DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY MADRAS

BOOK OF ABSTRACTS
CHEMISTRY iNHOUSE CHEMISTRY (CiHS 2020)

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Co-Convener, CiHS 2020

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MESSAGE FROM THE HEAD OF THE DEPARTMENT

Dear Faculty, Staff, Students and Distinguished Invitees to the CIHS - 2020,

It gives me great pleasure to invite all of you to the Two-day Symposium organized by the Chemistry department, fondly known to all of us as Chemistry-In-House Symposium, or as CIHS 2020, during Dec 3 and Dec 4, 2020. When the first event was rolled out in 2011, it was a meeting ground for interactions between students and faculty within the department. It was also a unique event featuring a large number of Ph. D. Scholars of the department as presenters, both in oral and poster format. The organizers of the event in 2011 had hoped that this would sustain and develop into an annual event with more and more active participation. Their expectations have been brilliantly carried forward and realized successfully by successive organizing teams; COVID 19 could only limit the meeting format to online Conference but could not dampen the enthusiasm of all participating scientists, young and old. This year being the tenth year of CIHS, the department faculty agreed to take this to the International arena. The faculty, staff and students are privileged to have the participation and a Key Note Address by one of its most distinguished Alumni and a renowned theoretical chemist, Prof. Krishnan Raghavachari from Indiana University, Bloomington, Indiana, USA. An M. Sc. student of this department during 1973-75 when most of our current students were not even born, Prof. Krishnan brings an unmatched wealth of experience in teaching, philosophy and excitement of original and focussed research to the young students and scholars as well as a freshness in research ideas and applications which are truly interdisciplinary to the faculty. There are several faculty members and many students who will give oral presentations and many others will showcase their posters in the allotted time. I want to place on record, the intense and sincere efforts by Professors Rajakumar, Dr. Kartik Mondal, Dr. Kothandaraman and Dr. Anbarasan in organizing the Symposium and all faculty and students who have agreed to present their research. The challenge they had to face in not being able to bring cuiliniary pleasures and free-hand poster sessions to a serious scientific meeting, due to social distancing is quite big too! The spirit of scientific inquiry will still prevail in the online meeting and take us forward. The primary focus and objective of this program have been and will be to bring together the Ph. D. Scholars, staff and faculty of the Department of Chemistry, IIT Madras for one day every year and share their research findings with all students, particularly the M. Sc. and beginning Ph. D. students. My best wishes to a successful and memorable event on the two days that follow.

K. Mangala Sunder

Prof. K. Mangala Sunder

Head, Department of Chemistry

MESSAGE FROM THE CONVENER

3rd December 2020

Exactly a decade back, in the international year of chemistry 2011, few of our colleagues went out to Krishna hostel gate for a cup of Tea. During our usual discussions, an idea of having a one-day in-house symposium every year was sprouted. We all just walked into our HOD’s office and proposed this to Prof. Sankararaman, our then HOD. He was very happy about the proposal and asked us to form a team and conduct it. The first in-house symposium named as Chemistry inHouse Symposium (CiHS) was conducted by Prof. Sundargopal Gosh as the convener and myself as co-convener. Trust me, it was an overwhelming response from the Department and everyone in the Department has participated in that CiHS with tons of enthusiasm. It was the first and a very successful inHoue symposium. That success gave us lots of motivation to continue it every year. In fact, it is not an exaggeration, if I say that we all look forward for this day every year. Ever since, it has been conducted on the third Wednesday of August of every year under the convenorship of one of our colleagues.

We thought of having this 10th CiHS in a very big way by inviting distinguished alumni of our Department and conduct it for two days. However, due to this pandemic, all our plans were changed. At one point of time, we were not sure if we could be able to conduct the CiHS 2020 at all. When this was proposed in one of our faculty meetings, only one statement was heard and it was ‘why should we stop our very important academic activity at all for any reason and we can go online’ and that’s how the 10th one, which is virtual was sprouted. This year’s CiHS is organized by Dr. Kothandaraman, Dr. Anbarasan and Dr. Kartik Mondal along with me.

This CiHS 2020 is comprised of one keynote lecture by Prof. Krishnan Raghavachari, one of our distinguished alumni from Indiana University; four invited lectures by our faculty colleagues, two short invited lectures by our newly joined colleagues and ten oral presentations by the students from ten different groups covering all main streams of chemistry. In addition, twenty nine posters are being presented electronically by the research scholars, even though the current strength in the Department is much less than the usual strength due to Covid-19. However, we deeply miss our fabulous dinner, which is one of the attractions in our CiHS, where all the students, staff, faculty and their families meet in OAT and have great time. I am very proud to be a part of this Department to say that nothing could kill our enthusiasm. This re-union on an electronic platform shows our academic commitment and I am sure we will continue to strive with added enthusiasm every year in the years to come. I take this opportunity to thank each and everyone in the Department for giving me this memorable opportunity to convene my favorite event, CiHS. Long live CiHS! I wish everyone to have a wonderful symposium.

Rajakumar Balla

Convener, CiHS 2020

Department of Chemistry
Chemistry inhouse symposium (CiHS-2020)
Indian Institute of Technology Madras

Day one **03-12-2020, Thursday**

2:00 – 2:30 PM		**Inauguration**
		Invocation
		Address by the Convener, CiHS 2020
		Address by the Head of the Department
		Inaugural address by the Director, IIT Madras
		Vote of thanks by the Co-Convener, CiHS 2020
2:30 – 3:45 PM	**Session I**	**Chairperson: Prof. Archita Patnaik**
2:30 – 2:45 PM	SIL1	Dr. Hema Chandra Kotamarthi
2:45 – 3:00 PM	SOP1	Rintu Robert (KV)
3:00 – 3:30 PM	IL1	Prof. Debashis Chakraborty
3:30 – 3:45 PM	SOP2	Mr. B. Ramesh (MJM)
4:00 – 5:15 PM	**Session I**	**Chairperson: Prof. K. Vidyasagar**
4:00 – 4:15 PM	SOP3	Mr. Debayan Roy (BB)
4:15 – 4:30 PM	SOP4	Mr. Rajeev Chand Nishad (AR)
4:30 – 4:45 PM	SOP5	Mr. V. Surya Kumar (PS)
4:45 – 5:15 PM	IL2	Prof. Edamana Prasad
5:45 – 7:00PM	**Session III**	**Chairperson: Prof. K. Mangala Sunder**
	Keynote Lecture by Prof. Krishnan Raghavachari	

Department of Chemistry

Chemistry inhouse symposium (CiHS-2020)

Indian Institute of Technology Madras

Day two **04-12-2020, Friday**

9:30 – 10:45 AM	**Session IV**	**Chairperson: Prof. G. Sekar**
9:30 – 9:45 AM	SIL2	Dr. Chaitanya Sharma Yamijala
9:45 – 10:00 AM	SOP6	Ms. K. Jayasree (KCM)
10:00 – 10:30 AM	IL3	Dr. P. Venkatakrishnan
10:30 – 10:45 AM	SOP7	Mr. Subham Pal (AD)

11:00 AM– 12:15 PM	**Session V**	**Chairperson: Prof. Sanjay Kumar**
11:00 AM **–11:15 AM**	SOP8	Ms. Tamil Selvi (KRR)
11:15 AM**– 11:45 AM**	IL4	Prof. K. Mangala Sunder
11:45 AM **–12:00 PM**	SOP9	Mr. Suman Dana (MB)
12:00 PM **– 12:15 PM**	SOP10	Mr. Abdul Sattar (AP)

12:30 – 1:00 PM **CONCLUDING SESSION**

Concluding remarks by Prof. S. Sankararaman

Address and Prize distribution by Prof. Ravindra Gettu, Dean IC&SR

National Anthem

KEYNOTE LECTURE

G4 Accuracy at DFT Cost: Eliminating Systematic Errors in DFT to Derive Accurate Energies for Complex Chemical Processes

Sibali Debnath, Eric Collins, Sarah Maier, Arkajyoti Sengupta, Bishnu Thapa,
*Krishnan Raghavachari**

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The failure of available density functional (DFT) methods to compute accurate electronic structures and energies for complex systems is well documented. In particular, there is often a large variation in the computed energies associated with complex reactions using different popular density functionals. While newly developed dispersion corrected and long-range corrected density functionals offer improved results, the errors are often greater than 5 kcal/mol for many chemical processes. Moreover, the lack of a universal DFT or a generic protocol to assess DFT errors has compounded the associated problems in quantum chemistry. Herein, we demonstrate that the disparate results from different density functionals stem from the systematic errors in the underlying chemistry representing the elementary changes in the bonding environment between reactants and products. We have developed a rigorous protocol to correct for these systematic errors and obtain dramatically improved results with deviations of only 0–2 kcal/mol for most density functionals. An important characteristic of our protocol is that the corrected results are largely independent of the nature of the underlying density functionals, and approach the accuracy obtained from state-of-the-art composite methods such as G4 theory. The performance of a range of DFT methods for a set of challenging problems – such as pericyclic reactions representing complex electronic rearrangements, bond dissociation energies in large biofuel molecules, redox potentials for diverse organic molecules, or accurate pK_a calculations for drug molecules containing several functional groups – is analyzed and assessed in this work.

SHORT INVITED LECTURES
(SILs)

SIL 1

Deciphering the chemo-mechanical coupling mechanisms of ATP-dependent enzymes using single-molecule force spectroscopy

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Energy-dependent enzymes perform many key cellular processes such as protein degradation and disaggregation, and act as biological molecular motors converting chemical energy from hydrolysis of ATP to mechanical energy. These enzymes utilize this energy to perform activities such as protein unfolding and translocation that are essential for protein degradation. Although the biochemical mechanisms of these enzymes are well-understood, the biophysical properties such as kinetics, translocation velocities and the stepping dynamics, as well as the energetic costs of these individual mechanical processes have not been studied in detail. Single-molecule force spectroscopic tools such as optical tweezers have enhanced our understanding of protein mechanics and the mechanism of action of molecular motors by complementing the bulk biochemical/biophysical methods. Single-molecule measurements allow examination of individual processes of a multi-step reaction as well as highlight the heterogeneity in their molecular properties that are masked in bulk averaging. In the current talk, I will discuss my recent research on the application of optical tweezers to understand the role of protein substrate directionality on protein degradation by an ATP-dependent protease, ClpAP. We show that ClpAP mechanically unfolds a model protein substrate, titin^{I27}, from the N-terminus with one or a few power strokes and is much faster than C-terminal unfolding, although translocation is only mildly affected by the direction. Our results highlight the paramount role of local stability in protein degradation and provide clues as to how the placement of degradation signals on a substrate may evolve to minimize the energetic cost of degradation[1]. Continuing on the mechanism of ClpAP, I have deciphered the role of individual ATPase motors in a double-ring ATPase enzyme, ClpAP. I have shown that ClpAP inactivated in the one of the rings is partially defective in unfolding, and pauses frequently during translocation, revealing that one ring functions as a booster motor assisting the more powerful other ring[2]. In addition, I will briefly discuss my research on application of single-molecule atomic force microscopy to co-relate the structure, sequence and mechanical stabilities of proteins using β-grasp proteins as model examples[3]. Further I will elaborate on my future research projects on application of optical tweezers and spectroscopic techniques to elucidate the differences in proteasomes vs proteases, both of which perform the same function of protein degradation, as well as determine the relation between polypeptide-amino acid composition and its translocation efficiency by ATPases.

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[2] Kotamarthi, H.C.; Sauer, R.T.; Baker, T.A. *Cell Reports.* **2020,** *30*, 2644.

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SIL 2

Adiabatic and Nonadiabatic dynamics: Applications in Catalysis, Batteries, and Organic Photovoltaics.

*Sharma S. R. K. C. Yamijala**
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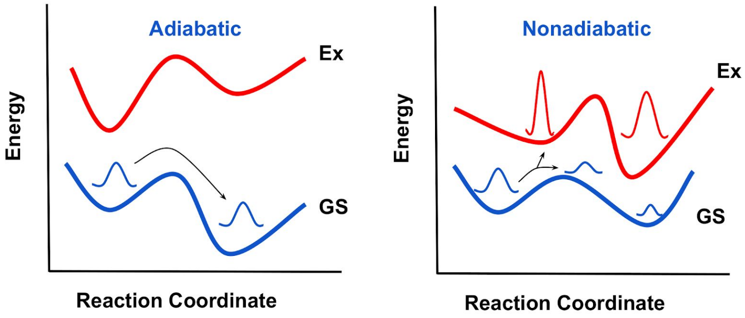
Many of us are aware of the Jablonski diagram, which explains fluorescence and phosphorescence processes using the concept of potential energy surfaces (PESs). As shown in that diagram, electrons hop between excited (say, S_1) and ground states (say, S_0). In other words, in photochemical processes, electronic amplitudes evolve over several PESs, and to capture these electronic processes accurately, we need to go beyond the ground state methods like DFT. If the photochemical reaction of our interest also includes the dissociation/formation of bonds, then we need to include the nuclear dynamics as well. If the nuclear dynamics is governed by a single PES (say, S_0 or S_1), then it is known as *adiabatic dynamics*, and if it involves more than one PES, then it is known as *nonadiabatic dynamics*. Adiabatic dynamics can be readily captured using many molecular dynamics (MD) packages such as CP2K, Quantum-Espresso, etc. However, the implementation and utilization of nonadiabatic dynamics is an ongoing research topic. In my talk, first, I will discuss the Fewest-Switches-Surface-Hopping method (a nonadiabatic dynamics method) that I implemented in the DFTB+ package,[1] and show its application in the field of organic photovoltaics.[2] Next, I will discuss a few applications that we recently explored in the areas of catalysis and energy storage devices using the traditional electronic structure and Born-Oppenheimer MD simulations.[3-5] Finally, I will present the future research interests that I would like to pursue at IIT-Madras.



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= equal author

INVITED LECTURES
(ILs)

IL 01

Subtle Features in Lactide Polymerization: Effect of Metal, Ligand(s) and Geometry of Catalyst in PLA Synthesis

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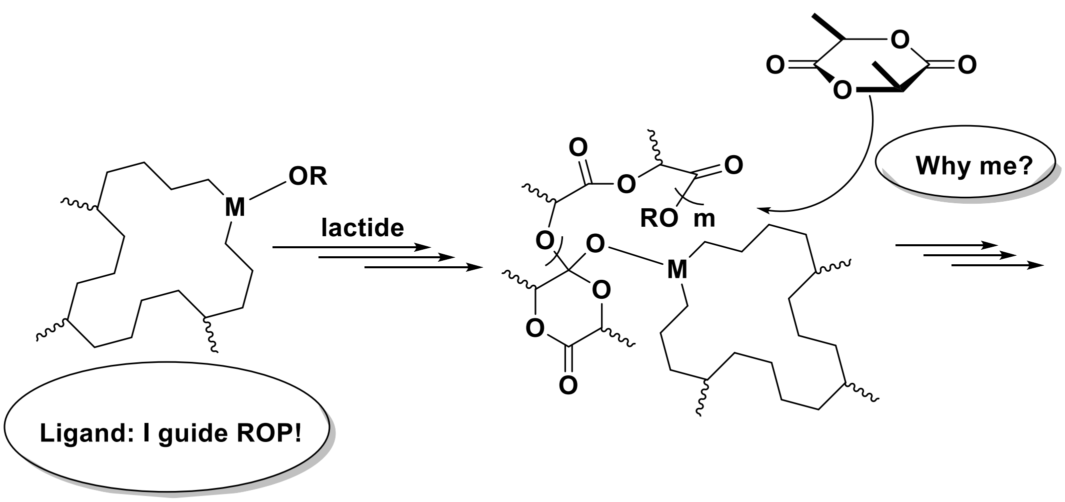
In the recent years, there has been a heuristic impetus towards the search for polymers from sustainable feedstock that are completely biodegradable and compostable thus contributing a circular economy in terms of raw material resources. This necessity stems from the pollution hazards associated with conventional plastics.[1] In this regard, a material that has attracted considerable research attention is poly(lactic acid) (PLA) which is conventionally produced using ring-opening polymerization (ROP) of the cyclic dimer of lactic acid popularly called as lactide. This methodology provides a better control over the polymerization parameters and produces PLA with desired molecular weights and molecular weight distributions under mild reaction conditions.[2,3] Rigorous studies over the past few years have revealed that the stereochemistry observed in the PLA is largely dependent upon the thermodynamic preference of the initiating monomer molecule from a racemic mixture of lactide enantiomers.**[4-6]** It is understood by us that the genesis of an unsymmetrical transition state produced from lactide and the catalyst plays a vital role in governing the stereospecificity of the propagation step which finally decides the final stereochemistry of the PLA. Most of the existing literature does not specify the optimum symmetry of the transition state that is necessary for a stereospecific propagation. The objective of the lecture is an appreciation of understanding towards the control of the molecular parameter as well as the tacticity of the PLA using recent examples from our research. Finally, it will be shown that the stereochemistry of the PLA can be controlled using non-centrosymmetric ligand/catalyst or by employing chirality in the ligand framework.



