

Research Scholars Day – 2023 – Oral Presentations (15th April 2023)

09:30	Inauguration: Head, Department of Chemistry	
	Chair: Dr. Ritika Gautam	
09.40	Abhishek K. Yadav	Advanced nitrogen-rich energetic materials: Facile Synthesis and Energetic Performance
10.00	Sikha Gupta	Facile formation of a Mn(III)-O-Ce(IV) species and its electron transfer equilibria with high valent Mn(IV)(OX) (X = Sc or H) complexes
10.20	Shitanshu Bajpai	Temperature Accelerated Sliced Sampling using OpenMM
10.40	Dharmendra Yadav	Design and Discovery of Chloroacetamide based anticancer drugs via Electrophile-First Approach
11.00-12.00	Tea + Poster session I (Odd number posters)	
	Chair: Dr. Venkata Suresh Mothika	
12.00	Suchismita Gosh	Investigating the Photosensitivity of Koneramines for Cell Imaging and Therapeutic Applications
12.20	Manorama Dey	Probing Virus Binding to Giant Plasma Membrane Vesicles with Fluorescence Microscopy Technique
12.40	Ganesh Chandra Upreti	Pd-Catalyzed Photochemical Alkylative Functionalization of C=C and C=N Bonds
13.00-14.40	Lunch Break	
	Chair: Dr. Parthasarathi Subramanian	
14.45	Shuvadip Ghosh	Quantum Thermal Switch and Rectifier
15.05	Ashwini Kumar	Copper(II) Complexes of 2-hydroxybenzaldehyde Analogues Facilitating Chemodynamic Therapy via Glutathione-Depletion and Lipid Peroxidation
15.25	Manish Kumar	(A) Triphenylamine and terpyridine–zinc(II) complex based donor–acceptor soft hybrid as a visible light driven hydrogen evolution photocatalyst. (B) A fascinating strategy for the Development of efficient heterogeneous photocatalysts in organic synthesis.
15.45	Ritu Gupta	Proton-coupled electron transfer combined redox process showcasing supercapattery in Cu(tpy) ₂ thin films
16.05	Pooja Aggarwal	Energy Funneling from Water-Dispersed Perovskites to Chromophores
16.25-17.25	High Tea + Poster session II (Even number posters)	
	Chair: Dr. Dharmaraja Allimuthu	
17.30-18.15	Prof. Nisanth N. Nair	Exploring Rugged Energy Landscapes of Chemical Reactions
18.15	Vote of thanks	

RSD-2023 Poster Presentations

(Odd Number: 11.00-12.00 and Even Number:16.25-17.25)

SL	Name	Title of the Poster
1	Sona Tiwari (DA)	Modulating reactivity of isatoic anhydrides between lysine and cysteine using chemical handles
2	Sai Kumari Vechalapu (DA)	Iron complexation-driven mitochondrial impairment triggers caspase-cascade and apoptosis in cancer cells
3	Parkhi Sharma (AD)	Mechanistic insight of (μ -Peroxo)(μ -hydroxo)dicobalt(III) Complexes supported by electron-rich Tris(2-pyridylmethyl)amine Ligands
4	Raju Eerlapally (AD)	Spectroscopic characterization and reactivity of a putative Cu(III)-OH species supported by a proline-based pseudo peptide
5	Ritama Kar (NN)	Modelling Chemical Reactions using Molecular Dynamics at the Fourth Rung of DFT Functionals
6	Shreyasi Banik (SD)	Synthesis, characterization, testing, and detonation performance studies of fused pyrazole-based fluorescent energetic materials
7	Parasar Kumar (SD)	Facile synthesis of thermally stable tetrazolo[1,5-b][1,2,4]triazine substituted energetic materials: Synthesis and characterization
8	Manajit Mandal (PCM)	Circular Polarized Light-Enabled Chirality Regulation of Nickel-Cysteine Nanoparticles
9	Neha Singh (PCM)	Giant electron transport properties of functionalized superparamagnetic nanoparticles
10	Hariom Birla (TG)	Effect of functional group on the switching efficiency of Azobenzene derivatives on graphite
11	Richa Arjariya (TG)	Dynamic Polymorph formation of a Trimesic acid derivative at solid liquid interface
12	Abhijit Dutta (PS)	Photophysics of thiocoumarin 1 (TC1) in bulk solvent media and effect of encapsulation inside the OA cavity
13	Kuldeep Singh Negi (PS)	Associated Water Modulation might explain the Protein-specific effect of Osmolyte
14	Shivangi Gupta (SKK)	CuO NPs catalyzed synthesis of quinolines, pyridines, and pyrroles via dehydrogenative coupling strategy
15	Siddharth Singh (VGR)	Interfacial hole transfer dynamics between CsPbBr ₃ perovskite nanocrystals and functionalized ferrocene derivatives
16	Kajal Chaudhary (RG)	Broad Spectrum Antimicrobial Metallopharmaceutical Agents Targeting MRSA and VRSA
17	Ayushi Chaudhary (RG)	Cellular Accumulation and Endoplasmic Reticulum-Localized Iridium(III) Complexes as Efficient Photodynamic Therapy Agents
18	Nidhi Gupta (MR)	Growth Of Silicene On Ag(111) Surface: A Kinetic Monte Carlo And DFT-Based Study
19	Shantanu Sen (SV)	Palmitoylated peptide conjugate: an excipient for averting insulin fibrillation
20	Ankita Jaiswal (SV)	Single-platform, attomolar detection of multiple biomarkers by flexible SERS sensors
21	Priya (MS)	On the Pauli potential for open shell systems.
22	Krishna Kant Singh (DG)	Examining Sample Chamber Site - selectivity in Femtosecond Optical Trapping.
23	Deepak Kumar (DG)	Theoretical Investigation on Multi-particle Femtosecond Optical Trapping.

