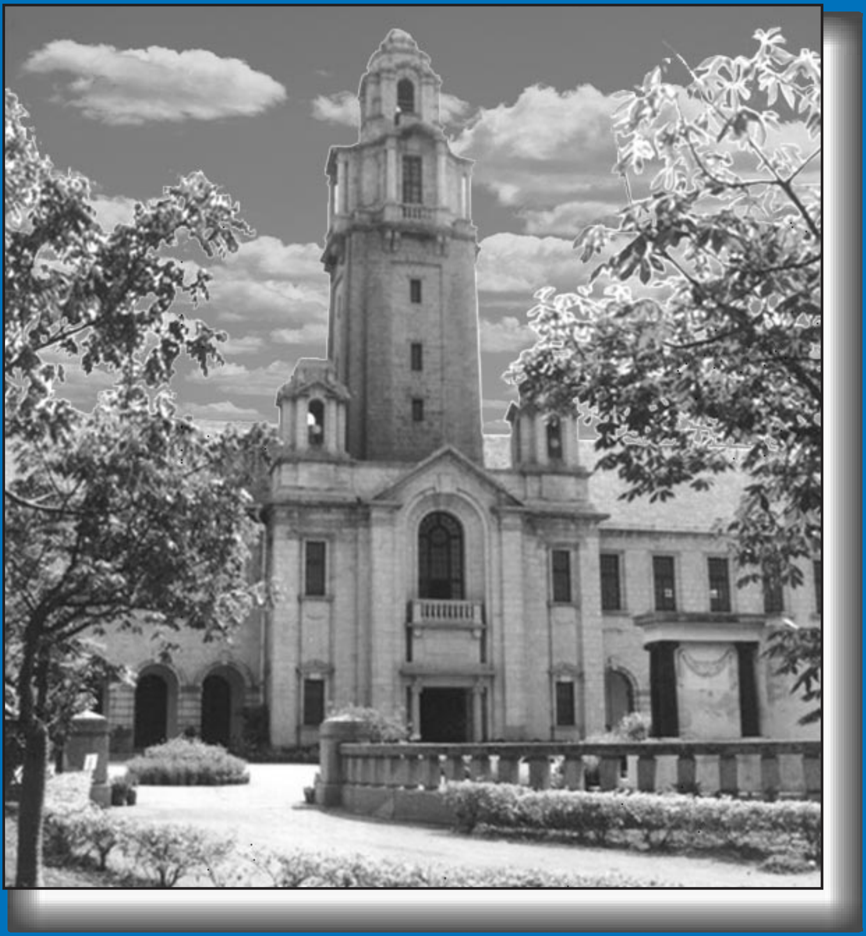
10th ANNIVERSARY OF CRSI NATIONAL SYMPOSIUM IN CHEMISTRY (NSC-10)

CHEMICAL RESEARCH SOCIETY OF INDIA
ESTABLISHED 1999

FEBRUARY 1 – 3, 2008



ABSTRACTS

INDIAN INSTITUTE OF SCIENCE
BANGALORE 560 012

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- Indian Institute of Science
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FOREWORD

About ten years ago the first national symposium in chemistry was held in the J.N.Tata Auditorium at Indian Institute of Science, Bangalore. It was the chemist's way of celebrating 50 years of Indian independence. Through the visionary guidance of Prof. C.N.R. Rao, the celebration culminated in the birth of a new society "The Chemical Research Society of India". Since then the "CRSI National symposium in Chefmistry" has been held in various parts of our great country. This is the tenth anniversary and it is being held in Bangalore again, which is now called Bengaluru. Suswagatha (Welcome)!

The symposium has evolved with time but maintains a few unique features. One of them is the opportunity given to chemists who have distinguished themselves over the years to present their work. This is done in the form of medal lectures, bronze, silver and gold and the names of the medal winners can be seen in the programme. Foreign fellows of the academy will also be given an opportunity to present their work. This year is no exception. Moreover, three special named lectures will also be delivered on this occasion. Quite aptly, the first C.N.R. Rao award lecture is to be given by M. Ratner of Northwestern University. In addition, we have the A Chakravorty award lecture to be given by E. Solomon of Stanford University and the Mizhushima-Raman lecture that will be delivered by K. Morokuma of Kyoto University.

In addition to these special lectures, there will also be an exciting half-day symposium on "Weak Interactions and their Strong Manifestations". By weak interactions, we mean hydrogen bonding and van der Waals interactions, which have recently been classified as non-covalent interactions. These interactions manifest rather strongly and pretty much control life on earth. Hydrogen bonding makes water what it is, the molecule that is always searched for in other planets as the first sign of life. Hydrogen bonding leads to the double helix structure of DNA and the triple helix in collagen. This and other interactions lead to polymorphism in solids, which plays a crucial role in drug activity. Drug manufacturing is a multi-billion dollar industry and one can see the rather strong manifestations of these weak interactions. Their strength arises from numbers and co-operativity is crucial which is often thought of as a signature of hydrogen bonding. From India, about 5800 papers have been published on hydrogen bonding so far out of which 3600 have appeared since the year 2000. This is 6 % of all the papers that have appeared on hydrogen bonding after year 2000. The special symposium features talks on experiments and theory, gas and condensed phase, in chemistry and biology.

Young scientists from all over the country are given an opportunity to present their talent in poster presentations. This year we have nearly 280 posters spread over two days. We trust, you will have enough food for thought after lunch on the 1st and 2nd of February.

E. Arunan
A. G. Samuelson

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Programme

2nd RSC-CRSI SYMPOSIUM ON THE CHEMICAL SCIENCES

31st JANUARY 2008

Venue: National Science Seminar Complex, Indian Institute of Science, Bangalore,

9.00 **WELCOME WORDS by Prof. A. Chakravorty, President, CRSI and Dr Alejandra Palermo, Manager, Special Projects, RSC Chair Prof. S. Chandrasekaran, IISc, India**

9.30 ***"Engineering Lanthanide Complexes for Sensing and Imaging"***
Professor David Parker
Chemistry Department, Durham University

10.00 ***"Studies on Peptides Containing Heteroaromatic Amino Acids"***
Dr. T.K. Chakraborty
IICT Hyderabad

10.30 ***"Creating Chiral Surfaces: From Nanoscale Control to Macroscale Amplification"***
Professor Rasmita Raval
Chemistry Department, Liverpool University

11.00 **COFFE BREAK**

Chair Professor Ray Jones, Loughborough University, UK

11.30 ***"Synthesis and Structure Determination of Natural Products"***
Dr Jonathan Burton
Chemistry Department, Oxford University

12.00 ***"Zinc Hydrolases and Bacterial Drug Resistance"***
Professor G. Mugesh
IISc, Bangalore

12.30 ***"Dynamical Tunneling: Mechanism and control"***
Professor K. Srihari
IIT, Kanpur, India

13.00 **LUNCH/DISCUSSION**

Chair Professor A.G. Samuelson, IISc, Bangalore, India

14.30 ***Short introduction to Innovation in RSC Publishing***
Dr Graham Mc Cann
Publisher, RSC

14.45 ***“Bridging the Gap Between Solution and Solid State Studies in the Self Assembly of Nanoscale Molecules and Clusters”***
Professor Lee Cronin
Chemistry Department, Glasgow University

15.15 ***“Shape Dependant Electro-Catalytic Properties of Pt and Rh Nanostructures”***
Dr. K. Vijayamohanan
NCL, Pune

15.45 TEA BREAK

Chair Professor David Parker, Durham University, UK

16.15 ***“Some Applications of Isonitrile Multicomponent Reactions to the Synthesis of Heterocycles”***
Dr Andrew Plant
Syngenta, Research Chemistry, Jealott’s Hill International Research Centre, UK

16:45 ***“Regio- and Stereoselective Synthesis of Novel Organophosphonates”***
Professor I.N.N. Namboothiri
IIT, Bombay, India

17.15 Concluding Remarks from chairs

FRIDAY 1ST - SUNDAY 3rd FEBRUARY 2008

10TH CRSI NATIONAL SYMPOSIUM IN CHEMISTRY-2008

VENUE: National Science Seminar Complex, I. I. Sc.

31st Jan 2008

08:00 - 16:00	**REGISTRATION**

1st February 2008

08:00 - 09:00	**REGISTRATION**
09:00 - 10:45	**Session 1: INAUGURATION AND SPECIAL LECTURES**
09:00 - 10:00	**INAUGURATION and PRESIDENTIAL ADDRESS**
10:00 - 10:45	**C.N.R. RAO AWARD LECTURE** *“Molecular Junction Transport – Beyond Tunneling to Function”* M. Ratner, Northwestern University, USA.
10:45 - 11:15	**HIGH TEA**
11:15 - 12:55	**Session 2: MEDAL LECTURES**
11:15 - 11:45	*“The Baylis-Hillman Reaction: Twenty Three Years of Our Research Experience”* D. Basavaiah, University of Hyderabad, Hyderabad
11:45 - 12:15	“*Double Trouble: Essays in NMR”* N. Chandrakumar, Indian Institute of Technology, Madras
12:15 - 12:35	*“Hydrogen Bonding and Hydrogen Bond Radii: A Microwave Spectroscopist’s View”* E. Arunan, Indian Institute of Science, Bangalore
12:35 - 12:55	*“Cyclodiphosphazanes as Neutral 2e, 4e, 6e or 8e Donors: Mononuclear to Octanuclear Rings, Cages, 1D- and 2D-Coordination Polymers of Transition Metals, Catalytic Investigations and Biological Studies”* M. S. Balakrishna, Indian Institute of Technology, Bombay

13:00 - 16:00	**LUNCH & POSTER SESSION I**
14:30 - 15:45	**CRSI COUNCIL MEETING (Members only)**
16:00 - 18:30	**Session 3: SPECIAL AND MEDAL LECTURES**
16:00 - 17:00	**CRSI 10th Anniversary Special Lecture** *“The Liquid-Liquid Interface as a Medium to Generate Materials”* C. N. R. Rao, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore.
17.00 - 17.30	*“Expanded Porphyrin: third order optical materials”* T. K. Chandrashekar, National Institute for Interdisciplinary Science and Technology (NIIST),Trivandrum.
17:30 - 17:50	*“Azides in Organic Synthesis: Stereoselective Synthesis of Biologically Active Molecules”* S. Baskaran, Indian Institute of Technology, Madras.
17:50 - 18:10	*“Modeling, Synthesis, evaluation of PPARa/gdual activators”* P. V. Bharatam, National Institute of Pharmaceutical Education and Research (NIPER), Punjab.
18:10 - 18:30	*“Observation of an Anomalous Luminiscence Property in Poly(Propyl Ether Imine) (PETIM) Dendrimers”* N. Jayaraman, Indian Institute of Science, Bangalore.
18:30 - 18:45	**TEA BREAK/POSTERS SESSION I CONTD.**
18:45 - 19:30	**Mizhushima-Raman Lecture** *“Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”* K. Morokuma, Kyoto University, Japan.

2nd February 2008

09:00 - 10:30	**Session 4: SPECIAL LECTURES**
09:00 - 09:45	**A. Chakravorty Endowment Lecture:** *“Spectroscopic Methods in Bioinorganic Chemistry: Blue to Green to Red Copper Sites”* E. I. Solomon, Stanford University, USA

09:45 - 10:15	*“Make It Count: Quantitating Low-Copy-Number Proteins in a Single Cell by Direct Counting”* R. N. Zare, Stanford University, USA
10:15 - 10:45	*“Carbohydrate Chemistry and Biology: New Challenges and Opportunities”* C-H Wong, Academia Sinica, Taiwan.
10:45 - 11:05	**TEA BREAK**
11:05 - 13:15	**Session: 5: 10th CRSI SPECIAL SYMPOSIUM on STRONG MANIFESTATIONS OF WEAK INTERACTIONS – I**
11:05 - 11:15	**Introductory comments** G. R. Desiraju, Hyderabad University
11:15 - 11:45	*“Weak noncovalent interactions among biomolecular building blocks can be surprisingly strong”* Pavel Hobza, Academy of Sciences of the Czech Republic, Prague, Czech Republic.
11:45 - 12:15	*“Hydrogen Bonding in Multi-functional Crystals”* Ashwini Nangia, University of Hyderabad, Hyderabad.
12:15 - 12:45	*“Electrostatics and Molecular Tailoring for Exploring Molecular Clusters”* Shridhar R. Gadre, University of Pune, Pune.
12:45 - 13:15	“ZEKE Probe for Isomer Assignment of Hydroquinone-water Complex” *Sanjay Wategaonkar, Tata Institute for Fundamental Research, Mumbai.*
13:15 - 16:00	**LUNCH & POSTER SESSION II**
16:00 - 17:50	**Session 6: MEDAL LECTURES**
16:00 - 16:30	*“Odyssey with Radical Ions”* Ganesh Pandey, National Chemical Laboratory, Pune.

16:30 - 16:50	"Applications of Norbornyl a-Diketone Building Blocks in Natural and Unnatural Products Syntheses" *F. A. Khan, Indian Institute of Technology, Kanpur.*
16:50 - 17:10	*"Studies on Some Metal-assisted Ligand Transformations"* Samudranil Pal, University of Hyderabad, Hyderabad.
17:10 - 17:30	*"Polypyridyl-Based Metal Complexes of Ruthenium(II) and /or Osmium(II): Synthesis, Characterization, Photoinduced Activity and Ion Recognition Study"* P. Paul, Central Salt and Marine Chemicals Research Institute, Bhavnagar.
17:30 - 17:50	*"Ketene dithioacetal chemistry: Synthesis of heterocyclic non-natural amino acids and thiophenes"* H. S. P. Rao, Pondicherry University, Pondicherry.
17:50 - 18:15	**TEA BREAK/POSTER SESSION II contd.**
18:15 - 19:00	**CRSI GENERAL BODY MEETING (Presentation of medals/ awards)**
19:00 - 19:45	**GOLD MEDAL LECTUR 1** *"Gibbs Excess Adsorption & Binding Interaction of Components in Chemical and Biological Systems"* D.K.Chattoraj, Jadavpur University, Kolkata
19:45 - 20:30	**GOLD MEDAL LECTURE 2** *"Theoretical Electrochemistry: Some Perspectives"* S.K. Ranagrajan, Indian Institute of Science, Bangalore.

3rd February 2008

09:00 - 11:20	**Session 7: SPECIAL AND MEDAL LECTURES**
09:00 - 09:30	*"Coordination Chemistry with Radicals: Where are the (Valence) Electrons?"* K. Wieghardt, Max-Planck-Institut für Bioanorganische Chemie, Germany.
09:30 - 10:00	*"Modeling Strongly Correlated Systems in Chemistry and Physics"* S. Ramasesha, Indian Institute of Science, Bangalore.

10:00 - 10:20	*“Use of Multinucleating Ligands for* M_p *(M = Co, Ni; p = 1, 2, 4) Complexes: Template Reactions and Coordination Assembly”* Debashis Ray, Indian Institute of Technology, Kharagpur.
10:20 - 10:40	*“Titanocene(III)-Mediated Radicals in Organic Synthesis”* Subhas C. Roy, Indian Association for the Cultivation of Science, Jadavpur.
10:40 - 11: 00	*“Molecular Dynamics Insights Into The Structure And Stability Of Collagen”* V. Subramanian, Central Leather Research Institute, Chennai.
11:00 - 11:20	**TEA BREAK**
11:20 - 13:20	**Session 8: 10th CRSI SPECIAL SYMPOSIUM on STRONG MANIFESTATIONS OF WEAK INTERACTIONS - II**
11:20 - 11:50	*“Charge density Analysis in Molecular Crystals: A route to quantify weak and strong interactions?”* T.N. Guru Row, Indian Institute of Science, Bangalore.
11:50 - 12:20	*“Stereospecific interactions involving sulfur in protein structures”* P. Chakrabarti, Bose Institute, Kolkata.
12:20 - 12:50	*“Molecular packing influencing solid state properties in alkoxy substituted oligo-phenyleneethynylenes”* *G.U. Kulkarni, Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore*
12:50 - 13:20	*“Solid State Reactivity and Supramolecular Synthons”* P.Venugopalan, Panjab University,Chandigarh.
13:20 - 13:30	**CONCLUSION**
13:30	**LUNCH**

Lecture Abstracts
(RSC-CRSI)

Dr. David Parker

David Parker is a native of the North-East of England and graduated with a First in Chemistry from the University of Oxford in 1978. He completed a D.Phil with Dr John M Brown in 1980 on mechanistic studies in asymmetric catalysis. Following a NATO post-doctoral fellowship with Prof Jean-Marie Lehn in Strasbourg, he returned to Durham to take up a Lectureship in Chemistry in 1982. In 1992 he was promoted to a Professorship in Chemistry. He received the RSC Hickinbottom Fellowship for 1988/9, the Corday-Morgan Medal and Prize in 1989, the ICI Prize in Organic Chemistry in 1991, the RSC Interdisciplinary Award in 1996, a Royal Society Leverhulme Trust Senior Research Fellowship (1998/9), the inaugural IBC Award for Supramolecular Science and Technology in 2000, the first RSC award for Supramolecular Chemistry in 2002, and a Tilden lectureship and medal in 2003. In 2002 he was elected as a Fellow of the Royal Society and currently he is a Wolfson RS Merit Award holder. He was the Chairman of Durham Chemistry from 1995-8 and during 2003-6.

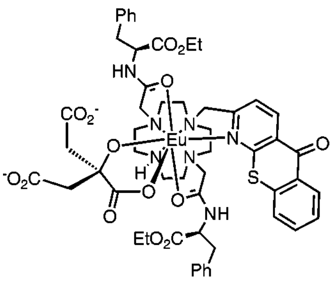
Engineering Lanthanide Complexes for Sensing and Imaging

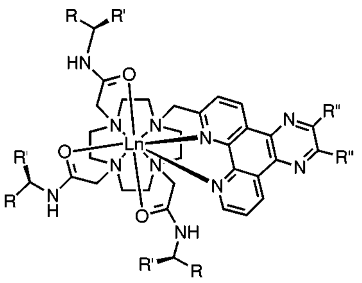
David Parker, Robert Pal, Elizabeth J. New, Craig P. Montgomery and Filip Kielar

Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK;
email: david.parker@dur.ac.uk

Well defined complexes of the lanthanide(III) ions allow the devlopment of both luminescent probes and magnetic resonance agents for use in the detection, analysis and imaging of bioactive species. Emissive probe complexes that are suitable for conjugation to proteins or various targeting entities have been developed, and examples of their usage in time-resolved FRET assays for kinase/phosphatase inhibition defined. Furthermore, complexes engineered to report on the local concentration of bioactive species such as bicarbonate, citrate, and phosphorylated tyrosine sites in peptides have been devised [1]. In addition, various amphipathic charged complexes have been studied that exhibit a marked tendency to be taken up by different cell types. Certain complexes bind reversibly to DNA and localise selectively in the cell nucleus [2], while others appear to target ribosomal RNA, e.g. within the nucleolus of the cell [3,4].

Strategies that allow the usage of these complexes as sensors in vitro or as imaging probes in *cellulo* will be aired [5,6,7], future key chemical and photophysical challenges described, and the scope for exploiting paramagnetic 19-F MR probes defined [8].





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5. Poole, R., Kielar, F., Parker, D. and Richardson, S.L. *Chem. Commun*., 2006, 4084.
6. Pal, R. and Parker, D., *Chem. Commun*., 2007, 474; C. P. Montgomery, L. Lamarque and D. Parker, *Chem. Commun*., 2007, 3841.
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Dr. Tushar Kanti Chakraborty

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Education: Ph.D. in 1984 from Indian Institute of Technology, Kanpur under the supervision of Prof. S. Chandrasekaran; Postdoctoral Fellow during 1984-87 at University of Pennsylvania, Philadelphia with Prof. K. C. Nicolaou.

Research Areas: Organic synthesis, peptides and peptidomimetics; designing new amide-linked molecular entities based on sugar amino acids and related compounds and studying their three-dimensional structures and properties.

Published over 131 papers in international journals.

Selected Publications: (1) Chakraborty, T. K.; Arora, A.; Roy, S.; Kumar, N.; Maiti, S. *J. Med. Chem.* **2007**, *50*, 5539-5542; (2) Chakraborty, T. K.; Koley, D.; Ravi, R.; Kunwar, A. C. *Org. Biomol. Chem.* **2007**, *5*, 3713-3716; (3) Chakraborty, T. K.; Roy, S.; Koley, D.; Dutta, S. K.; Kunwar, A. C. *J. Org. Chem.* **2006**, *71*, 6240-6243; (4) Chakraborty, T. K.; Samanta, R.; Das, S. *J. Org. Chem.* **2006**, *71*, 3321-3324; (5) Chakraborty, T. K.; Srinivasu, P.; Tapadar, S, Mohan, B. K. *J. Chem. Sci.* **2004**, *116*, 187-207; (6) Chakraborty, T. K.; Srinivasu, P.; Bikshapathy, E.; Nagaraj, R.; Vairamani, M.; Kiran Kumar, S.; Kunwar, A. C. *J. Org. Chem.* **2003**, *68*, 6257-6263; (7) Chakraborty, T. K.; Ghosh, S.; Jayaprakash, S.; Sharma, J. A. R. P.; Ravikanth, V.; Diwan, P. V.; Nagaraj, R.; Kunwar, A. C. *J. Org. Chem.* **2000**, *65*, 6441-6457; (8) Chakraborty, T. K.; Jayaprakash, S.; Diwan, P. V.; Nagaraj, R.; Jampani, S. R. B.; Kunwar, A. C. *J. Am. Chem. Soc.* **1998**, *120*, 12962-12963.

Awards and Honors: (a) Elected Fellows of the Indian National Science Academy in 2007, Indian Academy of Sciences in 2003 and the National Academy of Sciences, India in 2000; (b) Ramanna Fellowship by DST, India in 2007; (c) NASI-Reliance Industries Platinum Jubilee Award in Physical Sciences in 2006; (d) Andhra Pradesh Scientist Award in 2005; (e) Shanti Swarup Bhatnagar prize for Chemical Sciences in 2002; (f) Chemical Research Society of India Bronze Medal in 2002; (g) Dr. Basudev Banerjee Memorial Award of the Indian Chemical Society in 1999; (h) CSIR Young Scientist Award in 1991; (i) A. P. Akademi of Sciences Young Scientist Award in 1991.

Studies on Peptides Containing Heteroaromatic Amino acids

Tushar Kanti Chakraborty

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A common approach to restrict the conformational degrees of freedom in small peptides involves designing structurally rigid non-peptide scaffolds which, when inserted in the appropriate sites in peptides, produce the specific secondary structures required for binding to their receptors leading to the development of potent agonists/antagonists. The number of reports on the development of constrained non-peptide scaffolds used in peptidomimetic studies is increasing rapidly. Newer concepts are emerging where the fundamental building blocks used by nature, like amino acids, sugars and nucleosides, are amalgamated to produce nature-like, and yet unnatural, de novo structural entities with multifunctional groups anchored on a single ensemble. Furan amino acids (Faa) and pyrrole amino acids (Paa) belong to a new class of heteroaromatic amino acid building blocks that have been developed by us recently and used extensively in peptidomimetic studies.

It is now well known that the secondary structural motifs so common in proteins are not restricted to the a-peptide backbone alone, but can be seen in many designer oligomers. Among the most studied families of non-natural oligomers that show interesting secondary structures are the b-, g- and d-peptides, which bear particular significance because of their similarity to a-peptides. The conformationally constrained scaffolds of furan and pyrrole amino acids, which belong to the family of g- and d-amino acids, have emerged as important synthetic monomers leading to many *de novo* structural entities that have displayed interesting secondary structures and also useful properties like binding with DNA and G-quadruplex. The presentation will give a brief overview of some of our latest results in these areas of research.

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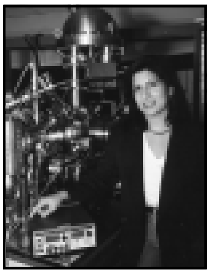
Shamala, N.; Karle, I. L.; Balaram, P. *Chem. Eur. J.* 2007, 13, 5917-5926
Nowick, J. S. *Org. Biomol. Chem.* 2006, *4*, 3869-3885; Chakraborty, T. K.; Arora, A.; Roy, S.
Kumar, N.; Maiti, S. *J. Med. Chem.* 2007, *50*, 5539-5542.

Dr. Rasmita Raval

The Surface Science Research Centre and
Department of Chemistry, University of Liverpool, UK



Professor Rasmita Raval is currently the Director of the Surface Science Research Centre and a Professor in the Department of Chemistry at the University of Liverpool. She received her PhD from the University of East Anglia (1986, with Prof. M.A.Chesters) on the development of the RAIRS technique to study complex adsorbates at surfaces. Her post-doctoral research with Prof. Sir David A. King at the Universities of Liverpool and Cambridge were on molecular adsorbate induced metal surface reconstructions. In 1990, she took up her first permanent faculty position as Lecturer at the University of Aberdeen, and in 1994 moved back to Liverpool. She is internationally known for her pioneering work on creating chiral 2-dimensional surfaces. Her multidisciplinary research on surface chirality combines 'bottom-up' assembly of molecular chiral architectures and concurrent development and utilisation of powerful surface spectroscopic tools to elucidate the nature of such interfaces at the atomic and molecular level. This work has spawned enormous academic interest and the scientific implications of this fundamental research cross many research fields, notably nanostructured self-assembly, heterogeneous enantioselective catalysis, single-molecule recognition, molecular electronics, and abiotic theories on the homochiral evolution of life-forms. Prof. Raval has given numerous invited plenary and keynote lectures at international conferences. She was awarded the 2003 Mott Lectureship by the Institute of Physics, named the 2002 Schuit Lecturer in Catalysis, Netherlands, and was awarded the 2002 E-Synergy/National Endowment for Science, Technology and Arts (NESTA) Innovation Prize.

Creating Chiral Surfaces: From Nanoscale Control to Macroscale Amplification

R.Raval

The Surface Science Research Centre and Department of Chemistry,
University of Liverpool, L69 3BX, UK.

3-dimensional expressions of chirality (or 'handedness') occur across a huge length-scale, encompassing spiral galaxies, biomineralisation, asymmetric crystalline materials, DNA and protein structure. How does the transfer of chirality from the molecular to the microscopic and the macroscopic scale occur? Despite 150 years of scientific study of chirality, it is only now, with the advent of scanning probe techniques and ultra-sensitive surface spectroscopies, that the nanoscale breaking of mirror symmetry in 2-dimensions is being understood. Technologically, the manifestation of chirality at surfaces has important implications in asymmetric catalysis, molecular recognition, and optoelectronics.

This talk will outline how adsorption and self-organisation of organic molecules can lead to the expression of chirality across a large length-scale, from the creation of nanoscale chiral motifs and clusters to highly organised chiral assemblies that are propagated at the macroscale [1,2]. On certain surfaces, chirality is bestowed at an even deeper level via reconstruction of the surface atoms to create chiral metal footprints [3], with chiral propagation occurring electronically from the chiral centres of the molecule to the metal surface. It will be shown that chiral surfaces can be highly responsive and self-adaptive, and are capable of sophisticated function such as single-molecule chiral recognitions events that can be revealed by direct imaging [4]. Finally, amplification mechanisms that drive mirror-symmetry breaking from the nanoscale to the macroscale will be outlined

Reference:

[1] *'Extended Surface Chirality from Supramolecular Assemblies of Adsorbed Chiral Molecules',* M.Ortega-Lorenzo, C.J.Baddeley, C.Muryn and R.Raval, Nature, 404 (2000) 376.

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Dr. Jonathan Burton

Jonathan Burton obtained a 1st degree in Natural Sciences (Chemistry) from Oxford University (1989-1993) where he spent a very productive honours year with Prof. George Fleet working on the chemistry of sugar lactones. He moved to Cambridge University for his Ph.D. (1993-1997) under the supervision of Prof. Andrew Holmes FRS and completed a total synthesis of (+)-laurencin. Towards the end of his Ph.D. he was elected to a Research Fellowship at Corpus Christi College which enabled him to continue research with Prof. Holmes on medium-ring ether/lactone chemistry. During this time he had a one year post-doctoral sojourn with Prof. Alexandre Alexakis at the Université Pierre et Marie Curie in Paris funded by a Royal Society European Exchange Fellowship. In 2000 he was awarded a Royal Society University Research Fellowship and began his independent academic career and he was recently appointed to a University Lectureship at the University of Oxford. His research interests include, total synthesis and structure determination of complex molecules; oxidative radical reactions mediated by manganese(III); catalytic asymmetric hydrogenation; hypervalent iodine chemistry.

Synthesis and Structure Determination of Natural Products

Jonathan Burton

Chemistry Deartment, Oxford University

The structures of complex natural products are best confirmed by independent synthesis or *X*-ray crystallography. Advances in NMR spectroscopy over the previous twenty years have greatly improved the ease with which the structures of complex molecules are solved; however, in cases where crystallography is not possible, regio and stereo-controlled synthesis is still the best method for structure confirmation. In many cases through-heteroatom connectivity becomes a significant challenge in structure assignment using NMR especially in otherwise closely related molecules.

The *lecture* will exemplify the difficultly of unambiguously assigning natural product structures by NMR methods. The total synthesis of the originally proposed structures of two halogenated marine natural products will be presented along with our current efforts to unambiguously assign the actual structures to these natural products using biosynthetic analysis, computer modelling and total synthesis.

Dr. G. Mugesh

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Education:

Ph. D. in Inorganic Chemistry, July 1998. Advisor: Prof. Harkesh B. Singh, Department of Chemistry, Indian Institute of Technology, Bombay

Dissertation: "*Studies on Novel Organochalcogen Derivatives; Synthesis, Structure, Reactivity, and Biomimetic Activity*"

M. Sc. in Chemistry, April 1993, Bharathidasan University, Thiruchirapalli, India.

B. Sc. in Chemistry, April 1990, University of Madras, Chennai, India.

Research Areas:

- Anti-thyroid and anti-oxidant activity of synthetic compounds
- Redox regulation of protein tyrosine phosphatases – understanding the unusual modifications at the active site of enzymes
- Antibiotic resistance and metallo-â-lactamases – understanding the role of zinc metals in bacterial drug resistance
- Biochemical haloganations/dehalogenations by metalloproteins.

Honors/Awards

- July 2006: Ramanna Fellowship, Department of Science and Technology (DST), New Delhi
- June 2006-to-date: Associate Editor, Bioinorganic Chemistry and Applications (BCA), Hindawi Publishing Corporation, USA.
- IUPAC Young Chemist Award, 40th IUPAC Congress, Beijing, China.
- January 2002, honored as a Skaggs Postdoctoral Fellow by the Skaggs Institute for Chemical Biology, The Scripps Research Institute, San Diego, USA.
- September 2001–October 2002: Post-doctoral Research Fellowship awarded by the Scripps Research Institute, San Diego, USA.

Zinc Hydrolases and Bacterial Drug Resistance

G. Mugesh* and A. Tamilselvi

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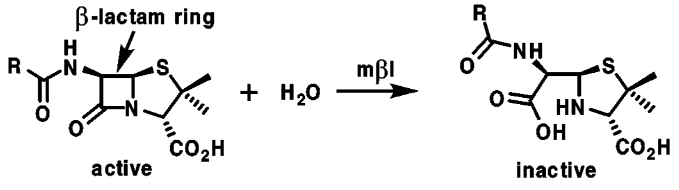
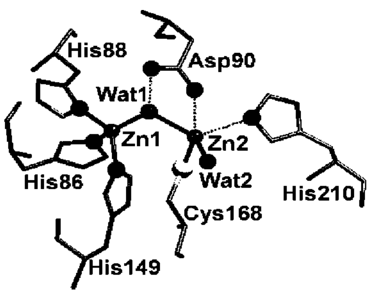
Antimicrobial resistance to b-lactam antibiotics has become a serious problem in the treatment of patients with bacterial infections. This drug resistance originates from the expression of certain enzymes called b-lactamases that catalyze the hydrolytic cleavage of the amide bond of b-lactam antibiotics. Of the four structural classes of this enzyme, the metalloproteins (metallo-b-lactamases, mbl, class B) represent a unique subset of zinc hydrolases that hydrolyze the b-lactam ring in several antibiotics including cephamycins and imipenems, which are generally resistant to the serine-containing b-lactamases (class A, C and D). Therefore, the medicinal application of the most commonly used antibiotics is severely compromised in bacteria that produce the metalloenzymes. In contrast to the serine-containing b-lactamases, the metalloenzymes are not inhibited by the clinically employed inhibitors such as clavulanic acid, sulbatctam and tazobactam.



Hydrolysis of b-lactam antibiotics by metallo-b-lactamases



Active site of mbl from *Bacillus cereus*

In view of the clinical problems associated with b-lactam antibiotics, we are working on the mechanism of the hydrolysis of b-lactams by natural enzymes and their synthetic mimics and the inhibition of metallo-b-lactamases. We have recently shown with the help of functional mimics that the presence of a second zinc ion is required for a quantitative hydrolysis of the antibiotics. In this lecture, the hydrolysis of b-lactam antibiotics such as penicillin, oxacillin and cephalosporins by mbl and its synthetic analogues will be discussed.

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Dr. K. Srihari

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Honors/awards: SPS (Physics honor society)
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Dynamical Tunneling: Mechanism and control

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Controlling quantum phenomena in atomic and molecular systems has been ‘the dream’ for a long time. The dream has started to become reality due to the formulation of several ingenious control strategies [1, 2, 3]. The ultimate quantum without doubt, is tunneling. We now know[4] that generalized forms of tunneling, called as dynamical tunneling, can manifest in a wide variety of systems with observable and crucial consequences. Is it possible to control tunneling? In fact we will ask a more provocative question - is it possible to control tunneling using insights obtained from the underlying classical dynamics?

This talk will try to answer the question using two examples. The first example is the driven double well which is a paradigmatic model for several control schemes with relevance in areas ranging from quantum dots to quantum computing. Using a novel measure to construct the strong-field control landscape[1] we will show that delocalized quantum states can interfere with the control process *i.e.*, dynamical tunnelling assisted by classical chaos spoils the perfect control[5]. The second example illustrates the subtle mixing of zeroth-order vibrational states due to Fermi resonances. It was conjectured nearly three decades ago that such state mixings are an example of dynamical tunneling and imply a purely quantum route to energy flow in an isolated molecule [4]. In this case we establish the mechanism and control the energy flow using local phase space structures [6].

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Lee Cronin is a Professor of Chemistry in the Department of Chemistry at the University of Glasgow. He graduated with a first class honours degree in Chemistry in 1994 from the University of York, and obtained a DPhil. in bio-inorganic chemistry in 1997 at the University of York under the supervision of Prof. P. H. Walton. In October 1997 he moved to the University of Edinburgh to take up a postdoctoral fellowship with Dr. N. Robertson in macrocyclic ligand design and in the summer of 1998, he took a two-month leave-of-absence to work at the University of Hokkaido, Japan, Institute of Electronic Science with Prof. T. Nakamura in the area of molecular conductors and magnetism. In August 1999 he began a Alexander von Humboldt Research Fellowship with Prof. A. Müller at the University of Bielefeld in Germany on the synthesis and crystallographic analysis of very large polyoxometalate clusters. He was appointed to a lectureship at the University of Birmingham in 2000 In 2002 he moved to take up a Lectureship in Glasgow and was promoted to Reader in 2005 and to Professor in 2006, and he was recently awarded a five year EPSRC Advanced Research Fellowship to allow him to spend more time focussing on his research interests. He has published over 100 papers.

Research Summary: My research interests are diverse and span aspects of inorganic (polyoxometalate cluster chemistry, classical coordination chemistry), organic (heterocyclic compounds, ligand design), nanoscale (self assembly of nano-scale clusters) and theoretical chemistry (modelling and DFT studies of clusters) with a particular thrust to collaborate at the discipline edges with engineers, physicists and materials scientists. In particular I am interested in understanding complexity in chemistry at a fundamental level including self assembly in complex systems and applying this to work towards the design, synthesis and evolution of devices and molecular systems.

Bridging the gap between solution and solid state studies in the self assembly of nanoscale molecules and clusters

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One of the big challenges in supramolecular chemistry and inorganic self assembly is the correlationbetween solution and solid state studies. The revolution crystallography during the last two decadesmeans that the structure determination of very large and extremely complicated molecules and supramolecular aggregates has outstripped the progressidentifying such species in solution before crystallisation. NMR and solution mass spectroscopic techniques have revolutionised organic and biological chemistry, but the application of these techniques to inorganic systems or supramolecular systems has been limited using mass spectrometry due to the unstable,rapidly exchanging, and highly charged systems. Furthermore,NMR studies are limited by rapid exchange and by paramagneticspecies or nuclei with low receptivity and these limitations are even more pronounced in polyoxometalate chemistry. Here I will present a methodology1-3 that aims to bridge the gap between mechanistic and solid state studies using a class of gigantic inorganic molecules called polyoxometalates.4 Gigantic polyoxometalates based on molybdenum oxide frameworks are extremely interesting since the are assembled under one pot conditions, are many nanometers in size, and are based upon a range of structurally conserved building blocks, see Fig. 1.

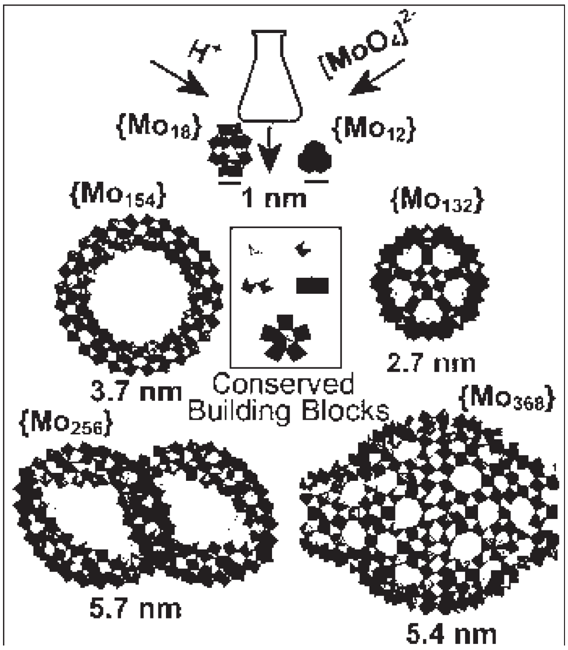

***Fig. 1.** Representations of the structures of some POM clusters, all synthesised under 'one-pot – 'one-step'reaction conditions (Polyhedral plot showing the MoOx units with conserved building blocks coloured) from thewell known and studied {M12} / {M18} Keggin / Dawson ions to the {Mo154} /{Mo132} and {Mo256} / {Mo368}clusters.]*

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Education:
- Ph.D. (Materials Chemistry), Indian Institute of Science, Bangalore, India, 1989
- M.Sc.(Chemistry), University of Kerala, India, 1982

Research areas:
- Surface functionalization using self-assembled monolayers, monolayer protected nanoclusters, hybrid materials and their electrochemistry
- Development of organo-inorganic nanocomposites for electrochemical power sources like lithium batteries, ultracapacitors and fuel cells

Honors/Awards:
- Received the MRSI Medal by the Materials Research Society of India (1996), the Affiliate Membership of IUPAC in 1997, Scientist of the year award of NCL Research Foundation in 2003 and the Chemical Research Society of India (CRSI) Bronze Medal (2004);
- Editorial Member, Bulletin of Materials Sciences(2006), Bangalore

Shape Dependant Electro-Catalytic Properties of Pt and Rh Nanostructures

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Nano-structured materials have attracted much attention recently due to the possibility of tailoring their dimensionality to facilitate a change in their fundamental properties including mechanical, electrical, optical or electrochemical behavior in comparison with similar behavior of their bulk analogues. Consequently, much effort has been directed towards the fabrication of shape selective nanostructures because of their exquisite size and shape dependent properties and also their technological relevance in diverse areas such as catalysis, photochemistry, chemical sensors and optoelectronics. These nanostructures are generally synthesized in many forms including highly monodispersed spherical nanoparticles to several anisotropic nanostructures such as wires/rods, tubes and ribbons. It is generally accepted that the morphology of a nanostructure could be remarkably tuned during the synthesis by controlling pertinent parameters such as temperature, nature of surfactant, metal ion to capping molecule ratio, and the concentration of other additives in order to control the physical and chemical properties of these materials. As a result, various methods have been developed to generate many of these nano level architectures with good shape control including the use of many soft as well as hard templates.

In the past, several nanostructured materials like silver, gold, platinum and palladium have been prepared by our group with or with out using templates to unravel their distinct behavior and a comparison with the properties of bulk materials show their promise for many new applications[1]. As a part of our continuing quest for preparing hybrid materials with novel or enhanced properties, this presentation will discuss the impact of nanotechnology on materials research citing specific examples of these metallic nanorods, nanowires and Y junction structures of gold, silver, platinum and rhodium. We will also demonstrate the utility of hierarchically developed alumina templates for the formation of platinum Y-junction nanostructures for fuel cell applications[2]. The present method of fabrication of Y-junction nanostructures using hierarchical alumina templates could be extended to other metallic/semiconducting systems facilitating more opportunities for such hierarchical designs in nanoelectronics.

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2. Synthesis of Platinum Y-Junction Nanostructures using Hierarchically Designed Alumina Templates and their Enhanced Electrocatalytic Activity for Fuel Cells Applications, Subhramannia Mahima, Ramaiyan Kannan, Indulekha Komath, Mohammed Aslam and Vijayamohanan K. Pillai, Chem. Mater. (2007 press)

Dr. Andrew Plant

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Andrew Plant studied chemistry at the University of Liverpool, obtaining his B.Sc in 1985 and his Ph.D in 1988, the latter working under the supervision of Dr. Derek Chadwick on synthetic heterocyclic chemistry. He was then awarded a Royal Society Fellowship to conduct postdoctoral research with Professor Dieter Enders at the RWTH (Technical University) in Aachen, Germany, working in the area of asymmetric synthesis. In 1991 he joined Bayer AG in Germany where, over a ten year period, he worked in Central Research, as well as the Animal Health and Crop Protection Businesses. Andrew returned to the UK in 2001 to join Syngenta, where today he holds the position of Group Leader, Herbicide Chemistry. His research interests span the chemistry of crop protection and heterocyclic chemistry in general.

Some Applications of Isonitrile Multicomponent Reactions to the Synthesis of Heterocycles

Andrew Plant

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In recent years isonitrile multicomponent reactions (IMCRs) have featured prominently in the lead generation and lead optimisation programmes of a number of industrial laboratories [1]. In particular the Passerini and Ugi reactions have been applied to the synthesis of a variety of heterocycles of biological interest [1-2]. In this communication we will outline novel syntheses of a number of polycyclic ring systems (e.g. Figure 1) that have been developed as part of lead generation programmes at Syngenta, Jealott's Hill, UK [3].

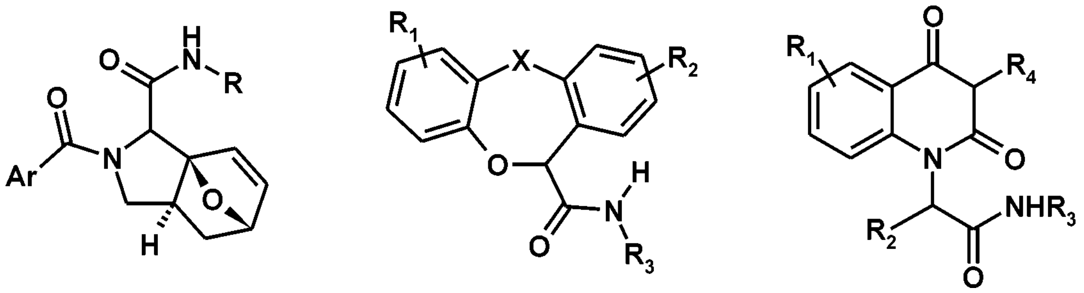

Figure 1.: Polycyclic heterocycles prepared utilising IMCRs.

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[3] Presented in part at the 17th Lakeland Heterocyclic Symposium, Grasmere, UK, May 8th, 2005 and at the 13th FECHEM Conference on Heterocycles in Bio-Organic Chemistry, Sopron, Hungary, May 31st, 2006.

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Education

MSc. Mangalore University, 1988, *Ph D:* Indian Institute of Science, Bangalore, 1994; *Postdoctoral:* Bar-Ilan University, Israel, 1995-96; University of North Texas, 1997-98; Columbia University, 1999; *Employment:* Senior Research Scientist, Sabinsa Corporation, New Jersey, 2000; Assistant Professor: IIT Bombay, 2001-2005; Associate Professor: IIT Bombay, 2005-Present.

Research areas

Organic synthesis, physical organic chemistry, reaction mechanisms
(a) Development of new synthetic methodologies
(b) Synthesis of ‘unnatural products’ and novel materials with interesting properties
(c) Study of various reaction pathways

Regio- and Stereoselective Synthesis of Novel Organophosphonates

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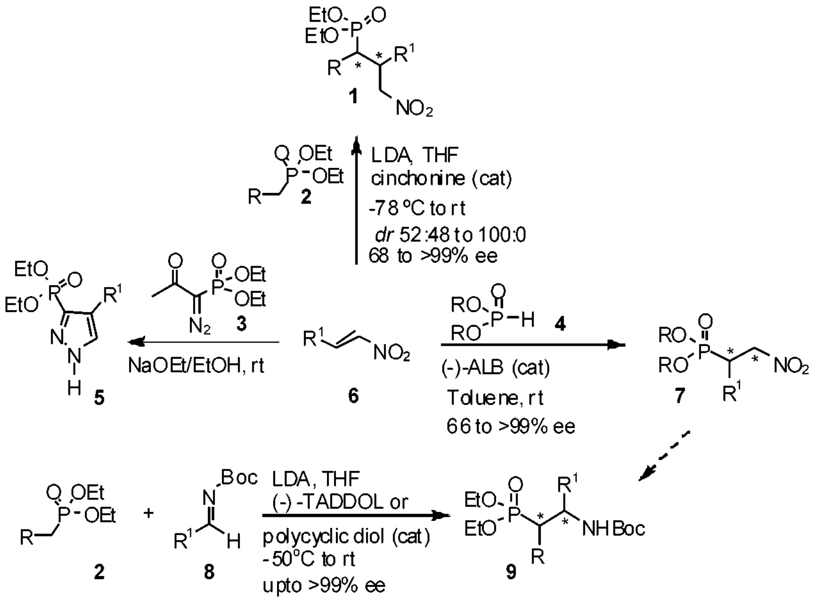
Organophosphorus compounds are distinguished by their diverse and potent biological properties. Phosphonates linked to other functional groups and heterocycles exhibit enhanced biological activity. For instance, aminophosphonates, the isosteric analogs of corresponding amino acids, serve as haptens for catalytic antibodies and as key intermediates for other biological processes. Herein, we report efficient routes for the regioselective synthesis of phosphonylpyrazoles and stereoselective synthesis of b- and g-nitrophosphonates.



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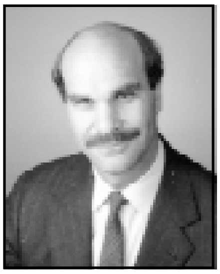
Lecture Abstracts
(CRSI)

Dr. Mark Ratner



Mark Ratner was in junior high school when Sputnik was launched, and that occasioned his becoming a scientist. He finished high school in Shaker Heights, Ohio, college at Harvard, and doctoral work at Northwestern (in 1969). Following postdoctoral work at Aarhus in Denmark (where he worked on the kind of very formal theory that attracts young scientists), and in Munich, he began his career in the Chemistry Department at New York University. His first student there, Ari Aviram, was really the person who launched modern investigations into the area of molecular electronics.

Ratner returned to Northwestern as Professor of Chemistry in 1975. He has chaired the Chemistry Department at Northwestern, served as Associate Dean of the College of Arts and Sciences, and now holds the Morrison Professorship in the Department of Chemistry.

Ratner is interested in structure at the nanoscale, function at the nanoscale, and the theory of fundamental chemical processes. More specifically, he tries to bring together structure and function in molecular nanostructures, based on theoretical notions, on exemplary calculations, and (very importantly) on collaborations with experimentalists and other theorists, in the United States and around the world. Some principal areas of interest are molecular electronics, theories of self-assembly, nonlinear response in molecules, and exact and approximate theories of quantum dynamics. His newest interest is in using nanoscience to attack the energy problems facing this world. In the interstices of these, he spends as much time trout fishing as he possibly can.

Ratner is a member of the National Academy of Sciences, the American Academy of Arts and Sciences, the International Academy of Quantum Molecular Sciences and the Royal Danish Academy of Sciences. He has received the Langmuir Award from the American Chemical Society and the Feynman Award from the Foresight Institute. He also has also been a member of the Faculty Teaching Honor Roll at Northwestern eleven times, and has taught roughly five thousand students in General Chemistry in the last dozen years. He is the coauthor of two non-technical books on nanotechnology.

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Molecular Junction Transport – Beyond Tunneling to Function

Mark Ratner

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The behavior of molecular transport junctions in the coherent tunneling (Landauer-Imry) regime is rapidly becoming understood. But vibronic and electronic polarization effects characterize molecules, and understanding how they act in such junctions is a significant issue. This talk will deal with the role of both weak and strong vibronic interactions in molecular junctions. The weak mixing appears in Inelastic Electron Tunneling spectra, and can be handled by perturbation theory in the coherent tunneling limit. Strong vibronic interaction requires a more elaborate analysis. Hysteresis and switching behaviors will be discussed, and some remarks about Coulomb blockade will be ventured.

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Education

M.Sc.	Banaras Hindu University , Varanasi-221 005 (Organic)
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Post-doctoral work:	Purdue University, USA, with Professor H.C. Brown (1980-1983)

Research Interests:

The Baylis-Hillman Reaction
Chiral Catalysis
Biotransformations

Honors/Awards:

1. CRSI Silver Medal-2008
2. Elected Fellow of the Indian National Science Academy (FNA) 2006
3. CRSI Bronze Medal-January 2000
4. Professor T. R. Govindachari 60th Birthday Commemoration Endowment
5. Award in Organic Chemistry 1999-2000
6. Elected Fellow of the Indian Academy of Sciences (FASc) Bangalore 1997
7. First Rank in M. Sc. Chemistry, Awarded B. H. U. Gold Medal 1972
8. Awarded A. P. National Scholarship on the Merit of B. Sc. Marks 1970

The Baylis-Hillman Reaction: Twenty Three Years of Our Research Experience

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The Baylis-Hillman reaction is an atom-economy three component carbon-carbon bond forming reaction involving the coupling of the a-position of an activated alkene with carbon electrophile under the influence of a catalyst or catalytic system producing densely functionalized molecules whose applications in various organic transformation methodologies have been well documented [1-5]. We have been working, for the last twenty three years on different aspects of this fascinating reaction with a view to develop this reaction as one of the most useful synthetic tools in organic synthesis and also to develop the Baylis-Hillman adducts as a valuable source for synthetic methodologies and also for one-pot multi-step / reaction strategies [6-15]. This talk will describe our recent efforts on various aspects of this reaction.

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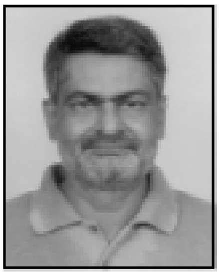

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Research Areas:
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Honors/Awards:
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2. Bruker NMR Award for Young Scientists (1985)
3. CSIR Young Scientist Award (Chemical Sciences 1987)
4. Elected Fellow of the Indian Academy of Sciences, Bangalore (FASc, 1993)
5. CSIR New Idea Fund Award (1996)
6. S.S. Bhatnagar Prize (Chemical Sciences, 1996)
7. Elected Fellow of the Indian National Science Academy (FNA, 1997)
8. Millennium Medal (Science Congress, 2000)
9. R.K. Asundi Memorial Lecture, INSA (2002)
10. K. Rangadhama Rao Memorial Lecture, INSA (2004)

Double Trouble: Essays in NMR

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Some of our recent work in the development and application of novel NMR experiments is presented, in the areas of high resolution NMR and spatially resolved NMR.

The first theme discussed will be the homonuclear correlation of spin pairs involving rare isotopes, a chemically important problem relevant for example to ^{13}C, ^{29}Si and ^{183}W applications. The standard approach has been to measure the double quantum spectrum (**INADEQUATE**) because the normal single quantum correlation spectrum such as **COSY** would be bedeviled by extremely strong diagonal peaks arising from isolated spins. We have developed an alternative approach that relies on diagonal suppressed single quantum correlation and optimizes sensitivity – and could also offer advantages in terms of reduced magnetization losses due to spin relaxation. The approach relies on recognizing coupled spin pairs by employing a double quantum filter, then immediately transferring to single quantum single transitions followed by mixing with a zero quantum Hamiltonian. This results in a diagonal suppressed display of correlation cross peaks, each cross peak comprising only one of the four possible 2D multiplet components. Sensitivity matches the unitary bound on coherence transfer. We have termed this approach **L**ow **A**bundance **S**ingle transition correlation **S**pectroscop**Y** (**LASSY**) and have dubbed it **CLASSY** for ^{13}C applications. Approaches to recover information on shifts and couplings from such an experiment are outlined. The relaxation behavior is briefly discussed. Possible applications to the solid state are also pointed out.

The second theme discussed will be the *in vivo* homonuclear correlation of protons. Under *in vivo* conditions, the spin echo mode of correlation spectroscopy has been found to be advantageous. However, the SECSY format also suffers from a pseudo diagonal, *viz*., the peaks at $F_1 = 0$, which often mask correlations in the neighborhood. By manipulating undesired magnetization components to generate delayed echoes beyond the detection time interval, we have developed a novel experiment that permits diagonal suppressed proton correlation in the spin echo format. We term this experiment **DI**agonal **S**uppressed **S**pin **E**cho **C**orrelation spec**T**roscopy (**DISSECT**). Initial results on phantoms are shown.

Finally, we present some applications of spatially resolved NMR to process monitoring. The specific examples we discuss are volume localized spectral measures of the time course of: (i) fruit ripening; and (ii) drug dissolution. It is shown that in both cases the molecular imprint of the processes in question may be captured by this approach, as also the relevant process kinetics.

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Molecular and van der Waals Spectroscopy, hydrogen bonding, chemical kinetics and dynamics, applications of ab initio electronic structure and other theoretical methods in spectroscopy and kinetics.

Honors/Awards:
Chairman of the IUPAC task group (2004-2007) on Categorizing hydrogen bonding and other intermolecular interactions; International Editorial Advisory Board Member for Physical Chemistry Chemical Physics, a Royal Society of Chemistry journal; CRSI Bronze medal for the year 2008.

Hydrogen Bonding And Hydrogen Bond Radii: A Microwave Spectroscopist's View

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Hydrogen bonding has been in the literature for close to a century now (for history see for example: Pimentel and McClellan [1]; Desiraju and Steiner [2]). It should then come as a surprise that there has been a continuous debate/discussion about the nature of hydrogen bonding and even the meaning of the term 'hydrogen bond'. Following our initiative, IUPAC has recently formed a task group with 15 international experts to propose a modern definition of hydrogen bond (Arunan [3]). Another question that has bothered chemists during this period is whether hydrogen bonding is unique or not. The answer is quite subjective and ranges from 'most certainly' to 'absolutely not'. Our group has been addressing these questions (Raghavendra and Arunan [4]) using various experimental and theoretical approaches and this talk will give a brief summary.

A home-made pulsed nozzle Fourier transform microwave spectrometer (Arunan et al. [5]) is used to study weakly bound complexes that are characterized as 'hydrogen bonded' or 'van der Waals' complexes. Complexes of H_2O and H_2S ($B{\bullet\bullet\bullet}H_2X$ where B could be any 'hydrogen bond' acceptor) have been investigated as the former is widely recognized as a hydrogen bonding molecule while the latter is not. Microwave spectroscopic results from our laboratory and others show that complexes of both H_2O and H_2S have significant structural similarity (Goswami et al. [6]) at the equilibrium. However, the barrier for large amplitude tunneling/internal rotation motions within the complex and the binding energy are smaller for the H_2S complex than the analogous H_2O complex. These structural and energetic details are used to provide a definition for the hydrogen bond from a microwave spectroscopist's view.

Pauling had defined covalent, ionic, metallic and van der Waals radii for several atoms in the periodic table (Pauling [5]). However, while discussing bonding, he also discussed hydrogen bonding in addition to the interactions bearing these names. Is there a hydrogen bond radius which eluded Pauling? We have recently defined hydrogen bond radii for donors and acceptors and shown that these radii vary with the dipole moment of the donor (Arunan and coworkers [4,7,8]). Interestingly, extrapolating to zero-dipole moment of the donor leads to the accepted van der Waals radius for the hydrogen atom (Pauling [5]). These radii can be used to explain both hydrogen bonding at longer inter-nuclear distances and the lack of it at shorter inter-nuclear distances.

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PDF, Chemistry Department, University of Alberta, Edmonton, Canada.
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Associate Professor 2000-2005 (Indian Institute of Technology Bombay, Mumbai, India)
Professor 2005- present (Indian Institute of Technology Bombay, Mumbai, India)

Research Areas:

- Main group Chemistry of Phosphorus, Nitrogen, Silicon and chalcogens.
- Transition Metal Organometallic Chemistry
- Homogeneous Catalysis

Cyclodiphosphazanes as Neutral 2e, 4e, 6e or 8e Donors: Mononuclear to Octanuclear Rings, Cages, 1D- and 2D-Coordination Polymers of Transition Metals, Catalytic Investigations and Biological Studies

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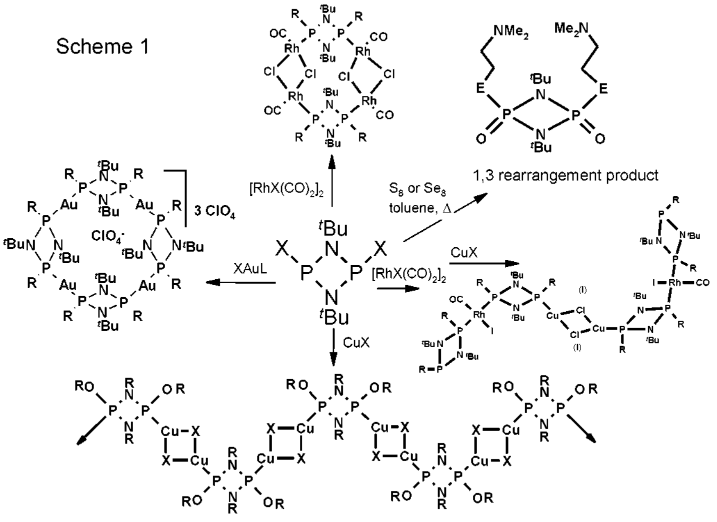
The saturated four-membered rings of the type $[XP(?\text{-}NR)]_2$ containing alternating phosphorus(III) and nitrogen atoms are known as cyclodiphosphazanes or diazadiphsophetidines. The recent revived interest in these well-known heterocycles is due to their excellent synthetic utility in the construction of macrocycles and as neutral and anionic ligands and also as catalysts for ethane polymerization reactions. Although, the rigid and nearly-planar neutral P_2N_2 rings resemble $[Cu(?\text{-}X)]_2$ (X = Cl, Br or I) rhombic units ($[Cu(?\text{-}X)]_2$ are known for giving a variety of structures with suitable ligands), their utility in designing high-nuclearity clusters, cages or coordination polymers is yet to be explored. In this context, we fine tuned the coordinating ability of these ligands by incorporating pendant hemilabile functionalities on phosphorus centers which resulted in the isolation of several interesting molecules (Scheme 1) [1]. The details will be presented.



Scheme 1

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Brief Biodata of Professor C.N.R. Rao

Prof. C.N.R. Rao (born on 30 June 1934, Bangalore, India) is the National Research Professor as well as Honorary President and Linus Pauling Research Professor at the Jawaharlal Nehru Centre for Advanced Scientific Research. He is also an Honorary Professor at the Indian Institute of Science. His main research interests are in solid state and materials chemistry. He is an author of over 1400 research papers and 41 books. He received the M.Sc. degree from Banaras, Ph.D. from Purdue, D.Sc. from Mysore universities and has received honoris causa doctorate degrees from 46 universities including Purdue, Bordeaux, Banaras, Delhi, Mysore, IIT Bombay, IIT Kharagpur, Northwestern, Notre Dame, Novosibirsk, Oxford, Stellenbosch, Uppsala, Wales, Wroclaw, Caen, Khartoum, Calcutta, Sri Venkateswara University and Desikottama from Visva-Bharati.

Prof. Rao is a member of all the major science academies in the world including the Royal Society, London, the National Academy of Sciences, U.S.A., the Russian Academy of Sciences, French Academy of Sciences, Japan Academy as well as the Polish, Czechoslovakian, Serbian, Slovenian, Brazil, Spanish, Korean and African Academies and the American Philosophical Society. He is a Member of the Pontifical Academy of Sciences, Foreign Member of Academia Europaea and Foreign Fellow of the Royal Society of Canada. He is on the editorial boards of several leading professional journals.

Among the various medals, honours and awards received by him, mention must be made of the Marlow Medal of the Faraday Society (1967), Bhatnagar Prize (1968), Jawaharlal Nehru Fellowship (1973), Padma Shri (1974), Centennial Foreign Fellowship of the American Chemical Society (1976), Royal Society of Chemistry (London) Medal (1981), Padma Vibhushan (1985), Honorary Fellowship of the Royal Society of Chemistry, London (1989), Hevrovsky Gold Medal of the Czechoslovak Academy (1989), Blackett Lectureship of the Royal Society (1991), Einstein Gold Medal of UNESCO (1996), Linnett Professorship of the University of Cambridge (1998), Centenary Medal of the Royal Society of Chemistry, London (2000), the Hughes Medal of the Royal Society, London, for original discovery in physical sciences (2000), Karnataka Ratna (2001) by the Karnataka Government, the Order of Scientific Merit (Grand-Cross) from the President of Brazil (2002), Gauss Professorship of Germany (2003) and the Somiya Award of the International Union of Materials Research (2004). He is the first recipient of the India Science Award by the Government of India (2005) and received the Dan David Prize for science in the future dimension for his research in Materials Science. He was named as Chemical Pioneer by the American Institute of Chemists (2005), “Chevalier de la Légion d’Honneur” by the President of the French Republic (2005) and received the Honorary Fellowship of the Institute of Physics, London (2006) and Honorary Fellowship of St. Catherine’s College, Oxford (2007).

Prof. Rao is Chairman, Scientific Advisory Council to the Prime Minister, past President of The Academy of Sciences for the Developing World (TWAS), Member of the Atomic Energy Commission of India and Chairman, Indo-Japan Science Council. He is Founder-President of both the Chemical Research Society of India and of the Materials Research Society of India. Prof. Rao was President of the Indian National Science Academy (1985-86), the Indian Academy of Sciences (1989-91), the International Union of Pure and Applied Chemistry (1985-97), the Indian Science Congress Association (1987-88), and Chairman, Advisory Board of the Council of Scientific and Industrial Research (India). He was the Director of the Indian Institute of Science (1984-94), Chairman of the Science Advisory Council to Prime Minister Rajiv Gandhi (1985-89) and Chairman, Scientific Advisory Committee to the Union Cabinet (1997-98) and Albert Einstein Research Professor (1995-99).

The liquid-liquid interface as a medium to generate materials

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The air-water interface is generally employed to prepare particle assemblies and films of metals and semiconductors. On the other hand, the interface between water and an organic liquid has not been investigated adequately for preparing nanocrystals and thin films of materials. The liquid-liquid interface provides an excellent medium for preparing ultrathin nanocrystalline films of metals, metal chalcogenides and oxides. The method involves the reaction at the interface between a metal-organic compound in the organic layer and an appropriate reagent for reduction, sulfidation, selenidation etc. in the aqueous layer. The formation of ordered thin films of nanocrystals at the interface has been examined by diffuse x-ray scattering and in-situ atomic force microscopy. Rheological measurements have also been carried out at the interface. Some of the two-dimensional nanomaterials so obtained are of Au, Ag, Pd, Au-Ag alloys, CuS, ZnS, PbS, CuSe, CdSe, CuO, ZnO and Cu(OH)2. Interestingly, many of the films are single crystalline. The results demonstrate the versatility and potential of the liquid-liquid interface for preparing nanomaterials and ultrathin films and encourage further research in this area. Results of studies on the effect of thiols as well as surfactants on the structure and the surface plasmon band of metal films will be presented.

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Degree	Subject	Class	Year	University
B.Sc.	Physics, Chemistry	I	1976	Mysore
M.Sc.	Chemistry	I	1978	Mysore
Ph.D.	Bioinorganic Chemistry	-	1982	I.I.Sc, Bangalore
Post-Doc.	Photochemistry and Physical Chemistry	-	1982-84	Massachusetts, Boston, USA
Research Associate	Biophysical Chemistry	-	1984-86	Michigan State East Lansing, USA

Research areas

Chemistry of tetrapyrrole pigments and related macrocycles for their use as:

1. Photosensitizer for photodynamic therapy
2. Model compounds for photosynthetic intermediates
3. Molecular receptors for neutral, cationic and anionic substrates
4. Catalysts for organic conversions
5. Supramolecular systems for molecular devices

Awards and Honours

1. Alexander Von Humblodt Fellowship: 1993-1994
2. Fellow of National Academy of Sciences, Allahabad-1996
3. Fellow of Indian Academy of Sciences, Bangalore-1999
4. CRSI Bronze medal for significant contributions in Chemistry: 2000
5. Shanti Swarup Bhatnagar Prize in Chemical Sciences for the year 2001
6. Fellow of Indian National Science Academy, New Delhi-2002
7. J. C. Bose National Fellowship for the year 2006

“Expanded Porphyrin: third order optical materials”

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Syntheses, spectroscopic, electrochemical, and third-order nonlinear optical susceptibilities of a series of 22π smaragdyrins and their corresponding Rh(I) derivatives bearing phenylacetylene substituents and ferrocene-containing substituents are reported. The synthetic strategy involved a [3+2] acid-catalyzed oxidative coupling reaction of the appropriate dipyrromethane and oxatripyrrane. The desired meso substituents, such as phenylacetylenylphenyl and the ferrocenes, were incorporated to the dipyrromethane unit prior to the oxidative coupling reaction. The optical absorption, emission characteristics, and the quantum yield of the smaragdyrin conjugates depends on the nature of the substituent, nature of linker group, and the spacer length. Theoretical studies at the DFT level suggest high delocalization of electrons confined to only four of the five available heterocyclic rings for the free bases. Upon Rh(I) metalation, the π-electron delocalization is extended to all the heterocyclic rings. The two-photon absorption cross section (TPA) values $\sigma^{(2)}$ measured through the open aperture Z-scan method, increases linearly with enhanced π-electron delocalization for the smaragdyrins containing phenylacetylene substituents. The meta branching of substituents decreases $\sigma^{(2)}$ values. Introduction of Rh(I) to the smaragdyrin cavity enhances the $\sigma^{(2)}$ values by about 3-10 orders of magnitude, attributed to the increased aromatic character upon Rh(I) insertion. The calculated molecular electrostatic potential (MESP) and harmonic oscillator model of aromaticity (HOMA) for the free bases and the Rh(I) derivatives justifies such a conclusion. A linear correlation observed for the second oxidation potential of Rh(I) derivatives and corresponding free bases also support the increased aromaticity upon Rh(I) insertion. The electrochemical data for ferrocene-containing smaragdyrins reveal easier ring oxidation by about 50-130 mV and harder ferrocene oxidation by 40-180 mV suggesting electron-donating nature of the ferrocene upon linking with the smaragdyrin π-system. The TPA cross section value of 88782 GM observed for Rh (I) smaragdyrin represents one of the highest values known for a metalloexpanded porphyrin derivative.

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Development of New Synthetic Methodology and Apply in the Stereoselective Synthesis of Biologically Active Molecules.

Honors:
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Azides in Organic Synthesis: Stereoselective Synthesis of Biologically Active Molecules

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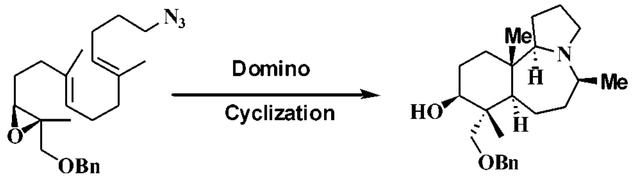
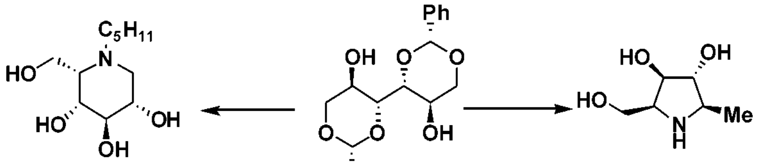
Biomimetic cation-initiated polyolefin cyclization is now a well-established protocol that allows the synthesis of fused polycyclic ring systems, in a highly stereoselective manner. Although, several initiators and terminators are designed and developed for the effective construction of carbo- and heterocyclic ring systems, azide has not been used as a cation terminator in polyolefin cyclization.

Recently, we reported a novel and general method for the stereoselective construction of 5-hydroxymethyl azabicyclic ring system based on epoxide-initiated cationic cyclization of azide. The scope of this methodology is further extended to hitherto unknown *domino epoxy-olefin-azide cyclization*. For the first time, azide has been used as a cation terminator in polyolefin cyclization leading to novel azapolycyclic compounds in a highly stereoselective manner. In addition, synthetically useful and highly functionalized chiral intermediates have been prepared from *bis*-benzylidene acetal of D-mannitol by regioselective reductive cleavage and applied this strategy in the stereoselective synthesis of biologically active molecules such as anti-cancer agent OGT2378, glycosidase inhibitors and fucosyltransferase inhibitors. In this presentation, our approaches towards the development of new synthetic methods and their applications in the stereoselective synthesis of biologically active molecules will be highlighted.





OGT2378
Anti-cancer Agent

Fucosyltransferase Inhibitor

References:

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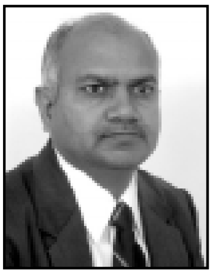

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3. CRSI Bronze medal 2008

Modeling, Synthesis, evaluation of PPARa/g dual activators

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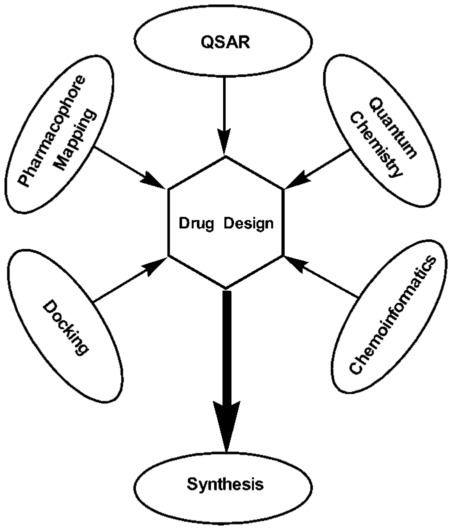

PPARa and PPARg are well known targets of anti-triglyceridemic and anti-diabetic activities respectively and dual activators of these targets are being designed as synergistically acting agents. Designing the dual activators using 3D-QSAR, Pharmacophore mapping, Molecular docking, Virtual screening, Pharmacoinformatics methods is being practiced in our laboratory [1-20]. Understanding the chemistry, biochemistry and basics of drug action of the glitazone series of compounds and applying the basics to design new molecules is also the major activity in our institute. For example studies on the rapid racemization, sulfur oxidation, of rosiglitazone, pioglitazone was taken up at our laboratory using quantum chemical methods [12]. 3D QSAR methods have been employed to design [10] several new leads. The designed molecules have been synthesized and biologically evaluated [3]. The pharmacophoric features of metformin and other related drugs have been explored [7,9]. The design of GSK3 inhibitors also was taken up [4,5]. The chemistry and biochemistry of several of the anti-diabetic agents was explored using quantum chemical methods [1,6,8,11,13,14-20]. The results of computer aided design, synthesis and biological evaluation of PPARg activators will be presented in this lecture.

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Education:	M.Sc. (Annamalai University, 1988) Ph.D. (Indian Institute of Technology, Kanpur, 1994) (Supervisor: Professor S. Ranganathan) Postdoctoral Fellow (University of Birmingham, UK and University of California, Los Angeles, USA; Mentor: Professor J.F. Stoddart)

Research areas:

Carbohydrate chemistry, carbohydrate-protein interactions, dendrimers and hyperbranched macromolecules, liquid crystals, organic synthesis and organometallic chemistry

Awards and Honors:

Young Observer, IUPAC General Assembly, Ottawa, August 2003.
Professor Swaminathan Endowment Lecture, University of Madras, 2007

Observation of an Anomalous Luminiscence Property in Poly(Propyl Ether Imine) (PETIM) Dendrimers

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Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012

Poly(propyl ether imine) (PETIM) dendrimers possess repeating units consisting of tertiary amine, ether and propyl groups. A divergent synthetic method has been established to prepare the series of PETIM dendrimers up to six generations, requiring the iterative reactions of alternating Michael reactions and functional group reductions. The molecular structure of a fifth generation dendrimers is shown in **Figure 1**. In studying the properties of dendrimers, we have identified recently that the dendrimers exhibit emission behavior, in spite of not having any chromophore or fluorphore within the molecular structure. A systematic study was conducted and it was found that the dendrimers present a λ_{em} at 390 nm, with λ_{ex} 330 nm, in a range of hydroxylic solvents (**Figure 2**), namely, water, MeOH and ethylene glycols. The emission intensity is solvent viscosity dependent, pH dependent, with acidic pH having more pronounced emission intensity. The emission profile is temperature independent, nor exposure to air, nitrogen and aging of the solutions for several months affect the fluorescence. The quantum yields are up to 5%, as measured by a relative method, and there exists at least two species with life times ~3 ns and ~7 ns, responsible for the emission behavior. Further efforts showed that few inorganic anions, such as perchlorate, periodate, nitrite and pyridinium methyliodide, could quench the fluorescence to varied extent and quantified by the classic Stern-Volmer constants. The presentation will provide the results of the fluorescence behavior of the PETIM dendrimers briefly.

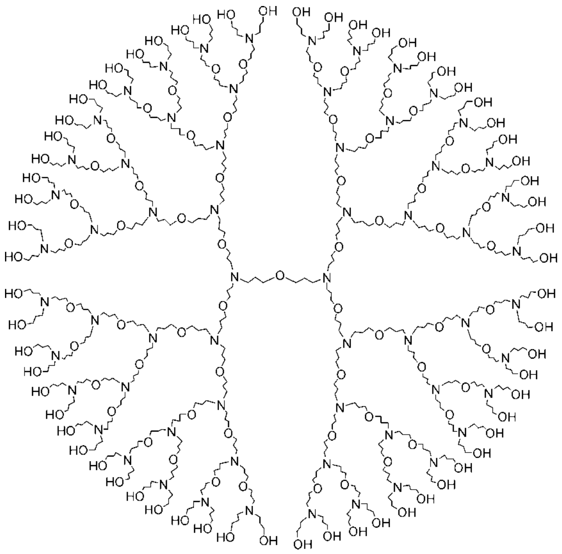

Figure 1. Molecular structure of a fifth generation hydroxyl group terminated PETIM dendrimer.

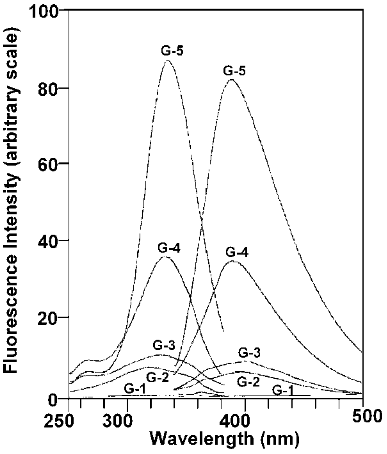

Figure 2. Emission and excitation spectra of PETIM dendrimer generations in MeOH (0.5 mM). λ_{ex} = 330 nm.

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1. International Academy of Quantum Molecular Science (IAQMS) Annual Award, 1978
2. The Chemical Society Award, The Chemical Society of Japan, 1992
3. The Schrödinger Medal, The World Association of Theoretical Organic Chemists (WATOC), 1993
4. The Fukui Medal, Asian Pacific Association of Theoretical & Computational Chemists, 2005

Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions

Keiji Morokuma

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The chemical reaction which creates, destroys, reorganizes chemical bonds to produce new compounds is the most important subject of chemistry. I have been absorbed by this fascinating world of chemistry from the beginning of my career almost fifty years ago, when a hand-powered calculator was used to solve Hückel secular equations for frontier electron densities of simple aromatic hydrocarbons. Theoretical/computational studies have come a long way and are now playing the central role in understanding the mechanism and dynamics of chemical reactions and in helping designing more useful chemical reactions and catalysts. The theory can study not only the reaction of the ground state of molecules in gas phase but also reactions of excited electronic states as well complicated reactions of complex molecular systems. The information theoretical/computational studies can provide is often complementary to the information experimental studies provide, and research on chemical reactions is becoming impossible without strong collaboration between theorists and experimentalists.

I will discuss recent examples of our own theoretical/computational studies on A. gas phase photochemical and ion-molecule reactions of small molecules and ions; C. self-assembly reactions of small carbon clusters to form fullerenes and carbon nanotubes; B. homogeneous catalytic reactions and reactions of transition metal and organometallic compounds; and D. reactions of metalloenzymes and the effects of protein environment.

Reference:

K. Morokuma, Theoretical Studies of Chemical Reactions – A Fascinating World of Chemistry from Gas Phase Elementary Reactions through Nanostructure Formation and Homogeneous Catalysis to Reactions of Metalloenzymes, Bull. Chem. Soc. Jpn, 80, 2247-2261 (2007).

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Princeton University, Ph.D. 1972
H. C. Ørsted Institute, Postdoctoral Fellow 1973 – 1974
California Institute of Technology, Postdoctoral Fellow 1974 - 1975

Research Areas:
The fields of Physical-Inorganic and Bioinorganic Chemistry emphasizing the application of a wide variety of spectroscopic and computational methods to determine the electronic structure of transition metal complexes. Areas of present interest include:

1) Electronic structure contributions to electron transfer in blue copper, Cu_A and iron sulfur sites;
2) O_2 and N_2O activation by Cu cluster active sites;
3) Structure/function correlations over non-heme iron enzymes;
4) Development of new spectroscopic and electronic structure methods in bioinorganic chemistry.

Honors and Awards:
1. Monroe E. Spaght Professor of Humanities and Sciences and SSRL Professor
2. Dean's Award of Distinguished Teaching
3. ACS Awards: Inorganic Chemistry, Distinguished Service in the Advancement of Inorganic Chemistry, Ira Remsen Award
4. Centenary Medal from the Royal Society of Chemistry, UK
5. Wheland Medal from the University of Chicago
6. Bailar Medal from the University of Illinois
7. Numerous lectureships including First Glen Seaborg Lecturer (U C Berkeley)
8. National Academy of Sciences, American Academy of Arts and Sciences and Fellow, American Academy for the Advancement of Science

Spectroscopic Methods in Bioinorganic Chemistry: Blue to Green to Red Copper Sites

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A wide variety of spectroscopic methods are now available which provide complimentary insights into the electronic structures of transition metal complexes. Combined with calculations these define key bonding interactions, enable evaluation of reaction coordinates, and determine the origins of unique spectroscopic features/electronic structures that can activate metal centers for catalysis. This presentation will summarize the contributions of a range of spectroscopic methods combined with calculations in elucidating the electronic structure of an active site using the blue copper site as an example. The contribution of electronic structure to electron transfer reactivity will be considered in terms of anisotropic covalency, electron transfer pathways and protein contributions to the geometric and electronic structure of blue copper related active sites.

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Research areas:
Physical Chemistry
Analytical Chemistry

Honors/Awards:

1. George C. Pimentel Award in Chemical Education, American Chemical Society, 2008
2. Honorary Fellowship, Chemical Research Society of India (CRSI), 2007
3. Dudley R. Herschbach Award for Excellence in Research in the field of Collision Dynamics, Dynamics of Molecular Collisions Meeting, Santa Fe, 2007
4. Honorary Doctorate, Chalmers Institute of Technology, Göteborg, Sweden, 2007
5. Oesper Award, University of Cincinnati and Cincinnati Section of the American Chemical Society, 2006
6. Chandler Medal, Department of Chemistry, Columbia University, 2005
7. Pupin Medal “for service to the nation,” Columbia University School of Engineering, 2005
8. Wolf Prize in Chemistry, Israel, 2005
9. Nichols Medal, New York Section of the American Chemical Society, 2005
10. James Flack Norris Award for Outstanding Achievement in the Teaching of Chemistry, Northeastern Section of the American Chemical Society, 2004

Make It Count: Quantitating Low-Copy-Number Proteins in a Single Cell by Direct Counting

Richard N. Zare

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One of the great challenges in chemistry is to penetrate the world of the ultra small, to view nearly infinitesimal spaces, and to recognize their importance. Indeed, the analysis and manipulation of volumes so tiny that they are almost beyond comprehension is a critical element of the emerging field of chemical nanosciences and nanotechnology. These capabilities unlock secrets of nature. These secrets underlie how cells function, how reactions occur, how energy and information is stored and transported and how such structures can be tailored to be useful devices for mankind from sensors to motors to computers. I want to take this opportunity to present my own adventures in exploring how to analyze the chemical contents of individual cells.

Several studies have reported recently the ability to examine individual proteins inside a single cell using labeling reactions followed by fluorescence detection. This approach, however, is limited to special cases where the environment of the cell does not cause changes in the fluorescence of the reporter molecules and where quenching and endogenous fluorescence does not interfere with measurements. Moreover, in vivo approaches are restricted to viewing one or perhaps a few species at the same time. We are pioneering a different approach, which is based on manipulating, capturing, and lysing an individual cell, labeling of the contents, if necessary, followed by the analysis of the single cell lysate using electrokinetic separations. Specifically, we have developed a microfluidics device that can quantify the low-copy-number protein or protein complexes in a single cell using single-molecule counting.

This presentation will describe the hardware necessary to accomplish this task and illustrate its application to naturally fluorescent compounds found in cyanobacteria and to nonfluorescent proteins found in an insect cell. Future directions will be proposed for continuing these studies. Support from the U.S. National Science Foundation is gratefully acknowledged.

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Carbohydrate Chemistry and Biology: New Challenges and Opportunities

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Protein glycosylation is the most complex post-translational process; more than 90 percent of human proteins are glycosylated. The significance of glycosylation at the molecular level is however not well understood, and as such the pace for the development of carbohydrate-based drug discovery and diagnosis is relatively slow. It is thus important to develop new tools to study the effect of glycosylation on the structure and function of proteins and other biologically active molecules. This lecture will focus on the development of new methods for the synthesis of homogenious glycoproteins with well defined glycan structure, glycoarrays for the high-throughput analysis of protein-glycan interaction and design of click-induced fluorescent probes for use to identify new cancer biomarkers for diagnosis and drug discovery.

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Honors/Awards:
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3. Photon Science Institute, The University of Manchester, fellow

Weak noncovalent interactions among biomolecular building blocks can be surprisingly strong

Pavel Hobza

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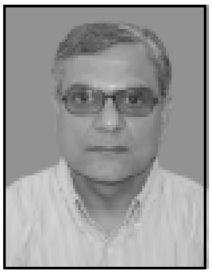
Stabilization energies of noncovalently bound molecular clusters playing a role in biodisciplines are investigated. Specifically, we consider H-bonded and stacked structures of DNA base pairs and amino acid pairs in the gas phase as well as within various chemical environments. Structures of pairs are either optimized or taken from experiment. Benchmark stabilization energies of complexes studied are determined at the Complete Basis Set (CBS) limit of the CCSD(T) calculations. The role of CCSDT level is also discussed. Resulting stabilization energies of H-bonded and stacked pairs are very larger, much larger than considered before. This is especially true about stacked DNA base pairs and amino acid pairs. Stabilization energies of these structures originate exclusively in the London dispersion energy and only high-level wave function theories can be applied. The partitioning of the total interaction energy to the components is performed using the DFT-SAPT method. The use of density functional theories, including the recently introduced hybrid meta GGA functionals, is discussed.



Professor Ashwini Nangia is at the School of Chemistry, University of Hyderabad. His research interests are in host–guest inclusion compounds, crystal design via hydrogen bonds and halogen bonds, and polymorphism. He is Topic Editor of ACS journal *Crystal Growth & Design*. He is a Fellow of the Indian Academy of Sciences and the Royal Society of Chemistry.

Hydrogen Bonding in Multi-functional Crystals

Ashwini Nangia

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A major challenge in the crystal engineering of multi-functional molecules is to know *apriori* how the individual functional groups will interact when several of them are simultaneously competing with each other. It is important to understand self-assembly in the “real” competitive milieu to rank H bond preferences in complex chemical systems. Not only the nature of functional groups but also their placement in the molecule, e.g. regioisomeric compounds, can change the intermolecular interactions or synthons in the crystal structure. With this objective we analyzed hydrogen bonding and crystal packing in *N*-X-phenyl-*N*¢*p*-nitrophenyl ureas (X = H, F, Cl, Br, I, CN, C°CH, CONH$_2$, COCH$_3$, OH, Me). These structures are classified into two families depending on the hydrogen bond pattern: urea tape structures contain the well-known a-network assembled *via* N–H···O hydrogen bonds. In non-urea tape structures the N–H donors H bond with NO$_2$ group or solvent O acceptor atoms but the C=O group hardly accepts strong H bonds. A structural model to understand how functional group, molecular conformation, hydrogen bonding, and crystal packing are closely related and influence each other in subtle yet definitive ways is presented for diaryl ureas. A supramolecular HSAB principle for crystal engineering of multi-functional molecules emerges from this study.

Crystal Structures of N-Aryl-N¢4-Nitrophenyl Ureas: Molecular Conformation and Weak Interactions Direct the Strong Hydrogen Bond Synthon

References:

L. S. Reddy, S. K. Chandran, S. George, N. J. Babu, and A. Nangia
Cryst. Growth Des., **2007**, *7*, DOI: 10.1021/cg070155j.

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Education :
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Research areas :
Theoretical and Computational

Honors/Awards :

1. Fellow of the Indian Academy of Sciences, Bangalore (1992)
2. Shanti Swarup Bhatnagar Prize in Chemical Sciences (1993)
3. Fellow of the Indian National Science Academy, New Delhi (1996)
4. J. C. Bose National Fellowship (2007).

Electrostatics and Molecular Tailoring for Exploring Molecular Clusters

Shridhar R. Gadre

Department of Chemistry, University of Pune, Pune 411 007.

Structures and properties of weakly bound molecular clusters have attracted considerable attention over the last two decades. These clusters are experimentally probed by employing several spectroscopic methods. Electrostatic complementary of interacting moieties can be exploited[1] for building up the initial geometries of such clusters. These are subsequently optimized employing HF, DFT or MP2 level of theory. Molecular Tailoring Approach (MTA), a linar scaling method developed in our group, has been employed for geometry optimization of large molecular clusters. Several applications such as hydration[2] of crown ether; IR spectra of acetylene[3] in argon and nitrogen matrices as well as $(CO_2)_n$ clusters; estimation of intramolecular O-H…. interaction energies[4] etc. will be presented.

