During the visit of Prof. R. Graham Cooks, Purdue University, Dec. 14, 2018.

Pictured above are, from left to right: 1st row (sitting) - Shibalik Mukherjee, Sandeep Bose, Debasmita Ghosh, Rabiul Islam, Jayoti Roy, C. K. Manju, Dr. Wakeel Ahmed Dar, Prof. T. Pradeep, Prof. R. G. Cooks, Anil Kumar, Dr. Angshuman RayChowdhuri, Sritama Mukherjee, Atanu Ghosh.


4th row (standing) - Ankit Nagar, Srikrishnarka Pillamarri, Asish Kurian, Manav Shah, Dr. Kamalesh Chaudhari, E. Sundarraj, Dr. P. Ganesan, Shamil Iqbal, Jyotirmoy Ghosh, Pallab Basuri, Harsh Dave, Md Azhardin Ganayee.

Not pictured: A. Suganya, Arijit Jana, Ramesh Kumar, Swathly Ravindran, Vishal Kumar, Dr. Krishnan Swaminathan.

ANNUAL REPORT | 2018

PRADEEP RESEARCH GROUP, INDIAN INSTITUTE OF TECHNOLOGY MADRAS

Annual reports of 2014, 2015, 2016 and 2017 are also available (click the respective year).
OUR TEAM

Thalappil Pradeep FNA, FASc., FNASC, FNAE, FRSC, FTWAS, FAAAS

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Deepak Parekh Institute Chair Professor and Professor of Chemistry
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Ph.D. Students

Abhijit Nag
Amrita Chakraborty
A. Anil Kumar
Ankit Nagar
Arijit Jana
Biswajit Mondal
Debasmita Ghosh
Esma Khatun
Gaurav Vishwakarma
Jayoti Roy
Jyoti Sarita Mohanty*
Jyotirmoy Ghosh
S. Jenifer *
M. P. Kannan*
Dr. Krishnan Swaminathan
MD FRCP (Edin)*
Madhuri Jash
C. K. Manju
Md Bodluzzaman

Md Rabiul Islam
Mohd. Azhardin Ganayee
Pallab Basuri
Papri Chakraborty
Paulami Bose
Sandee Bose
Shridevi Bhat
Spoorthi B. K.
Sritama Mukherjee*
Sudhakar Chennu
Sukanya Bagchi*
A. Suganya*
K. S. Sugi
Srikrishnarka Pillalamari*
J. R. Swathy*
Tanvi Gupte*
Tripti Ahuja
S. Vidhya*
Vishal Kumar*

*Joint students
**Postdoctoral/Research Associates**
- Dr. P. Ganesan
- Dr. Sourav Kanti Jana
- Dr. G. Velmurugan
- Dr. Wakeel Ahmed Dar
- Dr. T. K. Rahul
- Dr. Gopi Ragupathy
- Dr. Angshuman RayChowdhuri
- Dr. Avijit Baidya

- Institute postdoctoral fellow
- National postdoctoral fellow

**Administrative Officer**
- K. Priya

**Project Technicians**
- E. Sundarraj
- Asish Kurian

**Project Associates**
- Karthigai Meena
- M. Bhaskar

**Architect**
- Shamil Iqbal

**Industrial Consultant**
- Dr. Kamalesh Chaudhari

**M.S. Students**
- Ramesh Kumar
- Ananthu Mahendranath

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**WHAT’S INSIDE?**

- Glimpses of 2018
- Awards & Honors
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- A New Initiative – ICCW
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**Summer & Winter Student(s)/Fellow(s)**

- Keerthana Unni
- Meera P. Ragunath
- M. P. Hridya
- Sankavi
- Jesswin Lobo
- T. Athira
- Pooja Duhan
- Aniruddha Jana
- Dipannita Saha
- V. S. Amal
Prof. T. Pradeep has been elected the fellow of The World Academy of Sciences (TWAS) and the American Association for the Advancement of Science (AAAS).

Papri Chakraborty won a Karnataka DST Nanoscience Fellowship at Bengaluru INDIA NANO, 2018.

Ramesh Kumar and J. R. Swathy received a Gandhian Young Technological Innovation (GYTI) award from the President of India in a function held at the Rastrapati Bhavan, New Delhi on March 19, 2018. From left: Prof. R. A. Mashelkar, Dr. Harsh Vardhan (Minister, GOI), Shri Ram Nath Kovind (President of India), Prof. Ashutosh Sharma (Secretary, DST).

Pallab Basuri and Depanjan Sarkar (not in picture) received a Gandhian Young Technological Innovation (GYTI) Appreciation Award from Dr. Harsh Vardhan (Minister, GOI) in a function held at the Rastrapati Bhavan, New Delhi on March 19, 2018. Prof. R. A. Mashelkar and Prof. Ashutosh Sharma are also in the picture.
Awards and Honors

1. Prof. T. Pradeep was awarded The World Academy of Sciences (TWAS) prize in chemistry for his discovery of novel nanomaterials and development of products using such materials, leading to applications which support a clean environment, affordable clean water and ultrasensitive devices, November 27, 2018.

2. Prof. T. Pradeep has been awarded IITM Alumni Association Award for Faculty in Innovation by IIT Madras Alumni Association during a function held at Hotel Leela Palace, Chennai, September 29, 2018.

3. Prof. T. Pradeep has been elected as a fellow of The World Academy of Sciences (TWAS) and the American Association for the Advancement of Science (AAAS).

4. Prof. T. Pradeep has been invited to be a member of the advisory board of the Royal Society of Chemistry (RSC) journal, *Nanoscale Advances*.

Publications

JOURNAL PUBLICATIONS*


2. UPLC and ESI-MS analysis of metabolites of Rauvolfia tetraphylla L. and their spatial localization using desorption electrospray ionization (DESI) mass spectrometric imaging, Mohana Kumara P., Uma Shaanker R. and T. Pradeep, Phytochemistry, 2018. (Just Accepted)

3. Sustainable and affordable composites built using microstructures performing better than nanostructures for arsenic removal, Sritama Mukherjee, Avula Anil Kumar, Chennu Sudhakar,
Ramesh Kumar, Tripti Ahuja, Biswajit Mondal, Srikrishnarka Pillalamarri, Ligy Philip and T. Pradeep, ACS Sustain. Chem. Eng., 2018 (DOI: 10.1021/acssuschemeng.8b05157). (Just Accepted)


5. Rapid isotopic exchange in nanoparticles, Papri Chakraborty, Abhijit Nag, Ganapati Natarajan, Nayanika Bandyopadhyay, Ganesan Paramasivam, Manoj Kumar Panwar, Jaydeb Chakrabarti and T. Pradeep, Science Advances, 2018. (Just Accepted)


27. Fullerene functionalized monolayer protected silver clusters: $[\text{Ag}_{29}(\text{BDT})_{12}(\text{C}_{60})_{n}]^{3-}$ (n=1–9), Papri Chakraborty, Abhijit Nag, Ganesan Paramasivam, Ganapati Natarajan and T. Pradeep, ACS Nano, 12 (2018) 2415–2425 (DOI: 10.1021/acsnano.7b07759).


PUBLICATIONS WITH OTHER GROUPS


*Some of these papers will appear in 2019.

Patent Applications


**PCT applications**


**Patents Granted**

**Indian**


**PCT Patents Granted**


**Graduation**

**PhD (viva completed, convocation 2019)**

   ‘Chemical Approaches for Reliable Superhydrophobic Coatings: Synthesis and Applications’.

2. **Shridevi S. Bhat** has submitted her PhD thesis and is waiting for the viva to be finished.

**M.Sc. (graduated in 2018)**

   ‘Wood Mimicking Composite with Superior Mechanical Properties’.

   ‘Real Time Raman Analysis of Ambient Sprays’.


2. Reactions between nanoparticles, ACS on Campus, the American Chemical Society’s premier outreach program hosting professional development events at University of Delhi, India on Monday, February 5 and IIT Roorkee, India on Wednesday, February 7, 2018.
17. Reactions between noble metal clusters, Chemical Frontiers Goa @ 10, August 19-22, 2018.
21. From materials to clean water: Growing companies from wet labs, IISER Tirupati, India, September 14, 2018.
22. Reactions between nanoparticles, One Day Symposium on Recent Advances in Nanoscience and Technology, Department of Atomic and Molecular Physics, MAHE, India, September 24, 2018.