24	Riya Gupta (DM)	Cooperativity between intermolecular hydrogen and carbon bonding interactions
25	Sujan Singha (DM)	Building a helium nanodroplet spectrometer for studying chemistry at ultracold temperatures
26	Sanjay Choudhary (JKB)	Acceptorless dehydrogenation of primary alcohol to acid salt catalyzed by bifunctional Cobalt(II) Complex
27	Moumita Patra (JKB)	Hemilability-Driven Regioselective Cyclotrimerization of Alkynes by a Pincer Ni(II)-NHC Complex
28	Prabhakar Kumar Pandey (JKB)	An Efficient Ni(II) Pincer NHC Catalyst for the Borylation of Alkyl and Aryl Halides
29	Anjali (GA)	Cd(4,5-Imdb) MOF with Lewis sites for the Synthesis of α -Amino Nitrile and Picric acid Sensing.
30	Rhitwika (GA)	Co(III)-NHC complexes as novel catalysts for selective cycloaddition of carbon dioxide to epoxides.
31	Dolly Chandel (SPR)	Modulation of Supramolecular Chirality by Stepwise Axial Coordination in a Nano Size Zn(II)porphyrin Trimer
32	Paulami Chakraborty (SPR)	Diheme Cytochrome c: Effect of Heme-Heme Interactions on the Spin State of Iron
34	Nitin Shukla (AKP)	Time-Resolved luminescence-based Europium(III) Sensor for Selective detection of high-energy physiological phosphates and G-series chemical warfare mimics
35	Subhankar Pradhan (BS)	Allenyl Carbonate as Butadiene Surrogate in Cobalt-Catalysed Crotylation of Aldehydes
36	Bholanath Garai (BS)	Cp*Co(III)-Catalyzed C(8)-Nucleophilic Cascade Cyclization of Quinoline N-Oxide with 1,6-Enyne
37	Bharat Singh (MKG)	<i>Catalytic Aminium Radical-Cation Salt Induced, Autocatalytic SN2-type Ring-Opening transformations of Aziridines with O/S/N/C-Nucleophiles & ROC Applications/Formal Synthesis of (R)-Halostachine.</i>
38	Suraj (MKG)	<i>A Synthetic Route to Polyheterocyclic spiro-Oxindoles via Friedel-Craft type C-3 Alkylation/Pictet-Spengler Reactions of Indoles with spiro-Epoxy oxindoles/Aldehydes, and Study of their non-linear Properties.</i>
39	Juhi (AKP)	Quaternary Ru(ii) complexes of terpyridines, saccharin and 1,2-azoles: effect of substituents on molecular structure, speciation, photoactivity, and photocytotoxicity
40	SHIVANI ARORA (AS)	Polyhalogenated and Deuterated Dihydroisoquinolinones from Alkyl Halides: Haloalkyl Radical Generation <i>via</i> Visible light Mediated Halogen Atom Transfer
41	N. S. Reddy (AS)	Photocatalytic, Intermolecular Olefin Alkylcarbofunctionalization Triggered by Haloalkyl Radicals Generated <i>via</i> Halogen Atom Transfer
42	Kavita (VKS)	Kinetic Resolution of Electron Deficient Bromohydrins <i>via</i> Cu(II) Catalysed C-C Bond Cleavage
43	Khushboo (VKS)	Enantioselective Dearomative [4+2] Cycloaddition Reaction of 1-Naphthols with In-situ Generated ortho-Quinone Methides
44	Abhilash Chandra (AC)	Theoretical Vibrational Sum Frequency Generation Spectroscopy of Liquid-Vapour Interfaces of Aqueous Solutions of Monovalent and Divalent Metal Nitrates
45	Himanshu Kumar Vishwakarma (AC)	Terahertz spectrum of aqueous solutions of divalent metal chlorides from molecular simulations using polarizable models

Exploring Rugged Energy Landscapes of Chemical Reactions

Nisanth N. Nair*

Molecular Dynamics (MD) simulation techniques have transpired as a powerful computational tool to predict mechanism and free energetics of chemical reactions, and structural transformations in soft matter systems. However, several challenges remain, especially in modelling complex enzymatic reactions. We introduced a set of novel methods to address these challenges. We applied our methods to study the mechanism of antibiotic resistance due to β -lactamases. Of major concern, these enzymes can efficiently hydrolyze most of the β -lactam antibiotics, including the carbapenem group of antibiotics that are the last-reserved therapeutics for infections caused by multidrug-resistant bacteria. Based on the molecular-level understanding of the hydrolysis mechanism obtained from our simulations and computation of the underlying free energy landscapes, we propose a set of novel β -lactamase inhibitors against β -lactamases.

Advanced nitrogen-rich energetic materials: Facile Synthesis and Energetic Performance

