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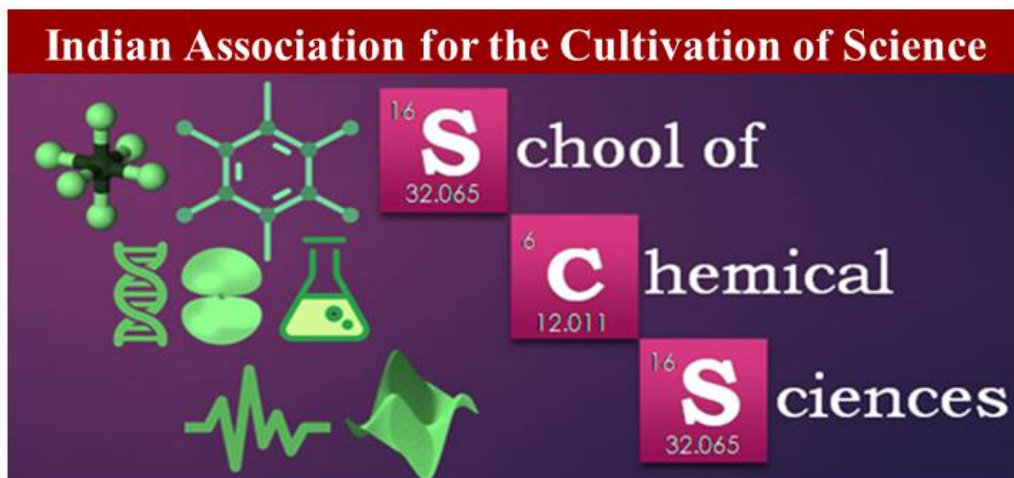
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Innovations and Advances in Chemical Sciences (InAdvanCS-2021-2)
March 02, 2021

The research domain of Chemical Sciences is growing at a phenomenal pace. It is necessary to organize symposia and conferences on various aspects of it at regular intervals for the benefit of the researchers in Chemical Sciences. Considering the potential interdisciplinary applications of Chemical Sciences, it would be desirable to have interactions among the practitioners of this field. With this objective in mind, the School of Chemical Sciences, Indian Association for the Cultivation of Science (IACS), is organizing a symposium on *Innovations and Advances in Chemical Sciences-2021-2* on March 02, 2021 at IACS, Kolkata. The objective of the symposium is to provide state-of-the-art review of the recent innovations and advances in Chemical Sciences and to project future directions aiming at addressing the pressing issues of the time. It is hoped that this meeting will bring together scientists in a stimulating and friendly environment that would foster collaborations between researchers and students. The lecture sessions will be supplemented by discussions to encourage the research students and young scientists for intensive academic interaction with the leading scientists. The webinar will be a stimulating and exciting meeting at IACS.

Speakers

Prof. Tapan Paine, IACS
Prof. Abhishek Dey, IACS
Prof. Suhrit Ghosh, IACS
Dr. Joyram Guin, IACS
Prof. Ayan Datta, IACS
Dr. Debashree Ghosh, IACS

Chairs

Prof. J. N. Moorthy, Director, IISER TVM
Prof. G. Muges, Dean, IISc
Prof. R. B. Sunoj, IIT Bombay

Further information on the symposium can be found in the following web site:
<http://www.iacs.res.in/school-chemical-sciences-scs.html>



Innovations and Advances in Chemical Sciences, (InAdvanCS-2021-2)

School of Chemical Sciences
Indian Association for the Cultivation of Science

Date: March 02, 2021

Programme Schedule

Link: meet.google.com/vee-pduv-gof

10:15 AM - 10:30 AM Inaugural address by Prof. Santanu Bhattacharya, Director, IACS

Session 1

Chairperson: Professor J. N. Moorthy, Director, IISER Trivandrum

Time	Speaker	Title of the talk
10:30 AM -11.30 AM	Prof. Suhrit Ghosh	Programmed Supramolecular Assembly of (Macro)molecules and Protein
11.30 AM -12.30 PMn	Dr. Joyram Guin	Oxidative Radical C-H Bond Functionalization with O ₂

