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সম্বৰ্ধনা অনুষ্ঠান

Editorial ...

"Keep exploring. Keep dreaming. Keep asking why. Don't settle for what you already know. Never stop believing in the power of your ideas, your imagination, your hard work to change the world."

- Barack Obama

Just like the rainbow after the rain, joy will emerge after the sorrow. The second wave of COVID-19 is coming to an end, and it has been more devastating than the previous one. We don't know how many waves are still out there waiting in a queue, but as more and more people get vaccinated, it is for sure that the pandemic has to bite the dust, and we human beings have to bite off more than we chew to welcome a post-COVID lifestyle.

Life after COVID-19 will be a new basket of challenges, like a portal that welcomes us into a new world. For a post-Covid lifestyle, we have to become adjustable enough to maintain a balance among everything, mostly health. People like to say that it would take a lot of time to return to our normal lives. But returning will never be the same as turning back to the life we had lived in the past. With changing circumstances, our life will never be the same as before. But our dreams and aims are still intact, and we shouldn't lose our hope.

Though we were bound during the last two lockdowns, technology has developed faster than before and brought everything that seemed impossible into the grasp of our hands. So let's not give up on our dreams and keep chasing them until we can build a better tomorrow for ourselves. The motto of "the Chemical Axis" had always been to ignite, inspire and nurture the creative instincts of young minds to mold them for a better tomorrow. In this regard, various articles relating to the present scenario and other fields of research are enlisted.

The series of Bhatnagar awardees, History of Chemistry and Chemistry in movies has been continued throughout this edition too.

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Place: Guwahati

The abstract sketched on the cover page has been designed by ***Yoshita Chakravarty*** *on the quotation*

‘‘The task is not to see what is never been seen before but to think what has never been thought before about what you see everyday."

- Erwin Schrödinger

Hope is like the sun, which, as we journey toward it, casts the shadow of our burden behind us. Multiple waves of the COVID-19 are challenging humanity as never before. But the spirit of hope has helped us cope through the ages and is the reason we are able to slowly bring the pandemic under control. The Chemical Forum of Department of Chemistry of B. Borooah College would like to offer our heartiest gratitude to all those who are the rays of this hope, the doctors,nurses, administrative staff, etc and most importantly the researchers who have been working day and night to develop various vaccines against the virus and slowly helping us win over the pandemic.Hope is not a peace of mind but hope is taking action and doing something. So we shouldn't let go of our hopes on our goals and keep moving forward step by step for a better tommorow.

Contents

Students' Section

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Biosynthesis of Metal Nanoparticles from Plant Extract

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Abstract: Metal nanoparticles are of vast importance owing to their interesting catalytic, electronic, optical properties and their potential applications in sensing, catalysis, surface-enhanced Raman scattering (SERS) spectroscopy and biomedical engineering. Nanomaterials especially, metal nanoparticles can also be synthesized using the natural bioresources such as microorganisms, plant and fruit extracts as well as animal tissues as a potential source of reducing and stabilizing agents in laboratories even on large scale. This is considered as an eye-catching viewpoint for eco-friendly or so-called green synthesis. Eco-friendly synthesis of biocompatible nanomaterials and their potential biomedical applications introduces the concept of nanobiotechnology. The lower cost and lesser side effects as compare to chemical methods of synthesis are the main advantages of biosynthesis. This paper describes briefly the green synthesis of metal nanoparticles using plant extracts with special emphasis on their various applications.

Keywords: nanoparticles, plant extracts, biosynthesis, biomedical applications, nanobiotechnology

1. Introduction

A new branch of nanotechnology is nanobiotechnology, which can combine biological principles with physical and chemical processes to synthesize nanoparticles with specific functions.[1] The development of eco-friendly cost-effective green protocol for the synthesis of nanomaterials is an important aspect of nanotechnology. More specifically, one can define nanobiotechnology involving synthesis of nanomaterials using microorganisms, including bacteria, viruses, fungi as well as plant and animal based products.[1, 2] Synthesis of nanomaterials using bioresources can be classified into the following types: I) Use of microorganisms like fungi, yeast, or bacteria, II) use of plant extract, fruit extract and honey, III) use of biological templates like DNA, membranes, viruses and diatoms, IV) use of animal tissues. Currently, there is growing need to develop eco-friendly synthetic protocols of various nanoparticles of different shapes and sizes for avoiding the adverse effects in comparison to traditional chemical methods. There is much scope of further improvement in the synthesis of nanoparticles by biogenic methods using different biological resources as the source of reducing and stabilizing agents and their potential applications particularly in relation to improving the monodispersity of the nanoparticles and modulating their size and shape, as well as in reducing the time required for nanoparticle synthesis.

It is bit difficult to find out the exact mechanism of these biosynthetic protocols. However, one can classify or identify the probable reducing and stabilizing agents in the bio-resources e.g., nitrate reductase in bacteria; cytochrome c in fungi; hydrolysable tannins; antioxidants in fruits; reducing sugars in plant leaves; fructose sugars, proteins in honey; metallothioneine in animal tissues etc.[1, 2]

Gold and silver nanoparticles are the most common ones used for biomedical applications and in emerging interdisciplinary field of nanobiotechnology.[2, 3] For example, oligonucleotide capped gold nanoparticles have been used for polynucleotide or protein detection using various detection/characterization methods.[4] Furthermore, gold nanoparticles have been employed in immunoassay, protein assay, cancer nanotechnology, especially in the detection of cancer cells.[5] After cellular uptake, they can act as precise and powerful heaters (thermal scalpels) to kill cancer cell.[6] Moreover, gold nanoparticles are capable of inducing apoptosis in B cell-chronic lymphocytic leukemia (chronic lymphoid leukemia).

Silver nanoparticles are of tremendous interest to researchers due to their excellent optical, electrical, catalytic and antibacterial properties.[7-9] The antibacterial activities of silver ions and salts have studied since early days and they can be utilized to control the bacterial growth in various applications such as prostheses, catheters, burn wounds etc.[10] Antimicrobial properties of silver nanoparticles can be utilized in various fields of medicine, various industries, animal husbandry, packaging, accessories, cosmetics, health and military. Silver nanoparticles show potential antimicrobial effects against infectious microorganisms such as *Escherichia coli, Bacillus subtilis, Vibria cholera, Syphillis typhus and Staphylococcus aureus.*[11] Silver nanoparticles can also exhibit excellent catalytic activity due to its high surface area to volume ratio and high surface energy making them extremely reactive. Therefore, silver nanoparticles of various sizes and shapes can be used as an effective catalyst in various catalytic reactions including chemical, electrochemical and photochemical.[12, 13]

The aim of this paper is to provide an updated overview on the synthesis of metal nanoparticles of various shapes and sizes using plant extract and their potential applications in optics, optoelectronics, chemical and biosensors, biomedical applications and catalysis. Due to space limitations, a complete review of all recent work on this important subject is not possible. However, we only summarize a few representative examples, including our own work.

2. Synthesis of gold and silver nanoparticles using plant extract

An important protocol for the eco-friendly biosynthesis of nanoparticles is the application of plant extract.[14] Use of different plants in the synthesis is a novel idea leading to true green chemistry.[14] **Figure 1** shows some popular plants which can be used for the extract preparation. The biological synthesis of metal nanoparticles (especially, gold and silver nanoparticles) using various plants (inactivated plant tissue, plant extracts and living plant) had received more attention as a suitable alternative to chemical and physical methods for the synthesis of nanoparticles.[14] Synthesis of metal nanoparticles using plant extracts is very cost effective, and therefore can be used as an economic and valuable alternative for the large-scale production of metal nanoparticles. Extracts from plants may act both as reducing and stabilizing agents in nanoparticle synthesis.[14] The bio reduction of metal nanoparticles by combinations of biomolecules found in plant extracts (e.g. enzymes, proteins, amino acids, vitamins, polysaccharides, and organic acids such as citrates) is environmentally benevolent, yet chemically complex. Plants have shown tremendous prospect in heavy metal accumulation and detoxification.[15] Several studies based on detoxification and hyper-accumulation of toxic metals by plants, such as *Arabidopsis halleri* and *Thlaspi caerulescens* had been reported.[14-16] Different kinds of plants such as *Acanthopanax sciadophylloides, Maytenus founieri, Brassica juncea, Sesbania drummondii,* and *Clethra barbinervis* have potential capacity for phytoremediation of heavy metals.[14-16] Trace elements (heavy metals and metalloids) are important environmental pollutants, and are toxic even at very low concentrations. The use of plant biomass for the removal of metals from aqueous solutions (known as biosorption) gained attention due to the great promise exhibited by them for the removal of contaminants from effluents in an eco-friendly approach. Researchers pay attention to use of plants with potential in phyto mining and phytoremediation of heavy metals in order to phyto synthesize metal nanoparticles.

Gardea-Torresdey et al. had reported for the first time the formation of gold and silver nanoparticles inside living plants.[17] They synthesized gold and silver nanoparticles within live *Medicago sativa* (alfalfa) plants by gold and silver ion uptake, respectively, from solid media. The alfalfa plants were grown in an AuCl4 rich environment. The information about uptake and formation of these nanoparticles was confirmed by X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM). The gold nanoparticles were in crystalline state. Additionally, icosahedral particles (~ 4 nm) and face-centered cubic (fcc) twinned particles (6–10 nm) were formed.

Murali Sastry and his group had used the leaves of geranium plant *(Pelarogonium graveolens)* to synthesize gold nanoparticles.[18] It should be noted that there is also a plant associated fungus which can produce compounds such as taxol and gibbarellins. There is an exchange of intergenic genetics between fungus and plants. Nanoparticles obtained using *Colletotrichum sp* fungus related to geranium plant has a wide distribution of sizes with mostly spherical shapes. However, rod and disk shaped nanoparticles can be synthesized using geranium plant extract. The extract used for reduction of Ag^+ ions to Ag^0 was prepared by taking 20 g of thoroughly washed and finely cut geranium leaves in a 500 mL Erlenmeyer flask with 100 mL of distilled water. The suspension was boiled for 1 min followed by addition of 5 mL of pure broth to 100 mL of 10^{-3} M aqueous solution of $AgNO_3$. The bio reduction of the Ag^+ ions was monitored by measuring the UV-vis spectra of the solution. **Figure 2** shows the UV-vis spectra recorded from the aqueous silver nitrate-geranium leaf extract reaction medium as a function of the reaction time.

Biological synthesis of gold nanoparticles using *Magnolia kobus* and *Diopyros kaki* leaf extracts had been reported.[19] There are reports about the synthesis of gold nanoparticles using *Murraya koenigi* leaf,[20] Lemon grass,[21] Aloe vera leaf,[22] Neem leaf,[23] *Tamarindus indica* leaf,[24] and silver nanoparticles using *Murraya koenigi* leaf.[25] Similarly, we find the synthesis of gold and silver nanoparticles using Krishna tulsi leaf extract[26] and *Hibiscus rosa sinensis*.[27]

A simple protocol using *Aloe vera* leaf extract had been reported for the synthesis of gold nanotriangle and spherical silver nanoparticles.[22] The kinetics of gold nanoparticles formation was monitored by UV-vis absorption spectroscopy and transmission electron microscopy (TEM). The effect of the amount of leaf extract on the synthesis of gold nanotriangles was investigated by observation of the reaction product formed. Addition of *Aloe vera* extract to 10^{-3} M aqueous solution of $HAuCl_4$ led to the appearance of a red color in solution after about 5 h of reaction. An analysis of the percentage of triangles formed in the reaction medium as a function of varying amounts of the *Aloe vera* extract showed that more spherical particles were formed with increasing amount of added extract.

Triangular gold nano prisms can be synthesized biologically[21] in high yield at room temperature by the reduction of aqueous chloroaurate ions ($AuCl_4$-) by using the plant lemongrass *(Cymbopogon flexuosus)* extract. Dr. Murali Sastry of Physical & Materials Chemistry Division, Dr. Absar Ahmed of Biochemical Sciences Division of National chemical laboratory (NCl), Pune and the team had demonstrated biological synthesis of large amounts of triangular gold nano prisms by a single-step, room-temperature reduction of gold salt solution by the extract of the plant, lemongrass *(Cymbopogon flexuosus)*. The lemongrass extract on mixing with gold salt solution exhibits a change of color from pale yellow to a vivid ruby red. The reaction mixture is allowed to stand for six hours to yield a large number of triangular gold nanoparticles of 8 -18 nm thickness with an edge length of 200-500 nm.[21, 28] **Figure 3** shows the TEM image of gold nanotriangles synthesized by the reduction of aqueous $HAuCl_4$ solution with lemon grass extract. The scientists also enhanced the yield of gold nanotriangles in the reaction medium up to ninety-five per cent of the nanoparticles population by repeated centrifugation. The reducing sugars (aldoses) present inside the lemongrass extract were found to reduce the Au^{3+} into nano prisms as proposed by Shiv Shankar et al.[28] By simple variation in the concentration of the lemongrass extract in the reaction medium, it is possible to vary the size of the nano prisms, thereby, the longitudinal SPR band in the NIR region can be easily tuned as shown in the UV-vis-NIR spectra of gold nanoparticles synthesized by adding different amount of lemongrass leaf extract (see **Figure 4**).

It had been reported that tamarind leaf extract can also be used as the potential bioresource for the reducing agent for making gold nanotriangles.[24] On treating aqueous Au^{3+} solution with tamarind leaf extract, rapid formation of flat and thin single crystalline gold nanotriangles was observed. The effect of different organic solvent vapors such as methanol, benzene, and acetone on the conductivity of these gold nanotriangles was investigated by measuring the corresponding I-V features. The results suggest that these nanotriangles can be used as vapor sensors. *Cinnamomum zeylanicum* leaf broth can be used as reducing agent to reduce Au^{3+} to obtain gold nanoprisms.[29] Nanoparticles of diverse shapes such as hexagon, truncated triangle, and triangle can also be synthesized by reducing aqueous chloroauric acid solution with the extract of seaweed, Sargassum *sp.,* at room temperature.[30]

Shiv Shankar et al. had reported the biosynthesis of silver and gold nanoparticles by the reduction of aqueous Ag^{+} and Au^{3+} ions and also the synthesis of bimetallic core-shell nanoparticles of gold and silver by simultaneous reduction of aqueous Ag^{+} and Au^{3+} ions with the broth of neem leaves *(A. indica)*.[23] They observed that the metal nanoparticles were stable in solution even four weeks after their synthesis. Moreover, stabilizing the nanoparticles was possibly facilitated by reducing sugars and/or terpenoids present in the neem leaf broth. The silver nanoparticles formed were predominantly spherical in shape and polydisperse in nature with diameters ranging between 5 to 35 nm.

Sastry et al.[22] had reported the green synthesis of gold and silver nanoparticles with various shapes (spherical and triangular) and sizes using *Aloe vera* plant extracts. It was explained that only biomolecules of molecular weights less than 3 kDa caused reduction of chloroaurate ions, leading to the formation of gold nanotriangles. Nevertheless, the bio reduction of silver ions proceeded merely in the presence of ammonia.

The extracellular biosynthesis of gold nanoparticles was carried out[31] by mixing aqueous solution of gold ions with *Coriandrum sativum* leaf extract and nanoparticles with spherical, triangle, truncated triangle and decahedral morphologies ranging from 6.75 nm to 57.91 nm were obtained. These nanoparticles were stable in solution over a period of one month at room temperature.

The extract from Black Tea had been employed as a reducing agent for the green synthesis of Au and Ag nanoparticles.[32] Three different extracts were prepared from Black Tea: (i) tea leaf broth, (ii) ethyl acetate extract and (iii) CH_2Cl_2 extract. Metal nanoparticles were synthesized by addition of aqueous solution of $AgNO_3$ or $HAuCl_4$ to any of the three extracts. The formation and growth of the nanoparticles was monitored with the help of absorption spectroscopy and transmission electron microscopy.

Vilchis-Nestor et al.[33] had employed green tea *(Camellia sinensis)* extract to produce gold and silver nanoparticles in aqueous solution at ambient conditions. They also investigated control of size, morphology, and optical properties of the nanostructures and reported initial concentrations of metal ions and tea extract as controlling factors. It was investigated that when the amount of *C. sinensis* extract was increased, the resulted nanoparticles were slightly bigger in size and more spherical in shape. The authors of this study believed that phenolic acid-type biomolecules present in *C. sinensis* extract were responsible for the reduction and stabilization of metal ions to produce silver and gold nanoparticles. Caffeine and theophylline present in tea extracts might also be responsible for catalysis and synthesis of nanoparticles.

Mude et al.[34] had reported the green synthesis production of spherical silver nanoparticles (60–80 nm) using callus extract of Carica papaya. Proteins and other ligands seemed to be responsible for the synthesis and stabilization of silver nanoparticles. Furthermore, fcc silver nanoparticles (10–20 nm) were synthesized by using the latex of *Jatropha curcas* as reducing and capping agent.[35]

Jha et al.[36] employed biotechnological protocol for the green synthesis of silver nanoparticles. They demonstrated that Cycas leaf extract could be used in order to synthesize stable silver nanoparticles. It is a common gymnospermic plant and a commercial source of sago. This plant is rich in flavonoids largely belonging to the mixture of phenolic compounds. The *Cycas* extract solution was treated with 20 mL of 0.25 M $AgNO_3$ solution and heated on the steam bath for 20 min until the color of solution changes to brown. X-Ray data indicated that silver nanoparticles had fcc unit cell structure. Phytochemicals such as polyphenols, glutathiones, metallothioneins, and ascorbates possibly were responsible for formation of the nanoparticles. Glutathione was concerned to play an important role in plants exposed to metal stress, and metallothioneins have the capacity to bind both xenobiotic (e.g. cadmium, silver, mercury, and arsenic) and physiological (e.g. zinc, selenium, and copper) heavy metals through the thiol group of their cysteine residues. Antioxidant action of phenolic compounds (compounds consist of catechin, taxifolin, procyanidins of various chain lengths formed by catechin and epicatechin units, and phenolic acids) is due to their high tendency to chelate metals. Phenolic compounds possess hydroxyl and carboxyl groups, which may inactivate iron ions by chelating and additionally suppressing the superoxide driven Fenton reaction, which is believed to be the most important source of reactive oxygen species (ROS). Therefore, plants with high content of phenolic compounds (e.g. Pinus species) are one of the best candidates for the green synthesis of nanoparticles. **Table 1** illustrates some examples of biosynthesis of nanoparticles using plant extract.

3. Applications of metal nanoparticles

The major intention of biological synthesis of nanoparticles is to develop eco-friendly and synthetic protocols with minimum cost of production and applications, specially in the biomedical field. Obviously, large number of researchers diverted their attention towards the use of biological systems for the synthesis of biocompatible metal nanostructures. The silver nanoparticles obtained by biosynthesis can be used in catalysis, data storage, energy storage, microelectronics etc.[37] Duran et al.[38] reported silver nanoparticles incorporated cloths are sterile and can be useful in hospitals to prevent or to minimize infection with pathogenic bacteria. Ankamwar et al.[24] used biogenic gold nanotriangles films as vapor sensors. The high absorption coefficient of these gold triangles in the NIR region make them useful in fabricating photonic devices such as optical sensors and NIR absorbers. Another application based on the large NIR absorption of the gold nanoparticles could be in hyperthermia of tumors.[39] The extremely flat nature of the nanoparticles would facilitate excellent thermal contact between the nanotriangles and tumor cells. The gold nanoparticles synthesized in aqueous medium using *Murraya koenigi* leaf extract can be used for cancer therapy due to anti-carcinogenic properties of biomolecules present in the extract. Ankamwar et al.[40] had reported the study on the biocompatibility of Fe_3O_4 nanoparticles evaluated by in vitro cytotoxicity assays using normal, glia and breast cancer cells.

Nanocatalysis has recently been a rapidly growing field which involves the use of nanoparticles as catalysts. The catalytic properties of gold and silver nanoparticles varied from their sizes and synthesis method. It is well-known that metals like Au, Ag and Pt and metal ions can catalyze the decomposition of H_2O_2 to oxygen. In addition, these metal ions can catalyze luminal-H_2O_2 systems. It was observed that by the addition of Ag colloids, chemiluminescence emission from the luminal-H_2O_2 system can be greatly enhanced.[41] Silver is also the most popular catalyst for the oxidation of ethylene to ethylene oxide and methanol to formaldehyde. When Au nanoparticles less than 5 nm in size are supported on base metal oxide or carbon, very active catalysts are produced. Understanding the interaction between Au nanoparticles and their support material is a key issue.[42] Au nanoparticle catalysts are highly active for the oxidation many compounds, particularly CO and trimethylamine. Gas sensors based on Au nanoparticles have been developed for detecting a number of gases, including CO and NO_x.[43] Pd-coated silver nanoparticles are very effective catalyst for remediation of trichloroethene (TCE) and common organic pollutants in ground water.[44]

Recently, Ankamwar et al.[45] reported the biosynthesis of anisotropic Au nanotriangles at room temperature using the flower extract of *Neolamarckia cadamba.* The biosynthesized gold nanoparticles were used both as a photocatalyst to enhance formation of hydroxyl radicals generated from the photolysis of H_2O_2 and also as an efficient SERS-active substrate using methylene blue as Raman probe molecule. The SERS result suggests that a chemical sensor can be developed using the SERS active biosynthesized Au nanoparticles. Ankamwar et al.[46] also reported the photocatalytic activity of biologically synthesized silver nanoparticles using flower extract of *Neolamarckia cadamba.* They also used the biosynthesized silver nanoparticles obtained from leaves extract of *Neolamarckia cadamba* as SERS active substrate to detect bacteria.[47] Using this biocompatible SERS active substrate, they had differentiated Gram positive from Gram negative bacteria. The SERS data presented in their study was highly stable, uniform and reproducible, which showed the versatility of their SERS active substrate. The SERS based detection of bacteria using biosynthesized Ag nanoparticles was highly sensitive with a limit of detection of 10^3 CFU/ml) for *E. coli.* SERS based pathogen detection method can be especially useful for the analysis of slow-growing bacteria, which typically may take weeks during laboratory tests.

4. Conclusions

Various bioresources like bacteria, fungi, actinomycetes, plants, fruits, honey as well as animal tissues can be used as a potential source of reducing and stabilizing agents for the synthesis of nanomaterials such as metal nanoparticles. This review article demonstrates the role of various plants extracts for the synthesis of metal nanoparticles mainly gold and silver with an overview of their potential applications.

