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# भारतीय प्रेोद्योगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

**Prof. T. G. Sitharam** Ph.D Waterloo (Canada) FICE (UK), FIGS, FISET

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Message from the Director

It is a matter of great pride and it gives me immense pleasure that the Department of Chemistry at IIT Guwahati is organizing the flagship biennial event "Frontiers in Chemical Sciences – 2022 (FICS – 2022) on December 2-4, 2022. I take this opportunity to welcome all the dignitaries and participants to FICS – 2022. I am sure that our esteemed visitors would enjoy our beautiful campus in addition to the eventful scientific sessions. I am delighted to know that this conference provides a platform for budding scholars not only to interact with emerging academicians/industrialists from various institutes/universities across the globe but also showcase their research endeavors. It is commendable that the current version of FICS has been successful in attracting over more than 400 participants including close to 45 speakers of international repute.

A Conference of this nature would not only bring greater awareness about the field but also enhance the research potential in this region through interaction with globally acclaimed researchers in the broader area of Chemical Sciences. I strongly believe that the conference will expand the intellect of young researchers across the nation while strengthening the scientific-base of the North-East region. I hope that the scientific community at IITG would be greatly benefitted by the new ideas, research interventions and potential collaborations likely to be generated during the event. Hearty congratulations to the organizers and warm wishes to all the participants. I do hope that the symposium will be a successful, eventful and memorable one.

Prof. T. G. Sitharam 24/11/22





# Message from the Head, Department of Chemistry

The Department of Chemistry, IIT Guwahati is going to organize its flagship biennial international conference on **Frontiers in Chemical Sciences (FICS - 2022)** from 2<sup>nd</sup> to 4<sup>th</sup> December 2022. In 2010, we started our journey and it has been almost 12 years, and we are organizing this event successfully. With great pleasure and honor, on behalf of the Department of Chemistry of IIT Guwahati, we warmly welcome you to the beautiful campus on the banks of the mighty river Brahmaputra. The scientific program will consist of plenary sessions, invited talks, oral and poster presentations. It will be a great platform to share our thoughts and exchange our scientific ideas.

Once again, I would like to take this opportunity to heartily welcome all the participants from across the world to the conference. To put a conference of this magnitude together is not a small task. To that end, I would like to acknowledge the contribution of the conference organizers and the student volunteers. The team will make your stay a memorable one during the conference. Lastly, I would like to thank all of the conference participants for their contributions to making the conference a grand success.

I wish you all an engaging and productive conference participation. My best wishes for the conference and hope it will be a great success.

hopal Das

(Prof. Gopal Das) Head, Department of Chemistry

	Day 01. 02-12-2022 (Friday)	
Day 01. 02-12-2022 (I Huay)		
7:00 – 8:00 AM	Breakfast	
8:00 – 9:00 AM	Registration	
9:00 – 9:45 AM	Inaugural Session	
	Chair: Prof. T. G. Sitharam	
	Guest of Honor: Prof. Mihir Kanti Chaudhuri	
9:45 – 10:15 AM	Inaugural Lecture, Prof. J. N. Moorthy	
	Molecules to Materials by Exploitation of Steric Effects	
10:15 – 10:45 AM	KL-1, Prof. Andreas Terfort	
	Self-Assembled Monolayers: Extremely useful Materials	
10:45 – 11:05 AM	Теа	
	Chair: Prof. T. Punniyamurthy	
11:05 – 11:25 AM	IL-1. Prof. Chandra M. R. Volla	
	Allenes in Metal-Catalyzed C-H Activation Reactions	
11·25 – 11·45 ΔM	II-2 Dr. Sakva S. Sen	
11.23 11.43 AM	Amidinatohypersilylsilylene: A New Synthon in Silicon	
	Chemistry	
44.45.40.05 DNA		
11:45 – 12:05 PIVI	IL-3, Prof. Ananya Debnath	
	Membrane Phase Transition Dictated Heterogeneity	
	Length and time scale of interface water	
12:05 – 12:25 PM	IL-4, Prof. Subrata Kundu	
	Anaerobic Oxidative Modifications of Phenolic Substrates	
	at Copper(II) Sites: Implications of Proton-Coupled-	
	Electron-Transfer (PCET) Route	
12:25 – 12:45 PM	IL-5, Prof. Ponneri C. Ravikumar	
	Breaking Inert Bonds for Making Heterocyclic Derivatives	
	Using Co-catalyst Through Weak Chelation	
12·45 – 2·00 PM	Lunch	
	Chair: Prof. Parameswar Krishnan Iver	
2·00 - 2·20 DM	KI_2 Prof Toshiki Nokami	
2.00 2.30 F W	Synthesis of Cyclic Oligosaccharides via Automated	
	Flectrochemical Assembly	
2:30 – 2:50 PM	IL-6, Prof. Pijus Kumar Sasmal	
	Aggregation-Induced Emission Active Iridium Complexes	
	for Tackling Antimicrobial Resistance	

2:50 – 3:10 PM	IL-7, Prof. Joyram Guin
	Asymmetric N-Heterocyclic Carbene Catalysis via Non-covalent
	Interaction
3:10 – 3:30 PM	IL-8, Prof. Mrinmoy De
	Surface Chemistry of 2D-MoS <sub>2</sub> and Related Applications
3:30 – 3:45 PM	IndL-1, Shri Pankaj Goswami
	Role of Oil Field Chemicals in Energy Transition
3:45 – 4:00 PM	Теа
	Chair: Prof. Jubaraj Bikash Baruah
4:00 – 4:20 PM	IL-9, Prof. Ajay Venugopal
	Cationic Magnesium and Calcium Hydrides: Catalysts or Pre-
	Catalysts?
4:20 – 4:40 PM	IL-10, Dr. Santosh Kumar Gupta
	Switching to Rare Earth Independent Light: a step towards
	Aatmanirbhar Bharat
4:40 – 5:30 PM	OP1-5, Student Oral presentation
	OP-1, Arup Das Kanungo
	Exploration of the Excited State Intramolecular Proton Transfer
	Process in Solid Organic Fluorophore 2.2'-(1,4-
	phenylenebis(1H-benzo[d]imidazole-1,2diyi) diphenol an AIEE
	OB 2 Dinankar Barman
	Organocatalytic Asymmetric Inverse-Electron-Demand-Diels-
	Alder Reaction between Alkylidene Pyrazolones and Allyl
	Ketones: Access to Tetrahydropyrano [2.3-c]Pyrazoles
	OP-3, Himangshu Sharma
	Total Synthesis of Bioactive Natural Product: Thailandamide
	Lactone
	OP-4, Ibanrishisha Mawa
	Unravelling the excited state relaxation pathways in two
	nitrile-substituted 2-(oxazolinyl)-phenols
	OP-5, Gopabandhu Panigrahi
	Effect of Chalcogen's (Q) Size and Vacancy of Metals in
	Controlling the Dimensionality of Lanthanide (Ln) Containing
	Quaternary $Ba_2 - OLn_1 - xivin_2 - yQ_5$ Unalcogenides
5:30 – 7:00 PM	Poster Session (P1 – P81)

7:00 – 9:00 PM Dinner

	Day 02: 03-12-2022 (Saturday)
7:00 – 8:00 AM	Breakfast
	Chair: Prof. Abu Taleb Khan
9:00 – 9:40 AM	<b>PL-1, Prof. David Crich (Virtual)</b> Remote Conformational Control of Reactivity in the Formation and Cleavage of Glycosidic Bonds: From the Lab Bench to Nature
9:40 – 10:10 AM	KL-3, Prof. G. Naresh Patwari To ROAM or NOT?
10:10 – 10:30 AM	IL-11, Prof. Madhab C. Das MOFs and HOFs toward Plausible Energy Applications
10:30 – 10:50 AM	IL-12, Prof. Kalyaneswar Mandal Reciprocally chiral recognition to block red blood cell invasion by malaria parasites
10:50 – 11:10 AM	Теа
	Chair: Prof. Sourav Pal
11:10 – 11:50 AM	<b>PL-2, Prof. Rahul Banerjee</b> Covalent Organic Frameworks and Reticular Nano- Synthesis
11:50 – 12:20 PM	KL-4, Prof. Christof Wöll Programmed Assembly of Functional Molecular Solids from Building Blocks: The SURMOF Approach
12:20 - 12:40 PM	IL-13, Prof. Rajarshi Samanta Migratory Insertion of Quinoid Carbene: Useful Tool for Step-Economic Construction of Azaheterocycles
12:40 – 1:00 PM	IL-14, Prof. Geetharani K. Development of N-Heterocyclic Carbene Complexes of Cobalt for Carbon-Boron Bond Formation
1:00 – 2:00 PM	Lunch

	Chair: Prof. Gopal Das and Prof. Mohd. Qureshi
2:00 – 2:20 PM 2:20 – 2:40 PM	<ul> <li>IL-15, Prof. Biplab Maji</li> <li>Proximity and Interlocking in Photoredox/Nickel Dual</li> <li>Catalysis</li> <li>IL-16, Dr. Sandeep Kumar Dey</li> <li>Selective Recognition and Extraction of Oxyanions by Urea-</li> <li>Functionalized Tripodal Receptors</li> </ul>
2:40 – 3:00 PM	IL-17, Prof. Krishna Pada Bhabak Turn-on Fluorogenic Donors of Hydrogen Sulfide (H <sub>2</sub> S): Fascinating Approaches toward Drug Delivery
3:00 – 3:20 PM	IL-18, Prof. Anukul Jana Redox Mediated Synthesis of Main-Group Based Open-Shell Compounds
3:20 – 3:40 PM	IL-19, Prof. Apurba Lal Koner Sub-Cellular Intercom and Understanding Local Physical Properties
3:40 – 4:00 PM	IL-20, Prof. Sabuj Kundu Methanol as a Sustainable Reagent: Our Journey
4:00 - 4:15 PM	Теа
4:00 - 4:15 PM	Tea Chair: Prof. Biplab Mondal
4:00 - 4:15 PM 4:15 – 4:55 PM	Tea Chair: Prof. Biplab Mondal PL-3, Prof. Maurice Brookhart (Virtual) Mechanistic and Synthetic Aspects of Olefin Polymerizations Using Late Transition Metal Catalysts
4:00 - 4:15 PM 4:15 - 4:55 PM 4:55 - 5:10 PM	Tea Chair: Prof. Biplab Mondal PL-3, Prof. Maurice Brookhart (Virtual) Mechanistic and Synthetic Aspects of Olefin Polymerizations Using Late Transition Metal Catalysts IndL-2, Shri Prasad Bidwe
4:00 - 4:15 PM 4:15 - 4:55 PM 4:55 - 5:10 PM 5:10 - 5:30 PM	<ul> <li>Tea</li> <li>Chair: Prof. Biplab Mondal</li> <li>PL-3, Prof. Maurice Brookhart (Virtual)</li> <li>Mechanistic and Synthetic Aspects of Olefin Polymerizations</li> <li>Using Late Transition Metal Catalysts</li> <li>IndL-2, Shri Prasad Bidwe</li> <li>SYNTHIA<sup>TM</sup>-Retrosynthetic Design Software</li> <li>OP6-7, Student Oral presentation</li> <li>OP-6, Madhusmita Devi</li> <li>Comprehending the Efficacy of Whitlock's Caffeine-Pincered Molecular Tweezer on β-Amyloid Aggregation</li> </ul>
4:00 - 4:15 PM 4:15 - 4:55 PM 4:55 - 5:10 PM 5:10 - 5:30 PM	<ul> <li>Tea</li> <li>Chair: Prof. Biplab Mondal</li> <li>PL-3, Prof. Maurice Brookhart (Virtual)</li> <li>Mechanistic and Synthetic Aspects of Olefin Polymerizations</li> <li>Using Late Transition Metal Catalysts</li> <li>IndL-2, Shri Prasad Bidwe</li> <li>SYNTHIA<sup>TM</sup>-Retrosynthetic Design Software</li> <li>OP6-7, Student Oral presentation</li> <li>OP-6, Madhusmita Devi</li> <li>Comprehending the Efficacy of Whitlock's Caffeine-Pincered Molecular Tweezer on β-Amyloid Aggregation</li> <li>OP-7, Ritobrata De</li> <li>Oxadiazole-adorned Heterocoronene Discotics as Ambipolar Organic Semiconductors</li> </ul>
4:00 - 4:15 PM 4:15 - 4:55 PM 4:55 - 5:10 PM 5:10 - 5:30 PM 5:30 - 7:00 PM	TeaChair: Prof. Biplab MondalPL-3, Prof. Maurice Brookhart (Virtual)Mechanistic and Synthetic Aspects of Olefin PolymerizationsUsing Late Transition Metal CatalystsIndL-2, Shri Prasad BidweSYNTHIA™-Retrosynthetic Design SoftwareOP6-7, Student Oral presentationOP-6, Madhusmita DeviComprehending the Efficacy of Whitlock's Caffeine-PinceredMolecular Tweezer on β-Amyloid AggregationOP-7, Ritobrata DeOxadiazole-adorned Heterocoronene Discotics as AmbipolarOrganic Semiconductors

7.00 0.00 0.00	Day 03: 04-12-2022 (Sunday)
7:00 – 8:00 AM	Breakfast
	Chair: Prof. Anil K. Saikia
9:00 – 9:40 AM	PL-4, Prof. Kavirayani R. Prasad
	Towards the total synthesis of Strychnine
9:40 – 10:00 AM	IL-21, Prof. Debashis Adhikari
	A Radical-Promoted Olefin Hydrogenation en route to $\alpha$ -
	Alkylation Reaction
10:00 – 10:20 AM	IL-22, Prof. Madhurima Jana
	Introducing a New Class of Boron-Based Heterocyclic
	Anion Receptor Additives in Li-Ion Battery Electrolyte: A
	Combined DFT and Computer Simulation Study
10:20 – 10:40 AM	IL-23, Prof. Prabal Banerjee
	Organic Electrochemistry: A Sustainable and
	Environmentally Benign Tool for Accessing Structurally
	Diverse Molecular Architectures
10:40 – 11:00 AM	IL-24, Prof. Nagaraja C. Mallaiah
	Strategic design of framework materials for catalytic
11.00 11.20 ANA	
11:00 – 11:20 AIVI	Tea
	Chair: Prof. Aditya Narayan Panda
11:20 – 11:50 AM	KL-5, Prof. Shu-Li You (Virtual)
	Recent Progress on Catalytic Asymmetric Dearomatization
	Reactions
11:50 – 12:10 PM	IL-25, Prof. Seelam Prasanth Kumar
	1D alignment of metalated porphyrin based self-
	assembled nanowires for photocatalytic hydrogen
	evolution
12:10 – 12:30 PM	IL-26, Prof. Pankaj Kumar Koli
	A step-wise reduction of nitrate $\rightarrow$ nitrite $\rightarrow$ nitric oxide
	derivatives
12:30 – 12:50 PM	IL-27, Prof. Srabanti Chaudhury
	An Insight into Protein-DNA Interactions Using Discrete-
	State Stochastic Models
12:50 – 2:00 PM	Lunch

	Chair: Prof. Sandip Paul
2:00 – 2:30 PM	KL-6, Prof. Satrajit Adhikari
	The effects of surface temperature on molecule-surface
	scattering processes: vibrational quantum and surface
	atoms recoil effects
2:30 – 2:50 PM	IL-28, Prof. Dipankar Srimani
	Activation of Alcohols for Sustainable Catalytic
	Transformations
2:50 – 3:10 PM	IL-29, Dr. Joyee Mitra
	Reversible Toxic Gas Adsorption & Catalytic Applications of
	Supramolecular Metallogels
3:10 – 3:30 PM	IL-30, Prof. Susmita De
	Understanding the Language of Proteins through Chemistry
3:30 – 4:00 PM	OP8-10, Student Oral presentation
	OP-8, Sayani Maity
	Nitrogen Dioxide Reactivity of Copper(II) complex with
	tetradentate amine ligand followed by ligand nitrosation
	OP-9, Smiti Rani Bora
	Tuning the charge transfer and optoelectronic properties of
	tetrathiafulvalene based organic dye-sensitized solar cells: a
	theoretical approach
	OP-10, Subhradeep Kar
	Bi-Catalysed Unprecedented 1,2-Reactivity of Spiro-Cyclopropyl
4.00 4.15 DNA	
4.00 - 4.15 Pivi	Ted Chair: Prof. Ashish Kumar Gunta
Δ·15 – Δ·35 PM	OP11-12 Student Oral presentation
4.13 4.33110	$OP_{-11}$ Tirupati Roy
	Synthesis ontical properties and cation mediated tuning of
	reduction notentials of core-annulated nanothalene diimide
	derivatives
	OP-12 Vasudha Sharma
	A Robust low coordinate Co(II) Catalyst for Efficient
	Conversion of CO- into Mothanol Under Mild Conditions
4·35 – 4·50 PM	Ind 3 Dr. Sunil Dhole and Shri Tushar Wagh (Virtual)
	Chemistry and Chemical Engineering at Service
4·50 – 5·05 PM	Indl-4 Dr. Prathana Siriyara Jagannatha (Virtual)
	Bridging the Gan Between Flectron and X-Ray Diffraction
5:05 – 5:30 PM	Valedictory Program
7:00 – 9:00 PM	Dinner

# **Inaugural Speech**

# Molecules to Materials by Exploitation of Steric Effects

Jarugu Narasimha Moorthy

School of Chemistry, IISER Thiruvananthapuram, Vithura, Thiruvananthapuram, Kerala and Department of Chemistry, IIT Kanpur, Kanpur, Uttar Pradesh

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#### Abstract:

We consider molecular structure as an embodiment of organic reactivity as well as macroscopic bulk property. By dealing with design at the molecular level, it is possible to control organic reactivity as well as properties of macroscopic solids.

I will present some results of our research in the last few years on how one may control molecular reactivity and develop functional materials in a bottom-up fashion. I will exemplify rational molecular design for the development of organic functional materials, namely, photochromic materials,<sup>1</sup> and porous materials (metal-organic frameworks (MOFs) and porous organic polymers (POPs)).<sup>2</sup>

#### **References:**

- Moorthy, J. N.; Mandal, S.; Mukhopadhyay, A.; Samanta, S. J. Am. Chem. Soc. 2013, 135, 6872; b) Mukhopadhyay, A.; Maka, V.; Moorthy, J. N. Photochem. Photobiol. Rev. C. 2016, 29, 73; c) A. Mukhopadhyay, V. Maka, G. Savitha, J. N. Moorthy, Chem (Cell Press), 2018, 4, 1069. d) Jana, K.; Moorthy, J. N. Chem. Eur. J. 2022, Accepted.
- P. Chandrasekhar, A. Mukhopadhyay, G. Savitha, J. N. Moorthy, *Chem. Sci.* 2016, 07, 3085. b) P. Chandrasekhar, A. Mukhopadhyay, G. Savitha, J. N. Moorthy, *J. Mater. Chem. A.* 2017, 5, 5402. c) A. Mukhopadhyay, V. Maka, G. Savitha, J. N. Moorthy, *Chem* (Cell Press), 2018, 4, 1069. d) V. Maka, A. Mukhopadhyay, Moorthy, J. N. *Nanoscale*, 2018, 10, 22389. e) V. Maka, A. , J. N. Moorthy, *Chem. Eur. J.* 2019, 25, 3835. f) Maka, V. K.; Tamuly, P.; Jindal, S.; Moorthy, J. N. *App. Mater. Today* 2020, 19, 100613. g) Yadav, C.; Maka, V. K.; Payra, S.; Moorthy, J. N. *J. Catal.* 2020, 384, 61. h) Jindal, S.; Maka, V.K.; Anjum, G.; Moorthy, J. N. *ACS Applied Nano Materials* 2021, 04, 449. i) Tamuly, P.; Sama, F.; Moorthy, J. N. *Adv. Mater. Interfaces* 2022, 2200337. J) Yadav, C.; Payra, S.; Moorthy, J. N. *J. Catal.* 2022, 414, 769

# **Inaugural Speech**

# **Brief Biodata**



Dr. J. N. Moorthy obtained Ph.D degree from the Organic Chemistry Department of Indian Institute of Science, Bangalore in 1994. He pursued postdoctoral research in University of Houston, USA, University of Wuerzburg, Germany and University of Victoria, Canada prior to joining the Chemistry Department, IIT Kharagpur in 1998. After a 5-month stint, he moved to IIT Kanpur. He has been a full professor at IITK since 2008. He moved to IISER Thiruvananthapuram as the Director in April 2019.

He is a recipient of AvH postdoctoral research fellowship, Germany (1995-96), young chemist award, and bronze and silver medals of Chemical Research Society of India (CRSI), India. He received Shanti Swarup Bhatnagar Prize in Chemical Sciences, India (2008), and Sastra-CNR Rao award in Chemical Sciences (2020). He is a Fellow of Indian Academy of Sciences Bangalore (2010), Fellow of Royal Society of Chemistry (2014) and Fellow of Indian National Science Academy (2018). He has also been a J. C. Bose National Fellow since 2015. He has been on the editorial boards of New J. Chemistry, J. Chem. Sci. and Int. J. Photoenergy. He is presently an associate editor of J. Chem. Sci.

His interests are in the areas of supramolecular chemistry, organic materials, mechanistic organic chemistry and organic photochemistry.

# Remote Conformational Control of Reactivity in the Formation and Cleavage of Glycosidic Bonds: From the Lab Bench to Nature

David Crich

Department of Pharmaceutical and Biomedical Sciences Department of Chemistry, Complex Carbohydrate Research Center University of Georgia, Athens, GA 30602, USA Email: David.crich@uga.edu

As has long been recognized, the reactivity of glycosyl donors is influenced by a multitude of factors, most prominently relative configuration and nature of protecting groups. In the last twenty-five years, beginning with the discovery of the benzylidene-directed  $\beta$ -mannosylation reaction, this list has been supplemented with the conformation about the exocyclic C-C bond in the donor side chain. This lecture will begin with a brief outline of systematic studies into the manner in which side chain conformation influences glycosyl donor reactivity and selectivity, with examples from the sialic acids and other higher carbon sugars. The lecture will continue with a discussion of recent work in our laboratory to exploit the phenomenon in simple hexopyranosyl donors using a dummy ligand at the 6-position to restrict side chain conformation. The lecture will then address the question as to whether nature has pre-empted organic chemistry by restricting substrate side chain conformation to maximize catalysis by glycoside hydrolases and glycosyl transferases. Finally, the lecture will conclude with a description of recent work in our laboratory toward the design of improved glycosidase inhibitors that exploit this general phenomenon.



David Crich received his Ph.D. in 1984 in Organic Chemistry from the University of Paris-XI under the supervision of Derek Barton. He pursued his post-doctoral research at the Institute for Natural Products Chemistry in Gif-sur-Yvette jointly with Barton and Pierre Potier. His independent career began at University College London in 1985 and has continued with appointments at the University of Illinois at Chicago (1990-2007), Wayne State University (2007-2009 and 2011-2019), the Institute for Natural Products Chemistry (2009-2011) and since 2019 at the University of Georgia. He is interested in carbohydrate chemistry, organic chemistry and medicinal chemistry and has won various awards for his endeavours in these areas.

# PL2

### **Covalent Organic Frameworks and Reticular Nano-Synthesis**

Rahul Banerjee

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur Campus, Mohanpur 741 252

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Covalent Organic Frameworks (COFs) represent a new class of highly porous, crystalline polymers with uniformly arranged ordered pore channels. Even though COFs have been used for the storage of a wide variety of molecular species like gases, nanoparticles, enzymes, and drugs, the benefits of their ordered pore channels for molecular separation are hardly extracted. The key issue behind this problem is fabricating COF particles into a self-standing, stable membrane form. Apart from the processability, the other formidable obstacle preventing the utilization of COFs in real-life applications is i) chemical stability, ii) complicated synthetic procedures and iii) scalability. In this context, we have successfully overcome the chemical stability problem of COFs, by synthesizing  $\beta$ -ketoenamine based frameworks. Irreversible enol to keto tautomerism resulted in exceptional stability within the frameworks. While processability, synthetic hurdles, and scalability of COFs still remain unexplored. To address these critical issues, we have developed a straightforward, scalable, and novel methodology by which COFs can be synthesized by simple mixing and heating of the reactants. Using this method, COF can be processed into self-standing covalent organic framework membranes (COMs). The resultant COMs display higher porosity and crystallinity over their reported powder form. These self-standing COMs are flexible, continuous, devoid of any internal defects or cracks, show long-term durability. It retains structural integrity in the water, organic solvents, and mineral acid (3 N HCl). We have utilized these COMs for separation applications such as wastewater treatment and recovery of valuable active pharmaceutical ingredients [APIs] from organic solvents. Our result highlights that COMs could satisfactorily address the world's most challenging separation problems, including wastewater treatment and drug recovery from organic solvents in pharma industries.





Prof. Rahul Banerjee received his PhD degree from University of Hyderabad, Hyderabad in 2006. After a postdoctoral work in UCLA (2006-2008), he joined CSIR-National Chemical Laboratory, Pune, India in 2008 as a Scientist. Prof. Rahul Banerjee is currently an Associate Professor at Indian Institute of Science Education and Research (IISER) Kolkata. His research interests include the study of structural chemistry with the flavor of chemical synthesis to design new porous materials. His work represents an important blend of fundamental as well as applied research, as these materials might selectively capture and store hydrogen and carbon dioxide as a reservoir. Apart from the gas storage application, his group was further able to utilize the ordered pores of COFs for gas and liquid separation application, by making the first COF membranes. Prof. Rahul Banerjee has published over 160 publications and 24 patents applications from CSIR-National Chemical Laboratory and Indian Institute of Science Education and Research (IISER) Kolkata on various porous framework materials since 2010. His current h-index is 80

## PL3

# Mechanistic and Synthetic Aspects of Olefin Polymerizations Using Late Transition Metal Catalysts

#### <u>Maurice Brookhart</u> Department of Chemistry, University of Houston, Houston, TX 77204 USA mbrookhart@unc.edu

This presentation will begin with a brief discussion of the properties of polyethylene and the synthesis of various forms of polyethylene via early metal catalysts and via free radical processes. Following this I will trace the development, polymerization activity and mechanistic aspects of Ni(II) and Pd(II) diimine-derived late metal catalysts. The talk will finish with a discussion of issues surrounding copolymerization of ethylene and polar vinyl monomers and a mechanistic dissection of the copolymerization of ethylene with vinyl trialkoxysilanes using both Pd(II) and Ni(II) diimine catalysts.



Maurice Brookhart (b. 1942) grew up in the mountains of Western Maryland and attended Johns Hopkins University in Baltimore where he received an A.B. degree in chemistry in 1964. He carried out his doctoral work in physical organic chemistry at UCLA under the direction of Saul Winstein. After finishing the Ph.D. degree in 1968, he spent six months as a National Science Foundation postdoctoral fellow at UCLA with Winstein and Frank Anet, followed by a year of study at Southampton University as a NATO postdoctoral fellow. Brookhart joined the University of North Carolina faculty in 1969 and retired as a William R. Kenan, Jr. professor of chemistry in 2014. In 2015 he joined the faculty at the University of Houston to conduct joint research with Prof. Olafs Daugulis.

Brookhart has spent research leaves in Rennes, Oxford, Berkeley, Seville, Marburg and at the Max Planck Institute in Muelheim. He served as associate editor of *Organometallics* (1990-95) and received ACS Awards in Organometallic Chemistry(1992), Polymer Chemistry(2003) and the Somerjai Award for Creative Research in Catalysis(2015). He was elected to the National Academy of Sciences in 2001 and received the North Carolina Award in Science in 2008 and the Willard Gibbs Medal in 2010.

Brookhart's research interests span mechanistic, synthetic, and structural organometallic chemistry and catalysis. Most of his work has focused on the development and mechanistic understanding of late transition metal complexes for olefin polymerizations and the employment of C-H and Si-H bond activation processes in catalytic transformations of small molecules, particularly hydrocarbons.

# PL4

# Towards the total synthesis of Strychnine

Kavirayani R. Prasad

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Our research group has been involved in the total synthesis of polyketide natural products using chiral pool tartaric acid and chiral furyl carbinols as the four carbon four hydroxy synthon. During the course of our synthesis of the natural product schulziene B, we had an unexpected entry to the realm of sulfinimine chemistry. This led to us to develop procedures for the direct addition of ketones, substituted methyl enones and other nucleophiles to non-racemic sulfinimines. In this talk, our efforts in application of the above methods in the total synthesis of alkaloids including the approach for the total synthesis of strychnine will be discussed.<sup>1-5</sup>



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Prasad (b.1969) obtained his B. Sc (Chemistry) from Andhra University, Visakhapatnam and MSc from Sri Krishnadevaraya University, Anantapur Andhra Pradesh. He obtained PhD from University of Pune in 1997 in asymmetric catalysis working at the National Chemical Laboratory (NCL), Pune under the guidance of Dr. N. N. Joshi. He held post-doctoral positions as the Alexander von Humboldt Foundation fellow (1998-2000) at the University of Muenster, Germany with Prof. Dr. Dieter Hoppe and another post-doctoral stay with Prof. Franklin A. Davis at Temple University, Philadelphia, PA, USA. After a brief stint as scientist in Medicinal Chemistry at Praecis Pharmaceuticals (presently GlaxoSmithKline) in Waltham, MA, USA, Prasad joined Department of Organic Chemistry, Indian Institute of Science in November 2003 where currently he is currently Professor.

Prasad's research interests are concerned with the development of synthetic strategies for the total synthesis of natural products of therapeutic significance and their evaluation as potent therapeutics.

Prasad is recipient of the Swarnajayanthi fellowship of the Department of Science and Technology (2006-2007), National Academy of Sciences-SCOPUS young scientist award administered by Elsevier (2009), Prof. N. S. Narasimhan Endowment lecture award of the University of Pune (2013), Rajib Goyal Prize (2012-2013) and the Shanti Swarup Bhatnagar Prize in chemical Sciences (2014). Prof. Prasad is an elected fellow of the Indian Academy of Sciences, (2015) and the National Academy of Sciences, India (NASI).

Prof. Prasad is an Associate Editor of *Organic Letters*, a premier journal in organic chemistry published by the American Chemical Society.

### KL1

# Self-Assembled Monolayers: Extremely useful Materials

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After their establishing about 30 years ago, self-assembled monolayers (SAMs) are now been employed in many areas of natural science and technology to adjust many different properties of surfaces and interfaces.

In this talk, I will show that the area still bears many surprises, room for improvement and – in conjunction with new problems – very innovative solutions. In this context, a major field of technological progress, (opto)electronics based on organic molecules, strongly benefits from the use of SAMs, as the devices contain many different interfaces, the properties of which have to be carefully adjusted. Starting from approaches to obtain extraordinarily highly ordered systems, we will discuss the problems of semiconductor growth on surfaces and on how to optimize charge carrier injection in such devices, even leading to complex logic circuitry.

In the second part of my talk, new uses of SAMs shall be discussed, in which the monolayers become altered in a way that they can be lifted off their substrates. The resulting nanometer thick membranes can be used as supports e.g. in transmission electron microscopy or can be further converted into graphene derivatives with interesting properties.

Finally, I want to introduce SAMs as templates for growth of metal-organic frameworks (MOFs), which due to their defined crystal structure formed from a diversity of organic ligands and metal ions gain a lot of interest. SAMs help to control the growth of these materials not only in two dimensions, but also regarding the orientation of these often highly anisotropic materials, which themselves also show an interesting surface chemistry.



Andreas Terfort studied chemistry in Göttingen and Regensburg (PhD: 1994). After a postdoc stay with George M. Whitesides, he returned to Hamburg, Germany in 1996 to pursue his Habilitation (2003). Following a series of (locum) professorships in Bochum, Frankfurt and Marburg, he finally was appointed as full professor at the Goethe-University of Frankfurt in 2008. His research aims at understanding the fundamentals of surface phenomena for the development of surfaces with pre-determined ('designed') properties, such as bio-compatibility, disinfection, corrosion inhibition, or sensing.

# KL2

# Synthesis of Cyclic Oligosaccharides via Automated Electrochemical Assembly

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We have developed "automated electrochemical assembly" which is an electrochemical method to synthesize middle-sized molecules including oligosaccharides in automated manner.<sup>1</sup> In this lecture, synthesis of three different cyclic oligosaccharide using automated electrochemical assembly will be introduced. Cyclic  $\beta$ -1,6-oligo *N*-acetylglucosamine was the first example of cyclic oligosaccharides synthesized via automated electrochemical assembly.<sup>2</sup> Synthesis of cyclic  $\alpha$ -1,4-oligo *N*-acetylglucosamine "Cyclokasaodorin<sup>®</sup>" was achieved via electrochemical polyglycosylation-isomerization-cyclization process developed by our group.<sup>3,4</sup> Cyclic  $\beta$ -1,3-,  $\beta$ -1,6-glucan dodecasaccharide is the largest and most complex cyclic oligosaccharides in this presentation. Although synthesis of its linear precursor hexasaccharides has already been achieved by automated electrochemical assembly,<sup>5,6</sup> retrosynthetic analysis is particularly important to synthesize the protected precursor of dodecasaccharide via the electrochemical dimerization-cyclization process.



Figure 1. Target natural and unnatural cyclic oligosaccharides.

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#### **EDUCATION**

1999, 03: (BA) Department of Industrial Chemisry, Kyoto University (Professor Makoto Harada) 2001, 03: (MS) Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University (Professor Jun-ichi Yoshida)

2004, 03: (PhD) Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University (Professor Jun-ichi Yoshida)

#### **RESEARCH EXPERIENCES**

2001, 04 - 2004, 03: Recipient of JSPS Research Fellowships for Young Scientists

2004, 04 - 2005, 02: Postdoctoral Fellow, Swiss Federal Institute of Technology (ETH) Zurich (Professor Peter H. Seeberger)

2005, 03 - 2011, 03: Assistant Professor, Department of Synthetic Chemistry and Biological Chemistry,

Graduate School of Engineering, Kyoto University (Professor Jun-ichi Yoshida)

2011, 04 - 2012, 10: Senior Lecturer, Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University (Professor Jun-ichi Yoshida)

2012, 11 - 2019, 09: Associate Professor, Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University (Professor Toshiyuki Itoh)

2019, 10 - present: Professor, Department of Chemistry and Biotechnology, Tottori University

#### **RESEARCH INTERESTS**

Carbohydrate Chemistry, Organic Electrochemistry, Synthetic Organic Chemistry, Ionic Liquid

#### AWARDS

2008, 02: Meiji Seika Kaisya Award in Synthetic Organic Chemistry
2009, 03: The 5<sup>th</sup> Progress Award in Organic Electrochemistry
2012, 03: The 26th Young Scholar Lecturer of CSJ
2012, 05: The 52th Research Grant Award of the UBE Foundation
2012, 09: The 15th Incentive Award of the Japanese Society of Carbohydrate Research
2017, 02: The 62th Scientific Research Achievement Award of Tottori University
2017, 11: The 40th Incentive Award of the Chugoku-Shikoku Branch of the Society of Synthetic Organic Chemistry, Japan

#### SELECTED PUBLICATIONS

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Original Papers: 107, Reviews: 15

## KL3

# **To ROAM or NOT?**

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A unimolecular dissociation process leading to two fragments emerging out of a single reactant possess an attractive yet flat potential in the exit channel, in the 3-8 Å region, resulting in dynamically complex trajectories that do not necessarily follow Arrhenius kinetics of crossing over a barrier, are termed as reactions undergoing "ROAMING" mechanism . The photodissociation of formaldehyde is a celebrated example of reaction with roaming radical mechanism.[1] In this talk, I will discuss two examples of photo-induced reactions, (i) intermolecular coulombic decay in molecular clusters and (ii) photodissociation of nitrobenzenes, probed using velocity map imaging technique, wherein the roaming mechanism is expected to play vital role in the reaction dynamics.



**Figure 1**. Velocity map image of NO radical produced following 266 nm photolysis of nitrobenzene and the corresponding translational energy distribution profile. Note that the translational energy distribution profile shows two components, the fast and slow which arise due two different mechanisms.

The photodissociation of nitrobenzene yields NO with a bimodal translational energy distribution, which suggests the presence of two distinct NO elimination channels resulting in slow and fast translational energy components. It has been proposed that the fast translational energy component results from the NO formation via an oxaziridine ring intermediate in the triplet state, while the slow translational energy component is result of photoisomerization of nitro group to nitrite group in the ground state either through a roaming transition state or a tight transition state.[2,3] However, the origin of the slow component has been a subject of debate due to the presence of multiple singlet-triplet crossings in the case of nitrobenzene. In order to delineate the role of roaming mechanism in the NO formation, we have investigated the dissociation dynamics of hetero-nitroaromatics using Velocity Map Imaging method. The hetero-nitroaromatics molecules provide a cleaner system which demarcate the roaming transition state.

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Naresh Patwari Ganpathi is a professor at the Department of Chemistry, IIT Bombay. After master's degree from University of Hyderabad in 1994, he joined Tata Institute of Fundamental Research for the PhD program and graduated in 2000. He was a JSPS postdoctoral fellow at the Tohoku University (2000-2002)followed another postdoctoral stint at the University of Illinois at Urbana-Champaign (2002-2003). He joined IIT Bombay in 2003 as an assistant professor and became professor in 2012. He was also a visiting scientist at Genesis Research Institute, Japan in 2010. His current research addresses variety of phenomena involving intermolecular interactions using both experimental and theoretical methodologies. In 2017, for the fundamental contributions to hydrogen bonding I was awarded Shanti Swarup Bhatnagar Prize in Chemical Sciences.

# KL4

# Programmed Assembly of Functional Molecular Solids from Building Blocks: The SURMOF Approach

#### Christof Wöll

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Realizing molecular "Designer Solids" by programmed assembly of building units taken from libraries is a very appealing objective. Recently, metal-organic frameworks (MOFs) have attracted a huge interest in this context. Here, we will focus on MOF-based electrochemical, photoelectro-chemical, photovoltaic, and sensor devices. Internal interfaces in MOF heterostructures are also of interest with regard to photon-upconversion and the fabrication of diodes.

Since the fabrication of reliable and reproducible contacts to MOF-materials represent a major challenge, we have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on appropriately functionalized substrates. The resulting films are referred to as SURMOFs [1,2] and have very appealing properties in particular with regard to optical applications [3]. The fabrication of hetero-multilayers is rather straightforward with this lbl method. In this talk, we will describe the principles of SURMOF fabrication as well as the results of systematic investigations of electrical and photophysical properties exhibited by empty MOFs and after loading their pores with functional guests. We will close with discussing further applications [4] realized by loading MOFs with nanoparticles or quantum dots and by creating molecular solids lacking inversion symmetry for second harmonic generation (SHG).[5]

In the last part of the presentation we will point out that SURMOFs are very well suited for unattended experimentation approaches. Using robot systems controlled by machine learning (ML) algorithms allows to efficiently optimize thin film properties (orientation, crystallinity, roughness). We will discuss this point in particular in connection with the fabrication of SURMOF-based sensor systems.

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Since 2009 he is the director of the Institute of Functional Interfaces at the Karlsruhe Institute of Technology. After his studies of physics at the University of Göttingen he received his PhD in 1987 from the Max-Planck-Institut of Dynamics and Self-Organization in Göttingen. After a postdoctoral time (1988 to 1989) at the IBM research laboratories, San Jose, USA he accepted a position equivalent to Assistant Professor at the Institute of Applied Physical Chemistry, University of Heidelberg. After his habilitation he took over the chair for Physical Chemistry at the University of Bochum (until 2009). He received the following awards: Heisenberg scholarship funded by the German DFG 1994-1996, Max-Planck Medal for PhD thesis (Max-Planck Society) 1998, van't Hoff Prize of the German Bunsen Association (DGB) 2016, From 2026-2018 he was Spokeperson of the Surface Physics Division of the German Physical Society and from 2016 until 2019 Elected member of the Council on Physical Chemistry of solid-State Bodies, Surfaces, and Characterization of Materials of the German Science Foundation (DFG). He is a Member of German National Academy of Sciences (Leopoldina). In 2019 he was awarded an honorary doctorate by the Southern Danish University of Odense for his services in the development of organic thin films in general and especially for his work in the development of so-called organometallic scaffold compounds (SURMOFs). His reaserch areas include Fundamental processes in Surface Physics and Surface Chemistry, Development and advancement of techniques for the characterization of molecular adsorbates and oxide surfaces, Organic surfaces, Metal-organic frameworks (MOFs).

# **Recent Progress on Catalytic Asymmetric Dearomatization Reactions**

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Dearomatization reactions are widely recognized as powerful methods for the synthesis of highly functionalized three-dimensional structures from simple planar aromatic compounds. Among those, catalytic asymmetric dearomatization (CADA) reactions are very attractive due to the abundance and ready availability of aromatic compounds and the direct access to enantiopure polycycles and spirocycles offered by them. That latter are frequently the key motifs in biologically active natural products and pharmaceuticals. However, due to the extra stability of "aromaticity" of the arenes, their dearomatization reactions with good enantioselective control has been a great challenge. In this talk, we present our recent results toward the development of catalytic asymmetric dearomatization reactions. The dearomatization reactions of indoles, pyrroles, phenols, naphthols, and pyridines have been achieved, affording various highly functionalized heterocycles bearing all-carbon quaternary chiral centers in most of the cases. These results provide not only the efficient synthesis of highly enantioenriched spiro- or polycycles, but also a novel concept in asymmetric catalysis.

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Shu-Li You was born in Henan, China, and received his BSc in chemistry from Nankai Univ. (1996). He obtained his PhD from Shanghai Institute of Organic Chemistry (SIOC) in 2001 under the supervision of Prof. Lixin Dai before doing postdoctoral studies with Prof. Jeffery Kelly at The Scripps Research Institute. From 2004, he worked at the Genomics Institute of the Novartis Research Foundation as a PI before returning to SIOC as a Professor in 2006. He is currently appointed as director of the State Key Laboratory of Organometallic Chemistry and deputy director of SIOC. His research interests mainly focus on asymmetric C-H functionalization and catalytic asymmetric dearomatization (CADA) reactions. Professor You has published over 300 research papers in internationally peer-reviewed journals (>24000 citations). He is the recipient of AstraZeneca Excellence in Chemistry Award (2011), RSC Merck Award (2015), Ho Leung Ho Lee Foundation Prize for Scientific and Technological Innovation (2016), State Natural Science Award (2nd class) (2017), and Xplorer Prize (2019). Prof. You has been an Associate Editor for JACS since Jan 2021.

#### KL6

# The effects of surface temperature on molecule-surface scattering processes: vibrational quantum and surface atoms' recoil effects

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The studies on molecule-surface scattering processes have enormous importance in understanding the heterogeneous catalytic reactions. The effect of surface mode vibrations and their state distribution at a specific surface temperature for H<sub>2</sub>/D<sub>2</sub>-Cu(111) dissociative chemisorption systems is explored for those molecules in their rovibrational ground state (v=0, j=0). We assume weakly correlated interactions between molecular degrees of freedom (DOFs) and surface vibrational modes through a Hartree product type wavefunction<sup>1</sup> within the linear and quadratic (anharmonic) molecular DOFs-surface modes coupling regime. While constructing the six-dimensional effective Hamiltonian, we employ (a) a chemically accurate potential energy surface according to the static corrugation model<sup>2</sup>; (b) normal mode frequencies and displacement vectors calculated with different surface atom interaction potentials<sup>3-5</sup> within a cluster approximation; and (c) initial state distributions for the vibrational modes according to Bose–Einstein probability factors. We perform 6D quantum dynamics<sup>6-7</sup> with the so-constructed effective Hamiltonian and calculate sticking and state-to-state scattering probabilities. As observed in the experiments,<sup>8-9</sup> the surface mode vibrations affect the chemisorption dynamics by displaying vibrational quantum and surface atoms' recoil effects in the regions of low and high collision energies of incoming diatom. The comparisons between our present results and experimental and other theoretical outcomes are demonstrated to discuss the novelty of our theoretical method.<sup>6,7,10</sup>

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Dr. Satrajit Adhikari is a Senior Professor of Theoretical Chemistry in Indian Association for the Cultivation of Science, Kolkata, India and adjunct Professor at IISER Kolkata. He received his Ph.D. from the Physical Chemistry Department of the same institute. He worked with Professor G. D. Billing for Post-Doctoral research at Copenhagen University, Denmark. Then he served as visiting Scientist at The Fritz Haber Research Center, The Hebrew University, Jerusalem. Currently Professor Adhikari's research focuses on: i) Beyond Born- Oppenheimer theoretical development and its applications on spectroscopic and scattering processes; ii) Methodological development for following the dynamics of multi-electronic multi-mode molecular systems; iii) Thermal effects on molecule-surface scattering; iv) Reaction dynamics for triatomic systems on single (adiabatic) and multiple (diabatic) potential energy surface(s); v) Selective photodissociation dynamics of bonds in small molecules and vi) Role of Jahn-Teller effect in the phase transition of orthorhombic rare earth crystals. He has published close to 151 articles on his areas of research in various international peer-reviewed journals. Professor Adhikari has delivered numerous talks at various national as well as international symposiums and training schools.

# IL 1

# **Allenes in Metal-Catalyzed C-H Activation Reactions**

Chandra M. R. Volla

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The invention of metal-catalyzed directing group assisted C-H activation has opened up new avenues for providing diverse array of decorated ring structures. Toward the development of sustainable earth-abundant metal catalysts, our research group has been investigating a series cobalt and nickel catalyzed C(sp2)-H activation with under-utilized p-systems like allenes, methylenecyclopropanes and oxabenzonorbornadienes. The key challenge in engaging these p - systems are the regiocontrol in the migratory insertion with organometallic species.



In this seminar, we will discuss our investigation into these less explored p-components in CH activation, demonstrating the capacity of these scaffolds for accessing a wide range of heteroannulation and dienylation reactions. Unique mechanistic implications in all of these transformations will also be described.

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Chandra M. R. Volla was born in Parvathipuram (Andhra Pradesh, India). He received his M. Sc. in chemistry from University of Hyderabad in 2005 and graduated with a Ph. D. in organic chemistry from Ecole Polytechnique Federale de Lausanne (EPFL), Switzerland working under the guidance of Prof. Pierre Vogel in 2009. In 2010 he joined the group of Prof. Magnus Rueping at RWTH Aachen, Germany as a Swiss National Science Foundation Fellow. After two and half years in Germany, he moved to Stockholm University, Sweden for pursuing postdoctoral studies funded by Wenner-Gren Foundation with Prof. Jan.-E. Backvall. In October 2014, he returned to India to join as an assistant professor in the department of chemistry, IIT Bombay and in May 2018, he was promoted to Associate Professor in the same department. His research interests include the study and development of different activation modes in metal and organocatalysis and their application in dual catalysis. He was awarded with INSA Medal for Young Scientist-2018, NASI-Young Scientist Platinum Jubilee Award-2018, Alkyl Amines Young Scientist Award-2018, IRCC Early Achiever Award-2017, Thieme Chemistry Journal Award-2021, AVRA Young Scientist Award-2020, Merck Young Scientist Award-2021 and OPPI Young Scientist Awards-2021.
## Amidinatohypersilylsilylene: A New Synthon in Silicon Chemistry

Sakya S. Sen

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At the "10th International Symposium on Organosilicon chemistry" in Poland in 1993, Nils Wiberg termed tris(trimethylsilyl) moiety as "hypersilyl" moiety (hereinafter we shall follow Wiberg's nomenclature) to distinguish it from the very related tri(*tert*butyl)silyl group, which he named "supersilyl" group. The advantages of the hypersilyl group are not only the good  $\sigma$ -donation or pronounced steric bulk, but the commercial availability of the precursors and possibility of further functionalization due to the presence of the SiMe3 moieties. In our part, we have prepared a new silylene connected with a hypersilyl moiety<sup>1</sup> and studied its reactivity towards small molecules.<sup>1,2,3</sup> Functionalization of the TTSS moiety led to the formation of unsymmetric disilenes.<sup>4</sup> The chemistry was subsequently extended to germanium and tin.<sup>5</sup>

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Dr. Sen received his Ph.D in 2010 at the University of Göttingen, Germany. Postdoctoral work followed (2011-2013) working with Prof. Holger Braunschweig at the University of Würzburg, Germany, supported by AvH Foundation. In 2014, he was appointed as a senior scientist at CSIR-NCL, Pune, where he is currently serving as a Principal Scientist since 2018. Dr. Sen is the recipient of CSIR-Young scientist award in 2017, INSA medal for Young Scientist in 2018, Merck Young Scientist Award, 2019, NCL-RF Scientist of the year in 2020, Swarnajayanti fellowship in 2021, CRSI-Bronze Medal 2022. He has been selected as a ChemComm Emerging Investigator 2018, Early Career Advisory Board Member of ACS Catalysis (2019-2021), Young Associate of Indian Academy of Science (2017-2020) and featured in "75 under 50 Scientists Shaping Today's India" (DST) (2021).

