



Now in the 64th year

Atomically Precise Metal Clusters

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Gas phase

PRODUCTION OF LARGE SODIUM CLUSTERS (Na_x , $x \leq 65$) 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

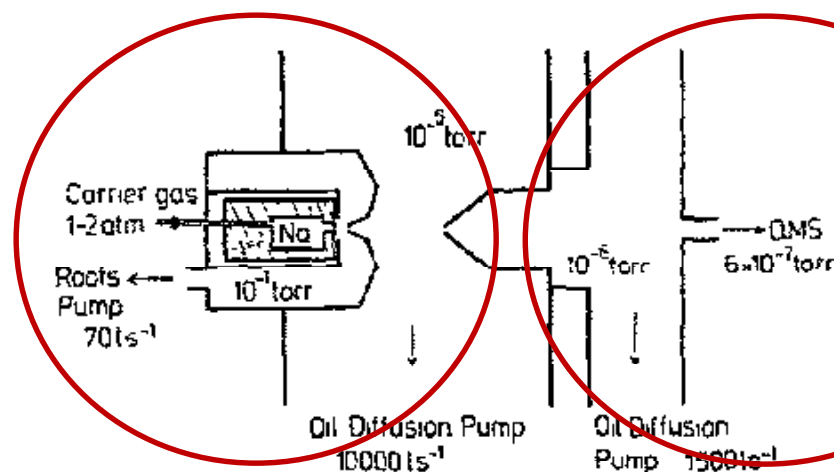


Fig. 1 Schematic of the seeded-beam apparatus.

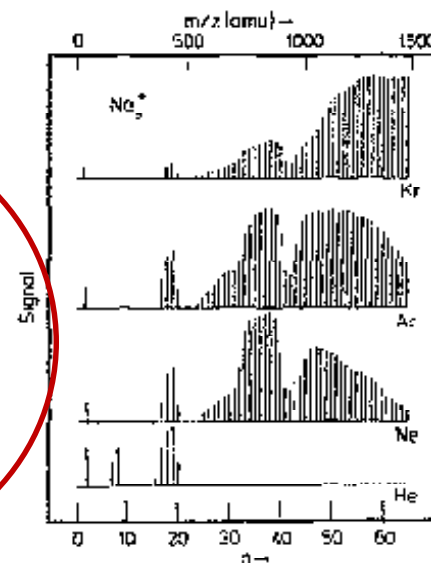
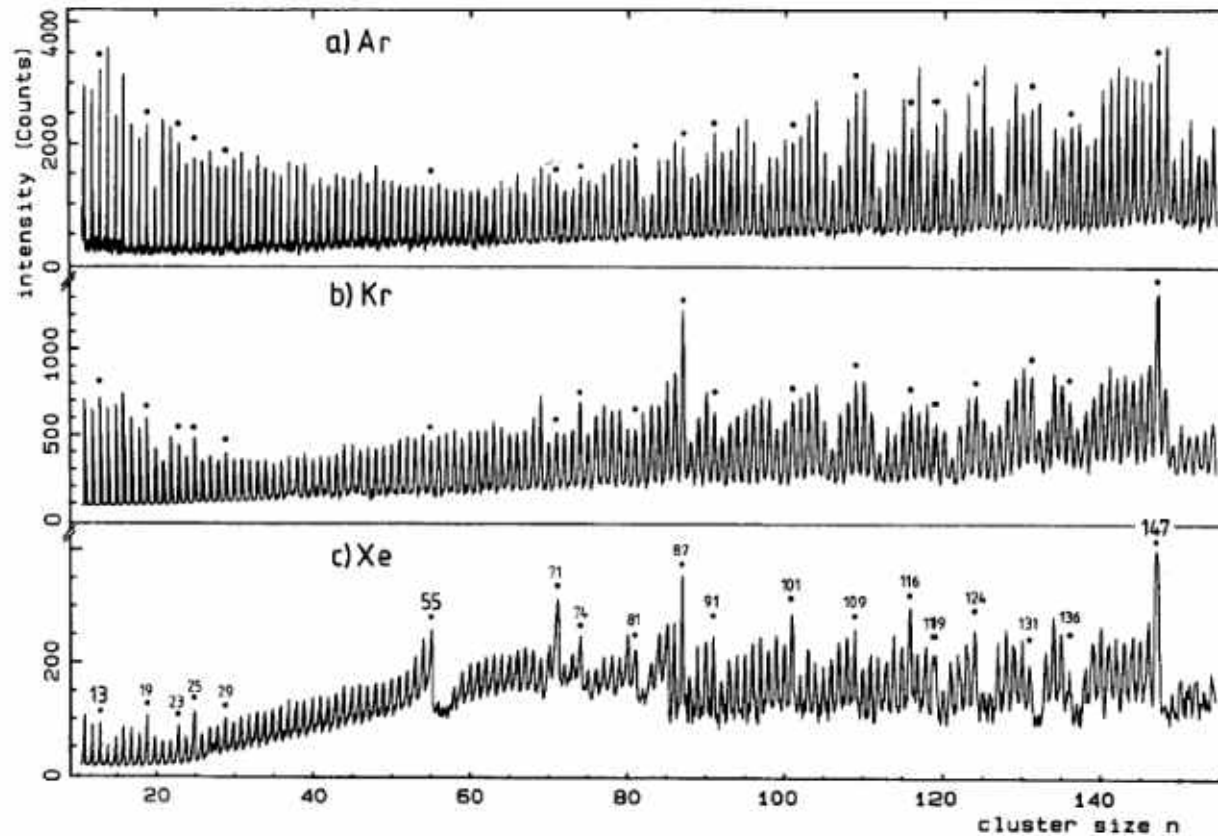


Fig. 3. Data sets showing the results of high-mass scans measured for four different backing gases. The mass spectra upon which these representations are based were obtained at a resolution ($m/\Delta m$) of 400 and a maximum signal-to-noise ratio of 20. Backing pressures were 1-3 atm for all three gases. 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.

Gas phase

International Journal of Mass Spectrometry and Ion Processes, 74 (1986) 33-41
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)

33

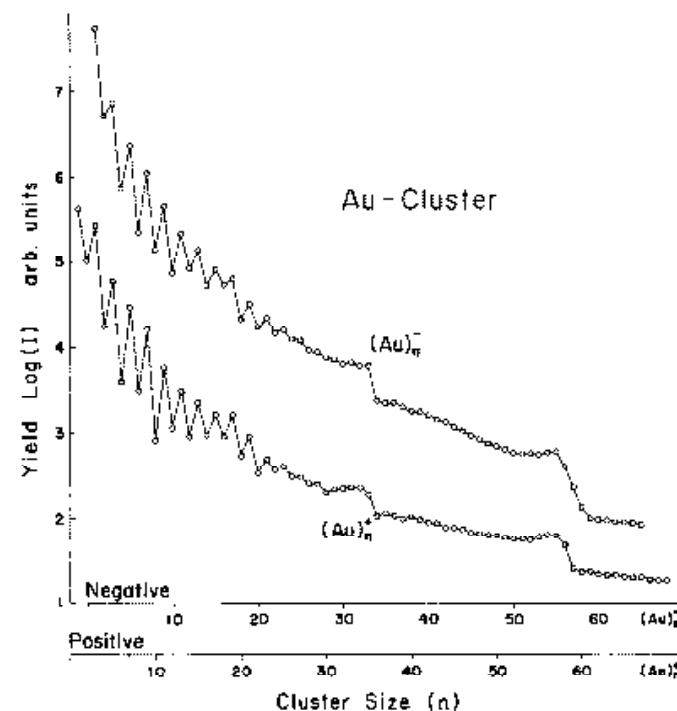


Fig. 2. Size distributions of gold clusters. $(Au)_n^-$ (upper curve) and $(Au)_n^+$ (lower curve), plotted on a logarithmic scale.

Magic clusters

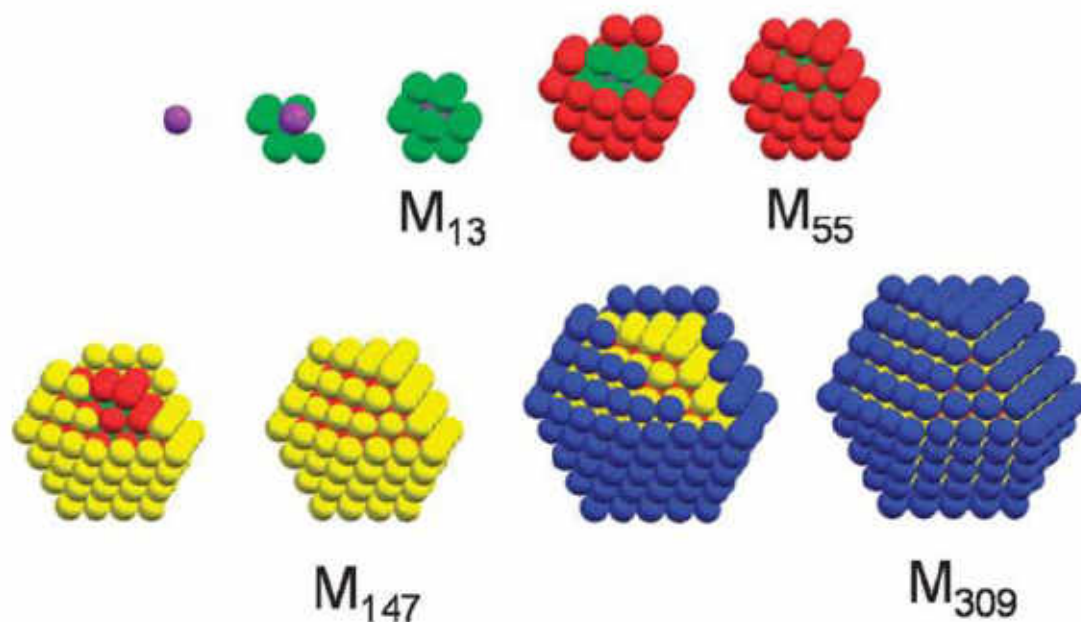


Fig. 1 Organization of full-shell clusters: a first single atom (purple) is surrounded by 12 others (green) to give a one-shell cluster M_{13} . 42 atoms (red) can be densely packed on the 12 green atoms ending with the M_{55} two-shell cluster, followed by 92 atoms (yellow) and 162 atoms (blue) to give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

C₆₀: 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

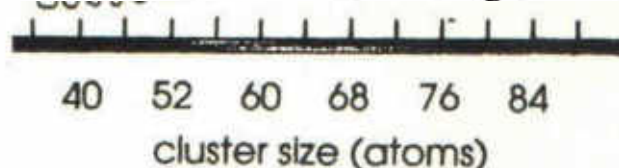
During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells¹, graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what 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 C₆₀ 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.

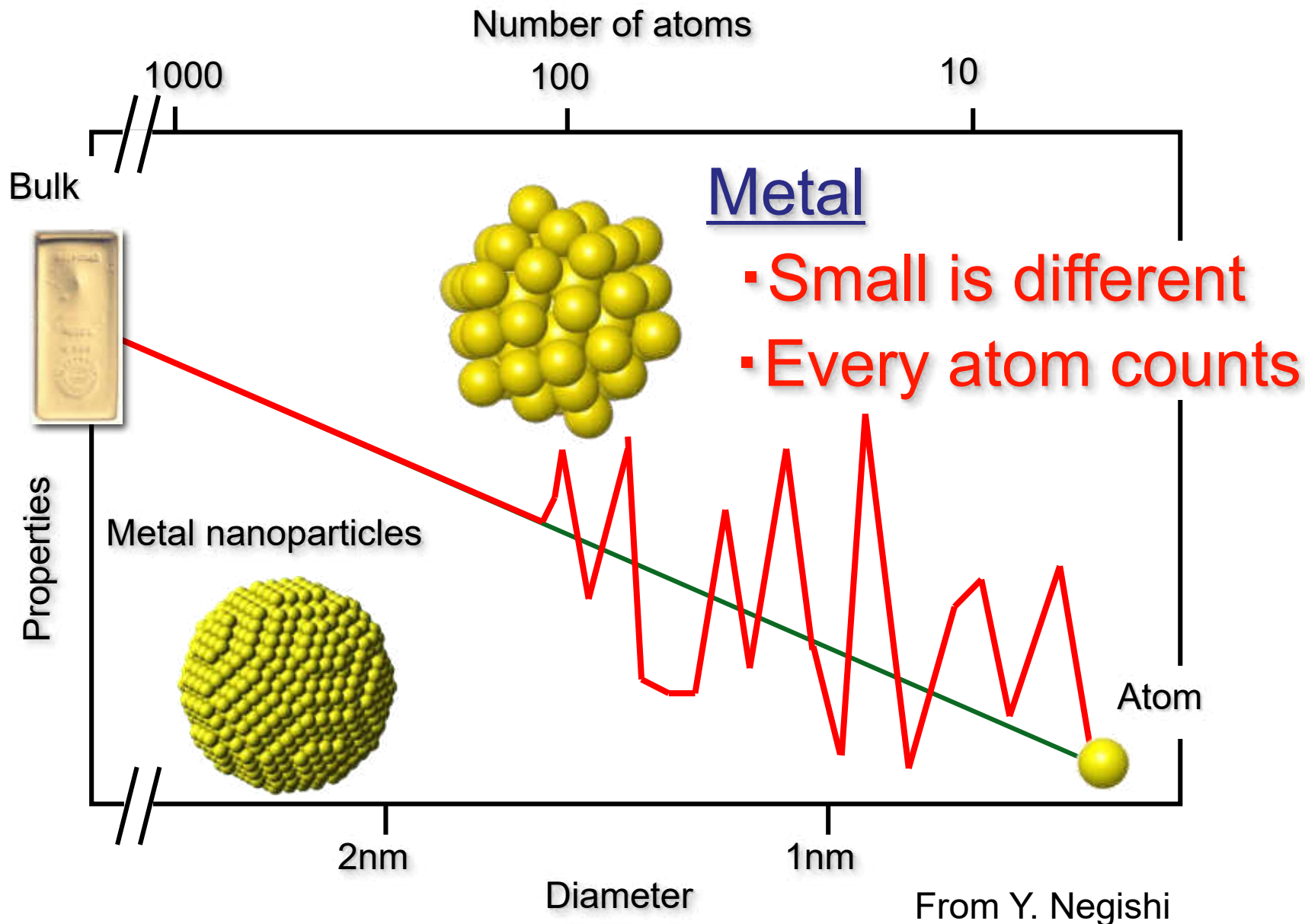
Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C₆₀ molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

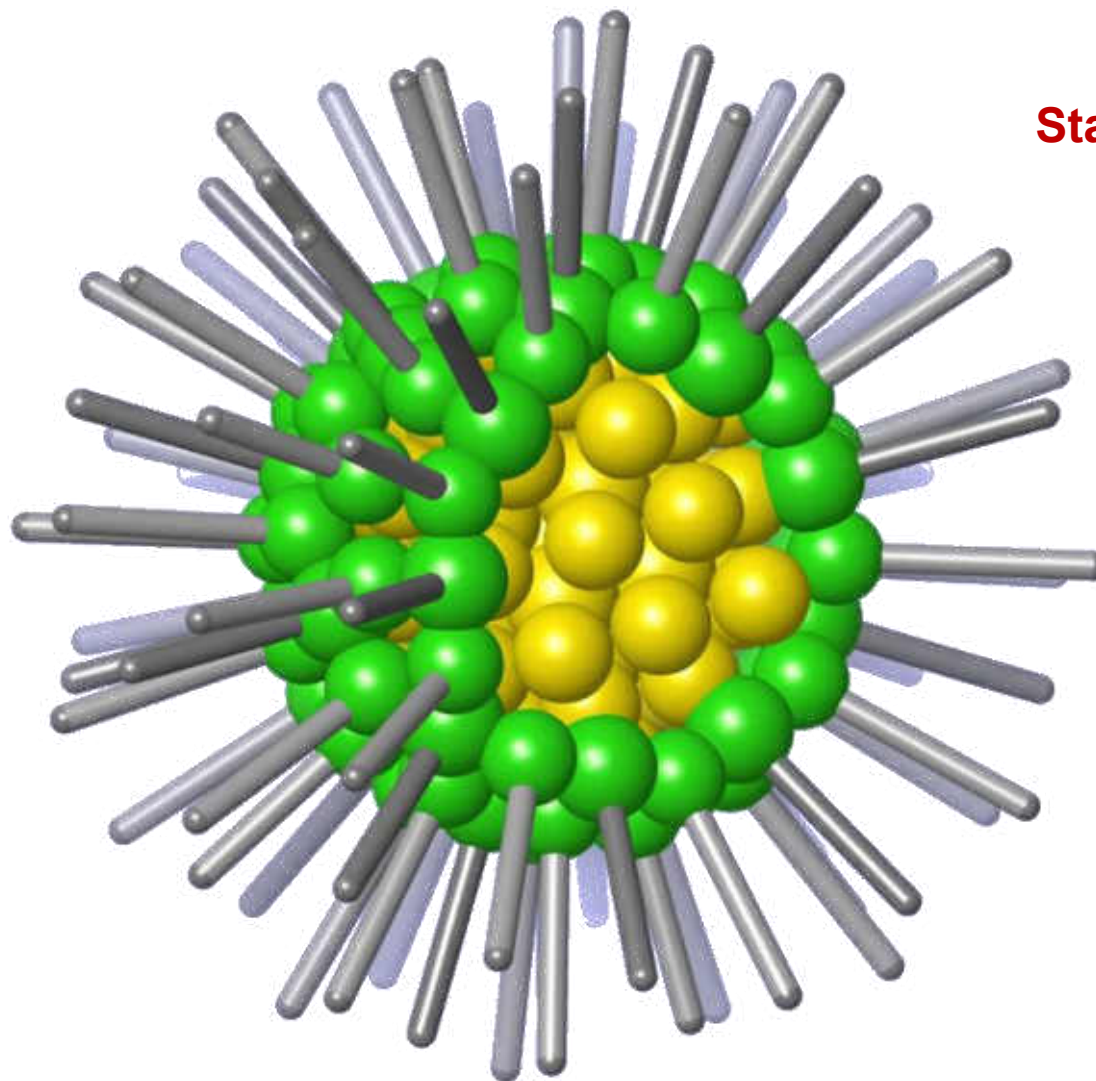


graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions 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







Stable clusters

From Y. Negishi



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	Isotopes of elements Atomic weights using MS ⁶	← 100 Aston (130) ⁵	← 100 Aston (~100) ⁵
1918	Electron ionization ¹³⁵			
1936-37	Secondary ion MS ¹³⁶			
1946	Time of flight ¹³⁹	1940s Organic mass spectrometry, Mixture of organic analytes could be separated by GC-MS ⁶	← 1,000 TOF (4000-5000 at m/z ~100) ¹³⁷	← 1,000 Magnetic sector (~2000) ¹³⁸
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	1980s high molecular-weight polymers, peptides, proteins, nucleic acids, ESI for macromolecules ⁶ 1996 Analysis of intact live viruses ¹⁵⁶	← 10,000 W geometry ortho-TOF (70,000 at m/z 316) ¹⁴⁷	← 10,000 FTICR (~29,000) ¹⁴⁸
1967	Tandem MS ¹⁴⁶			
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 quadrupole ¹⁵²			
1981	Fast atom bombardment MS ¹⁵³	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-2000 NPs ¹²⁴	← 1,00,000 Orbitrap (6,00,000 at m/z 195) ¹⁵	← 1,00,000 MALDI TOF (~2,00,000) ¹⁵⁸
1987	MALDI ^{10,154}			
1999	Orbitrap ¹⁴			
2004	Desorption electrospray ionization ¹⁵⁵			
		Analysis of materials with MS	← 10,00,000 FTICR (20,00,000 at m/z 66,000) ¹⁵⁷	← 10,00,000 Cryo MALDI TOF (~20,00,000) ¹⁵⁹

Charge detection MS

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

Synthetic methods

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

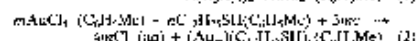
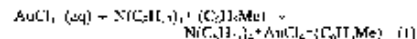
Department of Chemistry, The University of Liverpool, PO Box 147, Liverpool, UK L69 3BX

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 time¹ 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 losing 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 Fajana,⁴ who reduced an aqueous gold salt with phosphorus in carbon disulphide 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 monolayer-coated 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 tetrabutylammonium bromide as the phase-transfer reagent and reduced with aqueous sodium borohydride in the presence of dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$). 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



source of electrons is BHT.⁷ The conditions of the reaction determine the ratio of thiol to gold, i.e. the ratio m/n . The preparation technique was as follows. An aqueous solution of hydrogen tetrachloroaurate (20 ml, 0.1 mmol dm⁻³) was mixed with a solution of tetrabutylammonium bromide in toluene (80 ml, 50 mmol dm⁻³). The two phase mixture was vigorously stirred until all the tetrachloroaurate was transferred into

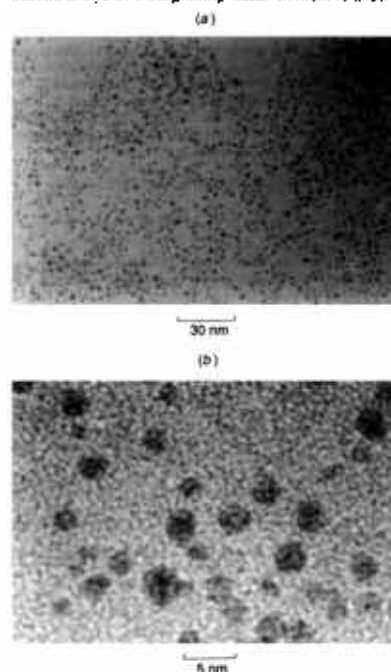


Fig. 4 TEM pictures of the thiol derivatised gold nanoparticles: (a) low and (b) high magnification

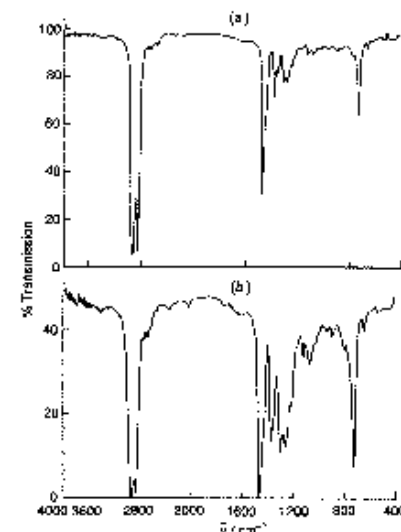


Fig. 2 IR spectra of (a) dodecanethiol and (b) nanoparticles prepared in toluene solvent. The particles were deposited on an NaCl disc by evaporation of a drop of a toluene solution.