It is bit difficult to find out the exact mechanism of these biosynthetic protocols. However, one can classify or identify the probable reducing and stabilizing agents in the bio-resources e.g., nitrate reductase in bacteria; cytochrome c in fungi; hydrolysable tannins, antioxidants in fruits; reducing sugars in plant leaves; fructose sugars and proteins in honey; metallothioneine in animal tissues etc.

The other significant characteristic of green synthesis is that it will operate mostly at mild conditions with the use of less toxic chemicals at ambient conditions such as room temperature and atmospheric pressure making it affordable and cost effective. It is expected that green synthesis of nanomaterials using biomolecules will receive utmost importance both from environmental and commercial point of view.

5. Acknowledgements

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Table 1:

Some examples of biosynthesis of nanoparticles using plant extract

Plant origin	**Synthesized nanoparticles**	**Morphology**
Aloe vera	Gold & silver	spherical, triangular
Acalypha indica	Silver	spherical
Azadirachta indica (neem)	Gold, silver & silver-gold alloys	spherical, triangular & hexagonal
Black tea leaf extracts	Gold & silver	spherical, prism
Camellia sinensis (green tea)	Gold	spherical, triangular
Carica papaya	Silver	spherical
Cinnamomum camphora	gold & silver	triangular, spherical (Au) and quasi-spherical (Ag)
Citrus limon (lemon)	Silver	spherical, spheroidal
Coriandrum sativum (coriander)	Gold	spherical, triangular, truncated triangular, decahedral
Cymbopogon flexuosus (lemongrass)	Gold	spherical, triangular
Emblica officinalis (indian gooseberry)	gold & silver	--------------------
Eucalyptus citriodora (neelagiri)	Silver	spherical
Hibiscus rosa sinensis	gold & silver	spherical and prism
Medicago sativa (alfalfa)	Gold	tetrahedral,hexagonal platelet, decahedral, icosahedral
Medicago sativa (alfalfa)	iron oxide	crystalline
Murraya koenigii	Silver	crystalline, spherical
Murraya koenigii	Gold	spherical, triangular
Ocimum sanctum (tulsi; root extract)	Silver	spherical
Ocimum sanctum (tulsi; leaf extract)	Gold	crystalline, hexagonal, triangular

Figure 1. Photograph of some plant which can be used for extract preparation in metal nanoparticles synthesis (photo courtesy: Dr. Balaprasad Ankamwar)

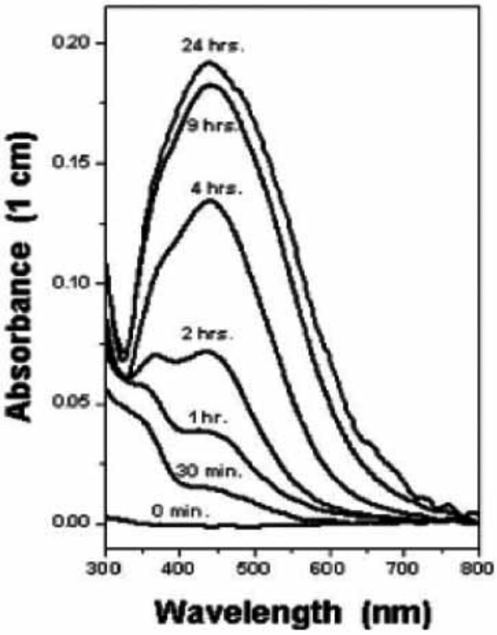

Figure 2. The UV-visible absorption spectra recorded from the aqueous silver nitrate-geranium leaf extract reaction medium as a function of the reaction time. (Reproduced with permission from Shiv Shankar et al. Copyright (2003) Wiley).

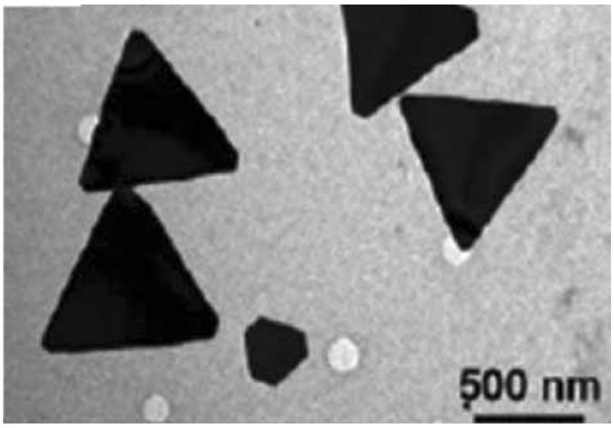

Figure 3. TEM image of gold nanotriangle synthesized by the reduction of aqueous HAuCl4 solution with lemon grass extract. (Reproduced with permission from Shiv Shankar et al. Copyright (2005) American Chemical Society).

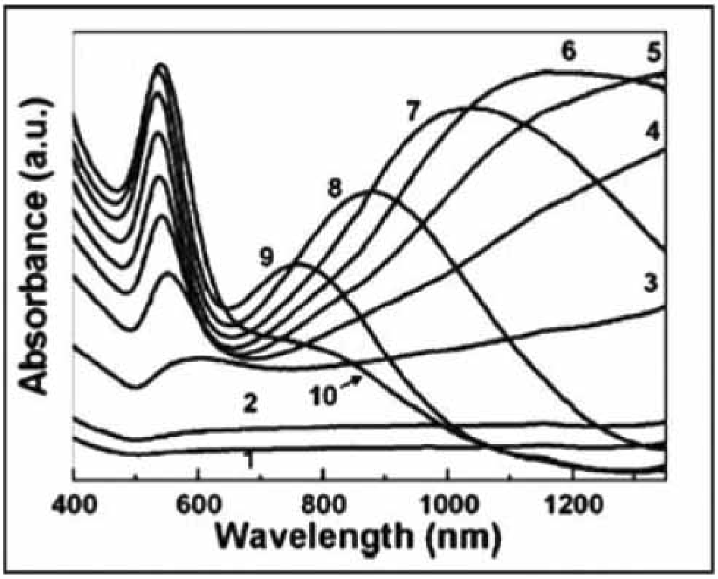

Figure 4. The UV-vis-NIR spectra of gold nanoparticles synthesized by adding different amount of lemongrass leaf extract. (Reproduced with permission from Shiv Shankar et al. Copyright (2005) American Chemical Society)

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Synthesis of Triazole Precursors, 4-Amino-3, 5-Dimethyl-1, 2, 4-Triazole, Phosphorus Containing Triazole and Their Reactivity Study with Metal

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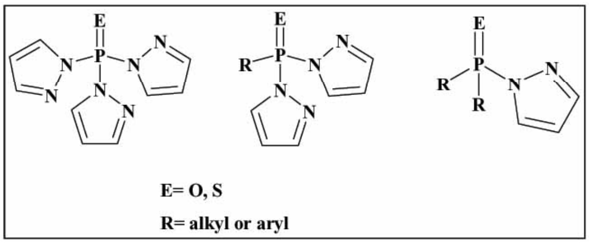
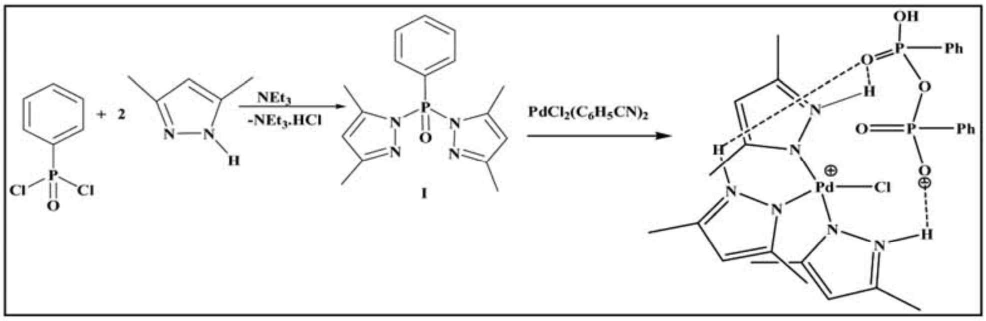
Abstract : The triazole precursor, 4-amino-3, 5-dimethyl-1, 2, 4-triazole **1** has been synthesized. The solid state structure of **1** showed extensive intermolecular N-H…N hydrogen bonding between amino groups at the 4-position and ring nitrogens leading to a 2D-sheet structure. Metalation reaction of **1** with Cu $(OAc)_2$ afforded a trinuclear copper cluster similar to the copper triangles known for copper pyrazolates. In order to synthesize phosphorus containing multi-coordinated ligand systems we studied reactions of **1** with $POCl_3$ and $PSCl_3$. The reaction with $POCl_3$ yielded **2** and **2a** where incomplete substitution of triazoles has been identified.

Introduction : Polypyrazolyl borates $[HB(Pz)_3]^-$ and $[H_2B(Pz)_2]^-$ (Pz = pyrazole or substituted pyrazole) are one among the most widely studied multidentate ligand systems.[1, 5] This is due to the following three factors: (a) they are readily synthesized in very good yields by a one- step synthesis, (b) they have excellent binding properties toward a large range of transition and lanthanide metal ions,[6, 9] and (c) these ligands can easily be modulated by varying the stereo-electronic properties of the substituents on the pyrazolyl groups.[10, 13] Because of these favorable binding properties pyrazolyl borates have found application as ligands in various research themes including organometallic[14, 15] and bioinorganic chemistry.[16, 17] By getting idea of the versatility of polypyrazolyl borates scientist tried to synthesize the corresponding phosphorus analogues such as $P(Pz)_3$, $(E)P(Pz)_2$, or $R_2P(E)(Pz)$ [E=O, or S ; R=alkyl or aryl]. But till date the reports for phosphorus based pyrazolyl ligand systems in metal complexes have been limited to a few examples.[18, 19]

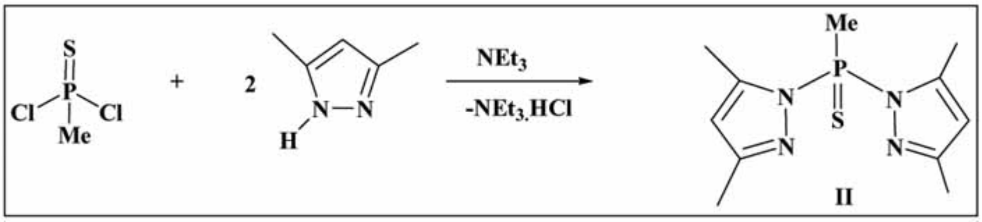


One of the chief defects of the phosphorus based pyrazolyl ligands appears to be the hydrolytic sensitivity of the P-N bond particularly after interaction of the ligand with transition metal ions. The general inclination of these ligands towards hydrolytic cleavage upon coordination with metal ions has been observed in many reactions involving acyclic and cyclic phosphorus based pyrazolyl systems.

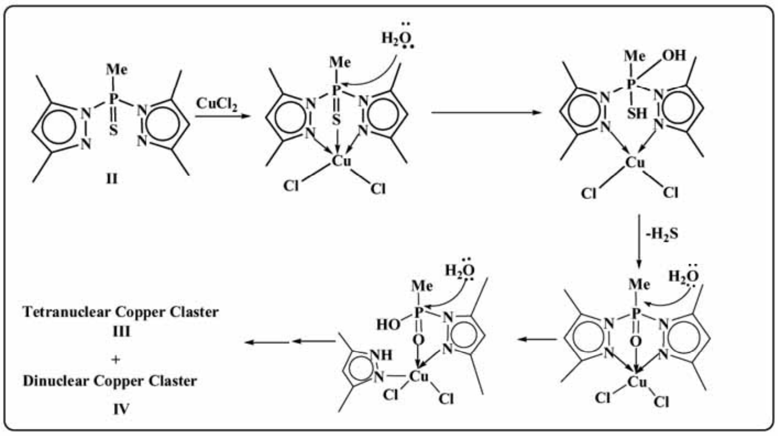
In a representative example the pyrazolyl complex $PhP(O)(3,5\text{-}Me_2Pz)_2$, **I,** synthesized by the reaction of P, P'-dichlorophenylphosphine oxide with 3, 5-dimethylpyrazole in presence of triethylamine as a hydrogen chloride scavenger, found to undergo a facile metal assisted P-N bond cleavage reaction. The reaction of **I** with $PdCl_2(C_6H_5CN)_2$ yielded an yellow crystalline material identified as $[Pd(3,5Me_2Pz)_3Cl]^+$ $[PhP(O)(OH)OP(O)_2Ph]^-$ in which P-O bonds were found to be present instead of any P-N bond. It is inferred that coordination of Pd with the terminal N-donor of the pyrazolyl moiety enhances the electrophilicity at the phosphorus centre which results in the nucleophilic attack by H_2O present in adventitious amounts in the solvent medium.[20]



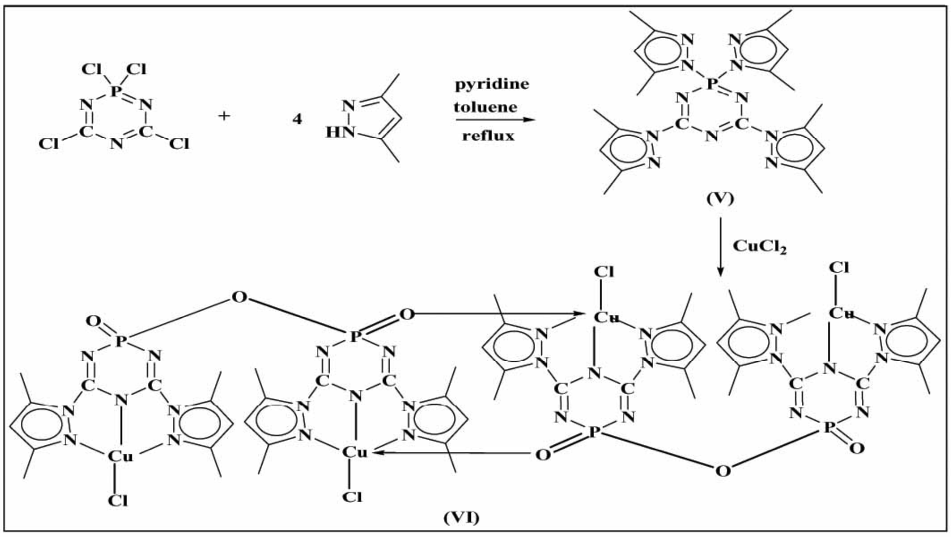
In another instance where a similar P-pyrazolyl ligand, $MeP(S)(3,5\text{-}Me_2Pz)_2$, was found to undergo a metal assisted hydrolysis and desulfurization reaction upon coordination with Cu^{+2} ion.



Reaction of **II** with $CuCl_2$ results in the formation of a tetranuclear and dinuclear Cu(II) clusters in which no P-N and P=S bonds were present. The metal assisted hydrolysis and desulfurization reaction is believed to undergo in a pathway which involves the nucleophilic attack of water on the initially formed complex and successive expulsion of H_2S. The resulting mononuclear complex undergoes further hydrolysis leading to the formation of **III** and **IV**.[21]



Not only acyclic P-pyrazolyl systems undergo metal assisted hydrolysis but cyclic systems such as pyrazole substituted cyclocarbaphosphazene are also found to undergo the same metal assisted hydrolytic reaction. The tetra pyrazolyl cyclocrbaphosphazene **(V)** was shown to undergo a regioselective P-N bond cleavage in presence of Cu^{2+} ions.



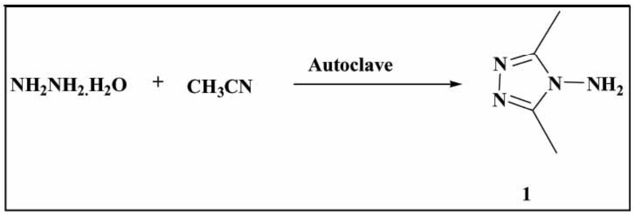
The reaction of **(V)** with $CuCl_2$ afforded the tetranuclear Cu(II) complex **(VI)**, the formation of which involves a regiospecific hydrolytic P-N bond cleavage reaction involving the phosphorus-pyrazole unit although the ligand **(V)** does not possess hydrolytic sensitivity as identified from ^{31}P- NMR experiment.[22]

In all the above examples the P-N bond cleavage was envisaged and resulted in fortuitous P-N bond cleavage leading to interesting multi-nuclear metal clusters. Hence we propose that if the pyrazole or any other heterocycle is attached to P-centre by a spacer will result in the P-analogue of tris (pyrazolyl) borate which will remain stable during metalation reactions.

Herein we report the synthesis of 4-amino-3, 5-dimethyl-1, 2, 4-triazole and its interaction with $POCl_3$, $PSCl_3$ and cyclocarbaphosphazene precursors. Treatment of 4-amino-3, 5-dimethyl-1, 2, 4-triazole with P-Cl groups will lead to the reaction of the primary amino group at its 4-position and result in formation of stronger P-N bonds as found in most amino substituted P(V) ligands.

Results and Discussion:

Synthesis of 4-amino-3, 5-dimethyl-1, 2, 4-triazole: 4-amino-3, 5-dimethyl-1, 2, 4-triazole, **1** was prepared by the literature procedure.[23] This involves the direct reaction of hydrazine hydrate and acetonitrile in an autoclave as shown in the scheme 1.



Scheme 1

The ESI-mass, ^{1}H-NMR and melting point values obtained from **1** matched with the literature reported values indicating the formation of 4-amino-3, 5-dimethy-1, 2, 4-ltriazole. In order to establish the supramolecular structure we have re-done X-ray crystal structure of **1**. In the solid state, **1** forms an extensive 2D-sheet structure aided by intermolecular hydrogen bonding between amino groups at the 4-positions and triazole ring nitrogens. The metric parameters for this hydrogen bonded assembly points to strong hydrogen bonds (figure 1).

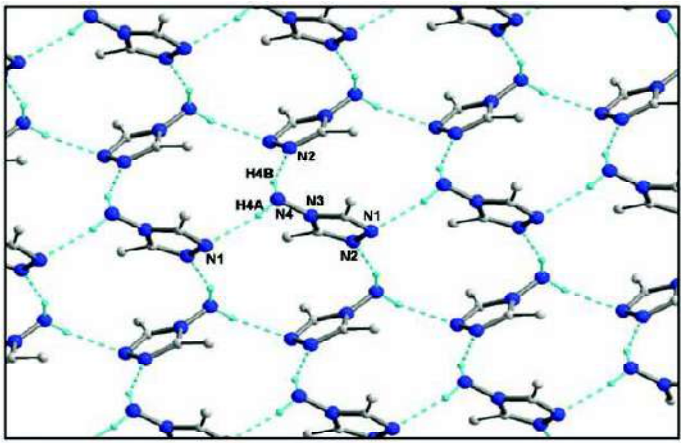


Figure 1: 2D-sheet structure formed by 1. D(N4-H4A-N1): 2.252(1)Å; <(N4-H4A-N1): 167.7(1); D(N4-H4B-N2): 2.212(1)Å; <(N4-H4B-N2): 156.28(0)

Reactivity : After synthesizing the triazole ligand **1** we were curious to see its metalation reactions with metal ions such as copper. Reaction of **1** with $Cu(OAc)_2$ was attempted in

MeOH in presence of a base such as NaOEt. It was presumed that NaOEt will be able to deprotonate the NH_2 group and facilitate its bonding with Cu^{2+} ions. Hexagonal crystals were isolated from a methanolic solution after one week. The single X-ray crystal analysis revealed the formation of trinuclear copper cluster where the NH_2 groups of the ligands remained intact (figure 2). The molecular structure of the trinuclear copper cluster is very much similar to the copper triangle known for copper pyrazolates.[24]

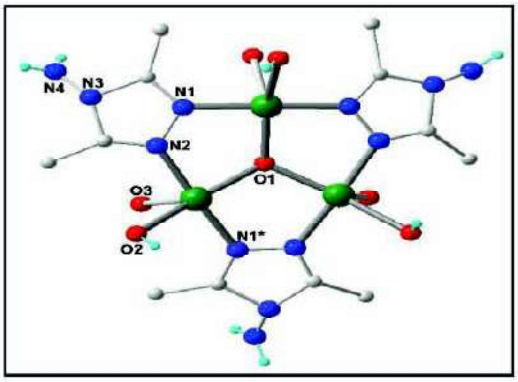
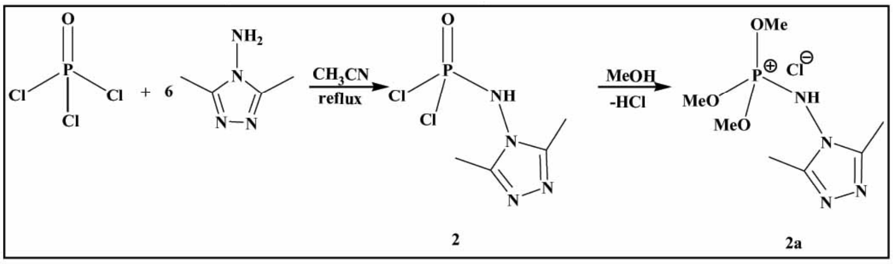


Figure 2: Molecular structure of the trinuclear copper complex. The disordered amino groups, methyl carbons and hydrogens, and hydroxyl groups are not shown for clarity. Detailed bond-lengths and angles have not shown due to poor X-ray data

Each copper is bound to two triazole ligands which act as μ_2-bridging ligands. The coordination environment of each copper consists of two triazole ring nitrogens (N1 and N2) one terminal aqua ligand (O3) and one terminal hydroxyl group (O2) and a one µ3-bridiging hydroxyl group. We were unable to locate the hydrogens attached to O1 and O3 due to poor X-ray data. But the principal attachments to copper have been verified by comparisons with structurally similar trinuclear copper pyrazolates. There are two additional hydroxyl groups outside the cluster core which provides the necessary charge balance to the cluster.

