



Asian Meeting on Metal Oxide Assemblies 2017 (AMMOA 2017)

Abstract Book

9th May 2017 – 10th May 2017

Scope of the conference

Design and application of functional architecture is an immediate challenge in chemistry. Owing to the coordinative flexibility, redox variation and existence of multiple metal centres coupled with the possibility of super-structure and hybrid materials formation, metal oxide based assemblies have emerged as an inorganic material of choice for designing of such diverse functional architecture. Since the structure is known in atomic details down to the last atom and the structure can be tailored following the functional requirement such assemblies have found applications ranging from catalysis, medicine to materials design. This meeting will present a synthesis of fundamental oxometalate design and their diverse applications from catalysis to medicine threaded together by their nanoscopic nature. The focus will be to demonstrate how as a coordination chemistry model system oxometalate nanoarchitecture branch out to diverse aspects of materials design that finally leads to diverse applications and it will highlight the efforts of Asian researchers in the milieu of leading international practitioners in design and application of metal oxide assemblies.

Invited speakers

Prof. Craig L. Hill

Dr. Graham Newton

Prof. Yoshihito Hayashi

Prof. R. Murugavel

Prof. Anjali Patel

Dr. Sebastian Peter

Prof. A. Ramanan

Prof. Samar K. Das

Dr. C. P. Parameswaran

Dr. Ayan Banerjee

Dr. Boomi Shankar

Program of Asian Meeting on Metal Oxide Assemblies 2017

9th May 2017:

- 8:30 Registration
9:45 Inauguration
Welcome address
Prof. R. N. Mukherjee, Director, IISER Kolkata
- Session 1: Polyoxometalates in Catalysis*
Chair: Prof. R. N. Mukherjee, IISER Kolkata.
- 10:00-10:45 “Polyoxometalates in Solar Fuels Research”
KL-1: Prof. Craig L. Hill, Emory University, USA
- 10:45 Tea break
Chair: Dr. Abhishek Dey and Dr. Sayan Bhattacharyya
- 11:00-11:30 “Ab initio synthesis of polyhedral zinc phosphates and their polyoxometallate conjugates”
IL-1: Prof. R. Murugavel, IIT Bombay, India
- 11:30-12:00 “Hybrid molecular metal oxides as tunable catalysts and supramolecular building blocks”
IL-2: Dr. Graham Newton, Nottingham, UK
- 12:00-13:00 Soundbites *Coordinator: Dr. Sayam Sen Gupta*
13:00 Lunch
14:30-16:00 Poster Session
- Session 2: Polyoxometalates and Materials Science*
Chair: Prof. S. Bhattacharya, Jadavpur University, Kolkata
- 16:00-16:45 “Vanadium Chemistry of Polyoxometalates”
KL-2: Prof. Yoshihito Hayashi, Kanazawa University, Japan
Chair: Dr. Venkataramanan Mahalingam, IISER Kolkata.
- 16:45-17:15 “Keggin type Polyoxomolybdates: From Design to Catalytic Applications”
IL-3: Prof. Anjali Patel, MS University Baroda, India
- 17:15-17:45 “Decavanadate Based Hetero-metallic Inorganic-organic Hybrids as Highly Active Electrocatalysts for Hydrogen Evolution”
IL-4: Dr. Sebastian Peter, JNCASR, India
Chair: Dr. Suman De Sarkar, IISER Kolkata.
- 17:45-18:05 “Iridium(III) Mediated Reductive Transformation of Closed-Shell Azo-Oxime to
Open-Shell Azo-Imine Radical Anion”
CL-1: Dr. Sanjib Ganguly, St. Xavier’s College, Kolkata, India
- 18:05-18:25 “Stabilization of Open Shell Pi-Radicals and their Activities”
CL-2: Dr. Prasanta Ghosh, R. K. M. Residential College, Narendrapur, Kolkata, India
- 18:30 Dinner

10th May 2017:

Session 3: Polyoxometalates and Crystal Engineering

Chair: Dr. Chilla Malla Reddy, IISER Kolkata

10:00-10:45 “Crystal engineering of photoluminescent chromium molybdate cluster based solids”

KL-3: Prof. A. Ramanan, IIT Delhi, India

10:45 Tea break

Chair: Prof. D. K. Maiti, University of Calcutta, India.

11:00-11:30 “Supramolecular Chemistry with Polyoxometalates: Molecule to Material, Unusual Isolation and Catalysis”

IL-5: Prof. Samar K. Das, UoH, India

11:30-12:00 “Hybrid polyoxometalates as multifunctional materials, photoresists, green catalyst and antioxidants”

IL-6: Dr. C. P. Parameswaran, IIT Mandi, India

12:00-13:00 Soundbites-II *Coordinator: Dr. Sayam Sen Gupta*

13:00 Lunch

14:30-16:00 Poster Session

Session 4: Polyoxometalates and diverse applications

Chair: Dr. Debajyoti Ghoshal, Jadavpur University, Kolkata.

16:00-16:30 “Pens with Bubbles: Patterning SOMs using microbubbles in thermo-optical tweezers”

IL-7: Dr. A. Banerjee, IISER Kolkata

16:30-17:00 “Functional Metal Oxide and Metal Halide Self-assemblies Supported by Multi-Site Main Group Ligands”

IL-8: Dr. Boomi Shankar, IISER Pune, India

Chair: Dr. Biplab Maji, IISER Kolkata.

17:00-18:00 Student Lectures (4 lectures 15 minutes each)

18:00 Vote of thanks

18:05 High Tea and Departure

Organizers

Prof. R. N. Mukherjee (Patron)

Dr. Soumyajit Roy (Convener)

Dr. Venkataramanan Mahalingam (Co-convener)

Dr. Raja Shunmugam (Co-convener)

Dr. Chilla Malla Reddy

Dr. Pradip Kumar Ghorai

Dr. Ratheesh Vijayaraghavan

Dr. Pradip Kumar Tarafdar

Dr. Sanjio S. Zade

Dr. Priyadarshi De

Dr. Supratim Banerjee

Dr. Suresh K. Devrajalu

Dr. Sayam Sen Gupta

Dr. Suman De Sarkar

Dr. Biplab Maji

Dr. Dibyendu Das

Dr. Mousumi Das

Contents

Keynote Lectures	8-10
Invited Lectures	12-21
Contributed Lectures	23-24
Student Lectures	26-28
Posters	30-53

Keynote Lectures

Polyoxometalates in Solar Fuels Research

Craig L. Hill

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Transition-metal oxygen-anion clusters (polyoxometalates or “POMs”) have become very popular targets of fundamental and applied research because they are compatible with air and water, highly tunable through synthesis, and have extensive redox and acid-base properties. This ensemble of properties makes POMs attractive for use in several applications, with several catalytic ones already commercialized. Solar fuel production (artificial photosynthesis) is the direct conversion of sunlight and low energy molecules (primarily H₂O and CO₂) into fuel (H₂ or carbon-based fuels) and O₂. Three components or tasks are needed to generate solar fuel(s): (a) a photosensitizer (PS; molecule or material) that absorbs light and separates charge in its excited state; (b) a water oxidation catalyst (WOC) that can capture the positive hole in the excited state and accumulate the four oxidizing equivalents needed to oxidize H₂O to O₂; and (c) a reduction catalyst that can take the electrons from the PS excited state (supplied by H₂O via the WOC) and reduce either H₂O to H₂ and/or CO₂ to carbon based fuels.

POMs have proven to be versatile, yet robust PS, WOCs and reduction catalysts or components of these. POMs have enabled many fundamental aspects of catalytic water oxidation to be examined, including electron transfer to molecular PS, such as [Ru(bpy)₂]^{2+*} or photoelectrodes. The synthetic, physical, electrochemical, catalytic and photochemical aspects of POM WOCs, PS and reduction catalysts will be presented.

Vanadium Chemistry of Polyoxometalates

Prof. Yoshihito Hayashi
Kanazawa University, Japan

The smaller ionic radius of vanadium prefers the smaller coordination number, and VO_4 , and especially VO_5 square pyramidal coordination mode is typical in polyoxovanadate chemistry. The representative polyoxovanadate is decavanadates and only polyoxovanadates that are stable in aqueous solution. The availability of VO_4 , VO_5 , and VO_6 coordination spheres gave a unique character in the vanadates. Despite the fact that only stable polyoxovanadate is a decavanadate, there are many polyoxovanadate species not yet explored, when the equilibrium and the lability of vanadium atoms is controlled in organic solvent. Many new polyoxovanadate architectures emerge with a block, spherical or disk structures and those has a flexible nature inherent in vanadium chemistry. The increasing number of new polyoxovanadates are demonstrated and the implication in a future polyoxometalate chemistry.

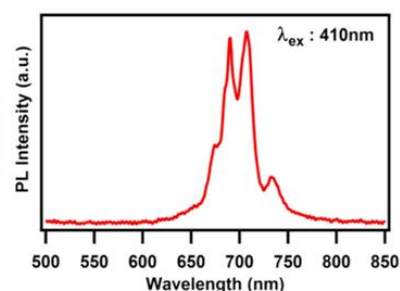
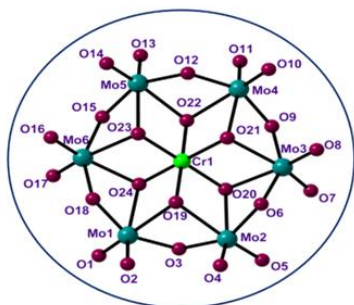
Crystal engineering of photoluminescent chromium molybdate cluster based solids

Arunachalam Ramanan

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Rational design of crystalline solids with built in functional properties still remains a dream. In this context, questions relating to the prediction of a target framework, for example, polyoxomolybdates (POM) is significant.¹ POM are well-known class of metal–oxo anionic clusters that encompasses species with a large variety of shapes and compositions, as well as applications in fields of catalysis, electronics, magnetism, medicine, energy. POM cluster based solids may be better understood if we adopt *a posteriori* analysis of the crystal structures in terms of the reactivity between chemically conceivable molecular building blocks. Among the POMs, the disk-shaped Anderson-Evans cluster anion, $\{XMo_6O_{24}\}^{n-}$ is well-known which occurs as a building block in several POM based solids. The in situ formed cluster is a versatile ligand to assemble into multidimensional structures with appropriate molecules or metal complexes either through H-bonding or metal-ligand interaction or both. The

chromium analogue is particularly unique as it exhibits red emission and can be considered as molecular equivalent of ruby (chromium doped alumina). The unique photoluminescence behavior of the Anderson-Evans cluster, $[H_xCrMo_6O_{24-x}]^{n-}$ was



first investigated by Yamase and his group almost two decades ago. In this talk, we discuss our recent results on the engineering of new photoluminescence materials employing $\{CrMo_6O_{24}\}$ as a building block coordinated with lanthanide ions that are potential emitters.

