Since 1959

Atomically Precise Matter

T. Pradeep

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https://pradeepresearch.org/

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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.

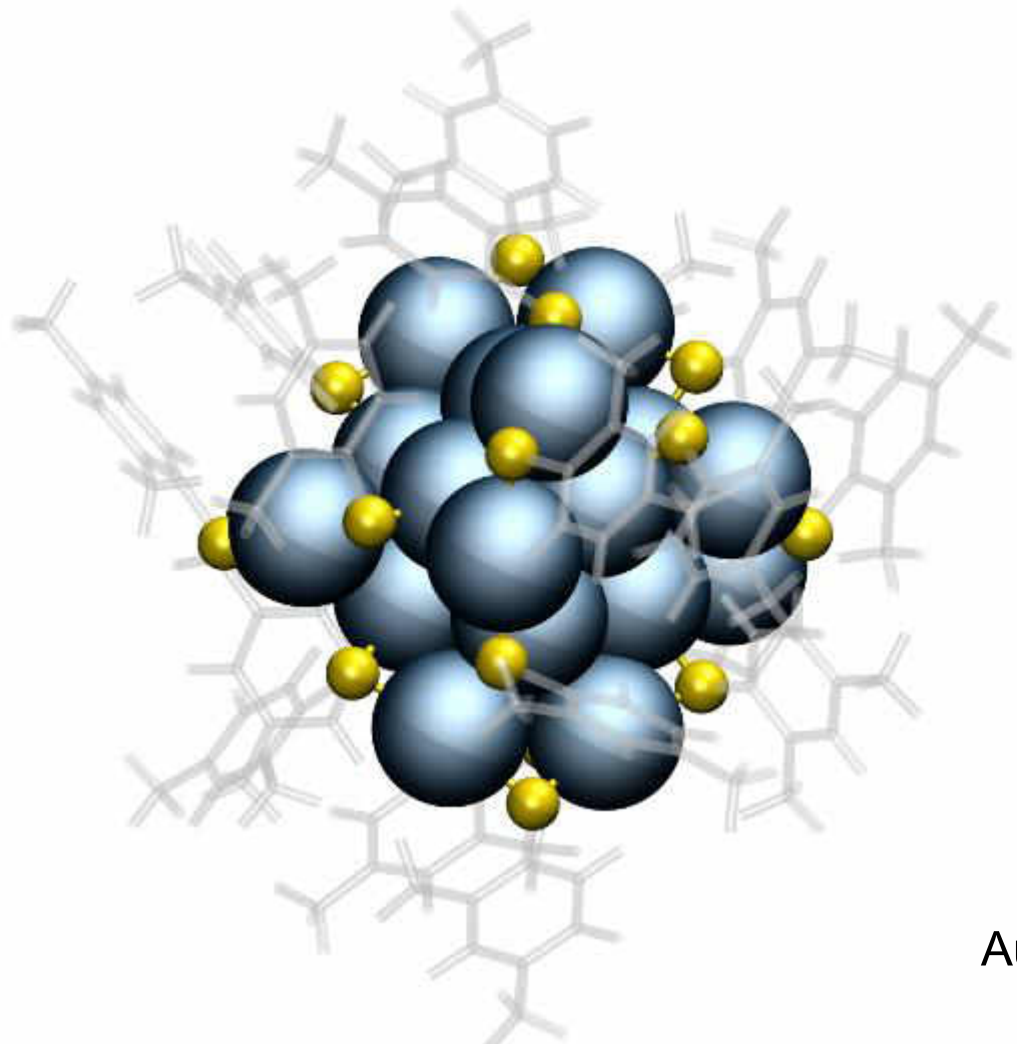
Associate Editor ACS Sustainable Chemistry & Engineering

Professor-in-charge

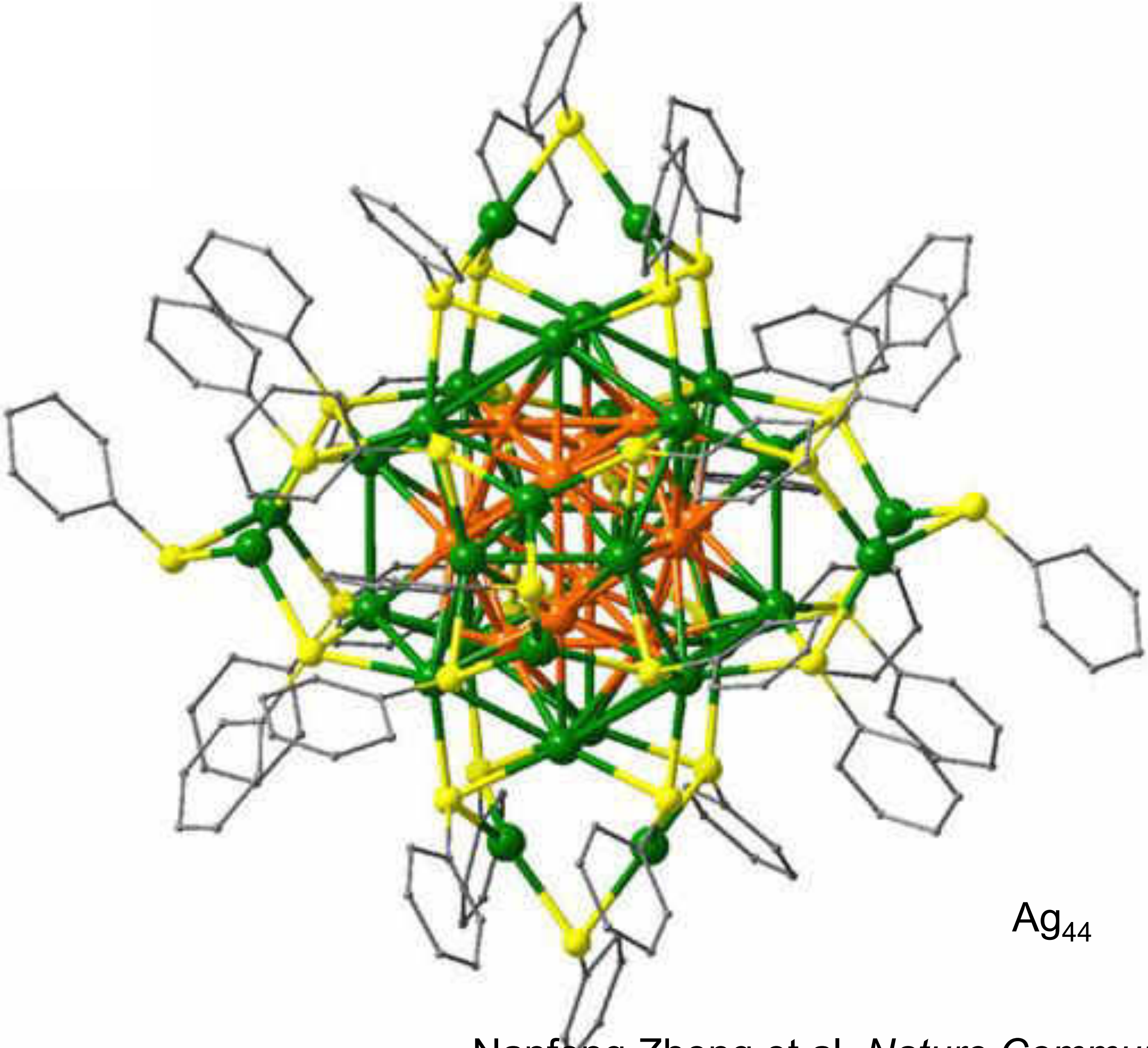
International Centre for Clean Water

Emerging Frontiers of Chemical Sciences, Farook College, Kozhikode, December 19-21, 2023

New molecules

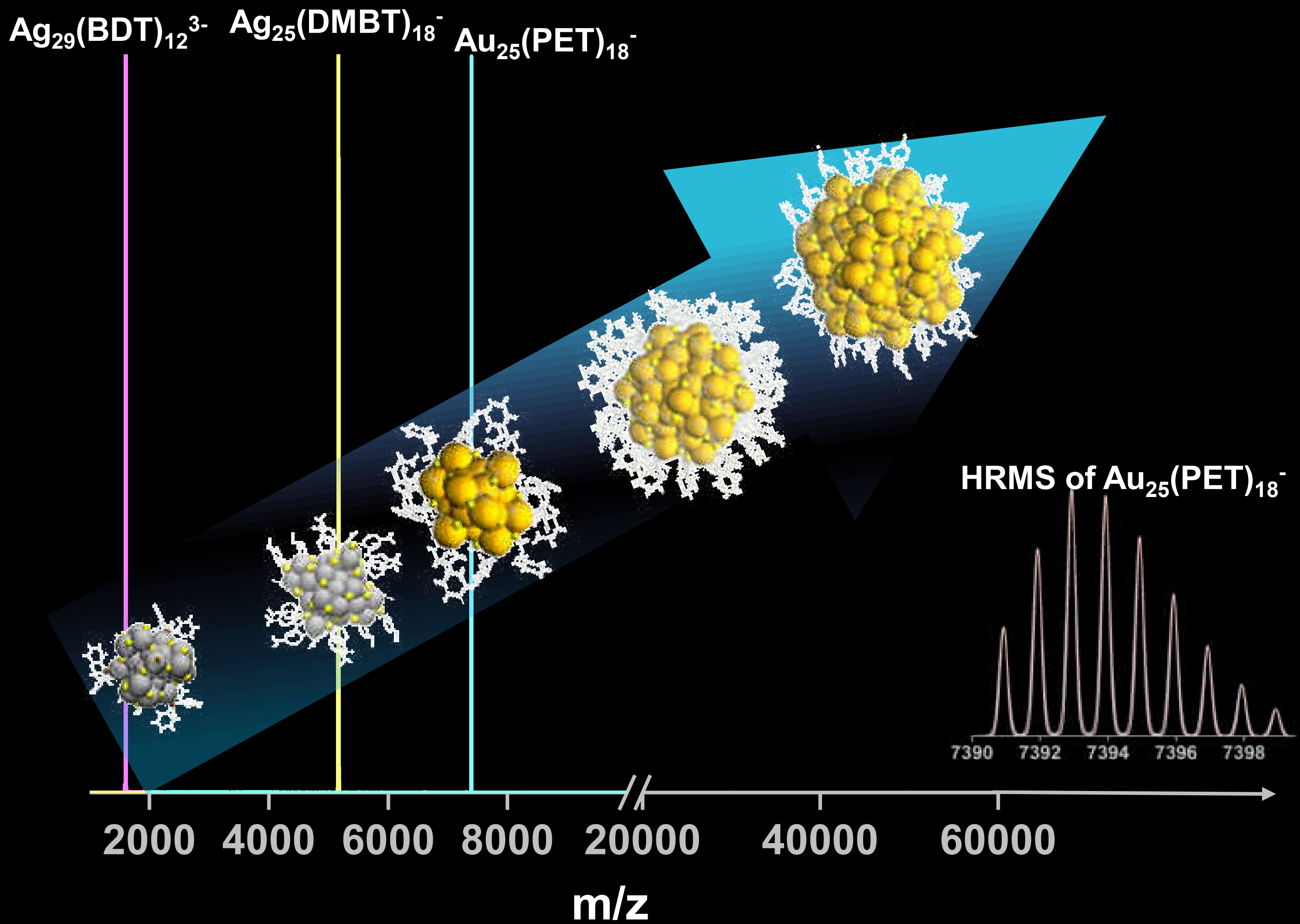


Au_{25}, Ag_{25}, Ag_{29}



Ag_{44}

Nanfeng Zheng et al. *Nature Communications*, 2013
Terry Bigioni et al. *Nature* 2013



$Ag_{29}(BDT)_{12}^{3-}$
$Ag_{25}(DMBT)_{18}^{-}$
$Au_{25}(PET)_{18}^{-}$
HRMS of $Au_{25}(PET)_{18}^{-}$
7390
7392
7394
7396
7398
2000
4000
6000
8000
20000
40000
60000
m/z

CHEMICAL REVIEWS

Review

pubs.acs.org/CR

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

Indranath Chakraborty[†] and Thalappil Pradeep*

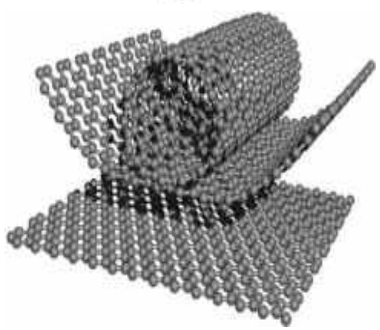
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

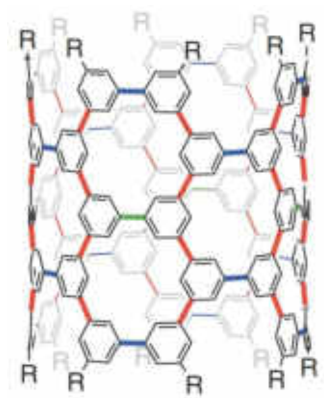
Supporting Information

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 $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{102}(SR)_{44}$ as well as $Ag_{25}(SR)_{18}$, $Ag_{29}(S_2R)_{12}$, and $Ag_{44}(SR)_{30}$ (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.

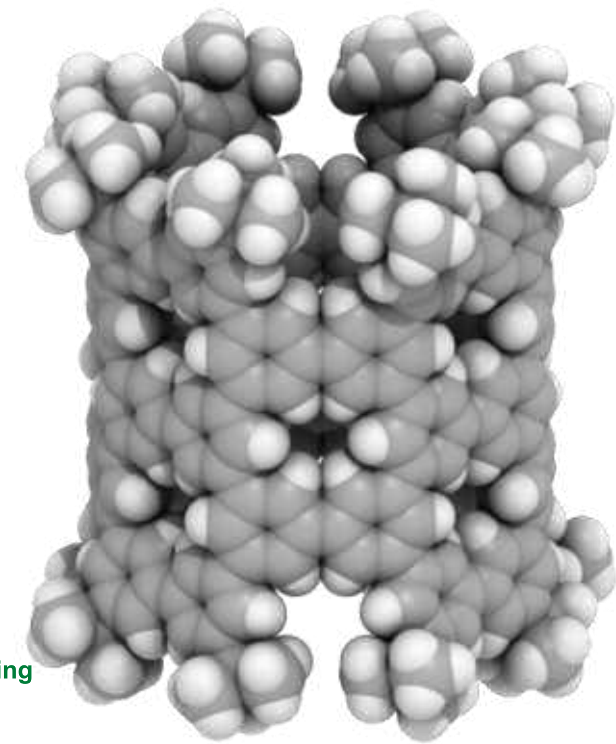
Phenine nanotube (pNT)