IR spectrum of the complex recorded in KBr pellets showed peaks at 3437cm^{-1} and 3202cm^{-1} respectively indicating the presence of O-H groups and N-H groups respectively. In addition C-H stretching frequencies in the range of 2920 and 3200 cm^{-1} have been observed. The EPR spectra of **2** in solid state and solution state have been taken. The ESR spectrum of the solid sample of **2** showed respective $g_{\parallel}$ and $g\perp$ values of 2.109 and 2.054 at the field strengths of 319.92 and 328.38 mT respectively. The ESR spectrum of the methanolic solution of **2** showed $g_{\parallel}$ and $g\perp$ values of 2.194 and 2.133 respectively at the respective fields of 307.15 and 315.93 mT. These EPR spectra showed the paramagnetic nature of the complex both in the solid and solution state indicating the presence of copper in its +2 oxidation state.

Preparation of acyclic P(V)-triazole ligand systems : The triazole precursor **1** was treated with $POCl_3$ in presence of excess of NEt_3 in dry CH_3CN (scheme 2) and then refluxed for 3 days under stirring condition. The homogeneous solution obtained is then cooled to room temperature. The solution was reduced to one third of its volume to yield a white crystalline precipitate. The precipitate was then extracted with $CHCl_3$ to remove $Et_3N.HCl$ by-product. The insoluble residue was filtered off and dried to obtain **2** as a moisture-sensitive compound. The ^{31}P NMR spectrum recorded on a methanolic solution of **2** showed a peak at chemical shift of -20.8 ppm ($CDCl_3$ as locking agent; 85% H_3PO_4 as reference) indicating the presence of a phosphate environment (figure 3). The infrared spectrum of **2** showed a strong absorption at 1258 cm^{-1} characteristic of P=O group in addition to N-H and C-H absorption peaks. The ESI-mass spectra gave a single peak at 238.46[M^+] which matched with the formulation of trimethoxy (4-amino-3, 5-dimethyltriazolyl) phosphonium cation **2a**. The incomplete substitution of the triazole in **2** may be attributed to the extensive hydrogen bonding of amino protons to the ring nitrogens. Hence a stronger organometallic base such as n-BuLi may be required to break these hydrogen bonds enabling complete substitution. The possible formation of **2a** may be due to the protonation of the corresponding dichloro (4-amino-3, 5-dimethyltriazolyl) phosphine oxide **2** by the in-situ generation of Hydrogen chloride followed by methoxide ion exchange.



Scheme 2

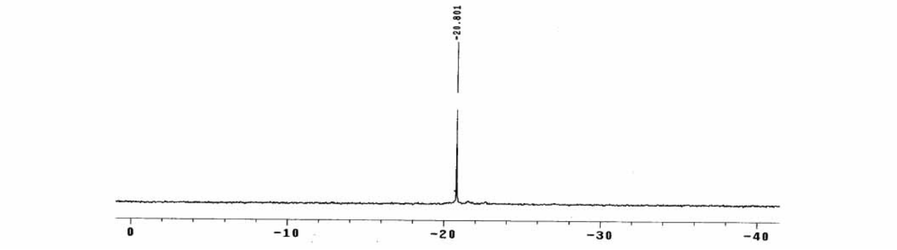


Figure 3: ^{31}P-NMR of **2** in $CDCl_3$

We also carried out a reaction between $PSCl_3$ and **1** in presence of Et_3N in dry CH_3CN using the same procedure as described above in order to synthesize tris(4-amino-3,5-dimethyltriazolyl)phosphine sulfide. But we were unable to isolate a pure product as indicated by ^{31}P-NMR spectra (figure 3). We are still in the process of improving the reaction conditions to obtain a pure product.

Conclusion : In conclusion we synthesized 4-amino-3, 5-dimethyl-1, 2, 4-triazole ligand and studied their reactivity with copper acetate and P(V)-Cl precursors. The reaction of the ligand **1** in presence of copper acetate and sodium ethoxide yielded a trinuclear copper cluser similar to the known copper pyrazolates. While the reaction of the triazole with

$POCl_3$ is incomplete in presence of Et_3N as hydrogen chloride scavenger, the corresponding reaction with cyclocarbaphosphazene in presence of n-BuLi proceeded cleanly.

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The Janus Particles

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Most popular and most studied artificial swimmer is self-propelled Janus particles. There is considerable development in the field of artificial micro-swimmer based on extensive research on self-propelled Janus particles. We mainly emphasize the swimming mechanism and transport properties of artificial micro-swimmer of Janus kind. The name 'Janus Particle' was first introduced by Professor Pierre-Gilles de Gennesin his Nobel lecture in 1991.The word Janus comes from the two-faced Roman god Janus who has two different faces. A typical Janus particle contains two distinct surfaces with different physical and chemical properties.

Figure 1: Schematic of spherical Janus particles with two distinct hemispheres with different interaction with solvent (left one), light absorbing properties (middle one) and catalytic properties (right one).

As for examples [1-8] (see Fig.1), (i) one surface of a spherical particle may be hydrophilic, another one is hydrophobic, (ii) one surface can catalyze chemical reaction however another surface cannot, (iii) one heme-sphere can absorb light but another cannot.

1.1 Outline of Janus particle synthesis

There are a number of technical difficulties that one encounters when synthesizing the Janus Particle in a laboratory [9-10]. The central as well as challenging issues here are to create different functional behaviour on two sides of the same particle. The three main procedures for Janus particle synthesis are: masking, phase separation, and self-assembly are schematically show in Fig 2.

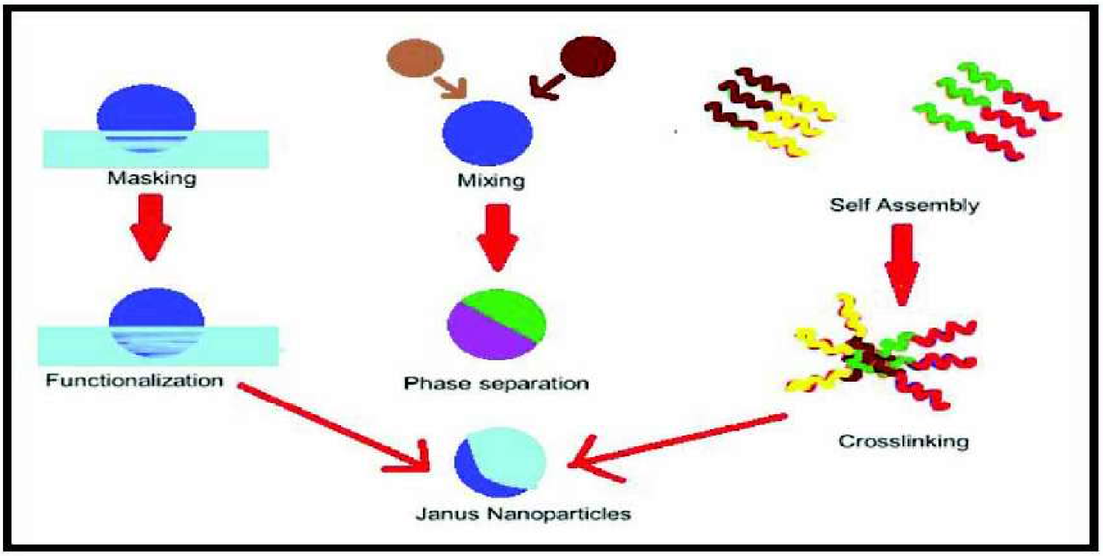

Figure 2: Outline of scheme for Janus particle synthesis in laboratory.

1.2 Self-propelled Janus particles:

All the two faced particles are not motile. A special kind of Janus particles can propel themselves by extracting energy from the surrounding medium. Research on motile Janus particles started receiving attention in chemical physics and biology when Sen et al [11] designed and synthesized a micro-sized Janus particle with one face containing platinum which can catalyze decomposition of hydrogen peroxide. These types of particles were synthesized to design 'nano-motors' for applications in biological sciences and nanotechnology. Thereafter, thinking of potential applications, several pioneer researchers have given significant input in this field of designing and characterizing self-propelled Janus particles with different goals. Few years later Sano et. [12]. synthesized a new type of self-propelled Janus particles which were powered by a different mechanism [Fig.3]. Later on, Prof. Bechinger's group [18] (Universität Stuttgart, Germany) experimentally explored very interesting transport features self-propelled Janus particles in a patterned environment and have shown that such active particles can be used as a light driven diffusing tracer. This pioneering work made self-propelled Janus particles more widely acceptable and versatile model systems for experimental tests of theories related to non-equilibrium phenomena [13-20]. The actual mechanisms of self-propulsion rest on some kind of phoretic process at the propeller - solvent interfaces. As for examples, suppose the self-propulsion is the result of chemical reactions or light absorption selectively one of the hemispheres. In the former case, asymmetric chemical gradients resulting from catalytic reactions push the particles to a specific reaction. Another example, selectively one hemisphere of the Janus particle becomes warmer by absorbing light. Thus, a fluid velocity gradient is produced at the vicinity Janus-particle solvent interface (Fig.3).

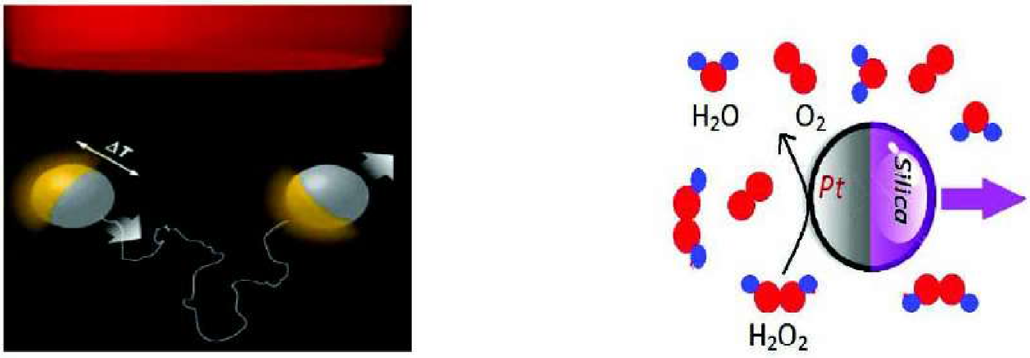

Figure 3: Schematic self-propulsion mechanisms. Left - Self-propulsion based on the thermophoresis. Right - diffusiophoresis is responsible for self-propulsion.

1.3 Peculiar dynamical properties and transport features of self-propelled Janus particles

Self-propelled Janus particles are a very interesting dynamical system to study as they exhibit very unusual transport features. Depending upon their self-propulsion mechanism Janus particles can diffuse a few hundred times faster than normal colloids of the similar sizes. When they diffuse through spatially periodic structures with broken inversion symmetry, interestingly, autonomous motion is observed. The spatial periodic structures can either be energetic potential or channel with varying cross-section. Note that in this interesting ratcheting effect detail balance is broken due to non-equilibrium correlated fluctuations of external origin. More interestingly, in some situations particles exhibit absolute negative mobility, that is, Janus particles spontaneously move to the opposite direction of the driving force. We discuss diffusion and peculiar transport features (autonomous motion or ratcheting and negative mobility) with more details in the following.

1.4 Diffusivity of Janus particles

Diffusion is one of the important quantifiers to analyze transport of nano-to-micro size particles in viscous medium. Diffusion is the act of spreading from a point. Generally it is estimated by calculating mean square displacement as a function time in the large time limit. In case of normal diffusion it is given by,

$$\left\langle \Delta x^2 \right\rangle = 2\mathrm{Dt} \quad \text{or,} \quad D = \lim_{t\to\infty}\left[\frac{\left\langle \Delta x^2 \right\rangle}{2t}\right] \qquad - \quad - \quad - \quad (1.1)$$

Where D is the diffusion coefficient. For a normal colloidal particle of size a diffusing through a viscous medium (with viscosity η) at the temperature T, diffusivity is given by,

$$D = \frac{\mathrm{k_B}T}{6\pi\eta\, r_0} \qquad - \quad - \quad - \quad (1.2)$$

This expression is referred to as the Stoke-Einstein relation. Note that kB is the Boltzmann constant. However, diffusivity of active particles contains another component due to self-propulsion motion.

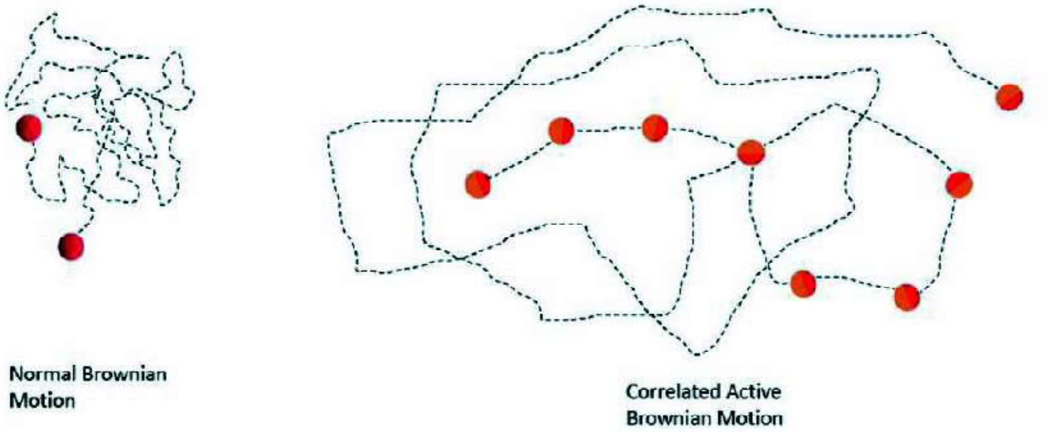

Figure 4: Schematic of trajectories of normal (left) and self-propelled (right one) Janus particles. Normal colloidal particles motion is completely uncorrected, where as self-propelled particles exhibits correlated motion.

In most of the previous studies of the dynamics of Janus particles, generally, it was assumed that the velocity is directed along the self-phoretic force. The phoretic force acts with respect to specific particles' axes. Moreover, rotational diffusion as well as other non-equilibrium fluctuations keeps the direction of self-phoretic change. As a result, Janus particles exhibit random motion, however, the net fluctuating forces acting on the particles are time correlated. Diffusion coefficient of such particle is given by,

$$D = \frac{k_B T}{6\pi\eta r_0} + \frac{v_0^2 t_R}{4} \quad - \quad - \quad - \quad (1.3)$$

Where the first component is the diffusion constant due to thermal translational motion, and the second is due to correlated phoretic motion. The phoretic contribution to diffusion is directly proportional to the square of self-propulsion velocity (v_0) and persistence time (τ_R). The persistence time is inversely related to the rotational diffusion constant, $\tau_R = 1/D_R$.

In general, the contribution in diffusion due to self-propulsion is overwhelmingly large in comparison to the thermal translational part. Thus, Janus particles can diffuse much faster than the passive Brownian particles of the same size. As for example, a Janus particle made of silica bead with radius 2.13 μm one hemisphere-coated with 20 nm thick gold layer has diffusivity about 7.84 μm^2/second, where as a passive silica spheres have diffusivity about 0.03 μm^2/second [21].

1.5 Autonomous motion

One of the most interesting features of self-propelled Janus particles is ratcheting or autonomous motion. In the field of chemical physics and biophysics ratchet models are used to explain mechanisms for directional transport. The Basic idea came from the Feynman Ratchet and pawl machine [22-30]. Through ratcheting mechanism one can extract energy out of nonequilibrium fluctuations of the surrounding. The essential ingredients for autonomous motion are: (a) spatial symmetry must be broken in the substrate potential (it may be energetic or entropic in nature [see Fig.5) and (b) the fluctuating forces acting on the system must be time correlated in nature. These ingredients are known as Pierre Curie's conjecture.

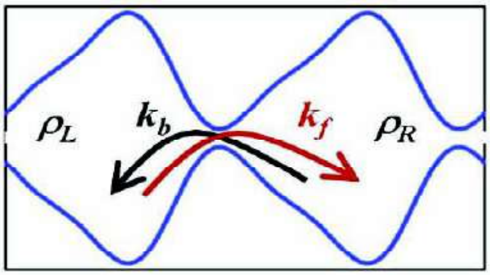

Figure 5: Schematic of two adjacent compartments of an asymmetric periodic channel.

If we consider a colloidal Brownian particle in a periodic channel with broken spatial symmetry, it will exhibit diffusive motion with net average velocity zero. Thus, neither they flow to left nor to right. This is due to the fact that a lacking source of external fluctuations system remains in the equilibrium state and the condition for detailed balance prevails.

$$\rho_L k_f = \rho_R k_b \quad - \quad - \quad - \quad (1.4)$$

This relation assures detailed balance in the system. That forward rate from any channel compartment is balanced by back flow of an exactly equal amplitude.

On the other hand when a Janus particle is placed in a coagulated channel or spatially periodic system with broken symmetry they spontaneously flow to a particular direction depending upon the nature of spatial periodic structures. Self-propelled Janus particle acquires an external source of energy due to phoretic mechanism, thus particles are no more in equilibrium with the surrounding medium and detailed balanced symmetry is broken,

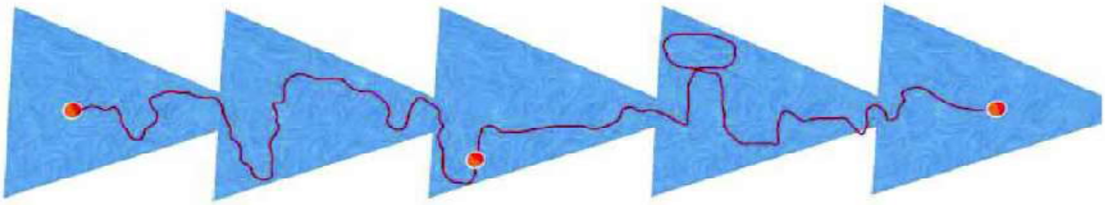

Figure 6: Schematic of an asymmetric periodic channel (adopted in reference [31]) along with a trajectory of active particle. Here compartments are triangle shape, thus spatial symmetry is broken.

A recent study based on numerical experiments shows that self-propelled artificial microswimmer like Janus particles exhibit autonomous motion in the periodic channel. They show that in the case of triangular compartmentalized channel ratcheting efficiency is orders of magnitude larger than thermal ratchet. This offers great robustness, thus, one can much easily access the ratcheting effects in experiments. More interestingly, just a few Janus particles are enough to pump a crowd of Janus particles.

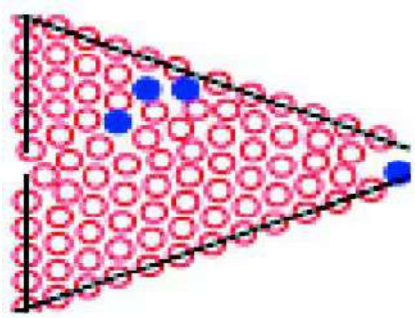

Figure 7: Snapshot of a few Janus particles (solid blue circles) in the crowd of passive particle (hollow red circles). Here only one compartment of a triangle channel has been shown [31].

1.6 Negative mobility

One of the most conspicuous features of self-propelled particles, under certain conditions, exhibits absolute negative mobility. This is basically a non-equilibrium phenomena, where a Brownian particle moves to the opposite direction of the applied force. The essential ingredient is that the system must be driven out of equilibrium as well as having no current. This effect is, generally, misunderstood with current reversal. However, the subtle difference should be noticed. Recently, Ghosh et. al. [32], have shown that suitably designed self-propelled Janus particles in a channel can swim against external bias of small amplitude. Thus, particles can exhibit absolute mobility. The underlying mechanism for such interesting phenomena rests on the interaction between walls and the Janus particles. To be specific, authors in ref [32] considered interaction between elliptical particles and roughness of channel walls, which make orientation of self-propulsion against the external drive

1.7 Eccentric micro-swimmers

In practice the center of force may not coincide with the propeller center mass. Moreover, orientation of self-propulsion may not be rigidly related to particles' rotation. Thus, the orientation can fluctuate around an average position. A new model has been proposed in ref [33-34] to describe dynamics of swimmers taking into account these issues. Self-propellers here are referred to as "eccentric swimmers". Figure 8 depicts a typical eccentric swimmer where the center of the force is located at the point P, which is apart from the center of the mass O. If the instantaneous self-propulsion force (with a

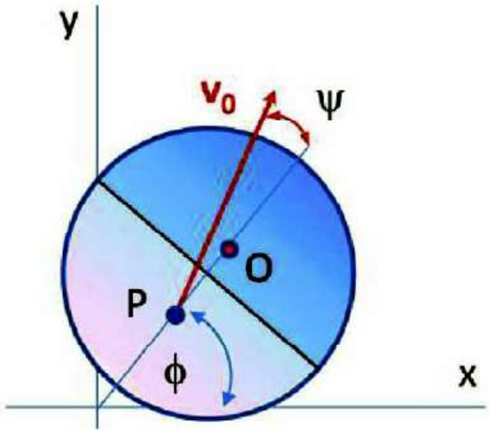

Figure 8: A self-propelled Janus particle with center of mass (O) and center of force at different position (P).

constant modulus v_0) makes an angle Ψ with respect to the molecular axis (OP in the Fig.8). However, Ψ fluctuates with respect to the molecular axis. The fluctuation of Ψ is characterized by a relaxation time and variance, and for the sake of simplicity it is modeled by a stationary Ornstein–Uhlenbeckprocess [33-34]. As the center of force does not coincide on the center of mass, the particle experiences a torque which makes the particle rotate with a frequency Ω which depends on the moment of inertia, amplitude of self-propulsion, as well as Ψ

Application: Janus particle has wide range of application in different branches of science for e.g. drug delivery, robotic microsurgery, cell biology, chemical industry, design and operation of micro-robots, separation the colloidal particle etc [1-7]. All of this application is based on the controlled transport of active particle.The motility transfer technique could be used to -increase the rate of the motility of weak sperm cells and to govern the reaction rate in a chemical reactor [35].

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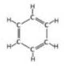
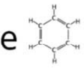
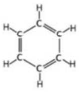
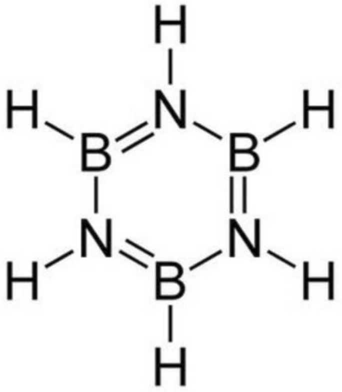
Me: Mom can we have  ?

