

(P249)

**Polyacrylamide Zirconium (IV) iodate as a new adsorbent for removal of lead from aqueous solution: equilibrium, kinetics and column study**

Uzma Haseen and Nafisur Rahman

Department of Chemistry, Aligarh Muslim University, Aligarh

Heavy metal pollution is a common environmental problem all over the world. The purpose of the research is to examine the applicability of polyacrylamide zirconium (IV) iodate as an adsorbent to remove Pb(II) from aqueous solutions. The effects of solution pH, adsorbent dose, initial Pb(II) concentration, contact time and temperature on the removal process were investigated. The lead adsorption was found to be maximum at pH 7.5. The sorption equilibrium time was observed in 90 min. The equilibrium sorption data were analysed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. Langmuir isotherm was found to be applicable in terms of high correlation coefficients, which indicate that the adsorption between Pb(II) and adsorbent was favourable. The kinetics of Pb(II) was discussed by pseudo-first order and pseudo-second order models. It was observed that the adsorption of Pb(II) was described by pseudo-second order kinetic model. Thermodynamic analysis showed that the adsorption of Pb(II) was spontaneous and endothermic under the experimental conditions. The column studies were also performed for practical function of the adsorbent which revealed high removal efficiency. All the results illustrated that polyacrylamide Zirconium (IV) iodate was a very attractive adsorbent for efficient removal of Pb(II) from contaminated aqueous solutions.

(P250)

**Selective separation and preconcentration of Aluminium through chelation on a synthesized resin containing N, O donor atoms for quantitative analysis of environmental and biological samples.**

Aminul Islam, Hilal Ahmad, Noushi Zaidi

Analytical Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh

Amberlite XAD-16 functionalized with Glyoxal-bis(2-hydroxyanil) through an azo linkage (-N=N-) was synthesized and used as a new chelating resin for preconcentration and determination of Al(III) in water samples. The resin was characterized by elemental analysis, Scanning Electron Microscopy along with Energy Dispersive X-ray Spectroscopy, Fourier transform infrared spectroscopy, and thermo gravimetric analysis. The resin was selectively bind aluminium over a large number of competitive cations ( $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ). Metal ion sorption equilibria were reached within 15 min. The sorbed metal ions were eluted by 5 mL of 2 M HCl within 2.5 min with the desorption recovery of  $\geq 98\%$ . Determination of the metal ions was carried out by flame atomic absorption spectrophotometry. The resin shows fast kinetics ( $t_{1/2}$  10 min), high preconcentration flow rate (5.0 mL min<sup>-1</sup>), very high sorption capacity (24.28 mg g<sup>-1</sup>), and low preconcentration limit (3.3 ppb). The preconcentration factor was 300 for a 1500 mL sample. Langmuir, Freundlich, Scatchard and Dubinin-Radushkevich adsorption models were applied to fit adsorption equilibrium data. Thermodynamic study showed that adsorption of Al(III) onto resin was spontaneous and endothermic in nature. This new method gave a good accuracy in column system as indicated by the recovery of  $\geq 98\%$  for the extraction of Al(III) ions and R.S.D. less than 5% (n=5). The detection limit and limit of quantification after preconcentration was 1.3 and 4.4  $\mu\text{g L}^{-1}$ ,

respectively. The resin has been successfully applied for the preconcentration and determination of trace Al(III) in dialysis fluid, packaged drinking water, rum and soft drink samples.

**(P251)**

**Development of a novel, selective flame atomic absorption spectrometric method based on systematic approach for the trace aluminium determination after an off-line column preconcentration**

Aminul Islam, Noushi Zaidi, Hilal Ahmad

Analytical Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh

Novel chelating resin 2-(2-hydroxyphenyl) benzoxazole anchored Amberlite XAD-16 was synthesized and tested for preconcentration and selective separation of ultra-trace aluminium over a large number of competitive cations prior to flame atomic absorption spectrometric determination. Experimental conditions, selected as a compromise between sensitivity and analytical frequency; for effective sorption of Al (III) were optimized systematically and were found to have fast kinetics ( $t_{1/2}$  7 min), high preconcentration flow rate (5.0 mL min<sup>-1</sup>), eluent concentration (5 mL of 2 M HCl), and low preconcentration limit (2.7 ppb). The maximum sorption capacity of the sorbent was 21.58 mg g<sup>-1</sup>. The experimental data were fitted to Langmuir and Freundlich isotherms. The monolayer sorption of Al (III) on XAD-HPB was confirmed by a good fit for Langmuir adsorption isotherm ( $r^2 = 0.999$ ). The function of the resin was ascertained by preconcentrating Al (III) from sample solution of different interferent to analyte ratio. The reliability was confirmed through the analysis of trace aluminium in the standard reference materials and from the recovery experiments. Accuracy (recovery = 98.9%- 101.3%,  $n = 3$ ), confidence limit, precision (RSD <5%), and detection limit (2.8 ppb) were evaluated to check the analytical characteristics of the method. The applicability of the proposed method was demonstrated by analysis of trace aluminium in tap water, fruit juice, dialysis fluid, and packaged drinking water samples.

**(P252)**

**Development of an analytical method for preconcentration and determination of trace metal ions using a novel chelating resin of enhanced hydrophilicity**

Aminul Islam, Mohammad Asaduddin Laskar, Akil Ahmad

Analytical Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh

A stable extractor of metal ions was synthesized through azo linking of p-hydroxybenzoic acid with Amberlite XAD-4 and was characterized by elemental analyses, infrared spectral and thermal studies. Its water regain value and hydrogen ion capacity were found to be 15.80 and 7.52 mmol g<sup>-1</sup>, respectively. Both batch and column methods were employed to study the sorption behavior for the metal ions which were subsequently determined by flame atomic absorption spectrophotometry. The optimum pH range for Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) ions were 10.0, 8.0-9.0, 7.0, 7.0-8.0 and 7.0-8.0, respectively. The half-loading time,  $t_{1/2}$ , are 6.0, 8.0, 8.0, 8.0 and 4.0 min, respectively. Comparison of breakthrough and overall capacities of the metals ascertains the high degree of column utilization (>75%). The breakthrough capacities for Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) ions were found to be 0.46, 0.43, 0.42, 0.09 and 0.06 mmol g<sup>-1</sup> with the corresponding preconcentration factor of 460, 460, 460, 360 and 260, respectively. The limit of preconcentration was in the range of 4.3-7.6  $\mu\text{g L}^{-1}$ .

The detection limit for Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) were found to be 0.47, 0.45, 0.50, 0.80, and 1.37  $\mu\text{gL}^{-1}$ , respectively. The Student's t (t-test) values for the analysis of standard reference materials were found to be less than the critical Student's t values at 95% confidence level. The AXAD-4-HBA has been successfully applied for the analysis of natural water, multivitamin formulation, infant milk substitute, hydrogenated oil and fish.

**(P253)**

**Rate and fixed time methods for determination of Nortriptyline hydrochloride in commercial dosage forms Initial**

Sumaiya Khan, Shahroora Sameen and Nafisur Rahman  
Department of Chemistry, Aligarh Muslim University, Aligarh

A kinetic spectrophotometric method has been developed for the determination of nortriptyline hydrochloride in pure and commercial dosage forms. The method is based on reaction of drug with potassium permanganate in alkaline medium at room temperature ( $30 \pm 1 \text{ }^\circ\text{C}$ ). The reaction was followed spectrophotometrically by measuring the increase in absorbance with time at 608 nm and the initial rate and fixed time ( at 10 min ) methods were adopted for constructing the calibration graphs. All the calibration graphs are linear in the concentration range of 10.0 – 100.0  $\mu\text{g/ml}$ . The limits of detection for initial rate and fixed time methods were 1.42 and 2.33  $\mu\text{g/ml}$ , respectively. The intraday and interday precisions were also calculated and found to vary in the range of 0.62-1.21 % and 0.28-1.92 % , respectively. The variables were optimized and the proposed methods are validated as per ICH guidelines. The method has been further applied to the determination of nortriptyline hydrochloride in commercial dosage forms. The analytical results of the proposed methods when compared with those of the reference method show no significant difference in accuracy and precision and have acceptable bias.

**(P254)**

**Poly-o-touidine zirconium(IV) ethylenediamine as an important nitrate selective composite material : synthesis , characterization and applications.**

Mohammad Fazeel Khan and Nafisur Rahman  
Department of Chemistry, Aligarh Muslim University, Aligarh

Various samples of poly-o-toluidine Zirconium(IV) ethylenediamine composite material was synthesized under varying conditions. The sample which showed maximum anion-exchange capacity ( 2.02 meqg-1) was selected for further studies. The material has been characterized on the basis of chemical composition, FTIR, X-ray diffraction, SEM-TEM and TGA-DTA studies. The adsorption of various anions has been carried out at room temperature. The material has high selectivity for nitrate ions. The effects of solution pH, adsorbent dose, initial nitrate concentration, contact time and temperature on the removal of nitrate ion were investigated. The equilibrium sorption data were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. Langmuir isotherm was found to be applicable which indicate that the adsorption between nitrate ion and adsorbent was favourable. Thermodynamic analysis showed that the adsorption of nitrate ions was spontaneous and endothermic under the experimental conditions. The results illustrated that poly-o-toluidine zirconium (IV) ethylenediamine was very attractive adsorbent for efficient removal of nitrate ion from aqueous solutions.

(P255)

**Silica gel modified with 3-aminopropyltrimethoxysilane and thiosalicylic acid for the removal of Pb(II), Cr(III), and Cu(II) from aqueous solutions.**

Mohd Nasir and Lutfullah

Department of Chemistry, Aligarh Muslim University, Aligarh

Thiosalicylic acid molecules were covalently immobilized onto silica gel previously functionalized with 3-aminopropyltrimethoxy silane (Sil-NH<sub>2</sub>) producing a Sil-Thsa surface. The synthesized material was characterized by FTIR, TGA, DTA and SEM studies. The modified silica gel was used to adsorb divalent cations from aqueous solution. The effects of solution pH, adsorbent dose, initial metal ion concentration, contact time and temperature on the uptake of metal ions were studied. The sorption data were analyzed by Langmuir and Freundlich isotherm models, which indicated the favourable adsorption of Pb(II), Cr(III) and Cu(II) on the modified silica gel. The selectivity sequence was found in the order; Pb(II) > Cr(III) > Cu(II).

(P256)

**Fabrication of ion selective electrode based on poly-o-toluidine zirconium (IV) iodosulphosalicylate as an electroactive material for determination of Cr(III).**

Nafisur Rahman

Department of Chemistry, Aligarh Muslim University, Aligarh

An inorganic-organic composite material, poly-o-toluidine zirconium(IV) iodosulphosalicylate, was synthesized by mixing poly-o-toluidine into the gel of zirconium(IV) iodosulphosalicylate. The distribution coefficient values of various metal ions were determined which showed high selectivity for Cr(III). Due to its Cr(III) selective nature, the composite material was used as an electroactive material for the fabrication of an ion selective membrane electrode. The membrane was characterized by XRD, SEM and AFM studies. It was observed that the PVC based ion-selective electrode displayed a useful analytical response with excellent reproducibility, low detection limit ( $1.58 \times 10^{-6}$  M), wide working pH range (3.0-7.0) and quick response time (10s). The electrode responds to Cr(III) in a linear range from  $3.16 \times 10^{-6}$  M to  $1 \times 10^{-1}$  M with Nernstian slope of 22 mV per decade change in concentration. The life span of electrode was found to be 12 weeks. The sensor has been applied to the determination of Cr(III) ions in water samples of different origins. The sensor has been used as indicator electrode in potentiometric titrations of Cr(III) ion with EDTA.

(P257)

**Amine functionalized tetraphenylethylene: A novel fluorescent probe nitrite and nitrate based on the aggregation-induced emission**

Diprati G. Khandare, Mainak Banerjee and Amrita Chatterjee\*

Department of Chemistry, BITS, Pilani

Contamination of rural drinking water supplies with nitrate and nitrite ions by livestock waste, organic wastes, and chemical fertilizers continues to be a problem throughout the world. Investigation of nitrite level in food stuff and drinking water is of very important because it reacts with dietary component in stomach and produces nitrosamine. Nitrite ions have ability to convert oxyhemoglobin into methemoglobin when present in the blood stream and thereby

interfering with oxygen transport in the blood. So the detection of nitrate and nitrite become especially significant.

Recently, aggregation-induced emission (AIE)-active materials have shown potential applications in the sensing fields. AIE-active molecules display no emission in solution, but an intense emission when aggregated or in the solid state because of nonradiative deactivation associated with restricted intramolecular rotations. Tetraphenylethylene (TPE) is one of such molecules that shows intense blue fluorescence when aggregated. Keeping this in mind a TPE-NH<sub>2</sub> was designed and synthesized. By taking advantage of the aggregation-induced enhanced emission feature, a convenient fluorescence-based assay for nitrite and when coupled with to a reduction step, nitrate has been developed. TPE amine in 6% THF-water shows a intense fluorescence, which after addition of nitrite (pH 1) shows gradual reduction of fluorescence intensity. The probe was also utilized for the analysis of real sample. High sensitivity and selectivity, fast reaction coupled with cost effective synthesis make this probe highly amicable for practical use.

**(P258)**

**Optimization of Supercritical Carbondioxide Extraction parameters of essential oils from various plants**

Aarti Singh, Meraj Alam Khan, Fauzia Khan, Seraj Anwer Ansari and Anees Ahmad  
Department of Chemistry, A.M.U.

The environment friendly green technologies and use of products for human consumption obtained from natural resources is the need of time and key of sustainability. This paper presents the review of literature and methods of extraction of essential oils and found that very little work has been done on Supercritical CO<sub>2</sub> extraction which is a green technology as it is free from solvents. The extraction of essential oils in industries is generally done in the traditional manner using either solvents or distillation which is a time consuming and costly process. The use of SC-CO<sub>2</sub> is cheap, green and faster process. So there is a lot of scope of work in this field. SC-CO<sub>2</sub> extraction method can be used to get numerous bioactive compounds from natural resources especially the non-consumable parts of fruits. This work will allow a shift in paradigm of research from synthetic to natural through green chemistry with green path. Optimization of extraction parameters will cause a breakthrough in this area and environmental friendly solution to the industry.

**(P259)**

**Fabrication and characterization of a novel cation exchanger polyaniline Sn(IV) tungstophosphate : its analytical applications for removal of heavy metal ions from waste water**

Arshia Akhtar, Md. Dilwar Alam Khan, S. A. Nabi

A crystalline 'organic-inorganic' cation exchanger has been synthesized via sol-gel mixing of an electrically conducting polymer into inorganic precipitate having a good ion exchange capacity, reproducibility and selectivity for heavy metal ions. The physical properties of the material were characterized by TGA-DTA, FTIR, XRD, SEM and TEM. From XRD analysis it is clear that the material is a crystalline material. The physico-chemical properties (IEC, pH titrations, elution, effect of concentration and effect of temperature etc.) and the preliminary study of the material

were also carried out. The pH titration curve for alkali metal ions shows a mono-functional behaviour whereas for alkaline earth metal ions show the two inflexion points which infer bi-functional behaviour of the exchanger. On the basis of distribution studies of several metal ions in different electrolyte solution with varying concentrations, the material was found to be highly selective for Pb(II), a highly toxic component of environmental waste water. The analytical applications of this material has been explored by achieving some binary separation of heavy metal ions from synthetic mixture as well as from waste water on its column, showing great promise in analytical chemistry. Thus, the newly synthesized “organic-inorganic” hybrid material offers a variety of exciting technological opportunities to decreases the toxicity of environmental waste water.

**(P260)**

**Facile synthesis and characterization of a polymer based nanocomposite and its analytical applicability towards waste water detoxification.**

Md. Dilwar Alam Khan and S. A. Nabi

Analytical Research Laboratory, Department of Chemistry, Aligarh Muslim University

A novel polymer based organic-inorganic nanocomposite cation exchanger has been synthesized by the incorporation of inorganic precipitate of Sn(IV)iodophosphate into the polymer matrix of electrically conducting polyaniline via sol-gel method. The morphological characterization of the nanocomposite has been done by simultaneous TGA-DTA, XRD, FTIR, SEM and TEM. The physico-chemical properties like functionality behaviour, ion exchange capacity, elution behaviour, thermal stability etc were also carried out to characterize the material. The XRD analysis reveals the amorphous nature of the composite indicating its suitability for ion exchange process. The cation exchanger is stable up to 300 °C with the retention of 90.8% of its initial ion exchange capacity. The TEM analysis shows the formation of particle size of nanometre range. On the basis of distribution studies (K<sub>d</sub> values) the composite was found to be highly selective for Hg (II) and Pb(II). Some analytically important binary separations were also carried out quantitatively with recovery >98% which reflects the potentiality of the exchanger. The synthesized nanocomposite cation exchanger has been successfully employed for the quantitative determination of Hg (II) and Pb(II) in industrial waste water.

**(P261)**

**Estimation of Glucose using Molecularly Imprinted Polymer-Modified Screen Printed Electrodes**

Kislay Singh, Bhim Bali Prasad\*

Department of Chemistry, Banaras Hindu University

A new sensor has been designed for the evaluation of Glucose in human serum samples. The sensor was designed by immobilizing Molecularly Imprinted Polymer (MIP) particles on the surface of Screen Printed Electrodes. The linear range of Glucose was found to be 2.39 mg/L to 11.76 mg/L in aqueous and Serum samples. The sensor is cost effective and economic and practically viable for glucose evaluation in diabetic patients.

(P262)

**Aqueous mediated Henry reaction by novel binuclear catalysts**

R. Arunachalam and P.S. Subramanian\*

Discipline of Inorganic Materials and Catalysis, CSIR-Central Salt and Marine Chemicals  
Research Institute, Bhavangar

Nitro-Aldol Henry reaction is an important C-C bond coupling reaction with potential industrial applications. Geometrically saturated and unsaturated complexes incorporated with Cu(II), Co(II), Cr(II) and Ln(III) etc., are generally used for this catalytic purpose. Herein we have synthesized a series of wisely designed binuclear metal complexes  $[\text{Cu}_2(\text{L}1)_2]^{4+}$  (1),  $[\text{Cu}_2(\text{L}1)_3]^{4+}$  (2),  $[\text{La}_2(\text{L}2)_3]^{6-}$  (3) with geometrically saturated and unsaturated coordination sites using pyridine based ligands. These complexes possessing highly cationic and anionic coordination sphere, their application as catalyst in nitro-aldol reaction was examined as shown in scheme 1. These catalysts being intrinsically chiral, attempt to separate their enantiopure form is under progress. However using this binuclear metal complexes, the preliminary attempt to understand their catalytic nature following the formation of -nitroalcohol has encouraged us by their isolated yield 75-80% with 5 mol% catalyst in  $\text{H}_2\text{O}:\text{CH}_3\text{OH}$  solvent medium; 8hrs reaction time and  $T = 45^\circ\text{C}$ . The synthesis, characterization and the efficiency of the catalyst, effect of solvent, temperature, and substitution will be discussed in detail Scheme.

Reference

1. Gerard Roelfes and Ben L. Feringa, *Angew. Chem., Int. Ed.*, 2005, 44, 3230.
2. P. M. Selvakumar, S. Nadella, K.J. Prathap, R.I.Kureshy, E.Suresh, P.S. Subramanian *Inorg. Chim. Acta.*, 2011, 375, 106.

(P263)

**1-Alkyl-1,2,4-Triazolium Based Brønsted Acidic RTILs as Benign Catalyst for The  
Synthesis of Dihydropyrimidines**

Sankaranarayanan Nagarajan, Elango Kandasamy

Research and development on synthesis of dihydropyrimidines (DHPMs) is inevitable. Since, they are pharmaceutically relevant anti-inflammatory, antitumor, antibacterial and antiviral agents.<sup>1</sup> And hence the demand for supply of DHPMs has been increased along with the usage of commercial organic solvents and metal based catalyst. Most of the organic solvents and metal based catalyst are potentially hazardous compounds to environment.<sup>2</sup> Numerous environmentally benign routes such as microwave-assisted technique, ionic liquids, ultrasound irradiation, solvent-free techniques and also many new catalysts have been reported to eliminate such hazardous compounds.<sup>3</sup> Among them the room temperature ionic liquids (RTILs), especially the azolium based RTILs are established well. The most studied RTILs in the azolium family are imidazolium based.<sup>4</sup> Based on the literature, the catalytic studies of 1,2,4-triazolium based RTILs are very few. In the present study, we have synthesized Brønsted acidic 1-alkyl-1,2,4-triazolium based RTILs and evaluated their catalytic studies in Bignelli reactions.

References:

1. Graaff, D.; Ruijter, E.; Orru, R. V. A. *Chem. Soc. Rev.* **2012**, 41, 3969.
2. Murata, H.; Ishitani, H.; Iwamoto, M. *Org. Biomol. Chem.* **2010**, 8, 1202.

3. Isambert, N.; Genisson, Y.; Rodriguez, J. Chem. Soc. Rev. **2011**, 40, 1347.
4. Hallett, J. P.; Welton, T. Chem. Rev. **2011**, 111, 3508.

**(P264)**

**Metal Incarcerated CNT Nanoreactors for Asymmetric Catalysis**

Poonam Sharma and Rakesh K Sharma

Indian Institute of Technology Jodhpur, Old Residency Road, Ratanada, Jodhpur, Rajasthan

Enantiomerically enriched compounds are of great contemporary interest to both academia and industry. So far most successful asymmetric catalysts are homogeneous. The drawbacks often associated with homogeneous catalytic processes are that of recyclability and product contamination by metal leaching. Heterogeneous asymmetric catalysis offers a great opportunity to overcome these drawbacks [1]. Carbon nanotubes (CNTs) are smart materials as a support for catalysts [2]. The metal incarceration in CNTs could tune them to nanoreactors for catalytic conversion. Modification of such CNTs with appropriate chiral source could provide prospects for the development of new heterogeneous chiral catalytic materials. Here we present highly active metallic nanocatalysts (Pd and Pt) modified by a chiral reagent incarceration in CNTs. These heterogeneous systems catalyse the asymmetric allylation of imines and aldehydes with high enantioselectivity under mild conditions. The homogeneous version of these reactions have already been reported[3,4]. The high activity and enantioselectivity are accredited mainly to the unique properties of the nano channels of the CNTs as they can readily enrich both chiral modifier and the reactants. After a catalytic run, the catalyst can be recycled and reused without loss of activity.

References:

1. Gladysz, J. A. Chem. Rev. **2002**, 102, 3215.
2. Chen, L.; Ma, D.; Zhang, Z.; Guo, Y.; Ye, D.; Huang, B. Cat. Lett. **2012**, 142, 975.
3. Sharma, R. K.; Samuelson, A. G. J. Chem. Sci. **2006**, 118, 569.
4. Sharma, R. K.; Samuelson, A. G. Tetrahedron Asymmetry **2007**, 182, 387.

**(P265)**

**First Application of Nickel Catalysed C (sp<sup>2</sup>)-O cross coupling to Access Vinyl-Aryl Ethers**

Debasish Kundu, Pintu Maity, Sabir Ahammed, Biju Majhi and Brindaban C. Ranu\*

Indian Association for the Cultivation of Science, Jadavpur

The vinyl C(sp<sup>2</sup>)-O bond forming reaction is of much interest as vinyl/styrenyl ethers are employed as useful intermediates in a wide variety of reactions like cycloaddition, cyclopropanation, metathesis reactions etc. They are also found as core units of several biologically active molecules and natural products. Recently Ni-catalysts have attracted much attention due to their relatively low cost and interesting catalytic features and have been successfully used for the synthesis of important organic molecules. This prompted us to explore the hitherto unreported application of Ni-catalyst for the vinylation of phenols without using any ligand. In a preliminary experiment we found that Ni-salt alone cannot initiate the reaction of vinyl bromide and phenol; however presence of a Cu-salt accelerated the reaction. Thus, as a part of our continuing program on transition metal catalyzed reactions, we report here a Cu-accelerated Ni-catalyzed ligand free cross-coupling of aromatic alcohols with styrenyl and vinyl



halides (I and Br). To the best of our knowledge, we are not aware of such C(sp<sup>2</sup>)-O cross coupling by nickel/Cu catalyst. Different types of phenols bearing both electron donating and withdrawing groups and various types of vinyl and styryl halides undergo coupling without any difficulty. The other advantages of this protocol are broad functional group tolerance including strong electron withdrawing functionality, high stereoselectivity, low catalyst loading, ligand-free condition, operational simplicity and high yields.

**(P266)**

**Bifunctional Titania Float for Metal Ion Reduction and Organics Degradation, via Sunlight**

Laveena P. D'Souza, Sindu Shree, and Geetha R. Balakrishna\*

Jain University

The present study demonstrates the use of a bifunctional titania float in sunlight to cause the simultaneous oxidation of formic acid and reduction of Cr (VI) to Cr (III). Nanosized, anatase TiO<sub>2</sub> was synthesized by wet chemical methods and characterized by various microscopy and spectroscopy techniques. A float has been fabricated with the above nano powder for water purification via sunlight mediated photocatalysis. The impracticable reduction of chromium in sunlight was made feasible by the use of photoactive nano Titania unlike the UV light which requires only the acid for complete reduction of chromium. The organic's (formic acid) degradation and Cr (VI) reduction were observed to support each other till the completion of both oxidation and reduction respectively. Formic acid with the catalyst (in the form of a float) in sunlight causes indirect scavenging of holes to enhance the catalytic efficiency and bring up the reduction rate on par with UV light making the water purification an environmental friendly and recyclable process.

**(P267)**

**Correlation analysis of reactivity in the oxidation of organic sulfides by benzimidazolium dichromate – A kinetic and mechanistic aspects**

Seema Kothari<sup>(a)</sup> and Dinesh Panday<sup>(b)</sup>

Department of Chemistry, J.N.V. University, Jodhpur, India<sup>(a)</sup>; Department of Chemistry, M.L.S.. University, Udaipur, India<sup>(b)</sup>

The oxidation of a number of monosubstituted aryl methyl sulfides by benzimidazolium dichromate (BIDC) in dimethyl sulfoxide (DMSO), to the corresponding sulfoxides, is first order with respect to BIDC. Michaelis-Menten type kinetics were observed with respect to sulfide.. The reactions are catalysed by hydrogen ion and the order is less than one. It appears that the BIDC-H<sup>+</sup> is the active electrophile. A ternary intermediate of composition Sulfide-BIDC-H<sup>+</sup> has envisaged. The best correlation is obtained with Charton's LDR and LDRS equations, the polar regression coefficients being negative. The oxidation of para- and ortho-substituted phenyl methyl sulfides is more susceptible to the delocalization effect than is the oxidation of meta-substituted compounds, which display a greater dependence on the field effect. The relatively small positive value of  $\eta$  suggests the presence of an electron-deficient transition state, in the rate-determining step, with moderate charge separation. The analysis of solvent effect by Swain's equation indicated that though both the anion- and cation-solvating powers of the solvent contribute to the observed solvent effect, the role of cation-solvation is major. A mechanism involving the formation of a 1:1 complex by an S<sub>N</sub>2 attack of sulfide-sulfur on

BIDC-H<sup>+</sup> in a rapid pre-equilibrium, followed by a rate-determining oxygen atom transfer from oxidant to sulfide, via a cyclic transition state, to give corresponding sulfoxide is postulated.

**(P268)**

**Facile and selective synthesis of 1,2-disubstituted benzimidazole using nanoporous material**

S. Senthilkumar & M. Kumarraja\*

Centre for Research and Post-graduate Studies in Chemistry, Ayya Nadar Janaki Ammal College, Sivakasi

A highly ordered nanoporous zeolite (NPZ) was synthesized using a commercially available zeolite as the framework source and organic surfactant was used as a template [1]. The nanoporous zeolite (NPZ) was characterized by SEM, TEM, EDAX and Powder XRD and has been employed as a catalyst for various organic transformations. In the present study, the reaction between *o*-phenylenediamine and aldehyde, the selectivity in forming the 1,2-disubstituted benzimidazoles is an issue of high interest. The resulting products are biologically potent and an important pharmacophore in drug discovery as they emerged as potent non-nucleoside inhibitors of HIV -1 reverse transcriptase and NS5B Polymerase of the Hepatitis C Virus(HCV) [2], also having anti-viral, anti-cancer, anti-hypertension and anti-ulcer properties. Many of the earlier reported processes have limitations such as use of some toxic acid as a catalyst, drastic reaction conditions, low yields, high temperature, and tedious work up procedures. All the above disadvantages are overcome by zeolite catalyst [3] such as shorter reaction time, use of inexpensive and environmentally benign catalyst, high yield and simpler work-up procedure.

References:

- [1]. H. J. Park, J. K. Jeon, J. M. Kim, H. L. Lee, J.H. Yim, J. Park and Y. K. Park, *J. Nanosci. Nanotech.* **2008**, 8, 5439.
- [2]. (a) S. D. Sharma and D. Konwar, *Synth. Commun.* **2009**, 39, 980-991. (b) M. S. Alamb, D. Pathaka, N. Siddiqui, B. Bhargava and W. Ahsanb, *Der Pharm. Lett.* **2010**, 2, 27-34.
- [3]. (a) M. Kumarraja and K. Pitchumani, *J.Mol.Catal.A:Chem.* **2006**, 256, 1. (b) S. Chassaing, M. Kumarraja, P. Pale and J. Sommer, *Org. Lett.* **2007**, 9, 3889.

**(P269)**

**CuO Impregnated mesoporous silica KIT-6 an efficient catalyst for benzene hydroxylation**

N S Sanjini and S Velmathi\*

Organic and Polymer Synthesis Laboratory, Department of Chemistry, National Institute of Technology, Tiruchirappalli

Highly ordered mesoporous three dimensional 3D copper oxide doped KIT-6 material was synthesized by simple wet impregnation method. The ordered nature of CuO-KIT-6 material was analyzed by low angle X-ray diffraction. The high surface area, pore diameter and mesoporous nature of the materials was confirmed by BET surface area analyzer. Si-O-Si, Si-OH and Cu-O-Si bonds in the framework CuO-KIT-6 was verified by FTIR spectroscopy. The Cu<sup>2+</sup> ← O<sup>2-</sup> charge-transfer transitions and d-d transitions of dispersed Cu<sup>2+</sup> were investigated by DRS UV-Vis spectroscopy. The morphology of the synthesized materials and percentage of copper oxide present in the material were analyzed by HR-SEM-EDAX. The catalytic activity of synthesized

CuO-KIT-6 was explored for hydroxylation of benzene with 30% aqueous H<sub>2</sub>O<sub>2</sub>. 10 mg of CuO-KIT-6 showed a good conversion (32%) with 100 % selectivity of phenol. Acetonitrile act as the solvent for this simple benzene hydroxylation reaction. At room temperature, small amount of CuO-KIT-6 (10 mg) showed 10.3% conversion of benzene. The optimization studies of catalyst amount, temperature etc., were done. The results will be presented in the conference.

**(P270)**

**Oxidation kinetics of antibacterial drug Norfloxacin by lipopathic oxidant, Cetyltrimethylammonium permanganate: A mechanistic study**

Sarita Garnayak and Sabita Patel

Department of Chemistry, National Institute of Technology, Rourkela

The oxidation of potent antibacterial drug Norfloxacin ((1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinolonecarboxylic acid, (NFX)) by lipopathic oxidant cetyltrimethylammonium permanganate (CTAP) in acetonitrile yields 7-amino-1-ethyl-6-fluoro 1,4-dihydro-4-oxoquinoline-3-carboxylic acid in presence of acetic acid. The kinetics of oxidation of norfloxacin by CTAP in water-acetonitrile mixture was investigated with change in [acid], [norfloxacin], [CTAP], [surfactant], temperature and solvents. The reaction was found to be fractional order with respect to norfloxacin, acetic acid and CTAP. Michaelis-Menten-type kinetics was observed with respect to norfloxacin and the Michaelis-Menten constant was found to be  $2.8 \times 10^{-4}$  M. The solvent kinetic isotope effect was found to be  $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})=1.18$ . The observed experimental data suggest that the reaction path involves the intermediate formation of a complex between norfloxacin and CTAP, which undergoes decomposition to give the product. The effect of [CTAP] on the rate shows micellar type aggregation at higher CTAP concentration. The kinetics of oxidation of NFX in presence of different ionic and nonionic surfactants has been studied, and found that CTAP is partitioned towards the micellar phase with the formation of mixed micellar aggregates with the surfactants while NFX remain in bulk non micellar solvent phase. The oxidation reaction occurs in bulk medium rather than the interface. High negative entropy of activation ( $\Delta S^\ddagger = -227 \text{ J K}^{-1} \text{ mol}^{-1}$ ) proposes a cyclic transition state. Suitable mechanism has been proposed on the basis of experimental results.

**(P271)**

**Synthesis, characterization and photocatalytic activity of some chromite spinel nanoparticles**

Swapnil Prabhulkar and R. M. Patil

Department of Chemistry, Institute of Science, 15, Madame Cama Road, Mumbai

Some chromite spinel nanoparticles with the formula  $\text{Ni}_x\text{Cu}_{1-x}\text{Cr}_2\text{O}_4$ , where  $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$  were studied for the photocatalytic degradation of Thiazole Yellow G an azo dye indicator in the present work. The nanoparticles were synthesized by simple, economic and ecofriendly coprecipitation method and were characterized by various physicochemical techniques such as X-ray diffraction analysis, Infra-red spectroscopy, Field Emission Gun – Scanning Electron Microscopy and Energy Dispersive Spectroscopy for the determination of crystallinity, metal-oxygen bonding, nanosized nature and elemental composition respectively. Various parameters affecting the photocatalytic dye degradation such as time, catalyst quantity

and catalyst composition were studied. This study provides clean and benign photocatalytic route for the degradation of the environmentally hazardous Thiazole Yellow G an azo dye.

**(P272)**

**Novel synthesis of tetrahydropyridines using polyphosphoric acid intercalated zirconia pillared montmorillonite**

Purabi Kar and Braja Gopal Mishra  
National Institute of Technology

Clays are one of the most economic materials that have been widely used as adsorbents and as catalyst to carry out several acid catalysed reactions in industries. Although clays are used as catalysts but they have certain disadvantages such as low thermal stability, loss of Brønsted acidic sites and collapsing of interlayer space at higher temperature. To overcome these limitations, several surface and interface modifications have been done to enhance the thermal stability, pore volume, surface area and acidity of the clay. The most prominent among them is pillaring of clay. The pillaring of the clay is done by the exchange of the interlayer cations by the inorganic polyoxocations, which is then subjected to thermal treatment to form stable metal oxide clusters which act as pillars that hold two clay sheets apart firmly thereby increasing interlayer spacing and preventing the collapse of clay sheets during high temperature applications. In this work, we report the synthesis, characterization and catalytic application of polyphosphoric acid-zirconia pillared clay nanocomposite system. The zirconia pillared clay (Zr-P) was prepared by the intercalation of  $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$  cationic species into the clay interlayer using dilute zirconium oxychloride solution as the oligomeric cationic source. The PPA supported zirconia pillared clay materials were synthesized using different preparative strategies to maximize the dispersion of the active polymeric component inside the inorganic clay matrix. The synthesized materials were subsequently characterized by XRD, UV-Vis, FTIR, SEM-EDAX, and TGA. The expansion of the clay interlayer on pillaring is clearly illustrated from the XRD. FTIR and UV-Vis study illustrates the structural integrity of the PPA species intercalated in the interlayers of the pillared clay. The catalytic activity of the PPA intercalated Zr-P pillared clay materials have been evaluated for the synthesis of the tetrahydropyridines under mild conditions. The PPA-Zr-P composite was found to be highly active for the multicomponent one pot synthesis of structurally diverse tetrahydropyridines under environmentally benign conditions.

**(P273)**

**Palladium-hydrogel nanocomposite for C-C coupling reactions**

Mitasree Maity, Uday Maitra\*  
Indian Institute of Science, Bangalore

Metal nanoparticles supported on a variety of matrices have received considerable attention owing to their enormous potential applications in various fields. In this work, palladium nanoparticles are conveniently synthesized by the sodium borohydride reduction at room temperature using calcium cholate hydrogel fibers as the template. The resulting Palladium nanoparticles self organize into the gel fiber, which assist the controlled growth as well as stabilization of palladium nanoparticles. Palladium nanoparticle containing xerogel was successfully used as a catalyst for C-C coupling reaction in water under aerobic conditions

without the use of expensive phosphine ligand. The catalysts are active and recyclable to some extent. The results from our preliminary studies will be presented in this poster.

**(P274)**

**Development of Soft-Nanohybrids for Modulating Enzyme Activity within Reverse Micelle**

Krishnendu Das, Deep Mandal and Prasanta K Das\*

Department of Biological Chemistry, IACS, Jadvapur

Improvement in catalytic efficiency of enzymes is of constant demand due to its potential importance in the field of biotechnology. Enzymology in membrane mimicking systems like reverse micelle associated with the idea of developing superior host where enzymes can be sheltered and protected from detrimental effects of solvent. 'Space' in the vicinity of the biomolecule is a key factor to modulate their efficacy in reverse micelle. Carbonaceous nanomaterials (single walled carbon nanotube (SWNT), graphene oxide (GO)), gold nanoparticles (GNP) having comparable dimension with the interfacial parameters, fitted well in the microenvironment of water-in-oil (w/o)-microemulsion and can efficiently modulate the interfacial area. We included nanomaterials such as GO and SWNT-GNP nanocomposite (GNP decorated SWNT surface) within CTAB reverse micelle to develop soft nanohybrid. Catalytic activity of surface active lipase enhanced up to 3.9 fold within GO and SWNT-GNP nanocomposite doped CTAB reverse micelles 1.2 than only CTAB reverse micelle. Interfacially localized GO or SWNT along with the water pool solubilized GNP presumably augmented the interfacial area of reverse micelle that helped in smooth occupancy of lipase and high local concentration of enzyme and substrate resulting in remarkable improvement in lipase activity.

References:

(1) D. Mandal, M. Ghosh, S. Maiti, K. Das, and P. K. Das, *Colloids and Surfaces B: Biointerfaces* **2014**, 113, 442.

(2) K. Das, S. Maiti, M. Ghosh, D. Mandal, and P, K, Das, *J. Colloid Interface Sci.* **2013**, 395, 111.

**(P275)**

**Synergistic catalysis using N-Heterocyclic carbenes and Palladium catalysts for direct allylation of aldehyde carbonyls**

Milind M.Ahire and Santosh B. Mhaske

The first, direct and highly regioselective allylation of aldehyde carbonyls has been achieved by synergistic catalysis using Palladium/N-Heterocyclic Carbene. Thus providing an efficient access to valuable  $\beta,\gamma$ -unsaturated ketones at milder reaction conditions starting from easily accessible allylic carbonates and aldehydes without any pre-activation. This catalytic method paves a new way in the area of C-allylation.

**(P276)**

**Development of Soft-Nanohybrids for Modulating Enzyme Activity within Reverse Micelle**

Krishnendu Das, Deep Mandal and Prasanta K Das\*

Department of Biological Chemistry, IACS, Jadvapur

Improvement in catalytic efficiency of enzymes is of constant demand due to its potential importance in the field of biotechnology. Enzymology in membrane mimicking systems like reverse micelle associated with the idea of developing superior host where enzymes can be sheltered and protected from detrimental effects of solvent. 'Space' in the vicinity of the biomolecule is a key factor to modulate their efficacy in reverse micelle. Carbonaceous nanomaterials (single walled carbon nanotube (SWNT), graphene oxide (GO)), gold nanoparticles (GNP) having comparable dimension with the interfacial parameters, fitted well in the microenvironment of water-in-oil (w/o)-microemulsion and can efficiently modulate the interfacial area. We included nanomaterials such as GO and SWNT-GNP nanocomposite (GNP decorated SWNT surface) within CTAB reverse micelle to develop soft nanohybrid. Catalytic activity of surface active lipase enhanced up to 3.9 fold within GO and SWNT-GNP nanocomposite doped CTAB reverse micelles 1.2 than only CTAB reverse micelle. Interfacially localized GO or SWNT along with the water pool solubilized GNP presumably augmented the interfacial area of reverse micelle that helped in smooth occupancy of lipase and high local concentration of enzyme and substrate resulting in remarkable improvement in lipase activity.

References:

- (1) D. Mandal, M. Ghosh, S. Maiti, K. Das, and P. K. Das, *Colloids and Surfaces B: Biointerfaces* **2014**, 113, 442.
- (2) K. Das, S. Maiti, M. Ghosh, D. Mandal, and P, K, Das, *J. Colloid Interface Sci.* **2013**, 395, 111.

**(P277)**

**Mn(III) based binaphthyl Schiff base complex heterogenized over organo-modified SBA-15: Synthesis, characterization and catalytic application**

Priti Sharma, Anish Lazar, A P Singh\*  
CSIR-National Chemical Laboratory

A heterogenized organocatalyst was synthesized by the covalent anchoring of the complex chloro (S,S)(-)[N-3-tert-butyl-5-chloromethyl salicylidene]-N-[3,5-di-tert-butyl salicylidene] 1,1'-binaphthyl-2,2'-diamine manganese(III) over modified mesoporous surface of SBA-15 through the reactive 3-aminopropyl trimethoxysilane (3-APTMS) group. The surface properties of the functionalized catalyst were analyzed by a series of characterization techniques such as elemental analysis, XRD, N<sub>2</sub> sorption measurement isotherm, FT-IR, TGA-DTA, XPS, and solid state <sup>13</sup>C NMR. The XRD and N<sub>2</sub> sorption measurement, UV reflectance and CP MAS NMR spectroscopy (<sup>13</sup>C and <sup>29</sup>Si) of the catalyst confirmed the structural integrity of the mesoporous hosts and the spectroscopic characterization technique proved the successful anchoring of the metal complex over the modified mesoporous support. The screening of the catalyst Mn(III)-L-SBA-15 and neat Mn(III)-L complexes was done in the oxidation reaction of thioanisole (methyl phenyl sulfide) by using TBHP as an oxidant. Mn(III)-L-SBA-15 catalyst shows higher activities and turnover number (TON) and exhibit enhanced enantiomeric excess comparable to homogeneous catalyst [Mn(III)-L]. [Mn(III)-L-SBA-15] catalyst was found more active than homogeneous catalyst [Mn(III)-L]; Moreover bulkier alkene like 1,2-dihydronaphthalene was also efficiently epoxidised with the synthesized supported catalyst.

(P278)

**Chiral VIVO-Sal-Indanol complex over modified SBA-15: An efficient, reusable enantioselective catalyst for asymmetric sulfoxidation reaction**

Anish Lazar, Priti Sharma, A P Singh\*  
CSIR-National Chemical Laboratory

A reusable, mesoporous, heterogeneous vanadium complex, VIVO-Sal-Ind-SBA-15 has been synthesized first time from (1R,2S)-(+)-Cis-1-amino-2-indanol for enantioselective sulfoxidation reaction. The physico-chemical properties of the functionalized catalyst were analyzed by a series of characterization techniques like XRD, N<sub>2</sub> sorption measurement isotherm, TEM, FT-IR, XPS, EPR, DRS UV-Visible, ICP-OES and solid & liquid state <sup>13</sup>C, <sup>29</sup>Si and <sup>51</sup>V NMR spectroscopy. Powder X-ray diffraction patterns, TEM and N<sub>2</sub> physisorption analysis confirmed the retention of mesoporous structure after various modifications. Solid-state NMR (<sup>13</sup>C CP-MAS NMR, <sup>29</sup>Si MAS NMR) and FT-IR analysis certified the integrity of organocatalyst residing inside the pore channels of the mesoporous support. Further, XPS, EPR, <sup>51</sup>V NMR and DRS UV-Visible analyses help to find out the oxidation state and coordination environment of vanadium in VIVO-Sal-Ind-SBA-15. Catalytic evaluation in asymmetric sulfoxidation reaction of sulfides indicated that VIVO-Sal-Ind-SBA-15 exhibited higher catalytic activity, stability, reusability and comparable enantioselectivity than SBA-15, PrNH<sub>2</sub>-SBA-15, neat VIVO-Sal-Indanol complex and without catalyst. The effect of different catalysts, temperature, solvents and substrates on sulfoxidation reaction was examined in order to optimize the conversion and enantioselectivity of thioanisoles to sulfoxides.

(P279)

**Oxidation of S- phenylmercaptoacetic acid by piperidinium chlorochromate**

K. Anbarasu, P. Selvi

The kinetics of oxidation of glycolic acid with piperidinium chlorochromate has been studied in 50 % aqueous acetic acid medium. The reaction order is one with respect to oxidant, substrate and fractional order with respect to hydrogen ion concentration. Decrease in dielectric constant of the medium increases the rate of reaction. No appreciable change in the rate is observed by increasing the ionic strength of the medium. The reaction does not induce the polymerization of acrylonitrile. From the kinetic data obtained, the activation parameters have been calculated and plausible mechanism has been proposed. A suitable rate law is derived.

(P280)

**Synthesis, Spectral, Chiroptical and Catalytic Investigation on Some Chiral Cu(II) Schiff base complexes**

P.M. Selvakumar<sup>c</sup>, Prabakar<sup>c</sup>, E. Chinnarajaa, P.S. Subramaniana<sup>b\*</sup>, Anjan Dasa<sup>b</sup>, and R.I. Kureshya<sup>b\*</sup>

<sup>a)</sup> CSIR-Central Salt and Marine Chemicals Research Institute, Bhavnagar-364002, Gujarat, India. <sup>b)</sup> Academy of Scientific and Innovative Research, New Delhi. <sup>c)</sup> Karunya University Tamil Nadu.

Enantiopure trianionic tetradentate ligands LSS, LRR and their respective Cu(II) mononuclear complexes 1-4 were synthesized where LRR and LSS are Schiff base ligands of 2-Hydroxy-

naphthaldehyde with (1R,2R)-2-amino-1-(4-nitrophenyl)propane-1,3-diol and (1S,2S)-2-amino-1-(4-nitrophenyl)propane-1,3-diol respectively. Both these ligands and complexes [Cu(LRR)], (1), [Cu(LSS)], (2) and Cu(LRR)<sub>2</sub> (3), Cu(LSS)<sub>2</sub> (4) were characterized using various spectroscopic techniques such as IR, UV-vis, NMR and MS. Since the ligands and their respective Copper(II) complexes are chiral in nature, they were screened as catalyst for asymmetric nitro-aldol reactions. The enantiopure ligand LSS and LRR depicting exactly opposite dichroic sign in the CD spectra, the respective complexes Cu(Lss), Cu(LRR) and Cu(LSS)<sub>2</sub>, Cu(LRR)<sub>2</sub> also retains the chirality. The complexes 3 and 4 with 1:2 ratio of Cu(II):ligand stoichiometric show almost negligible catalytic activity, but the respective 1:1 complexes 1 and 2 has been identified as catalytically active in the conversion of series of substituted benzaldehyde to respective nitroalcohol with high yield (78-88%) with moderate ee (upto 50%).

**(P281)**

**The influence of combination of oximes on the reactivating and therapeutic efficacy of antidotal treatment of organophosphate poisoning**

Rahul Sharma, Bhanushree Gupta, Arvind Sahu, Kallol K. Ghosh\*

School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur

Highly toxic Organophosphate compounds (OPC) including chemical warfare agents (CWA) and pesticides used by terrorist and military conflicts emphasize the necessity of development of effective medical countermeasures. Their acute toxicity effects are based on the phosphorylation of acetylcholinesterase (AChE) leading to the irreversible inhibition of its active sites. The subsequent over stimulation of post synaptic cholinergic receptor due to accumulation of acetylcholine in the synapses of the central nervous system and peripheral nervous system leads to massive disturbance of numerous body functions and finally leads to death by respiratory failure. The standard treatments with atropine and cholinesterase reactivators (oximes) are considered to be ineffective with certain nerve agents due to low affinity. Despite of extensive research over decades, none of the individual oxime has turned out to be a broad spectrum reactivator to cover all OP threatening agent. In search of a universal reactivator as antidotes, a new strategy is proposed i.e a combination of various oxime reactivators instead of using a single oxime alone. Here in we have used different combination of bis-oximes reactivators aiming to enhance their antidotal efficacy. The observed result may provide promising way to overcome the drawback of single oxime and make them more efficient to counteract toxic effects of OPC.

**(P282)**

**Mild and Efficient Copper Terephthalate Metal Organic Framework Catalyzed C-N Cross Coupling of Arylboronic Acids and Imidazole**

Nainamalai Devarajan and Palaniswamy Suresh\*

Madurai Kamaraj University

Metal Organic Frameworks (MOFs) are employed as heterogeneous catalysts for a variety of organic transformations.<sup>1</sup> The N-arylimidazoles has attracted significant interest in pharmaceutical molecules, natural products and carbene chemistry. Chan-Lam coupling reaction<sup>2</sup> is a valuable alternative cross-coupling in the construction of carbon heteroatom bonds. However, in almost all cases, stoichiometric amount of copper salts are the only choice to



promote the reaction in combination with different ligands, bases and solvents. In the present work, copper terephthalate MOF is found to be an efficient heterogeneous catalyst for C-N cross coupling reaction between imidazole and phenylboronic acids in ethanol under mild condition using TEA as base. The coordinatively unsaturated metal site present in copper MOF efficiently catalyzes the C-N coupling using catalytic amount only. A series of N-arylimidazoles (35 compounds) are synthesized with good to excellent yields. The present catalyst show wide range of functional group tolerance and favor with diverse heterocycles. The present catalyst eliminate stoichiometric amount of copper salts for Chan-Lam coupling and proceeds under ligand free condition. The catalyst is reused for several times without lose in catalytic activity. The observed results are rationalized by proposing a suitable mechanism.

#### References:

1. A. Corma, H. García, F. X. L. i Xamena, Chem. Rev. **2010**, 110, 4606–4655.
2. K. S. Rao, T. S. Wu, Tetrahedron **2012**, 68, 7735-7754.

#### (P283)

### **Asymmetric Ring Opening of meso-Epoxides with Aromatic Amines Using (R)-(+)-BINOL-Sc(OTf)<sub>3</sub>-NMM Complex as an Efficient Catalyst**

Ganesh V. More and Bhalchandra M. Bhanage\*

Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai

Enantiomerically pure  $\beta$ -amino alcohols are found in many biologically active natural products, novel therapeutic agents,  $\beta$ -blockers, insecticidal agents, antimalarial agent and oxazolines. In context, Hou et al. (1) reported a ring opening of meso-epoxides with anilines using Yb(OTf)<sub>3</sub> at -78 °C temp. which only 18% ee for aromatic epoxide. This seminal work was then followed by a report from Kobayashi et al. on using chiral bipyridine and Sc(DS)<sub>3</sub> as a catalytic system for the asymmetric ring opening of meso-epoxides with amines. However reported methods suffer from one or more drawbacks such as low enantioselectivity, longer reaction time, use of additives, use of expensive, and multistep synthesized chiral ligands.

