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Atomically Precise Clusters: Towards Megadalton Molecules

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

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 Supporting Information

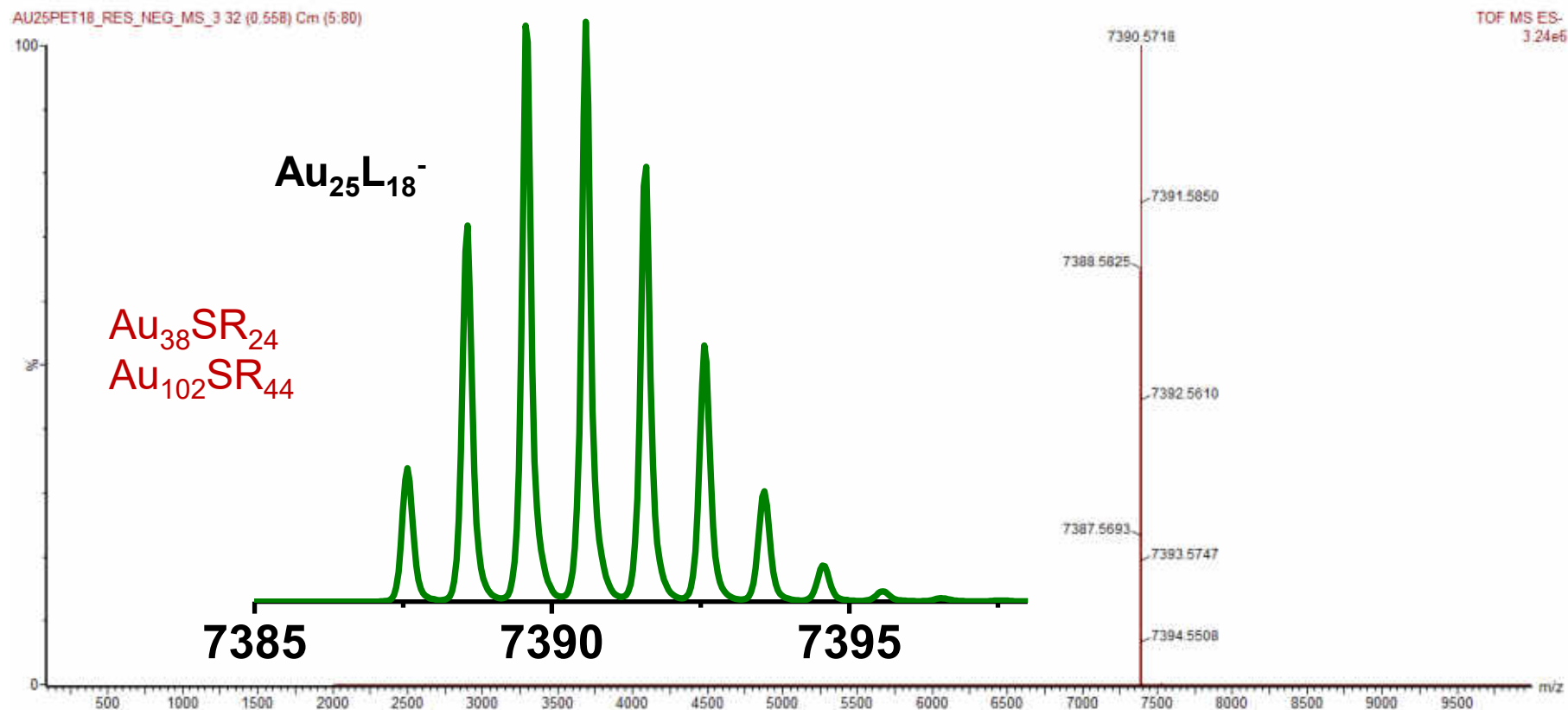
Citations: >1700

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

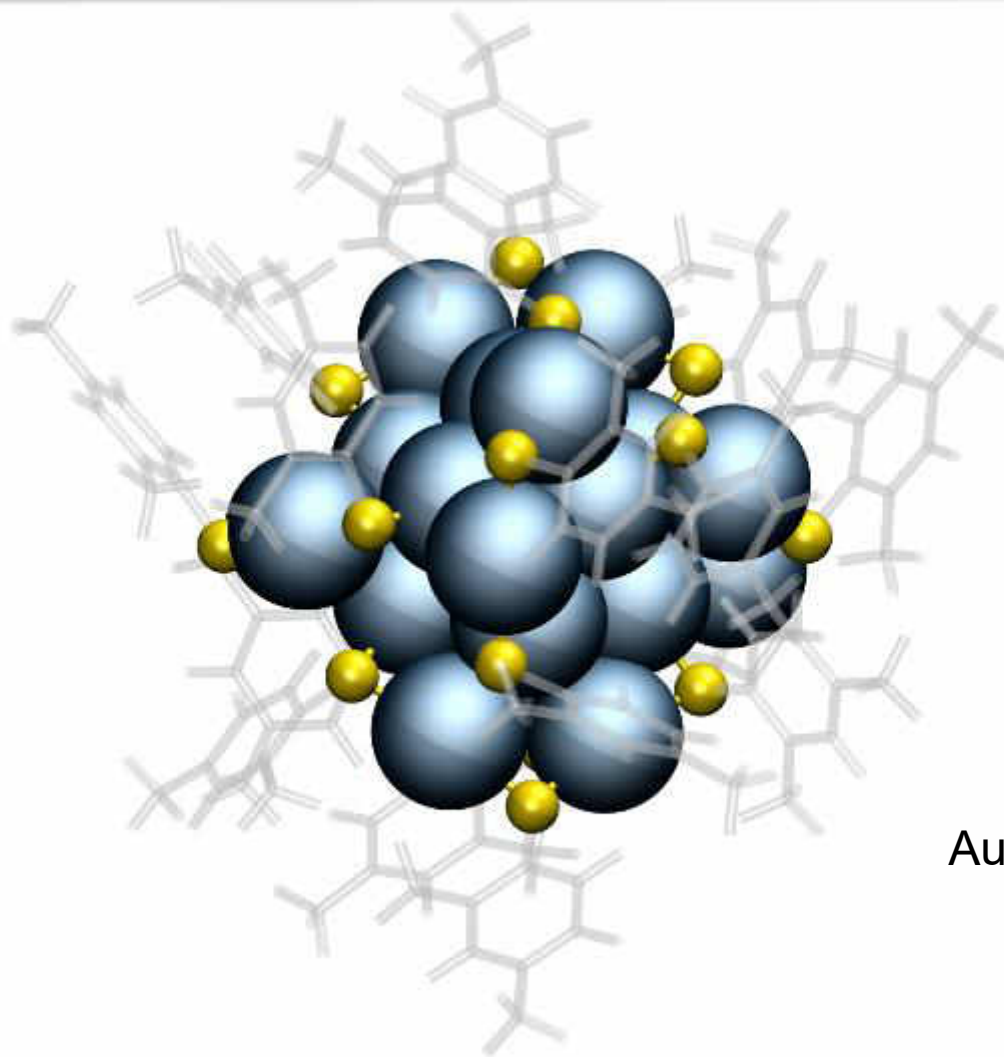


Also the pioneering work of R. W. Murray, Robert L. Whetten, Uzi Landman, Tatuya Tsukuda, Yuichi Negishi, Hannu Hakkinen, Rongchao Jin, Nanfeng Zheng, Terry Bigioni, Osman Bakr, Kornberg, Jianping Xie, C. M. Aikens, Thomas Buergi, Amala Dass, Ackerson, De-en Jiang, A. W. Castleman Jr., H. Schmidbauer,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

Molecular formula, Molecular weight

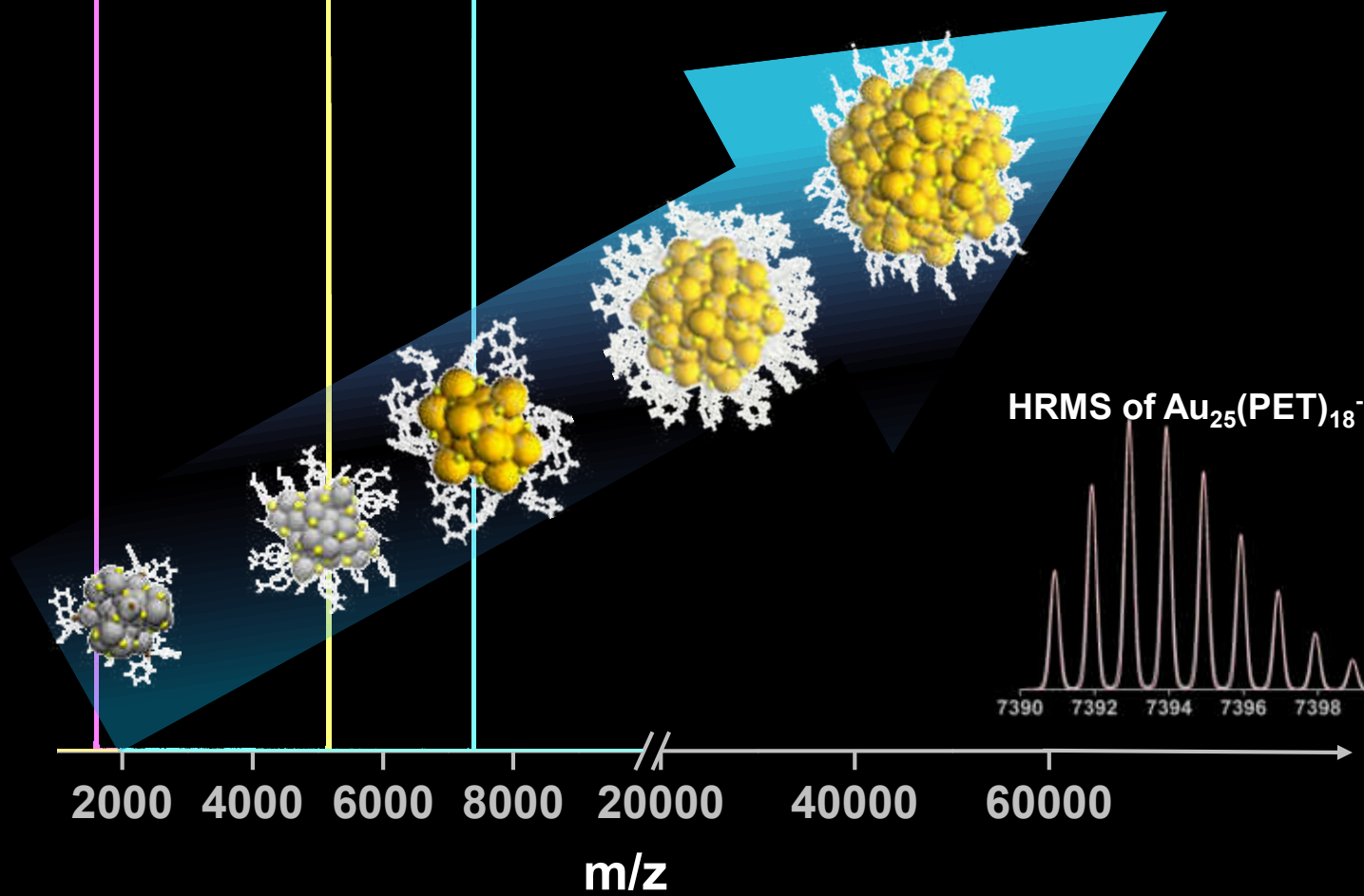


New molecules

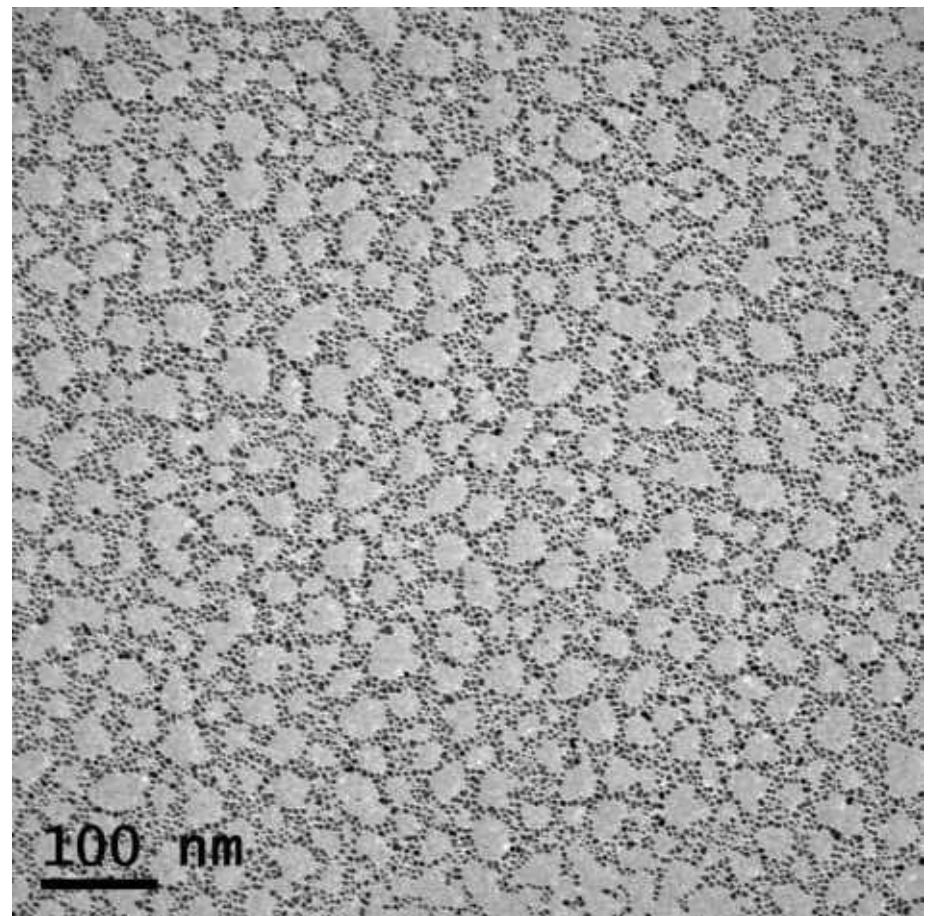
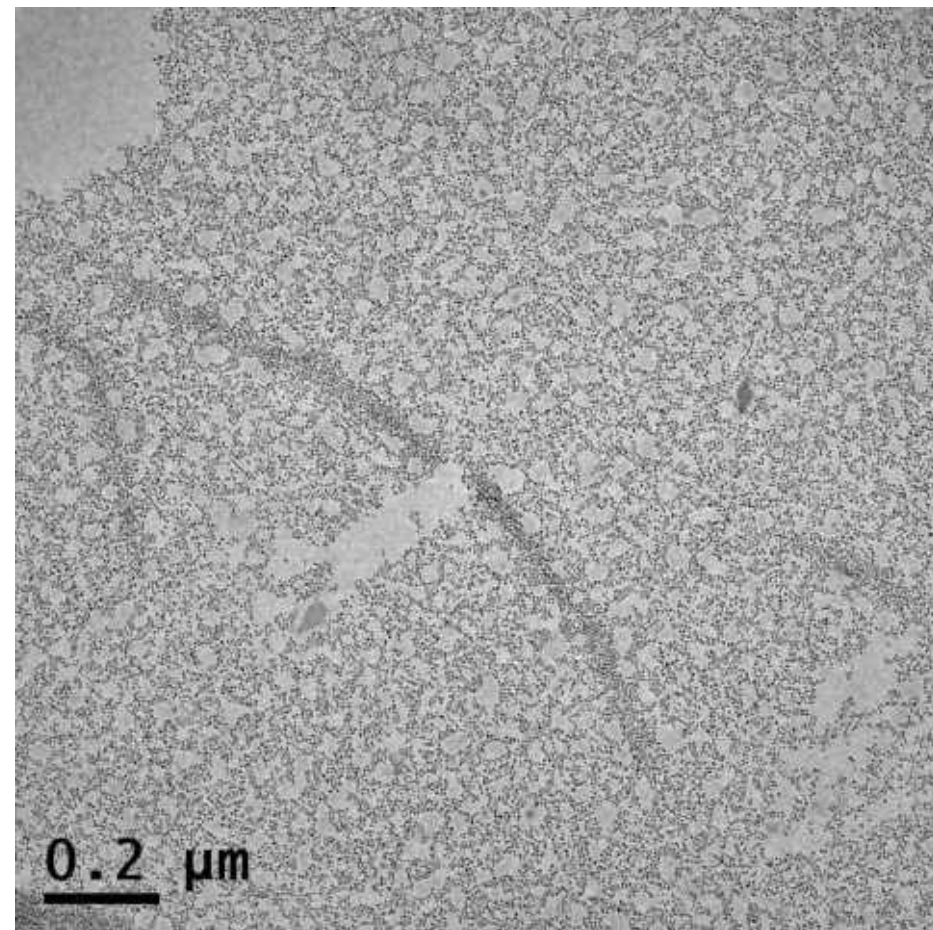


$\text{Au}_{25}, \text{Ag}_{25}, \text{Ag}_{29}$

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



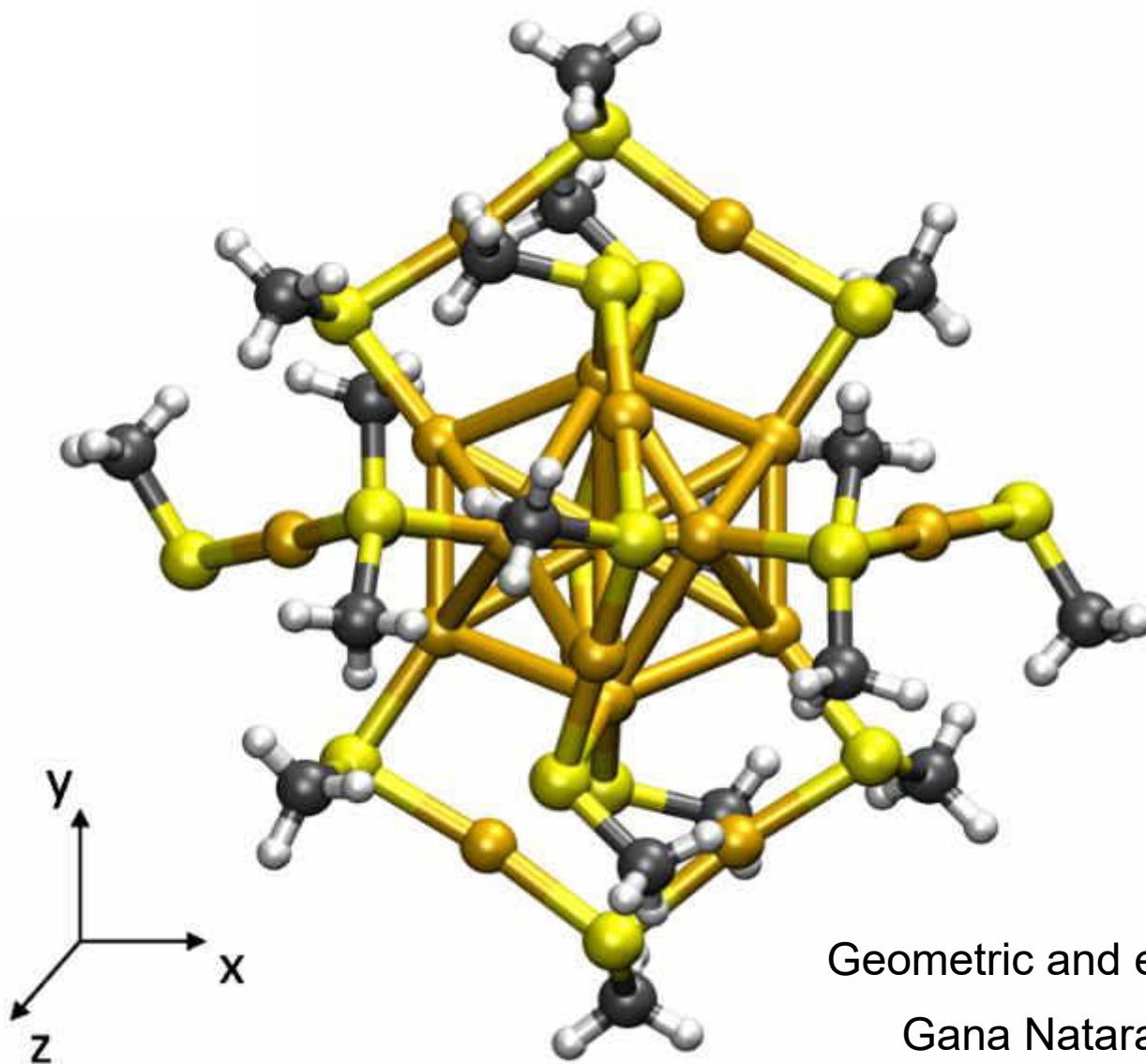
TEM images of Au₂₅ and Au₁₄₄



They make high quality crystals

50 μm

Molecular structure



Geometric and electronic shells

Gana Natarajan

Molecular materials

ACCOUNTS

of chemical research

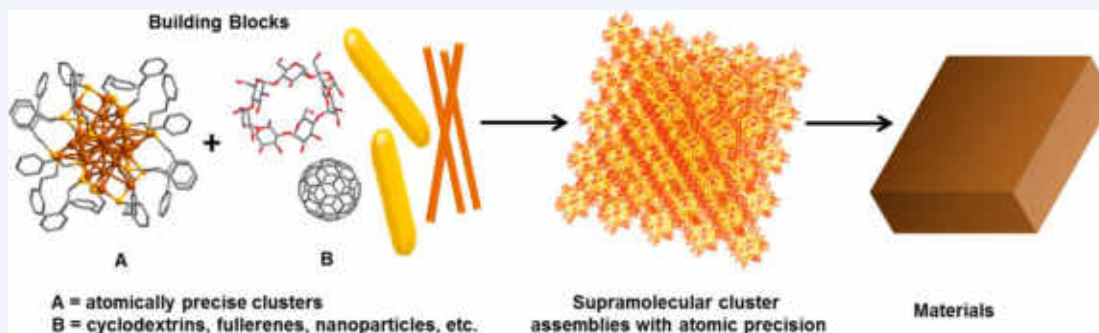
Article

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

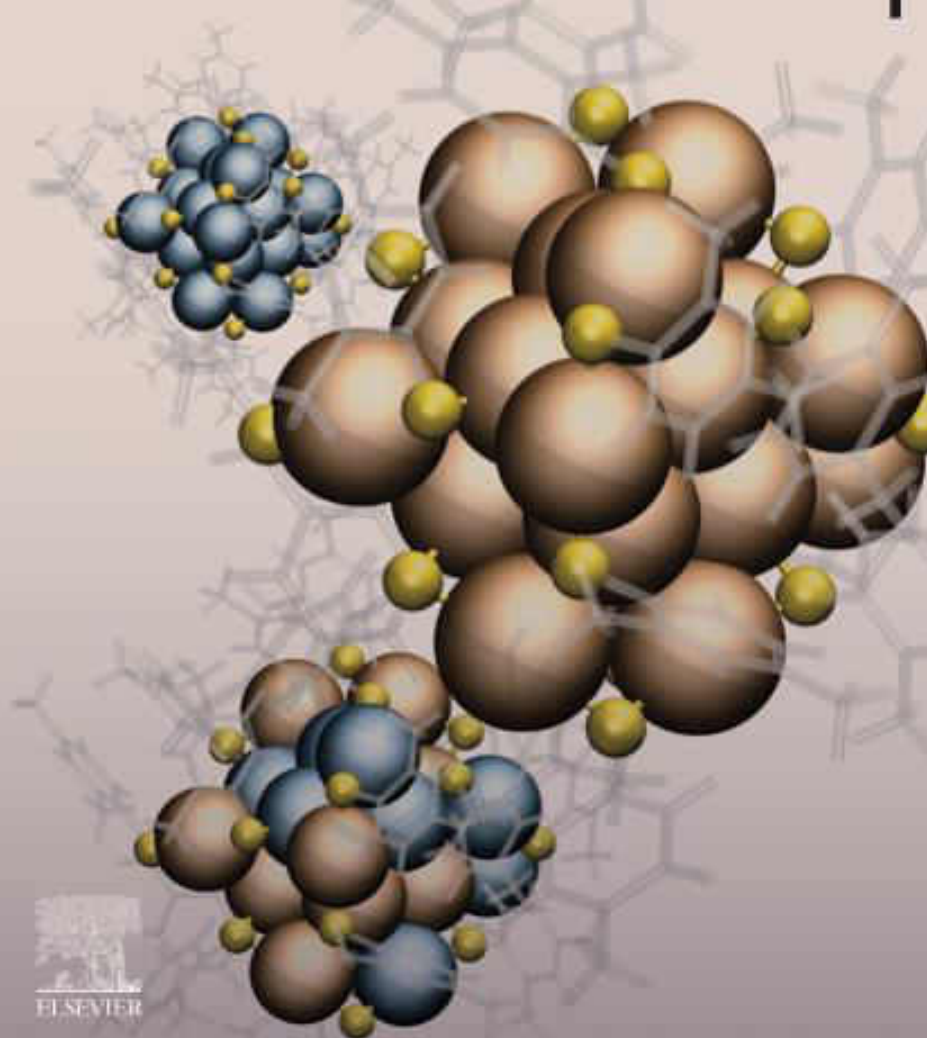
Molecular formula
Molecular weight
Molecular structure
Molecular absorption and emission
Molecular reactions
Molecular assembly
Molecular co-crystals

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

Future?

Edited by
Thalappil Pradeep

ATOMICALLY PRECISE METAL NANOCCLUSERS



Molecular reactions



Reactions on clusters
Reactions between clusters

Inter-cluster reactions



Article

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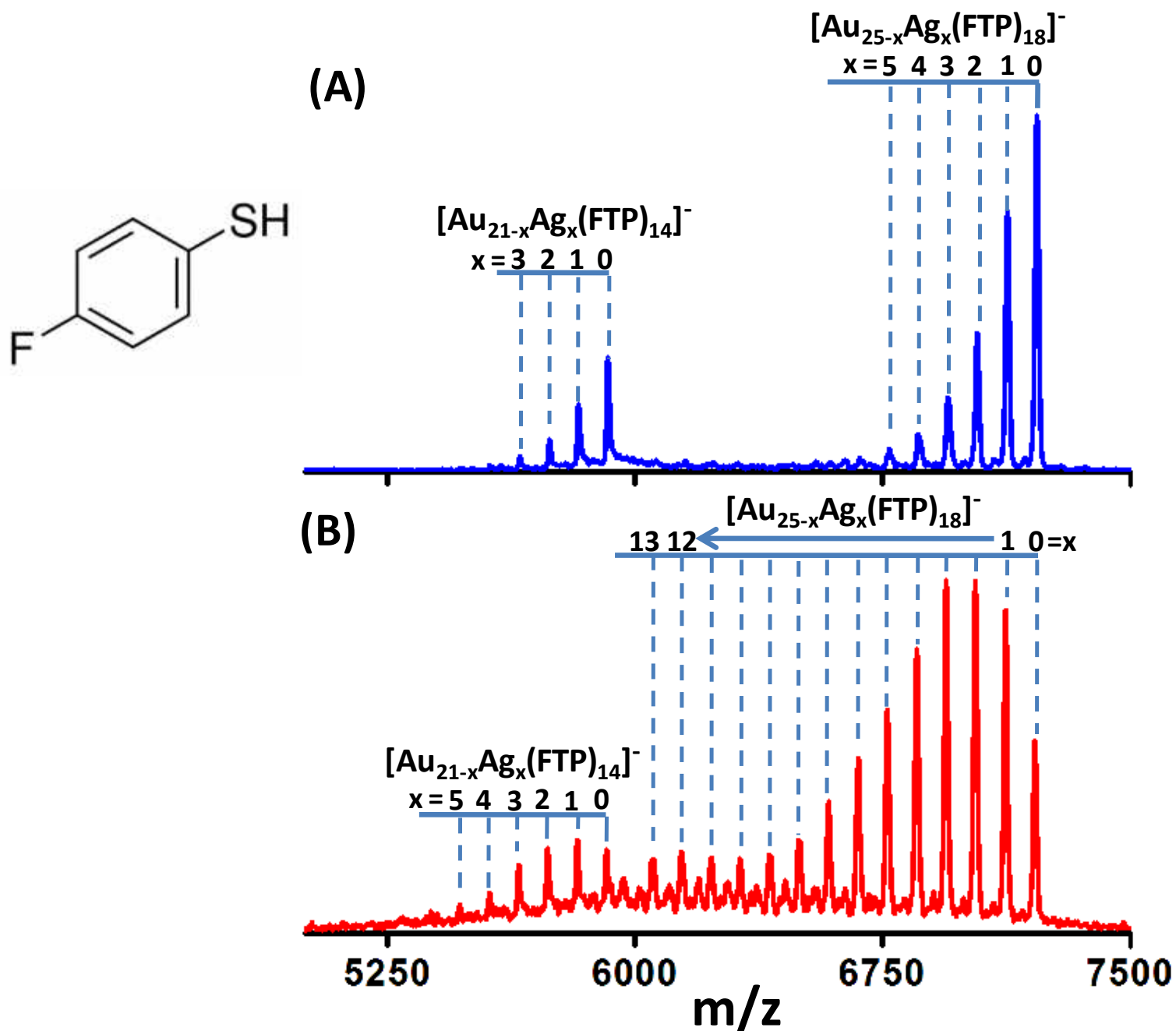
Intercluster Reactions between $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Ag}_{44}(\text{SR})_{30}$

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





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

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

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

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

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

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

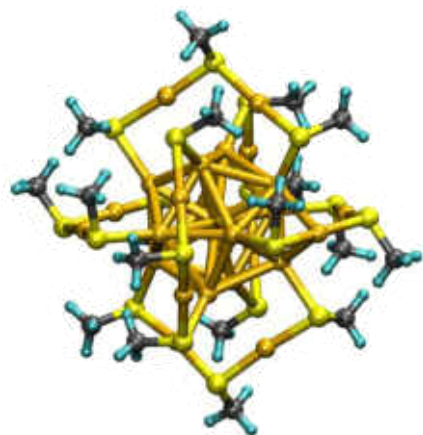
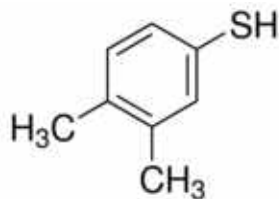
Location of Ag in $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$	I	D_{cv}	D_{cf}	S
C	-0.015	+0.564	+0.388	+0.226
I	-0.486	+0.093	-0.083	-0.245
S	-0.276	+0.303	+0.127	-0.035

Ag₂₅-Au₂₅ experiments

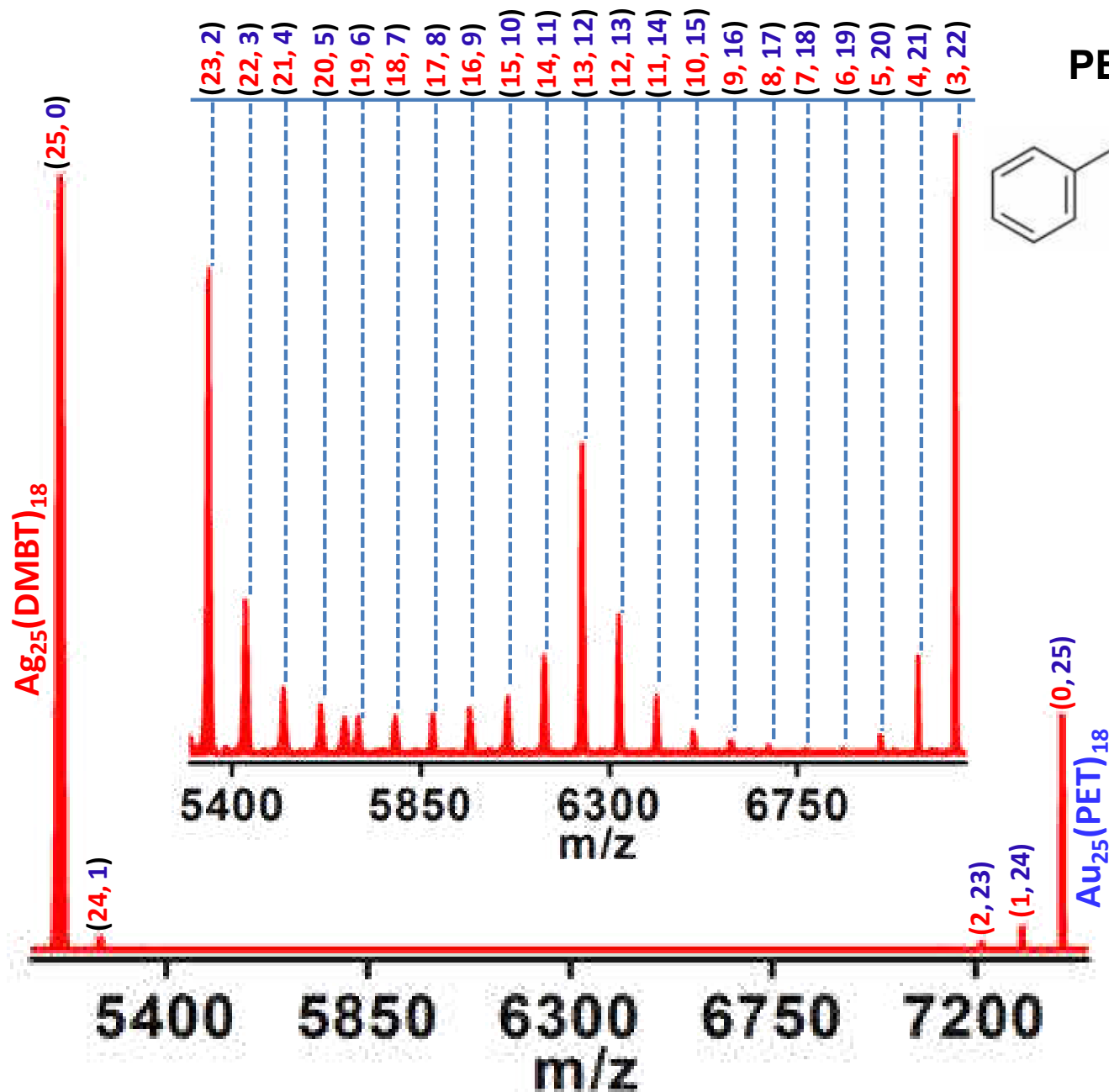
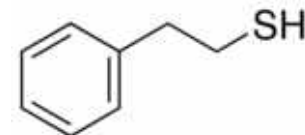
K. R. Krishnadas et al. *Nature Commun.* 2016

