Now in the 65th year

Atomically Precise Clusters

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Hydromaterials Pvt. Ltd.
EyeNetAqua Solutions Pvt. Ltd.
DeepSpectrum Innovations Pvt. Ltd.

Associate Editor

ACS Sustainable Resource Management

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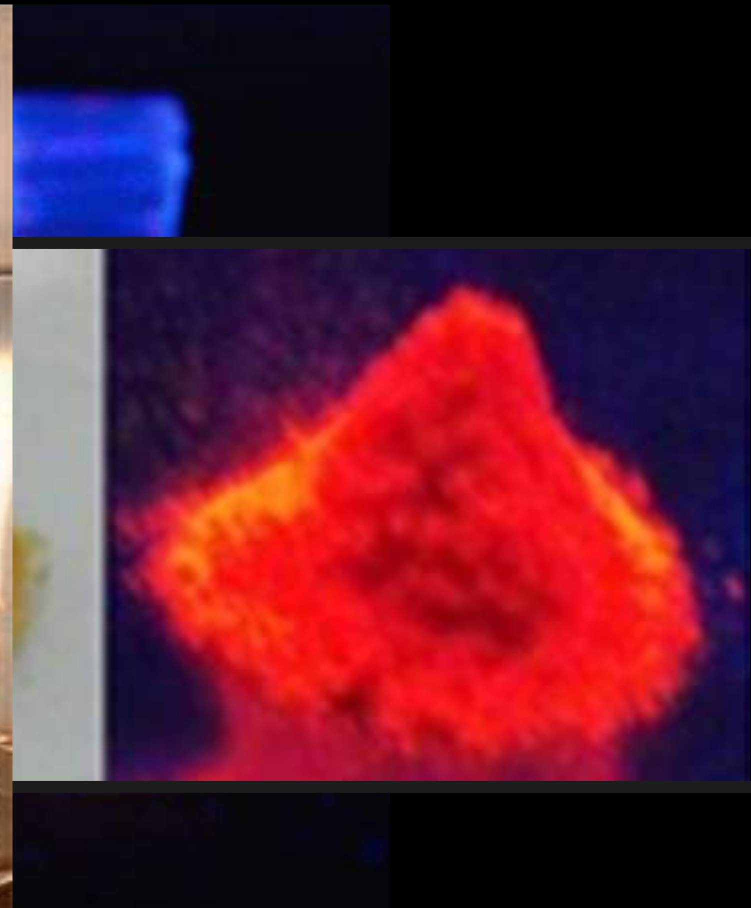
International Centre for Clean Water

Prof. R. P. Mitra Memorial Lecture, Department of Chemistry, Delhi University, April 25, 2025

Quantum Dots – Seeds of Nanoscience

KUNGL. VETENSKAPS-AKADEMIEN

THE ROYAL SWEDISH ACADEMY OF SCIENCES

THE NOBEL PRIZE IN CHEMISTRY 2023

The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Chemistry 2023 to

©Johan Jarnestad/The Royal Swedish Academy of Sciences

Moungi G. Bawendi

Massachusetts Institute of Technology [MIT], Cambridge, MA, USA

Louis E. Brus

Columbia University, New York, NY, USA

Alexei I. Ekimov

Nanocrystals Technology Inc., New York, NY, USA

‘for the discovery and synthesis of quantum dots’

THE NOBEL PRIZE IN CHEMISTRY 2023

How small are these ‘Quantum Dots’?

A quantum dot is a crystal that often consists of just a few thousand atoms. In terms of size, it has the same relationship to a football as a football has to the size of the Earth.

Remembering pioneers

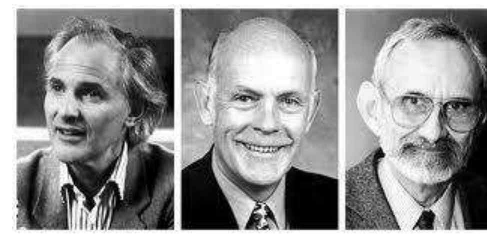
THE NOBEL PRIZE IN CHEMISTRY 2023

Michael Faraday – Divided metals

Lord Kelvin – Melting depends on size?

Richard Feynman, Nobel Prize 1965 –
Plenty of room at the bottom

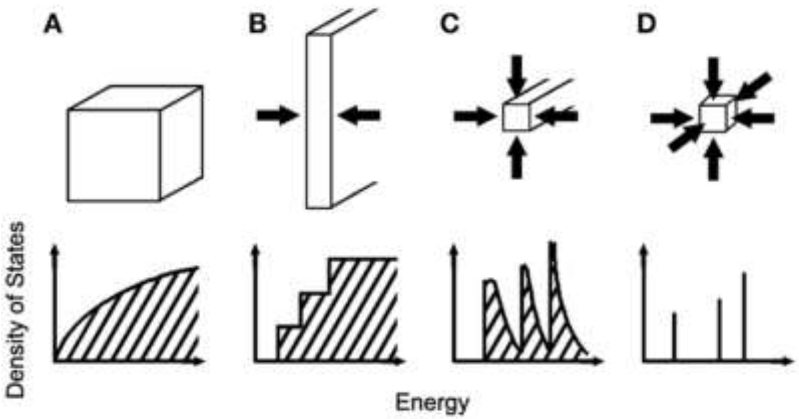
Harold W. Kroto, Richard E. Smalley and **Robert F. Curl,** Nobel Prize 1996



Andre Geim and Konstantin Novoselov, Graphene, Nobel Prize 2010

Jean Pierre Sauvage, J. Fraser Stoddart, and Bernard Lucas Feringa, Molecular machines Nobel Prize 2016

Quantum effects arise when particles shrink in size



Energy levels of semiconductor crystallites with different dimensionalities.

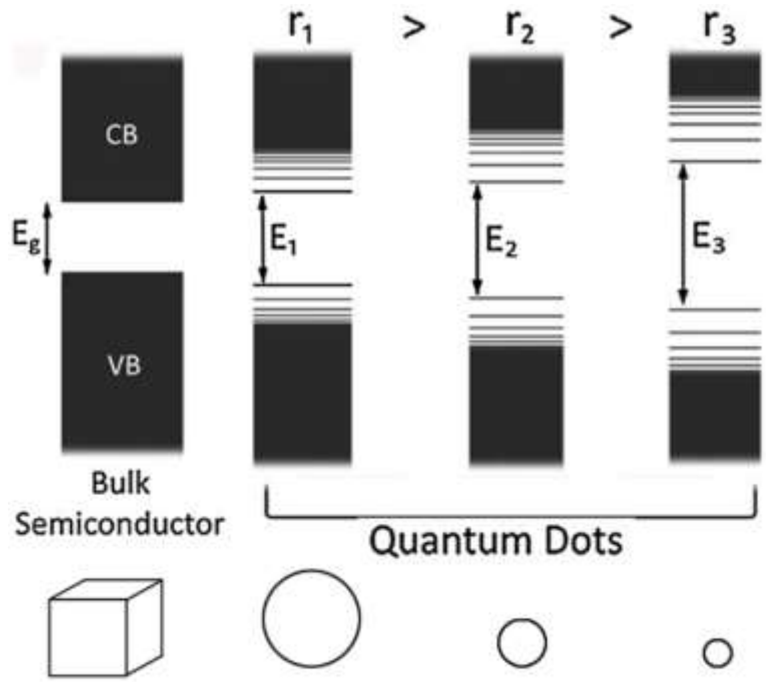


Illustration of size-dependent bandgap.

G. Dong, H. Wang, G. Chen, Q. Pan, J. Qiu, Frontiers in Materials 2015, 2.

Gas phase

PRODUCTION OF LARGE SODIUM CLUSTERS (Na_x, $x \leqslant 65$) BY SEEDED BEAM EXPANSIONS

Manfred M. KAPPES, Roland W. KUNZ * and Ernst SCHUMACHER
Institute of Inorganic and Physical Chemistry, University of Bern, CH-3000 Bern 9, Switzerland

Received 10 August 1982

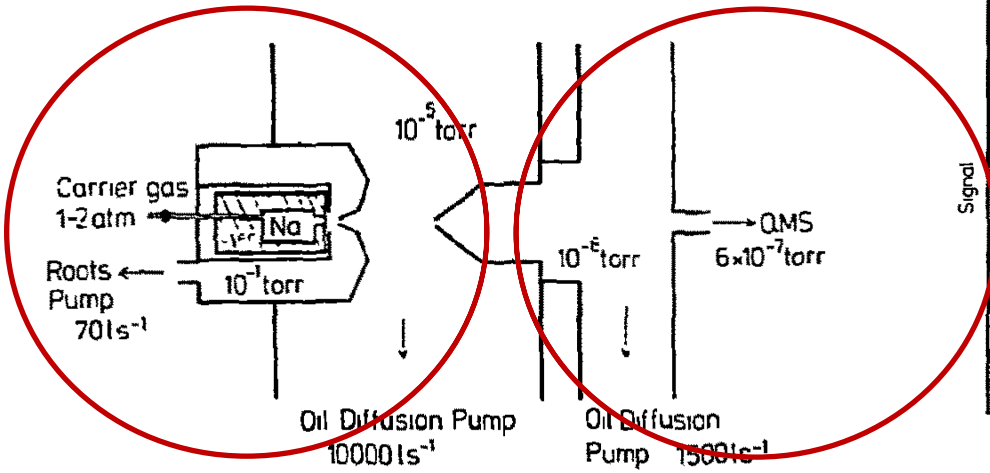


Fig. 1. Schematic of the seeded-beam apparatus.

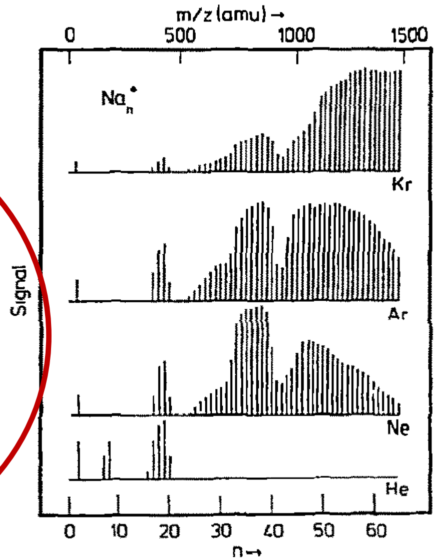
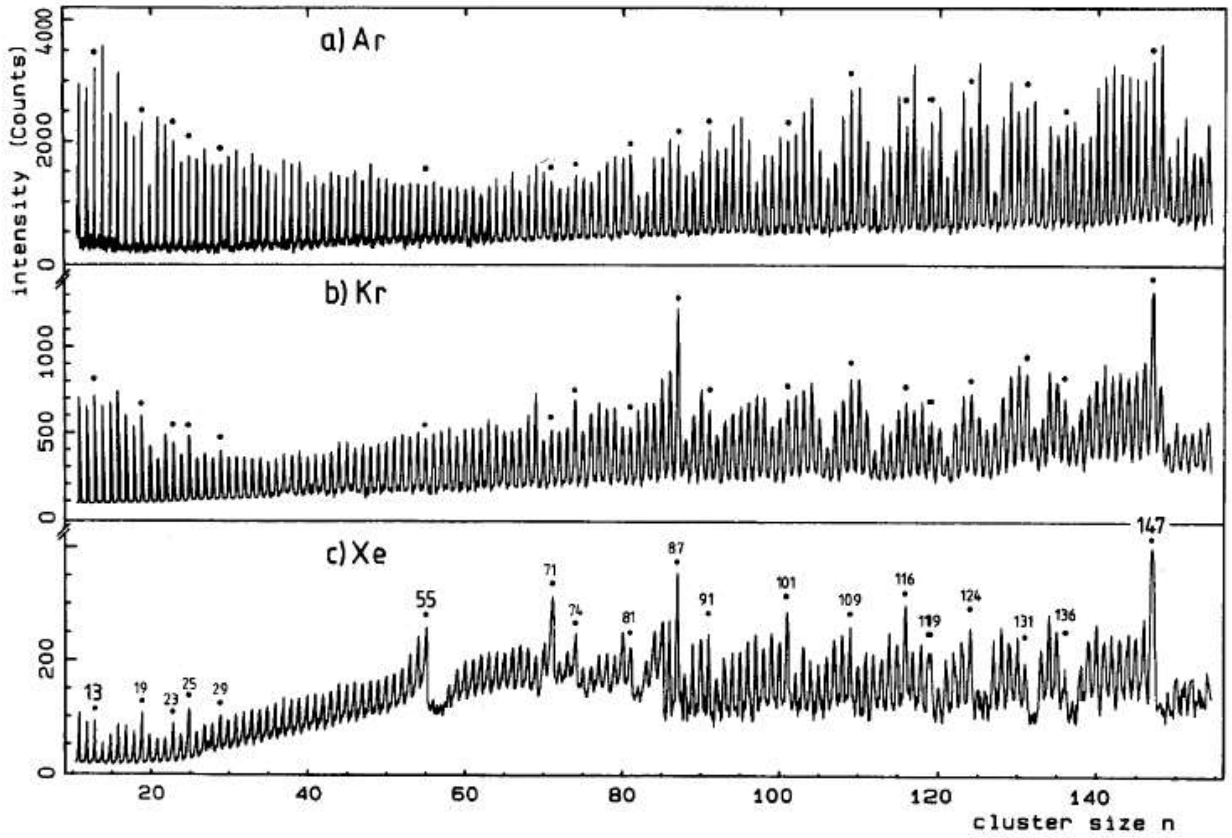


Fig. 3. Data sets showing the results of high-mass scans measured for four different backing gases. The mass spectra upon which these representations are based were obtained at a resolution ($m/\Delta m$) of 400 and a maximum signal-to-noise ratio of 20. Backing pressures were 1.3 atm for all three gases. A 1.5 mm aperture skimmer was used. With krypton, argon and neon, ions were detected up to m/z = 1495 corresponding to Na_{65}^+.

Gas phase cluster spectroscopy

Gas phase



Ti_8C_{12}

Fe, Al clusters

Mass spectra of positively charged Ar, Kr, Xe clusters, W. Miehle, O. Kandler, T. Leisner, and O. Echt. (**1989**) *J. Chem. Phys.*, 91, 5940.

Magic clusters

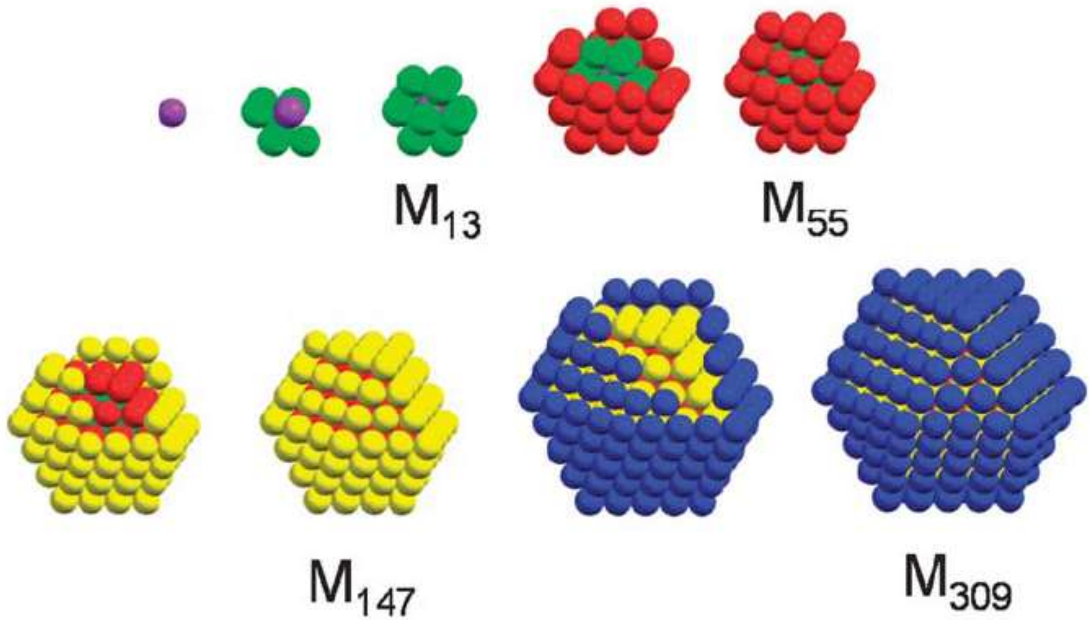


Fig. 1 Organization of full-shell clusters: a first single atom (purple) is surrounded by 12 others (green) to give a one-shell cluster M_{13}. 42 atoms (red) can be densely packed on the 12 green atoms ending with the M_{55} two-shell cluster, followed by 92 atoms (yellow) and 162 atoms (blue) to give M_{147} and M_{309}, respectively.

From Gunter Schmidt, *Chem. Soc. Rev.* **2008**, *37*, 1909–1930

C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

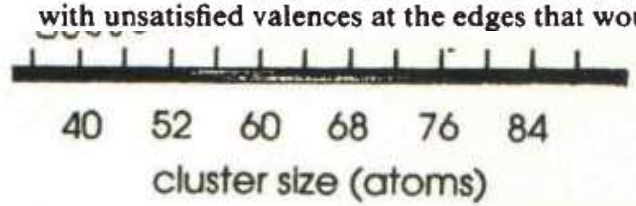
Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

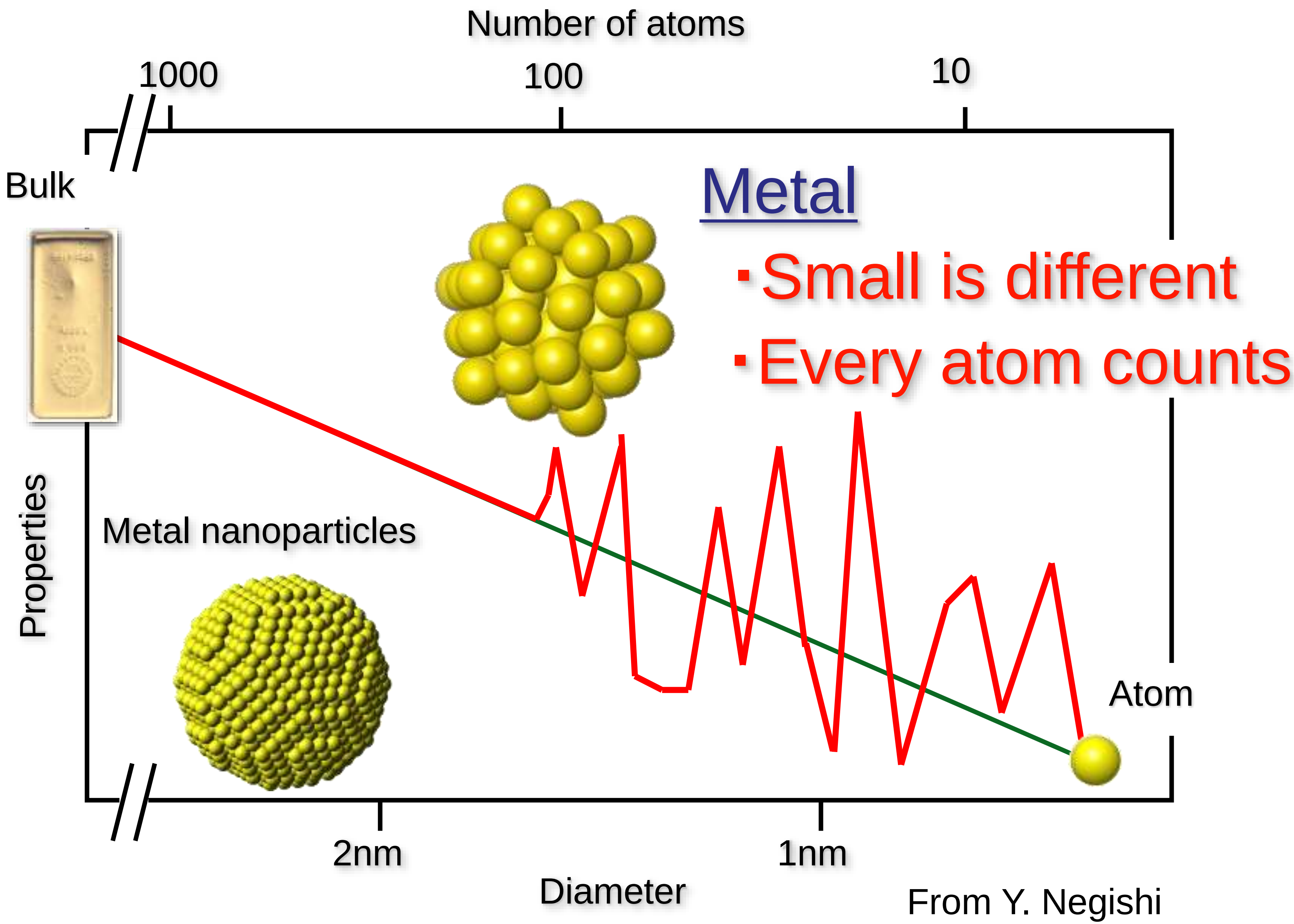
During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

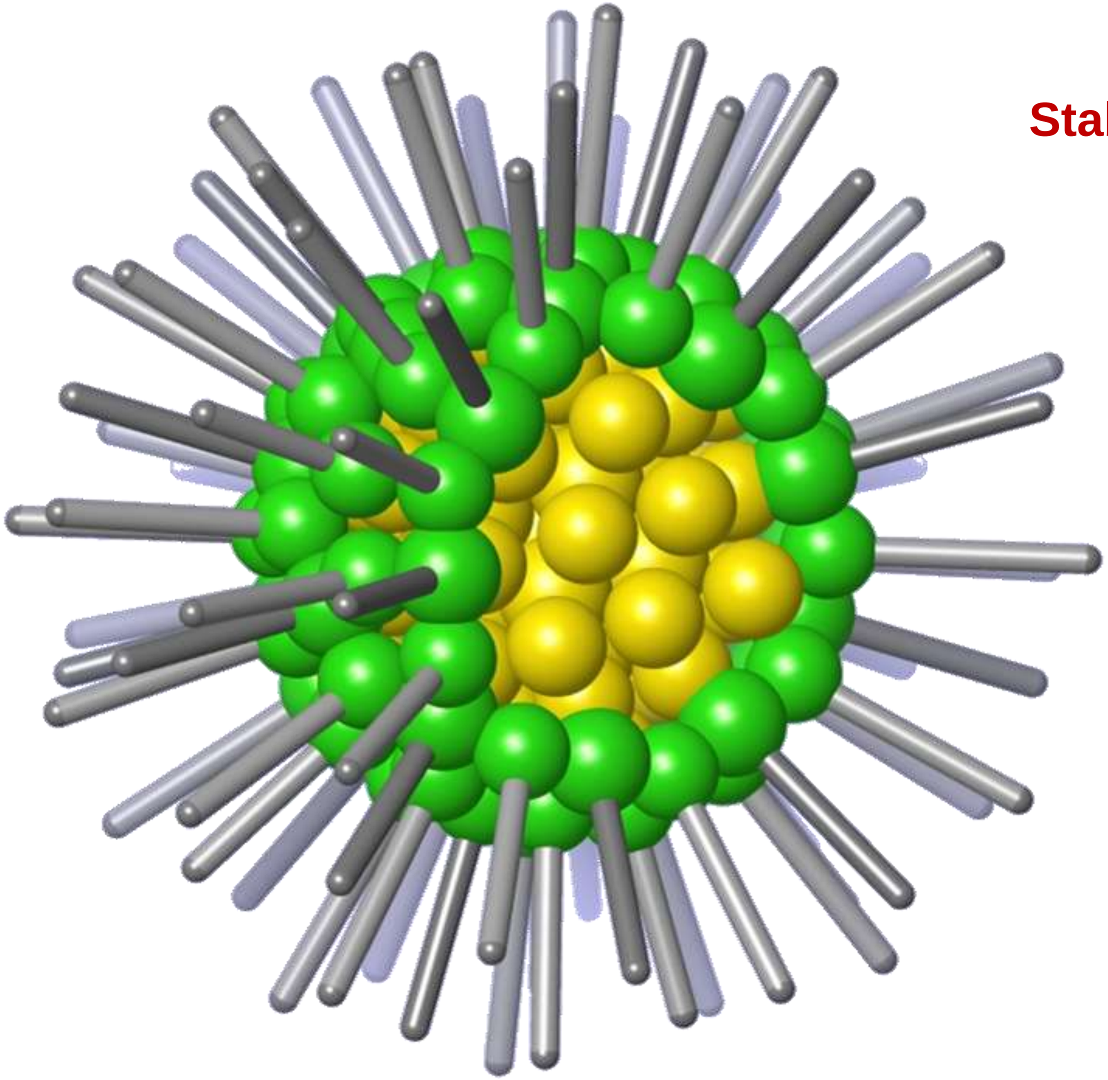
graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise




Number of atoms
1000
100
10
Bulk
Metal
·Small is different
·Every atom counts
Properties
Metal nanoparticles
Atom
2nm
1nm
Diameter
From Y. Negishi

Stable clusters



From Y. Negishi

Synthetic methods

J. CHEM. SOC., CHEM. COMMUN., 1994

Synthesis of Thiol-derivatised Gold Nanoparticles in a Two-phase Liquid–Liquid System

Mathias Brust, Merryl Walker, Donald Bethell, David J. Schiffrin and Robin Whyman
Department of Chemistry, The University of Liverpool, PO Box 147, Liverpool, UK L69 3BX

Using two-phase (water–toluene) reduction of $AuCl_4^-$ by sodium borohydride in the presence of an alkanethiol, solutions of 1–3 nm gold particles bearing a surface coating of thiol have been prepared and characterised; this novel material can be handled as a simple chemical compound.

Colloidal solutions of metals have been known for a long time[1] and a large variety of preparative techniques is now available.[2,3] Depending on the preparative conditions, the particles have a tendency to agglomerate slowly, eventually lose their disperse character and flocculate. The removal of the solvent generally leads to the complete loss of the ability to reform a colloidal solution. Preparation of colloidal metals in a two-phase system was introduced by Faraday,[4] who reduced an aqueous gold salt with phosphorus in carbon disulfide and obtained a ruby coloured aqueous solution of dispersed gold particles. Combining this two-phase approach with the more recent techniques of ion extraction and monolayer self-assembly with alkane thiols,[5] a one-step method for the preparation of an unusual new metallic material of derivatised nanometre-sized gold particles is described.

The strategy followed consisted in growing the metallic clusters with the simultaneous attachment of self-assembled thiol monolayers on the growing nuclei. In order to allow the surface reaction to take place during metal nucleation and growth, the particles were grown in a two-phase system. Two-phase redox reactions can be carried out by an appropriate choice of redox reagents present in the adjoining phases.[6] In the present case, $AuCl_4^-$ was transferred from aqueous solution to toluene using tetraoctylammonium bromide as the phase-transfer reagent and reduced with aqueous sodium borohydride in the presence of dodecanethiol ($C_{12}H_{25}SH$). On addition of the reducing agent, the organic phase changes colour from orange to deep brown within a few seconds. The overall reaction is summarized by eqns. (1) and (2), where the

$$AuCl_4^-(aq) + N(C_8H_{17})_4^+ (C_6H_5Me) \rightarrow N(C_8H_{17})_4^+AuCl_4^-(C_6H_5Me) \quad (1)$$

$$mAuCl_4^-(C_6H_5Me) + nC_{12}H_{25}SH(C_6H_5Me) + 3me^- \rightarrow 4mCl^-(aq) + (Au_m)(C_{12}H_{25}SH)_n(C_6H_5Me) \quad (2)$$

source of electrons is BH_4^-. The conditions of the reaction determine the ratio of thiol to gold, *i.e.* the ratio n/m. The preparation technique was as follows. An aqueous solution of hydrogen tetrachloroaurate (30 ml, 30 mmol dm^{-3}) was mixed with a solution of tetraoctylammonium bromide in toluene (80 ml, 50 mmol dm^{-3}). The two-phase mixture was vigorously stirred until all the tetrachloroaurate was transferred into

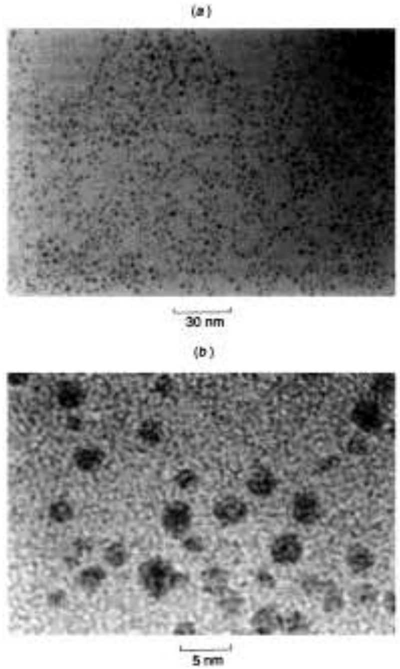


Fig. 1 TEM pictures of the thiol derivatised gold nanoparticles at (*a*) low and (*b*) high magnification

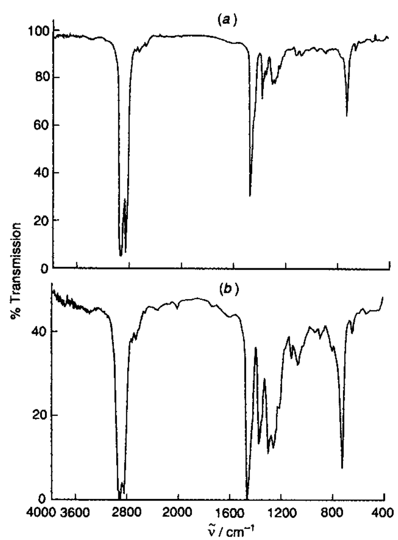


Fig. 2 IR spectra of (*a*) dodecanethiol and (*b*) nanoparticles prepared in the present work. The particles were deposited on an NaCl disc by evaporation of a drop of a toluene solution.

Observing such clusters

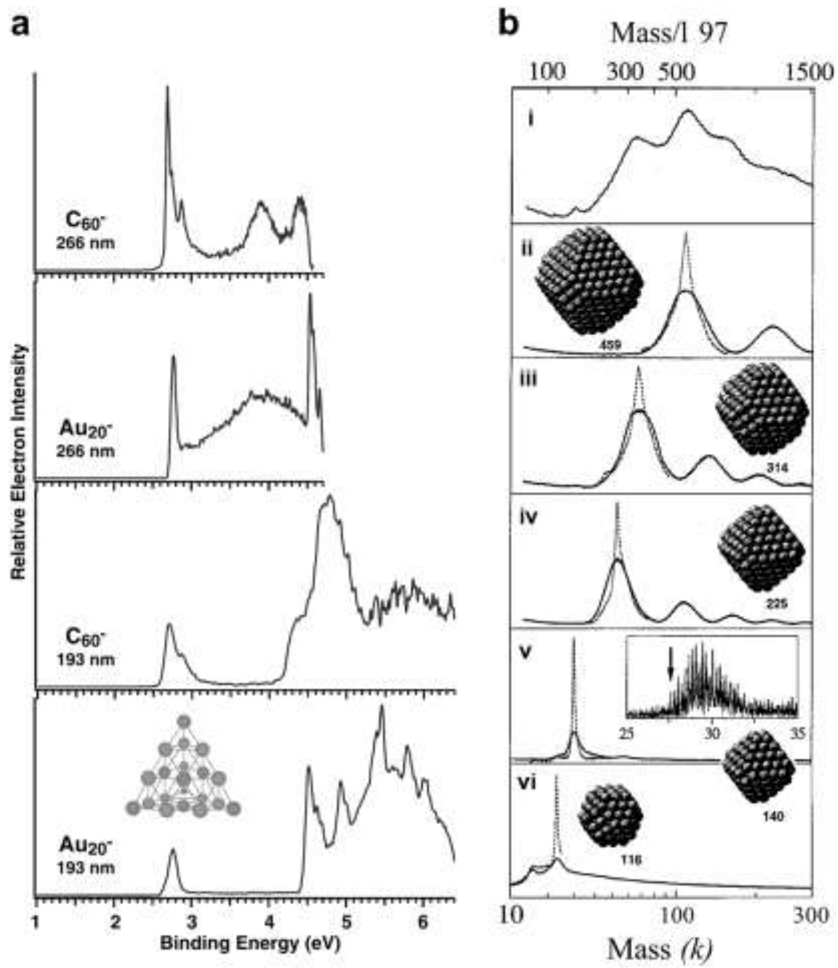
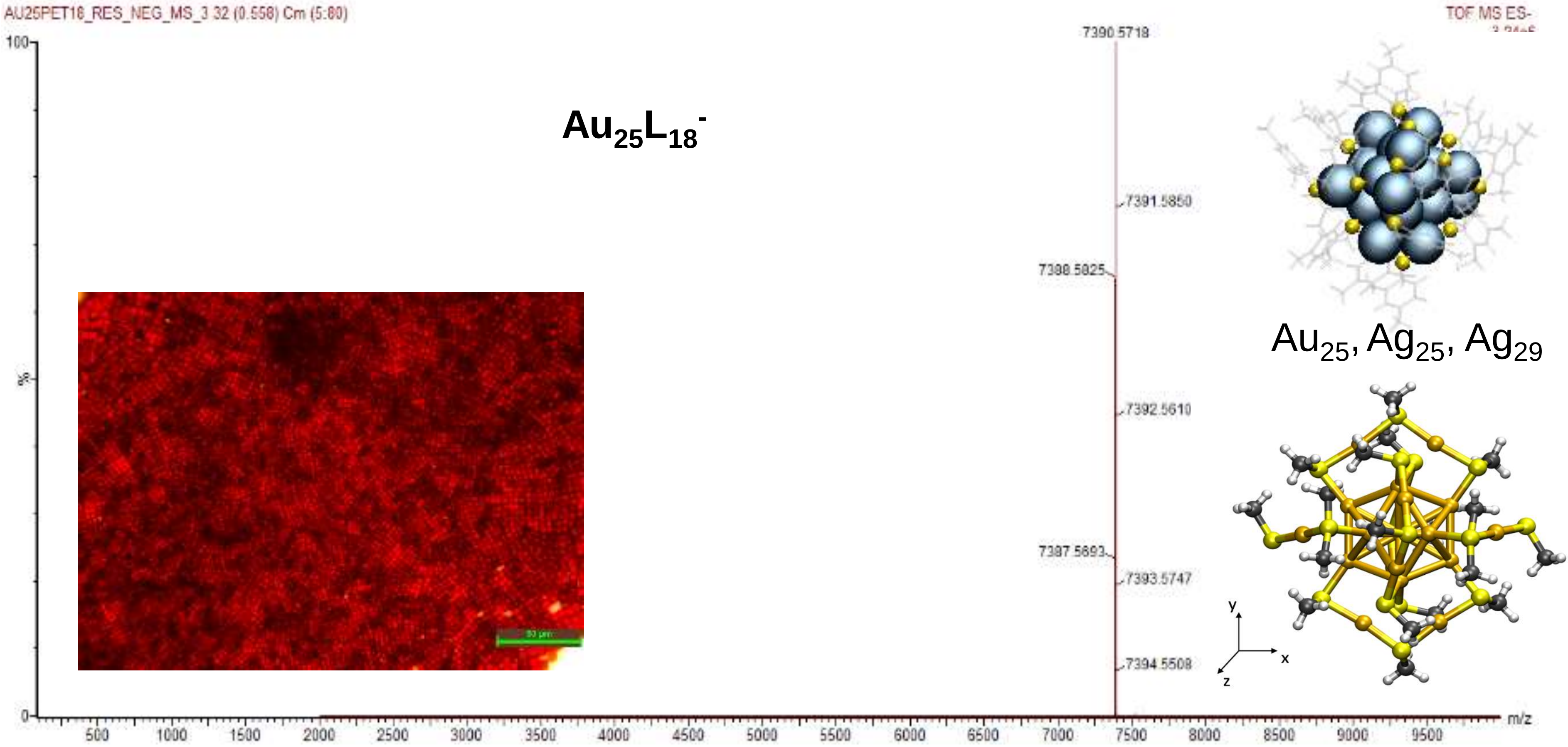


Fig. 2 Early stages of MS of noble metal clusters. a Photoelectron spectra of Au_{20}^{-} cluster compared with C_{60}^{-} at 193 nm and 266 nm[45]. (Copyright© 2003 the American Association for the Advancement of Science) **b** Mass spectra obtained by laser desorption ionization of dodecanethiol thiol-protected gold clusters, (i) crude mixture of clusters and (ii–vi) separated fractions[47]. (Copyright© 1996 John Wiley and Sons)

Chakraborty and Pradeep *NPG Asia Materials* (2019) 11:48
https://doi.org/10.1038/s41427-019-0149-3

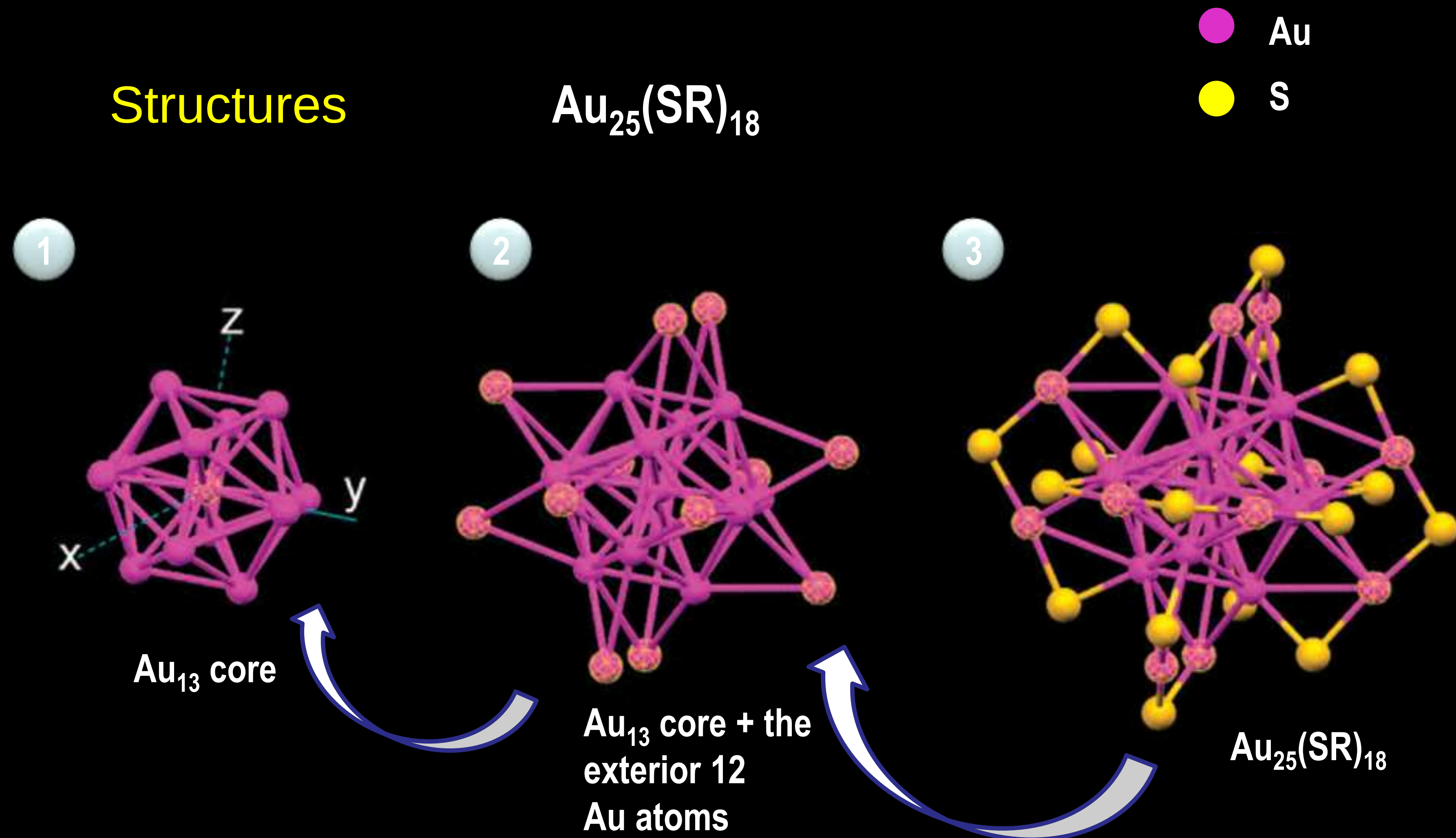
Atomically precise metal clusters as materials



T. Pradeep et. al. *Acc. Chem. Res.* 2018; 2019.

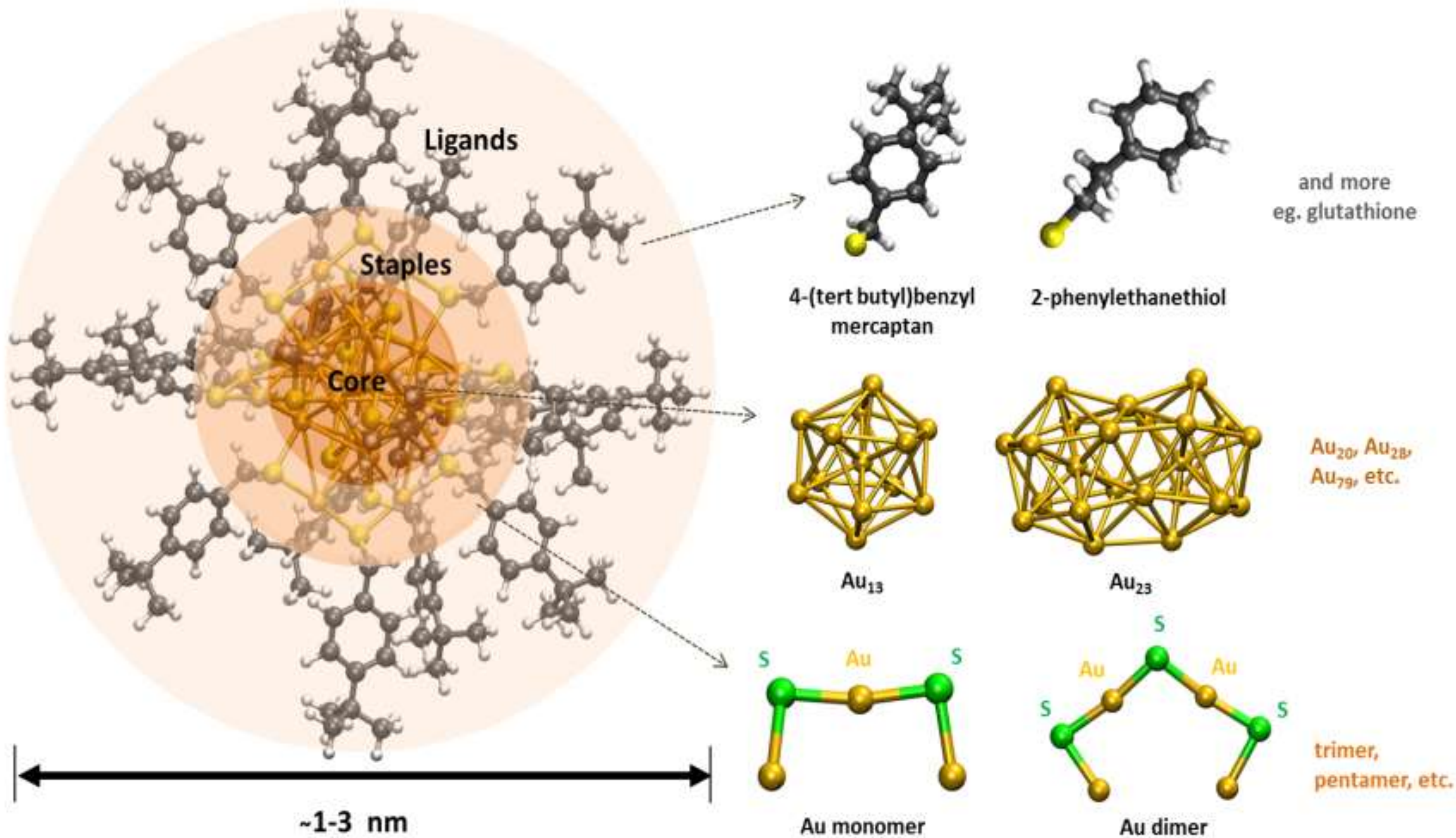
Structures

$Au_{25}(SR)_{18}$

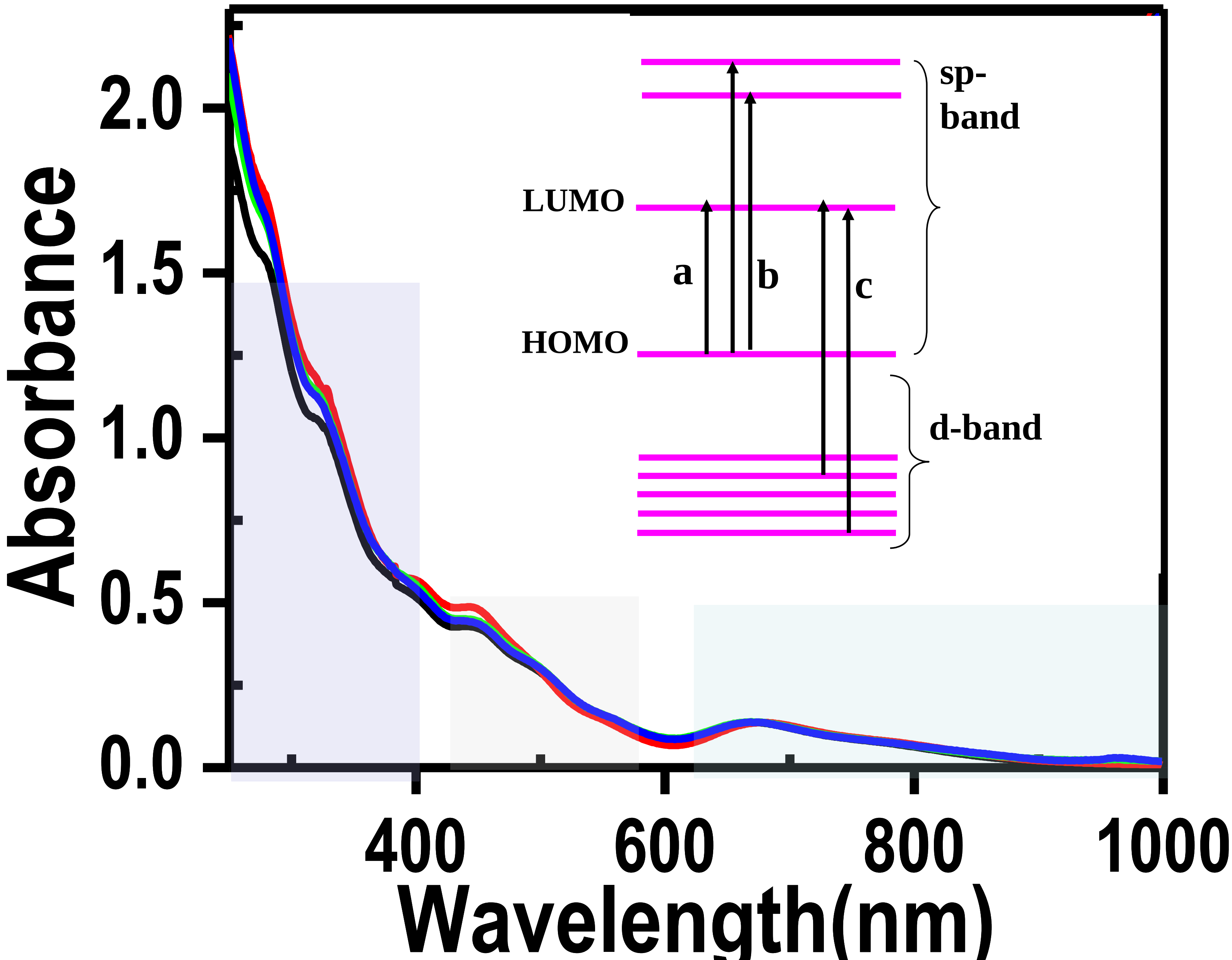


>150 such clusters

Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. *J. Am. Chem. Soc.* **2008**, *130*, 5883-5885.



