Department of Chemistry
IIT Madras

Chemistry In-House Symposium - 2023
(CiHS-2023)

Book of Abstracts

Chemistry In-House Symposium-2023

CiHS-2023

Program Committee

- **Dr. Kartik C Mondal (Convener)**
- **Dr. Sooraj Kunnikuruvan (Co-convener)**
- **Professor Jeganmohan M (member)**
- **Professor Mahiuddin Baidya (member)**

Advisory Committee

- **Professor Prasad Edamana**
- **Professor Sekar G**
- **Professor Ramesh Gardas**
- **Professor Muraleedharan K M**
- **Professor Debashis Chakraborty**
- **Professor Kothandaraman R**
- **Professor Murthy N N**

Poster Evaluation Committee

- **Dr. Palani Selvam T (Physical Chemistry)**
- **Dr. Chaitanya S Yamijala (Theoretical & Computational Chemistry)**
- **Dr. Arnab Rit (Inorganic Chemistry)**
- **Dr. Venkatakrishnan P (Organic Chemistry)**

FACULTIES & STAFF AT THE DEPARTMENT OF CHEMISTRY

Professors

Anbarasan P
Archita Patnaik
Arti Dua
Baskaran S
Beeraiah Baire
Bhyrappa P
Debashis Chakraborty
Dhamodharan R
Dillip Kumar Chand
Indrapal Singh Aidhen
Jeganmohan M
Kothandaraman R
Mahiuddin Baidya Md.
Mishra A K
Muraleedharan K M
Murthy N N
Prasad Edamana
Rajakumar B
Ramesh Gardas
Ranga Rao G
Sanjay Kumar
Sekar G
Selvam P
Pradeep T
Sundargopal Ghosh

Associate Professors

Arnab Rit
Venkatakrishan P
Kartik Chandra Mondal

Assistant Professors

Chaitanya Sharma Yamijala
Dawande Sudam Ganpat
Hema Chandra Kotamarthi
Palaniselvam T
Sooraj K

Emeritus Professors

Mangala Sunder K
Sangaranarayanan M V
Sankararaman S

Visiting Faculties

Nabil Omri
Subramanian V

Adjunct Professors

Balasubramaniam K K
Hadas Mamane
Viswanathan K S
Raman Vedarajan

STAFF AT THE DEPARTMENT OF CHEMISTRY

Technical Staff

Dr.Baskar R
Mrs.Beena MV
Mr.Chiranjeevi P
Dr. Elias Jesu Packiam D
Mr. Jothi Murugan S
Dr. Narayanan A
Mr. Naveen Menni
Mr. Ponnarsu Ravikumar
Mr. Ram Kumar V
Mr.Ravi V
Mrs. Srividya

Office Staff

Mrs.Geetha Vedachalam
Mr.Govindarajan
Mrs.Kavitha B
Mrs.Mallika M
Mr.Nagarajan T
Mrs. Shakila G

MESSAGE FROM THE HEAD OF THE DEPARTMENT

It gives me immense pleasure to invite all faculty colleagues, Postdoctoral Fellows, Research Scholars and Associates, students, and staff to the Chemistry-In-House Symposium (CiHS) 2023, scheduled on 23 August 2023.

CiHS is a unique event where the entire members of the Department come together and spend time discussing, sharing, and brainstorming their recent research findings. Department of Chemistry has been conducting the in-house symposium since 2011, without fail, except during the Covid pandemic time (2021).

I urge Ph.D. scholars, Postdoctoral Fellows, Research Associates, and M.Sc. students of the Department to participate in the event actively and utilize this rare opportunity to enhance their learning process. One will certainly benefit from the symposium and also will be able to comprehend the overall departmental research activities.

Many thanks to the organizing team of CiHS-2023 for its sincere efforts in arranging the symposium and to all faculty members and students who have agreed to present their research.

Wishing all a successful and memorable symposium!

Dr. Sanjay Kumar
Professor & Head
Department of Chemistry

MESSAGE FROM THE CONVENER, CiHS-2023

Chemical processes are immensely important for the survival of life on this planet. Chemists are revolutionizing the world with evolving chemical reactions. We need chemistry and chemical processes in every moment of our life. Chemistry Department at IIT Madras possesses over thirty-five research groups in diverse areas of chemistry, chemical physics, and chemical biology. The expertise of each faculty member provides enormous research opportunities to the research scholars in our department. Our faculty members are also rigorously teaching MSc students and Ph.D. scholars having expertise related to the topics they are practicing in our department. Every research group is focused on their own research topics. However, Chemistry in-house symposium (CiHS) that, started in 2011, will bring all the faculty members, research scholars, MSc students, and postdoctoral researchers under one roof for a day to showcase and/or share their research works/ideas. This mass gathering will give them a unique opportunity to exchange their findings and innovative ideas with each other. It is expected to spark huge research interests among newcomers to this department.

A day-long CiHS-2023 event starts at 8.30 with the registration followed by inauguration at 9.0 am by the Director and the Research Dean of IIT Madras. There are three plenary lectures, three invited lectures, three short invitation lectures, and eight student oral presentations with short interaction time with the speakers. Fifty-five posters will be presented from different research groups on diverse topics. Over twenty student volunteers will be engaged to help the event go smoothly. There will be a tea/coffee session in the morning, lunch and snacks for the participants. A grand dinner has also been arranged in the evening session. We have two major sponsors and several other minor sponsorships to finance our CiHS-2023 in a grand manner. I cordially invite all of you to this departmental event to make it a grand success.

I thank Prof. Sekar, Prof. Edamana Prasad, and Dr. Sooraj (Co-convener) for their great help in every moment.

With best wishes,

Dr. Kartik Chandra Mondal

Convener, CiHS-2023

Chemistry In-House Symposium-2023
CiHS-2023

Date: 23rd August 2023

Venue: ICSR Auditorium, IIT Madras

Program Schedule

08.30 AM- 09.00 AM Registration

09.00 AM – 09.30 AM Inauguration

- **09.00 AM -09.05 AM Welcome by Convener, CiHS 2023**
- **09.05 AM -09.10 AM Address by Head of the Department, Chemistry**
- **09.10 AM -09.20 AM Inaugural Address by Director, IIT Madras**
- **09.20 AM -09.25 AM Address by Dean Academic Research, IIT Madras**
- **09.25 AM -09.30 AM Vote of Thanks by Co-Convener, CiHS 2023**

09.30 AM -10.55 AM Session I Chair: Professor T Pradeep

09.30 AM -10.00 AM PL-1 Professor Archita Patnaik

Tryst with Science

10.00 AM -10.25 AM IL-1 Professor B Rajakumar

Temperature Dependent Kinetics of Criegee Intermediate with N-Butyraldehyde and Isobutyraldehyde

10.25 AM -10.40 AM SOP-1 Prathap Ravichandran

Activation of Singlet Carbenes with Aryne: A easy way for C2-Blocking and Aryl Migration

10.40 AM- 10.55 AM SOP-2 Jijith Mepperi

A knotty tale: Unfolding, untying and refolding of a fluorescent Knotted Protein

10.55 AM -11.15 AM Tea/Coffee

11.15 AM -12.45 PM Session II Chair: Professor Indrapal Singh Aidhen

11.15 AM -11.45 AM PL-2 Professor A K Mishra

Extending the Frontiers of Fluorescence Spectroscopy: Some Contributions from our Laboratory

11.45 AM -12.10 PM	**IL-2 Professor S Baskaran**
	New Synthesis and Application of Functionalized Sulfones
12.10 PM -12.30 PM	**SIL-1 Dr. Sudam G Dawande**
	Domino Reactions of α-imino Rhodium(II) Carbenoids: Synthesis of privileged polycyclic indole scaffolds
12.30 PM – 12.45 PM	**SOP-3 Pandidurai S**
	Organocatalyzed Enantioselective Synthesis of Chiral Heterocyclic Compounds using Domino Cycloaddition/Rearrangement
12.45 PM -01:00 PM	**Group Photo**
01:00 PM -01.45 PM	**Lunch**
01.45 PM -03.00 PM	**Session III Poster Session**
03.00 PM -04.25 PM	**Session IV Chair: Professor P Bhyrappa**
03.00 PM -03.30 PM	**PL-3 Professor P Selvam**
	Heterogeneous Catalysts - The High-Tech Materials: New Developments and Applications in Energy Conversion and Environmental Remediation
03:30 PM -03:55 PM	**IL-3 Professor Sundargopal Ghosh**
	Diboranes
03:55 PM -04.10 PM	**SOP-4 Manaswini Ray**
	Tale of a molecular prism
04.10 PM -04.25 PM	**SOP-5 Sriparna Sarkar**
	Monometallic and Bimetallic Al(III) compounds: Catalysts for Synthesis of Biodegradable Polyesters and Polycarbonates
04.25 PM - 04.45 PM	**Tea/Coffee**
04:45 PM -05.30 PM	**Session V Chair: Professor G Ranga Rao**
04.45 PM -05.00 PM	**SOP-6 Richa Sharma**
	Chitosan, Malic acid & Urea Based Machinable Material
05.00 PM -05.15 PM	**SOP-7 M Bakkiyaraj**
	Rhodium Catalyzed Asymmetric C-H Bond Functionalization: Enantiodivergent Synthesis of 3-Vinylphthalides

05:15 PM-05.30 PM SOP-8 Shuchi Sharma

Enhanced photoelectrochemical water splitting on Y_2O_3@TiO_2 photoanodes

05.30 PM-06.30 PM Session VI Chair: Professor E Prasad

05.30 PM -05.45 PM SIL-2 Professor K Mangala Sunder

Excited State Spectra of Rotational States of Molecular Complexes

05.45 PM -05.55 PM SIL-3 Professor E Prasad

The Link between Teaching and Research: Myth Breaking

05.55 PM - 06.15 PM Felicitation to Professor S Sankararaman & Professor K Vidyasagar

6.15 PM – 6.30 PM Concluding remarks by Professor Dillip K Chand

National Anthem

07.00 PM -10.00 PM Dinner @ ICSR

PLENARY & INVITED LECTURES

PL-01

Tryst with science

Archita Patnaik

Department of Chemistry, IIT Madras

E-mail: *archita@iitm.ac.in*

Three decades of work is a precious treasure and capturing it under one roof is unthinkable. In this abstract, I try narrating a concise account of some of its work elements.

Supramolecular self-assembly at interfaces[1] takes advantage of i. molecular pattern formation over a broad length scale as excellent platforms for two-dimensional molecular-recognition[2], host-guest chemistry, devising sensors, and ii. the tunability of electronic structure and transport properties with frontier molecular orbital alignment towards hybrid interfaces for organic semiconductor applications[3,4]. This new frontier in Chemical Physics uniquely combines designing and modelling molecular systems under controlled conditions, versatility in interfacial synthesis and physics of interfaces.

References

1. Bartels, L.; Ernst, K.-H.; Gao, H.-J.; Thiel, P. A. *J. Chem. Phys.* **2015**, *142*, 101501.
2. Sarangi, N. K.; Ramesh, N.; Patnaik, A. *J. Chem. Phys*. **2015**, *142*, 024702.
3. Kumar, K. S.; Patnaik, A. *Chem. Eur. J.* **2011**, *17*, 5327.
4. SS Gayathri and Archita Patnaik, *Chem. Commun*. **2006**, 1977.

IL-01

Temperature dependent kinetics of criegee intermediate with n-butyraldehyde and isobutyraldehyde

Amit Debnath[a] *and Balla Rajakumar*[a,b]

[a]*Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036*

[b]*Centre for Atmospheric and Climate Sciences, Indian Institute of Technology Madras, Chennai, 600036, India*

E-mail: *rajakumar@iitm.ac.in*

Atmospheric ozonolysis of olefins produces short-lived Criegee intermediates (CH_2OO), which act as a dominant oxidant in the troposphere and get scavenged mostly by the carbonyl compounds. n-Butyraldehyde (nBD) and iso- Butyraldehyde (iBD) are class of oxygenated volatile organic compounds (OVOCs), widely used in the synthetic rubber resins, accelerators, solvents and plasticizers manufacturing industries, flavouring agents in foods like hard and soft beverages, candy, ice cream, baked stuff, etc..[1]. Hence, it is essential to understand their atmospheric removal processes. In this study, the reaction kinetics for CH_2OO with nBD and iBD were determined by direct probing of CH2OO using a highly sensitive custom-built Cavity Ring-down Spectrometer (CRDS) at room temperature and 50 Torr/N_2 of total pressure [2].

A pulsed laser beam of 355 nm was used for the in-situ generation of CH_2OO at the reaction zone by photolyzing CH_2I_2 in the presence of excess O_2. The concentration of the CH_2OO was monitored by CRDs using another pulsed laser beam at 360 nm. The kinetic decay traces of CH_2OO from 50 to 1000 ms during the reaction with nBD and iBD are depicted in Figure 1. The kpseudo values obtained from the fit of Figure1 and are plotted against the nBD and iBD concentration, the slope of which give the bimolecular rate coefficient (k).

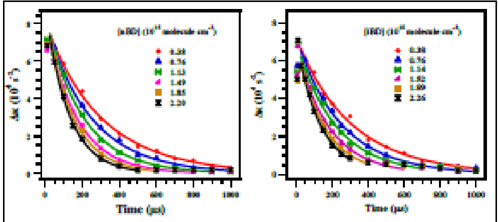


Figure 1: CH_2OO Decay traces at various concentration of nBD, and iBD in the temperature range 253-318 K

$$CH_2I_2 \xrightarrow{h\nu\ (355\ nm)} CH_2I + I \qquad R1$$

$$CH_2I + O_2 + M \xrightarrow{k_2} CH_2OO + I + M \qquad R2$$

$$CH_2OO + CH_2OO \xrightarrow{k_3} 2HCHO + O_2 \qquad R3$$

$$CH_2OO + CH_3CH_2CH_2CHO\ (nBD) \xrightarrow{k_{nBD}} Products \qquad R4$$

$$CH_2OO + CH_3(CH_3)CHCHO\ (iBD) \xrightarrow{k_{iBD}} Products \qquad R5$$

A negative temperature dependence was observed for the rate coefficient in the studied range of 253-318 K. The Arrhenius equations obtained are $k_{nBD}(T = 253 - 318\ K) = (11.51 \pm 4.33) \times 10^{-14}\exp\ (918.1 \pm 107.2)/T$ and $k_{iBD}\ (T = 253 - 318\ K) = (6.23 \pm 2.29) \times 10^{-14}\exp\ (1051.4 \pm 105.2)/T$ cm^3 $molecule^{-1}$ s^{-1}. Computational calculations (CVT/SCT and MESMER) were performed to verify the rate coefficients in terms of various possible reaction channels. Atmospheric implication of the studied reactions was also drawn in terms of atmospheric life time of nBD and iBD.

References

1. Opdyke, D. L. *Food Cosmet Toxicol*. 1997, *17*, 731–734.

2. Debnath, A.; Rajakumar, B. *Phys. Chemosphere*, **2023**, 312, 137217.

PL-02

Extending the Frontiers of Fluorescence Spectroscopy: Some Contributions from our Laboratory

Ashok Kumar Mishra

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036

Email: *mishra@iitm.ac.in*

This talk will present some glimpses of the research carried out in our laboratory at IIT Madras over the past three decades. After introducing fluorescence spectroscopy and the relevant photophysical processes, the talk will focus on two major components: (i) our research ON fluorescence spectroscopy, which will present some new understanding of fluorescence inner-filter effect, the fluorescence of ‘complex multifluorophoric systems’, as well as our contribution to the growing research on fluorescence instrumentation; and (ii) our research WITH fluorescence spectroscopy, which will present some new fluorescent molecules and new fluorescence based probing concepts introduced by us, which were used for understanding a variety of soft matter systems.

References

More details on the research in our laboratory is available at

https://akm-research-group.in & http://chem.iitm.ac.in/faculty/ashok

IL-02

New Synthesis and Application of Functionalized Sulfones

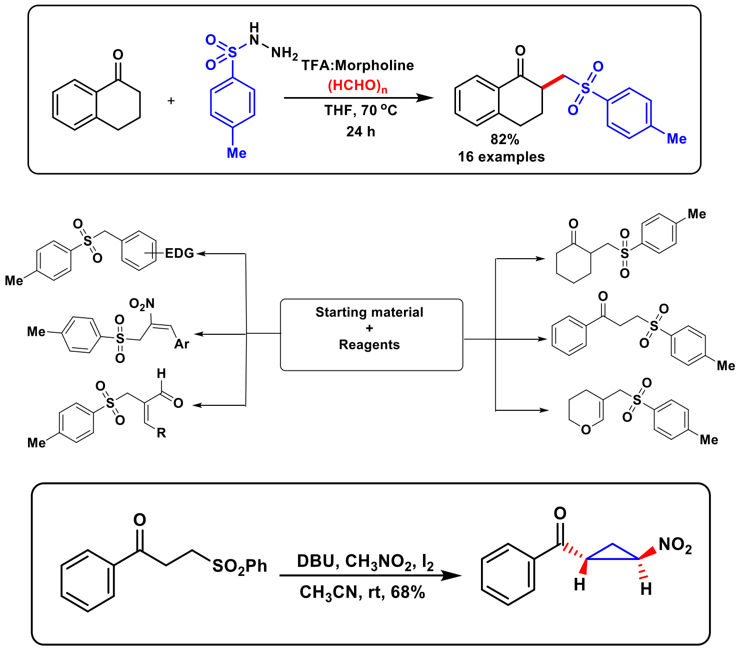
Sundarababu Baskaran

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036

E-mail: *sbhaskaran@iitm.ac.in*

The sulfone moiety is a unique functional group present in many pharmaceuticals, agrochemicals, and natural products. Molecules bearing sulfone group are known to exhibit a broad spectrum of biological activities such as antibacterial, antifungal, antimalarial, cysteine protease inhibitor, anti-HIV, anti-proliferative and anti-cancer.

Our effort towards achieving sustainable chemical transformations has resulted in the development of a novel, metal-free method for the synthesis of functionalized sulfones (Scheme). In this reaction, aryl sulfonyl hydrazide-formaldehyde reagent system serves as a novel “-CH_2-SO_2-Ar” transfer agent. Using this protocol, a facile one-carbon homologation method has been developed for the synthesis of γ-ketosulfone from ketone. Syntheses and applications of functionalized sulfones will be presented.



Scheme: Synthesis and application of various sulfone derivatives.

References

1. a) Whitham, G. H.; Organosulfur Chemistry; Oxford University Press: Oxford/New York, 1995. b) Oae, S.; Organic Chemistry of Sulfur; Plenium Press: New York, 1977. c) Meadows, D. C.; Sanchez, T.; Neamati, N.; North, T. W.; Gervay- Hague, J. *Bioorg. Med. Chem*. **2007**, *15,* 1127.
2. Konduru, N. K.; Dey, S.; Sajid, M.; Owais,M.; Ahmed, N. *Eur. J. Med. Chem.***2013**,*59*, 23.Xiang,J.; Ipek, M.; Suri, V.; Tam, M.; Xing, Y.; Huang, N.; Tobin, J.; Mansour, T. S.; Mckew, J.*Bioorg. Med. Chem.***2007**,*15*, 4396.

SIL-01

Domino Reactions of α-imino Rhodium (II) Carbenoids: Synthesis of privileged polycyclic indole scaffolds

Sudam G. Dawande

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036

E-mail: *sg.dawande@iitm.ac.in*

Domino reactions involving cycloaddition/rearrangement cascade of metal carbenoids have emerged as an indispensable strategy for the synthesis of nitrogen-containing polycyclic molecular frameworks. Herein, we presented the design and synthesis of a new class of isatin and phthalimide tethered *N*-sulfonyl-1,2,3-triazoles as surrogates of diazo compounds and their rhodium (II)-catalyzed domino reactions with indoles to synthesize azepino fused diindoles and indolyl tetrahydro pyrrolo[2,1-a]isoindoles respectively. In both cases, the reaction initiates via denitrogenative generation of α-imino rhodium carbene intermediate followed by intramolecular carbonyl oxygen insertion to give a carbonyl ylide, which then depending on the structure of carbonyl ylide reacts with indole distinctly and follows different reaction pathways to deliver corresponding products in moderate to excellent yields. Further, the synthetic utility of the products obtained has been demonstrated.

References

1. Padwa, A. *Chem. Soc. Rev.,* **2009**, 38, 3072.
2. Gulevich, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.,* **2013**, 52, 1371.
3. Anbarasan, P.; Yadagiri, D.; Rajasekar, S. *Synthesis,* **2014**, 3004.
4. Davies, H. M. L.; Alford, J. S. *Chem. Soc. Rev.,* **2014**, 43, 5151.
5. Kahar, N.; Jadhav, P.; Reddy, R. V. R.; Dawande, S. *Chem. Commun.,* **2020**, 56, 1207.

PL-03

HETEROGENEOUS CATALYSTS - THE HIGH-TECH MATERIALS:

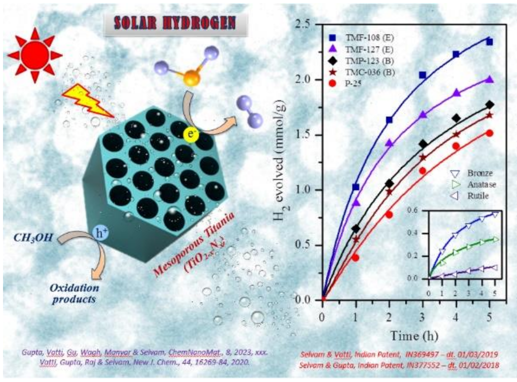
New Developments and Applications in Energy Conversion and Environmental Remediation

Parasuraman Selvam

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036

Email: selvam@iitm.ac.in

The discovery and development of periodic porous materials of well-defined pore geometry with precise and easily controllable pore shape and size are of great importance in many areas of modern science and technology. Mesoporous and hierarchical molecular sieves, including metal-organic frameworks resembling zeolites, represent the latest class of organized porous materials characterized by extensive surface area, sizable pore entrances, and substantial pore volumes. On the one hand, the unique flexibility of these materials, in terms of synthetic conditions, pore size tuning, large internal hydroxyl groups, framework substitution, etc., has created new avenues not only in catalysis but also in the areas of advanced energy materials and environmental pollution control strategies.



Gupta, Vatti, Gu, Wagh, Manyar & Selvam, ChemNanoMat., 8, 2023, xxx.
Vatti, Gupta, Raj & Selvam, New J. Chem., 44, 16269-84, 2020.

Selvam & Vatti, Indian Patent, IN369497 – dt. 01/03/2019
Selvam & Gupta, Indian Patent, IN377552 – dt. 01/02/2018

Furthermore, preparing and characterizing high-quality materials with well-defined pore characteristics are paramount for many applications in nanomaterials, catalysis, adsorption, and separation. In designing such materials, several characteristics of pore structure may be addressed, which include their shape, size, pore interconnectivity, etc. Likewise, traditional preparation methods of supported catalyst systems are neither efficient in generating/dispersing uniform-sized clusters nor chemically inert toward the guest molecules. Nevertheless, the confinement of nanoclusters/nanofilaments/enzymes in the cavities/voids/pores of nanostructured matrices is attracting much attention as a way to stabilize highly dispersed materials in the form of atoms, clusters, colloids, or filaments, and prevent their coalescence into to larger, ill-defined aggregates. In this context, the self-assembly of nanoparticles into ordered pore structures, i.e., encapsulation of the nanosized materials in zeolitic pores, is a promising option. Therefore, this presentation will discuss the recent progress in the development of numerous nanoscale materials and their applications in the areas of Bioprocessing, Energy, and Environmental Technology.

IL-03

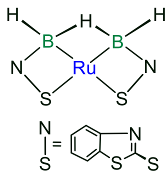
"Diboranes"

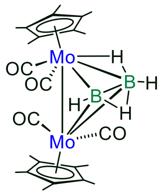
Sundargopal Ghosh

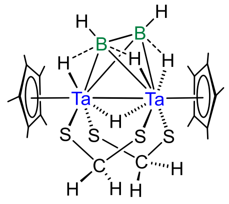
Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036

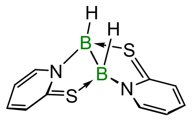
E-mail: *sghosh@iitm.ac.in*

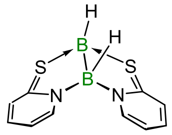
The fascinating aspect of metallaborane chemistry is that several classic organometallic complexes that defined fundamental structural and bonding paradigms are mimicked by many isoelectronic metallaborane analogues.[1] In this connection, diborane compounds not only mimics several classic organometallic compounds but also they have been extensively explored for the broad understanding of the chemical bonding and catalysis.[2] For example, we have recently synthesized and structurally characterized a bimetallic diborane(4) which mimics the Cotton dimolybdenum–alkyne complex $[\{CpMo(CO)_2\}_2C_2H_2]$.[3]











Also, we have isolated the first classical diborane(5) $[B_2H_5]^-$, in which the sp^2-B center is stabilized by the electron donation from tantalum.[4] Very recently, we have developed an uncatalysed synthetic pathway to generate the doubly base stabilised symmetrical and unsymmetrical diborane(4) species from the thermolysis reaction of 2-mercaptopyridine with $[BH_3.THF]$.[5] The key results of this work will be described.

References

1. (a) Saha, K.; Roy, D. K.; Dewhurst, R. D.; Ghosh, S.; Braunschweig, H. *Acc. Chem. Res*. **2021**, *54*, 1260. (b) Ghosh, S.; Noll, B. C.; Fehlner, T. P. *Angew. Chem. Int. Ed.* **2005**, *44*, 6568.
2. (a) Trageser, T.; Bolte, M.; Lerner, H. -W.; Wagner, M. *Angew. Chem. Int. Ed.* **2020**, *59*, 7726. (b) Bamford, K. L.; Qu, Z. -W.; Stephan, D. W. *J. Am. Chem. Soc.* **2019**, *141*, 6180. (c) Anju, R. S.; Roy, D. K.; Mondal, B.; Yuvaraj, K.; Arivazhagan, C.; Saha, K.; Varghese, B.; Ghosh, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 2873. (d) Borthakur, R.; Saha, K.; Kar, S.; Ghosh, S. *Coord. Chem. Rev.* **2019**, *399*, 213021.
3. Mondal, B.; Bag, R.; Ghorai, S.; Bakthavachalam, K.; Jemmis, E. D.; Ghosh, S. *Angew. Chem. Int. Ed.* **2018**, *57*, 8079.
4. Saha, K.; Ghorai, S.; Kar, S.; Saha, S.; Halder, R.; Raghavendra, B.; Jemmis, E. D.; Ghosh, S. *Angew. Chem. Int. Ed.* **2019**, *58*, 17684.
5. Ahmad, A.; Gayen, S.; Mishra, S.; Afsan, Z.; Bontemps, S.; Ghosh, S. (unpublished results).

SIL-02

Excited State Spectra of Rotational States of Molecular Complexes

Mangala Sunder Krishnan

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036

E-mail: *mangal@iitm.ac.in*

Molecular rotation and its detection by microwave spectroscopy and rotational Raman spectroscopy are most important in determining the ground state molecular properties such as their structures, dipole moments and nuclear quadrupole moments. Stable molecules have enormously large number of rotational states associated with each vibrational state of the molecule and for even a low degree of vibrational excitation of the 3N-6 or 3N-5 vibrational degrees of freedom (where N is the number of atoms in the molecule) there are often thousands of transitions which need to be identified in gas phase rotational-vibrational spectra. This challenge has been addressed quite well for several decades. Molecular complexes such as van der Waals complexes, are not able to support more than one or two excited vibrational states involving the weak bond of the complex and the rotational spectra of such complexes, despite having very few excited states are difficult to characterize due to the non-rigidity of the complex. I shall summarize the theory developed by my students, past and present, and will give examples of a couple of successful fitting of spectral lines of the ubiquitous molecular complex, namely benzene-water van der Waals complex.

References

For more information see

https://chem.iitm.ac.in/Faculty/mangala/

SIL-03

The Link between Teaching and Research: Myth Breaking

Edamana Prasad,[a,b]

[a]*Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036*

[b]*Head, Teaching Learning Centre (TLC), IIT Madras*

E-mail: *pre@iitm.ac.in*

For the past several years, research performance has been the main, and quite often the only, criterion towards selection and / or promotion of teachers in higher education institutes. At the same time, all higher education institutions always proclaim that the primary job of the faculty members is teaching. In order to justify the scenario, a general perception has been generated that high-quality research enhances teaching skills of the faculty members. However, this has never been tested or supported by any kind of scientific data. Conversely, some of the existing studies indicate negative correlation between the two.

The present talk compares the desired goals/characteristic features of a teacher and a researcher, which indicates that most of the features are rather independent and unique to the domain! Hence the question: the link between teaching and research: is it a myth?