Synthesis does not limit us today



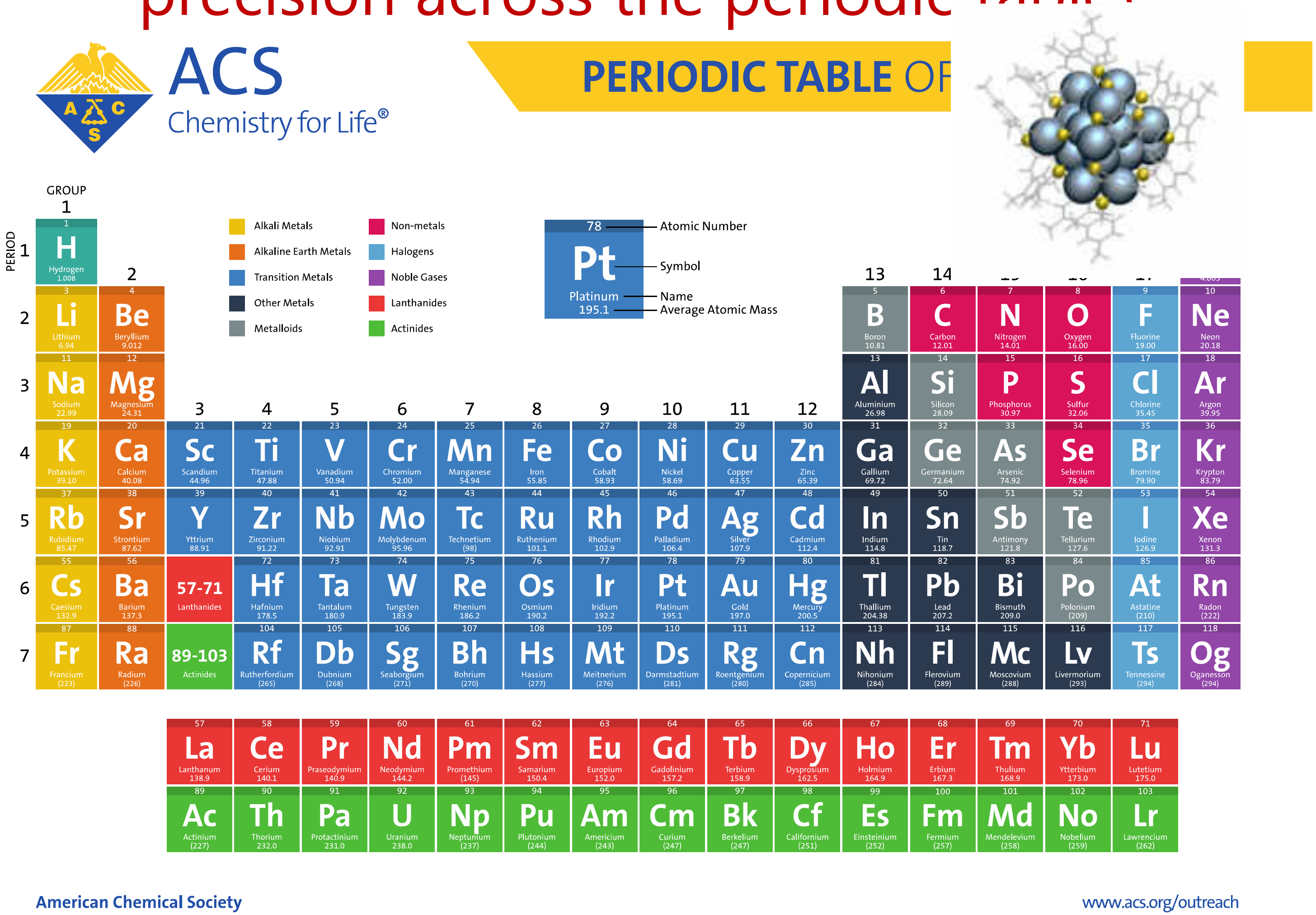


— Yamamoto coupling
— Suzuki-Miyaura coupling
— **Bäurle/Yamago/Isobe coupling**



H. Isobe *et al*. *Science* **2019**, *363*, 151

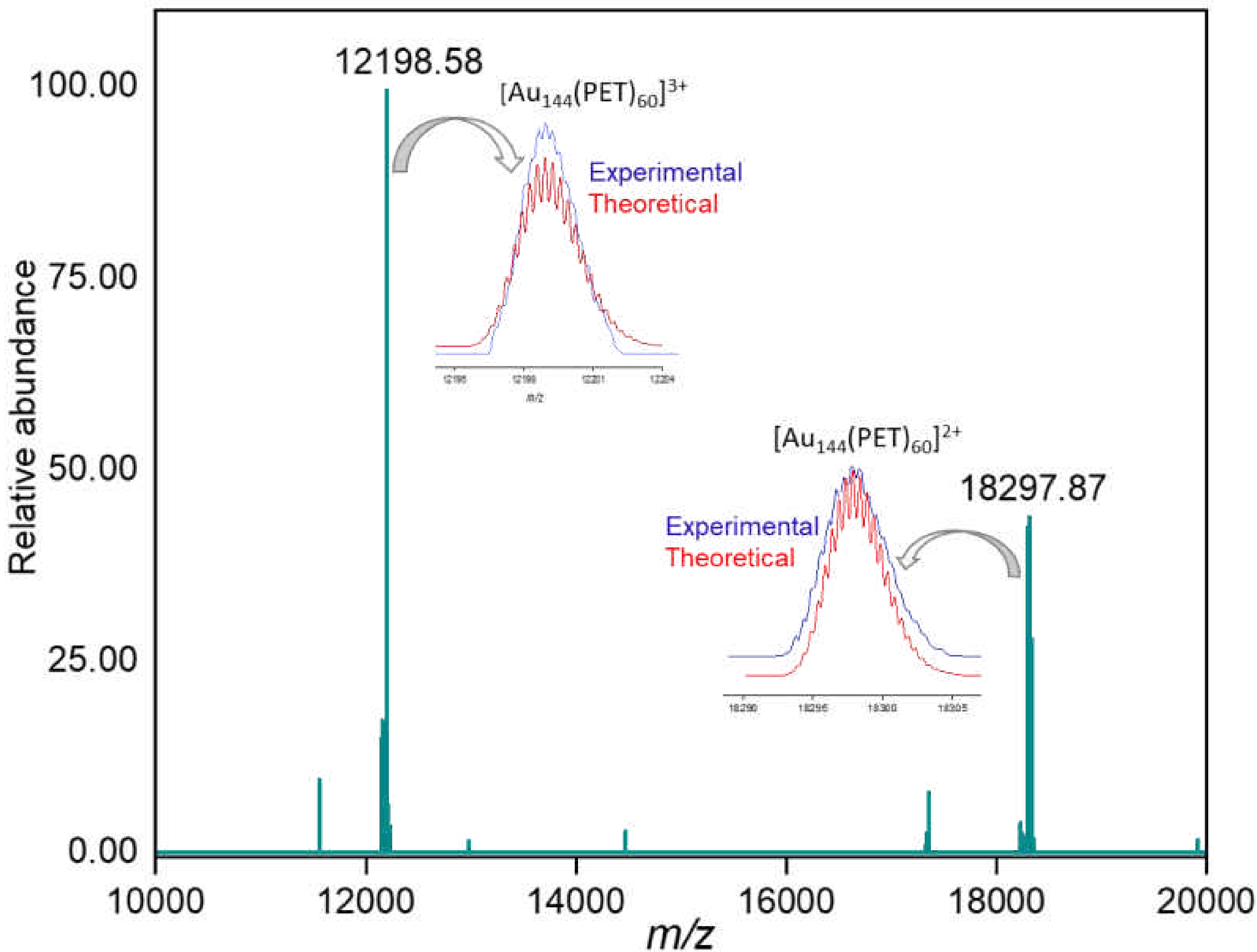
Can we create materials of atomic precision across the periodic table?



CARBON RECYCLING INTERNATIONAL

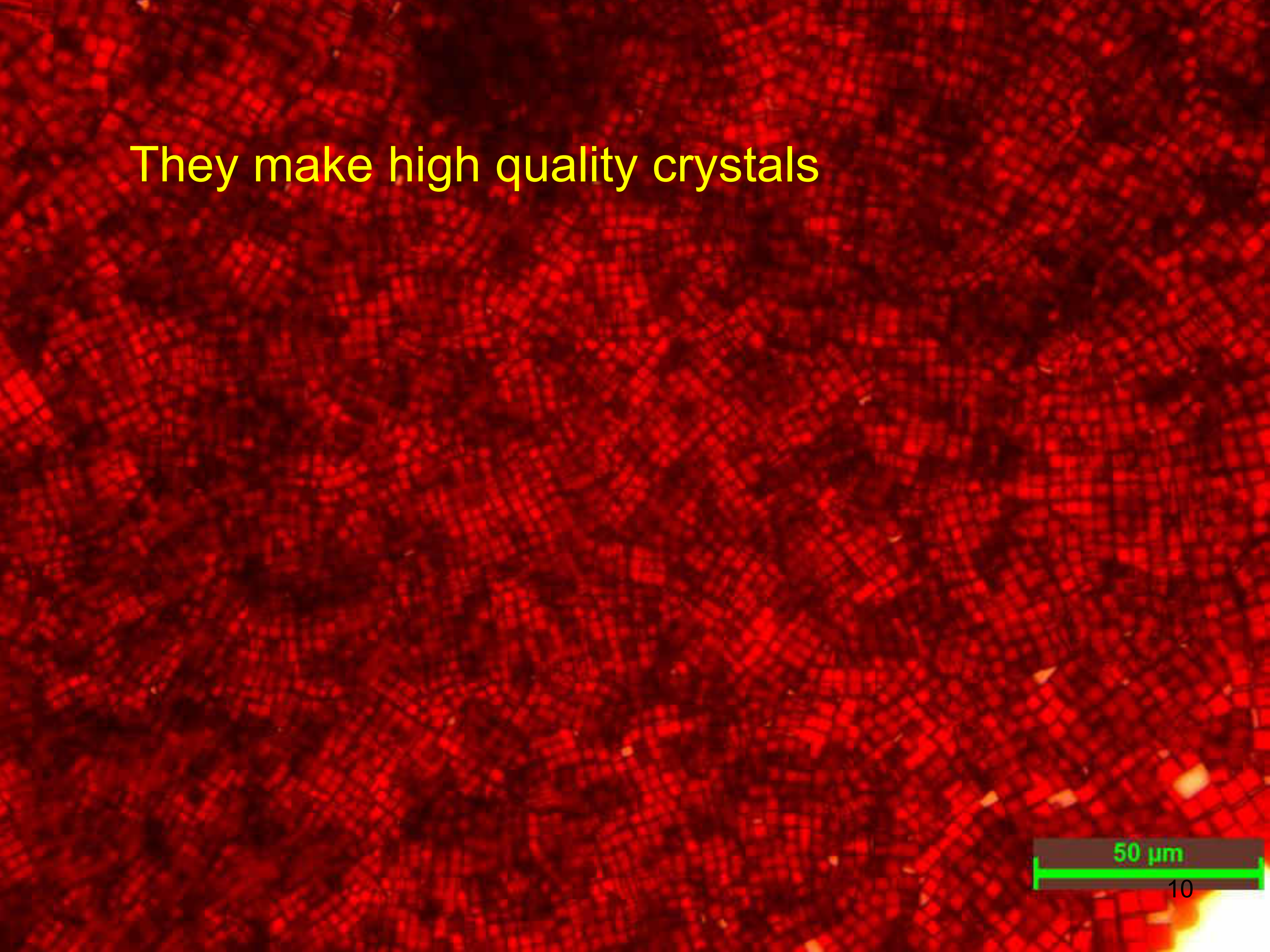
World's largest CO_2 to MeOH plant (Kopavogur, Iceland)

$Au_{144}(PET)_{60}$

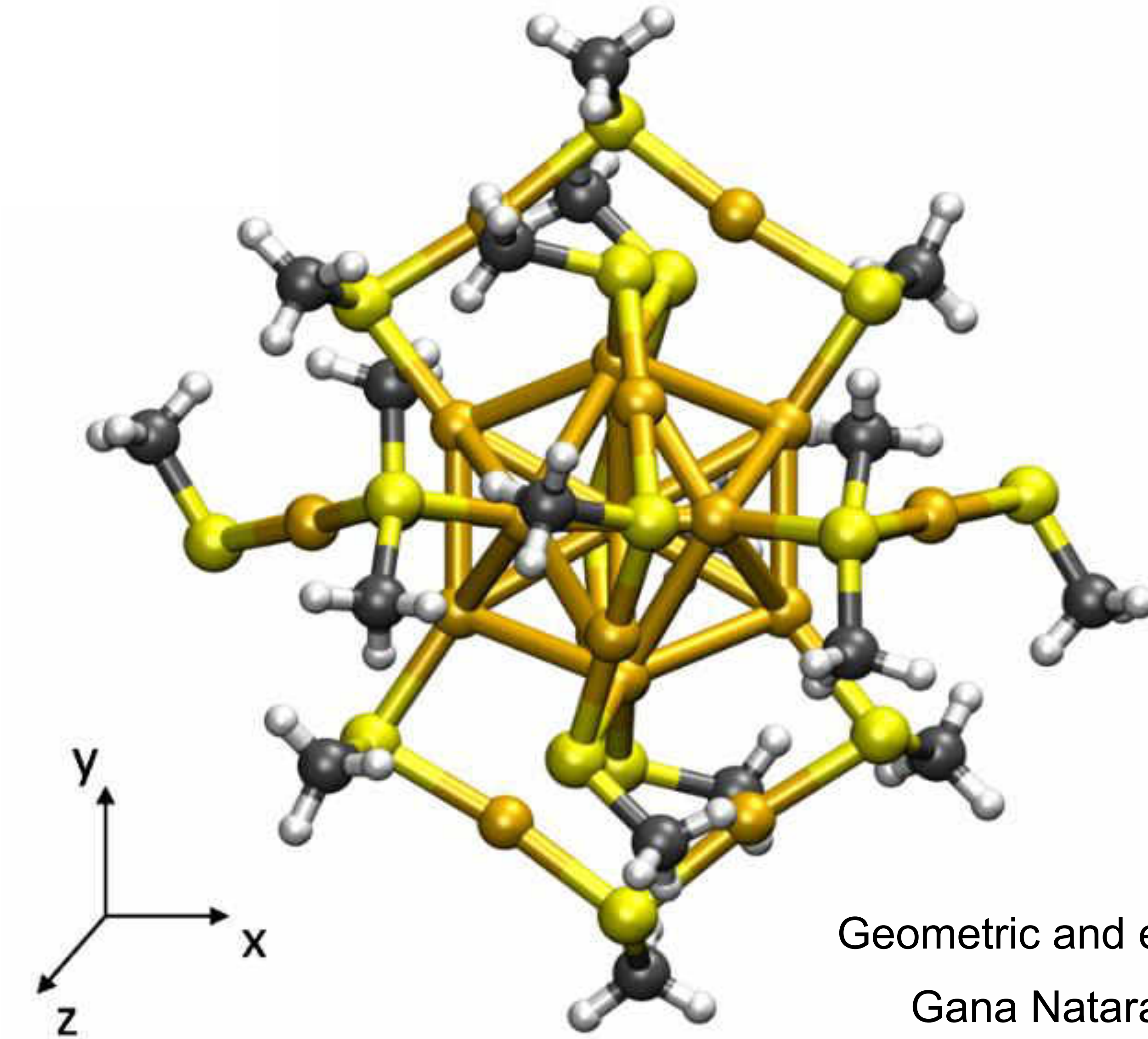


12198.58
$[Au_{144}(PET)_{60}]^{3+}$
Experimental
Theoretical
$[Au_{144}(PET)_{60}]^{2+}$
18297.87
Experimental
Theoretical
Relative abundance
100.00
75.00
50.00
25.00
0.00
10000
12000
14000
16000
18000
20000
m/z

They make high quality crystals



Molecular structure



Molecular materials

ACCOUNTS of chemical research

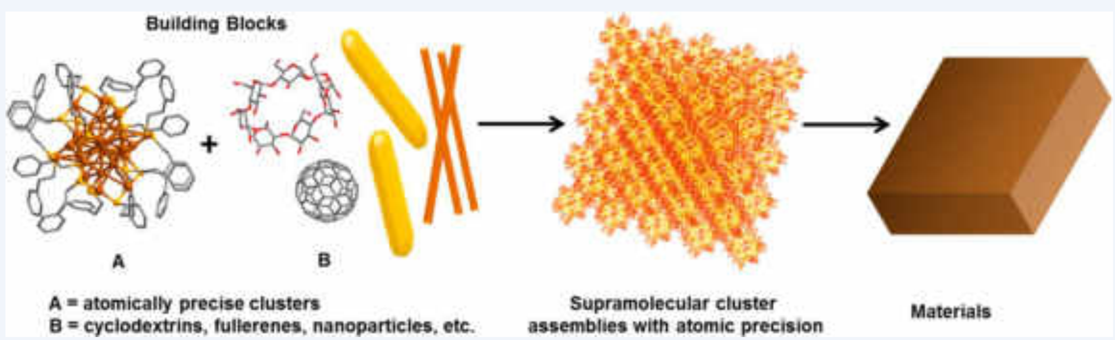
Article

pubs.acs.org/accounts

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



Molecules and their properties

Chemical formula	H_2O
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. $\times 10^{-12}$m^2/N
Coefficient of thermal expansion, 25°C	256.32 $\times 10^{-6}$ K^{-1}
Thermal Conductivity, 25°C	0.608 W/m.K

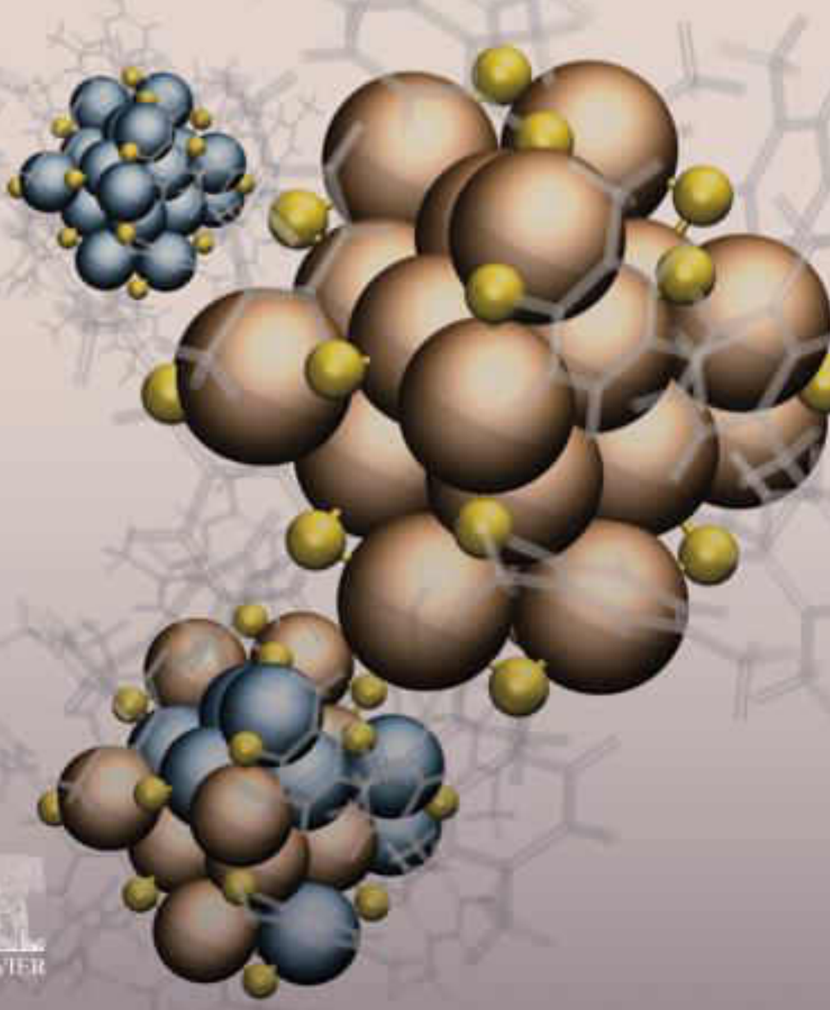
Molecular formula
Molecular weight
Molecular structure
Molecular absorption and emission
Molecular reactions
Molecular assembly
Molecular co-crystals
Ionization potential
Electron affinity

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

Future?

