

# TUE 2014 THEMATIC UNIT OF EXCELLENCE





This brochure showcases the activities of a research centre at IIT Madras. Some of you many not have seen our previous brochures and therefore, let me give you a brief introduction to our activities.

Thematic Unit of Excellence (TUE) on Water Purification Using Nanotechnology is an initiative of the Department of Science and Technology under the Nano Mission. Creation of this unit is firstly a recognition of our continuous efforts in the area and secondly a demonstration of the DST's commitment to one of the most important areas where solutions of advanced science and technology are needed. This unit coexists with the DST Unit of Nanoscience, another initiative of the Nano Mission.

The TUE at IITM looks at a number of areas such as nanomaterials, photocatalysis, dendrimers, porous concrete, aquaporins, membranes, capacitive deionisation, electrospun fibres and solar desalination as solutions for water purification. Several associated aspects such as water quantity monitoring, modelling, prototype development, performance evaluation, field trials and technology transfer are under its purview. Conduct of discussion meetings, conferences, dissemination of information through various media and capacity building through short term projects and refresher courses are other areas of activity.

All of these will be possible only with team effort. Besides me, Professors Sarit Kumar Das, Ligy Philip, Edamana Prasad, Manu Santhanam, C. Vijayan, and K. Srinivasa Reddy are participating in this effort. There are several Indian and international collaborators. While some of the efforts are at an advanced stage and technologies have been rolled out, others are being initiated and early results are available. The institute has recognised the importance of the activity and a new laboratory is being created and it is expected to be ready soon. There is a need for more people to join this effort and in the coming years, we hope that the nucleus created will be expanded further.

What we could accomplish in the last year is showcased here. All of these have been possible due to the support of our coworkers, collaborators and funding agencies. I thank each one of them.

The content is pictorial in nature and in case you wish to know more, please contact us. We are aware that much more effort is needed to accomplish our goal.





**Professor T. Pradeep** 







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**Amitava Srimany**, Balasubramanyam Jayashree, Subramanian Krishnakumar, Sailaja Elchuri and T. Pradeep *Rapid Commun. Mass Spectrom.*, (2014) (Just accepted)

Various disease conditions, particularly tumours, can be understood easily by studying changes in the lipid profile of cells. While lipid profiles of tissues have been done by desorption electrospray ionization mass spectrometric (DESI-MS) imaging, there is paucity in standardized protocols for sample preparation involving cell cultures to generate reliable results. In this study, we report a method for the direct analysis of lipids from cultured cells by incorporating them onto Whatman 42 filter paper as a substrate for reliable DESI-MS analysis.

WERI-RB1 cell line was spotted on commonly used substrates for DESI-MS analysis, such as glass slide, Teflon coated glass slide, thin layer chromatography (TLC) plate, and Whatman 42 filter paper. A comparison of mass spectrometric images with two different lipids was made to understand the behaviour of different surfaces when the same sample was spotted on them. Relative intensities of different lipid peaks in WERI-RB1 cell line were

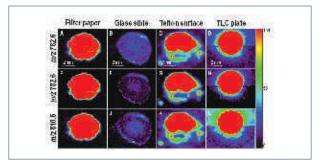
July Market Comment

Schematic of sample preparation using cell cultures. Cell suspensions are dropped on Whatman 42 filter paper, dried, the paper is cut to the required size and mounted on a slide for DESIMS analysis. A spectrum is also shown.

compared and relative lipid abundances were also compared across two different human retinoblastoma cell lines; WERI-RB1 and Y79.

The study demonstrates that good lipid signals can be obtained by DESI-MS when the cells were spotted on Whatman 42 filter paper. Tandem mass spectrometry was performed to identify the lipids as glycerophosphocholines (PC). Better lipid images from assembly of cells were obtained with distinct boundary when they were spotted on Whatman 42 filter paper than other surfaces.

We demonstrate the use of a simple substrate for reliable DESI-MS analysis of cultured cells. This method has the potential to understand various interactions of cells with other external agents. The current method would help in the application of DESI-MS for biology in general and medical sciences in particular.

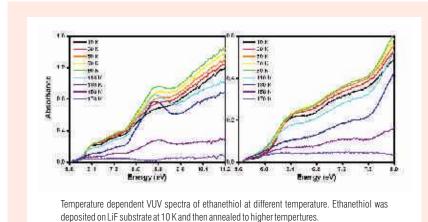


DESI MS images of lipid distribution of WERI-RB1 cells spotted on different surfaces. Top and bottom row show images without any noise reduction in BioMAP. Middle row shows images with noise reduction. The scale bars of top row apply to all images across each column. Intensity is colour coded; from black (low) to red (high).



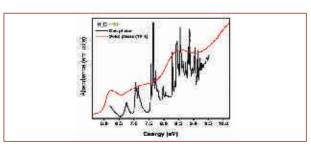


**Radha Gobinda Bhuin,** Bhalamurugan Sivaraman, J.-I. Lo, Raja Sekhar B. N., Bing-Ming Cheng, T. Pradeep and Nigel Mason *J. Chem. Phys., 141 (2014) 231101 [DOI: 10.1063/1.4903840].* 

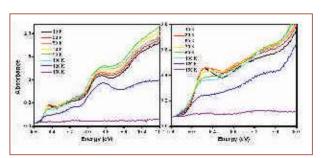


Following the recent identification of ethanethiol in the interstellar medium (ISM) we have carried out Vacuum UltraViolet (VUV) spectroscopy studies of ethanethiol (CH<sub>3</sub>CH<sub>2</sub>SH) from 10 K until sublimation in an ultrahigh vacuum chamber simulating astrochemical conditions. These results are compared with those of methanethiol (CH<sub>3</sub>SH), the lower order thiol also reported to be present in the ISM. VUV spectra recorded at higher temperature reveal conformational changes in the ice and phase transitions whilst evidence for dimer production is also presented.





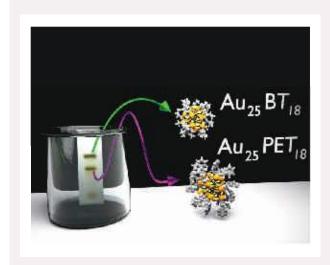
VUV spectrum of methanethiol ice, formed at 10 K, compared with the gas phase spectrum.



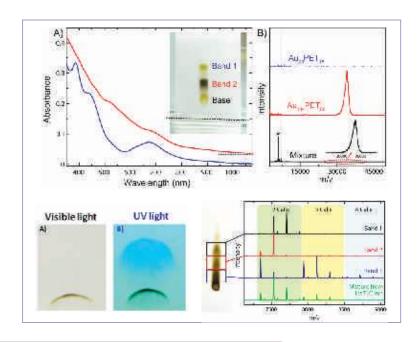
Temperature dependent VUV spectra of methanethiol at different temperature. Methanethiol was deposited on LiF substrate at 10 K and then annealed to higher temperatures.



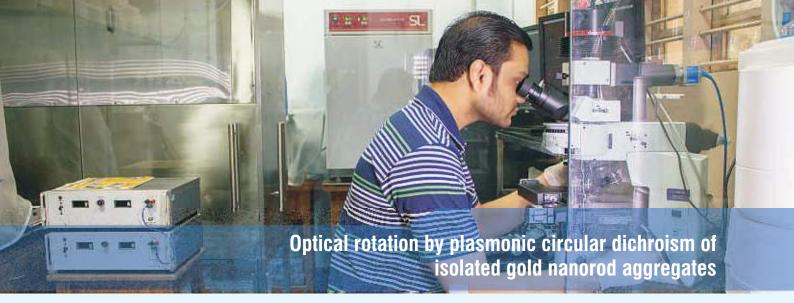
**Atanu Ghosh**, Jukka Hassinen, Petri Pulkkinen, Heikki Tenhu, Robin H. A. Ras and T. Pradeep *Anal. Chem., 86 (2014) 12185–12190 [DOI: 10.1021/ac503165t].* 



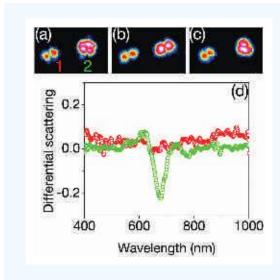
There is an urgent need for accessible purification and separation strategies of atomically precise metal clusters in order to promote the study their fundamental properties. Although the separation of mixtures of atomically precise gold clusters  $Au_{25}L_{18}$ , where L are thiolates, has been demonstrated by advanced separation techniques, we present here the first separation of metal clusters by thin layer chromatography (TLC), which is simple yet surprisingly efficient. This method was successfully applied to a binary mixture of  $Au_{25}L_{18}$  with different ligands, as well as to a binary mixture of different cluster cores,  $Au_{25}$  and  $Au_{144}$ , protected with the same ligand. Importantly, TLC even enabled the challenging separation of a multi-eomponent mixture of mixed-monolayer-protected  $Au_{25}$  clusters with closely similar chemical ligand compositions. We anticipate that the realization of such simple yet efficient separation technique will progress the detailed investigation of cluster properties.



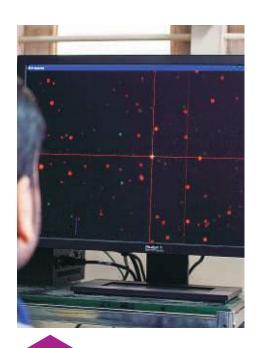


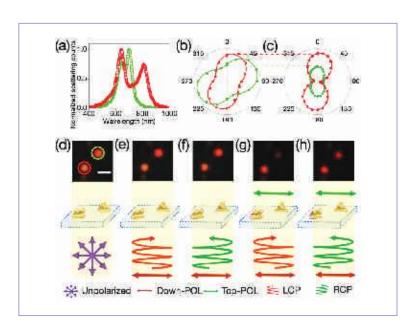


**Kamalesh Chaudhari** and T. Pradeep *Appl. Phys. Lett.*, 105 (2014) 203105 [DOI: 10.1063/1.4902318].



We show that plasmonic chirality in single gold nanorod (GNR) aggregates leads to the rotation of polarization of the scattered light. 3D glasses in conjunction with linearly polarized dark field scattering microspectroscopy were used to study the chirality of single GNR aggregates. Using this hetero-polarizer setup, we not only detect but also quantify their chirality. A polar mapping strategy was used for providing direct evidence for the emergence of light of different polarization angles when chiral GNR aggregates were excited with circularly polarized light of different handedness. Further, we have developed a methodology to eliminate fluctuations in the scattering intensity by averaging and normalizing the data. This allows calculation of plasmonic circular dichroism scattering spectra with high accuracy.

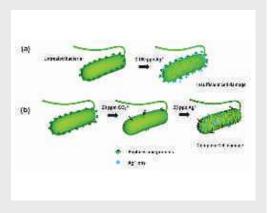


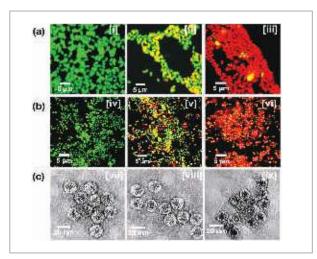




J. R. Swathy, M. Udhaya Sankar, Amrita Chaudhary, Sahaja Aigal, S. Anshup and T. Pradeep Sci. Rep., 4 (2014) 7161 [DOI: 10.1038/srep07161].

Silver is an indispensable metal but its use has to be minimised for sustainable growth. Much of the silver lost during use is unrecoverable; an example being its use as an antimicrobial agent, a property known since ages. While developing methods to create an affordable drinking water purifier especially for the developing world, we discovered that 50 parts per billion (ppb) of  $\mathrm{Ag}^+$  released continuously from silver nanoparticles confined in nanoscale cages is enough to cause antimicrobial activity in conditions of normal water. Here we show that the antibacterial and antiviral activities of  $\mathrm{Ag}^+$  can be enhanced  $\sim\!1,000$  fold, selectively, in presence of carbonate ions whose concentration was maintained below the drinking water norms. The protective layers of the organisms were affected during the carbonate-assisted antimicrobial activity. It is estimated that  $\sim\!1,300$  tons of silver can be saved annually using this new way to enhance its antimicrobial activity.





The fluorescence microscopy and HRTEM images demonstrating the defective outer membrane/capsid in microbes caused due to  $Aq^+ + CQ_3^2$  treatment.

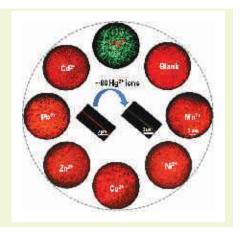
Line (a): Fluorescence microscopy images of E. coli: ([i] Input bacteria, [ii] 50 ppb  $Ag^+$ -treated bacteria and [iii] 50 ppb  $Ag^+$  + 20 ppm  $C0_3^{2-}$ -treated bacteria after staining with syto9 and propidium iodide. Line (b): Similar fluorescence microscopy images of S. aureus: [iv] Input bacteria, [v] 50 ppb  $Ag^+$ -treated bacteria and [vi] 50 ppb  $Ag^+$  + 20 ppm  $C0_3^{2-}$ -treated bacteria. Line (c) TEM images of MS2 bacteriophage: [vii] Input viruses, [viii] pput viruses, [viii] 50 ppb  $Ag^+$  + 20 ppm  $C0_3^{2-}$ -treated viruses after staining with 0.2% uranyl acetate. Images (vii) and (viii) appear the same as they are not damaged, while image (ix) appears dark as damage in the capsid allowed the stain to pass through it. (vii) and the stain to pass through it.