Student Oral Presentations (SOP)

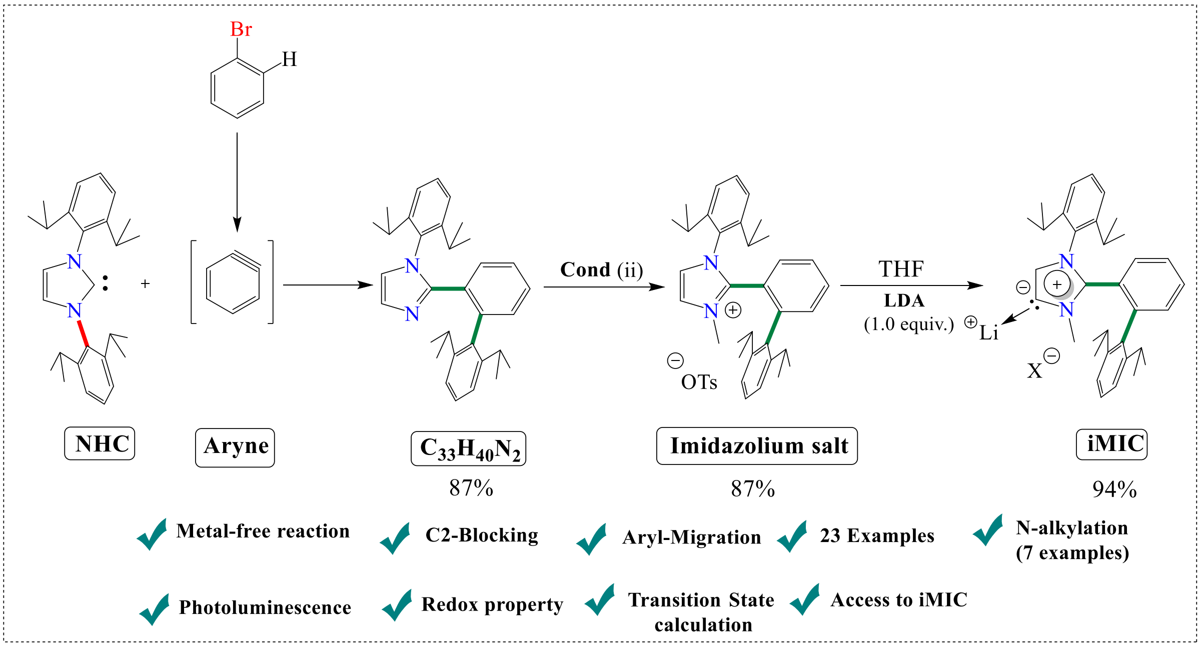
SOP-1

Activation of Singlet Carbenes with Aryne: A easy way for C2-Blocking and Aryl Migration

*Prathap Ravichandran, Kartik Chandra Mondal**
Department of Chemistry, IIT Madras

E-mail. csdkartik@smail.iitm.ac.in

Herein, we report a single-step C−N bond activation, C2 arylation, and aryl group migration of the singlet carbene [carbene = cyclic alkyl amino carbene (CAAC) and N-heterocyclic carbene (NHC)] with aryne in the absence of any metal catalyst. Bright light emitter can be produced by proper selection of the arynes. N-alkylation of these derivatives provides air and moisture-stable redox-active pyrrolium and imidazolium salts further converted to neutral mono radicals as well. Notably, imidazolium salts are a direct precursor for accessing mesoionic carbene (iMICs), where confirmed by forming an acetone adduct and cationic Nickel complex.



Scheme 1: Reaction of NHC with Aryne.

References

1. Aldeco-Perez, E.; Rosenthal, A. J.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Science* **2009**, *326*, 556-559
2. Merschel, A.; Glodde, T.; Neumann, B.; Stammler, H. G.; Ghadwal, R. S. *Angew. Chem. Int. Ed*. **2021**, *60*, 2969-2973

SOP-2

A knotty tale: Unfolding, untying and refolding of a fluorescent Knotted Protein

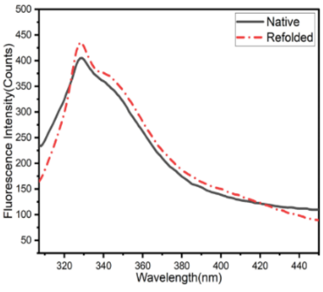
*Jijith Mepperi, Khushboo Goel and Dr. Hema Chandra Kotamarthi**

Department of Chemistry, IIT Madras

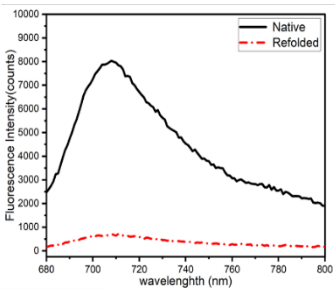
E-mail: cy21d301@smail.iitm.ac.in , hemachandra@iitm.ac.in

Proteins attain their functional structure from their amino acid chain by undergoing several intra and intermolecular interactions during protein folding. It is well accepted that a protein can spontaneously fold to its native structure if the surrounding environment is supportive since the protein folding takes place to minimize the energy[1]. Knotted proteins are special classes of proteins in which the polypeptide backbone cross over themselves to form topological knots. Even though ~1% of the protein data bank (PDB) entries are knotted in nature, the physiological significance of the knots in the proteins is yet to be identified[2]. The presence of the knot in the protein structure may give additional thermodynamic and kinetic stress to the protein folding process[3].

An unknotted protein once unfolded, refolds to its native folded state if the unfolding environment is removed. In this study, we tried to understand whether a 4_1-knotted protein miRFP709[4] would undergo the cyclic folding process under the successive exposure and removal of the chemical unfolding agent GnHCl.The choice of miRFP709 as the model protein for this study helps to have two independent probes to understand the changes in structure and ligand binding capacity of the protein during unfolding/refolding processes; Tryptophan-based UV fluorescence and Biliverdin-based NIR fluorescence of miRFP have been used to probe the structural changes in the protein.



Tryptophan



Biliverdin fluorescence

From the study, it is observed that during successive unfolding and refolding environments, the protein attained a compact folded structure but was different from its native structure and showed a significant loss in the ligand binding capacity. It is hypothesized that the unknotting during unfolding by the chemical denaturant prevents the protein from attaining its native folded and knotted state upon refolding.

References

1. Englander, S. W.; Mayne, L. The Nature of Protein Folding Pathways. *Proceedings of the National Academy of Sciences of the United States of America*. National Academy of Sciences November 11, 2014, pp 15873–15880.
2. Dabrowski-Tumanski, P.; Rubach, P.; Goundaroulis, D.; Dorier, J.; Sukowski, P.; Millett, K. C.; Rawdon, E. J.; Stasiak, A.; Sulkowska, J. I. KnotProt 2.0: A Database of Proteins with Knots and Other Entangled Structures. *Nucleic Acids Res* **2019**, *47* (D1), D367–D375.
3. Lim, N. C. H.; Jackson, S. E. Molecular Knots in Biology and Chemistry. *Journal of Physics Condensed Matter* **2015**, *27* (35).
4. Baloban, M.; Shcherbakova, D. M.; Pletnev, S.; Pletnev, V. Z.; Lagarias, J. C.; Verkhusha, V. V. Designing Brighter Near-Infrared Fluorescent Proteins: Insights from Structural and Biochemical Studies. *Chem Sci* **2017**, *8* (6), 4546–4557.

SOP-3

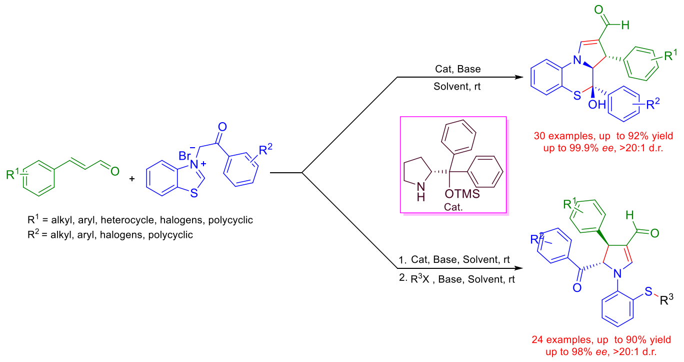
Organocatalyzed Enantioselective Synthesis of Chiral Heterocyclic Compounds using Domino Cycloaddition/Rearrangement

*Pandidurai S, Venkata Surya Kumar Choutipalli, Venkatesan Subramanian and G. Sekar**

Department of Chemistry, Indian Institute of Technology, Madras, Chennai-600036

E-mail: gsekar@iitm.ac.in

1,4-Thiazine, benzo[1,4]thiazine, pyrrolo[1.4]thiazine and their polyhydro derivatives are privileged N, S-containing heterocyclic forms of the core present in many bioactive and pharmacological reagents.[1-2] Over the past decades, many discoveries in the medicinal chemistry, organic synthesis, and catalysis have led to new synthetic methods for the synthesis of 1,4-thiazine derivatives. Several methods have been developed over the past decades to construct pyrrolo[1,4]thiazine derivatives.[3] In comparison to racemic methods, the enantioselective synthesis of chiral pyrrolo[1,4]thiazine and its derivatives received much less attention. Recently, Feng *et al*. reported the synthesis of chiral hydropyrrolo-thiazoles and [1,4]thiazine derivatives via catalytic asymmetric [3+2] cycloaddition and rearrangement of benzothiazloium salt with various dienophiles using chiral *N,N´*-dioxide/metal complex catalysts.[4] Herein, we report a proline-derived organocatalytic enantioselective synthesis of pyrrolo[1,2-*d*][1,4]thiazine-2-carbaldehydes using domino 1,3-dipolar cycloaddition/rearrangement of benzothiazolium salt with α,β-unsaturated aldehyde. This domino process produced fluorescent emissive chiral molecules with three contiguous stereocenters, having one chiral quaternary center in a single step, with excellent yield, enantio-, and diastereoselectivity. This strategy was extended to the stereoselective one-pot synthesis of novel chiral *N*-phenyl thioether-tethered tetrasubstituted dihydropyrrole-3-carbaldehydes via 1,3-dipolar cycloaddition/rearrangement, followed by ring-opening/C-S bond formation to afford in good yield with excellent enantio- and diastereoselectivity (Scheme 1). Computational studies explained the reaction path and offered an in-depth understanding of the reaction mechanism. In-silico study showed that the synthesized pyrrolo-thiazine-2-carbaldehyde scaffolds have substantial anticancer activity.



Scheme 1. Enantioselective synthesis of chiral heterocyclic compounds.

References

1. a) Badshah, S. L.; Naeem, A. *Molecules*. **2016**, *21*, 1054. b) Selvakumar, N.; Reddy, B. Y.; Kumar, G. S.; Khera, M. K.; Srinivas, D.; Kumar, M. S.; Das, J.; Iqbal, J.; Trehan, S. *Bioorg. Med. Chem. Lett*. **2006**, *16*, 4416.
2. a) Matralis, A. N.; Kourounakis, A. P. *J. Med. Chem.* **2014,** *57*, 2568-2581. b) Corelli, F.; Manetti, F.; Tafi, A.; Campiani, G.; Nacci, V.; Botta, M. *J. Med. Chem*. **1997**, *40*, 125.
3. Thielmann, T.; Guentert, M.; Koepsel, M.; Werkhoff, P. *Tetrahedron Lett.* **1989,** *30*, 4507.
4. Zhang, X.; Liu, X.; Zhang, J.; Zhang, D.; Lin, L.; Feng, X. *Org. Chem. Front.* **2018,** *5*, 2126.

SOP-4

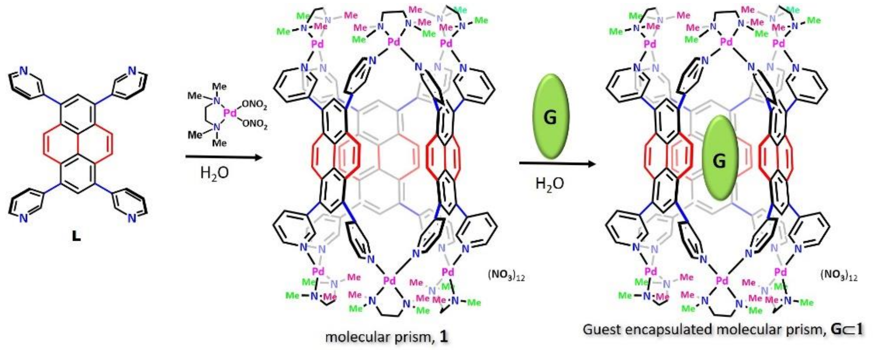
Tale of a molecular prism

*Manaswini Ray, Shobhana Krishnaswamy, Asit K. Pradhan and Dillip K. Chand**

Department of Chemistry, IIT Madras

E-mail: ray.manaswini2009@gmail.com, dillip@iitm.ac.in

A prism is a three-dimensional solid object with identical polygonal bases connected through rectangular sides; in a typical prism the base is trigonal. Molecular architectures resembling to the shape of a prism can be called as a molecular prism. In this work, we have used a non-chelating tetradentate ligand and *cis*-protected Pd(II) to prepare a self-assembled coordinating architecture, **1** of **$Pd_6L'_6L_3$** composition. The shape of complex **1** resemble to a prism and it is soluble in water. The molecular prism, **1** has been characterized by NMR spectroscopy, ESI-MS and single crystal XRD techniques.[1] The water-soluble molecular prism has ability to trap nonpolar/polar/anionic-aromatic guest molecules in water medium. The confined nanospace of the prism can encapsulate nonpolar aromatic guest molecules having length and width in the limits of ~9.5 and ~ 5.5 Å, respectively. The binding preference for the guests follows the order nonpolar < polar < anionic. The structural design of our molecular prism could bind radical initiators like **AIBN** and **HMPP** inside the cavity and protect them from light even upon irradiation. The half-life of encapsulated **AIBN** was found to be significantly increased (305 times) compared to half-life of the same in absence of host. On demand release of **AIBN** from the molecular prism and it's use in Wohl-Ziegler bromination reaction has been demonstrated.



Scheme 1. Synthesis of molecular prism, **1** and guest encapsulation by the prism

References

1. Ray, M.; Krishnaswamy, S.; Pradhan, A. K.; Chand, D. K. *Chem. Mater.*, **2023**, *35*, xxx-xxx (DOI: 10.1021/acs.chemmater.3c00749) (Cover page)

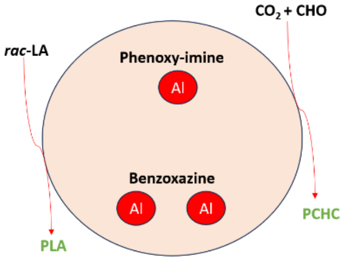
SOP-5

Monometallic and Bimetallic Al(III) compounds: Catalysts for Synthesis of Biodegradable Polyesters and Polycarbonates

Sriparna Sarkar, Sourav Singha Roy and Debashis Chakraborty[*]
Indian Institute of Technology, Madras Chennai – 600036
E-mail: dchakraborty@iitm.ac.in

Conventional plastics (e.g., polyethylene), which have wide applications in our daily life, are derived from non-renewable crude oil and take longer to degrade, adding further to the environmental waste.[1] It has led researchers to find alternative sources to replace conventional plastics in the long run. In this regard, the aliphatic polyesters [Polylactide (PLA)] and aliphatic polycarbonates [polycyclohexene carbonate (PCHC)] are potential candidates as their starting materials are completely or partially derived from renewable feedstocks.[2,3] The PLA is produced from the ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA) and PCHC is produced by the ring-opening copolymerization (ROCOP) of cyclohexene oxide (CHO) with CO_2. The field of homogeneous catalysis for ROP and ROCOP studies has been dominated by divalent or trivalent metal compounds such as Mg, Al, Zn, Cr, and Co.[4] The salan and salen based aluminum compounds have been widely explored in the literature due to excellent Lewis acidity and abundance of aluminum on Earth.

In this study, we explored the catalytic activities of monometallic Al(III) compounds supported by phenoxy-imine moiety and bimetallic Al(III) compounds supported by ethylenediamine bridged benzoxazine proligands for the ROP and ROCOP studies.[5,6] The compounds in the respective series (monometallic or bimetallic) differed from each other either in the substituent attached to the phenolate core or the number of ligands coordinated to the central metal atom. The catalytic activities of the bimetallic Al(III) compounds were observed to be higher than the monometallic Al(III) compounds. The plausible reason for such an observation is the cooperativity that exists between the two Al(III) center in the bimetallic compounds.



References

[1] Thompson, R. C.; Swan, S. H.; Moore, C. J. Vom Saal, F. S. *Philos. Trans. R. Soc. B* **2009**, *364*, 2153–2166.

[2] Tong, R. *Ind. Eng. Chem. Res.* **2017**, *56*, 4207–4219.

[3] Cao, H.; Liu, S.; Wang, X. *Green Chem. Eng.* **2022**, *3*, 111–124.

[4] Fazekas, E.; Lowy, P. A.; Rahman, M. A.; Lykkeberg, A.; Zhou, Y.; Chambenahalli, R.; Garden, J. A. *Chem. Soc. Rev.* **2022**, *51*, 8793.

[5] Singha Roy, S.; Sarkar, S.; Sudhadevi Antharjanam, P. K.; Chakraborty, D. *Mol. Catal.* **2023**, *540*, 113053.

[6] Singha Roy, S.; Sarkar, S.; Sudhadevi Antharjanam, P. K.; Chakraborty, D. *Eur. J. Org. Chem.* **2023**, e202300371.

SOP-6

Chitosan, Malic acid & Urea Based Machinable Material

Richa Sharma and R. Dhamodharan*

Department of Chemistry

Indian Institute of Technology Madras, Chennai 600 036, India

E-mail: sharma.richa829@gmail.com

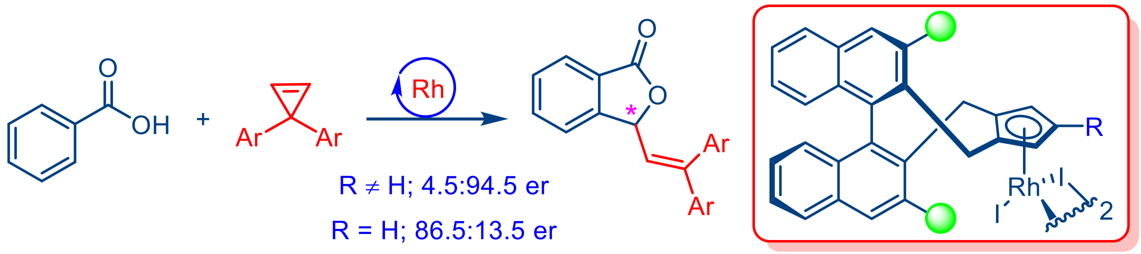
The synthesis of chitosan-based material (CHMAUR) of different forms (foam, porous and non-porous tough gels, porous dry) through crosslinking, facilitated by using urea in the presence of malic acid as the organic acid, is explored. The porosity of the material is determined using helium gas pycnometry, ethanol displacement method while its morphology is examined using scanning electron microscopy. The application of the new material towards absorption of water, support of compressive load and machinability (drilling and sawing) are examined. In the foam form CHMAUR is found to be suitable for smaller compressive loads and for water absorption to the extent of 5000 to 8000 %. In the porous dry form, CHMAUR is observed to support compressive load of up to 15 MPa, with the ability to be machined using conventional tools.

SOP-7

Rhodium Catalyzed Asymmetric C-H Bond Functionalization: Enantiodivergent Synthesis of 3-Vinylphthalides

Marimuthu Bakkiyaraj, Pazhamalai Anbarasan*
Indian Institute of Technology Madras, Chennai-600036
E-mail: anbarasansp@iitm.ac.in

Development of methods for the construction of chiral molecules in its enantiopure form is an evergreen interest in synthetic community. Particularly, achieving an enantiodiversity employing single chiral catalyst would be dream approach for an any given transformation. Most of the known asymmetric transformations were driven by transition metal catalysis where chirality is introduced through chiral ligands. In the past few decades, Cp*M^{III}-catalyzed C-H bond functionalization has emerged as efficient strategy for the construction of various chiral scaffolds, but their asymmetric approaches are rather limited.[1] In this context, chiral C2-symmetric cyclopentadienyl ligands have demonstrated excellent reactivity and stereoselectivity, particularly with group 9 metal, the studies are in its infancy.[2,3] Inspired by the chiral C2-symmetric cyclopentadienyl-Rh^{III} catalyst, the asymmetric synthesis of chiral 3-vinylphthalides have been envisaged from arylcarboxylic acids and cyclopropenes, a surrogate of vinylcarbenes. The detailed synthesis of catalyst, optimization, and scope for the synthesis of 3-vinylphthalides with high enantioselectivity and yield will be discussed in the presentation.



References

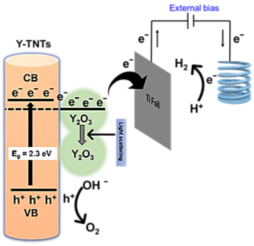
1. Mas-Roselló, J.; Herraiz, A. G.; Audic, B.; Laverny, A.; Cramer, N. *Angew. Chem. Int. Ed.* **2021**, *60*, 13198.
2. Ye, B.; Cramer, N. *J. Am. Chem. Soc.* **2013**, *135*, 636.
3. Ye, B.; Cramer, N. *Synlett* **2015**, *26*, 1490.

SOP-8

Enhanced photoelectrochemical water splitting on Y_2O_3@TiO_2 photoanodes

Shuchi Sharma[1], R.B. Harikrishna[1], G. Ranga Rao[1], A.M. Kannan[2]
[1]*Department of Chemistry, Indian Institute of Technology, Madras, Chennai, Tamil Nadu, India*
[2]*Ira A. Fulton Schools of Engineering Arizona State University, Mesa, AZ, USA*
Presenting author email address: shuchisharma.chem@gmail.com

Y_2O_3 is electrodeposited on TiO_2 nanotube arrays (Y_2O_3@TNTs) through anodization on Ti foil, followed by chronopotentiometry technique using the yttrium nitrate solution as Y source. Deposition time is varied with constant current supply of 1 mA cm^{-2} to deposit different amounts of Y^{3+}. Deposition of Y^{3+} leads to no change in the cell parameters and, hence the cell volume as confirmed through XRD analysis, evident that yttrium is not doped into the TiO_2 lattice. XPS analysis shows that yttrium is present in +3 oxidation state. The photoelectrochemical analysis of prepared TNTs as photoanodes is done in 1 M KOH with Xe arc lamp source equipped with AM1.5G filter under 1sun. Y_2O_3@TNTs as photoanodes are effective than TNTs in terms of photocurrent, photostability and charge separation properties. The Y_2O_3 deposited for 10 min time shows 2.75 times higher photoconversion efficiency as compared to pristine TNTs. This study shows that yttrium deposition significantly affects the photoelectrochemical properties of the photoanodes and that the current electrochemical approach of metal electrodeposition can be used for enhancing the PEC water-splitting activity and for green H_2 production.



Proposed mechanism of charge transfer in Y_2O_3 electrodeposited on TNTs.

References

1. Sharma, S.; Shanmugam, R.; Harikrishna, R.B.; Prasad, U.; Ranga Rao, G.; Kannan, A.M. *Int. J. Hydrog. Energy* **2023**. Published.
2. Cho, H.; Joo, H.; Kim, H.; Kim, J.E.; Kang, K.S.; Yoon, J.*Chemosphere* **2021**, *267*, 129289-129300.
3. He, J.; Wang, M.; Wu, X.; Sun, Y.; Huang, K.; Chen, H. *J. Alloys Compd.* **2019**,*785*, 391–397.

POSTERS

INORGANIC CHEMISTRY
(P1-P13)

P1

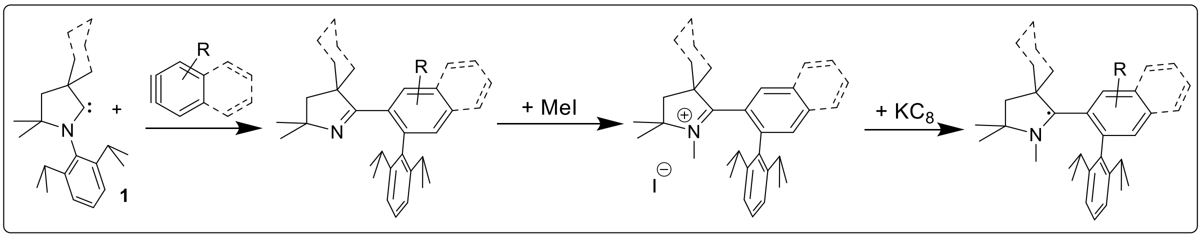
A brief overview on activating carbene-aryl bond using metal-free approach

Prathap Ravichandran, *Kartik Chandra Mondal**
Department of Chemistry, IIT Madras

E-mail. csdkartik@smail.iitm.ac.in

Carbene and aryne are unsaturated electron-deficient chemical species that are two electrons fewer from the attainment of the outer shell 8 electrons closed shell configuration. The introduction of hetero-atom(s) adjacent to the carbene carbon atom led to the isolation of singlet stable carbene that is bottled and stored at ambient conditions. It has been a common chemical reagent in the laboratory for over two decades. On the contrary, arynes are singlet exotic species and are yet to be isolated in pure form at ambient conditions. These arynes have a low HOMO-LUMO energy gap and lower-lying LUMO [HOMO = highest occupied molecular orbital and LUMO = lowest unoccupied molecular orbital]. In the past benzyne/aryne were shown to activate the strong covalent electron-sharing bonds of stable chemical species.

We have observed the splitting of one C−N bond of singlet carbenes (carbene = cyclic alkyl amino carbene (CAAC) and N-heterocyclic carbene (NHC)) when it reacts with aryne to form a blocking of C2 carbene carbon followed by the unexcepted migration of Dipp group in the absence of a metal catalyst. The molecule behaves like a bright light emitter (blue and near white light) that could be produced by proper selection of the aryne. N-alkylation of the product led to the formation of redox-active Zwitterionic abnormal carbene (aNHC) precursor that can be converted to neutral mono radical as well. The same observation was found in N-heterocyclic carbene also.



Scheme 1: Reaction of CAAC with Aryne.

References

3. Aldeco-Perez, E.; Rosenthal, A. J.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Science* **2009**, *326*, 556-559
4. Merschel, A.; Glodde, T.; Neumann, B.; Stammler, H. G.; Ghadwal, R. S. *Angew. Chem. Int. Ed.* **2021**, *60*, 2969-2973

P2

Synthesis and characterization of new low-dimensional quaternary sulfides, $Tl_2Cu_2GeS_4$, $Tl_2Ag_2GeS_4$ and $Tl_2Ag_2SnS_4$

*D. Sujeeth Kumar and Kanamaluru Vidyasagar**

Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036, India

E-mail: kvsagar@faculty.iitm.ac.in

Three new low-dimensional quaternary sulfides, namely, $Tl_2Cu_2GeS_4$(**1**), $Tl_2Ag_2GeS_4$(**2**) and $Tl_2Ag_2SnS_4$(**3**), were synthesized by solid state reactions and characterized by single crystal X-ray diffraction, diffuse reflectance spectroscopy and thermal analysis. The compounds **1**, **2** and **3**, respectively, have centrosymmetric layered, noncentrosymmetric layered and noncentrosymmetric one-dimensional structures, in which the Cu^+, Ge^{4+} and Sn^{4+} ions have tetrahedral coordination and Ag^+ has linear, trigonal planar and tetrahedral coordinations. The compounds **1**-**3** are semiconductors with the band gap values in the range of 1.68-2.02 eV.

P3

Syntheses and structural characterization of calcium organosulfonates

*Rupansha and Kanamaluru Vidyasagar**

Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036, India.

e-mail: kvsagar@faculty.iitm.ac.in

The solid state chemistry of metal organophosphonates[1] such as Zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, is well-documented and interesting from the point of view of their wide range of compositions, structural diversity and various applications such as sorbents, ion exchangers, sensors, catalysts etc[2]. However, when compared to the metal organophosphonates, the number of metal organosulfonates reported[3-7] is small and therefore, their solid state chemistry known is somewhat less. It is envisaged that calcium benzenesulfonate, $Ca(O_3SC_6H_5)_2$ would have the same layered structure of compositionally similar zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, for which the single crystal x-ray structure is not yet reported. In this context, a study of synthesis and characterization, primarily by single crystal X-ray diffraction, of organosulfonates of calcium has been taken up. The present work pertains to $Ca(O_3SC_6H_5)_2\cdot H_2O$(**1**), $Ca(O_3SC_6H_5)_2$(**2**), $Ca(H_2O)_6(O_3SC_6H_5)_2$(**3**), $Ca(O_3SC_6H_4CH_3)_2\cdot 4H_2O$(**4**) and $Ca(O_3SC_2H_4SO_3)$(**5**) compounds, which are benzenesulfonates, tolylsulfonate and ethanedisulfonate of calcium. They have zero-, two- and three-dimensional structures. They were characterized by X-ray diffraction, thermal analysis and solid state NMR spectroscopic methods.

References

1. (1) Clearfield, A.; Demadis, K. (eds) *Metal Phosphonate Chemistry: From Synthesis to Applications.* RSC **2012**.
2. (2) Brunet, E.; Colon, J. L.; Clearfield, A. (eds) *Tailored Organic-Inorganic Materials.* Wiley 2015.
3. (3) Salami, T. O.; Patterson, S. N.; Jones, V. D.; Masello, A.; Abboud, K. A. *Inorg. Chem. Commun.* **2009**, *12*, 1150–1153.
4. (4) Shimizu, G. K. H.; Enright, G. D.; Ratcliffe, C. I.; Rego, G. S.; Reid, J. L.; and Ripmeester. J. A. *Chem. Mater.* **1998**, *10*, 3282–3283.
5. (5) Cote, A P.; Ferguson, M. J.; Khan, K. A.; Enright, G. D.; Kulynych, A. D.; Dalrymple, S. A.; and Shimizu, G. K. H. *Inorg. Chem.* **2002**, *41*, 287–292.
6. (6) Pöllmann, H.; Stöber, S.; Wagner, C.; Merzweiler, K. *Acta Crystallogr. Sect.*, **2006**, 62, s211–s211.
7. (7) Amirthakumar, C.; Valarmathi, B.; Chakkaravarthi, G.; Kumar, R. M. *Bull. Mater. Sci.* **2020**, *43* (1), 1–10.