12.30 PM – 1:50 PM: Lunch Break

Session 2

Link: <https://meet.google.com/nrj-oujm-ttr>

Chairperson: Professor G. Mugesh, Dean. IISc Bangalore

Time	Speaker	Title of the talk
2:00 PM - 3:00 PM	Prof. Tapan Kanti Paine	Bioinspired Approaches to Selective Catalytic Oxidations by Nonheme Iron Complexes
3.00 PM – 4.00 PM	Prof. Abhishek Dey	Rational Design of Electrocatalyst for CO ₂ Reduction

Session 3

Link: <https://meet.google.com/rbv-nmbp-zte>

Chairperson: Professor R. B. Sunoj, IIT Bombay

Time	Speaker	Title of the talk
4:00 PM - 5:00 PM	Prof. Ayan Dutta	Tunneling and Oriented External Electric Field: Harnessing them for Catalysis
5.00 PM – 6.00 PM	Dr. Debashree Ghosh	Singlet Triplet gaps in polyaromatic hydrocarbons - role of spin frustration and strong correlation

Abstracts

Programmed Supramolecular Assembly of (Macro)molecules and Protein

Suhrit Ghosh

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Abstract: Classical surfactants or amphiphilic block-copolymers produce distinct nanostructures, relevant in applications ranging from biology to materials science. Nevertheless, their immiscibility-driven aggregation does not endow the opportunity to precisely regulate the internal order, predictable morphology or functional group display, which are highly desirable, especially in the context of biological applications. We have introduced a new class of amphiphiles (polymers, small molecules and proteins) in which the assembled-structure can be fully regulated by the specific molecular-recognition motif of an appended hydrophobic Supramolecular-Structure-Directing-Unit (SSDU), which is fundamentally different than the repulsive solvent-immiscibility driven aggregation of traditional amphiphiles. This has enabled: (i) Entropy-driven precision aqueous self-assembly of SSDU-attached hydrophilic polymers with predictable morphology by superseding the classical packing parameter-based norms (ii) Synthesis of unsymmetric polymersome with distinct functional group display at the inner and outer membrane and (iii) Formation of stimuli-responsive protein-nanostructures with remarkable stability (against thermal denaturation or enzymatic hydrolysis) and temperature/ redox-responsive enzymatic activity regulation. Such well-defined nano-assemblies exhibit specific biomolecular surface recognition by efficient multivalent binding, resulting in excellent antibacterial activity, glycocluster effect and enzyme inhibition. This presentation will discuss recent results from our group in this area.

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Oxidative Radical C-H Bond Functionalization with O₂

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Abstract: Oxidative functionalization of ubiquitous and inert C-H bonds has occupied an important place in organic synthesis. In view of the growing demand toward green and sustainable chemical process, molecular oxygen (O₂) is recognized as an ideal oxidant for the oxidative organic transformations. In the seminar, the concept of generating several valuable alkyl/acyl radicals via aerobic oxidation of aldehyde will be introduced. It will be shown that O₂ is capable of promoting direct acylation/alkylation of unactivated C-H bond via radical addition¹, addition/cyclization² and addition/migration cascade reactions.³ Furthermore, dioxygen activation employing auto-oxidation of aldehyde and its utilization in developing Pd-catalyzed aerobic C-H hydroxylation process will be presented during the lecture.⁴ In addition, some recent findings of our group on asymmetric NHC-catalysis will be discussed during the lecture.⁵

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Bioinspired Approaches to Selective Catalytic Oxidations by Nonheme Iron Complexes

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Dioxygen activating nonheme iron enzymes catalyze a diverse array of biological oxidations such as hydroxylation of aliphatic C-H bonds, *cis*-dihydroxylation/epoxidation of alkenes, halogenations etc.^[1] High-valent metal-oxo intermediates have been implicated as active oxidants in these enzymatic reactions. Inspired by the biological oxidations by nonheme enzymes, several synthetic iron catalysts have been developed.^[2,3] However, selective electron transfer for the reductive activation of dioxygen without quenching the active species remains a major issue in performing bio-inspired oxidation catalysis with dioxygen. Hence, most of the bio-inspired catalysts developed so far had to shunt this reduction process with peroxides or other oxidants.^[3] But many of the catalytic systems often exhibit non-selective oxidation of substrates due to the involvement of free radicals generated in the catalytic conditions.

