

Major Research Initiatives for the Academic Year 2012-2013 to 2015-2016
Department of Chemistry
Indian Institute of Technology Roorkee

Dr. R. N. Goyal completed a major research initiative supported by CSIR (2011-2014) and directed to develop voltammetric sensors based on nanomaterials for the determination of antibiotics in biological fluids. In this project, nanomaterials modified electrode have used for the determination of variety of antibiotics and drugs by voltammetric methods. Square wave voltammetry and cyclic voltammetry have been used for the determination of these compounds. Compared to a bare electrode, nanomaterials modified electrode exhibits an apparent shift of the oxidation or reduction potentials and a marked enhancement in the voltammetric peak current response of the biomolecules and drugs. The interference studies showed that the modified electrode exhibited an excellent selectivity in the presence of hypoxanthine, xanthine, uric acid and ascorbic acid. The proposed procedure was successfully applied to detect number of biomolecules and drugs such as, halobetasol propionate, mometasone furoate, cefpodoxime Proxetil, sulfacetamide and norfloxacin in human blood plasma and urine, without any pre-treatment. In all the cases a low detection limit (in nM) range is observed.

Dr. Anil Kumar initiated a research on “Synthesis of Biotemplated Colloidal Nanostructures of Iron Oxide(s) - Analysis of correlation between their Morphologies and Properties” funded by CSIR in 2014. For the last few years they have been involved in developing a wide range of nanomaterials *viz.* carbonaceous, semiconductors, metals, and their composites of varied dimensionalities, size(s) and shape(s). We have synthesized a few layer(s) thick N-functionalized and ultra-thin graphene sheets. Some of these materials are found to be highly conducting with fairly high value of specific capacitance at higher current densities exhibiting potential for supercapacitor applications. Among semiconductors during this period we have focused on synthesis of nanosized CdS, ZnS, PbS, PbSe, ZnO, CuO, β -Fe₂O₃, γ -Fe₂O₃ and β -FeOOH, have been carried out. Their optical, optoelectronic, fluorescence and magnetic, catalytic and biological properties have been analyzed and optimized. Present investigations are focused on developing energy materials such as biotemplated, integrated and composite nanostructures with enhanced properties.

Dr. M. R. Maurya initiated research on the “structural and functional models of haloperoxidases” through eight different projects funded by DST and CSIR (1998-2015). In this research, emphasis has been made to synthesize vanadium complexes which can be considered as structural models of enzymes “Vanadate dependent haloperoxidases”. Their catalytic activity for oxidation of various organic substrates in addition to the oxidative halogenation (i.e. functional models) have carried out. Another research area i.e. the development of metal complexes based heterogeneous catalysts have been developed. Major emphasis in this area of research has been the synthesis of vanadium complexes, their encapsulation in the cavity of zeolite-Y and immobilization on organic polymer and use them as recyclable and sustainable catalysts for catalytic oxidation of organic substrates. Effort was also made to identify the intermediate(s) to understand the mechanism of the catalytic reactions.

Dr. U. P. Singh initiated a research on “Organic and Metal-Organic Framework using anthracene based Azoles for selective Sorption of Gases and Catalysis funded by CSIR in 2015. They have constructed Zn(II)/ Co(II) MOFs using flexible ligands i.e., 9,10-bis(imidazole-1-ylmethyl)anthracene/9,10-bis(1H-triazole-1-ylmethyl)anthracene and different substituted sulfonic acids. These coordination polymer has been employed for the tailoring of isostructural two dimensional flexible metal organic framework. All MOFs were characterized by IR, SC-XRD analysis and the thermal stability of the frameworks was supported by TGA/DSC analysis. Single crystal X-ray diffraction analysis reveals that the complexes are isostructural and show flexibility in the framework. Furthermore, the photophysical properties of complexes in the solid state and adsorption studies are also investigated.