#### (P284)

### **Anchoring of palladium(II) Schiff-base moiety in mesoporous silica: Preparation, characterization and catalytic study**

Soma Das and Subratanath Koner\*

Department of Chemistry, Jadavpur University

The scope of palladium has proven to be most useful in coupling chemistry, demonstrating palladium as a “jack of all trades” and often offering improved selectivity over the other metals. There are some drawbacks in using homogeneous Pd-complexes like poor reusability whereas using heterogeneous Pd-catalysts has great economic and environmental importance as they can be easily separated. Herein a new highly efficient and eco-friendly heterogeneous catalyst has been successfully prepared by immobilizing palladium(II) onto the surface of post synthetically modified mesoporous silica, MCM-41 via silicon alkoxide chemistry. Functionalization was carried out by inclusion of 3-[(2-aminoethylamino)propyl]trimethoxysilane (ATMS) onto MCM-41 followed by condensation with o-vanillin generating a tridentate Schiff base moiety in the porous matrix. The Schiff base moieties were used to anchor palladium (II) sites upon reaction

with [PdCl<sub>4</sub>]-2 ions. The catalyst has been characterized by elemental analysis, small-angle powder X-ray diffraction, FTIR, electronic spectroscopy, TEM study etc. The prepared catalyst efficiently catalyzes the Suzuki cross-coupling reactions of various aryl bromides with arylboronic acid derivatives in a 20% aqueous ethanol solution at 60 °C. The cross-coupling reaction between p-nitrobromobenzene and p-methoxyphenylboronic acid demonstrates a TOF (turn-over frequency) of 6867 h<sup>-1</sup> with a low palladium loading (1.13 × 10<sup>-2</sup> mol%) in the catalyst. This indicates high efficiency of the catalyst. The catalyst can be recycled and reused at least 5 times without any significant loss of its catalytic activity. The performance of catalyst endows the new system to constitute a highly valuable practical advantage for both academic study and industrial applications.

**(P285)**

**Effect of Connecting Linkers in the Reactivation Potency of Bis-oximes against Nerve Agent Inhibited-AChE**

Bhanushree Gupta, Rahul Sharma, Kallol K. Ghosh\*

School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur

Acetylcholinesterase (AChE), a serine hydrolase enzyme plays an essential role in human neuronal system degrading neurotransmitter acetylcholine (ACh) within a synaptic cleft. Organophosphate compounds elicit their strong toxic effects by irreversible inhibition of AChE activity. Consequently, the physiological function of enzyme is discontinued and reflected in permanent stimulation of cholinergic receptors leading to failure of breath centre in central nervous system and subsequent death from suffocation. The therapeutic approach involves the use of oxime nucleophile as a reactivator of poisoned-AChE. Several reactivators have been designed and synthesised, but only few are in clinical use, as 2-PAM and obidoxime. Up to date no oxime is available as a broad spectrum reactivator. In search of a universal reactivator several modifications have been introduced. It is observed that bis-oximes are superior to mono-pyridinium oximes. In the present investigation efficacy of bis-oximes, connected to different linkers (like butane, butene and xylene) have been kinetically evaluated against different OP-inhibitors such as Sarin & VX. The results of the present study may provide further insight into structural requirements in terms of connecting linker for oxime reactivators.

**(P286)**

**Asymmetric organic transformations for the synthesis of bioactive compounds**

N. Gupta, S. H. R. Abdi, R. I. Kureshy, N. H. Khan, H. C. Bajaj

Discipline of Inorganic Materials and Catalysis, CSIR-Central salt and Marine Chemicals Research Institute, G. B. Marg, Bhavnagar

Chirality, a geometrical phenomenon in molecular terms outcomes in the “dual existence” (termed as enantiomers) of a molecule having same chemical structure and mirror image to one another which are essentially not superimposable. In this context it is not surprising that the biological and therapeutic activity of a chiral substance a lot depends upon their stereochemistry, since the living organisms have a highly chiral environment. The one enantiomer of the racemic compound (eutomer) shows the desirable biological activity whereas the other (distomer) is either fatal or inactive at best. This is the reason that more than one third of the marketed drugs are chiral in nature and the regulator will approve the new drugs as a single isomer only where

there is a possibility of existence as racemates. Metal-salen catalysed asymmetric organic transformations forms a large part of the synthetic methodologies reported in the literature for the production of optically pure compounds. Despite turn out to be a very good catalytic system in terms of high yield and enantioselectivity for the various organic transformations still there is an additional room for improvement in catalyst design particularly to make it better recyclable. Our group are working on the design and synthesis of recyclable homogeneous and heterogeneous metal salen type of complexes and subsequently test them for different catalytic organic transformation such as asymmetric epoxidation, nitro-aldol, cyanation etc with high degree of recyclability. Further to show the general applicability of these catalytic systems are shown in the synthesis of several pharmaceutically active compounds in a multigram scale.

**(P287)**

**Catalytic activity of Copper (II) Complexes Derived from Succinoyldihydrazones**

R. Borthakur and R. A. Lal\*

Department Of Chemistry, Centre for Advanced Studies, North Eastern Hill University,  
Shillong

Copper-catalyzed cross-coupling reactions have lead to the formation of C–N, C–O, C–S and C–C bonds and have been recognized as one of the most useful strategies in synthetic organic chemistry. Actually, the past decade has witnessed a sharp increase on the attention to Cu catalyzed coupling transformations due to the low cost and low toxicity and also due to important discovery on organic ligand facilitated copper catalysis, which significantly lowered the demand on reaction conditions and expanded the compatibility of Cu-catalyzed couplings.<sup>1</sup> As an important step towards the ideal synthesis of atom economics, employing the Cu-catalyzed coupling reaction in the design of tandem reactions is now gaining worldwide attention for their great efficiency in assembling structurally diversified small molecules. Copper catalysts have been proven to tolerate a great variety of different reaction conditions. Accordingly, the research on exploring new application of Cu-catalyzed coupling has gained extensive interest. So, in importance and our interest in copper complexes<sup>2</sup> playing an important role in catalysis, we, present in here copper complexes of succinoyldihydrazones<sup>3</sup> which have been synthesized, characterized and their catalytic properties studied in the synthesis of 1,3-diynes. The dihydrazones used as ligands for complex formation are multidentate ligands possessing as many as eight bonding sites and can utilize utmost six bonding sites simultaneously in bonding to the metal ions. The complexes show equal reactivity both with electron donating and electron withdrawing substituted phenylacetylenes in good yields. The advantages of the present protocol are low catalytic loading of the catalyst (1 mol%) with good yields in less time. The 1,3-diynes play a significant role in the construction of macrocyclic annulenes, organic conductors, supramolecular switches and carbon-rich materials.

**(P288)**

**Synthesis, Characterization and Photocatalytic properties of Silver oxide coupled TiO<sub>2</sub> Core-Shell nanocomposites**

Bilal Masood Pirzada, Owais Mehraj, Suhail Sabir  
Department of Chemistry, Aligarh Muslim University

A simple approach to the synthesis of Ag<sub>2</sub>O/TiO<sub>2</sub> core-shell nanocomposites with uniform octahedral structure in solution phase was employed. Freshly synthesized Ag<sub>2</sub>O was used as precursor, and titanium tetraisopropoxide (Ti(iOPr)<sub>4</sub>), diluted with ethanol, was preliminary hydrolyzed by water to get a fine condensed layer on the Ag<sub>2</sub>O surfaces. A mixture of water and ethanol was then dropped into the reaction system to completely condense (Ti(iOPr)<sub>4</sub>) around the Ag<sub>2</sub>O to form Ag<sub>2</sub>O/TiO<sub>2</sub> core-shell nanocomposites. This method is suitable for the formation of uniform integrated TiO<sub>2</sub> shells and their thickness can be controlled by adjusting the ratio of water/ethanol. The synthesized core-shell nanocomposites were characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Fourier Transform Infra Red (FTIR). The thermal properties of the composites were studied by the TGA/DSC thermograms. Surface characteristics were studied by the BET analysis. Optical properties were studied by UV-Vis Spectroscopy, XPS and Fluorescence spectra. The photocatalytic properties were studied by the degradation of Rhodamine B dye in presence of UV and Visible light sources. The structural characteristics and the subsequent photocatalytic properties of the core-shell nanocomposites were optimized by varying the percentage of Ag<sub>2</sub>O and also the selection of surfactants during the synthesis process.

**(P289)**

**Chiral Cu(II)-Amino Alcohol Based Complexes for Asymmetric Aza-Henry Reaction of N-Ts Imines**

Manoj K. Choudhary, Anjan Das, R. I. Kureshy, Manish Kumar, N.H. Khan, S. H. R. Abdi, and H. C. Bajaj

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI)

Aza-Henry reaction is an important C-C bond forming reaction in organic chemistry where the end products can easily be transformed into vicinal diamines and  $\alpha$ -amino carbonyl compounds having direct application in pharmaceuticals. In this direction chiral metal complexes based on BINOL, bis-oxazolines and salen ligands with Cu, Zn, La, and organo-catalysts have been explored for this reaction giving good catalytic activity but there is a nagging issue of separation and recycling of the catalyst. Therefore, a series of chiral ligands viz. (S)/(R) 1,1'-bi(2-naphthol)-bis-aldehyde/ piperazine-bis-aldehyde and various aminoalcohols viz., (1R,2S)-(-)-2-aminodiphenylethanol, (1S,2R)-(-)-2-aminodiphenylethanol, (1R,2S)-1-amino-2,3-dihydro-1H-inden-2-ol and (R)-valinol were synthesized. In situ generated complexes of the chiral ligands with copper salts were used as catalyst for asymmetric aza-Henry reaction of a variety of N-tosylimines with different nitroalkanes at RT to afford good yields (80%) with excellent enantioselectivity (ee >99%) in 24 h with nitromethane and high syn selective products with excellent enantioselectivity with nitroethane. The chiral Cu(II) complex with the Cu(OAc)<sub>2</sub>.H<sub>2</sub>O and the ligand derived from (R)-1,1'-bi(2-naphthol)-bis-aldehyde, (1R,2S)-(-)-2-aminodiphenylethanol were proved to be the best in terms of activity as well as selectivity and several times recyclability. This protocol was further used for the synthesis of (S)-Levamisole in 1g level.

**(P290)**

**Amine functionalised MCM-41 as a green, efficient, and heterogeneous catalyst for the regioselective synthesis of 5-aryl-2-oxazolidinones from CO<sub>2</sub> and aziridines**

Deepak B. Nale and Bhalchandra M. Bhanage\*

Department of Chemistry, Institute of Chemical Technology, N. Parekh Marg, Matunga, Mumbai

Covalently linked amine functionalised MCM-41 catalysts were investigated as an efficient, heterogeneous and recyclable catalyst for the coupling of carbon dioxide (CO<sub>2</sub>) and aziridines providing high conversion with excellent regioselectivity towards 5-aryl-2-oxazolidinones under mild and solvent free conditions. The effect of various reaction parameters, such as temperature, time, and CO<sub>2</sub> pressure for the synthesis of 5-aryl-2-oxazolidinones using amine functionalized MCM-41 catalyst was investigated. The optimized protocol was applied to a wide variety of 1-alkyl-2-arylaziridines producing the corresponding 5-aryl-2-oxazolidinones with good yield and excellent regioselectivity. Amine functionalized MCM-41 catalysts were characterized by FT-IR, TG/DTA, high and low angle XRD, and solid state <sup>29</sup>Si CPMAS NMR analysis. Furthermore, the catalyst was effectively recycled for five consecutive cycles without any significant loss in its catalytic activity and selectivity under the described reaction conditions. Readily available reagents, mild reaction conditions and effective catalyst recyclability make this protocol simple, convenient, practical and environmentally friendly.

**(P291)**

**Heck reaction catalysed by organic-inorganic hybrid MMT-Clay exchanged Ammonium tagged carbapalladacycle in aqueous media**

Vasundhara Singh, Amanpreet Kaur, Navneet Kaur, Satwant Kaur

This paper highlights our efforts to attach an ionic tag to an oxime palladacycle [1]. Complete characterization of ammonium tagged oxime carbapalladacycle was done using IR, NMR, TGA, AAS, mass spectral and elemental analysis. Further, heterogenization of synthesized ammonium tagged carbapalladacycle onto Na<sup>+</sup>-MMT clay was done by ion exchange method. The intercalation was confirmed by IR, XRD and BET surface area analysis. The thermal stability of heterogenized ammonium tagged oxime carbapalladacycle clay nanocomposite was determined by thermo gravimetric analysis. Application of ammonium tagged oxime carbapalladacycle and its heterogenized clay nanocomposite as catalysts was studied for executing Heck reaction in water as solvent. High yields of desired products with excellent TONs and TOFs were obtained in all the cases. Recoverability of the heterogeneous catalytic system has been measured by the 'quantitative' catalyst recovery after each cycle.

Reference:

[1] V. Singh, R. Ratti, S. Kaur, J. Mol Catal: A Chem. **2011**, 334, 13-19.

**(P292)**

**Study of silica bound sulphonic acid catalyst for few acid catalysed reactions**

Amanpreet Kaur, Vasundhara Singh

PEC University of Technology, Chandigarh

The challenge of developing protocols for use of solid acid catalysts in important chemical transformations is of interest keeping in mind all the advantages associated with the use of heterogeneous catalysts. In light of the same we have synthesized a silica supported imidazolium based sulphonic acid catalyst and complete characterization of silica supported imidazolium based sulphonic acid catalyst was done using IR, NMR and XRD analysis. The catalytic activity of the synthesized solid acid catalyst has been tested for few acid catalysed reactions to develop an efficient protocol for the same with all the advantages of heterogeneous catalyst. High yields of desired products with excellent TONs and TOFs were obtained in all the cases.

**(P293)**

**Dicationic aluminium salen complexes immobilized on montmorillonite type of clay: A highly recyclable catalyst for the synthesis of cyclic carbonate**

Shailesh Verma, Rukhsana I. Kureshy\*, Tamal Roy, Noor-ul H. Khan, Sayed H. R. Abdi and Hari C. Bajaj

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI), Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar

36 billion metric tonnes of CO<sub>2</sub> is produced annually all over the world leading to significant adverse effect on the atmosphere of earth. This eventually results in extensive research in the area of CO<sub>2</sub> utilization for the production of value added compounds with economical interest. Cyclic carbonates are one of the most significant molecules in this category due to their versatile industrial application mainly as electrolytes for lithium ion batteries, as solvents and chemical intermediates. Among the several catalytic systems reported so far for their production monometallic and bio-metallic salen type of systems developed by North et al. at its infancy forms a significant part. In the present work we have synthesized a number of dicationic aluminium salen complexes and immobilized them on montmorillonite type of clay via intercalation method. These complexes were proved to be excellent catalyst for the production of cyclic carbonate in high yield (>99%) and selectivity (>95%) in 24h with a wide variety of 1,2-epoxides at very mild reaction condition using only atmospheric CO<sub>2</sub> pressure. Further catalytic activity even remained intact in 100mmol scale which shows general applicability of the catalytic system. Moreover the immobilized catalytic system was recycled by simple centrifugation and reused for 6 cycles showing no sign of diminishing activity.

**(P294)**

**Asymmetric Friedel - Crafts Addition of Indoles to N-Sulfonyl Aldimines Catalyzed by Cu(II) Chiral Amino Alcohols Based Schiff base Complexes**

Prathibha Kumari, Prasanta Kumar Bera, Noor-ul H. Khan,\* Rukhsana I.Kureshy, Sayed H. R. Abdi, Hari C. Bajaj

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI), Council of Scientific and Industrial Research (CSIR), G. B. Marg, Bhavnagar

Friedel-Crafts alkylation of arenes is an important C-C bond forming reaction in organic chemistry. Asymmetric version of this reaction can provide a useful strategy for the synthesis of enantio- enriched alkylated arene products, which are potential starting materials for various

biologically active compounds. Although excellent results in term of yield and enantioselectivity have been reported in Friedel-Crafts alkylation of indoles with imines; the synthetic protocol for the reported catalysts are multi-steps and silent on catalyst recyclability, which is an important aspect for the acceptability of these catalysts in industries. We have synthesized the recyclable copper(II) chiral amino alcohol based Schiff base complexes which smoothly catalysed the Friedel-Crafts alkylation of indole with aryl aldimine with good yields (up to 98%) and enantioselectivities up to 97%. To understand the mechanism of the catalytic Friedel-Crafts addition reaction, the kinetic investigation was carried out with different concentrations of the catalyst Cu(II)-Schiff base complex, indole and N-(3-nitrobenzylidene)-4-methylbenzene sulphonamide as a model substrate. The Friedel-Crafts alkylation reaction of N-(3-nitrobenzylidene)-4-methylbenzene sulphonamide was first order with respect to the concentration of the catalyst and the nucleophile but did not depend on the initial concentration of the substrate (aryl aldimine). An appropriate mechanism of the Friedel - Crafts alkylation reaction is proposed.

**(P295)**

**A tailor made support for Copper nanoparticles: Green approach to N-arylation using simple, effective and heterogeneous catalyst**

Nirav Barot, Harjinder Kaur\*

Department of Chemistry, School of Sciences, Gujarat University

Copper nanoparticles (Cu NPs) were directly deposited onto Functionalized resin XAD-4 base by deposition reduction method. The functionalized resin is used as support and found to have important role in catalytic activity of catalyst. Stability of metal nanoparticles is achieved by functionalization of XAD-4 resin. Functionalizing support can control quantity of metal nanoparticles deposited on it. The catalyst is characterized by various techniques such as X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The average diameter of Cu NPs as observed under TEM was found to be 6-9 nm. The catalytic activity of Cu NPs was tested for the N-arylation of various aromatic amines and nitrogen heterocycles with various aryl halides to afford the corresponding coupled products in good yields without using external ligands, surfactants or additives. The reactions were carried out in methanol-water system which is green solvent. The progress of the reaction was monitored by TLC and products after isolation were characterized by mass spectrometry and <sup>1</sup>H NMR. The catalyst can be easily recovered quantitatively by simple filtration and reused without loss of catalytic activity.

**(P296)**

**Highly Enantioselective sulfide oxidation with chiral iron complex using aqueous hydrogen peroxide as terminal oxidant**

Prasanta Kumar Bera, Sayed Hasan Razi Abdi,\* Noor-ul Hasan Khan, Rukhsana Ilays Kureshy, Hari Chandra Bajaj

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI), Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar

Chiral sulfoxides are valuable compounds for their application as chiral auxiliaries, ligands, organo-catalysts and in pharmaceutical industries. The direct and most efficient synthetic route

to synthesize chiral sulfoxides was simultaneously developed by Kagan et al. and Modena et al. by using modified Sharpless epoxidation catalytic system. Since then there was spurt of activity in this area of research and the last two decades have seen important piece of works. Considering the toxicity of metal and atom efficiency the use of iron as metal source and H<sub>2</sub>O<sub>2</sub> as oxidant always been preferable. Here in this study a new series of amino alcohol derived Schiff base ligands and their corresponding iron complexes were synthesized in situ to catalyse the asymmetric oxidation of prochiral sulfide using aqueous H<sub>2</sub>O<sub>2</sub> as a terminal oxidant. One of these complexes was found to be very efficient catalyst for the enantioselective oxidation of methyl phenyl sulfide. During the optimization process the electron donating benzoic acid derivative or its Na salt as additive was found to be beneficial to improve both conversion and enantioselectivity. Finally the applicability of this catalyst was tested on different aryl alkyl sulfides. The catalyst provided good to excellent enantioselectivity (75 to 98% ee) with good conversion and excellent chemo selectivity (up to 98%).

**(P297)**

**Palladium complexes of heterobidentate ligands: Active catalysts for acylation reactions via C-H activation**

Kokil Saikia and Dipak Kumar Dutta

Materials Science Division, CSIR-North East Institute of Science and Technology, Jorhat

Palladium catalyzed C-H activation reactions has attracted considerable interest in recent times [1-4]. Insertion of metal into the carbon-hydrogen bonds via oxidative addition has long been investigated [5], which often is the key step for majority of transformations leading to many pioneering discoveries in the field of catalysis [1,2]. Herein, we report two palladium complexes (1a, 1b) of heterobidentate Pd<sup>0</sup>S ligands. The complexes are characterized by different spectroscopic techniques together with the single crystal X-ray structure determination. The catalytic activities of the synthesised complexes were investigated towards acylation of aryl halides with aldehydes and good to excellent yields were obtained. 1b shows better catalytic activity over 1a which may be attributed to the higher stability of the pentagonal ring of 1a. The chelating heterobidentate ligands are expected to show hemilabile behavior during the catalytic cycle by dissociating the weaker bond to generate vacant coordination site at the metal centre and reassociate after the completion of the reaction.

References:

- [1] J.Wencel-Delord, T.Dro<sup>u</sup>ge, F.Liu, F.Glorius, Chem. Soc. Rev., **2011**, 40, 4740.
- [2] J.Ruan, O.Saidi, J.A.Iggo, J.Xiao, J. Am. Chem. Soc., **2008**, 130, 10510.
- [3] B.J.Borah, D.Dutta, P.P.Saikia, N.C.Barua, D.K.Dutta, Green. Chem., **2011**, 13, 3453.
- [4] K.Saikia, B.Deb, B.J.Borah, P.P.Sarmah, D.K.Dutta, J. Organomet. Chem., **2012**, 696, 4293.
- [5] D.K. Dutta, B.Deb, Coord. Chem. Rev., **2011**, 255, 1686.

**(P298)**

**Small Molecule as a Chiral Organocatalyst for Asymmetric Strecker Reaction**

S. Saravanan, Noor-ul H. Khan,\* Ajay Jakhar, Rukhsana I. Kureshy, Sayed H. R. Abdi, Hari C. Bajaj



<sup>a</sup> Discipline of Inorganic Materials and Catalysis, <sup>b</sup> Academy of Scientific and Industrial Research, Central Salt and Marine Chemicals Research Institute (CSMCRI), Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar

Chiral-amino acids and its derivatives are the class of compounds required in their high enantiomeric purity, due to their high-end application in the area of genetic engineering, pharmaceuticals and asymmetric catalysis. Strecker reaction represents one of the simplest and atom economic multi-component reaction to afford  $\hat{\pm}$ -amino nitrile, which on subsequent hydrolysis gives natural and unnatural  $\hat{\pm}$ -amino acids. Metal based and metal free protocols using various cyanide sources have been documented but ironically, ethylcyanoformate, one of the safest cyanide source did not find a place with organo-catalyst for asymmetric Strecker reaction. This study reveals the application of simple organo-catalyst for Strecker reaction using ethylcyanoformate. A novel chiral amide based organocatalyst was synthesized from readily available starting materials. A variety of N- substituted imines were found to be suitable substrates with *i*-PrOH as an additive in the presence of chiral organocatalyst at 0 °C with ethylcyanoformate as a source of cyanide for the synthesis of chiral  $\hat{\pm}$ -amino nitriles. High yield (up to 91%) with excellent enantioselectivity (up to 99%) were achieved in 24 - 30 h in case of N- substituted imines. To understand the mechanism of the catalytic Strecker reaction, nmr studies and kinetic investigations were carried out. We further extend our study, using chiral  $\hat{\pm}$ -amino nitrile for the synthesis of chiral amino amide and hydantoin in high yield with high ee.

**(P299)**

**Investigation of biocatalytic application and stability assessment of steapsin in supercritical carbon dioxide**

Kirtikumar C. Badgajar and Bhalchandra M. Bhanage\*

Department of Chemistry, Institute of Chemical Technology, Matunga

Biocatalysis through enzyme, either immobilized or non-immobilized has gained special importance in research field in recent years, or has been considered as the most efficient way of producing fine synthetic chemicals in a near future. In this study, we have used steapsin as a biocatalyst for the synthesis of the valuable 25 food flavour esters using supercritical carbon dioxide. The results obtained signify three fold increments in the catalytic activity of steapsin as compare to the non-aqueous reaction media. In addition to this, the immobilized biocatalyst was effectively used for five consecutive recycles. Furthermore, we also investigate the influence of various reaction parameters like temperature, pressure, and exposure times on the activity of steapsin. Various characterization tools were used to demonstrate the change in the morphological study of steapsin.

**(P300)**

**Asymmetric organic transformations for the preparation of biologically important chiral compounds: Development of novel chiral catalysts**

R. I. Kureshy

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI), Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar

Over one third of all the marketed drugs worldwide are chiral which equals to a net worth of \$100 billion. Most of the chirally pure products are produced either by optical resolution of respective racemic compounds or by direct catalytic intervention, which is environmentally and economically more desirable. However, developing chiral catalysts those can perform the target reaction with high reactivity and enantioselectivity is a major challenge. Towards this end I have targeted some of the industrially important asymmetric transformation and developed suitable catalysts for them. The targeted reactions are asymmetric epoxidation, desymmetrization of meso epoxide, aminolytic kinetic resolution (AKR) of terminal trans and aryloxy epoxides, hydrolytic kinetic resolution (HKR) of racemic terminal and aryloxy epoxides with amines/amine derivatives /water and nitroaldol reaction of aldehydes. Our efforts in designing of chiral metal complexes for the synthesis of enantio-pure products as key intermediate for pharmaceuticals will be presented.

**(P301)**

**An Efficient One Pot Multi Component Reaction for Synthesis of Indolo[2,3-c]quinolines Using Bismuth Nitrate penta-hydrate as Environmental Benign Catalyst**

Prabal P Singh\* and Deepak K. Das  
GLA University, Mathura

Various Indolo[2,3-c]quinolines and its derivatives have been synthesized in a single step three component reaction [1] using environmental benign catalyst like bismuth nitrate pentahydrate [2]. Aryl amines, aromatic aldehydes and indoles were treated in a pot with  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  taking acetonitrile as solvent. Tetrahydroquinone an intermediate product formed was in situ oxidized to corresponding quinolines using  $\text{MnO}_2$  as oxidizing agent in good to excellent yields. The current method is applicable to broad substrate scope and holds significant potential in constructing polyheterocyclic quinolines. Structures of all the synthesized compounds were confirmed by FTIR, FTNMR and HRMS.

References:

- [1] Organic Preparations and Procedures International, **2009**, 41, 1-68.  
[2] Tetrahedron Letters, **2005**, 46, 7747-7750,

**(P302)**

**Manganese Complexes with Non-porphyrin N4 ligands as recyclable catalyst for the Asymmetric Epoxidation of Olefins**

Nabin Ch. Maity, Prasanta Kumar Bera, Debashis Ghosh, Sayed H. R. Abdi,\* Rukhsana I. Kureshy, Noor-ul H. Khan, Hari C. Bajaj

Discipline of Inorganic Materials and Catalysis, Academic of Scientific and Innovative Research (AcSIR), Central Salt and Marine Chemicals Research Institute (CSMCRI), Council of Scientific & Industrial Research (CSIR), Bhavnagar

Catalytic asymmetric epoxidation is an important reaction as resulting enantiomerically pure epoxides are highly useful intermediates and building blocks. Host of works have been carried out on catalyst design with prime focus on achieving the targeted epoxide with high enantioselectivity and yield. Mn-salen catalysts, Shi's ketone based system and Porphyrin-

inspired catalysts are excellent methods to epoxidize a wide range of olefins with high enantioselectivity (>99% ee), yet substantial room for improvement remains in terms of catalyst loading, enantioselectivity and use of ecofriendly oxidants with high atom efficiency. While numerous variants of salen ligands have been reported, only handful of bio-inspired non-heme N4 ligands with Mn have been studied. Nevertheless, these N4 ligands have shown very interesting results in asymmetric epoxidation of olefins with ee up to 96% in selected substrates but mostly at -20 °C or below temperatures. Moreover, the synthetic protocols of these ligands are tedious, multi-step and often require expensive chiral starting materials. With this backdrop, we have come up to a simple methodology to synthesize chiral N4 ligands with readily available chiral cyclohexanediamine and 2-acetylpyridine as starting materials in three convenient steps and used their manganese complexes in the asymmetric epoxidation of olefins with low catalyst loading (0.1 mol%) to get the product epoxide in ee 44-88% with high turnover number (1000 which reached up to ~2500 after 3 catalytic cycles) in short reaction time (45-60 min) for the epoxidation of olefins, -unsaturated ketone and chromenes with H<sub>2</sub>O<sub>2</sub> as an oxidant and acetic acid as an additive at 0 °C.

**(P303)**

**Effect of Phase Change Behaviour of Nanocrystalline TiO<sub>2</sub> using Functionalized Ionic Liquids**

Satwant Kaur Shahi, Vasundhara Singh

Department of Applied Sciences (Chemistry), PEC University of Technology, Chandigarh.

TiO<sub>2</sub> nanocrystals were prepared in functionalised ionic liquid by different methods such as Sol-Gel and hydrothermal methods. The materials obtained were analyzed and characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and Raman spectroscopy to study the phase which gives the evidence of formation of anatase TiO<sub>2</sub> nanoparticles. Ionic liquids have many distinct properties such as negligible vapour pressure, high ionic conductivity, recyclable, provide a wide liquidus range for organic catalysis and inorganic synthesis. Functionalized ionic liquids act as solvents, structure-directing agent and templates in the synthesis of nanoparticles with controllable structure and morphologies. In the present work we will present the preliminary work done on phase change of nanocrystalline TiO<sub>2</sub> using functionalised ionic liquid and by varying the pH of the solution.

**(P304)**

**A distinct approach for the synthesis of spirooxindole derivatives catalyzed by sulphated ionic liquid heteropolyacid salt**

Shailesh P. Satasia, Piyush N. Kalaria and Dipak K. Raval\*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar- 388 120, Gujarat, India

A new type of heteropolyanion-based ionic liquid (HIL) has been found to be very effective for the diversity oriented synthesis (DOS) of spirooxindole derivatives. The catalyst and synthesized compounds were well characterized by sophisticated instrumental techniques. The HIL showed promising features for the reaction such as shorter reaction time, high product yields (about 90-95%), simple work up procedure, easy removal and recycling of the catalyst. It was reused several times without significant loss in its efficiency which made the protocol sustainable and economic.

(P305)

**Cu(N-Heterocyclic Carbene)chloride: An efficient catalysts for multicomponent Click Reaction for the synthesis of 1,2,3-triazoles in water**

Vishal B. Purohit, Sharad C. Karad, Dipak K. Raval and Kirit H. Patel \*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

A novel water soluble Cu(NHC)Cl complex was conveniently synthesized and characterized by NMR spectroscopy. It was employed for three component Click reaction of benzyl chlorides (1a-e), alkynes (2a-c) and sodium azide (3) in water as solvent at room temperature. All the synthesized compounds (4a-o) were characterized by elemental analysis, IR, <sup>1</sup>H NMR and mass spectrometry. The catalyst was easy to prepare, very versatile, reusable and was found to be highly active at low catalyst loading towards the reaction.

(P306)

**Merrifield resin supported -SO<sub>3</sub>H functionalized ionic liquid as novel heterogeneous catalyst for Fisher indole synthesis**

Jemin R. Avalani\* and Dipak K. Raval

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar- 388 120, Gujarat, India

A highly convergent, efficient and practical heteroannulation protocol for the synthesis of indole derivatives has been developed. Reactions involving Merrifield-SO<sub>3</sub>H mediated one-pot two component synthesis of substituted phenyl hydrazines and various ketones (methyl ethyl ketone,  $\hat{I}\pm$ -tetralone, cyclohexanone, 1-Indanone) resulted in the highly substituted indole derivatives. All the products have been characterized by elemental analysis and spectral techniques. Easy recovery of the catalyst and high yield made the protocol attractive, sustainable and economic. The catalyst was found to be stable and reusable in the described protocol.

(P307)

**Triple C-H Functionalisation/Activation: Palladium Catalyzed Selective Synthesis of Benzofurans from Phenols and Olefins**

Upendra Sharma, Soumitra Agasti, Togati Naveen, Debabrata Maiti\*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai

Transition metal-catalyzed C-H activation/functionalization for the C-C or C-heteroatom bond formation is one of the most challenging and attractive way to synthesize heterocyclic moieties. Heterocyclic compounds particularly with oxygen as heteroatom are prominent structures found in biologically active natural and synthetic products. Benzofuran derivatives are ubiquitous in natural products agrochemicals and pharmaceuticals. Over the years, several effective strategies involving transition metal catalyzed inter/intra-molecular heteroannulation reactions have been reported for synthesizing benzofuran scaffolds. However, synthesis of 2- or 3-substituted benzofurans by simply reacting phenol and unactivated olefin is most straight forward and atom economical approach.<sup>1</sup> This methodology enables three C-H bond functionalisation and result in the construction of C-C and C-O bond. In this presentation, palladium catalyzed selective synthesis of 2-, 3- and 2,3-disubstituted benzofuran along with mechanism will be discussed.

## References

1. U. Sharma, T. Naveen, A. Maji, S. Manna and D. Maiti. *Angew. Chem. Int. Ed.*, 2013, 52, 12669.

### (P308)

#### **Iron Catalyzed Oxidative Arylation of Phenol: A Direct Approach towards Arylated Quinones by C-H Functionalization**

Arghya Deb and Debabrata Maiti\*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 40076

Arylated quinones (Quin-Ar) have emerged as an important structural motif to exhibit a wide variety of biological and pharmacological activities. The unique electron transfer property has enhanced their importance in photosynthesis and dye industry. Several synthetic strategies have been invented for Quin-Ar compounds because of their attracting features. Among them, traditional cross-coupling approaches were limited by the expensive catalyst. Thus the mere success was attributed by the prehalogenated quinones which are difficult to synthesize due to chemo- and regioselectivity problems. Though radical reactions have become an effective alternative approach but the use of hazardous diazonium salts make it less practical. Despite of high importance, quinone arylation methods are infrequent due to the scarcity of derivatized quinones as starting material and also its high expense. In order to address this problem, herein we are describing the protocol combining in situ selective oxidation of phenols to quinones and then arylation by C-H functionalization.

### (P309)

#### **Water dispersible, long time stable copper nanoparticles: Synthesis and catalytic activity**

Ravneet Kaur<sup>1,3</sup>, Surinder K. Mehta<sup>3</sup>, Cristina Giordano<sup>2</sup> and Michael Gradzielski<sup>1</sup>

<sup>1</sup>: Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, Sekr. TC7, D-10623 Berlin, Germany <sup>2</sup>: Max-Planck Institut (MPI) für Kolloide und Grenzflächen, Department of Colloid Chemistry, Research Campus Potsdam-Golm, D-14424 Potsdam, Germany <sup>3</sup>: Department of Chemistry and Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh-160014, India

Cu NPs are favorite candidates for catalyzing many organic reactions due to their cheap availability and mild reaction conditions. But their high reactivity towards oxygen necessitates not only their synthesis but also storage in a strictly inert environment, which is the biggest disadvantage. The present work focuses on two key aspects; firstly Cu NP synthesis using metallosurfactant under atmospheric conditions, with water as the solvent and secondly analysis of the catalytic efficiency of as synthesized metal nanoparticles. Stable, water dispersible Cu NPs were obtained by reducing metal complex in the presence of polyacrylic acid (PAA). Interestingly enough, other protecting agents such as polymers (polymethacrylic acid (PMAA)) or surfactants (dodecylamine, dodecylamine acetate) prove to be less efficient to prevent surface passivation of NPs. Reduction of nitrobenzenes was chosen to test the catalytic effect of the nanoparticles. By employing PAA capped Cu NPs, the catalytic activity was remarkably improved, given the fact that PAA is also efficiently preventing the oxidation of the Cu NPs.

## References:

1. Deb, A.; Manna, S.; Maji, A.; Dutta, U. *Eur. J. Org. Chem.* 2013, 24, 5251-5256. 2. Fujiwara, Y.; Domingo, V.; Seiple, I. B.; Gianatassio, R.; Del Bel, M.; Baran, P. S. *J. Am. Chem. Soc.* 2011, 133, 3292.

**(P310)**

**N-Formylation of Amines by Carbon Nanotube-Gold Nanohybrids**

N. Shah, E. Gravel, A. Hagege, H. Li, D. V. Jawale, E. Doris and I. N. N. Namboothiri  
Department of Chemistry, IIT-Bombay

Carbon nanotube(CNT)-metal nanohybrids are novel heterogeneous catalyst systems for a variety of organic reactions. Low catalyst loading, high turnover number (TON) and turnover frequency (TOF), high selectivity, simple and mild conditions, recyclability of the catalyst and ability of CNT to stabilize higher oxidation state of metal are some of the salient features of CNT-metal catalyzed reactions. CNT-Au nanohybrid has been recently employed as efficient catalysts for the oxidation of alcohols and reductive amination of aldehydes. Herein we report the direct N-formylation of amines with aqueous HCHO as formyl source under the catalytic influence of CNT-Au nanohybrid. The reaction proceeded under ambient conditions with 0.4 mol % of the catalyst to provide N-formylated amines in excellent yield. The scope of the reaction was demonstrated with alkyl and aryl amines. The catalyst was also recyclable upto four times without any loss of activity.

**References**

1. Advances in Carbon Nanotube-Noble Metal Catalyzed Organic Transformations, J. John, E. Gravel, I. N. N. Namboothiri and E. Doris, *Nanotechnol. Rev.* 2012, 388, 300-305.
2. Carbon Nanotube-Gold Nanohybrids for Selective Catalytic Oxidation of Alcohols, R. Kumar, E. Gravel, A. Hagege, H. Li, D. V. Jawale, D. Verma, I. N. N. Namboothiri and E. Doris, *Nanoscale* 2013, 5, 6491-6497.
3. Direct Reductive Amination of Aldehydes Catalyzed by Carbon Nanotube/Gold Nanohybrids, R. Kumar, E. Gravel, A. Hagege, H. Li, D. Verma, I. N. N. Namboothiri and E. Doris, *ChemCatChem* 2013, DOI: 10.1002/cctc.201300490.

**(P311)**

**Synthesis and Structural Properties of N,N,N',N'-tetraalkyl-3,4- and 3,5-pyridinedicarboxamide and its Ag(I), Hg(II) AND Pd(II) Complexes**

Love Karan Rana and Maninder Singh Hundal\*

Department of Chemistry, Centre for Advanced Studies in Chemistry,  
Guru Nanak Dev University, Amritsar, Punjab, India

The use of divergent polydentate ligands in metal coordination instead of the traditional convergent chelating ligands can be very helpful in extending the coordination network through space in one-, two- or three-dimensional architectures<sup>1</sup> and a good innovation for crystal engineering of coordination networks. The dimensionality of the resulting coordination network can be increased by non-covalent interactions, like hydrogen bonds,  $\pi$ - $\pi$ , C-H- $\pi$  and/or other van der Waals interactions,<sup>2</sup> affecting the final topology and properties of the supramolecular organization. Non-macrocyclic, multidentate carboxamides ligands derived from pyridine-3,4 and 3,5-dicarboxylic acids provide a variety of divergent coordination sites for binding to metal

ions in contrast to the well-studied carboxamide complexes of 2,6-pyridine-dicarboxylic, nicotinic and picolinic acid which provide convergent coordination sites.<sup>3</sup> Our interest in N,N,N',N'-tetraalkylpyridine-3,4- and 3,5-dicarboxamides is to investigate the different coordination geometries around the metal ions. These types of ligands may provide divergent coordination sites leading to supramolecular frameworks due to coordination and/or H-bonding or may result in simple monomeric coordination complexes due to convergent coordination sites and be useful as metallo-ligands by using the free coordination sites. To the best of our knowledge there is no crystal structure of any complex reported for them. The crystal structures of the complexes of Hg(II), Ag(I) and Pd(II) with N,N,N',N'-tetra-isopropyl/isobutyl-pyridine-3,4-dicarboxamide (IP34PD, IB34PD) and N,N,N',N'-tetra-isopropyl/isobutyl-pyridine-3,5-dicarboxamide (IP35PD, IB35PD) show versatile coordination complexes from monomers to 1D chains to 2D H-bonded networks.

#### References:

1. S. R. Batten, *J. Solid State Chem.*, 2005, 178, 2475.
2. (a) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885. (b) K. Biradha, *CrystEngComm*, 2003, 5, 374. (c) A. M. Beatty, *Coord. Chem. Rev.*, 2003, 246, 131. (d) P. Erk, H. Hengelsberg, M. F. Haddow and R. van Gelder, *CrystEngComm*, 2004, 6, 475; (e) M. Nishio, *CrystEngComm*, 2004, 6, 130. (f) S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, 34, 109. (g) J. M. Pollino and M. Weck, *Chem. Soc. Rev.*, 2005, 34, 193. (h) D. Braga, L. Brammer and N. R. Champness, *CrystEngComm*, 2005, 7, 1.
3. (a) P. Kapoor, A. P. S. Pannu, M. Sharma, G. Hundal, M. S. Hundal and R. Kapoor, *J. Coord. Chem.*, 64, 256 (2011). (b) P. Kapoor, A. P. S. Pannu, M. Sharma, M. S. Hundal, R. Kapoor, M. Corbella and N. Aliaga-Alcalde, *J. Mol. Struct.*, 981, 40 (2010). (c) P. Kapoor, A. P. S. Pannu, M. Sharma, G. Hundal, M.S. Hundal and R. Kapoor, *J. Coord. Chem.*, 63, 3635 (2010). (d) A.P.S. Pannu, P. Kapoor, G. Hundal, R. Kapoor, M. M. Ripoll, R. Butcher and M. S. Hundal, *Polyhedron*, 2011, 30, 1691. (e) A. P. S. Pannu, P. Kapoor, G. Hundal, R. Kapoor, M. Corbella, N. A. Alcade and M. S. Hundal, *Dalton Trans.*, 2011, 40, 12560.

#### (P312)

#### **Crystal Engineering Approach for the Design of Mechanically Flexible Organic Crystals by Introducing Slip planes in Structure**

G. Rama Krishna, Ramesh Devarapalli, Garima Lal and C. Malla Reddy\*

Department of Chemical Sciences, Indian Institute of Science Education and Research, Kolkata, Mohanpur Campus, West Bengal.

Utilization of organic single crystal materials is increasing day by day owing to their promising applications in organic light emitting diodes, organic solar cells, mechanochromic luminescence and tabletability of APIs etc (Ref.1) These desirable functions, especially mechanical properties, can be achieved by imparting soft nature in organic materials, however unfortunately there is no simple strategy to attain this. Till date all the findings are serendipitous discoveries, so a rational design strategy is necessary to accomplish such soft mechanical behavior in molecular crystals. Here we propose a design strategy to attain plastically deformable organic materials by introducing slip planes in the crystal structures. The high plasticity can be achieved by substituting hydrophobic groups, such as t-Bu, -OMe, -Me and multiple -Cl (or) -Br groups on -

Ar building blocks, for example on naphthalene diimide (NDI), which leads to the formation of slip planes in the crystal structures (Ref.1(c)), hence facilitate the bending.

References:

1. (a) Briseno, A. L. et al. *Nature.*, 2006, 444, 913. (b) Sundar, V. C. et al. *Science.*, 2004, 303, 1644. (c) Krishna, G. R. et al. *Adv. Funct. Mater.*, 2013, 23, 1422. (d) Bag, P. P. et al. *Cryst EngComm.*, 2012, 14, 3865.

**(P313)**

**Celecoxib cocrystal polymorphs with cyclic amides: Synthons of sulfonamide drug with carboxamide conformers**

Geetha Bolla, Sudhir Mittapalli, and Ashwini Nangia\*  
University of Hyderabad, Hyderabad.

Celecoxib (CEL) is a well-known non-steroidal anti-inflammatory drug (NSAID) and selectively used from coxib family. Cocrystals of the celecoxib were screened in this study to improve the poor aqueous solubility and bioavailability of the drug. Cyclic syn-carboxamides (lactams) produced cocrystals with different supramolecular synthons in sulfonamide of celecoxib. Cocrystals with five to eight member ring lactams were screened in this report. Further, valerolactam (VLM) attributes trimorphic cocrystals with synthons varieties in CEL sulfonamide functional group (dimer and catemer) and others gave only one form exclusively. The binary systems including trimorphic cocrystals are systematically characterized by IR, PXRD, DSC, SEM and finally confirmed by single crystal X-ray diffraction. The binary adducts assembled via N-H $\cdots$ O and followed by C-H $\cdots$ O, C-H $\cdots$ F hydrogen bonds. In addition, solubility and dissolution study of all the cocrystals were carried out in 50% EtOH-water medium and cocrystals showed improved solubility compared to CEL. Interestingly, we found there is a correlation between Hirshfeld surface analysis, stability and it follows CEL-VLM-I > CEL-CPR > CEL-VLM-II (39.8 > 38.1 > 34.5). In extent major 2D finger print Hirshfeld follows the stability order of the trimorphic cocrystals.

**(P314)**

**Structural Characterization of Axial Ligand Modified High Valent Tin (IV) Porphyrins**

Rahul Soman, Subramaniam Sujatha and Chellaiah Arunkumar

Bio-inorganic Materials Laboratory, Department of Chemistry, School of Natural Sciences,  
National Institute of Technology Calicut, Kerala, India.

Six coordinate tin (IV) porphyrins with trans-axial ligands were prepared from 5,10, 15, 20-tetrakis(4-carboxymethylphenyl)porphyrin [H<sub>2</sub>T(4-CMP)P] upon metallation with stannous chloride using the reported methods<sup>1</sup>. The formed tin dichloro porphyrin complexes were converted into their dihydroxy derivatives [dihydroxo[5,10,15,20-tetrakis(4-carboxymethylphenyl) porphyrinato] tin(IV) [Sn(OH)<sub>2</sub>T(4-CMP)P], which have strong affinity towards oxy-anionic ligands such as carboxylates and aryloxides. These synthesized tin(IV) porphyrins were characterized using UV-Visible and <sup>1</sup>H NMR spectroscopic methods. The <sup>1</sup>H NMR spectra of Sn(OH)<sub>2</sub>T(4-CMP)P shows a broad signal at -7 ppm because of the presence of axial hydroxyl groups and the  $\beta$ -pyrrole protons appears as sharp singlet along with satellite signals due to the coupling of <sup>119</sup>Sn and <sup>117</sup>Sn with  $\beta$  pyrrole protons. Sn(OH)<sub>2</sub>T(4-CMP)P is



reacted with various substituted phenols and aryl carboxylic acids. We successfully obtained the single crystals  $\text{Sn}(\text{Cl})_2\text{T}(4\text{-CMP})\text{P}$  and 4-nitrophenol condensed product,  $\text{Sn}(\text{O-ph-NO}_2^-)\text{2T}(4\text{-CMP})\text{P}$ . From the crystal structure, it is found that the axial ligands shows a distance of 2.419 Å and 2.067 Å for Sn-Cl and Sn-O respectively. It is interesting to note that the axial chlorine ligand is having a weak interaction with  $\beta$ -pyrrole carbon with 3.368 Å to form one dimensional array and in  $\text{Sn}(\text{O-ph-NO}_2^-)\text{2T}(4\text{-CMP})\text{P}$ , there is a strong interaction between the oxygen of nitro group and  $\beta$ -pyrrole hydrogen.

References:

1. (a) Arnold, D.P; Blok, J. *Coord. Chem. Rev.*, 2004, 248, 299-319; (b) Shetti, V.S.; Pareek, Y.; Ravikanth, M. *Coord. Chem. Rev.*, 2012, 256, 2816-2842.

**(P315)**

**Noncovalent Interactions in Trans-Porphyrins: Synthesis and Structural Characterization**

Jagadeesan Ramesh, Subramaniam Sujatha and Chellaiah Arunkumar

National Institute of Technology

Non-covalent interactions involving halogen play an important role in supramolecular chemistry [1] which provides stability to form molecular assemblies especially in the absence of strong intermolecular forces [2]. Here, we report the synthesis of trans-porphyrin namely, 5,15-bis(pentafluorophenyl)-10,20-bis(4-bromophenyl) porphyrin from 5-(pentafluorophenyl) dipyrromethane and 4-bromobenzaldehyde. And, its metal complexes ( $\text{M} = 2\text{H}$ ,  $\text{Zn}(\text{II})$ ,  $\text{Cu}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Co}(\text{II})$ ,  $\text{Mn}(\text{III})$  and  $\text{Fe}(\text{III})$ ) were prepared and all the porphyrins were characterized by UV-Visible,  $^1\text{H}$  NMR and Mass spectroscopic techniques as well as by single crystal X-ray analysis. Crystal structure of these porphyrins exhibit interesting weak intermolecular interactions referred as F-Br, F-F, C-F.. $\pi$ , C-Br..H and C-F..H which controls the packing motif. Interestingly, in free base and copper derivatives, the F-Br interaction is found to be 3.295 and 3.280 Å respectively which is not seen in zinc complex. The single crystal X-ray analysis of other porphyrin derivatives is in progress.

References:

1. (a) Kaur, G.; Panini, P.; Chopra, D.; Choudhury, A. R. *Cryst. Growth Des.* 2012, 12, 5096. (b) Dunitz, J. D. *ChemBioChem.* 2004, 5, 614. (c) Chopra, D.; Guru Row, T. N. *CrystEngComm.* 2011, 13, 2175. (c) Thalladi, V. R.; Weiss, H. C.; Blaser, D.; Boese, R; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* 1998, 120, 8702.
2. (a) Reichenbacher, K.; Suss, H. I.; Hulliger, J. *Chem. Soc. Rev.* 2005, 34, 22. (b) Hayashi, N.; Mori, T.; Matsumoto, K. *Chem. Commun.* 1998, 1905.

**(P316)**

**Construction of Helical 1D-Polymeric Chain in Hg(II) : Synthesis, Crystal Structure and DNA Binding.**

Anoop Kumar Saini<sup>a</sup>, Shaikh M.Mobin<sup>a</sup>, Mohammad Akbar<sup>a</sup>, Veenu Mishra<sup>a</sup> and Amit Kumar<sup>b</sup>

<sup>a</sup> Department of Chemistry Indian Institute of Technology Indore, Khandwa Road, Indore

452017. <sup>b</sup> Department of Bioscience and Bioengineering Indian Institute of Technology

Indore, Khandwa Road, Indore.

Reaction of  $[C_{22}H_{19}O_2N_4Hg]PF_6$  (1) with 3-aminobenzoic acid in the presence of acetonitrile at ambient temperature yields 1D-polymeric chain(2). This compound was characterized by elemental analysis and single crystal X-ray crystallography. Each Hg(II) in 2 is hepta-coordinated via Hg-O and Hg-N bonds possess pentagonal bipyramidal geometry. The inter and intra molecular non bonding interactions in 2 leads to formation of hydrogen bonded 2D-network. Moreover, 1D-polymeric chain in 2 is bound to another layer of neighbouring 1D-polymeric chain via hydrogen bonded in a helical shape. This prompted us to look for DNA interaction in 2. 2 on reacting with DNA show considerable fluorescence quenching.

**(P317)**

### **Crystallographic and thermal studies of o-hydroxy Schiff bases**

Kumkum Sharma, Satish Kumar Awasthi\*

Chemical Biology laboratory, Department of Chemistry, University of Delhi, India.

Schiff bases derived from o-hydroxy acetophenone and aliphatic amine have been prepared by microwave-induced organic reaction enhancement (MORE) technique in quantitative yields and assessed by spectroscopic and crystallographic techniques. The experimental protocol involves the condensation of equimolar quantities of o-hydroxyacetophenone and different primary amines.

