School
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Annual Symposium 2022

Time	Day 1: March 10th, 2022 C. V. Raman Hall	
	Session 1: Chairman, Prof. Bimalendu Dev	
10:00-10:20	*Ishita Bhattacharya*	**Quadruple bonding conundrum in C2 and isoelectronic dimers: A molecular orbital approach**
10:20-10:40	*Sumanta Ghosh*	**A machine learning approch to predict the configuration interactions of Heisenberg model systems.**
10:40-11:00	*Tanmoy Nandi*	**Fluorination Affects Drastically the Photophysical Properties of Tryptophan**
11:00-11:20	*Subhra Sankar Dutta*	**Structure analysis of Curcumin by Ion Mobility Mass Spectrometry**
11:20-11:40	***Tea Break***	
	Session 2: Chairman, Prof. Shyamal Saha	
11:40-12:00	*Debasish Saha*	**Identifying the Template for Oligomer to Fibril Conversion for Amyloid-β (1-42) oligomers using Hamiltonian Replica Exchange Molecular Dynamics**
12:00-12:20	*Sumitava Kundu*	**Orientational behaviour of colloidal crystal of hard polyhedra**
12:20-12:40	*Joy Dutta*	**The effect of surface temperature on the scattering of H2/D2- Cu(111) using a chemically accurate PES**
12:40-13:00	*Pranab Gain*	**High Pressure Chemistry of Some Iron Complexes**
13:00-14:40	***Lunch Break***	
	Session 3: Chairman, Prof. Prasanta K. Das	
14:40-15:00	*Sourav Bera*	**Nitrile containing linker based metallogels: synthesis, characterisation and effect of nitrile on melanoma**
15:00-15:20	*Manik Jana*	**Comparative anion receptor abilities of linear N-Confused tripyrrole Vs. N-Confued fused Macrocycles**
15:20-15:40	*Manotosh Bakt*	**Light-induced aerobic radical C-H functionalization of heteroarenes**
15:40-16:00	*Kushnood Fatma*	**DNA G-quadruplex mediated telomerase inhibition by small molecules**
16:00-16:20	*Dhiman Saha*	**Asymmetric Total Synthesis of Amphirionin-2**
16:20-16:40	*Priyanka Dinda*	**Thermoresponsive Amino-acid-derived Polymer and its Antifouling**

Time	Day 2: March 11th, 2022 C. V. Raman Hall	
	Session 4: Chairman, Prof. Sudip Malik	
10:20-10:40	*Ambreen Rashid*	**A bis-heteroleptic imidazole-bipyridine functionalized iridium (III) complex for fluorescence lifetime-based sensing of phosphate and pyrophosphate**
10:40-11:00	*Abhishek Das*	**Effect of Secondary Interactions on the Stability and Reactivity of a Chiral Nonheme Iron(IV)-Oxo Species**
11:00-11:20	*Kamal Hussain*	**Pentasulfido Chain in a Binuclear Zn(II) Complex**
11:20-11:40	*Arnab Nath*	**Reactive Intermediates of Copper Bound Aβ peptides and their association with Alzheimer's Disease**
11:40-12:00	*Aishik Bhattacharya*	**Reduction of Sulfur Dioxide to Sulfur Monoxide by Ferrous Porphyrin**
12:00-14:30	***Lunch Break***	
	Session 5: Chairman, Prof. Tarun K. Mandal	
14:30-15:00	*Avisek Das*	**Structure and Mechanism in Peptide Self-assembly: Insights from Atomistic Computer Simulations**
15:00-15:30	*Kanishka Biswas*	**Enhanced Atomic Ordering Leads to Ultra-High Thermoelectric Performance**
15:30-16:00	*Dibyendu Das*	**Substrate induced catalyst formation under non-equilibrium conditions**
16:00-16:30	*Rajib Goswami*	**Total Synthesis of Bioactive Natural Products: Carolacton and Alveolaride C**
16:30-17:00	*Rahul Banerjee*	**Covalent Organic Frameworks and Reticular Nano-Synthesis**
17:00-17:30	*Debojyoti Ghosal*	**Flexibility in metal-organic frameworks and their functional recompense**

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Abstracts

Quadruple bonding conundrum in C2 and isoelectronic dimers: A molecular orbital approach

Ishita Bhattacharya

School of Chemical Sciences, Indian Association for the Cultivation of Science

The bonding nature of C2 has been an intensely debated issue over the last decade with opinions sharply divided between the practitioners of Valence Bond (VB) and Molecular Orbital (MO) theory. VB theory investigations have suggested the presence of quadruple bonding in C2. However, these findings have been challenged. It is safe to state that Molecular Orbital (MO) based techniques enjoy more confidence, when it comes to the issues of electronic structure of molecules. As the debate rages, it must be noted till date no theoretical study has suggested any reliable experimentally verifiable evidence which will either establish beyond reasonable doubt the utter lack or existence of the quadruple nature to the bond in C2. Here, we have investigated the nature of the Potential Energy Surfaces of High Spin Sigma states of C2, N2, Be2 and acetylene through Multi-Reference Based techniques. The subsequent analyses not only afford crucial evidence in favor of quadruple bonding nature of the bond in C2 but the inference drawn from the theoretical evidence can be experimentally verified. Furthermore, we have extended our hypothesis to species which are isoelectronic to the carbon dimer such as BN, BeO and LiF. We observed that the trend in bonding exactly follows Lewis model of bonding.

A machine learning approach to predict the configuration interactions of Heisenberg model systems.

Sumanta Ghosh

School of Chemical Science, Indian Association for the Cultivation Science.