Dr. R. K. Peddinti successfully completed a major research on “Domino Reactions and Asymmetric Reactions of Benzoquinone Derivatives” in 2012-2015 under the financial support of DST. A practical chemical protocol for the synthesis of highly substituted bicyclo[2.2.2]octenone derivatives in regio- and stereo-selective manner from the corresponding 4-haloguaiacols has been developed. A simple and efficient one-pot synthesis of 5-(benzoxazol-2'-yl)bicyclo[2.2.2]octen-2-one derivatives from readily accessible starting materials by domino oxidative cyclization-acetalization-Diels-Alder protocol has been developed. We have demonstrated an efficient method for the synthesis of unsymmetrical oxygenated aryl alkyl/aryl disulfides by nucleophilic addition of thiols on *in situ* generated *o*-benzoquinone monoketals under catalyst-free conditions. Mild and aerobic conditions, enhanced regio-selectivities are the other merits of this protocol. We have also developed an unprecedented diacetoxyiodobenzene induced direct arylation of guaiacol derivatives and electron-rich arenes using Lewis-acid as activator to furnish highly oxygenated biaryls without pre-functionalization of both coupling partners. A simple and efficient method for the direct Friedel-Crafts reaction of 2-hydroxy 1,4-benzoxazine derivatives with various electron-rich arenes in the presence of BF₃.etherate has been developed to afford a series of densely substituted 2-aryl-1,4-benzoxazine derivatives of potential biological significance. An efficient methodology has been developed for the synthesis of pyrrolobenzoxazine and 3-arylamino coumarin derivatives promoted by trifluoroacetic acid. They have synthesized several sugar-based thiourea organocatalysts. These organocatalysts have been utilized in asymmetric transformations. An efficient, catalyst-free methodology has been developed for the Michael addition reaction of D-Glucosamine derivatives to provide novel sugar-derived vinylogous carbamates in high chemical yields and excellent stereoselectivity.

Dr. R. K. Peddinti initiated an another research on “Novel Dearomatization of Phenols into Benzoquinone Derivatives: Rapid Access to Bicyclo[2.2.2]octenones, Phenoxazines and other Heterocyclic Systems” in 2015 under a CSIR sponsored scheme. One of the objectives of the project is to synthesize novel bicyclo[2.2.2]octenone derivatives via Diels-Alder reaction of benzoquinone monoketals generated *in situ* by hypervalent iodine reagents mediated oxidation of the corresponding guaiacol derivatives. Another objective is to generate *o*-benzoquinone monoimides with hypervalent iodine reagents and Michael-type addition of *o*-aminophenols to produce phenoxazine derivatives.

Dr. K. Ghosh initiated two major research initiatives on “Synthesis and characterization of novel ruthenium nitrosyl complexes and their biological activity studies” and “Chemistry of non-innocent ligands: Synthesis of phenoxyl radical and related complexes and their applications” funded by CSIR and SERB respectively. The major highlights of the research are:

- (1) Design and synthesis of nitric oxide (NO) donating molecules for controlled and target specific delivery of NO.
- (2) DNA and protein interaction and nuclease and protease activity studies.
- (3) C-H activation and synthesis of ruthenium(III) organometallics.
- (4) Oxidation chemistry and mimicking of activities of metalloproteins through bioinorganic coordination chemistry.

Dr. K. R. Justin Thomas initiated research on solar cell organic materials in 2011. The projects are funded by CSIR and DST. Metal free organic dyes suitable for application as sensitizers in dye-sensitized solar cells have been successfully synthesized and characterized by optical and electrochemical measurements. The electronic structures of the dyes were also modeled by theoretical computations using density functional theory. These organic dyes are attractive when compared to the promising organometallic dyes containing ruthenium core due to their low cost and promising and tunable light-harvesting properties by slight structural modifications. They have tuned the optical properties and photovoltaic performances of the fluorene-based organic dyes by incorporating additional donors and varying the conjugation pathway. The nature of the conjugation pathway between the donor and acceptor and also between the donor and the auxiliary linker played crucial role in determining the functional efficacy of the dyes. Electron-rich conjugation pathway was found to red-shift the absorption wavelength and enhances the charge separation. The DSSC efficiency was improved higher than 7% by slight structural modifications. Simple dyes with low molecular mass have been found to function efficiently in the DSSC. Higher efficiency observed for these dyes are attributed presence of more dyes on the TiO₂ surface when compared to the bulky organic dyes.

Dr. K. R. Justin Thomas also completed a CSIR sponsored research on “Pyrenoimidazole Based Dipolar Compounds for Photovoltaics”. New organic materials based on pyrene, pyrenoimidazole and polyaromatic hydrocarbon bearing imidazoles were developed as emitting materials for organic light-emitting diodes or sensitizers for application in nanocrystalline TiO₂-based dye-sensitized solar cells. All the compounds were thoroughly characterized by spectral methods (¹H & ¹³C NMR and Mass) and further investigated for their absorption, emission and electrochemical properties. Promising dyes were demonstrated as functional ingredients in electronic devices such as organic light-emitting diodes and dye-sensitized solar cells. Pyrenoimidazoles bearing different chromophores such as carbazole, triphenylamine, pyrene and anthracene exhibited bright blue luminescence with excellent photoluminescence quantum efficiency. Polyaromatic hydrocarbons present on the imidazoles nucleus plays vital role to determine the absorption and emission properties of these blue-emitting compounds. Anthracene and pyrene containing derivatives exhibited blue photoluminescence with high quantum yield