Infrared (IR) spectra of Schiff base was recorded in the range of 4000-400  $cm^{-1}$  at room temperature. The spectrum showed a medium broad band centred at 3448  $cm^{-1}$  due to intramolecular hydrogen bonding  $\nu(O-H)$ . The existence of intramolecular hydrogen bonds between the hydroxyl oxygen and the nitrogen atom of imine group is further confirmed by X-ray structural data. The very strong and sharp band observed at 1617  $cm^{-1}$  is assigned to the  $\nu(C=N)$  stretching vibrations of azomethine group. Also  $\nu(C-N)$  absorption band observed at 1290  $cm^{-1}$ . The phenolic  $\nu(C-O)$  stretching band is observed as sharp singlet at 1237  $cm^{-1}$ , which is the evidence for the existence of the enol-imine form in the solid state. Absorption bands with the wave numbers of 2958 - 2853 ( $\bar{\nu}$  C-H) and 1464  $cm^{-1}$  ( $\bar{\nu}$  C=C) were also observed. Thermal study including TGA, DTA, DSC were also done. These Schiff bases can be used to make transition metal complexes.

References:

1. Durr, H. *Angew. Chem., Int. Ed.* 1989, 28, 413-431.
2. Kundu, A; Shakil, N. A.; Saxena, D. B.; Pankaj; Kumar, J.; Walia, S. J. *Env. Sci. Health Part B*, 2009, 44, 428-434.
3. Nazir, H.; Yildiz, M.; Yilmaz, H.; Tahir, M. N.;  $\tilde{A}elk\tilde{A}^{1/4}$ , D. *J Mol Struct.* 2000, 524, 241-50.

**(P318)**

### **Finely Tuned Cu(II)-Hg(II) Mixed Metal 1D-Polymeric Chain: Synthesis and Crystal Structures**

Veenu Mishra, a Shaikh.M.Mobin,\* Pradeep Mathur\*

School of Basic Sciences, Discipline of Chemistry, Indian Institute of Technology Indore

Mixed metal polymer has shown great interest due to their potential application in electrical conductivity, sensing, catalysis and magnetic behavior. Reaction of 3,5-Diisopropylsalicylic acid (DIPSA) and bipyridine with  $Cu(CH_3COO)_2$  and  $Hg(CH_3COO)_2$  in acetonitrile gives mixed

metal polymers 1 and 2. 1 and 2 are formed by fine tuning in reaction time. Formation of monomer 3 was observed during the recrystallization of polymer 2 in MeOH. The mixed metal polymers contain alternate dimeric unit of Cu(II) and Hg(II) forming 1D- polymeric chain, with varying geometry around Cu(II) and Hg(II) ions.

**(P319)**

**Thermally Induced Single Crystal to Single Crystal Transformation of Monomeric Ionic Co(II) complex to Dimeric Neutral Co(II) Complex**

Akbar Mohammad, Shaikh M. Mobin\*

School of Basic Sciences, Discipline of Chemistry, Indian Institute of Technology Indore

The recent upsurge in the field of single-crystal-to-single-crystal (SCSC) transformations reveals new routes to systematically studying the properties of the solid materials. SCSC transformation at discrete and polymeric level by heat, vapor or light has gain considerable interest due to its potential application in sensor technology, magnetic properties, gas storage and catalysis. SCSC process involves breaking and formation of bonds while retaining its crystallinity which makes the process challenging. The SCSC process at polymeric level is well documented, however very few reports are known at discrete level. The monomeric complex  $[\text{Co}(\text{hep-H})(\text{H}_2\text{O})_4]\text{SO}_4$  (1) has been synthesized from 2-(2-hydroxyethyl)pyridine (hep-H) and cobalt sulfate in a 95:5 (v/v) MeOH-H<sub>2</sub>O mixture at 298 K. Co(II) ion in 1 is linked by one hep-H ligand and four coordinated water molecules which is stabilized by one sulfate anion. The light orange crystal of 1 on exposure to heat at 120°C transforms to the neutral pink dimeric complex  $[\text{Co}(\text{hep-H})(\text{H}_2\text{O})_2(\mu\text{-sulfato-O,O})]_2$  (2). The facile SCSC transformation is accompanied by removal of two coordinated water molecules in 1 and concurrent formation of two new covalent bonds from anionic sulfate O atom to Co(II) atom. SCSC transformation involves anionic sulfate to coordinated to Co(II) to form neutral complex.

References:

- (1) (a) Niel, V.; Thompson, A. L.; Muoz, M. C.; Galet, A.; Goeta, A. E.; Real, J. A. *Angew. Chem., Int. Ed.* 2003, 42, 3760. (b) Cheng, X.-N.; Zhang, W.-X.; Chen, X.-M. *J. Am. Chem. Soc.* 2007, 129, 15738.
- (2) (a) Toh, N. L.; Nagarathinam, M.; Vittal, J. J. *Angew. Chem., Int. Ed.* 2005, 44, 2237. (b) Ouyang, X.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* 2003, 125, 12400. (c) Papaefstathiou, G. S.; Zhong, Z.; Geng, L.; MacGillivray, L. R. *J. Am. Chem. Soc.* 2004, 126, 9158.
- (3) (a) Pan, L.; Liu, H.; Lei, X.; Huang, X.; Olson, D. H.; Turro, N. J.; Li, J. *Angew. Chem., Int. Ed.* 2003, 42, 542. (b) Sawaki, T.; Aoyama, Y. *J. Am. Chem. Soc.* 1999, 121, 4793. (c) Zhang, J.-P.; Lin, Y.-Y.; Zhang, W.-X.; Chen, X.-M. *J. Am. Chem. Soc.* 2005, 127, 14162. (d) Kim, Y.; Jung, D. P. *Inorg. Chem.* 2000, 39, 1470. (e) Suh, M. P.; Moon, H. R.; Lee, E. Y.; Jang, S. Y. *J. Am. Chem. Soc.* 2006, 128, 4710. (f) Choi, H. J.; Suh, M. P. *J. Am. Chem. Soc.* 2004, 126, 15844.
- (4) M. M. Shaikh, A. K. Srivastava, P. Mathur and G. K. Lahiri, *Inorg. Chem.*, 2009, 48, 4652.

**(P320)**

**(±)-2,8 and (±)-4,10-di imidazolium-6H, 12H-5, 11-methanodibenzo[b,f][1,5]diazocines :  
Synthesis and Structural Studies**

Arruri Sathyanarayana, Ganesan Prabusankar\*  
Department of Chemistry, Indian Institute of Technology Hyderabad, ODF Estate,  
Yeddumailaram, Andhra Pradesh 502 205, India

The synthesis of functionalized ( $\pm$ )-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine analogues have been the subject of focus in various applications such as enantioselective recognition, enzyme inhibition, DNA intercalation, ligands in asymmetric synthesis and as a molecular torsion balance.<sup>1-2</sup> Herewith we report the synthesis of ( $\pm$ )-2,8 and ( $\pm$ )-4,10-diimidazo-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocines by the condensation reaction of anilines with paraformaldehyde under acidic (TFA) condition to yield the target molecules in excellent yield. These newly prepared molecules have been readily converted for the first time into ( $\pm$ )-2,8 and ( $\pm$ )-4,10-diimidazo-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocines tethered pre-N-heterocyclic carbene derivatives by alkylation RX (X = halides), and characterized by multinuclear (<sup>1</sup>H, <sup>13</sup>C, DEPT, HMBC, HSQC) NMR, FT-IR, UV-vis, elemental analysis and single crystal X-ray diffraction techniques.

**(P321)**

**Ru(III)-NCN Pincer Complexes as Catalysts for the Transfer Hydrogenation of Ketones**

Jerome P and R Karvembu

Department of Chemistry, National Institute of Technology, Tiruchirappalli 620015, India

Pincer complexes can act as efficient catalysts for many industrially important organic transformations under environmentally benign and mild conditions. Aromatic, aliphatic, alicyclic and heterocyclic alcohols play a vital role in pharmaceutical and perfumery industries. Among the different methodologies available, transfer hydrogenation of ketones is the simple and straight forward route to produce the alcohols due to its operational simplicity and easy availability of reductants. Eventhough several hydride sources are available, i-PrOH/NaOH finds more attraction because of its stability, easy accessibility, inexpensive and environmentally benign nature. Ru(III)-NCN pincer complexes were synthesized from [RuCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] and disubstituted isophthalamides in presence of triethylamine. The prepared ligands and the Ru(III)-NCN pincer complexes were characterized by analytical and spectral studies. Ru(III)-NCN pincer complexes were found to be an efficient catalyst for the transfer hydrogenation of ketones in i-PrOH/NaOH medium. Scope of the system was extended with various substituted aromatic ketones. Some heterocyclic ketones were also been tested and the results were found to be comparable with previous literatures.

**(P322)**

**Base-Promoted Expedient Access to Spiro-Isatins: Synthesis and Anti-Tubercular Evaluation of 1H-1,2,3-Triazole-Tethered Spiro-Isatin-Ferrocene, Isatin-Ferrocene and  $\beta$ -Lactam-Ferrocene Conjugates**

Kewal Kumar, Vipin Kumar

Department of Chemistry, Guru Nanak Dev University, Amritsar, India

The use of sodium hydride provides a convenient access in the synthesis of C-5 functionalized spiro-isatins with the absence of typical drawbacks associated with conventional protocols. The synthesized precursors' viz. N-alkylazido spiro-isatins and their unprotected counterparts were

explored in Cu-mediated azide-alkyne cycloaddition reactions for probing the anti-tubercular structure activity relationships (SAR) within isatin-ferrocene-triazole conjugate family.<sup>1,2</sup> Further the (SAR) is compared with the  $\beta$ -lactam-ferrocene based hybrids<sup>3,4</sup> The anti-tubercular evaluation studies of the synthesized conjugates revealed an improvement in the minimal inhibitory concentration (MIC) with the introduction of ferrocene nucleus as evidenced by spiro-isatin-ferrocene and isatin-ferrocene hybrids.

References:

1. K. Kumar, C. Biot, S. Carrère-Kremer, L. Kremer, Y. Guérardel, P. Roussel, V. Kumar, *Organometallics* 2013, DOI: 10.1021/om4009229.
2. K. Kumar, S. Carrère-Kremer, L. Kremer, Y. Guérardel, C. Biot, V. Kumar *Organometallics* 2013, 32, 5713.
3. K. Kumar, P. Singh, L. Kremer, Y. Guérardel, C. Biot, V. Kumar, *Dalton Trans.* 2012, 41, 5778.
4. K. Kumar, S. Carrère-Kremer, L. Kremer, Y. Guérardel, C. Biot, V. Kumar, *Dalton Trans.* 2013, 42, 1492.

**(P323)**

**A Greener Approach to Ruthenium Catalyzed Synthesis of Amides From Aldehydes**

Deepika Tyagi, Ambikesh D. Dwivedi, Rohit K. Rai, Sanjay K. Singh\*

Indian Institute of Technology Indore

Aldehydes are highly desirable starting materials for amide synthesis because of their easy availability and non-toxicity.[1] The earlier reported reactions reveal that, the desired amide formation takes place in good yield but the longer reaction time and high temperature along with N<sub>2</sub> atmosphere required for these reactions is a major drawback.[2] Generally the amide syntheses involve the wasteful procedures using organic solvents which lead to potential environmental threats.[3] So, keeping the environmental concern in mind the synthesis of primary amides with the coupling of aldehydes and hydroxyl amines using water as a solvent was undertaken by our research group. To continue in this context, we developed a ruthenium complex as a catalyst which led to the one pot synthesis of primary amides, in high yields within shorter duration of time and at lower temperature in a greener way.

References

1. García-Álvarez, R.; Díaz-Álvarez, A. E.; Borge, J.; Crochet, P.; Cadierno, V. *Organometallics* 2012, 31, 6482.
2. García-Álvarez, R.; Díaz-Álvarez, A. E.; Crochet, P.; Cadierno, V. *RSC Advances* 2013, 3, 5889.
3. Allen, C. L.; Williams, J. M. *J. Chem. Soc. Rev.* 2011, 40, 3405.

**(P324)**

**Carbon-hydrogen bond activation and synthesis of ruthenium (III) cyclometallates**

Rajan Kumar, Sushil Kumar, Kaushik Ghosh\*

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, India

Carbon-hydrogen bond activation by ruthenium complexes is an important area in chemical research. In this regard  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  played important role in different organometallic and organic syntheses such as oxidations, reductions, cross-couplings, cyclizations, isomerization etc. Reaction of precursor complex  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  with bidentate Schiff base (LSB) and azo (LAZ) ligands gave rise to orthometallated ruthenium complexes  $[\text{Ru}^{\text{III}}(\text{LSB})(\text{PPh}_3)_2(\text{Cl})]$  (1) and  $[\text{Ru}^{\text{III}}(\text{LAZ})(\text{PPh}_3)_2(\text{Cl})]$  (2) respectively.[1] Herein we report ruthenium complexes obtained by cyclometallation reaction.  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  reacted with bidentate ligands L1H2 and L2H2 and afforded orthometallated ruthenium(III) complexes  $[\text{Ru}^{\text{III}}(\text{L1})(\text{PPh}_3)_2(\text{Cl})]$  (3) and  $[\text{Ru}^{\text{III}}(\text{L2})(\text{PPh}_3)_2(\text{Cl})]$  (4) respectively (where L1H2 and L2H2 are 2-((4-(dimethylamino)phenyl)diazenyl)benzoic acid and 3-nitro-N-(quinolin-8-yl)benzamide respectively). Both the complexes 3 and 4 were characterized by UV/Vis, IR and EPR spectral studies. Molecular structure of complex 3 was determined by X-ray crystallography. Plausible mechanism for C-H bond activation will also be discussed.[2]

#### References

- [1] (a) Ghosh, K.; Kumar, S.; Kumar, R.; Singh, U. P. *Eur. J. Inorg. Chem.* 2012, 929. (b) Ghosh, K.; Kumar, S.; Kumar, R.; Singh, U. P.; Goel, N. *Organometallics* 2011, 30, 2498. (c) Ghosh, K.; Kumar, S.; Kumar, R.; Singh, U. P.; Goel, N. *Inorg. Chem.* 2010, 49, 7235.  
[2] Ghosh, K.; Kumar, R.; Kumar, S.; Singh, U. P. (communicated).

#### (P325)

##### **Stimulated DNA binding by metalloinsertors having Knoevenagel condensate $\beta$ -diketimine Schiff bases: Synthesis and characterization**

N.Pravin and N.Raman  
VHNSN College, Virudhunagar.

In the present investigation, Knoevenagel condensate  $\beta$ -diketimine Schiff base ligands and their metal complexes have been synthesized and characterized by using FTIR, NMR, UV-Vis., elemental analysis and mass analytical techniques. The molar conductance values indicate that these complexes are non electrolytes. The UV-Vis. data exhibit that the complexes adopt square-planar geometry. In addition, the DNA binding studies have been performed using absorption spectroscopy, viscosity measurements and cyclic voltammetry studies. The experimental evidence reveal that the synthesized complexes interact with calf thymus DNA through intercalation with intrinsic binding constants ranging from  $0.2 \times 10^4$  to  $1.5 \times 10^5$  which are relatively higher than the parent ligands. The electron transfer mechanism of these complexes is identified by cyclic voltammetry.

#### (P326)

##### **Directing Group Assisted Copper-Catalyzed Chemoselective O-Aroylation of Phenols and Enols Using Alkylbenzene**

Nilufa khatun, Saroj Kumar Rout, Srimanta Guin, Arghya Banerjee, Anupal Gogoi and Bhisma K. Patel\*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, India

Esterifications are traditionally achieved by reacting alcohols with carboxylic acids or its derivatives which often require auxiliary chemicals.<sup>1</sup> Besides the recently improved traditional esterification of alcohols,<sup>2</sup> the oxidative esterification of aldehydes<sup>3</sup> and carbonylation of

hydrocarbons are some alternative approaches to ester synthesis.<sup>4</sup> Of late, construction of C-C and C-X bonds via cross dehydrogenative couplings (CDC) are attractive because it does not require substrate prefunctionalizations and is atom economic.<sup>5</sup> The importance of C-O bonds in synthetic organic chemistry have resulted in the development of a variety of C-H bond functionalization methods mediated by various transition metals.<sup>6</sup> In this context the ester synthesis is in the vanguard. Recent synthesis of esters involve reactions of acids with cyclic ethers where the C-O bond formation takes place at the sp<sup>3</sup> carbon atoms alpha-to the ethereal oxygen.<sup>7</sup> Besides these a number of CDC based approaches employing metal catalysts such as Cu,<sup>3k</sup> Ru,<sup>8</sup> Rh,<sup>9</sup> Ir,<sup>10</sup> Pd,<sup>11</sup> and Fe<sup>12</sup> have been reported. Pushing the ester synthesis to an extreme limit of C-H activation we have developed a metal free (Bu<sub>4</sub>NI and TBHP) CDC approach for the synthesis of benzylic esters involving only alkylbenzene(s) as a self or a cross coupling partner(s).<sup>13</sup> Very specifically on the substrate directed coupling for the synthesis of esters via O-arylation processes there are only two reports where 2-acetylphenols and beta-dicarbonyl derivatives or their analogs have undergone directed O-arylation using aldehydes as the coupling partners.<sup>3d,14</sup> Alkylbenzenes have been excellent aroyl surrogates<sup>15</sup> and are the best alternatives to Friedel Crafts aroylations. Benzylic esters are obtained by the CDC coupling of aldehydes and alkylbenzenes using Cu(II) catalyst.<sup>3k</sup> In this work,<sup>16</sup> Using alkylbenzenes as aroyl surrogates a copper(II) catalyzed chemoselective O-arylation of 1,3-dicarbonyl compounds and phenolic -OH ortho to carbonyl (-CHO, -COR) groups have been achieved. A dual mechanism operating in tandem for these transformations has been supported by a crossover experiment.

#### References:

1. Otera, J.; Nishikido, J. *Esterification: Methods, Reactions, and Application*, Wiley-VCH, Weinheim, 2003.
2. (a) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* 2005, 127, 10840. (b) Owston, N. A.; Parker, A. J.; Williams, J. M. *J. Chem. Commun.* 2008, 624. (c) Gunanathan, C.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* 2009, 131, 3146. (d) Miyamura, H.; Yasukawa, T.; Kobayashi, S. *Green Chem.* 2010, 12, 776. (e) Gowrisankar, S.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed.* 2011, 50, 5139. (f) Liu, C.; Wang, J.; Meng, L.; Deng, Y.; Li, Y.; Lei, A. *Angew. Chem. Int. Ed.* 2011, 50, 5144. (g) Bai, X.; Ye, F.; Zheng, L.; Lai, G.; Xia, C.; Xu, L. *Chem. Commun.* 2012, 48, 8592. (h) Liu, C.; Tang, S.; Lei, A. *Chem. Commun.* 2013, 49, 1324.
3. (a) Gopinath, R.; Patel, B. K. *Org. Lett.* 2000, 2, 577. (b) Kiyooka, S.; Ueno, M.; Ishii, E. *Tetrahedron Lett.* 2005, 46, 4639. (c) Lerebours, R.; Wolf, C. *J. Am. Chem. Soc.* 2006, 128, 13052. (d) Yoo, W.; Li, C. *J. Org. Chem.* 2006, 71, 6266. (e) Ekoue-Kovi, K.; Wolf, C. *Chem. Eur. J.* 2008, 14, 6302. (f) Marsden, C.; Taaming, E.; Hansen, D.; Johansen, L.; Klitgaard, S. K.; Egeblad, K.; Christensen, C. H. *Green Chem.* 2008, 10, 168. (g) Hashmi, A. S. K.; Lothschütz, C.; Ackermann, M.; Doepp, R.; Anantharaman, S.; Marchetti, B.; Bertagnolli, H.; Rominger, F. *Chem. Eur. J.* 2010, 16, 8012. (h) Liu, C.; Tang, S.; Zheng, L.; Liu, D.; Zhang, H.; Lei, A. *Angew. Chem. Int. Ed.* 2012, 51, 5662. (i) Tschäen, B. A.; Schmink, J. R.; Molander, G. A. *Org. Lett.* 2013, 15, 500. (j) Huang, J.; Li, L.; Li, H.; Husan, E.; Wang, P.; Wang, B. *Chem. Commun.* 2012, 48, 10204. (k) Rout, S. K.; Guin, S.; Ghara, K. K.; Banerjee, A.; Patel, B. K. *Org. Lett.* 2012, 14, 3982. (l) Gopinath, R.; Barkakaty, B.; Talukdar, B.; Patel, B. K. *J. Org. Chem.* 2003, 68, 2944.
4. (a) Brennfürer, A.; Neumann, H.; Beller, M. *ChemCatChem* 2009, 1, 28. (b) Liu, Q.; Zhang, H.; Lei, A. *Angew. Chem. Int. Ed.* 2011, 50, 10788. (c) Xie, P.; Xie, Y.; Qian, B.;

- Zhou, H.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* 2012, 134, 9902.
5. (a) Li, C. *J. Acc. Chem. Res.* 2009, 42, 335. (b) Scheuermann, C. *J. Chem. Asian J.* 2010, 5, 436. (c) Le Bras, J.; Muzart, J. *Chem. Rev.* 2011, 111, 1170. (d) Yeung, C. S.; Dong, V. M. *Chem. Rev.* 2011, 111, 1215.
6. (a) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* 2004, 126, 2300. (b) Desai, L. V.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* 2004, 126, 9542. (c) Giri, R.; Liang, J.; Lei, J.-G.; Li, J.-J.; Wang, D.-H.; Chen, X.; Naggar, I. C.; Guo, C.; Foxman, B. M.; Yu, J.-Q. *Angew. Chem. Int. Ed.* 2005, 44, 7420. (d) Chen, X.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* 2006, 128, 6790. (e) Ye, Z.; Wang, W.; Luo, F.; Zhang, S.; Cheng, J. *Org. Lett.* 2009, 11, 3974.
7. Chen, L.; Shi, E.; Liu, Z.; Chen, S.; Wei, W.; Lei, H.; Xu, K.; Wan, X. *Chem. Eur J.* 2011, 17, 4085.
8. (a) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* 2005, 127, 10840. (b) Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Milstein, D. *Dalton Trans.* 2007, 107, 113.; (c) Gunanathan, C.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* 2009, 131, 3146. (d) Owston, N. A.; Parker, A. J.; Williams, J. M. J. *J. Chem. Commun.* 2008, 624.
9. Zweifel, T.; Naubron, J.-V.; Grützmacher, H. *Angew. Chem. Int. Ed.* 2009, 48, 559.
10. (a) Suzuki, T.; Morita, K.; Tsuchida, M.; Hiroi, K. *J. Org. Chem.* 2003, 68, 1601. (b) Dam, J. H.; Osztrovszky, G.; Nordstrøm, L. U.; Madsen, R. *Chem. Eur. J.* 2010, 16, 6820. (c) Watson, A. J. A.; Maxwell, A. C.; Williams, J. M. J. *Org. Lett.* 2009, 11, 2667. (d) Shimizu, K.-I.; Ohshima, K.; Satsuma, A. *Chem. Eur. J.* 2009, 15, 9977.
11. (a) Gowrisankar, S.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed.* 2011, 50, 5139. (b) Liu, C.; Wang, J.; Meng, L.; Deng, Y.; Li, Y.; Lei, A. *Angew. Chem. Int. Ed.* 2011, 50, 5144. (c) Liu, C.; Tang, S.; Zheng, L.; Liu, D.; Zhang, H.; Lei, A. *Angew. Chem. Int. Ed.* 2012, 51, 5662. (d) Reddy, R. S.; Rosa, J. N.; Veiros, L. F.; Caddick, S.; Gois, P. M. P. *Org. Biomol. Chem.* 2011, 9, 3126.
12. Luo, F.; Pan, C.; Cheng, J.; Chen, F. *Tetrahedron* 2011, 67, 5878.
13. Majji, G.; Guin, S.; Gogoi, A.; Rout, S. K.; Patel, B. K. *Chem. Commun.* 2013, 49, 3031.
14. Kumar, G. S.; Maheswari, C. U.; Kumar, R. A.; Kantam, M. L.; Reddy, K. R. *Angew. Chem. Int. Ed.* 2011, 50, 1.
15. (a) Guin, S.; Rout, S. K.; Banerjee, A.; Nandi, S.; Patel, B. K. *Org. Lett.* 2012, 14, 5294. (b) Yin, Z.; Sun, P. *J. Org. Chem.* 2012, 77, 11339. (c) Wu, Y.; Choy, P. Y.; Mao, F.; Kwong, F. Y. *Chem. Commun.* 2013, 49, 689. (d) Weng, J.; Yu, Z.; Liu, X.; Zhang, G. *Tetrahedron Lett.* 2013, 54, 1205. (e) Xu, Z.; Xiang, B.; Sun, P. *RSC Adv.* 2013, 3, 1679.
16. Rout, S. K.; Guin, S.; Banerjee, A.; Khatun, N.; Gogoi, A.; Patel, B. K. *Org. Lett.* 2013, 15, 4106.

(P327)

**Mono and Dialkyne Insertion Reactions of Cyclopalladated N,N',N''-Triarylguanidines, [(C,N)Pd( $\mu$ -Br)]<sub>2</sub> and cis/trans-[(C,N)Pd(Lewis base)Br]: Scaffolds for Enlarged, Rearranged and Zwitterionic Palladacycles through Ring Contraction cum Amine Imine Tautomerisation**

Priya Saxena,<sup>a</sup> Natesan Thirupathi,<sup>a,\*</sup> and Munirathinam Nethaji<sup>b</sup>

<sup>a</sup>Department of Chemistry, University of Delhi, Delhi, India, <sup>b</sup>Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India



Insertion reactions of six-membered cyclopalladated  $N,N',N''$ -triarylguanidines of the types  $[(C,N)Pd(\mu-Br)]_2$  and  $[(C,N)PdBrL]$  ( $C,N$  = guanidine derived monoanionic  $\kappa^2C,N$  scaffold,  $L$  = Lewis base) with various symmetrical and unsymmetrical alkynes afforded diinserted eight-membered and monoinserted six-membered palladacycles, respectively in 87–93% yields. The '[C,N]Pd' ring size of the di- and monoinserted palladacycles is smaller than anticipated due to ring contraction cum amine imine tautomerisation upon the formation of these palladacycles. Palladacycle,  $[(C,N)PdBrL]$  upon insertion reaction with  $MeO(O)CC\equiv CC(O)OMe$  afforded a zwitterionic annulated palladacycle,  $[(C,C)PdBrL]$  ( $C,C$  = diinserted guanidinium derived monoanionic  $\kappa^2C,N$  scaffold) in 76% yield which upon reaction with  $AgOTf$  afforded the corresponding ionic palladacycle,  $[(C,C)Pd(H_2O)L]$  in 78% yield. The new palladacycles were characterized by  $^1H$  and  $^{13}C$  NMR, IR spectroscopic techniques and elemental analysis. Further, molecular structures of six diinserted and three monoinserted palladacycles have been determined by single crystal X-ray diffraction. The plausible mechanisms of the formation of the new palladacycles have been proposed. The influence of the nuclearity of the starting palladacycles and substitution pattern of alkynes upon the types of products and their solution behavior will be discussed.

**(P328)**

**Some Unusual Reactions of Organotellurium Ligands with Metal Carbonyls**

Mohd Tauqeer, S. M. Mobin, Pradeep Mathur, G. K. Lahiri

Department of Chemistry, IIT Bombay

Use of ferrocenylacetylene with metal carbonyls and chalcogen stabilized metalcarbonyl clusters to synthesize several new ferrocenyl containing metal carbonyl cluster compounds has been investigated earlier in our group.<sup>1-3</sup> Diferrocenylditelluride reacts with different mononuclear metal carbonyl to form different coordinated products which can be interconverted to each other. It also gives novel halo compound when reacted with halogens. Also, a new ligand, (*Z*)-1-ferrocenyntelluro-1-ferrocenyl-4-ferrocenyl-1-buten-3-yne have been reacted with metal carbonyls to give novel tellurium coordinated complexes. These complexes are important in cluster growth purposes as not only the alkyne group but also the double bond and tellurium are involved in coordination.

References:

- (1) Mathur, P.; Singh, A. K.; Singh, V. K.; Singh, P.; Rahul, R.; Mobin, S. M.; Thöne, C. *Organometallics* 2005, 24, 4793-4798.
- (2) Mathur, P.; Singh, V. K.; Singh, A. K.; Mobin, S. M.; Thöne, C. J. *Organomet. Chem.* 2006, 691, 3336-3342.
- (3) Mathur, P.; Chatterjee, S.; Das, A.; Mobin, S. M. J. *Organomet. Chem.* 2007, 692, 819-823.

**(P329)**

**Syntheses of Homo and Heterometallic 3D-Coordination Polymers of Triorganotin Compounds and Application in Gas Adsorption**

Chandrajeet Mohapatra and Vadapalli Chandrasekhar

Indian Institute of Technology Kanpur, Kanpur, India.

Organostannoxanes are an important family of main-group-element-containing organometallic compounds that have been attracting considerable interest in view of their enormous structural diversity. In particular, the formation of organostannoxanes in the reactions of organotin oxides, hydroxides, and oxide hydroxides with protic acids has been investigated in great detail. Recently, the use of dicarboxylic acids and other difunctional reagents to assemble various types of metal–organic frameworks (MOFs), involving transition-metal ions or their complexes as nodes, suggested us the similar efforts on main-group elements should also be of interest. We describe different strategies to generate 3D-coordination polymers by utilizing organotin motif as node and dicarboxylic acids as ligands. We have synthesized a 4-connected triorganotin 3D-coordination polymer in a sqc topology which shows selective gas adsorption, preferring CO<sub>2</sub> and H<sub>2</sub> over N<sub>2</sub>. We also describe a step-wise conversion of a 2D-coordination polymer of Cu(II) to a heterometallic 3D-coordination polymer in a sqc topology containing both Cu(II) and organotin motif as nodes by utilizing trimethyltin as adhesive between two 2D-coordination polymers of Cu(II).

**(P330)**

**Synthesis, Structural Aspects and Solution Behavior of Rhodium (III) Half Sandwich Complexes Ligated by N, N',N'' - Triarylguanidinate Ligands**

Ram Kishan, Natesan Thirupathi, and Munirathinam Nethaji

Department of Chemistry, University of Delhi, Delhi-110007 and Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore

[( $\eta_6$ -C<sub>5</sub>Me<sub>5</sub>)RhCl( $\mu$ -Cl)]<sub>2</sub> was subjected to a bridge-splitting reaction with N,N',N'' - triarylguanidines, (ArNH)<sub>2</sub>C=NAr in the presence of NaOAc in methanol under reflux condition to afford [( $\eta_6$ -C<sub>5</sub>Me<sub>5</sub>)RhCl{ $\kappa_2$ (N,N')(ArN)<sub>2</sub>C-N(H)Ar}] (Ar = C<sub>6</sub>H<sub>4</sub>Me<sup>-2</sup> (1), C<sub>6</sub>H<sub>4</sub>(OMe)<sup>-2</sup> (2), and C<sub>6</sub>H<sub>4</sub>Me<sup>-4</sup> (3)) in 85%, 92%, and 95% yields, respectively. Complexes 1–3 were further treated with excess of NaN<sub>3</sub> in methanol at ambient condition to afford [( $\eta_6$ -C<sub>5</sub>Me<sub>5</sub>)RhN<sub>3</sub>{ $\kappa_2$ (N,N')(ArN)<sub>2</sub>C-N(H)Ar}] (Ar = C<sub>6</sub>H<sub>4</sub>Me<sup>-2</sup> (4), C<sub>6</sub>H<sub>4</sub>(OMe)<sup>-2</sup> (5), C<sub>6</sub>H<sub>4</sub>Me<sup>-4</sup> (6)) in 82%, 88%, and 90% yields, respectively. Complex 5 upon treatment with dimethylacetylenedicarboxylate in CH<sub>2</sub>Cl<sub>2</sub> at ambient condition afforded [( $\eta_6$ -C<sub>5</sub>Me<sub>5</sub>)Rh{N<sub>3</sub>C<sub>2</sub>(C(O)OMe)<sub>2</sub>}{ $\kappa_2$ (N,N')(ArN)<sub>2</sub>C-N(H)Ar}] (Ar = C<sub>6</sub>H<sub>4</sub>(OMe)<sup>-2</sup>; 7) in 65% yield. Complexes 1–7 were characterized by IR, NMR (1H and 13C) spectroscopy, and elemental analysis. Complexes 1–5 and 7 were also characterized by single crystal X-ray diffraction. Variable temperature 1H NMR spectroscopic measurements carried out on 1 showed the presence of five species in solution at low temperatures while those carried out on 2 showed the presence of only one species throughout the temperature range studied. A plausible mechanism of formation of 1–3 via N–H activation process and the fluxional behavior of 1 and 2 will be discussed.

**(P331)**

**Reactivity of 1,2,3-triseleno[3]ferrocenophane towards transition metal carbonyls**

Abhinav Raghuvanshi and Pradeep Mathur

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai

[n]ferrocenophanes (n ≥ 3) are of great interest because of the unique chemical properties resulting from the functionality of the side arm. In the past, a series of [3]-ferrocenophanes with

trichalcogen chains -S<sub>3</sub>-, -Se<sub>3</sub>-, -SSeS-, -STeS-, -SeSSe-, -SeTeSe-, -Te<sub>3</sub>- as bridging groups has been synthesized. Though a large number of chalcogen-containing iron carbonyl clusters are known, manganese carbonyl and osmium carbonyl selenide clusters are very less. In this context 1,2,3-Triseleno[3]ferrocenophane has been found to be a suitable precursor for the preparation of some new metal carbonyl selenide clusters. Presentation will describe the reactions of 1,2,3-Triseleno[3]ferrocenophane with [Fe(CO)<sub>5</sub>] [Mn<sub>2</sub>(CO)<sub>10</sub>] and [Os<sub>3</sub>(CO)<sub>12</sub>], that involve facile synthesis of manganese, iron and osmium carbonyl selenide clusters, respectively.

**(P332)**

**In vitro antitumor activity of 3-((2-(diphenylstannoxy)ethylimino)methyl-4H-chromen-4-one complex**

Imtiyaz Yousuf and Farukh Arjmand

Department of Chemistry, Aligarh Muslim University, Aligarh, India

Organotin(IV) complexes have gained tremendous research impetus owing to their proven candidature for the treatment of solid malignancies. A novel diphenyltin(IV) derivative, (1) 3-((2-(diphenylstannoxy)ethylimino)methyl-4H-chromen-4-one was synthesized by the method described previously from the Schiff base of 3-formylchromone and ethanolamine. The corroborative results of the biological and computational studies of 1 revealed that the complex avidly binds to ct DNA and can act as an efficient chemotherapeutic drug candidate for cancer. Therefore, the in vitro cytotoxic activity of 1 was screened by microculture Sulforhodamine B test (SRB) assay on a panel of human cancer cell lines of different histological origin viz., A2780(ovary), Hop62 (lung), U373MG (CNS), PC3 (prostate), MCF7 (human breast), K562 (leukemia) and HCT15 (colon) lines. The results revealed that (1) demonstrated excellent cytotoxic activity with GI<sub>50</sub> values <10 against all cancer cell lines. Herein, we report % control growth curves at different concentrations of (1) and adrimycin (ADR) as control (μg/ml against human carcinoma cell lines).

References:

- (1) F. Arjmand and I. Yousuf, J. Organomet. Chem. 743 (2013) 55-62
- (2) S. Tabassum and C. Pettinari, J. Organomet. Chem. 691 (2006) 1761-1766

**(P333)**

**Synthesis, Scope and Utility of Backbone Functionalized NHC- Metal Complexes**

V.Karthik and G. Anantharaman

Department of Chemistry, Indian Institute of Technology, Kanpur

Functionalization of carbenes with heteroatom containing functional groups is an active area of research due to its ability to form interesting metal complexes by utilizing its extra coordinating sites [1], to modulate the electronic property enabling new catalyst design [2], to enhance the stability in some cases. Of these, both N-functionalization and backbone functionalization(4- and 5-positions) of imidazol-2-ylidenes/imidazolium salts is known in the literature but the latter method is more effective in tuning the electronic properties but synthetic methods are not straightforward and often involves the intermediacy of free carbenes. Herein we present a simple and elegant method to achieve functionalization at the backbone position of imidazolium salts,

and the metal-imidazolylidene complexes and their utility in catalysis and as photoluminescent materials.

References:

- [a] Arduengo, A. J., III; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. J. Am. Chem. Soc. 1997, 119, 12742. [b] Khramov, D. M.; Rosen, E. L.; Er, J. A. V.; Lynch, V. M.; Bielawski, C. W. Tetrahedron, 2008, 64, 6853. [c] Mendoza-Espinosa, D.; Donnadiou, B.; Bertrand, G. J. Am. Chem. Soc. 2010, 132, 7264. [d] Mendoza-Espinosa, D.; Donnadiou, B.; Bertrand, G. Chem. Asian J. 2011, 6, 1099.
- Karthik, V.; Bhat, I. A.; Anantharaman, G. Organometallics, 2013, DOI: 10.1021/om400585b.

**(P334)**

**Novel Selenium and Tellurium Derivatives of NCN-Pincer Ligand**

Anand K. Gupta,<sup>a</sup> Harkesh B. Singh,<sup>a,\*</sup> and Ray J. Butcher<sup>b</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, India;

<sup>b</sup>Department of Chemistry, Howard University, Washington

New air-stable organoselenium and -tellurium compounds based on the NCN pincer ligand aryldiamine,  $[C_6H_3(CH_2-NMe_2)_2-2,6]^-$  are reported here. The compounds include  $[2,6-(CH_2-NMe_2)_2C_6H_3]_2Te$  (1),  $[2,6-(CH_2-NMe_2)_2C_6H_3]Te-n-Bu$  (2),  $[2,6-(CH_2-NMe_2)_2C_6H_3Se]^+Br^-$  (3),  $[2,6-(CH_2-NMe_2)_2C_6H_3]_2Se$  (4),  $[2,6-(CH_2-NMe_2)_2C_6H_3]TeBr_3$  (5),  $[2,6-(CH_2-NMe_2)_2C_6H_3]_2Te-PdCl_2$  (6),  $[2,6-(CH_2-NMe_2)_2C_6H_3]Te-PdCl_3$  (7),  $[2,6-(CH_2-NMe_2)_2C_6H_3]_2TeO]^{2+}.X^{2-}$  where  $X^{2-} = 2Br^-$  (8),  $2[Cl_3Pd(DMSO)]^-$  (9) and  $[Hg_2Cl_6]^{2-}$  (10). Compound 1 and 2 have been synthesized as the mixture from the reaction of  $[2,6-(CH_2-NMe_2)_2C_6H_3]Li$  with Te powder, whereas compound 3 and 4 have been synthesized by the use of Se powder and Se(dtc)<sub>2</sub> respectively. The compound 5 was prepared by the reaction of 2 with Br<sub>2</sub> at 0 °C in dry CCl<sub>4</sub>. The dinuclear cationic telluroxides 8 and 10 were synthesized from 5 by the treatment of NaOH and HgCl<sub>2</sub> respectively, in CHCl<sub>3</sub>. Similarly, the palladium containing compounds 6, 7 and 9 were synthesized from the reaction between 1 and different palladium precursors, PdCl<sub>2</sub> or (PhCN)<sub>2</sub>PdCl<sub>2</sub> at different reaction conditions. All the compounds were characterized by NMR, ESI-HRMS, elemental analysis and single crystal X-ray analysis (except 2).

**(P335)**

**Reactivity of Dihaloselenones: Synthesis of Cationic Diselenides and Aryltellurenyl Adducts of Selones**

Sangeeta Yadav,<sup>a</sup> Harkesh B. Singh,<sup>a,\*</sup> and Ray J. Butcher<sup>b</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, India;

<sup>b</sup>Department of Chemistry, Howard University, Washington

The reactions of various substituted benzimidazolin-2-dihaloselones with elemental iron and zinc lead to the formation of dicationic diselenides supported with metal halide complexes as counter anion. In these reactions dihaloselones act as oxidizing agents. The reaction with iron afforded dicationic diselenide as a single product while the reaction with zinc gave a mixture of dicationic diselenide and the selenone coordinated metal halide adduct as the products. The structures of

the dicationic diselenides have been confirmed by common spectroscopic techniques and single crystal X-ray analysis. Selones form aryltellurenyl complexes by heterolytic cleavage of Te-Te bond in mixed valent dihalides of ditellurides. Aryltellurenyl shows resemblance with iodonium ion.

**(P336)**

**Late-transition Metal Complexes of Triazole Derived N-heterocyclic Carbene ligands:  
Structure, Bonding and Related Application Studies**

Anuj Kumar and Prasenjit Ghosh\*

IIT Bombay

Series of late-transition metal complexes supported over three different triazole-derived N-heterocyclic carbene ligands namely, (i) a chelating Namido- functionalized N-heterocyclic carbene ligand precursor of the type [1-(R)-4N-(furan-2ylmethyl)acetamido-1,2,4 triazolium chloride [R = Et(1a), i-Pr (2a), CH<sub>2</sub>Ph(3a)], (ii) a chiral N-heterocyclic carbene ligand precursor of the type 1-((1S,2S,5R)-2-i-propyl-5-methylcyclohexyl -4-(R) 1,2,4 triazolium bromide [R = Et(1a), allyl(IIa), CH<sub>2</sub>Ph(IIIa) and (iii) an alkyl-bridged N-heterocyclic carbene ligands precursor of the type [1,1'-(R)-4,4'-CH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>- 1,2,4 triazolium dibromide [R = i-Pr , n =0 (1p), R = i-Pr , n =1 (2p), R = menthyl, n =0 (3p), R = menthyl, n =1 (4p) have been designed. The corresponding ruthenium and gold complexes were synthesized from the reaction of the silver analogue with [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> and (SMe<sub>2</sub>)AuCl respectively. The silver complexes were synthesized from the respective N-heterocyclic carbene ligand precursor by the direct treatment with Ag<sub>2</sub>O. The PEPSI themed palladium complexes were synthesized by the direct reaction of corresponding N-heterocyclic carbene ligand precursors with PdBr<sub>2</sub> in presence of K<sub>2</sub>CO<sub>3</sub> as a base and pyridine as a solvent. Furthermore, the nickel, palladium and platinum complexes were also synthesized by the reaction of corresponding N-heterocyclic carbene ligand precursors with NiCl<sub>2</sub>•6H<sub>2</sub>O, PdBr<sub>2</sub> and PtBr<sub>2</sub> respectively in the presence of base under reflux conditions.

**(P337)**

**Palladium Complexes Hinged on Abnormal N-heterocyclic Carbenes as Potential Catalysts  
for Cross-coupling Reactions**

Sudipta Modak and Prasenjit Ghosh\*

IIT Bombay

Crafting superior catalysts for the construction of the C-X (X=C, N, O) bonds are of great importance to chemical synthesis. Metal complexes of abnormal N-heterocyclic carbenes (aNHCs) are promising new entrants in this area since its inception in 2001 and have been found superior than their normal counterparts (nNHCs) on several occasions. Bearing this in mind, we have embarked on synthesizing palladium complexes of mono-aNHCs as well as bis-aNHCs with imidazole cores and mono-aNHCs with 1,2,3-triazole cores. These complexes have been well characterized with various spectral and analytical tools including single crystal X-ray diffraction technique. As a ligand having a better sigma donating ability enhances the electron density at metal center as was observed earlier in palladium complexes based on mono-aNHCs that entail better performance than the mono-nNHCs, it is thus conjectured that in palladium complexes based on bis-aNHCs will outperform those with mono-nNHCs as well as bis-nNHCs in catalysis front.

**(P338)**

**New class of phosphine oxide donor-based Re (I)-complexes from an in situ phosphine oxidation**

Palani Elumalai, Virender Singh, Bhaskaran Shankar, Dhanraj T. Masram, Malaichamy Sathiyendiran  
University of Delhi

The synthesis of rhenium(I)-based cyclic complexes using predesigned transition metal-based acceptors and organic donor precursors, is a thriving area of materials and medicinal chemistry. Due to their rich photophysical properties and potential applications in sensors, catalysts, flasks, anticancer agents, light harvesters, and nanomaterials, efforts are being directed toward making new complexes with improved properties. As a continuation of the research on the development of rhenium(I)-based complexes using various neutral donors, neutral phosphine oxide donor coordinated complexes have been synthesised and reported herein. It is well known that P=O donor ligands have been utilized as coordinating ligands between the metal centres in coordination polymers, metal–organic frameworks, and discrete lanthanide-based complexes, rhenium-based metallacycles with a phosphine oxide donor building unit are scarce. The complexes were prepared by a combination of the fac-Re(CO)<sub>3</sub> acceptor, bis-chelator donors, and a neutral phosphine donor. The complexes were characterized by elemental analysis, FT-IR, and NMR spectroscopy. The molecular structures of complexes were further confirmed by single crystal X-ray diffraction analysis.

**(P339)**

**Rhenium(I) carbonyl complexes containing redox active moiety and heterocyclic units for biological applications**

Deepak Gupta, Bhaskaran Shankar, Malaichamy Sathiyendiran.  
Department of Chemistry, University of Delhi

The design, synthesis and biological studies of complexes possessing metal core, [M(CO)<sub>3</sub>] (M = Re<sup>+</sup> or Tc<sup>+</sup>) have attracted immense attention in medicinal chemistry.<sup>1</sup> In particular, neutral complexes with simple N, O donors of the fac-M(CO)<sub>3</sub>-core having intermediate lipophilicity is an advantage in living systems and also have been proved to be powerful radiopharmaceutical precursor for the labelling of biomolecules. As a continuation of our work on fac-M(CO)<sub>3</sub>-core based complexes,<sup>2</sup> we envision that the introduction of biomimetic ligands as an ancillary part and [Re(CO)<sub>3</sub>] into the redox active core would lead to the generation of biologically active complexes. Herein, a new family of neutral heteroleptic dinuclear complexes containing fac-Re(CO)<sub>3</sub> cores, redox active chelator and heterocyclic unit is presented. Preparation of the complexes was achieved using Re(CO)<sub>3</sub>-corner, dianionic bis-chelating donor, and nitrogen donors in a one-pot process. The complexes were characterized by elemental analysis, FT-IR, and NMR spectroscopy. The molecular structures of two complexes were further confirmed by single crystal X-ray diffraction analysis. Potential medicinal applications of the complexes are also studied.

**(P340)**

**Reactivity of Diruthenium and Dirhodium Analogues of Pentaborane (9): Agostic versus Boratrane Complexes**

R. S. Anju, Dipak Kumar Roy, Bijan Mondal, K. Yuvaraj, C. Arivazhagan, Koushik Saha, Babu Varghese and Sundargopal Ghosh\*  
Department of Chemistry, Indian Institute of Technology Madras, Chennai, India

Novel Agostic, bis-sigmaborate ruthenium complexes and a rhodaboratrane were synthesized from diruthenium and dirhodium analogues of pentaborane (9). The bis-(sigma) borate complex has been identified as the intermediate for the formation of the agostic ruthenium complex. To the best of our knowledge, the first structurally characterized example of neutral diborane (6) ruthenium analogue was successfully isolated. All the complexes have been characterized by standard spectroscopic techniques, elemental microanalysis and single crystal X-ray diffraction method. The synthetic route to these complexes is interesting, since it does not suffer from the limitations intrinsic to the stability of the precursors. DFT calculations were performed to gain insight on the structure and bonding in the aforementioned complexes. The key results of this work will be described.

#### References:

1. D. K. Roy, S. K. Bose, R. S. Anju, B. Mondal, V. Ramkumar, S. Ghosh, *Angew. Chem. Int. Ed.*, 2013, 52, 3222–3226.
2. Y. Gloaguen, G. Alcaraz, A.-F. Pecharman, E. Clot, L. Vendier, S. Sabo-Etienne, *Angew. Chem. Int. Ed.*, 2009, 48, 2964–2968.
3. R. Dallanegra, A. B. Chaplin, A. S. Weller, *Angew. Chem. Int. Ed.*, 2009, 48, 6875–6878.
4. A. F. Hill, G. R. Owen, A. J. P. White, and D. J. Williams, *Angew. Chem. Int. Ed.*, 1999, 38, 2759–2761.
5. H. Braunschweig, A. Damme, R. D. Dewhurst, A. Vargas, *Nature. Chem.*, 2013, 5, 115–121.
6. T. B. Marder, Z. Lin, *Contemporary Metal Boron Chemistry I. Borylenes, Boryls, Borane s-complexes, and borohydrides*, Vol. 130, Springer, Berlin, 2008.

#### (P341)

##### **Group 7 Metallaboranes from Metal Carbonyl Compounds and Their Utilization as Catalyst for Alkyne Cyclotrimerization**

V. P. Anju, Subrat Kumar Barik, Bijnaneswar Mondal, V. Ramkumar and Sundargopal Ghosh\*  
Department of Chemistry, Indian Institute of Technology Madras, Chennai, India

Photolysis of  $[M_2(CO)_{10}]$  ( $M = \text{Re}$  or  $\text{Mn}$ ) with  $[\text{BH}_3 \cdot \text{thf}]$  at room temperature yielded arachno-1 and 2,  $[(\text{CO})_8\text{M}_2\text{B}_2\text{H}_6]$  (1:  $M = \text{Re}$ , 2:  $M = \text{Mn}$ ) in good yields. Both the compounds show butterfly structure with 7 skeletal electron pairs and 42 valence electrons. This result presents a new approach for the general access to low-boron-content metal-boron compounds without cyclopentadienyl ligand at the metal centers. This new synthetic method is found to be remarkable to the existing procedures as this evades the use of  $[\text{LiBH}_4]$  and metalpolychlorides for which the synthesis is very tedious. Compound 1 catalyzes the cyclotrimerization of a series of internal and terminal alkynes to yield mixtures of 1,3,5- and 1,2,4-substituted benzenes. The reactivity of 1 with alkynes demonstrates for the first time that an introduction of  $[\text{B}_2\text{H}_6]$  moiety into the  $[\text{Re}_2(\text{CO})_{10}]$  framework significantly enhances the catalytic activity. Note that  $[\text{Re}_2(\text{CO})_{10}]$  catalyzes the same set of alkynes under drastic conditions and prolonged period of time. Quantum-chemical calculations with DFT methods have been used to provide further

insight into the electronic structure, stability and bonding of 1 and 2. The key results of this work will be described.

References:

1. King, R. B. *Inorg. Chem.* 2004, 43, 4241.
2. Saito, S.; Yamamoto, Y. *Chem. Rev.* 2000, 100, 2901.
3. Geetharani, K.; Tussupbayev, S.; Borowka, J.; Holthausen, M. C.; Ghosh, S. *Chem. Eur. J.* 2012, 18, 8482.
4. Anju V. P.; Roy D. K.; Anju R. S.; Ghosh S. J. *Organomet. Chem.* 2013, 733, 79.