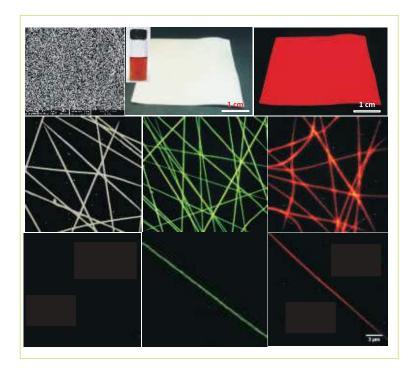




**Atanu Ghosh**, Vedhakkani Jeseentharani, Mohd Azhardin Ganayee, Rani Hemalatha, Kamalesh Chaudhari, Cherianath Vijayan and T. Pradeep *Anal. Chem., 86 (2014) 10996–11001 [DOI: 10.1021/ac502779r].* 

A new methodology has been demonstrated for ultra trace detection of  $Hg^{2+}$ , working at the limit of a few tens of metal ions. Bright, red luminescent atomically precise gold clusters, Au@BSA (BSA –bovine serum albumin), coated on Nylon-6 nanofibers were used for these measurements. A green emitting fluorophore, FITC (fluorescein isothiocyanate), whose luminescence is insensitive to  $Hg^{2+}$  was pre-eoated on the fiber. Exposure to mercury quenched the red emission completey and the green emission of the fiber appeared which was observed under a dark field fluorescence microscope. For the sensing experiment at the limit of sensitivity, we have used individual nanofibers. Quenching due to  $Hg^{2+}$  ions was fast and uniform. Adaptation of such sensors to pH paper-like test-strips would make affordable water quality sensors at ultralow concentrations a reality.



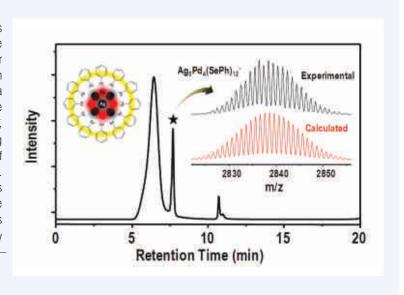


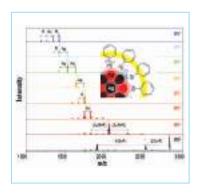




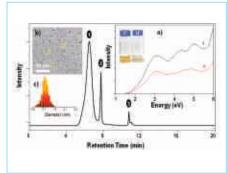
**Sreya Sarkar, Indranath Chakraborty,** Manoj Kumar Panwar and T. Pradeep *J. Phys. Chem. Lett.*, *5* (2014) 3757–3762 [DOI: 10.1021/jz5019509].

A selenolate protected Ag-Pd alloy cluster was synthesized using a one pot solution phase route. The crude product upon chromatographic analyses under optimized conditions gave three distinct clusters with unique optical features. One of these exhibits a molecular peak centered at m/z 2839, in its negative ion mass spectrum assigned to Ag<sub>5</sub>Pd<sub>4</sub>(SePh)<sup>12-</sup>, having an exact match with the corresponding calculated spectrum. Tandem mass spectrometry of the molecular ion peak up to MS9 was performed. Complex isotope distributions in each of the mass peaks confirmed the alloy composition. We find the Ag<sub>3</sub>Pd<sub>3</sub>—core to be highly stable. The composition was further supported by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X ray photoelectron spectroscopy (XPS).





MS/MS data of m/z 2839. Repeated MS/MS were done with the most intense fragments closer to the parent ion (marked by grey star in all traces, except the last one). Multiple losses were seen for each case and they are indicated on the arrow. Up to MS³ was achievable with reasonable intensity. Spectra have been shifted vertically for clarify.



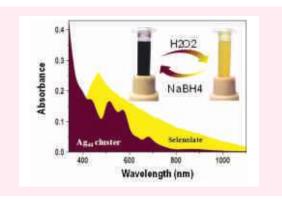
HPLC chromatogram of the crude cluster in acetonitrile at room temperature (30 °C) using the isocratic mode. Flow rate was optimized at 0.25 mL/min. The UV/Nis detector was used for analysis. Three distinct peaks correspond to clusters 1, 2 and 3. Inset: a) UV/Nis spectra of as-synthesized crude (i) & 2 (ii) clusters; inset of inset shows the corresponding photographs of the cluster solutions (marked as i' & ii', respectively). b) HRTEM image of cluster 2 and c) shows the size distribution. A few particles are marked with yellow circles.

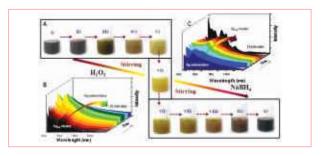




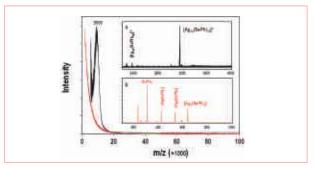
Indranath Chakraborty and T. Pradeep Nanoscale, 6 (2014) 14190-14194 [DOI: 10.1039/C4NR03267E].

The cluster  $Ag_{44}(SePh)_{30}$ , originally prepared from silver selenolate, upon oxidative decomposition by  $H_2O_2$  makes the same cluster back, in an apparently reversible synthesis. Such an unusual phenomenon was not seen for the corresponding thiolate analogues. From several characterization studies such as mass spectrometry, Raman spectroscopy, etc., it has been confirmed that the degraded and as–synthesized selenolates are the same in nature, which leads to the reversible process. Possibility of making clusters from the degraded material makes cluster synthesis economical. This observation makes one consider cluster synthesis to be a reversible chemical process, at least for selenolates.





A: Photographs of the  $Ag_{st}(SePh)_{30}$  cluster solution showing time dependent changes during oxidation (i to vi) and reduction (vi to x). Oxidation was accomplished by  $H_2O_2$  and reduction was by NaBH $_4$ . B: Time dependent UV/Vis spectra during oxidation of  $Ag_{44}$  cluster to form selenolates. C: Time dependent UV/Vis spectra for the reduction of selenolates to form the  $Ag_{44}$  cluster. Each spectrum has been collected at 1 min interval.



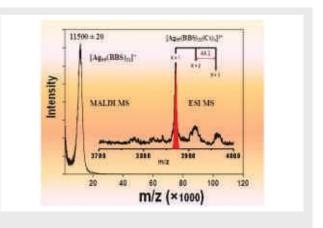
MALDI MS data of  $Ag_{ut}(SePh)_{uv}$  cluster (black trace) and selenlate 1 (red trace). Inset shows the ESI mass spectra of  $Ag_{ut}$  cluster (a) and selenolate 1 (b), respectively. All the peaks are marked.

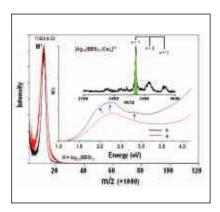




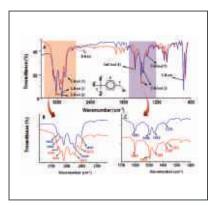
Indranath Chakraborty, Shrabani Mahata, Anuradha Mitra, Goutam De and T. Pradeep Dalton Trans., 43 (2014) 17904–17907 [DOI: 10.1039/c4dt02476a].

TA stable, Ag $_{55}$  cluster protected with 4-(tert-butyl) benzyl mercaptan (BBSH) was synthesized which exhibits two prominent absorption bands with maxima at 2.25 and 2.81 eV. A molecular ion peak at m/z 11,500 $\pm$ 20 in matrix assisted laser desorption ionization mass spectrum (MALDI MS), assigned to Ag $_{55}$ (BBS) $_{31}$  was observed. Electrospray ionization (ESI MS) shows a prominent trication along with higher charged species. An analogous Ag $_{55}$ (PET) $_{31}$  (PET  $\geq$  2-phenylethanthiol, in the thiolate form) was also synthesized under optimized conditions which proves the amenability of this cluster and the synthetic methodology to other ligands.





MS spectra of the as-synthesized crude cluster (red trace) and the purified  $Ag_{\rm so}$  cluster (black trace). Inset shows the UV/Vis spectra for the same (a: the crude cluster, b: purified cluster) plotted as a function of energy. Jacobian-corrected intensities are plotted (details are given in supporting information). The purified cluster shows two prominent bands at 2.25 and 2.81 eV and a weak band at 1.93 eV (marked) whereas the crude one shows only a broad band at 2.28 eV. Inset of inset shows the ESI mass spectrum of the purified cluster (in positive mode) which shows a prominent peak at m/z 3870 corresponding to  $[Ag_{\rm so}(BBS)_{\rm in}CS]^{3+}$ . The corresponding calculated isotope distribution is shown in green.



A: FT-IR spectra of pure BBSH (blue trace) and Ag<sub>ss</sub>(BBS)<sub>31</sub> cluster (red trace). The -SH stretching feature at 2586 cm<sup>-1</sup> in BBSH is marked by a dotted -eircle which is absent in the cluster. Structure of BBSH is shown as an inset in which different IR-active parts are numbered. The expanded views of C-H stretching and bending regions are given as B and C, respectively. For clarity, the spectra have been shifted slightly.



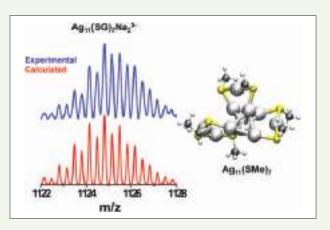




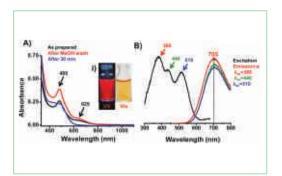


**Ananya Baksi**, M. S. Bootharaju, Xi Chen, Hannu Hakkinen and T. Pradeep *J. Phys. Chem. C*, 118 (2014) 21722–21729 [DOI: 10.1021/jp508124b].

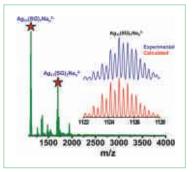
We report a one-step and high yield synthesis of a red luminescent silver cluster with the molecular formula,  $Ag_{11}(SG)_7$  (SG:glutathionate) via reduction of silver ions by sodium borohydride in the presence of the tripeptide, glutathione (GSH). The as-prepared cluster shows prominent absorption features at 485 and 625 nm in its UV-vis absorption spectrum. Aging of the as-prepared cluster solution led to the disappearance of the 625 nm peak, followed by broadening of the 485 nm peak to give three maxima at 487, 437, and 393 nm in its absorption spectrum. These peaks remain unchanged even after polyacrylamide gel electrophoresis (PAGE), where a single band was observed confirming high purity of the cluster formed. Electrospray ionization mass spectrometry (ESI MS) reveal the composition of the cluster to be Ag<sub>11</sub>(SG)<sub>7</sub> with multiple sodium attachments to the ligand to give -3 and -2 charged species. These compositions match well with their calculated isotope patterns. Extensive MS/MS was performed to understand the fragmentation. Potential atomic structures are



discussed based on density functional theory calculations and comparisons for optical absorption spectra using  $Ag_{11}(SCH_3)_7$  as the model. Photoluminescence of this cluster was selectively quenched in the presence of Hg(II) and Cu(II) separately. Detection limit was found to be below their permissible limits in drinking water set by US EPA.  $Ag_{11}(SR)_7$  cluster is reported for the first time.

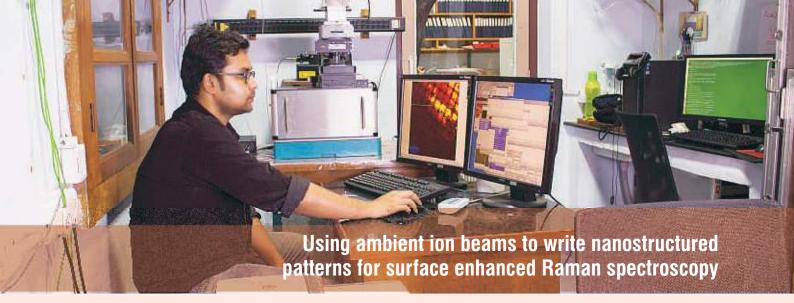


(A) UV—vis absorption spectra of as-synthesized, washed, and aged silver cluster. The clusters show two peaks at 485 and 625 nm (black and red traces) where the 625 nm peak disappeared with time and the other peak broadened into three smaller humps positioned at 393, 437, and 487 nm (blue trace). Photoluminescence spectra are shown in B, where all the three excitation maxima (385, 440, and 510 nm) resulted in a single emission maximum at 705 nm. Photographs of the as-synthesized cluster under UV and visible light are shown in inset (i).