In spite of the impressive progress of computational chemistry in recent years, strongly correlated systems pose still a bigger challenge in this arena. Full CI or even complete active space-based methods have unavoidable exponential scaling problem. This exponential basis increment often tackled through stochastic sampling methods. These methods usually involve multiple times diagonalization or sometimes diagonalization of larger Hamiltonian matrix. Artificial Neural Networks (ANNs) are potential candidates to circumvent such problems. For model Polyaromatic hydrocarbons (pAHs), we have used such methods to train configuration interaction coefficients (will be called as ANN-CI here) and it has been shown to perform excellently. More importantly, ANN-CI method can be trained with comparative efficiency with smaller space training data i.e., Monte Carlo configuration interaction (MCCI) data. The trained model achieves excellent accuracy and performance is tested in terms of variational energy, sensitivity and specificity etc.

[1] S.K, Ghosh, M., Rano, D., Ghosh, JCP 154 (2021) 094117 (Editor's Pick).

Title: Fluorination Affects Drastically the Photophysical Properties of Tryptophan

Tonima Nandy

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Abstract: 7-Fluorotryptophan (7F-Trp) is an important noncanonical derivative of tryptophan (Trp) which depicts high in vivo stability for the positron emission tomography (PET) imaging of Trp metabolism[1]. The photophysical properties of 7F-Trp in ethanol (ETH), 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-propan-2-ol (HFIP) have been investigated using spectroscopic technique, quantum chemical calculation, molecular dynamics simulation and compared with Trp to understand the role of fluorine in its fluorescence behavior. The presence of fluorine on tryptophan perturbs the interaction of its backbone containing COO^- and NH_3^+ with the chromophoric indole group which probably decreases the barrier of the conical intersection leading to decreased fluorescence intensity of 7F-Trp compared to Trp. The photophysical properties of Trp in alcoholic solvents is controlled mainly by solvent polarity whereas the weak interaction mediated by the fluorine of 7F-Trp with the fluorine and OH groups of fluorinated solvents plays an important role in modulation of its photophysical properties[2]. It has been found that, unlike Trp, 7F-Trp shows an additional emission feature at 430 nm which is highly dependent on the acidity of the solvents. Based on the experimental and quantum chemical calculation data, the specific emission feature of 7F-Trp has been assigned to the excited state protonation of 7F-Trp by the virtue of the proton transfer from solvents depending on its acidity[3].

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Structure analysis of Curcumin by Ion Mobility Mass Spectrometry

Subhankar Dutta

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Curcumin, the main bio-chemically active molecular component of turmeric, and is widely used as a medicinal compound. In a solution, the compound exists in two distinct tautomeric forms, diketo- and keto-enol, and the biochemical activities of the two forms have been shown to be different. We report here the structure analysis of this compound, both in the solution and in the gas phase, by employing HPLC coupled with UV-VIS absorption spectroscopy and ion mobility mass spectrometry. The two tautomeric forms are well separated by HPLC but their absorption spectra are significantly overlapped. An estimate of their relative abundances in a water-methanol mixture has been made by combining the mass spectrometric and spectroscopic data with the theoretically calculated absorption cross-section values. Electrospray ionization method, which is widely used for ionization of the non-volatile molecules in order to mass-separate by different mass analyzers, is shown here to have a significant effect on the isomeric conversion of the the curcumin. The isomeric differences are also revealed in the collision induced fragmentation pattern of the molecule. Quantum chemical calculation has been used extensively in aid for interpretation of the experimental findings.

Identifying the Template for Oligomer to Fibril Conversion for Amyloid-β (1-42) oligomers using Hamiltonian Replica Exchange Molecular Dynamics

Debasis Saha
School of Chemical Science, Indian Association for the Cultivation of Science

The oligomer to fibril conversion for amyloid-β (Aβ) peptides have been proposed to be the root cause for several incurable neurodegenerative diseases. With evidences suggesting high toxicity for small Aβ oligomers, lack of structural information regarding these systems poses a major challenge for the development of proper therapeutics against such diseases. In our study, we investigate low molecular weight Aβ 13-42 oligomers having two, three, four and five peptide chains using extensive all-atom molecular dynamics (MD) simulations. We have employed Hamiltonian replica exchange method (HREM) through solute tempering (REST2) to identify the key conformations for these oligomers in aqueous solution. Using a combination of intra-chain and inter-chain contacts as reaction coordinates, we obtain the free energy surface (FES) for these small Aβ42 oligomers. Consequently, the stable conformations for these systems have been identified and their structural features have been characterized. Our analysis finds that the conformations belonging to the most probable structures possess higher propensity to form β-sheets for residues 17-21, 30-36 and 39-41. For identifying the tendency to form fibril like interactions among these residues, we have defined a parameter that measures the fibril like contacts within these structures. Our analysis finds that among the groups of residues studied, residues 30-36 possess higher tendency to form fibril like contacts across oligomers of different sizes. The observations have been verified with different starting conformations for our HREM simulations. While we find higher interaction energy among residues 30-36, these particular group of amino acids are also found to be more shielded from water compared to other residues within the aggregates. With previous experimental studies finding these residues to be more crucial for the stability of Aβ42 oligomers, we propose from this study that this patch within the peptide chains could act as template for conversion of oligomers into disease relevant fibrils.

Orientational behaviour of colloidal crystal of hard polyhedra

Abstract : Orientational motion of hard anisotropic particles in self-assembled colloidal crystal has been a subject of interest in the field of soft-condensed matter. Due to the anisotropic shape of the building blocks, the crystal might have an orientationally ordered, disordered i.e. plastic crystal or orientational glass phase instead of having translational symmetry breaking in the system. The correlation of the phase behavior of entropic colloidal crystal to the shape attributes of the building blocks has been investigated, which is useful to predict the existence of plastic crystal phase and orientational glass without doing any simulations.

The effect of surface temperature on the scattering of H_2/D_2-Cu(111) using a chemically accurate PES

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The effect of surface modes vibrations on H_2/D_2 scattering from a Cu(111) surface at different temperatures is being explored for hydrogen/deuterium molecules in their rovibrational ground state (v = 0, j = 0). We assume weakly correlated interactions between molecular degrees of freedom and surface vibrational modes through a Hartree product type wavefunction [1]. While constructing the six-dimensional effective Hamiltonian, we employ (a) a chemically accurate potential energy surface according to the static corrugation model [2]; (b) normal mode frequencies and displacement vectors calculated with different surface atom interaction potentials [3-5] within a cluster approximation; and (c) initial state distributions for the vibrational modes according to Bose–Einstein probability factors. We perform 6D quantum dynamics [6] with the so-constructed effective Hamiltonian and calculate sticking and state-to-state scattering probabilities. The surface mode vibrations affect the chemisorption dynamics. The results display physically meaningful trends for both reaction as well as scattering probabilities compared to experimental [7] and other theoretical [2] results.