P4

SYNTHESIS AND CHARACTERIZATION OF NEW QUATERNARY $AMSnS_4$ (A = Na, K, Rb, Cs; M = V, Fe) SULFIDES

*K. Aneka and K. Vidyasagar**
Department of chemistry, Indian institute of chemistry Madras, Chennai 600036, India

E-mail: kvsagar@faculty.iitm.ac.in

The quaternary metal sulphides are an attractive class of solid state compounds that not only display structural diversity but also exhibit a variety of properties such as ion-exchange[1], strong second harmonic generation response[2], gamma ray detection[3] and wide band gap semiconductors[4]. In continuation of our previous studies[1], eight new quaternary $AMSnS_4$ (A = Na, K, Rb, Cs; M = V, Fe) sulphides have been synthesised by two methods employing CS_2 and thiosulphate flux. Their layered structure was inferred from powder X-ray diffraction studies. The ion-exchange properties of $KFeSnS_4$ with other mono- and di-valent cations have been investigated.

References

1. Yohannan, J. P.; Vidyasagar, K. Syntheses; *J. Solid State Chem.* **2016**, *238*, 291.
2. (2) Liu, B.W.; Zeng, H.Y.; Zhang, M.J.; Fan, Y.H.; Guo, G.C.; Huang, J.S.; Dong, Z.C. . *ChemInform* .**2015**, *46* ,16.
3. (3) Li, H.; Malliakas, C. D.; Liu, Z.; Peters, J. A.; Jin, H.; Morris, C. D.; Zhao, L.; Wessels, B. W.; Freeman, A. J.; Kanatzidis, M. G. *Chem. Mater.* **2012**, *24* , 4434.
4. (4) Chen, Z.; Mei, D.; Jiang, X.; Zhao, J.; Wu, Y.; Wang, J.; Wen, S.. *J. Solid State Chem.* **2022**, *312*.

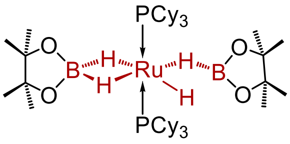
P5

σ- Borate Complexes of Osmium

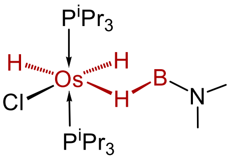
*Faneesha Assanar, Sourav Gayen and Sundargopal Ghosh**

Indian Institute of Technology Madras, Chennai, India
E-mail: sghosh@iitm.ac.in

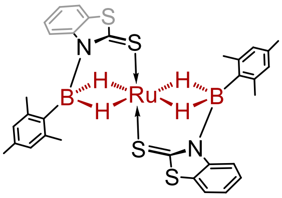
The organometallic chemistry has witnessed significant growth ever since the introduction of poly(pyrazolyl)borate in 1966 by Trofimenko.[1] Transition metal (TM) *σ*-borane/borate complexes are very appealing for various organic reactions as well as catalytic reactions due to their unique bonding modes and tendency to undergo hydroboration, C-H functionalization and dehydrogenation reactions. The importance of transition metal complexes showing an [M]···H–B interaction (σ or agostic) has been realized in metal- catalyzed B–H activation and hydroboration reactions.[2] Recently, we have established that 1,3-*N,S*-chelated ruthenium borate complexes, $[\{\kappa^2\text{-}N,S\text{-L}\}(PPh_3)Ru\{\kappa^3\text{-}H,S,S'\text{-}H_2B(L)_2\}]$ having polar Ru-N bonds shows C-H, B-H and Si-H bond activation.[3] With an objective to isolate osmium borate complexes, we have treated $[(PPh_3)_3OsCl_2]$, with heterocyclic borate ligands, $Na[H_3B(L)]$(L= 2-Mercaptobenzothiazolyl/ 2-Mercaptopyridine), that led to the formation of σ-borate complexes having unusual coordinations. For example, σ-borate species $[(PPh_3)_2Os(H)\{\kappa^3\text{-H,S,S'-}H_2B(L)_2\}]$ featuring a direct M−H bond, and $[(\kappa^2\text{-N,S-L})PPh_3Os\{\kappa^3\text{-H,S,S'-}H_2B(L)_2\}]$. Along with the Os-σ-borate species these reactions also yielded cis-$[(\kappa^2\text{-N,S-L})_2Os(PPh_3)_2]$, which is prone to borane activation through hemilabile ring opening of Os-N bond. The key results of this work will be discussed.



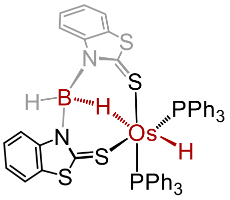
Sabo-Etienne, **2002**



Esterueals, **2010**



Ghosh, **2022**



This work

References

1. Trofimenko, S.; *J. Am. Chem. Soc*. **1966**, *88*, 1842.
2. (a) Saha, K.; Roy, D. K.; Dewhurst, R. D.; Ghosh, S.; Braunschweig, H. *Acc. Chem. Res.* **2021**, *54*, 1260−1273; (b) Montiel-Palma, V.; Lumbierres, M.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc. **2002***, *124*, 5624–5625.
3. Zafar, M.; Ahmad, A.; Saha, S.; Rongala, R.; Roisnel, T.; Ghosh, S. *Chem. Sci.* **2022**, *13*, 8567−8575.
4. Esteruelas, M. A.; Fernandez-Alvarez, F. J.; Lopez, A. M.; Mora, M.; Onate, E. *J. Am. Chem. Soc.* **2010**, *132*, 5600–5601.

P6

Macropolyhedral *syn*-$B_{18}H_{22}$, the “Forgotten” Isomer

Deepak Kumar Patel, B. S. Sooraj, Thalappil Pradeep, and Sundargopal Ghosh
Department of Chemistry, IIT Madras, Chennai 600036, India
E-mail: pradeep@iitm.ac.in, sghosh@iitm.ac.in

As the search for new and unusual molecules and materials in various fields intensifies, boron hydrides emerge as fascinating candidates with properties substantially different from those of organic molecules.[1-4] The chemistry and physics of macropolyhedral $B_{18}H_{22}$ clusters have attracted significant attention due to the interesting photophysical properties of *anti*-$B_{18}H_{22}$ (blue emission, laser properties) and related potential applications. We have focused our attention on the “forgotten” *syn*-$B_{18}H_{22}$ isomer, which has received very little attention since its discovery compared to its *anti*-$B_{18}H_{22}$ isomer, presumably because numerous studies have reported this isomer as nonluminescent. In our study, we show that in crystalline form, *syn*-$B_{18}H_{22}$ exhibits blue fluorescence and becomes phosphorescent when substituted at various positions on the cluster, associated with peculiar microstructural-dependent effects. This work is a combined theoretical and experimental investigation that includes the synthesis, separation, structural characterization, and first elucidation of the photophysical properties of three different monothiol-substituted cluster isomers, [1-HS- *syn*-$B_{18}H_{21}$] 1, [3-HS- *syn*-$B_{18}H_{21}$] 3, and [4-HS- *syn*-$B_{18}H_{21}$] 4, of which isomers 1 and 4 have been proved to exist in two different polymorphic forms. All of these newly substituted macropolyhedral cluster derivatives (1, 3, and 4) have been fully characterized by NMR spectroscopy, mass spectrometry, single-crystal X-ray diffraction, IR spectroscopy, and luminescence spectroscopy. This study also presents the first report on the mechanochromic shift in the luminescence of a borane cluster and generally enriches the area of rather rare boron-based luminescent materials. In addition, we present the first results proving that they are useful constituents of carbon-free self-assembled monolayers.[5] The key results of this work will be discussed.

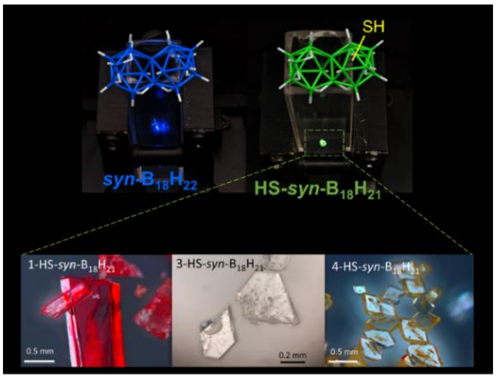


Figure: *syn*-$B_{18}H_{22}$ displays blue fluorescence in crystalline form, transforming to green phosphorescent when substituted.

References

1. Huang, Z.; Wang, S.; Dewhurst, R. D.; Ignat’ev, N. V.; Finze, M.; Braunschweig, H. Boron: Its Role in Energy-Related Processes and Applications. *Angew. Chem., Int. Ed.* **2020**, *59*, 8800– 8816
2. Mukherjee, S.; Thilagar, P. Boron Clusters in Luminescent Materials. *Chem. Commun.* **2016**, *52*, 1070– 1093

3. Dash, B. P.; Satapathy, R.; Maguire, J. A.; Hosmane, N. S. Polyhedral Boron Clusters in Materials Science. *New J. Chem.* **2011**, *35*, 1955
4. Cerdán, L.; Braborec, J.; Garcia-Moreno, I.; Costela, A.; Londesborough, M. G. S. A Borane Laser. *Nat. Commun.* **2015**, *6*, 5958
5. Patel, D. Kumar; Sooraj, B. S.; Kirakci, K.; Machacek, J.; Kucerakova, M.; Bould, J.; Dusek, M.; Frey, M.; Neumann, C.; Ghosh, S.; Turchanin, A.; Pradeep, T.; Base, T. Macropolyhedral *syn*-$B_{18}H_{22}$, the “Forgotten” Isomer *J. Am. Chem. Soc.*, **2023**. *(Just accepted)*

P7

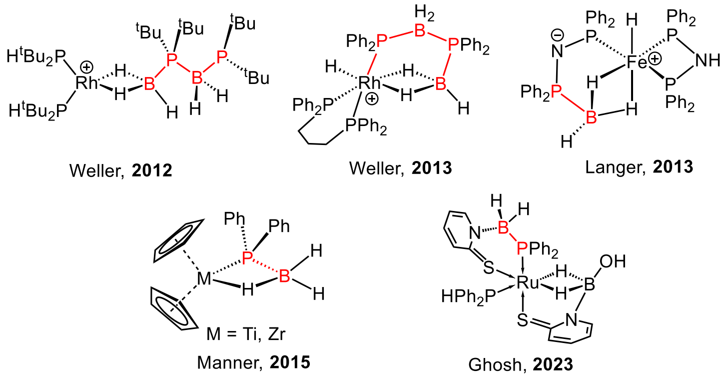
B-P Coupling: Metal Stabilized Phosphinoborate Complexes

*Sampad Shyamal, Sourav Gayen and Sundargopal Ghosh**

Department of Chemistry, IIT Madras, Chennai 600036, India

E-mail: sghosh@iitm.ac.in

The formation of homonuclear or heteronuclear bonds containing p-block elements is of significant interest in functional soft materials, hydrogen storage materials as well as coordination chemistry. Metal-catalysed dehydrocoupling reactions are considered as viable routes to form main group homonuclear (e.g. Si-Si, Ge-Ge, Sn-Sn etc.) as well as heteronuclear (e.g. P-N, B-Si, P-Si etc.) bonds. Meanwhile, bonds containing groups 13 and 15 elements have attracted immense attention because of their formal charge separation after being valance isoelectronic with C-C bond. The development of novel and facile metal catalysed B-P bond formation by Manners and co-workers is a major contribution in phosphinoborane chemistry[1]. Besides, Langer demonstrated the formation of a unique iron hydrido phosphine-borane complex by the formal insertion of BH_3 into the Fe-P bond[2]. With an adjective to establish B-P coupling reactions without using phosphine-borane dehydrocoupling agent, we have developed a new synthetic methodology employing Ru(σ-borate)(dihydridoborate)[3] complex and PPh_2Cl. We also have synthesized some novel phosphinous (III) acid incorporated Ru(σ-borate)(dihydridoborate) complexes by treating secondary phosphine oxide ($HPPh_2O$) and phosphite with Ru-bis(dihydridoborate) species. The key results of this work will be discussed.


Weller, **2012**

Weller, **2013**

Langer, **2013**

Manner, **2015**

Ghosh, **2023**

Figure: Examples of phosphine-borane complexes generated through B-P coupling reaction.

References

1. Schäfer, A.; Jurca, T.; Turner, J.; Vance, J. R.; Lee, K.; Du, V. A.; Haddow, M. F.; Whittell, G. R.; Manners, I. *Angew. Chem. Int. Ed.* **2015**, *54*, 4836 –4841; b) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. *Chem. Rev.* **2010,** *110,* 4023–4078.
2. Frank, N.; Hanau, K.; Flosdorfa, K.; Langer, R. *Dalton Trans.* **2013**, *42*, 11252-11261.
3. a) Saha, K.; Roy, D. K.; Dewhurst, R. D.; Ghosh, S.; Braunschweig, H. *Acc. Chem. Res.* **2021**, *54,* 1260–1273; b) Pathak, K.; Gayen, S.; Saha, S.; Nandi, C.; Mishra, S.; Ghosh, S. *Chem. Eur. J.* **2022**, *28*, e202104393.
4. a) Huertos, M. A.; Weller, A. S. *Chem. Commun.* **2012**, *48*, 7185-7187; b) Huertos, M. A.; Weller, A. S. *Chem. Sci.* **2013**, *4*, 1881-1888.
5. Gayen, S.; Shyamal, S.; Mohapatra, S.; Antharajanam, P. K. S.; Ghosh, S. (Submitted for publication)

P8

New Structural Motifs in Metallaborane Chemistry

*Soumen Giri, Punyo Nampi, Chandan Nandi and Sundargopal Ghosh**
Department of Chemistry, IIT Madras, Chennai 600036, India
E-mail: sghosh@iitm.ac.in

Metallaborane chemistry has grown in a pleasing fashion based on its structural, bonding and reaction chemistry. Over the last fifty years, many main group pioneers, such as Lipscomb,[1a] Grimes,[1b] Fehlner,[1c] Kennedy,[1d] and us[2] developed various synthetic strategies that led to the emergence of many single-cage and condensed metallaborane clusters having unique geometries (Chart1). However, syntheses of these large polyhedra from small building block units are generally uncontrolled and mechanistically undefined. The progress in this area was further enhanced by the development of both electron counting rules and isolobal principle that provided the groundwork for understanding the structural relationships between different clusters and their bonding motifs. In this regard, we have isolated various single-cage and fused polyhedral clusters from the reaction of [(Cp*CoCl)$_2$], (Cp* = η^5-C$_5$Me$_5$) with [LiBH$_4$·THF] followed by the thermolysis with excess of [BH$_3$·SMe$_2$]. These higher-nuclearity clusters are unique in terms of their bonding and electronic structures.[3] The key results of this work will be described.

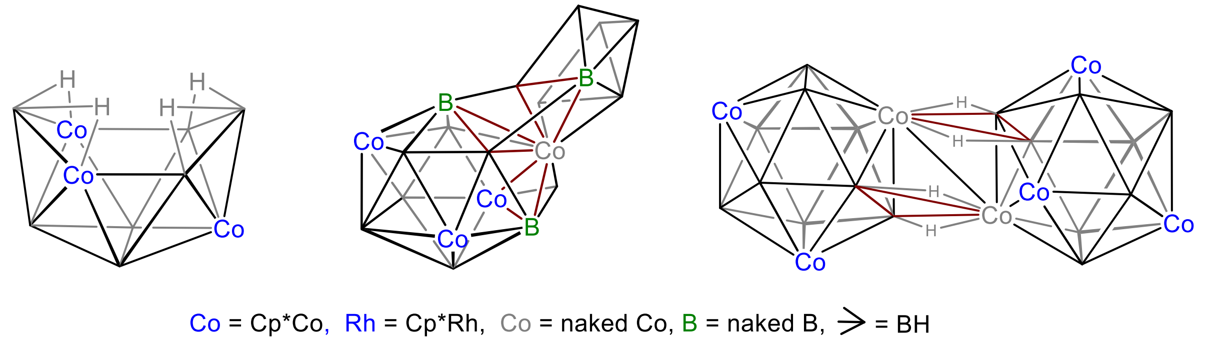


Chart 1. Examples of single-cage and fused polyhedral metallaboranes.

References

1. Lipscomb, W. N. Boron Hydrides; Dover Publications Inc.: Mineola, New York, 2012. (b) Grimes, R. N. Carboranes, 3rded.; Elsevier: Oxford, UK, 2016; pp 929. (c) Fehlner, T. P.; Halet, J. -F.; Saillard, J. -Y. Molecular Clusters. A Bridge to Solid-State Chemistry. University Press, Cambridge, UK, **2007**. (d) Kennedy, J. D. The Polyhedral Metallaboranes Part II. Metallaboranes Clusters with Eight Vertices and More. *Prog. Inorg. Chem.* **2007**, *34*, 211.
2. (a) Kar, S.; Pradhan, A. N.; Ghosh, S. Polyhedral Metallaboranes and Metallacarboranes. In Comprehensive Organometallic Chemistry IV; Elsevier, 2022; pp 263. (b) Zafar, M.; Kar, S.; Nandi, C.; Ramalakhsmi, R.; Ghosh, S. Cluster Fusion: Face-Fused Macropolyhedral Tetracobaltaboranes. *Inorg. Chem.* **2019**, 58, 47.
3. (a) Mingos, D. M. P. Polyhedral Skeletal Electron Pair Approach. *Acc. Chem. Res.* **1984**, *17*, 311. (b) Jemmis, E. D.; Balakrishnarajan, M. N.; Pancharatna, P. D. Electronic Requirements for Macropolyhedral Boranes. *Chem. Rev.*, **2002**, *102*, 93.

P9

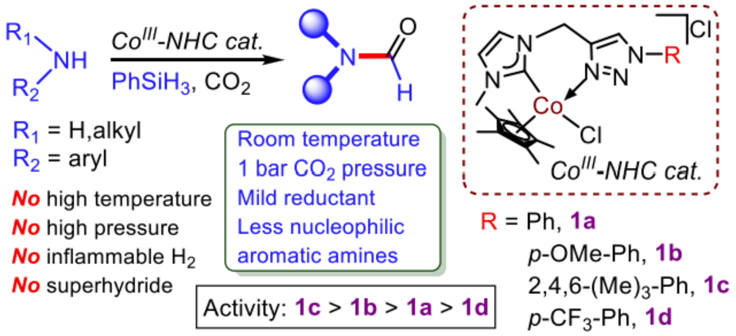
Heteroditopic Chelating NHC Ligand Supported Co^{III}-Complexes: Catalysts for the Reductive Functionalization of Carbon Dioxide under Ambient Conditions

*Misba Siddique, Biswaranjan Boity, and Arnab Rit**

Department of Chemistry, Indian Institute of Technology Madras, Chennai, India.

E-mail: arnabrit@iitm.ac.in

Synthesis and characterization of heteroditopic chelating NHC ligand supported air stable Co^{III}-NHC complexes (**1a-d**), featuring variable triazole N-substituents are reported.[1] These complexes were detected to be very effective catalysts for the reductive functionalization of CO_2 with aromatic amines using hydrosilane under ambient conditions (1 bar CO_2 pressure and RT) to yield diverse N-formylated amines and importantly, catalytic activity of the complexes was found to be reasonably tuned by the triazole N-substituents, which is probably due to some electronic modulations, rather than any considerable steric alterations as indicated by the percent buried volume calculation. Notably, the corresponding *in-situ* generated Co^{III}-NHC complexes were also found to be equally effective. It is worth mentioning that this is the first report on the effective N-formylation of less nucleophilic aromatic primary amines by employing a homogeneous Co-complex, to the best of our knowledge.[2] Further, the control experiments suggest that this protocol proceeds *via* a Co-hydride and formoxysilane intermediate formation.[3]



References

1. Illam, P. M.; Donthireddy, S. N. R.; Chakrabartty, S; Rit, A. *Organometallics* **2019**, *38*, 2610-2623.
2. Daw, P.; Chakraborty, S.; Leitus, G.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. *ACS Catal.* **2017**, *7*, 2500-2504.
3. Siddique, M.; Boity, B.; Rit, A. *Organometallics* **2023**, *42*, 1395-1403.

P10

Structurally aesthetic coordination metal clusters with diversified properties

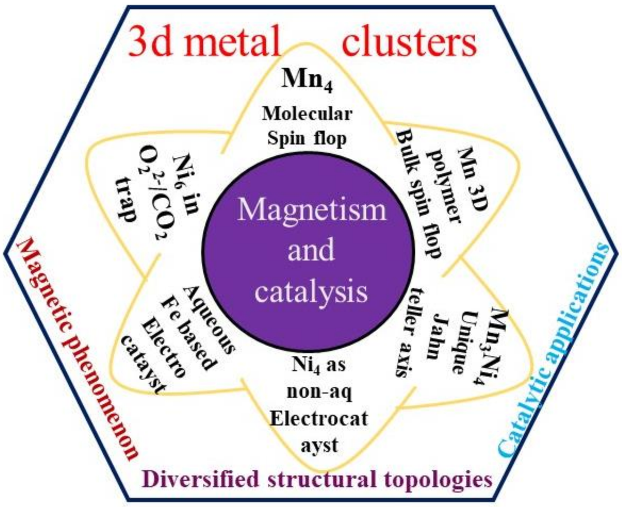
Jayasree Kumar, Kartik Chandra Mondal

Department of Chemistry, IIT Madras, Chennai 600 036

E-mail: csdkartik@iitm.ac.in

This presentation comprises a summary of my doctoral thesis work. As the inorganic metal clusters containing the Schiff base ligand are structurally significant and exhibit attractive properties[1], those areas was focused. The synthesized coordination complexes are 3d-transition metal based with various structure related properties.

Mn_4 tetramer with a butterfly core showing a spin frustration of molecular origin. The spin flop arises from the degree of frustration associated with the triangular lattice units. The Mn-schiff base containing coordination cluster is of antiferromagnetic in behavior and display bulk spin flop behavior. Such intriguing magnetic phenomenon were investigated by specific heat capacity measurements and DFT calculations. A Mn-Ni based coordination cluster was isolated as a heptanuclear disc and known for spin frustration behavior. An another fascinating complex, Mn_2Ni_4 able to show both Jahn teller compression and elongation at their each Mn Jahn teller axis in the same system. A Ni tetranuclear complex was thoroughly characterized and investigated its artificial nitrogen binding activity through control experiments and computational calculations. This complex able to show the maximum faradaic efficiency of 26.5 % in a non-aqueous system with Ni based cluster. Finally, a couple of Fe-schiff base mononuclear complexes are studied for electrochemical N_2 reduction in an aqueous medium.



Reference

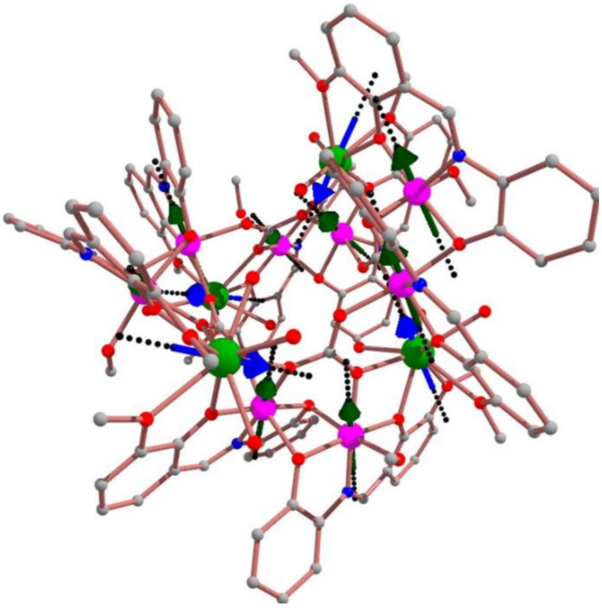
1. Liu, X.; Manzur, C.; Novoa, N.; Celedón, S., Carrillo, D.; Hamon, J. R. Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: Synthesis, functional materials properties, and applications to catalysis. *Coord. Chem Rev.*, **2018**, 357, 144-172.

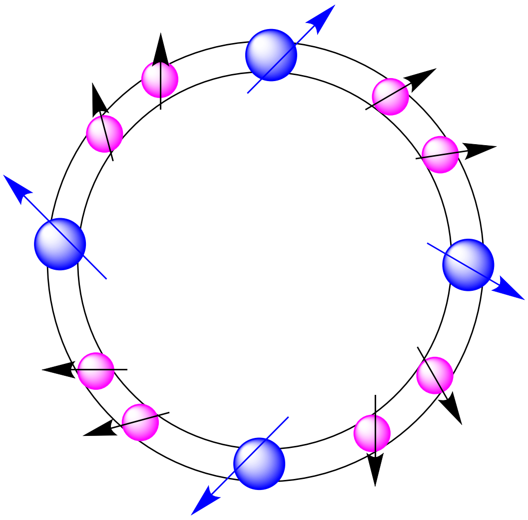
P11

Magnetic Toroid in Ni_8Dy_4 Coordination Cluster

*Christel Livia Mascarrenhas, and Kartik Chandra Mondal**
IIT Madras, Chemistry Department
E-mail: cy22d122@smail.iitm.ac.in

Molecular wheels having anisotropic paramagnetic metal ions are of huge interest due to the fact that they are rich of different phenomena like single molecule magnet, spin frustration, magnetic toroid and etc.[1] Herein, we represent a hetero-dinuclear Ni_8Dy_4 molecular wheel having four carbonate bridges display magnetic toroid a low temperature. The magnetic hysteresis loop at low temperature show steps like behavior. Detailed ab initio calculations have confirmed that the existence of magnetic toroid like behavior in the core of this complex.





References

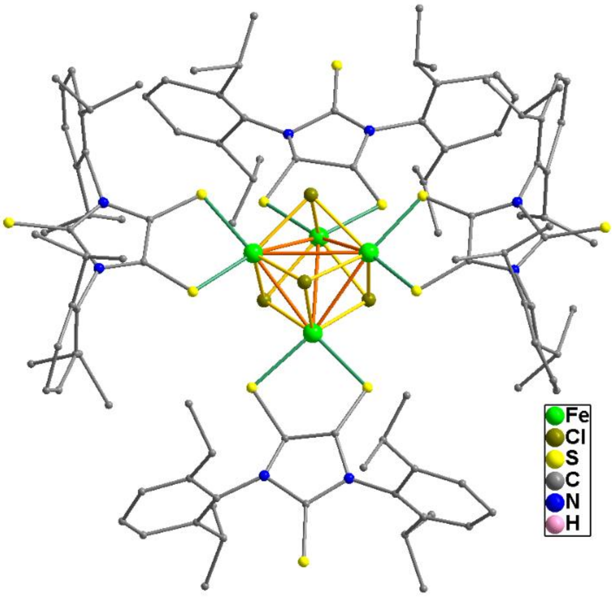
1. H.-L. Zhang, Y.-Q. Zhai, L. Qin, L. Ungur, H. Nojiri, Y.-Z. Zheng. Single-Molecule Toroic Design through Magnetic Exchange Coupling. *Matter* **2020**, *2*, 1481–1493.

P12

The radical character of dithiolene ligands in transition metal complexes

Sujit Das, and Kartik Chandra Mondal
IIT Madras, Chemistry Department
E-mail: sujitdas3051@gmail.com

Metal−dithiolene complexes, extensively studied since the early 1960s [1−5] are intriguing not only due to their unique structural and bonding motifs but also for their remarkable capabilities in such disparate fields as materials science[2,5] and biological systems.[1,6] While both molybdenum and tungsten enzymes contain the dithiolene unit, transition metal−bis-dithiolene, possessing unique optical, conductive, and magnetic properties, have shown promise in the development of optoelectronic devices. Gregory H. Robinson laboratory recently reported a stable lithium dithiolene radical anion, via the reaction of the N-heterocyclic dicarbene with elemental sulfur. Interestingly, radical may well serve as a novel platform to explore the dithiolene chemistry of the main group elements and transition metals. We have synthesized few transition metal complexes with this dithiolene radical, which are having interesting magnetic properties.



References

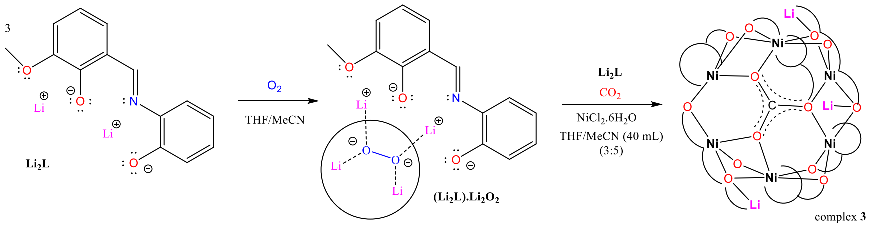
1. Stiefel, E. I., John Wiley & Sons: Hoboken, NJ, **2004.**
2. Kato, R. Chem. Rev. **2004**, 104, 5319−5346.
3. Hine, F. J.; Taylor, A. J.; Garner, C. D. Coord. Chem. Rev. **2010**, 254, 1570−1579.
4. Garreau-de Bonneval, B.; Ching, K. I. M.-C.; Alary, F.; Bui, T. T.; Valade, L. Coord. Chem. Rev. **2010**, 254, 1457−1467.
5. Kobayashi, A.; Fujiwara, E.; Kobayashi, H. Chem. Rev. **2004**, 104, 5243−5264.
6. Holm, R. H.; Kennepohl, P.; Solomon, E. I. Chem. Rev. **1996**, 96, 2239−2314.