Mom: we have  at home.

 at home:



Series

Shanti Swaroop Bhatnagar Awardees in Chemical Science: Mushi Santappa; The Ninth Recipient

The Shanti Swaroop Bhatnagar Award for Science and Technology is a science award in India given annually by the Council of Scientific and Industrial Research (CSIR). The award was instituted in 1958 with the objective to recognize conspicuously important and outstanding contribution to human knowledge and progress - fundamental and applied. The award is named after the founder director of the CSIR, Shanti Swaroop Bhatnagar. It was first awarded in 1958.Any citizen of India engaged in research in any field of science and technology up to the age of 45 years is eligible for the award. In 1967, Mushi Santappa was awarded the prestigious Shanti Swaroop Bhatnagar Award for his contribution to chemical science. Herein, brief information of the great scientist is given. Mushi Santappa was an Indian polymer chemist, leather technologist and a vice chancellor of Sri Venkateswara University and the University of Madras. He was one of the founder directors of Avanti Leathers Limited and was known for his researches on the synthesis of graft copolymers, the properties of macromolecules, and osmotic techniques. The Council of Scientific and Industrial Research, the apex agency of the Government of India for scientific research, awarded him the Shanti Swaroop Bhatnagar Prize for Science and Technology, one of the highest Indian science awards, in 1967, for his contributions to chemical sciences.

Early Life:

Mushi Santappa was born on 2 October 1923 in Jonnagiri village in the south Indian state of Andhra Pradesh to Arikeri Basappa-Rajoli couple. He graduated in chemistry from the University of Madras in 1943. His master's degree was from Banaras Hindu University in 1946 after which he secured a PhD from the University of London on a Government of India scholarship in 1949, mentored by R. W. West. Staying back in the UK, he obtained another PhD in 1951 from Manchester University, working under the guidance of Meredith Gwynne Evans, a Fellow of the Royal Society; his thesis was based on the physical chemistry of high polymers.

Academic Work:

After returning to India, he joined the University of Madras as a reader of physical chemistry in 1952 and in 1958, he was transferred to the Madurai Extension Centre (present day Madurai Kamaraj University) as a professor. He later returned to Chennai in 1963 as the head of the department of physical chemistry. Serving as a UGC Senior Professor at the University from 1966 onward, he also worked as a director at Central Leather Research Institute (CLRI) from 1972.

In 1979, he was appointed as the vice chancellor of Sri Venkateswara University, Tirupati. On expiry of his tenure in 1980, he returned to Chennai and took up the assignment as the vice chancellor of the University of Madras in 1981 where he stayed till 1984.

While working as the UGC professor he co-founded Avanti Leather Limited, a public limited company involved in the manufacture and export of leather products in 1976.

Scientific Work:

- Santappa's early researches during his doctoral studies were related to vinyl monomers, and its free radical polymerization using light, but later he shifted his focus to the study of kinetics of vinyl polymerization during his stint at the laboratory of Meredith Gwynne Evans.
- Through these studies he propounded that vinyl monomers could be polymerized using photo polymerization.
- He also demonstrated the synthesis of graft polymers by simple chain transfer process and also studied oxidation of number of organic substrates
- His researches have been published in over 350 articles and he guided 59 research scholars on the doctoral studies and also published a comprehensive text on the State of the Art in Polymer Science and Engineering in India.
- He along with Santi k. Palit, promoted research in polymer science at the Indian Association for the cultivation of science and was one of the organizers of the International Symposium on Polymers, under the aegis of the International Union of Pure and Applied Chemistry (IUPAC), held in Chennai in 1983.

Honours and Awards:

- The council of scientific and industrial research awarded Santappa the Shanti Swaroop Bhatnagar Prize, one of the highest Indian science awards in 1967.
- He received the Sir J.C. Ghosh Memorial Medal of the Indian Chemical Society in 1982 and the FICCI Award for Science and Technology of the Federation of Indian Chambers of Commerce & Industry in 1985.

- He was also a recipient of the Sri Kanchi Mahaswani Trust and the Voice Award for Science and Technology of Leather.
- He received an honorary DLitt from Gulbarga University and the degree of Doctor of Science (honoris causa) from Andhra University, Madras University, Sri Krishna Devaraya University and Madurai Kamaraj University.
- He was an elected fellow of all the three major Indian sciences academies, Indian Academy of Sciences (1961), Indian National Science Academy (1971) and National Academy of Sciences, India (1983).
- He was also a fellow of Royal Institute of Chemistry (1970) and the New York Academy of Sciences (1985) and a founder fellow of the Academy of Sciences Chennai.
- The Society for Polymer Science, India has instituted an annual award, Professor M. Santappa Award, in his honor, which recognizes excellence in research in polymer chemistry.

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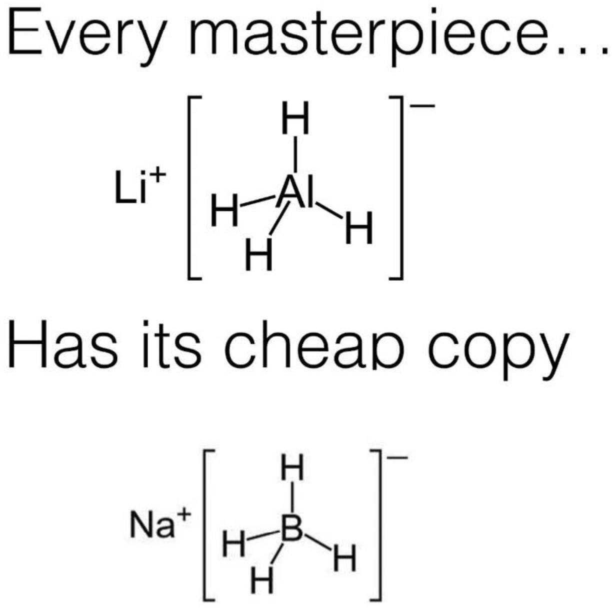

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Birth and Rise of Oriented External Electric Fields (Oeefs) As a Future Green Catalyst

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"Oriented external electric fields (OEEFs) as 'smart reagents' are no longer a theoretical dream," was written by Prof. Sason Shaik in his *Nature Chemistry* 'perspective' soon after the groundbreaking 'blinking experiment' carried out by Aragonès et. al. which was later recognized as a 'proof of principle'. The extraordinary idea of OEEF as a catalyst was first sparked to Shaik in 1974 while he was attending a scientific talk, sitting in a small, dim lecture hall at the University of Washington in Seattle, US. The lecturer at the hall was explaining the dissolution of tertiary butyl chloride in the ether and a smaller percentage of molecules split at the C – Cl bond. On addition of simple salt, lithium perchlorate, at a high concentration (5.5 M), however, increases the rate of the reaction by million-folds. From a chemist's point of view, it is not a very useful reaction itself, but its novelty appears after the addition of simple salt which increases the rate of the reaction enormously. Realizing the role of lithium perchlorate, he thought that at a very high concentration, each catalyst molecule could only have surrounded by two solvent molecules which probably form a liquid crystal-like matrix and somehow generates an electric field in the solution. At that moment, Shaik did not go to the bottom of how exactly the lithium perchlorate catalysis operates as he was trying to find a research career in chemical reactivity using Valence Bond Theory (VBT). However, the question was constantly stuck to his mind and after completing three decades in 2004, he turned it on again. Shaik started looking into his revolutionary idea by considering the active oxidant 'Compound I' found in many enzymes including the cytochrome P450 superfamily. Thereby, he published his first research article in a very prestigious Journal of *American Chemical Society,* entitled *"External Electric Field Will Control the Selectivity of Enzymatic-Like Bond Activations".* This successful step encouraged him and he began to think of something bigger and bold. After that, he tried to investigate the effect of OEEF to control the reactivity and *endo/exo* selectivity of the Diels-Alder reaction. However, it gave him a very tough time while publishing the results, and only succeeded in the year 2009. Latter Shaik said that it got tricky to publish anything, "So, I left the field for a while." Afterwards, several years passed, and suddenly in March 2016, everything was changed in a moment with the wave of a cellphone ring. A journalist called Shaik and told him that his concept of OEEF catalyzed Diels-Alder's reaction was becoming real. It was Michelle Coote,

from the Australian National University in Canberra, and Nadim Darwish, the University of Barcelona in Spain, groups set up such an extremely satisfying experiment that made the theoretical dream of OEEF catalyzed reaction realistically. In their paper, Coote and her colleagues wrote: *"This ability to manipulate chemical reactions with electric field offers proof-of-principle for a change in our approach to heterogeneous catalysis."*

The effects of OEEF while controlling the energetics of a reaction can be understood using the VBT and MOT concepts. Let us start our discussion by considering the simplest homonuclear molecule such as H_2 and Li_2. Albeit the covalent character is the most dominant structure for H_2 and Li_2, there exist two dormant ionic structures for each molecule. As can be seen in Figure 1a, the bond axes of these two molecules are oriented in the z-axis and therefore with the application of z-OEEF induces the significant bond ionicity leading to waking up the dormant ionic structures. On the other hand, the bond ionicity solely depends on two factors: molecular polarizability and field strength. Therefore, one can easily extend the bond ionicity by increasing the OEEF strength and purposefully alter these ionic structures with just reversal of the OEEF direction. As shown in Figure 1a, in no field case, the bonding electron density symmetrically localizes on the σ MO. In presence of OEEF, however, the orbitals mix and rehybridize, acquiring higher contributions on either the right or left

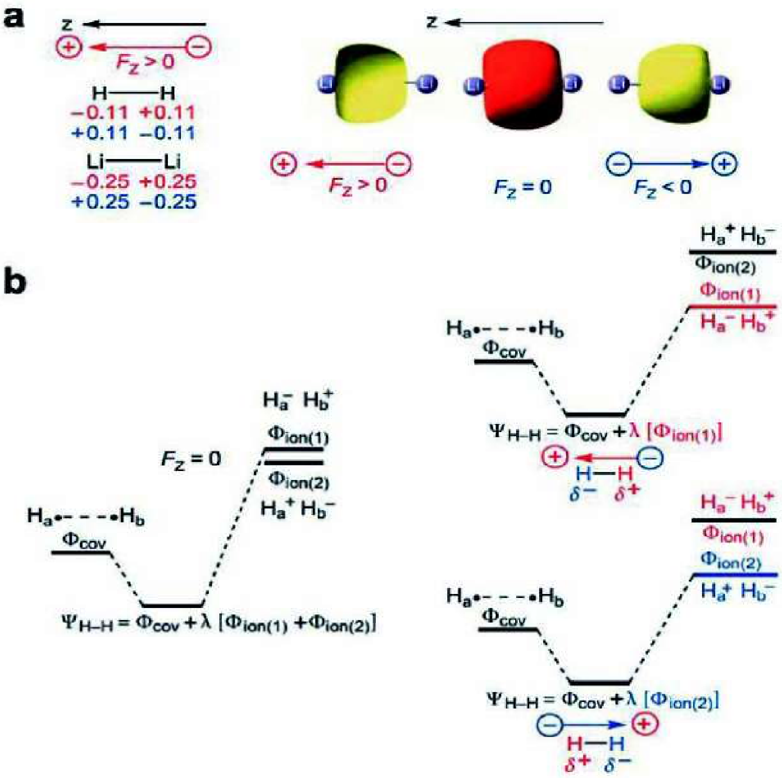

Figure 1: MO and VB analyses of the manner by which an OEEF, oriented along the bond axis, generates charge distributions and dipole moments in two homonuclear bonds, H-H and Li-Li. **(a)** OEEF-induced ionicity in H_2 and Li_2 for positive and negative fields along the bond-axis. The MO-based polarization mechanism due to σ–σ* mixing. **(b)** The VB-based polarization mechanism: the bond-wave-function ($\Psi_{H\text{–}H}$) without a field (left) arises due to equal mixing of the covalent structure (Φ_{cov}) with the degenerate ionic structures ($\Phi_{ion(1)}$, $\Phi_{ion(2)}$), producing a non-polarized covalent bond. $F_z < 0$ and $F_z > 0$ (right) exert selective stabilization of the ionic structure that opposes the field's polarity. The selective covalent–ionic mixing thereby leads to polarized bond wavefunctions.

atoms, depending on the direction of the applied field. Let us understand this phenomenon using Valence Bond Theory taking the H-H bond as a prototype (See Figure 1b). In a zero-field case, the bonding electron pair of H-H bond possesses a covalent structure (Φ_{cov}) that equally mixes with two degenerate ionic structures, i.e., $\Phi_{ion}(1)$ and $\Phi_{ion}(2)$. As a result, the bond-wave function ($\Psi_{H\text{-}H}$) for the H_2 molecule describes an a polar bond in where both the ionic structures behave as hidden dormant in the wave function. At this point, if we apply a z-OEEF on the H-H bond that will stabilize the ionic structure $\Phi_{ion}(1)$ that can now preferentially mix with the dominant covalent structure leading to the formation of a bond with ionicity oriented as in $\Phi_{ion}(1)$. On the other hand, reversing the direction of z-OEEF will stabilize the ionic structure $\Phi_{ion}(2)$, which can now mix preferentially with the covalent structure resulting in a bond with the ionicity of $\Phi_{ion}(2)$. Hence, it is now worthy to state that with increasing the OEEF strength, the dormant ionic structures become more dominant or stabilized and cross below the covalent structure resulting in bond heterolysis. Therefore, a polar bond can easily undergo a bond heterolysis at significantly weaker OEEF. Thus, catalyzing the bond heterolysis using OEEF is much like with the $LiClO_4$ catalysis of S_N1 reactions of polar bonds.

With the development of this exciting research area, it sets up the first rule for the researchers in this field which is famously known as the *"Reaction Axis Rule"*. The reaction axis is the direction along which electron pairs undergo reorganization from reactant-like to product-like bonding. *Applying an OEEF with the right polarity will stabilize the TS and catalyze the reaction. Flipping the OEEF in the opposite direction will cause inhibition.*

Let us take *"Diels-Alder reaction"* as an example to understand the reactivity and selectivity control of a reaction using OEEF. While digesting this new concept, we first need to understand the energy curves generated throughout the reaction coordinate for a generic reaction R → P in VB representation. Figure 2a shows the covalent structures (Φ_{cov}) describing the covalent bonds of reactants (R) and products (P). The mixing of these two VB structures generates the VB state shown in the bold curve; Ψ_{TS} is the transition state. Figure 2b is the same as the previous one, but here added all the ionic- and CT-structures ($\Phi_{ion}/(\Psi_{CT})$. The downward arrow indicates the mixing of these structures into the TS-wave function. Once we have understood the generic reaction concept, we can move to a more complex system like the Diels-Alder reaction. Figure 3 shows the VB representation of energy curves for generic.

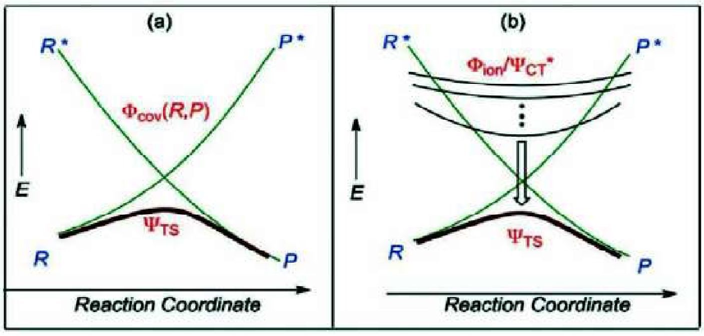

Figure 2: VB representation of energy profile diagram for a generic reaction R → P.

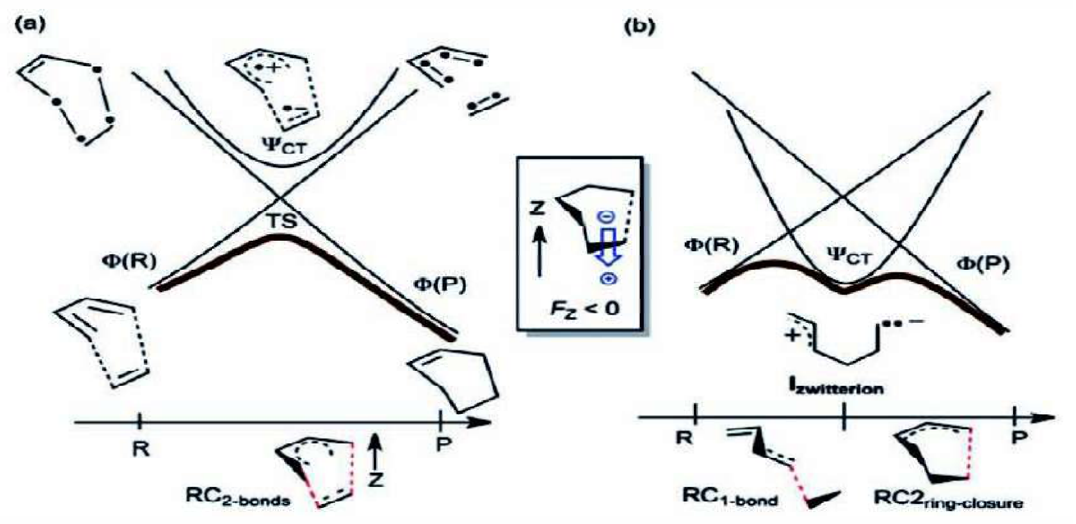

Figure 3: VB diagrams showing the construction of the energy profiles (in brown color) for a generic Diels-Alder reaction, and leading to predictions of z-OEEF effects on catalysis/inhibition and mechanistic-crossovers in the reaction

Diels-Alder reaction describing the various phenomenon like the formation of TS and its barrier height as well as the behavior of the reaction under OEEF oriented along the reaction axis. Figure 3a shows that the barrier and TS arise from the mixing of the reactant's (Φ_R) and product's (Φ_P) state curves that cross one another along the concerted reaction coordinate. As already discussed, here too there exists a CT-state (Ψ_{CT}), which involves an electron transfer directed from diene to dienophile. Ψ_{CT} shares the same symmetry as the TS and the mutual mixing lowers the barrier and endows the TS with some ionicity. It is clear that $F_z < 0$ along the reaction-axis will stabilize this Ψ_{CT} state and will cause greater TS stabilization, which will catalyze the reaction. By contrast, flipping the OEEF direction to $F_z > 0$ will destabilize Ψ_{CT}, and will thereby raise the barrier and inhibit the reaction. Furthermore, as shown in Figure 3b, at a critically high $F_Z < 0$, Ψ_{CT} should be sufficiently stabilized to cross well below the principal state curves and change thereby the mechanism from a concerted- to a stepwise cycloaddition via a zwitterionic intermediate ($I_{zwitterion}$). [Here, we will not discuss the controlling of *endo/ exo* selectivity due to the complexity of the subject area; interested readers may go through the following review paper- *https://doi.org/10.1039/C8CS00354H]*

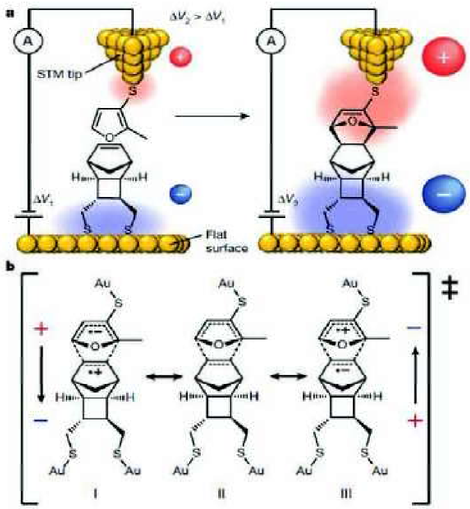

Figure 4: Experimental set up for electrostatic catalysis of a Diels – Alder reaction

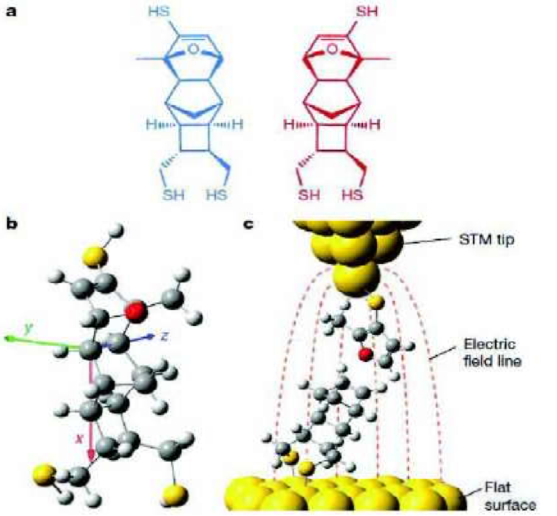

Figure 5: Computational modelling of the Diels – Alder reaction describing the experimental set up

Finally, we end up our discussion by showing the experimental setup to accomplish this revolutionary idea (See Figures 4 and 5). In this section, we do not go through the detailed experimental description, however, we provide a diagrammatic explanation that may help the reader to understand this groundbreaking unprecedented experimental setup (See Figure 4a). This setup was used to study the effects of an external electric field on the reaction rate by using single-molecule STM-BJ conductance measurements, which provide the oriented electric-field stimulus and also count reaction events. While carrying out the Diels-Alder reaction under this condition, the diene or furan is attached to the STM tip via a thiol group using 'S' linkage, and the dienophile is attached in a known orientation to a flat gold surface via two thiols. In this reaction, there are four structurally distinct products may be formed, each having two diastereoisomers however, here they showed the kinetically favored product only. Similarly in Figure 4b, they reported the possible resonance structures of the transition state geometry. When an electric field is present, minor contributors I or III may be stabilized enough to undergo resonance with II, lowering the reaction barrier. The vertical arrows show the field direction most likely to stabilize I or III, with I expected to experience greater stabilization at a given field magnitude. Coming to Figure 5; where (a) shows the two diastereoisomers of the *exo-syn* product of this reaction. These were the kinetically favored products; the six other possible products had much higher reaction barriers over the experimental range of field strengths. In the blue diastereomer, the substituents of the furan are located on the left of the molecule; in the red diastereomer, these substituents are located on the right. In (b), the coordinate axes are used to orient the field with respect to the molecule. The *z*-axis lies along with the double bond of the dienophile, while the *x*-axis is directed along the NB backbone. In (c), the scenario being modeled, showing the NB bridge sitting in the experimentally determined orientation with respect to the surface of the STM plate and to the electric field lines, which are passing through the reaction center at an oblique angle to the NB double bond.