Observing such clusters

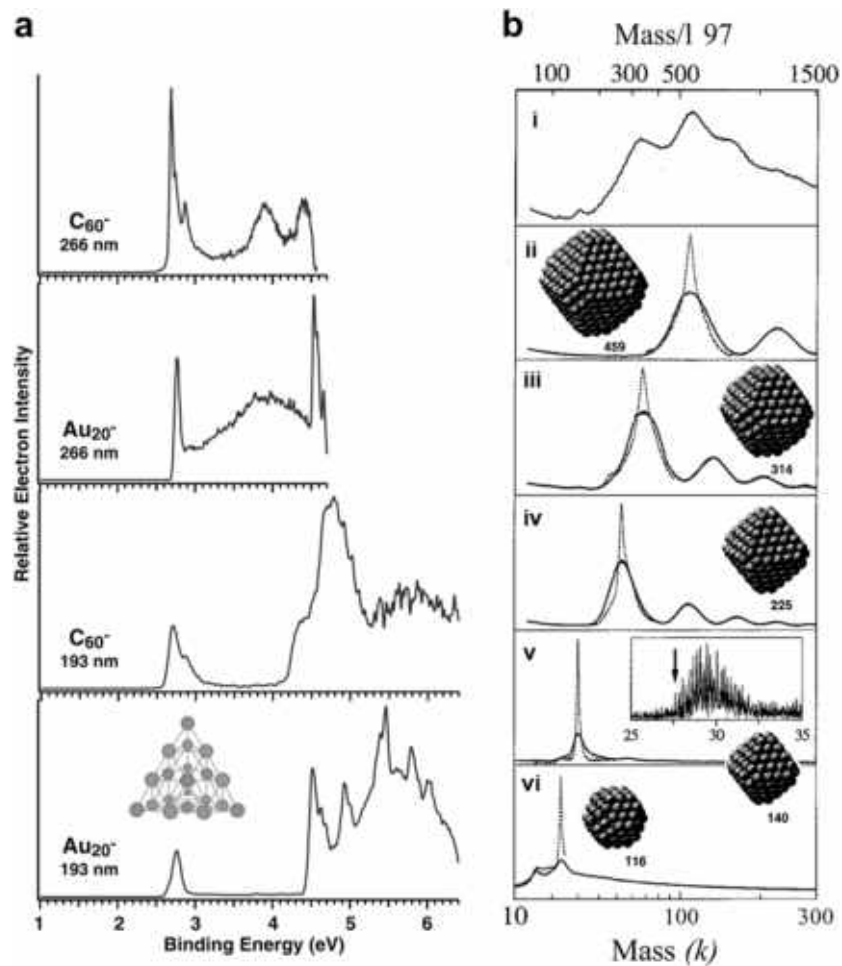
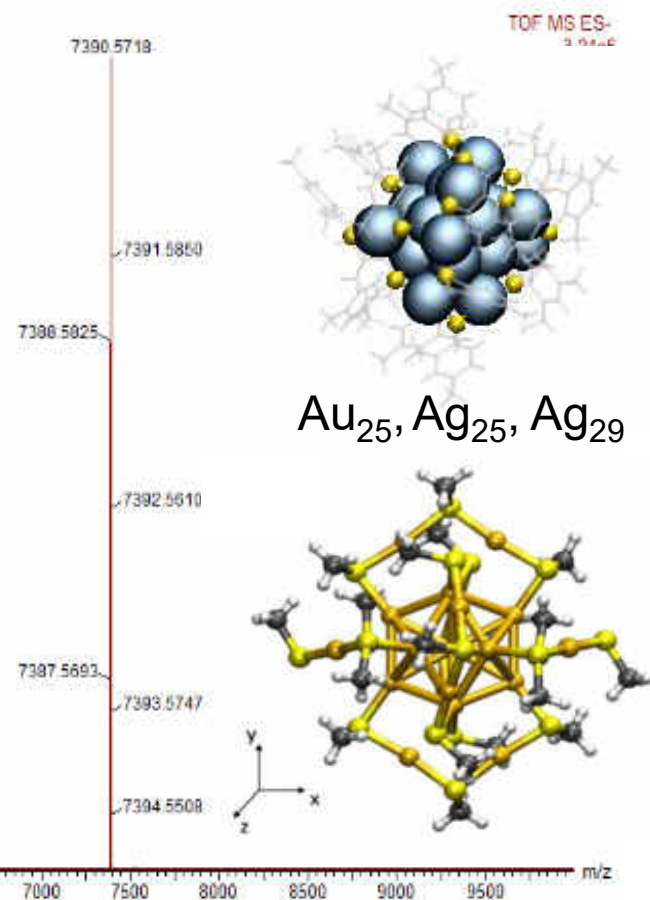
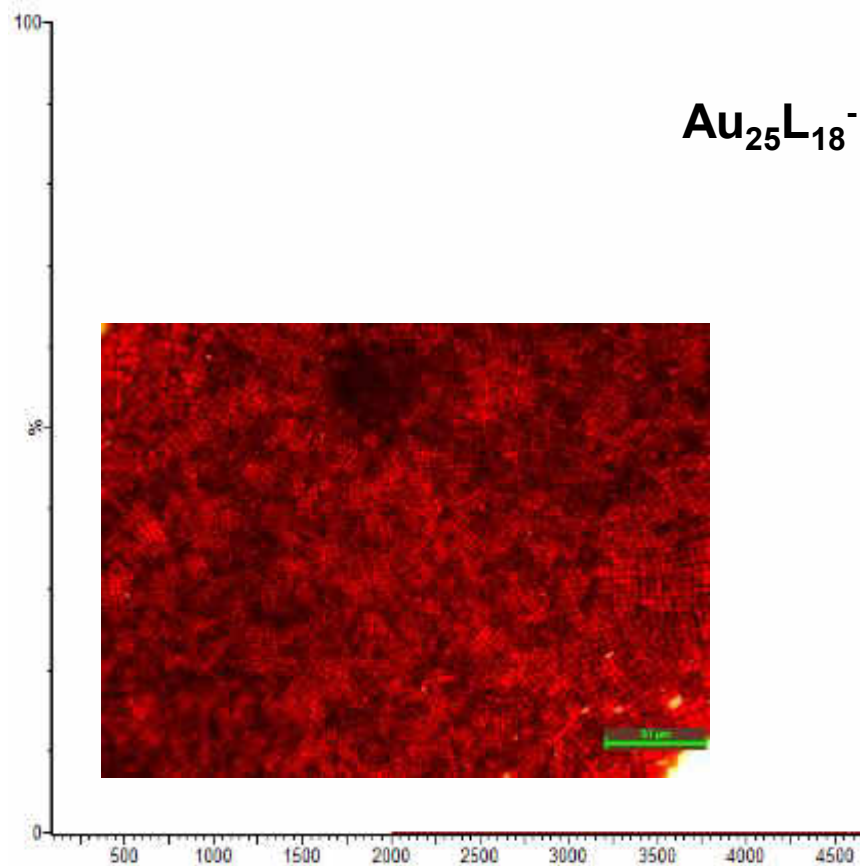


Fig. 2 Early stages of MS of noble metal clusters. **a** Photoelectron spectra of Au_{20}^- cluster compared with C_{60}^- at 193 nm and 266 nm⁴⁵. (Copyright© 2003 the American Association for the Advancement of Science) **b** Mass spectra obtained by laser desorption ionization of dodecanethiol thiol-protected gold clusters, (i) crude mixture of clusters and (ii–vi) separated fractions⁴⁷. (Copyright© 1996 John Wiley and Sons)

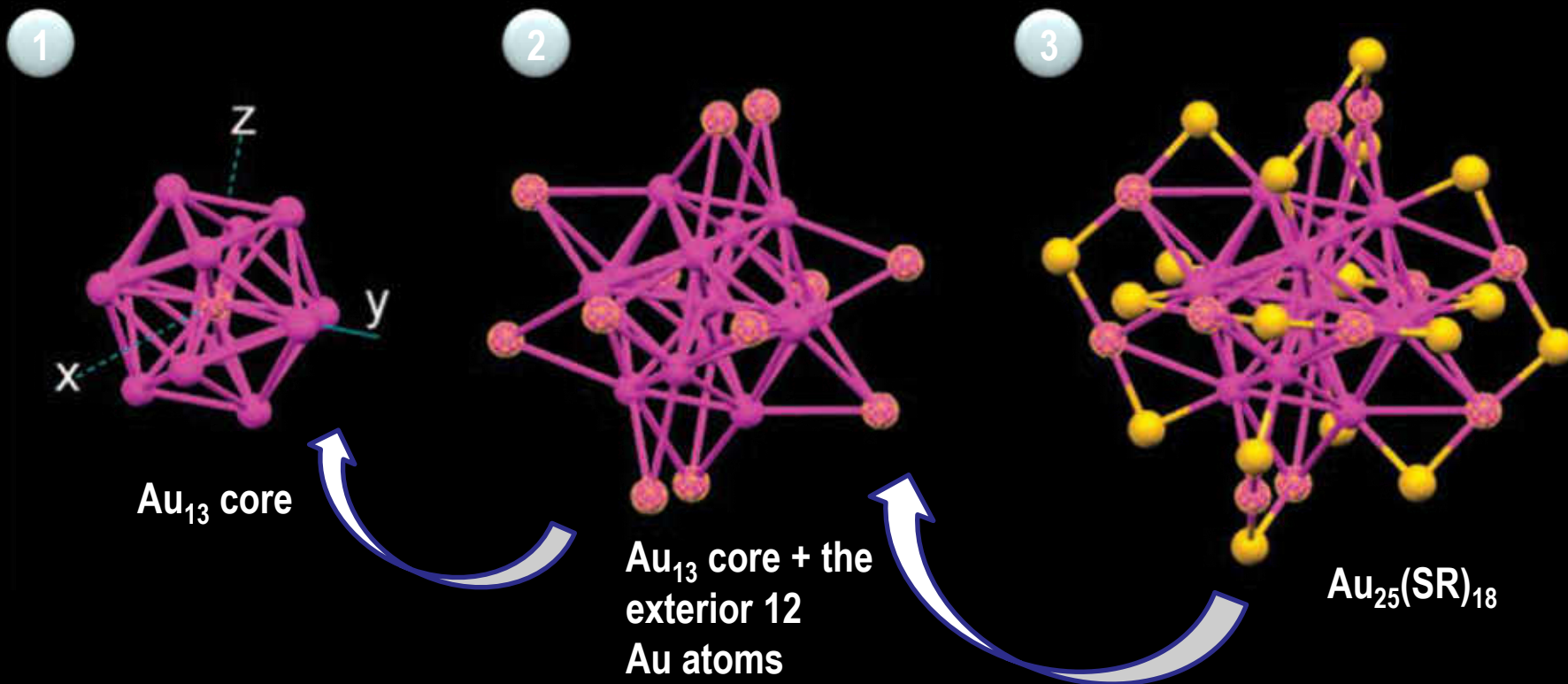
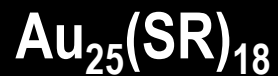
Atomically precise metal clusters as materials

AU25PET18_RES_NEG_MS_3 32 (0.558) Cm (5:00)

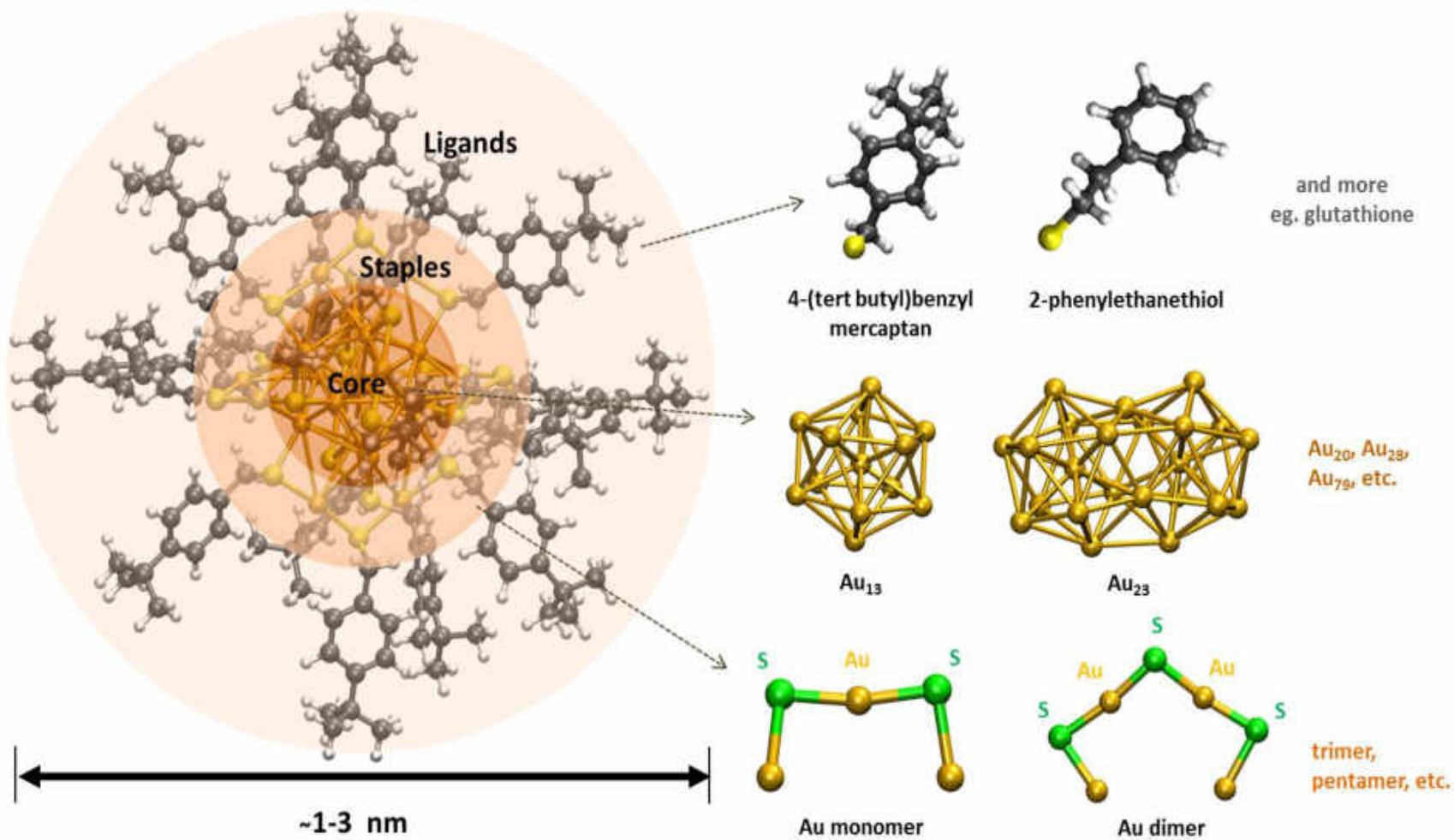


T. Pradeep et. al. *Acc. Chem. Res.* 2018; 2019.

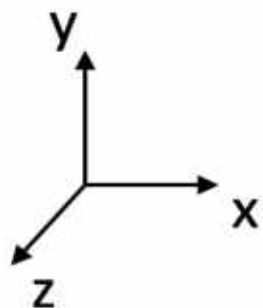
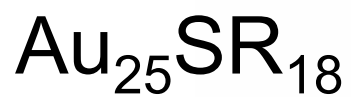
Structures



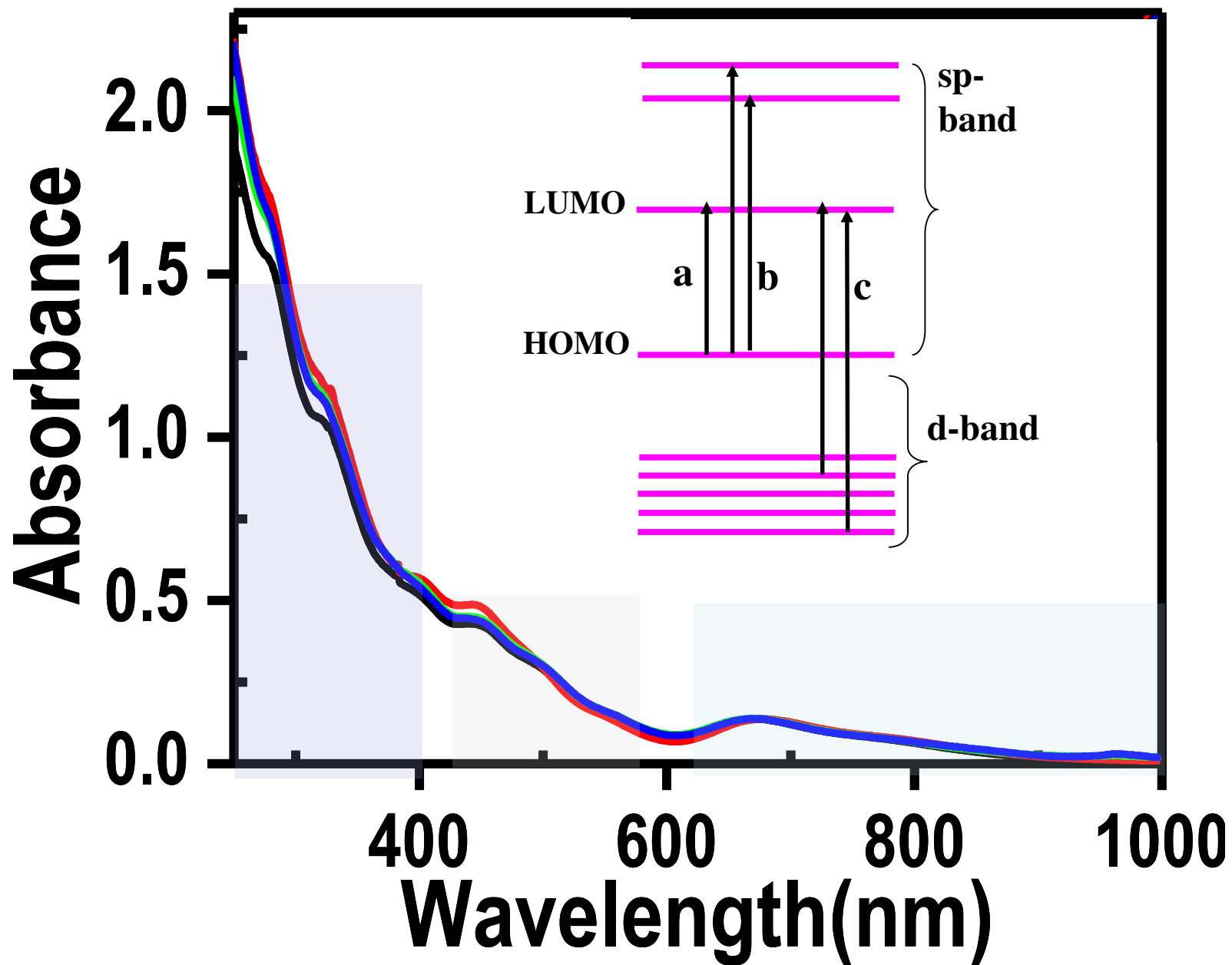
>150 such clusters



(a)



Geometric and electronic stability

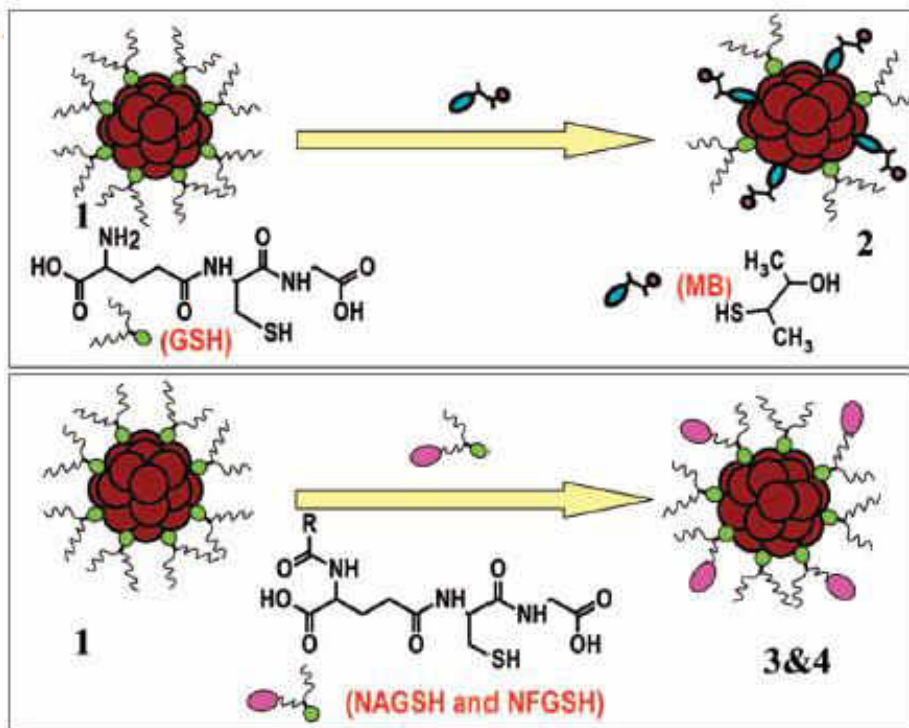


Ligand Exchange of Au₂₅SG₁₈ Leading to Functionalized Gold Clusters: Spectroscopy, Kinetics, and Luminescence

