

REPORT
Science Academies' Lecture Workshop on
ADVANCES IN SUPRAMOLECULAR CHEMISTRY AND NANOSCIENCE

3rd & 4th March 2017

ORGANIZED BY PG AND RESEARCH DEPARTMENT OF CHEMISTRY
ST.JOSEPH'S COLLEGE IRINJALAKUDA

Science Academies' Lecture Workshop on advances in supramolecular chemistry and nanoscience was organized at St.Joseph's college, Irinjalakuda, Kerala on 3rd and 4th March 2017. There were 154 participants, 27 teachers and 128 students from various colleges of Kerala. The overall aim of this workshop is to inculcate knowledge in the field of in supramolecular chemistry and nanoscience. The workshop is a unique platform for the faculty and the students to showcase their research to the scientific community. It provided an opportunity for them to interact, share and exchange their experiences with resource persons. Well experienced resource persons could motivate and induce research aptitude in the participants in their respective thrust areas.

The inauguration function started at 9.30am in the seminar hall with prayer song. Dr. Jessy Emmanuel, Co-ordinator of the workshop offered a warm welcome to all those who were present for the inaugural function. Dr.Sr.Lilly PL, Principal of the college delivered the presidential address in which she stressed the importance of scientific interactions. Dr.K.George Thomas, Convenor of the workshop, inaugurated the function.

Dr.K.George Thomas IISER, TVM gave keynote address. In his keynote address, he explained the significance of supramolecular chemistry and nanoscience in this current Chemistry world. Sr.Lilly K.O vice principal of the college, offered the formal vote of thanks.

After the tea break, Dr.Reji Varghese, Professor,IISER, TVM delivered the first lecture on 'Supramolecular Chemistry and DNA. The session ended at 11.30am. The second session began at 11.45am, Dr. Sukendu Mandal, Professor, IISER, TVM talk about

'Atom Precise Metal Nanoclusters,.After lunch the third session began at 1.30. Dr.K.George Thomas,Professor, IISER, TVM, talk about 'Plasmonic Nanomaterials and their applications and Semiconductor Quantum dots and their applications. The session got over by 4.00 pm. After a short tea break, the last session began. Ms.Nonu Davis, Ms Harsha Paul, Ms Nivedita Sudheer, Ms.P. P. Moly ,presented their research papers in this session. Dr.Manoj CL , Assistant professor St.Joseph's college, chaired the session.

The second day the first session was engaged by paper presentation. Mr. V.Vignesh, , Ms. A.Gifty Priscilla ,Mr.Nishad K.M., presented their papers.

from 10 AM to 11:15 AM
Dr.S. Sampath, professor, IISc Bangalore, gave an inspiring class on Electrochemical Properties of Nanostructured Materials. Third session was handled by Dr.K M Sureshan, IISER, Trivandrum. The topic of the lecture was 'Supramolecular Chemistry with Sugars'. After the lunch break, fourth session began at 1.30. Dr Mahesh Hariharan, Professor, IISER, TVM, talk about 'Ultrafast Processes in Chemistry and Biology'. Concluding session in which the participants expressed their views regarding the conduct and content of the workshop. The lectures and presentations were well appreciated by all the participants. They were truly benefited and enriched with new facts. Evaluation forms were filled by all the participants. They expressed their satisfaction and gratitude towards the conduct of the workshop. And the whole programme ended by 5.30 pm in a good note.

The following are a brief note on the ^{eight} six lectures that were delivered during the workshop.

Dr. K. George Thomas: Plasmonic Nanomaterials and their applications and Semiconductor Quantum dots and their applications.

The presentation will summarize some of the fundamental processes in plasmonic as well as excitonic systems with emphasis on the translating of these knowledge to devices. Precise assembly of plasmonic materials of desired size and shape allows modulation of their optical and field effects, opening up several plasmonically powered processes such as hot electron injection and surface enhanced spectroscopy. Plasmonic effects are significantly high when the gap between nanoparticles is less than 15 nm and the Raman signal enhancement factors at the hot spots follow a distance (d) dependence of $1/d^n$ with $n=1.5$. These studies provided fundamental insight on plasmon coupling and surface enhanced spectroscopy. By adopting these principles, we have designed platforms having arrays of well-organized plasmonic structures with precise nanogaps, which can generate multiple hot spots. These plasmonic platforms were further used for the identification of molecules of importance in health, environment and safety. These aspects will be discussed in the first part of the talk. The second part of the presentation will illustrate efforts to remodel the surface ligands on semiconductor quantum dots and its consequence on electron transfer process. By modifying the surface ligands on QDs, we could generate stable radicals of methyl viologen (paraquat) at ambient conditions by preventing back electron transfer from CdSe quantum dots. Paraquat is widely used as herbicide owing to its high efficiency even though banned in many countries due to its extreme toxicity. The high solubility of paraquat in water results in its downstream movement by rain, which affects the whole ecosystem adversely by contaminating the water sources. The biological activity of paraquat originates from its high reductive nature (reduction potential of -0.45 V vs NHE) which blocks electron transport processes in the living systems. Direct SERS detection of these radicals at ambient conditions using plasmonic platforms will be presented.