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Invited Lectures

***Ab initio* synthesis of polyhedral zinc phosphates and their polyoxometallate conjugates**

Ramaswamy Murugavel

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Our laboratory has been employing an organic soluble organophosphate (ArO)P(O)(OH) (Ar = 2,6-diisopropylphenyl) as the primary building unit (PBU) to assemble polyhedral molecules that resemble one or more zeolite secondary building units (SBUs).¹⁻⁵ Reaction of this phosphate with a divalent metal ion (e.g. Zn²⁺) in a donor solvent (L) predominantly leads to the isolation of stable tetranuclear metal phosphates [(ArO)PO₃Zn(L)]₄ which possess a Zn₄O₁₂P₄ inorganic core resembling the zeolitic D4R SBU. In recent times we have unraveled that it is possible isolate other SBUs from the same set of reactants by making small variations in the reaction conditions.¹⁻⁶ Thus, the hitherto unknown discrete D6R and D8R SBUs (which possess Zn₆O₁₈P₆ and Zn₈O₂₄P₈ cores, respectively) have been isolated by switching the solvent from methanol to acetonitrile and the co-ligand from DMSO to either 4-formylpyridine or 4-cyanopyridine.^{5b} A rationalization of these building principles and the application of this type of compounds will be presented, with particular emphasis on the catalysis by zinc phosphate-polyoxometallate hybrid materials. A part of the talk will also highlight on the aspects of oxo-imine exchange reactions in hexamolybdate systems.⁷

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Hybrid molecular metal oxides as tunable catalysts and supramolecular building blocks

Graham Newton

University of Nottingham, Nottingham

Molecular metal oxides are characterised in large part by their rich redox and photochemistry, leading to applications in catalysis, nano-scale electronics and magnetism. They can be organofunctionalised to form organic-inorganic hybrid systems with new synergic properties. Here recent findings on the tunable redox properties, photochemistry and supramolecular assembly of hybrid molecular metal oxides will be discussed.

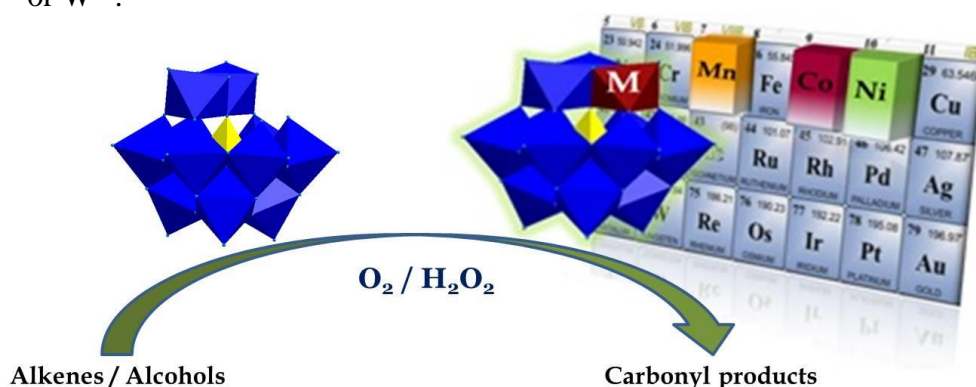
Keggin type Polyoxomolybdates: From Design to Catalytic Applications

Prof. Dr. Anjali Patel

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Polyoxometalates (POMs) are a rich class of inorganic metal-oxide cluster compounds with transition metals in their highest oxidation state and have the general formula $[X_nM_mO_y]^{n-}$, in which X is the hetero atom, usually a main group element (e.g. P, Si, Ge, As) and M is the addenda atom, being a d-block element in high oxidation state, usually V^V , Mo^{VI} or W^{VI} .



Our research is mainly focused towards the developing of new generation catalysts based on modified precursors of POMs with enhanced properties of acidity, redox potential and stability [1,2]. The modification of properties can be basically done by tuning the structural properties at the atomic or molecular level in two ways: (i) By creating defect (lacuna) in parent POM structures (i.e. Lacunary Polyoxometalates, LPOMs) and (ii) incorporation of transition metals into the defect structures (Transition Metal Substituted Polyoxometalates, TMSPOMs). Further modification can be done by functionalization of TMSPOMs.

The present talk describes the design of various catalytic materials based on phosphomolybdates as well as utilization of Lacunary Phosphomolybdates and Transition Metal Substituted Phosphomolybdates as redox catalysts in a number of organic transformations such as oxidation of alkenes and alcohols using environmentally benign oxidants [3-5].

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Decavanadate Based Hetero-metallic Inorganic-organic Hybrids as Highly Active Electrocatalysts for Hydrogen Evolution

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Polyoxometalates (POMs), a class of redox facile metal-oxy anion clusters, are strongly emerging as efficient, cheap, precious-metal-free electrocatalysts for hydrogen evolution reaction (HER).^{1,2,3} We have synthesized, three decavanadate ($V_{10}O_{28}^{6-}$) based supramolecular inorganic-organic hybrids (**1**, **2** and **3**) using different ligands (2,2'-bipyridine: **1**, 4-amino pyridine: **2**, and ethylene diamine: **3**) and Cu as the secondary transition metal (in two of them, **1** and **2**) for electrocatalytic HER applications. Single crystal analysis revealed that in **1**, the Cu (octahedrally coordinated) was directly linked to the decavanadate unit while in **2**, Cu formed a separate octahedral complex that was linked to the decavanadate unit only through non-covalent interactions. **3** exhibited excellent HER activity as cathode in acidic media with an onset overpotential of only 80 mV, charge transfer resistance (R_{CT}) as low as 90 Ω at -100 mV (vs RHE) and the catalytic current density of 50 mA.cm⁻² was reached at an overpotential of 200 mV. The Tafel slope, 87 mV.dec⁻¹, indicates that HER follows spill over mechanism in case of **3**. The comparative activity order followed as 3>2>1, where the onset overpotential for **2** and **1** were at 130 mV and 260 mV respectively. The trend suggests that there is a synergistic effect of both the transition metals (Cu and V) towards the catalysts' HER activity. Theoretical and experimental studies are going on to understand the role of structural, electronic and conductive properties of the three hybrids in determining the relative HER activity.

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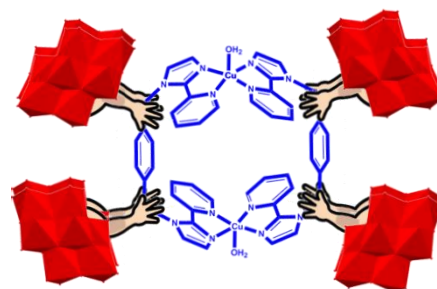
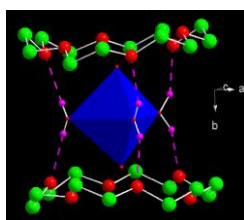
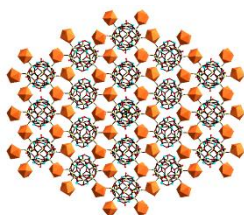
Supramolecular Chemistry with Polyoxometalates: Molecule to Material, Unusual Isolation and Catalysis

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In “Inorganic Supramolecular Chemistry”, the self-assembly through metal coordination has shown remarkable potential for the construction of well-defined architectures. The use of supramolecular interactions in the creation of new types of functional materials with interesting properties is a challenging task in contemporary chemical research. In the course of our supramolecular research, we have been working towards the construction of supramolecular functional systems that have potential applications. Supramolecular aspects of polyoxometalate (POM) chemistry will be described under following headings: the co-existence of some crown ethers and POM cluster anions, in which it will be demonstrated that POM cluster anions play an important role in stabilizing unusual supramolecular structures;^{1,2} bringing other metal-macrocycle systems into POM matrices to demonstrate the influence of POM cluster anion on the properties of metal-macrocycle coordination complexes;³ metallomacrocycle formation in a POM matrix;⁴ breathing of ionic crystals consisting of POM anions and trinuclear basic carboxylates (as cations). Subsequently, the linking propensity of some well-defined POM clusters to obtain metal-oxide based new materials⁵⁻⁷ will be discussed including the role of Keggin-type heteropolyanion in the self assembly of metal phosphonate architectures.⁸ Finally, catalytic organic transformations of industrial importance, catalyzed by POM supported metal coordination complexes, will be demonstrated.⁹



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Hybrid polyoxometalates as multifunctional materials, photoresists, green catalyst and antioxidants

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Polyoxometalates based organic-inorganic hybrids have attracted attention for a wide variety of applications. However, the design and development of hybrid polyoxometalates for specific applications is still a challenging task for synthetic chemists. The talk will focus on our attempts to develop new Class I and Class II type hybrid polyoxometalates for their applications in some less explored areas. The first part of the talk will be on the development of a new class of multifunctional aromatic sulfonium polyoxometalate hybrids. A series of aromatic sulfonium counter ions, triflate salts of which act as ionic liquids, have been developed based on a fundamental aromatic sulfonium counter ion motif that allows structural and electronic fine-tuning by introducing substituents at multiple locations. Using these counter ions, hybrid POMs of formulae $(AS)_4[Mo_8O_{26}]$, $(AS)_3[PMo_{12}O_{40}]$ and $(AS)_4[SiMo_{12}O_{40}]$, where AS = various aromatic sulfonium counter ions, have been developed and we showed that the photochromic properties of these POM hybrids can be fine-tuned by systematically varying the substitutions on the counter ion motif. These hybrids also exhibited catalytic properties, in some cases as self-separating catalysts, towards various organic transformations. Second part of the talk will be on the development of new class II type hybrids based on $[P_{12}V_3W_{15}O_{62}]^{9-}$, Mn-Anderson and $[H_3V_{10}O_{28}]^{3-}$ type clusters and their applications i) as photoresist materials for patterning sub-25 nm features under extreme ultraviolet lithography (EUVL) conditions ii) as synthetic antioxidants and iii) as light sensitive polymeric materials for fabricating photoresponsive devices. Finally, the development of a POM based hybrid supramolecular framework material as green catalyst for the selective oxidation of sulfides in water with hydrogen peroxide as reagent will be discussed.