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J. Dutta and S. Mandal contributed equally to this work.

High Pressure Chemistry of Some Iron Complexes

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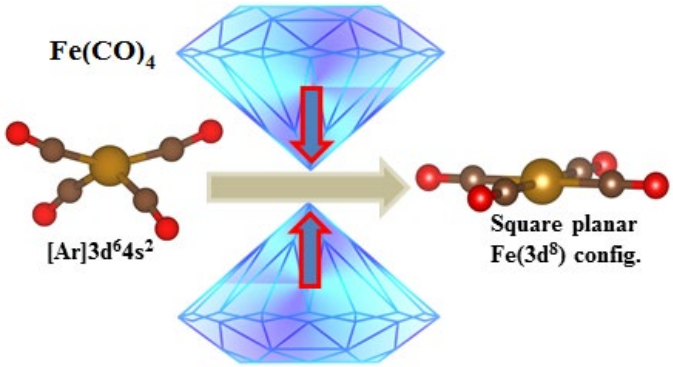
Abstract: Diamond anvil cells are able to produce isotropic pressures as high as 150 GPa in the laboratory. One of the important consequences of such high pressure is that electrons in the valence orbitals can be excited to realize excited states which can never be attained otherwise. The effect of pressure on the structural reorganization of ferrocene, Fc = $(C_5H_5)_2Fe$ is studied using density functional theory (DFT) calculations assisted by evolutionary crystal structure prediction algorithms. Pressure brings the individual molecules in close contacts and above 220 GPa, the 18-electron closed-shell molecular unit undergoes polymerization through the formation of quasi-one-dimensional (1D) chains, $[(C_5H_5)_2Fe]_\infty$. In the next project, we have reported that at pressure above 2 GPa, iron tetracarbonyl, $Fe(CO)_4$ attains a square-planar geometry with a sixteen electron count. Compression overcomes the $[Ar]4s^23d^6$ (S=2) $\rightarrow$ $[Ar]4s^03d^8$ (S=0) excitation energy to stabilize a closed-shell $Fe(CO)_4$ with d^8-configuration. Strong $\sigma(4CO) \rightarrow Fe$ ($d_{x^2-y^2}$) bonding alongwith Fe(d_{xz}, d_{yz}) and Fe(d_{xy}) $\rightarrow \pi (CO)_4$* back-bonding assists the formation of square-planar $Fe(CO)_4$ under pressure.



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Nitrile containing linker based metallogels: synthesis, characterisation and effect of nitrile on melanoma

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Nitrile functional group is an attractive option for the synthesis of metal based coordination polymers due its stability and influence on coordination polymer formation. Development of chiral coordination polymers starting from an achiral linker containing nitrile functional group is a challenging task. On the on other hand nitrile is relatively nontoxic to the living system unlike cyanide. For this reason, we designed a nitrile containing achiral linker and synthesized coordination polymers with it. Effects of solvents and anions on the structures were thoroughly studied using SXRD. Previous reports suggested that nitrile containing molecules showed activity against cancer cells due to its stability. Furthermore, it is a bioisostere of many functional groups (halogen, carbonyl etc.). We have tried to obtain gels from those coordination polymers, as gels can be applied topically for the treatment of melanoma. Cytotoxic effect of xerogels against melanoma cell line (B16-F10) was studied thoroughly to understand the effect of nitrile. Finally, the mode of cell death was investigated by flow cytometry and SEM.

Comparative anion receptor abilities of linear N-Confused tripyrrole Vs. N-Confued fused Macrocycles

Manik Jana, Harapriya Rath*

Abstract: Pyrrole and pyrrole based acyclic/cyclic systems have been widely exploited in the design of anion receptor due to their ability to form strong hydrogen bonds.[1] While linear oligopyrrole moiety are susceptible to change conformation to fit the size and shape of the negatively charged species and exhibit better binding ability towards anion compared to their cyclic congeners such as calix[4]phyrin. Contrarily, what remains scientifically elusive is the structural isolation of acyclic N-confused pyrrole based entity owing to synthetic challenges. On the other hand, though, N-confused porphyrinoids are well versed as anion receptors, their *meso*-saturated analogues such as calixphyrins are not yet studied as anion receptor(s). Thus, the first part of my talk will be focused on synthesis, solid state structural isolation, Spectroscopic and DFT-level theoretical studies of partially conjugated acyclic N-confused tripyrrane(s) and their cyclic counter parts i.e. N-confused calixphyrins. The second part of my talk will be directed towards the comparative study of these acyclic and cyclic N-confused pyrrole building blocks as anion receptors.

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Light-induced aerobic radical C-H functionalization of heteroarenes

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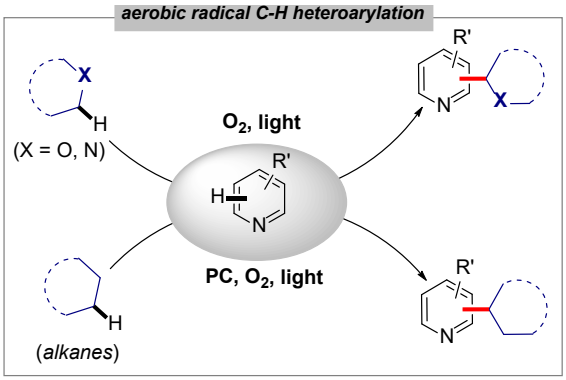
Functionalized N-heteroarenes are prevalent structural motifs in many natural products and pharmacologically active molecules. Direct incorporation of feedstock chemicals (ethers, amides, alcohols, ketones and alkanes) at C-H bond of N-heteroarenes through Minisci reaction remains the most appealing strategy to such compounds. Many different protocols for such transformations have been reported.[1-5] Recently, our group has introduced a novel strategy for the radical C-H functionalization of N-heteroarens using light as the source of energy and air as the sole oxidant.[6] In the presentation, studies towards the reaction development, substrate scope and mechanistic investigation of the aerobic radical C-H functionalization process will be discussed in detail.