Abhishek Kumar Yadav, and *Srinivas Dharavath**

To fulfil the requirements of energetic materials research, synthesis of new compounds with improved energetic performance and lower sensitivity to heat, shock, impact, and friction has attained considerable attention in recent interest. One of the most attractive strategies for preparing highly dense and thermally stable energetic compounds is to comprise nitrogen-rich azoles in the framework due to their synthetic accessibility. In this study, we have reported different series of high performing energetic materials and salts based on pyrazole-oxadiazole, pyrazole-triazole and triazole-oxadiazole with different explosophoric groups, which were designed and synthesized in a simple and straightforward manner. All the newly synthesized compounds were fully characterized by IR, ESI-MS, multinuclear NMR spectroscopy, elemental analysis, and thermogravimetric analysis–differential scanning calorimetry measurements. Further, ^{15}N NMR and Single-crystal X-ray diffraction studies supported the structures of some compounds. All the synthesized energetic molecules exhibited higher density (1.75 to 1.94 g cm $^{-3}$), good thermal stability (186 to 397 °C), excellent detonation performance (7689 to 9248 m s $^{-1}$) and are insensitive to impact (>30 J) and friction (>360 N). Among them, many compounds show high detonation velocity (9072 to 9248 ms $^{-1}$) and onset decomposition temperature (T_d between 238 and 397 °C) than the benchmark energetic materials RDX (VOD = 8878 ms $^{-1}$, T_d = 210 °C), HMX (VOD = 8878 ms $^{-1}$, T_d = 279 °C), and thermally stable HNS (VOD = 7164 ms $^{-1}$, 318 °C). Additionally, the melting and decomposition temperatures of 5-amino-1,3,4-oxadiazole-2-carbohydrazide (T_m = 92 °C, T_d = 242 °C) indicate that it can be used as a melt-cast explosive. The novelty, synthetic feasibility, and energetic performance of all the molecules suggest that they can be used as potential secondary explosives in defence and civilian fields.

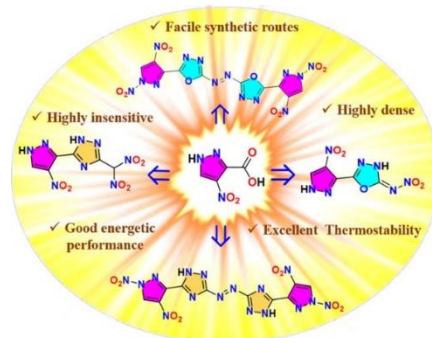


Figure 1. Unsymmetrical functionalization of 4-nitro-1H-pyrazole-3-carboxylic acid.

- (a) A. K. Yadav, V. D. Ghule, S. Dharavath, *ACS Appl. Mater. Interfaces*, **2022**, *14*, 49898-49908. (b) A. K. Yadav, V. D. Ghule, S. Dharavath, *Chem. Commun.*, **2023**, Advance Article.
- T. M. Klapötke, *Chemistry of High-Energy Materials. Chem. High-Energy Mater.* **2022**.
- A. K. Yadav, V. D. Ghule, S. Dharavath, *J. Mater. Chem. A*, **2022**, *10* (23), 12702–12712.
- J. Zhang, S. Dharavath, L. A. Mitchell, D. A. Parrish, J. M. Shreeve, *J. Am. Chem. Soc.* **2016**, *138* (24), 7500–7503.

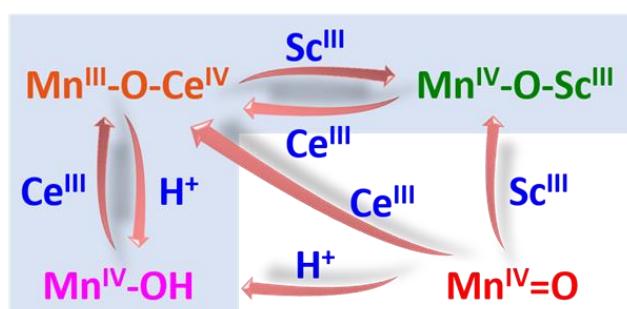
Facile formation of a Mn(III)-O-Ce(IV) species and its electron transfer equilibria with high valent Mn(IV)(OX) (X = Sc or H) complexes

Sikha Gupta, Pragma Arora, Rakesh Kumar, Bittu Chandra, Ayushi Awasthi, Raju Eerlapally,

Yisong Guo*, Lawrence Que, Jr.,* and Apparao Draksharapu*

High-valent manganese oxo species have been entreated as key intermediates in most enzymatic systems, particularly water oxidation by the oxygen-evolving complex (OEC) of photosystem II (PS-II).¹ In the OEC, the Ca^{2+} ion acts as Lewis acid that plays a crucial role in the O-O bond formation step. However, the essential role of the calcium ion has yet to be clarified.² A large number of artificial model compounds have been developed in the last two decades to understand the structural and mechanistic aspects of PS-II. Cerium(IV) ammonium nitrate (CAN) is a chemical oxidant that has been frequently used in artificial water oxidation reactions.³ In addition, several reports emerged recently where CAN acts as an oxidant and Lewis acid.⁴

Here we report the synthesis of a unique $[(\text{BnTPEN})\text{Mn}(\text{III})-\text{O}-\text{Ce}(\text{IV})(\text{NO}_3)_4]^+$ adduct (**2**), by the reaction of $(\text{BnTPEN})\text{Mn}(\text{II})$ (**1**) with 4 eq. ceric ammonium nitrate (CAN). **2** has been characterised using UV/Vis absorption, EPR, and resonance Raman spectroscopy, as well as by mass spectrometry. Treatment of **2** with $\text{Sc}(\text{III})(\text{OTf})_3$ results in the formation of the $(\text{BnTPEN})\text{Mn}(\text{IV})-\text{O}-\text{Sc}(\text{III})$ adduct (**3**), while HClO_4 addition to **2** forms $(\text{BnTPEN})\text{Mn}(\text{IV})-\text{OH}$ (**4**), reverting to **2** upon $\text{Ce}(\text{III})(\text{NO}_3)_3$ addition. **2** can also be prepared by the oxidation of 1 eq. $\text{Ce}(\text{III})(\text{NO}_3)_3$ with $(\text{BnTPEN})\text{Mn}(\text{IV})=\text{O}$ (**5**). These results demonstrate the existence of elegant equilibria between $\text{Mn}(\text{III})-\text{O}-\text{Ce}(\text{IV})$ and $\text{Mn}(\text{IV})$ species. When **2** is screened for electron transfer with ferrocenes, it is found that the binding of redox-active $\text{Ce}(\text{IV})$ enhances electron transfer efficiency. Despite having a component only in the $\text{Mn}(\text{III})$ oxidation state, **2** can nevertheless carry out O-atom and H-atom transfer reactions.