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

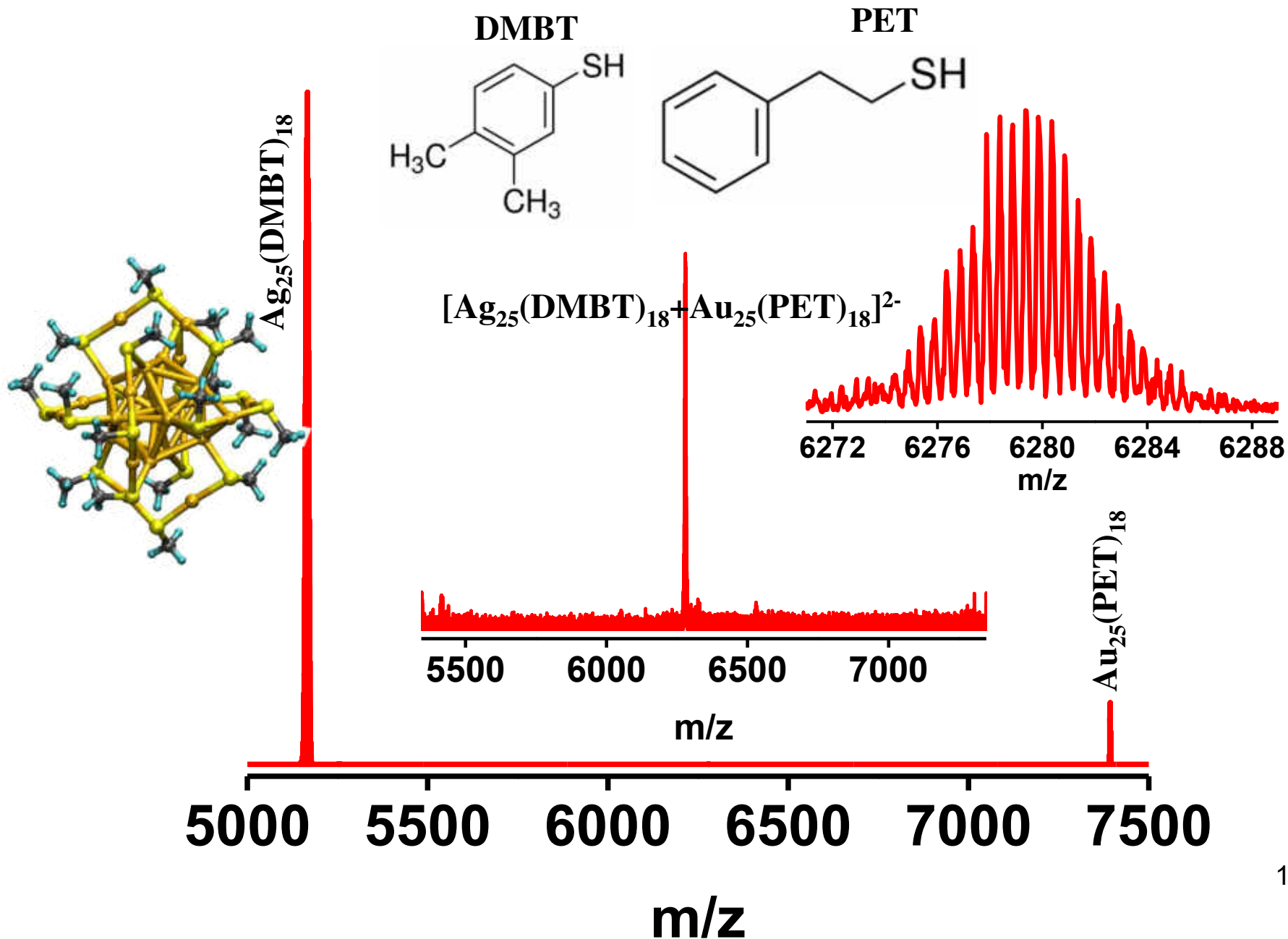
DMBT



PET

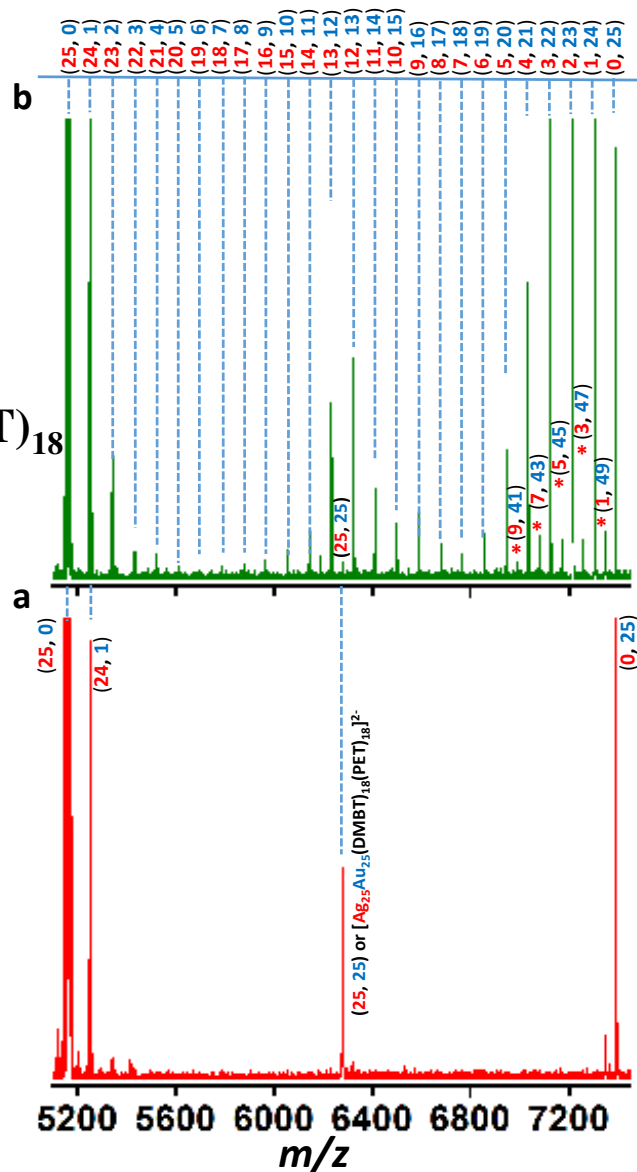


$[\text{Ag}_{25}(\text{DMBT})_{18} + \text{Au}_{25}(\text{PET})_{18}]^{2-}$



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

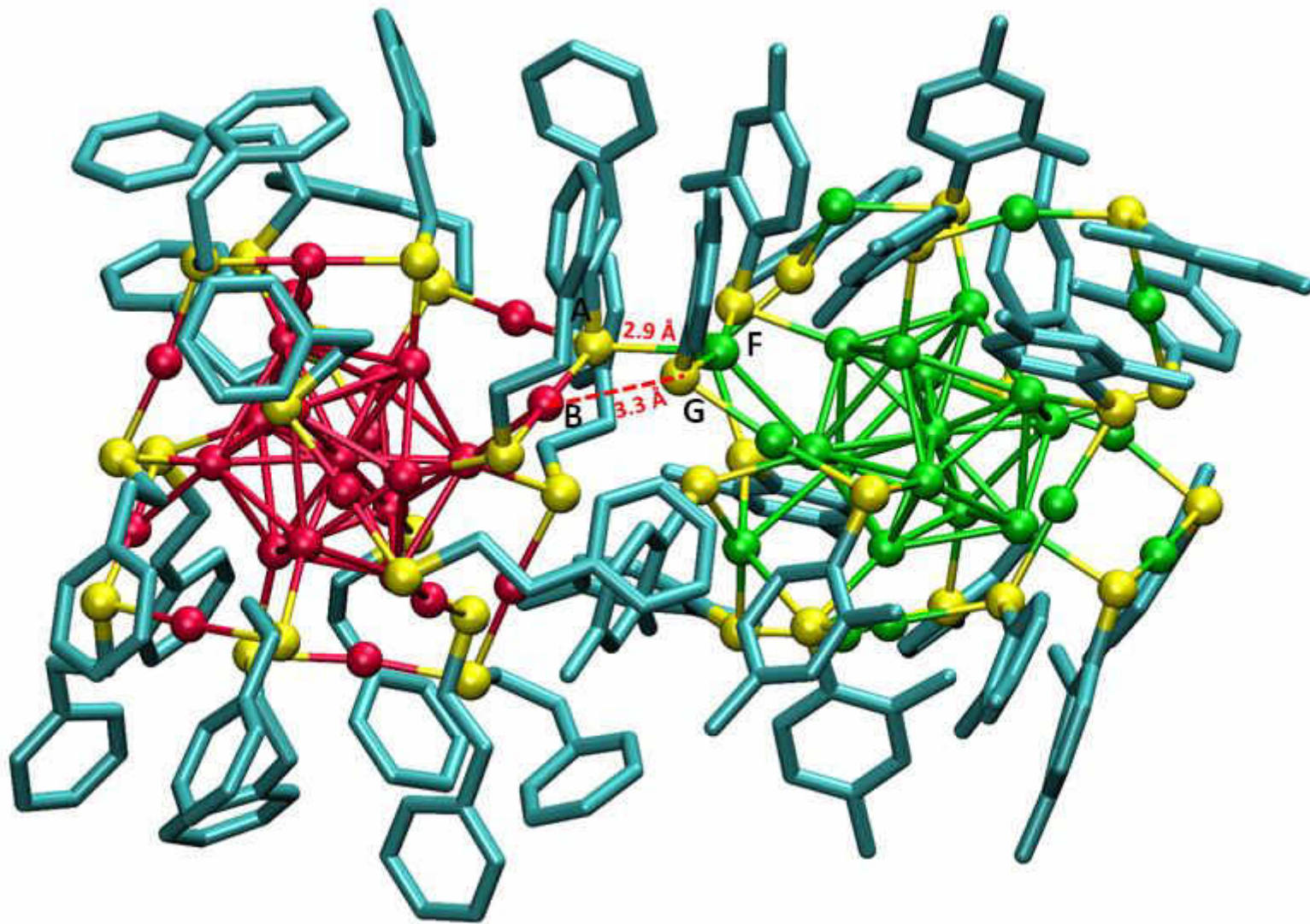
$\text{Ag}_{25}(\text{DMBT})_{18}:\text{Au}_{25}(\text{PET})_{18}$
0.3:1.0

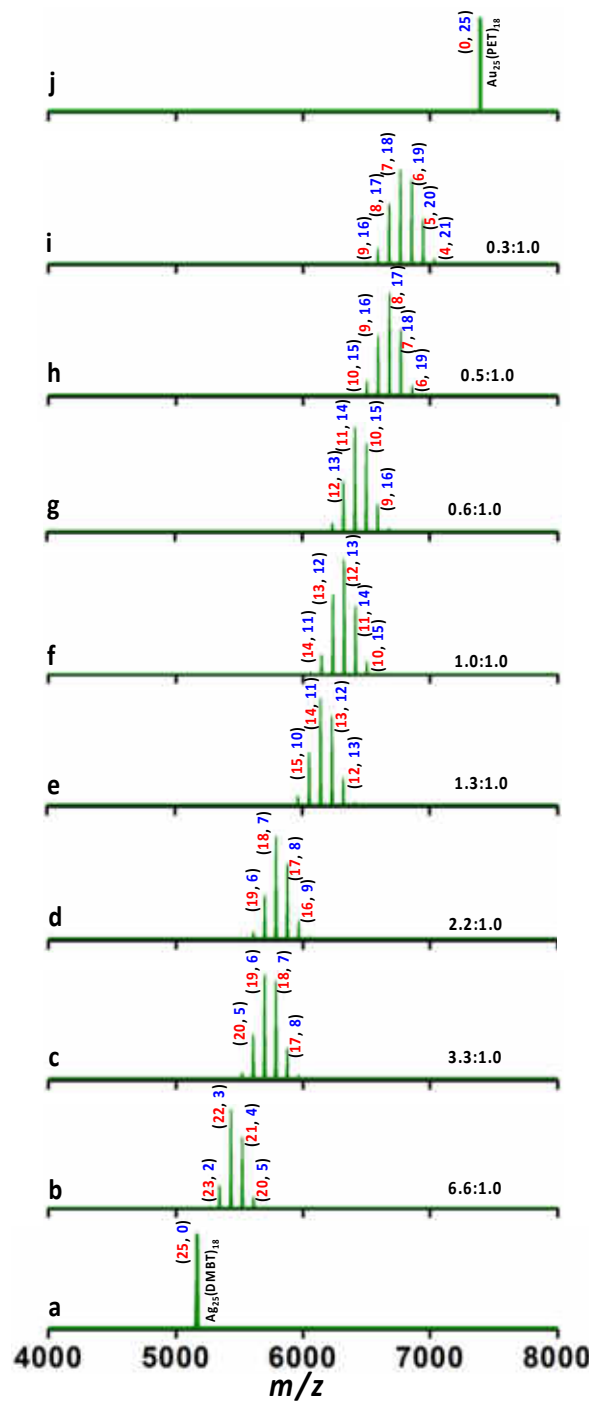


within 5 min

within 2 min

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

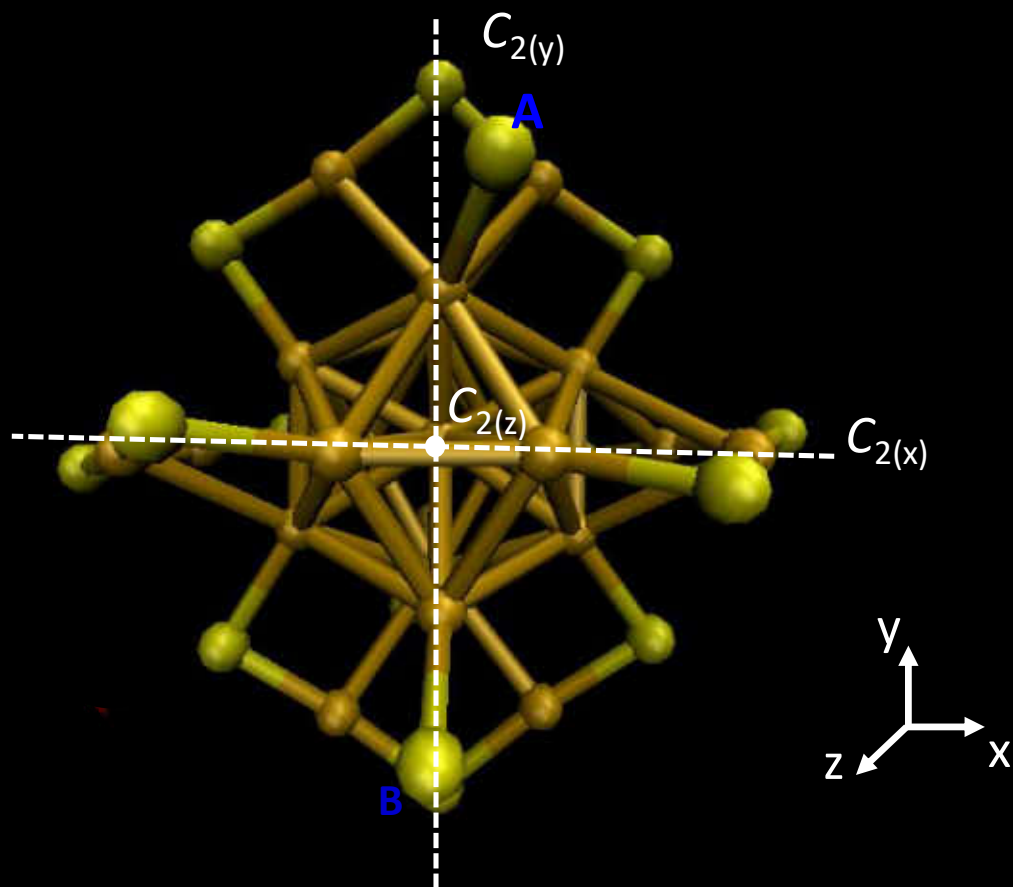




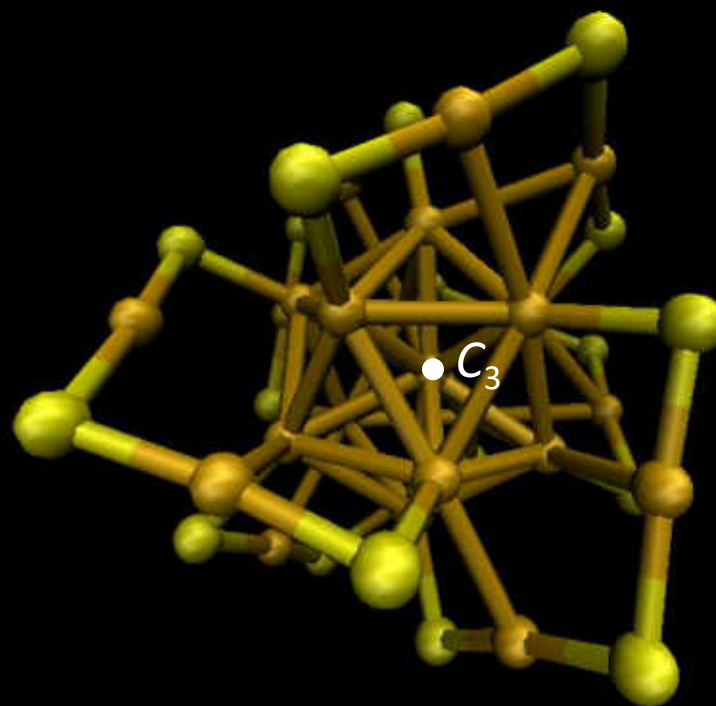
How do we comprehend this?

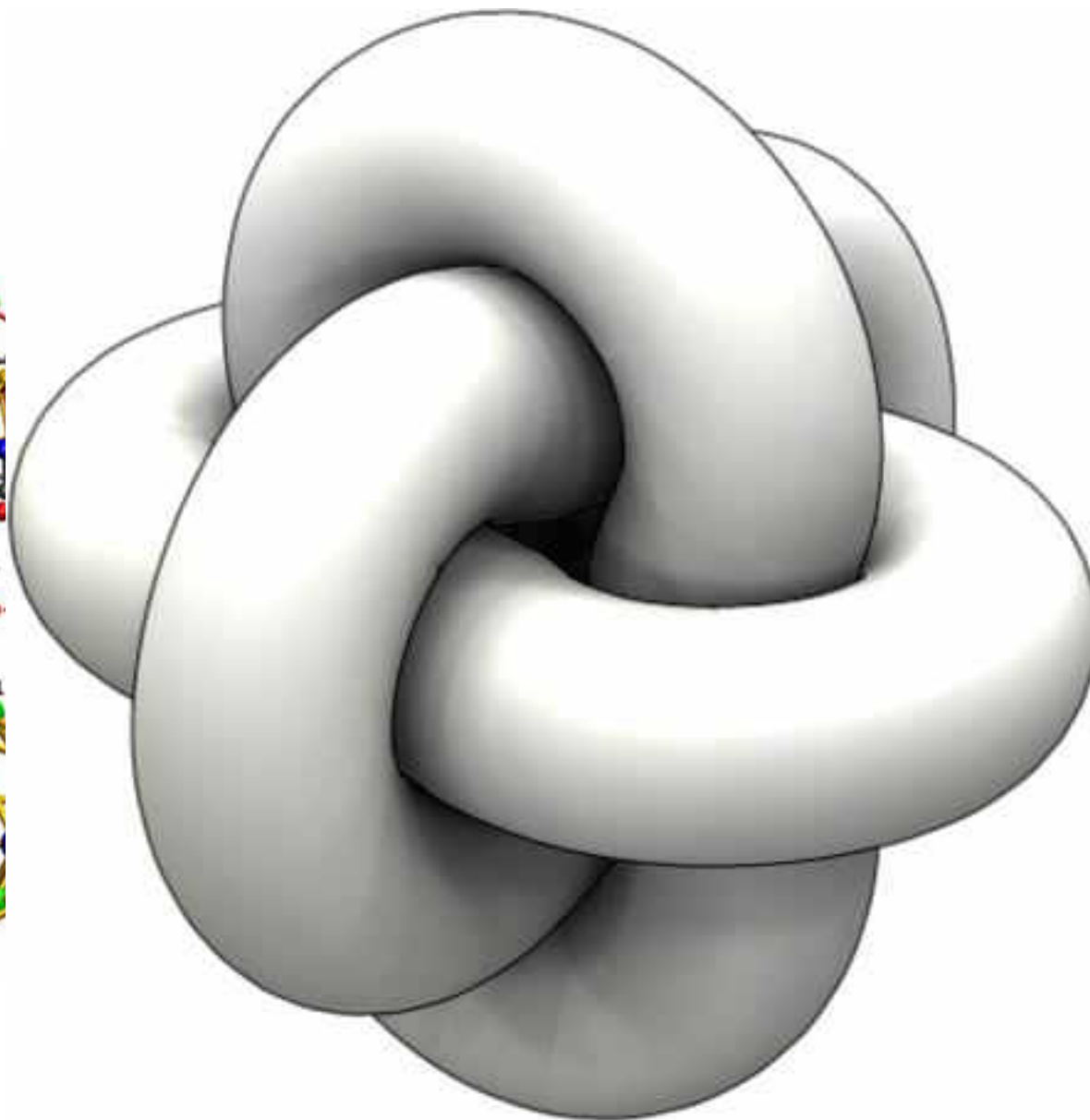
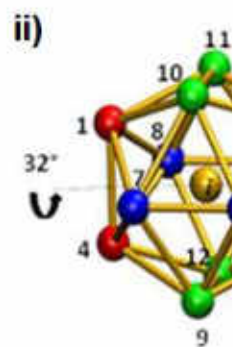
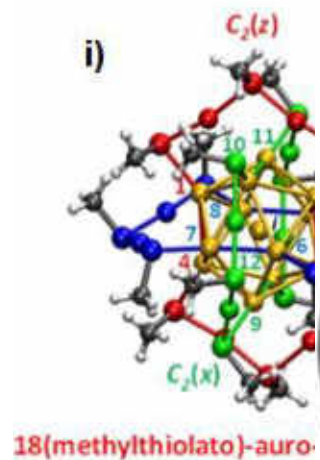
Nomenclature

1) Edge projection



2) Face Projection





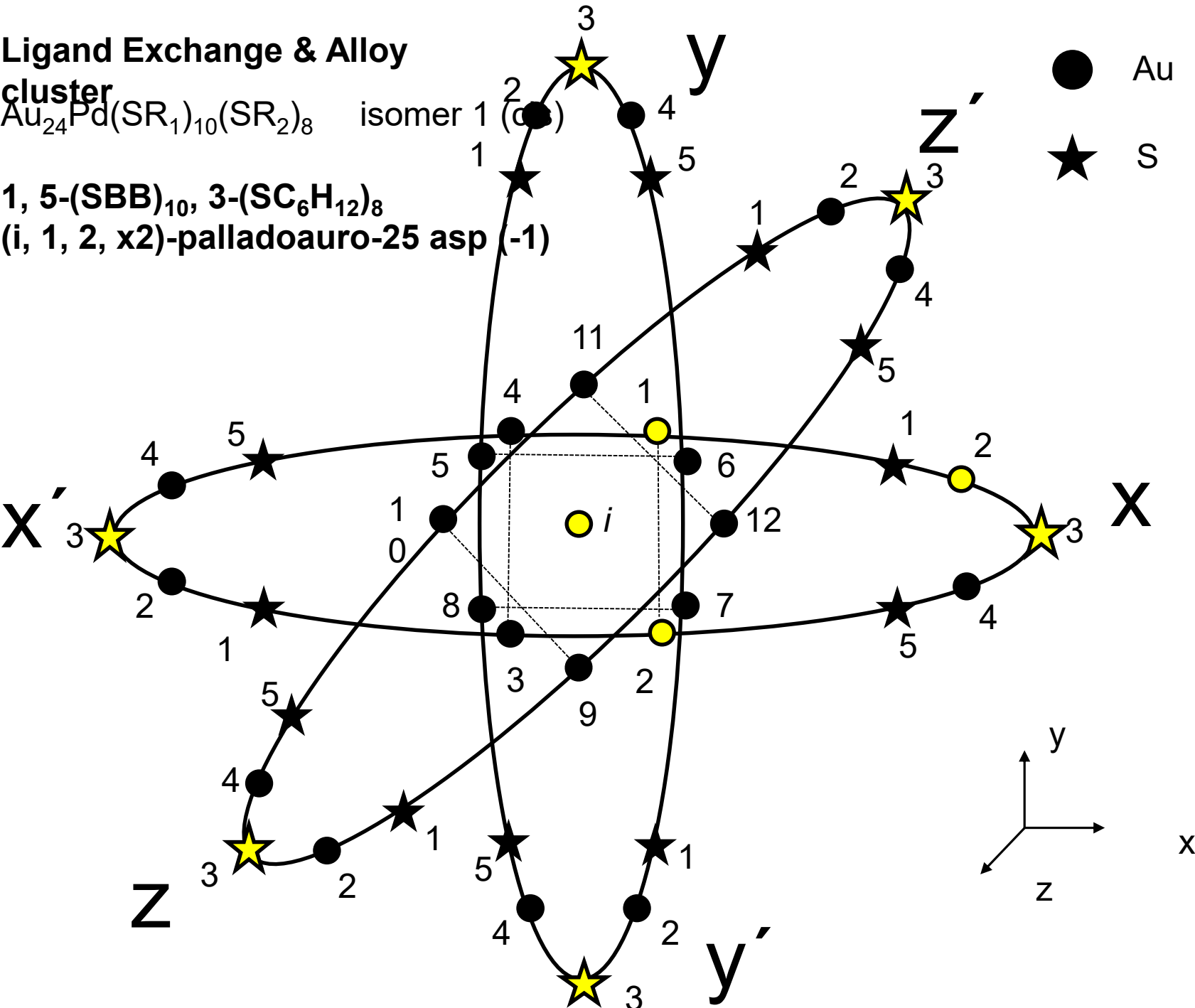
Aspicules

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

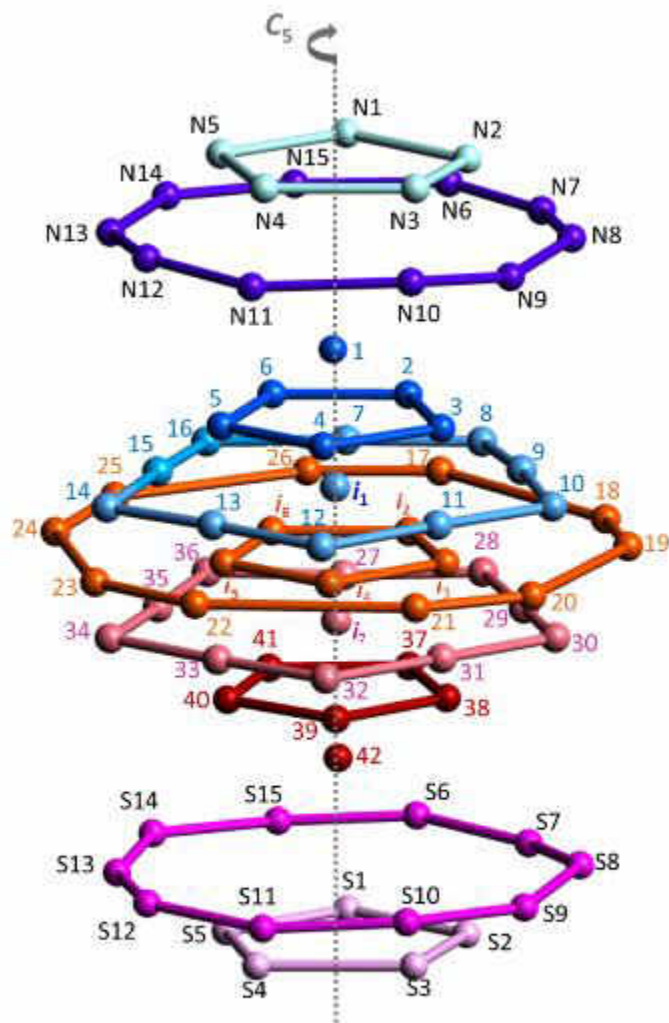
Ligand Exchange & Alloy cluster

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

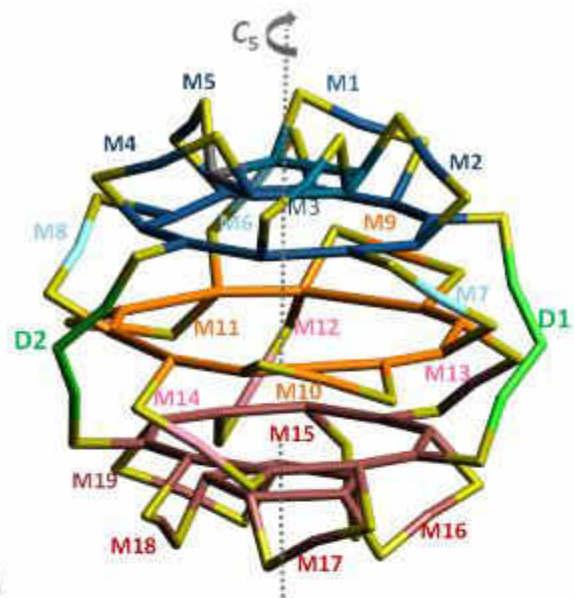
1, 5-(SBB)₁₀, 3-(SC₆H₁₂)₈
(i, 1, 2, x2)-palladoauro-25 asp (-1)



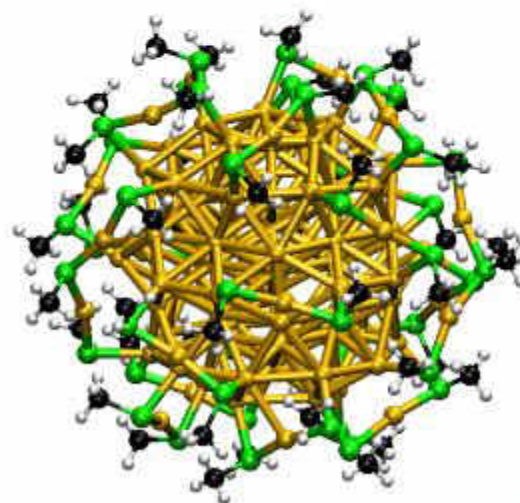
(A)



(B)



(C)



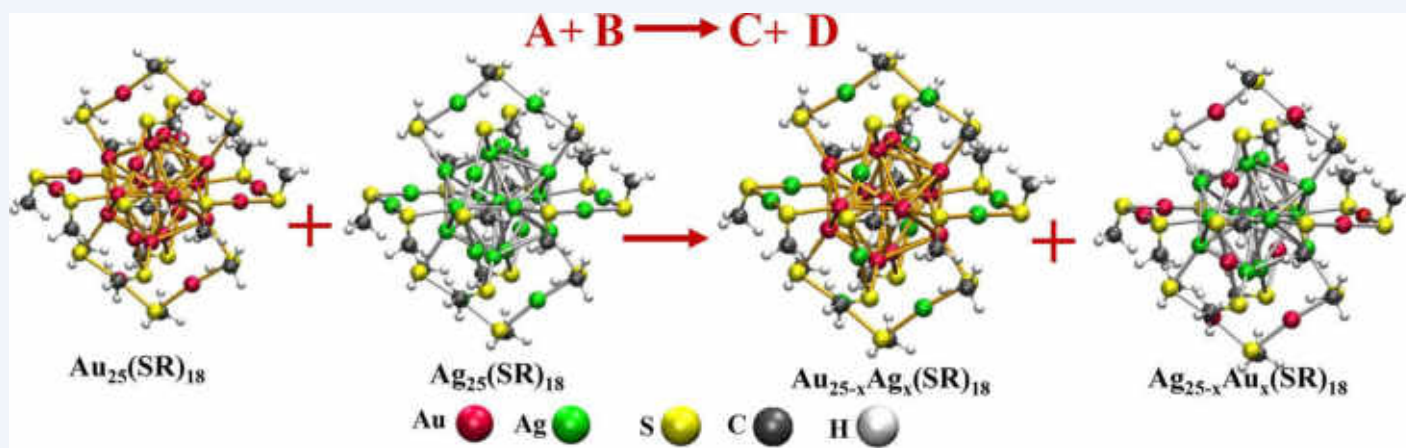
R-44(methylthiolato)-auro-102 aspicule(0)