Edited by
Thalappil Pradeep

ATOMICALLY PRECISE METAL NANOCLUSTERS



ELSEVIER

Molecular reactions

Reactions on clusters

Reactions between clusters

Inter-cluster reactions

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

Intercluster Reactions between $Au_{25}(SR)_{18}$ and $Ag_{44}(SR)_{30}$

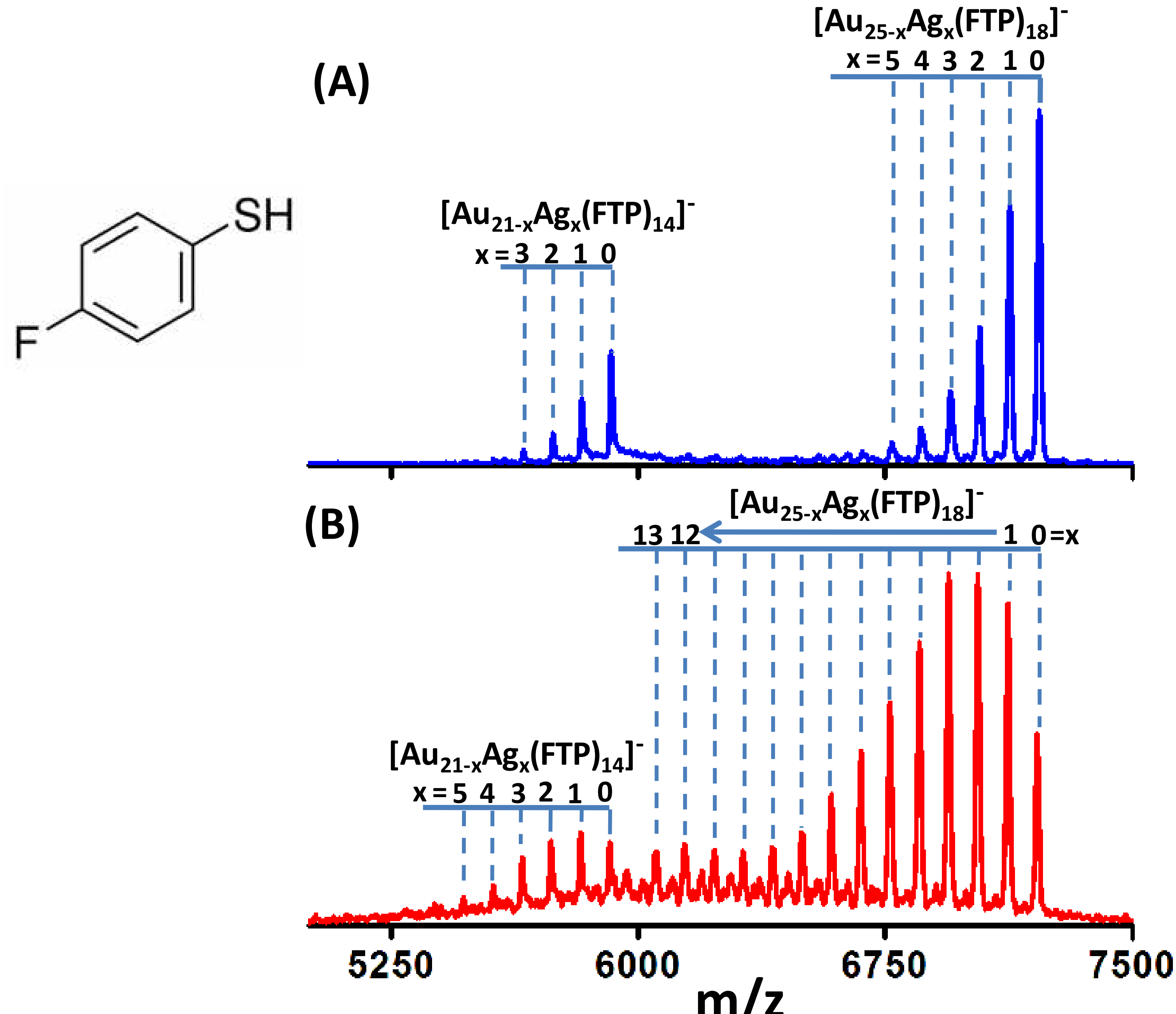
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

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

A + B → C + D

$Au_{25}(FTP)_{18} + Ag_{44}(FTP)_{30} \rightarrow Au_{25-x}Ag_x(FTP)_{18}$

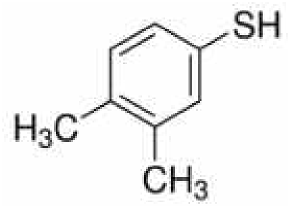


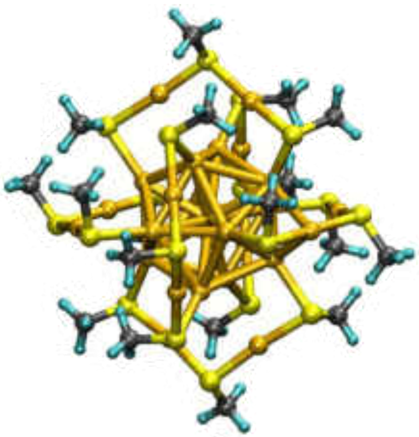
Ag_{25}-Au_{25} experiments

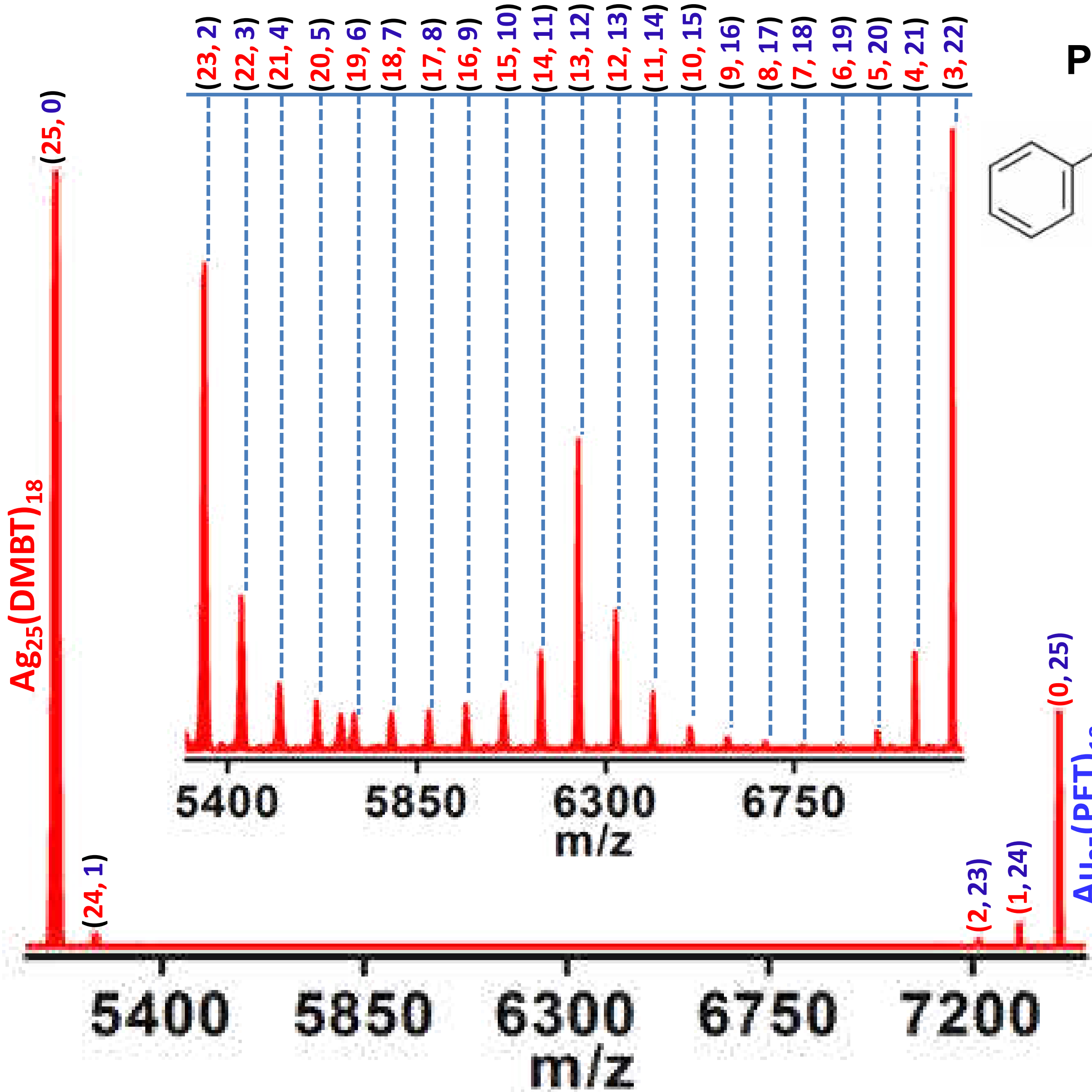
K. R. Krishnadas et al. *Nature Commun.* 2016

Reaction between $Au_{25}(PET)_{18}$ and $Ag_{25}(DMBT)_{18}$

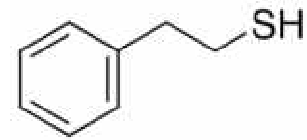
DMBT



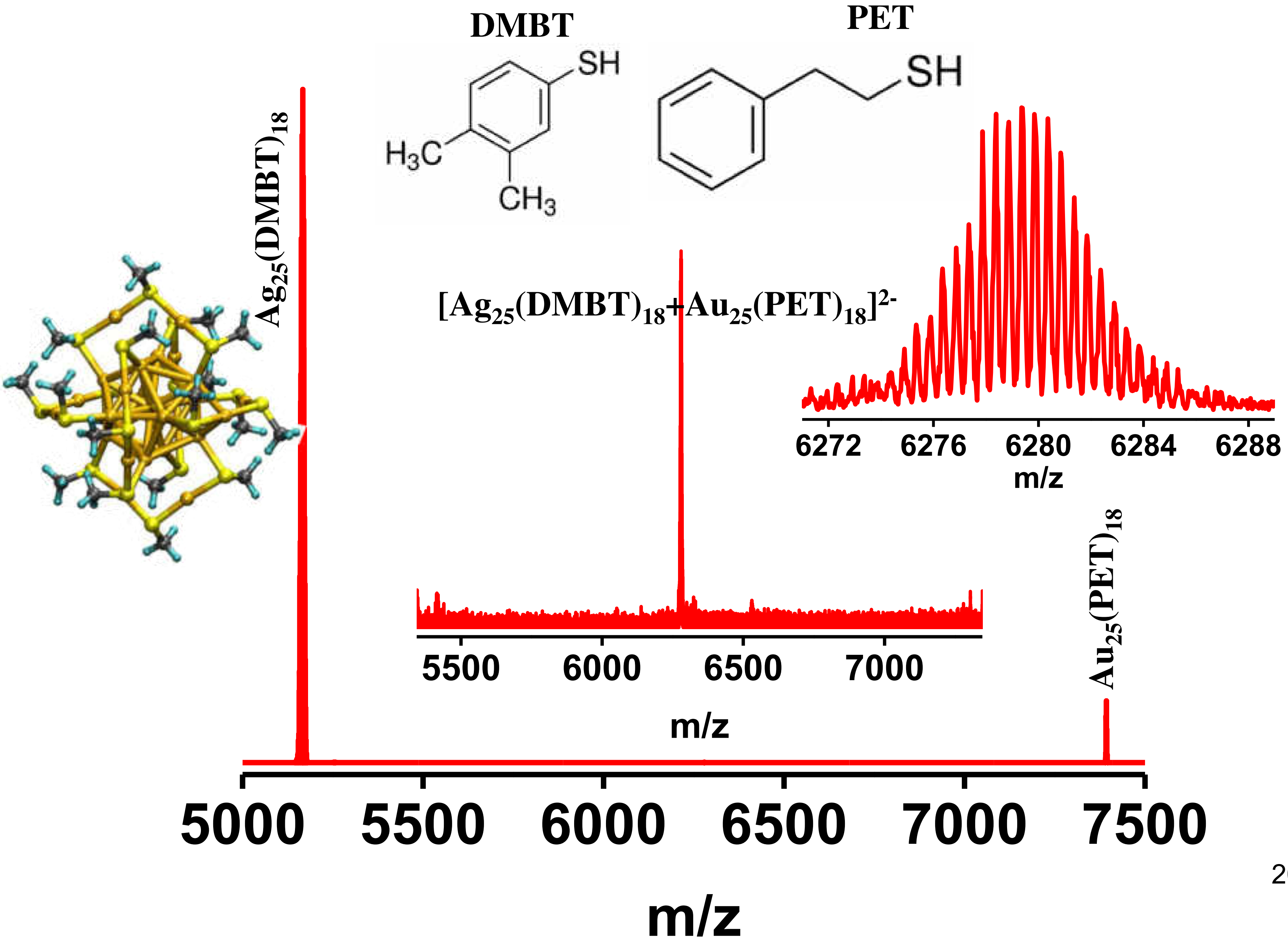




PET

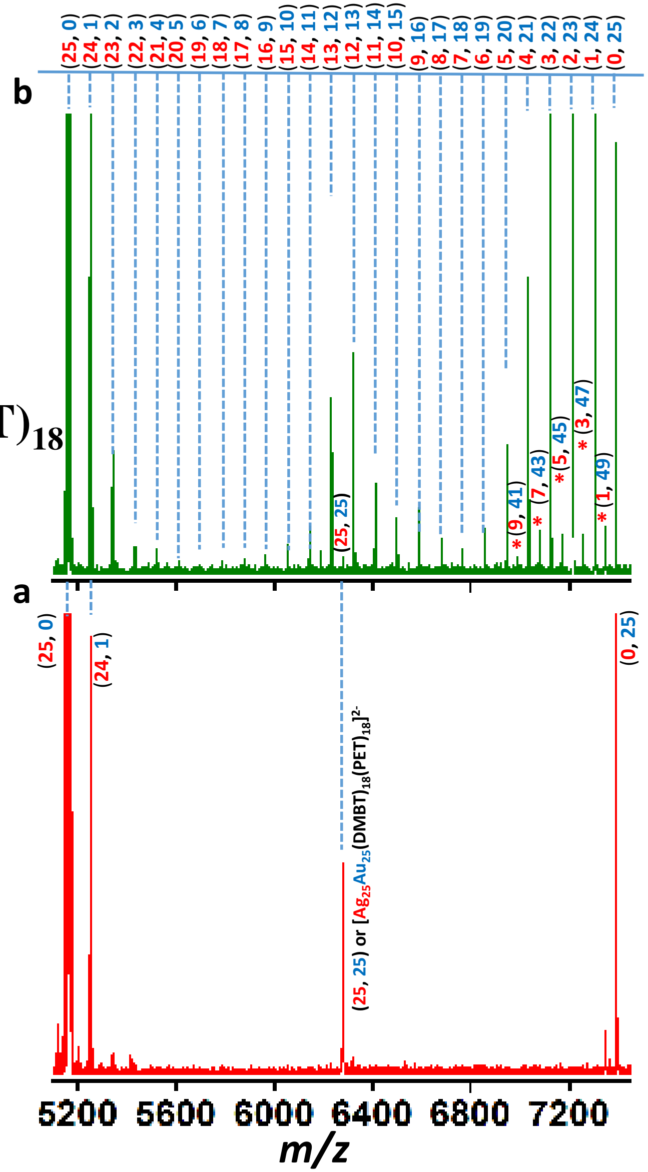


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

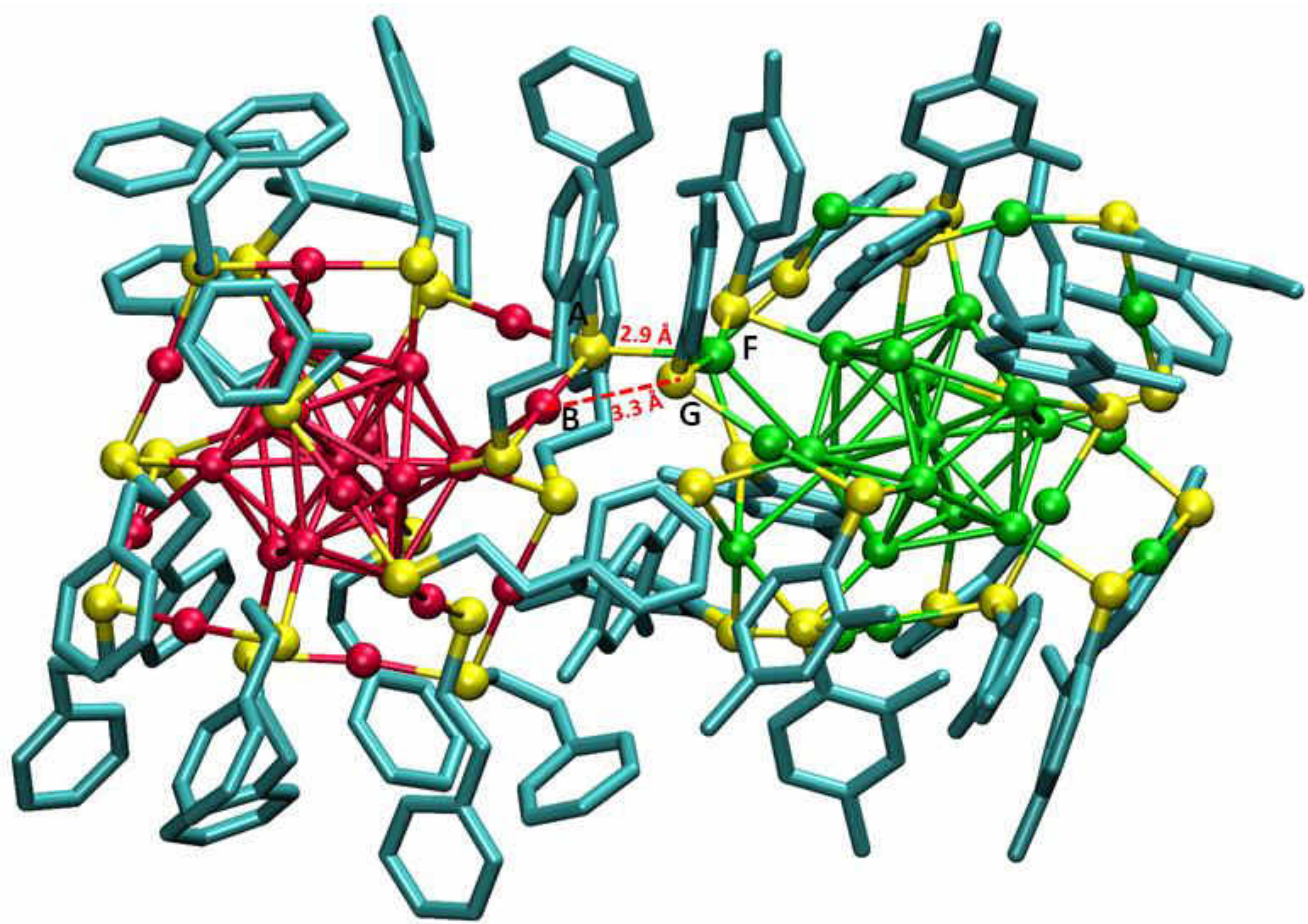
$Ag_{25}(DMBT)_{18}:Au_{25}(PET)_{18}$
0.3:1.0

