



Since 1959

Open Questions in Cluster Research

Thalappil Pradeep

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Co-founder

InnoNano Research Pvt. Ltd.

InnoDI Water Technologies Pvt. Ltd.

VayuJAL Technologies Pvt. Ltd.

Aqueasy Innovations Pvt. Ltd.

Hydromaterials Pvt. Ltd.

EyeNetAqua Pvt. Ltd.

Deepspectrum Analytics Pvt. Ltd.

Professor-in-charge



International Centre for Clean Water





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DST-JSPS Joint Workshop on Atomically Precise Materials for Sustainability, Chennai, February 1-3, 2025

Atomically Precise Clusters of Noble Metals: Emerging Link between Atoms and Nanoparticles

Indranath Chakraborty[†] and Thalappil Pradeep^{*}

DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

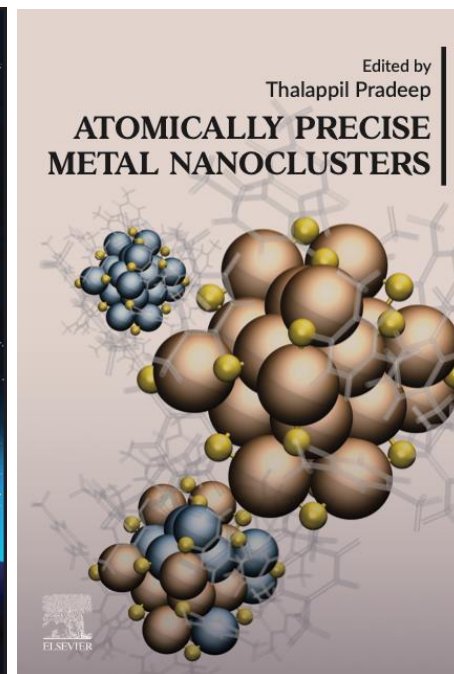
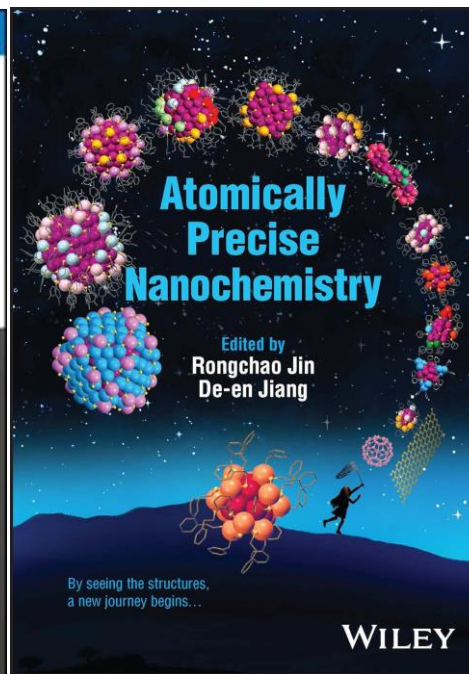
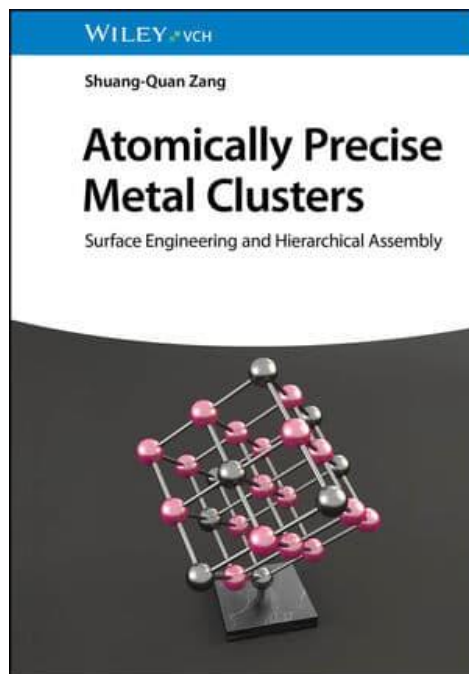
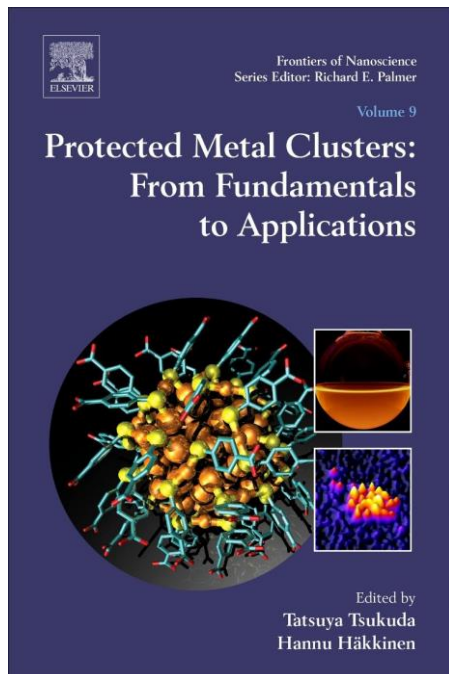
Supporting Information

ABSTRACT: Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$, and $\text{Au}_{102}(\text{SR})_{44}$ as well as $\text{Ag}_{25}(\text{SR})_{18}$, $\text{Ag}_{29}(\text{S}_2\text{R})_{12}$, and $\text{Ag}_{44}(\text{SR})_{30}$ (often with a few counterions to compensate charges) are known now. They can be made reproducibly with robust synthetic protocols, resulting in colored solutions, yielding powders or diffractable crystals. They are distinctly different from nanoparticles in their spectroscopic properties such as optical absorption and emission, showing well-defined features, just like molecules. They show isotopically resolved molecular ion peaks in mass spectra and provide diverse information when examined through multiple instrumental methods. Most important of these properties is luminescence, often in the visible–near-infrared window, useful in biological applications. Luminescence in the visible region, especially by clusters protected with proteins, with a large Stokes shift, has been used for various sensing applications, down to a few tens of molecules/ions, in air and water. Catalytic properties of clusters, especially oxidation of organic substrates, have been examined. Materials science of these systems presents numerous possibilities and is fast evolving. Computational insights have given reasons for their stability and unusual properties. The molecular nature of these materials is unequivocally manifested in a few recent studies such as intercluster reactions forming precise clusters. These systems manifest properties of the core, of the ligand shell, as well as that of the integrated system. They are better described as protected molecules or *aspicules*, where *aspis* means shield and *cules* refers to molecules, implying that they are “shielded molecules”. In order to understand their diverse properties, a nomenclature has been introduced with which it is possible to draw their structures with positional labels on paper, with some training. Research in this area is captured here, based on the publications available up to December 2016.

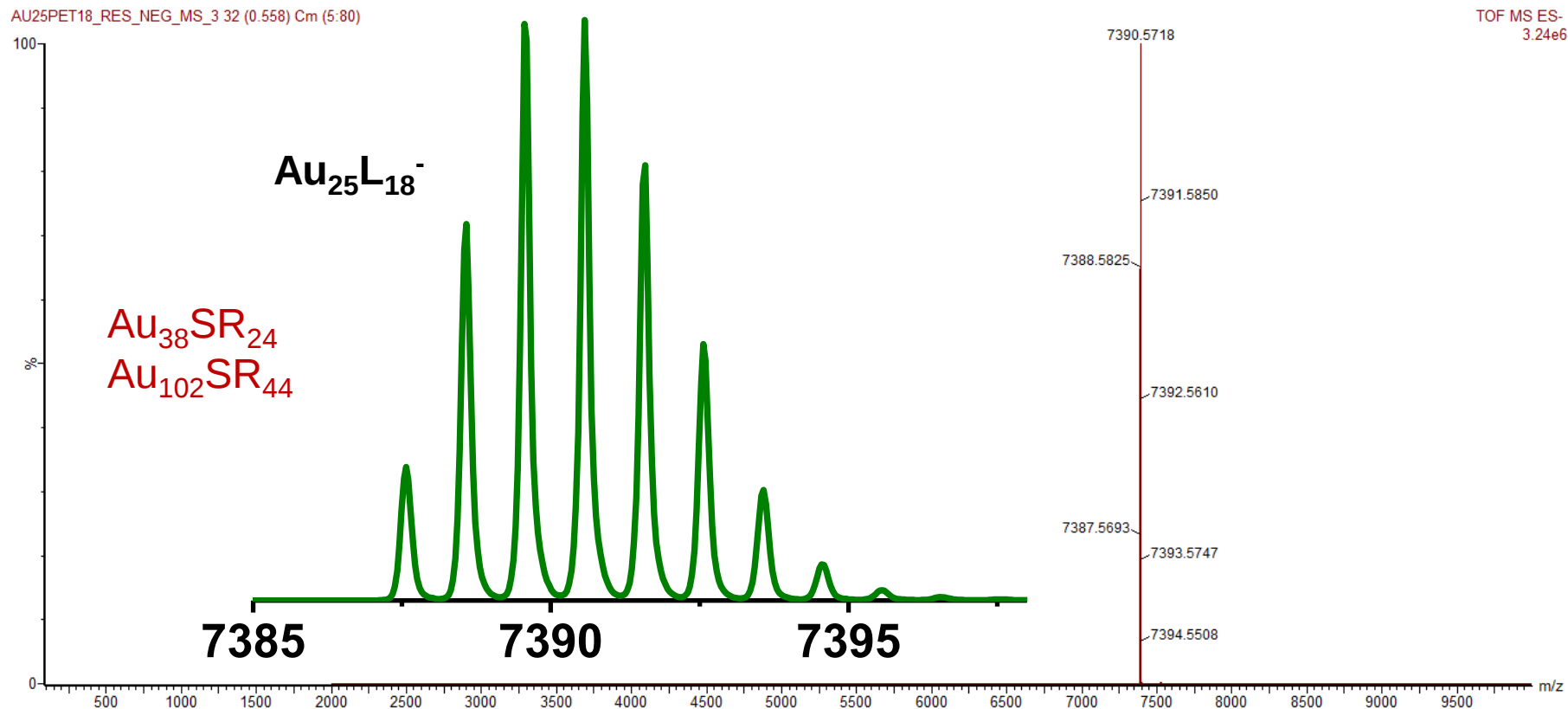


Based on the pioneering work of R. W. Murray, Robert L. Whetten, Uzi Landman, Tatuya Tsukuda, Yuichi Negishi, Hannu Hakkinen, Rongchao Jin, Nanfeng Zheng, Terry Bigioni, Osman Bakr, Kornberg, Jianping Xie, C. M. Aikens, Thomas Buergi, Amala Dass, Ackerson, De-en Jiang, Sukhendu Mandal, Christine Aikens, A. W. Castleman Jr., H. Schmidbauer, Robin Ras, Olli Jukkala,...

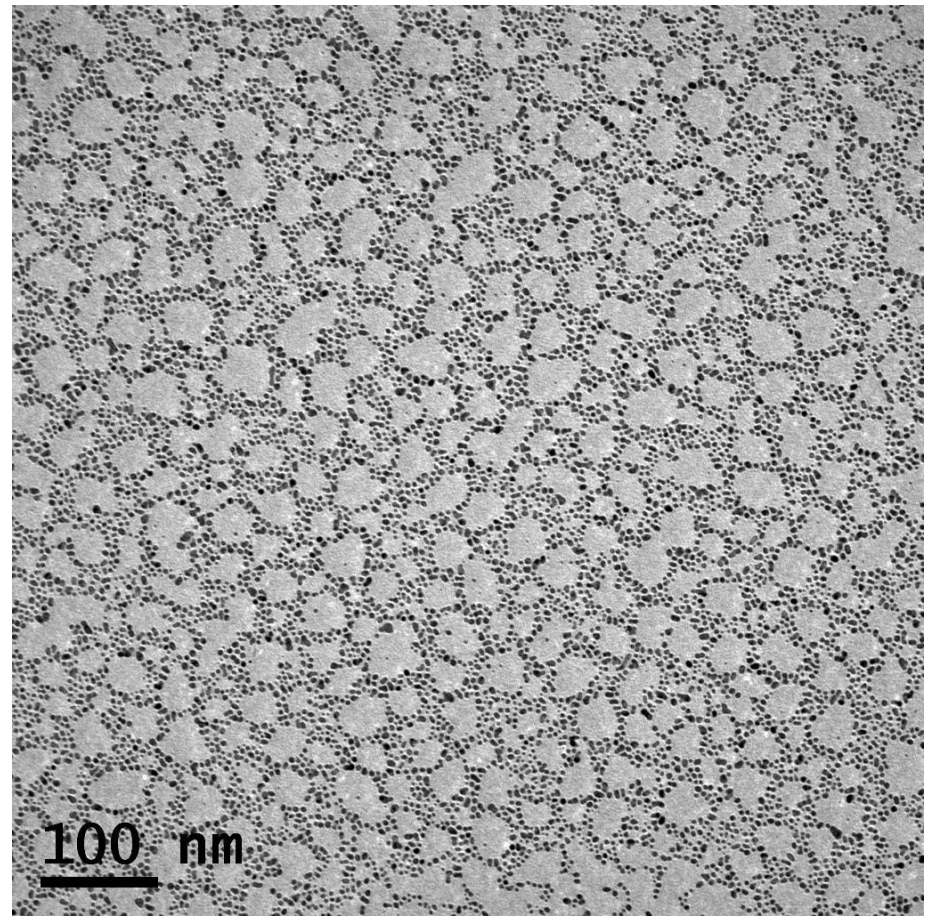
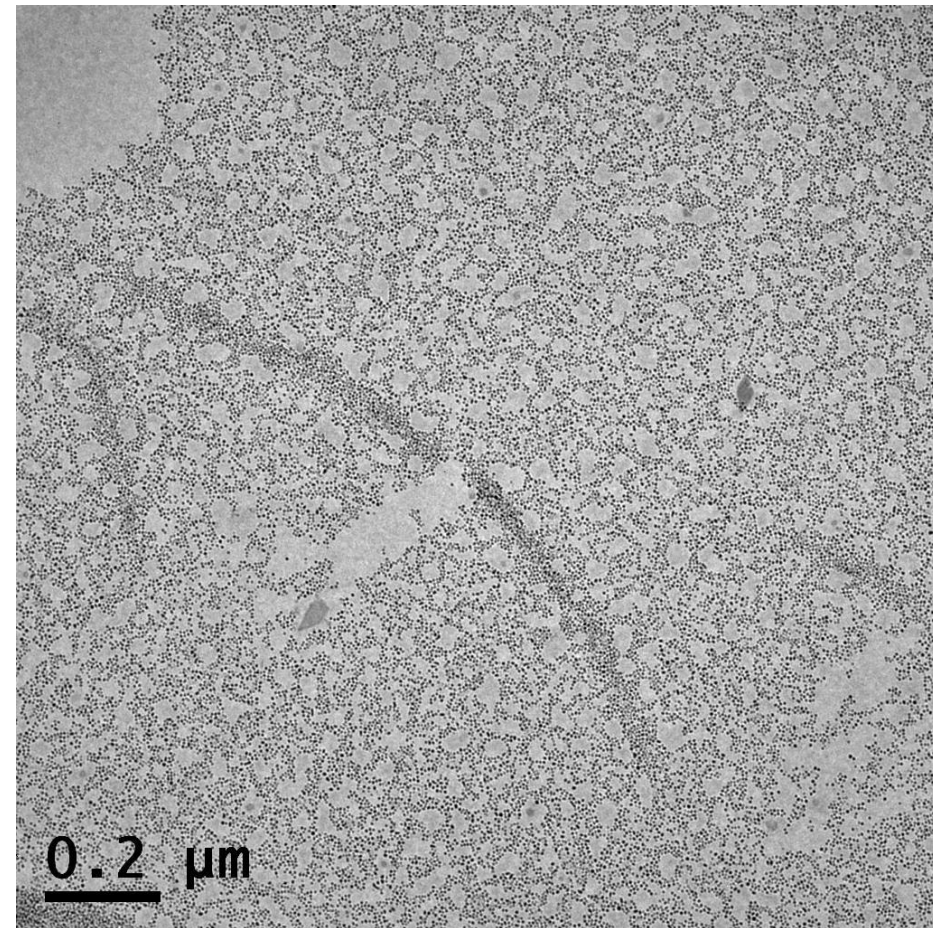
The area has exploded



Molecular formula, Molecular weight



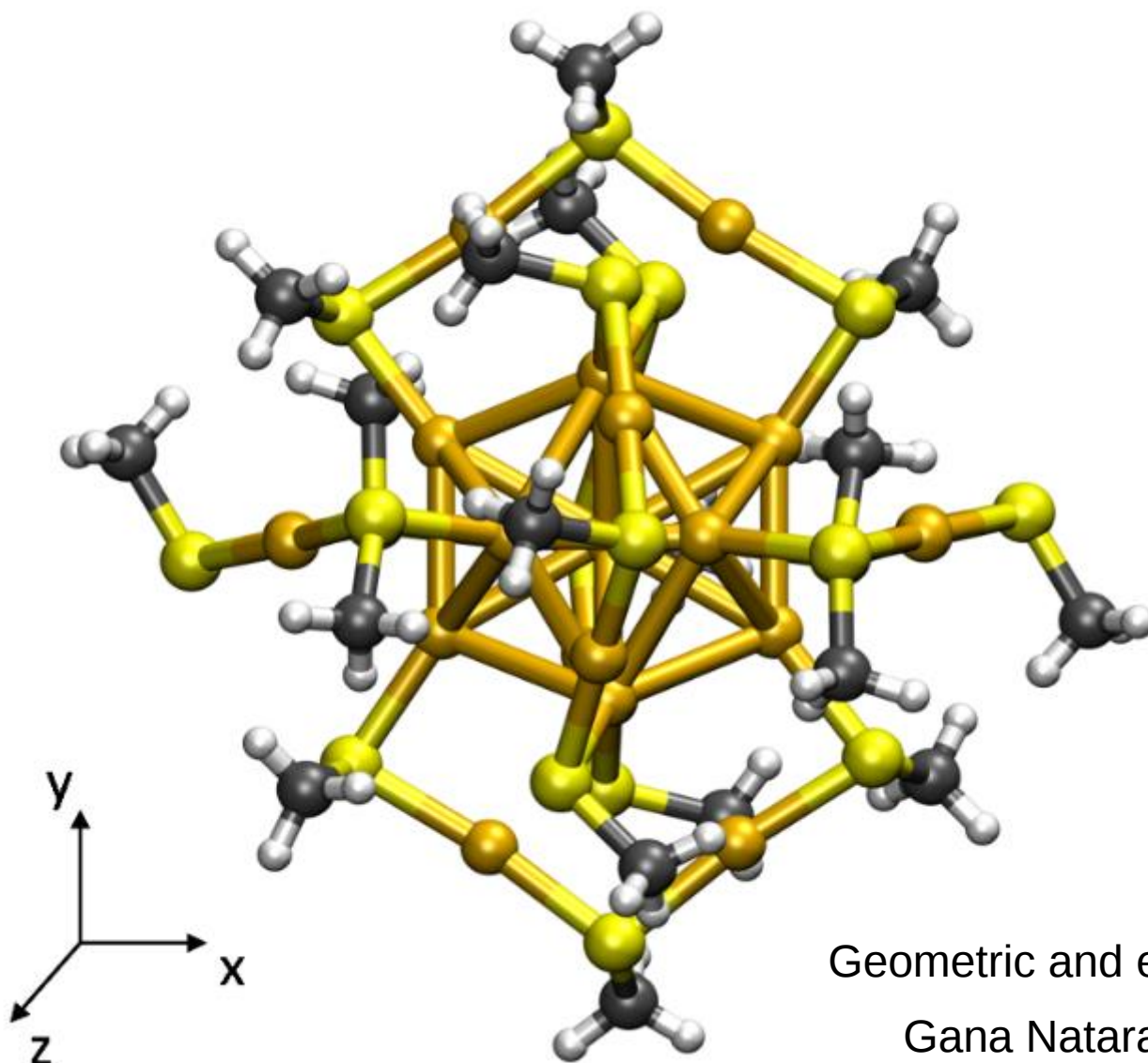
Seeing them - Au₂₅ and Au₁₄₄



They make high quality crystals

50 μm

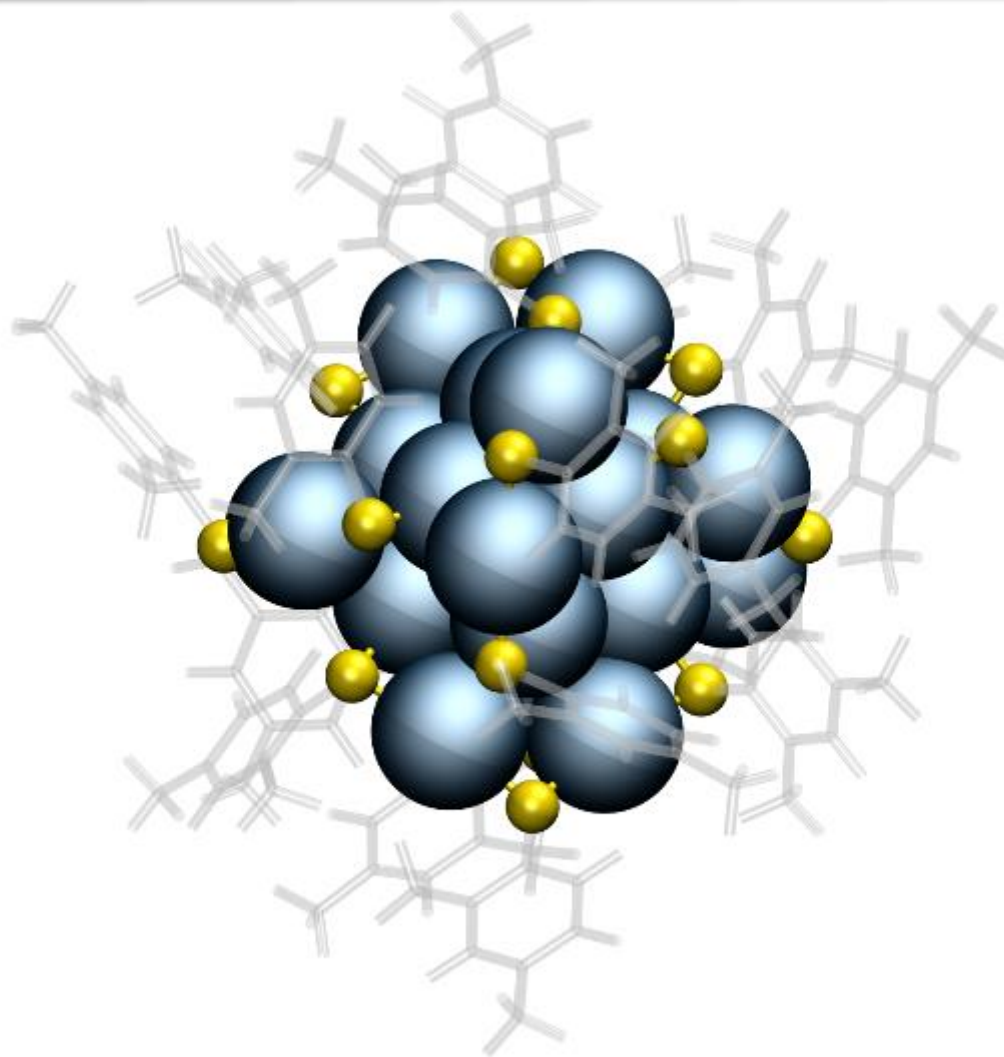
Molecular structure



Geometric and electronic shells

Gana Natarajan

Molecules, but...



Molecular materials

ACCOUNTS

of chemical research

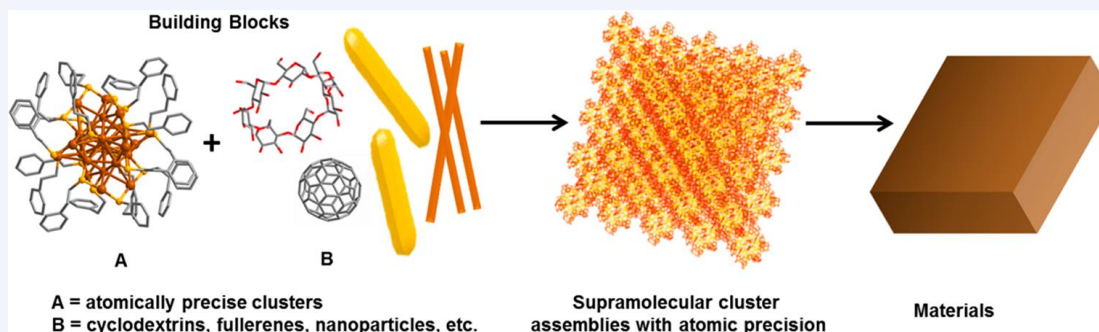
Article

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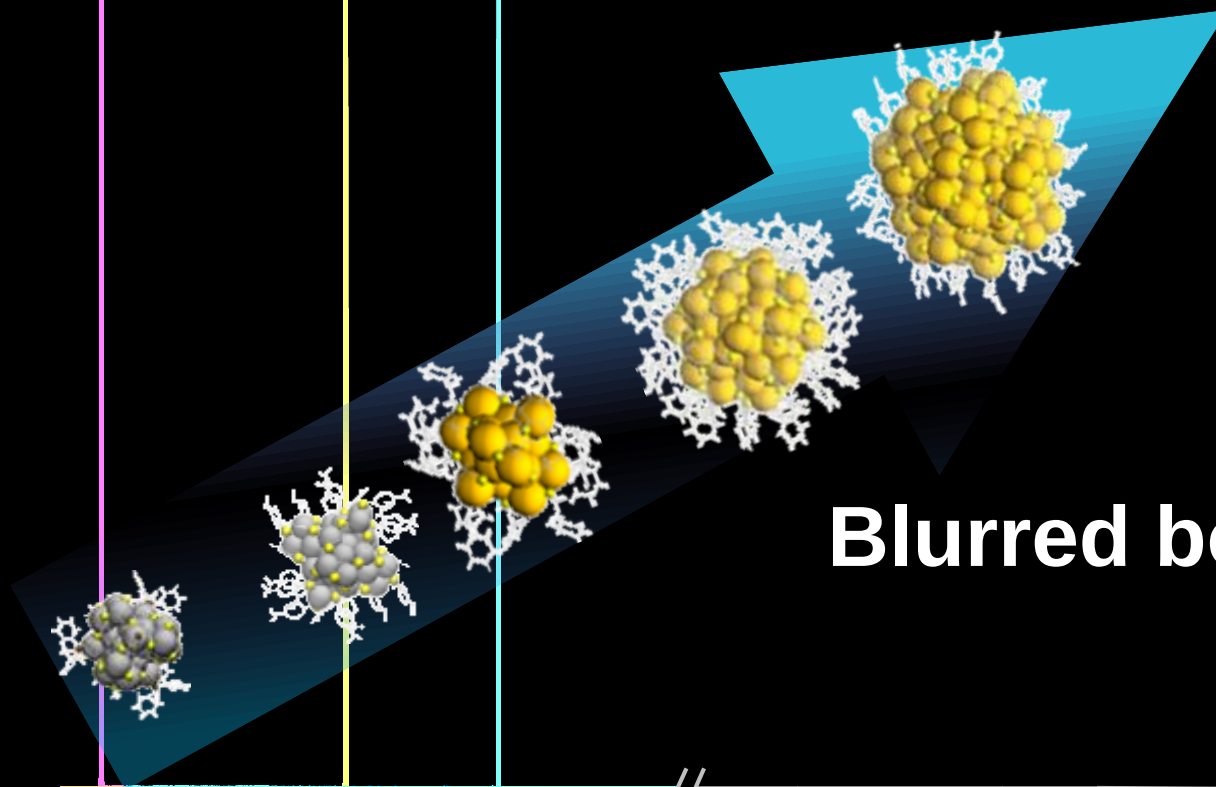
Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

Papri Chakraborty, Abhijit Nag, Amrita Chakraborty, and Thalappil Pradeep*

DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India



$\text{Ag}_{29}(\text{BDT})_{12}^{3-}$ $\text{Ag}_{25}(\text{DMBT})_{18}^{-}$ $\text{Au}_{25}(\text{PET})_{18}^{-}$



Blurred boundary

2000 4000 6000 8000 20000 40000 60000

m/z

Formula, structure and spectroscopy

Challenge 1. We do not know enough

Structures – we have over 300, yet...