# Membrane Phase Transition Dicated Heterogeneity Length and Time Scale of Interface Water

## Ananya Debnath

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Water assists in retaining the activity of a cellular membrane under physiological conditions. However, the correlation between the dynamics of water and membrane organization relevant for their activities and survival under physiological and low temperature conditions is not quantified and largely unknown. To this objective, a total of  $11.55 \sim 11.55 \mu$ s all-atom molecular dynamics simulations of 1,2-dimyristoyl-sn-glycerol-3-phosphocholine lipid membranes reveals a supercooling driven strong slow-down in heterogeneity time scale and structure-dictated drastic growth in heterogeneity length scales of the interface water (IW) at the fluid to the ripple to the gel phase transitions of the membranes. A universal violation and preservation of Stokes-Einstein relation is observed for the time scales derived from different quantities manifesting dynamical heterogeneity. The spatio-temporal scales follow an activated dynamical scaling solely within the gel phase similar to the random first order transition theory. The heterogeneity length scale of the IW becomes temperature evidence of probing ripple size of the membrane through the heterogeneity length scale of the interface water. The work opens up a possibility to characterize any domain-associated structural alterations of the membrane through the heterogeneity length scales of the IW in the full scale of the membrane through the heterogeneity length scale of the IW in the gel phase temperature invariant at the ripple size of the membrane through the heterogeneity length scale of the interface water. The work opens up a possibility to characterize any domain-associated structural alterations of the membrane through the heterogeneity length scales of the IW in the future



Ananya Debnath received the B. Sc. degree in Chemistry honours with Physics and Mathematics as minors from Calcutta University, in 1999, the MSc degree in Chemistry from Calcutta University, in 2001, with specialization in Physical Chemistry, and the PhD degree from the Department of Inorganic and Physical Chemistry, IISc Bangalore, in 2007. She did ther post doctoral research in Department of Chemical Engineering, IISc ad Max Planck Institute for Polymer, Mainz and University of Frankfurt. She joined IIT Jodhpur in 2013 as an Assistant Professor. Since 2019, she has an Associate Professor with the Chemistry Department, IIT Jodhpur. Her current research interests include multiscale modelling of soft and bio molecules. Dr. debnath was a recipient f the Max Planck Fellowship by Max Planck Society, Germany in 2009-2012. She is a Review editor if frontiers with speciality section Biophysics and an active referee of many international journals.

# Anaerobic Oxidative Modifications of Phenolic Substrates at Copper(II) Sites: Implications of Proton-Coupled-Electron-Transfer (PCET) Route

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Oxidatively modified tyrosine (Tyr) derivatives, such as nitro-tyrosine (Tyr-NO<sub>2</sub>) and chloro-tyrosine (Tyr-Cl), serve as biomarkers for cardiovascular, neurodegenerative, and various inflammatory diseases conditions related to aging.<sup>[1]</sup> Although oxygenase-type modifications of phenolic substrates by different reactive copperoxygen intermediates such as dicopper(II)-peroxo and dicopper(III)-(bis-u-oxo) have gained enormous interest over several decades.<sup>[2]</sup> The examples of phenol oxidation under anaerobic and ambient conditions, however, remain poorly understood. Notably, utilizing a nitrito-copper(II) cryptate, our previous study outlines phenol oxidation coupled to the reduction of  $NO_2^-$  to NO through proton-coupled-electron-transfer (PCET).<sup>[3]</sup> Intriguingly, the phenol reactivity of the nitrito-copper(II) cryptate with a protonated outercoordination-sphere has been illustrated to provide an unusual anaerobic route for phenol nitration.<sup>[3,4]</sup> Aiming to disclose the underlying mechanism for such anaerobic oxidations of phenol, our present efforts are dedicated to design new ligand scaffolds with systematic alterations of the first and second coordination sphere functionalities around the copper(II) site.<sup>[5]</sup> Unlike the copper(II) complexes of tripodal N-benzyl-tris-(2aminoethyl)amine) (L<sup>3H</sup>), the copper(II)-nitrite or -chloride complexes of N-nitroso-N-benzyl-tris-(2aminoethyl)amine) (L<sup>3NO</sup>) facilitate the anaerobic oxidations of various phenolic substrates resulting in nitrophenol and chlorophenol derivatives, respectively. Detailed kinetic investigations, including kinetic isotope effect (KIE) and Evring analyses, reveal a proton-coupled-electron-transfer (PCET) as the ratedetermining step for phenol chlorination mediated by copper(II)-Cl complex of L<sup>3NO</sup>. While other plausible phenol oxidation routes have also been considered, our work outlines that copper(II) sites supported by suitable coordination environments can mediate proton-coupled-electron-transfer (PCET) under anaerobic conditions.

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Subrata Kundu graduated with B.Sc. and M.Sc. from Jadavpur University (2007) and IIT Kanpur (2009), respectively. He obtained his Ph.D. from Humboldt-Universität zu Berlin (2013) under the supervision of Prof. Kallol Ray. Subsequent to a postdoctoral stint (Feb/2014-July/2017) in the group of Prof. Tim Warren (at Purdue University and Georgetown University), Subrata's independent career began as an assistant professor of Chemistry at Indian Institute of Science Education and Research Thiruvananthapuram (IISER-Tvm). Fascinated by the diverse bioactivities of metalloenzymes, his research efforts broadly focus on bioinspired coordination chemistry and elucidation of reaction mechanisms.

# Breaking Inert Bonds for Making Heterocyclic Derivatives Using Co-catalyst Through Weak Chelation

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During the last century, direct functionalization of inert bonds such as C-C and CH has mainly been ignored due to their high bond strength and inertness. Since the beginning of the 21<sup>st</sup> century, there has been renewed interest in functionalizing these inert bonds through metal catalysts to synthesize many useful organic molecules. In this talk, I will briefly introduce sustainable C-H activation reaction and our work using first-row transition metal catalysts through weak chelation. Many transformations have been developed, such as alkylation, alkenylation, and concomitant cyclization. Further, I will talk about the in-situ water generation from trifluoroethanol, which provides novel catalytic transformation through inert C-H and CC bond functionalization. Several mechanistic and control studies support the proposed catalytic cycle, which shows the unique catalytic efficiency of Co(III)-catalyst along with weak coordination.



Figure 1. Transition metal-catalyzed C-C and C-H bond functionalization of organic motifs.

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Dr. Ponneri C. Ravikumar obtained his B.Sc. (Chemistry) and M.Sc (Organic Chemistry) from the University of Madras. He completed his Ph.D. at the Indian Institute of Science (IISc), Bangalore, India, under the guidance of Prof. A. Srikrishna. Subsequently, he moved to the USA for his postdoctoral stint, first at Duquesne University, Pittsburgh, with Prof. Fraser F. Fleming and then at Yale University, New Haven, with Professor Seth B. Herzon. He joined as Assistant Professor at the Indian Institute of Technology (IIT), Mandi, Himachal Pradesh, in the year 2010. He continued there until December 2015; then, he moved to the National Institute of Science Education and Research (NISER), Bhubaneswar, Odisha, where he is currently an Associate Professor. He has received teaching excellence award as well as best faculty award for institute service while serving at IIT Mandi. Apart from teaching and Infrastructure) at IIT Mandi and Head, Estate Management and Works Department at NISER Bhubaneswar. The Chemical Research Society of India (CRSI) recently conferred him Bronze Medal for the year 2023 for his significant contribution to research in chemistry.

# Aggregation-Induced Emission Active Iridium Complexes for Tackling Antimicrobial Resistance

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Antimicrobial resistance (AMR) is a major global threat to human health and currently one of the leading causes of death worldwide due to the rapid emergence of multi-drug resistant (MDR) bacteria.<sup>1</sup> Since over the past 30 years no new antibiotics have been discovered, the World Health

Organization (WHO) has already warned of dire consequences as we are swiftly edging towards the "post-antibiotic era". This scenario clearly projects that there is an urgent and unmet need for the development of new classes of antibacterial agents to combat against MDR superbugs. However, the development of probes for rapid diagnosis of bacteria with desired sensitivity and selectivity, along with antibacterial activity against MDR bacteria has remained a great challenge. To address this, we have developed aggregation-induced emission (AIE) active cyclometalated iridium(III) polypyridine complexes for simultaneous rapid detection and elimination of drug-resistant bacteria in aqueous solutions.<sup>2</sup> The complexes can detect different Gramnegative and Gram-positive bacteria by fluorescence spectroscopy at concentrations as low as 1.2 CFU/mL within 5 min in spiked water samples. Detection of bacteria by these complexes is also visible by naked eye and fluorescence microscopy imaging at higher (10<sup>8</sup> CFU/mL) cell concentrations. More notably, the complexes show potent antibacterial activity against drug-resistant bacteria with low minimum inhibitory concentrations (MICs)  $\leq 5 \mu g/mL (1-4 \mu M)$  *via* ROS generation and cell membrane disintegrity. Interestingly, these complexes exhibits higher specificity toward bacterial cells compared to mammalian cells.

In this presentation, briefly we will also talk on the development of AIE-active iridium(III) complexes as antimalarial agents that demonstrates dual capability for imaging and killing of MDR malaria parasites. Further, we will discuss the design of AIE-active iridium probes engineered with antisense oligonucleotides (ASOs) to specifically target distinct conserved regions of the SARS-CoV-2 RNA for rapid detection of COVID-19 infection within 10 min at room temperature.



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Pijus Kumar Sasmal obtained his M.Sc degree from the Department of Chemistry, Indian Institute of Technology (IIT) Guwahati in 2005 and Ph.D degree (Advisor- Prof. Akhil R. Chakravarty) Department of Inorganic & Physical Chemistry, Indian Institute of Science (IISc) Bangalore in 2010. He did his postdoctoral research at the University of Marburg, Germany (October 2010-September 2012), Rutgers University, USA (November 2012-June 2014), and Princeton University, USA (July 2014-September 2015) with Prof. Eric Meggers,

Prof. KiBum Lee, and Prof. Robert K. Prud'homme, respectively. He joined the School of Physical Sciences, Jawaharlal Nehru University (JNU), New Delhi, India, in 2015 as an Assistant Professor. His group is working in the interdisciplinary research areas of chemistry and biology. His main research interest is the design and synthesis of metal-based diagnostic and therapeutic agents for tackling different diseases such as cancer and microbial infections (e.g. bacterial, malarial, and viral).

# Asymmetric N-Heterocyclic Carbene Catalysis via Non-covalent Interaction

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N-Heterocyclic carbenes (NHCs) have occupied an important place in asymmetric organocatalysis. The ability of NHC to activate substrates via covalent or non-covalent interaction provides a unique opportunity to develop numerous asymmetric transformations via NHC-catalysis.<sup>1</sup> Indeed, NHC-catalyzed many impressive asymmetric transformations have already been developed involving covalent interaction with substrates possessing activated carbonyl functional groups or with Lewis acidic silicon or boron reagents. On the contrary, the non-covalent mode of asymmetric NHC-catalysis, which undoubtedly widen the scope of NHC-catalysis, is in its infancy. Our group is actively working on developing novel enantioselective organic transformations using both covalent and non-covalent mode of NHC-catalysis. Some recent findings of our group on asymmetric NHC catalysis will be presented, during the lecture.<sup>2</sup>



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#### **Education:**

- Ph.D. (2004-2007): International Graduate School of Chemistry, Westfälische Wilhelms-Universität, Muenster, Germany (Advisor: Professor Armido Studer)
- M.Sc. (2002-2004): Indian Institute of Technology, Kharagpur, India
- B.Sc. (1999-2002): University of Calcutta, India

## **Positions Held:**

- Professor (since January 2021): School of Chemical Sciences, IACS, India
- Associate Professor (2017-2020): School of Chemical Sciences, IACS, India
- Assistant Professor (2013-2016): Department of Organic Chemistry, IACS, India
- Postdoctoral Fellow (2010-2012): Max-Planck-Institut für Kohlenforschung, Germany
- (Advisor: Professor Benjamin List, Nobel laureate 2021)
- Postdoctoral Fellow (2008-2010): University of Geneva, Switzerland

(Advisor: Professor Jerome Lacour)

## Awards and Honors:

- Associate of the Indian Academy of Sciences (IASc), 2019
- Thieme chemistry journals award, 2014
- Max-Plank fellowship for post-doctoral research at MPI für Kohlenforschung, Germany, 2011
- Alexander von Humboldt (AvH) fellowship for postdoctoral research, 2010

### **Research Areas:**

- The development of new generation method for organic synthesis using molecular oxygen (O<sub>2</sub>) as the source of oxygen atom or benign oxidant
- Asymmetric organocatalysis using N-heterocyclic carabenes (NHCs) Organic synthesis involving visible-light-mediated photocatalysis

## Surface Chemistry of 2D-MoS<sub>2</sub> and Related Applications

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Two-dimensional  $MoS_2$  nanosheets (2D- $MoS_2$ ) have been widely used in many biological applications due to their distinctive physicochemical properties. In the past, it was theorized that chemically exfoliated  $MoS_2$  can be modified using thiol chemistry (Raybaud, P, et al. Phys. Rev. Lett. 1998, 80, 1481). In this regard, we provide the first experimental evidence for this process using a facile solution based method. By chemically engineering the ligands, we then show ability to modulate the surface charge of the MoS<sub>2</sub> sheets. In doing so, we demonstrated the ability to tune the surface of the conjugates for selective enzyme targeting, inhibition and antibacterial activity. Moreover, 2D-MoS2 generally exists in two different polymorphic structures, metallic (1T phase) and semiconducting (2H phase). The functionalization of 2H phase is even more difficult due to the inertness of the surface. We report a new method for the exfoliation and direct functionalization of 2H- $MoS_2$  using surfactant molecules with thiol functionality. We found that the exfoliated  $MoS_2$  using thiolated ligands are functionalized with desired functionality and the processing scheme can be extended to other TMDs. Further, the development of surface modification using thiolated ligands allows us to use them for many specific applications. Apart from that, effect of possible ligand exchange on 2D-MoS<sub>2</sub> has never been explored, which can play an important role in diverse biological applications. Recently we have observed the ligand exchange phenomenon on  $2D-MoS_2$  in presence of different thiolated ligands. We have used that phenomenon for detection of several bio-thiols and drug delivery application. This strategy can be applied to the development of 2D-TMD based materials for various biological applications related to ligand exchange.



Figure: Functionalization and place exchange of thiolated ligands on 2D-MoS<sub>2</sub> and related applications.

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Mrinmoy De did his B.Sc. in Chemistry from Midnapore College, Vidyasagar University (2000) and received his M.Sc. from Indian Institute of Technology, Bombay (2002). Followed by he completed his Ph.D. from University of Massachusetts at Amherst under the supervision of Prof. Vincent M. Rotello (2009) and was a CCNE and NSEC postdoctoral fellow at Northwestern University. Since 2014 he has been at the Indian Institute of Science, Bangalore, where he is an associate professor at department of organic chemistry. His research focuses on the preparation various nanomaterials and their application towards development of nanoantibiotics, nanozymes, sensors and photocatalysis.

Awards:

2022 - Recipient of CRS Silver Medal by Chirantan Rasayan Sanstha

2021 - Recipient of Ignite Life Science Foundation Grant.

2015 – DST Young Scientist Award by Science and Engineering Research Board (SERB).

2010 – Outstanding Researcher Award by NSF Nanoscale Science & Engineering Center (NSEC)

2008 – Graduate Student Travel Grant Award by University of Massachusetts.

2007 - Procter & Gamble Outstanding Graduate Student Research Award.

2006 – Marvin Rausch Outstanding Poster Award Sponsored by Fisher Scientific.

2000 - Gold Medalist in 2000, B.Sc. Chemistry, Vidyasagar University, India.

## Cationic Magnesium and Calcium Hydrides: Catalysts or Pre-Catalysts?

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 $MgH_2$  and  $CaH_2$  find applications as reducing agents in organic chemistry. [1] They have generated significant interest as hydrogen storage materials. To understand elementary chemical reactions involved with  $MgH_2$  and  $CaH_2$ , chemists ventured into the isolation of the molecular hydrides. [2] Today, we find a handful of examples of molecular hydrides of alkaline earth metals showing relevance in the stoichiometric and catalytic reduction of unsaturated molecules. [3] Our studies on cationic alkyl, amides, and alkoxy derivatives [4] have opened the possibilities in accessing reactive hydride compounds. While there are no straightforward routes to obtain cationic hydrides, we have identified the challenges and developed new ways. [5,6] Investigations on the elementary reactions involving these newly synthesized hydrides have provided vital proof for understanding their roles as catalysts and pre-catalysts in the hydroelementation of unsaturated organic molecules. [6]

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Ajay Venugopal is an Associate Professor at the Indian Institute of Science Education and Research Thiruvananthapuram and works in main group chemistry. In 2016, he established a state-of-art laboratory on the scenic new campus. His research primarily focuses on understanding the structure and bonding in reactive main group compounds, stabilization of unusual coordinate modes, activation of inert chemical bonds, and Lewis acid catalysis. Curiosity-driven research in isolating reactive main group cations comprising magnesium, zinc, aluminum, antimony, and bismuth has led his group to explore their potential as Lewis acids in catalytic hydrosilylation.

# Switching to Rare Earth Independent Light: a step towards Aatmanirbhar Bharat

Santosh Kumar Gupta

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Commercial white-light LED lamps are typically made with InGaN blue LEDs coated with yellow phosphors containing rare-earth elements, such as cerium-doped yttrium aluminum garnet (YAG:Ce<sup>3+</sup>). Other red, blue, and green commercial phosphor also employs  $Eu^{3+}$ ,  $Dy^{3+}$  and  $Tb^{3+}$  ions. It is of great interest to develop rareearth-free phosphors to reduce the synthesis cost and more importantly the long-term adverse effects on the environment associated with the extraction and processing of the rare-earth materials. Also it is also being reported that rare earth ions have narrow excitation spectra due to the 4f-4f forbidden transitions, resulting in low absorbances. In recent years, a new group of Zn-Ga-Ge-O spinels, namely zinc gallate, zinc germanate, zinc stannate and their solid solutions, and has been developed for applications as RE free in both downconversion and persistent luminescence. In this talk, I will be speaking about our recent work on defect based downconversion and persistent light emission from zinc gallate, zinc germanate and zinc gallo germanate & stannate. These molecules under high temperature treatment generates abundance of vacancies, interstitials and antisite defects which not only act as emissive agent but also work as a trap in providing longer persistent light emission even on switching off the light source. Due to the complete separation of two processes, --excitation and emission--, minimal tissue absorption, and negligible autofluorescence can be obtained during biomedical fluorescence imaging using persistent luminescent materials. We could achieve ultra bright emission, tunability, radioluminescence and longer afterglow in these materials by virtue of defect engineering. To achieve commercial success these powder particles are also forcespun into polymer fiber. These molecules we believe have great potential to become a highly efficient new phosphor that is also earthabundant, non-toxic, and low-cost for applications in solid-state lighting and display.

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Dr. Santosh Kumar Gupta joined the 53<sup>rd</sup> batch of Bhabha Atomic Research Centre Training School and subsequently joined the Radiochemistry Division in 2010. Dr. Gupta is a graduate of Delhi University (B.Sc.), Indian Institute of Technology, Delhi (M.Sc.), and the Homi Bhabha National Institute at Mumbai, India (Ph.D.) Dr. Gupta is the recipient of several awards notable among them are Fulbright, Indo-US and JSPS Fellowship, DAE Young Scientist and Group achievement award, Scientific India Young Scientist award, Society of Materials Chemistry and Indian association of Nuclear Chemists and allied scientists Bronze medal for year 2021. He has also been bestowed with membership of Indian national young academy of sciences (INYAS) & National academy of sciences and young associate of Maharashtra academy of sciences MASc for the year 2021. He has received Royal society of Chemistry certificate for among 10% most cited author and ICDD certificate for contribution of new XRD pattern. He was featured in Top 2% most Influential scientists worldwide based on the Scopus publications impact consecutively for the year 2020 and 2021 prepared by Prof. John PA Loannidis of Stanford University and his team and published by Elsevier. As of today, he has published more than 200 journal articles with around 4600 citations and h-index of 42 and i-10 index of 113. His area research focuses on designing light emitting materials for health, energy and environment etc.

## **MOFs and HOFs toward Plausible Energy Applications**

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The presentation includes the discussion on design strategy, synthesis and various applications of tailored porous metal organic frameworks (MOFs) and hydrogen-bonded organic frameworks (HOFs) performed in the 'Framework Laboratory' at IIT-KGP. The frameworks are microporous with considerable solvent accessible volume and form channels with the dimensions ranging from  $\sim$ 3-7 Å. As the stability in presence of water and/or moisture is a topic of significant importance while considering them for practical applications, these frameworks do reveal high stability towards moisture and water as well. The high CO<sub>2</sub> separation selectivity over N<sub>2</sub> and CH<sub>4</sub> along with its moisture/water/pH stability makes these MOFs potential candidates for CO<sub>2</sub> separation from flue gas mixture and landfill gas mixture respectively. Besides gas separations, performances of MOFs and HOFs as superprotonic solid state conductors for plausible usage in fuel cells as PEMs will also be presented.

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- "Immobilization of a Polar Sulfone Moiety onto the Pore Surface of a Humid Stable MOF for Highly Efficient CO<sub>2</sub> Separation under Dry and Wet Environment through Direct CO<sub>2</sub>-Sulfone Interactions" A. Pal, S. Chand, D. G. Madden, D. M. Franz, L. Ritter, B. Space, T. Curtin, S. C. Pal and M. C. Das\* ACS Applied Materials & Interface. 2020, 12, 41177-41184.
- "A 2D Mg(II)-MOF with High Density of Coordinated Waters as Sole Intrinsic Proton Sources for Ultrahigh Superprotonic Conduction" S. Chand, S. C. Pal, D.-W. Lim, K. Otsubo, A. Pal, H. Kitagawa\*, M. C. Das\* ACS Materials Letters. 2020, 2, 1343-1350.
- 9. "Polycarboxylates Templated Coordination Polymers: Role of Templates for Superprotonic Conductivities up to 10<sup>-1</sup> S cm<sup>-1</sup>" S. M. Elahi, S. Chand, W.-H. Deng, A. Pal and M. C. Das\* Angew. Chem., Int. Ed. 2018, 57, 6662-6666.



Madhab C. Das received his B.S. (2002) from Midnapore College and M.S. (2004) in Chemistry from Vidyasagar University. He completed his Ph.D. in Supramolecular Chemistry at IIT Kanpur under the supervision of Professor P.K. Bharadwaj (2009). Then, he worked with Professors Banglin Chen at the University of Texas at San Antonio, George K.H. Shimizu at University of Calgary, and Hiroshi Kitagawa at Kyoto University as postdoctoral fellow (2009–2013) before joining IIT Kharagpur as Assistant Professor in 2013. Since 2019, he is an Associate Professor at IIT Kharagpur. His work is focused on functional Metal-Organic Frameworks (MOFs).

# Reciprocally chiral recognition to block red blood cell invasion by malaria parasites

### Kalyaneswar Mandal

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Apical membrane antigen 1 (AMA1) and rhoptry neck protein 2 (RON2) are two key *Plasmodium falciparum* proteins responsible for the moving junction formation that triggers malaria parasite entry into red blood cells. Identifying a suitable small protein to interfere with the interactions between AMA1 and the extracellular domain of RON2 would be an ideal strategy to snap off the junction formation, which, in turn, will stop the invasion process. We are using a unique combination of 'chemical protein synthesis' and 'mirror-image phage display' to systematically identify mirror-image protein molecules (consisting of all D-amino acids and glycine) that will have potential to interfere with the AMA1-RON2 interactions. Mirror-image proteins are resistant to proteolysis and less immunogenic. Therefore, a suitably engineered mirror-image protein molecule would be superior to a conventional natural peptide/protein as a candidate antimalarial therapeutic.



Kalyaneswar Mandal is an Associate Professor of Chemistry and Chemical Biology at the Tata Institute of Fundamental Research (TIFR), Hyderabad. He received his Ph.D. from IIT Bombay in organic chemistry. After completing his Ph.D. he worked at The University of Chicago, first as a Postdoctoral Fellow and later as a Research Professional Associate. In 2016, he joined the TIFR faculty at Hyderabad. He is a recipient of the DBT/Wellcome Trust India Alliance Intermediate Fellowship award. Dr. Mandal's research focuses on the synthetic protein chemistry combined with biophysical methods to elucidating and controlling the molecular basis of protein function.

# Migratory Insertion of Quinoid Carbene: Useful Tool for Step-Economic Construction of Azaheterocycles

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The diazo quinone or quinone diazide compounds have been extensively utilized to introduce phenol/naphthol moieties into hydrocarbons or nitrogen-containing heterocycles under transition metal catalysis. The reactions proceed via C–H insertion or migratory insertion of metal carbenes.<sup>1</sup> Due to site-selectivity issues, directed C–H metalation, metal–quinoid carbene formation followed by migratory insertion has achieved considerable attention.<sup>2</sup> In this presentation, regioselective arylation of quinoline scaffolds to provide 8-azaBINOL,<sup>3</sup> methyl- arylation,<sup>4</sup> based on the migratory insertion of quinoid carbenes will be discussed. Further, the racemic synthesis of important phosphine ligands like QUINAP, METHOX, PINAP, PHENAP will be discussed.<sup>5</sup> Construction of indolocoumarin using this strategy will also be explained.<sup>6</sup> Finally, a mild *N*-arylation using a similar strategy will also be presented.<sup>7</sup>



Figure. Migratory insertion of quinoid carbene for the site-selective arylation

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- 7. Bera, S.; Roy, S.; Pal, S. C.; Anoop, A.; Samanta, R. ACS Catal. 2021, 11, 10847-10854.



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Rajarshi Samanta did his bachelor's (2002) and master's (2004) from Jadavpur University. He received his PhD from the Indian Institute of Chemical Technology, Hyderabad in 2010 under the supervision of Prof. Tushar Kanti Chakraborty. Subsequently, he moved to Max Planck Institute, Dortmund, Germany for his postdoctoral work under Prof. Andrey P Antonchick as Max-Planck postdoctoral researcher. Then he joined at Indian Institute of Technology, Kharagpur as an assistant professor in September 2013 and was successively promoted to associate professor in August 2019. He received Associateship for the Indian Academy of Sciences (2019-2022) and was selected as an Emerging Investigator, *New Journal of Chemistry* (2021).

## **Current Research Interest:**

- Development of transition metal-catalyzed step economic transformations especially using diazo compounds via the formation of metallocarbenes/nitrenes.
- Synthesis of bioactive natural products using the developed methods.
- Direct late-stage modifications of various complex heterocyclic molecules in a catalytic way.
- Development of step-economic methods for the construction of heteroatomcontaining organic extended  $\pi$ -conjugated systems and screening their activity in biological assays as well as organic material.

# Development of N-Heterocyclic Carbene Complexes of Cobalt for Carbon-Boron Bond Formation

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Given their importance in utility as versatile precursors to a wide range of other valuable families of molecules, introducing diverse functionality into the organoboron compounds will enhance its use as a synthetic handle in target-directed synthesis.<sup>1</sup> Several efficient synthetic routes has been established and most of them rely on heavy metal based catalysts such as Pd, Rh, Ir etc. which suffers from inherent toxicity, cost and sustainability concerns.<sup>2</sup> This obviously put forth the needful for the development of catalytic systems based on earth abundant metals like Mn, Fe, Co etc. We have developed *N*-heterocyclic carbene supported cobalt catalysts for the synthesis of variety of boronic ester derivatives using cheap as well as challenging precursors, such as aryl and alkyl halides<sup>3,4</sup>, substituted alkenes,<sup>5</sup> N-heterocycles and aldehydes. The key results will be discussed.



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- (5) Verma, P. K.; Sethulekshmi, A. S.; Geetharani, K. Org. Lett. 2018, 20, 7840-7845.



Geetharani was born and raised in Madurai, Tamilnadu, India. She began her independent research career as an Assistant Professor at department of inorganic and physical chemistry, Indian Institute of Science Bangalore, India in 2016. She was promoted to an Associate professor in 2022. She is a recipient of DST-Inspire Faculty Award. She has been elected as Young Scientist/Affiliate by all three Science Academies in India. She received the SERB-Women Excellence Award from the President of India. She is also an Editorial member of Chemistry – An Asian Journal and a member of the Early Career Advisory Board of the European Journal of Inorganic Chemistry. Her research interests are in the areas of catalysis, main group and organometallic chemistry.

## **Representative Publications:**

- 1. Verma, P. K.; Meher, N. K.; Geetharani, K.\* Homolytic Cleavage of Diboron(4) Compounds by Diazabutadienes. *Chem Commun.* **2021**, *57*, 7886 7889. Highlighted on the Cover Page of the Article.
- 2. Siddiqui, S.; Bhawar, R.; Geetharani, K.\* Iron-Based Catalyst for Efficient Borylation of Unactivated Alkyl Halides. J. Org. Chem. 2021, 86, 1948-1954.
- 3. Verma, P. K.; K. Sujit Prasad.; D. Varghese.; Geetharani, K.\* Cobalt(I)-Catalyzed Borylation of Unactivated Alkyl Bromides and Chlorides. *Org. Lett.* **2020**, *22*, 1431-1436.
- 4. Verma, P. K.; Setulekshmi, A. S.; Geetharani, K.\* Markovnikov-Selective Co(I)-Catalyzed Hydroboration of Vinylarenes and Carbonyl Compounds. *Org. Lett.* **2018**, *20*, 7840-7845.
- Mandal, S.; Verma, P. K.; Geetharani, K.\* Lewis Acid Catalysis: Regioselective Hydroboration of Alkynes and Alkenes Promoted by Scandium triflate. *Chem. Commun.* 2018, 54, 13690-13693. Highlighted in Synfacts 2019, 15 (02), 0150.
- Verma, P. K.; Souvik, M.; Geetharani, K.,\* Efficient Synthesis of Aryl Boronates via Cobalt-Catalyzed Boryla-tion of Aryl Chlorides and Bromides. *ACS Catal.* 2018, *8*, 4049-4054. Highlighted in Synfacts 2018, 14(07), 0746.

# IL 15 Proximity and Interlocking in Photoredox/Nickel Dual Catalysis

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Covalent organic frameworks (COFs) are a promising toolbox in heterogeneous catalysis.[1] In this hot field, we recently reported a dual metallation (iridium and nickel) strategy in a single 2D-COF TpBpy to perform a variety of C-N cross-coupling reactions.[2] Moving from the traditional approach, [3] we focus on the COF-backbone as a host for metal-catalyzed photosensitive C-N coupling reactions. The controlled metallation and recyclability without deactivation of both catalytic centers are unique for previously reported coupling strategies. We also prepared a single metal decorated highly conjugated COF to enable metallaphotoredox catalysis for light-harvesting cross-coupling reactions.[4,5] The interlocking of Ni metal in the COF backbone helped to explore eight different C-X (X = B, C, N, O, S) cross-coupling reactions. We performed various photoluminescence and electrochemical studies with Hammett correlations to understand the mechanism. These protocols enable selective and reproducible coupling of a diverse range of amines (aryl, heteroaryl, alkyl), carbamide, sulfonamide, thiol, acid, and electron-rich -neutral, and -poor (hetero)aryl iodides. Keeping this strategy in perspective, we explored the activity to produce nonsteroidal anti-inflammatory drug Fulfenamic acid, strong pharmacophore N,5-diphenyloxazol-2amine, Food and Drug Administration (FDA) approved drugs Flibenserin, Tripelennamine and did late-stage diversification of the derivatives of ibuprofen, naproxen, gemfibrozil, helional, glycine, ketoprofen, ibuprofen, geraniol, menthol, and ɛ-aminocaproic acid.



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1987: Born, Howrah, India

**2007**: B.Sc. University of Calcutta (Chemistry Hons.)

**2009**: M.Sc. Indian Institute of Technology Kanpur (Chemistry)

2012: PhD Ludwig Maximillan Universität Munich, Supervisor: Prof. Herbert Mayr

2013-2015: Postdoc: Chubu University, Mentor: Prof. Hisashi Yamamoto

**2016**: Alexander von Humboldt fellow: Westfälische Wilhelms-Universität Münster, Mentor: Prof. Frank Glorius

**2016-2021**: Assistant Professor, Indian Institute of Science Education and Research Kolkata

2021-: Associate Professor, Indian Institute of Science Education and Research Kolkata

Research focus: Organic synthesis, catalysis, and mechanistic studies.

## Awards:

2021: "2021 Young Investigator Award ", Sponsored by Molecules

2021: Merck Young Scientist Award (runner-up) in Chemical Science

**2021**: INSA Medal for Young Scientists

2021: Associate of the Indian Academy of Sciences (IASc)

2020: NASI-Young Scientist Platinum Jubilee Award (2020) in Chemical Sciences

2019: Thieme Journal Award

## Selected publication:

- P. Rai, K. Maji, S. K. Jana, B. Maji, Chem. Sci. 2022, doi: 10.1039/D2SC04005K.
- K. Das, S. Waiba, A. Jana, B. Maji, Chem. Soc. Rev. 2022, 51, 4386-4464.
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# Selective Recognition and Extraction of Oxyanions by Urea-Functionalized Tripodal Receptors

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Selective recognition of an oxoanion by a hydrogen bond donor (HBD) scaffold demands design and synthesis of suitable receptors which could discriminate between anions of identical size and shape or basicity.<sup>1</sup> TRENbased urea and thiourea functionalized anion receptors have extensively been studied over the past two decades.<sup>2</sup> However, selective recognition of noxious oxoanion such as arsenate and chromate has always remained a challenging task in the field of anion recognition chemistry. We have established that second-generation hydrogen bond donor (HBD) anion receptors with an inner amide cavity and an outer urea cavity can selectively recognize and efficiently extract a specific oxoanion from water in the presence of competitive anions, depending on the nature of the peripheral aryl substitution.<sup>3</sup> The selectivity of a second generation oxoanion receptor has also been confirmed by crystallization experiments and density functional theory-based binding (interaction) energy calculations. Our current research showcases the synthetic modification of first generation tripodal receptors into oxoanion selective second generation receptors and unfolds the numerous possibilities of obtaining anion selectivity by mere structural alteration of known HBD organic receptors.



Figure 1. Selective arsenate encapsulation by an arsenate selective second generation HBD receptor.

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- S. K. Dey, B. Gil-Hernández, V. V. Gobre, D. Woschko, S. S. Harmalkar, F. R. Gayen, B. Saha, R. L. Goswame and C. Janiak, *Dalton Trans.*, 2022, 51, 15239–15245, (b) S. K. Dey, Archana, S. Pereira, S. S. Harmalkar, S. N. Mhaldar, V. V. Gobre and C. Janiak, *CrystEngComm*, 2020, 22, 6152–6160.

## Dr. Sandeep Kumar Dey

#### **Present Position**

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1. M.Sc. in Chemistry, North Eastern Hill University, Shillong, Meghalaya, India (Aug 2004–Dec 2006).

2. Ph.D. in Chemistry, IIT Guwahati, Assam, India (Jan 2008–Jan 2013), Supervisor: Prof. Gopal Das.

3. Postdoctoral Fellow at Academia Sinica, Taipei, Taiwan (May 2013– April 2014), Supervisor: Prof. S. S. Sun

4. Alexander-von-Humboldt postdoctoral Fellow at Institute of Inorganic and Structural Chemistry, Heinrich-Heine

University (HHU) Dusseldorf, Germany (Aug 2014–Dec 2016), Supervisor: Prof. Christoph Janiak

5. INSPIRE Faculty Fellow at Department of Chemical Sciences, Goa University, India (May 2017- Feb 2021).

#### Selected Publications (Total International Publications: 30, Book Chapters: 2)

1. S. K. Dey, B. Gil-Hernández, V. V. Gobre, D. Woschko, S. S. Harmalkar, F. R. Gayen, B. Saha, R. L. Goswamee and C. Janiak, *Dalton Trans.*, 2022, 51, 15239–15245.

2. **S. K. Dey,** Archana, S. Pereira, S. S. Harmalkar, S. N. Mhaldar, V. V. Gobre and C. Janiak; Selective encapsulation and extraction of hydrogenphosphate by a H-bond donor tripodal receptor; *CrystEngComm*, 2020, 22, 6152-6160.

3. **S. K. Dey,** N. D. Amadeu and C. Janiak; Microporous polyurethane material for size selective heterogeneous catalysis of the Knoevenagel reaction, *Chem. Commun.*, 2016, 52, 7834–7837.

4. **S. K. Dey,** and Gopal Das; Selective inclusion of PO<sub>4</sub><sup>3-</sup> within persistent dimeric capsules of a tris(thiourea) receptor and evidence of cation/solvent sealed unimolecular capsules, *Dalton Trans.*, 2012, 41, 8960–8972.

5. **S. K. Dey,** R. Chutia and Gopal Das; Oxyanion-encapsulated caged supramolecular frameworks of a tris(urea) receptor: Evidences of hydroxide- and fluoride-ion-induced fixation of atmospheric  $CO_2$  as a trapped  $CO_3^{2^-}$  anion, *Inorg. Chem.*, 2012, 51, 1727–1738.

6. **S. K. Dey,** and Gopal Das; A selective fluoride encapsulated neutral tripodal receptor capsule: solvatochromism and solvatomorphism, *Chem. Commun.*, 2011, 47, 4983–4985.

7. **S. K. Dey,** and Gopal Das; Fluoride selectivity induced transformation of charged anion complexes into unimolecular capsule of a  $\pi$ -acidic triamide receptor stabilized by strong N-H···F<sup>-</sup> and C-H···F<sup>-</sup> hydrogen bonds, *Cryst. Growth Des.*, 2011, 11, 4463–4473.

#### **Research interests**

1. Selective recognition and extraction of oxoanions using amide and urea-based organic receptors.

2. Hydrogen-bonding supramolecular capsules and Hydrogen-bonded Organic Frameworks (HOFs).



# Turn-on Fluorogenic Donors of Hydrogen Sulfide (H<sub>2</sub>S): Fascinating Approaches toward Drug Delivery

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In the year of 1777, a Swedish-German chemist Carl Wilhelm Scheele, discovered an essential bio-active gaseous molecule (gasotransmitter) popularly known as hydrogen sulfide (H<sub>2</sub>S). Although H<sub>2</sub>S was earlier considered as toxic gas, its important biological implications and benefits were explored rather recently. In mammals, the bio-synthesis of H<sub>2</sub>S is primarily governed by few key enzymes such as, cystathionine- $\gamma$ -lyase (CSE), cystathionine- $\beta$ -synthase (CBS) and 3-Mercaptopyruvate sulfurtransferase (3-MST). Moreover, the dietary sources of H<sub>2</sub>S include several allium and cruciferous vegetables (garlic, onion, broccoli, asparagus etc). In addition to these natural donors, the active research on the development of synthetic donors of H<sub>2</sub>S and the exploration their detailed pharmacological applications began after 1980.<sup>1</sup> Over last two decades, a number of non-fluorogenic organic donors of H<sub>2</sub>S are being developed for a slow and sustained donation of H<sub>2</sub>S as this was found to be crucial for mimicking its endogenous production with potent pharmacological implications. However, a real-time monitoring of H<sub>2</sub>S donation from non-fluorogenic donors is a major inconvenience with the existing knowledge. Therefore, the present talk will primarily highlight our recent strategies in developing the bio-analyte-responsive turn-on fluorogenic donors of H<sub>2</sub>S (Figure 1).



Figure 1. Schematic representation for the bio-analyte-responsive turn-on fluorogenic H<sub>2</sub>S donation strategies.

Few aspects regarding the development of polysulfide-based synthetic organosulfur compounds as potent sources of  $H_2S$  will be discussed. Inspired by the presence of allylic organopolysulfides in garlic, the exploration of very convenient and selective synthetic methodology for the symmetrical organosulfides (monosulfides, disulfides and trisulfides) will be described.<sup>2</sup> Subsequently, for a convenient and noninvasive monitoring of  $H_2S$  donation process, strategies for the external stimuli-responsive turn-on fluorogenic donors of  $H_2S$  for a sustained release will be discussed.<sup>3,4</sup> Finally, mechanistic pathways for the anti-cancer potential of organotrisulfides as  $H_2S$  donors in breast cancer cells will be highlighted.<sup>5</sup>

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- 5. D. Bhattacherjee, K. Raina, T. K. Mandal, R. P. Thummer and K. P. Bhabak, *Free Radic Bio Med*, **2022**, *191*, 82-96.



## **Professional Experience**

Professional Experienc	e
Jun, 2021 - Present	Associate Professor, Department of Chemistry, IIT Guwahati, Assam, India
Apr, 2015 - Jun,	Assistant Professor, Department of Chemistry, IIT Guwahati,
2021	Assam. India
Feb. 2013 - Apr.	Assistant Professor, Department of Chemistry, Presidency
2015	University Kolkata India
Nov. 2012 - Feb.	Post-doctoral Researcher University of Oxford United
2013	Kingdom
Jul 2010 - Oct 2012	Post-doctoral Researcher (Alexander von Humboldt Fellow)
oui, 2010 Oct, 2012	Humboldt University Berlin Germany
Aug 2009 - Iun	Research Associate IISc Bangalore India
Aug, 2007 - 5un, 2010	Research Associate, fise Dangalore, fildia
2010	
Education	
Aug 2006 - Jul 2009	Ph.D. Department of Inorganic & Physical Chemistry IISc
Aug, 2000 - Jul, 2007	Rangalora India (Supervisor: Prof G Mugash)
Aug 2003 Apr	M S. in Chamical Science, IISa, Pangalara, India
Aug, 2005 - Apr,	M.S. III Chefinical Science, IISC, Dangalore, India
2000 Awa 2000 Jul 2002	D.S. (Chamietry Hone) Demokrishen Mission Desidential
Aug, 2000 - Jul, 2005	B.Sc. (Chemistry Hons.), Ramakirshina Mission Residential
	Conege, Narendrapur, University of Calculta, India
Awards/Fallowshins	
Awarus/renowsnips	INSPIDE Equilty Award by Department of Science and
Jan, 2015	Tashnala av (DST) India
Dec. 2010	Dest Thesis Award by Eli Lilly and Commonly Outstanding Thesis
Dec, 2010	Best Thesis Award by Eli Lilly and Company Outstanding Thesis
NA 2010	Award 2010 in Asia
Mar, 2010	Alexander von Humboldt Fellowship for Post-doctoral
	Researcher by Alexander von Humboldt Foundation, Germany

### **Research summary**

The major research interests of the group are in the field of (i) developing fluorogenic and non-fluorogenic donors of hydrogen sulfide (H2S) and studying their biological implications; (ii) targeted delivery of anti-cancer/anti-inflammatory compounds/drugs using fluorogenic drug delivery systems; (iii) design and synthesis of potential bio-active organochalcogen compounds.

**Publications**: 39 Patents (filed): 02 **PhD students**: 01 (completed) and 10 (ongoing)

# **Redox Mediated Synthesis of Main-Group Based Open-Shell** Compounds

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In molecular chemistry, the redox processes are very much important for various synthetic transformations. For a molecule to participate in redox reactions, it must contain electron-donor and/or electron-acceptor motif(s). Several electron-donor and electron-acceptor motif(s) are known.

In this talk, I shall discuss the effort of my research group in developing convenient synthetic routes for synthesizing compounds that contain mono-/bis-alkenes as electron-donor motifs<sup>1</sup> and mono-/biscyclic/acyclic carbocations/iminium cations as electron-acceptor motifs.<sup>2</sup> Utilization of these molecules as synthons for isolating radical-cations, diradicals, radical-trications, and diradicaloids under redox (reduction/oxidation) reaction conditions will be elaborated.<sup>3</sup> The use of borane as an electron-acceptor motif combined with a carbocation or an electron-rich alkene to synthesize boron/carbon-based  $\pi$ -conjugated molecules, will be discussed.4

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Dr. Anukul Jana obtained his Ph.D. in 2009 from University of Göttingen, Germany under the guidance of Professor Herbert W. Roesky. His doctoral thesis focused on the chemistry of compounds with low-valent Group 14 elements. He did his first postdoctoral research work as an Alexander von Humboldt fellow in the group of Professor Paul Knochel, LudwigMaximilians-Universität, Germany. Later on, he moved to pursue his second postdoctoral research in the group of Professor David Scheschkewitz, Universität des Saarlandes, Germany. In early 2014, Dr. Anukul Jana started his independent career at TIFR Hyderabad. His current research interest is mainly in the chemistry of low-valent lowcoordinate Group 13-15 elements. Dr. Anukul Jana received Indian National Science Academy (INSA) Medal for Young Scientist 2019

## **Sub-Cellular Intercom and Understanding Local Physical Properties**

#### <u>Apurba Lal Koner</u>,\* Kaushik Pal, Suprakash Biswas, Tanoy Dutta, Akshay Silswal, and Barsha Chakraborty

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Cellular organelles are primarily considered as individual entities of a particular composition entitled to specific functions to implement several intracellular events.<sup>1</sup> Nevertheless, such solitary roles are no longer pertinent, as defied by the recent scientific advancements in inter-organelle communication. Organelles exchange information *via* certain biomolecules and metabolites to maintain long-term cellular homeostasis through different modes of communication.<sup>2</sup> Such communications are tightly regulated by various chemical reactions and are vital for cellular health.<sup>3</sup> The fate of chemical reactions is controlled by microenvironmental properties such as polarity, viscosity, potential, etc. Intracellular responses to external stress and their pathophysiological implications are associated with micro-environmental properties have been extensively studied. Such stress-induced responses of local physical properties of an organelle are essential parameters to be quantified for early disease diagnosis. Nevertheless, the current literature is yet to have a quantified approach to studying these processes with small molecule fluorescent reporters as chemical tools.



In this presentation, I plan to discuss the design principle of small fluoroprobes (see above Figure) with specific targeting abilities to the sub-cellular organelles. Further, the inter-organelle communication and quantitation of sub-cellular physical properties associated with cellular stress will be highlighted.<sup>4-8</sup>

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#### Methanol as a Sustainable Reagent: Our Journey

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For synthesis of various functionalized molecules utilization of readily available methanol as a C<sub>1</sub> building block is indisputably atom economical and greener strategy compare to the conventional methods. Employing methanol as a sustainable building block, we reported tandem transformation of various nitro compounds and nitriles to the corresponding N-methylated amines; synthesis of αbranched methylated ketones via multicomponent reactions.<sup>1</sup> Notably, several N,N-dimethyl and N-monomethyl amines were synthesized selectively using methanol from numerous simple starting materials.<sup>2</sup> Remarkably, cobalt catalysed tandem transformation of aldoximes to Nmethylated amides and synthesis of quinazolinone scaffolds using methanol.<sup>3</sup> Practical application facets and mechanistic investigation of these catalytic systems will be presented.



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Sabuj Kundu obtained his PhD in 2009 from Rutgers, The State University of New Jersey, USA under the supervision of Professor Alan S. Goldman. He worked as a postdoctoral fellow with Professor William D. Jones at University of Rochester, NY (2009-11) and Professor Maurice Brookhart at University of North Carolina at Chapel Hill (2011-13). Subsequently, in 2013 he returned to India and joined as an Assistant Professor at the Department of Chemistry, Indian Institute of Technology Kanpur, where he is presently an Associate Professor. He received the DST-INSPIRE Faculty fellowship, India. From IIT Kanpur, he also received P.K. Kelkar research fellowship. His group is focused on various aspects of homogeneous and heterogeneous catalysis for sustainable chemical transformations.

# A Radical-Promoted Olefin Hydrogenation en route to α-Alkylation Reaction

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Hydrogenation of an olefin is an important process and that becomes further appealing when the source of the hydrogen is alcohol. We have developed a nickel catalyst where the ligand backbone contains an azo motif.<sup>1-3</sup> With the help of the azo/hydrazo, 2e<sup>-</sup>/2H<sup>+</sup> redox couple the catalyst can easily dehydrogenate alcohols and redelivers the stripped hydrogen on an in situ generated enone.<sup>4</sup> In this lecture, the details of hydrogenation following a radical pathway will be described. This is in contrast to the metal-ligand bifunctionality-driven hydrogenation reactions where the intermediacy of the metal-hydride is ubiquitous. Furthermore, the traditional Noyori-type hydrogenation involving metal-hydride follows a two-electron pathway. Our investigated pathway offers a complementary hydrogenation path to this two-electron chemistry.