Ligands
Staples
Core
~1-3 nm
4-(tert butyl)benzyl mercaptan
2-phenylethanethiol
and more
eg. glutathione
Au13
Au23
Au20, Au28,
Au79, etc.
S
Au
S
Au monomer
S
Au
Au
S
S
Au dimer
trimer,
pentamer, etc.



Absorbance
2.0
1.5
1.0
0.5
0.0
400
600
800
1000
Wavelength(nm)
sp-
band
LUMO
HOMO
a
b
c
d-band

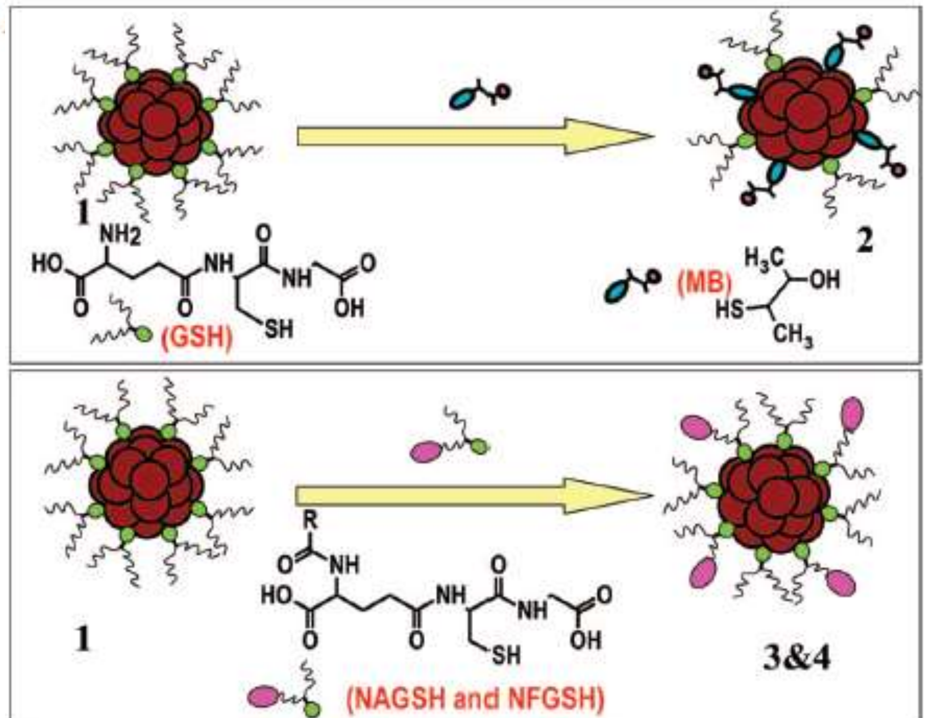
12168 J. Phys. Chem. C 2008, 112, 12168–12176

Ligand Exchange of $Au_{25}SG_{18}$ Leading to Functionalized Gold Clusters: Spectroscopy, Kinetics, and Luminescence

E. S. Shibu,[†] M. A. Habeeb Muhammed,[†] T. Tsukuda,[‡] and T. Pradeep*[,†]

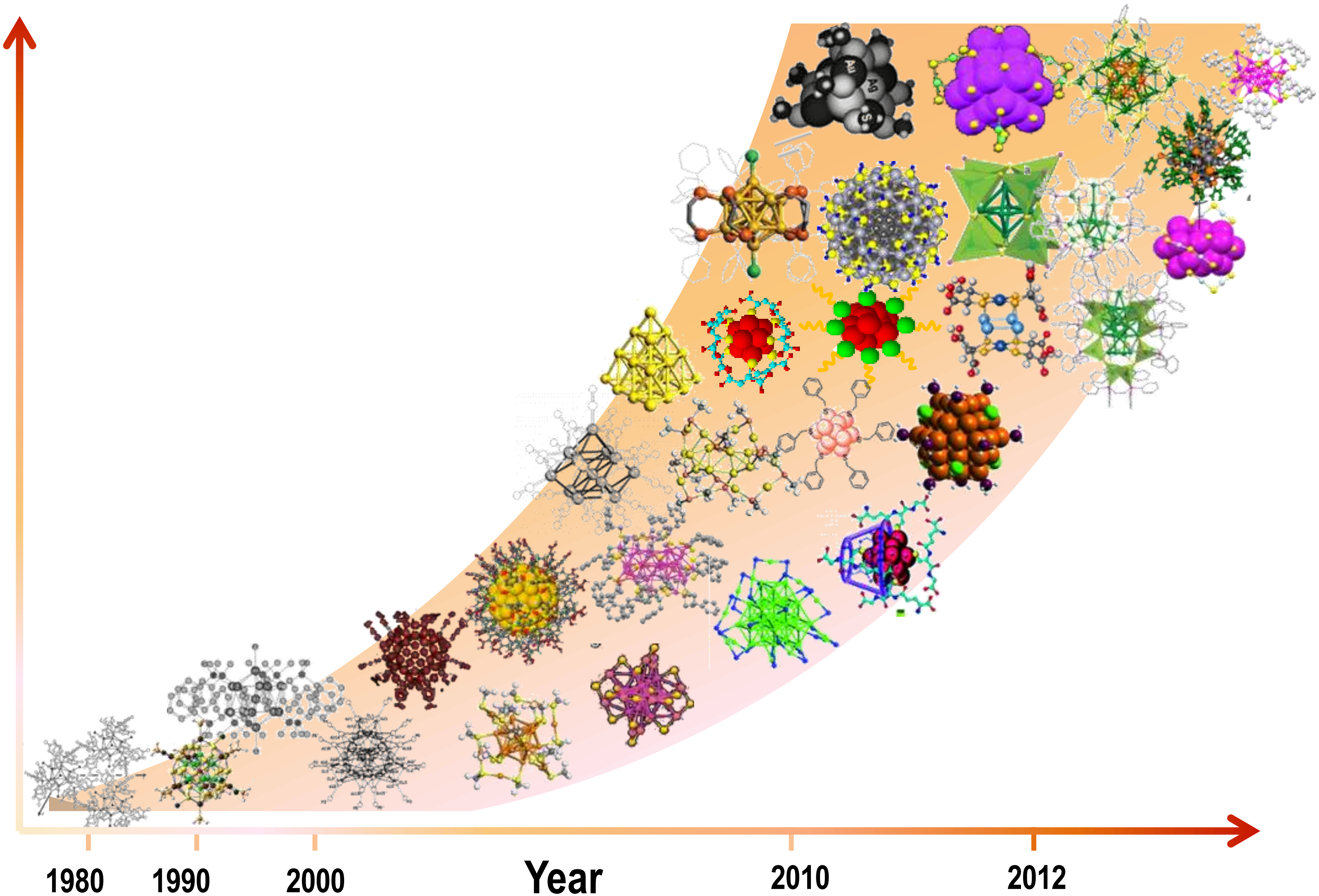
DST Unit on Nanoscience (DST UNS), Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Madras, Chennai 600 036, India and Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Received: January 18, 2008;



With Tatsuya Tsukuda

Evolution of noble metal clusters



I. Chakraborty and T. Pradeep, *Chem. Rev.* 2017

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

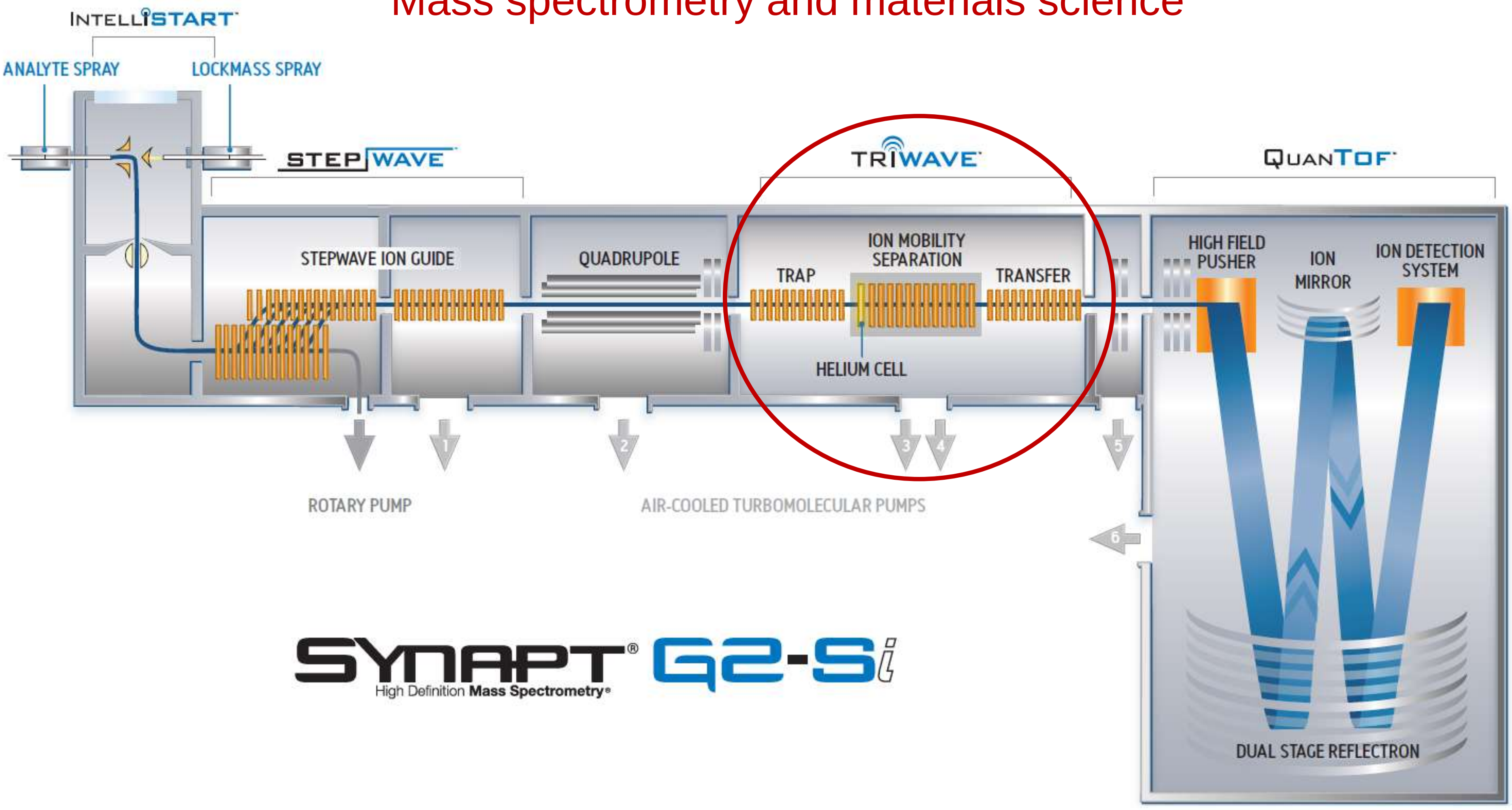
Citations: >2000

Supporting Information

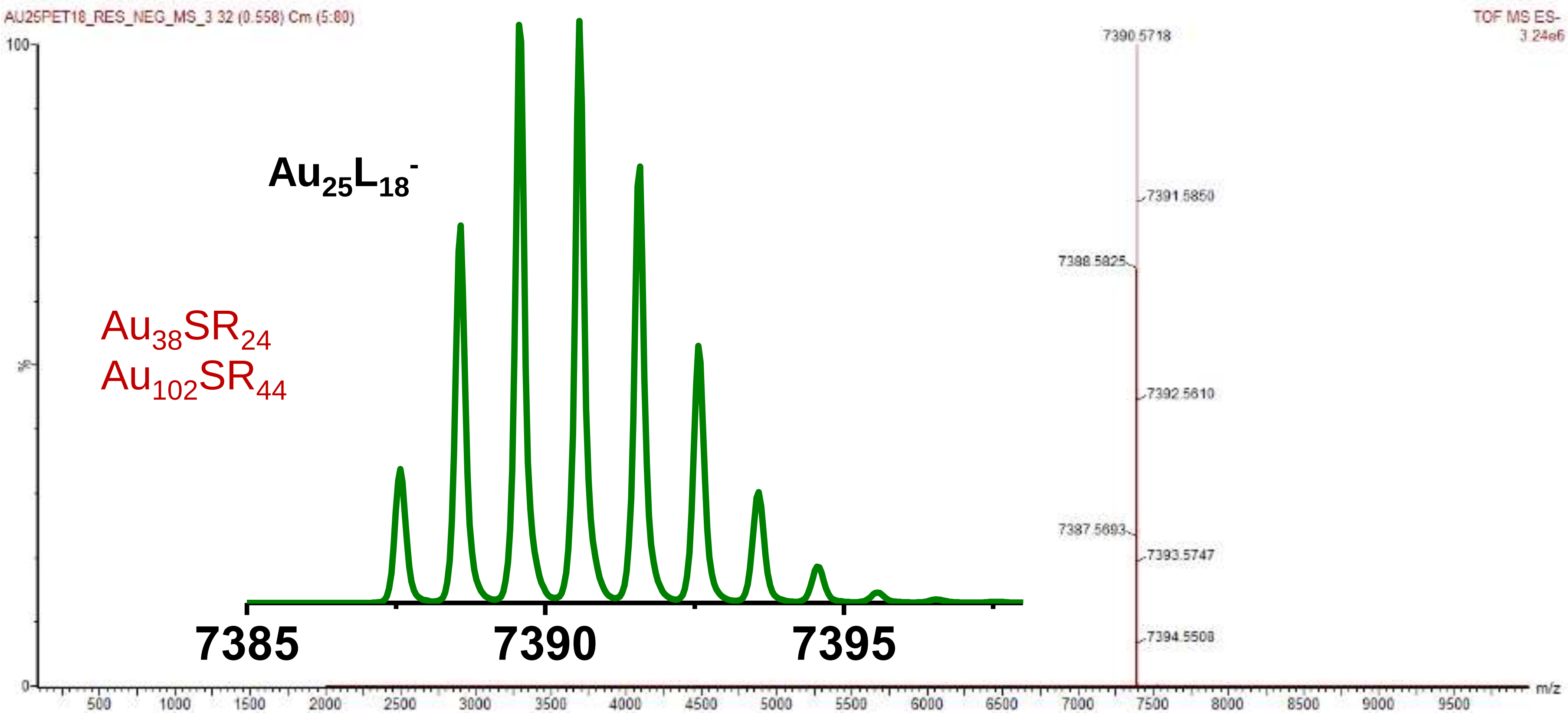
ABSTRACT: Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{102}(SR)_{44}$ as well as $Ag_{25}(SR)_{18}$, $Ag_{29}(S_2R)_{12}$, 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.

Also 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, …. A. W. Castleman Jr., H. Schmidbauer, …. Robin Ras, Olli Ikkala

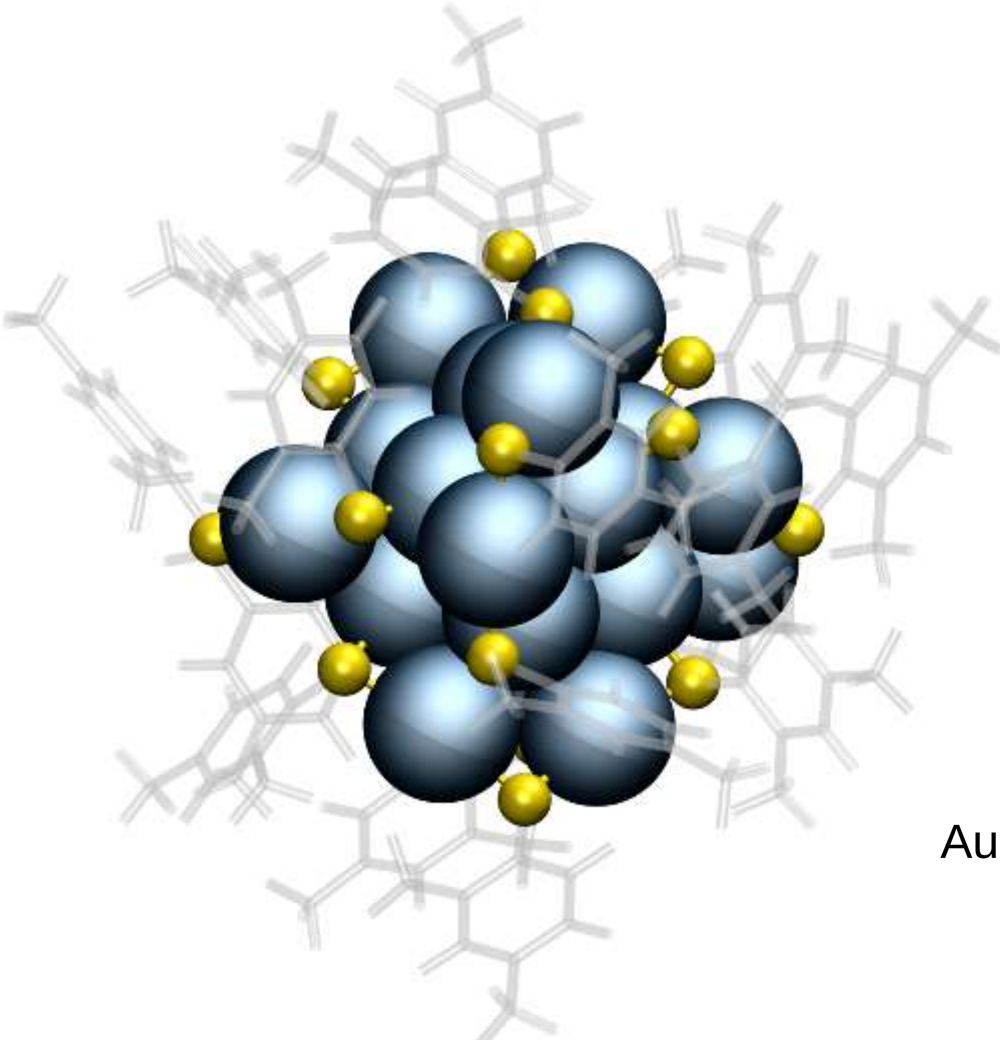
Mass spectrometry and materials science



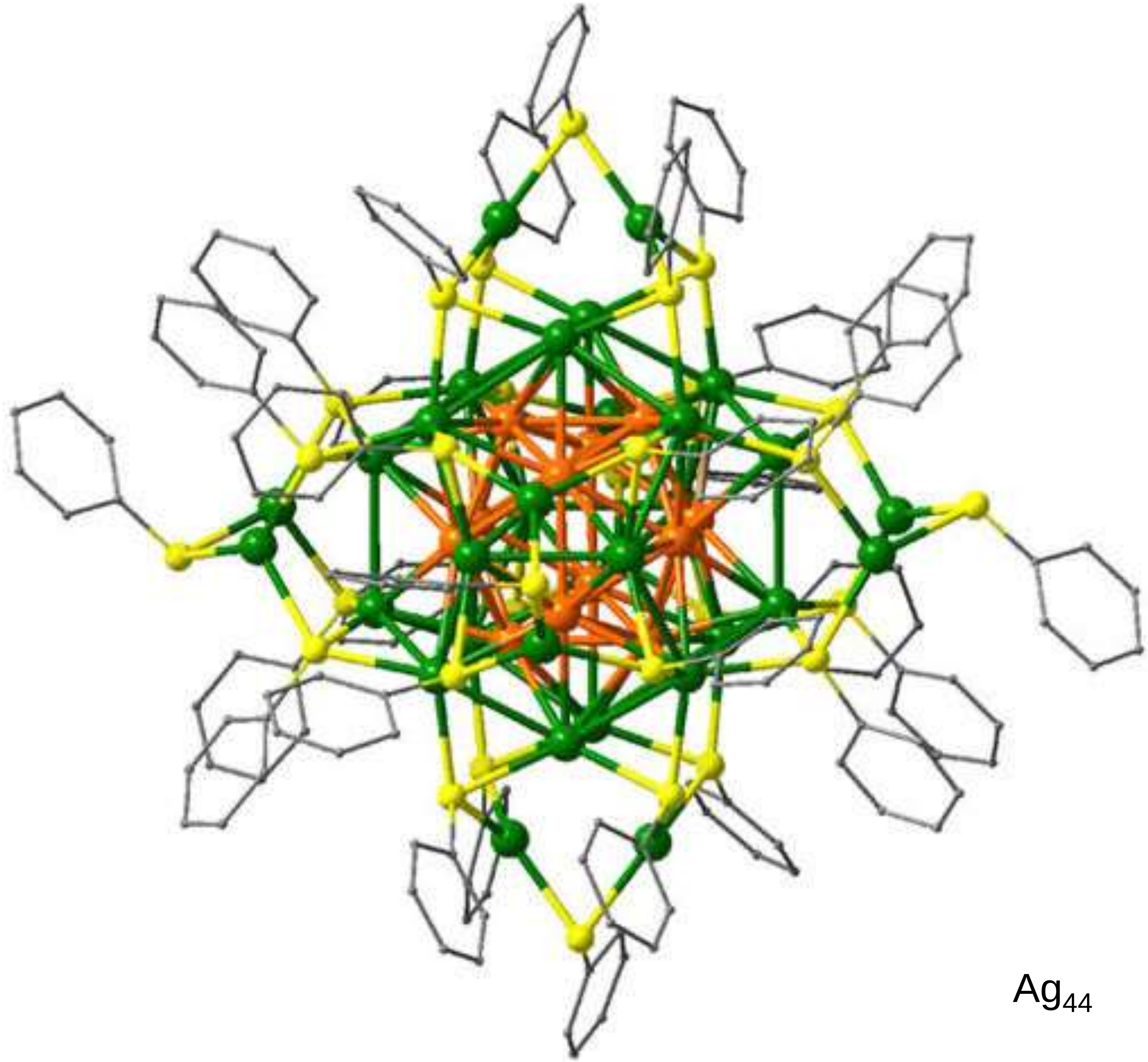
Molecular formula, Molecular weight



New molecules



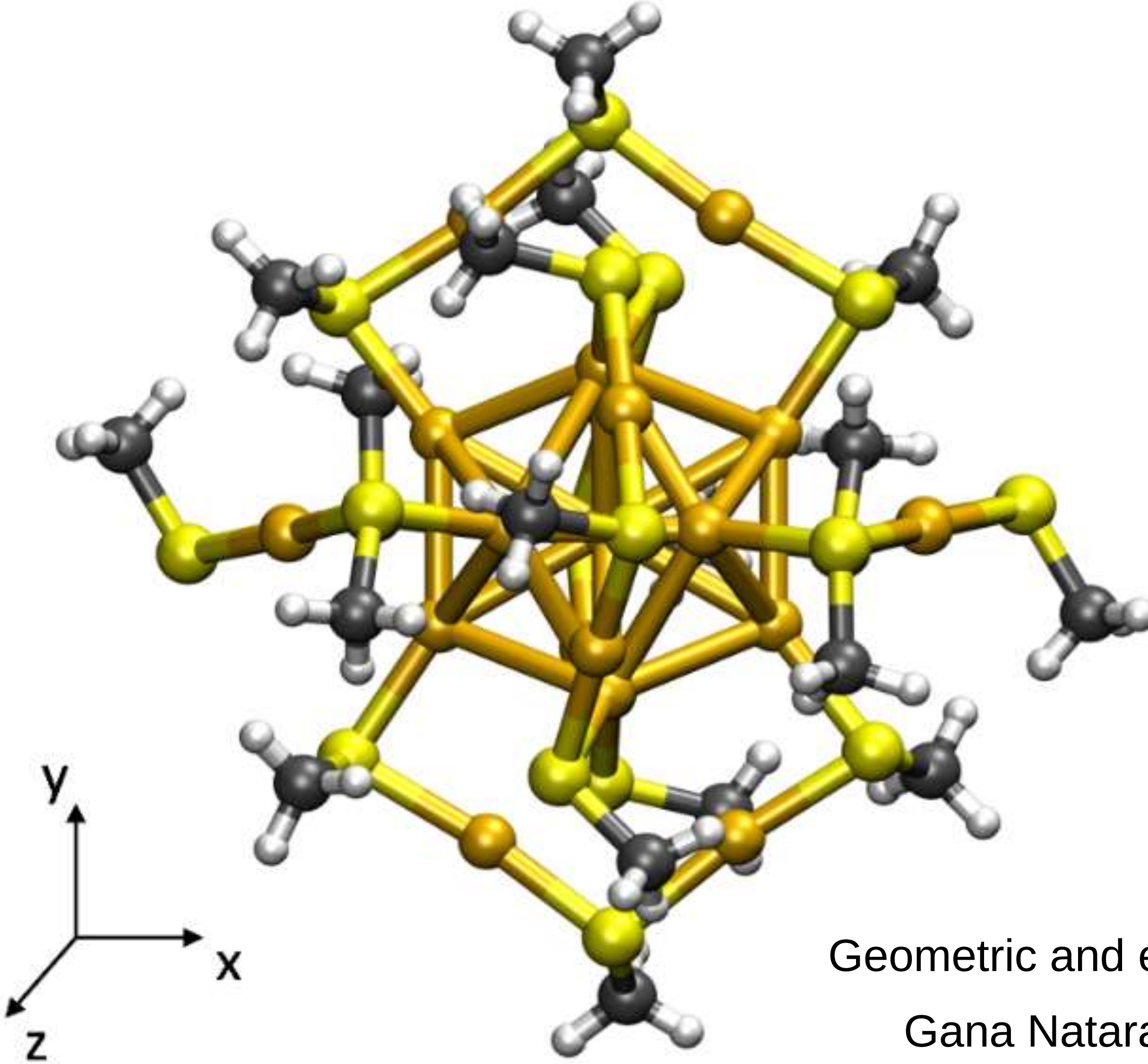
$Au_{25}, Ag_{25}, Ag_{29}$

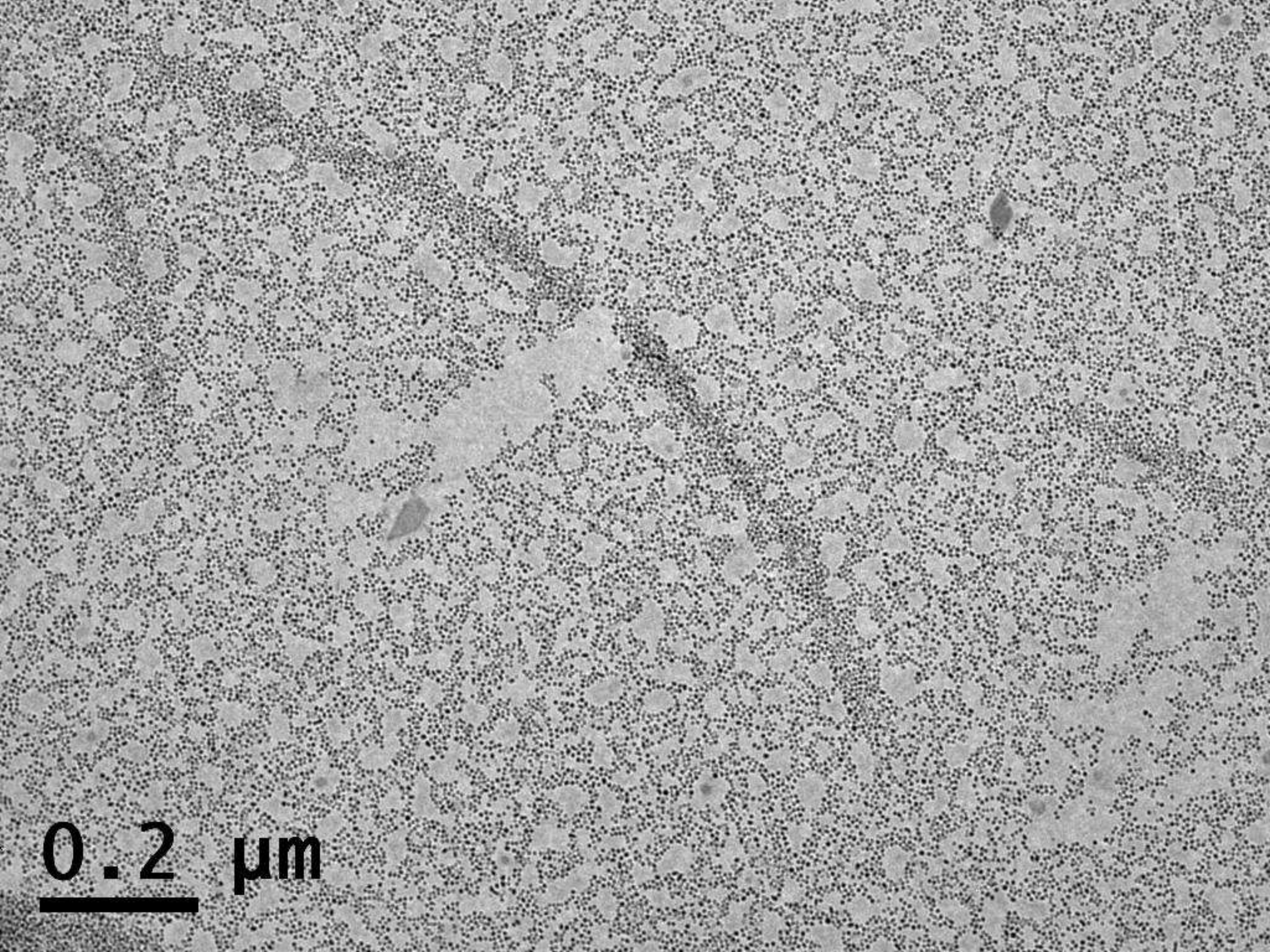


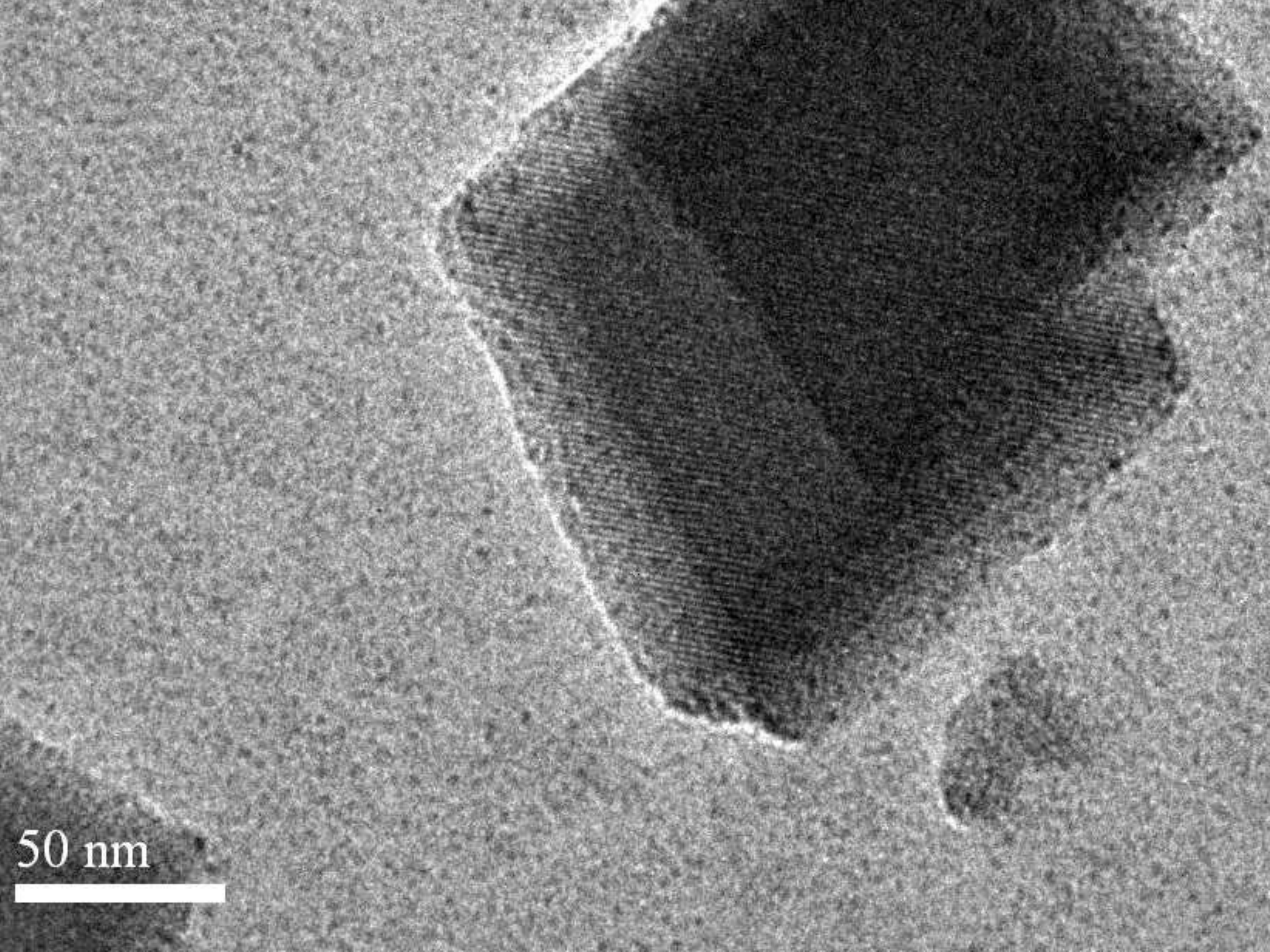
Ag_{44}

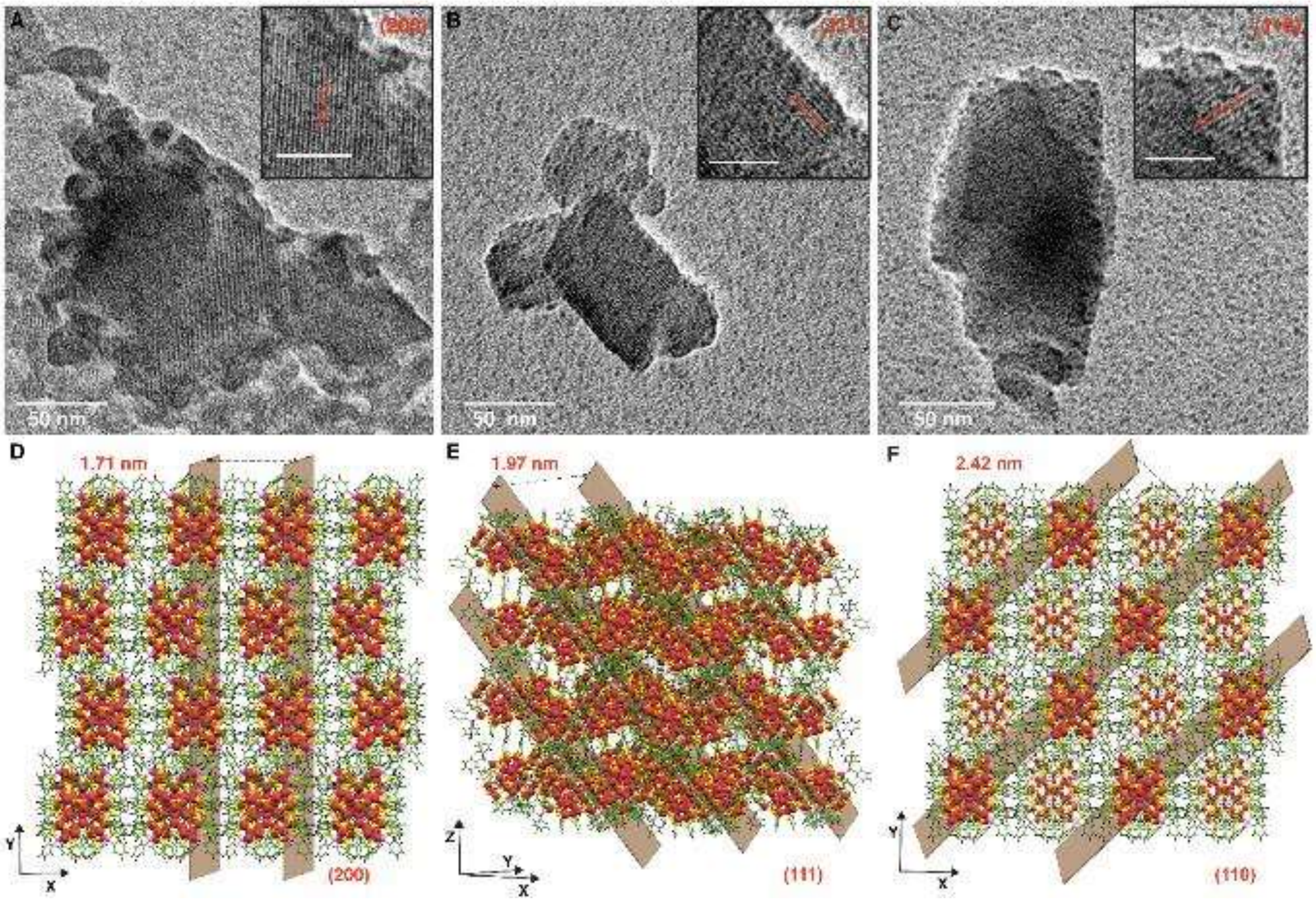
Nanfeng Zheng et al. *Nature Communications*, 2013
Terry Bigioni et al. *Nature* 2013