Scheme 1. Schematic diagram illustrating the equilibria between $\text{Mn}(\text{III})-\text{O}-\text{Ce}(\text{IV})$ and $\text{Mn}(\text{IV})$ species.

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3. A. Draksharapu, W. Rasheed, J. E. M. N. Klein, L. Que Jr., *Angew. Chem. Int. Ed.*, **2017**, 56, 9091.
4. D. G. Karmalkar, M. Sankaralingam, M. S. Seo, R. Ezhov, Y. -M. Lee, Y. N. Pushkar, W. -S. Kim, S. Fukuzumi, W. Nam, *Angew. Chem. Int. Ed.*, **2019**, 58, 16124.

Temperature Accelerated Sliced Sampling using OpenMM

Shitanshu Bajpai¹, *Brian Petkov*², *Muchen Tong*², *Charles Abreu*^{*3}, *Nisanth N. Nair*^{*1}, *Mark E. Tuckerman*^{*2}

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Enhanced sampling techniques based on Collective variable (CV) are widely used today for accelerating barrier-crossing events in molecular simulations. A class of these methods, which includes Temperature Accelerated Molecular Dynamics (TAMD)/driven-Adiabatic Free Energy Dynamics (d-AFED).¹ Unified Free Energy Dynamics (UFED).² uses an extended variable formalism to achieve quick exploration of conformational space. These techniques are powerful, as they permit enhancing the sampling of a large number of CVs simultaneously compared to other techniques. Extended variables are kept at a much higher temperature than the physical temperature by ensuring adiabatic separation between the extended and physical subsystems and employing rigorous thermostating. Here we present challenges associated with the above methods and how we overcome them using Temperature Accelerated Sliced Sampling (TASS).³ We also present a computational platform to perform extended phase space enhanced sampling simulations using the open-source molecular dynamics engine OpenMM. The implementation allows users to have interoperability of sampling techniques, as well as employ state-of-the-art thermostats. We also present some protocols to determine critical parameters and procedures for reconstructing high dimensional free energy surfaces. As a demonstration we present TASS simulation results on the high dimensional conformational landscape of Trp-cage mini protein in explicit water.

¹. (a) L. Maragliano, E. Vanden-Eijnden, *Chem. Phys. Lett.* 2006, 426, 168, (b) B. Abrams and M. E. Tuckerman, *J. Phys. Chem. B* 2008, 112, 15742

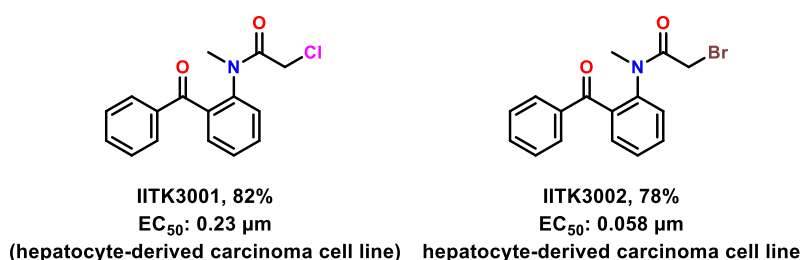
². Chen M, Cuendet MA, Tuckerman ME., *J Chem Phys.* 2012, 137, 024102

³. (a) S. Awasthi, N. N. Nair, *J. Chem. Phys.* 2017, 146, 094108, (b) S. Awasthi, N. N. Nair, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 2019, 9, e1398

Design and Discovery of Chloroacetamide based anticancer drugs via Electrophile-First Approach

Dharmendra Kumar Yadav, and *Dharmaraja Allimuthu**

Cancer is the leading cause of mortality across the globe and the emergence of drug resistance for commercially used anticancer agents warrants new therapeutic modalities. Several unique strategies targeting cancer therapy are in development, targeted protein inhibitors, small molecule-based proteolysis activating chimeras (PROTACs), chimeric antigen-directed T-cell (CAR-T cell) therapy, and antibody-drug conjugates amongst them. While the advanced technologies mark a huge success, most of them are in the clinical phase or personalized medicines. Over the past decades, covalent small molecules have been used to treat various diseases for more than a century, but the tools which facilitate the rational design of covalent drugs have emerged more recently. Some of the most prominent molecules including FDA-approved EGFR inhibitor afatinib, and the BTK inhibitor ibrutinib contain mildly reactive electrophilic covalent warheads and are directed to inhibit specific protein functions. By keeping the concept of reactivity, potency, and selectivity in our mind Here we have developed a library of electrophilic small covalent molecules using electrophile-first approaches and observed their reactivity with N-acetyl cysteine by thiol reactivity study. Further, we have used all concepts of the chemoproteomics platforms for Ligand screening, selectivity profiling, and target identification of these electrophilic covalent molecules against various cancer cell lines including lung cancer and hepatocyte-derived carcinoma cell line. We observed the nanomolar potency of IITK3001 and IITK3002 molecules through CTG cell viability assay against hepatocyte-derived carcinoma cell lines. After that, we proved the “ferroptosis” cell death biological pathway of the IITK3001 and IITK3002 molecules by using a combination cell viability assay with doxorubicin, staurosporine, RSL3, and fer-1 known anticancer drugs. Finally, we observed selective protein target labeling of IITK3001 and IITK3002 by using the concept of activity-based protein profiling assay via the click chemistry tool. By protein pulldown assay we are in process of further validation of the remaining concept of the chemoproteomics platform for finding potent ligands for selectively labeled target proteins.