**(P342)**

**Synthesis of Organochalcogen Derivatives of 2-Chlorocyclohex-1-ene-1,3-diimine**

Krishnan Venkateshwaran, Kandhasamy Gopal, Harkesh B. Singha  
Department of Chemistry, Indian Institute of Technology Bombay, Powai

Arylselenium compounds having two ortho coordinating groups show unusual reactivity and lead to the formation of unusual species like low-valent seleninene ester, selenospirocyclic compound, cyclic selenenate ester, cyclic tellurate ester and selenonium cation. In order to explore the chemistry of the analogous alkylselenium compounds, the reactions of 2-chlorocyclohex-1-ene-1, 3-diimine (1) with in-situ generated disodium dichalcogenides have been studied. The reaction of in-situ generated  $\text{Na}_2\text{E}-2$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ) with compound (1) afforded monochalcogenide (2, 3 & 4) instead of dichalcogenide. The mechanism for the formation of monochalcogenide has been proposed. The formation of the compounds has been confirmed by common spectroscopic techniques and single crystal X-ray analysis. The reaction of selenoheterocycle with dichlorodicyanoquinone (DDQ) leads to unexpected selenium cation 5.

**(P343)**

**Study of new ternary binuclear copper (II) complexes with isomeric ligands based on the antibiotic dapsone**

Ran Bahadur Yadav<sup>1</sup> and N. D. Kulkarni<sup>2\*</sup>

<sup>1</sup>Department of Applied Chemistry, Faculty of Technology and Engineering Kalabhavan, The M. S. University of Baroda, Vadodar

<sup>2</sup>Department of Chemistry, Faculty of Science, M. S. University of Baroda, Vadodara

In recent years the study of binuclear copper (II) complexes has been a subject of considerable interest. This is mainly because of the special structural, magnetic and ESR properties associated with them. Some of these compounds can also provide good models for bi/multinuclear active sites in metalloenzymes. The catalytic activity of these binuclear centers can be probably attributed to their redox characteristics which are expected to be affected by the magnetic exchange and existence of a suitable path to mediate the spin / electronic exchange. Unlike complexes with single atom bridges where direct super exchange can take place, polyatomic bridging units function in a more complex manner. Various studies involving bridging groups providing the  $\sigma$ - and/or  $\pi$ -orbitals for propagating the coupling have clearly indicated that the spin exchange is dependent on the availability of bridge molecular orbitals with the correct symmetry and energy to propagate interaction between the metal orbitals in which the unpaired electron resides.



The present work deals with seven new ternary binuclear Copper(II) complexes with a general formula,  $[ACu(\mu-B)CuA](ClO_4)_2$ , where A = 2,2'-bipyridine or 1,10-phenanthroline and B are four binucleating Schiff base ligands derived by condensation of the antibiotic, Dapsone, i.e. 4,4'-diaminodiphenylsulphone (4-DPS) and its isomer 3,3'-diaminodiphenylsulphone (3-DPS) with 2-hydroxynaphthaldehyde or 2-hydroxy-3-methoxybenzaldehyde. The complexes have been synthesized and characterized using elemental analysis, conductivity and various spectroscopic methods such as IR, electronic spectra, ESR and mass spectrometry. The variable temperature magnetic susceptibility (90K to 300K) measurements indicate the presence of weak antiferromagnetic to ferromagnetic exchange interaction between the proximate metal ions in the complexes. Molecular modeling has been used as a tool to calculate various geometrical parameters in the complexes which have been correlated with the observed magnetic property. The influence of isomerism in the bridging ligands on magnetic exchange has also been discussed.

**(P344)**

**Single-Molecule Magnet Behavior of Two New Tetranuclear Dy(III) Complexes**

Sourav Das and Prof. V. Chandrasekhar

Single-molecule magnets (SMMs) are a new class of molecular materials that exhibit slow relaxation of the magnetization at low temperatures. These materials have several possible applications arising from their ability to store and process magnetic information at the molecular level. Among the various families of chemical compounds those containing 4f ions are attracting a lot of interest. This is because of the significant magnetic anisotropy of certain lanthanide ions arising from their strong spin-orbit coupling in low-symmetry crystal fields. We describe the synthesis and complexation behavior of compartmental hydrazine-based ligands. Two new tetranuclear lanthanide complexes were prepared and structurally characterized. Magnetic measurements revealed that the Dy(III) derivatives were SMM.

**(P345)**

**Syntheses, crystal structures and spectroscopic correlation of discrete, one-dimensional and cocrystalline Cu(II)/Ni(II)-U(VI) systems derived from Schiff base ligands**

Sagarika Bhattacharya, Sasankasekhar Mohanta\*  
University of Calcutta, Department of Chemistry

Design of weak interactions directed self-assemblies is a major objective in crystal engineering. This report presents syntheses, crystal structures of nine finite cocrystals, one 1-D cocrystal, four discrete dinuclear compounds and one dinuclear-based 1-D system of copper(II)/nickel(II) and uranyl(VI). These complexes are obtained on reacting copper(II) metallo-ligands, derived from single-/double-compartment Schiff base ligands, with uranyl nitrate hexahydrate. Type of cocrystals described here are: (i)  $[1 \times 2 + 1 \times 1]$  cocrystals of two mononuclear Cu(II) or Ni(II) units and one  $[(UVIO_2)(NO_3)_2(H_2O)_2]$  moiety; (ii)  $[1 \times 1 + 1 \times 1]$  one-dimensional cocrystal of one mononuclear Cu(II) unit and one  $[(UVIO_2)(NO_3)_2(H_2O)_2]$  moiety; (iii)  $[2 \times 1 + 1 \times 4]$  cocrystals of four mononuclear Cu(II) units and one  $[(UVIO_2)_2(\mu-H_2O)_2(NO_3)_4]$  moiety. The cocrystals are interesting examples of weak interaction directed self assemblies. The cocrystals are formed due to the strong tendency of one/two water molecule (s) to interact with the O(phenoxo)2O(methoxy/ethoxy)2 compartments of the double-compartment ligands. In the

discrete diphenoxo-bridged dinuclear CuII–UVI compounds, U(VI) center is linked with ligand (both single- and double-compartments) through two bridging phenoxo oxygen atoms. One dinuclear-based 1-D system is formed due to interlinking of the dinuclear units by nitrate or uranyl oxygen atoms. The d-d spectra of most of the above-mentioned complexes and corresponding mononuclear systems have been recorded, revealing excellent correlation of d-d band position with displacement of CuII center (dCu) from least-squares basal plane. However, some inconsistency is also observed in some cases.

**(P346)**

**Highly Selective Detection of Nitro Explosives by a Luminescent Metal–Organic Framework**

Sanjog S. Nagarkar, Biplab Joarder, Abhijeet K. Chaudhari, Soumya Mukherjee, and Sujit K. Ghosh\*

Indian Institute of Science Education and Research (IISER), Pune

Rapid and selective detection of high explosives has become one of the most pressing issues concerning homeland security, military applications and environmental monitoring. The fluorescence based detection method is gaining increased attention due to high sensitivity, simplicity, short response time and can be employed both in solution and solid phase. Although extremely high sensitivity towards nitro-aromatic explosives has been demonstrated, the quick and selective detection of nitro-aromatics is still an unexplored area. Targeting specific chemical or physical property in addition to strong electron affinity can be better approach to overcome this problem. The MOF materials exhibit fast, highly sensitive and reversible explosive sensing but, the selective detection of nitro-explosives in presence of other nitro-aromatic compounds is still remains a great challenge. We have reported a highly fluorescent MOF for detection of nitro-aromatic explosive. The highly selective fluorescence quenching response of MOF towards TNP (2,4,6-Trinitrophenol) at ppm level concentration was obtained. First time the unprecedented selectivity for TNP in presence of other nitro-aromatic compounds has been demonstrated in MOF. This selectivity is ascribed to electron as well as energy transfer mechanisms and electrostatic interactions between TNP and MOF. The high selectivity and sensitivity along with water stability makes material promising candidate for highly selective detection of TNP.

**(P347)**

**Ferrocene-based Compartmental Ligand for the Assembly of 3d-4f Heterometallic Complexes**

Amit Chakraborty and Vadapalli Chandrasekhar

Heterometallic 3d-4f metal complexes are of interest in molecular magnetism.<sup>1, 2</sup> Compartmental ligands in general and Schiff-base ligands in particular are quite useful for assembling such complexes. One of the compartments in such ligands can be specific for 3d metal ions while the other compartment can be utilized for specifically accommodating f-block metal ions. We have utilized ferrocene to build new compartmental ligands<sup>3</sup> which have been used to synthesize the heterometallic complexes. The syntheses, structures, electrochemical behavior and magnetic properties of these complexes will be presented.

(P348)

**Synthesis And Characterization Of Co-Zr doped SrCoxZrxFe(12-2x)O19 (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 0.6, 0.7, 0.8, 0.9, 1.0) Ferrites Applying Citrate Precursor Sol-Gel Method**

Prabhjyot kaur, S.K. Chawla\*

Department of Chemistry, Guru Nanak Dev University, Amritsar

M-type hexaferrites denoted as MFe<sub>12</sub>O<sub>19</sub> (M refers to Ba, Sr, or Pb) have attracted a lot of attention because of their excellent magnetic properties and potential application in various fields [1–3], which account for about 90 wt% of the annual production of permanent magnets [4]. These ferrites share large volume of the market of permanent magnetic materials. They find extensive use in electronic material industry, radio industry, computer, and medicine owing to a favorable combination of sufficiently high magnetic properties, chemical stability, and low cost. In the present context, changes in the structural and magnetic properties of substituted M-type strontium hexaferrite SrCoxZrxFe(12-2x)O<sub>19</sub> ferrimagnets where magnetic (Co<sup>2+</sup>), and non-magnetic (Zr<sup>4+</sup>) ions have been substituted for Fe<sup>3+</sup> are probed at the microscopic levels employing Xray diffraction analysis (XRD) and Vibration Sample Magnetometer (VSM) techniques. Synthesis of compounds (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0) was accomplished by employing sol-gel method using citric acid as fuel and NH<sub>4</sub>NO<sub>3</sub> as oxidizer. The synthesis was accompanied by applying following stoichiometric equation SrCO<sub>3</sub> + (12-x) Fe(OH<sub>3</sub>)<sub>3</sub> + xCo(NO<sub>3</sub>)<sub>2</sub> + xZrO(NO<sub>3</sub>)<sub>2</sub> -----> SrCoxZrxFe(12-2x)O<sub>19</sub> The characterization of compounds was done by thermo-gravimetric analysis (TGA-DTA), FT-IR, XRD, energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM).

References

1. Jacobo, S.E., Civale, L., Blesa, M.A.: Evolution of the magnetic properties during the thermal treatment of barium hexaferrite precursors obtained by coprecipitation from barium ferrate (VI) solutions. *J. Magn. Magn. Mater.* 260, 37–41 (2000)
2. Oliver, S.A., Chen, M.L., Kozulin, I., Vittoria, C.: Structure and magnetic properties of barium hexaferrite films deposited at low oxygen pressures. *J. Magn. Magn. Mater.* 213, 326–334 (2000)
3. Yang, N., Yang, H., Jia, J., Pang, X.: Formation and magnetic properties of nanosized PbFe<sub>12</sub>O<sub>19</sub> particles synthesized by citrate precursor technique. *J. Alloys Compd.* 12, 263–267 (2007)
4. Sivakumar, M., Gedanken, A., Zhong, W., Du, Y.W., Bhattacharya, D., Yeshurun, Y., Felner, A.: Nanophase formation of strontium hexaferrite fine powder by the sonochemical method using Fe(CO)<sub>5</sub>. *J. Magn. Magn. Mater.* 268, 95–104 (2004).

(P349)

**Amino Acid Based Dynamic Metal–Biomolecule Frameworks**

Biplab Joarder, Abhijeet K. Chaudhari, Sanjog S. Nagarkar, Biplab Manna, Sujit K. Ghosh  
Indian Institute of Science Education and Research (IISER), Dr. Homi Bhabha Road, Pashan,  
Pune

Flexible or soft porous coordination polymers (PCPs) have been of immense importance for high performance molecular recognition, separation and related technologies.[1] Owing to their

dynamic nature, these MOFs have yielded unique interesting properties, like selective and hysteretic sorption, magnetic bistability, reversible photochemical responses, selective sensing, etc.[1] MOFs synthesized from biomolecular linkers, termed as metal–biomolecule frameworks (MBioFs), are receiving great attention due to their biocompatible nature and low environmental impact. Although there are few reports of rigid MBioFs, the dynamism in MBioFs has not been explored much so far. So, combining biocompatibility with dynamism should be a rational strategy to generate dynamic MbioFs (DMBioF), which might provide interesting properties, like soft-giant biomolecules. On the other hand, coordination polymer-based nanostructures, like nanofibers, are efficient materials for light harvesting applications and could give rise to new electronically, optically and biologically active materials. Keeping in mind these aspects, herein we present the synthesis and characterization of two isostructural homochiral CuII coordination frameworks based on amino acid (dand l-PGA, PGA= pyroglutamic acid). Dynamic behavior by solid-state structural transformation in single crystal-to-single crystal fashion is demonstrated. The extent of structural dynamism is shown by guest inclusion studies. Reversible sol-gel formation and anion-tuning morphology of the compounds are also discussed.[2]

#### References

[1] (a) Yanai, N.; Kitayama, K.; Hijikata, Y.; Sato, H.; Matsuda, R.; Kubota, Y.; Takata, M.; Mizuno, M.; Uemura, T.; Kitagawa, S. *Nat. Mater.* 2011, 10, 787. (b) Manna, B.; Chaudhari, A. K.; Joarder, B.; Karmakar, A.; Ghosh, S. K. *Angew. Chem. Int. Ed.* 2013, 52, 998.

[2] Joarder, B.; Chaudhari, A. K.; Nagarkar, S. S.; Manna, B.; Ghosh, S. K.; *Chem. Eur. J.* 2013, 19, 11178.

#### (P350)

##### **Synthesis and characterization of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of 2-amino-3-(4-hydroxyphenyl)-N'-(2-hydroxyphenyl)methylene]propanohydrazide**

Ph. Pengkiliya and R. K. Lonibala

Manipur University

Neutral Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of a new Schiff base, 2-amino-3-(4-hydroxyphenyl)-N'-(2-hydroxyphenyl)methylene] propanohydrazide (amph) derived from L-tyrosine hydrazide were isolated from the aqueous solution at pH ~7.0 and characterized based on the elemental analyses, pHmetric, molar conductance, electronic, IR, NMR and ESR spectral data. <sup>1</sup>H and <sup>13</sup>C NMR and IR spectra suggest the bonding of the ligand with the metal ions as a dinegative tridentate species. All the complexes were nonelectrolytes. Elemental and pHmetric data conform with 1:1 metal:ligand stoichiometry. Distorted octahedral geometry for Cu(II) complex was indicated by ESR and electronic spectra. The ESR spectrum of the complex is anisotropic at room temperature while it is isotropic at LNT. The trend in g-values indicates that the unpaired electron is present in the b<sub>1g</sub> (d<sub>x<sup>2</sup>-y<sup>2</sup></sub>) orbital. Formation of a high spin octahedral Mn(II) complex is suggested by the magnetic moment value and ESR spectral feature of the complex while magnetic and electronic spectral data of Co(II) and Ni(II) complexes are compatible with octahedral stereochemistry around the metal ions. We have also synthesized adducts from the ethanolic solutions and the complexes are yet to be characterized. We are making efforts to grow single crystals of the complexes. In absence of single crystals, we

proposed the tentative structures of the complexes. SEM-EDAX are used to obtain morphological information of the complexes and identification of chemical composition.

**(P351)**

**Rational Synthesis of Metal Phosphonates Based on Multidentate Organically Templated Phosphosphonic Acids**

Sunil K. Sharma and Ramaswamy Murugavel

Indian Institute of Technology Bombay, Powai, Mumbai-400 076, India

Polyphosphonic acids have long been known for their ability to bind with many metal ions (per acid group) and form polymeric metal phosphonates. The chemistry of metal phosphonates has undergone a significant expansion in recent years not only due to their potential applications in sorption, catalysis, ion exchange and intercalation chemistry, but also for their intriguing variety of architectures and fascinating new topologies. We have synthesized mesitylene and durene based mono-, di-, and tri- phosphonic acids, and their 2D alkali metals layered phosphonates and tetranuclearvanadium-phosphonates. Furthermore, 2D hydrogen bonded and  $\pi$ -stacked architectures of durene-1,4-bis(methylenephosphonic acid) with organic bases (pyridyl/piperdine) have been isolated as single crystals and structurally characterized by XRD.

References

1. Clearfield, A. Metal phosphonate Chemistry from Synthesis to applications; RSC publications, 2011.
2. Murugavel, R.; Choudhury, A.; Pothiraja, R.; Walawalkar, M. G.; Rao, C. N. R. Chem. Rev. 2008, 108, 3549.
3. Murugavel, R.; Shanmugan, S. Dalton Trans. 2008, 5358 - 5367.
4. Murugavel, R.; Kuppaswamy, S. Angew Chem. Int. Ed. 2006, 45, 7022.

**(P352)**

**Solution Processable Luminescent Nanoscale GdIII-OPE MOF: Multimodal Imaging and Explosive Sensing**

Venkata M Suresh, Snehajyothi Chatarjee, Rahul Modak, Vivek Tiwari, Amit B Patel, Tapas K Kundu and Tapas Kumar Maji\*

Multifunctional metal-organic frameworks (MOFs) that combine a set of well-defined properties like porosity and magnetism or magnetism and conductivity or porosity and optical properties are next generation of functional materials owing to their various possible applications in diverse fields. However, limited hydrolytic stability and large (in the millimetre range) size of bulk-crystalline phase MOFs restrict their intravenous administration and hence applications in biological and biomedicine fields. Nanoscale porous metal-organic frameworks (NMOFs) of uniform shape, size and permanent porosity with good hydrolytic stability are attractive due to their high solution processability, easy internalization into cell lines for bio imaging and drug delivery application. Here in, we report self-assembled highly luminescent metal-organic nanostructures of  $\{[\text{Gd}(\text{OPE})(\text{NO}_3)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}$  (1), (OPE=Oligo-phenyleneethynylene dicarboxylate) synthesized by coordination driven self-assembly of oligo-phenyleneethynylene dicarboxylic acid (OPEA) and Gd(III) in polar solvent under solvothermal conditions. This nanostructure has been characterized by powder X-ray diffraction, FESEM, TEM and adsorption

study. Interdigitation of 1D coordination polymer chains through alkyl chains results in a porous supramolecular 3D framework. Framework shows permanent porosity revealed by type-I CO<sub>2</sub> uptake profile. FESEM and TEM studies of 1 reveal nanorod like morphology with square type cross section with dimensions of 50-100 nm diameter and 0.5 - 0.8 μm length. High magnification TEM images show long range structural ordering present in 1 with uniform dark lines having an interspacing distance of 0.95 nm. Physiological stability, low toxicity and strong luminescence features of 1 have been exploited for imaging internalization into mammalian cultured cell lines HEK 293T and H1299. Furthermore, orderly aligned GdIII centers present in 1 have been explored for magnetic resonance imaging applications. Inherent microporosity of ordered luminescent 3D framework has been explored for explosive sensing applications in solution and vapor phase of analytes. These results demonstrate that introduction of paramagnetic metal centers, luminescence and porosity in particular MOF give multifunctional metal-organic nanostructures with efficient multimodal imaging and sensing applications.

**(P353)**

**Mechanistic Insights and Structural Evidences on An Iron(III)-Triggered Conformational Rotary Switch**

Rampal Pandey, Amit Kumar, Rakesh Kumar Gupta, and Daya Shankar Pandey\*  
Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi

An elegantly designed extremely fluorescent, chromogenic, fluorogenic and Fe<sup>3+</sup> recognizing conformational rotary switch imidazo-quinazoline 1 has been synthesized and structure of its both the conformations verified using X-ray single crystal analyses (Figure 1). The ambiguity regarding conformational switching induced by either Fe<sup>3+</sup> or pH has been resolved adopting various studies. Remarkably, quantum yield for 1 estimated 100% in methanol enables it to be used as reference for PLQY determination. Both the conformations have been clearly discriminated by basic analytical tools, naked eye, optical signalling and theoretical calculation. The conformation efficiency from 1 to 1' is 100% which is in fact thermoreversible. The DFT calculations suggested greater stability of 1 thus it needs external force to get converted into 1' which is provided by Fe<sup>3+</sup>. Ultimately, the concept has been supported by developing a model compound. As far as conformational rotation in any small molecule is concerned, it has been observed for the first time crystallographically that selective Fe<sup>3+</sup>-induced new conformation 1' excludes iron in the ensuing product. This approach will be helpful to investigate various organic and bio-molecular reactions to discriminate the conformational changes induced by either metal or pH.

**(P354)**

**An anionic metal-organic framework: adsorption study and cation exchange leading to versatile applications**

Anindita Chakraborty, Sohini Bhattacharyya and Tapas Kumar Maji  
JNCASR

A three dimensional porous anionic metal-organic framework [ $\{Zn_3(L)_2\} \cdot 6H_2O \cdot 2DMA$ ] (1) [L= 5,5'-(1,4-phenylenebis(methylene))bis(oxy)diisophthalic acid; DMA=CHONHMe<sub>2</sub><sup>+</sup>] has been synthesized and structurally characterized. The framework contains guest-accessible channels along different directions; smaller pore is hydrophilic while the larger one is hydrophobic in

nature. Upon guest removal, the framework generates robust structure with permanent porosity as realized by gas adsorption measurements. The remarkable and selective adsorption of CO<sub>2</sub> over gases like N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> is attributed to the high quadrupole moment of CO<sub>2</sub> and presence of electron cloud in the pore surface. Vapour adsorption study shows single-step hysteretic adsorption with H<sub>2</sub>O and MeOH, double-step hysteretic adsorption for EtOH and single-step gate-opening behavior with benzene. More interestingly, the counter cations (DMA) can be readily exchanged by various metal cations like Cu(II), Co(II), Ni(II), Mn(II); with highest inclusion with Cu (II) because of its versatile and flexible coordination geometry. 1 also shows significant exchange with heavy metal ions like Pb(II), Hg(II) and Cd(II); which could usher novel route to capture toxic heavy metals. Antenna effect has been observed when 1 was exchanged with various lanthanide ions [Eu(III), Tb(III), Dy(III) and Sm(III)].

**(P355)**

**Regiospecific C (naphthyl)-H Bond Activation by palladium(II): Synthesis, Characterization and Crystal structure of Isomeric Cyclopalladates**

Kanak Roy,<sup>a</sup> and Satyadeep S. Chhetri\*<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of North Bengal, Raja Rammohunpur, Siliguri 734013, India; <sup>b</sup> Department of Chemistry, Sikkim Govt. College, Gangtok

One of the mildest ways to achieve selective functionalization of C-H bonds in organic molecules is cyclometallation reaction [1]. In the present study, tetrachloropalladate ion has been found to activate both C2(naphthyl)-H and C8(naphthyl)-H bonds in a group of alkylsulfanylazonaphthalenes, affording cyclopalladates at room temperature. However, selectivity of C(naphthyl)-H bonds in the sulfanyl naphthylazo substrates has been shown to be controlled by the presence of acidic or basic additives. Regiospecific C2(naphthyl)-H has been achieved in presence of Et<sub>3</sub>N, leading to the formation of orthopalladate. On the other hand, regiospecific activation of C8(naphthyl)-H resulted in presence of acetic acid affording peripalladate. The structures of representative cyclopalladates have been determined by single crystal X-ray diffraction method. In the cyclopalladates, alkylsulfanylazonaphthalenes, bind palladium(II) via C(naphthyl), N(diazene), S(sulfanyl) donor set in terdentate fashion and the fourth position is occupied by a chloride ion. Both ortho-palladates and peri-palladates contain five-membered carbopalladacycles [C,N], whereas the [N,S] chelate rings are five-membered in orthoisomers but six-membered in peri-isomers. Photochemical transformation of the peripalladates into the ortho-palladates i.e. C8(naphthyl)-Pd → C2(naphthyl)-Pd has been achieved over a period of few days.

References

1. (a) I. Omae, *Coord. Chem. Rev.*, 2011, 255, 139; (b) M. Albrecht, *Chem. Rev.*, 2010, 110, 576.

**(P356)**

**Synthesis, Crystal Structure and Spectral Properties of Mixed Polyhalides of a Cu(II) tris – chelate**

Ramavath Babu and M. V. Rajasekharan\*

School of Chemistry, University of Hyderabad, Hyderabad

A tris-chelate of dafone is crystallized as a salt of mixed polyhalide anions.  $\text{Cu(dafone)}_3[\text{I}_2\text{Br}_3]_{0.5}[\text{I}_2\text{Br}_6]$  was synthesized, using  $\text{CuBr}_2$ , dafone (dafone = 4, 5-diazafluoren-9-one), iodine and excess of bromine solution. The only other tris-chelate of dafone is the previously reported  $[\text{Cu(dafone)}_3]\text{I}_2$ .<sup>[1]</sup> The  $\text{Cu(II)}$  complex cation is magnetically diluted in the anion matrices leading to well resolved EPR spectrum. Raman and electronic spectral details will also be presented.

#### References

1. Menon, S.; Rajasekharan, M. V. *Inorg. Chem.* 1997, 36, 4983.

#### (P357)

##### **AIEE Active Hexaarylbenzene Derivatives as Chemosensors for Picric Acid**

Vandana Bhalla, Sharanjeet kaur and Sandeep kaur  
Guru Nanak Dev University, Amritsar

Recently, development of cost efficient, selective, portable, fast and sensitive methods for detection of nitro derivatives has attracted great research interest. Among various nitro derivatives, detection of picric acid (PA) is important due to its wide usage in the manufacture of rocket fuels, fireworks, deadly explosive, sensitizer in photographic emulsions and as a component in matches, etc. Also picric acid has been recognized as an environmental contaminant and is harmful to wildlife and humans. Fluorescence signaling is one of the first choices among various methods used for detection of nitro derivatives due to its high sensitivity and selectivity. Thus, we have designed and synthesized hexaaryl derivative which exhibits aggregation induced emission enhancement (AIEE) in mixed aqueous medium due to presence of free rotors to give fluorogenic aggregates. Interestingly, the aggregates of derivative have strong affinity for  $\text{Hg}^{2+}$  ions and undergo the metal induced modulation in the presence of metal ion. Further, supramolecular assemblies of hexaarylbenzene derivative- $\text{Hg}^{2+}$  ensemble behave as highly selective chemosensor for picric acid with very low detection limit and very high quenching constant. Besides, we have used these metal induced aggregates for fabrication of fluorescent paper strips which can be helpful for practical detection of traces of PA.

#### (P358)

##### **Facile Synthesis of Arginine Functionalized Gold Nanoparticles and their Interaction with Bovine Serum Albumin**

M. Karuppu Raja and S. Murugesan\*

Department of Inorganic Chemistry, School of Chemistry, Madurai Kamaraj University,  
Madurai

Syntheses and characterizations of metal nanoparticles such as gold, silver and copper have gained considerable interest due to their attractive size and shape dependent optoelectronic and physiochemical properties. Particularly, the synthesis of gold nanoparticles (AuNPs) in conjugation with amino acids has received much attention because of the high stability, good biocompatibility and high affinity of AuNPs with biomolecules. In this work, the Au NPs have been synthesized using arginine as reducing and stabilizing agent and were characterized by UV-vis spectroscopy, energy dispersive X-ray spectroscopy, X-ray diffraction and Scanning electron microscopy analyses. The Au NPs size is found to be  $\sim 20$  nm. The binding tendency of Au NPs



with bovine serum albumin (BSA) has been investigated through UV-vis and fluorescence spectral methods. The results revealed that the Au Nps interact with BSA through ground state complex formation. The calculated apparent association constant ( $K_{app}$ ), quenching constant ( $K_q$ ), binding constant ( $K_b$ ) and number of binding sites ( $n$ ) are found to be  $7.482 \times 10^2 \text{ M}^{-1}$ ,  $4.241 \times 10^4 \text{ M}^{-1}$ ,  $2.341 \times 10^2 \text{ M}^{-1}$  and 0.499 respectively. The circular dichroism technique was employed to analyze the conformational changes in BSA induced by Au NPs and the results indicated that the biological activity of BSA could be influenced by arginine stabilized Au NPs.

**(P359)**

**Exploring the scope of Salen-type (N,N'-bis(salicylidene)ethylenedi amine) metalloligands towards heterometallic entities of diverse functionalities**

Soumavo Ghosh and Ashutosh Ghosh\*

Department of Chemistry, University College of Science, University of Calcutta

The supramolecular chemistry initiative has given birth to various strategies including the utilization of several metalloligands (metal complex as ligand) to build homo- and heterometallic complexes. Among them the chelates of tetradentate Salen type Schiff bases and its derivatives are one of the primary precursors as bidentate metalloligand. It alone makes a dictionary of homo- and hetero- polymetallic complexes with closely organized metal centers for a number of metal ions belong to s-, p-, d- and f-block. We have used some neutral tetradentate chelates of N,N'-bis(salicylidene)-1,3- propanediamine or its derivative [ $H_2L$  or  $H_2L'$  respectively] to prepare heterometallic coordination clusters (CCs) e.g.  $[ML]_2M'$  and  $[ML]M'$  (where, M is NiII or CuII and  $M'$  is a 3d-, 4f- or 5f- metal ions). Firstly, two pseudopolymorphic 2D coordination polymers (CPs) have been prepared using  $[NiIII]_2CoII$  as nodes and dicyanamido spacers by varying the solvent for synthesis. They show antiferro- to ferromagnetic switching due to conformational changes of the heterometallic nodes. Secondly, using Cu chelates of the same ligand we synthesized a new member of an earliest  $[CuL]_2Ln$  system ( $Ln = EuIII, GdIII$ ) described by Gatteschi et al derived from TbIII. This complex was suitably dimerized by a 4,4'-bipyridyl molecule. Both the complexes show ferromagnetic coupling below 5 K. On the other hand they displayed single molecule magnet properties in the presence of an applied magnetic field. Finally we have extended this strategy to actinides to built 1:1 adducts of  $[CuL]$  and  $[CuL']$  with  $UO_2(NO_3)_2 \cdot 6H_2O$  for the first time. Photophysical investigations reveal that the uranyl luminescence in solution can be completely turned off with the coordination of the Cu-chelates. These adducts crystallized as various solvates with exciting changes of supramolecular interactions.

**(P360)**

**Fluorescent pyridoxal based Schiff base ligands for sensing copper (II): biological applications**

Senjuti Mandal, Sudipta Chatterjee, Sushil Kumar Mandal, Ritwik Modak, Yeasin Sikdar, Barnali Naskar, Debadrita Modak, Sanchita Goswami, Anisur Rahman Khuda-Bukhsh, Tapan Kumar Mondal

Department of Chemistry, University of Calcutta; Department of Chemistry, Serampore College; Department of Zoology, University of Kalyani, Department of Chemistry, Jadavpur University

Three new copper complexes have been synthesized using two different N<sub>2</sub>O donor Schiff base ligands [((2-(dimethylamino)ethylimino)methyl)-5-(hydroxymethyl)-2-methylpyridin-3-ol] (HL1), [((2-(diethylamino)ethylimino)methyl)-5-(hydroxymethyl)-2-methylpyridin-3-ol] (HL2). All the compounds are well characterized by a variety of physical techniques including elemental analysis, FTIR, UV-Vis spectroscopy, NMR, single crystal X-ray diffraction studies. X-ray diffraction analysis reveals that complex 1 has distorted square pyramidal geometry with Addison parameter value,  $\tau = 0.24$ . Complexes 2 and 3 have  $\tau_4$  values of 0.114 and 0.15 respectively, indicate slightly distorted square planar geometry around the central metal ions. As pyridoxal containing moieties are fluorescent in nature, its potential as a fluorescent probe is cultivated. It is found that, Cu(II) ions selectively quenches the luminescence intensity of HL1. The association constant for Cu(II) was estimated to be  $6.06 \times 10^8 \text{ M}^{-1}$  in methanol by the linear Benesi-Hildebrand equation. The linear nature of steady-state Stern-Volmer plot ( $K_{sv} = 28.85 \times 10^6 \text{ L mol}^{-1}$ ,  $R^2 = 0.977$ ) suggests that only static quenching mode is present. But for HL2, the emission intensity is not quenched selectively by Cu(II) ions. The test for cytotoxicity of HL1 is performed and intracellular Cu<sup>2+</sup> imaging behavior of HL1 is studied on HeLa cells by fluorescence microscopy. Time dependent DFT calculations are carried out to correlate spectral output.

(P361)

**Computational Modeling of Spin state Dependent Reactivity of Bio-Inspired Model Complexes of Mononuclear Non-Heme Enzymes**

M. Jaccob, A. Ansari, B. Pandey and G. Rajaraman\*

Department of Chemistry, Loyola College, Chennai – 600 034, Tamil Nadu, India

Email: madhavanjack05@gmail.com

Activation and chemical transformation of molecular oxygen is a crucial process in biologically important chemical reactions. In nature, metalloenzymes use diverse active sites such as heme and non-heme (mono- and dinuclear) iron sites to activate dioxygen.<sup>1</sup> High-valent iron-oxo intermediates are found to be the active species in the catalytic cycles of oxygenation reactions. These intermediates can be also found to promote a broad range of synthetically and industrially relevant reactions such as hydroxylation, epoxidation, cis-dihydroxylation, heterocyclic ring formation and oxidative aromatic ring cleavage.<sup>2</sup> In order to tune the efficiency and selectivity of the oxidation catalyst, we need to evaluate the catalytic mechanisms of the enzymes under scrutiny in detail. On the basis of experimental and computational mechanistic investigations, various close-lying spin states of high-valent ferryl-oxo complexes are energetically accessible and this may lead to spin-crossover. The product distribution and yield depend not only on the ground but also on excited states (two- or multistate reactivity). Experimental proof for reaction mechanism involving various spin states is not a simple matter and in such a situation, computational chemistry has been playing an essential role in providing mechanistic data and structural information about unstable intermediates involving various spin states.<sup>3</sup> In this poster, I would like to present the overview about the spin state dependent reactivity of bio-inspired model complexes using DFT methods  $[(L)M^{IV}=X]$  (where  $M = \text{Fe, Mn}$ ;  $X = \text{O, NTs}$ ;  $L = \text{bispidine, H}_5\text{buea and H}_3\text{bupa ligands}$ ).<sup>4</sup> With the help of computation, we have shown that one can control the relative height of activation energy barriers upon modifying the steric and electronic factors of ligand skeletons. This paved a way to tune their catalytic selectivity and

efficiency of the oxidation catalysts and these predictions can lead to the new experimental studies.

#### References:

1. A. Gunay and K. H. Theopold, Chem. Rev. **2010**, 110, 1060.; W. Nam, Acc. Chem. Res., **2007**, 40, 522-531.
2. B. Meunier, S. P. de Visser, S. Shaik, Chem. Rev. **2004**, 104, 3947.; L. Que, Jr. and R. Y. N. Ho, Chem. Rev. **1996**, 96, 2607-2624.
3. Hirao, H.; Kumar, D.; Que, L. Jr.; Shaik, S., J. Am. Chem. Soc. **2006**, 128, 8590.
4. M. Jaccob et al, Dalton Trans., **2011**, 40, 11276-11281.; Dalton Trans. **2012**, 41, 10430-10439; Dalton Trans., **2013**, accepted.

#### (P362)

##### **P<sub>3</sub>F<sub>9</sub><sup>2-</sup>: An all-pseudo- $\pi^*$ 2 $\pi$ -aromatic**

Chakkingal P. Priyakumari<sup>a</sup> and Eluvathingal D. Jemmis<sup>b</sup>

<sup>a</sup>School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, CET Campus, Thiruvananthapuram, 695 016, Kerala, India and <sup>b</sup>Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Although numerous studies have been done on triangular phosphacycles with tri-coordinate phosphorus, corresponding penta-coordinate analogs have not received much attention.<sup>1</sup> There are very few reports on 3-membered rings containing penta-coordinate phosphorus<sup>2</sup>; interestingly, penta-coordinate triphosphirane (**1-4**) is yet to be studied. Schematically triphosphiranes **1**, C<sub>3h</sub> and **2**, C<sub>s</sub> are constructed from trigonal bipyramidal (tbp) PH<sub>5</sub> using one axial and one equatorial bond. Two more structures (**3**, **4**) are obtained starting with an approximate square pyramidal (spp) PH<sub>5</sub>, the species involved in the turnstile mechanism. These are not calculated to be minima. A qualitative MO analysis suggests (PH<sub>3</sub>)<sub>3</sub><sup>2-</sup> as a candidate for an all-pseudo- $\pi^*$  2 $\pi$  aromatic; however computational studies show that this is also not a minima. Fluorine substitution which increases the contribution of p orbitals on P in the pseudo- $\pi^*$  MO makes (PF<sub>3</sub>)<sub>3</sub><sup>2-</sup> a minimum, and aromatic. The 2 $\pi$  aromaticity arising from the bonding combination of the three pseudo- $\pi^*$  fragment MOs is comparable to that in C<sub>3</sub>O<sub>3</sub><sup>2-</sup> and is another example for the analogy between CO and PF<sub>3</sub>.<sup>3</sup> The dianion, (PF<sub>3</sub>)<sub>3</sub><sup>2-</sup> forms the first example of a 3-membered ring with all the vertices constituted by penta-coordinate phosphorus.<sup>4</sup> The ability of PF<sub>3</sub> to form the all-pseudo- $\pi^*$  2 $\pi$ -aromatic system is not shared by the heavier analogs, AsF<sub>3</sub> and SbF<sub>3</sub>.

#### References

- (1) Tho Nguyen, M.; Dransfeld, A.; Landuyt, L.; Vanquickenborne, L. G.; Schleyer, P. v. R. Eur. J. Inorg. Chem. **2000**, 2000, 103. Tokitoh, N.; Tsurusaki, A.; Sasamori, T.; Phosphorus, Sulphur Silicon Rel. Elem. **2009**, 184, 979.
- (2) Ehle, M.; Wagner, O.; Bergsträßer, U.; Regitz, M. Tetrahedron Lett. **1990**, 31, 3429. Sase, S.; Kano, N.; Kawashima, T. J. Am. Chem. Soc. **2002**, 124, 9706. Sase, S.; Kano, N.; Kawashima, T. J. Org. Chem. **2006**, 71, 5448.
- (3) Bao, X.; Zhou, X.; Lovitt, C. F.; Venkatraman, A.; Hrovat, D. A.; Gleiter, R.; Hoffmann, R.; Borden, W. T.; J. Am. Chem. Soc. **2012**, 134, 10259.
- (4) Priyakumari, C. P.; Jemmis, E. D. J. Am. Chem. Soc. **2013**, 135, 16026.

**(P363)**

**Employing Arynes in Transition-Metal- Free Monoarylation of Aromatic Tertiary Amines**

Sachin Suresh Bhojgude, Trinadh Kaicharla, and Akkattu T. Biju\*

Organic Chemistry Division, CSIR-National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune

Aromatic amines are ubiquitous in various natural products, pharmaceuticals, agrochemicals, dyes, materials, and are useful synthetic building blocks.<sup>1</sup> Traditionally, the formation of Caryl-N bonds has been achieved by classical methods such as nucleophilic aromatic substitution, electrophilic nitration followed by reduction, and by the copper-mediated arylation of amines, amides, or carbamates following the Ullmann-Goldberg protocol.<sup>2</sup> However, with the advent of transition-metal catalysis, the N-arylation of amines is more dominated by the use of Pd, Cu and Ni catalysts in well-established Buchwald- Hartwig or Ullmann-type coupling of aryl halides with amines as well as the Chan-Lam coupling between organoboron compounds and N-H containing compounds.<sup>3</sup> Interestingly, however, whereas the transition-metal-catalyzed arylation of primary and secondary amines is well- established, the analogous Caryl-N bond construction using aromatic tertiary amines, to the best of our knowledge, has not been reported. We have recently reported an efficient and facile transition-metal-free, selective mono N-arylation of aromatic tertiary amines using aryne as the aryl source.<sup>4</sup> High levels of functional group compatibility especially with halogen containing substrates, dyes and donor-acceptor systems, and high yields of products are the notable features of this method. The details of the work including preliminary mechanistic investigation will be presented.

References

- 1.(a) Amines: Synthesis Properties and Applications (Ed.: Lawrence, S. A.), Cambridge University Press, Cambridge, 2004. (b) Rappoport, Z. Ed. The Chemistry of Anilines, Wiley-VCH, Weinheim, 2007.
2. For reviews, see: (a) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* 2003, 42, 5400. (b) Kunz, K.; Scholz, U.; Ganzer, D. *Synlett* 2003, 2428. (c) Monnier, F.; Taillefer, M. *Angew. Chem., Int. Ed.* 2009, 48, 6954.
- 3.(a) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* 1998, 31, 805. (b) Hartwig, J. F. *Acc. Chem. Res.* 2008, 41, 1534. (c) Qiao, J. X.; Lam, P. Y. S. *Synthesis* 2011, 829.
4. Bhojgude, S. S.; Kaicharla, T.; Biju, A. T. *Org. Lett.* 2013, 15, 5452.

**(P364)**

**Transition-Metal-Free Aryne MCRs Initiated by N-Heterocycles**

Anup Bhunia, Digvijay Porwal, Tony Roy and Akkattu T. Biju\*

Organic Chemistry Division, CSIR-National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune

Arynes are highly electrophilic reactive intermediates, which have been extensively utilized in various carbon-carbon and carbon-heteroatom bondforming reactions.<sup>1</sup> Recent developments in aryne chemistry have been devoted to transition-metal-free reactions, which mainly include the initial addition of nucleophiles to aryne and subsequent trapping of the aryl anion intermediate with electrophiles. We have recently developed a transitionmetal- free multicomponent reactions

involving arynes, N-heterocycles and various carbonyl compounds.<sup>2</sup> With (iso)quinoline as the nucleophile, and carbonyl compounds such as aldehydes, ketones, and N-substituted isatins as electrophiles, the reaction afforded oxazino (iso)quinoline derivatives and the reaction proceeded via 1,4-dipolar intermediates. Interestingly, when the nucleophilic trigger used is pyridine, the reaction furnished indolin-2-one derivatives, and it is probable that the reaction proceeds via a pyridylidene intermediate. The details of this work will be presented.

#### References

- 1.(a) Bhojgude. S. S; Biju, A. T. *Angew. Chem. Int. Ed.* 2012, 51, 1520. (b) Tadross, P. M.; Stoltz, B. M. *Chem. Rev.* 2012, 112, 3550. (c) Bhunia, A.; Yetra, S. R.; Biju, A. T. *Chem. Soc. Rev.* 2012, 41, 3140.
- 2.(a) Bhunia, A.; Roy, T.; Pachfule, P.; Rajamohanan, P. R.; Biju, A. T. *Angew. Chem., Int. Ed.* 2013, 52, 10040. (b) Bhunia A.; Porwal D.; Gonnade R. G.; Biju A. T. *Org. Lett.* 2013, 15, 4620.

#### (P365)

##### **Synthesis of AAT Containing Bacterial Glycoconjugates**

Ananda Rao Podilapu, Srinivasulu Avvathula, Madhu Emmadi & Suvarn S. Kulkarni\*  
IIT Bombay

2-Acetamido-4-amino-2,4,6-trideoxy-D-galactopyranoside (AAT) is present on cell surface of many bacterial polysaccharides such as *Shigella sonnei*,<sup>1</sup> *Streptococcus pneumoniae*,<sup>2,3</sup> and *Streptococcus mitis*.<sup>4</sup> Recent studies on zwitterionic polysaccharides revealed that, they can elicit a T-cell dependent immune response, this is mainly because of the positive and negative charge present on them. In these species positive charge originates from the 4-amino functionality whereas negative charge comes from the phosphate or ester. To understand the specific function of AAT containing polysaccharides in drug or vaccine therapy, one need to have the pure compounds for biological studies.

Recently our lab established a efficient protocol to synthesize AAT building block from cheaply available D-mannose in few steps with good yields.<sup>5,6</sup> Currently we are exploring this protocol for the synthesis of O-linked bacterial glycoconjugates.

#### References:

1. Kenne, L.; Lindberg, B.; Petersson, K.; Katzenellenbogen, E.; Romanowska, E. *Carbohydr. Res.* 1980, 78, 119-126.
2. Lindberg, B.; Lindqvist, B.; Långren, J.; Powell, D. A. *Carbohydr. Res.* 1980, 78, 111-117.
3. Karlsson, C.; Jansson, P.-E.; Sörensen, U.B.S. *Eur. J. Biochem.* 1999, 265, 1091-1097.
4. Bergström, N.; Jansson, P.-E.; Kilian, M.; Sörensen, U.B.S. *Eur. J. Biochem.* 2000, 267, 7147-7157.
5. Emmadi, M.; Kulkarni, S. S. *Nat. Protoc.* 2013, 8, 1870-1889.
6. Emmadi, M.; Kulkarni, S. S. *Org. Biomol. Chem.* 2013, 11, 3098-3102.

#### (P366)

##### **Metal free regioselective C2 Amidation of Indole with Quinazolinone and Pyrimidone led to novel Indolylquinazolinone/ pyrimidones**

Suman Kr Ghosh, Rajagopal Nagarajan\*

Regioselective functionalization on the biologically 'privileged' skeleton like indole and pyrrole always engender interest among the chemists<sup>1</sup>, particularly amidation of indole and pyrroles remained a challenge to the synthetic community. Very few reports regarding amidation at C2 of indoles<sup>2</sup> and pyrroles<sup>3</sup> are available, but direct metal free amidation at the C2 position of indole still remain unexplored. Quinazolinone and pyrimidones are well known due to their diverse range of biological properties. Functionalization of quinazolinone's amide N-H increases the activity of the motif, though heterocycles like indole, pyrrole and cyclic amides have not been explored elaborately as functionality. Hence, a mild metal free protocol was developed for the regioselective C2 amidation of various indoles and pyrroles with quinazolinone and pyrimidone derivatives, which led to novel indolyl/pyrrolylquinazolinone and pyrimidones in moderate to good yields. Further we utilised our protocol to synthesize a highly functionalized 1,3-diazapine compound, which may contain useful biological properties.<sup>4</sup>

References:

1. Shiri, M. Chem. Rev. 2012, 112, 3508.
2. Kumar, A. S.; Nagarajan, R. Org. Lett. 2011, 13, 1398.
3. Wu, J.; Vetter, W.; Gribble, G. W.; Schneekloth, J. S.; Jr., Blank, D. H.; Gorls, H. Angew. Chem. Int. Ed. 2002, 41, 1740.
4. Ghosh, S. K.; Nagarajan, R. (Communicated).

**(P367)**

**Synthesis of Anthracene and Naphtho[b] Thiophene analogs Involving Lewis /Bronsted Acid -Mediated Regioselective Annulation**

Sivasakthikumar, R, Nandakumar, M and Arasambattu K. Mohanakrishnan  
Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai

In recent times, the anthracene derivatives have been widely explored in OLEDs,<sup>1a</sup> molecular switches<sup>1b</sup> and other optical applications.<sup>1c</sup> Due to its low electronic band gap and strong blue fluorescence, they have been extensively used as fluorescent chromophores in the construction of chemosensors for many applications.<sup>2</sup> It has been confirmed that the incorporation of anthracene units as pendant groups led to the formation of films with excellent optical quality.<sup>3</sup> Herein we report a one-pot synthesis of annulated heterocycles involving Lewis/Bronsted acid-mediated regioselective annulation of unsymmetrical 1,2- diarylmethinedipivalates<sup>4</sup>/diols in DCM at room temperature led to the formation of annulated arenes and heteroarenes.

References

- 1.(a) Chen, Y.-H.; Lin, S.-L.; Chang, Y.-C.; Chen, Y.-C.; Lin, J.-T.; Lee, R.-H.; Kuo, W. J.; Jeng, R. J. Org. Electronics 2012, 13, 43-52.(b) H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, R. Lapouyade, Chem. Soc. Rev. 2000, 29, 43-55.(c) Thangthong, A.; Meunmart, D.; Prachumrak, N.; Jungstittiwong, S.; Keawin, T.; Sudyoatsuk, T.; Promarak, V. Tetrahedron 2012, 68, 1853-1861.
2. Jadhav, J. R.; Bae, C. H.; Kim, H.-S. Tetrahedron Lett. 2011, 52, 1623-1627.
3. Boyd, T. J.; Geerts, Y.; Lee, J.-K.; Fogg, D. E.; Lavoie, G. G.; Schrock, R. R.; Rubner, M. F. Macromolecules 1997, 30, 3553-3559.

4.Sivasakthikumar, R.; Nandakumar, M.; Mohanakrishnan, A. K. J. Org. Chem. 2012, 77, 9053-9071.

**(P368)**

**A facile three-component expedient approach for the assembly of naphthoquinone-eboracin hybrid heterocycles**

S.Vivek Kumar, B. Devi bala, S.

Muthusubramanian and S. Perumal\*

Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University  
Madurai

Multi-component reactions (MCRs) have emerged as one of the most prevailing synthetic tools for the expedient and convergent access of molecular libraries needed in lead identification and drug discovery programmes.<sup>1</sup> 1,4-Naphthoquinones are considered as an essential class of natural products with widespread biological applications ascribable to their ability to modify DNA.<sup>2</sup> Eboracin, a substituted indenopyrrole, exhibits anti-convulsive activity against mice.<sup>3</sup> Due to the biological properties of these moieties, we were prompted to report the synthesis of naphthoquinone-eboracin hybrids, viz. (4bR\*,11bR\*)-4b,11b-dihydroxy-5-phenyl-4b,5-dihydrobenzo[f]indeno[1,2-b]-indole-6,11,12(11bH)-triones regioselectively in good yields from the threecomponent sequential reaction of 2-hydroxy-naphthalene-1,4-dione, substituted anilines and ninhydrin in PEG-400 medium in the presence of formic acid as catalyst under microwave irradiation at 100 °C. This transformation presumably proceeding via Michael addition/regioselective annulation via intramolecular condensation sequence stems as a part of our research programme recently launched on the synthesis of novel naphthoquinone based heterocyclic systems.<sup>4</sup>

References

- [1] (a) Domling, A. Chem. Rev. 2006, 106, 17; (b) Zhu, J. Eur. J. Org. Chem. 2003, 1133; (c) Cariou, C. C. A. ; Clarkson, G. J. ; Shipman, M. J. Org. Chem. 2008, 73, 9762.
- [2] (a) Hussain, H.; Krohn, K.; Ahmad, V. U.; Miana, G. A.; Greend, I. R. Arkivoc 2007; (ii) 145; (b) Powis, G. Pharmacol. Ther. 1987, 35, 57; (c) de Almeida, E. R. The Open Natural Products Journal 2009, 2, 42.
- [3] Alexander, G. J.; Alexander, R. B.; Kopeloff, L. M. Pharmacol biochem behave., 1985, 22, 53.
- [4] Devi Bala, B.; Balamurugan, K.; Perumal, S. Tetrahedron Lett., 2011, 52, 4562; (b) Michael Rajesh, S. Devi Bala, B. Perumal, S.; Menéndez, J. C. Green Chem., 2011, 13, 3248; (c) Devi Bala, B. Michael Rajesh, S.; Perumal, S. Green Chem., 2012, 14, 2484; (d) S. Muthusarayanan.; C. Sasikumar.; B. Devi bala. Green Chem. (In press) (e) Devi Bala, B. Muthusarayanan, S.; Perumal, S. Tetrahedron Lett. 2013, 54, 3735.