This extraordinary experimental masterpiece has revived the brainchild of Prof. Sason Shaik. Before this experimental verification or 'proof of principle' of his thought, it was very frustrating for him to publish any theoretical works in this context. Soon after this publication, however, he had written the *'Nature Perspective'* and started once again to nurture this research field. Since 2016, he has published a plethora of research articles covering various aspects of this field. Recently in 2021, several professors from all over the globe contributed their valuable knowledge in the form of written documents and Shaik was able to edit the first book of this field which is entitled *"Effects of Electric Fields on Structure and Reactivity: New Horizons in Chemistry"*. In the end, we would like to conclude by stating that this newly born OEEF catalysis research field may have a revolutionary impact on future research in different disciplines, more specifically in organic and green chemistry.

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Tackling Coronavirus with WP1122 – A Prodrug of 2-Dg

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Introduction :

WP1122 is a prodrug of 2-DG, a well-known antimetabolite with the ability to inhibit glycolysis and alter glycosylation, two processes critical to coronaviruses like SARS-CoV-2, the virus responsible for COVID-19. Although 2-DG has shown activity against SARS-CoV-2, other coronaviruses and other non-coronaviruses, it is believed that its therapeutic potential is limited by its inherent lack of drug-like properties. WP1122 was designed to improve the drug-like characteristics of 2-DG, specifically, increasing circulation time and tissue and organ uptake and concentration (often referred to as improved "pharmacokinetics"). In vitro analyses shows activity of WP1122 against coronaviruses superior to that of 2-DG alone, as well as preclinical animal tumor models (WP1122 was originally developed as a potential cancer drug) showing the improved pharmacokinetics of WP1122.

2-DG, the active compound in WP1122, reduced in vitro replication of SARS-CoV-2 by 100%.

Based on preclinical data, there are reasons to believe that WP1122 may be effective against COVID-19. This is based on the vital roles that glucose plays in the proliferation of SARS-CoV-2. Viruses like SARS-CoV-2 place increased demand on glucose and upregulate their host cell's metabolic processes. Some of the most important of these processes are believed to be glycolysis and glycosylation.

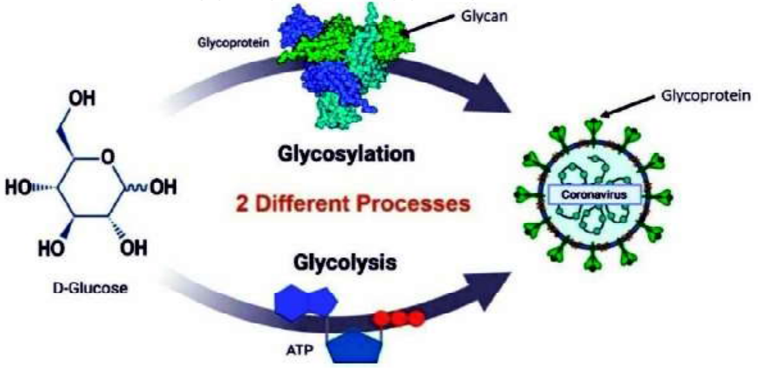


***Fig.:** Glucose provides energy in the form of adenosine triphosphate (ATP) to viral host cells via glycolysis, as well as enabling glycan formation supporting creation of glycoproteins during glycosylation.*

Understanding this is the key to understanding why WP1122 may represent a potential treatment. Glycolysis and glycosylation sound similar, but they are very different, even though they rely on the same base material, glucose, which is essentially sugar. In highly simplified terms, *glycolysis* converts glucose into fuel and *glycosylation* uses glucose to help build important protein structures that enable the way our cells function with each other and respond to changes in their environment. When viruses like SARS-CoV-2 invade our cells, they co-opt these processes to increase both their infectivity and their replication.

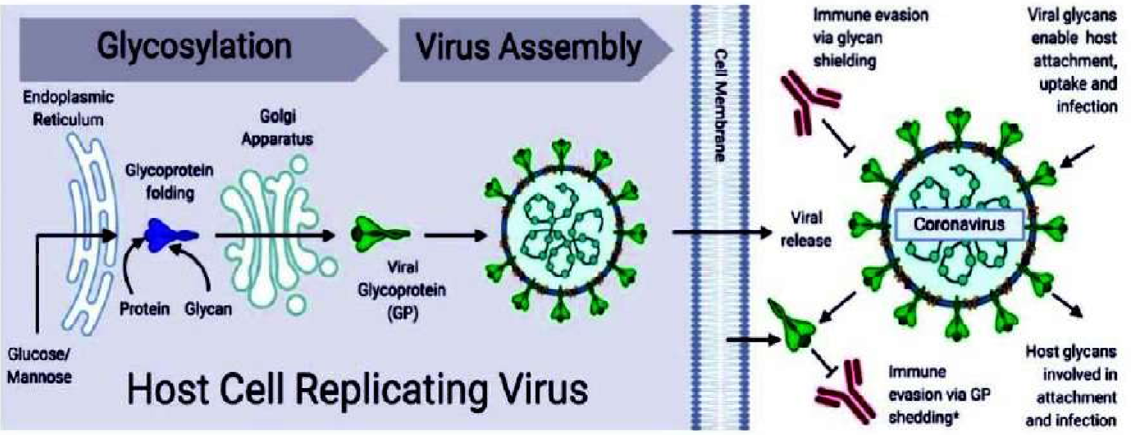


Fig.: *Enveloped viruses depend on glycosylation, which begins by hijacking the host cell secretory pathway, where combinations of sugar molecules (including glucose and mannose) called "glycans" are combined with proteins, as "folding" provides 3-dimensional structure. These viral "glycoproteins" mediate the assembly and budding of new virions. The host's immune system can be evaded through "shedding" of these glycoproteins (*for some viruses, not yet confirmed for coronaviruses) and through "glycan shielding." Glycans are crucial for viral attachment and infection of host cells.*[1]

Most of us are now familiar with the physical appearance of the spikes forming the corona around the coronavirus that gives it its name. These spikes are called *glycoproteins* and they play a vital role in the ability of coronavirus to infect host cells and to replicate.1 They also form a kind of camouflage that protects the virus from our immune systems. Like the name implies, a glycoprotein is the combination of glycans (see explanation in figure above) with proteins and the process of forming glycoproteins within the host cell is called *glycosylation.* Without proper glycosylation, viruses like the coronavirus cannot survive.

The role of glycosylation in viruses is widely discussed, but less so *glycolysis.* Glycolysis is the process by which cells convert glucose into energy. A recent study demonstrated that viruses induce an anabolic state in their host cells, which causes these infected cells to upregulate their production of energy using glycolysis as compared with their healthy neighbors.[2]

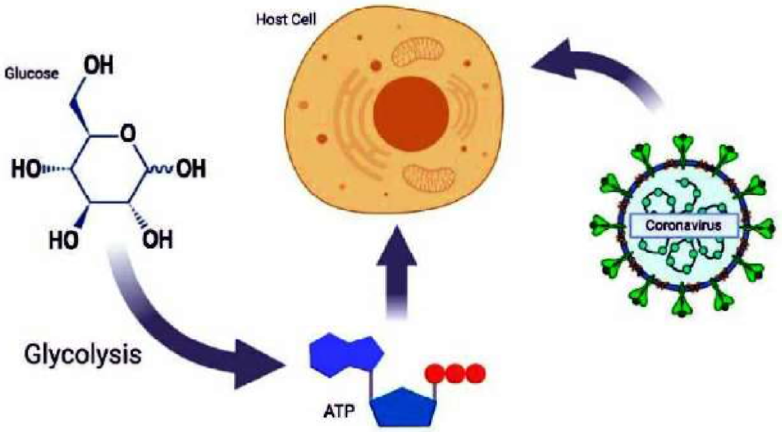


Fig.: *Viruses induce an anabolic state in host cells, which in turn makes them highly dependent upon glycolysis for adequate energy production.* [2, 3]

Given the roles of both glycosylation and glycolysis, it becomes apparent why glucose is critically important to the coronavirus. Given how important glucose is to these vital processes, one potential strategy for attacking viruses is to use their dependence upon glucose against them. And, this is where 2-DG potentially comes in. 2-DG stands for 2-Deoxy-D-Glucose and it is referred to as a *glucose decoy.* To cells, 2-DG looks like glucose, but it has one of the hydroxyl groups (the OH symbol shown here in red) found in the chemical structure of natural glucose removed. This missing hydroxyl group is just enough of a change that 2-DG won't actually convert into energy or support proper glycosylation.

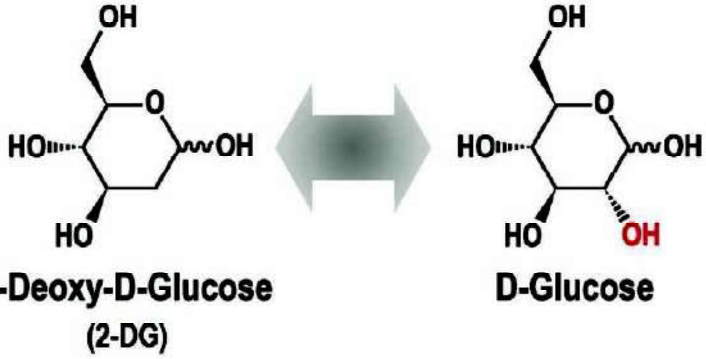


Fig.: *2-DG appears to the body to be natural glucose, but its lack of one hydroxyl group (shown in red on D-Glucose above) means that 2-DG will not convert into energy via glycolysis and it will not form the proper building-blocks for glycan formation during glycosylation.*

Importantly, multiple independent studies have shown the disruption of both glycolysis and glycosylation can have a potent effect against viruses like coronavirus.[2, 3, 4, 5, 6, 7]. This was, in fact, demonstrated in vitro in a range of viruses. These include rhinovirus, herpes and others, as well as porcine epidemic diarrhea virus, which is another coronavirus.

Researchers in Frankfurt, Germany, demonstrated the effect 2-DG has on SARS-CoV-2. In an unreviewed article submitted to NatureResearch (https://*www.researchsquare.com/article/rs-17218/v1*) by Bojkova, D et al (March 11, 2020; DOI: 10.21203/rs.3.rs-17218/v1), the authors reported that blocking glycolysis with **non-toxic concentrations of 2-DG completely prevented SARS-CoV-2 replication** in human cells (graph shown here). This is a significant milestone and it is believed that it supports an aggressive effort to pursue the use of 2-DG in clinical trials.

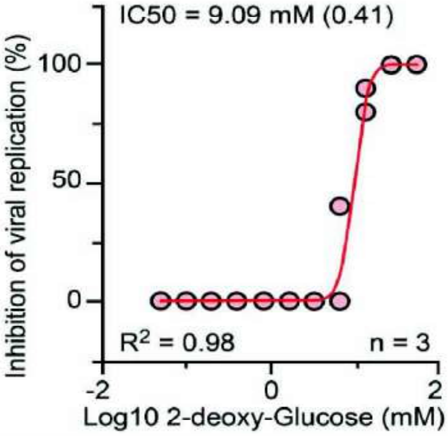


Fig.: *Effect of in vitro incubation of non-cytotoxic levels of 2-DG in Caco-2 cells on viral replication of SARS-CoV-2.*

Fortunately, there is already a lot of clinical data supporting the safety and tolerability of 2-DG in humans.[8,9,10,11,12,13,14] But there is a problem with 2-DG. The problem is that its capability in vitro does not translate well into animals and humans. This is because 2-DG lacks what we call "drug-like properties." It is too rapidly metabolized, and it fails to reach the necessary concentration levels in tissue and organs. Essentially, it hasn't been possible to get enough 2-DG into a patient and taken up by the critical tissue and organs in enough concentration in order to stop viruses.

Dr. Waldemar Priebe, Professor of Medicinal Chemistry at MD Anderson Cancer Center, discovered a way to dramatically improve the drug-like properties of 2-DG. He did this by creating a *prodrug* of 2-DG that greatly improved its drug-like properties.

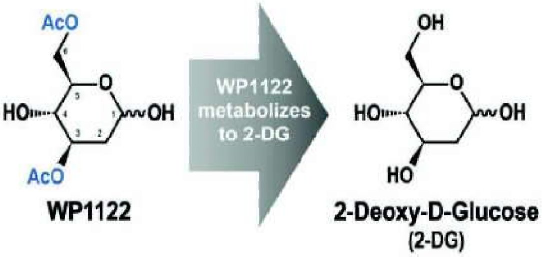
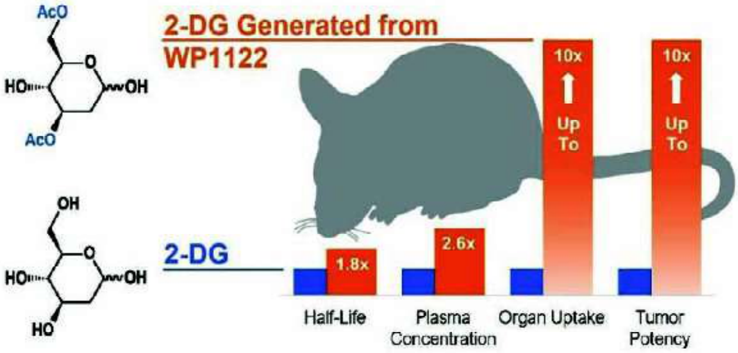


Fig.: *The presence of two acetyl groups (shown in blue) in WP1122 forms esters with hydroxyl groups at positions C-3 and C-6 and greatly enhances its tissue/organ uptake and retention.*

So, what is a "prodrug?" A prodrug is a medication or compound that, after administration, is metabolized into a pharmacologically active drug. In the case of WP1122, chemical modification of 2-DG creates a molecule that, after being administered, is transformed by normal metabolic processes into the active agent, which in this case, is 2-DG. In short, 2-DG is the active fragment of WP1122.

And, in fact, when one compares WP1122 to 2-DG alone in vivo, we see much higher concentrations of 2-DG in tissue and organs when that 2-DG is delivered by WP1122.15 Supplying 2-DG via WP1122 nearly doubles its half-life and almost triples its peak concentration in plasma. But where we see the biggest improvement is in organ uptake and potency. Until the advent of COVID-19, the bulk of the development work has been in the area of cancer treatment and depending on the tumor model, as much as 10 times the level of potency is seen from equimolar doses of WP1122 when compared with 2-DG alone.



With the most recent in vitro demonstration that 2-DG is effective in vitro against SARS-CoV-2, it is believed that WP1122 could represent a potential therapy for COVID-19 and other viral diseases. The goal is to have WP1122 in a clinical trial in 2021.

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Electro-Organic Conversion: A Modern Strategy for Organic Synthesis

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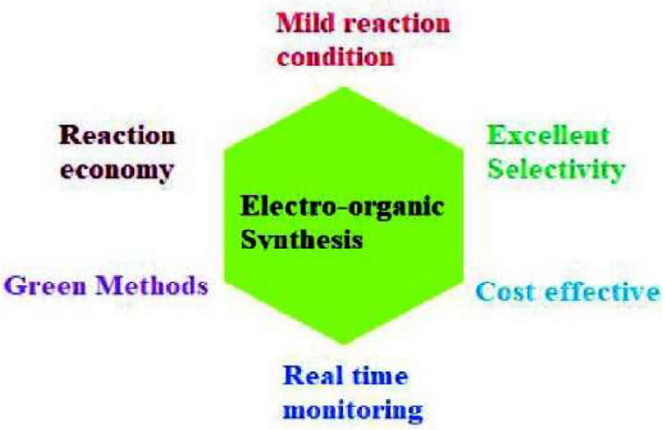
Introduction



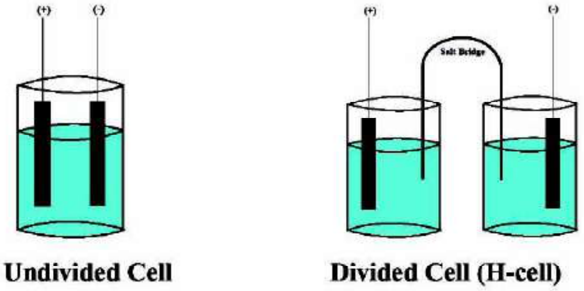
Over the last few years, electro-organic conversion has been attracting the attention of scientific community as a cost effective and environmentally friendly synthetic method. In principle, electrochemical synthesis involves the application of an external electric potential which provides the driving force to proceed a reaction far from its thermodynamic equilibria. Although preparative electrochemical transformations are common practices for inorganic transformations, the application of electrochemical methods for organic transformation was previously underdeveloped. Over 170 years ago, Kolbe demonstrated the potential application of electricity as a tool for organic transformation, but this technique was not accepted by the organic chemistry community as a common practice due to their complex reaction setup, boundless numbers of reaction variables and the common misconception that only aqueous solvents can be used for such transformation.[1] However, the concept of electro-organic synthesis is now re-emerging as an important technique for organic transformation since it possesses several profits over traditional chemical reagents such as high functional group tolerance, mild reaction conditions, real time monitoring, distinctive scalability and sustainability.[2]

Herein, a brief introductory information and a few modern research directions in the field of electrochemical organic-transformations has been presented, primarily directing to the young readers of this journal.

Basic set up of an electrochemical reactor

The essential needs for scheming a device for electrochemical organic conversion are the electrodes, which are coupled to an external power supply. The electrodes are the sites of the electron transfer process. Depending on the nature of material used, the electrodes can be of different shorts. Some electrode material such as platinum, graphite, glassy carbon is inert toward the reaction condition, whereas some electrodes prepared from metal like Mo, Ni and Pb produce insoluble high valent species which are active agent for the electrochemical transformation. Next to the electrodes, the other necessity are the electrolytes and the appropriate solvents. In more general term the combination of electrodes, electrolytes and solvents are known as 'cell'. Electrolytes supports the electrodes in completing the overall electrochemical cycle whereas solvents help in dissolving the reacting substances to facilitate the movement of ion in the reaction system. The commonly used electrolytes in electrochemical organic synthesis are Bu_4NBF, $LiClO_4$ and Et_4NClO_4; whereas Methanol, Acetonitrile and Water are three foremost solvents for electro-organic conversion.[3]

Further, depending on the types of organic transformation, the electrochemical cell can be of two types-divided or undivided. In undivided cell, both the electrodes are kept in the same vessel dipping into the electrolyte and solvent mixture. Whereas in divided cell, the two electrodes are separated so that two half-cell reaction does not interfere to give unnecessary side products. Figure 1 shows two schematic representations for divided and undivided cells.

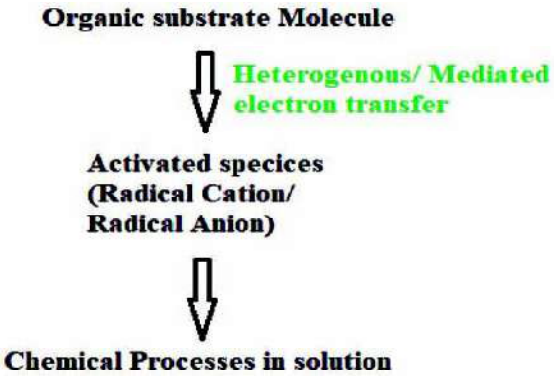


Undivided Cell **Divided Cell (H-cell)**

Figure 1: Schematic diagram of undivided and divided cell (H-cell)

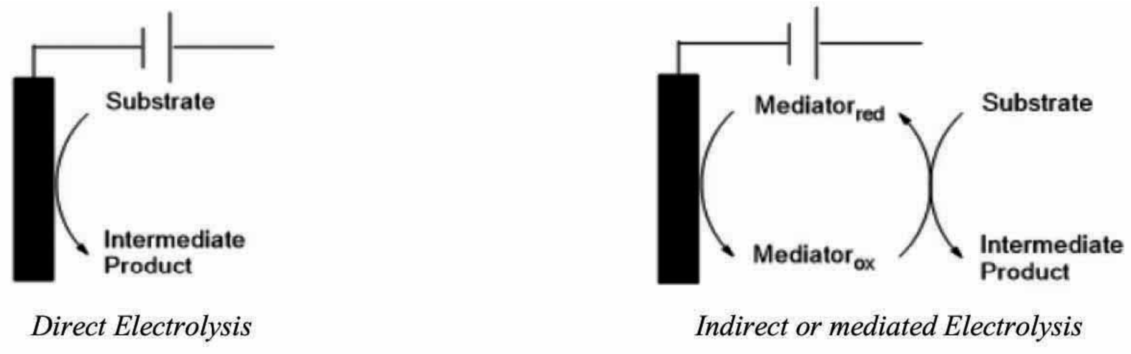
Principle of electro-organic conversion

During the electrochemical synthesis, the organic molecules are activated either by addition or removal of electron to/from their LUMO or HOMO respectively. In Oxidative process, electrons are removed from the HOMO of the organic molecule to form activated radical cation species, whereas in reductive processes electrons are added to the LUMO of the organic molecules to form



activated radical anion species. The activated species then undergo different short of chemical transformation in the solution depending on the reaction condition.[4]

The process of electron transfer can occur either directly or indirectly. In direct electrolysis, the electron transfer happens heterogeneously between the electron and the organic molecules. Early literature on electrochemical organic synthesis shows that most of the them were based on direct electrolysis strategy. Kolbe's decarboxylation, Shono's oxidation are well known examples of such direct electrolysis.[5] However, recently the concept indirect or mediated electrolysis is gaining more attention among the scientific community as it eliminates many of the drawbacks of direct electrolysis such as possibility of unnecessary side reactions, overcoming of the potential barrier present in the electrode surface in heterogenous process, low reaction rate and many others. In indirect process, initially the electron transfer process happens between the electron and a carrier molecule which is commonly known as redox mediators. The carrier molecules thereafter transfer the electron to the target substrate molecules.[3]



Direct Electrolysis

Indirect or mediated Electrolysis

Figure 2: Schematic representation for direct and Indirect electrolysis

Recent directions in the field of electrochemical-organic transformation

■ Strategy for scale up and designing of robust reactor

As electrochemistry is growing as a promising methodology for synthetic organic chemistry, focuses have been increasing on the development of strategy for scaling up for large scale molecular synthesis. Although several wonderful small-scale methodologies have been developed so far, however bulk scale electrochemical organic synthesis is still a challenging problem. In addition, reproducibility is also an issue for many well-developed electrochemical transformations. Therefore, proper understanding of the mechanistic pathways, role of the electrode surface, effect of the solvent system, effect of the power density, kinetics of the reactions are essential points to be investigated.