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# Introducing a New Class of Boron-Based Heterocyclic Anion Receptor Additives in Li-Ion Battery Electrolyte: A Combined DFT and Computer Simulation Study

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It is well known that electrolytes in battery technology play an indispensable role to serve as the medium for the charge transfer process. Among many, rechargeable Li-ion batteries (LIB) have enabled a revolution to replace conventional batteries for their use in tiny electronics to aerospace due to their unique characteristics. Mostly, the electrolyte of LIBs contains at least one Li salt, majorly LiPF<sub>6</sub> and nonaqueous cyclic/acyclic organic carbonates as electrolyte solvents. However, at high voltage, the conventional carbonate solution becomes less stable, destabilizing electrolytes and reducing the cycle life of battery performance.[1] Suitable additives such as anion receptors can be added to the cyclic carbonate electrolytes to improve the cyclability and performance of LIBs. Several experimental and computational studies showed that boron-based anion receptors having aromatic groups could be the potential additives to improve LIB power capability. [2,3] The movement, transport, and Li<sup>+</sup>-solvent interactions in bulk electrolytes are topics of interest, as such properties play an important role in interphase chemistry in battery science. Further, the ionpair formation is one of the key factors limiting the ionic conductivity of electrolytes in the LIBs. In this presentation, I shall introduce a new class of potential anionic receptors containing an electron-deficient boron site which can be used as an alternative to tris(pentafluorophenyl) borane (TPFPB) in LIB electrolytes. [4] The comparative efficacy of the designed additives in regulating solvation and transport properties of Li<sup>+</sup> ions in ethylene carbonate electrolyte in the presence and absence of an electric field will be discussed. [5]

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# Organic Electrochemistry: A Sustainable and Environmentally Benign Tool for Accessing Structurally Diverse Molecular Architectures

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Electroorganic chemistry has emerged as one of the most promising platforms for harnessing the reactivity profiles of various intermediates and expediting the development of new reaction manifolds.<sup>1</sup> After being neglected for several decades, the major cause for its re-emergence lies in its ability to use the traceless electrons as reagents that make this technology environmentally benign and sustainable.<sup>1</sup> The successful adoption of this technology can be recognized from the reports demonstrating its utilization in several Cheteroatom,<sup>2a</sup> C-C<sup>2b</sup> bond-forming reactions. Also, recent literature on the construction of several natural products<sup>3</sup> and drug molecules<sup>2a</sup> exhibits the practicality of this sustainable strategy. Inspired and motivated by the success of the electrochemical strategies, our group in 2018, aimed to establish this environmentally benign protocol in our laboratory. After almost two years of our efforts, in 2021, our group demonstrated an electrochemical protocol for accessing benzimidazolone and guinazolinones derivatives via *in situ* generation of isocyanates.<sup>4</sup> In the same year, we utilized our affirmative experiences in the area of donor-acceptor cyclopropanes (DACs) and reported the electricity-driven 1,3-oxohydroxylation of DACs providing an access to  $\beta$ -hydroxy ketone analogs.<sup>5</sup> Followed by this, we evinced the electrooxidative generation of non-stabilized azomethine ylides.<sup>6</sup> Next, in 2022, we extended our expertise in the ring-opening annulation of cyclopropanes via electrochemical generation of Ncentered radical intermediates that provided access to cyclopentane analogs.<sup>7</sup> Encouraged by the success of these protocols, in 2022, we decided to utilize our experiences for redesigning the synthetic route of a well-known API, paracetamol. Delightfully, we established a direct synthesis of paracetamol via site-selective electrochemical Ritter-type C-H amination of phenol.<sup>8</sup> In addition, we have also developed the electrochemical site-selective C-H sulfinylation of phenol which aims to render the aromatic sulfoxides.<sup>9</sup>



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**Career Profile:** 

2016-till date Associate Professor, Department of Chemistry, IIT Ropar.
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2007-2009 Postdoctoral Fellow, Purdue University, U. S. A.
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2002-2004 Senior Research Fellow, CSIR, India.
1999-2002 Junior Research Fellow, CSIR, India.

#### Significant awards/achievements

2021 CRSI Bronze medal
2010-2013 DST Young Scientist Award scheme
2007-2009 NIH post-doctoral fellow
2005-2007 DFG post-doctoral fellow
1999-2005 CSIR JRF and SRF

#### **Representative publications**

1. Debarshi Saha, Irshad Maajid Taily, Nakshatra Banerjee, and Prabal Banerjee,\* "Electricity Mediated [3+2]-cycloaddition of *N*-sulfonylcyclopropanes with Olefins via *N*-centered Radical Intermediates: Access to Cyclopentane Analogs" *Chem commun.*, **2022**, *28*, 5459-5462.

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3. Debarshi Saha, Irshad Maajid Taily, and Prabal Banerjee,\* "Electricity Driven 1,30xohydroxylation of Donor-Acceptor Cyclopropanes: a Mild and Straightforward Access to  $\beta$ -Hydroxy Ketones" *Euro. J. Org. Chem*, **2021**, 5053-5057.

4. Debarshi Saha, Irshad Maajid Taily, Sumitra Naik and Prabal Banerjee,\*

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5.Rakesh Kumar, Irshad Maajid Taily, and Prabal Banerjee,\* "Electrochemical SiteSelective C-H Sulfinylation of Phenols with Sulfides: A Metal- and Oxidant-free CrossCoupling for the Synthesis of Aromatic Sulfoxides" *Manuscript Communicated*.

# Strategic design of framework materials for catalytic conversion of carbon dioxide to value-added chemicals

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The concentration of carbon dioxide in the atmosphere is increasing exponentially with time exceeding 410 ppm, currently. This rapid increase in the atmospheric  $CO_2$  content is leading to serious environmental issues. Therefore, it is highly desirable to mitigate the increasing concentration of atmospheric carbon dioxide by its selective capture and utilization as a C1 feedstock to synthesize value-added chemicals and fuels. Especially, selective carbon capture and utilization (CCU) from direct air has attracted tremendous attention owing to its practical applications. In this direction, we have been working on the rational design of functional framework materials incorporating  $CO_2$ -philic and catalytic sites capable of simultaneously capturing and converting carbon dioxide into value-added chemicals at mild conditions. The strategic design, synthesis, and catalytic investigation of the framework materials developed in our group for the fixation of  $CO_2$  will be presented.

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# 1D alignment of metalated porphyrin based self-assembled nanowires for photocatalytic hydrogen evolution

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Light-stimulated water splitting into hydrogen has received significant attention for the cleanest energy production and storage.<sup>1</sup> Organic photocatalyst consisting of larger surface area, control in diffusion adsorption, nanostructures and electronic properties has been of greater interest to enhance hydrogen production on a large scale.<sup>2</sup> Considering these criteria's we have developed a series of transition metalated porphyrin-napthalimide based donor-acceptor systems (PN1-PN5).<sup>3-5</sup> We have designed and synthesized these five (D-A) materials consists of free base and transition metals and studied their morphology, electronic properties and catalytic behavior. Detailed investigation of these studies suggests that the Co (II) substituent D-A systems. Optical and electrochemical properties revealed that metalated derivatives displayed efficient intramolecular electron transfer from the donor to acceptor than free base. Microscopic data and diffraction analysis suggested that the precise molecular packing of Co(II) substituent PN2 exclusively formed aligned nanowires among other derivatives. (PN2) displayed a well aligned one-dimensional (1D) nanowire with high electrical conductivity ~33 mScm<sup>-1</sup> promoting remarkable photo catalytic hydrogen production rate (18 mM  $g^{-1}h^{-1}$ ) when compared to that of porphyrin-based derivatives reported until now. Hence these best results are displayed by using self-assembled PN series resulting in improvement of conductivity property and photo catalytic hydrogen production rate (Figure 1). Consequently, transition metal substituted macrocyclicbased D-A systems to be explored in detail for realistic challenges in clean and green technology.



Figure 1. Schematic illustration of Co(II) metalated porphyrin–napthalimide based selfassembled nanowires for hydrogen evolution

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# A step-wise reduction of nitrate → nitrite → nitric oxide and vice versa: Biological homeostasis of NO and its derivatives

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Nitric oxide (NO) plays a significant role in various physiological processes such as neurotransmission, vascular regulation, platelet disaggregation, and immune response to multiple infections.<sup>1</sup> Therefore, to maintain an optimal concentration of NO, nitrate reductase (NR), nitrite reductase (NiR)<sup>2</sup>, and nitric oxide synthase (NOS)<sup>3</sup> enzymes are available for NO biosynthesis. The above enzymatic reactions have not been explored extensively; therefore, the exact mechanism of these reactions is yet to be discovered. NR catalyse the conversion of the NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> via the O-atom transfer reaction via Mo/W-based enzymes. NiR enzymes catalyse the conversion of NO<sub>2</sub><sup>-</sup> to NO in the presence of 2 equivalent protons (H<sup>+</sup>).<sup>2</sup> When NO crosses the optimal level, NOD enzymes oxidize NO back to the NO<sub>3</sub><sup>-</sup>. This cycle continues in the biological system and maintains NO homeostasis to sustain life. In this report, we are exploring the new mechanistic aspects of acid-induced nitrite reduction of Co<sup>II</sup>-NO<sub>2</sub><sup>-</sup> (1)<sup>4</sup>, oxygen atom transfer chemistry of Co<sup>II</sup>-NO<sub>3</sub><sup>-</sup> (2)<sup>5</sup>, and NO oxidation reaction of {CoNO}<sup>8</sup> (3)<sup>6</sup> to understand the mechanistic aspects of these reactions. A new pathway for NiR enzyme activity was observed in the Co<sup>II</sup>-NO<sub>2</sub><sup>-</sup> (1) reaction with one equivalent proton (H<sup>+</sup>), which generates corresponding {CoNO}<sup>8</sup> (3) with H<sub>2</sub>O<sub>2</sub>. The detailed mechanistic investigations using <sup>15</sup>N-labeled-



 $NO_2^-$  demonstrate that N-atom in the {CoNO}<sup>8</sup> is derived from  $NO_2^-$  ligand, and  $H_2O_2$  came from the homolysis of ON-OH moiety of a nitrous putative acid intermediate  $[Co^{II}ONOH]^{2+}$ . In addition, 1 & 2 generate (3) in the presence of an equivalent amount of oxygen abstracting reagent (VCl<sub>3</sub>). These reactions suggest oxygen atom transfer from Co<sup>II</sup> bound  $NO_3^{-}/NO_2^{-}$  moieties to reagent X, forming  $\{CoNO\}^{8}$  with oxidized species O=X (VOCl<sub>3</sub>). Further, to complete the NO-biological cycle, we reacted the (3) with  $OH^{-}/O^{2-}$ , showing the formation of the  $Co^{II}$ -NO<sub>2</sub>, in contrast to one of our previous reports of  $\{CoNO\}^8$  with  $O_2$ , leading the generation of Co<sup>II</sup>-NO<sub>3</sub> (NOD product).<sup>7</sup> We also find out that complexes 2 and **3** generate the  $\{CoNO\}^8$  upon reaction with NO.

Figure 1.

Interconversion of nitrate  $\rightarrow$  nitrite  $\rightarrow$  nitric oxide and vice versa

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Academic Qualification							
S.No.	Degree	Year	Subject		University/Institution	% of mar	ks
1.	B. Sc.	2006	Chemistry (Hons	5)	AMU, Aligarh	68.0%	
2.	M.Sc.	2008	Analytical Chem	istry	AMU, Aligarh	72.4%	
3.	Ph.D.	2013	Bioinorganic Ch	emistry	III Guwahati	Awarded	
Work H	Experience	e					
S. Position Held		Name of the Inst	titute		From	То	
No.							
1.	Assist. Pro	of.	IISER, Tirupati, I	ndia		06/2017	Ongoing
2.	Assist. Pro	of.	M.M. university,	Mullana,	Haryana, India	06/2016	05/2017
3.	PDRF		CBS, Ewha Wom	ans Univ	ersity, Korea	03/2013	02/3016
Profess	ional Reco	gnition	/ Award/ Prize/ C	Certificat	e, Fellowship		
S. No. Name of Award						Year	
1.	1. Humboldt Experienced Research Awards			ards		2021-2024	
2. DAAD Experienced Resear			ch Awarc	lS li in		2021	
⊿	<b>3.</b> World Class University (WCU) Fellowship 2013-20				2013-2016		
4. Senior Research Fellowship 5 Junior Pescarch Fellowship						2011	
5. 6.	5. Junior Research Fellowship 6 National Eligibility Test		Eligibility Test				2003
						,	
Selected	d Publicat	ions					
1. Das, S	1. Das, S.; Kumar, P.* & coworkers <i>Chem. Sci.</i> , 2022, 13, 1706.						
2. Kulbir, K.; Kumar, P.* & coworkers <i>Chem. Sci.</i> , 2021, <i>12</i> , 10605.							
<b>3.</b> Yenuganti, M.; Das, S.; Kulbir; <b>Kumar, P.*</b> <i>Inorg. Chem. Front.</i> <b>2020</b> , <i>/</i> , 48/2-4882.							
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List of ]	Publicatio	ns					
S. No.	Publis	her		Journa	S		
1	ACS (.	5)		JACS (3	), IC(1), ACS Omega (1	)	
2	Willey	-VSH (	1)	Angewa	ndte Chemie (1)		
3	RSC (	15)		Chem. S	Sci. (3)Chem. Commun.( Trans. (6) PCCP (1) PS	3), ICF (1) C Advances (	7)
4	Floori	or (1)		Daluha	Inon (2) IC A (2)	C murunees (	· /
-	Elsevi Elsevi	er (4)		T Orynea	10n (2), ICA (2)		
3	Elsevi	er Scien	ice Direct (1)	<i>JMC (1)</i>	1		

### An Insight into Protein-DNA Interactions Using Discrete-State Stochastic Models

Srabanti Chaudhury\*

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Protein search for specific sequences on DNA is a fundamentally important process that marks the beginning of all major cellular transformations. The dynamics of protein-DNA interactions in *in vitro* settings is well investigated in a large number of experimental and theoretical studies and the mechanism of facilitated diffusion has been proposed and verified. The cellular environment is complex in live cells where multiple biochemical and biophysical processes can interfere with the protein search dynamics. In this talk, I will discuss a theoretical method that explores the effect of crowding in the cellular environment during the protein search and the target search dynamics in quorum sensing cells. The method employs a discrete-state stochastic framework that accounts for most relevant physical and chemical processes in the system. In the context of bulk crowders, the scenario of static and dynamic crowders has been explored and the role of protein crowder interactions in search dynamics has also been investigated. A comparison with existing experimental and theoretical results will be presented.

Quorum sensing is a bacterial cell-cell communication process that regulates gene expression. The search and binding of the autoinducer molecule (AHL)-bound LuxR-type proteins to specific sites on DNA in quorum-sensing cells has been studied in the context of Gram- negative bacteria based on this discrete-state stochastic approach. It is shown that several factors such as the rate of formation of the AHL-bound LuxR protein within the cells and its dissociation to freely diffusing AHL, the diffusion of the latter in and out of the cells, positive feedback loops, and the cell population density play important roles in the protein target search and can control the gene regulation processes. In all cases, our calculations of the dynamic properties using this analytical description has been supplemented by Monte Carlo computer simulations.

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Prof. Srabanti Chaudhury did her PhD in theoretical Chemistry from IISc Bangalore in 2009. She joined as a postdoctoral fellow at Rice University followed by University of Texas at Austin and at Los Alamos National Laboratory. She started her independent career as an Assistant Professor at IISER Pune in the department of Chemistry in 2013. She is the recipient of CRSI Bronze Medal, 2022. She is the Associate Editor of the journal Frontiers Biophysics.

#### **Research Interests:**

Using concepts of statistical mechanics to develop theoretical models to investigate stochastic fluctuations in chemical physics, biology and soft condensed matter.

### **Positions Held:**

- 1. Associate Dean (Doctoral Studies) Academics, IISER Pune (2018-2022).
- 2. Assistant Professor IISER Pune (2013-2019)

### Activation of Alcohols for Sustainable Catalytic Transformations

Dr. Dipankar Srimani

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Due to the rapid depletion of fossil fuels, there is an increasing demand for developing new valuable compounds using renewable starting materials. Because alcohols can be easily produced from lignocellulosic biomass, they are renewable. Thus, the activation of alcohols for the synthesis of valuable chemicals using a green and sustainable approach is a vital goal in catalysis. In present time, Acceptorless Dehydrogenation (AD) and Borrowing Hydrogen (BH) catalysis evolved as useful tools for producing a diverse range of fine chemicals using alcohols in a sustainable manner.<sup>1</sup> Instead of releasing toxic chemical wastes, one of the main advantages of AD and BH catalysis is that it can either release dihydrogen molecules without any sacrificial hydrogen acceptor or use dihydrogen molecules in the hydrogenation step.

We have recently developed new air-stable transition metal catalysts and explored their activity toward different AD coupling reaction and BH catalysis.<sup>2</sup> The scope and limitation of these complexes towards various useful chemical transformations have been investigated. The lecture will cover the fundamental concepts of AD and BH catalysis and the details of these works.

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Dipankar Srimani received his PhD (2011) from IACS, Kolkata under the supervision of Prof Amitabha Sarkar. He pursued his post-doctoral research (2011–2014) at Weizmann Institute of Science with Prof. David Milstein. In 2015, he joined the DST-INSPIRE faculty at IIT-ISM Dhanbad. In the same year, he moved to the Indian Institute of Technology-Guwahati and joined the Dept. of Chemistry as an Assistant Professor. Since 2019 he has been an Associate Professor at IIT-Guwahati. His research mainly focuses on the development of air-stable earth-abundant transition metal complexes and metal doped supported materials for catalytic applications.

# **Reversible Toxic Gas Adsorption & Catalytic Applications of Supramolecular Metallogels**

Dr. Joyee Mitra

Inorganic Materials & Catalysis Division, CSIR-Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002, Gujarat.

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Low molecular weight gelator (LMWG)-based supramolecular gels are a fascinating class of soft materials, arising from the self-assembly of small molecules into anisotropic structures that subsequently entangle to form a network that immobilizes solvent molecules via surface tension & capillary forces. <sup>1,2</sup> These materials are attracting widespread interest across academia and industry owing to their intriguing properties and multiple potential applications. Presence of metals can incorporate additional metal-specific properties in the metallogels.<sup>3</sup> In this regard, we have designed Ni(II)-based supramolecular organogel and organic-aqueous gels using primary amine appended triazole ligand, having varying morphology and rheological properties.<sup>4</sup> These gels are self-healable and moldable or injectable respectively depending on the absence or presence of water in the gelation medium. The formation and rupture of hydrogen bonds assisted by the solvent movement is responsible for the self-healing nature of the gels. The Ni(II)-organogel could recover 88% of its original fracture stress upon storage. In addition, the gels show reversible adsorption of H<sub>2</sub>S gas, an industrial pollutant, via gel-to-gel transformation. The dynamic nature of Ni-Ntriazole interactions has been utilized in achieving the reversible gas/vapor responsive behavior of the metallogels, which could be suitable in developing smart stimuli-responsive gel-based colorimetric probes for the detection of toxic gases in the future. Considering the availability of pendant -NH2 groups that aids in the interaction with CO2, the metallogel was also utilized as a heterogeneous catalyst for CO<sub>2</sub> activation & conversion.

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Dr. Joyee Mitra is working as a Senior Scientist in the Inorganic Materials & Catalysis Division of CSIR-Central Salt & Marine Chemicals Research Institute, Bhavnagar, since 2019. She has completed her B.Sc. (with Honors in Chemistry) in 2005 and Masters (with specialization in Inorganic Chemistry) in 2007 both from Jadavpur University, Kolkata. She completed her doctoral thesis in 2013 from Indian Institute of Technology Kanpur, under the supervision of Prof. S. Sarkar, exploring the design and reactivity of synthetic analogues to the molybdenum enzymes. Thereafter, she moved to the University of Illinois, Urbana Champaign for her post-doctorate, where she worked on small molecule activation and the catalytic upgradation of lignocellulosic biomass to chemicals, as a part of her post-doctoral research. She is the recipient of the DST-INSPIRE Faculty award. Her present research interests include supramolecular metallogels, and metal-free ionic and hydrogen bonded systems, mainly focusing on their catalytic applications.

### Understanding the Language of Proteins through Chemistry

Dr.Susmita De

Associate Professor, Department of Chemistry, University of Calicut, Malapurram – 673635, Kerala, India E-mail:dr\_susmita\_de@uoc.ac.in

We can put a set of alphabets together in innumerable permutations to make words each with its own meaning and with words we can make sentences, but only certain combinations in a particular order are meaningful for communications. Likewise, an endless number of poly-amino acid sequences can be formed with varying amino acid composition connected via peptide bonds. However only a certain, though roughly millions, number of possible amino acid sequences are represented in nature as proteins, each having a specific function. The function of protein is linked to the unique 3D structure attained by folding of the polypeptide chain, where the composition, sequence and position of specific amino acid are accountable. How the changes in the position, sequence and composition of the amino acid residues affects the activity of a protein at the molecular and atomic level towards controlling protein function and regulation of activity will be discussed based on recent works on ion channels,[1,2] immune proteins[3] and enzymes.[4]

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Susmita De obtained her Ph. D. in 2010 from University of Hyderabad under the guidance of Prof. Eluvathingal D. Jemmis. She has gained research experience in various area of theoretical chemistry by working with Prof. Gernot Frenking at the Department of Chemistry, Philipps-University Marburg, Germany, Prof. Keiji Morokuma at the Fukui Institute for Fundamental Chemistry, Kyoto University, Japan and Prof. Martin Zacharias at the Department of Physics, Technical University Munich, Germany. Her current research focus is on the detailed molecular-level understanding of structure and mechanism of complex molecular, biomolecular and materials systems by molecular dynamics simulations and quantum mechanical/molecular mechanical methods. She applies the knowledge of chemical bonding to predict the properties and reactivities of complex systems. Her foundation in chemistry had helped her to translate the molecular level knowledge to the areas of Biology and Material science, which can establish a synergy between theory and experiment to realise fruitful prediction of theory-driven experiments and synthesis.

Honours and recognitions:

EMBO visiting scientist fellowship in Germany, 2018

INSPIRE Faculty Award, 2012

DST Fast Track early career project for Young Scientist, 2011

# IndL 1

### **Role of Oil Field Chemicals in Energy Transition**

Mr. Pankaj Kr Goswami Director-Operations Oil India Limited

OIL India has been operating in the Nort Eastern part of the country since 1959. Most of its fields are matured with more and more oilfields entering the high water cut period & their efficient development faces severe challenges. Chemical injection is regarded as an effective method for enhanced oil recovery (EOR). High-performance, cost effective, and environmentally friendly chemicals are drastically required in the oil production and transportation process. Complicated interface phenomena and transport in porous media process also need to be highlighted for chemical design and EOR processes.

In addition, oilfield chemicals are necessary in unconventional reservoir development & drilling. Research into and the development of oilfield chemicals towards tight/shale reservoir development are required to address the technical challenges involved so as to enhance oil production in the country and to reduce import dependency irrespective of the fact that the world is looking towards cleaner fuel. The recent trends towards carbon net zero and the development of renewable energy, hydrogen etc. as an alternative source to fossil fuels has resulted in a major environmental focus being placed on decarbonisation with a big emphasis on the potential for carbon capture, utilisation and storage (CCUS).



Mr. Pankaj Kumar Goswami is the Director Operations of Oil India Limited, the second largest upstream National Oil Company of Govt. of India. As Director Operations, he looks after the entire gamut of Oil India's production and transportation activities in India and abroad.

He is also a board member of international joint venture companies such as WorldAce Investments Limited, Cyprus; JSC Vankorneft, Russia and LLC TYNGD, Russia.

With about 34 years of diversified experience in oil & gas production activities, Mr. Goswami has conceptualized many out-of-box ideas, which greatly helped in maintaining Oil India's production profile from the very old and mature oil fields in its main producing areas. He is a hard-core Oilman with deep understanding of geology, drilling, production and transportation activities in some difficult exploration terrains in the country with a specific reference to North East India. He is also credited with conceptualization and implementation of a number of projects for enhancing production of oil & gas. A thorough technocrat, Mr. Goswami has participated in several technical conferences relevant to the energy industry both at national and international level.

His educational qualification includes a Bachelor of Mechanical Engineering degree and a Post Graduate Diploma in Management.

# IndL 2

### SYNTHIA<sup>™</sup>-Retrosynthetic Design Software

Mr. Prasad Bidwe Commercial Marketing Manager Chemical Synthesis Merck Life Sciences, Mumbai

The most significant challenge in organic chemistry is finding viable synthetic pathways by painstakingly navigating the complex matrix of retrosynthetic possibilities while simultaneously accounting for what has been done, what could be done, and what starting materials are available.

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EXPERIENCE of  $\sim$  17 years

January 2018 till date- Commercial Marketing Manager- Merck Life Sciences, India

September 2014 to Feb 2017- Strategic Alliance Manager- Advinus Therapeutics Ltd Pune

Feb 2010 to Aug 2014- Assistant Manager-Project Management, Syngene International Ltd, Bangalore

Nov 2006 to Jan 2010- Senior Research Associate-Medicinal Chemistry, Jubilant Biosys Ltd, Bangalore

Mar 2005 to Oct 2006- Executive Process R&D- Sai Life Sciences, Hyderabad

### **Educational Qualifications:**

PGCHM	IIM, Calcutta (April 2017-Feb 2018)
MSc Organic Chemistry	Pune University(2004) -1994)
BSc Chemistry	Pune University(2002)

# IndL 3

### Chemistry and Chemical Engineering at service

Dr. Sunil Dhole and Shri Tushar Wagh Director, ChemDist Group of Companies, Plot No 144 A, Sector 7, PCNTDA Bhosari Pune – 411026, Maharashtra, India.

During the deadly second Covid-19 wave (April-21) in India, the entire medical system was caught off-guard specially because of the non-availability of the Medical Grade Oxygen. Entire country was dependent on the foreign suppliers for the basic equipment like Oxygen Concentrator. The present talk will share the short story of how a chemical engineering came handy to develop and commercialize an Indian made Portable Oxygen Concentrator (CD-OXY by ChemDist) within two weeks. The Oxygen concentrator developed by the team of Chemdist Membrane Systems Pvt. Ltd. Pune has been approved by Principal Scientific Advisor's board and PMO. It was distributed through the PM Cares project to the remotest locations in India.

Similarly, Sunil's team at Technorbital has innovated a specialty polymer using which they have produced a water filtration membrane which works without electricity. At present this innovation is serving around six million people in India per day with the clean and safe drinking water.

The speakers will briefly discuss about these innovations and challenges faced while commercializing these technologies.



Dr. Sunil Dhole After completing his bachelor's in Chemical Engineering from Amravati University Maharashtra did Masters (2002) and Ph. D. (2006) from IIT Kanpur. After a post-doctoral research fellowship at *non-Newtonian Rheology group at UCL, Belgium* (2007-2008) he joined Reliance Technology Group as Senior Research Scientist (2008-2011). His journey of entrepreneurship started in 2011 with the formation of Kanpur based company *"Technorbital Advanced Materials Pvt. Ltd."* The company has been started with the objective of converting potential lab-scale research in to the commercial reality.

Sunil's expertise is in *new generation water filtration membranes*, air purification membranes, and new generation waste water treatment technologies. The non-electric water purification solutions commercialized (e.g., Tata Swach Desire Plus, Tata Swach Crystella Advanced, Tech Jal Inline, Tech Jal community water purifier, GRAFiL industrial UF membranes) by Technorbital are serving around 5 million people in India per day.

Dr. Sunil Dhole is currently:

- Founder and director at Technorbital Advanced Materials Pvt. Ltd., Kanpur
- Founder and director at Chemdist Membrane Systems Pvt. Ltd., Pune
- Technical director at Espin Nanotech Pvt. Ltd., Kanpur
- Founder and director at Indeema Fibers Pvt. Ltd., Kanpur
- Founder and director at Vivocon Technologies Pvt. Ltd., Pune

He has published numerous research articles in the international peer reviewed journals, has multiple patents and is felicitated with various awards in the field of drinking water technologies.



Mr. Tushar Wag obtained Masters in Business Administration (MBA) Dual Specialization in Marketing & Finance from PUMBA prior to a Bachelor of Chemical Engineering from M.I.T Pune He has total 18+ yrs of experience in the field of Process Design, Sales & Marketing and Business Development for the Capital Equipment Industry. Founded CHEMDIST in 2012 with focus on Process Technology, Process Engineering, Process Equipments and Process Plants. Expertise in Process Application Technologies, Products & Services in the field of Distillation, Evaporation, Heat Transfer, Mixing & Reaction, Environmental, Effluent Treatment & Membrane Technologies.

Before venturing into entrepreneurship he has worked with Sulzer Chemtech and Thermax Ltd

Co-founded Chemdist Membrane Systems in 2018 with focus on developing innovative products and technologies for Membrane based industrial applications. Recently, during the deadly second Covid-19 wave (April-21) in India, Tushar and his team of Chemdist Membrane Systems Pvt. Ltd. Pune developed and commercialized an Indian Portable Oxygen Concentrator (CD-OXY) within 2 weeks. The uniqueness of the technology developed for CD-Oxy is that, it requires only half the quantity of the precious zeolite media as compared to the conventional Oxygen concentrator technologies. The CD-Oxy oxygen concentrator has been approved by Principal Scientific Advisor's board and PMO. It is currently being distributed through the PM Cares project thought out India.

**Chemdist Membrane Systems Pvt. Ltd.** has also launched a **new generation low opex Ethanol Production** Technology based on their innovative Membrane Distillation (MD) and Pervaporation (PV) Membranes. The MD technology also holds the excellent potential to replace the high opex multiple effect evaporation (MEE) in the wide industries varying from food, pharma, chemicals, etc.

**Chemdist Membrane Systems Pvt. Ltd.** has recently started a Centre Of Excellence at IIT Guwahati. The focus of the this research centre is to develop multiple derivatives (pharma, chemicals, etc.) from Ethanol and other distillery waste streams.

He has published numerous research articles in the international peer reviewed journals and has multiple patents.

# IndL 4

#### **Bridging the Gap Between Electron and X-Ray Diffraction**

Prathapa Siriyara Jagannatha,<sup>1</sup> M. Adam,<sup>2</sup> A. Abboud,<sup>2</sup> R. Durst,<sup>2</sup> J. Graf,<sup>3</sup> C. Michaelsen,<sup>3</sup> T. Stuerzer<sup>2</sup>

<sup>1</sup>Bruker India Scientific Pvt. Ltd. India <sup>2</sup>Bruker AXS GmbH - Karlsruhe (Germany)

<sup>3</sup>*Incoatec GmbH - Geesthacht (Germany)* 

Structure determination on ever smaller and more weakly diffracting crystals is one of the biggest challenges in crystallography. Traditionally, in-house X-ray crystallography covers sample sizes down to a lower limit of approximately 50 µm. Consequently, electron diffraction is receiving a lot of attention, as electron diffraction methods promise structure determination on significantly smaller samples. However, while micro-ED can cope with samples in the nm regime, an upper limit in the range of approximately 1 µm exists. At the same time crystallization of suitably small crystals can be difficult and grinding larger samples to the bring them into suitable sizes can add a severe threat to electron diffraction methods. On the other hand, the formation of crystals in sizes of the few micrometers often can be easily accomplished. Equipment for structure determination closing the gap for samples between 50 to 1 micrometer in size would be highly desirable. Fortunately, the 50 micron 'limit' for in house X-ray diffraction is not a hard border anymore. At Bruker and

Incoatec we are continuously exploring the technical restrictions of X-ray diffraction instrumentation in order to find ways to push or even overcome some of the limitations This holds for all elements in a system, and in particular for main components, such as detectors, sources, and goniometers. We will discuss the latest innovations and present selected results from crystallography.



**Dr. Prathapa Siriyara Jagannatha** Affiliation:

Product Manager and Application Scientist

Bruker India Scientific Pvt. Ltd.

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Dr. Prathapa Siriyara Jagannatha obtained his PhD in Crystallography from University of Bayreuth, Germany with over 14 years of experience in the field of Single crystal X-ray diffraction. Title of the PhD thesis is "Dynamic charge densities of amino acids and proteins". Specialized in accurate charge density study using the multipolar formalism and the maximum entropy method.

**Recipient of Claude Leon Foundation Postdoctoral fellowship from University of the Witwatersrand Johannesburg, South Africa.** Postdoc research project was on the "developing techniques for the structure determination of liquid fuels (biodiesel) and control of their physical properties.

After the postdoctoral research, worked as an X-ray diffraction Technician at Institut Català d'Investigació Química (ICIQ), Tarragona, Spain.

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# Exploration of the Excited State Intramolecular Proton Transfer Process in Solid Organic Fluorophore 2.2'-(1,4-phenylenebis(1H-benzo[d]imidazole-1,2diyl)diphenol an AIEE Active Material Applying to Green Light OLED

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We made 2.2'-(1,4-phenylenebis(1H-benzo[d]imidazole-1,2-diyl)diphenol (BDHPBI), a triple emissive in liquid and dual emissive in solid-state organic fluorophore in which double excited state intramolecular proton transfer (ESIPT) exhibiting systems were present.[1] The BDHPBI fluorophore displayed typical enol emission from twisted conformer and cis keto emission, as well as trans keto emission from quasi-planar conformer following the non-radiative isomerization process. This non-radiative process resulted in a very low fluorescence yield in the tautomer emission (0.09 in cyclohexane). However, we took use of the properties of aggregation-induced enhanced emission (AIEE), which caused some perturbation in the process of non-radiative isomerization and demonstrated significant fluorescence yield. We used dynamic light scattering (DLS) and a field emission scanning electron microscope (FESEM) to determine the size and form of aggregated particles in a 90% water-THF mixture. [2] In addition, we investigated the photophysical characteristics of BDHPBI in solid-state and water-THF mixtures using UV-visible spectrophotometry, photoluminescence, and time-resolved photoluminescence. In general, most fluorophores in the literature are less emissive in the solid state and more emissive in the liquid state, but the BDHPBI demonstrated very strong emission in the solid state as compared to the liquid state, with a very high fluorescence yield (0.59) in the solid state.



Figure 1. Graphical abstract of an AIEE active green emitting OLED material

We also took fluorescence imaging of the BDHPBI in the THF-water mixture and solid state. As the BDHPBI had a very high emission in the solid state, we used it to build an organic light-emitting diode (OLED) device.[3] Most notably, the molecule showed its promise as an OLED manufacturing candidate by exhibiting a maximum brightness value of 350.16 cd/m2 with a turn-on voltage of 10 V and a greater luminescence efficiency value of 5.55 cd/A with CIE coordinate values of (0.20, 0.42).

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### Organocatalytic Asymmetric Inverse-Electron-Demand-Diels-Alder Reaction between Alkylidene Pyrazolones and Allyl Ketones: Access to Tetrahydropyrano[2,3-c]Pyrazoles

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Herein we report a catalytic asymmetric inverse-electron-demand-Diels-Alder reaction between alkylidene pyrazolones and allyl ketones. Allyl ketone gets activated by bifunctional thiourea catalyst and acts as a dienolate in this reaction. The trisubstituted tetrahydropyrano[2,3-c]pyrazoles were obtained in moderate to good yields with high diastereo- and enantioselectivities. Few applications including a decarbonylation reaction have been demonstrated.





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### **Total Synthesis of Bioactive Natural Product: Thailandamide Lactone**

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#### Abstract:

Natural product served as important sources for powerful therapeutics against pathogenic microbes by virtue of their lethal and selective action. Therefore, development of synthetic routes to access these useful natural products are always important to understand them in details. Hertweck and co-workers in 2008 and 2010 have isolated novel polyketide natural product thailandamide A<sup>1</sup> and its genetically engineered analogue thailandamide lactone<sup>2</sup>. Broad biological screening of thailandamide A revealed its selective and potential inhibitory activity against different pathogenic Gram-positive and Gram-negative bacteria with specific mode of action. However, the antibacterial activity of thailandamide lactone remained undisclosed. Highly challenging architectural features, natural scarcity, lack of synthetic route together with our continual interest in natural products chemistry encouraged us to envisage the total synthesis of thailandamide lactone as well as evaluation of its antibacterial potential. In this presentation, the state of art associated with the first asymmetric total synthesis of bioactive genetically engineered natural product thailandamide lactone will be discussed.<sup>3</sup>



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### Unravelling the excited state relaxation pathways in two nitrile-substituted 2-(oxazolinyl)-phenols

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Molecules undergoing excited-state intramolecular proton transfer (ESIPT) show interesting applications in various fields ranging from bio-sensing to optoelectronic devices, molecular probing and so on. Recently, low molecular weight and single-benzene based fluorophore (SBBF) that are ESIPT active were synthesized.[1] These molecules were found to be weakly emissive in the solvent phase, but their properties changed in the crystalline form. In this work, the ground and excited state properties were theoretically investigated in the gas phase, and in two solvents of different polarities. A systematic study comprising of static calculations and non-adiabatic dynamics at various levels of theory, including density functional theory (DFT) and wave function theory (WFT) were performed. We found that the proton transfer (PT) process in the S<sub>1</sub> state is thermodynamically favored in the gas, cyclohexane (CH) and methanol (MeOH). Following PT, a non-radiative channel was identified driven by inter-ring torsional motion from the keto structures. This pathway was found to be accessible and more probable in the gas and CH due to small barriers in comparison to MeOH. Our dynamics simulation at TDDFT level predicted the average PT time to be around 11-15 fs. In addition, the first approach to conical intersection region was found to proceed from 500 fs onwards.[2]



Figure 1. Graphical abstract of the excited state dynamics studies

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# OP-5

# Effect of Chalcogen's (Q) Size and Vacancy of Metals in Controlling the Dimensionality of Lanthanide (Ln) Containing Quaternary $Ba_{2-\delta}Ln_{1-x}Mn_{2-y}Q_5$ Chalcogenides

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We present the syntheses, characterization, and physical properties of a series of disordered lanthanide (Ln) containing quaternary chalcogenides belonging to the quaternary Ba-*Ln*-Mn-*Q* (*Ln* = Pr/Gd/Nb/Yb and *Q* = S/Se/Te) system. The single crystals of these cation deficient chalcogenides are synthesized by the high-temperature molten flux method. All these compounds crystallize in the monoclinic crystal system with space group *C*2/*m* with different dimensionalities. The magnetic studies on a polycrystalline sample of Ba<sub>2</sub>Gd<sub>2/3</sub>Mn<sub>2</sub>Te<sub>5</sub> did not reveal any long-range magnetic order down to 5 K. The effective magnetic moment ( $\mu_{eff}$ ) of 10.37 µB calculated from the Curie–Weiss law is in good agreement with the theoretical value ( $\mu_{cal}$ ) of 10.58 µB. The resistivity and optical bandgap studies for the polycrystalline Ba<sub>2</sub>Gd<sub>2/3</sub>Mn<sub>2</sub>Te<sub>5</sub> (1.0(1) eV) and Ba<sub>1.88</sub>Gd<sub>0.56</sub>Mn<sub>1.95</sub>Se<sub>5</sub> (1.7(1) eV) samples confirm their semiconducting nature.



**Figure 1.** (a) The 3D (tunnel) and (b) 2D (layer) structures of  $Ba_{2-\delta}Ln_{1-x}Mn_{2-y}Q_5$ , and (c) magnetic plot of  $Ba_2Gd_{2/3}Mn_2Te_5$ .

	I	П	III
a (Å)	15.246(3)	14.3511(3)	13.986(3)
<b>b</b> (Å)	4.5479(9)	4.2727(2)	4.1422(8)
c (Å)	10.688(2)	10.0973(5)	10.116 (2)
β°	117.20(3)	118.555(3)	121.68(3)
$V(\text{\AA}^3)$	659.1(3)	543.83(5)	498.7(2)

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### Comprehending the Efficacy of Whitlock's Caffeine-Pincered Molecular Tweezer on β-Amyloid Aggregation

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Alzheimer's disease (AD) is one of the most prevalent neurodegenerative disorders, causing cognitive impairment, with no cure and preventive therapy. [1,2] Misfolding and extracellular aggregation of Amyloid- $\beta$  (A $\beta$ ) peptides are believed to be the primary cause of AD development, culminating in the formation of toxic AB oligomers and the deposition of  $\beta$ -amyloid plaques in the brain which serve as the hallmarks of AD. [3] Drug development for the potentially curative treatment of Alzheimer's is, therefore, a tremendous challenge for the scientific community. In this study, we investigate the potency of Whitlock's caffeine-armed molecular tweezer in combating the deleterious effects of AB aggregation, with special emphasis on the seven residue  $AB_{16,22}$  fragment. Extensive all-atom molecular dynamics simulations are conducted to probe the various structural and conformational changes of the peptides in an aqueous media in the presence and absence of inhibitors. To explore the specifics of the interactions between the peptide residues and the inhibitors, radial distribution functions, coordination number of water and inhibitor molecules around the peptide residues, nonbonding energy calculations, and hydrogen-bonding interactions are computed. In order to forecast the development of aggregates, the potential of mean force (PMF) is calculated using the free-energy profiles. The central hydrophobic core, more importantly, the aromatic phenylalanine residues are crucial in the development of the harmful amyloid oligomers. It is worth noting that, all the analyses demonstrate decreasing interpeptide interactions in the presence of inhibitors, thereby preventing amyloid aggregation. Furthermore, the study also reveals the effectiveness of molecular tweezers in destabilizing preformed amyloid fibrils.



Figure 1. Graphical abstract manifesting the inhibition and destabilization of amyloid fibrils.

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## **Oxadiazole-adorned Heterocoronene Discotics as Ambipolar Organic Semiconductors**

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Development in modern technologies has enforced a quest for new semiconducting materials in optoelectronics where self-assembled liquid crystalline (LC) materials can play a potential role.<sup>1,2</sup> Molecular engineering of disc-shaped LCs (DLC) with suitable organic moieties, especially heterocyclic units, can lead to a control over their columnar architecture in the nano-scale regime, which holds the key to tuning the charge-transport properties of the system.<sup>3</sup> We have successfully designed and synthesized room-temperature DLCs (1.1, 1.2 and 1.3) with 1,3,4-oxadiazole functional units acting as electron-deficient linkers between a central heterocoronene core and the peripheral alkoxy phenyl units. All the derivatives exhibited a broad columnar hexagonal mesophase range with high isotropic temperatures, as characterized from polarizing optical microscopy, and thermal as well as X-ray scattering studies.



Figure 1. Graphical abstract of the ambipolar DLC semiconductors

When employed in space-charge limited current (SCLC) devices, the DLC materials showed ambipolar charge transport behaviour with the maximum hole and electron mobilities in the order of  $10^{-3}$  and  $10^{-5}$  cm<sup>2</sup>/Vs, respectively, which substantiates them as effective organic semiconductors for optoelectronic device applications.

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## Nitrogen Dioxide Reactivity of Copper(II) complex with tetradentate amine ligand followed by ligand nitrosation

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Nitrogen dioxide (NO<sub>2</sub>) is known as a strong oxidant that can trigger lipid auto-oxidation and the key intermediate for protein tyrosine nitration. In biological system, NO<sub>2</sub> can be generated via several reactions, including the oxidation of NO by O<sub>2</sub>, the decomposition of ONOO<sup>-</sup>, and the oxidation of nitrite (NO<sub>2</sub><sup>-</sup>) by hydrogen peroxide in the presence of peroxidases.[1] So the reaction of NO<sub>2</sub> with metal ions is an interest in chemistry with a goal of redox transformations between various NOx complexes. Herein, we synthesized a copper(II) complex [Cu<sup>II</sup>(L)(CIO<sub>4</sub>)<sub>2</sub>], **1** by reacting equivalent amount of ligand **L** (**L** = N,N'-bis(2-pyridylmethyl)-1,3-diaminopropane) and Cu(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O. Complex **1** readily reacts with NO<sub>2</sub> in acetonitrile medium under inert condition resulted dinitrosation of the ligand at the aliphatic amine sites along with the formation of complex [Cu<sup>II</sup>(H<sub>2</sub>O)<sub>4</sub>(µ-CIO4<sup>-</sup>)](OH<sup>-</sup>), **2.**[2] The reaction mechanism was investigated by FT-IR, UV-visible and EPR spectroscopic techniques. The formation of NO<sub>3</sub><sup>-</sup> along with generation of a transient {Cu(NO)}<sup>9</sup> intermediate during the course of the reaction was evident by characteristics IR stretching frequency and X-band EPR spectrum of frozen reaction mixture.[3]



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## Tuning the charge transfer and optoelectronic properties of tetrathiafulvalene based organic dyesensitized solar cells: a theoretical approach

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The main goal of  $21^{st}$  century is to develop solar energy based technology due to it's safe and renewable nature for the environment.[1] The constant rise in energy demand brought on by the growth of environmental concerns has facilitated an intensification of research on solar energy conversion. The photo emission phenomena used by the photovoltaic systems and solar cells convert sunlight into electrical energy.[2] Since 1991, the discovery of dyesensitized solar cells (DSSCs) by O'Regan and Grätzel has attracted most researchers due to their improvements in comparison to all other kinds of solar cells.[3, 4] Various structural modifications have been performed on DSSCs by synthesizing many new organic photosensitizers which can absorb light in higher wavelength range and exhibit higher power conversion efficiency (PCE).[5] Here, we are going to review our efforts with a series of tetrathiafulvalene based dyes following the donor- $\pi$ -acceptor (D- $\pi$ -A) architecture.[6]

Firstly, we have designed a series of dyes following the donor- $\pi$ -acceptor (D- $\pi$ -A) architecture by incorporating tetrathiafulvalene (TTF) as the donor unit and phthalazine (PTZ), diketopyrrolopyrrole (DPP) and quinoxaline (QNX) as the acceptor units, along with the thiophene unit as  $\pi$ -bridge. The designed dyes have been designated as TTF-PTZ, TTF-DPP and TTF-QNX respectively. Besides, we have used cyanoacrylic acid and bidentate carboxylate groups as the anchoring groups to enable the adsorption of the designed dye-sensitizers to the TiO<sub>2</sub> semiconducting surface. These anchoring groups have been proven to be the most ideal anchoring mode in DSSCs.[7] Under the regime of density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods, we have studied the structural, electronic and photochemical properties of the designed dyes. This study reveals that our designed dyes are likely to exhibit facile charge transport. Moreover, the electronic properties of the dye-TiO<sub>2</sub> clusters strengthen the performance of the dyes compared to those of the isolated dyes. Hence, our study provides good recommendations for the further design of dyes to enhance the performance of DSSCs.

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## Bi-Catalysed Unprecedented 1,2-Reactivity of Spiro-Cyclopropyl Oxindoles with Dithianediol: Access to Spiro-Heterocycles

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Efficient and diastereoselective Bi-catalyzed 1,2-reactivity of spirocyclopropyl oxindoles has been described with dithianediols as the sulphur surrogate to furnish spiroheterocycles at moderate temperature (Fig 1).<sup>1</sup> The procedure provides a potential approach for the construction of spiro-tetrahydrothiphene scaffolds with functional group diversities. The catalytic 1,2-reactivity of cyclopropanes, mechanistic investigation, diastereoselectivity of the products and additive-free mild reaction conditions are the salient features.



Figure 1. (3+2)-Annulation of Spiro-Cyclopropyl Oxindoles with Dithianediols.

Cyclopropanes are the smallest carbocycles and are known for their versatile activity as three-carbon synthon in chemical space.<sup>2</sup> Despite having a ring strain of 115 kJ mol<sup>-1</sup>, the cyclopropane ring does not easily tend to open up voluntarily in situ. However, specific substitution patterns, including the installation of donor and acceptor (DA) moieties on vicinal positions, endows heterolytic cleavage of the C-C bond in presence of either heat or Lewis acid and provides pivotal driving force to generate 1,3-dipolar species. In this vein, the ring enlargement of oxindole derived DA spiro-cyclopropanes has professed a substantial attention in recent years owing to the abundance of oxindole-core in potent pharmacophore moieties. On the other hand, aside from the classical 1,3-reactivity, DA cyclopropanes have recently been documented to unveil a new fascinating 1,2-dipolar system,<sup>3</sup> although formation of such an even-numbered dipole is still a fledging topic. Further, S-containing heterocycles are one of the privileged heterocyclic units, ubiquitous in myriads of natural products and pharmaceuticals with promising anticancer, antimicrobial and antihypertension activities. Consequently, the blend of the sulphur moieties into spirocycles could lead to construct the fascinating bio-mimetic scaffolds. On the other hand, being non-toxic and eco-benign, the reactions involving bismuth(III)-salts as catalyst have been referred to as one of the highly sought-after transformations in scientific fronts. Herein, we report an efficient Bi(III)-catalyzed unprecedented 1,2-reactivity of spirocyclopropyl oxindoles with dithianediols as the sulphur surrogate to assemble spirotetrahydrothiophene structural frameworks at mild reaction conditions.