P13

O_2 Reduction by Lithium-Phenoxide, employing Ni^{2+} ions and a Competition for Carbonate formation from CO_2

*Saurav Ghosh and Dr. Kartik Chandra Mondal**
Department of Chemistry, Indian Institute of Technology Madras
E-mail: csdkartik@iitm.ac.in

Dioxygen activation with transition metal complexes is highly important for the oxygenation catalyst development.[1,2] Compared to the other 3d-transition metals, less focus has been given towards Ni-O_2 systems. This could be due to the high resistance of Ni towards formation of high valent complexes, due to their stable d^8-configuration in +2 oxidation state.[2] Ni(II) systems have been found to be unreactive towards dioxygen and react with the partially reduced forms, peroxide (O_2^{2-}) and superoxide (O_2^-).[2] Hence, scientists have started showing more interest towards the peroxo (O_2^{2-}) and superoxo (O_2^-) complexes of Ni(II). An intense literature survey on such complexes reveals that the Ni(II)-peroxide linkage is highly stable, and is mostly formed by the metal itself. In this work, we report two Ni(II)-carbonate and a Ni(II)-peroxide complexes, synthesised from $NiCl_2 \cdot 6H_2O$ and the Schiff base, Li_2L. In case of our complex, the ligand reduces atmospheric oxygen to peroxide ion, not the metal precursor. We have studied the mechanism of their formations in detail. We also studied the catalytic activity of the Ni(II)-peroxide complex.



Scheme 1. Reaction condition for the formation of the Ni(II)-Carbonate complex

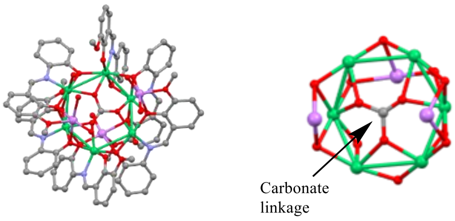


Figure 1. Crystal structure of Ni_6-Carbonate complex (Left), with its core (Right).

References

1. Duan, P.-C.; Manz, P.-H.; Dechert, S.; Demeshko, S.; Meyer, F. *J. Am. Chem. Soc.* **2018**, *140*, 4929.
2. Kim, J.; Shin, B.; Kim, H.; Lee, J.; Kang, J.; Yanagisawa, S.; Ogura, T.; Masuda, H.; Ozawa, T.; Cho, J. *Inorg. Chem.* **2015**, *54*, 6176.
3. Kieber-Emmons, M. T.; Schenker, R.; Yap, G. P. A.; Brunold, T. C.; Riordan, C. G. *Angew. Chem. Int. Ed.* **2004**, *43*, 6716.

ORGANIC CHEMISTRY

(P14-P31)

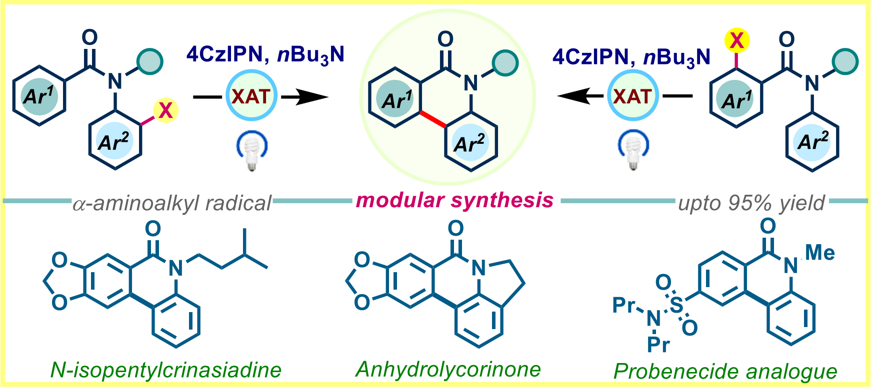
P14

A Visible Light Induced *α*-Aminoalkyl Radical Mediated XAT Process Towards Modular Synthesis of Phenanthridinone Alkaloids

*Karunamayee Mondal and Mahiuddin Baidya**

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

E-mail: karunamayeemondal97@gmail.com and mbaidya@iitm.ac.in



Visible light-induced photocatalysis plays a crucial role in sustainable organic synthesis, fetching significant attention from the synthetic community.[1] In this regime, a XAT strategy utilizing *α*-aminoalkyl radicals[2] is developed for the generation of challenging aryl radicals at room temperature and applied for intramolecular cyclization reactions *en route* to biologically relevant alkaloids.[3] Starting from simple halogen-substituted benzamides under visible light irradiation in the presence of an organophotocatalyst (4CzIPN) and $n\mathrm{Bu_3N}$ allows the modular construction of the phenanthridinone core, which gives facile access to drug analogs and alkaloids, e.g., from the Amaryllidaceae family.[3] The reaction pathway most likely involves a quantum mechanical tunneling-enabled transfer event to achieve aromatization-halogen atom transfer.[4] This poster presentation provides an exposition of the captivating synthetic protocol's development and comprehensive investigations unravelling mechanistic intricacies.

References

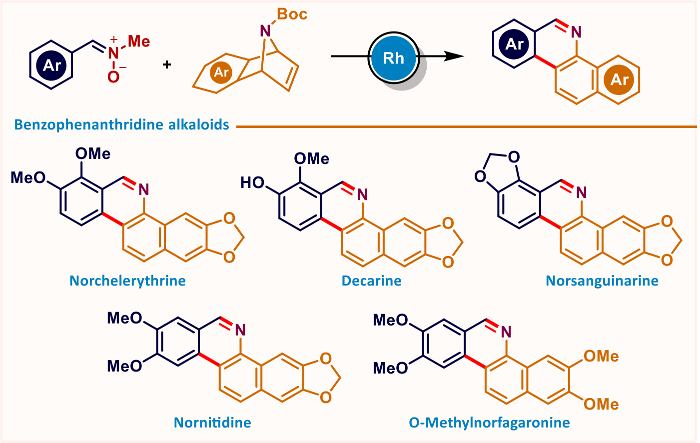
1. (a) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322–5363. (b) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075–10166. (c) Sahoo, H.; Mandal, A.; Dana, S.; Baidya, M. *Adv. Synth. Catal.***2018**, *360*, 1099–1103.
2. (a) Neff, R. K.; Su, Y. L.; Liu, S.; Rosado, M.; Zhang, X.; Doyle. *J. Am. Chem. Soc.* **2019**, *141*, 16643–16650. (b) Constantin, T.; Juliá, F.; Sheikh, N. S.; Leonori, D. *Chem. Sci.* **2020**, *11*, 12822–12828.
3. Mondal, K., Mallik, S.; Sardana, S.; Baidya, M. *Org Lett.* **2023**, *25,* 1689−1694.
4. Constantin, T.; Górski, B.; Tilby, M. J.; Chelli, S.; Juliá, F.; Llaveria, J.; Gillen, K. J.; Zipse, H.; Lakhdar, S.; Leonori, D. *Science* **2022**, *377*, 1323–1328.

P15

One Pot Synthesis of Benzo[*c*]phenanthridine Alkaloids from 7-Azabenzonorbornadienes and Aryl Nitrones

<u>Narasingan Aravindan</u> and Masilamani Jeganmohan
E-mail:mjeganmohan@iitm.ac.in

The Benzo[*c*]phenanthridine are naturally available alkaloids widely applied in the pharmaceutical industry. Among these alkaloids, *O*-methyl norfagaronine, norchelerythrine, decarine, norsanguinarine and nornitidine analogs are well-known because of their broad range of biological activities and potential candidates for developing new drugs.[1] Over the few decades, the transition-metal-catalyzed C-H activation/annulation has been recognized as one of the reliable approaches in modern organic synthesis because it enables the construction of complex cyclic molecules in a step- and atom-economical way.[2] However, introducing and removing the directing team requires additional steps, creating unnecessary waste. Therefore, the directing group, which can avoid extra steps and ensure high selectivity, would be highly desirable. Thus, the development of a straightforward protocol using readily available precursors would facilitate the construction of these biologically active molecules and assist the subsequent modification of these molecules. In this reaction, the nitrones functions as a directing as well as leaving group, which avoids the need for extra steps. Herein, we report a Rh(III)-catalyzed cyclization of aryl nitrones with azabicyclic alkenes to synthesize benzophenanthridines via tandem C-C and C-N bond formation.[3]



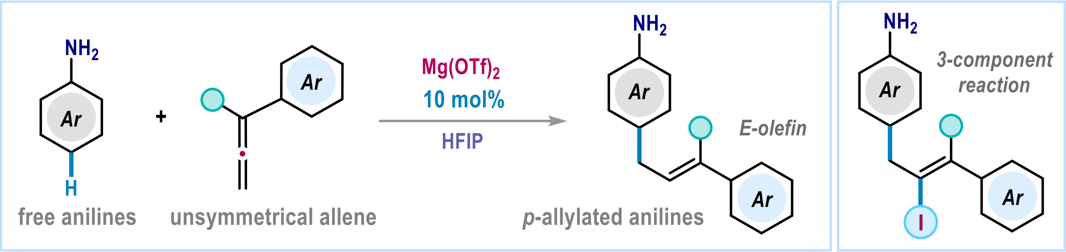
References

1. Lv, P.; Huang, K. L.; Xie, L. G.; Xu, X. H. *Org. Biomol. Chem.* **2011**, *9*, 3133. (b) Kumar, S. V.; Yen, A.; Lautens M.; Guiry, P. J. *Chem. Soc. Rev.*, **2021**, *50* , 3013.
2. (a) Reddy, M. C.; Jeganmohan, M. *Chem. Sci.* **2017**, *8*, 4130. (b) Gensch, T.; Hopkinson, M. N.; Glorius, F.; Wencel-Delord, J. *Chem. Soc. Rev.* **2016**, *45*, 2900.
3. Aravindan, N.; Jeganmohan, M. *Org. Lett.* **2023**, *25*, 3853.

P16

Magnesium-Catalyzed *para*-Allylation of Anilines with Aryl Allenes in Hexafluoroisopropanol

*Suman Ghosh and Mahiuddin Baidya**
Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
Email: sumanghosh2041@gmail.com; mbaidya@iitm.ac.in



Regio- and stereoselective allylation reactions are one of the most important synthetic maneuvers in organic chemistry as the allylic functionality constitutes a variety of transformations that found potential applications in synthesizing complex natural products and pharmaceuticals.[1] In this work, we envisioned exploring allenes as allylic synthons in a catalytic reaction modality. This choice is intriguing as allenes typically exhibit a distinct reaction modality owing to the presence of two orthogonal double bonds.[2] Herein, we report the development of this approach and delineate exclusive *para*-selective allylation of *N*-unsubstituted anilines with allenes in the presence of a catalytic amount of $Mg(OTf)_2$ in an HFIP medium.[3] Notably, despite the utilization of unsymmetrical allenes, we observed regioselective functionalization at the terminal position of allenes, and products were isolated with the sole *E*-selectivity in high yields. The protocol is operationally simple, scalable and can be performed with *N*-unprotected anilines. The methodology was also suitable for the regioselective allylation of indole and can be advanced in a three-component reaction mode using NIS activator. The alteration of the catalytic system with TfOH resulted in the regioselective difunctionalization of allenes, which follows an allylation/hydroarylation cascade mechanism.[3]

References

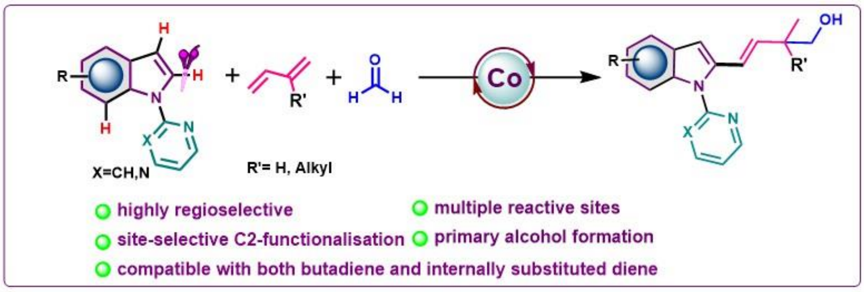
1. Mishra, N. K.; Sharma, S.; Park, J.; Han, S.; Kim, I. S. *ACS Catal.* **2017**, *7*, 2821–2847.
2. Yu, S.; Ma, S. *Angew. Chemie. Int. Ed.* **2012**, *51*, 3074–3112.
3. Ghosh, S.; Saha, S.; Baidya, M. *Org. Lett.* **2023**, *27*, 5073.

P17

Co(III)-Catalyzed three-component assembling of *N*-(2-pyrimidyl) indoles with dienes and formaldehyde though C-H bond activation

*Priyambada Prusty and Masilamani Jeganmohan**
Department of Chemistry, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India,
E-mail: mjeganmohan@iitm.ac.in

Over the past few decades, transition–metal–catalysed C–H bond functionalisation has garnered a great deal of attention in the field of synthetic organic chemistry and has been widely applied in fields from drug discovery to material sciences.[1] In recent years, sequential three-component C–H bond addition across π-bond isosteres (such as butadiene, internally and terminally substituted dienes, alkynes, acrylates, enynes, alkenes, allenes and strained ring systems) followed by coupling with different functionalities (*viz*: carbonyl compounds, and cyanating, aminating, halogenating, oxygenating, and alkylating reagents) has become a powerful tool in the hands of synthetic chemists.[2] This strategy includes simple chemical inputs with mild reaction conditions, which lead to diversity-oriented synthesis of complex molecular scaffolds. Homoallylic alcohols are the common building blocks that can be functionalised into complex molecular motifs and hence have widespread applications in pharmaceuticals (*viz*: ascorbic acid, entecavir, eldecalcitol *etc.*) and natural product synthesis.[3] Further the ubiquitous indole framework has been proven to be the most privileged class of heterocyclic compounds due to its widespread presence in a broad variety of natural, pharmaceutical, and biologically active molecules. Hence, the direct and selective C–H functionalization of indoles has received ample attention in medicinal and organic chemistry research areas.[4] In this regard, we have developed a highly regio- and chemoselective three-component assembling of *N*-pyrimidyl indoles with dienes and formaldehyde in the presence of a Co(III) catalyst. The scope of the reaction was investigated with a variety of indole derivatives to synthesize substituted homoallylic alcohols. Both butadiene and isoprene units were compatible with the reaction and provided the desired products containing a stereogenic centre and an acyclic quaternary centre respectively. The easily available formaldehyde is used which acts as a crucial C1 building block and can be modified into different functional groups. To understand the reaction mechanism, various investigations were carried out, and suggested the plausibility of a reaction mechanism involving C–H bond activation as a key step.



References

1. Gensch, T.; Hopkinson, M. N.; Glorius, F.; Wencel-Delord, J. *Chem. Soc. Rev.* **2016**, *45*, 2900.
2. Brandes, D. S.; Ellman, J. A. *Chem. Soc. Rev.* **2022**, *51*, 6738.
3. Hu, H.; Xu, W. H.; Kang, W. X.; Sun, W.; Sun, R.; Wei, X. H.; Sun, M. *Org. Chem. Front.* **2021**, *8*, 4459.
4. Kim, Y.; Park, Y.; Chang, S. *ACS. Cent. Sci.* **2018**, *4*, 768.

P18

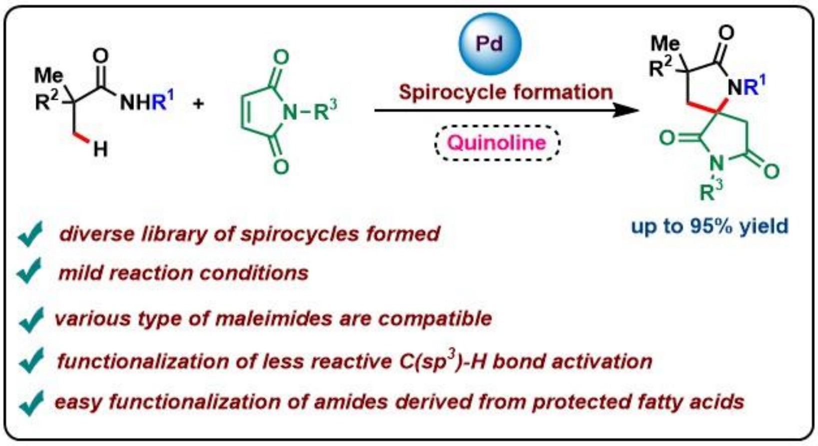
Palladium-Catalyzed Aerobic Oxidative Spirocyclization of Alkyl Amides with Maleimides *via* β-C(sp^3)-H Activation

*Ananya Dutta and Masilamani Jeganmohan**

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India

E-mail: mjeganmohan@iitm.ac.in

Spirocyclic scaffolds are a diverse set of compounds that are extracted from many biological sources, ranging from plants to marine life. These compounds have gained significant importance throughout many years due to their vast application in drug discovery and chiral ligand development.[1] The spiro molecules consist of two or more rings linked to each other *via* the sharing of only one common atom, where the rings can be of same or different size. Among various categories of spiro motifs present, nitrogen-based heterocycles generally referred to as spirodiamine scaffolds have been widely isolated from many biologically active compounds and also exhibit antiviral, antipsychotic and antitumor activities. Owing to the importance of such scaffolds, there has been many synthetic approaches to spirodiamine molecules but strategies involving transition metal catalyzed C(sp^3)-H bond activation followed by functionalization are hardly explored.[2]



Therefore, an efficient method for the synthesis of bicyclic spirodiamine molecules *via* β-C(sp^3)-H bond activation of aliphatic amides followed by cyclization with maleimides has been developed. The reaction proceeds through an amide directed β-C(sp^3)-H bond activation of alkyl amides and subsequent cyclization with maleimides. The methodology is highly compatible with a wide variety of maleimides. Amides derived from biologically active aliphatic acid and fatty acids were also found to be highly compatible with the protocol. A palladacycle was synthesized and is found to be the active intermediate in this reaction. A plausible reaction mechanism was also proposed to account for this spirocyclization.

References

1. Li, L.; Wang, S.; Luo, P.; Wang, R.; Wang, Z.; Li, X.; Deng, Y.; Peng, F.; Shao, Z. Direct access to spirocycles by Pd/Wing Phos-catalyzed enantioselective cycloaddition of 1,3-enynes. *Nat. Commun.* **2021**, *12*, 5667.
2. Ramesh, B.; Tamizmani, M.; Jeganmohan, M. Rhodium(III)-Catalyzed Redox-Neutral 1,1-Cyclization of *N*-Methoxy Benzamides with Maleimides *via* C−H/N−H/N−O Activation: Detailed Mechanistic Investigation. *J. Org. Chem.* **2019**, *84*, 4058-4071.

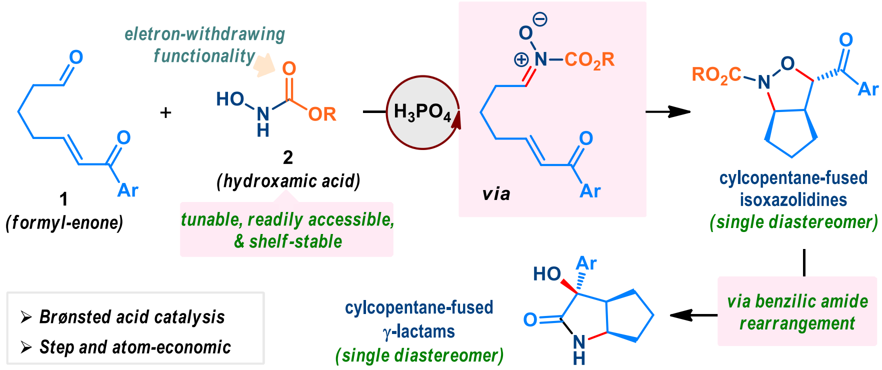
P19

Brønsted Acid Catalyzed Diastereoselective Annulation towards Cyclopentane Fused Isoxazolidines and their Benzilic Amide Rearrangement

*Swati Lekha Mondal and Mahiuddin Baidya**

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

E-mail: swatilekha.slm@gmail.com and mbaidya@iitm.ac.in



The isoxazolidine framework specifically, cyclopentane fused isoxazolidine derivatives are marked as a core constituent of many pharmaceuticals and natural products. Among the diverse methods to construct isoxazolidine scaffolds, the 1,3-dipolar cycloaddition reaction of nitrones with olefins remained most significant.[1] In this context, readily available hydroxamic acids were leveraged to access challenging nitrones in the presence of H_3PO_4 as Brønsted acid catalyst and engaged in intramolecular (3+2) annulation reaction to make valuable cyclopentane fused isoxazolidines in high yields and excellent diastereoselectivity.[2] The protocol is scalable and accommodates diverse functional groups. The glitches during ex-situ preparation of nitrones has been surmounted, while the ease in *N*-deprotection without perturbing the N–O bond garners synthetic versatility.[3] The products were further utilized in a base-promoted unique benzilic amide rearrangement[4] to garner cyclopentane fused γ-lactams bearing a quaternary center as a single diastereomer.[2]

References

1. Romeo, G.; Chiacchio, U.; Corsaro, A.; Merino, P. *Chem. Rev.* **2010**, *110*, 3337–3370. (b) Kaur, K.; Kumar, V.; Sharma, A. K.; Gupta, G. K. *Eur. J. Med. Chem.* **2014**, *77*, 121–133. (c) Berthet, M.; Cheviet, T.; Dujardin, G.; Parrot, I.; Martinez, J. *Chem. Rev.* **2016**, *116*, 15235–15283.
2. Cogent Synthesis of Cyclopentane Fused Isoxazlidines and their Benzilic Amide Rearrangement, Mondal, S. L.; Baidya, M. *Manuscript under review*.
3. (a) Guinchard, X.; Vallée, Y.; Denis, J. N. *Org. Lett*. **2005**, *7*, 5147–5150. (b) Gioia, C.; Fini, F.; Mazzanti, A.; Bernardi, L. and Ricci, A. *J. Am. Chem. Soc.*, **2009**, *131*, 9614–9615. (c) Gini, A. ; Segler, M.; Kellner D. and Mancheño, O. G. *Chem. A Eur. J.*, **2015**, *21*, 12053 –12060.
4. (a) Eastham, J. F.; Selman, S. ***Q. Rev. Chem. Soc.*** **1960**, ***14***, 221–235. (b) Moutayakine, A.; Burke, A. J. *Chem. Commun.* **2021**, *57*, 2585–2590. (c) He, Y-P.; Quan, R.; Li, X-Z.; Zhu, J.; Wu, H. *Angew. Chem., Int. Ed.* **2023**, *62*, e202217954.

P20

Ruthenium(II) Catalyzed C–H Bond Activation and Annulation Reaction: Coupling of Arenes with Diazonaphthoquinones towards Benzocoumarins

Sudeshna Mondal and Mahiuddin Baidya

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
E-mail: sudeshna03131@gmail.com and mbaidya@iitm.ac.in

Polycyclic benzocoumarin frameworks constitute an increasingly demanding field of research owing to their prevalence in natural products, drug candidates, and applications in functional materials.[1,2] They are particularly acknowledged for antibacterial and antitumor activities. Notable examples include ravidomycin, chrysomycins, and gilvocarcins, a novel class of aryl C-glycoside antibiotics.[2] Consequently, various synthetic protocols have been reported to access these motifs, where, in general, the cross-coupling-based strategy leading to intra- or inter-molecular biaryl formation was predominant.[3] In addition, the transition metal-catalyzed cyclization reaction of functionalized enediyne derivatives has been established.[4] However, the majority of these strategies require suitably adorned prefunctionalized substrates, multistep reactions, and cumbersome processes. Thus, engineering modular strategies delineating operational simplicity, step-economy, and ready substrate accessibility is highly desirable. Herein, we report an annulative coupling of arenes bearings synthetically useful various directing groups, for example, acid, amide, benzimidate, aldoxime, nitrone, and sulfoxonium ylide, with diazonaphthoquinones as a concise route towards high-value polycyclic benzocoumarin scaffolds under ruthenium catalysis.[5] The protocol harnesses weak and strong coordination assistance, displays high reaction yields with broad functional group tolerance, and was fruitful in the presence of diverse pharmacophore scaffolds. The reaction involves a reversible C–H metalation step and the intermediacy of a ruthenium(IV) species, an underdeveloped regime in C–H bond activation chemistry.

References

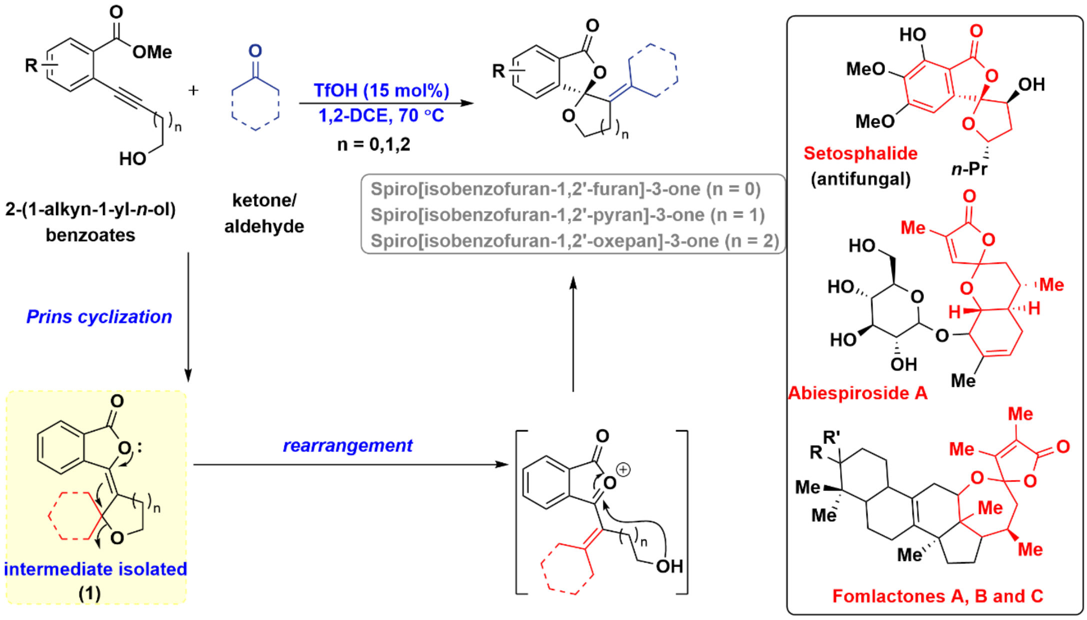
1. Garazd, Y. L.; Garazd, M. M. *Chem. Nat. Compd.* **2016**, *52*, 1–18.
2. Tibrewal, N.; Pahari, P.; Wang, G.; Kharel, M. K.; Morris, C.; Downey, T.; Hou, Y.; Bugni, T. S.; Rohr, J. *J. Am. Chem. Soc.* **2012**, *134*, 18181–18184.
3. James, C. A.; Snieckus, V.; *J. Org. Chem.* **2009**, *74*, 4080–4093. (b) Ahmed, A.; Dhara, S.; Ray, J. K. *Tetrahedron Lett.* **2013**, *54*, 1673–1676.
4. Chen, C. C.; Hsu, C. L.; Wu, M. J. *Tetrahedron* **2019**, *75*, 1034–1043.
5. Coupling of arenes with diazonaphthoquinones enabled by Ru(II) catalyst under the assistance of diverse common functional groups: A cogent synthesis of polycyclic benzocoumarins, Mondal, S.; Giri, C. K.; Baidya, M. *manuscript under review.*

P21

Synthesis of Spiro[isobenzofuran-1,2'-furan/pyran/oxepan]-3-ones through Brønsted Acid Catalyzed Alkynyl-Prins Cyclization

*Surabhi Mishra and Prof. Beeraiah Baire**
Department of Chemistry, Indian Institute of Technology Madras, Chennai, India.
*E-mail: beeru@iitm.ac.in**

The Prins cyclization reaction holds significance in organic synthesis as it enables the single step formation of both C−C and C−X (heteroatom) bonds.[1] It will provide an access to generate many biologically relevant oxa-polycyclic systems as well spirocyclic frameworks, such as spiroketals. As a result, many biologically active natural products have been successfully synthesized by employing this approach.[2] The spiroketal units are emerging as privileged structures in drug discovery. They are also omnipresent in the natural products domain.[3] Inspired by their importance, we designed and developed a Brønsted acid catalyzed alkynyl-Prins cyclization between ketones/aldehydes and 2-(1-alkyn-1-yl-*n*-ol) benzoates. Here, the intermediate vinylic carbocation was intercepted intramolecularly, by an *o*-carboxylate resulting in the formation of intermediate 1. This 1, under reaction conditions further underwent a rearrangement[4] to give the spirolactone product. The reaction was found to be tolerant towards large variety of different aldehydes, ketones and alkynols. To prove the mechanistic pathway, we performed control experiment and isolated the intermediate. The complete details will be presented in this poster.