### Student Activities

**National Conferences:**


2. ‘Molecular imaging of morphologically different rice varieties through mass spectrometry’ by Suganya Arunan in 22nd CRSI National symposium in chemistry, Pt. Ravishankar Shukla University, Raipur, February 2-4, 2018.

3. ‘Thirty-fold enhancement of photoluminescence quantum yield in \( \text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_{3})_{4} \) by modifying the secondary shell structure’ by Esma Khatun in 22nd Chemical Research Society of India Symposium, CRSI 2018, Pt. Ravishankar Shukla University, Raipur, February 2-4, 2018.


5. ‘Fullerene-functionalized atomically precise silver nanoclusters’ by Papri Chakraborty in International Conference on Nanoscience and Technology (ICONSAT), IISc, Bengaluru, March 21-23, 2018.

6. ‘Atomically Precise Nanocluster Assemblies Encapsulating Plasmonic
Gold Nanorods’ by Amrita Chakraborty in International Conference on Nanoscience and Technology (ICONSAT), IISc, Bengaluru, March 21-23, 2018.


12. ‘Fullerene-functionalized monolayer-protected silver clusters: [Ag_{29}(BDT)_{12}(C_{60})_{n}]^{3-} (n=1-9)’ by Papri Chakraborty in Bengaluru India Nano, Lalit Ashok, Bengaluru, December 5-7, 2018.


14. ‘Camouflaging Structural Diversity: Co-crystallisation of Two Different Nanoparticles having Different Cores but the Same Shell’ by Md Bodiuazzaman in Bengaluru India Nano, Lalit Ashok, Bengaluru, December 5-7, 2018.
15. Oral presentation titled ‘A new type of interparticle reaction: silver-silver intercluster reaction leads to formation of co-crystals of Ag$_{16}$ and Ag$_{17}$’ by Wakeel Ahmed Dar in Frontiers in Chemical Science, FICS-2018, Department of Chemistry, Indian Institute of Technology Guwahati, December 6-8, 2018.

**International Conferences:**


17. ‘Probing the mechanical response of luminescent dithiol protected Ag$_{29}$(BDT)$_{12}$(TPP)$_{4}$ cluster crystals’ by K. S. Sugi in Noble metal nanoparticles, Gordon research conference, GRC 2018, Mount Holyoke College in South Hadley, MA, June 17-22, 2018.

18. Oral and poster presentation titled as ‘Fullerene-functionalized atomically precise silver clusters: [Ag$_{29}$(BDT)$_{12}$(C$_{60}$)$_{n}$]$^{3-}$ (n=1-9)’ by Papri Chakraborty in Gordon Research Seminar and Conference on Noble Metal Nanoparticles (GRS and GRC 2018), Mount Holyoke College, South Hadley, MA, United States, June 16-17, 2018.


20. ‘[Ag$_{59}$(2,5-DCBT)$_{32}$]$^{3-}$: A new cluster and a precursor for three well-known clusters’ by Esma Khatun in Gordon Research Conferences, Nobel metal nanoparticles, Mount Holyoke College, South Hadley, MA United State, June 17-22, 2018.


24. ‘Camouflaging Structural Diversity: Co-crystallisation of Two Different Nanoparticles having Different Cores but the Same Shell’ by Md. Bodluzzaman at the 7th EuCheMs international conference on ‘Molecular frontiers & global challenges’ held at ACC Liverpool U.K., August 26-30, 2018.


27. Oral and poster presentation titled ‘An unprecedented 1000 - fold enhancement of antimicrobial activity of metal ions by selective anion treatment’ by J. R. Swathy, II edition of the International Conference on Water Energy NEXUS – Advanced Technology and Best Practices – Taste the Future, The Sanitary Environmental Engineering Division (SEED) of the University of Salerno (Italy) in cooperation with Advanced Institute of Water Industry at Kyungpook National University (Korea) and with The Energy and Resources Institute, TERI(India), Salerno, Italy, November 14 – 17, 2018.


Recognition

Students

2. **Pallab Basuri** and **Depanjan Sarkar** won the Gandhian Young Technological Innovation Appreciation Award (GYTI), for the ‘Detection of hydrocarbons by laser assisted paper spray ionization mass spectrometry (LAPSI MS)’, Rastrapati bhavan New Delhi, March 19, 2018.

3. **Ramesh Kumar** and **J. R. Swathy** received the prestigious Gandhian Young Technological Innovation (GYTI) Award from the honorable President of India for a prototype of rolling water purifier titled ‘RollPure’, March 19, 2018.

4. **Md Bodiuzzaman** has received the best poster prize of the Royal Society of Chemistry, U.K. at the 7th EuCheMs international conference on ‘Molecular frontiers & global challenges’ held at ACC Liverpool U.K., during August 26-30, 2018.


7. **IIT Madras** wins the best exhibitor award at Bengaluru INDIA NANO, December 5-7, 2018. The exhibit was designed and presented by our research group.

8. **Papri Chakraborty** has been awarded a Karnataka DST Nanoscience Fellowship at Bengaluru INDIA NANO, December 5-7, 2018.

9. **Papri Chakraborty** received one of the best poster awards at International Conference on Nanoscience and Technology (ICONSAT), March 21-23, 2018.

10. **Md Bodiuzzaman** won the best poster award in Bengaluru India Nano, December 5-7, 2018.

11. **Pallab Basuri** received overseas visiting doctoral fellowship from Science and engineering research board of India, 2018.
Alumni News

1. In a Germany-wide competitive selection Dr. Xavier received ‘Joachim Hertz Fellowship for Interdisciplinary Sciences’ for his planned research stay at Harvard.

2. Dr. Subramaniam Chandramouli got promoted as Associate Professor, Dept of Chemistry IITB from April, 2018.

3. Awarded the IIT Bombay Impactful research award for 2017 for research relating to low-power, portable device for desalination of Indian groundwater.

4. Dr. Ammu Mathew joined as ORISE Fellow in the department of Nanotechnology Core Facility of National Center for Toxicological Research, U.S. Food & Drug Administration.

5. Harwinder Singh Sidhu graduated from Texas A&M university with MS in Chemical Engineering and started working as a Design Engineer at Intel in Oregon, USA.

6. Dr. N. Sandhyarani got promoted as Professor at NIT Calicut in the School of Nano Science and Technology in April, 2018.

7. Dr. V. Suryanarayanan have been promoted as Principal Scientist from Senior Scientist at CECRI, Karaikudi.

8. Dr. V. Suryanarayanan also has been awarded ‘Distinguished Scientist in Electrochemistry’ by Venus International Foundation, which recognizes the ‘Expertly Qualified Research Professionals’.

9. Neeru Mittal, one of the former summer interns has received:
   a) President's gold medal for best allround performance in BS-MS at IISER-Mohali.
   b) Excellence award for best performance in Chemistry majors.

Ongoing Research Grants

1. Thematic project on frontiers of nanoscience and nanotechnology (TPF), DST, Rs. 541 lakhs (principal investigator).

2. Dust free glass, Saint-Gobain Research India Ltd. Rs. 36 lakhs (principal investigator, with Prof. R. Nagarajan).

3. Development of a novel combined arsenic filtration/monitoring system for community-scale water supplies, India-UK project supported by GITA, total funds Rs. 130 lakhs (principal investigator along with InnoNano Research Pvt. Ltd.).

4. Arsenic free South 24 Parganas district, DST, Rs. 374.88 lakhs (principal investigator).
5. Cluster composite nanofibre membranes for rapid, ultra-trace detection of waterborne contaminants, India-German Science and Technology Forum, Total funds Rs. 191.324 lakhs (principal investigator along with InnoNano Research Pvt. Ltd.).

**Grants Sanctioned in 2018**


2. WATER-IC for SUTRAM of EASY WATER, DST, 2018 – 2023, Rs. 9 Cr. (Ligy Philip, principal investigator, T. Pradeep, Co- principal investigator).