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DNA G-quadruplex mediated telomerase inhibition by small molecules

Kushnood Fatma

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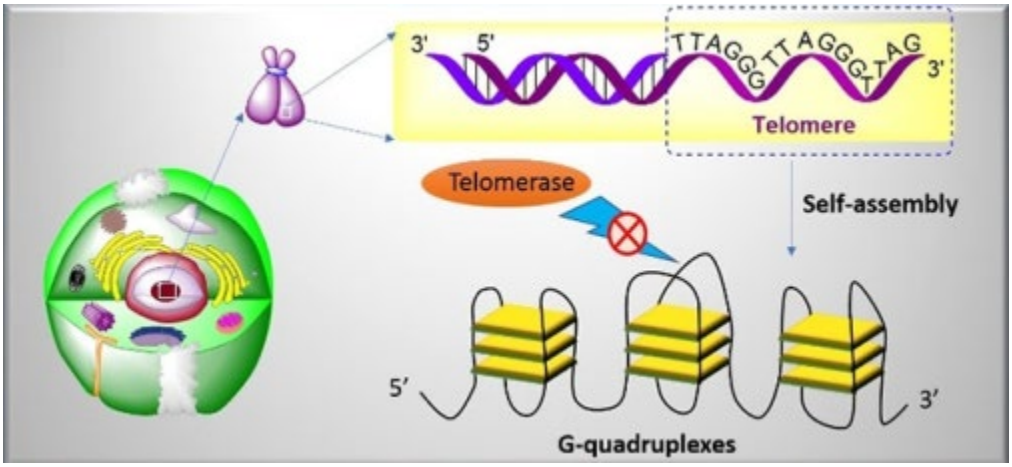
G-quadruplex (G4) structures are non-canonical higher-order structures formed by guanine-rich (G-rich) DNA sequences in presence of cations like Na^+ and K^+. The structural unit of G4 called G-quartet consists of four guanine bases held in plane by Hoogsteen hydrogen bonding. G4s present at telomere ends have been found to be biologically relevant. Stabilisation of G-quadruplex structures formed from telomeric DNA with G4-selective ligands, leads to inhibition of the telomerase enzyme and reduction of telomere elongation. We have synthesized small molecules that stabilize the telomeric G-quadruplex and inhibit the activity of telomerase in cancer cells. We have studied the interaction of small molecules with telomeric G4 using different biophysical and biological assays to ascertain the selectivity and biological effect of the molecules.

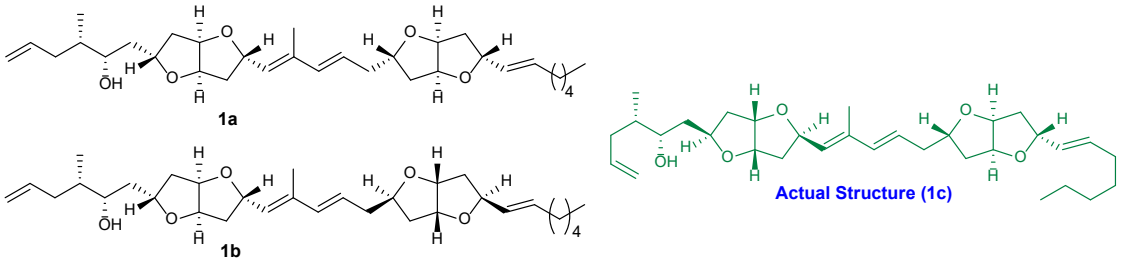


Asymmetric Total Synthesis of Amphirionin-2

Dhiman Saha, *Gour Hari Mandal and Rajib Kumar Goswami**

Amphirionin-2 was isolated from marine dinoflagellates *Amphidinium* species by Tsuda and coworkers in 2014. The molecule displayed anticancer activity against human colon carcinoma (IC_{50} 0.1 µg/ mL) and lung adenocarcinoma (0.6 µg/ mL). It also showed cytotoxicity against cervix adenocarcinoma Hela cells. The linear skeleton is embedded with two hexahydrofuro[3,2-b] furan units connected by two conjugated olefins. The correlation between the hexahydrofuro[3,2-b] furan units remained unknown during its isolation. Thus, we first prepared two possible structures (Figure 1, **1a** & **1b**) proposed by the isolation group which was further revised by the Fuwa *et al* (*Chem. Sci.* **2021**, *12*, 872) as compound **1c**.

Figure 1. *Chemical Structure of Amphirionin-2.*



Finally, the route developed by us was extended to achieve the total synthesis of the actual structure (**1c**) of amphirionin 2. The key features of our synthesis comprised Sharpless asymmetric dihydroxylation, followed by cycloetherification, Wittig olefination, Julia–Kocienski olefination, and Crimmins propionate aldol reaction. The natural product was synthesized in 30 longest linear steps with 0.3% overall yield starting from D-aspartic acid.