Acknowledgements : Financial support from C-DAC and NRB is gratefully acknowledged.

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4. M. M. Deshmukh, L. J. Bartolotti and S. R. Gadre, J. Phys. Chem. A 110, 12519 (2006); M. M. Deshmukh, C. H. Suresh and S. R. Gadre, J. Phys. Chem. A 111, 6472 (2007).

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Education:
Ph.D. in Chemistry

Research areas:
Supersonic jet spectroscopy, Spectroscopy of *van der Waal's* and H-bonded clusters, Investigations of intramolecular phenomena under jet cooled conditions.

ZEKE Probe for Isomer Assignment of Hydroquinone-water Complex

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In recent years the study of van der Waals and hydrogen-bonded interactions has been a subject of lot of interest for a simple reason, viz., the bulk properties of most of the materials are manifestations of these weak interactions. In this context various spectroscopic techniques are used to obtain the microscopic details of such complexes. In this talk I will describe the use of the ZEKE photoelectron spectroscopic method to assign the isomer specific REMPI spectrum of the hydroquinone-water complex.

Like the monomer the Hydroquinone-Water 1:1 complex (HQW) also shows the presence of two isomers, each belonging to the cis and trans monomeric precursor. The LIF as well as the REMPI spectrum of the HQW complex show characteristics very similar to that of the monomer spectrum i.e. transitions due to both isomers are present, the band origins are separated by similar amount, and the Franck-Condon activity among various normal modes is also very similar to that of the monomer. Therefore the assignment of the transitions in the REMPI spectrum of the HQW complex was done using an analogy to that of the monomer i.e. the lowest energy Band origin transition and features associated with it were assigned to the trans conformer. There has not been any direct spectroscopic evidence to support this assignment. Besides, the ab-initio computed relative energies of the cis and trans conformer show trend exactly opposite to that of the monomer, i.e., the cis–HQW complex is computed to be more stable in the ground state relative to the trans conformer. The observed relative ratio of the two BO transition intensities however does not support the theoretical results. Hence there is some amount of ambiguity in the assignments of the HQW complex isomers. In order to resolve this issue we have resorted to the ZEKE spectroscopy of complex as the ZEKE spectrum of the monomer shows that the two isomers have different FC activity in a few normal modes. I will present the ZEKE spectroscopic data on these complexes obtained in our laboratory and discuss the assignments based on this data.

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Education
Banaras Hindu University, Varanasi , Ph. D. (1980)
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Research Area:
Radical ion chemistry
Development of Newer Synthetic Methodology
Total Synthesis of Natural Products

Honors:

1. S. S. Bhatnagar Prize
2. B. M. Birla Science Prize
3. Vigyan Ratna, Govt. U.P.
4. J. C. Bose Fellowship
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ODYSSEY WITH RADICAL IONS

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Our research endeavor over the years revolves around developing a comprehensive and fundamental approach towards generating and understanding the dynamics of radical ions. The intent has been to develop systematically this field for achieving selectivity in creating radical ion pairs in polyfunctional organic molecules for synthetic manipulations. The basic understanding of the dynamics of these radical ion species has generated fundamentally new chemistry from a variety of substrates. For example, direct nucleophilic substitution of arenes has been achieved via arene radical cation. An important application of this chemistry is demonstrated by stereoselective synthesis of Montanine type of alkaloids. Amine radical cations which upon loosing proton or trimethyl silyl group from their *alpha* position, culminated in the convenient generation of important reactive intermediates viz., nitrones, iminium cation, a-amino radical and azomethine ylides. The significance of the methodology has been shown either by synthesizing appropriate natural product or a suitable precursor.

Furthermore, a new and non-conventional approach for the generation of electrophilic selenium species (PhSe+) for performing important selenoetherification reaction and an organic way of effecting enyne cyclization has been developed. Another interesting concept of PET-reactions is designed for redox reactions using triphenylphosphine as sacrificial electron donor. This particular discovery has led to develop a strategy of harnessing solar light into chemical energy useful for initiating new reaction strategies.

Inexorable pleasant voyage with radical ions in organic synthesis would be shared.

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Education :
Dr. Faiz Ahmed Khan was born in Koppal (Karnataka), India in 1965 and graduated with a M.Sc. degree in Organic Chemistry in 1987, from Gulbarga University. He obtained Ph.D. in the field synthetic organic chemistry from University of Hyderabad in 1994 and subsequently held postdoctoral position (Humboldt Fellow) at the Technische Universität Dresden Germany, prior to joining IIT Kanpur in 1996.

Research Interests:
His research interests are in the area of Synthetic Organic Chemistry, Transition Metal-Mediated Reactions in Organic Synthesis, Discovery of New Methodologies and Control of Stereochemistry in Organic Synthesis, Chemical Synthesis in Ionic Liquids, and Supported Catalysts.

Honors/Awards:

Dr. Khan is the recipient of INSA medal for Young Scientist (1997), Young Associate of the Indian Academy of Sciences Bangalore (1997), A.K. Bose Memorial Award by INSA (2001), B. M. Birla Science Prize in Chemical Sciences (2003), Young Muslim Scientist Award (2003) by the Muslim Association for the Advancement of Science – MAAS, Swarnajayanti Fellowship in Chemical Sciences (2003), B.M. Birla Science Prize (2003) and AVRA Young Scientist Award (2006).

Applications of Norbornyl a-Diketone Building Blocks in Natural and Unnatural Products Syntheses

Faiz Ahmed Khan

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The tetrachloronorbornene derivatives have been serving as important building blocks by rendering themselves as a powerful, inextricable template in the synthesis of complex natural and unnatural products.[1] We have reported, for the first time, the selective exploitation of bridgehead halogens for C-C bond formation[2] and subsequently disclosed[3] the utility of vinylic halogens to obtain synthetically useful a-diketones in high yield via ruthenium catalyzed oxidation.[3] Novel and structurally diverse molecular entities were synthesized expeditiously utilizing the norbornyl a-diketones as building blocks.[4] Some recent results in this direction from our group will be discussed.

References:

1. Khan, F. A.; Prabhudas, B.; Dash, J. *J. Prakt. Chem.* **2000**, *342*, 512.
2. Khan, F. A.; Prabhudas, B. *Tetrahedron Lett.* **1999**, *40*, 9289.
3. a) Khan, F. A.; Prabhudas, B.; Dash, J.; Sahu, N. *J. Am. Chem. Soc.*, **2000**, *122*, 9558. b) Khan, F. A.; Sahu, N. *J. Catal.* **2005**, *231*, 438.
4. For some applications of norbornyl ?-diketones from our group, see: a) Khan, F. A.; Dash, J.; Sahu, N.; Gupta, S. *Org. Lett.* **2002**, *4*, 1015. b) Khan, F. A.; Dash, J. *J. Am. Chem. Soc.* **2002**, *124*, 2424. c) Khan, F. A.; Dash, J.; Sahu, N.; Sudheer, Ch. *J. Org. Chem.* **2002**, *67*, 3783. d) Khan, F. A.; Dash, J. *J. Org. Chem.* **2003**, *68*, 4556. e) Khan, F. A.; Dash, J.; Sudheer, Ch. *Chem. Eur. J.* **2004**, *10*, 2507. f) Khan, F. A.; Dash, J. *Eur. J. Org. Chem.*, **2004**, 2692. g) Khan, F. A.; Satapathy, R; Dash, J.; Savitha, G. *J. Org. Chem.*, **2004**, *69*, 5295. h) Khan, F. A.; Dash, J.; Rout, B. *Tetrahedron Lett.* **2004**, *45*, 9285. i) Khan, F. A.; Satapathy, R.; Sudheer, Ch.; Rao, C. N. *Tetrahedron Lett.* **2005**, *46*, 7193. j) Khan, F. A.; Dash, J.; Sudheer, Ch.; Sahu, N.; Parasuraman, K. *J. Org. Chem.* **2005**, *70*, 7565. k) Khan, F. A.; Rout, B. *Tetrahedron Lett.* **2006**, *47*, 5251. l) Khan, F. A.; Rao, C. N. *Tetrahedron Lett.* **2006**, *47*, 7567. m) Khan, F. A.; Dwivedi, V.; Rout, B. *Tetrahedron Lett.* **2007**, *48*, 207. n) Khan, F. A.; Krishnakumar, K. S.; Sudheer, Ch. *Synthesis*, **2007**, 1054. o) Khan, F. A.; Rao, G. H. M.; Satapathy, R.; Karuppasamy P. *Org. Lett.* **2007**, *9*, 1581. p) Khan, F. A.; Sudheer, Ch.; Soma, L. *Chem. Commun.* **2007**, 4239.

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Coordination chemistry, Organometallic chemistry

Studies on Some Metal-assisted Ligand Transformations

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Metal-assisted transformations of organic functionalities are of immense interest primarily due to the continuous pursuit for new and convenient synthetic methods and regio- and stereoselective processes. We have been working on transition metal complexes with various hydrazine based Schiff bases for quite sometime. During our study, we have encountered some metal-assisted transformations of ligands. These transformations are due to imine to imidate conversion, reductive amination of imine, oxidative C-C coupling and activation of C-H followed by C-P bond formation. These results will be discussed in this presentation.

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Research areas:
Synthesis of designed metal complexes for structural study, structure-property correlation, metal-promoted organic transformation, photoactive supramolecular metal complexes to study energy/electron processes and molecular sensor for ion recognition.

Honors/Awards:
BOYSCAST Fellowship was awarded by DST, Govt. of India.

Polypyridyl-Based Metal Complexes of Ruthenium(II) and/or Osmium(II): Synthesis, Characterization, Photoinduced Activity and Ion Recognition Study

Parimal Paul

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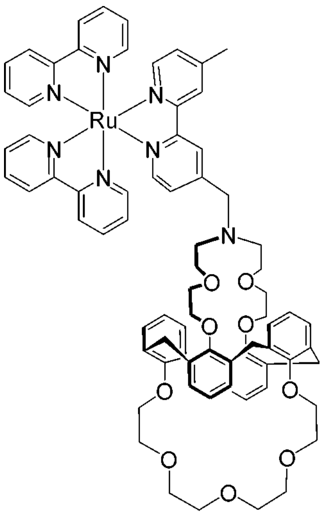

Photoactive metal complexes are currently being much investigated because of their rich photophysical properties and potential applications as electronic and photomolecular devices. A judicious choice of building blocks and spacers, and an appropriate designing of the structure can, in fact, allow the occurrence of intramolecular energy/electron transfer processes. Covalent linking of a suitable ionophore with the photoactive center also serves as a fluorescent molecular sensor, which is an important area and has been widely used by chemists, biologists and environmentalists for the recognition of various ions. In these systems, the key component is the spacers, the size, shape and electronic nature of the bridge controls the electronic communication between the chromophores. New spacers containing fully conjugated extended aromatic moieties, and their homo- and heterometallic bi- and oligonuclear complexes of ruthenium(II) and osmium(II) have been synthesized. All of these complexes exhibit interesting solution property as evident from concentration dependent ^{1}H NMR and mass spectrometry. Electrochemical behaviour of these complexes has also been studied. These complexes also exhibit strong metal-to-ligand charge transfer (MLCT) absorption and ^{3}MLCT luminescence at room temperature. The luminescence intensity and emission lifetime data suggest that in the heterodinuclear complexes energy transfer from Ru(II) to Os(II) center occur across the bridging ligand.

A series of new fluoroionophores comprising of azacrown or calix-crown hybrid molecule as ionophore and Ru(II)-bipyridyl/Re(I)-carbonyl moiety as fluorophore (as shown in the figure) have been synthesized and characterized. All of the Ru(II)-based fluoroionophores exhibit strong ^{3}MLCT luminescence at room temperature. Ion recognition property of these fluoroionophores has been evaluated on the basis of changes in luminescence property using various metal ions under different experimental conditions. Electrochemical and other spectroscopic properties of theses complexes have also been studies. All these results will be presented.

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Educational Qualifications:

Degree	Year	Institution	Field
B.Sc. (spl.)	1973	Osmania University	Chemistry
M.Sc.	1975	Osmania University	Organic Chemistry
Ph.D.	1980	Indian Institute of Science (Bangalore)	Organic Chemistry

Research Background:

1975-80:	Ph. D, Indian Institute of Science, Bangalore.
1980-82	(PDF) Rice University, Houston, 1982-85 (PDF) University of Minnesota, Minneapolis, and 1984-85 (PDF): University of Hyderabad, Hyderabad (PDF).
1999-2K & 2K2:	(Visiting Scientist): University of Nijmegen, Nijmegen.

Current Research Interests:
Synthesis and stereochemistry of sulfur, nitrogen and oxygen heterocycles; Asymmetric synthesis with chiral amino-alcohols.

Teaching:

1985-88:	North-Eastern Hill University, Shillong, Meghalaya.
1988 – Present:	Department of Chemistry, Pondicherry University, Puducherry.

Academic Distinctions:
1. National Merit Citation, 1969; National Associate Award, UGC, India, 1985-88.
2. S.I. Perumal Endowment Award, 1997.
3. Visiting Professor, North-Eastern Hill University, Shillong, Meghalaya, May-June, 1998.
4. Editorial Board Member, *Indian Journal of Heterocyclic Chemistry* (India).
5. NSR Center Award, University of Nijmegen, The Netherlands, 1999-2000 & 2002.
6. National Organic Symposium Trust 2007-2011 – Council member;
7. IGNOU – Expert in Organic Chemistry; NAAC – National Panel of Experts

Ketene dithioacetal chemistry: Synthesis of heterocyclic non-natural amino acids and thiophenes

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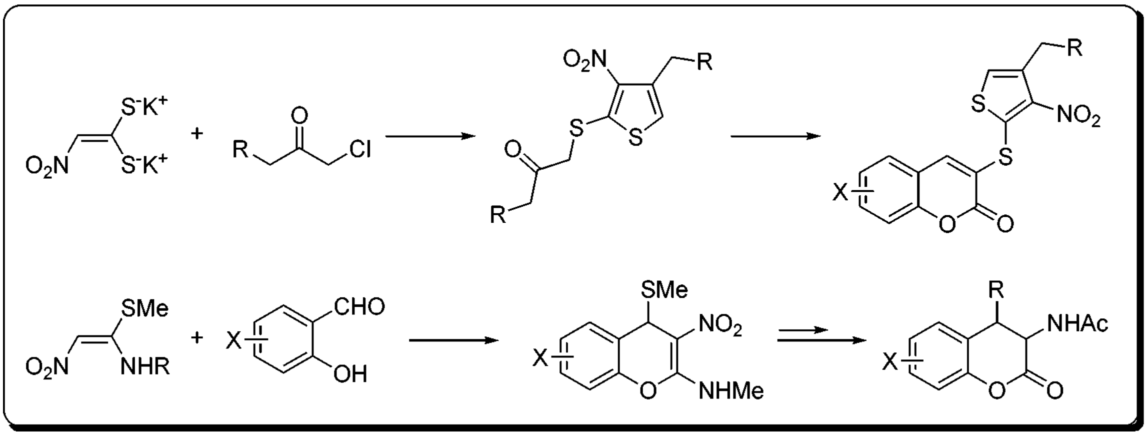
The ketene dithioacetals are versatile two-carbon synthones amenable for reactions with a variety of nucleophiles to provide heterocyclic molecules of biological importance. The ketene dithioacetals can be assembled readily from carbon disulfide, active methylene compound and alkylating agent. For example, the potassium hydroxide mediated condensation of carbon disulfide with nitromethane produces dipotassium salt of nitroketene dithioacetate, which on alkylation with alkyl halide with neighboring electrophilic center provides 3-nitrothiophenes. The thiophenes on condensation with salicylaldehydes provide 3-nitro-2-thienyl-sulfanylcoumarins. Similarly, the condensation reactions of ketene dithioacetals with molecular entities possessing nucleophilic and electrophilic centers furnish coumarins, chromenes, flavone-coumarin hybrids etc. Further synthetic elaboration of chromene products provides some unusual amino acids, like isomers of DOPA. Above and other latest results from our laboratory will be disclosed in the symposium.



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ii. Rao, H. S. P.; Sivakumar, S. *J. Org. Chem.* **2006**, *71*, 8715 – 8723.
iii. Rao, H. S. P.; Sivakumar, S. *Beilstein J. Org. Chem.* **2007**, *3*:31 (doi:10.1186/1860-5397-3-31.

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Education : .
Prof.Chattoraj passed Matriculation Examination in 1944. He obtained B.Sc (Hons) degree in Chemistry in 1949 and M.Sc degree in Chemistry with Physical Chemistry as special paper in 1951 both from the University of Cacutta. He started his research work on Stability of Hydrophobic Colloids and got PhD degree in Chemistry in 1957 Later on he carried out independent research on Thermodynamics of Adsorption and was awarded D.Sc degree from the Calcutta University.

Research Areas:
Research areas of Professor Chattoraj is mainly Surface Science including Monolayers, Adsorption of surfactants and Bioplymers on solid –liquid, liquid-liquid and vapor –solid interfaces, electrophoresis of adsorbed biopolymers ,surfactant –biopolymer binding interaction, food emulsions, colloidal properties of human bile ,protein-nucleic acid and protein- lipid interactions etc.He has published altogether 170 papers. Along with Prof.K.S.Birdi, he published a Monograph entitled " Adsorption and Gibbs Surface Excess" published by Plenum Press ,New York.(1984)

Honors/ Awards : Prof.Chattoraj delivered Professor J N Mukherjee Award Lecture {2006) and Professor P.K.Bose Memorial Lecture (1996) of Indian Chemical Society and was presented life –time Achievement award in 2007 for his contributions in Chemical Sciences He also delivered .Professor B.N. Ghosh Memorial Award Lecture (2003))of Indian Society of Surface Science and Technology and ,Prof. Sushil Mukherjee 90th Birthday Oration Award in the same, year sponsored by West Bengal Academy of Science and Technology ,, Prof.Chattoraj received P.C.Ray Memorial Award from 93rd Indian Science Congress Assciation for his Life Time Achievement in Surface Chemistry and Biophysical Chemistry. He also served as Sectional President in Biochemistry, Biophysics and Molecular Biology in 80th Session of ISCA(1993).Prof.Chattoraj was elected Fellow of INSA (1989) and Foundation Fellow of West Bengal Academy of Science and Technology.

GIBBS EXCESS ADSORPTION & BINDING INTERACTION OF COMPONENTS IN CEMICAL AND BIOLOGICAL SYSTEMS

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Excess adsorption of solute and solvent on solid-liquid solid-gas, liquid –liquid and ,liquid-gas systems respectively have been discussed in terms of absolute compositions of solute and solvent components forming inhomogeneous state of the surface phase The absolute surface composition of the components in all these systems will always be positive or zero but never negative. In contrast to this, the excess concentrations of these components may be positive, negative or zero depending upon the bulk composition of the solution. The Magic feature of the Gibbs dividing plane in this respect has been quantitatively explained. The Gibbs adsorption equations valid for all these systems have been properly integrated to obtain expressions for the standard free energy of adsorption whose values are either positive or negative. Similar to the adsorption process, excess binding of surface –active solute or neutral salt to biopolymer or their mixtures in aqueous media have been evaluated from experiments and absolute binding of solute and solvent components and free energies of excess binding of components respectively have been evaluated using same types of procedures followed for adsorption process.

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Theoretical Electrochemistry: Some Perspectives

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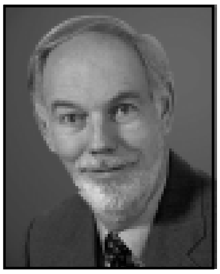
The role of theory in providing the basis for understanding electrochemical phenomena as well as a framework for generalising/ unifying these is the central theme of this talk. Questions posed at various levels viz.macroscopic, molecular and electronic are considered as illustrations.



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Research Interests:
Inorganic and bioinorganic chemistry.
Synthesis, reactivity and structure determination of transition metal complexes; mechanism of electron transfer reactions; polynuclear metal centers in chemistry and biology.

Education and Postdoctoral Training:
Diplom-Chemiker Hauptexamen 1967, Universität Heidelberg;
Ph.D.: Institut für Anorganische Chemie, Universität Heidelberg(laboratory of Professor Hans Siebert), 1969;
Postdoctoral Fellow, Universität Heidelberg, Institut für Anorganische Chemie (laboratory Professor H. Siebert and Professor J. Weiss), 1969 - 1972;
Sabbatical leave, University of Leeds (England)
(laboratory of Professor A.G. Sykes), 1972 - 1973;
Habilitation at the Universität Heidelberg, 1974.

Awards:

1. French-German Alexander von Humboldt Research Award, April 1995
2. Wilhelm-Klemm-Medal, German Chemical Society, 2000
3. John-Bailar-Medal, University of Illinois, 2000
4. Centenary Medal, Royal Society of Chemistry (London), 2002
5. ACS Award in Inorganic Chemistry, 2006
6. Ruhrpreis, 2005

Memberships:

GDCh
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Royal Society of Chemistry
Elected Member of the Deutsche Akademie der Naturforscher Leopoldina
Honorary Member of the Chemical Research Society of India

Academic Career:
Director at the Max-Planck-Institut für Bioanorganische Chemie,
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August 1994 – present
Professor of Inorganic Chemistry, Ruhr-Universität Bochum, Germany
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Associate Professor of Inorganic Chemistry, Universität Hannover, Germany
1975 - 1981
Assistant Professor of Inorganic Chemistry, Universität Heidelberg, Germany
1974 - 1975

Coordination Chemistry with Radicals: Where are the (Valence) Electrons?

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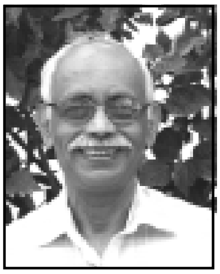
For any coordination compound, educated chemists can derive a *formal* oxidation number for the central metal ion by applying a given set of rules. It has been taught that you cannot *measure* this formal number since it has no real, physical basis. That's fine. On the other hand, when chemists talk about an iron(III) complex they often imply a well-defined d^n electron configuration (in this case n = 5), which is a measurable quantity. In other words, we no longer mean formal oxidation numbers but physical (or spectroscopic) oxidation states (C. K. Jørgensen). In common practice, these two (formal and spectroscopic oxidation numbers) are often used as synonyms – they are not!! The concept of innocent *vs.* non-innocent ligands (C. K. Jørgensen) is accepted by the community but requires the use of physical oxidation numbers.

I will demonstrate how difficult life can be when organic radicals are coordinated to open-shell transition metal ions.



Professor Ramasesha obtained his MSc and PhD degrees from IIT Kanpur. He was a postdoctoral fellow at IISc, Bangalore, Oxford University, UK, Louisiana State University, USA and Princeton University, USA, before taking up a faculty position at IISc in 1984, where he continues as a professor in the Solid State and Structural Chemistry Unit. His research interests are development and application of numerical quantum many-body methods for the study of electronic structure of conjugated systems, intermolecular electronic processes in organic electronic devices, low-dimensional magnets, single molecule magnets and photomagnets. He has extensive research collaborations in India and abroad. He has been a visiting professor at Princeton University; University of Arizona; Bordeaux University; Ecole Normale Superiere, Cachan, and ISMN, Bologna.

Modeling Strongly Correlated Systems in Chemistry and Physics

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The role of electron correlations in determining optical, electronic and magnetic properties of atoms, molecules and solids has been recognized almost from the beginning of quantum mechanics. However, a quantitative study of electron correlation effects has been difficult for mathematical and theoretical reasons. The study of correlated electronic structure theory in large systems requires developing theoretical models as well as numerical techniques for their solution. In this talk model Hamiltonians used in studying electronic and magnetic properties of molecular as well as low-dimensional systems will be introduced. This will be followed by a brief overview of numerical methods such as exact diagonalization [1] methods, density matrix renormalization group methods [2,3] and quantum Monte Carlo methods [4] for obtaining low-lying states, thermal properties and dynamic properties of correlated model Hamiltonians. Some applications of these methods to dimerized and frustrated spin chains [5], single molecule magnets [6], conjugated polymers [7] and electronic processes in organic light emitting diodes [8,9] will be discussed.

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2. **S. Ramasesha**, Swapan K. Pati, Z. Shuai and J.L. Br´edas, (2000) “The density matrix renormalization group method: Application to the low-lying electronic states in conjugated polymers”, Advances in Quantum Chemistry **38**, 121.

3. S.K. Pati, **S. Ramasesha** and D. Sen, (2002) “Exact and approximate theoretical techniques for quantum magnetism in low-dimensions”,Magnetism Molecules to Materials Vol 4 Eds. J.S. Miller and M.Drillon, Wiley VCH Series (New York).

4. M.P. Nightingale and C.J. Umrigar (Eds.) (1999), “Quantum Monte Carlo Methods in Physics and Chemistry”, NATO ASI Series, Kluwer Academic Publishers

5. R. Chitra, S.K. Pati, H.R. Krishnamurthy, D. Sen and S.Ramasesha, (1995), Phys. Rev. B **52**, 6581.

6. C. Raghu, I. Rudra, D. Sen and **S. Ramasesha**, (2001), Phys. Rev. B **64** 064419-1.

7. **S. Ramasesha** and Kunj Tandon, (1998) “Symmetrized DMRG method for conjugated polymers”, in Density Matrix Renormalization Eds. I. Peschel et al, Springer, Dresden.

8. M. Wohlgenannt, Kunj Tandon, S. Mazumdar, **S. Ramasesha** and Z.V. Var-deny, (2001) “Formation cross-sections of singlet-triplet excitons in p -conjugated polymers”, Nature, **409**, 494

9. Kunj Tandon, **S. Ramasesha** and Sumit Mazumdar, (2003), Phys. Rev. B **67**, 045109.

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M.Sc. (1985), Burdwan University
Ph.D. (1989), IACS, Kolkata

Research areas:
Targeted synthesis and characterization of paramagnetic 3d metal complex assemblies. Template ligand assisted inhibition of transition metal ion coordination driven hydrolysis and anion centered assembly.

Honors/Awards:
1. University Gold Medal (1985) and Barddhaman Sammilani Medal (1985).
2. Associate of Indian Academy of Sciences (1990-1995).
3. INSA Young Scientist Medal (1994).
4. IUPAC Affiliate Member (1992-1993; 1994-1995; 1999-2000).
5. Visiting Fellow of JNCASR (1995).
6. BOYSCAST fellow (1995).
7. AvH fellow (2002).
6. CRSI (Chemical Research Society of India) Bronze Medal (2008).

Use of Multinucleating Ligands for M_p (M = Co, Ni; p = 1, 2, 4) Complexes: Template Reactions and Coordination Assembly

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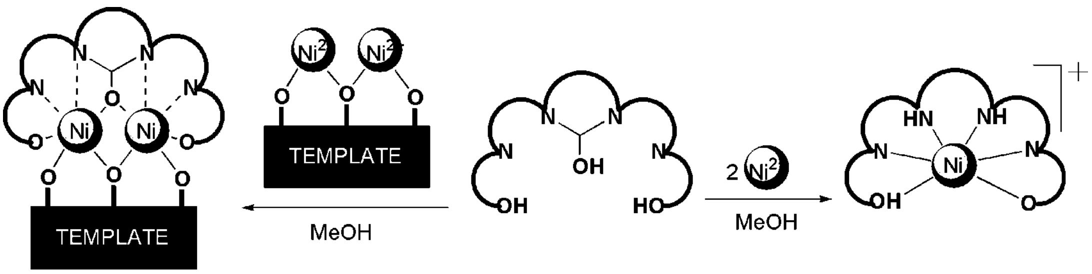
Complexation reactions of a multinucleating ligand H_3L, in certain conditions, with Mn^{III}, Fe^{III}, Co^{III}, or Cu^{II} lead to the hydrolysis of the central imidazolidine ring and even the destruction of one of the terminal imine bond. Ni^{II} also triggers the hydrolysis and the Ni_1 complex resulting from the hydrolyzed ligand, H_2L^1 can be isolated from the reaction medium. The hydrolysis can be prevented from the template reactions by use of 2-formylphenol (Hfp) and 2,6-diformyl-4-methylphenol (Hdfp) as co-ligands leading to stable Ni_2 complexes of H_3L. The first complex is a structural model of the active site of urease, featuring a carbonyl moiety (mimicking urea) coordinated to one Ni^{II} and one molecule of water to the other Ni^{II} center.



The substitution reaction of the coordinated water molecule was tested in a reaction with NaN_3 which provides a 1D chain complex that links Ni_2 neutral fragments by $(H_2O)NaN_3$ units. The co-ligand not only inhibits hydrolysis of L^{3-} but also serves as a template to stabilize bivalent cobalt ions in Co_2 complexes. The Ni_4 inverse metallacrown with the inverse 12-MC-4 motif, has been assembled *via* simultaneous chelation and bridging of butan-2,3-dionemonoxime and 2-amino ethanol.

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Education:
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Research areas:
Synthetic Organic Chemistry

Titanocene(III)-Mediated Radicals in Organic Synthesis

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Radical mediated reactions in modern synthetic organic chemistry has become an inevitable tool in recent years for stereoselective synthesis of complex bio-active naturally occurring compounds and related molecules. The discovery[1] of titanocene(III) chloride (Cp_2TiCl) as a radical generator has added a new dimension in this area of research. We have a significant contribution in this field for the last two decades or so by stereoselective synthesis of bio-active natural products[2] such as lignans, antitumour antibiotics, benzopyranone-natural products etc. We have also developed several novel and synthetically significant methodologies for the synthesis of medium-sized heterocyclic rings,[3] radical rearrangements etc[4] using the radical technology. Details will be discussed in the talk.

References:

1. T. V. RajanBabu and W. A. Nugent, *J. Am. Chem Soc*., 1994, *116*, 986.
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3. (a) B. Banerjee and S. C. Roy, *Eur. J. Org. Chem.*, 2006, 489; (b) S. K. Mandal and S. C. Roy, *Tetrahedron Lett.*, 2006, *47*, 1599.
4. (a) S. Jana, C. Guin and S. C. Roy, *Tetrahedron Lett.*, 2004, *45*, 6575; (b) S. Jana, C. Guin and S. C. Roy, *J. Org. Chem.*, 2005, *70*, 8252; (c) S. Jana, C. Guin and S. C. Roy, *Tetrahedron Lett*., 2005, *46*, 1155; (d) S. K. Mandal, S. Jana and S. C. Roy, *Tetrahedron Lett.*, 2005, *46*, 6115; (e) S. Jana and S. C. Roy, *Tetrahedron Lett.*, 2006, *47*, 5949.

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Molecular Dynamics Insights Into The Structure And Stability Of Collagen

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Collagen is an important protein due to its presence in the human body as well as its biomedical and commercial applications. The triple helical domain and the unique Gly-X_{AA}-Y_{AA} repeating triplet units are characteristic structural features of collagen [1]. The large size of collagen makes the direct study of structure and stability cumbersome. This is overcome through the use of the model collagen like peptides [2]. It is evident from earlier studies that the presence of proline and hydroxyproline in the X_{AA} and Y_{AA} positions confers maximum stability to model collagen like peptides whereas the presence of other amino acids in the same positions lead to variations in the global thermal stability and this also modulates the local stability [2]. Research in this area has raised several fundamental questions concerning the structure and stability of collagen. Some of which focused in this investigation are

- (i) What is the structural basis for the stability offered by various amino acids at X_{AA} and Y_{AA} positions?
- (ii) What is the minimum number of triplets necessary to carry out studies on the model collagen like peptides?
- (iii) What is the optimal amino acid sequence and composition for modeling collagen like peptides?
- (iv) What is the role of water around the collagen?

With a view to address these questions, a detailed classical molecular dynamics simulation has been carried out on various model collagen like peptides using AMBER force field employing the AMBER package. The molecular dynamics studies have provided valuable information about the origin of the stability, propensity of various amino acids to form collagen like conformation, hydrogen bonding pattern, significance of water and its dynamics. Molecular dynamics has also revealed importance of the other interactions involved in the stabilization of collagen [3, 4]. Salient observations and conclusions drawn from these studies would be presented.

References

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[2] B. Brodsky, A. V. Persikov, *Adv. Protein Chem.* 2005, *70*, 301.
[3] S. S. Raman, R. Parthasarathi, V. Subramanian, T. Ramasami, *J. Phys. Chem. B.* 2006, *110*, 20678.
[4] S. S. Raman, R. Parthasarathi, V. Subramanian, T. Ramasami, *J. Phys. Chem. B.* In Press.

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B.Sc(Hons)	Physics	Bangalore University	1969
M.Sc	Solid state physics	Bangalore University	1971
Ph.D	Organic Chemistry	IISc Bangalore	1976

Major area of research:
Chemical Crystallography and Materials Design

Honours and Awards:

Associate Member, Indian Academy of Sciences, 1983-1986
Young Scientist, CSIR, India 1987
Member, International Center for Diffraction Data 2002
Associate Editor, Journal of Indian Institute of Science 2002
Bronze Medal, Chemical Research Society India (CRSI) 2003
Editorial board, Bulletin of Materials, IASc 2005
Vice President, Indian Crystallographic Association 2005
Fellow of The Indian Academy of Sciences, 2005
Editorial Board, Acta Crystallographica E, 2007

Charge density Analysis in Molecular Crystals: A route to quantify weak and strong interactions?

T.N. Guru Row

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The role of intra- and inter-molecular interactions has been intensely studied in recent times, particularly in the context of supramolecular assembly and crystal engineering. The geometrical features analyzed by X-ray diffraction studies in molecular crystals have paved the way for the discovery of synthons[1]and subsequently to the characterization of weak and strong interactions based on bond lengths and angles. Designing new solids with desirable physical and chemical properties has been the main motivation of chemists and the emphasis is on the synthesis of representative model compounds to generate required packing modes of molecular species in a crystalline framework. The understanding of intermolecular interactions, the so-called elements of crystal engineering, is of paramount significance in this context. In their review on 'Chemical applications of X-ray charge density analysis' Koritsánszky and Coppens[2] concluded that 'X-ray charge density analysis has grown into a mature field and like in the development of structure determination, the methods have been standardized to a large extent so that more routine use becomes possible.' Analysis of charge density distributions in molecular crystals has received considerable attention in the last two decades both from high-resolution X-ray diffraction studies and from high-level theoretical calculations. An overview of the progress made in deriving one-electron properties, intermolecular interactions in terms of the AIM approach[3,4]will be outlined with special emphasis on improvements in charge density models and development of both experimental and theoretical techniques to interpret, analyze and quantify the nature of weak intermolecular interactions.

References:

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Stereospecific interactions involving sulfur in protein structures

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Cysteine (Cys) and methionine (Met) are sulfur-containing residues in protein structure. Two Cys residues can be involved in disulfide bridge, conferring stability to the structure. The stereospecific interactions of the thioether group with other nucleophiles and electrophiles have been established through analyses of small molecule structures [1,2]. If the sulfur-containing groups in protein structures can exhibit similar features, in spite of the presence of myriad of other weak noncovalent interactions, has been addressed [3] and would be discussed. The sulfur···aromatic interaction is of common occurrence in proteins and the geometrical features of their interaction in proteins [4] and small molecules would be considered.

References

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[3] Chakrabarti, P. and Bhattacharyya, R. *Prog. Biophys. Mol. Biol.* 95, 83-137 (2007).
[4] Bhattacharyya, R., Pal, D. and Chakrabarti, P. *Protein Eng.* 17, 795-808 (2004).

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Ph. D – Solid State and Structural Chemistry, Indian Institute of Science, 1992
Postdoctoral research at Indian Institute of Science, 1992 - 1993
Postdoctoral research at Cardiff University ,UK1993-95
Visiting Scientist at Cardiff University during 1998, 2001
Visiting Scientist at Tokyo University, 2004.

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Sudborough medal and the Best Thesis award from Chemical Sciences Division, Indian Institute of Science, 1993
Material Research Society of India Lecture medal, 1999
Sir C. V. Raman Young Scientist award, 1999
B.M.Birla Science prize in Chemistry, 2003
Chemical Research Society of India Lecture medal, 2003

Publications
Papers in international journals ~150; Contributions in 5 books

Molecular packing influencing solid state properties in alkoxy substituted oligo-phenyleneethynylenes

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The *p*-phenyleneethynylene based oligomers and polymers are of greater interest in the recent research scenario owing to their interesting electronic and photo conducting properties.[1] The various electronic transport properties shown by this class of molecules includes one-dimensional conduction, electronic transport controller, rectification and switching behavior.[2] It is quite well established that these properties in phenyleneethynylene oligomers and corresponding polymers are due to the change in electronic states on substitutions and conformational changes in phenyleneethynylene backbone.[2] Recent literature reports on the control of these properties achieved by phenyleneethynylene backbone by suitably substituting various electron donating, withdrawing or the combination of the both the groups.[3] In addition, there are studies on tuning the properties of these molecules by inducing geometric changes on rigid rod-like conjugated p system.[1b] In order to elucidate the role weak interaction such as C-H… p and chain-chain interactions, we have carried out a detailed study on alkoxy substituted oligo(phenyleneethynylne) using X-ray crystallography in conjunction with theoretical calculations on molecular transmission. We find that the weak interactions play a major role in determining the molecular transport via the geometry of the conjugated backbone.

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SOLID STATE REACTIVITY AND SUPRAMOLECULAR SYNTHONS

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In the filed of crystal engineering, an advantageous approach to the crystal structure prediction and engineering relies on the identification and exploitation of certain patterns of association i.e. supramolecular synthons that are robust and decisive in the crystal packing. The specific molecular associations thus obtained can induce solid state reactivity. In this context, the identification of dimer motifs akin to that of carboxylic acids, which derive stabilization from multiple C-H…O hydrogen bonds, would be discussed. The manifestation of these types of interactions is shown in the high-energy cyclic form of water hexamer trapped in an organic supramolecular complex with bimesityl dicarboxylic acid. We have shown that it is important to consider the strong and weak hydrogen bonding interactions jointly in the analysis and design of crystal structures. Particularly important was, how the weaker C-H…X and X…X (X=Halogen) interactions mediate the unprecedented helical assembly of sterically encumbered carboxylic acids. These analyses not only unravel a motif that is unprecedented, but also underscore the role of weaker interactions in modifying the supposedly 'robust' supramolecular motif in a decisive manner.

The X-ray structural investigations of halogen substituted aromatic carboxaldehydes reveal that the well-known C-H…O interactions control their crystal packing. This can result in channel-type organization sustained by weak C-H..O and C-H…N interactions that have decisive role in solid-state photobehavior. In addition, the intramolecular C-H…X interaction causes the C=O…X interactions to manifest in a readily recognizable pattern of association, i.e., a supramolecular synthon. The robustness of this synthon is amply suggested from the isostructurality exhibited by four dichloro- and dibromo- dialdehydes. Further, it is found that the aldehyde which can exploit the C=O…Br interactions in two distinct ways crystallizes in two crystal modifications. In another structural analysis, 2-thioureidobezoxazole shows that the crystal lattice is build up of stacks of dimers generated by N-H…S hydrogen bonds. The supramolecular assembly is dictated by weaker N-H…S interactions to the exclusion of stronger N-H…X (X=O, N) hydrogen bonds, which are normally expected.

Poster
Abstracts

Synthesis, Characterization, Micellization and Antimicrobial Studies of Some Mixed-ligand Complexes of Chromium(III) Metallosurfactants

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Surface active mixed-ligand complexes of Cr(III) containing one of the chelating ligands *viz*., ethylenediamine (en), triethylenetetramine (trien), 2,2 bipyridyl (bpy), 1,10 -phenanthroline (phen) as equatorial and with different axial amine ligands (dodecylamine or cetylamine) were synthesised and characterized by UV-Visible, IR, NMR, and elemental analysis. The critical micelle concentration (CMC) values of these surfactant metal complexes in aqueous solution were determined as a function of temperature using conductometric technique. Thermodynamics of micellization (ΔG_m^0, ΔH_m^0 and ΔS_m^0) were evaluated. Dodoecyl/cetyl amine metal surfactant complexes obtained were tested for its antibacterial and antifungal activity and it was found to have good antibacterial and antifungal activities.

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P 2

Tris (2-aminoethyl) amine based Pentafluorophenyl-substituted Urea Receptor for Inorganic Phosphate

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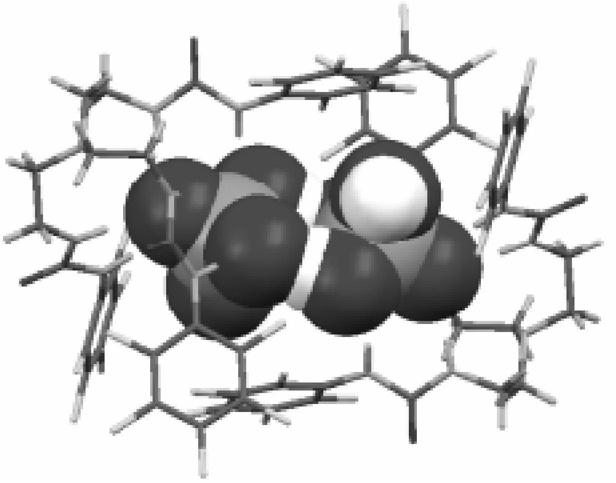
The design and synthesis of receptors capable of binding specific anionic guests is of crucial importance due to its potential application in environmental and biological processes. Phosphates and phosphate esters are ubiquitous in biology, playing roles in signaling, energy transduction, and information storage and expression. A novel type of non-covalent forces between electron deficient aromatic systems and anions namely anion-p interactions are the subject of numerous theoretical and experimental studies in recent. Solid state investigation of the new pentafluorophenyl-substituted tripodal urea receptor shows the formation of a cage type dimer via different non-bonding interactions of pentafluorophenyl units. Further, two units of this C_{3v} symmetric neutral receptor encapsulates a dimer of dihydrogenphosphate as a guest inside the cavity via sixteen hydrogen bonding interactions with the urea moieties and solvent molecules along with two anion/pi interactions. The receptor also shows significantly a higher binding and selectivity for dihydrogenphosphate over other oxyanions in solution state calculated by ^{1}H NMR titration.



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Coordination Polymers and Discrete High-Nuclearity Transition Metal Complexes Using 2-Pyridylalkylamine-Carboxylates

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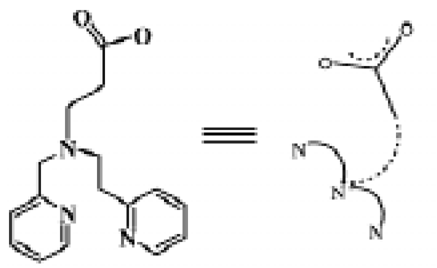
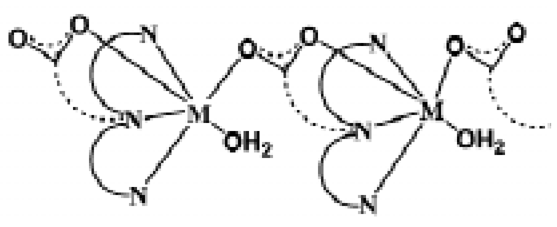
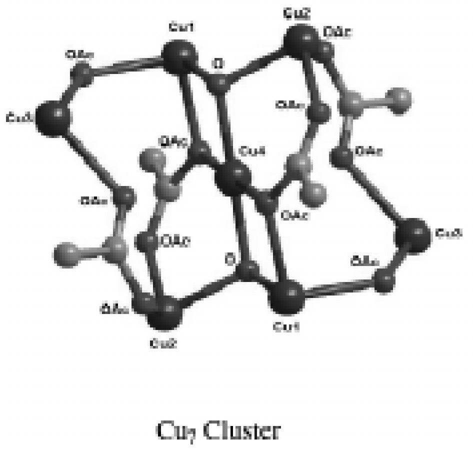
Polynuclear transition metal complexes exhibit a fascinating variety of unusual symmetries and structural patterns [1]. The synthetic techniques that provide access to these complexes [2], and the magnetic properties associated with a large number of interacting paramagnetic centers in a single cluster [3] add to their interest. It is well known that a carboxylate group can bridge two metal ions to give rise to a wide variety of polynuclear complexes ranging from discrete entities to multi-dimensional systems. Here we report the syntheses and characterization of coordination polymers ($\{[M^{II}(L1^-)(H_2O)][ClO_4]\}_n \cdot 2H_2O$, M = Mn, Co; $\{[M^{II}(L1^-)][ClO_4]\}_n \cdot 2H_2O$, M = Cu) and discrete high-nuclearity (Cu_4, Ni_4, $Cu_7^{[4,5]}$, Ni_8) transition metal complexes using 2-pyridylalkylamine-carboxylates.

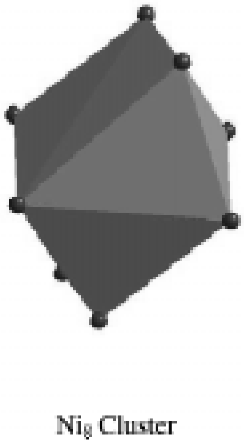


L1⁻



M = Mn, Co





Cu_7 Cluster

Ni_8 Cluster

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Synthesis, Structure, Molecular Switching and Catalytic Activity of Ethane and Ethylene Bridged Fe(III) Bisporphyrins

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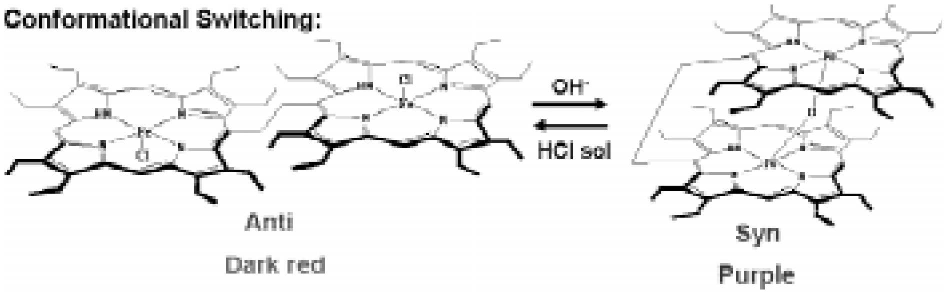
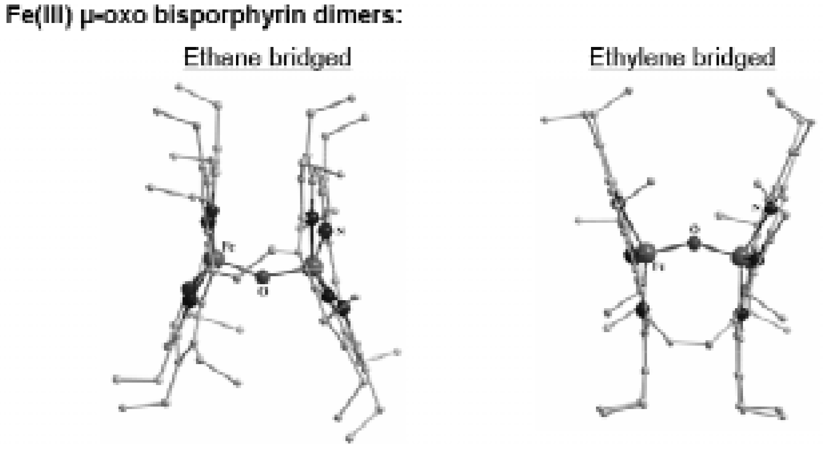
Iron porphyrins are important class of molecules found in Haemoglobin, Myoglobin, Cytochrome P-450 and in many other biological systems. Another type of porphyrins called cofacial bisporphyrins that are present in photosynthetic reaction centers (PRC). X-ray crystal structures of pure PRC proteins from *Rhodopseudomonas viridis (R.v.)* and *Rhodobacter spheroids (R.s.)* have been analyzed. Cofacial bisporphyrins are also known to catalyze small molecule reactivity such as asymmetric epoxidation, selective oxidation, reduction of oxygen to water etc [1, 2]. Interplanar distance between these types of facially disposed subunits has great importance upon small molecule reactivity.

To investigate the structure, properties and reactivities of the Fe(III) bisporphyrin, we have synthesized ethane and ethylene bridged Fe(III) bisoctaethylporphyrin chlorides and its μ-oxo derivatives, some of them are shown below. The electronic structure and molecular geometry, conformational switching, redox and catalytic activities will be discussed.





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Hydrated Iron(III)-Oxide Loaded Resin For Arsenic Removal – Kineticc And Equilibrium Studies

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Adsorption/co-precipitation with iron oxyhydroxides is the most commonly adopted method for arsenic removal from contaminated water because the method is both effective and cheap compared with other methods. In the present work, iron(III) was loaded onto the sulphonic acid sites of Duolite C26, a commercial cation-exchanger, and was then converted into hydrated ferric oxides (HFO) disbursed throughout the macropores of the ion exchanger beads by treating with mixture of NaOH and NaCl solutions. The resulting hydrated iron(III)-oxide loaded cation exchange resin (HFOLR) was tested for its ability to remove arsenic [As(V) and As(III)] present in water by batch adsorption. The pH_{pzc} of HFOLR was found to be 8.4 is higher than the naïve Duolite. For an initial concentration of 10 mg/L, a maximum adsorption of 99.6 and 90.8 % of As(V) and As(III) on HFOLR was occurred at pH 4.0 and 7.0 respectively. The effect of ionic strength on As(V) and As(III) adsorption onto HFOLR provided a measure of the relative bonding affinity of these ions for surface hydroxyl groups. Surface complex theory was successfully applied to explain the nature of interaction of As species with the surface functional groups of HFOLR. Positive identification of adsorbed arsenate species was provided using the FTIR and XRD techniques too. The XRD patterns for the adsorbent did not yield any crystalline peaks due to the fact that the crystallization of iron oxides is strongly retarded by the presence of the anionic resin particles. Specific interaction with As(V) was noted from XRD patterns of As(V)–laden HFOLR. The surface morphology and microstructure of the samples HFOLR and As–laden HFOLR were analysed by the SEM observation. Energy dispersive analysis of X-ray was used for characterizing the elements associated with the adsorbent before and after adsorption and prominent signals corresponding to As are observed for As–laden HFOLR. The mechanism for the removal of As by adsorption was explored by using the intraparticle diffusion model. To establish the most proper relationship for the equilibrium curves, isotherm studies were performed using Langmuir isotherm equation. The maximal adsorption capacities of As(V) and As(III) were found to be 36.2 and 25.8 mg/g respectively at 30 ^{0}C. The simulated water samples based on groundwater of New Jersey, USA, which contained arsenic together with cations of Al, Mg, Fe, Ca and Mn as well as anions like, fluoride, chloride, sulphate and carbonate, were treated by HFOLR to demonstrate its efficiency in removing As ions. Arsenic content could be brought down from 1.0 mg/L to well below 0.01 mg/L, the maximum permissible level as per WHO norms, with an HFOLR dose of 2.5 and 3.0 g/L for As(V) and As(III) respectively.

Electrochemical Sensing of L-Cysteine Using Flat Oriented Phthalocyanine Modified Electrodes

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L-cystine/L-cysteine redox couple is generally used as a model for the role of the disulfide bond and thiol group in proteins [1]. Moreover, it is an important amino acid owing to its crucial roles in many biological systems. For example, it could be used as a prospective radiation protector and cancer indicator. Therefore, it is very important to study its redox behavior and detection with high selectivity and sensitivity. Usually at naked metal electrodes no electrochemical response was observed for L-cysteine at physiological pH. Hence, in the present study we investigated the electrochemical determination of L-cysteine using self-assembled monomolecular films of 1,8,15,22-Tetraaminophthalocyanatocobalt(II) (4a-Co^{II}TAPc) and 2,9,16,23-Tetraaminophthalo- cyanatocobalt(II) (4b-Co^{II}TAPc) (Chart 1) on Au surfaces. Electrochemical and Raman studies confirm that 4a-Co^{II}TAPc adopts parallel orientation whereas 4b-Co^{II}TAPc adopts perpendicular orientation on Au surface [2]. Among the two electrodes, flat oriented 4a-Co^{II}TAPc electrode shows well defined oxidation peak for L-cysteine whereas perpendicularly oriented 4b-Co^{II}TAPc shows no pronounced response (Fig.1). Thus 4a-Co^{II}TAPc modified electrode was used for the determination of L-cysteine. Interference studies, detection limit and pharmaceutical analysis of L-cysteine will be presented in the poster.

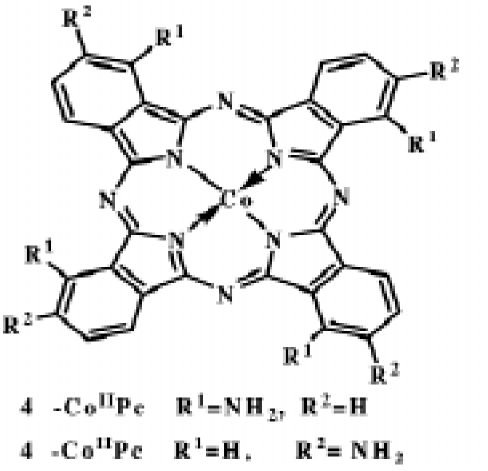

Chart 1. Structure of phthalocyanines

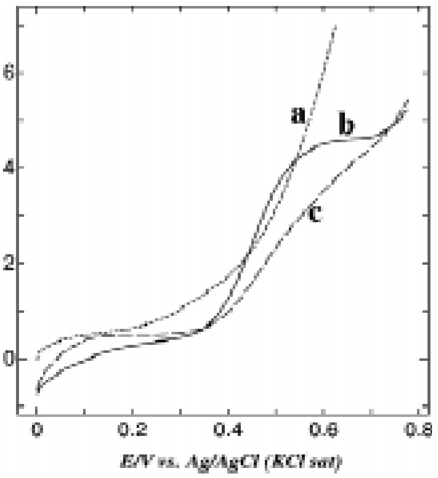

Fig.1. LSVs of L-cysteine at (a) bare Au, (b) Au/4a-Co^{II}TAPc and (c) Au/4b-Co^{II}TAPc electrodes in PB solution.

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Adsorption of Cu^{2+} from Aqueous Solution of Copper Sulphate On Functionalized Silica Gel with Different Loading of Aminopropyltrimethoxysilane

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Silica Gel (G) and amino functionalized silica gel (GN) with different loading of aminopropyl groups (GN1: 0.49, GN2: 1.01 and GN3: 1.45 mM/g,) were synthesized and used for the adsorption of Cu^{2+} from aqueous solution. The amino group was anchored on the surface of silica gel (GN) by refluxing gel in toluene solution containing appropriate amount of 3-aminopropyltrimethoxysilane for 24h. The GN adsorbent was filtered and washed with toluene. Elemental analysis (CHN) using Perkin-Elmer CHNS/O Series II, 2400, was carried out to quantify the number of organic moieties grafted on the silica gel [1]. The changes in the surface area and pore structure caused by the grafting of organic moieties were determined by nitrogen physisorption at 77.4K using surface area analyzer ASAP2010 Micromeritics USA. The surface area of silica gel decreases with the increases in the loading of aminopropyl groups [574 to337 (m^2/g)]. Adsorption study of Cu^{2+} on functionalized silica was investigated. The batch adsorption experiment was conducted at room temperature (303K$\underline{+}$ 1). $CuSO_4.5H_2O$ was used to prepare the Cu^{2+} solutions. The adsorption isotherm of copper (II) was measured using 0.1 g of adsorbent containing metal ions. The initial and final concentrations of the metal in the solution were analyzed by inductively coupled plasma, atomic emission spectrometry (ICP-AES, Perkin-Elmer optical emission spectrometer optima 2000DV). The adsorptions isotherms of Cu^{2+} were fitted with different models such as Langmuir, Frundlich, Sip and Redllich-Peterson. Sips modal was found to give the best fit [2]. It has been observed that when loading of NH_2 group (number of NH_2 groups) is increased from 0.49 to 1.01 mM/g, mono layer adsorption capacity of Cu^{2+} remain unchanged. The loading of NH_2 group in GN1 and GN2 was 0.49 and 1.01 mM/g, (NH_2/Cu ratio is 0.96 and 1.84 M/M respectively) and in the case of GN3, the loading of amino group was 1.47 mM/g (NH_2/Cu ratio 1.38 M/M). This study indicates that the number NH_2 per unit area (population density) determines NH_2/Cu ratio at saturation of Cu^{2+} on the functionalized silica gel. Diffuse reflectance spectroscopy (DRS) data indicate the complex formation of copper.

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Nickel Selective Electrode Based on Liquid Membrane Containing N_4 Macrocycle As Ionophore

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Determination of nickel assumes importance due to its toxic nature, widespread use in catalytic processes and its presence in various effluents. The toxicity of nickel can cause dermatitis, asthma and disorder of central nervous system [1]. The first nickel-selective electrode was reported by Pungor and co-workers using a nickel-dimethylglyoxime complex[2]. We have constructed a new PVC membrane nickel ion-selective electrode using N_4 compound as a neutral ionophore. Effect of various plasticizers, viz. o-nitrophenyloctyl ether (o-NPOE), dibutylphthalate (DBP), bis 2-ethyl sebacate (BES) was studied and improved membrane performance was observed [3]. The electrode was prepared with 4% ionophore, 63% o-NPOE (as plasticizer) and 33% PVC. The electrode gave Nernstian slope 29 mV/decade over the concentration range of 1.5×10^{-5} to 1.0×10^{-1} M of Ni^{2+} ions in the pH range of 3.5–8.5. The limit of detection was 3.1×10^{-6} M. It has a response time of <20 s and can be used for at least three months without any considerable divergence in potentials. The proposed electrode shows good discrimination of Ni^{2+} ion from several cations. The effect of organic solvents on electrode response was examined. The results show that this electrode can be used non-aqueous media up to 20% (v/v) concentration without interference. The electrode was used as an indicator electrode in the potentiometric titrations. It was also successfully applied to the determination of Ni^{2+} ions in chocolate samples.

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Synthesis, Spectroscopy and Cyclic Voltammetry of New iron(III) Complexes with Bio-relevant Pyrazolyl Thiosemicarbazone.

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The remarkable therapeutic success [1] of several heterocyclic thiosemicarbazones for removing excess iron from iron-loaded mice through chelation therapy has accelerated further research in this specific area. In continuation of our earlier work [2], We report here the synthesis and physico-chemical characterization of a new iron(III) complexes with 5-methyl-3-formylpyrazole N(4)-cyclohexylthiosemicarbazone (HMPz4Cy). The complexes have the general composition $[Fe(MPz4Cy)_2]X \cdot nH_2O$ ($X = Cl, NO_3, ClO_4$; n = 2-3). I.R. data for the free ligand and its complexes indicate that the ligand acts as an uninegative NNS tridentate (MPz4Cy) through the pyrazolyl nitrogen (tertiary), azomethine nitrogen and thiolato sulphur. Electronic spectral data (solid and MeOH) are suggestive of a distorted octahedral environment for the hexacoordinated iron(III) species. X-ray crystallographic identifications of iron(III) complexes with similar ligands support the proposed geometry of the complexes. E.p.r. data (r.t. and l.n.t.) show the presence of a low-spin iron(III) cation with $d_{xz}^2 d_{yz}^2 d_{xy}^1$ configuration. Cyclic voltammograms of iron(III) complexes indicate a quasireversible Fe^{+3}/Fe^{+2} couple. X-ray crystallographic identification of the species, $[Co(MPz4Cy)_2]Cl \cdot 2.75H_2O$ supports that the same ligand, HMPz4Cy exhibits almost identical coordination behaviour with cobalt(III) chloride salt in like solvent. Cyclic voltammograms of cobalt(III) complexes also show a quasireversible Co^{+3}/Co^{+2} couple [3].

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Second Sphere Coordination In anion Binding: Synthesis, Characterization And Single Crystal X-ray Structure of Tris(1, 10-Phenanthroline) Cobalt(III) Periodate Dehydrate, $[Co(phen)_3](IO_4)_3.2H_2O$

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In continuation of our interest in cationic cobalt(III) complexes[1-3] as anion receptors, we synthesized single crystals of $[Co(phen)_3](IO_4)_{3,}$ by slowly mixing the separately dissolved tris(1,10-phenanthroline)cobalt(III)chloride with sodium metaperiodate in aqueous medium in 1:3 molar ratio. Elemental analyses, spectroscopic studies (IR, UV/Visible, ^{1}H and ^{13}C NMR) and solubility product measurements were performed to characterize the complex salt. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 11.6865(3), b = 19.9546(4), c = 16.6808(3) Å, b = 98.473(1) °, V = 3847.5(6) Å^3, Z = 4. X-ray structure determination revealed an ionic structure consisting of one $[Co(phen)_3]^{3+}$, three $[IO_4]^-$ ions and two water molecules. The six nitrogen atoms, originating from three 1, 10-phenanthroline ligands (each bidentate) show distorted octahedral geometry around the central Co(III) metal ion. Supramolecular hydrogen bonding networks between ionic groups $[Co\text{-}phenCH^{d+}\cdots O^{d-}_{anion}]$ by second sphere coordination besides electrostatic forces of attraction have been observed that stabilize the crystal lattice. The structural studies suggest that $[Co(phen)_3]^{3+}$ is a potential anion receptor for the periodate ion, $(IO_4)^-$ in aqueous medium.

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Interaction of Vanadium (IV) Complexes with DNA

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The application of the macrocyclic transition metal complexes is of great interest as they are used as artificial restriction enzyme for cleaving nucleic acid (DNA, RNA). The intrinsic specificity for the hybridization between the two complementary DNA chains has been used as a bio recognition event in the design of DNA biosensor [1]. The vanadium compounds exhibit antitumor activity by inhibiting growth of numerous malignant cell lines including L1210 leukemia, Hela cells and human ovary carcinoma, by induction of cell cycle arrest and / or cytotoxic effects and is widely implicated in many biological systems as insulin mimetic and antitumor agents. Reaction of VCl_3 with one equivalent of ligand [L: N,N' Bis(salicylidene)-1,2-phenylenediamine; N,N'Bis(salicylidene)-3, 4-diaminotoluene; N,N'Bis(salicylidene)-3, 4-diaminobenzoic acid; N,N'Bis(salicylidene)-1, 2-ethylenediamine; N,N'Bis(orthohydroxyacetophenone)-1, 2-ethylenediamine] in air resulted the formation of [V^{IV}OL] complexes. The structure of [V^{IV}OL] (L: N,N' Bis(salicylidene)-1,2-phenylenediamine) has been shown in Fig. 1. These complexes were further used for the interaction study with DNA, through absorption and emission spectroscopy, melting temperature and viscosity experiment and cleavage study with gel electrophoresis (Fig. 2).

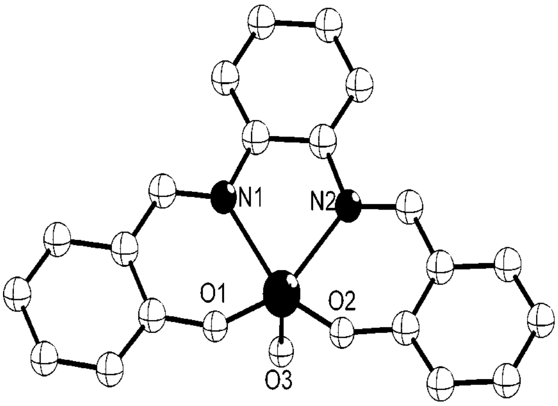

Fig.1

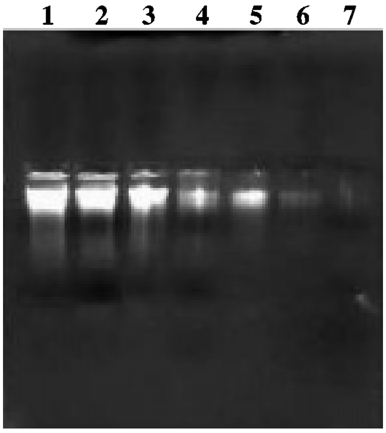

Fig.2 Cleavage study with gel electrophoresis

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Studies on the DNA Binding Properties of Half Sandwich Complexes of Ruthenium(II)

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Ruthenium is the one of the most promising metals after platinum in the treatment of cancer. In comparison with platinum based drugs, ruthenium based anticancer drugs are expected to exhibit low general toxicity and greater specificity. Some prominent examples of ruthenium drugs under investigation are the ruthenium (III) complexes [imidH][trans-$RuCl_4$(DMSO)(imid)] NAMI-A and [indH][trans-$RuCl_4$$(ind)_2$] KP1019 [1]. More recently, increasing attention has been focused on organometallic compounds, specifically on ruthenium (II) arene complexes. A series of complexes with the general formula [(h^6-arene)RuCl(en)][PF_6] [2] have been studied for their *in vitro* anticancer activity. The mechanism by which these complexes show anticancer activity is assumed to be similar to that of cisplatin.

On the basis of our earlier studies on copper(I) complexes with P(III) ligands [3], we wished to investigate the effect of replacing en with P(III) ligands. We present the synthesis of some neutral and cationic piano stool complexes containing different P(III) ligands. The reaction of these complexes with DNA was investigated in biologically relevant media by spectroscopic methods and viscosity measurements. The thermodynamic aspects of the aquation reaction in different half sandwich complexes were investigated using the Jaguar program available in the Schrodinger suite. Subsequently their interaction with DNA was probed using the ONIOM method available in the Gaussian suite of programs. A protocol for carrying out a computational study on the drug-DNA adduct will be described. An attempt is made to understand the activity of these complexes on the basis of drug-DNA interactions.

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Kinetics and Mechanism of Reaction between 4-Nitrophenol and Carbonates of Nickel, Zinc, and Cadmium in Solid State

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4-Nitrophenol [4-NP] has always been in analytical uses [1] and its biological, biochemical and medicinal studies have been the topic of interest [2, 3]. The formation of coordination complexes in solution is well understood. However, general solid state coordination chemistry has not yet picked up. Despite the increased attention that has been paid to solid state reactions in recent years, it remains confined to mostly inorganic-inorganic or organic-organic processes; references to inorganic-organic systems are few. 4-NP appears to have strong coordinating action in solid state as well. In continuation of our work [4, 5], the present work reports the kinetics and mechanism of the solid state interaction of 4-NP with metal carbonates (MCO_3; M = Ni, Zn and Cd). The data for the lateral diffusion for each reaction fitted the rate equation $X^n = k\,t$, where X is the thickness of the product layer at time t, and n and k are constants. When kinetics was studied gravimetrically, the data followed the equation $\Delta W = k'$ t, where Δ W is the change in the product's weight at any time t, and k' is the rate constant. The activation energies calculated from the progress of the reaction studied by either technique are different for the low and high temperature ranges. At lower temperatures, the rate of the processes is reaction controlled, whereas at higher temperatures, it is diffusion controlled. In lower temperature range, the diffusion is faster than the chemical reaction and as the temperature is raised, a situation is reached where the chemical reaction becomes faster and consequently n decreases gradually with increasing temperature turning the rate equation parabolic in case of lateral diffusion studies. 4-NP diffuses into metal carbonate grains; penetration to the grains occurs via vapor phase and the possibility of surface migration is negated as the reaction propagated at the same rate with different lengths of the air-gap between the reactants. In gravimetric method, a deviation was observed in the case of [$ZnCO_3$-(4-NP)] reaction where rate constant deviated from the normal straight line of Arrhenius plot at 90°C and above. At and above 90°C, the decomposition of $ZnCO_3$ becomes appreciable and thus the expected increase in weight due to reaction is marred by the decrease in weight resulting from its decomposition. The reactions were followed by chemical analysis, IR spectral studies, X-ray diffraction, and thermal and conductivity measurements. A single addition product [(MCO_3-(4-NP)] was obtained in all cases.

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Removal of Dyes Using Solid Wastes from Tanneries: Dual Advantage Technology

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Solid waste emanating from tanneries poses a serious challenge to environmentalists. Raw trimmings of hides/ skins from a tannery constitute a huge percentage of this solid waste from tanneries. In this study, raw trimmings, after a pretreatment with glutaraldehyde, have been used as adsorbent material for removal of dyes from wastewaters. Various parameters like adsorbent dosage, dye concentration and pH have been optimized. The effect of neutral salts on the dye adsorption capacity of trimmings has been studied. The adsorption of dye by aldehyde treated trimmings follows Langmuir isotherm. Above 95% dye removal efficiency has been achieved. Commercial trials prove the potential use of trimmings as adsorbent for dye containing waste waters. Also, the dye loaded trimmings have been employed in the manufacture of a tanning salt, which can be used in leather industry, thus giving a holistic solution to the challenging solid waste disposal problem.

Stannoxane Capping Derived from Chiral Tridentate NNO Donor Ligand for Nickel and Copper Macrocycles: Comparative Binding Studies of Stannoxane Moiety and its Modulated Copper Complex with CTDNA

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Novel stannoxane type dinuclear tin complex $C_{16}H_{13}N_4O_2Sn_2Cl_7$ **1** and its modulated macrocyclic complexes $[C_{24}H_{36}N_{10}O_3Sn_2CuCl_7]\ ClO_4$ **2** and $[C_{24}H_{34}N_{10}O_2Sn_2NiCl_7]\ ClO_4$ **3** were synthesized and characterized by elemental analysis and various spectroscopic techniques (IR, ^1H, ^{13}C, ^{119}Sn NMR, ESI-MS, EPR and Uv-Visible). ^{119}Sn NMR shows the presence of two tin metal centers in different environment. The proposed pseudo octahedral geometry of copper in complex **2** and square pyramidal geometry of nickel in complex **3** were established by the analysis of spectroscopic data. Absorption and fluorescence spectral studies and viscosity measurements have been carried out to assess the comparative binding of dinuclear stannoxane complex **1** and its modulated copper complex **2** with calf thymus DNA. The intrinsic binding constants K_b of the complex **1** and **2** were determined as $4.4 \times 10^4\ M^{-1}$and $7.5 \times 10^4\ M^{-1}$, respectively. Cyclic voltammetric studies have also been employed to ascertain the binding of complex **2** with CTDNA. The results suggest that the complex **2** binds to CTDNA twice in the order of magnitude compared to complex **1** [1]. Interaction studies of complex **2** with guanosine 5'-monophosphate further confirm the binding via N_7 position of guanine and phosphate moiety [2].

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Bis-calix[4]pyrrole: Potential Host for Cooperative Anion Binding

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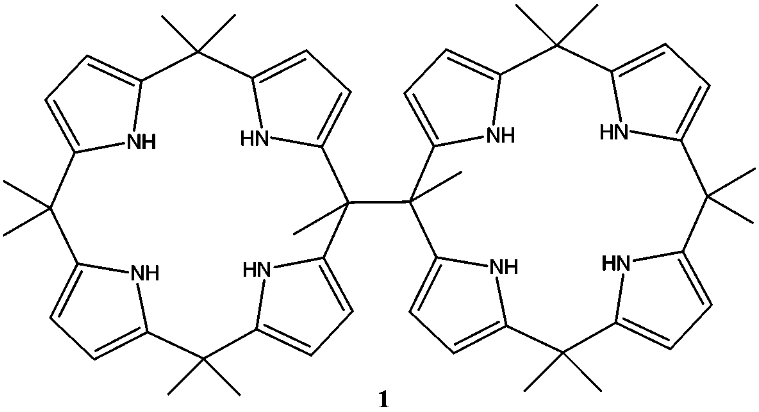
Over the last two decades, considerable effort has been devoted towards the synthesis of neutral host molecules that can bind guest molecules in a cooperative manner[1]. However systems that can effect cooperative binding, remain rare[2]. While powerful anion binding agents, albeit monomeric hosts are difficult to prepare. By contrast, the calix[4]pyrroles, an alternative class of pyrrole-based anion receptors, are easy to synthesize and functionalize too[3].

While calix[4]pyrrole itself binds to a variety of anions[3] and it's strapped derivatives show a great selective towards anions, but none of them show any cooperative effect toward anions. Sessler et. al. tried to make calix[4]pyrrole dimmers bearing rigid spacers to observe limited success. The present investigation deals with a very simple strategy to synthesize biscalix[4]pyrrole,1 in about 10 % yield, in two steps starting from 2,3-butanedione and it's preliminary anion binding study.



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Iron(IV)corrole-catalysed oxidations by *m*-chloroperbenzoic acid: Search for reactive intermediates

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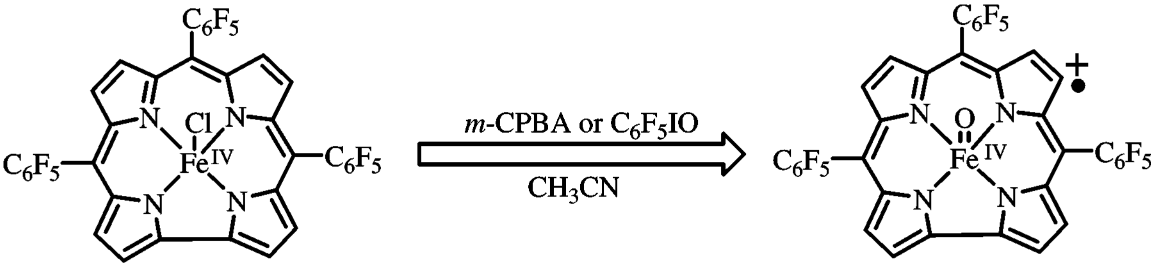
Since the breakthrough discovery of facile synthetic methodology [1] for the preparation of corroles, a tremendous amount of interest has been generated in the chemistry of this contracted macrocycles [2]. However, the mechanistic study of metallocorroles catalyzed oxidation reactions is still in its infancy [3]. In this present study we have explored simple methods that can enable us to predict the reaction pathway and to identify the intermediates involved. The reaction of *m*-chloroperbenzoic acid (*m*-CPBA) with meso-tris(pentafluoro-phenyl)corrolatoiron(IV) chloride [(F_{15}TPC)FeCl] has been studied in acetonitrile medium. The reactive intermediates formed have been quantitatively trapped by 2,4,6-tri-t-butylphenol (TTBP). Kinetic analysis of the (F_{15}TPC)FeCl-catalysed oxidation of TTBP has been found to be consistent with rapid reaction of organic substrate with an intermediate formed in the first and rate-determining step. The intermediate has been identified as an Iron(IV)-oxo corrole radical cation based on electronic and EPR spectral data.



"Compound I" type intermediate

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Synthesis and Characterisation of Penta and Hexa Coordinated Silicon compounds with Schiffs Bases containing NCS functionality

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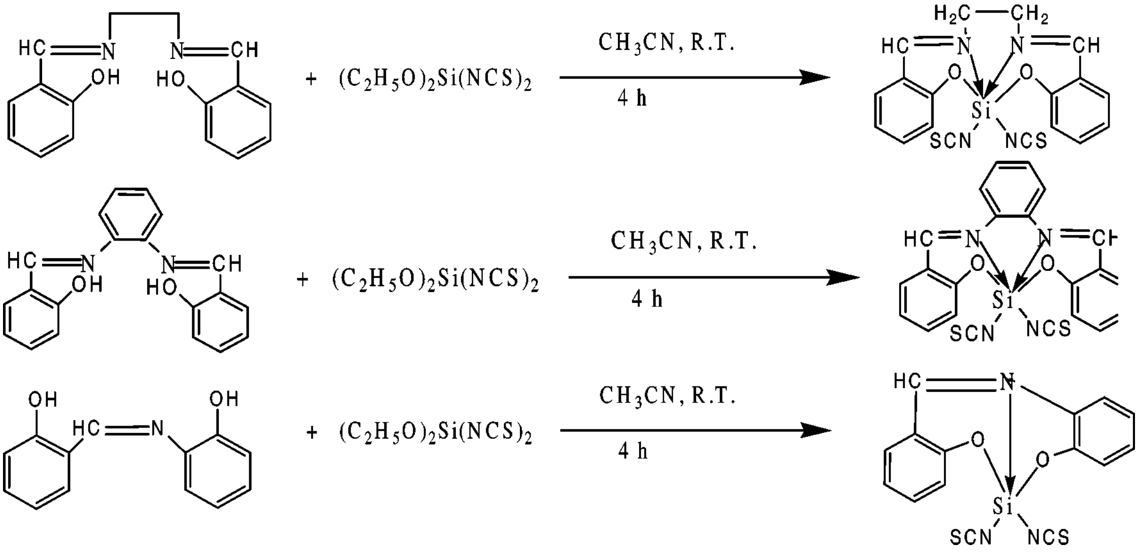
All the compounds were prepared in a one pot reaction between diethoxydiisothiocyanato silane and the corresponding ligands in 1:1 molar ratio under mild conditions according to the proposed scheme as below.



All these compounds are hygroscopic in nature and are found to be soluble in solvents like dimethylsulfoxide and dimethylformamide. The compounds have been characterized by elemental analysis, Infrared and multinuclear (^{1}H, ^{13}C and ^{29}Si) NMR studies.

Mapping the Reaction Coordinate for the Oxidative Addition of Molecular Hydrogen to a Metal Center

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The binding of molecular hydrogen to a metal center leads to the elongation of the H-H bond and subsequently to its cleavage along the reaction coordinate for the oxidative addition of H_2. There has been considerable interest in the study of the activation of dihydrogen and map out the reaction coordinate for the homolysis of H_2 on a metal center. A large number of H_2 complexes reported to date possess H-H distances ranging from 0.8 to 1.0 Å. A relatively fewer examples of *elongated* dihydrogen complexes wherein the H-H distances fall in the range of 1.0 to 1.5 Å, are known. Study of the *elongated* dihydrogen complexes is of great significance because of its relevance in important catalytic processes such as hydrogenation, hydrogenolysis, and hydroformylation. One of the current goals is to study the smooth gradation of the H-H distances along the continuum for the oxidative addition of H_2 to a metal center. In order to accomplish this, the electron donor abilities of the phosphorus coligands was systematically varied in the metal complexes such that the back-donation from the M(dp) to the H_2(s*) is increased in small increments. We synthesized a series of new ruthenium dihydrogen complexes bearing the 1,2-bis(diarylphosphino)ethane ligands wherein the aryl group is a benzyl moiety with a substituent (*p*-fluoro, H, *m*-methyl, *p*-methyl, *p*-isopropyl); in this series of complexes, a small increment in the electron donor ability of the chelating phosphine ligand results in an elongation of the H-H bond in a systematic manner.**[1]** We also synthesized a series of 16-electron dicationic dihydrogen complexes bearing *elongated* dihydrogen ligand.**[2]** In addition, we prepared a series of dihydrogen complexes of the type $[Cp/Cp^*Ru(PP)(h^2\text{-}H_2)]^+$ (PP = chelating phosphine) containing *elongated* H_2 ligand (d_{HH} = 1.0 to 1.17 Å) which shows smooth increment of the H-H distances along the reaction coordinate for the oxidative addition of H_2.**[3]**

The H-H bond lengths vary in small increments, correlating with the donor properties of the substituents (Hammett substituent constants) on the benzyl moiety of the chelating phosphine ligand. We have thus constructed H_2 complexes along the reaction coordinate for the oxidative addition of H_2 to a metal center. The results of these studies will be presented.

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Ruthenium(II) Complexes of Bipyridine - Glycoluril and their Interactions with DNA

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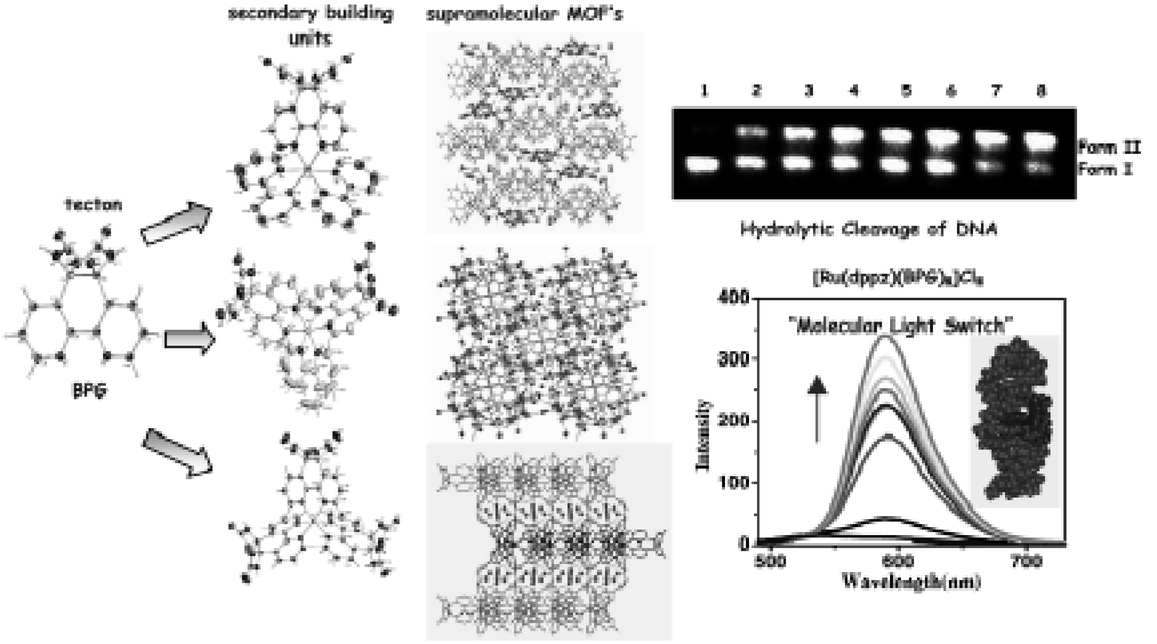
The synthesis, structural and photophysical characterization, DNA binding and cleavage by Ru(II) polypyridyl complexes of the type $[Ru(N\text{-}N)_2(BPG)]Cl_2$ **1-4**, $[Ru(BPG)_3]Cl_2$ **5** and $[Ru(N\text{-}N)(BPG)_2]Cl_2$ **6-9** where N-N is 2,2‘-bipyridine (bpy), 1,10-phenanthroline (phen), dipyrido[3,2-d:2‘,3‘-f]quinoxaline (dpq), dipyrido[3,2-a:2‘,3‘-c]phenazine (dppz) which incorporates the bipyridine glycoluril ligand have been studied to investigate the influence of the ancillary ligand. The X-ray structure of urea fused bipyridine ligand **BPG** reveal inherent H-bond donor (N-H) and acceptor groups (C=O) which exhibit a potential to generate supramolecular motifs as well as offer H-bonding groups for DNA binding. Single crystal X-ray analysis of **1**, **5** and **7** indicate a butterfly like structure for the cationic secondary building units evidencing this H-bonding capacity which results in a supramolecular self-assembled metal-organic frameworks (MOF) forming channels in **1** and **5** encapsulating tetradecameric water cluster, mixed water-dimethylsulfoxide cluster and a network of water molecules and chlorine anions surrounding secondary building units in **7**. The binding ability of these complexes to DNA is dependent on the planarity of the intercalative polypyridyl ligand, which is further influenced by the ancillary bipyridine-glycoluril ligand. Interaction of complexes **1-9** with plasmid *pBR322* DNA reveals that all complexes cleave DNA efficiently at micro molar concentrations under dark and anaerobic conditions probably by a hydrolytic mechanism. Molecular mechanics calculations of these systems confirm two different binding modes for the complexes.



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DNA-Binding And Photocleavage Activities of Metallointercalators Containing Immidazo-phenanthroline Ligand: $[Ru(en)_2(aip)]^{2+}$ and $[Co(en)_2(aip)]^{3+}$

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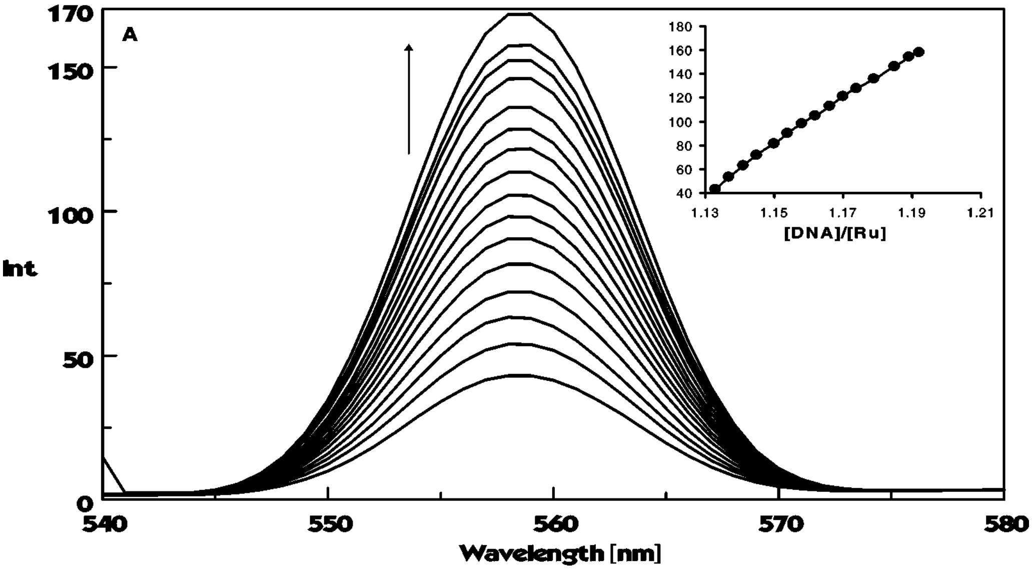
Two novel Ruthenium(II) complexes **(1)** $[Ru(en)_2(aip)]^{2+}$, and **(2)** $[Ru(en)_2(pyip)]^{2+}$, have been synthesized and characterized. The interaction of these complexes with calf thymus DNA was investigated by absorption (UV/vis), emission spectroscopy, viscosity measurements, DNA melting and DNA photo cleavage, the results suggest that the two complexes bind to DNA via intercalative mode and complex **2** binds more strongly to CT DNA than complex **1**. Moreover, these two complexes have been found to promote the photocleavage of plasmid DNA pBR322 under irradiation.



Emission spectrum of complex 1 with DNA concentration increasing (5,10,15.....

Synthesis and Characterization of ORGANOSILANOLS Bearing Pendant Carbosilyl Groups

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The organosilanols, the silicon analogues of alcohols are the compounds containing two or more Si-OH bonds. The synthesis and characterization of organosilandiols with general formula $R_3SiCH_2CH_2Si(OH)_2$ have been carried out. The primary interest in these studies is focused to understand the role of bulky R_3Si substutents (R_3 = PhMe, Ph) linked to CH_2CH_2 groups on the stabilty of organosilanediols.The following organosilanediols (1-4) have been prepared by controlled hydrolysis of their corresponding diorganodichlorosilanes derivatives in the ether mixture in presence of Et_3N which acts as scavenger.

1.CH_2=CHSi(p $OCH_3C_6H_6$) $(OH)_2$ _
2. $Ph_2MeSiCH_2CH_2Si$(p $OCH_3C_6H_4$)$(OH)_2$
3.$Ph_3SiCH_2CH_2SiPh(OH)_2$
4.$Ph_2MeSiCH_2CH_2HexSi(OH)_2$

The organosilanediols thus obtained are viscous liquids, soluble in organic solvents and are characterize by IR and proton NMR spectroscopy.

To study the Hydrogen bonding interactions in amine adduct of these organosilanediols (1-4) have been prepared and characterized by IR and 1HNMR spectroscopy.

A no of organic amines such as 4, 4' bipyridyl, 2, 2' bipyridyl, pyrazine, 3, 5 dimethoxyaniline and N, N-dimethyaniline have been investigated.