3. Affordable clean water in arsenic affected areas, Millennium Alliance, 2018-2020, Rs. 50 lakhs (principal investigator along).


6. DESI MS technique to image molecular distribution in tissues, L’Oreal India Private Limited, 10- 2018 – 07- 2019, Rs. 5 lakhs (principal investigator).

**Visiting Faculty**

Prof. P. M. Ajayan of Rice University (and our Distinguished Professor) visited us under the VAJRA (Visiting Advanced Joint Research) faculty scheme of the DST. He visited IITM thrice in this period. The VAJRA project is with Prof. Pradeep.

**Other Faculty**

1. Dr. Debal Deb and Prof. Mousumi Poddar visited us on September 10, 2018.
2. A group of faculty members of Chemistry and Biological Chemistry of Nanyang Technological University, Singapore visited the lab on September 18, 2018. The team comprised of Roderick BATES, Mihaela STUPARU, Richard D. Webster and Weng Kee LEONG.

3. Prof. R. Graham Cooks of Purdue University and our Distinguished Professor visited IITM during December 8-15, 2018.

4. Prof. Amit Goyal, Director of RENEW Institute @ SUNY, Buffalo and a Fellow of the National Academy of Engineering visited IITM during December 17-20, 2018.

Other than this, a number of scientists and professionals including Prof. Zuowei Xie, Chinese University of Hong Kong, Shri. Vashishta Johri, Advisor CRR, Ms. Ziaa Lalkaka, HD Parekh Foundation, Mumbai, Mr. Dilip Sanghvi, Founder of Sun Pharmaceuticals, the largest Indian pharma company and Chairman, Board of Governors, IIT Bombay, Mr. Madhu Reddy and Mr. Ruyintan Mehta of Wheels Global Foundation, Mr. Krish Gopalakrishnan, Executive Chairman of Infosys, India, Mr. Rajesh Bhojwani from D Tech Dental Technologies, Pune, India, Prof. J. N. Goswami, Physical Research Laboratory, Ahmedabad, Mr. Ray Stata - Founder Chairman of Analog Devices, Dr Nicholas Philip Chadwick, Dr Loukas Constantinou, Dr Christopher James Johnson from Bio Nano Consulting, London, Mr. Tullio Servida, CEO, Idropan, Italy, Prof. Joseph Klafter, President, Tel Aviv University, Israel and others visited the group in 2018.

**Visiting Fellows**

1. **Mr. Egor Mosses**, Busitema University, Uganda, June - November, 2018.

2. **Mr. Zhaoheng Chen**, Tokyo University of Science, Japan, July - September, 2018.
Service 2018

1. Member, Nanoscience Advisory Committee, Nano Mission, Department of Science and Technology, 2015-2018.
3. Member, Editorial Board of the journals, Chemistry of Materials, ACS Nano, Scientific Reports (Nature Group), Nanoscale, Particle, Surface Innovations and International Journal of Water and Wastewater Treatment.
4. Associate Editor of the journal, ACS Sustainable Chemistry & Engineering
5. Visiting Professor, Manipal University, 2018 onwards.
6. Member, Program advisory committee of inorganic and physical chemistry, DST, 2018 onwards.
7. Member, Industry relevant R & D expert committee, DST, 2018 onwards.
8. Member, DST JSPS committee.

A New Initiative - ICCW

A new initiative to build the International Centre for Clean Water (ICCW) has begun. It aims to be one of the best ecosystems of its kind in the world to ideate, nurture and translate disruptive technologies for sustainable clean water, with collective participation of the global community, delivering first rate science, leading to wealth and social good simultaneously, in the process building water professionals of tomorrow. Construction for the establishment of ICCW has started at the IITM Research Park. Glimpses of the empty site and a view of the research park are below.
Incubation

Vayujal received funding of 1 crore INR for the development of atmospheric water capture from Engineers India Limited.

InnoDi received a tax holiday of 3 years.

InnoDi received govt. of Karnataka startup grant of 35 lacs.

Technology reach

AquEasy is implementing a new technology based on sustainable materials for clean water.

Arsenic and iron removal technologies are now delivering clean water to 900,000 people each day.

In Punjab, the community purifier has crossed accumulative water output of 10 million liters each day.

All are co-owned by IIT Madras.

Popular Science

Prof. Pradeep wrote about the fate of talented researchers at crossroads as the job market for PhDs in science becomes increasingly competitive. “How far does a PhD go?”: Published in The Hindu.
The Hindu writes about our arsenic-removal technology.

A student-driven project at the IIT-M is being widely used to eliminate arsenic from water.

A professor and his students at the Indian Institute of Technology - Madras (IIT-M) have developed a technology to remove arsenic from water and make it potable. Over a period of 30 days, the technology is tested at various locations in Tamil Nadu and Kerala.

DTNext talks about “Roll Pure”.

According to a report by “National Samachar Office (NSO)”, about 54% of the Indian women from rural areas draw water from 200 to 250 metres, five kilometers daily to get drinking water.

Thus, a water purifier with built-in water purification system called Roll Pure is helping people who don't have access to clean water.

Rajyasabha TV covers the detection of hydrocarbon in coconut oil.

The project lead Dr. Ranjith Kumar sent this in order to test the oil, water volume 50-100 litres is filled inside the collecting two open water bottles and then is subjected to the point of red Bea. During grinding, residual material fills available biological contaminants and solid debris of same is filtered. Penrose’s differential centrifugal for liberation of solid debris and chemical contaminants is developed by bellows.
Publication Analysis

Source: Scopus, December 30, 2018.

Source: Google Scholar, December 30, 2018.

Cited by

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Probing the mechanical response of luminescent dithiol protected
Ag$_{29}$(BDT)$_{12}$(TPP)$_4$ cluster crystals

Korath Shivan Sugi, Gangapuram Mallikarjunachari, Anirban Som, Pijush Ghosh and T. Pradeep
ChemNanoMat., 4, 2018, 1-9 (DOI: 10.1002/cnma.201700371)

Abstract: Atomically precise clusters of noble metals are considered to be an important class of advanced materials. Crystals of these clusters composed of inorganic cores and organic ligands are fascinating owing to their tunable and unique properties. Understanding their mechanical properties can give more insight into the design of nanocluster-based devices. Here, we probe the mechanical response of single crystals of Ag$_{29}$(BDT)$_{12}$(TPP)$_4$ cluster (BDT=1,3 benzenedithiol, TPP=triphenylphosphine) under both quasi-static and dynamic loading conditions. Surprisingly, the measured reduced Young's modulus (E$_r$) and hardness (H) were 4.48 and 0.285 GPa, respectively, similar to those of polymers and much smaller than the values for bulk silver. These observations indicate a significant role of capping ligands on the physical properties of such materials. The observed storage modulus, loss modulus and loss factor were also found to be similar to those of polymers. The magnitude of loss factor suggested the ability of nanocrystals to absorb energy under dynamic loading. These studies of mechanical properties of cluster materials could be useful in developing their applications.

Understanding proton capture and cation-induced dimerization of
[Ag$_{29}$(BDT)$_{12}$]$^{3-}$ clusters by ion mobility mass spectrometry

Papri Chakraborty, Ananya Baksi, Sathish Kumar Mucedla, Abhijit Nag, Ganesan Paramasivam, Venkatesan Subramanian and T. Pradeep*

Abstract: Proton transfer reactions have been a topic of fundamental interest in several areas of chemistry and biology. However, such reactivity has not been explored in detail for nanoscale materials. In this article, we present a unique reaction of an atomically precise monolayer-protected silver nanocluster, [Ag$_{29}$(BDT)$_{12}$]$^{3-}$, with a proton (H$^+$. Under controlled conditions, the strong proton affinity facilitated a
complete conversion of the cluster to its protonated form, \([\text{Ag}_{29}(\text{BDT})_{12}\text{H}]^{2-}\). Moreover, binding of alkali metal ions (Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\) and Cs\(^+\)) induced specific structural changes and also favored dimerization of the cluster. In this case, the cations acted as a bridge between the two clusters and the degree of dimerization was specific to the size of the cations. The conformational changes and separation of the alkali–metal ion bound dimers from their respective monomers have been investigated by ion mobility mass spectrometry (IM MS) and tandem mass spectrometric studies. Density functional theory (DFT) calculations have been used to determine the possible structures of the monomers and the dimers. Similar reactivity of the cluster can also be extended to other metal ions. While the present study helps to expand the ion-chemistry of atomically precise clusters, gas-phase basicity of the molecule can be explored in further detail and this can find applications in the areas of sensing and materials in general.