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## Synthesis, optical properties and cation mediated tuning of reduction potentials of core-annulated naphthalene diimide derivatives

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Napthalene diimides (NDIs) are attractive candidates for electrical energy storage owing to the stabilisation of complexes between eletrogenerated dianions and cations. However, stability of such complexes are often compromised due to the monodentate nature of the electrogenerated carbonyl anions. This limitation may be overcome by the lateral addition of co-ordinating groups on the NDI core.Imidazo[1,2-*a*]pyridines are an important class of nitrogen fused heterocycles, which have been used in various fields including material science, optics and organometallics, and medicinal applications. Inspired by the fascinating properties of imidazo[1,2-*a*]pyridines and NDIs, we aimed to amalgam the two moieties by attaching the former moiety to NDI laterally, converting the dyes into multidentate ligands, overcoming the earlier dilemma of NDI and herein we show the synthesis, electrochemical, and optical properties of core-annulated naphthalene diimides *a*ImPyDI and *b*ImPyDI. We investigated the reduction potentials of the ImPyDIs in presence of acid and  $Zn^{2+}$  ions. In both cases, reduction potentials were altered significantly compared to the parent dyes. Even though, there is no LUMO contribution at the imine nitrogen atoms, they hold the cations in close proximity with the carbonyl groups. The electro-generated dianions are stabilised with the help of those cations. As a result, both the redox processes were found to be facile.



**Fig 1:**(Left) Structure of the dyes; (Right) (a) Schematic illustration of a two-electron transfer reduction for an *a*ImPyDI molecule. (b) Cyclic voltammograms of *a*ImPyDI (green), [(aImPyDI)Zn<sub>2</sub>](OTf)<sub>4</sub> (purple), *b*ImPyDI (red), and [(*b*ImPyDI)Zn<sub>2</sub>](OTf)<sub>2</sub> (blue). Measurements for ligands were done in chloroform and for zinc-complexes in acetonitrile.

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## A Robust low coordinate Co(II) Catalyst for Efficient Conversion of CO<sub>2</sub> into Methanol Under Mild Conditions

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*M*ethanol currently ranks among the top five commodity chemicals with an annual production of 70 million per tons, therefore making it the most attractive CO<sub>2</sub>-derived C1 building blocks. Realizing the high demand of methanol in the market as an alternate fuel, it becomes extremely desirable to have a cost-effective, sustainable and large-scale production from renewable sources. <sup>[1]</sup> Regardless of high activity shown by heterogenous catalysts and many other noble metal based homogenous systems, use of harsh reaction conditions, selectivity and stability issues raise the need to look for non-noble, earth-abundant homogenous metal catalysts. Undoubtedly, many first- row transition metal (Ni, Fe, Co, Mn) based catalysts have been recently reported, yet the use of highly flammable H<sub>2</sub> gas, or toxic silanes/boranes as hydride source, Lewis- acid/base, amines as additives and harsh reaction conditions sometimes reduce the activity and stability of the catalyst. <sup>[2]</sup> Therefore, in this line of interest, we have successfully synthesized the bulky amido–cobalt(II) complex which is a three-coordinate system in solution <sup>[3]</sup>, and has been found to work efficiently under moderate conditions. This system being a selective single site catalyst; has evidently reduced CO<sub>2</sub> to CH<sub>3</sub>OH with excellent TONs up to 11,171. Moreover, this is the most active cobalt catalyst and first low coordinated system yet reported for such reductions, yielding TOFs as high as 508 h<sup>-1</sup>. In this presentation, we are going to evaluate our genuine efforts in making a small contribution towards mitigating increased CO<sub>2</sub> concentration in the earth's atmosphere.



Figure 1. Graphical abstract of the CO<sub>2</sub> conversion into methanol using low co-ordinate cobalt(II) catalyst.

By employing CCS (Carbon Capture and Storage) Policy , we found our cobalt catalyst to be efficient enough in not only reducing pure CO<sub>2</sub> but also selectively converting CO<sub>2</sub> from vehicle exhaust with TOF as high as  $3000 h^{-1}$ , which is unprecedented. Spectroscopic studies have successfully identified the formation of B(OMe)<sub>3</sub> as the pre-product which on hydrolysis yields CH<sub>3</sub>OH. A series of related stoichiometric reactions have shed further light on identifying the active form of catalyst L<sub>3</sub>Co-( $\eta^1$ -BH<sub>4</sub>) which has been explicitly proven by <sup>1</sup>H, <sup>11</sup>B-NMR and ESI-MS techniques; and hence, is supporting our proposed mechanism. As a whole, this study further indicates that modulating the coordination space around the 3d-metal system can rival the practicality of precious noble metal-based systems in catalytic transformations of small molecules. With these significant results, we are heading towards in taking up our work from a laboratory level to an industrial scale.

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## Pyridinedicarboxylate salts of imidazole tethered anthracene derivatives and their impact on photophysical properties

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Impacts on aggregation induced emissions in the solid state of self-assemblies of salts of 9-N-(3imidazolylpropylamino)methylanthracene (Hanthraimida) with pyridinedicarboxylic acid and cocrystals with 1,3dihydroxybenzenes were analysed. Salts and cocrystals exhibit proton transfers and different structural features. An unusual composition of  $2[(H_3anthraimida)]^{2+}[(26pdc)^{2-}2(H26pdc)^{-}]\cdot(H_226pdc)\cdot CH_3OH (1)$  was shown by the salt of Hanthraimida with 2,6-pyridinedicarboxylic acid (H<sub>2</sub>26pdc). Various anionic and neutral forms of acid molecule formed chain-like arrangement via hydrogen bonding, where the cations H<sub>3</sub>anthraimida<sup>2+</sup> were accommodated in two distinct supramolecular environments. Whereas, the conventional composition of (H<sub>3</sub>anthraimida)<sup>2+</sup>(35pdc)<sup>2-</sup> ·4H<sub>2</sub>O (2) was observed for the salt of 3,5-pyridinedicarboxylic acid (H<sub>2</sub>35pdc) with Hanthraimida. This salt consists of octameric water clusters bonded to 35pdc<sup>2-</sup> ions in its lattice through hydrogen bond. While the introduction of resorcinol in such salts yielded ionic cocrystals, namely  $[(H_3anthraimida)]^{2+}[(26pdc)]^{2-}$ ·resorc·H<sub>2</sub>O· CH<sub>3</sub>OH (3) and  $2[(H_3anthraimida)]^+[(35pdc)]^{2-}.2(resorc) (4).$ 



Figure 1: Reactants, products, salts and ionic cocrystals of Hanthraimida.

There are emissions at longer wavelengths in salts and ionic cocrystals with varied compositions and distinct cationic forms of the same fluorophore, according to a combined structural and theoretical investigation on the observed photoluminescence of these compounds. For the purpose of illustrating the potential for aggregation-induced emissions in the solid state by **1-4**, DFT calculations on the neutral and ionic species were performed.

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## Stimuli-responsive Prodrug of Diclofenac: Sustained Drug Release with Turnon Near-infrared Fluorescence

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Non-steroidal anti-inflammatory drugs (NSAIDs) are commonly prescribed for the treatment of acute and chronic inflammatory diseases.[1, 2] However, prolonged uses of NSAIDs at higher doses induce undesired side-effects with non-selective cyclooxygenase (COX) inhibition.[3, 4] We report herein the first example of reactive oxygen species (ROS)-responsive near-infrared (NIR) fluorogenic prodrug **DCI-ROS** for the sustained release of the widely used NSAID, Diclofenac (**DCF**).[5] Inflammation-induced elevated ROS at the site of inflammation would enable the cleavage of the boronate ester moiety in **DCI-ROS** facilitating the sequential self-immolative processes for the release of active drug (**DCF**) with simultaneous turn-on NIR fluorescence (Figure 1).



Figure 1. Schematic representation of ROS-responsive prodrug of Diclofenac (DCI-ROS) and its uncaging process.

UV-Vis and fluorescence spectroscopic studies along with HPLC and ESI-MS analyses confirmed the feasibility of drug release process in aqueous medium. Moreover, the prodrug was found to be non-toxic in cancer cells and exhibited turn-on red emission with endogenous ROS under fluorescent microscopy indicating release of the active drug. Anti-inflammatory activity of the prodrug was validated further with the inhibition of COX-2 expression in the inflammation-induced macrophage cells (RAW 264.7). The inflammatory stimuli (ROS)-responsive sustained release of **DCF** along with NIR fluorescence emission would certainly be helpful for the site-selective delivery of the NSAID with convenient real-time fluorogenic monitoring for the treatment of inflammatory diseases in future.

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## Guerbet-Type $\beta$ -Alkylation Reaction Catalyzed by Pincer Metal Complexes Based on 3d Metals

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The construction of C-C bond is considered as a significant transformation in synthetic organic chemistry having numerous applications in agrochemicals, pharmaceuticals, fine chemicals and others<sup>1</sup>. Among various protocols reported for sustainable chemical synthesis, the transition metal catalyzed  $\beta$ -alkylation of secondary alcohols with primary alcohols through "Hydrogen Borrowing" pathway stands out as an exceptionally promising approach. Despite the overwhelming response of noble metal-based catalyst featuring high catalytic activity for such reactions, their low abundance, high cost and biological toxicity have prompted researchers to look for alternatives. The recent trend in contemporary catalysis is to substitute scarce precious metals by less expensive and earth abundant metals. Over the years, the first-row transition metals complexes have proven to be efficitive catalyst for variety of organic transformations. In this context, the current study sheds light on the efforts being carried out in our group towards the synthesis of NNN (*bis*-imino)pyridine/*bis*-benzimidazole pincer-metal complexes based on first-row 3*d* transition metals and their possible application in Guerbet-Type  $\beta$ -alkylation of alcohols.<sup>2-5</sup>

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## Development of pro-drug type peptides for the intervention of Amylinaggregation.

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The contemporary peptide based amyloid inhibitors have a pre-installed breaker element. These breaker elements are designed to develop a kink in the back bone of the inhibitor peptide which, inhibits amyloid formation. The kink in itself significantly reduces the target site recognition efficiency of the amyloid inhibitor. We have developed a new strategy for amyloid disruption. The designed peptide efficiently binds to the target site as a normal peptide. The peptide undergoes cascade of chemical reactions and transforms into the actual breaker peptide and thereby enhances the amyloid inhibition efficiency of the peptide. The designed peptideminetics have demonstrated significant efficiency in the inhibition of Amylin aggregates.



Figure 1: Pictorial representation of the proposed action of the amyloid inhibitor with pre-installed breaker elementand the inhibitor based on pro-drug mechanism. [1]

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### **Organocatalytic Dearomative Spirocyclization Reaction of Naphthalenones**

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Spirocarbocyclic frameworks are abundant in many bioactive compounds, also they have been employed as the fundamental building blocks for a variety of functional materials and chiral ligands.<sup>1</sup> Because of this, synthesising the special structure of spirocarbocycles has garnered the keen interest of organic chemists.<sup>2</sup> Highly functionalized spirocarbocycles can be produced efficiently and practically using dearomatization processes based on phenols and naphthols via an intramolecular or intermolecular spirocyclization.<sup>3</sup> These dearomatization reactions are efficient transformations which can convert readily available aromatic compounds into a variety of non-aromatic ring systems.<sup>4</sup> In this presentation, we are going to demonstate Brønsted base catalyzed dearomative intramolecular spirocyclization of a newly designed substrate having anyl enone motif tethered with  $\alpha$ -naphthol moiety (Scheme 1).



Scheme 1. Organocatalyzed dearomatization of Naphthalenone derivatives

We prepared the Naphthalenone derivatives in few steps and then executed the desired dearomative spirocyclization reaction in dichloromethane at room temperature with triethylamine. We got the products with upto 90% yield and >20:1 dr ratio in all the cases.

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## Design and development of mixed matrix membrane forselective separation of biomolecules

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Mixed Matrix membranes had been developed by introducing  $\beta$ -cyclodextrin as filler into polysulfone (PS) polymer matrix by phase inversion technique for adsorption applications. The prepared functional materials (PS- $\beta$ -CD-M) were characterised by techniques like Fourier transformation infrared spectroscopy (ATR-FTIR), nuclear magnetic resonance spectroscopy (NMR), X-ray diffraction (XRD) and Scanning electron microscopy (SEM). ATR-FTIR, NMR and XRD studies indicated hydrogen bonding interactions between polysulfone and  $\beta$ -CD network. The SEM micrographs of the PS- $\beta$ -CD-M were porous and asymmetric in nature and also the distribution of the  $\beta$ -CD throughout the polymer matrix was asymmetric. Adsorption properties of biomolecules such as amino acid and flavonoids were investigated on the prepared adsorptive membranes with the aim to provide an efficient method thatcan combine both the selectivity of adsorption and the flow behaviour of membranes.



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## Dually Reactive Multilayer Coatings Enable Independent Functionalization of Underwater Superoleophobicity and Oil Adhesion

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Fish-scale inspired underwater non-adhesive superoleophobic materials as commonly and artificially constructed by creating hierarchical surface topography on water-compatible materials, including polymeric hydrogels, metal oxides, electrostatic multilayers, etc. While promising, these methods do not allow for the underwater superoleophobicity and oil adhesion to be independently tuned, which limits their potential applications. Here, we design a dually reactive multilayer coating whose underwater superoleophobicity and oil adhesion can be independently tuned through the orthogonal functionalization of two different reactive moieties at ambient conditions. Moreover, the cooperative assembly of amphiphiles on the modified underwater superoleophobic coating gives rise to a reversibly switchable oil adhesion while retaining the extreme oil-repellency. The reversible change in the oil adhesion of the underwater superoleophobic coatings depends on the interplay between the molecular structure and concentration of the amphiphiles and the pH of the aqueous solution. Building on these findings, we developed underwater superoleophobic sensors that enable the naked eye real-time identification of (1) the charge of the head group of ionic surfactants and (2) the concentration of bile acids without complex equipment and procedures.<sup>1</sup>



Scheme. (A-B) Scheme showing dually reactive multilayer coating (A) and 1,4-conjugate addition reaction (B). (C-E) Schematic illustration of reversible functionalization of underwater superoleophobic interfaces with amphiphiles at specific pH.

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## Simultaneous Sensing and Photocatalytic Degradation to Free Water from Toxic Dye Pollutants for Possible Agricultural and Household Applications: Role of Generated Holes and Hydroxyl Radicals

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Careless discharge of textile/industry effluents containing carcinogenic organic dyes into local water bodies like lakes, rivers, and ponds has become the major source of wastewater pollution, threatening public health in India. Therefore, herein for the first time, we have developed  $I^{5+}/TiO_2$  as a smart catalyst serving a dual role. Thus, the catalyst is efficient in (a) colourimetric visual sensing/discrimination of methyl orange (MeO) and Methylene blue (MeB) in water through colour change and (b) degradation of such dyes upon irradiation of light ( $\lambda$ >400 nm). The I<sup>5+</sup>/TiO<sub>2</sub> has been synthesized through a simple thermal-assisted chemical synthesis route which has shown the specific interaction with MeO resulting in colour change through various photophysical experiments. We have established our synthesized nanomaterial as an excellent photocatalyst with excellent ability in photo-assisted catalytic degradation of MeO and MeB dyes within 60 min. The role of various active species in the photocatalytic reaction as well as the degradation pathway of the targeted dyes have also been thoroughly studied. To establish the effectiveness of our photocatalyst, we have further extended our study to find the effect of the treated water on the germination of Vigna radiata (green gram seeds) and monitored the plants' growth until the 16<sup>th</sup> day. Additionally, we also tested the treated water on HEK293 mammalian cell lines for cytotoxicity analysis. The results obtained suggested that the treated water is completely safe and devoid of any toxicity toward plants and human health. Therefore, the I<sup>5+</sup>/TiO<sub>2</sub>-assisted photocatalytic treated dye water can be utilized for agricultural and other household activities like washing, cleaning and gardening.



## Onium and alkyl amine decorated protein nanoparticles acts as an inherent antimicrobial agent and carrier of antibiotics to promote synergistic antibacterial and antibiofilm activities

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The unprecedented cases of antimicrobial resistance and scarcity of effective antibiotics against resistant strains demand the development of proficient drugs and their stewardship. The antibiotics carriers and the adjuvants which can counteract the resistance mechanism and revive the activity of existing antibiotics can be the promising tool to fight against the antimicrobial resistance mechanism. Herein we have reported the antimicrobial activity of the sulfoniumlinked albumin protein, which embraces the benefit of biocompatibility and drug-carrying capability. The scanning electron microscope, transmission electron microscope, and hydrodynamic diameter showed that the modified protein forms the nanoaggregate in the aqueous environment. The sulfonium and lauryl amine conjugated nanoaggregate was utilized to encapsulate the clinically approved antibiotics, and it displayed the release of antibiotics in a controlled manner. Antibiotic encapsulated carrier composite exhibited synergistic antimicrobial activity against Gram-negative and Gram-positive bacterial strains, plummeting the antibiotic's effective dose. Thus, the synthesized antimicrobial carrier molecule revitalizes the activity of the antibiotics and is a cost-effective strategy. Subsequent studies showed that the modified protein was capable enough to breach the biofilm barrier, and at minimum inhibitory concentration, biofilm lost its viability. The antimicrobial activity of the compound was proved to be membrane-directed and had negligible toxicity against erythrocytes and mammalian cell lines.



Figure 1. Schematic representation of the formation of modified BSA-based PNAs and their antibacterial activities

## Sterically Frustrated Cyclo[2]Dipyrrins Internally Linked with Anthracene Subunits

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Enantiopure helical systems have potential applications in circularly polarized luminescent materials (CPL), nonlinear optical materials, spin filters,<sup>1</sup> circularly polarized organic light emitting diodes (CP-OLEDs), and bioimaging applications.<sup>2,3</sup> Chirality in porphyrinoids is an emerging field recently realized with large and flexible macrocycles with appropriate linking subunits. Expanded porphyrinoids with a minimum of eight cyclic units reduce their bond angle strain by undergoing two half twists ( $T2_0$ ) i.e., figure of eight structure, and exhibit helical chirality.<sup>4</sup> The optical resolution of these macrocycles is often difficult to achieve owing to their dynamic interconversion between two conformers. In this work, we demonstrate the synthesis, structure, and chiroptical properties of a conformationally stable, helically locked, and twisted Cyclo[2]Dipyrrins 1 containing two dipyrrin units separated by anthracene subunits. The synthetic strategy utilizes a non-planar building block, 1,5-dipyrrylanthracene (1,5-DPA), which was subjected to acid-catalyzed condensation with 2,3,4,5,6-Pentafluorobenzaldehyde. The non-planar nature of macrocycle enhances the solubility and helps in structural characterization. Macrocycle 1 crystallizes as a racemic mixture as revealed from X-ray crystallographic analysis and adopts a highly twisted non-planar conformation which is supported by DFT method. Due to its high racemization energy barrier, optical resolution of the two (M, M) and (P, P) enantiomers were easily carried out and the CD spectrum of the two fractions showed clear mirror images of one another.



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## Metal-free greener approach for an oxidative cross-dehydrogenative-coupling reaction: Synthesis of a new class of 3-sulfenylindole derivatives from 4hydroxythiocoumarin and indole

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By employing an oxidative cross-dehydrogenative-coupling reaction, the synthesis of a new class of 3sulfenylindole derivatives is achieved from 4-hydroxythiocoumarin and indole using 10 mol% of molecular iodine, and TBHP (1 equiv.) in DMSO in room temperature. The salient features of this reaction are mild reaction conditions, good yields, and broad substrate scope. Furthermore, some of the synthesized 3-sulfenylindole compounds have been converted to biologically active sulfones. Antiproliferative activity of a few of the sulfone derivatives has also been studied on breast cancer (MCF7) cell lines that reacted with cellular reactive species.



Figure 1. Synthesis of 3-sulfenylindole and some of the sulfone derivatives

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## Citric acid based poly(ester amide urethane) thermoset as a sustainable coating material

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In recent times, poly(ester amide)s have loomed up us an appealing group of polymeric materials constituting excellent mechanical and thermal properties on ground of typical confinement of ester and amide connectivity in polymeric chains. However, substantial usage of polymers derived from conventional petroleum sources is serving as a major ultimatum to ecosystem sustainability. In this pursuit, a bio-based water-soluble poly(ester amide) was synthesized using an environmentally benign route devoid of usage of any solvent. Citric acid, glycerol and hexamethylenediamine were used as core raw materials for carrying out the synthetic reaction via a polycondensation route. The parent polymeric resin was characterized using various spectroscopic techniques such as Fourier transform infrared (FTIR), <sup>1</sup>H-NMR (Nuclear magnetic resonance), <sup>13</sup>C-NMR etc. In turn, poly(vinyl alcohol) was introduced to modify the texture of the resin. Isophorone diisocyanate was used fundamentally as a curing agent and subsequently, various compositions of resin/poly(vinyl alcohol)/ isophorone diisocyanate were prepared. Evaluation of their performances was carried out by conducting various mechanical, thermal and chemical resistance tests. The polymeric films displayed splendid mechanical attributes namely tensile strength, toughness and elongation at break along with satisfactory thermal stability feature. Elaborate aging studies (heat, UV and chemical) have also been carried out to estimate the robustness of the prepared material under stringent conditions. Moreover, the polymeric materials were also found to be biodegradable in nature. Hence the studied materials bear potential applications in diverse fields, notably as coating materials.

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## Light triggered H<sub>2</sub>S release from β-Carboline Photocage in the Organic Nanoparticles and Hydrogel platform

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Hydrogen sulfide ( $H_2S$ ) is a newly recognised gasotransmitter that exerts critical physiological functions such as biological regulation and cytoprotection. The physiological effect of  $H_2S$  in highly concentration dependent.[1-2] Thus to better understand the role of  $H_2S$ , there is a need of novel  $H_2S$  donors that can produce  $H_2S$  as required at the specific cite of action. Photoremovable protecting groups (PRPGs) have shown great potential for the spatio-temporal control over the release of various active molecules.[3] We report herein a novel UV and NIR light activatable  $H_2S$ donor (BCS) based on  $\beta$ -carboline PRPG.



Figure 1. Graphical abstract of the  $\beta$ -carboline based H<sub>2</sub>S donor in nanoparticle and hydrogel form

For the biological application purpose we formulated the  $\beta$ -carboline based H<sub>2</sub>S donor into pluronic coated organic nanoperticles (Plu@BCS nano) as well as pluronic-hydrogel (Plu@BCS hydrogel). The advantages of Plu@BCS nano/hydrogel H<sub>2</sub>S donors are i) simple synthesic procedure, ii) good solubility under physiological conditions, iii) fast and clean release of H<sub>2</sub>S, and ii) spatio-temporal control over the H<sub>2</sub>S release. These properties, together with the facile synthetic procedure, make the Plu@BCS nano/hydrogel an intriguing candidate for potential applicative research studies where spatiotemporally regulated H<sub>2</sub>S delivery is required.

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## Rose bengal photocatalyzed Knoevenagel condensation of aldehydes and ketones in aqueous medium

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Knoevenagel condensation is widely used in organic synthetic chemistry and several reaction conditions have been demonstrated. These reactions in a neutral medium are challenging. In this report, we present a sustainable and greener method for Knoevenagel condensation reaction between carbonyl compounds (both aldehydes and ketones) and active methylene compounds using rose bengal photosensitized hydrogen atom transfer (HAT) strategy in an aqueous medium. This protocol works smoothly for aromatic aldehydes and ketones containing both electron-donating and electron-withdrawing substituents.



Figure 1. Rose bengal photosensitized Knoevenagel condensation protocol by HAT reaction

We have developed first time a novel, simple, efficient, greener, and sustainable photocatalyzed protocol for Knoevenagel condensation reaction applicable for both aldehydes and ketones. This protocol does not require acidic, basic, or thermal conditions. Singlet oxygen generated by the photocatalyst triggers the formation of active methylene radicals by the HAT mechanism. We also found that the reaction can be accomplished with household bulbs. Among the several organic photocatalysts examined, rose bengal gave desired results due to its favorable singlet oxygen yield. The mechanism was elucidated with several control experiments and DFT theoretical calculations. The protocol is compatible with wider substrate scope and high-value product synthesis. This protocol is scalable and can be applied for the synthesis of chromene derivatives in a one-pot reaction. Further applications of this protocol are currently under investigation.

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## A Benzimidazole based fluorogenic probe for selective detection of Al<sup>3+</sup> ion.

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Sensing of metal ions has gained lot of interest and having relevance towards a wide range of environmental, biological and industrial processes.[1-2] Over the years, chromogenic and fluorogenic sensors have gained prominence for detecting various metal ions in very low concentration.[3] Benzimidazole moiety play an important role in heteroatomic molecular system for sensing & bioimaging [4], photovoltaics, non-linear optics, and optoelectronic devices.[5] The unexploited fluorescent properties and biological importance of benzimidazole group help us to design and synthesis of a benzimidazole based non-fluorescent probe for recognition of suitable metal ions.



Herein we have report an electron rich benzimidazole based probe L1 that can suitably detect  $Al^{3+}$  ion in mixed aqueous solvent system. With the gradual addition of  $Al^{3+}$  ion, the fluorescence intensity of L1 rapidly increased through an internal charge transfer fluorescence "TURN-ON" mechanism. Job's plot revealed the stoichiometry to be 1:1 and the binding constant of the metal complex was calculated to be  $2.09*10^{4} M^{-1}$ . The detection limit for  $Al^{3+}$  ion was determined as 0.98 nM. Further the probe can also be successfully employed for  $Al^{3+}$  ion detection in real water samples.

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## Electrocatalytic N<sub>2</sub> Reduction Activity of Core-Shell Iron Nanoalloy Catalysts - A Density Functional Theory (DFT) Study

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Exploring binary nanoalloy catalyst with high activity, selectivity, and stability is essential for building a novel electrocatalyst for ammonia synthesis.[1] In an industrial scale, ammonia production occurs through traditional routes Haber-Bosch process under extreme condition, following  $N_2$  and  $H_2$  react over Fe based catalyst.[2] In the present work, we have investigated the role morphology of iron alloy catalysts exposed with (110) facet to improve the electrochemical  $N_2$  reduction reaction (NRR) activity.



**Figure 1.** Cuboctahedral (Fe<sub>65</sub>) and core-shell ( $M_{15}$ @Fe<sub>50</sub>) nanoclusters (NC) investigated for nitrogen reduction reaction (NRR) and hydrogen evolution reaction (HER) activity. The violet and yellow colors represent the inner core with 15 late transition metal (M) atoms and the outer shell with 50 Fe atoms in  $M_{15}$ @Fe<sub>50</sub> NC.

Using the density functional theoretical calculations, we demonstrate that the presence of Cu in core of the iron nanocluster (NC) catalyst can favour the electrocatalytic ammonia synthesis selectively against hydrogen evolution reaction (HER) compared to pure iron NC and pristine Fe(110).[3-4] These findings open a scope in terms of scrutinizing the position and compositional effects of substituted elements on nanoalloys with long-term stability for the discovery of efficient NRR eletrocatalysts using machine-learning technology.

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## Conversion of scrap iron into ultrafine α-Fe<sub>2</sub>O<sub>3</sub> nanorods for efficient visible light photodegradation of ciprofloxacin

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Industrial wastes often contain metals and adversely affect human health and ecosystems. Scrap iron is one of the metal wastes contributed by both industrial and domestic activities.<sup>1</sup> One of the ways to mitigate such impacts is to deduce sustainable metal management by recycling. Such processes not only help in protecting the environment but also act as secondary sources and aid resource recovery.<sup>2</sup> According to a data available by EPA a total of more than 19,000 tons of ferrous waste has been generated in past each year. So a proper methods has to be devised not only to handle the waste effectively but to harness its potential in environmental remediation. In the present work we have proposed a method to integrate iron oxide generated from random scrap iron samples and exploit it in degradation of ciprofloxacin water toxicants thereby aiding to an effective remediating technology.

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## Photoactive g-C<sub>3</sub>N<sub>4</sub> as a visible light photo-initiator for the development of reinforced hydrogel

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Graphitic carbon nitride  $(g-C_3N_4)$  is considered an efficient metal-free photo-initiator utilized for various purposes such as energy conversion, wastewater remediation, or organic and polymer synthesis. [1] The suitable band gap of  $g-C_3N_4$  in the visible region and its excellent physicochemical stability allows it to be a potential candidate for the synthesis of hydrogel. In the present work, a facile one-pot synthesis of hydrogel has been carried out under visible light by employing  $g-C_3N_4$  as a photo-initiator. However, along with its photocatalytic property,  $g-C_3N_4$  also acts as a reinforcing agent within the hydrogel matrix. [2,3] The developed hydrogel shows much higher mechanical properties along with good absorbing capacity compared to those initiated by common free radical initiators like ammonium persulphate (APS).



Figure 1. Schematic diagram of photo-polymerisation

Moreover, a detailed study revealed that the developed hydrogel possesses the photocatalytic activity of  $g-C_3N_4$ . And it is also found that by varying the  $g-C_3N_4$  content, both the mechanical property and photocatalytic activity of the hydrogel can be tuned. Thus this carbon nitride-based hydrogel opens up new opportunities for the development of functional hydrogel with high mechanical strength and photocatalytic properties.

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### Visible-Light-Mediated Synthesis of Thio-Functionalized Pyrroles

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Figure 1. Graphical abstract of light-mediated synthesis of thio-functionalized pyrroles.

An inimitable illustration of the green-light-induced synthesis of thio-functionalized pyrroles has been established using  $\beta$ -ketodinitriles and thiophenols as the reacting partners and eosin Y as the photocatalyst. Large-scale synthesis and some useful synthetic modifications of the thio-functionalized pyrroles are also demonstrated.

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## Side-chain fatty acid containing crystalline block copolymers with polyisobutylene segment

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Fatty acids and their derivatives are essential bio-renewable resources due to their easy accessibility, low cost, biocompatibility, with myriads of applications.<sup>1</sup> Our group has previously well explored homopolymers of long-chain fatty acids, where crystallinity was observed due to the crystallisation of side-chain *n*-alkyl fatty acid moieties, having side-chain alkyl carbons  $C \ge 12.^2$  Since decades, researchers are very interested in modifying polymer crystallinity in order to have control over the final physical and mechanical characteristics of the polymers.<sup>3</sup> In this context, the introduction of inorganic, amorphous, or other elements have become increasingly significant in fine-tuning crystallinity within the polymer matrix.<sup>4</sup> Thus, we became motivated to synthesize block copolymers by incorporating an amorphous polyisobutylene (PIB) segment into side-chain fatty acid-based crystalline polymers and to investigate their influence on the side-chain crystallinity of the block copolymers (Figure 1). We used a combination of living cationic and reversible addition-fragmentation chain transfer (RAFT) polymerization to develop a series of PIB and side-chain fatty acid containing block copolymers with variable n-alkyl side-chains.<sup>5</sup> The effect of amorphous PIB segment on the crystalline behaviour of fatty acid side-chain polymers was studied utilising differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), polarised optical microscopy (POM), transmission electron microscopy (TEM), etc. Altogether, the amorphous PIB segment inside the fatty acid-containing block copolymer changes the orderliness of the lamellar orientation, resulting in a novel approach towards designing materials with desired physical characteristics.



Figure 1. Graphical abstract of fatty acid-based block copolymers containing PIB segment.

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## Dihydroindolo(2,3a)carbazole-based macrocycles with benzo[α]-annulated BODIPYs for Near-IR applications

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BODIPYs [4,4-difluoro-4-bora-3a,4a-diaza-s-indecenes] based macrocycles have attracted attention in recent years owing to their bio-labeling/imaging, optical sensing, photodynamic therapy, and organic photovoltaics applications.<sup>[1]</sup> Structural modification in the meso/peripheral of the BODIPY skeleton often led to an alteration in the photophysical and optical properties.<sup>[2]</sup> Particularly, annulation at the  $\alpha$ -position of BODIPY's tends to narrow energy gaps through the lowering of LUMO levels while maintaining modest change in HOMO levels which are essential for photovoltaics and near-IR applications.<sup>[3]</sup> Dihydroindolo(2,3a)carbazoles are nitrogen-containing polyaromatic alkaloids, which contain two pyrrole subunits in a rigid, linear, conjugated planar structure with high solubility, and stability towards air, light, and heat.<sup>[4]</sup> Since the dihydroindolo(2,3a)carbazole framework possesses benzo-annulated pyrrole at the  $\alpha$ -position it could be an inherent source for  $\alpha$ -fused BODIPY's. In this presentation, I will briefly introduce the synthetic strategy adopted to prepare such macrocycles (**InCarbz-S**) embedded with dihydroindolo(2,3a)carbazole and their  $\alpha$ -fused BODIPY (**InCarbz-SBOD**). These interesting air and acid-stable mono-BODIPY's exhibit extended conjugated with narrow energy gaps.<sup>[5]</sup>



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### Charge variable cholic acid-based polymers for insulin fibril inhibition

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In recent decades, insulin amyloid fibrillation has received great attention in the biomedical field due to its involvement in a wide range of devastating pathological conditions, especially diabetes [1]. Therefore, it remained challenging to design suitable effective inhibitors that can inhibit the fibrillation process and ameliorate the treatment of diabetes. Recently polymers have gained significant attention in this regard due to their ability to control various parameters like molecular weight, architecture, functionality, etc. [2,3]. In this presentation we are reporting the effect of cholic acid-based charge variable polymeric architectures on the insulin fibrillation process.



Figure 1. Graphical abstract of the inhibition of insulin protein fibrillation by cholic acid-based polymers.

In this work, we have synthesized side chain cholic acid containing cationic, anionic, and neutral polymers by reversible addition-fragmentation chain transfer (RAFT) polymerization technique to understand the effect of cholic acid-based charge variable polymeric architectures in modulating the insulin aggregation process [4]. Using a combination of biophysical and calorimetric techniques, we found the fact that the cationic polymer with cholate pendant acts as a potent inhibitor, prevented the growth of fibrils in a dosedependent manner, and showed better efficacy than cationic polymer without cholate moiety in preventing the insulin aggregation process. Furthermore, the anionic and neutral polymers with and without cholate pendants showed very less inhibitory effects in inhibiting the insulin aggregation process. We have also addressed that both electrostatic polar and hydrophobic forces of interactions are equally important for inhibiting the formation of insulin fibrils [5]. With these intriguing aspects, we believe that these polymers can be used as a template to design novel polymer-based inhibitors with the ability to efficiently combat amyloidogenic diseases.

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## Genaration of a non-heme Cobalt(IV)-oxo complex using <sup>t</sup>BuOOH as an oxidant

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Genaration of non-heme terminal metal-oxo complexes of late transitional metal like Co, Ni, Cu are still long distance challenge.[1] Metal-oxo complexes play vital role in different oxidation processes due to their thermal unstability and high reactivity. Different oxidants like hydrogen peroxide ( $H_2O_2$ ), tert-butylhydroperoxide ('BuOOH), *m*-chloroperbenzoic acid (*m*-CPBA), peracetic acid (CH<sub>3</sub>CO<sub>3</sub>H) are used to generate the metal-oxo complexes. Herein we synthesized [Co(bpzpya)(CH<sub>3</sub>CN)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>, **1** [bpzpya = [N,N-Bis(3,5-dimethylpyrazol-1-ylmethyl)-2-aminomethylpyridine)],[2] which was characterized spectroscopically as well as by single crystal-XRD. In acetonitrile solution at -40 °C this Co(II)-initial complex reaction with 'BuOOH and followed by Et<sub>3</sub>N finally gives its corresponding [Co<sup>III</sup>-OH] complex *via* a thermally unstable Cobalt(IV)-oxo intermediate.[3] This intermediate was characterized by different spectroscopic methods. Formation of cobalt(IV)-oxo complex was also confirmed by using some commonly organic substrate namely fluorine, xanthene, diphenyl methane which give their corresponding oxidized product 9-fluorenone, 9-xanthone and benzophenone respectively.



Complex 1

**Figure 1**. Reaction of complex **1** with <sup>t</sup>BuOOH followed by  $Et_3N$ . [S] = substrate

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## Black Turmeric (*Curcuma caesia* Roxb.) Rhizome Derived Phytotoxic Essential oil: Screening, Effectiveness, Chemical Basis, Uptake and Mode of Transport

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Plant-based phytotoxins play an important role in plant-plant interaction and are of great promise for the development of bioherbicide. In this study, screening of essential oils from six different *Curcuma* rhizomes identified black turmeric (*Curcuma caesia* Roxb.) oil as an efficient growth inhibitor in wheatgrass coleoptile bioassay (IC<sub>50</sub> 57.1 µg/mL). The phytotoxic efficacy of this oil was further confirmed through the dose-dependent (10.0-300.0 µg/mL) inhibition of germination, coleoptile and radicle growth of wheatgrass seeds in water medium (IC<sub>50</sub> 176.7, 90.6 and 93.0 µg/mL respectively) and the pre-germinated seeds in agar medium. Activity-guided fractionation and purification of the crude oil identified curzerenone, a major furanosesquiterpene in this oil as the most active phytotoxin (IC<sub>50</sub> 13.0 µg/mL in coleoptile bioassay; 188.3, 34.7 and 36.7 µg/mL respectively in water medium). Structure-activity relationship study indicated the importance of all the functional groups for its phytotoxicity. A significant contribution by the oxygenated monoterpenes towards oil phytotoxicity was also evidenced. Though inhibitory efficacy of the oil was comparatively weak in soil, a profound activity through aerial diffusion was observed against germination and/or growth of fresh and pre-germinated wheatgrass seeds (IC<sub>50</sub> 1.4-6.2 mg/L air).





The study also confirmed the uptake of active phytotoxins with no detectable transformation by the seeds in water and their persistence in the soil for at least one and half months. Further, its applicability was demonstrated through an efficient post-emergence growth inhibition (IC<sub>50</sub> 37.0-81.4  $\mu$ g/mL) of bermudagrass weed in water and agar medium.

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## Study of Metal's Presence in Rice Beer Prepared by Two Indigenous Tribal Communities: *viz* Rabha and Sonowal Kachari of Assam, India

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The two major tribal indigenous communities of Assam i.e.; Rabha and Sonowal Kachari prepare their homemade alcoholic beverages. Rabha people are subdivided into seven subtribes; Koch Rabha, Pati Rabha and Rangdani Rabha are three of them. Rangdani Rabha is the upper class of Rabha people and they pay special importance to their alcoholic beverages. All the subtribes of Rabha tribe and Sonowal Kachari tribe consume alcoholic beverages and they serve it in their local functions including marriage parties and pujas. Alcoholic beverages are of different names among different tribal communities, i.e., Makham or Juguli and Jonga or Chokko are two popular alcoholic beverages prepared by Rangdani Rabhas of Goalpara district; Pati Rabhas of Baksa district prepare 4 different types of rice beer, i.e., black rice beer, sticky rice beer, general rice beer and distilled rice beer; Koch Rabhas of Bongaigaon district prepare two types of rice beer i.e., distilled beer and sticky rice beer; Sonowal Kacharis of Dibrugarh district prepare two fermented rice beer i.e., Sepa and Rohi. Here we have reported the metal content in most frequently used rice beers among the tribes such that people can be aware of daily average intake of metals from the consumption of alcoholic beverages. Jonga of Rangdani Rabha, Sticky rice beer of Koch Rabha, Sticky rice beer of Pati Rabha and Rohi of Sonowal Kachari are the four most frequently used alcoholic beverages among the communities.

Heavy metal consumption is very toxic and cause severe adverse effect to human health. This adverse effect to human health depends on the amount of consumption, frequency of consumption etc. By using atomic absorption spectroscopy, the concentration of 11 metals like Cd, Co, Cr, Cu, Fe, K, Mn, Na, Ni, Pb, Zn in 4 different alcoholic beverages are determined after digesting the samples with concentrated nitric acid and concentrated sulphuric acid and the results are compared with the permissible limit of WHO. The estimated daily intake and target hazard quotient for each metal in different alcoholic beverages are reported here. Sticky rice beer of Pati Rabhas has highest total hazard quotient, still it can be marked as safe by comparing with WHO's permissible limit and it is almost free from contamination of toxic metals like cobalt and chromium.

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## A Temperature Tunable Synthesis of Tetrahydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-ones and Dihydro-1*H*-benzo[*b*]azepines from 2-Aminobenzonitriles and Donor-Acceptor Cyclopropanes

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Over the past two decades, donor-acceptor (D-A) cyclopropanes have been considered as versatile building blocks in organic synthesis mainly due to their easy accessibility and diverse reactivity.[1] The high reactivity of D-A cyclopropanes in the reactions is attributed to the presence of inherent strain in the cyclopropane ring plus the additional strain bestowed by the push-pull effect of the donor-acceptor substituents. Thus, the synthetic potential of D-A cyclopropanes can be expanded enormously by varying the donor and acceptor groups or placing a suitable group in the other vicinal position. Among different types of reactions of D-A cyclopropanes, their ring opening triggered by Lewis acids and/or nucleophiles constitutes one of the effective means for synthesizing various cyclic and acylic products [2] We have developed a temperature tunable one pot synthesis of tetrahydro-4H-pyrrolo[3,2c]quinolin-4-ones and dihydro-1*H*-benzo[*b*]azepines from 2-aminobenzonitriles and donor-acceptor cyclopropanes mediated by SnCl<sub>4</sub> (Scheme 1). The reaction proceeds via sequential ring opening of donor acceptor cyclopropane ring followed by nucleophilic and electrophilic attack of amine and nitrile to the newly generated cation and anion and subsequent unprecedented rearrangement leading to two sets of structurally diverse molecules. The reaction is compatible to many electron-donating as well as electron-withdrawing functional groups in both the substrates giving moderate to good yields. This methodology can be extended towards the synthesis of tricyclic hexahydropyrrolo[3,2c]quinolinone derivatives which constitutes the tricyclic core of martinelline, a series of alkaloids possessing antibacterial activity and potent antagonist activity toward bradykinin (BK) B1 and B2 receptors.[3]



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# Visible- light-mediated synthesis of $\beta$ -keto sulfones by using graphitic carbon nitride as recyclable photocatalyst under sustainable conditions

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Owing to their high stability, easy handling, and recyclable nature, carbon-based materials have emerged as effective catalytic systems in synthetic organic chemistry. [1] Among others, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a metal-free polymer, synthesized by thermal polymerization of easily accessible and cheap starting materials like urea. [2] Graphitic carbon nitride absorbs light in the visible region (band gap of 2.7 eV;  $\lambda_{max} \sim 460$  nm) and because of which they have utilized extensively as photocatalyst. [1,3] Visible-light-mediated reactions are one of the trending topics in modern synthetic chemistry. [4] Herein, this polymeric recyclable heterogeneous photocatalyst was synthesized, characterized and applied for the synthesis of biologically important  $\beta$ -keto sulfones in presence of blue light irradiation. [5]  $\beta$ -keto sulfones, were disclosed by using commercially available phenylacetylenes or ketones as precursors and sodium sulfinates, as the sulfonyl source. Potent biologically active compounds like anti-analgesic agents and CES1 inhibitors were synthesized by the present protocol. To explore the applicability, a few post-synthetic modifications of  $\beta$ -keto sulfones were also carried out. Finally, to show the greener aspects of the protocol, green chemistry metrics was also calculated. The eco-scale value of the current procedure was also found to be acceptable (with both acetylene and acetophenone). Besides this, metal, base and ligand-free reaction conditions, recyclable photocatalyst (up to five cycles) and wide substrate variability are some additional advantages of this methodology.



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## Chiroptical Properties of Fluorinated Carbo[6-8]helicenes: A Computational Study

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In this article, the effects of di- and octafluorination on chiroptical and structural properties of carbo[6-8]helicenes is reported. From each parent carbohelicene, two fluorinated derivatives are designed. In the cases of di-fluorination, one ortho hydrogen of each terminal ring is substituted by a fluorine atom. Similarly, all the four hydrogen of each terminal ring is replaced by four fluorine atoms in the cases of octafluorination. Excited states properties such as UV-vis and CD spectra of all the six fluorinated carbohelicenes are computed at the ADC(2)/def2-TZVP level and compared the results against the results of their respective parent carbohelicene. At the same level, CPL properties are computed. In the case of carbo[6]helicene (6H),  $g_{CPL}$  decreases with increase in the degree of fluorination. Difluorination in carbo[7]helicene (7H), and both di- and octafluorination in carbo[8]helicene (8H) produce improved  $g_{CPL}$  results compared to their respective parent. Among the all, in the case of difluorinated 8H both the  $g_{CPL}$  and fluorescence rate constant (K<sub>f</sub>) increase, simultaneously.



## Role of weak noncovalent interactions in polyproline II (PPII) helical stability

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Polyproline II (PPII) helix is a left-handed secondary structure (SS) which is the third most abundant SS after  $\alpha$ -hleix and  $\beta$ -sheet. The propensity of forming cis amide geometry in N-acetylated proline (pro) is higher than any other amino acids, and an oligomer of proline residue or poly-Pro (poly-P) tract can adopt either a polyproline I (PPI, all cis amide) or a polyproline II (PPII, all trans amide) helical conformation.[1] However, it is not well studied about the stability of trans amide proline residues in PPII helices. Recent studies on N-acetylated proline residues by Prof. Raines group has suggested CO···CO orbital interactions from the N-terminal carbonyl to the C-terminal carbonyl group stabilizes the trans geometry of the proline amide bond.[2] Another investigation from Prof. Sarma's group have shown a reciprocal variation of CO···CO interaction in diacyl hydrazide which mimic the dihedral angles essential for a PPII helix.[3] In this current study we show the presence of reciprocal CO···CO interactions that extend over the whole PPII helical region. Interestingly, the CO···CO interactions strengthen with the increase in the PPII helical chain length and the inner CO groups possess stronger CO···CO interactions, which could explain the reduced cis abundance of the inner Pro residues of a poly-P tract.[4] We also identified a much stronger (~0.9 kcal·mol<sup>-1</sup>)  $n_0 \rightarrow \sigma^*_{C\alpha-C\beta}$  interaction between the N-terminal CO oxygen lone pair and the antibonding orbital ( $\sigma^*$ ) of their  $C_{\alpha^-}$  $C_{\beta}$  bonds. As the  $n_{O} \rightarrow \sigma^{*}_{C\alpha-C\beta}$  interaction is possible only in the trans isomers of Pro, this interaction should be crucial for the stabilization of a PPII helix. Finally, an unusual  $n_N(amide) \rightarrow \sigma^*_{C-N}$  interaction (~0.3 kcal·mol<sup>-1</sup>) was observed between the peptidic nitrogen lone pair (n<sub>N</sub>) and the antibonding orbital ( $\sigma^*_{C-N}$ ) of the subsequent C-terminal peptide C-N bond. We propose a cumulative effect of these interactions in the stabilization of a PPII helix. Collagen triple helices comprises of three individual PPII helix. Deciphering the role of PPII helix stability would help in understanding the formation of collagen triple helices.[5]



Figure 1. Graphical abstract of the weak noncovalent interactions in polyproline II (PPII) helix and collagen triple helix stability.

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## Ruthenium Pincer Catalyzed Selective Synthesis of Alkanes and Alkenes via Deoxygenative Coupling of Primary Alcohols

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The selective conversion of alcohols to alkanes and alkenes is a captivating but extremely difficult process. Herein we explored the activity of an acridine-derived SNS-Ru pincer complex in the selective conversion of primary alcohols into both long-chain alkenes and alkanes. Both homo- and cross-coupling reactions provide good yields of the desired products with excellent selectivity. Various control experiments, mechanistic and kinetic studies suggest that the reaction sequence is dehydrogenation, aldol-condensation, deformylation, and hydrogenation. <sup>1,2,3</sup>



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### **Transformable Transient Directing Group Assisted C(sp<sup>2</sup>)** H Activation: Synthesis and Late-Stage Functionalizations of o-Alkenylanilines Bubul Das, Bhishma K Patel\*

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The isocyanate group in aryl isocyanates serves as a transformable transient directing group in a Ru(II)-catalyzed *o*-olefination leading to *o*-alkenylanilines. In alcoholic solvents, aryl isocyanates are transformed into carbamates which initiate the insertion of acrylates *via o*-C–H activation. The alcohol reacts with electrophilic isocyanate and form carbamate as a transient directing mediator (TDM), which actually directs the incoming alkene. However, after the desired transformation carbamate breaks into an amine. In particular, <sup>*t*</sup>AmOH serves the dual role of solvent-cum transient directing mediator. The *o*-alkenylanilines are converted to azacoumarins and subsequently into C-4 aryl-substituted azacoumarins using aryl iodides as coupling partners *via* Pd(II) catalyzed C–H functionalizations



Figure 1. Graphical abstract for transformable transient directing group.