Molecular structure

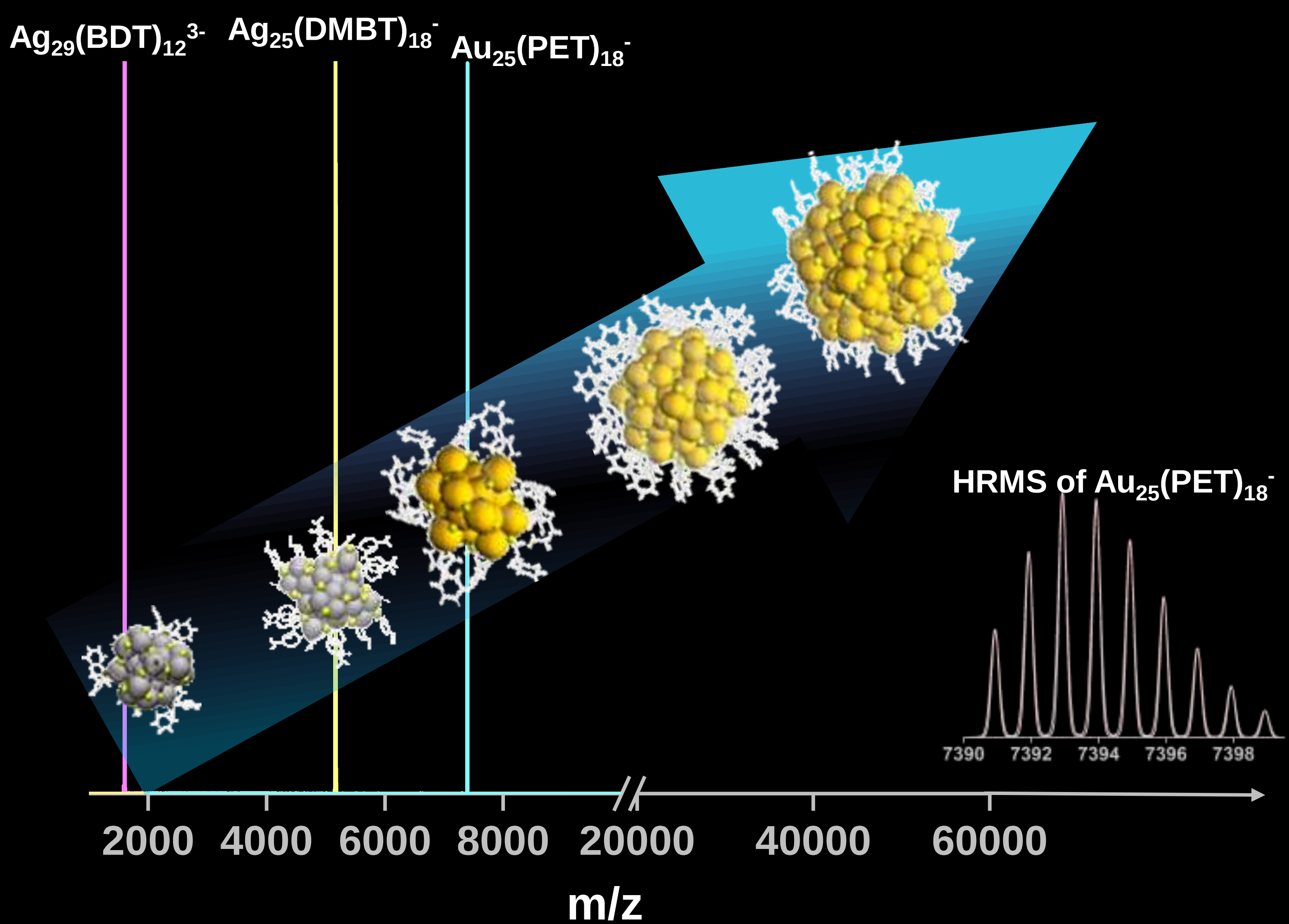



0.2 µm


50 nm



Ananthu Mahendranath et al. Chem.Comm.2021



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

Molecular materials

ACCOUNTS of chemical research

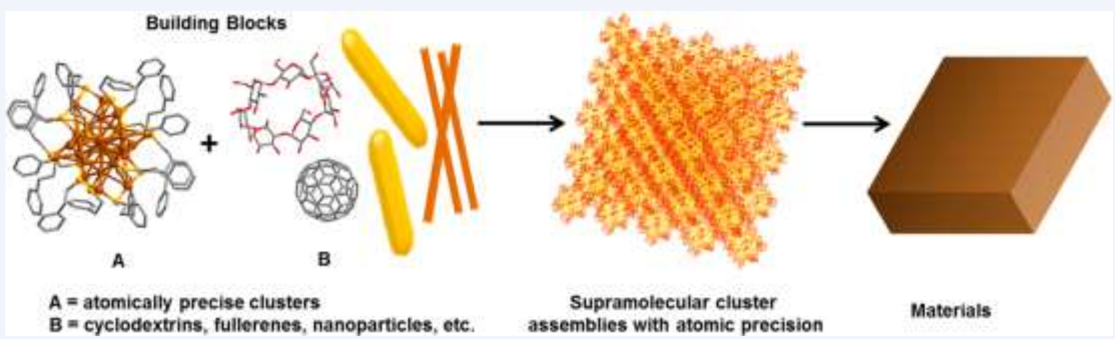
Article

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

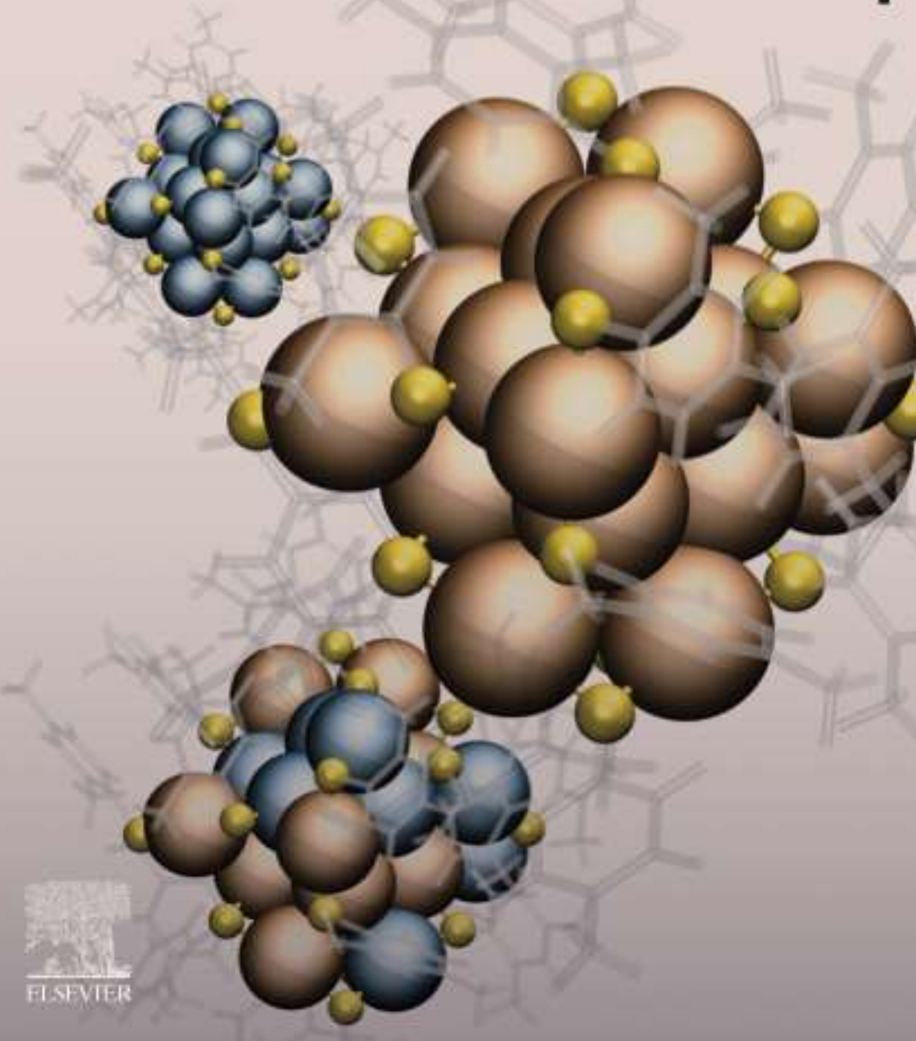
Molecular formula
Molecular weight
Molecular structure
Molecular absorption and emission
Molecular reactions
Molecular assembly
Molecular co-crystals

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 <u>between</u> clusters

Inter-cluster reactions

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

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

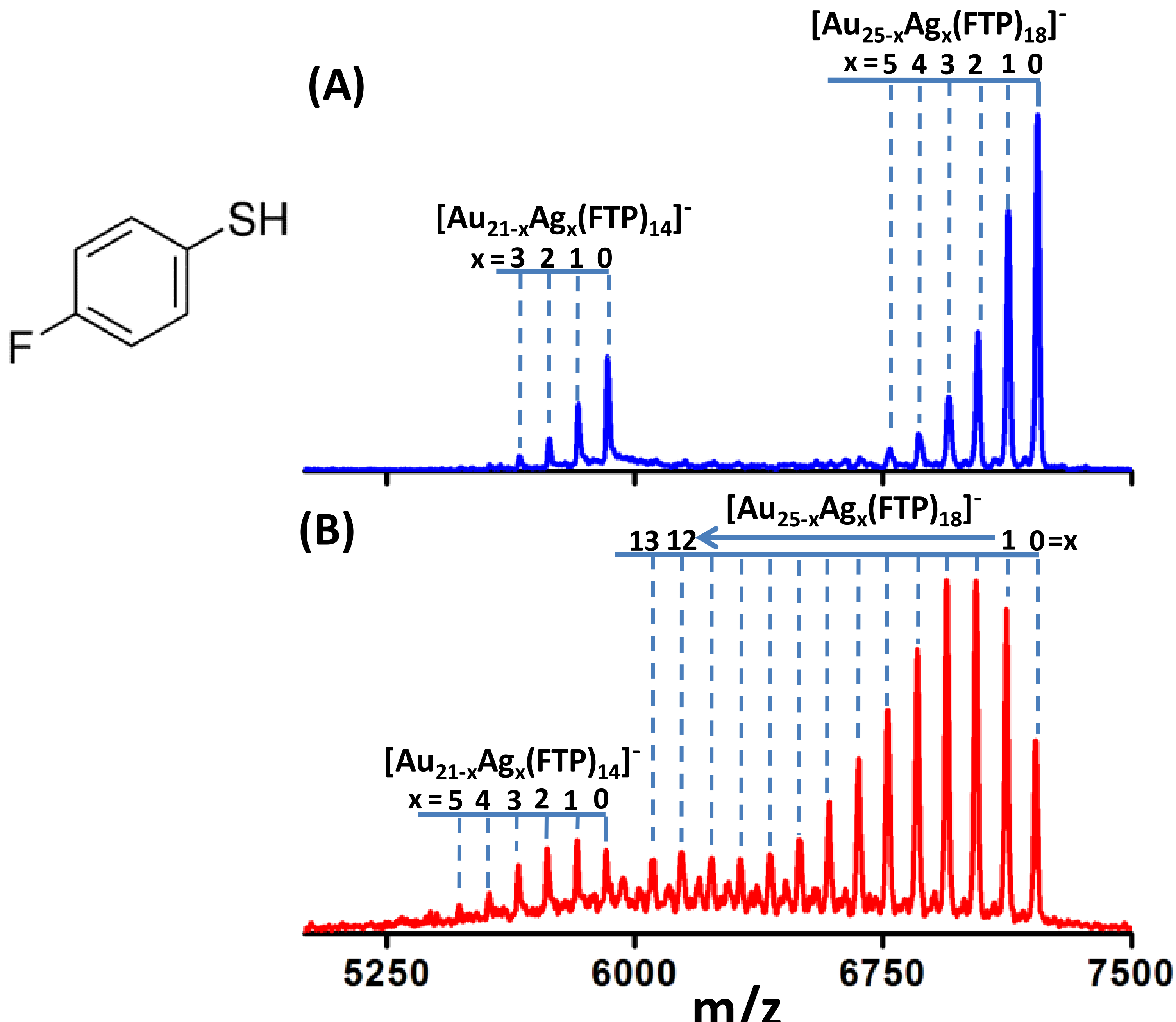
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

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

$$A + B \rightarrow C + D$$

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



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

(A)

Location of Au in $Au_xAg_{44-x}(SR)_{30}$	ΔE/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 $Au_{25-x}Ag_x(SR)_{18}$	ΔE/eV
Central atom (C)	+0.71
Icosahedron (I)	+0.23
Staples (S)	+0.44

(C)

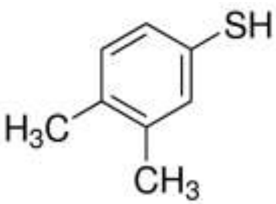
Location of Ag in $Au_{25-x}Ag_x(SR)_{18}$	Locations of Au in $Au_xAg_{44-x}(SR)_{30}$: I	D_{cv}	D_{cf}	S
C	-0.015	+0.564	+0.388	+0.226
I	-0.486	+0.093	-0.083	-0.245
S	-0.276	+0.303	+0.127	-0.035

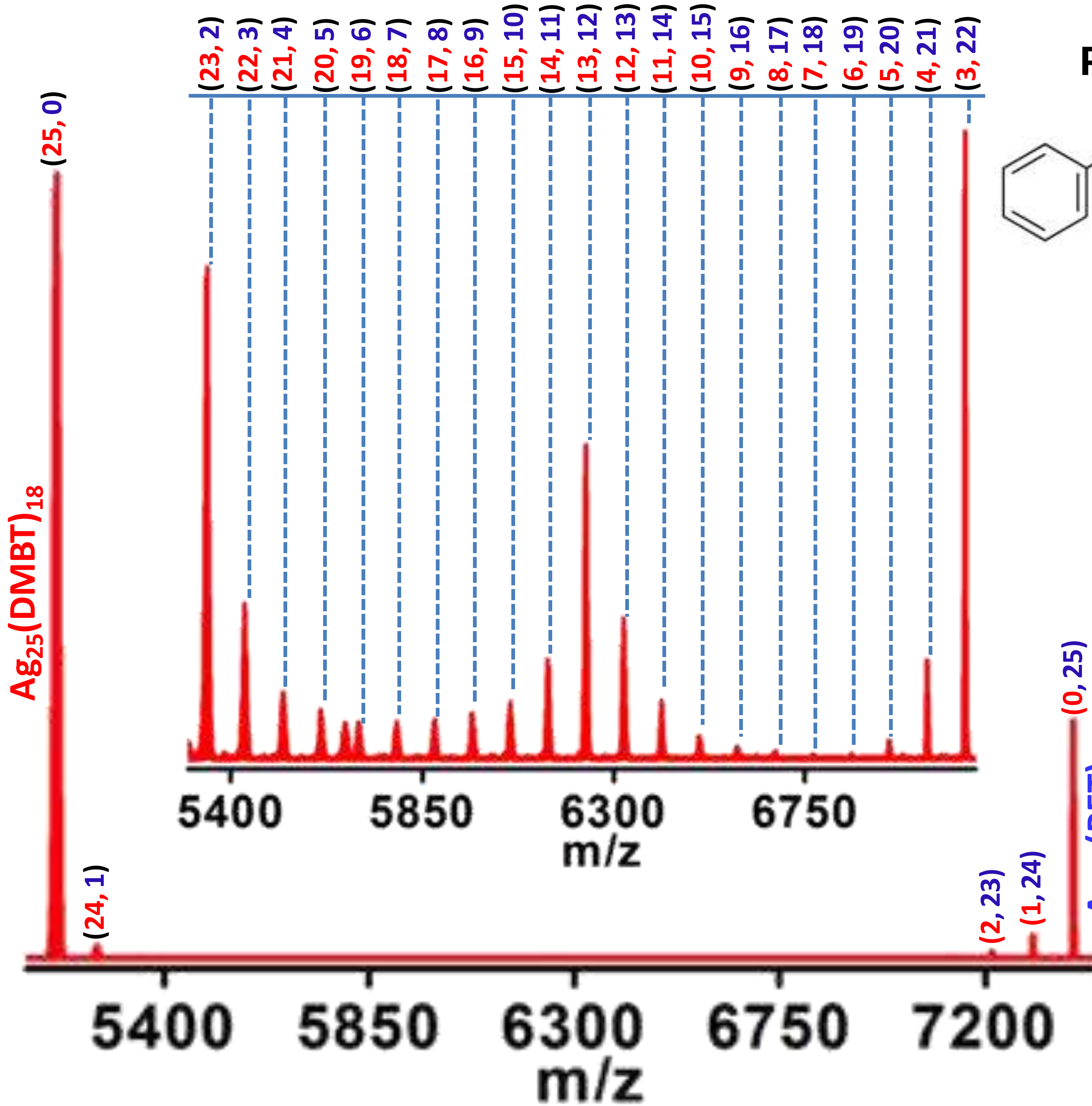
Ag_{25}-Au_{25} experiments

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

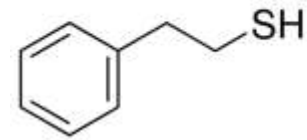
Reaction between $Au_{25}(PET)_{18}$ and $Ag_{25}(DMBT)_{18}$

DMBT

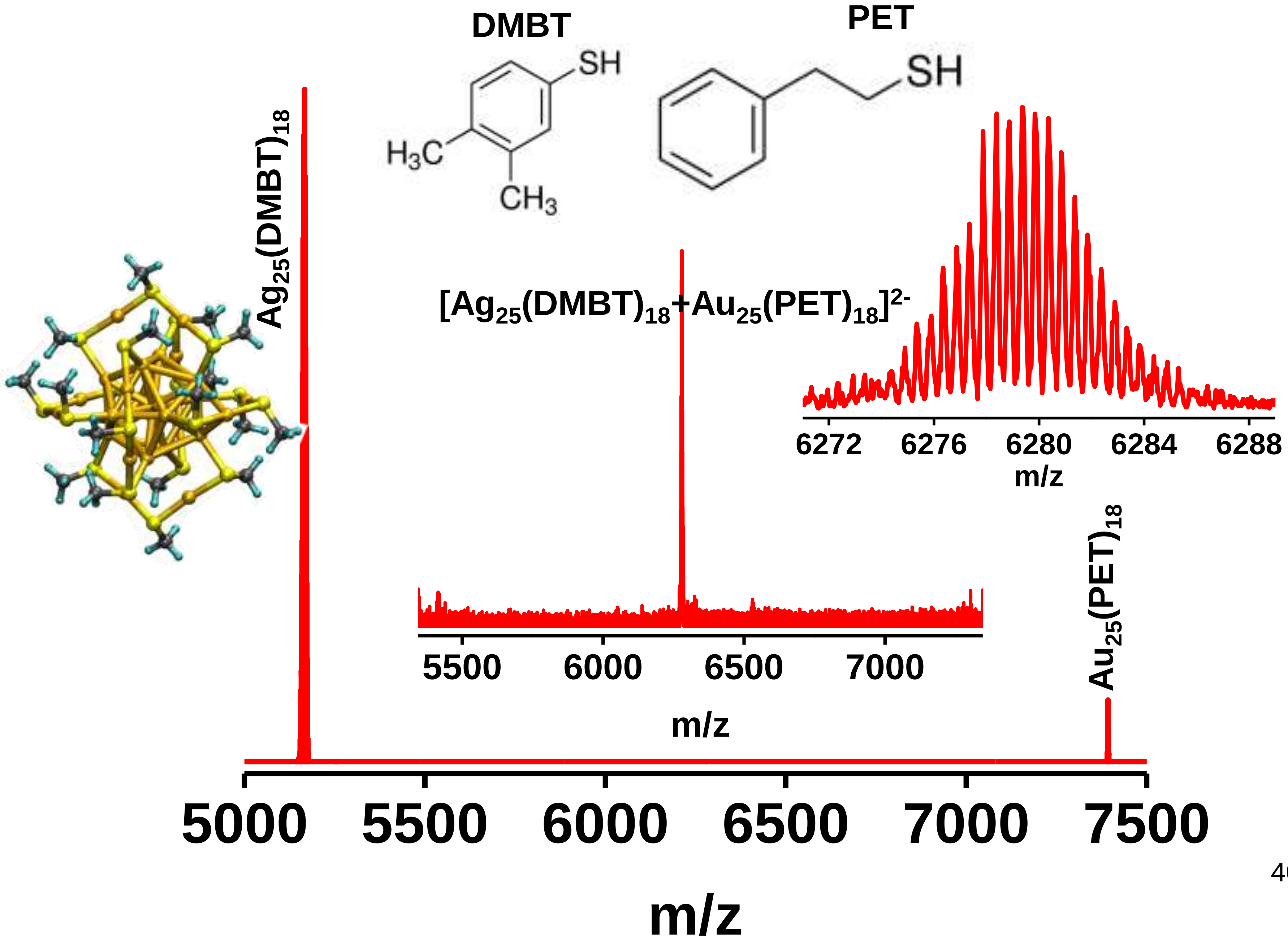




PET

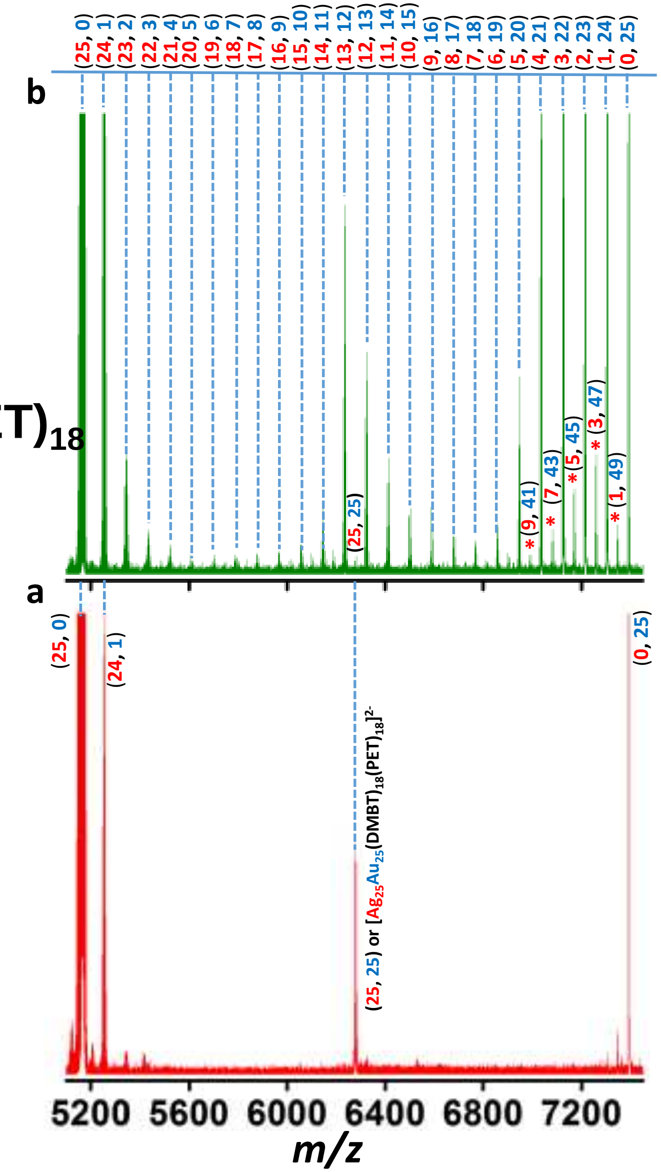


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

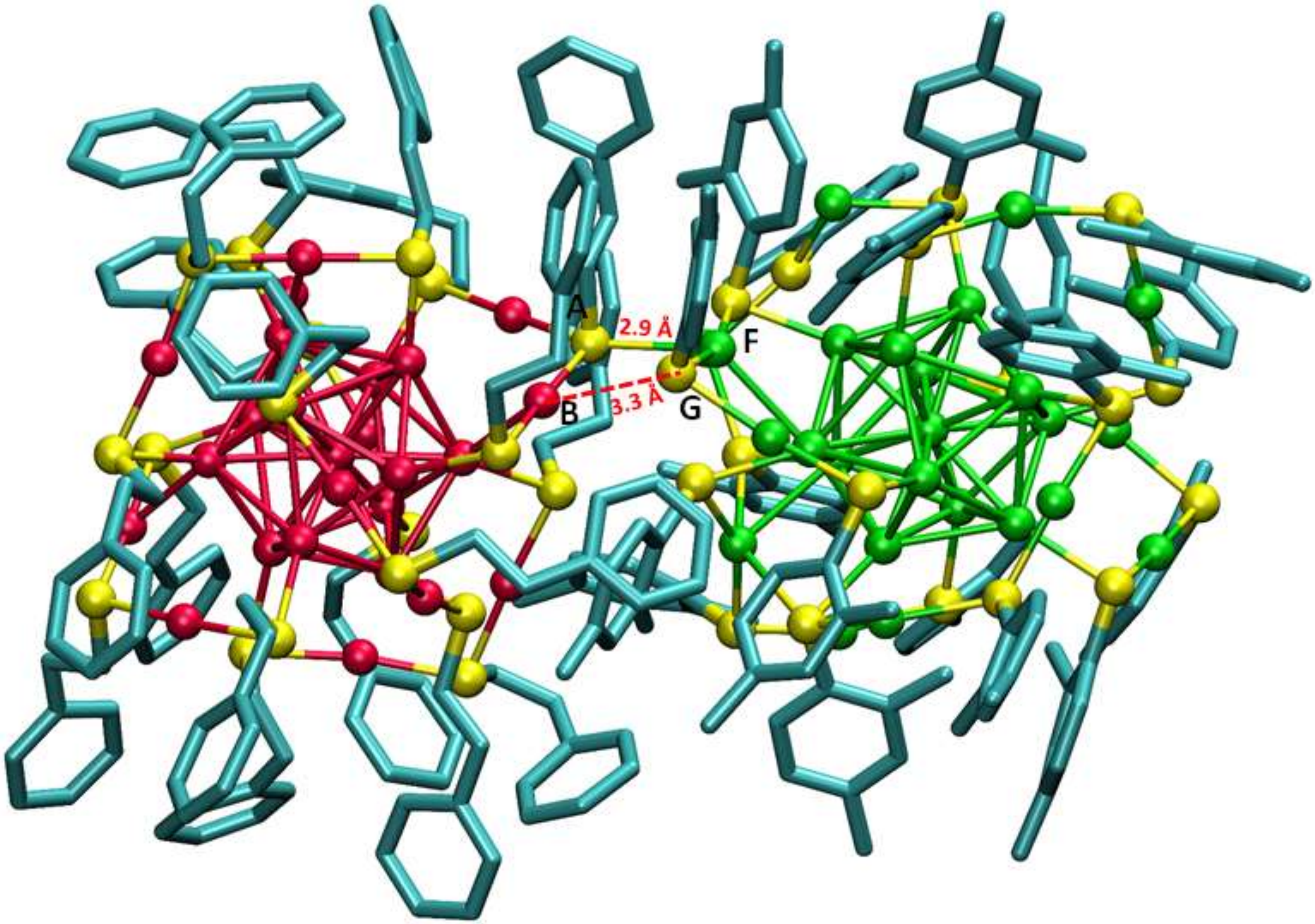
$Ag_{25}(DMBT)_{18}:Au_{25}(PET)_{18}$
0.3:1.0

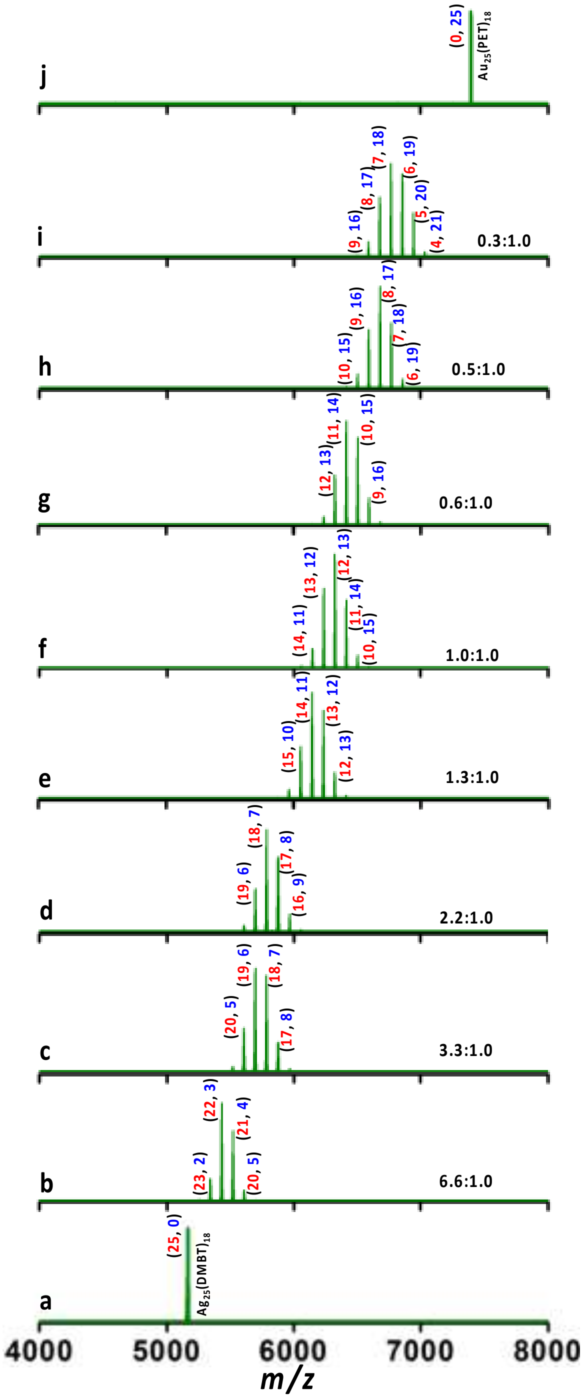


within 5 min

within 2 min

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



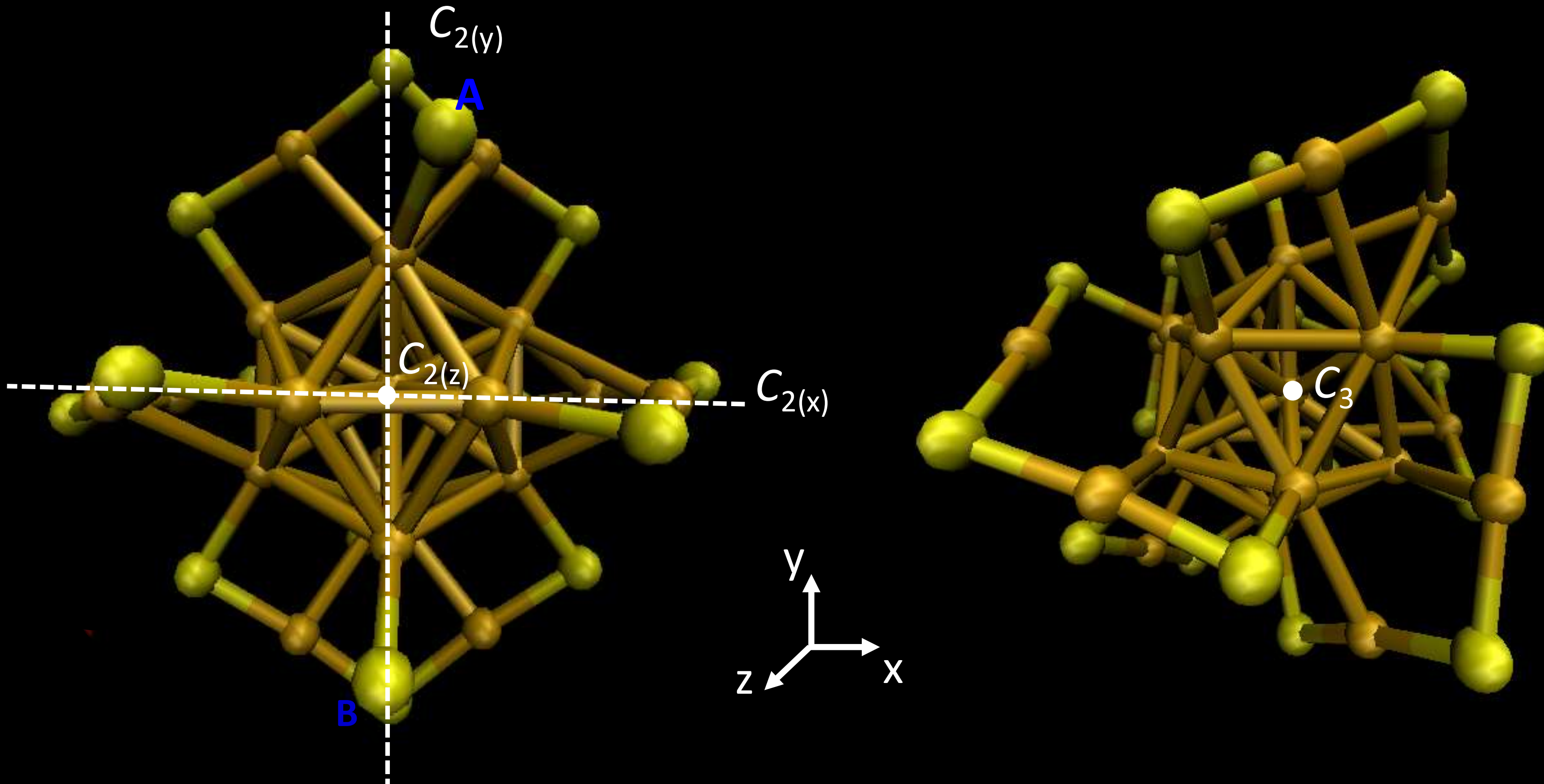

j
(0, 25)
Au$_{25}$(PET)$_{18}$
i
0.3:1.0
(9, 16)
(8, 17)
(7, 18)
(6, 19)
(5, 20)
(4, 21)
h
0.5:1.0
(10, 15)
(9, 16)
(8, 17)
(7, 18)
(6, 19)
g
0.6:1.0
(12, 13)
(11, 14)
(10, 15)
(9, 16)
f
1.0:1.0
(14, 11)
(13, 12)
(12, 13)
(11, 14)
(10, 15)
e
1.3:1.0
(15, 10)
(14, 11)
(13, 12)
(12, 13)
d
2.2:1.0
(19, 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)
Ag$_{25}$(DMBT)$_{18}$
4000
5000
6000
7000
8000
m/z

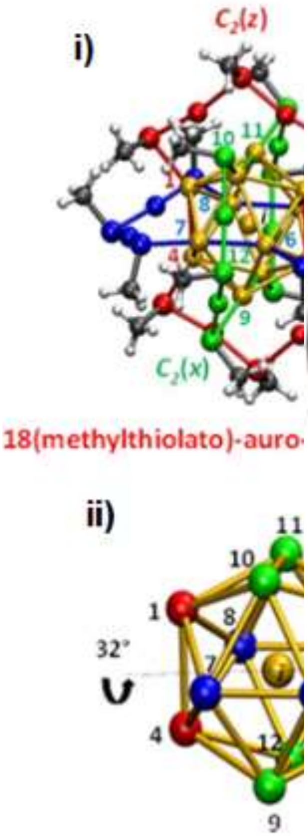
How do we comprehend this?

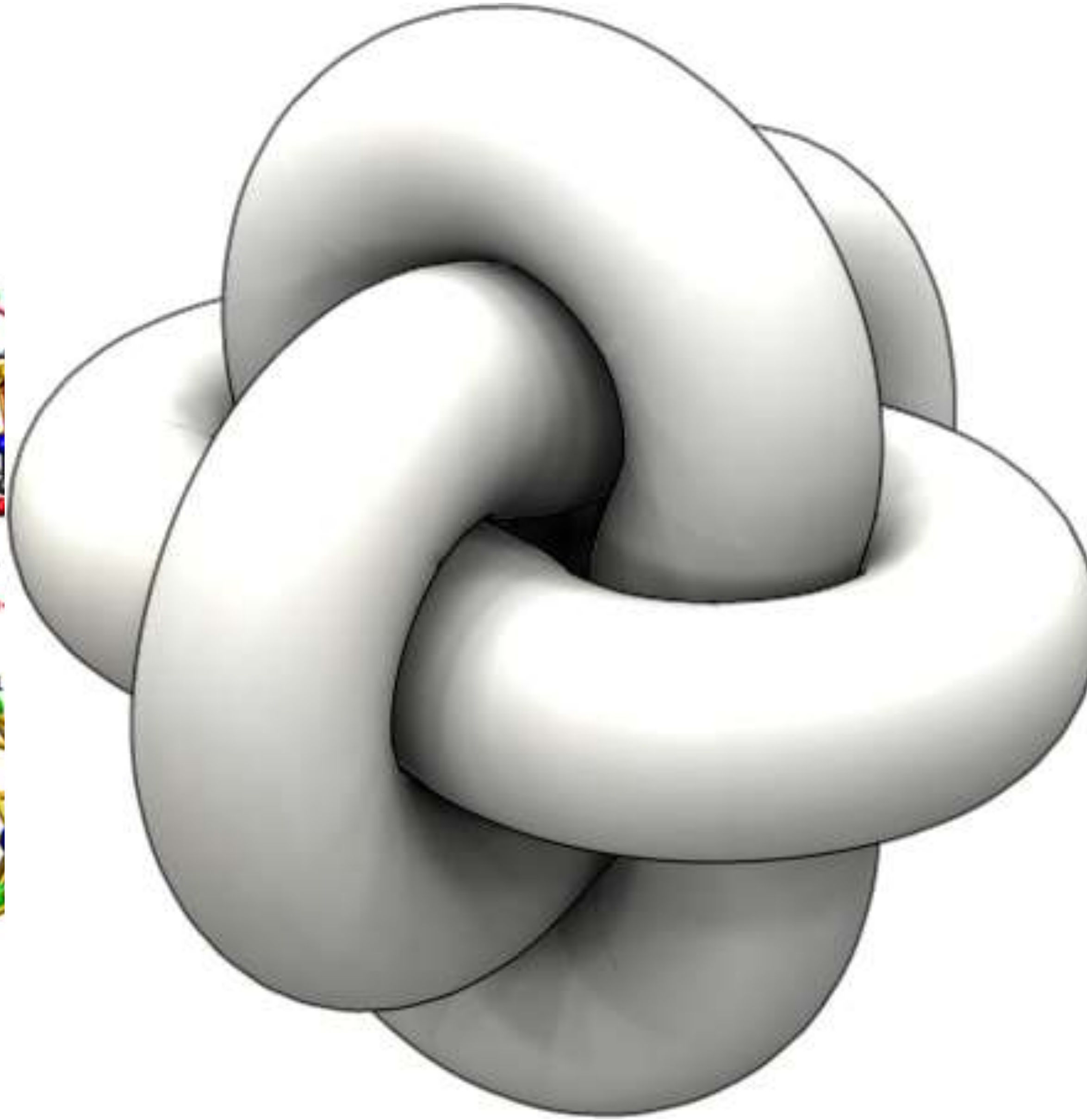
Nomenclature

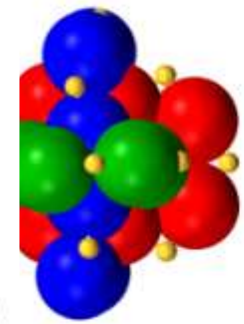
1) Edge projection

2) Face Projection









Gana Natarajan et. al. *JPC C* 2015

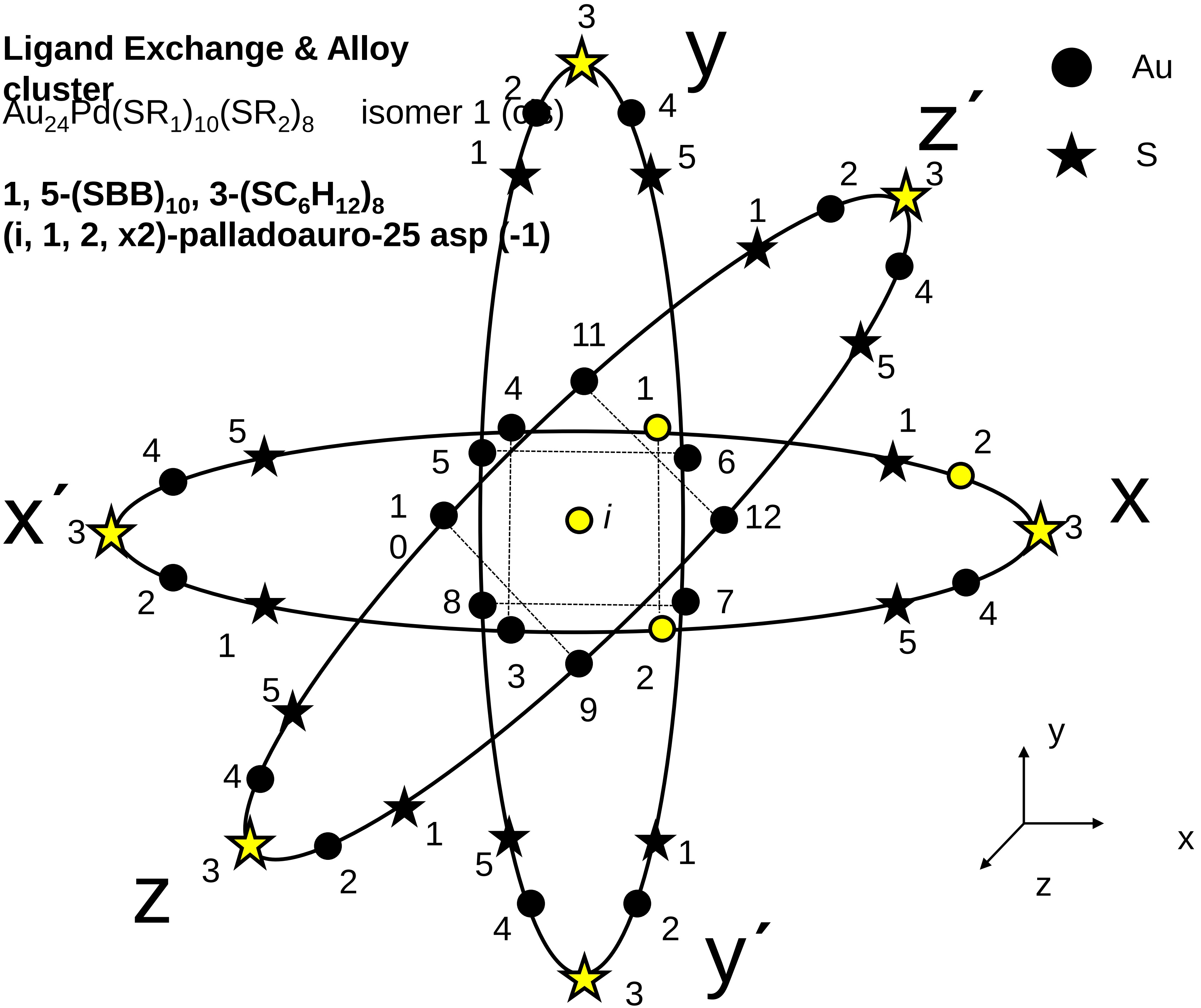
Aspicules

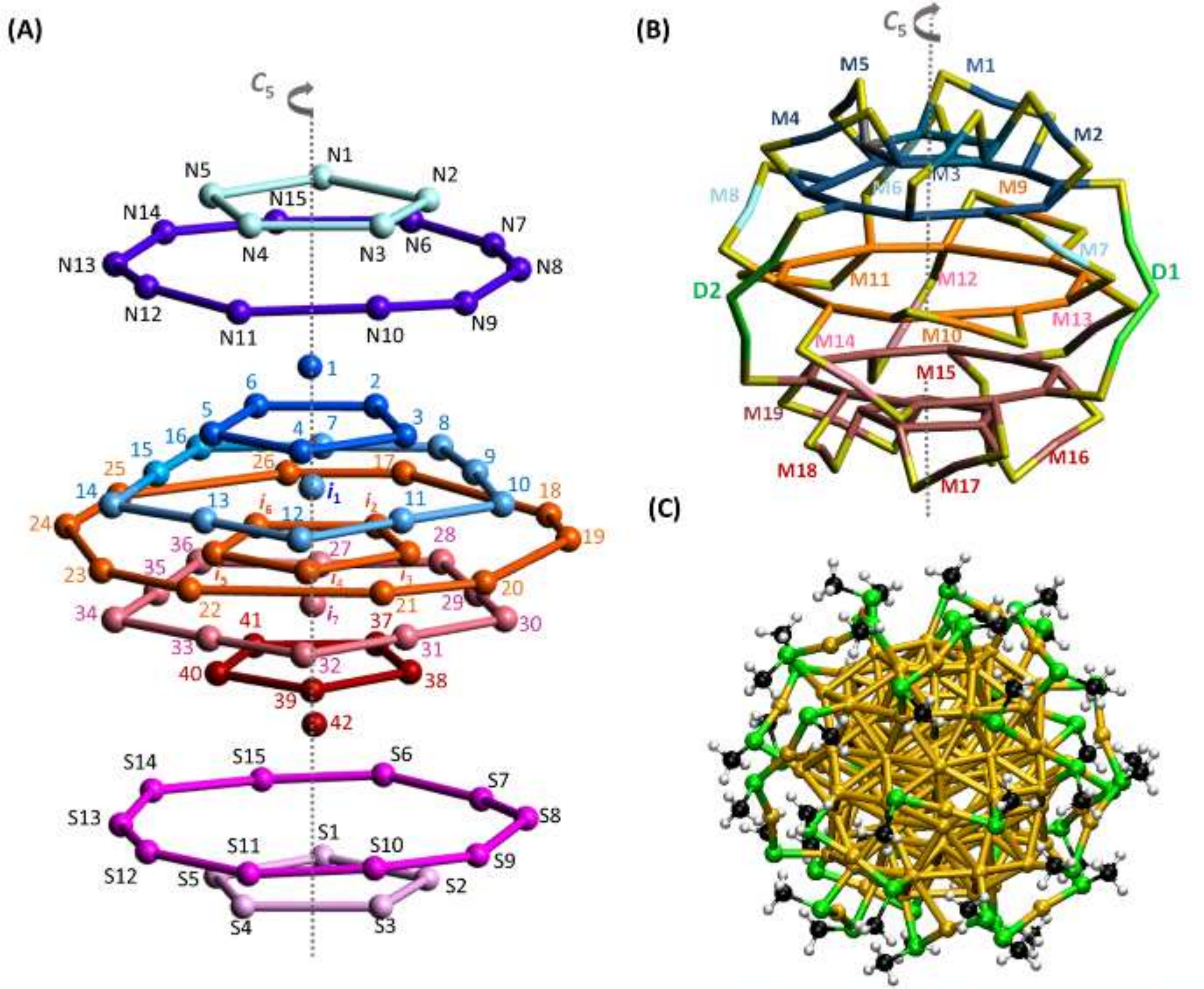
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule(1-)