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

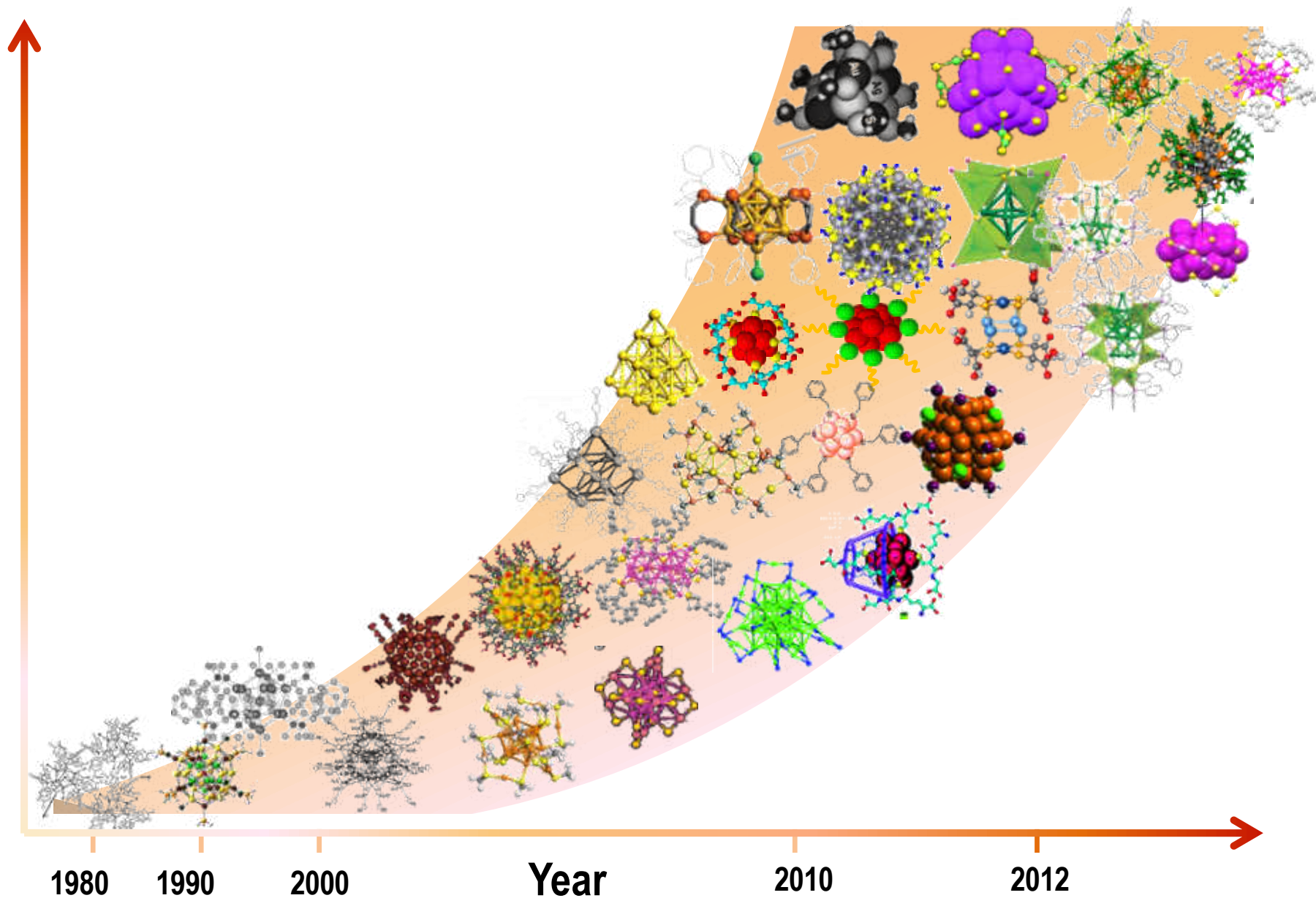
DST Unit on Nanoscience (DST UNS), Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Madras, Chennai 600 036, India and Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Received: January 18, 2008;

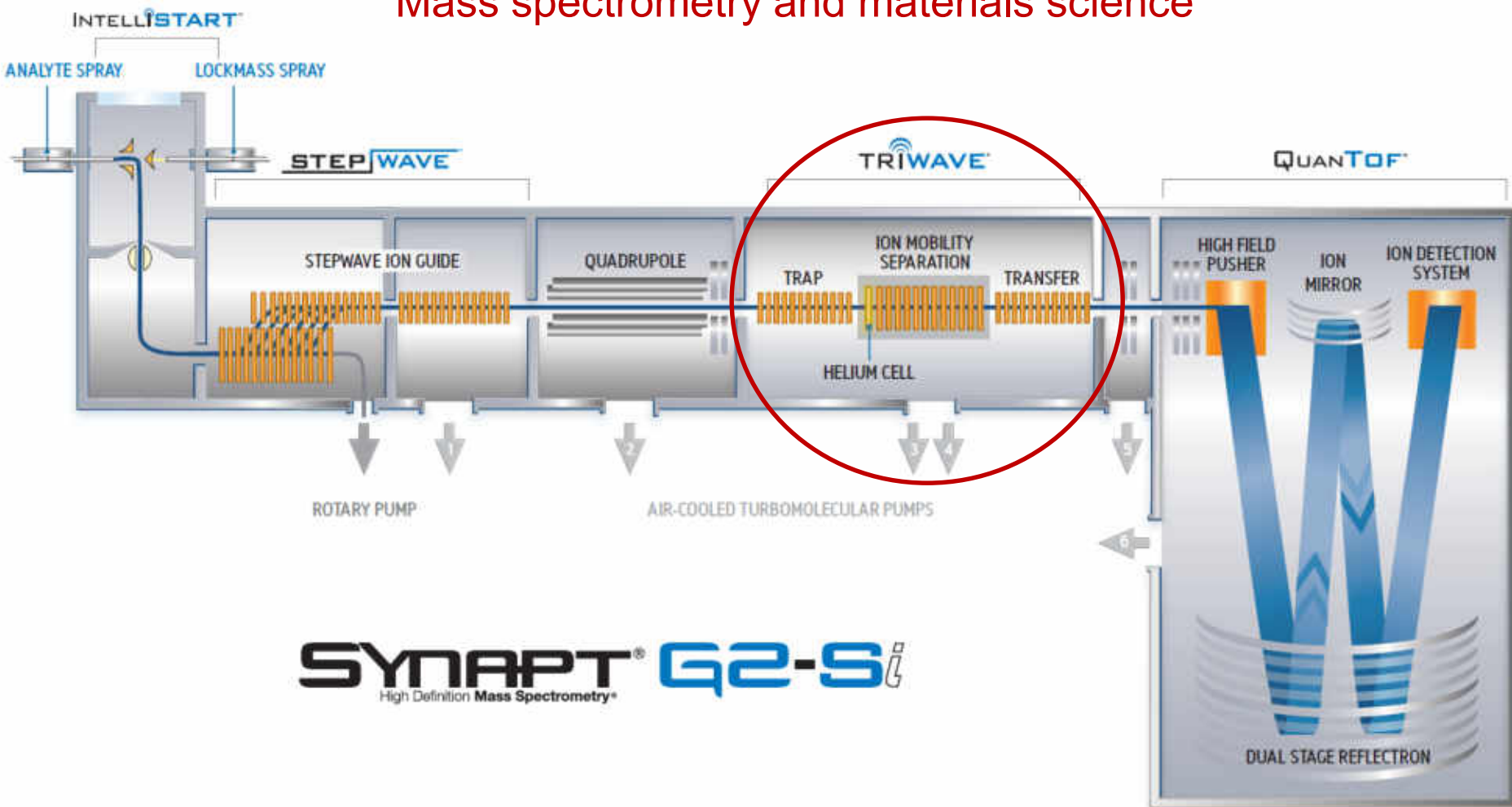


With Tatsuya Tsukuda

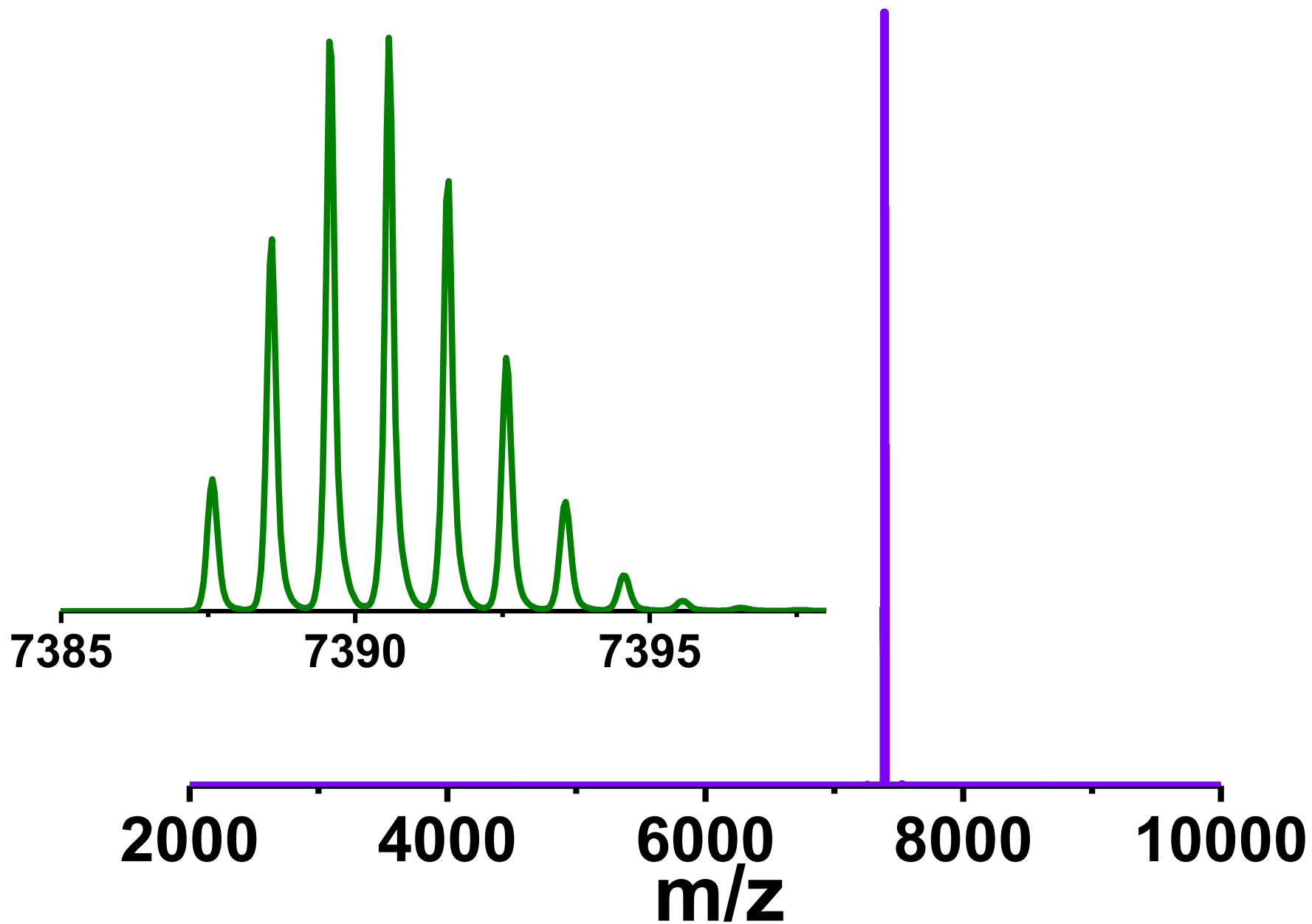
Evolution of noble metal clusters



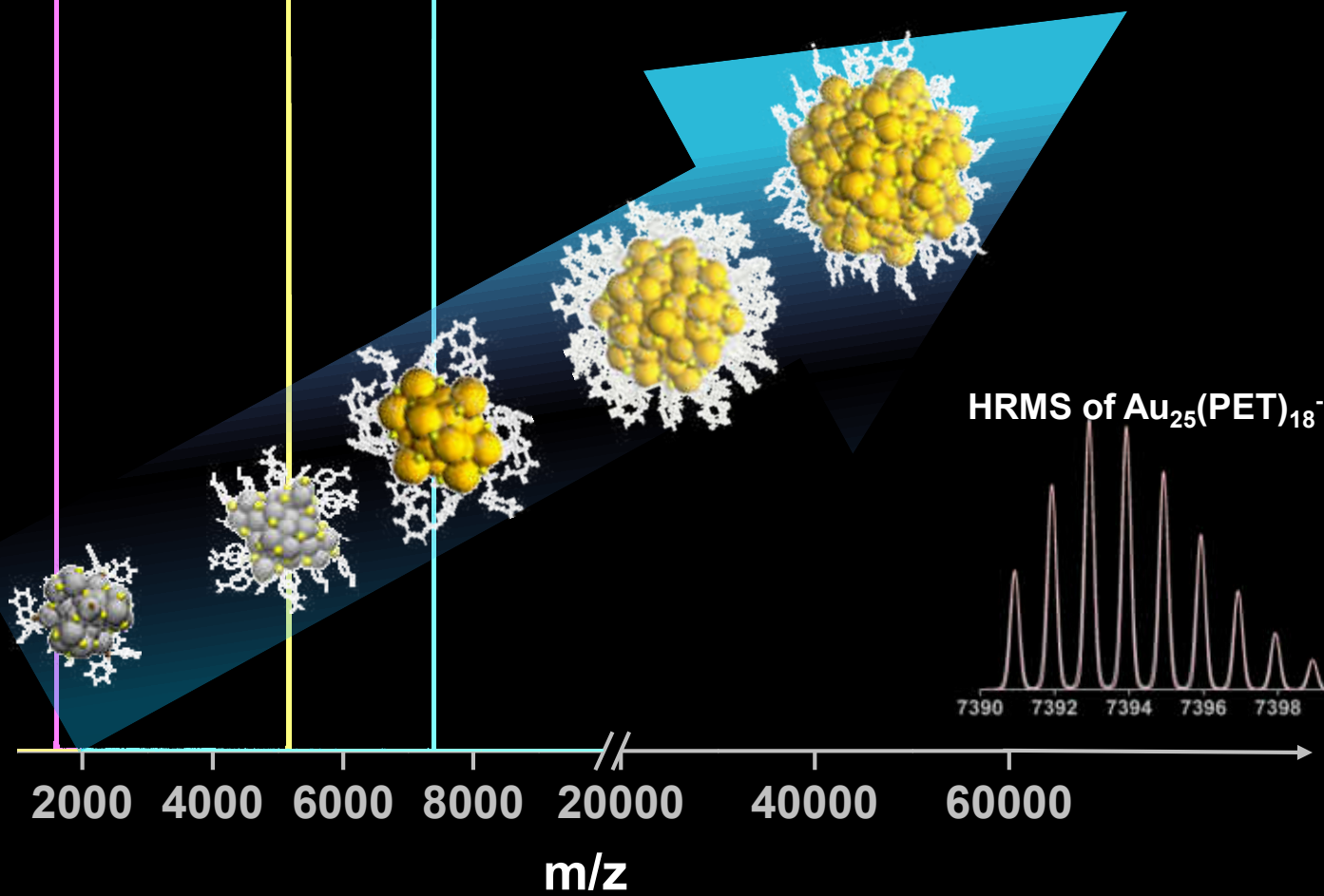
Mass spectrometry and materials science



$\text{Au}_{25}(\text{PET})_{18}^-$



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



Molecular materials

ACCOUNTS

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Article

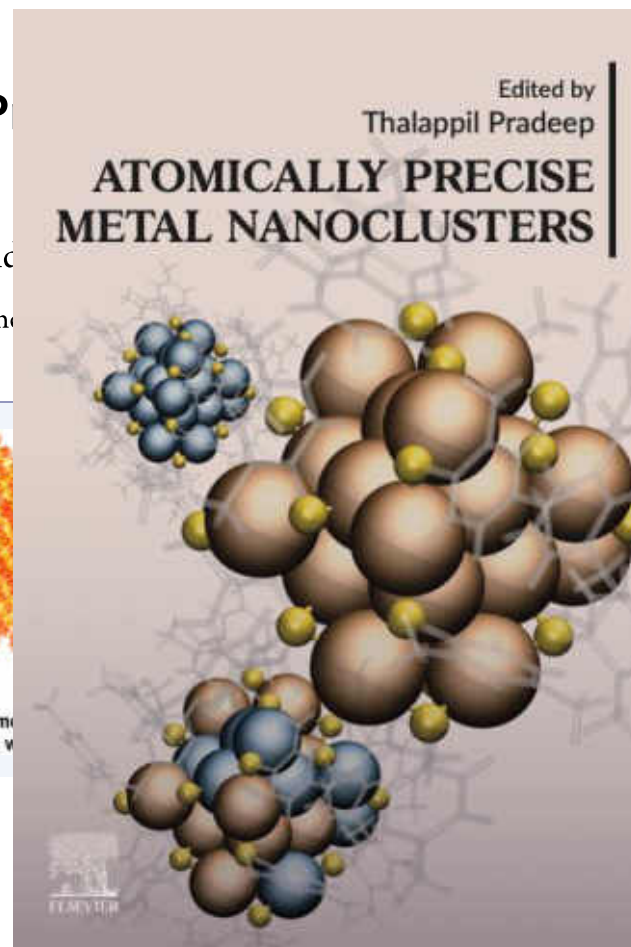
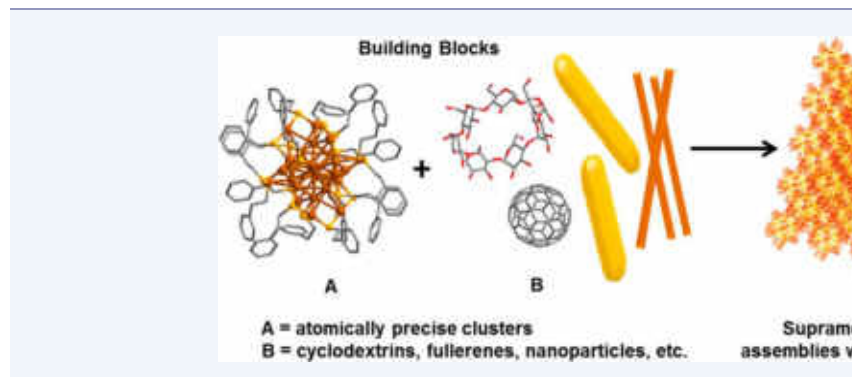
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1 Approaching Materials with Atomic Precision 2 Cluster Assemblies 3

4 Papri Chakraborty, Abhijit Nag, Amrita Chakraborty, and

5 DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence

6 Technology Madras, Chennai 600 036, India



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

Ionization potential

Electron affinity

Phases - phase transitions

Physical properties

Electrical, magnetic

Mechanical properties

Electrochemical properties

Future?