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## Stepwise synthesis of a rigid trinuclear [Co<sup>3+</sup>–Zn<sup>2+</sup>–Co<sup>3+</sup>] chiral complex with a labile Zn(II) site at the centre

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Using L-threonine derived ligand ( $H_2L^{L-thr}$ ), we first synthesized the rigid chiral mononuclear Co(III) complex [Co( $L^{L-thr}$ )<sub>2</sub>]<sup>1-</sup>. The complex at solid-state is a coordination polymer where bis-complexes are connected through Na<sup>+</sup> counter ion. The addition of Zn(II) salt replaces the Na<sup>+</sup> forming a trinuclear [Zn{Co( $L^{L-thr}$ )<sub>2</sub>}(H<sub>2</sub>O)] complex. The two phenolates from the bis Co(III) complex are in *cis* orientation, which coordinates with Zn(II), forming the heterobimetallic complex. Structural characterization shows that the Zn(II) at the centre is surrounded by H-bond capable carboxylates within the  $C_2$  symmetric chiral environment. The Penta-coordinated Zn(II) has an easily replaceable water molecule in the axial position. The resultant architecture where a Zn(II) bound water surrounded by H-bond capable chiral environment is reminiscent of the active site of hydrolytic enzymes. The complex has the potential to be used for catalysis, namely deamination reaction<sup>1</sup> and ring-opening reaction<sup>2</sup>. The choice of Co(III) and Zn(II) metal ions is such that the complex formed will be NMR active. In our case, we could assign each <sup>1</sup>H NMR peak to a proton of the trinuclear complex. This will allows us to study the multinuclear complex's interaction with the guest molecules in the solution state<sup>3</sup>.



**Figure 1**. (A) schematic representation of the reaction pathway, (B) X-ray structure highlighting the coordination geometry and space-filled model, and (C) <sup>1</sup>H NMR spectra of heterobimetallic complex  $[Zn{Co(L^{L-thr})_2}_2(H_2O)]$ 

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## Anisotropic Compartmentalization of Liquid-Liquid Interface using Dynamic Imine Chemistry

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The temporal and spatial sculpting of liquids has garnered interest in designing a nonequilibrium system for possible applications in catalysis, energy conversion, three-dimensional (3D) printing, and soft robotics. The liquid–liquid interface offers a fascinating avenue for generating such architectures that can be reversibly modulated after fabrication. [1-3] The basis of the liquid–liquid interfacial interaction is the reaction between individual components of the two phases. Such interactions result in an overall reduction of interfacial tension between the two liquids due to the formation of a two-dimensional (2D) network at the interface. Once the assemblies are formed, the interface can be transformed into various nonequilibrium structures [4]



Figure 1. Graphical abstract of anisotropic compartmentalization of liquid-liquid interface

In this study, oil-soluble aromatic aldehydes and water soluble polyethylenimine were used as biphasic components to construct imine-mediated assemblies at the oil-water interface. The successful jamming of imine mediated assemblies was observed when a compressive force was applied to the droplet. Thus, the anisotropic compartmentalization of the liquid-liquid interface was created and it was later altered by changing the pH of the surrounding environment. Finally, a proof-of-concept demonstration of pH triggered cargo release across the interfacial membrane confirmed the feasibility of stimuli responsive behaviour of dynamic imine assemblies. [5]

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## A benevolent direction to environmental suitability: ionic liquid immobilized MoO<sub>3</sub> nanoparticles used in the efficient visible lightdriven photocatalytic degradation of antibiotics

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Ionic liquids, mainly room temperature ionic liquids (RTILs) unveil exceptional features which make them different from most of the conventional organic solutions [1,2] and they act as a media for the preparation and stabilization of nanostructured materials such as nanoparticles, nanowires, and nanotubes. It also plays a deliberate role in the shape of the metal oxides as a capping agent as the ionic liquid possesses an alkyl chain and can be easily removed. In the environment matrices worldwide, antibiotics are ubiquitous and are used widely in the environment and are dispersed via emissions such as excrements, sewage irrigation, and sludge compost and enter the soil and impact negatively the natural ecosystem of the soil. Photocatalysis is regarded as an efficient green technology to remove toxic and persistent antibiotics. [3] In this presentation, we report the synthesis of an ionic liquid linked MoO<sub>3</sub> (MoO<sub>3</sub>-IL) system which is highly stable, capable of absorbing visible light, and may induce the breakdown of emerging organic water pollutants including antibiotics.





The photocatalyst has been prepared via a facile precipitation technique and the morphological, structural, and photocatalytic properties were analyzed by FT-IR, powder XRD, SEM-EDX, TEM, XPS, UV-DRS, and PL studies. Under visible light irradiation, the immobilized functionalized ionic liquid material displayed considerably enriched photocatalytic activity for the degradation of ciprofloxacin and metronidazole. It exhibited a degradation efficiency of 92.07% for ciprofloxacin while it recorded complete degradation of metronidazole in 60 minutes with a 0.0391min<sup>-1</sup> rate constant. The synergism of nano MoO<sub>3</sub> and ionic liquid, lower bandgap, and late recombination of photoinduced charge carriers are the major factors of its high photocatalytic activity. Furthermore, the trapping experiments were conducted to confirm the photoactive radicals involved in the degradation process.

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### Catalytic Evaluation of Bimetallic [Fe^Ir] Catalysts in Artificial Photosynthesis

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One of the biggest challenges that Scientists face nowadays is the green production of renewable fuels. Our global community is largely dependent on fossil fuels for their energy demands. But the combustion of these fossils fuels can increase the level of CO<sub>2</sub> circulating in our ecosystem which eventually causes global warming. Therefore, development of new technologies with the help of renewable energy sources which can replace fossil fuels has become a necessity for a cleaner & greener future. Artificial photosynthesis is one such example wherein it mimics the natural process of photosynthesis to convert sunlight, water and carbon dioxide into carbohydrates and oxygen. Researchers are trying to mimic this process in laboratory. We have synthesized a few bimetallic [Fe^Ir] complexes and characterized by NMR, HRMS, CV, and SCXRD. These complexes are employed for the catalytic oxygen production from water in presence of ceric ammonium nitrate (CAN) which is nothing but half artificial photosynthesis (Figure 1). The evolved oxygen is measured using oxytherm. Both the metals cooperatively participate in substrates activation and easily execute the job. Detailed mechanism and advantage of using both the metals (Fe and Ir) will be discussed in details.



Figure 1: Water oxidation with bimetallic catalyst

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## Electricity Mediated [3+2]-Cycloaddition of N-Sulfonylcyclopropanes with Olefins via N-Centered Radical Intermediates: Access to Cyclopentane Analogs

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In this modern arena, electroorganic chemistry has emerged as a new innovative technology for the development of sustainable methodologies.<sup>1</sup> Recent years have experienced a huge renaissance in this domain and have witnessed the participation of several synthetic laboratories for the development of novel methodologies.<sup>1</sup> Inspired and motivated by the synthetic utility of this chemistry, we envisaged that by employing this technology *N*-centered radicals can be generated that can be further utilized for the ring opening annulation process providing an access to cyclopentane analog. Henceforth, in this work, we designed an external oxidant-free strategy for the  $\beta$ -scission of strained C-C bonds of cyclopropane and utilized it towards a [3+2] cycloaddition for accessing the di- or tri-substituted cyclopentane analogs. Further, the detailed mechanistic studies ascertained that the methodology encompasses *N*-center radical intermediate.<sup>2</sup>



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## Twisted molecular donor and TCNQ based co-crystal: Structure-property relationship

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Organic single and multicomponent supramolecular charge-transfer complexes possess multiple noncovalent interactions, highly ordered structures, and multifunctional properties. This allows further to explore the fundamental investigation of photophysical pathways and the exploration of optoelectronic devices. In this context, cocrystallization is regarded as an efficient but simple method to achieve high performance and multifunctional optoelectronic materials. However, finding a suitable donor is a key challenge to construct efficient co-crystals for optoelectronic functions. In this work, three highly twisted donor molecules DBF-PTZ, DBF-ANT, and DBF-CBZ were synthesized by varying donor units with different capacities. Among the three, only DBF-PTZ molecule formed a kinetically controlled supramolecular charge transfer (CT) complex with an acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) in water, organic solvent, and solvent-free methods. A single crystal analysis is performed to understand the molecule's self-assembling and co-assembling molecular packing. However, the formation of the CT complex was characterized by FT-IR, Raman, Powder XRD, FETEM, and TGA analysis. Further, CT interactions and modulation of energy band gap were investigated *via* absorbance kinetics and density functional theory (DFT) calculations revealing an efficient co-crystallization strategy and achieving a new class of semiconducting materials.

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## Gold(I)-Catalyzed Cycloisomerization-Indole Addition Cascade: Synthesis of 3(2H)-Furanone Incorporated Unsymmetrical 3,3'- Bis(indolyl)methanes

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Bis(indolyl)methanes (BIMs) are one of the major skeletal fragments of several pharmaceutically important compounds and present in a variety of bioactive natural products, agrochemicals and functional materials.<sup>[1]</sup> An unprecedented Au(I)-catalyzed domino intramolecular carbonyl-alkyne cyclization/indole addition strategy has been developed.<sup>[2]</sup> This generalized strategy enables the synthesis of 3(2H)-furanone incorporated unsymmetrical 3,3'-bis(indolyl)methanes with generation of a stereocentre at the furanone junction. A variety of easily accessible indole-tethered 1,2-alkynediones and indoles were found efficient for this catalytic cycloisomerization method. In addition, this present protocol was also extended for the synthesis of a number of indolyl-(hetero)arylmethanes by employing a variety of (hetero)arenes (e.g. pyrrole, furan, thiophene, azulene) as nucleophile coupling partner.



**Figure 1**. Graphical abstract of the Gold(I)-catalyzed synthesis of 3(2*H*)-furanone incorporated unsymmetrical 3,3'-bis(indolyl)methanes

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## CuFe<sub>2</sub>O<sub>4</sub>@MIL-101(Cr): A magnetically retrieval nano-catalyst for the synthesis of benzodiazepine triazole scaffold in aqueous medium

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Magnetically recoverable metal nanoparticles are an important class of material in the field of catalysis due to their large surface-to-volume ratio. Because of their high surface energy, nanoparticles tend to agglomerate during the reaction process thereby decreasing their stability and efficiency. Hence they require to be stabilized using solid support material.[1] Meanwhile, metal-organic frameworks (MOFs) have emerged as a potential candidates in catalysis due to their high specific surface area, tuneable pore size, etc. MIL-101(Cr) being one of the stable MOFs has gained much interest due to its easy preparation procedure, high surface area, and high thermal stability.[2,3] Hence, magnetically recoverable  $CuFe_2O_4@MIL-101(Cr)$  has been synthesized and characterized by various spectroscopic techniques for application in catalysis. On the other hand, benzodiazepines are important *N*-heterocyclic compounds that exhibit anti-depressive, anti-inflammatory, anti-anxiety, analgesic, and hypnotic activities.[4,5] Further, triazoles are also an important heterocyclic compound having significant biological and pharmaceutical activities.[6] Therefore, in this study,  $CuFe_2O_4@MIL-101(Cr)$  was utilized for the synthesis of benzodiazepine triazole scaffold in an aqueous medium. A library of 21 derivatives has been synthesized using a variety of substrates. A high yield of 87-96% of the products, easy recovery, and reusability of the catalyst up to six consecutive runs are some of the salient features of this protocol. In addition, a yield of 86 % in the gram-scale level implies that this protocol can be implemented in industrial applications as well.[7]



Figure 1. CuFe<sub>2</sub>O<sub>4</sub>@MIL-101(Cr) catalyzed synthesis of benzodiazepine triazole scaffold.

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### Lewis Acid-assisted Transition-metal-free Aminocyanation of Alkynes with Arylamines and N-cyanosuccinimide

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 $\beta$ -substituted acrylonitrile, particularly  $\beta$ -aminoacrylonitrile derivatives are essential precursors for the synthesis of natural products, unnatural amino acids and pharmaceutical compounds. The development of an efficient and straightforward route for synthesizing  $\beta$ -substituted acrylonitriles and their derivatives has attracted much attention within the synthetic chemistry arena. Cyanofunctionalization of alkynes is the competent way for the synthesis of  $\beta$ -substituted acrylonitrile derivatives. The cyanofunctionalization of alkynes is possible via the direct addition of X–CN (X= C or heteroatom) to C=C multiple bonds or alternatively by using a cyanide source and a partner functional group from two different molecules in a step-economic manner. Majorly, cyanofunctionalization reactions were accomplished with transition-metal-based catalytic systems. In addition, the selection of non-toxic cyanide sources for such kind of intermolecular reactions is challenging. Mostly organic molecules have been used as a non-toxic cyanide source in past decades.

A transition-metal-free aminocyanation of aryl alkynes has been achieved using indium tribromide InBr<sub>3</sub> or tris(pentafluorophenyl)borane B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as a Lewis acid. This aminocyanation protocol features with non-toxic cyanide source, a good substrate scope and potentially valuable aminocyanation products. Mechanistic studies reveal the complex formation between Lewis acid and alkyne to produce *in situ* alkyne nitrile as a key intermediate. Further hydroamination of alkyne nitrile with arylamines affords the *E*-selective (*E*:*Z*= 70: 30 to 90:10)  $\beta$ -aminoacrylonitrile derivatives.



Figure 1. Aminocyanation of aryl alkynes with aryl amines.

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## Relaxometry and in-vivo study of water soluble Fe(III) based complex for potential application as MRI contrast agent

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MRI is one of the most powerful non-invasive imaging modality used now-a-days to investigate anatomic details. To improve sensitivity, more than 50% scans are done after administration of contrast agents, which are basically complexes of Gd(III), Mn(II), and Fe(III). Gd(III) being toxic, its use is recently forbidden by FDA. More biogenic Mn(II) and Fe(III) metals could be efficiently explored to achieve efficient contrast. Fe(III) give highly thermodynamically stable complexes which are least toxic. But, Fe- based contrast agents are mostly T<sub>2</sub> based and due to darkening effect, images are often confusing. Herein, we have reproduced water soluble ligand H<sub>4</sub>bedik and corresponding hexa-coordinated Fe(III) complex (complex 1) with excellent thermodynamic stability (log  $K_{ML}$  = 19.49). Detailed relaxivity studies showed capability of the complex as a T<sub>1</sub>-weighted MRI contrast agent with impressive longitudinal relaxivity value (0.99 mM<sup>-1</sup>s<sup>-1</sup>, at 37 °C). Physiological and kinetic stability of the aforementioned complex showed convincing data. *In-vivo* toxicity was tested and henceforth, complex was injected in healthy mice to test its pre-clinical signal enhancing ability. Successfully, we observe strong signal enhancement in the gall bladder and kidney of the mice, confirming the potential of complex 1 as gall-bladder and kidney targeting T<sub>1</sub>-weighted MRI contrast agent.

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## **P-42**

## Supramolecular polymorphism via solvent and temperature dependence in *peri*-naphthoindigo-boron difluoride aggregate systems

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Peri-Naphthoindigo is the naphthalene analogue of indigo, but exists in mono-enol form. The mono- $BF_2$  complex of this dye that was prepared shows high planarity, with the Fluorine atoms on the outside on both sides. Due to its ambipolar nature, it has the tendency to exhibit aggregation in polar and non-polar solvents.

For the study of aggregation properties, a mixture of 1,2-DCE and Methylcyclohexane in the ratio of 1:99 was chosen as the non- polar medium. An increase in extinction co-efficient, an additional shoulder and increased emission was seen, compared to the dye solution in 1,2-DCE. SEM images exhibited the formation of linear nanoaggregates. In a mixture of water: THF, nanoellipsoids Agg2 is seen at 80:20 ratio, while at 70:30 mixture, the dye exists as monomeric in nature. Thus a 76:24 ratio is chosen, at which Agg2 can be converted to Agg3 through a process of heating and re-cooling. SEM images show Agg3 to be spherical, which is also explainable based on SA/V ratios.

Thus we have synthesized a dye derivative which has the potential to exhibit supramolecular polymorphism by the utilization of a temperature and solvent polarity pathway.



Scheme 1: Synthesis of boron difluoride complex of *peri*-naphthoindigo



**Figure.** Diagrammatic representation of different aggregates accessed through unique pathways(left)and absorption spectra of Agg2 and Agg3 alongside that of the monomer(right)

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## Isolation of bioactive compounds with anticancer activity from indigenous bacterial community and their versatile role in green synthesis of gold nanoparticles

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Several bacterial species, such as *Clostridium, Klebsiella, Pediococcus, Lactobacillus, and Pseudomonas* have been found to have potential anticancer activity. More than 1500 active compounds are under development, and 500 are under clinical trial.[1-5] In this study, we have isolated a bacterial strain (GB\_SG\_008) from the soil, which shows high anticancer activity against specific tumor cells.



Figure 1. Images showing the bacterial population (GB\_SG\_008) growing on an LB agar plate (left) and AuNPs synthesized from extracellular supernatant of the same bacteria (right).

In this work, we have also discovered that the extracellular metabolites containing the bioactive compounds were found to reduce gold salt to produce gold nanoparticles (AuNP). The AuNP was found to have a spherical shape with around 40 to 60 nm in diameter. The AuNP also possesses a sheath over the surface, which possibly came from the reducing agent present in the extracellular supernatant and working as a capping agent for the AuNP. Finally, a cell viability assay was performed, and it was found that the AuNP and the extracellular supernatant from GB\_SG\_008 both have anticancer activity against human cancer cell lines. The bacterial strain was further subjected to 16s sequencing to understand the identity of the aforementioned bacterial strain.

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## A Molecular Dynamics Perspective on Interaction between Amino Acid functionalized Perylenediimide and Amyloid-β fibrils

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Non-covalent interactions such as hydrogen bonding,  $\pi$ - $\pi$  stacking, cation- $\pi$ , anion- $\pi$ , etc., are the backbone in drug designing, protein-ligand interaction, construction of macromolecules, designing of optoelectronic materials, and many more. [1-4] Designing of drug molecule for Alzheimer's disease (AD) is one of the most challenging tasks in the scientific community. This disease is associated with the aggregations of the amyloid- $\beta$  peptides, including the formation of senile plaque, oligomers, fibrils, and protofibrils—this different species are highly toxic. [5-6] Here we investigated the amino acids derivatives of perylenediimide (PDI) compounds [7] with the hexamer model of amyloid- $\beta$  fibrils using a molecular docking study followed by the multi-ns molecular dynamics simulation to understand the molecular binding nature and inhibitory properties. Further, to understand the nature of interactions at the quantum level between the amino acid fragments of the amyloid amyloid- $\beta$  fibrils and the modulated PDI molecules, symmetry-adapted perturbation theory (SAPT) and quantum theory of atoms in molecules (QTAIM) were implemented.

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### **EDTA and Thiol Functionalized Graphene oxide and Chitosan-Based Conjugated Polymeric Nanosheet for The Effective Adsorption of Antibiotics** Himadree Das<sup>1</sup>, Lal Mohan Kundu<sup>\*1</sup>

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The discharge of industrial effluents contains various organic and inorganic pollutants like broad-spectrum toxic contaminants, including heavy metals and antibiotics and organic dye. Because of their bioavailability and toxicity and the possibility of entering the human food chain directly or indirectly, their presence in surface water poses a threat to aquatic ecosystems and human beings.<sup>1</sup> The proper removal of heavy metals is of great concern around the world. Adsorption is the most promising because of its versatility, extensive applicability, economic feasibility, and ease of operation.<sup>2</sup> In the current study, we have synthesized graphene oxide by chemical oxidation of graphite powder by modified hummers method with some minor modifications, which maintains various benefits because it is costeffective and produces a high yield. (GO-CS-EDTA) is synthesized by modified covalent binding and electrostatic interaction process. Accordingly, the thiol functionalization is done by EDC-NHS coupling reaction. The synthesized (GO-CS-EDTA-Cys) nanosheets were primarily characterized by using Fourier Transform Infrared spectrum to investigate the functional groups present in the adsorbent. Crystallinity and phases were analyzed by XRD spectroscopy using an X-ray diffractometer. Dynamic light scattering was used to determine the size distribution of the nanoparticles. Thermal stability was tested using a thermogravimetric analyzer, in an N<sub>2</sub> environment. Surface morphology was determined by both Field emission transmission electron microscope and Field emission scanning electron microscope. All the batch adsorption tests were carried out on a laboratory scale with stock solutions of tetracycline. The optimum parameters such as pH of the solution, adsorbent doses, time of contact, effluent doses have been observed for the material. The kinetics of the adsorption process were evaluated using the pseudo-first-order, pseudo-second-order and intra-particle diffusion models. Additionally, graphs demonstrated the excellent fittings of the experimental data from the adsorption with the pseudo-second order model. Tetracycline's adsorption onto GO-CS-EDTA-Cys was thus adequately explained.

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## New synthesis approaches for antiaromatic indenofluorene regioisomers and their $\pi$ -extended derivatives

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Fully conjugated non-alternant indenofluorene (IF) isomers are the formally antiaromatic analogues of pentacene.<sup>1</sup> Among all the IF isomers, indeno[1,2-*b*]fluorene and indeno[2,1-*c*]fluorene found their applications in field-effect transistor and organic bulk-heterojunction devices, while example of indeno[2,1-*a*]fluorene is limited to one example because of instability.<sup>1</sup> The usual synthesis route to the IFs utilized addition of nucleophilic aryl/ethynyl groups to the benzo-diketone precursor and followed by SnCl<sub>2</sub>-mediated reduction of the formed diol to afford the desired IFs. This route to diketone precursors suffers from harsh reaction conditions including potentially high temperatures (220-280 °C), and also it lacks introduction of unsymmetrical disubstituent to the apical carbons of five-membered rings.<sup>1b</sup>





Lately we reported a mild synthetic approach to make [2,1-c]IF 1,<sup>2</sup> and further extended our approach to synthesize the unsymmetrically disubstituted [2,1-c]IFs 2-4,<sup>3</sup> as well as a  $(4n+2)\pi$  tetraradicaloid *s*-indacenodifluorene (*s*-IDF) **5** with small HOMO-LUMO and singlet-triplet energy gap (Figure 1) that absorbed in the near-IR region.<sup>2</sup> Adopting a similar synthetic approach and utilizing the steric crowding of bulky mesityl substituent, a steric promoted synthesis of symmetrical and unsymmetrical [1,2-b]IFs 6 and **7** including benzo-extended **9** and **10** were reported (Figure 1).<sup>4</sup> Notably, use of less bulky pentafluorophenyl group as one of the substituent afforded a mixture of IF regioisomers **8** and **11** which could be purified by silica gel column chromatography in air. Our experimental and theoretical studies showed **11** to possess greater degree of antiaromaticity than isomeric **8**, which was explained by Gimarc's principle of topological charge destabilization.<sup>4</sup>

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## Visible-Light Mediated Solvent-Switched Photosensitizer-Free Synthesis of Poly-functionalized Quinolines and Pyridines

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A solvent (TFE vs. EtOH) switched synthesis of quinolines and pyridines is illustrated from (E)-2-(1,3-diphenylallylidene)malononitriles via a Pd(II)-catalyzed photochemical process. The active catalyst generated from Pd(OAc)<sub>2</sub>/2,2'-bipyridyl complex by virtue of metal-to-ligand charge transfer (MLCT) serves as an exogenous photosensitizer. Photoexcitation, redox trans-metalation with arylboronic acid, and carbopalladation of nitrile followed by an intramolecular C–N bond formation offer exclusive Z-alkenylated quinolines and pyridines in respective solvents. Further, large-scale synthesis and few interesting post-synthetic modifications have been demonstrated.



Figure 1. Graphical abstract for the synthesis of Quinolines and Pyridines

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### Rotational synchronization of pinned spiral waves

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Coupled rotors can spontaneously synchronize, giving rise to a plethora of intriguing dynamics. We present here, a pair of spiral waves as two synchronizing rotors, coupled by diffusion. The spirals are pinned to unexcitable obstacles, that enables us to modify their frequencies and restrain their drift. In experiments with the Belousov-Zhabotinsky reaction we show that two counter-rotating spiral rotors, pinned to circular heterogeneities, can synchronize, in frequency and phase. The nature of the phase synchronization varies depending on the difference in their characteristic frequencies. We observe in-phase and out-of-phase synchronization, lag synchronization and phase-resetting across the experiments. The time required for the two spirals to synchronize is found to depend upon the relative size of their pinning obstacles and the distance separating them. This distance can also modify the phase-lag of the two rotors upon synchronization. Our experimental observations are reproduced and explained further on the basis of numerical simulations of an excitable reaction-diffusion model.

### Title: Oxidation properties of Ni complex of meso 5,10,15,20-tetrakis(3,4,5trimethoxyphenyl) porphyrin with antimony pentachloride using UV visible spectroscopy and cyclic voltammetry

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Many research focuses currently on the redox properties of several transition metal complexes with porphyrin. Meso5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)porphyrin  $[T(3,4,5-(OCH_3)_3)PP]$  and its coordination compound with Nickel, Ni $[T(3,4,5-(OCH_3)_3)PP]$  has been synthesised. [1,2] With the addition of antimony pentachloride, the complex's oxidation properties were investigated using ultraviolet visible spectroscopy and cyclic voltammetry (CV). The UV-visible absorption spectrum of oxidation of Ni porphyrin Ni $[T(3,4,5-(OCH_3)_3)PP]$  with stepwise addition SbCl<sub>5</sub> has shown red shift and appearance of new bands .These are in agreement with formation of radicals. The oxidation process has been confirmed by using cyclic voltammetry .[3-6]

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## **Recognition of Caffeine and Theophylline by 5-[(pyren-9-ylmethyl)amino]isophthalic acid : a crystal engineering approach**

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There are many heterocyclic compounds with closely related structures having different biological activities. Caffeine and Theophylline are examples of heterocyclic compounds that show wide apart biological activities as food constituents; former is stimulant and latter assists in respiration. The difference in the structures of these two compounds arises from the presence or absence of N-H group in their structural backbone as shown in the figure a. Based on this fact, we have studied recognition properties by using fluorescence spectroscopy of these two biologically important compounds by the pyrene based receptor 5-[(pyren-9-ylmethyl)amino]isophthalic acid shown in figure b. We have found that the fluorescence emission intensity of the receptor was affected in an opposite manner upon addition of these two compounds independently; accordingly those two compounds could differentiate easily in solution.



In addition to those solution studies, we had carried out structural studies on the solvates, various salts ionic cocrystals of the pyrene derived dicarboxylic acid. Accordingly, the self-assemblies of 5-[(pyren-9-ylmethyl)amino]isophthalic acid with DMF a 1:1 solvate, 1:1 co-crystals with 6-phenyl-1,3,5-triazine-2,4-diamine, 4,6-dimethylpyrimidin-2-amine or caffeine and a 2:1 co-crystal with phenazine and 1:1 salts with 4,4'-bipyridine were structurally characterised. The  $\pi$ - $\pi$  stacking among pyrene rings in each case was compared. The competitive roles of N-H··· $\pi$  interactions were elucidated and their probable roles in the quenching of fluorescence emission of the receptor were explored.

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### Oxidative dehalogenation of halophenols by high-valent nonheme iron(IV)oxo intermediates

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Mononuclear high-valent iron(IV)-oxo intermediates are excellent oxidants towards oxygenation reactions by heme and nonheme metalloenzymes and their model systems.<sup>1</sup> One of the most important functions of these intermediates in nature is to detoxify various environmental pollutants. Organic substrates such as halogenated phenols are known to be water pollutants which can be degraded to their less hazardous forms through an oxidation reaction by iron(IV)-oxo complexes.<sup>2</sup> Metalloproteins in the Nature utilize various types of second-coordination sphere interactions to anchor the substrate in the vicinity of the active site. This concept of substrate-binding is well-known for natural enzymes, but quite elusive for the relevant biomimetic model systems. Herein, we report the oxidative reactivity patterns of an iron(IV)-oxo intermediate,  $[Fe^{IV}(O)(2PyN2Q)]^{2+}$ , (2PyN2Q = 1,1-di(pyridin-2yl)-N, N-bis(quinolin-2 ylmethyl)methanamine) with a series of mono-, di- and tri-halophenols. A detailed experimental study shows that the dehalogenation reactions of the halophenols by such iron(IV)-oxo intermediate substrate-bound species forms, that is a phenolate adduct to the ferric species - which thereafter leads to the formation of the corresponding products.



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Munshi, S.; Jana, R. D.; Paine, T. K.; *Dalton Trans.*, **2021**, *50*, 5590-5597.

## Carbon Dots-Decorated g-C<sub>3</sub>N<sub>4</sub> as Peroxidase Nanozyme for Colorimetric Detection of Cr (VI) in Aqueous Medium

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Conversion of biomass waste to create novel nanomaterials for various applications is a promising concept of 'waste to wealth' in the modern world of nanotechnology. In this work, biomass derived carbon dots (CDs) on (graphitic carbon nitride) g-C<sub>3</sub>N<sub>4</sub> was fabricated to obtain a metal free nanozyme possessing inherent peroxidase mimic functions. Here, the CDs were obtained from biomass (chicken blood). The formation of CD/g-C3N4 was confirmed by different characterization techniques. The CD/g-C<sub>3</sub>N<sub>4</sub> exhibits distinguished peroxidase mimic activities confirmed by the catalysed oxidation of a chromophore TMB (3, 3', 5, 5', -tetramethylbenzidine) in presence of H<sub>2</sub>O<sub>2</sub> along with colour change from transparent to blue. The peroxidase mechanistic study revealed that H<sub>2</sub>O<sub>2</sub> was catalysed by CD/g-C<sub>3</sub>N<sub>4</sub> to generate reactive oxygen species. In an acidic medium, the presence of Cr (VI) can faster the rate of decomposition of H<sub>2</sub>O<sub>2</sub> to •OH radicals thereby enhancing the TMB oxidation rate. Therefore, a visual colorimetric sensor was designed for Cr (VI) detection with limits of detection (LOD) 0.31  $\mu$ M, based on the accelerated electron transfer between TMB and H<sub>2</sub>O<sub>2</sub> with the assistance of CD/g-C<sub>3</sub>N<sub>4</sub>.



Figure 1. Graphical abstract of the peroxidase activity of CD/g-C<sub>3</sub>N<sub>4</sub>

This work demonstrates the synthesis of  $CD/g-C_3N_4$  that could decompose  $H_2O_2$  to generate •OH radicals, which oxidizes the peroxidase substrate TMB. In an acidic medium, the presence of Cr (VI) can faster the rate of decomposition of  $H_2O_2$  to •OH radicals thereby enhancing the TMB oxidation rate. Therefore, a visual colorimetric sensor was designed for Cr(VI) detection based on the peroxidase mimic activity of  $CD/g-C_3N_4$  nanozyme.

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### Synergistic effect of iron and copper in Hydroxyapatite nanorods for Fentonlike oxidation of organic dye

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In this report, we deal with the synthesis process of pure hydroxyapatite (HAp) nanorod by facile hydrothermal method, followed by dual metal doping (Fe-Cu@HAp) via an ion-exchange method. To explore the catalytic reactivity of this novel heterogeneous Fe-Cu@HAp nanocatalyst, it was employed in the degradation of polluting dyes through an advanced oxidation process involving  $H_2O_2$  as an environmentally benign oxidant.[1,2] The structural, morphological, and optical properties of the as-synthesized nanocatalysts were examined by various analytical techniques such as PXRD, FTIR, Raman, UV-DRS, SEM-EDS, HR-TEM, and XPS. It was observed that the Fe-Cu@HAp exhibited superior catalytic activity compared to pristine HAp for the degradation of organic pollutants in the presence of green oxidant  $H_2O_2$ . Moreover, several reaction parameters like initial solution pH,  $H_2O_2$  dosage, catalyst loading on the kinetics of the degradation process were investigated. The degradation of dyes with Fe-Cu@HAp followed first-order kinetics and the rate constants for methylene blue and malachite green were 0.05113 min<sup>-1</sup> and 0.0613 min<sup>-1</sup> respectively, which were higher than those with pure HAp. Furthermore, quenching experiments were carried out to confirm the involvement of hydroxyl radicals generated in the degradation process. The plausible mechanism for the degradation of organic pollutants with Fe-Cu@HAp was also proposed. The recyclability of Fe-Cu@HAp for Methylene Blue (MB) and Malachite Green (MG) dye degradation were also explored.



Figure 1. Plausible mechanism for Fenton-like dye degradation

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## Sequestration of cationic dyes from polluted water resources using an effective polymeric organogel

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Human exploitation has been a serious cause of concern for nature. Environment-related contamination, for instance, related to water, soil, and air has drastically increased. However, the aquatic environment has been affected at an alarming rate due to the discharge of unwanted materials by heavy manufacturing industries directly into the water bodies.

The textile industry has a major contribution to polluting aquatic sources raising serious environmental issues.[1] Although usage of dyes has been used for fabrics, they are amply used in paper industries, cosmetics, food sources as well as photographic and pharmaceutical industries.

Easy solubility of the dyes in water rapidly increases their anthropogenic activities causing complexities in separating dyes from water bodies. To cope with the factor affecting the aquatic ecosystem, a polymeric organogel has been specifically used for extracting cationic dyes from dye-polluting sources. The highest removal efficiency was found to be 99.35% within a time of 60minutes making it capable of removing carcinogenic dye molecules from the water surface providing a safer marine environment suitable for humans as well as aquatic terrestrials.

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## 1,6-addition of sulfonylphthalide to *para*-quinone methides: Selective synthesis of addition and Oxidative Hauser-Kraus annulated products

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### Abstract:

Hauser-Kraus annulation is well known for the construction of multiheterocycles including bioactive molecules and natural products from phthalide anions and  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds through the Michael addition then Dieckmann condensation<sup>1</sup>. The reactions of sulfonylphthalide with both cyclic and acyclic Michael acceptors result in two possible products i) addition product ii) annulation product. Although annulation products are more favored in most cases, some of the acyclic Michael acceptors provide either annulated<sup>2</sup> or a mixture of both addition and annulated products<sup>3</sup>. Here we have demonstrated the selective synthesis of addition and unprecedented oxidative annulated products through 1,6-addition of sulfonyl phthalide to *p*-quinone methides using KO'Bu as a base. The addition product was predominantly obtained using KO'Bu as a catalyst. The oxidative H-K annulated product was obtained using the excess quantity of KO'Bu. Highlights of both these protocols are selectivity, shorter reaction time, high yields, and mild reaction conditions. Synthesized products were also successfully transformed into new functionalized heterocyclic molecules.



Scheme 1: Selective synthesis of addition and Oxidative Hauser-Kraus annulated products.

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### Ligand and Activator-Free Nickel Bromide Catalyzed Suzuki-Miyaura Coupling Reaction

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C–C bond formation reactions finds various applications in synthesis of several complex molecules such as natural products, drugs, pharmaceuticals, optoelectronic materials and biologically active compounds.[1,2] Tetraarylatedanthracene based materials that emits blue light with high efficiency in OLEDs, can be synthesized by the formation of C-C bond from tetrabromoanthracene and various arylboronic acids via Suzuki cross coupling reaction.[3,4] The Suzuki-Miyaura cross-coupling reaction is the most efficient tool for synthesis of C<sub>aryl</sub>-C<sub>aryl</sub> bond using transition metal based catalysts. Palladium and nickel based catalysts are widely used in this reaction, the latter

being more abundant and low cost yet less common. For the first time, we have reported commercially available and low-cost 3d-metal salt NiBr<sub>2</sub> as efficient catalyst for Suzuki-Miyaura coupling reaction in high yields with good functional group tolerance.[5] The valuable new polycyclic hydrocarbons (PAHs) have been synthesized by multi-fold Suzuki coupling employing NiBr<sub>2</sub>. The reactivity of the aryl halide follows Ar-I> Ar-Br> Ar-Cl according to the order of bond strength Ar-Cl> Ar-Br> Ar-I. The EPR analysis, mercury-drop experiments and reactions with radical scavenger such as TEMPO point towards the involvement of well-defined molecular species that operate via a Ni(0)/Ni(II) catalytic cycle where oxidative addition of the aryl halide to Ni(0) is likely to be the rate –determining-step.



Figure 1. NiBr<sub>2</sub> catalyzed Suzuki-Miyaura coupling reaction

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## A two-dimensional ion-pump of a vanadium pentoxide nanofluidic membrane

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The reactive surface and layered crystal structure of vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) are exploited here to prepare a two-dimensional (2D) ion pump that transports ions against their concentration gradient. The exfoliated layers of V<sub>2</sub>O<sub>5</sub> were assembled into membrane form to create ion-channels with excellent nanofluidic transport characteristics. At the surface-charge-governed regime, the flexible and freestanding membrane of V<sub>2</sub>O<sub>5</sub> showed a remarkable proton conductivity (~0.01 S cm<sup>-1</sup>). The activation energy of proton conductivity (0.066 eV) suggests that the exceptional mobility of H<sup>+</sup> ions ( $5.2 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) inside V<sub>2</sub>O<sub>5</sub> ion-channels originates from the coordinated hopping of charges between the two-dimensionally arranged water molecules.



Figure 1. Ion pumping with a triangular nanofluidic device.

The transport characteristics of V<sub>2</sub>O<sub>5</sub> ion-channels can also be tuned just by tailor-cutting its lamellar membranes into different shapes. While rectangular devices of V<sub>2</sub>O<sub>5</sub> membranes exhibit linear I–V curves, the triangularly cut membranes display a diode-like non-linear I–V curve. The ionic current rectification in the V<sub>2</sub>O<sub>5</sub> triangle was found to originate from a combination of the unipolar conductivity of counter-ions inside the 2D nanochannels and geometrical asymmetry. The 2D ion rectifier of V<sub>2</sub>O<sub>5</sub> also pumps ions at the rate of  $3.32 \times 10^{-8}$  amps<sup>-1</sup> againsta 1000-fold concentration gradient under a fluctuating external potential with zero mean.

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## Phytoremediation and Purification of Wetland Water of Dipor Bil by Aquatic Plants having Metal Hyperaccumulating Properties

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Dipor Bil, due to its rich wetland biodiversity recognized as Ramsar Site and is located in Guwahati, Kamrup district, Assam, India (26° 7′ 48″ N, 91° 39′ 36″ E). But the water of the wetland gradually become polluted due to settlement of industries around the periphery, domestic wastewater discharge from city which effect adversely to large segment of flora and fauna and also local peoples. Phytoremediation is a cost effective, ecofriendly and a plant-based metal uptake method is utilized in this research to purify the wetland water. [1] The present study began with the collection and identification of abundantly available 20 aquatic/wetland plants from Dipor Bil Wetland site for finding plants species with potentiality to accumulate four hazardous heavy metals as Ni, Pb, Cd and Hg from the site. [2] Among 20 aquatic/wetland plants three plants such as Trapa natans, Nelumbo nucifera and Nymphaea nouchali were shortlisted in the laboratory based on higher translocation factor (TF>1) in uptaking the four different heavy metals from contaminated site. These three plants were then treated with Dipor Bil Water for 28 days. [1] Phytoremediation ability of plants was also studied by analyzing the improvement in Dipor Bil Water quality (in terms of pH, DO, BOD and COD values and heavy metal contents) after their treatment.

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## Mechanistic insights of electrochemical Cl<sub>2</sub> and O<sub>2</sub> generation from lanthanum cobalt manganese oxide

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The chlorine evolution reaction holds a core role in the chemical industries and water-treatment plants. To overcome the high power input supplied for Cl<sub>2</sub> generation at industrial scale an efficient and durable electrocatalyst is always on hunt. Double perovskite oxides have been used previously for oxygen evolution reaction (OER) and have shown outstanding results on the ground of dual surface active site mechanism. Here, La<sub>2</sub>CoMnO<sub>6</sub> (LCMO) have been explored for the electrochemical Cl<sub>2</sub> and O<sub>2</sub> generation. The electrocatalytic studies were performed in 5 M NaCl (*p*H ~ 2.2) for CER and 1 M KOH (*p*H=13.5) for OER. The LCMO shows enhanced catalytic activity with onset and overpotential of 75 mV and 280 mV for CER. Further, the kinetics of the catalytic reaction was determined by the Tafel slope values that was calculated to be 44 mV/dec for CER. The interfacial charge transfer resistance value at 11  $\Omega$  tells the insight mechanism by facilitating more interaction between electrode-electrolyte interfaces. In addition to this, wettability analysis of LCMO showed a contact angle as low as 23°. The present study paves a way for double perovskites to be used as an electro-catalyst for the chlor-alkali process.



Figure: Excellent electrochemical performance of lanthanum cobalt manganese oxide based double perovskite system towards chlorine and oxygen evolution

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### The Solubilization of Diphenyl diselenide in Surfactant Solutions

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Solubilization of diphenyl diselenide (DPDS) was studied in Cetyl trimethyl ammonium bromide (CTAB), Octylphenol ethoxylate with 10 moles of ethylene oxide (OPE-10) and sodium dodecyl sulphate (SDS) surfactant solutions. Solubility of DPDS increases with increase in the surfactant concentration due to its solubilization in micelles. H<sup>1</sup> NMR and FT-IR spectroscopy was used to study the interaction, location of diphenyl diselenide in the micelle. The change in free energy for solubilization of DPDS in micellar media confirmed the favorable solubilizations in SDS, OPE-10 and CTAB solutions. The DPDS solubility was higher in OPE-10 and CTAB compared to SDS surfactant aqueous solutions.

## Efficient Metal-Free Green Syntheses of 4*H*-Chromenes and 3-Aminoalkylated Indoles Using Reusable Graphite Oxide Carbocatalyst under Aqueous and Solvent-Free Reaction Conditions

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With the continuous increasing concern for the environment, the development of sustainable and environmentally benign protocols has been given priority in many corners of synthesis.<sup>1</sup> The use of eco-friendly and green protocols in all phases of chemical construction by innovative research that widely addresses the issues of atom economy, the economy of steps, avoidance of hazardous chemicals, and volatile organic solvents can be appreciated.<sup>2</sup> Catalyst plays a vital role in environmentally benign organic synthesis as it satisfies one of the main principles of green chemistry. Graphite oxide (GO) is a 2D multilayer carbon nanomaterial that is an oxidized form of graphite.<sup>3</sup> It meets the requirement of a sustainable and green catalyst due to its extraordinary characteristics like high surface area, oxidizing ability, easy and low cost of preparation, and recyclability.<sup>4</sup>



Figure 1. Synthesis of 4H-Chromenes and 3-amino alkylated indoles using GO as the catalyst.

Graphite Oxide (GO) was prepared according to the modified Hummer's method and was then characterized using spectroscopic techniques such as FT-IR, XPS, SEM, TEM, SAED, EDX, PXRD, Raman, and TGA analysis to confirm its formation and thermal stability. Then, the synthesized GO was utilized for the one-pot three-component synthesis of pharmaceutically important 4*H*-chromenes and 3-aminoalkylated indoles in water and solvent-free reaction conditions, respectively. These said protocols provide green and sustainable reaction conditions, including excellent catalytic activity, good to excellent yield of the products, high functional group tolerances, gram-scale synthesis, and reusability of the catalyst. Further, the present methodologies exclude the problems of metal toxicity, metal waste disposal, metal contamination in the products, and the use of volatile organic solvents.

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## A facile synthesis of crystalline graphene quantum dots derived from indoor dust: Unveiling Material Science in the Kitchen

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Graphene quantum dots (GQDs) are not new to the world of materials science. They are well-known for their remarkable properties and related applications in therapeutics, sensing, imaging, solar cells, catalysis, and other fields [1]. GQDs can be synthesized by both the top-down and bottom-up approaches, with varying particle sizes, morphologies and characteristic properties for various applications. In bottom up method, alternate sources of carbon precursors such as biomass/bio-waste are being used, as an eco-friendly and sustainable choice, in the preparation of carbon-based quantum dots, widening the possibilities of bio-waste mitigation. However the synthesis of crystalline, homogeneously sized graphene quantum dots via bottom-up methods from these sources is scarce [2].



Figure 1. Graphical abstract of the synthesis, characterizations and biological application of GQDs

We have attempted the first synthesis of crystalline graphene quantum dots (GQDs) from indoor dust particles; a ubiquitous waste material with no practical applications [3]. A simple and facile hydrothermal approach was used to convert indoor household dust into crystalline GQDs with an average particle size of 5.23 nm. Various spectroscopic techniques, such as XRD, FTIR, Raman spectroscopy, XPS, AFM, and TEM, were used to characterize the GQDs, which were then evaluated for their antibacterial activity and cytotoxicity. GQDs showed cytotoxic effects against two human breast epithelial adenocarcinoma cell lines MDA-MB-231 and MCF-07 resulting in apoptosis-related changes on the cells. Amongst the four different pathogens tested, GQDs exhibited the highest antibacterial activity against Pseudomonas aeruginosa.

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### Dramatic rate-enhancement of oxygen atom transfer by an iron(IV)-oxo species by equatorial ligand field perturbations

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Nonheme iron dioxygenases are efficient enzymes with relevance for human health that regio- and stereospecifically transfer an oxygen atom to substrates. How they perform this task with such selectivity remains unknown, but may have to do with substrate binding, positioning and oxidant approach. To understand substrate approach on a catalytic reaction centre, we investigated the structure and reactivity of a biomimetic oxidant with ligand features that affect the interactions between oxidant and substrate. Thus, we report here the synthesis and characterization of an iron(IV)-oxo complex with pentadentate nonheme ligand, where structurally induced perturbations in the equatorial ligand field affect the spectroscopy and reactivity of the complex. We tested the activity of the complex with respect to oxygen atom transfer to and hydrogen atom abstraction from substrates. This oxidant shows improved reaction rates toward heteroatom oxidation with respect to the nonsubstituted ligand complex by  $\sim 10^4$  fold. The origin of the enhanced reactivity is explained with a series of density functional theory studies that show an enhanced electron affinity of the oxidant through equatorial ligand perturbations.



Figure 1. Reactivity of oxidants towards oxygen atom transfer reactions with substrates.

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## Excellent photocatalytic activity of a novel hydroxyapatite based composite, ZnFe<sub>2</sub>O<sub>4</sub>/HAp-Sn<sup>2+</sup> towards degradation of ofloxacin and norfloxacin antibiotics

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Antibiotic contamination in wastewater has become a matter of great concern due to the rapid industrial progress. The majority of antibiotic pollution in the environment occurs due to the waste from animal farms, aquaculture, sewage from antibiotic factories and hospitals. [1-3] Therefore, it is vital to develop efficient and ecologically friendly photocatalysts for the degradation of such pollutants. In this paper, we report synthesis of ZnFe<sub>2</sub>O<sub>4</sub>/HAp-Sn<sup>2+</sup>, a novel nanocomposite by three-step processes using hydrothermal treatment followed by calcination. The as-synthesized composite was characterized by Fourier transform infrared spectroscopy (FT-IR), ultraviolet diffused reflectance spectroscopy (UV-DRS), polycrystalline (or power) X-ray diffraction (PXRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM), thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS).



Figure 1. Plausible mechanism for the antibiotic degradation by ZnFe<sub>2</sub>O<sub>4</sub>/HAp-Sn<sup>2+</sup>

The as-prepared composite exhibited excellent photocatalytic activity in the degradation of two antibiotics namely ofloxacin (OFL) and norfloxacin (NFL) under natural sunlight without use of any oxidizing or reducing agents. [4-5] Scavenger studies were also carried out to ascertain the active radicals such as superoxide and hydroxyl radical during the photodegradation process.