R-(SMe)₄₄-auro-102 aspicule(0) and L-(SMe)₄₄-auro-102 aspicule(0) ²⁸

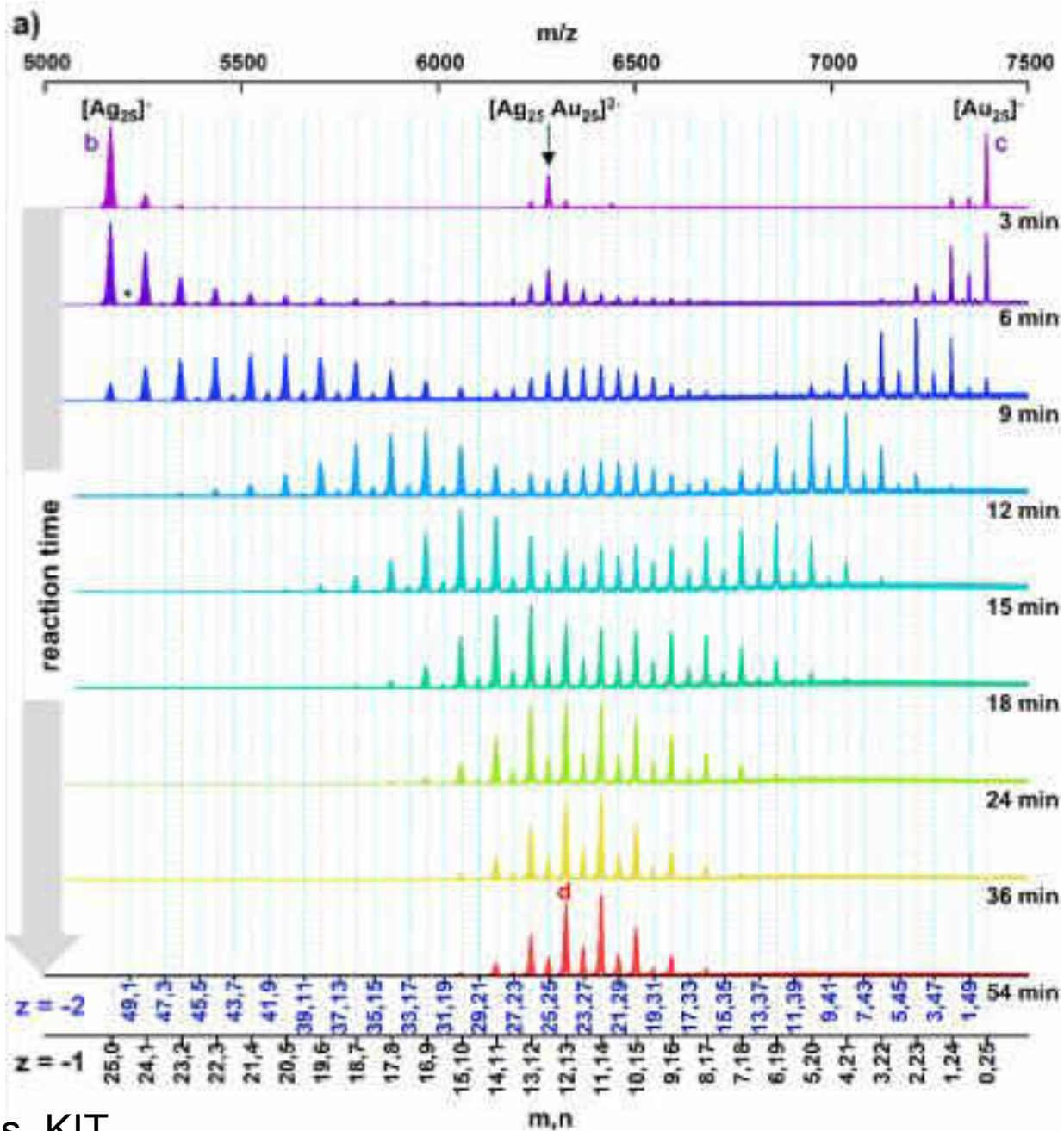
Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

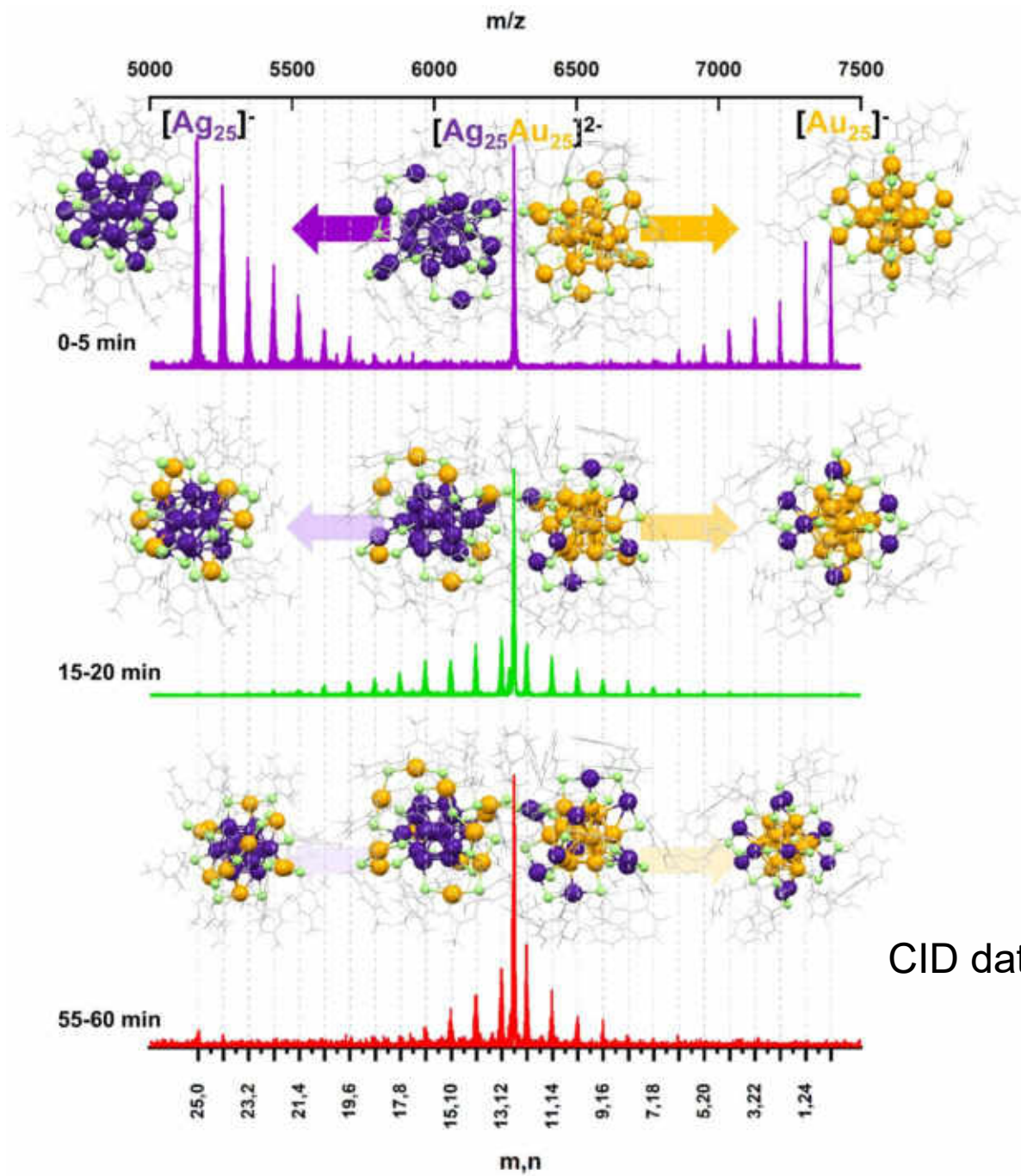
K. R. Krishnadas, Ananya Baksi,[†] Atanu Ghosh, Ganapati Natarajan, Anirban Som, and Thalappil Pradeep^{*ID}

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



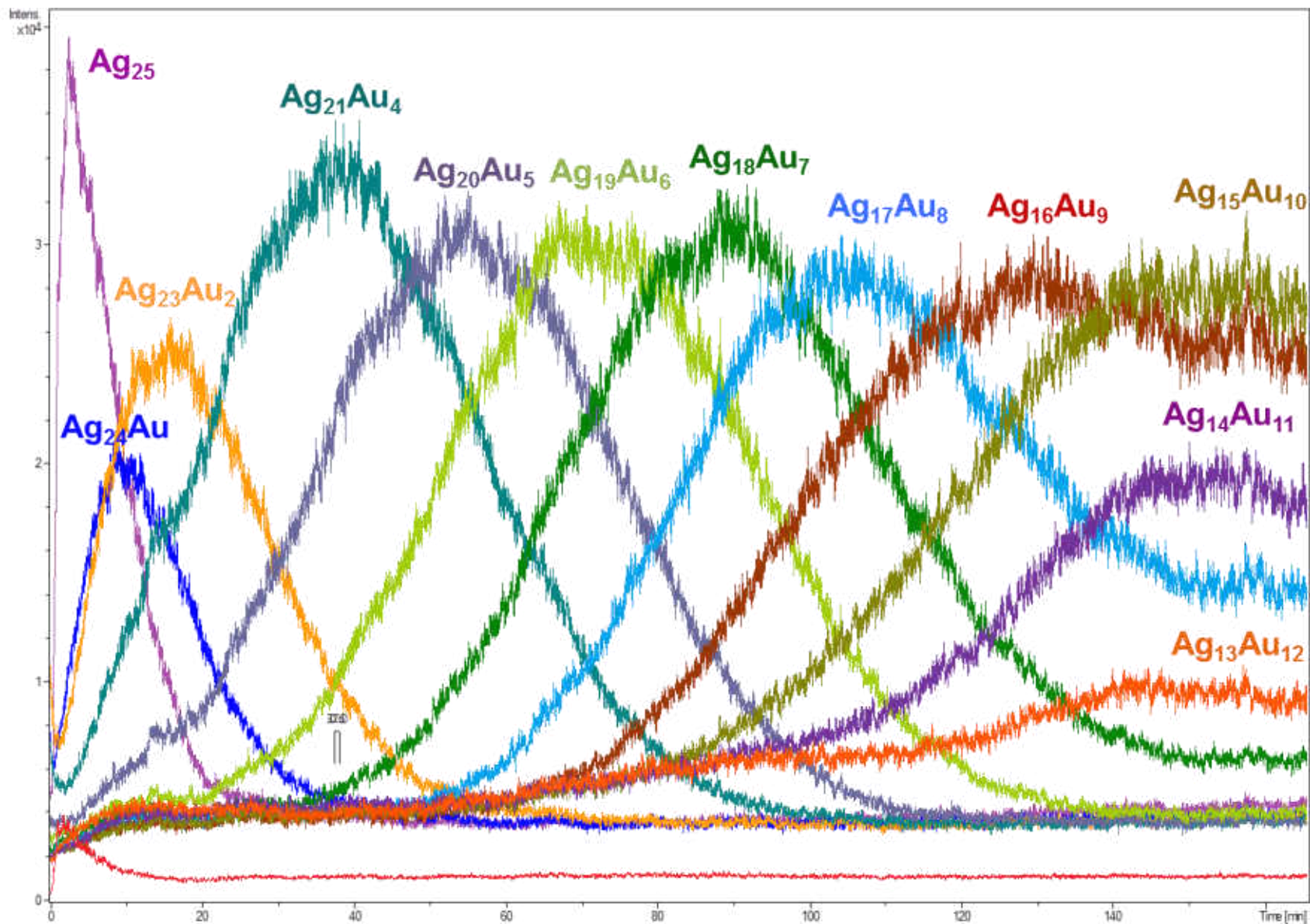
CONSPECTUS: Nanoparticles exhibit a rich variety in terms of structure, composition, and properties. However, reactions between them remain largely unexplored. In this *Account*, we discuss an emerging aspect of nanomaterials chemistry, namely, interparticle reactions in solution phase, similar to reactions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





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

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



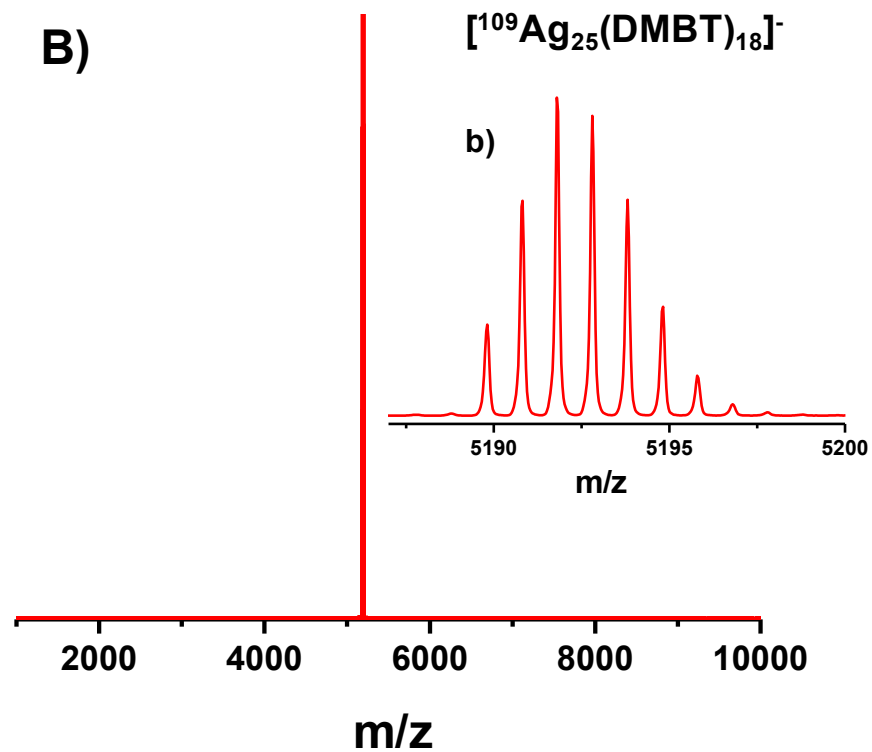
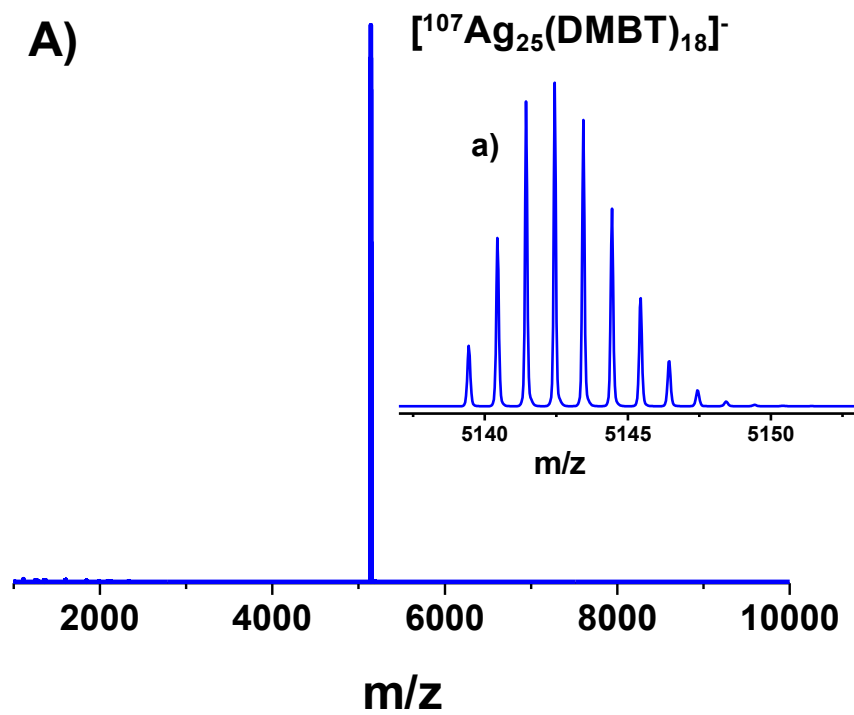
CONDENSED MATTER PHYSICS

Rapid isotopic exchange in nanoparticles

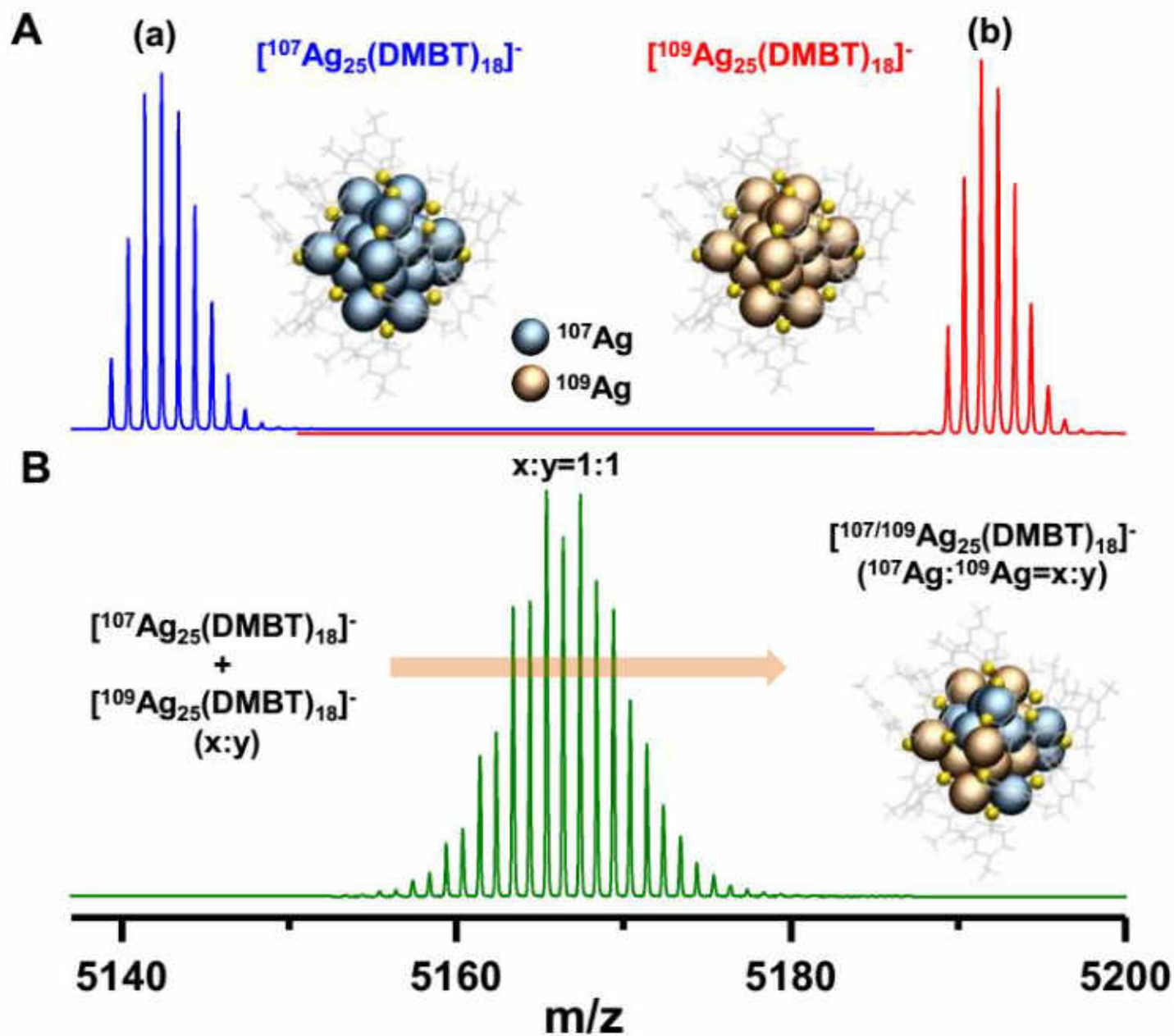
**Papri Chakraborty¹, Abhijit Nag¹, Ganapati Natarajan¹, Nayanika Bandyopadhyay¹,
Ganesan Paramasivam¹, Manoj Kumar Panwar¹, Jaydeb Chakrabarti², Thalappil Pradeep^{1*}**

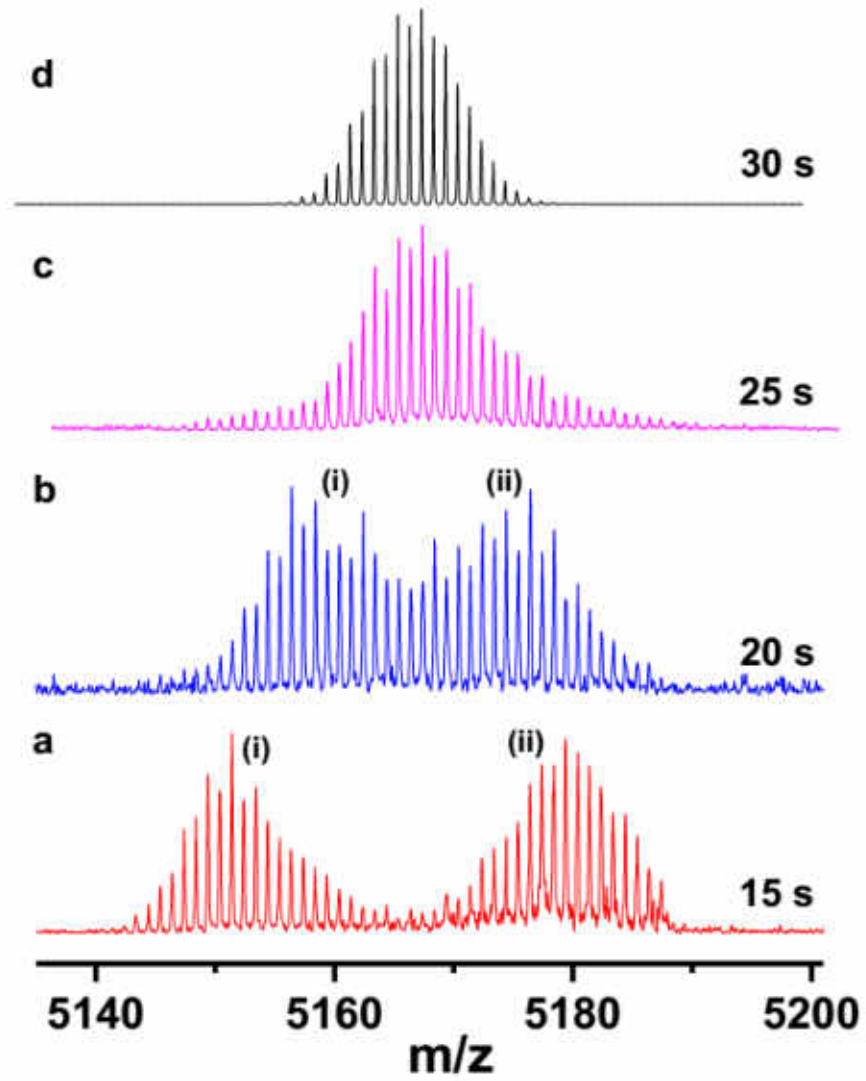
Rapid solution-state exchange dynamics in nanoscale pieces of matter is revealed, taking isotopically pure atomically precise clusters as examples. As two isotopically pure silver clusters made of ^{107}Ag and ^{109}Ag are mixed, an isotopically mixed cluster of the same entity results, similar to the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

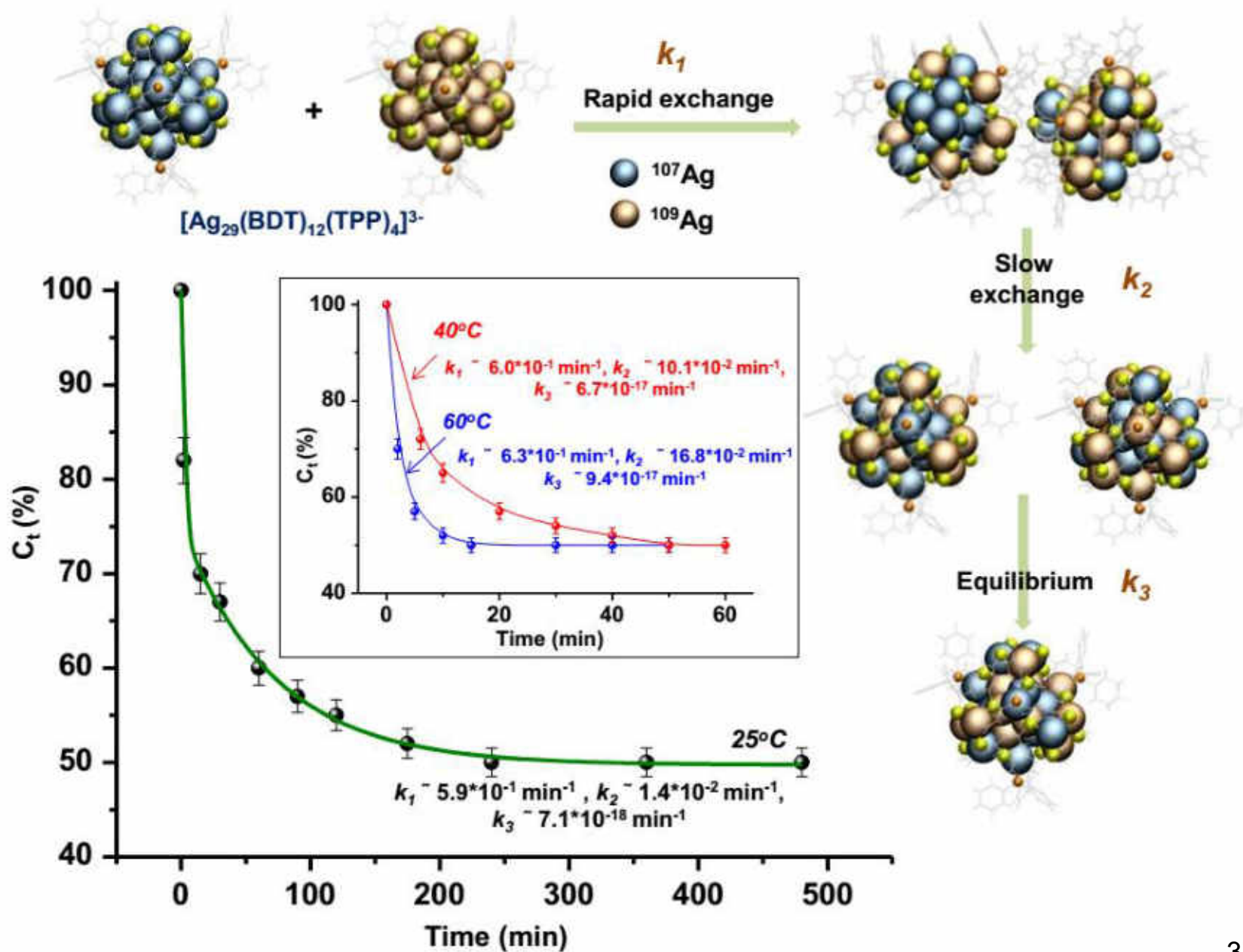
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ESI MS of **A)** $^{107}\text{Ag}_{25}(\text{DMBT})_{18}$ and **B)** $^{109}\text{Ag}_{25}(\text{DMBT})_{18}$. Insets shows the respective isotope patterns.

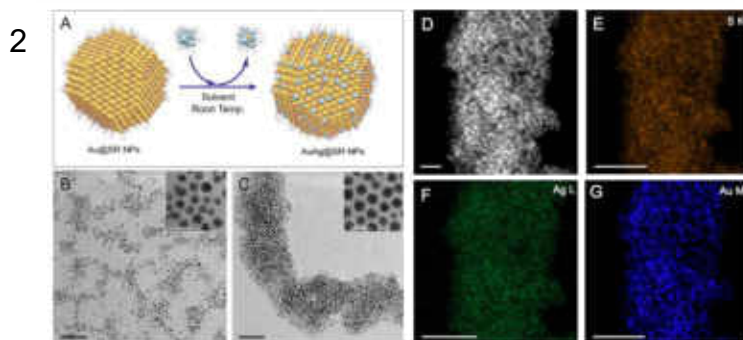
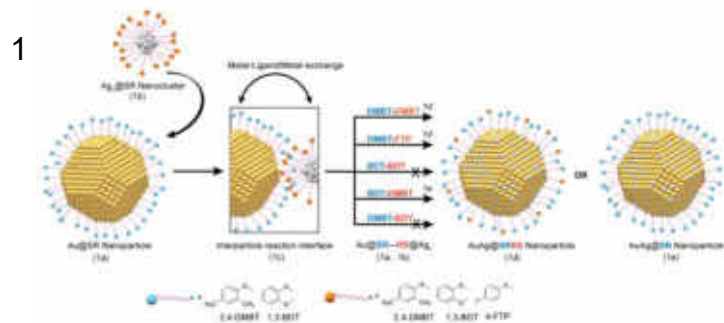




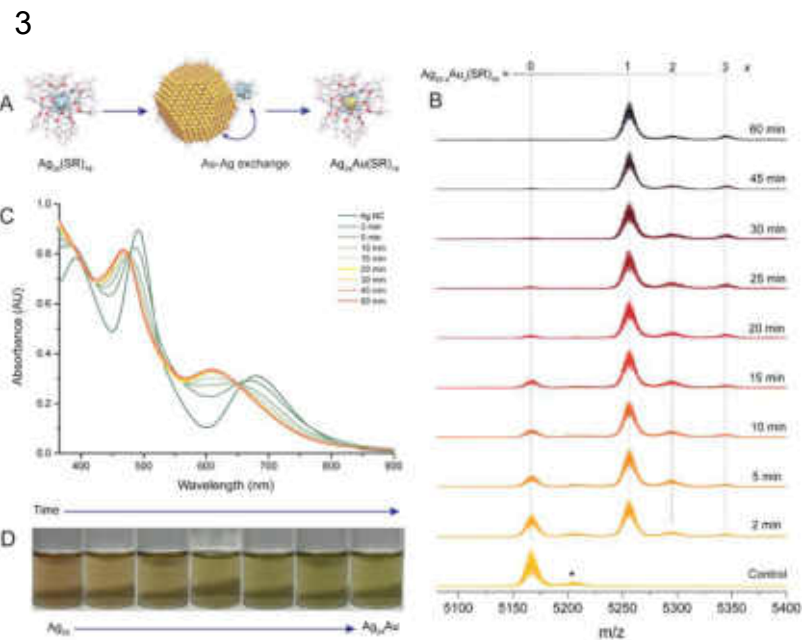


Can clusters react with nanoparticles?

Ag₂₅ with Au nanoparticles

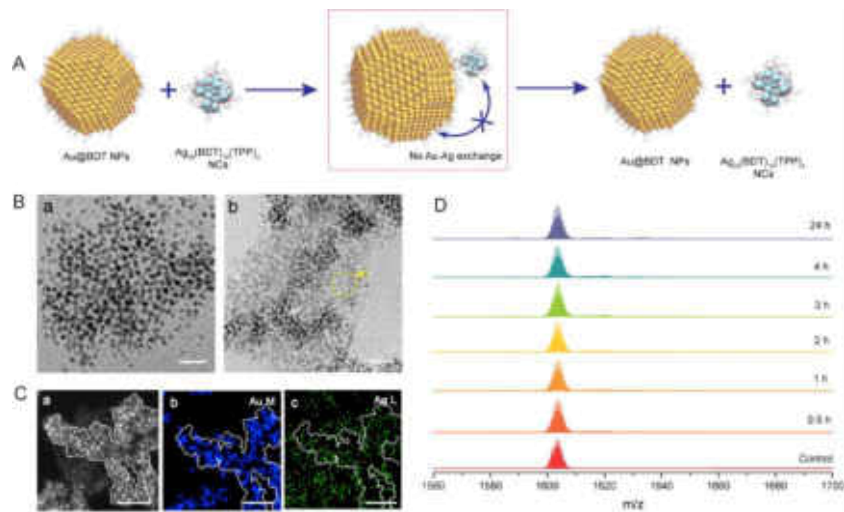


Scale bars: 50 nm (B-G) and 10 nm (insets of B and C).