A strong evidence in favor of HYDROGEN bonding (O-H….N) in these adducts have been obtained from IR spectra. Due to strong intermolecular hydrogen bonding interactions of Si-OH groups with amines, the IR stretching frequencies ÖO-H vibrations is shifted to lower frequency compared to that of free organosilanediols.

μ-Oxo-Bridged Dinuclear Iron(III) Complexes of Tripodal 4NLigands as Functional Models for methane Monoxygenase Enzymes

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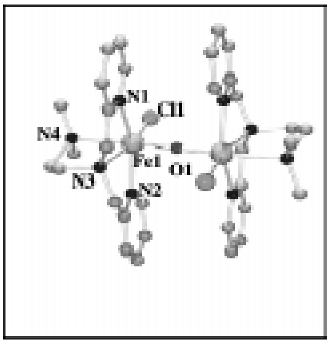
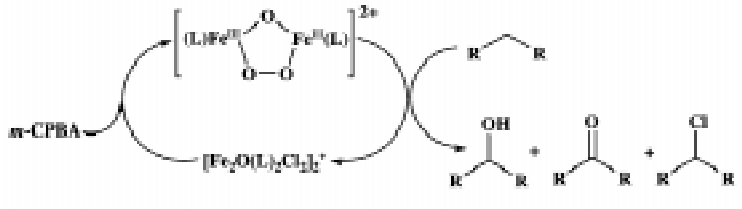
The soluble methane monoxygenase (sMMO) isolated from methanotropic organism catalyzes the transformation of methane to methanol. Several intermediates in the catalytic cycle of sMMO have been characterized but the mechanism of catalytic hydroxylation of unactivated C-H bonds is not fully understood. Modeling of sMMO has been receiving much attention due to development of bio-inspired iron based catalysts for the efficient and selective hydrocarbon oxidation. Three new iron(III) complexes $[Fe_2(\mu\text{-}O)(L1)_2Cl_2]Cl_2$ **1** and $[Fe_2(\mu\text{-}O)(L2)_2Cl_2]Cl_2$ **2**, where L1 = *N*,*N*-dimethyl-*N*',*N*'-bis(pyrid-2-yl- methyl)ethylenediamine and L2 = *N*,*N*-diethyl-*N*',*N*'-bis(pyrid-2-ylmethyl)- ethylenediamine, have been isolated as functional models for sMMO and successfully employed as catalysts for C-H activation of alkanes. All the complexes have been characterized using absorption spectral and electrochemical techniques. The molecular structure of $[Fe_2(\mu\text{-}O)(L1)_2Cl_2]Cl_2$ **1** has been determined by single crystal X-ray diffraction. The complex **1** possesses an Fe-O-Fe core and the coordination geometry around each iron(III) center is distorted octahedral. The tetradentate ligand L1 occupies four coordination sites, (μ-oxo) bridging O atom lies at the fifth position and the labile Cl^- ion occupies the sixth coordination position of iron(III) center. The $-NMe_2$ group in **1** forces the Fe-O-Fe core to be linear as revealed from the Fe-O-Fe bond angle of 180°. In the presence of *m*-CPBA cyclohexane is selectively (A/K: **1**, 6.9; **2**, 6.1) oxidized to cyclohexanol and small amounts of cyclohexanone (CyO) and 1-chlorocyclo- hexane are also observed as oxidative ligand transfer (OLT) reaction product. Interestingly, the oxidation of adamantane by **1** and **2** affords 1-adamantanol exclusively (40%), 2-adamantanol (6.0%) and small amount of adamantanone (2.1%) with enhanced yield within 30 mins. The diiron(III) complexes **1**-**2** have the potential to be developed into selective and efficient catalysts for epoxidation and alkane fictionalization.





Scheme 1: Oxidative transformation of alkanes by diiron(III) complexes

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P 24

Lanthanide complexes of tetradentate macrocyclic ligand: Synthesis and Spectroscopic investigation

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In the present paper, the lanthanide complexes derived from 1,5,8,12-tetraaza-2,4,9,11-tetramethyl cyclotetraaza-1,4,8,11-tetraene were synthesized. The general composition of the complexes is $[Ln(L)X_2.H_2O]X$, where M = La, Ce, Nd, Sm and Eu and X = NO_3^- and Cl^-. The ligand was characterized on the basis of elemental analyses, IR, Mass, and ^{1}H NMR spectral studies. All the complexes were characterized by elemental analyses, molar conductance measurements, magnetic susceptibility measurements, IR and electronic spectral techniques. The ligand acts as a tetradentate chelate and coordinates through four nitrogen atoms of azomethine groups. The lanthanum complexes are diamagnetic while the other Ln(III) complexes are paramagnetic due to the presence of $4f^n$ unpaired electrons. The spectral parameters i.e. nephelauxetic effect (b), covalency factor ($b^{1/2}$), Sinha parameter (d%) and covalency angular overlap parameter (h) have been calculated from absorption spectra of Nd(III) and Sm(III) complexes. These parameters suggest the metal-ligand covalent bonding. In the present study, the complexes show the coordination number seven.

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{Ru^{II}-NO}^{6} and {Ru^{II}-NO$^\cdot$}^{7}: Formation, Reactivity and Photorelease of Metal Bound Nitrosyl to the Biological Target

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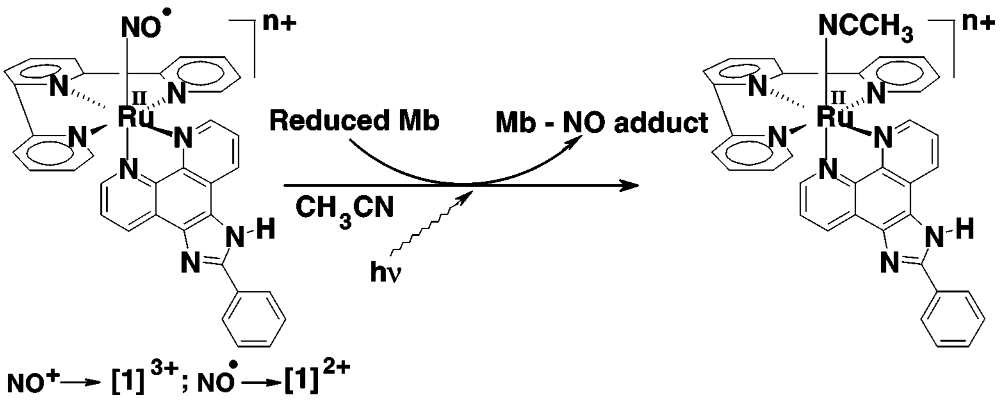
The relevance of nitric oxide (NO) in a wide range of biological processes have introduced a renewed interest in developing alternative molecular devices capable of functioning as efficient "NO" donors under biological conditions. In that context the present report demonstrates nitrosyl complexes with {Ru-NO}^{6} and {Ru-NO}^{7} configurations in the framework of $[1]^{3+}$ and $[1]^{2+}$, respectively. $[1]^{3+}$ exhibits NO$^+$® NO$\cdot$ and NO$\cdot$ ® NO$^-$ reductions at +0.49 and –0.26 V versus SCE. A sizeable shift (300 cm^{-1}) in n(NO) frequency takes place on moving from {Ru-NO$^+$} to [{Ru^{II}-NO$\cdot$}. The simulation of the EPR spectrum of {Ru^{II}-NO$\cdot$} suggests partial metal contribution (1/3) to the SOMO. The {Ru-NO$^+$} is transformed to the corresponding {Ru-NO2$^-$ } in the presence of OH$^-$ with k = 2.02 ´ 10^{-4} s^{-1} at 303 K. In the presence of a steady flow of dioxygen gas {Ru^{II}-NO$\cdot$} state oxidizes to {Ru-NO$^+$} through an associatively activated pathway with k/s^{-1} of 5.33 ´ 10^{-3}. On irradiation with light {Ru^{II}-NO$\cdot$} undergoes facile photo release of NO (k_{NO} = 2.0 x 10^{-1} min^{-1} and $t_{1/2}$ » 3.5 min) with the concomitant formation of the solvate species $[Ru(trpy)(L)(CH_3CN)]^{2+}$. The photoreleased NO can be scavenged by myoglobin as Mb-NO adduct.



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Cobalt(III) Catalysed Oxidation of Ethylbenzene Under Enviromentally Friendly Conditions

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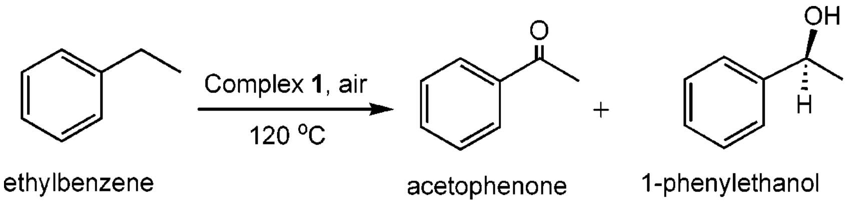
Although cobalt(II) catalysts are well known for aerobic oxidation of alkylaromatics, cobalt(III)-based catalysts also have been shown to be effective for the oxidation of alkylaromatic hydrocarbon feedstock [1]. Olive green oxo-bridged Co(III) cubane complexes $Co_4(?_3\text{-}O)_4(?\text{-}O_2CMe)_4(py)_4$ (**1**) and $Co_4(?_3\text{-}O)_4(?\text{-}O_2CPh)_4(4\text{-}CNpy)_4$ (**2**) – py, pyridine and 4-CNpy, 4-cyanopyridine – have been prepared by H_2O_2 oxidation of a mixture of Co^{2+}, RCO_2^- and py/4-CNpy in methanol at an elevated temperature and tested as catalysts for ethylbenzene oxidation [2].

Using complexes **1** and **2** as homogeneous catalysts air oxidation of neat ethylbenzene has been investigated



under atmospheric pressure at 120ºC. While the reaction catalyzed by **1** has resulted in 68.6% yield of acetophenone at 99% selectivity, compound **2** catalyzes the reaction giving acetophenone in 60% yield and 94% selectivity at the end of 22h at 120 ℃.

The above combination of yield and selectivity shows that cobalt(III) complexes having a cubane-like $[(Co^{III})_4(?\text{-}O)_4]^{4+}$ core are highly active in the aerobic oxidation of ethylbenzene under solvent free, hence environmentally attractive conditions.

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Synthesis, Adsorption Studies and Analytical Applications of N-Cetyl-N, N-Trimethyl Ammonium Bromide Based Cerium(IV) Phosphate: A Novel Surfactana Based Hybrid Fibrous Ion Exchanger

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A recent interest has been developed in the synthesis of hybrid fibrous ion-exchangers [1] due to their outstanding chemical, mechanical and thermal stability, in addition to metal ion selectivity. It has been observed that the introduction of organic species into an inorganic material enhances its reproducibility in ion-exchange behavior and its chemical stability to some extent. A large number of hybrid fibrous ion-exchange materials [2-6] have been synthesized in these laboratories by incorporating organic monomers/polymers with inorganic ion-exchange materials, showing the promising ion-exchange characteristics. Surfactants or surface-active agents have shown the enhancement in adsorption of metal ions on the surface of ion exchangers [7-9] by reducing the interfacial tensions between the material (solid) and aqueous phase (liquid). Efforts have, therefore, been made in these laboratories to synthesize some surfactant based hybrid fibrous ion-exchange materials. Surfactant, when present in the matrix of inorganic ion-exchanger not only, enhances the ion-exchange capacity of the material but also the adsorption of metal ions. The present work deals with the synthesis of N-cetyl-N, N, N-trimethyl ammonium bromide based cerium (IV) phosphate (CTAB-CeP) as a new surfactant based hybrid fibrous ion-exchanger.

CTAB-CeP was synthesized by mixing the solutions of ceric sulphate, phosphoric acid and N-cetyl-N, N, N-trimethyl ammonium bromide of optimum concentrations to obtain a material having good ion-exchange capacity (2.95 meq/dry g).

Adsorption studies have been performed for alkaline earths and heavy metal ion in different concentrations of HCl, HNO_3 and $HClO_4$ media. On the basis of the adsorption studies, the material has been found highly selective for Cd (II) ions, one of the most toxic heavy metals. Hence, its analytical utility has been established by achieving some binary separations of Cd (II) from other ions on its column, as:

Hg(II)-Cd(II), Mg(II)- Cd(II), Sr(II)- Cd(II) and Ni(II)- Cd(II).

The synthesized material (CTAB-CeP) has been found to have higher ion-exchange capacity than the other hybrid ion-exchangers [2-7], prepared earlier. Further, it has been found Cd (II)-selective, exploring its potential role in environmental and pollution chemistry where the separation of this ion is needed/required.

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Synthesis, Structural And Complexation Studies of Pentaerythritoxy-Bridged and Lariat Ether Type Cyclocarbaphosphazenes

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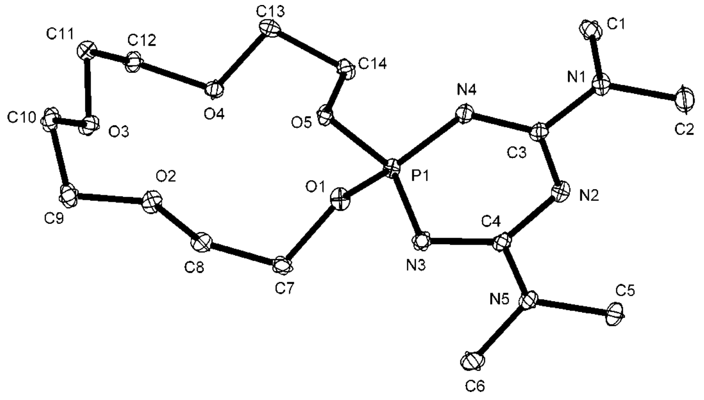
Reactions of dilithiated diols [$HO(CH_2)_3OH$, and $HO(CH_2CH_2O)_nH$, $n = 2$, 3 and 4] with 3, 5- bis (N, N-dimethylamino)-1,1-dichlorodicarbaphosphazene (**1**) in THF in 1:1 molar ratio have been carried out to afford the first examples of lariat ether type spirocyclic dicarbaphosphazene derivatives. The tetrasodium salt of pentaerythritol also reacts with **1** in 1:2 molar ratio to give a pentaerythritoxy-bridged spiro-spiro product. All the new compounds were stable to hydrolysis and have been characterized by spectroscopic and analytical methods and a few also by X-ray diffraction method. Complexation studies of spirocyclic compounds with Na^I, K^I, Ag^I and Cu^{II} ions were carried out by conductance measurements. The studies indicate mostly 1:1 complex formation between the metal ions and the lariat ether type cyclocarbaphosphazene derivatives. The reaction of dicarbaphosphazenes with aza-18-crown-6 and aza-15-crown-5 ethers resulted in the formation of azacrown derived carbaphosphazenes. The characterization and complexation studies of these compounds will also be presented.



Design and Synthesis of Redox Switched Ionophores and Their Use in Transport of Main Group Metal Ions Through Supported Liquid Membrane

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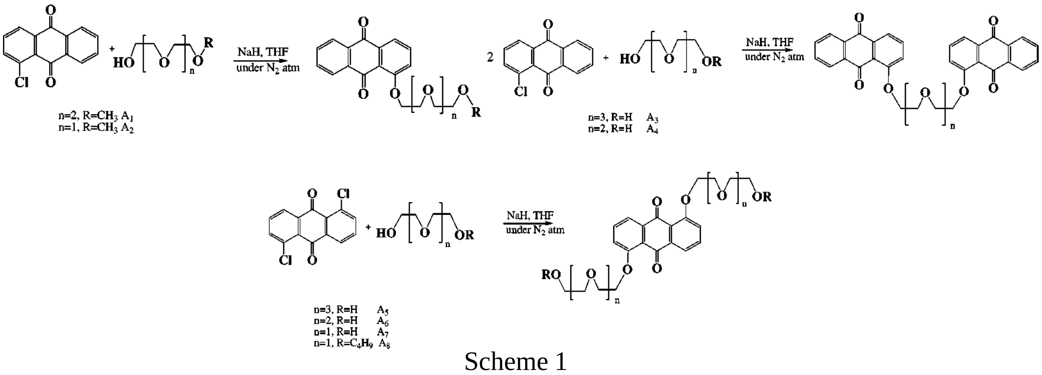
Carrier mediated transport through supported liquid membranes is one of the important applications of supramolecular chemistry. In the late 1960s Pedersen, Lehn, Cram Vogtle *et al* published [1-3] the synthesis of macrocyclic molecules (crown ether, cryptand, spherands, podands) that are able to selectively bind ions or small organic molecules via noncovalent interaction. Lariat ethers are combination of anthraquinone moiety with different podands; these were developed by G.W. Gokel [4]. Lariat ethers are macrocycic polyether compounds having one or more donor group bearing side arms. In the systems prepared to date, side arms are attached to carbon (carbon pivot lariat ethers).

A novel series of redox switched anthraquinone derived single armed [5], bridged and double armed lariat ethers (**A$_1$**) 1-(1-anthraquinonyloxy) 3, 6, 9-trioxanonane-9-methane (**A$_2$**), 1-(1- anthraquinonyloxy), 3, 6 -dioxahexane-6-methane, **(A$_3$)** 1, 11-(dianthraquinonyloxy) 3, 6, 9 trioxaundecane, **(A$_4$)** 1, 8-(dianthraquinonyloxy) 3, 6 dioxaoctane, (**A$_5$**) 1, 5 bis (2-(2-(2-(2-hydroxyethoxy) ethoxy) ethoxy) ethoxy) anthracene-9-10 dione, (**A$_6$**) 1, 5 bis (2-(2-(2-hydroxyethoxy) ethoxy) ethoxy) anthracene-9-10 dione , (**A$_7$**)1, 5 bis (2-(2-hydroxyethoxy) ethoxy) anthracene-9-10 dione (**A$_8$**)1, 5 bis (2-(2-(2-butoxy) ethoxy) ethoxy) anthracene-9-10 dione scheme1 have been synthesized by reacting anthraquinone moiety with different podands and characterized by m.p., TLC and spectral analysis. These redox switched lariat ethers were used in carrier-facilitated transport of main group metal ions across supported liquid membrane (SLM). These membranes were impregnated with ionophore (10^{-3} *M*) dipped at overnight and used as membrane support.

The results of SLM studies with ionophores (A$_1$-A$_8$) are listed in Table1 & 2. Ionophore A$_1$ having triethylene glycol side arm, shows strong binding affinity with small size of cation, so it forms stable complexes with Li^+ and Na^+. Therefore it shows less transport for K^+, Na^+ ion and no transport for Ca^{2+}, Mg^{2+}. Ionophore A$_2$ having diethylene glycol chain shows tremendous increased carrier ability as compared to A$_1$ and the trend for cation transport as $Li^+ > Na^+$.

Using cellulose nitrate membrane as support, ionophore A$_3$-A$_6$ shows carrier ability for all the cations. Ionophore A$_3$ & A$_5$ showing best result for K^+ ion due to long glycol chain moiety attached to the anthraquinone end group. Li^+, Na^+ & K^+ have ability to be transported by all the ionophores (A$_1$-A$_8$). Ca^{2+} and Mg^{2+} are not at all transported by ionophore A$_7$ & A$_8$, due to shorter glycol side arm. On the basis of selectivity ratio ionophore A$_3$ and A$_6$ shows higher transport for K^+ and Ca^{2+}. In SLM, ionophores do not move freely, they are fixed on the membrane and due to this their flexibility and mobility is checked. Hence sequence is different as observed in BLM [6] system. Electron microscope studies are in under process. Cellulose nitrate membrane is a better support as compared to onion membrane. This selectivity can be used in fabrication of sensors and redox switchable devices.



Scheme 1

Cationic Homo/Hetero Bi- And Tri-Nuclear Ruthenium Complexes

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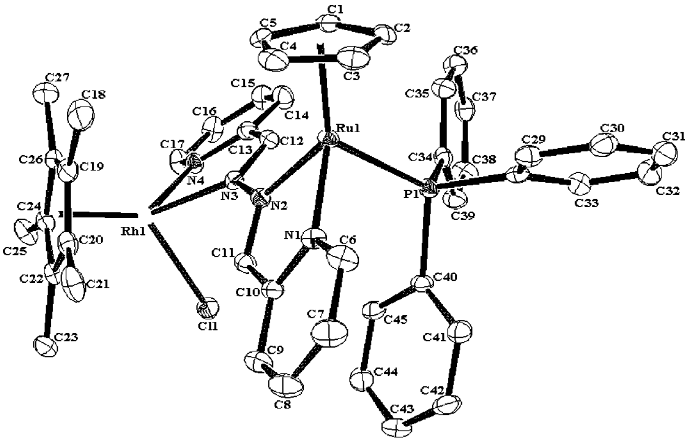
Considerable recent attention has been paid towards the synthesis and characterization of homo/hetero bi- or multinuclear complexes bridged by poly-pyridyl and azo aromatic ligands because of their potential use in various fields. In such complexes specific role of the bridging ligands is largely influenced by acceptor and donor properties of coordination sites, the length and rigidity of spacers, presence or absence of conjugated bonds, orientation of the substituents and scope of manipulating ligand charge. Although, poly-pyridyl ligands have extensively been used in this regard, closely related pyridyl azine ligands viz., pyridine-2-carbaldehyde azine (paa), *p*-phenylene-bis(picolino)-aldimine (pbp), *p*-biphenylene-bis(picoline)-aldimine (bbp) have relatively been less studied. To examine the applicability of such complexes in the synthesis of homo/hetero bi or tri-nuclear complexes, the representative complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\kappa^2\text{-paa})]PF_6$ and $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-dppm})(\kappa^2\text{-paa})]BF_4$ reported previously by our group have been used as potential metallo-ligand to produce a range of Ru/Ru, Ru/Rh, Ru/Pt homo/hetero dyads and Ru/Ru/Ru and Ru/Ru/Rh triads. [1]



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Specific Calcium Ion Fluorescence Sensor: Signaling by Conformatonal Switching Induced Pet Suppression in a Bichromophoric Acridinedione Foldamer

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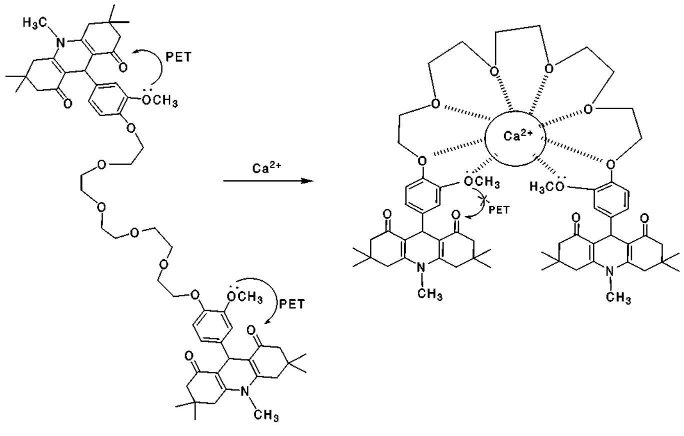
The design of chemosensors which are specific for the detection of biologically relevant cations, such as Na^+, K^+, Mg^{2+}, Ca^{2+}, is a topic of considerable interest [1]. Selective detection of Ca^{2+} in the presence of Na^+, K^+ & Mg^{2+} is important because many of the physiological processes are triggered, regulated or influenced by Calcium ion [2]. Even though a variety of crown-ether and related macrocyclic based chemosensors are known, the corresponding acyclic poly-ether (podand) based sensors are relatively rare [3]. Herein, we report the synthesis & selective binding studies of a novel acridinedione based bichromophore linked to an oxyethylene chain (podand) as the flexible recognition moiety. This bichromophore shows weak fluorescence due to the Photoinduced electron transfer (PET) from the electron rich –OMe group to the relatively electron deficient excited state of the fluorophore. The binding of Ca^{2+} ion induces conformational folding, in which Ca^{2+} binds with both the –OMe group. This binding suppresses the PET process and results in the fluorescence enhancement. This binding event was confirmed by ^{1}HNMR titration studies & time resolved fluorescence technique. Na^+, K^+ & Mg^{2+}ions do not show any significant variation, which clearly shows the unique ability of **1** to detect Ca^{2+} ions specifically. The binding of cations in noncyclic polyethers will mainly depend on the charge density & coordination number of the cation, which may be the reason for the specific binding of Ca^{2+} over other cations.



1 1.Ca²⁺

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Palladium Complexes of Some Semicarbazones Efficient Building Blocks for Heterodinuclear Complexes

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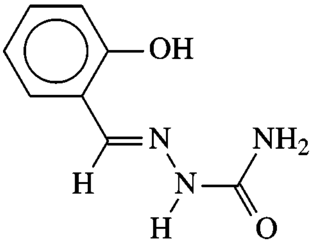
There has been considerable interest in the chemistry of transition metal complexes of the semicarbazone ligands, primarily because of their bioinorganic relevance and particularly because of their potentially beneficial biological (viz. antibacterial, antimalarial, antiviral, and antitumor) activities. However, we have been studying chemistry of the platinum metal complexes of the semicarbazone ligands with special reference to the variable coordination modes displayed by these ligands. In the present work, salicylaldehyde semicarbazone (1), and two related ligands (viz. 2-hydroxyacetophenone semicarbazone, and 2-hydroxynaphthaldehyde semicarbazone) have been chosen as the main ligands,



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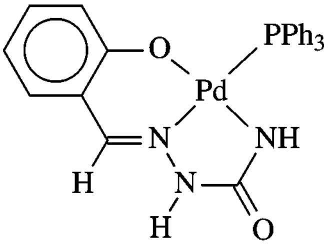

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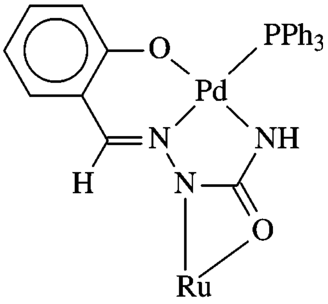

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and palladium has been selected as the metal. As the source of palladium the $[Pd(PPh_3)_2Cl_2]$ complex has been utilized. Reaction of $[Pd(PPh_3)_2Cl_2]$ with the selected semicarbazone ligands in the presence of a base has afforded a family of complexes (2), where the semicarbazones are coordinated to palladium as dianionic tridentate O,N,N-donors. Utilizing these palladium complexes (2) as the building block, interesting heterodinuclear complexes (3), containing ruthenium as the second metal) have been prepared. The chemistry of all these complexes is described in this presentation, with special reference to their formation and characterization.

Chlorocarbonyl Ruthenium(II) Complexes of Tripodal Triphos {$MeC(CH_2PPh_2)_3$}: Isolation and Structural Investigation

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Tridentate tertiary phosphines are recognized as one of the most important classes of ligands in homogeneous catalysis by transition metals. Recently, several ruthenium(II) carbonyl complexes containing polyphosphine ligands have shown interesting chemistry and catalytic activity which prompted us to synthesize ruthenium carbonyl complexes of tripodal tridentate phosphine ligand {$MeC(CH_2PPh_2)_3$} (tdpme) and to study their structural characteristics. $[Ru(CO)_2Cl_2]_n$ reacts with the tripodal triphos ligand {$MeC-(CH_2PPh_2)_3$},(tdpme), to form the di carbonyl complex $[Ru(CO)_2$\{$MeC(CH_2PPh_2)_3$\}$-Cl_2]$**(1)**, which exhibits two equally intense í(CO) bands at 2054 and 1988 cm^{-1} indicating *cis* disposition of carbonyl groups. The complex **1** underwent decarbonylation in dichloromethane to afford the monocarbonyl complex $[Ru(CO)$\{$MeC(CH_2PPh_2)_3$\}$Cl_2]$ (**2**) exhibiting a single terminal í(CO) band at 1959 cm^{-1}. The molecular structure of the complex **2** has been determined by Single Crystal X-ray diffraction (Figure 1). The complex $[Ru(CO)$\{$MeC(CH_2PPh_2)_3$\}$Cl_2]$ is monoclinic, Cc, with a = 21.8609(4) Å, b = 10.3959(2) Å, c = 18.5067(4) Å and a = 90°, b = 117.467(2)° and g= 90°. The ruthenium atom occupies the centre of a slightly distorted octahedral geometry. The complexes were characterized by elemental analyses, IR, ^1H NMR, ^{31}P NMR spectroscopy.

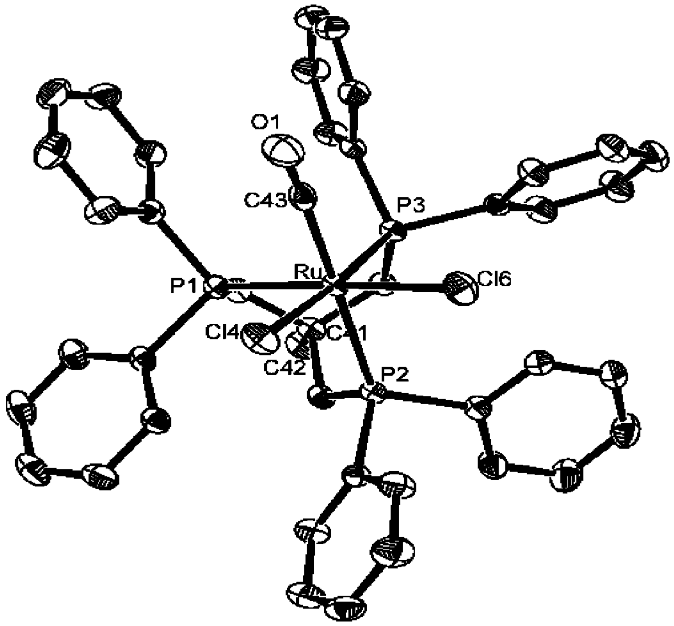

Fig 1. Single Crystal X-ray structure of $[Ru(CO)$\{$MeC(CH_2PPh_2)_3$\}$Cl_2]$.

Tripodalorganoselenoethers as Potential Ag(I) Extractant

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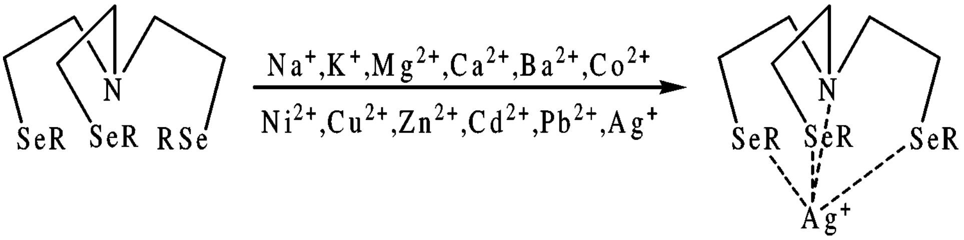
In continuation of our studies on the polychalcogen bearing species, we have synthesized a series of tripodalorganochalcogenoethers of the type N $(CH_2CH_2ER)_3$ [E= Se, Te].The tripodalorganoselenoethers exhibit a remarkable selectivity towards silver ions over a variety of other metal ions including alkali (Na^+, K^+), alkaline-earth(Mg^{2+},Ca^{2+},Ba^{2+}), transition and heavy metal ions(Co^{2+},Ni^{2+},Cu^{2+},Zn^{2+},Cd^{2+} and Pb^{2+}).Studies carried out on these tripodal ligands clearly indicated that the tripodalorganoselenoethers are able to extract out the Ag (I) ions highly efficiently in an extremely short span of time.



Metallaboranes of Earlier Transition Metals: Synthesis and Spectroscopic Characterization of Tantalaborane $\{h^5\text{-}C_5Me_5Ta\}_2B_5H_{10}(C_6H_4CH_3)$

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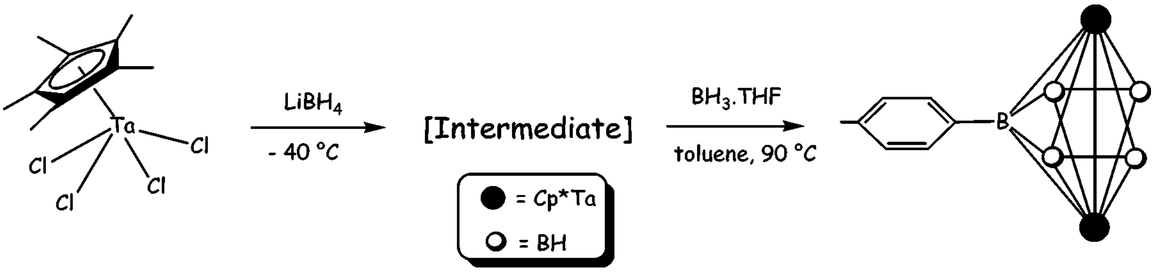
Reaction of 6 equiv of $LiBH_4$ with Cp^*TaCl_4 ($Cp^* = h^5\text{-}C_5Me_5$) followed by thermolysis with $BH_3\cdot THF$ in toluene at 95°C leads to the formation of electronically unsaturated tantalaborane, $\{Cp^*Ta\}_2B_5H_{10}(C_6H_4CH_3)$. The spectroscopic characterization and solid state X-ray structure shows that it is isostructural with Mo, Cr and W analogues and is best described as bicapped *closo* trigonal bipyramidal geometry.



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Synthesis and Characterization of La (III) Incorporated Carboxylated Chitosan Beads for Fluoride Removal

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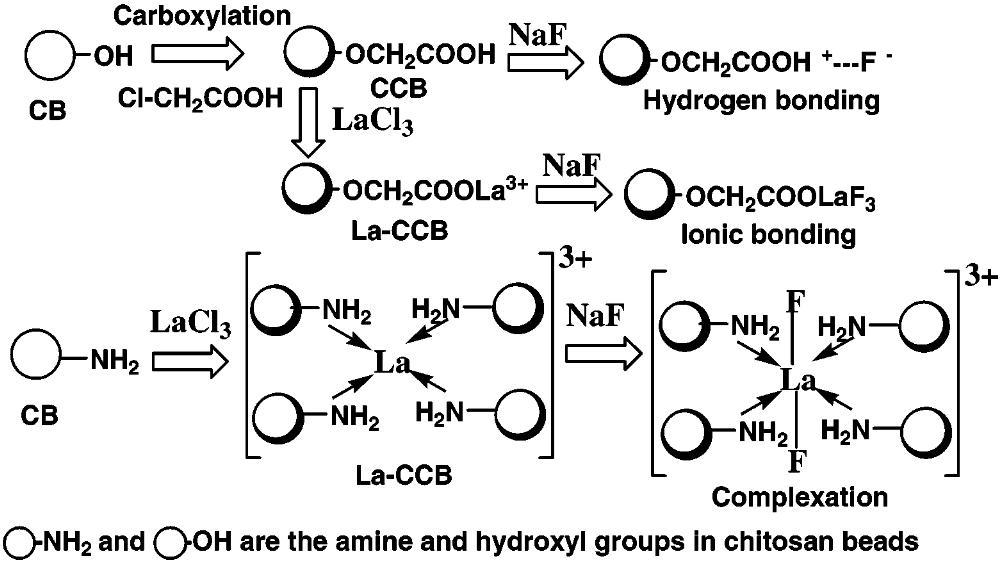
Chitosan beads (CB) as such have very low defluoridation capacity [DC] of 51mg F^- /kg has been modified by carboxylation and chelation with La^{3+} ion (La-CCB), in order to effectively utilize both hydroxyl and amine groups for defluoridation. The modified beads showed an enhanced DC to a very significant level of 4787 mg F^- /kg. The fluoride removal process is governed by both adsorption and complexation mechanism simultaneously (cf. Scheme 1). The sorbent was characterized using FTIR and SEM with EDAX. The sorption process follows both Freundlich and Langmuir isotherms. The experimental data have been fitted with kinetic models. Thermodynamic parameters such as DG^o, DH^o and DS^o were calculated to predict the nature of sorption is spontaneous and endothermic. A field trial was carried out with fluoride water collected from a nearby fluoride-endemic village to test the suitability of sorbent at field conditions. Suitable eluent was also identified for the continuous use of the sorbent.



Scheme 1. Mechanism of fluoride removal by La-CCB.

New Diorganotin(IV) Derivatives of Tyrosinylphenylalanine: Synthesis and Structural Characterization, Crystal Structure of Me_2Sn (TYR-PHE)

Mala Nath[1*], Hitendra Singh[1], George Eng[2], Xueqing Song[2]

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New diorganotin(IV) derivatives of tyrosinylphenylalanine (H_2Tyr-Phe) with general formulae R_2Sn(Tyr-Phe) where R = Me, *n*-Bu, Ph and *n*-Oct have been synthesized. The bonding and coordination behaviour in these derivatives are discussed on the basis of FT-IR, multinuclear ^{1}H, ^{13}C and ^{119}Sn NMR and ^{119}Sn Mössbauer spectroscopic studies. These investigations suggest that the dipeptide in R_2Sn(Tyr-Phe) acts as dianionic tridentate coordinating through COÕ, NH_2 and $N_{peptide}$ groups and the polyhedron around tin in R_2Sn(Tyr-Phe) is a trigonal-bipyramidal. It is further confirmed by the single crystal X-ray structure of Me_2Sn(Tyr-Phe) which shows two methyl groups and peptide nitrogen ($N_{peptide}$) are in the equatorial positions, while the two axial positions are occupied by the carboxylic oxygen(COÕ) and the amino nitrogen (NH_2) atom from the same ligand molecule and the tin atom is at centrally located position.

Cyclotriphosphazene appended with six porphyrins

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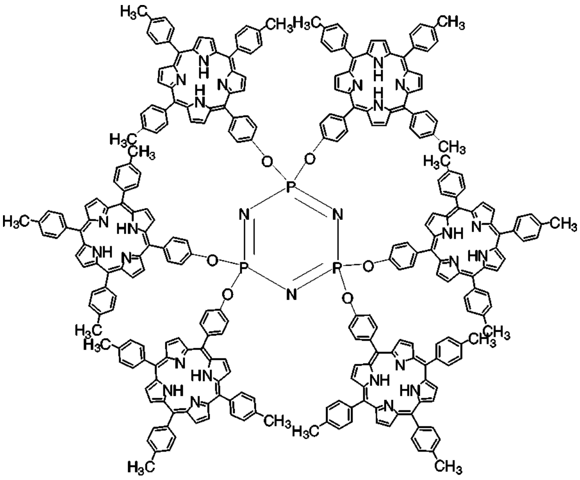
The design and construction of novel porphyrin architectures, in particular well-defined porphyrin arrays, is an area of increasing current interest. These porphyrin assemblies are of fundamental importance not only as models for the study of the energy and electron-transfer functions of the light-harvesting antenna and the photosynthetic reaction centers but also as building blocks for the construction of functional molecular devices, i.e., molecular scale wires, switches and photovoltaic devices, etc.[1] In the case of the natural antenna systems, the function and properties of the chromophoric arrays are controlled by the spatial arrangement and orientation of the molecules, which themselves are held in a specific architecture through predominantly noncovalent interactions within a protein and carotenoid scaffold. The resulting assemblies, which can consist of up to several hundred porphyrins, are able to transfer energy over large distances with a very high efficiency. The first step toward mimicking the properties of such systems is the development of techniques which enable the construction of well-defined multichromophore arrays. Our group has been involved in the synthesis of appropriate porphyrin building blocks with different porphyrin cores such as N_4, N_3S, N_3O, N_2S_2 etc and used them for the construction of porphyrin dyads, triads, tetrads including photonic wire[2]. In this poster, we present our recent results on new type of hexameric multiporphyrin arrays in which all porphyrin chromophores are anchored to cyclotriphosphazene. The synthesis and studies of such novel systems will be presented.



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Kinetics of Electron Transfer From Lactic Acid to Tris – (Dimethylgloximato) Nickelate (IV) in Aqueous Medium

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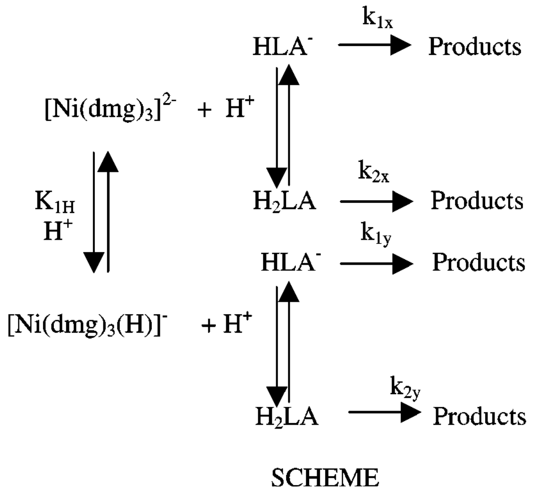
The kinetics of electron transfer from Lactic acid [S] to tris-(dimethylglyoximato) nickelate(IV), $[Ni(dmg)_3]^{2-}$ (dmg^{2-} = dimethylglyoximate anion), have been studied in aqueous medium at pH 11. The kinetics exhibit a pseudo-first order disappearance of $[Ni(dmg)_3]^{2-}$ when excess lactic acid is present. The pseudo-first-order rate constants k_{obs} are linearly dependent on $[S]_o$ for varying concentration of the reactant. The pH rate profiles with low $[S]_o$ show a monotonic decrease in rates with increasing pH. The results are interpreted in terms of a probable mechanism involving a rate-determining outer-sphere one-electron transfer from the reductant to the unprotonated and one protonated species of the Ni^{IV} complex present in the solution, followed by a subsequent and kinetically indistinguishable rapid reaction of the Ni^{III} intermediate (eq.1). The major product of the oxidation of Lactic acid by the Ni(IV) complex is pyruvic acid (eq.2).

$$[Ni^{IV}(dmg)_3(H)]^- + HLA^- \xrightarrow{k_1} [Ni^{III}(dmg)_3(H)]^{2-} + HLA^{\cdot}$$

$$[Ni^{III}(dmg)_3(H)]^{2-} + HLA^{\cdot} \xrightarrow{k_2} [Ni^{II}(Hdmg)_2] + dmg^{3-} + LA'$$

$k_2 >> k_1$, where LA' = dehydro lactate, H_2LA = Lactic Acid

$$CH_3CH(OH)\,COO^- + Ni(dmg)_3^{2-} + H_2O \longrightarrow Ni(dmgH)_2 + H_2dmg + CH_3CO\,COO^- \text{ ----- } (2)$$



SCHEME

P 40

Multinuclear Copper(II) Complexes: Effective Catalysts for Peroxidative Oxidation of Cyclohexane, Toluene and Benzene

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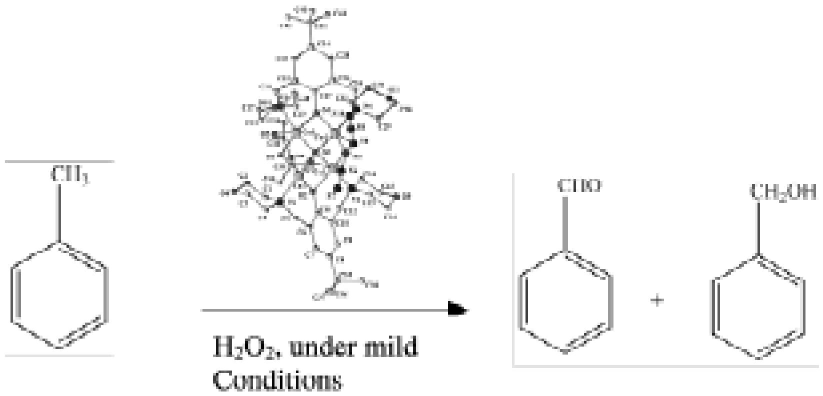
Large attention on multinuclear copper(II) complexes owes their origin to the effective role for catalytic enzymatic reactions.[1] Model enzymatic reactions for the oxidation of hydrocarbons in nature have been mimicked with copper complexes in the presence of several oxidants.[2] The study of the oxidation of cyclohexane assumes a special attention owing to the fact that its oxidized products are of immense industrial importance.[3] Benzene and substituted aromatic hydrocarbon (e.g. toluene) occupy a prominent position with regard to their role in commercial purpose as well as their hazardous impact on the environment.[4] We report here the syntheses and characterization of three copper(II) complexes with N_2O donor system, $[Cu_2(\mathbf{L_1})(\mathrm{m}_2\text{-pz})(CH_3COO)_2]$ (**1**)**,** $[Cu_4(\mathbf{L}_1)_2(\mathrm{m}_4\text{-O})(\mathrm{m}_2\text{-}CH_3COO)_2(\mathrm{m}_{1,1}\text{-}N_3)(N_3)]$ (**2**) and $[Cu_2(\mathbf{L_2})(\mathrm{m}_{1,1}\text{-}N_3))(\mathrm{m}_{1,3}\text{-}N_3)_2]$ ¥ (**3**) (where pz = pyrazolato, $\mathbf{HL_1}$ = 2,6-bis(morpholinomethyl)-4-*tert*-butylphenol and $\mathbf{HL_2}$ = 2,6-bis(morpholinomethyl)-4-methylphenol) X-ray crystallographic studies confirm the formation of di-, tetra- and polynuclear copper(II) complexes. These compounds show very effective catalytic property for the peroxidative oxidation of cyclohexane and toluene under mild conditions using H_2O_2 as the oxidant. The products are cyclohexanol and cyclohexanone in the case of cyclohexane oxidation; the corresponding products are benzyl alcohol and benzaldehyde for toluene. The oxidation of benzene to phenol has been carried out at 50 ºC using the same oxidant.



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DNA Binding And Nuclease Activity of Binuclear Copper(II) Complexes of Cuminaldehyde Thiosemicarbazones

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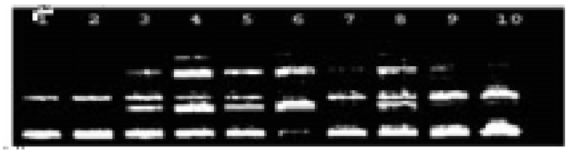
Binuclear copper(II) complexes of CTH, CMTH, CETH and CPTH (where CTH = cuminaldehyde thiosemicarbazone, CMTH = cuminaldehyde-4-methyl-3-thiosemicarbazone,CETH=cuminaldehyde-4-ethyl-3-thiosemicarbazone, CPTH = cuminaldehyde-4-phenyl-3-thiosemicarbazone) have been synthesized and characterized on the basis of elemental analysis, conductivity measurements, magnetic susceptibility data, electronic, IR and ESR spectroscopy. Electrochemical behaviour of these complexes has been investigated by cyclic voltammetry. All complexes undergo quasi-reversible one electron electrochemical reduction (Cu^{II}/Cu^{I}) in the potential range 0.505 – 0.545 V against Ag/AgCl reference electrode. The formula weight of the complexes is determined using LC-MS. The DNA binding of copper complexes with CT-DNA has been investigated using absorption spectrophotometry. The apparent binding constants for complexes are in the order of 10^7 to 10^8 M^{-1}. Based on the data obtained in the DNA binding studies is suggested that the complexes binds to DNA very effectively. DNA cleavage activity is carried on plasmid pUC18 DNA. All complexes show hydrolytic cleavage activity. The efficiency of cleavage activity is in the order $[Cu_2(CMT)_2Cl_2] > [Cu_2(CET)_2Cl_2] > [Cu_2(CPT)_2Cl_2]$.



Acylmethyl(aryl)tellurium(IV, II) derivatives: Restricted Rotation About Te-C(mesityl) Bond

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Electrophilic substitution of methyl ketones, $RCOCH_3$ (R = *i*-Pr,***1***; Et,***2***; Me,***3***) with aryltellurium trichlorides, $ArTeCl_3$ (Ar = 1-$C_{10}H_7$, Np, ***A***; 2,4,6-$Me_3C_6H_2$, Mes, ***B;*** 4-$MeOC_6H_4$, Anisyl, ***C***) at room temperature affords the corresponding acylmethyl(aryl)tellurium dichlorides. Reduction of the dichlorides, gives tellurides, $(RCOCH_2)ArTe$, ***1A***-***3C***, which give the corresponding dihalides, $(RCOCH_2)ArTeX_2$ (X = Cl, ***1Aa***-***3Ca***; Br, ***1Ab***-***3Cb***; I, ***1Ac***-***3Cc***) when reacted *in situ* with SO_2Cl_2, Br_2 and I_2. The unsymmetric tellurides are labile towards disproportionation and attempts to obtain them lead to the isolation of Ar_2Te_2 and Ar_2Te except in the case of *i*-PrMesTe (***2B***), which represents an interesting example of a kinetically stable aryl(alkyl)telluride. All the dihalomesityltellrium(IV) derivatives show separate ^1H and ^{13}C NMR signals for the *ortho* methyls irrespective of the sizes of R and X ligands. The telluride, ***2B*** with free rotation about Te-C(mesityl) bond show, like the unsymmetric diorganotellurium(IV) dihalides, only one ^{125}Te NMR signal. The 1,4-chelating behavior of the acyl ligand among diorganotellurium(IV) compounds is inferred from the X-ray diffraction data for **1Ac**, **1Ba**, **1Bb, 1Ca,**and **1Cc** which are indicative of the presence of intramolecular Te···O secondary bonding interactions (SBIs) at least in the solid state. Intermolecular C-H···O H-bonding interactions present in the crystal packings of**1Ba** and **1Bb** that are devoid of Te involved SBIs, appear to be retained in solution as well and result in the loss of rotational symmetry of the *ortho* methyl substituents of the mesityl ligands.

Synthesis, crystal, molecular structure and properties of some new phenylmercury(II) dithio complexes

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A series of new phenylmercury(II) dithio complexes $[(PhHg)_2cdc]$ (**1**; cdc^{2-} yanodithioimidocarbonate), $[PhHg Bu_2^n dtc]$ (**2**; $Bu_2^n dtc^-$ = di-n-butyldithiocarbamate), [PhHg morphdtc] (**3**; $morphdtc^-$ = morpholinedithiocarbamate), $[(PhHg)_2NED]$ (**4**; NED^{2-} = 1- nitroethylene – 2, 2 - dithiolate), [PhHg methoxethxant] (**5**; $methoxethxant^-$ = 2 – methoxyethyl xanthate) and $[PhHg Bz_2dtc]$ (**6**; Bz_2dtc **=** dibenzyldithiocarbamate) have been prepared and characterized by elemental analysis, UV – Vis., IR, ^1H and ^{13}C NMR spectra and mass spectrometry. The crystal structures of **2**, **3** and **6** showed almost linear Hg(II) core at the centre of the molecule. The weak intra- and inter-molecular Hg···S interactions provide stacked antiparallel molecular framework. Interestingly, the reaction of $PhHgOOCCH_3$ with $Bu_2^n dtc$ gave the known dimeric complex $[Hg(Bu_2^n dtc)_2]_2$ while the $Ni(O_2CCH_3)_2$ mediated reaction gave **2** instead of expected heterobimetallic complex $[PhHgNi(Bu_2^n CS_2)_2]OOCCH_3$. Upon excitation at 358 nm **6** exhibited a medium strong photoluminescence emission at 420 nm. All of the complexes are weakly conducting ($ó_{rt} \sim 10^{-12}$ S cm^{-1}). However **1** and **3** exhibited semiconductivity with band gaps 0.39 and 0.94 eV respectively. Density functional theory has been used to investigate the molecular structures of **1**, **4** and **5**.

Oxidation of Styrene Catalyzed by Cu(SALEN) Intercalated a-Zirconium Phosphate

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The heterogenization of tranistion metal complexes is an area of growing interest, particularly on zeolites, mesoporous silicate materials, polymers and activated carbon [1-3]. We have synthesized Cu(Salen) intercalated a-Zirconium phosphate [a-ZrP.Cu(Salen)] in situ by the flexible ligand method and characterized by XRD, SEM and IR spectroscopic techniques. Its catalytic behaviour for the epoxidation of styrene using *tert*-butylhydroperoxide and H_2O_2 as an oxidant was studied. Various parameters of the catalytic reaction along with kinetics will be presented.

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Synthesis, Derivatization, Transition Metal Chemistry and Catalytic Investigations of a Novel Tetraphosphorus Ligand

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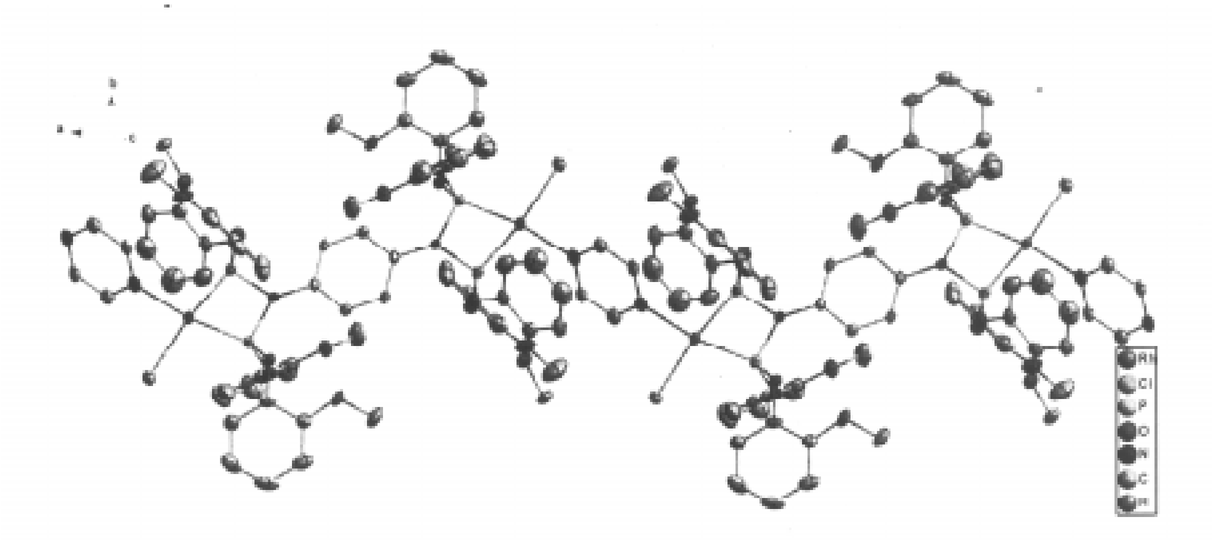
Metal complexes of phosphorus-based ligands play central role in various metal-catalyzed organic transformation reactions. In recent days, the progress on ligand chemistry and substantial development of high efficient catalytic systems become a major goal in the community of organic and inorganic chemists. In view of this, we present herein the synthesis, coordination chemistry and catalytic investigations of a new family of aminotetra(phosphines) derived from $[C_6H_4(NP_2Cl_4)_2\text{-}p]$ (**1**).[1] Molecular structure of **1** shows an unprecedented intermolecular P…P interactions leading to the formation of a 2-D sheet. The aminotetra(phosphonites), $p\text{-}C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$ (**2**) and $p\text{-}C_6H_4[N\{P(OMe)_2\}_2]_2$ (**3**) have been prepared by reacting **1** with appropriate amount of 2-(methoxy)phenol or methanol in presence of triethylamine. The oxidation reactions of **2** and **3** with H_2O_2, elemental sulfur or selenium afforded the tetrachalcogenides, $p\text{-}C_6H_4[N\{P(O)(OC_6H_4OMe\text{-}o)_2\}_2]_2$ (**4**), $p\text{-}C_6H_4[N\{P(S)(OMe)_2\}_2]_2$ (**5**) and $p\text{-}C_6H_4[N\{P(Se)(OMe)_2\}_2]_2$ (**6**) in good yield. The ligand **2** has been extensively used for the synthesis of several di-, tetra- and polynuclear late transition metal complexes. The use of these complexes towards various organic transformations such as Suzuki-Miyaura cross-coupling and transfer hydrogenation reactions will be presented.



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1,1’-Ferrocenedicarboxylate-bridged Redox-active Organotin and -tellurium-containing 16-membered Macrocycles. Synthesis, Structure and Electrochemistry

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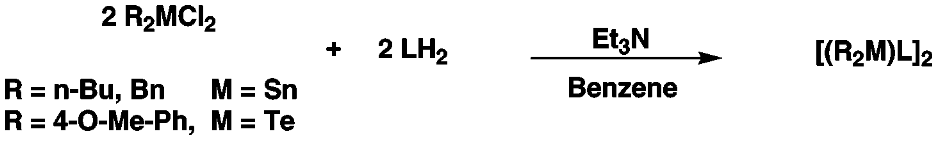
Recently there has been considerable interest in the application of inorganic rings and cages as scaffolds for the preparation of multiredox compounds [1]. Organostannoxane-supported multiferrocene assemblies are readily prepared in a reaction involving an organotin precursor and ferrocenecarboxylic acid [2]. Reactions of 1,1’-ferrocenedicarboxylic acid, LH_2, with $(nBu)_2SnO$ under solvothermal conditions at 180 ºC afforded a completely dealkylated octanuclear cage $[Sn_8O_4L_6]$ [3]. This compound was not electrochemically stable and decomposed under cyclic voltammetric conditions. We reacted LH_2 with diorganotin halides R_2SnCl_2 (R = n-Bu and Bn) and Ar_2TeCl_2 (Ar = 4-OMe-C_6H_4) in normal reflux conditions [4] and obtained molecular compounds. The molecular structures of these compounds have been confirmed by single crystal X-ray analysis. This reveals that the two main-group metal atoms within each macrocycle are bridged to each other by two ferrocenecarboxylate ligands. In the case of the organotin derivatives the ferrocenedicarboxylate ligand acts in an anisobidentate chelating manner leading to a hexacoordinate tin present in a skewed trapezoidal bipyramid geometry. In contrast, in the tellurium analogue the ferrocenecarboxylate ligand is monodentate leading to a tetra-coordinate tellurium in a see-saw geometry. ESI-MS studies on these macrocylic complexes reveal that they retain their structural integrity in solution. Electrochemcial studies reveal that $[n\text{-}Bu_2SnL]_2$ and $[Ar_2TeL]_2$ show two quasi-reversible oxidation processes. These compounds have low comproportionation constants (K_c) and can be described as being intermediate between no-coupling and weakly-coupled systems. $[Bn_2SnL]_2$ also shows two oxidation processes. However, in this instance, the second event is irreversible.



$$2\,R_2MCl_2 + 2\,LH_2 \xrightarrow[\text{Benzene}]{Et_3N} [(R_2M)L]_2$$

R = n-Bu, Bn M = Sn
R = 4-O-Me-Ph, M = Te

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Rhodium Catalyzed Regiospecific Multiple Carbenoid Insertion Approach to Indolophanes

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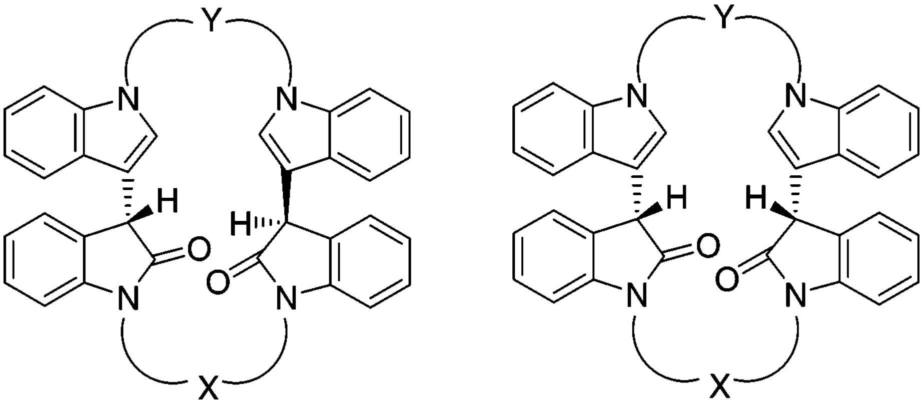
Cyclophanes have received much attention due to the structural versatility and opportunities for synthetic modifications, host-guest complexation, molecular self assembly and specific receptor activity [1,2]. However, aromatic groups contained in the cyclophanes are mainly carbocyclic rings such as benzene and naphthalene derivatives. Not many cyclophanes are reported with heteroaromatic ring systems. Herein, we report the $Rh_2(OAc)_4$ catalysed regiospecific intermolecular double carbenoid insertion reactions of cyclic diazoamides affording indolophanes via two carbon-carbon bonds formation in a single synthetic step.

Employing 3-diazo-1,3-dihydro-2*H*-indol-2-one as the carbene source, we recently described the first regioselective intermolecular carbenoid insertion reactions of cyclic rhodium(II) carbenoids to afford quantitative yields of intermolecular insertion products [3,4]. Our enticement in developing the new synthetic strategies using tandem reactions of diazocarbonyl compounds encouraged us to investigate the application of this methodology for the synthesis of cyclophanes. The $Rh_2(OAc)_4$ catalysed intermolecular double carbenoid insertion strategy has been successfully implemented for the synthesis of indolophanes as mixture of diastereomers. The notable details of our investigations will be presented.



X, Y = Aliphatic or aromatic Spacers

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Computational Studies on the Structures of $B_8H_8^{2-}$

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Several structures of $B_8H_8^{2-}$ species have been characterized at the Hartree-Fock and density functional (B3LYP) levels of calculation, using several basis sets in each case. Some of the previously suggested structures [1] (O_h, D_{3h} and D_{3d} symmetries) are seen not to correspond to true energy minima on the potential energy surface and some previously unreported stable structures are identified.

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Anion-Directed Synthesis of Metal-Organic Frameworks Based on 2-Picolinate Cu(II) Complexes: A Ferromagnetic Alternating Chain and Two Unprecedented Ferromagnetic Fish Backbone Chains

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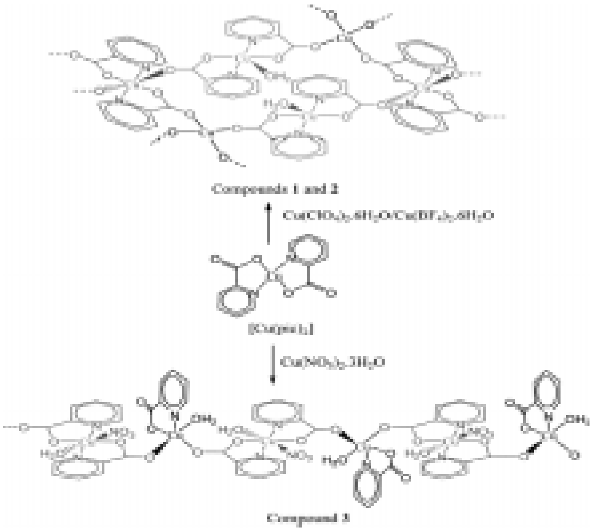
2-picolinic acid on reaction with Cu(II) salts produces discrete, mononuclear ‘inner metallic complex’ [Cu(pic)$_2$] which can potentially be used as a “metalloligand” building block to construct high-nuclearity copper complexes. In our study, three new polynuclear copper(II) complexes of 2-picolinic acid (Hpic), $\{[Cu_2(pic)_3(H_2O)]ClO_4\}n$ (**1**), $\{[Cu_2(pic)_3(H_2O)]BF_4\}n$ (**2**), and $[Cu_2(pic)_3(H_2O)_2(NO_3)]n$ (**3**), have been synthesized by the reaction of “metalloligand” [Cu(pic)$_2$] with the corresponding copper(II) salts. Crystal structure analyses show that compounds **1** and **2** are isomorphous and are constructed by “fish backbone” chains but **3** possess a very different polymeric network. Therefore, these compounds provide very interesting examples of the anion-directed template synthesis of metal-organic frameworks by using the versatile coordination mode of 2-picolinic acid. The present work shows how a slight change in coordination ability of the anion along with the difference in the H-bonding network can play a crucial role in determining the overall structure of the coordination network. Variable-temperature (2-300 K) magnetic susceptibility measurement shows the presence of weak ferromagnetic coupling for all three complexes that have been fitted with a fish back bone model developed for **1** and **2** (J = 1.74 and 0.99 cm^{-1}; J’ = 0.19 and 0.25 cm^{-1}, respectively) and an alternating chain model for **3** (J = 1.19 cm^{-1} and J’ = 1.19 cm^{-1}).



Anaerobic DNA Cleavage in Red-light by a Dicopper(II) Complex on Disulfide Bond Activation

Debojyoti Lahiri, Biswarup Pathak, Ashis K. Patra, Eluvathingal D. Jemmis
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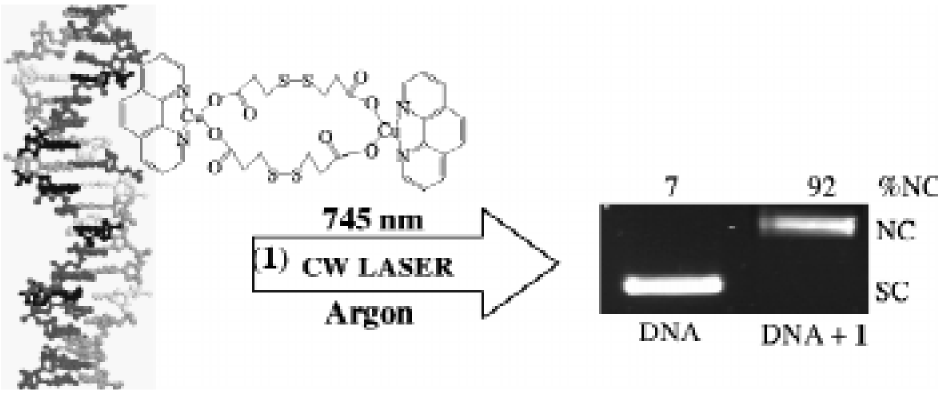
Anaerobic DNA damage is of immense biological importance. Cancer cells generally have hypoxic conditions within it. Therefore, compounds that are capable of cleaving DNA anaerobically are of potential use in the chemistry of new generation anticancer drugs. We have prepared a copper-based disulfide complex that shows efficient DNA strand scission on photolysis at red light under anaerobic conditions (argon atmosphere). The results are of importance in the chemistry of photodynamic therapy (PDT) of cancer [1]. The currently used PDT drug is Photofrin®. It is a porphyrin-based compound that cleaves DNA in red light aerobically involving singlet oxygen as the reactive species. Our dicopper(II) complex(1), in contrast, on photolysis in red light under argon leads to the formation of disulfide anion radicals as DNA cleaving species by accepting an electron from the electron donor solvent. The chemistry of photoactive compounds showing anaerobic DNA cleavage in red light is virtually limited. The organic dyes require aerobic conditions for their activity. It is thus of importance to develop the chemistry of metal-based compounds as anaerobic photocleaver of DNA for PDT applications.

In this work we report the synthesis, structure, DNA binding and cleavage properties of a ternary copper(II) complex $[Cu_2(3,3'\text{-dtdp})_2(phen)_2]$ (**1**). The complex displays efficient photonuclease activity on irradiation with monochromatic UV-A radiation of 365 nm or visible light of 647 and 745 nm wavelengths. The mechanistic pathway involves formation of disulfide anion radical as a reactive species.



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ZnO/Immobilised Resin Based Photo Catalyst Using for Transformation of Organic Molecule (Congo red)

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The Photo catalytic transformation of organic molecule (Congo red) has been investigated in ZnO /immobilized Resin aqueous suspension. It was attempted to determine the feasibility of such transformation by varying different parameters. In addition to prompt removal of the color, ZnO/immobilized resin based photo catalyst was simultaneously able to complete transformation of the organic molecules, with a complete mineralization of Carbon into CO_2, Sulphur a heteroatom into SO_4^{-2}. The mineralization of Nitrogen was more complex, Nitrogen atom in –3 oxidation state, such as in amino group, remain at this reduction degree and produces NH_4^+ cations, subsequently and strongly change into NO_3^- ions.

These results revels that ZnO/immobilized resin photo catalysis may be employed in methods for treatment of colored wastewater, not only for de-colorization, but also for de-toxification, in particular in textile industries in semi-arid countries.

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P 52

Photo-redox chemistry of cobalt (III) ammine complexes coordinated to unsaturated carboxylic acids: Product analysis and quantum yields determination

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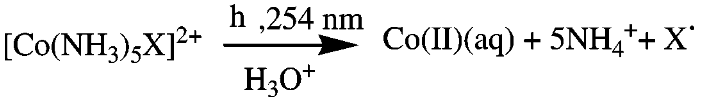
Cobalt(III) pentaammine complexes with unsaturated carboxylic acids coordinated to the metal lead to photoredox processes from the charge-transfer-to-metal (CTTM) excited states [Horvath et al (1)]. We have investigated the photoredox chemistry of the complexes of the type $Co(NH_3)_5 X^{2+}$ where X is crotonic acid, cinnamic acid or sorbic acid and examined in detail the nature of the decomposition products from the carboxylate free radical. The complxes on excitation in the CTTM band lead to the reaction



$$[Co(NH_3)_5X]^{2+} \xrightarrow[H_3O^+]{h\ ,254\ nm} Co(II)(aq) + 5NH_4^{+} + X^{\cdot}$$

The photooxidised ligand fragments were isolated and characterized by NMR, IR, UV-Vis and mass spectral analysis. The quantum yields were determined for the photoredox reaction. The formation of the organic molecules from the photooxidised carboxylic acids shows interesting reaction pathways, which will be presented.

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Probing Geometry of Complexes in Solution by Depolarized Hyper-Rayleigh Scattering

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Noncovalent interactions are important in a number of chemical and biological processes. It plays an important role in dictating structures of liquids, structure of DNA and the geometry of protein-ligand binding. These interactions may be as weak as van der Waals force or as strong as hydrogen bonding and charge transfer interactions. The smallest unit where we find the manifestation of these intermolecular interactions are 1:1 aromatic donor-acceptor complexes. Relative orientation of the component molecules in such complexes is determined by the nature of interaction and the two extreme geometries known are the parallel stacked and the T shaped geometries. In experiments, the main attention, so far, has been given to determine the geometries of such complexes in the solid state and in the gas phase. Though many groups have attempted to probe the structures of such complexes in solution by NMR spectroscopy, they were unable to provide the details of relative orientation in terms of the tilt and twist angles between the component molecules. In this work, we use depolarized hyper-Rayleigh scattering technique to probe the geometry of noncovalently bound 1:1 molecular donor-acceptor complexes in solution. It provides the characterization of structure of such complexes in solution in terms of the first hyperpolarizability tensor (b_{ijk}). The origin of second order optical nonlinearity is purely electronic in nature and thus the electronic structure of such complexes can be described in terms of its hyperpolarizality tensor elements in the molecular frame. The molecular anisotropy is defined as $u = \frac{\beta_{122}}{\beta_{111}}$ (where123 is the molecular frame, 1 being the direction of the principal axis of symmetry). We measure the depolarization ratio (D) in the laboratory fixed frame (XYZ, X being the direction of polarization and Z the direction of propagation of the incident light), where $D = \frac{<\beta^2_{XXX}>}{<\beta^2_{ZXX}>}$ (b_{XXX}, b_{XXZ} are the first hyperpolarizability tensor elements in the same frame) and correlate to u through co-ordinate transformation. How the symmetry of the molecules and that of light can be combined to find geometrical information will be illustrated in this poster with examples such as 1,2,4,5-tetracyanobenzene(TCNB)-1,2,4,5-tetramethylbenzene(durene), 2,3,5,6-tetrachloro-1,4-benzoquinone(Chloranil)-durene, and benzene-naphthalene pairs.

Synthesis and Sequestration of Au Nanoparticles by Alpha Amylase

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We shall present our recent results on the use of alpha amylase enzyme for the synthesis of Au nanoparticle (NP) as well as their sequestration. The sequestration could be the result of attachment of enzyme to the NPs after synthesis or it could be due to uptake from Au NP-starch composite following digestion.

We have for the first time synthesized Au NPs from $AuCl_4^-$ by using a pure enzyme such as α-amylase as the reducing agent [1]. We find that in the composite, the activity of the enzyme is retained, as revealed by the kinetics of starch digestion, which is similar to that of pure enzyme. The presence of free and exposed S-H groups is essential in the reduction of $AuCl_4^-$ to Au NPs as well as their stabilization.

Further, we have carried out systematic study of the kinetics as well as the mechanism of digestion of starch-Au NP composite by α-amylase [2]. This is relevant to starch-based polymers being used for pulsatile release of drugs, peptides and other bioactive agents and starch-encapsulated magnetic particles for superior magnetic resonance contrast agents. We observed that not only the digestion kinetics of the composite was similar to that of pure starch, but the enzyme also sequestered the NPs following digestion. Finally, it was established that the surface plasmon resonance of the Au NPs could be a direct probe for the study of digestion of starch (in the composite) by the enzyme. A qualitative model for the digestion of the composite by α-amylase has also been proposed, which is important for nanoscale drug delivery systems.

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The Model Study of Proton Transfer Phenomena in Various Forms of GC Base Pair

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The structural changes and destabilization of base pair are some of the important consequences of radical formation within DNA. The most energetic radicals can distort the flexible nucleic acid structure drastically [1]. The schematic representation of proton transfer within hydrogen bonding region of normal GC base pair has been compared with the proton transfer reactions through GC radical, GC cation and cationated GC radical to demonstrate the most favorable proton transfer pathway. There are significant differences in the energy levels of proton transfer in these systems and generation of cation and radical species at the equilibration region of proton transfer are distinctly indicated. The two local minima detected in the cationic radical types of proton transfer are $(GH^+)C$ and $G(H^+C)$, herein the minimum corresponding to $G(H^+C)$ occurs at lower energy level than the one for $(GH^+)C$ [2]. Hence the proton is more stable at the cytosine nucleobase rather than guanine. The formation of G^+ is found in cationated GC. Similarly two local minima are found at different energy levels in GC radical and cationated GC radical. Here we have studied only the energies for the single proton transfer mechanism within hydrogen bonding region, where the formation of cationated GC radical is found to be stable than the Watson Crick GC base pair. On the other hand the formation of CG^+ may drastically disturb the rate of proton transfer within normal DNA due to the stabilization of cationated species**.**

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P 56

Determination of Chloride in Liquid Detergent Using Ion-selective Electrode with a Method of Standard Addition

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Liquid detergent finds wide applications in cleaning of different instruments such as healthcare instruments, electronic components and various reactor components etc. Cleaning surfaces may involve large variety of construction materials viz. glass, metal, ceramic, plastic, cement and fiberglass. It is commonly used for leak detection on any system where there is a pressure differential. It is for this type of application in reactors i.e. leak test of certain facility that the presence of chloride in the liquid detergent becomes very crucial. The presence of chloride as impurity affects the physical properties of the metal and accelerates the rate of corrosion in the system [1-3]. Hence, the determination of chloride in the liquid detergent is very important.

The liquid detergent comprises of alkyl benzene sulfonate surfactant. It contains about 0.1 to 3 % of magnesium salt. The magnesium salt helps in improved cleaning performance and better skinning properties. Magnesium chloride, either anhydrous or hydrated (e.g., hexahydrate), is especially preferred in the formulation. The method contained in ISO 457:1983 standard for the determination of chloride is based on the titrimetry method. The method is applicable to detergents having chloride content equal to or greater than 0.1%. For the quantitative determination of chloride at trace level a new accurate method has been developed using chloride ion-selective electrode. The method of standard addition is frequently employed for samples of variable matrix; hence this was applied for the determination of chloride in liquid detergent.

In the method of standard addition to sample, the following equation was applied

$$C_0 = C_s / 10^{DE1/S} (1+V_0/ V_1) - V_0/V_1 \qquad (1)$$

Where S is the electrode calibration slope, V_0 and V_1 are the volumes; C_0 and C_s are the concentrations of the sample and the standard respectively. $DE_1 = E_1 - E_0$ where E_1 and E_0 are the potentials measured for the sample with and without standard addition. For this method, the slope of the electrode response curve must be known and should be linear, interfering species must be absent and, finally, the liquid junction potential between the reference electrode and the solution must not change.

Samples of liquid detergent were obtained from local market (Bright liquid detergent). The sample solution (1 mL) was taken in a polyethylene beaker. To this, 5 mL of 0.1 M KNO_3 was added and final volume was made up to 10 mL with deionised water. The KNO_3 solution is added to adjust total ionic strength of different samples. The potential of this solution was measured with an ion meter (Metrohm, Switzerland) using chloride selective electrode (Orion) and Ag/AgCl reference electrode. For standard addition appropriate volume of chloride standard solution (1 mg L^{-1}) was added in steps in the range 0.1 – 1 mL. The potential was measured after each standard addition. The concentration of the chloride ion was calculated by using the equation (1). The results obtained for two liquid detergents samples are presented in Table 1. The limit of detection for the determination of chloride is 10 mg mL^{-1} and the relative standard deviation was 5 % for the overall method.

Attempt was made to validate the method by measuring the chloride concentration in the samples by turbidimetry and ion chromatography (IC) method. Both these measurements were not successful because of serious interference from the matrix elements in turbidimetry and column contamination in IC methods. Hence the method has been validated by standard addition recovery studies.

A simple, rapid and accurate method has been developed for the determination of chloride in liquid detergent solutions. It makes use of readily available chemicals and equipment.

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Tunable optical and electronic property of Oligo(phenyleneethynylenes)

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Oligo(phenyleneethynylenes) (OPE) are a class of molecules, which are well known for their interesting electronic and photophysical properties.[1] The greater interest in these molecules is attributed to their tunable property by introducing various functional groups and inducing geometric changes. Among various functionalized OPEs and related polymers the alkoxy substituted phenylethynylenes are well studied for their interesting photo physical properties such as optical absorption and emission.[1b] Recent literature reports various studies on change in the fluorescence behavior of these molecules on suitable substitution of the phenyleneethyneylene backbone.[3] There are similar studies on the electronic properties of these molecules, and these studies confirm that the rearrangement of electronic states of conjugated p-backbone on substitution and conformational changes.[4] In order to understand the effect non-conjugated side chain in the transport characteristics of these molecules, we have carried out combined X-ray crystallographic and photophysical studies alkoxy substituted phenylene ethynylene molecules with varying alkoxy chain length. These molecules show high emission properties both in solution and solid state with large blue shift in the film. Interestingly, on varying the alkoxy side chain length of the alkoxy substitution, the molecules exhibit variation in planarity and in turn a systematic variation in molecular transmission.

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Adsorption kinetics of alkanethiols on Au nanocrystals in a 2D lattice using optical absorption spectroscopy

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We have investigated how the optical absorption property of a 2D lattice of metal nanocrystals can be tuned with alkane thiols of different chain lengths. This 2D lattice is a tightly packed assembly of gold nanocrystals obtained via a self assembly process at the liquid-liquid interface[1, 2]. The absorption band is situated at 700 nm for the pristine lattice which gets blue shifted upon adsorption of alkane thiols, the magnitude of the shift being proportional to the chain length. The disordered nanocrystals thus created ($\lambda_{max,}$ 530 m) are in equilibrium with the ordered nanocrystals in the lattice ($\lambda_{max,}$ 700 m) as indicated by an isosbestic point around 600 nm. The rate of interaction of thiols with the Au nanocrystal lattice decreases with decreasing chain length. The long chain thiols disintegrate or disorder the lattice more effectively, as evidenced by the increased population of the thiol-capped Au nanocrystals in the solution. The effect of an alkanethiol is specific and the effects with long and short chains are reversible. The changes in the Au plasmon band due interparticle separation has been satisfactorily modeled on the basis of the Maxwell-Garnett formalism [3].

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Exfoliated Graphite Oxide - Based Assemblies for Amperometric Sensing

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Exfoliated Graphite Oxide (EGO) is a layered material, lighter than graphite, both in colour and in density. It consists of oxidised graphite sheets with hydroxyl and epoxy functional groups in the basal plane and carboxyl and carbonyl functional groups at the edges. The functional groups make EGO hydrophilic and water molecules can readily intercalate into the interlayer galleries. Hence, EGO is regarded as graphite-type intercalation compound with covalently bound oxygen and non-covalently bound water between the carbon layers. The presence of a large amount of functional groups leads to the stabilization of negatively charged EGO as a colloid in a wide pH range of 2-11.

In the present studies, EGO is prepared by chemical oxidation of exfoliated graphite (prepared by thermal exfoliation of bisulphate ion intercalated graphite) and characterized using spectroscopic and electrochemical techniques. Thin film of EGO on glassy carbon electrode (GC) was formed by evaporation technique using colloidal EGO deposited on the GC surface. The EGO film is subsequently used to detect Pb(II) in aqueous medium. The detection limit is found to be picomolar and two linear calibration ranges are obtained in 1pM to 0.1 µM and 10 µM to 10 mM.

In the second part of the studies, electrostatic layer-by-layer assembly of EGO and redox protein (haemoglobin) is formed on a gold surface and their electrochemical properties are studied. An amperometric sensor is developed and the system is further applied to the electrocatalytic reduction of hydrogen peroxide.

Reference:
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Application of Majority Rule in the Self-assembly of Aminoacid Functionalized Oligo(*p*-phenylenevinylene)s

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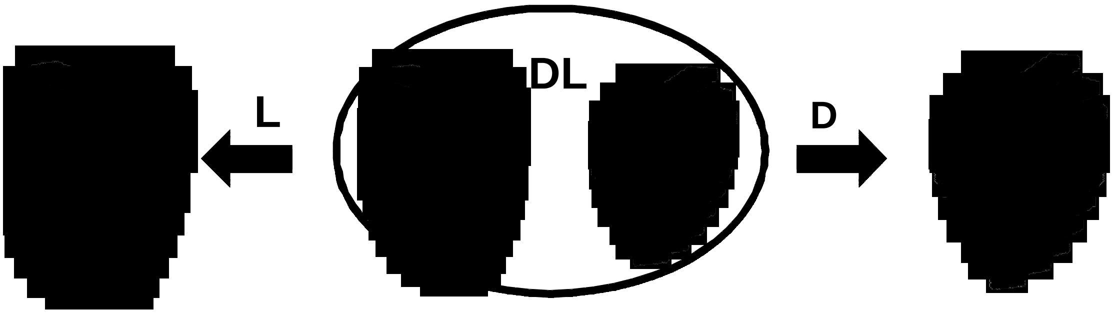
Manifestation of molecular chirality into supramolecular helicity in synthetic molecules, leading to a preferred handedness is a challenging task[1]. The “majority rule” approach reported by Green *et al.* have been used for chirality amplification in supramolecular assemblies, using a slight exess of one enantiomer that leads to a strong bias toward the helicity preferred by the enantiomer that is present in majority[2]. Oligo(*p*-phenylenevinylene)s (OPVs) are known to form helical assemblies and gels in nonpolar hydrocarbon solvents[3]. Herein we explore the possibilities of amino acid moieties as chiral motifs for the creation of helical assemblies of OPVs leading to the formation of gels even in moderately polar solvents such as chloroform and toluene. Addition of a very small concentration of the chiral molecule to the racemes mixture resulted in induction and amplification of chirality’s in the gel state. The enantiomeric excess and co-operating units will therefore act together to favour the helical sense preferred by the configuration of the majority and thereby making the expression of the chirality of a particular enantiomer from a racemic mixture. SEM and TEM studies gave further insight into the morphological features of these chiral OPV self assemblies. The details of these studies will be presented.



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Task Specific Ionic Liquid Bronsted Acid-clay Hybrid Nanocomposite Catalyzed Transesterification Reaction

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Transesterification is one of the important organic transformations that have relished numerous laboratory and industrial uses. The ester to ester transformation is particularly significant when the parent carboxylic acids are labile and difficult to isolate. b- ketoesters are muticomponent coupling reagents having electrophilic carbonyl and nucleophilic carbon which make them important synthons for the total synthesis of number of natural products. Since transesterification, used for the synthesis of new b- ketoesters, is an equilibrium process, it is accelerated by the simultaneous removal of low boiling coproduct alcohol during the process by distillation. This reaction is catalyzed by a number of chemical species like organic and inorganic acids, bases, anion exchange resins, DMAP, molecular sieves, Lewis acids, titanium tetra oxide, zeolites, clay, Mo-ZrO_2 , Envirocat EPZG to list a few. But all these procedures are flawed with one drawback or another like volatility and toxicity of acid catalysts, long reaction times, hostility of catalysts to environmental issues and their non-recoverability.

Due to rigorous environmental statutes, the scientific community is under great stress to develop ecocompatible synthetic methodologies. So present day chemistry is more inclined to re-scrutinize the existing synthetic procedures thereby making them more congenial. More than 60% of products and more than 90% of processes worldwide rely on the rapidly expanding field of catalysis. The use of ionic liquids as either solvents or catalysts is emerging as subject of considerable recent attention in accordance with prospects of ‘Green Catalysis’. Keeping in view these concerns we have synthesized a TSIL- bronsted acid and its clay hybrid which is successfully used as catalyst for the transesterification of b- ketoesters with various alcohols. The results of the same will be presented.

Novel Cyclic Trimeric Thermotropic Liquid Crystals: Synthesis and Characterisation

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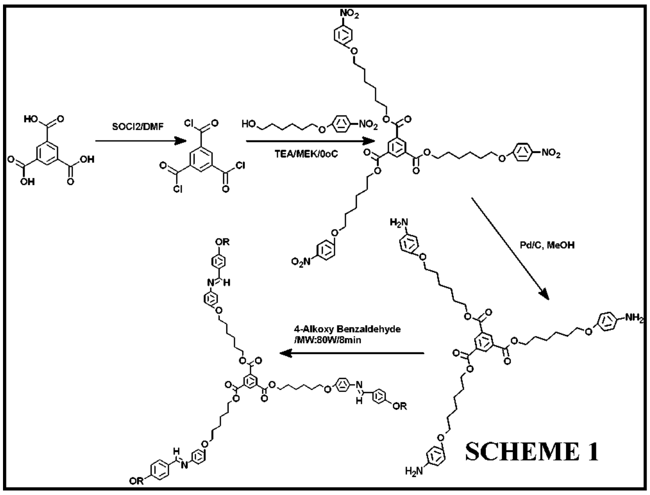
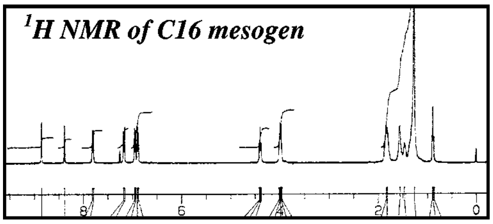
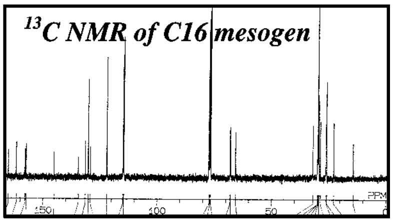
Thermotropic liquid crystals are recognized as an important class of organic electronics due to their sensitivity to external stimuli. From molecular structural point of view, they are primarily classified into calamitics and discotics. Usually, the mesogen consists of core made up of substituted phenyl rings connected through linking groups and flexible terminal units. In recent years, molecular topology of mesogen has been identified as one of the crucial factor in the formation of mesophase. The calamitic mesogens generally have linear like structures while discotics possessed disk-like cores. The cyclic trimers, on the other hand, show different topology leading to the formation of calamitic and columnar phases depending up on the terminal and linking units. Moreover, these oligomers (e.g. trimers) are considered as model compounds for polymeric liquid crystals. In the present work novel cyclic trimeric liquid crystals are synthesized using 1,3,5-tricarboxylic acid as precursor (Scheme 1). All the intermediates and target mesogens are characterized using FT-IR and ^{1}H and ^{13}C NMR spectroscopy (representative spectra are shown). The terminal alkoxy chains are varied from 2-16 (even series) and the mesophase characteristics like melting, clearing temperatures and phase stability is determined by optical polarizing microscope and DSC. The transition enthalpy values further confirm the mesophase identified by the microscope. Despite lower phase stability, the appearance of smectic polymorphism is an interesting feature of the series. The structure-property relationship with respect to core and terminal group chain length are discussed.