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Pens with Bubbles: Patterning SOMs using microbubbles in thermo-optical tweezers

Ayan Banerjee

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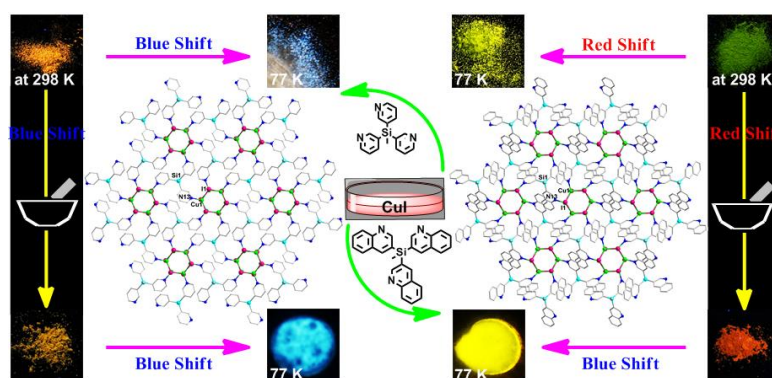
We describe our technique of writing patterns using SOMs by the use of a micro-bubble generated and manipulated by thermo-optical tweezers. Starting with a liquid dispersion of SOMs, we nucleate a microbubble due to absorption of SOMs from the tweezers laser. The bubble leads to the onset of Marangoni flows that causes self-assembly of the dispersed SOMs at its base, so that permanent patterns are formed when we subsequently translate the bubble using the tweezers. We form diverse patterns of both SOMs and other material which co-pattern with the SOMs, making the technique rather powerful as a potential microlithographic tool. Thus, we have developed catalytic chips where we patterned a SOM-based catalyst and preferentially carried out reactions on the patterns with high throughput, as well as solution processed electronic chips where we simultaneously synthesized, doped and patterned poly-pyrrole and poly-aniline (doped with Mo-based metal oxides) from a dispersion of the parent monomers and SOMs. We are presently exploring methods for fabricating solution processed micro-capacitors and bio-chips - where patterning proteins, antigens, etc. can have widespread applications in life sciences.

Functional Metal Oxide and Metal Halide Self-assemblies Supported by Multi-Site Main Group Ligands

Ramamoorthy Boomishankar

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Discrete assembly of polynuclear metal oxides and metal halides have been the topic of research in the past decades owing to their novel structural features. Interest in these materials in the recent years surrounds for their novel surface self-assemblies and their dynamic physical and chemical properties. In this effort, our group has focussed on stabilizing interesting self-assemblies of these metal-containing materials by employing diverse multi-site main group scaffolds. Earlier work from our laboratory has shown that several iso- and heteropolymolybdates and tungstates can be stabilized in presence of phosphazanium and phosphonium cations.^{1,2} In addition to their interesting supramolecular organization, these molecules have shown to exhibit efficient catalytic properties. In a similar strategy, we have developed interesting examples of discrete copper(I) iodide (CuI) clusters stabilized by N-donor functionalized P(V) and Si(IV) multi-site ligands. These materials were crystallized in the form of two-dimensional metal-organic frameworks (MOFs) consisting of discrete CuI clusters as secondary building units. These poly-nuclear clusters-MOFs show interesting types of thermochromic and mechanochromic luminescent behaviour due to the presence of emissive CuI-cluster core and also by the presence of certain fluorescent ligand functionalities (Figure).^{3,4} The multi-emissive nature of these cluster-MOFs has been substantiated by the presence of multiple low-lying excited states as well as by the rigidochromic effects exhibited by the cluster cores. During these studies we have also functionalized a flexible tetrameric main-group oxide termed as cyclotetrasiloxane as a ligand platform for constructing a multi-site ligand and utilized them for obtaining emissive CuI-Cluster MOFs.⁵



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Contributed Lectures

Iridium(III) Mediated Reductive Transformation of Closed-Shell Azo-Oxime to Open-Shell Azo-Imine Radical Anion

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The hydrogen bonded bis azo-oximato $[\text{IrCl}_2(\text{LNOH})(\text{LNO})]$ **A**, and its deprotonated form (Et₃NH) $[\text{IrCl}_2(\text{LNO})_2]$ **B**, have been isolated in the crystalline state by a facile synthetic method. The azo-oxime frameworks in **B** have been conveniently transformed to the azo-imine¹ by reduction with NaBH₄ or ascorbic acid. Notably, the coordinated azo-imines accept an extra electron thereby furnishing the azo-imine radical anion complex **C**. The underlying reductive transformation can be best described by proton-coupled electron transfer (PCET) process². The superior stabilization of the unpaired spin on the ligand array rather than metal has also been substantiated from EPR and DFT studies. Theoretical analysis reveals that the odd electron in **C** is delocalized over both the azo-imine moieties $[\text{IrCl}_2(\text{LNH}\bullet-)(\text{LNH})] \leftrightarrow ([\text{IrCl}_2(\text{LNH})(\text{LNH}\bullet-)]$, *i.e.* $[\text{Ir}^{\text{III}}\text{Cl}_2\{(\text{LNH})_2 \bullet-\}]$ with no apparent contribution from metal, and this type of ligand-centered mixed valence (LCMV) can be best expressed as Robin–Day class III (fully delocalized) in nature.

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Stabilization of Open Shell Pi-Radicals and their Activities

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The knowhow of the versatile activities of organic radicals is relevant in understanding several reactions in biology and catalysis. Stabilization of organic radicals in laboratory is one of the key steps to disclose their reactivities and also it opens up the opportunities to substantiate them by different spectroscopy, X-ray crystallography and DFT calculations. In addition to the relatively stable benzosemiquinonate, iminobenzosemi quinonate, diiminobenzo semiquinonate, iminothiobenzosemi quinonate, dithiobenzosemi quinonate, the reactive phenoxyl, anilino, aminyl, thiyl, azo, diimine and osazone anion radicals coordinated to transition metal ions were now established. However, the variety of the organic radicals is still rather limited in scope. Thus, stabilizing of organic radicals in complexes as closed shell singlet or open shell states is a challenge in chemical science. In this platform, I will talk on the relevant chemistry of open shell pi-radicals investigated recently in my laboratory.¹⁻⁴

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Student Lectures

Photochemical Reduction of Carbon Dioxide Coupled with Water Oxidation using Various Softoxometalate (SOM) Based Catalytic Systems

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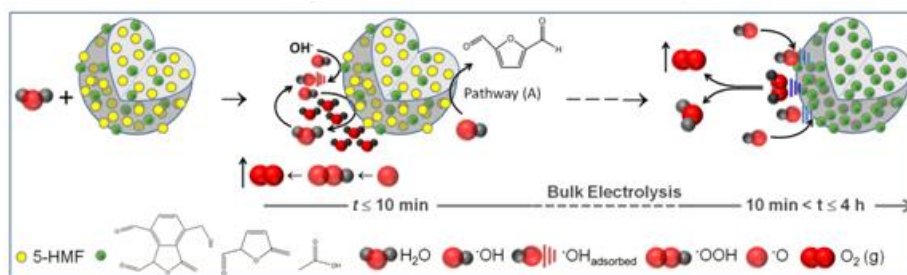
Simultaneous CO₂ reduction and water oxidation as a coupled process is an important challenge in the quest of clean energy production. In this work, we have synthesized a softoxometalate (SOM) based heterogeneous catalytic system which couples CO₂ reduction with water oxidation. Such a catalytic system can simultaneously oxidize water and release the generated electrons for reduction of CO₂ with a maximum turnover number as high as a million. The starting materials for this catalytic process are CO₂ and water while the end products are oxygen and formic acid and in few cases, formaldehyde. The prospect of using the formic acid generated during our process in fuel cells to generate green energy is also worth mentioning.

Carbon Dots with Tunable Concentration of Trapped Anti-oxidants as Metal-free Catalyst for Electrochemical Water Oxidation

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The challenging electrochemical water oxidation reaction to generate molecular oxygen requires low-cost efficient catalysts for their application in renewable energy technologies. The metal free carbon dot (C-dot) catalysts synthesized by microwave irradiation can trap an anti-oxidant, 5-hydroxymethyl-2-furaldehyde (5-HMF) inside the carbon framework. The C-dot with the highest concentration of 5-HMF act as a stable metal-free oxygen evolution reaction (OER) catalyst which operates at a decently low $0.21(\pm 0.03)$ V overpotential (η) and can generate current density up to $33.6(\pm 2.3)$ mA cm⁻².¹ With increased microwave reaction time, the concentration of 5-HMF inside the C-dots decreases at the cost of different furan derivatives which reduces the OER activity. The 5-HMF molecules in close vicinity to the catalytically active sites containing C=O groups can extract the $\cdot\text{OH}/\cdot\text{OOH}$ radicals and can increase the *in situ* H₂O concentration to facilitate the forward reaction of O₂ evolution (Scheme 1). During continuous electrolysis beyond 10 min, 5-HMF gets converted to 2, 5-diformylfuran entities, which increases the catalytically active sites and thereby maintains the OER activity of the C-dots for at least 4 h. The ability of microwave irradiated sucrose derived C-dots to electro-oxidize water is generalized with C-dots and graphene dots prepared from different precursors. This strategy of trapping anti-oxidant molecules capable of absorbing intermediate radicals inside nanostructured catalyst materials can be immensely useful for other fuel cell reactions as well.



Scheme 1: The OER mechanism with 5-HMF trapped C-dot as the catalyst.

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Visible light mediated photomechanical bending induced by topochemical polymerization reaction

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In recent years the research on conversion of light into mechanical form by photomechanical bending attracted great attention due to its applications in smart mini actuator devices. Photoreactions in highly ordered molecular crystals have been widely investigated as these reactions are generally accompanied by molecular scale motions, which lead to macroscale movement of the crystals. Here we demonstrate the concerted, fast and visible-light-induced topochemical polymerization and the associated macroscale anisotropic movement of the crystal on an interesting example of 1,1'-dioxo-1H-2,2'-biindene-3,3'-diyl didodecanoate.

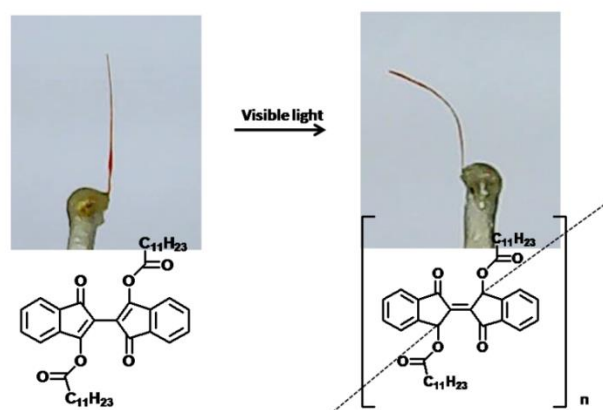


Fig. Photomechanical bending of a crystal under visible light mediated polymerization from single-crystal-to-single-crystal conversion.