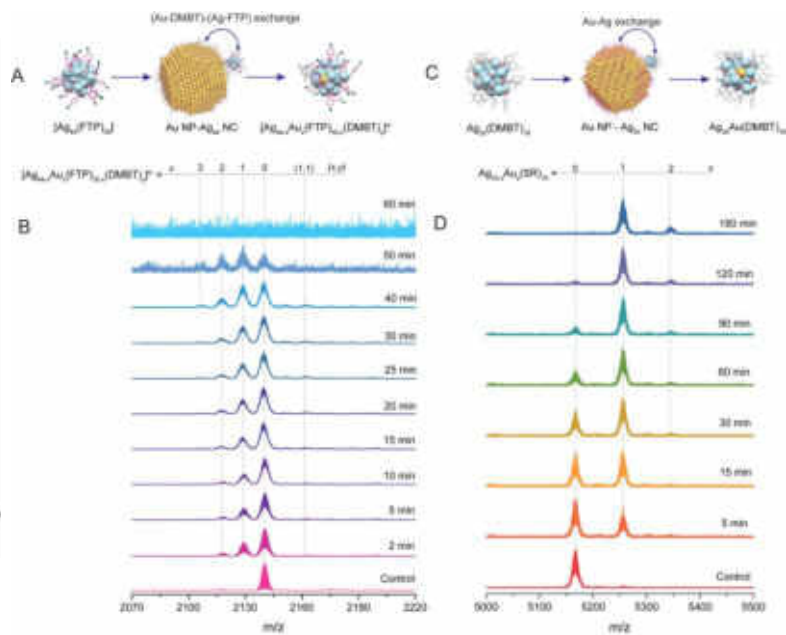


Interface controls the reaction

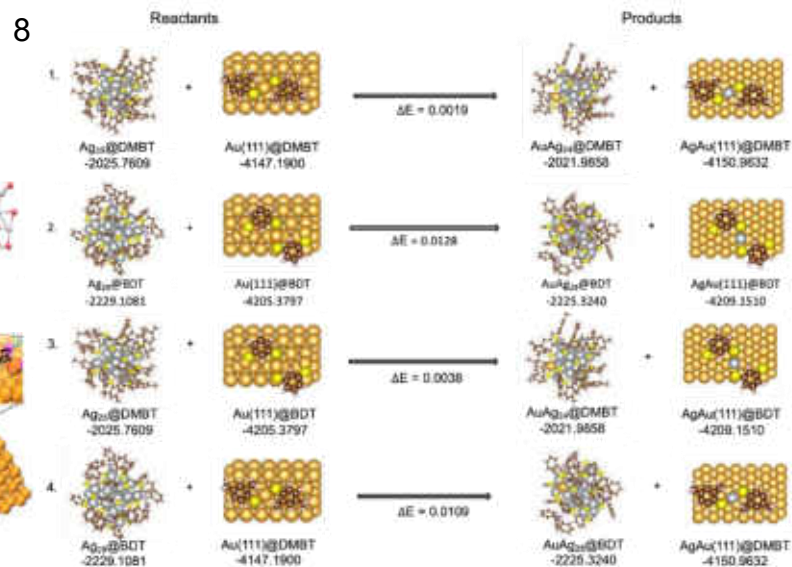
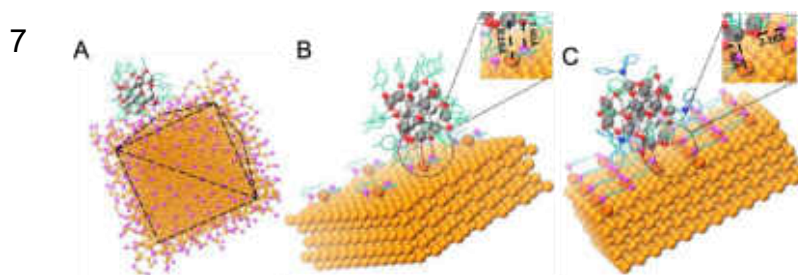
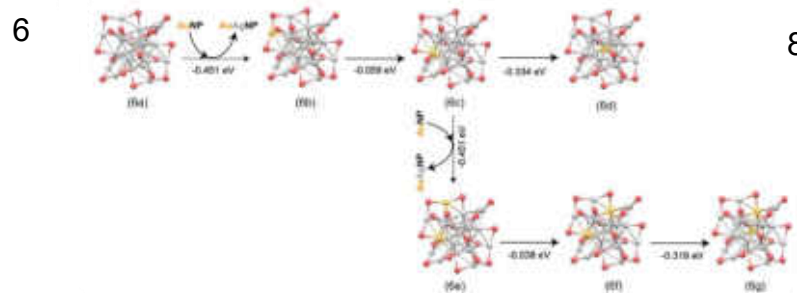
4



5



Computational insights



Reactions and new materials

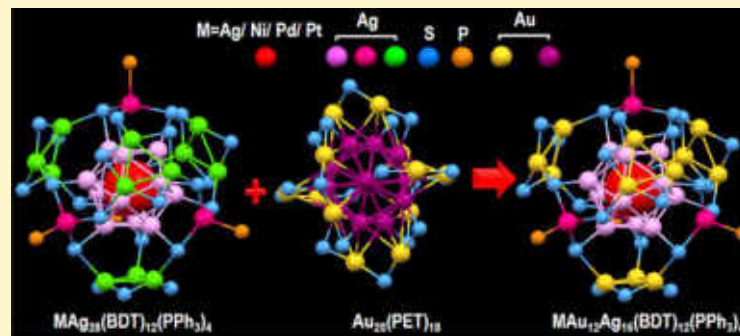
Intercluster Reactions Resulting in Silver-Rich Trimetallic Nanoclusters

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 $\text{MAg}_{28}(\text{BDT})_{12}(\text{PPh}_3)_4$ (BDT = 1,3-benzenedithiol and $\text{M} = \text{Ni}, \text{Pd}, \text{or Pt}$) and monothiol protected $\text{Au}_{25}(\text{PET})_{18}$ (PET = 2-phenylethanethiol) were used as model NCs. A mixture of trimetallic $\text{MAu}_x\text{Ag}_{28-x}(\text{BDT})_{12}(\text{PPh}_3)_4$ ($x = 1-12$) and bimetallic $\text{Ag}_x\text{Au}_{25-x}(\text{PET})_{18}$ ($x = 1-7$) NCs were formed during the reaction as understood from time-dependent electrospray ionization mass spectrometry (ESI MS). Detailed studies of intercluster reaction between $\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4$ and $\text{Au}_{25}(\text{PET})_{18}$ were also performed. Although both $\text{MAg}_{28}(\text{BDT})_{12}(\text{PPh}_3)_4$ ($\text{M} = \text{Ag}, \text{Ni}, \text{Pd}, \text{or Pt}$) and $\text{Au}_{25}(\text{PET})_{18}$ 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



Cite This: *ACS Nano* 2019, 13, 13365–13373

www.acsnano.org

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 $[\text{Ag}_{12}(\text{TBT})_8(\text{TFA})_5(\text{CH}_3\text{CN})]^+$ (TBT = *tert*-butylthiolate, TFA = trifluoroacetate, CH_3CN = acetonitrile) and $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$ (TPP = triphenylphosphine) abbreviated as Ag_{12} and Ag_{18} , respectively, react leading to $[\text{Ag}_{16}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$ and $[\text{Ag}_{17}(\text{TBT})_8(\text{TFA})_7(\text{CH}_3\text{CN})_3\text{Cl}]^+$, abbreviated as Ag_{16} and Ag_{17} , respectively. The two product NCs crystallize together as both possess the same metal chalcogenolate



Supramolecular chemistry

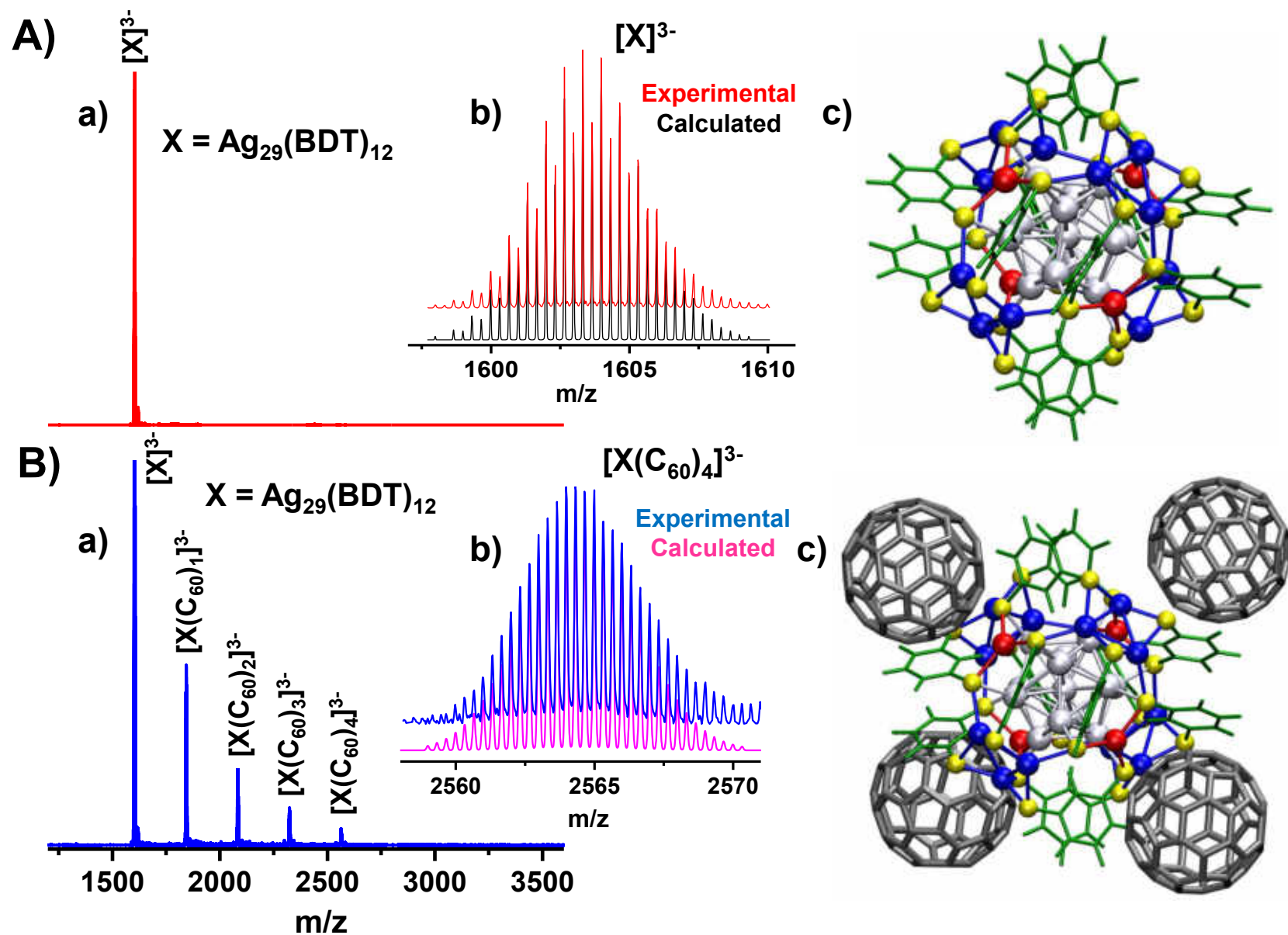


Figure 1. **A)** **(a)** Full range ESI MS, **(b)** experimental and calculated isotope patterns and **(c)** DFT optimized structure of $[Ag_{29}(BDT)_{12}]^{3-}$ cluster. **B)** **(a)** ESI MS of $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ ($n=1-4$) complexes, **(b)** experimental and calculated isotope patterns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

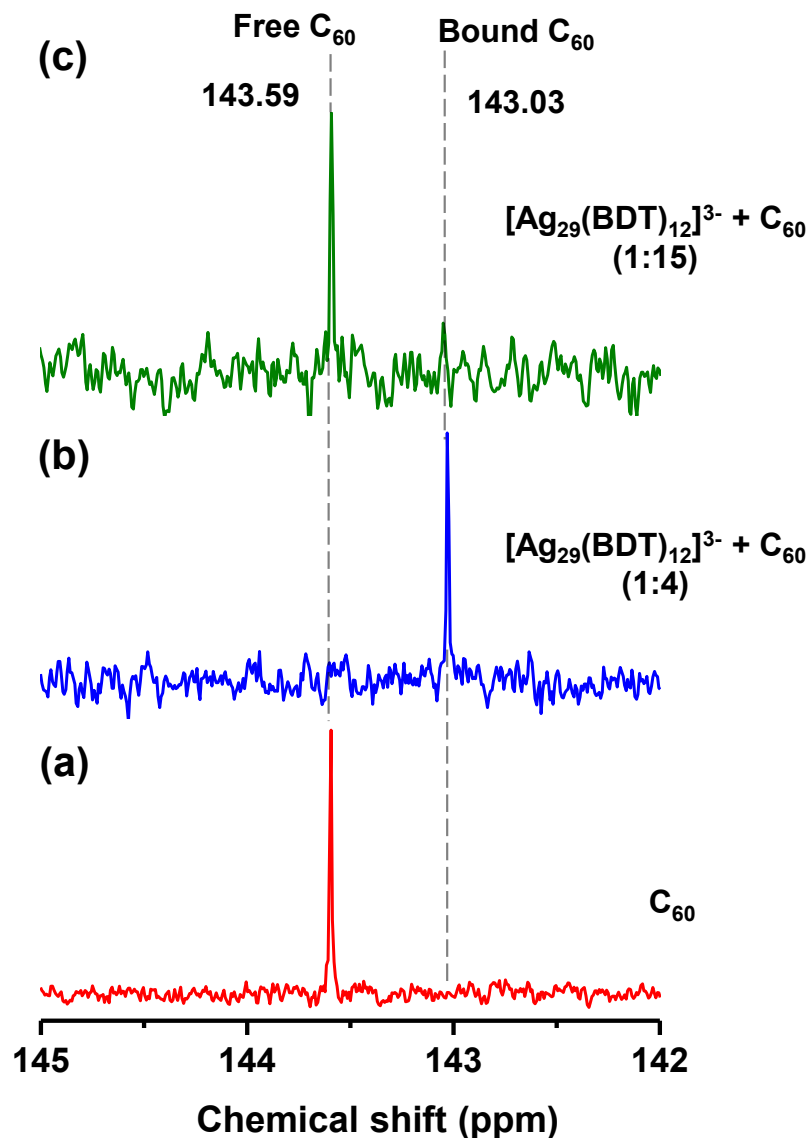
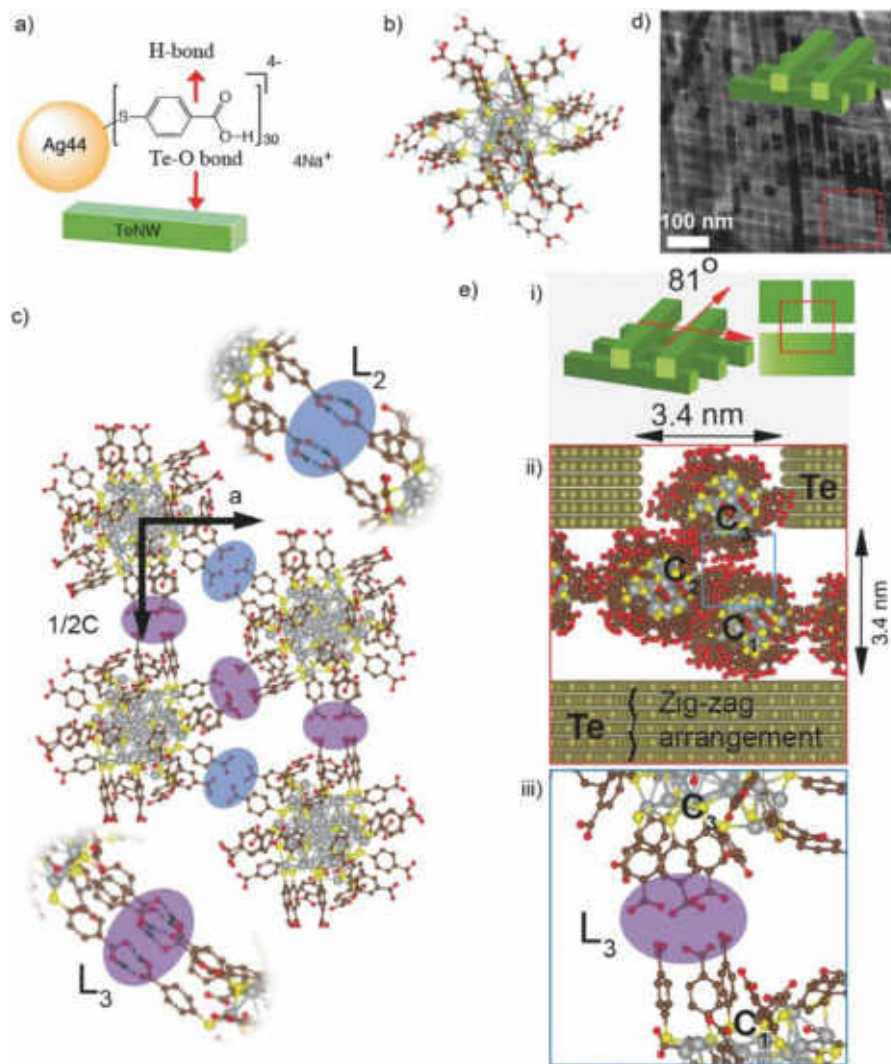
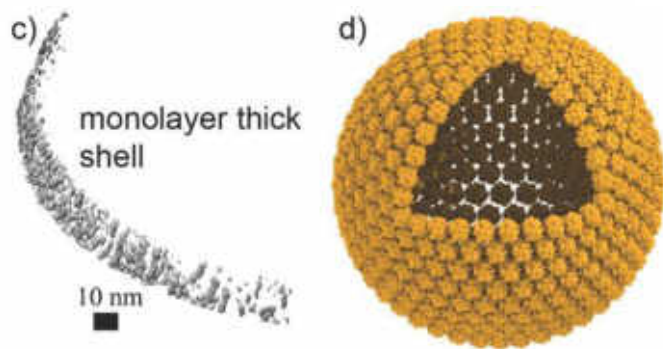
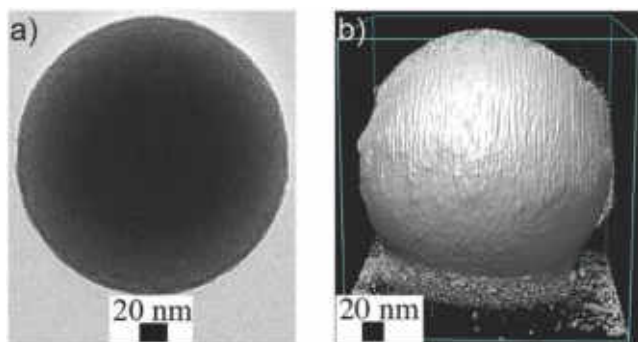
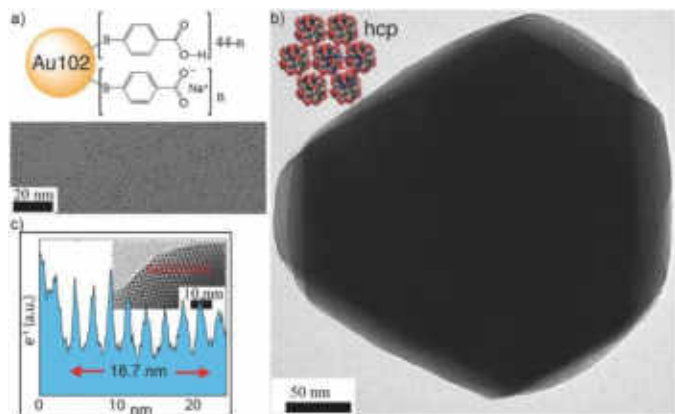


Figure 3. NMR of (a) C₆₀ showing peak at 143.59 ppm, (b) the adducts at a cluster:fullerene molar ratio of 1:4 showing peak at 143.03 ppm for the C₆₀ molecules in bound state and (c) the adducts at an excess concentration of C₆₀ (cluster:fullerene molar ratio of 1:15) showing a predominant peak for free C₆₀ (143.59 ppm) and a less intense peak for bound C₆₀ (143.03 ppm).

Assemblies and superstructures

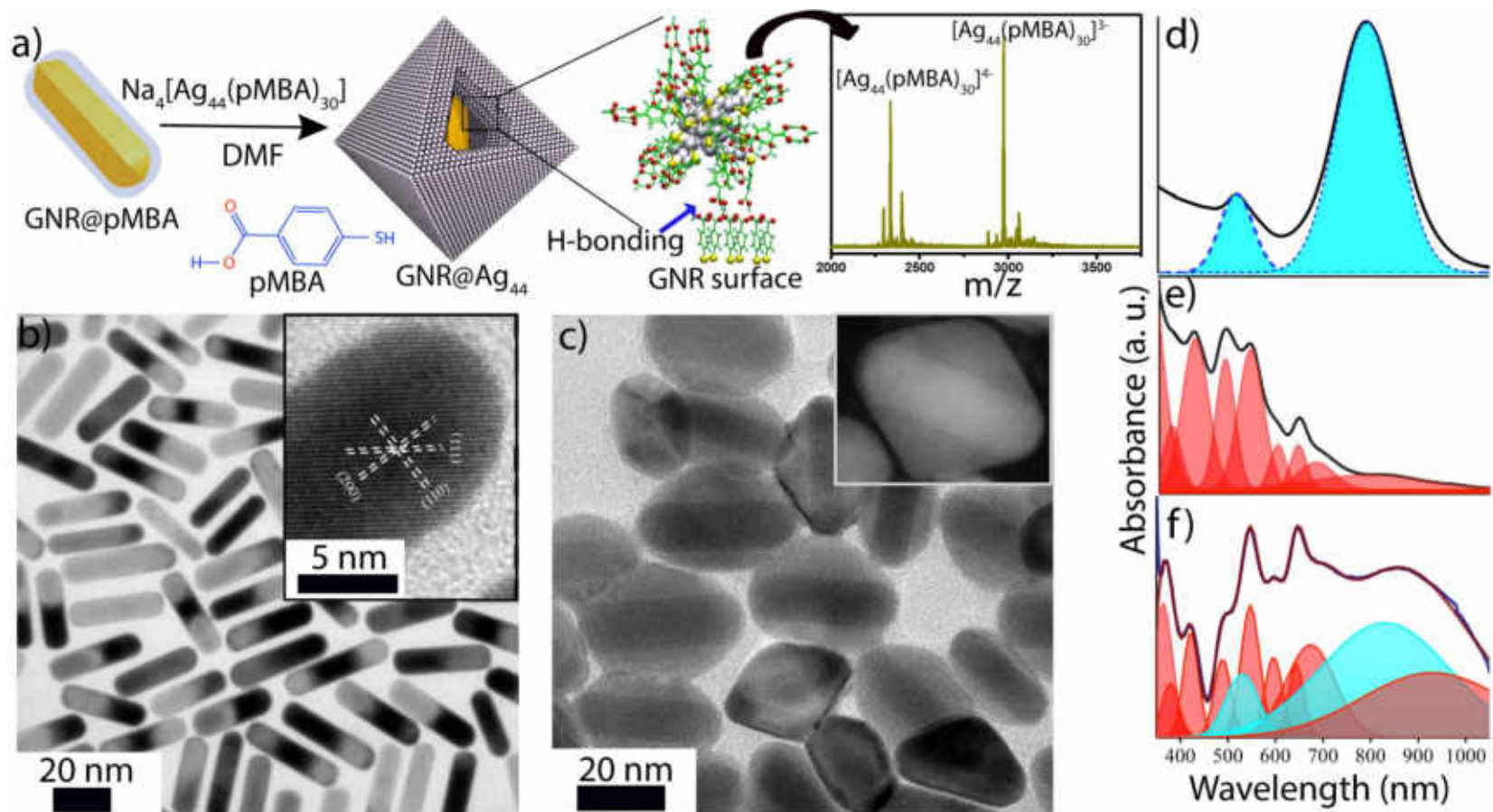
Nanoclusters in colloidal assemblies



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

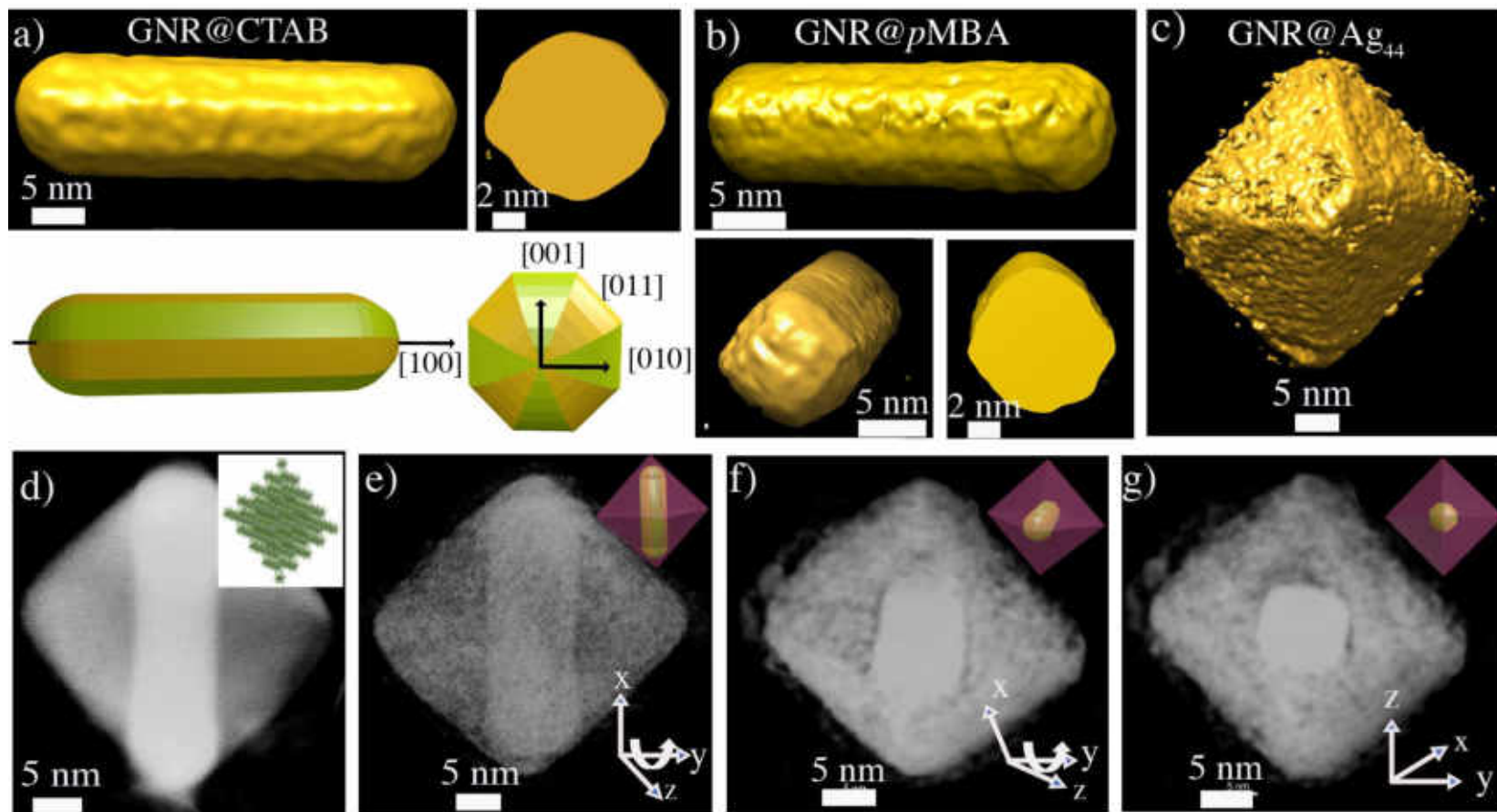
Nonappa et al., *Angew. Chem. Int. Ed.* **2016**, 55, 16035–16038.

Atomically precise nanocluster assemblies encapsulating plasmonic gold nanorods

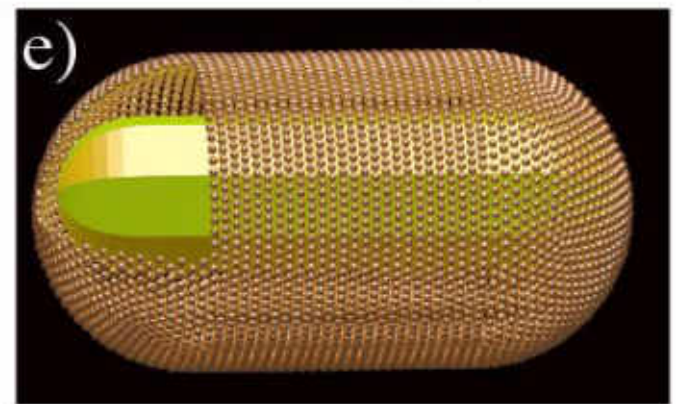
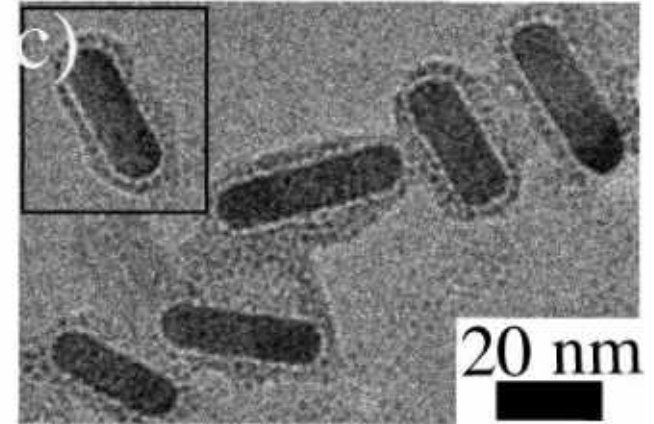
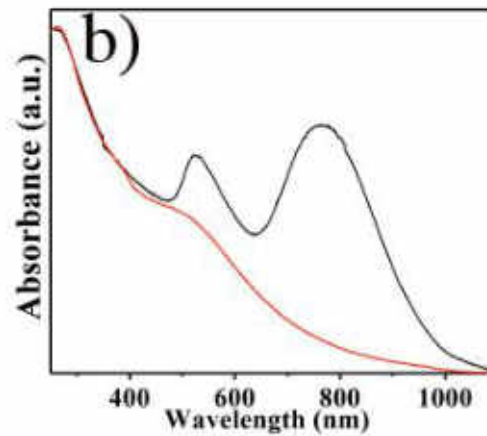
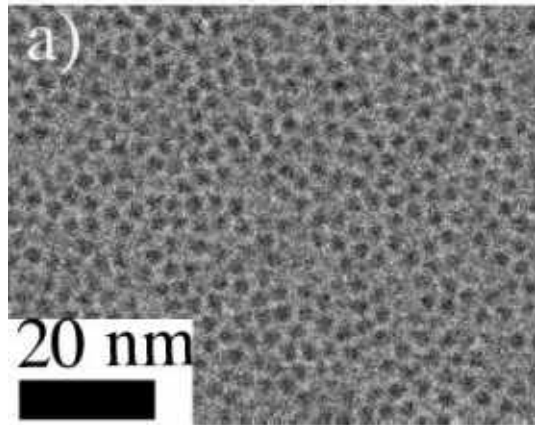


Chakraborty, A. et al., *Angew. Chem. Int. Ed.* **2018**, 57, 6522–6526.

3D morphological analysis

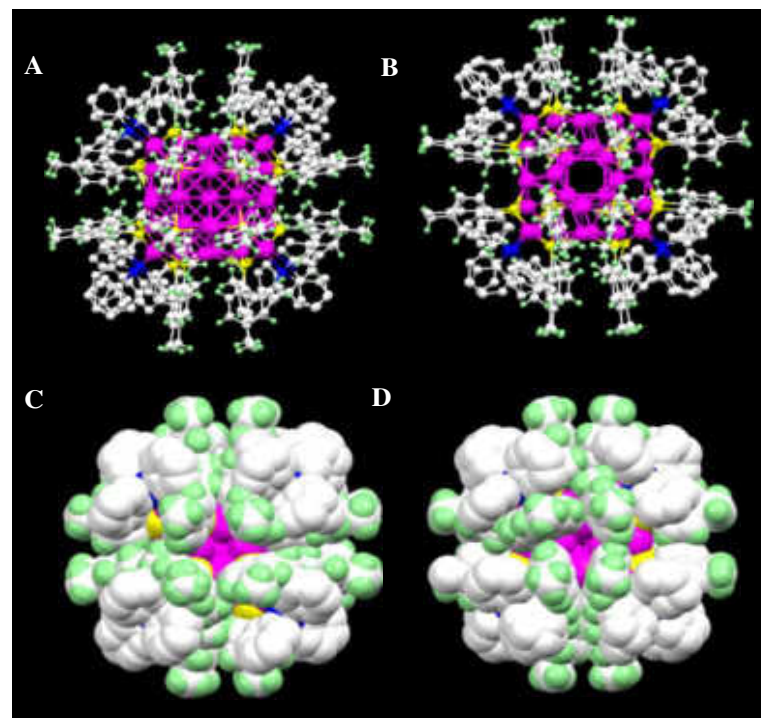
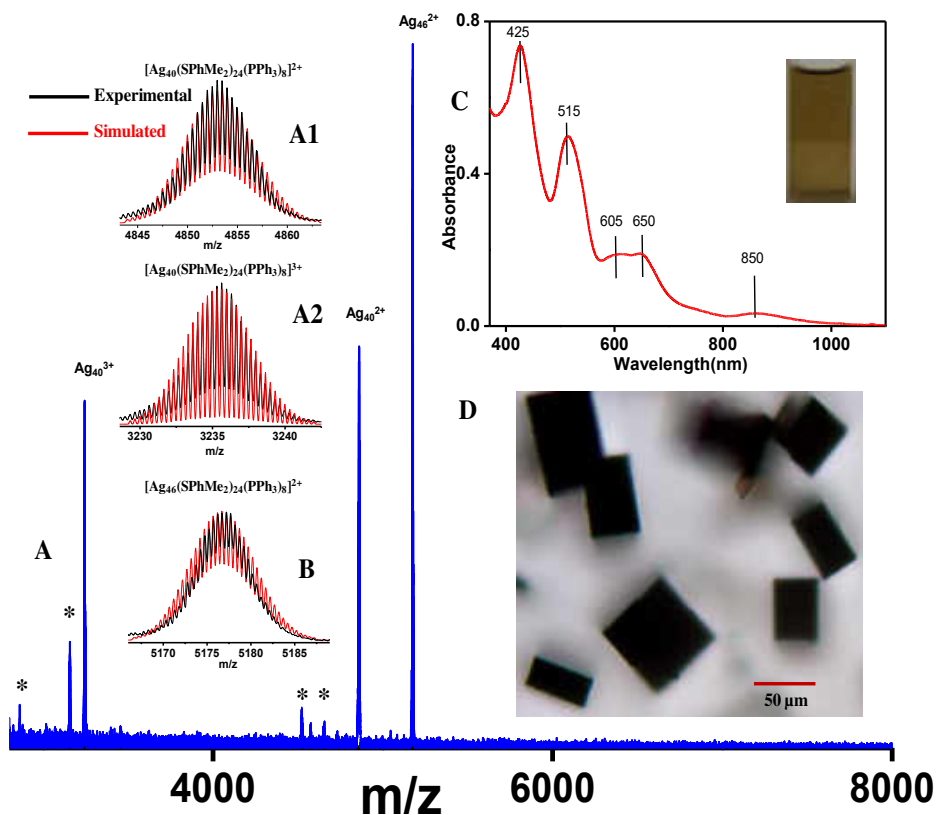