Scheme 1: Alkyne-Prins cyclization-based approach for the synthesis of spiro[isobenzofuran-1,2'-furan/pyran /oxepan]-3-ones.

References

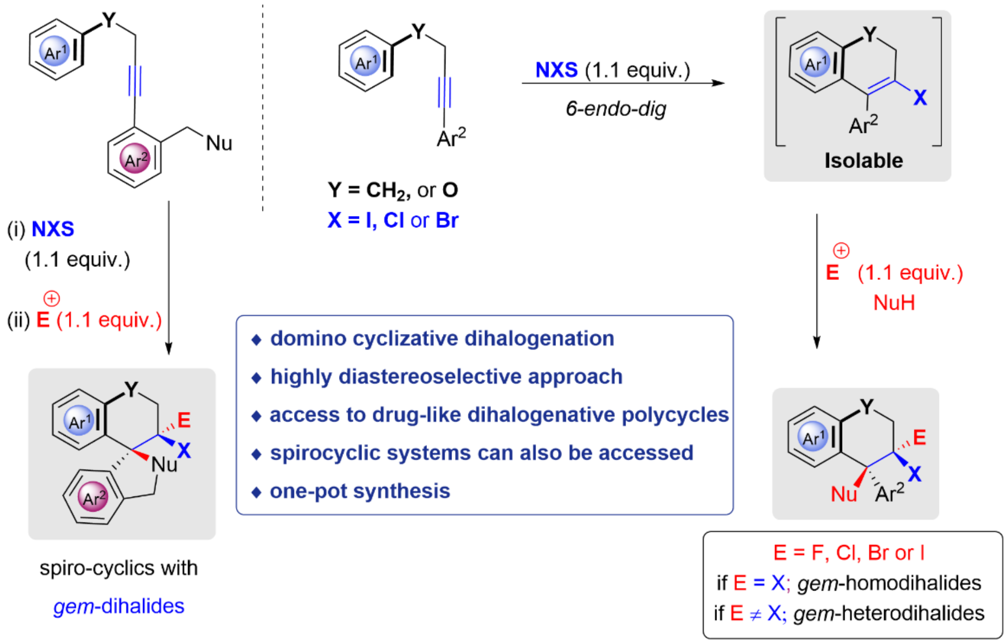
1. Abdul-Rashed, S.; Holt, C.; Frontier, A. J. *Synthesis* **2020**, *52*, 1991−2007.
2. Reddy, B. V. S.; Nair, P. N.; Antony, A.; Lalli, C.; Gree, R. *Eur. J. Org. Chem.* **2017**, 1805−1819.
3. Pesquet, A.; Marzag, H.; Knorr, M.; Strohmann, C.; Lawson, A. M.; Ghinet, A.; Dubois, J.; Amaury, F.; Daich, A.; Othman, M. *Org. Biomol. Chem.* **2019**, *17*, 2798−2808.
4. Shit, S.; Bora, S. K.; Sahu, A. K.; Saikia, A. K. *J. Org. Chem.* **2022**, *87*, 11634–11643.

P22

Highly diastereoselective, Domino construction of *gem*-Diheterohalogen based polycycles *via* NXS promoted functionalization of Alkynes

*Sindoori R Nair and Prof. Beeraiah Baire**
Department of Chemistry, Indian Institute of Technology Madras, Chennai, India
E-mail: beeru@iitm.ac.in

The compounds possessing a *gem*-di(*hetero*)halogen functional group are considered as privileged systems in medicinal chemistry,[1] and also useful building blocks in organic synthesis.[2] Many structurally diverse drugs have been found to possess *gem*-heterodihalogen moiety as an integral part with tunable properties.[3] Accordingly, many synthetic methodologies have been reported for the preparation of these privileged functional groups.[4] Earlier in our laboratory, we employed NXS-reagents as halonium ion (X^+) source for the construction of halogenated molecular frame works.[5] In continuation, we also developed strategies for the rapid generation of *gem*-diheterohalogen based compounds, which have relevance in medicinal chemistry and drug development. Our designed strategy involves the domino-cyclizative dehalogenation of alkynes in presence of NXS reagents for the rapid and highly diastereoselective construction of polycyclic systems possessing the *gem*-di(*hetero*)halogen functional group. A two-step process afforded the *gem*-hetero-dihalogenation, while a cascade process with excess of NXS reagent source gave us the corresponding *gem*-dihalogenation. We have further extended this approach for the construction of spiro-cyclics possessing the *gem*-diheterohalogen moiety. Further details and studies on the topic will be discussed in the poster.



Scheme 1: Diastereoselective, domino, cyclizative-*gem*-di(*hetero*)halogenation of alkynes.

References

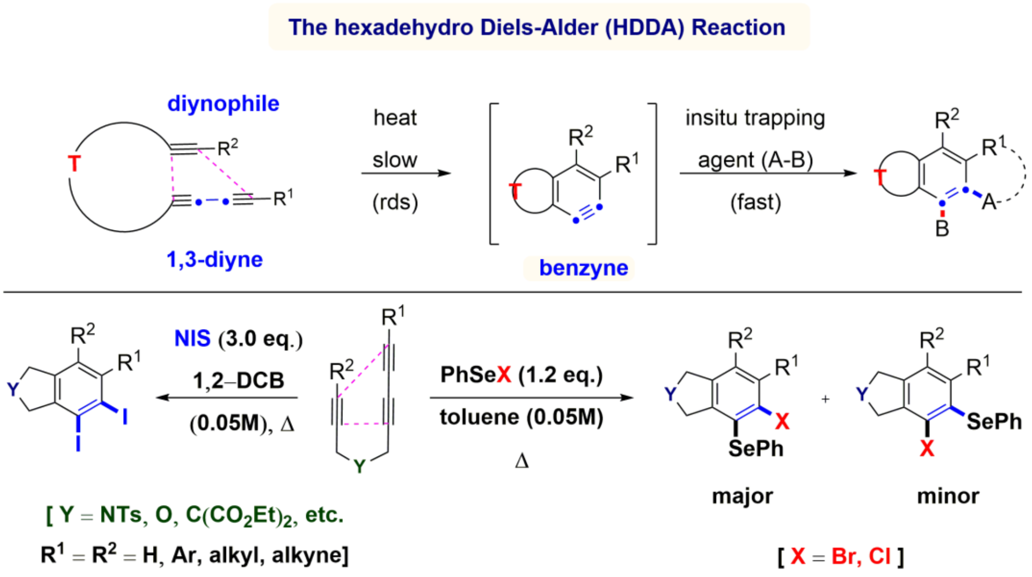
1. Emmanuvel *et al*. *Tetrahedron Lett.*, **2015**, *56*, 934.
2. Wu *et al.*, *Org. Lett.* **2019**, *21*, 6844−6849.
3. Schinazi et al., *J. Med. Chem.* **2017**, *60*, 5424−5437.
4. Schinazi *et al*., *J. Org. Chem.*, **2017**, *82*, 13171-13178.
5. Baire et al. *ChemistrySelect*. **2017**, *2*, 8500 – 8503

P23

The Di-halogenation and Pseudohalogenation Reactions of the HDDA Benzynes

*Siddique Khan, and Prof. Beeraiah Baire**
Department of Chemistry, Indian Institute of Technology Madras, Chennai, India
E-mail: beeru@iitm.ac.in

The hexadehydro-Diels-Alder (HDDA) reaction is a thermal [4+2] cycloaddition between an internally tethered alkyne (2π) and a 1,3-diyne (4π) unit to generate polycyclic benzyne intermediates.[1] The *in situ* generated benzyne can then be rapidly trapped by a variety of species to yield highly functionalized, structurally complex benzenoid products.[2] HDDA benzyne formation is a 100% atom-economic method for aryne generation without added reagents and triple-bond cycloisomerization, unlike other methods.[1] The di(*pseudo*)haloarenes are valuable systems in organic synthesis as well as medicinal chemistry. We designed and developed a versatile strategy for the construction of these systems by trapping the HDDA benzynes with various (pseudo)halogen sources.
Our strategy involves heating of a triyne/tetrayne in presence of *N*-halosuccinimide to give the di-iodinated polycylic arenes, *via* the trapping of the HDDA-benzyne. Organoselenium compounds offer potential biological activities like antiviral, antihypertensive, antioxidant, and antitumor properties. Therefore, we have further extended our strategy of dihalogenation of HDDA-benzynes for the simultaneous incorporation of a pseudohalide like arylselenyl along with the halides. Accordingly, the HDDA reactions were performed in presence of phenylselenium halides (PhSeX). The design and development of these strategies will be presented in this poster.



Scheme 1: The di(pseudo)halogenation of HDDA benzyne.

References

1. T. R. Hoye, B. Baire, D. Niu, P. H. Willoughby, B. P. Woods, *Nature.* **2012**, *490*, 208–212.
2. Lucas L. Fluegel and Thomas R. Hoye, *Chem. Rev.* **2021**, *121*, 2413−2444.
3. T.R. Hoye.*et al.*, *Org. Lett.* **2021**, *23*, 5448−5451.
4. K. Miyawaki, R. Suzuki, T. Kawano, I. Ueda, *Tetrahedron Lett.* **1997**, *38*, 3943-3946.
5. Y. Hu. *et al.*, *Chem. Commun.*, **2017,** *53,* 1542-1545.

P24

Silver(I)-Salt Catalyzed Selective Hydroboration of Isocyanates, Pyridines, and Quinolines

*Sangita Sahoo, Vipin K. Pandey and Arnab Rit**
Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.
E-mail: arnabrit@iitm.ac.in

Organoboranes are one of the versatile precursors in synthetic chemistry as they are widely employed in the synthesis of pharmaceuticals, agrochemicals, polyesters, dyes, natural products etc.[1] Among various potent functionalities, isocyanate is one of the least explored heterocumulenes for hydroboration and only three catalyst systems are known.[2-4] These systems suffer from some drawbacks such as low functional group tolerance, higher catalyst loading, limited substrate scope, and require specially designed ligands. Keeping all the above-mentioned disadvantages of the previous reports, herein, we report a simple silver salt catalyzed ligand-free selective mono- and deoxygenative hydroboration of isocyanates under mild conditions. Further, we explored the suitability of our protocol in pyridine hydroboration which regioselectively produces 1,4-hydroborated pyridines, playing an essential role in biological systems and as a reducing agent in organocatalysis. Additionally, the present protocol also works well for the double reduction of quinolines which upon hydrolysis produces 1,2,3,4-tetrahydro quinolines, integral components of numerous natural alkaloids, bioactive molecules, pharmaceuticals (Figure 1).[5]

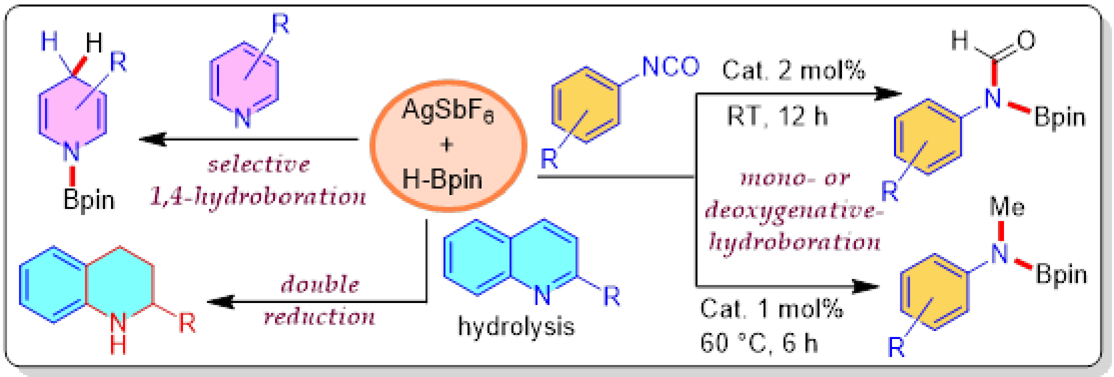


Figure 1: Schematic presentation of the present work

References

1. Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.* **2019**, *9*, 3307-3336.
2. Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima K.; Okuda, J. *Chem. Commun.* **2016**, *52*, 13155-13158.
3. Yang, Y.; Anker, M. D.; Fang, J.; Mahon, M. F.; Maron, L.; Weetman C.; Hill, M. S. *Chem. Sci.*, **2017**, *8*, 3529-3537.
4. Sahoo, R. K.; Sarkar N.; Nembenna, S.; *Angew. Chem., Int. Ed.* **2021**, *60*, 11991-12000.
5. Pandey, V. K.; Sahoo S.; Rit, A. *Chem. Commun.* **2022**, *58*, 5514-5517.

P25

S-Doped Non-planar Polycyclic Aromatic Hydrocarbons

*Raseswari Dash, Sudhakar Maddala and Venkatakrishnan Parthasarathy**
Department of Chemistry, IIT Madras, Chennai – 600036.
E-mail: pvenkat@smail.iitm.ac.in

In recent years, unusual topologies and chemistry of planar and non-planar polycyclic heteroaromatic hydrocarbons (PHAs) have been the subject of considerable attention. Hetero-[7]-quasicirculenes are an exciting class of PHAs having negative Gaussian curvature, which are promising in light of their potential applications for OLEDs, OFETs, and OSCs;[1] hetero-[7]-quasicirculenes and their corresponding circulenes are unexplored till now in the literature. Although the synthetic methods are available in some specific cases, a facile synthetic protocol of novel hetero-[7]-circulenes that provides ready access to property tunability is highly desirable. Considering the pressing need to address and extract their advantageous photophysical properties, we successfully synthesize novel hetero-[7]-quasicirculenes, which undergo π-extension to form the corresponding hetero-nanographene.[2] The design of the precursor for intramolecular oxidative coupling is the key to constructing novel hetero-[7]-quasicirculenes. Oxidative Scholl cyclization of simple heteroaromatic molecules is a powerful method to afford heteroatom-embedded quasicirculenes, circulene, and nanographene.[3] The scope and limitation of this transformation as well as the optical/electrochemical properties of the intriguing final products thia-[7]-quasicirculenes will be presented.

References

1. Gu, X.; Li, H.; Shan, B.; Liu, Z.; Miao, Q. Org. Lett. **2017**, *19*(9), 2246-2249.
2. Maddala, S.; Panua, A.; Venkatakrishnan, P. *Chem. Eur. J.* **2021**, *27*, 16013-16020.
3. Venkateswarlu, S.; Kumar, S.; Tao, Y. *Asian J. Org. Chem.* **2021**, *10*, 2251-2261.

P26

Synthesis of *O*- Glucosylated Moscatilin and Analogues

*Heera Lal and Indrapal Singh Aidhen**

Department of Chemistry, IIT Madras

E-mail: isingh@iitm.ac.in

Nature is abundant with glycosides and has inspired studies towards their isolation, structure elucidation, and evaluation of their properties, during the last few decades.[1] These glycosides from varied sources are either *O*- or *N*- or *C*-Glycosides and have been a good source as lead molecules for therapeutic applications.[2] Moscatilin **1** is a bibenzyl derivative extracted from the Indian orchid *Dendrobium pulchellum* of the *Orchidaceae* family.[3] Bibenzyl derivatives from nature in general have garnered considerable interest because of their potential therapeutic effects inducing apoptosis in melanoma cells, anti-proliferation, and anti-angiogenic inhibition.[4] The poor aqueous solubility of Moscatilin **1** has been one of the major limitations. In this context, we have aimed at the synthesis of hitherto unreported *O*-glucosides of Moscatilin, **2-4** including its analogous for assessing their anti-angiogenesis activity. The glucosyl residue in the targeted compounds is likely to improve water solubility and bioavailability. Two phenolic hydroxyls are the advantageous sites for *O*-glucosylation. Keeping this as the target, a convenient synthetic route using a building block approach has been developed for the synthesis of *O*-glucosylated Moscatilin and several analogues.

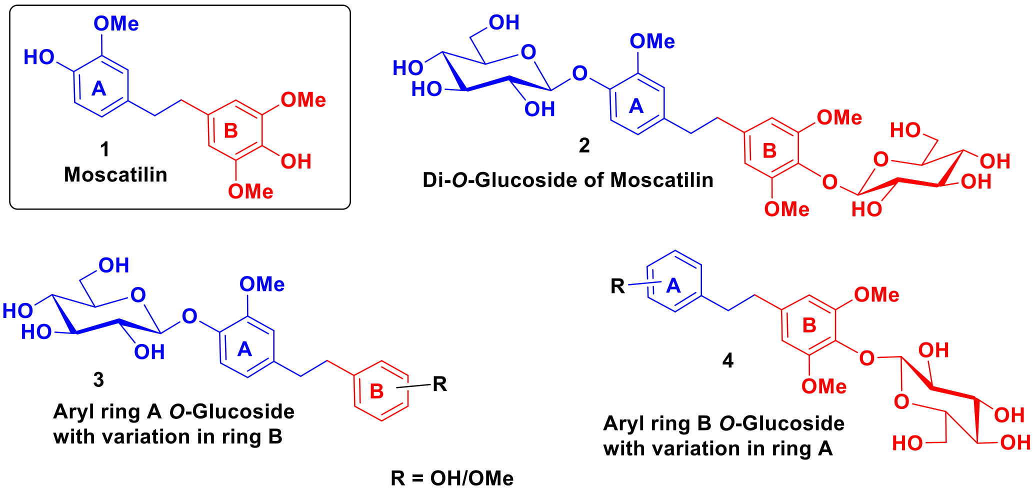


Figure: *O*-Glucosylated Moscatilin Derivatives and Analogues.

References

1. Aidhen, I. S.; Srikanth, S.; Lal, H. Eur. *J. Org. Chem*. **2022**, *2022 (35)*, 1-37 (e202200758).
2. Brito-Arias M., Synthesis, and Characterization of Glycosides. Brito-Arias M, (ed.) 2nd ed. New York, USA: Springer; **2016**.
3. Mnumder, P. L.; Sen, R. C.; *Phytochem*. **1987**, *26*, 2121-2124.
4. He, L.; Su, Q.; Bai, L.; Li, M.; Liu, J.; Liu, X.; Zhang, C.; Jiang, Z.; He, J.; Shi, J.; Huang, S.; Guo, L.; *Eur. J. Med. Chem*. **2020**, *204*, 112530.

Fluorescence-Raman (SERS) Dual Mode Detection Method for Monitoring H_2S Levels in Biological Samples

Archana. P. P, Muraleedharan. K. M *
Indian Institute of Technology Madras, Chennai, Tamil Nadu - 600036
E-mail: mkm@iitm.ac.in

Hydrogen sulfide (H_2S) is an endogenous gasotransmitter having key signaling roles in various pathophysiological processes[1]. H_2S concentration can vary significantly in the blood plasma during the onset and progress of systemic inflammatory response syndrome (sepsis), a severe medical condition. Since it could be used as a biomarker for sepsis, fast and accurate detection of H_2S during the early stages of sepsis can reduce the mortality rate in intensive care units. Small molecule fluorescent chemical probes are considered an effective tool for H_2S detection because of their good selectivity, sensitivity, and biocompatibility. In this context, we have developed a dual-mode detection probe for the fast detection of H_2S in biological media by fluorescence and surface-enhanced Raman (SERS) techniques [2,3]. Probe **1** will undergo thiolysis upon reacting with H_2S and generate compounds **2** and **3** which can be quantified using fluorescence and SERS methods respectively. Probe **1** showed a linear response toward H_2S in a concentration range of 0-100 μM with a limit of detection of 7 nM. The reaction was very fast (within 1 min) and showed good selectivity towards H_2S compared to other bio-thiols. The probe was successfully used to quantify H_2S in human blood plasma and for SERS-imaging of endogenous H_2S in HepG2 cells.

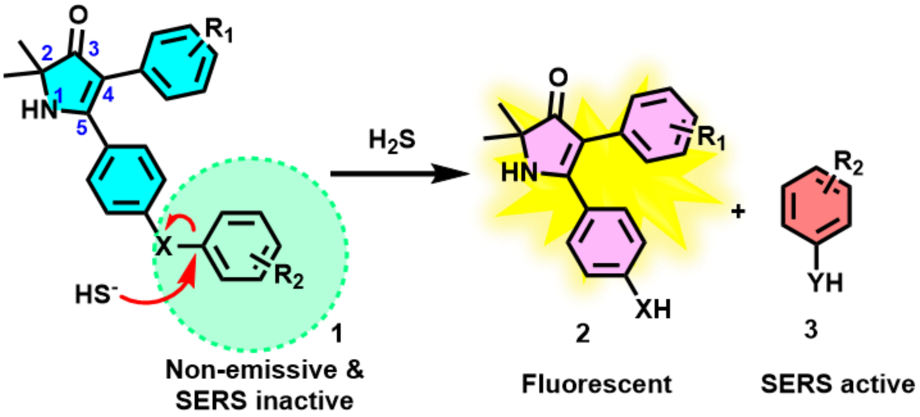


Figure 1. Dual-mode detection of H_2S using Probe **1**.

References

1. Filipovic, M. R.; Zivanovic, J.; Alvarez, B.; Banerjee, R. *Chem. Rev*. **2018**, *118 (3)*, 377-461.
2. Archana, P. P.; Shamjith, S.; Kurian, J.; Kesavan, A.; Sen, A.K.; Thangaraj, P.R.; Maiti, K.K.; Manheri, M.K. *Anal. Methods*, **2023**,*15*, 2853-2860.
3. 1*H*-pyrrol-3(2*H*)-one scaffold for the design of multimodal diagnostic probes and therapeutic agents, Muraleedharan Kannoth Manheri, Archana Panthalattu Parambil, Jais Kurian, Akila Kesavan, Patent Application No: 202241034179; date of Filing: 15/06/2022 (IDF 2353, IIT Madras)

P28

Development of Multi-drug Drug Delivery Systems with tunable polarity characteristics

*Akshaya K. V., Muraleedharan K. M.**

Indian Institute of Technology Madras, Chennai, Tamil Nadu - 600036

E-mail: mkm@iitm.ac.in

Combination therapy is becoming inevitable in almost all therapeutic areas due to the potential risk of resistance induction with monotherapy. Though promising, difference in physicochemical properties and pharmacokinetics of individual drugs could adversely affect their availability at the target site, which ultimately affect their performance. In this context, development of new approaches which give good spatio-temporal control in the distribution of individual drugs have become very essential. As part of our interest in this area, we have been working on a new class of synthetic lipids, characterized by the presence of hydroxylated oxanorbornane skeleton as the head group.[1-4] This presentation will summarize the results from studies involving a new group of lipids from this category with different charge characteristics on the head group. To demonstrate their potential use as multi-drug delivery system, we have covalently linked an H_2S donor moiety on the head group and have used the aggregates of resulting lipid to entrap other drugs such as ibuprofen. Synthetic details, drug loading and release profiles and characterization details will be discussed during this presentation.

References

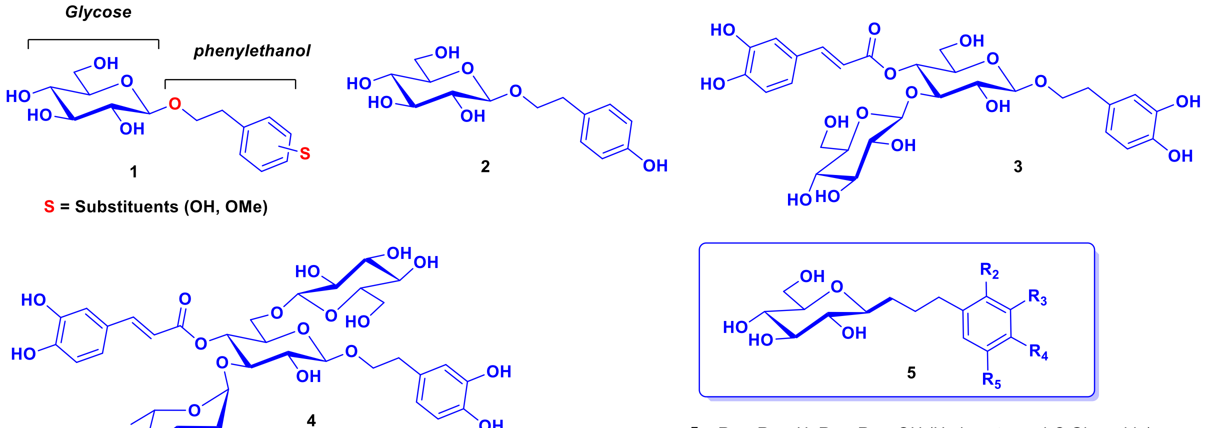
1. Saroj, S; Janni, D. S; Reddy, U. C.; Muraleedharan, K. M. *Materials Science & Engineering C*, **2020,** *112*, 110857.
2. Ganesan, M.; Muraleedharan, K. M. *RSC Adv*. **2012**, *2*, 4048-4051.
3. Janni, D. S.; Reddy, U. C.; Saroj, S.; Muraleedharan, K. M. *J. Mater. Chem*. B. **2016**, *4*, 8025-8032.
4. Janni, D. S.; Muraleedharan, K. M. *Langmuir* **2013**, *29*, 15182-15190.

P29

SYNTHESIS OF C-GLUCOSIDE ANALOGUES OF NATURAL PHENYLETHANOID *O*-GLYCOSIDES

*Amudala Subramanyam, Sumit and Indrapal Singh Aidhen**
Department of Chemistry, IIT Madras
E-mail: isingh@iitm.ac.in

Natural products offer diverse structures and biological abilities, proving valuable in discovering innovative pharmaceuticals. Structural modifications of natural substances have been highly effective in developing new drugs.[1] Phenylethanoid glycosides (PEG) **1** as natural compounds have attracted great attention due to their promising biological activities. The biological activities include neuroprotection, antioxidant, immunoregulation, anti-inflammatory, and analgesic effects, as well as antitumor, antiviral, and hepatoprotective abilities.[2]. PEG consists of a phenethyl alcohol group linked to a glucose molecule predominantly through β-*O*-glucoside linkage. The aryl ring carries varied substituents, such as -OH and -OMe with the substitution pattern being either resorcinolic or catecholic. Three potent PEGs, salidroside **2,** acteoside **3**, echinacoside **4**, and, are gaining renewed interest in this class of compounds. [3] Being *O*-glycosides, PEG have low bioavailability due to factors like poor intestinal permeability, enzyme hydrolysis, and interaction with gut bacteria. The work presented in this poster will be the first report on the synthesis of *C*-glucoside analogues **5** of PEG. The synthesized *C*-analogues are expected to be hydrolytically stable and are likely to address the limitations of naturally occurring *O*-linked PEGs.



S = Substituents (OH, OMe)

5a: $R_2 = R_5 = H$, $R_3 = R_4 = OH$ (Hydroxytyrosol *C*-Glucoside)
5b: $R_2 = R_3 = R_5 = H$, $R_4 = OH$ (Tyrosol *C*-Glucoside)
5c: $R_2 = R_5 = H$, $R_3 = R_4 = -OCH_2O-$
5d: $R_2 = R_4 = H$, $R_3 = R_5 = OH$ (resorcinolic pattern, 3,5)
5e: $R_2 = R_5 = H$, $R_3 = OH$, $R_4 = OMe$

Figure 1. Important Natural Phenylethanoid glycosides (PEG) **1 – 4** and proposed synthetic analogues of PEG **5**.

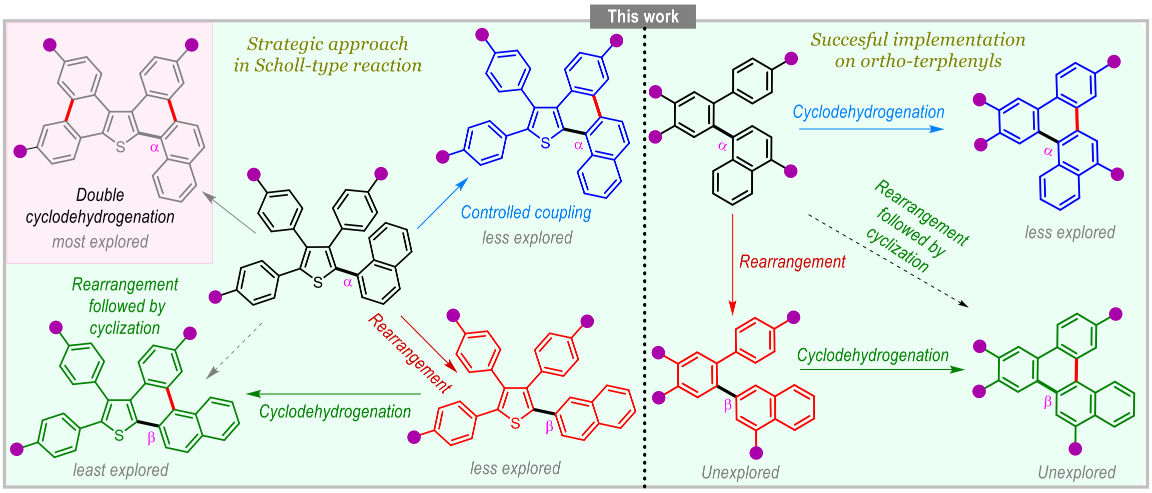
References

1. Fu, G.; Pang, H.; & Wong, Y. *Curr. Med. Chem.* **2008**, *15*, 2592-2613.
2. (a) Jimenez, C.; Riguera, R. *Nat. Prod. Rep.* **1994**, 11, 591 - 606. (b) Guangmiao, F.; Haihong, P.; Wong, Y. H. *Curr. Med. Chem.* **2008**, 15, 2592 - 2613.
3. Xue, Z.; & Yang, B. *Molecules* **2016**, *21*, 991.