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Thermoresponsive Amino-acid-derived Polymer and its Antifouling Behavior

Priyanka Dinda and Tarun K. Mandal

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Bioinspired stimuli responsive polymers have gained huge interest in the last few decades for their biodegradability and biocompatability and thus researchers have focused on developing biofriendly responsive polymeric materials as it mimics the functions of living system, offers a great perspectives ina the fields of tissue engineering, triggered drug delivery and therapeutics. However, there are significant developments on the responsive polymers that are programmed for various stimuli such as temperature, pH, light, etc. While such focus and progress remains mainly centered around conventional polymers compared to amino-acid-based polymers offering a diverse range of applications in biomedical area. Thus, this study focuses mainly on designing of a Boc-lysine-based monomer and its reversible addition fragmentation chain transfer (RAFT) polymerization to poly(Boc-L-lysinylacrylamide)s [P(Boc-lysA)s] of controllable molecular weights (M_ns) and low dispersities ($Đ$s ≤1.23). This RAFT polymerization follows first order rate kinetics with good control over M_n and excellent agreement with the theoretical value up to a very high monomer conversions (ca. 83.8%). P(Boc-lysA) exhibits an interesting reversible upper critical solution temperature (UCST)-type phase behavior in mixed solvents comprising of water and different polar organics (e.g., DMF, DMSO and MeOH). The UCST-type cloud point (T_{cU}) increases linearly with increase of molecular weight of P(Boc-lysA) and percentage of water content in the mixture. The addition of large organic cations in the aqueous solution of P(Boc-lysA) at pH 8.5 induces a lower critical solution temperature (LCST)-type transition with tunable cloud point (T_{cL}) with respect to polymer concentration and its M_n as well as nature of added ion and its concentration. Furthermore, the Boc-deprotection of P(Boc-lysA) produces zwitterionic PlysA, that shows excellent anti-protein-fouling property compare to those of conventional antifouling polymers when tested with bovine serum albumin (BSA) and monitored by DLS.

A bis-heteroleptic imidazole-bipyridine functionalized iridium (III) complex for fluorescence lifetime-based sensing of phosphate and pyrophosphate

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Phosphorescent iridium complexes have a wide variety of applications in the field of inorganic photochemistry,[1] organic light-emitting diodes (OLEDs),[2] chemosensors, [3] as biosensing agents,[4] and as catalysts[5] owing to their excellent photochemical stability, cell permeability, tunable excitation and emission wavelengths, high luminescent quantum yields, large stoke shifts, and relatively long phosphorescence [6].

Inorganic anions are a ubiquitous and integral part of our ecosystem.. However, above permissible limits they tend to show harmful effects. This concern necessitated the development of receptor molecules for selective recognition and sensing of anions. Most of the receptors rely on optical anion sensors via on-off type signal transduction. The time-resolved fluorescence method is advantageous over the conventional optical intensity-based method since the lifetime is independent of the instrumental parameters and can provide quantitative sensing of many analytes without the requirement for wavelength-ratiometric probes.

Over the past few years, significant research activities have been devoted to the development of materials for selective sensing, recognition, and extraction of anions. It's noted that the recognition of oxyanion of phosphates is a difficult task owing to their large size and low charge density. In this regard, herein we report a new ppy and imidazole functionalized bipyridine-based heteroleptic Ir (III) complex **Ir-1** ($C_{44}H_{42}F_{18}IrN_8P_3$) that can function as a selective as a fluorescent sensor probe for phosphate and pyrophosphate anions.An enhancement in the fluorescence intensities of **Ir-1** along with a concomitant increase in the excited-state lifetimes is seen with phosphate and pyrophosphate ion , thereby allowing **Ir-1** with an excellent opportunity for very sensitive detection of these two anions. Importantly, a higher selectivity towards phosphate over several other environmentally ubiquitous anions was displayed. Overall, a selective and sensitive fluorescence sensor for phosphate and pyrophosphate anion is reported which also operates through lifetime measurement.

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Effect of Secondary Interactions on the Stability and Reactivity of a Chiral Nonheme Iron(IV)-Oxo Species

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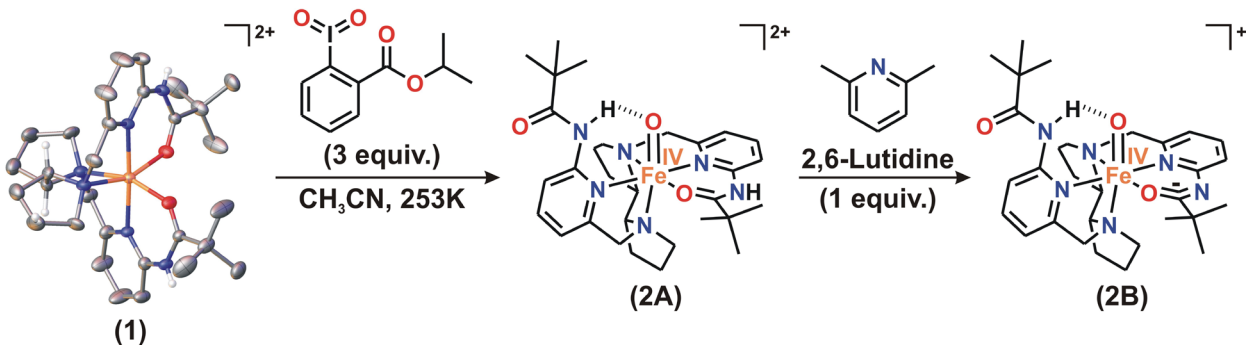
Many dioxygen-activating nonheme iron enzymes involve iron(IV)-oxo intermediates as the active oxidants in biological oxidations/oxygenations. Inspired by the enzymatic reactions, a good number of synthetic iron(IV)-oxo complexes have been isolated and spectroscopcally/structurally characterized.[1] These high-valent iron-oxo complexes display diverse reactivity.[2] Several factors such as nature of supporting ligands, spin-state of iron and other stereoelectronic properties control the stability and reactivity the iron-oxo intermediates.[3] Unlike protein backbones in enzymatic systems, secondary coordination interactions are absent in synthetic complexes. As a result, the efficiency and selectivity of oxidation/oxygenation reactions are often compromised. Thus, incorporation of secondary coordination interactions in bioinspired complexes are expected to tune the stability and reactivity of nonheme iron-oxygen species.[3]