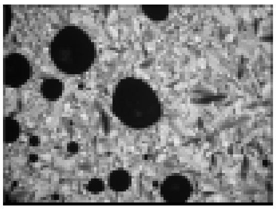
SCHEME 1



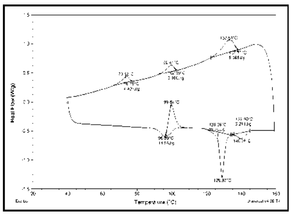
^{1}H NMR of C16 mesogen



^{13}C NMR of C16 mesogen



Focal conic fan texture of Smectic A of C6 Mesogen (OPM)



DSC trace (heating & cooling) of C16 mesogen

Mimicking Simultaneous and Selective Decoupling of Different Heteronuclei and Determination of Relative Signs of Dipolar Couplings Using Multiple Quantum Spin State Selection

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The non-selective excitation of a homonuclear multiple quantum in a heteronuclear spin system does not disturb the spin states of the heteronuclei resulting in the detection of single quantum transitions based on the spin states of the heteronuclei. The cross section taken along the single quantum dimension thus mimics the decoupling of heteronucleus. In addition, the spin state selected transitions are significantly lower in number compared to normal one dimensional spectrum, but suffice for the precise determination of homonuclear couplings. When more than two heteronuclei are involved, the technique can be extended for mimicking simultaneous decoupling of all the heteronuclei. Furthermore, the detection of any heteronuclear multiple quantum results in the selective decoupling of the passive heteronuclei. The methodology can thus be exploited for the analysis of the complex spectrum and for the determination of the relative signs of the dipolar couplings. The results of the work on different isotopomers of acetonitrile, $^{13}CH_3{}^{13}CN$, $^{13}CH_3C^{15}N$, $CH_3{}^{13}C^{15}N$ and $^{13}CH_3{}^{13}C^{15}N$ aligned in thermotropic liquid crystals, including the theoretical description of the behaviour of the spins using polarization operators will be discussed.

Effect Of Various Additives On The Gel-To-Liquid- Crystalline Phase Transition Temperature Of Dimethyldioctadecylammonium-Bromide Vesicles

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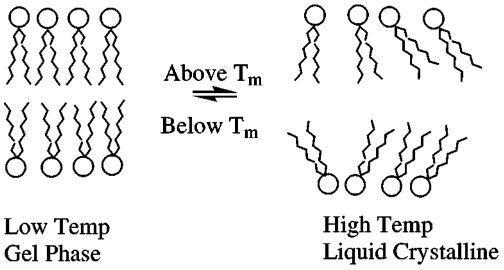
The effect of alkyltrimethylammonium bromides (Tetradecyltrimethyl-ammoniumbromide (TTAB), Hexadecyltrimethylammoniumbromide CTAB and Octadecyltrimethylammonium-bromide OTAB) and alkylpyridiniumhalides (Cetylpyridiniumbromide CPB and Cetylpyridiniumchloride CPC) on the gel-to liquid crystalline phase transition temperature (T_m) of spontaneously formed vesicle dispersions of dimethyldioctadecylammoniumbromide (DDOAB) have been examined using differential scanning calorimetry (DSC). The alkyltrimethylammonium bromides, affected the T_m in a complex manner, depending on the hydrocarbon chain length. OTAB elevated the T_m whereas TTAB and CTAB depressed the Tm of DDOAB vesicles. However, the planar pyridinium heads of CPC and CPB, having similar tail length as that of CTAB, affected the T_m only weakly, although the decreasing tendency of T_m is observable. In addition the shape of the main peak i.e. the gel-to-liquid crystalline phase transition peak shows very little sign of peak broadening. It seems that the lateral attraction between the DDOAB molecules of the bilayer is not reduced significantly by the penetration of the pyridinium moiety. The perturbing effect of aromatic hydroxyl compounds viz.; 1-Naphthol, 2-Naphthol, 2,3-Dihydroxynaphthalene and 2,7- Dihydroxynaphthalene on the gel-to-liquid-crystalline phase transition temperature of the vesicle membrane have also been studied using the same technique. A significant decrease in T_m was observed with the addition of these hydroxy compounds. However, for 2,7-dihydroxynaphthalene the Tm first decreases upto a certain concentration and then increases. The present study reveals some aspects of the interaction of various additives with spontaneously formed vesicles of DDOAB.



Gel to liquid crystalline transition

Photo Catalytic Activity of Lanthanide (Ce, Pr AND Nd) Molybdates

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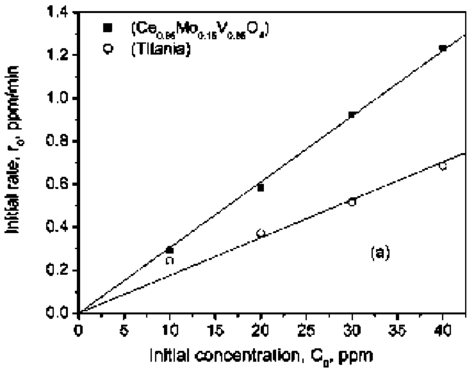
Lanthanide (Ce, Pr, and Nd) molybdovanadates were synthesized by the solid-state method. These compounds crystallize in the tetragonal space group *I41/amd* with $a = b = 7.3750$ (4) and $c = 6.4867$ (4) Å and $Z = 4$. The crystal structure has been analyzed by FTIR, UV-visible spectroscopy, and powder X-ray diffraction. Particle sizes are in the range of 300-400 nm as observed by scanning electron microscopy. Energy-dispersive X-ray analysis suggests the formation of $Ln_{0.95}Mo_{0.15}V_{0.85}O_4$ (Ln = Ce, Pr, and Nd) and the Rietveld refinements of the powder X-ray data substantiate this observation. Thermal analysis of these solids shows stability of the phase up to 800° C. These materials were investigated for photocatalytic activity by degrading different dyes such as methylene blue(MB), orange G (OG), Rhodamine B (RB), Rhodamine Blue (RBL), Alizarine Red S (ARS) and Remazol brilliant blue (RBBR) under solar and UV irradiation since they exhibited lower band gaps. The degradation rates for all the dyes show enhancement as compared to the commercial titania catalyst, Degussa P-25, both in UV and sunlight. These compounds degrade chlorinated phenols much faster than titania, which indicates selectivity toward chloro substitution.



Variation of the degradation rate of MB with initial concentration under solar radiation for Cerium molybdovanadate and Degussa P-25 titania.

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P 66

Ruthenium(II) Complexes of Bipyridine - Glycoluril and their Interactions with DNA

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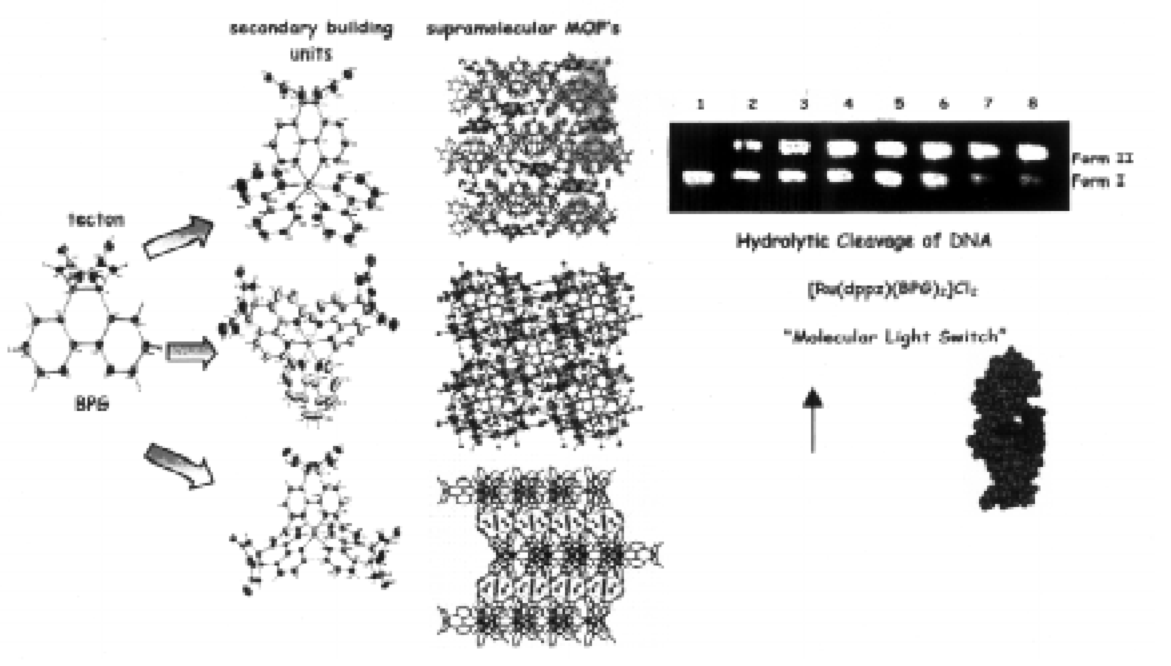
The synthesis, structural and photophysical characterization, DNA binding and cleavage by Ru(II) polypyridyl complexes of the type $[Ru(N\text{-}N)_2(BPG)]Cl_2$ **1-4**, $[Ru(BPG)_3]Cl_2$ **5** and $[Ru(N\text{-}N)(BPG)_2]Cl_2$ **6-9** where N-N is 2,2‘-bipyridine (bpy), 1,10-phenanthroline (phen), dipyrido[3,2-d:2‘,3‘-f]quinoxaline (dpq), dipyrido[3,2-a:2‘,3‘-c]phenazine (dppz) which incorporates the bipyridine glycoluril ligand have been studied to investigate the influence of the ancillary ligand. The X-ray structure of urea fused bipyridine ligand **BPG** reveal inherent H-bond donor (N-H) and acceptor groups (C=O) which exhibit a potential to generate supramolecular motifs as well as offer H-bonding groups for DNA binding. Single crystal X-ray analysis of **1**, **5** and **7** indicate a butterfly like structure for the cationic secondary building units evidencing this H-bonding capacity which results in a supramolecular self-assembled metal-organic frameworks (MOF) forming channels in **1** and **5** encapsulating tetradecameric water cluster, mixed water-dimethylsulfoxide cluster and a network of water molecules and chlorine anions surrounding secondary building units in **7**. The binding ability of these complexes to DNA is dependent on the planarity of the intercalative polypyridyl ligand, which is further influenced by the ancillary bipyridine-glycoluril ligand. Interaction of complexes **1-9** with plasmid *pBR322* DNA reveals that all complexes cleave DNA efficiently at micro molar concentrations under dark and anaerobic conditions probably by a hydrolytic mechanism. Molecular mechanics calculations of these systems confirm two different binding modes for the complexes.



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Performance Evaluation of Waste Activated Carbon from ‘Aquaguard’ as an Adsorbent for the Removal of Phenol from Aquatic Environment

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Water pollution is a persistent problem. Phenolic compounds widely exist in the effluents coming from industries such as oil refineries, coal tar, plastics, leather, textile, paint, varnishes, steel, phenol producing industries, explosive manufacturing industries, fertilizer and pesticide industries, pharmaceutical industries, coke oven plants, dye manufacturing industries, etc., and are acutely toxic. Also, during chlorination of phenol bearing wastewater, chlorophenols are produced. These chlorophenols are toxic and they are considered as persistent organic pollutants (POP). Among several processes available for the removal of phenolic compounds from wastewater, adsorption has been found to be an efficient and economically beneficial process. However, commercially available activated carbon remains to be a rather expensive material. In the present study the waste activated carbon from ‘Aquaguard’ water purifier after it is disposed of, was used for phenol removal. Removal of phenol by waste ‘Aquaguard’ carbon (WAC) was studied separately in batch and continuous mode. WAC was found to be very efficient, and it is almost a ‘no-cost’ material. Under optimized conditions ~98 % efficiency could be achieved for the removal of phenol when present even at a high concentration (20 mg/l). The kinetic studies showed that 4 hours shaking time was sufficient to achieve the equilibrium for phenol. The removal of phenol followed the pseudo-second order reaction kinetics. Study was conducted to see the effects of adsorbent dose on the removal of phenol using WAC. The pH was kept at 6.5±0.1. The optimum adsorbent dose was found to be 2 g/l. The effects of different parameters like pH, presence of different ions, temperature, agitation speed etc. were studied. The removal of phenol increased with increase in pH up to 6.0 and then decreased. There was no effect of agitation speed. The effect of different ions for the removal of phenol was within ±5 %. No effect of humic acid, 2, 4-D, atrazine and endosulfan was noticed. The removal of phenol decreased with increase in temperature. The adsorption isotherm was well described by the Freundlich isotherm model. The maximum adsorption capacity of WAC was found to be 25.57 mg/g for phenol having concentration 20 mg/l at 27±2°C. Evaluation of thermodynamic parameters revealed that the adsorption process was spontaneous and exothermic in nature. Fixed bed column studies were conducted for the removal of phenol from aqueous environment. The column with 2 cm diameter having bed depths of 5, 10 and 15 cm could treat 5.92, 12.11 and 16.65 liter of phenol bearing wastewater (phenol concentration 20 mg/l). The bed was almost 95 % saturated at the time of breakthrough. The adsorption rate constant (K) and adsorption capacity were found to be 0.013105 l/mg-h and 13.886 kg/m^3. Effect of flow rate and initial concentration was studied.

P 68

Estimation of Thermodynamic Properties of Cyclic Paraphenylacetylenes (CPPA) by Isodesmic and Homodesmic Reaction Methods

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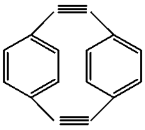
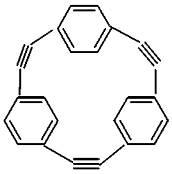
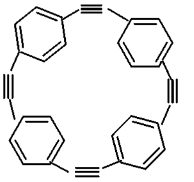
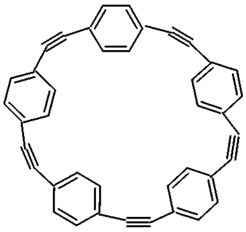
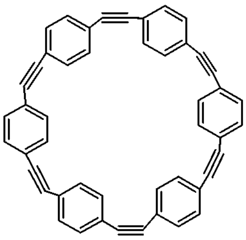
Polycyclic hydrocarbons containing phenyl rings connected to each other at the para positions by acetylenic bonds form a novel group of hydrocarbon molecules with potential applications in carbon nanotubes, molecular devices and molecular electronics.[1] The polymeric structures of polycyclic phenylacetylenes (n = 2 – 7) are given below:

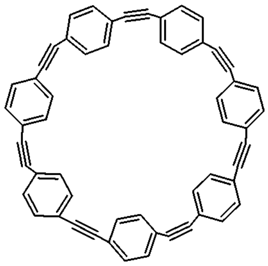












The strain energy becomes less as n increases leading to substantially different chemical stabilities for these compounds. Due to the strain many of these compounds are not yet synthesized in the laboratory, and accurate ab initio studies will hopefully provide for estimations of chemical properties. Isodesmic and homodesmic reactions[2] have been very useful tools in the past few years for performing theoretical calculations of thermodynamic properties. In this paper details of various schemes and the results of calculations performed with the help of Gaussian-03[3-4] will be described along with theoretical analyses for the variation of properties with n.

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In situ Cryo-Crystallisation of Chloro and Bromo Substituted Anilines and its Intermolecular Interactions.

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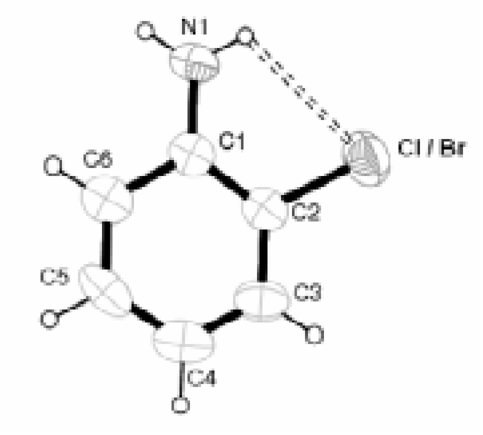
In situ cryo-crystallization of a liquid, the subsequent structure determination and its study of intermolecular interactions has emerged as an area of contemporary interest. *In -situ* cryo-crystallization of fluoro- substituted anilines and the evaluation of the variability in halogenated trifluoroacetophenones (Chopra *et a*l.[1, 2]) clearly bring out the importance of interactions generated by fluorine in crystalline lattices and establishes that indeed fluorine has a directing influence in molecular assembly. In order to evaluate the propensity of interactions in halogens in general, *o* - chloro and *o* -bromo anilines were crystallized from their respective liquids via *in situ* cryo crystallization method. The crystal structures are isostructural belonging to a trigonal system, space group $P\,3_1$. The crystal packing is due to intramolecular N-H…Cl / Br and intermolecular N-H….N hydrogen bonds. However, in the case of *o*-bromo aniline short Br…Br contacts (3.64 Å) are observed suggesting that this interaction is a consequence of the size of the Br atom.



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Electronic Properties of Transverse Substituted and Unsubstituted t-PA: a Comparative DMRG Study

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The optical properties of conjugated polymers have been a frontier area of research because of their potential applications in the non-linear optoelectronic devices. Strong photoluminesence (PL) is one of the most important requirements for making optoelectronic devices [1-3]. Designing of strong PL material requires complete understanding of mechanism involved in the optical phenomenon. According to Kasha's Rule, $E(2A_g)>E(1B_u)$ is the essential condition for strong PL. Trans-polyacetylene (t-PA) is an excellent example of non-emissive material. But replacement of H of t-PA chain by phenyl groups, or it's derivatives leads to strong . This behavior can be understood by considering coulomb interaction of the π electrons in these conjugated systems. Mazumdar *et. al* have considered electronic correlation in substituted t-PA and used Pariser Parr and Pople (PPP) model to study the Polydiphenylacetylene (PDPA) in the Single Configuration Interaction (SCI) picture In this work, we have used finite symmetrized Density Matrix Renormalization Group (SDMRG) method for Polydiethylacetylene (PDEA) and t-PA systems. To obtain $E(2A_g)$ and $E(1B_u)$ states, spatial symmetry $C_{2,}$ spin parity and electron hole symmetry are used. We find that there is no level crossing of $E(2A_g)$ and $E(1B_u)$ states as function of bond alternation, d up to 0.1. Singlet-Triplet gap does not go to zero in PDEA, but it vanishes for t-PA as ä goes to zero. We also compare the non-linear optical properties of these two systems.

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Large Scale Self Organization of Gold Nanorods Leading to One, Two and Three Dimensional Superstructures Induced by Monolayers

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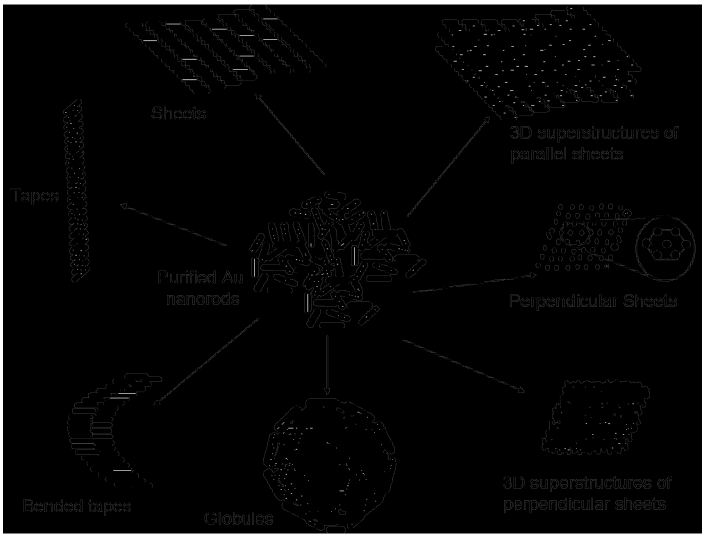
Gold nanorods are versatile material for diverse applications..[1] A method is described for assembling gold nanorods into one, two and three dimensional superstructures. The addition of dimercaptosuccinic acid (DMSA) into the nanorod solution was found to induce self assembly of nanorods into one-dimensional ‘tape-like’, two-dimensional ‘sheet-like’ and three-dimensional ‘superlattice-like’ structures depending on the DMSA concentrations. Assembly was found to be following smectic structure, where the nanorod long axes are parallel to each other. The rods are spaced 8.5±0.3 nm apart in the resulting structures, which extends over micrometer in length. We formed organization perpendicular to the grid also. The nanorod tapes were found to bend and form globular assemblies as well. The assembly and morphology of the nanorod structures were characterized by transmission electron microscopy (TEM) and UV-vis spectroscopy. The effect of DMSA concentration as well as the pH of the medium was also studied. Based on several control experiments utilizing several similar, charge neutralization of the nanorods by the carboxylic group of the DMSA was found to be the principal reason for such an assembly, while the mercapto groups render additional stability. A mechanistic model of the assembly is proposed [2]. This type of assemblies would plausibly function as plasmonic waveguides [3]) in potential nanodevices.



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A Computational Study Towards The Rotational Barriers of Thioamides

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Rotational barrier heights for several thioamides ($X_2NC(=S)$, H=Y, X) have been investigated in the gas phase by applying density functional theory. The calculated results suggest that the electrostatic and electronic effects can tune the planar form of amides to pyramidal forms. The variations of rotational barriers around the formally single C-N bond in all compounds are studied in comparative context with thioformamide. These results will be useful for the studies in immunosuppressant agent like FK506.

Rapid Measurement of $^{3}J(H^{N}\text{-}Ha)$ and $^{3}J(N\text{-}Hb)$ Coupling Constants In Polypeptides

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[2]NMR Research Centre, Indian Institute of Science, Bangalore-560012, India

We have developed two NMR experiments, (3,2)D HNHA and (3,2)D HNHB, for rapid and accurate measurement of $^{3}J(H^{N}\text{-}H^{a})$ and $^{3}J(N\text{-}H^{b})$ coupling constants in polypeptides based on the principle of G-matrix Fourier transform NMR spectroscopy[1] and quantitative *J*-correlation. These experiments, which facilitate fast acquisition of three-dimensional data with high spectral/digital resolution and chemical shift dispersion, will provide renewed opportunities to utilize them for sequence specific resonance assignments, estimation/characterization of secondary structure with/without prior knowledge of resonance assignments, stereospecific assignment of prochiral groups and 3D structure determination, refinement and validation. Taken together, these experiments have a wide range of applications from structural genomics projects to studying structure and folding in polypeptides[2].

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Intra and Intermolecular Hydrogen Bonding in Formohydroxamic acid

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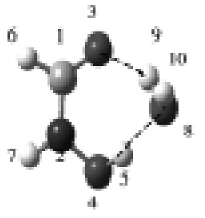
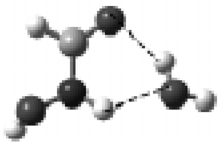
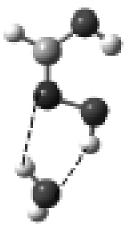
The hydrogen bonding of water with biomolecules like DNA, polypeptides and other molecules etc. significantly affect the structure and reactivity of these basic molecules of life. Hydroxamic acids are molecules of biological importance due to their applications as tumor inhibitors, antimicrobial agents, antituberculosis agents etc. The present theoretical studies suggest, inspite of the presence of multiple potential sites for hydrogen bonding in formohydroxamic acids(FHA), only one of the isomer 1Z shows H-bond interactions, though the distances between H-bond donor and acceptor are less than sum of their van der Waal radii, the X…H-A bond angle does not allow the H-bond stabilization. The aggregation of four lowest energy isomeric forms 1Z, 1E, 2Z and 2E with single water at MP2/Aug-cc-pVDZ level leads to stabilization energies in the range 3.5-10.9 kcal/mol, which indicate that the intermolecular H-bond is stronger than intramolecular H-bond. The dimerization of various isomeric forms at MP2/6-31+G* resulted in stabilization energies of the order 2.6-16.1 kcal/mol. 1Z-1Z(1) homodimer is most stable dimer and the optimized structure is having two symmetrical strong H-bond interactions between carbonyl oxygen of one FHA unit with the hydroxyl hydrogen of the second unit. Carbonyl oxygen is the strongest H-bond acceptor site in FHA as suggested by the dimerization and FHA-H_2O adduct studies. Cooperativity and synergic enhancement of intramolecular H-bonding is suggested in addition to the charge transfer and electrostatic interaction stabilization [1].



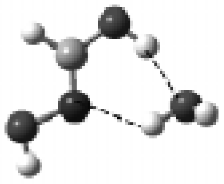
1ZW1



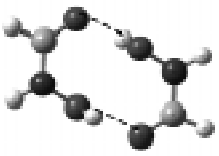
1EW1



2ZW1



2EW1



1Z-1Z (1)

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Anthracene-9,10-dione – A versatile Platform for Both Cation and Anion Chemosensors

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The development of new molecular systems for colorimetric detection of cations, anions and neutral molecules have attained prime significance due to their biological and environmental applications. Anthracene-9,10-diones due to their diverse chemical features depending on the substitution pattern have shown wide spread potential for the development of dye stuff materials, DNA intercalators, redox active and optical sensors. The possibility of color tuning and in-sights into the mechanisms responsible for these color changes can lead to further refinements in procedures.

The augmentation of electron-withdrawing or electron-donating groups on anthracene-9,10-dione moiety tunes the interactions of resulting receptors towards analytes bearing either negative or positive charge. Further the variation in electron density polarization tunes their selective or differential binding towards various heavy metal ions. The use of this meticulous control of varied binding sites in developing wide range of anthracene-9,10-dione based sensors for Cu^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Ag^{+} and F^{-} will be presented[1,2].

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Synthesis And Characterization of Heterogenised Chiral Schiff Base ligands with SBA-15, MCM-41, KIT-6 and its Application on the Enantioselective Reduction Prochiral Ketones

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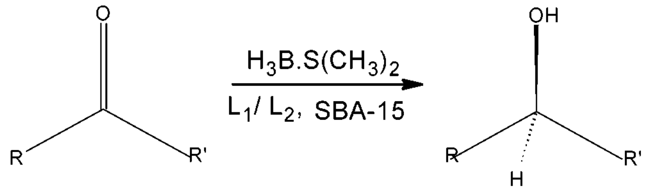
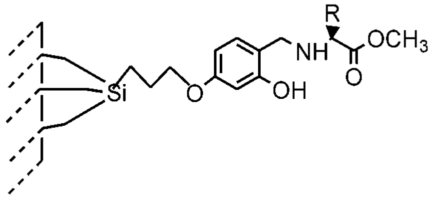
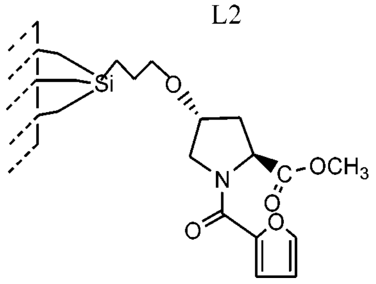
The novel chiral Ligands from Schiff bases of various amino acids such as L valine and L-proline amino acids with aldehydes, and heterogenised using various mesoporous materials like SBA-15, MCM-41, and KIT-6. These chiral Ligands were synthesized by the reported procedure[1] and confirmed its structures using FT IR, ^{1}H NMR, and ^{13}C NMR spectroscopic methods. These catalysts were then anchored with various mesoporous materials mentioned above using 3-chloropropyltriethoxysilane as a reactive surface modifier [2,3]. The immobilization of these chiral Ligands was confirmed by SEM, XRD, EDAX and Nitrogen adsorption-desorbtion methods[4]. These newly synthesized Ligands used as a catalyst for the reduction of various prochiral ketones, and the enantioselectivity was determined using chiral HPLC and Digital polarimeter. The ee(75-80%) determined shows that the catalyst immobilized in silica with larger pore diameters was found to be more active compare to homogeneous catalyst [5]. The catalysts were reusable with neither significant drop in enantioselectivity nor loss of mesostructures and recycled several times by simple filtration.



L1



L2



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Artemisinin and Synthetic Derivatives: a DFT Based Comparison

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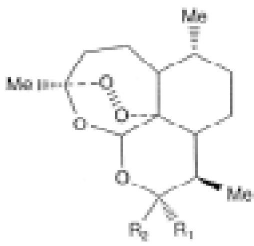
Malaria is one of the most worrying infectious diseases currently affecting the human race. Forty percent of the world's population is at risk of malaria infection causing around 300 to 500 million illnesses and up to 3 million deaths each year [1]. The worldwide malaria situation is serious since malarial parasites have developed resistance to the most common drugs. However, artemisinin, a sesquiterpene endoperoxide, isolated from a Chinese medicinal herb is found to be a potent antimalarial drug against the resistant strains of *Plasmodium falciparum*. But, still there is a need for better one and so numerous derivatives of this promising molecule are being synthesised to reach the goal [2]. Theoretical prediction prior to synthesis may be of great help in minimizing the cost and time factors while developing a better antimalarial drug.



R_1 = H, R_2 = OH	Dihydroartemisinin
R_1 = H, R_2 = OMe	Artemether
R_1 = H, R_2 = OEt	Arteether
R_1 = H, R_2 = $OCH_2C_6H_4CO_2H$	Artelinic acid
R_2 = H, R_1 = $O_2CCH_2CH_2CO_2H$	Artesunic acid

Figure: Artemisinin and derivatives

A theoretical comparison of artemisinin with few of its synthetic derivatives viz. dihydroartemisinin, artemether, arteether, artesunate and artelinate is reported. Geometries of the molecules are optimized by DMol3 software at an SGI-Altix 350 machine with various combinations of basis set and functional using Mulliken and Hirshfeld population analyses. Density functional theory (DFT) [3] based reactivity descriptors such as global softness (*S*), philicity (ω), Fukui function (f^+ & f^-) and relative nucleophilicity/ electrophilicity, calculated at the optimized geometries are used for searching and comparing the functionally important part of the molecules. The results obtained are in excellent agreement with the experimental reports.

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P 78

Structure and Electronic Properties of DNA Base-pairs and Modified DNA

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We have investigated the effect of metal electrodes and metal clusters on electronic properties of DNA bases and base-pairs. We find that Nucleobases trapped within two gold metals on either side undergo expansion. This primarily arises due to the concomitant increase in all the bond lengths in molecules. Such expansion of the molecules can be qualitatively understood on the basis of classical harmonic potentials in the bonds and loss of aromaticity in the rings, resulting in charge redistribution in the system. As a very important consequence of this, the nature of H-bonds potential change substantially within these electrodes. These hydrogen bonds have a single-well potential energy profile (of the type N…H…O and N…H…N) instead of double-well potentials (like N-H…O or N-H…N/N…H-N types) [1]. With such an understanding, we tried to capture the potential use the DNA bases for reversible H-bonding under ambient conditions. Protonation of DNA basepairs is a reversible phenomenon that can be controlled by tuning the pH of the system. We find that, under mild acidic pH conditions, the A:T basepair shows excellent nano-switch rectification behavior that is, however, absent in the G:C basepair. We also consider the noncanonical A:A basepair and find that it can be used as efficient pH dependent molecular switch. The switching action in the A:A basepair can be understood in the light of ð- ð interactions, which lead to efficient delocalization over the entire basepair [2].

We have also studied the alignment of magnetic ions, Cu^{2+} and Mn^{2+}, along a modified B-DNA helix. We find that doping with magnetic ions induces conducting states in the gap region of natural DNA. These magnetic ions are found to interact ferromagnetically along the DNA helix. Calculations of optical conductivity about the helical axis suggest that the origin of magnetic characteristics depend crucially on the metal ions; the Cu(Mn)-DNA favors in-plane(out-of-plane) *s (?)*-like delocalization over the base pairs. Such an alignment of magnetic ions offers promising perspectives for creating low-dimensional polarized spin channel within the DNA helix [3]. Similar alignment within stacking backbone (with V atoms) can also be used for creating half-metallic modified one-dimensional single-strand DNA motif for advanced Spintronics applications

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Universal Variation of Dielectric Behaviour Induced by Nanoscale Dopants in Dielectric Oxides: Evidence of Fractal Geometry

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Apart from the bulk (micron-sized) materials or nanomaterials, composites having matrix and filler with physically or chemically different properties have become the most challenging areas of current scientific and technological research. In order to tune the dielectric properties we decided to vary the range of interfaces on addition of nanoscale particles to micron-sized particles of the same composition "nμ-composites", to vary the interfacial density. Since the microstructure is influenced by the nature and extent of sinteribility we have looked at the microscopic features carefully along with detailed thermal studies and surface area analysis [1]. Our studies show that addition of nanoparticles to micron-sized particles leads to fractal geometry formation [2], which result in optimal dielectric properties at certain compositions. We have observed enhancement (decrease) of the dielectric constant (dielectric loss) by nearly 3 times of the bulk value at an optimum concentration of micron and nano sized particles [3]. This interesting variation of the dielectric constant with increase in the amount of nanoparticles in the nμ-composites is observed in many classes of titanates, zirconates, niobates and tantalates.

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Influence of Surface Properties on Controlled Drug Relesae from Mesoporous Oxide Drug Delivery Systems

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While considerable efforts are being made in the discovery of new drugs for treatment of several complex human ailments, controlled delivery of such drugs has also received almost similar attention. Out of several drug delivery systems (DDS) proposed in literature, systems based on mesoporous oxide (M. Vallet Regi et al [1]) materials (such as SiO_2, Al_2O_3, TiO_2) appear to be very promising for the sustained release of drugs at specific targets. Mesoporous materials several attractive features, such as large surface area (300-1000 m^2g^{-1}), tunable pore sizes (2-50 nm) and volumes (~ 1 cm^3g^{-1}), easier manipulation of surface properties and higher stability and biocompatibility. Among the various parameters of a mesoporous oxide material which influences drug release, surface acidity/basicity of the functional groups play a critical role. In this contribution we report a systematic study (S.K. Das et al [2]) of the dependence of drug loading and its rate of release on the surface functional groups of mesoporous alumina (abbreviated as MPA). MPA (BET surface area ~ 155 m^2g^{-1}; pore size ~ 5.8 nm) with varying degree of acidity and basicity were chosen as the DDS for the study. Contrary to the oft-employed methods proposed in literature, an alternative procedure was employed to impregnate MPA with drug ibuprofen (IBU), a non steroidal anti-inflammatory drug (NSAID). Our method of drug incorporation in MPA showed a significantly higher loading compared to proposed procedures in literature. The oxide-drug composites were characterized by using Fourier transform infrared (FTIR) spectroscopy, x-ray diffraction (XRD), thermogravimetric analysis (TGA) and N_2 adsorption/desorption. It was observed that the amount of drug loading is highest in case of acidic-MPA (26% of MPA-IBU w/w) in comparison to basic-MPA (22% of MPA-IBU w/w). Further, in vitro drug release was carried out in simulated body fluid (SBF) at room temperature with oxides varying in surface properties. Interestingly, basic-MPA exhibited faster IBU release compared to acidic-MPA. In case of basic-MPA 100% IBU release took place in 45 hours whereas in the time period, only 50% was released from acidic-MPA. Rate of IBU release from composites having a requisite mixture of basic and acidic MPA lay between the slower acidic MPA and faster basic MPA release rates. This information would suitably aid in tailoring controlled drug delivery systems. Release kinetics was also studied as a function of SBF Ph. The release kinetics for IBU from an acidic to a basic medium changed dramatically resembling a switching mechanism. Implications of this observation would benefit in the design of responsive DDS for specific purposes.

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Intersystem Crossing Effects in the O + Ethylene Reaction Dynamics

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Spin-orbit coupling (SOC) induced intersystem crossing (ISC) has long been believed to play a crucial role in determining the product distributions in the $O(^3P) + C_2H_4$ reaction. In this paper we will be presenting the first nonadiabatic dynamics study of the title reaction at two center-of-mass collision energies: 0.56 Ev, which is barely above the H-atom abstraction barrier on the triplet surface, and 3.0 Ev which is in the hyperthermal regime. The calculations were performed using a quasiclassical trajectory surface hopping (TSH) method with the potential energy surface generated on the fly at the unrestricted B3LYP/6-31G(d, p) level of theory. To simplify our calculations, nonadiabatic transitions were only considered when the singlet surface intersects the triplet surface. At the crossing points, Landau-Zener transition probabilities were computed assuming a fixed spin-orbit coupling parameter which was taken to be 70 cm^{-1} in most calculations. Comparison with a recent crossed molecular beam experiment at 0.56 Ev collision energy shows qualitative agreement as to the primary product branching ratios, with the CH_3 + CHO and H + CH_2CHO channels accounting for over 70% of total product formation. However, our direct dynamics TSH calculations overestimate ISC so that the total triplet/singlet ratio is 25:75, compared to the observed 43:57. Smaller values of SOC reduce ISC resulting in better agreement with the experimental product relative yields; we demonstrate that these smaller SOC values are close to being consistent with estimates based on CASSCF calculations. As the collision energy increases, ISC becomes much less important and at 3.0 Ev, the triplet to singlet branching ratio is 71:29. As a result, the triplet products CH_2 + CH_2O, H + CH_2CHO and OH + C_2H_3 dominate over the singlet products CH_3 + CHO, H_2 + CH_2CO, etc.

The possibility of Using Locally Available Garware Polyester Film (GPF) as UV dosimeter

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Polymers are becoming very popular in the field of radiation dose measurements [1] because of their low cost. The possibility of using CR-39 polymer as a UV dosimeter has been recently studied by Shweikani et al [2]. The lower LET (Linear Energy Transfer) radiations such as UV, X-rays, electrons and gamma on interacting with polymers produce the bulk changes in the form of many broken molecular chains, leading to change in bulk-etch rate and optical density. These changes can be used for the evaluation of radiation doses. In the present investigation, the effects of ultraviolet radiation produced by a lamp at 254 nm on locally available Garware Polyester Film (GPF) were studied. This was done by using two techniques: Bulk -etch technique and UV-Visible spectrophotometry. GPF sheets were exposed to UV light (» 254 nm) for different times (0.5, 1, 2, 4 and 8 hrs) at a fixed distance. The UV exposed detectors were then subjected to chemical etching using 6N NaOH as the etchant at 60°C for ~5 hrs for bulk-etch rate (V_B) measurements. Bulk-etch rate was found to increase with increase in UV exposure time. A linear relation was seen between the V_B and UV exposure time upto 4 hrs (Figure 1). In the case of UV-Visible spectrometry also, a linear relation was seen between the change in absorbance due to UV and the UV exposure time upto 4 hrs at a characteristic wavelength of 316 nm (Figure 2). From these studies, it can be concluded that locally available GPF can be used as a UV dosimeter. To see the changes induced by UV irradiation on GPF film, the bulk-etch rates were also determined at three different temperatures and the activation energy values for bulk etching were calculated by using Arrhenius equation. The activation energy values for bulk-etching were found to decrease with increase in UV irradiation time. The value of activation energy for 8 hrs UV irradiated sample was found to be 31.3 kJ/mole as compared to 49.9 kJ/mole for the unirradiated sample. This indicates that scission of the detector is taking place with UV irradiation.

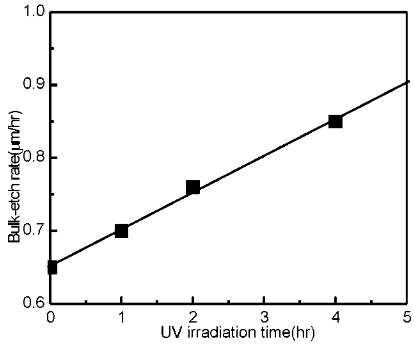

Figure 1. Plot of bulk-etch rate vs. irradiation time of UV-irradiated (254nm) Garaware polyester detector ^{o}C at 60

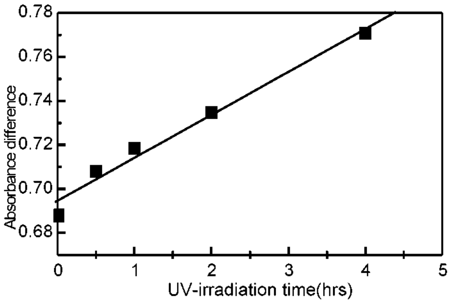

Figure 2. The plot of absorbance difference vs. UV-irradiation(254nm) time for garware polyester detector.

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Spider Web as Environmental Assessment Indicator of Carbon Nanotubes in Airborne Suspended Black Particulate Matter

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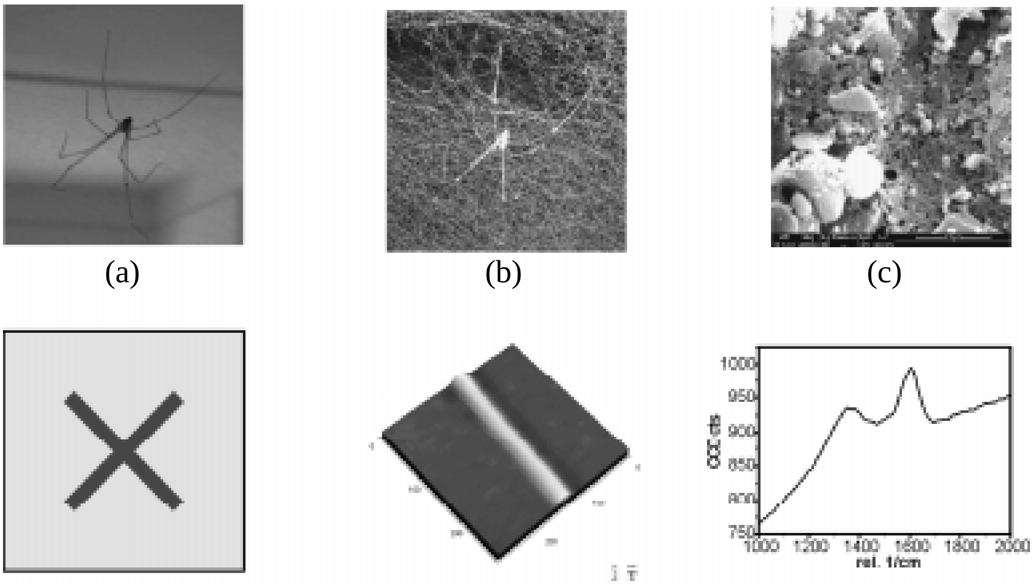
Since the discovery of carbon nanotubes in 1991 several facets of its utility have been predicted and a few are already showing result. The other part like the environmental problems caused by the nanoparticles have not been addressed. Recently the issue of global warming has been implicated mainly due to the green house effect. However the second contribution to the global warming is black carbon particulate present in the aerosols. In this work we want to demonstrate that the black particles which is popularly called black carbon associated with aerosols predominantly contains carbon nanotubes (CNT). Inside a room we generate these black particulates by day to day activities and outside the house excessive fossil fuel burning contributes to this at the maximum level. Using spider web (Fig.1a-b) as particulate matter indicator we have accessed these webs and found that the airborne particles do contain carbon nanotubes (Fig.1 c-f), and it is speculated that exposure to combustion-generated CNT in fine Particulates play a significant role in global warming and also in air pollution-related cardiopulmonary diseases. Therefore, CNTs from combustion sources in the environment could have adverse effects on human health along with its contribution to respirable diseases when inhaled inside the body.



(a) (b) (c)

(d) (e) (f)

Fig 1. (a) Indian domestic spider (b) Spider with its web
(c) SEM (d) TEM (e) AFM images of CNT (f) RAMAN Spectrum.

Topological and Thermodynamical studies of ternary mixtures: Molar excess volumes and Excess isentropic compressibilities

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Molar excess Volumes, V^E_{ijk} and speeds of sound , U_{ijk} of o- toluidine (i) + benzene (j) + toluene (j) or o- or p-xylene (k) ternary mixture have been measured as a function of composition at 308.15 K. The observed speeds of sound data have been utilized to determine excess isentropic compressiblities, $(\kappa_S^E)_{ijk}$ of ternary (i + j + k) mixtures. Moelwyn- Huggins concept [M.L.Huggins, Polymer **12**, 389 (1971)] between the surfaces of the constituents of binary mixtures has been extended for ternary mixtures (using the concept of connectivity parameter of third degree of a molecule, $^3\xi$, which in turn depends on its topology) to obtain an expression that describes well the observed V^E_{ijk} and $(\kappa_S^E)_{ijk}$ data. The observed data have also analyzed in terms of Flory theory.

Modification of Photochemical Behavior of trans-Strylpyridines Inside Cyclodextrin Cavities

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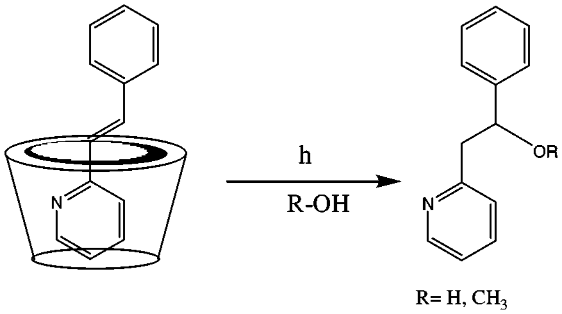
Cyclodextrins (CDs) are cyclic oligomers consisting of six, seven or eight D-(+)-glucose units (a-, b- and g-CDs respectively) with a hydrophobic inner cavity and a hydrophilic outside and are known to form inclusion complexes with a variety of organic guests. The inclusion phenomenon in CDs enables guest molecules to exhibit different and some times new properties from those of free molecules. In particular, the photochemical properties of a number of substrates are sensitive to the CD microenvironment. In this context, the modified polarity inside the cavities and the imposed steric constraints are among the main factors governing the photo reactivity of CD inclusion complexes[1].

Isomerisation and cyclization are the major photochemical reaction of styrylpyridines in isotropic media[2]. Photo physical behavior of various styrylpyridines has also been studied in isotropic media[3]. Baring a recent reports photochemical behavior of styrylpyridine inside cyclodextrin cavity has scarily been reported In the present study, photochemical behavior of various styrylpyridines and its methoxy substituted derivatives are studied inside cyclodextrin cavities. Modifications in photochemical behavior of styrylpyridines are observed inside cyclodextrin cavities. The change in the photochemical behaviors inside the cyclodextrin cavities are rationalized by mode of inclusion and proposing a suitable mechanism.



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Nanocrystalline Assisted Photoreduction of $Co^{III}(pn)_2LCl^{2+}$ in Water/1,4-Dioxane Mixtures

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Nanocrystalline titanium dioxide assisted reduction of $Co^{III}(pn)_2LCl^{2+}$ (L = $RC_6H_4NH_2$; R = *m-OCH*$_3$, *p-F*, H, *m-CH*$_3$, *p-CH*$_3$, *p-OC*$_2$*H*$_5$ and *p-OCH*$_3$) in a series of water/1,4-dioxane (Diox) mixtures (water/Diox = 100/0, 95/5, 90/10, 85/15, 80/20, 75/25, and 70/30) was monitored spectrally. Irradiation of nm-TiO_2 particles with λ_{max} = 254 nm flux leads to generation of Co^{II} species. In neat water the photo reduction yield ($\Phi_{Co(II)}$) is low, however, addition of 1,4 - dioxane causes a measurable rise in $\Phi_{Co(II)}$. That is, in nm-TiO_2 + Co^{III} + $h\nu \rightarrow Co^{II}$, ($\Phi_{Co(II)}$ is low, when x_2 = 0.0109 but it is high when x_2 = 0.0831, where x_2 is mole fraction of Diox). SEM images illustrate the growth of particle size upon irradiation and the changes in photo efficiency yields are interpreted in terms of correlation model expressions containing solvent empirical parameters. The particle size increases and the porosity get decreases. EDAX illustrate the amount of Co(III) present on the surface of the TiO_2 before and after irradiation. The binding property of Co(III) with TiO_2 surface was characterized using TEM.

Statistical Theory for Combinatorial Protein Design by Energy Landscaping

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Developing a predictive understanding of protein folding requires quantitative measures of sequence-structure compatibility. A foldability criterion accounts for this compatibility and is used in both structure prediction and protein design. A self-consistent theory is presented here which is used to estimate the number and composition of sequences consistent with a generalized foldability criterion. This generalized foldability criterion characterizes the properties of sequences by quantifying the energetic separation of the target state from the ensemble of unfolded states and the fluctuations of the energies in the unfolded ensemble The theory yields site-specific pair correlated monomer probabilities which is useful in exploring correlated mutations. The results of a simple lattice model are compared with the results of exact enumeration. The theory may provide a quantitative framework for design and interpretation of combinatorial experiments involving proteins, where a library of amino acid sequences is searched for sequences that fold to a desired structure.

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Potentiometric Sensor for Arsenate

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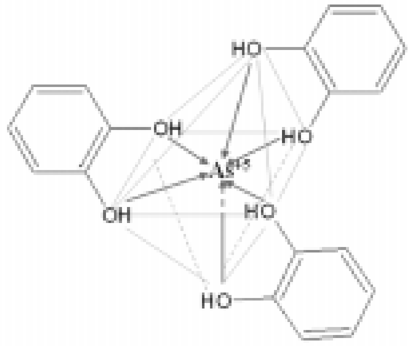
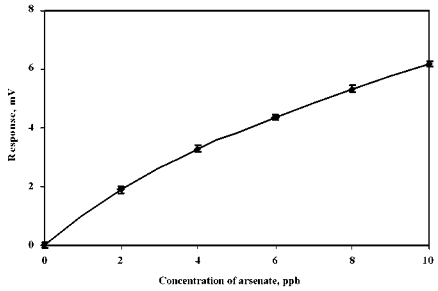
Arsenic is known as 'silent killer'. Consumption of arsenic contaminated water can cause skin melanosis, liver and kidney problems, gangrene, cancer etc. Because of the negative health effects of arsenic, World Health Organization (WHO) has established a maximum contamination level of 10 parts per billion (ppb) in drinking water. Nowadays a variety of techniques are available to detect arsenic in ppb level, but these methods require expensive instrumentation, highly skilled personnel and cannot be employed for on-site analysis. More over most of these methods are not suitable for detection below 10 ppb. We have developed potentiometric sensor for arsenic that utilizes a complexation reaction (Figure 1) between three molecules of Catechol and one molecule of Arsenate (Pal et.al. [1]). The change in concentration of arsenate due to this complexation reaction, was monitored potentiometrically. The sensor could estimate arsenic as low as a few ppb (Figure 2).





Complexation of Arsenate with Catechol Fig 2.
Calibration curve for Arsenate

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V_2O_5 as a new promising catalytic activator for Al-Zn sacrificial anodes

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Aluminum alloy sacrificial anodes are preferentially selected for cathodic protection of steel objects due to their high current capacity, low specific weight, high thermal and electrical conductivity and nominal cost. Conventionally a small amount of zinc (~5 %) is added to aluminum to prevent the formation of passive Al_2O_3 film on the anode surface. The major draw back of Al-Zn alloy sacrificial anodes is the noncolumbic corrosion loss and low galvanic efficiency. Incorporation of metal oxides in the interior of the alloy may refine the grains and suppressing the grain boundary corrosion that results in improvement of the anode performance. In the present study vanadium pentoxide (V_2O_5), one of the efficient catalysts in many electro chemical reactions was explode as an effective activator for Al-Zn alloy sacrificial anodes. The metallurgical suture of the anode was characterized by optimizing the casting parameters. The catalytic effect of V_2O_5 in the interior layer of the anode was characterized by different electrochemical techniques. The anode incorporated with optimum quantity of V_2O_5 (0.5 %) exhibited excellent galvanic performance under different experimental conditions in 3 % NaCl solution when they were indented to protect steel. There was a significant reduction in pitting, high and steady negative potential, very low polarization and high galvanic efficiency. The promising anodes were cost effective also.

Damping of Electronic Excited States Near Nanoscopic Systems

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Fluorescence Resonance Energy Transfer (FRET) is an interesting photo-physical process [1] that involves transfer of excitation energy from donor to acceptor in a non-radiative fashion. It has been extensively used in biology as a spectroscopic ruler to understand the conformational dynamics of biopolymers in the 10-100Å range. The rate of non-radiative damping of dye molecules near quenchers like other dye molecules is found to vary as R^{-6} where R is the distance between the donor and the acceptor. Recently, there has been tremendous interest towards using nanoscopic materials like nanoparticles, nanotubes etc. as energy acceptors. There have been reports of nanoparticle surface energy transfer (NSET) [2] between fluorescein and 1.4 nm diameter gold nanoparticle, both of which are connected by a DNA as a bridge. They observe an R^{-4} dependence of the rate on the distance, which is quite useful because it more than doubles the range of distances that could be measured using conventional FRET. There have also been attempts to explain the R^{-4} dependence for the case of nanoparticle [3]. We have done a detailed calculation of the rate of energy transfer from fluorescein to a 1.4 nm gold nanoparticle taking the electron-hole pair excitations as well as the plasmonic excitations explicitly into account.

Nanotubes have also been found to be efficient quenchers for the electronic excited states of molecules like pyrene . Interestingly, to the best of our knowledge, there are no reports of distance dependence of the rates of such processes, either experimentally or theoretically. A nanotube can be imagined to be a rolled up sheet of a single layer of graphite, graphene. The starting point for any theoretical investigation of the nanotubes is graphene. In view of this fact and the recent experimental advances in graphene, we have studied the distance dependence of the rate of damping of molecular electronic excited states near graphene. This would provide a starting point for the theoretical study of such states near nanotubes and motivation for the experimentalists to probe such processes.

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Nanoparticle Catalyzed Clock Reaction

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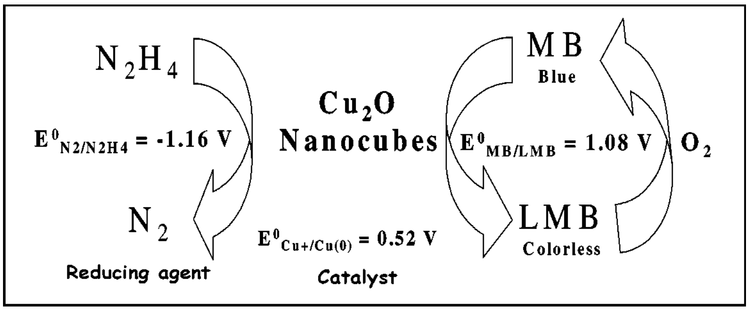
Bulk Cu_2O or cuprite is the only stable copper (I) compound present in plentiful amount in earth crust. It is a challenging job to take bulk Cu_2O to a nanoregime and to stabilize them in solution. No wonder that Cu_2O in its nanoregime would act as a photo catalyst. We report a synthetic protocol for the first time to obtain monodispersed, stable, exclusively cubic Cu_2O nanoparticles in surfactant free condition and its catalytic action for methylene blue (MB)–hydrazine reaction in aqueous medium. The blue color of the dye, MB faded away upon the addition of hydrazine producing colorless leuco methylene blue (LMB) indicating the progress of the redox reaction. The rate of this redox reaction has been found to be enhanced in the presence of the Nan catalyst, Cu_2O. The success of the reaction demonstrates a simple 'clock reaction'. An oscillation between a blue MB color and colorless solution due to formation of LMB is observed on periodic shaking. This oscillation continues for over fifteen cycles. Studies on the effect of bulk Cu_2O, nanoparticles of CuO and Cu(0) have not been successful for demonstration of the 'clock reaction'. Thus the importance of Cu_2O nanoparticles in the clock reaction is established beyond doubt. The Cu_2O nanoparticles were characterized by different physical methods. TEM studies authenticate the cube shaped monodispersed particles. The electrochemical studies indicate that nano-Cu_2O shows a couple of redox peaks which correspond to the redox Cu(II)/Cu(I) system. Kinetic studies authenticate first-order reaction mechanism. Further quantum chemical calculations reveal that the nanoparticles reduce the activation energy by ~17 kcal/mol thereby make the reaction 2.4×10^7 times faster compared to the gas-phase.



Scheme to show the catalytic activity of Cu_2O nanocubes for the 'clock reaction'.

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Surface Enhanced Raman Scattering with Core-Shell Nanoparticles

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In recent years, surface enhanced Raman scattering (SERS) has emerged as one of the most potent tools in ultra-trace molecular analysis. It blends single molecule sensitivity with chemical fingerprint capabilities, which make it a unique tool for biomolecular detection. Metallic nanoparticle substrates are one of the important requirements of SERS experiments, on which, molecules adsorb to exhibit enhanced Raman signatures. Conventionally, Ag and Au nanoparticles have been extensively used for SERS studies. Of late, core-shell nanoparticles have derived enormous attention in the field of SERS because of their unique optical properties like tunable surface plasmon.

In this paper, we present two novel techniques used to harness the core-shell properties of nanoparticles for biomolecular detection purpose:

1) We show the creation of electromagnetic hot spots in Ag core-Au shell nanoparticles, which provide enhanced optical fields for SERS. Further, we use them to detect biomolecules like p300 (a human transcriptional coactivator enzyme) at physiological concentrations.

2) We show the possibilities of using magnetic core-metallic shell nanoparticles for SERS applications. We synthesize, and use Fe_2O_3 core–Ag shell and Fe_2O_3 core–Au shell nanoparticles for SERS studies of bio-related molecules. Also, by performing SERS microscopy in the temperature range of 77 K to 473 K, we show that the metal-coated magnetic nanoparticles are robust with respect to variation in temperature.

Pd Nanoparticls as Efficient Catalyst for Carbon-Carbon Bond Formation

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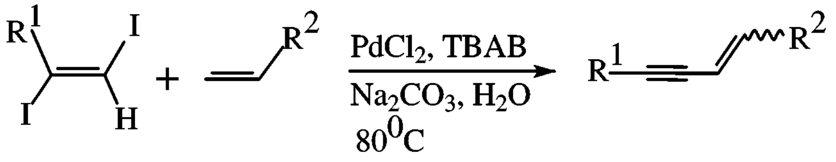
An efficient procedure for the stereo selective synthesis of (E)- and (Z)-2-alkene-4-ynoates and –nitriles by a simple reaction of vis-diido-(E)-alkenes with acrylic esters and nitrile catalyzed by in situ prepared Pd(0) nanoparticles in water has been developed.



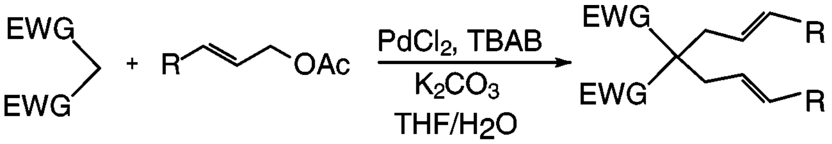
R^1= Aryl, alkyl

R^2= CO_2Me, CO_2Bu, CN

R^2 = CO_2Me / Bu, *E* isomer100 %

R^2 = CN, *Z* isomer 80 95 %

Palladium (0) nanoparticles have also been used as efficient catalyst for the bis-allylation of active methylene compounds by allyl acetate in one step in THF solvent without requirement of any ligand. Interestingly, the reaction in water provides monoallylated product with high selectivity.



R = H, Me, Ph.

EWG = electron withdrawing groups

The formation of Pd nanoparticles was detected from analysis of the reaction mixture by transmission electron microscopy (TEM) and Energy Dispersive X-ray spectroscopy (EDS). The TEM image and EDS showed the palladium nanoparticles with a size of 2-6 nm. The palladium nanoparticles were recycled for two runs with out any loss of efficiency.

P 94

Mesopores in Organic Cresol Formaldehyde MATRICES

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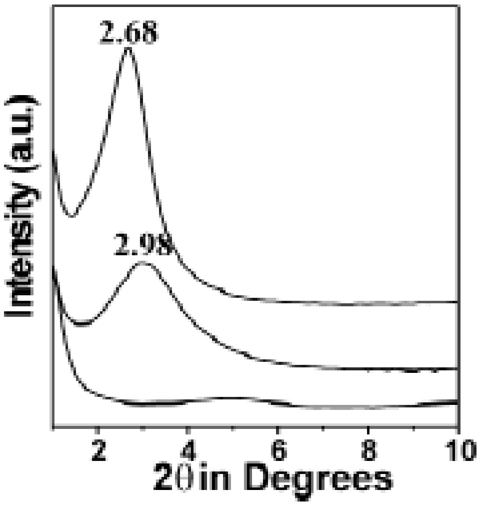
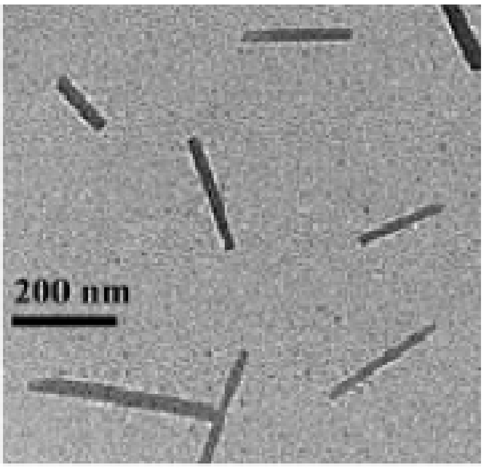
Cresol-formaldehyde resins are versatile polymer having numerous applications in ion exchange, catalysis, supercapacitors, photo resistant materials etc. Purely organic mesoporous materials are the area of major research interest in recent times [1-3], especially in the context of developing the low-k dielectric materials. Mesostructured cresol formaldehyde composites synthesized by template assisted route have not been explored much. Here we present a very simple procedure for the preparation of a nanostructured cresol-formaldehyde material through hydrothermal condensation of *m*-cresol and formaldehyde at 363 K under mild alkaline condition in the presence of supramolecular assembly of cationic surfactant, cetyltrimethyl ammonium bromide as structure directing agent or template. The resulting material was characterized by powder X-Ray diffraction, TEM, TG-DTA, UV-Vis and fluorescence spectroscopy. Removal of template from the as-synthesized material gave the template free mesoporous material. TEM image analysis revealed nanorod morphology with diameter of the rods of 30-40 nm. These nanorods have disordered wormhole-like nanostructure with pores of dimensions of *ca.* 2.5 nm. These composite materials exhibit photoluminescence property at room temperature, distinctly different from the material having non-porous resol matrix.





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Interaction of Superparamagnetic iron oxide nanoparticles with DNA

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Creation of nanostructures capable of sensing DNA interactions and screening DNA cleaving agents has been a major goal in bioinorganic and medicinal chemistry. Magnetic nanoparticles of iron oxides have been extensively exploited as the materials of choice for ferrofluids, high-density information storage, magnetic resonance imaging (MRI), tissue-specific releasing of therapeutic agents, labeling and sorting of cells, and separation of biochemical products. The reactivity as well as stability of particles has been shown to greatly increase, when they are prepared in core-shell structures. We have prepared the Fe_3O_4 nanoparticle using different stabilizers such as CTAB, Oleic acid and APS/SiO_2 to form modified core shell nanoparticles. The binding of core shell nanoparticle with herring sperm DNA has been investigated using spectral methods in Tris-HCl buffer pH 7.1. On titration with DNA, we observed hyperchromism in the 260 nm region. The surface or core modified iron oxide nanoparticles binding with DNA were also performed by emission and circular dichroism studies. In emission study the unmodified and APS core-shell were strongly binding with DNA than others and also same performance of circular dichroism.

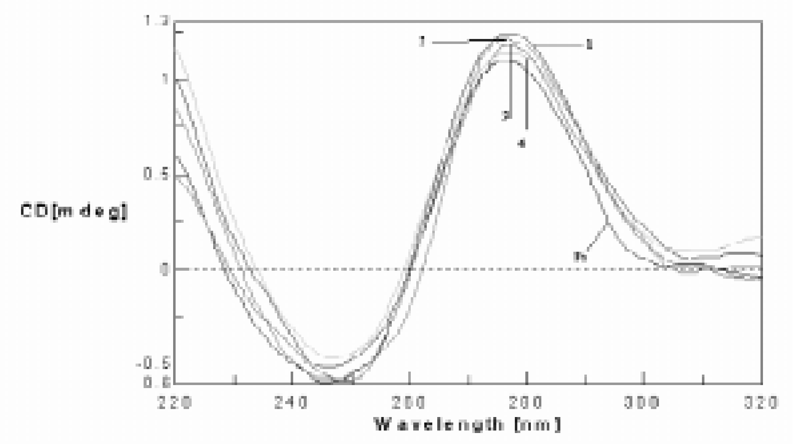

Fig.1. Circular dichroic spectra of Herring sperm DNA with Iron oxide nanoparticles

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Assembly and Encapsulation of Pd Nanoparticles in Organic/Inorganic Matrixes: A Highly Efficient Catalyst for Hydrogenation Reactions

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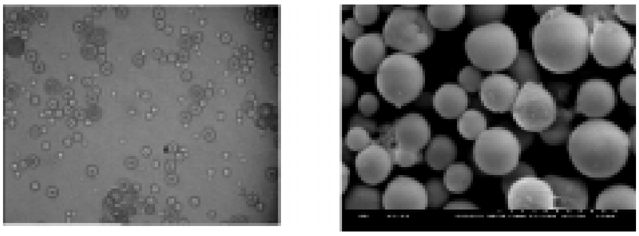
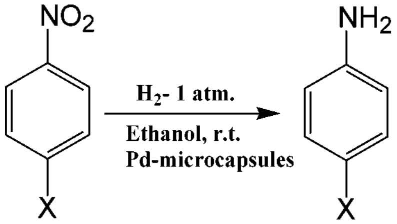
Polyelectrolyte chains can undergo counter ion condensation in certain salt solution to form polymer aggregates, and these ironically cross-linked polymer aggregates can lead to the rapid formation of ordered microcapsule structures [1]. The methodology used in this work, a tandem two-step process, in which, cationic polyamines form supramolecular aggregates with multivalent counter-ions via cross linking, and negatively charged nanoparticles deposit around the aggregates to form a multilayer thick shell [2]. Encapsulation of Palladium in silica hollow microcapsules was achieved by following the self-assembly route (Figure 1). First the microcapsules were prepared by assembling silica nanoparticles directed by ionically cross-linked polyamine aggregates of Poly L-Lysine and trisodium citrate. Then the Pd salt was absorbed into the shell and reduced to metallic nanoparticles by adding sodium borohydride. Thus prepared palladium nanoparticles assembled microcapsules were used as catalyst for various hydrogenation of nitro group to amine at room temperature (Scheme 1). The encapsulated Pd nanoparticles were accessible by the reactant and very active for the conversion. Moreover, the catalyst was efficiently recoverable by simple centrifugation and the separated catalyst could be reused with similar catalytic activity for the hydrogenation reaction.



(a) (b)

Figure 1: (a) & (b) Optical microscopy and Scanning electron microscopy images of Palladium assembled hollow microcapsules.



Scheme 1: Pd-catalysed hydrogenation of nitrobenzenes (X= -H, -CH_3, -OH, -Cl).

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Synthesis and Characterisation of Polymer Immobilised Gold and Silver Nanoparticles by Oxidative Coupling Reaction

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Nanocomposites of metal nanoparticles embedded in a polymer matrix can have synergetic or complementary between the polymer matrix and the inorganic nanoparticles [1,2]. The precise tuning of size and shape provides control over different physical and chemical properties of nano scale materials with technologically important application like biosensors, catalysts, optoelectronics, etc [3]. In this study we prepared mono dispersed gold and silver nanoparticles using metal salts ($AgNO_3$ or $HAuCl_4$) and dichloro phenol (DCP) /dimethyl methyl aniline (DMA) with 4-Aminoantipyrine (4-AAP) in presence of polymers. Here the DMA/DCP and 4-AAP act as reducing agent and metal salt act as oxidizing agent. The rate of nanoparticle formation was conducted by varying the nature of polymer (PVA, PEO and PVP), concentration of metal salt, pH of the reaction medium and reducing agent. The size, optical properties, structure and composition distribution of the resultant nanoparticles were characterized by transmission electron microscopy (TEM), UV-visible spectrophotometer, FT-IR spectroscopy and X-ray diffraction (XRD) analysis.

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Viscosities, Ultrasonic Velocities and Molar Isentropic Compressibilities of Binary Mixtures of Methanol with Acetonitrile and N,N-Dimethyl Formamide at 298.15 to 308.15 K

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The study of molecular interactions in binary liquid mixtures has attracted the attention of scientific community for more than a century. Mixed solvents rather than pure liquids are of greater industrial significance as they provide adjustment of desired properties of the medium. The composition dependence of viscosity and ultrasonic velocity of liquid mixtures has proved to be a useful tool to investigate the interactions between components of the mixtures. Though much work has been done in this area but the effect of temperature has been studied for only a few systems. In the present study density (d), viscosity (h), and ultrasonic velocity (U) of binary mixtures of methanol with acetonitrile and N, N-dimethylformamide over the entire mixture composition range at T=298.15,303.15,308.15 and 313.15K have been studied. The excess thermodynamic functions have also been calculated. Excess molar volume, (V^E), has been calculated from density $V^E = x_1 m_1 (1/d_m – 1/d_1) + x_2 m_2 (1/d_m – 1/d_2)]$ whereas excess viscosity (h^E) values have been computed from the measured viscosities $[h^E = h_m - (x_1 h_1 + x_2 h_2.)]$ Isentropic compressibilities ($K_{s)}$ have been calculated from the measured ultrasonic velocities $[K_s = 1/U^2 d]$ and used for calculation of excess isentropic compressibilities K_s^E The calculated values have been fitted to the Redlich Kister Polynomial equation to derive the coefficients and standard errors between the experimental and predicted values. The trend shown by the three parameters (V^E ,h^E and Ks^E) gives an indication of the effect of temperature on the molecular interactions of the systems under study.

New Open-Framework Materials: Synthesis, Structure, Porosity and Photocatalytic Properties

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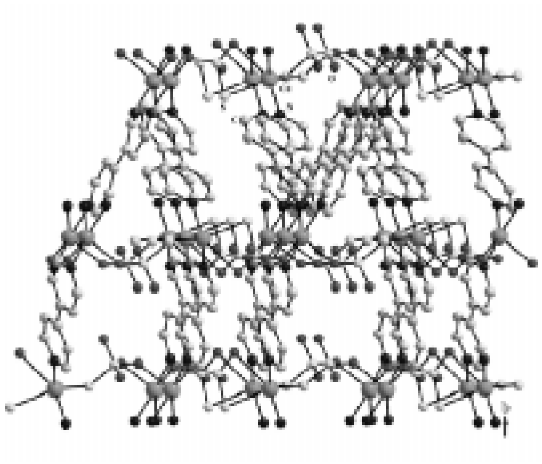
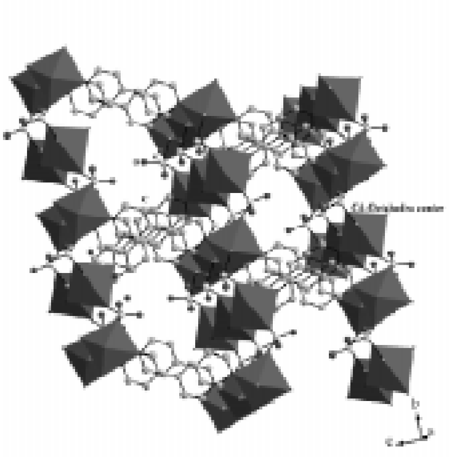
The literature is abound with large number of reports on open-framework structures formed by phosphates[1], phosphites[2], arsenates[3], sulphate, sulphites. There has not been any systematic study with thiosulfate as a network builder. It is likely that the thiosulfate would decompose under acidic condition and also under higher temperature and pressure to form sulfide and polysulfides. Thus, it is a challenge to explore the use of thiosulfate as a possible building unit in open-framework compounds. We have synthesized two new Cd(II)-thiosulfate compounds $[Cd_2(C_{10}H_8N_2)_{2.5}(S_2O_3)_2]$, **I,** and $[Cd(C_{10}H_8N_2)(H_2O)_2(S_2O_3)]$. $2H_2O$, **II,** employing mild hydrothermal methods in the presence of 4,4'-bipyridine. In both the compounds, the thiosulfate participate in network building forming a one dimensional structure, which are connected by the 4,4'-bipyridine ligand forming the three-dimensional extended structures (Fig. 1 and Fig. 2). In compound **I**, two types of trigonal bipyramidal cadmium centers are present containing CdN_3O_2 and CdN_2S_2O units. Whereas compound **II**, contains only $CdN_2SO(H_2O)_2$ octahedral unit. Both the compounds exhibit catalytic behavior for the decomposition of organic dyes in the presence of UV light. The water molecule inside the channels of **II**, can be reversibly adsorbed. The synthesis, structure, and photocatalytic properties of these compounds would be presented.



(Fig. 1)



(Fig. 2)

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'All-Solid-State' Electrochemistry of a Protein-Confined Polymer Electrolyte Membrane

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Interfacial redox behavior of a heme protein (hemoglobin) confined in a solid polymer electrolyte membrane, Nafion (a perfluoro sulfonic acid ionomer) is investigated using a unique 'all-solid state' electrochemical methodology [1,2]). The supple phase-separated structure of the polymer electrolyte membrane [3], with hydrophilic pools containing solvated protons and water molecules, is found to preserve the incorporated protein in its active form even in the solid state, using UV-visible, Fluorescence and DRIFT (diffuse reflectance infrared fourier transform) spectroscopy. More specifically, solid-state cyclic voltammetry and electrochemical impedance of the protein-incorporated polymer films reveal that the Fe^{2+}-form of the entrapped protein is found to bind molecular Oxygen more strongly than the native protein. In the 'all-solid state' methodology, as there is no need to dip the protein-modified electrode in a liquid electrolyte (like the conventional electrochemical methods), it offers an easier means to study a number of proteins in a variety of polymer matrices (even biomimetic assemblies). In addition, the results of the present investigation could find interesting application in a variety of research disciplines, in addition to its fundamental scientific interest, including protein biotechnology, pharmaceutical and biomimetic chemistry.

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Lead Molecule Selection from Natural Sources Revolutionizing Drug Discovery

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The possibility of finding new medicines from natural sources is one of the more commonly cited reasons for preserving biodiversity, and employing indigenous knowledge of traditional healing remedies greatly increases the likelihood of discovering these hidden medicinal compounds[1,2]. Many unconventional sources of natural products have escaped exploration by pharmacologists, yet they are likely to contain biologically active compounds, including valuable lead candidate's molecule for novel drugs[3]. Plants continue to provide us new chemical entitities (lead molecules) for the development of drugs against various pharmacological targets, including cancer, HIV/AIDS, malaria, Alzheimer's disease and pain. Like paclitaxel, camptothecin-derived analogues, arteether, galanthamine, tiotropium to name a few, and some are undergoing Phase II and Phase III clinical trials. A Marine sponges are the source of new active compounds discovered in the last twenty or thirty years in our seas. Novel natural products from cyanobacteria, actinomycetes elucidates their structures and biological activities as a starting point for the development of lead structures. Sea vegetables are powerfully antiviral and antiparasitic. Digenea (Ceramiales; Rhodophycota) produces an effective vermifuge (kainic acid). By using medicinal chemistry and combinatorial chemical and biosynthetic technology, novel natural product leads will be optimized on the basis of their biological activities to yield effective chemotherapeutic and other bioactive agents.

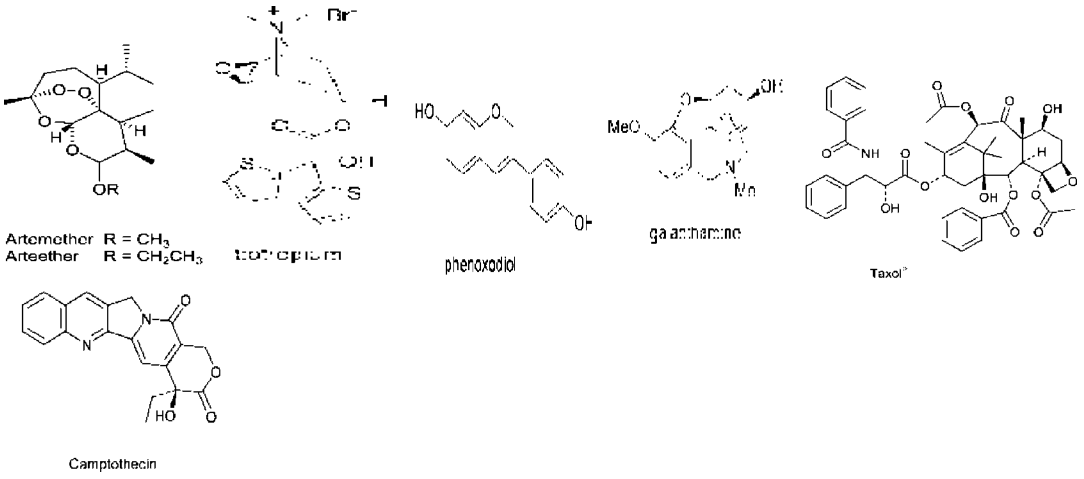

Figure 1. Chemical structures of plant-derived drugs.

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An Efficient Ssynthesis of Azetidine-2,3-Diones from L-(+)-Diethyl Tartrate

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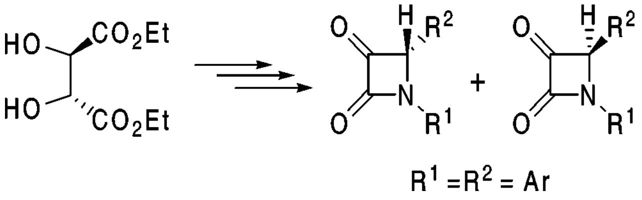
b-Lactams being a part of most widely used antibiotics [1] are a familiar class of compounds in organic synthesis. The resurgence of bacterial activity against traditional antibiotics has inevitably led to the discovery of newer b-lactam antibiotics with modified structures. Recent times have witnessed an upsurge in the number of new varied applications of b-lactams.[2,3] Among these, the most important application that has outgrown most other applications is the use of b-lactams as a synthon for biologically important molecules. One particularly important and useful class of synthons is substituted azetidine-2,3-diones. A convenient route to enantiopure azetidine-2,3-diones is described. The chiral ketene generated from commercially available L-(+)-diethyl tartrate on Staudinger cycloaddition with different imines gave spiro-b-lactams in good yields. These spiro-b-lactams were transformed into azetidine-2,3-diones in excellent yields in a two-step process (**Scheme-1**).



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Silica Chloride in Organic Synthesis

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Green chemistry has been defined as set of principles that reduces or eliminate the use of generation of hazardous substances Verma et al [1]. Along this line, using solid acids such as: heteropoly acids (HPAs), silica based sulfonic acid, Nafion-H, Dowex 50, Amberlite IR-112 and Permutit-Q have attracted more attention Downing et al [2]. In addition, there is current research and general interest in heterogeneous systems because of their importance in industry and also in developing technologies. Inorganic silica based solid acid is of great importance in terms of convenience, non-toxicity, economic, easy production, handling and insolubility in all organic solvents. Silica chloride is one such solid acid which can be used for different organic functional group transformations either as reagent or as catalyst under heterogeneous conditions Zolfigol at al [3]. The efficiency of silica chloride under operationally simple conditions has prompted us to explore the use of silica chloride for the synthesis of various building blocks Kaushik et al required in medicinal chemistry Fig. 1.

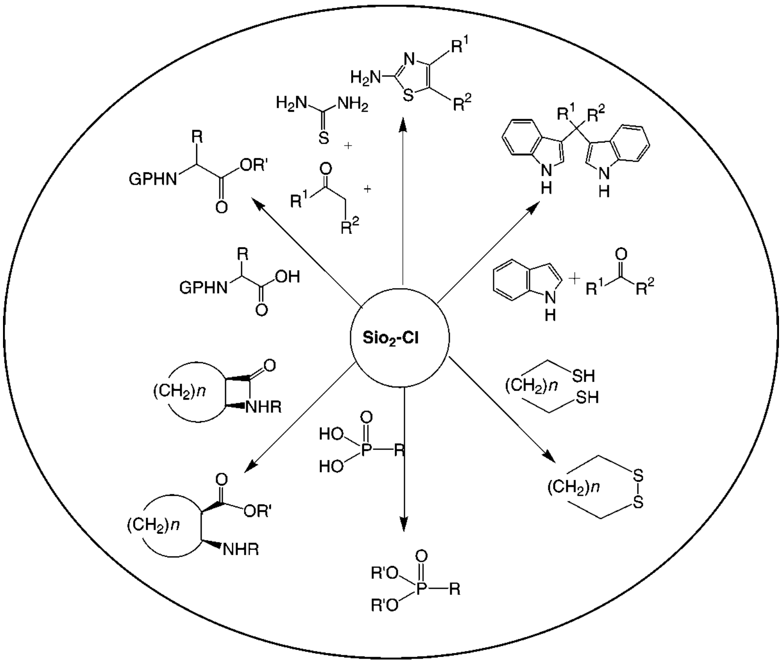

Figure 1

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Side Chain Modified 8-Aminoquinolines as Potential Antimalarial Agents

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Malaria is one of the most serious parasitic infections in the third world countries. Primaquine (PQ) an 8-aminoquinoline, is a clinical drug of choice for radical cure of relapsing *P. vivax* and *P. ovale* malaria. But PQ has some serious side effects, thus it is far from being an ideal antimalarial drug. The accumulation of 8-aminoquinolines in the parasite food vacuole is a part of their weak base properties and it can be increased by introducing basic groups either in the ring or in the side chain of 8-aminoquinolines. So a series of side chain modified analogs of PQ and other 8-aminoquinolines has been synthesized by attaching 1, 2, or 3 alkylamine linkers to the side chain of parent 8-aminoquinolines. Some compounds of this series have shown activities better than PQ against chloroquine (CQ) sensitive D6 and CQ resistant W2 strain. Such modification may lead to analogs which retain tissue-schizontocidal activity of PQ with improved blood-schizontocidal activity.

In this presentation, synthetic procedure followed to synthesize above mentioned side chain modified analogs of 8-aminoquinolines and their biological activity will be discussed.

Total Synthesis of Paroxetine and Formal Total Synthesis of Femoxetine: An Unusual Deoxodeprotection.

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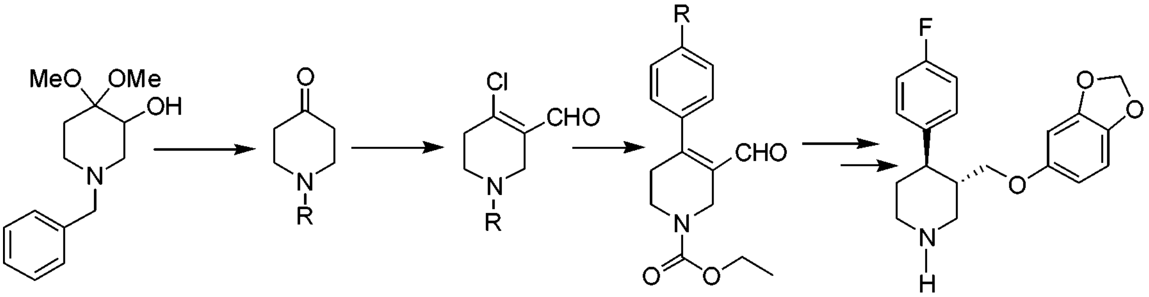
The selective activities of Paroxetine and Femoxetine as seritonin reuptake inhibitors [1]and their wide use as antideppressants created interest to develop their cost efficient synthesis in our group [2]. Use of piperidones for the synthesis of Paroxetine and femoxetine is not explored enough.



The synthesis commences from a-hydroxy acetal which was readily available with us. A novel one pot deprotection of acetal and deoxygenation is achieved in one step in order to prepare the piperidone. The advantage of Vilsmeir formylation [3] was taken to introduce the carbonyl functionality in regioselective manner, with halide at the beta position suitably placed for further manipulation . Suzuki coupling reaction of chloro aldehyde with phenyl boronic acids in aqueous condition provided the key intermeiate which was converted to Paroxetine as well as Femoxetine. The deatails of the above novel transformation and the synthesis of the two commercially important drugs would be described.

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Investigation of Prins Reaction of Paraformaldehyde with Substituted Styrene

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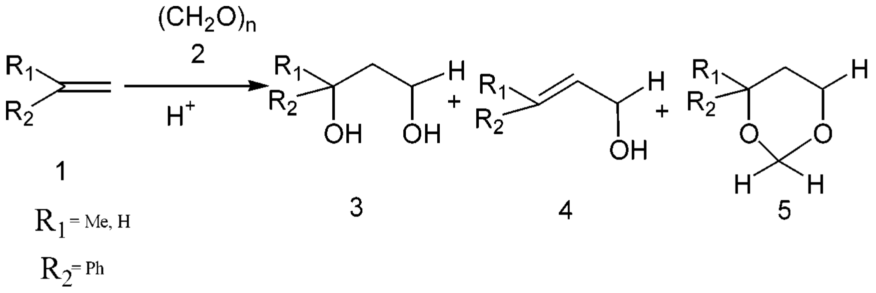
The importance of acid catalyzed Prins reaction may be judged from the numerous number of its synthetic use in C-C bond formation [1] reaction. Similarly,the Prins cyclization[2-3], is an important method in the formation of tetrahydropyran derivatives, because tetrahydropyran units are backbone of many natural products such as carbohydrates, polyether antibiotics and marine toxins**.** Many reported methods of the Prins reaction have suffered with some problems, such as longer reaction time, use of corrosive acid catalyst, high temperature reaction without product selectivity. As a result the development of new green methodologies for the Prins reaction is meaningful in terms of solvent-less condition, greater selectivity, shorter reaction time and simple work-up procedure. Here we are going to present the results of iodine catalyzed Prins reaction of substituted styrene with paraformaldehyde in different reaction conditions.



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Synthesis, Structure, DNA Binding and Oxidative Cleavage Activity of Ternary (L-Isoleucine) Copper (II) Complexes of Heterocyclic Bases

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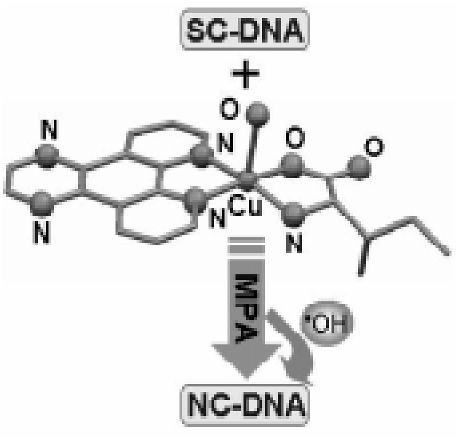
Three ternary α-amino acid copper(II) complexes of general formulation [Cu(AA)(B)(H_2O)](X) (**1–3**) where, AA is L-ile = L-Isoleucine (**1**-**3**), B is a N,N-donor heterocyclic base, *viz.* 2,2′-bipyridine (bpy,**1**), 1,10-phenanthroline (phen,**2**) and dipyrido[3,2:2′,3′-f]quinoxaline (dpq,**3**) and X = ClO_4^-/NO_3^- are synthesized, characterized, and their DNA binding and cleavage activity studied[1-3]. The structures of two new complexes of bpy and dpq with L-ile (**1, 3**) are characterized by X-ray crystallography [4]. These complexes show a distorted square-pyramidal (4+1) CuN_3O_2 coordination geometry. Complex [Cu(L-ile)(bpy)(H_2O)](NO_3) (**1**) crystallizes in the monoclinic space group $P2_1$ with unit cell parameters: a = 11.559(4) Å, b = 6.659(2) Å, c = 13.226(5)Å, α = 90.0°, β = 92.777(6)°, γ= 90.0° and V = 1016.8(6) Å^3. Complex [Cu(L-ile)(dpq)(H_2O)](ClO_4) (**3**) crystallizes in the triclinic space group $P1$ with unit cell parameters: a = 8.2524(19) Å, b = 11.940(3) Å, c = 13.440(3)Å, α = 109.257(4)°, β = 101.000(4)°, γ= 106.193(4)° and V = 1140.7(5) Å^3.