Works for $\text{Au}_{250}(\text{pMBA})_n$ and aqueous solvent



Co-crystals

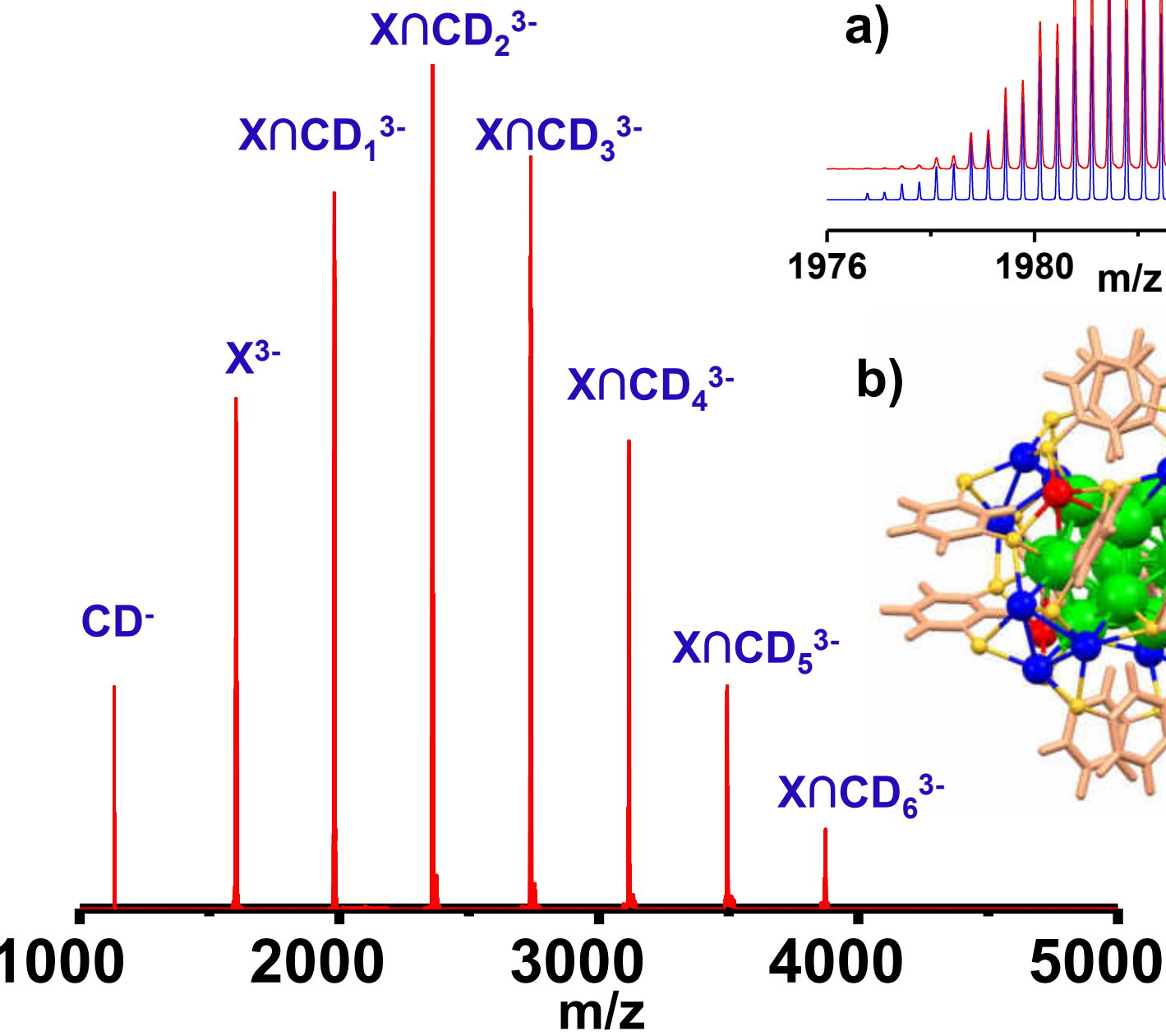
Ag_{40} and Ag_{46} with the same shell



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

Isomerism in supramolecular adducts

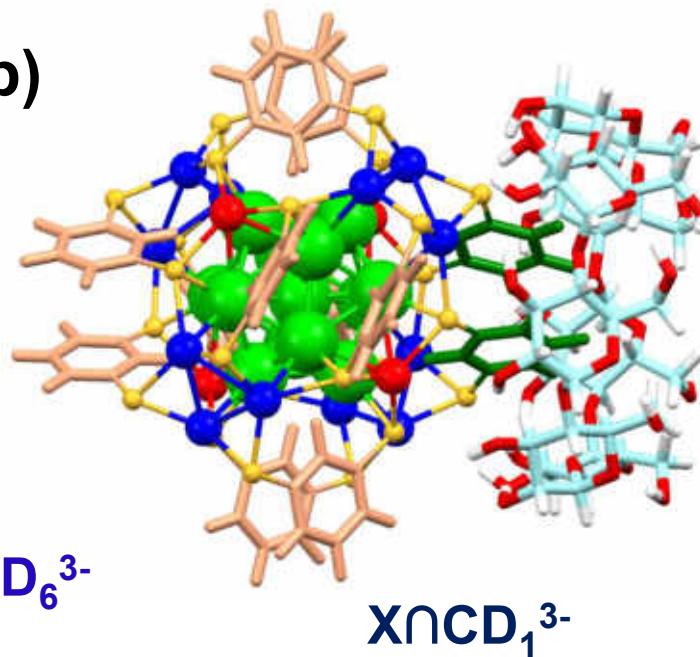
A)

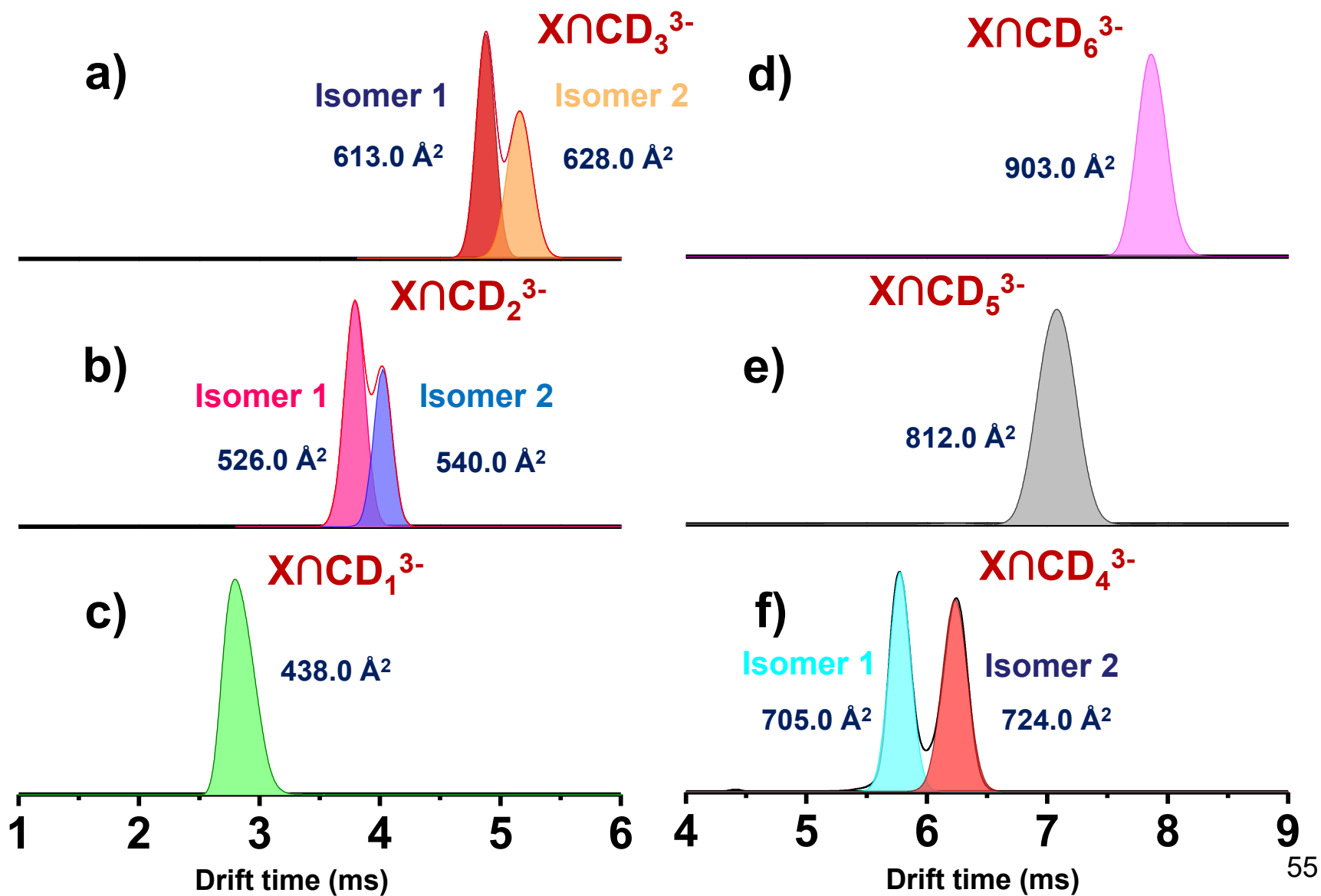
 $\text{Ag}_{29}\text{BDT}_{12} = \text{X}$ $\beta\text{-cyclodextrin} = \text{CD}$  XnCD_1^{3-}

a)

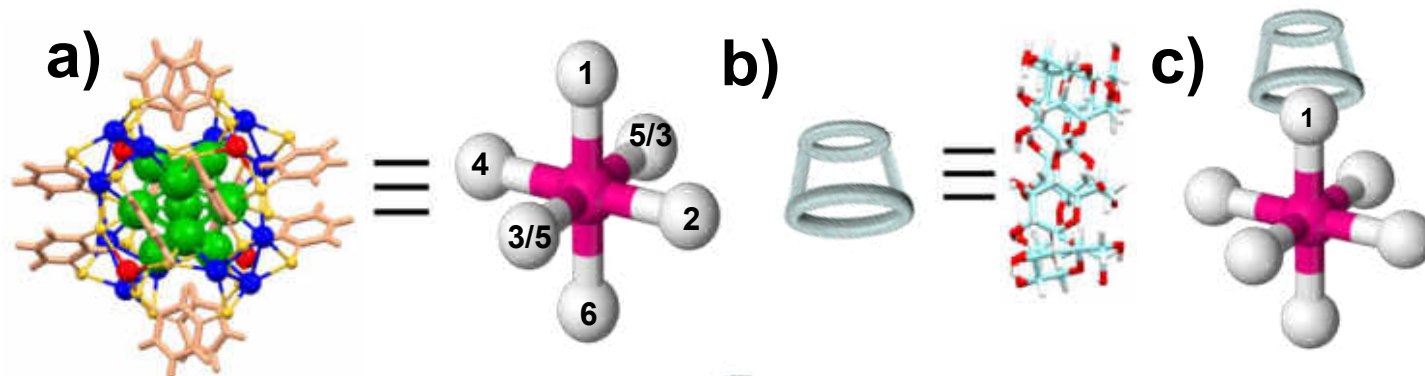
Calculated
Experimental1976 1980 1984 1988
 m/z

b)

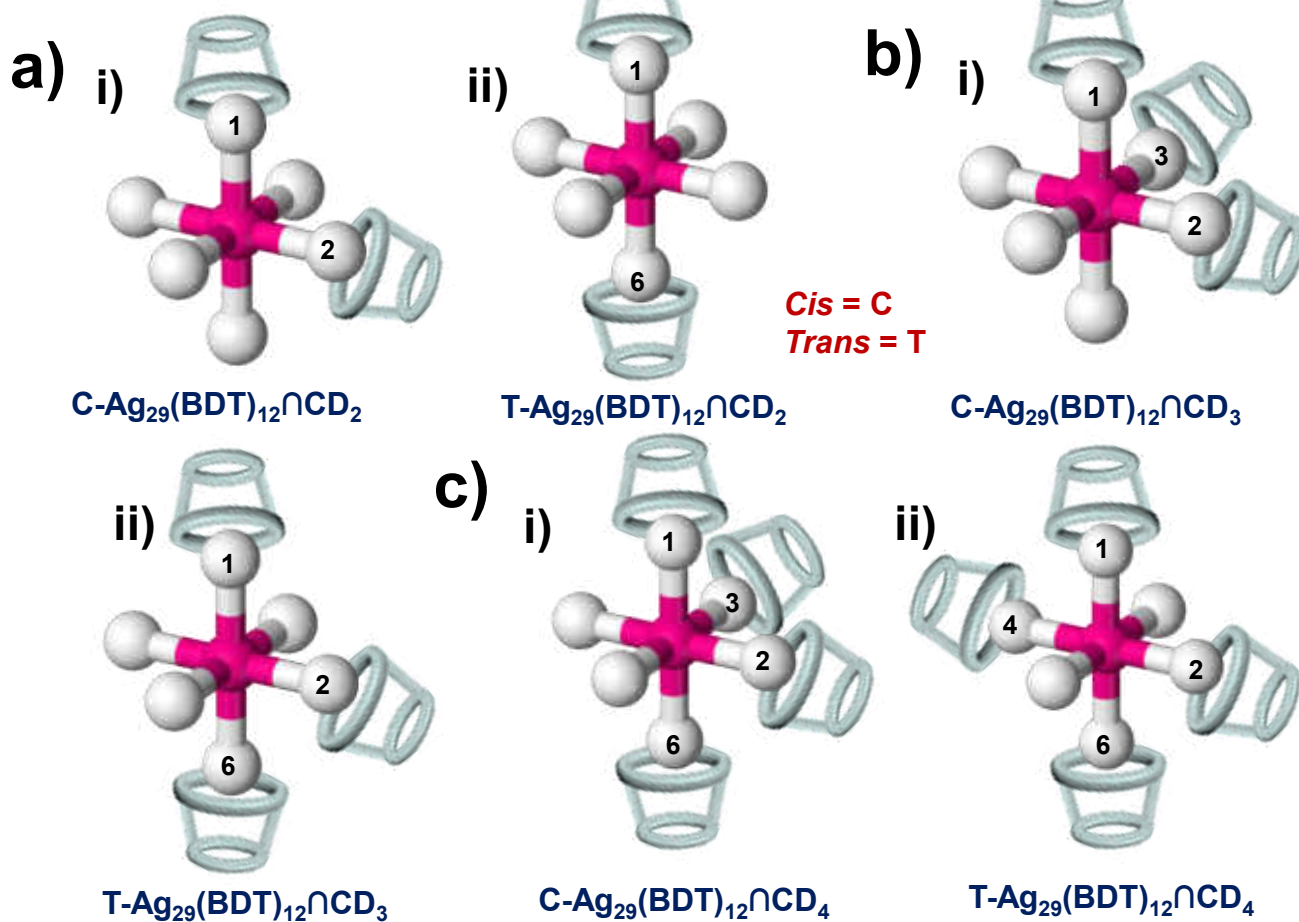




A)



B)



Where are they taking us to?

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

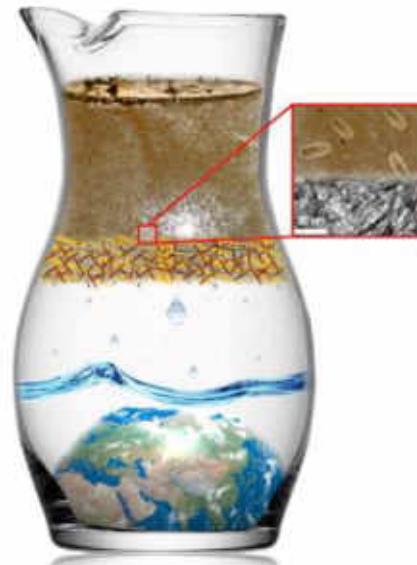
Mohan Udhaya Sankar¹, Sahaja Aigal¹, Shihabudheen M. Maliyekkal¹, Amrita Chaudhary, Anshup, Avula Anil Kumar, Kamalesh Chaudhari, and Thalappil Pradeep²

Unit of Nanoscience and Thematic Unit of Ex

Edited by Eric Hoek, University of California,

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

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



Madras, Chennai 600 036, India

(received for review November 21, 2012)

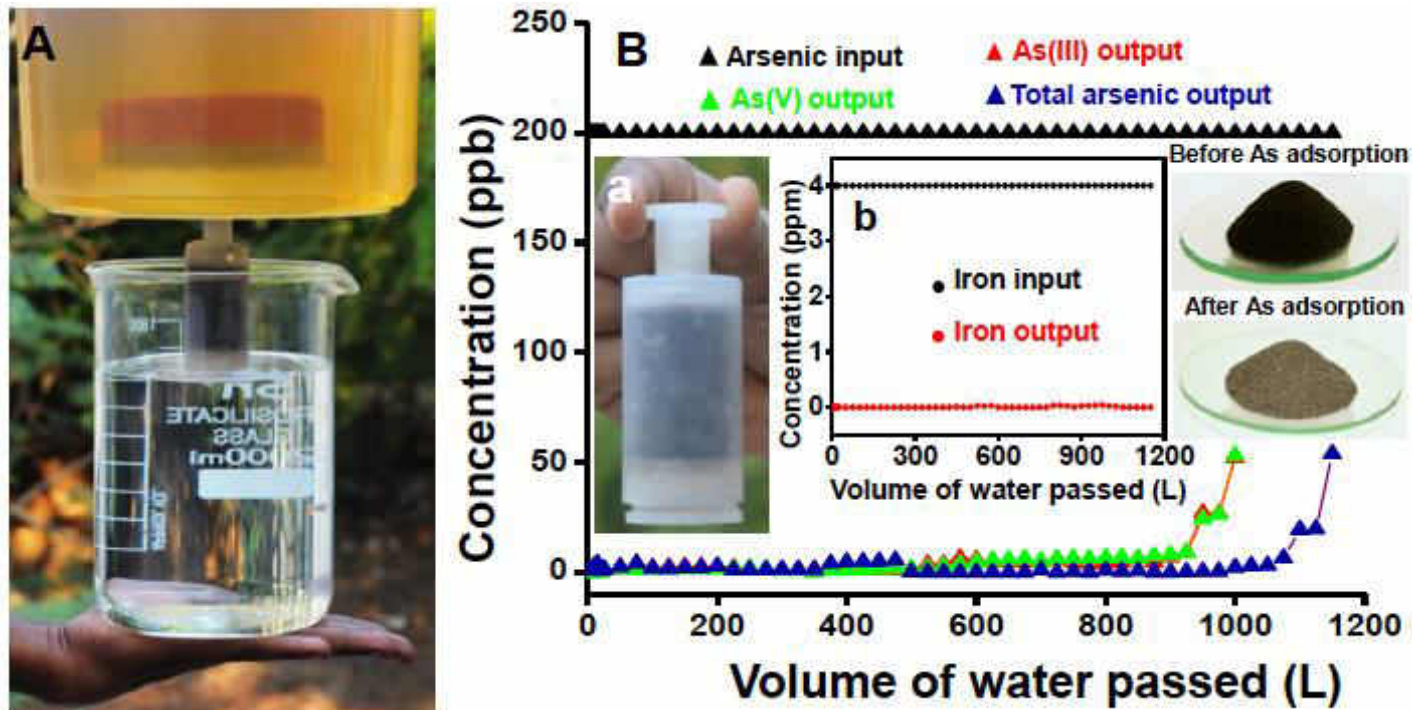
available; and (c) continued retention matrix is difficult.

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

RESULTS AND DISCUSSION

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

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



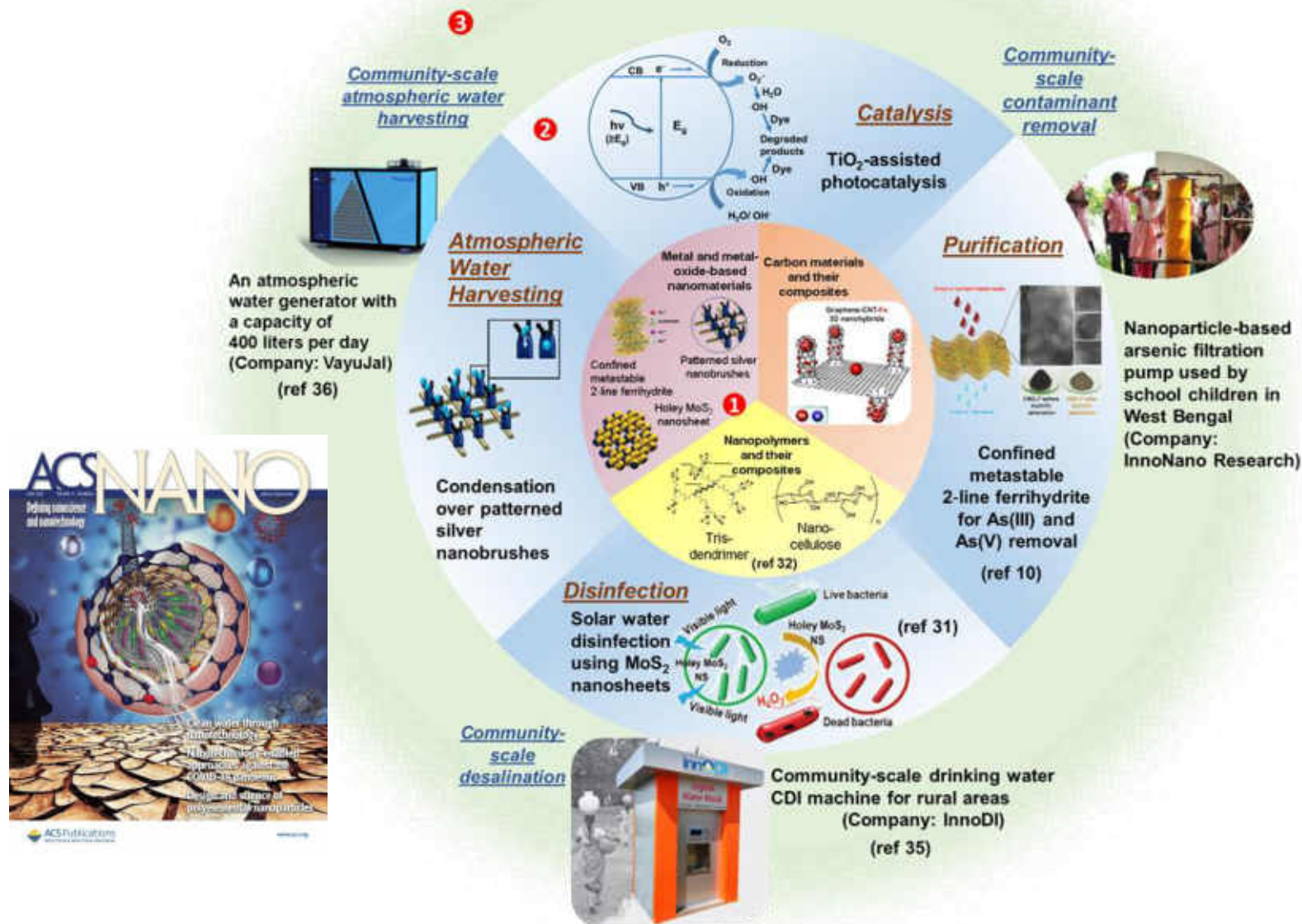
ACS Sustainable Chemistry & Engineering Editorial,
December 2016



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

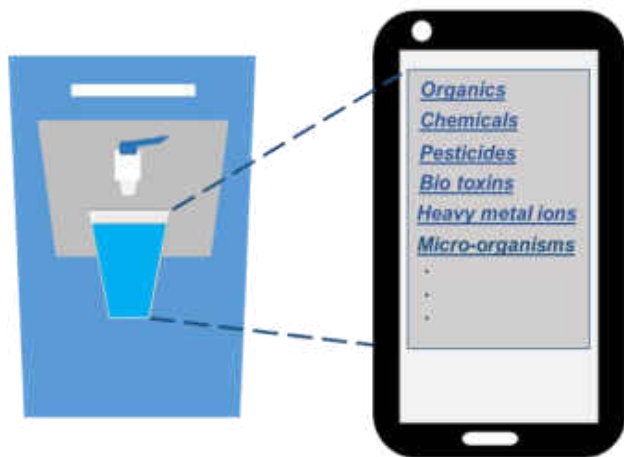
There are over 1700 community installations across the country, serving 1.3 million people with arsenic and iron-free water every day.

Evolution of materials to products



Smart water purifiers and big data

Smart Water Purifiers linked to IoT



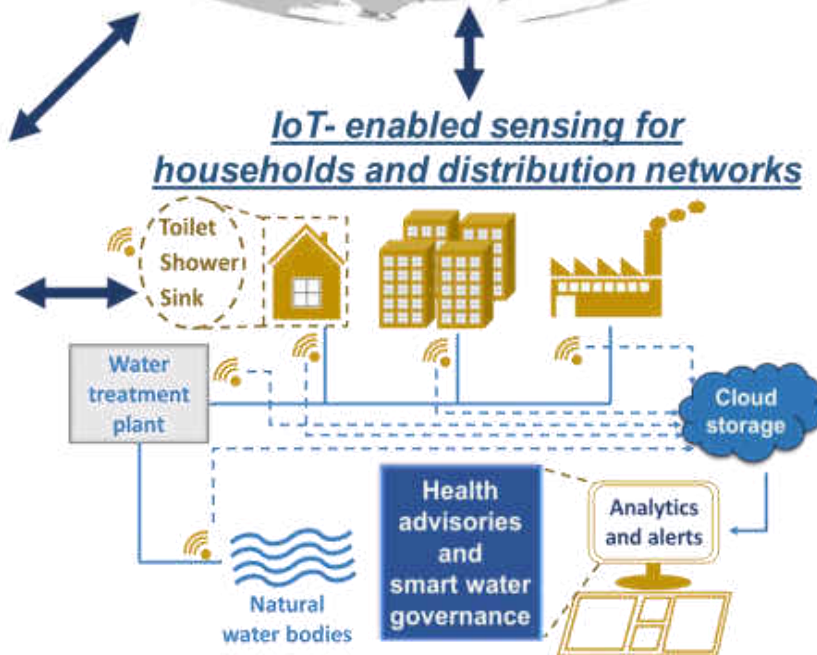
Cost-effective sensor accessory for point-of-use applications



Global Map of Water Health



IoT-enabled sensing for households and distribution networks



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)

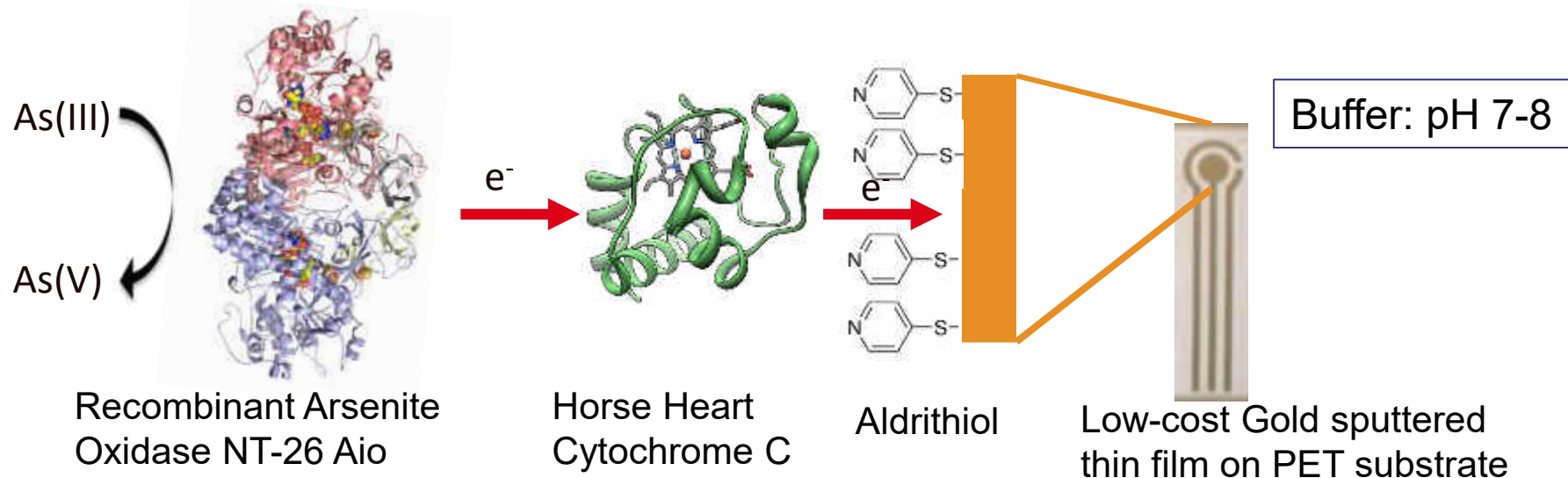


Water quality measurement – In the pipeline

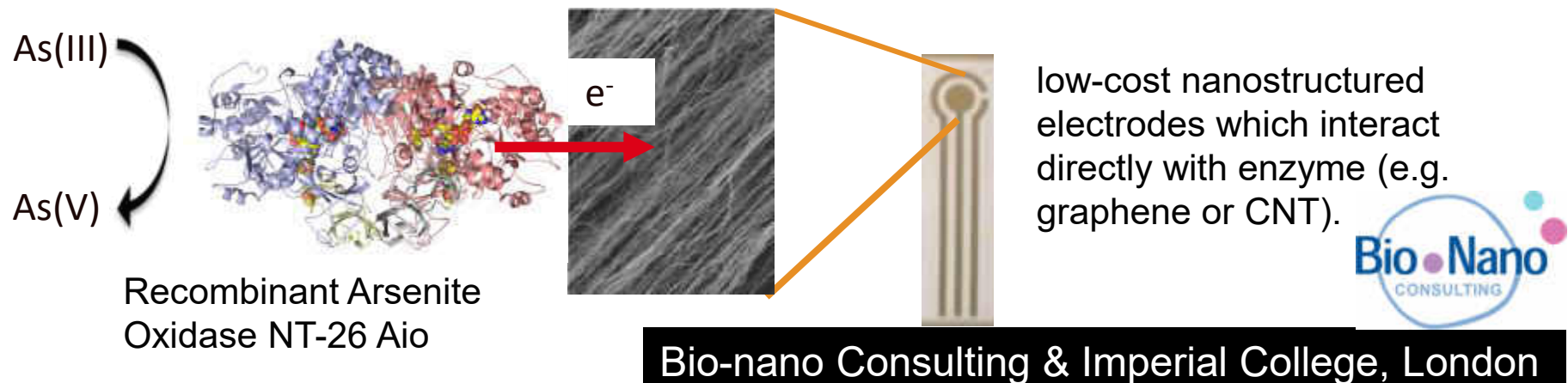
nano λ

Biosensor Design

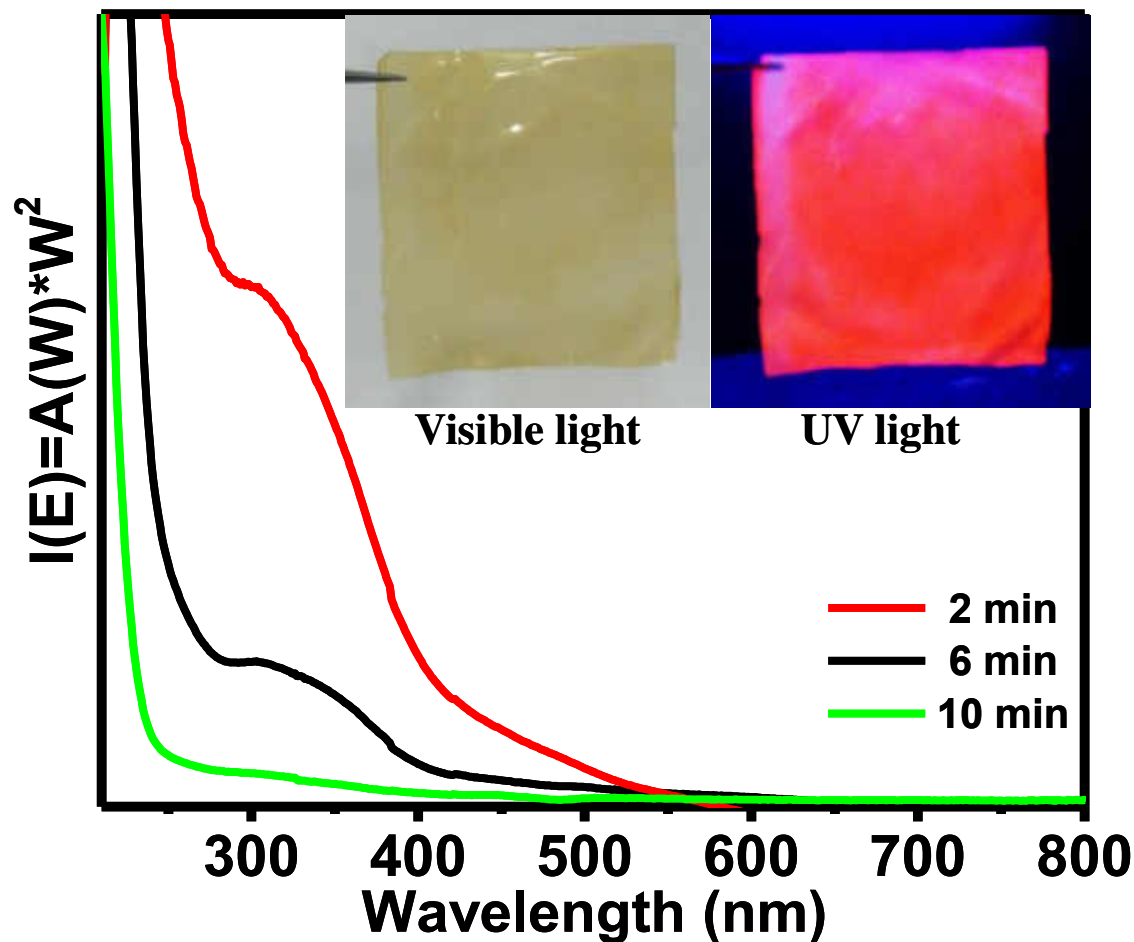
1st Generation Design (Mediated Electrochemistry)



2nd Generation Design (Direct Electron Transfer)