With an objective to probe the effect of secondary coordination interactions along with the ligand field of primary coordination sphere on the reactivity of iron(IV)-oxo complexes, we have prepared an iron(II) complex (**1**) of an amide-substituted 2-(((R)-2-((R)-1-(pyridin-2-ylmethyl)pyrrolidin-2-yl)pyrrolidin-1-yl)methyl)pyridine (PDP) ligand. The iron(II) complex reacts with IBX-ester at 253K in acetonitrile to afford the corresponding iron(IV)-oxo species (**2A**). Another iron(IV)-oxo species (**2B**) can also be generated from the iron(II) complex upon treatment with IBX-ester in the presence of 2,6-lutidine. Interestingly, the thermal stability of the **2B** is found to be higher than that of **2A**. Importantly, the oxidants exhibit enhanced stability compared to that of the iron(IV)-oxo complex of the parent PDP ligand,[4] and this provides an opportunity to explore the oxidizing ability of the intermediates particularly in asymmetric oxygenation reactions. The high-valent iron-oxo oxidants perform oxo atom transfer (OAT) reactions as well as hydrogen atom transfer (HAT) reactions. The activity of the iron(IV)-oxo species in oxidation/oxygenation reactions and the role of amide group on the supporting ligand in directing the selectivity will be presented.

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Pentasulfido Chain in a Binuclear Zn(II) Complex

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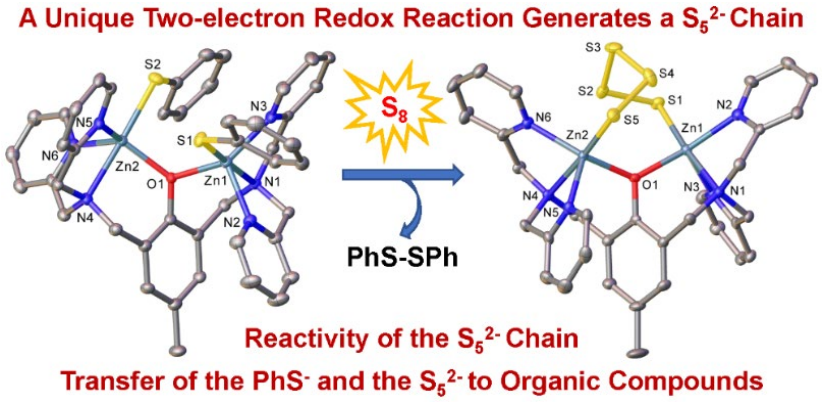
Zinc is an essential element for the growth and wellbeing of living organisms and zinc thiolates are common motifs in biological systems.[1, 2] There are a large number of mononuclear Zn(II) complexes with thiolate ligand and relatively less number of such complexes with hydrosulfide/polysulfide ligands.[3, 4] However, binuclear Zn(II)-thiolate complexes and their reactivity are much less explored[5, 6] while binuclear Zn(II)-polysulfido complexes are nonexistent. Here, we present the synthesis of a binuclear Zn(II)-bis(benzenethiolate) complex and its two-electron redox reaction with elemental sulfur (S_8) to yield an unprecedented binuclear Zn(II)-pentasulfido complex. The reaction of the binuclear Zn(II)-pentasulfido complex with phosphines generates a mixture of Zn(II) complexes featuring polysulfido chains of various sizes (S_n^{2-}, n = 2, 3, 4) and one such complex, (n = 4), could further be characterized by a molecular structure determination. Proteolysis reactions of the coordinated S_5^{2-} chain allowed access to more of new binuclear Zn(II) complexes, while the protonated S_5^{2-} chain liberated elemental sulfur and H_2S. Finally, transfer of the coordinated benzenethiolate ligands and the S_5^{2-} chain to selected organic compounds for the generation of organosulfur compounds has been demonstrated.[7]



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Reactive Intermediates of Copper Bound Aβ peptides and their association with Alzheimer's Disease

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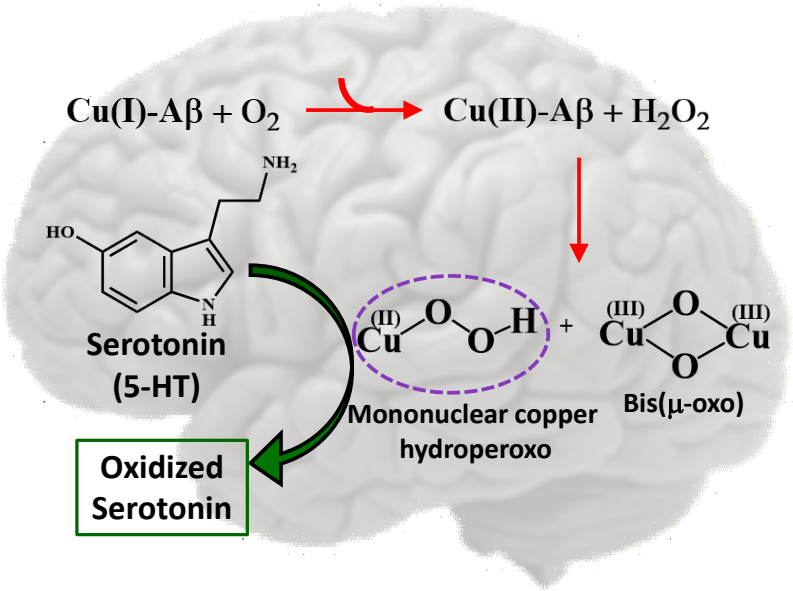
Alzheimer's disease (AD) is a terminal neurodegenerative disease that has generally been associated with the accumulation of amyloid beta (Aβ) peptides and characterized by the loss of neurons and neurotransmitters.[1] Transition metals like copper is found in abnormally high concentration in the oligomers and plaque of Aβ of AD affected brains.[1,2] This invokes the possible involvement of copper in AD. Copper can bind Aβ peptides and coexists in two different pH dependent forms at physiological pH.[3] We recently demonstrated that Cu-Aβ exhibits peroxidase activity[4] and can oxidize neurotransmitters like serotonin (5-HT) in the presence of H_2O_2, a biological oxidant. Reactive copper oxygen intermediates are supposed to be the active oxidants for the oxidative process. Cu-Aβ reacts with lower concentration of H_2O_2 (50 equivalent) to form a mixture of bis-μ-oxo-dicopper(III) and mononuclear end-on hydroperoxo copper(II) while in the presence of excess H_2O_2 (1000 equivalent), Cu-Aβ generates only the mononuclear end-on hydroperoxo intermediate. Both of these intermediates have been characterized using UV-Vis, EPR and Resonance Raman (rRaman) spectroscopy. Moreover, in the reduced state Cu-Aβ generates the same mononuclear hydroperoxo species in the presence of O_2 that carries out the oxidation of serotonin (5-HT). The ability of Cu-Aβ to oxidize neurotransmitters may provide a possible explanation for the neurodegeneration associated with AD.