Serendipity to Precision: Programming Rearrangements Under Scholl-type Reaction

*Nagaraju Ponugoti, Sudhakar Maddala, Venkatakrishnan Parthasarathy**
Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600 036.
E-mail: *pvenkat@iitm.ac.in*

Rearrangements in the Scholl reaction are commonly discovered through serendipity.[1] Factors including reaction conditions, molecular structure parameters, and the thermodynamic and kinetic stabilities of intermediates/products are crucial in facilitating rearrangements. Johnson and colleagues demonstrated 1,2-aryl shifts in a series of biaryls.[2] However, investigations of rearrangements on heteroles and *ortho*-terphenyls under Scholl-type reaction conditions are scarce.[3]



Scheme 1. Cyclization, rearrangement, and rearrangement-cyclization products of TATs and *ortho*-terphenyls under Scholl-type reaction.

In this study, we strategically designed the tetraarylthiophenes (TATs, Scheme 1) to control the cyclization to facilitate rearrangement. Unfortunately, our attempts to achieve the expected rearrangement of the naphthyl group under Scholl conditions resulted in cyclization instead. Nevertheless, we successfully accomplished the desired rearrangement by applying modified Johnson's conditions (treating with acid alone). By monitoring the progress of the rearrangement reaction, we have investigated the kinetics and obtained valuable insights into the activation parameters, including E_a, ΔH, ΔS, and ΔG. Ultimately, we achieved the rearrangement-cyclization product (step-wise) by introducing an oxidant into the same pot where the successful rearrangement occurred.[4] A similar study tested on *ortho*-terphenyls also yielded fruitful outcomes and justified our hypothesis.[4]

References

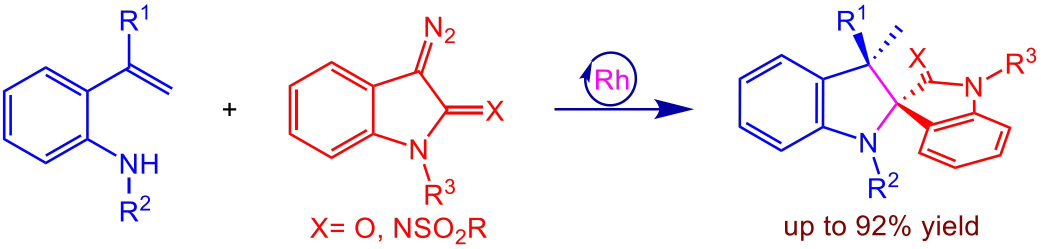
1. Ponugoti, N.; Parthasarathy, V. *Chem. Eur. J.*, **2022**, *28*, e202103530.
2. Skraba, S. L.; Brulet, J. W.; Song, M. K.; Johnson, R. P. *J. Org. Chem.*, **2017**, *82*, 13076-13083.
3. a) Wynberg, H.; Driel, H.; Kellogg, R. M.; Buter, J. *J. Am. Chem. Soc.*, **1967**, *89:14*, 3487-3494. b) Weinmayr, V.; Palmar, F. S.; Ebert, Jr. A. A. *J. Am. Chem. Soc.*, **1952**, *74*, 4361. c) Nakahara, H.; Yamaguchi, J. *Org. Lett.*, **2022**, *24*, 8083-8087.
4. Ponugoti, N.; Maddala, S.; Parthasarathy, V. *Manuscript under preparation.*

P31

Stereoselective Rhodium-Catalyzed Carbenylative Amination for the Synthesis of Spiroindoliness

Subramanian Srikriya, *Angula Chandra Shekar Reddy, Pazhamalai Anbarasan**
Indian Institute of Technology Madras, Chennai-600036
E-mail: anbarasansp@iitm.ac.in

Metal carbenes are serving as a pivotal intermediate for the synthesis of various complex heterocycles.[1] Among the diverse reactivity of metal carbenes, the generation of ylides with suitable Lewis base followed by trapping with reactive electrophiles has gained significant attention in the recent past.[2] Because these transformations offer access to construct the complex frameworks in high chemo and stereoselectivity. But the trapping of ylides with unactivated alkenes is rather limited. Recently, our group demonstrated the rhodium and palladium-catalyzed synthesis of indolines *via* the intramolecular trapping of *N*-ylides with alkenes.[3] Particularly, palladium-catalyzed carbenylative amination of *o*-vinylaniline has been demonstrated with *α*-diazocarbonyl compound derived from isatin derivatives to access spiroindolines as a single diastereomer.[4] In this poster, we will disclose the efficient rhodium-catalyzed stereoselective synthesis of spiroindoline derivatives under milder conditions employing *o*-vinylanilines with *α*-diazocarbonyls and *α*-diazoimines.



References

1. Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods For Organic Synthesis with Diazo Compounds: From Cyclopropanes To Ylides*; Wiley: New York, **1998**.
2. (a)Davies, H. M. L.; Morton. D. *Chem. Soc. Rev.* **2011**, *40*, 1857–1869. (b) Akter, M.; Rupa, K.; Anbarasan, P. *Chem. Rev*. **2022**, *122*, 13108–13205.
3. (a) Reddy, A.C.S.; Choutipalli, V. S. K.; Ghorai, J.; Subramanian, V.; Anbarasan, P. *ACS Catal*. **2017**, *7*, 6283– 6288. (b)Yadagiri, D.; Reddy, A. C. S.; Anbarasan, P. *Chem. Sci*. **2016**, *7*, 5934–5938.
4. Reddy, A. C. S.; Reddy, P. M.; Anbarasan, P. *Adv. Synth. Catal.* **2020**, *362*, 801–806.

PHYSICAL CHEMISTRY

(P32-P48)

P32

Nano-mechanical Investigations on Isomorphic Crystals of Tetranuclear Copper Nanoclusters

Amoghavarsha Ramachandra Kini [a], *Arijit Jana* [a], *Sanghamitra Debta* [b], *Tomas Base* [c]*,
Pijush Ghosh [b]* *and Thalappil Pradeep* [a]*
[a] *DST unit on nanoscience and Thematic unit of excellence (TUE), Department of Chemistry, IIT Madras, Chennai.*
[b] *Department of Applied Mechanics, IIT Madras, Chennai.*
[c] *Institute of Inorganic Chemistry, The Czech Academy of Science, Czech Republic*
E-mail: pradeep@iitm.ac.in

Metal nanoclusters with atomic precision form a novel category of materials, possessing a wide range of distinctive properties such as photoluminescence, catalysis, magnetism, conductivity, and more. These properties can be precisely adjusted through optimized synthetic protocols, introducing dopant metals, ligand engineering, and inter-cluster reactions.[1,2] Notably, the mechanical properties of molecular materials, particularly atomically precise nanoclusters, are of significant interest yet unexplored in the scientific community. Investigating the mechanical characteristics of nanocluster crystals allows us to gain insights into their behavior when subjected to stress. Ultimately, exploring the mechanical properties of nanoclusters empowers us to fabricate electronic devices with enhanced performance and functionality.[3]

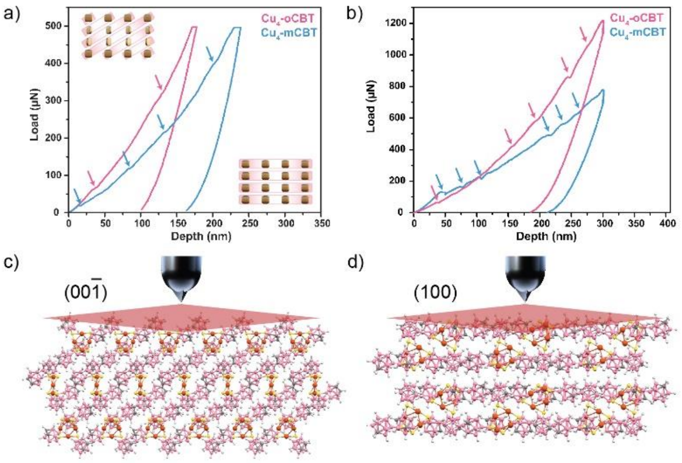


Figure 1. **a)** Load-displacement curves of both crystals under a fixed load of 500 µN using a load function of 5-10-5. Inset shows the schematic packing diagram of Cu4-oCBT (top) and Cu4-mCBT (bottom). **b)** Load-displacement curves with a fixed displacement of 300 nm. Arrows indicate pop-in events occurring during nanoindentation experiments. Extended order supramolecular packing of **c)** Cu4-oCBT and **d)** Cu4-mCBT along with the marked indentation planes.

Here we have probed the mechanical properties of isomorphic atomically precise copper nanocluster crystals protected by carborane-thiols using a Hysitron TI 950 Triboindenter. The clusters used are $Cu_4(o\text{-}CBT)_4$ and $Cu_4(m\text{-}CBT)_4$, protected by *ortho*-9-carborane thiol and *meta*-9-carborane thiol, respectively.[4]

The indentation data shows how the hardness and Young's modulus differ even when the two materials are almost identical. Probing the mechanical properties of molecular crystals can get us closer to establishing a better structure-property correlation in atomically precise nanoclusters.

References

1. Chakraborty, I.; Pradeep, T. *Chem. Rev.* **2017**, *117* (12), 8208–8271.
2. Jana, A.; Kini, A. R.; Pradeep, T. *AsiaChem Mag.* **2023**, *3* (1).
3. Sugi, K. S.; Bandyopadhyay, P.; Bodiuzzaman, M.; Nag, A.; Hridya, M.; Dar, W. A.; Ghosh, P.; Pradeep, T. *Chem. Mater.* **2020**, *32* (18), 7973–7984.
4. Jana, A.; Jash, M.; Dar, W. A.; Roy, J.; Chakraborty, P.; Paramasivam, G.; Lebedkin, S.; Kirakci, K.; Manna, S.; Antharjanam, S.; Machacek, J.; Kucerakova, M.; Ghosh, S.; Lang, K.; Kappes, M. M.; Base, T.; Pradeep, T. *Chem. Sci.* **2023**, *14* (6), 1613–1626.

P33

Purification and Optimization of *Mtb*'s Proteasomal complex to probe its oligomerization, unfolding, translocation and degradation mechanism.

*Pushpkant Sahu, Sohini Mondal, Sandipan Saha, Hema Chandra Kotamarthi**

Department of Chemistry, Indian Institute of Technology, Madras, 600036.

E-mail: hemachandra@iitm.ac.in

Proteolysis is a crucial cellular process that maintains the protein homeostasis by degrading folded and misfolded proteins. For this purpose, different kinds of proteases and proteasomes are present in all three domains of life[1]. Tuberculosis is a highly infectious disease and is caused by *Mycobacterium tuberculosis* (*Mtb*). It is a type of actinobacteria contains both proteasomes and regular bacterial proteases responsible for its pathogenicity in host cell[2]. Like other proteasomal complexes, the *Mtb* proteasomes are composed of two independent compartments (i) A hexameric ATPase compartment that recognizes, unfolds, and translocates the protein substrate by using ATP as an energy source. (ii) Peptidase compartment that degrades the polypeptide to small peptide fragments via amide bond hydrolysis[3] (Figure). In *Mtb*, Mpa (Mycobacterial proteasomal activator) acts as the ATPase which recognizes the intrinsically unfolded protein called Pup (Prokaryotic ubiquitin-like protein) and 20S CP acts as the peptidase, which is a four-ring cylinder made up of identical alpha and beta subunits in which each ring contains 7 units ($\alpha_7\beta_7\beta_7\alpha_7$). Mpa unfolds the pupylated protein by applying mechanical force and translocating it into the 20S CP peptidase for degradation using ATP as an energy source. To probe unfolding, translocation and degradation mechanism of *Mtb*'s Proteasomal complex using Optical tweezer based single molecule study and biophysical study, we have constructed, optimised and purified pupylated substrates (Pup-GFP & Pup-Titin^{I27}), Mpa, and 20SCP. To probe the oligomerization/de-oligomerization mechanism of Mpa, chemical denaturation study was performed based on fluorescence, Circular Dicroism and Native PAGE analysis.

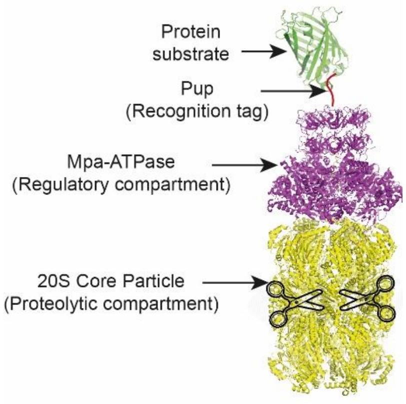


Figure: *Mtb*'s proteasomal complex

References

1. Greene, E. R.; Dong, K. C.; Martin, A. Understanding the 26S Proteasome Molecular Machine from a Structural and Conformational Dynamics Perspective. *Curr Opin Struct Biol* **2020**, *61*, 33–41.
2. Cerda-Maira, F.; Darwin, K. H. The *Mycobacterium tuberculosis* Proteasome: More than Just a Barrel-Shaped Protease. *Microbes Infect* **2009**, *11* (14–15), 1150–1155.
3. Sutter, M.; Striebel, F.; Damberger, F. F.; Allain, F. H.-T.; Weber-Ban, E. A Distinct Structural Region of the Prokaryotic Ubiquitin-like Protein (Pup) Is Recognized by the N-Terminal Domain of the Proteasomal ATPase Mpa. *FEBS Lett* **2009**, *583* (19), 3151–3157.

Rationally Designed Bimetallic Co-Fe-B Nanosheets for Electrocatalytic N_2 Reduction to Ammonia

*Vineet Mishra and G. Ranga Rao**

Department of Chemistry and DST Solar Energy Harnessing Centre (DSEHC), Indian Institute of Technology Madras, Chennai-600036

E-mail: grrao@iitm.ac.in

The activation of N≡N bond under ambient conditions is a great challenge in heterogeneous catalysis. A possible alternate path to activate nitrogen is electrocatalytic approach. Electrocatalytic nitrogen reduction reaction (e-NRR) under ambient conditions is expected to be an environment-friendly and sustainable pathway for ammonia production. However, the low ammonia yield and poor faradaic efficiency, attributed to the difficulty in N_2 adsorption, N≡N bond activation and competing hydrogen evolution reaction (HER) in aqueous electrolyte medium, inhibit its practical applications.[1-3] Hence, development of robust and efficient electrocatalyst is highly desirable. In this work, designing N_2 reduction catalyst is purely based on assembling two types of metals. First, a metal having low dissociation energy barrier and another metal with high dissociation energy barrier for N_2 to achieve optimised coverage of dissociated nitrogen atoms on the catalyst surface during electrocatalytic ammonia synthesis.[4] Apart from this, N_2 being Lewis base can preferentially be adsorbed on the Lewis acid boron over H^+ in acidic medium which further suppresses HER.[5-7] Hence, keeping all the above facts in mind, we have rationally designed a bimetallic cobalt-iron-boron (Co-Fe-B) nanosheets using high energy ball-milling method followed by high temperature annealing. The electrocatalytic N_2 reduction is performed in a two compartment H-cell separated by 211 nafion membrane using 0.05 M H_2SO_4 aqueous electrolyte. After the electrocatalytic N_2 reduction, the resultant NH_4^+ ion concentration in the electrolyte is quantitatively analysed with the help of indophenol-blue method. Absorbance of the solution is measured using UV-Visible spectrophotometer at a λ_{max} of 660 nm. As synthesised Co-Fe-B nanosheets show 11.2 μg h^{-1} cm^{-2} of NH_4^+ ion yield with the onset potential of 0.05 V vs RHE.

References

1. Maman, M. P.; Gurusamy, T.; Pal, A. K.; Jana, R.; Ramanujam, K.; Datta, A.; Mandal, S.; *Angew. Chem. Int. Ed.*, **2023,** *62*, e202305462.
2. Biswas, S. S.; Saha, A.; Eswaramoorthy, M.; *ACS Omega,* **2022**, *7*, 1874-1882.
3. Gurusamy, T.; Mohan, N. G.; Kandregula, G. R.; Murugaih, D. K.; Srinivasan, R.; Ramanujam, K. *Catal. Today*, **2022**, 423, 113898-113909.
4. Jacobsen, C. J. H.; Dahl, S.; Clausen, B. S.; Bahn, S.; Logadottir, A.; Norskov, J. K. *J. Am. Chem. Soc.*, **2001**, *123*, 8404-8405.
5. Biswas, A.; Kapse, S.; Ghosh, B.; Thapa, R.; Dey, R. S. *PNAS,* **2022**, *119*, 33, e2204638119.
6. Liu, C.; Li, Q.; Wu, C.; Zhang, J.; Jin, Y.; MacFarlane, D. R.; Sun, C. *J. Am. Chem. Soc.*, **2019**, *141*, 2884-2888.
7. Sultana, S.; Paramanik, L.; Mansingh, S.; Parida, K. *Inorg. Chem.,* **2022**, *61*, 131-140.

P35

Urea electrooxidation reaction promoted by Ni and Mo$_2$C catalysts

*Dilip Kumar Tiwari, and G. Ranga Rao**
Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036
Corresponding author e-mail: grrao@smail.iitm.ac.in

The energy crisis and environmental pollution have become two severe issues that need to be addressed with quick action[1]. Developing alternative and sustainable clean energy is an essential task due to the limited reservoirs of fossil fuels [2]. Hydrogen (H_2) has been regarded as a potential candidate to replace fossil fuels to solve the severe energy crisis and ever-growing environmental problems [3]. Urea-rich wastewater has been identified as a good source for H_2 fuel production in alkaline medium. Ni-based catalysts are deemed to be highly efficient catalysts in achieving high urea oxidation reaction (UOR) performance with low overpotential and high catalytic current [4]. The Ni@Mo$_2$C nanoparticles with three different Ni:Mo weight ratios with melamine are prepared and applied as anodic catalysts for the urea electro-oxidation reaction (Fig.1). The synergistic effect between Ni and Mo$_2$C could adjust the electron density states to boost the active sites and facilitate the catalytic activity of UOR as well as hydrogen evolution reactions (HER) [5]. The Ni@Mo$_2$C (1:2) catalyst exhibited superior catalytic activity, lower over-potential, better stability and superior electro-catalytic performance towards urea electro-oxidation compared with other Ni-Mo compositions, Ni@Mo$_2$C (1:1), Ni@Mo$_2$C (2:1), Mo$_2$C and Ni@C catalysts. The Ni@Mo$_2$C materials are characterized by XRD, SEM, TEM, Raman and XPS. The performance of urea oxidation has been tested by cyclic voltammetry, and the maximal current density of Ni@Mo2C (1:2) catalyst was 90.5 mA cm^{-2} at 420 mV vs. SCE in 1 M KOH electrolyte with 0.33 M urea. The Ni@Mo$_2$C (1:2) showed an improved performance with low over potential, small charge transfer resistance and low Tafel slope.

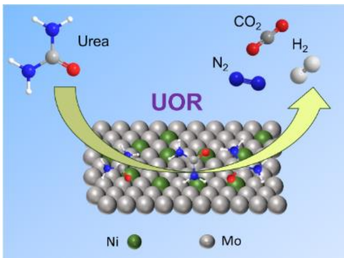


Figure 1: Electrooxidation of urea using Ni@Mo$_2$C (2:1) catalyst

References

1. L. Zhao, X. Shiji, S. Zhou, L. Jing, Q. Konggang. *Journal of Catalysis.* **2022**, 405, 606–613.
2. X. Wei, D. Dongwei, W. Zucheng, T. Shanwen. *New J. Chem*. **2017**, *41*, 4190.
3. Z. Jun, H. Ting, W. Mingda, Q. Ruijuan, D. Zehua, L. Hongfang, X. Bao. *Nano Energy*, **2019**, *60*, 894-902.
4. A. N. Rollinson, J. Jones, V. Dupont, M. V. Twigg. *Energy & Environ. Sci.* **2011**, *4*, 1216-1224.
5. B. K. Boggs, R. L. King, G. G. Botte. *Chem. Commun.* **2009**, *32*, 4859-4861.

P36

Effect of surfactants on the physicochemical and charge storage properties Cu_3TeO_6 material

*Pulak Mondal, Sweta Thangriyal, G. Ranga Rao**
Department of Chemistry, IIT Madras, Chennai 600036, India
E-mail: grrao@iitm.ac.in

In the search for an alternative renewable energy source, we have synthesized Cu_3TeO_6 as a supercapacitor electrode material. The facile hydrothermal method has been employed using different surfactants, PVP, CTAB and Tritan-X-100 in the synthesis. The synthesized Cu_3TeO_6 is characterized using XRD, IR and SEM techniques. In this study, we report the influence of the surfactants on the morphology, porosity and structural evolution as well as energy storage capacity of Cu_3TeO_6.[1] This is the first time report on this compound, when prepared in water, PVP, CTAB, and Tritan-X-100, shows the specific capacitance values of 515, 436, 246 and 500 F g^{-1} at a current density of 2 A g^{-1}, respectively. Benefiting from surfactant driven morphology, Cu_3TeO_6 shows different electrical conductivity and surface areas.[2] The compound Cu_3TeO_6 also exhibits variations in storage properties in terms of long cycling life, discharge current and charge transfer resistance.

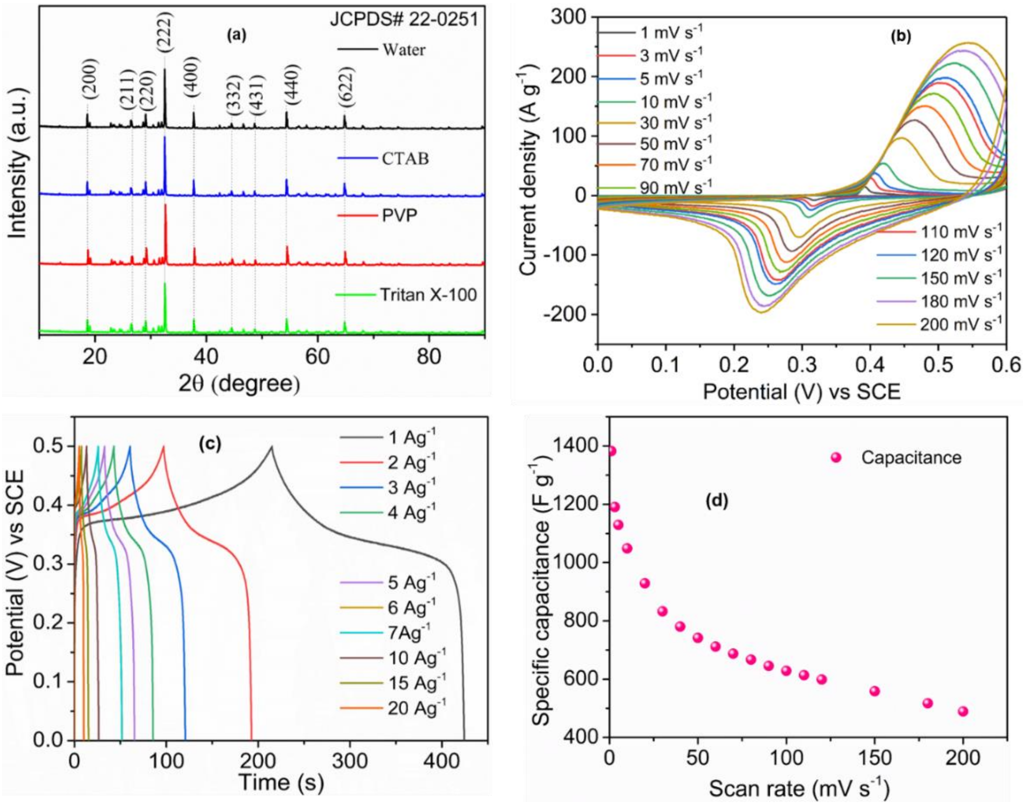


Figure 1. (a) XRD, (b) CV profiles at different scan rates, (c) CP profiles at different current densities, and (d) specific capacitance versus scan rate of Cu_3TeO_6 prepared using water as solvent.

References

1. Meher, S. K.; Justin, P.; Ranga Rao, G. *Nanoscale* **2011**, 3, 683.
2. Saravanakumar, B.; Radhakrishnan, C.;Ramasamy, M.; Kaliaperuma, R.; Britten, A. J.; Mkandawir, M. *Results in Physics* **2019,** *13,* 102185.

P37

A Spectroscopic Study on the Structural Stability of Hemoglobin in DBU- based Novel Protic ILs Media

*K. J. Jisha and Ramesh L.Gardas**

**Department of Chemistry, Indian Institute of Technology Madras, Chennai, India.*

E-mail: gardas@iitm.ac.in

Proteins are biopolymers that are formed by the condensation of amino acids and maintaining their structure in thermodynamically stable form is mandatory in many fields including therapeutics, biological processes as well as in diagnostics. Globular proteins, like heme proteins, are attaining stability by balancing the intermolecular interactions of their own functional groups and through the interactions with co-solvent molecules.[1] Co-solvents also affect the protein structure by altering the rigidity and flexibility of the polypeptide chains in the protein, which varies depending on the polarity of the medium chosen for the study. Academic and industrial communities have shown great interest in the selection of an apt solvent for biomolecules in suitable biocatalytic applications. When several additives were tested on protein molecules, Ionic Liquids (ILs) turned out to be a good choice because of their unique properties, which include greater thermal-chemical stability, minimal vapor pressure, and, most importantly, the capacity for reusing.[2,3] The choice of various ILs in many biological applications, such as protein separation, extraction, preservation, sensing of biomolecules, etc., is also influenced by their thermal stability, self-life, and stronger enzymatic activity. It's noteworthy to note that, depending on the protein molecule it is interacting with, each protein behaves differently according to the properties of the ionic liquids.[4,5] When ionic liquids are used as co-solvents, the cationic part suppresses the protein surface, particularly the hydrophobic surfaces, and therefore the protein aggregation is prevented which further enhances the solubility. The same IL can function as both a stabilizer and a denaturing agent depending on the experimental conditions. DBU (1,8-diazabicyclo [5.4.0] undec-7-ene), a tertiary amine with double heterocyclic structure, when paired with other heterocyclic molecules like Imidazole, Morpholine, and Triazole, there was synthesized a novel series of stable ILs. DBU-based ILs are least explored in biomolecule applications but are known for their high thermal stabilities. The interaction of these ILs with hemoglobin was analyzed using various spectroscopic techniques including UV-Visible spectroscopy, steady-state fluorescence, Fluorescence Time-Correlated Single Photon Counting (TCSPC), and Dynamic Light Scattering (DLS) to have a better insight into the effects of these ionic liquids on the structural stability of Hb molecule. All three IL systems were found to show hemoglobin-friendly behavior under the studied range of concentration and the triazole system was found to be more effective. Moreover, binding constant values obtained from the absorbance data have proved that there is no complex formation occurring during the IL-Hb interactions, and hence the studied ILs are suitable candidates to use as a cosolvent for hemoglobin-like globular proteins. Globular proteins which balance the stability via various inter- and intra-molecular interactions, require a medium that does not hinder the balancing. Our studies are a proof of concept that the DBU-based ILs used here can provide such kind of a medium without participating in the interactions.

References

1. Jha, I.; Attri, P.; Venkatesu, P. *Phys. Chem. Chem. Phys*. **2014**, *16*, 5514–5526.
2. Welton, T. *Biophys Rev*. **2018**, *10*, 691–706.
3. Guncheva, M. *Protein Journal*. **2022**, *41*, 369–380.
4. Schindl, A.; Hagen, M. L.; Muzammal, S.; Gunasekera, H. A. D.; Croft, A. K. *Front. Chem*. **2019**, *7*, 347.
5. Schröder, C. *Top Curr Chem*. **2017**, *375*, 25.