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# Synthesis of zinc sulphide quantum dots using green tea extract: Potential applications in protein binding, anti-bacterial activity, cell cytotoxicity and biosensing studies

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Discovering and developing new therapeutic compounds has become a crucial challenge due to increasing health disorders in today's world. In this regard, biocompatible quantum dots (QDs) have attracted a lots of attention in the biomedicinal domain due to their way of treating and diagnosing a wide range of diseases and many other biological applications,<sup>[1–3]</sup> such as drug delivery, bioimaging, biosensing, and antimicrobial activities. Herein, we have synthesized biocompatible ZnS QDs using green tea leaf extract, which acts as an immobilizing and stabilizing agent and explores the various biological activity, namely (1) anti-bacterial activity, (2) cell cytotoxicity, (3) bio-sensing and (4) protein binding properties. Treatment of synthesized ZnS QDs with *Escherichia coli* and *Escherichia faecalis* bacterial strains revealed that ZnS QDs inhibit the bacterial growth. It also shows cell cytotoxicity effects on treatment with HeLa cells. Biosynthesized ZnS QDs were found to be excellent sensor ability for the detection of bilirubin and rifampicin (RFP). QDs could assemble into complexes with biomacromolecules in the biological matrix. Therefore, we have investigated the interaction between carrier protein human serum albumin (HSA) and synthesized ZnS QDs. The intrinsic fluorescence of HSA was quenched upon interaction with ZnS QDs through static quenching mode. The presence of ZnS QDs enhances the binding affinities of HSA-quercetin and HSA-luteolin complexes. The findings of this work sound optimistic and will further interest for *in vivo* applications in the future.



Figure .: Biological applications of synthesized ZnS QDs

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## Photo-oxidation of 2-Naphthol to C2-Symmetric BINOL using Nano-Co<sub>3</sub>O<sub>4</sub>-V<sub>2</sub>O<sub>5</sub>/rGO: Asymmetric Induction Through Chiral Modification

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Asymmetric oxidative C-C coupling of 2-naphthol is regarded as important organic transformation reaction [1,2]. Different chiral and achiral metal catalyst has been used for the said oxidation reactions [1-3]. Cobalt oxide and vanadium oxide ( $Co_3O_4$ - $V_2O_5$ ) grafted on reduced graphene oxide (rGO) with a band gap of ~3.3 eV displayed as a suitable photocatalyst for the selective oxidation of 2-naphthol to BINOL [4]. Hydrogen peroxide was applied as the oxidant, and UV light was used to produce BINOL up to 92% yield. A newly synthesized chiral Schiff base ligand with a sigma-hole centre and cinchonidine with two chiral centres were used to induce chirality to the same catalyst. From numerous spectroscopic investigations and DFT simulations, it was clearly demonstrated how strongly the chiral modifiers interacted with the cobalt-vanadium oxide. The chirally modified heterogeneous nanocatalyst transformed the oxidative C-C coupling reaction with high enantioselectivity. Acetonitrile as the solvent and hydrogen peroxide as the oxidant allowed for high enantioselectivity of R-BINOL up to 87% ee. A noteworthy accomplishment was the production of S-BINOL when the cinchonidine-modified catalyst was used, and R-BINOL when the Schiff base ligand anchored chiral catalyst was used. It was discovered that the active reactive species in the UV-light-induced catalytic reaction was the hydroxyl radical. Relevant evidence for the photodecomposition of hydrogen peroxide on the catalyst surface leading to the creation of such species was provided by the spin trapping ESR and fluorescence experiment. It was discovered that supramolecular interactions such as O-H---*π* and H---Br contact were responsible for the chiral induction to the resulting product. The presence of sigma hole centre was believed to play significant role in naphtholate ion recognition during the catalytic cycle.



Figure 1. Graphical abstract of the photo-oxidative C-C coupling of 2-naphthol to BINOL by Co<sub>3</sub>O<sub>4</sub>-V<sub>2</sub>O<sub>5</sub>/rGO.

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## Detection and detoxification of imidacloprid in food samples through ionic liquid-stabilized CuNi alloy nanoparticle-decorated MWCNTs

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The change in environmental conditions as well as increasing population with the lack of grain stocks leads to the worldwide demand for food. Accordingly, to conquer the food demand, the utilization of pesticides has been extensively increased.[1] Despite the benefits in the agriculture field, pesticides/insecticides have raised negative consequences for wellbeing and food safety.[2] Imidacloprid has been globally utilized as an insecticide in several crops such as vegetables, maize, rice, potatoes, strawberries and fruits. Since 2003, imidacloprid has ranked constantly in top three insecticides that exceed the limit of concentration permitted by quality norms.[3] Likewise, as recommended by the rules provided by international association, the maximum residue level (MRL) and acceptable daily intakes (ADIs) for imidacloprid are 0.06 mg kg<sup>-1</sup> and 1 mg kg<sup>-1</sup> of body weight, respectively.[4] Moreover, the direct intake of imidacloprid can cause memory loss, neural tube disorder in infants, cardiac toxicity and acceleration of respiratory rates in humans.[5] Hence, highly specific and sensitive quantitative assessment and efficient degradation of imidacloprid in food, pharmaceutical and soil samples by an established method is necessitated to keep the above-mentioned hazardous side effects away.



Figure-1 Graphical Abstract for electrochemical sensing and catalytic degradation of Imidacloprid.

Herein, we developed a selective, sensitive, cost effective and efficient catalyst based on CuNi/IL@MWCNTs for electrochemical detection as well as catalytic detoxification of imidacloprid as shown in figure 1. The CuNi/IL@MWCNTs was successfully synthesized using the reduction method and AFM, FESEM, PXRD, and XPS confirmed the structure of CuNi/IL@MWCNTs and tested for the electrochemical detection of different pesticides and the results showed selectivity towards IMD and the comparison of Rct of CuNi/IL@MWCNTs with other electrocatalysts showed better electron transferability of CuNi/IL@MWCNTs. Moreover, the electrochemical quantification results showed good linearity (0.125–240  $\mu$ M) and excellent sensitivity (LOD = 11 nM). The developed CuNi/IL@MWCNTs has also been successfully validated by detecting the IMD in food samples with excellent recovery (97.4–101.2%). In addition to the quantification of IMD, the CuNi/IL@MWCNTs was successfully tested for catalytic degradation/detoxification of IMD, which was monitored using UV-visible spectroscopy and LC-MS with a degradation efficiency of 99.6% in 100 s. Furthermore, after usage, the easy extraction of CuNi/IL@MWCNTs utilizing a magnet makes the catalyst eco-friendlier, cost effective and reproducible. Hence, the proposed detection and degradation method could provide sensitive, selective, cost effective, quick and simple monitoring of insecticides' toxicity in food samples to help a safe world-wide food supply.

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#### Switch of Product Selectivity in Visible Light-induced Selenium Radicalmediated 1,4-Aryl Migration Process

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Photo redox catalysis triggered by visible light has evolved into a useful tool for creating a variety of organic trans-formations. The key factor of the exponential growth of visible light mediated organic transformations is its easy accessibility, soft and nontoxic nature that makes the overall process environmentally benign. Organoselenides, or compounds having C-Se bonds, are a common structural motif in a wide variety of natural products, agrochemicals, and medicinal chemistry.<sup>1</sup> Organoselenides offer a wide range of applications in synthetic organic chemistry, functional materials<sup>2</sup> catalysis<sup>3</sup> and fluorescence probe imaging.<sup>4</sup> Bis selenide alkene derivatives are found to be good anti-oxidant and antinociceptive agents in mice.<sup>5</sup> As a result, efficiently constructing selenide alkene skeletons is critical. Synthetic approaches that easily implant a selenium activity onto organic compounds are therefore highly desirable. Unsymmetrical tetrasubstituted acyclic alkene containing carboxylate functionality can be easily transformed into a wide range of functional groups, indicating that it has a wide range of applications in chemical manufacturing.<sup>6</sup> Thus, installation of selenium in such type of scaffold is worthy.



Figure 1. Graphical representation of visible light-induced selenium radical-mediated 1,4-Aryl migration process

Herein we have demonstrated a visible light induced selenium radical mediated domino reaction of aryl alkynoates, for the synthesis of 1,1-diselenide alkene derivatives and selenium containing  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid. The process is mild, metal free, easy to handle and scalable. Eosin Y and Cs<sub>2</sub>CO<sub>3</sub> are used to tune the product selectivity by inhibiting the decarboxylation step. The methodology shows good functional group tolerances and provided decent yield of the products. Further, the synthetic utility of this protocol was expanded further by preparing the allylic alcohol,  $\alpha$ ,  $\beta$ -unsaturated ester and vinylic halides.

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# Metal free, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> mediated sp<sup>3</sup> C-H α- hydroxylation of carbonyl compounds

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Oxidative transformation of the organic compounds using inexpensive reagent or oxidant is the most fascinating field in the synthetic chemistry.  $\alpha$ -hydroxycarbonyl compounds extend their applications in the field of pharmaceutical and material chemistry as intermediates for various synthetic conversions. [1][2] Also as templates in asymmetric catalysis.[3]Several methods have been reported for the sp<sup>3</sup> C-H  $\alpha$ -hydroxylation of carbonyl compounds using different oxidants, metal catalyst and metal free reagents.[4] Herein we reporting a highly efficient, metal free method for the sp<sup>3</sup> C-H  $\alpha$ -hydroxylation of carbonyl compounds using potassium iodide, persulfate in DMSO: H<sub>2</sub>O co-solvent system.



Scheme: Persulfate mediated α- hydroxylation of carbonyl compounds

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## Conjugated Polymer Nanoparticles as a Fluorescence Probe for Amplified Detection of Human Serum Bilirubin

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Bilirubin (BR), is a potent biomarker for jaundice and liver malfunction. However, its quantitative determination remains a bottleneck due to the interference of numerous biomolecules present in the blood serum. To overcome this, a conjugated polyfluorene derivative, poly1,1'-((2,7-dimethyl-9H-fluorene-9,9-diyl) bis(hexane-6,1-diyl)) bis(1H-benzo[d]imidazole) (PFBZ) was synthesized by incorporating it with a specific receptor benzimidazole for BR detection using a low-cost and straightforward oxidative coupling polymerization. The PFBZ polymer spontaneously forms nanoparticles in aqueous medium and unveils excellent sensitivity towards BR in an aqueous PBS medium with LOD 6.9 pM, which is far less than the clinically relevant range. The sensing mechanism is based on probe-analyte interaction chemistry and FRET, which were confirmed from both experimental and theoretical studies. This platform offers excellent sensitivity and selectivity, which motivated us to successfully explore the quantitative determination of BR in real serum samples. This method of sensing is straightforward, non-invasive and can be used as a biomedical sensor to diagnose the onset of jaundice and liver malfunction.



Figure 1. Graphical abstract for the selective detection of BR by PFBZ polymer NPs.

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### Sensing cyanide selectively with ESIPT based 2-(4'-diethylamino-2'hydroxyphenyl)-1*H*-imidazo-[4,5-b]pyridine (DHP)

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Cyanide plays important role in production industries for making synthetic fibres, acrylics polymers, in metallurgy for electroplating, gold mining, etc. Naturally, also cyanide has been found in apple seed bamboo, almonds, apricots seeds. Acute cyanide exposure is lethal therefore cyanide detection is crucial. Among various methods for sensing critical analytes, fluorescent techniques proved to be effective with high sensitivity, low cost synthesis and easy to operate. Excited state intramolecular proton transfer (ESIPT) based chemosensor 2-(4'-diethylamino-2'-hydroxyphenyl)-1H-imidazo-[4,5-b]pyridine (DHP) was developed as a sensitive probe for cyanide detection. The sensitivity study of the probe DHP were investigated by absorption and fluorescence studies. Interestingly, in partial aqueous medium (acetonitrile/H<sub>2</sub>O 9:1 v/v) and also in cetyltrimethylammonium bromide (CTAB) aqueous medium, the probe shows fluorescence turn on response. The fluorescence detection limit of cyanide was found to be  $0.6 \times 10^{-6}$  M, which is below the permissible limit for cyanide in drinking water according to World Health Organisation (WHO). The experimental result suggested the interruption of ESIPT by the cyanide leading to deprotonation of DHP giving turn-on anion emission. This mechanism were further supported by DFT and TD-DFT calculations and reversibility study.

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## Copper-Catalyzed Oxidative Dehydrogenative Reaction of Quinoline-N-Oxides with Donor-Acceptor Cyclopropanes: Installation of a Tertiary Alkyl Motif at C2 Position

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We have reported the copper-catalysed deoxygenative alkylation of quinoline *N*-oxides with donor-acceptor cyclopropanes to introduce a tertiary alkyl motif at the C2-position of quinoline. It is designed owing to the 1,3-zwitterion equivalent nature of donor-acceptor (D–A) cyclopropanes and the presence of ring strain (27.5 kcal mol<sup>-1</sup>) and vicinal substitution of D–A groups, whereby, we anticipated that D–A cyclopropanes might take part in [3+3]-dipolar cycloaddition reaction with *N*-oxides. This work uses molecular oxygen as a benign oxidant and supports excellent site selectivity at C2 position of quinoline with good functional group tolerance. The metal catalyst used is cheap and boasts of earth-abundant Cu(II)-metal. The mechanistic pathway has been investigated using both experimental and theoretical calculations which shows the involvement of a possible radical pathway.



Figure 1. Graphical abstract of C2 selective tertiary alkylation of N-oxides via oxidative dehydrogenative pathway

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## Room Temperature Columnar Liquid Crystalline Perylene Bisimide as a Novel Corrosion Resistant Surface Coating for Mild Steel Surface

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The corrosion process can be seen as a widespread phenomenon, which is both pervasive and unstoppable. This is an undesirable phenomenon that reduces the life of materials and takes away their beauty<sup>1</sup>. Potentiodynamic and electrochemical impedance tests are used to explore the corrosion inhibition abilities of a room temperature columnar liquid crystalline perylene bisimide (**PBI**<sup>O10</sup>)<sup>2</sup> on mild steel (MS) samples in 1M HCl. The inhibitor **PBI**<sup>O10</sup> demonstrated to be an outstanding corrosion inhibition, with a maximum inhibition efficiency of 76%. In the light of potentiometric polarization results, corrosion inhibitors. The protective layer was examined from SEM to confirm the protective coating generated on the MS surface<sup>3</sup>. The density function theory (DFT) approach was used to investigate the relationship between molecular structure and inhibitory efficacy.



Figure 1. The proposed mechanism of corrosion resistance of PBI<sup>O10</sup>.

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## Long Alkyl Chain Induced OFET Characteristic with Low Threshold Voltage in an n-Type Perylene Monoimide Semiconductor

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This work reports the fabrication of an n-channel OFET device using simple perylenemonoimide (**PMI**) derivatives by introducing a nonconjugated long alkyl chain (octadecyl) at the imide position. With poly(methyl methacrylate) (PMMA) as the dielectric, top-contact bottom-gate n-channel OFET were fabricated on an economical glass substrate using these simple **PMI** derivatives. Among them, PMI-C18 demonstrates OFET properties with electron mobility ( $\mu_e$ ) of  $1 \times 10^{-4}$  cm2 V<sup>-1</sup> s<sup>-1</sup> and current on/off ratio ( $I_{on/off}$ ) of  $8.8 \times 10^2$ . Moreover, the threshold voltage (V<sub>th</sub>) of 4.40 V obtained for **PMI-C18** was the lowest among all the reported perylenemonoimide core based OFET devices.

## Visible-Light Mediated One-Pot Synthesis of Five- And Six- Membered Heterocycles Using Fe<sub>3</sub>O<sub>4</sub>@RB@LDH as a Recyclable Photocatalyst

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Visible light has the advantages of being a low-cost and environmental friendly renewable source of energy. In recent decades, visible-light-induced reactions have become an attention-grabbing and influential appliance to enlarge the chemical transformations considering its environmentally kind properties. [1] Layered double hydroxides (LDHs) correspond to a family of highly ordered two-dimensional anionic clay materials which comprises of different M<sup>2+</sup> and M<sup>3+</sup> metal cations, interlayer anions and water. LDHs are engaged as excellent photocatalyst supports because of their relatively large surface area, straight forward preparation, high positive layer charge density, flexible composition and low cost. [2] The catalyst having electrostatic interaction amongst the positively charged LDHs, the anionic RB dye and negatively charged magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles can easily be prepared by ultrasonic irradiation in water which is considered as a green medium.



Figure 1. Graphical abstract of visible-light mediated one-pot synthesis of five- and six- membered heterocycles using Fe<sub>3</sub>O<sub>4</sub>@RB@LDH as a recyclable photocatalyst

In this presentation, an efficient and high yielding synthesis of pyran and pyrrolidinone derivatives through a recyclable photocatalyst under visible light in aqueous ethanol medium has been described. The photo catalyst was prepared and characterized by various analytical techniques viz., FT-IR Spectroscopy, TGA, TEM, FE-SEM and EDX analysis. Since it is magnetic, the prepared catalyst could be easily separated from the reaction mixture by using an external magnet. The advantages of this synthetic protocol are good to excellent yields, short reaction times, easy catalyst recovery and recyclability of the catalyst.

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# Facile green method for fabrication of MoS<sub>2</sub> decorated graphite rod and their application in H<sub>2</sub> evolution

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In the present study, a binder free method for the fabrication of electrode material has been designed. A one-pot solvothermal process has been used for the synthesis and decoration of  $MoS_2$  over graphite rod ( $MoS_2/GR$ )using soyabean oil at 200°C[1]. The powder X-ray diffraction confirms the formation of  $MoS_2$  over graphite rod. In this process, the  $MoS_2$  nanoparticles were directly grown on surface of graphite rod. SEM study confirms that  $MoS_2$  (~120 nm) particles are homogeneously distributed over graphite rod. The Vander Waal interaction between sulphur and graphite surface enhances the stability and catalytic activity[2]. The as decorated  $MoS_2/GR$  has been used as working electrode for the hydrogen evolution reaction[3]. The observed onset potential and overpotential of  $MoS_2/GR$  were - 21 mV and -257 mV respectively and the obtained onset potential is nearly three times lower than earlier reports while it shows good stability up to 10 h[4].



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## Accessing Complex Tetrahydrofurobenzo-pyran/furan Scaffolds via Lewis-acid Catalyzed Bicyclization of Cyclopropane Carbaldehydes with Quinone Methides/Esters

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We have reported an efficient and straightforward one-pot synthesis of tetrahydrofurobenzopyran and tetrahydrofurobenzofuran systems *via* an *in-situ* ring- expansion of the cyclopropane carbaldehydes followed by a [2+n] cycloaddition with the quinone derivatives. The transformation not only unveils a new reaction mode of cyclopropane carbaldehydes with quinone methides/esters but also promotes a step-efficient diastereoselective route to the sophisticatedly fused oxygen tricycles that can further be dehydrogenated to access the valued dihydro-2*H*-furo[2,3-*b*]chromene frameworks.



### Dual Matrix Influence on Ni(II) Rich Hybrid Catalyst for Electrochemical Methanol Oxidation Reaction

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The influence of two different surface matrix *viz* zeolite-Y and multi-walled carbon nanotube (MWCNT) on the electrocatalytic ability of Ni(OH)<sub>2</sub> combined with MnO<sub>2</sub> has been studied. The Ni and Mn loaded in different ratio exhibited different current density with respect to the change in the nature of support. The MnO<sub>2</sub>-Ni(OH)<sub>2</sub> catalyst decorated like a fish in a net-stock at the interface of the zeolite-Y and the MWCNT with high Ni(II) content provided the highest current density of 3.8 Amg<sup>-1</sup> and 3.6 Amg<sup>-1</sup> with platinum and graphitic rod as counter electrode, respectively. The study revealed that both the concentration of the Ni(II) as well as the nature of the support influenced the electrochemical behaviour of MnO<sub>2</sub>-Ni(OH)<sub>2</sub>. The electrochemical surface area as well as the durability of the catalyst having two different supports showed higher values in comparison to those in single matrix. The plot of current density vs. square root of scan rate showed diffusion control methanol oxidation process [1,2]. The results predicted that the MnO<sub>2</sub>-Ni(OH)<sub>2</sub> catalyst containing both zeolite-Y and MWCNT surface indicated that under the highly basic condition it can withstand for long period without significant loss in current density during the methanol oxidation reaction (MOR) process.



Figure 1. Mn-Ni nanoparticles were developed using zeolite-Y and MWCNT support for effective MOR

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## Multifunctional N-Doped Carbon Dots for Bimodal Detection of Bilirubin and Vitamin B12, Living Cell Imaging, and Fluorescent Ink

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A N-doped carbon dot (NCD) has been synthesized via a simplistic one-step hydrothermal technique using L-aspartic acid and 3,6-diaminoacridine hydrochloride. The NCDs exhibit a high quantum yield (22.7%) and excellent optical stability in aqueous media. Additionally, NCDs display good solid-state yellowish-green emission and are suitable for security ink applications. The remarkable fluorescence (FL) properties of NCDs are further applied to develop a multifunctional sensor for bilirubin (BR) and vitamin B12 (VB12) via fluorescence quenching. We have systematically studied the FL quenching mechanisms of the two analytes. The primary quenching mechanism of BR is via the Förster resonant energy transfer (FRET) pathway facilitated by the H-bonding network between the hydrophilic moieties existing at the surface of BR and NCDs. In contrast, the inner filter effect (IFE) is mainly responsible for the recognition of VB12. The practicability of the nanoprobe NCDs is further tested in real-sample analysis for BR (human serum and urine samples) and VB12 (VB12 tablets, human serum, and energy drink) with a satisfactory outcome. The in vitro competency is also verified in the human cervical cancer cell line (HeLa cell) with negligible cytotoxicity and significant biocompatibility. This result facilitates the application of NCDs for bioimaging and recognition of VB12 in a living organism.



Scheme 1. Blue emitting N-doped carbon dot for highly selective and sensitive detection of bilirubin, vitamin-B12, living cell imaging and fluorescence ink

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## A Portable Conjugated Polymer based Smartphone Platform for Sensitive Detection of Monoamine Neurotransmitter

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The development of diagnostic tools for neurotransmitter is of great importance in early diagnosis of life threating diseases such as alzheimer and cancer and for the development effective drugs or medicines. [1,2] However, current neurotransmitter detection approaches are limited to nonspecific detection, low spatiotemporal resolution and laboratory analysis.[3,4] To address this challenge, herein, we rationally designed and synthesised an anionic conjugated polyelectrolyte (CPE) Poly[(9,9-bis(4'- sulfonatobutyl)fluorene-co-alt-1,4-phenylene) sodium], PFPS to detect neurotransmitter serotonin (5-HT, also carcinoid biomarker) in a sensitive and selective manner. The PFPS CPE displayed turn off fluorescence response towards 5-HT with evident visual color fading under UV light. An exceptionally high Stern Volmer constant (Ksv) of  $1.14 \times 10^5$  M<sup>-1</sup> and a very low LOD of 35 nM/7.65ppb were obtained for 5- HT in 100% aqueous solution which is 100 times lower than clinical range (0.5-1.4µM) present in blood plasma. Moreover, the PFPS based protocol was transformed into low-cost portable system for accurate testing of 5-HT levels in real blood samples by measuring RGB values of visual response using color recognizing smartphone application. This smartphone based optical device holds enormous potential to advance the pathological research, clinical diagnosis and personalized health care devices.



Figure 1. Schematic illustration of conjugated polyelectrolyte based dual mode detection of serotonin.

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#### Chemically Modulated and Programmed Bursting of Liquid Marbles on a Water Pool

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Liquid Marbles are liquid droplets coated with hydrophobic particles at the liquid-vapour interface and are used for various industrial and bio-medical applications. However, the lifetime of liquid marble is quite low on water surfaces. It is observed that surface free energy and degree of hydrophobicity effects the lifetime of a liquid marble on water surface. Greater degree of hydrophobicity and smaller particle size allows for a greater lifetime on water surface. Keeping these points in consideration, we report the synthesis of chemically modified Halloysite Nanoclay based liquid marble which are stable on water surface for substantial amount of time. This stability of the marbles can be exploited as a reaction vessel and drug delivery capsules.



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# Synchronized redox pairs in metal oxide/hydroxide chemical analogues for efficient oxygen evolution reaction

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Alternative to noble metal-based materials, transition metal oxides, and hydroxides have drawn extensive attention as electrocatalytic oxygen evolution catalysts (OEC) due to their low cost, tunable morphological features, and susceptible electrochemical redox reactions. The major drawback of transition metal oxides lies in their high charge transfer resistance at the electrode-electrolyte interface. The mentioned drawback can be tackled by morphological tuning and surface modification. Herein we report a two-step electrodeposition of CoMn<sub>2</sub>O<sub>4</sub> and its chemical analogue CoMn(OH)<sub>x</sub> directly over Ni-foam yields an excellent water oxidation overpotential of 260 mA/cm2 with a Tafel slope of 29mV/dec and a four-fold increment in turnover frequency. Enhanced efficacy of the composite catalyst is realized through synchronized redox pairs and superior carrier transport. High stability, low cost, easy synthetic procedure, and environmentally friendly nature due to the use of the minimal number of metal atoms make this approach a model system for the futuristic catalytic systems to be used in industrial applications.

## High functioning CNF/epoxy green nanocomposite enriched with urethane linkages: Valorization of waste tea fibers to engineering material

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The depleting reservoirs of fossil-fuels and surging demand of petroleum resources are presiding today's world towards an inevitable scarcity of resources. Meanwhile, the growing concern towards environmental sustainability is mounting the reliance of the scientific community on inexhaustible resources.[1] Under these circumstances, the area of material engineering is experiencing crucial deviation from fossil derived synthons to naturally derived ones. Nanomaterial industry is one of such realms that endures significant advances by replacing synthetic nanomaterials by nature derived replacements, synthetic polymers by biopolymers in order to bring in sustainability into the picture.[2] Henceforth, this work has been objectified to produce cellulose nanofibers (CNF) from factory tea waste so as to add value to the later. Sunsequently, the prepared CNFs were grafted with toluene diisocyanate and ethylenediamine in order to provide right surface functionality. The resulted CNFs grafted with amine-terminated urethane linkages were charaterized with FTIR, XRD, and electron microscopic techniques. Afterwards, a green nanocomposite was fabricated using the grafted CNF as reinforcing agent and a tannic acid based bio-epoxy as the matrix. The amine groups of the grafted CNF further accelerated the curing process increasing the crosslinking density which refelcted in the mechanical properties. The prepared nanocomposites demonstrated good enhancement in tensile strength compared to the virgin one. Further, a primary investigation on the anticorrosive behaviour of the nanocomposites was carried out to explode its applicability to different practical domains.

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## Expedient Ni(OTf)<sub>2</sub>/Visible Light Photoredox-Catalyzed Annulation of Donor-Acceptor Cyclopropanes with Cyclic Secondary Amines

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Fused pyrrolidines and their synthetic analogs are ubiquitous in biological compounds and natural products.[1] Consequently, developing efficient methods to conceive such synthetically important scaffolds drives significant interest. Herein, we reported visible light-mediated organophotoredox stereospecific (3+2)-annulation of donor-acceptor cyclopropanes with cyclic secondary amines (Figure 1).[2] This method features synergistic action of Ni(II)-catalyzed ring-opening and photoredox catalyzed cross-dehydrogenative coupling of two distinct  $C(sp^3)$ -H bonds for the formation of C-C bonds. Optically active cyclopropanes are coupled with high enantiomeric purity (>99% ee). The current protocol provides straightforward access towards constructing fused pyrrolidine scaffolds in high yield with excellent stereospecificity.



**Figure 1**. N-H/ $\alpha$ -C(sp<sup>3</sup>)-H diffunctionalization to construct fuzed pyrrolidines.

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## Highly Stable Deep Red-to-NIR OLEDs with an External-Quantum Efficiency of 4.9% from Room Temperature Nanostructured Columnar Fluids based on Hetero Atom *bay*-Annulated Perylene Bisimides

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A series of electron deficient perylene bisimides (PBIs) bearing 3,4,5-tridecylphenyl substituents on the imide *N*atoms and *bay*-annulated with the hetero atoms like *N*, *S*, *Se* in the bay positions of the perylene core *via* Cadogan reaction have been synthesized. These compounds were liquid crystalline at room temperature exhibiting columnar hexagonal phase exclusively, with the exception of *S*-annulated PBI which exhibited columnar oblique phase. These self-organizing organic semiconductors in one-dimensional (1D) columnar structures, are unique by having better solubility, ease of purification, reproducibility and ease of handling in comparison to polymers or single crystals. Detailed photophysical studies of these compounds show that they exhibit high molar extinction coefficients with wide absorption spectra covering most of the visible spectrum and bright red fluorescence, makes them promising candidates for organic electronics. Further, they exhibited technologically important red electroluminescence. One of the solution-processed host-guest OLEDs (CBP as host at 1 wt% **PBI-N<sup>10</sup>**) exhibited a maximum EQE of 4.9%, a lifetime of 12.4 h with an initial brightness of 2900 cd/m<sup>2</sup> and a deep red/NIR emission. These results indicated that these materials exhibit significant potential in the field of columnar liquid crystal-based deep red/NIR emitters.



Figure 1. Graphical abstract of the red light emission in host-guest OLEDs.

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## A Comparative Study of Photophysical, Electrochemical, and Antimicrobial Properties of Dipyrazinyl pyridine Ligands

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N-containing aromatic heterocycles have gained much attention after the expansive onset of the application of terpyridines in recent years [1]. The structure-functional aspects of these nitrogen-based heterocycles and their metal complexes have been extensively studied using various photophysical parameters [2]. Large arrays of these compounds and their metal complexes have been exploited in DNA or BSA binding [3], anti-cancer [4], anti-HIV [5], and antimicrobial [6] experimentation. One N-based compound suitable for almost all of these applications is 2,6-di(pyrazin-2-yl) pyridine (dppy), an analog of terpyridine. This heterocyclic analog contains one pyridine ring and two pyrazine rings. The ligand, unlike terpyridine, can bind with three metals simultaneously instead of one. This structural difference might attribute to improved drug design and other biological applications.



**Figure 1**. Graphical abstract of the comparative photophysical, biological and theoretical studies of dppy ligands A one-pot method was used for synthesizing four 4-aryl-substituted 2,6-di(pyrazine-2-yl)pyridine (dppy) compounds **1-4**. The compounds differ in the 4-position with substituents like 4-dimethylaminophenyl (-NMe<sub>2</sub>), 4-methoxyphenyl (-OMe), 4-*p*-tolyl (-CH<sub>3</sub>), and 4-chlorophenyl (-Cl) designated with **1** to **4**, respectively. This paper investigates the impact of different electronic substituents on photophysical, thermal, electrochemical, and biological studies of dppy ligands. The effect of solvent polarity on optical properties has been studied. Structure optimization and theoretical studies with the help of Density Functional Theory (DFT) have been conducted to gain better insights into the compounds' nature. The trend of the HOMO-LUMO energy gaps of the synthesized compounds **1-4**, calculated from the electrochemical analysis, has been reflected in the theoretical observations. Moreover, the compounds were tested against different bacterial and fungal strains, and compounds containing electron-donating –NMe<sub>2</sub> and –OMe groups were quite active in both bacterial and fungal studies. Compound **3**, having the –CH<sub>3</sub> group, showed moderate activity against fungal strains.

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# Ring Opening of Pyrrolinium Ions Enabled Regioselective Synthesis of 4-alkyl N-arylpyrazoles

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An unprecedented method for the regioselective synthesis of 1,3-diaryl 4-alkyl pyrazoles has been reported. A wide variety of 1,3-diaryl 4-alkyl pyrazoles were synthesized as a single regioisomer via a ring-opening cyclization reaction of unsaturated pyrrolinium ions in the presence of aryl hydrazines. This method avoids the use of additional alkylation steps and hazardous oxidants which generally are essential for the synthesis of 4-alkyl N-arylpyrazoles.<sup>1</sup>



Figure 1. Regioselective synthesis of alkyl-N-arylpyrazole and its X-ray structure.

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#### Chimera and Cluster states in pinned rotors in chemical systems

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The collective behaviors have drawn great attention in recent years and opened a new branch in science. All of the natural systems and how they communicate can be modelled as a set of interconnected elements that affect each other's behavior bi-directionally. Therefore, studying complex systems is required and their mathematical modeling helps in understanding the nature and real life. Synchronization and Chimera are one of the important phenomena in nonlinear sciences. It has been seen that a portion of the human brain becomes more active and synchronized than the other part during epileptic seizure. That situation is closely related to chimera. Study on the synchronization becomes necessary to understand human brain, cardiac activity etc.

We have studied pinned spiral rotor in Belousov-Zhabotinsky (BZ) system. We carried out all our experiments in BZ system because it can generate sustainable waves. This system is also known as excitable system, so as our cardiac system. Electrical activity in the cardiac system can be understood from the simple ECG diagrams. Two dimensional spiral waves and three-dimensional scroll waves and their interaction pattern in a BZ reaction have potential to give better understanding of electrical activity of cardiac system. Pinned spirals or scrolls with heterogeneous obstacles are generally compared with the heart wave pinned to scar tissue. So, for better understanding we need to study the pinned spiral or scroll waves and their interactions and synchronization phenomena [1].

Chimera state is that where both synchronization and asynchronization states coexist. Here in this current work, we have locked the frequency of the rotors by pinning with obstacles of same diameter. We have made multiple pair of spirals, pinned and looked at their dynamics and phase synchronization phenomena. Here we observed the presence of cluster states as well as chimera states.

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## Microwave-Assisted Three-Component Reaction for the Synthesis of Spirooxindole-Pyrimidine Derivatives in Aqueous Medium

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Microwave-assisted synthesis has gained a lot of attention in the last few years for synthesizing the organic compounds rapidly and evolved into a new green method since it provides shorter reaction times, high yields of the products, high purity and absence of side-product formation. [1] Graphene-based nanomaterials have received immense interest because of their unique mechanical and electrical properties and found applications in many fields. Further, chemical modifications of graphene oxide have gained importance amongst synthetic and theoretical researchers because of its superior and magnificent electronic properties. Fluorination has been found to be one of the strategies adopted for the covalent functionalization of graphene as fluorine has high reactivity regarding catalytic properties. [2] Multicomponent reactions (MCRs) have been widely used for the synthesis of heterocyclic compounds as they have significant qualities such as few reaction steps, less time and energy consumption, high atom economy, operational simplicity. [3]



Figure 1. Graphical abstract of microwave-assisted three-component reaction for the synthesis of spirooxindolepyrimidine derivatives in aqueous medium

A highly efficient and sustainable procedure has been introduced for the three-component synthesis of spirooxindole-pyrimidine derivatives via a reaction of isatin, barbituric acids and cyclohexane-1,3-diones by utilizing Fluorinated Graphene Oxide (FGO) as an environmental friendly and metal-free recyclable carbocatalyst under microwave irradiation in aqueous medium. The method provides several remarkable advantages like easy recovery and reusability of the catalyst, operational simplicity, high yields of the products and short reaction times. The use of microwave irradiation makes this protocol probably very useful, rapid, clean and suitable. The synthesized catalyst was characterized by several analytical techniques *viz.*, UV–Vis, FT-IR Spectroscopy, TGA, TEM, FE-SEM and EDX.

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#### Photomechanical Effects Displayed by Sulfonylhydrazone Molecular Crystals

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The process of amplification of molecular motion into macroscopic mechanical motion has gained tremendous attention among materials scientists and the materials that are able to transduce external stimuli such as heat, light, mechanical force etc. into useful work which in turn find their application in a broad range of areas such as actuators, smart medical implants, artificial muscles, flexible electronics, dynamic components of micro fluidic device, robotics etc. In this work we explored a new class of molecules which are capable of switching between their E and Z isomers around -C=N- bond namely p-Tolyl sulfonylhydrazone derivatives. The four derivatives of p-Tolyl sulfonylhydrazone (o-Nitro, m-Nitro, p-Nitro and unsubstituted) were showed photoresponsive nature in the crystalline as well as solution state. On exposer to UV light long needle shape single crystals of m-Nitro derivatives displayed slow photomechanical bending, on the other hand single crystals of unsubstituted and p-Nitro derivatives of p-Tolyl sulfonylhydrazone did not perform any significant photomechanical bending in presence of UV light, the block shape crystals of o-Nitro derivatives of p-Tolyl sulfonylhydrazone did not perform any significant photomechanical bending in presence of UV light, the block shape crystals of o-Nitro derivatives of p-Tolyl sulfonylhydrazone did not perform any significant photomechanical property. The photoresponsive behaviour was further inspected with the help of different kinematic analysis.

## Intermolecular Dearomative [4+2] Cycloaddition of Naphthalenes via Visible-Light Energy-Transfer-Catalysis

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Dearomative cycloaddition reaction serves as a blueprint for creating three-dimensional molecular topology from flataromatic compounds.<sup>1</sup> However, dearomative cycloaddition of arenes system is highly challenging because of the high chemical stability inherent due to aromaticity. Further, severe reactivity, selectivity and reversibility issues make this process arduous.<sup>2</sup> One such process to overcome these challenges is the photochemical approach that induces the loss of aromaticity. Visible-light photocatalysis, in particular, has developed as an effective and ecologically beneficial mechanism for exploiting energy transfer and electron transfer, allowing for sustainable reactions including diverse dearomative reactions.<sup>3</sup> In this regard, we focus on the triplet energy transfer catalysis which in presence of sensitizers the arenes can be selectively excited from a ground state to a higher triplet state lowering the kinetic barriers significantly compared to thermal processes.<sup>4</sup> Chemists have developed a number of dearomative transformations of arenes via visible light catalysis, which are now essential tools for the synthesis of complex molecular scaffolds.<sup>5</sup> The current work emphasises the difficult issues of the dearomative cycloaddition reaction. We performed various photoluminescencs, electrochemical, UV-VIS and triplet energy quenching studies, to understand the mechanism. The developed protocol can be accessed for the cycloaddition reaction of feed-stock naphthalene molecules with vinyl benzenes where, structurally diverse 2-acyl naphthalenes, and styrenes with various functional groups could easily be converted to a diverse range of bicyclo[2.2.2]octa-2,5-diene scaffolds in high yields and selectivities. The reaction can be scale up to gram scale and is also amicable for late-stage modification of various complex molecules like menthol, borneol, cholesterol, gemfibrozil, clofibric acid, fenbufen, and ketoprofen. Furthermore, milder reaction conditions and substantially higher triplet energy of the dearomatized product prevent the reverse reaction resulting in higher product yields. The work will shed light on visible light energy transfer catalysis which is in the early stage of the chemical synthesis.



🗸 Triplet energy transfer catalysis 🔬 Dearomative (4+2) cycloaddition reaction of naphthalene system

 $\sqrt{}$  Three dimensional complex products  $\sqrt{}$  Late-stage functionalization of bioactive analoques

**Figure 1**. Visible light energy transfer mediated [4+2] cycloaddition of naphthalene

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#### Synthesis of benzoxepine derivatives via C-H activation

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Described herein are the C-H fictionalization reaction between 2-(1-hydroxyethyl)phenol and alkynes in presence of trace amounts of  $RhCl_2$  and  $Cu(OAc)_2$  via the activation of  $sp^3$  proton of 2-(1-hydroxyethyl)phenol. This reaction involves cleavage of terminal C-H bond of  $sp^3$ -C and brings out a valuable benzoxepine derivatives which forms the basic core of many molecules with pharmacological importance.

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## Multi-targeted Small Molecule Fluorescent Nano Dot for PotentialTreatment of Alzheimer's Disease

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The emergence of neurodegenerative diseases is connected to several pathogenic factors, including metal ions, amyloidogenic proteins, and reactive oxygen species. Recent studies suggest that cytotoxicity is caused by small, dynamic, metastable early-stage oligomeric species. Here, we introduced a small molecule-based red-emitting smart probe with increased reactivities against a variety of targets, metal-free amyloid-( $A\beta$ ), and metal-bound  $A\beta$ , and most importantly early-stage oligomeric species which are associated with the most common and widespread type of dementia, Alzheimer's disease (AD). In silico study revealed that the molecule binds with the hydrophobic region KLVFFA (amyloidogenic domain) specifically with high binding affinity and thus blocks the aggregationpathway of the peptide. The in vitro and cellular studies demonstrated that this highly biocompatible molecule effectively reduces the structural damage to mitochondria while shielding cells from apoptosis, scavenges ROS, and attenuates multifaceted amyloid toxicity.

# Synthesis of CuS-N- doped carbon nanocomposite for remediation of organic contaminants in aqueous solutions

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Persistent organic pollutants like dyes and phenols have caused a number of ecological problems in the aquatic environment. The water and soil contamination caused by this untreated discharge of toxic contaminants from industrial, agricultural, and household activities has been a serious health concern globally. Investigation of novel water purification technologies and conservation measures from these pollutants has become a major concern to the scientific community.[1] The organic contaminants are stable and traditional degrading approaches involving light, chemical, and biological treatments are less successful. Therefore, AOPs especially Fenton/Fenton-like reaction, are widely used to deal with the persistent organic pollutants in water owing to its simple operation, eco-friendly and high treatment efficiency.[2] CuS being a novel compound have outstanding catalytic activities but due to Cu leaching the stability of the catalyst reduces. The carbonaceous materials have significant advantages in terms of well-developed pore structure, large surface area, and highly active surface functional groups, for which they have been used in Fenton/Fenton-like systems for better support and as electron donors. Developing a catalyst that is environmentally benign and performs satisfactorily is therefore very crucial. Therefore, biomass derived carbonaceous material is chosen as a suitable candidate in this present context. These can activate H<sub>2</sub>O<sub>2</sub> to •OH to remove refractory organic pollutants.[3] Here, we reported a hydrothermal synthesis of CuS-N-doped carbon for Fenton activities. The formations of the synthesized nano-catalysts were thoroughly characterized with the help of spectroscopic and microscopic techniques.



Figure 1. Graphical abstract of the reaction mechanism of dye degradation.

It was found that doping of nitrogen in the carbon matrix contributes to more active sites. CuS nanoparticles embedded in carbon matrix can prevent the agglomeration of active nanoparticles which facilitates the catalytic process. The catalytic activities of the synthesized catalysts were tested for the degradation of MB from aqueous solutions. The results show that the complete degradation of MB was possible within 15 min of reaction time. The optimization of the reactions was done in terms of the reaction parameters such as catalyst amount, pH and amount of  $H_2O_2$ . The reusability of the catalysts was tested by performing the reactions with the spent catalysts up to fifth runs without significant loss of catalytic activities. The results of the work will provide a path towards an efficient catalyst synthesis and its applicability in waste water treatment in a sustainable way.

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## Ruthenium pincer complex catalyzed efficient synthesis of quinoline, 2styrylquinoline and quinazoline derivatives *via* acceptorless dehydrogenative coupling reactions

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The synthesis of *N*-heterocycles has been considered an emerging area of chemical research due to their extensive utilization in pharmaceuticals, materials science, and natural product synthesis. The development of green, atomeconomical, and sustainable strategies for the construction of *N*-heteroaromatic compounds by employing readily available starting materials is highly desired in the scientific community. In this context, alcohol is found as cheap, abundant in nature, and biorenewable substrate produced from diverse range of sustainable resources. The transition metal-catalyzed acceptorless dehydrogenative coupling (ADC) of alcohols provide a prominent synthetic strategy to synthesize the *N*-heterocycles in a sustainable and environmentally benign way, since only hydrogen and water are formed as the eco-friendly by-products. Herein, we report an efficient method for synthesis of quinoline, and quinazoline derivatives from 2-aminobenzylalcohols, secondary alcohols and nitriles *via* ADC of alcohols catalysed by bifunctional ruthenium NNN-pincer complex, with lower catalyst loading (0.1 mol%), base loading (1 mol%) and shorter reaction time (6 h) under aerial condition. Further, the catalyst was found to be effective for the synthesis of 2-styrylquinolines derivatives *via* one-pot three-component ADC strategy of 2-aminobenzyl alcohol, isopropanol, and primary alcohol. Notably, this catalytic system shown remarkably high TON of 4,40,000 for 2-phenylquinoline and TON of 2,90,000 for 2-phenylquinazoline, which are the highest reported values hitherto for the transition metalbased catalysts.



Figure 1. Graphical representation of ruthenium pincer complex catalyzed efficient synthesis of quinoline, 2styrylquinoline and quinazoline derivative

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### Red-Emitting Silver Nanoclusters for Dual-Mode Detection of Cu<sup>2+</sup> and Vitamin B<sub>12</sub> in Living Cell

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Biomolecule-stabilized metal nanoclusters (MNCs) exhibit enormous potential as unique luminescent materials in various applications. However, highly stable and bio-friendly fluorescent-MNCs synthesis is still a challenge. Here, we report a facile synthesis of red-emissive silver nanocluster (LYS-AgNCs) within a dithiothreitol (DTT)-reduced lysozyme (LYS) scaffold. The nanoclusters exhibit uniform size distribution, excellent water solubility, and superior photoluminescence property featuring a quantum yield of 6.1 %, massive (280 nm) Stokes shift, solid-state emission, and pH stability augments its applicability into dual-mode sensing platform for Cu<sup>2+</sup> and vitamin B<sub>12</sub> (VB12). Two contrasting fluorescence (FI) quenching mechanisms were responsible for the sensing; Cu<sup>2+</sup> –induced FI quenching occurs via a multifaceted mechanism involving both static and dynamic quenching, whereas the inner filter effect (IFE) and Förster resonance energy transfer (FRET) are mainly responsible for VB12-induced FI quenching. An inexpensive portable paper strip was fabricated using LYS-AgNCs for on-site field application, enabling instrument-free fast and visual detection of Cu<sup>2+</sup> and VB12. Moreover, LYS-AgNCs also possess favorable biocompatibility against human cervical cancer cells (HeLa), making them a suitable nanoprobe for cell imaging and an efficient agent for detecting Cu<sup>2+</sup> and VB12 inside live cells as well. Finally, we demonstrate the applicability of LYS-AgNCs for real-sample analysis of VB12 with a satisfactory outcome.



Scheme 1. Schematic illustration of the DTT reduced LYS-AgNCs synthesis.

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## Tropospheric Oxidation of CFC-alternatives Initiated by OH-Radical: A Computational Perspective

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Chlorofluorocarbons (CFCs) have an adverse effect on the environment as they enhance the ozone layer's depletion by reacting with different oxidants present in the atmosphere. [1] This resulted in the development of different CFC alternatives in accordance with the Montreal Protocol (1987) [2] and the Kyoto Protocol (1997). [3] However, depending on the lifetime of these alternatives, they also pose a threat to the ozone layer. In this work, we have studied the degradation of Dichlorofluoropropene, CF<sub>3</sub>CF=CCl<sub>2</sub> (CFP) initiated by OH-radical in the atmosphere. [4] The mechanism is believed to proceed via two processes: (i) Addition Reaction Channels (R1 & R2) and (ii) Abstraction Reaction Channels (R3 & R4). The addition reactions are found to be both thermodynamically and kinetically more favourable than the abstraction reactions. Optimization of all the species present in the pathway has been done using the density functional theory and the post-Hartree-Fock (MP2) method. The MP2 results were further refined using the coupled-cluster method to prepare the Energy Profile Diagram. The kinetics of each reaction channel and the overall rates were also studied using the transition state theory (TST). [5] These results were corrected using the Eckart tunneling. [6] The overall rate coefficient obtained by adding individual rate constants was calculated to be  $4.7 \times 10^{-12}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> using the M06-2X level, which is of the same order of magnitude as obtained by Tokuhashi et al. [7] However, the MP2 results show deviation from the experimental results (Figure 1). Additionally, Atmospheric implications (lifetimes, ODP, GWP, POCP) studies were also carried out to assess the harmful effect of CFP on the stratospheric ozone layer.



Figure 1. Rate comparison at the UM06-2X (Red) and UMP2 (Blue) levels of theory [4] with the experimental results obtained by *Tokuhashi et al.* (Black). [7]

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## Biothiol-responsive Turn-on Fluorogenic Probe for the Targeted Delivery of Potent GSTP1 Inhibitor

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Glutathione S-transferases (GSTs) constitute one of the most important families of detoxifying enzymes and are known to overexpress in cancer cells.<sup>[1]</sup> They are known to induce the development of multidrug-resistance in tumors. The ability of GSTs to promote conjugation of the tripeptide glutathione (GSH) with a variety of substrates leads to the inactivation of various reactive compounds including some anti-cancer drugs. Moreover, the overexpression of piclass isoform of GSTs, glutathione S-transferase Pi (GSTP1) in tumor cells is associated with the inhibition of apoptosis through direct interaction of this enzyme with the mitogen-activated protein kinase (MAPK) named c-Jun-N-terminal Kinase 1 (JNK1) and the scaffold protein TNF $\alpha$ -receptor-associated-factor 2 (TRAF2).<sup>[2]</sup> The inactivation of the highly reactive and electrophilic chemotherapeutic drugs by GSH-conjugation is mainly catalyzed by the overexpressed GSTP1 at the tumor micro-environment.<sup>[3]</sup> Therefore, a promising strategy for cancer treatment could be the development of potent and selective inhibitors of GSTP1. The nitrobenzoxadiazole derivative (NBD-HEX) is reported as a potent inhibitor of GSTP1 endowed with the outstanding anti-cancer activity in different tumor models.<sup>[4]</sup> Therefore, in the present study, a mitochondria-targeted turn-on fluorogenic delivery system has been developed for the selective delivery of GSTP1 inhibitor NBD-HEX to the mitochondria of cancer cells (Scheme 1).