Ligand Exchange & Alloy cluster

$Au_{24}Pd(SR_1)_{10}(SR_2)_8$ isomer 1 (cis)

1, 5-$(SBB)_{10}$, 3-$(SC_6H_{12})_8$
(i, 1, 2, x2)-palladoauro-25 asp (-1)





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

R-$(SMe)_{44}$-auro-102 aspicule**(**0**)** and L-$(SMe)_{44}$-auro-102 aspicule**(**0**)**

ACCOUNTS of chemical research

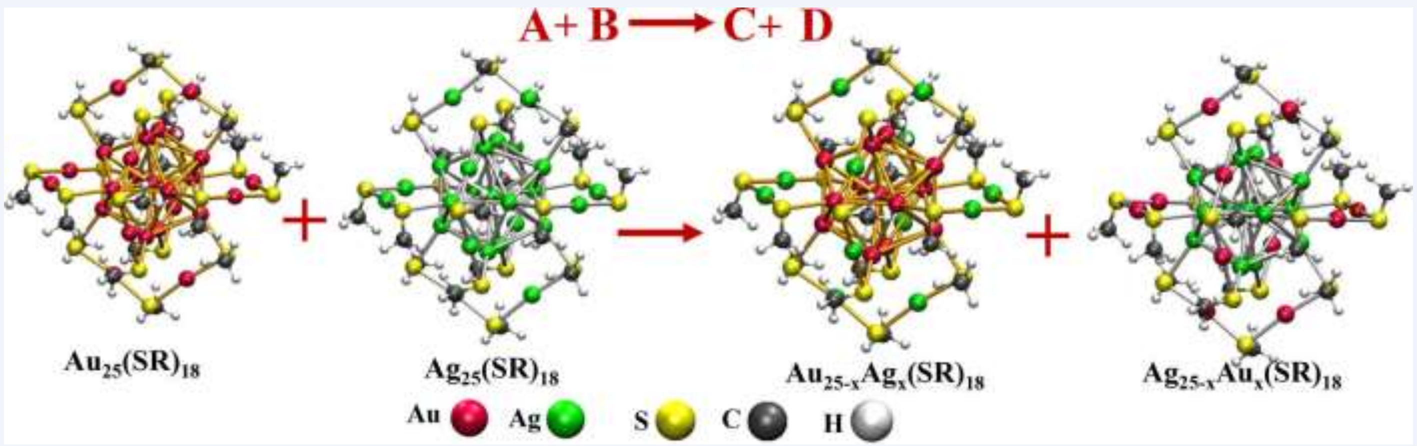
Article

pubs.acs.org/accounts

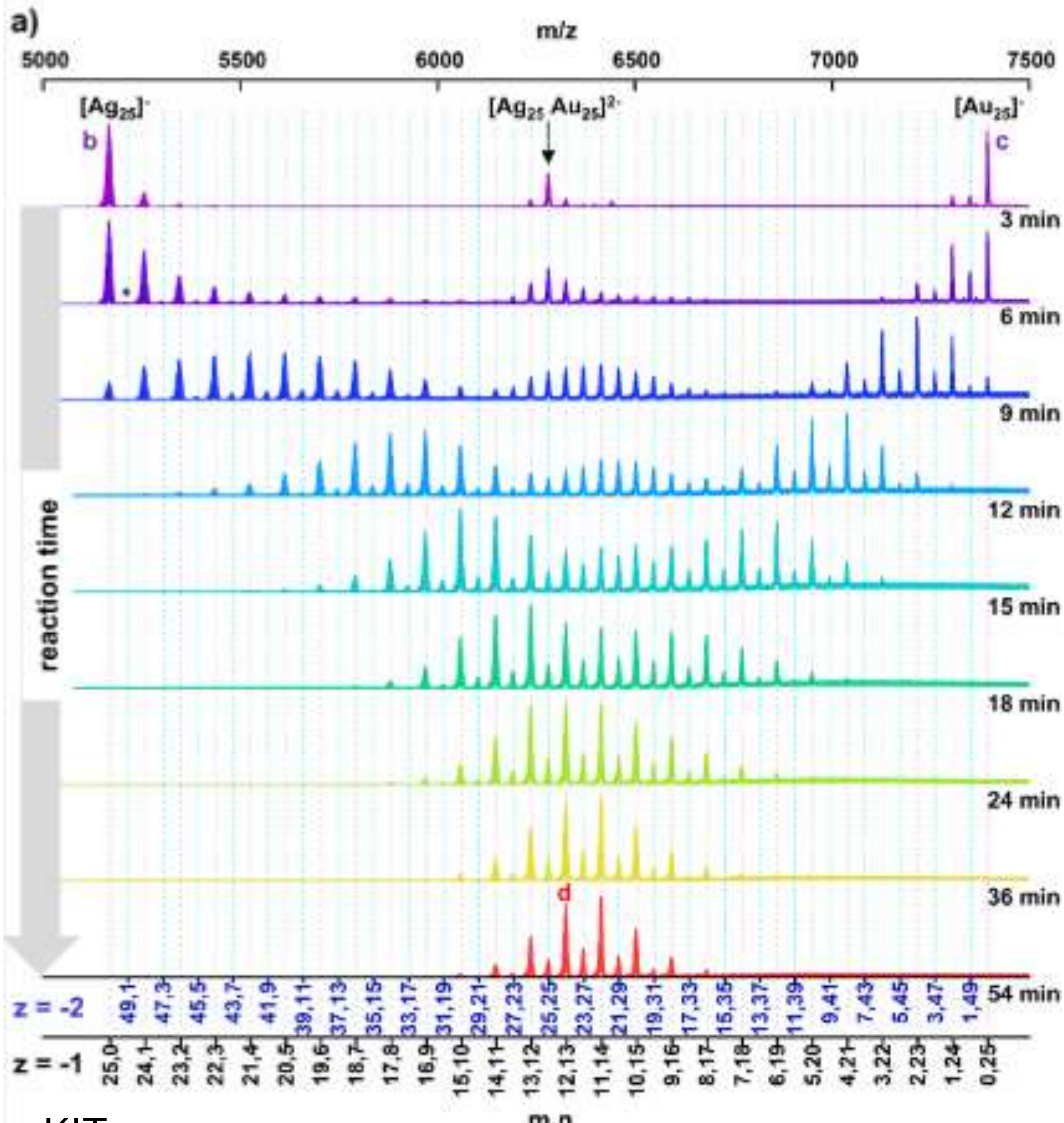
Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

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

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

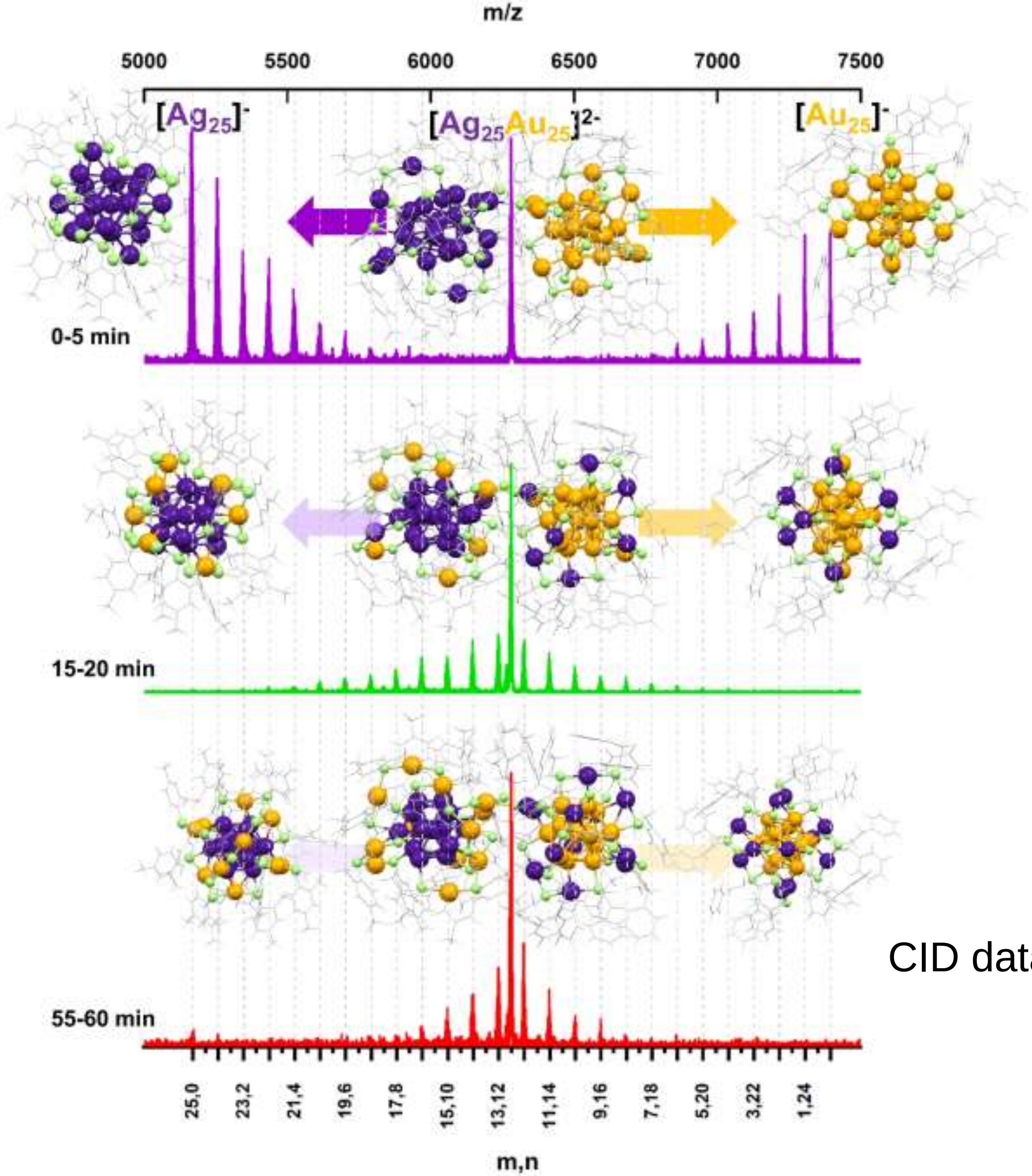


CONSPECTUS: Nanoparticles exhibit a rich variety in terms of structure, composition, and properties. However, reactions between them remain largely unexplored. In this *Account*, we discuss an emerging aspect of nanomaterials chemistry, namely, interparticle reactions in solution phase, similar to reactions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



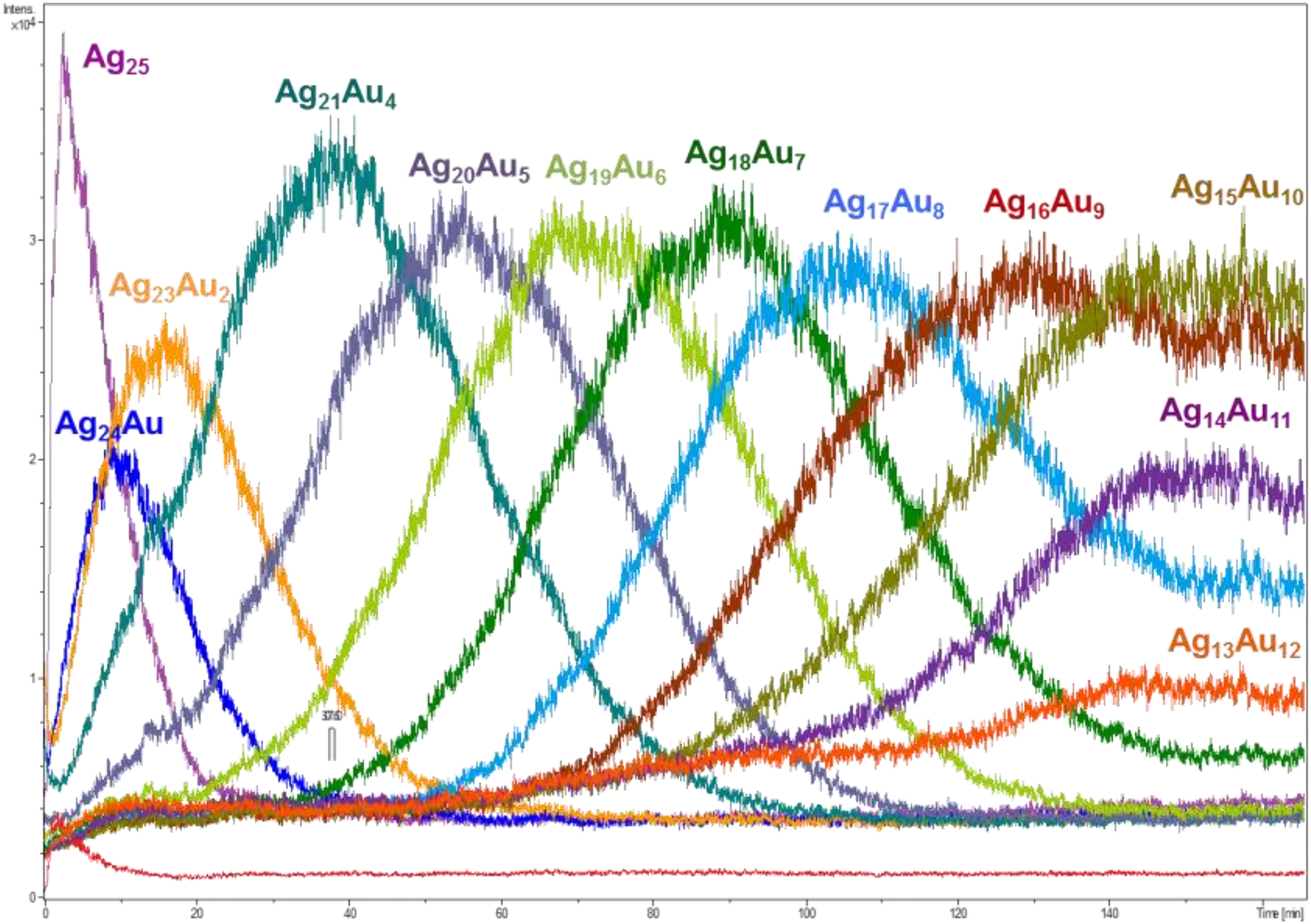
Manfred Kappes, KIT

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



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

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



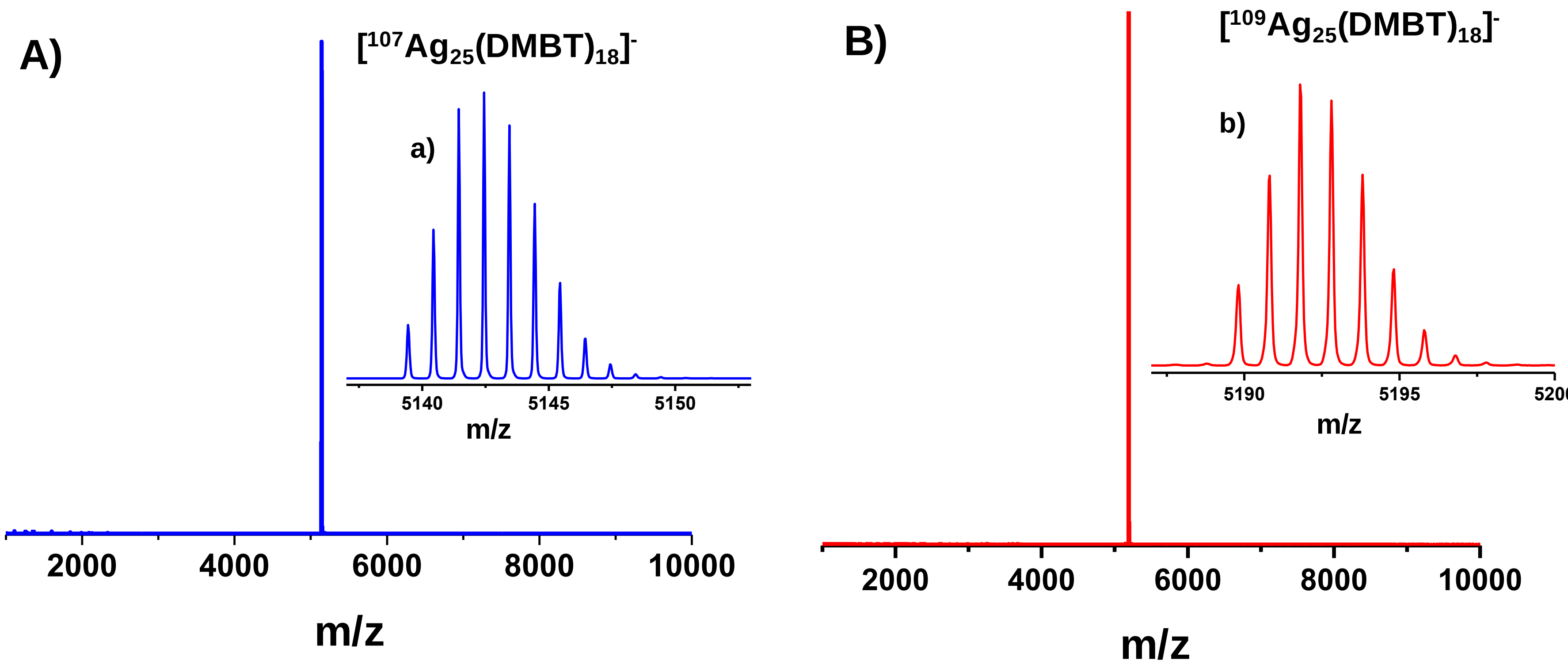
SCIENCE ADVANCES | RESEARCH ARTICLE

CONDENSED MATTER PHYSICS

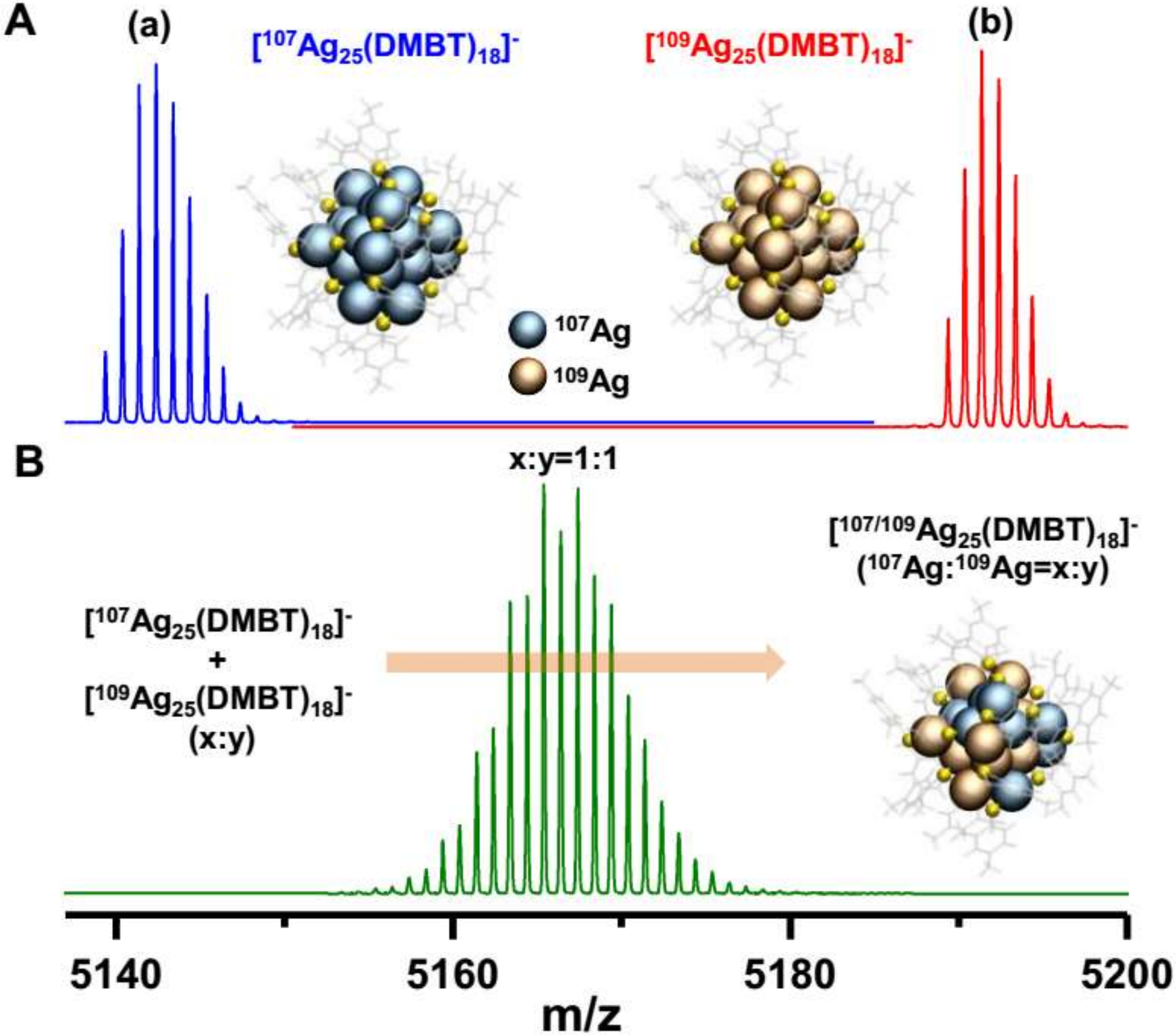
Rapid isotopic exchange in nanoparticles

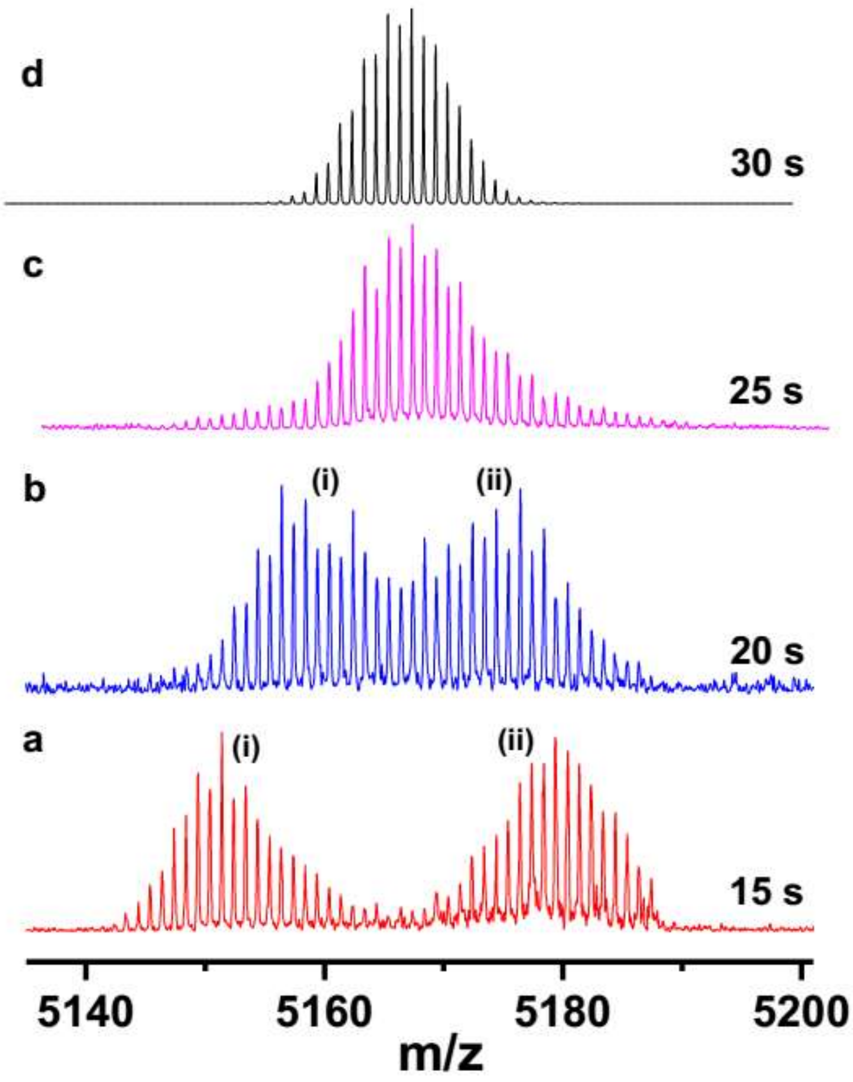
Papri Chakraborty[1], Abhijit Nag[1], Ganapati Natarajan[1], Nayanika Bandyopadhyay[1], Ganesan Paramasivam[1], Manoj Kumar Panwar[1], Jaydeb Chakrabarti[2], Thalappil Pradeep[1]*

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.

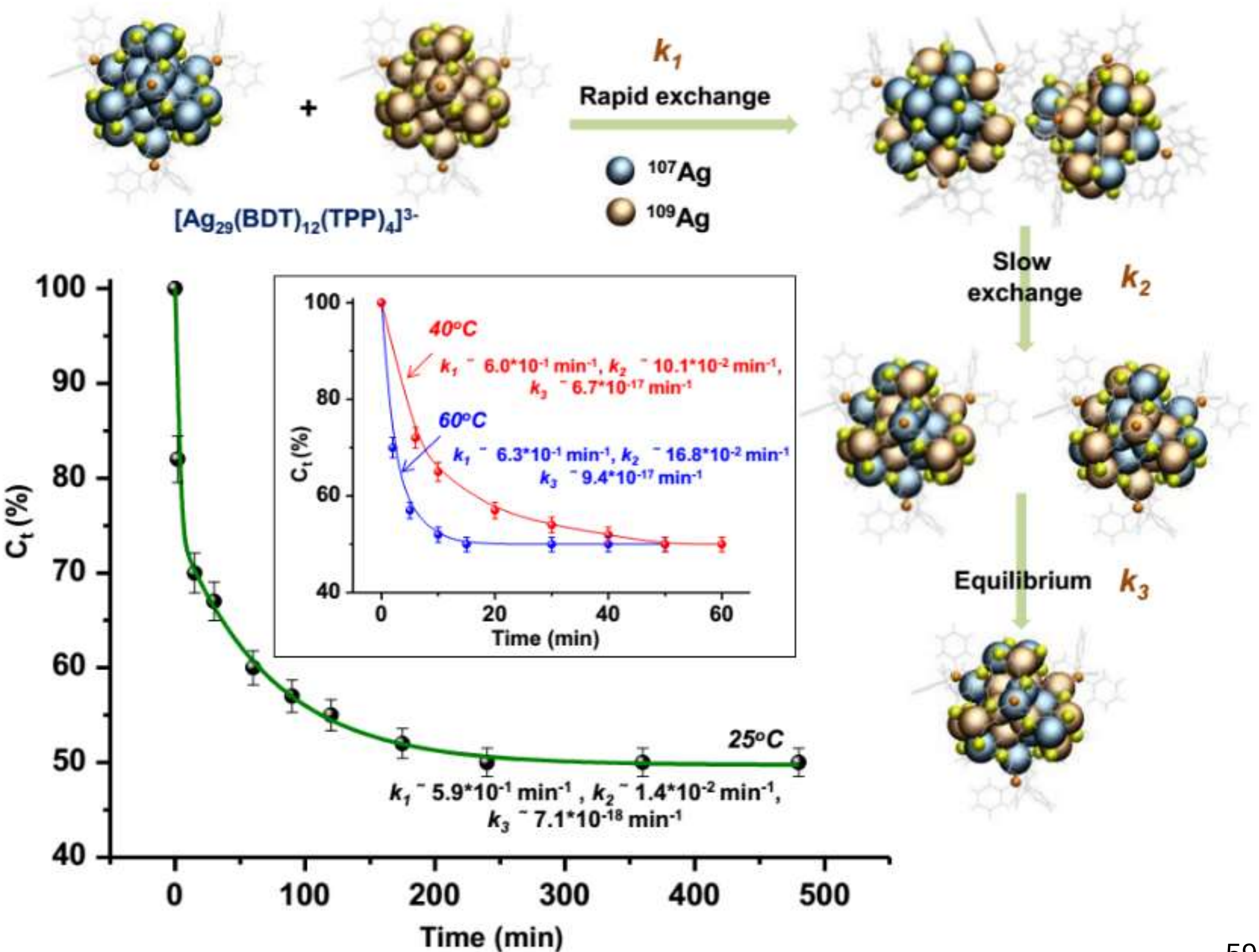


ESI MS of **A)** ^{107}Ag$_{25}$(DMBT)$_{18}$ and **B)**^{109}Ag$_{25}$(DMBT)$_{18}$. Insets shows the respective isotope patterns.


A
(a)
[$^{107}Ag_{25}(DMBT)_{18}]^-$
[$^{109}Ag_{25}(DMBT)_{18}]^-$
(b)
^{107}Ag
^{109}Ag
B
x:y=1:1
[$^{107/109}Ag_{25}(DMBT)_{18}]^-$
(^{107}Ag:^{109}Ag=x:y)
[$^{107}Ag_{25}(DMBT)_{18}]^-$
+
[$^{109}Ag_{25}(DMBT)_{18}]^-$
(x:y)
5140
5160
5180
5200
m/z



Papri Chakraborty, et. al. *Science Advances* 2019

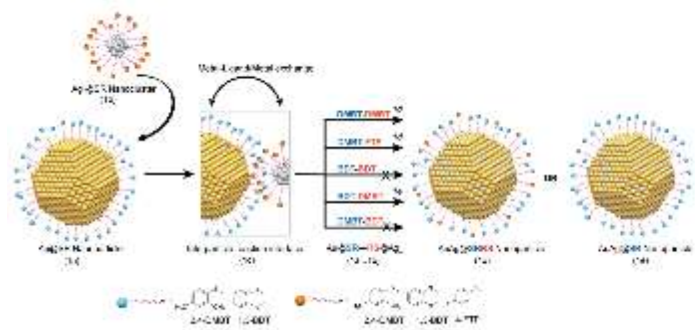


$[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$
k_1
Rapid exchange
^{107}Ag
^{109}Ag
Slow exchange
k_2
Equilibrium
k_3
C_t (%)
Time (min)
25°C
k_1 ~ 5.9*10^{-1} min^{-1} , k_2 ~ 1.4*10^{-2} min^{-1},
k_3 ~ 7.1*10^{-18} min^{-1}
40°C
k_1 ~ 6.0*10^{-1} min^{-1}, k_2 ~ 10.1*10^{-2} min^{-1},
k_3 ~ 6.7*10^{-17} min^{-1}
60°C
k_1 ~ 6.3*10^{-1} min^{-1}, k_2 ~ 16.8*10^{-2} min^{-1}
k_3 ~ 9.4*10^{-17} min^{-1}

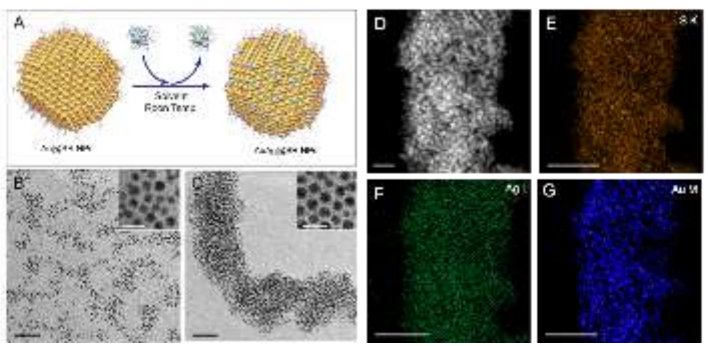
Can clusters react with nanoparticles?

Ag_{25} with Au nanoparticles

1

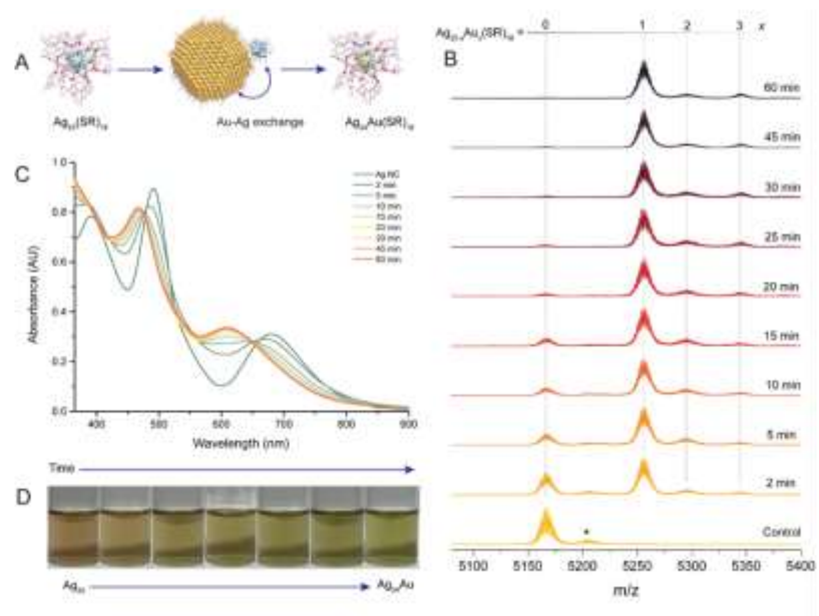


2



Scale bars: 50 nm (B-G) and 10 nm (insets of B and C).

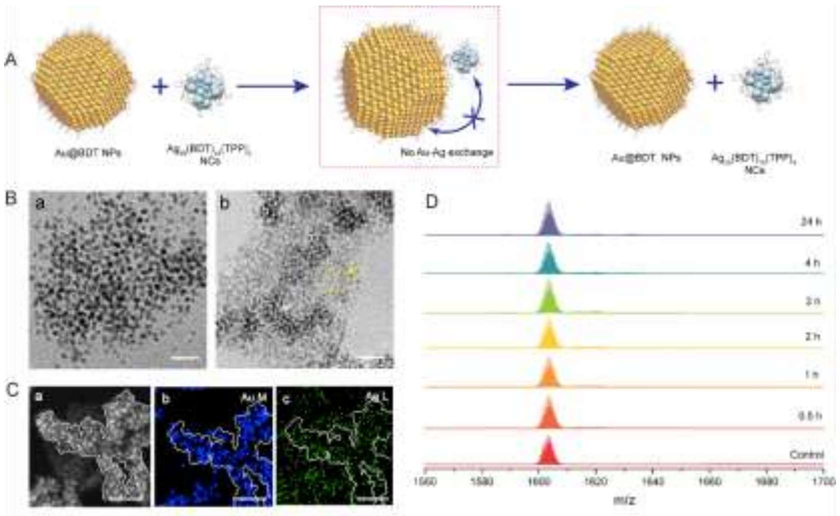
3



Paulami Bose, et al. *Chem. Mat.* 2024

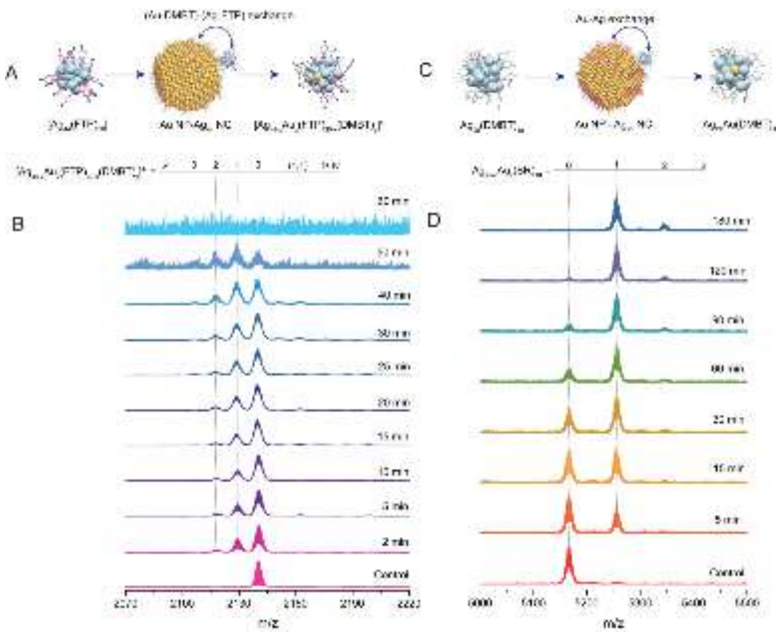
Interface controls the reaction

4

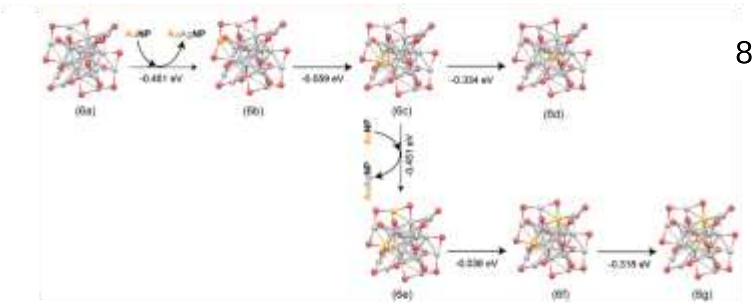


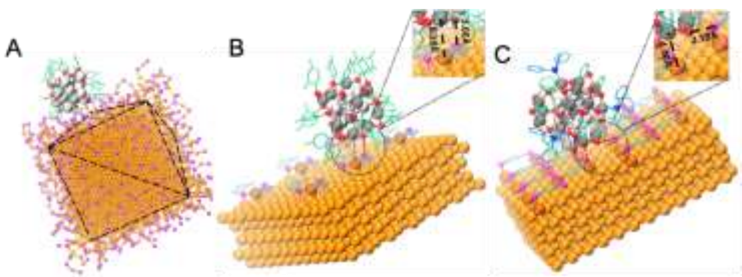
Scale bars: 20 nm

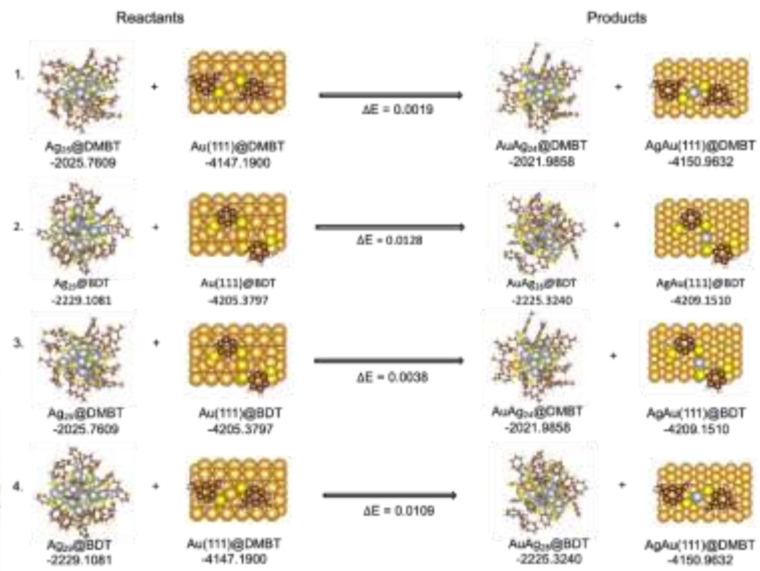
5



Computational insights

6


7


8


Reactions and new materials

CHEMISTRY OF MATERIALS

Article

Cite This: *Chem. Mater.* 2020, 32, 611−619

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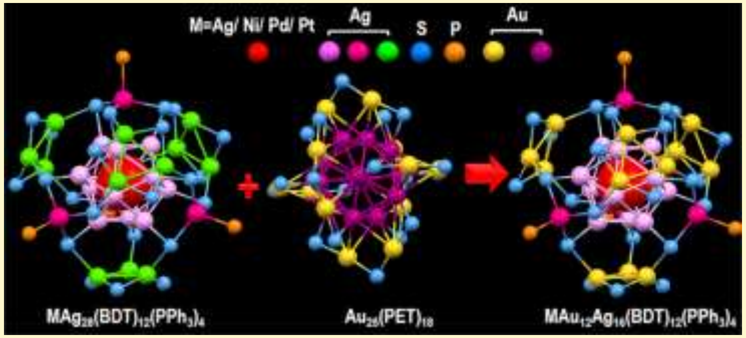
Intercluster Reactions Resulting in Silver-Rich Trimetallic Nanoclusters

Esma Khatun, Papri Chakraborty, Betsy Rachel Jacob, Ganesan Paramasivam, Mohammad Bodiuzzaman, Wakeel Ahmed Dar, and Thalappil Pradeep*

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

Supporting Information

ABSTRACT: Herein, we present an intercluster reaction leading to new trimetallic nanoclusters (NCs) using bimetallic and monometallic NCs as reactants. Dithiol protected bimetallic $MAg_{28}(BDT)_{12}(PPh_3)_4$ (BDT = 1,3-benzenedithiol and M = Ni, Pd, or Pt) and monothiol protected $Au_{25}(PET)_{18}$ (PET = 2-phenylethanethiol) were used as model NCs. A mixture of trimetallic $MAu_xAg_{28-x}(BDT)_{12}(PPh_3)_4$ (x = 1−12) and bimetallic $Ag_xAu_{25-x}(PET)_{18}$ (x = 1−7) NCs were formed during the reaction as understood from time-dependent electrospray ionization mass spectrometry (ESI MS). Detailed studies of intercluster reaction between $Ag_{29}(BDT)_{12}(PPh_3)_4$ and $Au_{25}(PET)_{18}$ were also performed. Although both $MAg_{28}(BDT)_{12}(PPh_3)_4$ (M = Ag, Ni, Pd, or Pt) and $Au_{25}(PET)_{18}$ contain 13 atoms icosahedral core, only a maximum of 12 Au doped NCs were formed for the former as a



Reactions leading to co-crystals

ACS NANO
Cite This: *ACS Nano* 2019, 13, 13365–13373
www.acsnano.org
ARTICLE

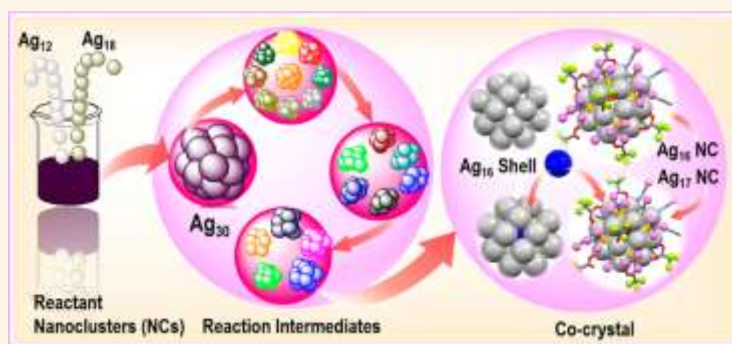
Interparticle Reactions between Silver Nanoclusters Leading to Product Cocrystals by Selective Cocrystallization