P38

Aggregation Behaviour and Drug Interaction of Bile Salt in the Presence of Mono- or Di-cationic Ionic Liquids

*Priyanka V. P., Ramesh L. Gardas**

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India

E-mail: gardas@iitm.ac.in

Ionic liquids (ILs) with unique properties such as their low vapour pressure, great thermal-chemical stability, and tunable nature when selecting anions and cations, make them important study targets in chemistry and biology [1]. Based on the structure of anions or cations, ILs also display surface active characteristics that explore numerous therapeutic applications. As a result of their poor water solubility, the majority of the pharmaceutically active substances perform poorly in biological systems. Surfactants with aggregation properties aid in the solubilization of drugs that are not readily soluble, by entangling them in the micellar system [2, 3]. Bile salts are well-known biological surfactants that help in increasing the solubility and bioavailability of hydrophobic drugs in water [4]. In comparison to traditional surfactants, the binary mixture of ILs and bile salts (mixed micellar system) exhibits improved surface characteristics [5]. The present study deals with the aggregation behaviour of sodium deoxycholate (bile salt) in water (micellar system) and in an aqueous solution of imidazolium-based mono- and di-cationic ionic liquids (mixed micellar system). The critical micellar concentration (CMC) of the studied systems was determined using conductivity and fluorescence experiments. Dynamic light scattering experiments were employed to understand the size of the aggregates formed. It was observed that the CMC value of sodium deoxycholate (NaDC) decreased with the incorporation of ILs into the system which points out the enhancement of the surface properties. The system containing hydrophobic mono cationic IL showed more affinity towards NaDC which reflects in the low CMC value of the system. As the wt% of IL increases, the CMC value of the mixed micellar system decreases which confirms the easy aggregation of NaDC in IL solution rather than the aqueous solution. The size of the aggregates increased as the wt% of ILs increased and after a certain wt%, it decreased. Further, the application of the studied micellar and mixed micellar system towards the interaction with ciprofloxacin (CIP) was evaluated using UV-Visible spectroscopy. The system containing 0.15 wt% of IL which has smaller aggregates was chosen for the interaction study because aggregates with smaller sizes should be capable of adsorbing more drug molecules. The determination of interaction parameters of micellar and mixed micellar systems with the drug was examined by the Benesi-Hildebrand equation.

References

1. Priyanka, V. P. and Gardas R. L. *Sep. Purif. Technol*, **2020**, *234*, 116048.
2. Vashishat, R.; Sananb, R.; Mahajan, R. K. *RSC Adv*, **2015**, *5*, 72132-72141.
3. Banjare, M. K.; Behera, K.; Kurrey, R.; Banjare, R. K.; Satnami, M. L.; Pandey, S.; Ghosh, K. K. *Spectrochim. Acta A Mol. Biomol. Spectrosc*, **2018**,*199*, 376-386.
4. Selvam, S. *J. Photochem. Photobiol, B*, **2012**, *116*, 105-113.
5. Makkar, R. S.; Rockne, K. J. *Environ. Toxicol. Chem*, **2003**, *22*, 2280-2292.

P39

Benign Solvents for Sustainable Chemical & Technological Developments

*K. K. Athira, Baiju Chenthamara, Indrajit Das, Sachind Prabha Padinhattath and Ramesh L. Gardas**
Department of Chemistry, Indian Institute of Technology Madras, Chennai, India.
E-mail: gardas@iitm.ac.in

Ionic liquids (ILs) are a class of versatile and fascinating compounds that have gained significant attention in recent years due to their unique properties and diverse applications. ILs exhibit a wide range of properties, which can be tailored by selecting specific combinations of cations and anions which allows to design ILs with desired characteristics, such as low volatility, high thermal stability, excellent electrical conductivity, and specific solvation abilities. Deep eutectic solvents (DES) are another promising class of materials that offer an innovative approach to the challenges posed by traditional solvents. DES offer a more sustainable and cost-effective alternative with similar or even improved properties. The unique characteristics of ILs and DES make them attractive for various applications across multiple fields, including chemistry, materials science, energy, and even biomedical research. Here, we are focusing on four main applications namely, extraction of DNA[1], CO_2 absorption[2], and extraction of micropollutant[3] using ILs and metal leaching[4] where DES is employed. The separation and purification of nucleic acid is a widely studied field as it has paramount importance. The disadvantages of conventional extraction methods include toxicity, complexity and time consumption. The first work constitutes the development of an efficient IL based aqueous biphasic system with Potassium phosphate buffer as a second phase forming component for the extraction of DNA from bacterial cells. The study includes a thorough investigation of the IL-DNA interactions along with the extraction studies and we have successfully developed a system for the extraction where the biological activity of the DNA is intact after the extraction. The next section deals with the need for an alternative solvent for Carbon dioxide (CO_2) capture where room temperature protic ILs (PILs) are identified as a potential absorbent. The method used in the present invention is energy efficient compared to conventional methods due to the Lewis acid-base interaction between IL and CO_2. Enhanced CO_2 trapping (0.56 moles per mole of IL) and recyclability up to seven cycles are the main advantages. Besides these applications, ILs have emerged as a promising candidate for wastewater treatment because of the ease in structure tunability and other unique chemical properties. Despite the existence of numerous conventional wastewater treatment techniques, an efficient method for removing micropollutants remains elusive. We have developed N-benzylethanolamine based ILs to eliminate diclofenac sodium, one of the top priority pharmaceutical micropollutants, from the aquatic environment. The interaction between ILs and diclofenac medium was evaluated computationally and liquid-liquid extraction (LLE) method was used for experimental studies. The ILs showed excellent extraction performance and found to be reusable up to six further cycles. The final section represents the application of DES for the leaching of $LiCoO_2$ from spent Li-ion battery. Here we have designed a choline chloride-carboxylic acid-based DES as an effective alternative to the conventional inorganic acids for the leaching process. This innovation capitalizes on the substantial chloride content present in the choline-based DES, combined with the reducing capabilities of carboxylic acid, to enhance the leaching procedure. Ultimately, we successfully achieved effective leaching, followed by the subsequent precipitation of metals. The extensive studies, ILs and DES present versatile solutions across various fields, contributing to innovative and sustainable advancements.

References

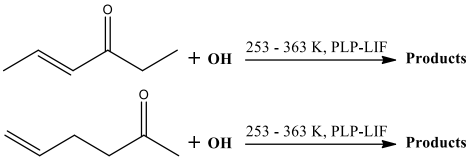
1. Athira, K. K.; Gardas, R. L. *Fluid Phase Equilib*. **2022**, *558*, 113463.
2. Das, I.; Swami, K. R.; Gardas, R. L. *J. Mol. Liq*. **2023,** *371*, 121114.
3. Padinhattath, S. P.; Gardas, R. L. *J. Mol. Liq*. **2023**, *378*, 121603.
4. Padinhattath, S. P.; Chenthamara, B.; Gardas, R. L. *Acta Innov*. **2021**, *38*, 62.

P40

GAS-PHASE KINETICS INVESTIGATION FOR THE REACTION OF UNSATURATED KETONES WITH OH RADICALS

Bishnupriya Kar[a], *Rajakumar Balla**[a,b]
[a]Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600036, India.
[b]Centre for Atmospheric and Climate Sciences, Indian Institute of Technology Madras, Chennai, 600036, India.
E-mail: rajakumar@iitm.ac.in

Unsaturated ketones are a class of organic compounds that contain both a ketone functional group (a carbonyl group, C=O) and one or more carbon-carbon double bonds (C=C) within their molecular structure. There are a number of different sources that contribute to the presence of unsaturated ketones, such as 4-hexen-3-one (4H3O) and 5-hexen-2-one (5H2O), in the environment; emissions from mechanical and biological treatment plants,[1] production as intermediate products in the synthesis of perfume, use of insecticides and fungicide,[2] and biomass burning.[3] Field and laboratory studies show that these compounds are also released into the atmosphere from the wounded leaves of a variety of plants.[4-9] The unsaturated nature of these ketones makes them interesting subjects for studying reaction kinetics, which is the branch of chemistry that deals with the rates of chemical reactions and the factors that influence them. In the present work, the temperature dependent kinetics for the reactions of unsaturated ketones with OH have been studied over the temperature range of 253 – 363 K using Pulsed Laser Photolysis – Laser-Induced Fluorescence (PLP-LIF).In the PLP-LIF experiment, a KrF excimer lasing at λ = 248 nm used for photolysis of precursor H_2O_2, a probe laser Nd:YAG pumped dye laser at 281.9 nm and a photomultiplier tube to detect the fluorescence at 308 nm were placed at a right angle to each other. The laser beams entering into the reaction cell through the windows at a Brewster angle. The rate coefficients for the reactions of 4H3O and 5H2O with OH radicals were found to be 3.80×10^{-11} and 3.24×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively.



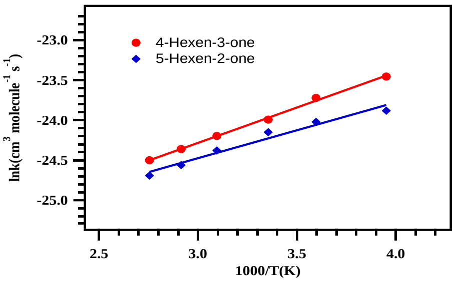


Figure 1. Arrhenius plots for the reactions of 4H3O and 5H2O with OH radicals over the temperature range of 253 – 363 K.

References

1. Marvin L. Poutsma. *The J. Phys. Chem. A* **2013**, *117* (4), 687-703.
2. Benni Du, Weichao Zhang. *Comp. Theor. Chem.* **2022**, *1213*, 113737.
3. Xueyu Wang, Bo Tang, Lei Bao, Heng Zhang, Maoxia He, Shiling Yuan. *J. Hazard. Mater.* **2022**, *424*, 127592.
4. Jan Niklas Illmann, Iulia Patroescu-Klotz, Peter Wiesen. *Phys.l Chem. Chem. Phys.* **2021**, *23* (5), 3455-3466.
5. Xueyu Wang, Lei Bao, Dandan Han, Yaoyao Wei, Maoxia He, Shiling Yuan. *Atmos. Environ.* **2021**, *246*, 118107.
6. Niklas Illmann, Rodrigo Gastón Gibilisco, Iustinian Gabriel Bejan, Iulia Patroescu-Klotz, Peter Wiesen. *Atmos. Chem. Phys.* **2021**, *21* (17), 13667-13686.
7. Niklas Illmann, Iulia Patroescu-Klotz, Peter Wiesen. *Atmos. Chem.Phy.s* **2021**, *21* (24), 18557-18572.
8. Weiran Li, Meifang Chen, Yi Chen, Shengrui Tong, Maofa Ge, Yucong Guo, Yunhong Zhang. *J. Environ. Sci.* **2020**, *95*, 23-32.
9. Rodrigo Gastón Gibilisco, Ian Barnes, Iustinian Gabriel Bejan, Peter Wiesen. *Atmos. Chem.Phys.* **2020**, *20* (14), 8939-8951.

P41

Vacuum ultraviolet photolysis of condensed methyl chloride in interstellar conditions and trapping of intermediates at inter-grain interfaces

Bijesh K. Malla[1]*, Gaurav Vishwakarma*[1]*, Soham Chowdhury*[1]*, and Thalappil Pradeep*[1*]

[1]Department of Science and Technology Unit of Nanoscience and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.

E-mail: pradeep@iitm.ac.in

Photochemistry generates chemical complexity efficiently in interstellar space due to processes occurring in the solid state under prevailing pressure and temperature conditions.[1] In the present study, using reflection absorption infrared spectroscopy (RAIRS), three different condensed phases of methyl chloride ice, namely, amorphous, crystalline, and polycrystalline, were detected in ultrahigh vacuum (UHV) ($p = 5\times10^{-10}$ mbar) and cryogenic conditions ($T = 10$-90 K). Upon vacuum ultraviolet (VUV) photoirradiation, crystalline methyl chloride leads to more photoproduct formation than amorphous and polycrystalline. This unusual finding is attributed to the rapid diffusion and reaction of photochemical intermediates in a crystalline matrix, whereas the intermediates are trapped at grain boundaries in the polycrystalline solid. Normally, the intermediate diffusion is high in the case of amorphous phase as compared to crystalline phase. The consequence of long-term irradiation leads to the removal of discontinuity in the polycrystalline solid, and the photoproducts accumulate in the crystalline matrix, as observed in the enhanced desorption of photoproducts in temperature-programmed desorption mass spectrometry (TPD-MS).

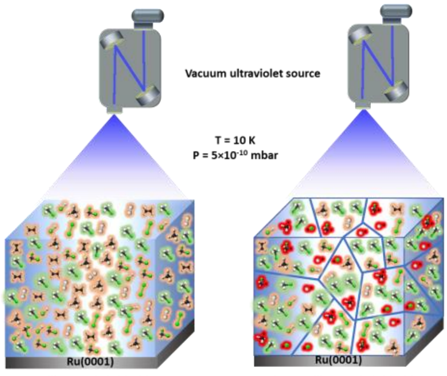


Figure 1. Diffusion of reactive species through the crystalline matrix forms more products, while trapping of the intermediates at the interface reduces product formation in the polycrystalline matrix.

Reference

1. Öberg, K. I. Photochemistry and Astrochemistry: Photochemical Pathways to Interstellar Complex Organic Molecules. *Chemical Reviews*. American Chemical Society September 14, 2016, pp 9631–9663. https://doi.org/10.1021/acs.chemrev.5b00694.

P42

Investigation of kinetics and mechanistic insights of the reaction of criegee intermediate (CH_2OO) with methyl-ethyl ketone (MEK) under tropospherically relevant conditions

Amit Debnath and Balla Rajakumar
Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036
E-mail: rajakumar@iitm.ac.in

Criegee intermediates are short-lived species formed in the ozonolysis of the unsaturated hydrocarbons in the troposphere. MEK is one of the most abundant oxygenated volatile organic compounds (OVOCs), emitted into the atmosphere from biogenic and anthropogenic sources, and is rated 10th in the Toxics Release Inventory (TRI) of EPA. Hence, it is essential to understand its atmospheric removal processes. In this study, the reaction kinetics of the simplest Criegee intermediate (CH_2OO) with MEK [$CH_3(CO)Et$] was performed at room temperature and 50 Torr/N_2 of total pressure using Pulsed Laser Photolysis-Cavity Ring-Down spectroscopy (PLP-CRDS)[1]. The CH_2OO was generated in situ at the reaction zone by photolyzing CH_2I_2 by 248 nm in the presence of excess O_2, and was subsequently probed at 360 nm with a laser repetition rate of 2 Hz.

$$\mathbf{CH_2I_2 \xrightarrow{h\nu} CH_2I + I}$$
$$\mathbf{CH_2I + O_2 \longrightarrow CH_2I + I}$$
$$\mathbf{CH_2OO + CH_2OO \xrightarrow{k_1} products}$$
$$\mathbf{CH_2OO + CH_3COCH_2CH_3 \xrightarrow{k_2} products}$$

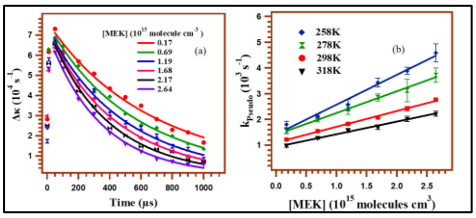


Figure 1. (a) CH_2OO Decay traces at various concentration of MEK, (b) Pseudo 1st order fits at various temperatures

The rate of self-reactions of CH_2OO and its reactions with species (ICH2OO, I, etc.) of comparable concentrations produced in the reaction zone are quite high. Therefore, they are essential to consider in case of this kinetic measurement[2]. The kinetic decay traces were plotted against reaction times ranging from 0 to 7.2 ms, and the σ-independent rate coefficient for the self-reaction was measured to be $k_{self}(298\,K) = (3.58 \pm 0.21) \times 10^6$ cm s^{-1} which was further employed to measure the bimolecular rate coefficient of the titled reaction. The decay behaviour of CH_2OO due to its reaction with MEK, was examined up to 1 ms and the corresponding traces are depicted in Figure 1(a). Variation of the k_{pseudo} values which were obtained from the decay traces, with respect to the concentrations of MEK are depicted in the Figure 1(b). The gradient of each linear fit yields the absolute rate coefficient of the title reaction. An inverse T-dependency of the kinetics was observed in the studied range of 258 - 318 (±2) K. The rate coefficient at 298 K and 50 Torr/N_2 was measured to be: $k_2(298\,K) = (6.39 \pm 0.20) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.

References

1. Debnath, A. and Rajakumar, B. *Chemosphere*, **2023,** *312*, 137217.
2. Chhantyal-Pun, R., Davey, A., Shallcross, D. E., Percival, C. J. and Orr-Ewing, A. J. *Phys. Chem. Chem. Phys.* **2015**, *17*, 3617–26.

P43

THE ATMOSPHERIC FATE OF BROMINE MONOXIDE RADICAL WITH PROPYL-PEROXY RADICAL USING CAVITY RING DOWNSPECTROSCOPY

Prasanna Kumar Bej, and B Rajakumar
Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036
E-mail: rajakumar@iitm.ac.in

The halogen compounds (X=F, Cl, Br, I) release from marine coastal area, anthropogenic sources, artificial resources are efficient catalyst in the reduction of ozone depletion layer in stratospheric atmosphere) [1,2]. Bromine substituents are more actively participating in the O_3 loss than the chlorine because majority of it reacts with $O(^3P)$ to remain as Bromine monoxide (BrO). The other reservoir form of Bromine like $BrONO_2$ is relatively instable and formation HBr most likely possible in the atmosphere. The most non methane abundant gas found in atmosphere is propane. So, the study of kinetics of BrO radical with Porpylperoxy (PrO_2) can play vital rule. The in-situ BrO radical generation was performed by photolysis n-propyl bromide in presence of O_3 molecule. Temperature and pressure dependence rate coefficient of Bro radical with PrO_2 was performed by using in-built pulsed laser photolysis-cavity ring-down spectroscopy (PLP-CRDS) technique. The probing wavelength of BrO radical was 344.04 nm at its (6,0) absorption band.

The rate coefficient pf BrO-radical with PrO_2 was measured as $(1.43 \pm 0.12) \times 10^{-12}$ cm^3 molecule $^{-1}$ s^{-1} at 298 K and 60 Torr. The concentration precursors n-Propyl bromide, O3 and O2 reactant species was maintained as $[O_2] >> [C_3H_7Br] > > [O_3]$ throughout the reaction to obtain the pseudo first order reaction condition. The rate coefficient was measured in the temperature range 263-338K at 95 Torr. There was negative temperature variation was observed withing this range. There is no significant effect of pressure change was observed in the range of pressure from 95-200 Torr.

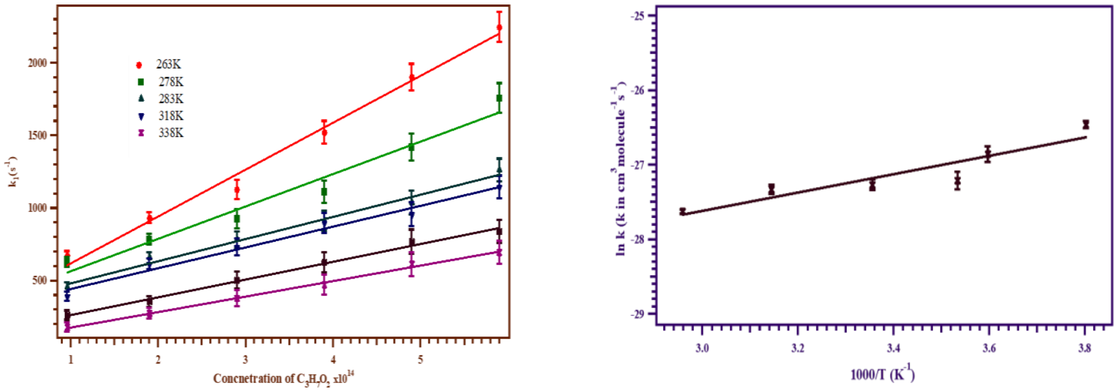


Figure 1. The temperature dependent rate coefficient of Bro radical with PrO_2 from 263-338 K at 60 Torr pressure (Left). The Arrhenius plot of Bro radical with PrO_2 at experimental temperature condition (Right)

References

1. Enami, S. and Kawasaki M., *J. Phys. Chem. A* **2007,** *111*, 3342-48.
2. Wheeler, M.D and Orr-Ewing, A. J, *J. Chem. Phys* **1998**, *285*, 346-351.

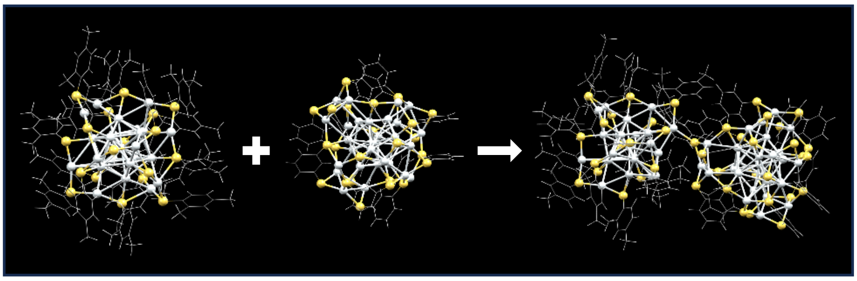
P44

Dissociative dimerization occurs during the reactions of atomically precise $[MAg_{24}(DMBT)_{18}]^-$ and $[Ag_{29}(BDT)_{12}]^{3-}$ clusters forming their 16 e^- super atomic adducts

Swetashree Acharya [a], *Jayoti Roy* [a], *Diptendu Roy* [b], *Anupriya Nyayban* [a], *Amoghavarsha Ramachandra Kini* [a], *Biswarup Pathak* [b]* *and Thalappil Pradeep* [a]*

[a] *DST Unit of nanoscience and Thematic unit of excellence (TUE), Department of Chemistry, IIT Madras, India*
[b] *Department of Chemistry, IIT Indore, India*
E-mail: pradeep@iitm.ac.in

One of the most recently explored materials at nanoscale dimension belongs to the family of atomically precise clusters.[1-3] Their chemical reactions, a newly discovered aspect of their science, show a wide variety and diverse aspects such as kinetics and thermodynamics, which are being explored intensely in recent days.[4] Although alloy clusters synthesized by Intercluster reactions possess certain common structural features, they exhibit distinctly different reactivities in their substitution reactions.[5] New insights derived from such science will further enrich the area of nanoscale materials. The availability of ligand protected clusters with accurately known structures opened the possibility to explore their chemistry in greater details. Interparticle reactions in solution phase, like reactions between molecules, involving atomically precise noble metal clusters was discovered earlier from our group.[6] These reactions demonstrate that the nature of the metal−thiolate interface, that is, its bonding network and dynamics, play crucial roles in dictating the type of exchange processes and overall rates. This spontaneous process is driven by the entropy of mixing and involves events at multiple time scales. It shows that we can further enhance our knowledge of reaction mechanisms in nanoscale by studying cluster reaction in more details. In this work, we have done reactions between center doped $[MAg_{24}(DMBT)_{18}]^-$ (M= Ag, Au, Pd, and Pt) and $[Ag_{29}(BDT)_{12}]^{3-}$ nanoclusters, to gain more insights about the reactivity of different central atom doped Ag_{25} clusters.



References

1. Chakraborty, I.; Pradeep, T. *Chem. Rev*. 2017, 117, 8208−8271.
2. Jin, R.; Zeng, C.; Zhou, M.; Chen, Y. *Chem. Rev*. 2016, 116, 10346−10413.
3. Fang, J.; Zhang, B.; Yao, Q.; Yang, Y.; Xie, J.; Yan, N. Coord. *Chem. Rev*. 2016, 322, 1−29.
4. Krishnadas, K. R.; Baksi, A.; Ghosh, A.; Natarajan, G.; Som, A.; Pradeep, T. *Acc. Chem. Res.* 2017, 50, 1988−1996.
5. Khatun, E.; Chakraborty, P.; Jacob, B. R.; Paramasivam, G.; Bodiuzzaman, M.; Dar, W. A.; Pradeep, T. *Chem. Mater*. 2020, 32, 611-619
6. Chakraborty, P.; Nag, P.; Chakraborty, A.; Pradeep, T. *Acc. Chem. Res.* 2019, 52, 2−11

P45

Electrochemical Reduction of Nitrate to Ammonia: Method for upcycling of pollutant to a value-added product

*Sumanta Giri, Soniya Mariya Varghese, Anju V G and G Ranga Rao**
Department of Chemistry, IIT Madras
E-mail: grrao@iitm.ac.in

Ammonia is the second most produced chemical in the world, used as an indispensable chemical in various industries, as well as an effective material for hydrogen storage.[1] However, an energy-intensive method like the Haber-Bosch (HB)process is used in the industrial production of ammonia which results in the production of 300 million metric tons of CO_2 per year.[2] The renewable synthesis of ammonia using electrochemical reduction of molecular nitrogen is gaining popularity as a replacement for the current HB process. However, due to low solubility, high energy required to activate the inert nitrogen triple bond, competing hydrogen evolution reactions, etc., the electrochemical reduction of nitrogen results in low faradaic efficiency and low ammonia generation rate. As a result, various strategies have been used to improve the process, including increasing the solubility of N_2 by employing hybrid electrolytes[3] or by using alternative nitrogen sources[4] that have substantial solubility in electrolyte solvents, particularly in water. Nitrate being a major pollutant, especially in industrial and domestic sewage, can serve as an alternative source of nitrogen for the electrochemical synthesis of ammonia.[4] It is well known that wastewater can be treated electrochemically[4] to eliminate nitrate ions. Nitrate ions are more susceptible to reduction[5] than inert N_2 molecules due to their high solubility in water and low bond dissociation energy.[6] Additionally, the approach of electrochemical nitrate reduction to ammonia serves two purposes: it produces ammonia in a sustainable manner while also removing a significant water pollutant. But due to the different valence states in nitrogen, nitrate reduction results in a variety of products like N_2, NH_3, N_2H_4, NO_2^- etc. Thus, selectively producing ammonia via nitrate reduction is crucial and challenging.[4]
The experiment (Figure 1) involves the synthesis of a transition metal doped boron carbon nitride-based catalyst for nitrate reduction. The work involves carefully tuning the composition of BCN and transition metal to achieve the electrochemical reduction of nitrate to ammonia with high faradaic efficiency and high conversion rate.

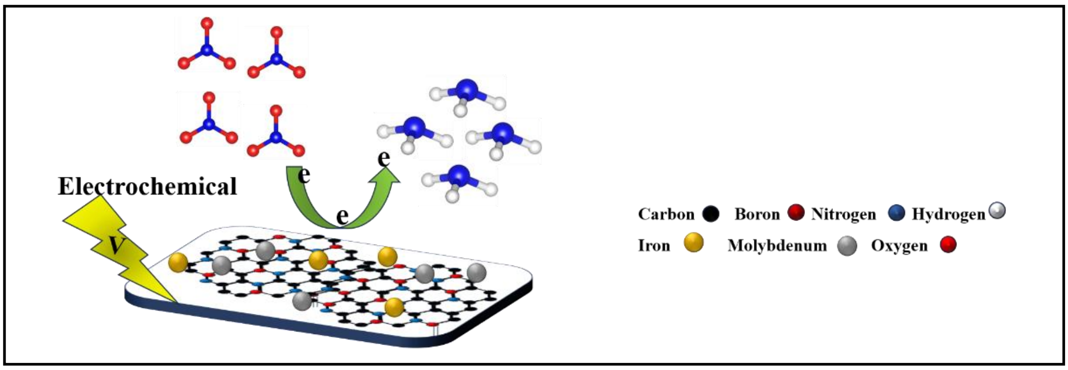


Figure.1. Electrochemical Reduction of nitrate to NH_3 using transition metal doped BCN as the catalyst.

References

1. Shelby, L. F.; Sergio, I. P. B; Royce, D. D.; Sharad, M.; Ross, D. M.; Shelley, D. M.; Michael, J.J.; Julie, N.R.; Lauren, F. G. *Nat. Catal.* **2018**, 1, 490.

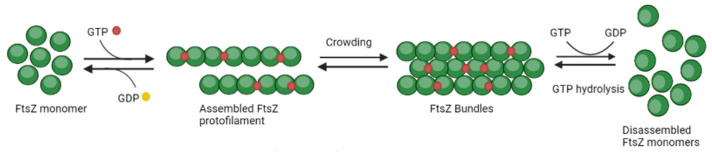
2. Humphreys, J.; Lan, R.; Shanwen, T. *Adv. Energy Sustainability Res*.**2021**,2, 2000043.
3. Ren, Y.; Yu, C.; Han, X.; Tan, X.; Wei, Q.; Li, W.; Han, Y.; Yang, J. *ACS Energy Lett.* **2021,** 6, 3844.
4. Zhen-Yu, W.; Mohammadreza, K.; Xue, Y.; Qizheng, H.; David, A. C.; Peng, Z.; Chuan, X.; Qunfeng, X.; Mohsen, S.; Feng-Yang, C.; Jung, Y. K.; Yang, X.; Kimberly, H.; Yongfeng, H.; Michael, S. W.; Qiling, L.; Gates, I.; Samira, S.; Haotian W. *Nat Commun.* **2021**,12, 2870.
5. Rao, G. R.; Mishra, B. G. *J. Porous Mater*. **2007**, 14, 205.
6. Dimitra, A.; Yvetee-van, B.; Emiel, J. M. H.; Figueiredo, M. C. *Electrochem Sci Adv* **2022,** 00, e2100220.

P46

In-vitro inhibitory targeting of the bacterial division protein, FtsZ, by small synthetic molecules

*Ragini Kumari, Suryakshi Bhunia, K.M. Muraleedharan, Hemachandra Kotamarthi**
Department of Chemistry, Indian Institute of Technology Madras
E-mail: hemachandra@iitm.ac.in

In spite of recent advances in our understanding of Mtb, it is difficult to find a cure for it. The fact that TB continues to develop antibiotic resistance is one of the main causes. Patients infected with a strain that is multi-drug resistant are essentially incurable. This stresses the requirement for fresh chemotherapeutic approaches. Division protein, FtsZ of the bacterial cytoskeleton is one of the novel targets for therapeutic drug discovery. It creates a "Z-ring" structure at the site of bacterial cell division, is essential for the division process. It has been studied for its potential as a target for treating Mycobacterium tuberculosis (Mtb) infections and addressing drug resistance, given the fact that it is not a key target for currently available anti-tuberculosis medications. FtsZ is a crucial protein for cell division in Mtb, and blocking it may prevent bacteria from replicating and growing.