Fullerene-functionalized monolayer-protected silver clusters: \([\text{Ag}_{29}(\text{BDT})_{12}(\text{C}_{60})_n]^{3-}\) \((n = 1–9)\)

Papri Chakraborty, Abhijit Nag, Ganesan Paramasivam, Ganapati Natarajan, and T. Pradeep

ACS Nano, 12, 2018, 3, 2415-2425 (DOI: 10.1021/acsnano.7b07759)

Abstract: We report the formation of supramolecular adducts between monolayer-protected noble metal nanoclusters and fullerenes, specifically focusing on a well-known silver cluster, \([\text{Ag}_{29}(\text{BDT})_{12}]^{3-}\), where BDT is 1,3-benzenedithiol. We demonstrate that \(\text{C}_{60}\) molecules link with the cluster at specific locations and protect the fragile cluster core, enhancing the stability of the cluster. A combination of studies including UV–vis, high-resolution electrospray ionization mass spectrometry, collision-induced dissociation, and nuclear magnetic resonance spectroscopy revealed structural details of the fullerene-functionalized clusters, \([\text{Ag}_{29}(\text{BDT})_{12}(\text{C}_{60})_n]^{3-}\) \((n = 1–9)\). Density functional theory (DFT) calculations and molecular docking simulations affirm compatibility between the cluster and \(\text{C}_{60}\), resulting in its attachment at specific positions on the surface of the cluster, stabilized mainly by \(\pi–\pi\) and van der Waals interactions. The structures have also been confirmed from ion mobility mass spectrometry by comparing the experimental collision cross sections (CCSs) with the theoretical CCSs of the DFT-optimized structures. The gradual evolution of the structures with an increase in the number of fullerene attachments to the cluster has been investigated. Whereas the structure for \(n = 4\) is tetrahedral, that of \(n = 8\) is a distorted cube with a cluster at the center and fullerenes at the vertices. Another fullerene, \(\text{C}_{70}\), also exhibited similar behavior. Modified clusters are expected to show interesting properties.
Fabrication of a waterborne durable superhydrophobic material functioning in air and under oil

Avijit Baidya, Sarit Das, Robin Ras, T. Pradeep


Abstract: A fundamental challenge in artificially structured or chemically modified superhydrophobic surfaces is their poor chemical, mechanical, and structural robustness toward different mechanical abrasions. This limits their application potential in different fields of science and technology. Herein, a stable waterborne superhydrophobic material composed of clay particles is developed through a one-pot chemical modification in ambient conditions, forming durable micro-nanodual-structured coatings at room temperature over a range of substrates, without adhesive. This chemical modification inverts the inherent hydrophilic nature of clay particles and provides an excellent superhydrophobic surface having a water contact angle >170° (±2°) and a contact angle hysteresis <5° (±2°). The coating shows excellent durability against various induced damages (mechano-chemical-environmental) and works efficiently both in air and within oils. The observed property is due to the controlled surface energy obtained by the incorporated chemical functionalities and enhanced surface roughness facilitated by the hydrophobic effect during slow evaporation of water from the coating material. Being a stable water dispersion, it enables large area coatings, thereby minimizing safety and environmental concerns. Use of this material to develop rugged waterproof paper for various paper-based technologies is also demonstrated. As clay is commercially available and economical, it is believed, this scalable organic-solvent-free superhydrophobic material will have a positive impact on various industries.

Detection of hydrocarbons by laser assisted paper spray ionization mass spectrometry (LAPSI MS)

Pallab Basuri, Depanjan Sarkar, Ganesan Paramasivam, T. Pradeep

Anal. Chem., 90, 2018, 4663−4668 (DOI: 10.1021/acs.analchem.7b05213)

Abstract: Here we introduce a new ambient ionization technique named laser assisted paper spray ionization mass spectrometry (LAPSI MS). In it, a 532 ± 10 nm, ≤10 mW laser pointer was shone on a triangularly cut paper along with high voltage, to effect ionization. The analyte solution was continuously pushed through a fused silica capillary, using a syringe pump, at a preferred infusion rate. LAPSI MS promises enhanced ionization with high signal intensity of polycyclic aromatic hydrocarbons (PAHs), which are normally not ionizable with similar ionization methods involving solvent sprays. LAPSI MS works both in positive and negative modes of ionization. A clear enhancement of signal intensity was visualized in the total ion chronogram for most analytes in the presence of the laser. We speculate that the mechanism of ionization is field assisted photoionization. The field-induced distortion of the potential well can be large in paper
spray as the fibers comprising the paper are separated at tens of nanometers apart, and consequently, the analyte molecules are subjected to very large electric fields of the order of 10^7 V cm\(^{-1}\). Ionization occurs from their distorted electronic states of reduced ionization energy, using the laser. Negative ion detection is also demonstrated, occurring due to the capture of produced photoelectrons. LAPSI MS can be used for monitoring in situ photoassisted reactions like the decarboxylation of mercaptobenzoic acid in the presence of gold and silver nanoparticles and the dehydrogenation reaction of 2,3-dihydro-1H-isoindole, which were chosen as examples. As an application, we have shown that paraffin oil, which is usually nonionizable by paper spray or by electrospray ionization can be efficiently detected using this technique. Impurities like mineral oils were detected easily in commercially available coconut oil, pointing the way to applications of social relevance.

Direct conversion of rice husk to silicon nanoparticles: Sustainable fluorophores for white light emission

Sandeep Bose, Mohd. Azhardin Ganayee, Biswajit Mondal, Avijit Baidya, Sudhakar Chennu, Jyoti Sarita Mohanty, T. Pradeep*

ACS Sustain. Chem. Eng., 6, 2018, 6203–6210 (DOI: 10.1021/acssuschemeng.7b04911)

Abstract: Silicon nanoparticles (Si NPs) exhibiting observable luminescence have many electronic, optical and biological applications. Owing to reduced toxicity, they can be used as cheap and environment-friendly alternatives for cadmium containing quantum dots, organic dyes and rare earth-based expensive phosphors. Here, we report an inexpensive silicon precursor, namely rice husk, which has been employed for the synthesis of Si NPs by rapid microwave heating. The as prepared Si NPs of ~ 4.9 nm diameter exhibit observable green luminescence with a quantum yield of ~ 60%. They show robust storage stability and photostability and have constant luminescence during long-term UV irradiation extending over 48 h, in contrast to other luminescent materials such as quantum dots and organic dyes which quenched their emission over this time window. Green luminescent Si NPs upon mixing with appropriate species are shown to be useful for energy-efficient white light production. The resulting white light has a color coordinate of (0.31, 0.27) which is close to that of pure white light (0.33, 0.33). The performance of our white light emitting...
material is comparable to that of a commercial white light emitting diode (WLED) bulb and is shown to be better than that of a commercial compact fluorescent lamp (CFL).