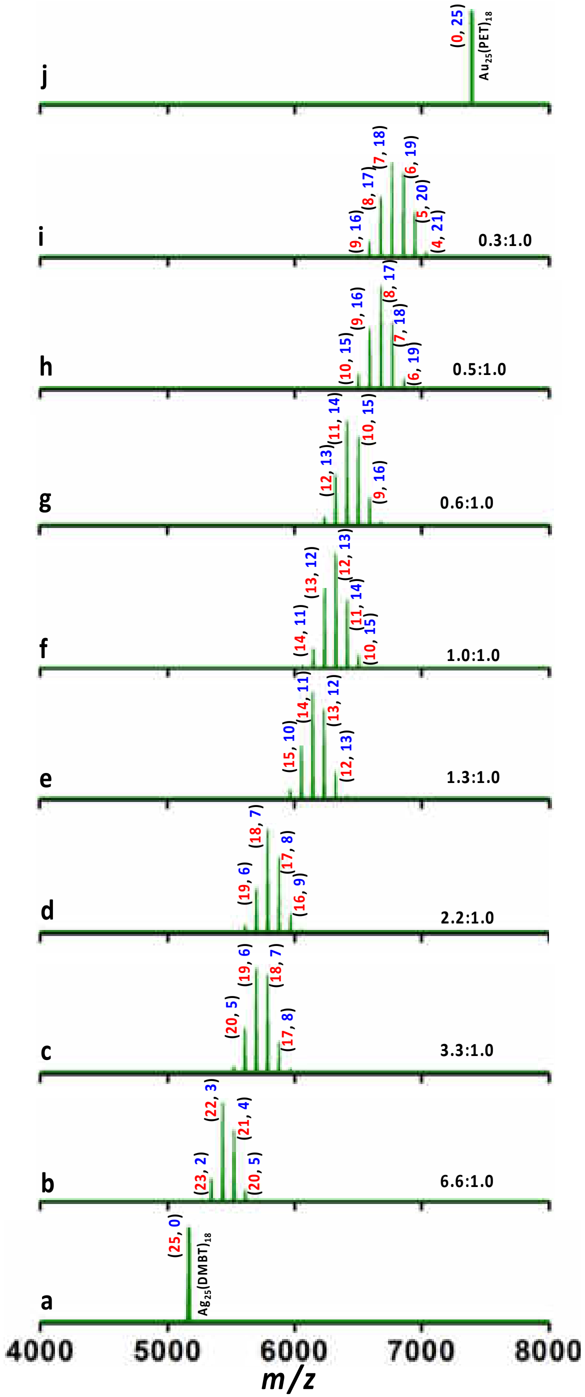


within 5 min

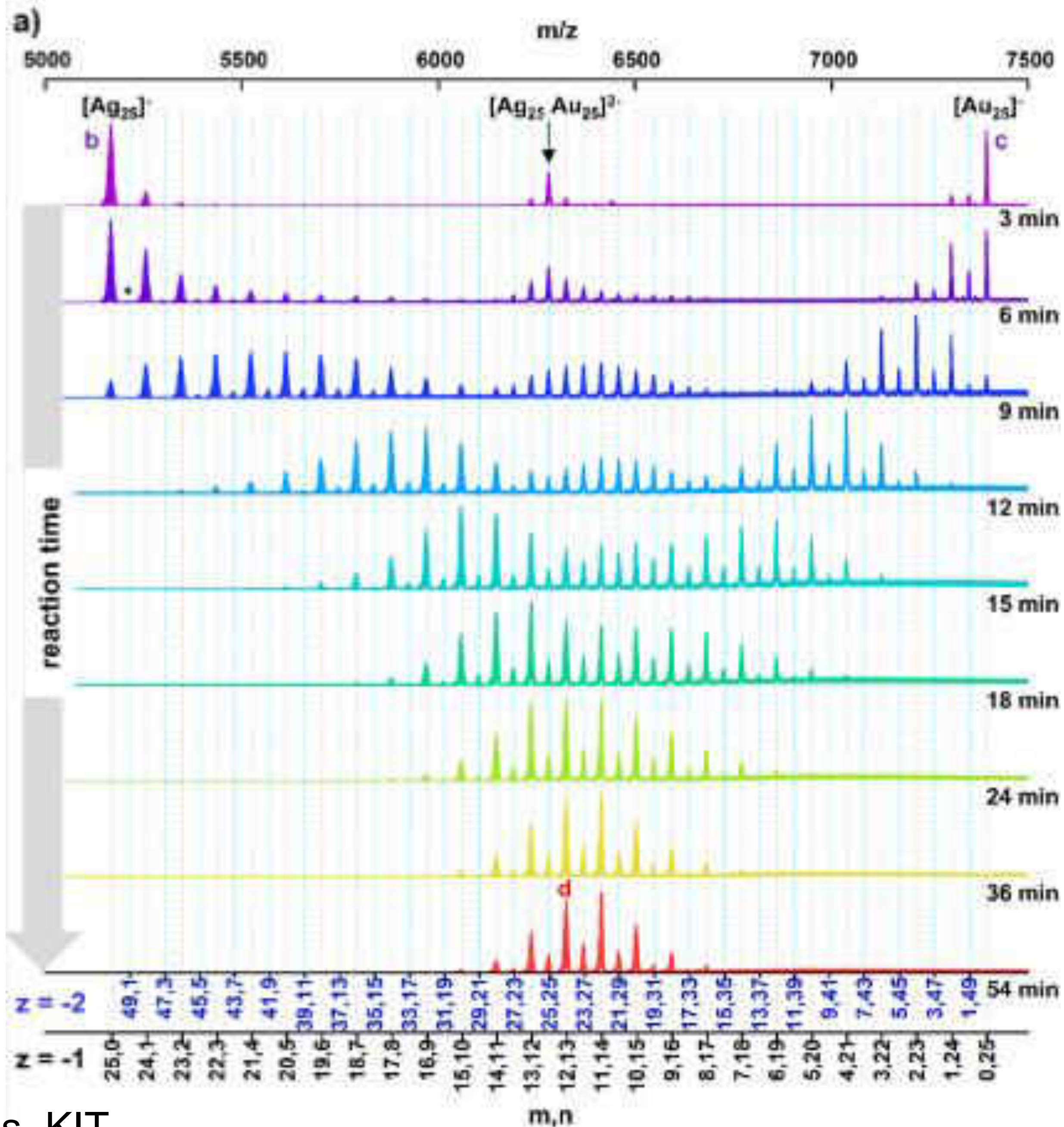
within 2 min

Optimized structure of $[Ag_{25}Au_{25}(DMBT)_{18}(PET)_{18}]^{2-}$





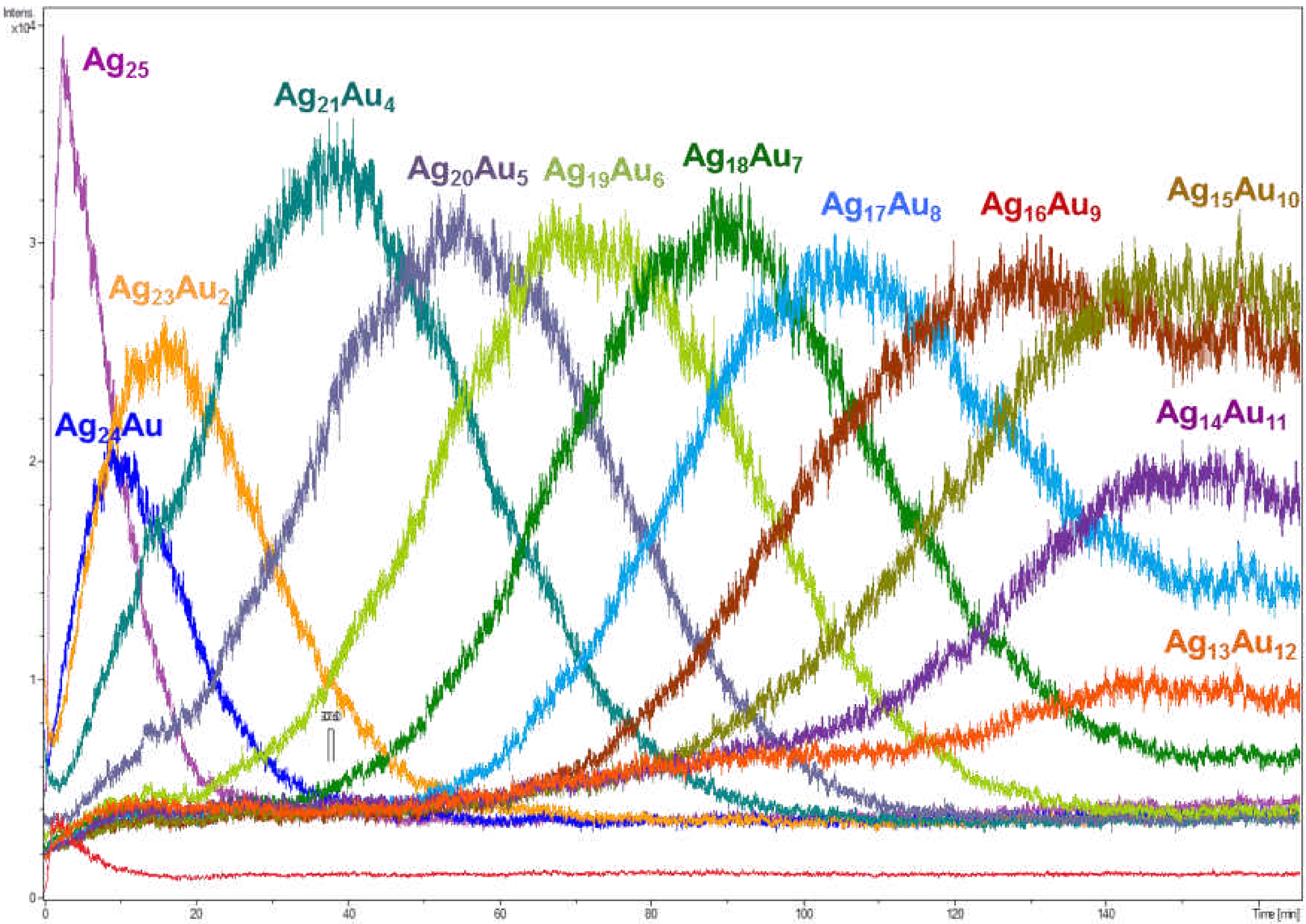
j
(0, 25)
Au25(PET)18
i
0.3:1.0
(9, 16)
(8, 17)
(7, 18)
(6, 19)
(5, 20)
(4, 21)
h
0.5:1.0
(10, 15)
(9, 16)
(8, 17)
(7, 18)
(6, 19)
g
0.6:1.0
(12, 13)
(11, 14)
(10, 15)
(9, 16)
f
1.0:1.0
(14, 11)
(13, 12)
(12, 13)
(11, 14)
(10, 15)
e
1.3:1.0
(15, 10)
(14, 11)
(13, 12)
(12, 13)
d
2.2:1.0
(19, 6)
(18, 7)
(17, 8)
(16, 9)
c
3.3:1.0
(20, 5)
(19, 6)
(18, 7)
(17, 8)
b
6.6:1.0
(23, 2)
(22, 3)
(21, 4)
(20, 5)
a
(25, 0)
Ag25(DMBT)18
4000
5000
6000
7000
8000
m/z



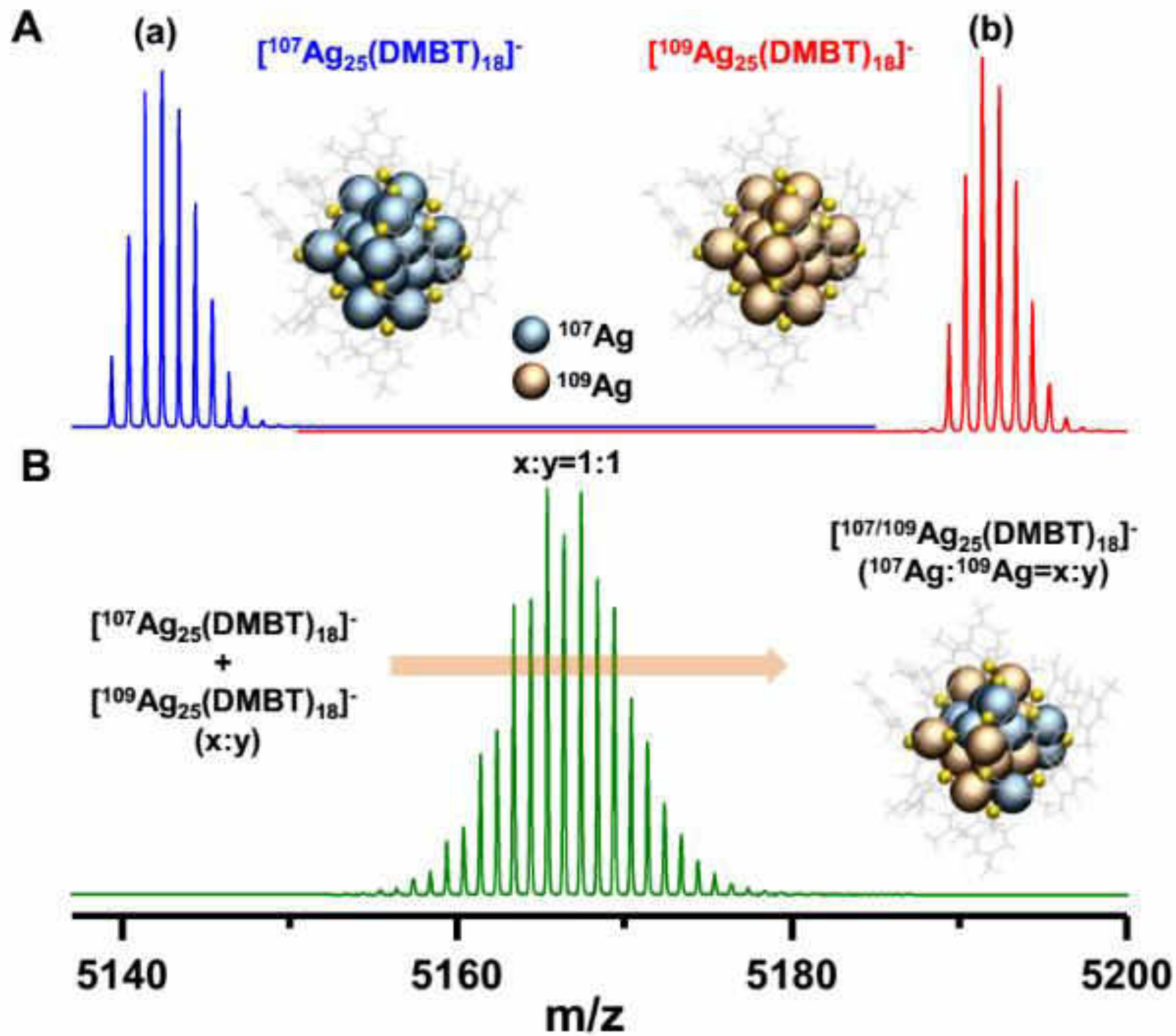
Manfred Kappes, KIT

M. Neumaier, A. Baksi, et. al., *JACS* 2021

Kinetics of the exchange (monitored on the Ag_{25} side)

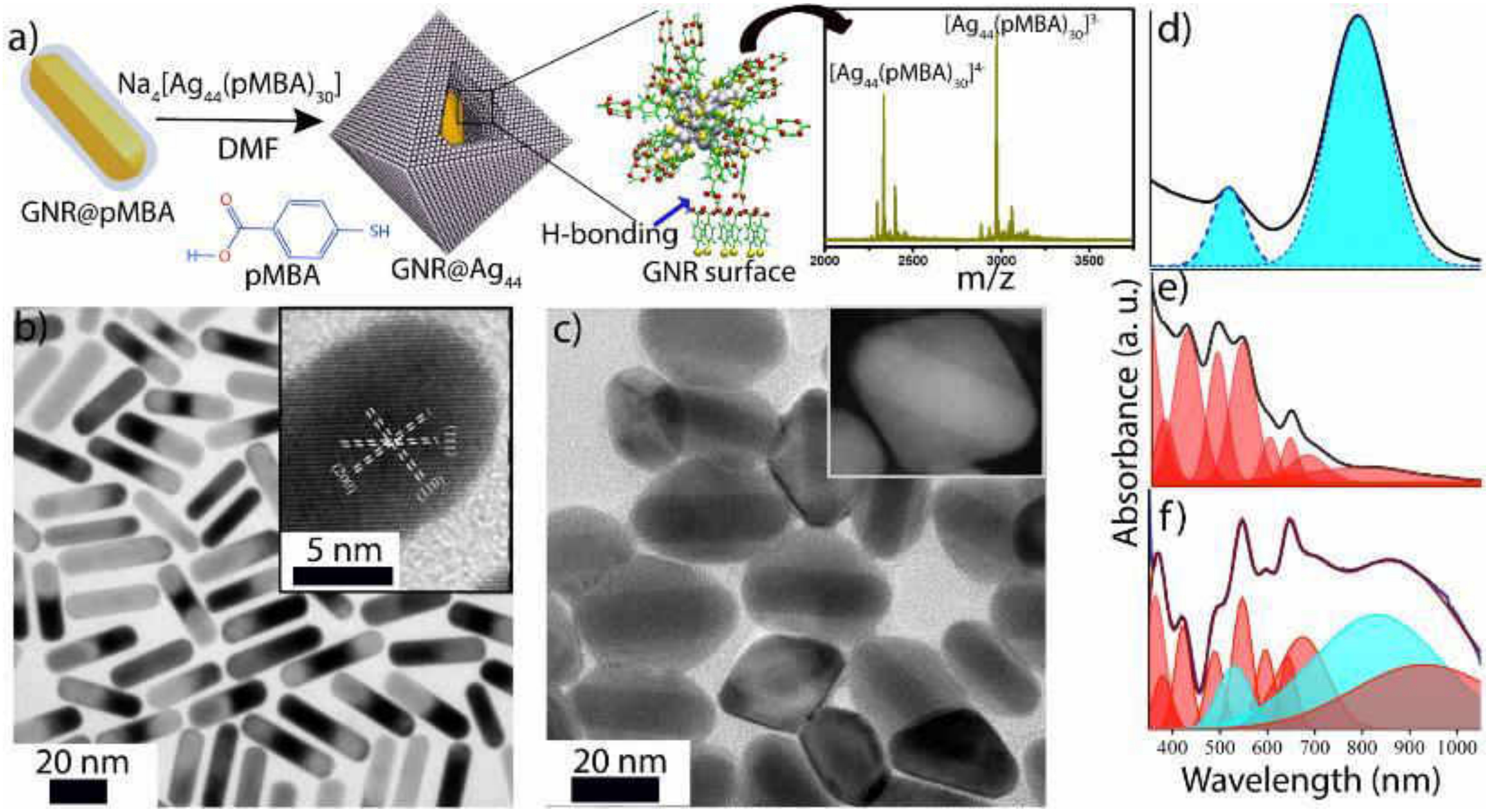


Isotopic exchange



Papri Chakraborti, et. al. Science Advances, 2019.