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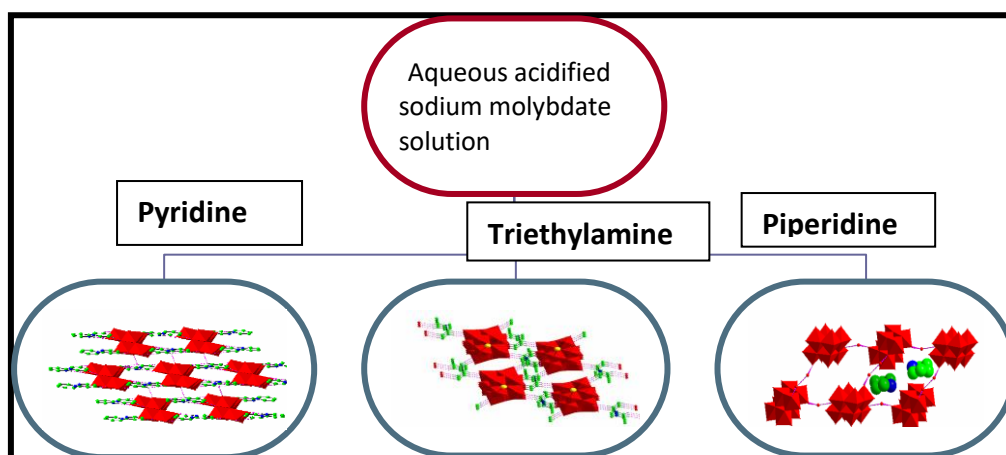
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Posters

A Gas-Liquid Synthetic Strategy in Polyoxometalate Chemistry: Potential Bag Filter for Volatile Organic Amines

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Diffusion of piperidine, pyridine and triethylamine into an acidified aqueous solution of Na_2MoO_4 , yields compounds $[(\text{pipH})_4][\text{Mo}_8\text{O}_{26}] \cdot 4\text{H}_2\text{O}$ ($\text{C}_5\text{H}_{11}\text{N}$ = piperidine = pip) (**1**), $[(\text{pyH})_4][\text{Mo}_8\text{O}_{26}]$ ($\text{C}_5\text{H}_5\text{N}$ = pyridine = py) (**2**), and $[\text{Et}_3\text{NH}]_3[\text{NaMo}_8\text{O}_{26}]$ (**3**) respectively. Compound **1** possesses supramolecular 3-D network and the relevant connectivity pattern generates channels of approximate dimensions of $10.76 \times 11.57 \text{ \AA}^2$, in which the piperidinium cations are located as guests. Multidimensional frameworks (3-D in compounds **1** and **3**, and layer type of network in compound **2**) have been made possible, as the organic cations and polyoxometalate (POM) anions are glued together by significant hydrogen bonding interactions. The synthesis of compounds **1–3** provides a unique “gas-liquid” synthetic route in POM chemistry that results in organic-inorganic hybrid materials with structural diversities.



Metal-oxo cluster supported Cu-pyrazole complex: hydrothermal synthesis, characterization and *in situ* oxidative cyclization of ligand

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Polyoxometalates (POMs) have received enormous attention because of their fascinating properties in the field of catalysis, electrical conductivity, medicine, and photochemistry. In recent time, functionalization of POM cluster surface with transition metal coordination complexes has been of great interest. In this poster, we present the synthesis and structural characterization of a POM supported copper pyrazole complex, $[\text{Cu}^{\text{I}}(\text{C}_{15}\text{H}_{12}\text{N}_2)_2]_3[\text{PW}_{12}\text{O}_{40}]$ (**1**). The single crystals of compound **1** have been synthesized hydrothermally and crystal structure of the compound **1** shows the presence of one Keggin anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and three mononuclear complexes of Cu(I). The coordination geometry of two of the Cu(I) center is T-shaped, that are attached to the Keggin anion by coordinate covalent bonds and third Cu(I) center being linear (not attached to the Keggin anion). One of the interesting aspects of this system is *in situ* formation of 1,5-diphenylpyrazole ligand (cyclic one) from cinnamaldehyde-phenylhydrazone [CINPH] Schiff base through oxidative cyclization. When the crystals of compound **1** (suspended in water, compound **1** is not soluble in water) are exposed to molecular oxygen (oxygen gas is purged through the suspension), compound **1** gets oxidized to compound $[\{\text{Cu}^{\text{II}}(\text{C}_{15}\text{H}_{12}\text{N}_2)_2\}\{\text{Cu}^{\text{I}}(\text{C}_{15}\text{H}_{12}\text{N}_2)_2\}][\text{PW}_{12}\text{O}_{40}]$ (**2**) with two mono-nuclear copper coordination complexes, in which one is Cu(II) complex and the other one is Cu(I) complex, as observed from single crystal X-ray crystallography of compound **2** (Fig. 1). Both compounds **1** and **2** are additionally characterized by EPR and electrochemical studies.

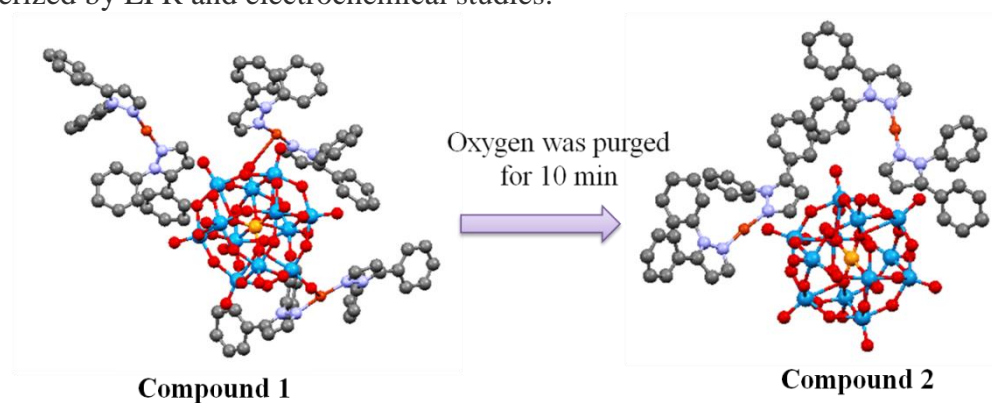
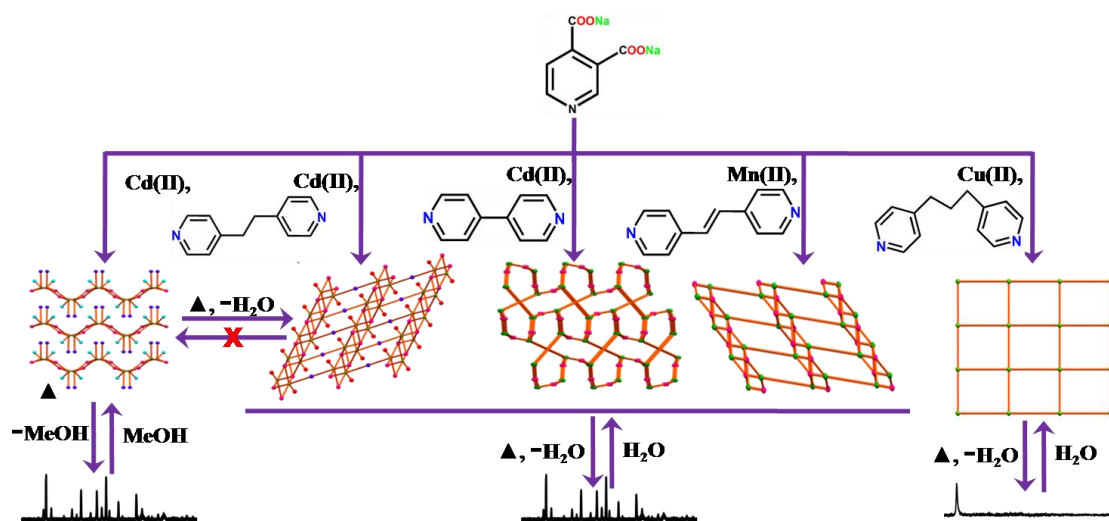


Fig. 1. Structural conversion of molecular structure of **1** to molecular structure of **2** (single crystal to single crystal conversion), when crystals of compound **1** are exposed to oxygen gas.

Flexible metal-organic frameworks: transformation, reversibility and sorption study

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In dynamic metal organic frameworks (MOFs), external stimuli like heat, light, pressure, solvent etc may introduce flexibility through chemical and physical changes. This flexibility may impose some unique selective, stepwise sorption which might be useful for gas and solvent separation. Besides, some dynamic MOFs exhibit nice molecular recognition and/or sensing applications of small molecules. Thus, inherently, such flexible materials have drawn attention for the designing of next generation functional materials. The expected way of such structural transformations is allied with the changes in coordination number of metal atoms, bond rearrangement and conformational changes in flexible organic linkers, removal or exchange of guest molecules. Continuous seek in this area of interest, shaped some nice example of reversible single-crystal-to-single-crystal transformation, crystalline-to-microcrystalline transformation [1] as well as some rare reversible crystalline-to-amorphous transformation [2].



We have synthesized some MOFs, $\{[\text{Cd}(3,4\text{-pyrdc})(\text{bpe})(\text{CH}_3\text{OH})].(\text{H}_2\text{O})\}_n$ (1), $\{[\text{Cd}(3,4\text{-pyrdc})(\text{bpe})_{0.5}(\text{H}_2\text{O})].(\text{H}_2\text{O})\}_n$ (2), $\{[\text{Cd}_2(3,4\text{-pyrdc})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2].(\text{H}_2\text{O})_4\}_n$ (3), $\{[\text{Mn}_2(3,4\text{-pyrdc})_2(\text{bpee})(\text{H}_2\text{O})_2].(\text{H}_2\text{O})\}_n$ (4) and $\{[\text{Cu}_2(3,4\text{-pyrdc})_2(\text{bpp})_2(\text{H}_2\text{O})_4].(\text{H}_2\text{O})_5\}_n$ (5) derived from divalent metal salt, 3,4-pyridinedicarboxylate (3,4-pyrdc) and four different N,N'-donor ligands; [bpe = 1,2-bis(4-pyridyl)ethane, 4,4'-bipy = 4,4'-bipyridine, bpee = 1,2-bis(4-pyridyl)ethylene and bpp = bis-pyridylpropane]. Compound 1 to 4 exhibits reversible crystalline-to-crystalline solid state phase transformation whereas compound 5 shows a rare reversible crystal-to-amorphous solid state phase transformation associated with a visible colour change upon desolvation and resolution. Moreover the desolvated phase of 1 undergoes irreversible transformation to 2 in presence of water. All the five compounds after the phase transformation, exhibit different gas adsorption behaviours with interesting solvent sorption behaviour.