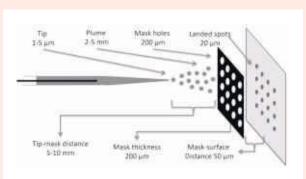
ESI MS of the clusters in the negative ion mode showing -2 and -3 charged species along with some thiolates. Main peaks are marked with the \*symbol. Experimental spectrum (blue trace) is in good agreement with the calculated mass spectrum (red trace) of the species as shown in the inset.



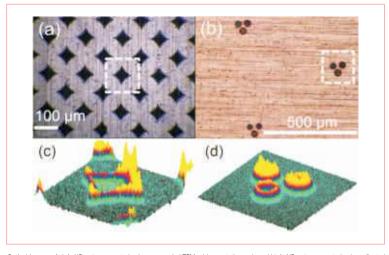


Anyin Li, Zane Baird, Soumabha Bag, **Depanjan Sarkar**, Anupama Prabhath, T. Pradeep and R. Graham Cooks *Angew. Chem. Int. Ed., 53 (2014) 12528-42531 [DOI: 10.1002/anie.201406660].* 

Electrolytic spray deposition was used to pattern surfaces with 2D metallic nanostructures. Spots that contain silver nanoparticles (AgNP) were created by landing solvated silver ions at desired locations using electrically floated masks to focus the metal ions to an area as little as 20 mm in diameter. The AgNPs formed are unprotected and their aggregates can be used for surface-enhanced Raman spectroscopy (SERS). The morphology and SERS activity of the NP structures were controlled by the surface coverage of landed silver ions. The NP structures created could be used as substrates onto which SERS samples were deposited or prepared directly on top of predeposited samples of interest. The evenly distributed hot spots in the micron-sized aggregates had an average SERS enhancement factor of 108. The surfaces showed SERS activity when using lasers of different wavelengths (532, 633, and 785 nm) and were stable in air.



Schematic of the ionization, focusing, and deposition experiment. The drawing is not to scale, but the important dimensions (diameters and distances) are labeled. As a result of the charge induced focusing effect, the spot sizes in the deposited patterns are 10 times smaller than those in the mask.



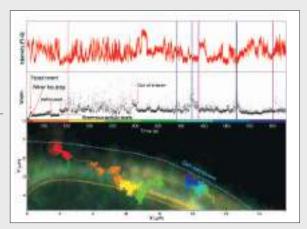
Optical images of a) AgNP patterns created using a grounded TEM grid as a static mask, and b) AgNP patterns created using a floated metal mesh as a mask while moving the copper target discontinuously underneath it. The movement created three-spot patterns visible at a number of locations. Images (c) and (d) are Raman maps of the selected (150150 mm2) regions in (a) and (b), respectively. Raman signals of the dropcast (3 mm diameter circle) crystal violet sample are only observable in the AgNP regions. The Raman intensity in the 1154 to 1204 cm² range was used for imaging. The highest peaks in the images correspond to a Raman signal (1176 cm² peak) of 41870 counts s²-mw1 in (d).



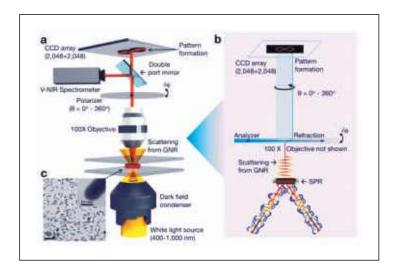


Kamalesh Chaudhari and T. Pradeep Sci. Rep., 4 (2014) 5948 [DOI: 10.1038/srep05948].

Spatiotemporal mapping of the position and orientation of nano-machinery inside complex and dynamic cellular environments is essential for the detailed understanding of many bio-physical processes. For the genuine observation of such biomolecular dynamics with high signal to noise ratio and reduced disturbance from the labeling probes, reduction in the size of nano-bio labels and simplification of techniques for their observation are important. Here we achieve this using polarized dark field scattering micro—spectroscopy (PDFSMS), in its simplest form so that it is deployable in several experiments. We not only locate tiny gold nanorods (GNRs) of size 30 (length) x 10 nm (diameter) inside HEK293 cells but also demonstrate mapping of their in-situ polarization patterns using a novel method. Real time observations of rotatingGNR with DFSMS and PDFSMS are used to resolve in-plane and out-of-plane rotational modes of GNR. We have shown that PDFSMS itself can provide complete information about the state of GNR. A step ahead, we demonstrate the application of PDFSMS to track



three dimensional rotational dynamics of transferrin-eonjugated GNRs inside live HEK293 cells. These first-time observations of the three dimensional intracellular rotational dynamics of tiny GNRs using PDFSMS present a new landmark in single particle scattering spectroscopy.

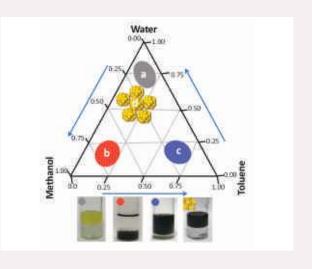




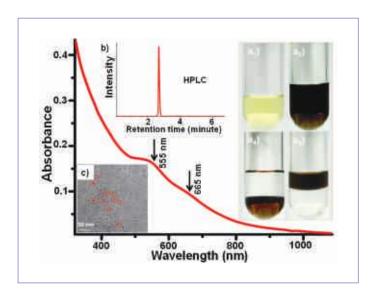


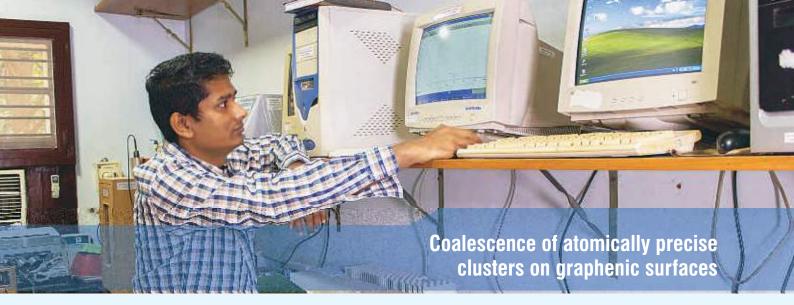
**Atanu Ghosh** and T. Pradeep *Eur. J. Inorg. Chem.*, 2014 (2014) 5271-5275 [DOI: 10.1002/ejic.201402587].

A new strategy to synthesize a diverse array of organic soluble, atomically precise silver clusters has been developed. The technique, based on the miscibility principle of solvents, uses no phase transfer agents and makes various clusters of masses 8.0, 13.4, 22.8, 29.2 and 34.4 kDa by changing the reactant compositions. We have also synthesized the well-known  $Au_{25}(SR)_{18}$  by the same method. Among the silver clusters formed, we have studied the new 13.4 kDa species with unique step-like features in the UV-vis spectrum in detail by mass spectrometry and other analytical techniques. The compound has been assigned as  $Ag_{68}(SR)_{34}$  which is reported for the first time. By time dependent studies, we have shown that the synthetic route follows the bottom up approach. The material forms microcrystals. We hope that the proposed synthetic strategy will extend the area of atomically precise clusters.

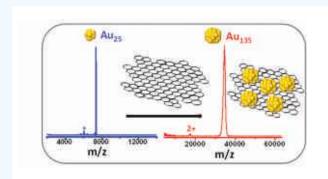






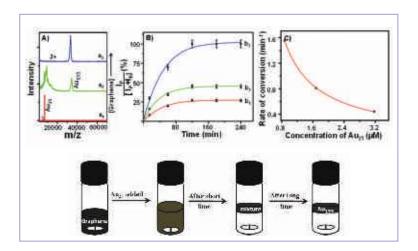


**Atanu Ghosh,** T. Pradeep and Jaydeb Chakrabarti *J. Phys. Chem. C*, 118 (2014) 13959–13964 [DOI: 10.1021/jp503001s].



Interaction of ultra-small metal clusters with surfaces of graphene is important for developing promising future applications of graphenic materials. In the experiment, chemically synthesized reduced graphene oxide (RGO) in water was mixed with  $Au_{\rm 25}SR_{\rm 18}$  (where SR, SCH\_2CH\_2Ph, is a ligand protecting the cluster core) in tetrahydrofuran (THF) and a completely new cluster, larger in mass, was formed at the liquid-liquid interface. Matrix assisted laser desorption ionization mass spectrometry (MALDI MS) of the product attached to RGO show that the peak due to  $Au_{\rm 25}SR_{\rm 18}$  disappears gradually upon reaction and a single sharp peak referred to here as '135 $\pm$ 1 kDa cluster' appears. The composition of the new cluster is very close to the well-known magic cluster,

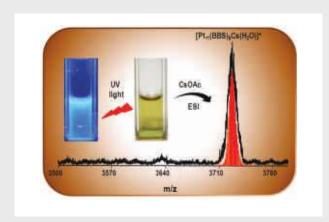
 $Au_{144}SR_{60}$  while the peak maximum is at  $Au_{135}SR_{57}$ . The formation of  $35\pm1$  kDa cluster from the parent  $Au_{25}$  is proposed to be governed by the trapping of smaller clusters in a deep potential well generated at the graphene surface. We theoretically model the active role of the surface in stabilizing the large clusters. Our studies indicate a general mechanism of stabilization of clusters of precise size via the competition between the interfacial fluctuations and the energy scales of interaction of the clusters with the surface. The chemical transformation occurs at deformable surfaces at reduced particle densities which is in good agreement with the theoretical model. Transformations of this kind are important in controlled tuning of particles at graphenic surfaces.



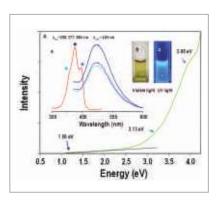




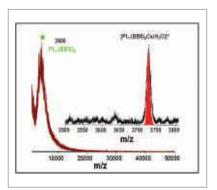
Indranath Chakraborty, Radha Gobinda Bhuin, Shridevi Bhat and T. Pradeep Nanoscale, 6 (2014) 8561-8564 [DOI: 10.1039/C4NR02778G].



A blue luminescent 11-atom platinum cluster showing step-like optical features and absence of plasmon absorption was synthesized. The cluster was purified using high performance liquid chromatography (HPLC). Electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) mass spectrometry (MS) suggest a composition, Pt<sub>11</sub>(BBS)<sub>8</sub> which was confirmed by a range of other experimental tools. The cluster is highly stable and compatible with many organic solvents.



UV/Vis spectrum of the as-synthesized Pt cluster plotted in terms of energy. Jacobian-corrected intensities are plotted. Spectrum shows two humps near 3.13 and 3.98 eV. Inset 'a shows the luminescence spectral data. Three emission spectra, collected at the maxima shown by the excitation spectrum are shown. The excitation spectrum was collected for emission at 450 nm, which is the maximum exhibited in all the emission spectra. Insets 'b' and 'c' are the photographs under visible and UV light, respectively.



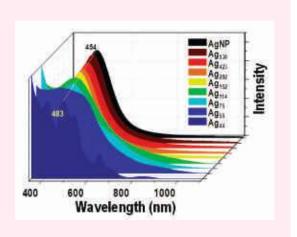
MALDI MS data of the purified cluster. Molecular peak at m/z 3600 was observed at threshold laser power. Inset shows the ESI mass spectrum of the purified cluster. CsOAc was used as ionization enhancer. The red sticks show the calculated spectra for the corresponding composition.

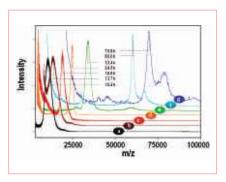




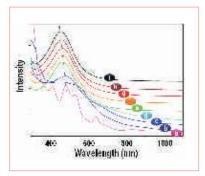
Indranath Chakraborty, Jayanthi Erusappan, Anuradha Govindarajan, K. S. Sugi, Thumu Udayabhaskararao, Atanu Ghosh and T. Pradeep Nanoscale, 6 (2014) 8024–8031 [DOI: 10.1039/c4nr00679h].

We report the systematic appearance of a plasmon-like optical absorption feature in silver clusters protected with 2-phenylethanethiol (PET), 4—flurothiophenol (4-FTP) and (4-(t-butyl)benzenethiol (BBS), as a function of cluster size. A wide range of clusters, namely,  $Ag_{44}(4\text{-FTP})_{30},\ Ag_{55}(PET)_{31},\ \sim Ag_{75}(PET)_{40},\ \sim Ag_{114}(PET)_{46},\ Ag_{152}(PET)_{60},\ \sim Ag_{202}(BBS)_{70},\ \sim Ag_{423}(PET)_{105},\ and\ \sim Ag_{530}(PET)_{100}$  were prepared. The UV/Vis spectra show multiple features up to  $\sim Ag_{114}$  and thereafter from  $Ag_{152}$  onwards, the plasmonic feature corresponding to a single peak at  $\sim 460$  nm evolves, which points to the emergence of metallicity in clusters composed of  $\sim 150$  metal atoms. A minor blue shift in the plasmonic peak was observed as cluster size increased and merged with the spectrum of plasmonic nanoparticles of 4.8 nm diameter, protected with PET. Clusters with different ligands such as 4-FTP and BBS also show this behavior, which suggests that the 'emergence of metallicity' is irrespective of the functionality of the thiol ligand.