Assembly and disassembly of FtsZ

FtsZ is a filamenting temperature-sensitive Z-ring protein. It has structural similarity with α-β tubulin.. FtsZ structure has two important domains – 1. N-terminal domain and 2. C-terminal domain. N-terminal domain is involved in FtsZ polymerization, forming filaments that make up the Z-ring. It contains a GTP-binding site, which is essential for the assembly and disassembly of FtsZ filaments. The later one, also called GTPase domain, contributes to FtsZ ring formation and stability. FtsZ is a GTP-binding protein and notably, the generation time/division time of bacteria depends on the GTPase activity of FtsZ. In the absence of Z-ring formation, the cell undergoes continuous growth, which enlarges the cell and makes it sensitive to the environment, causing cell lysis. In order to inhibit cell division, the GTPase activity or polymerization of FtsZ has to be disturbed. In this regard, the drugs that can affect the interaction between FtsZ monomers can be very useful antibiotics. Our aim is to understand the mechanism of interaction of small synthetic molecules that can inhibit the FtsZ assembly. We will analyze the chemical properties, binding sites, mechanism of action using in-vitro and in-silico methods. Further, we will also characterize the biophysical properties of FtsZ protofilaments.

References

1. Chen Y, Anderson DE, Rajagopalan M, Erickson HP. Assembly Dynamics of Mycobacterium tuberculosis FtsZ *. J Biol Chem. 2007;282(38):27736–43.
2. Hurley KA, Santos TMA, Nepomuceno GM, Huynh V, Shaw JT, Weibel DB. Targeting the Bacterial Division Protein FtsZ. 2016; 59(15): 6975–6998.
3. Hemaiswarya S, Soudaminikkutty R. Phenylpropanoids inhibit protofilament formation of Escherichia coli cell division protein FtsZ Printed in Great Britain. 2011;1317–25.
4. White EL, Ross LJ, Reynolds RC, Seitz LE, Moore GD, Borhani DW. Slow Polymerization of Mycobacterium tuberculosis FtsZ. 2000;182(14):4028–34.

P47

STUDY OF METAL OXIDE MONOLAYERS ON TRANSITION METAL CHALCOGENIDES FOR SUPERCAPACITOR APPLICATIONS

K. Thejasree[ab], M. L. Aparna[a], G. Ranga Rao[a]*, K. T. Ramakrishna Reddy[b]*.

[a]*Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.*

[b]*Solar Photovoltaic Laboratory, Department of Physics, Sri Venkateswara University, Tirupati, 517502, India.*

Ternary selenides are promising electrode materials for supercapacitors on account of their higher electronic conductivity, multiple oxidation states and better electroactivity. However, it is crucial to strategically engineer the electrode materials as nanostructured hybrid composites to achieve enhanced charge storage performance. Herein, we experimentally explore the electrochemical charge storage characteristics of $MoO_3@NiCo_2Se_4$ nanostructure. $MoO_3@NiCo_2Se_4$ is synthesized via hydrothermal route coupled with ball milling, varying the milling duration from 0 to 6 h. The $MoO_3@NiCo_2Se_4$ nanostructures obtained from 4-hour ball milling process, demonstrates optimal conditions for achieving uniform monolayer dispersion of polymeric molybdates on $NiCo_2Se_4$ nanostructures. The specific capacities obtained from 3-electrode electrochemical cell measurements are 147 C g^{-1}, 344 C g^{-1} and 476 C g^{-1}, respectively, for MoO_3, $NiCo_2Se_4$ and $MoO_3@NiCo_2Se_4$ nanostructures at 2 A g^{-1}. This study highlights the significance of MoO_3 monolayers in tuning the functional characteristics of $NiCo_2Se_4$ nanostructures for charge storage applications. The newly developed material shows significant promise as electrode material for further exploration and real-world implementation within the energy storage sector.

P48

Kinetics of OH-initiated Reaction of Allyl trifluoroacetate in the Troposphere

Fredy Joy and Rajakumar Balla
Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036.
e-mail: rajakumar@iitm.ac.in

Hydrofluoroethers (HFE) are widely synthesized and used as replacements for chlorofluorocarbons, hydrochlorofluorocarbons and hydrofluorocarbons in a variety of applications.[1] The reaction of HFE with OH radicals lead to the formation of fluorinated esters (FES). FES are have also seen potential uses as solvents in Li-ion batteries.[2] One such FES is allyl trifluoroacetate (ATA). The temperature-dependent kinetics of the reaction of ATA with OH radicals were measured using the Pulsed Laser Photolysis-Laser Induced Fluorescence (PLP-LIF) technique in the range of 268 – 363 K at 50 Torr/N_2 of total pressure. The OH radicals were generated by photolyzing concentrated hydrogen peroxide (H_2O_2) at 248 nm and were subsequently probed at 281.9 nm. The pseudo-1st order rate coefficients, which were obtained from the kinetic decay plot of LIF intensity from the OH radicals (Figure 1) at various concentrations of ATA, were used to calculate the absolute rate coefficients of the title reaction. The rate coefficient at room temperature was measured to be k_{ATA} (298 K) = $(1.21 \pm 0.07) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} which is in good agreement with the value reported by Rodriguez et al.[3]

To gain further details into the reaction kinetics, the temperature-dependent rate coefficients were also computed using canonical variational transition-state theory with small-curvature tunnelling (CVT/SCT) and interpolated single-point energies (ISPE). The parameters obtained were also used to compute the implications of the title reaction in the atmosphere viz. cumulative atmospheric lifetimes, radiative forcing (RF) and global warming potentials (GWP).

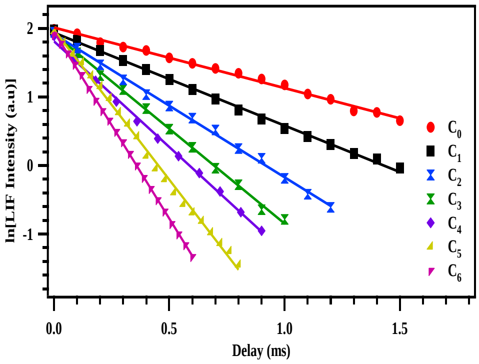


***Figure 1**. Pseudo-1st order kinetic decay of LIF intensity from excited OH radicals due to its reaction with ATA at*

References

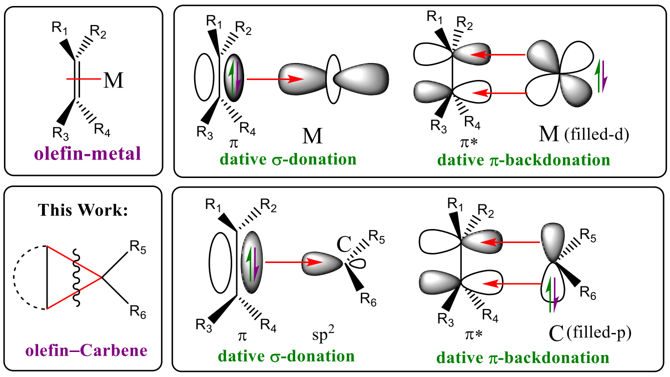
1. Tsai, W. T. *J. Hazard. Mater*. **2005**, *119*, 69–78.
2. Lu, W.; Xie, K.; Pan, Y.; Chen, Z.; Zheng, C. *J. Fluorine Chem*. **2013**, *156*, 136–143.
3. Rodríguez, A.; Bravo, I.; Rodríguez, D.; Tajuelo, M.; Diaz-de-Mera, Y.; Aranda, A. *RSC Adv*. **2016**, *6*, 21833–21843.

THEORITICAL & COMPUTATIONAL CHEMISTRY
(P49-P56)

Unveiling the Bonding in Cyclopropane Derivatives: Insights from EDA-NOCV Analysis

Sonam Suthar[a] *and Kartik Chandra Mondal**
[a]*Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu*
E-mail: csdkartik@iitm.ac.in

For over a hundred years, the reactivity of a three-membered cyclic compound consisting of a C3 ring (cyclopropane derivatives) has fascinated both synthetic and theoretical chemists. Several bonding models, such as the Bent-Bond model and the Walsh model, have been proposed and continue to be the subject of debate[1]. We have investigated a diverse set of organic compounds with various functional groups attached to them. The energy decomposition analysis coupled with natural orbital for chemical valence (EDA-NOCV)[2-3] is employed to gain a deeper understanding of the bonding characteristics and to propose a more general bonding model for this class of compounds. The results of the analysis revealed that, out of the 49 compounds studied, the majority (37/49) exhibited a preference for the formation of two dative covalent bonds within the cyclopropane ring. These bonds were found to occur between a singlet olefin and an excited singlet carbene, involving a vacant sp^2 orbital and a filled p-orbital. In some cases (7/49), two-electron sharing bonds between an excited triplet olefin and triplet carbene were observed. Additionally, a small number of compounds (5/49) exhibited flexibility, with the ability to adopt either sharing or dative covalent bonding. The findings from their bonding analyses were consistent with the results obtained through Quantum Theory of Atoms in Molecules (QTAIM) analyses. The interaction between the olefin-carbene group can be likened to the interaction observed in olefin-metal systems, as depicted in the figure below. In both cases, there is a transfer of electrons, with the olefin donating a sigma (σ) bond to the metal/carbene and the metal/carbene reciprocating by back donating a pair of electrons through a pi (π) bond to the olefin respectively.



References

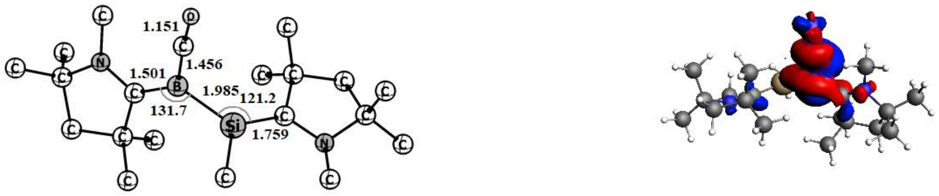
5. Craig, A. J.; Hawkins, B. C.; *Synthesis*, **2016**, *51*, A-M.
6. Mitoraj, M.; Michalak, A. *Organometallics* **2007**, *26*, 6576.
7. Michalak, A.; Mitoraj, M.; Ziegler, T. *J. Phys. Chem. A*, **2008**, *112*, 1933-1939.

P50

Exploring Sila/Germa Boryne Species: Analysis of Stability and Binding Efficiency Of CO/N_2 by EDA-NOCV Method

*Harsha S. Karnamkkott, Sujit Das and Kartik Chandra Mondal**
Indian Institute of Technology Madras, Chennai, 600036
E-mail: csdkartik@iitm.ac.in

The inability of p-block elements to participate in π back bonding restricts them from activating small molecules like CO, H_2 etc. However, the development of the Main-group metallomimetics became a new pathway where main-group elements like boron can bind and activate small molecules like CO and H_2. The concept of the Frustrated Lewis pair, Boron-Boron multiple bonds and Borylene are some of the reported classes of Boron metallo mimetics. Hence, we have theoretically modelled and studied CO/N_2 complexes coordinated to elusive species like sila/germa boryne[1] stabilised by donor base ligands (cAAC)BE(Me)(L), where E = Si, L = cAAC^{Me}, NHC^{Me}, PMe_3, E = Ge, L = cAAC^{Me} and (NHC^{Me})BE(Me)(cAAC^{Me})). The substitutional analogue of (cAAC^{R})BSi^{R1}(cAAC) and E = P, L = cAAC^{Me}) are also modelled to carbonyl complexes and considered under the DFT, NBO, QTAIM and EDA-NOCV[2] study. The EDA-NOCV analysis demonstrated stronger binding of CO than N_2. Also, an effective back bonding was analysed for carbonyl complexes of (NHC^{Me})B(CO)E(Me)(cAAC^{Me}) species. The Transition state and Kinetic study for CO/N_2 bond was also employed. The kinetic study done with the help of KiSThelp also indicated a slower reaction rate for nitrogen binding. The change of partial triple bond character to single bond nature of the B−Si bond reveals such species' ability to bind and activate the carbonyl ligand, thus mimicking the transition metals.



A B

Figure. A) The optimised geometry of CO complex at M06-2X/Def2-TZVPP. B) The deformation density denoting CO to B sigma donation from EDA-NOCV calculation at M06-2x/TZ2P level

References

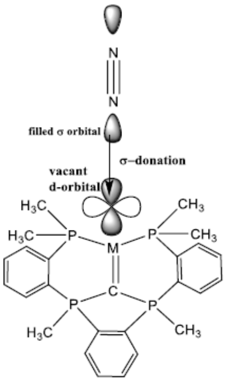
1. Das, S.; Devi, K.; Suthar, S.; Mondal, K. C. *J. Comput. Chem.* **2022**, *44*, 1673.
2. Morokuma, K. *J. Chem. Phys.* **1971**, *55*,1236.
3. Zeigler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

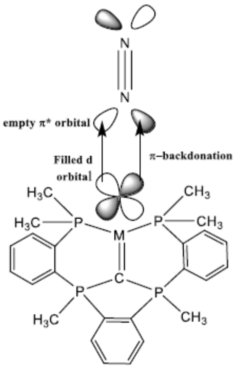
P51

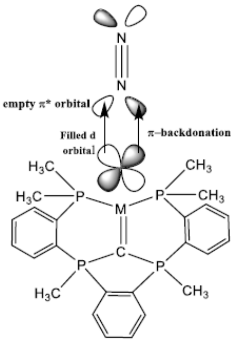
Bonding and Stability in Carbone−M−N_2 Complexes Relevant to FeMoco of Nitrogenase using EDA-NOCV Analyses: N_2 activation

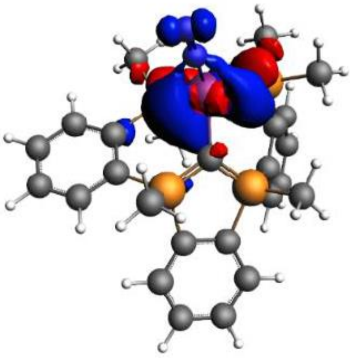
Sonia, and Kartik Chandra Mondal
IIT Madras, Chemistry Department
E-mail: soniadhull9191@gmail.com

The binding, activation, and reduction of N_2 to NH_3 by FeMoco of nitrogenase involve complex structural features. The complete mechanism of N_2 activation and role of interstitial C(4-)-atom have not been fully understood. Although several complexes have been studied before. In this thesis complete bonding scenario of M−N_2 and C(0)→M for (similar to Fe-sites of FeMoco) , a series of single dinitrogen bonded [(P_2-CDP)M(Mn/Fe/CoNi)−N_2] complexes (**1-4**) and double dinitrogen bonded [(P_2-CDP)M(Mn/Fe/Co/Ni)−$(N_2)_2$] complexes (**5-8**) with different 3d-metals/spin states containing a coordinated σ- and π-donor C(0)-atom which possesses eight outer shell electrons [carbone, $(Ph_3P)_2$→C(0);] and two phosphine ligands, have been studied by DFT, QTAIM46, and EDA-NOCV calculations. Bonding and interactions between M−N and C(0)−M has been investigated to get the information about extent of M→N_2 π-back donation and role of C(0)-atom in N_2 activation. Carbone increases the significant electron density on metal. Hence carbone play significant role in N_2 activation. Among the single dinitrogen bonded complexes (**1- 4**) cobalt shows maximum M→N_2 π-back donation (71.5%) and among doubly dinitrogen bonded complexes (**5-8**) manganese shows maximum M →N_2 π-back donation (87.9%).









References

1. ADF2017, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
2. G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, Chemistry with ADF. *J. Comput. Chem*. **2001**, *22* (9), 931-967.

P52

“AB stacked bilayer β_{12} borophene as anode material for Alkali- metal ion batteries: A first-principles study.”

Ankita Narwal,[1,2] *Subhadeep Banerjee,*[1,3] *and Sharma S. R. K. C. Yamijala*[1,2,3,4,*]

1. Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600036 India.
2. Centre for Atomistic Modelling and Materials Design, Indian Institute of Technology Madras, Chennai 600036, India.
3. Centre for Quantum Information, Communication, and Computing, Indian Institute of Technology Madras, Chennai 600036, India.
4. Centre for Molecular Materials and Functions, Indian Institute of Technology Madras, Chennai 600036, India.
E-mail: yamijala@iitm.ac.in

As the lightest 2D- material, monolayer borophene is found to exhibit a theoretical capacity as high as 1860 mAh g^{-1} for Li-ion batteries, which is four times higher than that of graphite and is one of the highest specific charge capacities ever reported on 2D sheets. Additionally, it showed high mechanical strength and a low diffusion barrier. However, borophene suffers from stability issues in its free-standing form and requires metal substrates for growth, which restricts the real-life applications of borophene. In this work, using first-principles calculations, we investigated the AB stacked bilayer β_{12} borophene and found it to be both energetically and dynamically stable, making it a promising candidate to exist in free-standing form. We further carried out the DFT calculations to investigate its potential as a high-performance anode material for alkali metal ion batteries. We find that it shows good electrical conductivity before and after the metal (Li/Na/K) adsorption. Further, AB stacked bilayer β_{12} borophene demonstrates strong adsorption energy (-0.89 to -1.44 eV /atom) and suitable average OCV (0.43 to 0.65 V), which plays a crucial role in preventing the dendrites formation and enhancing the battery’s cycle life. Moreover, the diffusion barrier as low as (0.13-0.49 eV) also meets the fast charge/discharge rate requirements. Our findings indicate that AB stacked bilayer β_{12} bilayer borophene could achieve a theoretical capacity upto (204.4 to 304.5 mAh g^{-1}), which is comparable to graphite (372 mAh g^{-1}). All the above findings suggest that the AB stacked bilayer β_{12} borophene can be a potentially favorable anode material.

Accurate Bond Dissociation Energies of Various Per- and Polyfluoroalkyl Substances: Achieving Chemical Accuracy Using Connectivity-Based Hierarchy Schemes

Samir Kumar Nayak,[1,2] *and Sharma S. R. K. C. Yamijala*[1,2,3,4,*]
1. Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600036 India.
2. Centre for Atomistic Modelling and Materials Design, Indian Institute of Technology Madras, Chennai 600036, India.
3. Centre for Molecular Materials and Functions, Indian Institute of Technology Madras, Chennai 600036, India.
4. Centre for Quantum Information, Communication, and Computing, Indian Institute of Technology Madras, Chennai 600036, India.
E-mail: yamijala@iitm.ac.in

Per- and poly-fluoroalkyl substances (PFASs) represent a class of chemical compounds extensively used across various industries due to their unique hydrophobic and oleophobic nature and exceptional thermal and chemical stability.[1,2] Despite their widespread industrial application, the inherent danger of PFASs to ecosystems and human health is a serious concern. Human exposure to PFASs primarily occurs through dietary intake and drinking water. The current situation demands addressing the environmental persistency of PFASs and accumulation within food chains, necessitating effective degradation strategies. The challenge in breaking down PFASs is due to the robust stability of the C–F bond. Predicting the activation barriers for their degradation can be facilitated by estimating accurate bond dissociation energies (BDEs). However, achieving reliable BDEs with density functional theory (DFT) is inconsistent as the sensitivity of DFT results depends on the functional and basis set choices.[3] Our study aims to determine BDEs for an extensive array of PFASs with high accuracy (~1 kcal/mol). To attain this level of accuracy, we employ the well-regarded quantum chemistry composite approach, G4, in conjunction with a connectivity-based hierarchy (CBH).[4] The CBH scheme offers a promising route in achieving BDEs within the 1 kcal/mol range. To enhance chemical accuracy, we have introduced a modified version of the CBH protocol called modified CBH (mCBH). By benchmarking mCBH with G4 energy values, we validated the performance of the mCBH scheme and compared it with the conventional CBH. Applying the mCBH protocol, we successfully calculated accurate BDEs for various C–C, and C–F bonds within a selected set of PFASs. This research contributes to a deeper understanding of PFAS degradation pathways and offers a robust computational approach to evaluate bond dissociation energies, ultimately addressing the environmental impact of these persistent compounds.

References

1. Manzetti, S.; van der Spoel, E. R.; van der Spoel, D. Chemical Properties, Environmental Fate, and Degradation of Seven Classes of Pollutants. *Chem. Res. Toxicol.* **2014**, *27* (5), 713–737.
2. Yamijala, S. S. R. K. C.; Shinde, R.; Wong, B. M. Real-Time Degradation Dynamics of Hydrated per- and Polyfluoroalkyl Substances (PFASs) in the Presence of Excess Electrons. *Phys. Chem. Chem. Phys.* **2020**, *22* (13), 6804–6808.
3. Zhao, Y.; Truhlar, D. G. How Well Can New-Generation Density Functionals Describe the Energetics of Bond-Dissociation Reactions Producing Radicals? *J. Phys. Chem. A* **2008**, *112* (6), 1095–1099.
4. Ramabhadran, R. O.; Raghavachari, K. Theoretical Thermochemistry for Organic Molecules: Development of the Generalized Connectivity-Based Hierarchy. *J. Chem. Theory Comput.* **2011**, *7* (7), 2094–2103.

P54

Charge transfer dynamics: A quantum mechanical approach

Deboki Reja, *Sanjay Kumar**

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
E-mail: sanjay@iitm.ac.in

The most prominent events in the interstellar medium, cometary atmosphere, and upper planetary atmosphere are ion-molecule collisions. These collisions may lead to elastic and inelastic rotational-vibrational excitations and charge transfer. We have carried out an elaborate study on the ion-molecule charge transfer reaction. The dynamics of these ion-molecule collisions are mostly found to evolve on highly coupled electronic potential energy surfaces. First, we have identified the various (excited) electronic states of the diatom going through the collision[1]. It is observed that the non-adiabaticity plays a dominant role in most of the cases. Our calculated results were found to be in accordance with the early available experimental data in the literature[23]. Experiments on the charge transfer scattering dynamics were carried out by the various research groups[45]. In the next phase of our study, we are focusing on calculating various dynamical attributes such as; scattering amplitudes, integral cross sections, and differential cross sections.

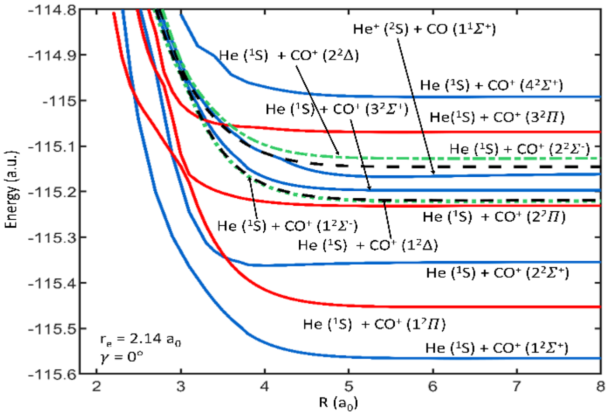


Figure 1. *Ab initio* adiabatic PECs of $(HeCO)^+$ system for the collinear geometry as function of R at $r_e = 2.14\ a_0$.

References

1. Reja, D.; Kumar, S. *Chem. Phys. Lett.* **2023**, *822*, 140535.
2. Dowek, D. *Phys. Rev. A* **1983**, *28* (5), 2838–2850.
3. Werbowy, S.; Kowalski, A.; Pranszke, B. *Chem. Phys. Lett.* **2015**, *641*, 136–140.
4. Gao, R. S.; Johnson, L. K.; Hakes, C. L.; Smith, K. A.; Stebbings, R. F. *Phys. Rev. A*, **1990**, 41, 5929.
5. Kusakabe, T.; Kitamuro, S.; Nakai, Y.; Tawara, H.; Sasao, M. *Plasma Fusion Res.* **2012**, *7*, 2401062.

Quantum Chemical and Microkinetic Investigation of the Mechanism of Formation and Structure of Humins: Applications to Cellulose-Based Biofuel Production

*Jogeswar Chhatria, Swetha Nair, Sankari N. Sunil, and Sooraj Kunnikuruvan**

Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600036

E-mail: soorajk@iitm.ac.in

Cellulose-based biofuel production is one of the key alternatives for non-renewable fossil fuels. Biofuel production from cellulose consists of the depolymerization of cellulose to glucose followed by glucose dehydration to form 5-hydroxymethylfurfural (HMF) with fructose as an intermediate. In addition to its potential as a biofuel precursor molecule, HMF is a vital platform chemical for diverse applications.[1,2] However, glucose to HMF conversion is known to have a very poor yield, especially in aqueous media.[3] This can be ascribed to the formation of various side products during glucose dehydration to HMF. Among the side products identified, humins, a blacked-colored tarry polymeric material, was found to be the major component.[4,5] Therefore, reducing humins formation is critical for improving the yield of HMF,

In this regard, we investigated the structure and mechanism of the formation of humins from glucose and fructose under acid-catalyzed conditions using density functional theory (DFT) based computations and microkinetic analysis. The results of this study indicate that pathways leading to the direct conversion of glucose/fructose to humins are insignificant. In contrast, the path involving acetal intermediate was found to contribute significantly. The results of these studies could explain most of the experimental observations and address the controversy over the structure of humins.[6] In addition to critical insights into the structure and the mechanism of the formation of humins, this study also suggests a catalytic system that can enhance the yield of HMF from glucose/fructose.[7]

References

1. Mascal, M.; Nikitin, E. B. Direct, *Angew. Chem., Int. Ed.* **2008**, *47*, 7924–7926.
2. Galbe, M.; Zacchi, G. *Appl. Microbiol. Biotechnol*. **2002**, *59*, 618–628.
3. Jing, Q.; Lu, X. Chin. *J. Chem. Eng*. **2008**, *16*, 890.
4. Girisuta, B.; Janssen, L. P. B. M.; Heeres, H. J. *Ind. Eng. Chem. Res*. **2007**, *46*, 1696–1708.
5. Patil, S. K. R.; Heltzel, J.; Lund, C. R. F. *Energy Fuels* **2012**, *26*, 5281–529.
6. Patil, S. K. R.; Lund, C. R. F. *Energy Fuels* **2011**, *25*, 4745–475.
7. *Jogeswar C.*, Swetha N., Sankari N. S., Sooraj K., *Manuscript under preparation*

P56

Lithium-Ion Solvation Structure in Carbonate-based and Ether-based Electrolytes for Lithium-Ion Batteries: Insights from Ab Initio Molecular Dynamics and Metadynamics Simulations

*Madhurja Buragohain and Sooraj Kunnikuruvan**

Department of Chemistry, Indian Institute of Science and Technology, Madras,
Chennai-600036
E-mail: soorajk@smail.iitm.ac.in

The electrode-electrolyte interface (EEI) formed by the decomposition of electrolytes on the electrode surface was found to have a crucial role in determining the performance of Li-ion batteries (LIBs).[1-3] An ideal EEI is a uniform protective layer, which allows the passage of ions and prevents further decomposition of an electrolyte by insulating electron conduction. The EEI formed on the anode surface is popularly known as the solid electrolyte interface (SEI). The critical factors that contribute to the kinetics of formation and the structure of the SEIs are the interaction of the electrolyte with the electrode surface as well as the interaction between ions and solvents that are part of the electrolyte.[5] Thus, to understand the mechanism of formation and the structure of SEI, it is vital to know the structure of the electrolyte. We noted from the literature that there are disparities over the structure of some of the commonly used electrolytes in LIBs, especially on the solvation structure. Moreover, the presence of Li-F bonds observed in some of the recent experimental studies was found to contradict previous experimental and computational studies where the anionic part of $LiPF_6$ was reported/considered to be outside the first coordination shell of Li ions.[6]

In this regard, we employed ab initio molecular dynamics (AIMD) simulations in conjunction with metadynamics simulations to scrutinize the Li-ion solvation structure of some of the commonly used electrolytes formed between carbonate-based and ether-based solvents with $LiPF_6$ salt. Our simulations indicate the presence of Li-F-P bridged complexes in the electrolyte. This study also brings light to the effect of the solvation structure of these electrolytes on their reactivity towards oxidation/reduction. The results of this study provide crucial information on the factors that are to be considered while employing interface engineering for developing high-performance batteries.

References

1. Wu, F.; Maier, J.; Yu, Y. *Chem. Soc. Rev* **2020**, *49*, 1569–1614.
2. Oh, S. M.; Song, J.; Lee, S.; Jang, I.-C. *Electrochim. Acta.* **2021**, *397*, 139269.
3. Goodenough, J. B.; Kim, Y. *Chem. Mater.* **2010**, *22*, 587–603.
4. An, S. J.; Li, J.; Daniel, C.; Mohanty, D.; Nagpure, S.; Wood, D. L. *Carbon* **2016**, *105*, 52–76.
5. Chen, X.; Li, H.-R.; Shen, X.; Zhang, Q. *Angrew. Chemie. Int.* **2018**, *57*, 16643–16647.
6. Chen, X.; Yao, N.; Zeng, B.-S.; Zhang, Q. *Fundam. Res.* **2021**, *1*, 393–398.

Major sponsorship

1. Digital Skill Academy
2. Teaching Learning Centre (TLC), IIT Madras, Chennai 600036