Further, designing of robust electrochemical reactor is additional challenge for the broad scale applications. Most of the electrochemical organic reactions require relatively longer time as the organic molecules are highly sensitive to the power density. However, application of broader current density is helpful to design robust and simple electrochemical reactors. But very few reactions are developed so far which are less sensitive to high current density.[3]

■ Designing of valuable redox mediators

As mentioned previously, the redox mediators assist the electron transfer process between the electrodes and the organic substrate molecules, which offer benefits over direct electrolysis. In recent years, focuses have been increasing to develop valuable redox radiator for large scale electrochemical organic transformation. So far researchers have developed numerous sorts of redox mediators based on main group compound (Halogen and Hypervalent Iodine based, Nitrate and Nitroxyl based), transition metal (Mn, Fe, Cu, Pd, Ru, Ir, Co, Ni, Rh -based), Organic molecules (Arene-based) and the attentions are still in the region to discover high efficiency novel redox mediator.[6]

■ The concept of paired electrolysis: utilization of maximum energy during the synthesis

Utilization of maximum energy during the synthesis is a new-fangled trend that is coming into the court of organic electrochemists in recent days. Strategies have been developed to exploit electrical energy from both the electrode simultaneously during the electrochemical synthesis, which is commonly recognized as 'paired electrolysis'. In such processes, at the same time two parallel electrochemical processes are carried out in the same electrochemical system which in combination leads to the products. The paired electrolysis process can be considered as the gold standard for energy utilization.[3] One well known example of paired electrolysis is the synthesis of p-tert-butyl benzaldehyde dimethyl acetal and phthalide BASF SE in a single paired electrolysis process (Figure 2).[7]

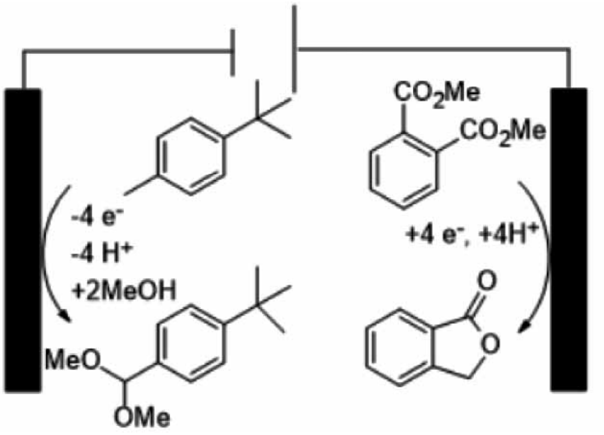


Figure 3: Synthesis of p-tert-butyl benzaldehyde dimethyl acetal and phthalide by paired electrolysis

■ Designing of stereoselective electro-organic transformations

Stereoselectivity, at all times is an important apprehension for the synthetic chemistry community as most of the natural products, synthetic drugs and other useful molecules holds chiral centers in them. As the area of electrochemical synthesis has been growing over the years, therefore it is of utmost concern to design stereoselective version of such synthetic methodologies to extend its applicability. To do so, introduction on a chiral source in the reaction medium is essential. Literature show that the first ever such approach was made by Miller group in 1975, where they designed a chiral graphite electrode for stereoselective electrochemical synthesis by treating the graphite with thionyl chloride followed by (S)-(-)phenylalanine methyl ester. The modified electrode was reported to use effectively for asymmetric cathodic reduction of 4-acetylpyridine.[8] The recent approach in the field of stereoselective electro-organic transformation was reviewed by M. Ghosh et al (2019),[9] which shows that several groups have designed effective chiral source such as chiral electrodes, chiral medium, chiral auxiliary for stereoselective electro-organic conversion and the pick of the bunch are yet to come for large scale application.

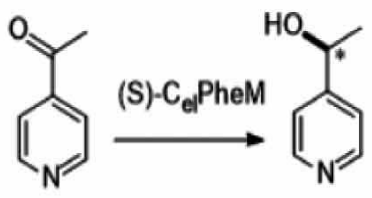


Figure 4: Asymmetric reduction of 4-acetylpyridine

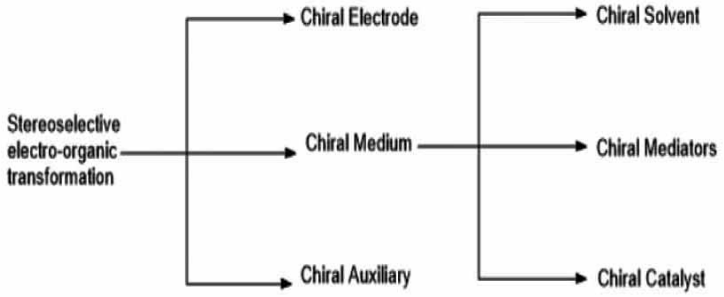
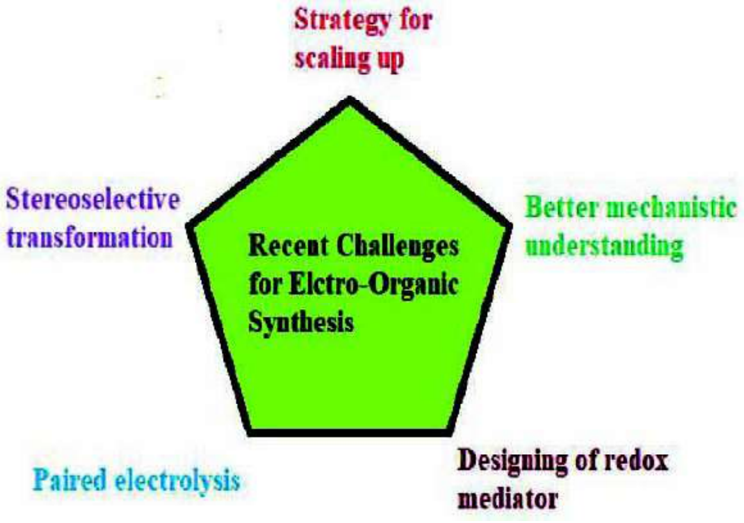


Figure 5: Strategy for designing of stereoselective electrochemical organic transformation

Outlook

As far as the problems of environmental contamination and global warming are concerned, for sure chemical industries have substantial contributions towards them. Therefore, it's the decisive time to look for green and atom economic chemical transformation to replace the traditional reagent-based methodologies. Recent progresses in the field of electro-organic synthesis directs that it has a solid potential to convert as an efficient and green technology in the coming future. However, in establishing so, it is job of the coming researchers to overcome the various challenges of electrochemical organic transformations and undeniably this is a growing area of research for the modern synthetic chemistry community.



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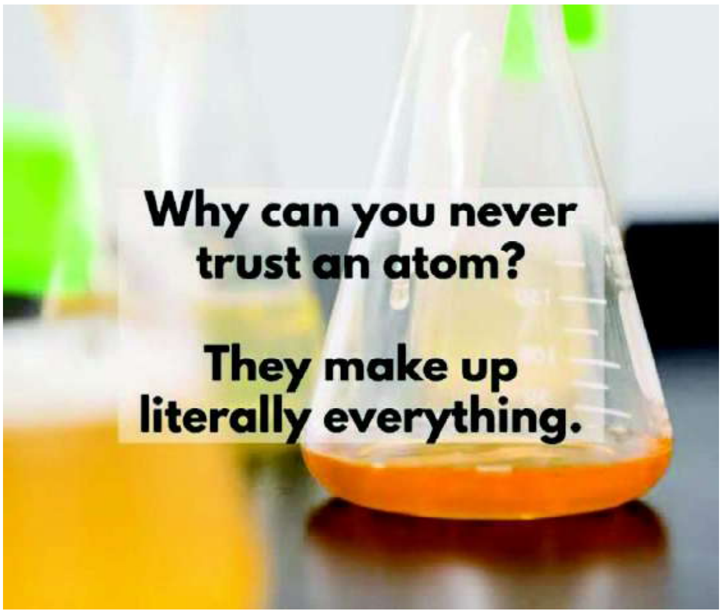

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Tempo and its Derivatives: A Potential Organo-Catalyst for Industrial Application

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1. Introduction:

The stable tetraalkylnitroxyl radical TEMPO is an effective and efficient well known oxidation catalyst which has a very potential and vast application in organic synthesis including oxidation of alcohols, sulphides and organometallic compounds. But TEMPO is an expensive catalyst, so industry mainly employs its derivatives such as 4-hydrooxy-TEMPO or 4-acetamido TEMPO as a catalyst in place of TEMPO to attain desirable product. TEMPO mediated homogeneous and heterogeneous oxidation processes are the useful route to synthesis a variety of products in fine chemicals and pharmaceutical industry.

1.1. What is TEMPO?

Chemical name: 2,2,6,6-tetramethylpiperidine-1-oxyl.

Chemical formula: $C_9H_{18}NO$.

Molecular weight: 156.25

Elemental analysis: C=69.18; H=11.61; N=8.96; O=10.24

It is a nitroxyl radical. It is colourless and has a fishy amine like odour.

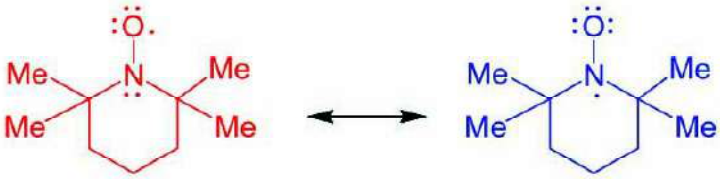

Figure 1: Structure of TEMPO

2. History:

In 1965, Golubev, Rozantsev and Neimann observed that treatment oxoammonium salt with excess ethanol produces acetaldehyde. In 1975, Cella demonstrated that alcohols can be oxidised to acid by treatment of p-choloroperbenzoic acid in presence of catalytic amount of 2,2,6,6 tetramethyl piperidine.

An important seminal contribution done by Cella to TEMPO mediated oxidation of carboxylic acid by showing oxoammonium salts can be employed catalytically for the conversion of primary alcohols to carboxylic acid.

In 1987, Anelli published a paper where in which it was shown primary alcohols can be oxidised either aldehydes or acids by treating the alcohol in a biphasic mixture with chlorine bleach in presence of $NaHCO_3$,KBr and a catalytic amount of TEMPO derivative 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl.

Very first Industrial oxidative process based on TEMPO include Novertis aerobic process with Cu^{2+}/O_2 developed by Semmelack in 1980s to synthesise retinal from retinol.

The continuous process was developed by Wacker Chemie to synthesise aldehydes with additional substituent in beta and gamma position and Pfizer's synthesis of bisnoraldehyde from bisnoralcohol using bleach and 4-hydroxy TEMPO.

3. Mechanism:

The oxidation reaction by TEMPO is carried out in organic solvent or biphasic reaction system affording aldehydes or ketones or in water.The available experimental data shows that the secondary oxidant transforms TEMPO or a related stable radical in an oxoammonium salt that operates as primary oxidant transforming alcohols to aldehydes. This results in the formation of a hydroxylamine that is oxidised to a TEMPO radical thus completing the catalytic cycle. The aldehyde in presence of water equilibrates with corresponding hydrate that oxidised to acid via similar mechanism.The oxidation of primary alcohols with oxoammonium salts can work via 5 -member T.S under basic conditions or a linear T.S under acidic condition. Under basic condition the oxidation is quicker and shows a greater selectivity. The oxoammonium cation formed by oxidation of TEMPO with hypochlorite at 0-4*c slightly basic conditions selectively oxidises a verity of alcohols. Instead of hypochlorite, a verity of different of primary oxidants can be used to generate the oxoammonium ion including a mild electric potential along with active metal catalyst like $Ru^{2+}/Mn^{2+}/Co^{2+}$ /Cu^{2+} and several other suitable oxidants.

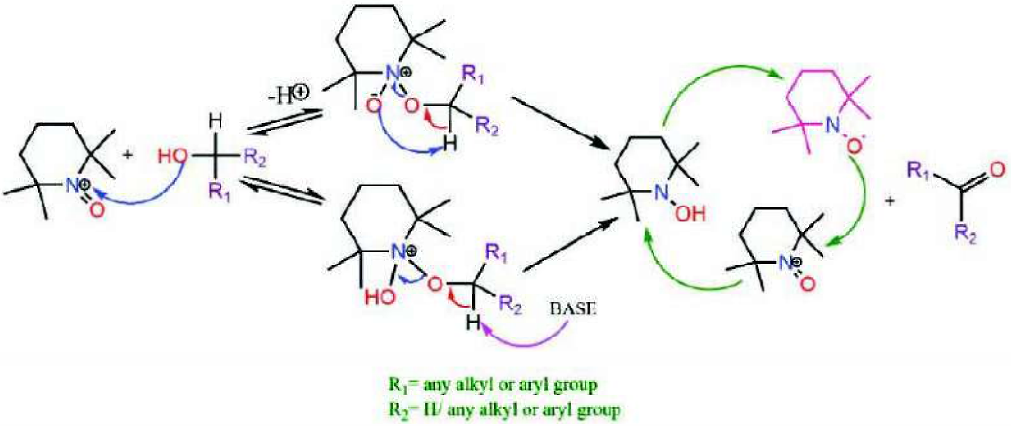

Figure 2: A possible mechanism for TEMPO catalysed reaction

Here I am trying to highlight some applications of TEMPO in industry as homogeneous and heterogeneous catalyst, its advantages and its limitations.

4. TEMPO as a homogeneous catalyst:

4.1. Bisnoraldehyde:

This 1st industrial example of Batch processwas developed by Pharmacia and Upjohn in the mid of 1990s by synthesing Bisnoraldehyde (BNA) from Bisnoralcohol. Nowadays BNA is synthesised from waste soya bean residue based on the oxidation of bisnoralcohol with bleach and 4-hydroxy-TEMPO.Bisnoraldehyde is used to produce steroids such as progesterone and corticosteroids.

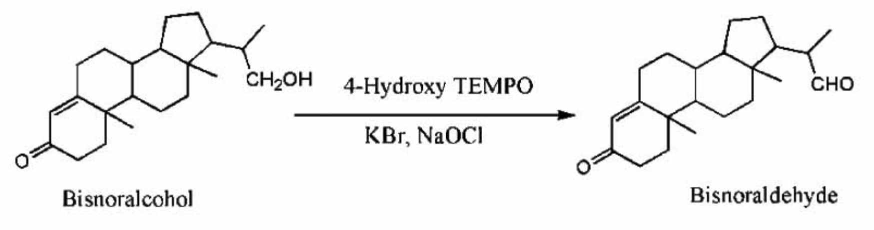

Figure 3: Preparation of bisnoraldehyde

The benefits of this process are

a. Heavy metals base oxidants like hexavalent Cr salt and complexes, manganese oxides or Pb salts could be avoided.

b. Doesn't produce any noxious emission like oxidants.

c. Increases utilization of soya sterol feedstock from 15% to 100%.

d. Produces nontoxic aqueous process waste stream and recoverable organic solvent waste stream.

e. Eliminates carcinogenic ethylene dicholoride by a conversion with recycled inventory.

4.2. HIV protease Inhibitor proline derivative and 5-HT2B receptor antagonist:

Recently multikilogram production of proline derivative has been developed via a ketone fluorination with deoxofluor. The required ketene for fluorination is prepared via oxidation with Nalco and catalytic TEMPO.Similarly Eli Lilly synthesised 2-Cyclohexylaldehyde from cyclohxylethanol by Anelli-Montanari protocol on a 20 kg scale. The synthesized aldehyde is used as synthone for synthesis of important 5-HT2B receptor.

4.3. Aerobic reaction:

The scientist of fine chemical manufacturer Neumann and co-workers invented this process. In aerobic reaction, 1 mol% polyoxametalate heteropoly acid, $H_5PV_2Mo_{10}O_{40}$ and 3 mol% TEMPO as co-catalyst are used. The oxoammonium cation is formed by one electron oxidation of TEMPO by $H_5PV_2Mo_{10}O_{40}$. Oxidation of alcohol by oxoammonium cation affords.

The hydroxyl amine TEMPOH followed by rate limiting oxidation of latter by a second equivalent of hetropolyacid. The reduced form, $H_5PV_2Mo_{10}O_{40}$ is readily reoxidized to oxygen. This reaction was found independent of oxygen pressure which means that it could work in oxygen or air without the need of pressure vessel.

4.4. Heterogenized Co-oxidant:

Sugar oxidation:

Holderich and his co-workers selectively oxidise primary hydroxyl group by using organic nitrosonium salt in aqueous solution. The oxidant is produced by disproportion of TEMPO in a batch reactor by silver catalyst and peroxides as primary oxidant.

5. TEMPO as Heterogeneous catalyst

5.1. SiliaCat TEMPO:

SilliCat TEMPO shows superior performance compared to homogeneously or other heterogeneously catalysed oxidation mediated TEMPO. It is prepared with innovative technology which comprises the sol-gel techniques of organically modified hybrid organic-inorganic silica.The catalyst enhances reactivity and selectivity drastically. For example, oxidation of benzyl alcohol with SiliaCat TEMPO to benzaldehyde is 3 times higher than silica supported TEMPO. In addition only benzaldehyde is produced. No trace amount of benzoic acid is found. The sol-gel entrapment phenomenon chemically and physically stabilises the radical species in sol-gel cage.Silicat TEMPO is solvent independent because organosilica neither shrinks nor swells nor can dissolves in solvent.It be used in various nitroxide mediated oxidations for production of pharmaceuticals, flavours, fragrances, cosmetics and agrochemicals.

5.2. FibreCat TEMPO:

This is superior heterogeneous catalyst and used to covert unreactive aliphatic primary alcohol to aldehydes selectively using bleach or Co (II) or Mn (II) as co-catalyst and molecular oxygen and air as terminal oxidants.

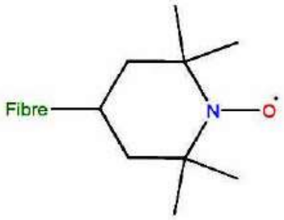

Figure 4: FibreCat TEMPO

Advantages of FibreCat TEMPO catalyst are Heterogenation of TEMPO provides a much simple purification and it is recyclable.

5.3. Polymer-supported TEMPO:

This is synthesized with the help of polyester or polystyrene to support TEMPO and commercialized by Aldrich and Novabiochem. Like other heterogeneous catalyst, these are highly reactive, recyclable and oxidise selectively to give desired product.

6. CONCLUSION:

The great synthetic value of TEMPO can bring a revolutionary direction in industrial chemistry and the oxidation product that range from steroids to silicon polymer, polysaccharides to aromatic aldehydes has a widespread application in fine chemicals, medicinalchemistry, industrial chemistry and agrochemistry. Some selected examples are discussed in this topic. Still researchers are trying to build up new innovative methodologies using TEMPO as co-oxidant, by which some selected organic compounds can be oxidized. The enormous scopes of TEMPO-catalyzed oxidation reaction will make TEMPO and its derivatives as one man army in organic synthesis and industrial field in future.

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Advancements and Importance of Heterocyclic Compounds

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An organic compounds consisting of a cyclic ring and at least one-heteroatom are known as heterocyclic compounds. Nitrogen, oxygen and sulphur are the most commonly and diversely known heteroatoms in heterocyclic chemistry.[1,2]

Heterocyclic chemistry is one of the central points of attraction for organic chemists since recent years. If ever eager to find a close relationship between chemistry and medicines, heterocyclic chemistry would be the one. The vigorous study of heterocyclic chemistry in recent times has significant contributions to scientific community as heterocyclic cores are most attractive in numerous chemical zone. Contribution of heterocyclic chemistry to mankind is truly remarkable in the field of biological, industrial as well as enhancement of life processes.[3] A large array of heterocyclic compound are of supreme importance initiating from cosmetics to plastics, electronics, agrochemicals, polymers, organometallics, co-ordination chemistry, supramolecules and so on. Pyridine moieties are also an important class of heterocycles that exhibits outstanding biological activities such as anticancer, antibacterial, antirheumatic, antihistaminic etc. Wide range of existing heterocycles that can be noted are pyran, furan, pyrazole, indole, thiophene, isoindole, benzothiazole, quinolines, isoquinolines, benzofurans, isobenzofurans, azoles, benzothiophenes, purines etc. Naturally occurring drugs such as theobromine, quinine, procaine, reserpine, morphine, atropine, emetine also consists of heterocycles. Furthermore, all the biological processes occurring in day to day lives are the basic manifestations of chemical reactions. These chemically occurring biological metabolisms are composed of heterocycles such as vitamins, nucleic acids, ATP, enzymes, co-enzymes, haemoglobin, chlorophyll etc. as major skeleton.[4-7]

The flexibility and effectiveness in their synthesis is a major reason promoting heterocyclic compounds to market drugs. Therefore, diverse synthetic methodologies have emerged for wide production of heterocycles. Various catalytic processes are progressing subsequently to synthesize medicinally active heterocycles through green and sustainable methods in recent years.[8] Some of the biologically important heterocycles are listed in Fig. 1.

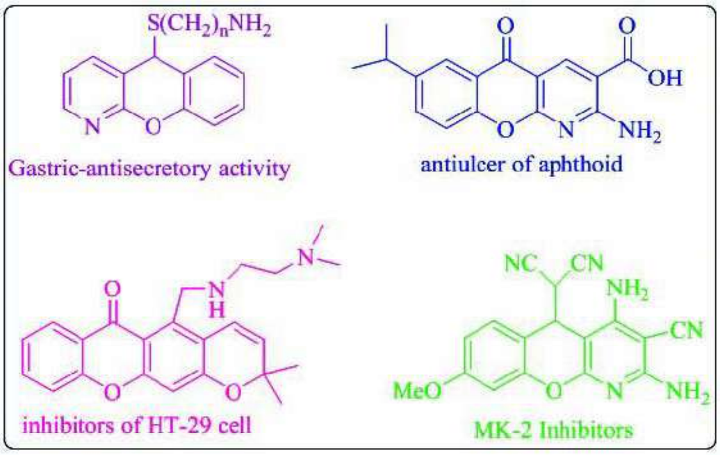

Fig. 1: Some of the biologically important Heterocycles.