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IL 02

Study of Fast Reaction Kinetics in Quantum Dots Using Transient Absorption Spectroscopy

Edamana Prasad *
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The present talk explains the basic principles involved in transient absorption spectroscopy, which is widely utilized in 'pump-probe' experiments. In the recent past, there has been an increasing interest in understanding the excited state dynamics of quantum dots due to their potential role in energy harvesting. 'Pump-probe' experiments can be used to get insightful information about the excited state process in quantum dots.[1] In the present study, the excited state dynamics of CdSe quantum dots (CdSe QDs) were monitored using femto second laser flash photolysis system, in the presence and absence of graphene quantum dots (GQDs). The results from the study indicate the evidence of electron transfer from CdTe QDs to GQDs with the hole-trapping process by surface defects. On the basis of the mechanistic study, an overall charge-transfer scheme that accounts for the faster bleach recovery of CdTe QDs in the presence of GQDs is proposed. More importantly, the consequences of improved charge transfer have been established through the measurements of enhanced photoconductivity (ie., from 1.39 (±0.12) × 10^{-4} S m−1 in the control system to 1.47 (±0.24) × 10^{-3} S m^{-1} in the system under investigation). These findings described in the present study are hoped to open up design strategies for developing light-harvesting inorganic−organic hybrid QD assemblies with better efficiency.

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IL 03

Coumarin[4]arenes: A Family of Fluorescent Macrocycles

Venkatakrishnan Parthasarathy*
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Design and synthesis of macrocyclic hosts with predetermined binding sites and conformationally tunable cavity size have always remained the topic of great interest for organic and supramolecular chemists.[1] Numerous synthetic hosts, such as, cyclophanes, cucurbiturils, calixarenes, resorcinarenes, pillararenes, etc., have been constructed and investigated for applications not limited to molecular recognition but for sensing, catalysis, materials science, and biomedical fields.[2] Under this category, a new class of bicyclic heteroaromatic cavitands, namely '*coumarin[4]arenes*' has been reported by our group recently (Figure 1).[3] These macrocycles are inherently blue-fluorescent and chiral. They can be readily synthesized using a mild two-step optimized protocol in high yields by employing the readily available reagents. Coumarin[4]arenes are found to rapidly interconvert between their two C_2-symmetric boat conformations in solution.[4] The conformationally-flexible coumarin[4]arenes are capable of binding to quaternary ammonium ions strongly. In continuation to these efforts, we have successfully achieved conformationally-locked C_4-symmetric coumarin[4]arenes by a simple pre-macrocyclization strategy, avoiding complex post-synthesis methods. Some aspects pertaining to the synthesis, characterization, conformational behavior, host-guest complexation of these coumarin-containing novel fluorescent macrocycles will be highlighted during this presentation.

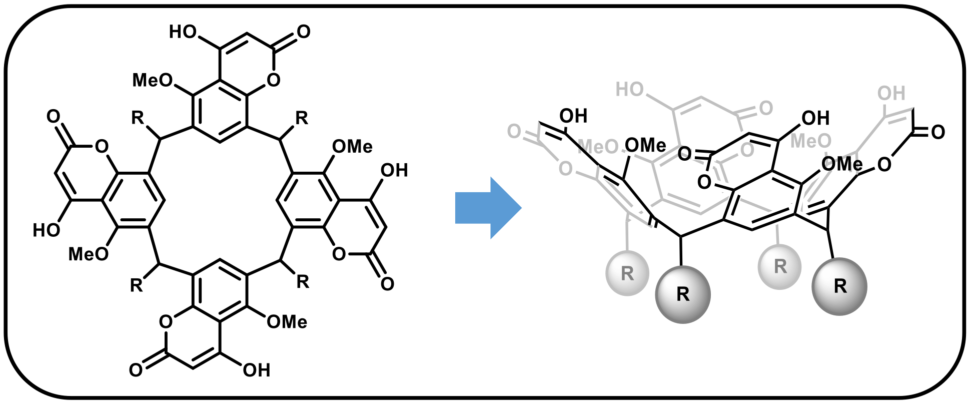

Figure 1. Structural representation of coumarin[4]arenes.

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IL 04

Revisiting benzene-water and and benzene-water-rare gas complexes microwave spectra with a Coriolis Coupling Model

Prasenjit Halder* and Mangala Sunder Krishnan* and E. Arunan**
** Department of Chemistry, IIT Madras, Chennai 600036*
*** Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, 560012.*

The microwave spectrum of benzene-water complex is nearly thirty years old and has been analyzed initially using a restricted torsional Hamiltonian and later using a more extended torsion-rotation coupling model. However, a few intense and prominent lines had to be omitted from the spectra to ensure that the errors of fitting of the remaining lines are close to experimental accuracy. Subsequently several complexes with benzene have been studied by others using the same model and in every one of them a similar inconsistency has been noticed with lines that could not be fit under the torsion-rotation coupling. The problem was revisited with a model of symmetric top, low frequency degenerate bending modes coupled strongly to overall rotation through Coriolis terms. The fits using this model appear remarkably consistent and the analysis has been extended to study a host of similar complexes. In every one of them, the revised model fits all lines observed without exception. This talk will give a summary of the efforts that led to this closure of a long-standing problem in microwave spectra of van der Waals complexes.

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[1]. Ref. Coriolis Interactions in Benzene-Water and Related Molecular complexes, Prasenjit Halder, Mangala Sunder Krishnan and e. Arunan, J. Molec. Spectrosc., **370**, 111277 (2020) includes both a brief history of earlier fits and details of the current model.

STUDENT ORAL PRESENTATIONS
(SOPs)

SOP 01

Syntheses and characterization of new quaternary phosphates, $Sr_3Nb_2P_2O_{13}$ and $Sr_3Ta_2P_2O_{13}$

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Abstract

Two new quaternary phosphates, $Sr_3Nb_2P_2O_{13}$ and $Sr_3Ta_2P_2O_{13}$, were synthesized by solid state reactions and characterized by X-ray diffraction and spectroscopic techniques. They are isostructural compounds and crystallize in noncentrosymmetric $P2_12_12_1$ space group. Single crystal X-ray structure determination of $Sr_3Nb_2P_2O_{13}$ compound revealed its unique layered structure, which consists of Sr^{2+} and discrete PO_4^{3-} ions between anionic $[Nb_2PO_9]^{3-}$ framework layers. The noncentrosymmetric structure is attributed to acentric coordination polyhedra, namely, distorted NbO_6 octahedron and PO_4^{3-} tetrahedron. The niobium and tantalum compounds have band gap values of 3.94 and 3.67 eV, respectively. Their second harmonic generation[1, 2] responses needs to be evaluated.

Reference

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SOP 02

Transition-Metal-Catalyzed Functionalization of Substituted Aromatics with Sulfonyl Chlorides or Alkenes

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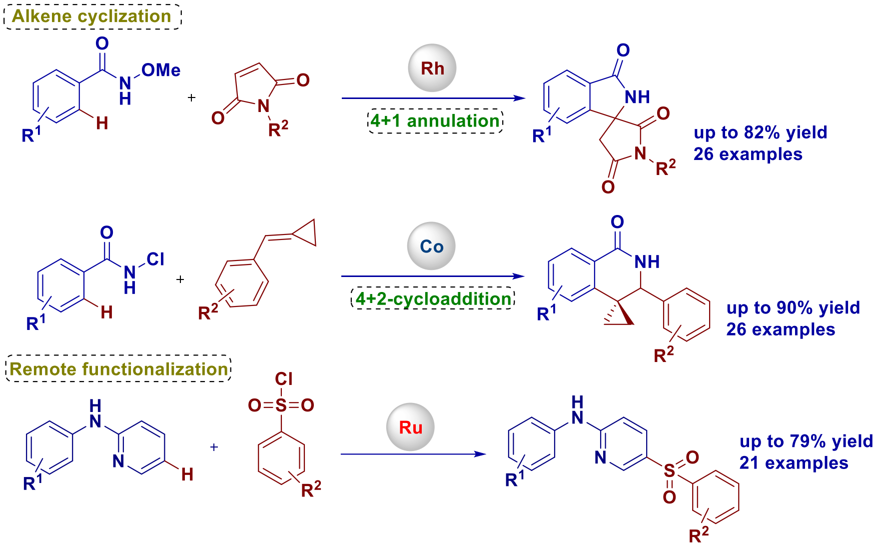
Transition-metal-catalyzed cyclization of substituted aromatics with carbon−carbon π-components *via* C−H bond activation is a promising method to construct carbocyclic and heterocyclic molecules in a highly atom- and step-economical manner.[1a] For these reactions, π-components such as alkynes, alkenes, benzynes, maleimides and alkylidenecyclopropanes are widely used. In addition, a stoichiometric amount of metal oxidant is needed to regenerate the active catalyst [Rh(I) to Rh(III) or Ru(0) to Ru(II) or Co(I) to Co(III)]. The development of new methods to avoid the use of stoichiometric amount of metal oxidant into catalytic amount of oxidant or redox-neutral manner is highly important.[2] With our continuous interest on transition-metal-catalyzed cyclization reactions, we have investigated reaction of substituted *N*-methoxy benzamides or *N*-chloro benzamides with maleimides or alkylidenecyclopropanes in a redox-neutral manner *via* [4+1] annulation and [4+2] cycloaddition strategy, respectively. *N*-Methoxy benzamides react with maleimides in presence of a Rh(III) complex afforded spiroindolinone moieties in moderate to good yields.[3] In the other hand, the reaction of *N*-chloro benzamides with alkylidenecyclopropanes in presence of a Co(III) catalyst provided 3,4-dihydroisoquinolinones in moderate to excellent yields.[4] During the past few years, σ-chelation-directed cyclometallation strategy is an emerging method for functionalization of *meta* position of aromatic ring systems.[1b] Herein, we disclosed a ruthenium-catalyzed remote C−H sulfonylation at the C5 position of the pyridine group of *N*-aryl-2-aminopyridines with aromatic sulfonyl chlorides *via* the C−H bond activation.[5]



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SOP 03

Functionalization of inactivated C(sp^3)-H bond by Brønsted acid catalyzed alkynyl Prins annulation and further studies

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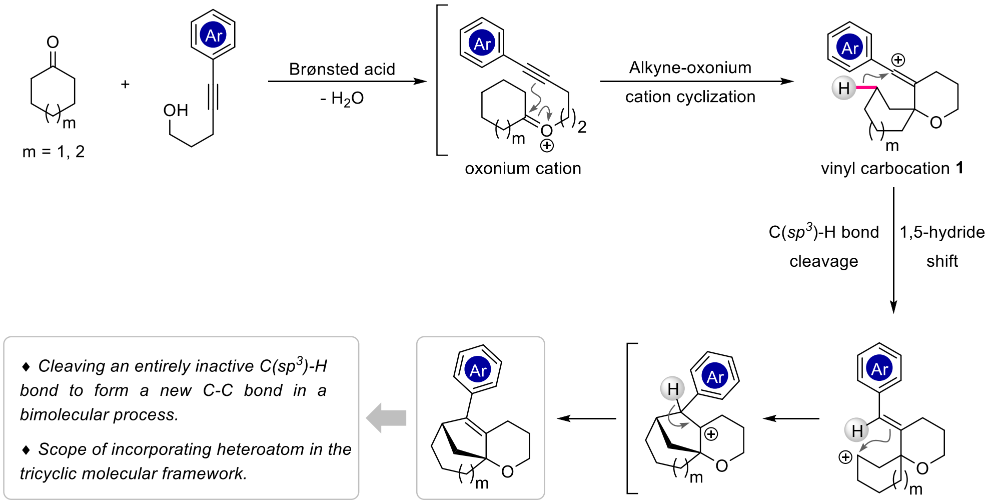
Selective catalytic functionalization of inactivated sp^3 hybridized C-H bond possesses a paramount challenge in organic synthesis owing to their high bond dissociation energy and high abundance in the organic molecules.[1-4] While dealing with Brønsted acid catalyzed alkynyl Prins reaction between ketones and alkynols, we presumed that the speculative vinyl carbocation intermediate **1** (Scheme 1) may offer such a spatial arrangement that would promote inactivated C(sp^3)-H bond functionalization leading to interesting tricyclic molecular architecture containing bicyclo[n.2.1] (n = 3, 4) moieties. Gratifyingly, our subsequent experimentation validated our proposition and we could achieve the synthesis of different bicyclo[4.2.1]nonene and bicyclo[3.2.1]octene containing tricyclic molecules. During this study, we were also introduced to various other molecular frameworks. The intricate mechanistic aspects and exploration of the potential of this novel methodology will be disclosed in this presentation.



- *Cleaving an entirely inactive C(sp^3)-H bond to form a new C-C bond in a bimolecular process.*
- *Scope of incorporating heteroatom in the tricyclic molecular framework.*

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SOP 04

Poly(N-Heterocyclic Carbene) Ligands: Applications in the Construction of Self-Assembled Molecular Architectures and Heterobimetallic Catalysis

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In the last few years, N-heterocyclic carbene (NHC) ligands have proven themselves as privileged successors of the classical ligands such as phosphines, carbonyls, cyclopentadienyls etc.[1] The strong σ-electron donation capability of NHCs and ease of alteration of their electronic as well as steric properties have made them popular in organometallic chemistry and catalysis.[2] Among various applications, NHC ligands are widely utilized for the synthesis of efficient transition metal based catalysts and for the construction of metal assisted three-dimensional assemblies. However, poly(NHC) ligands are relatively less explored although reported to be a wise choice as building blocks as well as ancillary ligands for the above mentioned chemistry. Herein, we present the synthesis of two new polyazolium salts [**L1**-H_3]$(X)_3$ (**1**) and [**L2**-H_2]$(X)_2$ (**2**) (X = Br, PF_6), precursors for NHC donors, featuring different coordination sites (Figure 1a) and their utilization in the generation of unique Ag^I-assisted self-assembled structures and synthesis of effective heterobimetallic catalyst systems (Figure 1b).[3] The hexanuclear complexes [(**L1**)$_4$$Ag_6$]$(PF_6)_6$ were obtained by reacting **1** with Ag_2O and they represent the unique examples of discrete polynuclear self-assemblies, obtained *via* rational design, which feature more than two poly-NHC ligands that are connected by means of exclusive Ag^I-NHC bonds. This polynuclear Ag^I-NHC complexes were successfully utilized as carbene transfer agents[4] to obtain diverse Au^I/Cu^I coinage metal-NHC complexes.[5] On the other hand, the sequential deprotonation cum metalation of the ligand **2** afforded the heterobimetallic Ir^{III}/Pd^{II} and Ir^{III}/Au^I NHC complexes. The synthesized heterobimetallic Ir^{III}/Pd^{II} complex was found to be effective in various tandem organic transformations such as transfer hydrogenation and Suzuki-Miyaura cross coupling or hydrodefluorination.