Dr.S. Sampath : Electrochemical Properties of Nanostructured Materials

Electrochemical capacitors are devices capable of higher charge storage several hundred times more than conventional capacitors. They are different from batteries and for certain types of application have several advantages. The state-of-charge is a simple function of voltage and this coupled with high power density and good cycle-life enable them to be useful in applications ranging from light-weight electronic fuses, memory back-up power sources, surge protection devices to pulse power sources for smart weapons. Such devices are also likely to help the global transition to more energy- efficient technologies. Recently, a new class of reversible electrochemical energy storage systems have been developed that use: (a) the capacitance associated with charging and discharging of the electrical doublelayer at the electrode-electrolyte interface and are hence called electrical double-layer capacitors (EDLCs), and (b) the pseudocapitance with electrosorption or surface redox reactions which are referred as pseudocapacitors. While EDLCs with capacities of many tens of farads per gram of the electrode material have been achieved employing high surface-area carbon powders, fibres, or felts, much higher capacitance values are accomplished with pseudocapacitors employing certain high surface-area oxides or conducting polymers. These electrochemical capacitors are being envisaged for several applications to complement the storage batteries. This article provides a brief introduction to scientific fundamentals and technological applications of electrochemical supercapacitors. It is also stressed that there is a substantial scope for technology development in this newly emerging area, where materials science and polymer technology will have a pivotal role in conjunction with electrochemistry.

Dr.Reji Varghese : Supramolecular Chemistry with DNA

Supramolecular chemistry refers to the domain of chemistry beyond that of molecules and focuses on the chemical systems made up of a discrete number of assembled molecular subunits or components. While traditional chemistry focuses on the covalent bond, supramolecular chemistry examines the weaker and reversible noncovalent interactions between molecules. These forces include hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π - π interactions and electrostatic effects. Important concepts that have been demonstrated by supramolecular chemistry include molecular self-assembly, folding, molecular recognition, host-guest chemistry, mechanically-interlocked molecular architectures, and dynamic covalent chemistry. The study of non-covalent interactions is crucial to understanding many biological processes from cell structure to vision that rely on these forces for structure and function. Biological systems are often the inspiration for

supramolecular research. In the presentation, individual supramolecular interactions with specific examples were discussed.

Electrostatic interactions: Electrostatic interactions are between cations and anions. Electrostatic interactions can be either attractive or repulsive, depending on the signs of the charges. Favorable electrostatic interactions cause the vapor pressure of sodium chloride and other salts to be very low. The electrostatic interactions within a sodium chloride crystal are called ionic bonds. But when a single cation and anion are close together, say on the surface of a protein, or within a folded RNA, those are favorable non-covalent electrostatic interactions. Electrostatic interactions can be very strong, and fall off slowly with distance ($1/r$).

Dipole Interactions: In a molecule composed of atoms of various electronegativities, the atoms with lowest electronegativities hold partial positive charges and the atoms with the greatest electronegativities hold partial negative charges. In a methanol molecule (CH_3OH), the electronegative oxygen atom pulls electron density away from the carbon atom. In a water molecule, the electronegative oxygen atom pulls electron density away from the hydrogen atoms. The oxygen atom carries a partial negative charge. The hydrogen atoms carry partial positive charges. This phenomenon of charge separation is called polarity. Water is a polar molecule.

Dipole-dipole interactions: The strength of a dipole-dipole interaction depends on the size of each dipole and on their relative orientation. The interaction energy between two dipoles can be either positive or negative. Parallel end-to-end dipoles attract while antiparallel end to end dipoles repel.

Dipole-induced dipole interactions: A molecule with a permanent dipole moment will induce a dipole moment in a second molecule that is located nearby in space. This phenomenon is called polarization. The strength of a dipole-induced dipole interaction depends on the size of the dipole moment of the first molecule and on the polarizability of the second molecule. Polarizability is a measure of the ease with which electrons are shifted by an external electronic field. Molecules with π electrons, such as phenylalanine and tryptophan, are more polarizable than molecules such as isoleucine that lack π electrons. Dipole-induced dipole interactions are important even between molecules with permanent dipoles. A permanent dipole is altered/ modulated by the dipole of an adjacent molecule. For example, the dipole of one water molecule will influence the electron distribution of an adjacent water molecule. The dipole of a water molecule will induce a change in the dipole of a nearby water molecule, compared to the permanent dipole of an isolated water molecule.

Dipole-charge interactions: A molecule with a permanent dipole can interact favorably with charged species. This type of interaction is why sodium chloride (cationic sodium ions and anionic chloride ions) and other salts tend to interact well with water (strong dipole).

Fluctuating dipoles (Dispersive interactions, London Forces): Molecules behave like oscillating dipoles. In molecules that are located nearby to each other the oscillators are coupled. The movements of the electrons in molecules are correlated. Electrons tend to run away from each because of electrostatic repulsion. Coupled fluctuating dipoles experience favorable electrostatic interaction known as dispersive interactions. The strength of the interaction is related to the polarizabilities of the two molecules (or atoms). Fluctuating dipole interactions fall off with $1/r^6$.