Protein protected clusters?

Molecules and their properties

Chemical formula	H ₂ O
Molecular weight	18.0148
Critical temperature	373.91°C
Critical pressure	22.05 MPa
Critical density	315.0 kg/m ³
Triple point temperature	0.01°C
Triple point pressure	615.066 Pa
Normal boiling point	100.0°C
Normal freezing point	0.0°C
Density of ice at normal melting point	918.0 kg/m ³
Maximum density, 3.98°C	999.973 kg/m ³
Viscosity, 25°C	0.889 mN s/m ²
Surface tension, 25°C	72 mN/m
Heat Capacity, 25°C	4.1796 kJ/kg.K
Enthalpy of vaporisation, 100°C	2,257.7 kJ/kg
Enthalpy of fusion, 0°C	333.8 kJ/kg
Velocity of sound, 0°C	1.403 km/s
Dielectric constant, 25°C	78.40
Electrical conductivity, 25°C	8 µS/m
Refractive index, 25°C	1.333
Liquid compressibility, 10°C	480. × 10 ⁻¹² m ² /N
Coefficient of thermal expansion, 25°C	256.32 × 10 ⁻⁶ K ⁻¹
Thermal Conductivity, 25°C	0.608 W/m.K

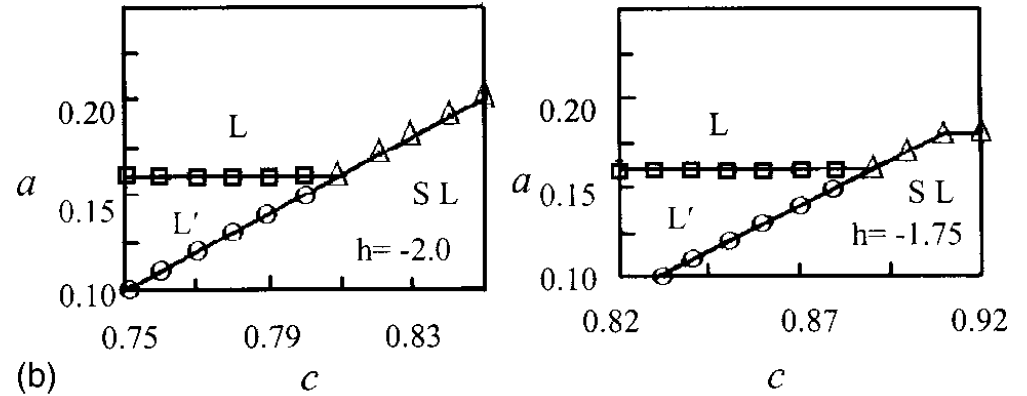
Molecular formula
Molecular weight
Molecular structure
Molecular absorption and emission
Molecular reactions
Molecular assembly
Molecular co-crystals

Phases - phase transitions
Physical properties
Electrical, magnetic
Mechanical properties
Electrochemical properties

Future?

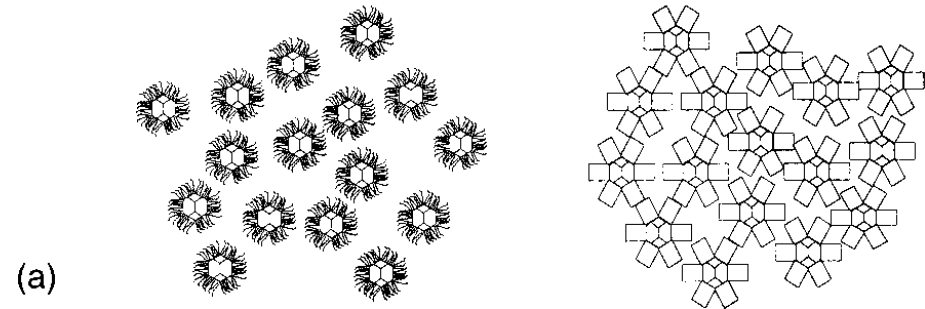
Physical properties

Phase diagram

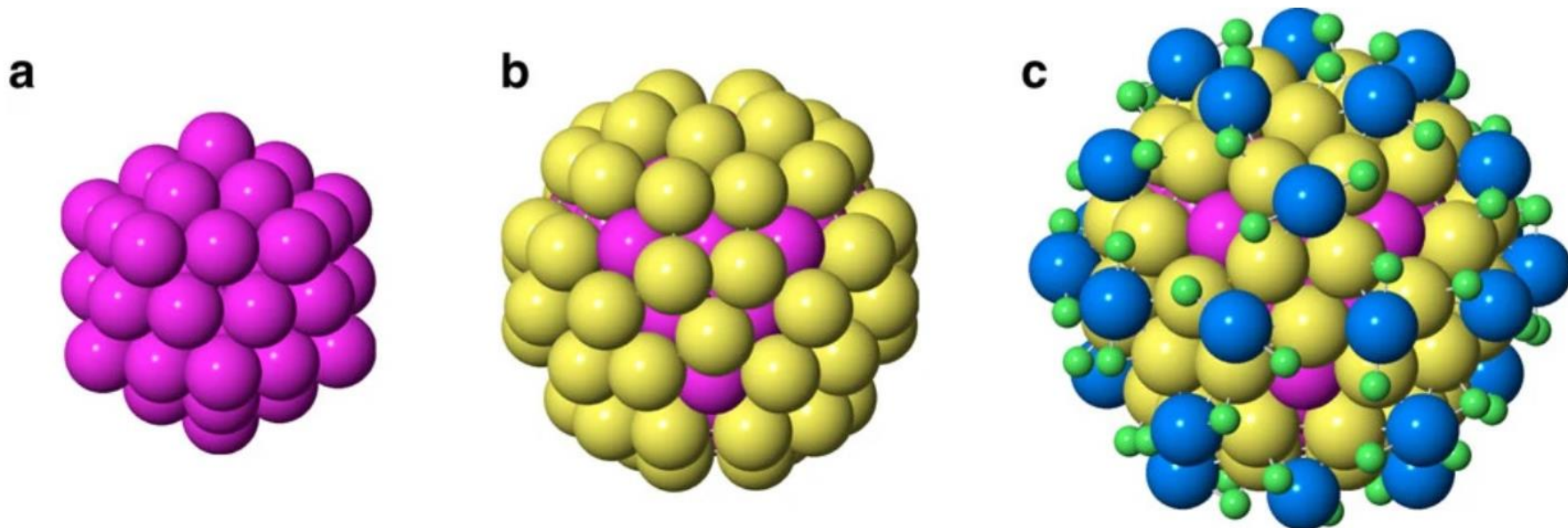


A

B

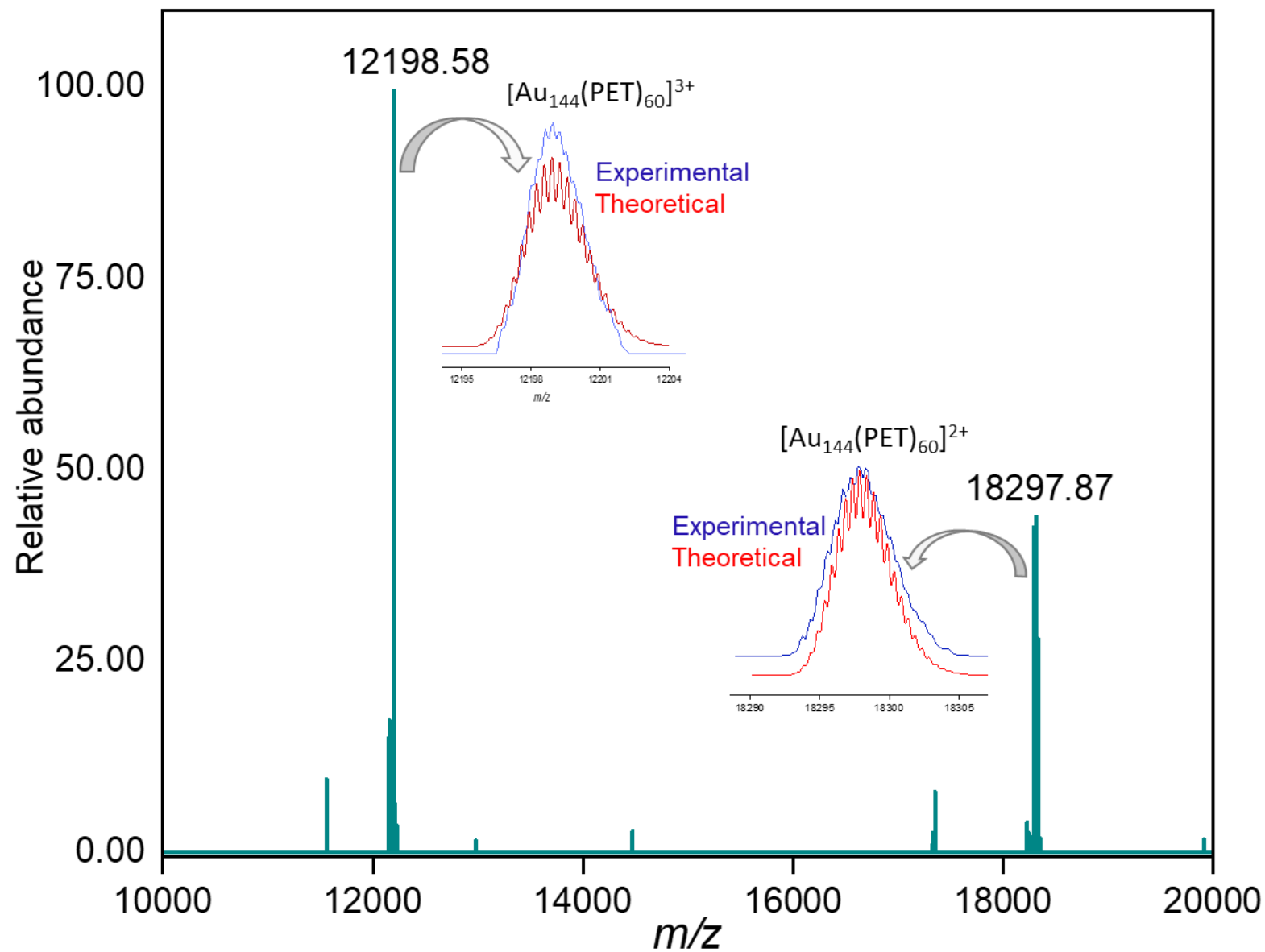


Do we know enough about structures?

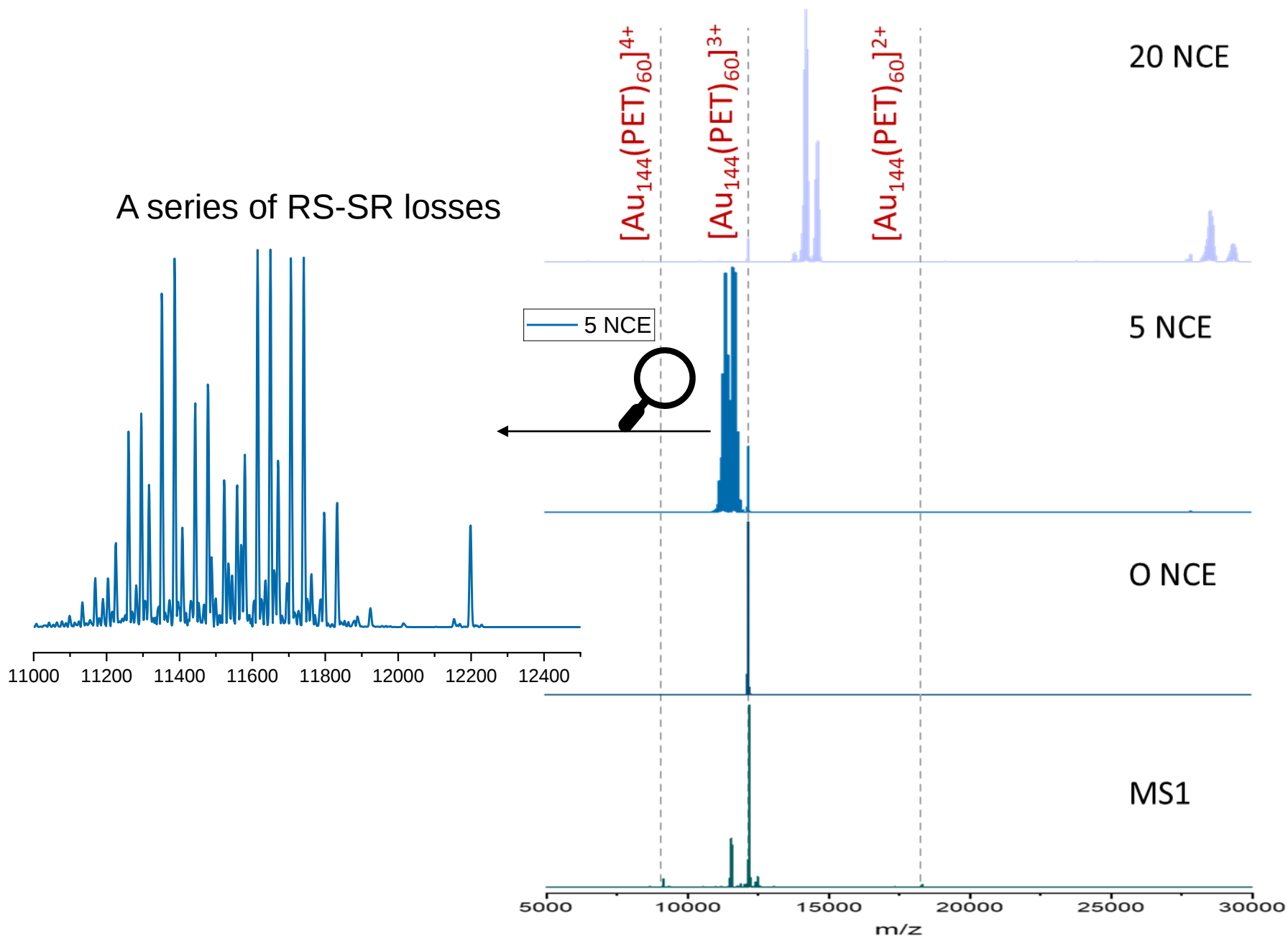


(a) Fifty-four atom gold core consisting of two Mackay icosahedron shells. (b) The icosahedral gold core (pink) is covered by 60 gold atoms (yellow) making up the grand core. (c) Total structure, where the grand core is covered in 'staples'—green atoms represent sulfur, whereas blue atoms represent gold in the staple structure. The organic carbon chains have been left out for clarity.

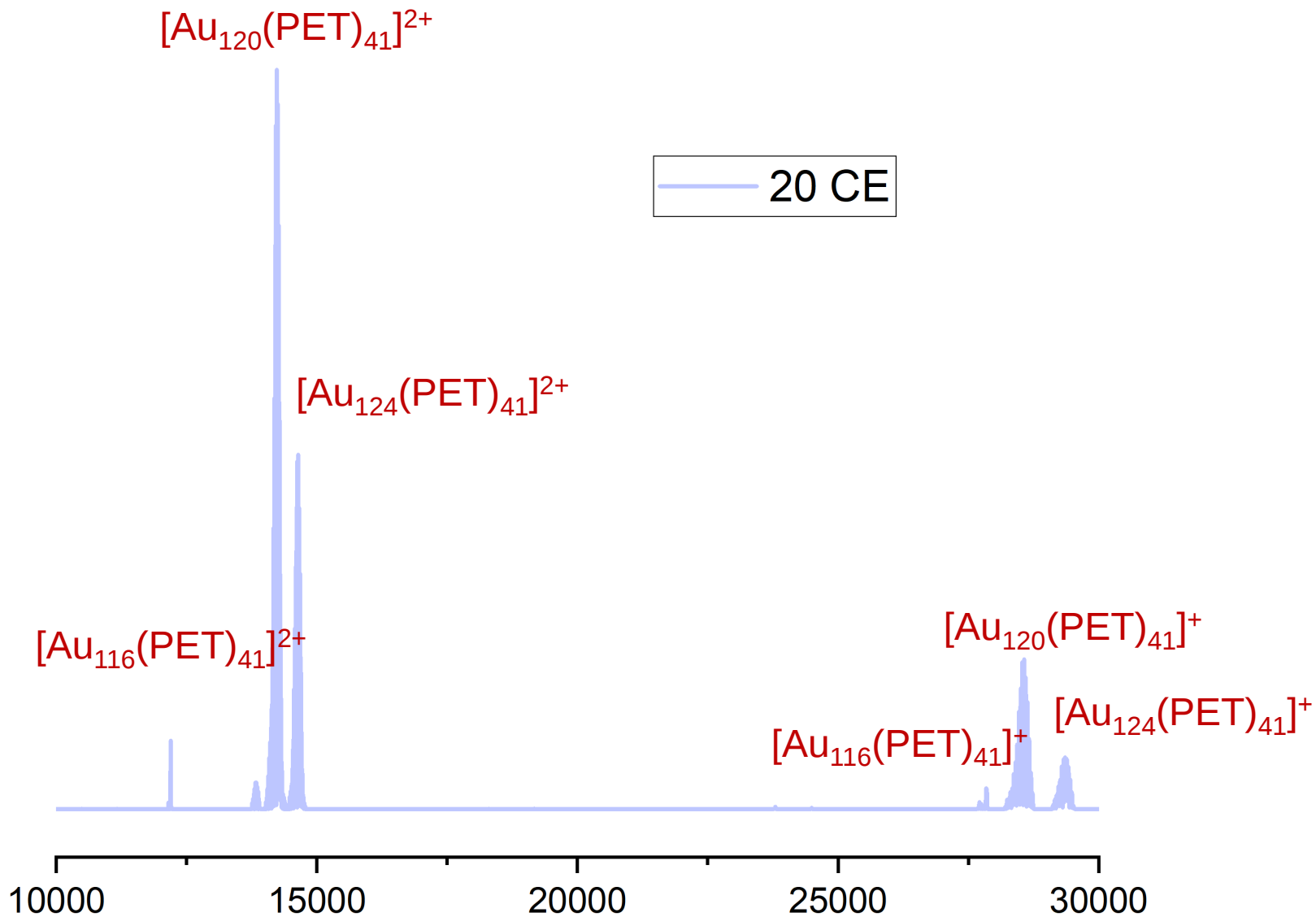
Jensen, K. M. Ø., et al. *Nat. Commun.*, 7, 2016, 11859.



MSMS of $[\text{Au}_{144}(\text{PET})_{60}]$



Transformation to a new core



Materials availability

nature

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Letter | Published: 07 July 1972

Electrochemical Photolysis of Water at a Semiconductor Electrode

[AKIRA FUJISHIMA](#) & [KENICHI HONDA](#)

[Nature](#) **238**, 37–38 (1972) | [Cite this article](#)

164k Accesses | **137** Altmetric | [Metrics](#)

Abstract

ALTHOUGH the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm (ref. 1).

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CLEAN AIR WITH PHOTOCATALYSIS

Akira Fujishima

Former President of Tokyo University of Science
Director, Photocatalysis International Research Center, TUS

Challenge 2. We do not make enough

Challenge 3. We do not know deep enough

Molecular reactions



Reactions on clusters
Reactions between clusters

Inter-cluster reactions



Article

pubs.acs.org/JACS

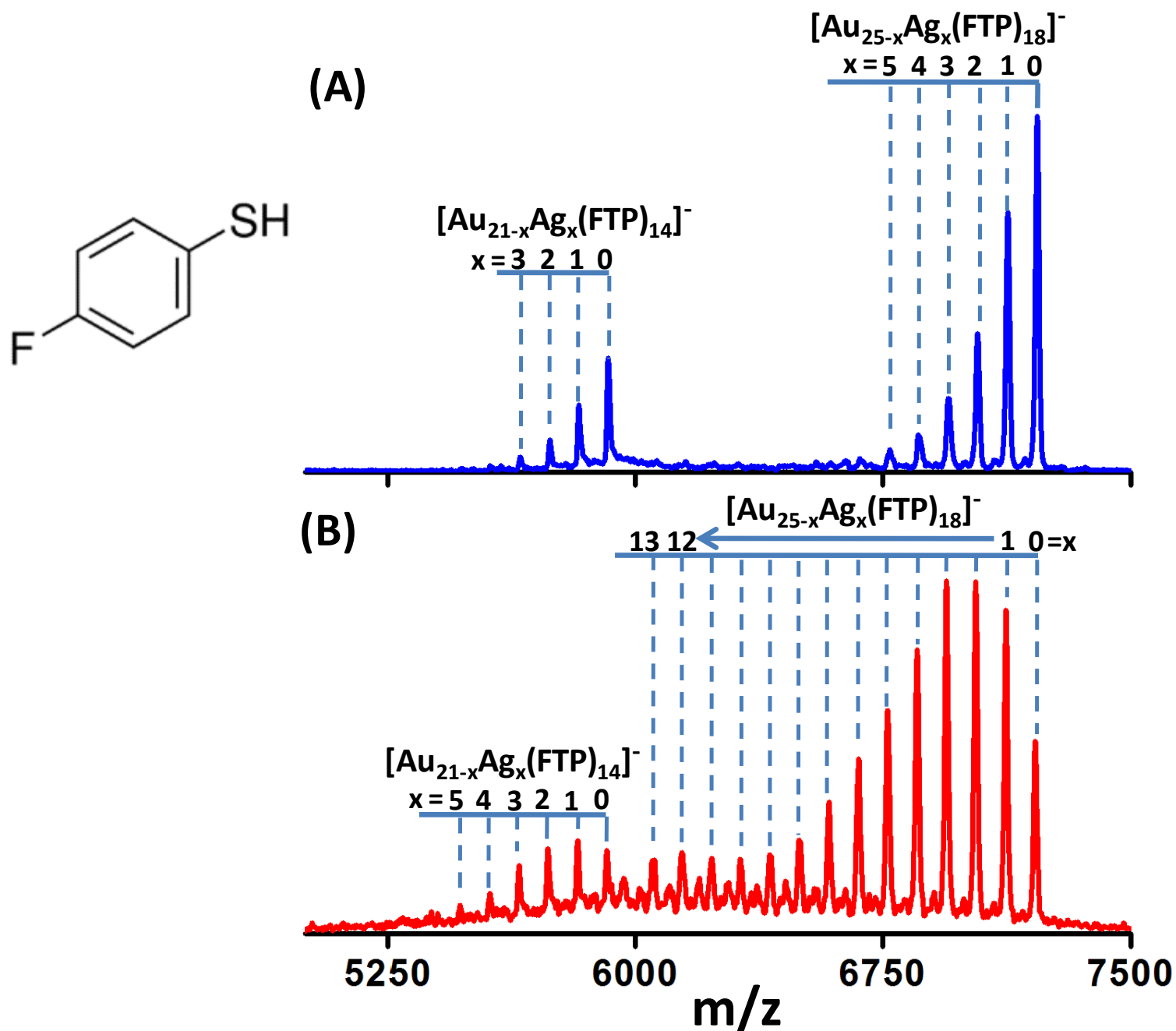
Intercluster Reactions between $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Ag}_{44}(\text{SR})_{30}$

K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India

 Supporting Information





Energies for the substitution reaction of (A) Au in $\text{Ag}_{44}(\text{SR})_{30}$, (B) Ag in $\text{Au}_{25}(\text{SR})_{18}$ and (C) the overall reaction energies (in eV) as a function of their positions in product clusters, $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$ and $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ for $x=1$

(A) Location of Au in $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$ $\Delta E/\text{eV}$

Icosahedron (I)	-0.72
Dodecahedron: cube vertex (D_{cv})	-0.14
Dodecahedron: cube face (D_{cf})	-0.32
Staples (S)	-0.48

(B) Location of Ag in $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ $\Delta E/\text{eV}$

Central atom (C)	+0.71
Icosahedron (I)	+0.23
Staples (S)	+0.44

(C) Locations of Au in $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$

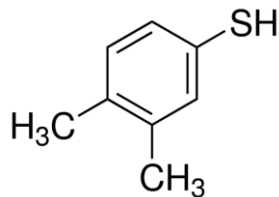
Location of Ag in $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$	I	D_{cv}	D_{cf}	S
C	-0.015	+0.564	+0.388	+0.226
I	-0.486	+0.093	-0.083	-0.245
S	-0.276	+0.303	+0.127	-0.035