Molecular reactions



Reactions on clusters
Reactions between clusters

Inter-cluster reactions



Article

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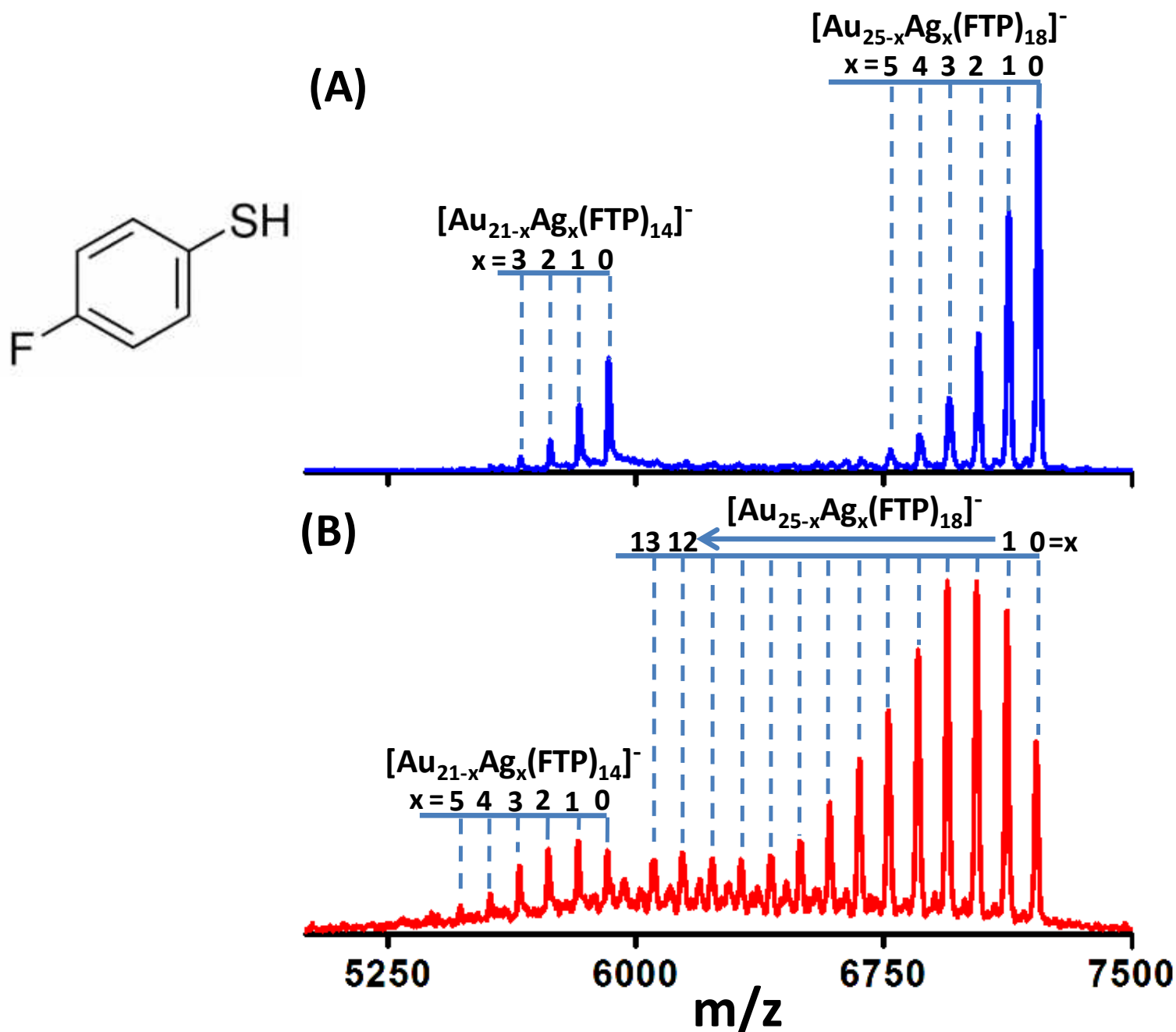
Intercluster Reactions between $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Ag}_{44}(\text{SR})_{30}$

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



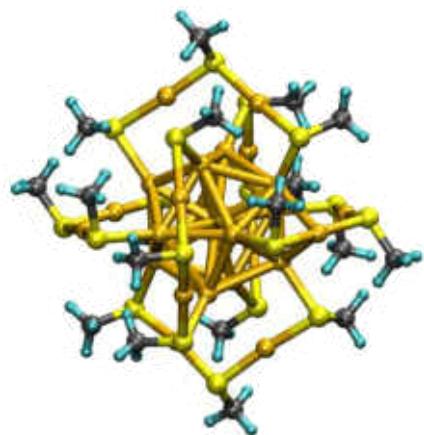
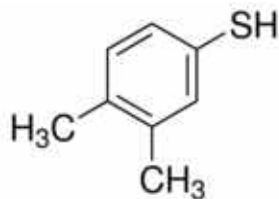


Ag₂₅-Au₂₅ experiments

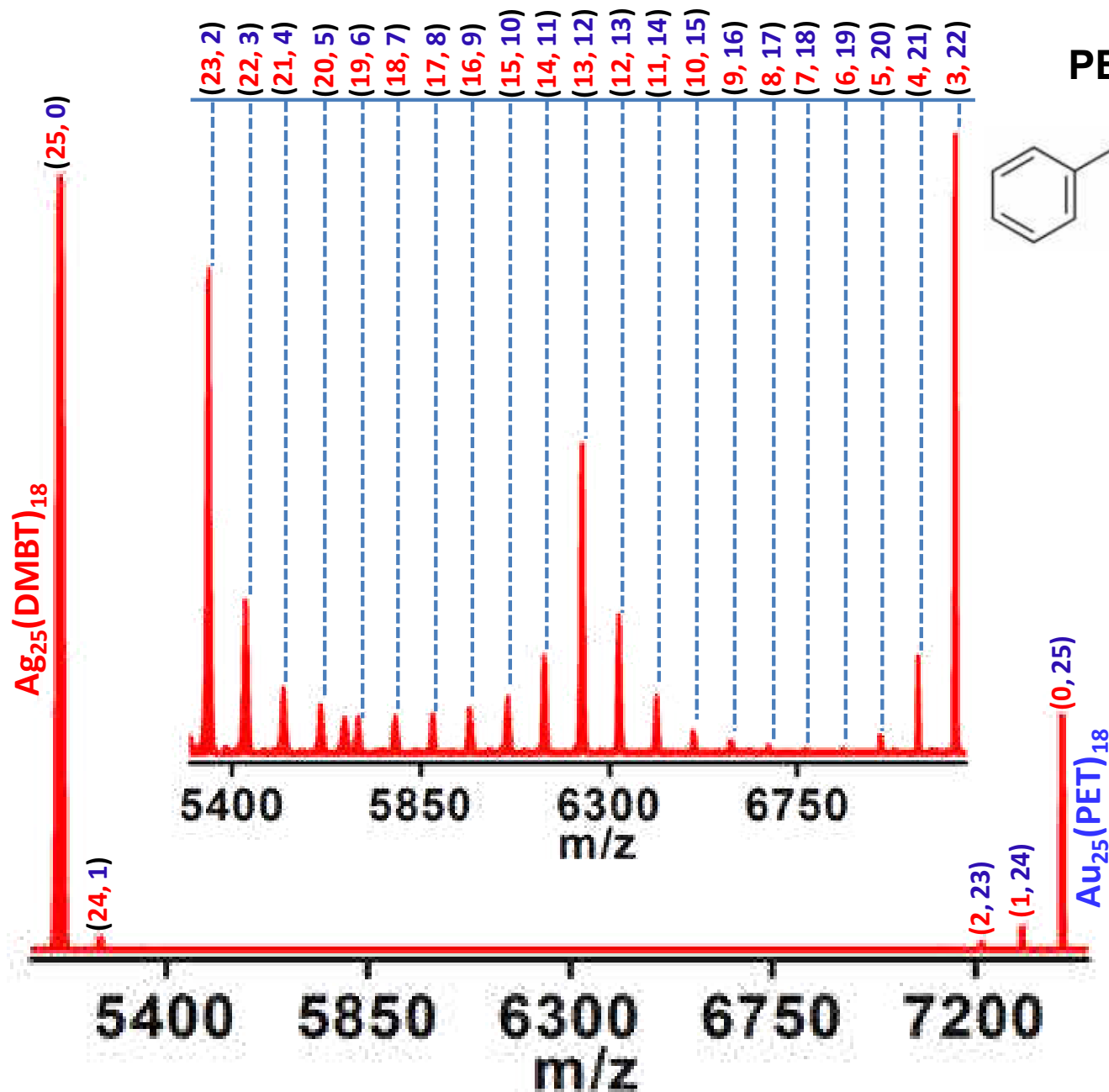
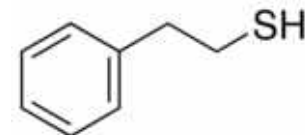
K. R. Krishnadas et al. *Nature Commun.* 2016

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

DMBT

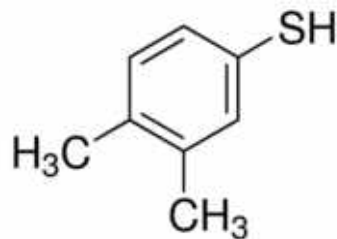


PET

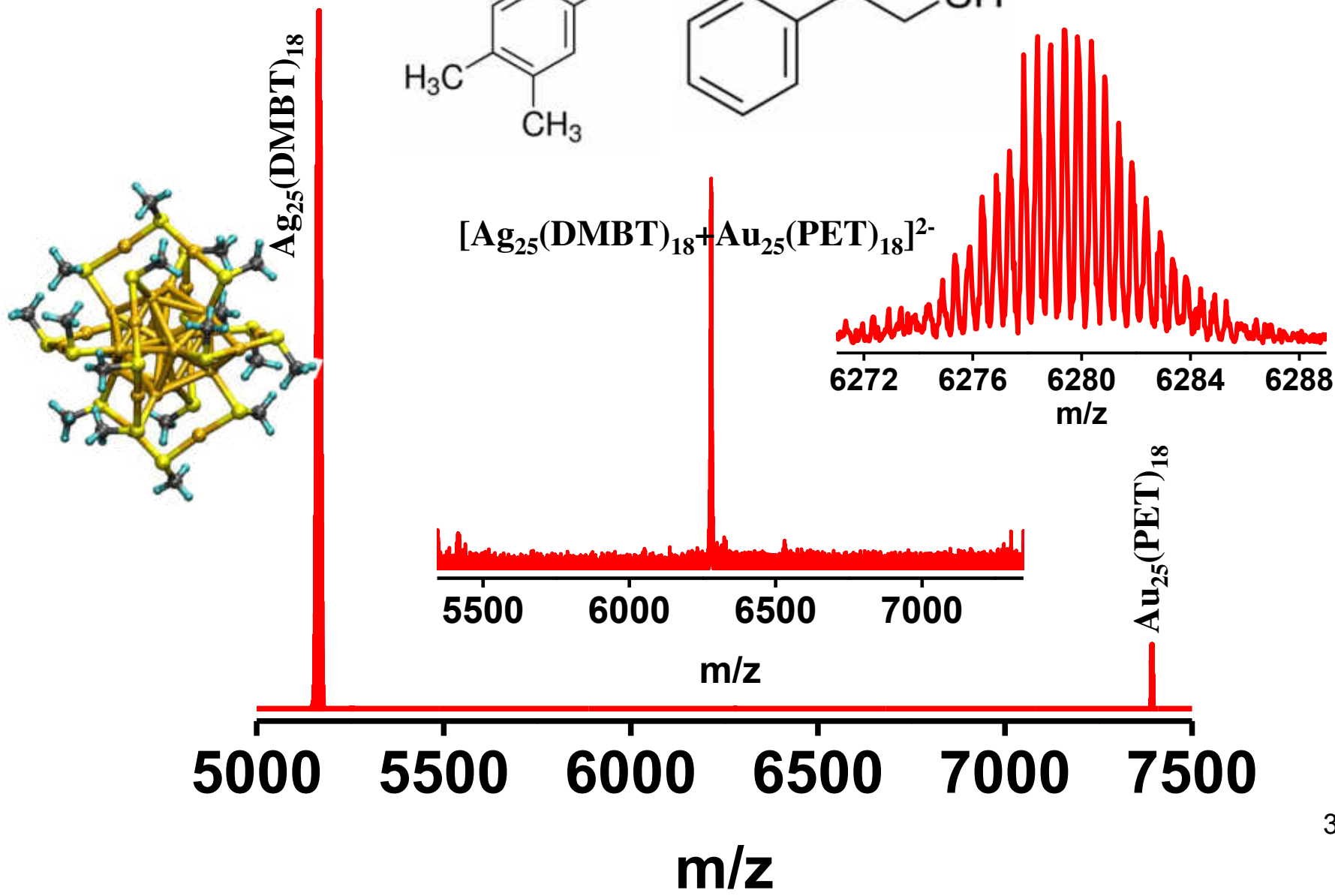
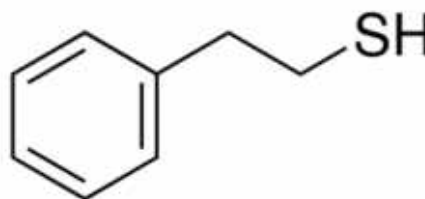




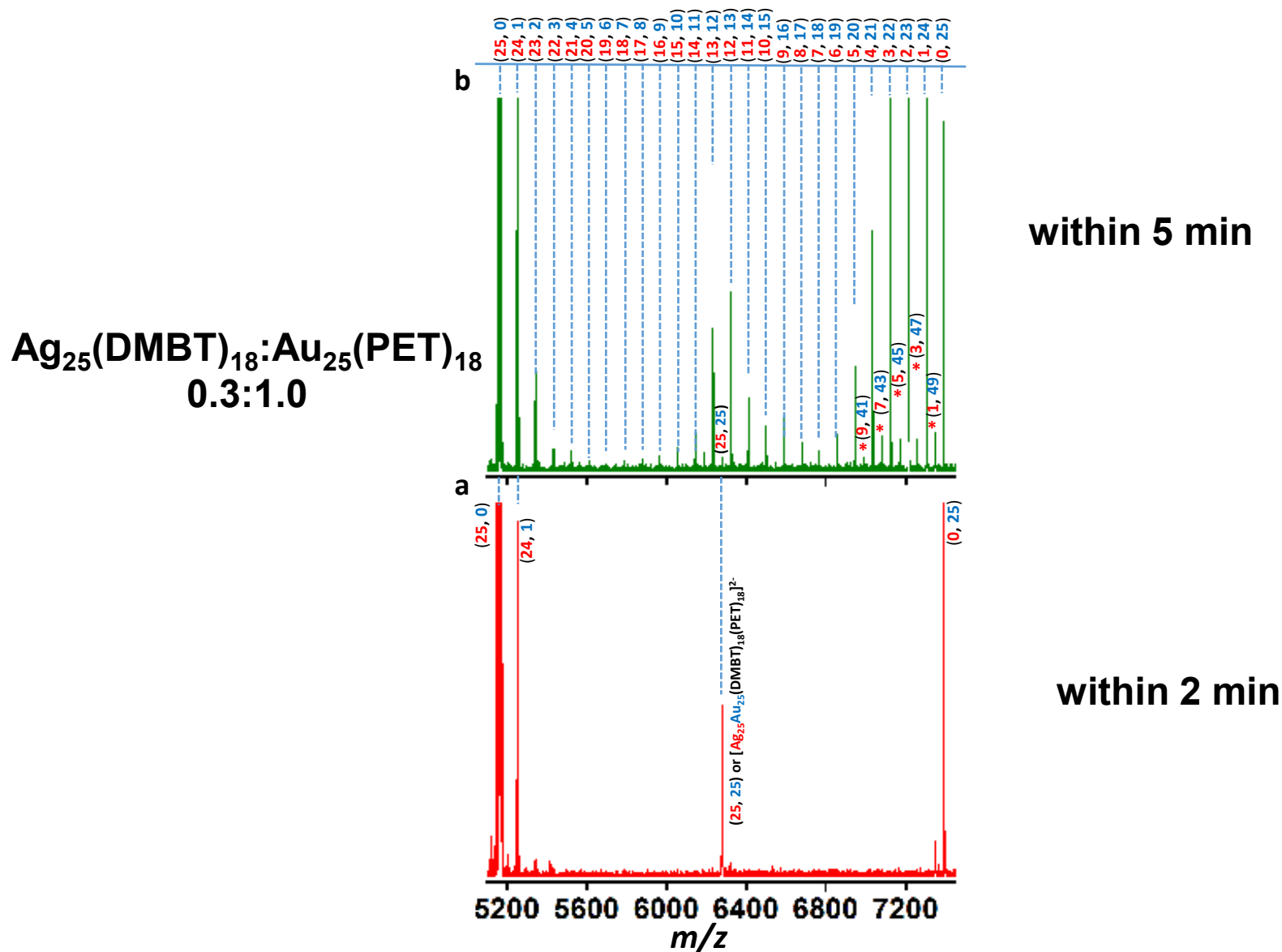
DMBT



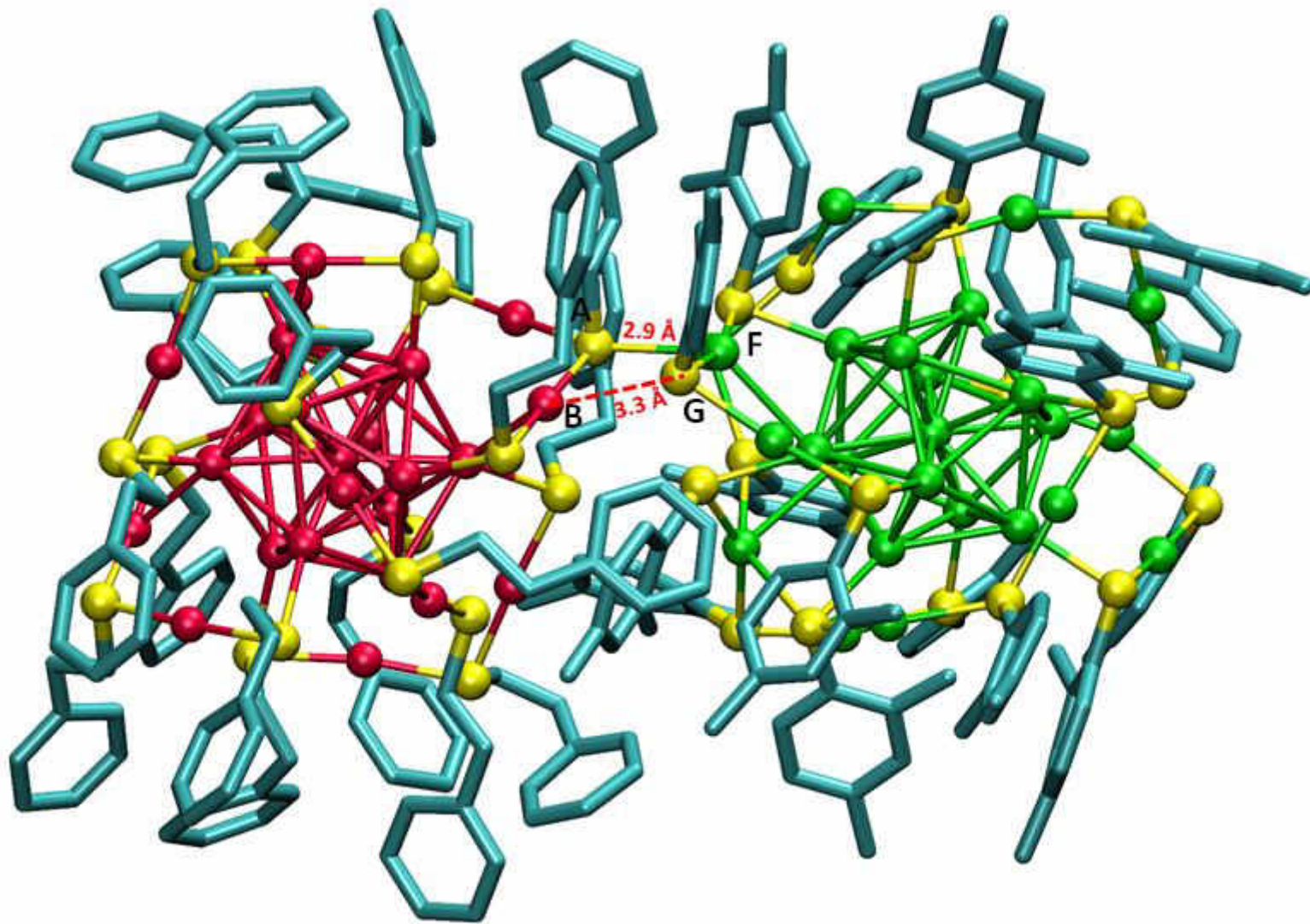
PET

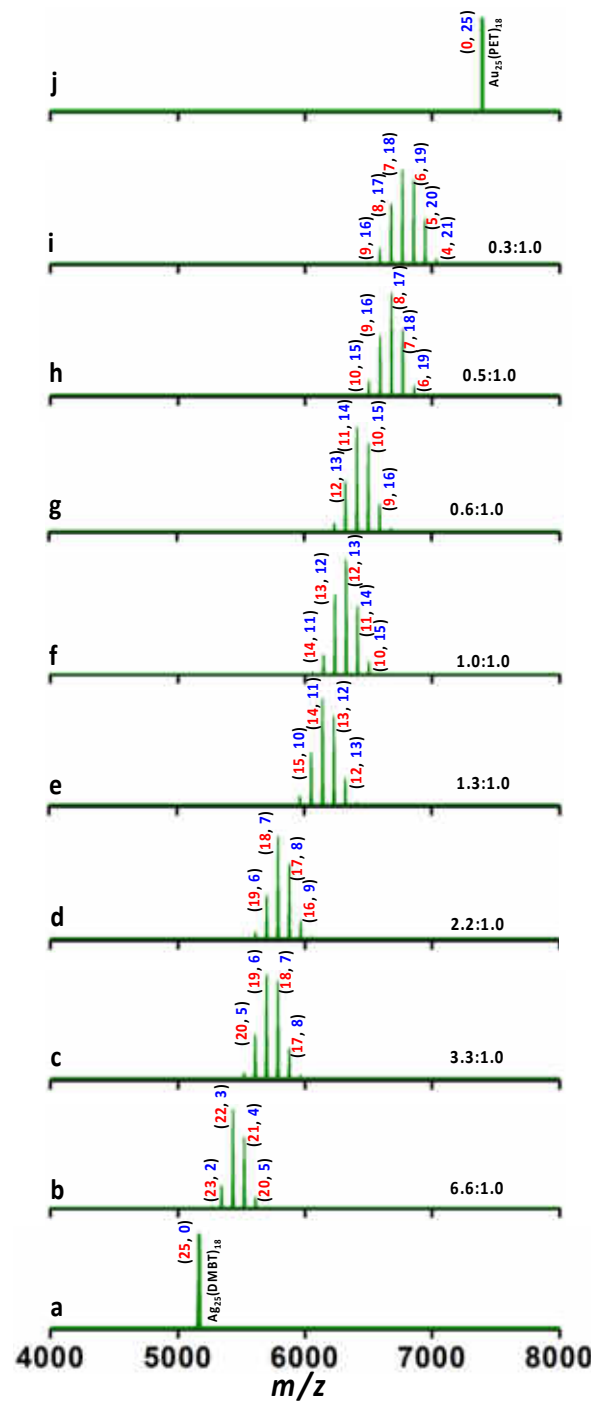


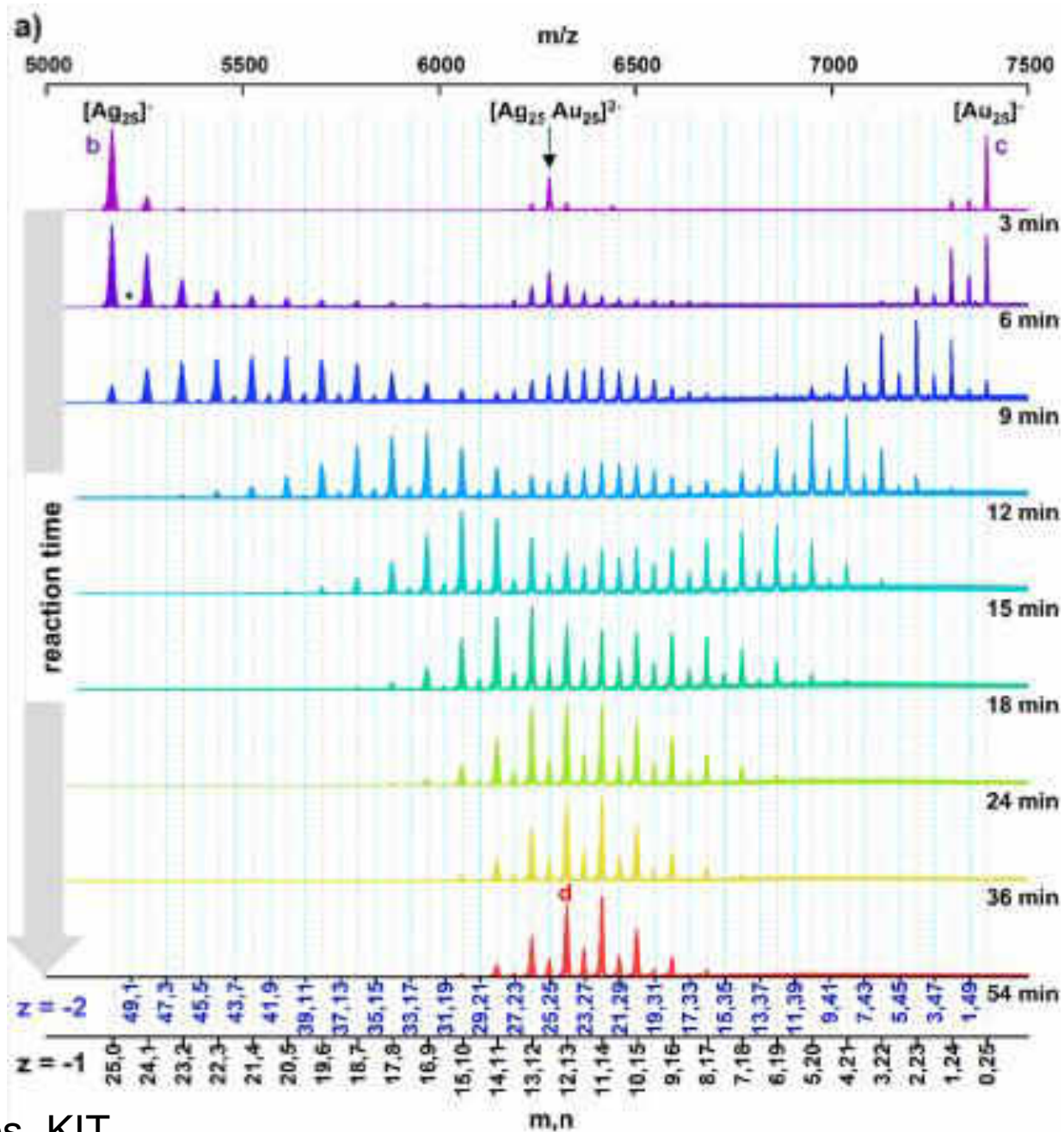
Evolution of alloy clusters from the dianionic adduct, $[\text{Ag}_{25}\text{Au}_{25}(\text{DMBT})_{18}(\text{PET})_{18}]^{2-}$