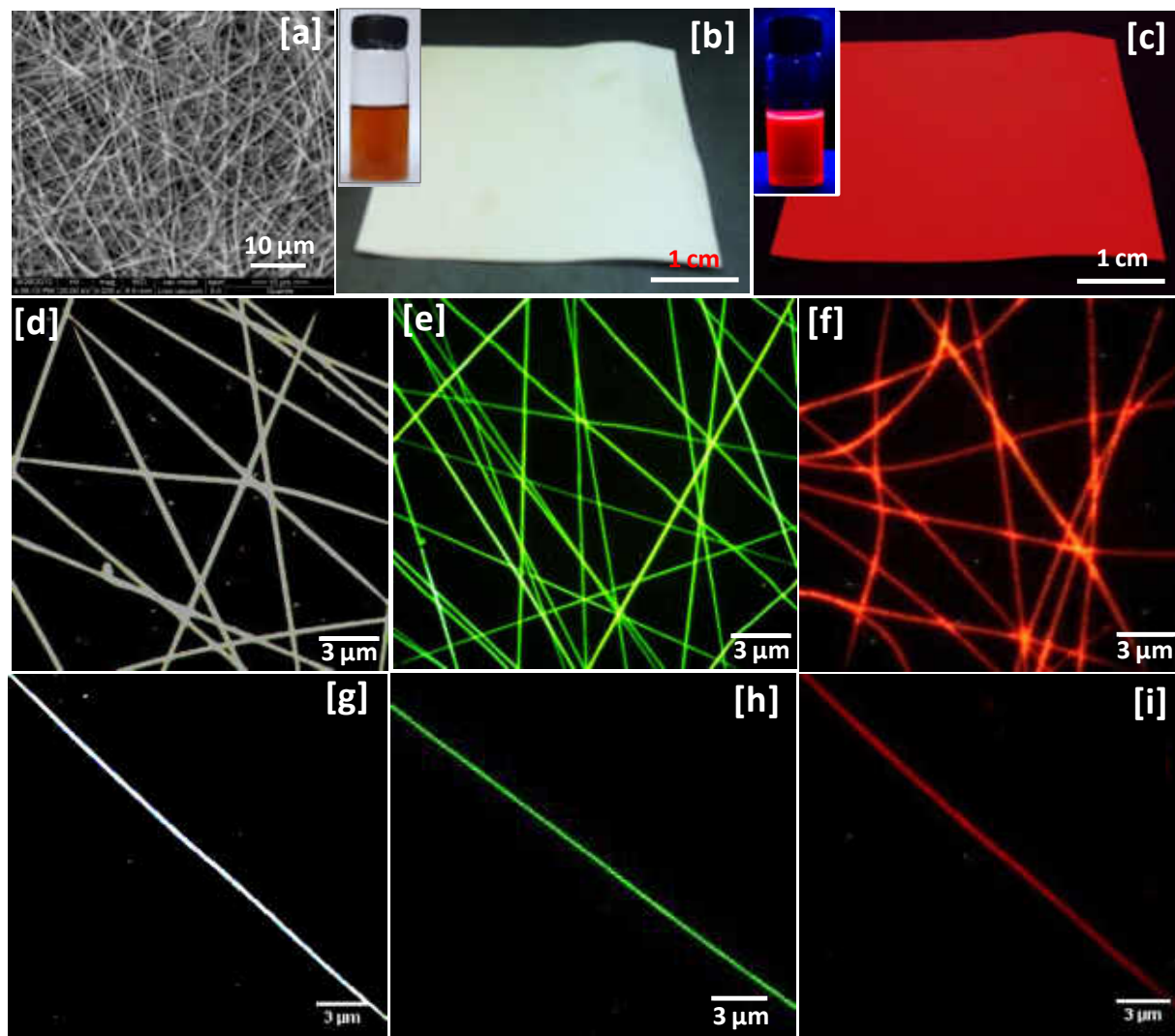


Cluster-based metal ion sensing

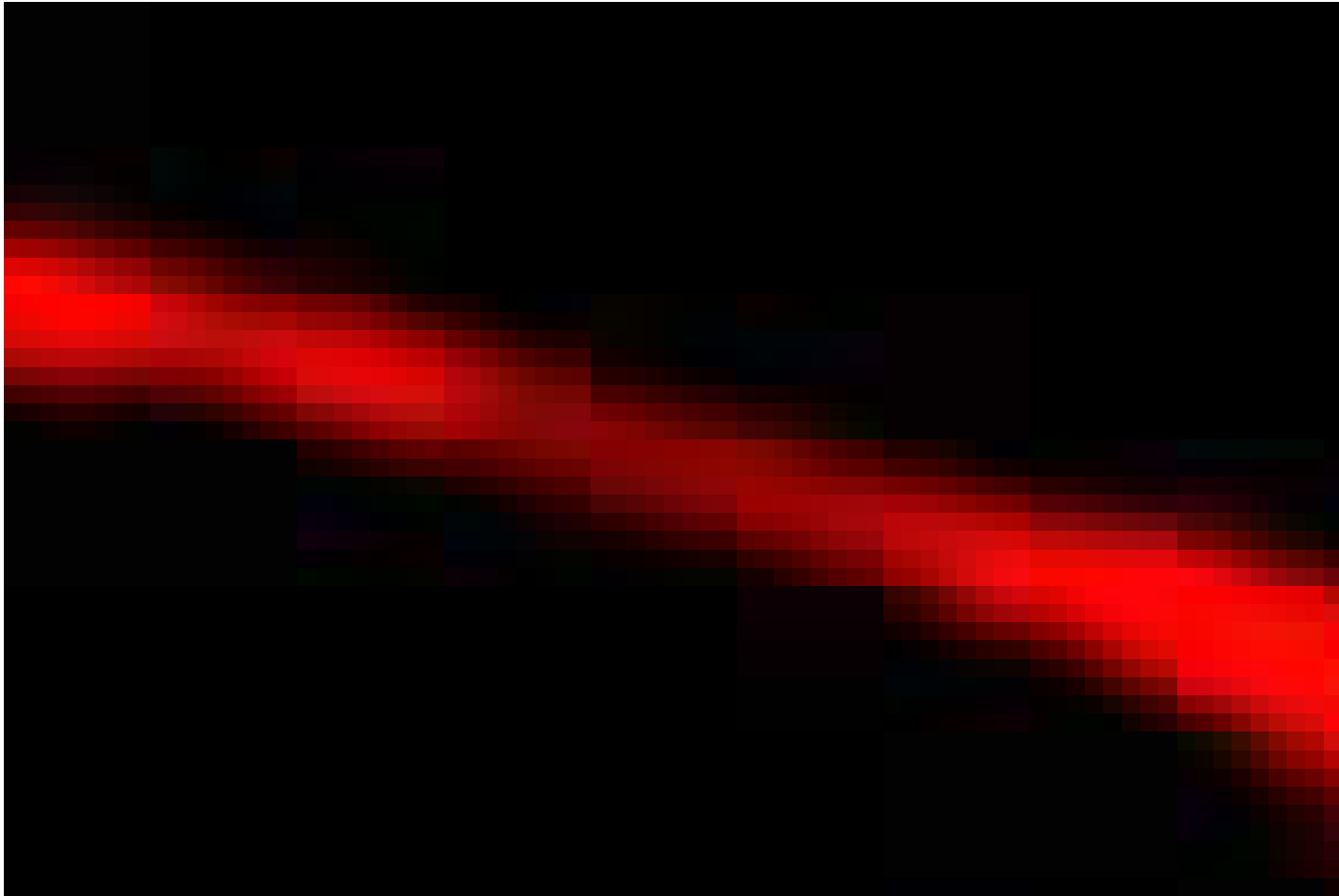


Decrease in the absorption of Au_{15} as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

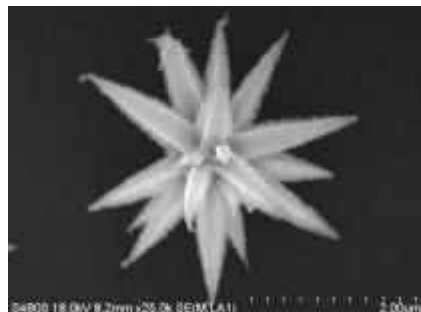
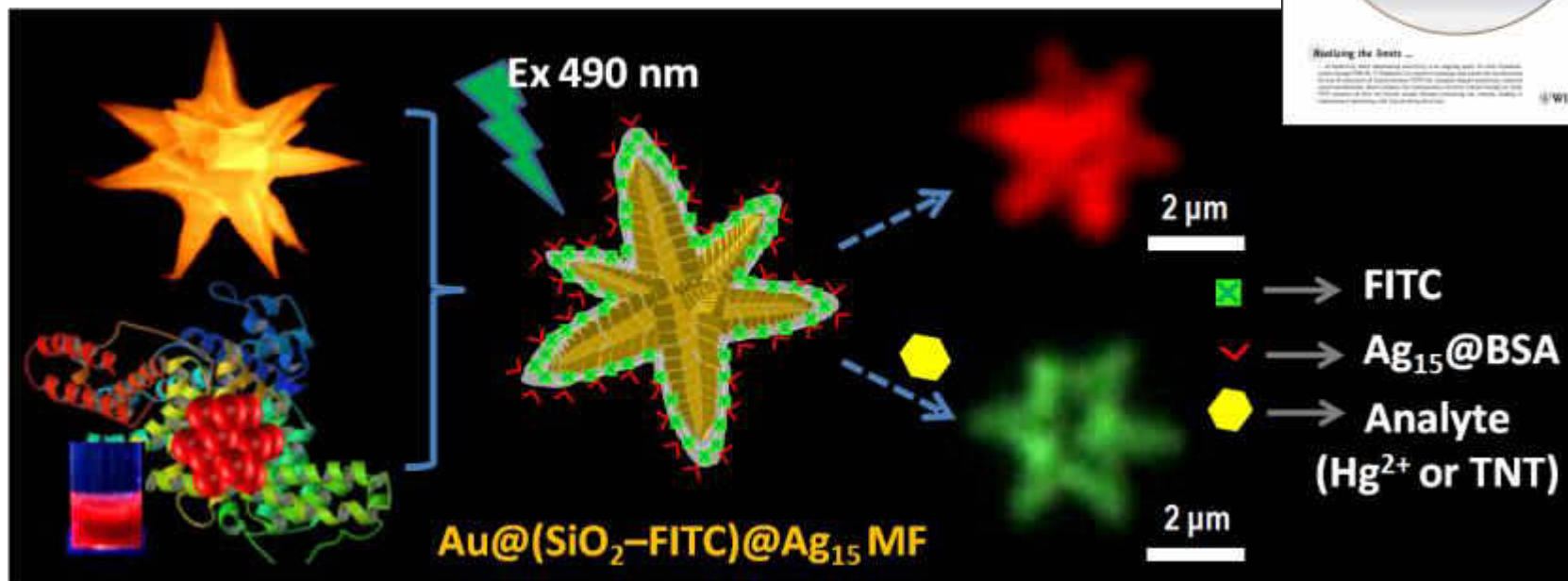
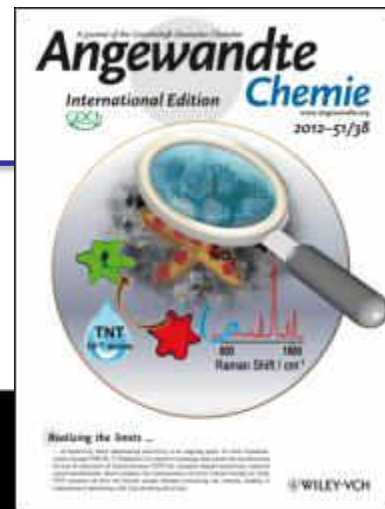
Approaching detection limits of tens of Hg^{2+}



Mercury quenching experiment using nanofiber



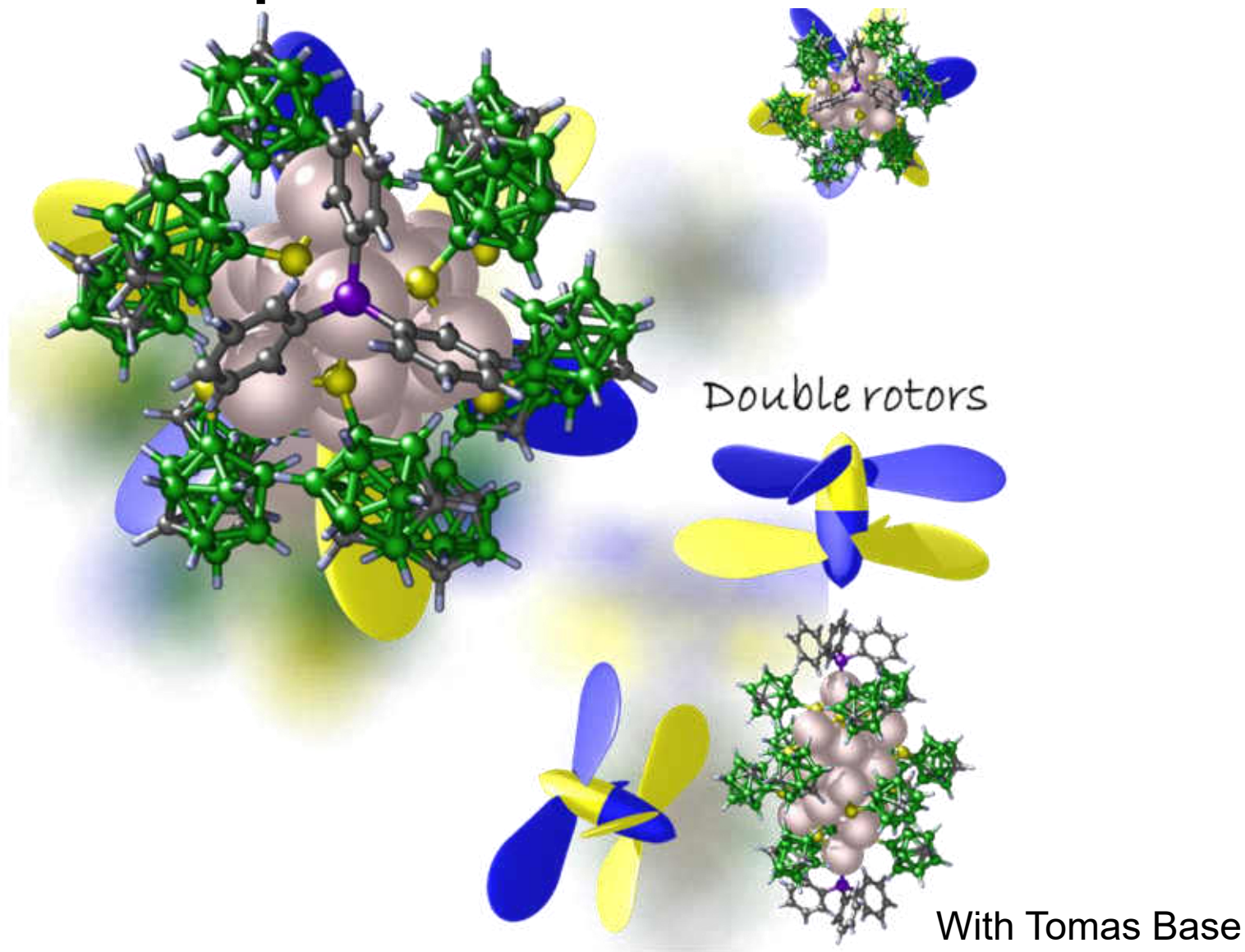
Sub-zeptomolar detection

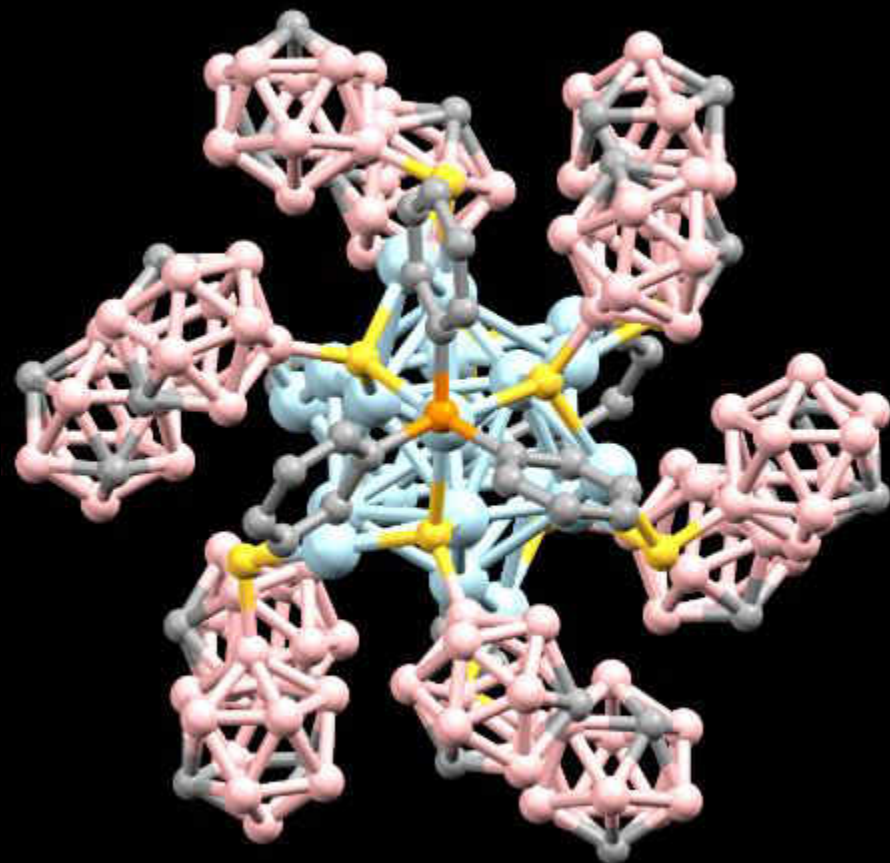
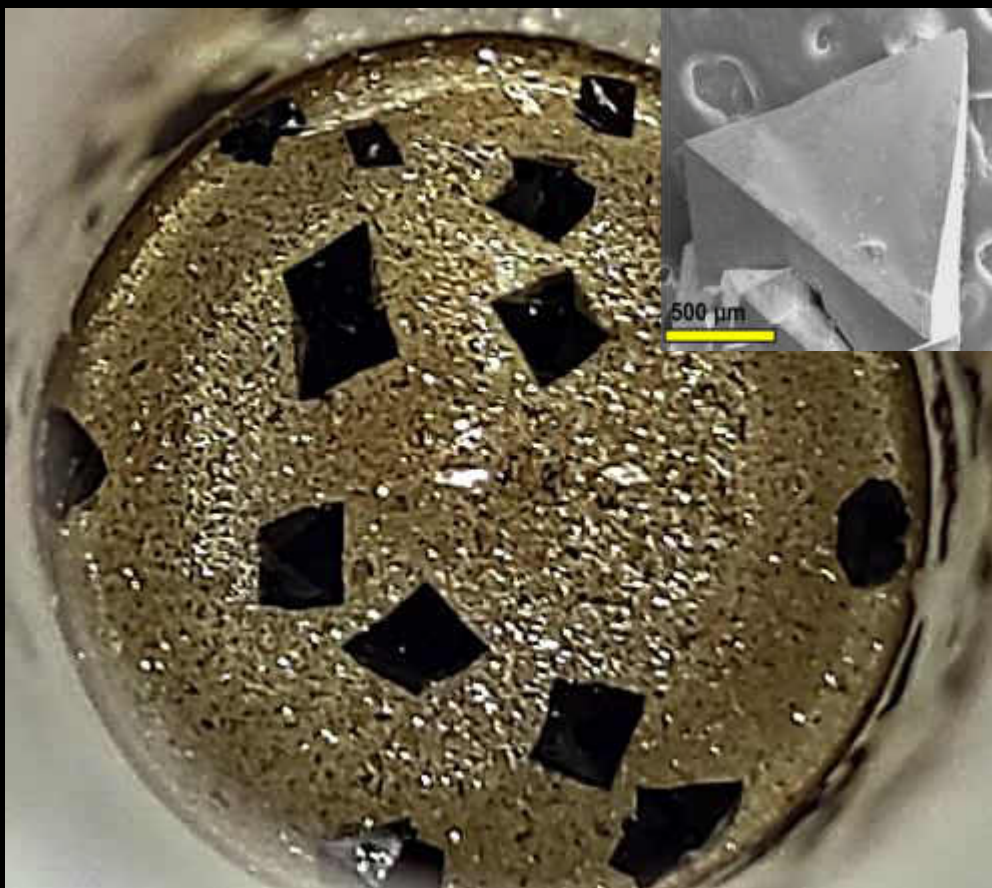


Featured in:
The Hindu, Telegraph, Times of India, etc.
C&E News
and many others

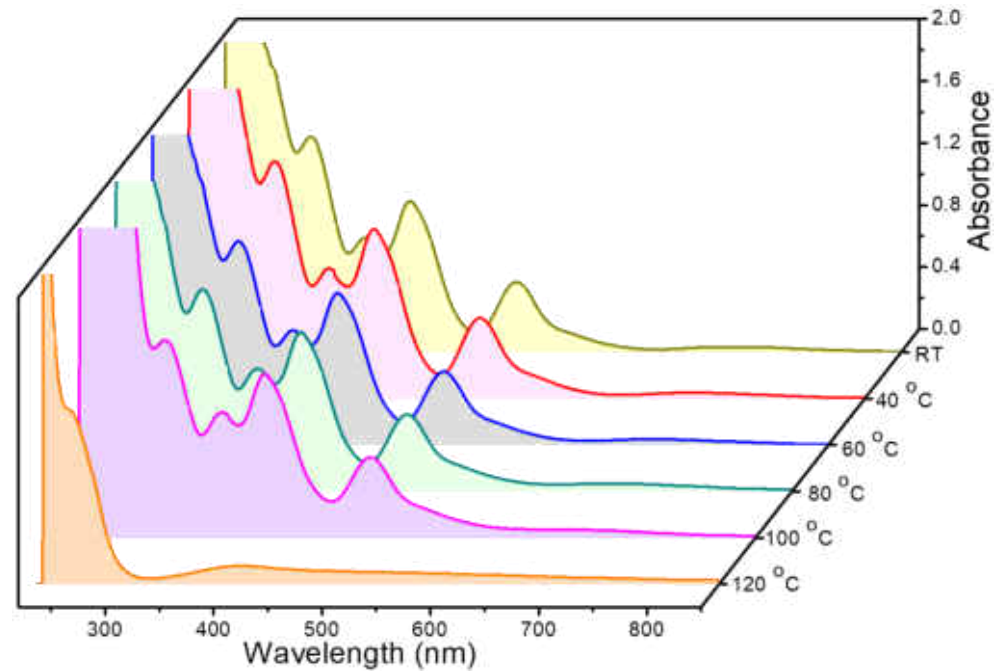
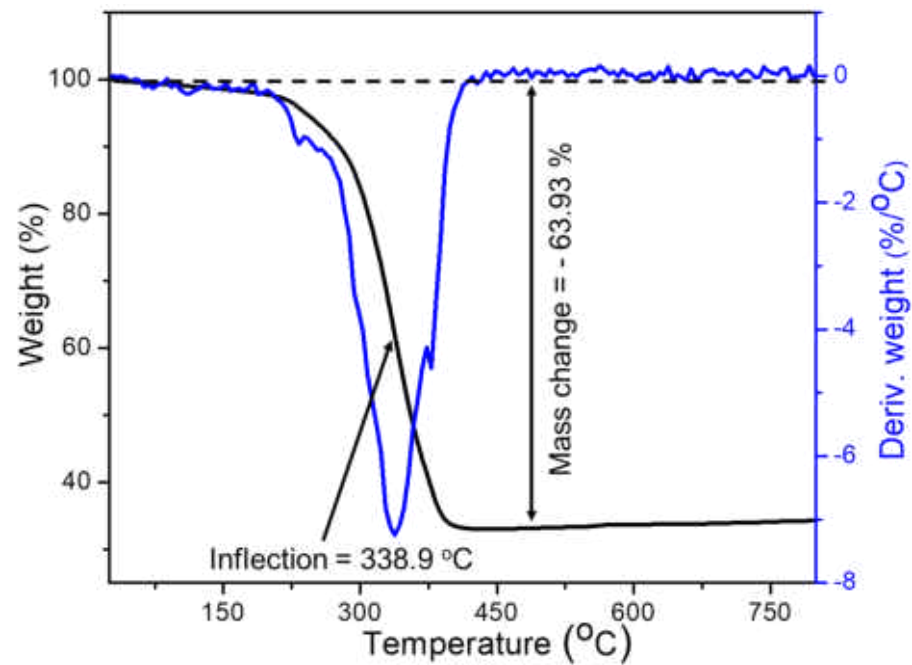
Ammu Mathew, et al. Angew. Chem. Int. Ed. 2012

Carborane-thiol protected silver nanomolecule

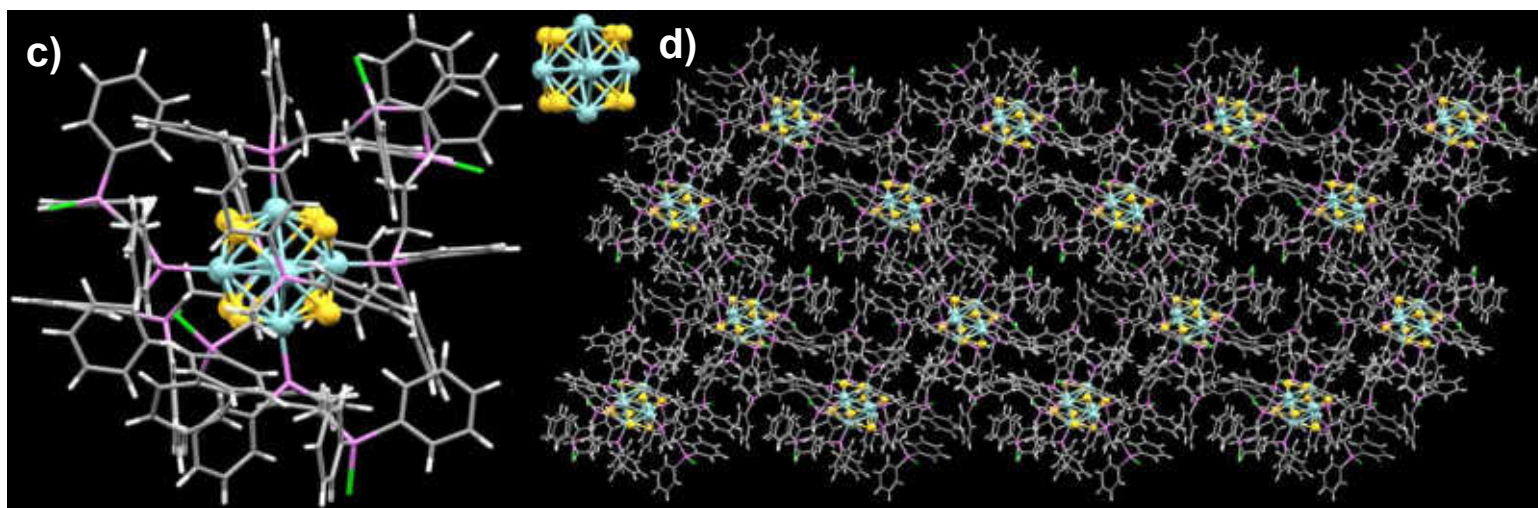
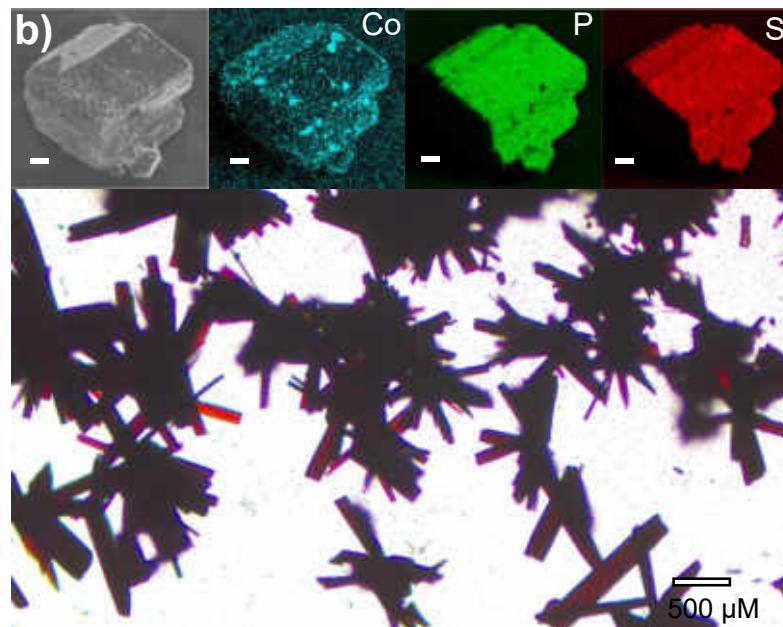
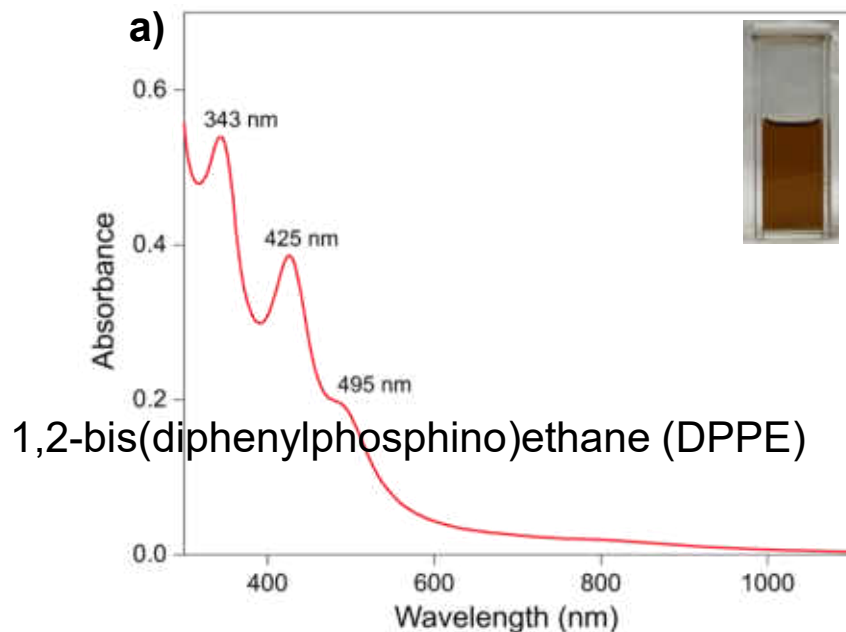




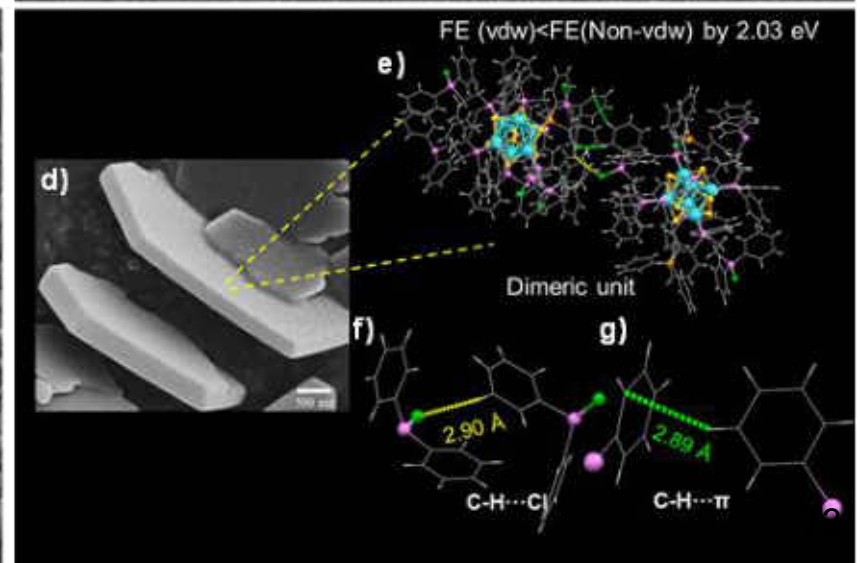
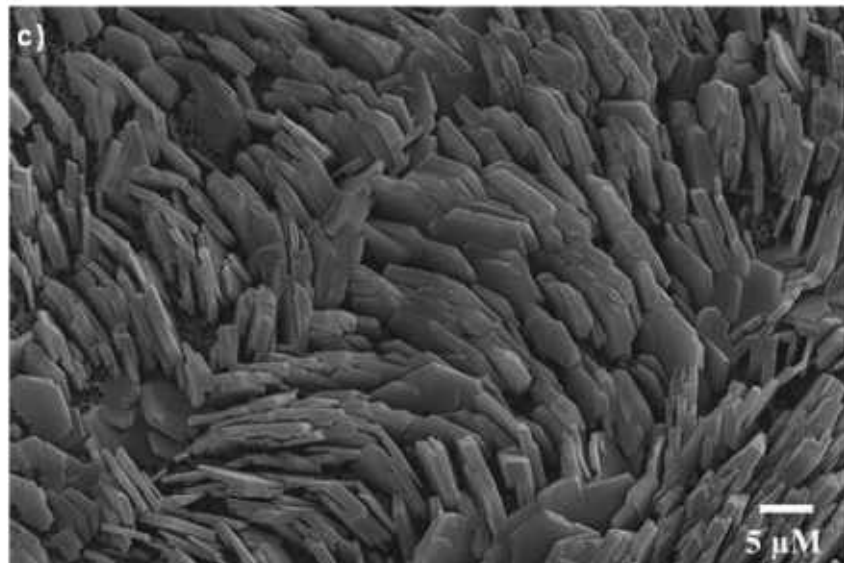
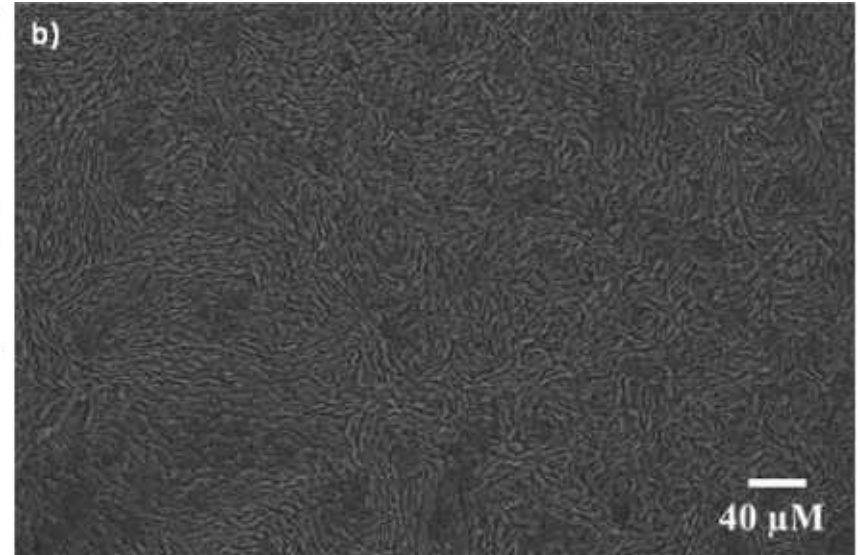
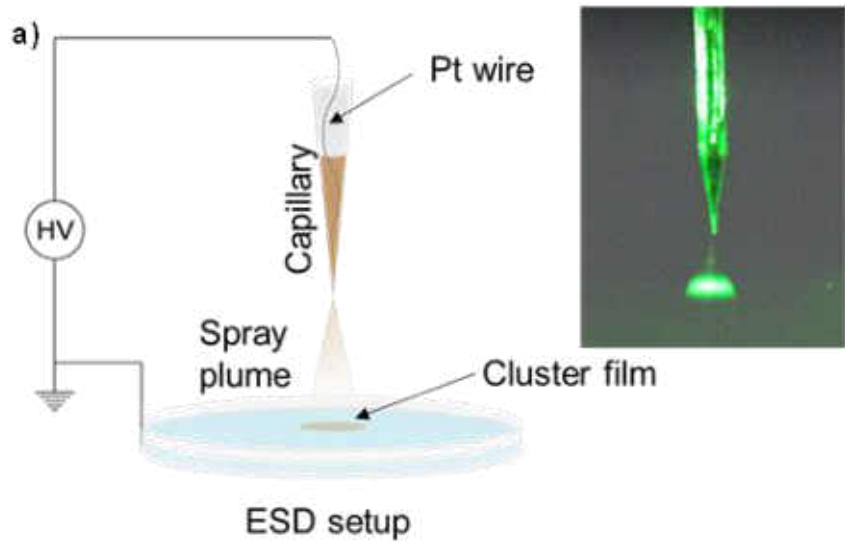
Thermal stability