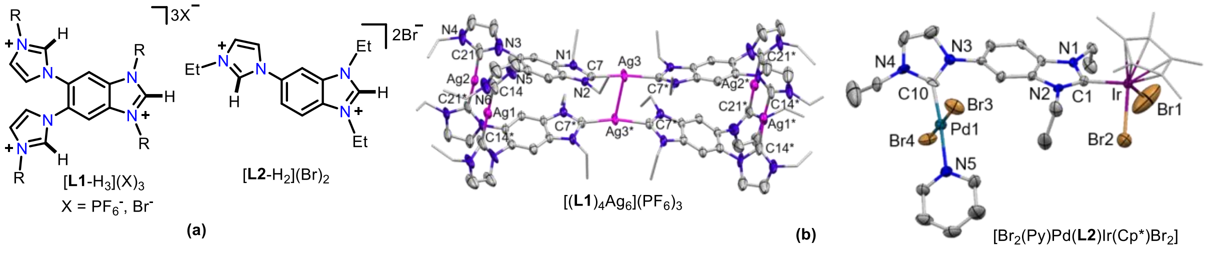

Figure 1: a) Mixed imidazole and benzimidazole derived ligands **1** and **2**. b) Crystal structures of the hexacation [(**L**$_1$)$_4$$Ag_6$]$^{6+}$ and heterobimetallic Ir^{III}/Pd^{II}-NHC complex.

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SOP 05

Emerging trends in degradation of pharmaceuticals in aqueous media and new challenges in development of ordered mesoporous titania photocatalyst

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Pharmaceuticals in environment in surface/ground water have led to tremendous concern over its severe impact on the human/animal health and ecosystem.[1] The current water treatment technologies are inefficient or ineffective to degrade completely the dissolved drug molecules in aqueous systems, e.g., famotidine, paracetamol, erythromycin, and more than 200 such drugs. Developing new advanced oxidation process for such purpose is a challenge for scientific community. In this regard, titania-based photocatalysts are the most extensively employed for such purpose. However, bulk titania has several limitations including its high exciton recombination rate, low surface area and limited light absorption properties. In this context, ordered porous materials are highly relevant with their unique textural, electronic, and optical properties. Hence, we have recently developed[2,3] high-quality 2D-hexagonal ordered mesoporous titania with well-crystallized framework porous structure and high surface area using P-123 and CTAB as structure-directing agents. The resulting mesostructured matrix are designed as TMP-123 and TMC-016/TMC-036, respectively. These high-quality nanostructured materials (Fig. 1a & 1b) show significant amounts of intrinsic defects, viz., Ti^{3+} centers as compared to commercial P25 photocatalyst (Fig. 1c & 1d), which in-turn promote the charge separation of photogenerated excitons, and therefore exhibit excellent degradation efficiency (DE) for famotidine (FAM; TMP-123: DE$_{100}$ = 75min; P-25: DE$_{100}$ = 120min; Fig. 1e). The superior activity of the synthesized catalysts is ascribed to: (i) light absorption extending into the visible region, (ii) low charge-transfer resistance and high carrier density, and (iii) intrinsic Ti^{3+} defects, as deduced from DRUV-Visible, photo-electrochemical and EPR studies, respectively. On the other hand, paracetamol (PAC) shows only a partial degradation (Fig. 1f) under similar reaction conditions. Further work is in progress.

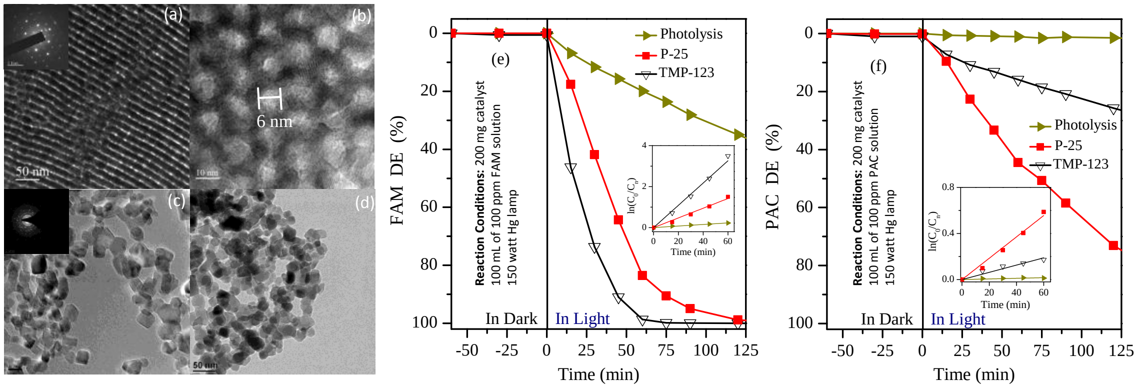

FIG. 1. TEM images of TMP-123 (a & b) and P-25 (c & d), and photocatalytic degradation of FAM (e) and PAC (f).

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SOP 06

Small coordination clusters: oligomerization, catalysis and magnetism

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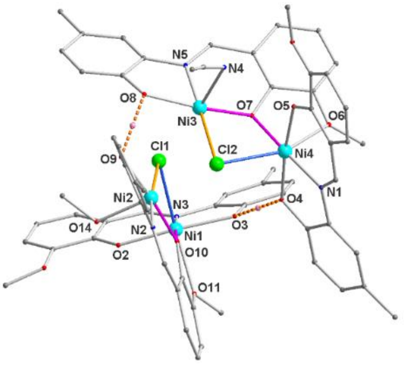
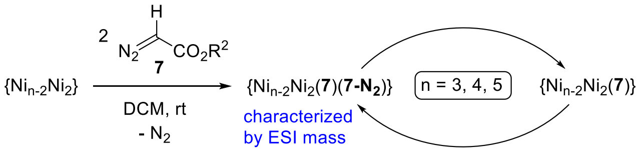
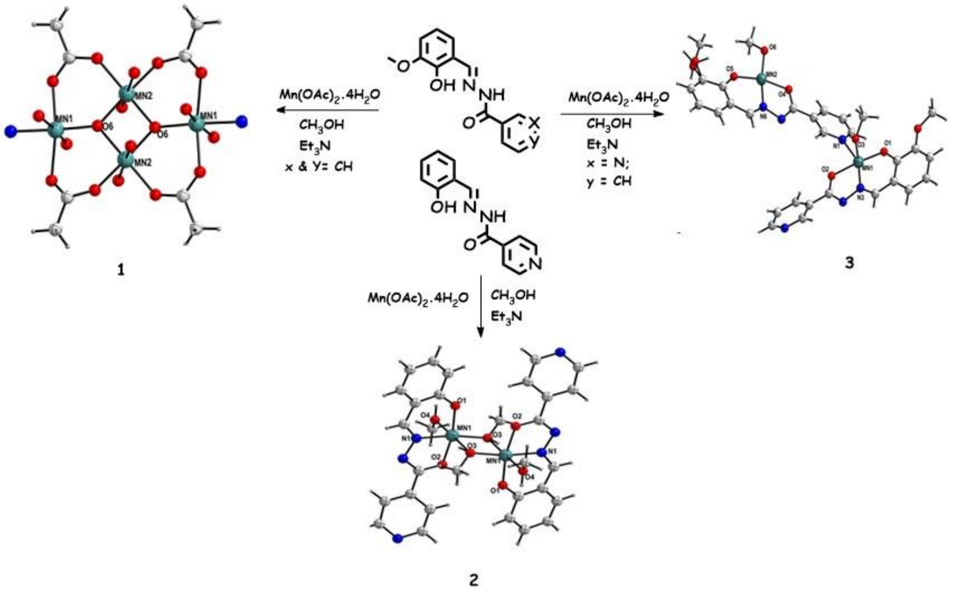
Transition metal based coordination complexes have been known for their catalytic and magnetic properties. The cluster with repeating monomeric units called oligomers which results upon the elimination of small molecules in the system.[1] Their sizes are confined and obtained through finite degree of polymerization. Original monomers undergo aggregation to yield oligomers. Such Nickel based oligomers originated from parent Ni_4 $[Ni_4((O^-)_2L\text{-}Me)_2((O_{al}^-)(OH)L\text{-}Me)_2Cl_2(MeOH)(MeCN)]$ compound (Fig. 1) are characterized using ESI mass spectrometry. The pentacoordinated Ni_4 compound acts as a catalyst for stereoselective cyclopropanation reactions of aromatic heterocycles along with diazoester as a carbene source. The catalytic activity of the tetranuclear complex studied on substituted aromatic heterocycles using various diazoesters.





Molecular structure of H-bonded tetramer (left) Plausible oligomeric $\{Ni(L\text{-}Me)\}_n$-catalyzed mechanism for cyclopropanation reaction (right).



Three different $Mn^{(III)}$ complexes $Mn_4(H_2hbhz)_2(OAc)_4(OMe)_4$ **1,** $Mn_2(H_2hihz)_2(OMe)_4$ **2** and $Mn_2(H_2hnhz)_n(OMe)_2$ **3** have been prepared with $Mn(OAc)_2.4H_2O$ by slightly tuning the substituents of the ligand. The interesting magnetic phenomenon exhibited by these three complexes were investigated.

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SOP 07

Modeling Single-Nanoparticle Catalysis

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Nanoparticle catalysis is intrinsically heterogeneous, and hence challenging to study in ensemble measurements. Single-molecule detection of fluorogenic reactions in which a catalytic conversion of non-fluorescent substrates (off states) to fluorescent products (on states), occurring one at a time on the surface of a single nanoparticle, captures intrinsic heterogeneity in catalytic cycle in terms of stochasticity in the waiting times between two consecutive off and on signals [1-4]. In this work, we show how a unified theoretical framework, based on the chemical master equation (CME), provides a novel way to infer catalytic mechanisms and rate parameters from different, seemingly unrelated, measures introduced in a series of experimental studies on single-nanoparticle catalysis [1-4]. Building on a previous work [5], we find that a Langmuir-Hinshelwood (LH) like mechanism is consistent with experimental data, provided it includes two important aspects of intrinsic heterogeneity at the single-molecule level, namely, fluctuations due to surface restructuring dynamics and multiplicity of catalytic sites[6]. For this, we propose a parallel-pathway LH mechanism with replicas. This mechanism, in its minimal form, provides excellent quantitative agreement with experimental data, and shows how the sign and magnitude of waiting time correlations between consecutive turnovers provides a sensitive indicator of intrinsic heterogeneity. Our work establishes that the statistical dependences of off and on signals in a single turnover, and temporal correlations between consecutive turnovers are crucially linked with multiplicity of catalytic sites. This rules out all previous single-site models of single-nanoparticle catalysis in which statistical independence of off and on signals is implicitly assumed [1-5].

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SOP 08

Fuel and Energy Production Using Electrocatalyst from Spent Zinc/C Battery

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Recycling of used batteries creates not only careful management of existing resources and prevents environmental breakdown from both ceaseless mining and the noxious waste being dumped in landfills, but also promotes sustainable economic development. In the current study, the recovered cathode material from the end-of-life batteries was repurposed as an electrocatalyst for electrochemical synthesis of ammonia (via nitrogen reduction) and electrochemical reduction of oxygen for metal (Zinc)-air battery applications.[1] Ammonia is essential to the global economy as a fertilizer feedstock, industrial and household chemical, and chemical precursor in addition to also being considered a future fuel alternative and hydrogen storage molecule. The production of synthetic ammonia remains dependent on the energy and capital-intensive Haber-Bosch process.[2] Extensive research in molecular catalysis has demonstrated ammonia production from di-nitrogen, albeit at low production rates. The transition to Haber-Bosch alternatives through robust, heterogeneous catalyst surfaces remains an unsolved research challenge.

The derived electrocatalyst ($ZnMn_2O_4$) demonstrated an excellent catalytic activity towards oxygen and nitrogen reduction reactions (ORR/NRR) in the aqueous medium. ORR onset potential is 0.86 V vs. RHE. During NRR, water present in the electrolyte produces competing hydrogen evolution reaction (HER) due to its closest reduction potential, thus causing a major selectivity issue in NH_3 production. Our study shows effective HER suppression promoting NRR in basic medium.

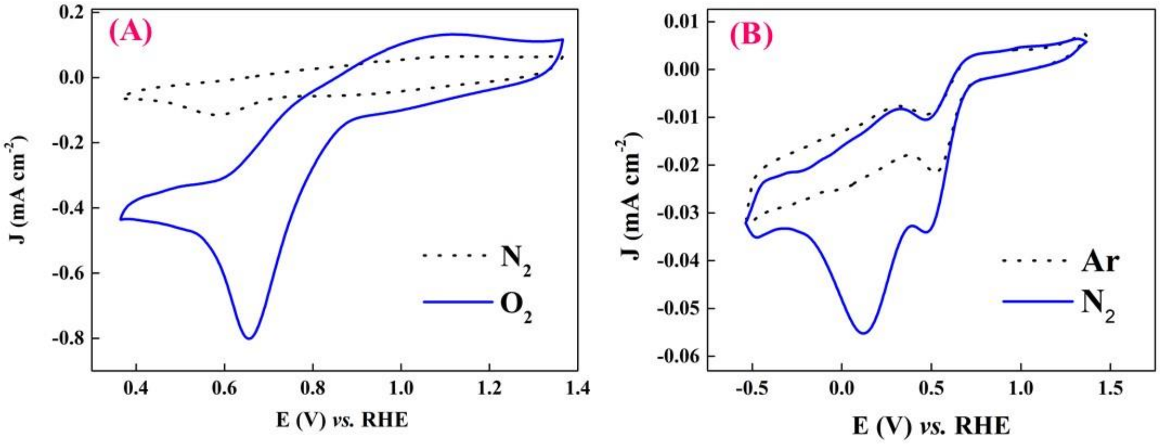

Fig. Cyclic voltammetry curves of $ZnMn_2O_4$ catalyst in (A) oxygen saturated and (B) nitrogen saturated 0.1 M KOH electrolyte

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SOP 09

Diversification of Arene Carboxylic Acid Feedstocks Through Ru(II)-Catalyzed C–H/C–H Coupling Reactions

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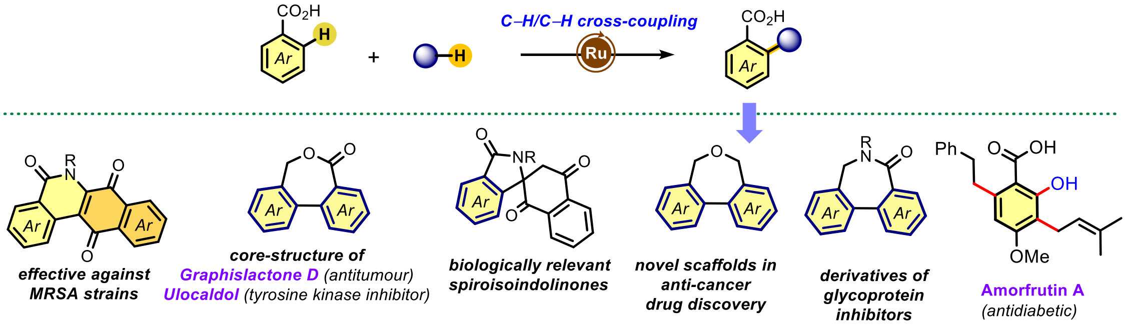
Arenes constitute the fundamental structures of numerous natural products, pharmaceuticals, clinical drug candidates, and many other high-value organic molecules. Thus, the development of novel synthetic strategies for the selective functionalization of arenes carries fundamental importance in synthetic organic chemistry. Conventionally, functionalized arenes are synthesized using transition-metal catalyzed cross-coupling reactions. But, these strategies requisite prefunctionalized precursors, expensive phosphine ligands, and generate superstoichiometric amounts of waste. In this aspect, directed C–H/C–H cross-coupling reactions with arenes have displayed tremendous potential owing to their sustainable nature and broader synthetic utility.[1] Unlike the cross-coupling reactions, we can obviate prefunctionalized precursors, which not only expedite the access of diverse functionalized arenes, but also expand the scope towards the late-stage derivatization of valuable organic molecules.[1] These synthetic approaches become inimitable, when native functionalities present in organic molecules are utilized for selective functionalization of arenes. In this regime, involving the commercial feedstock chemicals such as benzoic acids bear substantial importance, as these feedstock chemicals are available with diverse substitution pattern which can be manipulated to useful organic molecules through direct catalytic transformations. Even after the rapid growth of such strategies under expensive Pd, Rh, and Ir-catalysis, the advancement of Ru(II)-catalyzed direct C–H/C–H cross-coupling reactions is relatively slow. This synthetic space has encouraged us to develop novel direct C–H/C–H cross-coupling reactions under Ru(II)-catalysis. In this presentation, I will demonstrate few of our recent findings towards harnessing the innate potential of these feedstock chemicals through direct C–H/C–H cross-coupling to generate diverse array of functionalized arenes including heterocycles and spirocycles.[2]



effective against MRSA strains

core-structure of Graphislactone D *(antitumour)* **Ulocaldol** *(tyrosine kinase inhibitor)*

biologically relevant spiroisoindolinones

novel scaffolds in anti-cancer drug discovery

derivatives of glycoprotein inhibitors

Amorfrutin A *(antidiabetic)*

Scheme 1: Ru(II)-catalyzed C–H/C–H cross-coupling with benzoic acid derivatives and access to biologically relevant organic molecules.