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Palladium-Free Protocol for the Synthesis of Functionalized 1,2-Diaryl-, 1,2,3-Triaryl- and 1,2,3,4-Tetraarylbenzenes

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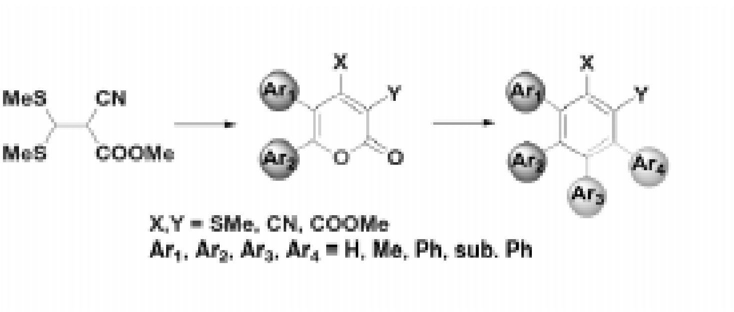
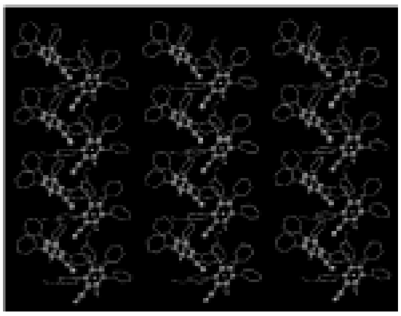
The demand of functionally congested arylated benzene scaffolds as versatile auxiliaries for asymmetric syntheses, as chiral phases for chromatography and as important substrates for chiral liquid crystalline materials has increased dramatically during the past few decades. [1] Palladium-catalyzed aryl-aryl cross-coupling between the electrophilic aromatic halides $Ar(X)_n$ (X being generally Br, I, and OTf; n being mainly 0, 1 or 2) and organometallic species Ar-M (M being Mg, Ni, Zn, Sn, and B) is a versatile synthetic method for the preparation of diverse arylatedbenzene. [2] Despite the wide synthetic generality of these aryl-aryl cross-coupling reactions, multiple coupling on tri- or tetrahalides to prepare triaryl- or tetraarylbenzenes places constraints on the choice of reagents or catalysts and produces either low yields of desired compounds or fails completely to fulfill the demand.

During the recent studies on the chemistry of a-pyrones, we observed [3] that a-pyrones prepared from a-oxo-ketene-*S,S*-acetal have promising structural topology as useful substrates for ring transformation reactions, flexible substitution pattern and the presence of a good leaving alkylsulfanyl group for generating molecular diversity. In this presentation, we describe a versatile palladium-free approach to preparing 1,2-diaryl-, 1,2,3-triaryl- and and 1,2,3,4-tetraarylbenzenes through simple stitching of a-oxo-ketene-*S,S*-acetals with active methylene molecular pieces in just two steps. Examination of the crystal packing in the structure of a nitrile substituted 1,2,3,4-tetraarylbenzene reveals a unique "**N…p interaction**", which enforces the molecules in a helical pattern.





Unique N...p interaction

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Synthesis of New Molecules to Discover Drug Candidates

Amit K. Srivastava, Siva S. Panda, Pankaj Khanna, Rajeev Sakhuja, Shilpi Khurana, Mukesh K. Pandey, Anjali Saxena, Khushbu Kushwaha, Nidhi Jain, Lata, Bharti Bhardwaj, Nusrat Jehan, Ritu Malik, Archana gupta, Sunita Bhagat and Subhash C. Jain*

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Plants have been an important source for discovery and developing new drugs especially for anticancer and antiinfectious diseases. In industrialized nations, about 50% of the prescribed drugs are derived or synthesized, taking lead from the natural products. Therefore, the role of organic synthesis is crucial for the development and production of new synthetic drugs, based on natural product templates.

Keeping above in mind, we have synthesized a large varieties of new molecules in order to discover a potential drug candidate. In the first place, we have developed a simple general method for the synthesis of 6-alkyl/alkenyl salicylic acids, 3-alkylpyridines, 6-alkyl/alkenyl anthranilic acids, 4-alkyl/alkenyl coumarins and 2-alkyl/alkenyl isoflavones of biological importance by exploiting sulfone chemistry. Some of these molecules are found to be active against P-388 murine leukemia cells at very low concentration.

The chemistry of spiro indoles and their fluorinated analogues has also been of considerable interest to us due to their pharmacodynamic nature and therapeutic importance. We have recently synthesized a series of novel spiro[indol-pyrazolinyl-thiazolidines], spiro[indol-indazolyl-thiazolidines] and spiro[indol-benzooxazines]. Realizing the importance of bis heterocyles, we have also developed an elegant and facile route for the synthesis of some novel bis spiro indoles containing an appropriate spacer. Structural variation in linker has been made by using biphenyl, biphenyl ether, piperazine and morpholine moieties.

While studying the catalytic reactivity and selectivity of azaphenothiazines, we came across a new eco-friendly method for the synthesis of some biologically active novel N-[n-(phthalimido)alkyl]-1-azaphenothiazines and azonia-spiro compounds. Azonia compounds were used to obtain different size N-heterocycles. This methodology is being extended to synthesize a large number of bioactive heterocycles containing lipophilic chains, in order to discover a suitable drug candidate. Some of the above new molecules have been screened for their varied biological activities. Detailed synthetic methodology along with the biological activity of new molecules will be presented at the Symposium.

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Speciation of Chromium after Extraction of Cr(VI) as an Ion-Association Complex with Tetrabutylammoniumiodide

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The increasing concern for environmental pollution has stimulated active research in the study of the toxicology of heavy metals. In this context, there has been a significant advancement in the growth of the analytical chemistry of various metals. Chromium is no exception to this. Chromium (VI) finds extensive use in electroplating and chromium (III) finds its application in leather tanning. Chromium (III) is required for normal glucose metabolism, whereas chromium (VI) is highly carcinogenic. In view of the toxic nature of chromium (VI) study of methodologies for the speciation of chromium assume significant importance.

A simple method has been developed for the speciation of chromium based on the extraction of its ion-association complex at 383 nm with tetrabutylammonium-iodide in acidic medium. The ion-pair was extracted using IsobutylMethylKetone (MIBK) as the solvent. The effect of various parameters such as acidity, aqueous phase volume, equilibration time, interfering ions etc. has been studied. The extracted chromium (VI) was back extracted into the aqueous phase to the non-toxic chromium (III) using ascorbic acid as the reducing agent. The organic phase after extraction and stripping was characterized using FT-IR spectroscopy. The calibration graph was linear in the range 0-1 mg mL^{-1} chromium (VI) with a relative standard deviation of 2%. A detection limit of 0.25 mg in 30 mL aqueous phase volume could be achieved and the validity of the proposed method was checked by applying it to study the recovery of chromium in a synthetic mixture of several other ions and electroplating waste water.

Mild Synthesis of a Family of Planar Triazinium Cations via Proton Catalyzed Cyclization of Pyridyl Containing Diazo Compounds and Studies on DNA Intercalation

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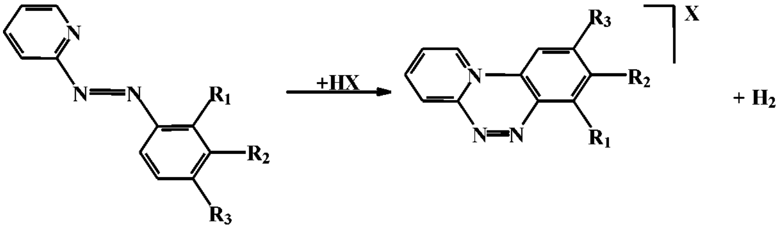
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032.

In this presentation we wish to disclose an efficient proton catalyzed synthesis of a family of flat triazinium cationic compounds [**2**]X from 2-(arylazo)pyridines. The methodology is new and has several distinct advantages over most of the available procedures of making heterocyclic cationic compounds. Characterization of the resulting compounds has been made by different spectroscopic, electrochemical techniques as well as single crystal structure determination of a representatitive [**2a**]ClO_4. The reference compounds can be reduced in two successive one-electron steps as probed by cyclic voltammetry and coulometry. The paramagnetic radical intermediate [**2**] is distinguished by sharp and intense EPR spectrum at g~2.0. The studies on DNA-[**2**]$^+$ interaction have revealed intercalative mode of binding.



1 **[2] X**

Compound	R_1	R_2	R_3	Yield (%)
[**2a**]Cl	H	H	H	65
[**2a**]ClO_4	H	H	H	62
[**2a**]NO_3	H	H	H	64
[**2a**]HSO_4	H	H	H	60
[**2b**]Cl	H	Me	H	62
[**2c**]Cl	H	H	Me	63
[**2d**]Cl	H	H	OMe	64
[**2e**]Cl	Cl	H	H	60
[**2f**]Cl	H	H	Cl	61
[**2g**]Cl	H	H	Br	64

Studies on the Synthesis, Spectral Studies and Pharmacological Activities of 5-Methyl- 5-Tolyl - D^2 - 1,3,4 -Thiadiazolines

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In recent years greater interest in shown in synthesising thiadiazole derivatives as they are reported to exhibit good antimicrobial activities. The antibacterial, antifungal, antitubercular and antiherbicidal properties of these thiadiazole derivatives have been well documented. In the present study we report the synthesis of 2 – (Acetamido) – 4 – acetyl – 5 – methyl – 5 – tolyl – D^2 – 1,3,4 –thiadiazoline(II) by hetrocyclisation of 4 – methylacetophenone thiosemicarbazone (I). The corresponding 4–acetyl–2–amino–5–methyl–5 –tolyl– D^2 –1,3,4 – thiadiazoline(III) was obtained by hydrolysing(II). The structures of the compounds synthesised were ascertained by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and Mass spectral data. These compounds were then assayed for antimicrobial activities against six selected bacteria and five fungi. The thiosemicarbazone(I) was found to be effective antibacterial activity against *Klebsiella pneumoniae, Proteus mirabilis,* and *Pseudomonas aeruginosa* and antifungal activity against *Candida albicans* and *Aspergillus fumigatus.* The compound(II) was found to be effective antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* and antifungal activity against *Mucor* sp. The compound(III) was found to be effective antibacterial activity against *Salmonella typhi, Klebsiella pneumoniae, Proteus mirabilis* and *Escherichia coli* and antifungal activity against *Candida albicans, Aspergillus fumigatus* and *Mucor* sp.

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Synthesis and Biological Evaluation of Novel Pyrimidines

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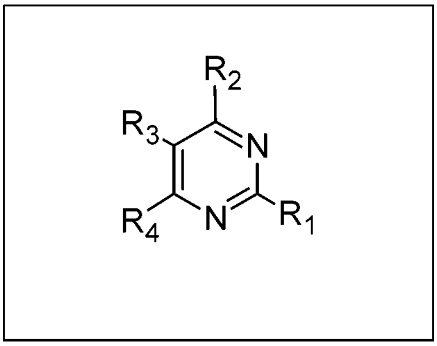
The key biochemical signal transduction pathways and transcription proteins have been explored and targeted to modulate the expression of the inflammatory proteins. One such protein that is highly expressed and plays a critical role in the pathogenic mechanisms of a number of chronic inflammatory conditions such as RA (rheumatoid arthritis), IBD (inflammatory bowel disease) and psoraisis [1] is the Tumor Necrosis Factor (TNF-a). From the discovery perspective, biological drugs targeting TNF-a have demonstrated to be effective in the treatments of patients with RA, IBD and psoriasis. Due to their potential adverse effects [1], developing orally active, small molecules that target TNF-a pose a great challenge. Herein we report the synthesis and biological activity of a series of pyrimidine analogs.



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New Strategies for Peripheral Functionalization of Hyperbranched Polymers

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Bengaluru 560012

Hyperbranched polymers have attracted sustained interest of researchers because of their ability to demonstrate many of the unique dendrimer-like properties, such as low solution/melt viscosities and large number of functionalizable end-groups, and the added advantage of far easier synthetic access [1]. Among the several molecular structural features that can be tailored, a particularly interesting one is the nature of the peripheral functionality; as they are primarily responsible in governing the solution properties of hyperbranched polymers and they also provide opportunity for post-polymerization functionalization.

During the past decade, we have developed a new melt-transetherification methodology for the preparation of polyethers and have utilized this approach to access and study a wide range of hyperbranched structures [2,3]. We have demonstrated that by the use of appropriate long chain alcohols, we can create core-shell type hyperbranched structures with hydrophilic core and hydrophobic shell or vise versa. We are presently examining the robustness and tolerance of this approach to a variety of functional groups, with the objective of developing strategies to incorporate different types of post-functionalizable terminal units at the molecular periphery of hyperbranched polymers. In this poster, we shall describe the different strategies that we have adopted to incorporate a range of peripheral functional groups, such as propargyl, norbornenyl and haloalkyl groups. Further complete derivatization of these peripheral functional groups to achieve different objectives, such as chromophore incorporation by “click chemistry” or chain initiation to incorporate water-soluble polymeric tethers, will be discussed.

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Bioisosterism and Organic Chemist's Gut Feelings for Molecular Modifications for Successful Drug Discovery

Brijesh Kumar Srivastava, Amit Joharapurkar, Jayendra Z. Patel, Saurin Raval, Rina Soni,
Preeti Raval, Nisha Sadhwani, Mukul R. Jain, Prasenjit Mitra, Bipin Pandey, Pankaj R. Patel

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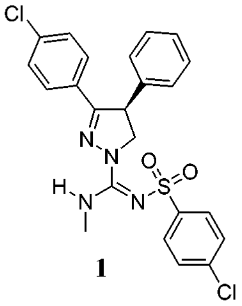
Bioisosterism and bioinformatics are the current buzzwords for accelerated new drug discovery protocols. While bioisosteric replacement of CB1 receptor antagonist SLV-319 **1** gave compounds **3** & **4,** which were found to be totally inactive, simple chemical modifications in the CB1 receptor antagonist and antiobesity drug Rimonabant **2** based on organic chemist's gut feelings led to a series of compounds **5,** with interesting and useful properties and opportunities. These results will be substantiated by *in vitro, in vivo* and pharmacokinetics profiles. The importance of various salts and chirality to optimize desired profiles will also be described.



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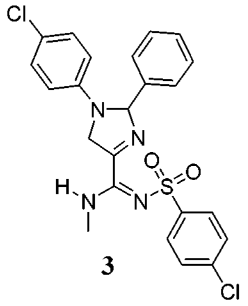
(SLV-319)



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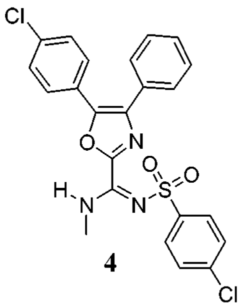

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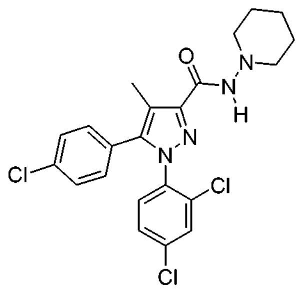

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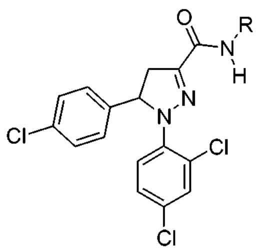

5

Acridone Based Hybrid Molecules as Cox-2 Inhibitors, Anti Cancer Agents and MDR Modulators: Design, Synthesis and Evaluations

Jatinder Kaur, Atul Bhardwaj and Palwinder Singh*

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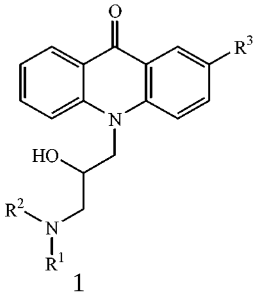
Along with its role in the production of prostaglandins (causing inflammation) during the arachidonic acid metabolism, the enzyme cyclooxygenase-2 (COX-2) is also responsible for the propagation of cancer and the development of multi drug resistance. One of the major limitations of the presently available highly selective COX-2 inhibitors is their cardiac toxicity which arises due to the decrease in the production of prostacyclin, a vasodilator.

Development of hybrid molecules by suitably combining the structural features of two molecules is always advantageous due to their multi target nature, less dose requirement and minimal side effects. In our current research programme, we have chosen acridone moiety (a DNA chelator, present in several anti-cancer drugs) as the template and introduced an amino hydroxyl substituent (active pharmacophore of multi drug resistance modulators) at the nitrogen or other different positions of acridone. The resulting molecules **1** and **2** have been synthesized and evaluated for COX-2 inhibition, for anti-cancer activities and for MDR modulating properties. The results of these investigations will be presented.



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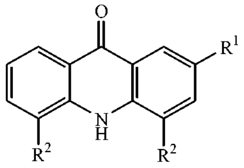

2

A Convenient Method for the Synthesis of Unsymmetrically Substituted Triphenylenes

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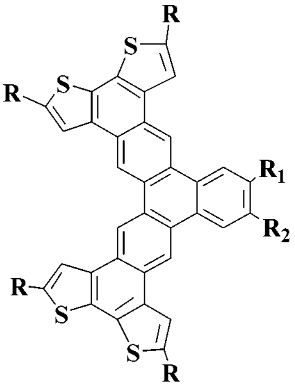
Punjab-143005

Triphenylene derivatives are the most widely synthesized and well characterized materials in the family of discotic liquid crystals (DLC's). The unsymmetrical peripheral substitution on triphenylene core has a large effect on the thermal behaviour of liquid crystalline materials. However, the properties of unsymmetrically substituted triphenylenes have been less explored due to paucity of methods for their synthesis. The only existing rational route involve the iodine promoted photocyclisation[1] or iron (III) chloride[2,3] promoted cyclisation of ortho-terphenyl which are prepared by Ullman coupling reaction under vigorous conditions or by palladium catalysed cross coupling reactions involving aryl boronic acids.



R, R_1 = alkyl chains, PEG

Design A

In the present investigation, we planned to synthesize unsymmetrically substituted triphenylene derivatives based on design A. During the course of our investigation we observed an unprecedented cyclisation of intermediate terphenyls in absence of any oxidising reagent. In this presentation, we will discuss the results of our investigations for development of a convenient method for the cyclisation of unsymmetrically substituted terphenyls.

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Vinylogous Carbonates in the Synthesis of Cyclic Ethers

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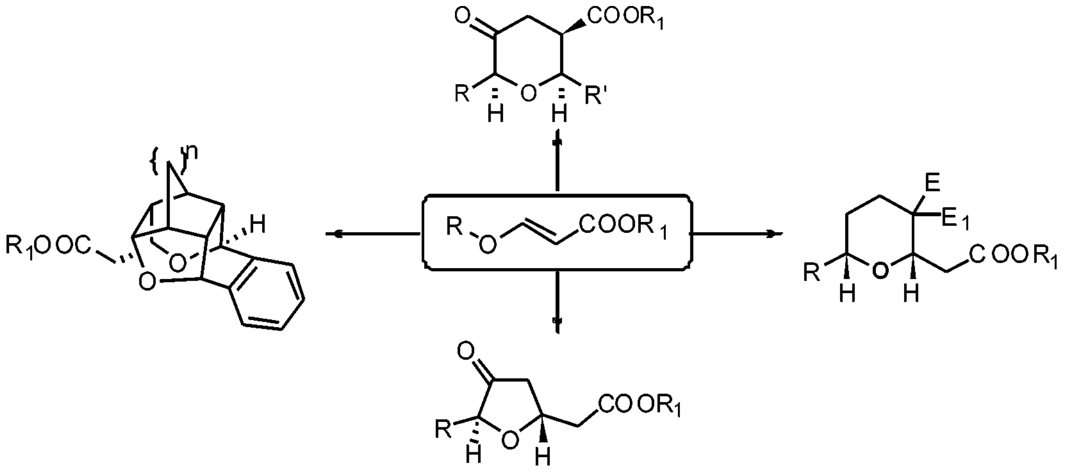
Cyclic ethers are ubiquitous in nature showing diverse biological activity [1]. Several unnatural cyclic ethers are aesthetically pleasing and have varied applications in theoretical and biological chemistry [2]. In recent years, vinylogous carbonates have been utilized as starting materials for the synthesis of cyclic ethers particularly in the radical cyclization reactions [3]. We have developed a highly stereoselective synthesis of new oxa-cages *via* alkyl radical cyclisation to vinylogous carbonates. To expand the scope of vinylogous carbonates in non-radical pathways, a highly diastereoselective method for the synthesis of cyclopropafuranones from vinylogous carbonates has been established. These *donor-acceptor* substituted cyclopropafuranones have been converted into diversely functionalized tetrahydrofuranones and pyranones by regioselective ring opening of the cyclopropane ring. In another direction, we have reported an efficient strategy for the synthesis of 1,2,2-trisubstituted indanes employing a tandem S_N2 - Michael sequence. Now, this strategy have been extended to the diastereoselective synthesis of 2,3,3,5-tetrasubstituted tetrahydropyran derivatives, demonstrating the utility of vinylogous carbonates as good Michael acceptors under non-radical pathway as well.The details of the above mentioned research finding will be exemplified in the poster-presentation.



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Synthesis of the Trisaccharide Related to the O-Antigen of E-coli Type8

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E. coli type 8 is a gram negative enterotoxic and enteropathogenic bacterium. Structure of the repeating unit of the O-antigen [1] is a mannose trisaccharide (Fig.1) containing **(**1® 2)-b-linked mannoside in the nonreducing end. Efficient synthesis of such linkage is scarce in the literature. We present herein the synthesis of the methyl glycoside of trisaccharide repeating unit of E.coli type 8 O-antigen. NIS/TfOH mediated glycosidation of phenyl or ethyl 2-O-acetyl-3,4,6-tri-O-benzyl-b-D-mannopyranoside (**2a** or **b**, Fig. 2) with methyl 3,4,6-tri-O-benzyl-a-D-mannopyranoside (**1**) furnished the corresponding disaccharide derivative (**3**) in high yield (82-88%). Zémplen deacetylation of (**3a**) followed by the reaction of resulting **3b** with the glycosyl donor, phenyl 4,6-O-benzylidene-2,3-di-O-benzyl- a-D-mannopyranoside (**4**) in the presence of 1-Benzenesulfinyl piperidine/Trifluoromethanesulfonic anhydride proceeded quite efficiently producing the corresponding trisaccharide derivative in 89% yield as a/b mixture from which the desired b-anomer was obtained in 68% yield. 10% Pd/C catalysed hydrogenolysis finally afforded the target trisaccharide as methyl glycoside.

b-D-Manp-(1>2)-a-D-Manp-(1>2)-D-Manp

Fig 1: Trisaccharide repeating unit of the O-antigen of E. coli type 8.

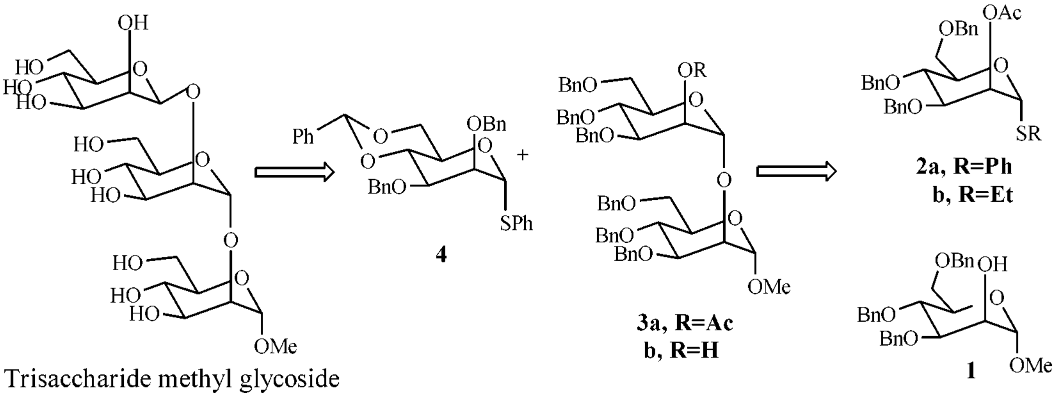

Fig. 2 Retrosynthetic analysis of the trisaccharide glycoside

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Synthesis of Chiral Phosphazene Bases and Their Applications in Catalytic Asymmetric Transformation

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Uncharged organic bases have been found to be efficient and irreplaceable reagents in base-mediated transformations in organic synthesis.[1] Among the several different families of strong neutral bases, phosphazenes[2] has emerged as a family of very strong and non-metallated organic bases[3]. These Schwesinger bases show extreme basicity (pKBH+ value of 50 in acetonitrile) or rather the lower nucleophilicity, is based on the increased steric hindrance and the participation of various donors to the conjugation in the cation structure make them suitable catatalyst for many base catalysed reaction such as Michael addition.

In our endeavor to utilize chiral Phosphazenes base for catalytic asymmetric organic transformation reaction, we have prepared chiral Phosphazene using L-prolinol and phosphotrinitrilic chloride in presence of triethyl amine in toluene in good yield. Possible use of this chiral Phosphazene as a catalyst in asymmetric organic transformations will also be discussed.

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Self Assembly of a Family of 2-oxo-3-cyano-4,6-Dimethyl Pyridyl Based Compounds that Show Face to Face and Edge to Face Orientation

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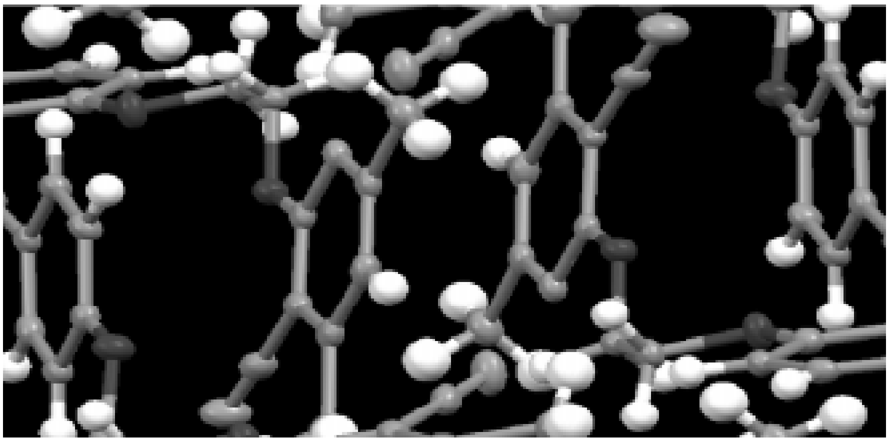
Interaction between aromatic units play a important role in many areas of chemistry and biochemistry, it is notably in molecular recognition and self assembly [1,2]. Extensive theoretical studies have shown face to face to edge to face in various molecular orientations [3].

Subtituent pyridine and phenyl rings with polymethylene linkers have been used as prototype for p- p interactions (parallel stacking as in DNA/RNA and perpendicular stacking as in proteins).

In x-ray crystallography we observed face to face and edge to face p- p interaction. Weak interactions in these compounds have been analysed by IR and ^{1}H NMR also in which we observed p- p , CN- p and hydrogen bonding as in x-ray crystallography. A number of inter-ring geometry have been observed from parallel face to face stacking to a edge to face orientation in which H atoms of one ring interact with negatively charged region on the other.



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Microwave– Assisted Synthesis and Study of the Stereochemistry of a, β̃ (9,10-Dihydroanthracene-9,10-diyl)-n’-(Ketimiyl)Succinimide

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A cage containing hydrazones having good biological activity but the synthesis of such type of hydrazones required relatively strenuous reaction condition namely refluxing substrates for several hours in the presence of an acidic catalyst. Introducing microwave technique , we synthesized a series of hydrazones having general formula a,b-(9,10-dihydroanthracene-9,10-diyl)-N’-(ketimiyl) succinimide which have been completed with in minutes and in high yield. This suggests that by applying microwave irradiation , the rate enhancement is due to selective absorption of microwave energy by polar molecules, nonpolar being inert to the MW dielectric loss. This represents an ecofriendly, green approach to these valuable hydrazones derivatives that avoids the harsh or highly contaminant conditions involving classical heating and offers a reduction or even elimination of solvent use and recovery, simplification of the work up procedures, facility of scale up and saving in energy consumption, in addition with higher yields.The hydrazones have been synthesized by utilizing N-aminoimide of anthracene-maleic anhydride adduct and alkyl-aryl ketones using microwave techniue and their stereochemistry have been characterized by IR and dynamic NMR spectroscopy. These hydrazones assume a preffered non-planar conformation about the N-N bond with the imine part (-N=CR_1R_2) lying *syn* to the cage moiety. The repulsive interaction of sp^2- nitrogen lone electron pair from the phenyl ring of the cage has been attributed to the stability of the hydrazones. Configurational isomers have been observed about the N=C bond , the major isomer being the one with the less bulky group lying cis to the cage moiety.

Microwave Mediated Synthesis of Aza Bissteroids

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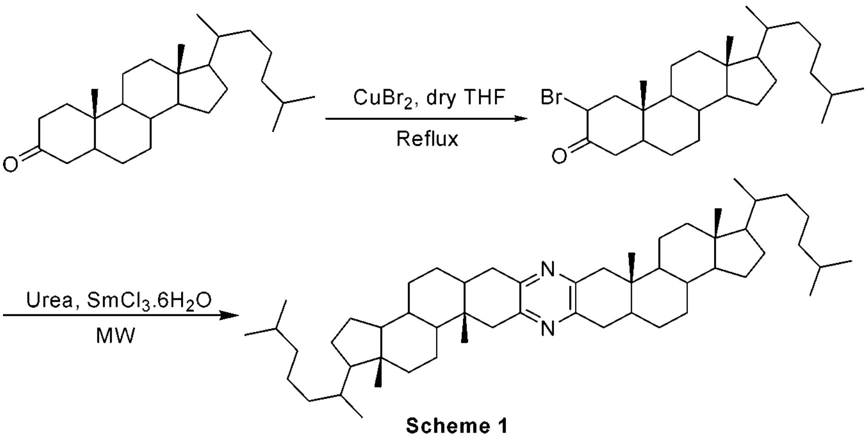
The steroidal heterocycles constitutes one of the most interesting classes of organic compounds and their biological importance is well documented [1]. Some aza-heterocycles viz. pyrazole, pyridine, pyrimidine, pyrazine etc. are more commonly appearing as an essential part of pharmacologically active heterosteroids. Recently a number of dimeric and oligomeric steroids have emerged as unique structural entities with characteristic chemical behaviour [2]. The pyrazine fused bissteroid cephalostatin, isolated from marine worm *Cephalodiscus gilchristi,* has shown powerful cell growth inhibition against P388 lymphocytic leukemia [3]. However, such compounds are rare marine natural products and available in only small amounts. The novel structures and exceptional activities of such bissteroids have attracted great interests of organic chemists for the synthesis of structurally related compounds. In spite of such growing interests literature shows only a few numbers of synthetic methods for the preparation of bissteroidal compounds. Herein, we report a convenient preparation of pyrazine-fused bissteroid from 3-keto steroids. In a two-step strategy cholestan-3-one was first converted to 2-bromo-cholestan-3-one and then reacted with urea in presence of $SmCl_3$ under microwave irradiation to afford the bissteroidal pyrazine (Scheme 1). The key step of the reaction is the utility of urea as a source of ammonia under microwave irradiation in presence of $SmCl_3$. The reaction has also been generalized using Lewis acid other than $SmCl_3$.



Scheme 1

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Stereoselective C-C Bond Formation via Enolate : Application of Memory of Chirality Concept for Chiral Induction

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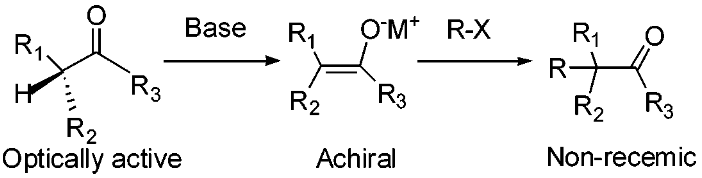
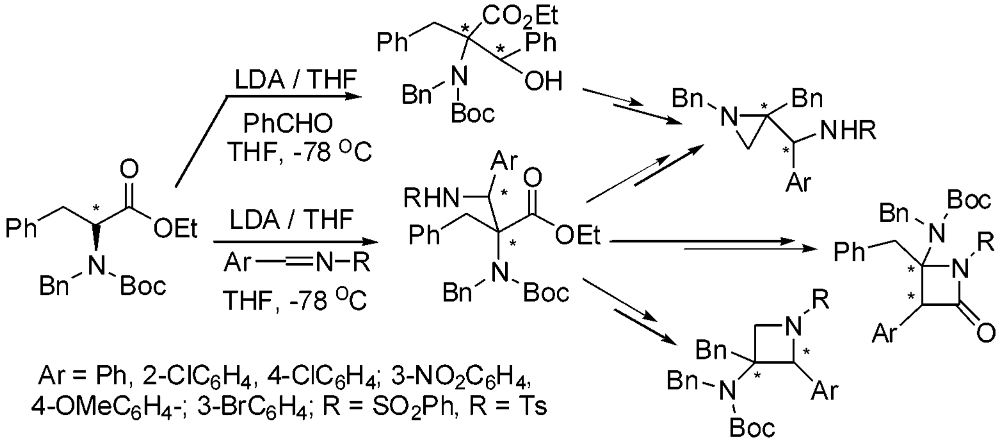
In recent years, a new stereoinduction principle, known as 'memory of chirality' (MOC) has emerged as an alternative to other classical methods in asymmetric synthesis.[1] Memory of chirality as per Fuji's definition is a phenomenon where a static central chirality of the starting material is preserved in the form of dynamic conformational chirality of the reactive intermediate.



Based on MOC principle we studied stereoselective C-C bond formation reaction of *N*, *N* diprotected amino acid ester enolates with various electrophiles especially to imines [2]. MOC concept has been successfully utilized for the synthesis of various synthetic targets of biological importance namely, a, b-diamino acid derivatives, b-lactums, aziridines, azitidines etc.



Ar = Ph, 2-ClC$_6$H$_4$, 4-ClC$_6$H$_4$; 3-NO$_2$C$_6$H$_4$, 4-OMeC$_6$H$_4$-; 3-BrC$_6$H$_4$; R = SO$_2$Ph, R = Ts

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Preparation of Food Colourant from the Carotenoids, Ssynthesized by Euglena SP

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Some algae have been reported to be very rich sources of carotenoids Tomohisa et al, 2006 [1], Olaizola, et al, 2003 [2], Yuan et al.2000 [3]. *Euglena sp*. is a microalga floats over the various ponds of Assam. The alga synthesizes a significant amount of astaxanthin. The amount of carotenoid present in this species was found to be 15.854± 0.238 mg/g of dried algae when collected from natural habitats Britton,1985 [4]. The individual carotenoids were separated, identified and estimated by HPLC. HPLC separation revealed that astaxanthin occurs mostly as esters of fatty acids. The hydrolysis of the extract carried out in 0.018M KOH solution Jian et al, 1999 [5]. The hydrolyzed extract on HPLC separation showed mainly two carotenoids i.e. astaxanthin (14.396±0.330mg/g of dry algae powder) and lutein (1.077±0.870mg/g of dry algae powder). E/Z isomers were also separated by HPLC.

Carotenoids are organic solvent soluble natural pigments with beautiful colours. From the alga carotenoids have been extracted and encapsulated in an oil-in-water emulsion. This emulsion was dried by spray- drying to produce some water- soluble beadlets. This beadlets are water dispersible. These beadlets can be used as colour additives of food. These encapsulated carotenoids are more stable than carotenoid pigments available in nature. Details of the procedure would be presented.

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A Novel Synthesis of 2-Trimethylsilyl-3-Methyl-Cyclohexen-1-one by the Wurtz-Fittig reaction

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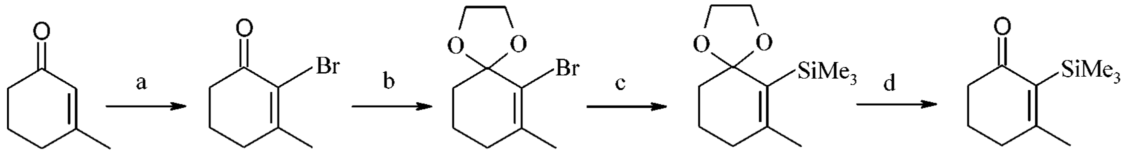
Cyclic vinylsilanes form an important class of compounds in synthetic organic chemistry [1]. Reports of cyclic vinylsilanes which have been functionalized have been few [2]. An important class of functionalized organosilicon compounds are á-trimethylsilyl-a, b-unsaturated cycloalkenones. These compounds are a-acylvinyl anionic synthons. The ketalised derivatives of the a-trimethylsilyl-a, b-unsaturated cycloalkenones: the 6-trimethylsilyl-1,4-dioxaspiro[4.n]cycloalk-6-enes are documented as masked acyl vinyl anion equivalents[3]. With this insight, the preparation of 6-trimethylsilyl-7-methyl-1,4-dioxaspiro dec-6-ene (**4**) and 2-trimethylsilyl-3-methylcyclohexenone (**5**) was taken up (**Scheme 1**). Even though the preparation of 2-trimethylsilyl-3-methylcyclohexenone (**5**) through the n-BuLi route, its ketalised derivative (**4**) is not reported in literature.



1 **2** **3** **4** **5**

(a) Br_2/Et_3N (56%) (b) $(CH_2OH)_2$/p-TsOH, C_6H_6 (70%) (c) Na/Cl-$SiMe_3$ (76%) (d) H_2O (98%)

Scheme 1

3-Methylcyclohexenone (**1**) was prepared by the Knoevenagel condensation of ethylacetoacetate with paraformaldehyde/piperazine using microwave irradiation. Bromination of 3-methyl-2-cyclohexenone (**1**) followed by dehydrobromination with triethylamine yielded 2-bromo-3-methylcyclohexenone (**2**). Subsequent ketalisation with ethylene glycol and p-toluene sulphonic acid/benzene gave the 6-bromo-7-methyl-1,4-dioxaspiro[4,5]dec-6-ene (**3**). The bromo-ketal (**3**) upon Wurtz-Fittig coupling reaction with 2 equivalents of metallic sodium and 4 equivalents of chlorotrimethylsilane in anhydrous ether solvent at (-) 40°C, gave the 6-trimethylsilyl-7-methyl-1,4-dioxaspiro[4,5]dec-6-ene (**4**). Acid catalyzed workup of (**4**) yielded 2-trimethylsilyl-3-methyl-cyclohexen-1-one (**5**). All the reactions were repeated a minimum of ten times each and the yields reported in **Scheme 1** are optimized. The mechanism of formation of the vinylsilanes is the trapping of the sodiated anion of **3** with chlorotrimethylsilane, to yield the cyclic vinyl silane: 6-trimethylsilyl-7-methyl-1,4-dioxaspiro[4,5]dec-6-ene (**4**).

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Recent Developments in the Chemistry of Forskolin

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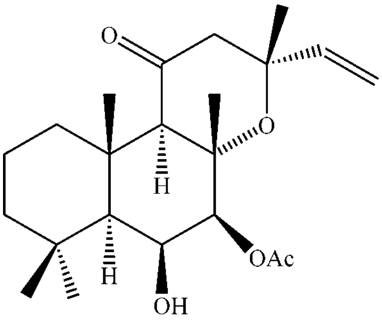
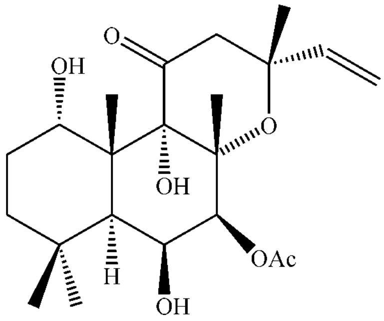
Forskolin, a highly oxygenated labdane diterpene isolated from roots of *Coleus forskohlli,* has been shown to activate adenylate cyclase and exhibit a wide range of physiological activities such as branchospasmolytic, antihypertensive, antiglucoma and positive inotropic effect etc. In addition, forskolin has been demonstrated to inhibit platelet aggregation as well as metastasis of tumors.

Labdane based molecular framework of forskolin accommodates eight asymmetric centers, seven of which are continuous. These structural features, together with its wide pharmacological profile have attracted attention of large number of synthetic chemists, which has led to the considerable synthetic approaches to forskolin skeleton. In our continuing efforts in the chemistry of forskolin we have achieved new synthetic route to labdane skeleton of forskolin and remote functionalization to obtain new molecules. Our recent efforts will be presented.



1,9- Dideoxy forskolin



Forskolin

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Amino Acid Based Amphiphilic Hydrogelators: Potent for Antibacterial Activity and Controlled Release

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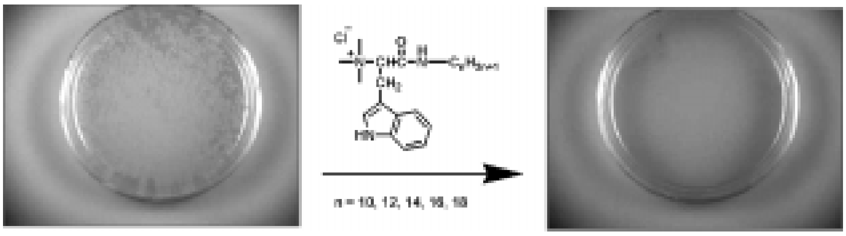

At the onset of this twenty first century, development of biomaterials, which are inherently antibacterial having broad-spectrum activity against both Gram-positive and Gram-negative bacteria with considerable biocompatibility, is of tremendous importance in biomedicinal chemistry. To this end, hydrogelating soft materials particularly from low-molecular-weight (LMW) gelators have generated significant interest in preparing and modifying biomedicinal implants. In our recent research effort, we have developed a series of L-tryptophan based cationic amphiphiles with varying degree of hydrophobicity, some of which are excellent gelator for plain water, an essential criterion for biological use. The alkyl chain induced hydrophobicity at the molecular level has remarkable influence in modulating water immobilization and thus giving rise to a wider efficiency of gelation, minimum gelation concentration (MGC) in plain water ranges from 15-0.2%, w/v. These amino acid based amphiphilic hydrogelators exhibited remarkable bactericidal activity against both Gram-positive (minimum inhibitory concentration, MIC = 0.1-75 mg/mL) and Gram-negative (MIC = 0.5-5 mg/mL) bacterial species. This bactericidal effect of cationic hydrogelators was greatly influenced by their alkyl chain length and interestingly it was quite comparable or in some cases markedly better than that of clinically available antibiotics. Most excitingly, they showed least toxicity to mammalian cells. These antibacterial as well as biocompatible hydrogels also have the ability to entrap and facilitate controlled release of biomolecules that may find prospective applications in drug delivery and biomedicines.

Reference
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A Novel System for Debenzylation of Sugars

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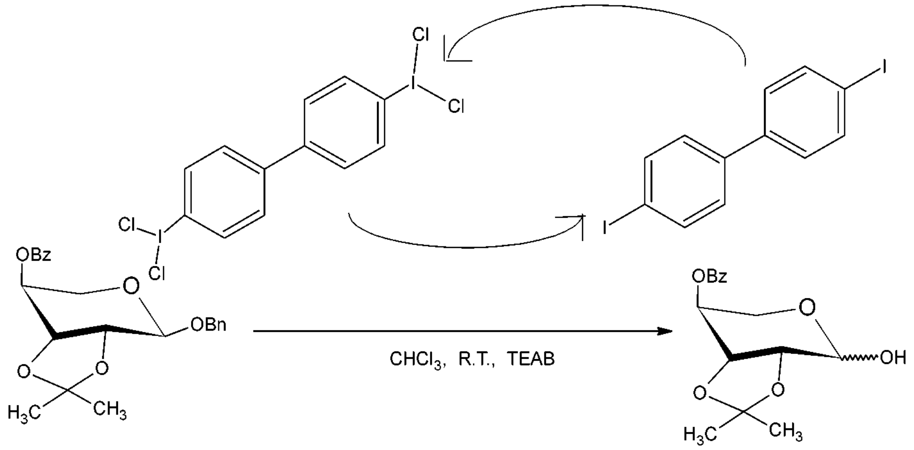
Debenzylation of sugars is an important reaction in glycol-chemistry due to its applications in medicinal chemistry and chiral dry intermediates. Although numerous methods are available for the removal of benzyl ethers (protective group) our novel method aims at elimination of the short comings of those methods. Our novel method involves use of 4,4'-Bis-(dichloroiodo)-biphenyl exclusively in presence of tetraethyl ammonium bromide (TEAB)at room temperature for selective debenzylation of sugars. The method is simple, mild and does not affect acetates, benzoates and sensitive glycosidic linkages as well as reagent can be recycled.



Microwave Assisted Synthesis of 9-Substituted Acridines

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Acridine is a heterocyclic compound with a wide variety of pharmaceutical/biological properties including DNA and RNA binding properties. Many drugs are known to bind DNA through intercalation between consecutive nucleosides in the DNA strand [1]. Derivatives of acridine have been first developed as pigments and dyestuffs by the end of 19th century. Other applications of Acridine and its derivatives are as antitumour agents, anticancer agents [2], bactericides, antimalarials, insecticides and antifungies.

The Bernthsen reaction, one of the earliest methods used for the synthesis of acridine and its derivatives. It consists of heating a mixture of an aromatic and aliphatic carboxylic acid with a diphenylamine and zinc chloride at 200-270 ℃ for about several hours [3]. Under conventional heating the reaction requires 20 hours [3], whereas under microwave irradiation, 2-12 min are required providing 9-substituted Acridine derivatives in varying yields. Instead of using Zinc Chloride we use P-toluene sulfonic acid (*p*-TSA) and shows its application for Bernthsen reaction. It is observed that both the aliphatic and aromatic carboxylic acids undergo Bernthsen reaction showing good yields in microwave heating with time economy observed. Thus microwave irradiation has proved to be a good way to optimize the Bernthsen reaction for aromatic and aliphatic carboxylic acids, shortening the reaction time, experimental simplicity and enhanced the reaction yields. More over, easy availability of p-toluene sulfonic acid, and easy wake-up process makes it improvement over existing methods. Use of microwaves also considerably raised the yields compared to the ‘classical’ method.

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Turn Mimics : Design and Synthesis

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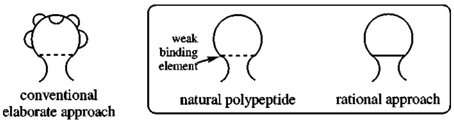
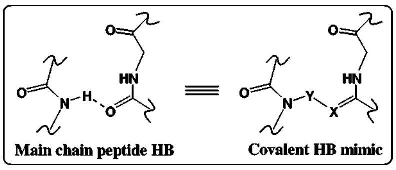
Turns (e.g. b-turns, a-helices, b-hairpins, g-turns) are common secondary structural motifs in proteins that play a role in protein folding and stability and participate in molecular recognition interactions. Most molecular recognition events involving proteins are owing to the intrinsic topology on the turn surfaces. These topologies are stabilized in short peptide sequences by weak, main chain peptide hydrogen bonding interactions, in proteins. Hydrogen bonding interactions however are too weak (1 – 2 kcal/mol) to stabilize these peptide sequences in native-like conformations when they are removed out of the context of the protein environment. Methods for such conformational stabilization have been developed over the past couple of decades [1]. Most conventional methods involve mutations of either or both of the peptide sequence and the backbone and are hence deficient to replicate the native molecular recognition topological surface of these short peptides and are applicable for stabilizing only specific turn systems. In a rational, atom-economic approach, we replace the hydrogen bonding interactions with covalent mimics (100–150 kcal/mol) to achieve conformational mimicry [2] of the functional surface in short peptide sequences.



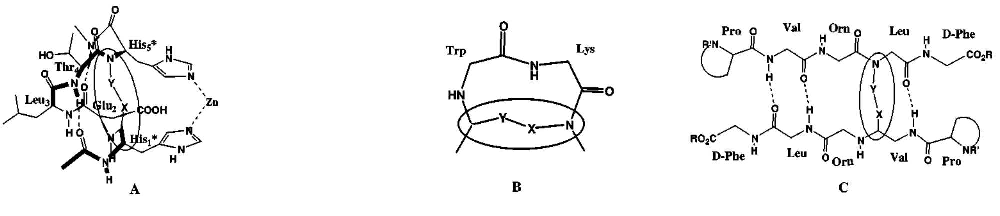
Conformational stabilization of turns: the conventional and the novel approaches.



In the covalent mimics for the peptide hydrogen bonding interaction between the amide NH of the i^{th} residue and the amide >C=O of the $i+n^{th}$ residue, trivalent species like –N< replace the peptide carbonyl oxygen and divalent species like -O-, -Se-, -CH$_2$-, replace the hydrogen atom.

The peptide hydrogen bonding interaction and its covalent mimics.

The functional topologies of three different short peptide sequences with varying biological significance are being replicated using the above philosophy. They are the Zn-binding HEXXH helical domain of angiotensin converting enzyme (ACE) & Thermolysin (**A**) [3], the type II b-turn in somatostatins (Trp-Lys) (**B**), and the type II' b-turn and the antiparallel b-sheets in gramicidin-S (**C**). In this presentation, we will discuss the design, synthesis and conformational studies of these constrained mimics.



Constrained mimics of the Zn-binding HEXXH helical domain of ACE & Thermolysin (A), the type II b-turn on the Somatostatins (Trp-Lys) (B), and the type II' b-turn and the antiparallel b-sheets in Gramicidin-S (C)

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Bifunctional Fluorogenic Chemosensors Based on Thiacalix[4] Arene

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Thiacalix[4]arene, regarded as second member of calix[4]arene family, has attracted a lot of interest in supramolecular chemistry. The presence of sulfur atom bridges in thiacalix[4]arene results in potentially useful properties, mostly unknown in classical calix[4]arene. Thiacalix[4]arene has excellent ability to act as pre-organizing complexing agents, carriers and potential biomimics as well as able to undergo multiple fuctionalization. Recently, we achieved the stereoselective synthesis of all four stereoisomers of bis(*O*-2-aminoethyl)-*p*-*tert*-butylthiacalix[4]arene, that is, vicinal *O,O'*- and distal *O,O"*-bis(2-aminoethyl) derivatives with *syn* and *anti* arrangements of the two substituents[1]. Using one of these isomers *syn* distal bis(*O*-2-aminoethyl)-*p*-*tert*-butylthiacalix[4]arene, we reported the synthesis of bisthiacalix[4]arenes in cone conformation[2]. Now, we have used *syn* distal bis(*O*-2-aminoethyl)-*p*-*tert*-butylthiacalix[4]arene to synthesize fluorescent sensor bearing two dansyl groups[3] in *cone* conformation. Further, we have also synthesized *p*-*tert*-butylthiacalix[4]arene based dipodal chemosensors bearing fluorogenic pyrene units conjugated to amide groups in cone conformation. These receptors behave as bifunctional fluorogenic sensor to soft metal ions (Cu^{2+} and Hg^{2+}) and biologically important inorganic anions (F^- and CN^-). The synthesis and photophysical behavior of these thiacalix[4]arene derivatives will be presented in the symposium.

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Green Strategy for a Novel Synthesis of Functionalized Dihydropyrimidines from Carbohydrates

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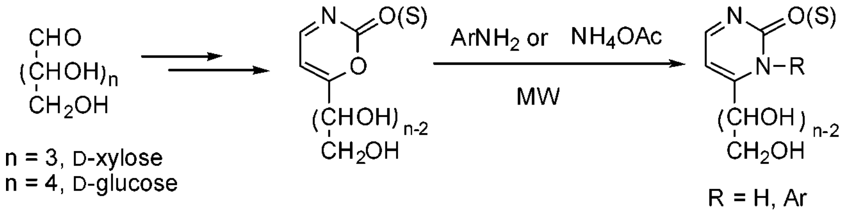
Functionalized dihydropyrimidines (DHPMs) represent a heterocyclic system of remarkable pharmacological efficiency. For example, appropriately functionalized DHPMs are orally active hypertensive agents, a_{1a} adrenoceptor selective antagonists as well as valuable new leads for anticancer and AIDS therapy [1]. Biorenewable resources are new and rapidly developing concept in the environmental and chemical sciences that concerns the wide use of biorenewable materials for industries. Carbohydrates are the major biorenewable feedstocks for synthesizing various industrially and biologically important compounds. In pursuing our work on functionalized pyrimidines [2,3], we have developed a green strategy for a novel synthesis of functionalized DHPMs using carbohydrates as biorenewable resources.



The synthesis is accomplished by reacting D-glucose/D-xylose semicarbazone or thiosemicarbazone-derived 1, 3-oxazin-2-ones/thiones with ammonium acetate/aromatic amines under solvent free microwave irradiation conditions in a one-pot procedure. The present synthetic strategy involves aza-Michael addition followed by dehydrative ring transformation leading to higher yields of functionalized DHPMs in a short reaction time.

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Asymmetric Synthesis of Benzo-Fused Oxa-Heterocycles Exploiting b-Hydroxy-a-Tosyloxy Ester Building Blocks

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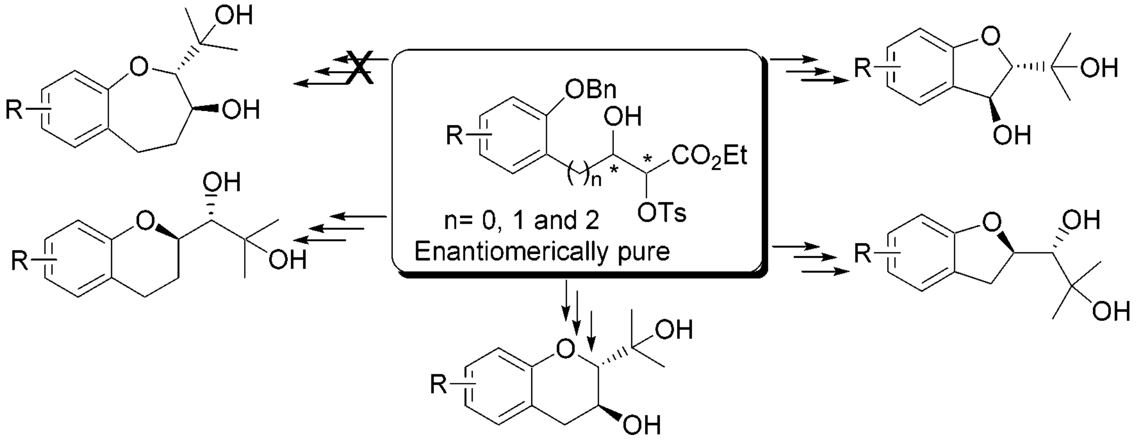
Over the past several years organic synthesis of natural product-like molecules received significant attention due to the growing use of small-molecule libraries for studies of protein function and discovery of novel drug leads.[1] Small-molecule libraries generated from core scaffolds derived from natural products are proving to be a valuable source of biologically active compounds that provide new probes for molecular targets. In this context, new methodologies have to be designed for stereoselective synthesis of small-molecule libraries with distinct skeletal frameworks *via* diversity-oriented synthesis (DOS).

As part of our research programme related to the diversity-oriented synthesis (DOS) and biological applications associated with benzo-annulated heterocycles,[2] we became interested in the enantioselective synthesis of natural product like small molecules containing dihydrobenzofuran, 1-benzopyran and 1-benzoxepin frame works by utilising b-hydroxy-a-tosyloxy esters. The details of our synthetic studies[3] will be presented.



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A Rapid and Pollutionless Microwave Asissted Efficient Extraction from Seeds of *nigella sativa*

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A simple, rapid and precise microwave-assisted extraction process was developed and optimized for preparing n-hexane extract from shade dried seeds of *N. sativa*. The seeds have a wide variety of application in traditional medicine, especially for the treatment of cough, fever, bronchial asthma and eczema Ali et al [1]. The occurrence of fats and fatty acids. Essential oils. Enzymers. Proteins and peptides. Alkaloids. Saponins, and polyols has been reported Al-Naggar et al [2] Atta-ur-Rahman et al [3]. Recent pharmacological investigation on the seed extract revealed a wide spectrum of activities such as anti-tumor, anti-inflammatory, analgesic, anti-pyretic and gastroprotective.

The newly developed process was compared with conventional soxhlet extraction, on their production and any change in number of components of both extract with their shape and R_f values. The major parameters studied showed effect on extraction efficiency including processing time, strength of radiation, moisture content, mesh size and irradiation with and without solvent. The most favorable conditions were obtained by using coarse powdered plant material for 10 min at 340 W with n-hexane solvent under moisture. There was no change in the composition of both extracts under microwave and conventional soxhlet extraction, further to evaluate chemical composition it was saponified and methyl ester of free acids were compared by TLC study. The GC-MS analysis was also performed of unsaponifiable oil fraction, hence this newly developed extraction procedure required less amount of solvents and saving the time also. It was beneficial to the environmental and normal health care. The alcohol and n-hexane extract were also analyzed and compared for their antimicrobial activities.

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Michael Addition of Dialkyl Succinate to α,β-Unsaturated Ketones – A New Addition to Dialkyl Succinate Chemistry

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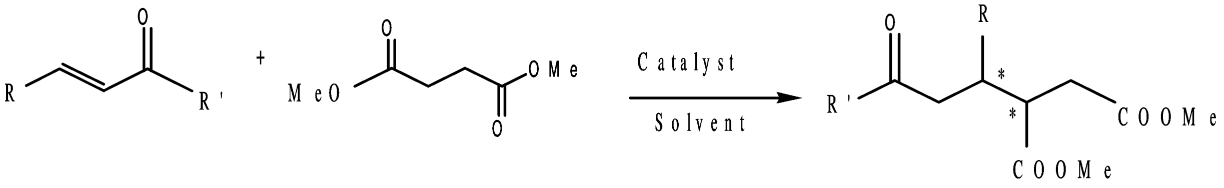
Dialkyl succinate has got intersecting chemistry such as acylation condensation, self-condensation, Stobbe condensation, etc. Acylation condensation of dialkyl succinate in the presence of TMSCl to yield 1,2-bis(trimethylsilyloxy)cyclobutene has been reported by Fadel and his colleagues [1]. Dialkyl succinate undergoes self-condensation to yield diethyl 2,5-dioxo-2,4-cyclohexanedicarboxylate in the presence of a strong base catalyst such as sodium hydride or alkoxides [2]. Condensation of dialkyl succinate with aldehydes or ketones to form monoesters of α-alkylidene succinic acids has appeared in a number of reports [3]. Other interesting chemistry of dialkyl succinate includes use of diethyl dilithiosuccinate in the synthesis of γ-butyrolactone synthesis, which is a useful intermediate in the synthesis of cyclopentenones. Mono- and dialkylation of succinates have been reported by Long and Rathke, and carbocyclization by Wilkening *et al.* and Mundy *et al.* We will report Michael addition of dialkyl succinates to α,β-unsaturated ketones as new additions to the already existing succinic acid ester chemistry. Addition of dimethyl succinate to α,β-unsaturated ketones results in the formation of two diastereomers. These and other relevant results will be discussed.



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Anti-Thyroid Drugs and Related Compounds Effectively Protect Against Peroxynitrite-Mediated and Peroxidase-Catalyzed Nitration and Oxidation Reactions

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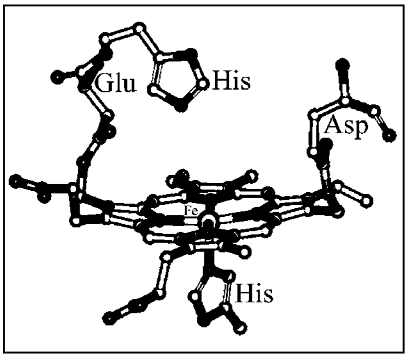
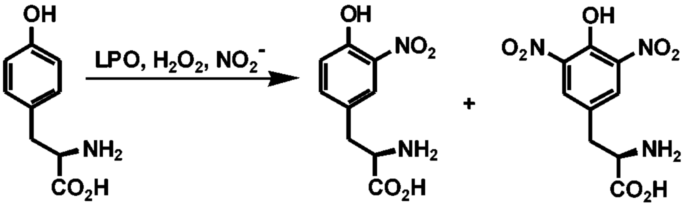
Nitrotyrosine, generated by enzymatic or non-enzymatic nitration of tyrosyl residues in proteins, has attracted much attention as a biomarker of oxidative and nitrative stress in inflammatory, allergic, and other diseases. Recent studies suggest that the non-enzymatic or chemical nitration of free and protein-bound tyrosine is caused mainly by peroxynitrite (PN), which is a strong biological oxidizing and nitrating species generated *in vivo* by the diffusion-controlled reaction of superoxide anion radical ($O_2^{\bullet -}$) and nitric oxide (•NO) whereas, the enzymatic nitration of free and protein-bound tyrosine is catalyzed by heme-peroxidases such as myeloperoxidase (MPO), eosinophil peroxidase (EPO), horseradish peroxidase (HRP), and lactoperoxidase (LPO) in the presence of hydrogen peroxide (H_2O_2) and nitrite (NO_2^-). Furthermore, other heme-proteins such as hemoglobin, myoglobin, and cytochrome C and free heme/iron also catalyze the nitration of tyrosine.



A. Active site of LPO.



B. LPO-catalyzed nitration of L-Tyrosine

As the nitration reactions inactivate a variety of enzymes and proteins by nitrating the tyrosine residues, much attention has been devoted to the inhibition of these nitration reactions. In the present study, we employed a number of commonly used anti-thyroid drugs and different synthetic organoselenium and organosulfur compounds as scavengers of peroxynitrite as well as the inhibitors for the lactoperoxidase(LPO)-catalyzed nitration of L-Tyrosine. We have also studied these compounds as inhibitors of LPO-catalyzed oxidation reactions.

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Diastereoselective Synthesis of Highly Functionalized Tetrasubstituted Tetrahydrofurans with 2,5-*trans* and 2,5-*cis* Relationships Using Iodocyclization Reaction

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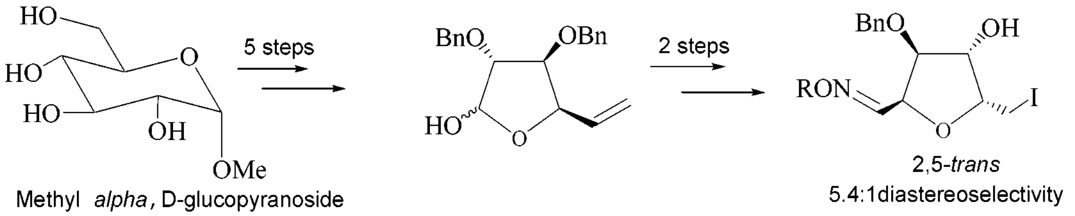
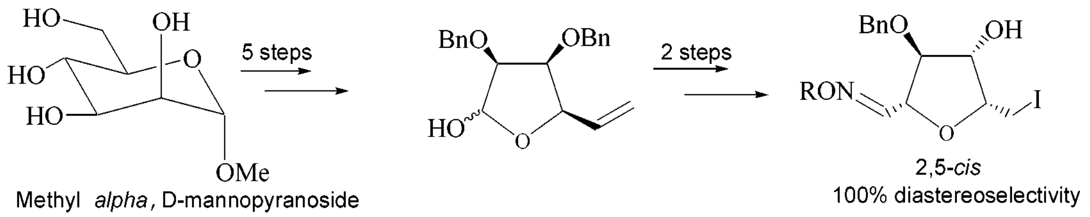
The tetrasubstituted tetrahydrofurans (THFs) are present in various natural products [1] and various biologically important molecules [2] like renealtins A and B, asitrocin, 2,4-*cis*- and *trans* asitrocinones, donnaienin, trilobatin B[3]. The iodocyclization reaction is one of the most commonly employed methods for the construction of tetrahydrofurans, and has been broadly employed in the synthesis of natural products.

Realizing the importance of the polyfunctionalized THFs, we envisaged new oxime substituted THF scaffolds, with 2,5-trans and 2,5-cis relationship, containing various diversification sites that allow amenability of the product transformation to biologically interesting molecules. By using iodocyclization reaction we have synthesized the chirally pure tetrasubstituted tetrahydrofuran diastereoselectively starting from commercially available pyranoside sugars. While a good selectivity was noticed in the case of glucopyranoside derived THFs, 100% selectivity was observed in the case of mannopyranoside derived THFs. The details of the work will be presented.





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An Asymmetric Dihydroxylation route to (*2R,3S,6S*)-2,6-Bis(hydroxymethyl)Piperidine-3-ol

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Functionalised piperidines are an important class of heterocycles and interest in their chemistry continues unabated because of their usefulness as biologically active agents.[1]A piperidine-3-ol bearing appendages with versatile functionality at 2-and 6-positions eg. **1** would serve as a building block for a large variety of piperidine alkaloids such as (+)-prosophylline, (+)-prosopinine,(+)-prosopine and (+)-micropine[2] (Figure1).

We have developed a new protocol for the synthesis of **1** starting from L-glutamic acid **2** as depicted in scheme1. Thus, L-glutamic acid **2** was converted into the intermediate **3** by standard synthetic transformations. Compound **4** was obtained in excellent diastereoselectivity by asymmetric dihydroxylation of olefinic ester derived from **3**. Subsequent synthetic manipulations led to the target compound **1**.

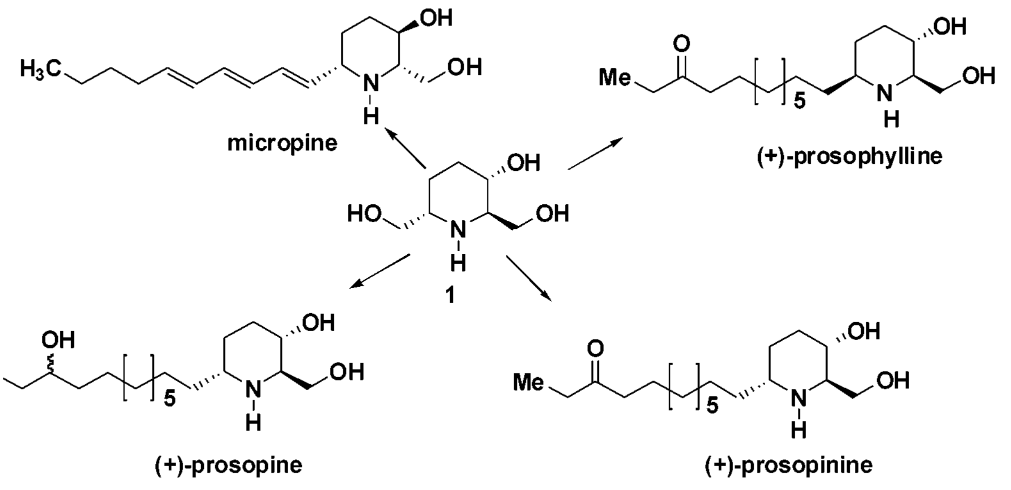
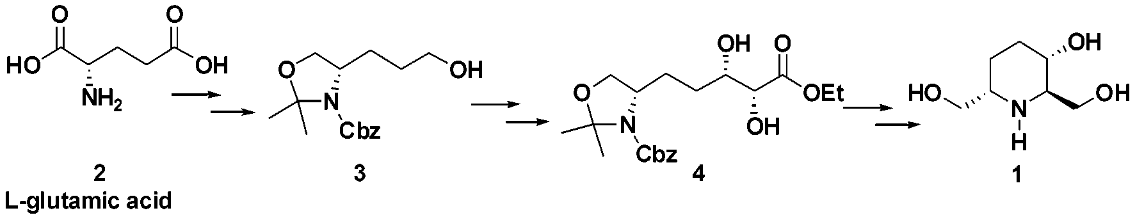


Figure 1



Scheme 1

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Carbamate Chemistry Using Mitsunobu's Chemistry

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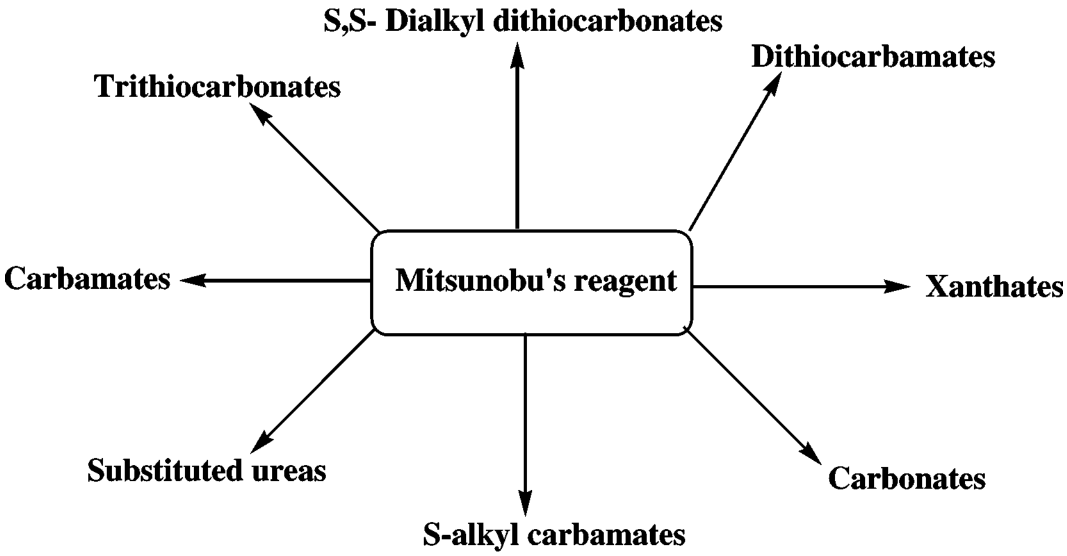
Mitsunobu reaction has been known for more than three decades, mediated by the redox combination of triaryl-phosphine/dialkyl azodicarboxylate.[1] Mitsunobu reaction is popular in organic synthesis and medicinal chemistry because of its scope, stereospecificity and mild reaction conditions. Mitsunobu reaction has extensively been used in the synthesis of various kinds of natural products[2], peptide chemistry[3] and combinatorial chemistry as well.

In the present talk, I would like to disclose our recent work for the synthesis of carbamates, dithiocarbamates, xanthates, carbonates, *S*-alkyl carbamates and substituted ureas using Mitsunobu's reagent from the various kinds of starting materials using cheap, abundant and safe reagents like CO_2/CS_2 respectively.



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Synthesis and Evaluation of 1-Benzhydryl-Sulfonyl-Piperazine Derivatives as Inhibitors of Tumor Growth and Tumor Angiogenesis of Mouse Ehrlich Ascites Tumor *in vivo*

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Angiogenesis is the formation of new capillary blood vessels from preexisting vessels, is a tightly regulated phenomenon that plays essential roles in reproductive functions, wound healing and embryonic development. It is clearly established that the aggressive growth of tumors and of their metastasis is strictly dependent on angiogenesis, thus suggesting that the inhibition of angiogenesis may represent an effective approach for blocking tumor progression. This has led to the development of a new class of novel products having antiangiogenic activity. Piperazines are currently the most important building blocks in drug discovery, with a high number of positive hits encountered in biological screens of this heterocycle and its congeners. In this perspective a series of novel 1-benzhydryl-sulfonyl-piperazine derivatives were synthesized by nucleophilic substitution reaction of 1-benzhydryl-piperazine with different sulfonyl chlorides and characterized by ^{1}H NMR, LC/MS, FTIR and X-ray crystallographic studies. The title compounds exhibited *in vivo* inhibition of Ehrlich ascites tumor (EAT) cell growth, increased the Median Survival Time (MST) and %ILS of EAT bearing mice. Further treatment of derivatives *in vivo* resulted in reduction of EAT cell number and ascites formation. The efficacy of the derivatives to inhibit the angiogenesis *in vivo* was evaluated in tumor bearing mice peritoneum and chorio allantoic membrane (CAM) model. The compounds suppressed the *in vivo* blood vessel formation in mice peritoneum and in chorio allantoic membrane. Among the compounds studied, **7e** demonstrated highest tumor inhibitory and anti-angiogenic effects against the mouse tumor. However this phenomenon needs detailed investigation.

L-Proline Catalyzed Simple and Efficient Synthesis of 1,8-Dioxo-Decahydroacridines in Aqueous Medium

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1,8-Dioxo-9-aryl-10-aryl-decahydroacridines and their derivatives have attracted strong interest due to the treatment of cardiovascular diseases, such as angina pectoris and hypertension. They have been also used to synthesize labeled conjugates with medicinals, peptides, proteins, and nucleic acids that exhibit anti-tumor and DNA-binding properties. Multi-Component Reactions (MCRs) constitute an especially attractive synthetic strategy for rapid and efficient library generation due to the fact that the products are formed in a single step and the diversity can be achieved simply by varying the reacting components.

Recently, organic reactions conducted in aqueous media have received much attention because water is nontoxic, cheap, abundantly available and benign to the environment. Although water not only increased the rate and the yield of a reaction but also, enhanced enantioselectivity in chiral synthesis, the major drawbacks of using water as a solvent are its poor ability to solubilize organic reactants and unsuitability for use with moisture sensitive organic compounds and catalysts. One of the more efficient and versatile methods of increasing solubility and one that does not require modification of the solute is to use an organic co-solvent. Some of the most commonly used co-solvents are the lower alcohols, DMF, acetone, and acetonitrile. Proline is an abundant bi-functional chiral molecule that is inexpensive and available in both enantiomeric forms. These two functional groups can both act as acid or base and can also facilitate chemical transformations in concert, similar to enzymatic catalysis.

Each of the reported methods for the synthesis of decahydroacridines has its own merit; however, these methods are also plagued by the limitation of poor yields, cumbersome work-up procedure and effluent pollution. Consequently, we thought that there is scope for further innovation towards milder reaction conditions, short reaction times, increase in variation of the substituents in the components and better yields in the synthesis of 1,8-dioxo-decahydroacridines which can possibly be achieved by choosing L-Proline as a catalyst for this multi-component reaction (MCR) in aqueous media.

An Efficient Heterobifunctinal Reagent for Construction of Oigonucleotide Microarrays

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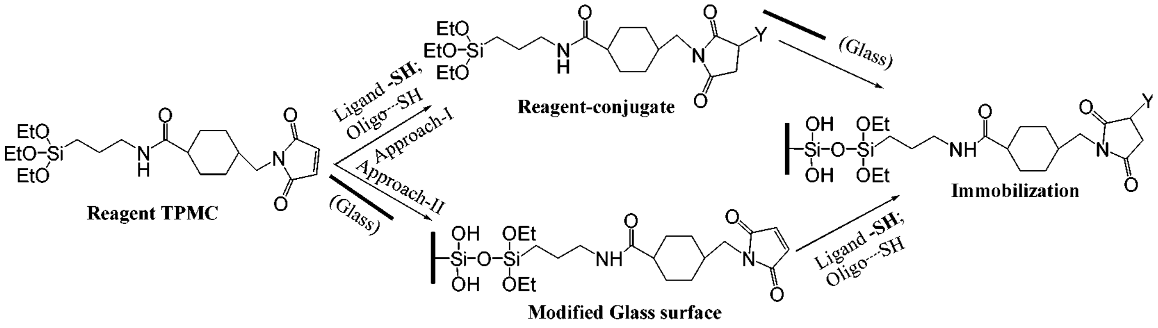
Varanasi -221 005.

In the light of utility of heterobifunctional reagents in microarray technology, a new heterobifunctional reagent N-(3-triethoxysilylpropyl)-4-(N'-maleimidylmethyl) cyclohexanamide (TPMC) has been developed in which the triethoxy functionality has specificity towards the glass surface while on the another hand the maleimide functionality has for thiol ligands like (-SH) modified oligonucleotides through stable thio-ether linkage. Immobilization of oligonucleotides has been achieved via two alternative approaches. In the first approach, reagent TPMC was treated with Oligonucleotide to get triethoxysilyl-oligonucleotide conjugate which was then immobilised on unmodified glass surface covalently via specific triethoxy functionality. In the second approach, the reagent was first treated with unmodified glass surface to generate maleimide functionality on the glass surface which was then utilized for the immobilization of Oligonucleotide via stable thio-ether linkage. The immobilised oligonucleotides and constructed microarrays were found stable. The immobilised oligonucleotide arrays were detected on the solid surface after hybridisation with the complementary fluorescently labeled oligonucleotides and were also successfully applied for discrimination of nucleotide mismatches.



Y= Ligand and HS-----Oligonucleotides

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Anion and Cation Sensing by an Adenine Based Colorimetric Sensor

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[b]Analytical Division, Chembiotek Research International, Kolkata.

Ion sensing has been a matter of extensive and intensive research for last few decades [1-2]. Present report deals with synthesis and characterization of p-nitrophenyl triazenyl purine [3] (PNTP) followed by its evaluation as a potential candidate for the anion and cation sensing. Addition of 2 equivalents of tetrabutylammonium salts of PF_6, BF_4^-, HSO_4^-, and ClO_4^- to the $2x10^{-5}$ $moldm^{-3}$ DMSO solution of PNTP at room temperature produced visible colour changes and Hypochromic as well as Hyperchromic shift at 398 and 575 nm UV-Vis spectral peaks of PNTP respectively. Among the chosen anions the sensitivity towards PF_6^- was the best.

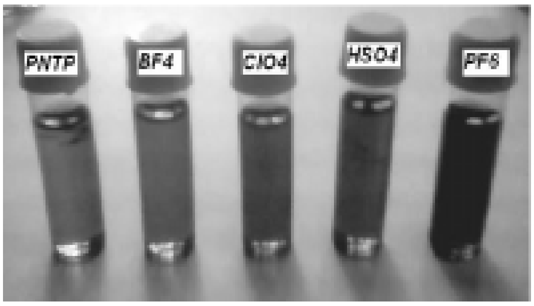

Fig.-1 Visible colour change of PNTP with chosen anions

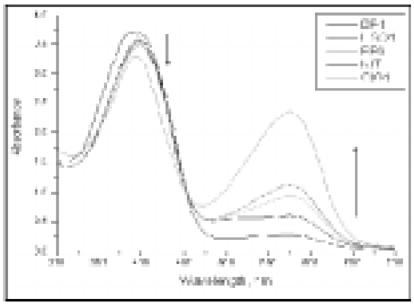

Fig.-2- Absorption spectra of solutions containing PNTP ($2x10^{-5}$ $moldm^{-3}$) and 2 equiv. of different anions in DMSO (300-700) nm.

Interestingly PNTP was able to sense Cd^{2+} among the mixture of Zn^{2+}, Cd^{2+}, and Hg^{2+}. For Cd^{2+} there was a bathochromic shift of ~70 nm in 575 nm absorption peak of the $2x10^{-5}$ $moldm^{-3}$ solution of PNTP. The sensing behaviour of PNTP with respect to other cations is still under progress.

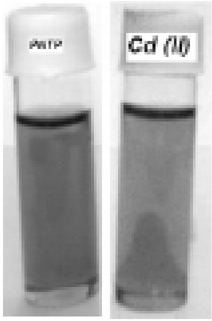

Fig. 3 -Visible colour change of PNTP with Cd^{2+}.

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Synthesis and Antimalarial Assessment of Bile acid Based 1,2,4-Trioxanes

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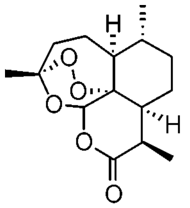
[a] *Division of Medicinal & Process Chemistry and* [b]*Division of Parasitology, Central Drug Research Institute, Lucknow-226001*

Malaria is a major parasitic disease affecting over 100 countries of the tropical and subtropical regions of the world including India. Around 300-500 million clinical cases of malaria are reported every year of which around 2-3 million die due to complicated cases of malaria[1].Situation is getting worse with the emergence of multidrug-resistant parasites. Therefore, development of highly efficacious and cost-effective treatments is urgently needed. The success and usefulness of peroxide antimalarials of the 1,2,4-trioxane class, such as artemisinin **1** and its derivatives e.g. arteether **2** ,artemether **3**, have opened new possibilities for the treatment of multidrug-resistant malaria [2].

As part of our endeavour to develop structurally simple and easily accessible 1,2,4-trioxanes [3], we have synthesized a new series of bile acid-based 1, 2, 4-trioxanes (prototype **4**) and assessed them for their antimalarial activity against multidrug- resistant *P.yoelii* in Swiss mice by oral and i.m. route. Several of these trioxanes have shown promising antimalarial activity.



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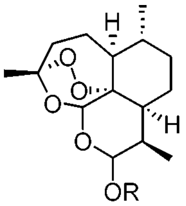
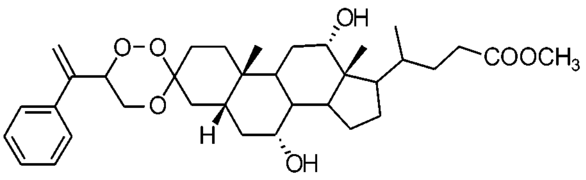


2R=Et
3R=Me



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Synthetic Studies toward the Total Synthesis of Penarolide Sulfate A_1

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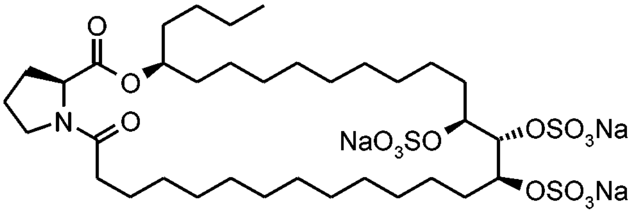
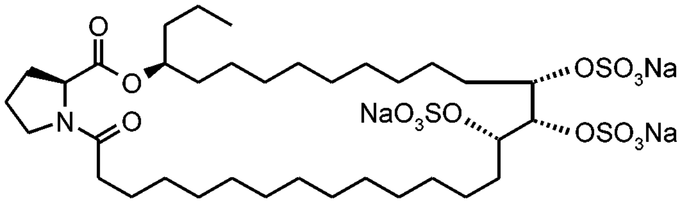
Penarolide Sulfate A_1 and A_2 inhibits a-glucosidase with IC_{50} values of 1.2 and 1.5 mg/mL respectively, isolated from the marine sponge Penares sp. [1]. Inhibitors of a-glucosidase are potential therapeutics for the treatment of diseases such as viral infections, cancer and diabetes. From structural standpoint these are unique 30 and 31 membered macrolides encompassing a proline residue and three sulfate groups.



Penarolide sulfate A_1



Penarolide Sulfate A_2

Fascinated by the important biological activity and unique structure, we have chosen these proline containing alkaloids as our synthetic target. Herein we will describe a highly efficient total synthesis towards penarolide sulfate A_1, featuring intramolecular Sonogashira cross coupling reaction for the construction of 30 membered macrolide ring. Regioselective Sharpless asymmetric dihydroxylation (SAD), Sharpless asymmetric epoxidation (SAE), Jacobsen Hydrolytic Kinetic Resolution (HKR) as the key steps have been disclosed.

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Preparation of Multivalent Dendritic Thiols and Assessment of their Metal Capping Efficiencies

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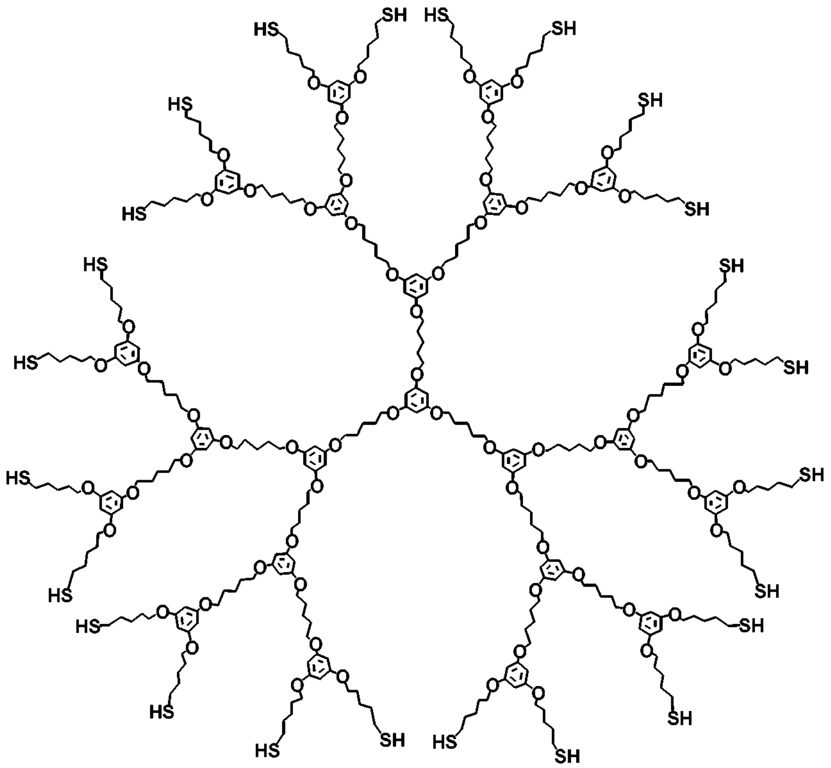
Dendrimers present the most well-defined structures among various macromolecular structures. The dendritic structures provide *endo*- and *exo*-receptor properties, resulting primarily from their unique architectures. The powerful strategy of multivalent presentation can be invoked systematically into the dendritic architectures and the general class of dendrimers are prominent due to these and more features. In a programme, we were interested to construct dendrimers, presenting multiple number of thiol groups at their peripheries. Preparation of multivalent dendritic thiols presenting 3, 6, 12 and 24 thiol groups at the peripheries of zero, first, second and third generation dendrimers respectively, was targeted. Phloroglucinol-based poly (alkyl aryl ether) dendrimers were utilized to prepare the multivalent dendritic thiols. Upon establishing the synthesis of thiols, their properties were explored, initially as capping agents of metal particles. Capping of gold particles with dendritic thiols are being conducted and the constitutions of the dendritic thiol-capped metal particles are assessed. **Figure 1** presents the molecular structure of the third generation dendritic thiol. Preparation of the dendritic thiols and their metal particle capping abilities will be presented in the poster.

Figure 1



Boric Acid Catalyzed Oxidative Bromination of a Variety of Organic Substrates: An Eco-Friendly and Practical Protocol

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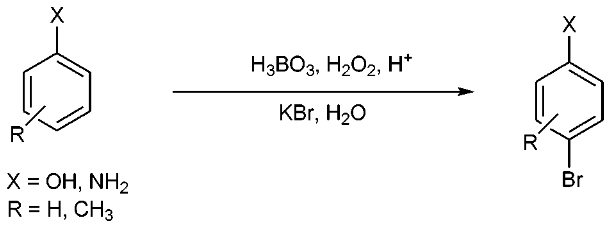
[1]*Centre for the Environment, Indian Institute of Technology Guwahati, Guwahati-781039, Assam*
[2]*Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, Tezpur University*

Brominated aromatic compounds are an important class of molecules in synthetic organic chemistry. They are key intermediates in a variety of reactions and widely used in industry.[1] Methods reported for bromination of aromatics involves use of molecular bromine and transition metal catalysts. However, the methods have several disadvantages like difficulty in handling and transport of bromine due to its hazardous nature, formation of HBr as a byproduct, low atom efficiency, and generation of large amount of byproducts causing serious environmental pollution.[2,3] Several improved procedures involving the *in situ* preparation of 'bromonium species' by oxidation of bromide ion with suitable oxidants under various homogeneous and heterogeneous reaction conditions have been reported, which is attractive and challenging from the standpoint of both green chemistry and synthetic chemistry.[1] Here we report an easy to operate and practical protocol for the regioselective bromination of aromatic compounds involving boric acid as a recycleable catalyst and potassium bromide as the source of bromide and hydrogen peroxide the oxidant in H_2O or C_2H_5OH.