Ag₂₅-Au₂₅ experiments

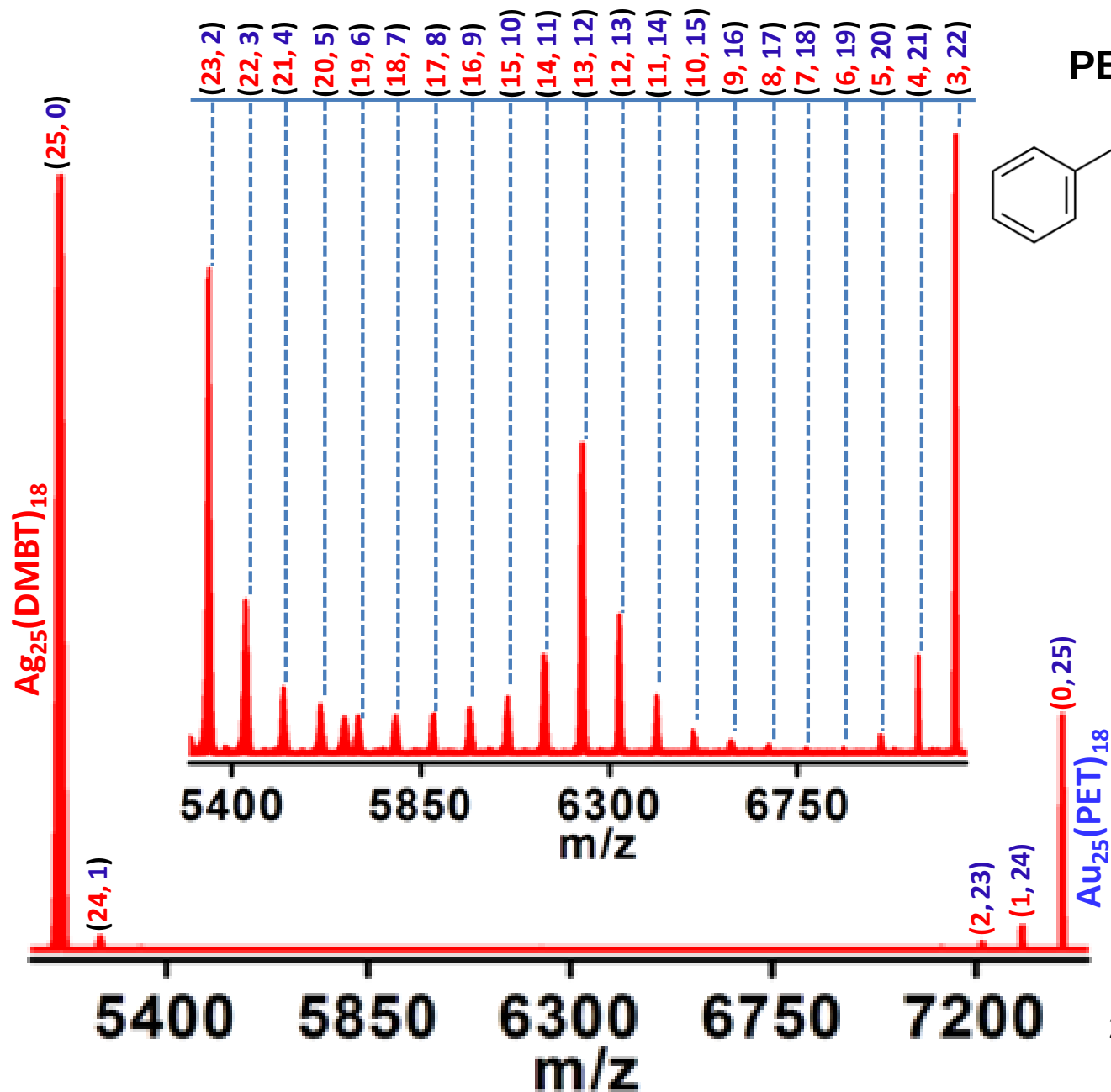
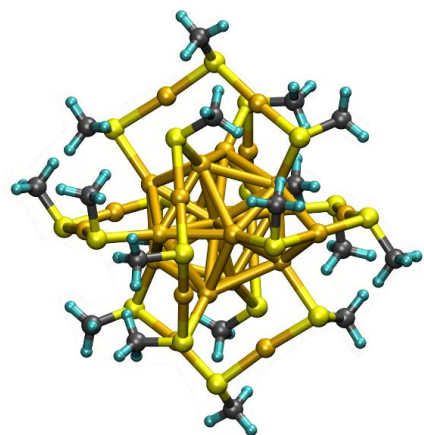
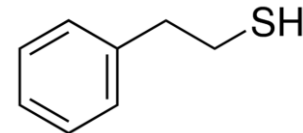
K. R. Krishnadas et al. *Nature Commun.* 2016

Reaction between $\text{Au}_{25}(\text{PET})_{18}$ and $\text{Ag}_{25}(\text{DMBT})_{18}$

DMBT

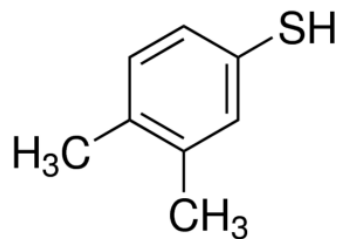


PET

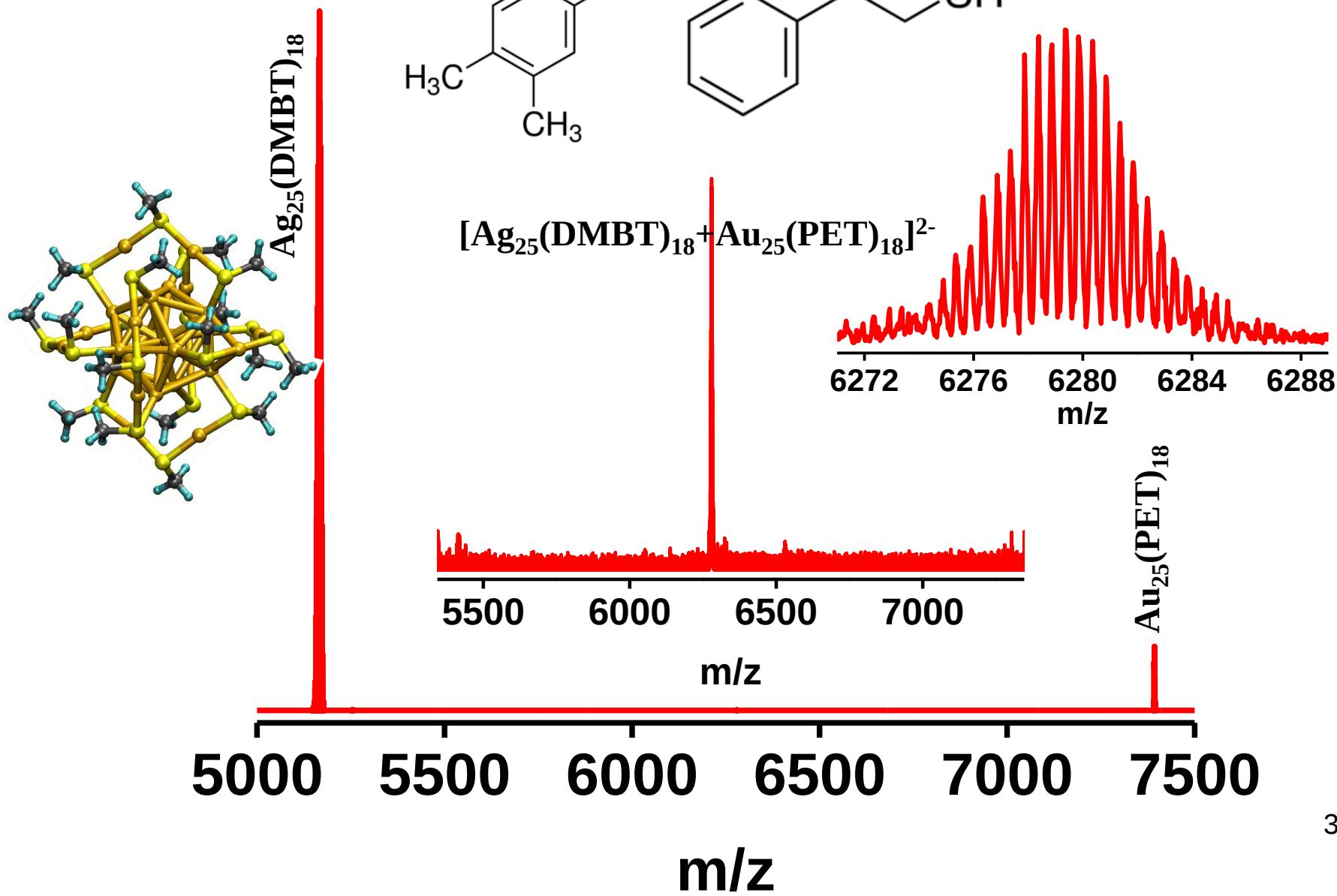
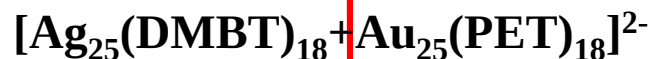
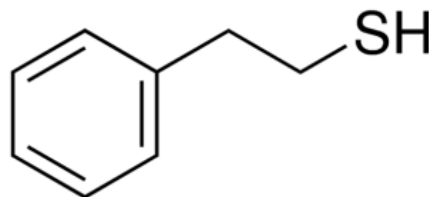




DMBT

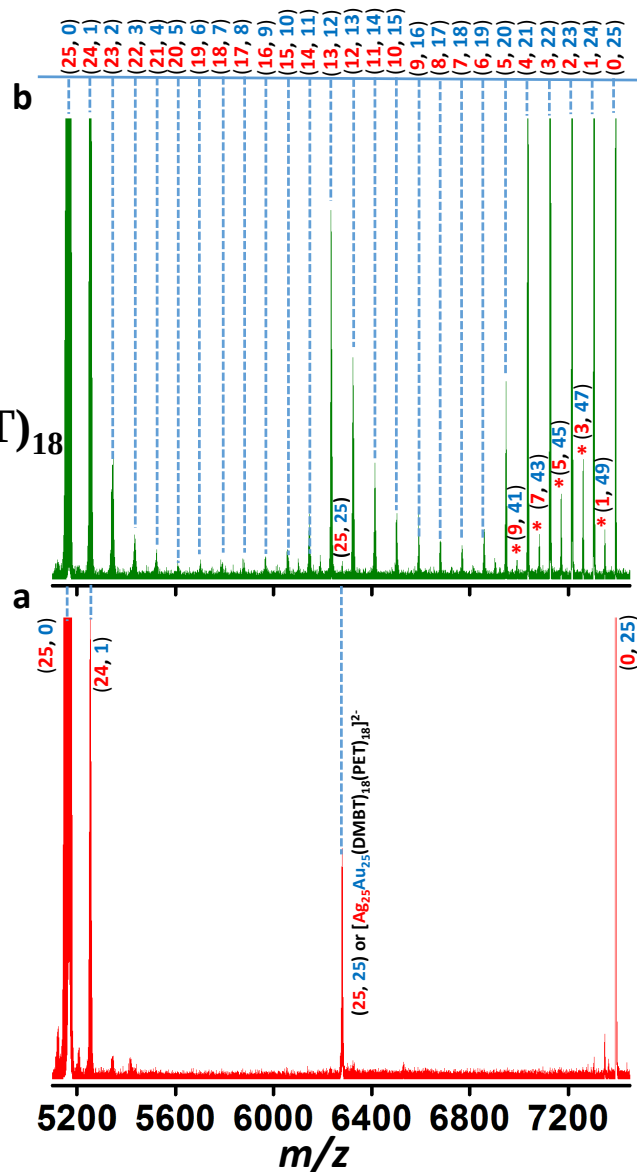


PET



Evolution of alloy clusters from the dianionic adduct, $[\text{Ag}_{25}\text{Au}_{25}(\text{DMBT})_{18}(\text{PET})_{18}]^{2-}$

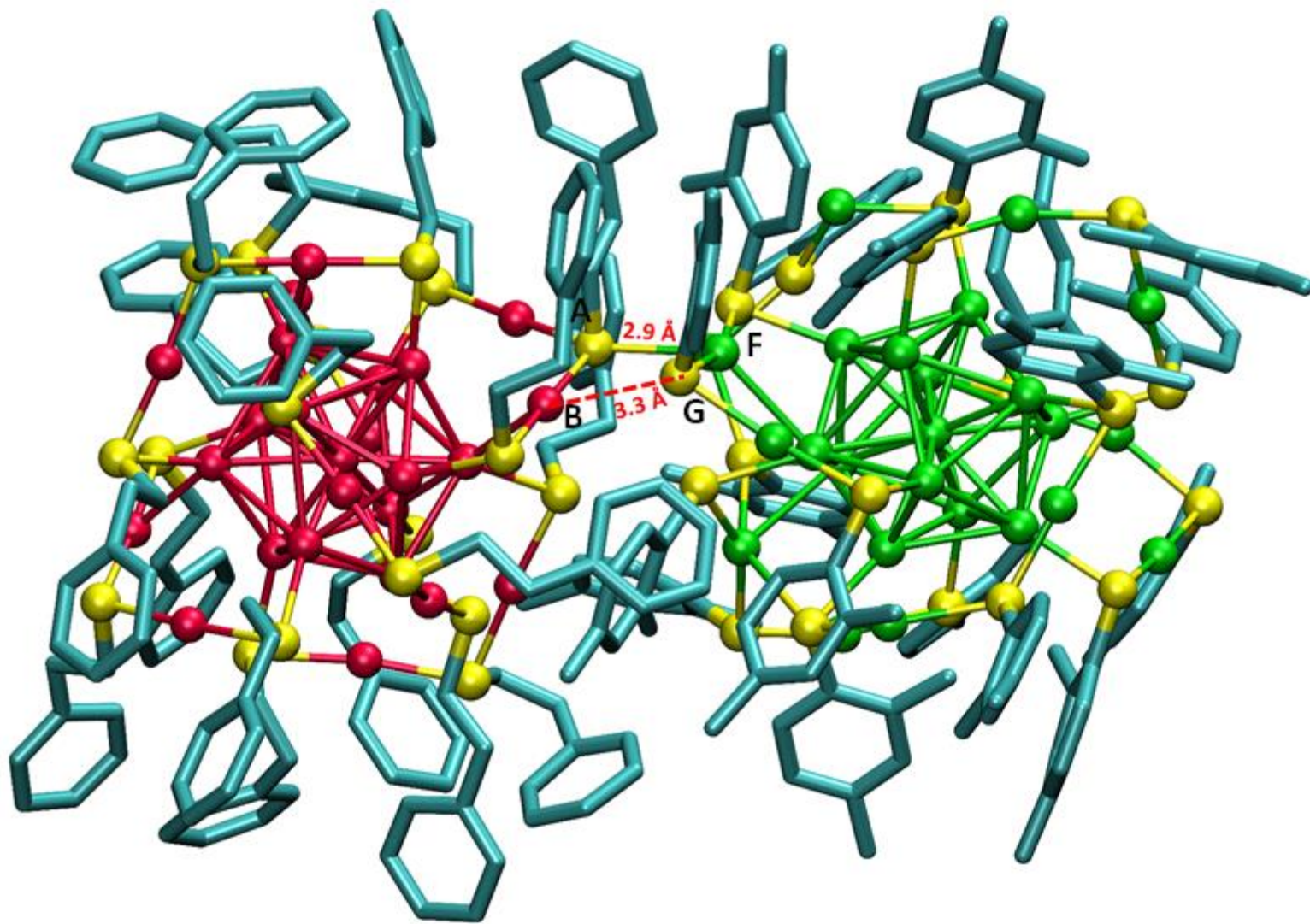
$\text{Ag}_{25}(\text{DMBT})_{18}:\text{Au}_{25}(\text{PET})_{18}$
 0.3:1.0

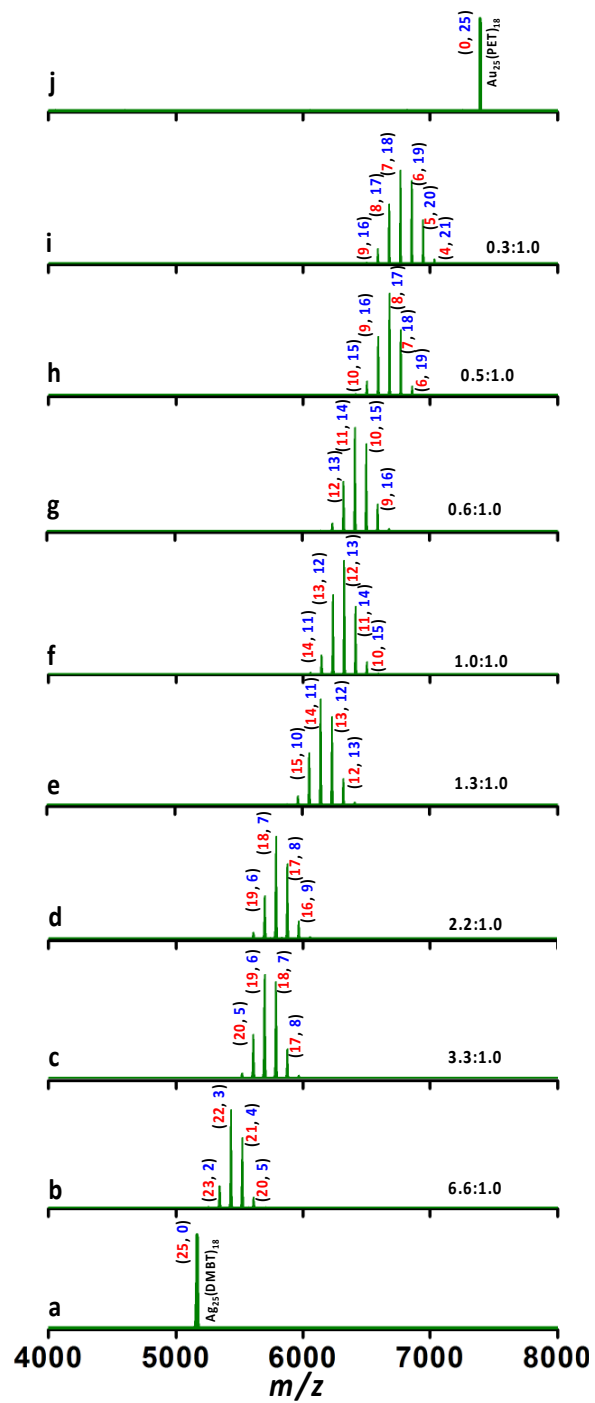


within 5 min

within 2 min

Optimised structure of $[\text{Ag}_{25}\text{Au}_{25}(\text{DMBT})_{18}(\text{PET})_{18}]^{2-}$

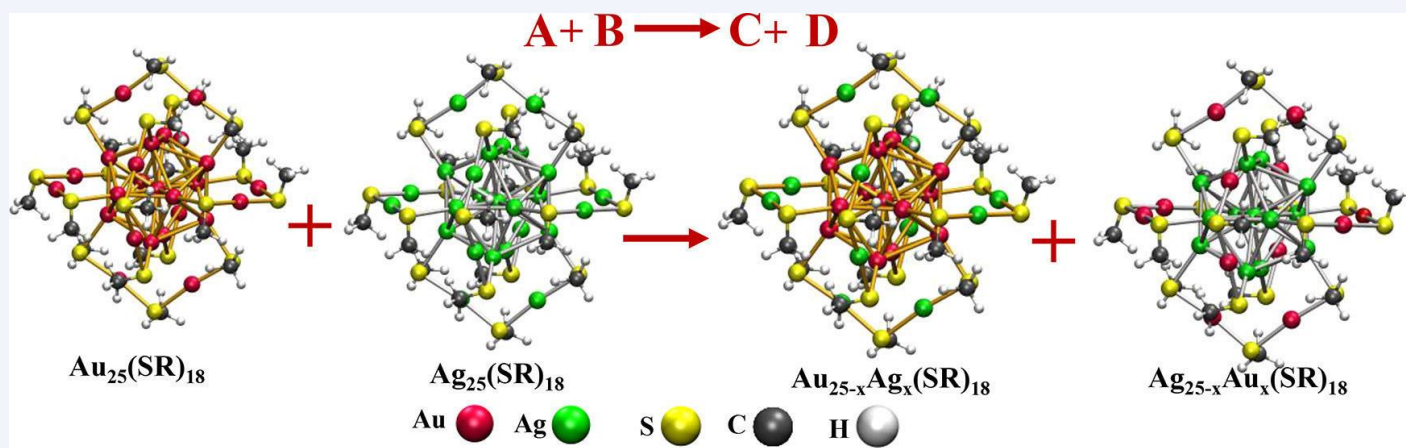




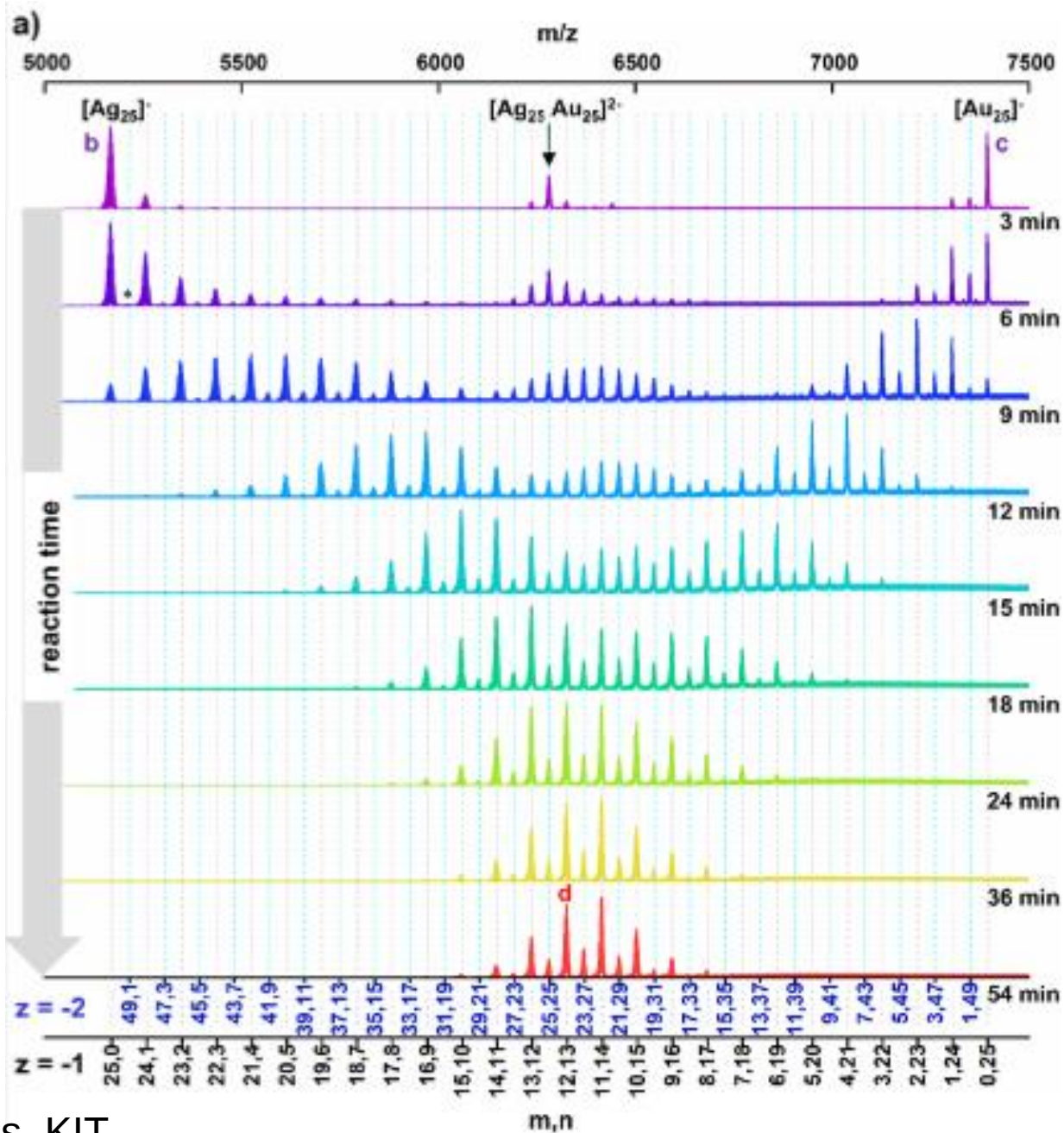
Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

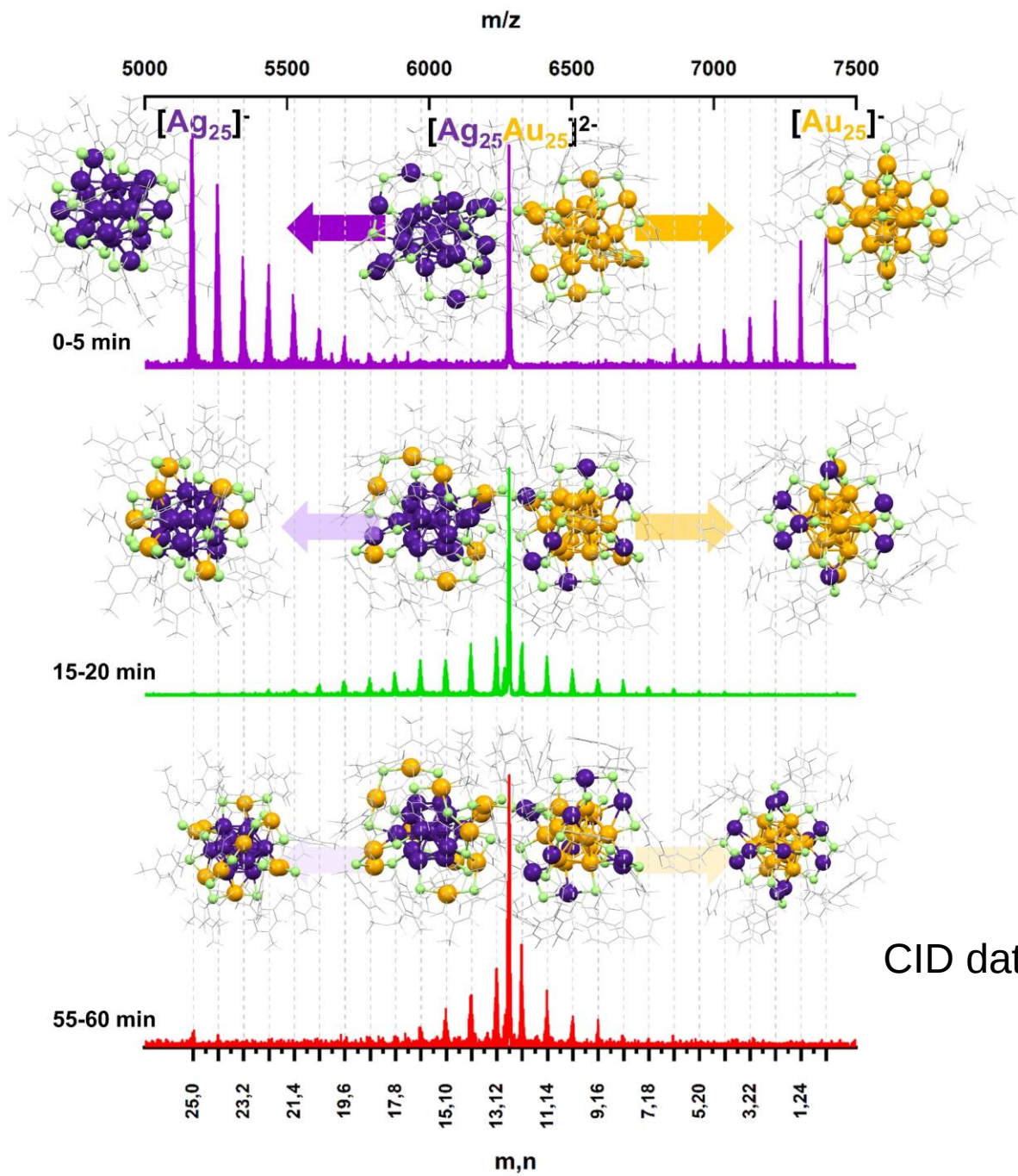
K. R. Krishnadas, Ananya Baksi,[†] Atanu Ghosh, Ganapati Natarajan, Anirban Som, and Thalappil Pradeep^{*ID}