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SOP 10

Controlling and Probing the Structured Interfaces of High-Performance Elastomers

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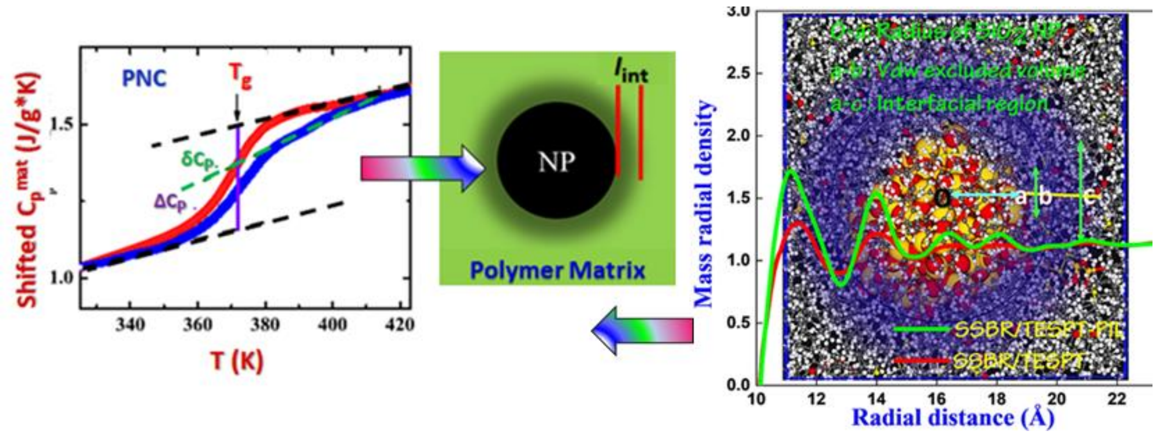
Nanocomposites are fundamentally new class of materials in which the nanoparticles (NPs) induce interfacial reconstruction[1] via multiple non-covalent interactions culminating in varied material properties. While it is known that the properties of polymer nanocomposites (PNCs) are largely dominated by the interfacial layer around the nanoparticles, the molecular parameters controlling the interfacial layer structure and dynamics are complex and remain feebly studied.[2,3] Here, we combined different static and dynamic experiments along with computational modelling to probe both the polymer and nanoparticle-specific parameters with a goal to control the local structure and dynamics in PNCs. Specifically, this work provides an in-depth analysis of the interface structure and associated chain dynamics of the silica NP-filled Styrene-butadiene and Natural rubber PNCs at a scale close to the relevant molecular processes, directly correlating their micro/macroscopic properties[4-7] utilizing ionic and ionic liquid modifiers and cross-linkers. Accordingly, improved thermal stability, high-temperature shifts in the glass transition, self-healing ability and dynamic-mechanical performance of the PNCs were accrued from the existence of a strengthened and thicker interfacial layer, tapped by systematic dielectric relaxation spectroscopy, temperature modulated differential scanning calorimetry and molecular dynamics simulations.



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POSTERS

PHYSICAL & THEORETICAL CHEMISTRY

PC 01

Confining an Ag_{10} Core in an Ag_{12} Shell: A Four-Electron Superatom with Enhanced Photoluminescence upon Crystallization

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Atomically precise analogs of noble metals, also called nanoclusters (NCs), have become an emerging category of nanomaterials, shown to be important in diverse applications such as sensing, catalysis, energy storage, drug delivery, cancer treatment, etc.[1] NCs have been used as nanoscale building blocks for creating solid-state materials.[2] Till now, more than 100 Au NCs with crystal structures have been reported. Contrary to this, only a few Ag NCs are known with their crystal structures, due to their ease of oxidation.[3]

Herein, we introduce a new Ag cluster co-protected by thiol and diphosphine ligands, $[Ag_{22}(dppe)_4(2,5\text{-}DMBT)_{12}Cl_4]^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane; 2,5-DMBT= 2,5-dimethylbenzenethiol), which has an Ag_{10} core encapsulated by an $Ag_{12}(dppe)_4(2,5\text{-}DMBT)_{12}Cl_4$ shell. The Ag_{10} core comprises two Ag_5 distorted trigonal bipyramidal units and is uncommon in Au and Ag nanoclusters. The electrospray ionization mass spectrum reveals that the cluster is divalent and contains four free electrons. An uncommon crystallization-induced enhancement of emission is observed in the cluster. The emission is weak in the solution and amorphous states. However, it is enhanced 12 times in the crystalline state compared to the amorphous state. A detailed investigation of the crystal structure suggests that well-arranged $C{-}H\cdots\pi$ and $\pi\cdots\pi$ interactions between the ligands are the major factors for this enhanced emission. Further, in-depth structural elucidation and density functional theory calculations suggest that the cluster is a superatom with four magic electrons.

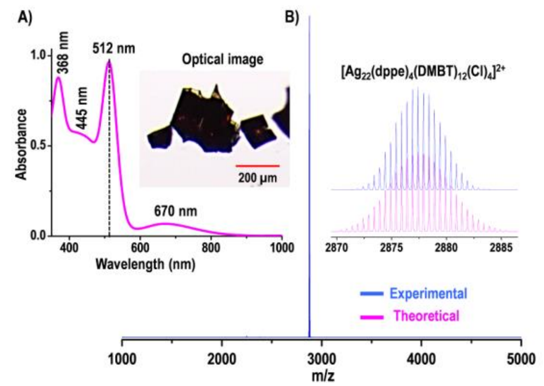

Figure. (A) Optical absorption spectrum and (B) HRESI MS of $[Ag_{22}(dppe)_4(2,5\text{-}DMBT)_{12}Cl_4]^{2+}$ which displays a peak at m/z 2876. Inset: Comparison of the theoretical and the experimental isotopic distributions.

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PC 02

Fabrication of a safe and energy-dense aqueous carbon/carbon supercapacitor with a wide voltage window

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Abstract

Amplification of energy density without compromising with power density is a major challenge in the field of capacitive science. Since energy density is quadratic dependent on voltage ($E= 1/2\ CV^2$), broadening an operating voltage window of the supercapacitors (SCs) could be an effective strategy to boost the energy density rather than improving the capacitance of the electrode. For extending the voltage window of the SC beyond the water electrolysis voltage limit in an aqueous medium, the chemistry of the electrode material and pH of the electrolyte plays an important role.[1,2] In the present work, activated carbon (ACTS-800) derived from Tamarind seeds, a bio-mass, pyrolyzed at 800 ºC is explored as a potential electrode material for fabricating a high voltage SC in aqueous 1 M Na_2SO_4. Interestingly, the beneficial interaction between the surface functional groups and electrolyte resulted in the high overpotentials for both hydrogen and oxygen evolution reactions in the neutral medium. As a result, the fabricated symmetric SC had shown a broad working voltage window up to 2.0 V with an attractive energy density of 28 Wh kg^{-1} at 248 W kg^{-1}. On the other hand, the formation of a stable electric double layer due to ion ordering at the interface, the symmetric SC exhibited a low leakage current of 0.33 mA at 2.0 V. Due to the attractive features such as eco-benignity, low leakage current, and high energy density of as developed SC we believe that it might qualify as one of the potential candidates for the next-generation energy storage applications.

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PC 03

Electrode and conductive additive compatibility yielding excellent rate capability and long cycle life for sustainable organic aqueous Zn-ion batteries

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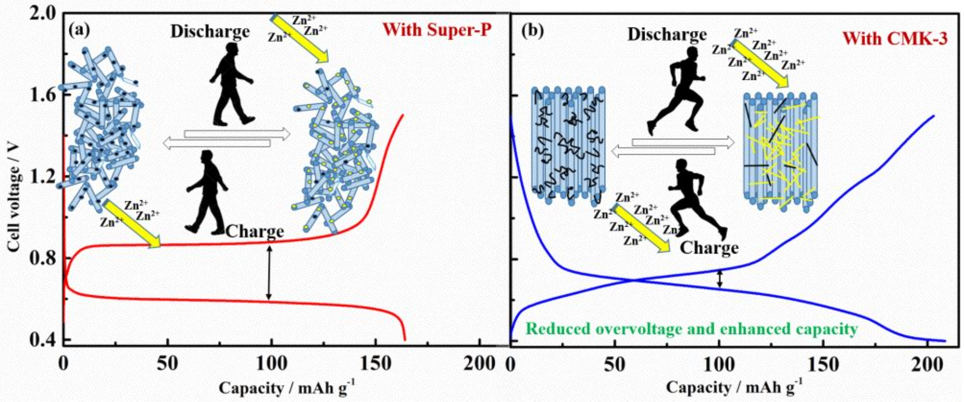
Aqueous Zn-ion battery has tremendous potential to penetrate the energy storage market, as an alternative to Li-ion batteries, given the high volumetric capacity of Zn (5853 mAh cm^{-3}), cost-effectiveness, earth abundance, and enhanced safety sprouting from using the aqueous electrolyte. But its performance is stunted due to poor rate capability and low cycle life originating from the degradation of cathode materials upon Zn^{2+} insertion/deinsertion. Thanks to the stability of aromatic organic cathode material with required intermolecular spacing, pentacene-5,7,12,14-tetraone (PT). Due to the poor conductivity of PT, Super P (low surface area mesoporous carbon, 60 m^2 g^{-1}), Ketjenblack (~1200 m^2 g^{-1} mesoporous carbon) and CMK-3 (high surface area ordered mesoporous with 981 m^2 g^{-1} area) are tried as conductive support. PT is encapsulated into CMK-3 conductive additive making it perform at rates as high as 20 A g_{PT}^{-1} (63C) with ~ 46% capacity retention. Such rates are common for supercapacitors; therefore, this work is distinct as outstanding faradaic behavior is obtained due to the chemical robustness of the cell. PT/CMK-3 electrode exhibited higher capacity than PT/Super P and PT/Ketjenblack electrode indicating the effectiveness of CMK-3 as suitable additive. Further, PT/CMK-3 composite electrode exhibited outstanding cycling stability up to 5000 cycles with more than 95% capacity retention at 2.5 A g_{PT}^{-1} mainly due to its ordered mesoporous nature. Galvanostatic intermittent titration proved that the Zn^{2+} diffusion is nearly two order higher in PT/CMK-3 than in PT/Super P thereby allowing fast charge/discharge of the battery.



Charge/discharge profile of **(a)**PT/Super P and **(b)**PT/CMK-3 at 0.08 A g^{-1} with PT/CMK-3 showing enhanced capacity and lower overvoltage.

PC 04

Experimental and modeling kinetics study of thermal decomposition of methyl-2-methylbutanoate behind reflected shock waves

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ABSTRACT

Fuel security and anthropogenic carbon dioxide emissions, which are associated with climate change, have arisen primarily from extensive fossil fuel use for energy generation in the last few decades. One attractive solution is biodiesel, which is an oxygenated, diesel-like fuel consisting of fatty acid alkyl esters[1]. These biofuels can have quite different combustion characteristics in terms of its reactivity, and pollutant formation due its oxygenated chemical structure[2]. These issues have thus driven our research towards the detailed study on the thermal decomposition of an ester like methyl-2-methyl butanoate (M2MB) using an in-built stainless-steel single pulse shock tube (SPST) facility with an ID of 50.8 mm and an internal smoothness of 10 µm, divided into 2 sections namely driver and the driven section. M2MB can be useful as biofuels, an alternative source of energy. In the present study, thermal decomposition of M2MB was studied behind reflected shock waves in the temperature range of 1018–1645 K using a single pulse shock tube (SPST) with argon as a diluent whereas helium was used as a driver gas . The post shock mixtures were analyzed both qualitatively and quantitatively using Gas Chromatography coupled with Mass Spectrometry (GC-MS) and Gas Chromatography coupled with flame ionization detector (GC-FID) respectively. Methane (CH_4), ethylene (C_2H_4), Methanol (CH_3OH) and Propene (C_3H_6) were the major decomposition products obtained from the decomposition product analysis of M2MB whereas the minor products were ethane (C_2H_6), propylene (C_3H_6) and methyl acrylate ($C_4H_6O_2$). All electronic structure calculations were carried out using the Gaussian 09 program suite[3]. The geometries of all stationary points on the potential energy surface of M2MB, were optimized with G3B3 level of theory. The minimum energy path (MEP) was obtained by intrinsic reaction coordinate (IRC) calculations to verify that the transition states connecting the reactants and products. The 'MESMER' package was employed along with master equation in the same temperature range to investigate the rate coefficients for the decomposition reactions.

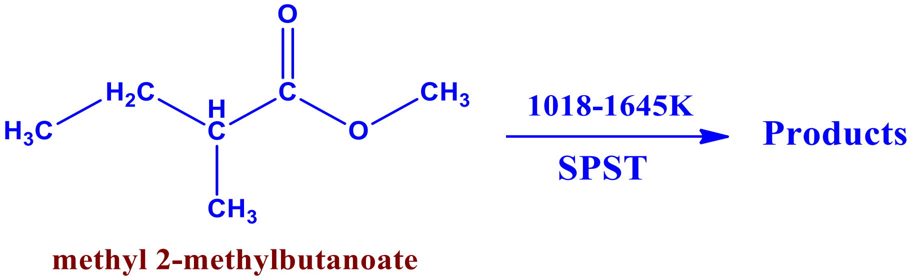

Figure 1. *Thermal decomposition of methyl-2-methylbutanoate behind reflected shock waves.*

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PC 05

Manifestation of Structural Differences of Atomically Precise Cluster-Assembled Solids in Their Mechanical Properties

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ABSTRACT: Cluster-assembled solids (CASs) formed by the self-assembly of monodispersed atomically precise monolayer-protected noble metal clusters[1] are attractive due to their collective properties. The physical stability and mechanical response of these materials remain largely unexplored. We have investigated the mechanical response of single crystals of atomically precise dithiol-protected Ag_{29} polymorphs,[2] monothiol-protected Ag_{46}, and a cocrystal of the latter with Ag_{40}[3] (formulas of the clusters have been simplified merely with the number of metal atoms). The Ag_{29} polymorphs crystallize in cubic and trigonal lattices (Ag_{29} C and Ag_{29} T, respectively), and Ag_{46} and its cocrystal with Ag_{40} crystallize in trigonal and monoclinic lattices (Ag_{46} T and $Ag_{40/46}$ M, respectively). The time and loading-rate-dependent mechanical properties of the CASs are elucidated by measuring nanoindentation creep and stress relaxation. The obtained Young's modulus (E_r) values of the CASs were similar to those of zeolitic imidazolate frameworks (ZIFs)[4] and show the trend Ag_{29} T > Ag_{29} C > $Ag_{40/46}$ M > Ag_{46} T. We have also studied the viscoelastic properties of all the four CASs and found that the value of tan δ/damping factor of monothiol-protected Ag_{46} T was higher than that of other CASs. The unusual mechanical response of CASs was attributed to the supramolecular interactions at the surface of nanoclusters. This observation implies that the stiffness and damping characteristics of the materials can be modulated by ligand and surface engineering. These studies suggest the possibility of distinguishing between the crystal structures using mechanical properties. This work provides an understanding that is critical for designing nanocluster devices capable of withstanding mechanical deformations.