MALDI MS spectra (collected in positive mode) of silver clusters prepared in solution. All the clusters were purified through solvent extraction before spotting for MALDI MS studies. Threshold laser fluence was used throughout the experiment to avoid fragmentation. The spectra show a series of clusters with peak maxima ranging from 10.2 to 70.9 k. Almost all of them (except 'f' and 'g' which have some other features with reduced intensity) show sharp single features which confirm the formation of one dominant cluster in each case. The FWHM varied from 1.5 to 5 kDa. The peaks (from bottom to top) were assigned as:  $Ag_{ss}(PET)_{ss}[g]$ ,  $\sim Ag_{ss}(PET)_{ss}[g]$ ,  $\sim Ag_{ss}(PET)_{ss}[g]$ ,  $\sim Ag_{ss}(PET)_{ss}[g]$ . Spectra have been shifted vertically for clarity.

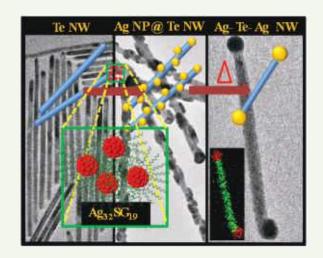


UV/Vis spectra of clusters with wavelength on the x-axis. From bottom to up:  $Ag_{st}$  [a],  $Ag_{ss}$  [b],  $\sim Ag_{rs}$  [c],  $\sim Ag_{rtt}$  [d],  $Ag_{rss}$  [e],  $\sim Ag_{sw}$  [f],  $\sim Ag_{sw}$  [g],  $\sim Ag_{sw}$  [h] and AgNPs [i]. Spectra have been shifted vertically for clarity. The spectra show multiple features up to 'd' (namely, eight bands for  $Ag_{st}$ , two energy bands for  $Ag_{sw}$  and  $Ag_{st}$ , and three for  $Ag_{rs}$ ). But from 'h' to 'i', only a single plasmon–like feature was observed with a small blue shift (i. e. at higher energy).

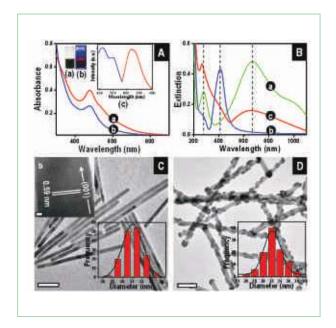




**Anirban Som**, Akshaya Kumar Samal, Thumu Udayabhaskararao, M. S. Bootharaju and T. Pradeep *Chem. Mater., 26 (2014) 3049–3056 [D0I: 10.1021/cm403288w].* 



Reactivity of two different nanosystems of silver, namely nanoparticles and atomically precise clusters, towards 1D tellurium nanowires (NWs) was probed and compared with the reaction of silver ions. While the reaction of nanoparticles and ions led to silver telluride nanowires, a different reactivity was exhibited by clusters which resulted in silver islands at different positions on the Te NWs. These hybrid Ag nodule-decorated Te NWs are sensitive to temperature and they transform to dumb—bell shaped silver-tipped Te NWs upon solution phase annealing. Differences in chemical reactivity of nanoparticles of two different size regimes with nanowires are demonstrated. Synthetic methods of this kind will be useful in creating complex nanostructures which are difficult to be made in the solution phase.





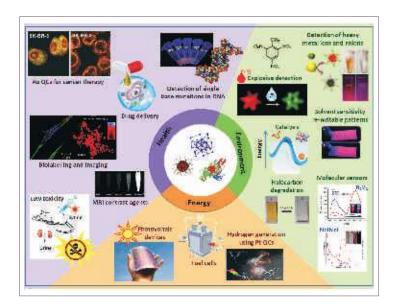


Ammu Mathew and T. Pradeep

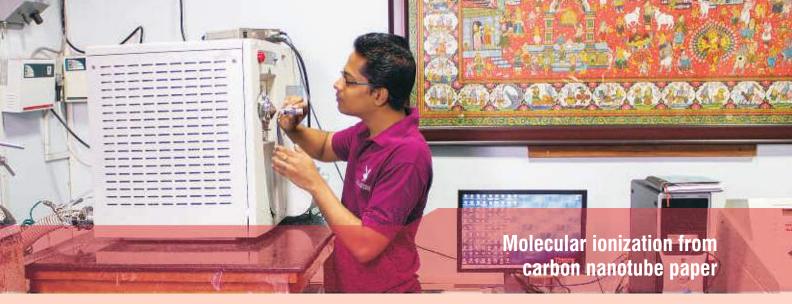
Part. Part. Syst. Charact., 31 (2014) 1017-1053 [DOI: 10.1002/ppsc.201400033].



Sub-nanometer-sized metal clusters, having dimensions between metal atoms and nanoparticles, have attracted tremendous attention in the recent past due to their unique physical and chemical properties. As properties of such materials depend strongly on size, development of synthetic routes that allows precise tuning of the cluster cores with high monodispersity and purity is an area of intense research. Such materials are also interesting owing to their wide variety of applications. Novel sensing strategies based on these materials are emerging. Owing to their extremely small size, low toxicity, and biocompatibility, they are widely studied for biomedical applications. Primary focus of this review is to provide an account of the recent advances in their applications in areas such as environment, energy, and biology. With further experimental and theoretical advances aimed at understanding their novel properties and solving challenges in their synthesis, an almost unlimited field of applications can be foreseen.

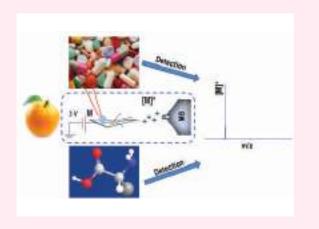


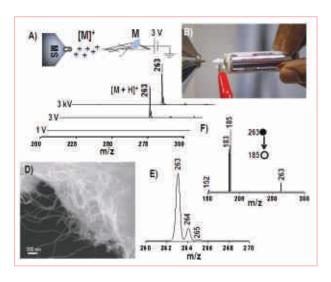




**Rahul Narayanan**, Depanjan Sarkar, R. G. Cooks and T. Pradeep *Angew. Chem. Int. Ed.*, *53* (2014) 5936 –5940 [DOI: 10.1002/anie.201311053].

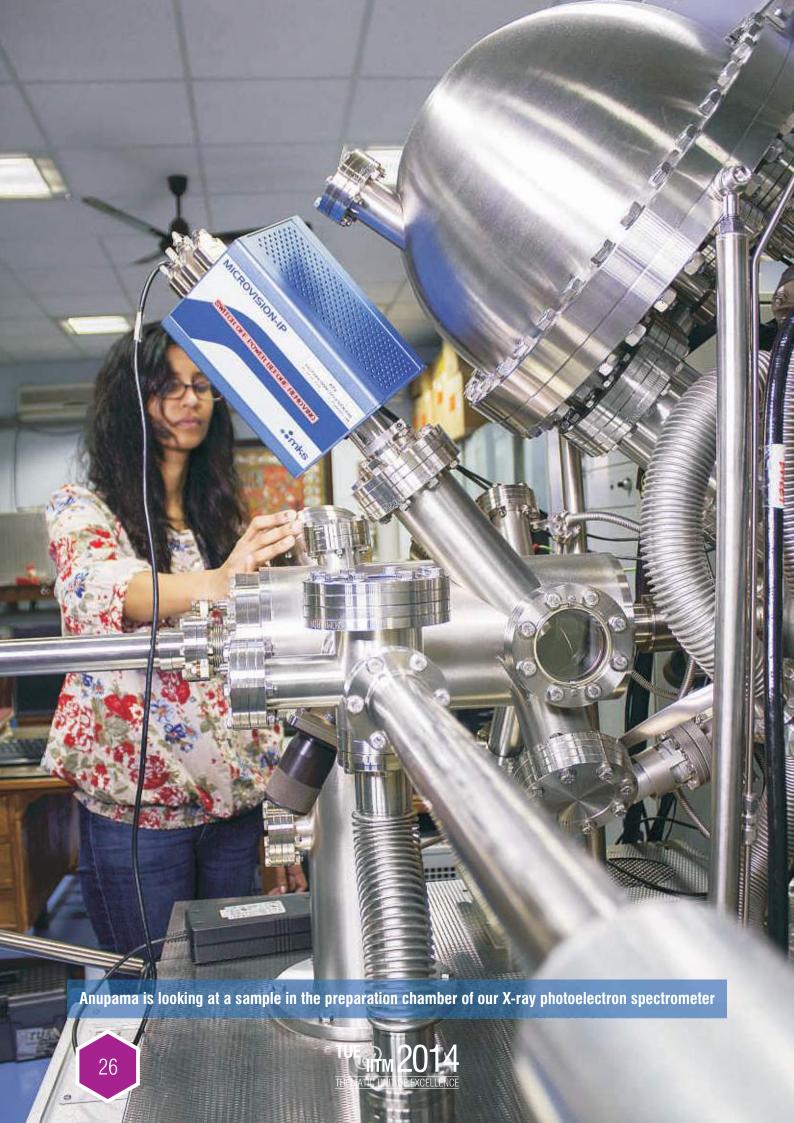
Ambient ionization is achieved by spraying from a carbon nanotube (CNT)-impregnated paper surface under the influence of small voltages ( $\geq 3$  V). Organic molecules give simple high—quality mass spectra without fragmentation in the positive or negative ion modes. Conventional field ionization is ruled out, and it appears that field emission of microdroplets occurs. Microscopic examination of the CNT paper confirms that the nanoscale features at the paper surface are responsible for the high electric fields. Raman spectra imply substantial current flows in the nanotubes. The performance of this analytical method was demonstrated for a range of volatile and nonvolatile compounds and a variety of matrices.

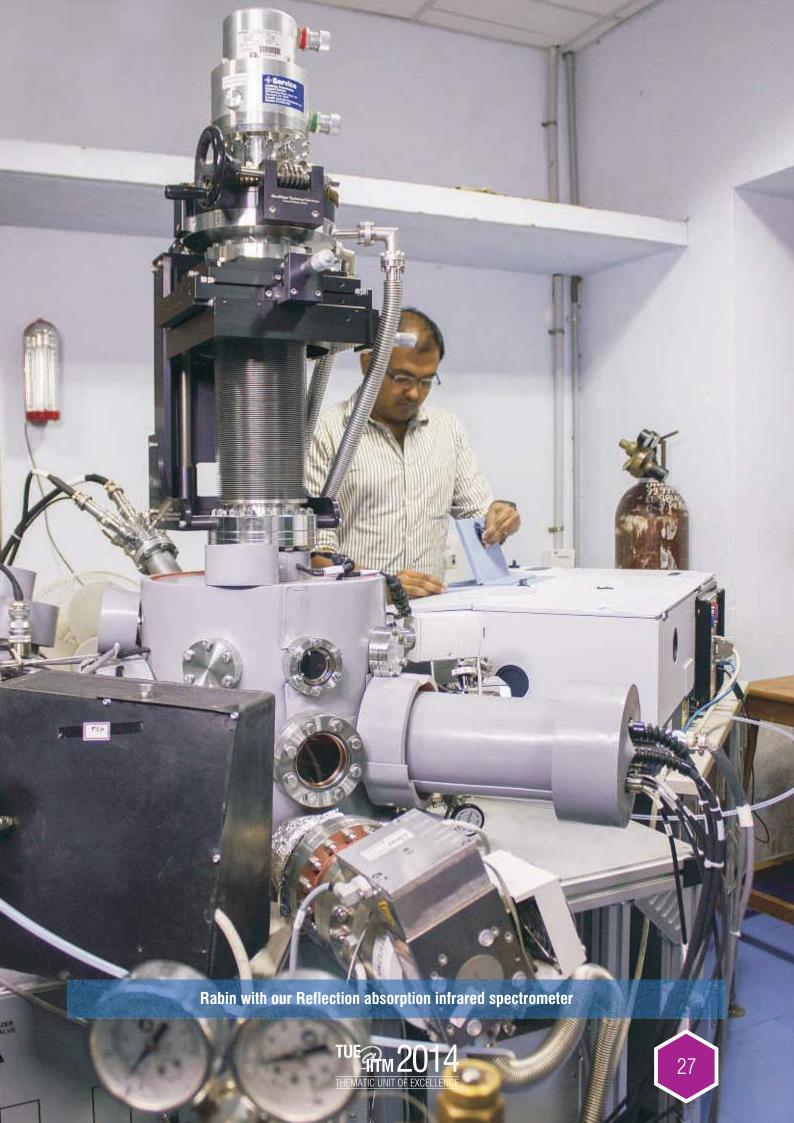




A) Schematic representation of the ionization process from CNT paper. B) Photograph of the ionization source showing paper triangle and battery along with a grounding electrical connection. C) Mass spectra of triphenylphosphine (M) at 3 kV, 3 V, and 1 V from wet CNT paper. D) Field emission scanning electron microscopy (FESEM) image of CNT-eoated paper. E) Isotope distribution of the protonated molecule at 3V. F) MS2 spectrum of the parent ion at m/2 263.