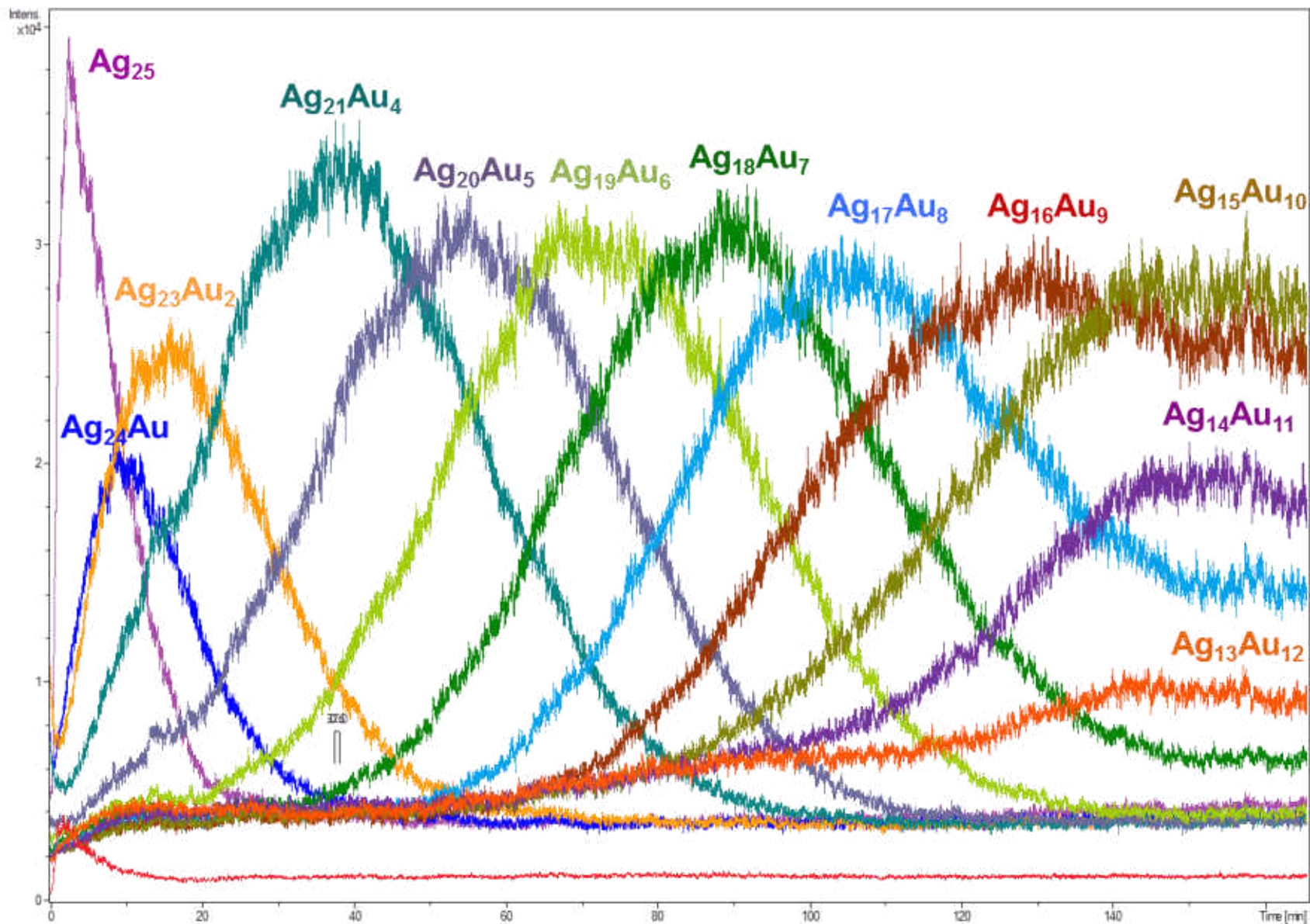
Optimized structure of $[\text{Ag}_{25}\text{Au}_{25}(\text{DMBT})_{18}(\text{PET})_{18}]^{2-}$



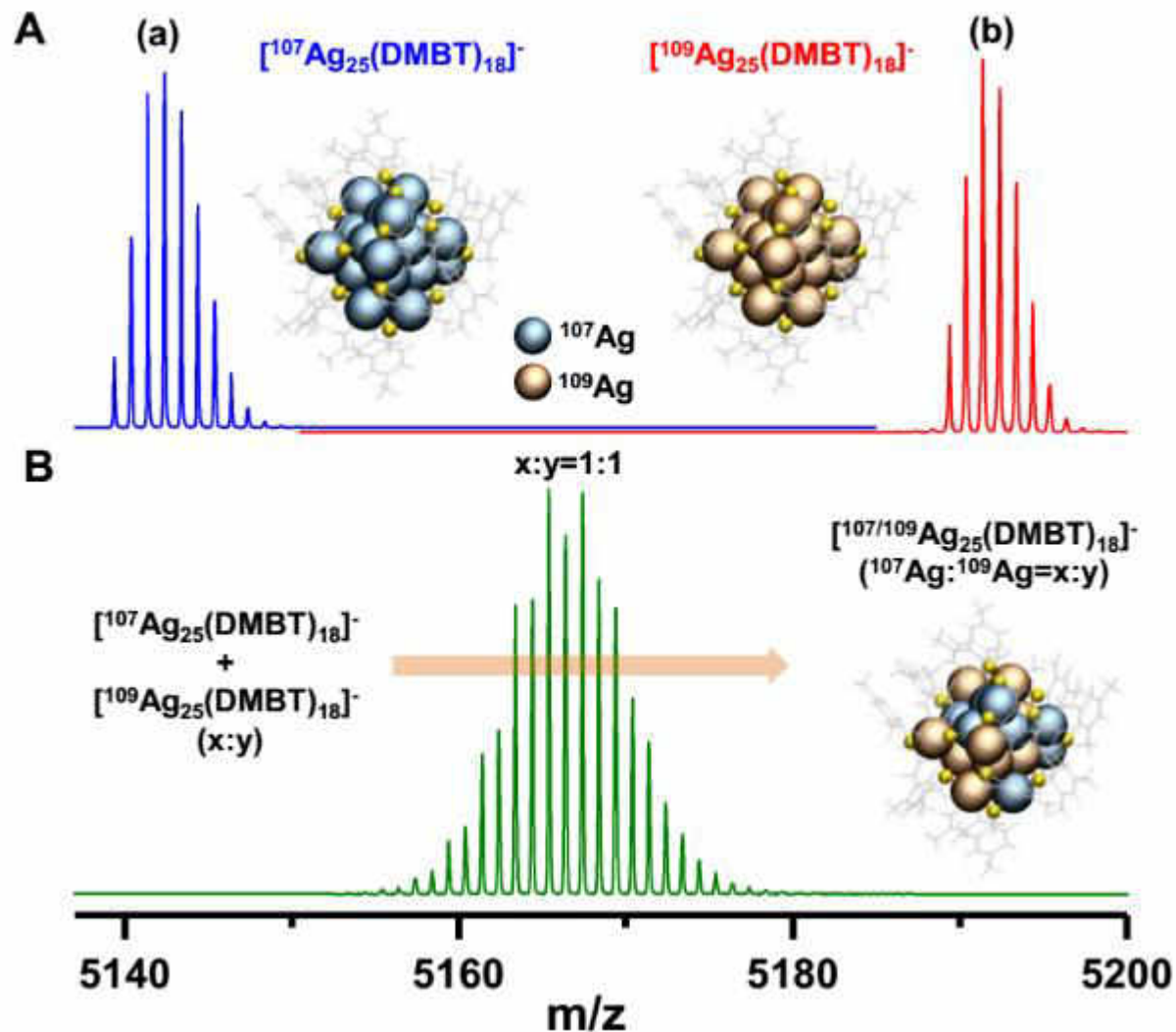




Kinetics of the exchange (monitored on the Ag₂₅ side)

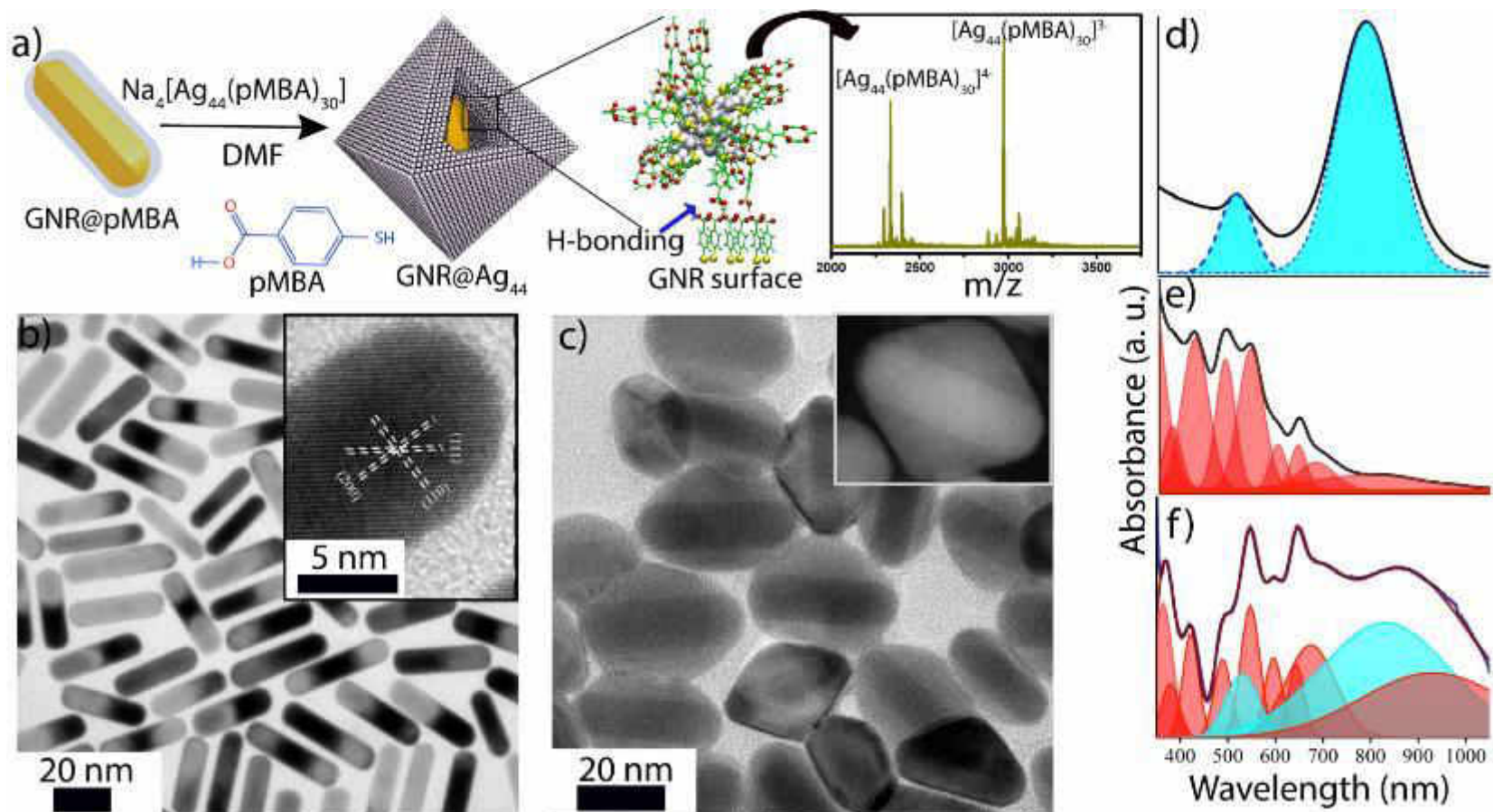


Isotopic exchange



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

Atomically precise nanocluster assemblies encapsulating plasmonic gold nanorods



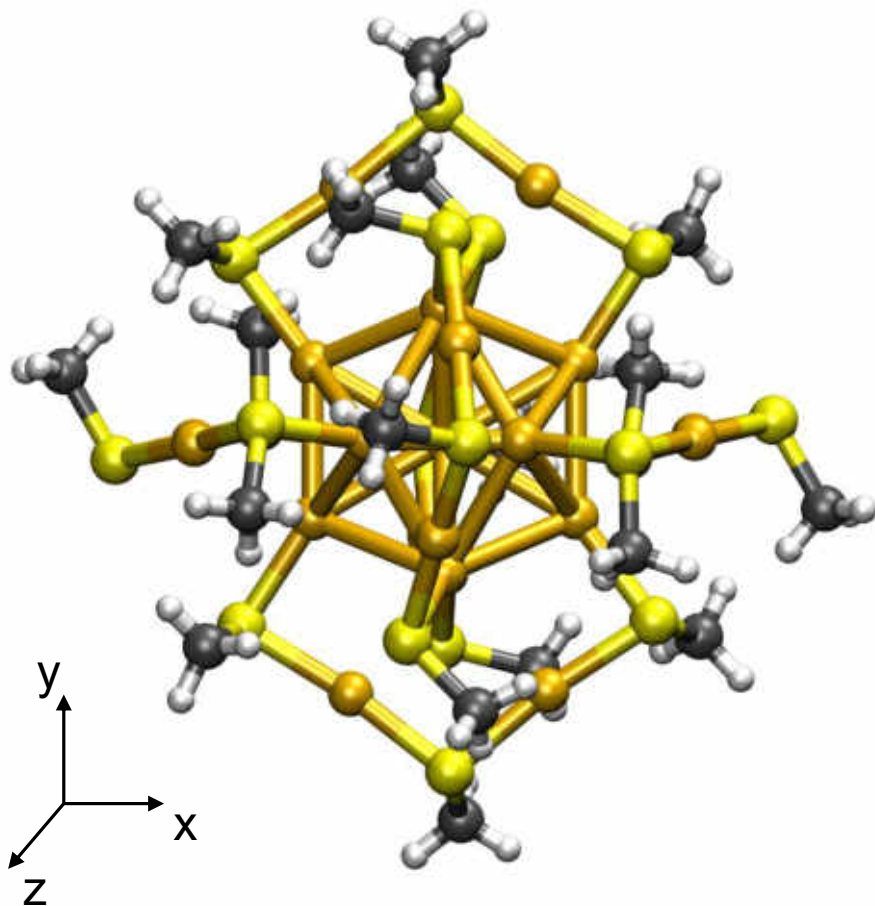
Chakraborty, A. et al., Angew. Chem. Int. Ed. **2018**, 57, 6522–6526.

A system of nomenclature

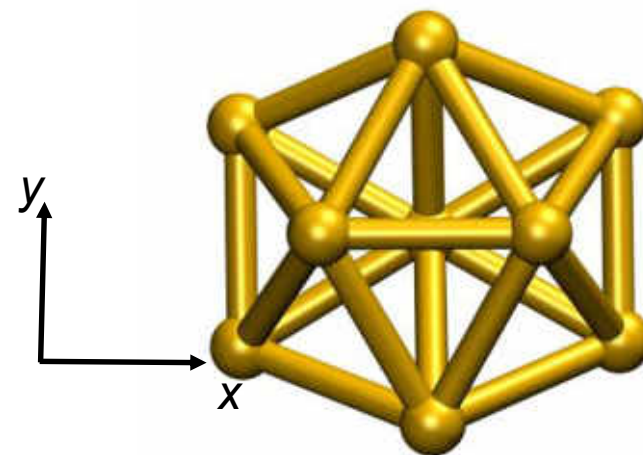
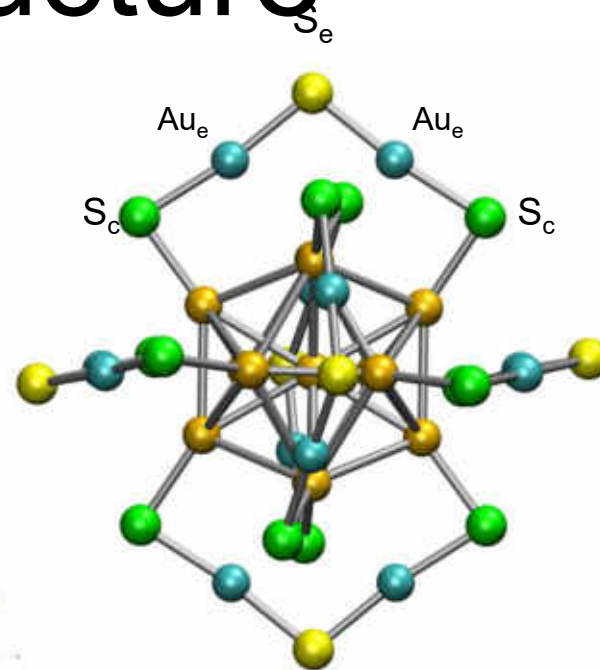
Aspicules



Ball and stick structure



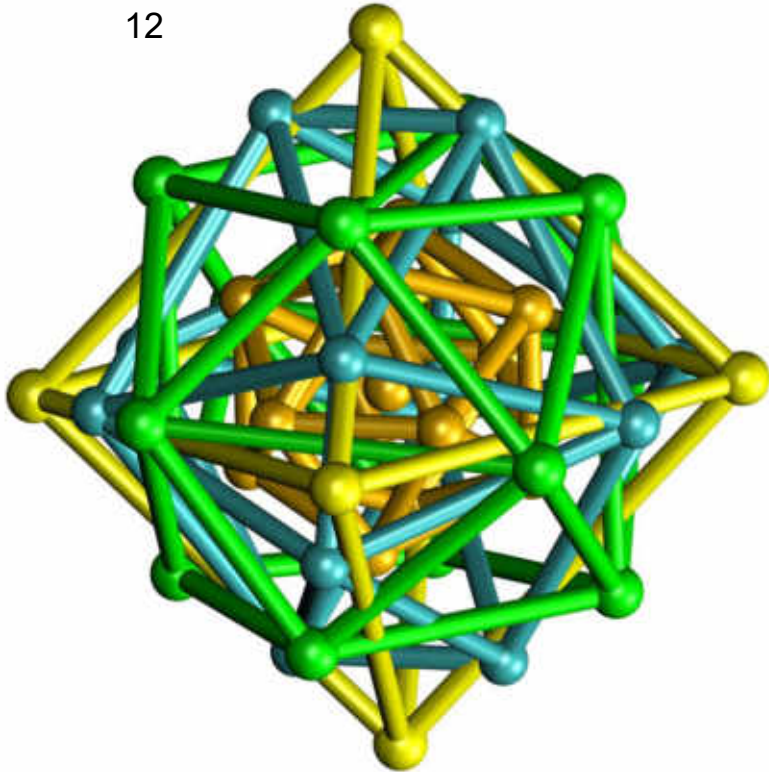
A view of gold methyl thiolate [25]aspicule ($\text{Au}_{25}(\text{SMe})_{18}$). Gold atoms colored gold, sulfur atoms by yellow, carbon dark gray, hydrogen atoms as white and (b) with the gold and sulfur atoms alone .