**Atomically precise nanocluster assemblies encapsulating plasmonic gold nanorods**

Amrita Chakraborty, Ann Candice Fernandez, Anirban Som, Biswajit Mondal, Ganapati Natarajan, Ganesan Paramasivam, Tanja Lahtinen, Hannu Häkkinen, Nonappa,* T. Pradeep*


**Abstract:** We present the self-assembled structures of atomically precise, ligand-protected noble metal nanoclusters leading to encapsulation of plasmonic gold nanorods (GNRs). Unlike highly sophisticated DNA nanotechnology, our approach demonstrates a strategically simple hydrogen bonding-directed self-assembly of nanoclusters leading to octahedral nanocrystals encapsulating GNRs. Specifically, we use the $p$-mercaptobenzoic acid ($p$MBA) protected atomically precise nanocluster, $\text{Na}_4\text{[Ag}_{44}(p\text{MBA})_{30}]$ and $p$MBA functionalized GNRs. High resolution transmission and scanning transmission electron tomographic reconstructions suggest that the geometry of the GNR surface is responsible for directing the assembly of silver nanoclusters via H-bonding leading to octahedral symmetry. Further, use of water dispersible gold nanoclusters, $\text{Au}_{n}(p\text{MBA})_n$ and $\text{Au}_{102}(p\text{MBA})_{44}$ also formed layered shells encapsulating GNRs. Such cluster assemblies on colloidal particles present a new category of precision hybrids with diverse possibilities.

**Metals in urine in relation to the prevalence of pre-diabetes, diabetes and atherosclerosis in rural India**

Ganesan Velmurugan, Krishnan Swaminathan, Ganesh Veerasekar, Jonathan Q Purnell, Sundaresan Mohanraj, Mani Dhivakar, Anil Kumar Avula, Mathew Cherian, Nalla G Palaniswami, Thomas Alexander, T. Pradeep*


**Abstract:**

**Objectives:** Diabetes and cardiovascular diseases are growing burdens in rural communities worldwide. We have observed a high prevalence of diabetes amongst rural farming communities in India and sought to evaluate the association of non-traditional risk factors, such as metals, with diabetes and other cardiometabolic risk factors in this community.

**Methods:** Anthropometric measurements, chemistries, and carotid intima media thickness were determined in 865 participants of KMCH-Nallampatti Non-communicable disease study-I (KMCH-NNCD-I, 2015 – A cross sectional study) conducted in a farming village from South India. Urinary heavy metal levels were determined by ICP-MS analysis and corrected to urinary creatinine level. Statistical analyses were
performed to study the association between urinary heavy metal levels and clinical parameters.

**Results:** 82.5% of the study population were involved in farming and high levels of toxic metals were detected in the synthetic fertilizers used in the study village. The prevalence of pre-diabetes, diabetes, and atherosclerosis were 43.4%, 16.2%, and 10.3%, respectively. On logistic regression analysis, no association of traditional risk factors like BMI, blood pressure and total cholesterol with disease conditions was observed. But urinary levels of metals such as arsenic, chromium, aluminium and zinc showed an association with diabetes while arsenic and zinc showed an association with pre-diabetes and atherosclerosis.

**Conclusions:** Our data suggest a probable role for metals in the etiology of diabetes and cardiovascular diseases in rural communities. Identifying and eliminating the causes of increased levels of these environmental chemicals could have a beneficial impact on the burden of non-communicable diseases in rural population.

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**Polymorphism of Ag_{29}(BDT)_{12}(TPP)_{4}^{3−} cluster: Interactions of secondary ligands and their effect on solid state luminescence**

Abhijit Nag, Papri Chakraborty, Mohammad Bodiuazzaman, Tripti Ahuja, Sudhadevi Antharjanam and T. Pradeep*

*Nanoscale, 10, 2018, 9851–9855 (DOI: 10.1039/C8NR02629G)

**Abstract:** We present the first example of polymorphism (cubic & trigonal) in single crystals of an atomically precise monolayer protected cluster, Ag_{29}(BDT)_{12}(TPP)_{4}^{3−}. We demonstrate that C-H–π interactions of the secondary ligands (TPP) are dominant in a cubic lattice compared to a trigonal lattice, resulting in a greater rigidity of the structure, which in turn, results in higher luminescence efficiency in it.

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**Towards atomically precise luminescent Ag_{2}S clusters separable by thin layer chromatograph**

C. K. Manju, Jyoti Sarita Mohanty, Depanjan Sarkar, Sudhakar Chennu and T. Pradeep*

*J. Mater. Chem. C, 6, 2018, 5754-5759 (DOI: 10.1039/c7tc05858f)*
Abstract: Here, we report the synthesis of monolayer protected, luminescent and atomically precise silver sulfide (Ag$_2$S) clusters. Cluster formation was studied by varying the conditions of the reaction. Matrix assisted laser desorption ionization mass spectrometry (MALDI MS) was used to monitor the growth of clusters to nanoparticles (NPs). Clusters of different nuclearity were obtained at a lower temperature, and were efficiently separated by thin layer chromatography (TLC). One of the clusters was assigned as Ag$_{158}$S$_{79}$(SBB)$_{32}$, where SBB is 4-tert-butylbenzyl mercaptan.

Species-specific uptake of arsenic on confined metastable 2-line ferrihydrite: A combined Raman-XPS investigation of the adsorption mechanism

Chennu Sudhakar, Avula Anil Kumar, Radha Gobinda Bhuin, Soujit Sen Gupta, Ganapati Natarajan, and T. Pradeep*

*ACS Sustain. Chem. Eng., 6(8), 2018, 9990–10000 (DOI: 10.1021/acssuschemeng.8b01217)

Abstract: The present study is targeted towards understanding the interaction between important and technologically relevant polymorphs of iron oxides/oxyhydroxides with arsenic species at neutral pH. The existence of various arsenic (As) species in solution was verified by Raman measurements. Their species-dependent adsorption on the affordable arsenic removal media, confined metastable 2-line ferrihydrite (CM2LF) was investigated. The results were compared with common adsorption media, hematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$). X-ray photoelectron spectroscopy was used to investigate the changes in the core levels of Fe 2p and As 3d resulting from the uptake of arsenic species. Binding of various As species with CM2LF was confirmed by FTIR studies. Raman adsorption data were found to fit a pseudo-second-order model. Results of this study show the synthesized nanocomposite of CM2LF to be very effective for the removal of As(III) and As(V) species in comparison to various materials at neutral pH. A model for the adsorption of As(III) and As(V) species in water on a ferrihydrite particle was developed. This accounted for the large uptake capacity.

Patterned nanobrush nature mimics with unprecedented water harvesting efficiency

Depanjan Sarkar, Anindita Mahapatra, Anirban Som, Ramesh Kumar, Ankit Nagar, Avijit Baidya and T. Pradeep*

**Abstract:** Water scarcity is one of the most alarming problems of the planet. An ambient ion-based method is developed to make hydrophilic-hydrophobic patterned silver nanowires (NWs) as humidity harvesters of unprecedented efficiency. Such water harvesters are developed by two-step surface modification of the as-synthesized NWs (known from a report earlier) using electrospray. These patterned NWs of ≈20 µm length and ≈200 nm width grown over a relatively large area (2 × 2 cm²) exhibit atmospheric water capture (AWC) efficiency of 56.6 L m⁻² d⁻¹, the highest reported so far. The whole fabrication process of the surface is performed under ambient conditions with a home-built nanoelectrospray ion source, without the help of any sophisticated instrumentation. The synthesized material combines and mimics two exciting examples of AWC in nature, which are cactae and Namib Desert beetles, which utilize AWC for their living. It is believed that the combination of the special features of the above two natural species helps to achieve the highest water capture efficiency reported till date. A working prototype using this surface for AWC is also fabricated.

![Diagram of water harvesting](image)

**Bent keto form of curcumin, preferential stabilization of enol by piperine, and isomers of curcumin∩cyclodextrin complexes: Insights from ion mobility mass spectrometry**

Abhijit Nag, Papri Chakraborty, Ganapati Natarajan, Ananya Baksi, Sathish Kumar Mudedla, Venkatesan Subramanian and T. Pradeep*

*Anal. Chem., 90, 2018, 8776–8784 (DOI: 10.1021/acs.analchem.7b05231)*

**Abstract:** A detailed examination of collision cross sections (CCSs) coupled with computational methods has revealed new insights into some of the key questions centered around curcumin, one of the most intensively studied natural therapeutic agents. In this study, we have distinguished the structures and conformers of the well-known enol and the far more elusive keto form of curcumin by using ion mobility mass spectrometry (IM MS). The values of the theoretically predicted isomers were compared with the experimental CCS values to confirm their structures. We have identified a bent structure for the keto form and the degree of bending was estimated. Using IM MS, we have also shown that ESI MS reflects the solution phase structures and their relative populations, in this case. Piperine, a naturally occurring heterocyclic compound, is known to increase the bioavailability of curcumin. However, it is still not clearly understood which tautomeric form of curcumin is better stabilized by it. We have identified preferential stabilization of the
Cyclodextrins (CDs) are used as well-known carriers in the pharmaceutical industry for increasing the stability, solubility, bioavailability, and tolerability of curcumin. However, the crystal structures of supramolecular complexes of curcumin∩CD are unknown. We have determined the structures of different isomers of curcumin∩CD (α- and β-CD) complexes by comparing the CCSs of theoretically predicted structures with the experimentally obtained CCSs, which will further help in understanding the specific role of the structures involved in different biological activities.