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2. Eduardo *et al. Anticancer Agents Med. Chem.* **2012**, 12 (6), 611.
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5. Liou *et al. J. Med. Chem.* **2004**, 47 (11), 2897.
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7. Conrad *et al, Nature*,2019,575, 693.

Investigating the Photosensitivity of Koneramines for Cell Imaging and Therapeutic Applications

Suchismita Ghosh, and Raja Angamuthu*

The photophysical properties of the anthracene appended koneramines (L^{An}) were analyzed and utilized as a chemosensor for the selective detection of Cd^{2+} and Zn^{2+} . The complexation-induced inhibition of PET (photo-induced electron transfer) from the chelating nitrogen atoms to the excited state of the anthracene moiety resulted in a fluorescence “turn-on” signal upon binding with Cd^{2+} and Zn^{2+} . The confocal microscopic imaging studies performed on the MCF-7 cells validated that the compound is potentially useful for detecting Cd^{2+} and Zn^{2+} inside the cells. The cadmium complex exhibited unique bactericidal activity against clinically relevant human pathogens. The excellent activity against multidrug-resistant *S. aureus* makes the complex useful as a new, easily synthesizable antibiotic. The cadmium complex $L^{An}CdCl_2$ was not cytotoxic against vero cells with a selectivity index of 40, exhibited concentration dependent bactericidal killing, was non-interactive with several other clinically approved standard drugs, exhibited prolonged post-antibiotic effect (PAE) against *S. aureus* ATCC 29213 and possesses antibiofilm activity.

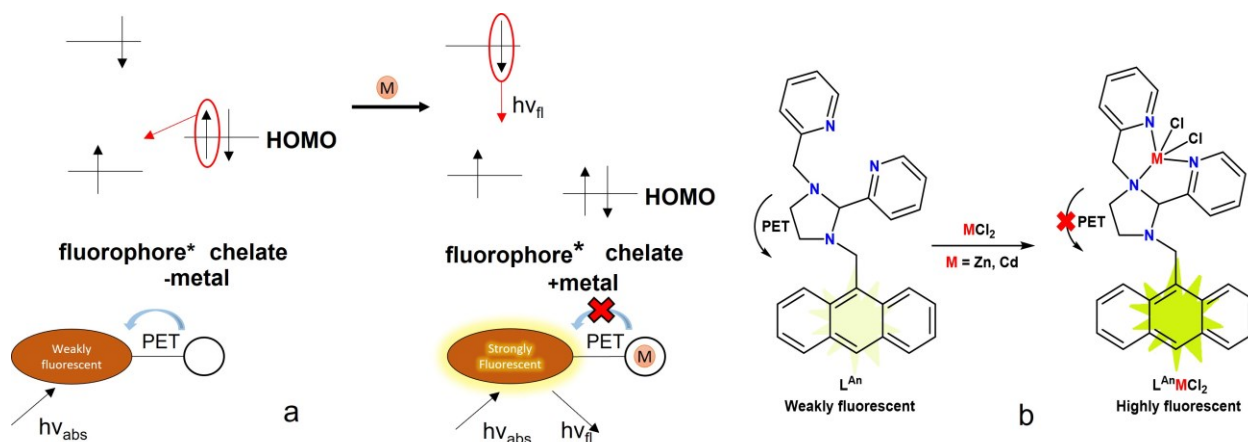


Figure 1. (a) Fluorescent mechanism of PET sensors; (b) Complexation-induced inhibition of PET and fluorescence enhancement in anthracene appended koneramine.¹

1. S. Ghosh, A. Akhir, D. Saxena, S. Singh, S. Sivakumar, S. Chopra and R. Angamuthu, *Dalton Trans*, 2022, **51**, 15659-15668.

Probing Virus Binding to Giant Plasma Membrane Vesicles with Fluorescence Microscopy Technique

*Manorama Dey, Nagma Parveen**

Giant Plasma Membrane Vesicles (GPMVs) are derived from the native plasma membrane of eukaryotic cells¹. They are applied as cell membrane mimics as well as model cells². While GPMVs retain the functionality of lipid and protein composition of the plasma membrane, some interesting observations were made about them such as they show the temperature-dependent phase separation behaviour and can form a planar cell surface mimetic Supported Plasma Membrane Bilayer (SPMB)³. The feature of phase separation has not been observed in the plasma membrane of intact cells and can be seen only in artificial Giant Unilamellar Vesicles (GUVs) with high cholesterol and saturated lipid content. Therefore, GPMVs provide an exciting platform to explore the lipid-protein interaction, protein dynamics, and host-pathogen interaction of the near-native composition of the plasma membrane⁴. There are multiple reports on the virus attachment, fusion, and even budding at the raft-like domains of the plasma membrane. Because of the small size and dynamic nature of the rafts in the plasma membrane, it is difficult to visualize the virus binding and fusion events at the rafts. To show that GPMVs are the suitable model system for virus binding and fusion studies we have established formulation of GPMVs from three different cell lines and employed fluorescence microscopy techniques to image the binding of fluorescently labelled viruses to the GPMVs (Fig 1A). The chosen cell lines have different levels of membrane receptors. Our imaging data confirm that the virus binding to the GPMVs follows the same trend as the binding of the virus to the respective host cells. This ensures that GPMVs retain the functional receptors in their membrane. Further, we have extended our work by introducing SPMB from GPMVs by adding artificial vesicles into it (Fig 1B). The extent of virus binding depends on the expression level of the membrane receptor in the GPMVs as confirmed upon imaging the virus binding at a single particle level.