Hydrogen Bonding: An acceptor atom (A) with a basic lone pair of electrons (i.e., a Lewis Base) can interact favorably with an acidic proton bound to an electronegative atom (D). A strong hydrogen bond requires that both atoms A and D are electronegative atoms. The most common hydrogen bonds in biological systems involve oxygen and nitrogen atoms. Sulfur can also engage in hydrogen bonds. Hydrogen bonds where atom D is a carbon atom are observed although these are relatively weak interactions. Hydrogen bonds are essentially electrostatic in nature, although the energy can be decomposed into additional contributions from polarization, exchange repulsion, charge transfer, and mixing. In traversing the Periodic Table, increasing the electronegativity of atom D strips electron density from the proton, increasing its partial positive charge, and increasing the strength of the hydrogen bond. Hydrogen bond strengths form a continuum. Strong hydrogen bonds of 20-40 kcal/mol, generally formed between charged donors and acceptors, are nearly as strong as covalent bonds. Weak hydrogen bonds of 1-5 kcal/mol, sometimes formed with carbon as the proton donor, are no stronger than conventional dipole-dipole interactions. Moderate hydrogen bonds, which are the most common, are formed between neutral donors and acceptors are from 3-12 kcal/mol. All these different supramolecular interactions were discussed with appropriate examples. Apart from this general introduction, two very recent research papers were also discussed in the talk.

Dr.Sukendu Mandal : Atom Precise Metal Nanocluster

Metal nanoclusters composed of precise number of atoms are of fundamental importance for investigating the evolution of the structure and physicochemical properties in going from the atomic state to the metallic state. These small clusters exhibit properties that depend strongly on the size of the cluster, which provides a unique opportunity to fabricate novel materials with desired properties. A great deal of research has gone into thiolated clusters of Au and Ag because of the stability afforded by the strength of the metal-sulfur bond and the resistance of these metals to oxidation.

These noble metal nanoclusters are of great interest due to their unique optical and electronic properties, and their small size makes them particularly suitable for catalysis^{1,2} and biological sensing³. However, most of the assemblies have been confined to gold and silver⁴ based clusters and there have been only selected works on platinum, known to be an important catalyst. In this talk first I will discuss the synthesis of these nanoclusters followed by structural evolution from molecular complex to nanocluster to bulk solids. Then I will discuss the optical and catalytic behavior of these nanoclusters.

Dr. K. M. Sureshan : Topochemical reactions in crystals and organogels

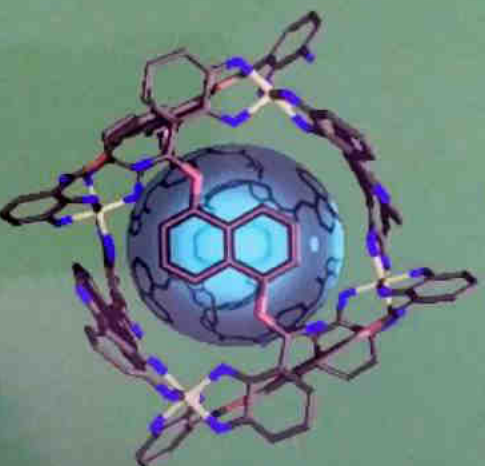
Polymeric gels, one form of the colloidal materials, have attracted much attention because of their application in cosmetics, medicine, food industry, controlled release, developing smart materials etc. Recently the focus has shifted to supramolecular gels formed by self-assembly, through noncovalent interactions, of small monomeric species due to their reversible nature, degradability, homogeneity and tunability over the polymeric gels. Different classes of Low Molecular Weight Organogelators (LMWOs) those can congeal a variety of organic solvents have been reported. However there are only limited examples of harvesting function from these novel materials. Exploration for novel functions from these soft materials continues to be a challenging and exciting task. Pursuing our interests in organogels and topochemical reactions, we have developed a few gelators which can congeal oils and hydrocarbon solvents to give strong and self-supporting gels and can undergo Topochemical reactions in gel-states. The design of these gelators and their possible application in various fields will be discussed.

Dr. Mahesh Hariharan: Ultrafast Processes in Chemistry and Biology

Mechanistic investigation of chemical reactions employs time-resolved spectroscopic techniques.¹ Use of such techniques has offered us detailed insights on the pathways involved in several fundamental and bio-relevant reactions. Many of the biological events, that include vision and photosynthesis, occur in ultrafast timescale. Scientists from various disciplines have collectively worked over several decades to understand such processes in chemical and biological systems. This talk will focus on nanosecond, picosecond and femtosecond spectroscopic measurements to understand some fundamental reactions that are important in chemistry and biology. This finding was recognized through the Nobel Prize in Chemistry in 1999 for Ahmed Zewail.

PROCEEDINGS OF SCIENCE ACADEMIES' LECTURE WORKSHOP
ON

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