Department of Chemistry, DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE) Indian Institute of Technology Madras, Chennai 600 036, India



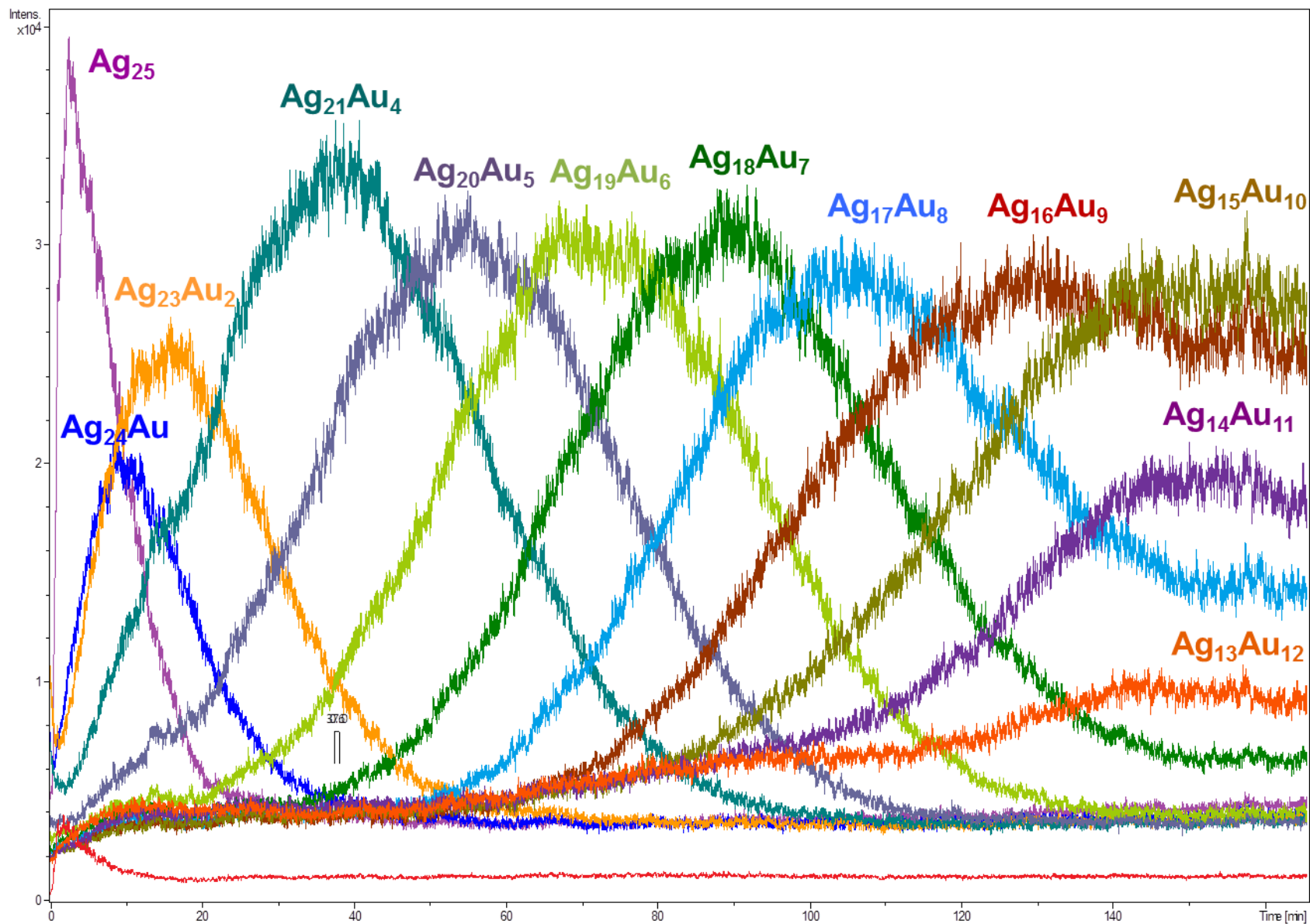
CONSPECTUS: Nanoparticles exhibit a rich variety in terms of structure, composition, and properties. However, reactions between them remain largely unexplored. In this *Account*, we discuss an emerging aspect of nanomaterials chemistry, namely, interparticle reactions in solution phase, similar to reactions between molecules, involving atomically precise noble metal clusters.





CID data of $[Au_{25}Ag_{25}]^{2-}$

Kinetics of the exchange (monitored on the Ag₂₅ side)



Mechanism

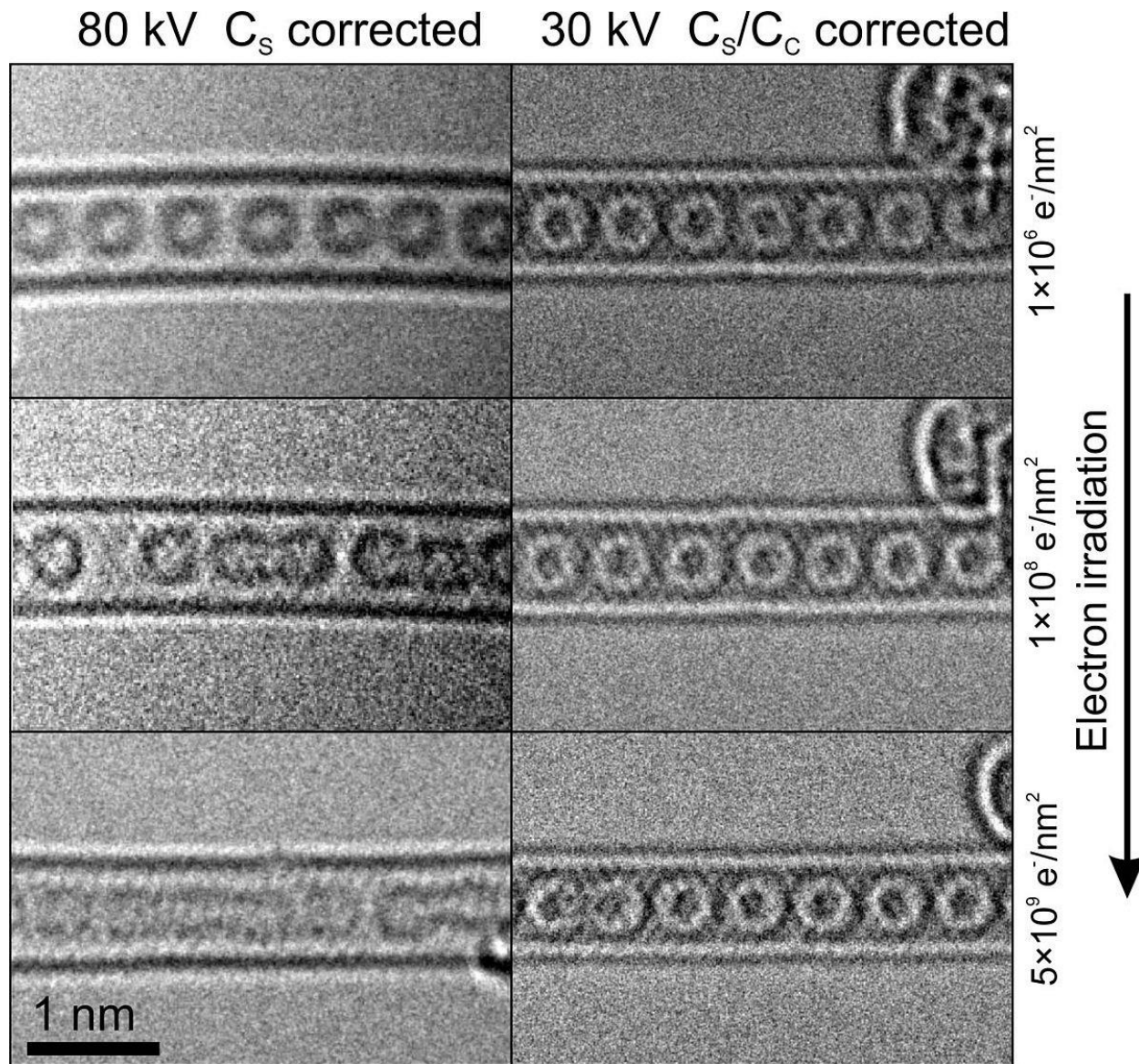
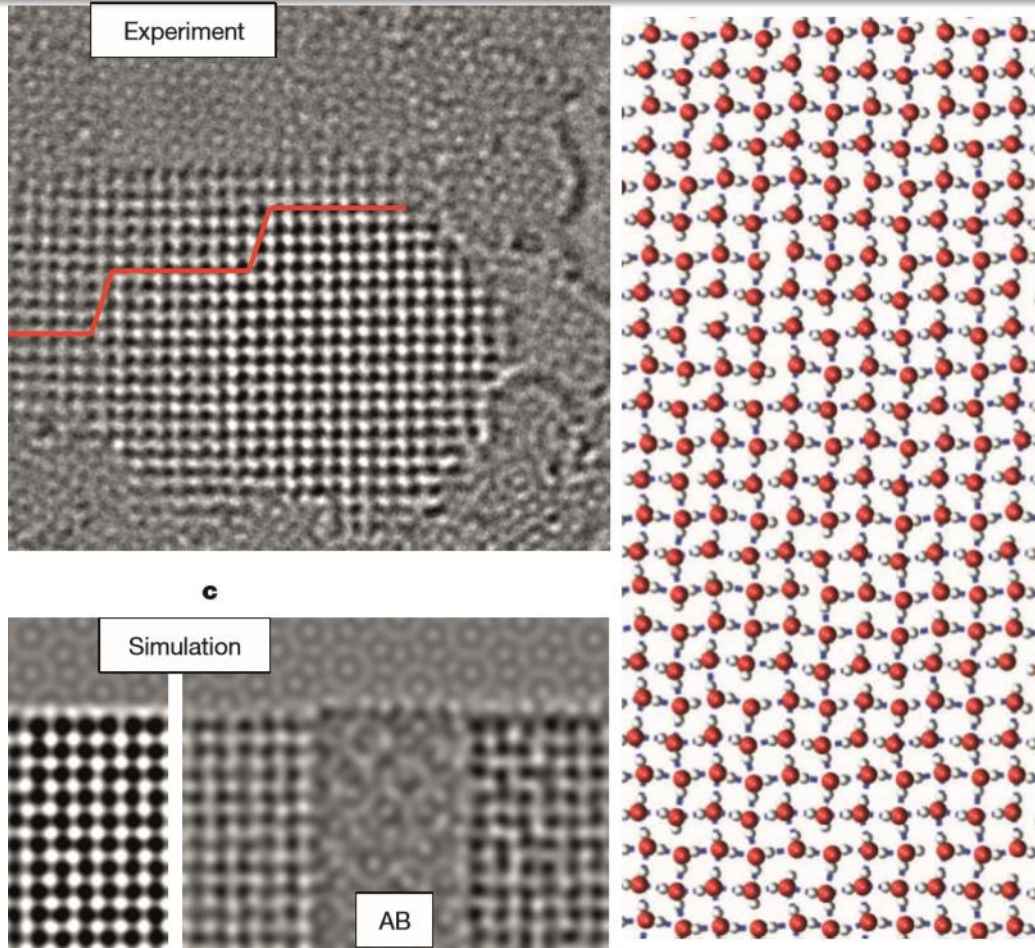


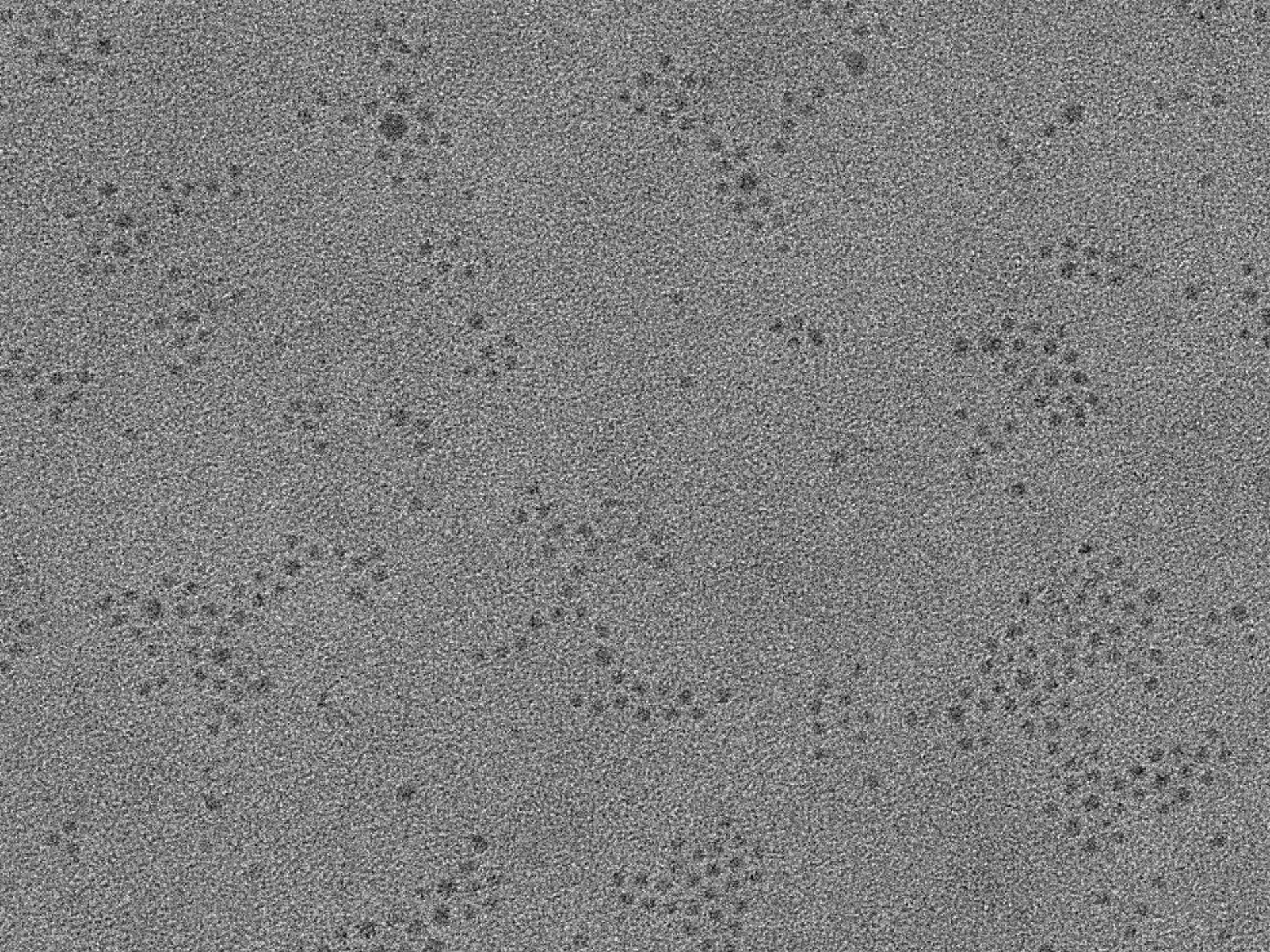
Fig. 1: Effect of electron irradiation of C60 molecules (fullerene) at different electron energies. At 30 kV the molecules do not undergo any structural changes. However, at 80 kV the C60 start to polymerize, first forming dimers and subsequently another tube within the original tube.

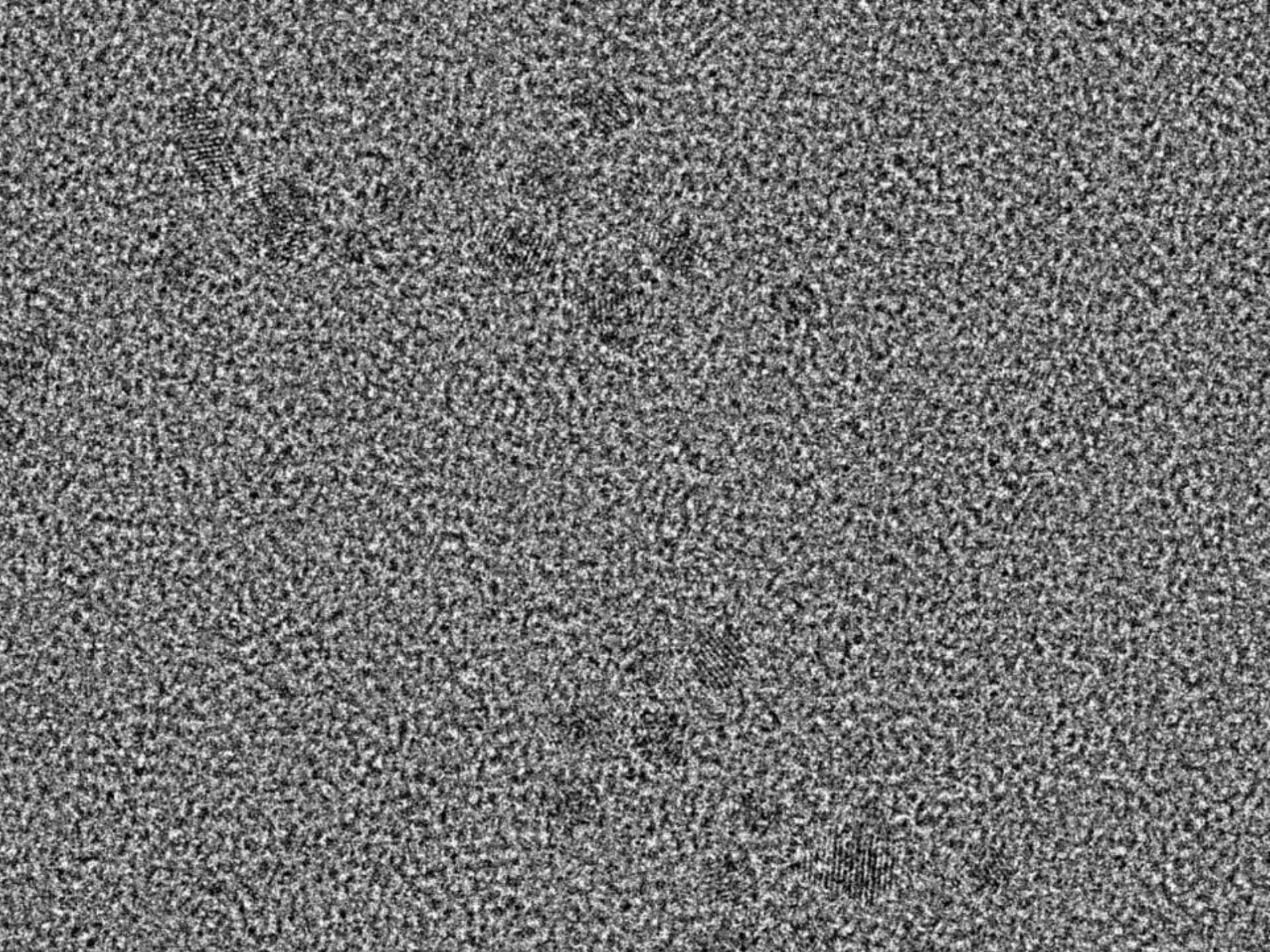


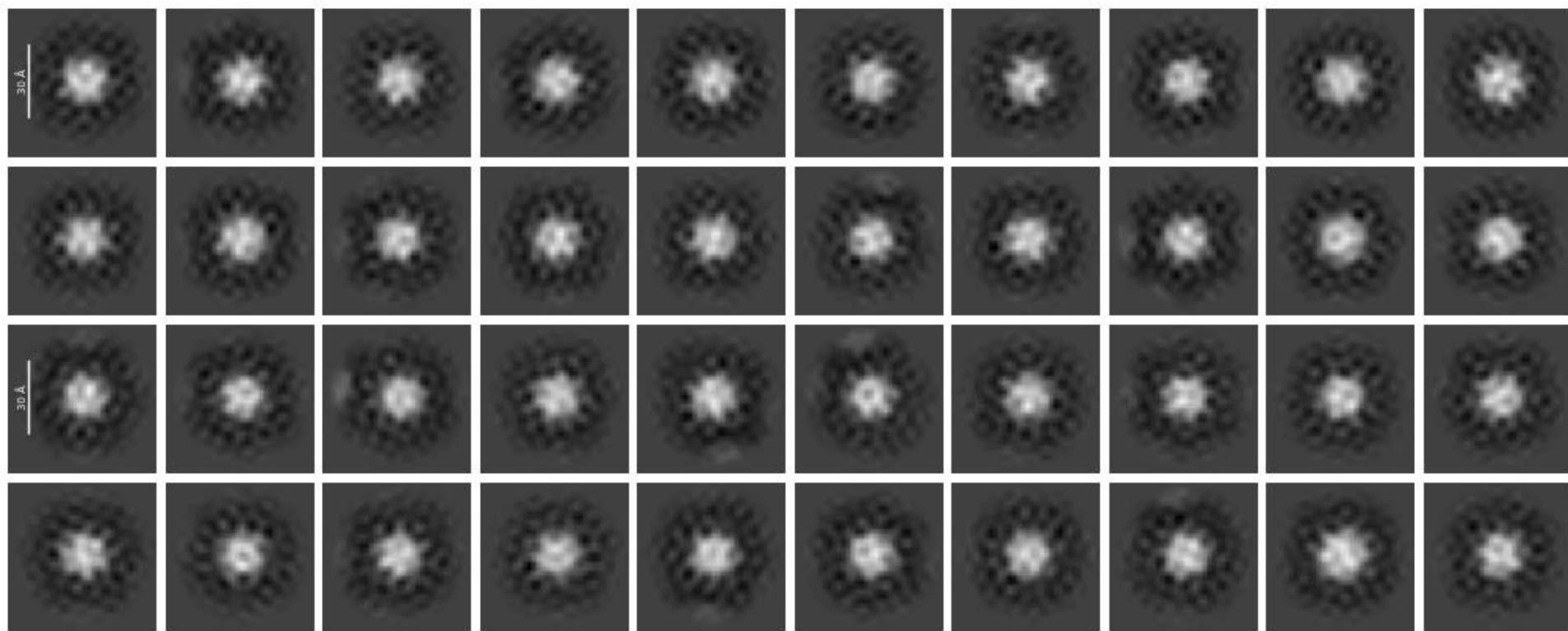
Observing water



Algara-Siller, G.; Lehtinen, O.; Wang, F. C.; Nair, R. R.; Kaiser, U.; Wu, H. A.; Geim, A. K.; Grigorieva, I. V., Square ice in graphene nanocapillaries. *Nature* **2015**, 519 (7544), 443-445.