**(P369)**

**Ring Opening-Ring Closing Olefin and Enyne Metathesis of Norbornene Derivatives to the Construction of Angularly Annelated Polycycles**

Ritabrata Datta, Anupam Jana, Sritama Bose, Pipaliya B. Viththlbhai and Subrata Ghosh\*

Junior Research Fellow Department of Organic Chemistry, Indian Association for the  
Cultivation of Science, Jadavpur, Kolkata

Domino ring opening (RO)- ring closing metathesis (RCM)<sup>1</sup> of norbornene derivatives offers a unique tool for direct construction of complex molecular structures. We have employed<sup>2</sup> this protocol for the synthesis of condensed and bridged ring systems present in several natural products. This protocol has been extended to construct angularly annelated tricyclic systems. Thus, treatment of appropriately constructed norbornene derivatives with Grubbs's<sup>TM</sup> second generation catalyst afforded highly functionalized angularly arrayed tricyclic ring systems having 5-7 membered in excellent yields.

Norbornene derivatives having alkyne unit was found to undergo tandem ring opening- ring closing enyne metathesis (RCEM) to give rise to conjugated diene. Diels-Alder reaction of this diene with dienophiles led to cycloaddition followed by 1,3-sigmatropic rearrangement of the resulting vinyl cyclopentane to form tetracyclic structures.

The results of this investigation will be presented in connection to natural products synthesis.

**(P370)**

**Synthesis characterization and electrochemical studies of some novel indole derivatives**

Gulzar Khan, Ratnesh Das

Department of Chemistry, Dr. Harisingh Gour University, Sagar, Madhya Pradesh

Nitrogen containing heterocycles find wide application as structural components in pharmaceuticals and agrochemicals due to their marked biological activities. Among biologically active heterocycles, Indole and its derivatives enjoys wide range of therapeutic and pharmacological properties as anti convulsant, analgesic, sedative anti-depressive, anti-carcinogenic and hypnotic agents. In this study a new series of novel indole derivatives were synthesized. Structure of the title compounds were elucidated by spectral techniques like UV-Vis., FT-IR and NMR. Electrochemical studies of the synthesized compounds were recorded on 797 VA computer. Their biological evaluation is in progress.

**(P371)**

**Synthesis of substituted 1,3-diaryl-6,7-dihydro-1H-indol-4(5H)-ones from 1-aryl-2-(arylamino)ethanones**

Selvam Kaladevi and Shanmugam Muthusubramanian\*

Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai  
625 021, India

Fused pyrroles are common structural motifs widely exist in nature. They often serve as "privileged structures"<sup>TM</sup> in many biologically active molecules and pharmaceutical substances. They display antibacterial, antiviral, anti-inflammatory, antitumor and antioxidant activities.<sup>1</sup> Owing to their biological importance, these derivatives attracts the attention of synthetic Organic Chemists. Many methodologies are available for synthesis of fused pyrroles involving cycloketone annulations,<sup>2</sup> metal-catalyzed cascade cyclization of alkynes<sup>3</sup> etc.

This presentation describes the synthesis of fused pyrroles from substituted 1-aryl-2-(arylamino)ethanones. Upon reflux with cyclohexane-1,3-dione in acetic acid, 1-aryl-2-(arylamino)ethanones lead to 1,3-diaryl-6,7-dihydro-1H-indol-4(5H)-ones in excellent yield.



## References

1. Jacobi, P. A.; Coultts, L. D.; Guo, J. S.; Leung, S. I. *J. Org. Chem.* **2000**, 65, 205.
2. Zhao, X.; Zhang, E.; Tu, Y.-Q.; Zhang, Y.-Q.; Yuan, D.-Y.; Cao, K.; Fan, C.-A.; Zhang, F. M. *Org. Lett.* **2009**, 11, 4002.
3. Nagafuji, P.; Cushman, M. J. *Org. Chem.* **1996**, 61, 4999.

### (P372)

#### **Design and Efficient Synthesis of Functionalized Flavone-Triazole-Tetrahydropyran Conjugates via Click Chemistry**

Naveen Kumar Konduru and Naseem Ahmed\*

IIT Roorkee

Flavonoids are plant secondary metabolites and are water soluble due to polyphenolic nature. They play vital role in the plants by protecting from microbes and insects attack as well as in human being intake of flavonoids relieve from hay fever, heart disease, asthma, and stroke. 1,2,3-Triazole basic moiety is present in many natural products and in medicinal agents. 1,2,3-Triazole derivatives have shown a wide range of applications in pharmaceutical and agrochemical products. Similarly, substituted tetrahydropyrans are common structural motifs in numerous biological molecules and core units in natural products that include (-)-centrolobine, bryostatin and pheromones. They have shown a large pharmacological profile such as good antiproliferative activity against various cancer cell lines; inhibit the growth of the fungal pathogen *Candida albicans* and in vivo antinociceptive activity etc.

Molecular hybridization is a new concept in drug design and development in which combines different bioactive substances to produce a new hybrid compound with improved affinity and efficacy compared to the parent drugs, it was proved by recent literature reports. Therefore, here we have selected flavone, triazole and tetrahydropyran derivatives to construct one entity. Herein, we report a mild and efficient method developed for synthesis of flavone-triazole-tetrahydropyran hybrids via click reaction. Under optimized reaction conditions the products such as 5-iodo and 5-H-1-(tetrahydropyran)-1,2,3-triazol-4-(3-methoxyflavone) derivatives were isolated in excellent yields (90-98%) within 1-3h.

### (P373)

#### **Design of indolocarbazole based novel organic dyes for dye-sensitized solar cell applications**

Kesavan Stalindurai and Chennan Ramalingan\*

Centre for Nanotech./Department of Chemistry, Kalasalingam University, Anand Nagar, Krishnankoil, Tamilnadu, India

In the recent days, an increasing demand for energy, the diminution of fossil resources and its allied environment pollutant grounds a great quest and necessitate for environmentally sustainable energy technologies. Dye sensitized solar cells (DSSCs), especially Gratzel's™ ruthenium based ones are one of the important classes of solar cells and play vital roles in providing better power conversion efficiencies. Although ruthenium based ones provide nearly 15% power conversion efficiency, the higher cost, environmental issues and non-flexibility of the same made the researchers around the globe to focus on the design of alternative metal free organic dyes as sensitizers in the field of dye sensitized solar cells. Further, metal free organic dyes could have larger absorption coefficients, could be widely designed and could be easily

synthesized as well. Currently, diverse ranges of novel organic dyes have been reported as efficient sensitizers in the field of dye sensitized solar cells, however, the power conversion efficiency has yet to be reached the one provided by ruthenium based dye sensitized solar cells. In an attempt to design efficient sensitizers for dye sensitized solar cells, various metal free indolocarbaole based novel organic dyes have been synthesized from simple and commercially available cyclohexadione using various organic reactions including condensation, double cyclization, alkylation, formylation, halogenations, Buchwald-Hartwig type reaction / Ullmann type coupling reactions etc. which would be discussed.

**(P374)**

**Synthesis of Imidazo[1,2-a] pyridine by using DABCO and its chalcone derivatives**

Vaishali Goswami and H.S.Joshi

Department of Chemistry, Saurashtra University, Rajkot

Imidazo[1,2-a]pyridine moieties represent important building blocks in both natural and synthetic bioactive compounds, and it also possesses diverse therapeutic activities [1]. The nature and the position of the substituent on the pyridinic moiety influence these activities [2]. The core structure of imidazo[1,2-a] pyridine has been synthesized in the most cheapest, non-toxic and safest solvent water. The synthesis has been carried out by the reaction of 2-amino-5-bromo pyridine, para methoxy phenacyl bromide in presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as base 1. Imidazopyridine chalcone derivatives were synthesized by reaction of 6-bromo-2-(4-methoxyphenyl)H-imidazo[1,2-a]pyridine-3-carbaldehyde 2 and different aryl acetophenone in the presence of catalytic amount of 40 % alkali to give (2E)-1-(6-bromo-2-(4-methoxyphenyl)H-imidazo[1,2-a]pyridin-3-yl)-1-arylprop-2-en-1-ones 3a-j [3]. Their IR, <sup>1</sup>H NMR, MASS spectral data and elemental analysis were in accord with assigned structure.

References:

[1]Hamdouchi, C.; Blas, J.; Prado, M.; Gruber, J.; Heinz, B. A.; Vance, L. J. Med. Chem. **1999**, 42, 50.

[2]Lhassani, M.; Chavignon, O.; Chezal, J. M.; Teulade, J. C.; Chapat, J. P.; Snoeck, R.; Andrei, G.; Balzarini, J.; De, Clercq. E.; Gueiffier, A. Eur. J. Med. Chem. **1999**, 34, 271.

[3]Joshi, M.; Vekariya, P.; Dodiya, B.; Ghetiya, R.; Joshi, H. J. Het. Chem. **2012**, 49, 130.

**(P375)**

**A Facile Metal-Free Oxidative Cross-Dehydrogenative-Coupling Reaction (CDCReaction) for Selective Formation of C-S Bonds.**

Varun Begur, Kandikere Ramaiah Prabhu

IISc. Bangalore

C-H functionalization is a longstanding goal owing to ease, efficient and environmentally benign method of synthesizing a variety of functionalised molecules that have industrial applications. Therefore, development of CDC methods is rapidly growing area in organic synthesis. The transformations via CDC-reactions are powerful tools, as they do not require pre-functionalization of starting materials. In the present work, a facile metal free oxidative CDC-reaction, involving selective formation of C-S bonds has been described. Present protocol provides an easy access to highly substituted aromatic derivatives in excellent yields. An

excellent protocol for synthesizing a variety of thioamides in excellent yields has also been discussed.

**(P376)**

**Highly Regioselective Addition of Organozinc Reagents to 2-Oxo-1,2-dihydropyrimidine-5-carboxylates**

Rakesh Chopra and Kamaljit Singh

Department of Chemistry, Guru Nanak Dev University, Amritsar, India

The 2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylates (Biginelli DHPMs) represent one of the most actively investigated class of compounds due to their importance as potential calcium channel blockers and have been known for more than a century. Some specific examples include Sch575948, dehydrocrambine A. As a result of their diverse pharmacological profile, synthetic investigations on DHPMs have received extensive attention by synthetic organic chemists and medicinal chemists alike. Herein, we report the incorporation of alkyl as well as phenyl groups at C-4 position of 2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylates, known to be a key position responsible for antagonist/agonist switching of the calcium channel blocking activity of these compounds, by the addition of organozinc reagents catalysed by BF<sub>3</sub>·OEt<sub>2</sub>. In addition, we describe theoretical studies supporting the formation of the products and the attendant regioselectivity of the process.

**(P377)**

**A green protocol for the construction of triazolo[3,4-b][1,3,4] thiadiazine possessing pyrazine nucleus.**

Jalpa R. Pandya and H.S.Joshi\*

\*Department of Chemistry, Saurashtra University, Rajkot- 360 005

In recent years, the focus is being shifted towards environmentally green and benign protocols to avoid use of hazardous organic solvents. The organic reactions carried out in aqueous media have attracted many chemists. As a solvent, water offers many economic and environmental advantages including wide availability, cheap in cost, non-hazardous and safe in handling [1-2]. Water has been heavily investigated recently as a replacement for more conventional organic solvents, because of its low cost and its avoidance of organic vapors; it has thus been identified as a "green" solvent [3]. With these aspects of clean and green protocols, we have developed a synthesis of triazolo[3,4-b][1,3,4] thiadiazine in aqueous media. [1,3,4] thiadiazine is investigated for many therapeutic activities [4-5]. The synthesis has been carried out by the reaction of 4-amino-5-(pyrazin-2-yl)-4H-1,2,4-triazole-3-thiol, substituted phenacyl bromide in presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as base.

References

1. Li, C. J. Chem. Rev., **2005**, 105, 3095.
2. Tiwari, V.; Meshram, J. Ultrasonics sonochemistry **2011**, 18, 911-916.
3. Pirrung, M. Chem. Eur. J., **2006**, 12, 1312-1317.
4. H.S.Joshi et.al. Acta Chim. Slov. **2011**, 58, 53-59.
5. Schenone, S.; Bruno, O.; Ranise, A.; Bondavalli, F.; Filippelli, W.; Falcone, G.; Giordano, L.; Vitelli, M. R. Bioorg. Med. Chem. **2001**, 9, 2149-2153.

**(P378)**

**Tetrazine Templated Synthesis of Mixed Ternary Glycoclusters**

Boddu Venkateswara Rao and Srinivas Hotha\*

Department of Chemistry, Indian Institute of Science Education and Research, Pune, India.

A chemical reaction wherein two individual molecules are coupled together covalently in the presence or absence of reagents is known as a conjugation reaction and if the reacting partners are biomolecules then it is known as bioconjugation. Bioconjugation of molecules is important for studying various cellular events such as protein-protein interactions, imaging of cells, for the measurement of distances between epitopes, for modification of materials, etc. Amidation, Native Chemical Ligation, Staudinger ligation, azide-alkyne involved [3+2] cycloaddition ('click' reaction), olefin metathesis, imine formation, tetrazine-based ligation, Michael addition are some of the bioconjugation methods; among these, Staudinger ligation, click reaction between azide and alkyne are the most popular and bioorthogonal. Tetrazine-ligations were probed independently by Fox and Hilderbrand. Most of the above methods are useful to study binary complexes as only two partners participate in the conjugation. However, stepwise conjugation of molecules to get ternary complexes in a modular fashion is still a formidable challenge. In this poster, our recent efforts for the general Ternary Conjugation Strategy will be discussed.

References:

[1] Schilling, C. I.; Jung, N.; Biskup, M.; Schepers, U. and Brase, S. Chem. Soc. Rev., **2011**, 40, 4840-4871 [2] Sletten, E. M.; Bertozzi, C. R. Angew. Chem. Int. Ed., **2009**, 48, 6974-6998; [3] (a) Blackman, M. L.; Royzen, M.; Fox, J. M. J. Am. Chem. Soc., **2008**, 130, 13518-13519; (b) Devaraj, N. K.; Weissleder, R.; Hilderbrand, S. A. Biocon. Chem., **2008**, 19, 2297-2299; [4] Rao, B. V.; Hotha, S. Chem. Commun., **2013**, 49 (92), 10808 - 10810.

**(P379)**

**Synthesis of Highly Functionalized Biaryls Using Allyl Cyanide**

Pratik Yadav, Surjeet Singh, Satyanarayan Sahu, Ramendra Pratap

Department of Chemistry, University of Delhi, North Campus

A simple and efficient route for the synthesis of highly functionalized biphenyls has been developed based on Baldwin Rules. A competitive intramolecular study has been done between 6-Exo-Trig and 6-Exo-Dig cyclization and it was found that reaction nicely follows Baldwin's ring closer rules and each case 6-Exo-Trig was preferred over 6-Exo-Dig attack. Reaction proceeds via in situ generation of carbanion at  $\alpha$  and  $\gamma$  positions of allyl cyanide followed by tandem one pot ring closer reaction with substituted 2H-pyran-2-ones.

**(P380)**

**A novel efficient entry to potential bioactive versatile heterocyclic-condensed purines:**

**Functional N-fused imidazole as building block**

Vikas Chaudhary, Sankar K. Guchhait

NIPER

Structural hybridization of marketed drugs and bioactive agents/natural products offers discovery of novel therapeutic agents/drugs. However, a relatively less is known in scaffold-hybridization.

An excellent example is azatoxin, a hybrid of etoposide and ellipticine (both anticancer drugs). As our contribution in this area, we have considered pyrido[1,2-e]purines, a structural amalgamation of purine class of compounds (purinone, adenine, guanine, xanthine, or purine-2,4-diamine or their analogs) and imidazo[1,2-a]pyridine/pyrazine, as novel purine analogs for anticancer activity. Heterocyclic-condensed purines are known for their various bio-activities, and possess enhanced selectivity. The imidazo[1,2-a]pyridine/pyrazine derivatives are present in marketed drugs such as zolpidem and zolmidine, and exhibit various pharmacological activities. Furthermore, our group has developed 3-aminoimidazo[1,2-a]pyridine/pyrazine derivatives as hTopoIII±â€ ATP-binding site inhibitory anticancer agents. Therefore, pyrido[1,2-e]purines as novel compounds will be important for their potential versatile pharmacological activities contributing to novel chemical space of biological relevance. We have explored imidazo[1,2-a]pyridine/pyrazine-2-carboxyethyl-3-amine as an important synthetic building block in the novel concise synthesis of pyridine/pyrazine ring enlarged analogs of purinone, adenine and its oxo/thio-congeners, guanine, xanthine, and purine-2,4-diamine. The designed building block has been prepared by an established Strecker-Ugi type multicomponent reaction using TMSCN as a functional isonitrile equivalent in one step and good yield.

**(P381)**

**Synthesis of 1-oxygenated Carbazole Alkaloids, Clausine E and Clausine F**

D. P. Kamat, a S. G. Tilve\*<sup>a</sup> and V. P. Kamata

<sup>a</sup>Department Of Chemistry, Goa University, Taleigao Plateau, Goa 403 206, India

Email: [durga.kamat.25@gmail.com](mailto:durga.kamat.25@gmail.com)

1-oxygenated carbazole alkaloids of plant origin are of interest due to promising biological activities. Clausine E1 and Clausine F2 were isolated from the stem bark of *Clausena excavata*. Clausine E showed inhibition of rabbit platelet aggregation and vasoconstriction. Recently its growth inhibitory activity against several cancer cell lines has been proved. Clausine F also showed inhibition of platelet aggregation and possess antitumor properties. A rapid entry into clausine E was established through Wittig reaction between triphenyl-Î±-methoxycarbonylhomoskatolidene phosphorane and glyoxylic acid followed by annulation step. Further synthesis of clausine F was achieved from clausine E in two steps. The details of this synthesis would be presented.

References

1. Wu, T.-S.; Huang, S.-C.; Wu, P.-L.; Teng, C.-M. *Phytochemistry*, **1996**, 43, 133.
2. Wu, T.-S.; Huang, S.-C. *Chem. Pharm. Bull.*, **1992**, 40, 1069.

**(P382)**

**Novel Dihydropyrimidine Analogues for Calcuim Channel Blocking activity**

K. Sri Latha, B. Shireesha

Medicinal Chemistry Research Division, Vaagdevi College of Pharmacy, Warangal

Calcium channel blockers (CCBs) or Antagonists are the most widely used class of drugs in cardiovascular disorders (hypertension, tachyarrhythmia and angina pectoris). Dihydropyrimines (DHPMs) proven as versatile chemical moiety with diverse pharmacological activities. DHPMs are structurally similar to Dihydropyridines (DHPRs), the established CCBs for the treatment of cardiovascular diseases. Several DHPMs were reported for the CCB activity and patented (eg:

US7687511 B2). In present study, we designed and synthesized some novel Mannich bases of DHPMs (B1-B7) and tested for their calcium channel blocking activity against the standard Dihydropyridine i.e., Amlodipine. O-Mannich bases were prepared regioselectively from DHPMs by using catalytic amount of base. The CCB activity was determined on isolated rat ileum. All the compounds have shown promising results. The compound B6 (Amine substituted derivative) have shown equal potency with an IC<sub>50</sub> value of 50 Åµg/ml when compared to standard Amlodipine (IC<sub>50</sub> 51.1 Åµg/ml).

**(P383)**

**Novel Curcumin Hybrids for Alzheimer's disease Therapeutics**

A. Rajasekhar Reddy<sup>1</sup>, B. Ramya Sree<sup>1</sup>, M. Bhagavan Raju<sup>2</sup>,  
A. Shireesha<sup>1</sup>

<sup>1</sup>Medicinal Chemistry Research Division, Vaagdevi College of Pharmacy, Warangal, India

<sup>2</sup>Gland Institute of Pharmaceutical Sciences, Kothapet, Medak Dt.

Alzheimer's disease (AD) is a progressive deteriorating disease of insidious onset that affects higher mental functions, usually appearing in late life. The present therapeutics of AD is only symptomatic. Further research is focused on disease modifying treatments based on its pathophysiology, mostly involving specific proteins (A $\beta$  and tau), enzymes (secretases and kinases) and other targets like nicotinic ACh, N-Methyl-D-Aspartate, serotonin, histamine and adrenergic receptors. Tacrine is the first FDA approved cholinesterase inhibitor for the treatment of AD, but its usage is limited by its multiple dosing per a day and its hepatotoxic metabolite 7-hydroxy tacrine. On the other hand, Curcumin was proved for wide range of pharmacological activities, and recently it has been reported that it can combat with AD also with the activities of scavenging radicals, blocking A $\beta$  aggregation, acetyl cholinesterase inhibition and chelation of metal ions. In the present study, some new hybrid molecules of Curcumin analogues and Tacrine were designed with assumption that these can decrease the possibility of formation of toxic metabolite of Tacrine with improved efficacy and bioavailability. These two molecules were combined with modification at active methylene link between both keto groups of Curcumin analogues with tacrine (a potent acetyl cholinesterase inhibitor) and formaldehyde by Mannich reaction to get the final products. The toxicity of the molecules was predicted by in silico approach by OSIRIS Property Explorer and also MetaPrint 2D for the prediction of possible metabolites. The molecules were evaluated for acetyl cholinesterase inhibition, antioxidant activity, A $\beta$  aggregation inhibition and compared with curcumin as well as tacrine and data was statistically analyzed to verify the significance of the results. The results have shown that the hepatotoxicity and other toxic effects like mutagenicity, tumorigenicity of tacrine were also minimized by hybridization with improved pharmacological efficacy.

**(P384)**

**Iodine catalyzed one pot synthesis of flavones from substituted o-hydroxyacetophenones and aromatic aldehydes**

Mayuri Naik, Vijayendra Kamat and Santosh Tilve  
Goa University

The flavones (2-phenylchromones) are naturally occurring heterocyclic compounds belonging to the flavonoid group. These are widely distributed in vascular plants [1]. They exhibit wide range of biological activities which includes leishmanicidal activity, ovipositor stimulant phytoalexins,

anti-HIV, vasodilator, antiviral, antioxidants, bactericidal, DNA cleavage, anti-inflammatory, anti-mutagenic, anti-allergic and anticancer [2]. Some flavonoids inhibit the histamine release from human basophils and rat mast cells [3]. Moreover it is known that some flavonoids have a repelling property against some phytophagous insects and a subterranean termite (*Coptotermes* sp.) acting as antifeedant [4]. A new, general and alternate method for the one pot synthesis of medicinally important flavones is described. Number of report on the flavones synthesis frequently makes use of chalcones or flavanones which in turn are prepared from o-hydroxyacetophenone and aromatic aldehydes. Our method directly converts o-hydroxyacetophenone and aromatic aldehydes to the required flavones via tandem condensation-oxidative cyclization using catalytic amount of base and iodine in DMSO solvent. Various derivatives containing electron donating as well as electron withdrawing groups synthesized in good to excellent yields proves the generality of this method.

#### References:

1. Harborne, J. B.; Williams, C. A. *Nat. Prod. Rep.* **2001**, 18, 310-333.
2. Seijas, J. A.; Vazques-Tato, M. P.; Carballido-Reboredo, R. *J. Org. Chem.* **2005**, 70, 2855-2858.
3. Yano, S.; Tachibana, H.; Yamada, K. *J. Agric. Food Chem.* **2005**, 53, 1812-1817.
4. (a) Morimoto, M.; Tanimoto, K.; Nakano, S.; Ozaki, T.; Nakano, A.; Komai, K. *J. Agric. Food Chem.* **2003**, 51, 389-393 (b) Ohmura, W.; Doi, S.; Aoyama, M.; Ohara, S. *J. Wood Sci.* **2000**, 46, 149-153.

#### (P385)

##### **Synthesis of soluble fulleropyrrolidines**

A. R. Parveen, V. Sughanya and S. Nagarajan\*

Department of Chemistry, Annamalai University, Annamalainagar- 608002 \*Department of Chemistry, Central University of Tamil Nadu

As a representative member of the fullerene family, C<sub>60</sub> has attracted ever-increasing attention since its discovery, due to its versatile building block nature. It has been immensely used in biological studies, optoelectronic and molecular devices. The chemical functionalization of fullerene sphere produces a large number of different derivatives that combine the desirable properties of C<sub>60</sub> with the solubilizing power of the side chains. The specific 1,3-dipolar cycloaddition of azomethine ylides produces the fulleropyrrolidine, in which the carbon atoms in the pyrrolidine ring can be functionalized. In the present investigation a novel fulleropyrrolidines substituted with long alkyl chains has been synthesized by the reaction of C<sub>60</sub> with aromatic aldehyde and sarcosine in toluene. The synthesized novel compounds were characterized by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic techniques.

#### (P386)

##### **High Regioselectivity in the Diels-Alder Reactions of 9-Substituted Anthracenes with Citraconic Anhydride**

Ruhima Khan and Moirangthem Dhaneshwar Singh\*

Department of Chemistry, Manipur University, Canchipur-795003, Manipur, India

DA of non-symmetrical 1,3-diene with unsymmetrical dienophiles has tremendous interest to organic chemists due to regio- and stereochemistry involved in the reaction. The use of chiral 9-

substituted anthracenes in highly diastereoselective Diels-Alder cycloadditions with maleimide and related dienophiles are well established. DA reaction of 9-substituted anthracenes with unsymmetrical dienophiles results into the formation of two regioisomers- the ortho and the meta adducts. However in most cases the ortho adduct has been found to be the major product. High meta selectivity in the Diels-Alder reactions of 9-substituted anthracenes and 2-acetamidoacrylate has also been reported. Herein, we wish to report our studies on DA reaction of 9-substituted anthracenes with citraconic anhydride. The regioselectivity in the Diels-Alder reaction of 9-substituted anthracenes having electron releasing substituents with citraconic anhydride has been investigated. The ortho regioisomer is preferred in all the cases with good yield. The reaction proceeded best under conventional heating conditions in Toluene.

**(P387)**

**Base Mediated Tandem Knoevenagel and Selective Reduction of Steroidalketones: A novel Route to Allylic Alcohols**

Mandakini Dutta and Romesh C. Boruah

Medicinal Chemistry Division, CSIR-North-East Institute of Science & Technology, Jorhat, Assam 785006, India

Allylic alcohols are an important class of organic compounds as they are versatile building blocks for functionalised molecules and serve as synthetic intermediates in natural and non-natural product synthesis.<sup>1</sup> They are useful in many synthetic applications including Claisen rearrangements, related Sigmatropic processes, SN<sub>2</sub>/ displacements with cuprate, palladium-catalysed  $\pi$ -allyl chemistry and cationic cyclizations, enantio- and diastereoselective hydroxyl-directed additions to alkenes and many more.<sup>2</sup> Varieties of method are available for the synthesis of allylic alcohol.<sup>3</sup> Some of the most prominent methods for synthesizing chiral allylic alcohol are the selective reduction of  $\alpha,\beta$ -unsaturated carbonyl compounds, coupling of alkenyl halides and aldehydes and coupling of alkyne and carbonyl compounds. Name reactions such as Baylis-Hillman reaction and Prins reaction are also applicable for the synthesis of allylic alcohols. In continuation of our interest towards development of newer strategy for A-ring annelated steroidal allylic alcohol, we describe here a base mediated synthesis of steroidal allylic alcohol from 3-ketosteroid in absence of any catalyst. The reaction strategy involves Knoevenagel condensation of steroidal 3-ketosteroid with aromatic aldehyde followed by selective reduction of steroidal ketone in isopropanol solvent.

**(P388)**

**Copper (I) Iodide-Catalysed Aerobic Oxidative Synthesis of Imidazo[1,2-a]pyridines from 2-Aminopyridines and Methyl Ketones**

Darapaneni Chandra Mohan, Ramachandra Reddy Donthiri, Sadu Nageswara Rao and Subbarayappa Adimurthy

Academy of Scientific & Innovative Research, CSIR-Central Salt & Marine Chemicals Research Institute, G.B. Marg, Bhavnagar. Gujarat (INDIA)

The transition metal catalyzed direct C-N bond formation through C-H activation by the formal loss of H<sub>2</sub> or H<sub>2</sub>O would enhance the existing toolbox of synthetic methods to build complex nitrogen heterocycles. In particularly imidazo[1,2-a]pyridine (IP) scaffolds are found in numerous pharmacologically important compounds. Many commercially available drugs including alpidem, olprinone, minodronic acid (to treat anxiety, heart failure and osteoporosis),



Zolimidine (peptic ulcer), necopidem, saripidem (sedative and anxiolytic) and optically active GSK812397 candidate(HIV infection)are derived from imidazo[1,2-a]pyridine-core entities. In continuation of our studies on the synthesis of imidazo[1, 2-a]pyridines, We report operationally simple copper-catalyzed synthesis of imidazo [1,2-a]pyridines through C-H activation with oxidative linkage of two C-N bonds under very mild conditions using molecular oxygen as a sole oxidant. The process allows the quick assembly of imidazo[1,2-a]pyridines including a marketed antiulcer drug Zolimidine at gram scale (2.411 g) from inexpensive and readily available 2-aminopyridines and methyl ketones with broad range of functional group tolerance. The mechanistic studies indicate the essential role of CuI and O<sub>2</sub> for the present investigation.

**(P389)**

**Catalyst- and Solvent-free, Pot, Atom and Step Economic Synthesis of Tetrahydroquinazolines**

Rupam Sarmaa, Debajyoti Bhuyanb and Dipak Prajapati  
Department of Chemistry, Nalbari College, Nalbari, Assam, India

The concept of pot, atom and step economy (PASE), first conceived by Clarke and co-workers,<sup>1</sup> provides a new line of approach towards developing environmentally friendly synthetic technologies. The formulation of the PASE concept is based on the introduction of the idea of pot economy and combining it with the already known ideas of atom and step economy. An atom economic procedure takes into consideration the number of atoms of all the reagents that constitutes the desired product, thereby regulating the waste generated in terms of participating atoms.<sup>2</sup> On the other hand, a step economic procedure regulates the efficiency of a procedure by minimising the number of steps required to synthesize the target molecule.<sup>3</sup> A method is considered pot economic if successive reaction steps can be carried out in one reaction vessel without the requirement of workup and isolation of the intermediate species.<sup>4</sup> The beauty of the PASE concept is that it brings together divergent aspects of green chemistry within a single umbrella so that one can plan, execute and monitor organic synthesis in a way that leads to minimal waste generation. A pot, atom and step economic (PASE) synthesis of tetrahydroquinazolines has been achieved via microwave-promoted four-component catalyst- and solvent-free aza-Diels-Alder reaction strategy. The key step of the methodology is the in situ generation of both the diene and the dienophile and their subsequent reaction to give the desired product.

**(P390)**

**Novel 2-Aryl-3-arylamino-imidazo-pyridine/pyrazines as Potent Antitubulin, Anticancer, and Apoptotic Agents**

Garima Priyadarshani, Sankar K. Guchhait\*

National Institute of Pharmaceutical Education and Research (NIPER) S. A. S. Nagar (Mohali), Punjab (India)

Inspired by the pharmacophoric features of natural product antitubulin combretastatin A-4 (CA-4) and their synthetic analogs,<sup>1</sup> a series of novel 2-aryl-3-arylamino-imidazo-pyridine/pyrazines were designed as potential antitubulin anticancer agents. They can be synthetically accessed by one-pot reaction of isocyanides prepared from the anilines via formylation and subsequent dehydration, and their multicomponent reactions with heterocyclic-2-amidines and aldehydes which allowed substitutional variation at 3-position.<sup>2</sup> Four compounds possessed similar tubulin

polymerization inhibitory activity to that of CA-4, potent anticancer activities in kidney, breast and colon cancer cell lines, and relatively low toxicity to corresponding normal cells. They also exhibited relatively higher anticancer activities than 5-fluorouracil. They have shown to cause apoptosis, and DNA and chromosomal damage inducing cell-arrest in the G2/M phase of cell cycle in HEK 293T. The molecular docking and molecular dynamics (MD) simulation studies revealed that these compounds occupied the colchicine binding site at the  $\hat{I}\pm, \hat{I}^2$ -tubulin heterodimer interface similar to that of CA-4, and stabilized the complex by forming multiple interactions with the key residues of the protein.

**(P391)**

**L-Proline: an Efficient Catalyst for Transamidation of Carboxamides with Amines**

Sadu Nageswara Rao, Darapaneni Chandra Mohan and Subbarayappa Adimurthy  
Academy of Scientific & Innovative Research, CSIR-Central Salt & Marine Chemicals Research  
Institute, G.B. Marg, Bhavnagar-364 002. Gujarat (INDIA)

The amide bond is one of the most important linkages in nature due to its presence in peptides and protein structures and has been well recognized in chemistry and biology. These amide bonds are usually prepared by the reactions of amines with carboxylic acid derivatives (alcohols, aldehydes, esters, chlorides and anhydrides). Alternatively, transamidation is an attractive tool and represents one of the most convenient and straightforward methods, that would exchange the constituents of two different amide groups. In the view of importance, we have developed a novel L-Proline Catalyzed transamidation process that can be selectively transaminated in an efficient manner. Compared to previously known transamidation catalysts, L-Proline is inexpensive, is readily available, and can be used conveniently. This strategy applicable for a wide range of benzylic, aromatic, aliphatic, propargylic, and heteroaromatic amines can be effectively used to produce corresponding transamidation products in good to excellent yields.

**(P392)**

**Palladium Catalyzed Base Free, Ligand Free Suzuki Cross Coupling Reactions in Ionic Liquids**

Diganta Sarma\* and Preeti Rekha Boruah  
Department of Chemistry, Dibrugarh University, Dibrugarh-786004, Assam, India

Suzuki reaction is a palladium-catalyzed cross coupling between organoboronic acid and halides or triflates. It is one of the important methods for the construction of biaryls. The coupling involves a base and a ligand. The Suzuki coupling reactions are generally carried out in THF and diethylether in presence of Pd(II) or Pd(0) catalysts which are soluble in these solvents. One of the important features of Suzuki coupling is that the boronic acid must be activated, e.g. with a base. Traditional bases such as KOH, NaOH,  $K_2CO_3$ ,  $NaHCO_3$ , NaOAc, triethylamine or tetrabutyl ammonium acetate are generally used in Suzuki couplings. This activation of boron atom enhances the polarization of the organic ligand, and facilitates transmetalation. In view of the fact that organic solvents are highly volatile and environmental hazardous, there is a greater need to replace them by environmental benign solvents. In this work, Suzuki couplings have been successfully carried out in basic ionic liquids in a base free and ligand free environment.

References:

1. Welton, T. Chem. Rev. **1999**, 99, 2071.

- 2.Kumar, A. Chem. Rev. **2001**, 101, 1.  
3.Kotha, S.; Lahiri, K.; Kashinath, D. Tetrahedron, **2002**, 58, 9633.  
4.Prechtl, M. H. G.; Scholten, J. D.; Dupont, J. Molecules, **2010**, 15, 3441.

**(P393)**

**An expedient domino [3+2] cycloaddition/intramolecular annulation reaction for the synthesis of novel hexacyclic fused systems**

Akilan Malathi and Raju Ranjith Kumar  
Madurai Kamaraj University

A series of novel hexacyclic fused system viz. 14a-hydroxy-12-methyl-10-(4-aryl)-8,9,9a,10,12,13,14,14a-octahydro-5H-10a,14-methanoindeno[2',1':4,5]azepino[3,4-b]pyrrolizine-5,15(7H,11H)-diones were synthesized through the one-pot three-component reactions of (E)-3-arylidene-1-methylpiperidin-4-ones, ninhydrin and proline. This reaction presumably occurs via domino 1,3-dipolar cycloaddition of azomethine ylide generated in situ from the reaction of ninhydrin and proline to (E)-3-arylidene-1-methylpiperidin-4-one followed by intramolecular annulation. The structure of these structurally intriguing hexacyclic compounds was elucidated unambiguously with the help of two-dimensional NMR spectroscopy and single crystal X-ray diffraction studies.

**(P394)**

**A Facile Atom Economic Synthesis of Novel Chromenopyridines**

Remani Vasudevan Sumesh, Akilan Malathi, Raju Ranjith Kumar  
Madurai Kamaraj University

The reaction of 3,5-diarylidene-1-methylpiperidin-4-ones with 1,3-cyclohexanedione, 2-hydroxy-1,4-naphthoquinone, 4-hydroxycoumarin or 4-hydroxy-1-methyl-2(H)-quinoline in acetic acid or ethanol/TEA under reflux conditions afforded novel chromeno[3,2-c]pyridin-9(2H)-ones, benzo[6,7]chromeno[3,2-c]pyridine-6,11(2H,12H)-diones, chromeno[3',4':5,6]pyrano[3,2-c]pyridin-6(7H)-ones or pyrido[3',4':5,6]pyrano[3,2-c]quinolin-6(7H)-ones respectively. These reactions proceed through an initial Michael addition followed by annulation to afford the product in excellent yields. The significance of these reactions includes readily available starting materials, simple procedure and no column chromatographic purification is necessary. Further, the atom economy of these reactions is very high since water is the only by-product of these reactions. The structure of all these novel heterocycles were elucidate with the help of one and two dimensional spectroscopic techniques.

**(P395)**

**Design, Synthesis and Cytotoxic Evaluation of 2-Imino-4-Thiazolidinone Derivatives**

Ravindra M Kumbhare<sup>1</sup>, Umesh B Kosurkar<sup>1</sup>, R. Pamanji<sup>2</sup>, J. Venkateswara Rao<sup>2</sup>, Sridhara Janardhan<sup>3</sup> and G. Narahari Sastry<sup>3</sup>  
Fluoroorganic<sup>1</sup>, Biology<sup>2</sup>, Molecular modeling<sup>3</sup> division  
CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad

The Thiazolidin-4-one ring system is a core structure in various synthetic pharmaceutical compounds, displaying a broad spectrum of biological activities. The biological activities of 2-imino-4-thiazolidinone derivatives (n=19) were evaluated to investigate their anti-proliferative/cytotoxic activities in four different types of human cancer cell lines. Most of the derivatives exhibited cytotoxic properties against all the cell lines in a concentration-dependent manner and exhibited activity less than 100 µg/ml concentration. It is apparent from the results that these 2-imino-4-thiazolidinone derivatives are found to be more potent on leukemia cell lines than the colon and melanocarcinoma cell lines.

#### References

1. Zhang, X.; Li, X.; Li, D.; Qu, G.; Wang, J.; Loiseau, P. M.; X. Fan, *Bioorg. Med. Chem. Lett.* **2009**, 19, 6280-6283.
2. El- GabyMohamed, S. A.; El- Hag Ali Gameel, A.M.; El-MaghrabyAhmed, A.; Abd El-Rahman Mohamed, T.; Helal Mohamed, H. M. *Eur. J. Med. Chem.* **2009**, 44, 4148-4152.
3. Hafez, H. N.; El-Gazzar Abdel-Rahman, B. A. *Bioorg. Med. Chem. Lett.* **2009**, 19, 4143-4147.
4. Shih, M. H.; Ying-Ke, F. *Bioorg. Med. Chem. Lett.* **2004**, 12, 4633-4643.

#### (P396)

##### **A “Turn-On” Type Chemodosimeter for Selective Detection of Aromatic Thiols**

Diprati G. Khandare, Mainak Banerjee and Amrita Chatterjee

Department of chemistry, Birla Institute of Technology and Science - K. K. Birla Goa Campus, NH-17B Bypass Road, Zuarinagar, Goa

Thiophenols having a broad synthetic utility as insecticides, pesticides, pharmaceuticals, they belong to a class of highly toxic and pollutant compounds. Because of the high toxicity of the widely existent benzenethiols and their ease of entrance into the human body by inhalation and skin absorption exacerbating grave systemic and central nervous injuries like burning sensation in throat, eyes and nose, laryngitis, shortness of breath, coma and even death etc. So the development of a probe molecule is worthy. Most of the optical probes developed could not able to distinguish between aromatic and aliphatic thiols. So in the present work we have designed and synthesized a “turn-on” type probe having a 2-(2-hydroxyphenyl)benzothiazole ring and a dinitrophenyl moiety which by aromatic nucleophilic substitution (S<sub>N</sub>Ar) at physiological condition can detect selectively thiophenols. All the fluorimetric studies were carried out in 45% DMF:PBS (pH = 7.0) buffer. The probe selectively responds to aromatic thiols only over other aliphatic thiols, with a turn-on type fluorogenic change from colorless to yellowish green with the formation of substituted benzothiazole which is strongly fluorescent. The probe is highly selective, cost effective and show detection limit of 3 ppb.

#### (P397)

##### **Synthesis of Tetrahydrobenzo[b]pyrans by using Ionic liquids in hydro-alcohol media.**

<sup>1</sup>Vijaya bhaskar.K, <sup>2</sup>Srinivasan.K.K.

<sup>1</sup>Manipal College of Pharmaceutical Sciences, Manipal University, Manipal

<sup>2</sup>Sri MadhwaVadiraja Institute of Technology and Management, Bantakal

One-pot synthesis of tetrahydrobenzo[b]pyrans by condensing aromatic aldehyde, malononitrile and 1,3-cyclohexanedione by using ionic liquid, 1-butyl, 3-methyl imidazolium

chloride([bmIm]Cl-) in hydroalcohol media. The addition of alcohol and water in the ratio of 1:2 keeps all the reactants in solution. This facilitates the reaction and makes the product formation very easy. The reaction is carried out at room temperature by stirring for short time ranging from 30 minutes to 120 minutes depends on the type of aromatic aldehyde used. This method has many advantages like, short reaction time, high yields and reuse of catalyst and avoiding the usage of hazardous chemicals. The compounds were characterized by using IR, NMR & Mass data.

**(P398)**

**Enantioselective Ring Opening Reaction of Epoxides with Anilines Catalyzed by Organo-catalyst**

Manish Kumar, Rukhsana I. Kureshy\*, Noor-ul H. Khan, Sayed H. R. Abdi, and Hari C. Bajaj  
Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI), Council of Scientific and Industrial Research (CSIR)

Chiral  $\hat{I}^2$ -amino alcohols are valuable intermediate for many biologically active compounds and play a very crucial role in asymmetric catalysis. Various efficient methods to achieve chiral syn- $\hat{I}^2$ -amino alcohols have been reported that include amino-hydroxylation of olefins, addition of  $\hat{I}^2$ -hydroxy ketones to imines and asymmetric ring opening (ARO)/aminolytic kinetic resolution (AKR) of meso/racemic terminal, trans epoxides with alkyl/aryl amines using different chiral metal catalysts. But in the metal catalyzed ring opening reaction, the contamination of metal in the product is always a challenge; therefore chiral organocatalyst is one of the efficient way to resolve the problem. Chiral organo-catalysts derived from the combination of chiral (S)  $\hat{I}^{\pm}$ -methyl benzylamine and chiral (S) ter-butylsulphinamide were prepared and characterized by various spectroscopic methods. These organo-catalysts were used for the first time in enantioselective ring opening reaction of various epoxides viz. meso-stilbene oxide, cyclohexene oxide, cyclopentene oxide, and cis-butene oxide, terminal epoxides with anilines as nucleophiles. Among both the catalysts screened in ARO of meso epoxides, 20 mol% of the catalyst with (S,S) configuration gave syn-beta-amino alcohols of the meso stilbene oxide with excellent enantioselectivity (up to 97%) and also with quantitative yield (up to 92%).

**(P399)**

**Synthesis and anticancer evolution of 3, 6-diphenylimidazo [2,1-b] thiazoles**

Satish Koppireddi, Sagana Sripriya, Sreenivas Avula, Komsani Jayaram Reddy, RambabuYadla\*  
Fluoroorganics division, CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad-500 607, India.  
E-mail: ryadla@yahoo.com

Cancer is one of the major cause for increasing mortality rate in many of developed and under developed countries in the world. In spite of tremendous progress in chemotherapy there has been substantial development in recent years in the number of new anticancer agents, with the emphasis on creating new DNA interactive drugs [1]. A major hitch of these compounds in clinical application is the development of drug resistance through the expression of efflux pumps, including P-glycoprotein (P-gp) and multi-drug resistance associated protein MRP [2]. So there is a challenge and need to develop newer anticancer agents which will be effective to treat MDR tumors and will have lesser side effect on other functional organs. A class of heterocyclic compounds is thiazoles having prominent role in medicinal chemistry. Thiazole

skeleton is pharmacophore unit found in many potent biologically active molecules such as Sulfathiazol (antimicrobial drug), Bleomycine and Tiazofurin (antineoplastic drug). Imidazo[2,1-b]thiazole derivatives exhibited good anti proliferative activities against a variety of human cancer cell lines [3]. In addition, the imidazo[2,1-b]thiazole derivatives of Levamisole have been reported as potential antitumor agents [4]. The above background prompted us to develop a series of novel 3, 6 -diphenylimidazo [2,1-b] thiazoles synthesized and evaluated for their anticancer activity. Some of the synthesized compounds have exhibited very good activity against and HELA, MDA-MB-231, A549, THP1 and DU-145 cell lines.

#### References:

1. Demeunynck, M.; Bailly, C.; Wilson, W.D. Wiley-VCH, Weinheim, Germany, 2002.
2. M. Lehnert, Eur. J. Cancer **32A (1996)** 912-920.
3. Andreani, A.; Leoni, A.; Locatelli, A.; Morigi, R.; Rambaldi, M.; Recanatini, M. Garaliene, V. Bioorg. Med. Chem. **8 (2000)** 2359-2366.
4. Andreani, A.; Bonazzi, D.; Rambaldi, M. Arch. Pharm. **315 (1982)** 451-456.

#### (P400)

##### **A One pot stereoselective synthesis of imidazo[2,1-b]thiazoles and benzo[d]thiazolo[3,2-a]imidazoles**

Tariq A. Shah, Niyaz A. Mir, Sarfaraz Ahmad, M. Muneer,\* Nigam P. Rath  
Department of Chemistry, Aligarh Muslim University, Aligarh -202002, India

Nucleophilic addition on dibenzoyl acetylene has been reported in a number of studies earlier. In the present study imidazo[2,1-b]thiazole and benzo[d]thiazolo[3,2-a]imidazole 3a-e analogues were synthesized stereoselectively using dibenzoylacetylene 1 and thiazole/benzothiazole 2a-e derivatives. The procedure was applied to a series of substrates to examine the extension and limitation of the methodology. The short reaction time, good yield, negligible by-product, fairly mild conditions and simple workup in this approach can be applied in the synthesis of biological and pharmaceutical molecules with imidazo[2,1-b]thiazole and benzo[d]thiazolo[3,2-a]imidazole skeleton. The structure of the products was characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass spectrometry and X-ray crystallography.

#### (P401)

##### **An Efficient Synthesis of Imidazo[1,2-a]pyridines via Copper Catalyzed Tandem C-N/C-C Bond Formation Reactions**

Pinku Kaswan, Kasiviswanadharaju Pericherla and Anil Kumar  
Department of Chemistry, Birla Institute of Technology & Science, Pilani 333 031, Rajasthan

Imidazo[1,2-a]pyridine, a bicyclic N-fused imidazole, is an important molecule present in several pharmacologically relevant structures, and have shown many biological activities such as anti-bacterial, anti-ulcer, anti-viral and anti-inflammatory.<sup>1</sup> Zolpidem, alpidem zolimidine and saripidem are some important drug molecules which contain imidazo[1,2-a]pyridine skeleton. In general, these privileged scaffolds have been synthesized by the reaction of 2-aminopyridines and  $\alpha$ -haloketones which are highly lachrymatory and toxic.<sup>2</sup> Lei et al. reported a simple and efficient method for the synthesis of imidazo[1,2-a]pyridines via oxidative coupling of 2-aminopyridines and alkynes in presence of Ag<sub>2</sub>CO<sub>3</sub>.<sup>3</sup> In continuation of our interest in synthesis of imidazo[1,2-a]pyridine derivatives,<sup>4,5</sup> we have developed a tandem approach for the synthesis

of imidazo[1,2-a]pyridines from simple and readily available acetophenones and 2-aminopyridines using inexpensive CuI as catalyst. The details of protocol will be presented.

References:

1. Montzka, T. A.; Starrett, J. E.; Crosswell, A. R. and Cavanagh, R. L. *J. Med. Chem.*, **1989**, 32, 2204-2210.
2. Paudler, W. W. and Kuder, J. E. *J. Org. Chem.*, **1966**, 31, 809-813.
3. He, C.; Hao, J.; Xu, H.; Mo, Y.; Liu, H.; Han, J. and Lei, A. *Chem. Commun.*, **2012**, 48, 11073-11075.
4. Pericherla, K.; Khedar, P.; Khungar, B. and Kumar, A. *Chem. Commun.*, **2013**, 49, 2924-2926.
5. Pericherla, K.; Khungar, B. and Kumar, A. *Tetrahedron Lett.*, **2012**, 53, 1253-1257.

**(P402)**

**Fe(III) complex of phenyl substituted biuret-amide based macrocyclic ligand as peroxidase enzyme mimic : Kinetic and mechanistic studies**

Santanu Pattanayak, Sayam Sen Gupta\*

National Chemical Lab. Pune

We have reported the synthesis and characterization of Fe(III) complex of a biuret-amide macrocyclic ligand (1) which showed excellent peroxidase activity, huge acid stability and has very low intramolecular deactivation rate in aqueous media. In another approach, we have been able to generate a high valent FeV=O reactive intermediate from 1 in organic media (Acetonitrile) and used for oxidation of unactivated C-H bonds (cyclohexane) at room temperature. However to check the electronics effect in the tail part of the biuret moiety, we introduced N-phenyl moiety in the parent biuret-amide macrocycle ligand instead of N-Me moiety and synthesized  $(Et_4N)_2[FeIII(Cl)(N\text{-phenyl-biuret-amide})]$  (2) successfully. Single crystal XRD data suggested that the incorporated phenyl group in complex (2) is perpendicular with respect to macrocycle plane. Detailed acid stability, inactivation parameter measurement and peroxidase activity of 2 is going on in our laboratory to decide whether substituted phenyl group has innocent or noninnocent character towards electron transfer in course of the reaction. In acetonitrile medium 2 reacts with mCPBA (1:1) at room temperature gives FeV=O species that was already characterized by EPR, HR-MS. This FeV=O species can able to do hydroxylation of unactivated C-H bond like cyclohexane. Suitable findings like electronics and steric around metal center would provide a great deal in synthetic organic transformation.

**(P403)**

**An efficient Domino Approach to Some Polyheterocycles Bearing a New Thiochromenoquinoline Molecular Framework**

Narsidas J. Parmari<sup>a</sup>, Balvantsingh M. Labana<sup>a</sup>, Rajni Kant<sup>b</sup>, Vivek K. Gupta<sup>b</sup>

<sup>a</sup>Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar. Dist. Anand, Gujarat, India <sup>b</sup>Post-Graduate Department of Physics, University of Jammu, Jammu Tawi, India

A series of some 18 polyheterocycles bearing a new thiochromenoquinoline molecular framework has been synthesized by combining 2-alkenyl-thiopyranoquinoline-3-carbaldehydes, which were derived from 2-mercaptoquinoline-3-carbaldehyde and citral, efficiently with heterocyclic mono/diketones in the presence of tetrabutylammonium hydrogen sulfate under

solvent-free conditions. The application of domino/Knoevenagel-hetero-Diels-Alder strategy tested for the first time on typically designed quinoline-based aldehyde substrates had been successful to achieve thiopyran biomolecules of pharmaceutical interest. The reaction proceeded through a highly diastereoselective mode that had covered even carbocyclic diketones as active methylene units against all these aldehydes to yield desired products. The stereochemistry of the products was confirmed by the single crystal X-ray diffraction and 2D NMR-NOESY data.