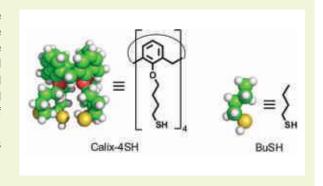


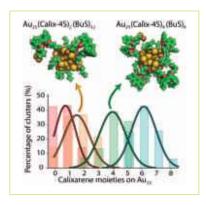


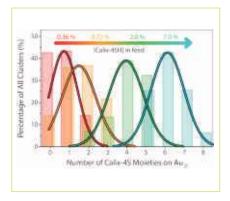


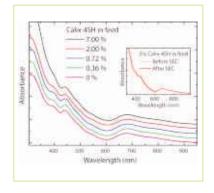
**Jukka Hassinen**, Petri Pulkkinen, Elina O. Kalenius, T. Pradeep, Heikki Tenhu, Hannu J. Häkkinen and Robin H. A. Ras *J. Phys. Chem. Lett.*, 5 (2014) 585–589 [DOI: 10.1021/jz500052h].

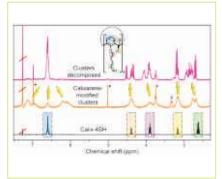
Although various complex, bulky ligands have been used to functionalize plasmonic gold nanoparticles, introducing them to small, atomically precise gold clusters is not trivial. Here, we demonstrate a simple one–pot procedure to synthesize fluorescent magic number  $Au_{25}$  clusters carrying controlled amounts of bulky calix[4]arene functionalities. These clusters are obtained from a synthesis feed containing binary mixtures of tetrathiolated calix[4]arene and 1–butanethiol. By systematic variation of the molar ratio of ligands, clusters carrying one to eight calixarene moieties were obtained. Structural characterization reveals unexpected binding of the calix[4]arenes to the  $Au_{25}$  cluster surface with two or four thiolates per moiety.



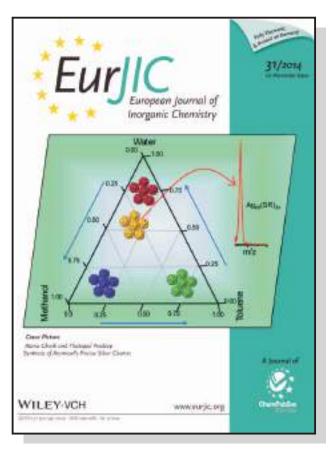


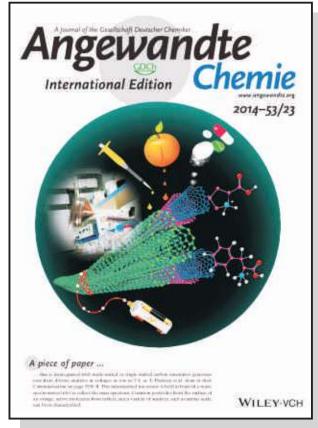
















# AMRIT



Presence of arsenic and iron in drinking water affects water quality significantly. Damage to human health due to the presence of arsenic in water is well-known. With the advent of nanotechnology, it is possible to address contaminants such as arsenic at affordable cost. A product, aptly titled AMRIT is presented here. AMRIT uses a composition based on iron oxyhydroxide to remove arsenic from water.

What is means in terms of performance and affordability? AMRIT composition can handled up to an input load of 5 ppm of arsenic and bring the output level below the typical detection limit (<1ppb). Complition is at least 5-6 times more efficient than any other adsorbant available currently. Since the contact time required for removal is fairly low (less than 1min), the composition is used in the size of 0.2 mm, thereby offering negligible pressure drop. This helps from several aspects: treatment cost reduces, filtration unit becomes smaller, filtration unit can be operated with minimum pressure, easily maintainable by local community and reduced sludge quantity.



The nanocomposite material



The arsenic filter assembly



#### InnoNano Research Pvt. Ltd

Registered Office

ce: Ady Em

7/30, II Main Road, Kastuibai Nagar, Adyar, Chennai 600020 HSB 270, IIT Madras, Chennai 600036 Email: udhayasankarm@live.com Phone: +91 9789037951

Parameter	Input water quantity	Output water quality
Turbidity	Up to 200 NTU	1NTU (WHO norm: 5 NTU)
Iron	Up to 15 ppm	<0.3 ppm (WHO and BIS norms)
Arsenic	Up to 5 ppm	<0.010 ppm (WHO norm:<0.05 ppm)
Allowed TDS	Upto 2000 ppm	No reduction from input
pH	6 to 9 7 to 8	

Product Name AMRIT —Arsenic Removal by Indian Technology
Product description An affordable domestic and community scale water

purification unit for iron and arsenic removal **Technical details** Iron and turbidity removal by physical filtration,

arsenic removal by adsorption **Product elements**One input water storage tank, one output water storage

tank kept on a stand along with purification cartridges

Material of construction Food grade polypropylene for plastic components.
Food grade ingredient for adsorbents
Mode of operation Manual pouring of water or through a pump, gravity

flow to the output tank

Electricity requirement No electricity required for operation, electricity may be used to operate the pump

Feed water quality
Turbidity: up to 200 NTU
Iron: up to 15 ppm
Arsenic: up to 5 ppm

Output water quality

Allowed TDS: up to 2000 rpm

Turbidity: 1 NTU (WHO and BIS norms: 5 NTU)

Iron: < 0.3 ppm (WHO and BIS norms)

Arsenic:<0.010 ppm (WHO norm, BIS norm: <0.005 ppm)

Arsenic: < U.010 ppm (WHU norm, Bis norm: < U.005 ppm)

Rate of water filtration 50-400 mL/min (domestic model), 100-500 L/h (community model). 500 L/h (online model)

Replacement frequency Yearly for arsenic removal media, 3-5 years for turbidity/iron

removal media

Expected life of the unit
Adaptability
Adaptability
removal media
15 years
Easy integration

Easy integration with existing water purification technologies

and products

#### Amrit during field trials

































## **Conferences conducted**



One day discussion meeting on Imaging in Mass Spectrometry, January 17, 2014, IC & SR, IIT Madras.



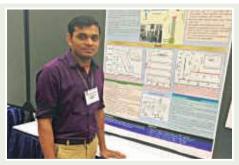
International discussion meeting on Low Energy Ion Scattering at Molecular Solids, January 18-19, 2014, IC & SR, IIT Madras.



Second international water conference on Emerging Technologies on Clean Drinking Water, October 23-24, 2014, IC & SR, IIT Madras.

### Students' Poster presentations





Radha Gobinda Bhuin@ 62nd ASMS Conference on Mass Spectrometry & Allied Topics-2014



Indranath Chakraborty & Anirbon Som@ICONSAT-2014



Rabin Rajan J M@IMSC-2014



Indranath Chakraborty@7<sup>th</sup> Bangalore India Nano-2014



Ananya Baksi@GRC, Noble Metal Nanoparticle Mount Holyoke College-2014



Rahul Narayanan@7<sup>th</sup> Bangalore India Nano -2014

- 1. 'Noble metal clusters in protein templates: Mass spectrometric understanding of cluster growth' by Ananya Baksi (Gordon Research Conference on Noble Metal Nanoparticle Mount Holyoke College, South Hadley, MA, USA).
- 2. 'Atomically precise silver clusters as new SERS substrates' by Indranath Chakraborty (Gordon Research Conference on Noble Metal Nanoparticle, Mount Holyoke College, South Hadley MA LISA)
- 3. 'Heterojunction double dumb-bell Ag<sub>z</sub>Te-Te-Ag<sub>z</sub>Te nanowires' by Anirban Som (International Conference on Nanoscience and Technology, ICONSAT 2014, Chandigarh, India).
- 4. 'Atomically precise silver clusters as new SERS substrates' by Indranath Chakraborty (International Conference on Nanoscience and Technology, ICONSAT 2014, Chandigarh, India).
- 5. 'Distinguishing amorphous and crystalline ice by ultralow energy collisions of reactive ions' by Radha Gobinda Bhuin (62nd ASMS Conference on Mass Spectrometry & Allied Topics, Baltimore, USA).
- 6. 'Development of ultralow energy (1 40 eV) ion scattering spectrometry coupled with reflection absorption infrared spectroscopy and temperature programmed desorption for the investigation of molecular solids' by Rabin Rajan J M (International Mass Spectrometry Conference, IMSC -2014, Geneva, Switzerland).
- $7. \quad \text{`Noble metal clusters in protein templates: } Understanding of cluster growth' by Ananya Baksi (7th Bangalore India Nano, Bangalore, India).$
- 8. 'Atomically precise silver clusters as new SERS substrates' by Indranath Chakraborty (7th Bangalore India Nano, Bangalore, India).
- 9. 'Molecular ionization from carbon nanotube paper' by Rahul Narayanan, (7th Bangalore India Nano, Bangalore, India).
- 10. 'Antimicrobial silver: An unprecedented anion effect' by Swathy Ravindran (2nd International Conference on Emerging Technologies for Clean Water, IIT Madras).
- 11. 'Confined metastable nanoscale 2 +ine ferrihydrite for affordable point -of -use arsenic free drinking water' by Anil Kumar (2nd International Conference on Emerging Technologies for Clean Water, IIT Madras).

#### Guests@our lab in 2014

- Dr. T. N. T. K. V. Prasad and A. Padma Raju, Vice Chancellor of Acharya N.G. Ranga Agricultural University, Hyderabad, January 08, 2014.
- Dr. Revathi Rajgopal & Dr. Merry Terry, Assistant Professor, Stella Maris College, Chennai, January 09, 2014.
- Prof. R. G. Cooks, Henry B. Hass Distinguished Professor, Purdue University, West Lafayette, Indiana, USA, January 14, 2014.
- 4. Dr. Demian R. Ifa, Assistant Professor, York University, Toronto, Canada, January 14, 2014.
- 5. Mr. Kevin Kuchta, Senior Scientist, Extrel CMS, Pittsburg, Pennsylvania, USA, January 16, 2014.
- Prof. Vicki Wysocki, Dept. of Chemistry and Biochemistry, Ohio State University, Columbus, Ohio, USA, January 18, 2014.
- 7. Dr. Helen Fraser, Faculty, Astronomy Research group, Open University, UK, January 18, 2014.
- Prof. Postawa Zbigniew, Institute of Physics, Jagiellonian University, Krakow, Poland, January 18, 2014.
- 9. Prof. Heon Kang, Dept. of Chemistry, Seoul National University, South Korea, January 18, 2014.
- 10. Prof. Steven Bernasek, Dept. of Chemistry, Princeton University, New Jersey, January 18, 2014.
- Dr. Varun Sheel, Associate Professor, Space & Atmospheric Science Division, PRL Ahmedabad, January 18, 2014.
- 12. Prof. Shikha Varma, Institute of Physics, Bhubaneswar, January 18, 2014.
- 13. Dr. R. Mukhopadhyay, Solid State Physics Division, BARC, Mumbai, January 18, 2014.
- 14. Prof. Amalendu Chandra, Dept. of Chemistry, IIT Kanpur, January 18, 2014.
- Prof. C. N. R. Rao, National Research Professor and Honorary President, JNCASR, Bangalore, January 21, 2014.
- 16. Prof. P M Ajayan, Materials Science and Nano Engineering Department, Rice University, Houston, Texas, USA, February 11, 2014 and April 25, 2014.
- 17. Dr. Bhalamurugan Sivaraman, Space & Atmospheric Science Division, PRL Ahmedabad, March 08, 2014.
- 18. Prof. Dr. Ron M. A. Heeren, FOM-AMOLF, Utrecht University, Netherlands, March 13, 2014.
- Prof. Pushan Ayyub, Dept. of Condensed Matter Physics and Materials Science, TIFR, Mumbai, March 20, 2014.
- 20. Mr. J. I. Sevak, Product Safety Manager Heubach India, March 25, 2014
- Dr. T. Devasena, Associate Professor, Centre for Nanoscience & Technology, Anna University, Chennai, March 28, 2014.
- 22. Prof. Peter Hodgson, Director, Institute for Frontier Materials, Deakin University, Australia, April 01,
- 23. Prof. Lingxue Kong, Deakin University, Australia, April 01, 2014
- 24. Dr. Arindam Ghosh, Associate Professor, Dept. of Physics, IISc, Bangalore, April 04, 2014.
- 25. Prof. Jaydeb Chakrabarti, SN Bose National Centre for Basic Sciences, Kolkata, April 07, 2014.
- 26. Dr. T. N. V. V. Rao, Regional Head, Underwriters Laboratories Inc, Bangalore, April 09, 2014.
- 27. Dr. Sushanta K Mitra and Dr. S. K. G. Naga, University of Alberta, Canada, April 11, 2014.
- Mr. Prithviraj and Mr. Vijay, Karnataka State Council for Science and Technology, Bangalore, April 12, 2014.
- 29. Mr. K Jayadev, Nano Digest, April 17, 2014.
- 30. Prof. B. Neppolian, SRM University, Chennai, April 22, 2014.
- 31. Mr. Sriram Tavanikanti IAS, Executive Director, IRDA, Hyderabad, April 23, 2014.
- 32. Dr. Sukhendhu Mandal, Assistant Professor, IISER Trivandrum, June 10, 2014.
- 33. Prof. Shekar Mande, Director, National Centre for Cell Science, Pune, June 10, 2014.
- Dr. Dhirendra Bahadur, Dept. of Metallurgical Engineering & Materials Science, IIT Bombay, Mumbai, June 21, 2014.
- Prof. Chandrabhas Narayana, Chemistry and Physics of Materials Unit, JNCASR, Bangalore, July 09, 2014.