**Electrohydrodynamic assembly of ambient ion-derived nanoparticles to nanosheets at liquid surfaces**

Depanjan Sarkar, Rajesh Singh, Anirban Som, C. K. Manju, Mohd Azhardin Ganayee, Ronojoy Adhikari, and T. Pradeep*

*J. Phys. Chem. C, 122, 2018, 17777−17783 (DOI: 10.1021/acs.jpcc.8b04169)*

**Abstract:** We describe an ambient ion-based method to create free-standing metal nanosheets, which in turn are composed of nanoparticles of the corresponding metal. These nanoparticle-nanosheets (NP-NSs) were formed by the electrospray deposition (ESD) of metal ions on a liquid—air interface leading to nanoparticles that self-organize under the influence of electrohydrodynamic flows, driven by the electric field induced by the applied potential. Such a two-dimensional organization of noble metals is similar to the assembly of molecules at liquid—air interface and has the possibility of creating a category of new materials useful for diverse applications. Enhanced catalytic activity of the formed NP-NSs for Suzuki–Miyaura coupling reaction was demonstrated, which was attributed to their large surface-to-volume ratios.

**Preparation of gas phase naked silver cluster cations outside a mass spectrometer from ligand protected clusters in solution**


*Nanoscale, 10, 2018, 15714–15722 (DOI: 10.1039/c8nr04146f)*

**Abstract:** Gas phase clusters of noble metals, prepared by laser desorption from the bulk have been investigated extensively in vacuum using mass spectrometry. However, such clusters have not been known to exist in ambient conditions till date. In our previous work, we have shown that in-source
fragmentation of ligands can be achieved starting from hydride and phosphine co-protected silver clusters leading to naked silver clusters inside the mass spectrometer. In a recent series of experiments, we have found that systematic desorption of ligands of the monolayer protected atomically precise silver cluster can also occur in the atmospheric gas phase. Here, we present the results, wherein, $[\text{Ag}_{18}\text{H}_{16}(\text{TPP})_{10}]^{2+}$ (TPP = triphenylphosphine) cluster results in the formation of naked cluster, $\text{Ag}_{17}^+$ along with $\text{Ag}_{18}\text{H}^+$ without mass selection, outside the mass spectrometer, in air. These cationic naked metal clusters are made by passing electrosprayed ligand protected clusters through a heated tube, in the gas phase. Reactions with oxygen suggest $\text{Ag}_{17}^+$ to be more reactive than $\text{Ag}_{18}\text{H}^+$, in agreement with their electronic structures. The more common thiolate protected clusters produce fragments of metal thiolates under identical processing conditions and no naked clusters were observed.

Detection of $[\text{Au}_{25}(\text{PET})_{18}(\text{O}_2)_n]^-(n = 1, 2, 3)$ Species by Mass Spectrometry

Shridevi Bhat, Raghu Narayanan, Ananya Baksi, Papri Chakraborty, Ganesan Paramasivam, Rabin Methikkalam, Abhijit Nag, Ganapati Natarajan, and T. Pradeep*


Abstract: $[\text{Au}_{25}(\text{SR})_{18}]^-$ nanoclusters have been tested as a model catalyst in multiple oxidation reactions involving CO, alkenes, cyclohexane, and alcohols. Oxygen is used as an oxidizing agent in most of the reactions. Hence, $\text{O}_2$ activation is of great interest in catalysis. The mechanism of these reactions, the role of intact nanoclusters as catalytically active species, and the utility of such nanoclusters as homogeneous catalysts are not completely clear. Herein, we investigate the interaction of $[\text{Au}_{25}(\text{SR})_{18}]^-$ in solution with $\text{O}_2$ using electrospray ionization mass spectrometry and density functional theory (DFT) calculations. Up to three $\text{O}_2$ molecules attach to an $[\text{Au}_{25}(\text{SR})_{18}]^-$ in dichloromethane (DCM) when $\text{O}_2$ gas is passed through a solution of the former. Oxygen addition to the nanocluster leads to its decomposition. The nanocluster is most stable in toluene and least stable in tetrahydrofuran when kept under a continuous flow of $\text{O}_2$, where no $\text{O}_2$ adduct peaks are observed. It shows intermediate stability in DCM in the presence of $\text{O}_2$, and the decomposition products, in this case, are of a different type compared to the former solvents. The appearance of $\text{O}_2$ adducts and the variation in the stability of the nanocluster in different solvents is assumed to be due to the difference in oxygen solubility.
in these solvents. DFT calculations suggest that the first two O2 molecules interact with the surface Au atoms through the cavities formed by the ligands and staples in the nanocluster and the third O2 interacts only with 2-phenylethane thiol ligands.

**Holey MoS_2 Nanosheets with Photocatalytic Metal Rich Edges by Ambient Electrospray Deposition for Solar Water Disinfection**

Depanjan Sarkar, Biswajit Mondal, Anirban Som, Swathy Jakka Ravindran, Sourav Kanti Jana, C. K. Manju and T. Pradeep*

*Global Challenges, 2018, 1800052 (https://doi.org/10.1002/gch2.201800052)*

**Abstract:** We introduce a new method for creating nanopores in single layer molybdenum disulfide (MoS_2) nanosheets (NSs) by the electrospray deposition (ESD) of silver ions on a water suspension of the former. Electrospray deposited silver ions react with the MoS_2 NSs at the liquid-air interface resulting in Ag_2S nanoparticles (NPs) which goes into the solution leaving the NSs with holes of 3-5 nm diameter. Specific reaction with the S of MoS_2 NSs leads to Mo-rich edges. Such Mo-rich defects are highly efficient for the generation of active oxygen species such as H_2O_2 under visible light, which causes efficient disinfection of water. We show 10^5 times higher efficiency in disinfection for the holey MoS_2 NSs in comparison to normal MoS_2 NSs. Experiments have been performed with multiple bacterial strains and a virus strain, demonstrating the utility of the method for practical applications. A conceptual prototype is also presented.

**Monolayer-Protected Noble-Metal Clusters as Potential Standards for Negative-Ion Mass Spectrometry**

Ananya Baksi, Papri Chakraborty, Abhijit Nag, Debasmita Ghosh, Shridevi Bhat and T. Pradeep

*Anal. Chem., 90, 2018, 11351-11357 (DOI: 10.1021/acs.analchem.8b02280)*

**Abstract:** A detailed mass-spectrometric study of atomically precise monolayer-protected clusters revealed the potential application of such materials as mass-spectrometric standards, mostly in negative-ion mode and in the high-mass range. To date, very few molecules are known that can be efficiently ionized and detected at lower concentrations as negative ions with...
high signal intensities beyond m/z 3000. Noble-metal clusters are molecules with definite masses, sizes, and shapes, which makes them excellent candidates to choose as standards over conventional low-molecular-weight polymers or clusters of ionic salts. They may be used as calibrants in all possible modes, including tandem mass spectrometry and ion mobility. With the advancement in materials science, more and more molecules are being added to the list that are inherently negatively charged in solution and can be examined by mass spectrometry. In this report, we demonstrate the use of three such model cluster systems for their potential to calibrate mass spectrometers in negative-ion mode. This idea can be extended to many other clusters known so far to achieve calibration in extended mass ranges.