**(P404)**

**Asymmetric Synthesis of Drug-like spiro [chroman-3,3'-indolin]-2'-ones through amination-catalysis**

Dhevalapally B. Ramachary,<sup>a\*</sup> M. Shiva Prasad,<sup>ab</sup> S. Vijaya Laxmi<sup>a</sup> and R. Madhavachary<sup>a</sup>  
<sup>a</sup> School of Chemistry, University of Hyderabad, Hyderabad. <sup>b</sup>Department of Chemistry, School of Basic and Applied Sciences, Central University of Tamil Nadu, Thiruvavur

Asymmetric synthesis of drug-like functionalized spiro[chroman-3,3'-indolin]-2'-ones 5 containing three contiguous stereocenters with high diastereo and enantioselectivities was achieved by using reflexive-Michael (r-M) reaction of unmodified hydroxyenals 1 with various (E)-3-alkylideneindolin-2-ones 2 in the presence of (R)-DPPOTMS/AcOH (R)-3/4b as catalyst at the room temperature. Chiral spiro[chroman-3,3'-indolin]-2'-ones 5 were transformed into the functionalized spiranes in good yields with high selectivity through Wittig, TCRA, acetal protection and reduction reactions, respectively. Supporting evidence for the reaction pathway through the formation of the important catalytic species of "aminals" were observed through NMR and ESI-HRMS analysis of an on-going reaction between 1 and (R)-3 in CDCl<sub>3</sub> and also shown by the structural requirement in hydroxyenals 1 to generate the "aminals" with (R)-3 through controlled experiments.

**(P405)**

**Enantioselective Reactions via Dual Activation using Hydrogen Bonding Organocatalysts**

Vinod K Singh  
IISER Bhopal

Nature is the source of diverse range of chiral molecules which have been used as organocatalysts for a variety of asymmetric transformations. Similar to amino acid and carbohydrate-based small molecule catalysts, cinchona alkaloids have also been widely exploited as organocatalysts in their native and modified forms. They possess unique molecular recognition ability due to presence of C-9 hydroxyl group and tertiary nitrogen present in the quinuclidine moiety, which together carry out organocatalysis through simultaneous activation (dual activation) of two reacting species. Interestingly, both the enantiomers of the chiral product could easily be accessed due to occurrence of these alkaloids in pseudoenantiomeric forms.

A number of reports from the group of Cannon, Jacobsen, Wang, Takemoto, Hiemstra and many others illustrating the use of cinchona alkaloid based thio(urea) catalysts in various stereoselective transformations clearly dictates the versatility of these catalysts and thus calls for further exploration. In this direction, our group has also successfully carried out several enantioselective organocatalytic transformations using these catalysts which will be discussed in this lecture.



**(P406)**

**Microwave assisted highly regio- and stereo- selective synthesis of [a]-annelated pyrazolo pyrroloindoles via insitu generated azomethine imine intramolecular 1,3 dipolar cycloaddition**

D.S. Sharada\*, Anand H. Shinde and S. Vidyacharan

Department of Chemistry, Indian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram, Andhra Pradesh, India.

The synthesis of [a]-annelated pyrazolo pyrroloindoles via intramolecular cycloaddition of insitu generated azomethine imine from N-allylated indole-2-carboxylaldehyde by using microwave irradiation has been described. [a]-Annelated indoles are unique structural features present in a wide range of heterocyclic compounds that play important roles in medicinal chemistry and organic synthesis. Among [a]-annelated systems, the pyrrolo[1,2-a]-indole scaffold is a primary target for synthetic chemists due to its structural diversity. After study in the field, we envisaged N-allylated indole-2-carboxylaldehyde can be exploited in order to access the mentioned tetracyclic framework and which in turn can be prepared from (Z)-methyl 2-(bromomethyl)-3-phenylacrylate by successive allylation and formylation reactions with 3-methyl indole. Initially, reaction of (Z)-methyl 2-(bromomethyl)-3-phenylacrylate with 3-methylindole gave N-allylated indole intermediate and further formylation using Vilsmeier-Haack conditions lead to the corresponding aldehyde in excellent yield (95%). Finally, the reaction of the N-allylated indole-2-carboxylaldehyde with phenyl hydrazine in ethanol by microwave irradiation successfully provided the desired tetracyclic [a]-annelated pyrazolo pyrroloindoles in good yield. We have synthesized variety of tetracyclic angularly fused [a]-annelated pyrazolo pyrroloindoles. The methodology has been carried out in one pot starting from 3-methyl indole and synthesized variety of [a]-annelated pyrazolo pyrroloindoles. Highly stereoselective nature of the reaction was clearly evidenced by <sup>1</sup>H NMR spectroscopy and X-ray crystal analyses.

**(P407)**

**A Green and Facile protocol for the Synthesis of 3-Aminoimidazo-Fused Heterocycles via Groebke-Blackburn-Bienayme Reaction Under Catalyst-Free and Solvent-Free Conditions**

Shinde Vidyacharan, Anand H. Shinde, Bishnupada Satpathi, and Duddu S. Sharada\*  
Indian Institute of Technology, Hyderabad

Multicomponent reactions (MCRs) comply with the principles of green chemistry and as a consequence of which, they have emerged as a significant tool in organic synthesis.<sup>1</sup> One of the strategies widely implemented is in developing alternative sustainable routes, among which catalyst-free and solvent-free reactions (CFR & SFR)<sup>2</sup> have gained importance recently. These approaches have several advantages over the conventional organic synthetic methods.

Imidazo-fused heterocycles are becoming more important in medicinal and organic chemistry, as they exhibit a broad spectrum of pharmacological and biological activities, such as antiviral, antibacterial, fungicidal, and anti-inflammatory properties.<sup>3</sup> In continuation of our interest in developing novel heterocyclic compounds via MCRs, herein, we report a novel and facile method for the synthesis of imidazo-fused heterocycles under catalyst-free and solvent-free conditions. It is a one-pot, catalyst, solvent, workup and column free synthesis of 3-aminoimidazo-fused heterocycles by three-component reaction of 2-aminoheterocycle, aldehyde, and isocyanide. This efficient and green protocol has several advantages.

Here we extended our protocol to synthesize wide variety of nitrogen and sulfur containing heterocycles by changing amine, aldehyde and isocyanide components. Our strategy resulted in some interesting and privileged heterocycles, having ring junction carbon attached to three heteroatoms. The important features of this procedure are mild conditions, high yield, operational simplicity, atom economy and environmental friendliness. Thus, this CFR & SFR methodology should prove useful for facile synthesis of such scaffolds on industrial scale.

References:

- 1 (a) Gu, Y. *Green. Chem.* **2012**, 14, 2091; (b) Ramachary, D. B.; Sangeeta, J. *Org. Biomol. Chem.*, **2011**, 9, 1277; (c) Jiang, Tu, S.-J.; Kaur, P.; Wever, W.; Li, G.-G. *J. Am. Chem. Soc.*, **2009**, 131, 11660; (d) Gawande, M.B.; Vasco, Bonifacio, D.B.; Luque, R.; Branco, P. S.; Varma, R. S. *ChemSusChem.*, **2013**, DOI.10.1002/cssc.201300485d;
- 2 (a) Martins, M. A. P.; Frizzo, C. P.; Moreira, D. N.; Buriol, L.; Machado, P. *Chem. Rev.*, **2009**, 109, 4140; (b) A. Kumar

**(P408)**

**Studies Directed towards Total Synthesis of 12-membered Macrolide Balticolid**

Sumit Saha, Rakesh Goud Battini, Ranajit Das

National Institute of Technology Sikkim

The Macrolides are a group of compound whose activity originates mainly from presence of large macrocyclic lactone ring. Recently several Macrolides have been isolated with different ring size and significant biological activity. Their biological activity and densely functionalized structural attracts the considerable attention of synthetic Organic Chemist. Cladospolide, Pandangolides are such kind of macrolide isolated from different marine sp and several reported synthesis in literature also imply necessity of development in this area. Balticolid, very recently isolated 12-membered macrolide from Ascomycetous Species, having considerable Antiviral activity<sup>2</sup>. We are interested in developing simple and general strategy for the synthesis of 12-membered macrolide considering Balticolid as synthetic target.

Synthesis was initiated with D Mannitol derived easily accessible optically active (R)-2,3-O-cyclohexylidene glycerinaldehyde which have great similarity in Chirality with target and molecule. The synthesis of an allyl alcohol, the common intermediate which will lead to three different fragment was performed using Chiral aldehyde. Combining the three fragment through some classical transformation may produce Balticolid.

References:

1. Krishna, P. R.; Prabhakar, S.; Ramana, D. V. *Tetrahedron Lett.* **2012**, 53, 6843
2. Shushni, M. A. M.; Singh, R.; Mentel, R.; Lindequist, U. *Mar. Drugs* **2011**, 9, 844.
3. Bonini, C.; Chiumminto, L.; Pullez, M.; Solladoe, G.; Colobert, F. *J. Org. Chem.*, **2004**, 69, 5015.

**(P409)**

**Design, synthesis, biological evaluation of some novel thiadiazole derivatives**

Sunil Makwane, S. D. Srivastava, S.K. Srivastava

Synthetic Organic Chemistry Laboratory, Department of Chemistry, Dr. Harisingh Gour University, Sagar (M.P.) 470003 India

Cyclization reactions are of increasing importance in the field of medicinal chemistry. Cyclization reactions can provide products with the diversity needed for the discovery of novel N and S containing heterocycles. Since, these compounds exhibited a variety of biodynamic activities such as antibacterial, antitubercular, anti-inflammatory, fungicidal, anticonvulsant. Herein we report synthesis and antimicrobial evaluation of some novel Thiadiazoles derivatives. Compounds were characterized by different spectral techniques like FT-IR, NMR and HRMS.

**(P410)**

**CuFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles: A simple and efficient catalyst for the synthesis of medicinally privileged pyrimidine derivatives**

Sonam Sharma, Anshu Dandia

In recent years, magnetic nanoparticles have emerged as a valuable assembly of heterogeneous catalysts in modern synthetic chemistry due to their high surface-to-volume ratios and unique electronic and surface properties. The separation of magnetic nanoparticles is simple, economical, and an attractive alternative to filtration or centrifugation as it prevents loss of catalyst and enhances reusability, making the catalyst cost-effective and promising for industrial applications.

The hexahydropyrimidine skeleton is present in a number of alkaloids, eudistomidines H and I, tetraoponerines, verbametrine and verbamethine. Hexetidine is a formaldehyde-releasing antimicrobial agent employed in mouthwashes and numerous products of veterinary and human drugs. Different N-substituted hexahydropyrimidines are synthetic intermediates for spermidine-nitroimidazole drugs for the treatment of A549 lung carcinoma. They form structural units in trypanothione reductase inhibiting ligands for the regulation of oxidative stress in parasite cells. Due to their significant biological activity and unique structural characteristics make them appealing candidate for effective and highly efficient synthesis.

In this regards<sup>1</sup>, we have developed a highly efficient, recyclable and magnetically recoverable CuFe<sub>2</sub>O<sub>4</sub> nanoparticles as a heterogeneous catalyst for the synthesis of highly substituted hexahydropyrimidines via three-component reaction of formaldehyde, aromatic amines and cyclic ketones in aqueous ethanol under mild reaction conditions(Fig-1). In this scenario, the magnetically separable heterogeneous catalyst tends to be a very appealing technique to furnish better handling properties and often possesses activities comparable to those of homogeneous and simple nanoparticles. The detailed synthetic strategy of these compounds will be presented in the conferences.

References:

1. (a) Dandia, A.; Parewa, V.; Jain, A. K.; Rathore, K. S. *Green Chem.* **2011**, 13, 2135. (b) Dandia, A.; Jain, A. K.; Laxkar, A. K. *RSC Adv.*, **2013**, 3, 8422. (c) Dandia, A.; Parewa, V.; Rathore, K. S. *Catal. Commun.* **2012**, 28, 90. (d) Dandia, A.; Parewa, V.; Gupta, S. L.; Rathore, K. S. *J. Mol. Catal A: Chem.* **2013**, 61, 373. (e) Dandia, A.; Jain, A. K. *J. Heterocyclic Chem.* **2013**, 50, 104.

**(P411)**

**Art of the diversity-oriented transformation for construction of spiro heterocycles: Stereochemical aspect of green chemical synthesis**

Dr. Anshu Dandia

Centre of Advanced Studies, Department of Chemistry, University of Rajasthan, Jaipur, India.

Exploration of nanotechnology as a doubly green dream is the major goal of present research as it offers the opportunity to make products and processes green from the beginning with their potent catalytic activity, possible processability, easy preparation, high stability, ease of recyclability. Besides, the intense interest in the development of spirooxindole system and related compounds as potential medicinal agents or biological probes, variety of novel spirooxindole derivatives were successfully synthesized via multi component 1, 3- dipolar cycloaddition, Mannich-type reactions and Knoevenagel condensations with interesting chemo, regio and stereo-chemical outcomes (Fig. 1). Greenness of the process was well instituted as water was exploited both as reaction media as well as medium for synthesis of catalyst. Overall, we intended to modify the laborious process of lead discovery by accumulating green methodologies in combination with aqueous media and nanocatalysts for the synthesis of a variety of novel spiro heterocycles which may prove to be biologically very vital.

References:

Anshu Dandia et al. RSC Adv. **2013**, 3, 8422-8430. J. Mol. Catal A: Chem. **2013**, 373, 61-71. Tetrahedron. **2013**, 69, 2062-2069. Cata. Commun. **2012**, 28, 90-94. Tetrahedron Lett. **2012**, 53, 3012-3017. Green Chem. **2011**, 13, 1852-1859. Ultrason. Sonochem. **2011**, 18, 1113-1117.

**(P412)**

**Michael addition of nitroalkane to nitroolefin in aqueous medium at neutral pH**

Porag Bora, and Ghanashyam bez\*

Department of Chemistry, North Eastern Hill University, Shillong

1,3-Dinitro compounds are versatile intermediates for a variety of 1,3-difunctionalized molecules, heterocycles, carbohydrate derivatives and potentially active energetic material<sup>1</sup>. Further, the nitro group can be converted into a variety of other functional groups like the carbonyl, the amino, the hydroxylamino, or the azo group.<sup>2</sup> The 1,3-dinitro compounds can be obtained by Michael addition of nitroalkanes to nitroolefins. Though, nitroolefins are widely used as Michael acceptors for the C-C bond formation reactions, because of its high reactivity it is difficult to control the addition of nitronate anion to nitroolefins and generates a mixture of oligomerized product.<sup>3</sup> Water plays an important role in biological processes, so it is considered to be helpful in understanding a chemical reaction in biological processes. In continuation to our interest<sup>4</sup> in the development of green synthetic protocols we have developed an efficient method for Michael addition of nitroalkane to nitroolefin in aqueous medium at neutral pH . The reaction affords very good yield and shows good to moderate distereoselectivity of 1,3-dinitro compounds.

References:

1. Ballini, R.; Palmieri, A.; Righi, P. Tetrahedron. **2007**, 63, 12099-12121.  
2. Zenz, I.; Mayr, H. J. Org. Chem. **2011**, 76, 9370-9378.  
3. Rabalakos, C.; Wulff, W. D. Synlett. **2008**, 18, 2826-2830.  
4. Bora, P. P.; Bez, G. Eur. J. Org. Chem. **2013**, 2922-2929.

(P413)

**1,3-Dipolar Cycloadditions of Diazosulfones with Electron Deficient Alkenes**

Deepa Nair, Prashant Pavashe, Rahul Kumar and Irishi N. N. Namboothiri

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400 076

1,3-Dipolar cycloadditions (1,3-DC) are efficient protocols for regio- and stereoselective synthesis of heterocycles. Pyrazole, a five membered nitrogen heterocycle, is prevalent as core moiety in many natural products as well as drug molecules. Due to their therapeutic properties such as anti-tumor, anti-bacterial, anti-inflammatory and CNS depressant properties, they are widely explored as pharmaceutical products and agrochemicals. In the past few years, our group has been actively involved in 1,3-DC reactions of diazo compounds with various electron deficient substrates, viz nitroalkenes, enones and alkynes. Among the most explored diazo compounds, Bestman-Ohira reagent ( $\alpha$ -diazo- $\beta$ -ketophosphonate, BOR), has proved to be a good cycloaddition partner for obtaining highly functionalized phosphonylpyrazoles. Similar to BOR,  $\alpha$ -diazo- $\beta$ -ketosulfone can also be used in regioselective 1,3-DC reactions. Herein we report the 1,3-DC reaction of diazosulfone with different electron deficient substrates such as chalcones and arylidenemalonates for the regioselective synthesis of functionalized pyrazoles in moderate to good yields.

References:

(a) Muruganatham, R.; Mobin, S. M.; Namboothiri, I. N. N. *Org. Lett.* **2007**, 9, 1125. (b) Muruganatham, R.; Namboothiri, I. N. N. *J. Org. Chem.* **2010**, 75, 2197. (c) Verma, D.; Mobin, S. M.; Namboothiri, I. N. N. *J. Org. Chem.* **2011**, 76, 4764. (d) Kumar, R.; Namboothiri, I. N. N. *Org. Lett.* **2011**, 13, 4016. (e) Kumar, R.; Verma, D.; Mobin, S. M.; Namboothiri, I. N. N. *Org. Lett.* **2012**, 14, 4070. (f) Verma, D.; Kumar, R.; Namboothiri, I. N. N. *J. Org. Chem.* **2013**, 78, 3482.

(P414)

**Total Synthesis of both Spiroketal Diastereomers of the Reported Structure of Cephalosporolide H**

Rodney A. Fernandes\* and Mahesh B. Halle

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, Maharashtra, India.

The 5,5-spiroketal moiety is found in many natural products like symbiospirol A (1a), ascospiroketal B, (1b) penisporolides A and B (1c) and cephalosporolides (1d,e). The increasing pharmacological and medicinal importance of natural products containing spiroketal framework has sparked intense interest in both their synthesis, chemical reactivity and biological activity. The rigid spiroketal structure with varying functional groups in vicinity poses greater challenges in target oriented stereoselective synthesis. We have completed the total synthesis of both spiroketal diastereomers of reported structure of cephalosporolide H in 12 steps with 9% overall yield. The key steps involved in the synthesis are Keck's allylation, cross metathesis to get the desired  $\hat{1}^2, \hat{1}^3$ -unsaturated ester, Sharpless asymmetric dihydroxylation to install the  $\hat{1}^2$ -hydroxy- $\hat{1}^3$ -lactone moiety and spiroketalization to access both spiroketal diastereomers of cephalosporolide H. (2)

References:

1.(a) Tsunematsu, Y.; Ohno, O.; Konishi, K.; Yamada, K.; Suganuma, M.; Uemura, D. *Org. Lett.* **2009**, 11, 2153. (b) Seibert, S. F.; Krick, A.; Eguereva, E.; Kehraus, S.; Konig, G. M. *Org. Lett.* **2007**, 9, 239. (c) Li, X.; Sattler, I.; Lin, W. J. *Antibiot.* **2007**, 60, 191. (d) Li, X.; Yao, Y.; Zheng, Y.; Sattler, I.; Lin, W. *Arch. Pharm. Res.* **2007**, 30, 812. (e) Ackland, M. J.; Hanson, J. R.; Hitchcock, P. B.; Ratcliffe, A. H. *J. Chem. Soc., Perkin Trans. I* **1985**, 843.  
(2). Fernandes, R. A.; Halle, M. B. *Asian J. Org. Chem.* **2013**, 2, 593.

**(P415)**

**Stereoselective Approaches to the Oxa-, Aza- and Thia-cycles**

Yogesh Shelke, Santosh J. Gharpure

IIT Bombay

Stereoselective synthesis of heterocycles is an important and challenging area in synthetic organic chemistry, because these motifs are commonly found in both natural products and pharmaceuticals. Stereoselective approaches for synthesis of heterocycles such as isoflavans, Morpholines, 1,4- oxathianes, thiazinoindoles and pyrroloindole will be presented. Densely substituted isoflavanes are synthesised by using intermolecular hetero Diels-Alder reaction of in situ generated o-quinone methides. Lewis acid mediated reductive etherification strategy is successfully used for construction of pharmaceutically important morpholines and 1,4-oxathianes. Pictet-Spengler reaction is a powerful and versatile tool for synthesis of heterocycles. Thia- Pictet-Spengler reaction is studied for construction of thiazinoindoles derivatives. Various N-fused indoles are prepared by using N-acyl iminium ion cyclization reaction.

**(P416)**

**Phytochemical investigation and bioactivity studies on the medicinal plant *azadirachta indica***

Sajin Francis K and Mangalam S Nair\*

Organic Chemistry Section, Chemical Sciences & Technology Division, National Institute for Interdisciplinary Science and Technology (CSIR), Trivandrum-695 019, India.

*Azadirachta indica* (commonly known in India as Neem; Family: Meliaceae) has universally been accepted as a wonder tree because of its diverse utility.<sup>1</sup> Almost all parts of the tree are used in traditional medicines for the treatment of various ailments.<sup>2</sup> Limonoids from *A. indica* have attracted considerable attention due to their cytotoxicity against human cancer cell lines. The present study therefore aimed at the isolation of the limonoids viz; epoxyazadiradione, azadiradione and azadirone<sup>3</sup> from *A. indica* seeds for their detailed anticancer studies. Structures of the compounds are given below. In vitro cytotoxicity of all the three compounds were determined against various human cancer cell lines. The results indicate that azadirone sensitizes human colon cancer cells to TRAIL through three distinct mechanisms: up-regulation of DR5 and DR4 signaling, down-regulation of cell survival proteins, and up-regulation of proapoptotic proteins. (Studies were carried out in collaboration with Dr. Bharat B. Aggarwal, University of Texas).

References

1. Brahmachari, G. *Chem. Bio. Chem.* **2004**, 5, 408-421.

2. Chopra, R. N.; Nayer, S. L.; Chopra, I. C. Glossary of Indian medicinal plants, CSIR, New Delhi, 1956, 31.
3. D. Lavie, E. C. Levy, M. K. Jain. Tetrahedron , 1971, 27, 3927-3939.

**(P417)**

**Synthesis of heteroanalogues of flavones**

R. B. Kshatriya, J. K. Machhi

University of Pune

Flavonoids are natural products having wide range biological activities. Flavonoids have anticancer, antimalarial, antibacterial, antiviral, antifungal activities. Flavones are prepared by Claisen-Schmidt, Baker-Venkatraman and many other methods. Flavonoids are formylated and heterocyclization is created at 8<sup>th</sup> position. These heterocyclic molecules are checked for anticancer activities. Our research reached up to synthesis of heteroanalogues. Next step is to check bioactivity.

**(P418)**

**Protecting Group-Free Diastereoselective Total Synthesis of (±)-Cleistenolide**

Pankaj S. Mahajan and Santosh B. Mhaske\*

A short, efficient and expedient protecting group-free diastereoselective total synthesis of (±)-Cleistenolide has been achieved in five steps with 60% overall yield. Achmatowicz reaction, chemoselective oxidation of secondary alcohol and diastereoselective 1,3-anti reduction of β-hydroxy ketone are the key features of this linear total synthesis. The synthetic strategy demonstrated herein has a potential to explore it for an asymmetric total synthesis of (–)-Cleistenolide and related bioactive natural products.

**(P419)**

**Synthesis of a Novel heterocyclic Steroid-Peptide Conjugates**

Preetismita Borah and P.K Chowdhury\*

Natural Products Chemistry Division, CSIR-North East Institute of Science & Technology,  
Jorhat-785006, Assam, India

Steroid -Peptide Conjugate hybrid molecules, in recent years, are gaining considerable importance because of their potential use as peptidomimetics. Most of those Steroid- Peptide conjugates were obtained via cleavage of A and D rings of steroids molecules. The conjugation of steroids to other chemically or biologically relevant molecules represents a valuable strategy to generate new properties in the resulting molecular hybrid. To the naturally occurring saponins many synthetic biomolecules, viz., steroid- conjugates have shown to possess biological and physico- chemical features arising out of the junction of the two molecular entities. It has been demonstrated that Peptide-Steroid conjugates have been used as synthetic receptors of oligopeptide sequences, as protease-like artificial enzymes and as mimics of the natural cationic peptide antibiotics. Ugi four component reactions (Ugi-4CR) have been found to be a versatile approach towards the formation of peptide-steroid conjugates. In the present work, synthesis of some hetero steroid-peptide conjugates has been pursued [Scheme1] in order to get some potentially new and interesting Steroid –peptide conjugates(2) through application of Ugi-4 CR

with some heterosteroids generated from Seco-steroid derivative which in turn obtainable from easily available starting material 16-DPA(1). This new class of heterosteroid-peptide conjugates might possess diverged biological properties.

References:

1. Hostettman K, Marston A Saponins Cambridge University Press: Cambridge, UK, 1995
- 2.a)Doemling, A Chem Rev. **2006**, 106, 17. b) Ugi, I, Werner, B, Doemling A Molecules, **2003**, 8, 53-66.
3. Borah Juri Moni, Chowdhury Pritish, Steroids **2011**, 76, 1341-45

**(P420)**

**Synthesis of Calothrixins and its Analogs Using FeCl<sub>3</sub>-Mediated Domino Reaction Protocol**

Bose Muthu Ramalingam, Velu Saravanan, and Arasambattu K. Mohanakrishnan\*

Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai

The quino[4,3-b]carbazole alkaloids, Calothrixin A and calothrixin B were isolated from the photoautotrophic cultures of Calothrix cyanobacteria by Rickards et al. in 1999.<sup>1</sup> The calothrixins A and B inhibit the human HeLa cancer cells and plasmodium falcipuram at nanomolar concentrations.<sup>2</sup> A novel one pot synthesis of calothrixin B and its analogs is achieved involving an FeCl<sub>3</sub>-mediated domino reaction of enamines in dry DMF at reflux give 39-50% overall yield.<sup>3</sup> The in vitro cytotoxicity assay of the synthesized Calothrixin B and its analogs are performed against cell lines such as MCF7 (Breast), MDA-MB-231(Breast) and He La (Cervical). All these calothrixins exhibited relatively better activity against HeLa cancer lines. Two of the synthesized analogs are found to be ten times more potent than the parent compound. Full details on synthesis of calothrixin B and its analogs will be presented in the poster.

References

- 1) Rickards, R. W.; Rothschild, J. M.; Willis, A. C.; de Chazal, N. M.; Kirk, J.; Kirk, K.; Saliba, K. J.; Smith, G. D. Tetrahedron **1999**, 55, 13513–13520.
- 2) Matsumoto, K.; Choshi, T.; Hourai, M.; Zamami, Y.; Sasaki, K.; Abe, T.; Ishikura, M.; Hatae, N.; Iwamura, N.; Tohyama, S.; Nobuhiro, J.; Hibino, S. Bioorg. Med. Chem. Lett. **2012**, 22, 4762–4764.
- 3) Muthu Ramalingam, B.; Saravanan, V.; Mohanakrishnan, A, K. Org. Lett., **2013**, 15, 3726-3729.

**(P421)**

**A-ring modified bioactive friedelan triterpenoids via BF<sub>3</sub>.OEt<sub>2</sub>-mediated oxidative transformation**

Antara Sarkar, Jayanta Das, Raju Subba, Bittu Saha and Pranab Ghosh\*

Natural Products and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, West Bengal

Organic molecules derived from higher plants are found to exhibit a remarkable wide range of chemical diversity and a multiplicity of biological properties. Of the natural products, the pentacyclic triterpenoids (PTs) are increasingly drawing attention due to their diverse scope of chemical modifications toward achieving their medicinal applications. Friedelin and its



derivatives are well known among the PTs to exhibit potential biological effects. Herein, a simple but unique protocol for a library of A-ring modified friedelan PTs are described. The key route of the derivatizations is the one-pot BF<sub>3</sub>.OEt<sub>2</sub>-mediated oxidative transformation of friedelin into friedel-2-en-3-ol acetate (1) and 2-keto-3-en-3-ol acetate (2). The product distribution was found to be dependent on the reaction temperature as well as on the molar ratio of reagents to substrates. The enol acetate and the 2-keto analogue were further oxidized to incorporate oxo groups at C2, C3 and C4. Further work is still in progress to have other novel friedelan derivatives via the enol acetates (1 and 2). Anticipated phyto- and cytotoxic evaluation of all the derivatives is also in progress.

(P422)

**A General and Divergent Enantiospecific Total synthesis of Butanolide and Butenolide Based Natural Products**

Laxmi Narayan Nanda, Santosh J. Gharpure\*  
IIT Bombay

Donor-Acceptor substituted cyclopropanes (DACs) are fast emerging as versatile building blocks in organic synthesis.<sup>1</sup> Typical DACs contain a heteroatom such as oxygen as donor and an electron withdrawing group like a carbonyl group as acceptor. Due to the captodative effect of these donor and acceptor substituent, they show remarkably diverse reactivity with very high selectivity for cleavage of one of the cyclopropane bond sandwiched between donor and acceptor groups.<sup>2</sup> Not surprisingly, this interesting reactivity of DACs has been exploited in the synthesis of natural products such as (-)-rocellaric acid, xylobovide and anti-oligoannelated THF.<sup>3</sup> Lactone bearing natural products display lot of structural diversity and also varied biological activity. The five membered  $\gamma$ -lactone unit containing butanolides and butenolides are quite prevalent among the bioactive natural products. Hagen's gland lactones were found in the glands located near the abdominal tips of the Braconid wasps which contain fragrant volatile biological control agents that are rich in lactones.<sup>4</sup> Juruenolide-C was isolated from seedlings and micropropagated leaves of *Virola surinamensis* myristicaceous having antifungal activity against *Cladospodium cladisporioides* and juruenolide-D was isolated from seedlings and micropropagated leaves of *Virola surinamensis* myristicaceous tree in the river banks of the Amazon.<sup>5</sup> Ancepsenolide the first bis-butenolide acetogenins, isolated from a marine organism *Pterogorgia anceps* acts as plant metabolites that have shown interesting antitumoral, antimalarial, immunosuppressive, as well as pesticidal activities. <sup>6, 7</sup> This presentation will address a general and divergent enantiospecific total synthesis of these butanolide and butenolide based natural products.

References:

1. a) Reissig, H. U.; Zimmer, R. *Chem. Rev.* **2003**, 103, 1151. b) Yu, M.; Pagenkopf, B. L. *Tetrahedron* **2005**, 61, 321.
2. Gharpure, S. J.; Shukla, M. K.; Vijayasree, U. *Org. Lett.* **2009**, 11, 5466
3. a) Bohm, C.; Reiser, O. *Org. Lett.* **2001**, 3, 1315. b) Yu, M.; Lynch, V.; Pagenkopf, B. L. *Org. Lett.* **2001**, 3, 2563-2566.
4. Gharpure, S.J.; Nanda, L.N.; Shukla, M. K. *Eur. J. Org. Chem.* **2011**, 6635.
5. Clive, D. L. J.; Ardelean, E. S. *J. Org. Chem.* **2001**, 66, 4841.
6. Lorenzo, M.; Brito, I.; Cueto, M.; D-Croz, L.; Darias, J. *Org. Lett.* **2006**, 8, 5001.

7. a) Trost, B. M.; and. Miiller, T. J. J. Am. Chem. Soc. **1994**, 116, 4985. b) Larson, G. L.; de Perez, R. M. B. J. Org. Chem. **1985**, 50, 5258. c) Podraza, K. F.; Sneden, A. T. J. Nat. Prod. **1985**, 48, 792. d) Rodriguez, A. D.; Ramirez, C. J. Nat. Prod. **1994**, 57, 339. e) Guo, Y-W.; Gavagnin, M.; Mollo, E.; Trivellone, E.; Cimino, G. J. Nat. Prod. **1999**, 62, 1194. f) Ghobril, C.; Kister, J.; Baati, R. Eur. J. Org. Chem. **2011**, 3416.

**(P423)**

**A Novel Synthesis of Isoxazole Tethered Quinone-Amino Acid Hybrids via 1,3-dipolar cycloaddition reaction as the key step**

P.Ravi Kumar, Dr.Manoranjan Behera, Dr.Y.Satyanarayana, A.Jayashree, M.Sambaiah, K.Venu, P.Nagaraju  
JNTU, Hyderabad

Naturally occurring quinones have captured human attraction for thousands of years initially by reason of their bright color with possible uses as dyes and drugs. The discoveries of antibiotic and antitumor properties assigned to several natural quinones have raised interest among scientists for use as pharmaceuticals. Isoxazole derivatives show hypoglycemic, analgesic, anti-inflammatory, antifungal, anti-bacterial and HIV-inhibitory activity. Unnatural amino acids, the non-proteinogenic  $\alpha$ -amino acids that either occur naturally or are chemically synthesized have been used widely as chiral building blocks and molecular scaffolds in constructing combinatorial libraries. They represent a powerful tool in drug discovery when incorporated into therapeutic peptidomimetics and peptide analogs. Synthesis of hybrid natural products has gained momentum in recent years (1-2). It is expected that combining features of more than one biologically active natural segment in a single molecule may result in pronounced pharmacological activity while retaining high diversity and biological relevance. There are a few reports describing the quinone-isoxazole, quinone-amino acids, sugar-oxasteroid-quinone, quinone-annonaceous acetogenins, conduritol-carba-sugar hybrids (3-7).

An efficient method for the preparation of novel t-butyl 1(-methoxycarbonyl)-2-(3-(3,6-dioxocyclohexa-1,4-dienyl)isoxazol-5-yl)ethylcarbamate and t-butyl 1(-methoxycarbonyl)-2-(3-(3,6-dioxocyclohexa-1,4-dienyl)isoxazol-5-yl)phenyl)ethylcarbamate hybrids via 1,3-dipolar cycloaddition followed by an oxidation reaction using CAN has been described. Using this method, various isoxazole-tethered quinone-amino acids hybrids were synthesized in high yields.

References

- (1) Tietze, L. F.; Bell, H. P.; Chandrasekhar, S. Angew Chem. Int. Ed. Eng. 2003, 42, 3996.
- (2) Mehta, G.; Singh, V. Chem. Soc. Rev. 2002, 31, 324.
- (3) Kotha, S., Mandal, K., Banerjee, S., Mobin, S. M. Eur. J. Org. Chem. 2007, 1244.
- (4) Ravi Kumar, P. Behera, M., Raghavulu, K., Jaya Shree, A., Yennam, S. Tetrahedron Lett. 2012, 53, 4108.
- (5) Kaliappan, K. P.; Ravikumar, V. Org. Biomol. Chem. 2005, 3, 848.
- (6) Hoppen, S.; Emde, U.; Friedrich, T.; Grubert, L. Koert, U. Angew. Chem. Int. Ed. Eng. 2000, 39, 2099.
- (7) Mehta, G.; Ramesh, S. S. Can. J. Chem. 2005, 83, 581.

(P424)

### Assembly Line Synthesis

Varinder Aggarwal

Bristol University

In this lecture I will present our work on the reactions of primary and secondary lithiated carbamates with boranes and boronic esters. These reactions furnish homologated boronic esters with high levels of stereocontrol. I will show how we use this chemistry to make complex natural and unnatural products in a single operation. Finally, I will also describe a new method for the stereospecific cross-coupling of secondary and tertiary chiral boronic esters with electron rich aryl halides.

(P425)

### Ring-Closing Metathesis Enabled Efficient Synthesis of $\gamma$ -Butenolide Antifungal Agent (-)-Incrustoporin and its Analogues

Pradnya H. Patil, Asim K. Chowdhury and Rodney A. Fernandes\*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, Maharashtra, India

An efficient ring-closing metathesis based synthesis of the antifungal agent (-)-incrustoporin<sup>1</sup> and analogues are achieved. The ready availability of various allyl alcohols through the Sharpless kinetic resolution<sup>2</sup> and esterification with a variety of substituted arylacetic acids followed by methylenation and the final RCM to get the targets would make this explored strategy suitable for rapid analogues development.<sup>3</sup> The development of strategy and synthesis of (-)-incrustoporin and its analogues will be presented in detail.

#### References

- (a) Zapf, S.; Anke, T.; Sterner, O. *Acta Chem. Scand.* **1995**, 49, 233-234;  
(b) Lorenzen, K.; Anke, T. *Curr. Org. Chem.* **1998**, 2, 329-364.
- (a) Sharpless, K. B.; Katsuki, T. *J. Am. Chem. Soc.* **1980**, 102, 5974-5976;  
(b) Guiry, P.J.; Singh, S. *Eur. J. Org. Chem.* **2009**, 1896-1901;  
(c) Paquette, L. A.; Sweeney, T. J. *Tetrahedron* **1990**, 46, 4487-4502;  
(d) Jamison, T. F.; Moslin, R. M.; Miller, K. M. *Tetrahedron* **2006**, 62, 7598-7610.
3. Fernandes, R. A.; Patil, P. H.; Chowdhury, A. K. manuscript submitted

(P426)

### Assembly of Amphiphilic Polyurethane by Intra-Chain H-Bonding

Tathagata Mondal

Indian Association for the Cultivation of Science

Polyurethanes based materials are promising for bio-medical applications due to their excellent physical properties and bio-compatibility. We envisioned revisiting this classical family of macromolecules in context of their self-assembly by H-bonding interaction among the self-complementary urethane functionality might produce new self-assembled structures in aqueous solution.

With this aim, we have prepared an amphiphilic polyurethane wherein the urethane linkages were placed periodically in the hydrophobic backbone to which pendant carboxylate groups were

attached for imparting amphiphilicity. In aqueous medium (pH ~ 8.0) it shows spontaneous polymersome assembly which was probed by dynamic light scattering (DLS), transmission electron microscopy (TEM) and atomic force microscopy (AFM) studies. These polymersomes could encapsulate a hydrophilic dye (Calcein) in the water pool inside the membrane as evident by fluorescence studies. Formation of the membrane and resulting polymersome is believed to be the consequence of folding of the polyurethane chains which can be stabilized by intra-chain H-bonding among the urethanes. This hypothesis was supported by urea induced denaturation of the membrane and solvent dependent FT-IR studies. Concentration dependent FT-IR and DLS experiments confirmed intra-chain H-bonding. Further, XRD of that sample also established the H-bonded folded structure. These assemblies were found to be kinetically very stable and biocompatible which can be attributed to their zwitterionic nature. Synthesis and self-assembly of these materials will be the topic of the presentation.

**(P427)**

**Synthesis of Pyrazole Terminated Dendrimers Stitched Together via Click and Staudinger/Aza-Wittig Reactions**

Shaziya Khanam, Ranjeet kumar, Archana Gaurav and Ranjana S. Khanna\*

Department of chemistry (center of Advanced study), Banaras Hindu University, Varanasi

Dendrimers are generally constructed with three main parts (i.e. the core, dendron, and periphery), which allow the design of novel multifunctional molecules. Due to these special structural properties, dendrimers have been attracting great attention among scientists in many disciplines including organic, inorganic, organometallic, polymer, physical and biochemistry as well as materials science.<sup>1</sup> Till date several kind of dendrimers have been synthesized. In this context, we have prepared pyrazole terminated dendrimers using two methodology i.e Cu(I) catalyzed click<sup>2</sup> and Staudinger/aza-Wittig<sup>3</sup> reactions, in which Cu(I)-catalyzed Huisgen [2 + 3] dipolar cycloaddition reaction was performed between an organic azide and a terminal alkyne to prepare different series of aldehyde functionalized dendrons which further stitched to the azide moieties of core molecules via Staudinger/aza-Wittig reactions for the construction of final dendrimers. The synthesis, characterization and scope will be presented in detail.

References

[1] S. M. Grayson, J. M. J. Frechet, Chem. Rev. **2001**, 101, 3819-3867.

[2] M. J. Joralemon, R. K. O. Reilly, J. B. Matson, A. K. Nugent, C. J. Hawker, K. L. Wooley, Macromolecules **2005**, 38, 5436-5443.

[3] J. W Lee, U. Y. Lee, S. C. Han, J. H. Kim, Bull. Korean Chem. Soc. **2009**, 5, 1001-1002.

**(P428)**

**Tailor-made pH-Responsive Poly(caprolactone) Vesicles for Oral Drug Delivery**

Bapurao Surnar and M. Jayakannan

IISER Pune

Oral drug delivery under gastrointestinal (GI) tract is one of the most challenging tasks since the drug molecules should be stable and retained in the active form under the harsh GI tract. pH-responsive synthetic polymers are particularly attractive because they can protect the drug molecules in the acidic stomach (pH < 2.0) and burst instantaneously under neutral or basic pH (pH > 7.4) in the small intestine to release the loaded cargoes. Among all the nanostructures,

vesicular assemblies are particularly important for drug delivery since they resemble the structure of the cell membrane and also have features for loading and delivering both hydrophilic and hydrophobic drugs. We have developed new classes of carboxylic functionalized poly(caprolactone) (PCL) block copolymer vesicles and utilized these nano-carriers as pH responsive-drug delivery vehicles for oral administration under GI tract. The carboxylic functionalized caprolactone monomer was prepared through multi-step synthesis and polymerized under controlled ROP using polyethylene glycol (PEG-2K) to produce amphiphilic diblocks, PEG-b-CPCL<sub>x</sub>, with x = 25, 50, 75 and 100. These copolymers were self-organized into 100-250 nm vesicular assemblies. The size and shape of the vesicular assemblies were confirmed by light scattering, Zeta potential and electron microscope. These vesicles were capable to encapsulate both hydrophilic molecules (like rhodamine B, Rh-B) and hydrophobic drugs (Ibuprofen (IBU) and camptothecin (CPT) in the core and layer, respectively. These pH responsive vesicles were stable in strong acidic conditions (pH < 2.0, stomach) and ruptures to release the loaded cargoes under neutral or basic pH (7.0 i,£ pH, intestine). The drug release kinetics under simulated GI tract had been studied comprehensively. These custom designed vesicles un-wrap a new area of pH stimuli responsive polymer vehicles for delivering multiple drugs in oral drug delivery for biomedical applications.

#### Reference

1. Bapurao Surnar; Jayakannan, M. Stimuli-responsive Polycaprolactone Vesicles for Dual Drug Delivery under GI Tract, *Biomacromolecules*, **2013**, ASAP Article

#### (P429)

##### **Preparation of hydrotalcite/chitosan biocomposite for lead removal**

Gopalakannan Venkatrajan, Kalimuthu Pandi, Natrayasamy Viswanathan\*

Department of Chemistry, Anna University, University College of Engineering - Dindigul, Dindigul, Tamilnadu, India.

Nowadays, biosorption is recognized as a promising technique for water treatment. A composite is a heterogeneous substance consisting of two or more materials which does not lose the characteristics of each component. In the present study, hydrotalcite/chitosan (HT/CS) biocomposite was prepared by dispersing hydrotalcite in the chitosan biopolymeric matrix. The synthesized HT/CS composite was utilized for lead removal in batch mode. Sorption studies were performed to optimize various equilibrium parameters viz., contact time, pH, initial lead concentration, temperature and competing co-ions. The presence of functional groups, elements and the surface morphology of the composite were confirmed by FTIR and SEM with EDAX analysis. The equilibrium sorption data were fitted to Freundlich and Langmuir isotherms. The values of thermodynamic parameters such as  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  indicate the nature of lead sorption.

Keywords: Hydrotalcite; Chitosan; Composite; Adsorption; Lead

#### References

- 1.N. Viswanathan, S. Meenakshi, *Appl. Clay Sci.* **2010**, 48, 607-611.
- 2.L. Xiao, W. Ma, M. Han, Z. Cheng, *J. Hazard. Mater.* **2011**, 186, 690-698.

#### (P430)

## **Viscosimetric Determination of the Radii of Gyration of Sodium Carboxymethylcellulose in 2-Ethoxyethanol-Water Mixed Solvent Media**

Ranjit De, Ajaya Bhattarai, and Bijan Das\*

Department of Chemistry, Presidency University, Kolkata

The viscosities of an anionic polyelectrolyte sodium carboxymethylcellulose have been reported in water and 2-ethoxyethanol-water mixtures in salt-free and salt-containing solutions as a function of temperature. The results were analyzed in terms of a phenomenological approach (1) for the viscosity of polymer solutions to determine the intrinsic viscosities of the polyelectrolyte samples. The results obtained have been used to determine the root-mean-square radii of gyration (2) of the polyion chains. The polyion coils are found to expand at low ionic strength and these collapse drastically with increasing ionic strength. Addition of 2-ethoxyethanol to the medium in which these samples are dissolved causes a contraction of the polyion chains, although this influence is less pronounced than that of the added salt.

### References

1. B. A. Wolf, *Macromolecular Rapid Communications*, **2007**, 28, 164.
2. G. Tanaka, *Macromolecules*, 1982, 15, 1028.

**(P431)**

### **Viscometric and Wear Performance of methacrylate based Lubricants**

Mahua Upadhyay, Gobinda Karmakar, and P.Ghosh

Natural Product and Polymer chemistry Laboratory

Department of Chemistry, University of North Bengal, Darjeeling, India

Methacrylate based lube oil additive of three different kinds viz, one homopolymer (polyhexadecyl methacrylate, PHDMA) and two of its copolymers (HDMA-1-decene and HDMA-styrene) have been synthesized, characterized and investigated for their Viscosity modifier (VM), Anti wear (AW) and Thickening performance at different concentrations in two different base oils. The VM properties in terms of VI (Viscosity Index), the AW properties through determination of wear scar diameter (WSD) using a four ball wear tester and thickening, i.e. rise in oil viscosity due to added polymer at a given polymer concentration were studied. The polymers studied have been found to show VM and AW properties under the experimental conditions. At a given polymer concentration thickening was found to increase in the order PHDMA-styrene > PHDMA-1decene > PHDMA. The intrinsic viscosity, a measure of polymers hydrodynamic volume, showed a higher value in lower viscosity base stock, as compared to the higher viscosity oil in the case of homopolymer and PHDMA-1decene copolymers. The decrease in viscosity with temperature followed the order PHDMA > PHDMA-1decene > PHDMA-styrene; indicating a better viscosity index for the SIP type.

### References

1. R.M.Mortier, *Chemistry and Technology of Lubricants*, Blackie (1992).
2. U.Schodel, "Polymethacrylated for tomorrow's multi grade oils". SAE 700054.
3. I. R. H. Crail and P.Haltersley, "The relative effectiveness of VI Improves on an in service viscosity bases", SAE 710840.
4. R. L. Stambaugh and R.J.Kopko, "Behaviour of non-Newtonian lubricants in high shear rate applications", SAE 730487.

5. E. H. Okrent, Engine friction and bearing wear, 4, 1961, 97.
6. M. Palacios and M.L.Bajon, Tribol. Int. 27.1983.
7. K. Yoshida, Jap.J.Tribol. 40(4), 1995.

**(P432)**

**Influence of torsional angle on polymer chain conformation and charge carrier mobility**

Satish Patil

SSCU, Indian Institute of Science, Bangalore

The development of molecular semiconductors for optoelectronic devices has tremendous impact on energy production. However, a major challenge to attain widespread implementation of this technology would be to develop materials by cost effective methods and achieve high stability. Although this can pose a great challenge, the concept of bulk heterojunction has provided the record breaking efficiency of as high as 9.2%. However, a clear relationship between the material properties and stability is still lacking. In this talk, the role of torsional defects in molecular semiconductor shall be discussed. Moreover, our recent results of design and synthesis of ambipolar  $\pi$ -conjugated polymers for organic field-effect transistors (OFET) will be highlighted.

**(P433)**

**Synthesis of C-2 and C-5 aryl L-Histidine libraries for Antimicrobial Peptidomimetics**

Amit Mahindra, Nitin Bagra, Rahul Jain

National Institute of Pharmaceutical Education and Research, S.A.S. Nagar, Punjab-160062

Short cationic antimicrobial peptides are emerging antibiotics due to multiple mode of action, selectivity for pathogen's cell membrane with less susceptibility for resistance. The key pharmacophoric feature of such peptides is cationicity and lipophilicity/bulk. The amino acids with such properties are histidine, arginine, tyrosine, tryptophan and phenylalanine etc. Modified L-Histidine has a balance of both features and therefore ring modified L-histidines are important synthon for newer peptidomimetics with improved biological activity and proteolytic stability. Improving the lipophilicity in peptides was targeted through arylated analogues and protocols for C-2 & C-5 aryl L-Histidine were established. Synthesis of 2-arylated L-histidines with  $\text{ArB(OH)}_2$  has done with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and catalytic  $\text{AgNO}_3$  in  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  (1:1) (Synlett, 2012, DOI: 10.1055/s-0031-1290381). Palladium catalyzed C-H functionalization affords 5-aryl L-histidines with  $\text{ArI}$ ,  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2\text{-PCy}_3$  in DMF under microwave irradiation (J Org. Chem. 2013, doi: 10.1021/jo401934q).

**(P434)**

**A novel solid phase extraction methodology for the recovery of precious metal palladium**

Shivani Sharma, A.SanthanaKrishnaKumar, R.Sudheer Reddy, N.Rajesh

Department of Chemistry, Birla Institute of Technology and Science, Pilani-Hyderabad Campus, Jawahar Nagar, Shameerpet Mandal, R.R. Dist-500 078(AP), India.

Biopolymers possess excellent properties that are suited for multifarious applications. Chitosan, a linear polysaccharide is the second most abundant biopolymer possessing  $\beta$ -linked D-glucosamine units and is endowed with features such as biodegradability and biocompatibility. The utility of palladium as a catalyst in various organic reactions is well known [1]. The

recovery of the precious palladium assumes considerable importance. Liquid-Liquid extraction is the widely used method to recover palladium. The inherent drawbacks of this method pave way for solid phase extraction [2] as the ideal choice. In this work, we present a novel method, wherein a room temperature ionic liquid, Aliquat-336 impregnated onto chitosan was utilized for the adsorption of Pd(II). The adsorbent was well characterized through various physico-chemical techniques like FT-IR, XRD, SEM and EDX analysis. The adsorption was found to be best at pH 3.5 giving an adsorption capacity of 188.67 mg g<sup>-1</sup>. Several parameters like effect of pH, amount of adsorbent, isotherms, kinetics and thermodynamics were studied in detail.

#### References

- [1] K. Mandai, T. Korenag, T. Ema, T. Sakai, M. Furutani, H. Hashimoto, J. Takad, Biogenous iron oxide-immobilized palladium catalyst for the solvent-free Suzuki–Miyaura coupling reaction, *Tet. Lett.*, **2012**, 53, 329–332.
- [2] R. Ruhela, K.K. Singh, B.S. Tomar, J.N. Sharma, M. Kumar, R.C. Hubli, A.K. Suri, Amberlite XAD-16 functionalized with 2-acetyl pyridine group for the solid phase extraction and recovery of palladium from high level waste solution, *Separation and Purification Technology*, **2012**, 99, 36–43.