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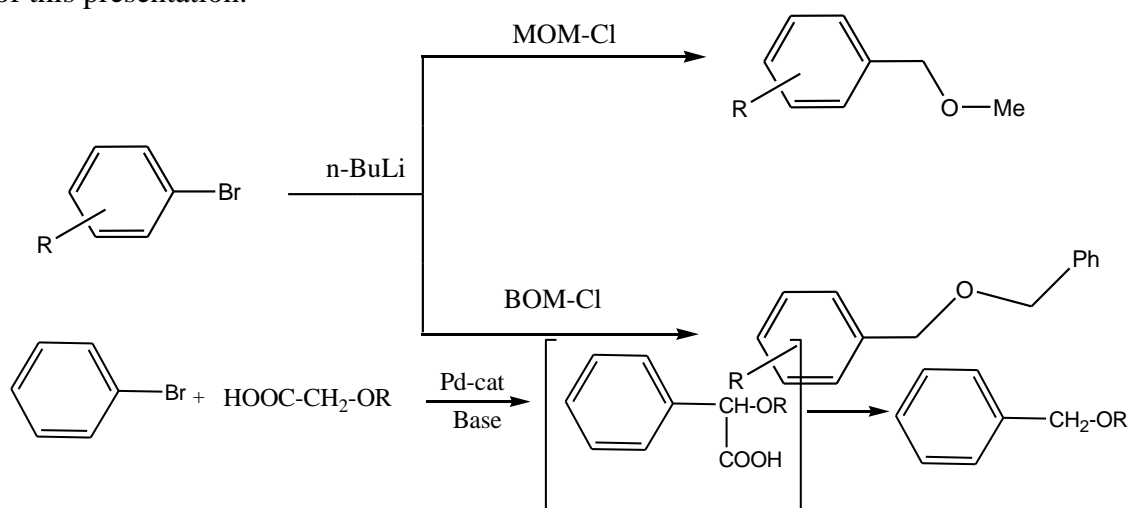
Methoxymethylation and Benzyloxymethylation of Aryl Bromides

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Methoxymethylation and benzyloxymethylation is a method for the preparation of benzyl ethers from aryl bromides. Only one report is available in literature from Migita et al., they have reported that the reaction of aryl bromides with methoxymethyl tributyltin in the presence of a catalytic amount of dichloro bis(triphenyl phosphine) palladium was found to give arylmethyl methyl ethers.¹ Although the reaction is a novel aromatic methoxymethylation, but it suffers from many disadvantages including not easy to preparation of methoxymethyltin compounds, long reaction times, use of toxic solvent (HMPA) etc. I have developed a transition metal free, high yielding one pot methodology for methoxymethylation and benzyloxymethylation of aryl bromides which will be the topic of this presentation.



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Study on the mechanism of the formation of pyran derivative from a propargylic ester under the catalysis of transition metal complexes

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For many years metal mediated pyran and furan ring formation has received a great deal of attention to the synthetic organic chemist. It is found that Pt [1], Au [2], Ag [3] metal salts are very effective in catalyzing reactions for generating five membered and six membered oxygen heterocycles [4]. We report our studies on the mechanism of the synthesis of pyran derivative from a propargylic ester under the catalysis of transition metal complexes. It was suggested that the formation of pyran derivative from propargylic ester occurs through the formation of allene complex. While proposing the mechanistic pathway of the formation of pyran derivative it was assumed that a carboxyl co-ordinated metal complex is formed as an effective intermediate to generate the final product. Our result suggests that the activation energy involved in this pathway is necessarily high. Our search for an alternative pathway reveals that the formation of pyran derivative goes through a solvent assisted proton transfer reaction.

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n-Capric Acid anchored Silanized-Silica-Gel; Its application to sample clean up of Th(IV) sorbed as a dinuclear species in quantified H-bonded-dimeric-metal-trapping-cores

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Selective separation, preconcentration and recovery of Th(IV) from aqueous solutions were investigated using reusable (>800 cycles @95% recovery) n-capric acid (nCA) impregnated silanized-silica-gel (SSG-nCA), through batch-column adsorption methods. SSG-nCA is a porous material (Pore volume: 2.21 mL g⁻¹) of high Brunauer–Emmett–Teller (BET) surface area (1820 m²g⁻¹). Dimethyldichlorosilane (DMDCS) binds SG skeleton-unit-cells (i.e., {Si(OSi)₄.xH₂O}_{θ=2.4}) via–{SiO₂}_{n=12}-O-Si(Me)₂-O- {SiO₂}_{n=12} 3-D networking to produce SSG through intra-particle silanization reaction. In SSG-nCA hydrophobic-long-hydrocarbon-chain of nCA being hooked at hydrophobic surface of SSG generates 121 μmol g⁻¹ H-bonded-dimeric-metal-trapping-cores (HBDMTC), projected towards hydrophilic mobile phase. It showed significant Th(IV) sorption (Break through Capacity (BTC): 235±15 μmol g⁻¹; minimum sorption-equilibrium time:> 12 minutes; high recovery(> 95% from large sample volume, 1000 mL) and high preconcentration factor(PF:192)). The ascertained dimeric-aqua- {Th₂(OH)₂(H₂O)₂}⁶⁺ sorbed species, anchored with an appreciable binding energy (-38.37 eV per mole) at optimum pH 5.0±0.4. The sorption process was endothermic (+ΔH), entropy-gaining (+ΔS) and spontaneous (-ΔG) in nature. It was found effective in presence of 0.125-0.150 mmol mL⁻¹ Na/K salts of coexisting ions. Sequential separation of Zr(IV), U(VI), Ce(IV), Th(IV) was achieved by exploiting the differences in pH for extraction (Zr(IV) at pH 2.5 and U(VI), Ce(IV), Th(IV) at pH 5.0±0.4) followed by their selective elution from respective extracted portion (Zr(IV):4M HNO₃ and U(VI):0.6M CH₃COOH, Ce(IV):1M CH₃COOH, Th(IV):0.5 HNO₃).

An environmentally benign one pot green synthesis of silica gel immobilized dithiozone based 3-D microarray, {SiO₂}@DZ for selective sample clean up of Cd(II) amidst several other congeners

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A facile synthesis of an ion-exchange material ({SiO₂}@DZ: Molecular weight: 313g) through the immobilization of dithiozone (DZ) on inorganic carrier (silica gel, SG) in an innocent solvent (dry diethyl ether) using dimethyldichlorosilane (DMDCS, a new silane coupling reagent¹⁻⁴) has been made by an instantaneous single step one pot reaction. Appearance of violet tint (for the formation of ether soluble DMDCS-DZ₂) of any degree indicates the completion of immobilization and was detected through naked eye. The material was found to be chemically inert up to 8M mineral acids (HNO₃, H₂SO₄, HClO₄ and HCl). The extractor was efficiently utilized for the extraction chromatographic sample clean up of Cd(II). The influences of some analytical variables for sorption (viz., pH, flow rate, temperature, concentration, interfering ions and volume of influent solution) and desorption (type and concentration of the eluent) of Cd(II) were systematically investigated. Cd(II) sorption was quantitative at the range of pH 4.25–4.5 and the analyte was retrieved (recovery > 98%) with 3 mL 0.8M perchloric acid. High level of maximum sorption capacity (274 μM gm⁻¹), an appreciable enrichment factor (264) and considerably high degree of re-usability (> 800 cycles) reflects the highness of the extractor. Optimized method was successfully applied for selective sample clean up of Cd(II) in some real samples too.

Keywords: Facile synthesis of {SiO₂}@DZ, Selective sample clean up of Cd(II), Break Through Capacity, Preconcentration factor, Re-usability

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Porous NiFe-oxide Nanocubes, Derived from Metal-organic Framework, as a Bifunctional Electrocatalyst for Overall Water Splitting

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Electrocatalytic water splitting, a combination of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) half-reactions, has been recognized to be one of the most promising ways to produce high-purity hydrogen. However, the commercialization of the system is hindered due to high cost of the noble metal electrocatalysts such as IrO₂ and Pt used for OER and HER, respectively.¹ The design of a bifunctional earth-abundant metal-based electrocatalyst for overall water splitting is therefore necessary to reduce cost of the system. In this respect, Ni-Fe based catalysts are very attractive towards electrochemical water splitting in alkaline medium due to their high corrosion-resistance, lower overpotential requirement and long term stability in comparison to pristine Ni-O and Fe-O.² Moreover the tunability of an electrocatalyst in terms of its porosity and morphology is essential to enhance the activity of the catalyst.^{3,4} Herein we derived a highly porous NiFe-oxide nanocube system as a bifunctional electrocatalyst from NiFe-PBA MOF which outperforms NiFe nanoparticles and requires very low overpotential for both OER and HER. They demonstrate an overpotential of 271 and 197 mV for electrochemical OER and HER, respectively in 1M KOH at 10 mA/cm² on carbon fiber paper (CFP) (2.2 mg/cm²) which is much better than the NiFe-oxide nanoparticles with the same composition. The latter requires 339 and 347 mV for achieving current density of 10 mA/cm² for OER and HER, respectively. The electrolyzer constructed using NiFe-oxide nanocubes in a two electrode configuration delivers a current density of 10 mA/cm² at a cell voltage of 1.67 V, which is impressive. The better catalytic activity of the nanocubes are observed because of its uniform morphology and high porosity which exposes maximum number of active sites. The nanocube-edges also play a significant role in the enhanced activity of the catalyst.