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PC 06

Highly-scalable, Affordable, Conducting Cloth as Wearable Breath Humidity Sensor

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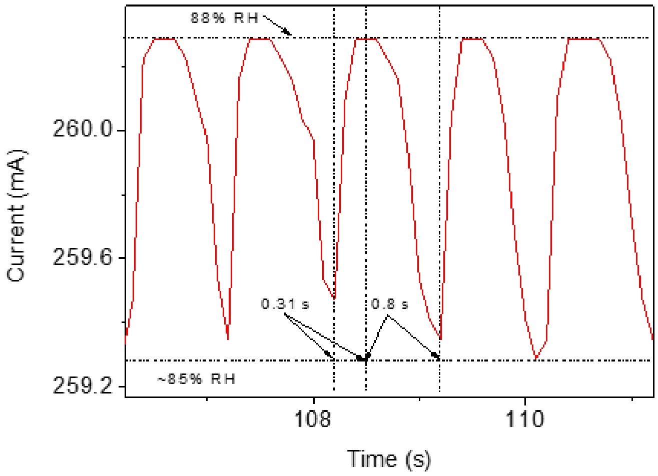
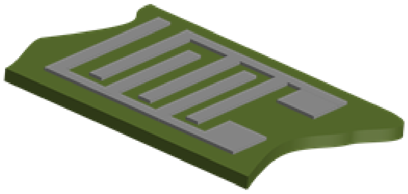
In the recent past, wearable and flexible sensors have gained an immense importance from medical and sensing applications,[1–3] in that perspective, there is a need for an affordable and a fast-responsive sensor for everyday health monitoring. Such sensors will be a potential tool to invasively monitor the breath patterns. In this regard, we fabricated a conducting cloth custom-made by *in-situ* polymerizing, polyaniline (PANI) on polypropylene (PP) non-woven cloth. Interdigitated silver conducting electrodes were screen printed on the top of this non-woven cloth making a micro-sensor unit. Being fabricated from cloth, this sensor is highly flexible and economical for large-scale production. A chronoamperometric study was performed for monitoring and recording the breath patterns of the exhaled air through nose and mouth of a healthy person. A potential of 3 V was applied across the electrodes at the scan rate of 0.1 s was used to monitor the breath cycles. We observed a fastest response of 0.31 s for the sensor to detect the change in relative humidity (RH) from room temperature to 85 % RH and a recovery of 0.8 s. The sensor was sensitive in the entire region of (0-95% RH) and responsive to ethanol. One good ending line is needed. Like such sensors can be used for alcohol detections or so, not sure but one solid line with future perspective.





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PC 07

A smartphone-based fluoride-specific sensor for rapid and affordable colorimetric detection and precise quantification at sub-ppm levels for field applications

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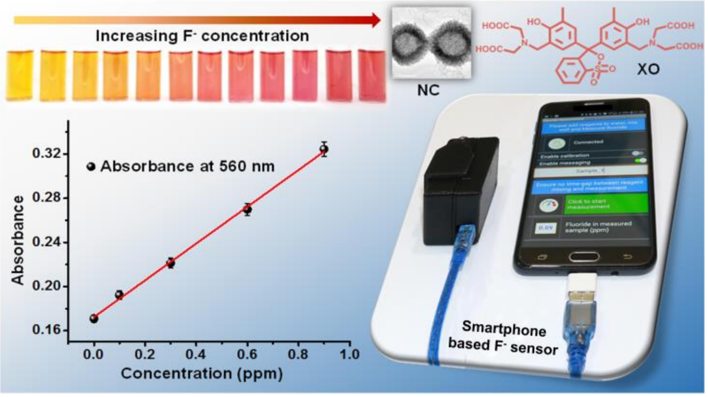
Higher levels of fluoride (F^-) in groundwater constitute a severe problem that affects more than 200 million people spread over 25 countries.[1] It is not only essential to detect but also accurately quantify aqueous F^- to ensure safety.[2] Need of the hour is to develop smart water quality testing systems that would be effective in location-based real-time water quality data collection, devoid of professional expertise for handling. We report a cheap, handheld, portable mobile device for colorimetric detection and rapid estimation of F^- in water by the application of the synthesized core-shell nanoparticles (near-cubic ceria@zirconia nanocages) and a chemoresponsive dye (xylenol orange). The nanomaterial has been characterized thoroughly and the mechanism of sensing has been studied in detail. The sensor system is highly selective towards F^- and shows unprecedented sensitivity in the range of 0.1 to 5 ppm of F^-, in field water samples, which is the transition regime where remedial measures may be needed. It addresses multiple issues expressed by indicator based metal complexes used to determine F^- previously. Consistency in the performance of the sensing material has been tested with synthetic F^- standards, water samples from F^- affected regions, and dental care products like toothpastes and mouthwash using a smartphone attachment and by naked eye. The sensor performs better than prior reports on aqueous F^- sensing.



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PC 08

Gas-phase ion chemistry of titanium oxofullerene anions, $[HxTi_{42}O_{60}L_y]^{n-}$ $[L= (OCH_3)_{42}(HOCH_3)_{10}(H_2O)_y$, $x = 7,12$; $y = 3,2$; $n = 1, 2]$

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Abstract

We investigated the gas-phase fragmentation events of highly symmetric titanium oxide fullerene (TOF) cluster ions, $[H_{12}Ti_{42}O_{60}(OCH_3)_{42}(HOCH_3)_{10}(H_2O)_2]^{2-}$ and $[H_7Ti_{42}O_{60}(OCH_3)_{42}(HOCH_3)_{10}(H_2O)_3]^{1-}$, simplified as $[HxTi_{42}O_{60}L_y]^{n-}$ ($L = (OCH_3)_{42}(HOCH_3)_{10}(H_2O)_y$; (when n = 2; x, y are 12, 2 and when n= 1; x, y are 7, 3 respectively) which contain a closed cage, fullerene-like $Ti_{42}O_{60}$ core, protected by a specific number of methoxy, methanol and water molecules acting as ligands. These dianionic and monoanionic species were generated in the gas-phase by electrospray ionization of $H_6[Ti_{42}(\mu^3\text{-}O)_{60}(O^iPr)_{42}(OH)_{12}]$ cluster (TOF-1).[1] Collision induced dissociation studies of TOF-1 revealed that upon increasing the collision energy, the protecting ligands were stripped off first, and $[Ti_{41}O_{58}]^{2-}$ was formed as the first cage fragment. Thereafter, systematic TiO_2 losses were observed giving rise to subsequent fragments like $[Ti_{40}O_{56}]^{2-}$, $[Ti_{39}O_{54}]^{2-}$, $[Ti_{38}O_{52}]^{2-}$, etc. Similar fragments were also observed for monoanionic species as well. About 23 such systematic TiO_2 losses were observed, which were followed by complete shattering of the cage. The fragmentation of TOF-1 was comparable to the fragmentation of fullerene ions, where systematic C_2 losses were observed.[2–4] The present study provides valuable insights into the structural constitution of TOF clusters and the stability of the parent as well as the resulting cage-fragments in the gas-phase.

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PC 09

Towards Vibrational Tomography of Citrate on Dynamically Changing Individual Silver Nanoparticles

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Trisodium citrate (TSC) has been used in the synthesis of colloidal nanoparticles (NPs) and has probably become the most common reducing and stabilizing agent in the history of noble metal nanomaterials.[1-3] In this work, we explored changes in binding modes of the most common ligand, citrate on silver nanoparticles (AgNPs) using single-particle surface-enhanced Raman scattering (SP-SERS). Single AgNPs of 50±10 nm diameter anchored on clean glass slides were monitored using time-dependent SP-SERS with 632.8 nm excitation, at 1.3 μW incident (0.5 μW absorbed) power per nanoparticle. We observed several distinct spectra of citrate during time-dependent SP-SERS. Analysis of 1400 spectra showed the existence of two major groups termed as favorable (F) and probable (P) spectra, based on their likelihood of appearance and intensities. These distinct spectra corresponded to a multitude of binding modes, structures, and variants of photocatalyzed products of citrate on the surface of dynamically changing AgNPs. Density functional theory (DFT) simulations were performed to model the structures and binding modes of citrate on an Ag(111) surface and corresponding Raman spectra were computed and compared with distinct spectral types. Experiments performed with deuterated (2,2,4,4-d_4) citrate-capped AgNPs provided additional evidence to understand the shifts in vibrational features obtained in SP-SERS of citrate-capped AgNPs. These systematic analyses of time-dependent SP-SERS spectra may be used for the reconstruction and vibrational tomography (VT) of ligands at the single-particle level. The proposed VT approach is similar to sectioning an object through a multitude of orientations and reconstructing its three dimensional structure, although the structures reconstructed here are molecular orientations.

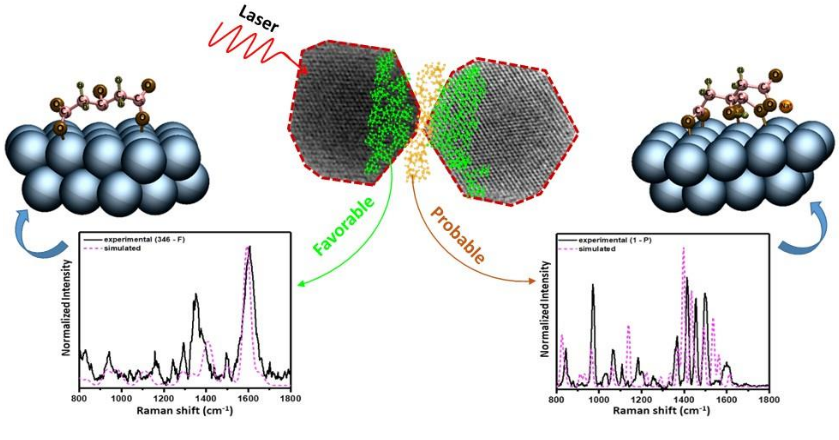

Figure 1. Laser interacting with citrate-protected AgNPs. SP-SERS measurements resulted in various binding modes and orientations of citrate on individual AgNP.

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 # I (Tripti Ahuja) am the presenting author.

PC 10

Can oxide monolayers increase the charge storage capacity? A case study of MoO_3 thin layers on $NiCo_2S_4$

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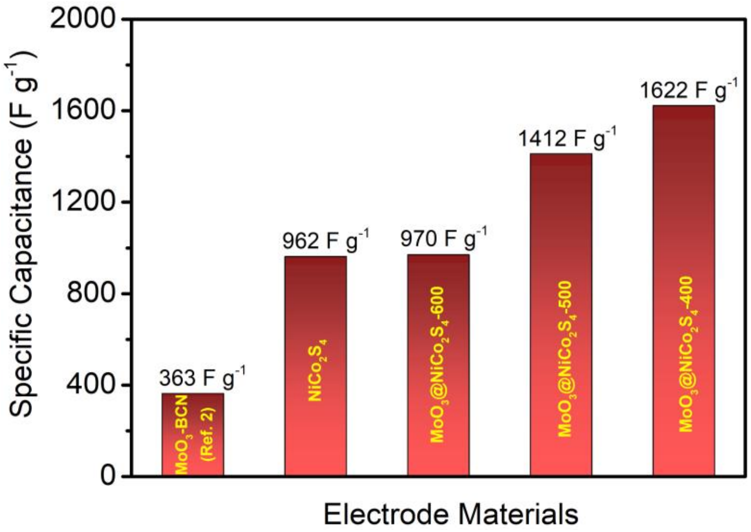
Abstract:

Charge storage is an interfacial phenomena. In order to verify this concept we have prepared monolayers of molybdenum oxide on $NiCo_2S_4$ substrate at different temperatures ranging from 400 to 600 °C. The sample prepared at 400 °C shows 1.7 times higher storage capacity compared to $NiCo_2S_4$ substrate at the same current density. The sample also shows good cyclic stability 93% capacitance retention after 3000 charge–discharge cycles at 8 A g^{-1}. This proves the concept of enhancing the charge storage using monolayer materials.



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PC 11

Synthesis and Characterization of Lanthanide based Metal-Organic Framework (MOF)

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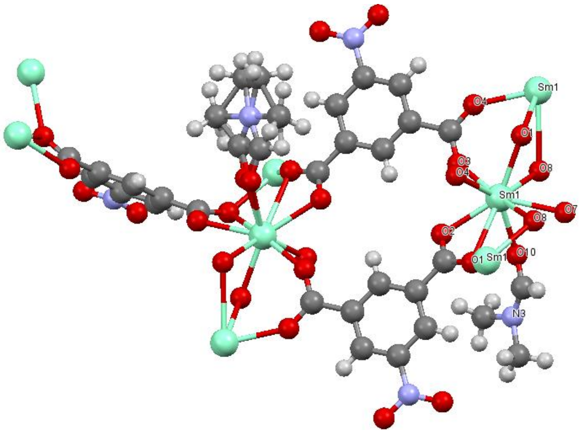
Abstract:

A novel lanthanide based metal-organic framework complex **Sm-H_2L** has been synthesized hydrothermally by using samarium metal and 5-nitroisophthalic acid (H_2L) as a ligand. The structural analysis of this complex has been done by single crystal X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD) and FT-IR. The complex **Sm-H_2L** is highly crystalline in which Sm forms bonds with H_2L ligands to give 3D structure as shown in the figure.



Structure of complex Sm-H_2L compound showing Sm (green), N (purple), O (red), C (grey) and H (light grey) atoms.

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PC 12

Understanding the Aggregation Behaviour of Urobilin and Stercobilin: Application in Water Quality Monitoring

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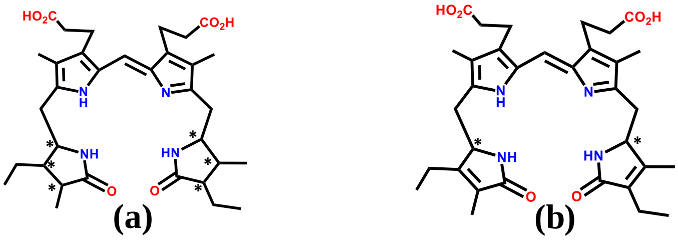
Faecal pigments (FPs) is considered as a primary source of the contaminant in water. The enhancement of urobilin (UB) and stercobilin (SB), fluorescence by Zn(II) is often used for the detection of FPs in aqueous media (Schlanger's test).[1] A detailed photophysical study of UB and SB was carried out. This work shows that in aqueous media FPs have the intriguing presence of multiple emitting species which indicate the coexistence of monomers (λ_{ex}= 525 nm, λ_{em}= 540 nm), lower-order H-aggregates (dimers) (λ_{ex}= 506 nm, λ_{em}= 516 nm), and higher-order H-aggregates (λ_{ex}= 480 nm, λ_{em}= 500 nm) even at a very low concentration.[2] Furthermore, the investigations conclude that FP-Zn(II) complexes have a lower solubility in water that results in the formation of molecular aggregates of the complexes. This is the primary region of time-dependent loss of FP-Zn(II) fluorescence which adversely affects the sensitivity of FPs detection in the aqueous medium. Density functional theory (DFT) calculations using the B3LYP functional and LANL2DZ basis set shows the contributions of $\pi-\pi$ stacking and hydrogen-bonding interactions towards the formation of H-aggregated dimer of FPs. The study was further extended by utilizing this aggregation-induced emission phenomenon of FPs by increase the viscosity of the primary alcohol. Among methanol, to 1-Octanol, we found that FP-Zn(II) has stable and maximum fluorescence intensity in 1-Hexanol. Furthermore, 1-Hexanol can also be used as an efficient extraction medium for FPs, which can enhance fluorescence as well as minimization of matrix components interference for high sensitivity detection (picomolar and sub picomolar concentration). These molecular-level understanding of FPs and FP-Zn(II) is expected to aid in the development of aqueous phase analytical strategy towards the fluorescence-based analysis of the faecal matter, an essential component of water quality analysis.