Atomically precise nanocluster assemblies encapsulating plasmonic gold nanorods



Chakraborty, A. et al., Angew. Chem. Int. Ed. **2018,** 57, 6522–6526.

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

PNAS PNAS PNAS

Mohan Udhaya Sankar[1], Sahaja Aigal[1], Shihabudheen M. Maliyekkal[1], Amrita Chaudhary, Anshup, Avula Anil Kumar, Kamalesh Chaudhari, and Thalappil Pradeep[2]

Unit of Nanoscience and Thematic Unit of Ex … Madras, Chennai 600 036, India

Edited by Eric Hoek, University of California, … (received for review November 21, 2012)

Creation of affordable materials for cons
water is one of the most promising ways
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 con
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.

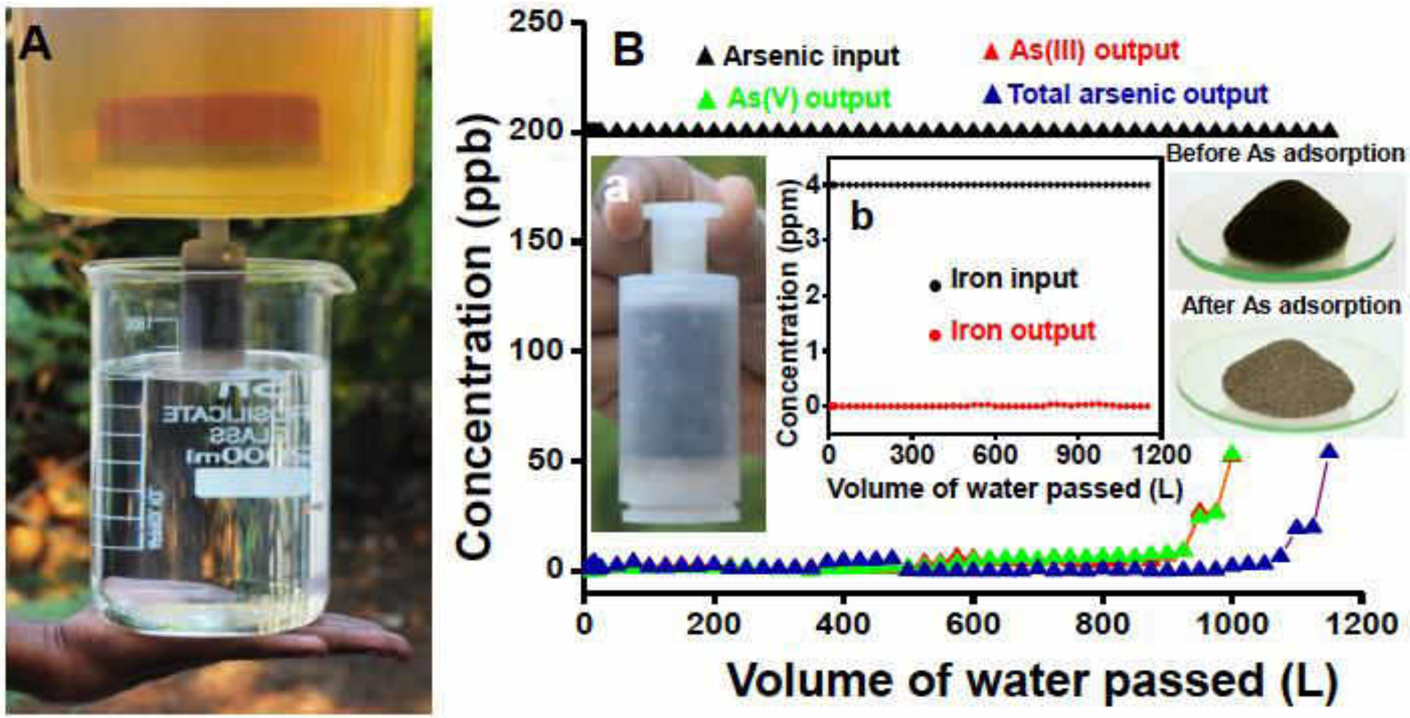
hybrid | green | appropriate technology | frugal science | developing world

vailable; 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
ts in water. We demonstrate an af-
device based on such composites de-
nd undergoing field trials in India, as
spread eradication of the waterborne
disease burden.

Results and Discussion

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

Range of materials, their affordability and safety



Safety of spent media, TCLP

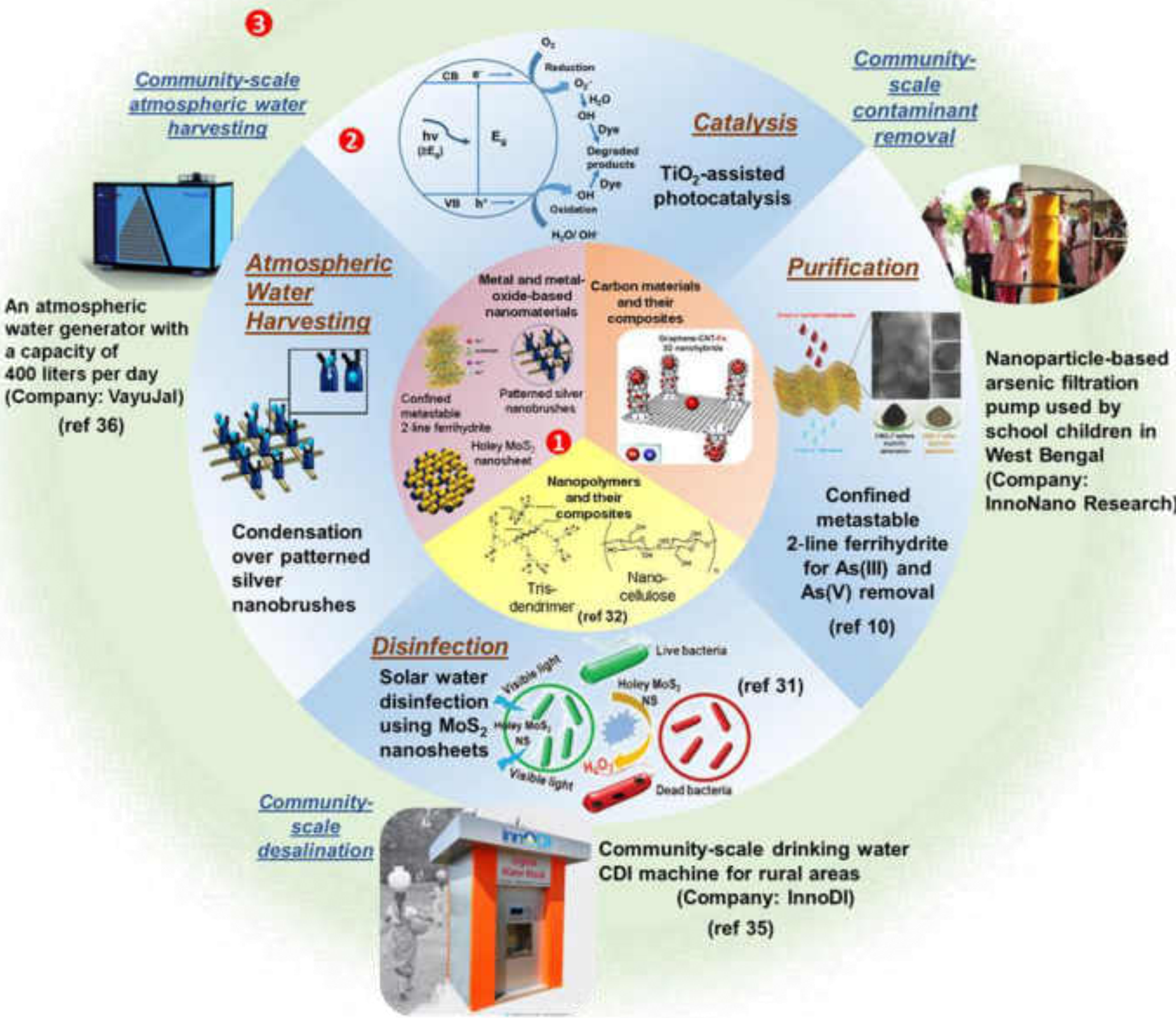
A. Anil Kumar, et. al. *Adv. Mater.*, 29 (2016) 1604260.

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.

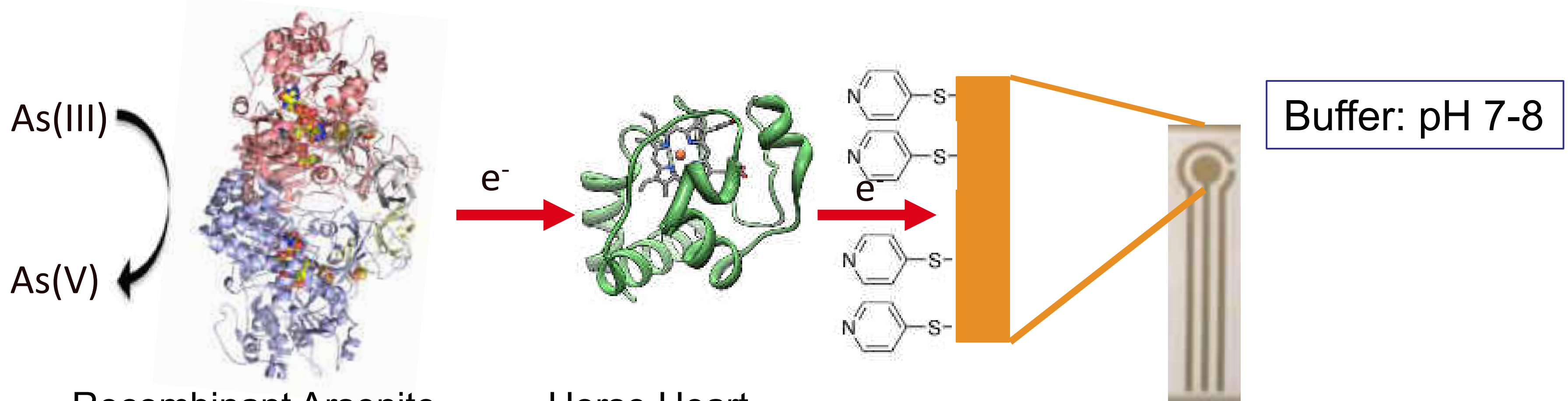
Evolution of materials to products



Ankit Nagar and T. Pradeep 14(2020). *ACS Nano*, 6420-6435

Biosensor Design

1st Generation Design (Mediated Electrochemistry)



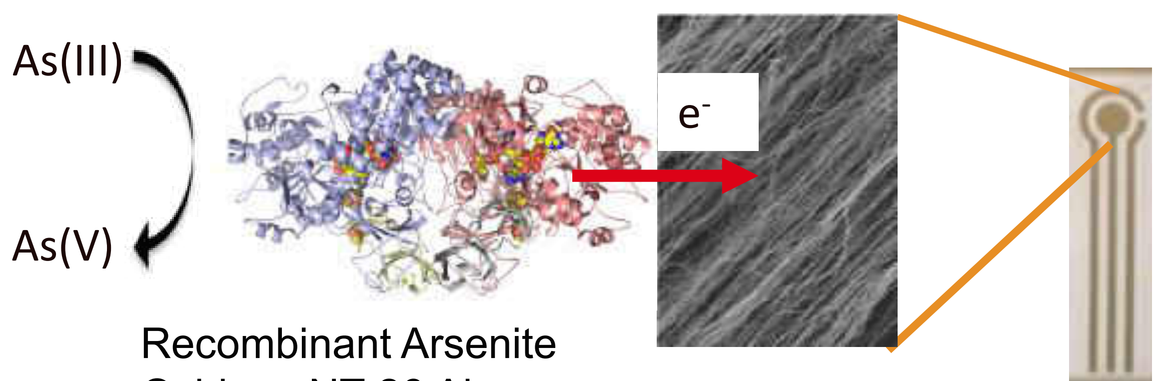
Recombinant Arsenite Oxidase NT-26 Aio

Horse Heart Cytochrome C

Aldrithiol

Low-cost Gold sputtered thin film on PET substrate

2nd Generation Design (Direct Electron Transfer)

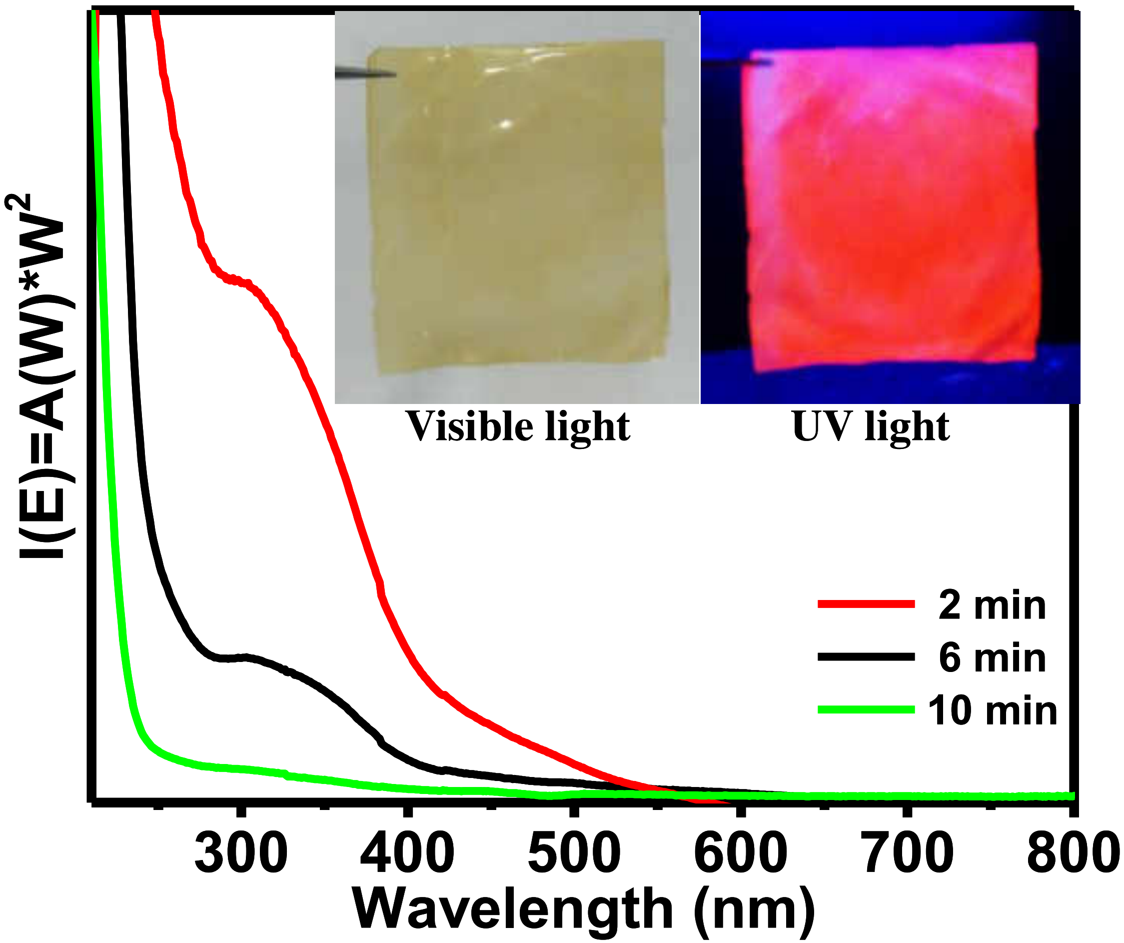


Recombinant Arsenite Oxidase NT-26 Aio

low-cost nanostructured electrodes which interact directly with enzyme (e.g. graphene or CNT).