Wakeel Ahmed Dar,[†] Mohammad Bodiuzzaman,[†] Debasmita Ghosh, Ganesan Paramasivam, Esma Khatun, Korath Shivan Sugi, and Thalappil Pradeep*

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

Supporting Information

ABSTRACT: We present an example of an interparticle reaction between atomically precise nanoclusters (NCs) of the *same* metal, resulting in entirely different clusters. In detail, the clusters $[Ag_{12}(TBT)_8(TFA)_5(CH_3CN)]^+$ (TBT = *tert*-butylthiolate, TFA = trifluoroacetate, CH_3CN = acetonitrile) and $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ (TPP = triphenylphosphine) abbreviated as Ag_{12} and Ag_{18}, respectively, react leading to $[Ag_{16}(TBT)_8(TFA)_7(CH_3CN)_3Cl]^+$ and $[Ag_{17}(TBT)_8(TFA)_7(CH_3CN)_3Cl]^+$, abbreviated as Ag_{16} and Ag_{17}, respectively. The two product NCs crystallize together as both possess the same metal chalcogenolate



Supramolecular chemistry

Papri Chakraborty, et,. al. *ACS Nano* 2018

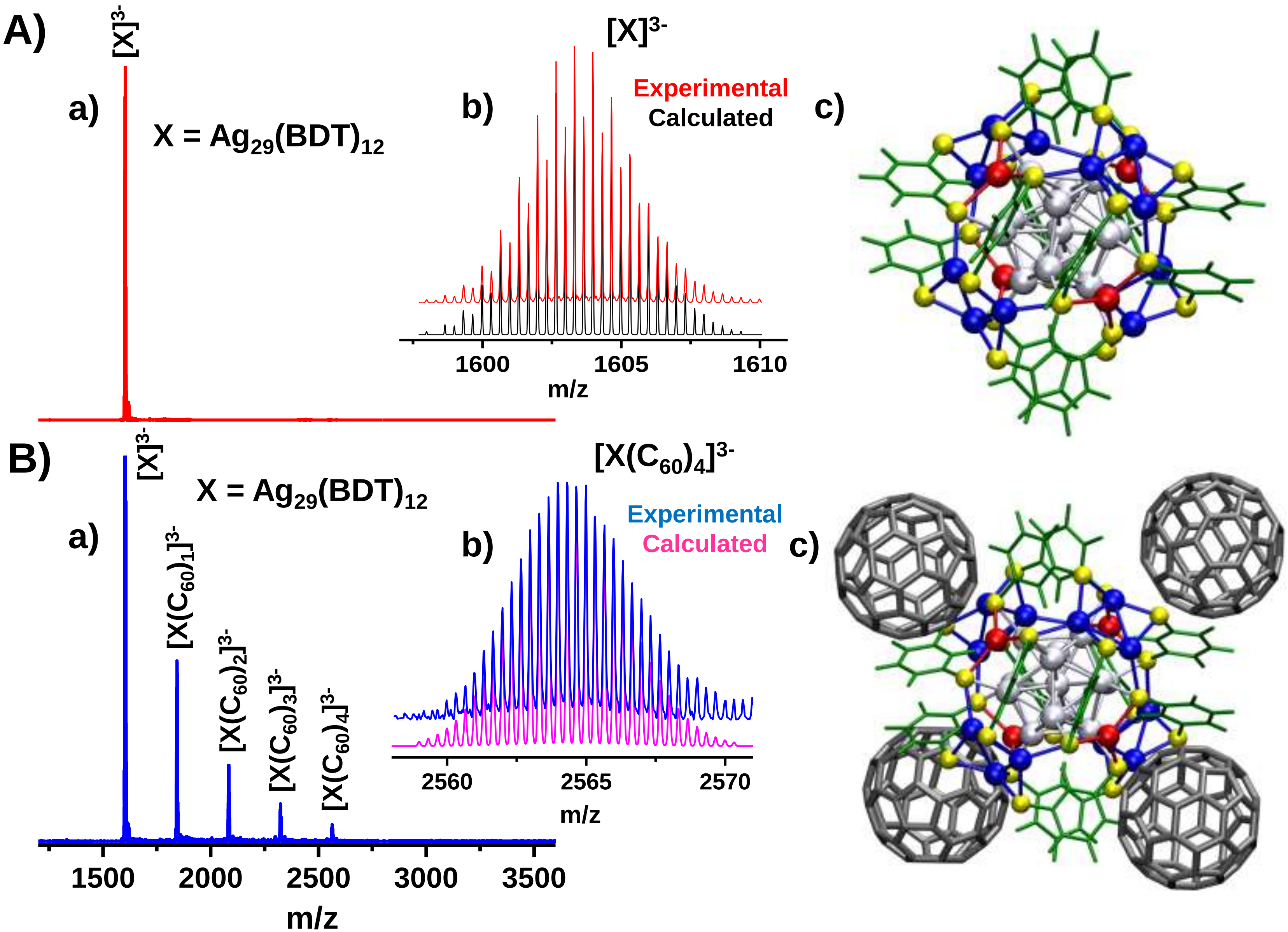
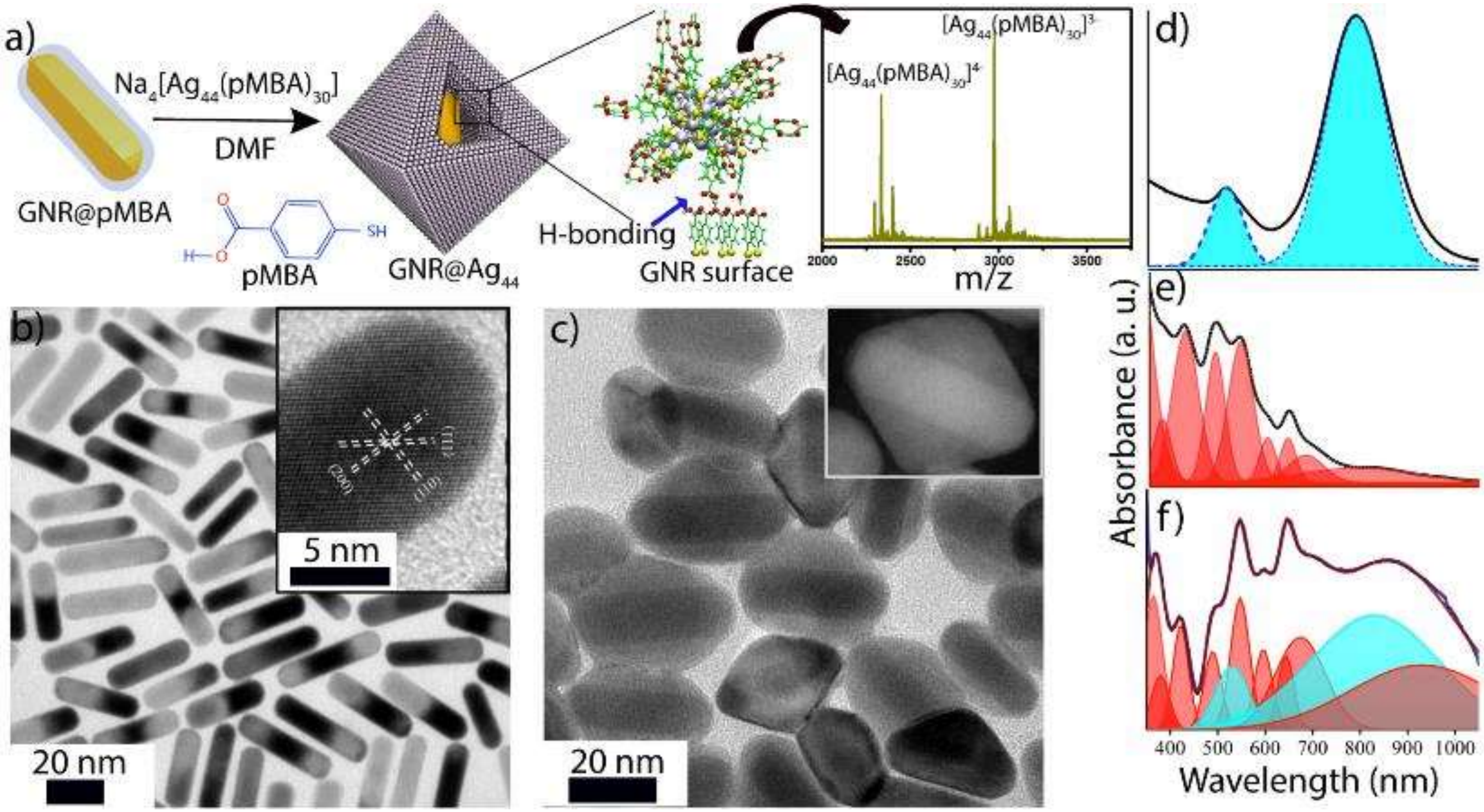


Figure 1. A) (a) Full range ESI MS, **(b)** experimental and calculated isotope patterns and **(c)** DFT optimized structure of $[Ag_{29}(BDT)_{12}]^{3-}$ cluster. **B) (a)** ESI MS of $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (n=1-4) complexes, **(b)** experimental and calculated isotope patterns of $[Ag_{29}(BDT)_{12}(C_{60})_4]^{3-}$ and **(c)** schematic of the possible structure of $[Ag_{29}(BDT)_{12}(C_{60})_4]^{3-}$.

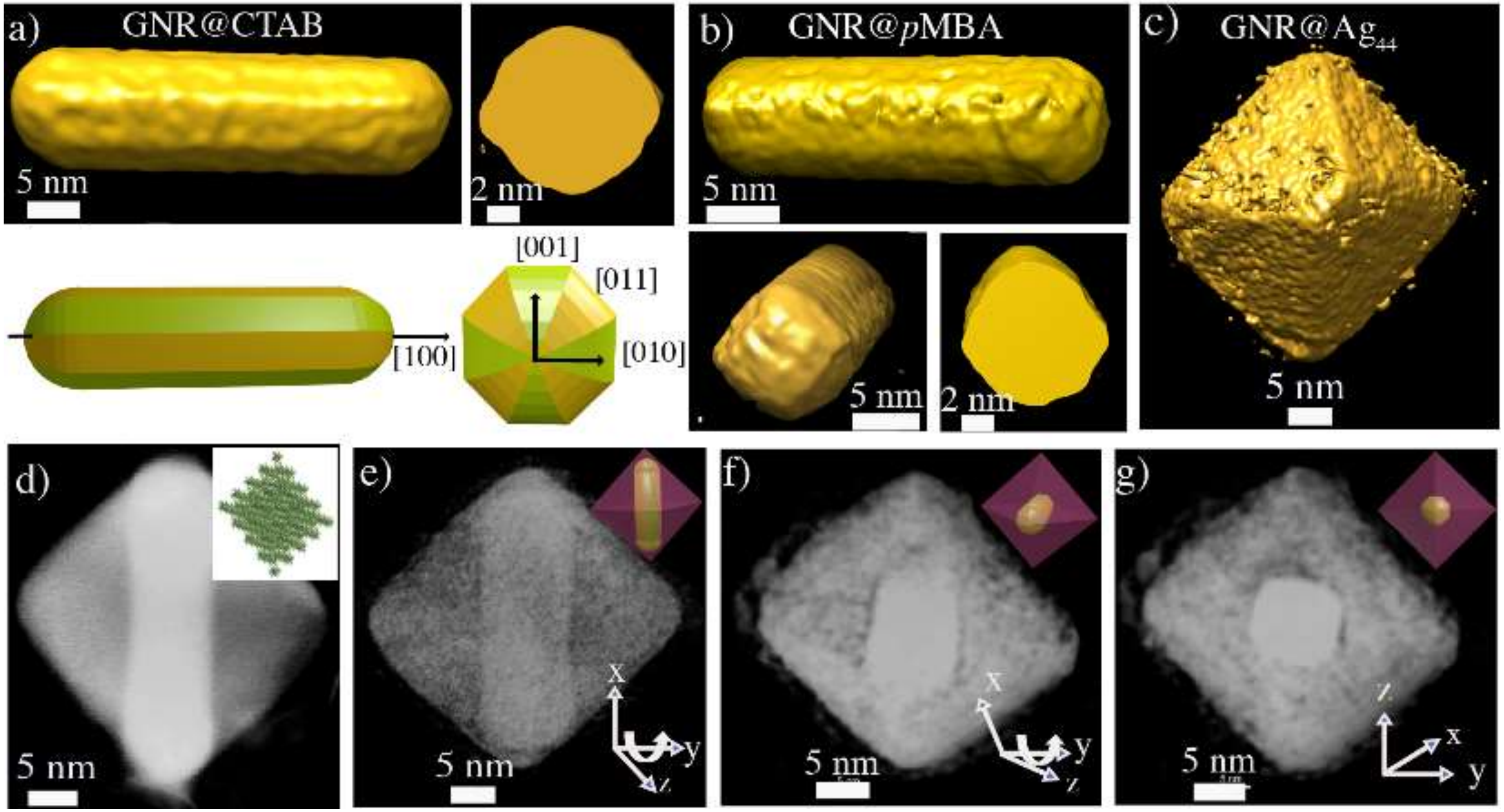
Assemblies and superstructures

Atomically precise nanocluster assemblies encapsulating plasmonic gold nanorods

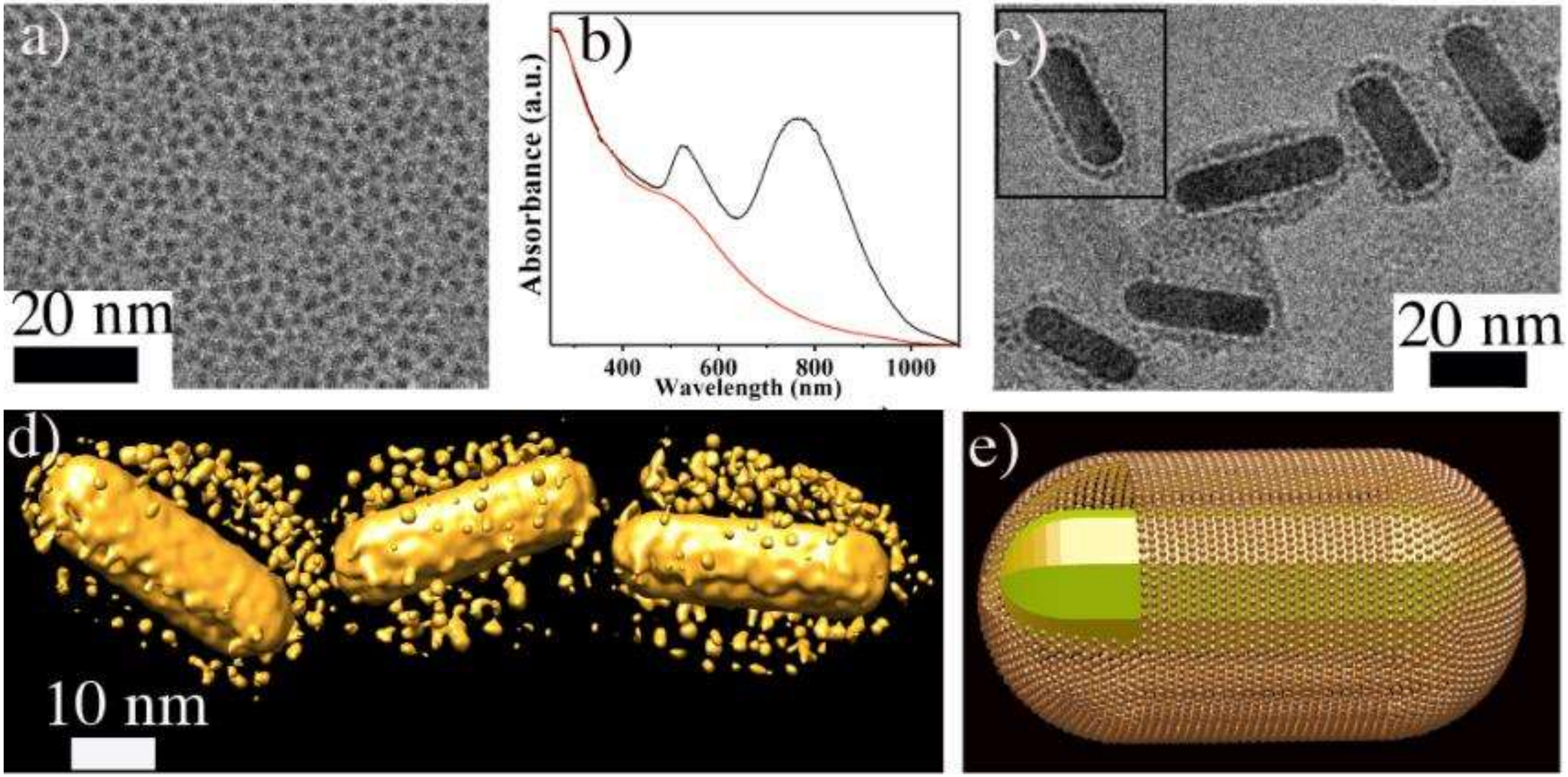


Chakraborty, A. et al., *Angew. Chem. Int. Ed.* **2018,** *57*, 6522–6526.

3D morphological analysis

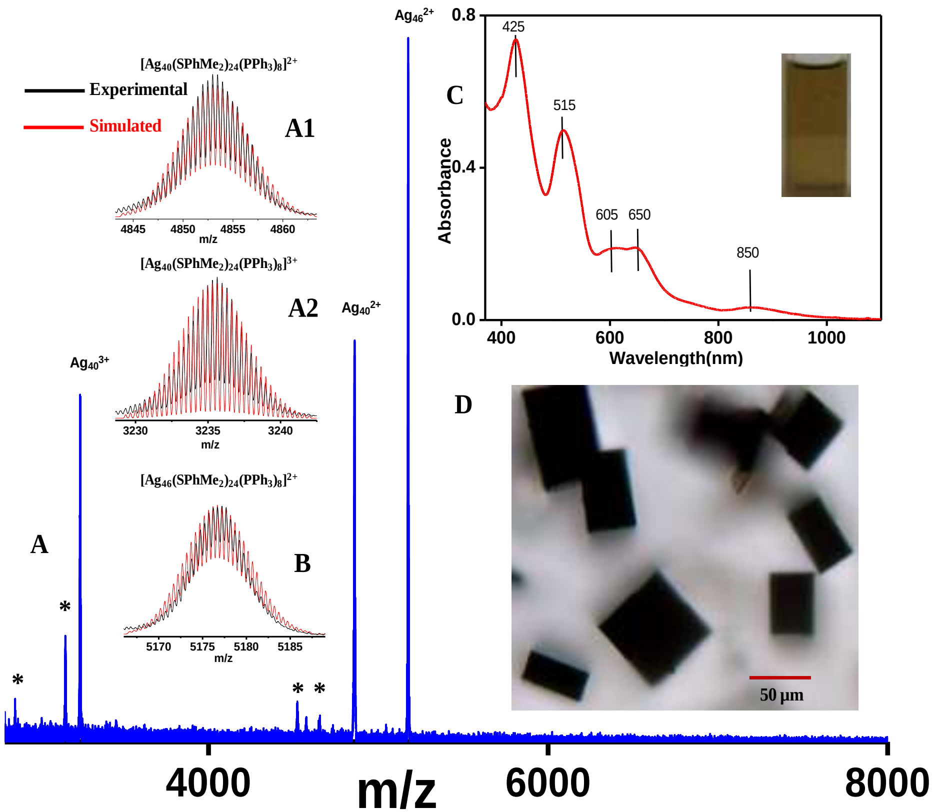


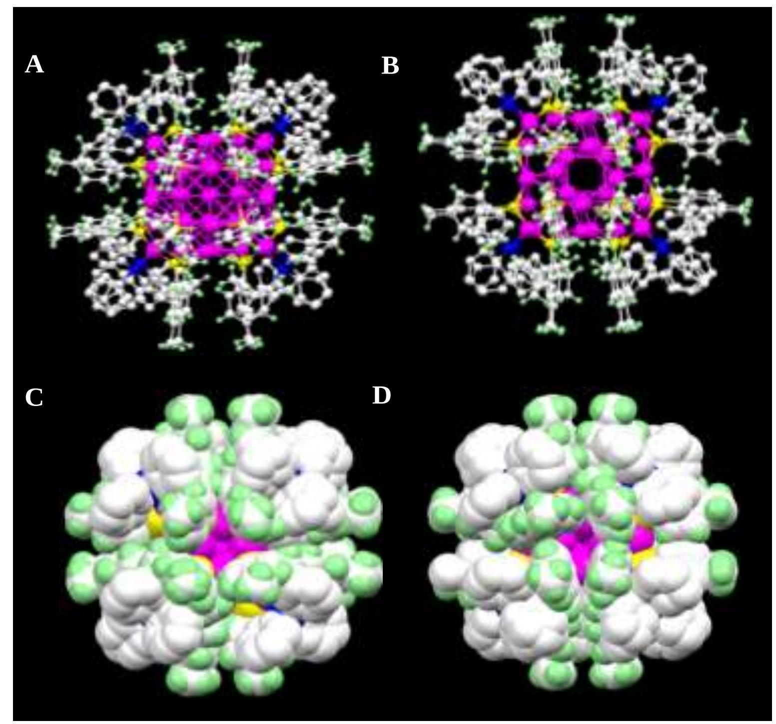
Works for Au_{250}(*p*MBA)$_n$ and aqueous solvent



Co-crystals

Ag_{40} and Ag_{46} with the same shell

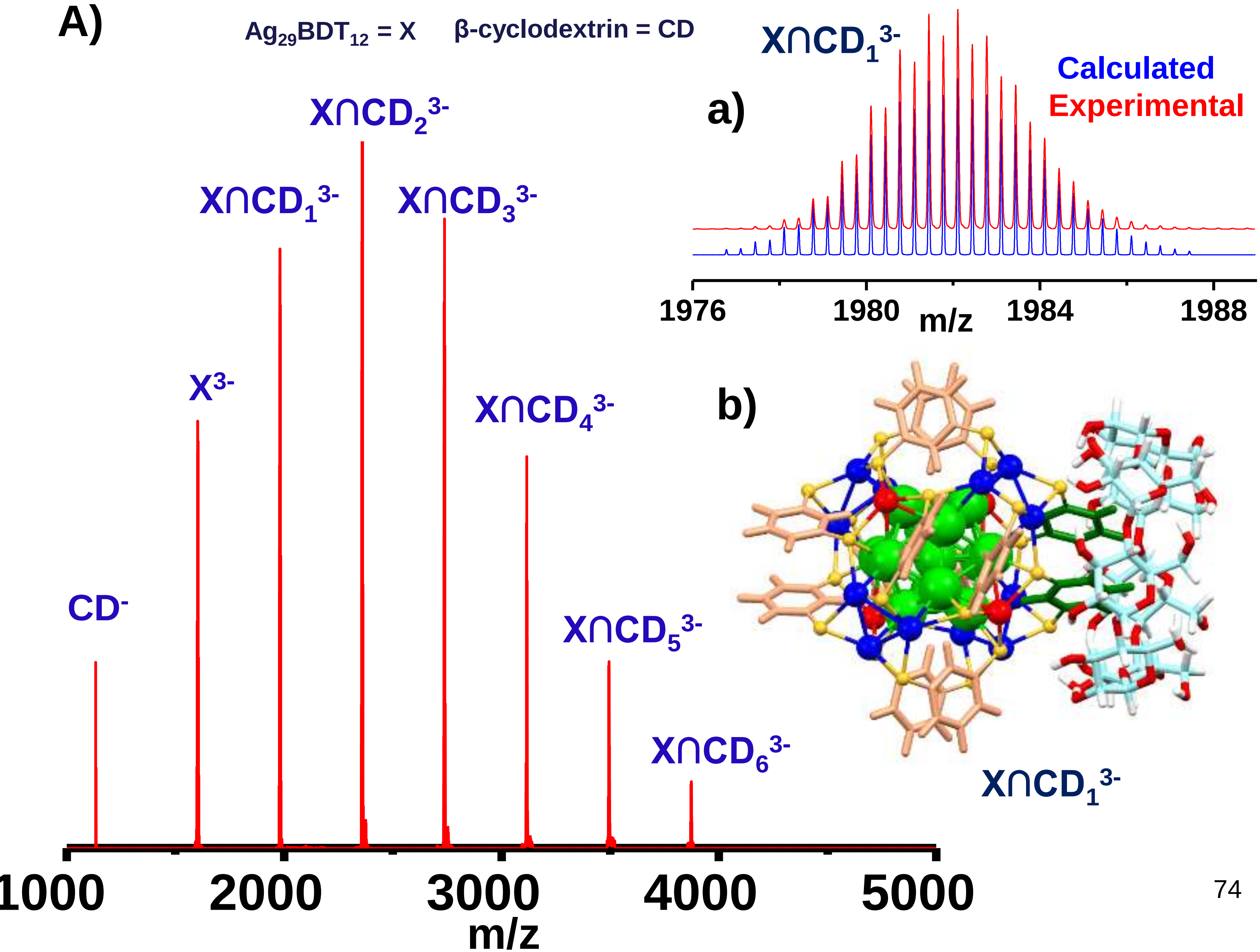




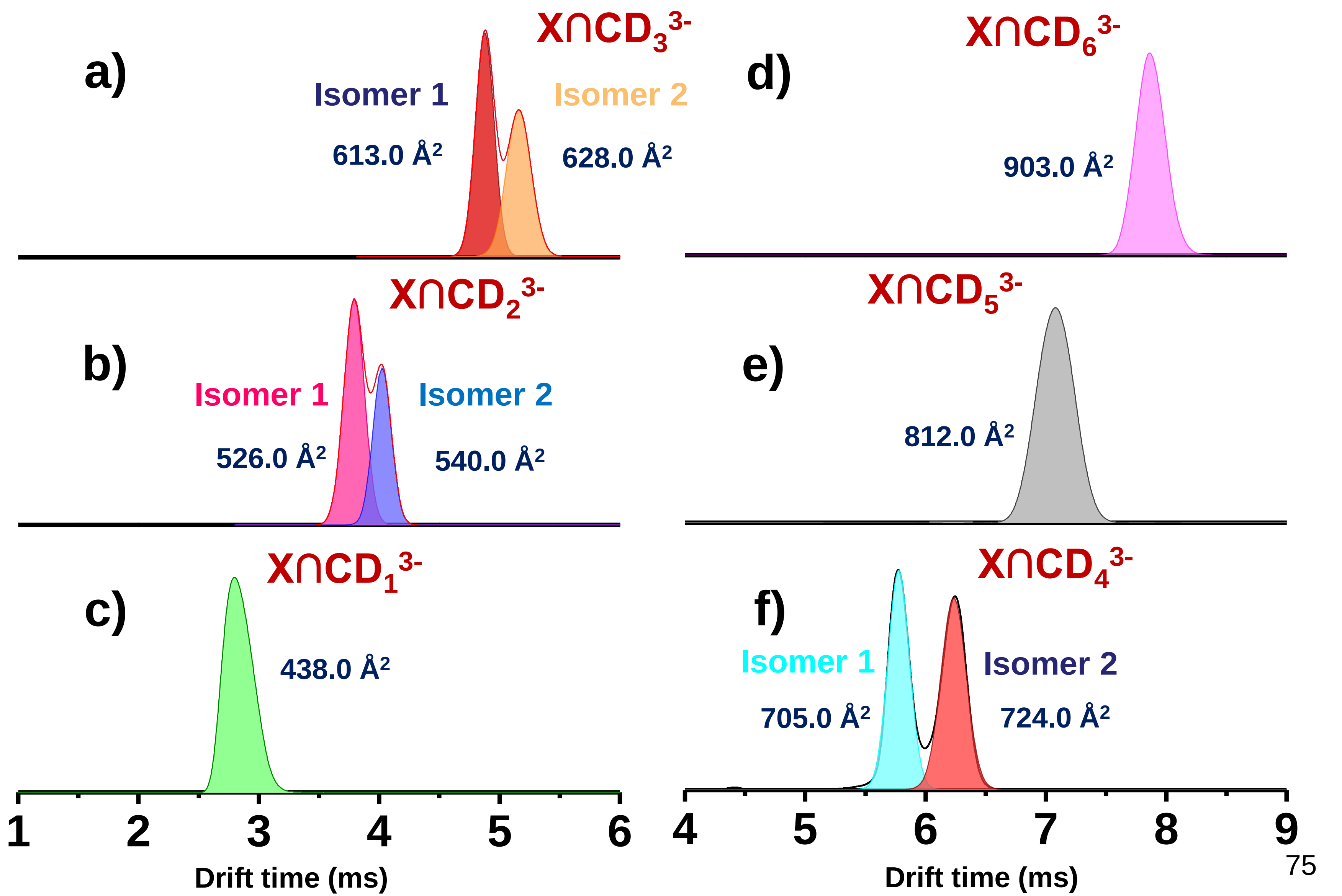
M. Bodiuzzaman, et. al. *Angew. Chem. Int. Ed.* **2018**

Isomerism in supramolecular adducts

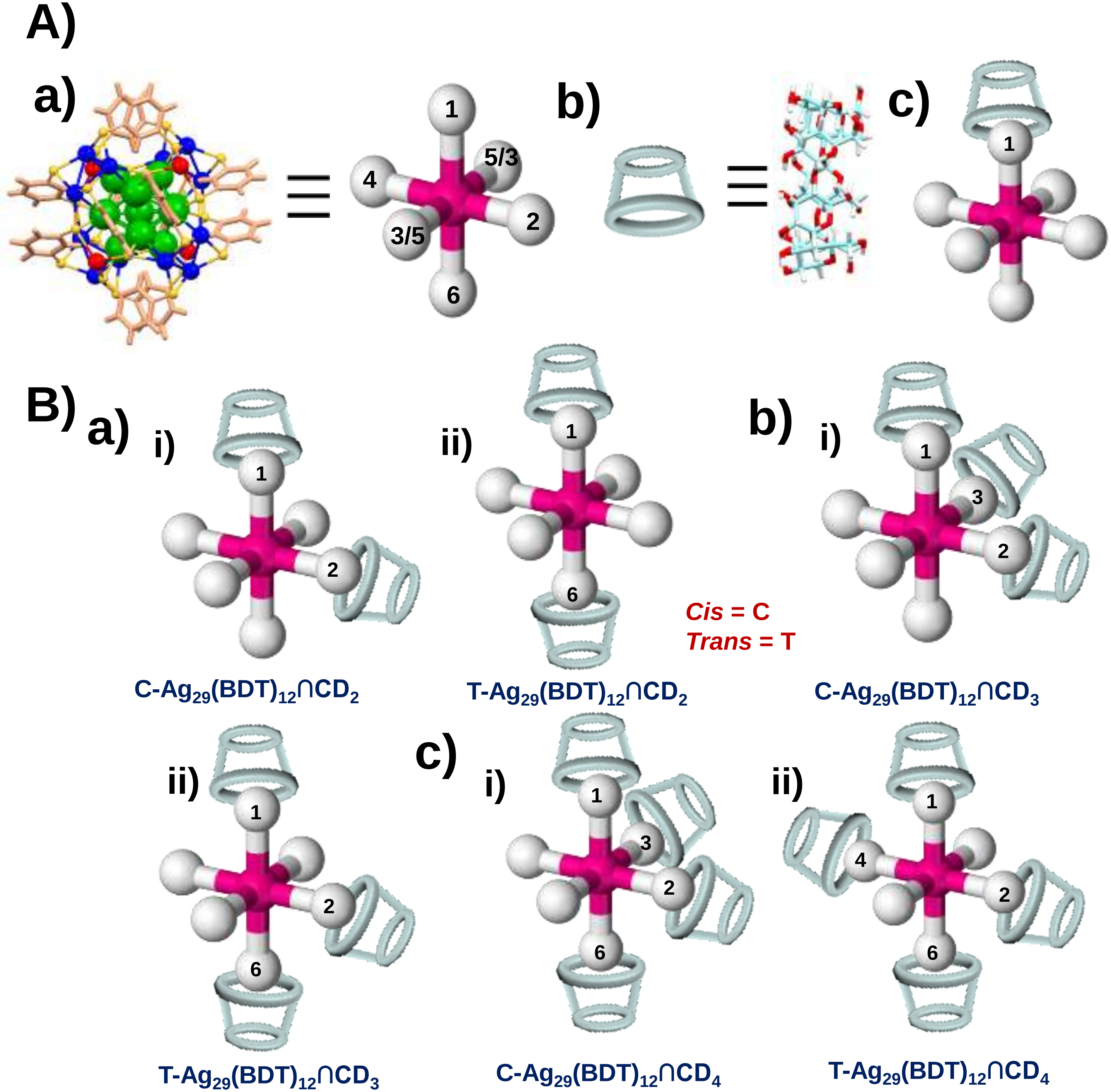
Abhijit Nag, et al. *JACS* 2018



A)
$Ag_{29}BDT_{12}$ = X β-cyclodextrin = CD
$X\cap CD_2^{3-}$
$X\cap CD_1^{3-}$
$X\cap CD_3^{3-}$
X^{3-}
$X\cap CD_4^{3-}$
CD^{-}
$X\cap CD_5^{3-}$
$X\cap CD_6^{3-}$
1000
2000
3000
4000
5000
m/z
$X\cap CD_1^{3-}$
a)
Calculated
Experimental
1976
1980
m/z
1984
1988
b)
$X\cap CD_1^{3-}$



a)
X∩CD3 3-
Isomer 1
613.0 Å2
Isomer 2
628.0 Å2
b)
X∩CD2 3-
Isomer 1
526.0 Å2
Isomer 2
540.0 Å2
c)
X∩CD1 3-
438.0 Å2
1
2
3
4
5
6
Drift time (ms)
d)
X∩CD6 3-
903.0 Å2
e)
X∩CD5 3-
812.0 Å2
f)
X∩CD4 3-
Isomer 1
705.0 Å2
Isomer 2
724.0 Å2
4
5
6
7
8
9
Drift time (ms)


A)
a)
1
5/3
4
2
3/5
6
b)
c)
1
B)
a)
i)
1
2
ii)
1
6
b)
i)
1
3
2
Cis = C
Trans = T
C-$Ag_{29}(BDT)_{12}∩CD_2$
T-$Ag_{29}(BDT)_{12}∩CD_2$
C-$Ag_{29}(BDT)_{12}∩CD_3$
ii)
1
2
6
c)
i)
1
3
2
6
ii)
1
4
2
6
T-$Ag_{29}(BDT)_{12}∩CD_3$
C-$Ag_{29}(BDT)_{12}∩CD_4$
T-$Ag_{29}(BDT)_{12}∩CD_4$

Where are they taking us to?

PNAS PNAS PNAS PNAS

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

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.

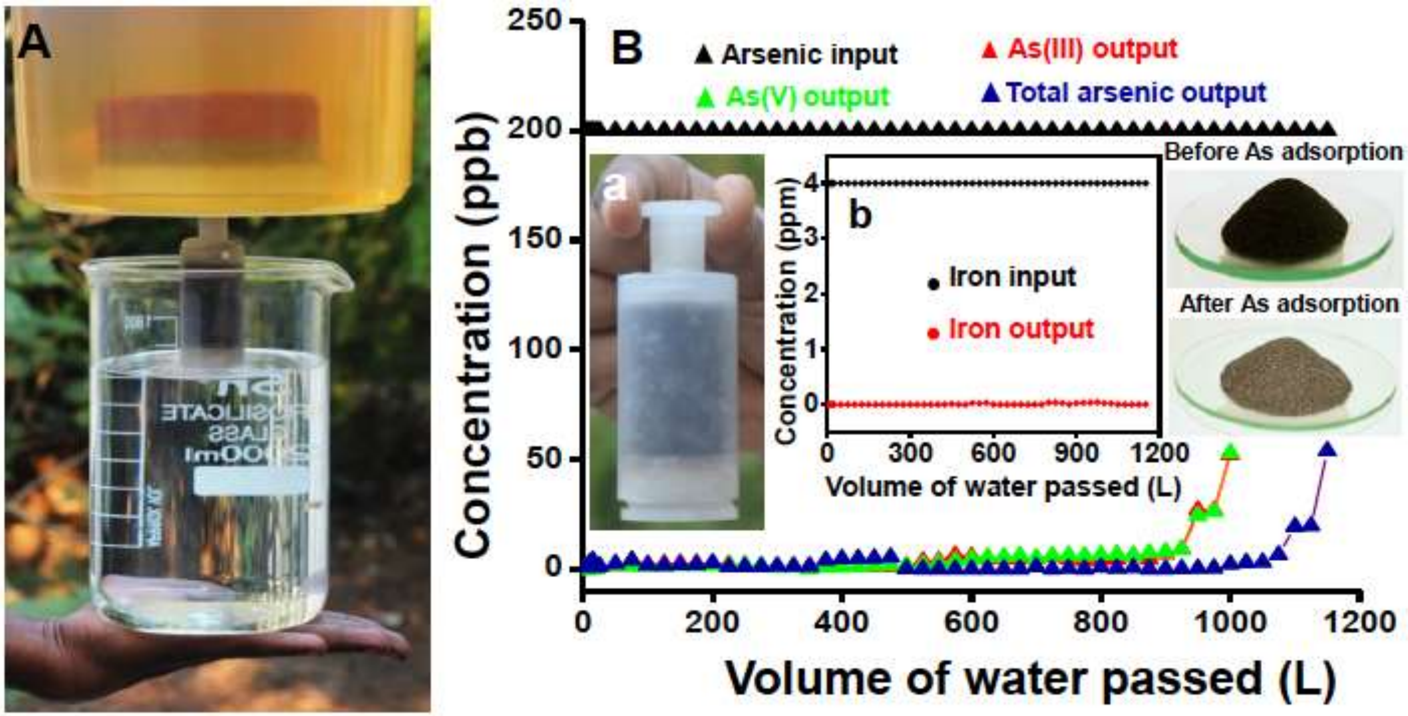
vailable; and (*c*) continued retention
matrix is difficult.
ate a unique family of nanocrystalline
n granular composite materials pre-
ature through an aqueous route. The
mposition is attributed to abundant -O-
on chitosan, which help in the crys-
oxide and also ensure strong covalent
surface to the 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
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
disease burden.

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

Results and Discussion

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

Range of materials, their affordability and safety



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

Safety of spent media, TCLP

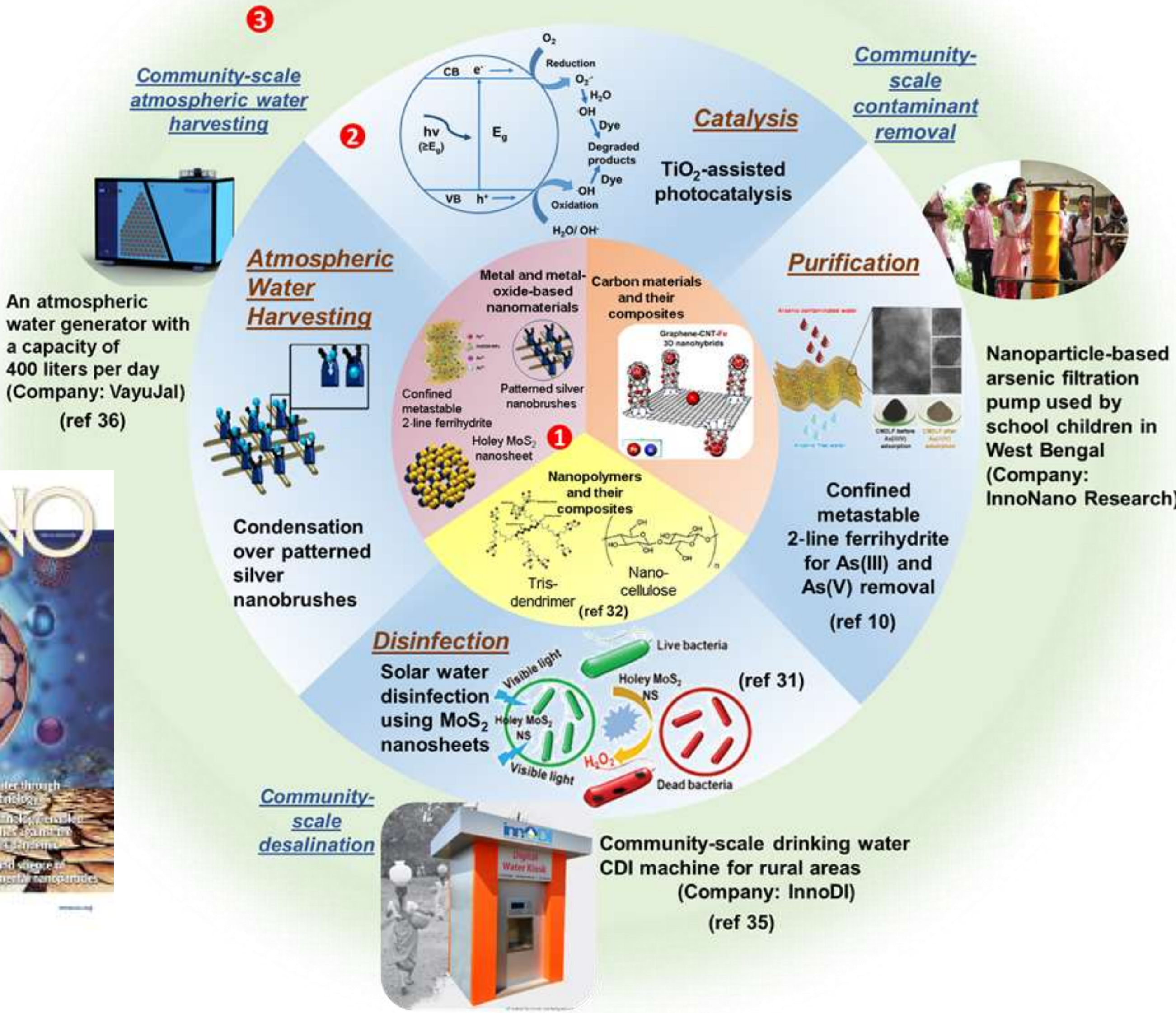
Clean water for everyone

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.