Scheme 1 Chemical structure of (a) Stercobilin and (b) Uroilin (Star mark indicate the chiral centres in the FPs molecule)

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PC 13

Synthesis of Mg-Sr-Al ternary layered double hydroxide for CO_2 capture

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Layered double hydroxides (LDHs) are promising materials for CO_2 capture in the temperature range 200-400°C.[1,2] The stable structural frameworks of LDH materials contain positively charged metal hydroxide sheets which are usually responsible for high uptake of CO_2. The synthesis of layered triple hydroxides (LTHs), also known as ternary layered double hydroxides (LDHs), has gained prominence for their potential applications to catalysis[3], supercapacitors[4], electrocatalytic water splitting[5] and CO_2 adsorption.[6,7] The CO_2 adsorption performance of these materials can be improved by chemical and structural modifications, such as increasing the interlayer spacing[8], replacing divalent cations[9], employing support materials like grapheme oxide[10], optimising the molar ratio of Mg/Al[11], controlling the particle size and morphology[12] and incorporating suitable charge compensation anions.[13]

In this work, we report hydrothermal synthesis of layered triple hydroxide (LTH) at controlled pH of 10. The proposed formula of this material is $\mathrm{Mg_{2.1}Sr_{1.0}Al_{1.4}(OH)_3(CO_3)_{\mathit{x}}(NO_3)_{\mathit{y}}(\,H_2O)_m}$. This material contains brucite-type octahedral nanosheets of LTHs with CO_3^{2-} and NO_3^{-} anions present in between the layers. The basal spacing for d_{003} plane is 0.84 nm. The material is thermally stable up to 470°C, and hence can be used for CO_2 capture in the temperature range 200–400°C at 1 bar pressure. The CO_2 absorption capacity of this material is being examined manometrically using iSorb HP1 gas sorption analyser.

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PC 14

Gas Phase Investigation of Kinetics of Phenyl Radical, the Simplest Aromatic Radical with Model Biofuels Using Cavity Ring-down Spectroscopy

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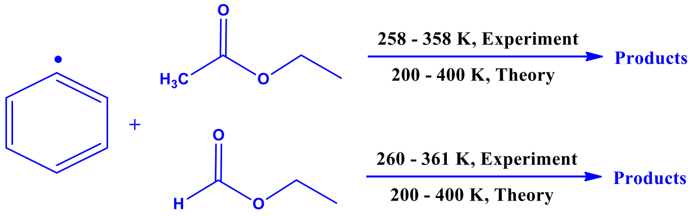
Phenyl radical ($C_6H_5^\bullet$) is one of the most reactive intermediates responsible for the production of soot and polycyclic aromatic hydrocarbons (PAHs) during a combustion process[1]. Being one of the major constituents of automobile emissions, kinetic investigation of $C_6H_5^\bullet$ reactions are essential not only to understand the environmental impact of vehicular emissions but also for designing more efficient and clean practical combustion engines in the future. Using our in-built cavity ring-down spectroscopy (CRDS) set-up[2], kinetics of the reaction of $C_6H_5^\bullet$ has been investigated in the temperatures and pressures of atmospheric interest, with ethyl acetate (EtOAc, EA) and ethyl formate (HCO_2Et, EF) which are considered to be potential biofuels and used widely in various applications of daily life such as food flavourings, confectionaries, in perfumes and printing industries[3]. Atmospheric oxidation of EA and EF by oxidants like phenyl radicals has the potential to contribute to regional as well as global air qualities.



CRDS was used to measure the absorption cross section of phenyl radicals at 504.8 nm ($^2B_1 \leftarrow {}^2A_1$ transition) using nitrosobenzene (C_6H_5NO) as the radical precursor at 248 nm and it was measured to be: σ_{phenyl} (504.8 nm, 298 K) = $(5.55 \pm 1.34) \times 10^{-19}$ cm^2 $molecule^{-1}$ which was found to be independent of the pressure (40-200 Torr in N_2). Moreover, the absolute rate coefficients for the reaction of $C_6H_5^\bullet$+EA and $C_6H_5^\bullet$+EF were measured over the temperature range of 258-358 K and 260-361 K respectively at (40±2) Torr of total pressure with N_2 using CRDS at a laser repetition rate of 2 Hz. The temperature dependent rate coefficient for the reaction $C_6H_5^\bullet$+EA over the studied temperature range was obtained to be $k_{\text{expt}}(258\text{-}358\ K) = (9.33 \pm 0.11) \times 10^{-16} \exp[(883.7 \pm 181.2)/T]$ cm^3 $molecule^{-1}$ s^{-1} with a rate coefficient of $k(T) = (2.20 \pm 0.12) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K whereas the same for the reaction of $C_6H_5^\bullet$+EF was measured to be $k_{\text{expt}}(260\text{-}361\ K) = (1.20 \pm 0.16) \times 10^{-13} \exp[-(435.6 \pm 50.1)/T]$ cm^3 $molecule^{-1}$ s^{-1} with a room temperature rate coefficient of $k(298\ K) = (4.54 \pm 0.42) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. In both the cases, the effect of pressure and photolysis laser fluences were found to be negligible within the experimental uncertainties for the studied range. In addition, to complement our experimental findings, the T dependent rate coefficients for the title reactions were investigated at CCSD(T)/cc-pVDZ//B3LYP/6-31+G(d,p) level of theory using canonical variational transition state theory in combination with small curvature tunnelling (CVT/SCT) corrections. At room temperature the reactivity of EF towards phenyl radicals was found to be ~2 times higher than that for EA.

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PC 15

Molecular memory and dynamic cooperativity in monomeric enzymes

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The classical Michaelis-Menten (MM) equation[1], represents a non-cooperative kinetic response of enzymes with either a single or non-interacting multiple binding site(s). The mean catalytic rate of several monomeric enzymes, however, shows deviations from this classical behavior.[2] This effect, termed as dynamic cooperativity, is believed to be associated with molecular mechanisms, stochastic reaction networks, that include enzymatic conformational fluctuations in product formation pathways. In spite of the latter, however, the present understanding of dynamic cooperativity is confined to mean kinetic measures, obtained from deterministic rate equations, which cannot account for fluctuations. Here, we consider a stochastic reaction network for a special class of monomeric enzyme, called mnemonical enzymes, which are known to exhibit both positive and negative (dynamic) cooperativity. We model their kinetics using the chemical master equation (CME)[3] to show how the emergence of dynamic cooperativity, at the molecular level, is inextricably linked to the multiplicity of monomeric enzyme numbers, enzymatic conformational fluctuations and molecular memory. Our results show that dynamic cooperativity is a transient phenomenon, which emerges due to temporal correlations between enzymatic turnovers, and vanishes as these correlations decay and molecular memory fades.[4]

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PC 16

Investigation of Absorption Cross-Sections of Ortho-Xylyl Radical in the Visible Region and its Effect on Temperature and Pressure Using Cavity Ring-Down Spectroscopy

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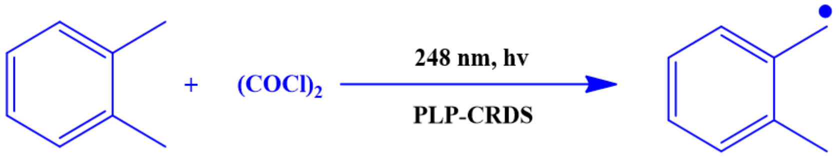
Aromatic hydrocarbons like xylenes are one of the essential components which are found in practical combustion engine fuels- gasoline and petroleum. Among all the isomers of xylene, o-xylene [ortho-$C_6H_4(CH_3)_2$] is used widely in paints, adhesives, feedstock for the production of phthalic anhydride etc[1]. It is also used widely as an anti-knock agent to reduce engine knocking[2]. When o-xylene reacts with atmospheric oxidants, it forms o-xylyl radical [ortho-$C_6H_4(CH_3)(^{\bullet}CH_2)$] which plays a significant role in the production of polycyclic aromatic hydrocarbons (PAHs) and can undergo decomposition as well as self-reaction to give substituted aromatic compounds such as Fulvenallene radical[3]. Thus, understanding the chemistry of o-xylyl radical is the need of the hour to better understand the kinetics as well as its combustion behaviour. This will also help in manufacturing more efficient future automobile engines emitting lesser pollutants into the atmosphere. To the best of our knowledge, there is no gas-phase spectroscopic data of o-xylyl radical prior to this study is available.



The absorption spectrum of o-xylyl radical has been measured at room temperature in the wavelength range of 460.1-475.1 nm, using an in-built pulsed laser photolysis-cavity ringdown spectroscopy (PLP-CRDS) setup. Broad absorption peaks were observed in the regions of 462-463 and 466-467 nm, whereas the sharp features were observed at 462.3, 463.9, 465.1, 468.3 (max), 469.1, 469.9, 471.7, 472.5 and 473.5 nm. At the absorption maxima of 468.3 nm, the absorption cross-section ($\sigma_{o-xylyl}^{468.3\ nm}$) was measured as $(1.58 \pm 0.38) \times 10^{-18}$ cm^2 $molecule^{-1}$ at (298±2) K and (40±2) Torr of pressure with N_2. In addition, the variation of $\sigma_{o\text{-}xylyl}$ with experimental temperatures and pressures have been deciphered in the ranges of 263-338 K and 40-95 Torr respectively. A negative temperature dependency with a very weak pressure dependency was observed. In order to complement our experimental findings, the time-dependent density functional theory (TD-DFT) was employed to investigate the electronic transitions of o-xylyl radicals in the visible region and the absorption maximum corresponding to the first electronic excitation was found at 468.2 nm.

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POSTERS

ORGANIC CHEMISTRY

OC 01

Biological Evaluation and Structure–Activity Relationships of Adenine-Modified Quinolones Conjugates against Malarial Parasite

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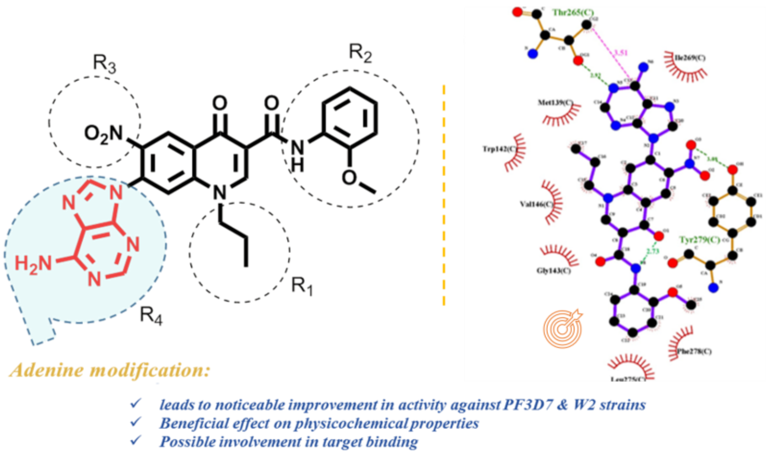
Malaria is an infectious disease with large mortality rate. Though many drugs such as chloroquine, mefloquine, atovaquone-proguanil and artemisinin-based combination therapy (ACT) *etc*. are available, an increased risk of resistance makes the need of new antimalarial drugs.[1,2] Quinolone class of compounds have shown great promise in this aspect, but the poor *in vivo* efficacy of some of the leads limits its application towards clinical development.[3-5] Here we attempted to improve the therapeutic potential of quinolone derivatives through detailed structural modifications and its SAR analysis. This study includes quinolones with alkyl or aryl-alkyl substitution at N-1 position, carboxamide unit at C-3, nitro or amino groups at C-6, and different heterocyclic rings such as piperidine, morpholine, piperazine or adenine moiety at the C-7 position. Interestingly, the adenine substituted derivatives at the C-7 position were observed to show enhanced antimalarial activities against chloroquine-sensitive (PF3D7) and resistant (W2) parasite strains with IC_{50} values of 0.38 μM and 0.75 μM respectively. Docking studies in the Qo site of cytochrome bc1 complex revealed the involvement of adenine unit in target binding.[6]



Adenine modification:

- ✓ *leads to noticeable improvement in activity against PF3D7 & W2 strains*
- ✓ *Beneficial effect on physicochemical properties*
- ✓ *Possible involvement in target binding*

Figure 1. Shows the SAR possibilities explored on quinolone scaffolds and the docking profiles of the most active compound in the Qo site of cytochrome bc1 complex.

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OC 02

Free Amine Directed Ruthenium-Catalyzed C–H Activation/Annulation of Anilines with Olefins

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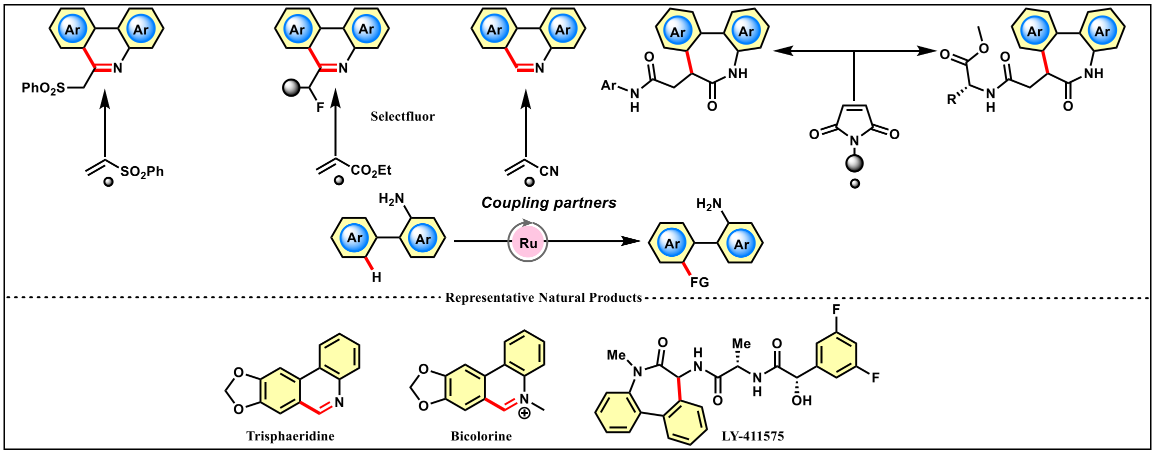
Over the last two decades, transition-metal-catalyzed C–H bond activation/functionalization has emerged as a vibrant area of research, allowing functionalization of otherwise unactivated C–H bonds and offering unconventional disconnection approach for the synthesis of complex molecules.[1] Directing group (DG) plays pivotal role in this strategy in controlling reactivity and regioselectity issue. Obviously, consideration of free amine functionality as a DG is highly rewarding as it is an important constituent of a large variety of natural products and can also be easily transformed into variety of other functionalities.[2] However, materialization of this concept constitutes several challenges, like formation of stable yet unreactive transition metal complexes, direct nucleophilic reactions with coupling partners, as well as competing undesired side reactions such as oxidative degradation and β-hydride elimination. With judicious tuning of reaction conditions, we have successfully engaged free amine functionality as a DG in arene C–H bond activation reactions under inexpensive ruthenium catalysis. A cross-ring (5+1) annulation reaction between 2-arylanilines and activated olefins has been established for the synthesis of phenanthridines frameworks.[3a] Following this strategy, bioactive natural products such as *trisphaeridine* and *bicolorine* were also prepared in high yields. When maleimides was employed as coupling partners with ruthenium(II) catalyst, dibenzo[*b*,*d*]azepinones, which represent the core of several bioactive molecules including LY-411575, were isolated in very high yields.[3b] Dibenzo[*b*,*d*]azepinones with side-chains derived from chiral amino acids were also obtained in one step, highlighting the synthetic utility of this protocol. Mechanistic investigation covering deuterium exchange studies and *KIE* experiments suggest that the C–H bond activation takes place via an organometallic pathway in these processes.



Scheme 1: Ruthenium-catalyzed free amine directed cross-ring annulation.