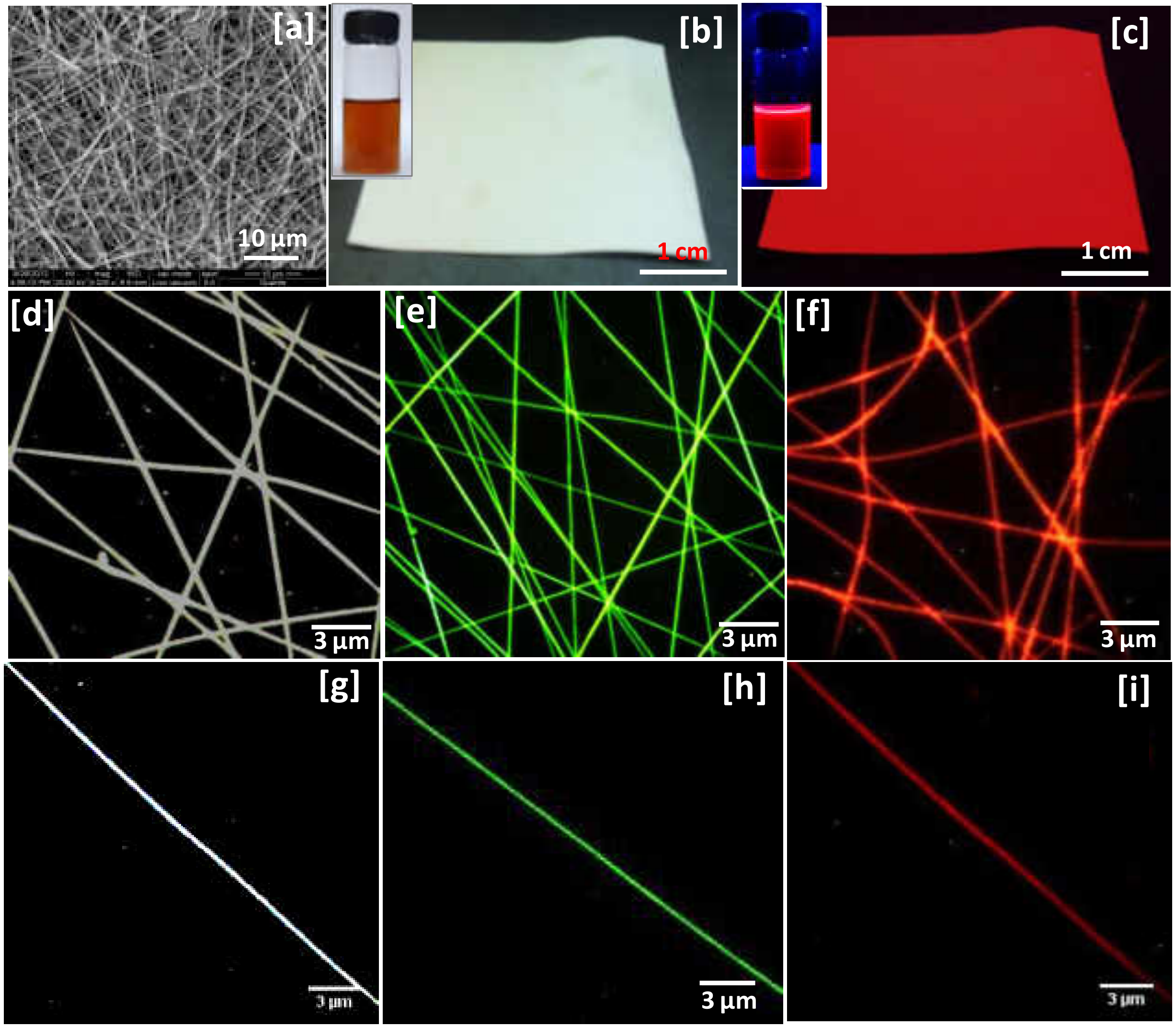
Bio-nano Consulting & Imperial College, London

Cluster-based metal ion sensing



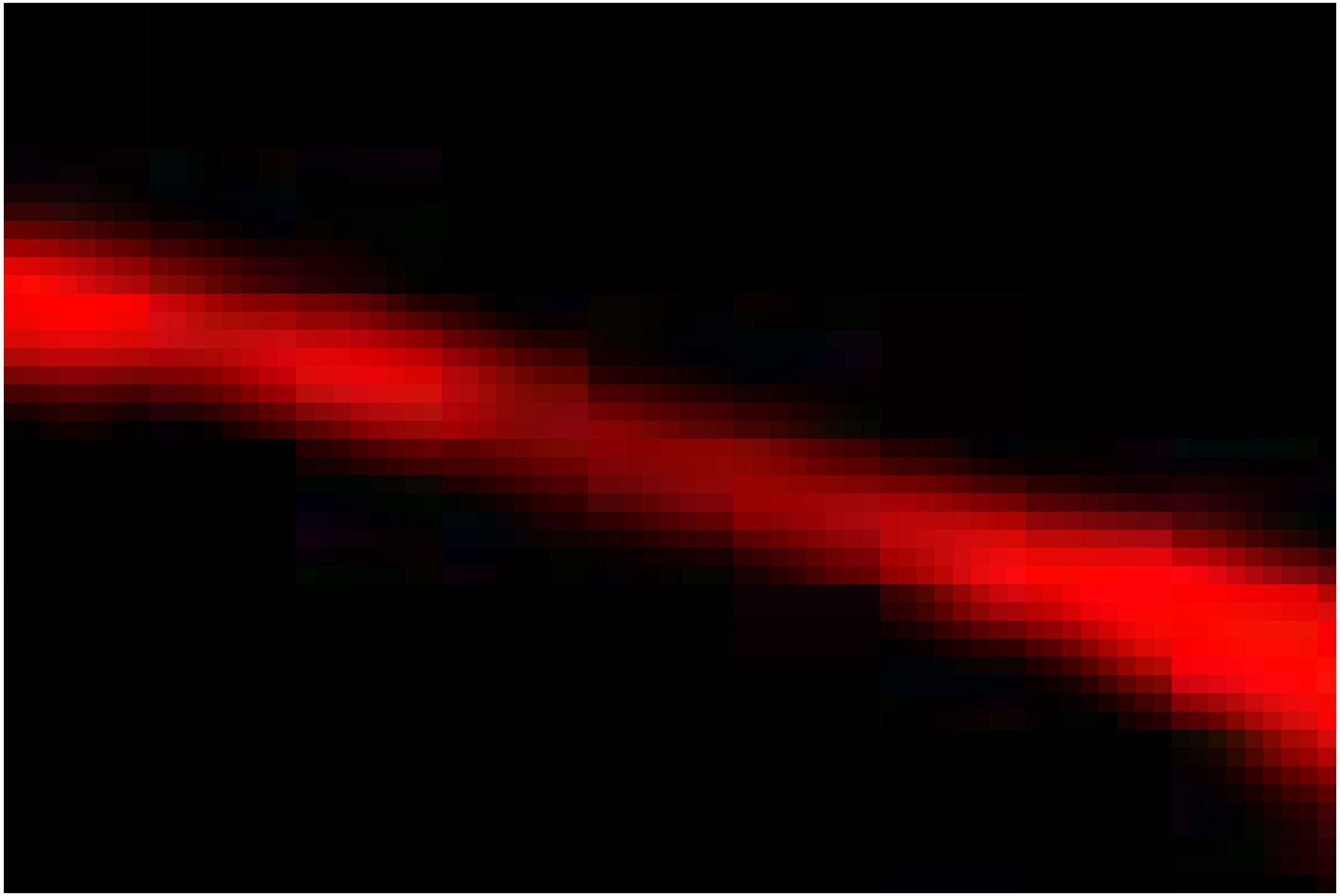
Decrease in the absorption of Au_{15} as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

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

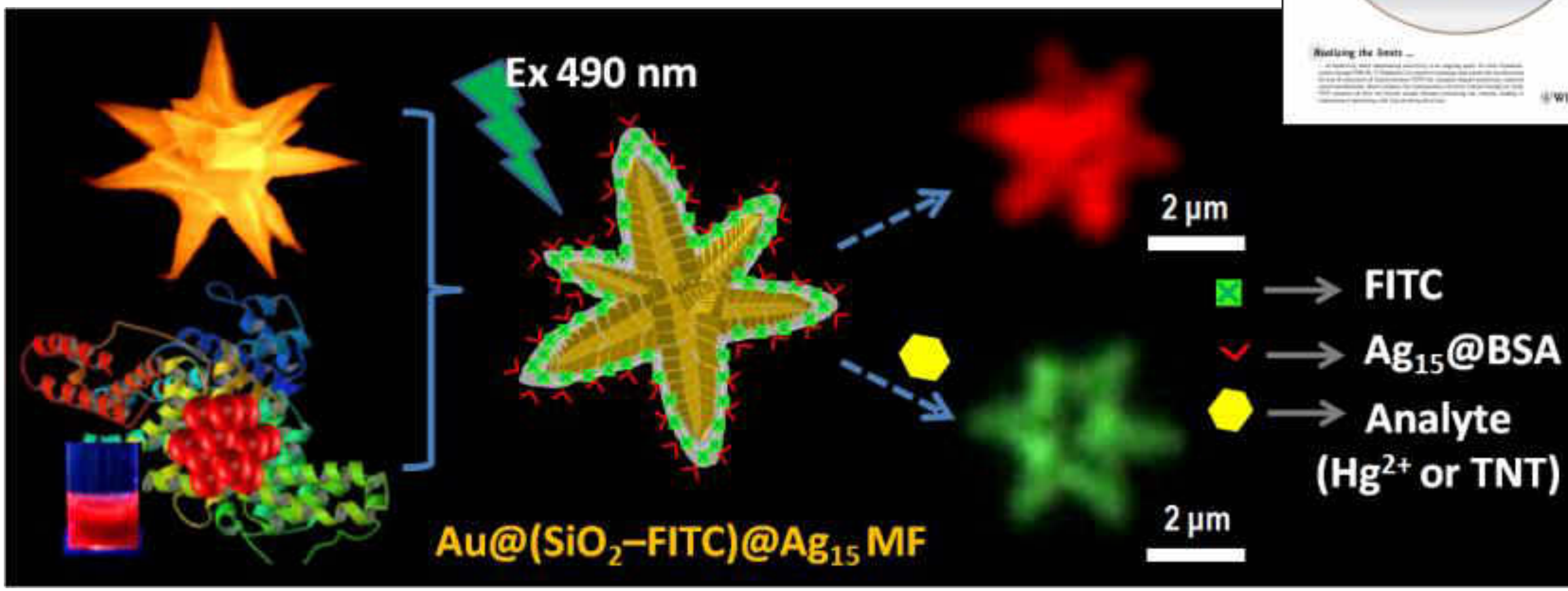


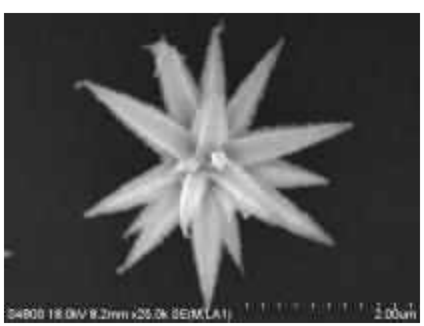
Atanu Ghosh et al. Anal. Chem. 2014.

Mercury quenching experiment using nanofiber



Sub-zeptomolar detection

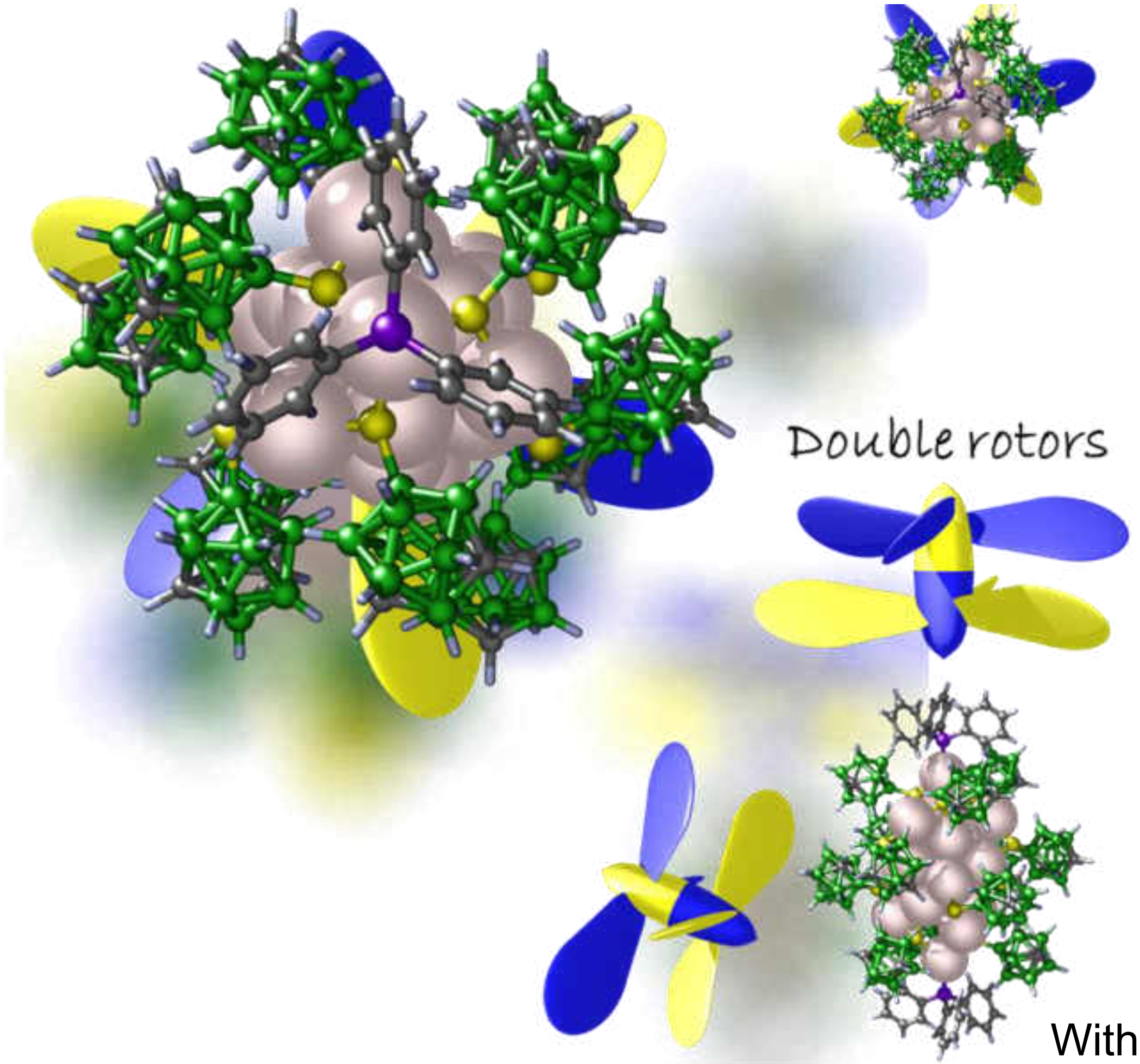




Featured in:
The Hindu, Telegraph, Times of India, etc.
C&E News
and many others

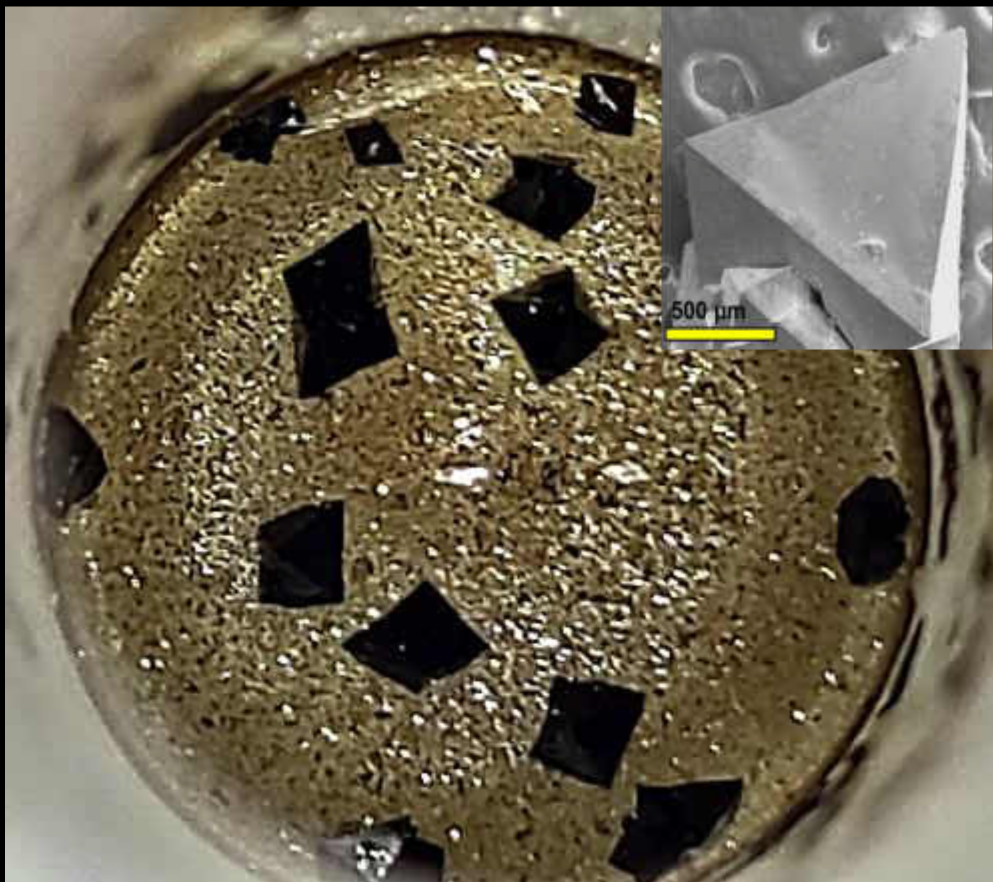
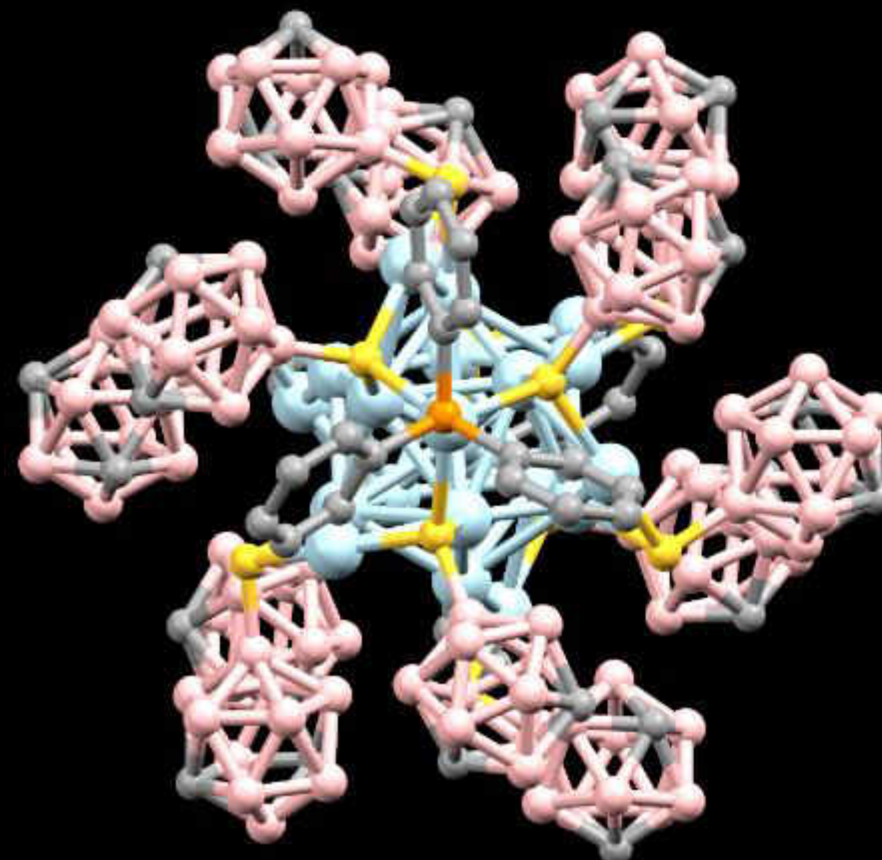
Ammu Mathew, et al. Angew. Chem. Int. Ed. 2012