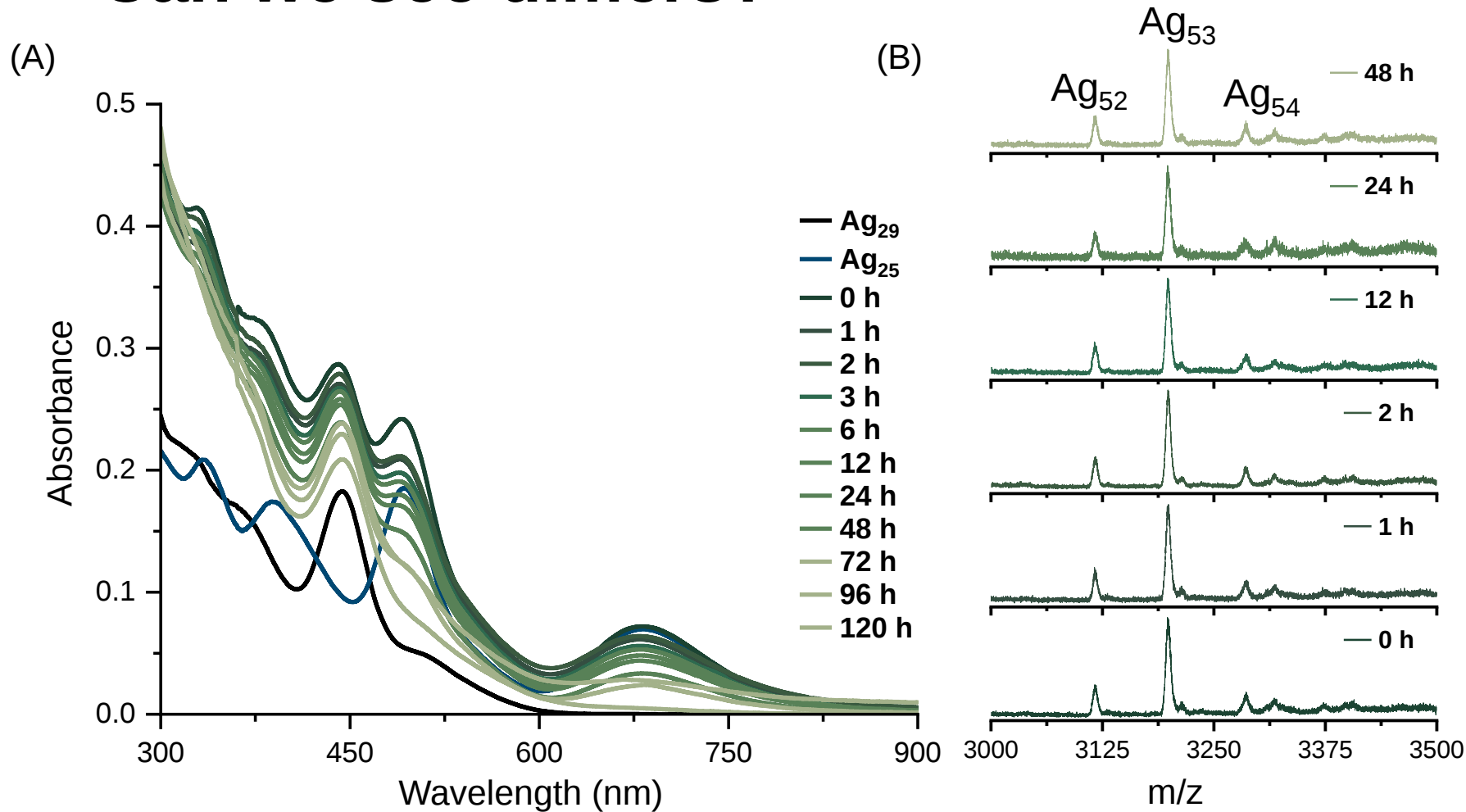


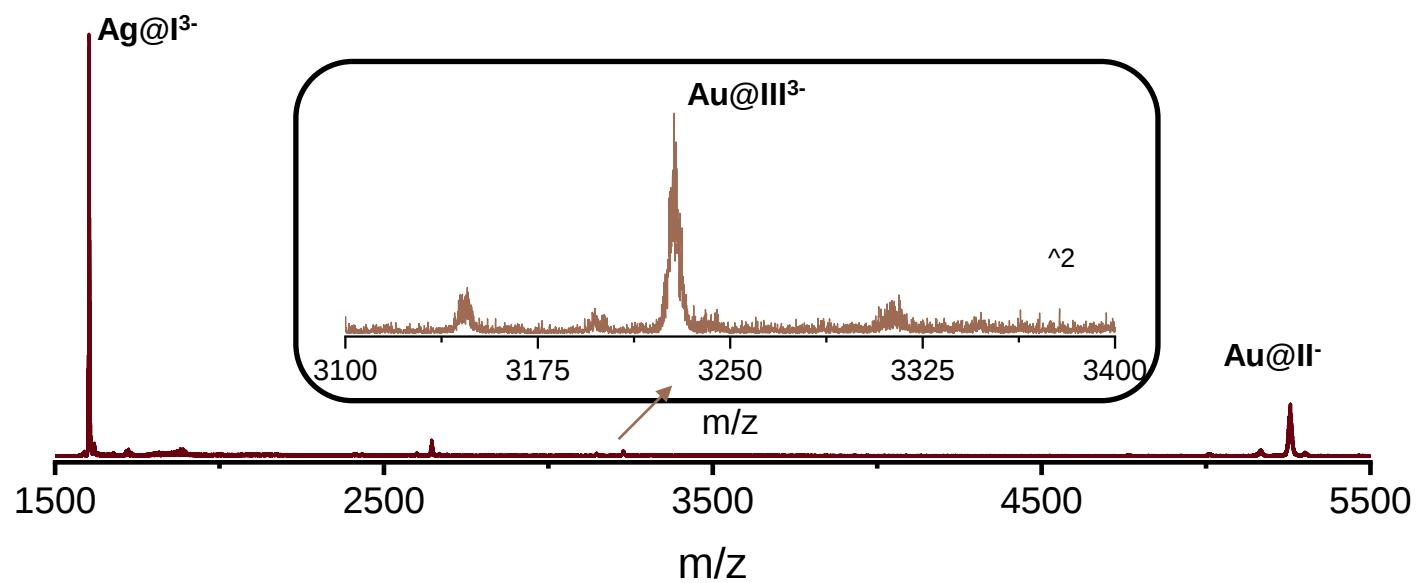
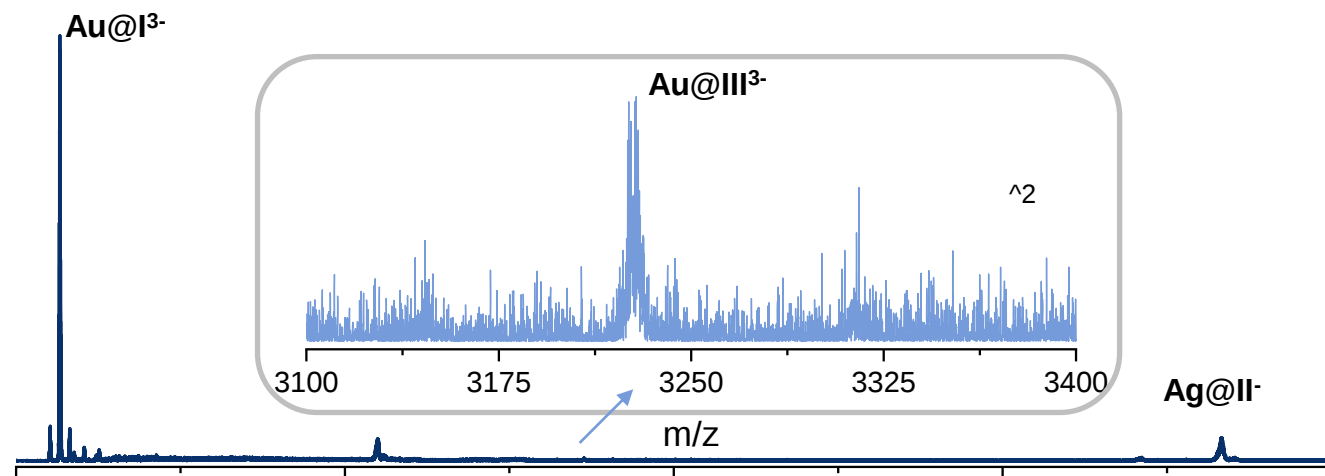




B. S. Sooraj, et. al. Unpublished

Can we see dimers?





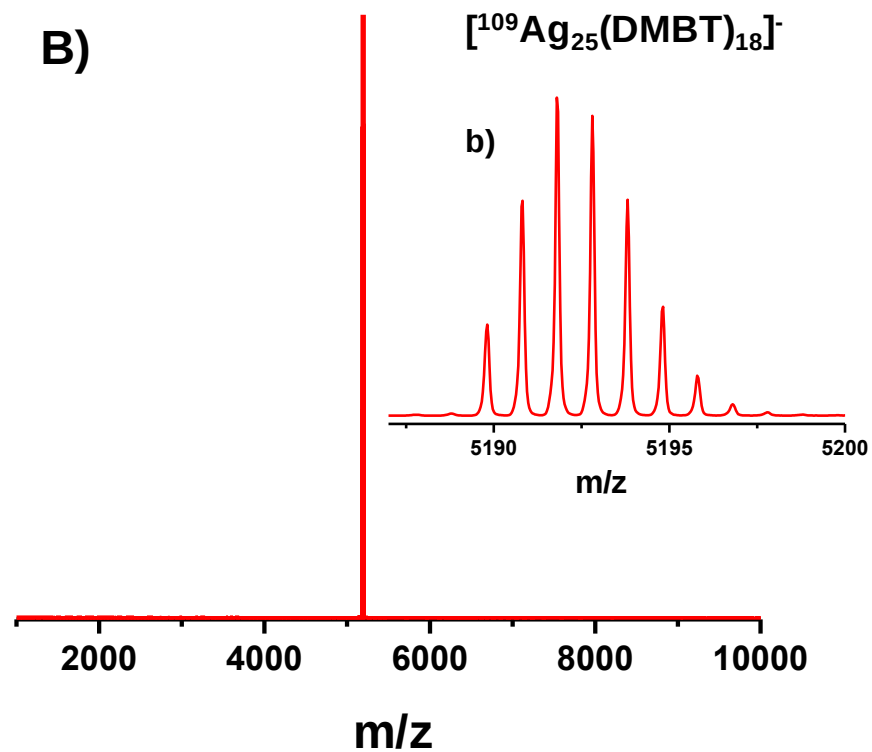
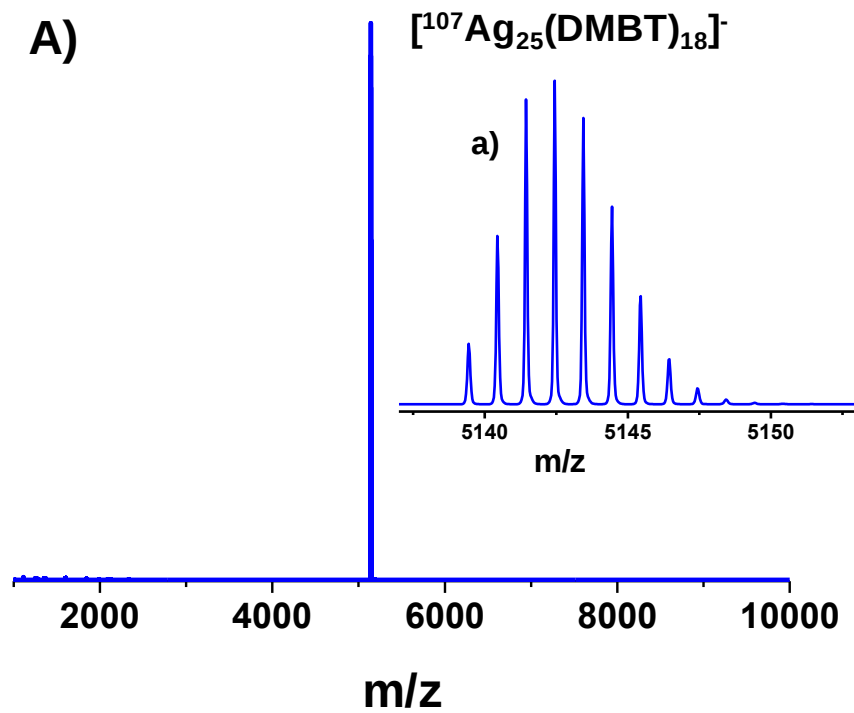
CONDENSED MATTER PHYSICS

Rapid isotopic exchange in nanoparticles

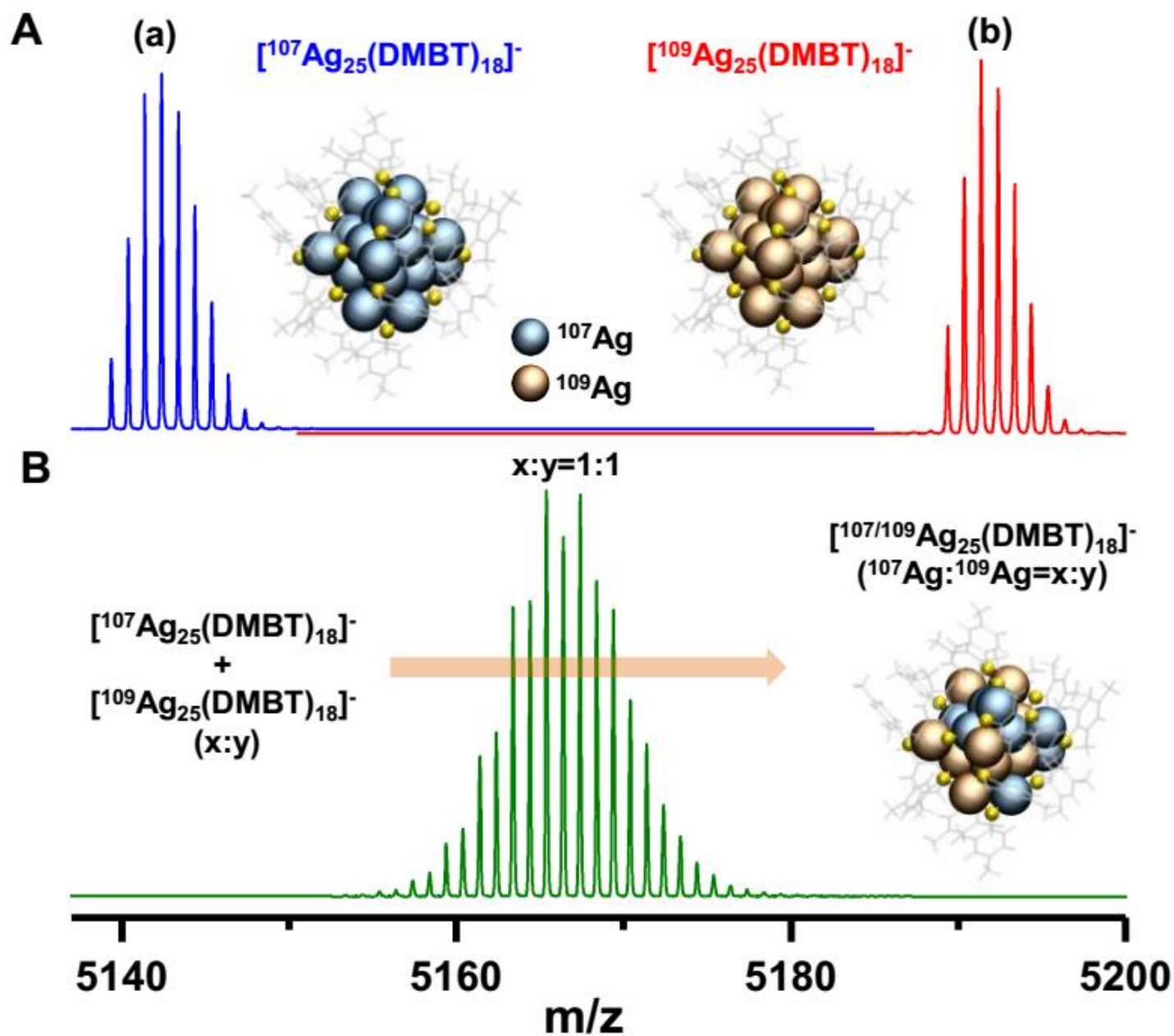
**Papri Chakraborty¹, Abhijit Nag¹, Ganapati Natarajan¹, Nayanika Bandyopadhyay¹,
Ganesan Paramasivam¹, Manoj Kumar Panwar¹, Jaydeb Chakrabarti², Thalappil Pradeep^{1*}**

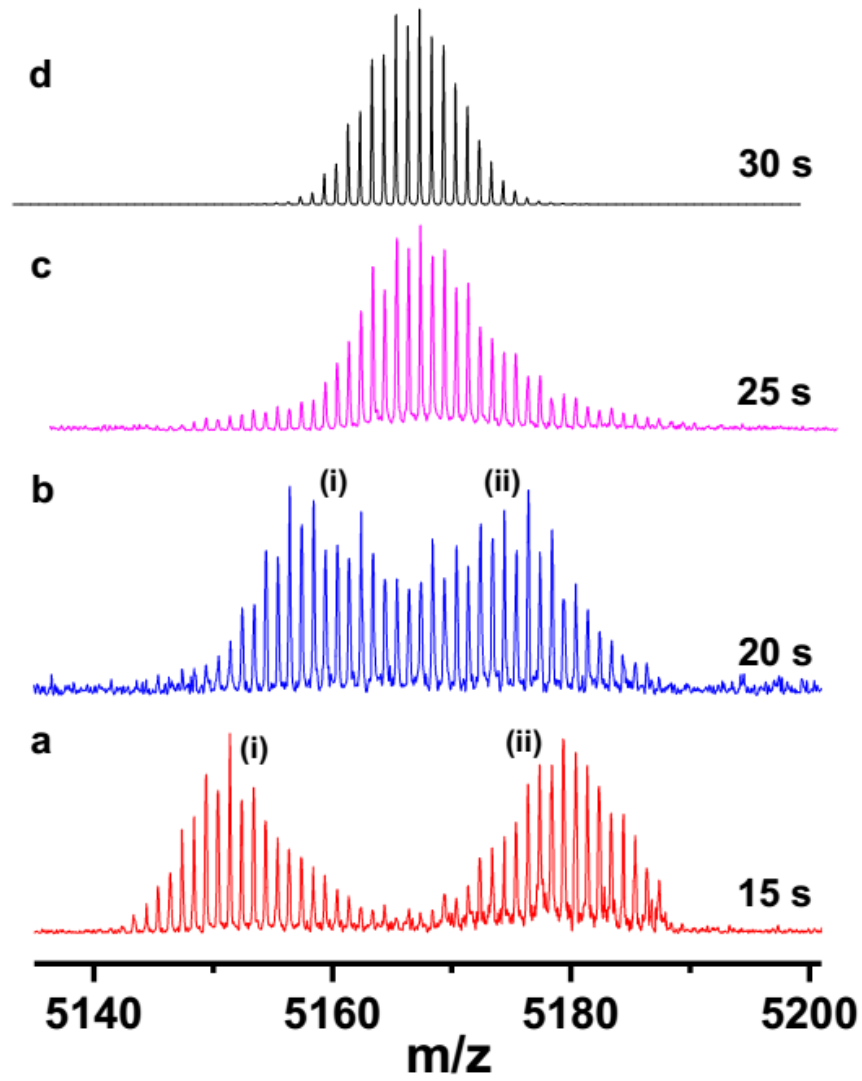
Rapid solution-state exchange dynamics in nanoscale pieces of matter is revealed, taking isotopically pure atomically precise clusters as examples. As two isotopically pure silver clusters made of ^{107}Ag and ^{109}Ag are mixed, an isotopically mixed cluster of the same entity results, similar to the formation of HDO, from H_2O and D_2O . This spontaneous process is driven by the entropy of mixing and involves events at multiple time scales.

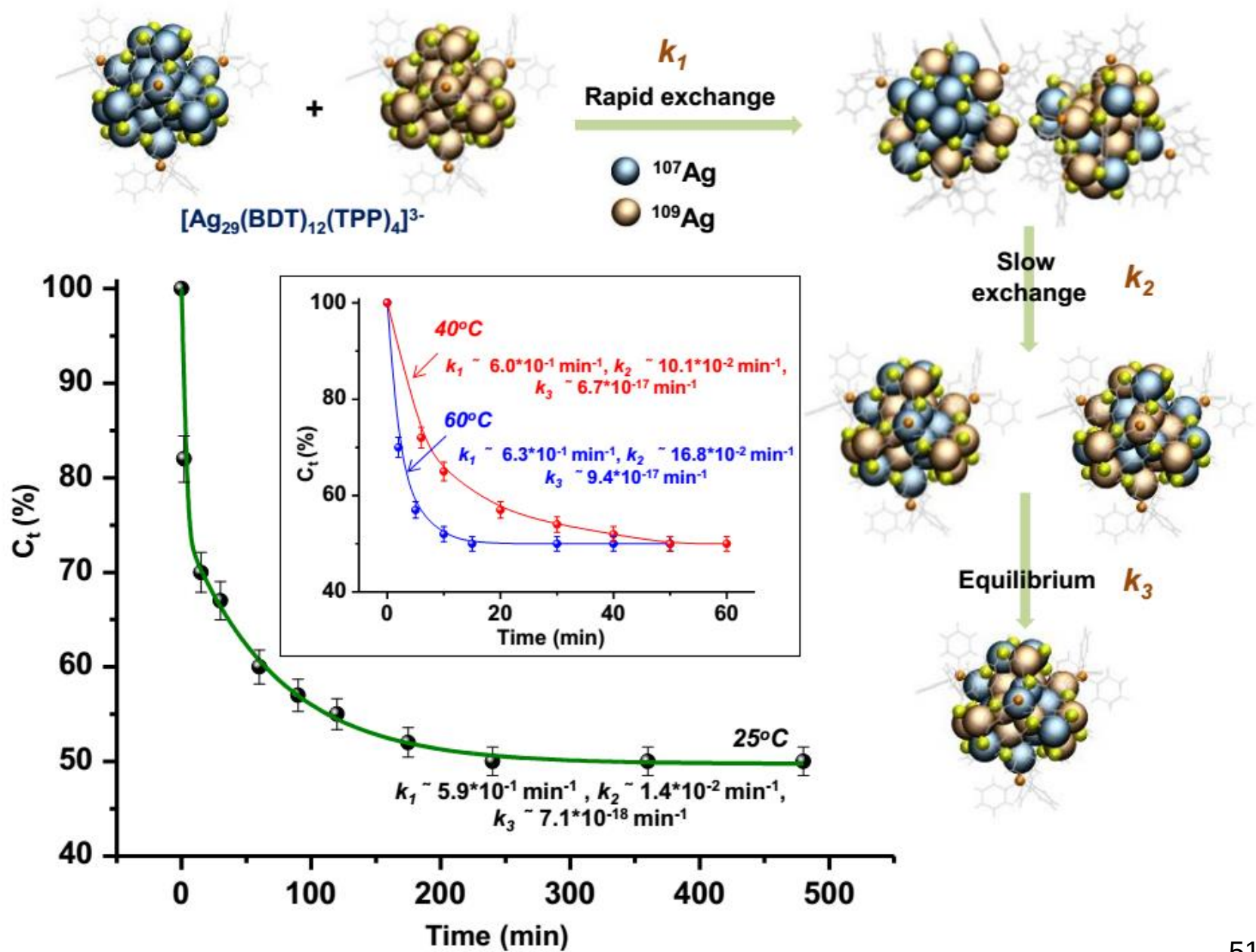
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ESI MS of **A)** $^{107}\text{Ag}_{25}(\text{DMBT})_{18}$ and **B)** $^{109}\text{Ag}_{25}(\text{DMBT})_{18}$. Insets shows the respective isotope patterns.





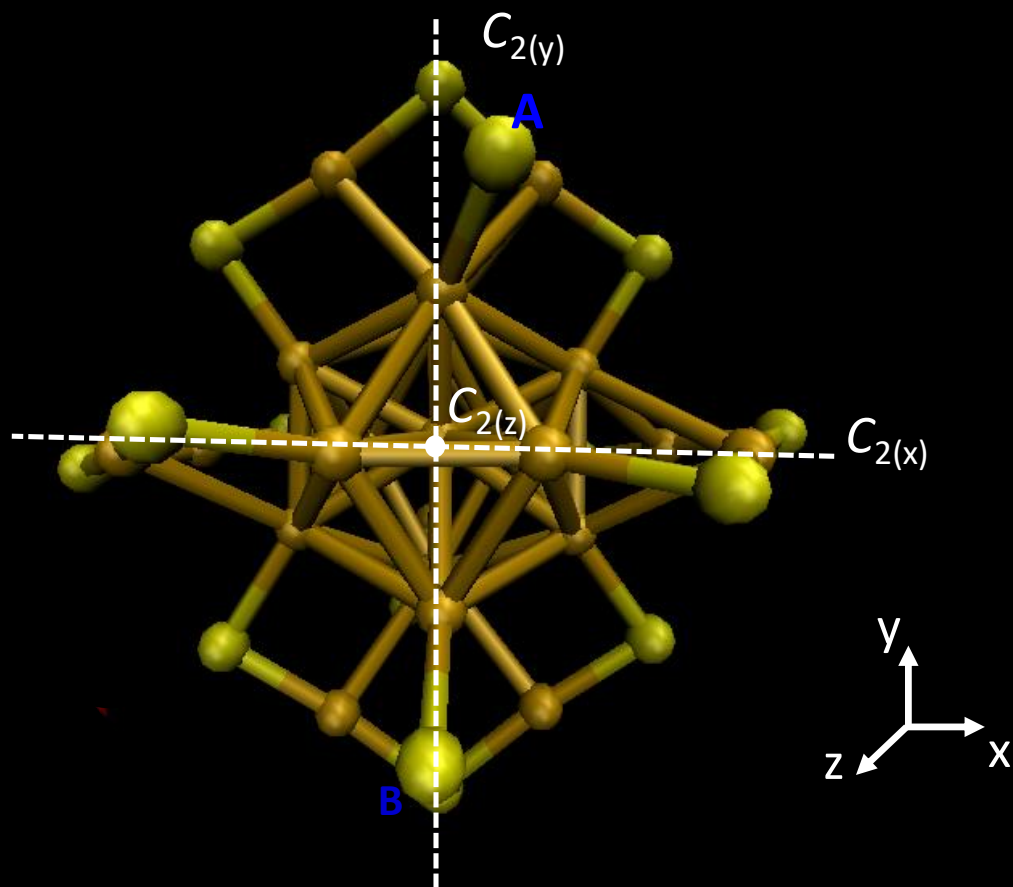


Dynamics

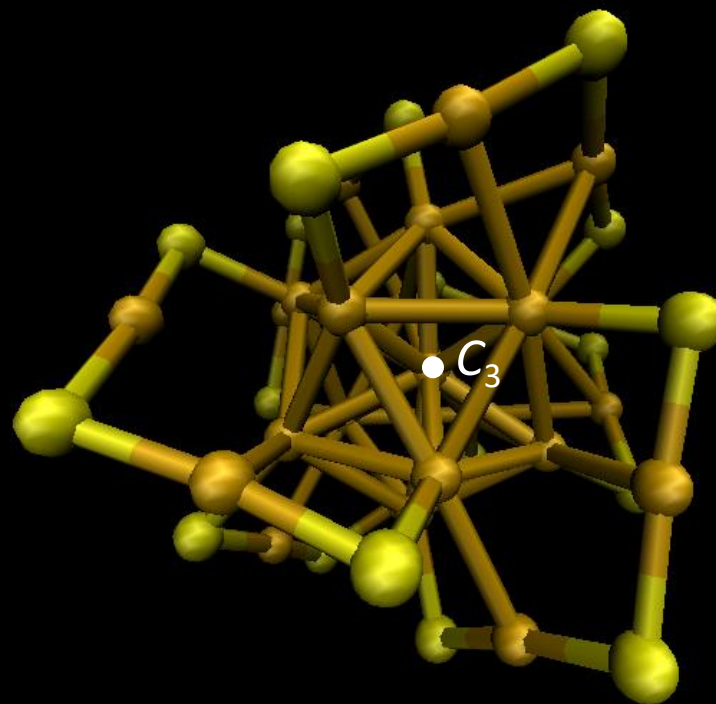
4. How to comprehend this molecular world?