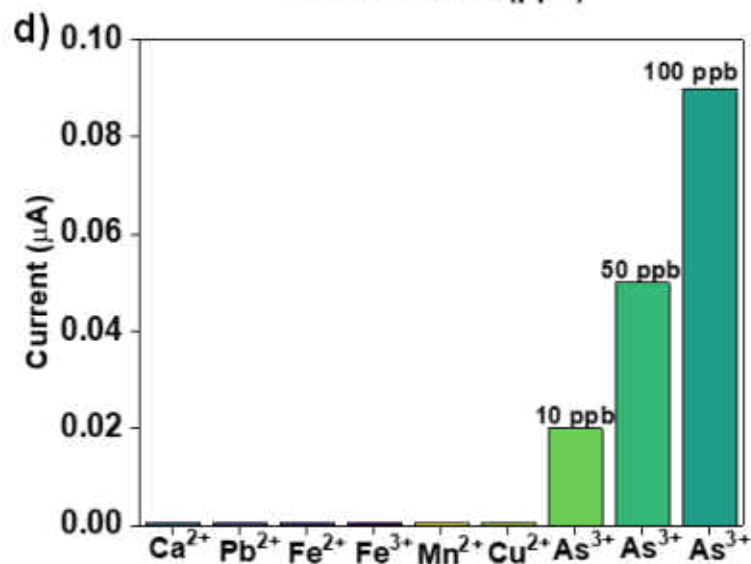
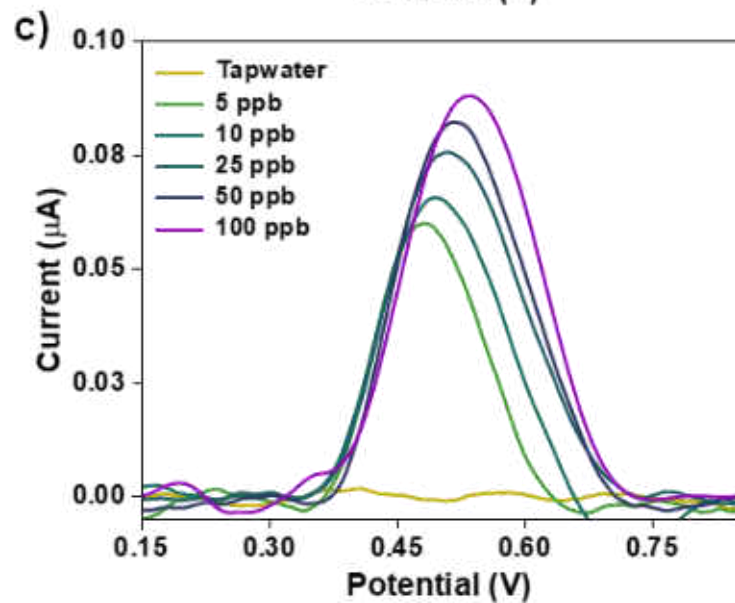
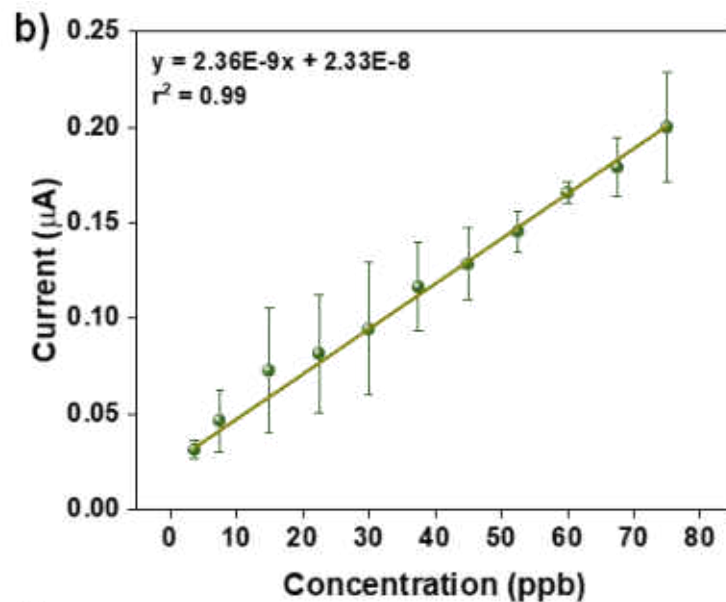
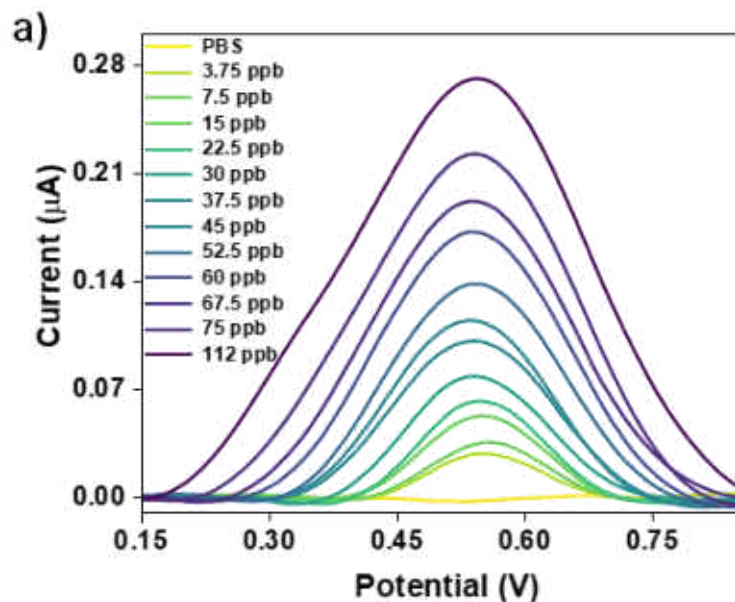
New electrodes - Aligned nanoplates of Co_6S_8



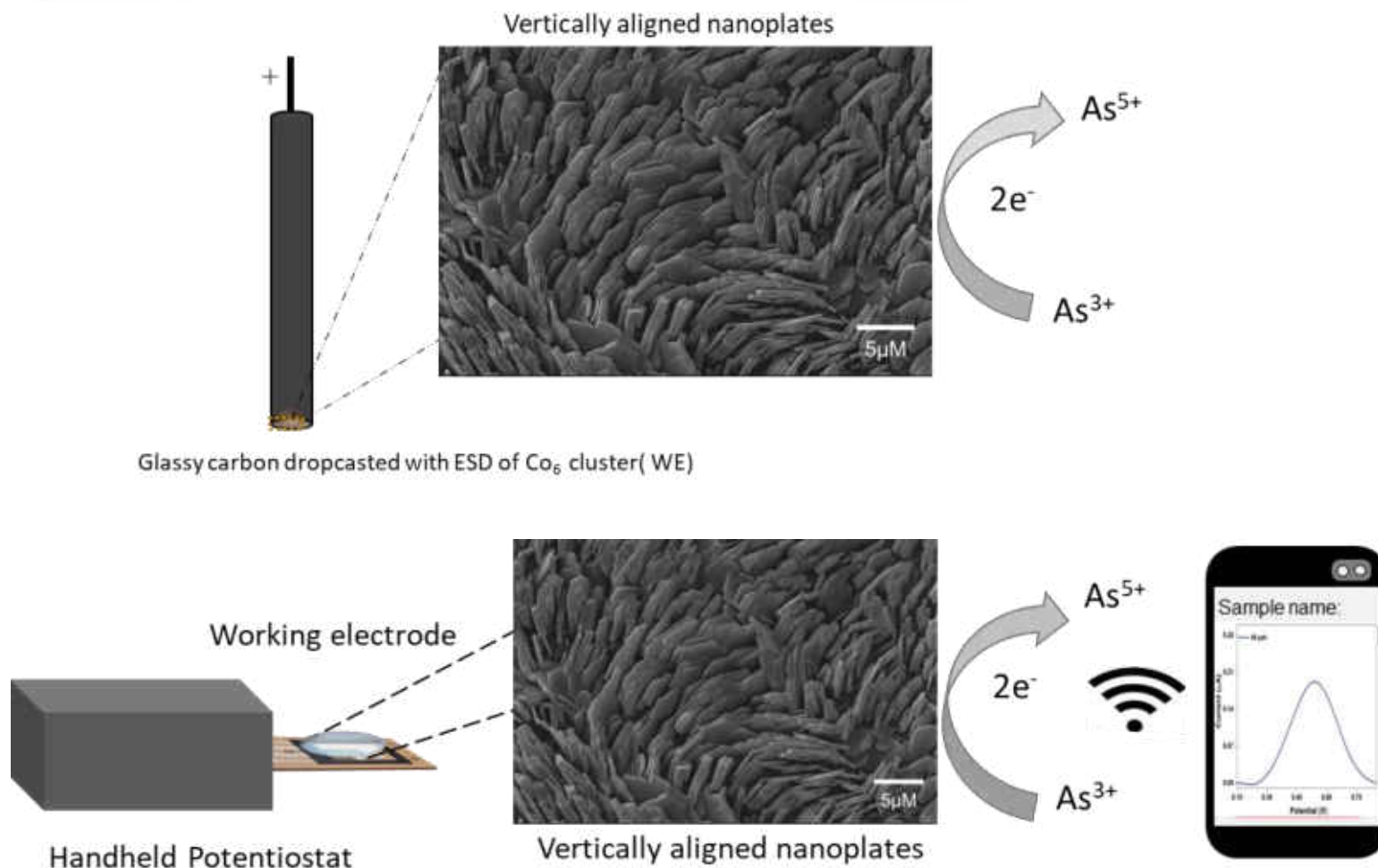
Electrospray deposition



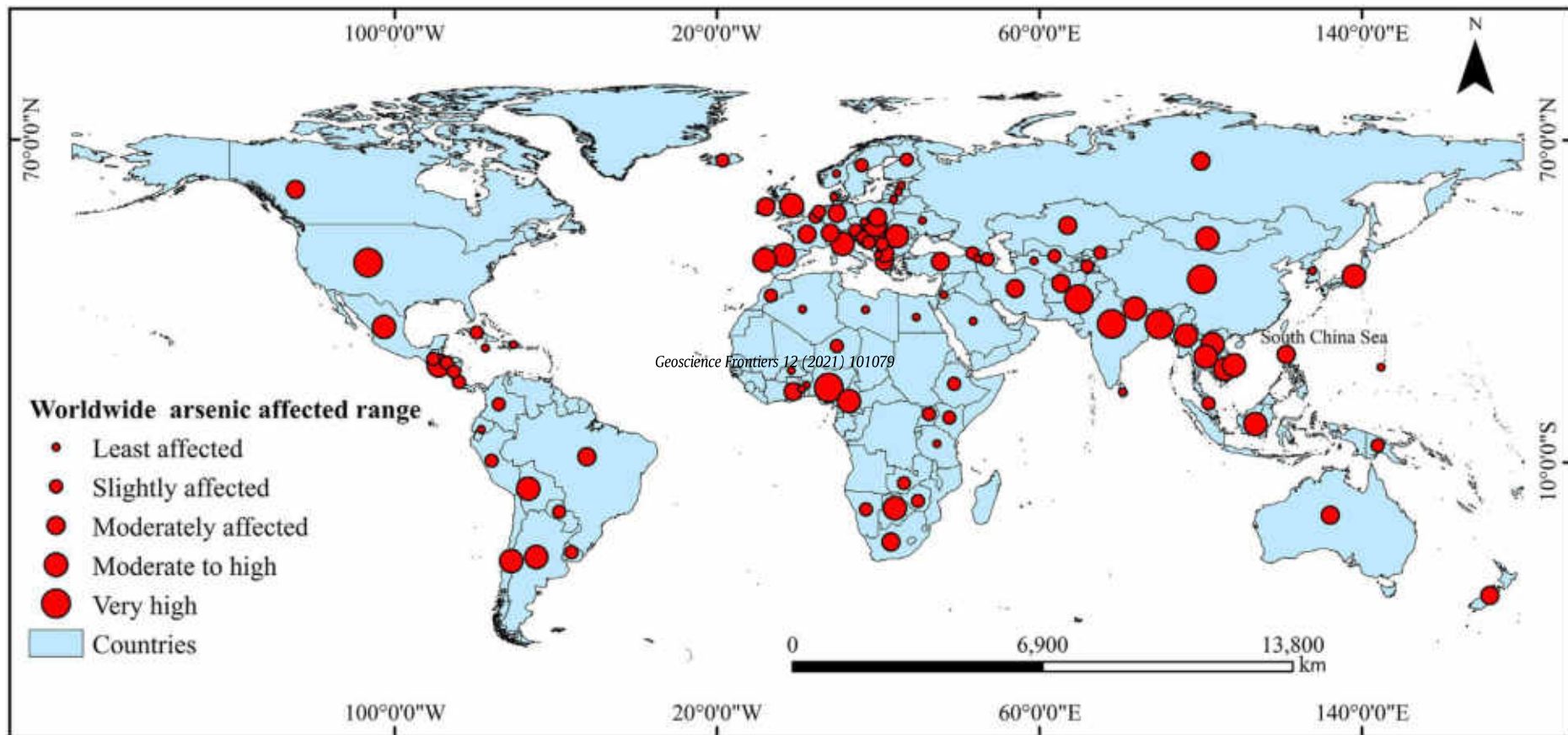
Sensing



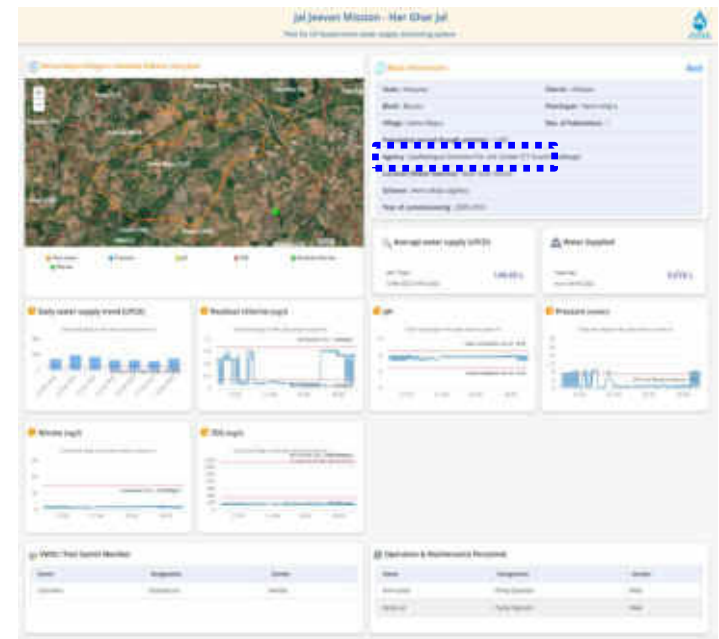
Working electrode



Arsenic poisoning across the world



Installations made by four companies

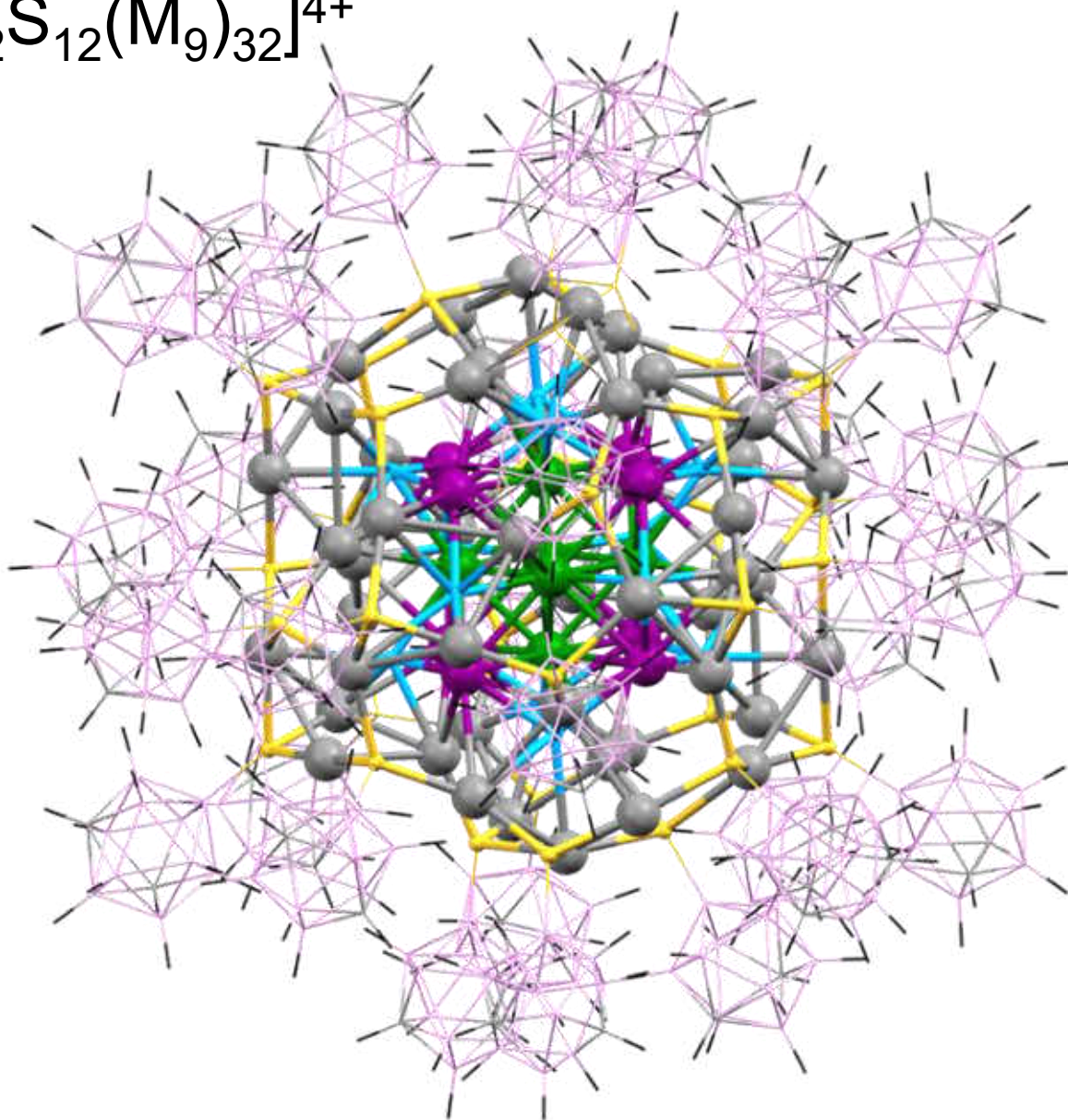
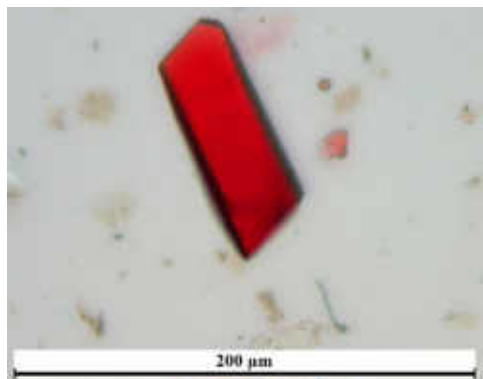
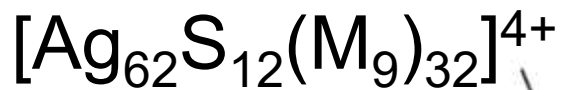


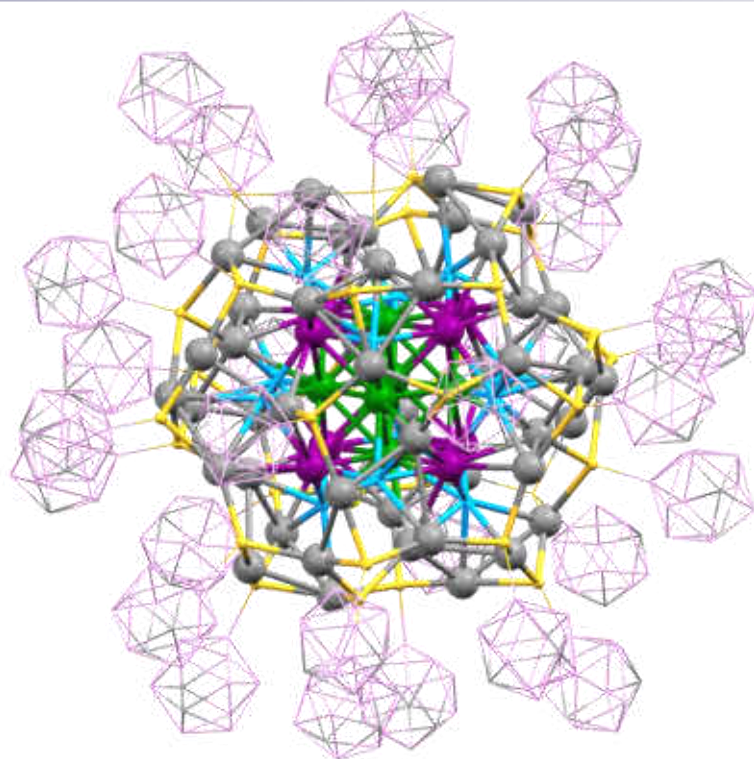
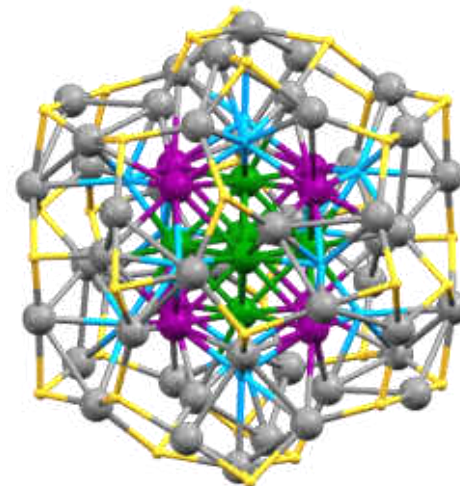
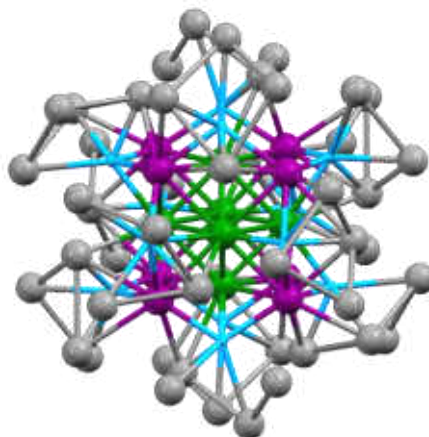
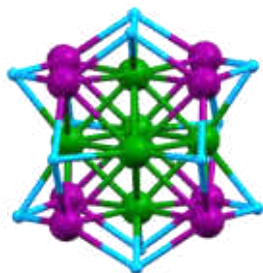
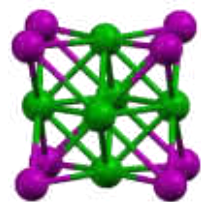


International Centre for Clean Water

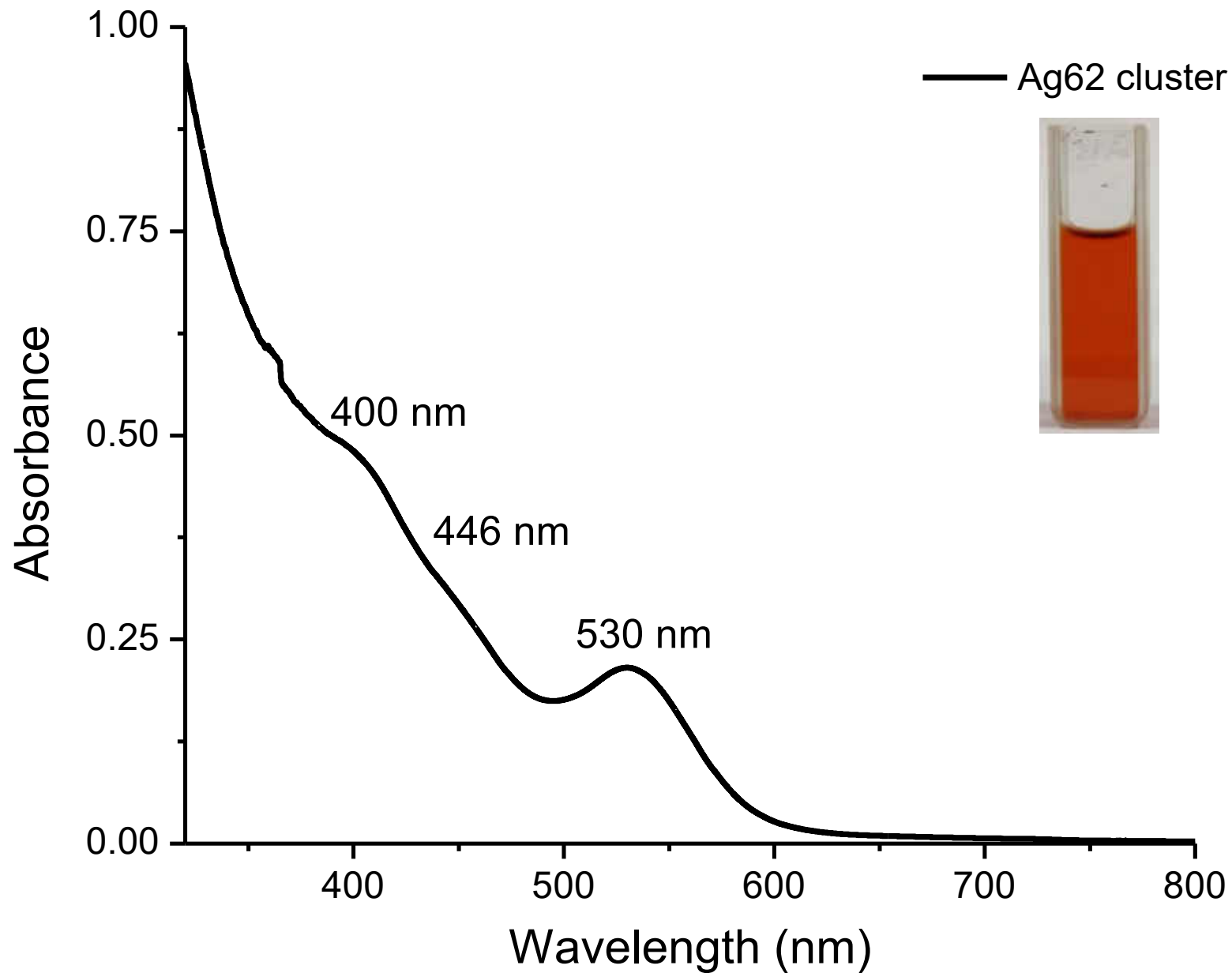
Very new science

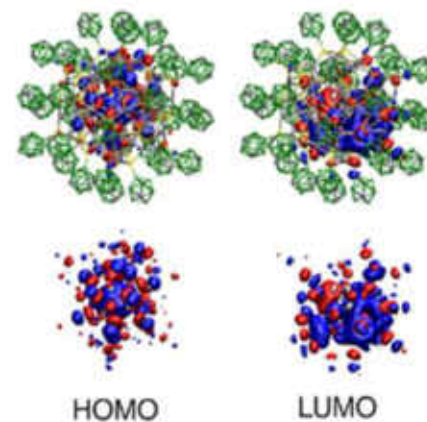
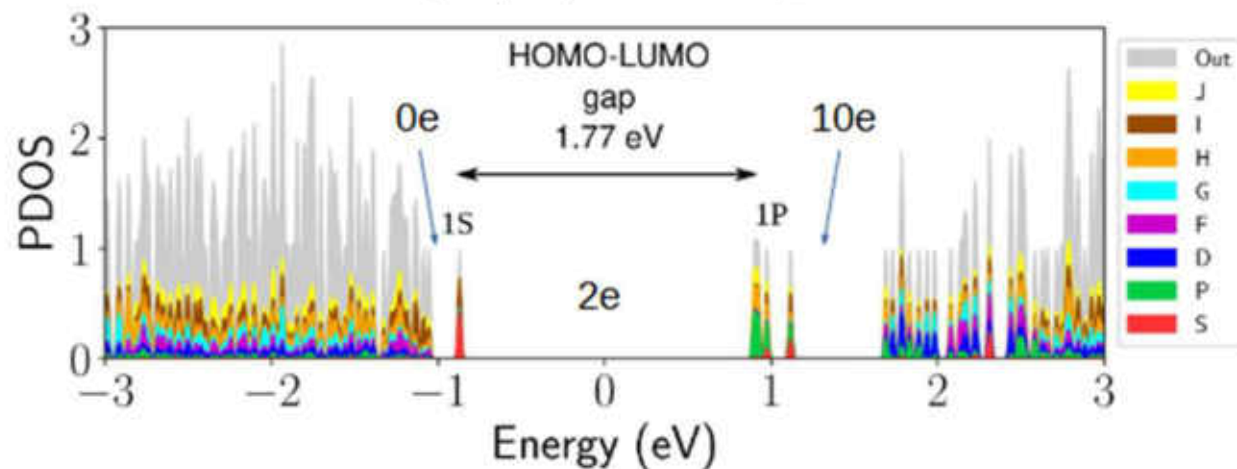
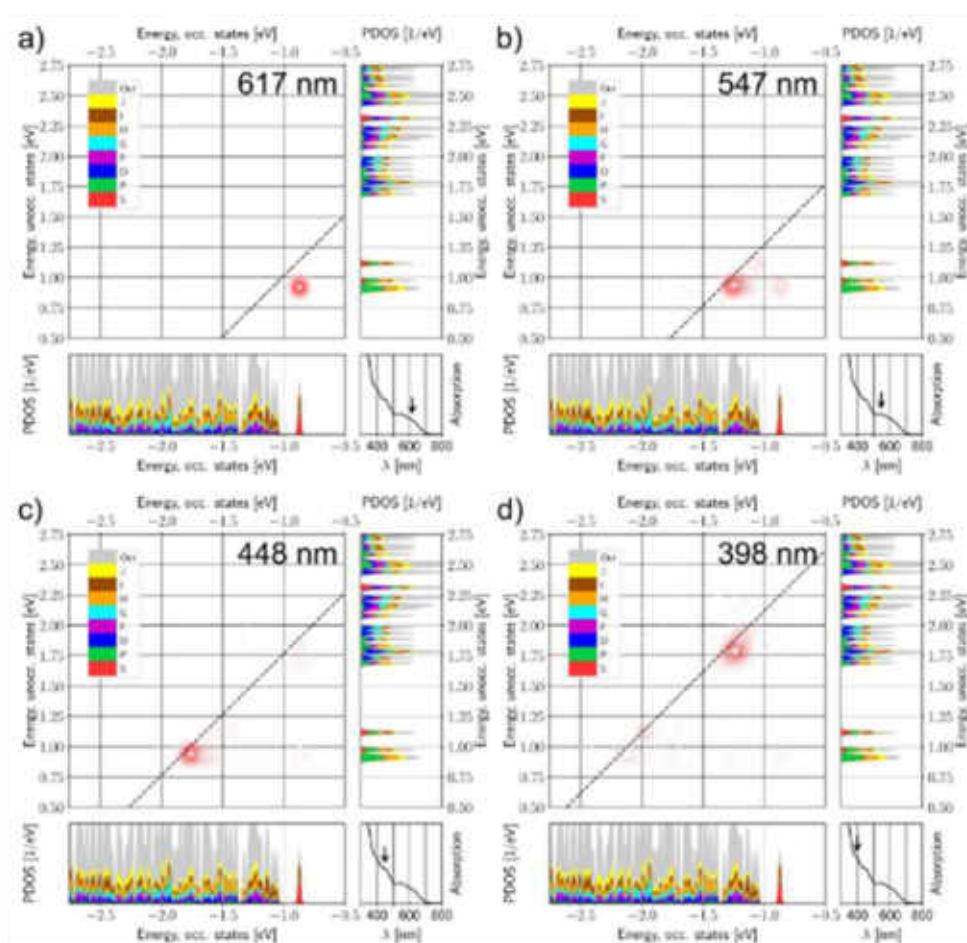
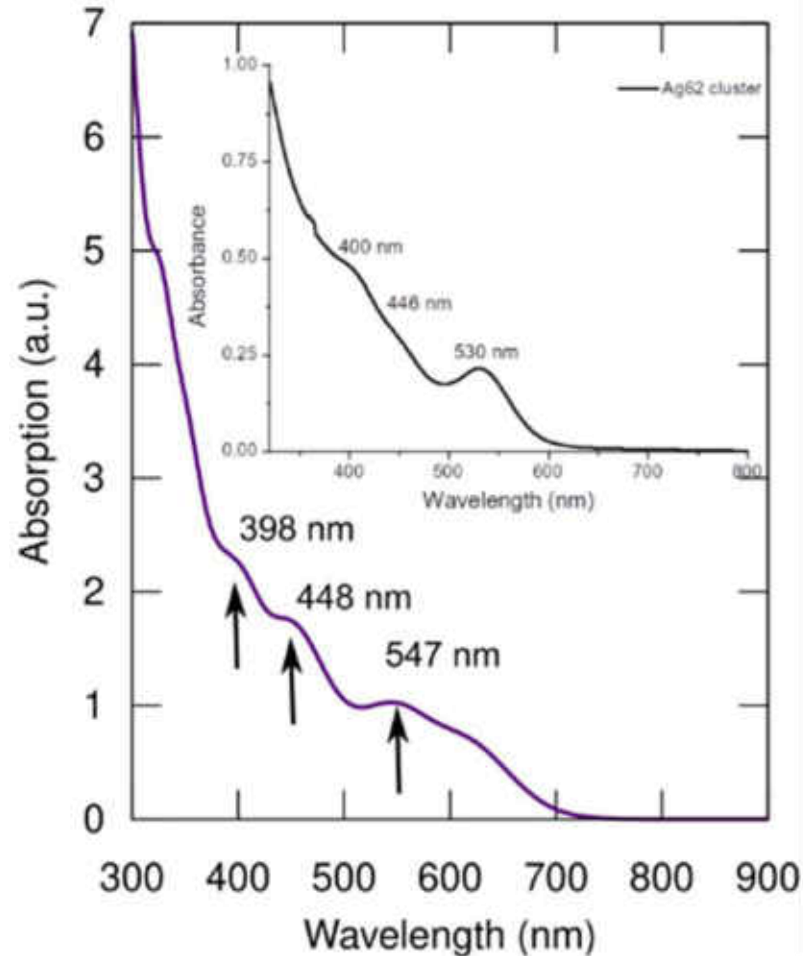
Unprecedented Polymorphism in Carborane-thiol Protected 2e-superatomic Spherical $[\text{Ag}_{62}\text{S}_{12}(\text{M}_9)_{32}]^{4+}$ Nanocluster