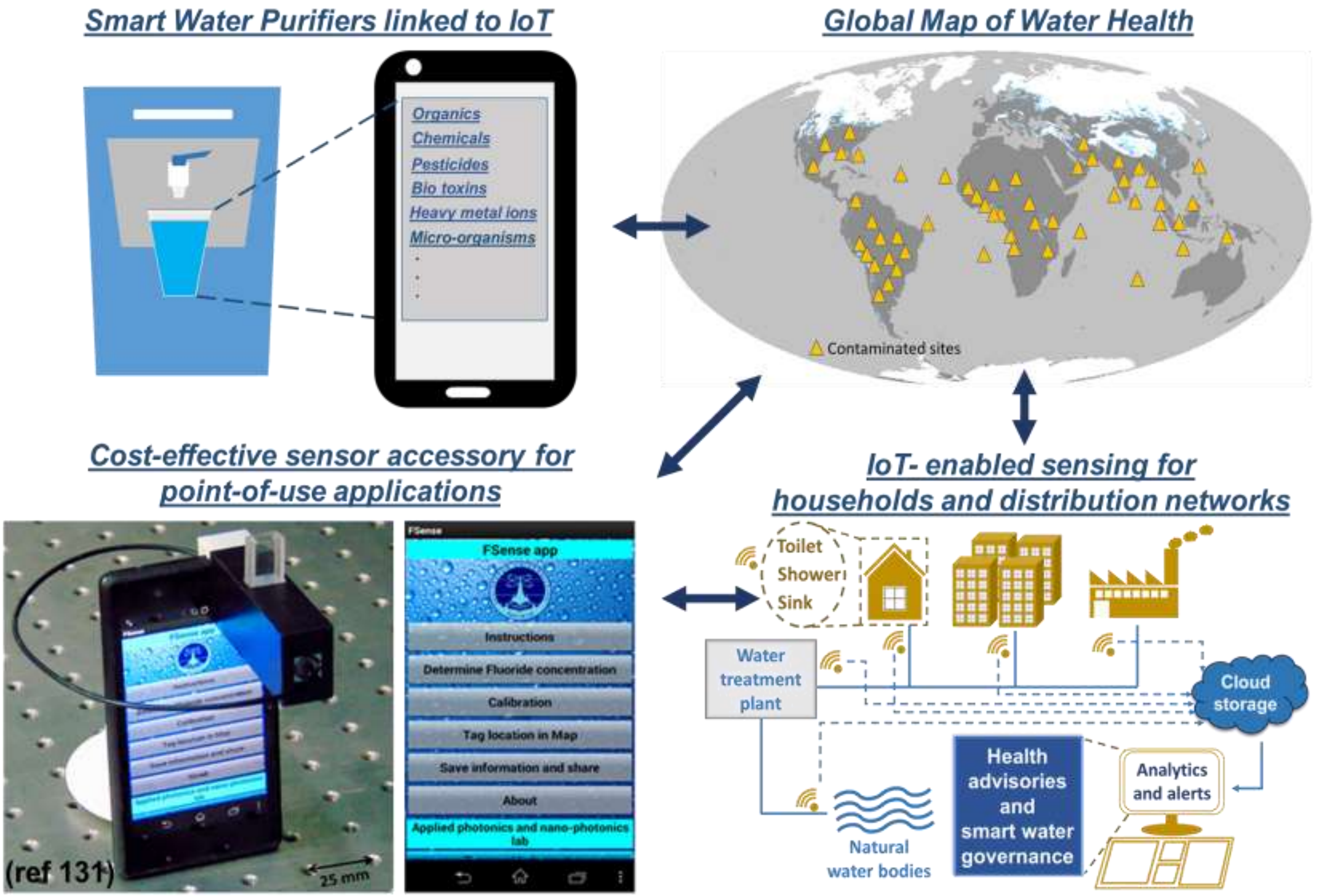
There are over 1700 community installations across the country, serving 1.3 million people with arsenic and iron-free water every day.

Evolution of materials to products



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

Smart water purifiers and big data

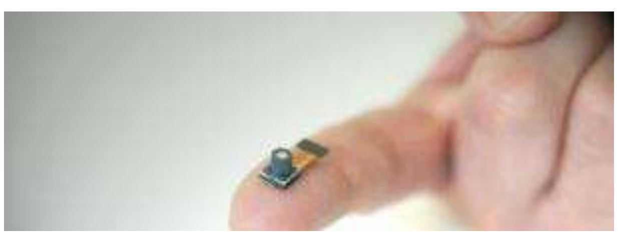


Ankit Nagar and T. Pradeep 14(2020). *ACS Nano*, 6420-6435

Sensors and new opportunities

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

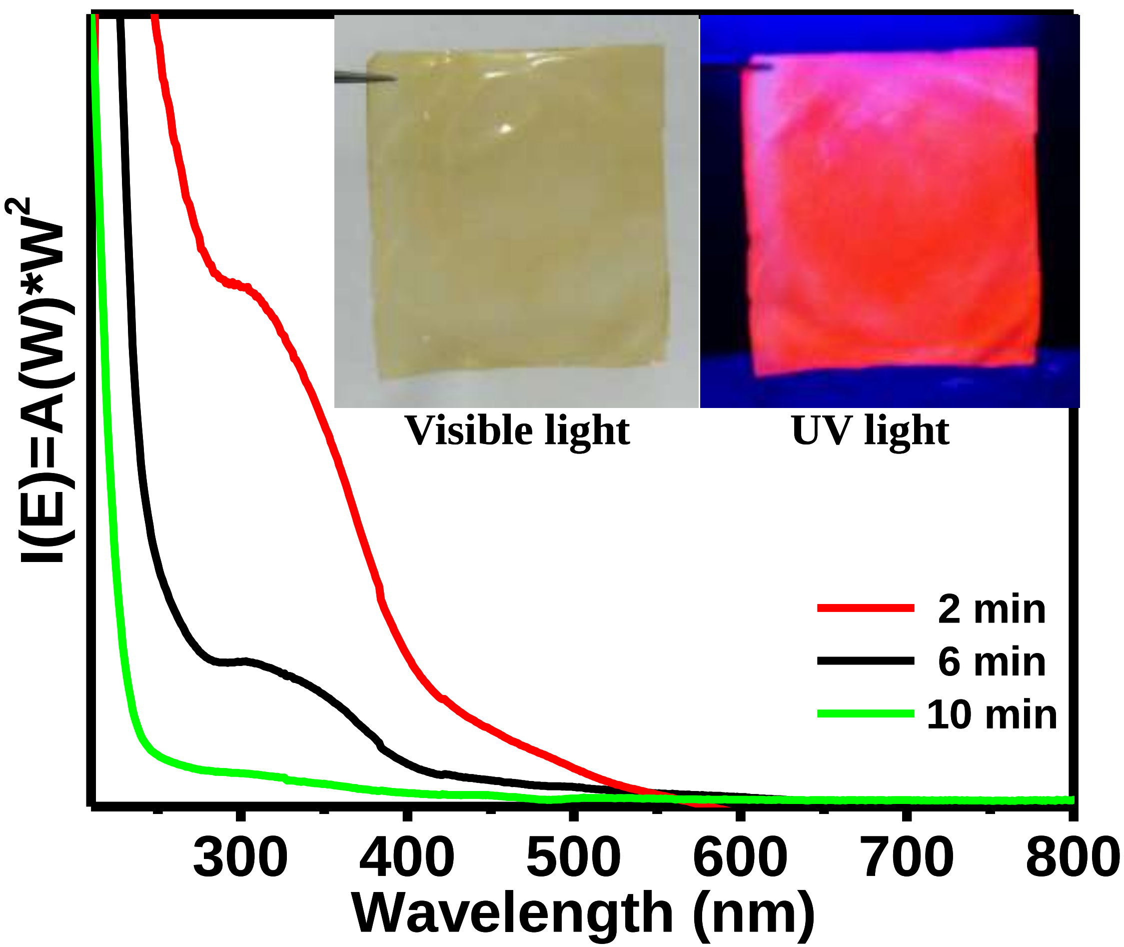
Ultra compact Low Cost
Spectral Sensor Module
~ Billions units (? 2027)



Water quality measurement – In the pipeline

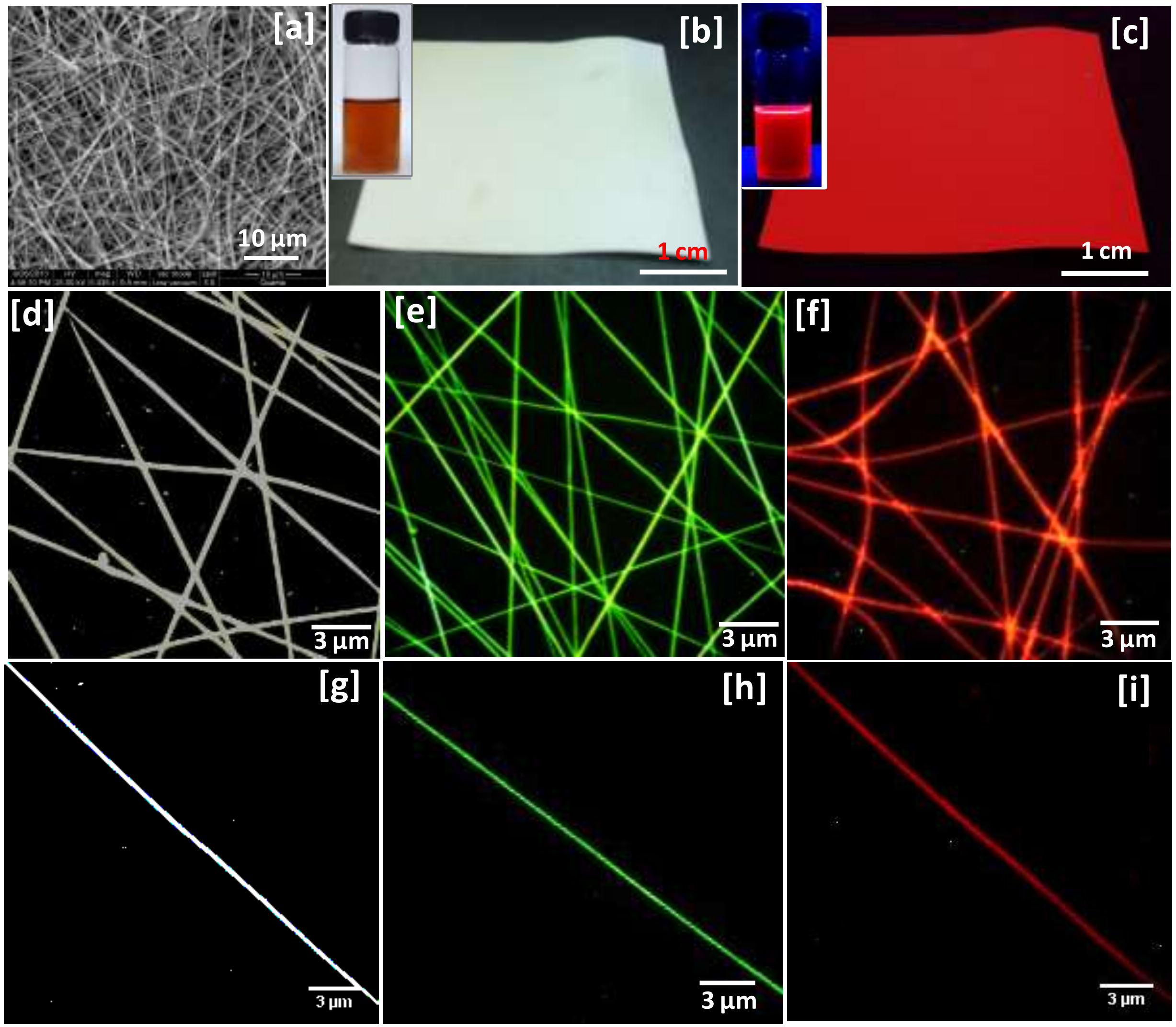
nanoλ

Cluster-based metal ion sensing



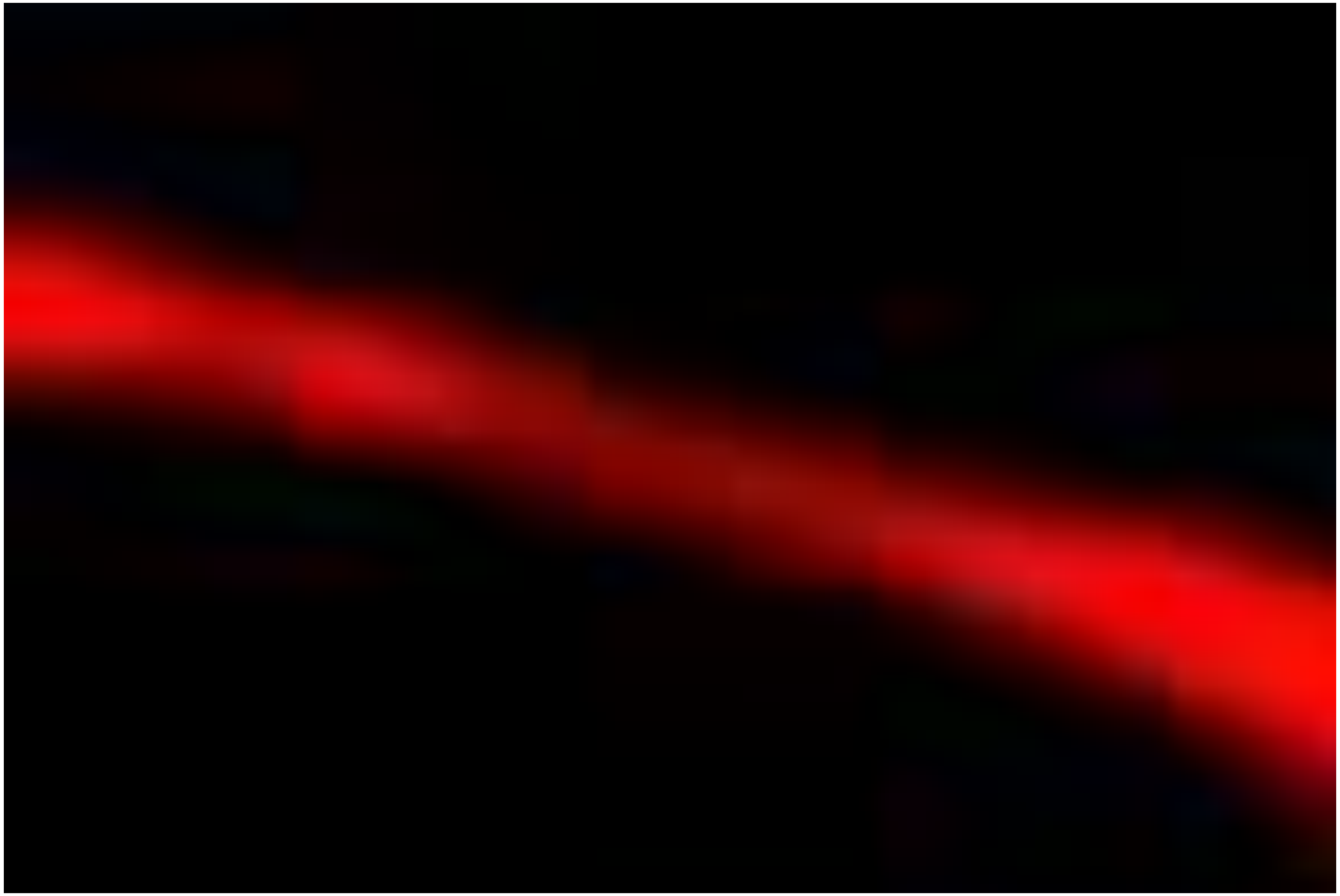
Decrease in the absorption of Au_{15} as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

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

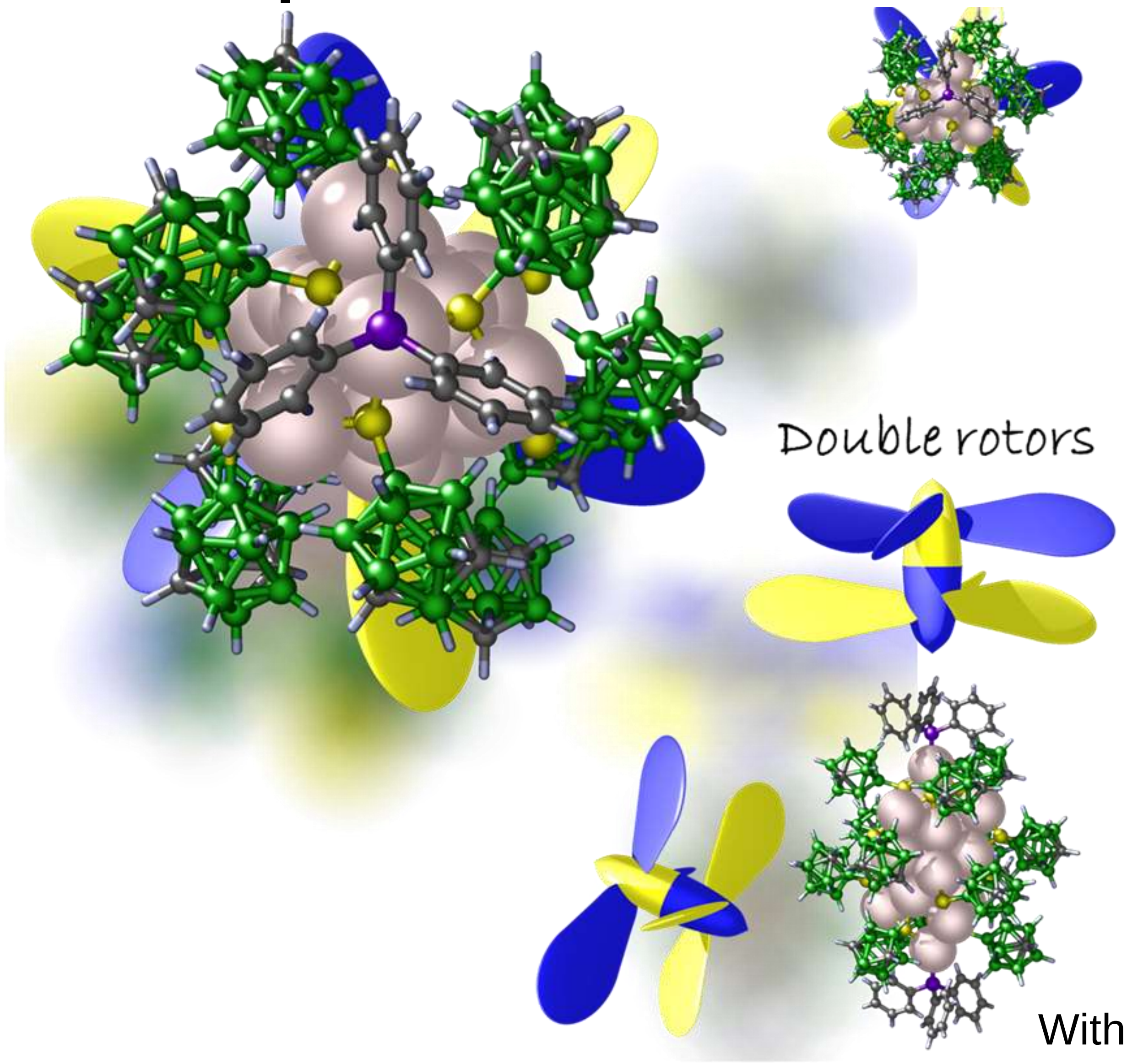


Atanu Ghosh et al. Anal. Chem. 2014.

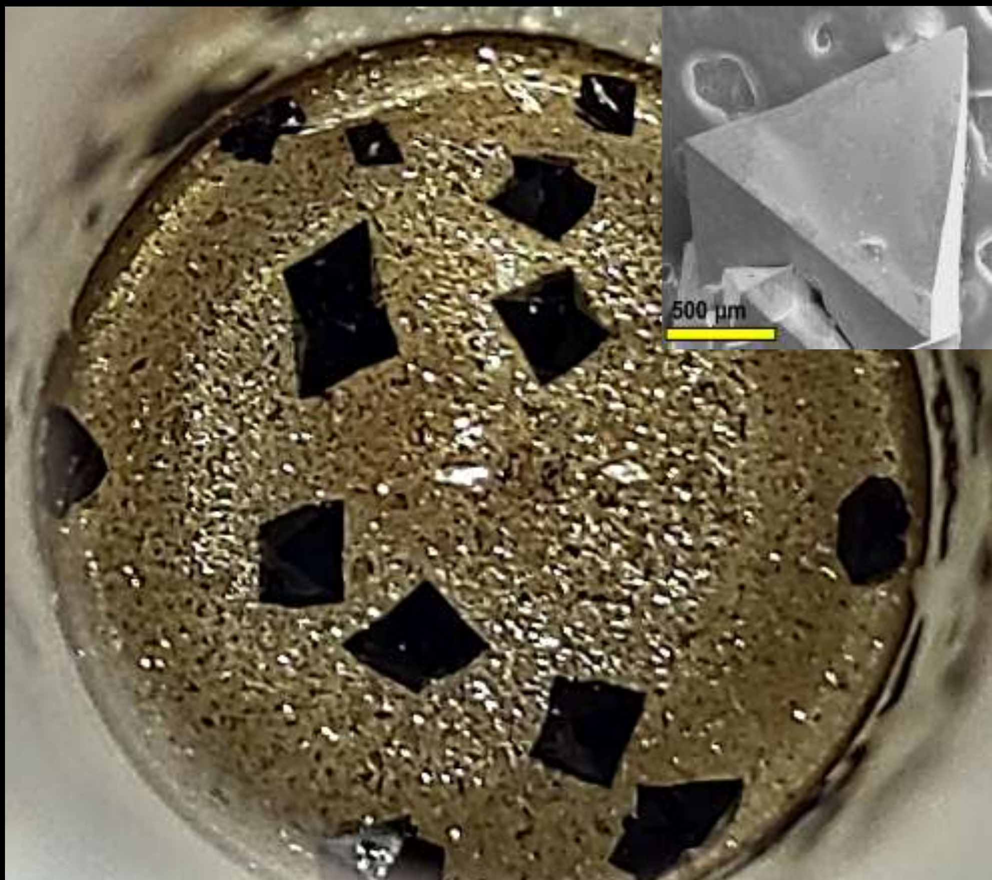
Mercury quenching experiment using nanofiber

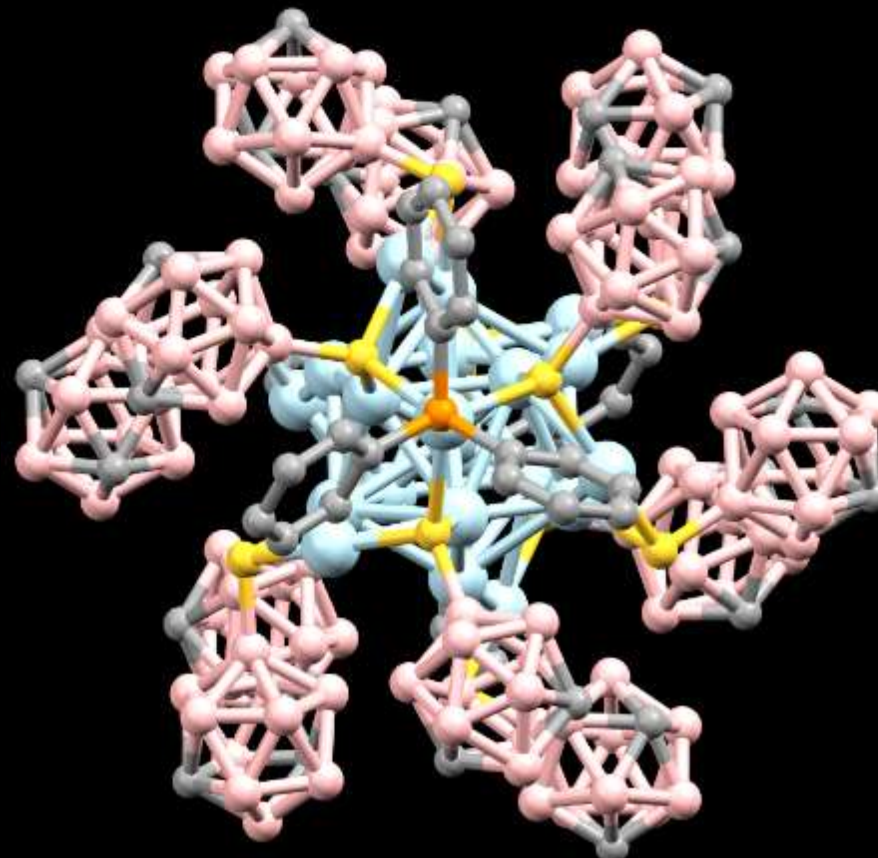


Carborane-thiol protected silver nanomolecule

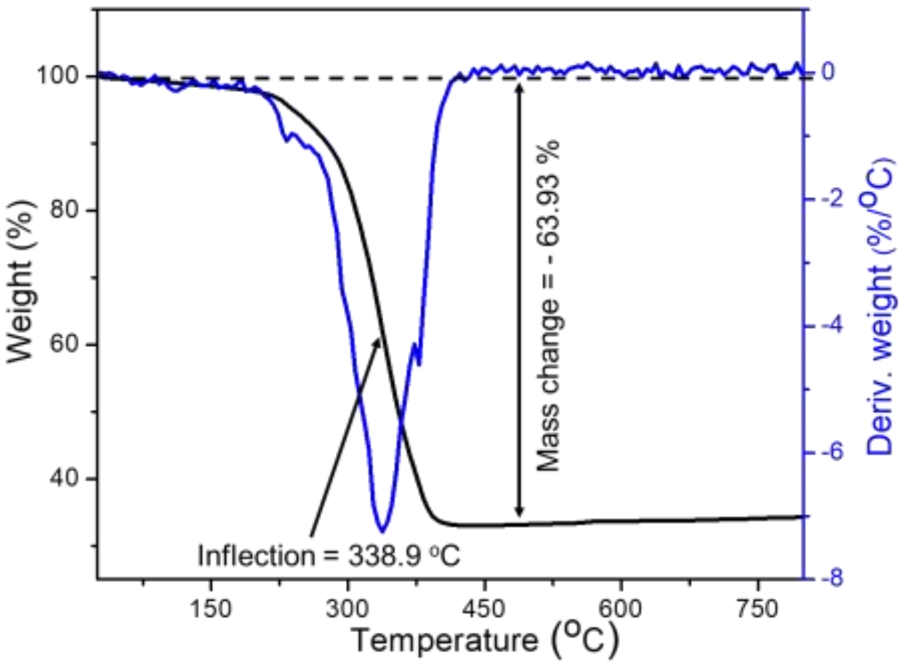


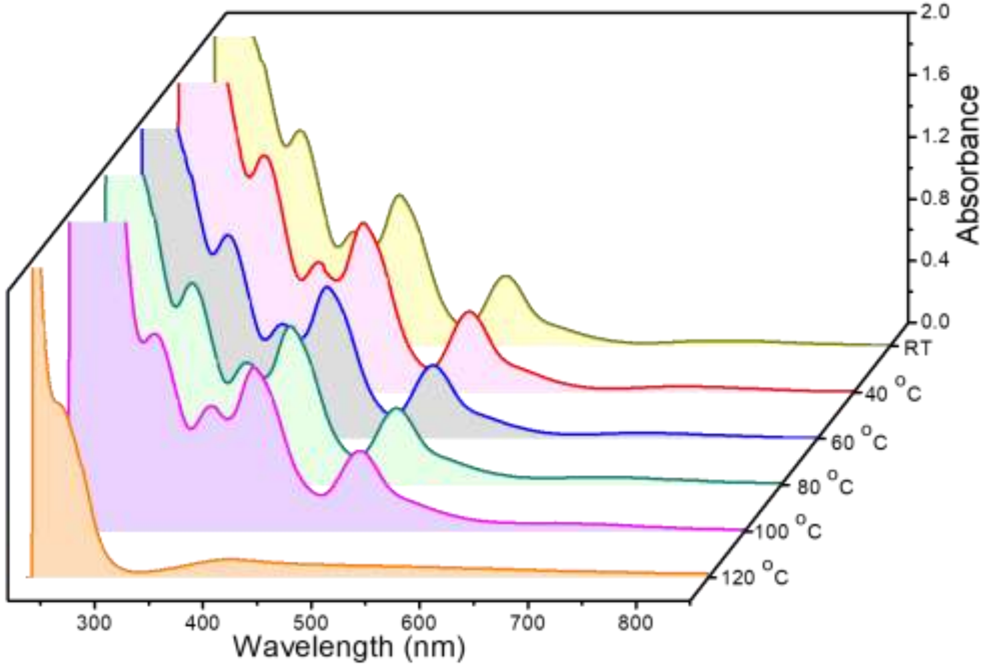
With Tomas Base


500 µm

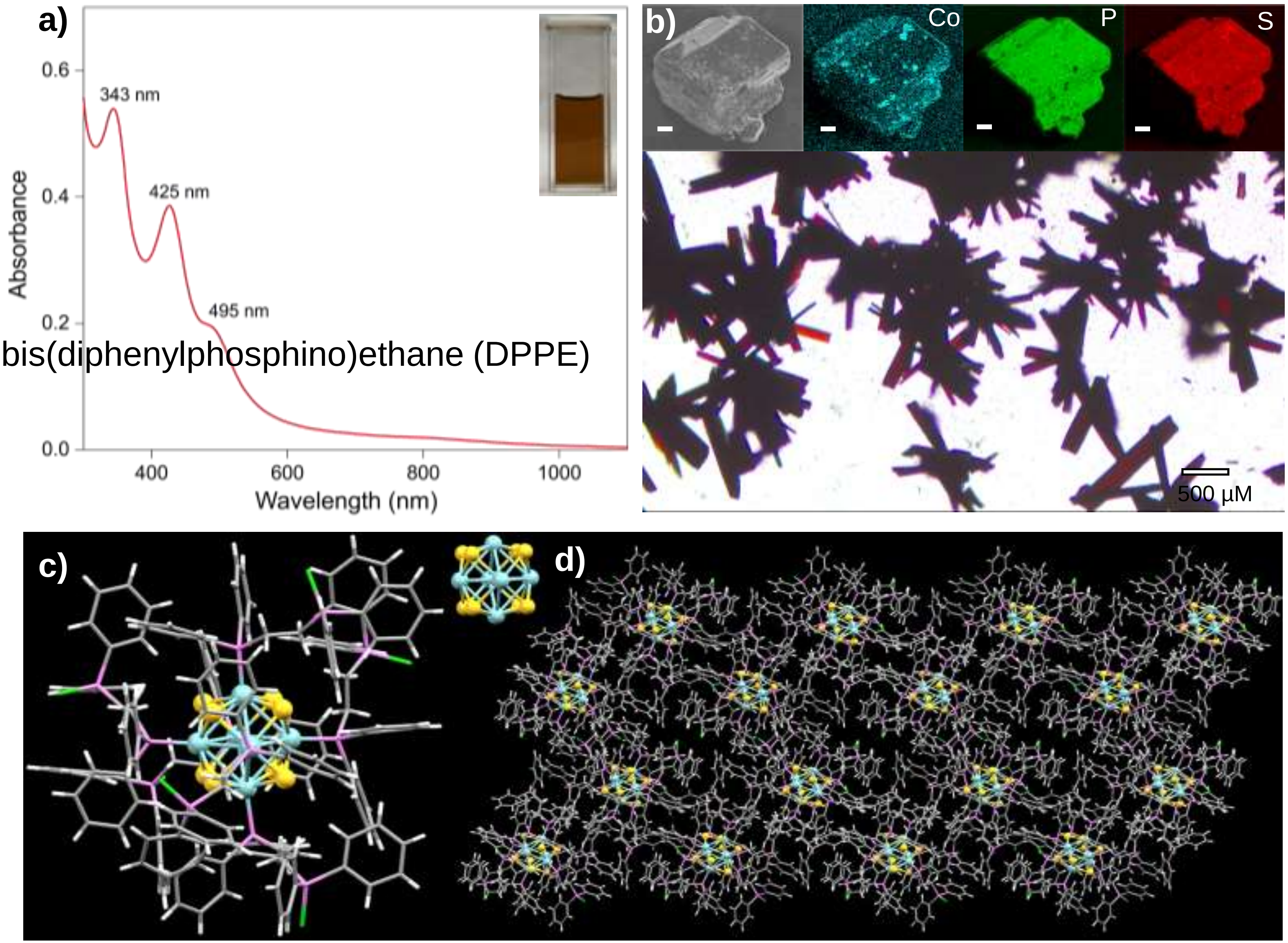


Thermal stability



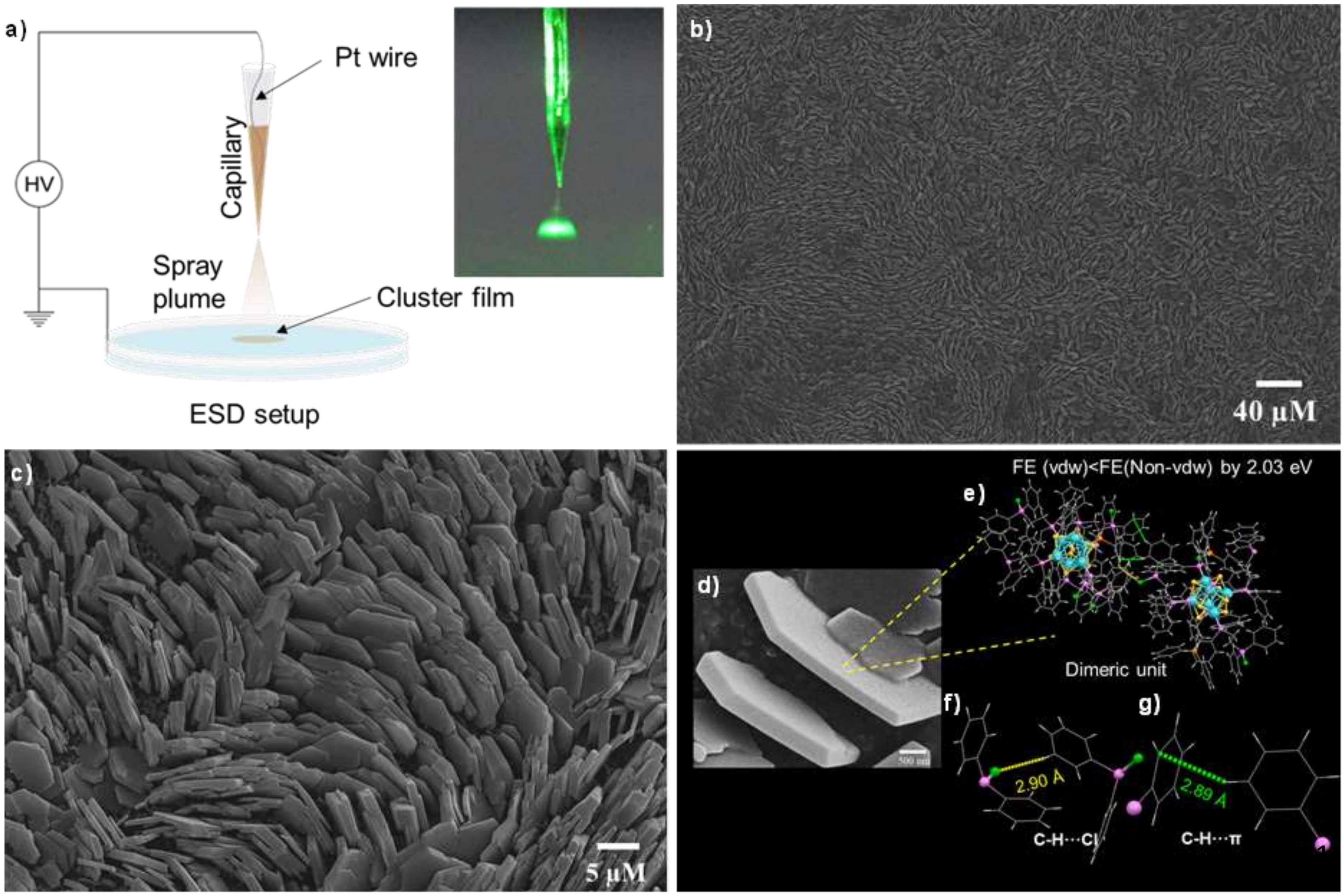


New electrodes - Aligned nanoplates of Co_6S_8

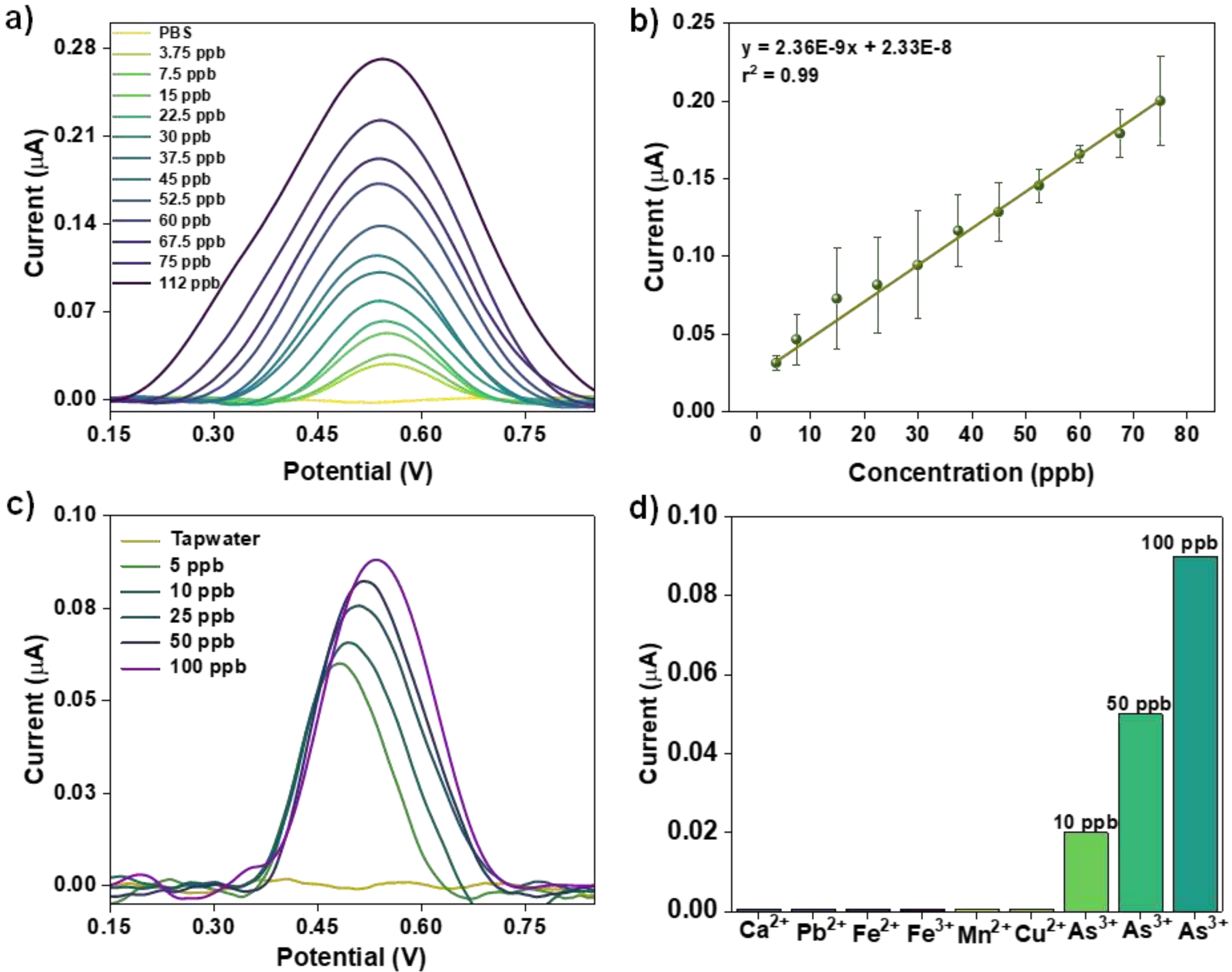


1,2-bis(diphenylphosphino)ethane (DPPE)

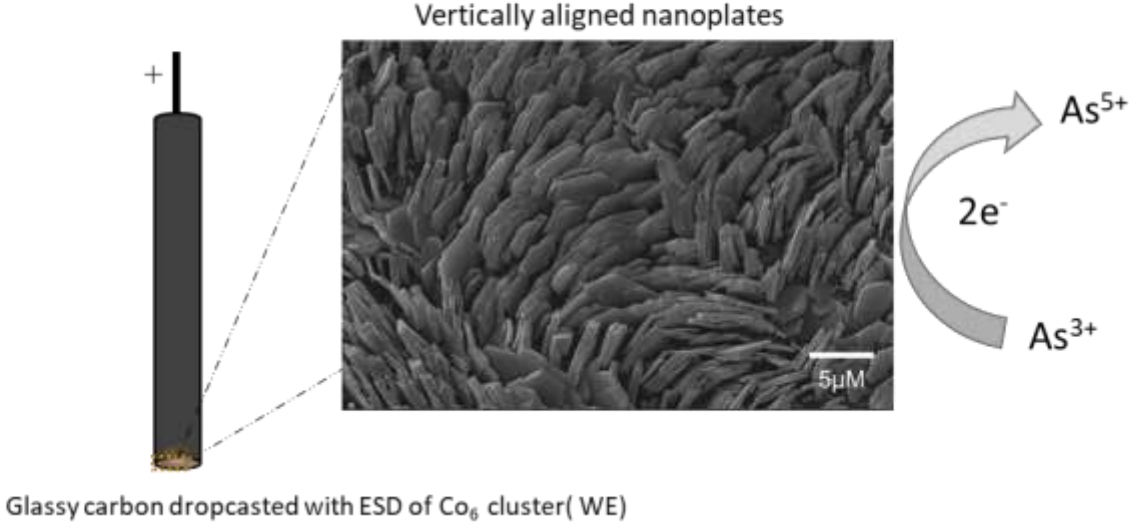
Electrospray deposition

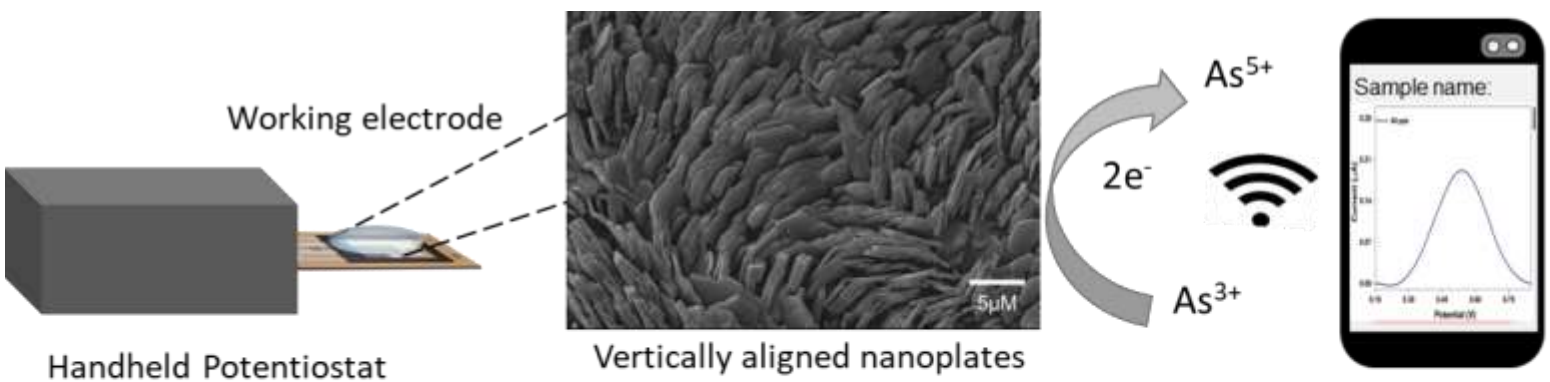


Sensing


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+

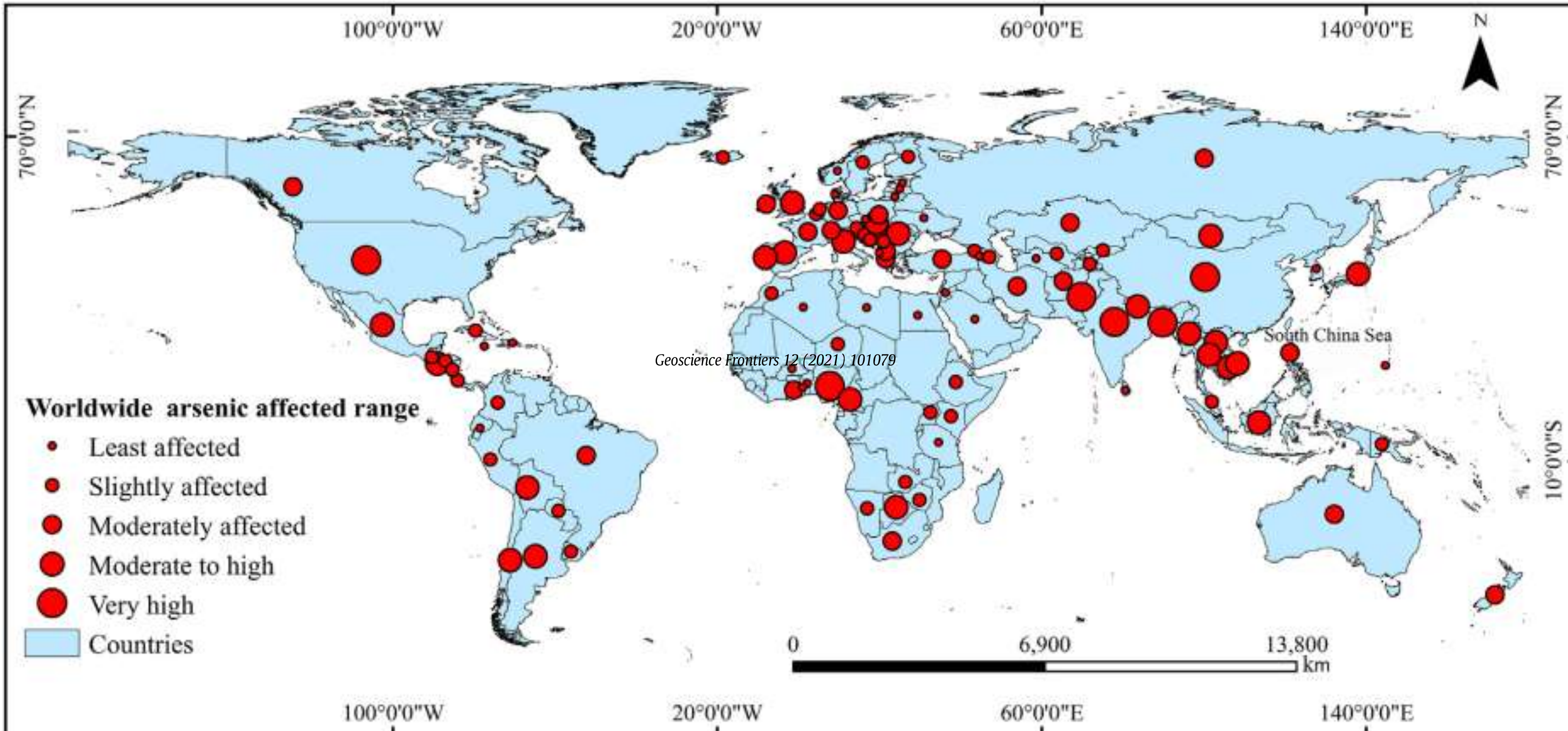
Working electrode





Anagha Jose et al. *ACS Materials Lett.*, 5 (2023) 893–899.