**Atomically precise cluster-based white light emitters**

Esma Khatun, Sandeep Bose, Madhuri Jash, and T. Pradeep*


**Abstract:** Materials emitting white luminescence are receiving increasing attention due to their potential applications in electroluminescent devices, information displays and fluorescent sensors. To produce white light, one must have either three primary colors, blue, green and red or two colors, blue and orange. In this paper, we have used thiol/phosphine protected red luminescent silver nanoclusters (Ag NCs), [Ag{sub 29}(BDT){sub 12}(PPh{sub 3}){sub 4}]^{3-} (BDT=1,3-benzenedithiol), [Au{sub x}Ag{sub 29-x}(BDT){sub 12}(PPh{sub 3}){sub 4}]^{x-} and Ag{sub 29}(LA){sub 12} (LA= lipoic acid) as one of the fluorophores for white light emission. These clusters are mixed with blue luminescent silicon nanoparticles (Si NPs) and green luminescent fluorescein isothiocyanate (FITC). The mixtures show white luminescence with CIE coordinates of (0.31, 0.34), (0.33, 0.35) and (0.29, 0.31) which are in good agreement with pure white light (0.33, 0.33). The other clusters with yellow, blue, orange, etc., luminescence can also be used to make white light. This work provides a prospective pathway for white light emission based on atomically precise noble metal nanoclusters.

**Thirty-fold photoluminescence enhancement induced by secondary ligands in monolayer protected silver clusters**

Esma Khatun, Atanu Ghosh, Papri Chakraborty, Priya Singh, Mohammad Bodiuazzaman, Ganesan Paramasivam, Ganapati Nataranjan, Jyotirmoy Ghosh, Samir Kumar Pal, and T. Pradeep*

*Nanoscale, 10, 2018, 20033-20042 (DOI: 10.1039/C8NR05989F)*

**Abstract:** In this paper, we demonstrate that systematic replacement of secondary ligand, PPh{sub 3} leads to enhancement in the near-infrared (NIR) photoluminescence (PL) of [Ag{sub 29}(BDT){sub 12}(PPh{sub 3}){sub 4}]^{3-}. While replacement of PPh{sub 3} with other monophosphines enhances luminescence slightly,
replacement with diphosphines of increasing chain length leads to drastic PL enhancement, as high as 30 times than the parent cluster, $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{-3}$. Computational modeling suggests that the emission is a ligand to metal charge transfer (LMCT) which is affected by the nature of the secondary ligand. Control experiments with systematic replacement of secondary ligand confirm the influence of it in the emission. The excited state dynamics shows this emission to be phosphorescence in nature which arises from the triplet excited state. This enhanced luminescence has been used to develop a prototypical $\text{O}_2$ sensor. Moreover, a similar enhancement was also found for $[\text{Ag}_{51}(\text{BDT})_{19}(\text{PPh}_3)_3]^{-3}$. The work presents an easy approach to the PL enhancement of Ag clusters for various applications.

Isomerism in supramolecular adducts of atomically precise nanoparticles

Abhijit Nag, Papri Chakraborty, Ganesan Paramasivam, Mohammad Bodiuazzaman, Ganapati Natarajan and T. Pradeep*

*J. Am. Chem. Soc., 140, 2018, 13590–13593 (DOI:10.1021/acs.jpcc.7b04559)*

Abstract: We present isomerism in a few supramolecular adducts of atomically precise nanoparticles, $[\text{Ag}_{29}(\text{BDT})_{12} \cap (\text{CD})_n]^{-3} \ (n = 1 - 6)$, abbreviated as I where BDT and CD are 1, 3-benzenedithiol and cyclodextrins ($\alpha$, $\beta$ and $\gamma$), respectively; $\cap$ symbolizes an inclusion complex. The different host-guest complexes of I were characterized in the solution state as well as in the gas phase. The CDs ($\alpha$, $\beta$ and $\gamma$) encapsulate a pair of BDT ligands protecting the $\text{Ag}_{29}$ core. This unique geometry of the supramolecular adducts makes the system similar to octahedral complexes of transition metals, which manifest various isomers. These isomers of I ($n = 2 - 4$) were separated by ion mobility mass spectrometry (IM MS). We proposed structures of all the inclusion complexes with the help of IM MS measurements and molecular docking, density functional theory (DFT), and collision cross section (CCS) calculations.

Camouflaging structural diversity: co-crystallization of two different nanoparticles having different cores but the same shell

Mohammad Bodiuazzaman, Aranu Ghosh, Korath Shivan Sugi, Abhijit Nag, Esma Khatun, Babu Varghese, Ganesan Paramasivam, Sudhadevi Antharjanam, Ganapati Natarajan, and T. Pradeep*

Abstract: Two ligand protected new nanoscale pieces of silver - namely, \([\text{Ag}_{46}(\text{SPhMe}_2)_{24}(\text{PPh}_3)_8](\text{NO}_3)_2\) and \([\text{Ag}_{40}(\text{SPhMe})_{24}(\text{PPh}_3)_8](\text{NO}_3)_2\) (abbreviated as \(\text{Ag}_{46}\) and \(\text{Ag}_{40}\), respectively) with almost the same shell but different cores were synthesized simultaneously. As their external structures were identical, the clusters were not able to distinguish each other separately and they got crystallized in the same crystal. The occupancy of each cluster was 50% in the co-crystal. The outer shell of both the clusters is composed of \(\text{Ag}_{32}\text{S}_{24}\text{P}_8\) which is reminiscent of fullerenes, and it encapsulates a well-studied core, \(\text{Ag}_{14}\) and a completely new core, \(\text{Ag}_8\) which correspond to a face-centred cube and a simple cube, respectively resulting in the \(\text{Ag}_{46}\) and \(\text{Ag}_{40}\) clusters. The presence of two entities (\(\text{Ag}_{40}\) and \(\text{Ag}_{46}\) clusters) in a single crystal and their molecular formulae were confirmed by detailed electrospray ionization mass spectrometry. The optical spectrum of the mixture showed unique features which were in good agreement with the results from time-dependent density functional theory (TD-DFT). Camouflaging diverse cores of this kind with unique shell may present a new paradigm in well-defined composite materials, leading to new properties.

Approaching materials with atomic precision using supramolecular cluster assemblies

Papri Chakraborty, Abhijit Nag, Amrita Chakraborty, and T. Pradeep*

*Acc. Chem. Res., 2018 (DOI: 10.1021/acs.accounts.8b00369)

Conceptus: Supramolecular chemistry is a major area of chemistry that utilizes weaker non-covalent interactions between molecules, including hydrogen bonding, van der Waals, electrostatic, \(\pi\cdots\pi\), and \(\text{C}-\text{H}\cdots\pi\) interactions. Such forces have been the basis of several molecular self-assemblies and host–guest complexes in organic, inorganic, and biological systems. Atomically precise nanoclusters (NCs) are materials of growing interest that display interesting structure–property correlations. The evolving science of such systems reaffirms their molecular behavior. This gives a possibility of exploring their supramolecular chemistry, leading to assemblies with similar or dissimilar cluster molecules. Such assemblies with compositional, structural, and conformational precision may ultimately result in cluster-assembled hybrid materials. In this Account, we present recent advancements on different possibilities of supramolecular interactions in atomically precise cluster systems that can occur at different length scales. We first present a brief discussion of the aspicule model of clusters, considering \(\text{Au}_{25}(\text{SR})_{18}\) as an example, that can explain various aspects of its atomic precision and distinguish the similar or dissimilar interacting sites in their structures. The supramolecular interaction of 4-tert-butylbenzyl mercaptan (BBSH)-protected \([\text{Au}_{25}(\text{SBB})_{18}]^{-}\) NCs with cyclodextrins (CD) to form \(\text{Au}_{25}\text{SBB}_{18}\cap\text{CD}_n\) \((n = 1–4)\) and that of \([\text{Ag}_{29}(\text{BDT})_{12}]^{3-}\) with fullerenes to form \([\text{Ag}_{29}(\text{BDT})_{12}(C_{60})_n]^{3-}\) \((n = 1–9)\) (BDT = 1,3-benzenedithiolate) are discussed subsequently. The formation of these adducts was studied by electrospray ionization mass spectrometry (ESI MS), optical absorption and NMR spectroscopy. In the subsequent
sections, we discuss how variation in intercluster interactions can lead to polymorphic crystals, which are observable in single-crystal X-ray diffraction. Taking $[\text{Ag}_{29} (\text{BDT})_{12} (\text{TPP})_4]^{3-}$ (TPP = triphenylphosphine) clusters as an example, we discuss how the different patterns of C–H···π and π···π interactions between the secondary ligands can alter the packing of the NCs into cubic and trigonal lattices. Finally, we discuss how the supramolecular interactions of atomically precise clusters can result in their hybrid assemblies with plasmonic nanostructures. The interaction of p-mercaptobenzoic acid (p-MBA)-protected Ag$_{44}$(p-MBA)$_{30}$ NCs with tellurium nanowires (Te NWs) can form crossed-bilayer precision assemblies with a woven-fabric-like structure with an angle of 81° between the layers. Similar crossed-bilayer assemblies show an angle of 77° when Au$_{102}$(pMBA)$_{44}$ clusters are used to form the structure. Such assemblies were studied by transmission electron microscopy (TEM).