and thermal stability. Also a series of non-conjugated fluorene-bridged bis- and tris-imidazole derivatives have been synthesized and characterized by their spectral, thermal and electrochemical properties. These dyes were functionally modified by slight chemical alternations to serve as sensitizers in dye-sensitized solar cells. DSSC with efficiency as high as 6.04% were fabricated using the dyes developed in this work.

Dr. K. R. Justin Thomas initiated a major research scheme sponsored by DST on “New Materials and Methods for the Efficient Organic Photovoltaic Devices” in 2015. They have synthesized new dithienopyrrole containing fluorene and used it as a linker or donor in the organic dyes featuring different donors (triphenylamine, fluorenyldiphenylamine, carbazole and phenothiazine) or acceptors, respectively. The dyes showed red shifted absorption and high molar extinction coefficients when compared to the control dye lacking donor or acceptor. Electronic richness of the fluorene appended DTP considerably influenced the optical and electrochemical properties of the dyes. In the future, they plan to design molecules which can show molar extinction coefficients more than $50,000 \text{ M}^{-1} \text{ cm}^{-1}$.

Dr. P. Jeevanandam initiated a research on “Synthesis and characterization of optically interesting nanocomposites” funded by CSIR. Various optically interesting nanocomposites such as fluorescent dyes incorporated in metal oxide and mixed metal oxide nanoparticles, semiconductor nanoparticles decorated nanocomposites, semiconductor nanoparticles incorporated in metal oxide with high band gap and nanocrystalline semiconductor alloys of the type $A_{1-x}B_xO$ and $A_{1-x}B_xS$ were synthesized. The synthetic methods employed for the preparation of the nanocomposites were sol-gel method and thermal decomposition method or both. All the synthesized nanocomposites were characterized using various techniques. The optical properties of the nanocomposites were investigated using diffuse reflectance spectroscopy and photoluminescence spectroscopy at room temperature and optical properties of the nanocomposites were compared with that of the individual constituents. After thorough characterization of the nanocomposites, applications such as photocatalytic degradation of toxic dyes in aqueous solutions were studied.

Dr. Naseem Ahmed completed a major research on “Design, Synthesis and Their Estrogen Receptors Binding Study of Some Novel Flavone, Flavone-Estradiol Adduct and Indanone based Ligands against Breast Cancer Cell Lines”. Breast cancer, a major women killer is 70-80% overexpressed with estrogen receptors (ERs). So, $ER\alpha$ and/or $ER\beta$ would be the legitimate target for prognostic marker and therapy. Estrogen receptor–ligand interactions produce diverse responses, which result in a complex and heterogeneous genetic alteration. Like, overexpression of ER suppresses p53 causes uncontrolled cell cycle and wild proliferations. Drugs are used either as antiestrogens or aromatase inhibitors, which gave adverse effects as endometrial proliferation or tumor flare or tumor-resistance in long use. Aim of our project is to design, synthesize and evaluate their ER binding affinity against human breast cancer cell lines for some

novel flavones, flavones–estradiol conjugates and indanone based tamoxifen analogs. Flavones are derivatized for better lipophilicity. Flavone–estradiols are linked with alkyl or alkynyl chain spacer via C-C bond for better stability, structural flexibility and biological activity. Tamoxifen is a vital chemotherapy drug, however optimal tissue selectivity has not yet been demonstrated. Thus, tamoxifen analogs as novel scaffolds are still a need for additional diversity and new chemical scaffolds for improved tissue selectivity. This scheme provided molecular level insights into biological processes and explored living systems in chemical biology. Potentially target-specific anti-tumor agents expected to give new drug candidates against breast cancer treatment.

Dr. Paritosh Mohanty completed a major research on “Inorganic-Organic Hybrid Nanoporous Materials for Carbon Dioxide Capture” during the period 2012-2015. The group achieved the development of materials capable to capture more than 23 wt % of CO₂.