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Human Hemoglobin : An Efficient Biomimetic Catalytic System for the Sulfoxidation Reactions

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Recently biocatalysts attracted much attention in the oxidation processes due to its clean, selective and efficient oxidation reaction under mild conditions.1 Human hemoglobin is an iron porphyrin metalloprotein which acts as an oxygen carrier in biological systems. Haemoglobin (Hb) and myoglobin (Mb) from various sources became the most popular subject proteins in oxidation studies because these proteins provided the researchers with the models of the catalase and peroxidase action that would be more convenient for kinetic studies than the enzymes per se, since Hb and Mb react with H_2O_2 notably slower than catalases and peroxidases do. On the other hand, it soon became clear that these proteins, when mixed with peroxides, become very active pro-oxidants, and their role in promoting oxidation of many substrate molecules has been investigated in vitro. In recent years, the reaction of the haem proteins with peroxides has been implicated in a number of pathological conditions thus bringing a new biomedical significance to the old story.2 In present study, we examined the biocatalytic activity of the human hemoglobin (HbA) for the chemo-selective oxidation reactions using hydrogen peroxide as an oxidant in a phosphate buffer. Recently we reported this system for oxidation of aryl sulfides. We observed this biomimetic catalytic procedure was simple, environmentally friendly, facile, selective and high yielding for sulfoxidation. Purified human oxyhemoglobin (HbA0), crude human oxyhemoglobin and ferryl oxy hemoglobin were used for oxidation. HbA0 and ferryl oxy hemoglobin (Fe+4 = O) efficiently catalyzes the sulfoxidation reaction of various sulfur containing compound without over oxidation product.

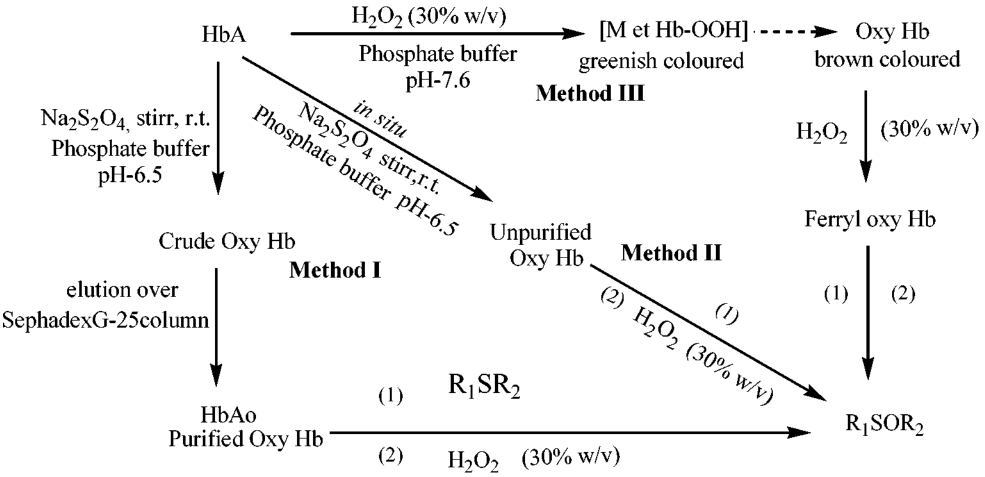

Figure 1: HbA/H_2O_2; A biomimetic catalytic procedure for sulfoxidation reaction.

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Design, Synthesis and Biological Evaluation of Derivatives of (+)-EHNA as Adenosine Deaminase Inhibitors

Sachin Kandalkar,_Yogesh Waman, Shubhangi Bhosale, Srinivasa Reddy B., Jagadeesh Mavinahalli, Dinesh Barawkar, Siddhartha De, Anita Chugh, Kasim Mookhtiar and Venkata P. Palle*

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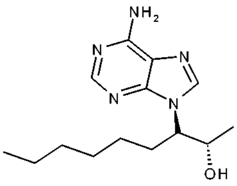
Adenosine deaminase (ADA) catalyzes the hydrolytic deamination of adenosine and 2'-deoxyadenosine to inosine and 2'-deoxyinosine, respectively. Inhibition of ADA activity has significant physiological consequences due to the accumulation of these substrates, which are important mediators of physiological signals through cell surface receptors, and thus offering therapeutic potential in various diseases [1].

From recently available crystal structures of ADA complexed with inhibitors [2], it has become clear that differences in inhibitor activity at the enzyme level derive from interactions in the adenine binding site and the hydrophobic pocket. In particular, the hydrophobic pocket seems to play an important role in this aspect [3]. We have modeled a series of derivatives of (+) EHNA (Structure 1), a known inhibitor of ADA and found that the hydrophobic pocket does make significant contributions to inhibitory activity (Figure I-III). Based on this finding, and other considerations, a series of (+)EHNA derivatives were designed and docked into ADA. Selected analogs were then synthesized for inhibitory studies. A complete account of these modeling studies, synthesis of new analogs and their biological evaluation will be presented.



1. (+)EHNA
(Ki = 1.13nM)

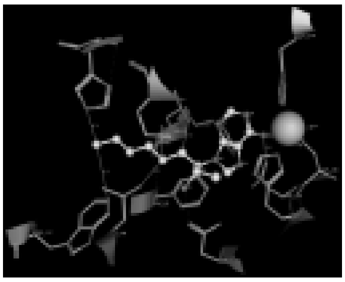


Figure I

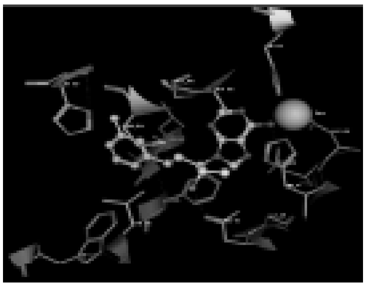


Figure II

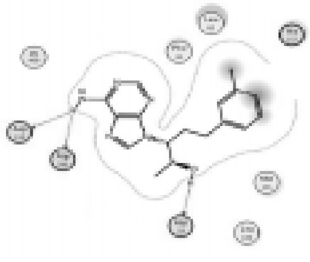


Figure III

\# Work carried out towards Ph.D. dissertation.

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Self-Assembly of Nanostructures *via* Directional Bonding Approach

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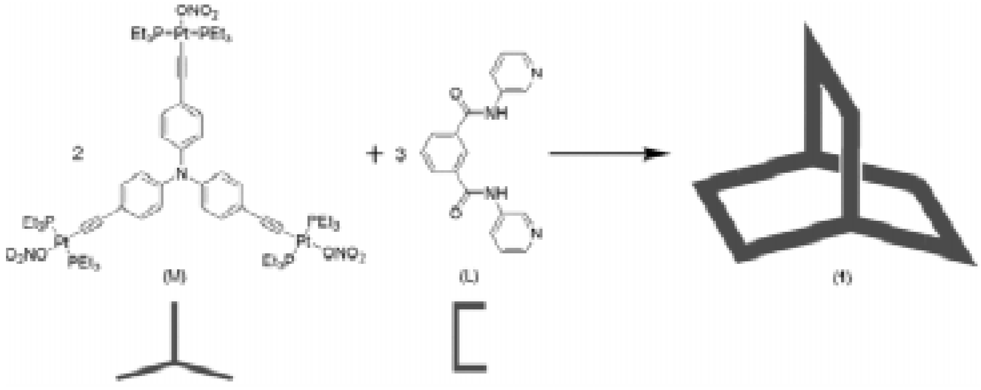
Bangalore-560 012, India

Coordination driven self-assembly is a useful technique for the construction of nanoscopic metal-organic assemblies of finite shapes and sizes. Square planar Pd(II) and Pt(II) have long been among the favorite metal ions used for this purpose because of their rigid coordination environment. In a majority of the cases, symmetrical dipyridyl ligands have been used with *cis*- protected metal centers to generate molecular squares, triangles, and rhomboids. Self-assembly using non-symmetric bridging ligands may result in the formation of several isomeric products. We have recently synthesized a few 2D nanoscopic assemblies using non-symmetric bridging ligands [1, 2] and self-selection for a single isomer was established in each case. Self-assembly of a trigonal prism *via* a new tritopic D_{3h} symmetric Pt_3 acceptor and an organic donor "clip" was achieved. The cage undergoes efficient fluorescence quenching by nitroaromatic compounds that are chemical signature of explosives. In addition to this, several Pd-based 3D cages were prepared by directional bonding approach using flexible linkers and characterized fully by NMR, ESI-Mass and crystal structure determination [3].



Scheme-1: Self-assembly of a Pt_3 trigonal prism (1) via directional bonding approach

References:

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Structural Characterization And Biological Evaluation Of Organotin(Iv) Complexes

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Hisar-125001(Haryana)

Organotin(IV) carboxylate complexes of the type $RSnCl_2(L)$, $RSnCl_2(L)$, $RSnCl(L)_2$, $RSnCl(L)_2$; and $RSn(L)_3$, $RSn(L)_3$ (where, R= Ph,Bu; L=1-Napthoxyacetic acid, 2-Napthoxyacetic acid) have been synthesized by the reaction of mono-organotin trichlorides with anionic form of ligand in desired molar ratio. All complexes have been characterized by elemental analysis and spectral (IR,^{1}HNMR,^{13}C NMR,^{119}Sn NMR) studies. On the basis of spectral (IR and NMR) studies coordination in complexes occur through carbonyl oxygen. The ligands behave as bidentate co-ordinating through carbonyl oxygen. The ligands and carboxylate complexes have been evaluated for in vitro antifungal activity against Aspergillus niger, Candida albicans and in vitro antibacterial activity against Gram negative Escherchia coli and Gram positive Staphylococcus aureus. Carboxylate complexes of organotin were found to be more potent than the parent ligands. Some of the complexes show significant antimicrobial activity (MIC >3.12mg/ml).

Synthesis of Novel Organotin(IV) Complexes with Varying Nuclearities Using Thioacetic Acid

Neetu Singh[a], Jyotsna Chaturevdi[a], M. Nethaji[b] and Subrato Bhattacharya[a*]

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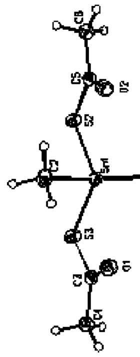
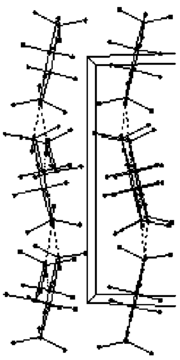
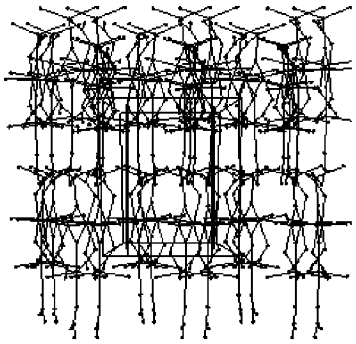
[b]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore

Organotin cages and clusters are well known class of compounds. A large number of such compounds have been prepared by the reactions of the organotin precursors with different acids (carboxylic, phosphonic, phosphinic acids etc). However, similar reactions with thiocarboxylic acids led to the formation of discrete monomeric molecular complexes and our attempts to stabilize bi/polynuclear thioacetate complexes using sulfide linkage always ended up yielding organotin sulfides with the loss of the thioacid ligand

On the other hand, we have also carried out a few reactions of diorganotin thioacetates with different nucleophiles such as methanol, water, sodium hydroxide and sodium acetate in different solvents (polar and non-polar) and under different conditions (in presence or absence of catalysts). The reactions yielded both mononuclear and polynuclear compounds. Among the polynucear ones, structures and properties of some representative (linear, sheet and three-dimensional) organostannoxane compounds will be presented.







Synthesis Of Novel Quinoline Crown Ethers Spectral Studies And Their Binding Property With Transition Metals

Malathi. M, Pitchai. P and Mohan. P. S*

Department of Chemistry, Bharathiar University, Coimbatore-46

There exists increasing interest in the synthesis of crown compounds due to their important diverse applications in supramolecular chemistry. Preparation of well defined, structurally challenging compounds which analytical chemists and biochemists required are essential and valuable goal. Quinolines have considerable interest in sensor field. The study of macrocyclic quinoline crown ethers has attracted great interest in last decades and their application as chemosensor is current growing thing. Here we have synthesized a novel Quinoline crown-6 using 2-Chloro-quinoline-3-carbaldehyde as a basic moiety, in two more stops. All details of experiments will be explained in presentation. All the products formed were confirmed by ^{1}H and C^{13} spectrum and binding character of the synthesized compound with transition metals are also studied using UV absorption spectrum. All the details of data will be given during poster presentation.

Synthesis, Characterization and role of spacer length on the final architecture in $[Ag(phSE)(NO_3)]_n$ (phSE = bis(phenylthio)ethane)

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a Department of Chemistry, Guru Nanak Dev University, Amritsar
b Department of Chemistry, M.M. Modi College, Patiala

Reaction of aqueous solution of $AgNO_3$ and methanolic solution of phSE resulted in the phSE propagated $[Ag(phSE)(NO_3)]_n$ [Fig 1] zigzag chains. Each chain is bridged to the similar one above it through oxygen of the nitrates. The previously known complexes $[Ag_2(phSM)_3(ClO_4)_2]_n$ and $[Ag_2(phSB)_3(ClO_4)_2]_n$ (phSM = bis(phenylthio)methane and phSB = bis(phenylthio)butane) are 1D pseudohelical and 4x4 grid respectively. The X-ray quality crystals of $[Ag(phSP)NO_3)]_n$ (phSP = bis(phenylthio)propane) could not be prepared. The structural difference has been discussed on the basis of steric effects due variation in the spacer of these ligands.

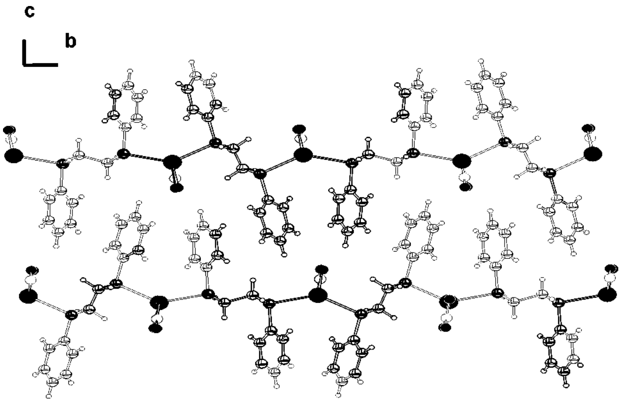

Fig 1 View along c-axis showing the 2D sheet structure of $[Ag(phSE)(NO_3)]_n$ (phenyl groups are omitted for clarity).

Structural and Pharmacological Studies of Conotoxins from Indian Marine Snails

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and
National Center for Biological Sciences, Tata Institute of Fundamental Research
GKVK, Bellary Road,Bangalore 560065, India

The conotoxins are a group of peptide based toxins that are produced by marine snails of the genus *Conidae*. The toxins have elicited tremendous interest among neuropharmacologists and neurobiologists because of the specificity with these toxins target sodium, potassium and calcium ion channels and also other pharmacologically important targets such as adrenergic, serotonin, NMDA and Nicotinic Acetyl Choline receptors. Thus the identification and characterisation of these peptides could serve as a valuable starting tool in the design of neuropharmacologically active drugs.

We have initiated a program to isolate and purify pharmacologically important peptides from Cone snails that inhabit the Indian coastal waters. It is estimated that ~ 77 species are unique to these waters. Physicochemical characterization of these peptides has relied almost exclusively on Mass Spectrometry and Multidimensional Nuclear Magnetic Resonance Methods with additional information from other spectroscopic methods. Electrophysiological methods have enabled us to identify specifically the ion channel targets of these peptides. The application of these methods to the charcterization of these peptides will be discussed.

Mild Oxidation of Alcohols to Carbonyl Compounds with Periodic Acid Catalyzed by $[Ru(acac)_2(CH_3CN)_2]PF_6$ in Water

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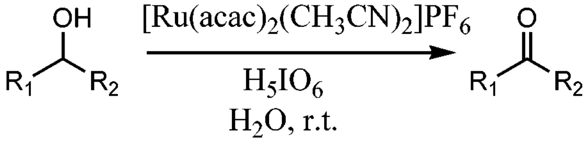
[a] *Department of Chemistry, National Institute of Technology, Tiruchirappalli - 620 015*
[b] *Syngene International Ltd., Bangalore - 560 099*

Various methods for the oxidation of alcohols to carbonyl compounds are available [1]. Although individually having some synthetic advantages, most conventional methods suffer from one or more experimental drawbacks, such as severe reaction conditions, complicated reaction procedures and the need to use toxic solvents. Therefore, the search for a mild but efficient oxidation method with easy handling and nontoxic solvent is still the subject of numerous interests. A new catalytic system, in which a variety of alcohols are converted into carbonyl compounds in good yields by using periodic acid as oxidant and $[Ru(acac)_2(CH_3CN)_2]PF_6$ as catalyst at room temperature, has been developed. This method is high yielding, safe and operationally simple.



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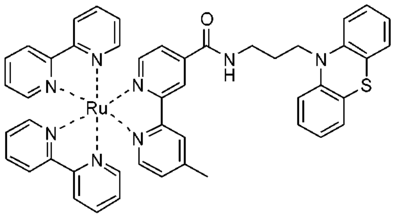
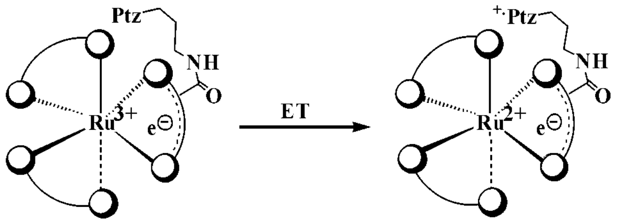
Long-lived Photoinduced Charge Separation in new Ru(bipyridine)$_3^{2+}$-Phenothiazine Dyads

G. Ajayakumar and K. R. Gopidas*

Photosciences and Photonics Group, Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum 695 019, India.

Ruthenium complexes based on 2,2'-bipyridine (bpy) ligands have been extensively studied and used by chemists for photoinduced electron transfer (PET) reactions because of their unique photophysical and electrochemical properties.[1] In the Ru(II) polypyridyl dyads reported,[2] readily reducible organic moieties (such as methyl Viologen, MV^{2+}) or readily oxidizable moieties (such as phenothiazine, Ptz) are attached to Ru(bpy)$_3^{2+}$ to give Ru(II)-A or Ru(II)-D systems, respectively. For the Ru(bpy)$_3^{2+}$ – D/A dyads, the CS state lifetimes are generally very short, in the order of a few hundreds of picoseconds. Herein we present the synthesis, photophysical and PET processes in a few Ru(bpy)$_3^{2+}$ - Ptz dyads. These dyads have one, two or three Ptz donors covalently linked to the bpy moieties through an amide linkage. Compared to the Ru-(CH$_2$)$_n$-Ptz systems reported earlier,[3] this report presents two new significant observations: (1) Charge separation in our systems is at least one order of magnitude faster and (2) BET occurs in the nanosecond time window which is about 100 time slower. In order to explain the fast charge separation and slow charge recombination rates, formation of a folded conformer where the Ptz group attached to one bpy residue comes closer to and associates with another bpy moiety is invoked.





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Hexavalent Chromium Removal from Aqueous Solution Using Activated Carbon

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This paper examines an efficient adsorption process for the treatment of Cr(VI) contaminated water. The ability of Eucalyptus bark carbon as an adsorbent for Cr(VI) ions in aqueous solution was studied. Result revealed that adsorption of chromium (VI) on eucalyptus bark carbon was endothermic in nature. Thermodynamic parameters such as the entropy change, enthalpy change and Gibbs free energy change were found out to be 1.39 kJ mol^{-1} K^{-1}, 1.08 kJ mol^{-1} and -3.85 kJ mol^{-1}, respectively. Cr (VI) removal was highly pH dependent and the results indicate that the optimum pH 3 for the removal. The maximum adsorption capacity of eucalyptus bark carbon was found to be 23mg.g^{-1}. Adsorption capacity was calculated by applying Langmuir isotherms. The results indicate that the Langmuir model fits the data better than the Freundlich adsorption isotherm model. The surface properties of adsorbent were characterized by the Scanning electron microscopy, Electron Dispersive X-Ray Spectroscopic analysis and Fourier Transform Infrared Spectroscopy techniques. It was concluded that Eucalyptus bark carbon adsorbent column could be used effectively for removal of hexavalent chromium from aqueous solution.

Orbital Compatibility for the Condensation of Polyhedral Boranes

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Bangalore 560 012

The mono polyhedral boranes condense to give macropolyhedral boranes with single atom sharing, edge sharing, face sharing and four atoms sharing [1].The *mno* rule [2] dictates the electron requirement for the condensation. But there are cases where polyhedron can form different structure with same electron counts. The number of shared atoms (i.e. one, two or three), the type of the polyhedra (i.e. *closo*-, *nido*- and *arachno*-), and the comparability of the fragment orbitals[3] of the individual polyhedra are some of the factors that controls the stability of the condensed structure. Theoretical studies at B3LYP/6-31G* level show that a large polyhedron prefers a small polyhedron for the condensation. For example, the condensation of f $B_{12}H_{12}^{2-}$ and $B_6H_6^{2-}$ is better than that of two $B_{12}H_{12}^{2-}$ units. The compatibility of the orbitals is shown schematically. According to this there are several *closo* macropolyhedral boranes which are more preferred than $B_{20}H_{16}$ and $B_{21}H_{18}^{-}$ which are already synthesized.

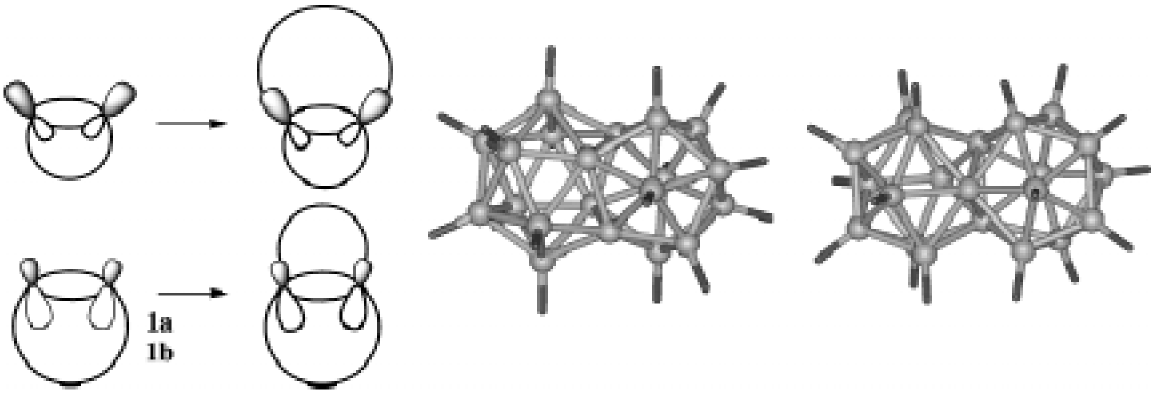

Figure **1a)** Schematic representation showing the orbital compatibility for the polyhedral condensation. **1b)** Structures of $B_{20}H_{16}$ and $B_{21}H_{18}^{-}$

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Synthesis and Characterization of Some Novel Functional organosilanes and their Applications

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Functional organosilanes seem very promising and versatile materials due to their distinctive characteristics like low temperature flexibility, high temperature stability, biocompatibility, hydrophobicity and oxid-ative resistance, etc. These have found wide range of technological applications ranging from aerospace to deep sea, medicinal field to agriculture area, electronics to structural applications, etc.

Hydrosilylation [1,2] is a well-established and facile process for the synthesis of organosilane derivatives. It involves the addition of Si-H group containing silicon compound on unsaturated functionalities whether these are terminal or non-terminal, cyclic or in conjugation**.** Catalyst plays vital role in hydrosilylation reactions, eg. platinum complexes [3] are used as catalysts due to their activity at relatively low concentrations keeping in view our general interest to synthesize functional organosilane via hydrosilylation reactions.

In the present investigation we wish to report a facile synthesis of functional organosilanes and their esters. A series of functional organosilanes, disiloxanes and polysiloxanes have been synthesized via hydrosilylation reaction of –Si-H group bearing organosilicon derivatives and maleic anhydride. The anhydride group bearing derivatives have been reacted with long chain primary alcohol in the presence of lower valent metal oxide catalyst to afford esters. The characterization of products has been carried out using FT-IR, ^{1}H and ^{13}C NMR techniques.

These esters have shown excellent lubricating properties having very low pour point(below -60^{0}C) and very high flash point ~ 200 ^{0}C (closed-cup) with excellent load bearing properties. These materials have also shown unique properties to facilitate the blending of mineral oil/synthetic esters with silicones, which in turn facilitate to tailor the properties of common lubricants as per requirement. Thus it acts as universal compatibilizer of organic lubricant and silicones.

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Rapid synthesis and characterization of Metallic $\mathrm{La_4BaCu_5O_{13+}}$d phase by the Nitrate-Citrate gel combustion method.

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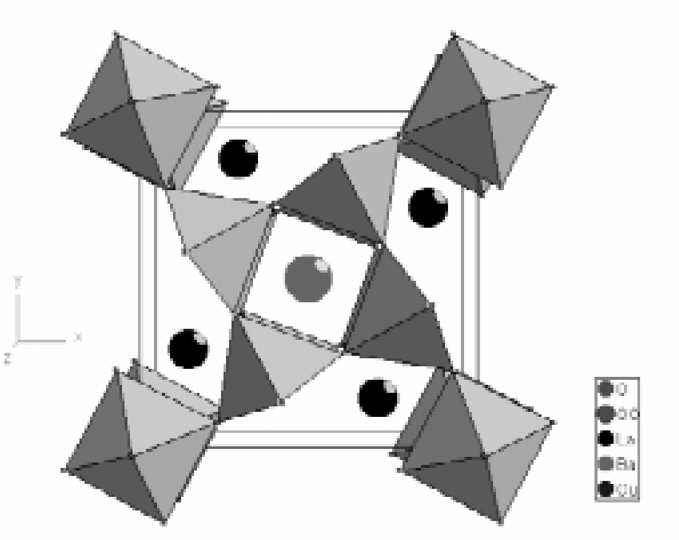
The oxygen-deficient defect perovskite of the formula $\mathrm{La_4BaCu_5O_{13+\mathit{d}}}$ is crystallizes in the tetragonal structure, space group *P*4/*m*, *a* » Ö5a_{p} = 8.644 Å, *c* » a_{p} = 3.867 Å, where a_{p} refers to a perovskite subcell. The model structure consists of groups of four corner-sharing $\mathrm{CuO_5}$ pyramids linked through $\mathrm{CuO_6}$ octahedra. Each octahedron shares four corners with four pyramids and two corners with two other octahedra; each pyramid is connected to four other pyramids and one octahedron. The framework exhibits one perovskite-like tunnel and two hexagonal tunnels per cell. $\mathrm{Ba^{2+}}$ and $\mathrm{La^{3+}}$ are ordered, with 12-coordinate $\mathrm{Ba^{2+}}$ in perovskite tunnels and 10-coordinate $\mathrm{La^{3+}}$ in hexagonal tunnels. $\mathrm{La_4BaCu_5O_{13+\mathit{d}}}$ is unique because of it shows metallic behaviour in the temperature range 10 – 600 K without undergoing superconducting transition. Solid state preparative methods require high temperature (1000 °C) and longer duration (2- 4 days).

In the present study is focused on the rapid synthesis and characterization of $\mathrm{La_4BaCu_5O_{13+\mathit{d}}}$ by the nitrate – citrate gel combustion process. As-synthesized compound is an amorphous in nature; single phase was observed on heating at 950 °C for 1 h. Structural parameters were refined by the Rietveld refinement method using powder XRD data. The compound crystallizes in the tetragonal structure (space group *P4/m*, No. 83) and exhibit metallic behaviour upto 15 K. Oxygen content was determined by the iodometric titration.



Pd-Catalyzed Stereoselective Synthesis of Phosphono- Butadienes, Benzofurans and Benzopyrans: Use of Environmentally Benign Conditions

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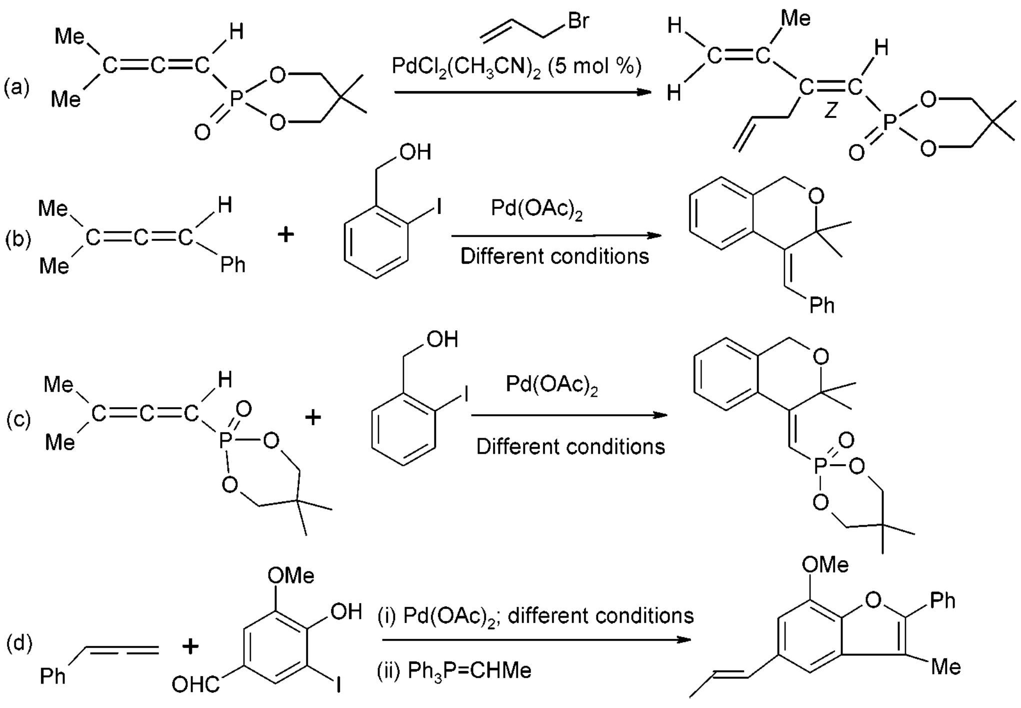
In continuation of our work on organophosphonate chemistry and Pd-catalyzed coupling and cyclization reactions of allenes with iodophenols [1], we have used allyl bromide, functionalized iodophenols and iodobenzyl alcohols in coupling reactions with allenes (both phosphorylated and nonphosphorylated). Some of the products can be used for the C-C bond forming reactions (e.g. HWE reaction). Herein, we present an environmentally friendly protocol (water or PEG-400 as a reaction medium) for the synthesis of benzofurans and benzopyrans and also a new simpler route to the unsubstituted Obovaten derivative when compared with the literature method [2]. Representative examples are shown in Scheme 1.

Scheme 1



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One Pot Wet Synthesis of Inorganic-Organic Hydride Materials with Polyoxometalates: Synthesis, Characterization and Catalytic Activity Towards the Oxidation of Alcohols

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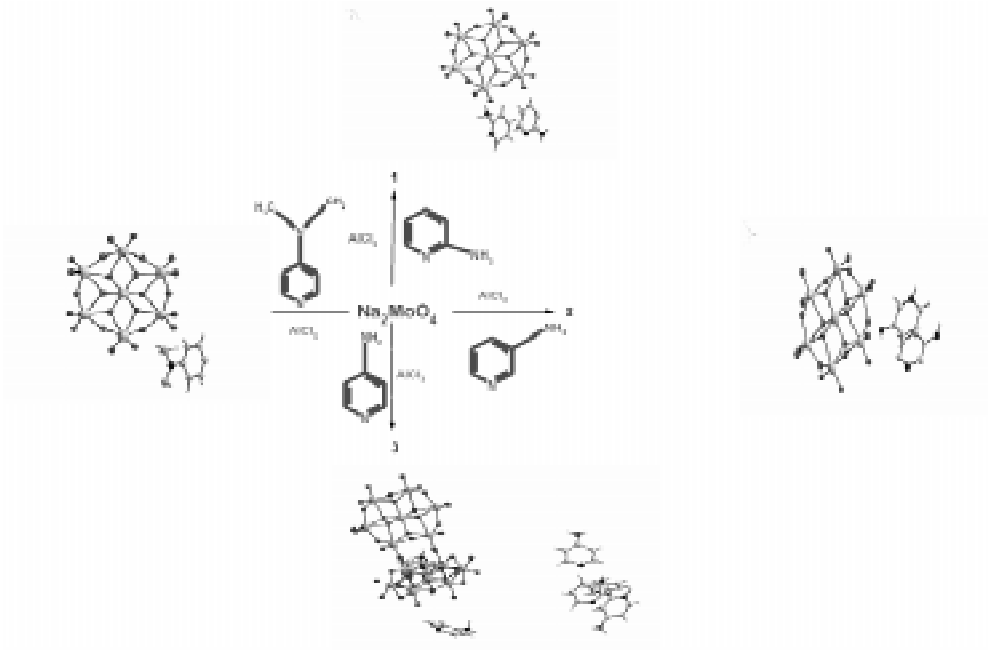
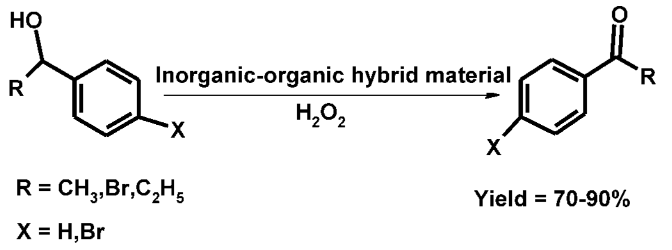
Inorganic-organic hybrid materials with polyoxometalates have immense applications in diverse areas including materials science. Even though, the reports on synthesis and crystal structures of inorganic-organic hybrid materials are numerous, the catalytic activities of these towards organic oxidations of industrial importance (for example, the oxidation of alcohols and epoxidation of alkenes) are less explored. Here, we describe the synthesis and crystal structures of four such hybrid materials that have Anderson cluster as a common POM anion with four different aminopyridines with diverse supramolecular interactions. We have also shown the catalytic activities of these new materials towards oxidation of alcohols.





Syntheses, Structural, Photophysical and Thermal Properties of Some Gadolinium (III) & Europium (III) Complexes

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Lanthanide complexes have variety of applications due to the excellent photophysical properties [1]. The reaction of $GdCl_3$ with one equivalents of 2,2' bipyridine (bipy) / 1,10 phenanthroline (phen) and one equivalent DNP yielded the complex [bipy][Gd(bipy)$(DNP)_3(OH_2)$] **1** and [Gd(phen)$(DNP)_3(OCH_3)$] **2** respectively, whereas the reaction of $EuCl_3$ with one equivalent of phen resulted the formation of complexes [Eu$(phen)_2Cl_3(OCH_3)$] **3**, The same reaction in the presence of one equivalent DNP yielded the complex [Eu(phen) $(DNP)_3(OCH_3)$] **4**. These complexes have been characterized by various methods including X-ray crystallographically. The X-ray studies demonstrated that complexes **1** and **4** crystallize in monoclinic space group *P21/n* with cell dimensions a = 9.7658(9) Å, b = 17.1398(14) Å, c = 19.2714 (16) Å for **1;** a = 9.7819(11) Å, b = 17.1049(17) Å, c = 19.259(2) Å for **4**. Complex **2** crystallizes in the triclinicspace group P-1 with cell dimensions a = 11.8499(7) Å, b = 12.9648(7) Å, c = 14.2279(7) Å and **3** crystallizes in the orthorhombic space group *P212121* with cell dimensions a = 11.0798(5) Å, b = 11.6775 (6) Å, c = 18.4319 (9) Å. The coordination number in **1** and **4** is nine, whereas in **2** and **3**, it is eight. The crystal packing views of complex **2** suggested a host-guest supramolecular structure (Fig. **1**). Thermo gravimetric analysis showed that after complete decomposition all the complexes resulted the formation of thermally stable oxide (Ln_2O_3) [Ln = Gd, Eu]. Room temperature Excitation and luminescence data of **3** and **4** showed that these complexes emit red fluorescence under ultraviolet light.

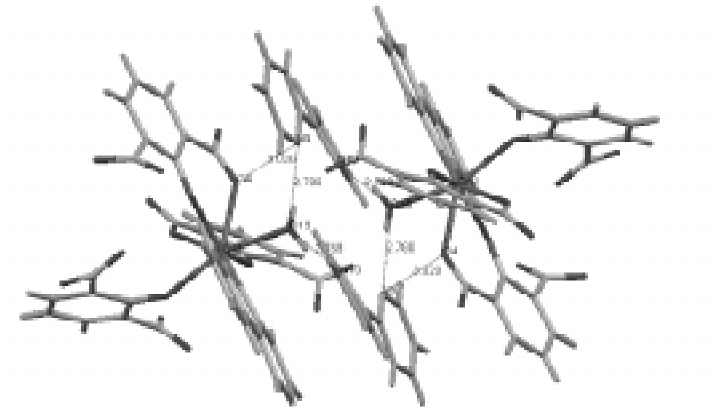

Fig. 1

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Coordination Chemistry With Amide – Based Macrocyclic & Open – Chain Ligands

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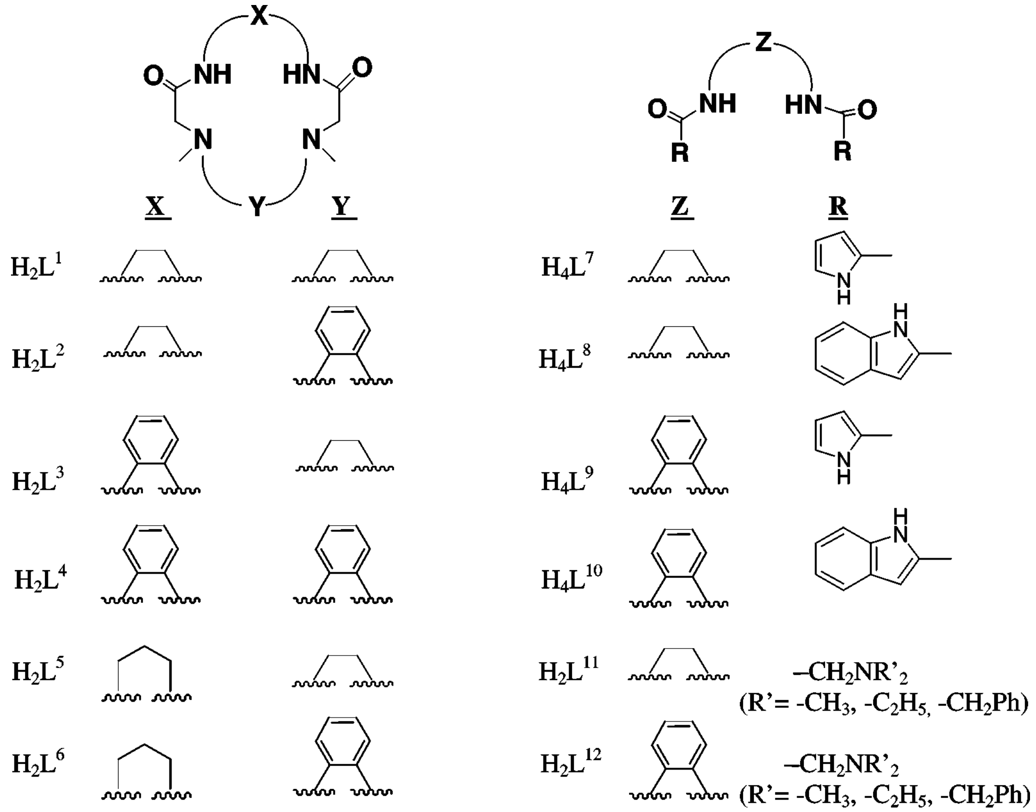
The present work illustrates the coordination chemistry of transition metal ions with amide-based macrocyclic and analogous open-chain systems. The design aspect includes tetradentate ligands having flexible or rigid backbone that provides the option for the ligand to coordinate a metal centre in different ways. The ligands coordinate either through two anionic *Namide* and two neutral *Namine* for the macrocyclic systems or two anionic *Namide* and two anionic *Npyrrole/indole* for the open chain systems. All ligands are intended to provide a similar N_4 primary coordination environment around the metal centre. The 12-membered macrocyclic ligands (H_2L^1 – H_2L^4) are able to stabilize both Ni(II) and Ni(III) state in a square–planar environment. The ligands H_2L^5 and H_2L^6 explore the effect of increasing the macrocyclic ring size from 12- to 13- membered on the electronic and redox properties of the Ni ion. The chemistry has further been extended to their flexible open–chain analogues, H_2L^{11} – H_2L^{12}, and results in interesting structures. The ligands H_4L^7 – H_4L^{10} in their tetra-anionic form $[L^n]^{4-}$, are expected to bring about the high oxidation state of the metal ions. Our preliminary studies indicate that these ligands form square–planar Ni(II) complexes with an accessible Ni(III) and Ni(IV) states. A comprehensive account of the mentioned work will be presented.



Thermodynamics and Solution State Studies on Some Quaternary metal complexes and their comparison with binary and ternary complexes

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Equilibrium studies on quaternary metal complexes of type M^1M^2AB where M^1 and M^2 are Cu^{II} and Ni^{II} or Cd^{II} or Co^{II} or Pb^{II}, A= o-phenylenediamine and B = Salicylic acid were carried out using Irving Rossotti titration technique at 30 ± 0.1, 40 ± 0.1 and 50 ± 0.1 °C and at fixed ionic strength, $\mu = 0.2$ $moldm^{-3}$ ($NaClO_4$). The separation of titration curves demonstrate the formation of mixed metal mixed ligand complexes of stoichiometry M^1 M^2 AB. All metal ion formation constant of the complexes, M^1 M^2 AB in addition to M^1AB, M^2AB M^1A_2 M^1B_2, M^2A_2 and M^2B_2 type of complexes for all metal ions were evaluated using for the Fortran IV computer program and the complex formation equilibrium data were pruned with the aid of speciation curves plotted with aid of Fortran IV computer program SPEPLOT. The stability order of metal complexes and solution structure of heterobinuclear M^1 M^2 AB Complexes have been discussed on the basis of basicity of ligands and coordination sphere of complexation.

Synthesis and spectral characterization of Ruthenium complexes containing h^6-cyclichydrocarbons and N-heterocyclic carbenes as ligands

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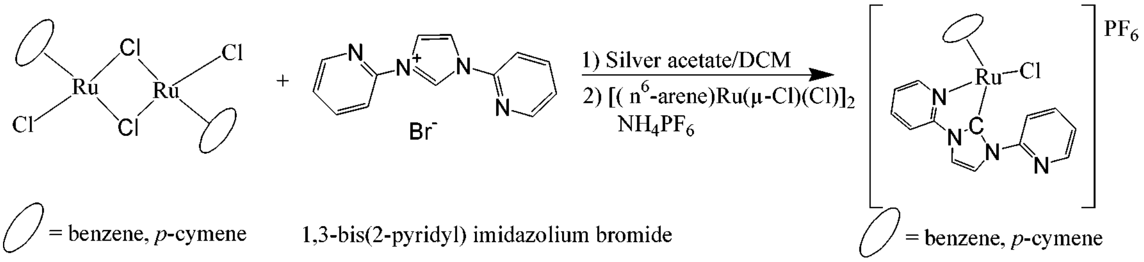
The N-heterocyclic carbene ligands such as 1,3-bis(2-pyridyl)imidazolium bromide (PyImiPy) and 1-methyl-3-pyridylimidazolium bromide (CH_3ImiPy) were synthesized according to literature procedure [1]. Reactions of N-heterocyclic carbenes (NHC) with silver acetate yielded the silver-NHC complexes. These silver NHC complexes on trans metallation with [(h^6-arene) Ru (μ-Cl)(Cl)]$_2$ {h^6-arene = benzene **(1)**, *p*-cymene **(2)**}, gave the corresponding ruthenium(II) half sandwich complexes such as [(h^6-*p*-cymene) Ru(PyImiPy)Cl]PF_6 **(3)**, [(h^6-*p*-cymene)Ru (CH_3ImiPy)Cl]PF_6 **(4)**, [(h^6-benzene)Ru(CH_3ImiPy) -Cl]PF_6 **(5)**, [(h^6-benzene)Ru(CH_3ImiPy)Cl]PF_6 **(6)** respectively. These complexes were characterized by using various techniques such as FT-IR, ^{1}H-NMR etc.



Scheme

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Dual Mode Recognition and Site Selective Binding of Serum Albumin by a Near-Infrared Absorbing Dye

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Serum albumin is the major protein constituent of blood plasma, which facilitates the disposition and transport of various exogenous and endogenous ligands to the specific targets [1]. The specific delivery of ligands by serum albumin originates from the presence of two major and structurally selective binding sites, namely, site I and site II. Recently, it has been reported that molecules possessing higher affinity for serum albumin and showing preferential binding at site II are found to exhibit efficient photodynamic therapeutical applications (PDT) [2]. In this context, detection and understanding the interactions of various ligands with serum albumin is important for the design of efficient drugs and photosensitizers for applications in PDT.

With the objective of developing infrared absorbing novel sensitizers for photodynamic therapeutical applications [3], we have investigated the interactions of a polyhydroxyl substituted squaraine dye (SQ) with bovine serum albumin (BSA) through absorption, steady state and time resolved fluorescence, circular dichroism (CD), cyclic voltammetry (CV), ^{1}H NMR, scanning electron and tapping mode atomic force microscopic techniques [3e]. Increase in addition of BSA resulted in increase in absorbance and fluorescence quantum yields (80-fold) of SQ, along with significant bathochromic shifts in the absorption and fluorescence maxima. Half-reciprocal analysis of the absorption data gave a 1:1 stoichiometry for the complex between BSA and SQ with a high association constant of 1.4×10^{6} M^{-1}. The complex formation was confirmed by observation of induced CD signal corresponding to the SQ chromophore, up-field shift of aromatic protons in NMR spectra and decrease in current intensity of SQ when bound to BSA. The picosecond time-resolved fluorescence studies indicated that the complex BSA-SQ exhibits biexponential decay with significantly enhanced lifetimes of 0.5 and 1.5 ns when compared to the lifetime of SQ (t = 121 ps) in the absence of BSA. Employing displacement cum fluorimetry using site specific binding ligands such as dansylproline and dansylamide indicated that SQ binds with protein selectively at site II involving hydrophobic, hydrogen bonding and electrostatic interactions. The uniqueness of this molecular system is that it interacts with BSA selectively at site II and signals the binding event through dual mode recognition of 'visual color' change and 'turn on' fluorescence intensity.

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Supercritical Fluid Extraction of Thorium from Tissue Paper Matrix Employing Organophosphorus Reagents

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Conventional techniques for the separation and purification of actinides (uranium, thorium, plutonium) from various matrices largely rely on solvent extraction, which results in generation of large amount of radioactive liquid volume. Supercritical fluid extraction (SFE) has inherent potential to minimize the liquid generation and offer faster, cleaner and efficient extraction owing to low viscosity, high density, low surface tension and better diffusivity properties. Owing to low viscosity and surface tension, SCF can penetrate deep inside the matrix, extracting the desired material. In SFE, solvent properties such as density can be varied by tuning pressure/ temperature conditions. Thorium is a fertile material and in reactor by absorbing neutrons gets converted into fissile ^{233}U. In present study supercritical fluid extraction of thorium from solid matrix (tissue paper) employing CO_2 as SCF and organophosphorus reagents as co-solvent.

(i) Among phosphates, if aromatic group is replaced by aliphatic group then extraction efficiency decreases e.g. TBP and TPP. (ii) Among phosphine oxides, higher the aliphatic chain length, higher is the extraction efficiency e.g. TOPO and TBPO. (iii) Among phosphine oxides, if phenyl group is attached to P i.e. TPPO then extraction efficiency is intermediate to TOPO and TBPO. (iv) On comparing phosphates with phosphine oxides, for aliphatic hydrocarbon, the extraction efficiencies are comparable e.g. TBP and TBPO. For aromatic ring, as in case of phosphine oxide extraction efficiency is higher than its phosphate analogue e.g. TPP and TPPO.

The reported solubility trend is supercritical CO2 is: TBP >TBPO> TOPO>TPPO [1]. The observed trend in extraction efficiency is not as per the reported trend of solubility, which indicates that extraction efficiency is influenced by the structure of the organophosphorus reagent. Organophosphorus reagents form coordinatively solvated compounds with actinides through P=O group. The electronegativity of the substituents around the phosphorous severely affects the extractive capacity. The more electronegative alkoxy group decreases the availability of electrons on the phosphoryl oxygen, the molecule becomes weaker extractant. Electron donating group attached to phosphorus increases availability of electrons on the phosphoryl oxygen, the molecule becomes stronger extractant. A phenyl group linked through oxygen to phosphorus reduces the extractive capacity as compared to when direct carbon-to-phosphorus bond exists [2].

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Structural Variations in PyridineN-Oxide Complexes of Manganese, Copper and Zinc

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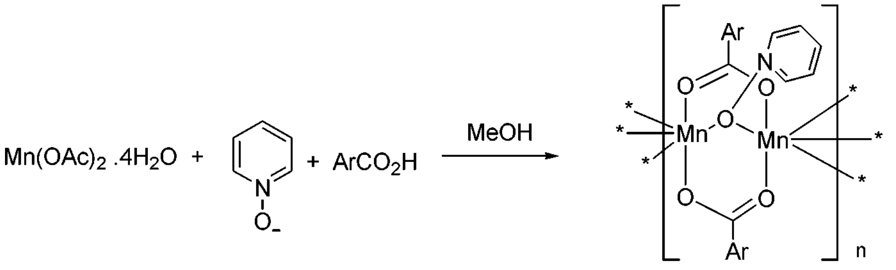
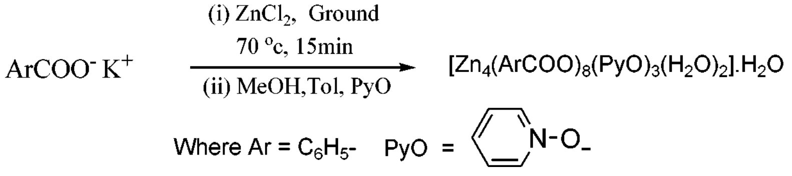
Pyridine N-oxide is an important reagent for oxo-transfer reactions. Transition metal complexes facilitate such reactions. The N-oxide containing metal complexes are also of special interest as magnetic material. As such we are interested in synthesizing 1st row transition metal carboxylates with pyridine N-oxide as supporting ligand. In this presentation a few of such complexes are reported.

A series of metal carboxylates containing pyridine N-oxide are prepared via one pot solution phase synthesis and solid phase synthesis. The structures of the products are found to be metal dependent; mononuclear, binuclear and polynuclear complexes are obtained. In the case of the reactions of manganese (II) acetate tetra hydrate with pyridine N-oxide in presence of aromatic carboxylic acids, 1-D coordination polymer with bridging aromatic carboxylate as well as bridging pyridine N-oxide are obtained. This is shown below



Where Ar = C_6H_5- , 4-NO_2-C_6H_4-

However analogous reaction with copper (II) acetate leads to mononuclear or binuclear paddle wheel carboxylate complexes with monodentate pyridine N-oxides. Finally solid phase reaction of zinc chloride with potassium benzoate prepared in situ and pyridine N-oxide leads to a tetra-nuclear zinc complex as shown in scheme 1.



.... Scheme 1

All the complexes are characterized by single crystal X-ray crystallography and other spectroscopic techniques. The structural features along with magneto chemistry of the pyridine N-oxide complexes will be discussed.

Reference:

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A Neutral Calix [4]Arene Semicarbazone Receptor For Recognition Of Hydrogensulphate Anion

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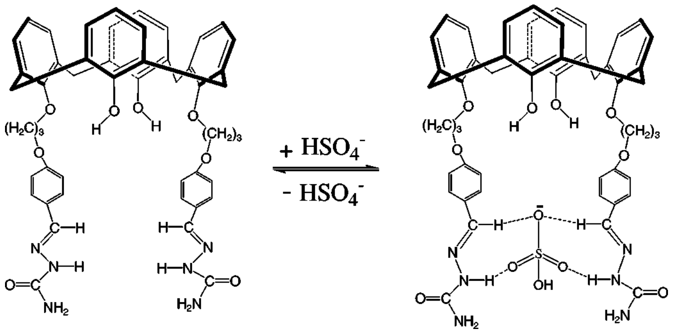
Anion recognition is extremely important for resolving biological, chemical and environmental issues [1]. Different strategies adopted for anion recognition essentially consist of either acquiring the positively charged molecular hosts or by utilizing the neutral molecular hosts. The former interact with anions through electrostatic forces while the later recognize anions through donor-acceptor attributes, hydrophobic effects and hydrogen bond. In this regard, it was envisaged that the phenolic oligomers represented by calix[*n*]arenes[2] could in principle provide excellent platforms for construction of attractive recognition sites for host-guest interactions and it should be possible to design molecular receptors for anion recognition by employing activated amides, urea and thiourea functionalities. We report herein, the synthesis, characterization and anion binding properties of novel calix[4]arene receptors[3] bearing two semicarbazone and thiosemicarbazone moieties at the distal 1,3-positions in calix[4]arene. These receptors have been found to demonstrate significant binding ability for tetrahedral HSO_4^- ions in preference to other anions including Cl^-, Br^-, I^-, ClO_4^-, $H_2PO_4^-$ and PF_6^-.



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Encapsulated Redox Centers

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Molecular recognition phenomena are important in biochemistry and in the emerging field of supramolecular chemistry. The host-guest chemistry opens the way to several desirable goals such as intelligent materials, new sensors and molecular devices and affords a deeper fundamental understanding of the intermolecular forces responsible for binding. The host-guest binding affinity can be controlled by the gain or loss of an electron by a host (or a guest) molecule which modifies its charge and electronic distribution. It leads to very significant changes in the magnitude and nature of the intermolecular forces between this molecule and its potential recognition partners. Important classes of receptors, calixarenes are used in our present work. The attractive property of this host is that we can modify their binding selectivity or we can introduce specific functional group. They are electro inactive, but the electrochemical parameters of redox active guests (quinones) are often strongly affected by the presence of these hosts. Quinones are good electron acceptors and also serve as efficient photosensitizers. In aprotic solvents, quinines can be reversibly reduced into radical anions and dianions. However, protonation of the reduced quinines and formation of hydrogen bonds can introduce substantial changes in the effective redox potential depending on the nature of the functional groups in the quinine ring. They are extensively used in the Photodynamic therapy. Anthraquinones, particularly, 1, 2-dihydroxy-9, 10-anthraquinones (Alizarin red) play an important role in the field of medicine. It is very sensitive to the solution pH and has defining acid-base properties. It behaves as monoanion at neutral medium, as dianion in basic and as neutral in the acidic conditions. The complexation of quinones with calixarene is detected both by electrochemical and spectrophotometric experiments and the results are reported and will be presented in the symposium. Also the pH plays an important role in determining the binding ability.

One-dimensional coordination polymers constructed on the skeleton of carboxylate ligands containing Metal (Cu^{II}, Zn^{II}) bipyridyls

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The chemistry of metal carboxylates has emerged as an important area of research .It includes not only mono and dicarboxylates of transition, rare earth, and main-group metals, but also a variety of hybrid structures. Some of the carboxylates possess novel adsorption and magnetic properties. Dicarboxylates and related species provide an effective means of designing novel porous materials and other related species. In some of these structures, the dicarboxylate acts as a linker between two inorganic units. Hybrid nanocomposites have also been noteworthy, for example; cadmium oxalate hosts lattices, which can accommodate extended alkali-metal halide structures. Additionally, 2, 2'-bipyridine based metal species, have also been used to control the assembly processes.

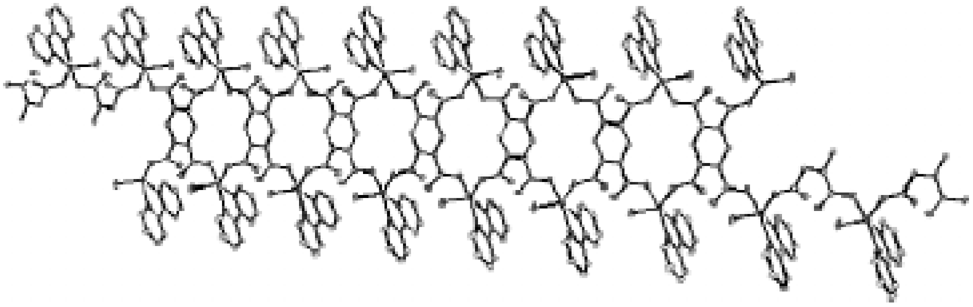

Fig. A Representation of Zn based one dimensional coordination polymer

In this context, we have synthesized few novels Zn^{II} and Cu^{II} bipyridine based coordination polymers containing carboxylate ligands. The complexes are characterized by their single crystal X-ray crystallography. Structural motifs resulting from their self-association through probable non-covalent interactions have been studied. A detailed account of such studies will be presented.

Analytical Applications Of 2, 6-Diacetylpyridinebis-4-Phenyl-3- Thiosemicarbazone And Determination Of Cu(II) In Foods And Water Samples

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New synthesized reagent 2, 6-Diacetylpyridine bis- 4-phenyl-3-thiosemicarbazone (2, 6-DAPBPTSC) is proposed as a sensitive and selective analytical reagent for the spectrophotometric determination of copper(II) at pH: 3.0 to form a yellowish orange colored 1:1 chelate complex. The absorbance was measured at a maximum wavelength 410 nm. This method obeys Beer's law in the concentration range 0.63 - 6.30 μg mL^{-1} and the correlation coefficient of Cu(II)- 2,6-DAPBPTSC complex is 0.942, which indicates an adequate linearity between the two variables with good molar absorptivity and sandell's sensitivity 0.847 x 10^{4} L mol^{-1}cm^{-1}, 0.0075 μg cm^{-2} respectively. The instability constant of complex calculated from Asmus' method 1.415 x 10^{-4} at room temperature. The precision and accuracy of the method is checked with calculation of relative standard deviation (n = 5), 0.777% and the detection limit value is 0.0056 μg mL^{-1}. The interfering effect of various cations and anions has also been studied. The method was successfully applied for the determination of Cu(II) in foods, and water samples and the performance of present method was evaluated in terms of Student '*t*' test and Variance '*f*' test, which is indicates the significance of present method is an inter comparison of the experimental values, using atomic absorption spectrometer (AAS).

P 176

Ferrocene-Naphthyridine Conjugate and Its Protonation

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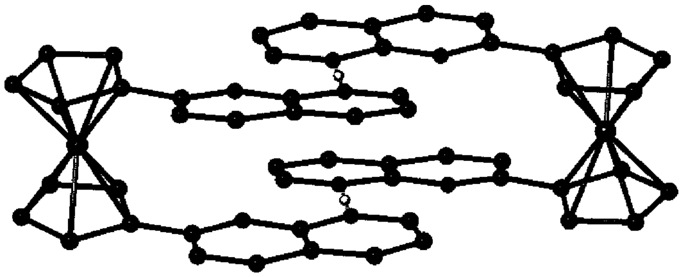
Proton pumping and conduction of charges in biological systems is governed by supramolecular interactions. Hydrogen bonded donor-acceptor assemblies serve as biomimetic model towards the understanding of electron/ charge transfer processes. Protonation of 1, 1¢bis (1, 8-naphthyrid-2-yl) ferrocene (FcNP$_2$) reveal remarkable changes in optical properties. Intra and inter-molecular hydrogen-bonded [FcNP$_2$•H$^+$] species have been identified. The protonated structures resemble closely to the Cu(I) complexes of FcNP$_2$. The colors of the protonated solids and their electrochemical responses are linked to their structures obtained from X-ray and DFT studies. Use of triflic acids with (1,8-naphthyrid-2-yl)ferrocene (FcNP) provide a novel trimer [Fe$^{IV}_3$O$_2$(O$_2$CCF$_3$)$_8$]; its proton-coupled electron transfer will be discussed.



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Palladium, Gold and Silver N-Heterocyclic Carbene Complexes asPotential Anticancer and Antimicrobial Metallopharmaceutical Agents

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A series of Pd, Au and Ag complexes of a non-functionalized N-heterocyclic carbene ligand displaying significant biological activity is reported. [Ray *et al, J. Am. Chem. Soc.* **2007**, in Press]. Specifically, two palladium complexes, **1a** and **1b**, displayed excellent anticancer activity, while the gold **1c** and silver **1d** complexes exhibited remarkable antimicrobial properties. Interestingly enough, the **1b** complex showed strong antiproliferative activity against three types of common human tumor cell lines, namely, cervical cancer (HeLa), breast cancer (MCF-7) and colon adenocarcinoma (HCT 116) in culture. Worth noting that, when examined under the same conditions, the **1b** complex was found to be considerably stronger (*ca*. 2-20 times) than the benchmark drug, cisplatin. The complex **1b** triggered the cell cycle arrest at the G2/M phase thereby inhibiting the proliferation of the tumor cells. With regard to the antimicrobial activity, the gold **1c** complex was found to be *ca*. 2 times more potent than its silver **1d** analog. Morphological studies revealed that the gold **1c** and silver **1d** complexes prevented the progression of cell cycle by blocking cytokinesis. It is noteworthy that the NHC complexes that exhibit anticancer properties do not show any antibacterial properties and the complexes, which show antimicrobial activities, do not display noticeable antitumor properties. The palladium complex **1a** was synthesized from the reaction of 1-benzyl-3-*t*-butylimidazolium chloride **1** with $PdCl_2$ in presence of K_2CO_3 as a base. The silver complex **1d** was synthesized by the reaction of **1** with Ag_2O. The other palladium complex **1b** and the gold complex **1c** were synthesized by following a transmetallation route from the silver complex, by treatment with $(COD)PdCl_2$ and $(SMe_2)AuCl$, respectively.

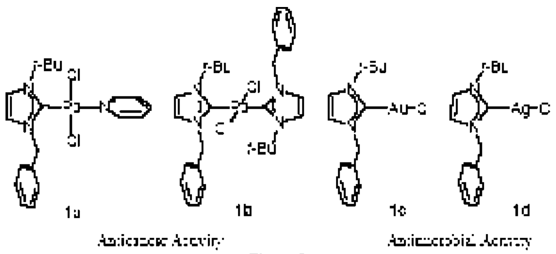

Figure 1.

Organotin(IV) complexes of 5-[(*E*)-2-(aryl)-1-diazenyl]-quinolin-8-ol: Synthesis, Structures and Assessment of cytotoxicity in Human Tumour Cell Lines

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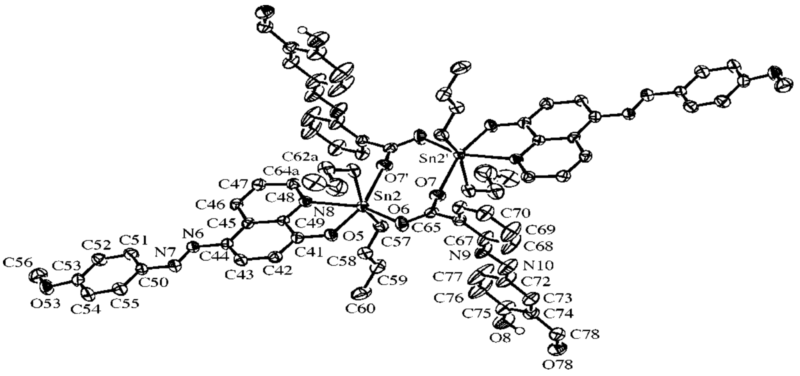
The chemical, biological and pharmaceutical properties of organotin(IV) complexes have been extensively studied. The structures-antitumour activity relations of di- and triorganotin(IV) quinolin-8-olate(s) and its derivatives are also documented. Owing to these applications, the structure and mechanisms of action of these compounds remain a matter of great interest. In addition, a large number of structural studies have been carried out in our laboratory on the organostannyl complexes involving diazenyl ligands.

As a part of an on going study, the 5-[(*E*)-2-(aryl)-1-diazenyl]-quinolin-8-ol framework has been used for the preparation of a great variety of organotin(IV) complexes. The mode of coordination was assessed on the basis of spectroscopic evidences (^{1}H, ^{13}C, ^{119}Sn NMR (including CP MAS), IR, and ^{119}Sn Mossbauer). A systematic structural study by X-ray crystallography provided various structural motifs in the solid state. A few unprecedented examples are also noted (e.g., see fig.). Various important structural features and antitumour properties of such organotin(IV) complexes will be presented.



HDA Strategy to Synthesize Tetrazines and their Characterization at Semiempirical level

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Hetero Diels Alder(HDA) cycloaddition reaction strategy has been explored to synthesize a number of tetrazines using various substituted dienophiles. The semiempirical studies (including AM1, PM3, MNDO Hamiltonian) have been performed to predict the possibility of product and reactivity of HDA. Moreover, some global electronic parameters like electrophilicity index (W), chemical potential (m) have also been evaluated to predict charge transfer flow in Diels Alder cycloaddition. These electronic parameters in addition with eigen functions were used to interpret experimental outcomes. The theoretical semiempirical results were found in good agreement with experimental results. All the experimentally synthesized compounds have been assayed for their purity by chromatographic resolution. Structures of all the synthesized compounds were characterized on the basis of elemental, ^{1}H NMR, IR, and mass spectral assignments.

Vortex Effects in the Current-Density of Helium Atom in a Time-Dependent Magnetic Field

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A few vortex effects, cyclonic and acyclonic, in the current-density of helium atom evolving in a time-dependent magnetic field are presented. The significance of these effects, which may contribute radically to the construction of exchange-correlation functionals of time-dependent current-density functional theory (TD[C]DFT), are discussed.

Dynamics of Polydisperse Supercooled Liquids

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In this work we investigate how polydispersity influences the potential energy landscape, fragility and heterogeneous dynamics of polydisperse Lennard-Jones (LJ) systems in super cooled regime near the glass transition [1, 2]. Polydispersity is found to have a significant effect on the potential energy landscape; the rate of fall of the average inherent structure energy with temperature decreases sharply with polydispersity. The average inherent structure energy decreases with polydispersity, which indicates that the packing is more efficient at higher polydispersity. However, increasing polydispersity at fixed volume fraction speeds up the relaxation and decreases the glass transition temperature. The fragility of glass formation decreases with polydispersity analogous to the "antiplasticization" seen in some polymeric melts [3]. An interesting temperature dependent crossover of heterogeneity with polydispersity is observed at low temperature due to the faster build-up of dynamic heterogeneity at lower polydispersity. Fragility is found to be correlated only to the dynamic heterogeneity and not to the intrinsic heterogeneity in the system.

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Hydrogen Bonding Interaction of Phenol with Trimethylamine: Origin of Blue Shifts of the C-H Stretching Vibrations in Complexes

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Normally hydrogen bond formation in a X-H…Y system is accompanied by a red shift and an infrared intensity increase of the X-H stretching vibration. Recently, theoretical [1] and experimental studies [2] have reported the existence of an unusual class of C-H…Y hydrogen bond that leads to C-H bond shortening along with a blue shift and an infrared intensity decrease of the C-H stretching vibration. Interestingly, blue shifting hydrogen bond can also occur where those C-H groups that do not themselves participate in hydrogen bond formation shifts to higher frequency. We present here the origin of such blue shift occurring at the groups not participating in a hydrogen bond for trimethylamine (TMA) and triethylamine (TEA) complexes with phenol. Density functional theory calculations with the hybrid B3LYP functional and the 6-31++G(d,p) basis set are performed to get optimized structures and frequencies of different species. The effect of hyper conjugation on the structure of free TMA, TEA and their phenol complexes is elucidated through a natural bond orbital (NBO) analysis. Our results clearly indicate an attenuation of the anomeric effect in complexed TMA and TEA. Contrary to general belief, it has been observed that blue shifts occurring at those C-H groups that do not participate in a hydrogen bond are mainly determined by a decrease of the n ® s*(C-H) hyper conjugative interaction [3]. A linear correlation is established between the C-H distances and the occupation of the corresponding s*(C-H) orbitals.

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Self-assembling Short Peptide and Pseudopeptide Based Nanomaterials

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Design and construction of various nanomaterials using ‘bottom up’ approach is really challenging one, in which proper selection of suitable self-assembling molecular building blocks plays a vital role in constructing selective nanomaterials. Two dipeptides containing an N-terminally positioned ω-amino acid residue (β-alanine/δ-amino valeric acid) self-assembles to form nanotubes in the solid state as well as in aqueous solution (Figure 1). Water molecules play an important role in the formation and stabilization of dipeptide nanotube structures in the solid state and it has been established using temperature dependent XRPD experiments. These nanotubes are proteolitically, thermally stable and they also exhibit stability over a wide range of pH (pH 1-13). These dipeptides can form an interesting class of short peptidic structure that can give rise to stable nanotubular structure upon self-assembly and these nanotubes can hold a future promise for potential nanotechnological applications.[1] Helical nanofibres can be successfully constructed using suitable chiral pseudopeptide-based molecular building blocks and reversing the handedness of these nanofibres can also be achieved using the enantiomeric molecular scaffolds (Figure 2). Straight nanofibres are obtained from the corresponding achiral molecular scaffolds establishing the fact that chiral nanoobjects can be made from only chiral molecular scaffold and the transfer of chirality from molecular to supramolecular and nanoscopic level[2]

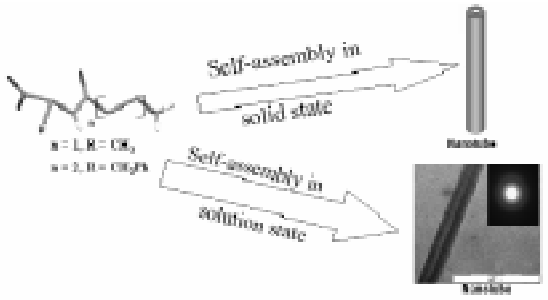

Figure 1

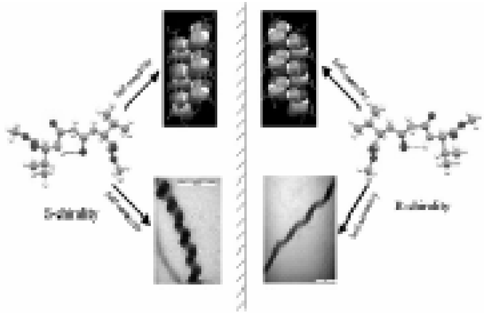

Figure 2

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Catalyst and Mixed catalyst effect on the Oscillatory behaviour of Gallic acid in presence of Methyl ketones

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The study of oscillatory chemical reactions has been dominated by Belousov-Zhabotinskii (BZ) reaction [1], which behaves like chemical clock. In these reactions which are far from equilibrium the concentrations of some reaction intermediates in the reaction system exhibits a regular change in time, a kind of self regulating function similar to what happens in an organism.

Amongst the various classes of BZ reactions, the metal-ion catalysed reactions are extensively studied [2, 3]. However, the present investigation pertains to the study on oscillatory behaviour of Gallic acid with potassium bromate in presence of some methyl ketones as Co-substrates and various metal-ions as catalysts in aqueous acid medium. The reactivity of single and mixed organic substrate systems and also to judge the relative efficiency of metal-ions as catalysts in these reaction systems. Besides, Mn^{2+} / Fe^{2+} couple was chosen to observe the Co-catalyst effect on both single and mixed organic substrate systems.

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Synthesis of Capped ZnS , CdS, ZnSe and CdSe Particles UsingTamarind Seed Polysaccharide

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There are various methods for the synthesis of capped nano particles using polymer matrices [1]. The use of bio-polymers in this field is gaining importance due to the “green” nature of the synthesis. In addition bio-polymers exhibit reductive as well as chelating functional groups. The bio-polymer (Tamarind seed polysachharide - TSP) used for the study were extracted from the seeds of tamarind seed powder. They belong to the galactoxyloglucan family with the composition of glucose: galactose: xylose 3:2:1 respectively. The bio polymer has a cellulose-type spine, which carries xylose and galactose in the branches[2]. They exhibit excellent dual nature of hydrophilic and hydrophobic character. TSP exhibit excellent binding properties and are used in various industries like paper and textile as a binding agent. The polysaccharide for the study was extracted from the tamarind seed following a simple procedure[3]. The obtained polymer was used to chelate cadmium and zinc metals and the made in to homogeneous. Sodium hydrogen sulphide and selenide particles were added to the above at constant stirring and heating under nitrogen atmosphere in DMF over a period of 12hr. The as synthesized bio-polymer capped metal sulphide and selenide particles were characterized using UV, IR, SEM and TEM.

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Butadiene Based Photoactive cholesteric Liquid Crystals for Full Color Data Storage Devices

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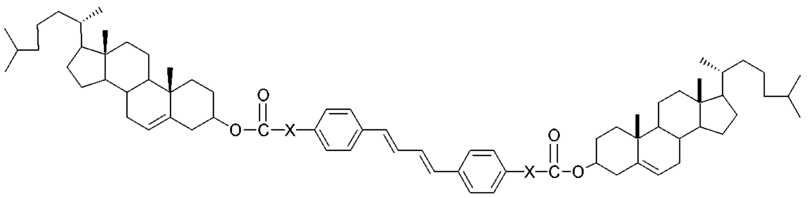
The study of photochemical processes of molecules in liquid crystalline matrices attracts considerable attention since the cooperative interactions and long range ordering of liquid crystalline molecules helps to amplify even weak photochemical processes into macroscopic phenomena such a phase transition or changes in the bulk alignment of the molecules. [1] Such materials whose light transmission/reflectance properties can be controlled using light itself as stimulus can find applications in a number of areas including molecular electronics as well as stimuli responsive lasers. [2] Of particular interest in this regard are chiral nematic liquid crystals (N* LCs) since in these systems the molecules self-organize into helically ordered structures, which lead to selective reflection of light, depending upon the pitch of the helix[3]. Our interest in designing inherently photoactive N* LCs with glass forming properties, led us to the synthesis and investigation of a series of novel symmetrically substituted diphenylbutadienes linked on either sides to cholesteryl moieties directly or via flexible alkyl chains (Chart 1). The synthesis, liquid crystalline properties, photo/thermoresponsive behaviour and polarized emission of these luminescent trimesogens will be presented.



DCBC1, X = -O-
DCBC8, X = -O-$(CH_2)_8$O-
DCBC12, X = -O-$(CH_2)_{12}$O-

(Chart 1)

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Spectrally Resolved Dynamics of Trap Staes invisible Light Emitting ZnO:MgO Nanocrystals

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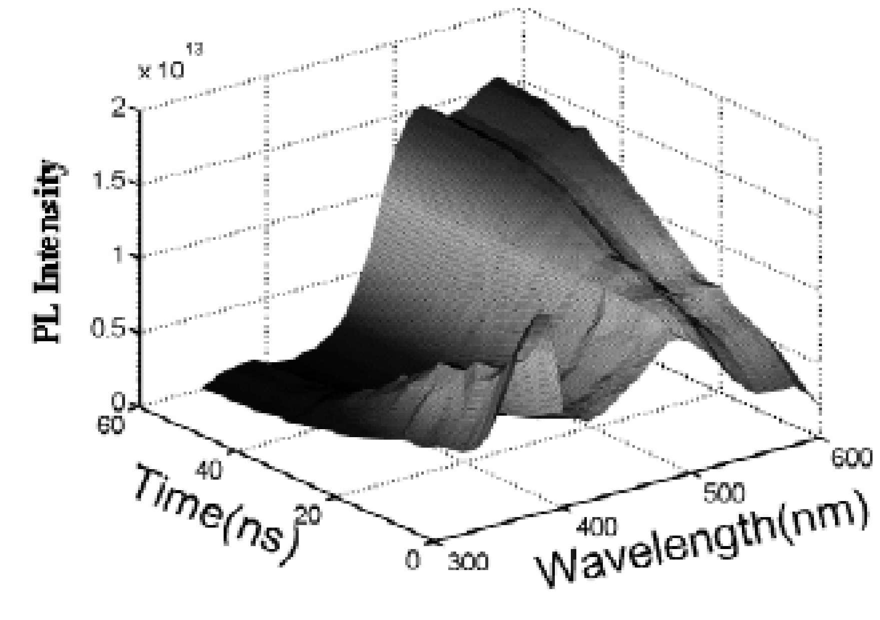
Semiconductor nanocrystals with size tunable photoluminescence are promising alternatives to organic dyes for fluorescence-based applications. II-VI semiconductors based on cadmium chalcogenides are the front-runners for such applications because of their intense absorption, high quantum yield. They do, however, suffer from the drawback that they involve elements that are toxic and pose an environmental hazard. ZnO, a II-VI semiconductor with a direct dipole allowed band gap of 3.4 eV in the near UV and a large exciton binding energy of 60 meV has been known as a luminescent material for close to a century. Nanocrystals of ZnO exhibit two emission bands – a narrow excitonic emission band at 380 nm and a broad intense blue green emission in the visible that has been attributed to trap states, but is as yet poorly understood. The ratio of the intensities of the visible trap emission to the UV excitonic emission is strongly dependent on particle size being larger the smaller the nanocrystals; for ZnO nanocrystals larger than 12 nm the visible emission is absent. Unfortunately capping agents that could, in principle, prevent particle growth, quenches the visible emission.

In this report, we show that capping ZnO nanocrystals with MgO by a sequential synthetic procedure to give ZnO:MgO core-shell nanocrystals exhibit stable visible emission between 460 nm and 580 nm. We use time resolved photoluminescence spectroscopy to investigate the dynamics of the trap states involved in the visible emission. We show that emission originates from recombination involving trapped electrons and holes respectively, with efficiencies that depend on the occupancy of the trap density of states.



O···H-O interaction or Hydrogen Bond?: A Critical Appraisal

Milind M. Deshmukh,[a] Carlo Gatti[b] and Shridhar R. Gadre[a*]

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In the literature, the presence of a (3,-1) molecular electron density (MED) critical point (hence forth called bond critical point BCP) has been taken to be the single most significant signature of a hydrogen bond. In the present work, a critical appraisal of such topographical criterion has been made for O-H···O interactions in water dimer, 1,3-propanediol and few monosaccharide molecules. The presence/absence of a (3,-1) MED BCP is a binary event in the sense that at some geometry one may see a (3,-1) MED BCP, however by very small variation in the geometrical parameters, a BCP may disappear. On the contrary, there is always some interaction present between interacting atoms and can be quite significant even in absence of (3,-1) MED BCP. In the present work, this interaction is gauged by the interaction energy estimate through MTA and some electron sharing indices viz. Delocalization index and Difference density value. It has been found that these indices are the continuous functions of geometrical changes and are quite parallel with each other. On the basis of examples, presented in this work, it is hard to find a cutoff distance as suggested in the contemporary literature such that below this distance a H-bond is present and above it is not in the sense of presence/absence of (3,-1) MED BCP. In conclusion, the present study highlights the use of continuous criteria as discussed above rather than a binary event such as presence/absence of a (3,-1) MED BCP for probing inter/intramolecular interactions such as hydrogen bond.

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Infrared and *ab initio* Studies of Conducting Molecules: 2,5-Diamino-3,6-Dichloro-1,4-Benzoquinone

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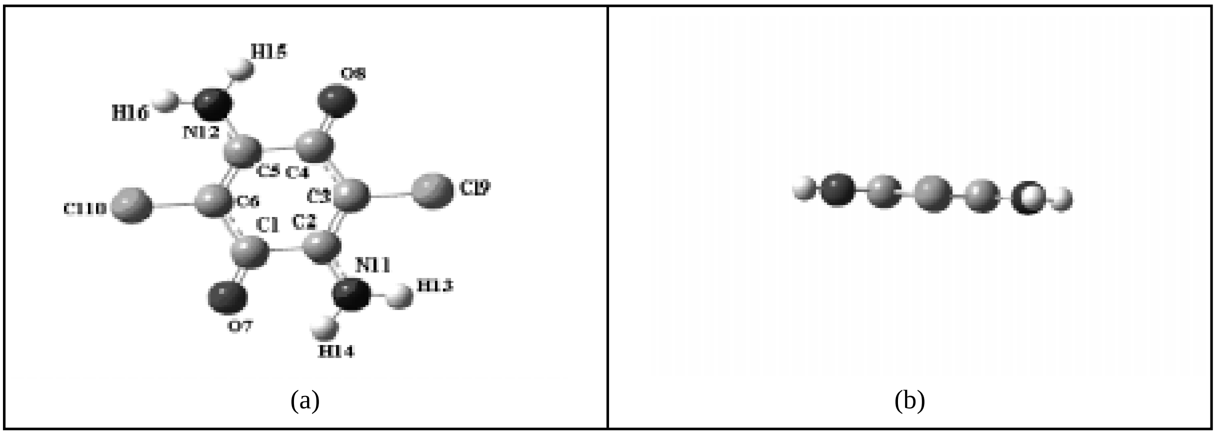
2,5-Diamino-3,6-dichloro-1,4-benzoquinone has been synthesized by modifying the procedure reported in literature. Its IR spectrum has been recorded in the solid phase in the range 4000 – 400 cm^{-1}. *ab initio* calculations have been performed using Gaussian 03 program[1] to compute optimized geometry, harmonic vibrational frequencies along with intensities in IR and Raman spectra and atomic charges at RHF/6–31+G^*, B3LYP/6-31+G^* and B3LYP/6-311++G^{**} levels. To make vibrational analysis Gaussian View software was used. The optimized molecular structure is found to possess C_{2h} point group symmetry. The observed IR frequencies have been assigned to different modes taking C_{2h} molecular symmetry with the help of pictorial view of normal modes. From the magnitude of the observed frequencies corresponding to the NH_2 stretching motions an indication of H – bonding is noticed[2]. From geometrical parameters of the molecule it appears that molecule is planar and two parallel sets of conjugated strands are formed in this molecule providing a route to conduct charges. The N – H bonds facing towards chlorine atoms are found to be shorter than those facing towards oxygen atoms indicating the presence of H - bonding between hydrogen atom of an NH_2 group and carbonyl (quinoid) oxygen atom.



(a) (b)

Fig. 1. (a) Optimized molecular structure and leveling scheme (planar view) and (b) side view of 2,5-Diamino-3,6-dichloro-1,4-benzoquinone(dadb).

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Nanostructured Gold Modified Electrode and its Sensor Application for Simultaneous Detection

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Nanosized metal particles are attracting much attention due to their intriguing properties and potential applications. The catalytic properties of gold nanoparticles (Au_{nano}) very much depend on the method of preparation and particularly, the size of the Au_{nano}. This is due to the large surface area to volume ratio and the activated catalytic surface that makes the metallic nanoparticles very attractive when compared to the bulk metal. In the filed of electrochemical sensor, gold nanoparticles act as best biocompatible flat form.

In the present work, a very simple and efficient electrochemical sensor was designed by electrochemically depositing Au on glassy carbon (GC) electrode. The nanostructured gold (Au_{nano}) modified glassy carbon electrode (GC/Au_{nano}) was found to efficiently electrocatalyze the oxidations of N_2H_4, SO_3^{2-} and NO_2^- in the absence of any other electron transfer mediator/enzyme immobilization in the GC/Au_{nano} modified electrode. The electrooxidation peaks appeared at 0.04, 0.35 and 0.72 V(SCE) for N_2H_4, SO_3^{2-} and NO_2^- at the GC/Au_{nano} modified glassy carbon electrode in Ph 7.2 with a large decrease in the over potentials. The electrochemical sensors designed using the GC/Au_{nano} modified electrode was found to be the best sensor for simultaneous detection of N_2H_4, SO_3^{2-} and NO_2^- present in a mixture. The GC/Au_{nano} modified electrochemical sensor was very stable, highly sensitive and showed fast response.

Exploring the Edge Effects in Gold Nanorods

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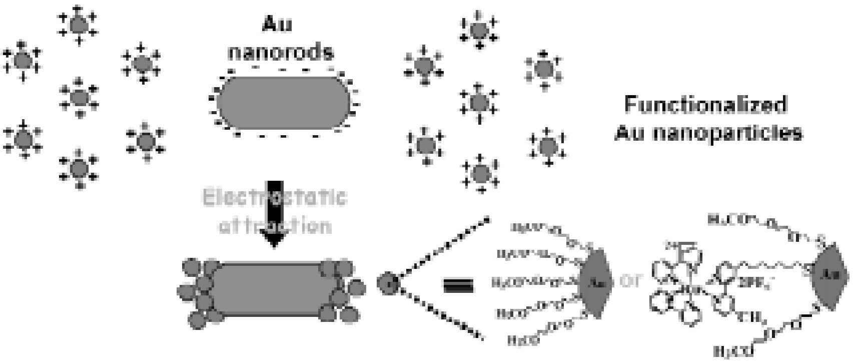
Significant progress has been achieved on the size and shape controlled synthesis of nanoscale building blocks (nanoparticles, nanotubes, nanorods etc.) and their integration into higher order nanostructured materials having desired optoelectronic properties.[1] However, site specific functionalization of nanomaterials still remains a major challenge. We have demonstrated a new methodology for the preferential end functionalization of Au nanorods by exploiting the unusual properties of Au nanorods such as high electric field and site selective reactivity of functional groups at their edges. It is theoretically proposed that the edges of Au nanorods have high electric potential compared to the lateral face. We have experimentally verified this aspect by investigating the electrostatic attractive interactions between oppositely charged nanorods and nanoparticles [1] The enhanced electric field at the edges of Au nanorods preferentially attract the nanoparticles having positive zeta potential, leading to the selective growth of Au nanorods in the longitudinal direction and a corresponding shift in their plasmon absorption. One of the interesting observations in the present study is the size dependency of the nanoparticle on the preferential growth of Au nanorods and these aspects will be discussed. This methodology was further extended for binding a variety of photo-, electro- and bioactive molecules selectively on to the edges of Au nanorods. Preferential alloying at the edges of nanorods with other metals like silver has been demonstrated and these aspects will be discussed. It is reported that {111} crystallographic facets dominate the edges of the Au nanorods and thiols have a specific reactivity on to this facet. These unique properties have been utilized earlier in our group for integrating Au nanorods into one-dimensional assemblies using electrostatic/supramolecular/covalent approaches and their utilization as sensors for the selective detection of biologically active molecules [2]. In the present poster we will also discuss the effect of linker molecules on the plasmon coupling between Au nanorods, with particular reference to dimmers [3].



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Modeling Studies of Ionic Liquids

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The influence of shear on the nanoscale molecular assembly of room temperature ionic liquids has been investigated. Coarse grained molecular dynamics simulations of an ionic liquid, 1-10-alkyl-3-methylimidazolium hexafluorophosphate have been performed and the cations were found to orient themselves along the direction of shear.