Carborane-thiol protected silver nanomolecule

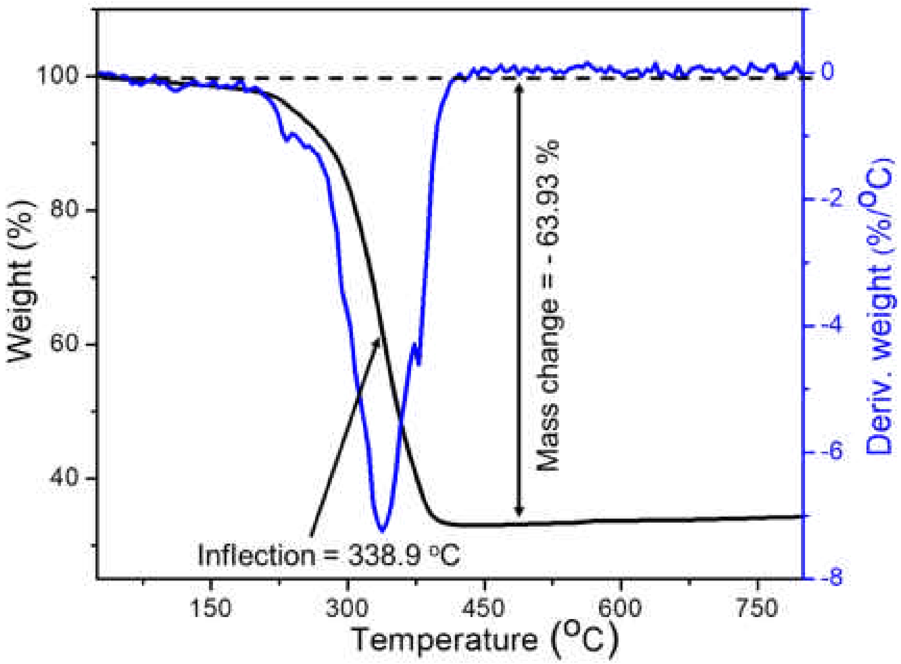


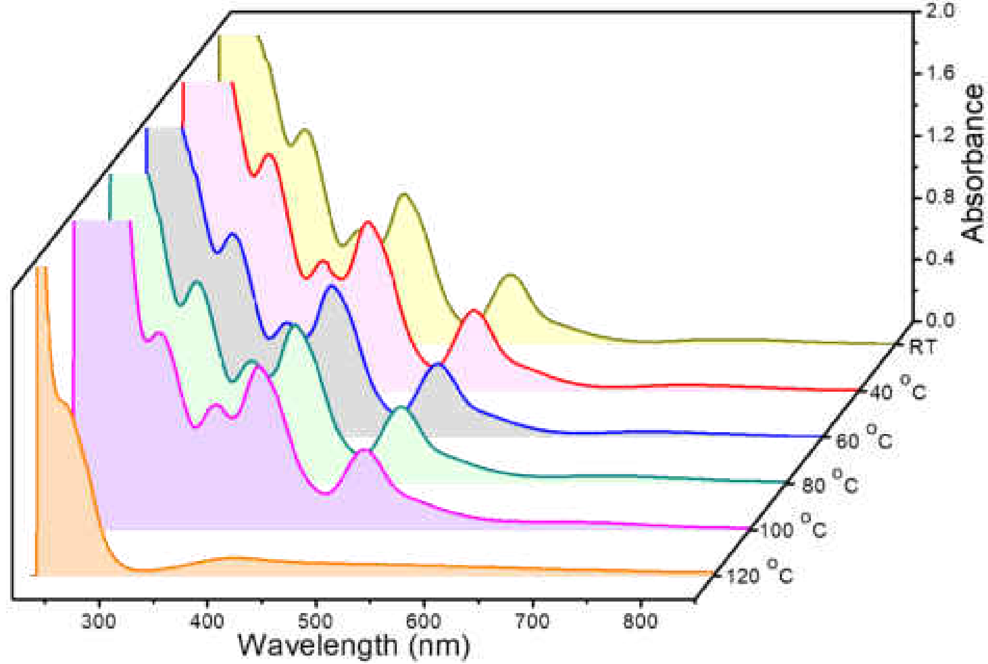
With Tomas Base

Jana *et. al*, Inorganic Chemistry (2022)

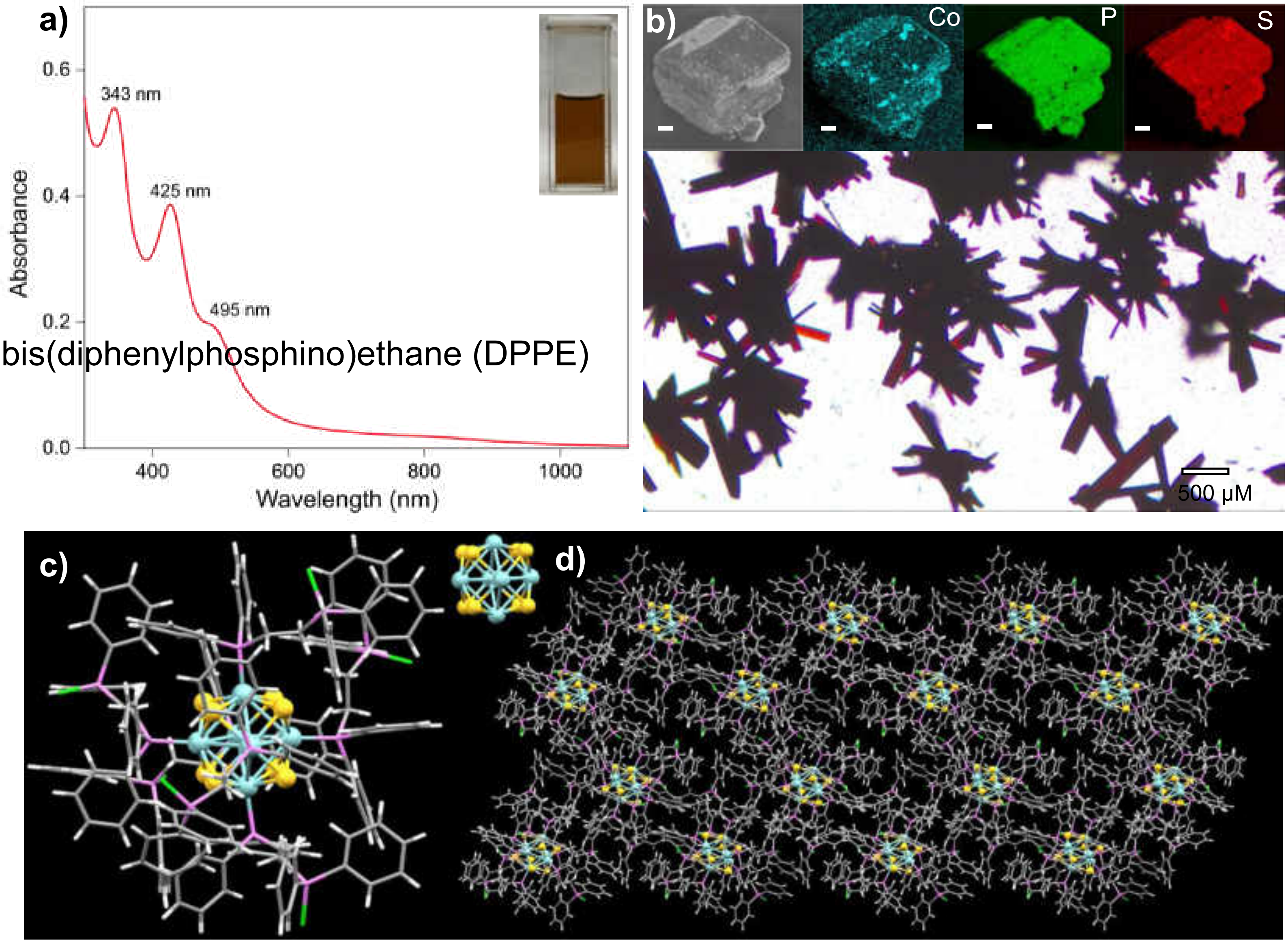

500 µm


Thermal stability



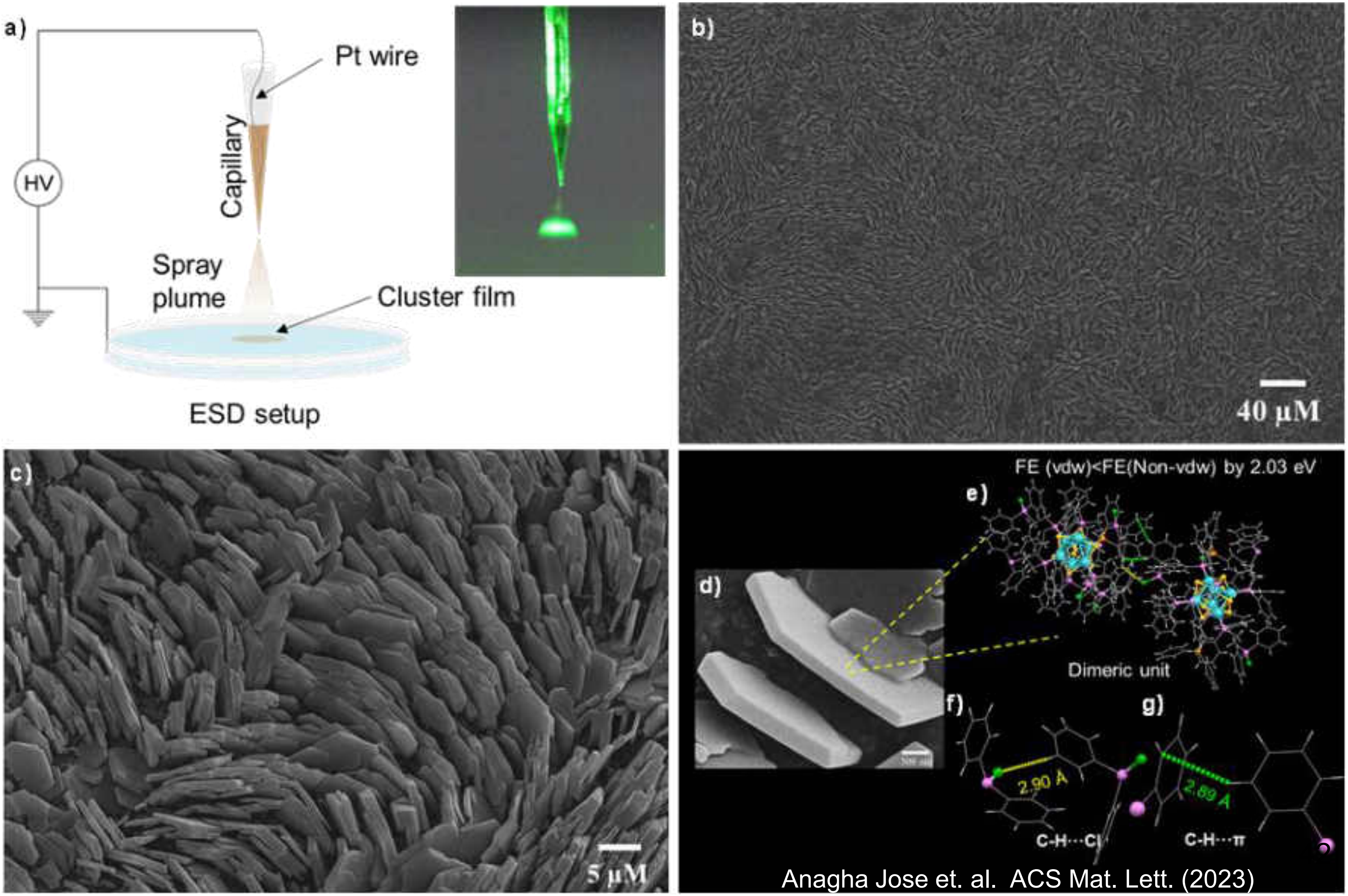


New electrodes - Aligned nanoplates of Co_6S_8



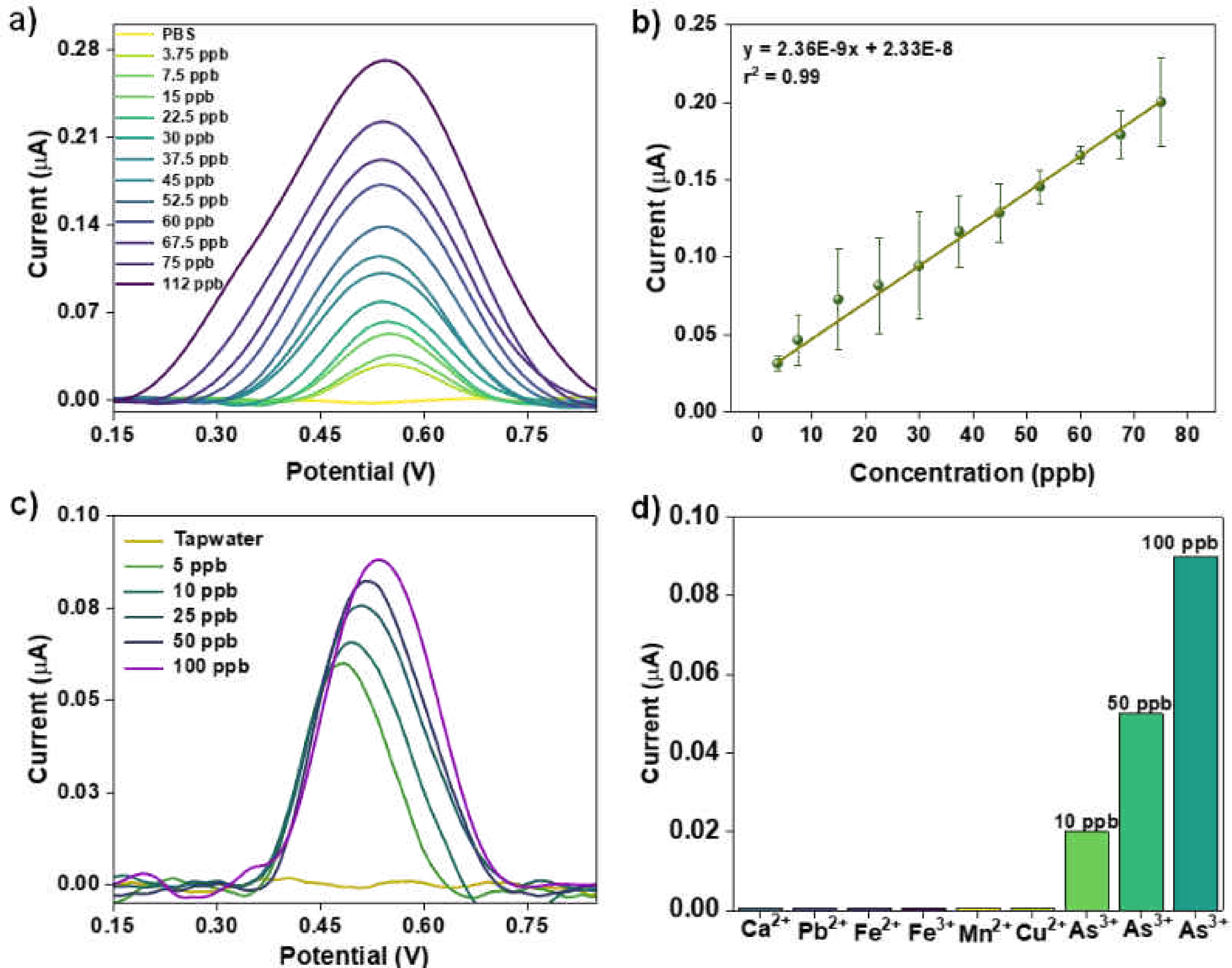
1,2-bis(diphenylphosphino)ethane (DPPE)