Dr. Anuj Sharma successfully completed a research on “Glyoxalic acid as an effective formaldehyde equivalent in imine-mediated isocyanide based multicomponent reaction cascades” during the period 2012-2015 using financial support from DST. New methodologies to discover GBB reaction on less reactive 2-amino azines as well as glyoxalic acid variant was developed. Moreover, Use of glyoxalic acid in Ugi and Passerini reaction to access 2-unsubstituted α -acylaminoamides was also successfully synthesized and their therapeutic potential was evaluated. This DST project was completed successfully in May 2015 with eight publications in esteemed journals.

Dr. Anuj Sharma initiated a DST sponsored research on “Copper catalyzed Novel bond forming strategies for potent Therapeutic Heterocyclic scaffolds” in 2015. In this research, novel copper catalysed methodologies for the synthesis of dibenzothiazepine and their post condensation MCR sequences will be developed. Use of new copper compounds and ligand combinations to prescribe novel synthetic accesses to novel heterocycles and their C-H activated arylations will be explored. The potential applications (therapeutic or others) of the synthesized molecules molecule will be developed in future. Still now three papers published in esteemed journals.

Dr. C. N. Ramachandran initiated a computational research on “Formation, Structure, Stability and Thermodynamic Properties of Mixed Gas Hydrates” in 2013 sponsored by SERB. This research aims to proposal aims to investigate the structure, stability and thermodynamic properties of mixed hydrates, in particular the mixed hydrates of lower hydrocarbons and those with the environmental hazardous gases. Study of gas hydrates at the molecular level requires modelling of these cages. Due to different orientation of hydrogen bonds, several isomers are possible for the cages and hence selection of a suitable host water cage is a great challenge. Using the concept of strong-weak effective bond (SWEB) model proposed originally for dodecahedral water cages earlier, we modelled various cages of different size and shape. These

include large cages such as tetrakaidecahedral (TD) and hexakaidecahedral (HD) which belongs to sI and sII types of gas hydrates. Later, we extended the above concept for modelling fused cages of dodecahedral, irregular dodecahedral, tetrakaidecahedral and hexakaidecahedral cages. Each of the above fused cages with maximum number of *tId* hydrogen bond was modelled using the minimum energy geometries of the component cages with maximum number of *tId* bonds. The encapsulation of various guest molecules and their spectroscopic properties are also studied. In addition, we also studied about the carbon dioxide induced bubble formation in CH₄-CO₂-H₂O-ternary system. The results indicated that with an increase in the concentration of CO₂ removal of dissolved CH₄ may be enhanced preventing the accumulation of methane in the liquid phase. The studies on the effect of nitrogen and other impurities in the bubble formation of CH₄ and CO₂ in their aqueous solutions are in progress.

Dr. Prasenjit Kar initiated two research schemes on “Small Molecules for Solution Processed Organic Solar Cell” and “Novel molecular design for Dye Sensitized solar cell”.

Dr. K. K. Sadhu initiated a SERB sponsored research on “Development of fluorescence based selective chemical sensor for Magnesium ion under physiological condition”.

Dr. Debasis Banerjee initiated a research scheme on “Enantioselective Dual Catalysis: A Sustainable Approach for Activation and Functionalization of Challenging C(sp² and sp³)-O Bond” sponsored by SERB.

References

1. S. K. R. Parumala, R. K. Peddinti, *Org. Lett.* **2013**, *15*, 3546-3549.
2. R. T. Naganaboina, R. K. Peddinti, *J. Org. Chem.* **2013**, *78*, 12819-12824.
3. R. T. Naganaboina, A. Nayak, R. K. Peddinti, *Org. Biomol. Chem.* **2014**, *12*, 3366-3370.
4. S. R. Surasani, S. K. R. Parumala, R. K. Peddinti, *Org. Biomol. Chem.* **2014**, *12*, 5656-5668.
5. S. K. R. Parumala, S. R. Surasani, R. K. Peddinti, *New. J. Chem.* **2014**, *38*, 5268-5271.
6. A. Sharma, J. Agarwal, N. B. Kamatham, R. K. Peddinti, *Synlett* **2015**, *26*, 1398-1402.
7. R. T. Naganaboina, R. K. Peddinti, *Tetrahedron* **2015**, *71*, 6245-6253.
8. S. K. R. Parumala, R. K. Peddinti, *Green Chem.* **2015**, *17*, 4068-4072.
9. A. Singhal, S. K. R. Parumala, A. Sharma, R. K. Peddinti, *Tetrahedron Lett.* **2016**, *57*, 719-722.
10. S. Sharma, R. T. Naganaboina, R. K. Peddinti, *RSC Advances* **2015**, *5*, 100060-100069.
11. S. K. R. Parumala, R. K. Peddinti, *Tetrahedron Lett.* **2016**, *57*, 1232-1235.
12. R. Muhammad, P. Rekha and P. Mohanty, *RSC Adv.*, **6**, 17100 (2016).
13. R. Muhammad, P. Rekha and P. Mohanty, *Greenhouse Gas: Sci. Tehno.*, **6**, 150 (2016).
14. K. R. J. Thomas and A. Baheti, *Mater. Technol.*, **2013**, *28*, 71-87.
15. A. Venkateswararao, K. R. J. Thomas, C.-P. Lee, K.-C. Ho, *Tetrahedron Lett.*, **2013**, *54*, 3985-3989.