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OC 03

Iridium(III) Catalyzed Intermolecular Allylic C H Amidation of Internal Alkenes with Sulfonamides

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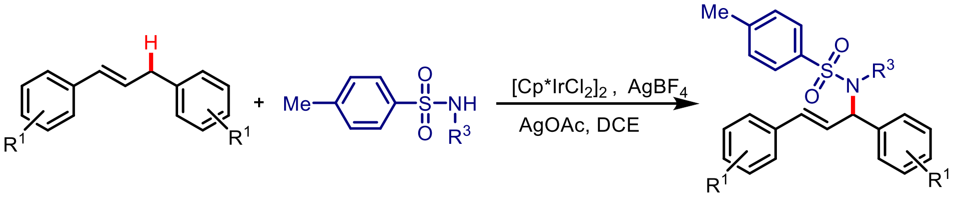
The transition metal catalyzed allylic C-H functionalization of alkenes with nucleophiles has gained tremendous attention in organic synthesis for the past few years for construction of various chemical bonds. The allylic C-H bond of terminal alkenes can be activated very effectively in the presence of a palladium catalyst (*via* π-allyl mechanism)[1] or low valent Iridium complexes[2] (by allylic substitution reactions) in the presence of labile leaving group at the allylic position are well known. The allylic C-H functionalization of internal alkene is very challenging as compared with the terminal alkene due to the high thermodynamic stability of internal alkene. Recently, Rh(III) and Ir(III) catalyzed intermolecular C-H amination, etherification and C-C bond formation of various alkenes with N, O and C nucleophiles has been reported. In this conference we are going to present Ir(III) catalyzed intermolecular allylic $C(sp^3)$-H amidation of highly challenging unactivated internal alkenes with sulfonamides *via* π-allyl intermediate.[3] The reaction was compatible with symmetrical and unsymmetrical internal alkenes as well as substituted sulfonamides. It is interesting to note that in the reaction of aryl-alkyl alkenes, the amidation selectively takes place at the alkyl substituted allylic carbon selectively. Meanwhile, the better selectivity was also observed in the unsymmetrical aryl-aryl alkenes having electron-withdrawing substituent at one of the aryl groups. The proposed mechanism was also supported by the deuterium labelling studies.



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OC 04

Cobalt (III)-Catalyzed Redox-Neutral Coupling of Acrylamides with Activated Alkenes via C–H Bond Activation

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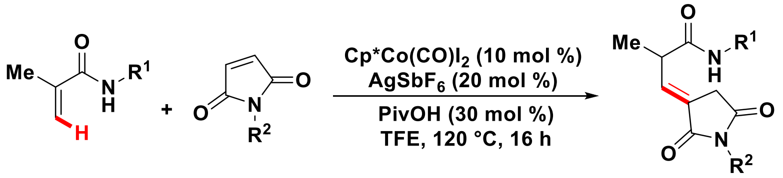
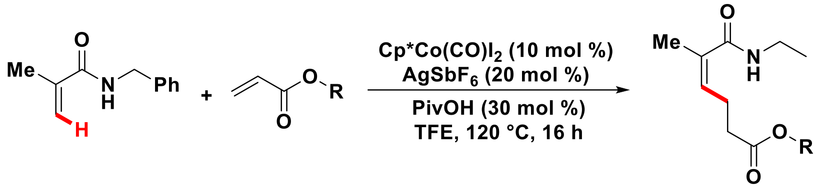
The transition-metal-catalyzed C–H functionalization reaction has evolved as an indispensable tool in synthetic organic chemistry to construct complex organic motifs in a highly atom- and step-economical manner.[1] The C-H functionalization of organic molecules catalyzed by the first row transition metals such as cobalt, nickel, copper and iron have gained much attention in synthetic organic chemists due to their high abundance and bio-compatability.[2] In particular, Cp*Co-catalyzed C–H bond activation reaction emerged as the promising alternative to the second and third row metal catalysts for the functionalization of organic molecules.[3] By employing the Cp*Co, the functionalization of aromatics and heteroaromatics has been extensively studied, however only few examples are reported to functionalize electron deficient vinylic C–H bonds, due to the ineffective formation of key cobaltocycle intermediate.[4] In this context we have investigated the reaction of acrylamides with activated alkenes using cobalt(III) catalyst under the redox neutral conditions. A possible reaction mechanism involving cobaltocycle intermediate is proposed and supported by deuterium labelling studies.[5]

Scheme 1. Alkylation of acrylamides with maleimides



Scheme 2. Alkylation of acrylamides with activated olefins



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OC 05

Highly Efficient and Enhanced Stability of Perovskite Solar Cell Based on Bicarbazole as Dopant Free Hole-Transporting Materials

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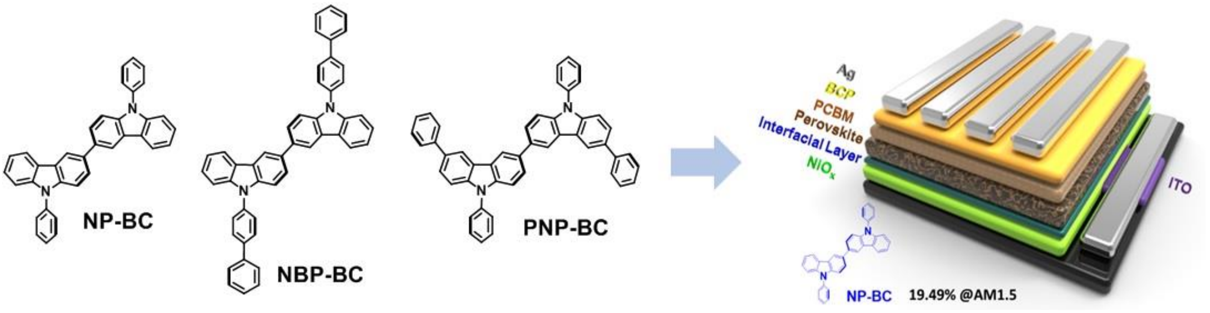
Molecules based upon a carbazole substructure have found widespread application in electronics, sensing and biological applications.[1] Bicarbazoles (**BC**) are more useful in organic electronics and Photonics. Especially substituted **BC** is playing a very important role as hole transporting material (HTM) for Perovskite Solar Cells (PSCs).[2] In our recent report,[3] it is shown that high-performance dopant-free p–i–n-type perovskite solar cells have been obtained using the 3,3´-bicarbazole (**BC**)–based compounds **NP-BC, NBP-BC**, and **PNP-BC** as simple HTMs. A metal-free oxidative coupling strategy using recyclable organic oxidants has been adapted for the synthesis of **BC**-HTMs in excellent yields (≥95%); synthesis involves low cost (34~120 USD/g) and avoids metal-impurities in the last step which enhance the PSCs performance. When **NBP-BC** was used as a dopant-free HTM in a p–i–n PSC device structure, it demonstrated a PCE of 13.03% under AM 1.5 conditions. Further optimization of the PSC performance was realized using p–i–n device structure ITO/NiO_x/interfacial layer (**BC**-HTMs)/perovskite/$PC_{61}BM$/BCP/Ag—that is, **BC**-HTMs were employed as the interfacial layer between the NiO_x and perovskite layers. The interfacial layer reduced the defect and improved the PSC film morphology, enlarged the grain sizes in the perovskite layer, and also dramatically enhanced the FF. The best performance was obtained when **NP-BC** was employed as the interfacial layer, which provided a short-circuit current density of 22.38 mA cm^{-2}, an open-circuit voltage of 1.09 V, and a FF of 79.9%, corresponding to an overall conversion efficiency of almost 20% (19.49%). Moreover, under an argon atmosphere, the PCE of the **NiO_x/NP-BC** PSC device decayed by 4.55% after 168 h; however, it retained 90.80% of its original PCE after 1000 h. The results of this project will be presented.



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OC 06

Ru(II)- or Rh(III)-Catalyzed Difunctionalization of Alkenes by Tandem Cyclization of N-Aryl Acrylamides with Alkenes

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Olefins are inexpensive wieldy available feedstock and can be readily functionalized into complex organic molecules. The unique reactivity of olefins has made alkene functionalization essential in organic synthesis. In particular, Transition-metal catalyzed dicarbofunctionlization of alkenes has gained special attention, because it can construct complex carbon skeletons by installing two carbon-carbon based entities across the double bond to generate the two C-C bonds. [1a] However, controlling regioselectivity is very challenging in this reaction due to the possibility of side reactions such as *β*-hydride elimination. Furthermore, this kind of reactions need a pre-functionalized starting material and produces more organic waste. The transition-metal-catalyzed chelation assisted oxidative cyclization of organic molecules *via* C-H activation is a practical method to synthesize annulated heterocyclic products in highly step and atom economical manner. [1b,c] Recently, difunctionalization of activated alkenes are proven to be most efficient method to synthesize oxindoles.[1d] Oxindoles are privileged heterocycles prevalent in numerous natural products, biologically active compounds and agrochemicals. In continuation of our research on Ru(II) or Rh(III)-catalyzed C-H activation, we have developed a Ru(II) and Rh(III)-Catalyzed domino cyclisation of *N*-aryl acrylamides with maleimides in the presence of copper(II) acetate to synthesize oxindoles.[2] The reaction mechanism involving *via* C-H alkylation and intramolecular oxidative cyclization sequence.

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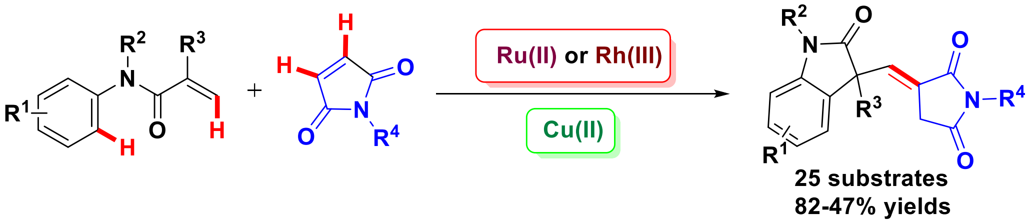

OC 07

Synthesis and Photophysical properties of Pyran-2-one Annulated Tetrabenzocoronene: A Large π-expanded coumarin

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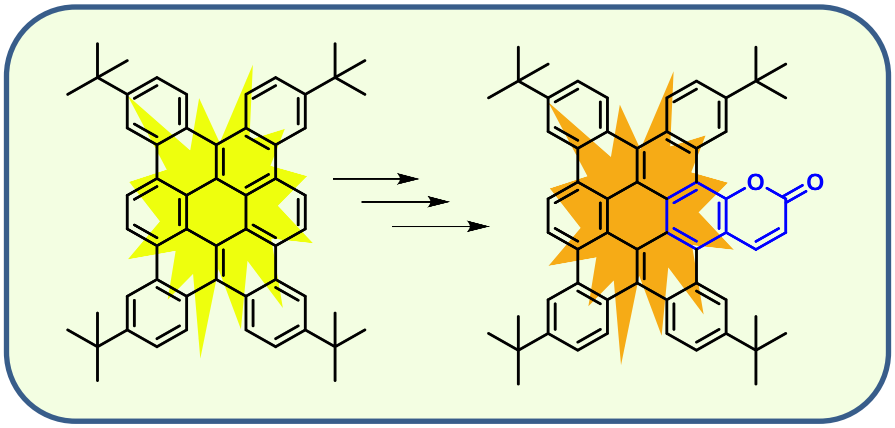
π-expansion has always been an important key to modulate the photophysical properties of polycyclic aromatic hydrocarbons, paving the way to synthesis of novel compounds with diverse applications in various fields.[1,2] The present report reveals the synthesis of the novel pyran-2-one annulated tetrabenzocoronene achieved by light driven electrocyclization followed by the deprotection and the modified Pechmann synthesis of coumarins. These large π-expanded systems possess interesting optical properties (in solution and solid state) and electrochemical properties, promising the applications in fields such as OLEDs, OFETs, fluorescent probes and in two-photon bio-imaging. [2,3]



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POSTERS

INORGANIC CHEMISTRY

IC 01

Ru^{II}-Heteroditopic NHC Complexes: Catalysts for C-N Bond Formation *via* Borrowing Hydrogen Strategy

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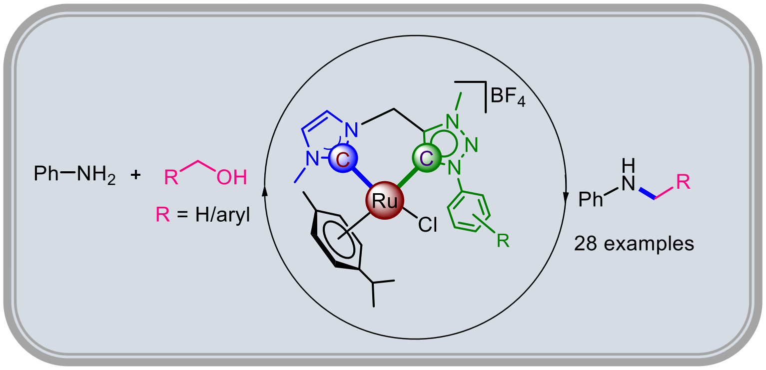
The identification of N-heterocyclic carbenes (NHCs) as improved alternatives of the classical ligands (especially sensitive phosphines) was the beginning of a new era in homogeneous catalysis. Owing to the flexibility in stereoelectronic modifications, NHCs became popular as ancillary ligands for metals in various oxidation states.[1] A recent breakthrough in this area is the development of easily accessible Click derived 1,2,3-triazolylidene (mesoionic carbene/MIC) as the congener of Arduengo type imidazolylidene (ImNHC). Along with the greater σ-donor nature, MICs offer diverse possibilities to fine-tune the activity of their transition metal complexes *via* flexible back bone.[2] In the past decade, synthetic chemists have started exploring the advantages of combining ImNHC and MIC donors in a single ligand frame which led to the identification of such heteroditopic systems as excellent ancillary ligands in the field of organometallic chemistry.[3] Herein, we present the synthesis and catalytic applications of various heteroditopic NHC-Ru(II)-complexes featuring varied steric and electronic profiles *via* simple alteration of the N-phenyl group substituents of the triazole moiety. The effect of ligand modification in the catalytic performances of these complexes was initially perceived through the transfer hydrogenation of imine functionality which disclosed that the bis-NHC-Ru(II) complex showed higher activity than the analogous monoNHC-Ru(II) complex with a secondary N-coordination.[4a] Motivated by this observation, we further explored the applicability of these complexes in diverse C-N bond formation reactions *via* borrowing hydrogen (BH) strategy which is a tandem extension of the transfer hydrogenation (Scheme 1). Wide range of aromatic, heteroaromatic and aliphatic amines as well as primary alcohols were successfully employed to obtain the corresponding diverse secondary amines. Also various N-methylated amines were realized using methanol as green methylating agent.[4b]



Scheme 1: Ru^{II}-NHC complexes catalyzed N-alkylation reaction *via* BH strategy.