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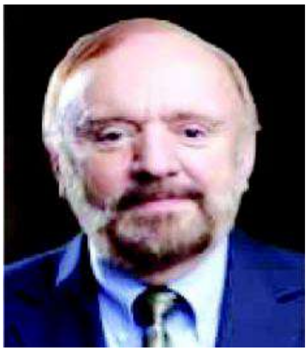
Series

History of Chemistry : 21st Century

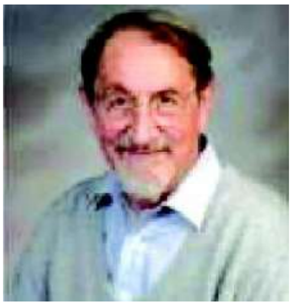
Chemistry is a branch of science that has been around for a long time. In fact, chemistry is known to date back to as far as the prehistoric times. Due to the amount of time chemistry takes up on the timeline, the science is split into four general chronological categories. From the mid 19th century, modern chemistry started and now in the 21st century, there has been a large amount of development being brought by chemistry and some of the renowned chemists in this field are:

Allen J. Bard (1993-): Allen J. Bard is a professor at the University of Texas, where he also serves as director of the Center for Electrochemistry and holds the Norman Hackerman-Welch Regents Chair. He received his Ph.D. from Harvard University in 1958. In 2011, Bard was awarded the National Medal of Science for his contributions in electrochemistry, including electroluminescence, semiconductor photo-electrochemistry, electro-analytical chemistry, and the invention of the scanning electrochemical microscope. His discovery of electrogenerated chemiluminescence (ECL) has enabled the medical community to detect the HIV virus and analyze DNA. Bard is considered the "father of modern electrochemistry." In 2013, President Obama awarded Bard with the National Medal of Science. Other awards he has received include the Wolf Prize in Chemistry in 2008, the Priestley Medal in 2002, and the Fellow of American Academy of Arts and Sciences in 1990.He has published three books: Electrochemical Methods, with Larry Faulkner, Integrated Chemical Systems, and Chemical Equilibrium. He has also published over 600 papers and chapters, while editing the series Electroanalytical Chemistry (21 volumes) and the Encyclopedia of the Electrochemistry of the Elements (16 volumes). He is currently editor-in-chief of the Journal of the American Chemical Society. Bard's current research focuses on harnessing the power of natural sunlight to produce sustainable energy. His lab at the University of Texas tests different chemical compounds in the hopes of discovering a material that will carry out artificial photosynthesis. Bard feels strongly that such discoveries must be sought and made because otherwise humanity will be in deep trouble as fossil fuels run out.

Jean M.J. Fréchet (1944 -): Jean M.J. Fréchet is a chemist and the Henry Rapoport Chair of Organic Chemistry in the department of chemistry at the University of California, Berkeley. He is also the vice president of research at the King Abdullah University of



Science & Technology in Saudi Arabia. Fréchet holds over 70 U.S. patents and his research is conducted in the areas of organic synthesis, polymer chemistry, nanoscience, and nanotechnology, in which he has authored nearly 800 articles, with a major emphasis on the design, fundamental understanding, synthesis, and applications of functional macromolecules. Fréchet, who was born in France, has received numerous awards, including the American Chemical Society Cope Scholar Award in 2001, the American Chemical Society Award in Polymer Chemistry in 2000, and the Society of Imaging Science and Technology's Kosar Memorial Award in 1999, among others. Fréchet is a member of the American Chemical Society, the National Academy of Sciences, the National Academy of Arts and Sciences, and Academia Europaea. He also serves as the associate editor of the Journal of the American Chemical Society. Fréchet's current research focuses on the fundamental and applied aspects of organic, polymer, and materials chemistry. He has noted that most of his projects involve three stages: (1) design; (2) synthesis; and (3) characterization, where the function of the structure and properties are tested.



Martin Karplus (1930 -): Martin Karplus, a theoretical chemist, Emeritus Professor and the Theodore William Richards Professor of Chemistry at Harvard University. He is also Director of the Biophysical Chemistry Laboratory, a joint laboratory between the French National Center for Scientific Research and the University of Strasbourg, France. In 2013, Karplus received the Nobel Prize in Chemistry, along with Michael Levitt and Arieh Warshel, for developing multi-scale models for complex chemical systems. Their contribution was ground-breaking, because they managed to make Newton's classical physics work side-by-side with quantum mechanics. This approach makes possible computer simulations that are so realistic they closely resemble the outcome of traditional laboratory experiments. Karplus earned his Ph.D. from the California Institute of Technology and was a National Science Foundation Postdoctoral Fellow at Oxford University. He has made many contributions to physical chemistry, quantum chemistry, and molecular dynamics. The Karplus equation, which describes the correlation between coupling constants and dihedral angles in protein nuclear magnetic resonance spectroscopy, is named after him. Karplus, who was born in Austria, has also made numerous contributions to the field of theoretical chemistry through textbooks, such as Proteins: A Theoretical Perspective of Dynamics, Structure and Thermodynamics, and Atoms and Molecules: An Introduction for Students of Physical Chemistry. His current research interests are concerned with the physical properties of molecules of biological interest.

Henry F. Schaefer III (1944 -): Henry F. Schaefer III is a theoretical and computational chemist and the Graham Perdue Professor of Chemistry and Director of the Center for Computational Chemistry at the University of Georgia. He is also a fellow with Discovery Institute's Center for Science and Culture. Schaefer received his Ph.D. from Stanford University and is known for inventing the field of computational quantum chemistry, developing it into a reliable quantitative discipline in chemistry. Using supercomputers and simulations rather than actual chemical substances, his lab uncovers chemical structures by crunching numbers. His theoretical research has been directed at one of the most challenging problems in molecular quantum mechanics, the problem of electron correlation in molecules. Schaefer is the author of more than 1,300 scientific publications, the majority appearing in the Journal of Chemical Physics and the Journal of the American Chemical Society. Some of his research challenges the work of Nobel Prize winner Gerhard Herzberg regarding the geometry of triplet methylene. In 2014, Schaefer will receive the American Chemical Society Peter Debye Award in Physical Chemistry. He also received the Alexander von Humboldt Award and the SURA Distinguished Scientist Award in 2012, among numerous other awards.

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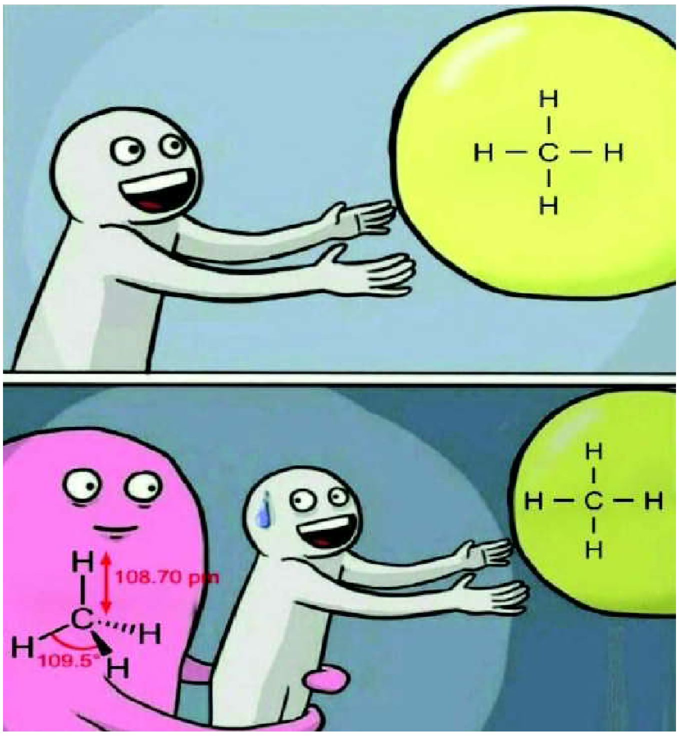

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Specific Ion Effect in Colloidal Systems: A Brief Overview

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A colloid has a dispersed phase (the suspended particles) and a continuous phase (the medium of suspension or dispersion medium). The dispersed phase particles have a diameter of approximately 1 nanometre to 1 micrometre [1]. Colloidal suspensions are the subject of interface and colloid science. Homogeneous mixtures with a dispersed phase in the colloidal size range may be called colloidal *aerosols, colloidal emulsions, colloidal foams, colloidal dispersions, or hydrosols.*

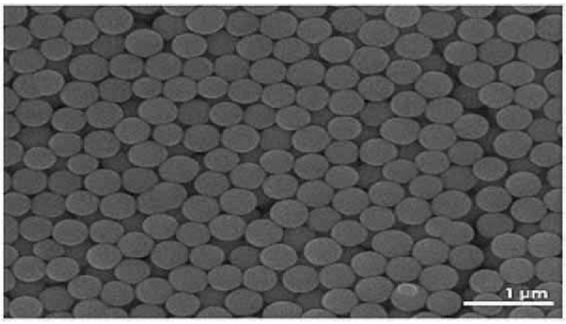

Figure 1: SEM image of a colloid (Source: *Wikipedia*).

Specific ion effects are important in numerous fields of science and technology. They have been discussed for over 100 years, ever since the pioneering work done by Franz Hofmeister, who was a pharmacologist and his group in Prague. Over the last decades, hundreds of examples have been published and periodically explanations have been proposed. However, it is only recently that a profound understanding of the basic effects and their reasons could be achieved. Today, we are not far from a general explanation of specific ion effects.

It is known to all about the important impact of salts e.g. on digestion, the nervous system and the properties of blood. However in the 19th century, it was difficult to understand such complex systems. Nevertheless measurements of ion effects are comparatively easier. For example swelling and precipitation of colloidal & biological systems can be detected with the naked eye. Addition of ions to an aqueous solution can significantly change their osmotic pressures and electrical conductivity, which were measurable already in the 19th century.

A good number of publications for specific ion effect especially in colloidal science and biology are reported whose basic concepts are summarized in a specific book [2]. Moreover a typical ordering, the so-called Hofmeister series of ions is also produced in the same book (Fig. 2).

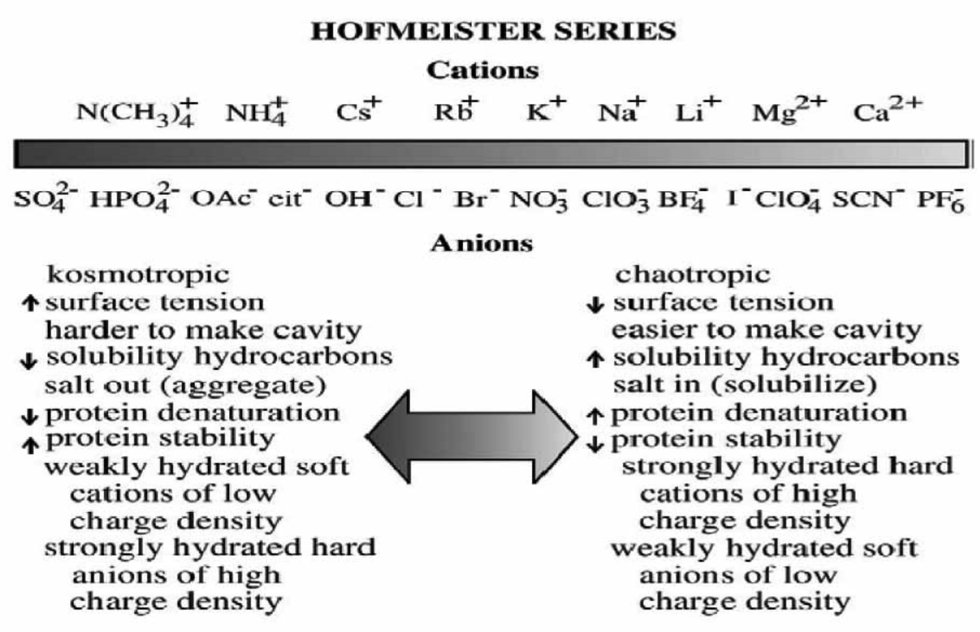

Figure 2: Ordering of cations and anions in a Hofmeister series [2].

Hofmeister and his co-workers reported several publications explaining the effects of various kinds of salts on phenomena like precipitation of proteins and mineral oxides, swelling of biological membranes etc. However Hofmeister works are related with the influence of salts but not individual ions. The ordering of the ions is not only unique but also reverse in the Hofmeister series which is quite interesting behavior in the context of specific ion effect. In this context, Fig 2 shows an opposite trend of ordering for the cations and anions. The cation series flows from soft weakly hydrated ions on the left to hard, strongly hydrated ions on the right, which being reversed for the anions. This can be attributed to the different charged groups being present on the accessible surface of biological molecules such as proteins. On the other hand regarding the solubility of organic or low polar molecules such as benzene or gases like oxygen and CO_2, soft, polarisable and organic ions are mostly salting-in and hard and highly charged ions are mostly salting-out, independently of the sign of their charge [3].

With reference to the classification of ions, the term structure-making and structure-breaking were used frequently. However, the experimental findings by Omta et al. misleads it, where they reported that at least monovalent ions do not influence the structure of water beyond the first hydration shell [4]. So a new terminology has been attributed known as "kosmotropic" (strongly hydrated) and "chaotropic" (weakly hydrated) for convenience in the context of classification of ions.

Generally the influence of cations are less pronounced than specific anion effects, because of absolute charge density in anions and stronger interactions with water than cations of the same size. Nevertheless, this statement is applicable when ion-water interactions are dominant for the specific ion effects. If direct ion-ion or ion-charged headgroup interactions are dominant then magnitudes of both specific cation and anion effects are similar [2].

The responsible interactions or more specifically the forces governing specific ion effect in different systems is also a subject of interest to researchers. Initially it was thought that dispersion interactions between ions in solution can satisfactorily explain ion specificity. But with this concept it was not possible to describe properly the experimentally determined surface tension increments with reasonable ion polarisabilities[5]. From the ion polarizability measurements in solution it is evident for chemists that iodide is more polarisable than chloride. But the opposite had to be assumed for sodium halides in order to describe properly the surface tension changes with salt concentration, as per the dispersion interaction models[6]. It is not like that only ion polarizabilities are responsible for specific ion effects. Because molecular dynamics simulation results confirms that the attraction of small inorganic ions to the water-air interface is dependent upon their charge density i.e. (the ratio of the charge to the ionic radius) but not explicitly on the ion polarizability [7]. Moreover at interfaces the structuring if water is a decisive factor. As an example, hydronium ions cannot be hydrated so favorably in water due to their particular charge distribution and geometry. Actually the H_3O^+ ions can enter the first water layer near to the air surface, where their hydration and geometry is energetically slightly more favorable than in the bulk [8]. Structure of water also plays a significant role on the adsorption of ions to hydrophobic interfaces. A simplified electrostatic consideration might be thought of to act during the adsorption of anions onto hydrophobic surfaces bearing some kinds of positive charges without taking into account the structure of water. Around the hydrophobic surface the water layering (the "hydrophobic structuring" of water) is energetically not very promising which helps in adsorption of large ions of low charge density such as iodide (halide ion) onto the hydrophobic parts [9].

Ion properties are dependent strongly upon the environment and in particular on the nature of counterions or headgroups in their vicinity. This dependence is also responsible for reverse Hofmeister series. In biology and colloidal chemistry, the interaction of ions with charged headgroups is a significant part of specific ion effects [2]. A useful concept was introduced in the pioneering work by Kim D. Collins which allows one to understand an assembly of experimental results in biology and colloidal science [10]. Collins' model is known as the "concept of matching water affinities". Ions are considered as a sphere with a point charge in the centre. When the ions are small in size, the surrounding water molecules are tightly bound (the ions are hard or kosmotropic), whereas when the ions are bigger, the hydration layer is only loosely bound (the ions are soft or chaotropic). This essential classification results from the relative strength of the ion-water interactions compared to water-water interactions, as illustrated in Fig. 3. Collins concept stated that a soft/hard ion pair is always separated by water and cannot form strong ion pairs. This is in tune with the general rule in chemistry that "like seeks like".

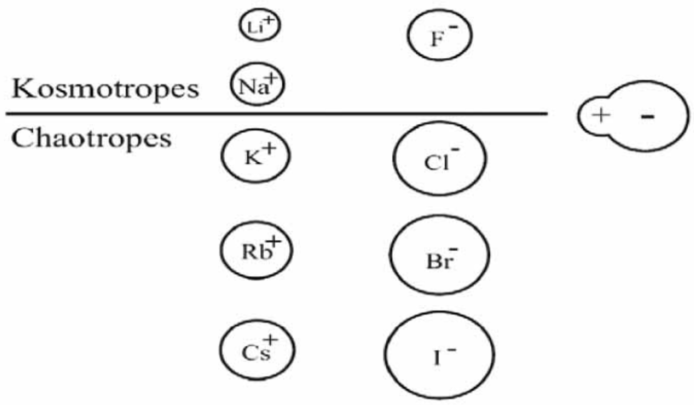

Figure 3: Classification of cations and anions into strongly hydrated kosmotropes and weakly hydrated chaotropes [2].

Specific ion effects are dependent upon salt concentration and, especially in the case of proteins, strongly pH dependent. Frequently, at very low salt concentrations (< 0.1 M) electrostatic effects dominant. However even at such a low concentration specific ion effects were also found effective. As an example in the adsorption of 3,4-dihydroxy benzoic acid (3,4-DHBA) onto α-Al_2O_3/water interface, a critical salt concentration (0.025 milimolar) determines positive and negative effects of different salts on the adsorption densities of 3,4-dihydroxybenzoic acid.

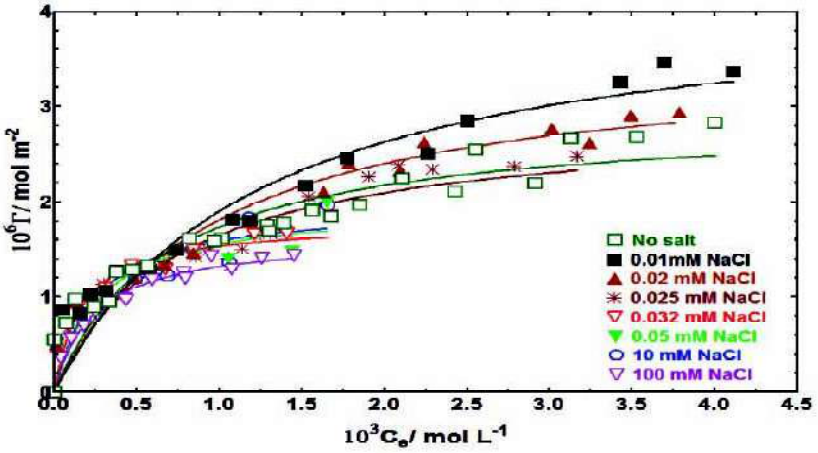

Figure 4: Plots of adsorption density vs. equilibrium concentration of 3, 4-DHBA in the absence and presence of NaCl [11].

Above critical salt concentration polarizability of ions was found to govern the adsorption density. Nevertheless the theoretical origin for explaining the specific ion effect would be different below and above the critical concentration (0.025 mM), which likely to be different for different systems.

On the other hand at intermediate concentration range (0.1– > 2 M) specific ion effects are often measured, because here the electrostatic interactions are significantly screened[2]. At very high concentrations, usually most of the water is captured in the ion hydration spheres and then even chaotropic ions can become salting-out.

With all the above discussions, it evident that such complex phenomena like specific ion effects cannot be fully described within a simple model. It appears somewhat hopeless to get some general idea about specific ion effects. Though modern computer power and multitude of experimental results have contributed to the understanding of specific ion effects, yet much more information is awaiting considering the different ions in different systems and their reversibility.

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Students' Section

Polymer Electrolytes for All-Solid-State Batteries without Dead Zones

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As the demand for electric vehicles rises, interest grows for all-solid-state batteries. These next generation batteries will replace Li ion batteries in future. Li ion batteries are inherently dangerous due to explosive nature. However, the low chemical stability of solid-state sulphide electrolytes is hindering the popularization of electric vehicles. To this, a POSTECH research team has recently developed a polymer electrolyte without a "dead zone", which lowers ion transport and is accelerating the commercialization of all-solid-state batteries.

A research team led by Professor Moon Jeong Park and Ph.D. candidate Jaemin Min of POSTECH's Department of Chemistry with Professor Chang Yun Son's research team from the Division of Advanced Materials Science have developed a novel block copolymer electrolyte that can control the structure through electrostatic interactions. Most of the energy storage devices still use Li-ion batteries. In a Li-ion battery, ions are moved by a liquid electrolyte. Even a small damage can leak into the electrolyte leading to a fire or explosion, and thus considered unstable. In order to overcome this disadvantage, an all-solid-state battery uses a solid-state electrolyte. In particular, due to the flexible nature of the polymer, the polyelectrolyte-based all-solid-state battery is stable even in a collision and has a low risk of fire since it is not flammable. In addition, compared to lithium-ion batteries of the same weight and size, the energy density is 1.5 to 1.7 times higher so it lasts longer.

Unlike lithium-ion batteries, all-solid-state batteries consist of only an electrode and an electrolyte without a separator between the negative electrode and the positive electrode. The research team developed a new nanostructured electrolyte by controlling the electrostatic interaction in the polymer electrolyte. The team synthesized a set of polymer electrolytes with different strengths of electrostatic interactions through sophisticated synthesis methods, and confirmed the nanostructures of these electrolytes by small-angle X-ray scattering (SAXS) profiles.

Professor Moon Jeong Park believed that this study provides a potential route to accelerating the commercialization of all-solid-state batteries and developing safe batteries."

Reference:

1. Jaemin Min, Ha Young Jung, Seungwon Jeong, Byeongdu Lee, Chang Yun Son, Moon Jeong Park, Enhancing ion transport in charged block copolymers by stabilizing low symmetry morphology: Electrostatic control of interfaces, *Proceedings of the National Academy of Sciences,* **2021,** *118,* 32.

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Students' Section

Ocean Acidification

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Introduction

Covering more than 70 percent of the Earth's surface, the ocean is one of planet Earth's most distinguishing characteristics. Over recent decades, a range of human activities such as the burning of fossil fuels is increasing the amount of carbon dioxide gas emitted into the atmosphere-and hence the amount that dissolves into the ocean. Now, so much carbon dioxide has been absorbed by the ocean that the chemistry of seawater is changing, causing the ocean to become more acidic, a phenomenon known as ocean acidification.