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Morphology and Crystallinity Dependence of Co-Fe-O Nanostructures in Catalyzing the Electrochemical Oxygen Evolution Reaction

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Morphology, crystallinity and elemental composition of a metal-based catalyst are few of the important tuneable parameters for regulating their electrochemical activity.¹ According to previous reports, earth abundant Co-Fe mixed metal oxides are one of the most promising catalyst for both oxygen evolution reaction (OER) and oxygen reduction reaction (ORR).² Herein we have reported two different morphologies i.e. nanoplates and nanoparticles of Co-Fe mixed metal oxides by using a common precursor but tuning the precipitating and reducing agents. The effect of crystallinity and elemental composition on the electrocatalytic activity of these catalysts was also investigated. It was observed that amorphous Co-Fe mixed oxide nanoplate with 2:1 ratio of Co and Fe demonstrates a superior activity as compared to the other Co-Fe-O electrocatalysts. This particular catalyst requires 276 mV overpotential to reach a current density of 10 mA/cm² with an excellent durability and 97.6 % power conversion efficiency under anodic condition. The best OER activity is attributed to the mesoporous plate like morphology with high electrochemically active surface area, presence of defects and coordinated unsaturated sites.³

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Solid Phase Extraction, Separation and Preconcentration of Rare Elements Th(IV), U(VI), Zr(IV), Ce(IV), Cr(III) amid several other foreign ions with Eriochrome Black T anchored to 3-D{SiO₂}_n microarray

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A presto and facile synthesis of a mesoporous (Pore Diameter: 46.2-47.1 nm) material (FSG-EBT) through the immobilization of azo dye (EBT) on functionalized silica gel (FSG) has been achieved. Synthesis needs no stringent reaction condition like refluxing. Its corresponding nano material has been well assessed (composition: $[\text{Si}(\text{OSi}\equiv)_3(\text{OH}) \cdot x\text{H}_2\text{O}]_n$ [-Si(CH₃)₂-NH-C₆H₄-N=N-EBT]₄; Structure: tetrahedral) and reiterated by density functional theory (DFT) calculation. Along with its good extractor qualities [like high Pore Volume, PV: 0.374689 cm³ g⁻¹; Surface Area, SA: 330.968 m² g⁻¹; BTC (Q₀ = 476.7 μmol g⁻¹); Column efficiency, CE: 296 and Preconcentration Factor, PF: 120.20 ± 0.04; reusability >1000 cycles; and faster rate of sorption-desorption], FSG-EBT possesses well demarcated spatial placement of HOMO-LUMO with a suitable band gap (η: 7.1471 eV). Here, HOMO-LUMO is well separated. It makes difficult for charge recombination by their mixing and shows its applicability as good donor-acceptor organic electronic device.

The present work reports the systematic studies on extraction, separation and preconcentration of Th(IV), U(VI), Zr(IV), Ce(IV) and Cr(III) amid several other foreign ions using EBT anchored {SiO₂}_n 3-D microarray. The effect of various sorption parameters, such as pH, concentration, temperature, sample volume, flow-rate and co-existing foreign ions were investigated. Quantitative sorption was ensured at solution pH: 6.0–6.5 for Th(IV), Ce(IV), Cr(III) and pH: 2.75–3.0 for Zr(IV), U(VI) couple. Analysis on extracted species and extraction sites reveals that $[\text{Th}_4(\mu^2\text{-OH})_8(\text{H}_2\text{O})_4]^{8+}$, $[\text{Ce}_6(\mu^2\text{-OH})_{12}(\text{H}_2\text{O})_5]^{12+}$, $[\text{Cr}_3(\mu^2\text{-OH})_4(\text{H}_2\text{O})]^{5+}$, $[(\text{UO}_2)_3(\mu^2\text{-OH})_5(\text{H}_2\text{O})_3]^+$ and $[\text{Zr}_4(\mu^2\text{-OH})_8(\text{H}_2\text{O})_{0.5}]^{8+}$ for the respective metal ions gets extracted at HOMO of the extractor. HOMO-{metal ion species} was found to be 1:1 complexation. Sorption was endothermic, entropy-gaining, instantaneous and spontaneous in nature. A density functional theory (DFT) calculation has been performed to analyze the 3-D structure and electronic distribution of the synthesized extractor.

KEYWORDS: EBT anchored {SiO₂}_n 3-D microarray; Solid Phase Extraction; Break-through Capacity is a function of frontier orbitals; HOMO-{metal ion species} 1:1 complexation; Sequential separation of Th(IV), Ce(IV), Cr(III), Zr(IV), U(VI)

FIVE DIMENSIONAL PLANE SYMMETRIC UNIVERSE IN CREATION FIELD COSMOLOGY

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We have taken an attempt to construct the Hoyle and Narlikar C-field cosmology in plane symmetric space time. We have assumed that $C(x, t) = C(t)$ that is the creation field C is a function of time 't' only. It is found that for each case of $2f < \alpha^2$, we get negative deceleration parameter indicating that the universe is accelerating. The universe becomes isotropic for large value of t. For a small of t, the ratio $\frac{\sigma}{\theta}$ tends to zero. Therefore, the model approaches to isotropy at late times. Also, we have observed that the matter density is inversely proportional to square of time t. Also, as the matter moves the further apart, it is assumed that more mass is continuously created to maintain the matter density. However, the matter density tends to zero when time will be infinitely large. Finally the exact solution of the field equations are obtained.

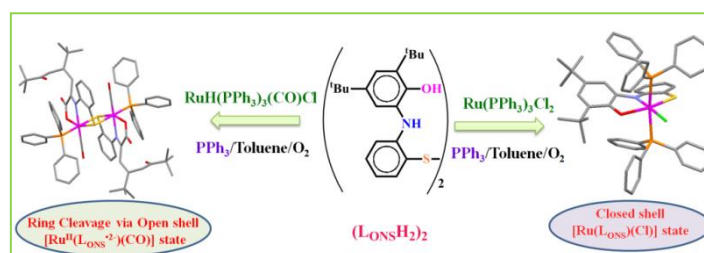
Key words- Five dimension plane symmetric metric, Holy-Narlikar C field cosmology, Dust, Disordered Radiation Universe, Stiff fluid case.

An ONS-Coordinated Open-shell π Radical: Oxidative Aromatic Ring Cleavage Reaction

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The coordination chemistry of 2,4-di-*tert*-butyl-6-((2-mercaptophenyl)amino)phenol ($L_{ONS}H_3$) which was isolated as a diaryl disulfide form, $(L_{ONS}H_2)_2$, with ruthenium ion is disclosed. It was established that the tri-anionic L_{ONS}^{3-} is redox non-innocent and undergoes oxidation to either a closed shell singlet, L_{ONS}^{1-} or an open shell π radical state, L_{ONS}^{2-} and the reactivities of $[Ru^{II}(L_{ONS}^{2-})]$ and $[Ru^{II}(L_{ONS}^{1-})]$ states are different. Reaction of $(L_{ONS}H_2)_2$ with $[Ru(PPh_3)_3Cl_2]$ in toluene in presence of PPh_3 affords a ruthenium complex of the type *trans*- $[Ru(L_{ONS})(PPh_3)_2Cl]$ (**1**), while the similar reaction with $[Ru(PPh_3)_3(H)(CO)Cl]$ yields a L_{ONS}^{2-} complex of ruthenium(II) of the type *trans*- $[Ru^{II}(L_{ONS}^{2-})(PPh_3)_2(CO)]$ (**2**). **1** is a resonance hybrid of $[Ru^{II}(L_{ONS}^{1-})Cl]$ and $[Ru^{III}(L_{ONS}^{2-})Cl]$ states. It is established that **2** incorporating an open shell π radical state, $[Ru^{II}(L_{ONS}^{2-})(CO)]$, reacts to *in situ* generated superoxide ion and promotes an oxidative aromatic ring cleavage reaction yielding a α -(*N*-aryl)imino- ω -keto-carboxylate (L_{NS}^{2-}) complex of the type $[Ru^{II}(L_{NS}^{2-})(PPh_3)(CO)]_2$ (**4**), while **1** having a closed shell singlet state, $[Ru^{II}(L_{ONS}^{1-})Cl]$, is inert in the similar condition. Notably, **2** does not react to dioxygen molecule, but reacts to KO_2 in presence of excess PPh_3 affording **4**. The redox reaction of $(L_{ONS}H_2)_2$ with $[Ru(PPh_3)_3Cl_2]$ in ethanol in air is different leading to the oxidation of L_{ONS} to a quinone sulphoxide derivative (L_{ONSO}^0) as in *cis*- $[Ru^{II}(L_{ONSO}^0)(PPh_3)Cl_2]$ (**3**), *via* **1** as an intermediate. The molecular and electronic structures of **1-4** were established by single crystal X-ray crystallography, EPR spectroscopy, electrochemical measurements and density functional theory (DFT) calculations.



Reference:

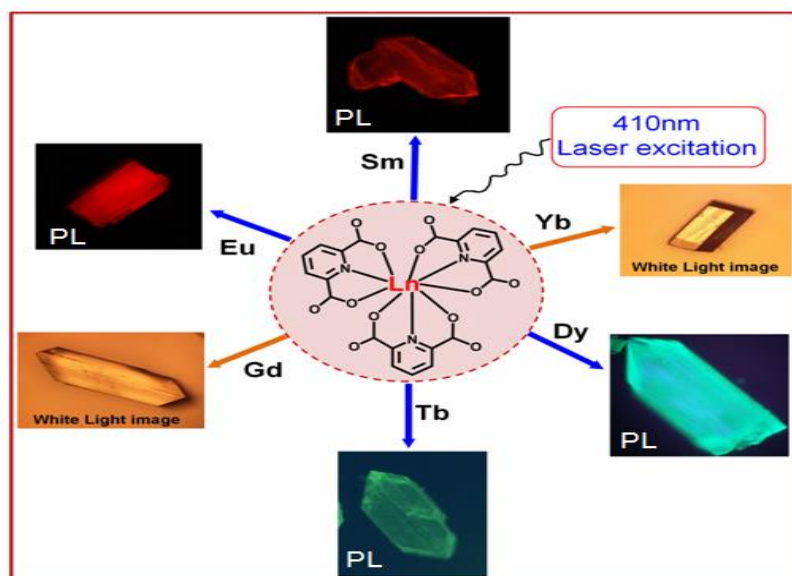
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Isostructural Series of Photoluminescent Solids: [$\{\text{Al}(\text{H}_2\text{O})_6\}\{\text{Ln}(\text{pda})_3\}\cdot 10\text{H}_2\text{O}$, Ln-Sm, Eu, Gd, Tb, Dy and Yb

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Our attempts to synthesize lanthanide coordinated Anderson-Evans cluster $\{\text{AlMo}_6\text{O}_{18}\}$, similar to its chromium analogue,¹ accidentally led to the isolation of a new isostructural series of solids of the composition $[\{\text{Al}(\text{H}_2\text{O})_6\}\{\text{Ln}(\text{pda})_3\}\cdot 10\text{H}_2\text{O}]$ where Ln = Sm, Eu, Gd, Tb, Dy and Yb. Single crystal X-ray analysis revealed that the structures of these solids are built of three major building blocks: lanthanide dipicolinate anion, $\{\text{Ln}(\text{pda})_3\}^{3-}$, the counter cation, $\{\text{Al}(\text{H}_2\text{O})_6\}^{3+}$ and a hexameric water cluster in chair form. The cations and the anions are linked through H-bonding forming a 2D sheet; the hexameric water cluster further stabilises the sheets through H-bonding with coordinated water molecules on aluminium. The poster will also discuss the photophysical properties of the lanthanide complex based crystals. The solids containing Sm, Eu, Tb and Dy showed characteristic emission of rare-earth ions while Gd and Yb based solids did not.