#### (P435)

##### **Exploring the Mechanism of Conversion of Monosulfiram into Disulfiram**

Rajesh Kumar Sharma, Ashutosh Gupta

Department of Chemistry, Udai Pratap Autonomous College, Varanasi

Monosulfiram (Tetraethyl Thiuram Sulfide) is a topical drug used in the treatment of scabies. However in presence of visible light it gets converted into disulfiram (Tetraethyl Thiuram Disulfide) which is used in the treatment of alcohol aversion therapy. In the present study, mechanism of conversion of monosulfiram into disulfiram is explored. Structure, geometrics, energetics of monosulfiram is obtained at MP2 and DFT level of theory. Its reactivity is assessed employing conceptual DFT. NBO charge distribution, bond dissociation energy and polarizability of the given molecule is determined. Spin density of free radicals generated during thermolysis & photolysis is characterized. Lowest singlet excited state of monosulfiram along with the potential energy surface of monosulfiram has been determined. It is found that conversion of monosulfiram into disulfiram occurs both by thermolysis and photolysis.

#### (P436)

##### **Self-sorting in Covalent Organic Cages**

Koushik Acharyya and Partha Sarathi Mukhejee

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Self-sorting<sup>1</sup> is a well-established synthetic protocol in biological world. It is defined as a spontaneous association through mutual recognition of complementary building units into a well-defined ordered architecture, within a random reaction mixture. In order to understand such nature's own process in a better way immense efforts have been paid off in last few decades to construct several artificial architectures utilizing non covalent interactions. On the contrary, hitherto covalent self-sorted systems are very few in the literature. In our recent work<sup>2</sup> we are successfully able to show for the first time unprecedented self-sorting of three-dimensional



nanoscopic organic cages driven by the dynamic imine bond. Individual cages were first synthesized by condensing a dialdehyde with a triamine to form [3+2] self-assembled cages and well characterized by various techniques. Interestingly reaction mixture of two aldehydes and one amine and vice versa, lead to the formation of one specific combination depending on the preference for a partner over another. We have further established that such self-“sorting process can be guided by supramolecular interaction especially by H-bonding.<sup>3</sup>

#### References

- 1.Saha, M. L.; Schmittel, M. *Org. Biomol. Chem.* **2012**, 10, 4651.
- 2.Acharyya, K.; Mukherjee, S. and Mukherjee, P. S. *J. Am. Chem. Soc.* **2013**, 135, 554.
- 3.Acharyya, K. and Mukherjee, P. S. *Chem. Eur. J.* (Accepted article)

#### (P437)

##### **Synthesis of novel unsaturated tricyclic proline and their application in synthesis of conformationally constrained SMAC mimetic as anticancer agent**

Rafat Ali, Sanjeev Meena<sup>§</sup> Dipak Datta<sup>§</sup> and W. Haq

Medicinal and Process Chemistry Division, <sup>§</sup>Biochemistry Division, Central Drug Research Institute, Lucknow

In past few years, significant attention has been made to synthesize non-proteinogenic (unnatural) amino acids. These unnatural amino acids introduced into the peptides to give modified peptides which have good control over conformational flexibility and improve pharmacodynamics, enzymatic stability and bioavailability compared to native peptides. Among the unnatural amino acids available, bicyclic proline analogues display interesting pharmacological activities and serve as building blocks for the synthesis of peptidomimetics. These factors inspire us toward the synthesis of new more constrained cyclic proline analogs. We describe the synthesis of fused tricyclic proline (1) starting from inexpensive pyroglutamic acid under solvent free condition. Presence of double bond enables compound 1 to synthesize various derivatives which emphasize the importance of this analogue. Due to strong ability of oxygen to form H-bond, we believe that when this tricyclic proline is introduced in the peptide sequence would result in important conformational changes which are useful in peptidomimetics study. Extensive studies reveal that overexpression of inhibitor of apoptosis (IAP) proteins makes cancer cells resistant to apoptosis induced by a variety of anticancer drugs and also Smac is a potent inhibitor of IAP. Therefore, the development of Smac peptidomimetics is considered as a highly promising approach for the treatment of cancer. To explore its biological importance we replace proline by the tricyclic proline in Smac AVPI in a step towards the development of conformationally constrained SMAC mimetic as anticancer agent. Our designed Smac mimic showed moderate activity in cancer, validating this unnatural amino acid as a building block to synthesize new anticancer agents. The details of study will be presented in poster.

#### References:

- [1] Zhang, B; Zhang, Y; Bai, L; Qui, Su; Wang, S; Wu, Y. Design, Synthesis, and Evaluation of Tricyclic, Conformationally Constrained Small-Molecule Mimetics of Second Mitochondria-Derived Activator of Caspases. *J. Med. Chem.* **2008**, 51, 7352-7355.
- [2] Fulda, S., Galluzzi, L. & Kroemer, G. Targeting mitochondria for cancer therapy. *Nature Rev. Drug Discov.* **2010**, 9, 447-464.

[3] Flygare, A, J; Beresini, M; Budha, N; Chan, H; Cheeti, S; Cohen, F; Feng, B; Wong, M; Wong, S; Yu, R; Zobel, K; Fairbrother, J, W. Discovery of a Potent Small- Molecule Antagonist of Inhibitor of Apoptosis (IAP) Proteins and Clinical Candidate for the Treatment of Cancer (GDC-0152). *J. Med. Chem.* **2012**, 55, 4101-4113.

**(P438)**

**A Copper-Catalyzed Cascade Three-fold C–N bond Formation Enroute to N–Pyridyl Heterocycles**

Parthasarathi Subramanian and Krishna P. Kaliappan\*

Department of Chemistry, Indian Institute of Technology –Bombay, Mumbai, INDIA

The recent advancement in transition metal catalyzed C–H activation and subsequent functionalization has led to the development of many efficient methodologies for the formation of C–C, C–X and C-heteroatom bonds.<sup>1</sup> Furthermore, this C-H activation strategy has been successfully utilized in the synthesis of several natural products<sup>2</sup> and biologically active molecules,<sup>3</sup> especially heterocycles. Among the heterocycles, nitrogen containing heterocycles have found widespread applications in pharmaceuticals, functional materials and agrochemical products. Imidazobenzimidazoles are one such class of nitrogen containing heterocycles, known for their wide spectrum of biological profile, have generated considerable interest among synthetic community and as a result many methodologies have been developed for their synthesis. However, the existing methods suffer from harsh conditions, narrow functional group tolerance, poor atom economy, low yielding and so; it warrants an efficient protocol for the syntheses of imidazobenzimidazole derivatives. Herein, we describe a one-pot Cu-catalyzed synthesis of N-pyridyl imidazobenzimidazole derivatives via oxidative sp<sup>2</sup> C–H activation to a cascade two fold C–N bond formations.

References

[1] a) R. G. Bergman, *Nature* 2007, 446, 391-393; b) M. S. Chen and M. C. White, *Science* 2007, 318, 783-787;

[2] a) M. C. Bagley, J. W. Dale, E. A. Merritt and X. Xiong, *Chem. Rev.* 2005, 105, 685-714; b) J. Kim and M. Movassaghi, *Chem. Soc. Rev.* 2009, 38, 3035-3050;

[3] T. W. Lyons and M. S. Sanford, *Chem. Rev.* 2010, 110, 1147-1169.

**(P439)**

**Synthetic Studies on (+)-Sch-642305 and Sch-725674**

Kota Ramakrishna and Krishna P. Kaliappan\*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai

The 1,3-dithiane has been utilized as an acyl anion equivalent in organic synthesis ever since its discovery by Seebach and Corey.<sup>1</sup> In 1994, the pioneering study done by Tietze on the alkylation of lithiated-1,3-dithianes led to the inception of linchpin coupling,<sup>2</sup> whose synthetic utility has been significantly demonstrated by Smith with their key scientific finding that tertiary amines such as HMPA, DMPU are capable of inducing a solvent controlled Brook rearrangement on lithiated-1,3-dithianes. Further, Smith introduced multicomponent linchpin couplings in context of synthesizing various complex molecules there by rendering the dithiane chemistry as an important tool for C-C bond formation in organic synthesis.<sup>3</sup>

(+)-Sch-642305, a bicyclic 14-membered macrolide, isolated from *Penicillium Verrucosum* (culture ILF-16214) in 2003 by a group of scientists from Schering-Plough and it was found to inhibit bacterial DNA primase with an EC<sub>50</sub> value of 70 μM as well as HIV-1 Tat with an IC<sub>50</sub> value of 1 μM.<sup>4</sup> The stereochemically densely substituted cyclohexenone with a fused 10-membered macrolide is a considerable synthetic challenge. Sch-725674 is another 14-membered macrolactone isolated by Yang and co-workers from a culture of *Aspergillus* sp., in 2005 and displayed antifungal activity against *Saccharomyces cerevisiae* and *Candida albicans*.<sup>5</sup> In continuation of our interest in synthesizing biologically active 14-membered macro lactones,<sup>6</sup> we devised a concise approach towards (+)-Sch-642305 and Sch-725674 involving linchpin coupling, Yamaguchi macrolactonization, trans annular Michael reaction and hydroxyl-directed ketone reduction as key steps respectively.

#### References:

1. Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, 4, 1075.
2. Tietze, L. F.; Geissler, H.; Gewert, J. A.; Jakobi, U. *Synlett* **1994**, 511.
3. (a) Smith, A. B., III; Condon, S. M.; McCauley, J. A. *Acc. Chem. Res.* **1998**, 31, 35. (b) Smith, A. B., III; Pitram, S. M.; Boldi, A. M.; Gaunt, M. J.; Sfougataki, C.; Moser, W. H. *J. Am. Chem. Soc.* **2003**, 125, 14435.
4. Chu, M.; Mierzwa, R.; Xu, L.; He, L.; Terracciano, J.; Patel, M.; Gullo, V.; Black, T.; Zhao, W.; Chan, T.-M.; McPhail, A. T. *J. Nat. Prod.* **2003**, 66, 1527.
5. Moretti, J. D.; Wang, X.; Curran, D. P. *J. Am. Chem. Soc.* **2012**, 134, 7963.
6. (a) Kaliappan, K. P.; Si, D. *Synlett* **2009**, 2441. (b) Si, D.; Sekar, N. M.; Kaliappan, K. P. *Org. Biomol. Chem.* **2011**, 9, 6988. (c) Si, D.; Kaliappan, K. P. *Synlett* **2012**, 23, 2822.

#### (P440)

#### **Chemical synthesis of damaged DNAs to study structure and function of Y-family polymerases**

Pratibha P. Ghodke, Pradeepkumar P. I.

Department of Chemistry, Indian Institute of Technology Bombay

DNA damage is a constant threat caused by endogenous and exogenous sources; presence of these damages block the progress of DNA replication process by replicative polymerases. An important mechanism to overcome this problem entails the use of specialized DNA polymerases (Y-family) to carry out Translesion synthesis (TLS). TLS is defined as the bypass of damaged sites by incorporation of a nucleotide across the damage, which can be error-free or error-prone. Compared to the replicative polymerases, additional little finger domain of the TLS polymerases enhances the binding with template DNA and influences fidelity and activity. Among the Y-family polymerases, the structure of DinB polymerase (DNA polymerase IV from *E. Coli*) is yet to be determined with damaged DNAs. A recent study suggests that DinB polymerase and its orthologs can efficiently bypass the different N2-dG potential lesions. To understand the structural and functional requirement of DinB polymerase, we carried out synthesis of oligonucleotides containing site-specific N2-modified-dGs. The clear perspective of lesion induced conformational changes in DinB polymerase with N2-modified-dG oligonucleotides is currently being studied by X-ray crystallography.

**(P441)**

**Anticancer Strategies via Specific Stabilization of Promoter G-Quadruplex DNAs by Small Molecules Endowed with Drug like Properties**

Diveshkumar K. V. and Pradeepkumar P. I.\*

Department of Chemistry, Indian Institute of Technology Bombay

G-quadruplexes are highly stable secondary structures that can be adopted by guanine rich nucleic acids mainly found in eukaryotic chromosomal ends (telomeres) and at the promoter regions of various proto oncogenes like C-MYC, C-KIT, BCL-2 and untranslated region (UTRs) of mRNAs. Stabilization of G-quadruplex structures by small molecules has been recognized as a promising strategy for anticancer drug therapy since they are involved in various biological processes like telomerase inhibition, inhibition of transcription and translation processes of various oncogenes. An ideal G-quadruplex stabilizing agent should be specific to the targeted quadruplex over other quadruplex topologies and duplex DNAs. Herein, we report a new class of indanone and indole based compounds that can selectively stabilize promoter quadruplex DNAs over telomeric and duplex DNAs. Various derivatives have been designed and synthesized by changing the number and length of side chains to target the loops and grooves of quadruplex structures. Interaction of these small molecules with quadruplex and duplex DNAs has been explored by various biophysical methods like CD spectroscopy and ITC experiments. Furthermore, stabilization of C-MYC quadruplex DNA was studied using concentration dependant Taq DNA polymerase stop assay. Results indicate that all the derivatives can induce and stabilize the promoter quadruplex DNAs (C-MYC and C-KIT) selectively over telomeric and duplex DNAs.

**(P442)**

**Intramolecular 1,5-closed shell type O....O interactions**

Chiranjeev Sharma, Ashawani Kumar Singh, Satish Kumar Awasthi

Chemical Biology Laboratory, Department of Chemistry, University of Delhi

Our current understanding and one of the most consistent observation suggest that the non-bonded intramolecular interaction between two oxygen atoms within a molecule exert the destabilizing force<sup>1</sup> with mechanistic implications.<sup>2</sup> Extensive literature survey reveals that in spite of the large number of publications on important bioactive molecules containing O-O distance still shorter than the sum of van der Waals radii, which can be ascribed to their steric demand per se, the possibility of non-bonded 1,5-type O-O interaction is either neglected or considered unremarkable.

As a part of continuing research work on synthesis of new antimalarials<sup>3</sup> and characterization of small organic molecules for the evaluation of rare and unusual interactions by X-ray crystal studies,<sup>4</sup> we recognized the non-bonded O...O distances between the oxygen atoms of the keto group and the carboxy ethyl ester group at C4 and C3 positions in quinolone (1) are significantly shorter than the sum of the corresponding van der Waals radii. We anticipated that the crystal structure of geometrically restricted organic molecules possessing  $\beta$ -keto/carboxy ester functionality should exhibit similar interactions. Different compounds (2,3, etc...) were also synthesized, characterized (by <sup>1</sup>HNMR, <sup>13</sup>C NMR and HRMS) and crystallized to validate the generality of our prediction. We chose hexane for crystallization because it is apparent that the use of the polar solvent might inhibit the intramolecular interaction by solvation.

The effect of temperature on the single crystals of these compounds was determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements in open aluminium pans under nitrogen atmosphere. Surprisingly, contrary to the reports on the thermal decomposition of 4-quinolonecarboxylates and related compounds evolving carbon dioxide much below 320°C, we found these compounds remain intact till 450°C. Theoretical calculations also reveal the positive electronic energy values  $h(r) = g(r) + v(r)$ . Thus we can conclude that the crystal structures and theoretical investigations of these compounds provide compelling evidence that intramolecular 1,5-closed shell type O•••O interactions. Though uncommon such interactions are energetically and structurally significant and further exploration will surely yield new insights.

References:

1. McCarrick, M.; Wu, Y. D.; Houk, K. N. J. Am. Chem. Soc., 1993, 114, 1499-1500.
2. Warner, R. N.; Elsey, G. M.; Maksimovic, L.; Johnston, M. R. T. Lett., 1995, 36(42), pp 7753-7756.
3. Dixit, S. K.; Mishra, N.; Sharma, M.; Singh, S.; Agarwal, A.; Awasthi, S. K.; Bhasin, V. K. Eur. J Med. Chem. 2012, 51, 52–59
4. Neupane, C. S., Awasthi, S. K. Tet letters, 2012, 53, 6067-6070.

**(P443)**

**Shape and Morphology of Nanocatalyst Makes the Difference: Cobalt oxide Flowers for Nanocatalysis**

Amitava Acharjya, Vivek Polshettiwar\*

Nanocatalysis Laboratories (NanoCat), Department of Chemical Sciences  
Tata Institute of Fundamental Research (TIFR)

The chemist's first choice for heterogeneous catalysts is often porous silica because of its high surface area. However, these surface areas are mostly due to the pores and are thus not always accessible. We have developed new kind of fibrous silica nanospheres (KCC-1)<sup>1</sup>. The material exhibits excellent physical properties, including a high surface area, a fibrous surface morphology, good thermal, hydrothermal and high mechanical stability. Its high surface area is due to these fibers and not pores. KCC-1 was found very useful for silica-supported catalysis, wherein accessibility of active sites were increased dramatically<sup>2-5</sup>. KCC-1 nitridated derivatives showed good CO<sub>2</sub> capture capacity<sup>6</sup>. Using KCC-1 synthesis protocol, herein we report synthesis of cobalt oxide nanoparticles in a greener way using soft template approach by microwave assisted solvothermal synthetic route and were then characterized by BET analysis, SEM, TEM, and XRD. Three different shapes of cobalt oxide have been obtained just by changing the reaction conditions. The basic mechanism behind their shape formation/growth was investigated. Catalytic activity of these three different shaped cobalt oxide are now under investigation.

References:

1. V. Polshettiwar, D. Cha, X. Zhang and J. M. Basset, Angew. Chem.Int. Ed. 2010, 49, 9652.
2. A. Fihri , M. Bouhrara , U. Patil , D. Cha , Y. Saih , and V. Polshettiwar, ACS Catalysis 2012, 2, 1425

3. V. Polshettiwar, J. T.-Cazat, M. Taoufik, F. Stoffelbach, S. Norsic and J.-M. Basset, *Angew. Chem. Int. Ed.* 2011, 50, 2747.
4. A. Fihri, D. Cha, M. Bouhrara, N. Almana, V. Polshettiwar, *ChemSusChem*, 2012, 5, 85.
5. M. Bouhrara, C. Ranga, A. Fihri, R. R. Shaikh, P. Sarawade, A. H. Emwas, M. N. Hedhili, and V. Polshettiwar, *ACS Sustainable Chem. Eng.*, 2013, 1, 1192.
6. U. Patil, A. Fihri, A. H. Emwas and V. Polshettiwar, *Chemical Science*, 2012, 3, 2224.

**(P444)**

### **Photoluminescence properties of Eu<sup>3+</sup> doped BaF<sub>2</sub> nanomaterials**

L. Priyobarta Singh, S. Krishna Srivastava

Manipur University

Alkaline earth metal fluorides MF<sub>2</sub> (M = Sr, Ca, Ba), characterized with low phonon energy has been potential fluorescent host matrix for doping rare-earth (RE) ions. Thus, these are widely used in microelectronics and optoelectronic devices such as wide-gap insulating over layers, gate dielectrics, insulators, and buffer layers in semiconductor-on-insulator structures and more advanced 3D devices. Reports reveal that BaF<sub>2</sub> activated with rare-earth ions exhibit unique luminescent properties and can be used as scintillators. This can be attributed to the cubic structure with a single-valued refractive index (1.47) of BaF<sub>2</sub> that significantly avoids light scattering and limits the self-quenching process of the lanthanide ions. Cubical crystalline 3 at.% Eu<sup>3+</sup> doped BaF<sub>2</sub> nanomaterials have been successfully synthesized by ethylene glycol route. The cubical crystalline structure of BaF<sub>2</sub> was confirmed by XRD analysis. The shape of the prepared nanoparticles is found to be changes from cubical to rod shaped with annealing up to 900 °C. Photoluminescence studies give the characteristic emission of Eu<sup>3+</sup> at 587 nm (5D<sub>0</sub>→7F<sub>1</sub>, magnetic dipole transition) and 613 nm (5D<sub>0</sub>→7F<sub>2</sub>, electric dipole transition). The decay time of as-prepared sample is longer than 900 °C annealed samples. The CIE chromaticity coordinates diagram shows the prepared nanomaterials can be used as orange-reddish emitter.

**(P445)**

### **Synthesis and characterization of cobalt sulfide nanocrystallites and its use as catalyst for photodegradation of methylene blue**

Amol S. Pawar and Shivram S. Garje

Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E)

Various methods have been reported for the preparation of cobalt sulfide including chemical precipitation, hydrothermal and ion exchange methods. Herein, we report a convenient method for the preparation of cobalt sulfide nanocrystallites using single-source molecular precursor approach. The precursor molecule of the type CoCl<sub>2</sub>(LH)<sub>2</sub> (where, LH = thiophene carboxyaldehyde thiosemicarbazone) was synthesized and characterized by elemental analysis, IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. It was further used as a single source precursor for the preparation of nanocrystalline CoS by pyrolysis and solvothermal decomposition methods. The materials obtained were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive analysis by X-rays (EDAX) and UV-visible spectroscopy. XRD shows formation of hexagonal phase CoS (JCPDS: 75-0605) and the 1:1 stoichiometry between cobalt and sulfur was confirmed by EDAX. TEM images show spherical shape morphology of the nanocrystallites obtained from both the methods. As synthesized CoS

nanocrystallites were further used as catalyst in the photodegradation of methylene blue. The materials are found to have good photocatalytic activity as evident from the absorption spectra of the dye.

**(P446)**

**Synthesis, Characterization and Structures of Pentanuclear, Dodecanuclear and Polymeric Lanthanide Phosphates**

Sandeep K Gupta, Subramaniam Kuppaswamy, and Ramaswamy Murugavel  
Department of Chemistry, IIT Bombay

Monoester of phosphoric acids,  $R(O)PO_3H_2$ , where R is an aryl or alkyl group are now well established as ideal candidates for the preparation of both main group and transition-metal phosphate clusters of medium to high nuclearity. Such compounds are now being extensively studied for their magnetic properties. A phosphate monoester with a bulky aryl substituent 2,6-diisopropylphenylphosphate (dippH<sub>2</sub>), has been used to synthesize pentanuclear, dodecanuclear lanthanide phosphate clusters and one-dimensional polymeric chains under various conditions. All compounds have been characterized by both analytical and spectroscopic technique. Further their molecular structure has been established by X-ray diffraction technique. To the best of our knowledge, these compounds represent the first examples of pentanuclear, dodecanuclear molecular lanthanide phosphate clusters and one-dimensional polymeric chains based on mono ester of phosphoric acid.

**(P447)**

**Synthesis and Characterization of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles synthesized in binary mixture of Ionic liquid and Ethylene glycol**

Preet Shikha, B.S Randhawa\*, Tejwant Singh Kang\*  
Department of Chemistry, Guru Nanak Dev University, Amritsar-143005 (India)  
E-mail: (shikha.preet2011@gmail.com)

The unique properties of nanomaterials brought revolution in various scientific fields. Materials in nanorange show contrasting behaviour as compared to bulk where quantum effects are negligible. Among various nanoparticles, magnetic nanoparticles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> draw a great attention due to attractive scientific, industrial and biological applications. Currently, the hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) in nanosize range can be synthesized by different conventional methods which require a lot of expensive apparatus and are time consuming. So the need to synthesized nanomaterials with cheap and effective methods is in a great demand. In view of above problems we have synthesized nanomaterials using binary mixture of an ionic liquid and ethylene glycol as a green solvent. In this work we have synthesized a series of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles by a very simple and efficient route using inherently green mixture of Ionic liquid and Ethylene glycol. A low temperature grinding of Fe(NO)<sub>3</sub>·9H<sub>2</sub>O in binary mixture of Ionic liquid and Ethylene glycol in the presence of NaOH yields nanocrystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The obtained nanoparticles have been characterized by XRD, SEM, TEM and Mossbauer spectroscopy. The effect of varying composition of solvent mixture on the morphology and characteristic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles has also been investigated.

(P448)

**Myristate as corrosion inhibitor for magnesium alloy ZE41: An electrochemical examination**

Nandini and A. Nityananda Shetty

The automobile industry hugely relies upon light-weight structural materials to target superior fuel efficiency. Magnesium is the lightest structural metal and hence its alloys are being increasingly employed for weight-critical applications in automobile industry. These alloys are highly vulnerable to corrosion; as a result most of their potential applications remain a practical challenge. ZE41 is one such rare earth containing cast alloy of magnesium. In this study, an anionic surfactant myristate (conjugate base of tetradecanoic acid) has been investigated as a inhibitor towards magnesium alloy ZE41 in sodium sulfate medium. The electrochemical techniques like potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) have been made use of. The scanning electron microscopy (SEM) and energy dispersion X-ray (EDX) analysis have been utilized for examination of surface morphology. Myristate is found to be mixed-type inhibitor with a predominant control over anodic process. The inhibition is possible outcome of adsorption which is found to follow Langmuir adsorption isotherm.

(P449)

**Cd doped ZnO Nanoparticle: Optical and Photocatalytic and Antibacterial Properties**

Jagriti Gupta

Cd-doped ZnO nanoparticles were synthesized through a facile soft-chemical approach. The detailed structural analysis was performed by XRD, X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM). X-ray diffraction and Raman spectra confirm the formation of highly crystalline single-phase hexagonal wurtzite nanoparticle. The optical studies of Cd doped ZnO nanoparticles confirms that band gap and near band edge emission of ZnO nanostructures are strongly dependent on the Cd concentration and the defect states. Furthermore, the increase in the intensity of green emission as increase in the Cd concentration from 0 to 7 % undoubtedly indicates the enhancement of defect states in the Cd doped ZnO nanoparticles. Further the red shift in the near-band edge emission (NEB) confirmed the incorporation of Cd ions in the ZnO with the increase of Cd concentration. A broad green defect emission is also observed at around 590 nm with the increase of Cd ions from 0 to 7%. Further increase in the Cd concentration 10 % suppresses the green defect emission. This type of deviation in Cd doped ZnO nanoparticles may be ascribed due to change in the dopant concentration dependent defects and nonradioactive energy transfer. Furthermore, we can say that the photocatalytic activity strongly depends on Cd concentration and defect concentration. Cd doped ZnO with very low Cd concentration (3% Cd) shows excellent photocatalytic effect under UV and Visible light as compare to pristine ZnO. Pristine ZnO and Cd doped ZnO nanoparticle shows the good antibacterial properties.

(P450)

**Modification of SiO<sub>2</sub> nanoparticles by organo-boron compounds**

Arunava Agarwala

Department of Chemistry, Manipal University Jaipur



Organo-boron surface functionalities are widely used in the context of sensing, catalysis, chromatography, surface doping, and more. Several reports demonstrate the introduction of organo-boron surface functionalities via molecular linking groups, where the organic linker group is reacted to form a covalent bond at the surface and the boron moiety is pendant at the surface. Formation of boron containing monolayers at SiO<sub>2</sub> nanoparticle surfaces is demonstrated under mild conditions. Monolayer formation is obtained by direct covalent bond formation between the boron functionality and surface silanol groups (Si-OH). Halo-borane derivatives are studied exhibiting different types of surface reactions. Surface reactivity towards SiO<sub>2</sub> nanoparticles and Si/SiO<sub>2</sub> interfaces was studied by FTIR, XPS, Thermogravimetric analysis (TGA), solid state <sup>11</sup>B NMR, ellipsometry, atomic force microscopy (AFM). Collectively, The results suggest the formation of monolayers via direct Si-O-B bond formation is highly attractive for a wide range of applications including sensing, catalysis, chromatography, surface doping. Annealing of SiO<sub>2</sub> nanoparticles modified with organo-boron compounds resulted incorporation of B atom in silica framework.

**(P451)**

**Surface modification of apple pomace as low-cost adsorbent for removal of Cd<sup>+2</sup> and Pb<sup>+2</sup> ions from aqueous solution**

Piar Chand and Yogesh B. Pakade\*

CSIR-Institute of Himalayan Bioresource Technology

Surface of apple pomace (AP) was modified with methyl acrylate in presence of strong oxidizing agent ammonium ceric nitrate (NH<sub>4</sub>)<sub>2</sub>[Ce (NO<sub>3</sub>)<sub>2</sub>] to enhance the adsorption capacity. Characterization of AP and methyl acrylate apple pomace (MAAP) were carried out by FTIR and SEM-EDS. Langmuir adsorption isotherm was found to be more suitable for AP and MAAP adsorption indicated by correlation coefficient (r<sup>2</sup>) than Freundlich isotherm. Kinetics study demonstrated the suitability of pseudo-second order kinetics with correlation coefficient (r<sup>2</sup>) of 0.99-1.0 and 0.94-0.99 for AP and MAAP. Thermodynamics study demonstrated that ΔH° was found positive for Cd<sup>+2</sup> and negative in case of Pb<sup>+2</sup> adsorption. FTIR spectra of AP and MAAP before and after adsorption indicated that polyphenols (-OH), esters (-COO), carboxyl (-CO) and amine (-NH<sub>2</sub>) groups may be responsible for metal adsorption onto surface. After surface modification the removal efficiency and adsorption capacity (mg/g) were increased significantly. Results demonstrated that utilization of MAAP as a low cost, easily applicable and environment friendly adsorbent for treatment of contaminated water.

**(P452)**

**Solubilization of polycyclic aromatic hydrocarbons in aqueous micellar solutions of some gemini and monomeric surfactants**

Toshikee Yadav, Deepti Tikariha, Jyotsna Lakra and Kallol K. Ghosh\*

School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, (C.G.)

Polycyclic aromatic hydrocarbons (PAHs) are potent atmospheric pollutants that consist of two or more benzene rings. PAHs have low solubility in water, their slow dissolution can contaminate large amounts of ground water for long period. Surfactants play a vital role in the solubilization of these hydrophobic organic compounds. The present study focused on solubilization of polycyclic aromatic hydrocarbons i.e. pyrene, acenaphthene and fluorene in

aqueous micellar solutions of some gemini (16-s-16, s = 10, 12) and monomeric surfactant viz. cetyltriethylammonium bromide (CDEEAB). Gemini surfactants (16-12-16, 16-10-16) have greater ability to solubilize the PAH's (Pyrene, acenaphthene and fluorene) than conventional surfactant CDEEAB. The solubilization parameters i.e. molar solubilization ratio (MSR), micelle-water partition coefficient (Km) and free energy of solubilization ( $\Delta G^\circ$ ) of PAHs have been discussed. The negative value of  $\Delta G^\circ$  shows spontaneity of solubilization process.

The results of this study will be useful to understand the role of appropriate surfactant system for the solubilization of toxic hydrophobic organic compounds.

**(P453)**

**Nano zero-valent iron supported activated carbon as adsorbent for the removal of heavy metal ions from water.**

Fauzia Khan, Meraj Alam Khan, Aarti Singh, Seraj Anwar Ansari and Anees Ahmad.  
Department of Chemistry, A.M.U., Aligarh, Aligarh.

Nowadays many water resources are polluted by anthropogenic sources including household and agricultural waste and industrial processes and human concern over the environmental impact of wastewater pollution has been increased. Several conventional wastewater treatment techniques, i.e. chemical coagulation, adsorption, ion-exchange, membrane filtration, electrochemical methods, etc., have been applied to remove the pollution; however there are still some limitations, especially that of high operation costs. The use of zero-valent iron as a reductive medium is receiving increased interest due to its low operation and maintenance costs. In addition, it is easy-to-obtain, with good effectiveness and ability for degrading contaminants. This paper reviews the use of zero-valent iron to remove heavy metals ions.

**(P454)**

**Probing the interactions at Magnetic Nanoparticles Interface with Serum Proteins**

Delina Joseph<sup>1</sup> and Shilpee Sachar<sup>2</sup>

<sup>1</sup> Dept. of Chemical Sciences, School of Science, SVKM's NMIMS, Vile Parle(W), Mumbai-400 056; <sup>2</sup> Dept. of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E), Mumbai-400 098

Magnetic nanoparticles (MNPs) constitute a class of nanoparticles with unique ability to be guided by an external magnetic field. These properties helps MNPs to play an important role in biomedical applications such as magnetic resonance imaging (MRI), targeted drug and gene delivery, tissue engineering, cell tracking and bioseparation. Hence its potential is being explored to its fullest in research. As a pre-requisite, MNPs need to be coated with appropriate materials to ensure the stability and bio-compatibility. There is a paucity of information on the binding affinities and other physicochemical parameters of various coating materials with respect to MNPs. This work aims to study the nature of association during the interaction of these nanoparticles with various potential coating materials, as the understanding of this dynamics would empower a researcher to choose an apt coating for designing more efficient MNPs for respective applications. In the present study, Iron Oxide Nanoparticles are first synthesized using chemical co-precipitation method. The synthesized MNPs are characterized by FTIR, XRD, DLS, Zeta potential and VSM studies. These bare nanoparticles are then studied for their interaction with serum protein (BSA) via fluorescence spectroscopy and dynamic light scattering techniques. The spectroscopic investigation helps in understanding the stability of the molecular

association in terms of binding and size. The thermodynamic parameters are also estimated using isothermal titration calorimetry technique. Further, the above system was studied in presence of a surfactant. Surfactant coating was found to stabilize the MNP: BSA system to a greater extent. The study can provide valuable insights at the interactions happening at the nanoparticles interface with different coating materials which would further aid in design of more competent MNPs.

**(P455)**

**Solution Thermodynamics of Ferrous Sulphate in aqueous lactose solutions at T= (298.15, 303.15, 308.15, and 313.15) K: A Viscometric and volumetric study**

Abhijit Sarkar, Bijan Kumar Pandit and Biswajit Sinha

University of North Bengal

Apparent molar volumes and viscosity B-coefficients for Ferrous sulphate in aqueous lactose solutions were determined from solution density and viscosity measurements at (298.15, 303.15, 308.15, 313.15) K as a function of FeSO<sub>4</sub> concentration. The standard partial molar volume and slopes obtained from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The viscosity data were analyzed using the Jones-Dole equation and the derived parameters A and B were interpreted in terms of solute-solute and solute-solvent interactions respectively. The standard volume of transfer and viscosity B-coefficients of transfer of ferrous sulphate from water to aqueous lactose solutions were derived to study various interactions in the ternary solutions. The activation parameters of viscous flow for the ternary solutions were also calculated and explained in terms of transition state theory. The structure making or breaking ability of ferrous sulphate has been discussed in terms of the sign of.

**(P456)**

**Thermophysical properties of binary mixtures of N,N-dimethylformamide with three cyclic ethers**

Rajendra Pradhan, Mousumi Das, Amarjit Kamath, Biswajit Sinha

University of North Bengal

Densities and viscosities of binary mixtures consisting of tetrahydrofuran (THF), 1,3-dioxolane (1,3-DO) and 1,4-dioxane (1,4-DO) with N,N-dimethylformamide (DMF) over the entire range of composition were measured at the temperatures 298.15, 308.15 and 318.15 K and at atmospheric pressure. The ultrasonic speeds of sound of these binary mixtures were measured at ambient temperature and atmospheric pressure ( $T = 298.15$  K and  $p = 1.01 \times 10^5$  Pa). The various experimental data were utilized to derive the excess molar volumes  $E(V_m)$ , excess viscosities ( $\hat{I} \cdot E$ ) and excess isentropic compressibilities  $E(\hat{I}^o s)$ . Using the excess molar volumes  $E(V_m)$ , the excess partial molar volumes ( $E V_{m,1}$  and  $E V_{m,2}$ ) and excess partial molar volumes at infinite dilution ( ${}^0 E V_{m,1}$  and  ${}^0 E V_{m,2}$ ) of each liquid component in the mixtures were derived and are discussed. The excess molar volumes  $E(V_m)$  as a function of composition at ambient temperature and atmospheric pressure were used to test further the applicability of the Prigogine-Flory-Patterson (PFP) theory to the experimental binaries. The excess properties were found to be either negative or positive depending on the nature of molecular interactions and structural effects of the liquid mixtures.

**(P457)**

**Synthesis and evaluation of phenanthridine analogues as anti-tubercular agents**

K. Mahalakshmi Naidu

Birla Institute of Technology & Science-Pilani

A series of ten new 6-(4-((substituted-1H-1,2,3-triazol-4-yl)methyl)piperazin-1-yl)phenanthridine analogues employing versatile 100% atom economy copper(I)-catalyzed azide-alkyne cycloaddition have been prepared. Structure of the newly synthesized compounds are confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, LCMS and evaluated for their anti-tubercular activity against Mycobacterium tuberculosis H37Rv strain by Microplate Alamar Blue Assay. Among the tested compounds, 7f and 7i exhibited good activity (Minimum Inhibitory Concentration of 3.125 µg/mL) against the growth of Mycobacterium tuberculosis H37Rv. In addition, 7f and 7i compounds were subjected to cytotoxicity studies against mouse macrophage (RAW264.7) cell lines and the selectivity index values are >15 indicating suitability of compounds for further drug development.

References:

1. Badger, G. M.; Seidler, J. H.; Thomson, B. J. Chem. Soc.,(Resumed) 1951, 0, 3207.
2. Meseroll, L. M. N.; McKee, J. R.; Zanger, M. Synthetic Communications 2011, 41, 2557.
3. Nagesh, H. N.; Mahalakshi Naidu, K.; Harika Rao, D.; Sridevi, J. P.; Sriram, D.; Yogeewari, P.; Chandra Sekhar, K.V.G.; Bioorg. Med. Chem. Lett. 2013. In press.
4. Chandra Sekhar, K.V.G.; Rao, V.S.; Kumar, D.; Bull. Korean Chem. Soc. 2011, 32, 2657.

**(P458)**

**Structural Optimization of Indole based Compounds for Anti-cancer activities**

Shaveta, Palwinder Singh

Department of Chemistry, Guru Nanak Dev University, Amritsar-143005. India

Based upon the biological potential of various natural moieties, it was planned to incorporate indole, pyrazole and pyrimidine in a single molecule, so that resulting compounds may have better medicinal value in comparison to their individual counterparts. A library of compounds was synthesized and evaluated for their tumor growth inhibitory activities over 60 cell line panel of human cancer cells. Certain compounds were found to be showing promising tumor growth inhibition at various human cancer cell lines with GI50 in µM range. On the basis of enzyme immunoassay and molecular modelling studies, dihydrofolate reductase (DHFR), was found to be the probable cellular target of these compounds. The rationale for design of molecules, details of their synthesis and biological studies will be presented.

**(P459)**

**The Extra Cellular Loop 2 (ECL2) of C5a Receptor. Structure by Folding\***

Dr. Soumendhra Rana

Chemical Biology Laboratory, School of Basic Sciences, Indian Institute of Technology, Bhubaneswar, OD, 751007, India

The C5a receptor (C5aR) is a major chemoattractant receptor of druggable proteome, phylogenetically related to the rhodopsin subfamily of the G-protein coupled receptors (GPCRs). Ubiquitously expressed in variety of cells, including the phagocytes, C5aR is involved in

numerous non-immunological and immunological signaling events, ranging from CNS development, tissue regeneration, chemotaxis, production of reactive oxygen species (ROS) to the release of enzymes. The plethora of biological responses, initiated by C5aR requires binding of complement component 5a (C5a), a robust pro-inflammatory polypeptide, generated by complement activation, an integral part of innate immunity. C5a engages the entire extracellular milieu of C5aR, where ECL2 is known to contribute predominantly toward C5a binding and signaling. However, in the absence of C5aR structure, exact binding mode of C5a to C5aR is unclear. From recent structural studies on rhodopsin family GPCRs, it is evident that the transmembrane region of most of these receptors shares a heptahelical bundle structure, whereas the ECL2s, the longest extra cellular loop displays a wide structural diversity, even within the subfamily. Thus, predicting ECL2 structure is as challenging as crystalizing C5aR in native state, though a high resolution molecular model is approachable combining experimental and computational studies. In our quest toward a high resolution structure of C5aR, we are evaluating allostereism in C5a and the foldability of ECL2 in C5aR, which will be discussed in detail. \*This research is supported by the seed grant, IIT Bhubaneswar

**(P460)**

**Rationally designed indole derivatives as highly effective 5-LOX inhibitors**

Parteek Prasher, Pooja, Palwinder Singh

Department of Chemistry, Guru Nanak Dev University, Amritsar-143005. India

Due to the production of pro-inflammatory prostaglandins and leukotrienes, arachidonic acid (AA) metabolism is being the target of the drugs used for treatment of allergic and inflammatory diseases. Leukotrienes are produced by 5-lipoxygenase (5-LOX) through the participation of 5-LOX activating protein (FLAP). Hence, decreasing leukotriene biosynthesis through the inhibition of 5-LOX has been extensively studied as a potential target for the development of novel therapies of 5-LOX associated diseases. Zileuton, MK-886 and MK-0591 and a few limited drugs are being clinically used for the treatment of LOX-mediated diseases. Based upon the structures of some known 5-LOX inhibitors, a set of compounds carrying appropriate substituents at N-1 and C-3 of indole were synthesized and investigated for 5-LOX inhibitory activities. Fifty percent inhibitory concentration (IC<sub>50</sub>) of these compounds ranges from 0.6 to 5  $\mu$ M and found to be comparable to that of clinically used 5-LOX inhibitor, Zileuton. During further refinement of the molecules, amino acid appended indoles were synthesized. IC<sub>50</sub> of these compounds ranges from 0.0086 to 8.33  $\mu$ M, better than that of the previous set of compounds. These compounds showed significant hydrogen bonding interactions with the amino acid residues in the active site of the enzyme as observed during their docking studies.

Rationale of the design of molecules, their synthesis, biological studies and molecular modeling will be presented.

**(P461)**

**QSAR study of Anti-bacterial activity of Mannich bases against  
*Pseudomonas aeruginosa***

Teena Pareek, Chanchala Joshi, A.V. Bajaj, Deepak Khare, Dheeraj Mandloi  
School of Chemical Sciences, DAVV, Indore

In the present study, we have made efforts to investigate Anti-bacterial activity of Mannich bases against *Pseudomonas aeruginosa*. The results have shown that Anti-bacterial activity of these compounds can be modeled excellently in tri-parametric models in which Weiner index W, Balaban index F and Topological index T played a dominating role. The predictive ability of the model is discussed on the basis of cross-validation method. The superiority of these indices over several other molecular descriptors is critically examined. The values obtained for the best model are-  $R^2 = 0.6278$ , Adjusted  $R^2 = 0.4417$ , Coefficient of variation = 0.2811 and F-ratio = 3.374.

**(P462)**

**Synthesis of 2-(piperidin-1-yl) quinoline based N-hydrazide biquinoline derivatives and their antimicrobial and antioxidant activity**

Gaurav G. Ladani and Manish P. Patel\*  
Sardar Patel University

A new series of N-hydrazide biquinoline derivatives bearing 2-(piperidin-1-yl) quinoline have been synthesized via a one-pot multicomponent reaction. All the title derivatives were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, mass spectra and elemental analysis. In vitro antimicrobial activity of the synthesized compounds was investigated against a representative panel of pathogenic strains using broth microdilution method (MIC). In vitro antioxidant activity was evaluated by ferric-reducing antioxidant power method.

**(P463)**

**Preferential Repair of Clustered Abasic Sites in TATA Box Consensus Sequence as Compared to CpG Island: Study through Molecular Dynamics and Enzyme Kinetics**

Vandana Singh, Bhavini Kumari, Banibrata Maity, Debabrata Seth and Prolay Das  
Indian Institute of Technology Patna

Radiation, chemicals and many endogenous processes cause spontaneous damage to the cell, in particular cellular DNA. Sometimes there may be creation of abasic sites in isolation or in clusters where two or more closely spaced damaged lesions like strand breaks, abasic sites, or oxidized bases occur within a few helical turn of DNA. Herein repair activity of APE1 enzyme on two different DNA sequences of genomic importance have been analysed; TATA box consensus sequence and CpG Island sequence.

The core sequences of TATA box and CpG Island are incorporated in the central positions of 51 bases long oligonucleotides having deoxyuracil residues that are convertible into abasic sites by treatment with UDG enzyme. Thus, clustered abasic site was created by two abasic sites close to one another in opposite strands at precise positions. Two model oligomer duplex systems in the form of TATA box core sequence and core CpG island sequence with bistranded abasic-clustered DNA damage were generated and rate of repair of those bistranded abasic-clustered DNA damages by APE1 enzyme were monitored by enzyme kinetics and fluorescence dynamics. For study of repair process using fluorescence dynamics, the oligomer duplex were saturated with EtBr and then treated with APE1 enzyme where time resolved fluorescence spectroscopy exhibit noticeable decrease in the weightage of the 21 ns component of the dye following APE1 reaction. This confirmed an increased APE1 enzyme activity on TATA box as compared to CpG island. In enzyme kinetics, the parameters showed higher  $K_m$  and lower catalytic efficiency for APE1 enzyme acting on CpG island mimicking sequence while low  $K_m$

and higher turnover for TATA box consensus sequence. Bistranded abasic clusters in TATA box can be repaired more efficiently, however the process is risky since unrepaired DSBs can be potentially lethal and mutagenic.

**(P464)**

**Synthesis of a New Class of Proteasome Inhibitors: Probing the Proteasome Biology**

Neena K K and PakkirisamyThilagar\*

Inorganic and Physical Chemistry Department, Indian Institute of Science, Bangalore-560012, India.

Since the discovery of lysosome it was believed that cellular proteins are degraded by this organelle. However, several independent researchers showed strong evidence for non-lysosomal intracellular protein degradation, but the mechanisms for this process were unclear until the discovery of proteasome. Proteasome is essential in regulating degradation of many vital regulatory molecules involved in apoptosis. Since then proteasome inhibition by targeting 26S proteasome become a novel approach for cancer treatment<sup>1, 2</sup>. Recently, a dipeptide boronic acid "Bortezomib" has been approved by FDA USA for multiple myeloma treatments. The antitumor activity of Bortezomib is involved in regulation of a broad array of cellular processes, such as cell cycle and division, regulation of transcription factors, and assurance of the cellular quality control. However, this drug causes adverse effects like thrombopenia, fatigue, peripheral neuropathy<sup>3</sup>. This may be due to the non-selectivity of drug to normal proliferating cells in addition to cancerous cells. These issues necessitate further studies on the design and development of novel proteasome inhibitors with improved selectivity. To address this problem, we have designed and synthesized a series of novel proteasome inhibitors and evaluated their cytotoxicity against normal and cancerous cells. Real time visualization of biological process with fluorescent probes has attracted much interest in recent years<sup>4</sup>. So to monitor the cellular drug uptake we conjugated the new proteasome inhibitors with highly luminescent BODIPY dyes<sup>5</sup>. The design, synthesis, docking studies and results from invitro evaluation of synthesized compounds in different cancer cell lines will be described in detail.

References:

- 1)W. Baumeister, Annu. Rev. Biochem. 1999, 68, 1015.
- 2)Michael Groll, Chem. Rev. 2007, 107, 687.
- 3)Paul. E. Fleming, Drug discovery today, 2010, 15, 243.
- 4)Injae Shin, ChemSoc Rev. 2013, 10.1039/c3cs60271k.
- 5)Neena K K, PakkirisamyThilagar\* unpublished work.

**(P465)**

**Folic acid functionalized grapheme quantum dots for cancer cell imaging**

Shobha Waghmode<sup>1</sup>, Preeti Nigam Joshi<sup>2</sup> and Dhiman Sarkar<sup>2</sup>

<sup>1</sup>Abasaheb Garware Arts and Sci.College, Pune 411004, India, <sup>2</sup>Combichem bioresource centre, NCL, Pune 411008, India

Graphene quantum dots (GQDs) have attracted significant attention in recent days due to its superior properties, such as high photo stability against photo-bleaching and blinking, biocompatibility, and low toxicity. Here we are reporting folic acid functionalized GQDs for

specific cancer cell imaging. Graphene was prepared from the raw graphite by sonicating H<sub>2</sub>SO<sub>4</sub> and strong oxidizing agent. Then reacted with H<sub>2</sub>O<sub>2</sub> or KO<sub>2</sub> which ends with graphene oxide (GO). GO treated with different reducing agents with 30 min sonication followed by 4 hour refluxing at 100°C. GQD prepared by using dialysis method by dialyzing graphene against deionised water for 24 hours. GQDs were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Raman spectroscopy, IR, UV-Visible and XRD. QDs exhibit excellent fluorescence properties and here we applied Folic acid (FA) functionalized GQDs for cancer cell imaging to achieve efficient and target specific delivery of a graphene quantum dot (GQD) using folic acid (HA) (GQD-FA) as a targeting agent. Folic acid binds with FA receptors on cell surface specifically. In vitro cellular imaging, exhibited strong fluorescence from FA receptor over expressed on MCF-7 (Breast cancer) and HepG2 cell lines which clearly indicate the efficacy of our FA functionalized graphene QDs in cell imaging.

**(P466)**

**Development of a novel class of pyrazoline and isoxazole derivatives as potential antimicrobial, antituberculosis, antimalarial and antioxidant agents**

Piyush N. Kalaria, Shailesh P. Sataasia and Dipak K. Raval\*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar- 388 120, Gujarat, India

The medical consequence of pyrazoline and isoxazole condensed systems and the raise in trouble of multidrug resistant bacteria pathogens has impelled us to synthesize substituted pyrazoline 6a-l and isoxazole 7a-l via the reactions of chalcones with hydrazinhydrate and hydroxylamine hydrochloride in ethanol. The title compounds were screened for their preliminary in vitro antibacterial activity against a panel of pathogenic strains and in vitro antituberculosis activity against Mycobacterium tuberculosis H37Rv. Compounds 6k, 6l, 7h and 7k exhibited excellent antibacterial activity and few of them have been recognized as moderate antituberculosis agents compared with the first line drugs. Consequently, they were also screened for their in vitro antimalarial activity against Plasmodium falciparum and in vitro antioxidant activity by ferric-reducing antioxidant power method. Among the synthesized compounds, half of the compounds exhibited terrific antimalarial activity and majority of compounds showed highest antioxidant potency.

**(P467)**

**An efficient one-pot synthesis and biological evaluation of some novel 2-amino-3-cyanopyridine derivatives bearing 5-imidazopyrazole nucleus**

Sharad C. Karad, Vishal B. Purohit and Dipak K. Raval\*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar- 388 120, Gujarat, India

A novel water soluble Cu(NHC)Cl complex was conveniently synthesized and characterized by NMR spectroscopy. It was employed for three component Click reaction of benzyl chlorides (1a-e), alkynes (2a-c) and sodium azide (3) in water as solvent at room temperature. All the synthesized compounds (4a-o) were characterized by elemental analysis, IR, <sup>1</sup>H NMR and mass spectrometry. The catalyst was easy to prepare, very versatile, reusable and was found to be highly active at low catalyst loading towards the reaction.



**(P468)**

**Investigation of potential application of Ferrocene-1,2,4-triazole-Carbohydrates hybrid compound in the breast Cancer cell bioimaging.**

Nilesh M. Kahar, Dr. Vidya Avasare

A sugar transporter (Glut5) is known to be overexpressed by breast cancer cell. Glut5 is responsible to transfer the fructose hence high fructose uptake by cancerous cell can be measured to identify the cancerous growth in the breasts. To observe the cancerous growth usually radioactive sugars have been used. Since fluorescent tagged sugars in particular fructose can be cheaper, safer and an impressive alternative to the radioactive probes in bioimaging of breast cancer cells hence it is very necessary to synthesis a florescent labeled sugars for the bioimaging. 1, 2 Recently, we have developed a new ferrocene embedded fluorophore which can be widely employed to tag various biomolecules. In the quest of better tool for the imaging of breast cancer cells, we have synthesized the ferrocene fluorophore labeled carbohydrates and we have been investgaing the prospective application of these compounds in the bioimaging of breast cancer cell lines.