Arsenic poisoning across the world

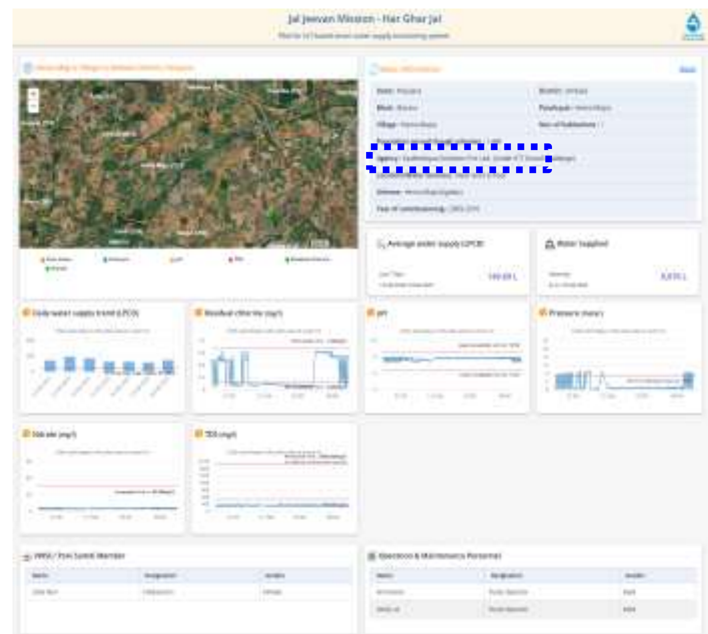


E. Shaji, M. Santosh, K. V. Sarath, Pranav Prakash, V. Deepch and B. V. Divya, Geoscience Frontiers, 12 (2021) 101079.

India's water is being monitored

IITM/IISc

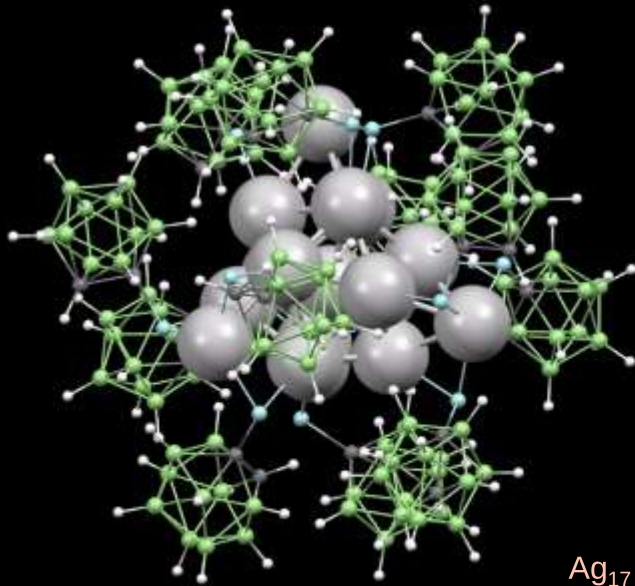
Installations made by four companies



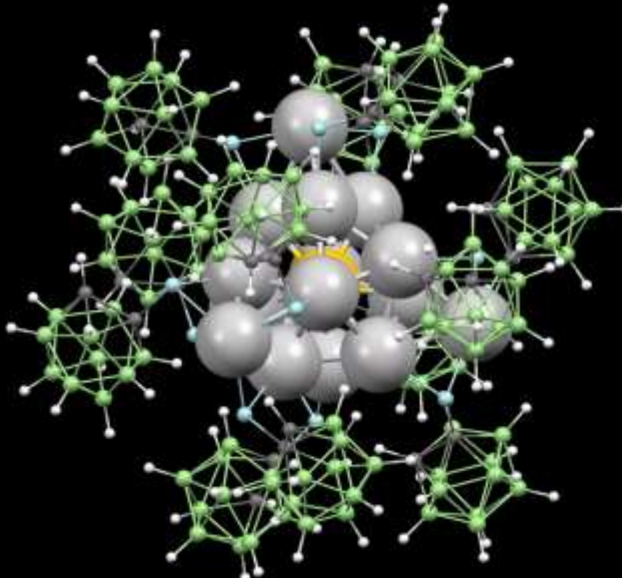
Ag_{17} $AuAg_{16}$ $Ag_{13}Cu_4$ $AuAg_{12}Cu_4$

Vivek Yadav, et. al., *Nature Communications*, 2025

Structure of M_{17} Nanoclusters

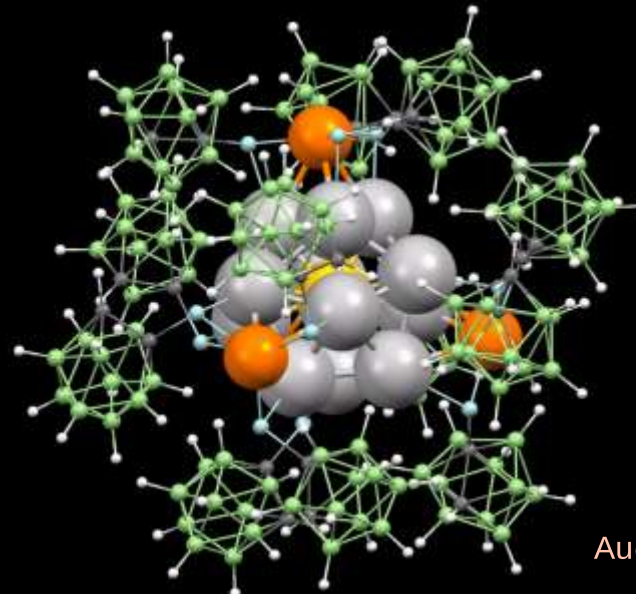


Ag_{17}



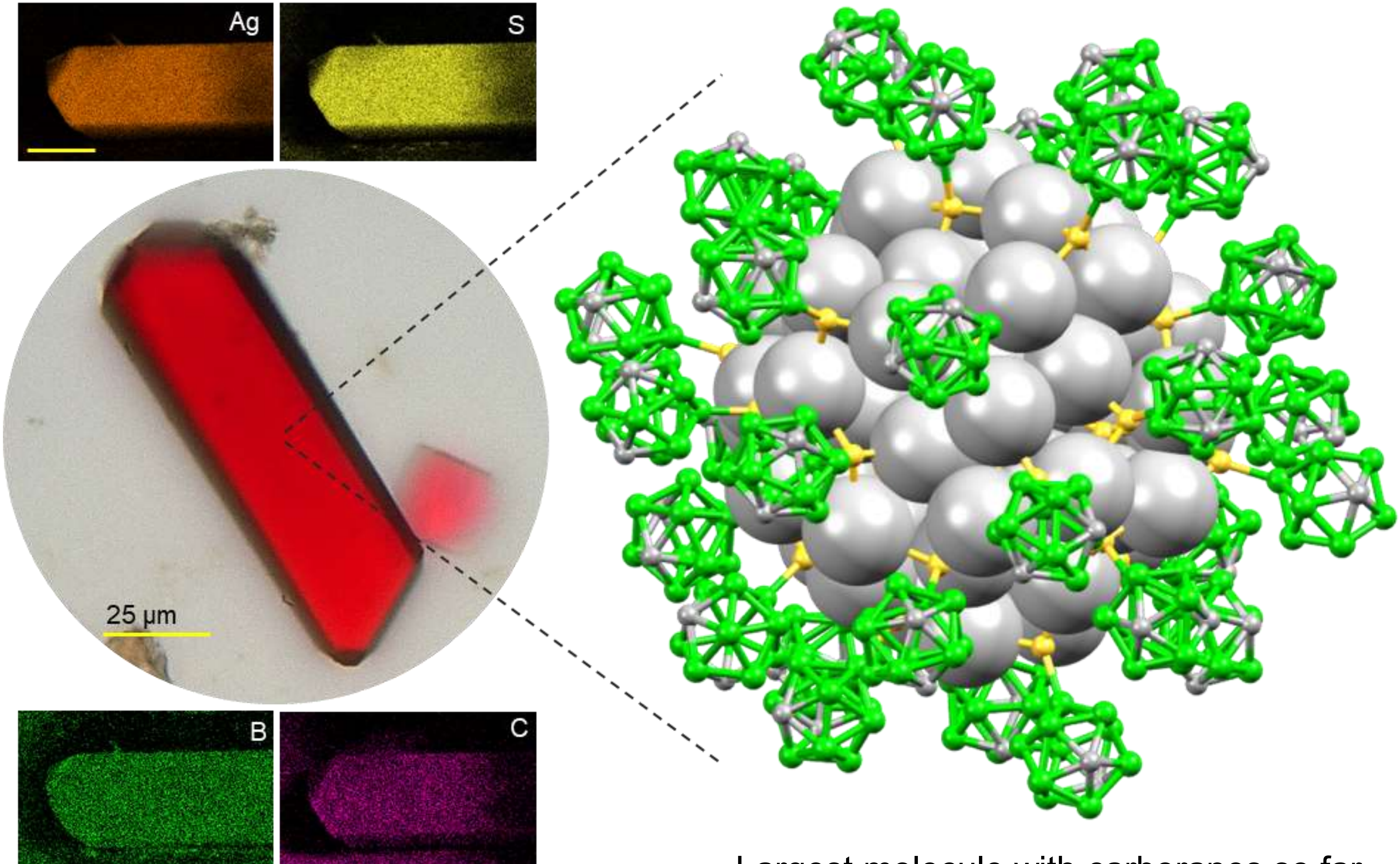
$Au@Ag_{16}$

$Ag_{13}@Cu_4$



$Au@Ag_{12}@Cu_4$

$[Ag_{62}S_{12}(CBT)_{32}]$ Nanocluster

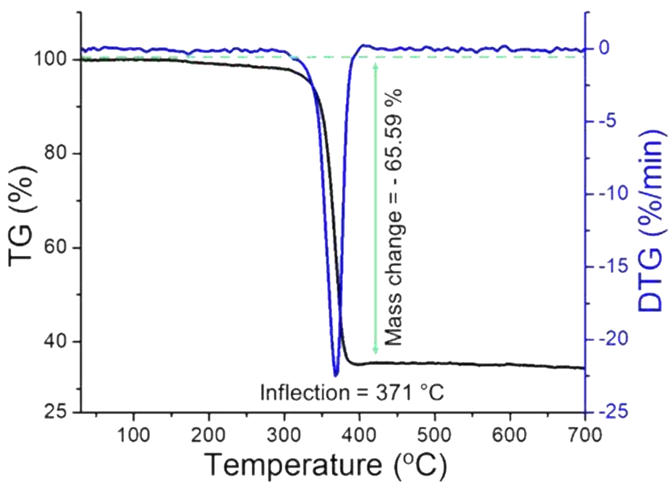


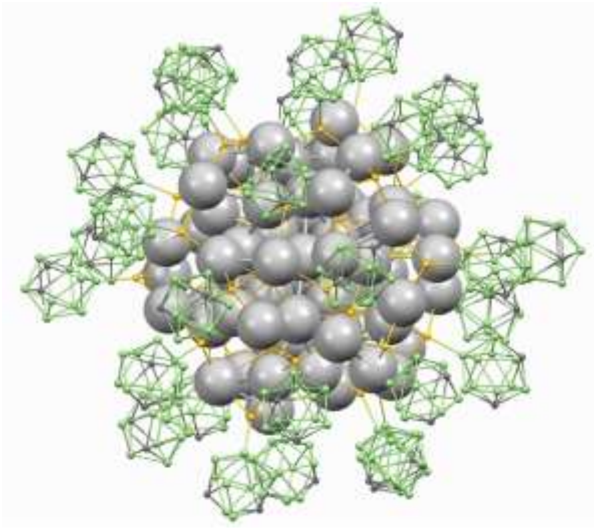
Largest molecule with carboranes so far….

Jana *et al.*, manuscript under preparation

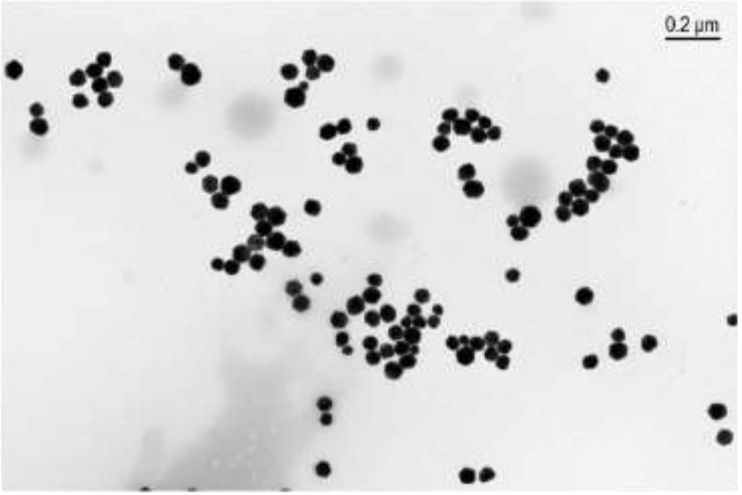
Summary

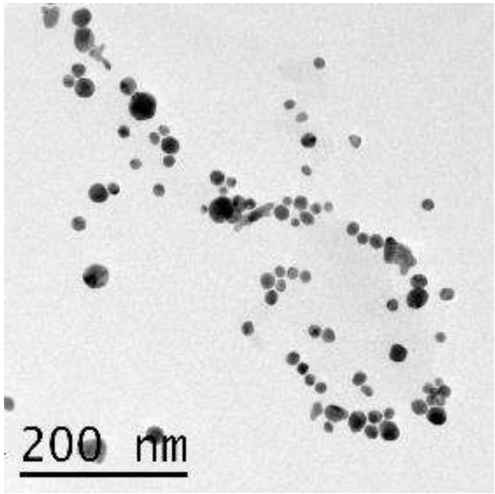
- Atomically precise clusters are a category of new materials
- They are molecules – properties, nomenclature,…
- Clusters are thermally stable up to 400° C.
- They exhibit useful applications
- Atomic precision across the periodic table
- An era cluster-based materials is being born



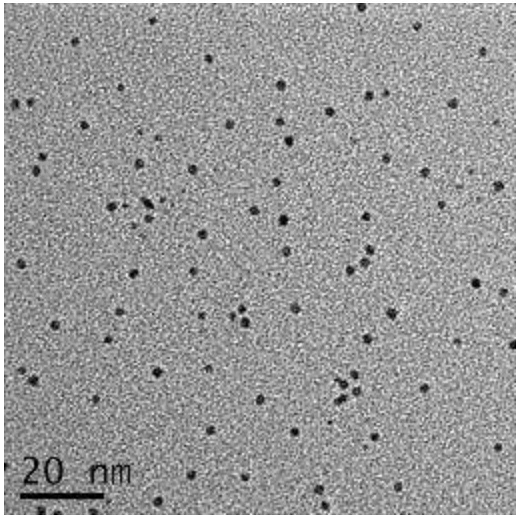


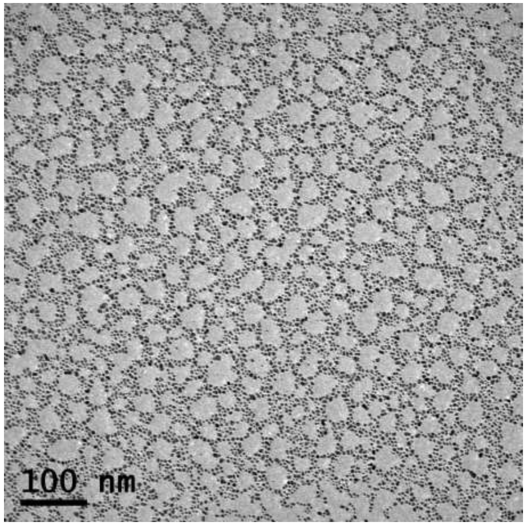
Larger clusters - TEM

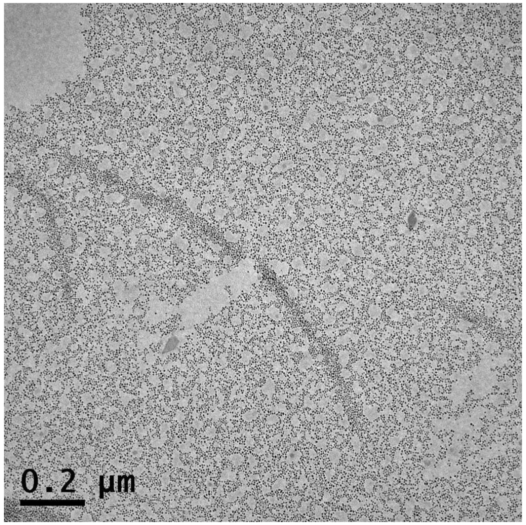




60 nm sized Au-citrate nanoparticles $Au_{\sim 246000}(MUTAB)_{\sim 6280}$



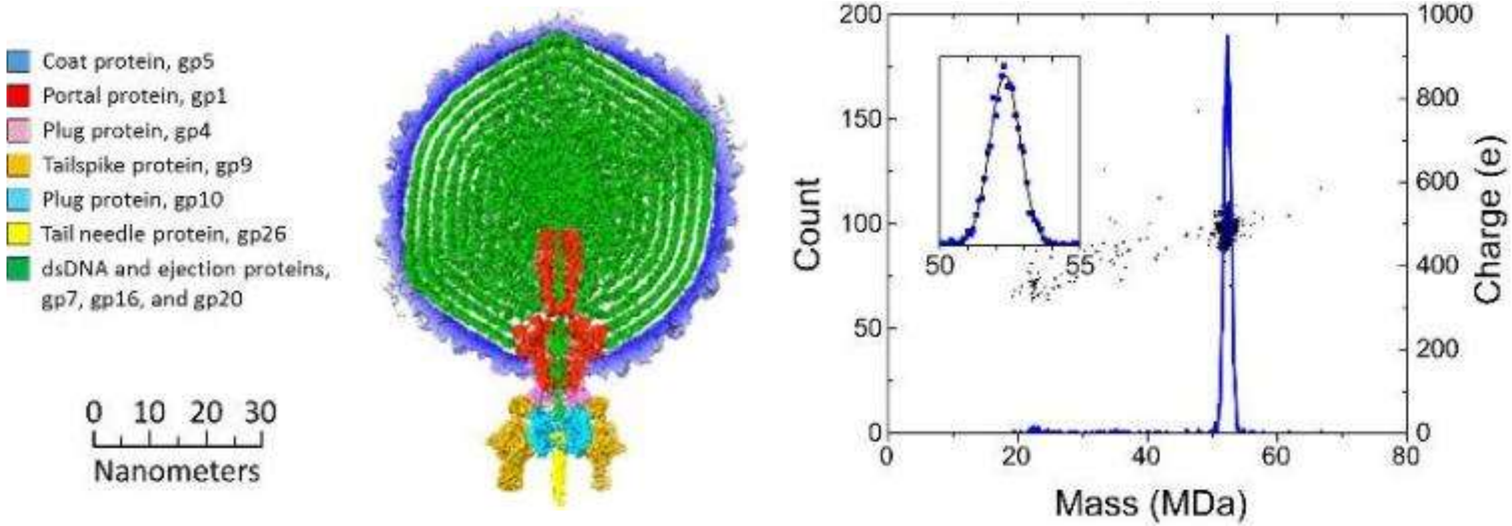




$Au_{279}(TBBT)_{84}$ $Au_{144}(PET)_{60}$ $Au_{25}(PET)_{18}$

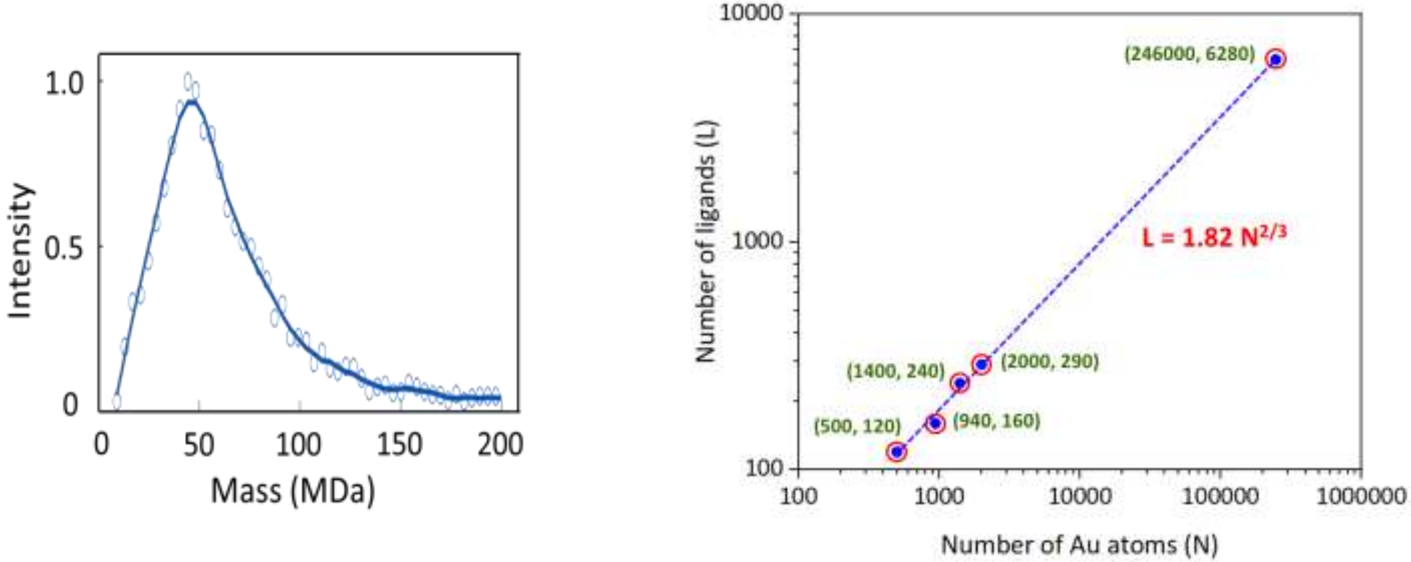
CDMS of viruses and nanoparticles

(a)

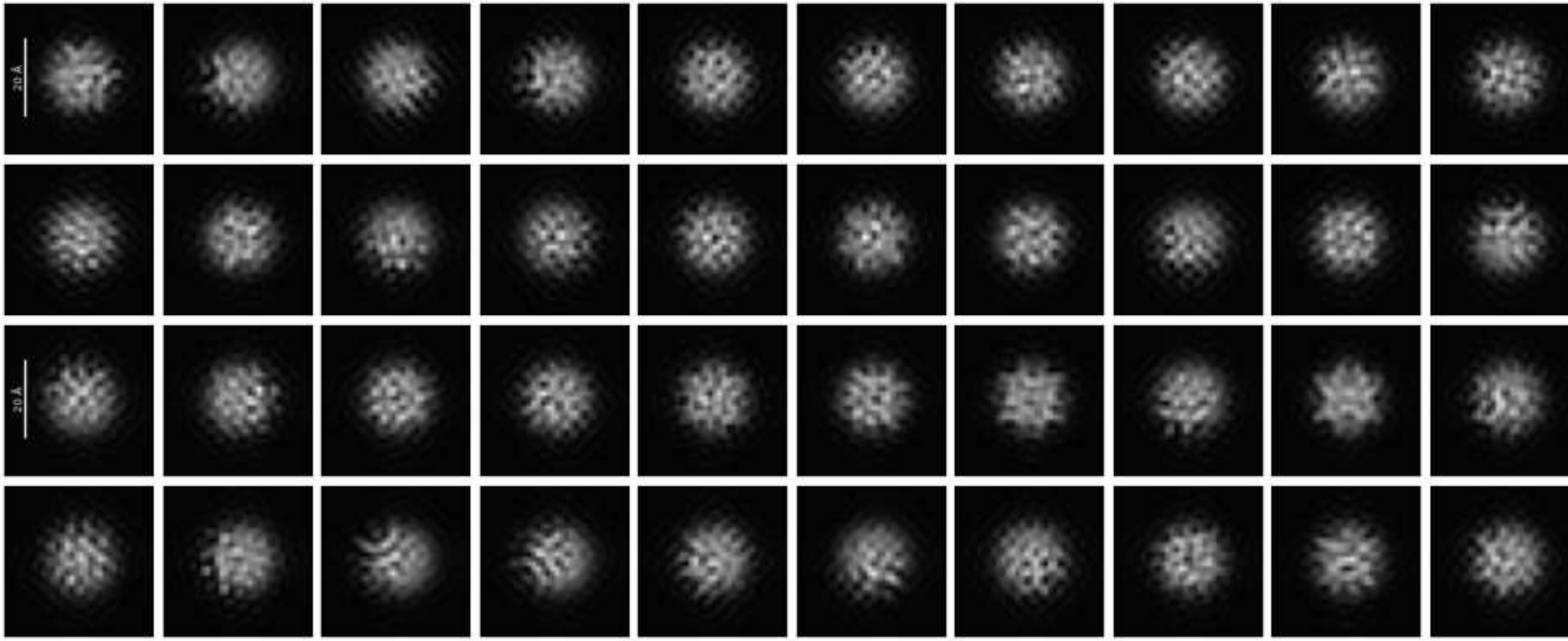


Keifer, D. Z.; Motwani, T.; Teschke, C. M.; Jarrold, M. F. Measurement of the Accurate Mass of a 50 MDa Infectious Virus. *Rapid Commun. Mass Spectrom.* **2016**, *30* (17), 1957–1962.

(b)



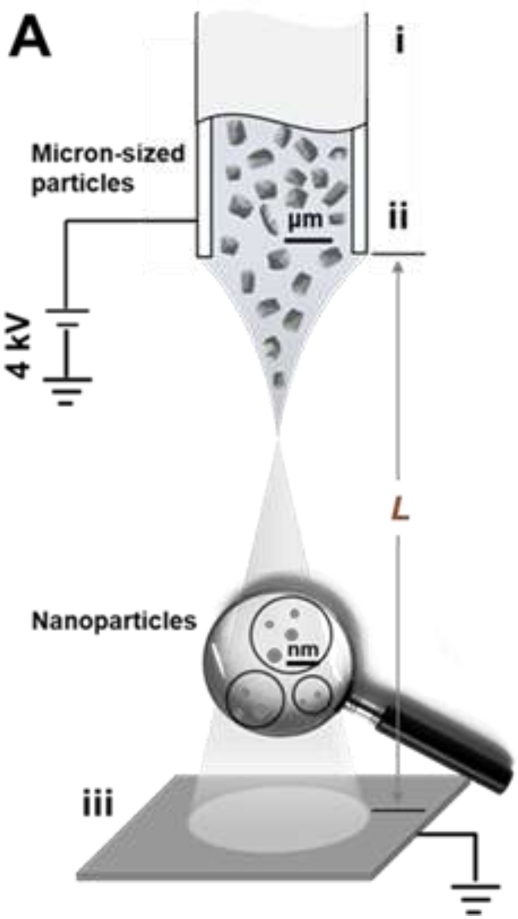
B. S. Sooraj, et. al. Unpublished

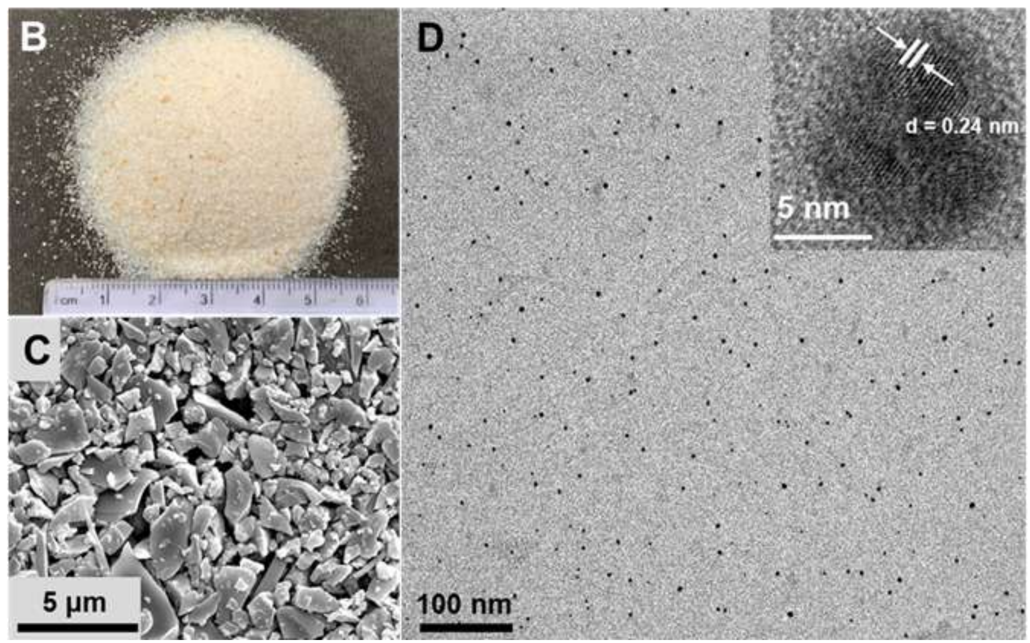


B. S. Sooraj, et. al. Unpublished

Weathering of Minerals in Microdroplets

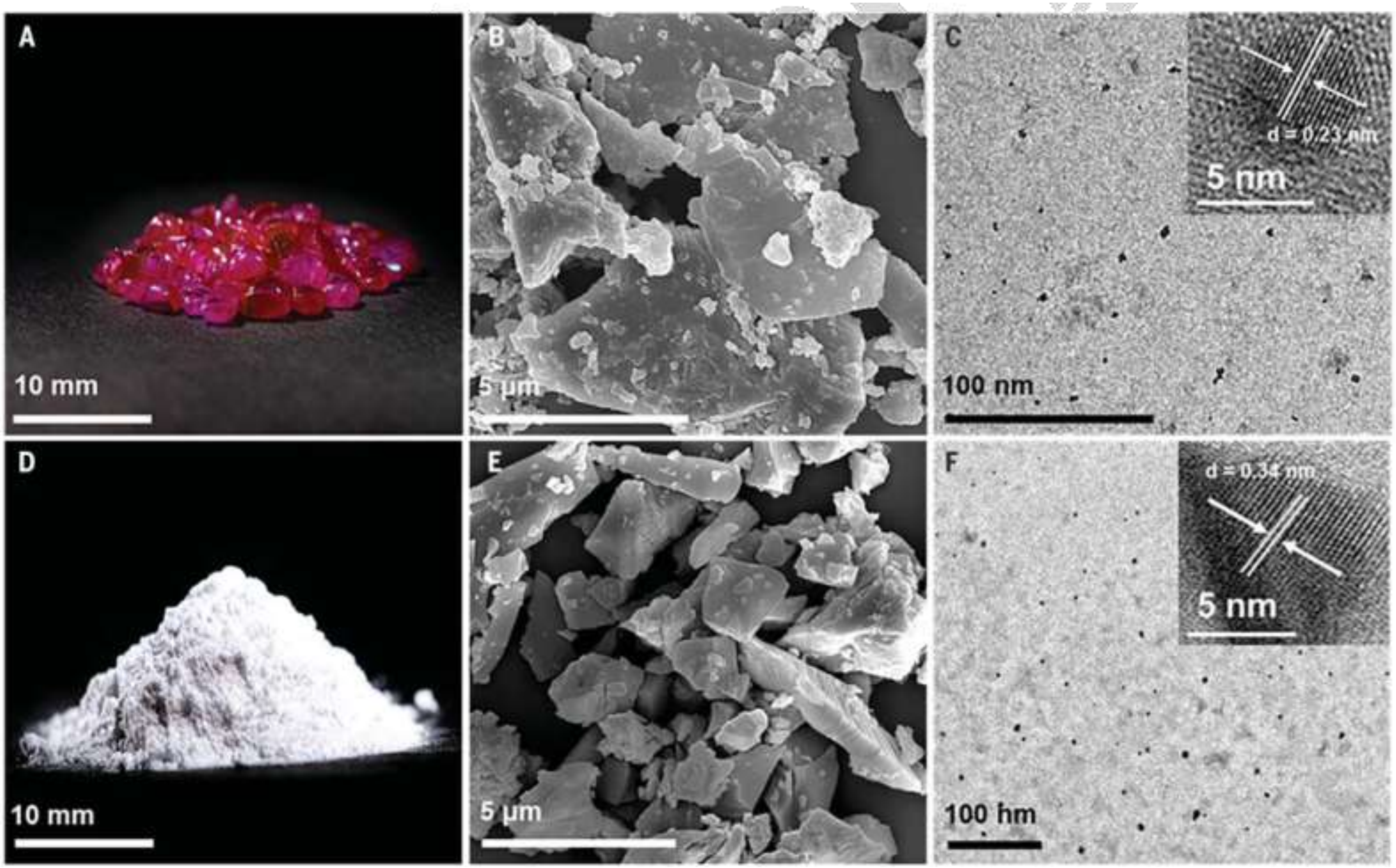
Spontaneous Weathering of Natural Minerals in Charged Water Microdroplets Forms Nanomaterials



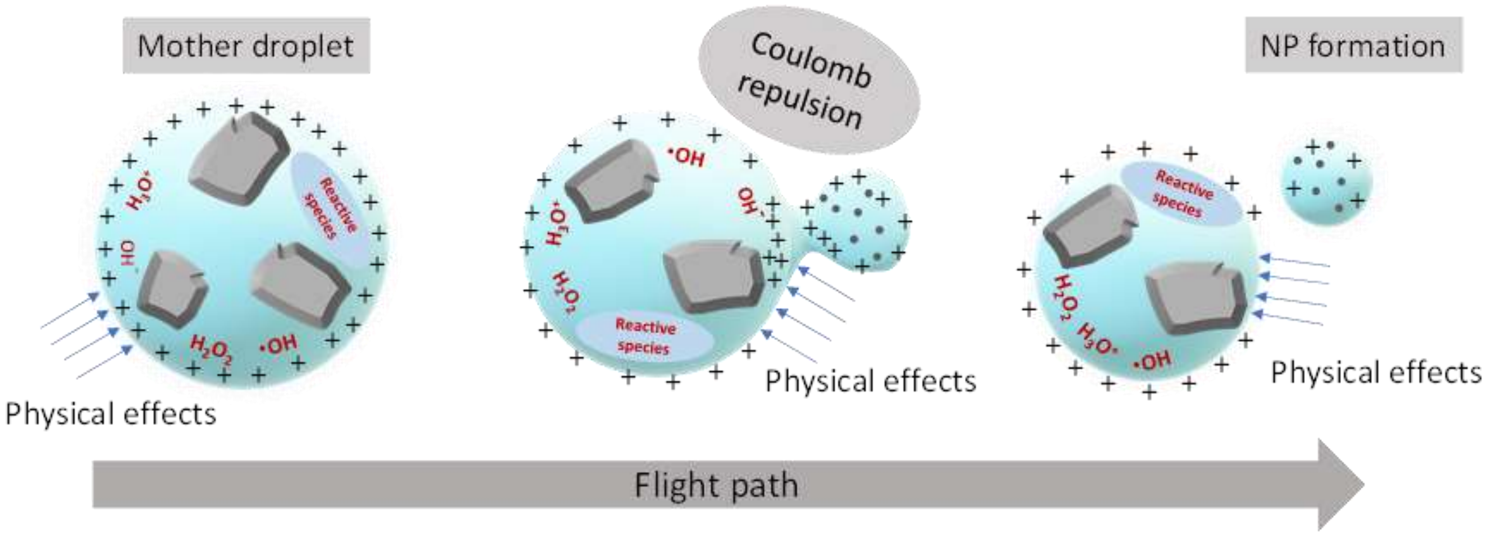


Spoorthi, et. al., *Science*, 384 (2024) 1012-1017.