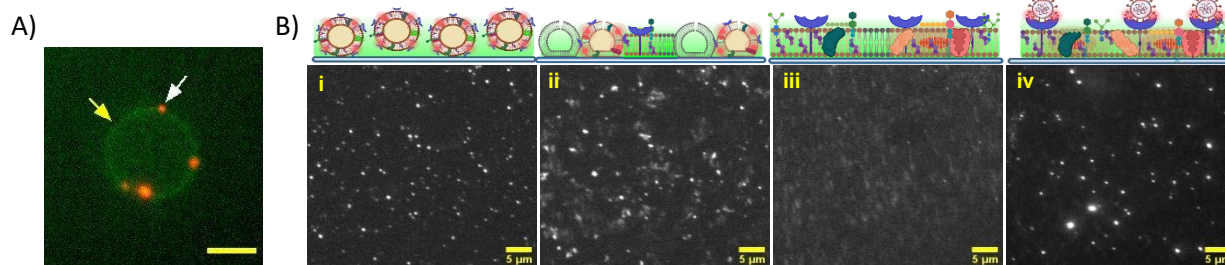


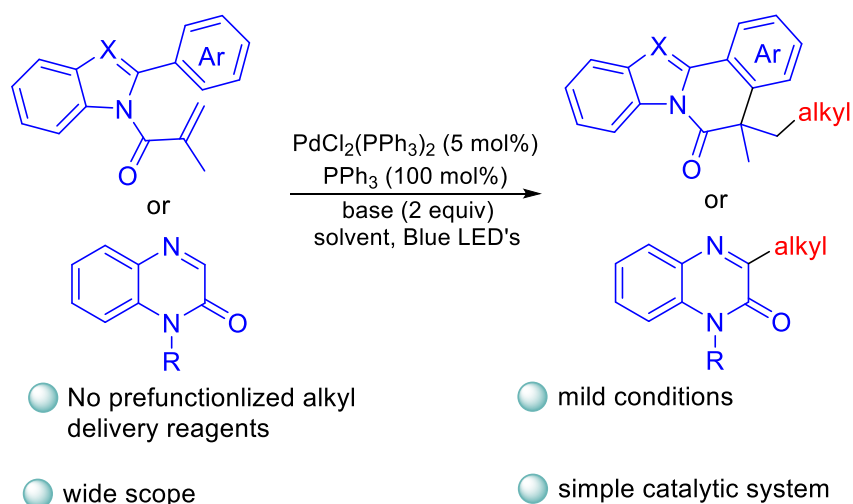
Figure 1. A) Epi-fluorescence micrograph of DiI labeled SARS-CoV-2 (indicated by white arrow) binding on DiO labeled GPMVs (yellow arrow) isolated from Vero cells. Scale bar 5 μm. B) TIRF micrograph of GPMVs at different time points showing SPMB formation in presence of DOPC vesicles (i-iii) and virus binding on SPMB (iv).

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2. Teiwes NK, Mey I, Baumann PC, Strieker L, Unkelbach U, Steinem C. *ACS Appl Mater Interfaces.* 2021;13(22):25805-25812.
3. Liu HY, Grant H, Hsu HL, et al. *ACS Appl Mater Interfaces.* 2017;9(41):35526-35538.
4. Yang ST, Kreuzberger AJB, Kiessling V, Ganser-Pornillos BK, White JM, Tamm LK. *Sci Adv.* 2017;3(6):1-13.

Pd-Catalyzed Photochemical Alkylative Functionalization of C=C and C=N Bonds

Ganesh Chandra Upreti, Tavinder Singh, Kirti Khanna, and Anand Singh*

Visible light photoredox catalysis emerged as an efficient and versatile tool for modern organic synthesis.¹ The photochemical Pd-catalysis opened a new avenue for the incorporation of sp³-hybridized unactivated alkyl halides for the cross-coupling reactions.² Here we have developed the excited-state palladium-catalyzed alkylative cyclization of acrylamides and the alkylation of quinoxalinones.³ The application of a variety of primary, secondary, and tertiary unactivated alkyl halides as alkyl radical precursors and the use of a simple catalyst system are the highlights of this reactivity manifold. The reactions exhibit wide scope, occur under mild conditions, and furnish the products in excellent yields.



1. C. Padon, D. Kurandina, V. Gevorgyan, *Angew. Chem. Int. Ed.*, **2019**, *58*, 11586.

2. G. Z. Wang, R. Shang, W. Cheng, Y. Fu, *J. Am. Chem. Soc.* **2017**, *139*, 18307.

3. G. C. Upreti, T. Singh, K. Khanna, A. Singh, *J. Org. Chem.* **2023**. [10.1021/acs.joc.2c03028](https://doi.org/10.1021/acs.joc.2c03028).

Quantum Thermal Switch and Rectifier

Shuvadip Ghosh, and Arnab Ghosh*

Our objective is to construct models which can be implemented as efficient quantum thermal devices that can control thermal currents in analogy to electronic devices that are used to control electric current in electronic circuit. We are now focusing on the formulation of thermal analog of rectifier and switch, two important electronic devices for controlling flow of electric current. Till now very few models have been proposed which can show switching and rectification effects.^[1,2] However, most of the works on quantum thermal rectifiers that have been proposed till now rely on either on temperature gradient of the bosonic reservoir or different coupling strengths between the system and the bath to break the mirror symmetry.^[3] Much less attention is paid in achieving thermal rectification by means of fermionic reservoirs, which may be the key ingredient for the formulation of more efficient thermal rectifier. Furthermore, previously proposed models rarely exhibit perfect rectification, and that is too under very limiting conditions.^[1,2,3]

We propose a minimal model [Fig. 1] of a Coulomb-coupled fermionic quantum dot thermal diode [4], that can act as an efficient thermal switch and exhibit complete rectification behavior, even in the presence of a small temperature gradient. Using two well-defined dimensionless system parameters, universal characteristics of the optimal heat current conditions are identified. It is shown to be independent of any system parameter and is obtained only at the mean transitions point “-0.5”, associated with the equilibrium distribution of the two fermionic reservoirs, tacitly referred to as “universal magic mean”.