To address these challenges, we have been exploring several biomimetic approaches towards dioxygen and peroxide activation.^[5a-h] These studies provided useful insight into the development of bioinspired catalysts. In case of peroxide activation, generation of metal-based oxidant through heterolytic O-O bond cleavage of iron(III)-OOH(R) may be tuned by using Lewis/protic acid or by taking the advantage of secondary coordination interactions.^[4] In that direction, we have developed several bioinspired iron complexes that activate dioxygen/peroxides leading to the generation of iron-oxygen oxidants.^[5] The active oxidants thus generated exhibit versatile reactivity toward hydrocarbon substrates. The role of Lewis/protic acid and secondary interactions on the reactivity of iron(III)-OOH(R) species have been evaluated.^[5d-e] The reactivity of the peroxide-derived iron-oxygen oxidants and the ability of the complexes in performing selective catalytic oxidations will be presented in the talk.

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Rational Design of Electrocatalyst for CO₂ Reduction

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Iron and Co complex with covalently attached proton transfer motifs are tuned to reduce CO₂ to CO as well as formic acid selectively under different experimental conditions. The selectivity is governed by relative binding affinity of the reduced Fe centre towards CO₂ and H⁺ which in turn can be tuned by utilizing the distal functional groups. Resonance Raman spectroscopy, FTIR and electrochemical techniques are used to elucidate the reaction mechanism. The role of different intermediates in governing the selectivity will be illustrated. The tailor-made complexes are demonstrated to be among the most selective and efficient electrocatalysts to be developed till date.

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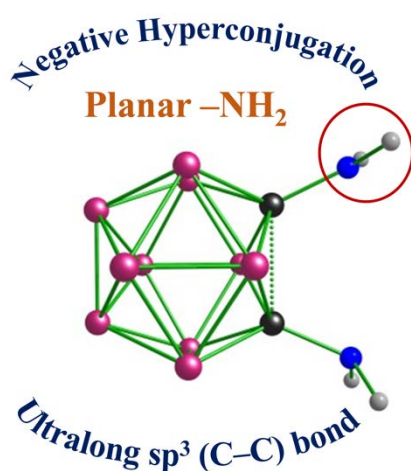
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Tunneling and Oriented External Electric Field: Harnessing them for Catalysis

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Abstract: Classical interpretation for the kinetics of chemical reactions involves the rate of crossing of barriers by the molecules. Hence, most of the mechanistic studies across chemistry have been to reduce the barrier height by stabilizing the transition state (TS). Nevertheless, many molecules undergo chemical transformations through direct quantum tunneling rather than climbing the barrier. This leads to counterintuitive products for many reactions particularly at low temperatures. The talk will focus on few computational studies on such reactions where tunneling plays a very important role even at not so low temperatures. Apart from tunneling oriented electric field has also been utilized to catalyze reactions. Few examples from our research group will be discussed.



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Singlet Triplet gaps in polyaromatic hydrocarbons - role of spin frustration and strong correlation

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Abstract: Polyaromatic hydrocarbons (PAHs) such as acenes have long been studied due to its interesting optical properties and low singlet triplet (ST) gaps, which has a plethora of applications from molecular magnetism to singlet fission. Earlier studies^{1,2} have already noticed that use of complete valence active space is imperative to the understanding of its excited state properties. Since complete active space based methods are computationally unaffordable for such large valence spaces, we have used density matrix renormalization group (DMRG)³ based approaches. Further small modification to the PAH topology shows interesting new phases of behavior in its optical gaps. We have understood the crucial effect of spin frustration from a combined molecular and model Hamiltonian perspective.⁴

While DMRG provides us with a powerful approach for pseudo 1D PAHs, it cannot be easily extended to more general cases. Therefore, new methods have been developed with artificial neural networks to stochastically model the Hilbert space of 2D PAHs.⁵

A rational design principle is suggested to tune the ST gaps and a robust general method is developed to compute these properties.

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