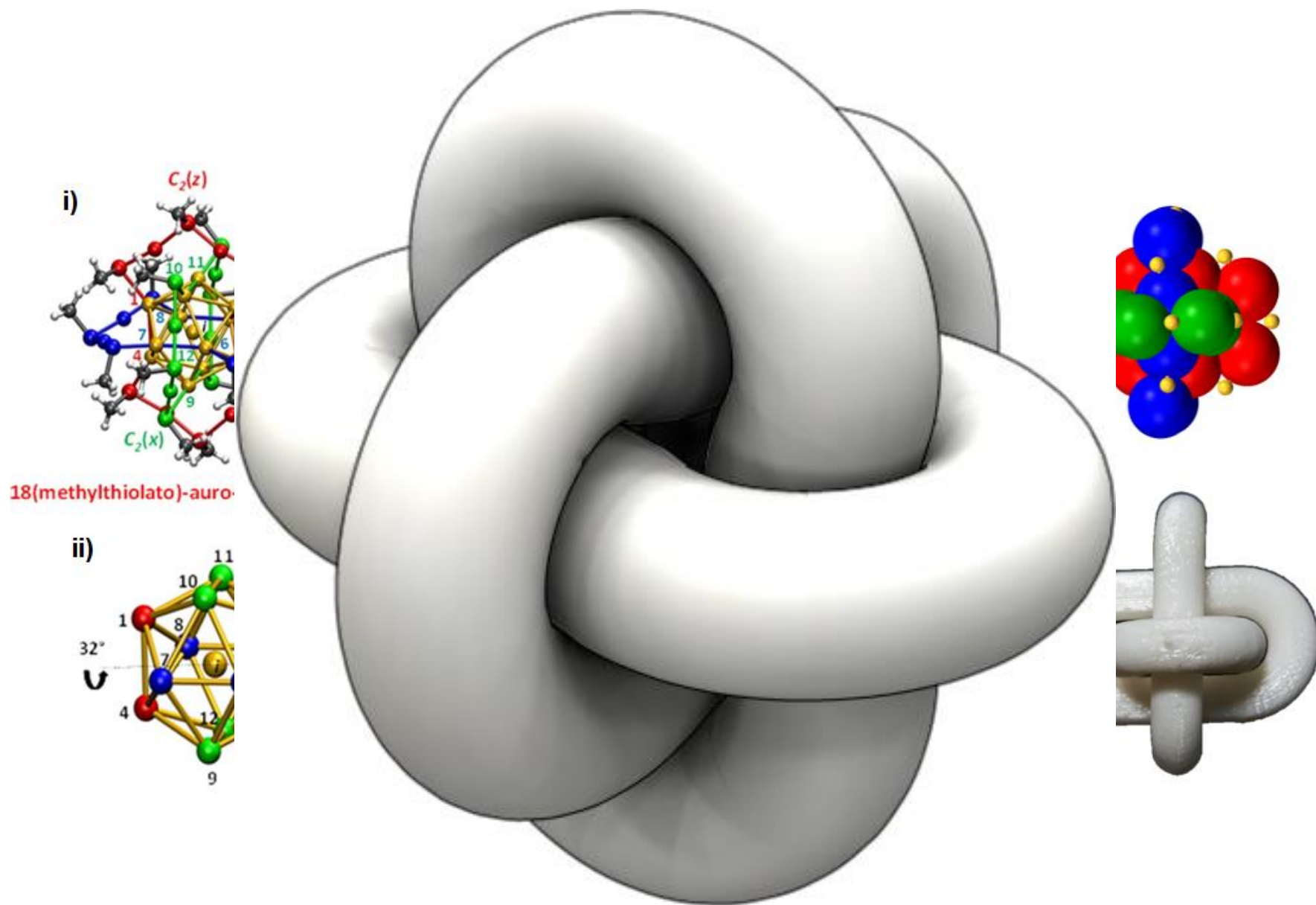
Nomenclature

1) Edge projection



2) Face Projection





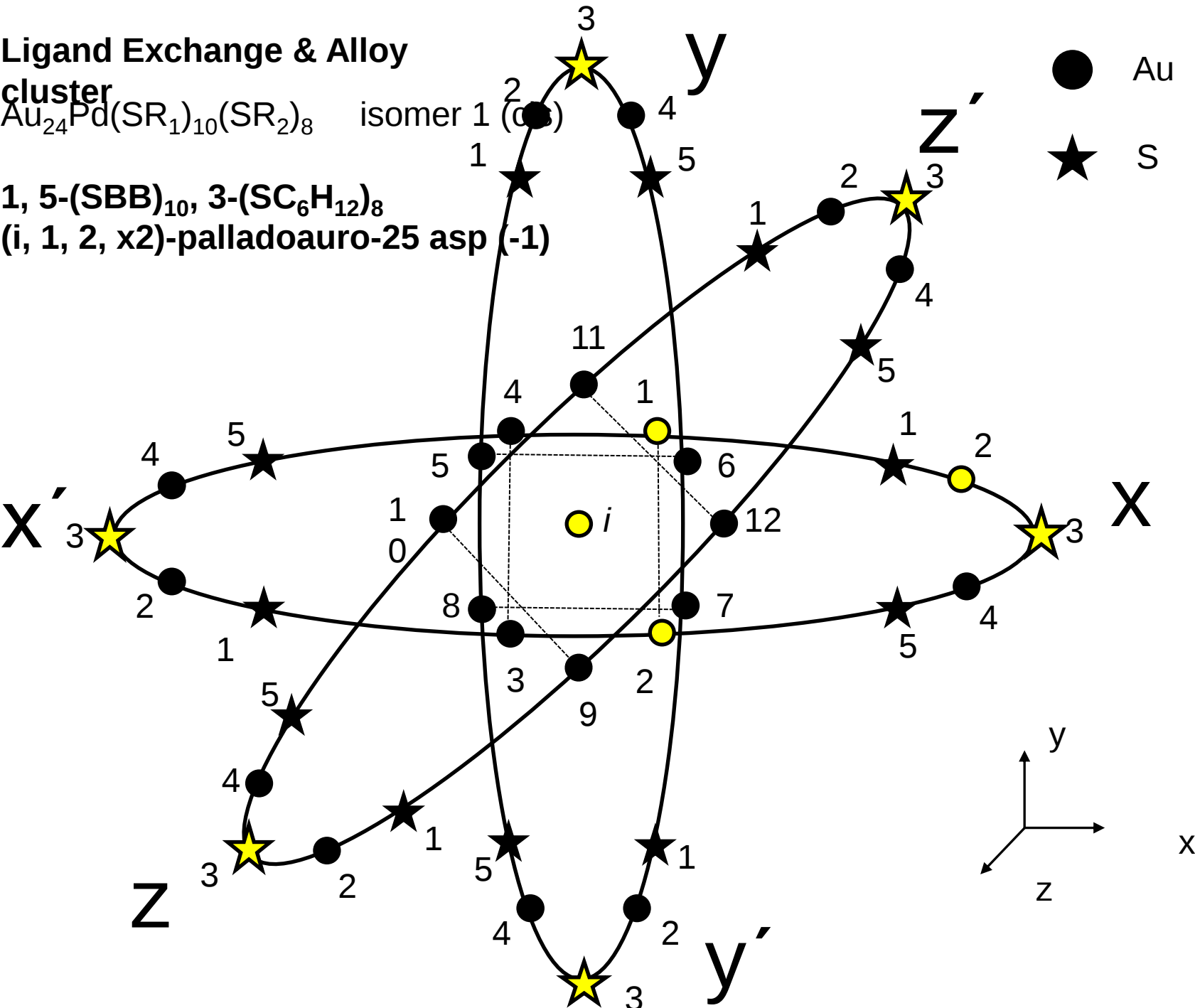
Aspicules

(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-(PET)₂,(SMe)₁₆-auro-25 aspicule(1-)

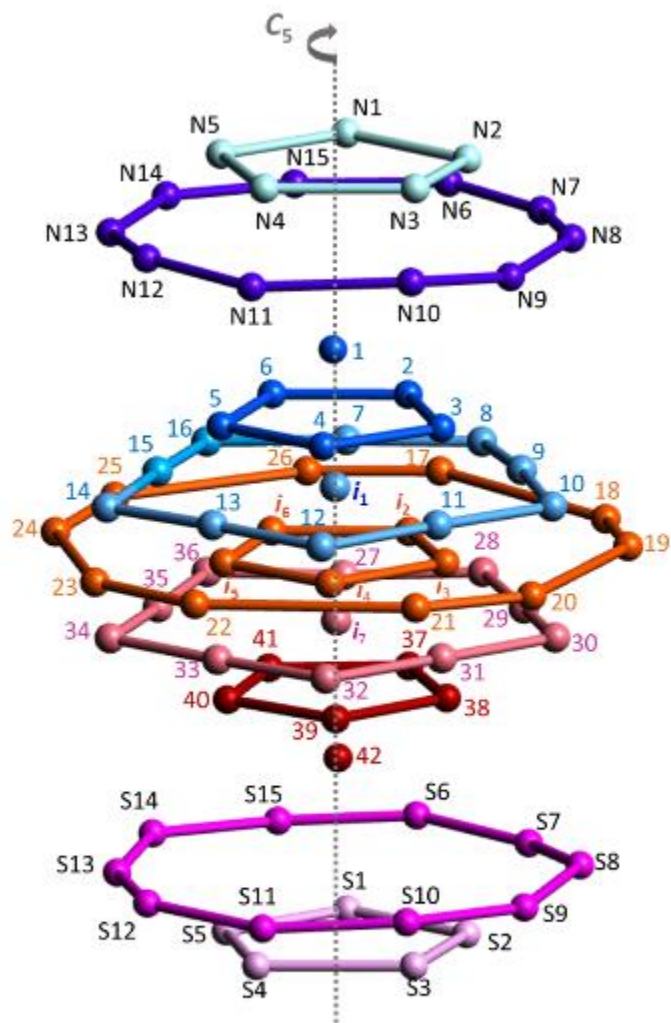
Ligand Exchange & Alloy cluster

$\text{Au}_{24}\text{Pd}(\text{SR}_1)_{10}(\text{SR}_2)_8$ isomer 1 (c)

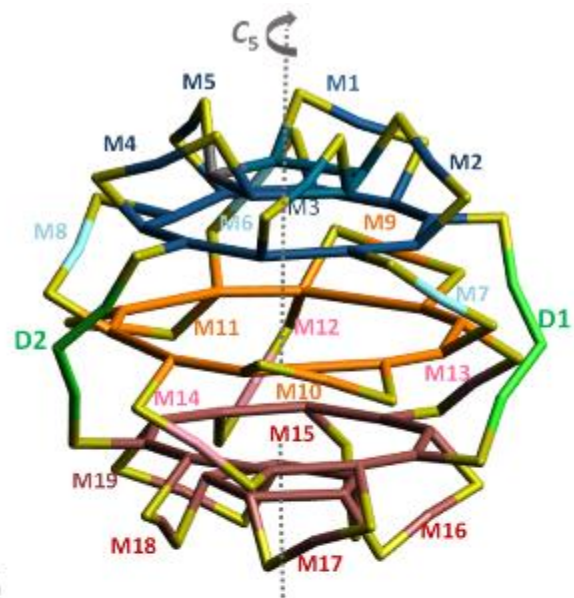
1, 5-(SBB)₁₀, 3-(SC₆H₁₂)₈
(i, 1, 2, x2)-palladoauro-25 asp (-1)



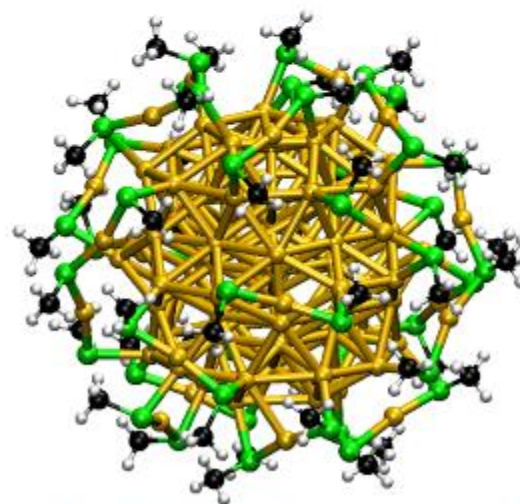
(A)



(B)



(C)



R-44(methylthiolato)-auro-102 aspicule(0)

R-(SMe)₄₄-auro-102 aspicule(0) and L-(SMe)₄₄-auro-102 aspicule(0) ⁵⁹

5. What for?

Devices, quantum, catalysis, energy, CO₂ conversion, biology,....

Where are they taking us to?

Biopolymer-reinforced synthetic granular nanocomposites for affordable point-of-use water purification

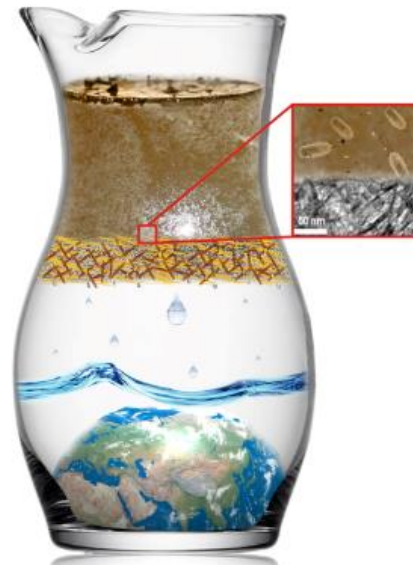
Mohan Udhaya Sankar¹, Sahaja Aigal¹, Shihabudheen M. Maliyekkal¹, Amrita Chaudhary, Anshup, Avula Anil Kumar, Kamalesh Chaudhari, and Thalappil Pradeep²

Unit of Nanoscience and Thematic Unit of Ex

Edited by Eric Hoek, University of California,

Creation of affordable materials for cons water is one of the most promising way drinking water for all. Combining the composites to scavenge toxic species other contaminants along with the ab affordable, all-inclusive drinking water without electricity. The critical proble synthesis of stable materials that can uously in the presence of complex s drinking water that deposit and caus surfaces. Here we show that such can be synthesized in a simple and effective out the use of electrical power. The na sand-like properties, such as higher shea forms. These materials have been used water purifier to deliver clean drinking ily. The ability to prepare nanostructu ambient temperature has wide releva water purification.

hybrid | green | appropriate technology | frugal science | developing world



Madras, Chennai 600 036, India

(received for review November 21, 2012)

available; and (c) continued retention matrix is difficult.

ate a unique family of nanocrystalline n granular composite materials pre- ature through an aqueous route. The mposition is attributed to abundant -O on chitosan, which help in the crys- oxide and also ensure strong covalent : surface to the matrix. X-ray photo-) confirms that the composition is rich ps. Using hyperspectral imaging, the aching in the water was confirmed. to reactivate the silver nanoparticle al antimicrobial activity in drinking osites have been developed that can its in water. We demonstrate an af- device based on such composites de- nd undergoing field trials in India, as :spread eradication of the waterborne

Results and Discussion

M. Udhaya Sankar, et. al. *Proc. Natl. Acad. Sci.*, 110 (2013) 8459-8464.

Clean water for everyone



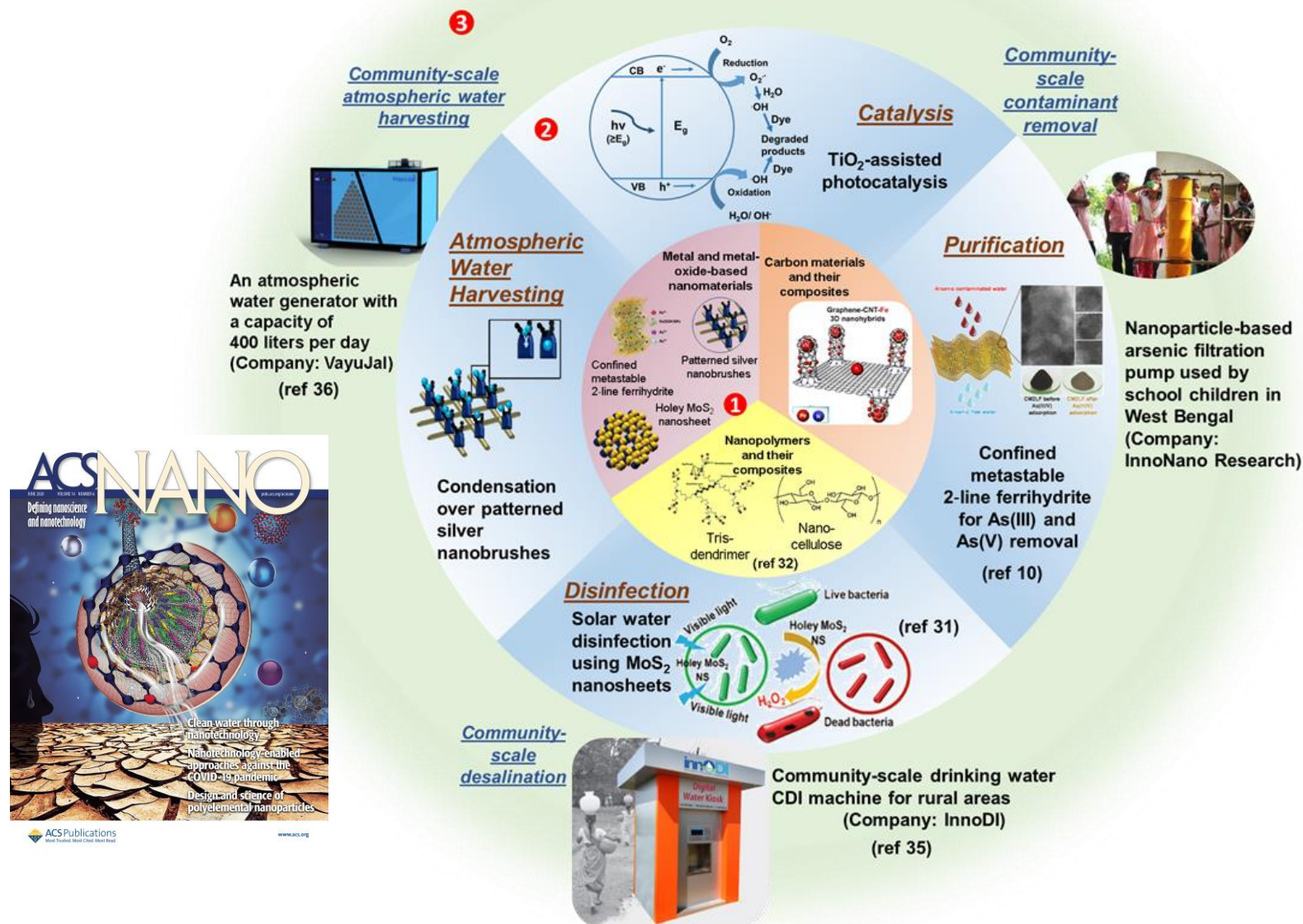
ACS Sustainable Chemistry & Engineering Editorial,
December 2016



We developed environmentally friendly water positive nanoscale materials for affordable, sustainable and rapid removal of arsenic from drinking water.

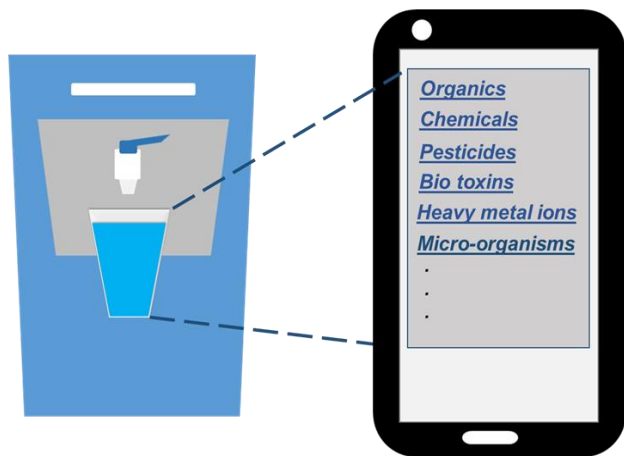
There are over 1700 community installations across the country, serving 1.3 million people with arsenic and iron-free water every day.

Evolution of materials to products

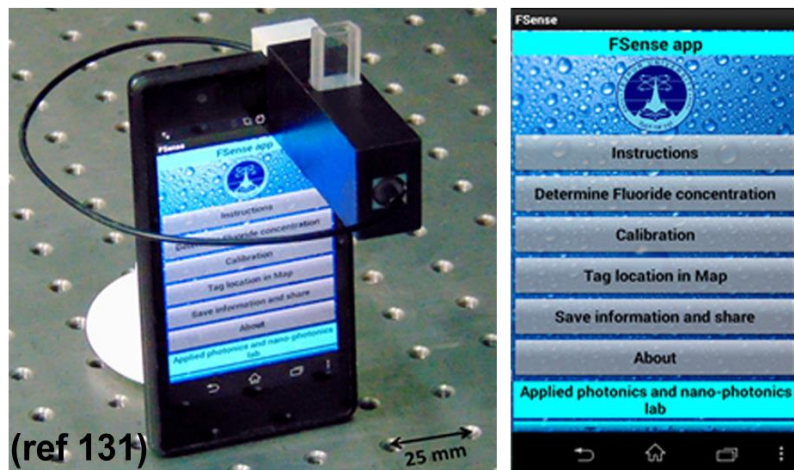


Smart water purifiers and big data

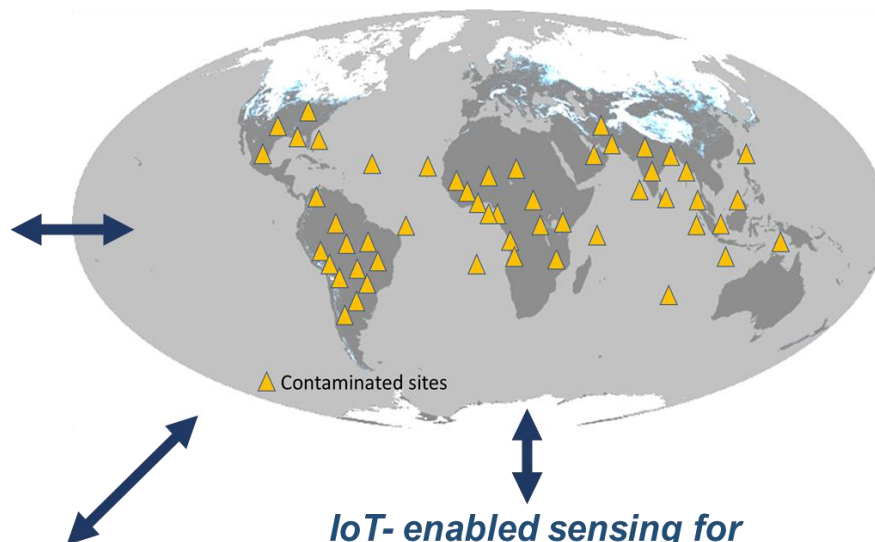
Smart Water Purifiers linked to IoT



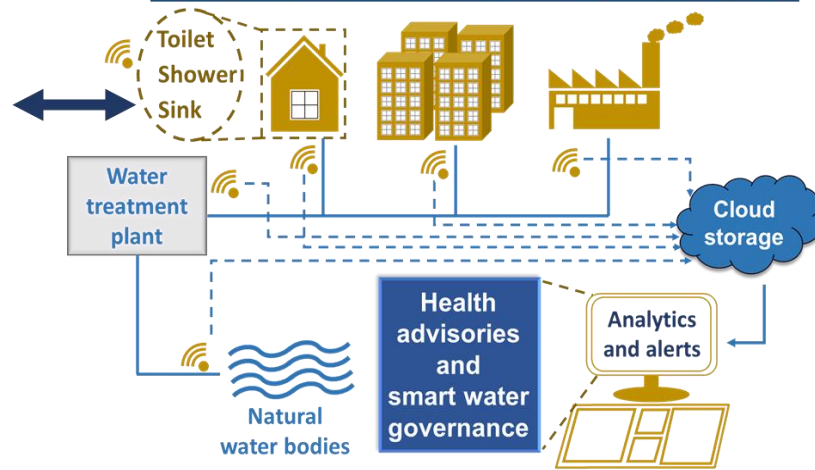
Cost-effective sensor accessory for point-of-use applications