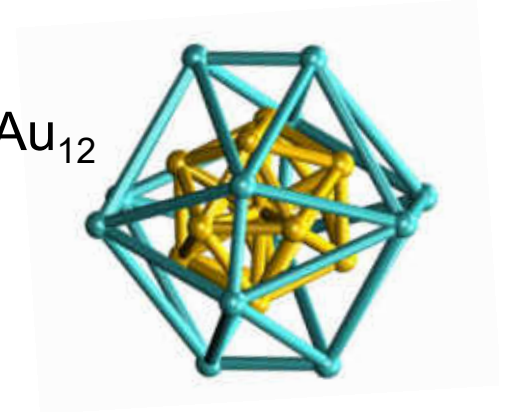
Shell Structure

(a) $\text{Au}@_{12}\text{Au}_{12}@_{12}\text{S}_6@_{12}\text{S}$

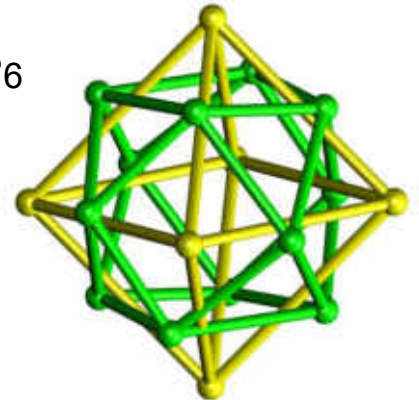
12



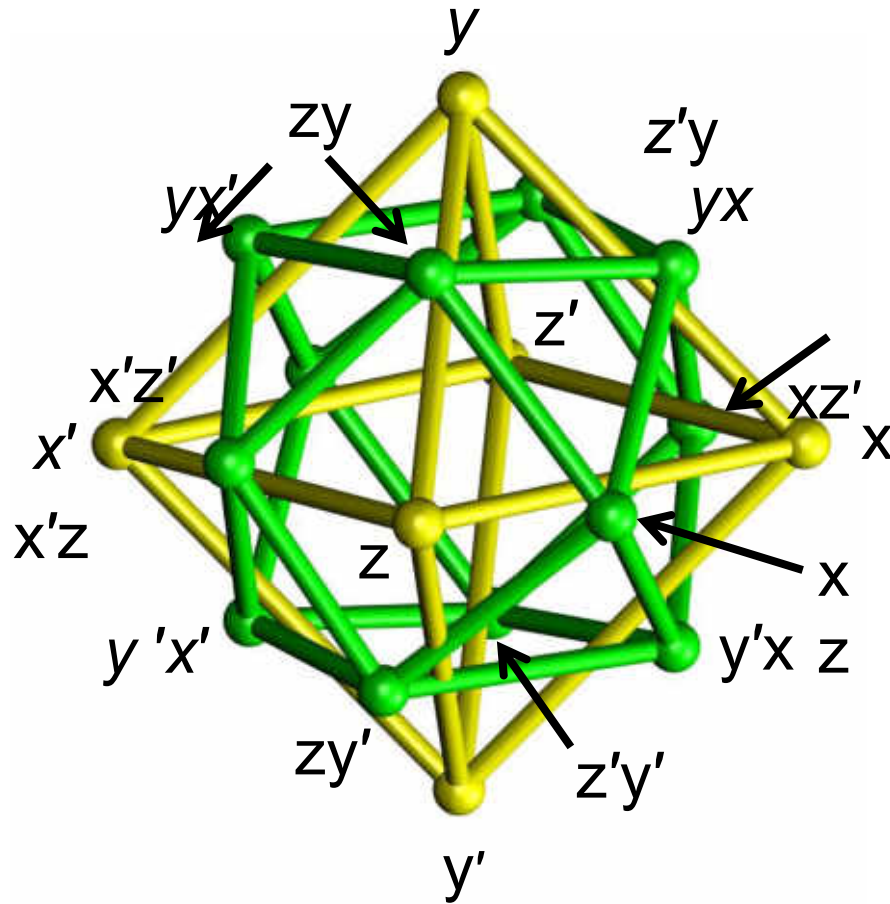
(b) $\text{Au}_{12}@_{12}\text{Au}_{12}$



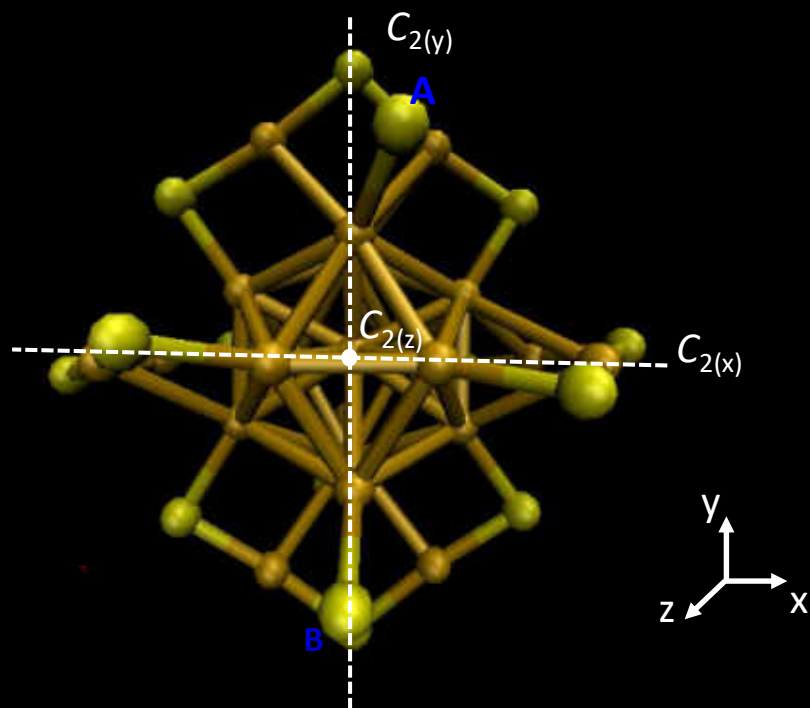
(c) $\text{S}_{12}@_{12}\text{S}_6$



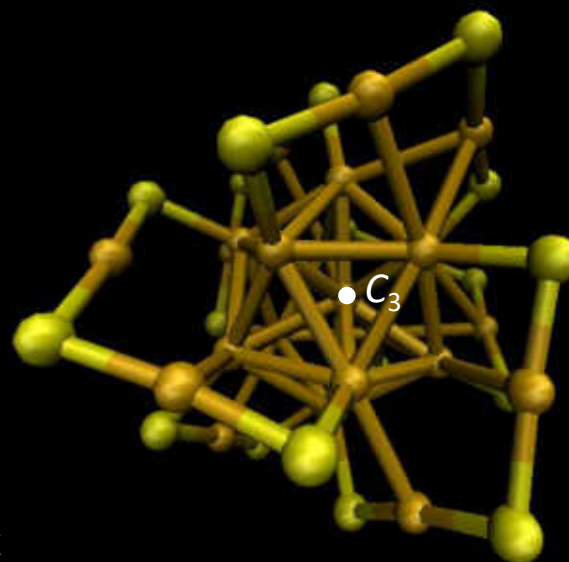
Terminologies



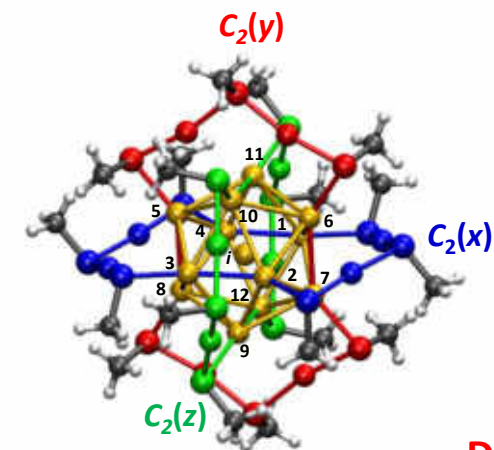
1) Edge projection



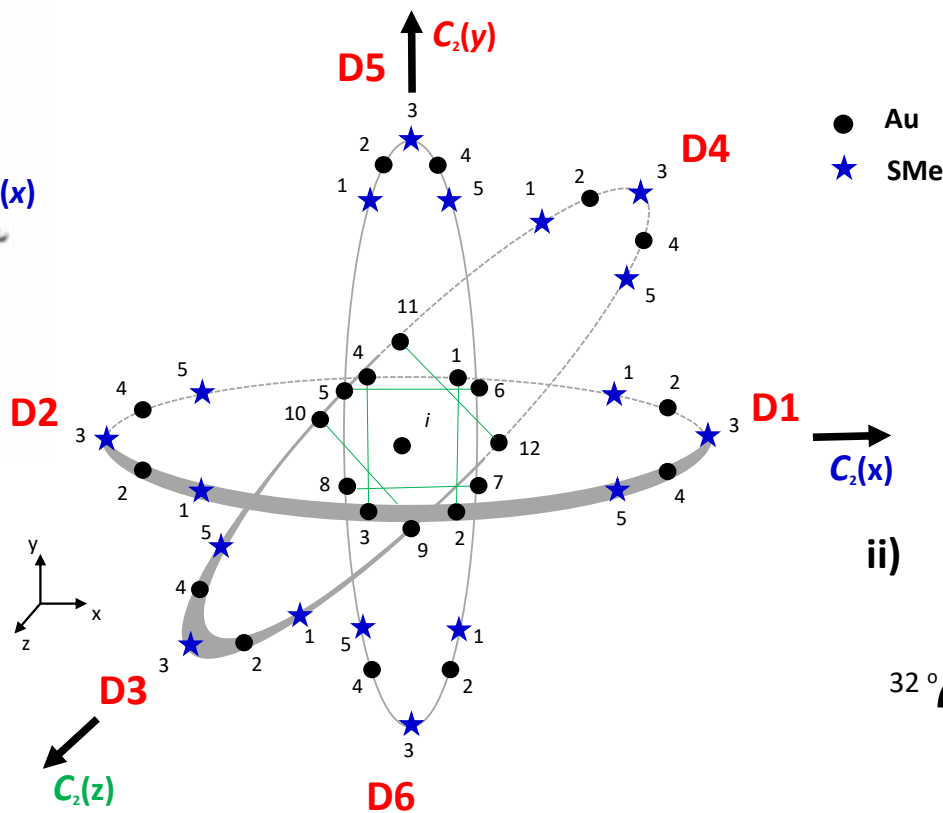
2) Face Projection



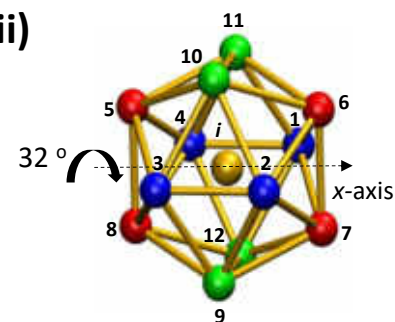
i)



18(methylthiolato)-auro-25
aspicule(1-)



ii)



18(methylthiolato)-auro-25 aspicule(1-)

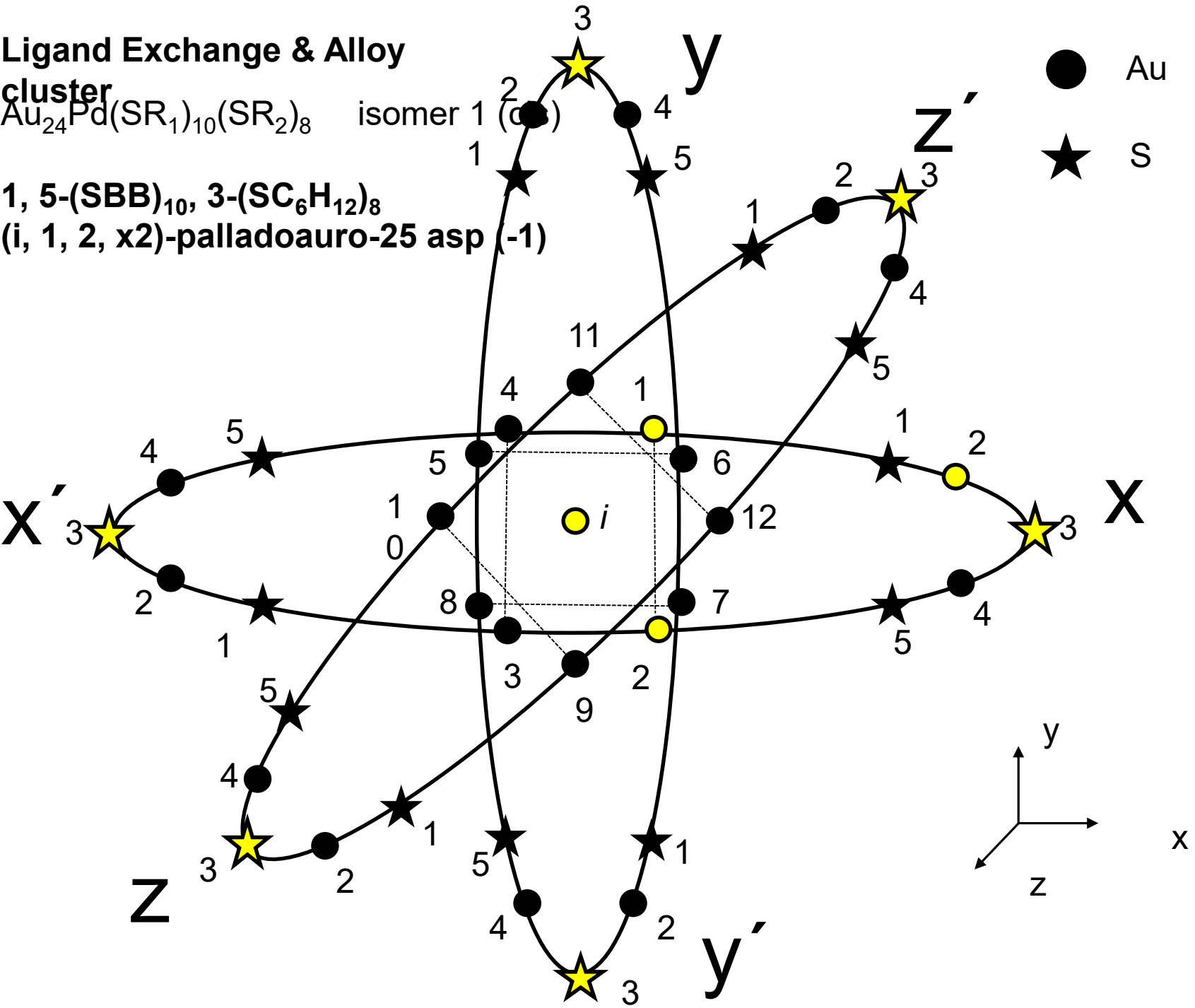
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-(PET)₂,(SMe)₁₆-auro-25 aspicule(1-)

Ligand Exchange & Alloy
cluster

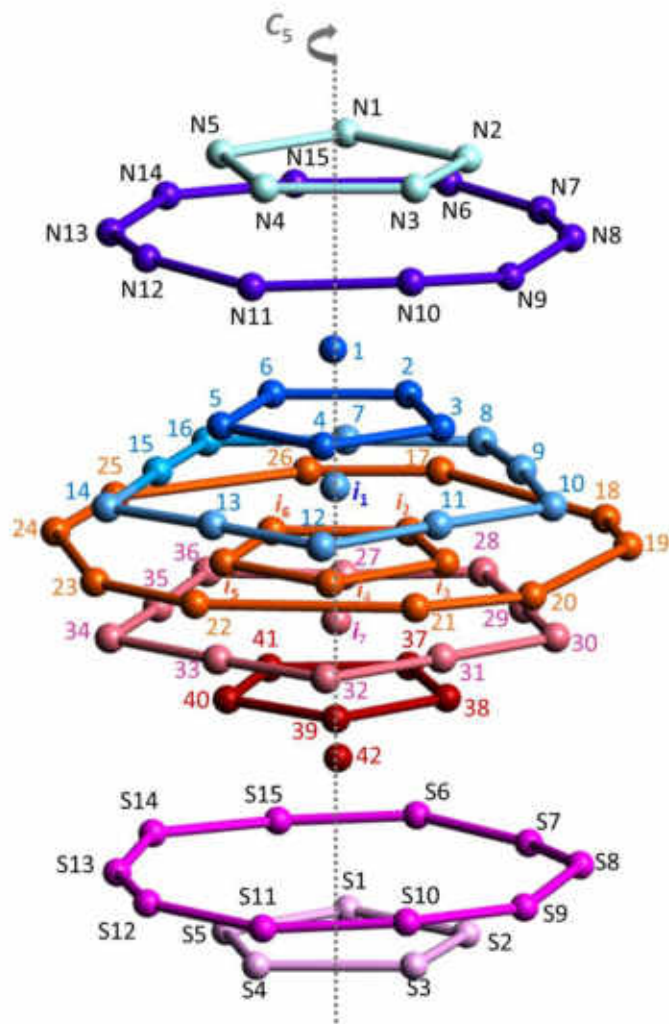
$\text{Au}_{24}\text{Pd}(\text{SR}_1)_{10}(\text{SR}_2)_8$ isomer 1 (c)

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

● Au
★ S



(A)



Biopolymer-reinforced nanocomposite for water purification

Mohan Udhaya Sankar¹, Saha Kamalesh Chaudhari, and Thangarasu

Unit of Nanoscience and Thematic Unit of Nanoscience

Edited by Eric Hoek, University of California, San Diego

Creation of affordable materials for water purification is one of the most promising drinking water for all. Combining nanocomposites to scavenge toxic species and other contaminants along with the use of biopolymers to form an affordable, all-inclusive drinking water purifier without electricity. The critical property is the synthesis of stable materials that can be used continuously in the presence of contaminants in drinking water that deposit and form a filter layer on surfaces. Here we show that such materials can be synthesized in a simple and effective manner without the use of electrical power. These materials have been used as a sand-like properties, such as high mechanical strength and high water forms. These materials have been used as a water purifier to deliver clean drinking water. The ability to prepare nanocomposites at ambient temperature has wide implications for water purification.

hybrid | green | appropriate technology



Work was featured in several journals



Nature Nanotechnology, July 2014 issue

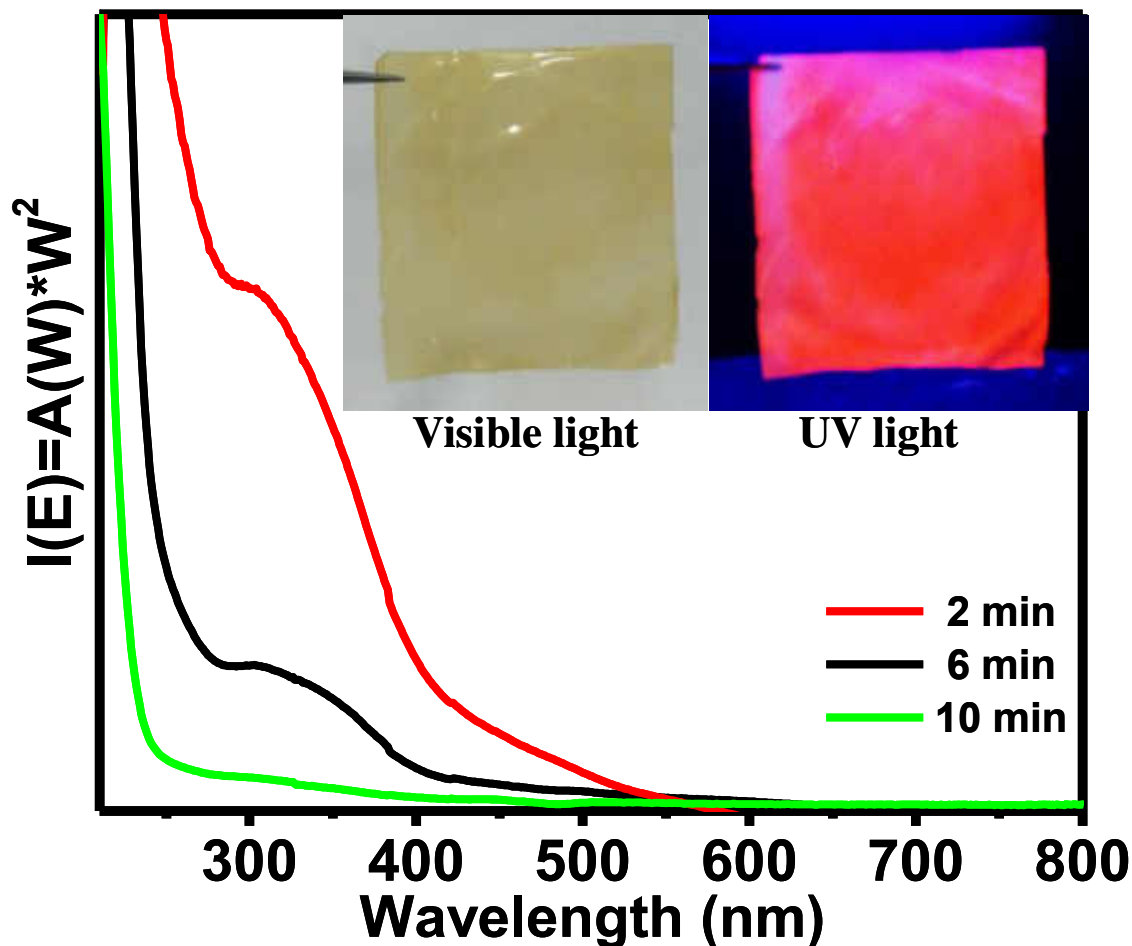


We developed environmentally friendly water positive nanoscale materials for affordable, sustainable and rapid removal of arsenic from drinking water.