References:

- 1) J. Levi, Z. Cheng, O. Gheysens, M. Patel, C. T. Chan, Y. Wang, M. Namavari, S. S. Gambhir Bioconjugate Chem. 2007, 18, 628-634.
- 2) Weissleder, R. Ntziachristos Nat. Med. 2003, 2 (2), 123-31.

**(P469)**

**Ferrocene Incorporated Small Molecule Fluorophore for Selective Detection of Zinc**

Shweta Yelgaonkar, Vidya Avasare

Syntheses of fluorophore have been significantly attracting scientific attention due to their enormous application in non-destructive measurements of biological events. Ferrocene has widely been employed in syntheses of catalysts, organometallic compounds, materials and biologically important drug molecules. However syntheses of ferrocene incorporated fluorophore have much less been explored.

Metalloneurochemistry has been dominated by d-block elements and Zn(II) is the second most abundant and important element among those in human brain. Hence, it is very essential to design fluorophore probes for selective Zn(II) detection in presence of Na(I), K(I), Ca(II) and Mg(II); which can be used to understand the role of Zn (II) in neurophysiology and neural disorders. The synthesis of Zn(II) selective fluorophore has mainly been inspired by Zinpyr.1 Hence we have designed the ferrocene incorporated fluorophore for the selective detection of Zn(II) ion in the presence of Na(I), K(I), Ca(II) and Mg(II).

**(P470)**

**Design, synthesis, physicochemical exploration, solvation dynamics, and DNA damage of quinolone appended chalcone derivative: A complete study**

Himank Kumar, A.Chattapadhyay, P.Bhavna and Sujit Kumar Ghosh (a\*)  
Visvesvaraya National Institute of Technology, South Ambazari Road, Nagpur

The design, synthesis, characterization and photophysics of a potential bioactive quinoline derivative ADMQ and its interaction with calf-thymus DNA (ct-DNA) has been reported using experimental and theoretical spectroscopic techniques. Absorption spectroscopy, steady state fluorescence spectroscopy, NMR and FTIR experimental spectroscopic techniques have been used along with the carcinogenicity/ cytotoxicity/ mutagenicity screening test and DNA electrophoresis studies. The experimental observations have been rationalized theoretically by density functional theory (DFT), ZINDO-CI molecular modeling calculations and molecular docking. The environmental effects have been studied in ground and excited state in a variety of solvents of different polarity. Photophysics of the molecule shows the Intramolecular charge transfer (ICT) and Twisted intramolecular charge transfer (TICT) in the excited state, followed by a structural change in the molecule. The compound does not exhibit any deleterious effect or toxicity to the bacterial cell in carcinogenicity/cytotoxicity/mutagenicity studies. Agarose gel DNA electrophoresis has shown partial cleavage of DNA by this potential drug ADMQ. Interaction of ADMQ with ct-DNA leads to dramatic decrease in the fluorescence intensity of the compound, suggests the binding of ADMQ with ct-DNA. The DNA-ligand (ADMQ) binding affinity has been predicted and verified using Molecular Docking Methodology. The experimental and theoretical spectroscopic research describe herein could be very useful to assess the mechanistic details of chalcone derivative in physiological conditions.

(P471)

**Push-pull chromophores as colorimetric chemosensors for cations**

Navdeep Kaur, Priya Singla, Paramjit Kaur and Kamaljit Singh  
Department of Chemistry, Guru Nanak Dev University, Amritsar, India

The field of chemosensors for the detection of anions and cations is a vibrant area of investigation due to their potential applications as diagnostic tools in medical, physiological and environmental applications. One of the most attractive approaches in this field involves the construction of colorimetric chemosensors since visual detection yields immediate qualitative information, which could then be quantified by using spectroscopic tools. Our investigation is aimed at using such organic molecules incorporated with push-pull system for the detection of analytes and developing the easy to make colorimetric sensors that can be utilized to sense and bind a variety of important ions with high selectivity and sensitivity.

In continuation our interest, herein, we shall present BODIPY dye and pyrene based chromophore which act as selective and sensitive colorimetric sensors for Pd<sup>2+</sup>/Hg<sup>2+</sup> and Hg<sup>2+</sup>/Ag<sup>+</sup> respectively.

(P472)

**PL heterogeneity near single molecule levels in solution-processed europium complex thin films**

Mir Irfanullah and Arindam Chowdhury  
Department of Chemistry, Indian Institute of Technology Bombay Powai, Mumbai

Organic chromophore sensitized luminescent complexes of europium have been extensively investigated using ensemble measurements. However, there is a dearth of literature reports about visible light induced luminescent behaviors of Eu(III) complexes near single molecule levels, which can often shed new insight on optoelectronic properties which are obscured in bulk

studies. To study such behaviors, a visible light excitable luminescent Eu(III) complex, Eu(OPH)<sub>3</sub> · 2CH<sub>3</sub>OH {where OPH = 9-oxidophenalenone} has been synthesized and characterized in solution. The photoluminescence spectrum of the complex at ensemble level displays both broad band ligand fluorescence and a characteristic sharp Eu(III) emission with long radiative lifetimes, which clearly points out to energy transfer to Eu(III) from the excited ligand. We have successfully imaged the luminescence emerging from the complex near single molecule levels by embedding these on glass and exciting the ligands using a 405 nm laser in an epifluorescence microscope capable of obtaining dispersed emission spectra. We find that the relative intensities of emission of the ligand and the Eu(III) center varies considerably for various spatially separated emission spots, which essentially points out to a remarkable degree of heterogeneity near single molecule levels. The investigations reveal that heterogeneity occurs due to a range of asymmetric geometries adopted by Eu(III) ions near single molecule levels.

(P473)

### **Synthesis and Spectrally Resolved Single Particle Photoluminescence Imaging of CdS Quantum Dots**

Ramya. C and Arindam Chowdhury\*

Indian Institute of Technology-Bombay, Powai

Ensemble photoluminescence measurements (steady state measurements) give the average behaviour of all the individual particles in the sample under study. The inhomogeneous broadening effect due to different factors can be known only if the nanocrystals can be probed at the single particle level. Single Molecule Fluorescence Microscopy is a powerful tool for imaging and probing the dynamics of individual fluorescent molecules and luminescent semiconductor nanocrystals (Quantum Dots). Cadmium Sulphide (CdS) Quantum Dots (QDs) have been synthesized in reverse micelle method, characterized, imaged and single particle level spectral studies have been carried out to understand the reason for spectral broadening.

Introduction

CdS Quantum Dots with different sizes can be synthesized using reverse micelle method by varying R value. Nikon Eclipse 2000U (inverted) epi fluorescence microscope was used to image the individual CdS nanocrystals.

Experiment/Methods

Imaging of CdS NCs were done by spin coating suitable concentration of sample on the microscope cover slip in order to get individual CdS quantum dots using epi-fluorescence microscope and exciting the sample with 405nm diode laser. The emitted light from the sample was allowed to pass through a CCD camera and collected movies with an exposure time of 500 ms. Movie collected shows blinking spots of diffraction limited particles. Spectrally resolved PL imaging of individual spatially isolated CdS NCs is done using a combination of slit and transmission grating. Each spectrum was calibrated with 3 different laser lines of wavelength 488, 532 and 633 nm and analyzed using ImageJ and Origin 8 softwares.

3.ResultsandDiscussion

PL study of two CdS samples (R15 and 10) synthesized by reverse micelle technique show broad defect emission peak with FWHM values of 237.9 nm and 172.9 nm and peak positions at 670.82 nm and 625.95 nm respectively. Broadening can happen both because of the size variation of particles in the sample and due to the inherent spectral broadening of individual CdS NCs. The possibility for the spectral broadening due to particle size distribution is ruled out since the CdS NCs selected for the present study (R 10 and R15) does not show any particle size

dependence. So the spectral broadening can be assumed due to the inhomogeneity due to the distribution of multiple defect states located on different nanocrystals.

References:

- [1] Layek, A; De,S; Thorat, R; Chowdhury, A. J.Phys.Chem.Lett. **2011**, 2, 1241-1247
- [2] Ethayaraja, M; Ravikumar, C; Muthukumaran, D; Dutta, K; Bandyopadhyaya, R. J.Phys.Chem.C. **2007**,111,3246-3252.
- [3] Smith, A. M.; Nie, S.M. Acc. Chem.Res. **2010**, 43, 190-200.

**(P474)**

### **Fluorescence Dynamics of Nanomaterials for Potential Applications**

Amitava Patra

Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata, India

There has been a growing interest on utilizing semiconductor quantum dot (QD) for technological applications for their attractive properties. The detailed understanding of the carrier relaxation dynamics is essential because it dictates the overall efficiency in various optoelectronics, photovoltaic, light harvesting and sensing applications. Recent studies reveal that the energy transfer between QD and dye is a Förster resonance energy transfer (FRET) process as established from  $1/d^6$  distance dependence.<sup>1-5</sup> Again, graphene-semiconductor composite nanostructures have been recently emerged as a new class of functional materials because of their potential applications i.e. solar energy conversion, optoelectronic devices, catalysis and sensing. We have analyzed the decays of the fluorescence of QD in GO-CdTe QD composite by using a proposed stochastic model to estimate the number of sites available and the fractional surface coverage of QD by GO sheet. The photoconductivity properties of GO-QD composites with visible illumination have been studied to understand transport properties of GO-QD composite.<sup>6</sup>

References

- 1 S. Sadhu and A. Patra, J. Phys. Chem. C, 2012, 116, 15167.
2. T. Sen, and A. Patra, J. Phys. Chem. C 2012, 116, 17307 (**Invited Feature Article**).
3. S. Sadhu and A. Patra, J. Phys. Chem. C, 2011, 115, 16867.
4. A. Kar and A. Patra, Nanoscale 2012, 4, 3608 (**Invited Feature Article**).
5. S. Sadhu and A. Patra, ChemPhysChem. 2013, 14, 2641 (**Minireview**).
6. S. Kundu, S. Sadhu, R. Bera, B. Pramanik and A. Patra, J. Phys. Chem. C, 2013,117, 23987-23995.

**(P475)**

### **Synthesis, Characterization and Bioassay of novel beta-lactams**

Devika Rana, Raman Bhadauria, Kuldeep Singh\*

Jaypee University of Information Technology Waknaghat

Selective functionalization of C-H bonds is one of the key challenges in recent synthetic organic chemistry. The advent of techniques such as directing group assisted C-H bond functionalization and cross dehydrogenative coupling have made possible to process the selective

functionalization of inert C-H bonds. Pertinent to these seminal achievements, protocols have been developed for the direct ortho-hydroxylation and ortho-arylation of 2-arylbenzazoles using Pd(OAc)<sub>2</sub> as the catalyst in the presence of suitable oxidants and solvents. In C-O bond formation approach (diacetoxyiodo) benzene (DIB) is acting as hydroxyl source whereas in the C-C bond formation approach aldehyde is acting as aryl equivalent. Both of these methodologies tolerate a diverse array of substituents giving good to excellent yields of corresponding ortho-hydroxylated and ortho-arylated products.

**(P476)**

**Diversity Oriented Approach to Triazole Based Peptidomimetics as Mammalian Sterile 20 Kinase Inhibitors**

Aruna Bitra, Deepthi Goyal, Ruchi Anand, Sambasivarao Kotha  
Department of Chemistry, Indian Institute of Technology Bombay, Mumbai, India.

Protein kinases are important drug targets as they are involved in several pathological conditions. Here, we demonstrate a strategy to develop small molecule inhibitors by using peptidomimetics compounds as target for serine/threonine kinases. In this regard, a unique approach to modified peptides by using copper catalyzed 1, 3-dipolar cycloaddition reaction between various azides and peptides containing alkyne moiety to create a triazole based peptidomimetic library was employed. Various mono- and di-triazole based peptidomimetics have been synthesized by this strategy. All the final products and the alkyne precursors were then screened for anti apoptotic activity against the apoptotic enzyme MST1 towards its substrate H2B. Interestingly, these compounds have yielded competent kinase inhibitors, exhibiting an IC<sub>50</sub> value of 1.2 μM for the pro-apoptotic Mammalian Sterile 20 1(MST1) kinase, which is an important drug target in cardiomyopathy. Further, kinase profiling studies were performed with a panel of kinases both within the Sterile 20 kinase family and also with PI-3K, that doesn't belong to Ste family. Results revealed that compound 7 is a competent MST1 kinase inhibitor, which exhibits high degree of selectivity and specificity for MST1 and does not inhibit the other tested kinases. In addition, docking studies shed light on the binding mode of these compounds. Hence, this knowledge can serve as a starting point for further development of triazole based peptidomimetics for designing selective serine/threonine kinase inhibitors.

**(P477)**

**Design, Synthesis, Characterization and In Silico molecular docking studies of Tetraaza Macrocylic Chelating Agent**

Neelam Yadav, B. Singh\*  
Department of Chemistry, Banaras Hindu University

The use of cyclic polyamine compounds as ligands for metals has expanded over years. Interest in the coordination chemistry of these chelators is due in part their relevance in bioinorganic and catalytic studies, as well as their application in biology, medicine and modern clinical imaging protocols. The macrocyclic complexes are considered to mimic the synthetic models of metalloporphyrins and metalocorrins due to their intrinsic structural properties. The macrocyclic complexes have also received special attention because of their mixed soft-“hard donor character and versatile coordination behaviour and their pharmacological properties, i.e., toxicity against bacterial growth. Macrocyclic ligands form metal complexes more

thermodynamically stable and also kinetically more inert. Acyclic ligands do not usually require harsh condition for complexation but they are more prone to release off the metal in-vivo because of transmetallation by endogenous metal ion competition or transchelation by endogenous ligands (eg. phosphates). A tetraaza mono-thia macrocyclic chelator [C10H20N4O2S] has been synthesized and characterized by IR, NMR (1H & 13C) spectroscopy and ESI-Mass spectrometry. DFT study based on B3LYP method with 6-311G\*\*(d,p) basis set for all atoms by Gaussian 03W programme which results dipole-moment, vibrational frequency and optimized structure of chelating agent. Energy, dipole moment and point group of optimized structure was found -1160.9941 a.u., 10.0831 Debye and C1. In silico study (molecular docking) of ligand with proteins OSC, HMGCR of human and mouse gives significant results in terms of free energy of binding, inhibition constant, VdW+H-bond+desolvation energy, electrostatic energy, total intermolecular energy and interaction surface which concludes this compound showed good binding affinity with these proteins (which are potential enzyme of cholesterol biosynthetic pathway), so have potential ability to reduce high cholesterol level by binding these proteins.

**(P478)**

**A new scale of electronegativity invoking other atomic properties**

Seema Dhail, Lalita Ledwani and Tanmoy Chakraborty\*  
Manipal University, Jaipur

The study of electronegativity is an active field of research. The concept of electronegativity is very much efficacious in chemical science to correlate the chemical binding, reactivity and many other physico-chemical properties of atoms and molecules over a long period of time. The electronegativity is not only ubiquitous in chemistry but also, in present times, finds application in physics, biology and geology. It has also been pointed out that electronegativity idea helps in the qualitative understanding and elucidation of quark chemistry. Since the concept of electronegativity is not a physical observable, the possibility of quantum mechanical evaluation of electronegativity can be ruled out. As we know, the periodic properties are interrelated, we have adopted that principle to evaluate a new scale of electronegativity. In this venture, we have tried to compute a new scale of electronegativity based on other atomic properties viz. absolute radii of atoms and atomic hardness invoking linear regression analysis. Our proposed ansatz for evaluating the electronegativity is as-  $\chi = a(\eta/r) + b$ , where  $\chi$ ,  $\eta$  and  $r$  represent atomic electronegativity, atomic hardness and absolute radii of the atoms and  $a$  and  $b$  are regression constants. The new scale of electronegativity satisfies all the "sine qua non" of the electronegativity. To validate our scale of electronegativity, we have applied our computed data to the real field. A nice correlation of experimental results with their theoretical counterparts strengthens our model of electronegativity.

**(P479)**

**A comparative study of the non-radiative decay channels in conjugated long-chain iminium ions and nitrones**

Praveen Saini, Anjan Chattopadhyay\*  
Department of Chemistry, BITS-PILANI, K.K. BIRLA Goa Campus,  
Zuarinagar, Goa, India

Conjugated long-chain iminium ions, such as retinyl iminium systems are well known for their ultrafast cis-trans isomerizations. Theoretical investigations have revealed the presence of conical intersections (CI) as the key player behind these processes. These S0/S1 intersections (TICT CI) are normally of the peaked types and goes through a barrierless one-bond-flip (OBF) process which occurs in the central part of the molecule. However, presence of proper substituents and approach of counter ions may shift the characteristic CI geometry or slow down the process by a sloped topography. Some evidences of the kinked CI through a Hula-twist (HT) path have also been reported; however, these are the primary routes for isomerization in neutral polyenes. In contrast, the nitron systems are not known for any ultrafast cis-trans isomerization processes through singlet states. The conjugated N-alkyl retinyl nitrones were reported to give stable oxaziridines under light, and these were found to convert back to nitrones in dark. Our present CASSCF/6-31G\* studies have explored the possible non-radiative channels in these types of nitrones. Conical intersection (S0/S1) geometries arising out from the OBF and HT motion in the central part of these nitrones are at higher energy (3.5-5 kcal/mol) level than the relaxed planar excited state and thereby reduces the chance of any cis-trans isomerization through these motions. Interestingly, a CI due to the twist in the terminal C-N-O part is found to be lowest in energy and seems to be heading towards the oxaziridine geometry. The allowed S0-S1 transitions in these nitrones are found to have transition moment values of 4.9 D which is comparatively lower than that of the conjugated iminium ion systems (~7.5 D).

**(P480)**

**A Computational Study of Homolytic Bond Dissociation Process Involved in the Initiation Process of Atom Transfer Radical Polymerization**

Chetana Deoghare, Raghu Nath Behera and Rashmi Chauhan

Department of Chemistry, Birla Institute of Technology & Science, Pilani – K. K. Birla Goa Campus, Zuarinagar, Goa, India

The paper presents a computational study on homolytic bond dissociation of a number of alkyl halides R-X (R = succinimide, ethyl-2-haloisobutyrate, X = Cl, Br, I) which can be potential initiators for the atom transfer radical polymerization (ATRP). The density functional theory with B3LYP functional and 6-31+G(d)/LanL2DZ basis sets is used in the prediction of geometries and energetics associated with the dissociation of R-X bond. The relative equilibrium constant for the ATRP activation/deactivation process is calculated from the free energy values, and its variation with system parameters (such as solvent, temperature and substituent) is investigated. Comparison with the known initiators for the ATRP shows that some of the studied compounds have potential to initiate the ATRP process.

**(P481)**

**Looping dynamics of a single chain with internal friction**

Nairhita Samanta and Rajarshi Chakrabarti\*

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai

The primary step in RNA and protein folding is loop formation between the two internal fragments and the quantity of prime interest is the average loop formation time ( $\bar{t}_{loop}$ ). Usually the looping time is calculated within Wilemski-Fixmann (WF) framework [1] and looping time was found to be proportional to the solvent viscosity. But recently a non-vanishing looping time

in polypeptide chain has experimentally been observed at extrapolated zero viscosity of the solvent. Subsequently this has been attributed to a solvent independent dry or "internal friction", present within the molecule and supposedly arise due to Hydrogen bonding, dihedral angle rotation etc [2]. We have calculated  $\tau_{loop}$  for a Gaussian chain with internal friction within Rouse as well as Zimm description following WF model and show that depending on the time scale involved with the internal friction, the looping time for a Rouse chain with internal friction increases by a factor of 2-15 as compared to the case of no internal friction, which supports experimental findings of Krieger et. al [3].  $\tau_{loop}$  also shows a fractional viscosity dependence as is observed empirically [2] and lower dependence on chain-length. Currently we are looking at the loop formation between interior monomers.

#### References:

1. G. Wilemski and M. Fixmann, J. Chem. Phys. 60, 866 (1974)
2. N. Samanta and R. Chakrabarti, Chem. Phys. Letts. 582, 71 (2013)
3. F. Krieger, B. Fierz, O. Bieri, M. Drewello and T. Kiefhaber, J. Mol. Biol. 332, 265 (2003)

#### (P482)

##### **Importance of synergistic effect in protein stabilization and counteraction of denaturing effect of urea by glycine betaine**

Narendra Kumar, Nand Kishore

Indian Institute of Technology Bombay, Mumbai

The counteraction of denaturing effect of urea by osmolytes has been one the most studied problem of osmolyte action. However, possible synergy in the osmolyte mixture has often been neglected. Here, we report synergy in glycine betaine (GB)-urea mixture by using a model peptide. The result shows that in GB-urea mixture, GB acts as stronger osmolyte and urea becomes a weaker denaturing agent which is clear from the increase in the exclusion of GB from the peptide surface and decrease in the interactions between peptide and urea. The reason for this synergistic behaviour is due to the direct interactions between GB and urea through hydrogen bonding and Lennard-Jones interactions between them, along with enhancement in strengthening of the hydrogen bonding network of water in GB-urea mixture. This study might be of potential importance in the field of agriculture, medicine and biotechnology and to our best of knowledge, is the first study showing the importance of synergy and providing the molecular level explanation for it.

#### References:

1. Narendra Kumar, Nand Kishore; J. Chem. Phys., 139 (2013) 115104.
2. Narendra Kumar, Nand Kishore; Phys. Chem. Chem. Phys., under review

#### (P483)

##### **The triplet-singlet gap in the m-xyllylene radical: a not so simple one**

Daniel Reta Maneru,<sup>1</sup> Arun K. Pal,<sup>2</sup> Iberio de P. R. Moreira,<sup>1</sup> Sambhu N. Datta<sup>2</sup> and Francesc Illas<sup>1</sup>

<sup>1</sup>Departament de Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, C/ Martí- i Franques 1, E-08028 Barcelona, Spain. <sup>2</sup>Department of Chemistry, Indian Institute of Technology, Bombay, Powai,



Mumbai, India.

Meta-benzoquinodimethane (MBQDM) or m-xylylene provides a model for larger organic diradicals, the triplet-singlet gap being the key property. In the present work this energy difference has been the object of a systematic study by means of several density functional theory based methods including B3LYP, M06, M06-2X, HSE and LC- $\omega$ -PBE potentials and a variety of wave function based methods such as Complete Active Space Self Consistent Field (CASSCF), Multi Reference Second Order Moller Plesset (MRMP), Difference Dedicated Configuration Interaction (DDCI) and Multireference Configuration Interaction (MRCI). In each case various basis sets of increasing quality have been explored, and the effect of the molecular geometry is also analyzed. The use of the triplet and broken symmetry (BS) solutions for the corresponding optimized geometries obtained from B3LYP and especially M06-2X functionals provide the value of the adiabatic triplet-singlet gap closer to experiment when compared to the reported value of Wenthold, Kim and Lineberger, (J. Am. Chem. Soc., 1997, 119, 1354) and also for the electron affinity. The agreement further improves using the full  $\omega$ -valence CASSCF(8,8) optimized geometry as an attempt to correct for the spin contamination effects on the geometry of the broken symmetry state. The CASSCF, MRMP and MRCI, even with the full  $\omega$  valence CAS(8,8) as reference and relatively large basis set, systematically overestimate the experimental value indicating either that an accurate description must go beyond this level of theory, including  $\omega$ <sup>3</sup> electrons and higher order polarization functions or perhaps that the measured value is affected by the experimental conditions.

**(P484)**

**Conformational dynamics of a short antigenic peptide in its free and antibody-bound forms gives insight into the role of beta-turns in peptide immunogenicity**

Rashmi Tambe Shukla and Yellamraju U. Sasidhar

Department of Chemistry, IIT Bombay

Immunological experiments on a synthetic 36 residue peptide (75-110) from Influenza hemagglutinin have been shown to elicit anti-peptide antibodies (Ab) which could cross react with the parent protein. To understand the factors behind the immunogenicity of a short peptide fragment, 98YPYDVDPDYASLRS110, from hemagglutinin protein and its conformational preferences in free and Ab-bound forms, we have studied this 13mer peptide in its free and Ab-bound forms using MD simulations with OPLS-AA/L force field at 293 K and 310 K. Our results show that the free antigen (Ag) peptide samples both 'native-like' and Ab-bound-like conformations in explicit water suggesting possible reasons for its immunogenicity and the cross-reactivity observed for the anti-peptide Ab towards the parent protein. The free Ag samples a type I  $\beta$ -turn involving the sequence 'DYAS' specifically at 310 K, which is important in Ab binding. On the other hand, the bound form of the Ag peptide samples two type I  $\beta$ -turns in tandem involving sequences 'YPYD' and 'DYAS' suggesting that conformational changes are induced in the 13mer Ag upon Ab binding. Our results also show that upon binding the conformational fluctuations are relatively more reduced for the interfacial residues in the Ag in comparison to the Ab. Further, in this study we have also discussed in detail the role of different residues involved in Ag-Ab binding and interaction.

**(P485)**

**Efficient nuclease active metal chelates: Synthesis, characterization and biocidal screening**

N.Raman and N.Pravin

VHNSN College, Virudhunagar

Coordination compounds of Cu(II) and Zn(II) coupled with Schiff bases [obtained by the Knoevenagel condensation of 2,4-pentanedione and benzaldehyde (3-benzylidene-pentane-2,4-dione) with p-substituted (X) aniline, where X = -NO<sub>2</sub> (L1), -H (L2), -OH(L3) and -OCH<sub>3</sub>(L4)] were synthesized. They were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, UV-Vis, IR, Mass, EPR, molar conductance and magnetic susceptibility measurements. All the complexes have square-planar geometry around the central metal ion. Moreover, the DNA cleavage efficiencies of these complexes with pBR322 DNA have been investigated by gel electrophoresis. The complexes were found to promote the cleavage of pBR322 DNA from the supercoiled form I to the open circular form II and the linear form III in presence of hydrogen peroxide. Finally, in vitro antibacterial activities of the Schiff bases and their metal complexes were screened against the bacteria *Staphylococcus aureus*, *Bacillus subtilis*, *Salmonella typhi*, *Escherichia coli* and *Pseudomonas aeruginosa* and fungi *Rhizoctonia bataticola*, *Fusarium Solani*, *Candida albicans*, *Culvularia lunata* and *Aspergillus niger*. The complexes show enhanced antifungal and antibacterial activities compared to the free ligands.

**(P486)**

**Sodium-Hydroxide-Mediated Synthesis of Highly Functionalized [1,6]-Naphthyridines in a One-Pot Pseudo Five-Component Reaction**

Satavisha Sarkar, Deb K. Das and Abu T. Khan\* Abu

IIT Guwahati, Guwahati

A one-pot pseudo five-component reaction has been developed for the synthesis of hitherto unreported 5-amino-7-alkoxy-2-methyl-2,4-aryl-1,2-dihydro-1,6-naphthyridine-8-carbonitriles using aryl methyl ketones/alkyl methyl ketones, malononitrile and alcohols in the presence of sodium hydroxide under reflux conditions. Following identical reaction procedure, various 5-amino-2-methyl-2,4-diaryl-7-(aryltio)-1,2-dihydro-1,6-naphthyridine-8-carbonitrile derivatives were also synthesized using aryl methyl ketones, malononitrile and thiophenols in presence of sodium hydroxide in ethanol. High-bond forming efficiency, good yields and use of readily available base are some of the salient features of this multicomponent reaction. Compiling all the results, this synthetic procedure displays the efficiency and synthetic value of the one-pot multicomponent reaction for the synthesis of substituted 1,6-naphthyridine in which two rings or six new bonds were formed in highly chemoselective manner.

**(P487)**

**Removal of zinc using a novel microbe-polysaccharide adsorbent**

Manasi, Vidya Rajesh, T. Sathvika, N. Rajesh

Department of Biological Sciences, Department of Chemistry, Birla Institute of Technology and Science, Pilani-Hyderabad Campus, Jawahar Nagar, Shameerpet Mandal, R.R. Dist, 500 078 (AP), India.

Electronic industry is one of the major contributors of heavy metal pollution [1]. Removal of these heavy metals by use of greener technologies is of paramount importance. Our work demonstrates the efficiency of novel *Halomonas* BVR 1 bacterial strain isolated from electronic industry effluents and its subsequent immobilization in chitosan for the removal of zinc. Active sites on chitosan involving hydroxyl and amino groups act as a host to welcome the guest, zinc ions [2]. This kind of a host guest interaction leads to an increase in the number of metal binding groups and enhances the adsorption capacity considerably. The characterization of the immobilized adsorbent was carried out using FT-IR and SEM-EDAX techniques. Various analytical parameters were studied such as the effect of pH, thermodynamics and kinetics. Concentration of zinc was analyzed using Atomic Absorption Spectrophotometry (AAS). Zinc was quantitatively adsorbed in the pH range 5-7. This system favored Freundlich isotherm with a Langmuir adsorption capacity of 38.75 mg g<sup>-1</sup>.

#### References

- [1] P. Kiddee, R. Naidu, M. H. Wong, Electronic waste management approaches: An overview, *Waste Manage.* 33 (2013) 714-721.
- [2] X. J.Hu, J.S Wang, Y.G Liu, X Li, G. M Zeng, Z.L.Bao, X.X Zeng, A.W.Chen, F.Long, Adsorption of chromium (VI) by ethylenediamine-modified cross-linked, magnetic chitosan resin: Isotherms, kinetics and thermodynamics, *J. Hazard. Mater.* 185 (2011) 306–314.

#### (P488)

##### **Tuning the photophysical properties of $\pi$ - conjugated copolymer based on thiophene-benzothiadiazole by controlling the solvent induced mode of aggregation**

Renjith S, T Prasada Rao, and Sudha J D\*

Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Trivandrum, Kerala, India

Research on solution processable  $\pi$ - conjugated polymers are receiving attention because of their unique optoelectronic properties and find applications in photovoltaics, super capacitors, sensors and so forth. Active layer morphology, exciton conjugation length and crystallinity are the key factors which govern the efficient performance of these devices. Literature reveals that solvent used for the fabrication of active layer plays an important role in the modulation of optoelectronic properties through the changes in its mode of aggregation . In the present work, we are addressing the role of solvent/nonsolvent ratio in tuning the photophysical properties of the copolymer based on 3-hexylthiophene and benzothiadiazole(PD3HTBT). Copolymer was synthesised by the chemical oxidative polymerisation using anhydrous ferric chloride in chloroform under reflux conditions. It was characterised for its chemical structure and solubility studies made using solvents of varying polarity index. Molecular aggregation studies were performed by changing non-solvent/solvent ratio. Significant non-solvent in solution makes solute-solvent interaction energetically less favorable and forcing polymeric chain segments to approach each other resulting in aggregation. The extent and mode of aggregation can be conveniently determined by UV-vis and fluorescent emission spectroscopic analysis. Variation of photophysical properties of PD3HTBT mainly involves radiative processes. From steady state and time resolved emission studies in chloroform-ethyl acetate, chloroform-ethanol and tetrahydrofuran-water mixtures revealed solvatochromic effects which have been related to the formation of J or H-aggregates. Aggregation is accompanied by the strong

quenching/enhancement of photoluminescence efficiency. These effects have been related to the conformational changes of the polymeric backbone which induce a modification of effective conjugation length causing optical shifts. The results generated in the present work can be exploited for the fabrication of photovoltaic devices with efficient performance.

#### References

- [1] Choudhury, P. K.; Bagchi, D.; Sangeeth, C. S. S.; Menon, R. J. *mater. Chem.* **2011**, 21, 1607-1614.
- [2] Scharsich, C.; Lohwasser, R. H.; Sommer, M.; Asawapirom, U.; Scherf, U.; Thelakkat, M.; Neher, D.; Köhler, Anna J. *polym. Sci. B* **2012**, 50, 442-453.
- [3] Traiphol, R.; Sanguansat, P.; Sriksirin, T.; Kerdcharoen, T.; Osotchan, T. *Macromolecules*, **2006**, 39, 1165-1172.
- [4] Ananthakrishnan, S. J.; Varathan, E.; Ravindran, E.; Somanathan, N.; Subramanian, V.; Mandal, A. B.; Sudha, J. D.; Ramakrishnan, R. *Chem. Comm.* **2013**.

#### (P489)

##### **Ferrocene Incorporated Small Molecule Fluorophore for Selective Detection of Zinc**

Shweta Yelgaonkar

Purdu

Syntheses of fluorophore have been significantly attracting scientific attention due to their enormous application in non-destructive measurements of biological events. Ferrocene has widely been employed in syntheses of catalysts, organometallic compounds, materials and biologically important drug molecules. However syntheses of ferrocene incorporated fluorophore have much less been explored. Metalloneurochemistry has been dominated by d-block elements and Zn(II) is the second most abundant and important element among those in human brain. Hence, it is very essential to design fluorophore probes for selective Zn(II) detection in presence of Na(I), K(I), Ca(II) and Mg(II); which can be used to understand the role of Zn (II) in neurophysiology and neural disorders. The synthesis of Zn(II) selective fluorophore has mainly been inspired by Zinpyr.1 Hence we have designed the ferrocene incorporated fluorophore for the selective detection of Zn(II) ion in the presence of Na(I), K(I), Ca(II) and Mg(II).

#### (P490)

##### **The First Phenalenone Based Receptor for Selective Iodide Ion Sensing**

Amrita Mitra,<sup>a</sup> Anand Pariyar,<sup>a</sup> Suranjana Bose,<sup>a</sup> Pinaki Bandyopadhyay<sup>a</sup>  
and Arindam Sarkar<sup>b\*</sup>

<sup>a</sup>Department of Chemistry, University of North Bengal, Siliguri, West Bengal, India. <sup>b</sup>Invictus Oncology Pvt Ltd, India Innovation Research Center, 465 Patparganj Industrial Area, Delhi, India.

Substituted phenalenones in the form of radical or in complexed form with elements such as Zn, B or Si have left their mark in the area of organic materials over the years[1]. Application of phenalenone in a non radical or non complexed form and as a fluorescent material is rarely reported. On the other hand, molecular devices capable of interacting with ions in solution and signaling their presence by changing optical properties (absorption or emission) offer a convenient method for their detection [2]. Detection of Iodide ion is particularly of importance

due to its biological functions such as thyroid and neurological activity. With the above underlying objective, we report, the synthesis and characterization of a highly fluorescent novel tris-phenalenone compound ( $C_{45}H_{36}N_4O_3$ ). A thorough study on the binding behaviour of the compound with  $I^-$  and other biologically relevant anions (viz.  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $CH_3COO^-$ ,  $N_3^-$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) in solution was performed by quantitative UV-visible and fluorescence spectroscopy. The novel compound is found to sense selectively iodide ion in solution among other above mentioned anions.

#### References

- [1] Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C.; Science **2002**, 296, 1443.
- [2] Bencini, A.; Lippolis, V. Coord. Chem. Rev. **2012**, 256, 149.

#### (P491)

### Low Melting High Energy Density Materials (HEDM): Design, Synthesis and spectroscopic studies

Sumit K. Panja, Ankita Ojha, Nidhi Dwivedi and Satyen Saha\*  
Banaras Hindu University

Energetic materials include explosives, propellants, and pyrotechnics that are used for a variety of civilian and military purposes. Many new energetic materials have emerged recently in order to meet the challenging requirements to improve the performance of existing products. The development and testing of energetic materials is an exciting and challenging area of chemistry, from applied as well as fundamental aspects[1, 2]. The key requirements include tailored performance, insensitivity, stability, vulnerability, and environmental safety. Recent development in ionic liquids has opened up a new promising series of HEDMs. It can be easily designed or modified to get nitrogen rich HEDMs. Here, we shall present; design and synthesize of some new energetic materials which are found to be low melting salts. We have synthesized a group of heterocyclic cations comprising triazolium, tetrazolium, mono and dication of imidazolium and pyrimidinium and paired with picrate, dinitramide and 5, 5-azobistetrazolate anion. Their spectroscopic characterizations will also be discussed.

#### References:

1. Singh, R. P.; Verma, R. D.; Mestri, D. T.; Shreeve, J. M. Chem. Rev. 2006, 45, 3584.
2. Sikder, A.K., Sikder, N. J. Hazard. Mater. A 2004, 112, 1.

#### (P492)

### Structural Insights into Transcription Mechanism of Antibiotic Regulation by a TetR-family protein from *Streptomyces coelicolor*

Hussain B.<sup>1,2</sup>, Ruchika B.<sup>1</sup>, Shamayeeta R.<sup>1,2</sup>, Anwasha B.<sup>1</sup>, Ruchi Anand\*<sup>1</sup>

<sup>1</sup>Department of Chemistry, Indian Institute of Technology Bombay, Mumbai, 400076, India

<sup>2</sup>IITB-Monash Research Academy, Indian Institute of Technology Bombay, Mumbai, 400076, India. E-mail: ruchi@chem.iitb.ac.in

*Streptomyces* species are well-known for their wide variety of biologically active secondary metabolites and contribute to two-third of naturally occurring antibiotics. Production of antibiotics in these species is dictated by transcriptional regulatory proteins that adapt quorum-sensing mechanism, which involves small diffusible molecules (autoinducers). A-factor (a  $\gamma$ -

butyralactone) is one such molecule, which along with the A-factor receptor protein (ArpA) controls the production of antibiotic, sporulation and morphological differentiation in *S. griseus*. The homologs of ArpA presides the secondary metabolism and morphogenesis in *S. coelicolor* A3(2) are proteins ScbR, CprA and CprB. While earlier studies have shown that deletion mutant of *cprB* gene from *S. coelicolor* A3(2) exhibits acute reduction in antibiotic production and sporulation, the identity of DNA sequences that CprB binds remain largely unknown. In the present work, we identify the cognate DNA elements that are recognized by CprB and demonstrate that CprB acts as an autoregulator. Further, we illustrate the molecular level mechanism of transcription regulation by employing a combination of X-ray crystallography, isothermal calorimetric and DNA retardation assays. The crystal structure of the CprB-DNA complex reveals that CprB exists as a tetramer and recognizes the dsDNA via the N-terminal helix-turn-helix motif. Moreover, its mode of binding is analogous to the broad spectrum multidrug transporter protein QacR from the antibiotic resistant strain *Staphylococcus aureus*. Finally, we show that CprB follows a sequential model of DNA binding with the first dimeric CprB unit priming the dsDNA for binding, and the second unit assisting in proper clamping of the DNA.

**(P493)**

**Design, Synthesis and Antiradical Activity of Bifunctional, C5a-Thio Structural Analogues of  $\alpha$ -Tocopherol**

Anil K. Singh\* and K. Gopu

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai – 400 076

$\alpha$ -Tocopherol (**1**) form of Vitamin E is a well-known antioxidant/radioprotective compound, which inhibits lipid peroxidation and other free radical-mediated reactions in the biological systems.<sup>1</sup> However, the largely hydrophobic character of these compounds make them poorly soluble in aqueous media, which in some cases, limits their therapeutic efficacy and this has a strong influence on their pharmacokinetic and pharmacodynamic properties. Further, oral administration of vitamin E compounds in biological systems is complex because of its oily nature. Efforts have been made to ameliorate these shortcomings by structural modifications at various positions of the parent molecules. In one of our earlier strategies, we have employed click chemistry to design novel glyco-conjugates of  $\alpha$ -tocopherol, some of which are solid, and show significant water solubility and radical scavenging activity.<sup>2</sup> The antioxidant/radioprotective activity of **1** is believed to be associated with its ability to scavenge reactive oxygen species via its phenolic group. With a view to obtain compounds with enhanced antioxidant activity, several sulphur atom-containing structural analogues of **1** have been designed over the years. We have demonstrated a simple and general method for the synthesis of bifunctionalized analogues of **1** containing sulphur atom at C-5a position. The influence of these structural changes on the dynamics of oxidation products formation has been investigated by DPPH and methyl linoleate peroxidation methods. The novelty of these compounds lies in their stability and bifunctional nature and, hence, enhanced radical scavenging activity.<sup>3</sup> Details of our efforts towards design, synthesis and bioassay studies together with an overview of the efforts made in the field with respect to their potential use in translational medicine and the future outlook on these and related compounds as new therapeutic agents will be discussed.

References

1. Cerecetto, H. and G. V. López (2007). Antioxidants derived from vitamin E: an overview. *Mini Reviews in Medicinal Chemistry* **7**: 315–38. Hosseinimehr, S. J. (2007) Trends in the development of radioprotective agents. *Drug Discovery Today* **12**: 794–805.
2. Singh, A. K. and K. Gopu (2010) Synthesis and antioxidant properties of novel  $\alpha$ -tocopherol glycoconjugates. **51**: 1180-1184.
3. Singh, A. K. and K. Gopu. Unpublished results

(P494)

### **Preparation and Fluorescence Behaviour of the Nanoparticles of 3-Styrylindoles**

Anil K. Singh\* and A. W. M. H. Ansari

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai

Organic nanoparticles (ONPs) have attracted a great deal of attention in recent years because of their projected applications in many areas like agriculture, biological, environmental, medical, opto-electronic, pharmaceutical, etc.<sup>1</sup> The fluorescent organic nanoparticles (FONs) are considered important as potential light emitting diode materials, efficient visible light-active photo-catalyst, and optical detection and bio-imaging probes.<sup>2</sup> The optimization of bioavailability and the control of optical properties of ONPs by controlling their size and supramolecular architecture are the objects of much current interest. In view of the potential applications of micremulsion-based nanoparticles in transdermal drug delivery and other biomedical applications, we had undertaken synthesis and characterization of cholesteryl nanoparticles with specific intention to understand the effect of molecular size and hydrophobicity on the nanoparticle formation, and produce stable nanoparticles of uniform size distribution.<sup>3</sup> To understand how optical properties develop as a function of size, which is of fundamental and technological interest, and our recent observations on the fluorescence properties of 3-styrylindoles in microheterogenous media and in the solid state<sup>4</sup> prompted us to investigate the fluorescence emission behaviour of differently substituted 3-styrylindoles in their nanoparticle form. Herein we disclose that FONs of 3-styrylindoles can be easily prepared by simple reprecipitation method in THF, using water as a nonsolvent.<sup>5</sup> The average diameter of these FONs is 20 to 57 nm. There is no significant change in the fluorescence intensity of 3-styrylindole, 3-(4-nitro phenylstyryl) indole, 5-bromo-(4-nitrophenyl) indole both in nano form and molecular form. However, the nanoparticles of 5-methoxy-(4-nitrophenyl) indole exhibit dramatic change of fluorescence intensity from the less fluorescent isolated single molecule in THF to the strongly fluorescent nanoparticles' suspension in THF/water mixtures, which is attributed to the extended conjugation and J-aggregation donor-acceptor nature of the compound. The increase in  $\Phi_f$  with increase in water percentage indicates specific aggregation of 5-methoxy-(4-nitrophenyl) indole in nanoform. The fluorescence intensity in nano form decreases after one week due to clumping of nanoparticles into bigger size. Specific orientation and aggregation of nanoparticles is essential for enhancement in fluorescence intensity which is clearly observed from TEM. Future work should focus on direct analysis of the nanoparticles and on the development of convenient biomedical applications of such formulations.

#### References

1. Utekhina, A. Yu. and Gleb B. Sergeev (2011) Organic nanoparticles. *Russ. Chem. Rev.* **80** 219-234.

2. Baker, S. N. and G. A. Baker (2010) Luminescent carbon nanodots: emergent nanolights. *Angew. Chem. Int. Ed.*, **49**, 6726-6744. Fery-Forgues, Suzzane (2013) Fluorescent organic nanocrystals and non-doped nanoparticles for biological applications. *Nanoscale*, **5**, 8428-8442.
3. Singh, A. K. and A. W. M. H. Ansari (2010) Synthesis of uniform narrow-size nanoparticles of cholesterol esters. *Nanosci. Nanotechnol. Lett.* **2**, 46-50.
4. Asefa, A. A. and A. K. Singh (2009) A fluorescence study of novel styrylindoles in homogeneous and microheterogeneous media. *J. Fluorescence* **19**, 921-930. Asefa, A. A. and A. K. Singh (2009) Fluorescence emission enhancement in substituted 3-styrylindoles in the solid state. *J. Luminescence* **130**, 24-28.
5. Singh, A. K. and A. W. M. H. Ansari. Unpublished results.

**(P495)**

**Total synthesis of marine alkaloid mansouramycin D via iminoannulation**

K. S. Prakash and R. Nagarajan\*

School of Chemistry, University of Hyderabad

Mansouramycin D, a class of isoquinoline quinone, was isolated from the ethyl acetate extract of marine streptomyces sp. Isolate Mei37 by Laatsch and co-workers in 2009. The structure of Mansouramycin D has been confirmed as 3-(1H-indole-3-yl)-7-methylaminoisoquinoline-5,8-dione by NMR and mass spectrometry. Mansouramycins showed cytotoxicity profiling against 36 cancer cell lines and found to have significant activity against various cancer cells. Specifically, high cytotoxicity against many human cancer cell lines with an IC50 value up to 0.089  $\mu$ M for lung cancer. We report herein the first, simple and concise route to total synthesis of Mansouramycin D. The core structure isoquinoline ring has been constructed from iminoannulation of 2-alkynylbenzaldehyde.

**(P496)**

**Effect of urea on gemini surfactant micelles: A steady-state and time resolved fluorescence spectroscopic study**

Sonu, Amit K. Tiwari and Subit K. Saha\*

Department of Chemistry, Birla Institute of Technology and Science, Pilani, Rajasthan

Effect of urea on gemini surfactant (12-4-12) micelles has been studied by steady-state and time resolved fluorescence spectroscopy. The critical micelles concentration (CMC) of 12-4-12 increased with increasing the concentration of urea. The micro environmental properties have been determined by using a twisted intramolecular charge transfer probe molecule. The microviscosity of the micellar system decreased in the presence of urea without altering the micropolarity of the same system. Solvent and rotational relaxations of C-480 also have been studied in the absence and presence of urea in gemini surfactant micelles. At lower concentration of urea the solvation times decreases and at higher concentration of urea the solvation times increases. The rotational relaxation time of C-480 decreased in the presence of urea.



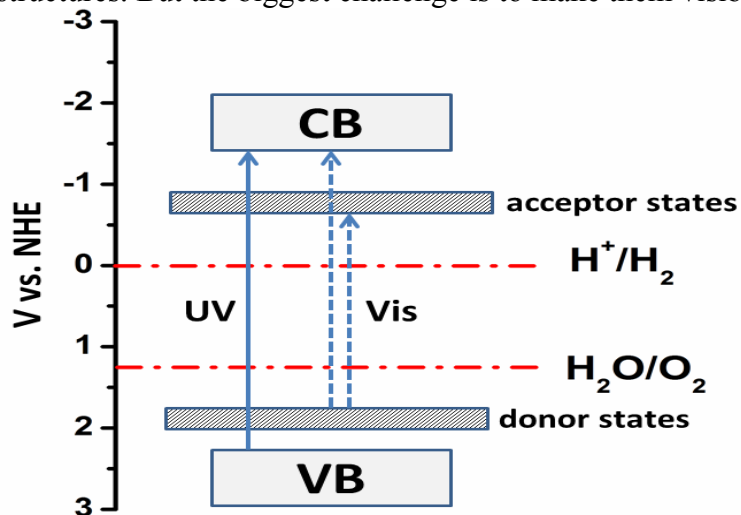
(P497)

### Ab initio Study on Materials for Visible Light Photocatalysis

Biswarup Pathak

Discipline of Chemistry, School of Basic Sciences, Indian Institute of Technology Indore,  
Indore, M. P., India

Hydrogen is one of the most promising alternatives to fossil fuel and photocatalysis of water is the cleanest and safest way to produce hydrogen. Therefore, the search for an efficient photocatalyst is the major concern for the hydrogen production. The metal oxides with layered perovskite structures are reported to be very efficient UV photocatalyst owing to their layered structures. But the biggest challenge is to make them visible light active.



The ideal band gap for any visible-light photocatalyst is around 2.0 eV for the effective utilization of the solar spectrum. But band gap is not only the sole criteria for the efficient photocatalysis. The semiconductor's band positions (Figure) with respect to the water oxidation/reduction potential are very much important for the efficient photocatalysis. Therefore, the controlled band gap engineering (1-3) is very important for the effective utilizations of the solar-to-hydrogen conversion. Here we will show how the atomistic modeling on materials can be useful for their band edge alignment for the effective utilization of visible solar light.

#### References

- [1] P. Liu\*, J. Nisar, B. Sa, B. Pathak\*, R. Ahuja, *J. Phys. Chem. C*, 117, 13845 (2013)
- [2] P. Liu\*, J. Nisar, R. Ahuja, B. Pathak\*, *J. Phys. Chem. C* 117, 5043, (2013).
- [3] X. Jiang, J. Nisar, B. Pathak, J. Zha, R. Ahuja, *Journal of Catalysis* 299, 204, (2013).
- [4] B. Wang, P. Kanhere, Z. Chen, J. Nisar, B. Pathak, R. Ahuja *J. Phys. Chem. C* 117, 22518, (2013).

(P498)

### Metaphenylene Based Nitroxide Diradicals: A Protocol to Calculate Intermolecular Coupling Constant in One-Dimensional Chain

Tumpa Sadhukhan, Shekhar Hansda, Iqbal A. Latif and Sambhu N. Datta\*  
Department of Chemistry, IIT Bombay

Intramolecular magnetic exchange coupling constants are determined for seven isolated metaphenylene based dinitroxide diradicals by unrestricted density functional methodology (UDFT) using a number of hybrid functional such as B3LYP, B3LYP-D3, M06-2X, HSE and LC- $\omega$ PBE. In all cases, B3LYP somewhat overestimate the coupling constant and M06-2X produces a more realistic value. The range separated HSE and LC- $\omega$ PBE functional yield large deviations from experiment. The nature of spin coupling agrees with spin alternation rule and the calculated spin densities which is in agreement with the McConnell rule. It can also be explained in terms of the non-disjoint SOMO effect. Furthermore, the calculated NICS(1) isotropic and zz, and hyperfine coupling constants also correlates with this. A method has been put forward to determine the intramolecular ( $J$ ) and intermolecular ( $J$ ) coupling constants from quantum chemical calculations on a one-dimensional chain of weakly bound diradicals. Two expressions are derived for the energies of different spin states in terms of  $J$  and  $J$ . Exemplary UDFT computations are done on the N-mers (N=2-6) of two diradicals for which the crystal coordinates are available. The intramolecular and intermolecular coupling constants are determined from the calculated UDFT energies. All these are in general agreement with the measured coupling constants.<sup>2</sup>

#### References

- (1) Sadhukhan, T.; Hansda, S.; Latif, I. A.; Datta, S. N. J. Phys. Chem. A (just accepted).
- (2) Rajca, A.; Takahashi, M.; Pink, M.; Spagnol, G.; Rajca, S. J. Am. Chem. Soc. 2007, 129, 10159-10170.