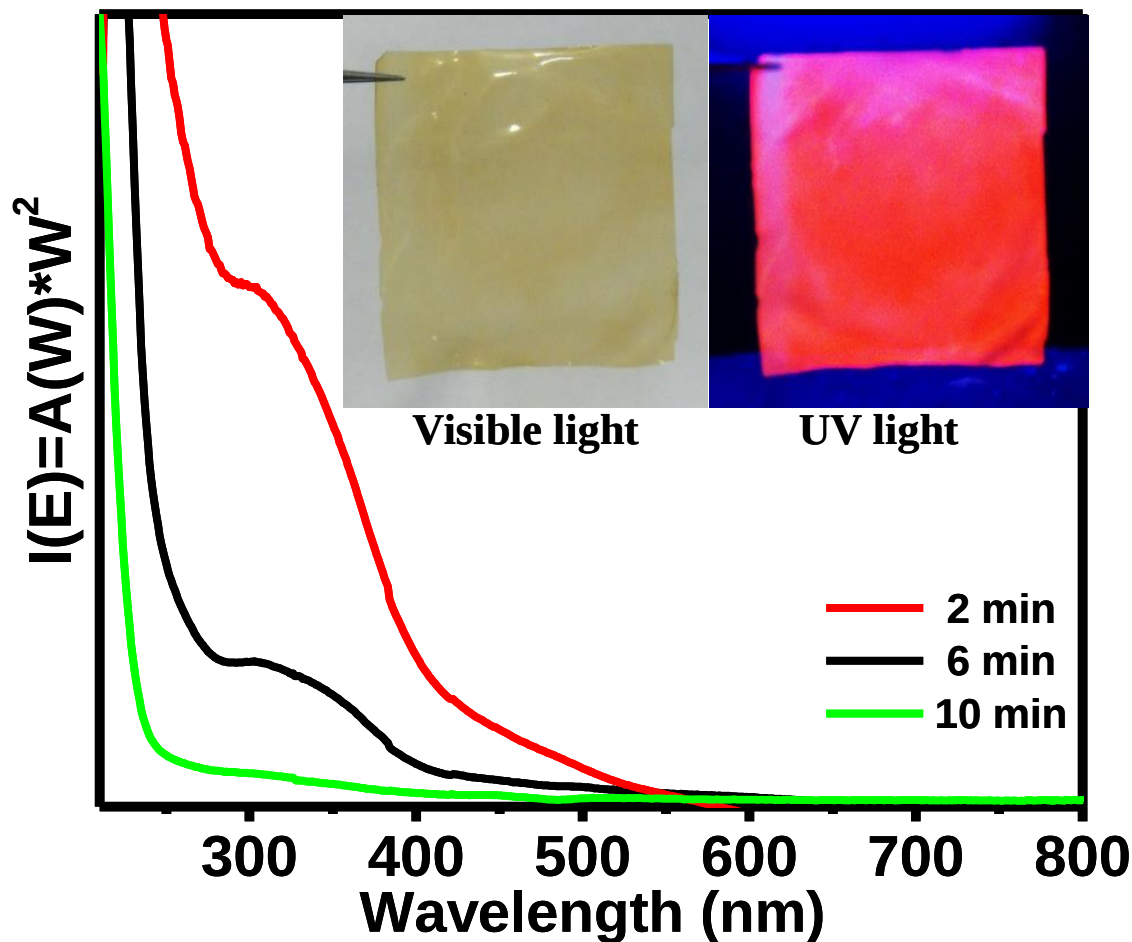
Global Map of Water Health



IoT-enabled sensing for households and distribution networks

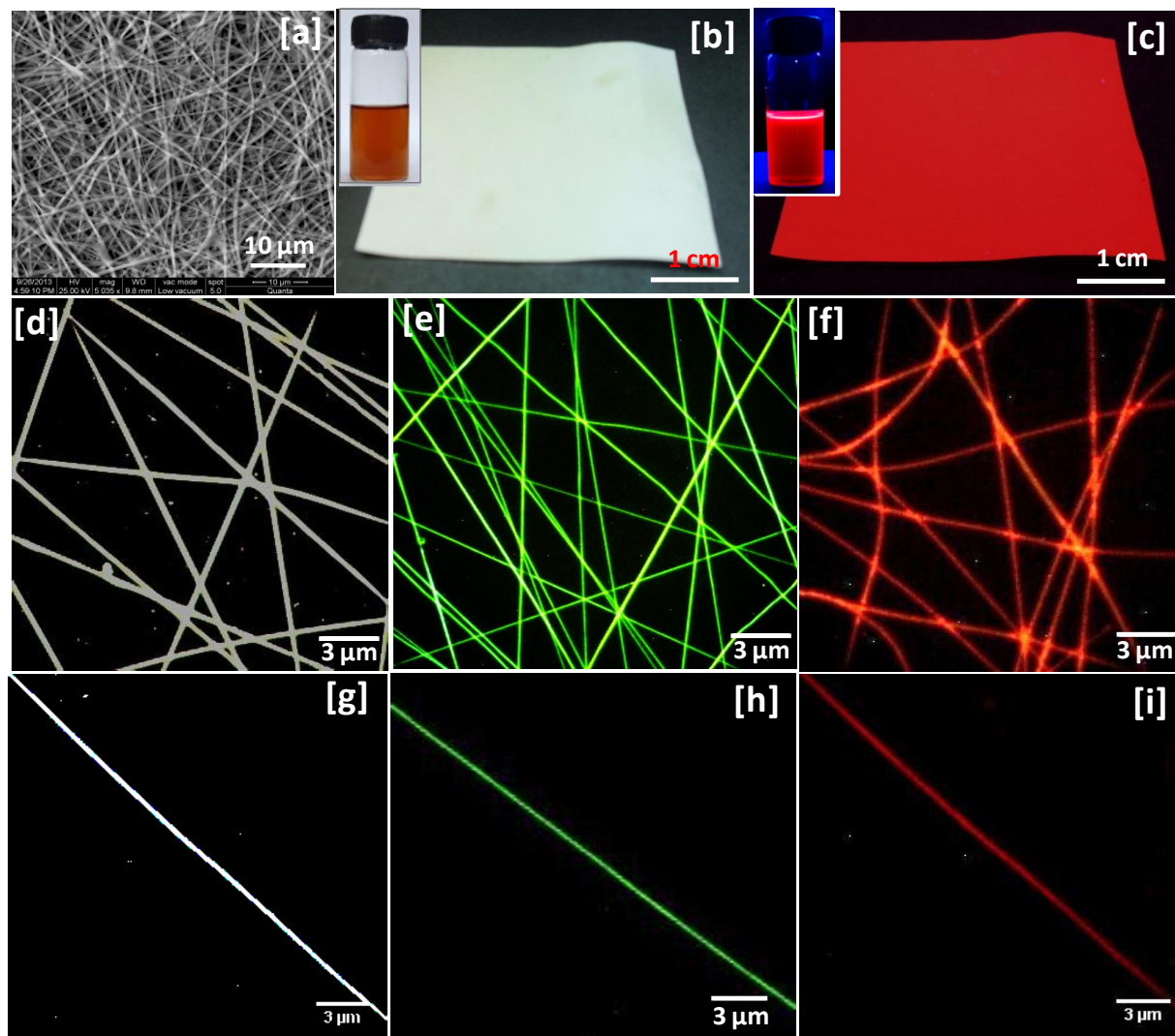


Cluster-based metal ion sensing

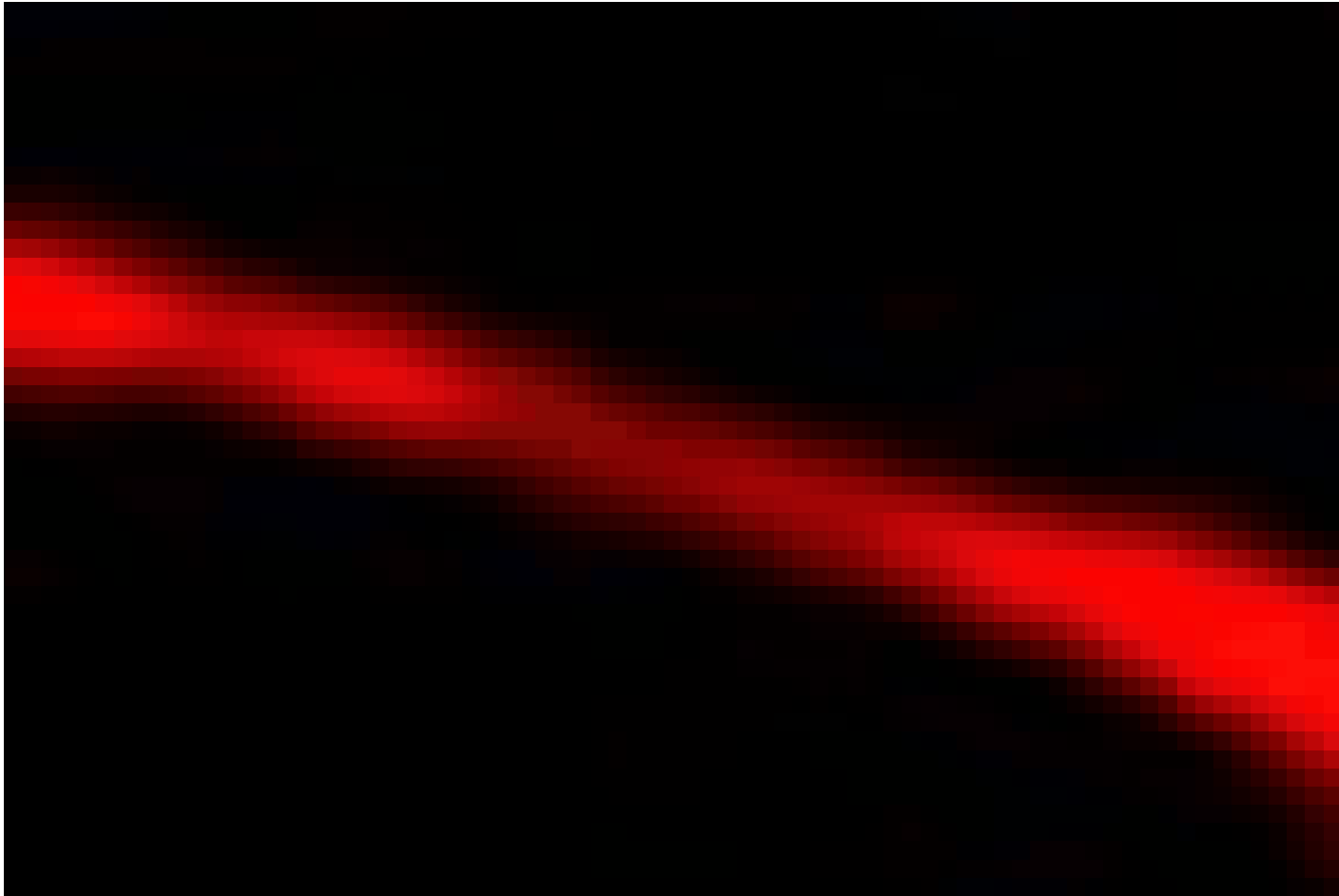


Decrease in the absorption of Au_{15} as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

Approaching detection limits of tens of Hg^{2+}

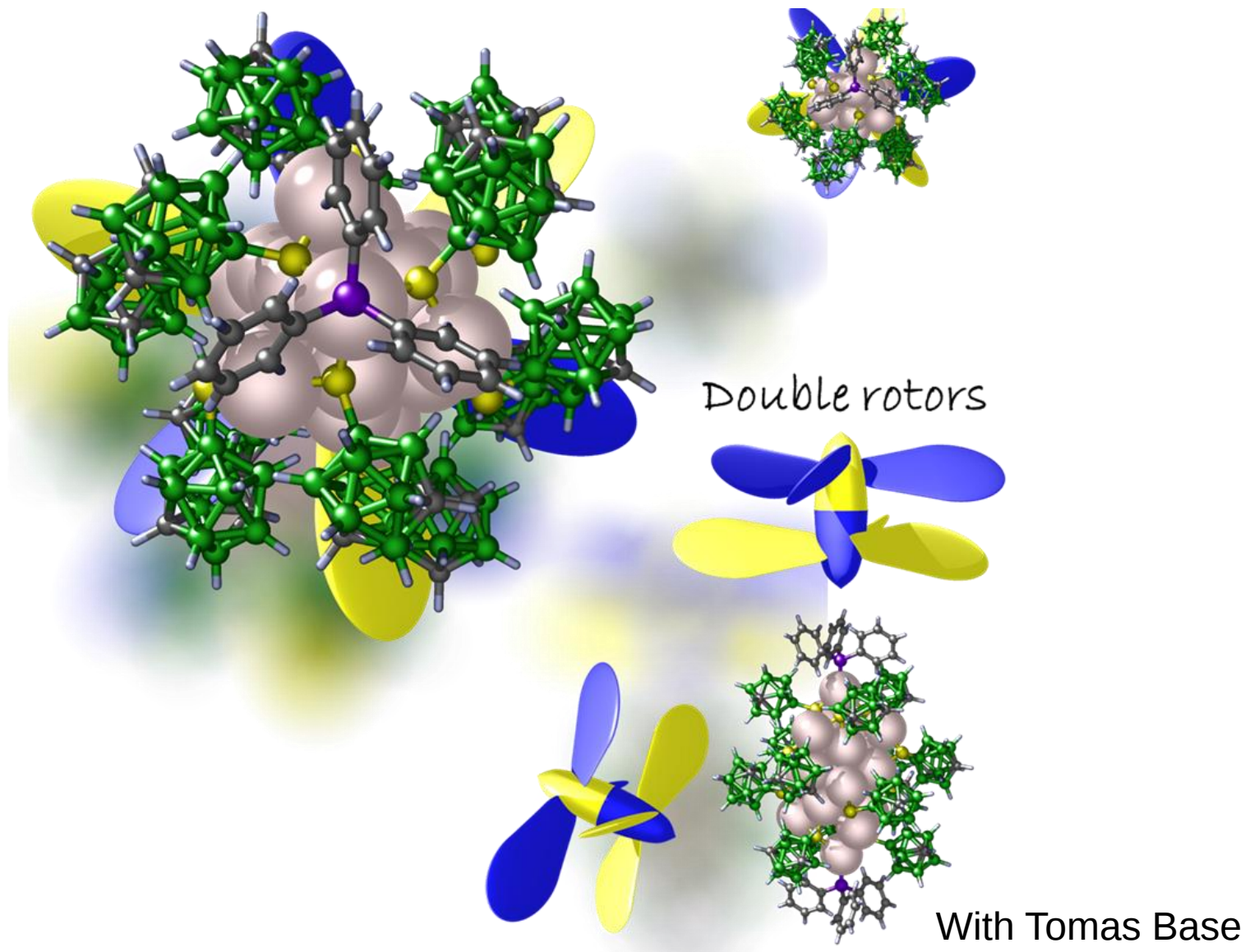


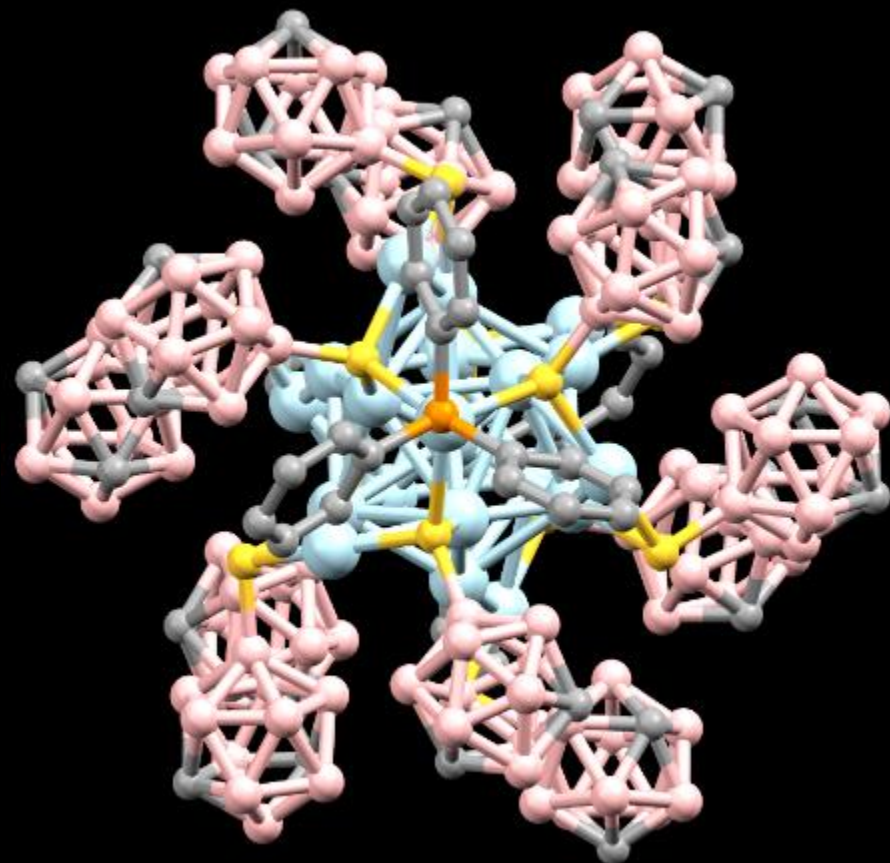
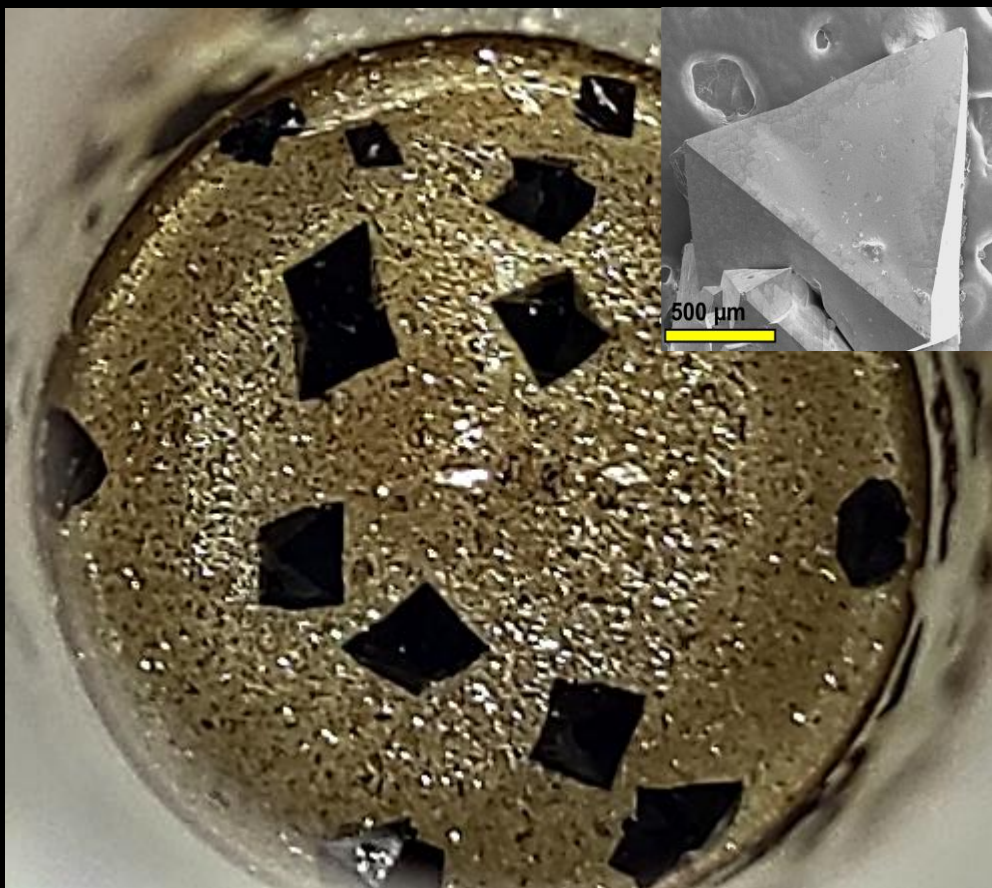
Mercury quenching experiment using nanofiber



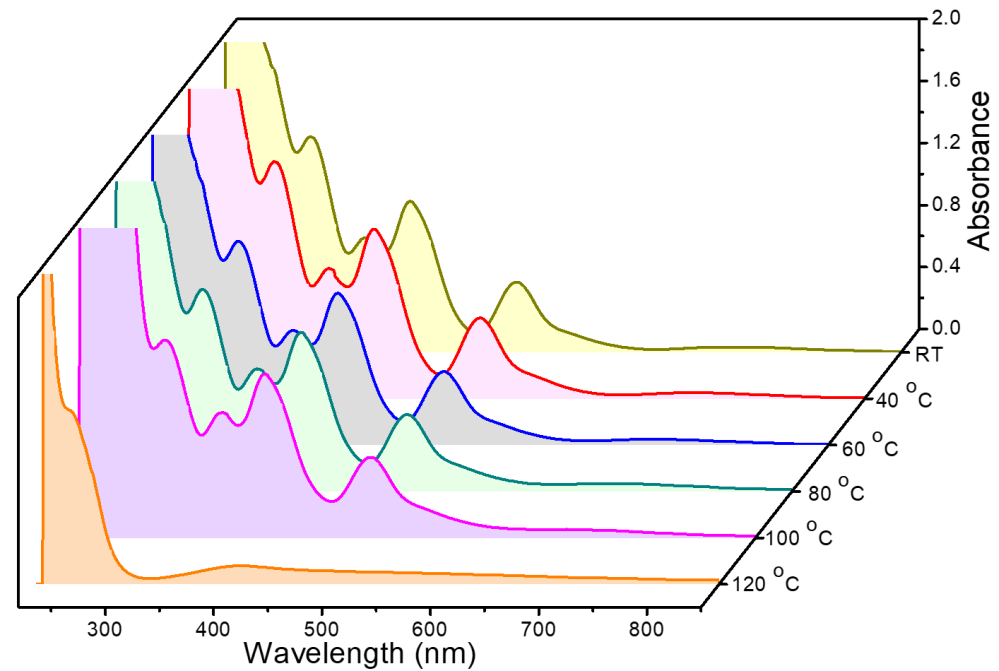
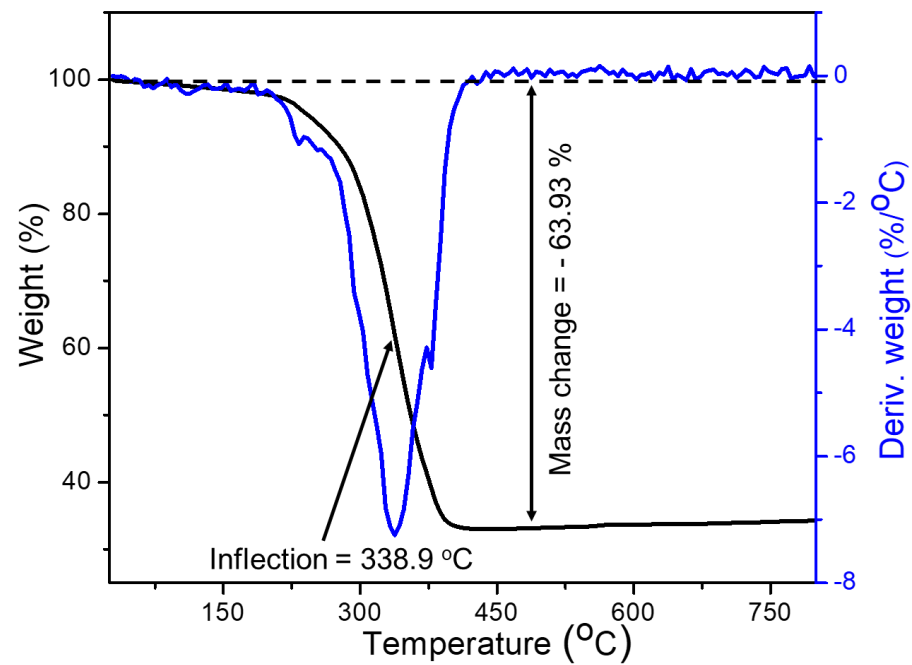
Stability

Carborane-thiols





Thermal stability



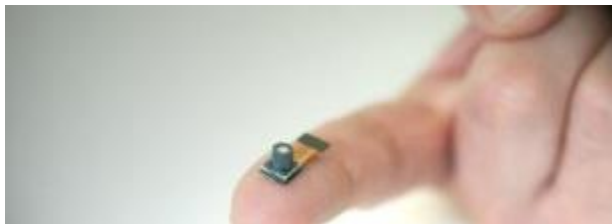
Sensors and new opportunities



Analog/Grating
Equipment
\$ 5~6 Billion (2017)
a few **100k units** (2017)



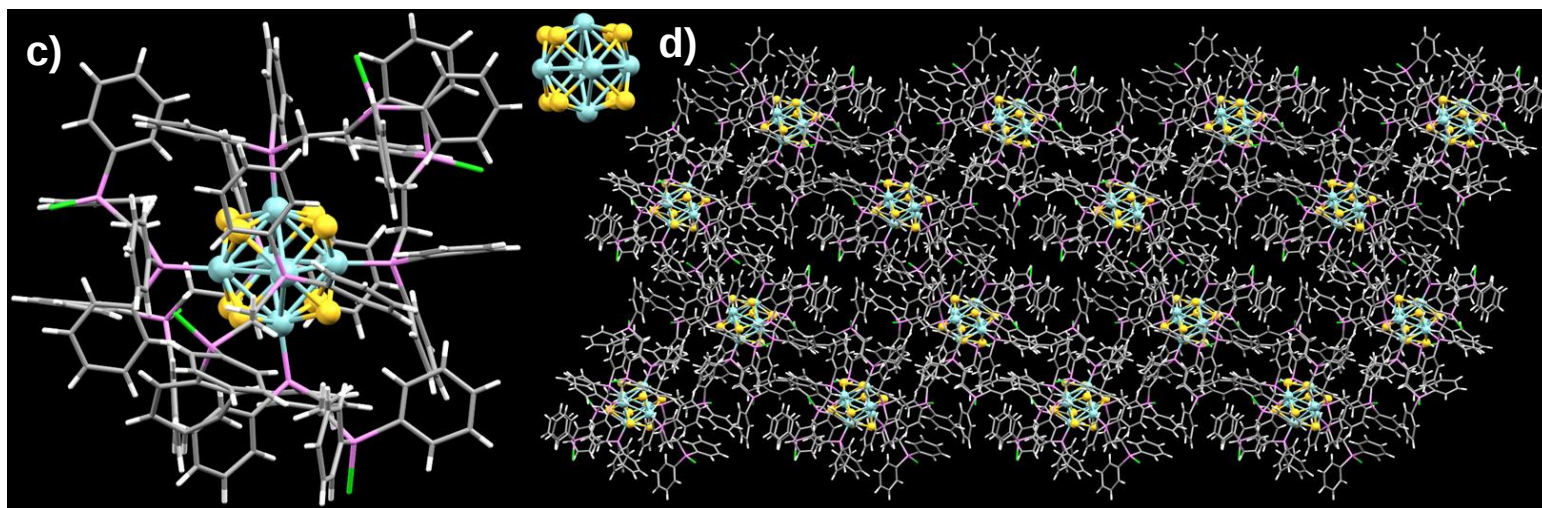
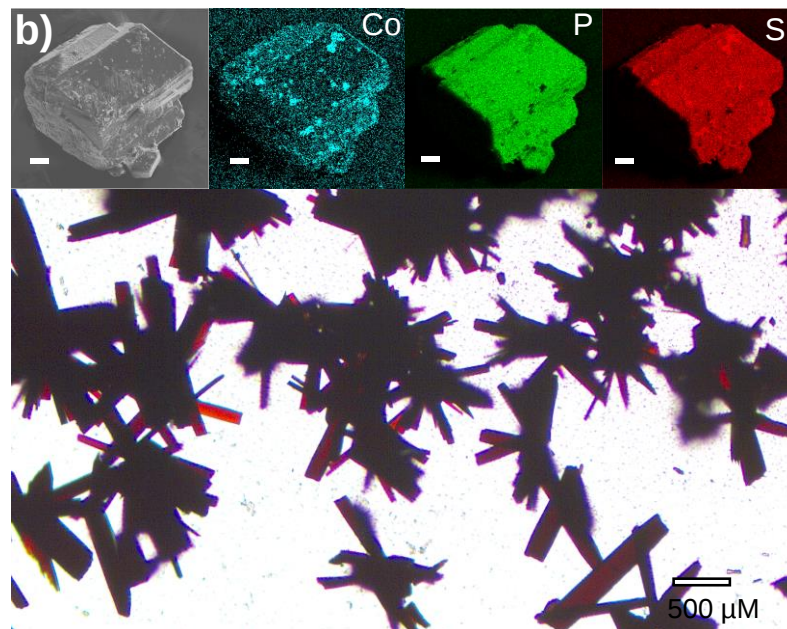
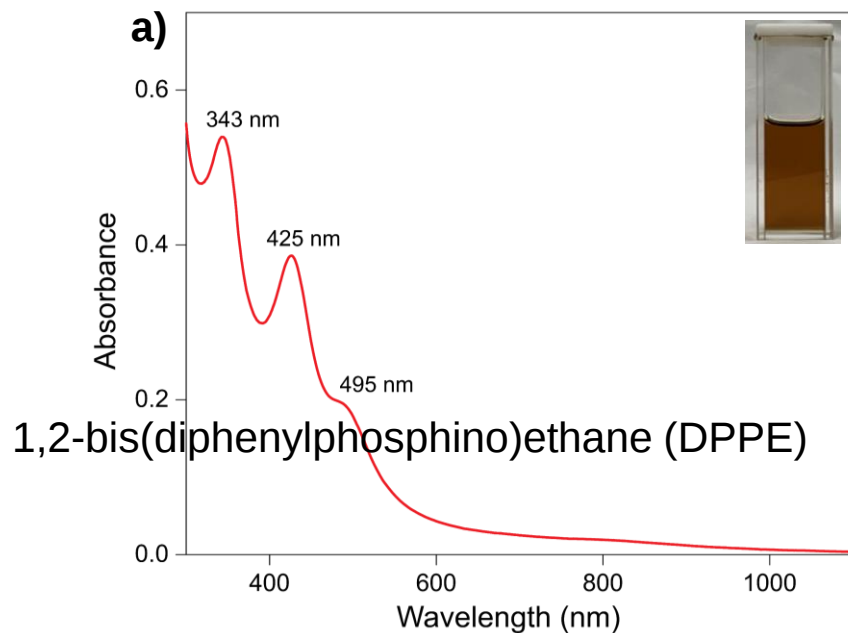
**Ultra compact Low Cost
Spectral Sensor Module**
~ **Billions units (? 2027)**