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Physicochemical Insights in Supramolecular Interaction between Chitosan and Adenosine triphosphate Coated Silver nanoparticles: Elucidation of their Antimicrobial & Anticancer Activities

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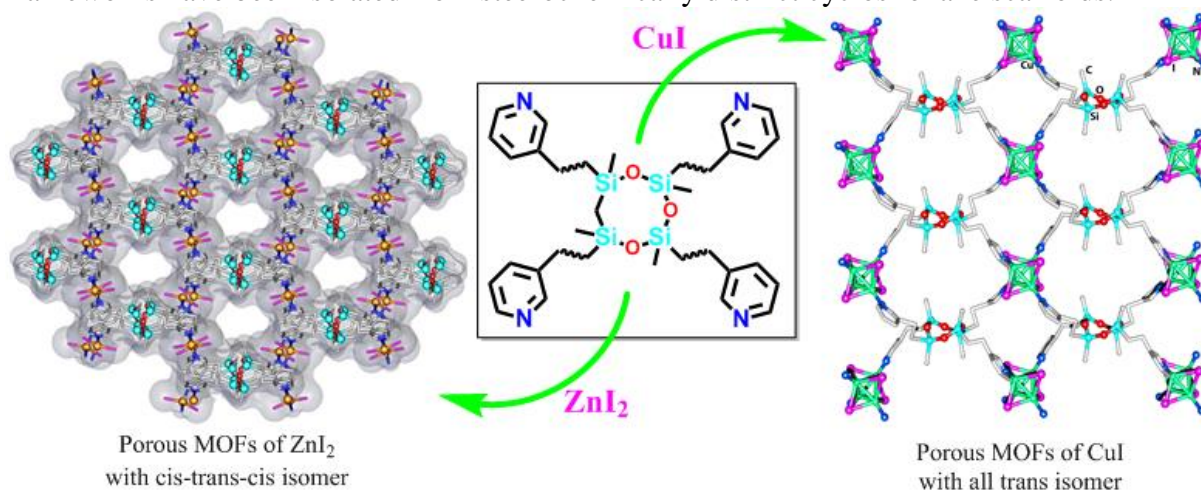
The feature of both pH and enzyme responsiveness within materials have attracted considerable attention from versatile areas of biomaterial science due to their stimuli responsive feature and diverse potential applications in wide range of human therapeutics. By tuning their physicochemical parameters, it is possible to add a plethora of functionality within materials. Herein, we have exploited the supramolecular chemistry to form nano-supraamphiphiles via interaction of cationic biopolymer chitosan with adenosine triphosphate (ATP) coated silver nanoparticles. These highly stable nano-supraamphiphiles are particularly appealing due to their excellent stability in normal physiological environment and stimuli responsive feature. The phosphatase driven dephosphorylation and pH responsiveness feature can be exploited as a model of cell instructed response. Thus gives an alternative way of nanomedicine to treat human cancer effectively. Besides the novel anticancer activity, this biocompatible nano-supraamphiphiles shows excellent bactericidal activity over both gram positive and gram negative bacilli.

Synthesis and separation of stereoisomers of cyclotetrasiloxanes containing 3-pyridyl substituents and their functional Metal-Organic Frameworks

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Functionalized cyclosiloxanes have been used as starting materials for obtaining silicon polymers having organofunctional moieties [1]. Among the cyclosiloxanes, the cyclic tetrasiloxanes were studied in detail owing to their high thermal stability and functional group tunability via chemical modifications [2]. Here we show the synthesis and separation stereoisomers of new cyclotetrasiloxane scaffolds containing peripherally functionalized 3-pyridyl moieties, $[\text{MeSiO}(\text{CH}=\text{CH}^3\text{Py})]_4$ (L^1) and $[\text{MeSiO}(\text{CH}_2\text{CH}_2^3\text{Py})]_4$ (L^2), and their reactivity studies with certain d^{10} metal ions. The ligand L^1 was obtained by the heck coupling reaction of tetramethyl tetravinyl tetrasiloxane (D_4^{vi}) and 3-bromopyridine in presence of the Pd(0) catalyst. The as-synthesized ligand L^1 shows the presence of three stereoisomers, cis-trans-cis (L^{1A}), cis-cis-trans (L^{1B}), and all-trans (L^{1C}) which were quantitatively separated by column chromatography. An interesting one-dimensional Zn(II) coordination polymer exhibiting a PtS network topology, assisted by supramolecular π - π interactions, has been obtained in the reaction of L^{1A} with ZnI_2 . A one-dimensional cationic coordination polymer has been obtained for L^{1B} consisting of an alternately arranged larger and smaller Ag_2L_2 macrocyclic repeat units. Two photoactive CuI-cluster MOFs consisting of Cu_2I_2 and Cu_4I_4 repeat units have been isolated for the ligands L^{1C} and L^{2C} , respectively. Separation of stereoisomers of cyclosiloxanes is a challenging task and the metal complexes reported based on these ligands is the first instance where topologically unique metal-organic frameworks have been isolated from stereochemically distinct cyclosiloxane scaffolds.



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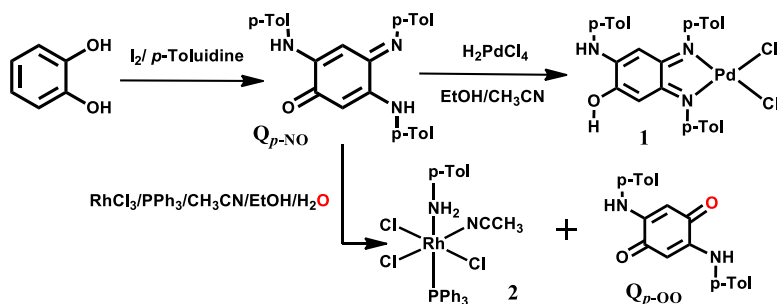
Metal Ion Promoted Tautomerization and C-N Bond Cleavage: Conversion of Catechol to a *p*-Benzoquinone Derivative

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Metal ion promoted tautomerization of *p*-iminoquinone to *o*-diiminoquinone and a C-N bond cleavage of 2,5-bis(*p*-tolylamino)-4-*p*-tolyliminobenzoquinone (Q_{p-NO}) leading to the conversion of catechol to a *p*-benzoquinone derivative are isolated. In presence of palladium(II) ion, Q_{p-NO} tautomerization to 3-hydroxy-4-(*p*-tolylamino)-*o*-bis(*p*-tolyliminobenzoquinone) (Q_{o-NN}) affording $[Pd^{II}(Q_{o-NN})Cl_2]$ (**1**) complex. However in similar reaction of Q_{p-NO} with $RhCl_3$ in presence of PPh_3 as co-ligands in moist MeCN/EtOH progresses further surprisingly with a C-N bond cleavage affording $[Rh^{III}(PPh_3)(p\text{-toluidine})(MeCN)Cl_3]$ (**2**) and 2,5-bis(*p*-tolylamino)-*p*-benzoquinone (Q_{p-OO}). The cleavage reaction progresses with an *o*-diiminobenzoquinone anion radical intermediate of rhodium (III) ion detected by the EPR spectrum of the frozen reaction mixture at 150 K with the *g* parameter at 1.996. Thus a new path of conversion of catechol to *p*-quinone derivatives is authenticated.



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Efficient Design to Monitor the Site Specific Sustained Release of Colorless/Non-emissive Cancer Drug

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Monomers namely norbornene derived chlorambucil (NOR-CHO), norbornene grafted PEG Folate (NOR-PEG-FOL) and norbornene derived Methyl Orange (NOR-MO) have been synthesized by attaching the anticancer drug chlorambucil, poly ethylene glycol with folate (PEG-FOL) and methyl orange (MO) to the norbornene backbone by ester linker for demonstrating pH responsive capabilities. Chlorambucil produces its anti-cancer effects by interfering with DNA replication and damaging the DNA in a cell. Presence of PEG-FOL functionality makes the system water-soluble as well as site-specific. The anti-cancer drug which we have used is not emissive in nature hence methyl orange has been used for making the system fluorescent active. Tri-block polymer of NOR-CHO, NOR-PEG-FOL and NOR-MO have been synthesized by Ring Opening Metathesis Polymerization (ROMP) using Grubbs (G₂) second generation catalyst. Successful formation of all the monomers, homopolymers and tri block co-polymer (NOR-CHO-FOL-MO) of corresponding monomers have been characterized by NMR-spectroscopy, Infrared spectroscopy and gel permeation chromatography. Drug release profile of the tri-block polymer system showed the drug release at acidic pH.

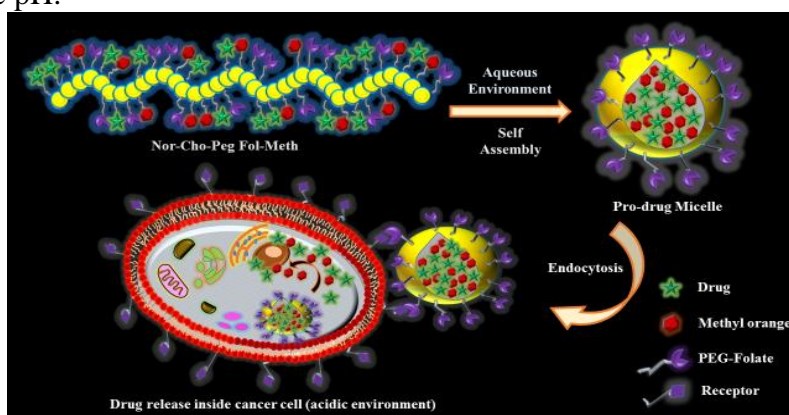


Figure 1: Cartoon representation of tri-block polymer (NOR-CHO-FOL-MO)

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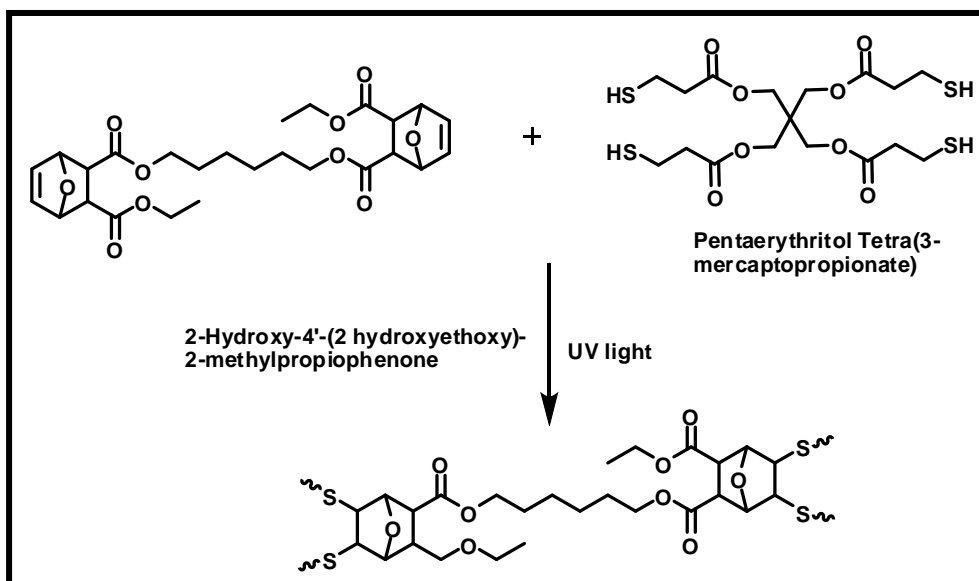
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Key words: Norbornene, Chlorambucil(CHO), methyl orange(MO), Ring Opening Metathesis Polymerization(ROMP), Grubb's second generation catalyst(G2 catalyst)