Prof. D. Chatterji



Prof. C.N.R. Rao



Prof. Ramakrishna Ramaswamy



Participants of the International Conference on Emerging Technologies for Clean Water

- 36. Dr. Rajnish Kumar, Chemical Engineering and Process Development, NCL Pune, July 10, 2014.
- Prof. Krishnan Balasubramaian, Dept. of Mathematics & Computer Science, California State University, Hayward, California, USA, July 09, 2014.
- 38. Mr. Ajau Garg, Saint Gobain research, July 25, 2014.
- 39. Mr. Rajesh Parishwad, Indian Representative RSC, August 12, 2014.
- 40. Mr. T. S. Tamizharasan, Elgi Ultra, August 16, 2014.
- 41. Dr. K. Krishnakumar, Ms. Nithya and team from Sankar Nethralaya, Chennai, August 27, 2014.
- 42. Dr. Ujjal K. Gautam, Associate Professor, JNCASR, Bangalore, September 09, 2014.
- 43. Prof. Jim Mayhew, Rose Hulman Institute of Technology, Indiana, September 11, 2014.
- 44. Mr. Virat Markendiya, ACS News Reporter, September 18, 2014.
- 45. Prof. Sankaran Subramanian, Former professor, Dept. of Chemistry, IIT Madras, September 19, 2014.
- 46. Dr. Rajnish Kumar, Chemical Engineering and Process Development, NCL Pune, September 26, 2014.
- 47. Prof. Jagat Kanwar, Deakin University, Australia, October 02, 2014.
- 48. Prof. Kankan Bhattacharya, Dept. of Physical Chemistry, IACS Kolkata, October 07, 2014.
- 49. Dr. V. Mohan, Mohan Diabetes Institute, Chennai, October 09, 2014.
- Prof. Jane Catherine, Analytical and Environment division, University of Johannesburg, South Africa, October 21, 2014.
- 51. Prof. Arup Sengupta, Dept. of Civil and Environmental Engineering, Fritz Engineering Laboratory, Lehigh University, Bethlehem, October 22, 2014.
- 52. Prof. Maria Aparecida Carvalho de Maedeiros, State University of Campinas, Brazil, October 22, 2014.
- 53. Dr. Zach Dovey, Fellow in Robotic Urology at OLV Clinic, Aalst, Belgium, October 22, 2014.
- 54. Prof. Franz Giessibl, University of Regensburg, Germany, November 03, 2014.
- 55. Dr. Rajnish Kumar, Chemical Engineering and Process Development, NCL Pune, November 04, 2014.
- 56. Dr. M. Balasubramnaim, Mohan Diabetes Research Foundation, November 05, 2014.
- $57. \quad \text{Prof. Ramakrishna Ramaswamy, Vice chancellor, University of Hyderabad, November 07, 2014.}$
- 58. Prof. Dipankar Chatterji, President, Indian Academy of Sciences, Bangalore, November 07, 2014.
- 59. Mr. Mitch Daniels, Purdue University President, Indiana, USA and team, November 07, 2014.
- Dr. Suresh Garimella, Executive Vice President for Research and Partnerships, Purdue University, Indiana, USA, November 07, 2014.
- 61. Mr. Phillip A. Min, American Consulate General, Chennai, November 07, 2014.
- 62. Prof. Pooya Rezai, Dept. of Mechanical Engineering, York university, Canada, November 10, 2014.
- Dr. Anilkumar. T. Dandekar, Assistant Professor of Agricultural, Engineering College of Agriculture, Bheemrayanagudi, Shahapur, Yadgiri, Karnataka, November 12, 2014.
- 64. Prof. V. Adaikkalam, Centre for Biotechnology, Anna University, November 21, 2014.
- 65. Dr. Samir Kumar Pal, S.N. Bose National Centre for Basic Science, Kolkata, December 04, 2014.
- 66. Dr. Rupinder Kanwar, Associate Professor, Deakin University, Australia, December 11, 2014.
- 67. Prof. Subodh Gupta, Cenovus Energy, Alberta, Canada, December 11, 2014.
- 68. Prof. Carlo Montemagno, Ingenuity Labs, University of Alberta, Canada, December 18, 2014.
- Mr. Arindam Phani, Dept. of Chemical and Materials, University of Alberta, Canada, December 18, 2014.
- 70. Prof. Sushanth Mitra, York University, Toronto, Canada, December 18, 2014.
- 71. Dr. Nithin S. Kale, ISENS, IIT Bombay, December 20, 2014.
- Mr. Kapil Bargeja, Chief Executive Officer, Nano Sniff Technologies Pvt. Ltd, IIT Mumbai, December 2014.
- Dr. C. G. Krishnadas Nair, Former chairman HAL, Honorary President, Society of Indian Aerospace Technologies & Industries (SIATI), December 26, 2014.
- 74. Prof. Madhu Viswanathan, University of Illinois, Urbana Champaign, December 28, 2014.
- 75. Dr. C. Subramaniam, Dept. of Chemistry, IIT Bombay, December 29, 2014.



Prof.CNR Rao with our group



Mr. Mitch Daniels, Prof. Suresh Garimella, Prof. Philip A. Min along with the IITM team



Prof. Ron M.A. Heeren



Dr. Zach Dovey

#### **Existing equipment and infrastructure**

- (1) PerkinElmer Lambda 25 UV Vis Spectrometer with temperature controller
- (2) PerkinElmer Lambda 25 UV-Vis Spectrometer
- (3) BalzerThermoStar Mass Spectrometer
- (4) PerkinElmer Spectrum One FT-IR Spectrometer and Pelletizer
- (5) Horiba Jobin Yvon Nano Log Spectrofluorometer
- (6) MALDI TOF MS Model: Voyager-DE PRO Bio-spectrometry with Workstation-Applied Bio-systems
- (7) High Resolution Transmission Electron Microscope (HRTEM) with EDAX (Jeol JEM 3010)
- (8) 3200 Q TRAP LC/MS/MS
- (9) Scanning Electron Microscope (FEI QUANTA 200) with EDAX
- (10) XPS-UPS-TPD (Omicron NanoTechnology)
- (11) Low energy Ion Scattering Spectrometer (EXTREL CMS)
- (12) WITec GmbH Confocal Raman Microscope (CRM -Alpha300 S) with Atomic Force Microscopy (AFM) and Scanning Near-field Optical Microscopy (SNOM) (lasers: 532, 633 nm) and Dark-field condenser attachment
- (13) PerkinElmer Gas Chromatograph Mass Spectrometer (GC-MS) Model: Clarus 600 C
- (14) Thermo Scientific Ion trap LTQ-XL Mass spectrometer with Desorption Electrospray Ionization (DESI) setup
- (15) CytoViva Hyperspectral Imaging System
- (16) Low energy Ion Scattering (Vera SpecTM) MS-RAIRS (Bruker Optics, VERTEX 70) TPD with Ion Gun from Kimball Physics (IGPS-4016B)
- (17) Leica Ultramicrotome
- (18) Ball Mill Grinder (Retsch, MM 200)
- (19) Kubota Refrigerated Centrifuge
- (20) Electrochemical Analyzer/Workstation (CHI600E, CH Instruments, Inc.)
- (21) Shimadzu Prominence HPLC system with accessories
- (22) Isothermal Microcalorimeter (MicrocaliTC 200)
- (23) Inductively Coupled Plasma Mass Spectrometry (ICPMS), PerkinElmer, NexION 300X
- (24) Metrohm Ion Chromatograph with Auto Sampler and Accessories (883 Basic IC Plus)
- (25) Eyela Rapid Sythesizer (PPS-2510-CE)
- (26) Rotavapor (BUCHI, R-200)
- (27) Eyela Freeze dryer (FDU-1200)
- (28) Ultrasonic Processor (Sonics Vibra Cell)
- (29) Mayura Gas Chromatography with Autosampler (Auto GC -1100)
- $(30) \quad \text{Needle Based Electrospinning Machine M No: ESPIN Nano-Physics Instruments Co, Chennai} \\$
- (31) Biocare Deep Freezer (800Cand 200C)
- $(32) \quad \text{Millipore Milli Q Laboratory Grade Water Purification/Deioniser System Model No: Integral 3}$
- (33) Mettler Toledo Digital Weighing Balance (AB 104-S)
- (34) CAS Digital Weighing Balance
- (35) Cintex Precision Hot Air Oven with digital display
- (36) REMI Laboratory Centrifuge (R-8 C)
- (37) EyelaRotary Evaporator (N-1200 BV-W)
- (38) EyelaFreeze Dryer (FDU 1200)
- (39) Eyela Personal Organic Synthesizer with Accessories (PPS-2511)
- (40) Leica Fluorescence Microscope with High resolution Digital Camera (DMI 3000 B)
- (41) Leica Inverted Phase Contrast LED Microscope (DMIL LED)
- (42) Anton Paar Microwave Sample Digestor (Microwave 3000)
- (43) ElmarcoNanospider Needleless Electrospinning Machine (NS Lab –200).
- (44) EutechMutiparameterMonitor for pH/Cond/Disso Oxy/ORP (Cyberscan PCD-650)
- (45) Medimeas Semi-Automatic Rotary Microtome (MRM-\$T)
- (46) Medimeas Full Automatic Cryocut Microtome (MCM-AT)
- (47) Remi Centrifuge (CM-12 Plus)
- (48) Sigma Hot Air Oven
- $(49) \quad \hbox{Shimadzu Digital Weighing Balance Model No: AY-220}$
- (50) Elico TDS Analyzer (CM  $\pm$  83 EC)
- (51) Sigma Scientific Rotary Shaker
- (52) Scigenics Biotech Orbital Shaker (Orbitek)





## New equipment and infrastructure added in 2014

- (1) Cryoscientific 4°C Laboratory Refrigerator
- (2) Shimadzu Nexera Advanced UHPLC system with Softa300S ELSD, Fluoresence and PDA Detector
- (3) Shimadzu Prominence Preparative -eum -analytical HPLC system with UV-VIS Detector
- (4) Programmable Spin Coating system Model: Spin NGX –Apex Instruments
- (5) Plimmer Alpha Capacitance Deionization (CDI) Water purification unit
- (6) Pfeiffer Vacuum HiCube 80 Eco Turbo molecular dual vacuum pump
- (7) ESCO Biological Safety cabinet (Installation pending)
- (8) Nabertherm 15000C Tube furnace
- (9) Kiethley 2611B Source/Measure meter





#### **Alumni News**

- M. S. Bootharaju joined KAUST, Saudi Arabia as a Post-Đoctoral Fellow
- C. Subramaniam joined Department of Chemistry, IIT Bombay as an Assistant Professor
- C. Subramaniam received the Young Science Gold Award from IUMRS
- T. S. Sreeprasad joined Rice University as a senior Post-doctoral fellow
- P.L. Xavier joined Max Plank Institute for Structure and Dynamics of Matter as a PhD student
- Sreya Sarkar joined Purdue University, Indiana as a PhD student

#### **Graduation**

**Soumabha Bag,** Department of Chemistry, IIT Madras, 2014 Low energy ion scattering at molecular solids

**M.S. Bootharaju,** Department of Chemistry, IIT Madras, 2014 Noble metal nanomaterials for water purification

**Robin John,** Department of Physics, IIT Madras, 2014 Investigations of the formation and inter-conversion of low dimensional carbon systems

**Kamalesh Chaudhari,** Department of Biotechnology, IIT Madras, 2014 (to be awarded in 2015) Single particle investigation of nano-bio interactions

**Ammu Mathew,** Department of Chemistry, IIT Madras, 2014 (to be awarded in 2015) Functional noble metal clusters: Synthesis, surface chemistry and applications



### Foreign students' visit



Anyin Li, Purdue University, USA and Jukka Hassinen, Aalto University, Finland



Veronique Raika Many, Paris Diderot University, France with Jessy, Swathy and Anuradha



Anyin Li with Radha Gobinda and Rabin

## Students' visit overseas

































- (1) **Avijit Baidya,** Aalto university, Finland, Prof. Robin Ras, 24th June 47th Sept, 2014
- (2) **Ananya Baksi**, Ohio State University, U.S.A Prof. Vicki Wyscoki, 21st-28th June, 2014
- (3) Indranath Chakraborty, University of Toledo, U.S.A-Prof. Terry Bigioni, June, 2014
- (4) **Kamalesh Chaudhari,** Energy, Environment and Sustainability Lab, SNU, Korea –Prof. Kim, Sung Jae, 1st –28th February, 2014
- (5) **Radha Gobinda Bhuin,** National Synchrotron Radiation Research center, Taiwan
  —Prof. B. M. Cheng, 4th -11th August, 2014
  Seoul National University, South Korea —Prof. H. Kang, 12th August -10th October, 2014



### **Awards / Recognitions**



#### T. Pradeep:

Member, Editorial Board, Chemistry-An Asian Journal

Member, Advisory Board, Nanoscale

Fellow of the Royal Society of Chemistry (FRSC).