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Reduction of Sulfur Dioxide to Sulfur Monoxide by Ferrous Porphyrin

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Reduction of SO_2 to fixed forms of sulfur can address the growing concerns regarding its detrimental effect on health and environment as well as enable its valorization into valuable chemicals. While the coordination of SO2 to transition metals are documented, its reduction using molecular catalysts has remained elusive. Alternatively, the naturally occurring heme enzyme sulfite reductase is known to reduce SO2 to H2S and is an integral part of the global sulfur cycle. However, its action is not yet mimicked in artificial systems outside of the protein matrix even after several decades of its structural elucidation. Here reduction of SO2 by iron (II) porphyrin, a synthetic analogue of heme, is demonstrated. A combination of spectroscopic and analytical methods indicates that SO_2 is reduced by $2e^-/2H^+$ by $Fe^{II}TPP$ to form an intermediate $[Fe^{III}\text{-}SO]^+$ species which releases SO. The SO obtained from the chemical reduction of SO_2 could be valorized in the form of a Diels-Alder adduct of butadiene resulting in an organic sulfoxide.

Structure and Mechanism in Peptide Self-assembly: Insights from Atomistic Computer Simulations

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Abstract

Peptides composed of gene-encoded library of twenty amino acids and their derivatives are known to form spontaneous noncovalent assemblies under *in vivo* and *in vitro* conditions. Availability of wide varieties of chemical functionalities in the building blocks and morphological features in the final assembled states have been exploited in the design of bio-compatible soft materials with targeted applications in a multitude of domains. Despite the wealth of information on the morphology of the assembled objects, atomic resolution details of molecular arrangements inside them are largely unknown. The mechanisms of the assembly processes are of fundamental interest and research in this area is still in its infancy. Our group is involved in complete understanding of the structure and mechanism in self-assembling peptide systems by a whole range of computer simulation techniques. In this talk, I will present our recent work on the spontaneous self-assembly of L-phenylalanine tripeptide in water. Our studies produced atomistic pictures of spontaneously assembled nanofibers composed of hundreds of peptide molecules. The dimensions of the nanofibers varied from 10 to 18 nanometres, with irregular helical twists along the long axes. Previously published experimental data, acquired under similar conditions, provided direct validation of the fibrous morphology and indirect support for the non-trivial helicity observed in our simulations. Quantitative analyses of peptide-water and peptide-peptide interactions revealed heterogeneous local environments of molecules across the nanometre length scales. Analyses of unbiased simulation trajectories revealed a stepwise mechanism with complex hierarchies. Importance of various chemical interactions during the main events of the assembly process furnished unprecedented details about the emergence of complex assembly phenomena from simple building blocks.

Enhanced Atomic Ordering Leads to Ultra-High Thermoelectric Performance

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With about 2/3 of all utilized energy is being lost as heat. Thermoelectric materials can convert waste heat to electrical energy, and it will have significant role in future energy management. High thermoelectric performance is generally achieved either by electronic structure modulations or through phonon scattering enhancements, which often counteract each other. A leap in performance requires innovative strategies that simultaneously optimize electronic and phonon transports. We demonstrate high thermoelectric performance with a near room-temperature figure of merit, zT ~1.5 and a maximum zT ~2.6 at 573 K by optimizing atomic disorder in Cd doped polycrystalline $AgSbTe_2$.[1] Cadmium doping in $AgSbTe_2$ enhances cationic ordering, which simultaneously improves electronic properties by tuning disorder-induced localization of electronic states and reduces lattice thermal conductivity via spontaneous formation of nanoscale (~2-4 nm) superstructures and coupling of soft vibrations localized within ~1 nm around Cd sites with local strain modulation. The strategy is applicable to most of other thermoelectric materials which exhibit inherent atomic disorder.

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Substrate induced catalyst formation under non-equilibrium conditions

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Abstract:
There remain critical gaps in our understanding of the emergence of functional biopolymers in the origins of Earth's biosphere. For instance, extant proteins, evolved over millions of years, carry out an impressive array of responsibilities, from catalysis and molecular recognition to motility and compartmentalization. One of the major goals of our lab is to investigate the possible origins of advanced enzymatic functions from folds of short peptide based paracrystalline phases. Further, we are excited about understanding the non-equilibrium structures of living systems.[1-6] I will show our recent discoveries of simple chemical systems that can be substrate-driven to access higher energy self-assembled states, just as seen in natural microtubules. Further, I will attempt to sketch our aims of developing self-assembled autonomous materials that can show temporal control of functions.[5,7-10]

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Total Synthesis of Bioactive Natural Products: Carolacton and Alveolaride C