**Scheme 1**. Schematic representation of the biothiol-responsive turn-on fluorogenic delivery of GSTP1 inhibitor NBD-HEX to the mitochondria of cancer cells.

Evidences from the UV-Vis and fluorescence spectroscopic studies confirmed the biothiol-triggered release of NBD-HEX in the aqueous medium with turn-on fluorescence. Moreover, while, the free NBD-HEX was found to have significant anti-proliferative activity, the probe was found to be relatively non-toxic in breast cancer cells and exhibited turn-on emission with endogenous biothiol under fluorescent microscopy indicating the release of the potent GSTP1 inhibitor under the cellular environment.

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## Palladium Nanoparticle Implanted Polymer Membrane for Reusable Dip-Catalysis of diverse C-C and C-X (X=O/S/N) coupling reactions

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The criteria for the development of a successful catalyst are simple yet cheap fabrication, high efficiency, stability, flexibility, straightforward recovery, reusability, and ease of scale up. There are reports of palladium nanoparticle (PdNPs)-based catalysts for performing carbon-carbon cross coupling reactions, but aforesaid criteria are rarely met in a single system. Moreover, a single catalyst system performing different types of C-C and C-heteroatoms cross-coupling reactions is very rare. Herein, we achieved the above-mentioned criteria by using a reusable polymer embedded PdNPs dip-catalyst membrane without any other ligands or additives under milder reaction conditions. The composite membrane was fabricated by simply depositing poly(4-vinyl pyridine) anchored PdNPs (average size 9.9 nm) on Nylon-6 membrane followed by UV cross linking.



The C-C bond formation reactions using diverse reagents (Suzuki-Miyaura, Heck, Sonagashira, Stille, Hiyama reactions) were achieved to give the desired products in high to excellent isolated yields while the C-X (X=N/O/S) bond formations were accomplished in moderate to good isolated yields. Plausible mechanisms for such diverse coupling reactions by a single catalytic membranes are also illustrated. The P4VP-PdNP dip-catalyst system was stable under the reaction conditions without significant leaching of Pd into the solution. The dip-catalyst membrane can be reused at least 10 times without losing any significant activity.

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#### Exploring Novel Mechanistic Insights in Fe(III) catalyzed Ullmann type Carbon-Heteroatom Cross-Coupling Reactions: A DFT Study <u>C. Rajalakshmi</u>, Praseetha Prakash, Krishnaveni. G, Vibin Ipe Thomas\*

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Iron-catalyzed Ullmann-type cross-coupling reactions have recently garnered considerable attention due to its costeffective and sustainable nature<sup>1-6</sup>. Despite advancement in the experimental protocols, the former's mechanistic details remain scanty in the literature. In the present work, an in-depth computational investigation into the mechanism of the Fe (III) catalyzed C-X (X=O) cross-coupling of phenols with aryl iodides, is carried out for the first time, using Density Functional Theory method employing B3LYP-D3 functional augmented with CPCM solvation model. A high spin iron (III)- bisphenoxy DMEDA complexes are found to be the active catalysts for Oarylation reactions. The DMEDA binds as a dianionic ligand. The study revealed that the reaction proceeds via a concerted nucleophilic substitution mechanism, which is in stark contrast with the conventional Fe-catalyzed C-C coupling reactions. This observation could be rationalized by the non-reducing nature of reaction media, instability of the higher oxidation state, and the ease of the Csp<sup>2</sup>-O bond forming reaction. The activation barriers 31.7 kcal/mol obtained were in close accordance with the experimental conditions. The present study could rationalize the impracticability of achieving DMEDA-assisted C-O cross-coupling in polar aprotic solvents like DMF owing to the poor stability of the anionic complexes. Frontier Molecular Orbital (FMO) analysis further revealed that the presence of an electron-withdrawing group (EWG) on aryl iodides tends to favor the reaction by reducing the energy of the LUMO. The present study could aid in the rational design and development of iron-catalyzed carbonheteroatom cross-coupling reactions.

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#### Surface Pourbaix Diagram: An Essential Tool for Electrocatalysis?

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Over recent years, there has been enormous efforts invested towards finding cleaner and renewable alternatives to fossil fuels. Many electrocatalytic aided reactions such as water oxidation, hydrogen evolution, oxygen evolution/reduction, nitrogen reduction, carbon dioxide reduction reactions are gaining popularity as they are accompanied by release or storage of "green" energy.[1-5] The development of abundantly available, low- cost, and efficient electrocatalysts is still an active field of interest in energy science. Among various factors, the performance of an electrocatalyst is influenced by the atomic structure on its surface while in contact with the electrolyte (Electrode/Electrolyte interface).[6] Thus, identifying the most stable surface terminations at electrochemical conditions (pH and potential) is essential in characterising the activity of the catalyst.



Figure 1. A representative surface Pourbaix diagram showing stable H (in blue) terminations in metal oxidebased electrocatalyst.

Surface Pourbaix Diagrams (SPD) can show the thermodynamically most favourable exposed surface termination of a given catalyst model as function of potential and pH. [7] The type of surface terminations depends on the catalytic reaction and the electrolyte conditions used for the study. In the present work we showcase some examples of SPDs we constructed to study the most favourable surfaces terminations during catalytic reactions including hydrogen evolution and Carbon dioxide reduction. [8,9] In summary, we will demonstrate the usefulness of SPDs in understanding the catalytic performance of an electrocatalyst a step closer to the realistic experimental findings by including the coverage effects at the surface.

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#### Electrochemical Generation of a Nonstabilized Azomethine Ylide: Access to Substituted N-Heterocycles

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Azomethine ylides are fascinating 1,3-dipoles for [3 + 2] cycloaddition reactions toward the construction of *N*-heterocycles. Herein, an efficient and environmentally benign electrochemical approach for the generation of a nonstabilized azomethine ylide has been established under metal-free and external oxidant-free conditions. The resulting 1,3-dipole undergoes a [3 + 2] cycloaddition reaction with olefins and aldehydes. This electrosynthetic methodology indulges a straightforward and facile approach for the construction of substituted pyrrolidines and oxazolidines.


## Ionic Thermoelectric Properties of Reconstructed Lamellar Vanadium Pentoxide Membranes

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In recent years, the application of ionic thermoelectric (TE) materials to convert low-grade waste heat into electricity has become a subject of intense scientific research. However, most of the efforts are focused on organic polyelectrolytes or ionic liquids embedded in polymeric gels. Here, for the first time, we have demonstrated that nanofluidic membranes of reconstructed layered materials like vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) exhibit excellent ionic TE characteristics. The high Seebeck coefficient (S =  $14.5\pm0.5 \text{ mV/K}$ ) of the V<sub>2</sub>O<sub>5</sub> membrane (VO-M) is attributed to temperature gradient-induced unidirectional transport of protons through the percolated network of atomically thin two-dimensional (2D) nanofluidic channels. The TE characteristics of VO-M have shown nearly 80% improvement (S =  $26.3\pm0.7 \text{ mV/K}$ ) upon functionalizing its percolated network with ionic polymers like Poly(4-styrenesulfonic acid) (PSS).



Figure 1. Graphical abstract of the diffusion of protons through the nanochannels of V<sub>2</sub>O<sub>5</sub>

Further, unlike organic polymer-based thermoelectric systems, the VO-M not only sustains exposure to high temperatures (~ 200 °C for 5 minutes) but also protects the PSS molecules intercalated into its interlayer space. Moreover, the V<sub>2</sub>O<sub>5</sub>-based TE materials can self-repair any damage to their physical structure with the help of a tiny droplet of liquid water. Thus, nanofluidic membranes of reconstructed layered materials like VO-Ms demonstrate vast robustness and great ionic TE performance, which could provide a novel platform for scientific studies and futuristic applications.

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# Donor-acceptor organic nanostructure based on conjugated polymer for improving visible-light-driven photocatalytic activity towards degradation of dye in aqueous medium

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Industrial wastewater is often tainted by organic dyes, which are typically non-biodegradable, resulting in serious environmental problems, and also have mutagenic and carcinogenic effects.<sup>1</sup> Donor-acceptor hybrid nanostructures based on conjugated polymers have attracted a lot of attention, primarily because of their potential use in photovoltaic and other electronic and optoelectronic devices.<sup>2</sup> Here, we have demonstrated a different aspect of these hybrid nanostructures toward efficient photocatalysis for the degradation of the organic dyes in an aqueous medium.



A simple process to form the hybrid donor-acceptor nanostructures by assembling the surface of an aminefunctionalized regio-regular P3HT nanostructure with a carboxylic acid-functionalized fullerene molecule (phenyl C-61 butyric acid) (PCBA) on its surface. The efficient photoinduced charge separation and charge transfer in the hybrid material were investigated by steady-state and time-resolved photoluminescence and photocurrent measurements.<sup>3</sup> The photocatalytic activity of the hybrid nanostructure in water under visible light irradiation (using a 20 W white LED bulb) was investigated, and it was found to show 82.5% dye degradation efficiency. To facilitate the reusability of the photocatalyst, a membrane-based dip-photocatalyst was developed from this material, and it shows 87.5% dye degradation efficiency and can be reused multiple times without a significant change in degradation efficiency.

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### Impact of industrial dyes on macromolecular structure and function

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Globalization, industrialization and rapid economic growth increase the demand for everything from food, clothes and to chemicals with the advancement of time. To meet the demands, lots of hazardous materials have been created knowingly or unknowingly, which causes adverse impacts on living organisms and the environment. Dyes are one of the most used toxic materials which significantly affects the quality of water bodies; it increases BOD & COD. More than 10,000 dyes are used in industrial purposes such as colouring and printing in textiles, papers, paints and leathers etc. Apart from these some of the dyes are used as a tracing agent in various scientific studies and even added to food illegally for aesthetic purposes. During those processes about 10-15% of the dyes are discharged into the water system: it reaches rivers and sewers and accumulates in the environment, wildlife and even humans through the food chain or nutrient transfer. Therefore, dyes are emerging as environmental pollutants over time. Recent studies have shown that dyes are carcinogenic, mutagens and they interact with living organisms at the molecular level. Usually, dyes are good binders towards biomacromolecules (protein, DNA, RNA etc.) and form stable complexes upon ligation. Thus, they affect both structure and function of the macromolecules which can be of serious concern from environmental, biological and chemical point of views.



Figure: 3D structures of serum-albumins

In general, protein interaction studies are essential for understanding different processes, actions and mechanisms of biological systems. They offer both the experimental and theoretical database for drug discovery, design and development of new drug targets. Interaction of dye molecules with proteins are also very important to understand the harmful impacts of such coloring agents. Here we report the binding interactions of different dyes like Methyleneblue, Methyl-orange, Rhodamine-B, Congo-red, Ethidium-bromide etc. towards serum albumin proteins. Spectroscopic investigations followed by molecular docking experiments confirmed the adverse effects on protein structures which eventually affect their functions as well. The result portrays the possible binding sites, binding constants, stoichiometry, mechanism and associated thermodynamics of dye-protein complexation. This study possesses the thread at the molecular level, for the dye molecules to compete with other essential ligands in biological systems; hence can provide important insights for further risk assessment of such chemical moieties.

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## Influence of Salt and Temperature on the Self-assembly of Cyclic Peptides in Water: A Molecular Dynamics Study

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It is found in the literature that the cyclic peptides (CPs) possess the property to self-assemble in water to form cyclic peptide nanotubes (CPNTs) and are used extensively in the field of nanotechnology. Several factors influence the formation and stability of these nanotubes in water. However, an extensive study of the contribution of several important factors is still lacking. The purpose of this study is to explore the importance of temperature and salt (NaCl) on the association tendency of CPs. Furthermore, the self-association behaviour of CPs in aqueous solutions at various temperatures are also thoroughly discussed. Cyclo-[(Asp-D-Leu-Lys-D-Leu)<sub>2</sub>] is considered for this study and a series of classical molecular dynamics (MD) simulations at three different temperatures, viz. 280 K, 300 K, and 320 K, both in pure water and in various concentrations of NaCl salt are carried out. The calculations of radial distribution functions, preferential interaction parameters, cluster formation and hydrogen bonding properties suggest a strong dependence of NaCl concentration facilitates the association of CPs. Besides this, the association of CPs is found to be enhanced at low temperature. Furthermore, the thermodynamics of CP association is predominantly found to be enthalpy driven in both presence and absence of salt. No crossover between enthalpy and entropy in CP association is observed. In addition, the MM-GBSA method is used to investigate the binding free energies of the CP rings that self-assembled to form nanotube like structures at all three temperatures.



**Figure 1**: Snapshots of the formation of CPNT like sturctures at (a) 280K, (b) 300K and (c) 320K (for simplicity only the backbone atoms of the cyclic peptide rings are shown)

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## Metal Oxide Solid Solutions for Photocatalytic Hydrogen Evolution Reaction

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Hydrogen generation by solar water splitting has been considered as a promising green energy technique as the solarenergy is an abundant natural resource and does not contribute to carbon footprints [1]. This also offers one of the best method to solve the energy crisis without causing any environmental issue that result from the burning of fossil fuels [2]. Recently, several kinds of oxide based semiconductors have been developed as photocatalysts for production of H<sub>2</sub> from water. To improve the photocatalytic hydrogen performance, various strategies such as morphology control, defect engineering, and band engineering have been developed. Among these methods, defect engineering is considered as an effective way to modulate the electronic band structure, charge carrier transfer and surface-active sites construction of photocatalysts. The synthesis of solid solutions is also the prime approach for band engineering, aiming at improving the light absorption and facilitating the photogenerated e-h pair separation. Here, the impact of oxygen vacancies and ZnO segregated phase on the photocatalytic activity has been discussed. In this work, we have synthesized  $ZnFe_{2-x}Ga_xO_4$  solid solutions via citrate-gel method and studied the water splitting activity for hydrogen generation in the presence of sacrificial agent. We found that the hydrogen production rate systematically increases from  $ZnFe_2O_4$  (3089µmolh<sup>-1</sup>g<sup>-1</sup>) to  $ZnGa_2O_4$  (3989µmolh<sup>-1</sup>g<sup>-1</sup>) in the series. Formationof additional ZnO phase with incorporation of  $Ga^{3+}$  in the  $ZnFe_2O_4$  structure improves the hydrogen evolution.

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# Role of spin-states in the dioxygen reactivity of non-heme iron mono-nitrosyl

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Iron heme and non-heme complexes bearing nitrosyl ligands have been the subject of study for decades due to the importance of iron nitrosyl fleeting intermediates in medicinal and biological chemistry. [1] Two non -heme iron nitrosyl complexes of same ligand framework ( $Pz_2Py = Bis[\{di(3,5-dimethyl-1H-pyrazolyl)methyl\}]-(2-pyridylmethyl)amine)$  having  $\{Fe(NO)\}^7$  configuration were synthesized and characterized spectroscopically as well as structurally. It has been found that the spin states (S = 3/2 or S = 1/2) of the complexes depends on the solvent used during synthesis. [2,3] The dioxygen reactivity of these complexes has been studied. The reactivity of these iron-nitrosyl complexes towards molecular oxygen, which presumably results in the formation of a metal peroxynitrite intermediate. This has been authenticated by the characteristic ring nitration of externally added phenolic substrate. Spectroscopic and analytical studies suggest that the spin state of the iron centre modulates the overall reactivity.



Figure 1. Dioxygen reactivity of high spin and low spin iron nitrosyl complexes.

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## Non-covalent confinement of Mn(II)-complex in porous silica nanosphere rendering dual mode MRI-contrast agent

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Magnetic resonance imaging is a powerful imaging technique for early diagnosis of various diseases. Being less sensitive, it is often accompanied with administration of contrast agents, which are mainly paramagnetic complexes of Gd(III), Mn(II) or Fe(III). Recent studies indicated that high doses of Gd(III) leads to nephrogenic systemic fibrosis in patients with renal failure. Mn(II) complexes being biogenic, is more preferred. But high relaxivity and stability is always a challenge for such contrast agents. Henceforth, synthesis of kinetically and thermodynamically stable Mn(II) complex (complex 1) with a hexa-coordinating ligand (H<sub>2</sub>PyDPA) with an inner-sphere water molecule is illustrated in the work. Relaxivity is further enhanced by confining the complex molecule within a biocompatible silica nanoparticle (complex  $1@SiO_2$ ) which imparted high kinetic stability to the system. The novel nanosystem showed  $r_1$ = 8.61 mM<sup>-1</sup> s<sup>-1</sup> and  $r_1$  = 34.59 mM<sup>-1</sup> s<sup>-1</sup> at physiological pH and temperature, measured at 1.41 T, which is almost 2.5 times higher than commercially used Gd(III) based contrast agents. Relaxivity values were found to be  $\sim 3$  times boosted when interaction with serum albumin is investigated.  $r_1 = 24.76 \text{ mM}^{-1} \text{ s}^{-1}$  and  $r_1 = 63.96 \text{ mM}^{-1} \text{ s}^{-1}$  was found for complex 1@SiO<sub>2</sub>NPs in presence of bovine serum albumin, at 1.41 T, physiological pH and temperature. Synthesized nanosystem was stable in 4-10 pH range and impervious to 200 equivalent excess of biologically relevant anions (bicarbonate, biphosphate and citrate) and found to be inert in presence of 40 equivalent excess of Zn(II) ions. Thus the availability of the inner-sphere water molecule is assured in biological conditions. Contrast ability of the complex confined nanosystem is visualized by recording concentration dependent clinical MR-images. The cell viability and internalization ability is also checked on *HeLa* cell-line and thereby, a potential  $T_1$ - $T_2$ -dual mode MRI contrast agent is proposed as an alternative to clinically used GBCAs.

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# Photoredox hydroxy-arylation of the terminal double bond of *n*-substituted 3-methyleneisoindolin-1-ones in visible light

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*N*-Substituted 3-hydroxyisoindolin-1-ones are useful structural scaffolds found in numerous bioactive natural products (Chilenine and Fumadensine) and pharmaceutical agents (CRR-228 and CRR-271) and used as a Raf kinase inhibitor and MEK protein kinase inhibitor.[1] Typically, 3-hydroxyisoindolin-1-ones are useful synthons[2] as they can be dehydrated to 3-methyleneisoindolin-1-ones or deoxygenated to bioactive isoindolin-1-one derivatives.[3] In view of the profound biological importance of 3-hydroxyisoindolin-1-ones, various synthetic routes have developed over the years.[4] We explored the feasibility of photocatalyzed synthesis of 3-benzyl-3-hydroxyisoindolin-1-ones in visible light. We anticipated that a Meerwein-photocatalytic approach might work on *N*-substituted 3-methyleneisoindolin-1-ones as starting materials and enable difunctionalization at the double bond. The entitled work describes a ruthenium-catalyzed and visible light-assisted hydroxy-arylation of the terminal double bond of *N*-substituted 3-methyleneisoindolin-1-ones. The reaction takes place with aryl diazonium salt as the arylating reagent and water as the hydroxyl source in visible light at ambient temperature.



Figure 1. Hydroxy-arylation of the terminal double bond of *N*-substituted 3-methyleneisoindolin-1-ones.

The strategy entails vicinal difunctionalization of alkene and enables construction of 3-benzyl-3-hydroxyisoindolin-1-one heterocyclic scaffolds in moderate to good yields. C–C and C–O bonds are formed in one pot without any external additive and oxidant through an in situ generation of a carbocation intermediate in green light. The catalysis initiates via a radical pathway and involves a carbocation intermediate. The strategy provides an easy access to these molecules with potential medicinal chemistry applications.

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# Organocatalytic Asymmetric Divergent Synthesis of Benzofuran Fused Azocine Derivatives and Spiro-Cyclopentane Benzofurans

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Divergent synthesis is a fascinating and efficient strategy that has attracted much attention from chemists for the synthesis of diverse isomers with different chemo-, regio- or diastereoselectivities from identical starting materials[1]. In fact, synthesis of two or more structurally and stereogenically different types of chiral products *via* divergent strategy is quite attractive. Herein, we reported a sequential chemodivergent enantio-, regio- and diastereoselective reaction between aurone-derived  $\alpha,\beta$ -unsaturated imine and ynones by combining bifunctional urea, DBU and PPh<sub>3</sub> catalysis has been developed. A variety of eight-membered cyclic azocine and spiro-cyclopentane benzofurans with contiguous tertiary and quaternary stereocenters were obtained in high yields with excellent stereoselectivities[2]. This method provides a new strategy for constructing enantioenriched eight-membered azocines and spiro cyclopentane and also demonstrates the practicability of ynones as C4/C3 synthon for the synthesis of chiral medium-membered rings.



Figure 1. Enatioselective Divergent synthesis of Benzofuran Fused Azocine Derivatives and Spiro-Cyclopentane Benzofurans

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# Insights into the Aggregation and Light-Harvesting properties of Naphthalimide-Based Amphiphile and Non-amphiphile AIEgen

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A comparative study has been depicted on naphthalimide attached amphiphile and non-amphiphile with their aggregation-induced emission properties. A synthetic manipulation of a hydrophobic tail on the framework repressed the ACQ-phoric fluorophore to an AIEgen.  $L_1$  and  $L_2$  remain in the dispersed form in organic solvent and exhibits aggregation and intense emission signal in water. Microscopy detailing of the aggregating process has been analyzed. The AIEgens are emissive in water as well as emissive in the solid state. The natural light-harvesting process is mimicked by the AIEgen, forming an energy transfer process between  $L_1$  and commercial dye. Disaggregation of the AIEgen has also been used in the detection of nitroaromatics. Analytical application of the AIE-gen is being demonstrated regarding the detection of nitro-explosives in aqueous media.



Figure 1. Graphical abstract of the aggregation and disaggregation process.

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# DFT Study on Binuclear Transition Metal Complexes with Macrocyclic Tetradentate Ligands: Structures, Relative Energies, and Metal-Metal (MM)Bond Lengths and Bond Orders

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We use DFT with the M06-L functional and LAN2LDZ basis set to study a series of homobinuclear transition metal complexes  $M_2L_2$  (M = Ti, V, Cr, Mn, Fe, Co, Ni), where L is a symmetrical macrocyclic tetradentate ligand  $C_8N_4H_8$ . Two orientations are taken for eachcase – (a) *orthogonal*, where the metal-metal (MM) bond axis is perpendicular to the ligand planes, and (b) *lateral*, where the MM bond axis is parallel to the ligand planes. By exploring a variety of low lying spin states, the ground state for each complex is predicted. Invariably, the orthogonal structures are lower in energy than the lateral structures, which predict that theformer would be more readily formed during synthesis. Our DFT findings concerning the ground state spin multiplicity and MM bond lengths are consistent with and relatable to experimental results on known binuclear tetragonal lantern-type complexes of vanadium, chromium, iron, cobalt and nickel having four bidentate ligands. The tetragonal structure which, however, possess only two ligands. The MM bond lengths span a wide range, and are assigned formal bond orders from zero to four. The valencies of the metalcentres in the ground state complexes begin with about 5 for the dititanium complexes, rise toabout 6 for the dichromium complexes, and fall to about 2 for the dinickel complexes.

#### Dual dynamic reversible bond derived self-healable waterborne polyurethane

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Self-healable waterborne polyurethane (SHWPU) is one of the prudent polymer because of its environmental benign character and its wide spectrum of applications. However, SHWPU exhibiting both efficient self-healing ability and high mechanical properties are highly anticipated which is a formidable challenge to material chemists because of the conflicting attributes of these two properties. Herein, a series of SHWPU films were prepared by using aminophenyl disulfide and alicylic diamine as asymmetric with other desired reactants (di-/poly-ols/-amine and diisocyanate). The dual dynamic reversible bond developed due to the presence of aromtic disulfide moiety and multiple hydrogen bonding raised from asymmetric urea linkages supplemented the high healing ability. Simultaneously, the rigid cylclic rings (both aromatic and aliphatic) improved the mechanical properties of SHWPU films. Owing to the precise molecular engineering, the resulting network exhibits good tensile strength, excellent elongation at break, and high thermal stability. Notably, all films shows oustanding self-healing ability on exposure to heat and microwave radiation. Furthermore, the soil burial studies of the films and subsequent SEM image analysis confirmed their biodegradability. Hence, the sustainable SHWPU films can be applied for multiple applications including self-healable films.



Figure 1. Graphical abstract of dual dynamic reversible bond derived self-healable waterborne polyurethane

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# Unprecedented C-C Bond Formation *via* Ipso Nucleophilic Substitution of 2,4-Dinitrobenzene Sulfonic Acid with Active Methylene Compounds Sandip Mondal and Bhubaneswar Mandal\*

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**ABSTRACT:** The removal of sulfonic acid functionality of an electron deficient benzene sulfonic acid via ipso nucleophilic substitution reaction with various active methylene compounds is leading to generate a new C-C bond. This method produces excellent yield without requirement of transition metal (Pd or Cu) catalyst, PTC and ligand, occurs under mild conditions, unwanted byproduct free. Therefore it is a highly effective strategy for incorporating of various types of active methylene compounds into the *o*-nitro substituted benzene ring. This method has been applied for synthesizing APIs as well as in materials chemistry. This is the first report of carbon-carbon bond formation by substituting a sulfonic acid group.

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## Exploring the Reactivity of *ortho*-[1-(p-MeOPhenyl) Vinyl] Benzoate (PMPVB) donors in C-O and C-S bond Formation Reactions

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The synthesis of ethers and thioethers is dominated by metal catalyzed dehydrative processes or coupling reactions involving stoichiometric or more amounts of activating agents of leaving groups or the nucleophiles. Here, we present a practically simple method for the synthesis of ethers and thioethers *via* Bronsted acid-catalyzed activation of *ortho*-[1-(p-MeOphenyl)Vinyl] benzoate (PMPVB) donors derived from alcohols. The donors are easily accessible from commercially cheap starting materials, bench-stable and can be stored over many months or even years. The mechanism of action is based on the remoted activation of an active alkene followed by intramolecular cyclization leading to a reactive intermediate that can react *via* a substrate dependant S<sub>N</sub>1 or S<sub>N</sub>2 mechanism with alcohols and thiol nucleophiles providing facile access to ether and thioether functionalities respectively.



Figure 1. Graphical abstract of the reactivity of ortho-[1-(p-MeOPhenyl) Vinyl] Benzoates (PMPVB) donor

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# Aggregation induced delayed green fluorescence from assembly of gold nanoclusters: Be used as an advanced probe for "background free" pyrophosphate recognition

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Aggregation induced emission (AIE) and aggregation caused quenching have recently become two well-known phenomena towards the development of advanced optical materials. In addition to interesting light emitting properties, these class of materials have important physical & chemical properties with useful applications in photochemistry, as luminescent materials, in solar energy harvesting applications, as biological photo sensors, etc.[1] In this regard, a recent advancement in the field of organic electronics has witnessed rational implementation of the concept of delayed fluorescence (DF).[2] Due to their long luminescence lifetime, DF materials, portend to be ideal candidates for eliminating background noise arising due to auto-fluorescence and thereby allowing accurate sensing and assay of chemical and biological species. On the other hand, phosphorescent materials, having high luminescence lifetime, are typically constituted of heavy metal atoms and are thus not environment friendly nor suitable for bio-sensing of molecules. Thus DF materials having sufficient luminescent lifetime & quantum yield are suitably poised to be used as futuristic, environmental friendly and bio compatible chemo sensors. In this regard, development of AIE based DF materials may be a way forward in the field of molecular and ion recognition.

In this presentation we report the conversion of a non-luminescent mercapto propanoic acid based gold nanocluster (Au NCs) into a highly luminescent material (Zn Au NCs) upon complexation reaction with zinc ions with Au NCs. The resultant bright green luminescence of Zn Au NCs arose due to AIE. In addition, Zn Au NCs also showed green delayed fluorescence with a high quantum yield of 6% and an average lifetime of 17.67  $\mu$ s. This green delayed fluorescence of the assembly of Zn Au NCs have been further used for "back ground free" probing for pyrophosphate anions. A schematic representation of the plausible mechanism leading to discernible detection of pyrophosphate is shown below:



**Figure 1.** Graphical abstract of schematic representation of the possible mechanism of quenching of delayed bright green luminescence of Zn Au NCs upon addition of sodium pyrophosphate.

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#### Azoheteroarene based probe for arginine and lysine detection

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Stimuli-responsive molecules are attractive because of the requirement of modulation of functions in numerous applications. Among the various external stimuli, light is the most non-invasive and tannable. Photoswitches are small organic molecules that are capable in altering their physiochemical properties in the presence of light. Azobenzene is a well-known photoresponsive unit, which isomerises between its native trans state to less stable cis form by irradiation with the light of suitable wavelength. [1] Herein, we have designed a simple azoheteroarene based probe for the efficient detection of arginine. Arginine plays an important role in many biological functions, whose detection is very significant.[2] As arginine is the only natural amino acids containing guanidine group, which has the strongest alkaline behaviour and highest isoelectric point and lysine has free amine group in it. Our azo based probe upon binding to arg/lys, induced a visible colour change from orange to pink. (Fig. 1) In comparison to arginine, the probe is little sensitive towards lysine and showed no response towards other amino acids. Mechanistically, in the absence of arginine/lysine, intramolecular hydrogen bonding occurs in the molecular system which gets disturbed when arginine is added due to intermolecular proton transfer from the probe to arginine takes place. Amino acid-probe complex has been investigated with the help of UV-vis, fluorescence, ESI-HRMS, <sup>1</sup>H NMR spectroscopic techniques. Through this contribution, we present the preliminary results.



Figure 1. (a) Schematic representation of arginine with probe; (b) Naked eye detection of arginine and lysine.

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## One-Pot Transition-Metal-Free Synthesis of Polysubstituted Fused Benzene Derivatives from Methyl Enol Ethers and Alkynes: Study of Solvatochromic Effect

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A mild and transition-metal-free one-pot strategy is established to prepare polysubstituted naphthalene and phenanthrene derivatives from methyl enol ethers (MEE) withalkynes. Significantly, this protocol is promoted by

BF3'OEt2 at room temperature. A wide variety of diversely functionalized naphthalene and phenanthrene derivatives were obtained ingood to excellent yields. Two distinct mechanistic pathways seem to be involved, one of them leading to an unusual product from *para*-methoxy substituted MEE. Due to fluorescent nature of naphthalene, selected compounds were screened for the solvatochromism study.



#### **Reference:**

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## Earth Abundant Manganese Complex Catalyzed Sustainable Synthesis of α-Hydroxycarboxylic Acids

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Conversion of readily available feedstocks to valuable platform chemicals via an eco-friendly catalytic pathway has always been one of the key focuses of synthetic chemists. In this context, herein, we report selective transformation of readily available feedstock, vicinal glycols, to value-added  $\alpha$ -hydroxycarboxylic acid molecules that are prevalent in bioactive molecules and biodegradable polymers<sup>[1]</sup> A bench stable earth-abundant metal complex {[HN(C<sub>2</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>]Mn(CO)<sub>2</sub>Br}, **Mn-I** catalyzed the reformation reaction at low temperature in high selectivity with a turnover number TON reaching 2400, surpassing previously used homogeneous catalysts for such a reaction. Hydrogen gas is evolved as a by-product without the need of any external acceptor. The developed protocol is applicable for both aromatic and aliphatic vicinal glycols, delivering the  $\alpha$ -substituted hydroxycarboxylic acids in high vields and selectivities.<sup>[2]</sup> Keeping in mind the additional functionalization required to obtain substituted vicinal glycols, further, we developed a more straight-forward approach for synthesizing  $\alpha$ -hydroxycarboxylic acid via the acceptorless dehydrogenative coupling of more readily available ethylene glycol and primary alcohol. The ADC reaction was catalyzed by another manganese complex with a triazine backbone. Mn-II. The ADC protocol could also be applied to synthesize various  $\alpha$ -hydroxycarboxylic acids in high yield, including a highly demanded platform chemical, lactic acid, which could be synthesized with a high turnover of  $>10^{4}$ .<sup>[3]</sup> Both the reactions are highly sustainable and eco-friendly giving water and hydrogen as the sole by-product. The latter is liberated without the need for any acceptor and can be stored and utilized. Furthermore, the ADC protocol was also applied for synthesizing  $\alpha$ amino acid,  $\alpha$ -thiocarboxylic acid, and several drugs and bioactive molecules, including endogenous metabolites, Danshensu, Enalapril, Lisinopril, and Rosmarinic acid. Further, various mechanistic studies, including kinetic experiments, NMR experiments were performed to delineate the mechanism involved in the reaction.



Figure 1. Earth abundant manganese complex catalyzed synthesis of  $\alpha$ -hydroxycarboxylic acids.

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## Transiently Breathing Multi-Luminescent Vesicles with Broad-Spectrum Tunability

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Capturing the fundamental physicochemical characteristics of cell membranes is an important objective of cytomimetic chemistry and a key step in the design of synthetic protocell models. The intricate manipulation and reorganization of lipids in biological membranes generally follow an out-of-equilibrium pathway, allowing communication between the intracellular and extracellular environment. To mimic the complex non-equilibrium dynamics of cell membranes, we present a pH responsive vesicular assembly that shows dynamic expansions and contractions i.e., "breathing" behaviour and broad-spectrum transient fluorescence oscillations under the influence of a chemically driven pH cycle. [1, 2, 3] The vesicular architecture acts as a versatile platform for establishing FRET interactions between multiple donor and acceptor fluorophores. The breathing effect was induced by the vesicle's spontaneously fluctuating interfacial charge during the pH cycle. It also altered the donor fluorophore's emission intensity, affecting the efficiency of FRET interactions between donor-acceptor pairs. This enabled multicolour as well as transient pure white light luminescence of the vesicles during the breathing events. Furthermore, the vesicles demonstrated excellent adaptability in terms of the durations of the breathing cycles and the tunability of the luminescence colour transitions.



Figure 1. Schematic illustration of transient luminescence in the pH responsive breathing vesicles under the influence of a pH clock.

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## Aqueous Processing of Chemical 'Inputs' to Derive Bio-inspired Coatings with Desired Outputs

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Inspired by the Nepenthes Pitcher plant, slippery liquid infused porous surface (SLIPS) become as an important avenue for various potential and practically realistic applications.[1] Solid slippery interfaces infused with fluorinated and non-fluorinated liquid often suffer from durability and contamination issues due to the leaching of environmentally non-viable lubricant.[2] Derivation of highly optically transparent and durable bio-inspired anti-wetting interfaces—following a simple, completely water-borne, non-fluorinated and scalable fabrication approach is an extremely challenging task to achieve. Here, a simple and mutual chemical reaction between selected thioester and amine groups is rationally extended for aqueous processing of strategically selected chemicals to derive desired output.



**Figure 1**. A) Schematic presentation of a mutual reaction between amine and thioester functional groups. B-C) Illustrating the derivation of desired 'outputs'—including bio-inspired wettability, water-borne process, durable and & optically transparent coating through the aqueous processing of small molecules based reactants having strategically selected chemical 'inputs' (i.e. self-polymerizable, hydrophilic, and hydrophobic moieties). D) Depicting the slippery behaviour of beaded droplets of different liquids on solid slippery coating. E) Illustrating the physical (tensile and compressive) deformations of fibrous and porous substrate that embedded with superhydrophobic coating. F) Schematic presenting tolerance of prepared coating towards some relevant and widely accepted abrasive exposures.

In the current design, a non-fluorinated small molecule that is decorated with both hydrophilic (sulfonate) and hydrophobic (hydrocarbon) moieties through thioester bond remained highly reactive to a primary amine containing another water soluble and self-polymerizable small molecule to provide a stable (for 30 days) dispersion of nanoparticles (size  $\sim 210$  nm) in aqueous medium. During the course of the mutual reaction between amine and thioester moieties, the hydrophilic moiety is released in the aqueous phase, and the polymerizable moiety attached covalently with hydrophobic long tail through amide bond formation. Further, this aqueous reaction mixture is extended to develop waterborne, transparent (above 85 %), physically and chemically durable lubrication-free slippery coating on a planar substrate and highly beaded droplets of various liquids (e.g., water, polar and non-polar solvents) having a wide range (70.2 mN/m to 22.3 mN/m) of surface tensions. On the other side, the synthesized superhydrophobic coating on porous and fibrous-substrate remained efficient in sustaining repetitive physical deformation and other relevant abrasive exposures. Such robust, transparent and waterborne bio-inspired wettability would be appropriate for various prospective applications in realistic settings.

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#### **Investigation of Supramolecular Self-Assembly of Dipeptides**

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Self-association of the small peptides resulted in various nanostructures; supramolecular self-association is important as their biocompatibility and biodegradability, capability for specific molecular recognition, chemical variety, and for application in medicinal chemistry.[1] Supramolecular non-covalent interactions stabilize the secondary structure of peptides or proteins. Alternating L/D amino acids containing peptide-based supramolecular structures are not explored enough.



Figure 1. Molecular self-assemble in crystalline state

Herein, we designed an alternating L/L and L/D amino acid-containing dipeptides Boc-L-Ile-L-Phe-OMe (1), Boc-L-Ile-D-Phe-OMe (2), Boc-L-Ile-L-Phg-OMe (3), and Boc-L-Ile-D-Phg-OMe (4) and investigated their supramolecular self-assemblies. The molecules in 1 self-assemble to form a single helix-like architecture, and the molecules in 3 self-associated around a water molecule to form a cylinder-like structure in the crystalline state. On the other hand, the observed supramolecular arrangements of 2 and 4 are similar but deviate from that of 1 and 3 due to the chirality difference. Peptides 2 and 4 exhibit a discontinued double helix-like structure in the crystalline state. Peptides 1 and 3 self-associate to form helical ribbon-like and nano tube-like structures in solution, respectively, whereas both 2 and 4 form nanorod-like structures in solution.[2]

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# Biophysical study on binding of Rhodamine B with ds-DNA: elucidation of binding mechanism and thermodynamics

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The interaction study of nucleic acids with small molecules such as drugs, dyes and metal complexes etc. has been very rewarding as it gives valuable knowledge for the design of novel and more efficient drugs. Ligand-DNA association reactions are extremely important as they provide valuable inputs in drug developments which specifically target DNA. Rhodamine B (RB), a xanthene dye, is widely used for printing and dyeing in industries; it is mutagenic after activation in in vitro systems and genotoxic in nature. Nucleic acid binding ability of such chemical compounds may provide an understanding to characterize the mechanism of ligand-receptor interactions. On the other hand, dyes are known for their polluting nature and can cause severe harm to biological bodies. So quantitative information about the effects of such dyes on structure and function of DNAs, are very much required. Thus, RB can be a potential target for ligand-DNA interaction study and here we report the binding of Rhodamine B with natural polymeric ds-DNA strands (HT DNA, deoxyribonucleic acid sodium salt from herring testes; derived from the sperm of herrings fish) using biophysical tools. The detailed binding mechanism and thermodynamics have been elucidated from UV-vis, fluorescence, infra-red (IR) spectroscopic data and complemented with computational methods. Spectral data analyses prove 1:1 stable, ground state complex formation. Cooperative binding mode via minor groove of the nucleic acid has been observed. The results obtained provide an understanding of the binding affinity, stoichiometry and structural details of the RB-HT DNA complex. The complexation is spontaneous; favoured by negative free energy change followed by entropy-enthalpy compensation and structural perturbation of the nucleic acid. Thus, overall structurefunction relationship and molecular aspects of binding have been established in the current piece of research work.



Figure 1: Structure of DNA (source: internet)

Figure 2: Structure of Rhodamine B

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## Conformational Features and Hydrogen Bonding Properties of Glycosaminoglycan-Interleukin8 Complexes in Aqueous Medium: An Insight from Computer Simulation Study

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Glycosaminoglycans (GAGs) are an important class of unbranched, negatively charged hetero-polysaccharides. They are the structural components of connective tissue and the extracellular matrix of higher organisms. GAGs are crucial in physiological, pathological, and cell signaling processes. [1] The structural diversity, highly anionic charged surface and their typical location in extracellular matrices make the GAGs molecules biologically important. The protein targets of GAGs are chemokines and growth factors. [2] GAGs bind with their protein targets in the extracellular matrix and participate in biological processes like angiogenesis and cancer, inflammation, neural development etc. [1] Due to the highly flexible nature of GAGs, the molecules can adopt many energetically alike conformational states, making the molecules more challenging for researchers. [3] Controlling GAG sulphation patterns is an important task that can be taken care of during molecular modeling to understand the behavior of different sulphated GAGs towards protein binding with varying sulphation positions.

In this work, we tried to identify different binding modes of GAGs to chemokine; Interleukin8 (IL8) by performing molecular docking experiments and extensive atomistic molecular dynamics (MD) simulations. Emphasis was given to investigating the conformational features, binding affinities, and hydrogen bonding properties of sulphated and non-sulphated GAGs in their free and bound form. [4, 5] The GAG molecules exhibit higher flexibility in the bound forms than the corresponding free forms, irrespective of their chemical structure. Estimation of Cremer–Pople Puckering Parameters ( $\Theta$ ,  $\Phi$ ) inferred that the GAG conformations primarily lie in chair form with occasional appearances of equatorial and tropical conformations in both free and bound states. Our study showed that the flexibility of the GAGs is mainly due to the flexibility in glycosidic linkages and the  $\omega$  rotation. The free landscape was generated with the help of two reaction coordinates,  $\varphi$ , and  $\psi$ , to understand the conformational pattern of the GAGs through the different glycosidic linkage involved in the GAGs. Our study further reveals the role of hydrogen bonds and conserved water in the binding process. The average lifetime of the IL8-GAG direct HB pairs was ~ ten times less than the IL8-GAG-shared water HBs. We find that despite the highly negatively charged surface of GAGs, the IL8 surface populated by non-cationic amino acids could serve as a promising binding site in addition to the cationic surface of the protein. [5]

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# Ligand mediated HNO release from a nitrosyl complex of Mn(II)porphyrinate having {MnNO}<sup>6</sup> configuration

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The one electron reduced form of well-known biological signaling molecule Nitric Oxide (NO), Nitroxyl (NO<sup>-</sup> or HNO) has some unique characteristics and can act as a therapeutic agent. But Nitroxyl is a short-lived species. Hence a donor molecule is required for its utilization. Metal nitrosyls (MNO) of suitable electronic configuration can be considered as potential HNO donor.<sup>1</sup> Herein we report a Manganese-nitrosyl complex having {MnNO}<sup>6</sup> configuration along with its synthesis and spectral characterization. The penta-coordinated {MnNO}<sup>6</sup> complex, **1** [Mn<sup>II</sup>(TTMP)(NO)] (TTMP = 5,10,15,20-Tetrakis(3,4,5-trimethoxyphenyl)porphyrin) acts as an HNO/NO<sup>-</sup> donor in presence of a sixth coordinating ligand such as BF<sub>4</sub><sup>-</sup>, DTC<sup>-</sup> (DTC = diethyldithiocarbamate) etc. which is confirmed by the presence of well-known NO<sup>-</sup> acceptor like [Fe<sup>III</sup>(TPP)CI] (TPP = tetraphenylporphyrin) and [Fe<sup>III</sup>(DTC)<sub>3</sub>]. Complex, **1** reacts with PPh<sub>3</sub> in presence of HBF<sub>4</sub>.Et<sub>2</sub>O to give either Ph<sub>3</sub>P=N or Ph<sub>3</sub>P=N.HBF<sub>4</sub> which confirms the NO<sup>-</sup> release. The release of NO<sup>-</sup> is further confirmed by the presence of N<sub>2</sub>O in the head-space gas of the reaction vessel.



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# Intramolecular cyclization of isothiocyanyl amino acids/peptide: arrival at unnatural thioxoimidazolidinyl/thioxooxazolidinyl amino acids

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A novel intramolecular cyclization of isothiocyanyl amino acids/peptide is reported to arrive at unnatural thioxoimidazolidinyl (TOI)/thioxooxazolidinyl (TOO) amino acids for the first time. Interestingly, analogous isothiocyanyl amines undera similar reaction condition either follow 5-endo-dig cyclization to offer 5-membered thiourea or acyclic diethylaminyl thiourea derivative instead of 6-membered cyclic thiourea.



**Figure 1.** Schematic presentation of cyclization of isothiocyanyl alanine (<sup>NCS</sup>Ala) to afford thioxoimidazolidine amino acid (**TOI**, 1) derivative, [BocN-**TOI**-CONMe(OMe); tert-butyl (R)-5-(methoxy(methyl)carbamoyl)-2-thioxoimidazolidine-1-carboxylate]

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#### Efficient silk dyeing by Camelia sinenesis and a mechanistic view

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In the recent years there is a growing interest in the use of natural dyes due to their eco-friendly nature and to get rid of health hazards from synthetic dyes.[1] The components present in natural dyes like polyphenolics, anthraquinones, flavonoids, anthocyanins, etc impart functional finishing properties to the coloured fibre like deodorizing, antimicrobial, antifungal, antioxidant, fluorescence, flame retardant, and UV protection properties.[2] Different solvents like methanol, ethanol, water etc. are compared to determine the best solvent for the extraction of phenolic compounds from the natural dye sources. [3] The use of aluminium potassium sulphate, zinc chloride and stannous chloride etc. as mordants in colouration increases the colour stability and enhancement in antimicrobial characteristics and UV protection ability.[4] In this presentation, we are going to focus on the extraction of functional components from green tea (*Camelia sinensis*) leaves and mordant dyeing of mulberry silk fabrics for antibacterial and UV protection ability.



Figure 1. Coloured silk dyed with green tea extract showing UV protection and antimicrobial activity

Silk fabrics dyed directly or with mordant exhibit golden yellow colours with excellent colourfastness to washing and rubbing in the grey scale rating of 4-5. The colour coordinates CIE L\*a\*b\* of dyed samples reveal the location amidst redness and yellowness spaces. The colour strength is expressed in K/S values and was found to be maximum with the dyed silk, dyeing with the extracts using methanol/water solvent systems. The green tea extract on silk fabric also exhibits good UV protection and antibacterial behaviours. To establish the mechanism of dyeing, catechin was used as a standard and mordant dyeing in silk, resulting in similar golden yellow colouration. Theoretical interaction energy ( $E_{interaction} = -13.836$  kJ/mol) calculation established good stability of mordanted catechin dyeing on silk and catechin stability in different solvents were in the order catechin-water > catechin-methanol > catechin-ethanol.

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#### Pd and photoredox dual catalysis assisted decarboxylative *ortho*-benzoylation of *n*-phenyl-7-azaindole

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Directing group assisted C-H activation plays a significant role in functionalizing specific C-H bonds and helps in the construction of diverse molecular scaffolds.[1] The involvement of precious transition metal catalysts such as palladium, copper, ruthenium and rhodium in activating sp<sup>3</sup>, sp<sup>2</sup> and sp C-H bonds has been quite extensively explored in the past few years.[2] Although, the utility of transition metal catalysts in organic synthesis cannot be undermined, they do possess certain limitations in terms of cost, harsh reaction conditions, and broad general applicability. Some of these challenges have been addressed by invoking dual catalysis approach assisted by photocatalyst in visible light.[3] Such dual catalytic systems have resulted in an organic metamorphosis, allowing distinct activation modes inaccessible through single catalytic system, and offering complementarity to traditional organic reactions. The entitled work describes the directing group assisted decarboxylative *ortho*-benzoylation of *N*-aryl-7-azaindoles with  $\alpha$ -keto acids by synergistic visible light promoted photoredox and palladium catalysis. Detailed mechanistic studies suggest that the decarboxylative photoredox cycle of Eosin Y with Pd proceeds via a radical process.



Figure: Directing group assisted decarboxylative ortho-benzoylation of N-aryl-7-azaindoles with  $\alpha$ -keto acids.

7-azaindoles are useful scaffolds found in many pharmacologically active compounds. Various methods for selective *ortho*-functionalization of *N*-phenyl-7-azaindoles under thermal conditions have developed in recent years.[4] However, an *ortho*-selective benzoylation of these molecules under thermal conditions has not been reported. We rationalized that through a synergistic 7-azaindole directed and palladium catalyzed C-H activation accompanied by photoredox assisted decarboxylation of  $\alpha$ -oxo acids, *ortho*-benzoylation of *N*-phenyl-7-azaindoles may be achieved by radical decarboxylative coupling under mild reaction conditions. Biological target predictions indicate that these molecules may serve as potential anti-cancer and anti-viral agents.