16. A. Baheti, K. R. J. Thomas, C.-P. Lee, K.-C. Ho, *Org. Electronics*, **2013**, *14*, 3267-3276.
17. D. Kumar, K. R. J. Thomas, C.-C. Lin, J.-H. Jou, *Chem. Asian J.*, **2013**, *8*, 2111-2124.
18. D. Kumar, K. R. J. Thomas, C.-P. Lee and K.-C. Ho, *J. Org. Chem.*, **2014**, *79*, 3159–3172.
19. S. Kumar, K. R. J. Thomas, C.-T. Li and K.-C. Ho, *Organic Electronics*, **2015**, *26*, 109–116.
20. P. Rekha, V. Sharma and P. Mohanty, *Microporous Mesoporous Mater.*, **219**, 93 (2016).
21. P. V. R. K. Ramacharyulu, R. Muhammad, J. P. Kumar, G. K. Prasad and P. Mohanty, *Phys. Chem. Chem. Phys.*, **17**, 26456 (2015).
22. P. Rekha, R. Muhammad, and P. Mohanty, *RSC Adv.*, **5**, 67690 (2015).
23. V. Sharma, A. Sahoo, Y. Sharma and P. Mohanty, *RSC Adv.*, **5**, 45749 (2015).
24. P. Rekha, U. Sahoo and P. Mohanty, *RSC Adv.*, **4**, 34860 (2014).
25. N. Ahmed, G. K. Pathe and B. V. Babu, *Tetrahedron Letters* **2014**, *55*, 3683 – 3687.
26. N. Ahmed, G. K. Pathe and B. V. Babu, *RSC Advances*, **2015**, 63095 - 63103.
27. G. K. Pathe and N. Ahmed, *Tetrahedron Letters* **2015**, *56*, 1555-1561.
28. G. K. Pathe, N. Konduru, I. Parveen and N. Ahmed, *RSC Advances*, **2015**, 83512-83521.
29. G. K. Pathe and N. Ahmed, *RSC Advance*, **2015**, *5*, 59114-59119.
30. G. K. Pathe and N. Ahmed, *Synthesis*, **2015**, *47*, 3542-3552.
31. V. Shilpi, S. P. Kaur and C. N. Ramachandran, *Chem. Phys. Lett.*, **2015**, *626*, 39-42.
32. V. Shilpi, S. P. Kaur and C. N. Ramachandran, *RSC Adv.*, **2015**, *5*, 74720-74723.
33. K. S. Sujith and C. N. Ramachandran, *Phys. Chem. Chem. Phys.*, **2016**, *18*, 3746-3754.
34. M. Khandelwal and A. Kumar, *Dalton Transactions*, **2016**, *45*, 5180-5195.
35. M. Khandelwal and A. Kumar, *J. Mater. Chem. (A)*, **2015**, *3*, 22975-22988.
36. M. Kaloti, A. Kumar and N.K. Navani, *Green Chem.*, **2015**, *17*, 4786-4799.
37. U. K. Gaur, A. Kumar and G D Varma, *J. Mater. Chem. C*, **2015**, *3*, 4297- 4307.
38. A. Kumar, B. Singh and K. Gupta, *J. Phys. Chem. (C)*, **2015**, *119*, 6314-6323.
39. A. Kumar and S. K. Gupta, *Green Chem.*, **2015**, *17*, 2524–2537.
40. A. Kumar and M. Khandelwal, *J. Mater. Chem. (A)*, **2014**, *2*, 20345–20357.
41. A. Kumar and S. K. Gupta, *J. Phys. Chem. (B)*, **2014**, *118*, 10543-10551.
42. U. Sharma and P. Jeevanandam, *J. Nanopart. Res.*, **2016**, *18*, 1-20