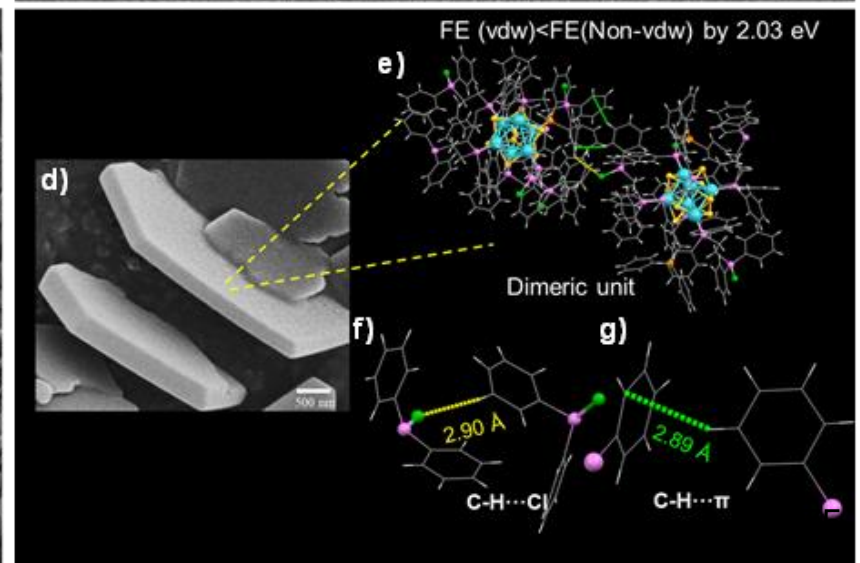
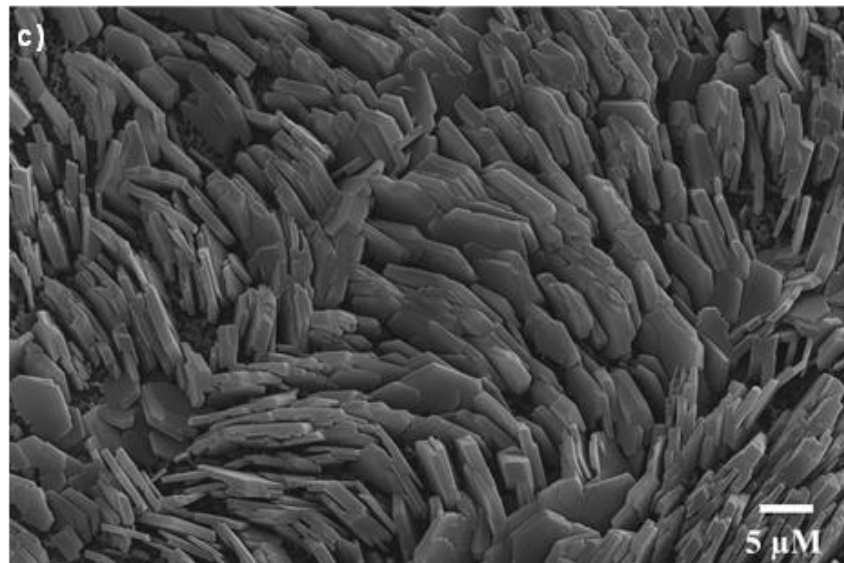
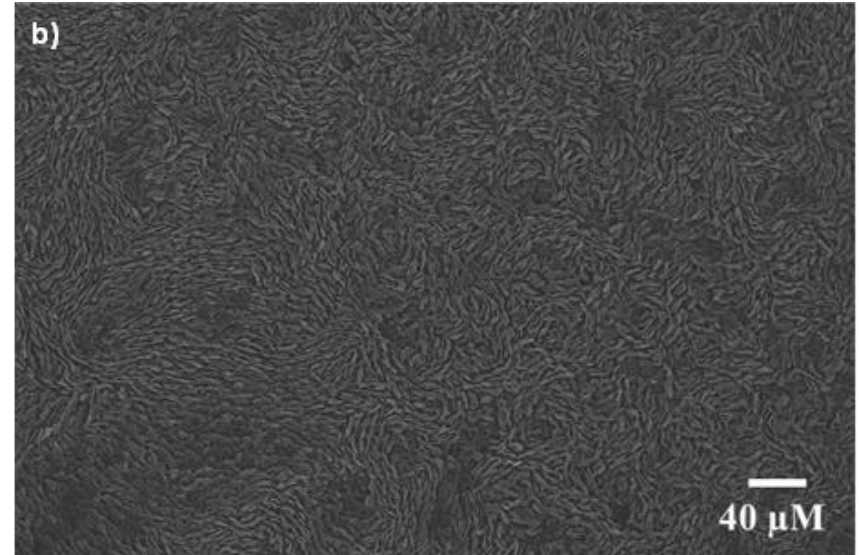
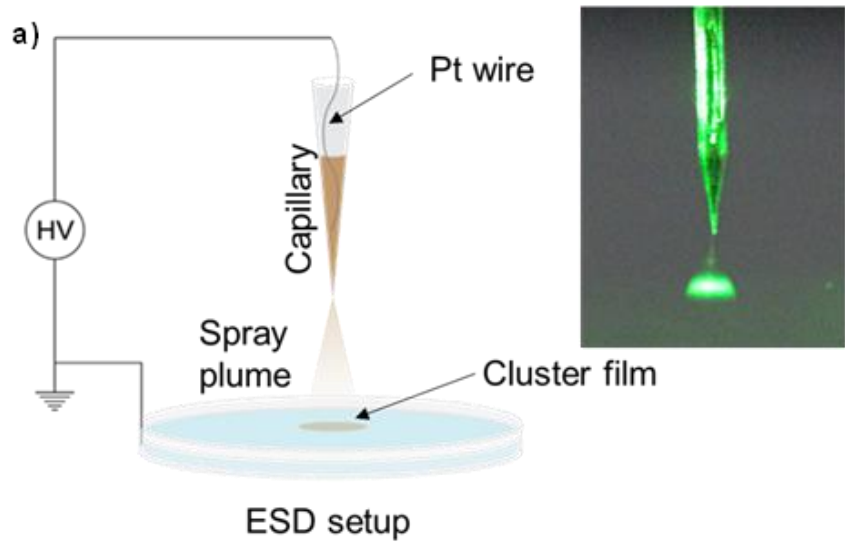
Water quality measurement – In the pipeline

nano λ

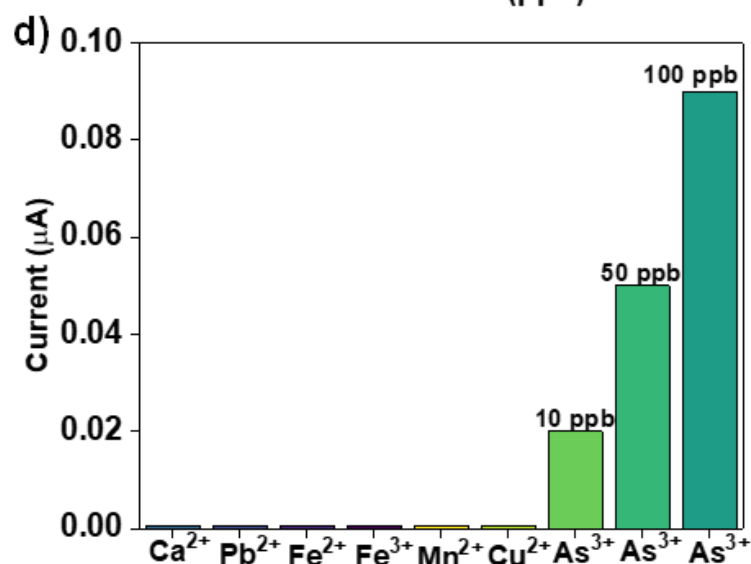
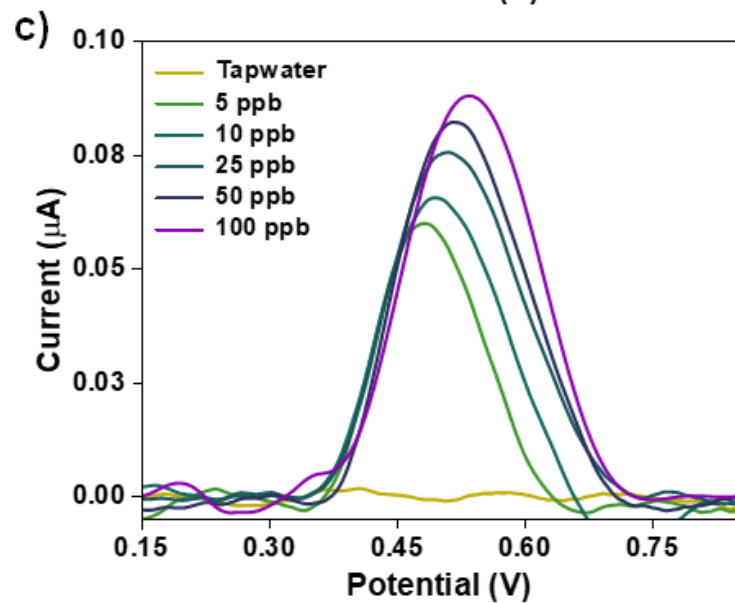
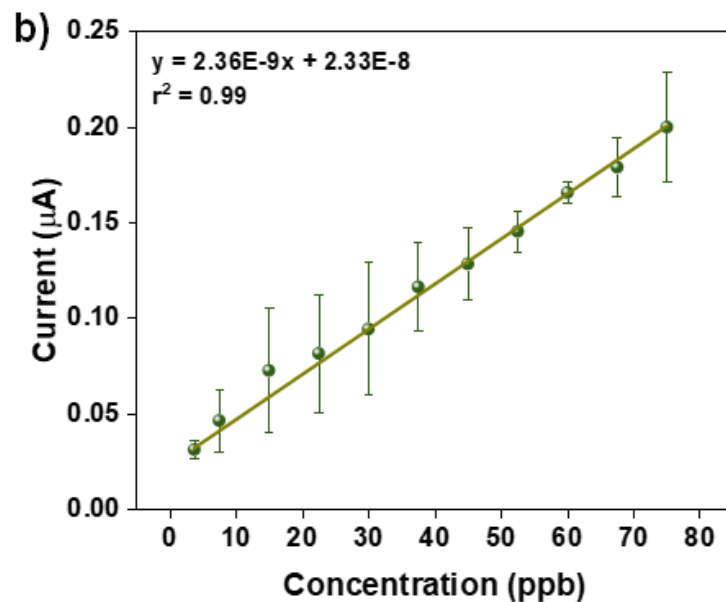
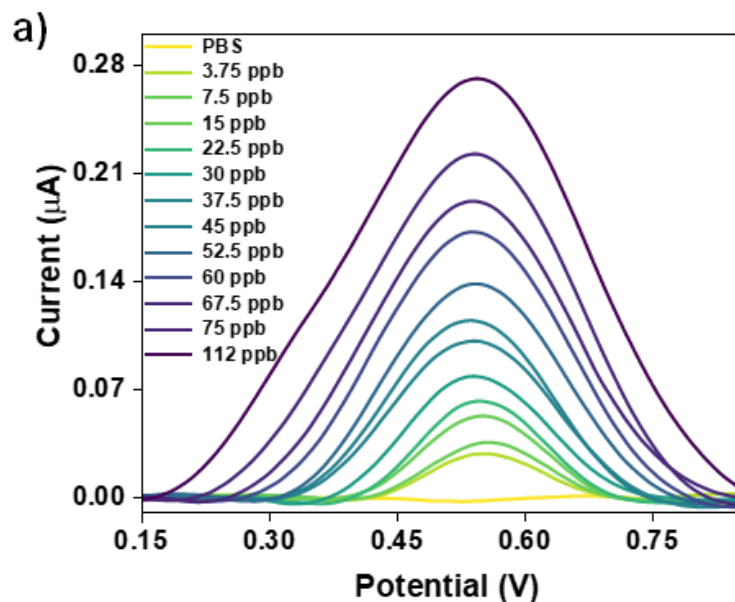
New electrodes - Aligned nanoplates of Co_6S_8



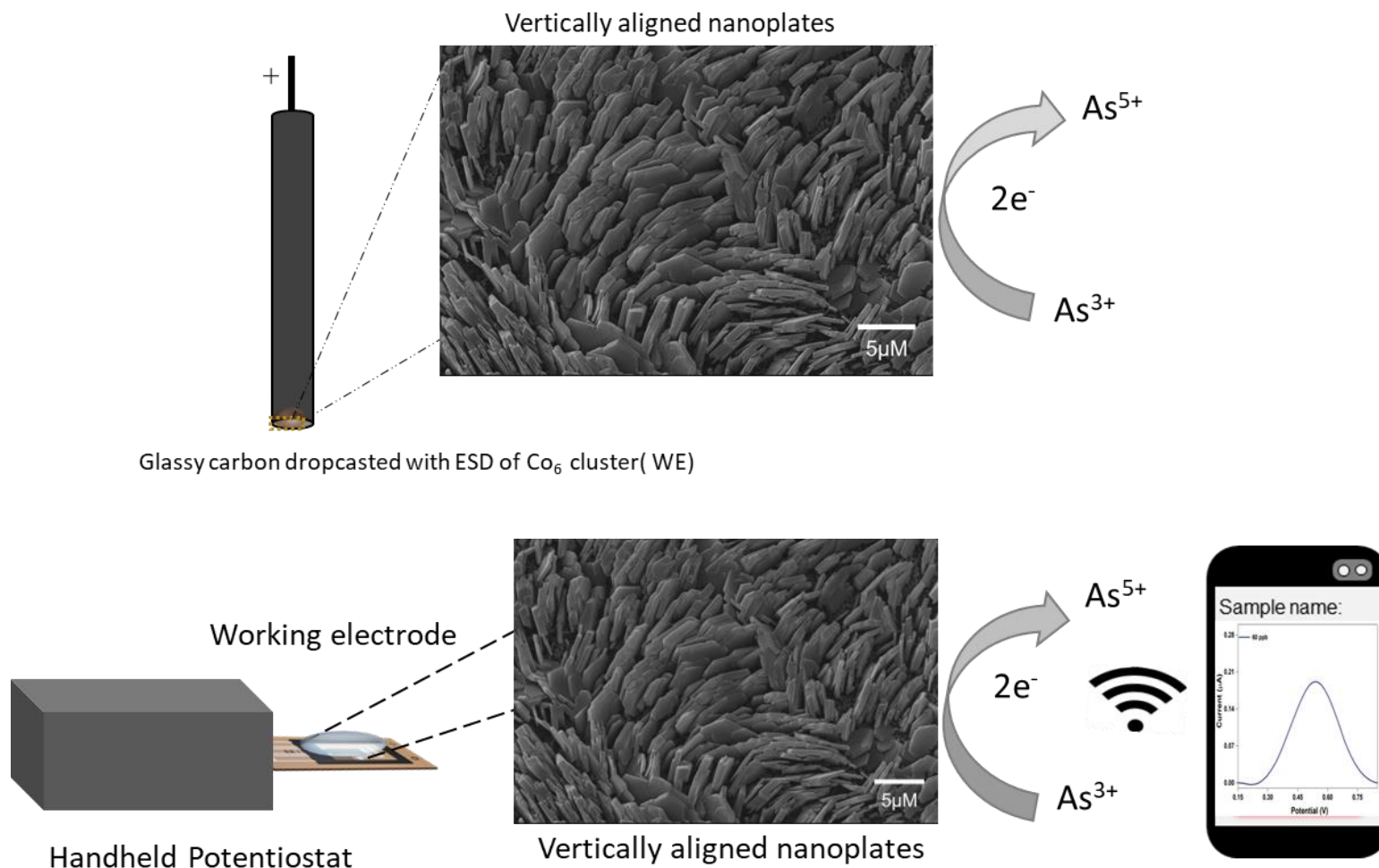
Electrospray deposition



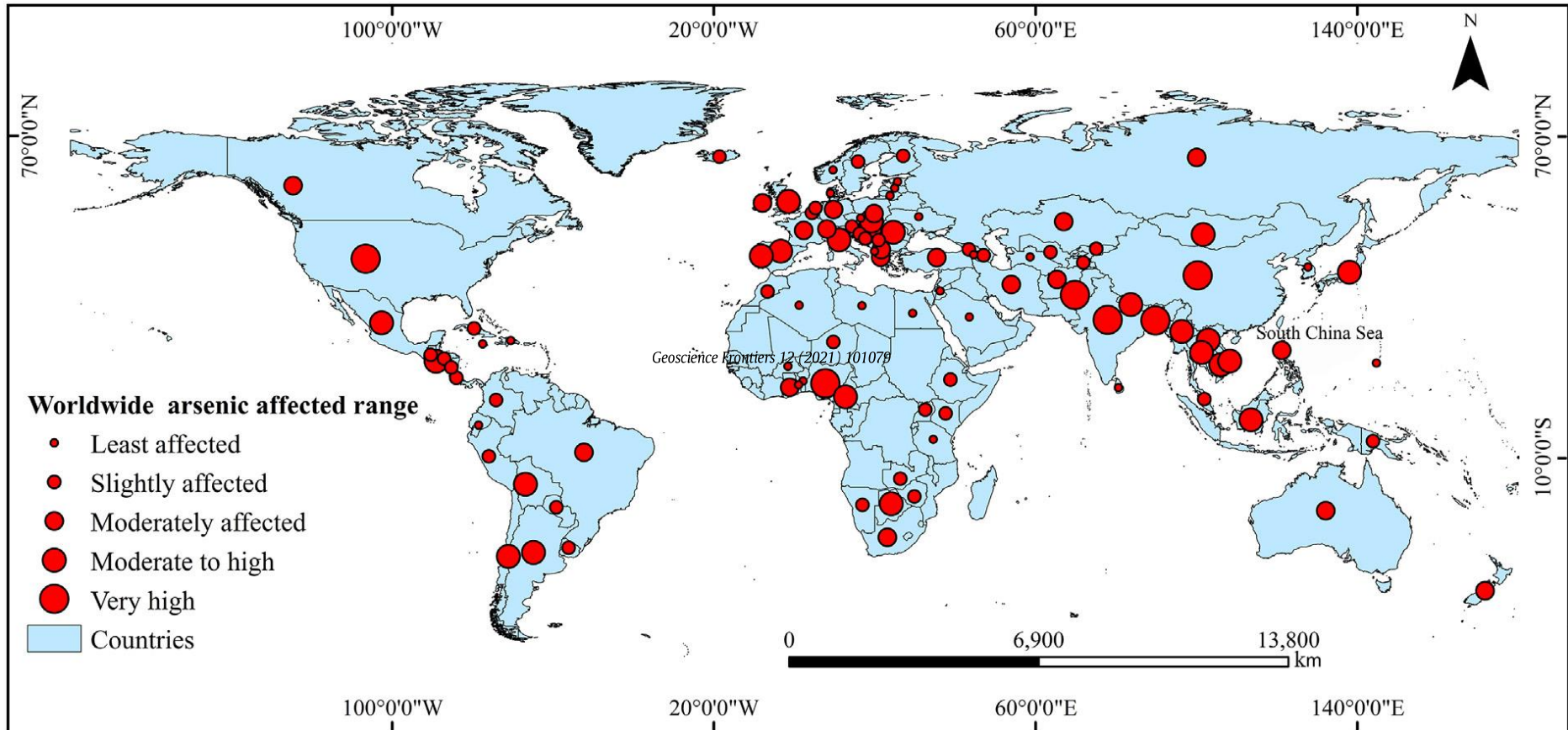
Sensing



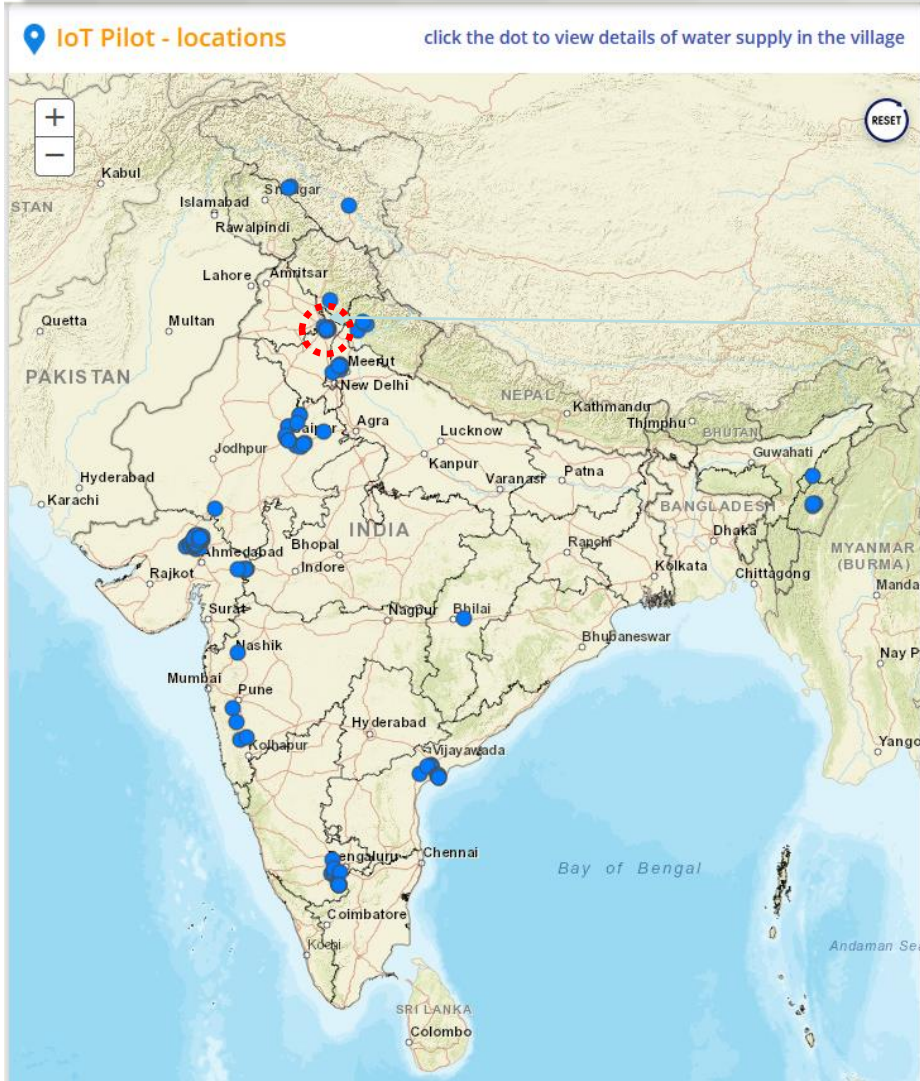
Working electrode



Arsenic poisoning across the world

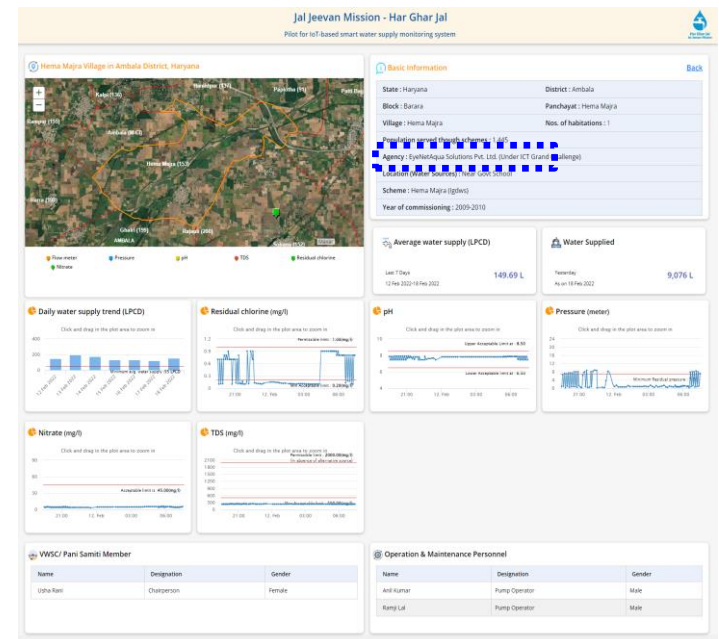


India's water is being monitored



IITM/IISc

Installations made by four companies





International Centre for Clean Water

Collaborators



Robin Ras

Nonappa

Tomas Base



Manfred Kappes

Olli Ikkala

Horst Hahn

Tatsuya Tsukuda,
Keisaku Kimura,
Yuichi Negishi,
Uzi Landman,
Hannu Hakkinen,
Rob Whetten



Shiv Khanna

Biswarup Pathak K. V. Adarsh

G. U. Kulkarni

Vivek Polshettiwar

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Thank you