Elected fellow of the Indian National Academy of Engineering

Associate editor, ACS Sustainable Chemistry & Engineering

#### Students:

Indranath Chakraborty - Malhotra Wiekfield Award

Indranath Chakraborty —best poster award in ICONSAT 2014, Chandigarh

Ananya Baksi —best poster award in Bangalore Nano-2014

**Anil Kumar, Prakash and Ramesh**—best exhibitor award for the year 2014 in the category of Innovative Display which was presented by Department of Information Technology, Biotechnology and Science & Technology, Government of Karnataka and Vision Group on Nanotechnology







#### Talks and lectures by Prof. T. Pradeep

- 1. Molecular ionization from carbon nanotube paper, International discussion meeting on low energy ion scattering at molecular solids, January 18-49, 2014.
- 2. Infinite possibilities of the infinitesimal!, Karnataka Science Congress, Gulbarga, January 30-31, 2014.
- 3. Biopolymer reinforced synthetic granular nanocomposites for affordable point-of-use water purification, Environmental Impact and Hazard Identification of Engineered Nanomaterials, Indo-UK seminar, Ahmedabad University, February 24-26, 2014.
- 4. Affordable clean water using nanotechnology, Nano for Young, ICONSAT 2014, Punjab University, Chandigarh, March 4, 2014.
- 5. Molecular Ionization from Carbon Nanotube Paper, Indian Society for Mass Spectrometry Workshop, Parwanoo, March 10, 2014.
- 6. Atomically precise clusters of noble metals, Two-Đay Workshop on Nano Science and Technology, IIT Madras, April 4-5, 2014.
- 7. Clusters, ions and advanced mass spectrometry, University of Hyderabad, April 28, 2014.
- 8. Affordable clean water using nanomaterials, Department of Applied Chemistry, University of Johannesburg, May 9, 2014.
- 9. Affordable point-of-use drinking water purification using nanomaterials, As2014, Argentina May 12 46, 2014.
- $10. \quad \text{A new form of ionization, International discussion meeting on Advanced materials: current trends \& future prospects, Manali, May 28-June 1, 2014.}$
- 11. Mass spectrometry and materials science, Advances in spectroscopy, IIT Madras June 20, 2014.
- 12. Affordable point-of-use drinking water purification using nanomaterials, Professor CNR Rao 80th Birthday Symposium, Chemistry Centre, Burlington House, London, June 23 24, 2014.
- 13. Affordable point-of-use drinking water purification using nanomaterials, University of Alberta, July 3, 2014.
- 14. Affordable point-of-use drinking water purification using nanomaterials, IIT Bombay, July 11, 2014.
- 15. Introduction to Nanoscience and Nanotechnology, Apollo Tyres Ltd., July 12, 2014.
- 16. Affordable point-of-use drinking water purification using nanomaterials, Amrita University, July 24, 2014.
- 17. Nanomaterials and emerging frontiers of mass spectrometry, Stella Maris College, Chennai, July 25, 2014.
- 18. Nanomaterials and emerging frontiers of mass spectrometry, IIST, Thiruvananthapuram, July 28, 2014.
- 19. A century of chemistry!, Inaugural Lecture of the Integrated Interdisciplinary Master of Science Program, IIRBS, M. G. University, Kottayam, August 19, 2014.
- 20. Luminescent gold molecules, IIT Madras, August 23, 2014.
- 21. Metals...not yet, SN College for Women, Kollam, September 29, 2014.
- 22. New ways of ambient ionization, JNC Conference on Chemistry of Materials, Thiruvananthapuram, October 11 -43, 2014.
- 23. Affordable point of use drinking water purification using nanomaterials, Plenary talk at Asia NANO 2014, Jeju, Korea, October 26-29, 2014.
- 24. New ways of ambient ionization, Department of Chemistry, Seoul National University, Korea, October 29, 2014.
- 25. Drinking water purification for tomorrow, National Academy of Sciences 3rd Policy Support Brainstorming on Safe Water and Sanitation, Allahabad, November 18–20, 2014.
- 26. New ways of ambient ionization for plant sciences, Department of Plant Biology & Biotechnology, Loyola College, Chennai, November 26, 2014.
- 27. New ways of ambient ionization, 5th DAE-BRNS Interdisciplinary Symposium on Materials Chemistry, BARC, Mumbai, December 9-43, 2014.
- 28. Affordable point-of-use water purification using nanomaterials, INAE Annual Convention, Jaipur, December 12-43, 2014.
- 29. A century of chemistry!, Science Talent Enrichment Programme (STEP), IISER Thiruvananthapuram, Dec 15-49, 2014.

# Prof. T. Pradeep's visit





With Prof. Jim Heath, March 4, 2014



With Marc Benhamon, Argentina, May 16, 2014



With Bhekie Mamba, Johannesburg Airport, May 19, 2014



With Ashutosh Sharma, Suresh Das, Milan Sanyal and K. Vijayamohanan, Manali, May 30, 2014



With Dr. K. Vijayamohanan and Anjali, Rohtang Pass, May 30, 2014



With Ashok Ganguli, Ajay Sood, C.N.R. Rao and Goutam De



With Sourav Pal, Manali



With Dr. P. B. Salim, District Magistrate, Nadia Dist., West Bengal, June 18, 2014



With the District Magistrate, Murshidabad Dist., W.B., June 18, 2014



With Anshup and Praveen Poddar, At an arsenic plant, WB., June 19, 2014



@Royal Society of Chemistry, June 23, 2014



With Prof. H. Rosky, Royal Society of Chemistry, June 24, 2014



@ Cardiff University, UK, June 26, 2014



With Carlo Montemagno, University of Alberta, July 2, 2014



With Thomas Thundat, University of Alberta, July 3, 2014



With Dr. Baldev Raj during INAE annual meeting, December 13, 2014

#### **Patents**



- - T. Pradeep, Depanjan Sarkar, M. K. Mahita, Anirban Som, R. Graham Cooks, Anyin Li, 6669/CHE/2014, filed on December 29, 2014.
- Method of extraction of silver by glucose,
  - T. Pradeep, Ananya Baksi, Mounika Gandi, Swathi Chaudhari, Soumabha Bag, 6730/CHE/2014, filed on December 30, 2014.
- Method for accumulation of silver by rice and possible metal extraction by agriculture,
  - T. Pradeep, Soujit Sengupta, Ananya Baksi, Debal Deb, 6846/CHE/2014, filed on December 31, 2014.

### **Technology development**

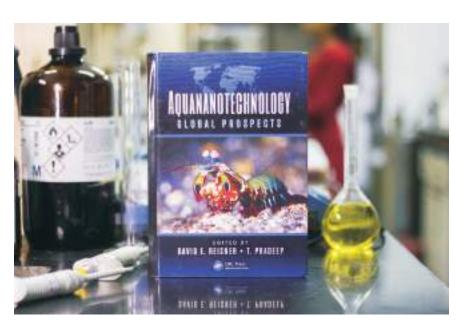


- AMRIT is undergoing installations across the country. It has now reached West Bengal, Bihar, Uttar Pradesh and Karnataka.
- A new AMRIT purifier with RFID-based delivery and internet-based data collection was displayed at Bangalore India Nano 2014.
- On-line AMRIT water purifiers attached to hand pumps have been developed recently.
- The pesticide removal technology has reached about Rs. 1.5 crores in royalty earnings, translating to the production of nearly 1.5 million filter units. The technology must have reached about 5 million people so far.

#### **Grants**

• Soft ionization ion mobility mass spectrometry of atomically precise clusters of noble metals, Rs.608 lakhs

#### **Books**





#### Aquananotechnology: Global Prospects.

David E. Reisner, T. Pradeep, CRC Press, New York, 837 Pages

### **Work in News**







#### **SCIENCE & TECHNOLOGY**

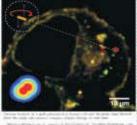
#### Novel way to produce safer drinking water

M

#### SCIENCE & TECHNOLOGY

#### Turning a simple optical microscope into a powerful tool

S



# THE

#### Honey, I shrunk the mass spectrometer

М

#### Carbon hanniche Coating Shrinks Size of Spactrometers



# the **ENGINEER**

Tricorder technology advances with nanoscale discovery



#### NANOTECH ON TAP



### PURDUE Purdue News



#### ScienceDaily



## PAPER SPRAY IONIZATION WITH A 3-V BATTERY

Like most ambient sample ionization Like most amorem sample contents, pa-methods used for mass spectrumetry, pa-per spray usually requires voltages in the kilovolt range. Such high ionization volt-ages can be dangerous and require large power supplies. Bahul Narayanan, Depan-jan Sarkar, and Thalappil Pradeep of the Indian Institute of Technology, Madras, in Chennai, and R. Graham Gooks of Pundue University now show that they can ionize samples with potentials as low as 3 V by using paper coated with carbon nunotubes (Angree Chem. Int. Ed., 2014, DOI: 10.1002) anie.aci311053). In a demonstration, the group used the low-voltage method to col-lect mass spectra of pesticides, medicines, amino acids, and other compounds. With out the nanotube coating, more than 500 V is required to produce any signal, they say. Electron micrographs of the coated paper show that nanotubes protrude from the surface. The researchers suggest that the nanotobes act as electrodes that induce an electric field between the paper tip and the mass spectrometer inlet. More recently, the team has found that they could obtain spec-tra by applying just 1 V, Pradeep says.—CHA



#### 7th Nano Expo, Bangalore





Research • Industry • Academia
December 4 - 6, 2014 | Bangalore

The DST unit of Nanoscience, IIT Madras participated in the 6th Nano expo held at Bangalore in December 2014. A mock-up of a village in West Bengal was created, where a demo of the AMRIT water filter was available. Arsenic contaminated water was purified in real-time to pure drinking water, and this water was in turn used to make tea in a tea shop, which was distributed to the delegates/visitors at the stall. The tea shop by itself was powered by a solar panel. The AMRIT water filter was demonstrated with an access control RFID device which is planned to be distributed to the villagers shortly. A domestic version of the AMRIT water filter, several nanotechnology based cutting tools and a few other developments spearheaded by various IITM faculty and research groups were also on display.

The stall won the Best Stall Award for the second consecutive year.

























**Ligy Philip**Dept. of Civil Engg.

# Modified TiO<sub>2</sub> based photocatalytic systems for water treatment

Prof. Ligy Philip's group has been working on removal of emerging compounds in water using semiconductor photocatalysis. The photocatalyst most widely used is TiO<sub>2</sub>, which has some disadvantages including poor absorbance in the visible and fast electron-hole pair recombination. The group has made significant progress to make  ${\rm TiO_2}$ photoactive in the visible and solar light. New improved  ${\rm TiO_2}$ catalysts have been synthesized employing latest advances in nanotechnology such as doping, sensitization, nanocomposites, etc. Group has conducted various batch experiments to optimize the various system parameters for removal of various contaminants like pesticides, pharmaceuticals etc. using the synthesized photocatalysts. A continuous photocatalytic rector was also developed using the optimized design parameters. The reactor has shown promising results in its application for disinfection and contaminant removal by harnessing the renewable solar energy.



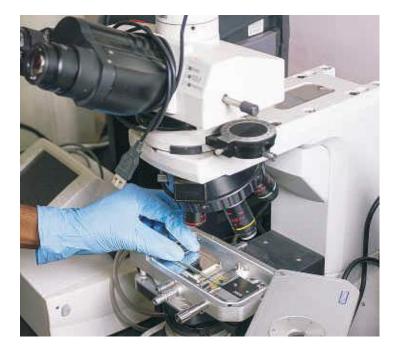
Bottom:

Batch photocatalytic reactor employing N-doped TiO<sub>2</sub> working under visible light













**Edamana Prasad**Dept. of Chemistry

# Hydrogel for water purification

A hydrogel has been prepared from acrylic acid and acrylamide in presence of glycogen for water purifying purpose. The hydrogel was characterized using SEM, FTIR, rheology and dynamic light scattering (DLS) studies. The developed hydrogel exhibits self-healing property at neutral pH, high swelling ability, high elasticity and excellent mechanical strength. The experimental results suggest that the polymer based hydrogel adsorbs toxic metal ions (Cd²+, Pb²+ and Hg²+) and organic dyes (methylene blue and methyl orange) from contaminated water with remarkable efficiency. The reusability of the hydrogel has been demonstrated by repeating the adsorption-desorption process over several cycles with identical results (B. Vivek and Edamana Prasad, manuscript submitted to J. Phys. Chem.).