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

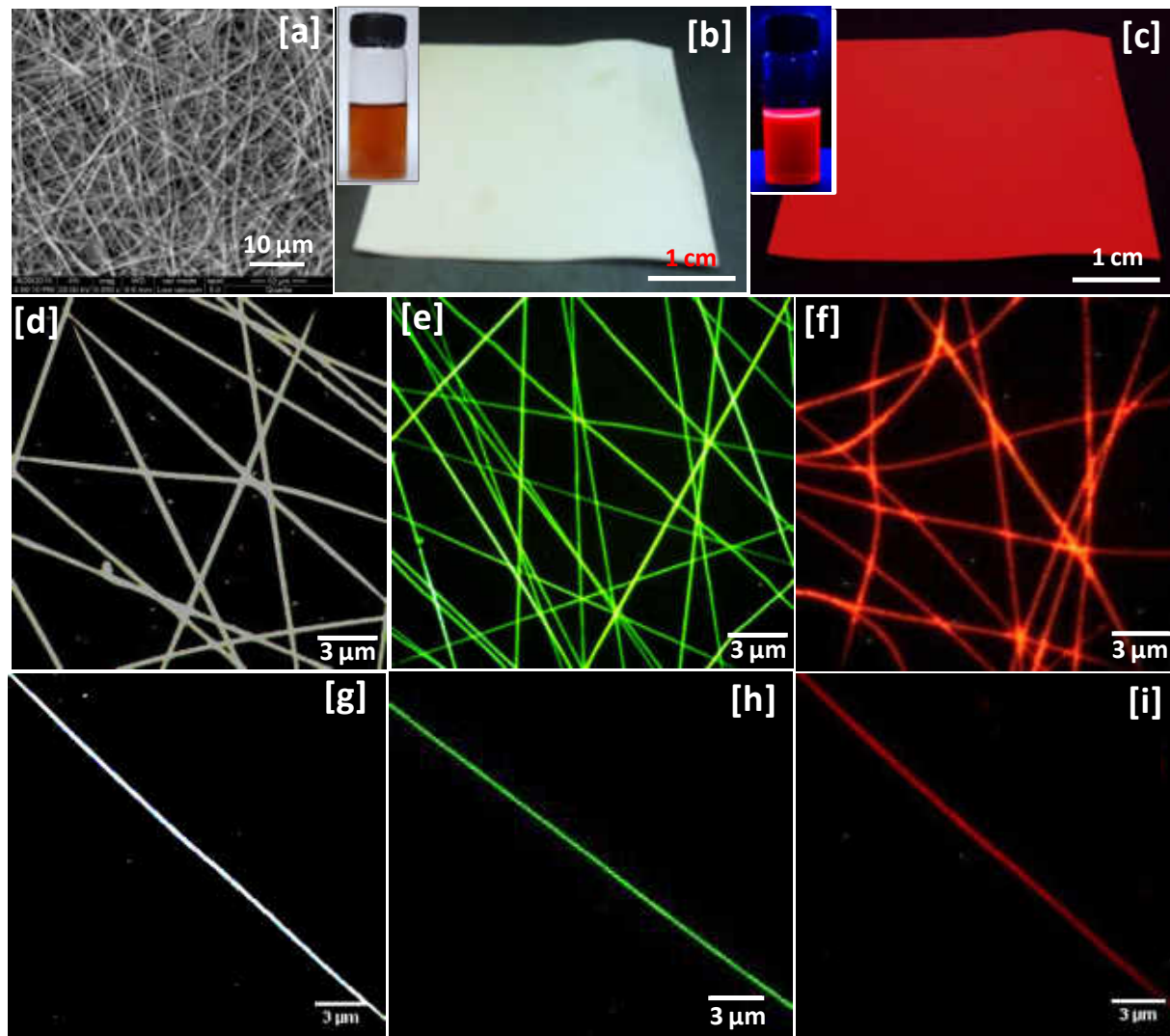
Quantum cluster based metal ion sensing paper

Large area uniform illumination using quantum cluster



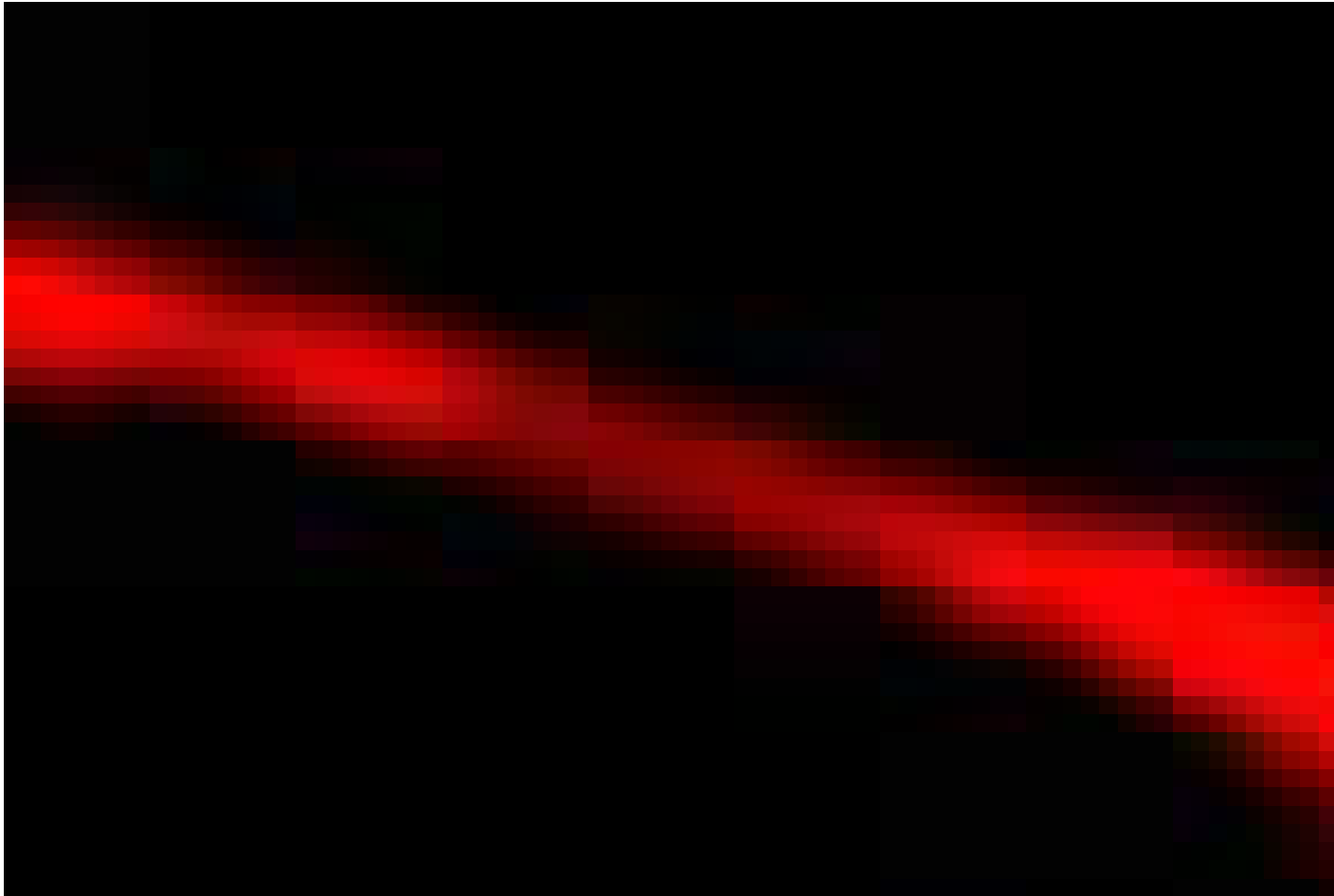
Decrease in the absorption of Au_{15} as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

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

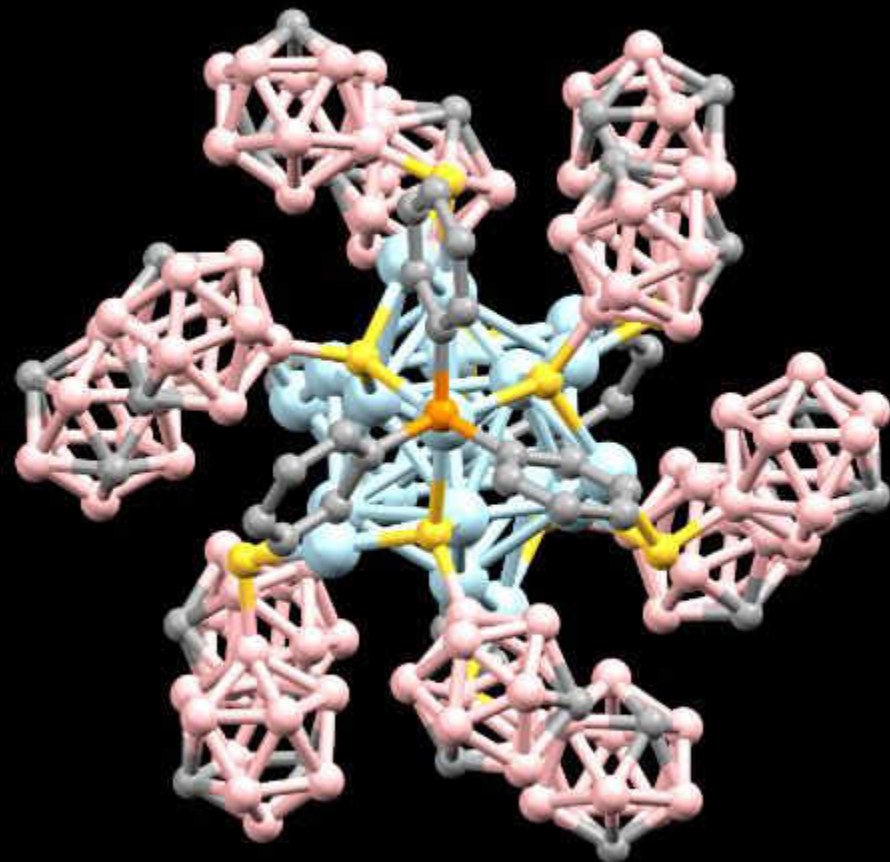
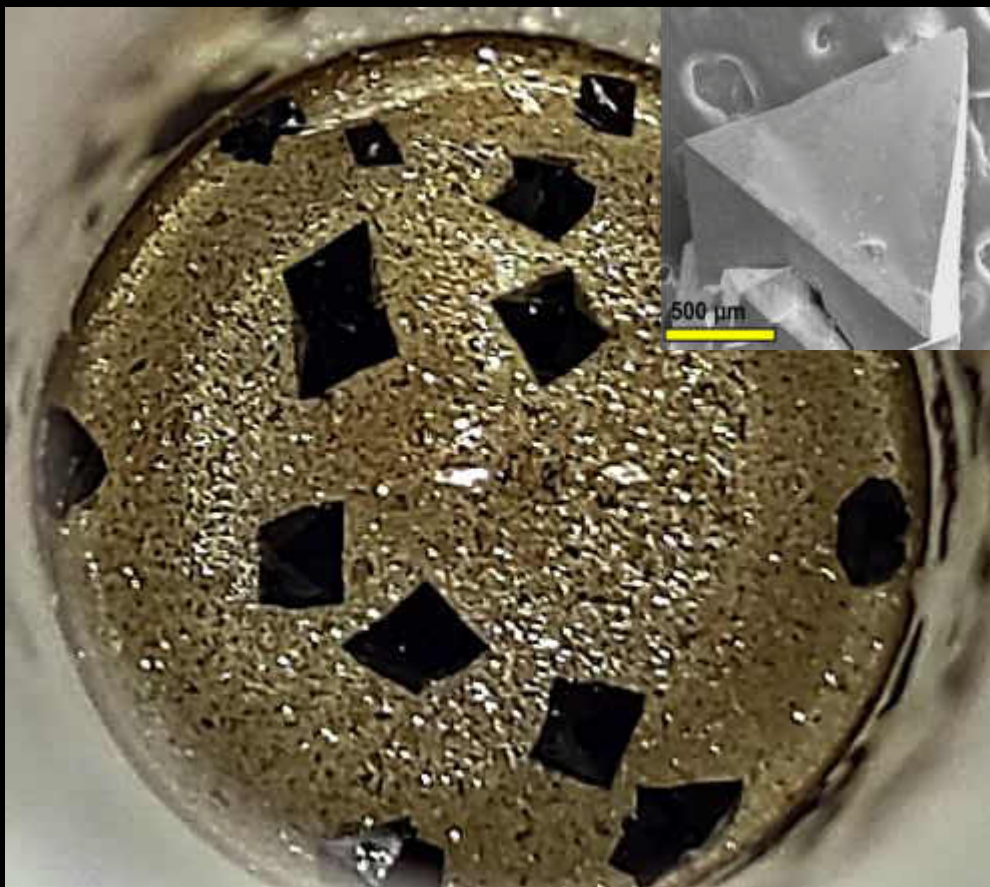


Atanu Ghosh et al. Anal. Chem. 2014.

Video of mercury quenching experiment using the nanofiber



Clusters stable up to 300 °C!



With Tomas Base

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

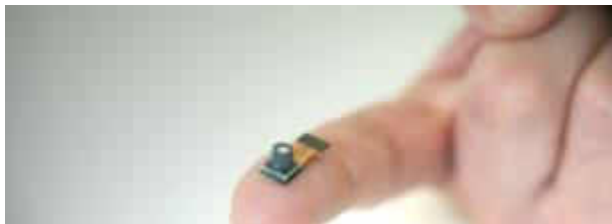
Sensors and new opportunities



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



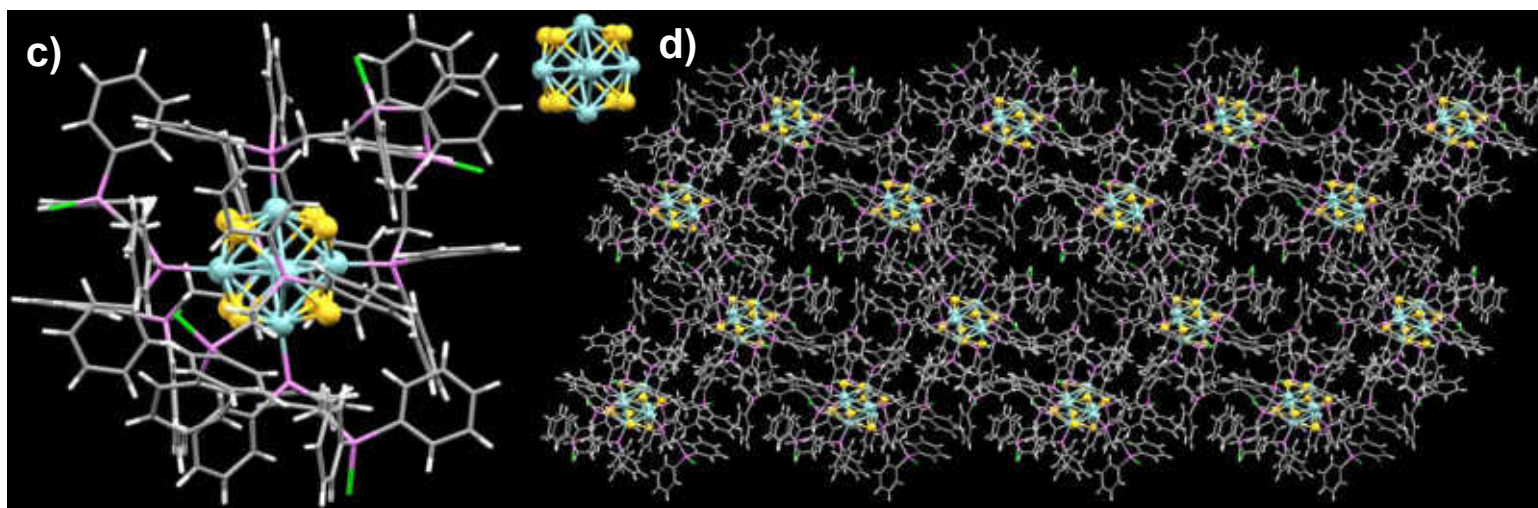
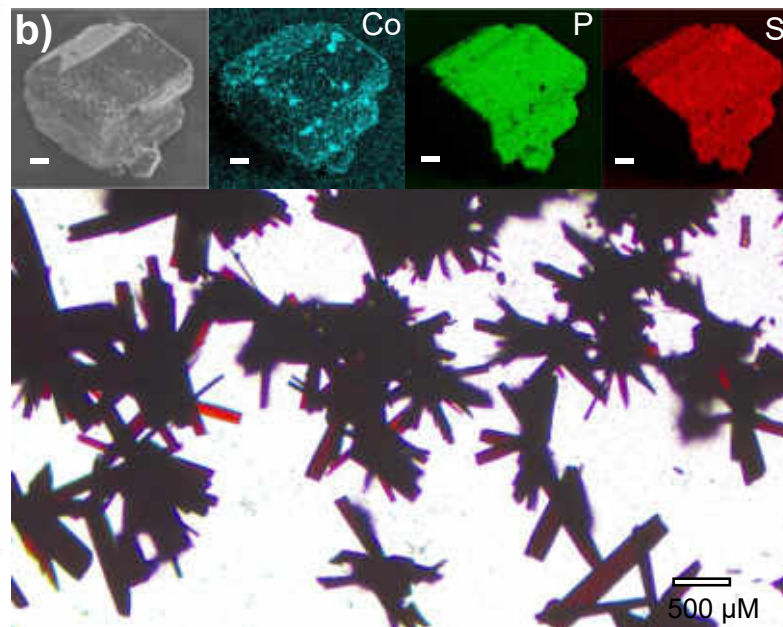
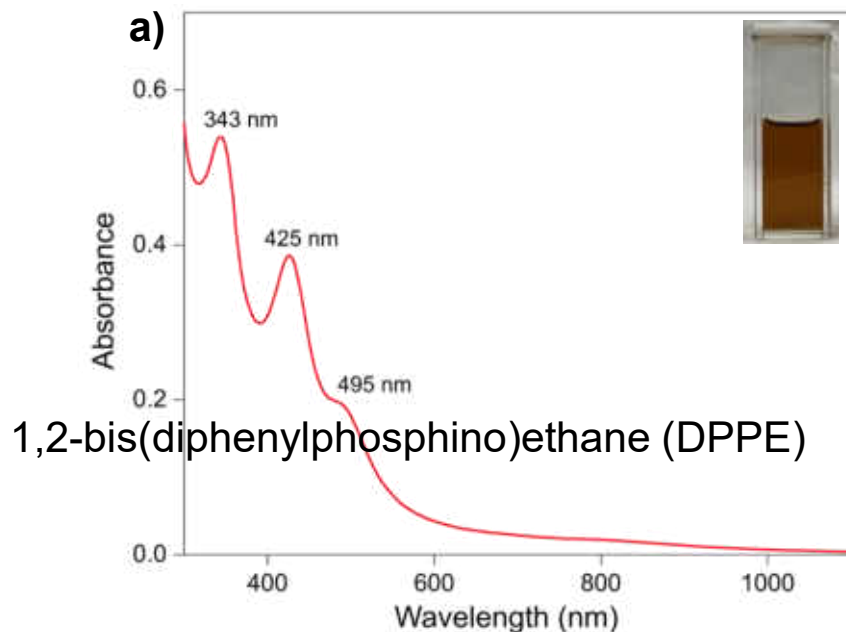
**Ultra compact Low Cost
Spectral Sensor Module**
~ **Billions units** (? 2027)