Electrospray deposition

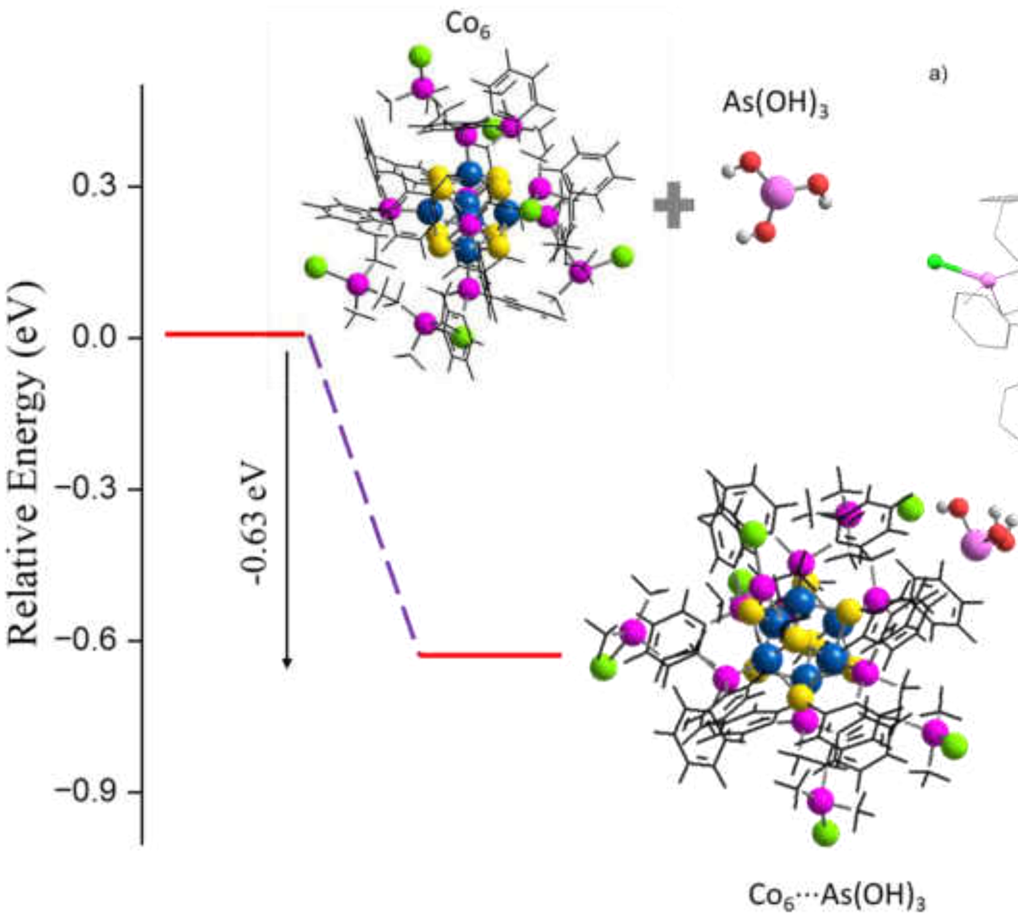


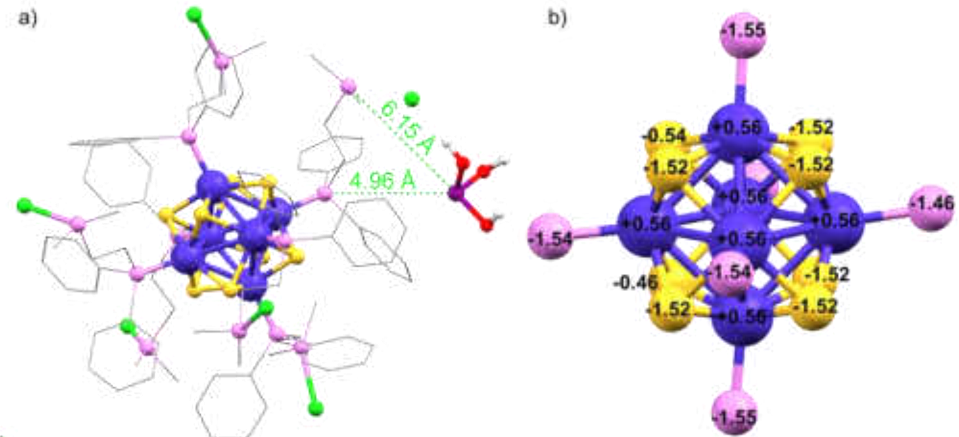
Anagha Jose et. al. ACS Mat. Lett. (2023)

Sensing

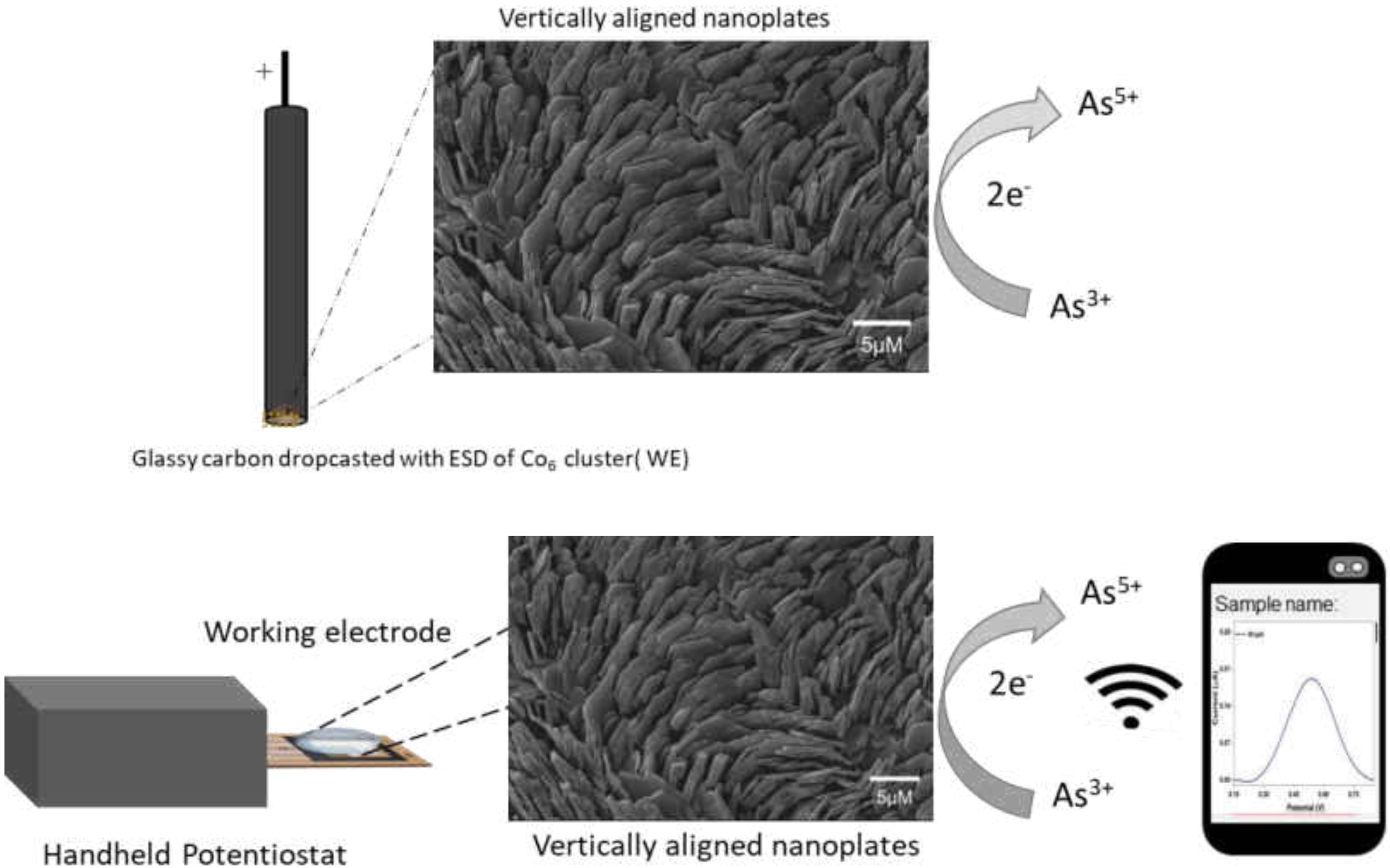

a)
PBS
3.75 ppb
7.5 ppb
15 ppb
22.5 ppb
30 ppb
37.5 ppb
45 ppb
52.5 ppb
60 ppb
67.5 ppb
75 ppb
112 ppb
Current (μA)
Potential (V)
b)
y = 2.36E-9x + 2.33E-8
r² = 0.99
Current (μA)
Concentration (ppb)
c)
Tapwater
5 ppb
10 ppb
25 ppb
50 ppb
100 ppb
Current (μA)
Potential (V)
d)
100 ppb
50 ppb
10 ppb
Current (μA)
Ca2+ Pb2+ Fe2+ Fe3+ Mn2+ Cu2+ As3+ As3+ As3+

Computational insights

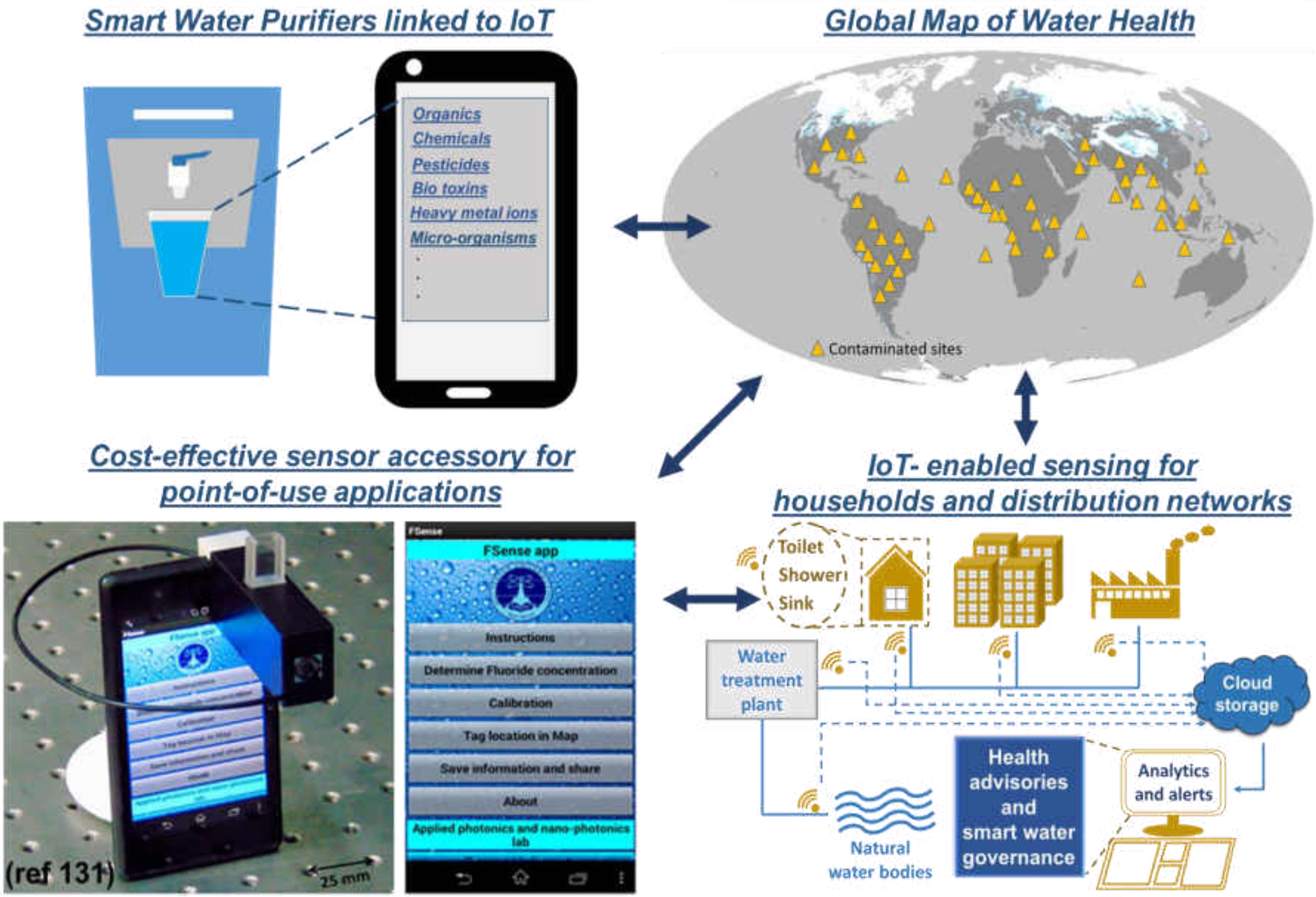




Working electrode

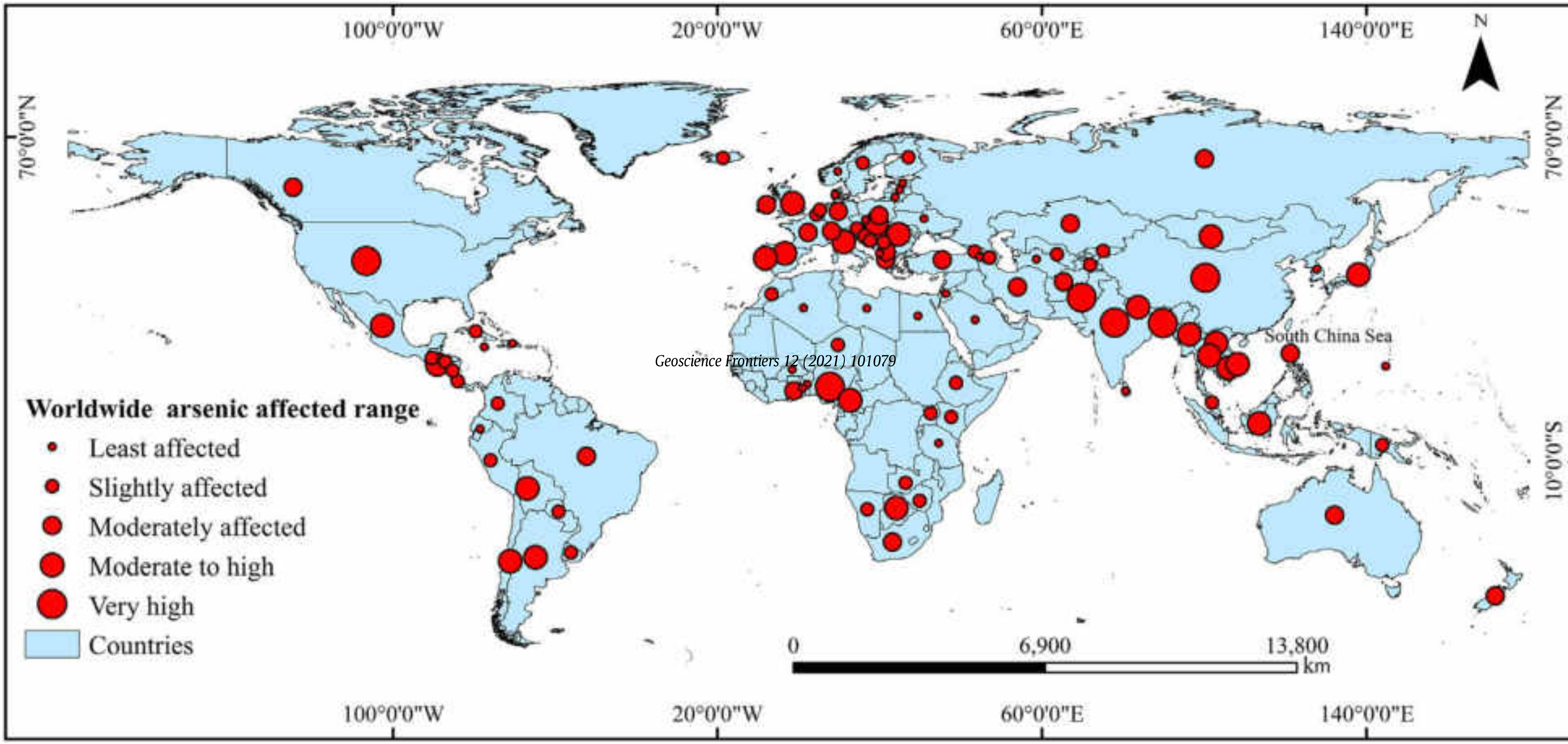


Smart water purifiers and big data



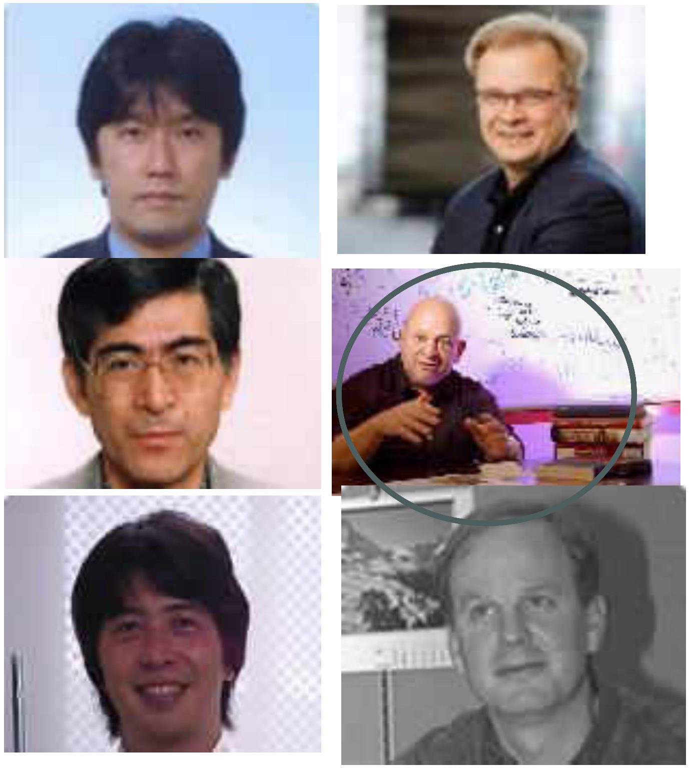
Ankit Nagar and T. Pradeep 14(2020). *ACS Nano*, 6420-6435

Arsenic poisoning across the world



E. Shaji, M. Santosh, K. V. Sarath, Pranav Prakash, V. Deepch and B. V. Divya, Geoscience Frontiers, 12 (2021) 101079.

Collaborators



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Thank you all