Precision in these hybrid assemblies of Te NWs was highly controlled by the geometry of the ligands on the NC surface. Moreover, we also present how Ag$_{44}$(p-MBA)$_{30}$ clusters can encapsulate gold nanorods to form cage-like nanostructures. Such studies involved TEM, scanning transmission electron microscopy (STEM), and three-dimensional tomographic reconstructions of the nanostructures. The hydrogen bonding interactions of the −COOH groups of the p-MBA ligands were the major driving force in both of these cases. An important aspect that is central to the advancement of the area is the close interplay of molecular tools such as MS with structural tools such as TEM along with detailed computational modeling. We finally conclude this Account with a future perspective on the supramolecular chemistry of clusters. Advancements in this field will help in developing new materials with potential optical, electrical, and mechanical properties.

**Appearance of SERS activity in single silver nanoparticles by laser-induced reshaping**

Kamalesh Chaudhari, Tripti Ahuja, Vasanthanarayan Murugesan, Vidhya Subramanian, Mohd Azhardin Ganayee, Thomas Thundat, and T. Pradeep*


**Abstract:** We report simultaneous plasmonic scattering and Raman spectroscopic observations of single citrate capped silver nanoparticles (AgNPs) which exhibit surface enhanced Raman scattering (SERS) upon meeting specific conditions induced by laser (532 nm) exposure. We show that nanoparticles which are not initially SERS active become SERS active by laser-induced reshaping/reorientation. A set-up developed for these observations enabled in-situ high speed time-lapse characterization using plasmonic and Raman spectroscopies in conjunction with dark-field microscopy (DFM). Changes in the AgNPs were confirmed by monitoring plasmonic scattering spectra and DFM images. Time-lapse observations have shown
that laser-induced changes in the plasmonic properties of AgNPs resulted in the appearance of SERS. Spectral matching between plasmon resonance and downward molecular vibronic transitions for molecules adsorbed on the surface of plasmonic nanomaterials is attributed to the nanoparticle SERS. We have further shown that release of silver ions by silver nanoparticles can be the probable reason for their plasmonic changes. Gold nanoparticles inert to such mild (850 µW, 532 nm) laser-induced changes do not exhibit appearance of SERS.

Rapid isotopic exchange in nanoparticles

Papri Chakraborty, Abhijit Nag, Ganapati Natarajan, Nayanika Bandyopadhyay, Ganesan Paramasivam, Manoj Kumar Panwar, Jaydeb Chakrabarti, T. Pradeep*

Sci. Adv., 2019; 5: eaau7555

Abstract: Rapid solution-state exchange dynamics in nanoscale pieces of matter is revealed, taking isotopically pure atomically precise clusters as examples. As two isotopically pure silver clusters made of $^{107}$Ag and $^{109}$Ag are mixed, an isotopically mixed cluster of the same entity results, similar to the formation of HDO, from H$_2$O and D$_2$O. This spontaneous process is driven by the entropy of mixing and involves events at multiple time scales.

Metal-ligand interface in the chemical reactions of ligand protected noble metal clusters

K. R. Krishnadas, Ganapati Natarajan, Ananya Baksi, Atanu Ghosh, Esma Khatun and T. Pradeep*

Langmuir, 2018, (DOI: 10.1021/acs.langmuir.8b03493)

Abstract: We discuss the role of the metal–ligand (M–L) interfaces in the chemistry of ligand-protected, atomically precise noble metal clusters, a new and expanding family of nanosystems, in solution as well as in the gas phase. A few possible mechanisms by which the structure and dynamics of M–L interfaces could trigger intercluster exchange reactions are presented first. How interparticle chemistry can be a potential
mechanism of Ostwald ripening, a well-known particle coarsening process, is also discussed. The reaction of $\text{Ag}_{32}(2,5-\text{DCBT})_{32}$ ($\text{DCBT} = \text{dichlorobenzenethiol}$) with $2,4-\text{DCBT}$ leading to the formation of $\text{Ag}_{44}(2,4-\text{DCBT})_{30}$ is presented, demonstrating the influence of the ligand structure in ligand-induced chemical transformations of clusters. We also discuss the structural isomerism of clusters such as $\text{Ag}_{44}(\text{SR})_{30}$ ($\text{SR} = \text{alkyl/aryl thiolate}$) in the gas phase wherein the occurrence of isomerism is attributed to the structural rearrangements in the M–L bonding network. Interfacial bonding between $\text{Au}_{25}(\text{SR})_{18}$ clusters leading to the formation of cluster dimers and trimers is also discussed. Finally, we show that the desorption of phosphine and hydride ligands on a silver cluster, $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$ ($\text{TPP} = \text{triphenylphosphine}$) in the gas phase, leads to the formation of a naked silver cluster of precise nuclearity, such as $\text{Ag}_{17}^+$. We demonstrate that the nature of the M–L interfaces, i.e., the oxidation state of metal atoms, structure of the ligand, M–L bonding network, and so forth, plays a key role in the chemical reactivity of clusters. The structure, dynamics, and chemical reactivity of nanosystems in general are to be explored together to obtain new insights into their emerging science.

Sustainable and affordable composites built using microstructures performing better than nanostructures for arsenic removal

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Abstract: Arsenicosis was recognized over 104 years ago. Elevated arsenic (As) concentrations in water is faced by about 200 million people worldwide, and has become one of the biggest challenges in the context of water purification. Providing sustainable and affordable solutions to tackle this menace is a need of the hour. Adsorption on advanced materials is increasingly being recognized as a potential solution. Here, we report various functionalized microcellulose-reinforced 2-line ferrihydrite composites which show outstanding As (III) and As(V) adsorption capacities. Green synthesis of the composite yields granular media with high mechanical strength which show faster adsorption kinetics in a wide pH range, irrespective of the presence of other interfering ions in water. The composites and their interaction with As (III) and As(V) were studied by XRD, HRTEM, SEM, XPS, Raman, TG and IR spectroscopy. Performance of the media in the form of cartridge reaffirms its utility for point-of-use water purification. We show that cellulose microstructures are more efficient than corresponding nanostructures for the purpose of arsenic remediation. We have also performed an evaluation of several sustainability metrics to understand the “greenness” of the composite and its manufacturing process.
Clathrate hydrates in interstellar environment
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Abstract: Clathrate hydrates (CHs) are ubiquitous in earth, under high-pressure conditions but their existence in the interstellar medium (ISM) remains unknown. Here we report experimental observations of the formation of methane and carbon dioxide hydrates in an environment analogous to ISM. Thermal treatment of solid methane and carbon dioxide-water mixture in ultra-high vacuum of the order of 10^{-10} mbar for extended periods, led to the formation of CHs at 30 and 10 K, respectively. High molecular mobility and H-bonding play important roles in the entrapment of gases in the in-situ formed 5^{12} CH cages. This finding implies that CHs can exist in extreme low-pressure environments present in the ISM. These hydrates in ISM, subjected to various chemical processes may act as sources for relevant prebiotic molecules.

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