In addition, the phase behavior, physical properties and organization in solutions of ionic liquid-water have been investigated using atomistic molecular dynamics simulations.

How to Enhance the Survival Duration of Charge-Separated Species

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The recent trends of photochemical research are to build various artificial photosynthetic devices i.e. model donor- acceptor linked bichromophoric and multihromophoric systems where primary charge separation within the redox component will be relatively much faster than the energy wasting charge recombination (k_{CR}) process. Using electrochemical, steady state and time resolved fluorescence techniques photochemical investigations on various novel synthesized intramolecular systems such as 4MBA, 4MBAS, 7MNT, 7MTCA, MNCA etc. reveal that the longevity of the charge-separated species, resulted from the photo induced electron transfer (PET), could be enhanced. In case of 4MBA and 4MBAS it is seen that by changing the nature of spacer from unsaturated to saturated the k_{CR} decreases while ion-pair yield increase. Again using beta-cyclodextrin (bCD) microenvironment the k_{CR} minimizes drastically with enhancement of the survival duration of the charge-separated species to large extent in case of 4MBA[1]. In case of rigid systems such as 7MNT and 7MTCA it is also seen that using bCD cavity the stabilization of the radical ions against destructive charge recombination process occurs [2]. Thus, bCD appears to be the suitable medium to achieve one of the key requirements for designing artificial photosynthetic devices both with the rigid and flexible donor-acceptor (D-A) systems where long-lived charge-separated species results by retarding the energy destructive charge recombination process. But a very interesting result is obtained by changing the donor part of 4MBA to constitute MNCA, it is seen that without any artificial device like cyclodextrin MNCA possesses better capability of storing charge-separated species relative to that of the previously studied dyad 4MBA. Again electrochemical, FT-IR, steady state and time resolved spectroscopic measurements were made on both the rigid systems i.e.7MNT and 7MTCA in presence of TiO_2 nanoparticles. The experimental results demonstrate the formations of charge-separated species both in the excited singlet and triplet states due to the intramolecular PET between the donor and acceptor functionalities present in 7MTCA. Interestingly, in this case TiO_2 does not take part in PET reactions with the organic solute but it modifies the duration of the longevity of the charge-separated species formed within this organic compound [3]. From the detailed investigations by using electrochemical and pico/nanosecond time resolved spectroscopic techniques it is seen that before energy wasting charge recombination starts the longevity of the charge separated species, resulted from the PET, could be enhanced either by changing the nature of the spacers or using the micro heterogeneous medium like b-cyclodextrin (bCD) or by changing the donor part of the system or adsorbing the organic substrates with semiconductor TiO_2 nanoparticles or through synthesis introducing proximity effect.

Adsorptive Stripping Voltammetric Determination of an Anticancer Drug: Tamoxiphene

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Electrochemical behaviour of tamoxiphene, non-steroidal anticancer drug was studied using a Hanging Mercury Drop Electrode (HMDE) from Differential Pulse Adsorptive Stripping Voltammetry (DPAdSV). The effect of pH, accumulation potential and accumulation time were examined and consequently analytical parameters were evaluated. Britton-Robinson (BR) buffer of pH 4.4 was found to be the best medium for the determination of the above drug. The calibration plot was found to be linear from 2 x 10^{-3} M to 1 x 10^{-7} M with a limit of detection of 5 x 10^{-9} M with an accumulation time of 60 sec. Further, this method was also applied successfully for the determination of Tamoxiphene in serum samples.

Temperature Dependent Studies of Acoustic Parameters in n-octane and Chloro-benzene and Application of Various Theories of Sound Speed

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Binary mixture of n-octane and chloro-benzene has been studied extensively from the view point of its acoustic behaviour at different temperatures (298, 308 and 318K) by measuring density (r) and sound-speed (u) measurements over the entire composition range.

Experimental values are used to compute derived parameters such as isentropic-compressibility (k_s) intermolecular free length (L_f) and acoustic-impedance (Z) using well established relations.[1-3] The sign and magnitude of excess parameters like excess intermolecular free length (L_f^E) deviation in isentropic-compressibility (Dk_s) excess molar volume (V^E) and excess acoustic impedance Z^E have been used to interpret the results in terms of intermolecular interactions between the components of the binary liquid mixture.[4]

$$\kappa_s = \frac{1}{u^2\rho} \qquad (1)$$

$$L_f = \frac{\kappa}{u\rho^{1/2}} \qquad (2)$$

$$Z = u\rho \qquad (3)$$

$$Y^E = Y_{mix} - (x_1Y_1 + x_2Y_2) \qquad (4)$$

Free Length Theory $u^{FLT} = \dfrac{K}{L_{fmix}\,\rho_{EXP}{}^{½}}$

Nomoto $u^{NOM} = \left(\dfrac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right)^3$

Impedance Dependence Relation

$$u^{IDR} = \frac{\sum x_iz_i}{x_i\rho_i}$$

Vandeal-Vangael Ideal $\left(\dfrac{1}{x_1M_1+x_2M_2}\right)\left(\dfrac{1}{u(VAN)^2}\right) = \dfrac{x_1}{M_1u_1{}^2+} + \dfrac{x_2}{M_2u_2{}^2}$

Theoretical evaluation of sound-speed in binary liquid mixtures and its comparison with the experimental values is very useful to validate. Theoretical models for liquids. Various theoretical approaches of sound-speed viz. free length theory (FLT), Impedance Dependence Relation (IDR), Nomoto's Relation (NR) and Vandeal-Vangeal Relation (VAN) have been applied to obtain the theory of best fit for the system at the temperatures taken for investigation[5-8]

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Photo induced electron transfer reactions of Coumarin 450 with Amines in Micelles

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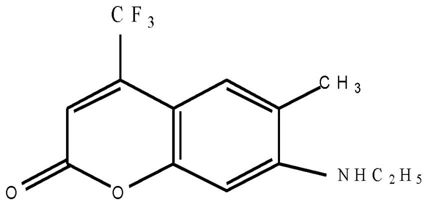
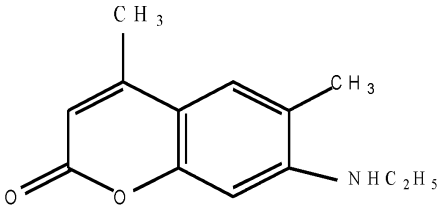
Photo induced electron transfer reactions involving Coumarin 503 and Coumarin 450 dyes with aromatic amines were carried out in anionic (Sodium dodecyl sulfate, SDS) and cationic surfactants (Cetyltrimethylammonium bromide, CTAB) by steady state and time resolved absorption and fluorescence techniques. Steady-State fluorescence quenching of the coumarin dyes by the amine quenchers shows a positive deviation from Stern-Volmer relationship, which is due to the presence of both static and dynamic quenching. A static quenching is due to the presence of high concentration of amines around the coumarin fluorophore in the micelles. The electron transfer due to static component is very fast and takes place within 50 ps. Time resolved fluorescence studies show the dynamic part of the quenching for the excited coumarin dyes by the amine quenchers and found to be less than diffusion controlled rate constant. The lower electron transfer rate constant in micellar media is attributed to the greater donor-acceptor distance in the micelles [1]. The location of the probe molecule in the micelles was confirmed by time resolved fluorescence anisotropy measurements.

Nanosecond laser flash photolysis studies were carried out in anionic and cationic micellar solutions. Photoionisation of coumarin dyes was observed in the both micelles on exciting with 355 nm. The photo ionization of coumarin dyes produce solvated electron and the dynamics of the solvated electron depend on the nature of micelles [2]. In the presence of amine a new transient was observed at 470 nm and this is attributed to the cation radical of the amine. The photo stability of coumarin dye increased on the addition of amine to the coumarin dye solution in micelles. The mechanism of the photo reaction of coumarin dyes with aromatic amines in micro heterogeneous medium provided by the two different micelles and will be presented in detail.



Coumarin 503



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Probing Ultra fast Dynamics of IR-125 dye, from DCM bulk medium to DCM-water interface

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Femtosecond transient absorption spectroscopy has proven to be an efficient technique to study the excited state dynamics in liquid phase [1, 3]. In a typical transient absorption experiment an excitation of the molecule is initiated by a strong pump pulse, and its dynamics is followed by recording the absorbance of a weak probe pulse as a function of the time delay between the pump and probe pulses [2]. Interfaces are ubiquitous. They occur everywhere. They are the boundaries that separate distinct physical and chemical regions of matter. The interface has unique chemical and physical properties which differ from either of bulk mediums. Because of these properties, the interface has fundamental scientific and technological importance. We have studied how the transient absorption changes as we move from IR125 dye in DCM bulk medium to DCM-water interface. Femtosecond excited dynamics of the dye molecule is observed to be strongly dependent on the position of probing of the dye molecule from bulk medium to interface. A gradual change in the transient absorption signal is observed from DCM bulk medium to DCM-water interface. The decay component which corresponds to the excited state lifetime is observed to increase from DCM bulk medium to DCM-water interface.

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Molecular modeling of the interaction of Hepatitis B virus B-cell Epitope antigen and antibodies

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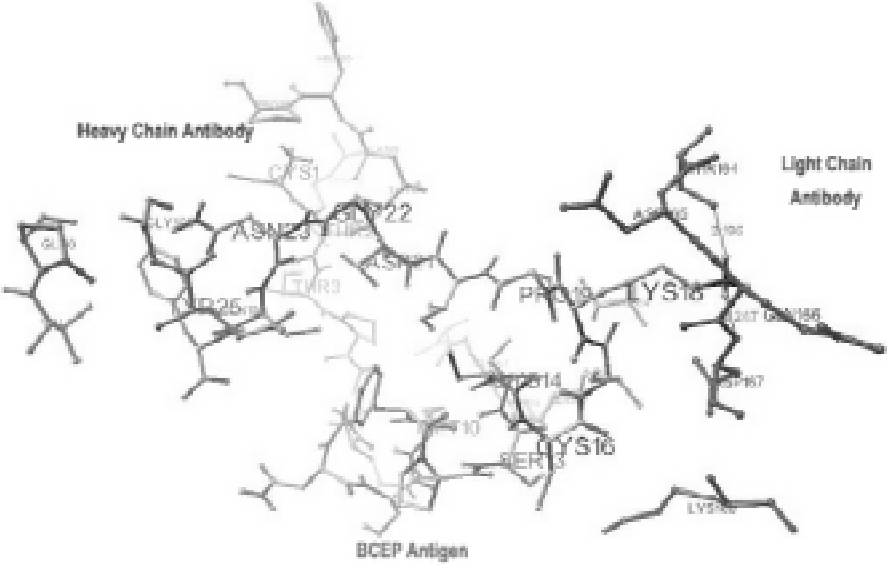
Recent advancements in the structure and genomic organization of the hepatitis B virus (HBV) resulted in the development of second and third generation HBV vaccines, containing entire or the fragment of hepatitis B surface antigen (HBsAg) to prevent the HBV infection [1]. The function of these anti-HB antibodies is to recognize a theoretically unlimited set of HBV antigens and to defend the vertebrate body against them. A significant attribute of antibodies is their specificity in binding with various types of antigens. Computational methods, involving molecular docking have become an increasingly useful tool for modeling antibody-antigen interactions [2]. In the present work, the 3D model for the BCEP antigen comprising amino acid residues CTTPAQGNSMFPSCCCTKPTDGNCY was constructed using homology modeling technique. The Lamarckian genetic algorithm (LGA) of Auto Dock 3.0.5 [3] was employed to locate the binding orientations and possible conformations of the BCEP antigen interacting with pre-S1 domain monoclonal antibody and antibodies IgG and IgM. The binding models were examined using van der Waals and hydrogen bonding interactions. The final docked energies of the binding conformation of BCEP antigen with the antibodies pre-S1 domain monoclonal antibody, IgG and IgM are -17.75, -10.1 and -8.1 kcal/mol respectively.



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Theory of Quasi-reversible Charge Transfer Reaction on Realistic Self-affine Fractal Electrode

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Theory of a long-standing problem of finite rate heterogeneous charge transport across an irregular interface is developed. The random surface irregularity is modeled as a surface fractal, which is characterized by, statistically self-affine fractal over a limited length scales. We use our general formalism developed earlier for the quasi-reversible heterogeneous charge transfer reaction current on random surface roughness, where reaction current is described in term of power spectrum of roughness. The power spectrum of a surface fractal is approximated in terms of white noise for low wave-numbers and a power law function for the intermediate wave-numbers. This description for roughness consists of four fractal morphological parameters. Our results unravel the connection between the potentiostatic current transient at fractal interface when diffusion is coupled with finite charge transfer rates. Finally, we analyze the dependence of reaction current on various fractal roughness parameters and discuss the crossover of reaction from quasi-reversible to Nernstian and quasi-reversible to sluggish charge transfer.

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Fullerene - Ferrocene DYAD linked by rigid Bilinkage: Synthesis and study of photophysical property

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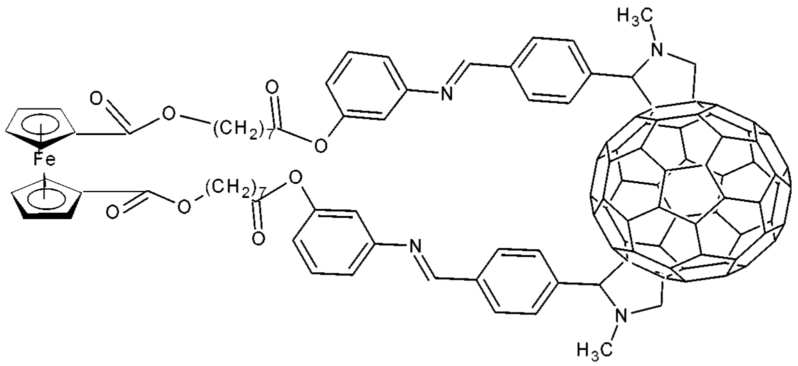
A novel Fullerene-Ferrocene based Donor-Bridge-Acceptor Dyads having rigid aromatic Schiff base bilinkage have been synthesized by adopting the reported 1,3 dipolar cycloaddition reaction[1]. The compound was charecterised by ^{1}HNMR, MALDI-MASS, FT-IR and elemental analysis. Such a dyad of Fullerene and Ferrocene joined by bilinkage is reported for the first time as compared to dyads having different monolinkers [2]. The linker comprised of ester as well as Schiff base groups which favours electron as well as energy transfer process. Photophysical properties of the dyad using Abrorption spectra and stedy state Fluorescence spectra were studied as a function of dielectric constant of the medium. Absorption spectra indicated a slight blue shift in lmax (202 nm) as compared to N-Methyl Fulleropyrrolidine having lmax (215nm) Fluorescence spectra of the dyad in Methylcyclohexane was studied with excitation at 449nm which showed weak emission spectra at 742 nm indicating efficient electron transfer from ferrocene to fullerene.



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Stability of Palladium Nanoclusters using Density Functional Theory

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Density functional calculations within the generalized gradient approximation (GGA) have been performed to investigate the lowest energy electronic and geometric structures of neutral, cationic and anionic Pdn (n=1–7) clusters in the gas phase. In this study, we have examined three different spin multiplicities (M= 1, 3 and 5) for different possible structural isomers of each neutral cluster. The calculated lowest energy structures of the neutral clusters are found to have multiplicities, M=1 for Pd1, Pd3, Pd5, Pd6 and Pd7 while M=3 for Pd2 and Pd4. We have also determined the lowest energy states of cationic and anionic Pdn (n=1–7) clusters, formed from the most stable neutral clusters, in three spin multiplicities (M=2, 4 and 6). Bond length, coordination number, binding energy, fragmentation energy, bond dissociation energy, ionization potential, electron affinity, HOMO-LUMO gap, chemical hardness and electric dipole moment of the optimized clusters are compared with experimental and other theoretical results available in the literature. Based on these parameters, we predict the four-atom palladium cluster to be a magic-number cluster.

Highly selective aerobic oxidation of alcohols to aldehydes and ketones heterogeneously catalysed by $H_5[PMo_{10}V_2O_{40}]\cdot32.5H_2O$ immobilized on ionic liquid-modified SBA-15

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The oxidation of alcohols to aldehydes and ketones plays a vital role in organic chemistry both at the laboratory and industry level. Catalytic oxidation with molecular oxygen is particularly smart from an economic and environmental point of view[1, 2]. Ionic liquids have become commonplace in recent years and are a significant alternative medium for the traditional organic synthesis and catalytic reactions. Moreover, since ionic liquids are expensive it is desirable to minimize the amount of ionic liquid used in usual biphasic reaction systems. This can be realized with the supported ionic liquid catalysis3, 4. We report, herein a mild and effective procedure for the immobilization of $H_5[PMo_{10}V_2O_{40}]\cdot32.5H_2O$ (V2) onto 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid-modified SBA-15. The supported ionic liquid catalyst, V2ILSBA, catalyzed the aerobic oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones respectively with no trace of over oxidation to carboxylic acids. The allylic alcohols were selectively oxidized to the allylic aldehydes. The activity and selectivity were comparable to those of the homogeneous analogue, and could be reused for 10 cycles without any loss in activity and selectivity. Hence this system provides an easy approach for the successful immobilization of V2 over ionic liquid modified SBA-15. In addition, the catalyst is reusable without any loss of catalytic performance.

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Iron Pentacarbonyl as Hydrogen Bond Acceptor: Density Functional Theory and Aim Calculations

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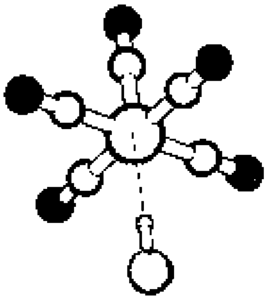
$Fe(CO)_5$ is chosen as the model system to study whether organometallic complexes can act as hydrogen bond acceptors. $Fe(CO)_5$ is a fluxional molecule. Theoretical calculations predict the most stable geometry of $Fe(CO)_5$ to be a trigonal bipyramidal. The square pyramidal geometry is also a minimum at B3LYP/6-311++G** level of theory. The C_{4v} structure exists in the gas phase as a transition state during a Berry pseudo rotation, which can further be stabilized by a sixth ligand. This has been observed in case of $Fe(CO)_5\cdots C_6H_6$ complex by FTIR spectroscopy in solution by Rose-Petruck et al [1]. However, still there is no direct observation of $Fe(CO)_5$ interacting with a sixth ligand in isolation.

In this work the C_{4v} geometry of $Fe(CO)_5$ and its interaction with different hydrogen halides, HX (X=F, Cl, Br) are considered. Optimized structures of the complexes were obtained using density functional theory (DFT) at B3LYP level using Gaussian 03. Frequency calculations were carried out to ascertain that the structures were true minima. Basis set superposition error corrections and zero point energy corrections are also done for the complexes. In all the complexes, the hydrogen of HX interacts with Fe through the sixth co-ordination site. The BSSE corrected stabilization energies of the complexes of $Fe(CO)_5$ with HF, HCl and HBr are –5.8, -3.7 and –3.4 kcal/mol respectively at B3LYP/6-311++G** level of calculation. From the calculations, the H-X bond shows a red shift during complex formation indicating that Fe acts as a hydrogen bond acceptor. QTAIM analysis of the complexes has also been carried out. This shows the presence of a bond critical point between the iron and the hydrogen of HX and hence bond formation. Moreover the numerical values of the electron density, $\rho(r_c)$ and Laplacian of the electron density, $\nabla^2\rho(r_c)$ at the hydrogen bond critical point [2] confirms the bond formed between $Fe(CO)_5$ and HX to be a hydrogen bond.



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Synthesis and characterization of Ultrafine $Ba_{1-2x}Ca_xSr_xTiO_3$ (x = 0.05, 0.10)

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Barium titanate is a type of perovskite oxide which has a wide application as a ferroelectric ceramic and dielectric material as well. It is mainly used as a capacitor due to its high dielectric constant. The dielectric properties are controlled by purity and microstructure which in turn are dependent on the method of preparation. Recent advances in nanotechnology such as: Multilayer capacitor (MLCs), Micro electro Mechanical systems (MEMs) and Dynamic Random Access Memories (DRAM) have resulted in the miniaturization of devices. These require nano size $BaTiO_3$. Various chemical routes like co-precipitation, sol-gel, Hydrothermal and reverse micelle are known to yield nano particle products. Most of the workers synthesized $BaTiO_3$ by conventional ceramic method at higher temperature. But ceramic method is not very useful for the preparation of high performance ceramic because the materials have very large particle size are non homogenous and have high impurity contents.

The main objective of this work is to synthesize Barium Calcium Strontium Titanate, $Ba_{1-2x}Ca_xSr_xTiO_3$ (BCST) and to trace out its peculiar applications. We have synthesized (BCST) powders (x = 0.05, 0.10) and also $Ba_{1-x}Sr_xTiO_3$, (BST) (x= 0.20) and $Ba_{1-x}Ca_xTiO_3$, (BCT) (x=0.20) by chemical route using citric acid and ethylene glycol. It was found that single phase was formed at 800 ^{0}C which was confirmed by XRD and TGA/DTA. There are no impurity peaks observed in the XRD patterns. All peaks are identified to be due to perovskite phase with tetragonal structure for all the three compositions. The lattice parameter was calculated from the XRD data. The lattice parameters decrease with increasing content of Sr and Ca. This is attributed to the fact that the ionic radius of Sr and Ca are smaller than that of Ba ion. Average grain size was calculated using Debye Scherrer's equation ($t = 0.9\,\lambda/B\cos\theta$), where t is the diameter of the grain, λ is the wavelength and B is the full width at half maximum. The DC resistivity was measured as a function of temperature. The dielectric constant and loss tangent were studied as a function of frequencies and temperature. To understand the conduction mechanism in the sample AC conductivity was measured with variation of temperature and frequency. The AC conductivity of BCST increases with increase in the frequency, which may be due to the strong hoping of ions.

Polarographic behavevior of heparin and molecular designing for increased anticoagulation potency to treat thrombotic disorders

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The identification of exact action and localization of anticoagulants on hemorrhage/ stroke i.e. thrombosis, is the area of major research interest. For this the molecular designing of heparin [anticoagulant] has been done, to increase its significant effectiveness for the prevention and treatment of thrombotic disorders. Electrochemical methods [Direct current polarography (D.C.P.) and Differential pulse polarography (D.P.P.) have been developed for the qualitative and quantitative analysis of heparin and its modified molecules in 0.2M NaOH as supporting electrolyte. The developed methods have been standardized for determination of heparin over the existing methods and its interaction with amino acids/ iron (Fe-II)/ albumin. The analytical results indicated 1:1 heparin: amino acids/ albumin ratio while 1:2 stoichiometric ratio for iron-heparin complex was observed. The pharmacological efficacy of modified molecules both in vitro [human citrated plasma] and in vivo [albino mice plasma], as their anticoagulation activity have been described. The plasma prothrombin time, an important pharmacological parameter as observed in vivo for parent drug heparin and modified molecules were found in the following order: Normal<Iron-heparin complex<Albumin-heparin < Heparin-cysteine < Heparin-methionine »< Heparin < Heparin-glutamic acid <Heparin-lysine. Significantly heparin-glutamic acid and heparin-lysine modified molecules showed 1.5 and 5.5 times higher anticoagulation efficacy with better tolerability and ensure faster functional recovery respectively as compared to the parent heparin drug.

As such the modified heparin-glutamic acid and heparin-lysine drugs may be recommended to the therapeutic experts for their possible use in the treatment of thrombotic disorders.

Correlating Weak Hydrogen Bonding and Electron Donor-acceptor Properties for Novel molecular Materials

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Two most ubiquitous non-covalent interactions are hydrogen (H)-bonding and electron donor acceptor (EDA) interaction. It is well know that, normally, the earlier interaction plays important role in stabilizing structure while later in transmitting signals. To understand such interactions at solid state level and make them work for the practical applications is a challenging task. Strong H-bonding and EDA interactions are studied at solid state level and were of increasing interest from late 1980's. But collectively both weak H-boding and weak EDA interactions are rarely studied at solid state level. My preliminary experiments show that, with the correct balance between these two non-covalent interactions one can tune various technologically important properties such as, molecular magnetism, newer sensors in such compounds.

1, 2, 4, 5-tetracyanobenzene (TCNB), an electron acceptor (with reversible ionization potential of –0.65 eV in acetonitrile at room temperature versus SCE), exist in dimeric form with weak CN$\cdots$HAr hydrogen bonding, but when treated with weak electron donor molecules, such as Phenol, it not only form expected charge transfer complex but also extend its dimeric CN$\cdots$HAr hydrogen bond to the ribbon like network, akin to host assembly. The single crystal X-ray diffraction study clearly shows that these ribbon-like networks generate cavities (Fig 1), where Phenol is incorporated as a guest molecule. The presence of CN$\cdots$HAr interaction is also evident from the spectroscopic (FT-IR and Raman, Fig 1) studies. Thus, it is evident that such a structure gets built using both charge-transfer as well as hydrogen bonding motif in the form of flexible host-guest assembly. On the contorollary this host formation becomes loose when stronger electron donor molecules such as TMPD (N,N,N′,N′-tetramethyl-*p*-phenylenediamine, a strong electron donor) is used instead of Phenol. The structure of later complex do not seem to show the usual π-π interaction between the two aromatic rings, but indicates the presence of n-π interaction localized between the nitrogen atom of TMPD and the cyano groups of TCNB. Magnetic measurements using SQUID magnetometer (5-20K) on powdered sample showed decrease in χT values with lowering temperature, weakly antiferromagnetic (θ=-0.85K). Thus I will present some interesting results, which show presence of weak H-bonding, and EDA interaction, and their interplay for generating new molecular materials.

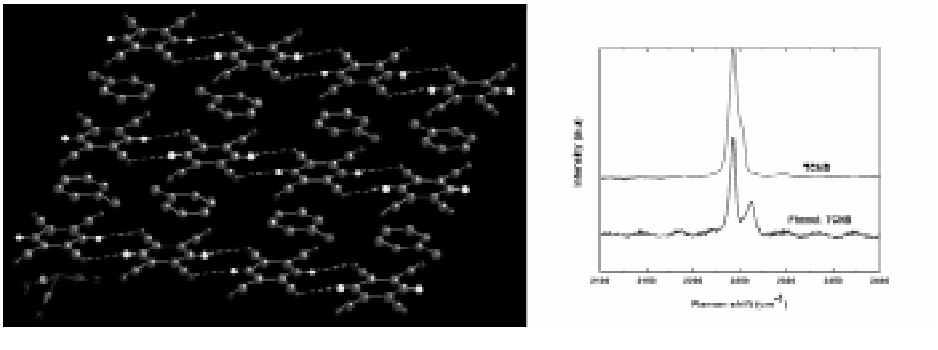

Figure1: Showing Presence of Stacking of EDA complex (X-ray, left) and CN…H Hydrogen bonding (Raman Scattering, right).

Interactions of Amino Acid Based Hydrophobically Modified Water-Soluble Polymer with Oppositely Charged Surfactants: Fluorescence Probe, Dynamic Light Scattering, and Calorimetric Studies

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The formation of complexes between the cationic surfactants (CTAB and DTAB) and hydrophobically modified polymer, poly(sodium N-acryloylglycinate-co-N-n-dodecyl-acrylamide), was investigated in dilute aqueous solutions by means of surface tension, turbidimetry, fluorescence, isothermal titration microcalorimetry, and dynamic light scattering. Surface tension studies resulted critical aggregation concentration (cac) values for the surfactants in presence of a given amount of polymer, which was found to be much lower than cmc of surfactant itself. The decrease in cmc value is much larger compared to that obtained in the presence of corresponding homopolymer, poly(sodium N-acryoyl-glycinate). Effect of salt concentration on the complex formation was investigated. Pyrene fluorescence studies suggest complexes formed have very compact structure due to their increased hydrophobicity. Decrease in anisotropy observed from fluorescence depolarization studies using DPH probe suggests morphological changes in complex upon addition of surfactant. Optical density measurements showed that upon addition of surfactant polymer/surfactant complex formed becomes water insoluble and the solution turns turbid and accompanied by the formation of large complex precipitates. The precipitate forms a stable dispersion in the presence of a large concentration of surfactant. The microcalorimetry results for the mixed systems characterize systematically the thermodynamics of their interaction and phase behavior was observed. The size of the water soluble complexes formed was determined by dynamic light scattering measurements.

NMR Investigation on the Interaction of b-Cyclodextrin and Ampicillin

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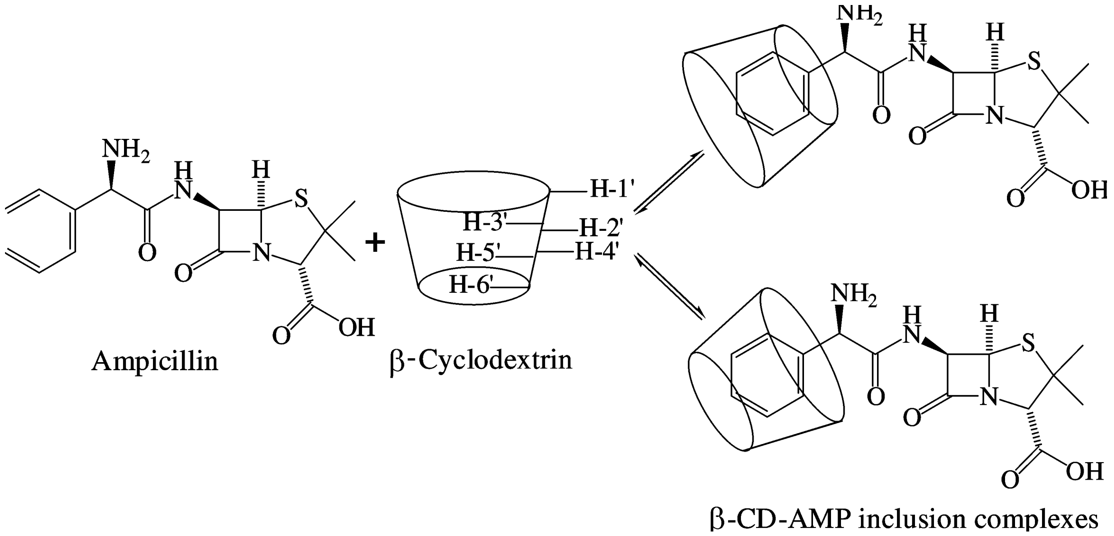
Cyclodextrins (CDs) are cyclic oligosaccharides of a-(1>4)-linked glucopyranose, which have a hydrophilic exterior and a hydrophobic cavity [1]. This structural feature allows CDs to encapsulate a variety of hydrophobic molecule, or part of it, inside their cavity through non-covalent interactions to form inclusion complexes [1]. CDs possess a special ability to complex with drugs enabling them to increase solubility, reduce bitterness, enhance stability, and decrease tissue irritation upon dosing [1, 2]. In this work, we used b-cyclodextrin (b-CD), which has 7 units of glucose to interact with ampicillin (AMP). AMP is a penicillin-like antibiotic drug currently used to treat infections, including gonorrhea and meningitis. NMR spectroscopy has become the most important tool for the structural elucidation of organic compounds, particularly in solution state [3]. The 2D ROESY (Rotating-frame Overhauser Effect SpectroscopY) has been found very helpful for the investigation of the interaction between CD and guest molecule and it gives the information about the mode of penetration i.e. narrower or wider rim side, the depth of penetration and orientation of the guest [3]. ^{1}H NMR spectroscopic study of varying ratios of b-CD and AMP in D_2O suggests the formation of a 1:1 inclusion complex. The assignment of resonances of guest (AMP) protons was made with the help of 2D COSY (Correlation Spectroscopy) spectral data. The stoichiometry and association constant were determined using the continuous variation (Job's Plot) method by the treatment of ^{1}H NMR titration data. 2D ROESY spectrum showed interaction between b-CD cavity protons (H-3' and H-5') and phenyl ring protons of AMP, suggests the complexation between b-CD and AMP. The structure for the b-CD-AMP inclusion complexes has been proposed taking into consideration the stoichiometry, ^{1}H NMR titration results and ROESY spectral data.



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Time Dependent Density Functional Theory Study of Charge Transfer Transition of $[PtBr_6]2^-$

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Ligand to Metal charge transfer transition of $[PtBr_6]^{2-}$ has been investigated computationally by time dependent Density Functional Theory in polarized continuum model . To calibrate the theoretical data, different extent of mixing of HF calculation was made in the exchange part of exchange –correlation functional. The hybrid exchange-correlation functional with different basis set gives a covalent ground state description. The excited state Geometry is optimized with a significant decrease in bond length which is indicative of Charge Transfer transition from Bromine to Pt(IV).

Excessive negative charge accumulation on $[PtBr_6]^{2-}$ in both the ground and excited state supports LMCT type transition.

Potential energy scan was done on to describe the bonding description of $PtBr_6^{2}$. The calculated ligand to metal charge transfer transition are shifted to lower energies compared to the experimental values**.**

Vertical excitation energies with different oscillator strength were computed for the first 60 singlet excited states, to reproduce the UV-visible spectra. The low lying excited states were supposed to be adiabatically connected which give rise to single expression for the exchange-correlation functional.

Partial molecular diagram of $[PtBr_6]^{2-}$ depict four type of transitions namely **i**. n1 corresponding to p®p* transition, **ii**. n2 Corresponding to p®s* transition, **iii**. n3 Corresponding to s®p* transition and **iv**. n4 Corresponding to s®s* transition. Each of these transitions is a group of transitions since excited orbital configuration gives rise to several different states of similar but not identical energies.

Transitions of n1 and n3 are absent in $[PtBr_6]^{2-}$ due to the t_{2g}^6 ground state configuration.

The experimental transitions of $[PtBr_6]^{2-}$ are at 370.37 -303.03nm and at 226.24 nm. As TDDFT requires both excitation and de-excitation operators and Gaussian 03 offers only the excitation operator, the relative oscillator strengths are not reliable, the lowest energy CT band is mainly from a nonbonding level to antibonding one, they should be broad. This is reflected by a third, low intensity vertical transition in all the theoretical methods. Comparison of the data revealed that the theoretical vertical excitation match closely with the experimental spectral data for BP86 method protocol with Stuttgart/Dresden effective core potential basis for Pt and 6-31+G(D) basis for Br. This 6-31+G(D) is specially designed for the calculation of anions. The experimental Pt-Br bond length is 2.5 Å in $[Pt(en)Br_{3]}$. The B3lyp/LANL2dz optimized bond distance is 2.6163 Å.

A Novel Amperometric Hydrogen peroxide Biosensor based on HRP incorporated in Organically modified Sol-Gel glass matrix with multiwalled carbon nonotube

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We herein report a novel hydrogen peroxide biosensor which has been constructed by immobilizing ferricyanide [hexacyanoferrate(III)] and horseradish peroxidase (HRP) in ormosil with multiwalled carbon nanotube modified within grapite paste electrode. Ferricyanide moieties have been chosen to serve as redox mediator for enzymatic peroxide reduction in ormosil network to maintain biosensor activity because it has an ideal electrochemistry and high electron transfer efficiency. Multiwalled carbon nanotubes (MWNTS) have been used because of having its unique electronic, chemical and structural features that make them very attractive for electrochemical studies. For example, they have distinct electrochemical activities and capabilities for facilitating mediated electrochemistry of enzymes/proteins from other carbon materials. Excellent electrochemical performance was exhibited using multiwalled carbon nanotubes (MWNTS) with redox mediator ferricyanide. In the present work, the effect of the electron transfer efficiency of the ferricyanide was expected to be promoted by adding multiwalled carbon nanotubes into the ormosil modified electrode. Preparation of graphite paste electrode by incorporating ormosil matrix encapsulated with enzyme and mediator/mwnts has been done to avoid their leaching under the operational conditions. Sensor was characterized by cyclic voltammetry and amperometry. Sensor without HRP showed no or little response whereas significant response signal enhancement could be obtained in presence of ferricyanide and ferricyanide/MWNTS with HRP respectively. In addition, the effect of solution pH on the response of peroxide biosensor was also investigated. Linear relationship is observed for hydrogen peroxide reduction at an applied potential of -0.2 V vs Ag/AgCl in phosphate buffer solution of 0.1M, pH 7.0 and detection limit is .20mM. Diffusion controlled redox process is proved by Randel-sevick plot (peak current vs scan rate$^{1/2}$) which obey the Randel-sevick equation. Performance of the sensor was evaluated with respect to response time, sensitivity as well as operational stability. The HRP/MWNTS encapsulated in ormosil modified graphite paste electrode is easy to prepare and achieved 95% of the steady state current within <10s. It has good reproducibility, wide linear range up to 550 mM and high storage stability of 4 months stored at 4^0C when not in use.

Influence of Subsurface Oxygen on Palladium Surfaces Towards CO-Oxidation at High Temperatures

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Noble metals are known for high oxidation capacity of carbon monoxide (CO) and they are essential ingredients in three-way catalytic converters employed in automobiles for emission control. In general, the rate of CO oxidation decreases above 550 K on metal surfaces and high rate of CO-desorption becomes a limiting factor in the CO oxidation[1-2] Recent reports [3] indicates oxygen-diffusion into the sub-surface/bulk of Pd-surfaces under ultra high vacuum (UHV) and >500 K, and Pd_xO_y formation at relatively high oxygen pressure (>10^{-3} mbar). Variations in the catalytic activity of oxidation reactions with Pd catalysts are reported and generally it is attributed to differences in activity between Pd and PdO. However, the interactions between oxygen and Pd-surfaces have important implications, especially towards oxidation reactions, and seldom detailed reports are available in the literature on the influence of sub-surface oxygen to oxidation reactions. In our efforts to understand the above aspect, we carried out CO oxidation reactions, by allowing a mixed molecular beam (MB) made of CO+O_2 on Pd(111) surfaces under a wide variety of conditions (T = 450 to 900 K, CO:O_2 = 7:1 to 1:10). A set of data is given in Figure 1 which shows the delay in CO_2 desorption in spite of large oxygen adsorption and presence of CO. Above studies provide the direct proof for CO-adsorption with significant sticking coefficient (s_{CO}) at high temperatures on Pd surfaces that contains significant sub-surface O-coverage. Indeed our results are highly relevant to the present generation catalytic converters employed under air-rich conditions, in which Pd is increasingly used as an active metal or the only active metal. More results will be presented in the poster.

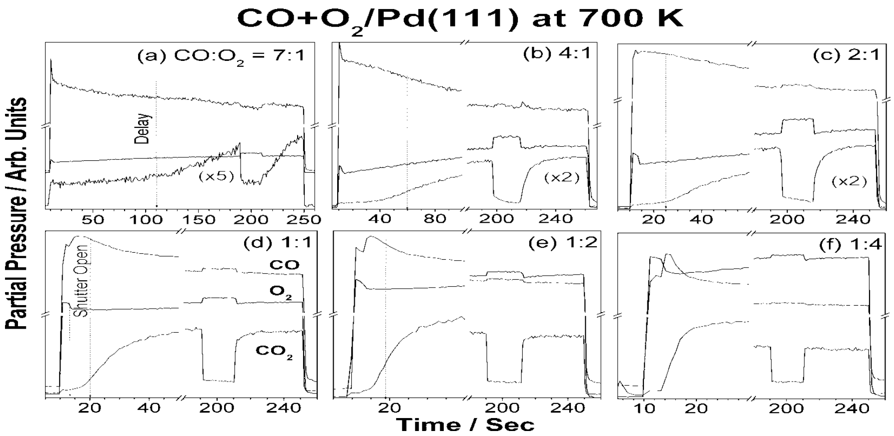

Figure 1: Temporal evolution of the partial pressure of CO, O_2, and CO_2 during the CO + O_2 reaction at 700 K on Pd(111) surfaces for different CO:O_2 ratios between 7:1 and 1:4. Dashed arrows indicate the shutter opening and dotted arrow indicates the onset of simultaneous CO adsorption and CO_2 desorption. Beam oscillation was carried out between t = 190-210 s to measure the steady state rate.

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Feasibility of Photogalvanic Solar Cells in Present Scenario of Energy Crisis

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There are not many people now days that need to remind the energy crisis all over the world. As we run out of the all the energy recourses we find a heavy stress due to earths limited energy resources. All the energy sources available as coal, Petroleum and Natural gases are quite low to serve all over the world for all energy requirements and these sources also increase the pollution and global warming. The day is not far on which all the stored energy resources will ends. So there is an urgent need to search a renewable energy source like solar energy. Photogalvanic conversion of solar energy in to electrical energy has attracted attention of scientists with bright future prospect. The photogalvanic effect reported first of all by Rideal and Williams [1]. The photogalvanic solar cells are based on some such chemical photochemical reaction, which give rise to high energy products on excitation by a photon. These energy rich products loose energy electrochemically. Recently we reported some photogalvanic solar systems by using some efficient dyes as photosensitizers [2-3]. The performance and conversion efficiency of photogalvanic cell composed of dye in presence of anionic surfactant has been studied and analyzed. The performance and conversion efficiency cell is observed. The effects of various parameters like pH, concentration of dye, concentration of surfactant, diffusion length and electrode area on cell's power generation was also observed. Finally feasibility of solar cells checked.

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Non-Covalent Charge Transfer Assemblies for Selective Sensing Of Anions in Water

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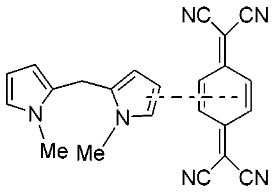
The development of new chemosensors for ions is an important area of investigation in supramolecular chemistry due to their fundamental roles in medical diagnostics, physiology and environmental applications. A number of examples of sensors based on mass changes, electrochemical devices, biosensors, chromogenic and fluorescent chemosensors have been reported over the past few years. Colorimetric sensing events have gained more importance owing to the ease in monitoring of the process without resorting to sophisticated techniques. A great effort has been invested in developing simple-to-make and use naked-eye diagnostic tools for sensing of metal ions.

Anions are ubiquitous in nature. Fluoride is the smallest nucleophilic anion, which is administered in the treatment of osteoporosis and is often added in dental pastes and water because of its beneficial effects. However, its excess may lead to the emergence of dental caries, fluorosis, urolithiasis etc. For these reasons, the development of probes that can sense this anion in water has become a topical objective.

In this poster presentation, synthesis and use of charge transfer assemblies such as dipyrromethane-7, 7', 8, 8'-tetracyanoquinodimethane (TCNQ) **1** as a selective receptor for fluoride ion (as Na$^+$ salt) in aqueous solutions shall be presented. Since the sensing process invokes a visible color change, this process can be described as "Naked eye" sensing [1]. Conceptually the present assembly utilises N-methylated pyrrole and thus does not rely on hydrogen bonding with fluoride but senses it through perturbation of the assembly due to weak p-interactions.



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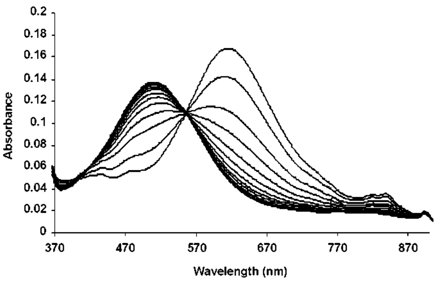

Changes in the absorption spectrum of **1**, upon addition of F$^-$ (Visual change: Blue to Pink).

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(b) Paramjit Kaur, Sandeep Kaur and Kamaljit Singh (Communicated)

Ruthenium(II) complexes of some thiosemicarbazones: Structural and DFT study

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Six new thiosemicarbazones have been prepared by reacting six different (4-aryl)thiosemicarbazides with thiophen-2-aldehyde. Reaction of the thiosemicarbazones with $Ru(PPh)_3Cl_2$ afforded compounds of formula *cis*-$[Ru(PPh_3)_2(L)_2]$ (L = deprtonated thiosemicarbazone ligand). X-ray single crystal structure determination of four of these complexes reveal that thiosemicarbazone ligands coordinate to the ruthenium center through the hydrazinic nitrogen and sulfur forming four-membered chelate rings with ruthenium in *cis*-N_2 *trans*-S_2 *cis*-P_2 coordination environment. The complexes undergo quasi-reversible one electron oxidation at ~0.5 V *vs* Ag/AgCl electrode. DFT calculations on these complexes indicate that HOMO has ~35% metal character and there is substantial delocalization of the electrons over ligand backbone. Thus assignment of the oxidation state of the metal ion for such molecules must be made with caution, as during the one electron oxidation of the complexes the electron is lost from a molecular orbital, having appreciable ligand contribution, rather than from a pure metal centered orbital.

Study of Catalysts Based On Non-Precious Metals for Applications in PEM Fuel Cells

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The search continues for catalysts, based on non-precious metals that can act as cathodes in proton exchange membrane (PEM) fuel cells. This is motivated by the cost of Pt for the mass production of automobiles using currently available technology. Key challenges for the development of new catalytic materials for this application concern activity for oxygen reduction, stability in acidic environment, and open circuit potential (OCP). Our research focuses on thin-film materials prepared by magnetron sputtering, and formed from Fe, Co and/or Ni in combination with S or Se. A fundamental approach is emphasized in which performances of the model catalysts are evaluated against a Pt standard. This paper will review the new information gained so far by characterizing these catalysts with such techniques as scanning Auger microscopy, X-ray photoelectron spectroscopy, micro-Raman spectroscopy and X-ray diffraction, before and after application of electrochemical tests. Thin films have been produced with OCP values approaching 0.9 V (vs. reversible hydrogen electrode).

Synthesis, Structural Elucidation, Electrochemical, DNA And Antimicrobial Studies Of Transition Metal Complexes Derived From A Tetradentate Schiff Base

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A new tetraaza macrocyclic Schiff base, synthesised from 3-hydroxy-4- nitrobenzylideneaceto-toluidide and *o*-phenylenediamine, acts as a tetradentate ligand and forms solid cationic complexes with Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}, Mn^{II}, VO^{IV} and Cd^{II} salts in ethanol. Microanalytical data, magnetic moment, electronic, IR , Mass and ESR techniques were used to characterize the structures of the synthesised Schiff base ligand and its complexes. Electronic absorption and IR spectra of the complexes suggest that all the complexes exhibit square-planar geometry while the oxovanadium complex shows square-pyramidal geometry. Elemental analysis and mass spectral data of the Schiff base and their complexes suggest that the general formula of the complexes is [ML]X where L=Ligand, X= $2Cl^-$ or SO_4^{2-}. Electrolytic behaviour of the chelates was assessed from their higher conductance data. Monomeric nature of the chelates was confirmed from their magnetic susceptibility values. Electrochemical studies of copper complex in DMF using cyclic voltammetry technique indicate the existence of unusual oxidation states such as Cu(III), Cu(I) which are stabilized by the ligand system. Antimicrobial study of the ligand and its complexes (MIC values) indicates that the complexes exhibit higher antimicrobial activity than the free ligand. The nuclease activity of the above metal complexes shows that the complexes cleave DNA through redox chemistry. In the presence of H_2O_2 , all the complexes are capable of cleaving Lambda DNA.

A Convenient synthesis of Palladium nanoparticles and Catalysis of Hiyama Coupling Reaction in Water

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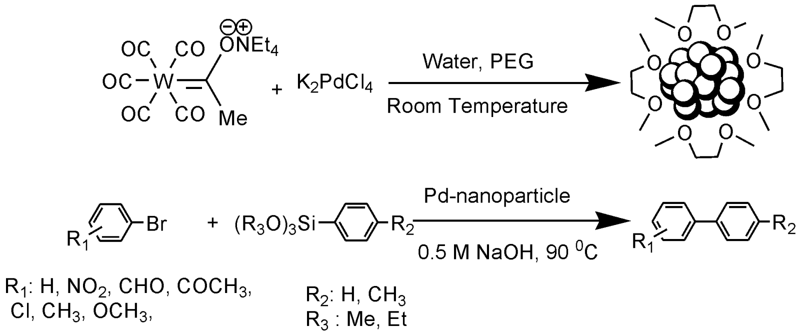
Transition-metal-catalyzed reactions have become an important tool of modern organic synthesis due to their high efficiency, selectivity and wide diversity of possible transformations. In homogeneous metal-catalyzed reactions, each metal complex molecule in solution functions as the catalyst or as a precatalyst. The ligand environment around the metal atom controls its reactivity and protects it from competitive decomposition pathways. In heterogeneous catalysis, the catalytic surface offers a limited number of 'active' sites for catalysis, often necessitating harsher reaction conditions for optimum catalytic efficiency. Of late, nanoparticles emerged as useful and unique catalysts whose efficacy is attributed to their characteristic high surface-to-volume ratio that translates into more number of active sites per unit area compared to standard heterogeneous catalysts.



We developed a mild synthetic method for the generation of colloidal palladium in water utilizing the reducing property of a Fisher carbene complex[1] of tungsten $[(CO)_5W{=}C(CH_3)O(-)\ NEt_4(+)]$ and PEG as capping agent. The colloidal palladium (1 mol%) efficiently catalyzes Hiyama Cross coupling reactions[2] performed in air. The major advantage of the protocol is three-fold: all operations are performed in water, no additive other than a small amount of PEG is required and temperture of reaction is usually lower than 100 °C. A range of substituted aryl bromides were used as substrates. Both electron withdrawing and electron donating substituents yielded excellent results. It was observed that the size of the nanoparticles decreases with increasing amount of the stabilizer PEG-6000 and the catalytic activity and stability of the nanoparticles were found to be inversely correlated. Encourage by these results we applied our catalytic system in other C-C cross-coupling reaction such as Suzuki, Stille, Heck and Sonogashira coupling reaction also. The present procedure is superior to several earlier methods in that it does not use any organic solvent except for work up, nanoparticles can be used straight after preparation without any purification step, and the entire operation is fluoride-free.

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The effect of salts on alcohol dehydrogenease Langmuir-Blodgett film

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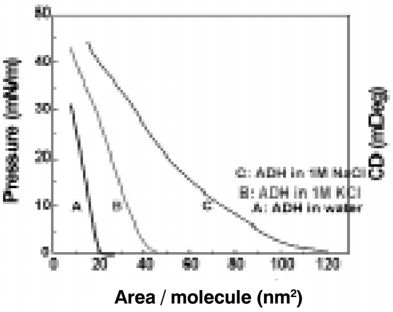
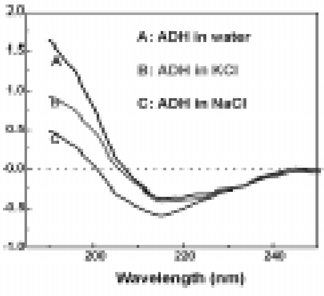
Studies of proteins have emerged considerable interest due to their prospective application in nanobioscience. Immobilization of protein/enzyme with minimum denaturation on a solid support has been found extensively valuable for various technological applications. Langmuir-Blodgett (LB) method is a tool among various developed techniques to study the monolayer and to immobilize biomaterials on solid surfaces. The fundamental points associated with protein/enzyme monolayer are, the structural and conformational regulation of protein monolayer, stability, surface coverage, biological activity and effects of salts/ions etc. We have studied here the basic property of alcohol dehydrogenease (ADH) monolayer and the effect of salts in the subphase on the surface activity of ADH. The ADH was purchased from Sigma. The interfacial surface activity of ADH in presence and in absence of salts was studied by monitoring the surface pressure (p)-area (*A*) isotherm measurement (Fig. 1) on a LB trough. The results show that the surface activity of ADH increases in salt containing subphase. A detail compressibility study was done to characterize the states of ADH monolayer and to select the optimum surface pressure to transfer a well-organized film onto a substrate surface. The conformational change of ADH in different media was studied by circular dichroism (CD) and FTIR spectroscopy. The peak at 215 nm in the CD spectra of LB monolayers (Fig. 2) confirms the formation of b-structure. CD and FTIR studies show that uses of salt perturb the protein monolayer. Therefore, a larger unfolding of ADH molecule is expected by using salt in subphase. The surface morphology of deposited ADH films at different conditions was analyzed by atomic force microscopy (AFM). Fig. 3A shows aggregated structure of ADH (20-30 nm in diameter) at lower pressure. However, at higher surface pressure, ADH is squeezed out from the monolayer and forms fibrillar networks (Fig. 3B). Micro and nano fibrils (Fig. 3C and 3D) are observed in LB-films lifted from salt containing subphases.





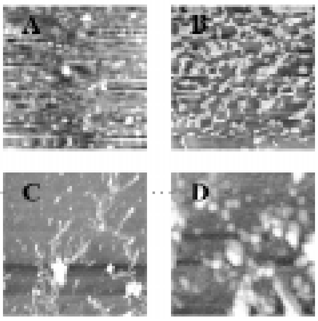


Fig.1. (*p*)-(*A*) isotherm Fig.2. CD spectra

Voltammetric Ultra Trace Determination of Gallium and Indium

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Indium is usually present with gallium in industrial processes using compounds of In and Ga for their semiconductor properties [1]. Further the electrochemical characteristics of In (III) are also considered very close to trivalent gallium [2]. Therefore in present study optimum conditions for the determination of indium and gallium and gallium down to 0.10 ìg/ml by adopting differential pulse polarography (DPP) were developed.

In the presence of 1 M sodium thiocyanate, In (III) and Ga (III) gave distinguishable DP peaks at -0.62 V and –0.77V, respectively. The possibility of interference from aluminate was examined and ruled out [3]. The calibration characteristics in both the cases showed a coefficient of Correlation (r) of 0.99. The DPP procedure was applied successfully for the determination of sub mg level indium and gallium in aqueous matrices where results were found quantitative in terms of recovery of 97.8°/8 and precision (SD ±0.02).

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Excitation wavelength dependence of solvation dynamics in the micelle and the gel phase of a PEO-PPO-PEO triblock copolymer

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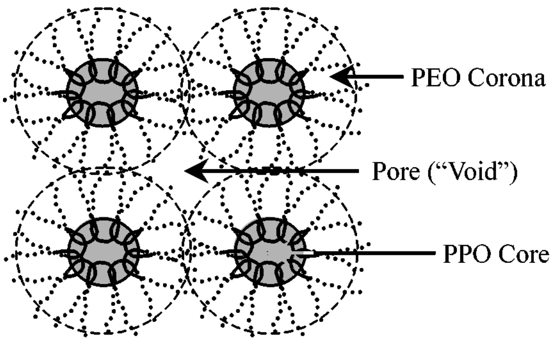
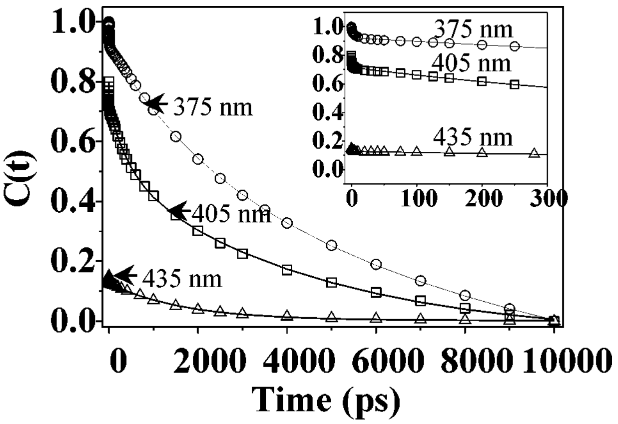
Excitation wavelength (λ_{ex}) dependence is used to spatially resolve the solvation dynamics in different regions of the micellar and gel phase of a water soluble triblock copolymer, PEO_{20}-PPO_{70}-PEO_{20} (Pluronic P123). This is studied by femtosecond and Pico second time resolved emission spectroscopy [1-2]. In the gel, the micelles associate to form an interconnected network with inter-micellar distance (140 Å) less than the sum (160 Å) of the radii of the micelles. Both the P123 micelle and gel, exhibits a large (~24 nm) red edge excitation shift (REES) due to heterogeneity in the environment. Solvation dynamics in the interior of P123 micelle and gel are found to depend strongly on the excitation wavelength. With increase in λ_{ex}, the contribution of the bulk-like exposed region having an ultrafast component ($\leq$2 ps) increases more than 10 times. There is concomitant decrease in the contribution of the ultraslow component arising from the buried region.





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Synthesis, spectroscopic and DFT study of potential ligands of N’-(2-methoxy-benzoyl)-hydrazine carbodithioate ester

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In the present work synthesis and spectroscopy studies of two new ligands, N’-(2-methoxy-benzoyl)-hydrazine carbodithioic acid benzyl ester (**1**) and N’-(2-methoxy-benzoyl)-hydrazine carbodithioic acid ethyl ester (**2**) are reported. The compounds (**1**) and (**2**) were synthesized by stirring a $CHCl_3$ / MeOH suspension of potassium [N’-(2-methoxy-benzoyl)-hydrazine]-carbodithioate with benzyl chloride / ethyl iodide for 3-4 h, respectively. On slow evaporation of the solution solid product were obtained. These compounds have been characterized by I.R., NMR and single crystal X-ray spectroscopy. The white single crystal obtained by slow evaporation of (**1**) after 1 day crystallizes in triclinic crystal system with space group P -1 which has unit cell parameters : a = 7.493(2), b = 10.230(3) , c = 11.212(4) 74.56(3), a = 81.49(3) , b = 77.61(2) , g= 805.3(4) and Z = 2. The molecular packing show intermolecular C-H…S and N-H…O (carbonyl oxygen) hydrogen bonding and N-H…O (2-methoxy group) intramolecular hydrogen bonding which have stabilized the molecular packing (Figure 1). A correlation of experimental and theoretical results concerning the geometric and electronic structure description of both ligands has been made. The theoretical investigation based on the density functional theory (DFT) was performed for these molecules. The theoretical results are in good agreement with the experimental data. The topological analysis of electron density (AIM theory) was applied to confirm the existence of intermolecular H-bond in the molecule. The molecular orbital diagrams of (**1**) and (**2**) have been calculated on the basis of DFT.

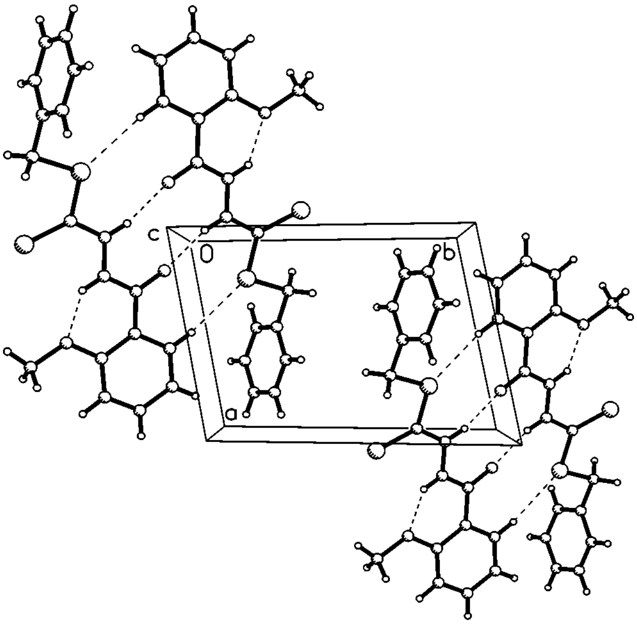

Figure 1. The molecular packing of 1 indicating intermolecular or intramolecular hydrogen bonding

Twisted Intramolecular Charge Transfer (TICT) Reaction in (Alkylamino)benzonitriles in Electrolyte Solutions: Concentration and Ion Size Dependences

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Steady state [1] and time resolved [2] spectroscopic studies have been performed with three intramolecular charge transfer molecules, 4-(1-azetidinyl) benzonitrile (P4C), 4-(1-pyrrolidinyl) benzonitrile (P5C) and 4-(1-piperidinyl) benzonitrile (P6C), in ethyl acetate and acetonitrile in presence of several perchlorate salts at room temperature to investigate the effects of electrolytes on the equilibrium constants and reaction rates in these TICT molecules. Electrolyte concentration and ion-size dependences of several spectroscopic properties such as quantum yield, absorption and emission transition moments, radiative and nonradiative rates, and changes in reaction free energies associated with $LE \rightarrow CT$ conversion have been determined for these molecules. Quantum yields have been found to decrease significantly upon addition of electrolyte for all these molecules. Formation of *charge transfer* (CT) state is found to be strongly favored over the *locally excited* (LE) state as the electrolyte concentration is increased, electrolyte effects being more pronounced in ethyl acetate than in acetonitrile. Changes in reaction free energies ($-\Delta G_r$) for the $LE \rightarrow CT$ conversion reaction in presence of electrolyte are more pronounced in ethyl acetate than in acetonitrile. While quantum yield is found to decrease with the increase in ion-size, ΔG_r remains largely insensitive to the variation in ion diameter. Time resolved studies with these molecules in ethyl acetate in presence of $LiClO_4$ indicate that the average reaction time for $LE \rightarrow CT$ conversion increases at low electrolyte concentration and then decreases to become comparable and even lower than that in the pure solvent. Except for Mg^{+2}, the average reaction time decreases linearly with the ion-size in 0.5(M) $LiClO_4$ solution of ethyl acetate. The observed electrolyte concentration dependence of the average reaction time for both the molecules agrees well with the calculated values from the theory of Zwan and Hynes [3] in the broad barrier over damped limit with barrier frequency, $\omega_b \approx 2x10^{12} s^{-1}$.

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Ferromagnetic carbons derived from low molecular weight organic compounds

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That ferromagnetism may occur in carbonaceous compounds has been predicted long ago, Mataga [1]. Only recently Esquinazi et al [2] observed ferromagnetic signals in highly oriented pyrolytic graphite. Here we report that combustion product of small organic molecules like toluene and naphthalene clearly shows ferromagnetic signals at 300K with saturation magnetization as high as $1X10^{-3}$emu/g, measured in a SQUID magnetometer. FTIR Studies showSp^2CH (arom) and sp^3CH_2 (sym&asym) stretching modes suggesting these are hydrogenated amorphous carbon. Electron diffraction diagram of these materials show essentially two rings, one corresponding to d_{002} of graphite and another at a still lower angle. Interplanner spacings (d values) increase as the carbon content of the parent material increases. TEM & SEM studies reveal that these are present in one phase and depicts 3-dimensional carbon network made up of nearly spherical globules of 50-80nm diameter. EDS study confirms absence of any magnetic contaminants. Hence the origin of ferromagnetism is intrinsic in nature and plausible reasons were discussed in details.

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Synthesis Of Thio-Sugar Based Amino Acids

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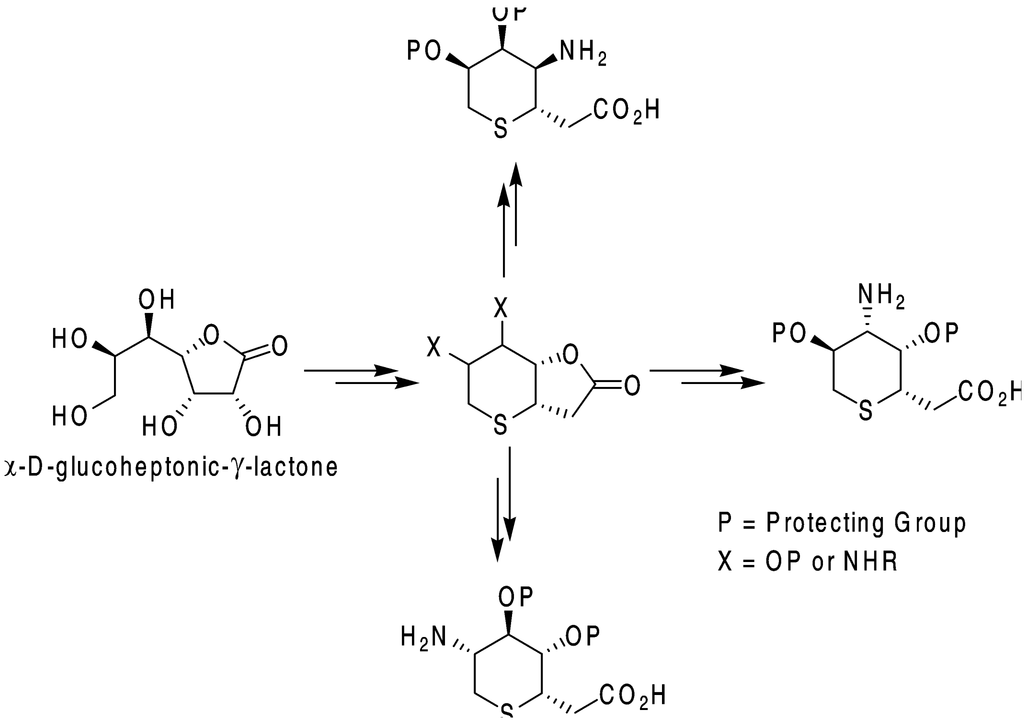
Synthesis of thio-sugar is of continuing interest in contemporary organic synthesis due to their importance in the glycosidase inhibition.[1] Additionally, sugar based amino acids are interesting and important class of templates in the area of peptidomimetic[2] and supramolecular studies.[3] So, the challenge lies in the synthesis of thio-sugars and thio-sugar based amino acids in an elegant manner. In our laboratory, we have demonstrated earlier the efficacy of sulfur transfer reagent, Benzyltriethylammonium tetrathiomolybdate [BnNEt$_3$]$_2$MoS$_4$. Herein, we present the synthesis of various thio-sugar based amino acids derived from a-D-glucoheptonic-g-lactone utilizing [BnNEt$_3$]$_2$MoS$_4$ as the sulfur transfer reagent.



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Modelling and Synthesis of GSK-3 Inhibitors, Targeting Substrate Binding Site

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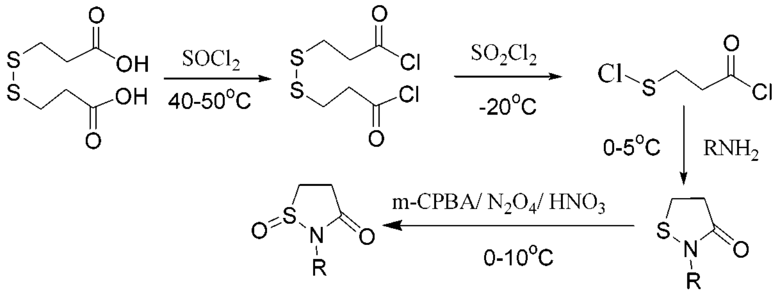
Glycogen Synthase Kinase-3 (GSK-3), a serine/threonine kinase, is an important target for anti-diabetic agent design [1]. Inhibition of GSK-3 activity can be achieved through three distinct mechanisms i) Metal-ion competitive approach at Mg^{2+} binding site, ii) ATP competitive manner in ATP binding pocket and iii) ATP non-competitive manner in substrate interaction domain. It is important to inhibit GSK-3 selectively over other phylogenitically related kinases, in order to achieve the net effect of inhibitors. In order to solve the problem of selectivity in ATP competitive inhibitors several rational approaches have been employed by different research groups [2, 3]. However, there are some possible problems with the ATP competitive GSK-3 inhibitors that have been developed so far. Here we report 2-substituted 1-Oxo-1 l^4-isothiazolidin-3-one as ATP Non-competitive GSK-3 inhibitors which bind GSK-3 at substrate binding site and consequently inhibit the activity of the enzyme. FlexX based molecular docking studies and virtual screening of the newly designed ligands was carried out to understand the interactions of these ligands in substrate binding site. Higher scored ligands have been screened for TOPKAT based *in silico* toxicity prediction. Ligands selected from this virtual screening exercise have been taken up for synthesis.

Scheme-1



Scheme for preperation of ATP Non-Competitive 2 substituted 1-Oxo-1λ^4-isothiazolidin-3-one ligands

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Rauhut-Currier Reaction of Conjugated Nitroalkenes

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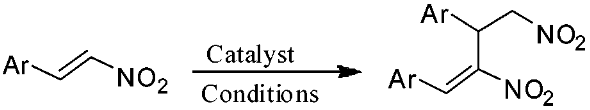
The self-coupling reaction of activated alkenes, commonly known as Rauhut-Currier reaction, is reported only with acrylates [1] and acrylonitriles.[2] While similar coupling between the a-position of activated alkenes with other electrophiles, the Morita-Baylis-Hillman (MBH) reaction, has received tremendous attention over the past decade, Rauhut-Currier reaction is less known because it suffered from limited substrate scope. This is not only because the reaction is a dimerization but also because the reactive intermediate involved is highly sensitive towards electronic and steric factors and readily undergoes oligomerization and/or polymerization.



As part of our programme towards highly efficient synthesis of multifunctional molecules that exhibit interesting properties including bioactivity,[3] we have investigated the Rauhut-Currier reaction of nitroalkenes. Extensive optimization of the reaction conditions by screening various nucleophilic Lewis bases and solvents enabled us to obtain the dimerization products from a variety of aromatic and heteroaromatic nitroalkenes in satisfactory yield. Efforts are currently underway towards the synthesis of heterodimers using mixture of two nitroalkenes as well as development of diastereo- and enantioselective versions of this reaction.

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Synthesis of New Isoellipticine Derivatives through Imino-Diels-Alder reaction

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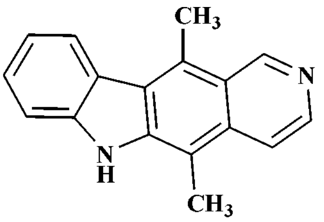
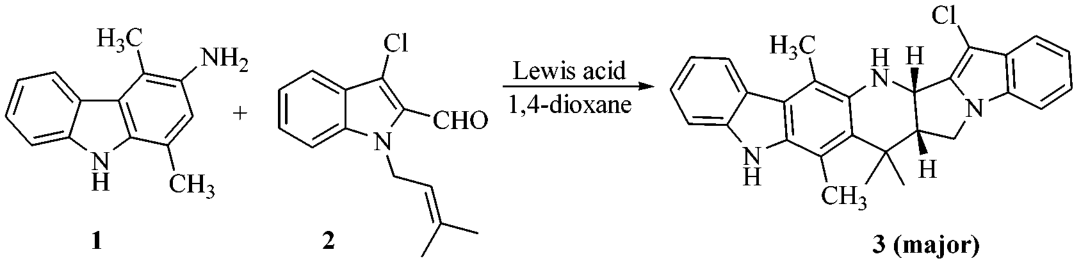
Ellipticine is a naturally occurring alkaloid of the 6*H*-pyridocarbazole family; this compound and its derivatives are endowed with antitumor and anticancer properties. They are DNA intercalating molecules and their high DNA binding affinity is thought to be responsible in part for this pharmacological properties.[1-2] 14-chloro-6,7,7,16-tetramethyl-5,7,7a,8,14b,15-hexahydrobenzo[5',6']pyrrolizino[2',1':5,6]pyrido[3,2-b]car-bazole derivatives, which are structurally similar to isomeric ellipticine fused with pyrroloindole moiety, have been synthesized.



Ellipticine



1 **2** **3 (major)**

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Site-Selective Functionalization Of Medicinally Potent Heterocycles

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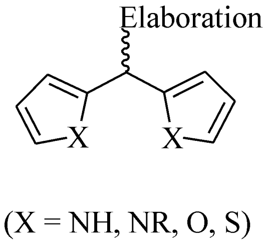
Heterocyclic chemistry continues to be in the focus of life science oriented research. Structural functionalisation is a unique tool for fine-tuning biological properties and offers extra bonus in this context. This poster presentation shall feature two pertinent issues. First, demonstration of lithiation – substitution sequence [1] in the field of some interesting bisheterocyclyl methanes **1**, intermediates for a variety of important (medicinally and otherwise) macrocyclic systems such as *meso*-porphyrins, calix[4]pyrroles etc. Second, novel and dependable routes to structural elaboration of dihydropyrimidinones **2** – potent cardiovascular agents and special emphasis shall be laid on the merit of the functionalisation approach [2].



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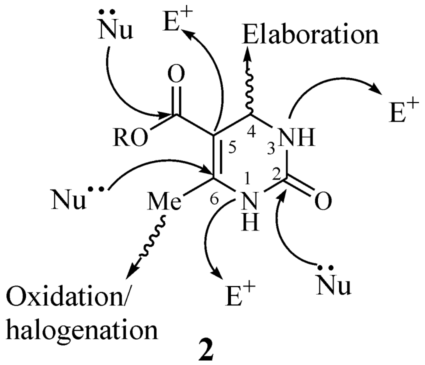

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Trehalose – Does It Entrap Or Replace Coupled Water In Amino Acid Solutions?

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Trehalose is known to stabilize protein structures in aqueous solutions. The molecular level understanding of such mechanism could be explained either by one of the two hypotheses; wherein the coupled water is either entrapped by trehalose in proteins or is replaced. The results from the present study on aqueous solutions of amino acids with trehalose demonstrate the partial replacement of water molecules in the near vicinity of amino acids resulting in enhancement of structural ordering of hydrated amino acids. This is reflected in the increased values of experimentally determined hydrodynamically coupled water using quartz crystal microbalance (QCM) and solid/liquid interfacial tension of aqueous solutions of amino acids with trehalose. The study suggests a Kosmotropic role of trehalose in Protein stabilization.

A Novel Organo-Catalyst For Chemo-Selective *O-Tert* -Butoxycarbonylation Of Phenols

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The occurrence (30% frequency) of hydroxyl groups [1] in the preparation of drug candidates makes their protection/deprotection an important and frequently needed exercise.[2] A common approach to protect hydroxyl groups is acylation [2,3] but the regeneration requires hydrolytic cleavage under strong alkaline conditions [2] and is detrimental to other functional groups. Chemoselective deacylation is achievable under neutral or virtually neutral and non-aqueous conditions following ‘demand-based thiolate anion generation’ protocols but these require elevated temperature and high boiling solvent.

The inertness of *tert*-butyl carbonates (*O*-*t*-Boc) for routinely adopted experimental conditions in organic synthesis, and the ease of removal under mild acidic environment, [2] makes *O*-*tert*-butoxycarbonylation an efficient alternative. However, the drawbacks of the limited methodologies for *O*-*t*-Boc formation of phenols necessitate the development of a better methodology. Although Lewis acid catalysed *N*-*tert*-butoxycarbonylation has recently gained importance, phenols forms the *tert*-butyl ethers with $(Boc)_2O$ in the presence of a strong Lewis acid highlighting the need for organo-catalyst for which DMAP is the only choice available. However, DMAP induces formation of symmetrical carbonates and carbonic-carbonic anhydrides and is toxic.

The present work will demonstrate a novel organo-catalyst for chemo-selective *O*-*tert*-butoxycarbonylation of phenols.

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Aqueous-Mediated Synthesis Of Heterocyclic Ketene Aminals

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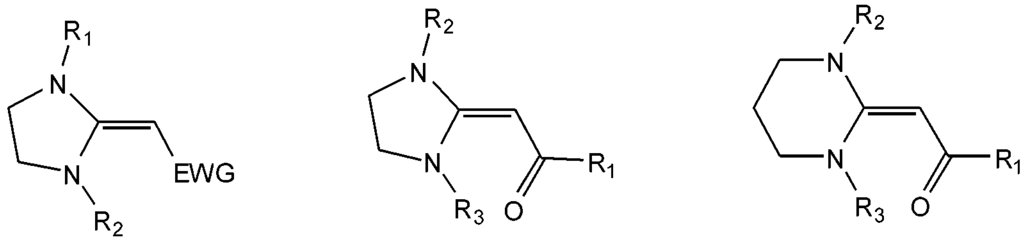
Heterocyclic ketene aminals are versatile ambident synthetic intermediates, which combine the nucleophilicity of enamines and the electrophilicity of enones. They have been utilized as building blocks for the synthesis of a wide range of heterocycles and natural products [1]. We wish to report herein an easy and green method for the synthesis of the heterocyclic ketene aminals **1, 2, 3** (**Scheme-1**). Our method involves the reactions of á-oxoketene dithioacetals [2] with various diamines and refluxing in ordinary water.



1 **2** **3**

EWG = NO_2, CN, CO_2Et, R_1= H, alkyl, aryl, R_2 = H, alkyl, aryl, R_3 = H, alkyl, aryl

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A Short, Enantioselective Synthesis Of 2-Hydroxy Piperidine Dderivatives From d-Hydroxy Lactones

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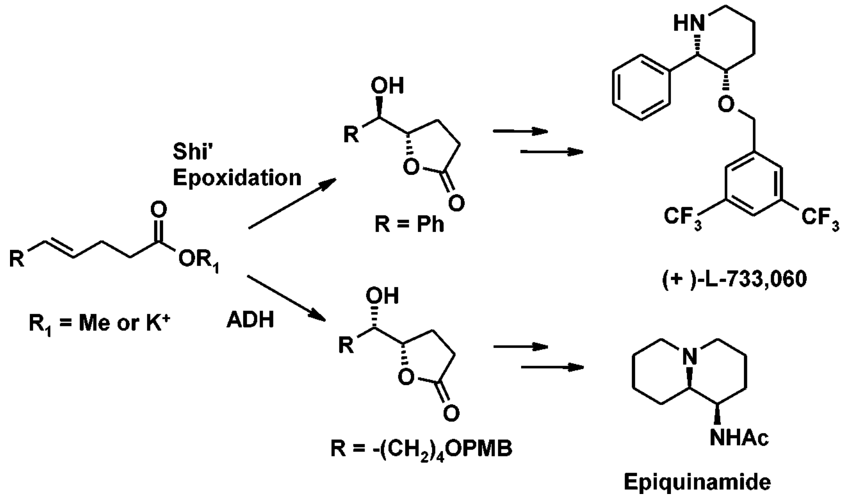
Substituted piperdine is often encountered in the biologically active alkaloids and possess diverse biological activities. The plant enzymes readily synthesize piperidine from amino acids. However, the construction of six-membered heterocycle of piperidine nucleus in the laboratory with fixed stereochemistry is challenging to chemists. Here, we present the synthesis of 2-hydroxypiperidine derivatives i.e (+)-L-733, 060 and epiquinamide. (+) L-733, 060 is a synthetic NK1 receptor antagonist to show clinical utility in a variety of disorders including migraine, rheumatoid arthritis and pains. Epiquinamide has been found to be highly selective for b2 nicotinic acetylcholine receptors (nAChRs), as such representing a new structural class of nicotinic agonists and could be considered a lead compound for the development of nAChR therapeutic agents. The synthesis of (+) L-733, 060 involves the Shi' epoxidation of g,d-alkenoate to get the d-hydroxy lactone with *trans* selectivity while the latter make use of asymmetric dihydroxylation to obtain the *syn* selectivity. Both the synthesis involve similar reaction sequences such as Johnson-Claisen rearrangement, formation of hydroxy lactone, inversion of hydroxyl group with azide, reductive cyclization of azidolactone to give the hydroxy piperidine. This route is practical and high yielding to construct the piperidine rings.



Synthesis Of Homoallylic Alcohols Using Cui As Catalyst

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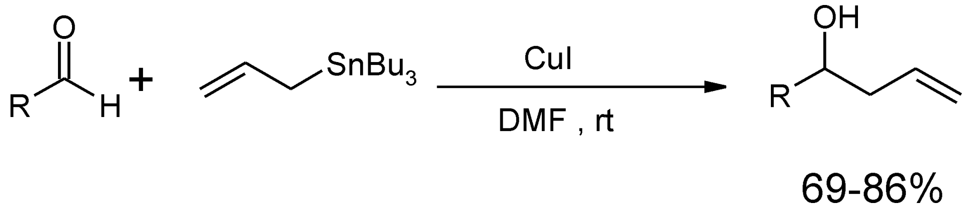
The addition of allyl metal reagents to aldehydes is an important method for carbon –carbon bond formation. In recent years, several Lewis acids, especially metal Lewis acids or transition metal complexes have been utilized extensively to catalyze this transformation. Most of these methodologies are fraught with limitations such as excess use of catalyst (or co-catalyst), moisture sensitive conditions, stoichiometric amount of promoter and poor substrate selectivity. There has been increasing interest in the development of new catalysts, which are cheap, air-stable and easily available commercially. Recently CuI has emerged as a very effective catalyst for various organic transformations. We have developed a simple methodology for the synthesis of homoallylic alcohols using allyl tributyl stannane as allylating agent in presence of CuI as catalyst (Scheme -1) [1].



Scheme-1

The reaction was carried out by stirring a mixture of an aldehyde (1 mmol), allyl tributylstannane (1.05 mmol) CuI (0.15 mmol) in DMF (2 ml) at room temperature. Both aromatic and aliphatic aldehydes underwent homoallylation efficiently to produce homoallylic alcohols in good yield (69-86%).

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Deoximation By Phase Transfer Oxidants Under Microwave Irradiation In Solvent Less System

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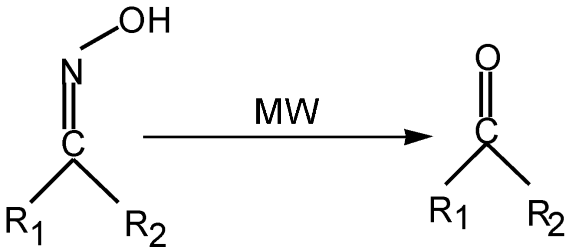
The protection of certain functional groups and the deprotection of the protected derivatives constitute important processes in the multistep synthesis of polyfunctional molecules. Regeneration of ketone and aldehyde from their oximes is an important reaction in synthetic organic chemistry as the oxime serves as an efficient protecting group for carbonyl compounds [1, 2]. Further, as the oxime can also be prepared from non-carbonyl compounds, the formation of carbonyl compounds from oximes represents a potential route for the synthesis of aldehyde and ketone[3]. Thus there has been continuing interest in the development of new reagents and methodologies for the regeneration of carbonyl compounds from their oximes and several deoximation reagents have so far been developed.

Solvent less reactions under microwave irradiation is gaining ground in organic synthesis, because of the increased emphasis on eliminating and if not possible minimizing the use of organic solvents. Further the use of microwave irradiation results in manifold reduction of reaction time. We have been investigating the use of cerium based phase transfer oxidants in the oxidation of alcohol as well as the oxidative deoximation of oximes to their parent carbonyl compounds both in homogeneous and heterogeneous systems. It has been observed that reactions under microwave irradiation take much less time, but give good yields. The reaction also involves easy work up procedures for the recovery of the products. Here in we report the use of two phase transfer oxidants cetyl dimethyl benzyl ammonium cerium nitrate and cetyl trimethyl ammonium cerium nitrate in the regeneration of carbonyl compounds from their oximes.



The carbonyl compounds were characterized by their spectroscopic analysis and the comparison of the data with authentic samples. Of the two reagents, cetyl trimethyl ammonium cerium nitrate was found to be a better and more effective deoximation reagent. Further, the nature of the other functional groups present in the neighbourhood was found to influence the efficiency of the deoximation reagents.

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Isolation Of Bioinsecticides From The Striped Tiger Butterfly, *Danaus Genutia* (Lepidoptera: Nymphalidae)

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Most of the attempts have centered on the idea of isolating and charecterizing the cardenolides derived from these insects or plants, however this is the first such attempt to study and analyze the effect of cardenolide containing extract as a source of potential bio-insecticides. We wish to analyse the possible effects of toxic alkaloids isolated from these butterflies as bio-insecticides.

All works reported here have been carried out under strict laboratory conditions at the Department of Entomology, College of Agriculture, UAS, GKVK with permission from respective departments. We took extracts from wholebody Striped Tiger butterflies, with 95% pre chilled ethanol, filtered and concentrated by HPLC and then spraying the extract on pre-trimmed mustard leaf (each concentration having a set of three petriplates with one leaf each having 10 Diamond Black Moth larvae released) with corresponding concentrations of the concentrated and diluted extracts. Then, we checked the mortality rate for each concentration every 24 hours for seven continuous days and reported the same.

At the end of 168 hours, i.e., after 7 days, 2% Extract showed a maximum of 68.99% of Corrected Mortality and a minimum of 41.11% of Corrected Mortality. 0.25% Extract showed a maximum of 42.91% of Corrected Mortality and a minimum of 14.44% of Corrected Mortality. This clearly shows that 2% Extract has given the best results followed by 0.25% Extract.

Thus, we showed that the Butterfly Extract contains toxic alkaloids & cardenolides that have the capacity to kill the larvae of the DBM, the pest of spinach. As expected results were interpreted and calculated and it was seen that the 2% concentration of extract showed the best results i.e., 68.99% mortality followed by 0.25% concentration of extract which showed 42.91% mortality. The data obtained from the graph shows the best results in 2% Extract, but the 3% extract has shown a diminished mortality rate because the larvae did not feed on such a higher concentration of extract sprayed leaf. Our next step is to procure more of 2% and 0.25% Extracts on a large scale basis and subject them to purification procedures of Dialysis and HPLC for separation at a highly concentrated manner, concentrating and characterization of the toxic alkaloids such that we can proceed to Field Trials on a broader axis.

A First One-Pot Synthesis, Isomerization And Synthetic Utility Of Mono And Bis Morita-Baylis-Hillman Adducts Of 1,1'-Ferrocenedialdehyde

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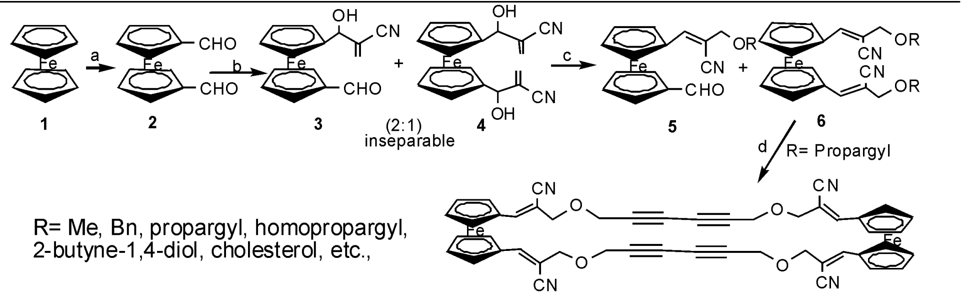
The chemistry of ferrocene is still an important research area due to its applications in the area of novel materials development, asymmetric catalysts, nonlinear optics, biological properties and electrochemistry [1]. Amongst various C-C bond forming reactions, the Baylis-Hillman reaction is an important reaction giving rise to densely functionalized molecules and is considered to be atom economic. Functionalisation of ferrocene under mild conditions is difficult task as it requires multi-step rigorous reaction condition. To address the problem and in continuation of our research in the area of novel synthetic applications of Baylis-Hillman adducts [2], particularly with ferrocene derivative, we have recently examined the reaction of Baylis-Hillman adduct of ferrocenealdehyde **2** with various oxygen and carbon nucleophiles in presence of montmorillonite K10 clay catalyst. The reaction was found to afford highly functionalised excellent yield of *E*- and *Z*-trisubstituted alkene derivatives of ferrocenealdehyde. This poster aims to explain on our recent findings of a novel and first one-pot synthesis of mono- and bis- adduct of Morita-Baylis-Hillman adduct of 1,1'-ferrocenedialdehyde. These adducts undergone a facile stereoselective isomerization reaction with a number of saturated, unsaturated, aromatic alcohols to yield highly functionalised trisubstituted alkene derivatives in excellent yield. Synthetic utility of mono and bis- propargyl derivative of 1.1'-ferrocenedialdeyde has been demonstrated in the synthesis of novel macrocycles. The study is shown in Scheme 1. The results will be discussed in detail.



a. *n*-BuLi, TMEDA, ether, DMF, reflux ; b. CH_2=CHCN, RT, 6h; c. ROH, montmorillonite K10 clay, heat, 3h; d. $Cu(OAc)_2$, MeOH-Py, Reflux, 1h

Scheme 1

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Synthesis Of Aminoethyl-a,b-Diaminopropionyl (Aedap) PNA - Strategic Modification To Reduce Hydrophobicity

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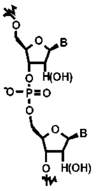
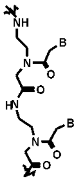
The astonishing discovery of Peptide nucleic acids (PNAs) by Nielsen et. al. [1] that bind with higher affinity to complementary nucleic acids than their natural counterparts, and obey the Watson-Crick base pairing rules resulted in the rapid establishment of a new branch of research focused on the diagnostic and therapeutic applications of this highly interesting class of compounds. PNA is a neutral DNA mimic derived by replacement of sugar-phosphate backbone with N-(1-aminoethyl)glycine units carrying natural nucleobases A, T, G and C with a carbonyl linker having a great potential to act as antisense agents.