Ruby, Fused Alumina



Mechanism of nanoparticle formation



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Atomically Precise Nanochemistry

Gordon Research Conference

Diversity, Symmetry and Functions of Molecular Materials

February 4 - 9, 2024

Chairs

Thalappil Pradeep and Stefanie S. Dehnen

Vice Chairs

Stacy Copp and Hannu Häkkinen

Contact Chairs

Grand Galvez

2024 Seawall Boulevard

Galveston, Texas, United States

Venue and Travel Information

Conference Description

The Atomically Precise Nanochemistry GRC is a premier, international scientific conference focused on advancing the frontiers of science through the presentation of cutting-edge and unpublished research, prioritizing time for discussion after each talk and fostering informal interactions among scientists of all career stages. The conference program includes a diverse range of speakers

Conference Links

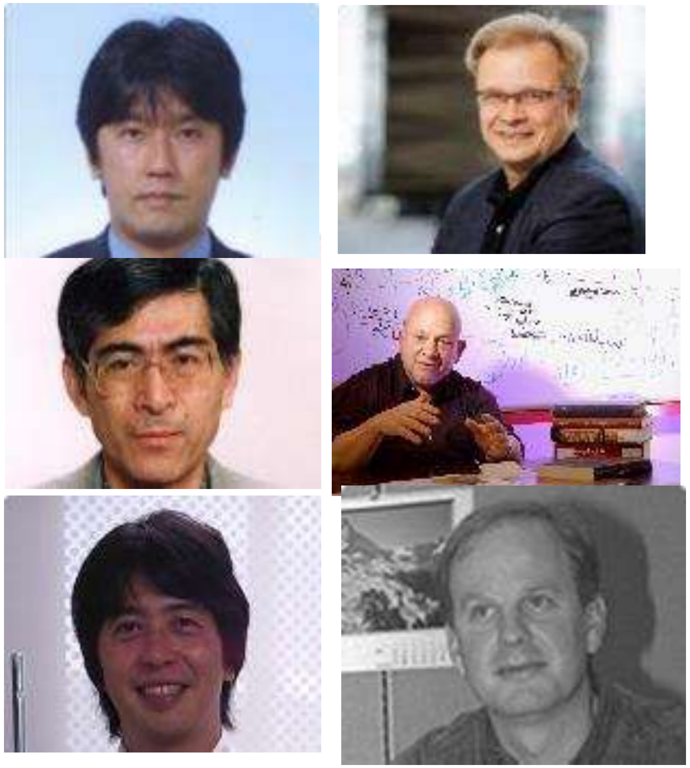
» Conference History

» Atomically Precise Nanochemistry (GRS)

Affordable, inclusive, sustainable and contextual excellence

The AMRIT Team, 2013

Collaborators



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

Robin Ras

Nonappa

Tomas Base

Manfred Kappes

Olli Ikkala

Horst Hahn

Biswarup Pathak

K. V. Adarsh

G. U. Kulkarni

Vivek Polshettiwar

Shiv Khanna

Water team at IIT: A. Sreekumaran Nair, Anshup, M. Udhaya Sankar, Amrita Chaudhary, Renjis T. Tom, T. S. Sreeprasad, Udayabhaskararao Thumu, M. S. Bootharaju, K. R. Krishnadas, Kalamesh Chaudhari, Soujit Sengupta, Depanjan Sarkar, Avijit Baidya, Swathy Jakka Ravindran, Abhijit Nag, S. Vidhya, Biswajit Mondal, Krishnan Swaminathan, Azhardin Gnayee, Sudhakar Chennu, A. Suganya, Rabiul Islam, Sritama Mukherjee, Tanvi Gupte, Jenifer Shantha Kumar, A. Anil Kumar, Ankit Nagar, Ramesh Kumar Soni, Tanmayaa Nayak, Sonali Seth, Shihabudheen M. Maliyekkal, G. Velmurugan, Wakeel Ahmed Dar, Ganapati Natarajan, N. Pugazhenthiran, A. Leelavathi, Sahaja Aigal, S.Gayathri, Bibhuti Bhusan Rath, Ananthu Mahendranath, Harsh Dave, Erik Mobegi, Egor Moses, Hemanta R. Naik, Sourav Kanti Jana, Tanmayaa Nayak, Sonali Seth…

Avula Anil Kumar, Chennu Sudhakar, Sritama Mukherjee, Anshup, and Mohan Udhaya Sankar

Funding: Department of Science and Technology, Government of India

Start-ups and partners:

PhD Theses: Bindhu Varughese, M. R. Resmi, M. Venkataramanan, N. Sandhyarani, R. Selvan, A. Sreekumaran Nair, M. J. Rosemary, Renjis T. Tom, C. Subramaniam, Jobin Cyriac, V. R. Rajeev Kumar, D. M. David Jeba Singh, Akshaya Kumar Samal, E. S. Shibu, M. A. Habeeb Muhammed, P. R. Sajanlal, T. S. Sreeprasad, J. Purushothaman, T. Udayabhaskararao, M. S. Bootharaju, Soumabha Bag, Robin John, Kamalesh Chaudhari, Ammu Mathew, Indranath Chakraborty, Radha Gobinda Bhuin, Ananya Baksi, Amitava Srimony, Anirban Som, Rabin Rajan Methikkalam, K. R. Krishnadas, Soujit Sengupta, Depanjan Sarkar, Atanu Ghosh, Rahul Narayanan, Avijit Baidya, Shridevi Bhat, Papri Chakraborty, Swathy Jakka Ravindran, C. K. Manju, Abhijit Nag, S. Vidhya, Jyoti Sarita Mohanty, Debasmita Ghosh, Jyotirmoy Ghosh, Md. Bodiuzzaman, Biswajit Mondal, Tripti Ahuja, Esma Khatun, Krishnan Swaminathan, K. S. Sugi, Amrita Chakraborty, Sudhakar Chennu, Sritama Mukherjee, Madhuri Jash, Sandeep Bose, Md. Rabiul Islam, Pallab Basuri, Mohd Azhardin Ganayee, Tanvi Gupte, Ankit Nagar, Srikrishnarka Pillalamarri, Arijit Jana, Paulami Bose, Gaurav Viswakarma, Vishal Kumar, Jayoti Roy, A. Anil Kumar, Jenifer Shantha Kumar

MS Theses: Ananthu Mahedranath, Ramesh Kumar Soni

>25 Post-doctoral fellows, >130 masters students and visitors

Department of Science and Technology, Government of India

Institute of Eminence

Many Outstanding Individuals

Indian Institute of Technology Madras

Associate Editor
ACS Sustainable Resource Management

Bhaskar Ramamurthi/V. Kamakoti

Pradeep Research Group

Manswita Mandal for help with the slides

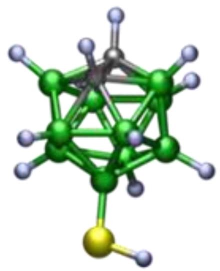
International Centre for Clean Water

People's Water Data

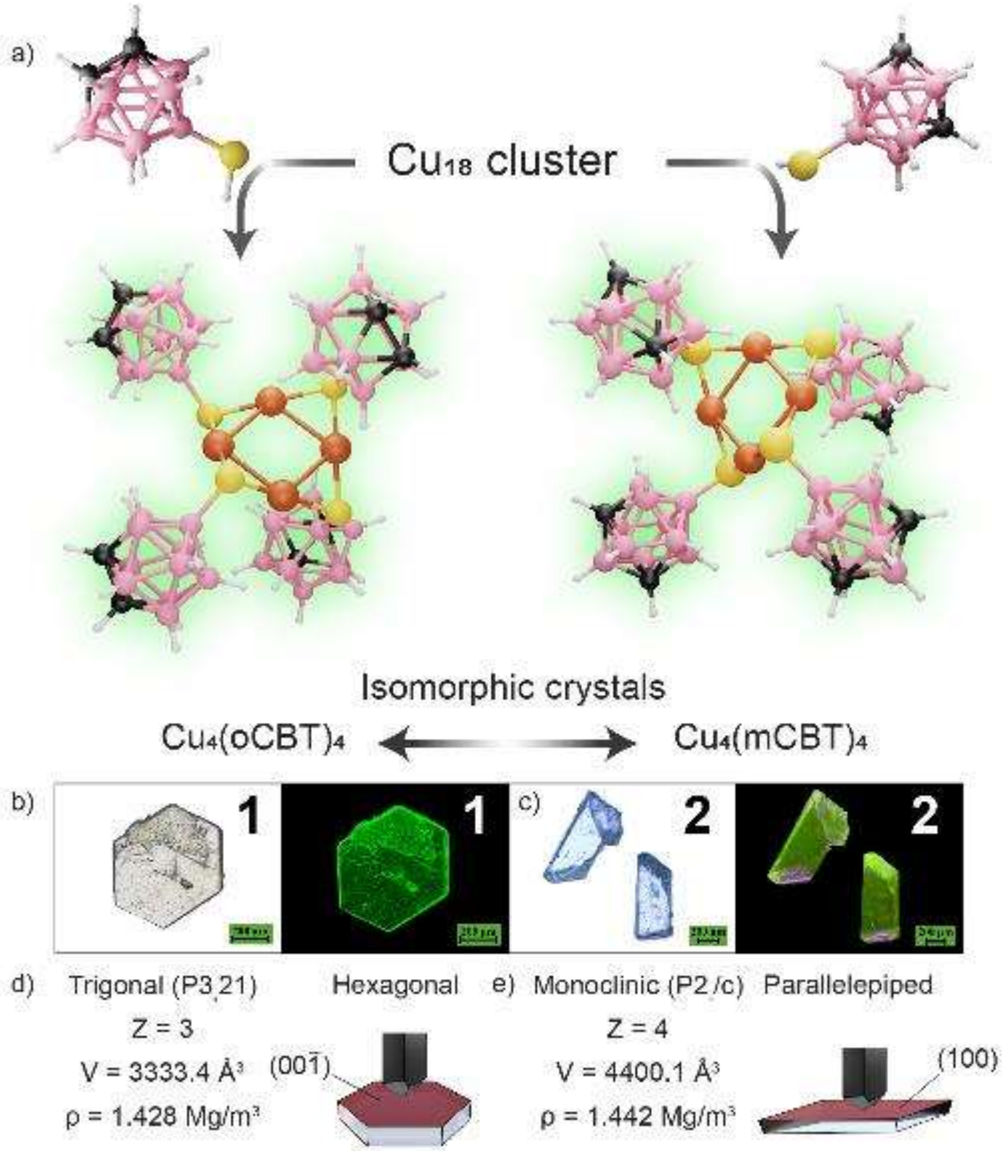
A course by IITM

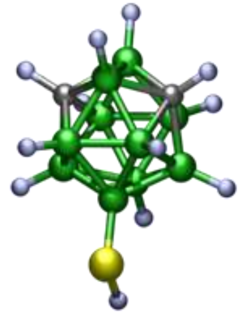
Properties

Nanomechanical Properties of Cu_4 Nanoclusters



9-HS-1,2-$C_2B_{10}H_{11}$

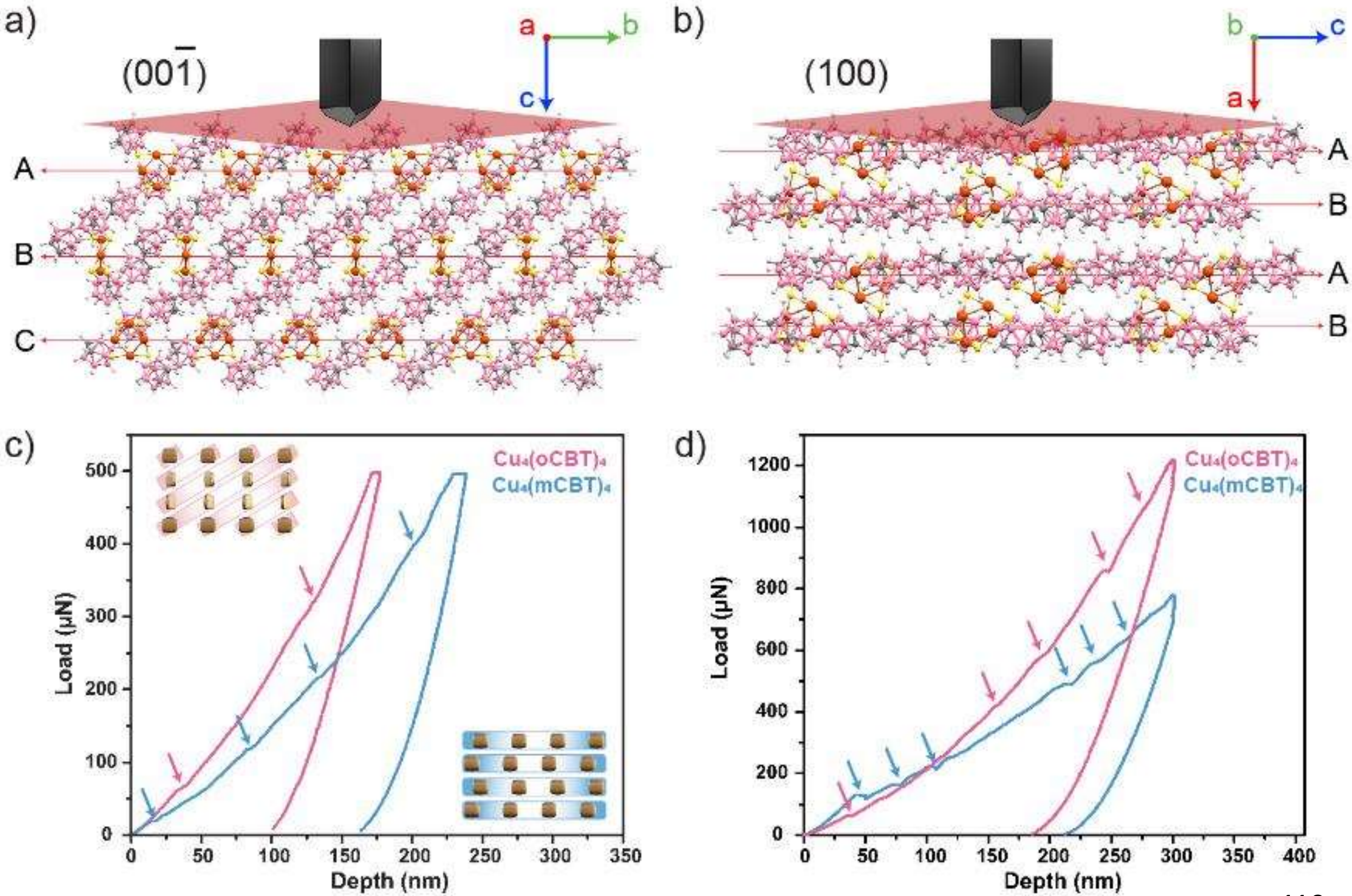




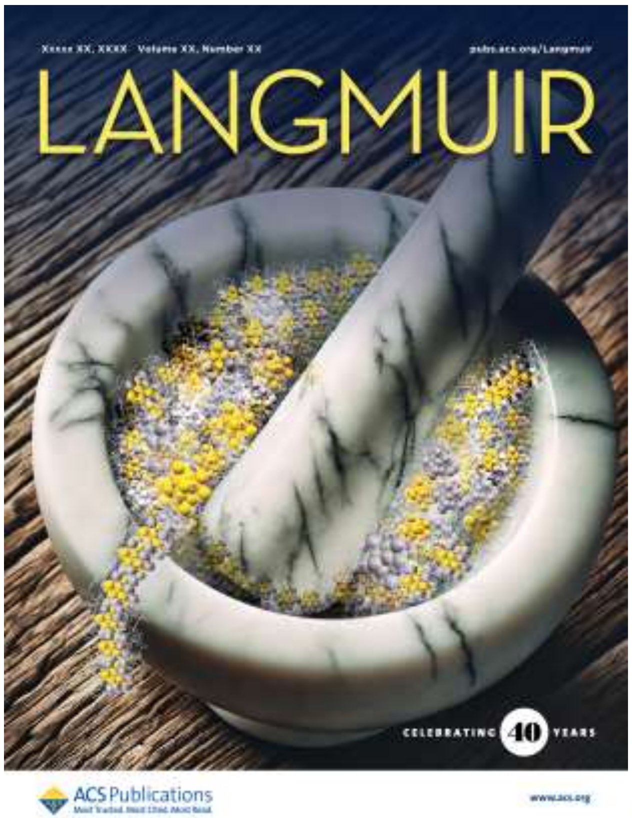
9-HS-1,7-$C_2B_{10}H_{11}$

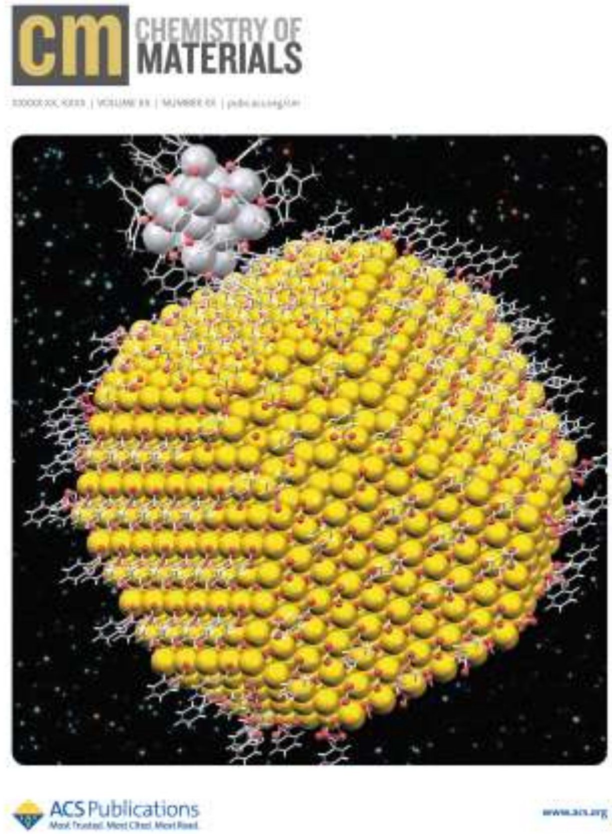
Amoghavasha Ramachandra Kini, et. al., *Chem. Mater.* 2025

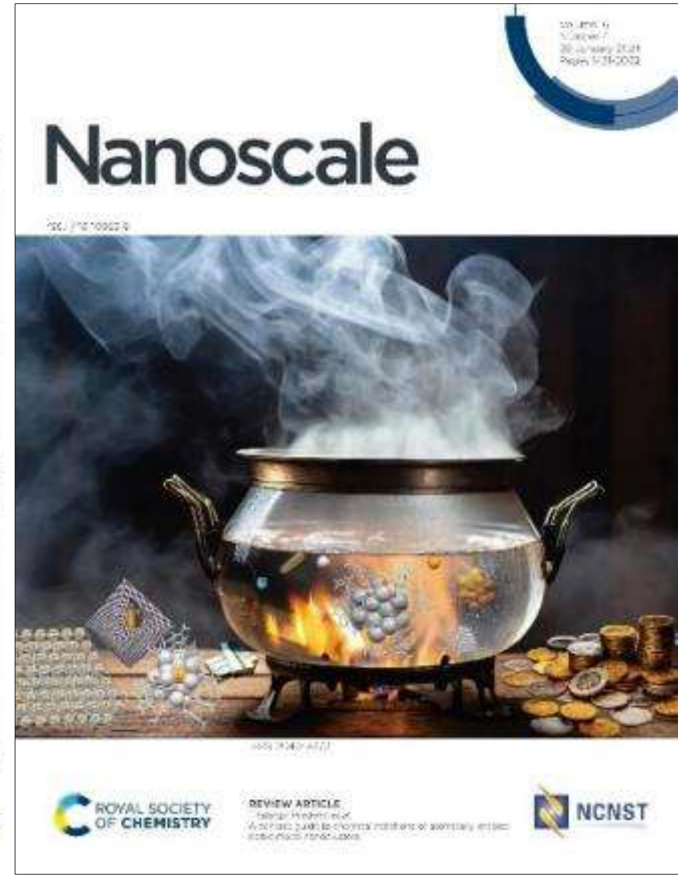
Nanomechanical Properties of Cu_4 Nanoclusters



❖ **Direct N^9-arylation of Guanine with Phenylboronic Acid Catalyzed by Cu-doped Silver Nanocluster**







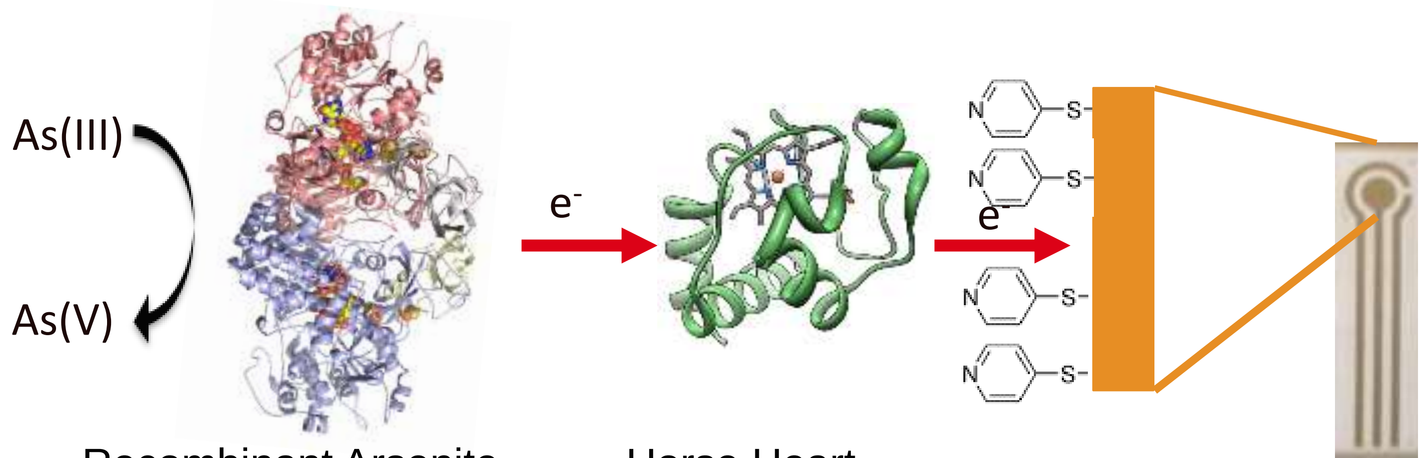
Department of Science and Technology

Institute of Eminence

Many Outstanding Individuals

Biosensor Design

1st Generation Design (Mediated Electrochemistry)



Buffer: pH 7-8

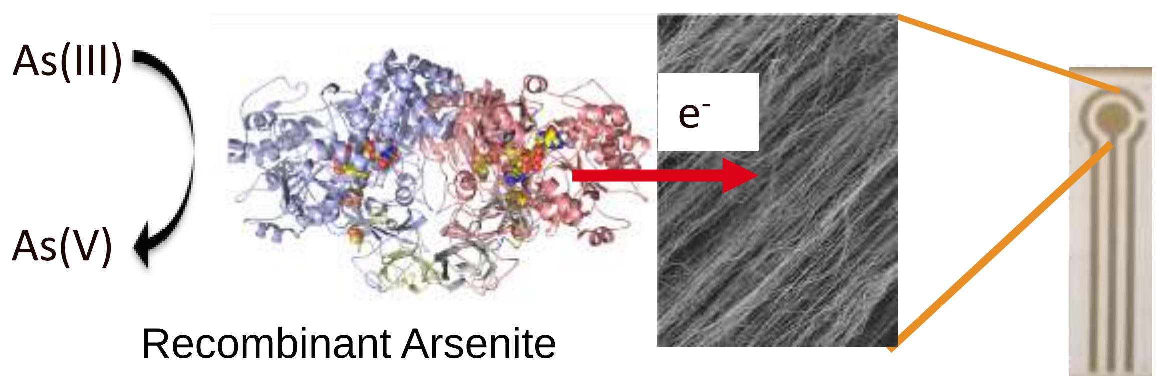
Recombinant Arsenite Oxidase NT-26 Aio

Horse Heart Cytochrome C

Aldrithiol

Low-cost Gold sputtered thin film on PET substrate

2nd Generation Design (Direct Electron Transfer)

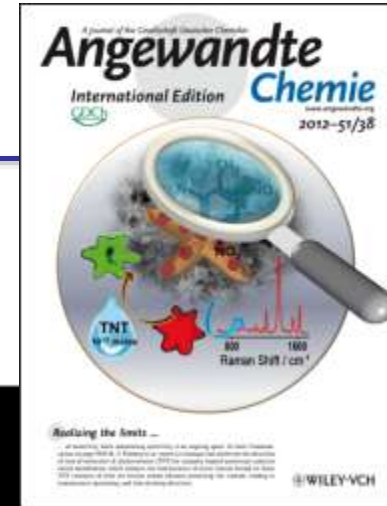


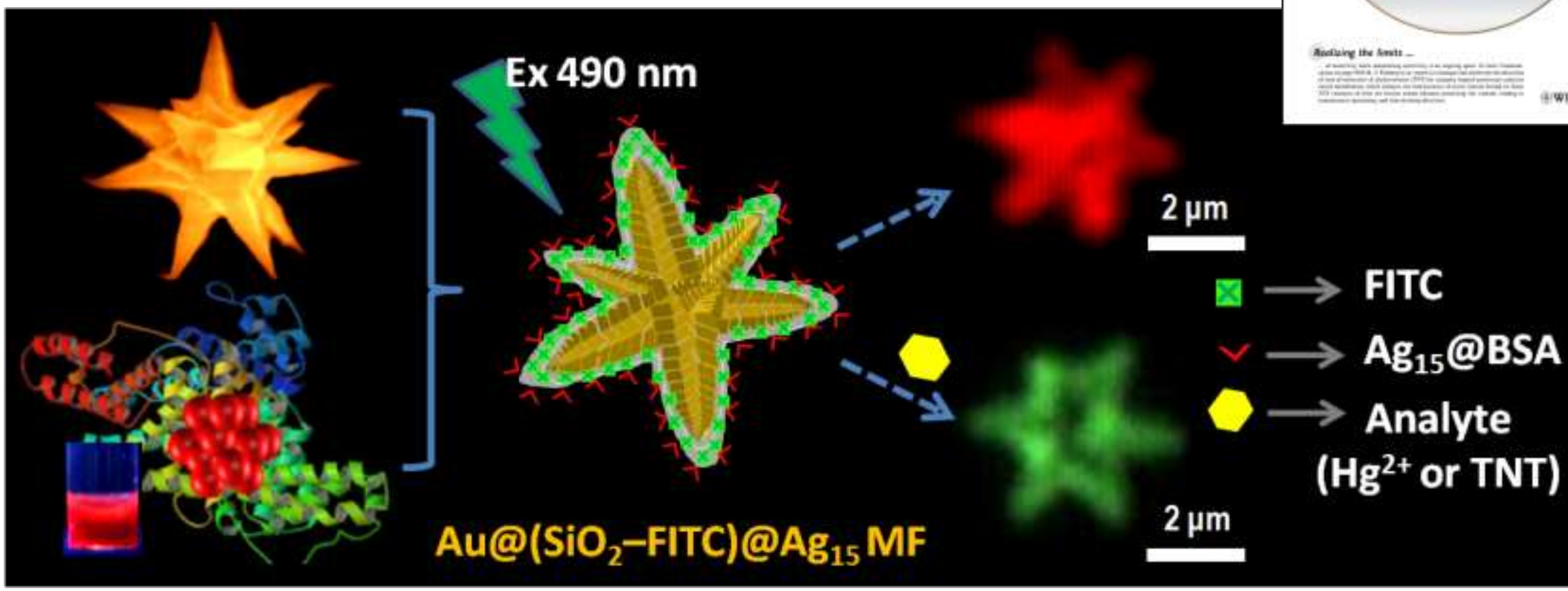
Recombinant Arsenite Oxidase NT-26 Aio

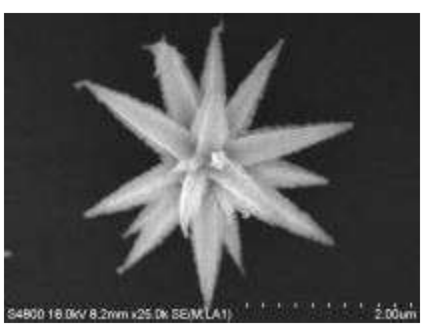
low-cost nanostructured electrodes which interact directly with enzyme (e.g. graphene or CNT).

Bio-nano Consulting & Imperial College, London

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

How do we know that they exist?

Table 1 Landmark events in the history of mass spectrometry and their importance in enabling the characterization of materials

Progress in instrumentation	Systems studied by MS		Resolution[6,134*,]	Mass range (m/z)[134,*]
1912 Measurement of m/z values by Thomson[3] 1918 Electron ionization[135] 1936-37 Secondary ion MS[136]	Isotopes of elements Atomic weights using MS[6]	early studies by MS	100 Aston (130)[5] 1,000	100 Aston (~100)[5] 1,000
1946 Time of flight[139] 1952 Double-focussing instruments[140] 1955 Advanced TOF[141] 1956 GC–MS,[7,8] high-resolution MS[142] 1953-58 Quadrupole analyzers[143] 1962 Ion mobility[144] 1966 Chemical ionization[145] 1967 Tandem MS[146]	1940s Organic mass spectrometry, Mixture of organic analytes could be separated by GC–MS[6]	Analysis of organic molecules	TOF (4000-5000 at m/z ~100)[137] 10,000 W geometry ortho-TOF (70,000 at m/z 316)[147]	Magnetic sector (~2000)[138] 10,000 FTICR (~29,000)[148]
1968 Electrospray ionization (ESI)[149] 1974 Fourier transform (FT) Ion cyclotron resonance[13], Atmospheric pressure chemical ionization[150] 1975 Surface-induced dissociation[151] 1978 Triple quadruple[152] 1981 Fast atom bombardment MS[153] 1987 MALDI[10,154] 1999 Orbitrap[14] 2004 Desorption electrospray ionization[155]	1980s high molecular-weight polymers, peptides, proteins, nucleic acids, ESI for macromolecules[6] 1996 Analysis of intact live viruses[156]	MS in proteomics and living cells	1,00,000 Orbitrap (6,00,000 at m/z 195)[15] 10,00,000	1,00,000 MALDI TOF (~2,00,000)[158] 10,00,000
	1985 Discovery of fullerenes by laser-induced vaporization[38] 1996 LDI for characterization of thiol-protected clusters[47] 2008 MS of intact $Au_{25}(PET)_{18}$ clusters[52] 2018 MS of $Au_{\sim 2000}$ NPs[124]	Analysis of materials with MS	FTICR (20,00,000 at m/z 66,000)[157]	Cryo MALDI TOF (~20,00,000)[159]

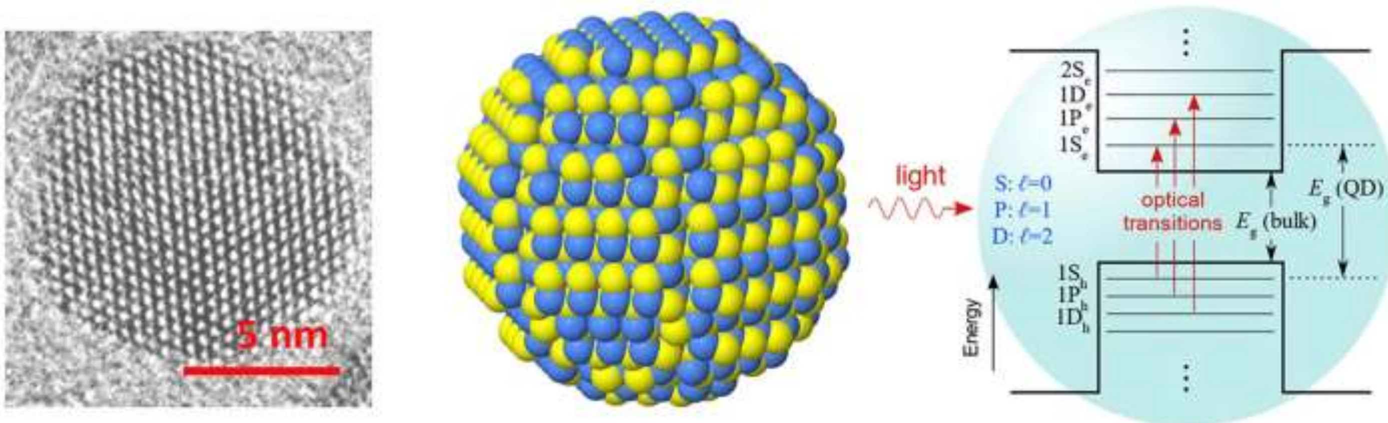
Charge detection MS

*Does not strictly correspond to the time evolution presented in the left column

Chakraborty and Pradeep *NPG Asia Materials* (2019) 11:48
https://doi.org/10.1038/s41427-019-0149-3

THE NOBEL PRIZE IN CHEMISTRY 2023

Illustration of quantum dots



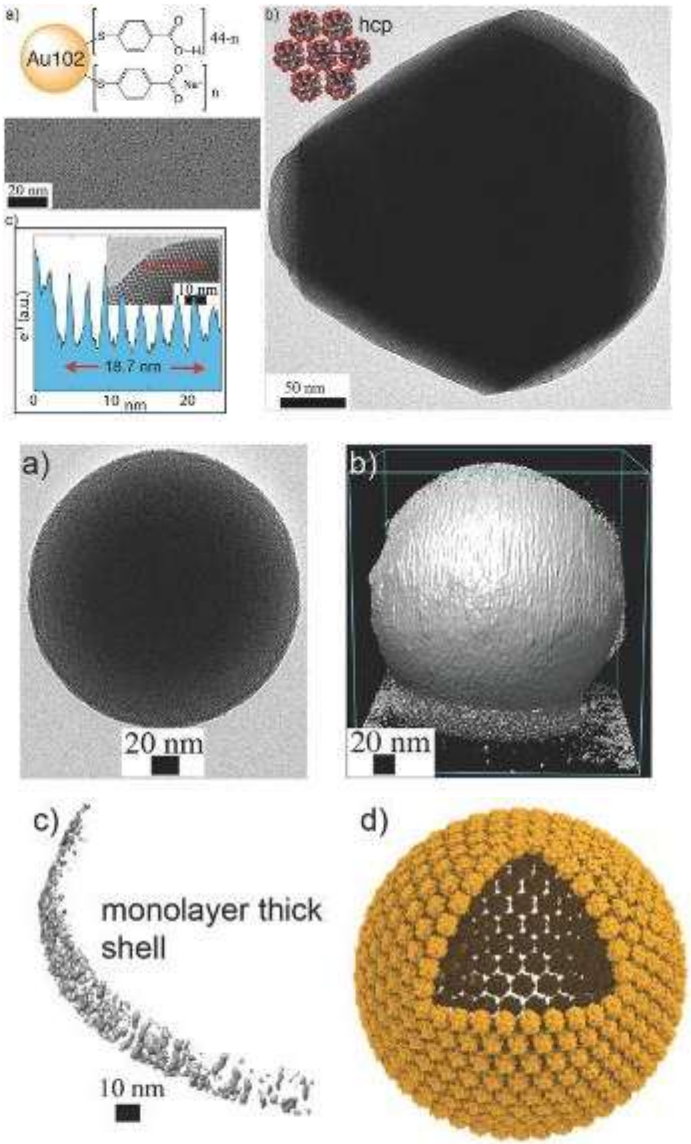
Left: transmission electron microscope image of a CdSe nanocrystal. Centre: Atomic structure of a nanocrystal. Right: Electronic states in a core-shell quantum dot, with the dot itself in the centre bracketed by a wide-bandgap shell.

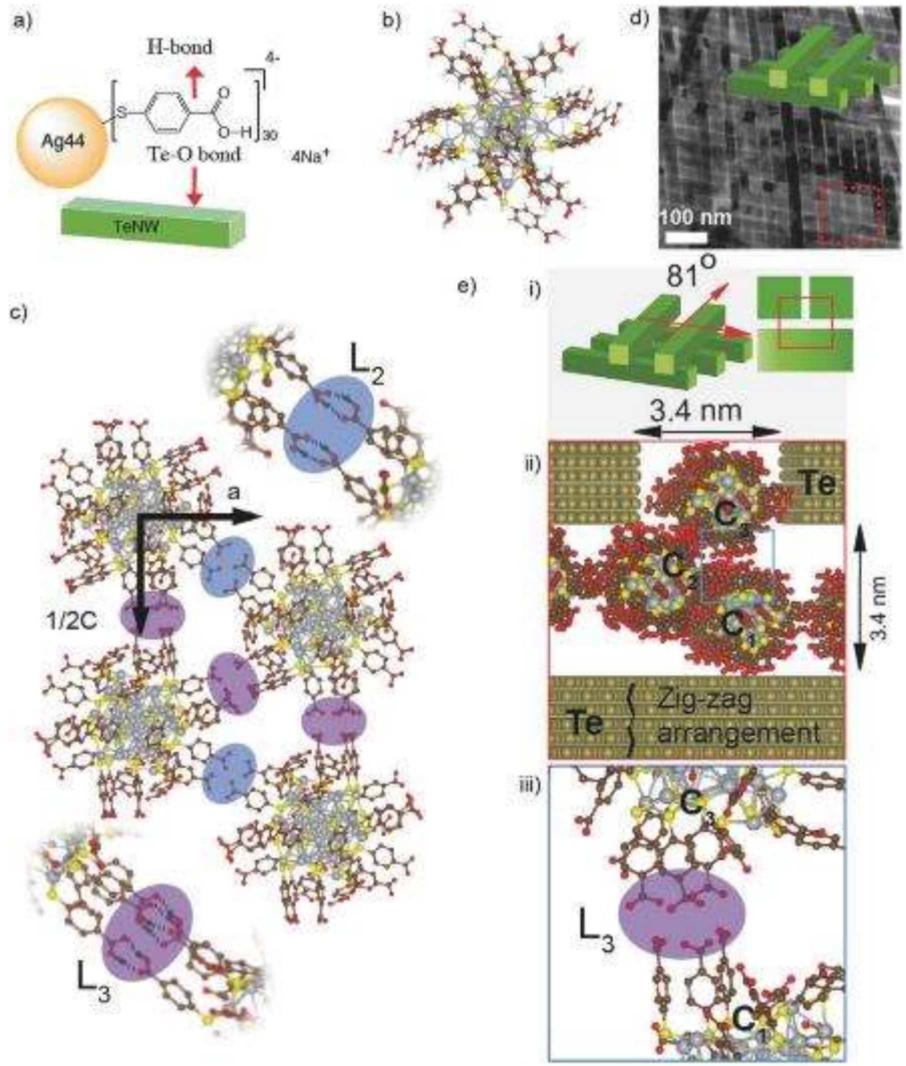
A. L. Efros and L.E. Brus, ACS Nano 15, 6192 (2021).

Today, ‘quantum dot’ refers to a nanostructure in which quantum mechanical effects manifest themselves in the electronic structure.

- Either through quantum size effects, many-body interactions (excitonic states) or high surface-to-volume ratio such that surface states dominate the electronic structure.
- In addition to a small size comparable to the carriers’ de Broglie wavelength, it is now recognized that the quantum phase coherence length (typically limited by inelastic scattering) needs to exceed the system size.

Nanoclusters in colloidal assemblies

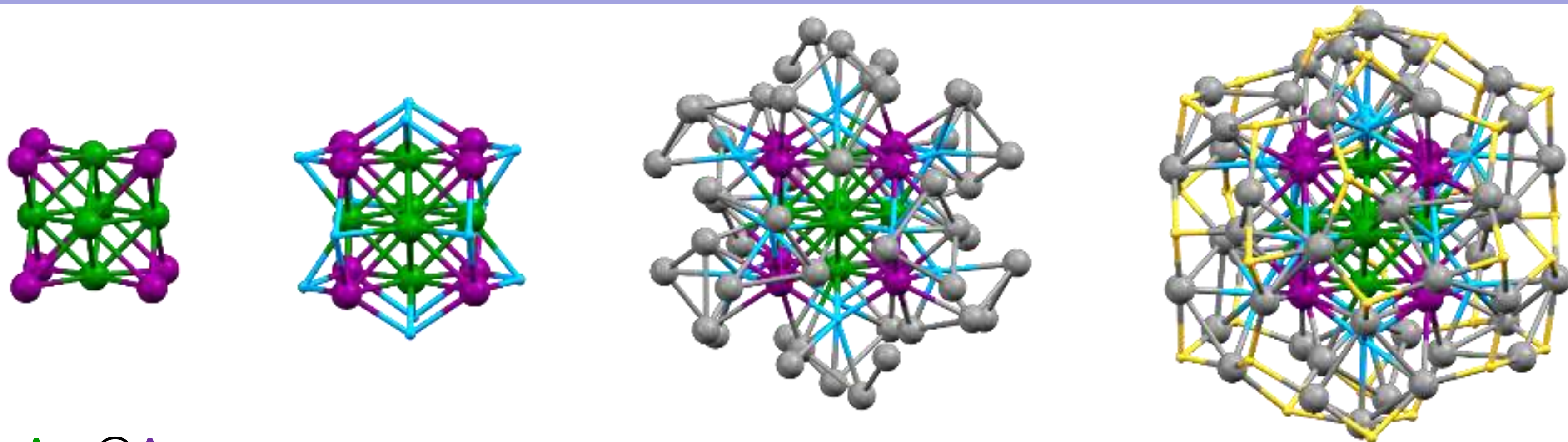




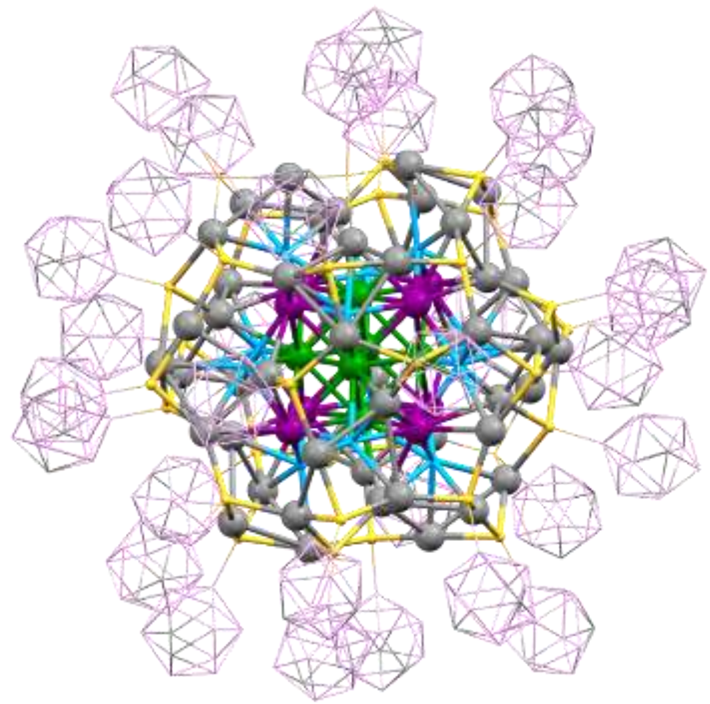
Som, A. et al., *Adv. Mater.* **2016**, *28*, 2827–2833

Nonappa et al., *Angew. Chem. Int. Ed.* **2016**, *55*, 16035–16038.

Structural anatomy of [$Ag_{62}S_{12}(CBT)_{32}$] Nanocluster

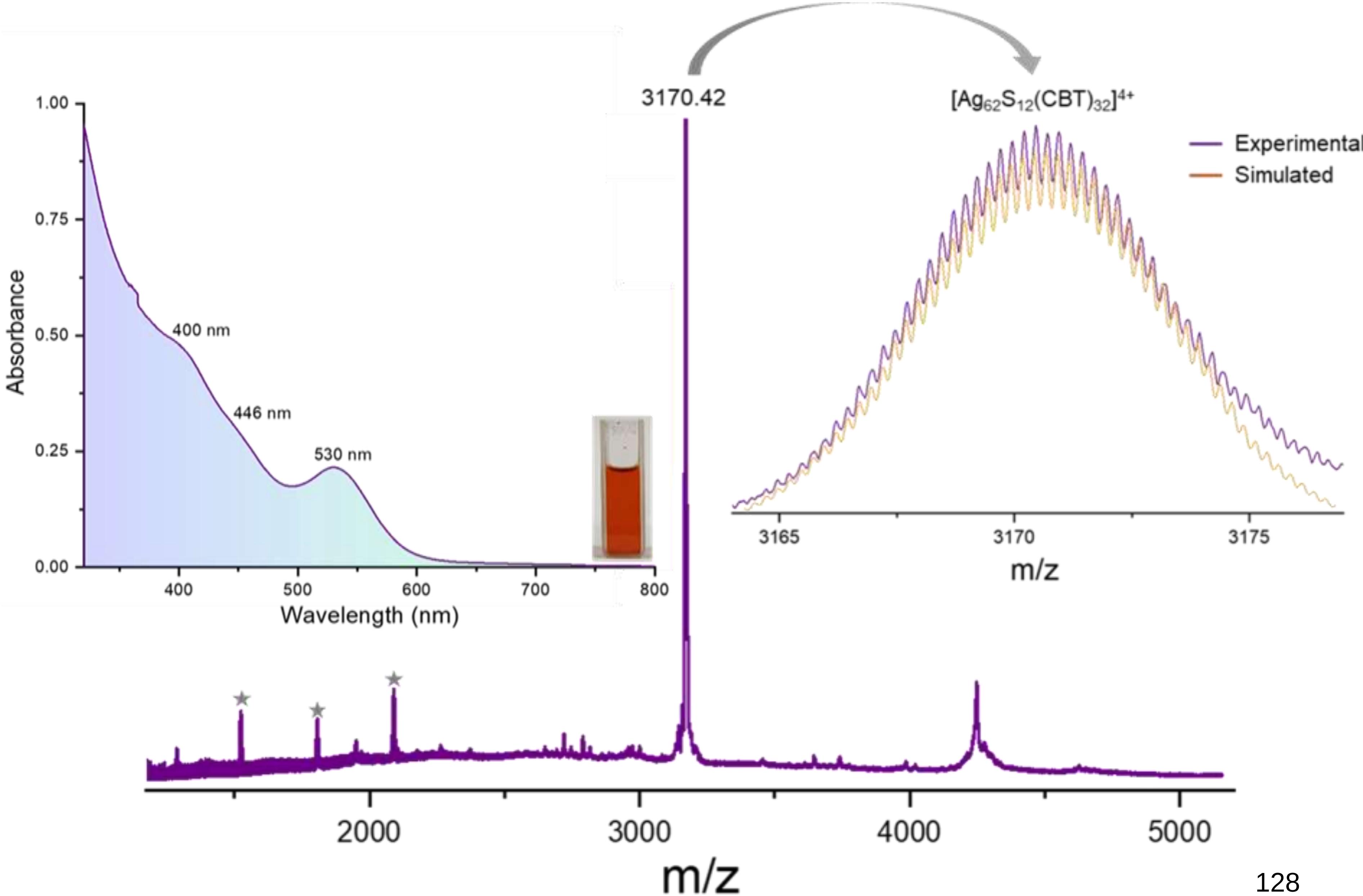


$Ag_6@Ag_8$ $Ag_6@Ag_8S_{12}$ $Ag_6@Ag_8S_{12}@Ag_{48}$ $Ag_6@Ag_8S_{12}@Ag_{48}S_{32}$



$Ag_6@Ag_8S_{12}@Ag_{48}S_{32}(CB)_{32}$

Characterization of Ag_{62} cluster



Gas phase

International Journal of Mass Spectrometry and Ion Processes, 74 (1986) 33–41 33
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MASS DISTRIBUTIONS OF NEGATIVE CLUSTER IONS OF COPPER, SILVER, AND GOLD

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(First received 6 May 1986; in final form 27 August 1986)

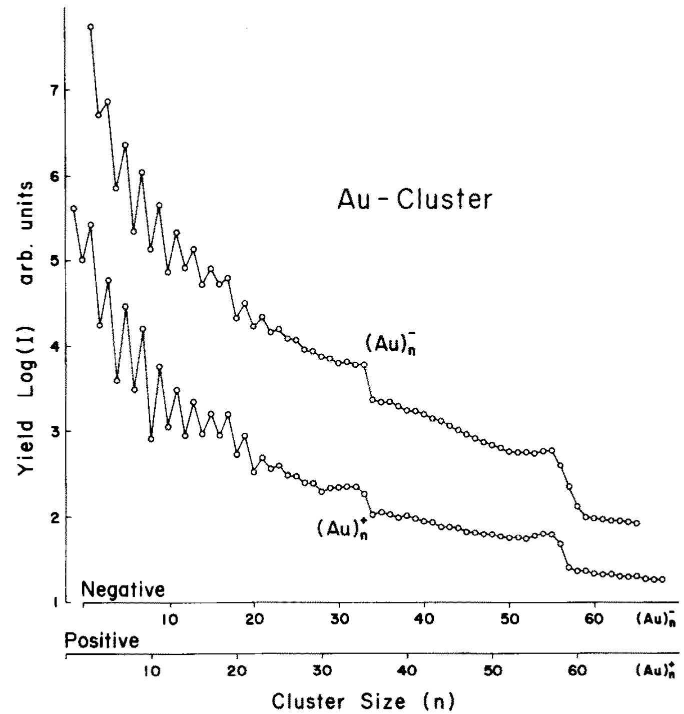

Fig. 2. Size distributions of gold clusters, $(Au)_n^-$ (upper curve) and $(Au)_n^+$ (lower curve), plotted on a logarithmic scale.