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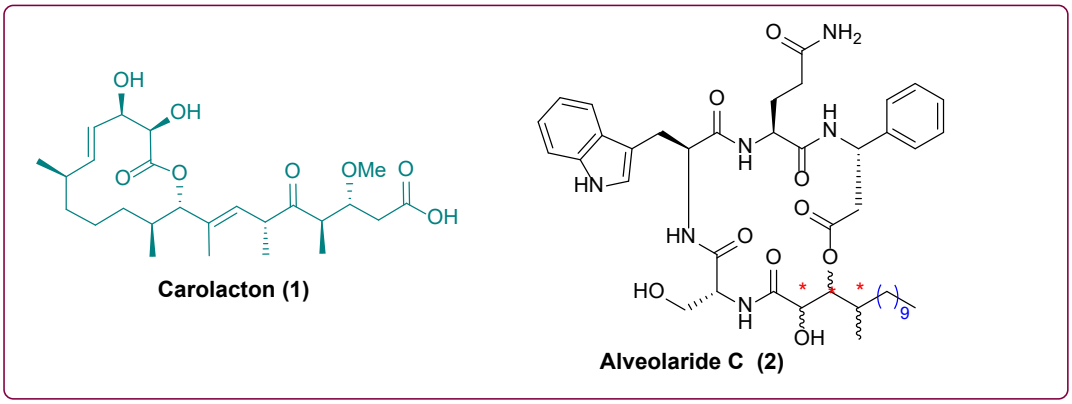
Abstract:

Total synthesis of natural product is one of the key backbones of many disciplines of science which attracted researchers due to their wide structural variations and broad range of biological activities. Carolacton (**1**) and alveolaride C (**2**) (Figure) are the bioactive secondary metabolites. Carolacton is a marine macrocyclic natural product which combats against *Streptococcus mutans* and *Streptococcus pneumonia*, the major bacterial pathogens responsible for human dental caries and pneumococcal infections, respectively, whereas. alveolaride C (**2**) is an antipathogenic marine natural product. The structure of alveolaride C was deduced partially by the isolation group. Attractive bioactivities of these secondary metabolites together with their natural scarcity as well as their structural uniqueness prompted us to develop synthetic routes to render them readily available which eventually would validate their structures. In this presentation, the state of art associated with the asymmetric total synthesis of bioactive carolacton (**1**)[1] and alveolaride C (**2**)[2] will be discussed.

Figure: Chemical Structures of Carolacton (**1**) and Alveolaride C (**2**).



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Covalent Organic Frameworks and Reticular Nano-Synthesis

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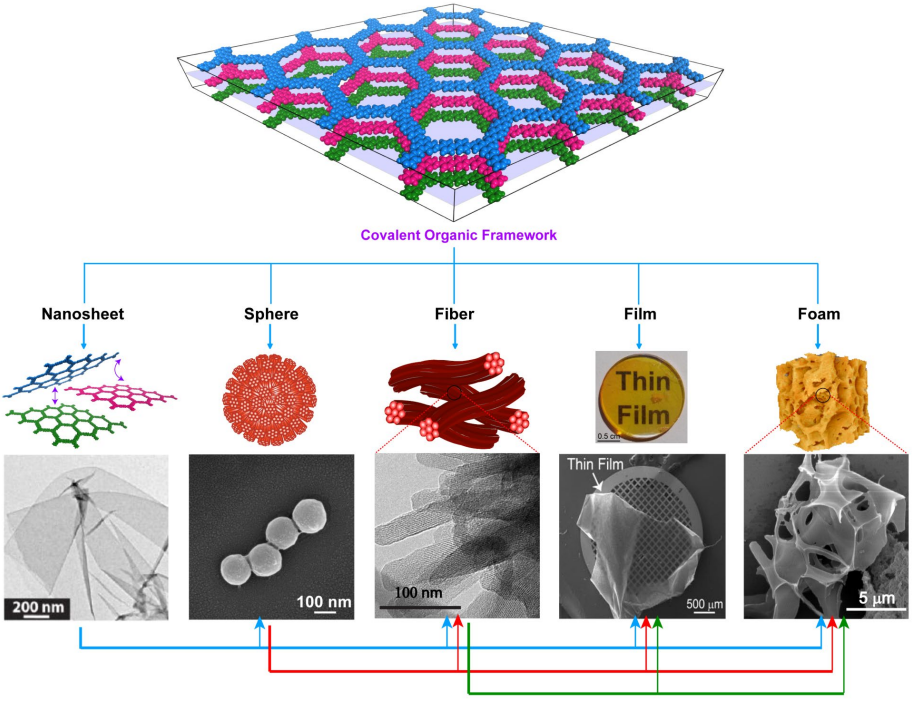
Covalent Organic Frameworks (COFs) represent a new class of highly porous, crystalline polymers with uniformly arranged ordered pore channels. Even though COFs have been used for the storage of a wide variety of molecular species like gases, nanoparticles, enzymes, and drugs, the benefits of their ordered 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 *β-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.



Flexibility in metal-organic frameworks and their functional recompense

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Flexible or dynamic metal organic frameworks (MOFs) have become a very promising field in contemporary research not only due to their study in understanding structural features but also for their potential applications in tailoring better functionality. The transformation of phase which is the fundamental thing of such structural flexibility can be initiated by various external stimuli like heat, light, pressure, solvent etc. This dynamism in the structure of MOF based material can proceeds through physical as well as chemical changes. Interestingly, it has been noted that for such flexible MOFs, the transformed phase may sometime display stepwise gas and/or solvent adsorption and also show selective gas adsorption. These functionalities in flexible MOFs might be found pretty useful for gas and/or solvent separation. Moreover, as the change of phase are generally taken place by some external stimuli, monitoring of the change in the structures of flexible MOF, can be used as a sensor for the responsive stimuli both as qualitative (molecular recognition and/or sensing) as well as quantitative (impurity measurement) way.

In many of our work, it has been observed that in the study of flexible MOFs with their structural flexibility most of them show reversible crystalline-to-crystalline transformation whereas in some cases rare reversible crystalline-to-amorphous transformation has also been observed. In every case, various external stimuli like heat, pressure, solvents etc, individually or cooperatively facilitate the transformations to another phase. There are several interesting properties have been observed for these transformed products. It has been also found that some flexible MOF shows excellent solvent dependent emission properties and those may be useful to detect the traces of water in solvents, and may sense the polarity of different organic solvents. A direct physical motoring of the single crystalline phase has been done in the light of the mechanical property of the crystal and an inter-relation has attempted with the structural flexibility and mechanical property of the crystal.