**Top:** Fluorimeter

Middle:

Optical Microscope

Bottom: Glove box



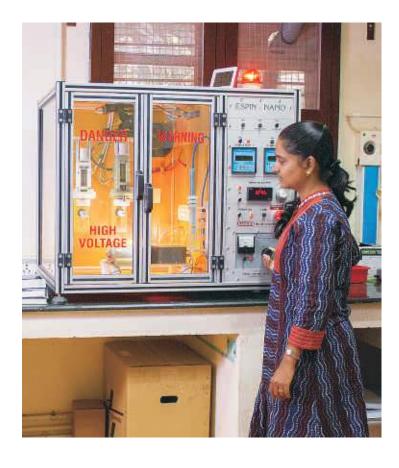
**C. Vijayan** Dept. of Physics

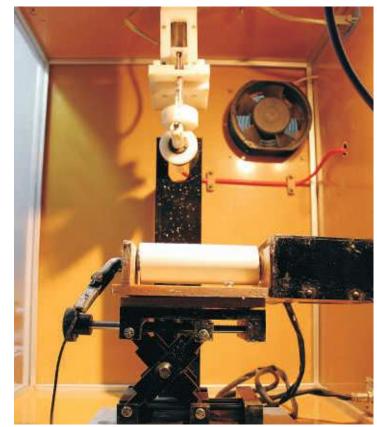
# **Electrospun** nanofibers

Electrospun fibers show very high surface area-to-volume ratio, making them suitable for applications such as filters, sensors and adsorbing media.

Nanoclay and new forms of luminescent nanoclusters have been successfully incorporated into a variety of flexible fibers such as those of PVA, PHB, Nylon and PMMA in our laboratory using a simple and low cost electrospinning method. Appropriate biochemical materials are being incorporated into the nanofiber-based membrane so as to enhance its efficiency as filters for different contaminants of water.

Our work focuses on understanding the Physics and Chemistry of these novel nanocomposite materials and utilizing them in applications such as detection of microorganisms in drinking water and purification by filtering.





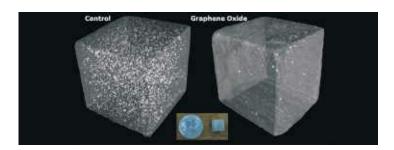
**Top:** Jessy is making electrospun mats for sensors

Bottom:

A closer view of the process of electrospinning











**Manu Santhanam** Dept. of Civil Engg.

# Porous concrete for water filtration

The primary purpose for which porous concretes were developed was to prevent collection and adsorption of water on pavements. They have also found applications in rain water harvesting and in reducing pavement — tyre interaction noise.

The objective of this project is to develop a porous concrete drinking water purification system. The developed system should be easy to fabricate, low cost, easy to clean, and effective in its filtration performance.

Several types are being designed, and tested for physical and mechanical properties. The water permeability of these systems are also being evaluated.

Modified enhanced porosity systems incorporating various nanomaterials are being developed. Water filtration performance will be measured and the microstructure will be assessed to determine the growth of biological species inside the concrete.

#### Top

Enhanced porosity concrete (EPC)

#### Second:

Closer view of EPC

#### Third:

X ray tomography image showing densification of paste with addition of graphene oxide nanoparticles

#### Bottom:

X ray tomography image showing internal void structure of EPC



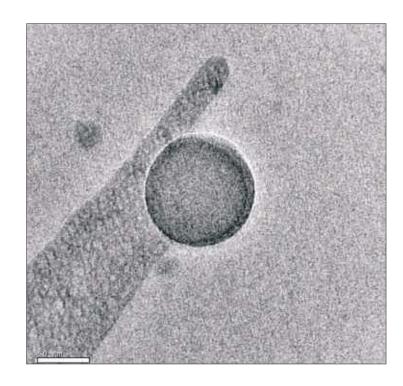
**Sarit Kumar Das**Dept. of Mechanical Engg.

# Nanofluid assisted solar desalination

Nanofluid assisted solar desalination project is a novel and useful technology for medium level water purification in coastal rural areas.

The technology works on the humidification—dehumidification (HDH) cycle in which saline water is evaporated in unsaturated air using sprays. The saturated air is then dehumidified in a heat exchanger using the incoming saline water to make it more energy efficient. In the intermediate stage, the saline water is heated by solar radiation. To avoid scaling of the solar collector at high temperature, an intermediate nanofluid (nano particle suspension) is used to keep the saline water away from the solar collector.

The technology has got scarce maintenance and low energy inputs to make it appropriate for village level desalination units in coastal areas.







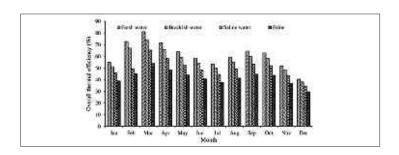
Top: CuO TEM

Middle: Fe<sub>2</sub>O<sub>3</sub> SEM

Middle:

Electrical Breakdown Voltage setup









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# Solar thermal desalination

Solar thermal desalination is an effective way to meet fresh water requirements of remote and rural communities. The distillate produced from solar thermal based desalination units are of high quality. Moreover, the technology is eco—friendly and can reduce green house gas emissions from conventional fossil fuel based desalination plants.

A novel multi-stage desalination system has been developed to cater the potable water demands of small communities in rural and remote areas. The desalination system works on evaporative cooling and the unit consists of multi-stage metal trays used for both evaporation and condensation. The heated feed water from solar collector is allowed to flow as a thin film over the trays such that due partial pressure difference mass transfer occurs from the evaporating to the condensing surface there by releasing latent heat to the next tray favoring enhanced evaporation in successive trays. The distillate yield from the unit is nearly four to five times higher than the conventional solar still. The unit can also be operated at low feed water temperature by evacuating the unit, thereby the area occupied by the solar collector required is minimized and hence favoring the unit to be more suitable even for urban applications. The desalination system can also be operated in tri-generation mode for effective utilization of solar energy in cascaded approach.

#### Top:

Multi stage evacuated solar desalination system

#### Middle

Year round performance of solar desalination Unit

#### Bottom:

Concentrating solar collector for desalination



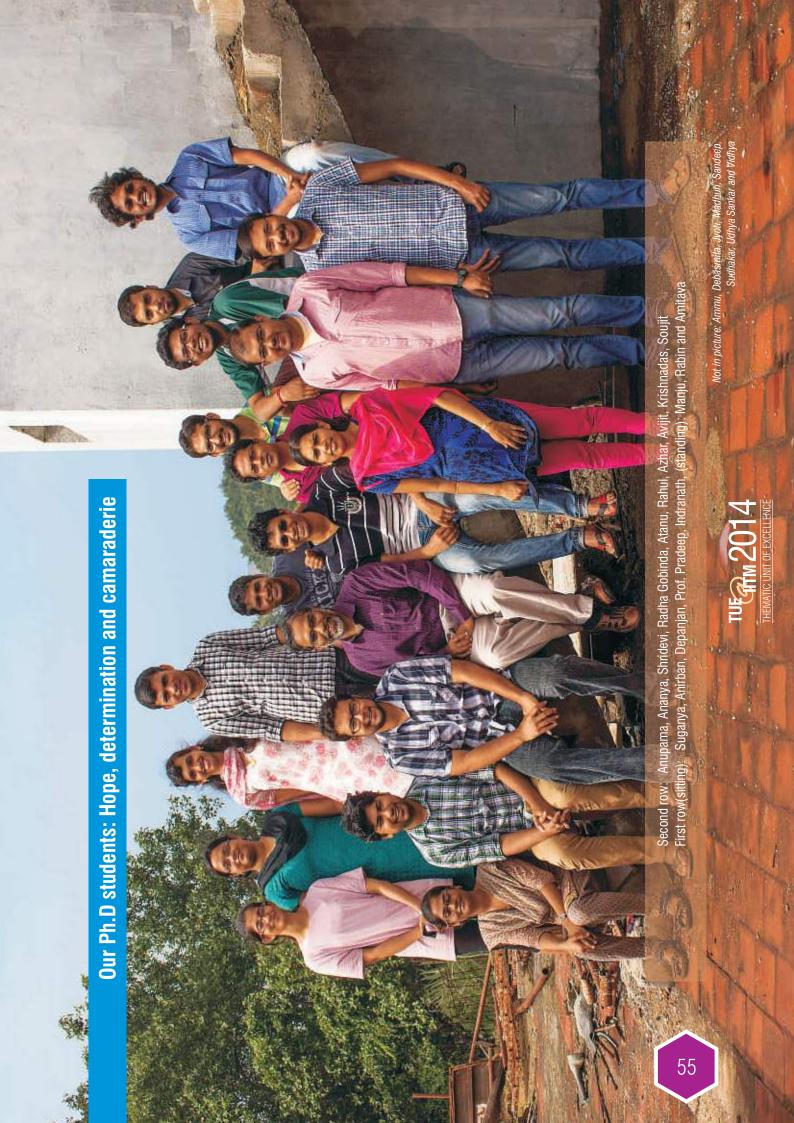




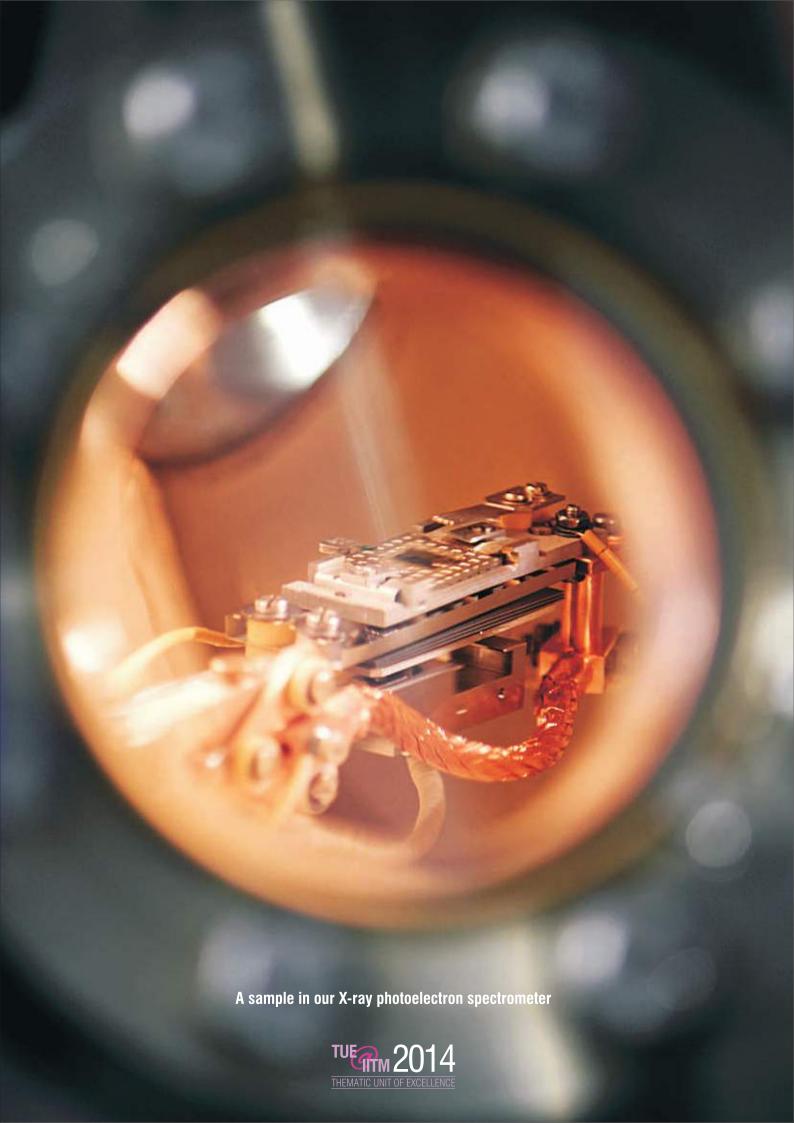
Not in picture: Ammu, Amrita, Anshup, Balaji, Biswajit, Debasmita, Jyoti, Krishnapriya, Madhuri, Manisha, Rajastree, Sandeep, Sudhakar, Udhya Sankar and Vidhya

Mahitha, Hema, Swathy, Suganya, Priya, Jessy, Hemanta, Radha Gobinda, Purushothaman, Prof. Pradeep, Ramesh, Rahul, Mohan, Saravanan, Tuhina, Anupama First row(sitting): Indranath, Gautham, Depanjan, Azhar, Anirban, Atanu, Raghu, Anil Manju, Vasudeva Bhat, Abhijit, Avijit, Soujit, Sundarraj, Vasanth

Third row:











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