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IC 02

Cluster Growth Reactions: Dimetallaboranes to Dimetallaheteroboranes of group 9 Metals

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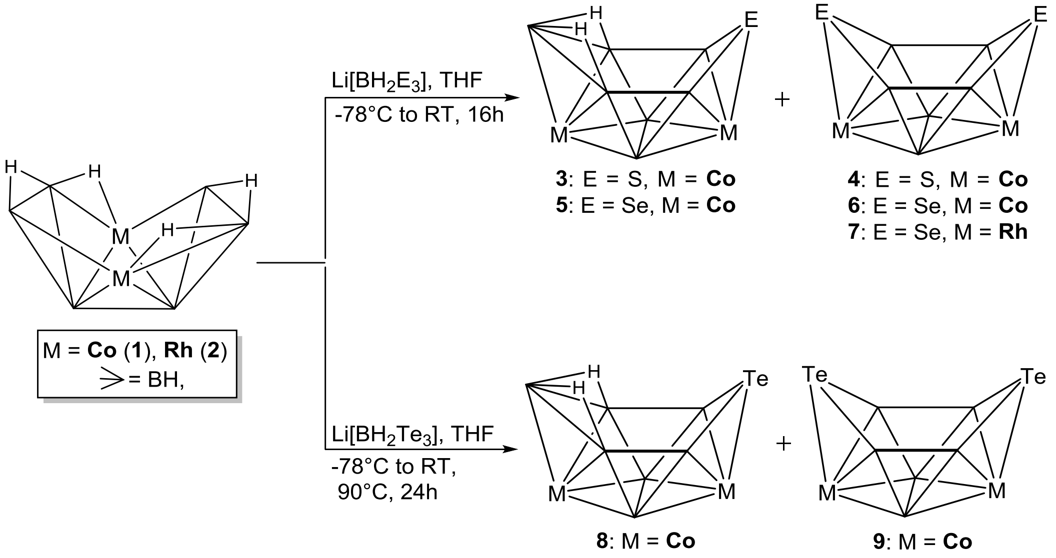
The growth of cluster moieties containing main group and transition metal fragments have gained enormous interest due to their numerous structural diversities.[1] The expansion of higher vertex polyhedral boron clusters allows one to investigate unique bonding and their exceptionally large-size electronic structures. Fehlner *et al.* showed two complementary approaches for the preparation of metallaborane clusters from transition metal complexes. For example, (i) condensation reaction involving monoborane reagents ($LiBH_4$·thf, BH_3·thf or $BHCl_2$·SMe_2, etc.; thf = tetrahydrofuran) and cyclopentadienyl metal chlorides and (ii) insertion or fragmentation involving "pre-assembled" borane fragments.[2] However, in most of the cases, these synthetic approaches ended up resulting in cluster fusion,[3] instead of core expansion of a single cage cluster. The group 9 metallaboranes, such as $[(Cp^*Co)_2B_6H_{10}]$, $[(Cp^*Rh)_2B_6H_{10}]$ are very reactive due to their open cage geometries. As a result, we have treated dimetallaoctaboranes (12) $[(Cp^*M)_2B_6H_{10}]$ ($Cp^* = \eta^5$-C_5Me_5), (**1**: M = Co and **2**: Rh) with $Li[BH_2E_3]$ (E = S, Se, Te), which led to the formation of 10-vertex *nido* **3-9**. This is a typical representation of cluster growth reaction. The key results of this work will be described.



Scheme 1: Syntheses of decaborane analogues of group 9 metals **3-9**

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IC 03

B-H functionalization of hydrogen rich divanadaborane, $[(Cp^*V)_2(B_2H_6)_2]$

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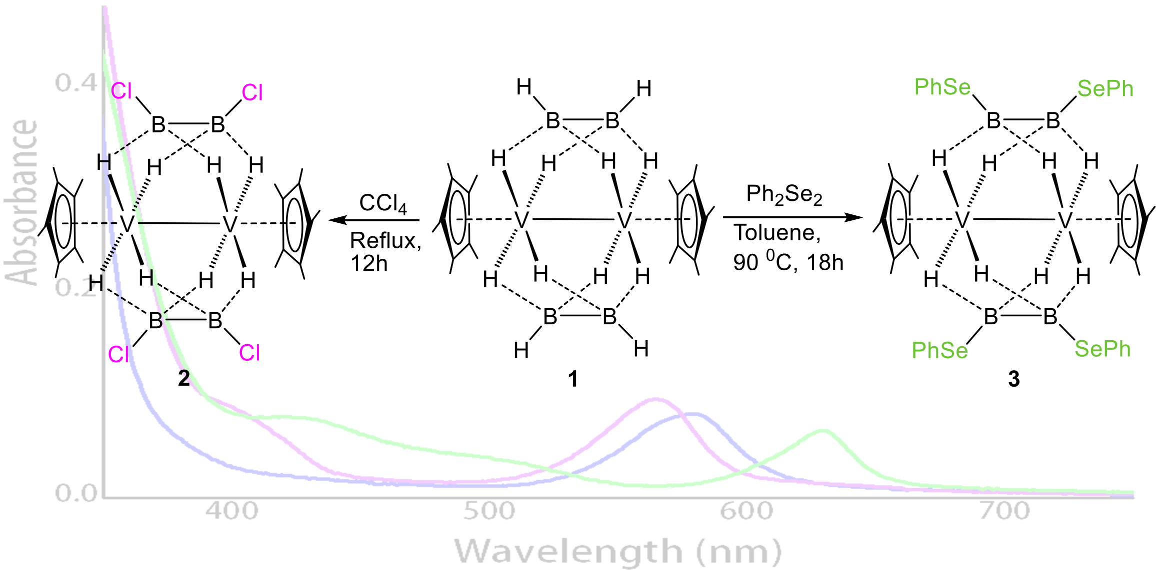
Metallaboranes incorporating early transition metals are less explored compared to late transition metals, and examples of structurally characterized group 5 metallaboranes are very less in number.[1] Although reactions with Cp_2VCl_2 is already explored, only a limited number of vanadaboranes like $[(CpV)_2(B_2H_6)_2]$ and $[(CpV)_2B_5H_{11}]$ are reported.[2] Hence in an attempt towards the synthesis of novel vanadaboranes, a vanadium trimer $(Cp^*VCl_2)_3$ was prepared.[3] Reaction of $(Cp^*VCl_2)_3$ with an excess of $[LiBH_4.thf]$ at low temperature followed by pyrolysis in the presence of $[BH_3.thf]$ resulted in formation of blue $[(Cp^*V)_2(B_2H_6)_2]$ (**1**) in good yield. In an attempt to obtain the terminal per functionalization, we treated $[(Cp^*V)_2(B_2H_6)_2]$ with chlorine and diphenyldiselenide that yielded $[(Cp^*V)_2(B_2H_4Cl_2)_2]$ (**2**) and $[(Cp^*V)_2(B_2H_4(SePh)_2)_2]$ (**3**) respectively. Photophysical properties of these compounds upon B-H functionalization were studied using UV-Vis spectroscopy. The key results of this work will be discussed.



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IC 04

Synthesis and reactivity of bis(σ)borate and bridging boryl complexes of ruthenium: Hydroboration of alkynes

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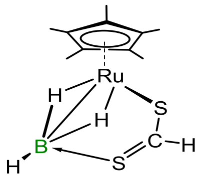
Recent years have witnessed significant growth in the field of transition metal borane chemistry, in particular with compounds comprising one or two boron atoms.[1] The reactivity of various chalcogen-based borate ligands with pentamethylcyclopentadienyl based metal halides has been explored by us and others that led to the formation of a wide range of complexes with interesting topologies.[2] In search of an alternative borane source for the synthesis of transition-metal−boron complexes, we explored the reactivity of a modified borohydride reagent, Na[BH$_3$(SCHS)] with [{Cp*RuCl(μ-Cl)}$_2$] (Cp* = η^5-C$_5$Me$_5$), which yielded ruthenium dithioformato [{Cp*Ru(μ,η^3-SCHS)}$_2$] (**1**) and diborinane complex [(Cp*Ru){(η^2-SCHS)CH$_2$S$_2$(BH$_2$)$_2$}] (**2**). Treatment of **1** with [BH$_3$·thf] resulted in the isolation of agostic-bis(σ-borate) complex [Cp*Ru(μ-H)$_2$BH(SCHS)] (**4**) which on reaction with a trace amount of Te-powder yielded bis(bridging-boryl) complex [{Cp*Ru(μ,η^2-HBS$_2$CH$_2$)}$_2$] (**5**). A series of hydroborated η^4-σ,π-alkene borane complexes [(Cp*Ru)(μ-H)BH{R^{1}C=C(H)R^2}{SC(H)S}] (**6a-g**) (**6a**: R^1 = H, R^2 = Ph; **6b**: R^1 = Ph, R^2 = H; **6c**:, R^1 = H, R^2 = *p*-Tol; **6d**: R^1 = *p*-Tol and R^2 = H, **6e**: R^1 = H, R^2 = CO$_2$Me; **6f**: R^1 = CO$_2$Me and R^2 = H; **6g**: R^1 = R^2 = CO$_2$Me) were isolated from the reaction of **4** with terminal and internal alkynes.[3] In addition, a new synthetic route for the synthesis of bridging boryl borylene complex [(Cp*Ru)$_2$(μ-HBS$_2$CH$_2$-κ^2B:κ^2S){μ-B(C$_6$H$_4$)C(CH$_3$)-κ^2B:κ^2C}] (**8**) has been established which involves the thermolysis of an *arachno*-ruthenaborane, [(Cp*Ru)$_2$B$_3$H$_8$(CS$_2$H)] (**7**) with phenylacetylene. Thermolysis of **7** on the other hand, afforded the ruthenium bridging bis(boryl) complex [(Cp*Ru)$_2$(μ-HBS$_2$CH$_2$-κ^2B:κ^2S){μ,η^2:η^2-SBH}] (**9**).[4] The key results of this work will be discussed.



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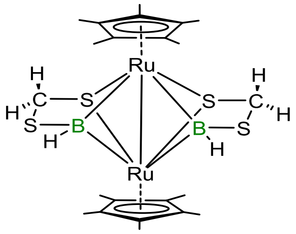

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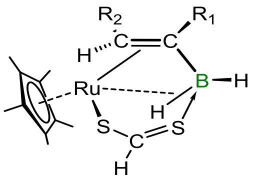
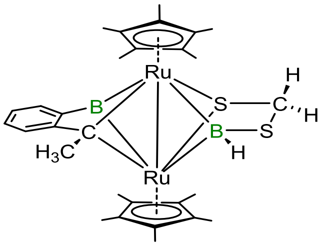


6a-g



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IC 05

Exclusive Diastereoselectivity in Low-Symmetry Self-Assembled Coordination Complexes

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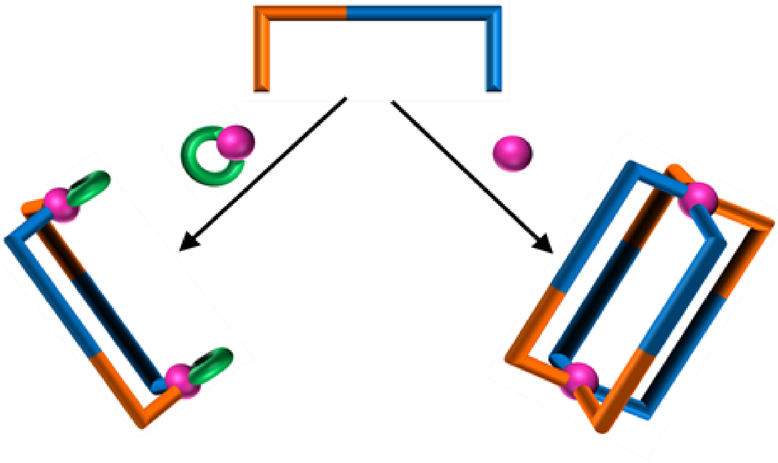
Abstract: Palladium(II) driven self-assembly has been proven to be efficient for the construction of discrete self-assembled complexes. Among the self-assembled palladium(II) complexes, quadruple-stranded binuclear complex of Pd_2L_4 formulation is the simplest and the most reported one. A pyridine/aniline appended unsymmetrical bidentate ligand *N*-(4-(4-aminobenzyl)phenyl)nicotinamide, investigated in this work has two well separated coordination sites. Combination of the ligand with *cis*-protected palladium(II) (i.e. PdL') and palladium(II) in separate reactions produced the corresponding $Pd_2L'_2L^{un}_2$ and extremely rare $Pd_2L^{un}_4$ type self-assembled binuclear complexes, respectively. Notably, both variety of complexes are prepared from a common ligand system. Two diastereomers (i.e. (2,0) and (1,1)-forms) are possible for $Pd_2L'_2L^{un}_2$ type complex whereas four diastereomers (i.e. (4,0), (3,1), *trans*(2,2) and *cis*(2,2)-forms) can be imagined for the $Pd_2L^{un}_4$ type complex. However, exclusive diastereoselectivity was observed and the complexes formed belong to (1,1)-$Pd_2L'_2L^{un}_2$ and *cis*(2,2)-$Pd_2L^{un}_4$ forms.[1] The diastereomers are predicted from NMR study in solution and DFT calculations in gas phase and implicit solvent media, however, single crystal structures of both the complexes provided unambiguous support. The rare $Pd_2L^{un}_4$ type complex is studied in further detail. Parameters like counter-anion, concentration, temperature and stoichiometry of metal to ligand did not influence the diastereoselectivity in complex formation. DFT calculations show the *cis*(2,2) form to be the most stable, followed by the (3,1) isomer. Lowest conformational strain in the bound ligand strands in the *cis*(2,2)-arrangement along with optimal intermolecular interactions makes it the energetically most stable of all the isomers. Molecular dynamics (MD) simulations were carried out to visualize the self-assembly process towards the formation of $Pd_2L^{un}_4$ type complex and the free energy difference between the *cis*(2,2) and (3,1) isomers. Snapshots of MD simulation elucidate the step-by-step progress of complexation leading to the *cis*(2,2)-isomer.[1]



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IC 06

Highly fluorescent aryl-cyclopentadienyl ligands and their tetra-nuclear mixed metallic potassium–dysprosium clusters

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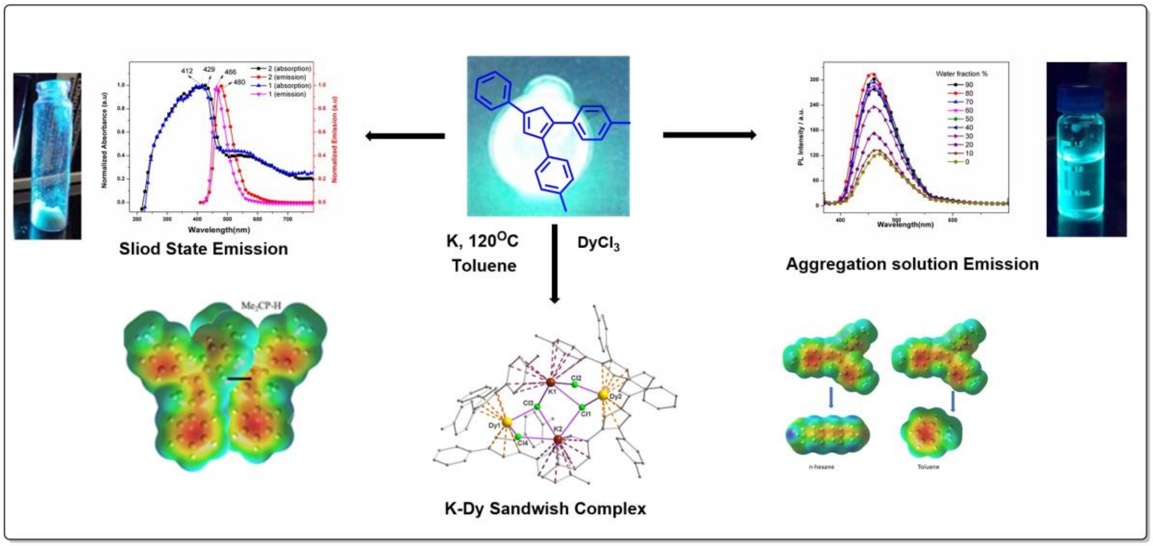
Two alkyl substituted triaryl-cyclopentadienyl ligands 4,4'-(4-phenylcyclopenta-1,3-diene-1,2-diyl)bis(methylbenzene) **(1)** and 4,4',4''-(cyclopenta-1,3-diene-1,2,4-triyl)tris(methylbenzene) **(2)**] have been synthesized via cross-aldol condensation followed by Zn-dust mediated cyclization and acid catalyzed dehydration reactions. The fluorescence properties of **1** and **2** have been studied in solution and solid state. The ligands exhibited aggregation-induced emission enhancement (AIEE) in THF/water solution. **1** and **2** have been found to be significantly more fluorescent in the solid state than in their respective solutions. This phenomenon can be attributed to the strong intermolecular C-H…π interactions present in **1** and **2** which leads to the tight packing of molecules in their solid-state. **1, 2** and their corresponding anions have been studied by theoretical calculations. Ligands **1** and **2** have been shown to react with anhydrous $DyCl_3$ in the presence of potassium metal at high temperature to afford two fluorescent chloride-bridged tetra-nuclear mixed potassium–dysprosium metallocenes $[(Me_2Cp)_4Dy_2^{(III)}Cl_4K_2].3.5(C_7H_8)$ (5) and $[(Me_3Cp)_4Dy_2^{(III)}Cl_4K_2].3(C_7H_8)$ (6), respectively in good yields.



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