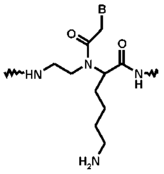
Despite advantages offered by the achiral PNA, it has been of interest to replace the glycine moiety of the backbone with chiral amino acids as mentioned by Corradini et. al.[2]. The side chains of the amino acids were envisaged to be valuable for controlling binding affinity, specificity, hydrophobicity and attachment of ligands to PNA. PNA oligomers incorporating chiral monomers retained the hybridization properties with tolerance for small and medium substituents at the glycine-a position. The lysine-modified oligomers (I) as reported by Haaima et al [3], are known to be more readily soluble in aqueous systems.



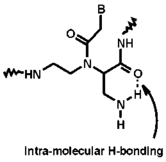
DNA (RNA)



aegPNA



I



Intra-molecular H-bonding

II

We aimed to synthesize PNA monomers having b-aminoalanine moiety in the backbone to get a modified PNA, aminoethyl a,b-diaminopropionyl) PNA (II), with a chiral backbone. This is expected to be stable due to the presence of intramolecular hydrogen bonding. In addition, due to the presence of hanging amine functionality, the low solubility and cellular penetration problems found in classical PNAs might be overcome.

The strategy towards the synthesis of target monomer used asparagine as the starting material. The a,b-diaminopropionic acid was synthesized from it, which after reductive alkylation gave the backbone of desired PNA. Later on, attachment of nucleobase (Thymine) via a methylene carbonyl linker to the backbone gave the desired monomer (II). All the intermediates and the final molecule have been characterized using ^{1}H, ^{13}C-NMR and MS analyses. The syntheses of oligomers were performed following Merrifield Solid Phase Oligomer Synthesis using Boc-strategy and MBHA resin. Sequential combination of the *aeg*-T monomer with our desired monomer were done at different positions of the oligomers e.g. N-terminal, C-terminal, middle modification etc. This was followed by their cleavage from the resin, purification and characterization using rp-HPLC and MALDI-TOF MS techniques respectively. The comparative biophysical studies with DNA/RNA that includes study of duplex and triplex stability by UV-T_m experiments are in the future plans.

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Un-symmetrical polyaza [N_{12}] macrocycle as a potential encapsulating agent: Spectroscopic and Electro–chemical characterization of homo–bimetallic complexes

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Coordination chemistry of polyaza macrocyclic ligands has been a fascinating area of investigations to coordination and bio-inorganic chemists. Macrocyclic ligands capable to bind two or more metal ions giving discrete homo or hetero–bimetallic / polymetallic complexes have received much attentions. However, un–symmetrical polyaza macrocycles which contain non – equivalent coordination sites to bind metal ions have attracted chemists only recently [1]. The polymetallic complexes of such macrocycles can be used as suitable models to elaborate the asymmetrical binding of various metal ions in the metallo–biosites. The individual metal ions exhibits different role in the functioning of the polnuclear metallo – enzyme. Recently, we have reported [2–3] that use of protected two armed reactive substrate, N,N'–bis(N-ethylaniline)propane,1,3-diimine generated from condensation of 1,3-diamionopropane with N-acetylaniline (1:2 mole ratio) induces (in–situ) cyclo–addition reactions with a mixture of amine and HCHO (1:3 mole ratio). This in turn results in stable dihydroperchlorate salt of big size 20–membered [N_8] or 32–membered [N_{12}] un-symmetrical dinucleating macrocycles as stable solid product. An analogous reactive substrate N,N'–bis(N-ethylaniline)–hydrazine-1,3-diimine obtained from reaction of N-acetylaniline and hydrazine (2:1 mole ration) also undergoes an in–situ cyclization process with mixture of 1,3-diaminopropane and HCHO (1:3 mole ratio) which in the presence of $HClO_4$ produces stable solid product identified as dihydroperchlorate salt of 26–membered un–symmetrical [N_{12}] macrocycle, 8,14,24,30 tetramethyl-7,15,23,31tetraphenyl[1,5,7,9,13,15,17,21,23,25,29,31] dodecaazacyclodotri aconta-8,14,24,30-tetraene.dihydroperchlorate. Here-in we report reactions of this macrocyclic ligand towards metal salts and their derivative complexes which afford affording stable solid metal encapsulated products. The products have been characterized using elemental analyses, FTIR, UV–visible (ligand field), FAB–mass spectral and magnetic moment measurements. The cyclic voltametric studies indicate formation of quasi–reversible redox couples $M^{III/II}$ and $M^{II/I}$ compatible with the flexible nature of the macrocyclic cavity.

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Time Resolved Resonance Raman Spectroscopy: A Journey from Nanosecond to Femtosecond Time Domain

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Time resolved resonance Raman (TR3) spectroscopy, a pump-probe technique in fast and ultrafast time domain, provides information directly about vibrational structure, reactivity and dynamics in the excited state [1]. The pump beam excites the molecule to the higher excited state and the probe beam detects the transient species thus formed after a certain delay time, governed either electronically or optically.

In presence of suitable hydrogen donor, aromatic ketones undergo hydrogen abstraction reaction in their excited triplet state. The triplet state thus formed, via intersystem crossing from singlet state, interacts with the ground state hydrogen donor to form a ketyl radical, which may undergo further photoreaction. The triplet state structure and reactivity of isomeric benzoylpyridines, heterocyclic analogues of benzophenone were studied using nanosecond TR3 spectroscopy. The shortening of triplet state lifetime and decrease in intersystem crossing yield is explained on the basis of position of the heteroatom that affects the charge density of carbonyl group and determines the characteristics of the excited state and its efficiency for the hydrogen abstraction reaction.

It is well known that solvent polarity brings out changes in the structure and dynamics of excited triplet state. Xanthone is structurally similar to benzophenone and well known for its solvatochromic behavior [2]. In the present study, effect of solvent polarity on structure in both ground and excited triplet state of xanthone will be discussed.

TR3 spectroscopy has its own limitations of interference from fluorescence background and due to transform limit it can't further be extended to subpicosecond time domain. Femtosecond stimulated Raman spectroscopy (FSRS) [3] can overcome all the above obstacles. FSRS produces good quality vibrational spectra, free from strong background fluorescence and provides quality information in femtosecond time domain. This technique uses two NIR-pulses, one picosecond narrow-bandwidth (5-20 cm^{-1}) Raman pump pulse centered at 787 nm and a broadband continuum Raman probe pulse (800-1050 nm). When the two fields overlap spatially and temporally on the sample, one observes gain features on top of the Probe beam. The ratio of the probe spectrum for Raman pump ON and Raman pump OFF, gives the gain spectrum. Recently FSRS set up is designed and developed in our research group. The preliminary SRS spectrum obtained from various solvents like benzene, CCl_4 and cyclohexane will be presented. Also the SRS spectra of b-carotene in two different solvents are reproduced to validate the setup.

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Synthesis Of Biscoumarins From 4-Hydroxycoumarin And Aaromatic Aldehydes–A Comparative Assessment Of Percent Yield Under Thermal And Microwave-Assisted Conditions

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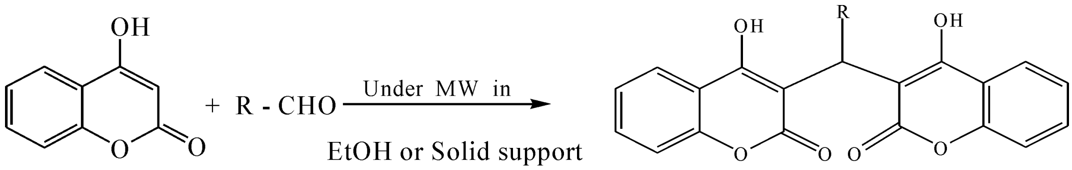
Coumarins form an important group of organic compounds possessing enormous pharmacological, industrial and biological value. 4-Hydroxycoumarin and its derivatives are known for their anticoagulant, spasmolytic, antibacterial and antifungal activity [1]. In addition to this, certain derivatives have also been reported as antitumor and anti-HIV agents [2]. Besides, coumarins find diverse applications as food additives, cosmetics, laser media, non-linear optical chromophores, agrochemicals as well as analytical reagents [3].

In this backdrop, efforts are being made to synthesize as many derivatives of 4-hydroxycoumarin and dicoumarols as possible using microwave eco-friendly methods. Herein, we report convenient syntheses of various biscoumarins by condensing a series of aldehydes with 4-hydroxycoumarin under microwave irradiation for the first time along with a comparative account of their syntheses under conventional conditions. Under microwave, the reaction time has been reduced considerably with improvement in yields in comparison to thermal conditions. Reactions have been carried out both under solvent as well as in solvent-free environment and the adopted procedure provides an energy and time-saving protocol.



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Triphase Catalytic Activity Of A New Insoluble Multi-Site Phase Transfer Catalyst In Etherification Of Methyl Salicylate

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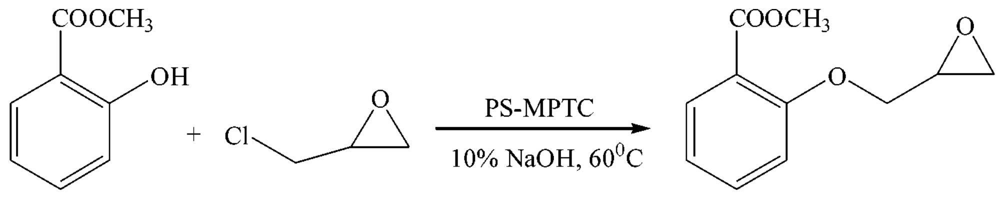
University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu.

Phase transfer catalysis emerged as an indispensable organic technique to carry out the reactions between two immiscible reagents. It is an environmentally friendly and economically profitable method to synthesize wide range of organic chemicals [1,2]. However, the removal and recovery of catalyst was found to be expensive and difficult process in the case of soluble PTCs. This problem can be overcome by immobilizing the PTC on a solid polymeric support i.e. insoluble polymer-supported PTC (PS-PTC) as introduced by Regen [3] and hence it can be easily separated by filtration and recycled. So far, numerous studies have been reported on the use of soluble and insoluble single-site PTCs for various organic reactions, but their activity was very poor due to the presence of single active-site. The important considerations in the selection of the catalyst are economy of scale and efficiency of the phase transfer catalysts specifically on the industrial-scale preparation of organic compounds. In order to fulfill these requirements, multi-site PTCs (MPTCs) containing more than one active-site were developed by Idoux et al. Further, there are only few reports available on the synthesis of polymer-supported MPTCs. In the present study, a new polymer-supported MPTC containing three active-sites has been synthesized, characterized and its catalytic activity was determined through etherification of methyl salicylate.

Initially, the polystyrene bound polymer beads were prepared by suspension copolymerization of styrene (73%), divinylbenzene (2%), and vinylbenzylchloride (25%) using AIBN as a free radical initiator. The resulting co-polymer beads containing pendant chloromethyl groups was condensed with triethyl methanetricarboxylate followed by reduction with $LiAlH_4$. The obtained condensed product was chlorinated using thionylchloride and then quaternized with triethylamine to form a new insoluble tri-site PS-MPTC. The new PS-MPTC was characterized by FT-IR technique, [chloride ion], and SEM analyses. The catalytic efficiency was ascertained through etherification of methyl salicylate using epichlorohydrin under pseudo-first order reaction conditions and compared the same with single-site PS-PTC. The rate constants were calculated by following the disappearance of substrate (methyl slaicylate) through Gas Chromatography. It was found that the tri-site PS-MPTC was » three-fold more active than single-site PS-PTC in terms of rate constant. The kinetic study was performed by varying the experimental parameters, viz., stirring speed, [substrate], [NaOH], [catalyst], and temperature. The observed results reveal that all the kinetic parameters are dependency of the rate of reaction. The activation energy and thermodynamic parameters viz. enthalpy, entropy and free energy change were also calculated. Based on the observed kinetic and thermodynamic results, an interfacial mechanism was proposed for the etherification reaction.



Methyl salicylate

Epichlorohydrin

methyl 2-((oxiran-2-yl) methoxy)benzoate

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Synthesis and Antibacterial Activity of Chalcone Dendritic Architectures

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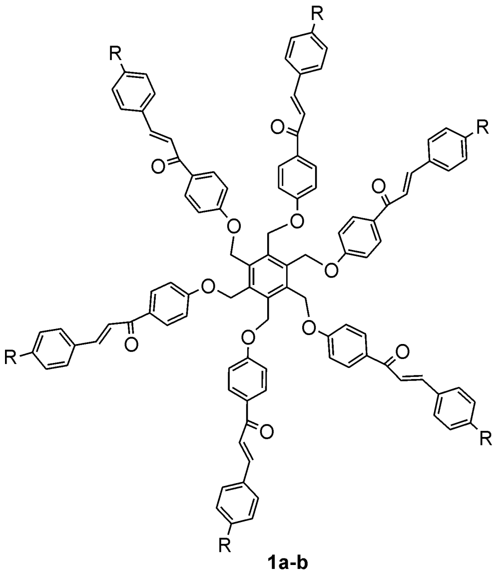
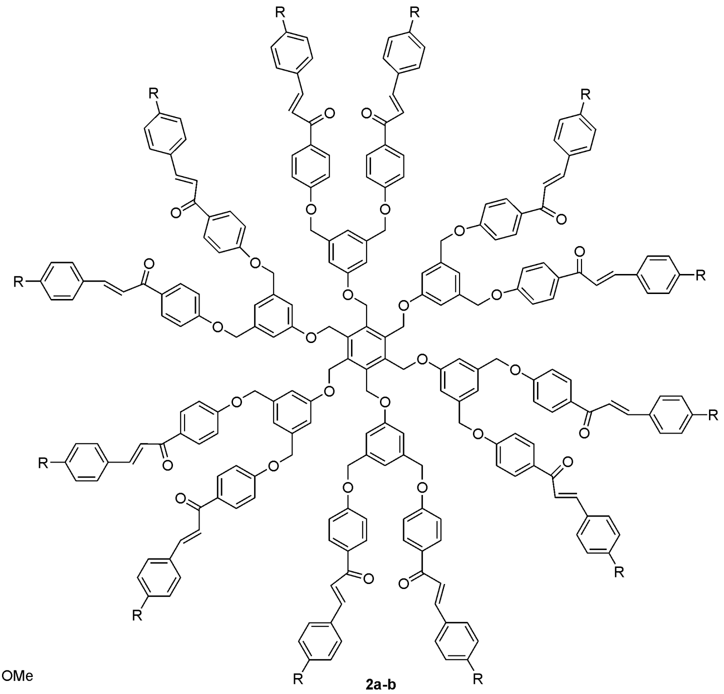
Dendrimers are a new class of spherical polymeric materials. They are highly branched, monodisperse macromolecules. Dendrimers occupies prominent role in macromolecules because of its various applications in the field of biology and material sciences.[1,2] In the recent years, biological applications of dendrimers have been of growing interest.[3] In view of this, chalcone nucleus an important precursor for many potentially bioactive compounds abundantly present in plants. Chalcone derivatives find application as antioxidant, antibiotic and antibacterial agents. However the synthesis of biological active chalcone based dendritic architecture are yet to be investigated. We describe herein the synthesis and antibacterial activity of chalcone based dendritic architectures **1a, 1b** and **2a, 2b**.



1a-b



2a-b

R = H,OMe

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New Ursane-Type Antiplasmodial Triterpenes from Tarenna Zeylanica Leaf

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Malaria, a leading cause of death continues to challenge the world [1]. Resistance of *Plasmodium falciparum* to chloroquine and some other antimalarial drugs continues to increase. In the present study, the phytochemical investigation was carried out on an active leaf extract of *Tarenna zeylanica* collected from forest in the locality of Bhubaneswar, Orissa, aimed at identifying the active antiplasmodials for further research.

Antiplasmodial activities were assessed using the parasite lactate dehydrogenase assay [2] and chloroquine and artemether were used as positive controls. Flash chromatography was performed using TLC grade silica gel (60G, 45ì) and for TLC studies, analytical silica gel 60F254 plates (Merck) were used. Spectra were acquired using NMR (Jeol ECA 600MHz), IR Spectroscopy (Digilab UMA 400) and EI-MS (Finnigan MAT 90 spectrometer) & Micromass Quattro Ultima HPLC- MSMS.

The leaf methanolic extract of *T. zeylanica* possessed antiplasmodial activity with low IC_{50} values, 14.2 and 31.4 µg/ml against chloroquine sensitive (3D7) and resistant (K1) strains of *P. falciparum* respectively. A Literature search revealed that no phytochemical studies have been reported on *T. zeylanica*. In the present study, seven constituents were isolated viz. ZAL1, ZAL3A, ZAL3B, ZAL7, ZAL15 and ZAL16. The activity of ZAL3A, ZAL3B and ZAL7 against strain K1 (IC_{50} = 6.12, 0.72 and 0.67 µg/ml respectively) confirms the activity of *T. zeylanica* seen in this study. The structural identification of these active compounds ZAL3A, ZAL3B and ZAL7 were established by IR, UV, EI & ES-MS and advanced NMR (1H, 13C, Dept, DQF Cosy, HMQC & HMBC) techniques. Compound ZAL 3A was identified as ursa-11, 13(18)-dien-3b, 28-diol and is reported for the first time. The identification of ZAL3B and ZAL7 is in progress and preliminary spectral analysis suggests that these compounds also ursane type of triterpenes.

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Click Chemistry On Sugar-Derived Alkynes And Azido-Alkynes

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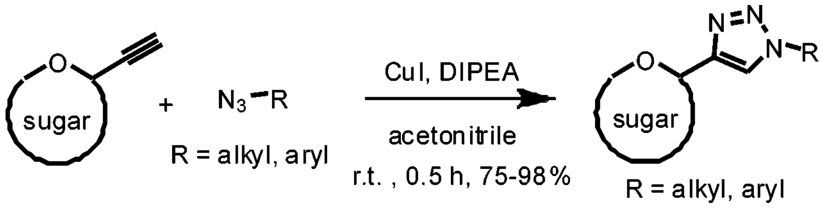
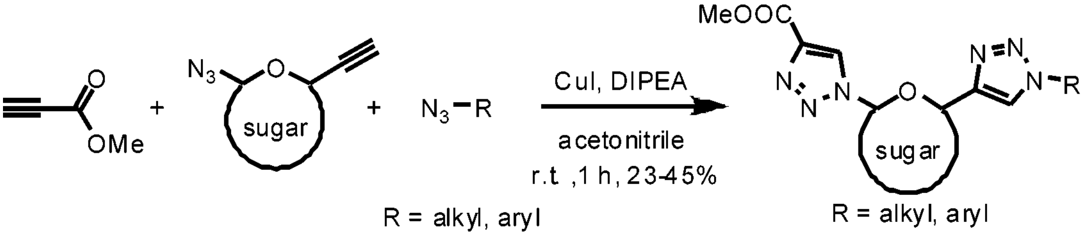
Click reaction is a reaction that is modular, wide in scope, gives very high yields, generates only inoffensive byproducts that can be removed by nonchromatographic methods, and be stereospecific. Its salient features are simple reaction conditions, the use of readily available starting materials and reagents, and water such solvent, and simple product isolation as well.[1,2] The word "click" was coined to describe the guiding principle. Among the various classes of click chemistry, Huisgen dipolar cycloaddition of azides and alkynes [3] to afford 1,4-triazoles in a regioselective manner, is extensively explored because of its pharmaceutical applications.

Single click chemistry: While click chemistry of sugar-derived azides is well known, that of sugar-derived alkynes is not much explored. We have studied Huisgen 1,3-dipolar cycloaddition of various sugar-derived alkynes with several alkyl and aryl azides using CuI, DIPEA and acetonitrile as the co-solvent to synthesize a number of 1,4-triazoles in excellent yields.



Double click in one pot: By a sequential addition of sugar-derived azido-alkynes and an azide in a proper time lag to a copper metalated alkyne, using CuI, DIPEA and acetonitrile, we have accomplished a double click in one pot to synthesize a number of bis-triazoles.



Our future plan, triple click in one pot, and the details of our single and double click work will elaborately be discussed in the poster.

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Metal Nanoparticles: A New Generation Catalyst For Organic Synthesis

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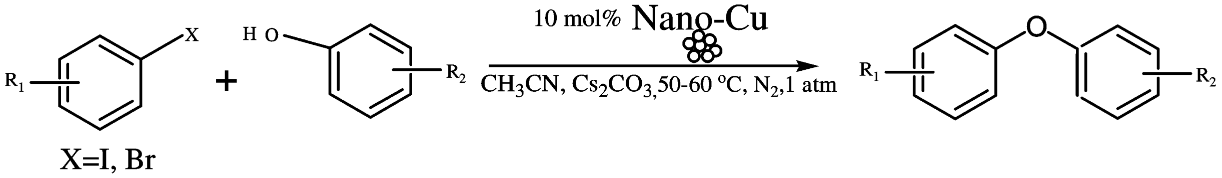
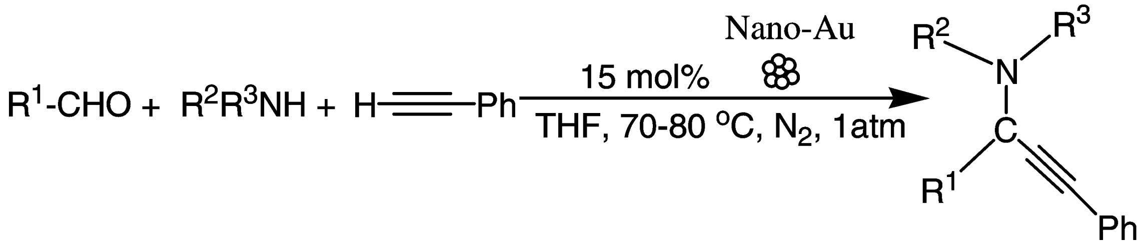
Nanoscience is a combination of "nano", from the Greek "nano" or Latin "nanus" meaning dwarf and the word "science". The word nano means 10^{-9}, so nanometer is one billionth of a meter. Two principal factors causes the properties of nanomaterials to differ from other materials are increased relative surface area and quantum effects. Nanoparticles are core base materials for implementing nanotechnology and have attracted researchers not only in field of chemistry but also in other fields such as physics, medicine, biology and material science, due to their current and promosing applications in organic synthesis, magnetic storage media, cell and DNA separation, drug delivery. In the growing field of metal nanoparticles they can also be used for the preparation of porous metallic ensembles and as filters for polymers. Metal nanoparticles provide an immense potential in organic synthesis and various organic transformations due to their characteristic, high surface to volume ratio and a higher concentration of partially co-coordinated surface sites than the corresponding bulk materials. The metal nanoparticles are supposed to environmentally benign as they can be readily recovered and reused, and thus economically acceptable.

Our research group has carried out several organic transformations [1] and synthesis of biological active moieties using various metal nanoparticles [2]. One of the recent work include A^3 coupling of aldehyde, amines and alkynes using Au(0) of 10-15 nm. nanoparticles to give propargylamines. We had also carried out Ulmann coupling to form diaryl ether from phenol and aryl halide using Cu(0) metal nanoparticles. Ni- metal Nanoparticle has immense potential for reduction and can perform reduction chemoselectively.





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Design, Synthesis and Evaluation of New Bis Pyridinium Oxime: Reactivators for Human Acetylcholinesterase Inhibited by Nerve Agent Sarin

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The extensive use of neurotoxic organophosphorus (OP) compounds as pesticides in the agriculture, as well as their potential use as mass destruction agents in chemical warfare (nerve agents) during military conflicts and terrorism, has attracted attention to the development of effective medical counter measures for such type of poisoning. The acute toxic effects of nerve agents such as sarin, soman, tabun, cyclosarin and VX are due to inhibition of activity of acetylcholinesterase (AChE), an enzyme that plays an important role in the nervous system by hydrolyzing acetylcholine, a neurotransmitter. This leads to a variety of cholinergic effects such as myosis, salivation, hypotension, bradycardia, muscle tremors, convulsions, and respiratory depression culminating in death due to respiratory failure.

Current medical protection against the toxicity of OP poisoning consists of a regimen of anti-cholinergic drugs, such as atropine, to counteract the accumulations of acetylcholine and oximes viz. 2-PAM, TMB-4, HI-6 and Obidoxime to reactivate OP-inhibited AChE. However the currently used reactivators are associated with limitations like poor lipid solubility and unstable in solution as well. Further an effective therapy by a single oxime for all the known nerve agents is still lacking. In view of the above a search is being continued to find out a universal reactivator which would be active against a broad spectrum of nerve agents.

In this regard we have synthesized a novel series of bis-pyridinium oximes connected by xylene linker and their *in-vitro* reactivation efficacy was evaluated for sarin inhibited human AChE. Reactivation efficacy of synthesized compounds was compared with 2-PAM and obidoxime. Among the synthesized compounds, the bis-pyridinium oxime *N*,*N'*-*p*-xylene-bis[(2,2'-hydroxyiminomethyl)-pyridinium] dibromide (2P-pX) exhibited 45% reactivation of human AChE inhibited by sarin as against 34% and 24% reactivation exhibited respectively by 2-PAM and obidoxime at a concentration of 10^{-4} M within 10 minutes. The time dependent reactivation profile of the new oximes indicated that the oxime 2P-pX was able to reactivate 56% of the sarin inhibited human AChE after 30 minutes.

Aqueous-Ionic Liquid Mixtures As Effective Reaction Media

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The use of ionic liquids (ILs) as “green” alternatives to the conventional organic solvents has been increasing over the last few years. With the ever increasing interest in the use of ILs as reaction media, there is a growing awareness about their shortcomings. The high viscosity of ionic liquids is believed to be one of the important detrimental factors affecting chemical transformations [1].

Water is known to reduce the viscosity of ILs to a great extent [2, 3]. The addition of water to ILs also affects other characteristic properties of ILs like the polarity parameters. In this work we have analyzed the various physicochemical properties (e.g. polarity, viscosity etc.) for a range of aqueous mixtures of ILs at several temperatures. We have then examined the effect of addition of water as a co-solvent on the progress of different C-C bond-forming organic reactions, including the Diels-Alder reaction. The correlation of the reactivities with the properties of binary mixtures leads to an in depth understanding of the solute-solvent interactions at the molecular level. The analysis indicates that use of water as a “viscosity-reducer” in ILs leads to highly-enhanced rates of reactions, but the other effects of change in polarity cannot be excluded. The binary mixture when used for organic reactions gives higher rates (as compared to ILs) and should be considered as a viable option in the scale-up stage of ILs.

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1,3-Dipolar Cycloaddition of Nitrile Oxides to (*r*)-1-(1-Phenylethyl)-3,5-bis[(*e*) -Arylmethylidene] Tetrahydro-4(1*h*)-Pyridinones: Formation of Novel Enantiomerically Pure di- and tri Spiroheterocycles

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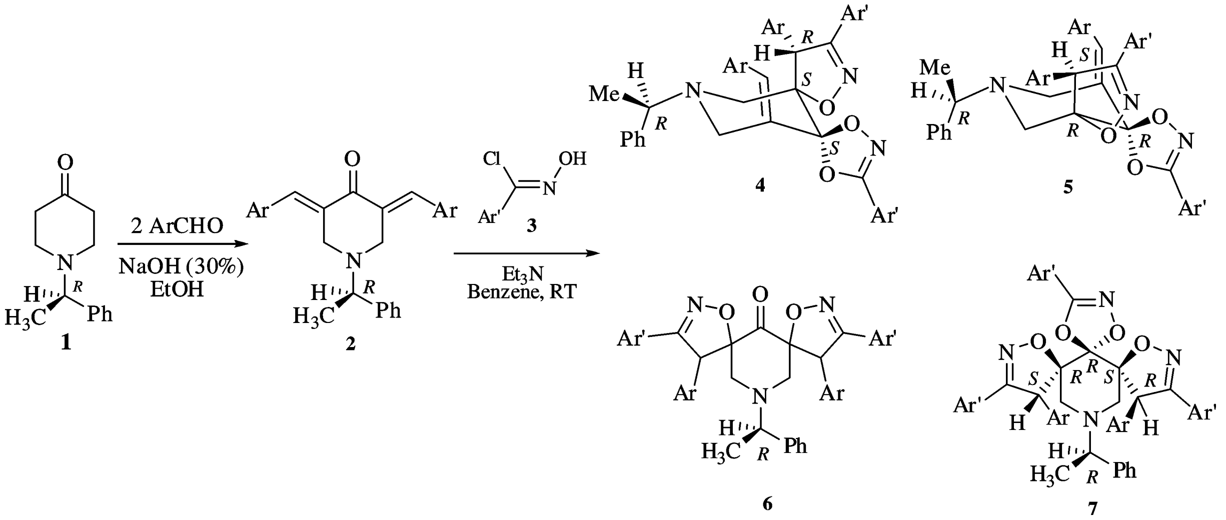
Enantiomerically pure (*R*)-(1-phenylethyl)-3,5-bis[(*E*)-arylmethylidene]tetrahydro-4(1*H*)-pyridinones (**2**) were synthesized for the first time in good yields (78-85%) by the reaction of (*R*)-1-(1-phenylethyl)tetrahydro-4(1*H*)-pyridinone (**1**) with aromatic aldehydes in the presence ethanolic sodium hydroxide and their 1,3-dipolar cycloaddition with nitrile oxides affording di- and tri-spiroheterocycles (**4**-**7**) regio- and stereoselectively in moderate yields is described.



Cinnamic Acid Derivatives Via Heck Reaction In Biphasic Catalytic System

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A biphasic [aqueous-organic] system for the Heck reaction of water-soluble olefins has been developed, which employs an organic phase soluble Pd complex catalyst. The catalyst and biphasic solvent system was tested for the coupling reaction of Na-acrylate with different aryl halides and found to be active for the synthesis of cinnamic acid derivatives. The reaction was facilitated by both organic as well as inorganic bases. The catalyst was recycled conveniently with no loss in the activity.

Catalyst product separation has always been a major issue in process development involving homogeneous catalysts [1,2]. With particular reference to Heck reactions, the multi-component system comprising olefin, aryl halide, vinylated product, base, base-halide adduct, phase transfer agent, catalyst and generally a polar solvent, requires a complex strategy for product separation and catalyst recovery [3] and recycle. To overcome the issues of catalyst – product separation, the use of biphasic systems has been reported for Heck reactions, which involves non-aqueous or aqueous biphasic systems. However, in a majority of the studies a detailed investigation on the catalyst recycle is not available for Heck reaction in aqueous media. Although the extremely active and stable Palladacycle catalysts give highly enhanced rates, conventional strategies of catalyst – product separation still need to be followed, which could lead to catalyst deactivation. There are no details on the recycle of Palladacycle catalyst for Heck reaction in the reported literature.

Heck reactions of water-soluble olefins like Na-acrylate are amenable to reactions in aqueous-organic biphasic systems using Pd complex catalysts solubilized in the organic phase. Such a biphasic system offers more advantages over conventional systems with respect to catalyst recycle and product recovery. The presence of water ensures an efficient removal of the halide byproduct, formed in the course of the Heck coupling of Na-acrylate with different aryl halides. The Heck reaction of acrylic acid salts with aryl halides, results in the synthesis of substituted cinnamic acid derivatives, which have wide ranging applications as UV absorbers, anti-oxidants in plastics, as intermediates for pharmaceuticals and also in medicinal chemistry.

Sodium hydroxide, carbonate and bicarbonate were found to be excellent bases for this reaction, and were efficient even though retained in the second, non-catalyst phase. The activity observed for the vinylation was highest for iodobenzene followed by bromobenzene. No reaction was observed with chlorobenzene. The palladacycle catalyst was stable in presence of water, and could be recycled for four times with no loss in the activity.

A biphasic [aqueous-organic] medium is shown to be feasible for the Heck reaction of water-soluble olefin-Na acrylate, with a very efficient catalyst product separation. The biphasic system developed has the following advantages viz- (i) efficient catalyst recovery and recycle, (ii) convenient product separation and (iii) efficient sequestration of the halide as base is in a soluble state. Strategies for total conversion of halide followed by an efficient catalyst recycle, isolation of product and a separate stage for recovery of the unreacted Na-acrylate has been outlined.

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Oxidative Conversion of a,a-Disubstituted Acetamides to Corresponding One Carbon Shorter Ketones

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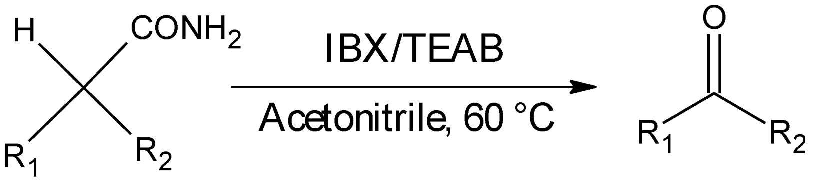
Our research interest is to explore the applications of hypervalent iodine reagents in development of new methodologies [1-2]. In persistence of our work by using IBX/TEAB system, a new route for synthesis of ketones is developed. a,a-Disubstituted acetamides on reaction with o-iodoxybenzoic acid in combination with tetraethylammonium bromide in acetonitrile at 60 °C gave corresponding one carbon shorter ketones.



Where R_1,R_2 = alkyl, cyclic, aryl, heteroaryl.

Generality of this transformation is studied and will be presented.

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Application Of Modified Pictet-Spengler Reaction For The Synthesis Of Novel Heteroaromatic Polycyclic Structures

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Indole alkaloids, such as b-carbolines are a large group of naturally occurring alkaloids with varying degree of unsaturation. The core structural element is present in the natural, synthetic organic compounds and in the clinically used drugs (Tadalafil and Abecarnil) exhibiting variety of important biological activities of therapeutic interest. Emulating these artistic frameworks of nature, many of the therapeutically important cyclic surrogates of the b-carboline could be designed which would open up the new avenues for therapeutic intervention. The synthesis of b-carboline framework is predominantly carried out using the century old Pictet-Spengler reaction. The latter involves acid-catalyzed intramolecular cyclization of an intermediate imine formed by condensation of carbonyl compound and b-arylethylamine. Despite being a powerful carbon-carbon bond forming reaction, traditionally, the Pictet-Spengler reaction has remained confined to only three aliphatic amine derived substrates: Trp/tryptamine, His/histamine and Dopamine/Tyrosine.

With the view to extend the application of this elegant reaction to substrates beyond b-arylethylamine, we envisioned that not only the aliphatic amine in these substrates could be replaced by aromatic amine but it could be also allowed to originate from either *C* or *N* in any activated heterocyclic template in a manner to facilitate 6-endo cyclization. Our assumption was based on the fact that the schiff base derived from aryl amine would be more electrophilic than the corresponding aliphatic amine, thus facilitating the *endo* cyclization. The application of our modified concept led to the identification of a variety of aryl amine-based second-generation substrates furnishing novel polycyclic structures when condensed with structurally diverse aldehydes. The most interesting aspect of our modified strategy is that our substrates underwent Pictet-Spengler reaction with aldehydes having either electron donating or electron withdrawing substituents, whereas traditional Pictet-Spengler substrates derived from aliphatic amine underwent cyclization only with aldehydes having electron withdrawing substituents. The outcome of this study will be discussed in detail.

Substrate for traditional Pictet-Spengler reaction

Substrate based on our modified strategy for Pictet-Spengler reaction

Figure 1.

Bioactive Studies Of Coumarin Coupled Benzimidazole-2-Thione Compounds

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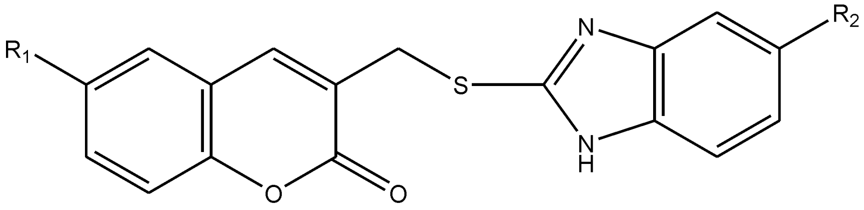
The 1–benzopyran-2-one moiety is the structural core of coumarins. It is often found in more complex natural products and it is frequently associated with biological activities, such as, anti-cancer, anti-fungal, anti-HIV and anti-clotting [1]. Similarly, benzimidazoles are also remarkably effective compounds both with respect of their biological activity and their favorable selectivity ratio [2]. In our present study, we would like to report the coupled products of different substituted 3-chloromethyl-coumarin derivatives with various substituted benzimidazole-2-thione compounds and all these compounds have been characterized using ^{1}H NMR, Mass spectral and FT-IR techniques. A preliminary investigation on antimicrobial activity against few bacterial as well as fungal pathogens of humans and plants were attempted with different microbes, such as, *Shigella dysenteriae*, *Solmonella typhi*, *Xanthomonas oryzae*, *Pseudomonas fluorescence*, *Epidermophyton sp*, *Trichophyton sp*, *Sclerotium sp* and *Alternaria alta*. These studies indicated that these compounds were more effective against bacterial pathogens. In particular, coupled products, **1** and **5** (**Figure 1**) were more effective than the rest of the compounds.



1 $R_1 = R_2 = $ -H
2 $R_1 = $ -H; $R_2 = -CH_3$
3 $R_1 = $ -Br; $R_2 = $ -H
4 $R_1 = $ -Br; $R_2 = -CH_3$
5 $R_1 = $ -Br; $R_2 = $ -COOH

Figure 1: Structures of Coumarin coupled benzimidazole derivatives (**1**-**5**)

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Chemoselective Reduction of a, b-Unsaturated Carbonyls with Thiourea Dioxide (TUDO)

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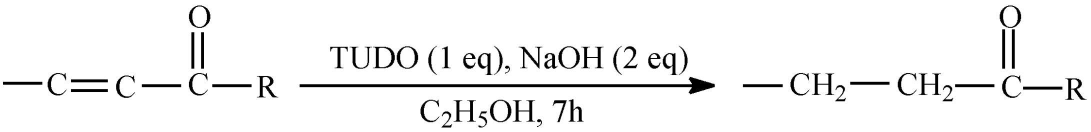
The continuing sophistication in and ever changing landscape of molecular targets for a myriad of applications ranging from biology to material sciences requires continuing evolution of synthetic methods, particularly selective inexpensive methodologies. The selectivity of reactions were earlier monopoly of enzymes. In the present investigation the chemoselective behaviour of thiourea dioxide has been explored. Thiourea dioxide has shown a remarkable selectivity for the 1, 4-reduction of a, b-unsaturated carbonyls (Chandrasekhar *et al* [1], Yang *et al* [2], Dhillon [3]) to the corresponding saturated carbonyls in excellent yields. The results of these studies will be presented.



$$—C{=}C—\overset{\overset{\displaystyle O}{\|}}{C}—R \xrightarrow[C_2H_5OH,\ 7h]{TUDO\ (1\ eq),\ NaOH\ (2\ eq)} —CH_2—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—R$$

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Synthesis of Pyrrolo [3,4-b] Quinolines: via Intramolecular Imino Diels-Alder Reaction

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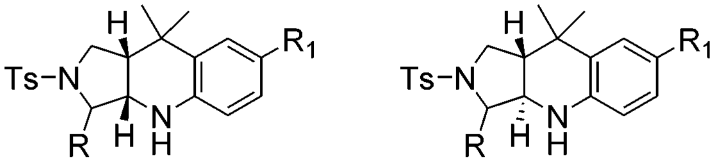
Hexahydroquinoline have been found in the essential part of many natural products such as alkaloids and pharmaceutically important compounds.[1] These compounds are considered to be prime candidates in the construction of bacterial topoimerase inhibitors.[2] Hence a number of synthetic methods have been developed for the synthesis of such molecules. We herein report the synthesis of novel hexahydropyrrolo [3,4-b] quinolines by imino Diels-Alder reaction using $InCl_3$ as a catalyst.[3]



Cis *Trans*

$R = H, CH_3CH_2$
$R_1 = H, CH_3, OCH_3, Cl, Br$

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Antimicrobial Activities of 5,7-Dihydroxy-6,8,4'-Trimethoxyflavone

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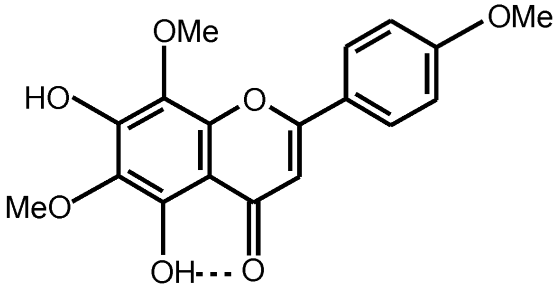
At the present scenario of scientific medicinal research, bioflavonoids are being considered much effective and useful due to their multidirectional therapeutic efficacies, very particularly as antioxidant and anticancerous agents [1,2]. This remarkable class of plant secondary metabolites also exhibits a wide range of biological activities [2]. In this new millennium, it may be urged that interest in herbal medicines and natural products in general is at an all time high. This phenomenon has been mirrored by an increasing attention to phytomedicines as form of alterative therapy by the health professions. Mankind has been utilizing plant products as traditional medicines, fragrances, spices, and colourants for thousands of years [3]. A multidirectional therapeutic uses of vast number of plant species in traditional way are known in India also since the *Vedic* times as *Ayurvedic* and *Unani* system of medicine.

In continuation of our works on medicinal plants, we have found *Limnophila heterophylla* (family: Scrophulariaceae as new and rich source for 5,7-dihydroxy-6,8,4'-trimethoxyflavone — a well-known natural bioactive flavonoid. *L. heterophylla,* a locally available herb, is an important Indian medicinal plant and finds lot of applications in the traditional system of medicine against various ailments. The petrol extract of the air-dried plant materials (aerial parts and roots) afforded the flavonoid characterized on the basis of detailed spectral studies (UV, IR, PMR, CMR, 2D-NMR, EIMS). In our preliminary studies, the flavonoid has been found to exhibit significant antimicrobial activities against the three bacterial strains, *Escherichia coli, Salmonella typhimurium* and *Staphylococcus aureus*, and one fungal strain, *Alternaria solani*.



(5,7-Dihydroxy-6,8,4'-trimethoxyflavone)

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Synthesis of 4-(Cyclohexylsulfanyl)-1,3-Diaryl-1H-Pyrazoles Using Vilsmeier's Reagent

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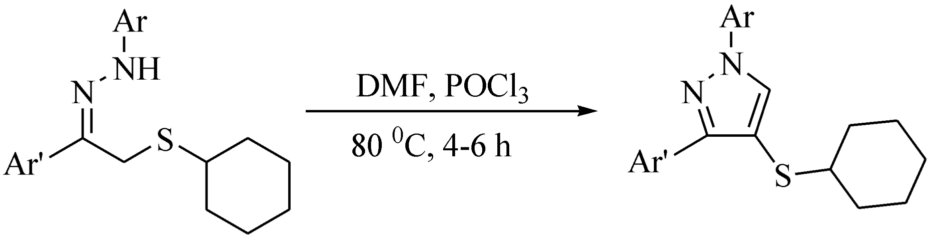
Pyrazoles find a wide range of pharmacological applications as analgesic, anti-inflammatory, antipyretic, antibacterial, antimicrobial [1], antipsychotic [2] and antimalarial [3] activity. Presence of sulfur as a substitutent in the pyrazole ring may enhance the biological activity of this ring system and hence it has been planned to synthesize 4-(cyclohexylsulfanyl)-1,3-diaryl-1H-pyrazoles. The starting materials identified for this synthesis are the hydrazones of 2-(cyclohexylsulfanyl)-1-(4-methylphenyl)-1-ethanone (**I**). The 1-arylpyrazoles have been previously synthesized from hydrazones using Vilsmeier's reagent. Upon treatment with phosphorous oxychloride and dimethyl formamide at 80 °C, the hydrazones **I** were quantitatively converted to the respective target pyrazoles, 4-(cyclohexylsulfanyl)-1,3-diaryl-1H-pyrazole (**II**). The synthesized compounds have been fully characterized by spectral data.



I **II**

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Synthetic Of Potentially Bioactive Mannich Bases Of 2-Chloro 4-Nitrobenzamide Derived From Secondary Amines

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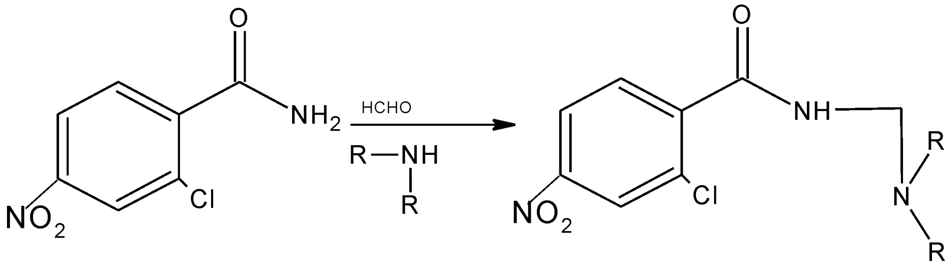
The Mannich derivative of 2-Chloro 4-Nitro benzamide with some secondary amines was prepared for study of antimicrobial effects. The chemical structure of synthesized compound was confirmed using elemental analyses, UV, IR and ^{1}H NMR spectroscopy. The novel synthesized Mannich bases were evaluated for antibacterial activity towards Gram- positive (*B.subtilis*) and Gram-negative bacteria (*P.aeruginosa*) at 40, 80 and 160 mg/ml respectively by disk diffusion method. The results were stastically analyzed. Meanwhile excellent antibacterial results were obtained against the pathogens under investigation and found to be low toxic as ascertained by LD_{50} test.



Oxidative Copolymerization of Aniline with *O*- and *P*-Toluidine by Ammonium per sulfate: Kinetic and pathway

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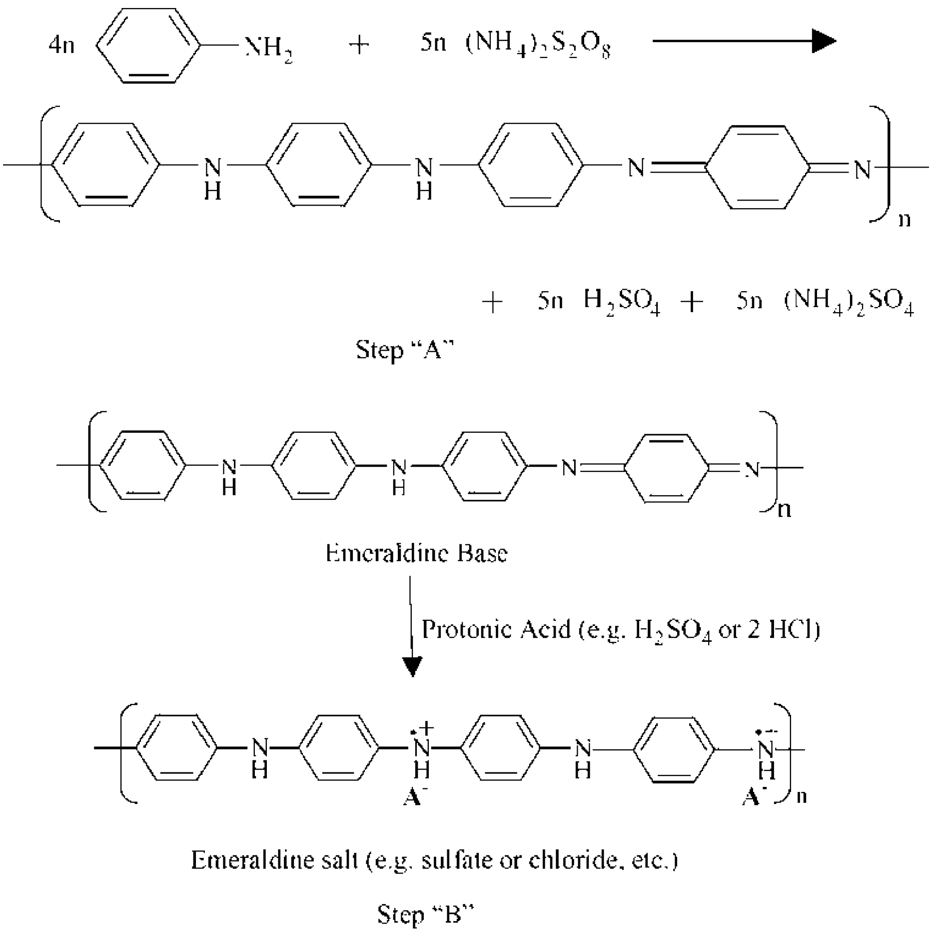
Department of Chemistry, Aligarh Muslim University, Aligarh - 202002

The kinetic study on the oxidation of aniline with *o*- and *p*-methylaniline by ammonium persulfate (APS) has been carried out. The course of copolymerization was investigated by UV-vis spectroscopic method. Structural characterization was studied by FT-IR spectral analysis. The electronic spectra of the copolymers poly(aniline-co-*p*-toluidine) and poly(aniline-co-*o*-toluidine) show hypsochromic shift. The shift has been observed in the bands corresponding to p ® p* transition as well as in the exciton transition. The increase in absorbance recorded during the reaction for different concentration of aniline, *o*- and *p*- toluidine at various times of intervals of polymerization reaction indicates a growth in the polymer formation. The degradation curve can be fitted reasonably well by an exponential decay of APS, suggesting first order kinetics. The resulting first-order rate constant was used to calculate the rate of copolymer formation using the rate equation $-d[A]/dt = kc^n$.



Bacterial Extract as a Biogenic Mineral Growth Modifier

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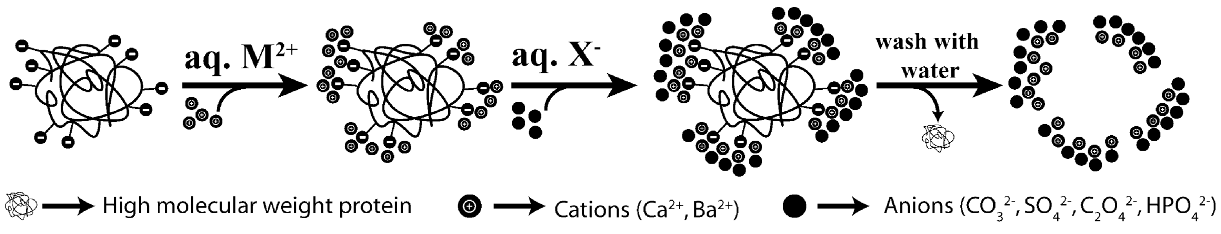
The formation of minerals and mechanisms by which bacteria could control the formation of minerals in natural habitats is now of current interest for material scientists to have an insight of the mechanism of *in vivo* mineralization, as well as to seek industrial and technological applications [1-3]. Crystalline superstructures of calcium and barium minerals formed micron-sized building blocks when synthesized in the presence of an organic matrix consisting of secreted protein extracts from three different lactic acid bacteria (LAB) *viz*: *Lactobacillus plantarum* MTCC 1325, *Lactobacillus acidophilus* MTCC 4495 and *Pediococcus acidilactici* CFR K7. LABs are not known to form organic matrix in biological materialization processes. The influence of these bacterial extracts on the crystallization behavior was investigated in details to test the basic coordination behavior of the acidic protein. The significant role of native form of high molecular weight bacterial protein extracts in the generation of nucleation centers for crystal growth is also established. A model for the formation of organic matrix-cation complex and the subsequent events leading to crystal growth is proposed (Scheme 1). Reproducibly formations of highly pure crystalline minerals phase are highlighted here.



Scheme 1. Proposed mechanism of template action of protein extract

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Cu Catalyzed Oxidation of Alcohols and Extension to Enantioselective Oxidation

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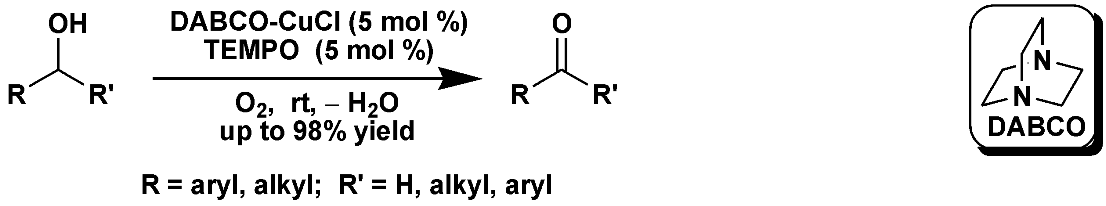
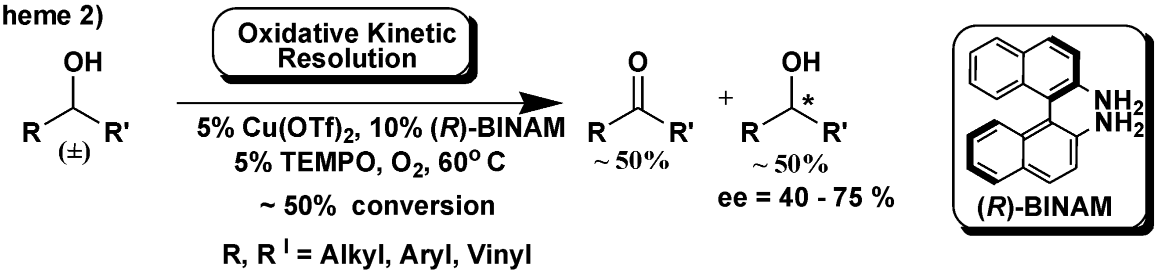
Enantiopure alcohols are very important structural units for the synthesis of a wide range of natural products, chiral ligands and biologically active compounds. Although, enantiopure alcohols are available by enantioselective reduction of ketones, resolution of racemic alcohols by oxidative kinetic resolution remains rare. Though chiral Ti, [1] Ru, [2] and Pd [3] catalysts are introduced in the field of oxidative kinetic resolution for the synthesis of enatiopure allylic and benzylic alcohols, expensive nature of these chiral complexes made to look for alternative catalysts, which are easily available and inexpensive. Very recently, we have developed an efficient methodology for the selective oxidation of alcohols to the corresponding aldehydes and ketones using DABCO-Cu complex as catalyst (Scheme-1) which catalyze the reaction at room temperature using molecular oxygen as sole oxidant. We extended our oxidation methodology for the oxidation of primary alcohols and aldehydes to the corresponding carboxylic acids in a very efficient manner under very mild conditions. For the very first time, continuation to our Cu catalyzed oxidation chemistry, using chiral Cu-BINAM complex as chiral catalyst we have developed an efficient oxidation method to resolve racemic secondary benzylic and allylic alcohols ((Scheme- 2) oxidative kinetic resolution).

(Scheme 1)



(Scheme 2)



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Reactivity Of α-Hydroxy Acids Towrds Imidazolium Fluorochromate Oxidation

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Imidazolium fluorochromate (IFC) is one of the Cr (VI) compound act as a mild oxidant [1]. The kinetics of oxidation of α–hydroxy acids such as glycolic acid, lactic acid and mandelic acid by imidazolium fluorochromate was followed in 100% aqueous medium. The influence of substrate, oxidant, H^+ ion, and dielectric constant on the reaction rates at varied temperatures was studied. The reaction following a Michaelis-Menton type [2] kinetics in the case of substrate shows a complex formation between IFC and substrate. Activation parameters have been calculated and suitable mechanism has been proposed. The relative reactivity *viz.*, glycolic acid > lactic acid > mandelic acid was explained.

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Highly Efficient, Recyclable Rhodium Catalyst Immobilized on Poly- ionic Resins: Application in the Heck-type Coupling reactions

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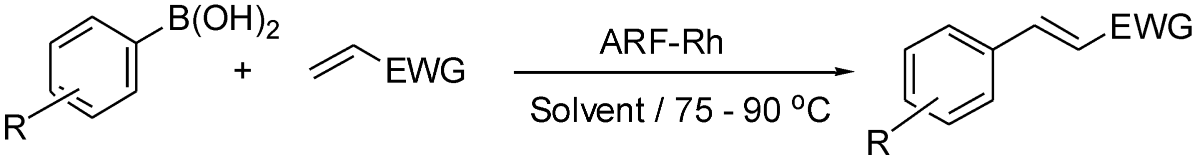
Transition metal catalysts have been widely used in organic synthesis, most notably in various carbon–carbon and carbon–heteroatom bond-forming reactions. Over the last two decades, efforts have been made to the development of novel polymer-supported reagents and catalysts for application in organic synthesis. [1] Supported metal catalysts can facilitate both the isolation and recycling of the catalyst by filtration, thus providing economic and environmentally clean processes.

Rhodium-catalyzed stereoselective 1,4-addition of organoboronic acids to a, b - unsaturated carbonyl compounds has attracted much attention in the recent years. [2] On the other hand, Heck-type coupling reaction between organoboronic acid and electron deficient alkene in presence of rhodium catalyst has also been reported. [3]

In connection with our interest towards development of heterogeneous resin-supported reagent and catalyst, we have recently developed a new technique to immobilize rhodium on a surface of Amberlite resin formate (ARF). The resulting poly-ionic resin bound rhodium [ARF–Rh] exhibits excellent catalytic activity in ligand-free Heck-type olifination reactions of organoboronic acids with alkenes. Easy preparation of the heterogeneous catalyst, high catalytic activity, stability, no-leaching and recycling of the catalyst for several runs remain the major facets of this poly-ionic resin-immobilized [ARF–Rh] catalyst. The details of our experimental findings will be presented here.



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Chemistry of Bile Acids: Applications in Supramolecular Chemistry and Materials Science

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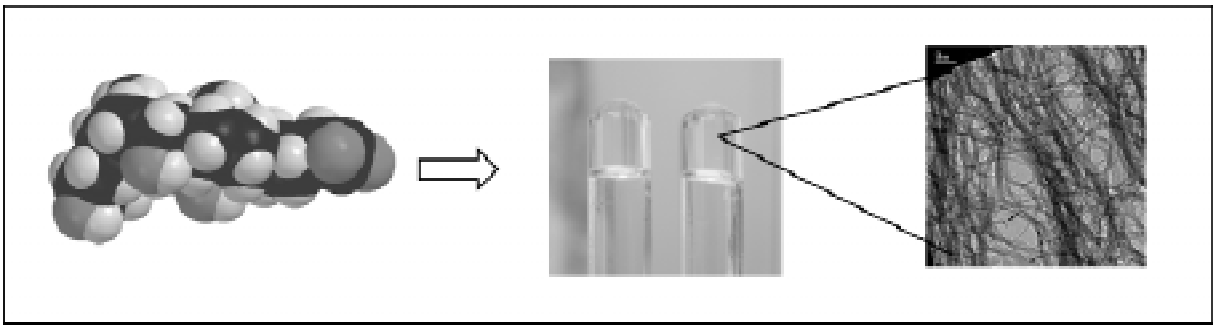
Bile acids are facially amphiphilic molecules of great biological significance. During the past few years our group has explored the chemistry of novel bile acid derivatives. These efforts have led to a number of applications of this class of molecules in synthesis, supramolecular chemistry and materials science. Bile acid derivatives serve as excellent chiral auxiliaries and templates [1] for asymmetric synthesis, good platforms for the design of small-molecule receptors[2**]** and sensors[3] exquisite monomers for dendritic constructions, fine capping agents for nanoparticle synthesis, efficient gelators of organic and aqueous liquids. This poster will highlight some of our ongoing work.



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2,4-Dihydroxybenzophenone- Melamine -Formaldehyde Terpolymer Resins and their Ion-Exchange Properties.

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Terpolymer resins (2,4-DHBPMF) were synthesized by the condensation of 2,4-dihydroxybenzophenone and melamine with formaldehyde in the presence of acid catalyst and using varied molar ratios of reacting monomers [1,2]. Terpolymer resin compositions have been determined on the basis of their elemental analysis and the number average molecular weights (Mn) of these resins were determined by conductometric titration in non-aqueous medium. The viscosity measurements were carried out in DMF indicates normal behavior. IR and NMR spectra were studied to elucidate the structure. The terpolymer resins have been further characterized by reflectance spectra in solid state, absorption spectra in non-aqueous medium.

A terpolymers 2,4-DHBPMF proved to be a selective ion-exchange polymer for certain metals. Chelating ion-exchange properties of these polymers were studied for Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, and Zn^{2+} ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurement of the distribution of given metal ion between the polymer sample and a solution containing the metal ion [3, 4]. The study was carried out over a wide pH range and in media of various ionic strength. The polymer showed a higher selectivity for Cu^{2+}, Fe^{3+} ions than for Co^{2+}, Ni^{2+} and Zn^{2+} ions.

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Photosentesized reaction of Diaminotolunes with Methylene blue

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The photosensitized deamination of isomeric diaminotolunes has been studied using methylene blue as a photosensitizer in alkaline medium. The deamination products have been identified and formation of molecular complex between diaminotolune and methlene blue has been observed. The effects of the pH, concentration of sensitizer, concentration of the substrate and the intensity of the light on the rate of the deamination have been studied. The quantum efficiency of the photodeamination has been evaluated using Potassium ferrioxalate as an actinometer. The mechanism of the photodeamination has been suggested.

The utility of *N*-Fmoc-Asp/Glu derived 5-oxozolidinones for side chain carboxyl group selective modifications

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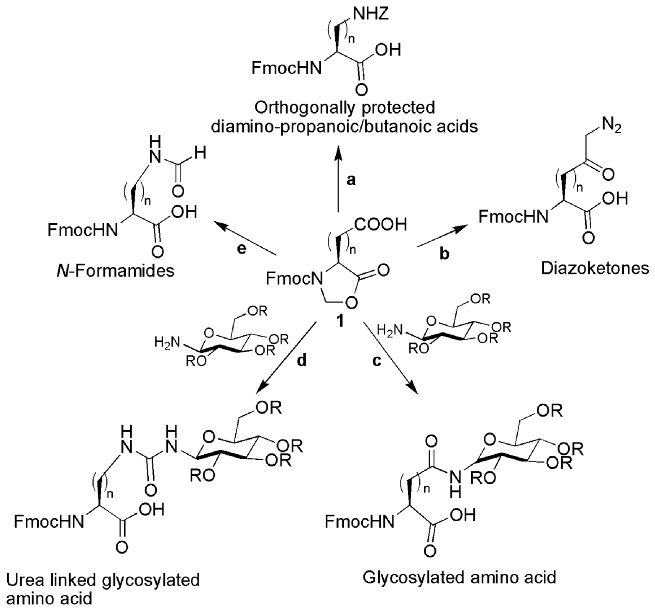
The site selective w-COOH group modifications have been carried out by adopting bidentate and internal protection strategy for N^a-amino and a-COOH groups. N-Fmoc-Asp/Glu has been condensed with paraformaldehyde to obtain the 5-oxazolidinones 1. The COOH group in 1 is activated and coupled to O-protected glycosyl 1-amines and diazomethane to obtain N-linked glycopeptides and diazoketones. The isocyanate derivatives of 1 have been utilized as key intermediates to prepare urea tethered neoglycopeptides, orthogonally protected diamino aliphatic acids and to introduce N-formyl group in the side chain. This approach produces the side chain derivatives of amino acids in less number of high yielding steps and allows to access isocyanates of normal a-amino acids.



a) 1. NMM/IBC-Cl, aq. NaN_3 2. BnOH/MW 3. 1N LiOH; b) 1. NMM/ EtOCOCl, CH_2N_2, 2. 1N LiOH; c) 1. HBTU, DIEA, 2. 1N LiOH; d) 1. EtOCOCl, NMM/ aq. NaN_3, 2. Toluene/MW, 3. glycosyl amine, DMAP, 4. 1N LiOH; e) 1.EtOCOCl, NMM/aq. NaN_3, 2. Toluene/MW, 3. formic acid, DMAP, 4. 1N LiOH

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Synthesis of α-Chlorostilbenes, the Combretastatin A-4 Analogues, Mediated By a Heterogeneous Si-Fe Catalyst

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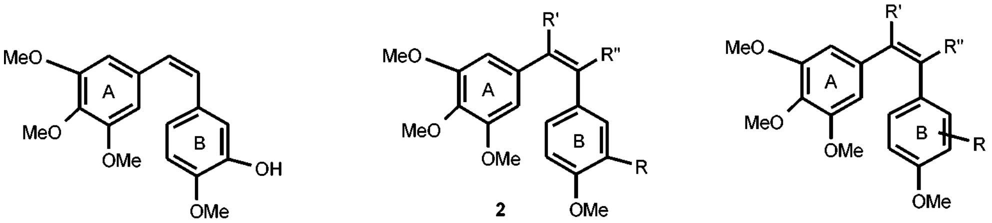
Various combretastatins, which are substituted stilbenes, exhibit significant anticancer activity. Structure-activity relationship studies in case of combretastatin A-4 **1** have indicated that the presence of 3,4,5-trimethoxy substituents on A ring, 4-methoxy substituent on B ring and cis orientation of the two aromatic rings are the essential structural features for anticancer activity [1]. Combretastatins and related substituted stilbenes are generally prepared by Wittig reaction of suitable aldehydes and Wittig salts. There are a number of publications reporting combretastatin analogues having the carbons representing the double bond of combretastatins as a part of ring system but the combretastatin analogues having substituents on double bond, as exemplified by general structure **2** in Figure 1, are limited [2]. Various halo-stilbenes are prepared by reductive homocoupling of benzotrichloride followed by consecutive reductive dechlorination to 1,2-dichlorostilbene effected in the presence of sodium formate as the reducing agent and Pd/C catalysts [3a], halogenation of acetophenones [3b] etc but combretastatin A-4 analogues with halides on double bond are not reported to our knowledge. As a part of our interest in developing novel anticancer agents, we intended to prepare substituted stilbenes **3**, based on our recent results **to** study the structure-activity relationship.



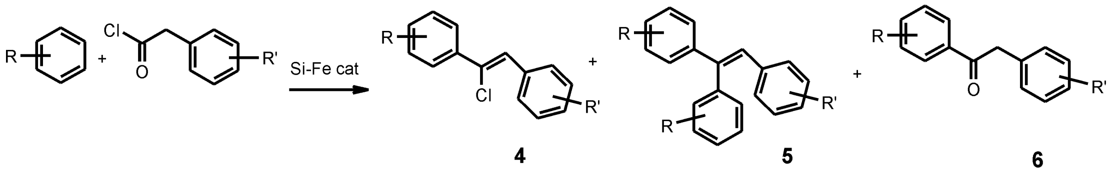
1: Combretastatin A-4

2
R=H, OH, NO_2, NH_2, OMEM
R', R"=H, CN, COOH, COOalkyl, $CONH_2$
CH_2OH, CHO, CH_2NMe_2

3
R', R"=H, halide, aryl

Figure 1

During our recent work, involving Friedel-Crafts acylation of aromatic substrates with acid chlorides in the presence of a heterogeneous Si-Fe catalyst, we found that α-chlorostyrenes were obtained in good yields in addition to the normal Friedel-Crafts acylation products. We envisioned that these results could be extended further to obtain α-chlorostilbenes by reaction of phenylacetic acid chlorides with aromatic substrates. The recent results in this direction are presented herein (Scheme 1).



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Synthesis Of Aryl Ketones By The Copper-Catalyzed Arene C-H Addition To Nitriles

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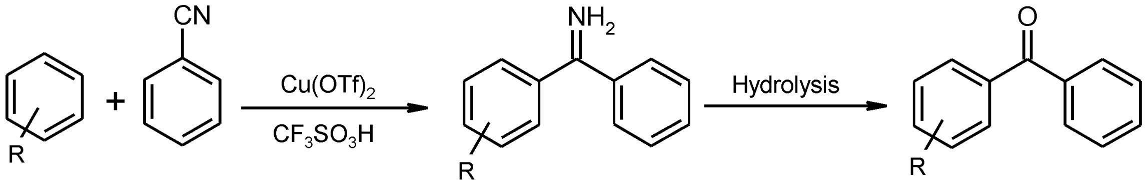
Developing novel methods for catalytic C-H functionalization has been a fascinating area in synthetic organic chemistry. The catalytic addition of C-H bonds to unsaturated substrates is one of the most devoted research topic for synthetic chemists for years. The transition metals such as Pd, Rh, Ru etc [1,2] have been used to catalyze C-H addition to unsaturated substrates. Very few examples have been reported for Cu catalysed C-H bond functionalization. To our knowledge, however, there are no examples for Cu catalyzed C-H addition to polar multiple bonds such as nitrile. Herein, we report for the first time intermolecular Cu catalyzed reaction of simple arenes and nitriles, which facilitate a useful and reliable method for the synthesis of aryl ketones. The unprecedented copper-catalyzed C-H addition of arenes to nitriles provides moderate to excellent yields of aryl ketones or the corresponding hindered imines. This novel chemistry is believed to involve copper-catalyzed C-H activation of the arene by electrophilic aromatic substitution. Similar reactions have been successfully developed employing arylboronic acids and nitriles.



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Synthesis and Characterization of Heterocycles Derived From N,N’-(4,4'-methylenebiphenyl)-bis-2-hydroxybenzylamine

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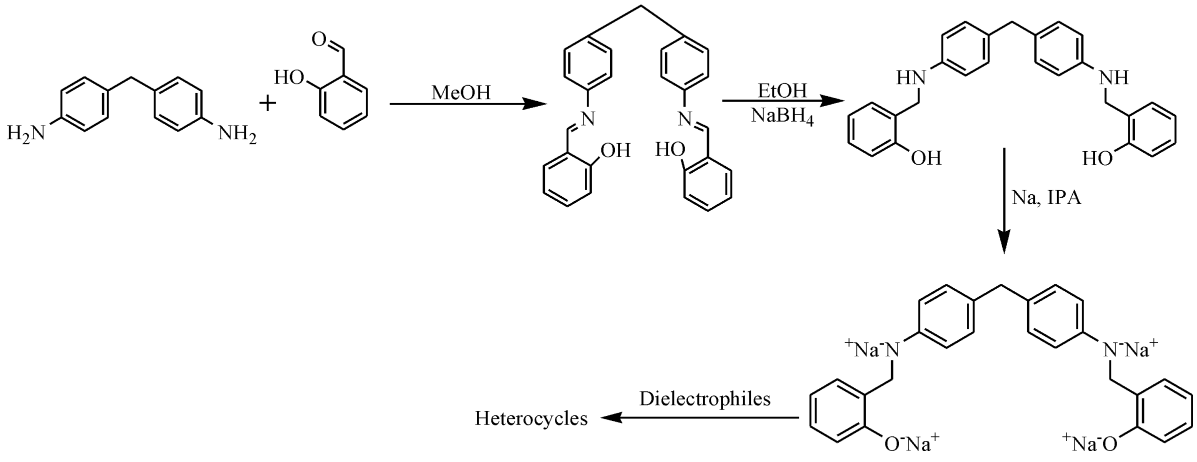
In the area of organophosphorus compounds the phosphonates are very important class of compounds in terms of biological activity [1]. They serve as inhibitors of gene expression in mammalian cells and antibiotics. They are also used as biocides (*viz.* fungicides, herbicides, insecticides etc.) and plant growth regulator.

In the present study we have synthesized a variety of heterocyclic moieties, consisting of phosphorus and silicon along with nitrogen and oxygen. The phosphorus heterocycles synthesized are all 6-membered (phosphonines). They are important from a synthetic point of view as, among other things, they can be useful starting materials, P-ligands and resolving agents, in addition, they all are structural analogue of the phosphoro-organic alkylating drug cyclophosphamide, which has outstanding cytotoxic and immuno-suppressor properties [2].

The oxazines, oxa-aza-cyclononane and hyprevalent silicon [3] heterocycles have also been synthesized using tetra-anion strategy.

The products were characterized by satisfactory elemental analyses and spectral (IR, ^{1}H, ^{13}C, ^{31}P, ^{29}Si and Mass) studies. A plausible mechanistic logic and concept utilized in the synthesis will be presented.



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N-chlorosuccinimide as a versatile reagent for the sulfenylation of ketones: a facile synthesis of a-ketothioethers

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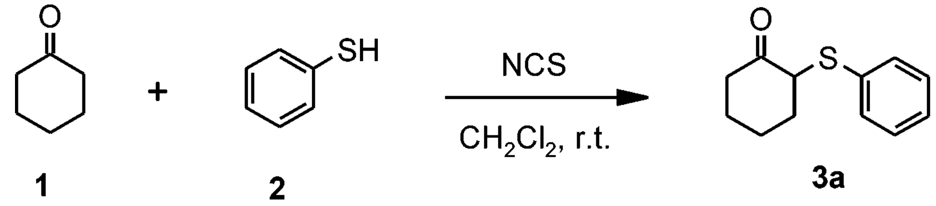
The sulfenylation of ketones (cyclic and acyclic) having a-hydrogen as been achieved using *N*-chlorosuccinimide (NCS) under mild reaction conditions to produce a-ketothioethers in excellent yields with high selectivity. The use of NCS makes this method quite simple, more convenient and practical. The most common methods for a-sulfenylation of ketones involve the reactions of enolates (generated from ketone using LDA in THF at –78 °C) [1-3] and enamines with various sulfenylating reagents such as PhSSPh, MeSSMe, methylmethanthiosulfate or PhSCl and *N*-(phenylthiourea) phthalimide or *N*-phenylthiocaprolactam. To our knowledge, no direct method for a-sulfenylation of unmodified ketones has been reported. In this article, we report a simple, direct, and efficient method for the preparation of a-ketothioethers from ketones and aromatic thiols.



Scheme, Sulfenylation of cyclohexanone

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Applications of allyl amines afforded from Baylis-Hillman adducts toward heterocyclic synthesis

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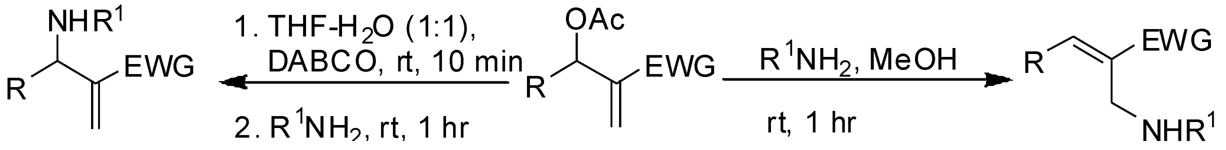
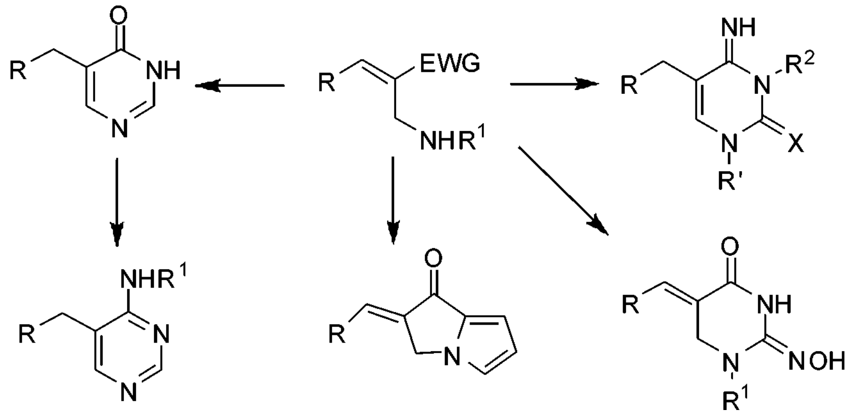
Stable synthetic intermediates with easy accessibility and multi-functionality are species of interest in the field of synthetic organic chemistry, provided they offer sufficient potentiality to be utilized in the synthesis of useful target molecules. Allyl amines are one such synthons which have been extensively utilized in the generation of a wide spectrum of molecules, including a- and b- amino acids, alkaloids, carbohydrates, heterocycles and others, through novel manipulations. Our interest in the allyl amine concerns with the one which are afforded via Baylis-Hillman chemistry. The acetyl derivative of Baylis-Hillman adducts reacts with amine in two different fashions to generate structurally different allyl amines. The first allyl amine is afforded by S_N2' displacement reaction between the acetate and amine, while the second one is yielded by successive S_N2'-S_N2' displacement reaction of acetate with amine (Fig. 1).



Owing to the presence of unique structural features, these allyl amines serve as excellent substrates for the generation of a variety of heterocyclic system. We have utilized such amines for the generation of cyclic uriedes, pyrimidin-4-ones, 4-pyrimidinamines 2-oximo pyrimidine-2, 4-dione, pyrrolizin-2-ones (Fig. 2). The detail results of these studies will be presented and discussed.



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Stereo controlled Approach to 2,5-Diaryl-3,4-Disubstituted Tetrahydrofurans Through a Highly Diastereoselective Aldol Condensation of a a-Chiral Ester Enolate. Total Synthesis of (-)-Talaumidin, (+)-Talaumidin and (-)-Virgatusin

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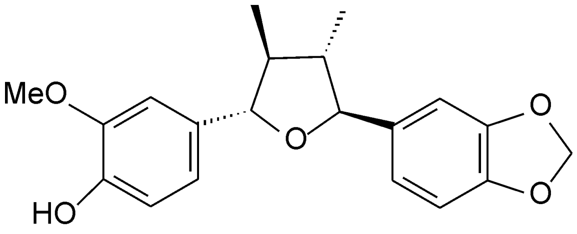
2, 5-Diaryl-3, 4-disubstituted tetrahydrofurans constitute an important class of lignans comprising of a large number of structurally and stereo chemically different plant derived metabolites. Structural diversity amongst the members of this family arises from different types of substituents at the 3, 4-positions as well as from the different nature of the aromatic ether substituents. Typical examples include talaumidin **1** [1] and virgatusin **2** [2]. Compounds of this family are associated with a host of interesting biological activities such as anti-tumor, anti-inflammatory, antioxidant, antiviral, neurotrophic, neuoroprotective, immunosuppressive etc. For example, (-)-talaumidin **1** exhibits neurotrophic activity in rats while (-)-virgatusin **2** is a potent inhibitor of the endogenous DNA polymerase of hepatitis B virus. In spite of their enormous therapeutic potential, synthetic activities in this area began only recently.

The synthesis of these lignans having four contiguous stereo centers either with all *trans* configuration as in **1** or with *cis*, *trans, trans* configuration as in **2** poses considerable synthetic challenge. Unlike the reported approaches [1,2] which involve sequential generation of the stereo centers, our approach relies on stereo controlled generation of three contiguous centers out of the four in a single step involving a highly diastereoselective aldol condensation of an ester-enolate with a a-chiral center. Our approach culminating in the total synthesis of (-)-talaumidin, (+)-talaumidin and (-)- virgatusin will be presented.



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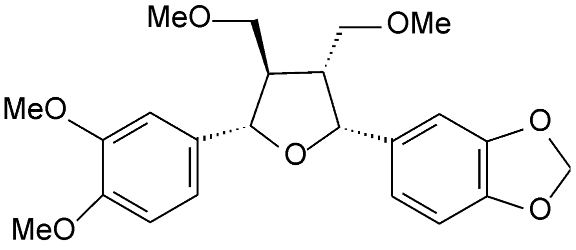

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Benzotriazole mediated one-pot facile synthesis of N^3-[1, 3, 4]-oxadiazol-2’-yl)-2-thioxo-2, 3-dihydro-1*H*- quinazolin-4-one under *MW* condition

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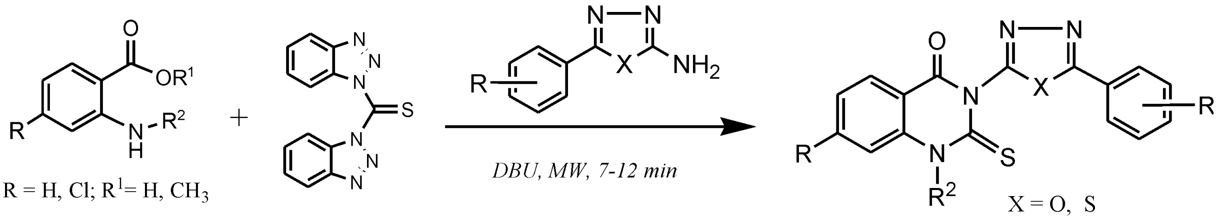
The quinazolinone skeleton is frequently encountered as building block for hundreds of naturally occurring alkaloids[1] displaying a wide range of biological activities against many of diseases and hence the exploration of this skeleton as privileged new chemical entities (NCE’s) in drug discovery research is beyond doubt a paramount importance for synthetic chemist. Methaqualone, a synthetic quinazolinone is the most well-known sedative hypnotic drug. Involvement of two or more steps, use of hazardous chemicals, long reaction times, low reaction yields and limited availability of starting materials are the serious drawbacks of earlier reported synthetic methods.

Tiodazosin, marketed as antihypertensive agents contain both the [1, 3, 4]-oxadiazoles and quinazoline heterocycles. Despite of the widespread biological activity of alone quinazolines and these heterocycles, there is no simple and short method for the synthesis of heterocycles that contains both these ring system. In this relevance, we turned our attention to *bis*-(benzotriazolyl)-methanethione, and decided to check for the possibility of finding a simple and direct one-pot procedure that may be compatible with other heterocyclic ring and substituents. Based on our experience and in continuation of our work to search new synthetic methodology,[2] we tried to synthesized N^3-thiazole, [1,3,4]-oxadiazoles and thiadiazole substituted 2-thioxo-2, 3-dihydro-1*H*-quinazolin-4-one by the *DBU* catalyzed reaction of corresponding heterocyclic amines with anthranilic acid or its ester derivative using the *bis*-(benzotriazolyl)-methanethione as our recently reported method, where we noticed that reaction was very sluggish and afforded compound comparatively in very low yield than previously used aliphatic and aromatic amines.



A microwave assisted simple, convenient, and high yielding synthetic methodology for the diverse thioquinozolinone were developed by the amidine base catalyzed one-pot reaction of anthranilate ester, bis-(benzotriazolyl)-methanethione, and heterocyclic amines having [1, 3, 4]-oxadiazoles and thiadiazole. The method is short, simple, convenient, safe, and high yielding with anthranilate ester. Results are encouraging and are needed to be investigated in an extensive manner to develop the total synthesis of natural products containing the thioxoquinazolinones skeleton.

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Intermolecular And Intermolecular Synergistic Activity Of Molecular Bioisosterism Of Indole-Indene Rings On Inflammation

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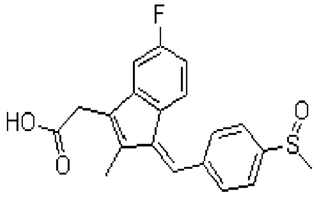
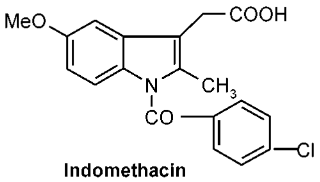
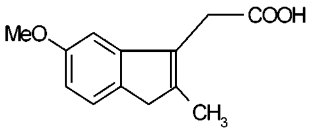
Indomethacin and sulindac both are one of the most potent NSAID having indole and indan ring respectively. The idea has been generated to synthesize similar bioisosteric ring having antiinflammatory activity. 6-methoxy-2-methyl-1-indene acetic acid has been synthesized by reaction of 3-methoxy-benzaldehyde with ethyl acetoacetate and diethyl amine by following Knovenagel condensation to get the bisacetoacetate, which on alkaline hydrolysis and subsequent acidification gives 3-methoxy-phenyl glutaric acid. This on ring cyclisation by sulfuric acid produces the 6-methoxy-3-indanone-1-acetic acid. This on treatment with formaldehyde and subsequent reduction by Clemmensen reduction and oxidation by selenium dioxide produced desired product, which is isosteres with indomethacin as well as sulindac. 3-methoxy-benzaldehyde has been prepared by nitration of benzaldehyde and subsequent reduction of nitro group into amino and then by diazotization and finally acid hydrolysis produced the phenolic group, which on methylation by dimethyl sulfate produced the 3-methoxy-benzaldehyde. Indomethacin has been hydrolyzed at amide linkage and reacting with the acid chloride of 6-methoxy-3-indanone-1-acetic acid produced indole-indene conjugate [1,2]. The toxicity parameters of the two have been intraperitoneally on mice and found the LD_{50} 68mg/kg (6-methoxy-2-methyl-1-indene acetic acid) and 82mg/kg (Indole-Indene Conjugate). LD_{50} for indomethacin has been found 50mg/kg.



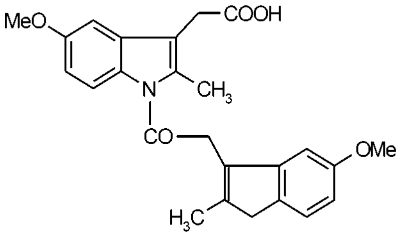
Sulindac



Indomethacin



6-Methoxy-2-methyl-1-indene acetic acid



Indole-Indene Conjugate

The antiinflammatory screening of the two compounds were performed on rat by plethismometer using rat-paw edema method by treating 6-methoxy-2-methyl-1-indene acetic acid to the first group and indole-indene conjugate to the second group having four animals each at 25mg/kg dose intraperitoneally. The % inhibition was calculated by %=[(Control-Test) ÷Control] ×100. The synergistic activity of the two test compounds were done by using indomethacin+6-methoxy-2-methyl-1-indene acetic acid and indomethacin+indole-indene conjugate and found that the duration of antiinflammatory activity remains persistent for 5th hour and 8th hour for the combination applications [3].

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Nucleophilic addition reaction of dye carbocations in mixed reversed micelles

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In the reaction systems containing surfactants, various physico-chemical properties are affected to large extent. The nucleophilic addition reaction of hydroxide with dye carbocations ion have been studied in mixed reversed micellar media formed with an anionic surfactant, AOT (sodium bis (2-ethyl-hexyl) sulfosuccinate) and non-ionic surfactants. The rate of the reaction, which follows psuedo-first order kinetics in reversed micellar media formed by AOT and non-ionic surfactant, have been measured and compared with that of the mixed reversed micellar systems. The effect of the variation of water pool, W_O ($[H_2O]/[\text{Surfactant}]$), ionic strength and additives in various reversed micellar system has also been investigated.

Thermodynamic activation parameters (standard enthalpy of activation, $\Delta H^{\#}$, standard entropy of activation, $\Delta S^{\#}$, etc.) of the reaction under different conditions have been determined. An attempt has been made to quantitatively analyse the kinetic data.

Lecture
Index

LECTURE INDEX

Special Lectures

CRSI-Medal Lectures

CRSI-Special Symposium Lectures

Poster
Index

Poster Author Index

POSTER INDEX

POSTER INDEX

POSTER INDEX

POSTER INDEX

POSTER INDEX

POSTER INDEX

POSTER INDEX

POSTER INDEX

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