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## Palladium-Catalyzed Auxiliary Guided C4-Selective Arylation of Indoles *via* C-H/C-H Bond Functionalization

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The heteroaromatic indole skeleton is one of the most studied organic motifs in the dominion of synthetic chemistry.<sup>1</sup> Specially, C4-functionalized indoles signify an important role in natural product synthesis, material science, as well as in crop protection and pharmaceutical industry.<sup>2-3</sup> Thus, the development of effective methods for regioselective C4-H functionalization of indoles has received intensive attention. An efficient Pd(II)-catalyzed weak chelation enabled regioselective C4-arylation of indoles using readily accessible unactivated arenes is outlined (Figure 1).<sup>4</sup> Here, arene acts as a coupling partner as well as the solvent of the reaction. The exclusive C4-selectivity, weak chelation, cross-dehydrogenative coupling (CDC),<sup>5</sup> and late-stage diversifications are the salient features.



Figure 1. C4-H Arylation of indole under Pd-catalysis

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# Concise Synthesis of N-Aryl Tetrahydroquinolines via a One-pot Sequential Reduction of Quinoline/Chan-Evans-Lam Coupling Reaction

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A boronic acid-catalyzed one-pot reduction of quinolines with Hantzsch ester followed by N-arylation via external base-free Chan-Evans-Lam coupling has been demonstrated. This step-economical synthesis of N-aryl tetrahydroquinolines has been accomplished from readily available quinoline, Hantzsch ester, and arylboronic acid under mild reaction conditions. The dual role of boronic acid as a catalyst (in the reduction of quinolines) and a reagent (in the N-arylation) has been realized for the first time. The use of cheap N-arylation protocol, aerobic reaction conditions, and functional group diversity is the important practical features.



Figure 1. Graphical representation for the one-step synthesis of N-aryl substituted THQs

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### Label-Free Detection of Ochratoxin A Using Aptamer as Recognition Probe at Liquid Crystal-Aqueous Interface

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The formation of biosensing systems for various analytes has made use of stimuli-responsive, thermotropic nematic liquid crystals (LC) at aqueous interfaces. These interfaces can easily report aptamer-target binding events at the LC-aqueous interface due to the orientational changes in LC. We demonstrate the use of aptamer as the recognition probe in a label-free, straightforward, and reliable method for the detection of Ochratoxin A (OTA). At the aqueous-LC interface, the cationic surfactant CTAB (cetyltrimethylammonium bromide) self-assembles, giving the LC a homeotropic orientation. The aptamer and CTAB produce a complex in presence of a negatively charged OTA specific aptamer and this complex results in the formation of planar/tilted ordering of LC. When OTA is present, it creates a strong and stable G-quadruplex structure of the aptamer, which causes CTAB to be redistributed at the LC-aqueous interface and causes the LC to undergo a homeotropic orientation. The LC aptasensor has a detection limit of 0.1 nM. We found that the pH and ionic strength had an impact on the sensitivity of LC aptasensor. Additionally, we showed how the developed LC aptasensor may be used to detect OTA in apple juice and tap water. In terms of manufacture, simplicity of use, and analysis, this technology is superior to traditional detection techniques.

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# L-Tryptophan Derived Ligand based Co<sup>III</sup>- Complex Receptor for Cationic substrate: Solid State and solution study

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Abstract. The tridentate amino acid derivative has been prepared using L-Tryptophan and was coordinated with Co(II) salt in the presence of triethyl amine as a base to generate  $(HNEt_3)[Co(L^{O-valtryp})_2][HNEt_3.CIO_4]$ . The complex has been characterized using FT-IR, UV-vis, 1H NMR, and SCXRD. As the Co(III)- complex formed is diamagnetic, it gave a well-recognized NMR spectrum, demonstrating the formation of Co(III)-bis complex having two eq. triethyl ammonium ions. The electronic spectrum of the complex was recorded using its DMF solution, and the existence of two d-d bands is consistent with the pseudo-octahedral geometry around the low-spin Co(III) ion.<sup>1</sup> Single-crystal X-ray analysis of the complex has revealed that the asymmetric unit contains one anionic complex molecule with one triethyl ammonium counter ion and one extra triethyl ammonium salt. The anionic Co(III) complex has conformationally flexible side arms bearing phenyl or indole substituents that fold themselves to form the cavity where the guest binds and non-covalent interactions play an important role in recognizing the achiral guest cation. Cavity-forming metal complexes of amino acid-derived reduced Schiff base ligands find their potential application towards various substrate recognition because of their flexibility, H-bonding ability, and inherent chirality.<sup>2,3</sup>



Figure 1. Structure of ligand and substrate-bounded metal complex cavity.

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## Copper-Catalyzed C7-Selective C-H/N-H Cross-Dehydrogenative Coupling of Indolines with Sulfoximines

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Cu-catalyzed cross-dehydrogenative coupling of C7 C-H bond of indolines with sulfoximines has been accomplished. The reaction can be extended to the cross-dehydrogenative coupling of N-aryl 7-azaindoles with mono selectivity. Sulfoximines feature as pivotal structural motifs of numerous compounds that are important in biological, medicinal and synthetic sciences. Efforts are thus made on the development of effective synthetic approaches for the construction of functionalized sulfoximines. Considerable progress has been made using the transition-metal-catalyzed C-N bond formation of sulfoximines with aryl halides and boronic acids as the aryl source. Recently, the rapid ascent of the cross-dehydrogenative coupling (CDC) has offered an effective synthetic tool to construct carbon-heteroatom bonds, obviating the requirement of prefunctionalized substrate precursors, thus enabling a step- and atom-economical alternative. To this end, harnessing the CDC strategy between sulfoximines with a class of imperative heterocycle structural frameworks would provide versatile aminated scaffolds.



Figure 1. Coupling of (Hetero)Arenes with Sulfoximines.

In this regard, the functionalization of indole has attracted a great deal of attention, as they are prevalent substructures of plentiful drug candidates and natural products. Among the available six C-H sites, the selective editing of the C7 C-H bond imposes a significant synthetic challenge. By virtue of the reduced indoline intermediate, the C7 C-H bond functionalization can be accomplished using a suitable directing group with transition-metal-catalysis. Thereby, engaging sulfoximines as an aminating coupling partner to afford the C7-amination of indolines in a cross-dehydrogenative manner would thus be valuable. Herein, we report an efficient Cu-catalyzed C7-sulfoximination of indolines via C-H and N-H dehydrogenative strategy using the removable pyrimidyl directing group. A broad range of sulfoximines covering (hetero)aryl and alkyl derivatives can be successfully coupled to deliver the aminated indoline scaffolds, which can be oxidized to the indole structural scaffolds in quantitative yields. Further, the late-stage functionalization of naturally occurring alcohol derivatives has been showcased to display the practical synthetic potential. Interestingly, the method can be extended to the coupling of substituted *N*-aryl azaindoles in good yields, which encompasses an important class of valuable indole moieties. These trans-formations highlight the use of abundant first-row Cu-catalysis with broad substrate scope and functional group compatibility.

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# Stereo-electronic Effect of Phenyl Substituents on Thermal Properties of Oxazine Ring-substituted Benzoxazine Monomers & Polymers

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Polybenzoxazine (PBZ) thermoset is prepared by thermal curing of 1,3-benzoxazine (BZ) monomers via ringopening polymerization (ROP) mechanism primarily under catalyst-free conditions, thus enables industrial sustainability. Furthermore, they offer several advantages, e.g., long shelf life, excellent mechanical strength and thermal stability, high char yield and limiting oxygen index (LOI), toxic volatile-free polymerization, etc. Recently 1,3-benzoxazines have been classified into four generations depending on their structural variety. [1] Oxazine ringsubstituted BZ is the the latest generation, also known as fourth-generation of benzoxazine. Thus, structural tailoring strategy to design newer BZ motifs is gaining advertency among polymer scientists. [2]

Here, in this presentation, oxazine ring di-substituted benzoxazine monomer, PH-fa-[2,4]ph, i.e., phenyl ring as a substituent at both the oxazine-ring sp<sup>3</sup> carbon centers is synthesized at ambient room temperature (rt) and thermally polymerized to earn highly cross-linked polybenzoxazine thermoset, poly(PH-fa-[2,4]ph), as depicted in Figure 1.



Figure 1: Graphical abstract of the Oxazine-ring di-substituted benzoxazine monomers and polymers.

The installation of phenyl rings at the oxazine moiety has ensured several advantages compared to the unsubstituted BZ entities. [3] For instance, ROP temperature is lowered, as evident from DSC analyses, because of formation of a stable benzylic carbocationic zwitterion due to the oxazine ring-cleavage. TGA of monomer indicated lowering in mass-loss (i.e., vaporization) and TGA-GC-MS studies help to understand the polymerization mechanism by identifying the volatiles formed during thermal curing of PH-fa-[2,4]ph. Corroborating 1D- and 2D-NMR analyses, SC-XRD investigation, and Natural Bond Orbital (NBO) calculation, it is found that various intramolecular noncovalent interactions such as  $n(O) \rightarrow \sigma^*(C-H)$ , CH- $\pi$ , etc. and stereo-electronic effect of phenyl ring as oxazine ring-substituents play an active role in regulating thermal properties of such monomers. Moreover, the high aromatic content and availability of polymerization sites in these BZ monomers results into a highly cross-linked PBZ with high thermal stability, char yield and LOI as detected in TGA analyses of polybenzoxazines. Hence, structural engineering at the molecular level appears to be an effective technique to regulate properties of monomers and polymers, thus, in turn, establishing the importance of designing the latest formaldehyde-free 4<sup>th</sup> generation high-performance PBZ thermosets. [4]

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# Copper(ii) and cadmium(ii) triggered hydrogelation of a simple trimethoxy terpyridine ligand

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Supramolecular chemistry is one of the most advanced and fascinating branches of the research area in chemistry nowa- days [1]. Last few years, there has been a great interest to design small molecule which has the property of self-assembly. In particular, low molecular weight supramolecular hydrogels find extensive applications in medicinal chemistry, optoelectronics, drug delivery and organic-inorganic hybrid materials [2-4]. The hydrogels have a characteristic of flexibility, strength and self-recovery nature [5]. It has also been observed that the metal-driven self-assembly with hydrogelators has re- sulted in gel formation via complexation [6-8]. It has also been shown that hydrogels and metallogels can be fluorescent in nature [9].



Figure 1. Graphical abstract of the copper(ii) and cadmium(ii) triggered hydrogelation of a simple trimethoxy terpyridine ligand

In this regard, terpyridine and their metal complexes gained considerable interest due to their usage in the field of ion sensing, halogen bonding, gelation etc [10]. Herein, we report Cd(II) and Cu(II) triggered hydrogelation behavior of a terpyridine ligand containing methoxy substituent 4' -(3,4,5-trimethoxyphenyl)- 2,2':6',2''-terpyridine **L**. The cadmium-based hydrogel exhibits green fluorescence, while the copper-based hydrogel exhibits non-fluorescence in the presence of UV light. The Crystal structure of CdCl<sub>2</sub>**L** is also reported here.

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# A MOF Chemosensor for Highly Sensitive and Ultrafast Detection of Folic Acid in Biofriendly Medium, Paper Strips and Real Samples

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A new zirconium-based dansyl anchored metal-organic framework (MOF) bearing UiO-66 topology was synthesised by solvothermal procedure. The as-synthesised and activated form of the materials were stable up to 215 °C, and structural integrity remained unaltered in common organic solvents as well as in a wide pH range (2-12). **UiO@Dansyl** has a specific BET surface area of 1026 m<sup>2</sup>g<sup>-1</sup>. The FT-IR, FE-SEM and EDX studies with **UiO@Dansyl** confirmed that the material was pure enough for the application purpose. The activated material was utilised for the fluorogenic detection of folic acid (FA) in PBS buffer (pH 7.4). The probe showed highly sensitive (detection limit: 1.3 nM) and ultrafast (< 5 s) response toward FA. The detection limit is lower than known MOF sensors for FA. The fluorescence quenching efficiency of the probe by FA was around 95% whereas for other competitive analytes, the quenching was only 2-5%. The Stern-Volmer constant was found to be 9.2 × 10<sup>5</sup> M<sup>-1</sup>. The **UiO@Dansyl** was also applied for the detection of FA in food samples, human blood serum and urine. To be applicable for real-field purposes, a paper-strip device was fabricated for the on-site detection of FA. The d-PET mechanism of quenching in fluorescence intensity by FA was investigated in a systematic way with the help of TRPL, UV-Vis spectroscopy, pH titration and theoritical calculations are also attached in support of that mechanism. The above experimental findings indicated the superiority of **UiO@Dansyl** for detection and quantification of FA in bio-friendly medium.



**Fig. 1.** Change in fluorescence response of **UiO@Dansyl** (a) upon incremental addition of 5 mM FA (c) with respect to time upon injecting 300  $\mu$ L 5 mM FA. (b) Digital image of cuvette before and after addition of FA (d) Bar diagram of selectivity toward FA in presence of competitive analytes. (e) Lifetime decay profile of **UiO@Dansyl** (f) Detection of FA in food supplements.

# Lewis acid catalyzed reactivity switch: pseudo three-component annulation of nitrosoarenes and (epoxy)styrenes

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A lewis acid-catalyzed annulation reaction via arene functionalization of nitrosoarenes and C–C cleavage of (epoxy)styrene to provide arylquinolines is reported. Generally, nitroso functionality participates in the reaction of nitrosoarenes and styrene to yield nitrone and axazolidine, where arene moeity stays abstained in the reaction. Here we have developed a reaction for the C-H functionalization of nitrosoarenes that incorporates the arene moiety into the product. Normal annulation pattern of 1,3-dipolar cycloaddition reaction between nitrosoarene and styrene, alters to Pavarov-type reaction in presence of oxophilic lanthanide-based lewis acid which finally helps to achieve C-H functionalization of a Yb and Cu-catalyzed pseudo-three-component annulation reaction of nitrosoarenes with styrene or epoxystyrene providing a wide range of aryl quinolines<sup>1</sup>.





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# Organocatalytic Asymmetric Reaction between α-Cyano Enones and Dioxindoles: Synthesis of Dihydrofuran-Spirooxindoles

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The organocatalytic enantioselective synthesis of dihydrofuran-spirooxindoles having a linkage at the 2position of the dihydrofuran motif has been developed. Dioxindoles and  $\alpha$ -Cyano Enones were employed in this method. The desired spirooxindole products were obtained via a Michael reaction followed by a Pinner reaction and isomerization and good to high yields with excellent diastereo (>20:1 dr) and excellent enantioselectivities (up to 98% ee) were observed.



Figure 1. Graphical abstract of synthesis of dihydrofuran-spirooxindoles

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# A Self-Cleaning Hydrophobic MOF Based Composite for Highly Efficient and Recyclable Separation of Oil from Water and Emulsion

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A hydrophobic MOF (1'@CF<sub>3</sub>) was synthesized by post-synthetic modification to anchor -CF<sub>3</sub> group to the Zr- BDC-OH MOF (1'). The hydrophobic property of the MOF was used for the preparation of a robust hydrophobic composite (1'@CF<sub>3</sub>@melamine) with melamine sponge. The water contact angle of 1'@CF<sub>3</sub>@melamine was found to be 145  $\pm$  1°. The hydrophobic composite was demonstrated to separate oil-water mixtures and water-in-oil emulsions even under harsh aquatic environments. The oil-water and emulsion separations were carried out in easy and fast way without the consumption of energy. The absorption capacity and separation efficiency of the composite for a wide variety of oils were found to be 27-37 g/g and 95-99%, respectively. The material showed high recyclability up to 50 cycles for oil-water separation and for 30 cycles for oil-water emulsion separation. In addition, the hydrophobic MOF coated glass substrate displayed excellent self-cleaning properties. Furthermore, inexpensive and facile gravity-driven filtration and against the gravity-based separation techniques for different oils were developed by employing the composite.



Figure 1. Bar plot of separation efficiency (%) of  $1'@CF_3@$  melamine composite towards separation of: (a) various oils from oil-water mixtures, and (b) EtOAc from different types of aqueous media. Each measurement was repeated six times.



Figure 2. (a) Bar plot for separation efficiency (%) and (b) flux of 1'@CF3@melamine composite for various waterin-oil emulsions.

Keywords: Emulsion separation, Hydrophobic, MOF, Oil-Water separation, Self-cleaning.

# Novel cyclic peptidomimetic with attached copper chelating ligand inhibits Aβ fibrillogenesis

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Amyloid-beta peptide ( $A\beta$ ) misfolding and formation of toxic oligomer followed by fibril formation is one of the major causes of Alzheimer's disease. On the other hand, excessive deposition of copper, zinc and iron also promotes amyloid aggregation. In recent times, several cyclic peptides modified in various ways have been used as potential amyloid inhibitors. Head-to-tail cyclic peptides with alternating D, L amino acids inhibits amyloid formation significantly. Herein, we report our designed head-to-tail cyclic peptidomimetics with only one D-amino acid in the sequence that shows significant inhibition of amyloid aggregation when used in 2-fold molar excess to that of  $A\beta$ . In one of our designed peptidomimetics we have attached a copper chelating ligand and investigated its efficacy towards amyloid aggregation inhibition and confirmed by various bio-physicals tools such as thioflavin T (ThT) fluorescence assay, dynamic light scattering (DLS), transmission electron microscopy (TEM), and Congo-red stained birefringence studies. The non-toxicity of our designed cyclic peptidomimetics was confirmed by the MTT assay on the mouse neuronal cell line. Such peptidomimetics works synergistically, firstly by restraining the conformational change in  $A\beta$ -peptide and also restores metal ion homeostasis. Such peptidomimetics can be of great help in understanding the mechanism of  $A\beta$ -aggregation and can prove to be a novel therapeutic approach.<sup>1</sup>



Figure 1. Graphical representation of working mode of the cyclic peptidomimetics inhibiting Aβ-aggregation

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# Application of waste from paper industry as heterogeneous base catalyst for synthesis of biodiesel from from cottonseed oil.

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In the modern day world, there has been observed a drastic upsurge in need for petroleum resources, but to meet this ever increasing demand these resources alone are not sufficient and have its own limitations and drawbacks. Firstly, their sources are on the verge of exhaustion and non-renewable. Secondly, they release toxic gases such as NO<sub>x</sub>, SO<sub>x</sub>, CO<sub>2</sub> etc harmful to the environmental in general and to animals and plants kingdoms in particular. [1]. Hence, an alternative source of motive power is of utmost importance to meet this global crisis. In this regard, present day world is shifting its focus on producing biodiesel from oils or fats from renewable sources like plants, animals and algae etc. [2]. In our work, we use non-edible oil such as cottonseed oil as feedstock for biodiesel and waste from paper industry as heterogeneous catalyst. The catalyst used has been characterized for surface morphology, elemental analysis, functional groups present, crystallinity, basic sites, surface area etc. using SEM, TEM, EDS, FTIR, CO<sub>2</sub>-TPD, BET.[3]. It has been observed during reaction that there is a correlation between activity of catalyst and its basicity. The variables known to effect directly in the production and yield of biodiesel such as reaction time, temperature, catalyst concentration, oil to methanol molar reaction has been studied.[4]. And finally the biodiesel hence produced has been characterized using FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR.

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# Design, Synthesis and Study of Thermal Bergman Cyclisation and Photophysical Properties of Donor-Acceptor Enediynes

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Natural enediynes due to their unique molecular framework shows potent biological activity via the formation of reactive diradical species following Bergman Cyclisation pathway which can abstract proton from the DNA phosphate backbone causing cancerous cell death.<sup>1</sup>

This work elaborates on the possibility of the interaction of aromatic  $\pi$  donor and acceptor enediyne molecules. We aimed at bringing the reactive centres in either arm of the enediynes together through CT/ $\pi$ - $\pi$ -stacking interactions leading to lower Bergman Cyclization temperature.<sup>6</sup> In this line, a series of D-D, D-A, A-A enediyne molecule have been synthesized using sequential Sonogashira Reaction with various donor/acceptor aromatics. Their solid phase reactivities have been studied using Differential Scanning Calorimetry.<sup>3,4</sup> In addition, UV-Vis Study was carried out to explore the charge transfer properties of the synthesized enediynes.<sup>6</sup>



Figure 1. Donor-Acceptor Enediynes.

The trend of the rate of thermal BC observed was A/A > D/A > D/D. Through bond delocalisation of electronic charge density, is seen to play a critical role in lowering the temperature of BC as is revealed in the trend.<sup>4</sup> This might be because of the strong overlapping between the reactive molecular orbitals. <sup>1,2</sup> A flow of charge from the donor in one arm to the acceptor moieties in another arm of the enediyne or to and from the central ring through a bond possibly plays a crucial role in controlling the BC.

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# Diastereoselective synthesis of 2,6-disubstituted tetrahydropyranones *via* Prins cyclization of 3-bromobut-3- en-1-ols and aldehydes

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Tetrahydropyrans are the most common heterocyclic structures ubiquitously present in bioactive molecules and natural products.[1] Among them, substituted pyran motifs are structural core unit of numerous biologically active natural products such as diosniponol B,[2] exiguolide,[3] bryostatin 1[4] etc. Although there are various methods for the synthesis of tetrahydropyran moiety, Prins cyclization reaction is most convenient tool due to its excellent diastereoselectivity and carbon-carbon, carbon-heteroatom bond formation in a single step. Here, we have demonstrated a highly diastereoselective synthesis of tetrahydropyranones from 3-bromo-but-3-en-1-ols and aldehydes mediated by  $BF_3 \cdot OEt_2$  in good yields via Prins cyclization reaction (Scheme 1). The methodology is extended for the synthesis of enol ether, ester derivatives and 4-hydroxy 2,6-disubstituted tetrahydropyrans with 2,4- and 4,6-trans configuration and also extended towards the synthesis of aminoguanidine derivatives which are considered as anticancer agent.





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### I(III) Catalysed Oxidative Rearrangement reaction of Unactivated Anilines

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An I(III)-catalyzed Oxidative rearrangement reaction using Bis(Triflouroacetoxy)iodo benzene as oxidant has been developed that convert unactivated anilines into indolo[1,2-C]quinazoline via an N-aryl nitrenoide intermediate.



Scheme: Synthesis of indolo[1,2-C]quinazoline.

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### Glycosyl Ortho-[1-(p-MeOPhenyl)Vinyl]Benzoates (PMPVB) as Universal Donors for *O*-, *S*- and *C*- Glycosylation

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We have developed glycosyl *Ortho*-[1-(*p*-MeOPhenyl)Vinyl]Benzoates (PMPVB) as stable, yet reactive glycosyl donors that can be activated under Brønsted acid catalysis. The ability to activate these donors under simple Brønsted acid catalysis allow the stereo & regeoselective construction of *C*-*O*, *C*-*S*, and *C*-*C* in a very elegant fashion. The remarkable activity of these donors has also been utilized in the construction of the challenging protecting group independent 2-deoxy  $\alpha$ -*O*-glycosides and 2-deoxy  $\beta$ -*C*-glycosides. The difference in the free energies of the anomeric intermediates disclose the reasons for the observed unique reactivity.



Keywords: • PMPVB donors • Organocatalytic • O-, S- & C-glycosylations

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# Designing efficient single atom catalysts through atomic dispersion on advanced functional material for electrocatalytic OER activity

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With an aim to achieve paramount catalytic activity by categoric utilization of all the active metal centres, Single Atom Catalyst (SAC) has proven to be extremely efficient in versatile field of applications like chemical, thermal and electrocatalysis.<sup>1</sup> It has successfully mitigated the drawbacks of both homogeneous and heterogeneous catalysts such as limited active metal centres, product selectivity and separation issues, on account of its strong metal-support and metal-ligand type stabilization.<sup>2, 3</sup> To augment the catalytic activity, utilization of advanced functional materials like Mxenes, LDH, MOFs etc as anchoring support materials for single atom stabilization has produced an exponential growth in overall performance of the catalyst through a synergistic effect. In this line of interest, we have successfully synthesized Ni-Cr LDH based Iridium SAC system that has proven to be extremely efficient for electrocatalytic OER activity, operating at mere 240 mV overpotential with negligible current decay over 36 h of stability study. Phenomenal stability in both alkaline and simulated sea water medium, the SAC system has the potential to beat the state of art  $IrO_2$ 



Figure 1: Graphical abstract for Ir@Ni-Cr LDH SAC based electrocatalytic OER activity

catalyst in all possible ways. In this presentation, we are going to scrutinize the characteristic structure and catalytic activity through advanced characterization techniques.<sup>4</sup>

The SAC system was synthesized from the base material through a wet chemical approach and the morphological analysis were performed through electronic microscopy. Concrete evidence of single atom existence has been confirmed through advanced characterization studies like XAS and HAADF-STEM, fundamentally assured a perturbed electronic environment of material. This electronic redistribution has been confirmed through XPS binding energy as well as XRD peak shifting. Further quantification of exact oxidation state with deconvolution of atomic environment and coordination number of metal centre has been done through XANES and EXAFS fitting. This modified electronic distribution along with enhanced catalytic active centres has proven to be vital in the experimental electrocatalytic study. Complete electrocatalytic study has been done to rationalize the mechanism of catalytic cycle. **References** 

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# Improving Stability, Solubility, and In Vitro Permeation Behavior of drug Famotidine via Molecular Salt formulation

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Crystal engineering technique has been employed to resolve stability issue and poor physiochemical properties of drugs such as solubility, permeation behaviour and bioavailability.[1] Famotidine (FAM) is a histamine H<sub>2</sub>-receptor inhibitor drug that is used to treat peptic ulcers, gastroesophageal reflux, etc. But, the drug shows low bioavailability and rapid degradation in an acidic condition.[2] To resolve these issues, we synthesized six molecular salts of drug FAM with two sets of coformers from GRAS list, i.e., ismomeric hydroxybenzoic acids (HBAs) and isomeric aminobezoic acids (ABAs) via mechanochemical grinding in 1:1 ratio.[3] The obtained multicomponent solids were subjected to stability and physicochemical properties studies. These molecular salts showed better phase stability in comparison to the parent drug in acidic pH condition. They also displayed improved solubility and superior membrane permeability when compared with pure API. Improved properties exhibited by these solid forms is due to conformational change in the drug molecule depends on the strength of hydrogen bond heterosynthons formed in the crystal structures.



**Figure 1**. Graphical abstract of the isomeric position change of functional groups in the coformer facilitated drug conformation change that substantiates improved permeation behaviour by the salt formulation.

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# Self-assembled benzoselenadiazole-capped tripeptidehydrogels with inherent *in vitro* anti-tumor and anti- inflammatory activity

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The increasing number of cancer diseases and their associated mortality is one of the greatest threats to human life in the modern century. The ability of malignant tumor cells to develop resistance to several chemotherapeutic drugs creates a major obstacle in the treatment of cancer and therefore the search for new peptide based biomaterials<sup>1</sup> as anti-cancer compounds is promising in current drug research. Selenium-based organic compounds have attracted the attention of researchers since the anticancer activity of selenium based organic compounds was established. Our current work depicts the development of aromatic benzo[2,1,3]selenadiazole-5-carbonyl (BSe)-capped tripeptide hydrogels for investigating their inherent anti-cancer and anti-inflammatory activities.<sup>2</sup> We have designed and synthesized two sets of aromatic rich tripeptides BSeLYF (L = L-leucine; Y = L-tyrosine; F

= L-phenylalanine) and BSeLYW (W = L-tryptophan) to evaluate their self-assembling behavior. Furthermore, the BSe-capped tripeptide hydrogels have been examined in vitro using MCF-7 and HEK 293T cell lines to investigate their anti-proliferation behavior and inflammatory response. BSeLYF formed the hydrogel in PB (pH 7.4, 0.1 M) and BSeLYW formed the hydrogel in PB (pH 6.7, 0.1 M). The CD spectra of different concentrations (0.015 to 1 mM) of the BSeLYF and BSeLYW hydrogels indicated the formation of helical structure and the PXRD revealed the distance between the interstrand spacing within the  $\beta$ -sheets. The viscoelastic properties of the hydrogels were determined by rheology experiments and the formation of nanofibrillar structures were confirmed from TEM images. The anti-cancer efficiency of these BSe-capped tripeptide hydrogels was screened against malignant MCF-7 and noncancerous human embryonic kidney 293T (HEK 293T) cell lines by a dose-dependent MTT cell viability assay. The MTT cell viability results show that both BSe-tripeptide hydrogels exhibit significant inhibition of cell proliferation toward cancerous MCF-7 cell lines in a concentration-dependent manner. The ROS and qRT-PCR studies suggested that BSeLYF and BSeLYW hydrogels induce ROS overproductionand activate the intrinsic apoptotic pathway by the activation of Bax, CytC, Apaf and Caspase-9. Furthermore, the anti-inflammatory responses of the BSe-capped hydrogels were determined by measuring the  $TNF-\alpha$  and IL-6secretion levels. Overall, we have successfully developed BSe-capped two tripeptide hydrogels which exhibited inherent anti-cancer as well as excellent anti-inflammatory behaviours.

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## Copper(I) Mediated Cascade Annulation *via* Dual C–H/C–H Activation: Access to Benzo[*a*]carbazolic AEEgens

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A Cu(I) mediated cascade cyclization/annulation of unprotected o-alkynylanilines with maleimides in one-pot is developed. The protocol offers sequential formation of two C–C and one C–N bonds to deliver fused benzo[a]carbazoles having free NH skeletons. The annulated products display fluorescence emission in the range 485–502 nm with large Stokes shift and serve as AEEgen. Cell viability assays enumerate biocompatible AEEgens, while their high intracellular fluorescence depicts cell imaging applicability.



Figure 1. Synthesis of Benzo[*a*]carbazolic AEEgens

This protocol avoids the use of expensive transition metal catalyst and efficiently offers two consecutive ring formations involving one new C–N and two C–C bonds formation in a single pot with excellent functional group diversity. This strategy overcame challenges such as: i) homocoupling of 2-alkynylaniline ii) competitive N–H/C–H annulation from the N–H side; iii) stoppage of reaction at 2-phenylindole via protonation and reluctant to undergo subsequent annulation and, iv) overcoming the binding of the active Cu catalyst by the free amine employing AgNO<sub>3</sub> (which is trapped as a transient silver-amine complex).

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### Understanding the Propensities of Fluorescent Carbazole Analogs towards the Inhibition of Amyloid Aggregation

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Amyloid aggregation is an extreme trait in age-related diseases, e.g., Alzheimer's and Type II diabetes, related to the self-assembly and misfolding of various proteins. Among many amyloidogenic proteins, spontaneous misfolding of islet amyloid polypeptide (IAPP) tempts the assembly of amyloid fibrils as extracellular deposition on the pancreatic  $\beta$ -cells, which is one of the key factors of Type II diabetes [1]. To date, there are no approved drugs/therapeutic agents which can cure the occurrence and progression of amyloidosis related disorders. These limitations create a high demand for the design and synthesis of structurally modified inhibitors. It is noteworthy that carbazoles have concerned great attention as the inhibitory activity of  $A\beta$  amyloid aggregation [2]. However, extensive studies on their activity toward the prevention of islet amyloid aggregation are still rare. Although several carbazole alkaloids like mahanine, koenidine, and mahanimbine, isolated from the leaves of the plant Murraya koenigii Spreng. (commonly known as Indian Curry Leaf plant, Fam. Rutaceae), showed efficacy as antidiabetic agents in in vitro and in vivo systems [3]. Inspired by this here we have explored the propensities of five structurally different carbazole analogs towards the inhibition of amyloid aggregation.



Figure 1. Graphical abstract of amyloid inhibitory activity of carbazole analogs

Herein, five structurally different synthetic (1-4) and naturally occurring (5, mahanimbine) fluorescent carbazole analogs are explored for their comparative amyloid aggregation inhibitory activities. Here we have used human insulin as a model amyloidogenic protein. First, we have tested the insulin amyloid aggregation inhibitory activity of carbazole analogs (1-5) with the help of the thioflavin T (ThT) fluorescence assay. Circular dichroism (CD) and Transmission electron microscopy (TEM) was used to validate the population of  $\beta$ -sheet structures and confirm the morphological changes of amyloid aggregation in the presence of test compounds respectively. Among these five analogs, 3 and 5 effectively showed the inhibitory activity of insulin amyloid aggregation in *in vitro* and molecular docking studies, which also involved human IAPP. Furthermore, 3 exhibited therapeutic propensity by inhibiting the islet amyloid deposition on the pancreatic  $\beta$ -cells of diabetic mice. Carbazole analogs 3 and 5 (non-toxic) also showed efficacy as fluorescent cell (MIN6) imaging agents.

In future, structures of such carbazole analogs can be tailored more precisely to develop low-cost and non-toxic therapeutic agents for Type II diabetes and other amyloidosis related diseases.

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# Visible-Light Mediated Oxidative C-C Coupling of 2-Naphthol and Benzyl Alcohol Oxidation *via* HNT Embedded Fe(III) Superoxide

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Selective oxidation of 2-naphthol to BINOL and benzyl alcohols to aldehydes was achieved by activation of molecular oxygen (O<sub>2</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) over a low-cost iron-oxide catalyst embedded in halloysite nanotube [1]. The involvement of superoxide radical bound Fe<sup>III</sup> species in these oxidation reactions was evident from Electron spin resonance spectroscopy (ESR), Raman and *insitu* FTIR spectroscopic analysis. The analysis suggested the end-on binding of superoxide radical with Fe<sup>III</sup>-centre of the catalyst [2]. Furthermore, the stability of such radical bound Fe<sup>III</sup>-species in HNT was analysed through density functional theory (DFT) calculations and the results suggested that end-on ( $\eta^1$ ) binding mode was favoured by 13.5 kcal/ mol than the side-on ( $\eta^2$ ) binding mode. A great degree of selectivity in the catalytic oxidation of benzyl alcohol and the oxidative C-C coupling of 2-naphthol was thought to be brought about by the creation of such reactive species. The existence of an appropriate band gap of ~2.14 eV enabled the catalyst to catalyse the process under visible light irradiation [3]. Both the reactions were tested in presence of oxidants O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> at ambient temperature. In order to comprehend their significance in catalytic processes, it was researched how various parameters, such as oxygen flow rate, peroxide amount, solvent type, and catalyst amount, affected the conversion and selectivity of the reactions. The successful oxidation of 2-naphthol using H<sub>2</sub>O<sub>2</sub> as an oxidant was a real success in overcoming the drawbacks of this process utilising H<sub>2</sub>O<sub>2</sub> as an oxidant [4].



Figure 1. Graphical abstract of the selective oxidation of 2-naphthol to BINOL.

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# Development of protease resistant cationic heptapeptides with enhanced antimicrobial activity by incorporating D-amino acids

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Exaggerated use of antibiotics to treat bacterial infections have resulted in the emergence of antibiotic resistance in which evolving microbes are no longer prevented by the existing antibiotics available in the markets. Almost five million people died from diseases caused by resistant microbes in 2019 alone and this figure is expected to turn fifty million annually by 2050 [1]. Therefore, there is dire need for the development of new antibacterial agents with improved potency to deal with the resistant microbes. Antimicrobial peptides (AMPs) are a class of short peptide molecules found to be present in almost all classes of living organisms and act as a first line of defense against microbial attacks. Applications of antimicrobial peptides clinically to treat microbial infections are however limited by their high cytotoxicity and poor proteolytic stability [2]. The AMPs found in the nature are composed of L-amino acids which are recognized by the proteolytic enzymes. Use of D amino acids in the AMP sequence is a strategy to develop protease resistance resistant AMPs.



Here in this work, we modified two of our previously reported peptides P4 and P5 [3] incorporating D-amino acids replacing the L-amino acids either fully or partially. Partially D-substituted peptides (P4A, P4B, P5A, P5B) were found to have diminished antimicrobial activities, on the other hand the peptides wholly substituted with D-amino acids (P4C and P5C) were found to either retain or gain antimicrobial properties. All D-substituted peptides (P4C and P5) were found to be stable in the presence of a cocktail of enzymes in comparison to their parent analogues i.e., P4 and P5. Effect of the modified peptides P4C and P5C on bacteria cells and bacterial cell mimics as well as mammalian cells and mammalian cell mimics were studied using several biophysical and spectroscopic techniques like fluorescence, CD, NMR, ITC, FESEM, FETEM, FACS, confocal microscopy etc.

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### Peptide-Templated Hydrogel Beads and Capsules with Tuneable Surface Functionalization

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Hydrogel beads are a novel type of soft material wherein the excellent qualities of macro-dimensional hydrogels are infused into small, easily controllable, and robust droplets. Polymeric gelling components are generally utilized as the main building block of the bead network in most of the reported hydrogel beads because of their high structural stiffness and stability. However, this may result in a compromise in the functional properties of the beads. Herein, we report a simple and effective method of making peptide-based hydrogel beads using PyKC, a dipeptide hydrogelator that forms a redox responsive hydrogel in aqueous solution. [1] Unlike other peptide-based hydrogels, PyKC-based hydrogel beads do not dissolve in bulk aqueous/non-aqueous medium and retain structural and functional characteristics for a longer period of time. Because of the beads can be coated with multiple layers of a polymeric cross-linked network formed using poly-acrylates and poly-amines using the versatile Michael addition reaction. [2] Later, the polymeric shell can be further functionalised with hydrophobic or hydrophilic residues to control the surface wettability, immobilise catalytic enzyme (HRP) and protein (BSA), and perform host-guest chemistry. Furthermore, the peptide hydrogel core can also be removed to create hollow capsules with variable porosity and size. The easy surface functionalization of the beads and the templated production of hollow capsules may find applications in the construction of macro-reactors, delivery vehicles, and smart devices for material as well as bio-medical application.



Figure 1. Graphical abstract illustrating the fabrication of the peptide-templated hydrogel beads and capsules with tuneable surface functionalization

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# Electrochemical Amidation: Benzoyl Hydrazine/Carbazate and Amine as Coupling Partners <u>Tipu Alam</u>, and Bhisma K. Patel\* Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, Assam-781039, India

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An electrochemical amidation of benzoyl hydrazine/carbazate and primary/secondary amine as coupling partners via concomitant cleavage and formation of  $C(sp^2)$ -N bonds has been achieved. This methodology proceeds under metaland exogenous oxidant-free conditions producing N<sub>2</sub> and H<sub>2</sub> as by-products. Mechanistic studies reveal the *in situ* generations of both acyl and *N*-centered radicals from benzoyl hydrazines and amines. The utility of this protocol is demonstrated through a large-scale, and synthesis of Bezafibrate, a hyperlipidemic drug



Figure 1. Graphical abstract for electrochemical amidation.

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# Weak Coordination-Guided C4-H Alkylation of Indoles with Cyclopropanols *via* Sequential C-H/C-C Bond Activation

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The *N*-heterocyclic indole scaffold is a privileged substructure in the myriad of natural products, bioactive molecules.<sup>1</sup> Thus, site-selective C-H functionalization of indole core has become an important pursuit in organic synthesis.<sup>2</sup> In particular, design of efficient methodology for the selective editing of C4-H bond of indoles has gained considerable interest due to their conspicuous biological activity.<sup>3</sup> A Rh-catalyzed weak chelation-assisted C4-alkylation of indoles has been accomplished using readily accessible cyclopropanols as an alkylating agent *via* the cascade C-H and C-C bond activation (Figure 1).<sup>4</sup> The substrate scope, functional group tolerance, and late-stage mutation of drug molecules are the important practical features.



Figure 1. C4-H alkylation of indole via C-H/C-C bond activation

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# A comparative study of COD removal of Acid Orange 8 catalysed by iron based heterogeneous nano-catalysts

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The use of iron based heterogeneous nano-catalysts (HNC) such as iron oxides, zero valent, iron disulfides has gained a lot of attention in recent years for the application of wastewater treatment [1]. They are known for their abundance, rich content, low cost, easy preparation, non-toxic and high catalytic activity. In this study, we have compared the COD removal efficiency of an azo dye, Acid Orange 8 (AO 8) by hydroxyl radicals generated by activation of hydrogen peroxide (HP) using two different iron-based nano-catalysts, i.e., iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and iron disulfide (FeS<sub>2</sub>).



Figure 1. Graphical abstract for the degradation of AO 8 by iron based heterogeneous nanocatalysts

Iron oxide has been prepared by co-precipitation method [2] and iron disulphide by simple hydrothermal method [3]. They were further characterized by TEM, SEM, VSM, powder XRD, Raman spectroscopy and FT-IR. In Fe<sub>2</sub>O<sub>3</sub>/HP system, the COD removal efficiency was increased from 0.66 to 87.41% when the treatment period was increased from 90 to 240 min at optimum parameters ([Fe<sub>2</sub>O<sub>3</sub>] = 2.0 g/L; [HP] = 7.0 mM; [AO 8] = 0.3 mM; pH= 3). In FeS<sub>2</sub>/HP system, the COD removal efficiency was found to be less as compared to Fe<sub>2</sub>O<sub>3</sub>/HP system i.e., 36.42% in 240 min at their optimum parameters ([FeS<sub>2</sub>] = 4.0 g/L; [HP] = 7.0 mM; [AO 8] = 0.3 mM; pH = 3). pH plays an important role in the degradation of AO 8. In both the systems, the pH was varied from 3 to 11. It was observed that the highest COD removal was achieved at pH 3. This is due to the higher oxidation potential of hydroxyl radicals at pH 3 [4].

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### In-situ generated biopolymer carbon dots on paper as pH-sensitive for separation of oppositely charged dyes

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In this work, we have synthesized carbon dots directly on paper from biopolymer chitosan using a simple one-step thermal method [1]. The formation of the biopolymer carbon dots was confirmed with UV-Vis and Fluorescence spectroscopy. The morphology and the distribution of the carbon dots on the paper was analyzed using Field Emission Scanning Electron Microscope, Energy Dispersive X-Ray (EDX), Atomic Force Microscopy (AFM), Laser Confocal Microscopy (LCSM), X-ray Diffraction (XRD), and X-ray photoelectron Spectroscopy (XPS). The Fourier Transformed Infrared and Zeta potential measurements confirm the interaction of the dye with the carbon dots on the paper. The paper showed selectivity for negatively charged dyes in acidic and neutral pH due to protonated amines of carbon dot. In basic pH, there was no adsorption of anionic dye. Thus, a base was exploited as a medium to desorb anionic dye from carbon dot paperwith slight agitation and upto 76% can be recovered. The selectivity for anionic in acidic and neutral pH conditions of biopolymeric carbon dots was used to separate cationic and anionic dye from a mixture. The selectivity was found to be above 98% for a pair of different cationic and anionic dyes. This work demonstrates the ability of natural bio-precursors in the separation of oppositely charged materials. Furthermore, using paper as support, we have created a cheaper and more sustainable approach for dye separation [2].

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# Condition Dependent Thio-Claisen Rearrangement: Easy Access to Thiopyran and Furan Fused Chromen-4-ones Derived from 4-Hydroxythiocoumarin

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The synthesis of a variety of sulfur heterocycles is accomplished by employing thio-Claisen rearrangement [1] in the present work. The precursors of thio-Claisen rearrangement study were prepared by propargylation and allylation of 4-hydroxythiocoumarin (1), where the sulfur acts as a nucleophilic center. The S-propargyl-4H-chromen-4-ones (2) were subjected to [3,3]-sigmatropic rearrangement, which led to the interesting observation that the reaction is solvent dependent and results in regioselective ring closure of the rearranged products to produce 4H,5H-thiopyrano[2,3-b] chromen-5-ones (3) and 3-methyl-4H-thieno[2,3-b]chromen-4-ones (4), respectively.[2] On the other hand, S-allyl-4H-chromen-4-one (5) is much more resistant to Claisen rearrangement, but a successful reaction was carried out in presence of triethyl amine as a nucleophilic catalyst followed by regioselective ring closure to form 3-methyl-2,3-dihydro-4H-thieno[2,3-b]chromen-4-one (6).[3]



Figure 1. Synthesis of new sulfur heterocycles via thio-Claisen rearrangement

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# Hydrogen by Deuterium Substitution in an Aldehyde Tunes the Regioselectivity by a Nonheme Manganese (III)-Peroxo Complex

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Mononuclear nonheme Mn<sup>III</sup>-peroxo complexes are important intermediates in biology, and take part in oxygen activation by photosystem II.[1,2] Herein, we present work on two isomeric biomimetic side-on Mn<sup>III</sup>-peroxo intermediates with bispidine ligand system and reactivity patterns with aldehydes. The complexes are characterized with UV-Vis and mass spectrometric techniques and reaction rates with cyclohexanecarboxaldehyde (CCA) are measured. The reaction gives an unusual regioselectivity switch from aliphatic to aldehyde hydrogen atom abstraction upon deuteration of the substrate, leading to the corresponding carboxylic acid product for the latter, while the former gives a deformylation reaction.



Figure 1. Oxidants investigated and products obtained in the deformylation of substrates by Mn<sup>III</sup>-peroxo intermediates

Mechanistic details are established from kinetic isotopic effect studies and density functional theory calculations. Thus, replacement of C-H by C-D raises the hydrogen atom abstraction barriers and enables a regioselectivity switch to a competitive pathway that is slightly higher in energy.

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### Hydroxyl radical mediated COD removal studies of water soaked with *Pinus kesiya*

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The subtropical pine (*Pinus kesiya*, the Khasi pine as is locally known) forests in India are found in Khasi and Jaintia Hills of Meghalaya, Arunachal Pradesh, Nagaland, and Manipur. The use of pine cone and bark as natural adsorbents in the recovery of low concentrations of heavy metals has gained importance in recent times as they have the capacity to bind and accumulate heavy metals [1,2]. A preliminary investigation undertaken in our laboratory shows that Chemical Oxygen Demand (COD) of water soaked with 10 g of dry pine cone in 100 ml water for 24 hours increased to 208 ppm against the permissible limit of 90±3 ppm. Thus, the environmental impact of the presence of huge amount of pine cone/bark/needle in water bodies of Meghalaya is a matter of concern. The hydroxyl radicals generated by the catalytic decomposition of  $H_2O_2$  (HP) by  $Fe^{2+}$  were used to study the COD removal efficiency (COD<sub>eff</sub>) of water soaked with pine cone (WPC). Optimization of concentration of  $Fe^{2+}$  and HP were carried out, the optimal parameters for effective COD removal was found to be 0.3 and 3.0 mM respectively. pH is an essential parameter for the generation of hydroxyl radical in this process [3], the effect of pH on COD<sub>eff</sub> was studied by varying the pH from pH 3 – 11, and the efficiency was found to be highest at pH 3.0. Under optimal parameters, the COD<sub>eff</sub> of WPC was found to be 51.61 % at 300 min of reaction. It was also found that the presence of anions inhibits the COD removal efficiency of WPC and it was found that Cl<sup>-</sup> possess highest inhibitory effect compared to  $SO_4^2$ - and  $NO_3^-$ .



Fig. 1: COD removal of WPC at different treatment period:  $[Fe^{2+}] = 0.3 \text{ mM}$ ; [HP] = 3.0 mM, pH = 3.0

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# **P-162**

# Insights into Molecular Conformation Directed Aggregation Induced Emission and Detection of Melamine in Adulterated Milk

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Substituted cyclohexane is an integral part of natural products and their conformational isomers have great importance in medicine, biology, and supramolecular chemistry. In our work, molecular conformation directed aggregation induced emission (AIE) luminogen NMICY (naphthalimide methylcyclohexane) was prepared and its pure equatorial conformer was isolated and characterized via single crystal X-ray diffraction (SC-XRD) analysis. In NMICY, the methyl-cyclohexane substituent adopted the most stable chair conformation which remarkably prevented the intermolecular  $\pi$ - $\pi$  interaction among the naphthalimide cores



Figure 1. Graphical abstract of the Confirmation directed AIE of NMICY and a-PET sensing of Melamine.

and introduced a unique concept of J\* aggregation pattern (first report). A large bathochromic shift of ~80 nm along with a large stroke shift of ~100 nm in NMICYs condensed state was observed and potentially transformed the aggregation-caused quenching (ACQ) 1,8-naphthalic anhydride (NA) molecule into aggregation induced emission (AIE) luminogen (NMICY). The condensed state structure property in aqueous media and supramolecular self-assembly behaviour of NMICY were optimized, and a facile strategy for melamine detection in milk and aqueous milk powder is reported with a limit of detection (LOD) value of 0.184 ppm (milk) and 0.101 ppm (milk powder) was achieved via the rare acceptor-excited photoinduced electron transfer (a-PET) sensing mechanism. Further, smartphone-based portable sensing analysis broadened and simplified the melamine detection process.

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