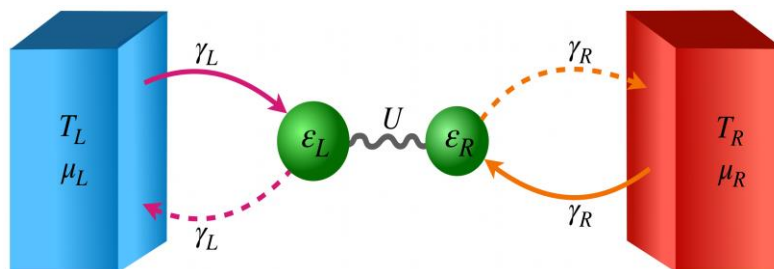


Figure 1: Model system for quantum thermal switch and rectifier. Adapted from *Entropy*. **2022**, 24(12), 1810.

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Copper(II) Complexes of 2-hydroxybenzaldehyde Analogues Facilitating Chemodynamic Therapy via Glutathione-Depletion and Lipid Peroxidation

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Transition metals has a vital role in various cellular processes. Iron(III) and Copper(II) metal ions are among the few that display high redox activity which makes them highly toxic. These transition metal ions participate in Fenton or Fenton-like reactions inside the tumor environment, also known as 'Chemodynamic Therapy' (CDT). CDT catalyzes excessive H_2O_2 within cancer cells to produce highly toxic hydroxyl radical ($\cdot OH$), thereby amplifying the oxidative stress and inducing cancer cells apoptosis. Because of the unique tumor microenvironment with high H_2O_2 concentration, the production of hydroxyl radicals would be limited to the tumor site. Compared with the normal cells, cancer cells are in a relatively high redox state and are more vulnerable to reactive oxygen species (ROS) attack. However, cancer cells usually adapt to oxidative stress through over-production of glutathione (GSH, an effective scavenger of ROS). Therefore, how to augment oxidative stress preferentially by decreasing GSH level in cancer cells is a scientific and reasonable therapeutic strategy to enhance CDT in anticancer drug development. Studies have found that the well-defined redox active Cu(II) complexes might be efficient anticancer agents; Cu(II) can convert GSH to oxidized glutathione (GSSG) and the resulting Cu(I) can further catalyze H_2O_2 to produce $\cdot OH$.

Herein, we have designed and synthesized a library of HDAC inhibitor (Sirtinol)-derived (ONO) ligands and their Cu(II)/Fe(III) complexes. All ligands were characterized by spectroscopic methods (1H and ^{13}C NMR, UV-vis) and ESI-MS mass spectrometry. The metal complexes have been characterized by ESI-MS mass, UV-Vis, EPR and SC-XRD. Biological activity of all the compounds have been studied on various cancer cell lines namely, MDA-MB-231, MCF-7, HCT-116, and A549. The compound **Cu-(L2)₂** displayed high antiproliferative activity ($IC_{50} = 5.32$ nm) on all the above-mentioned cancer cell lines and displayed the highest cytotoxicity on the breast cancer cell line MCF-7.

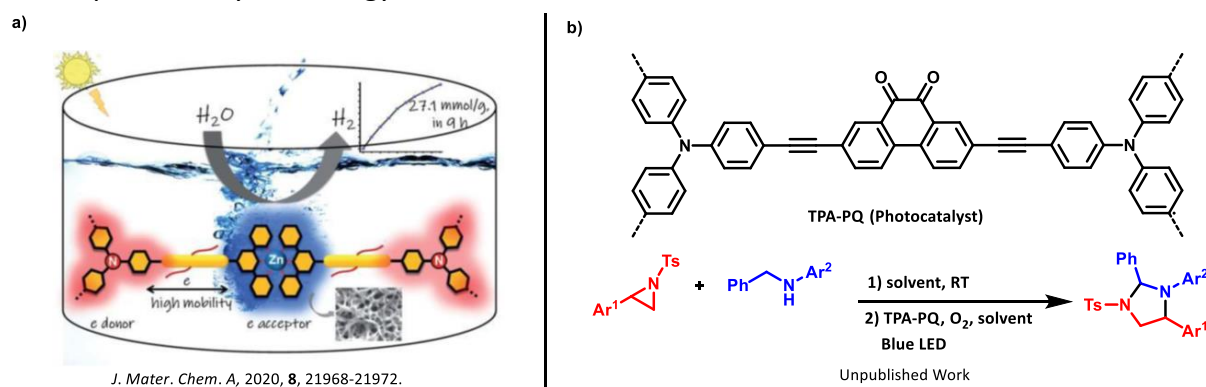
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(A) Triphenylamine and terpyridine–zinc(II) complex based donor–acceptor soft hybrid as a visible light driven hydrogen evolution photocatalyst.

(B) A fascinating strategy for the Development of efficient heterogeneous photocatalysts in organic synthesis.