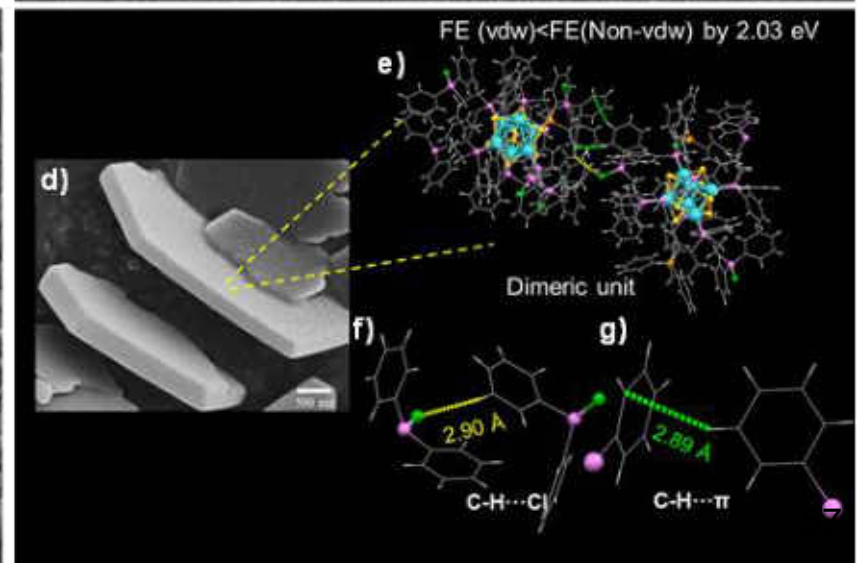
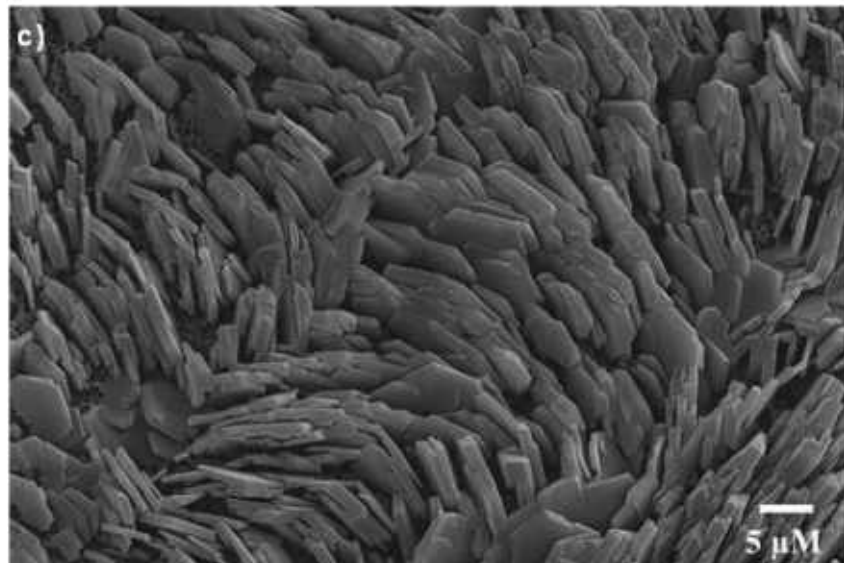
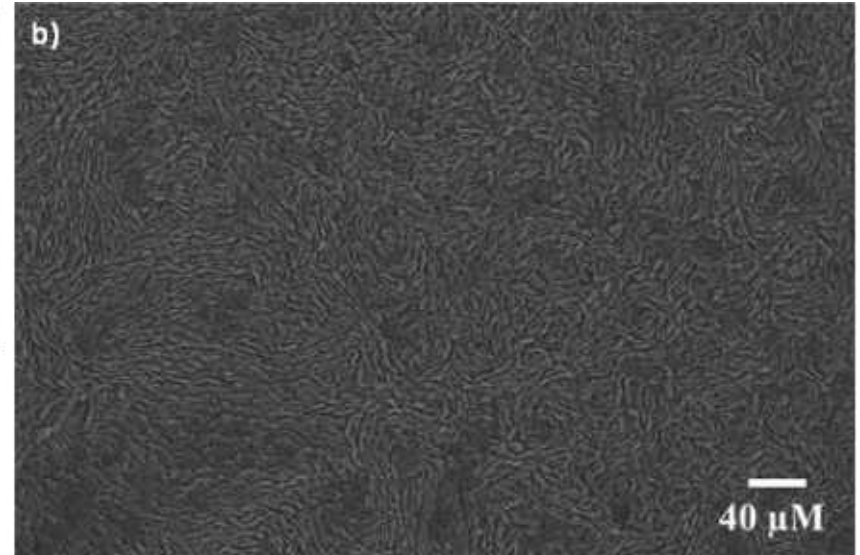
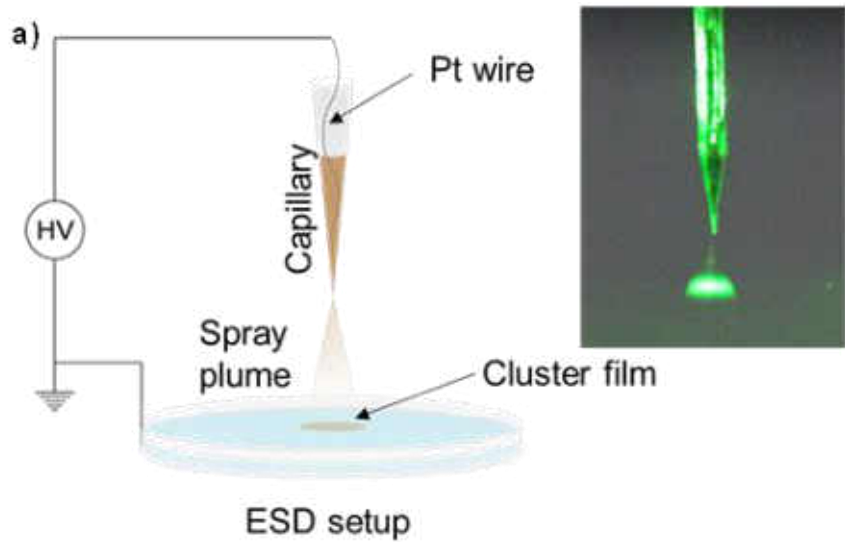
Water quality measurement – In the pipeline

nano λ

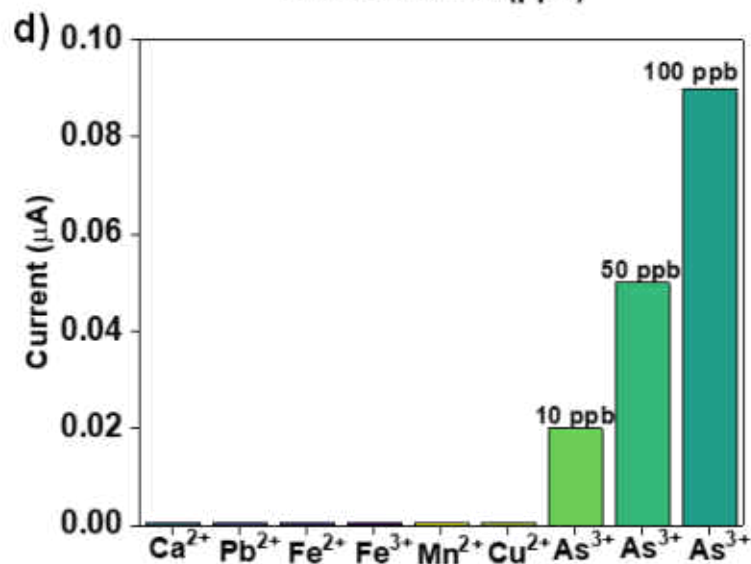
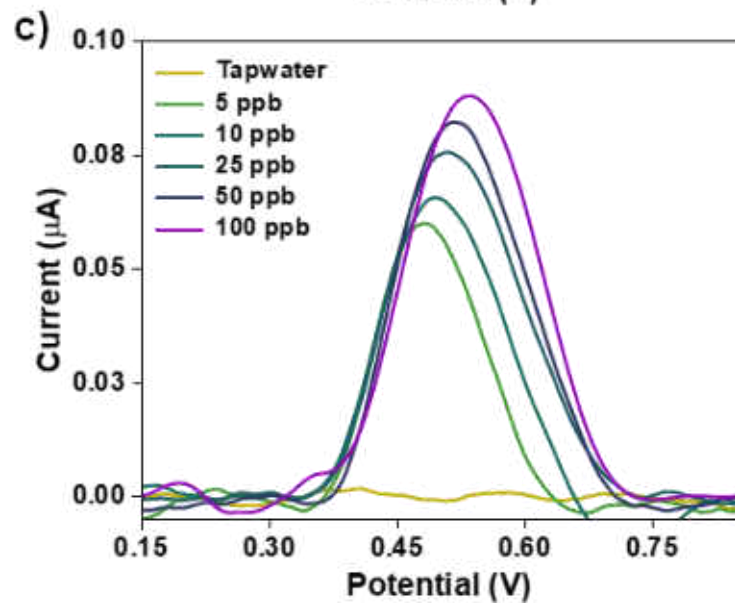
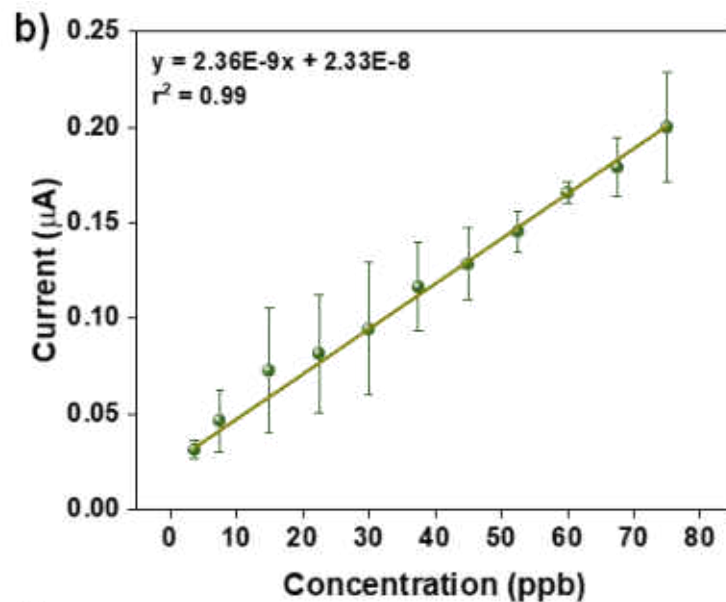
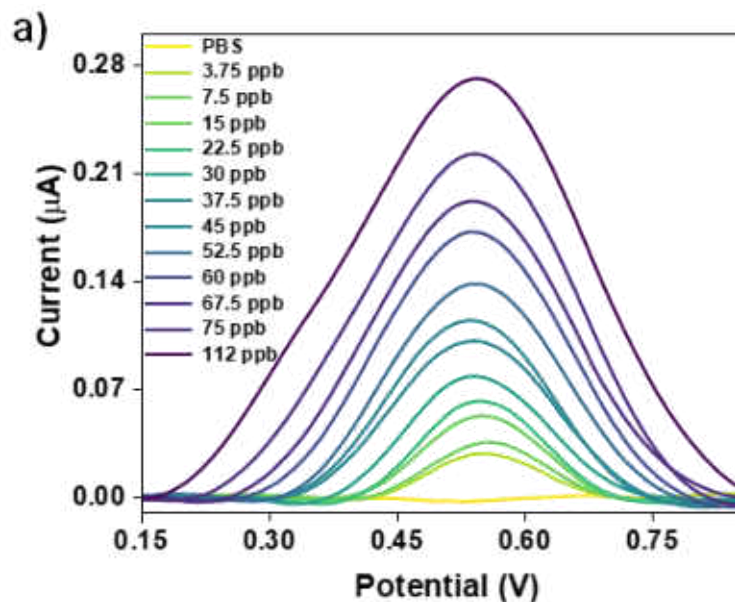
New electrodes - Aligned nanoplates of Co_6S_8



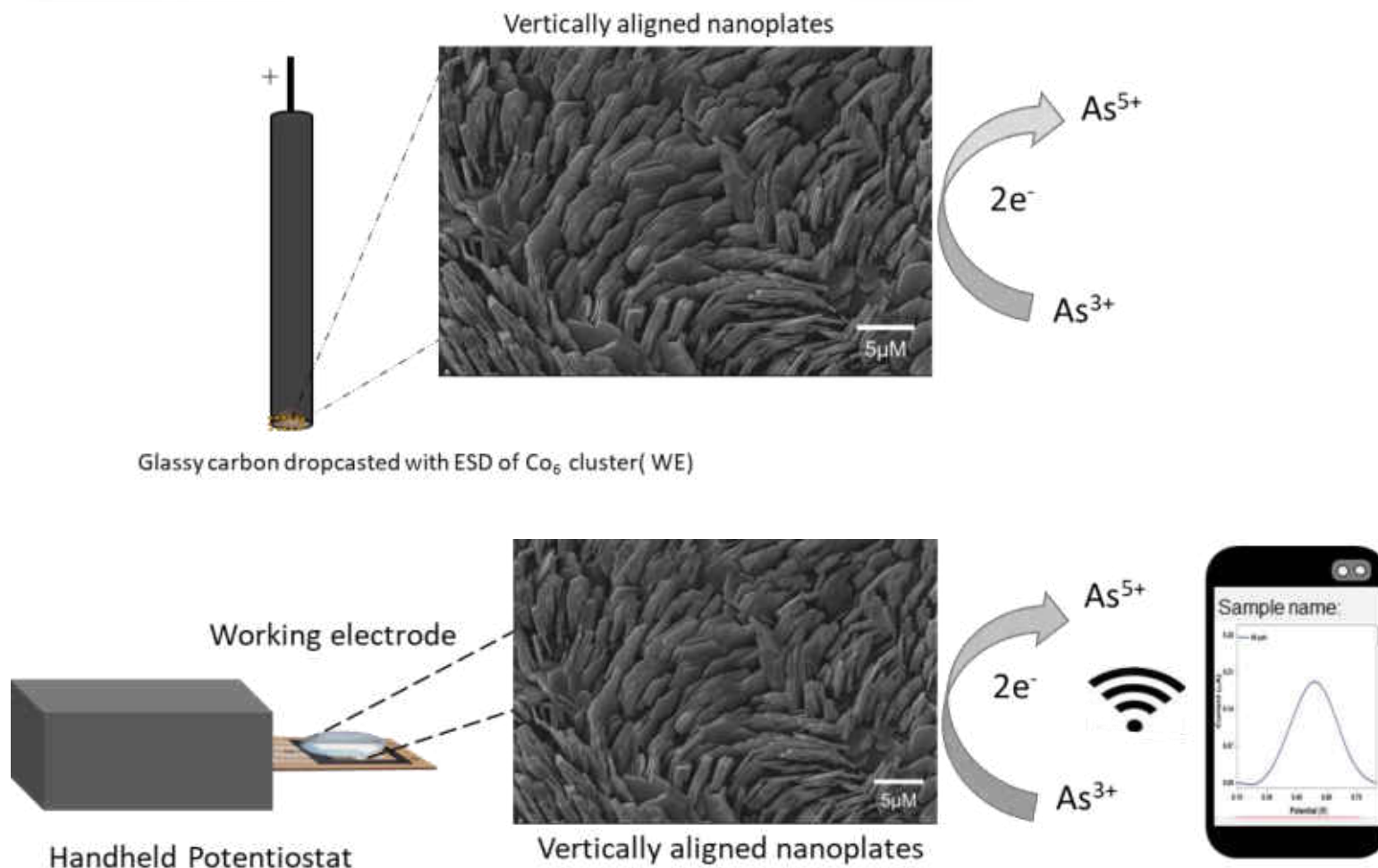
Electrospray deposition



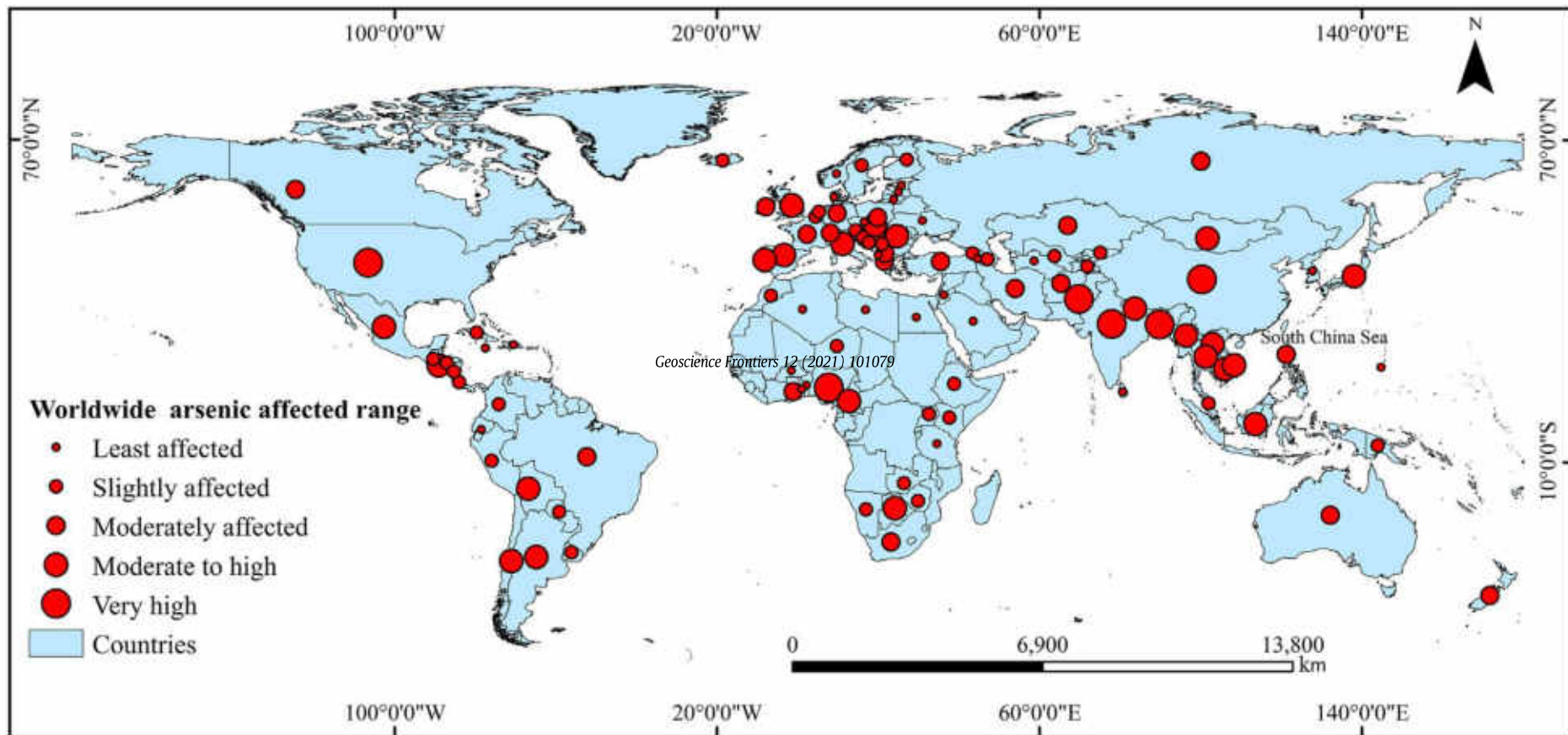
Sensing



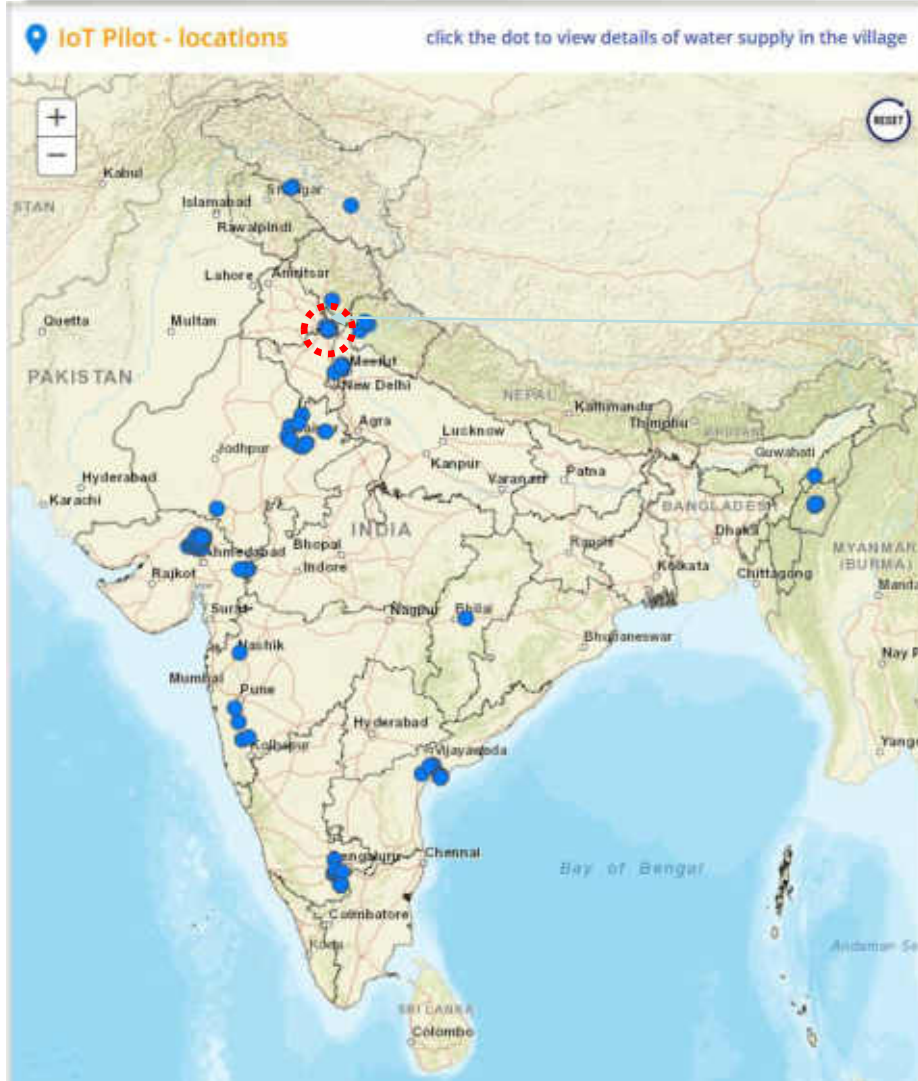
Working electrode



Arsenic poisoning across the world

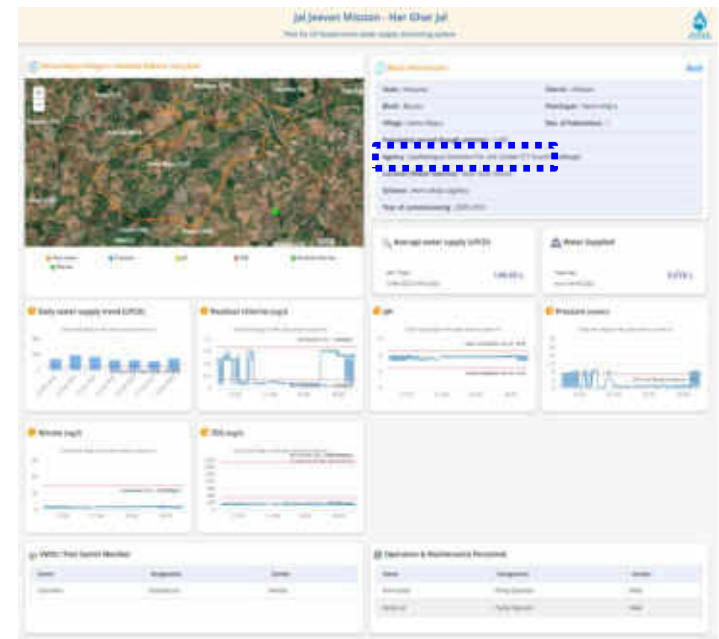


India's water is being monitored



IITM/IISc

Installations made by four companies





International Centre for Clean Water



IIT Madras Research Park

Collaborators



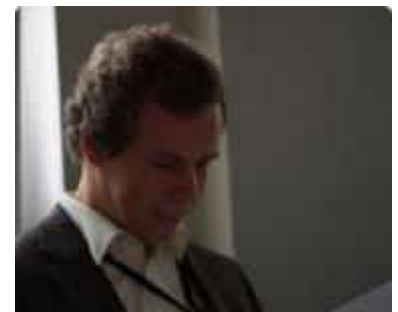
Tatsuya Tsukuda
Keisaku Kimura
Yuichi Negishi
Hannu Hakkinen
Uzi Landman
Rob Whetten
K. Vijayamohanan, Reji
Philip, Shiv Khanna



Robin Ras



Nonappa



Tomas Base



Manfred Kappes



Olli Ikkala



Horst Hahn



Biswarup Pathak



K. V. Adarsh



G. U. Kulkarni



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