Ocean acidification is one of the several effects of climate change on oceans. Ocean acidification has been compared to anthropogenic climate change and called the "evil twin of global warming" and "the other carbon dioxide problem".

Causes of Ocean Acidification

Ocean acidification is mainly caused by carbon dioxide gas in the atmosphere dissolving into the ocean. This leads to a lowering of the water's pH, making the ocean more acidic. Many factors contribute to rising carbon dioxide levels. Currently, the burning of fossil fuels such as coal, oil, and gas for the human industry is one of the major causes.

Deforestation is another reason for the rise of carbon dioxide as it leaves fewer trees to absorb the gas. Also, when plants are cut down and burnt or left to rot, the carbon that makes up their organic tissue is released as carbon dioxide.

Some parts of the ocean are naturally acidic, such as hydrothermal vent sites - underwater 'hot springs'. In the past, ocean acidification occurred naturally but over much longer periods. It is occurring faster now than in the last 20 million years.

The Chemistry of Ocean Acidification

When atmospheric carbon dioxide is absorbed by the ocean, it reacts with seawater to form carbonic acid (H_2CO_3). Almost immediately, carbonic acid dissociates to form bicarbonate ions (HCO_3^-) and hydrogen ions (H^+). As the concentration of hydrogen ions increases, the water becomes more acidic.

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$$

Some of the extra hydrogen ions react with carbonate ions (CO_2^{3-}) to form more bicarbonate. This makes carbonate ions less abundant-a problem for many marine species that absorb carbonate from seawater and use it to build calcium carbonate shells and skeletons.

Effects of Ocean Acidification

The changes in the chemistry of the ocean adversely affects the behaviour of the marine life, especially organisms like oysters and corals that make hard shells and skeletons by combining calcium and carbonate from seawater. However, as ocean acidification increases, available carbonate ions (CO_2^{3-}) bond with excess hydrogen, resulting in fewer carbonate ions available for calcifying organisms to build and maintain their shells, skeletons, and other calcium carbonate structures.

It also affects the behaviour of non-calcifying organisms. The ability of some fish, like clownfish, to detect predators is decreased in more acidic waters. Studies have shown that decreased pH levels also affect the ability of larval clownfish to locate suitable habitats. When these organisms are at risk, the entire food web may also be at risk.

Changes in marine ecosystems will also have a significant impact on human society. Humans are intricately linked with the health of the ocean. We humans have relied on the ocean for resources such as food, recreation, medication, and transportation. Consequently, we can say that ocean acidification has a pronounced effect on the overall ecosystem.

A solution to the problem of Ocean Acidification

Marine pollution is often difficult to control because pollution transcends international borders, making it difficult to make and implement regulations. Perhaps the most important strategic policy to reduce marine pollution is education. There are two ways to reduce this overall level of pollution. Firstly, either to reduce the human population or find a way to reduce the ecological footprint left by a common human. The second way is for humans to spread less pollution personally. This requires social and political will, as well as to create awareness so that more people respect the environment and harm it less.

Conclusion

Most anthropogenic pollution enters the ocean. Byrne Jenson wrote in his article, "anthropogenic pollution can decrease the biodiversity and productivity of marine ecosystems, thereby reducing and depleting human seafood resources". Most people are unaware of the harmful effects of sources of marine pollution and therefore fewer steps can be taken to deal with this situation. In order to make the public aware of all the facts, intensive research is needed to give full details of the situation. And then this information should be conveyed to the public.

References:

1. Barker, S. & Ridgwell, A. **2012** Ocean Acidification. *Nature Education Knowledge* 3 (10):21.
2. Booklet on Ocean Acidification by *National Research Council of the National Academics.*
3. Article on Ocean Acidification by *National Oceanic and Atmospheric Administration (NOAA).*
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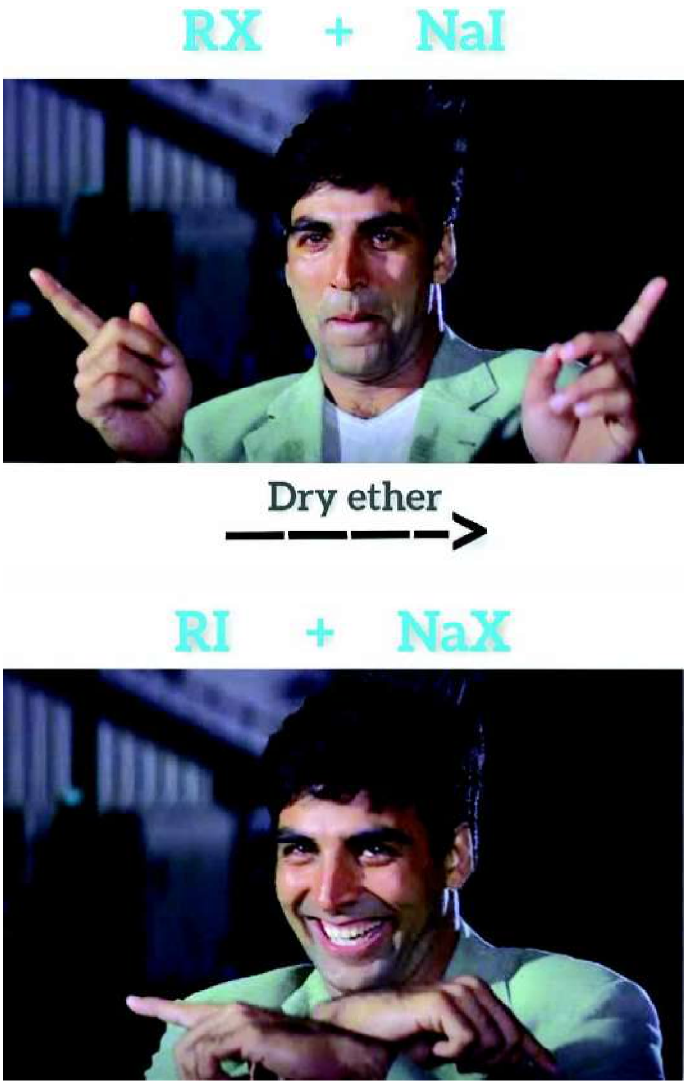

Nanocluster Discovery That Will Protect Precious Metal

Scientists have created a new type of catalyst that will lead to new, sustainable ways of making and using molecules and protect the supply of precious metals. Traditionally; catalysts are divided into homogeneous, when catalytic centers are intimately mixed with reactant molecules, or heterogenous, where reactions take place on surface of a catalyst. Usually, chemists must make compromises when choosing one type or another, as homogeneous catalysts are more selective and active, and heterogenous catalysts are more durable and reusable. However, the nanoclusters of palladium atoms appear to defy the traditional categories, as demonstrated by studying their catalytic behaviour in the reaction of cyclopropanation of styrene.

Catalysts enable nearly 80 percent of industrial chemical processes, the high demand for catalysts means that global supplies of many useful metals, including gold, platinum, and palladium, are becoming rapidly depleted. The challenge is to utilize each-and-every atom to its maximum potential. Exploitation of metals in the form of nanoclusters is one of the most powerful strategies for increasing the active surface area available for catalysis. The process of magnetron sputtering used by these researchers allowed them to produce metal nanoclusters that can be deposited on almost any surface. More importantly, the nanocluster size can be controlled precisely by experimental parameters, from single atom to a few nanometres, so that an array of uniform nanoclusters can be generated on demand within seconds.

Eco-Leather

For four years University of Delaware's, Affordable Composites from Renewable Sources program, began developing what they call "eco-leather" collaboration with the university's fashion and apparel studies department. Eco-leather is made with natural fibres such as flax or cotton mixed with palm, corn, soybean and other plant oils that are laminated together in layers to create something that looks and feels almost similar o as if it came from an animal. The designers love eco leather because it gives them a whole element of design that they didn't have before when they were trying to work with polyvinyl chloride (PVC) as an artificial leather substitute. It is breathable, and not like a plastic that would make the skin sweaty when worn. And unlike real leather, which requires tanning– a process that releases potentially toxic materials into the environment– the materials in eco-leather are sustainable and produce a low carbon footprint.

Zinc's oxidation state can be made +3, fundamentally changing the element's chemistry

Zinc traditionally has a valence of two, meaning two electrons take part in the element's chemical reaction. A new article shows that the chemistry of zinc can be fundamentally changed, making it trivalent–or a valence of three–with the proper reagent. This technology would enable us to manipulate chemistry at the fundamental level, making synthesis of new materials with tailored properties possible. While zinc is categorized as a transition metal element, its third electron shell–arranged around the nucleus and containing electrons–is full, and unlike regular transition metals, does not take part in zinc's chemical reaction and does not allow zinc to be magnetic. However, research has found, when reacted with highly stable trianions, zinc's properties can be changed. Its [third shell] d-electrons can be made to participate in chemical reactions and zinc could thus carry a magnetic moment. This study shows that fundamental chemical properties of an atom can be changed.

Reference:

1. *www.sciencedaily.com*
2. *www.acs.org*

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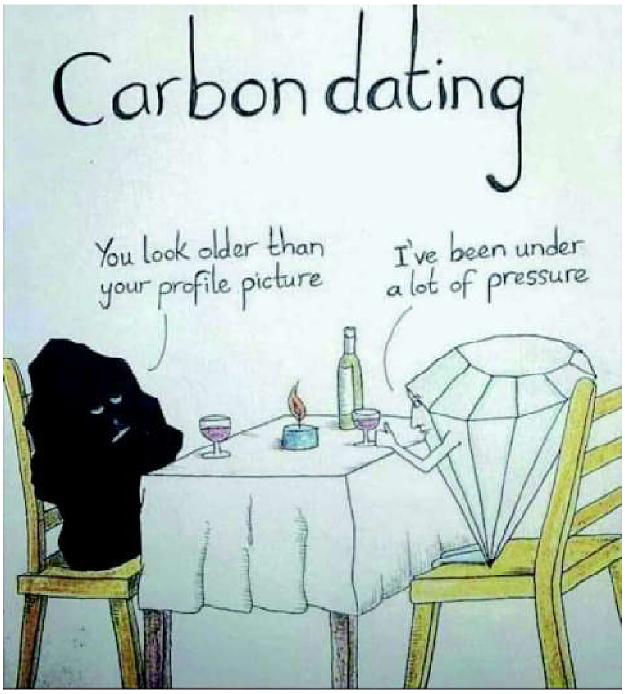
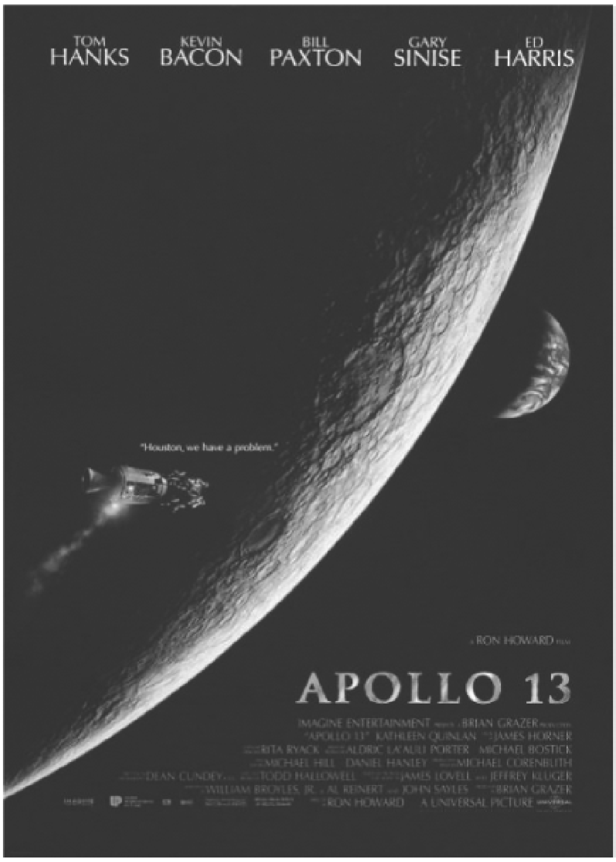


CHEMISTRY IN MOVIES

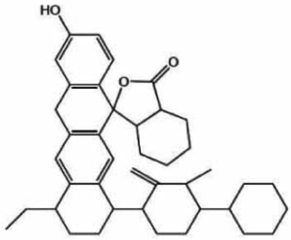
APOLLO 13 (1995)



During the Apollo 13 mission, an explosion in the Service Module forced the astronauts to shut down the Command Module and use the Lunar Module as a "lifeboat" while the spacecraft looped the moon and returned for an emergency reentry into the Earth's atmosphere. As the astronauts settled in the LM there was a gradual build-up of carbon dioxide gas. The environmental system in the LM depended on two lithium hydroxide (LiOH) filters to remove excess carbon dioxide (exhaled by humans as part of normal respiration) from the atmosphere. But with three astronauts to support instead of two, the filters did not have enough capacity to maintain safe carbon dioxide levels for the entire journey home. The CM environmental system had many unused LiOH filters that might be transferred to the LM. But the filters used in the CM were box-shaped and fit into box-shaped holders; those in the Lunar Module were cylindrical and fit into cylindrical holders. The engineers with the Mission Control team worked out a solution that cobbled together plastic bags, plastic coated cue cards from a three-ring reference binder, hoses from the lunar spacesuits, and lots of grey duct tape, then carefully radioed instructions to the astronauts in space. After about an hour, the new device, although not very elegant, worked perfectly.

MEDICINE MAN (1992)

A botanist goes to South America for a couple of years to work for a pharmaceutical company and look for ant carcinogens. He is then joined by a biochemist named Dr. Rae Crane, who fires up her gas chromatography (GC) mass spectrometer to analyze samples in the middle of the South American jungle. Somehow they are able to determine that one of the compounds ("Peak 37") in their mixture has anticancer activity. They show the wonderful chemical structure of the compound as in the figure below which doesn't seem to break any rules of chemistry, such as carbon with 5 bonds.



Peak 37 with Anti-cancer Activity

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Smart Clothes Keep an Eye on the Heart

In the past few months, the news of Apple watch saving many people through its ECG feature has become a popular topic. But there is no more need to wear your uncomfortable smart watches or chest straps to monitor your heart if your comfy clothes can do a better job.

The Brown School of Engineering lab of chemical and biomolecular engineer Matteo Pasquali reported in the American Chemical Society journal *Nano Letters* that it sewed carbon nanotube fibers into athletic wear to monitor the heart rate and take a continual electrocardiogram (ECG) of the wearer.

The fibers are just as conductive as metal wires, but washable, comfortable and far less likely to break when a body is in motion, according to the researchers. The researchers also noted that nanotube fibers are soft and flexible, and clothing that incorporates them is machine washable. The fibers can be machine-sewn into fabric just like standard thread. The zigzag stitching pattern allows the fabric to stretch without breaking them.

On the whole, the shirt they enhanced was better at gathering data than a standard chest-strap monitor taking live measurements during experiments. When matched with commercial medical electrode monitors, the carbon nanotube shirt gave slightly better ECGs.

The shirt has to be snug against the chest. The future studies are focusing on using denser patches of carbon nanotubes threads so there's more surface area to contact the skin.

Pasquali's lab introduced carbon nanotube fiber in 2013. Since then the fibers, each containing tens of billions of nanotubes have been studied for use as bridges to repair damaged hearts, as electrical interfaces with the brain, for use in cochlear implants, as flexible antennas and for automotive and aerospace applications. Their development is also part of the Rice-based Carbon Hub, a multiuniversity research initiative led by Rice and launched in 2019.

The original nanotube filaments, at about 22 microns wide, were too thin for a sewing machine to handle. Taylor said a rope-maker was used to create a sewable thread, essentially three bundles of seven filaments each, woven into a size roughly equivalent to regular thread.

Fibers woven into fabric can also be used to embed antennas or LEDs, according to the researchers. Minor modifications to the fibers' geometry and associated electronics could eventually allow clothing to monitor vital signs, force exertion or respiratory rate.

"We see that, after two decades of development in labs worldwide, this material works in more and more applications," Pasquali said. "Because of the combination of conductivity, good contact with the skin, biocompatibility and softness, carbon nanotube threads is a natural component for wearables."

He said the wearable market, although relatively small, could be an entry point for a new generation of sustainable materials that can be derived from hydrocarbons via direct splitting, a process that also produces clean hydrogen. Development of such materials is a focus of the Carbon Hub.

"We're in the same situation as solar cells were a few decades ago," Pasquali said. "We need application leaders that can provide a pull for scaling up production and increasing efficiency."

AMAZING FACTS

- The only two non-silvery metals are gold and copper.
- Glass is actually a liquid, it just flows very, very slowly.
- Superfluid Helium defies gravity and climbs on walls.
- Although oxygen gas is colorless, the liquid and solid forms of oxygen are blue.
- Hydrofluoric acid is so corrosive that it will dissolve glass. Although it is corrosive, hydrofluoric acid is considered to be a weak acid.
- Mars is red because its surface contains a lot of iron oxide or rust.
- The only letter not appearing on the periodic table is J.
- A rubber tire is technically one single, giant, polymerized molecule.
- Apple seeds are extremely poisonous. It contains amygdalin, which is turned into cyanide if chewed.

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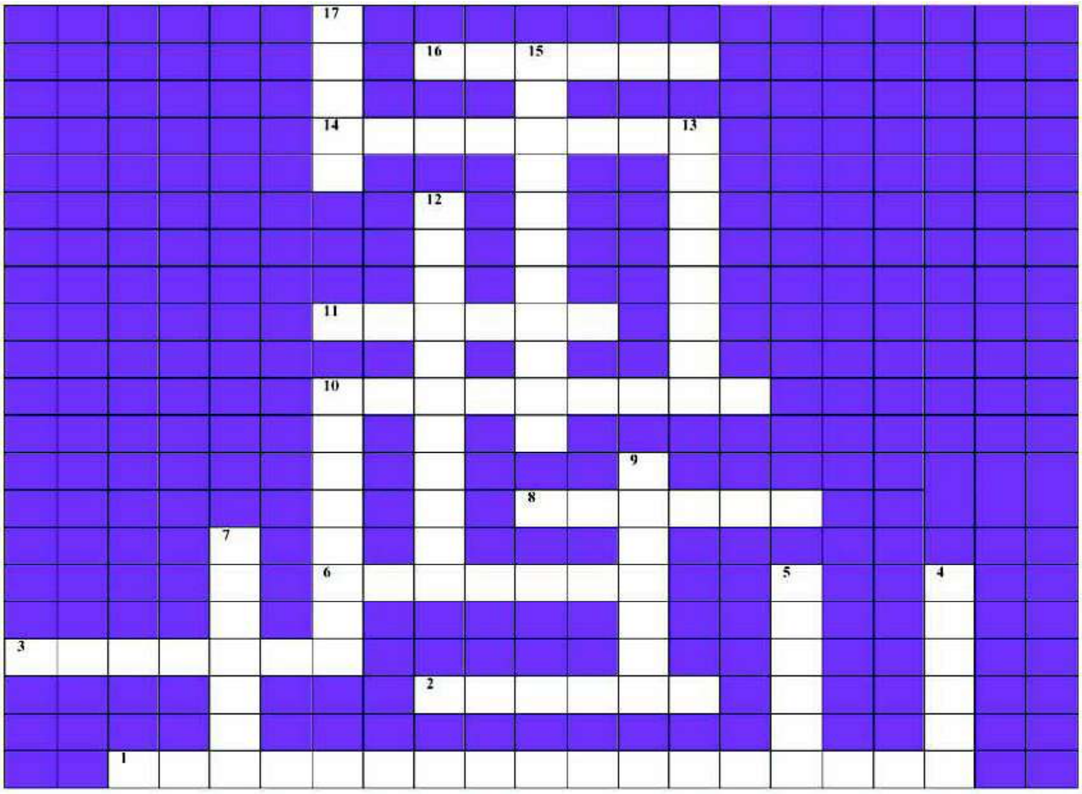
Chemistry Puzzle

Find the words related to Atomic Structure

K	Z	T	H	B	A	Q	U	B	M	Z	Q
C	O	M	P	O	N	E	N	T	S	B	E
W	V	F	M	H	W	K	O	S	S	X	L
S	S	Q	Z	R	N	N	T	O	R	A	E
N	H	W	Q	W	A	Q	L	M	P	T	M
Y	H	P	I	U	X	E	A	O	E	O	E
C	L	O	U	D	A	Z	D	T	N	M	N
Q	O	N	O	T	O	R	P	A	H	I	T
N	E	U	T	R	O	N	K	H	O	C	C
Q	L	E	D	O	M	B	R	T	J	F	U
P	O	U	M	O	T	A	Y	X	K	P	V
N	U	C	L	E	U	S	B	Q	G	X	H

Chemistry Crossword
APPARATUS



Down :

17. These come in pair and grip hot things.
15. You measure temperature with this.
13. A small cylindrical glass container used for experiments.
12. This tube may not always be hot but you can warm solutions in it.
10. Porcelain container to heat reactants in.
9. Sounds like French for 'little pip'-used to add liquids.
7. A spoon for chemists?
5. Named after a famous Robert, a burner used in chemistry.
4. Thick-walled glass cylinder to contain substances in the gas state.

Across :

16. Anagram of rotter, used as a stand
14. A metal mat used on a tripod when heating.
11. Funnels used to separate insoluble solids from liquids.
10. Anagram of dense corn-cold water through this to turn vapours into liquids
8. Three-legged metal support.
6. Despite its name, this shelf doesn't buzz
3. You can do titration with this long glass tube.
2. A mug for a chemist ?
1. Tall graduated container for measuring volumes of liquids.

N.B. Please send the answer to The Editor, 'The Chemical Axis', Department of Chemistry, B. Borooah College, Guwahati, Assam - 781007 on or before 10-10-2021
E-mail : thechemicalaxis@gmail.com

Any suggestion regarding the improvement of 'The Chemical Axis' will be solicited.
Please send your suggestion to The Editor, 'The Chemical Axis', Department of Chemistry,
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6. Present Occupation :
7. Period of study :
8. Course of study (PG/UG/HS) :
9. Any suggestion regarding development of the Forum :

Date :
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