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A donor–acceptor coordination polymer (TPA-Zn) was synthesized by Zn(II)-assisted self-assembly of an in-situ generated triphenylamine (TPA) cored tristerpyridine ligand. The polymer absorbs broad spectrum of light and exhibits visible light-assisted hydrogen generation (27.1 mmol/g over 9 h) from water with 2.9% quantum efficiency at 400 nm. Microscopic images show a mesoscale fibrous morphology and the Brunauer–Emmett–Teller (BET) analysis reveals the porous nature of TPA-Zn (surface area: 234.5 m²g⁻¹; d = 6.98 nm), both of which are helpful for substrate diffusion during catalysis. Apart from this, we are also working on metal-free conjugated organic polymer (TPA-PQ) as a photocatalyst for sp³ C-H functionalization in the presence of light and molecular oxygen, to synthesize imidazolidine derivatives from activated Aziridines, which serves as an alternative to the traditional metal-based photocatalysis strategy.



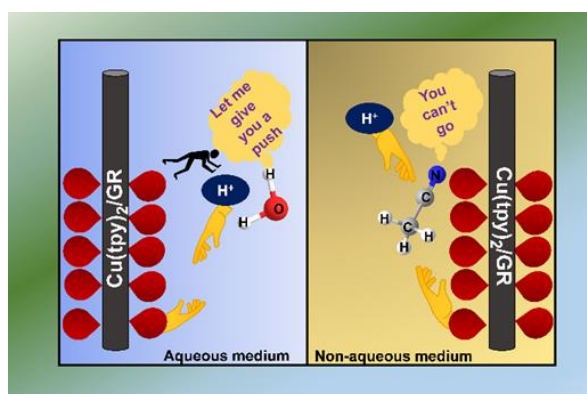
Scheme: (a) Schematic representation of the present work showing visible light-induced dihydrogen production by the mesoscale coordination polymer TPA-Zn and (b) Schematic representation of the present work showing light-induced C-H Functionalization to the synthesis of Imidazolidine derivatives in the presence of metal-free conjugated organic polymer (TPA-PQ) as photocatalyst.

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Proton-coupled electron transfer combined redox process showcasing supercapattery in $\text{Cu}(\text{tpy})_2$ thin films

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Polypyridyl metal complexes, due to their rich optical and electrochemical properties, have attracted significant attraction in the scientific community for various applications. Though the photophysical properties of polypyridyl complexes in solution and surface chemistry have been well-explored, electrochemical supercapacitor applications are scarce. Considering remarkable redox features occurring at a lower potential, fast electron transfer, and lower peak-to-peak separation, Cu^{2+} terpyridyl thin films could propel implementation toward low-cost, flexible energy storage applications. The work employs an electrochemical grafting method to covalently modify graphite rods (GRs) using diazonium salts of bis(4'-amino-phenyl terpyridine) Cu^{2+} , which form controllable, high yield, and highly reproducible thin films (18-20 nm).^{1,2} The molecular thin film shows an enhanced charge storage capacity as compared to the bare GR, which is predominantly due to three major contributions,³ (i) facile redox process due to $\text{Cu}^{2+}/\text{Cu}^+$, (ii) proton-coupled electron transfer (PCET) in acidic electrolyte due to the creation of free pyridinic nitrogen as electroactive sites and azo bond formation (-N=N-) during electrochemical grafting (iii) increase in active surface area. PCET pathway was successfully elucidated by methylation of free nitrogens and pH-dependent studies. Capacitive characteristics of the molecular thin films are found to be deeply dependent on the nature of the electrolytes (aqueous vs. non-aqueous). The work provides a dynamic insight into the surface wettability effect over the conductivity of electrolytic ions on the high performance of $\text{Cu}(\text{tpy})_2/\text{GR}$ electrodes as hybrid-capacitors toward the 'supercapattery' mimicking.



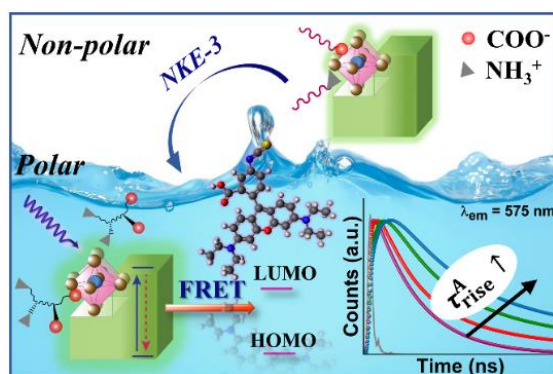
Scheme 1. Schematic illustrating the role of solvent (aqueous and non-aqueous) in $\text{Cu}(\text{tpy})_2$ modified graphite (GR) electrodes.

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Energy Funneling from Water-Dispersed Perovskites to Chromophores

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Cesium lead halide perovskite nanocrystals (PNCs) have enjoyed enormous attention in optoelectronics and photovoltaics.^[1,2] However, instability in polar conditions and limited energy/charge transport due to long-chain capping ligands restrict their large-scale applications.^[3] Herein, we have engineered a short-chain multidentate bola amphiphilic ligand (NKE-3), which provides synergistic passivation of the perovskite surface by one multidentate ionic terminal and localizes water molecules by another multidentate ionic terminal leading to the water-suspended colloidal solution of PNCs. NKE-3 allows efficient long-range dipole-based fluorescence resonance energy transfer (FRET) from perovskites to Rhodamine B isothiocyanate (RITC) in water, with FRET efficiency ranging from 96% to 98%. We calculated the FRET rate using the acceptor's rise-time component as it ensures no contamination from FRET-inactive donors.^[4] Moreover, we tuned the emission maxima of PNCs through halide exchange to optimize FRET efficiency. Such energy funneling to a suitable molecular photocatalyst is imperative to PNCs' potential applications.^[5]



The schematics illustrate the process of post-synthetic ligand exchange using the newly synthesized NKE-3, followed by the phase transfer of PNCs. Additionally, the diagram depicts the energy transfer from water-dispersed PNCs to a chromophore dye (RITC).

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