Photo cross-linked porous network for efficient solvent removal from aqueous phase

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Thiol–ene click chemistry in presence of UV light has emerged remarkably in popularity over the past few years as it enables the formation of homogeneous network.^{1,2} Cross linked network structures are drawing attention these days because of its ability to absorb organic solvent or oil spilled on water.^{3,4} In this work; we have end functionalized monomer with norbornene moieties, thus allowing simple, efficient photo initiated thiol–norbornene cross-linking chemistry to be utilized to form the cross linked network. Cross-linking with a tetra functional thiol was performed in a dry DCM solvent. The material possesses uniform porous nanostructure and shows high solvent uptake ability. The material can absorb toxic dyes (rhodamine B, methyl orange, Nile red) as well as water dispersible organic solvents from the textile and paint industries.



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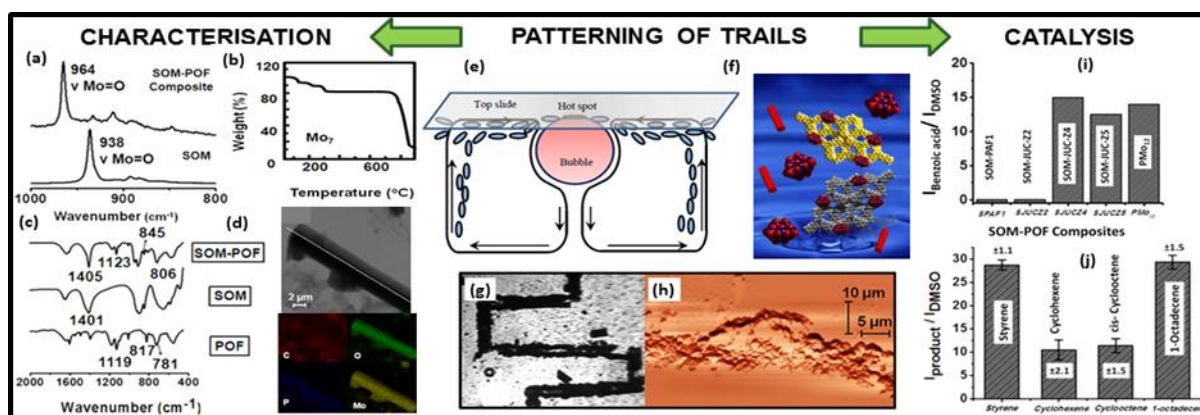
EXPLORATION OF SOFT OXOMETALATES IN PATTERNING AND ALLIED STUDIES

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Soft oxometalates or SOMs are the heterogeneous dispersions formed by polyoxometalates of colloidal length in solutions.[1] These are intermediate of molecular POM solutions and their crystalline counterparts. [1] In this presentation, we shall depict controlled nucleation of SOMs to form microdimensional arrays of POMs using laser irradiation of thermo-optical tweezers. [2] The patterning process involves a phase transition phenomenon where SOM colloids are transitioning to polycrystalline POM arrays (Figure 1 g. and 1 h.).[2] Further, these arrays have demonstrated their function as 2D catalytic chemical reactionwares, for instance, SOMs along with various POFs (Porous organic frameworks) have been shown to form inorganic-organic hybrids which on patterning act as robust catalysts (Figure 1 a- d)for oxidation of aliphatic and aromatic aldehydes (Figure 1 i). [3] Additionally trails formed from SOMs have exhibited catalysis of epoxidation of alkenes in a site specific fashion (Figure 1j). [4]



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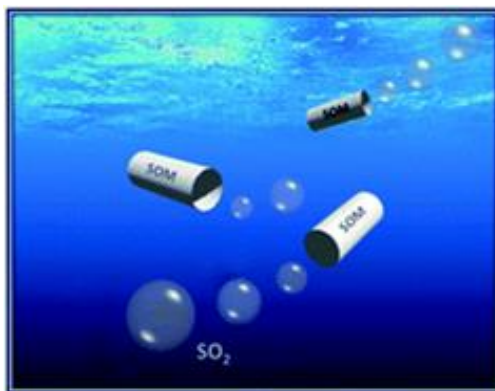
MICROMOTORS: AUTONOMOUS MOVEMENT INDUCED IN CHEMICALLY POWERED ACTIVE SOFT-OXOMETALATES (SOMS)

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Synthesis of autonomously moving soft and active matter [1] is an immediate challenge for modelling biological phenomenon. In nature various biological motors are present. For instance, eukaryotic cells contain several powerful biomotors which convert chemical energy from hydrolysis of ATP to mechanical work. Taking inspiration from these biological machines various groups across the world have started working with synthetic micromotors [2]. In recent times, although, moving matter has been designed, their synthesis is tedious. Here we will demonstrate a system based on soft-oxometalates (SOMs) [3, 4] which is very easy to synthesize and is used as a model system in our study. This system moves autonomously in response to chemical stimuli like that of a reducing agent-dithionite [5]. The redox active Mo^{VI} sites of SOMs are used for oxidizing dithionite to generate SO_2 to propel the micromotors. We explain this motion qualitatively and also show how surface interaction, adsorption isotherm of the evolved gas influence power conversion efficiency of these micromotors. This explains that using a simple redox system and exploiting this potential in SOMs it is possible to construct SOM micromotors and in principle possibilities exist for fine tuning their motion.



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LIGHT DRIVEN CARBON DIOXIDE REDUCTION COUPLED WITH OXIDATION OF PHENYLACETYLENE TO ACETOPHENONE.

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The abiological reduction of carbon dioxide to organic compounds is of interest due to increase in energy demand and green house gas emission. The photochemical reduction of carbon dioxide is set to become an indispensable key technology to address these global issues. This technique has been exploited to develop an approach to reduce carbon dioxide photochemically and simultaneously phenylacetylene is converted to acetophenone. Some efforts have been made to convert carbon dioxide into industrially useful organic products. However, such conversion remain extremely expensive. Most of the process simply report reduction process being carried out. It is an economic and environmental disincentive in the quest for clean energy and disrupts atom economy. Our approach retains it, but seeks to convert it into some industrially useful precursor.

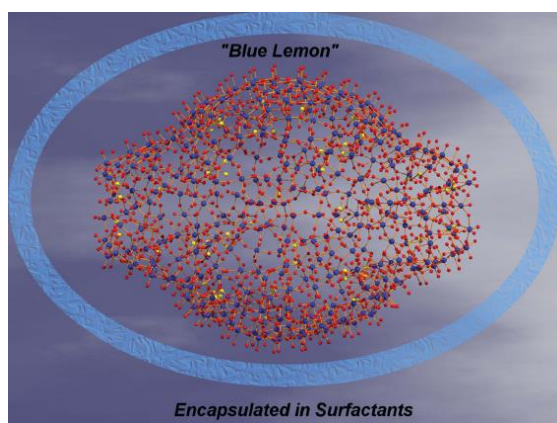
Manipulating the inner surface of spherical shaped Mo₁₃₂ capsule and outer surface of Hedhog-shaped Mo₃₆₈ cluster

Susovan Bhowmik

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The giant metal oxide spherical capsules of the type Mo₁₃₂ (more generally: (pentagon)₁₂(spacer/ligand)₃₀) allow versatile chemistry and applications as well as the option to study new phenomena of interdisciplinary interest owing to its widely tunable interiors. This lecture refers to the related fascinating manipulation of the interior surface of Mo₁₃₂ nano ball. This is also aimed at discussing exterior manipulation of the nano-hedhog Mo₃₆₈ cluster (or 'blue lemon') by embedment of hydrophobic shell of DODA cations/surfactants leading to formation of giant blackberry like vesicals.



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CO₂ fixation under ambient condition towards value added chemicals

Tanmoy Biswas and Venkataramanan Mahalingam*

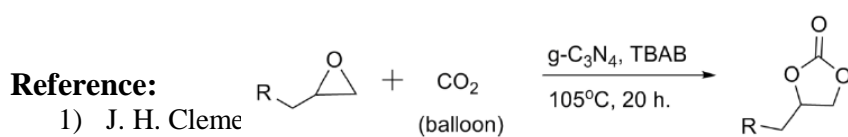
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Research on carbon dioxide fixation has attracted great attention due to global warming and climate change. Fossil fuels are the major source of energy and which is indispensable for our day to day life. The majority of our required chemicals are produced from the petroleum and the renewable energy utilization technology is not developed enough to replace the fossil fuel based system. This accumulates a huge amount of carbon dioxide (CO₂) every day in the atmosphere. Consequently, CO₂ utilization for the preparation of useful chemicals and fuel is necessary. Cyclic carbonates are well established as highly polar aprotic solvent, solvent for lithium ion battery, monomers of polycarbonates, etc.¹ Previously very few works had been reported for fixation of CO₂ using graphite carbon nitride (g-C₃N₄) or quaternary ammonium halides alone at relatively high CO₂ pressure.² Our objective is to develop methodologies for epoxide to cyclic carbonate formation at ambient CO₂ pressure. We prepared g-C₃N₄ from the thermal polycondensation of melamine.³ We have used catalyst mixture i.e. g-C₃N₄ and tetrabutylammonium bromide (TBAB) which operates synergistically for the conversion of epoxide to cyclic carbonate in solvent free condition. We have taken epichlorohydrin as model substrate and the optimum condition is 105°C for 20 h under CO₂ filled balloon condition. Our catalyst system is active for other substrates like styrene oxide, allyl glycidyl ether or phenyl glycidyl ether. The activity of our catalyst combination is remained almost same up to 7 cycles. The main scheme of the work is mentioned below (Scheme I).

Key words: Global warming, CO₂, g-C₃N₄, TBAB, epoxide, cyclic carbonate, balloon, solvent free etc.

Scheme I:



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