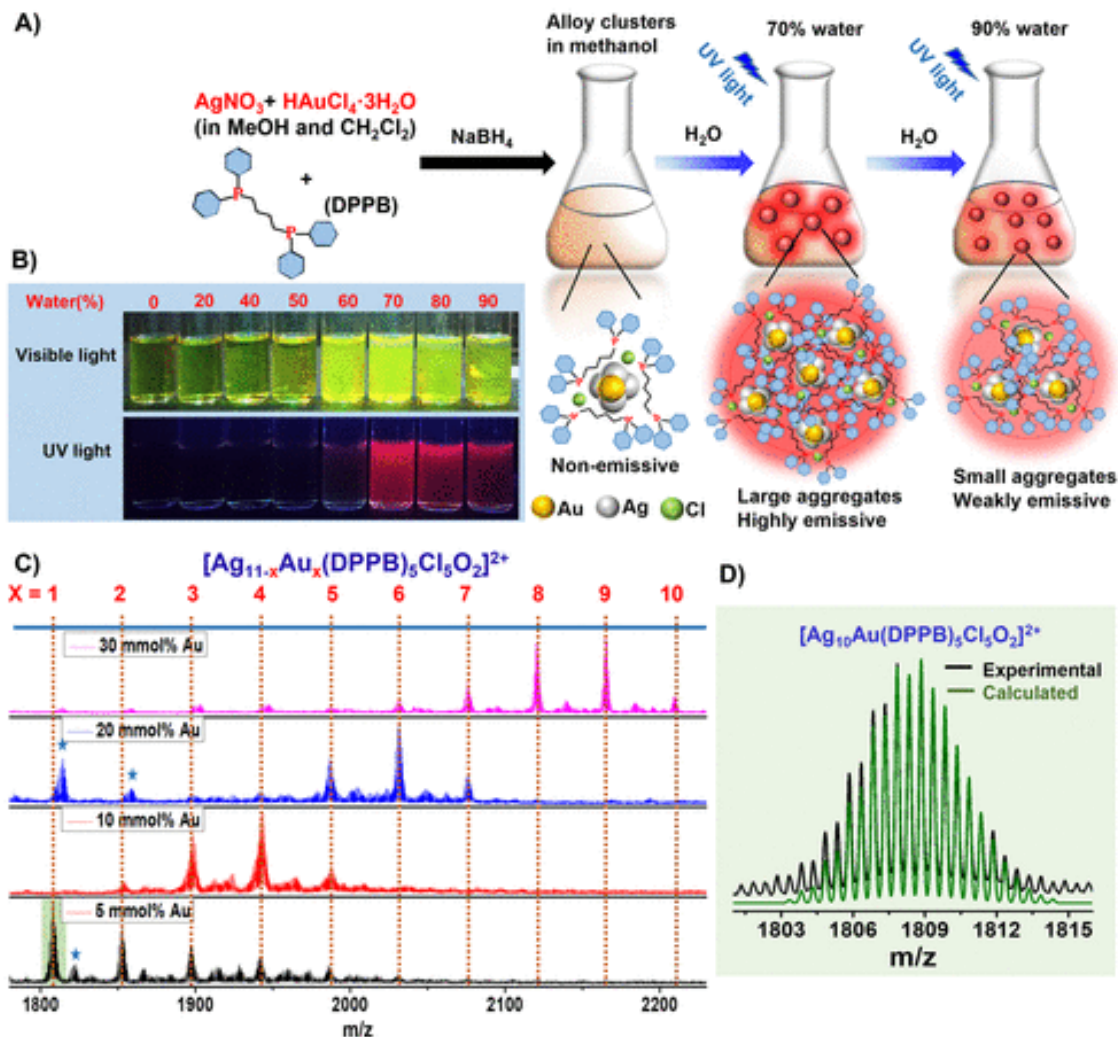
Absorption spectrum



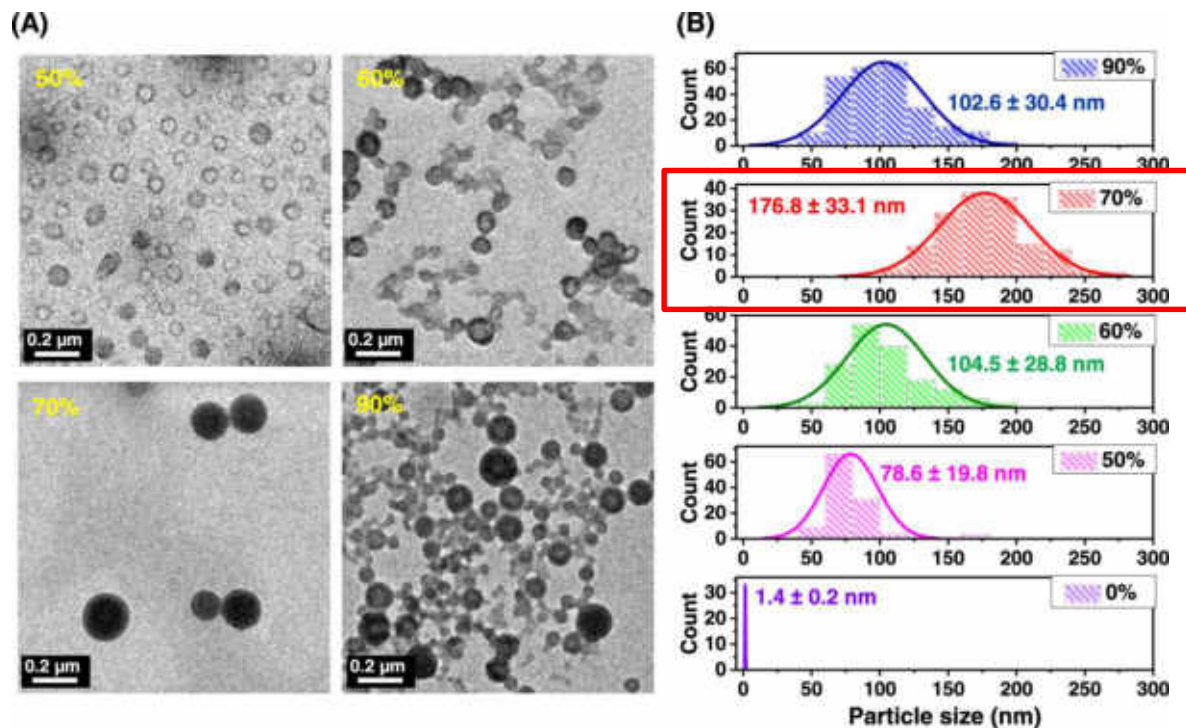


Cluster aggregates

Aggregates of clusters

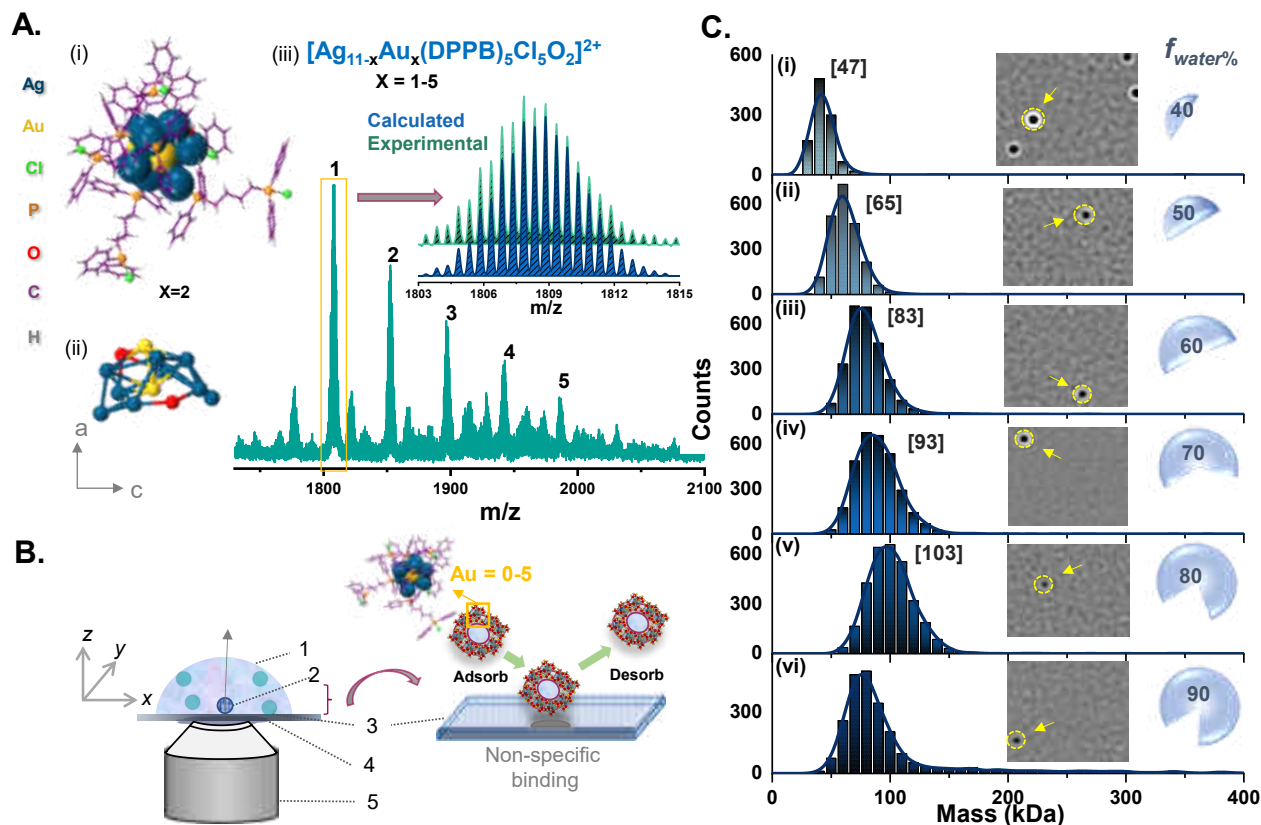


$[\text{Ag}_{11-x}\text{Au}_x(\text{DPPB})_5\text{Cl}_5\text{O}_2]$ Dynamic light scattering



(A) TEM images of phosphine protected $\text{Ag}_{11-x}\text{Au}_x$ alloy clusters formation of solvent-induced aggregates in the presence of 50, 60, 70, and 90% water.

Mass photometry



A (i) Calculated structure (x = 2), (ii) the metal, Ag_{11-x}Au_x, core (x = 2), and (iii) ESI MS of [Ag_{11-x}Au_x(DPPB)₅Cl₅O₂]²⁺ (x = 1-5) nanoclusters. In inset, calculated isotopic distribution is stacked with the experimental one. **B.** Concept and experimental implementation of MP. Parts in the graphic representation: 1: solvent mixture (sol mix) containing nanoclusters; 2: nanocluster aggregates in solution; 3: glass surface; 4: immersion medium; 5: objective lens. Single-particle landing event on a non-coated cover slide is shown on the right. **C.** A stacked plot of the MP histogram of various-sized nanoaggregates with the counts of particle landing events, with varying solvent composition. Mass (kDa) is shown on the x-axis. The corresponding $f_{\text{water}\%}$ of solvent mixture is labelled on each histogram.

With Vicki Wysocki

Aggregates with atomic precision

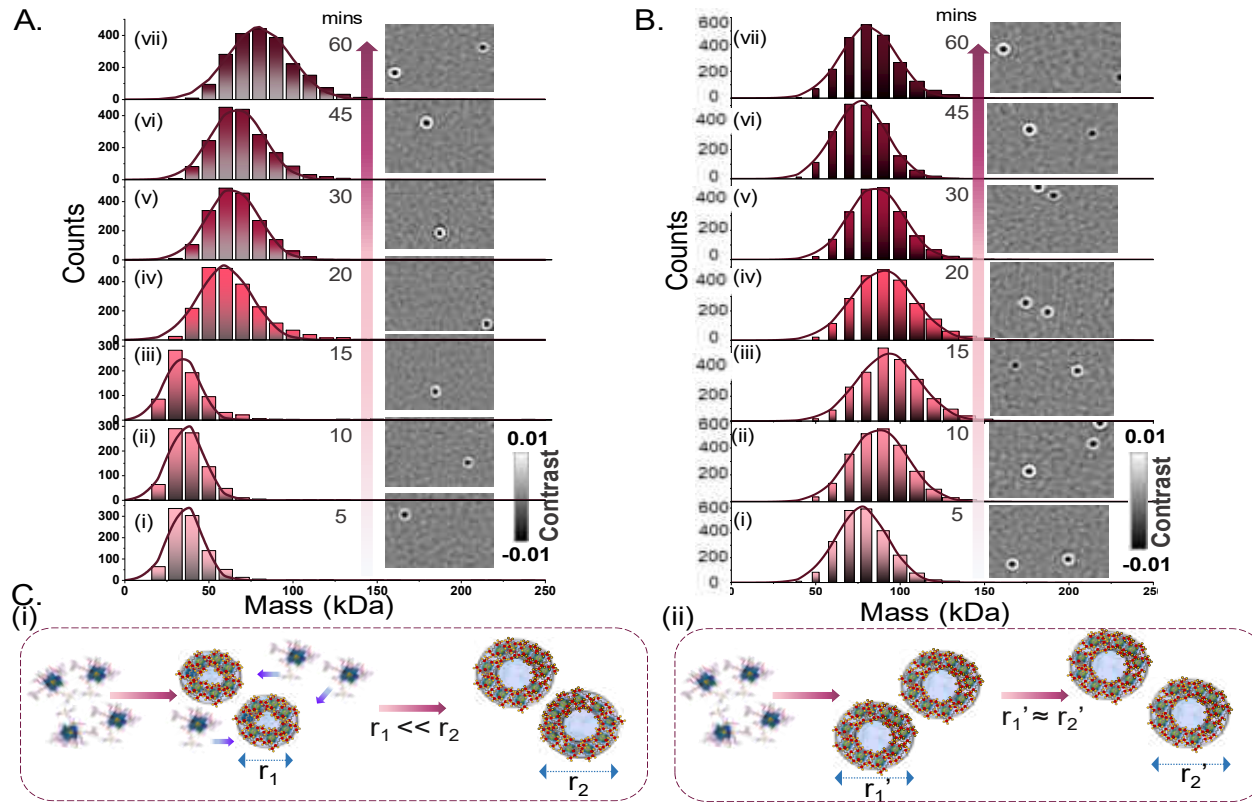
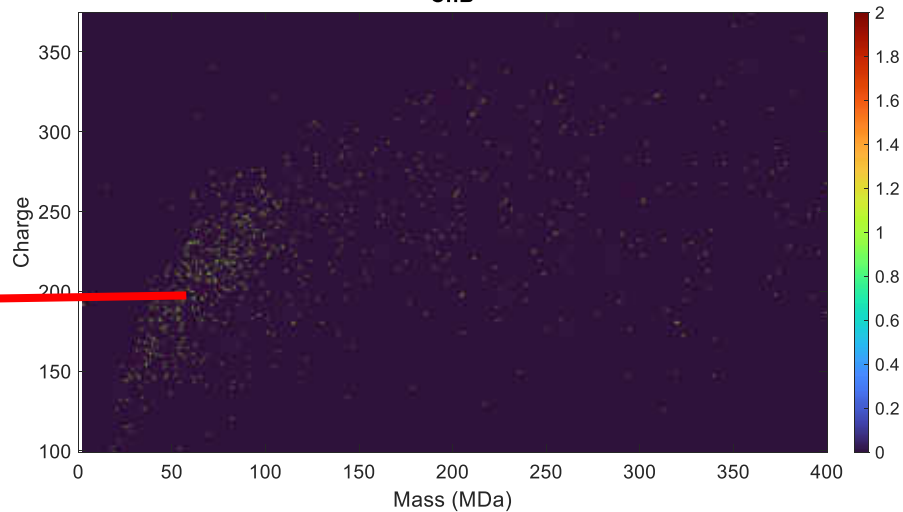
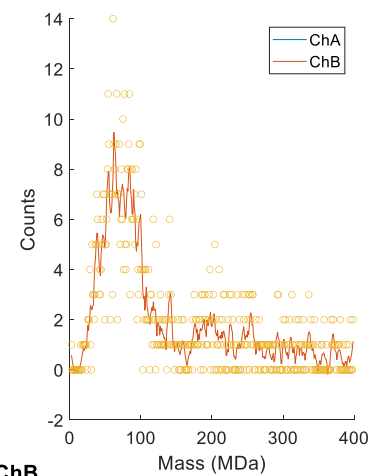
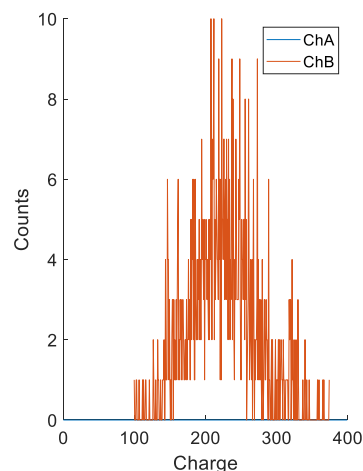
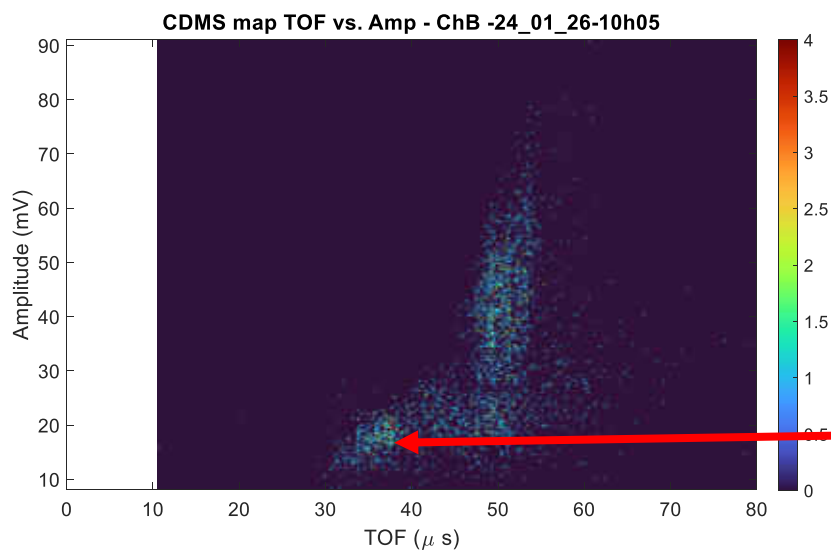


Fig. 2 Stacked plots of the time-dependent mass variation of nanoaggregates with normalized counts of single-particle landing events at (A) $f_{40\%}$ and (B) $f_{80\%}$ respectively, in MP. The time scale of each stack represents the time of data acquisition at a particular sol mix. The photographs of single-particle landing events at the glass-sol mix interface with increasing time are shown as insets with each measurement. (C) Schematic representation of the variation in diameter of nanoassemblies during NC-aggregation at (i) $f_{40\%}$ and (ii) $f_{80\%}$ respectively. r_1 , r_1' represent the diameter of the aggregates at the initial stage of growth, and r_2 , r_2' represent the same at the final stage.

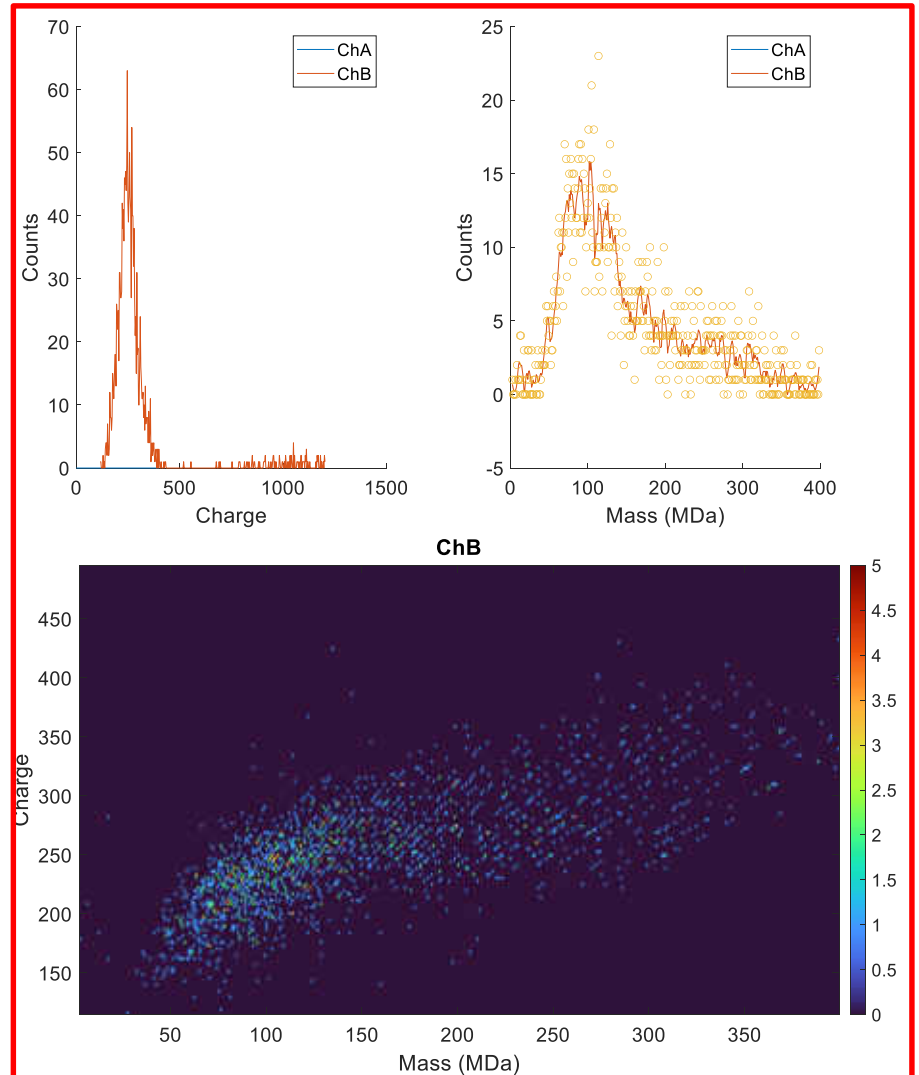
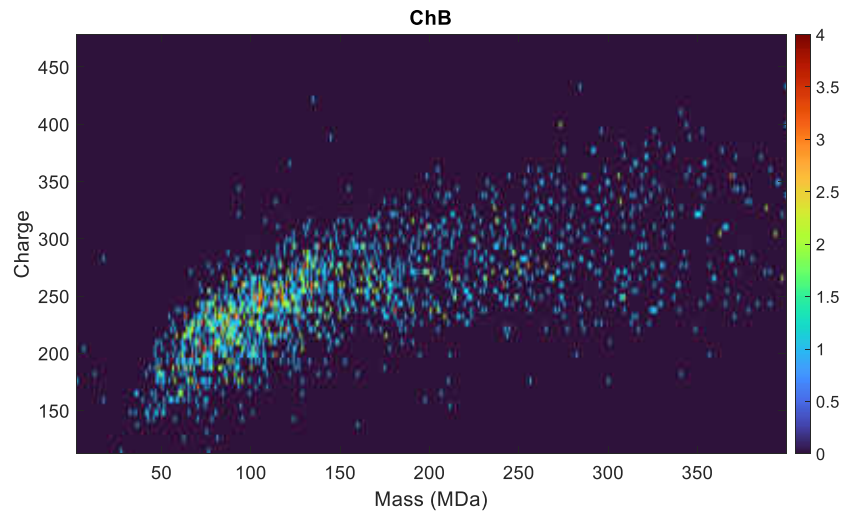
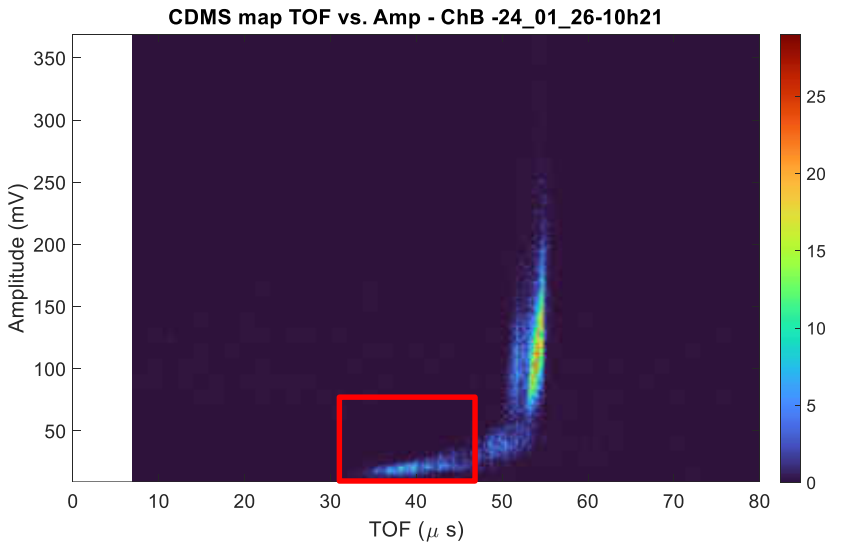
CDMS

- $\text{Ag}_{11-x}\text{Au}_x(\text{DPPB})_5\text{Cl}_5\text{O}_2$
- 30:70 methanol/water mixture
- Conc. of cluster 0.05 mg/ml



With Antoine Rodolphe, Lyon

Plasmonic nanoparticles



Molecular materials

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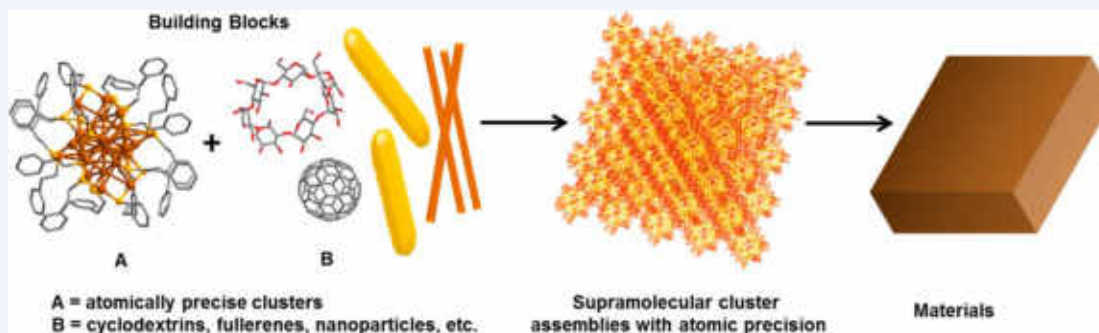
Article

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Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

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

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



Collaborators



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Nonappa

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Manfred Kappes

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



Shiv Khanna

Biswarup Pathak K. V. Adarsh

G. U. Kulkarni

Vivek Polshettiwar



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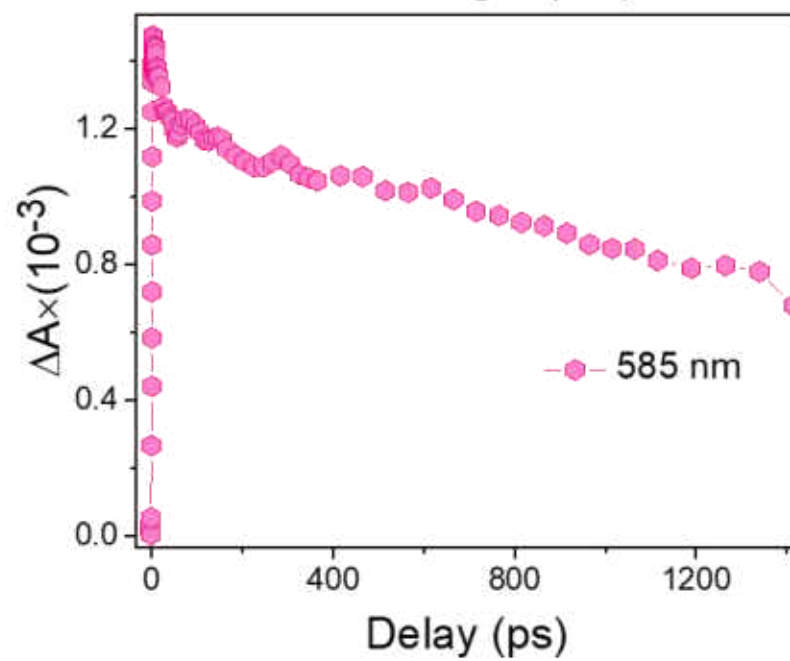
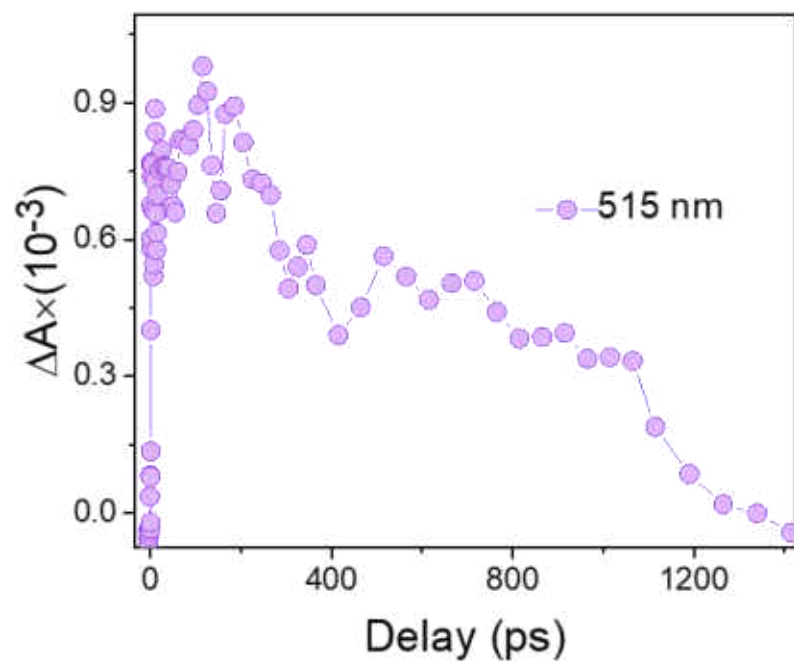
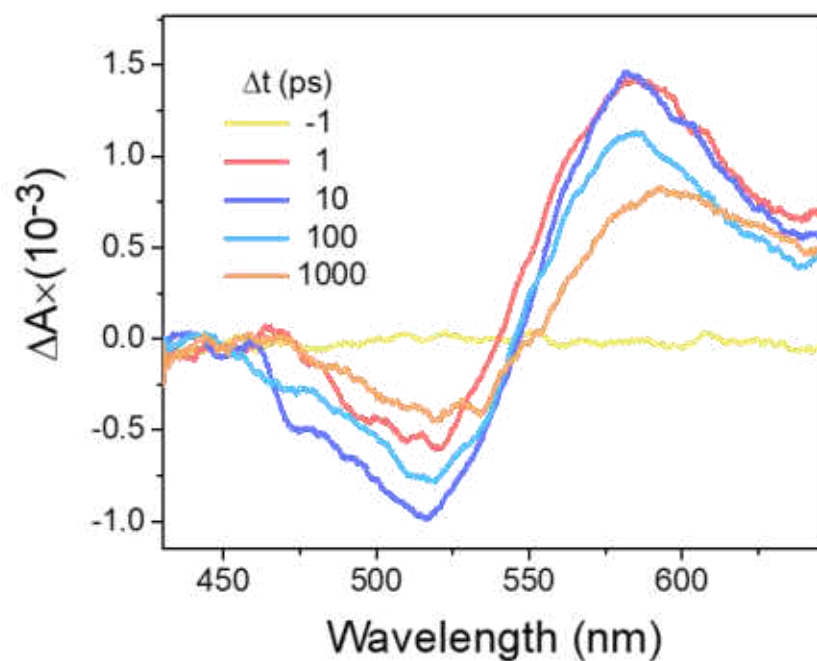
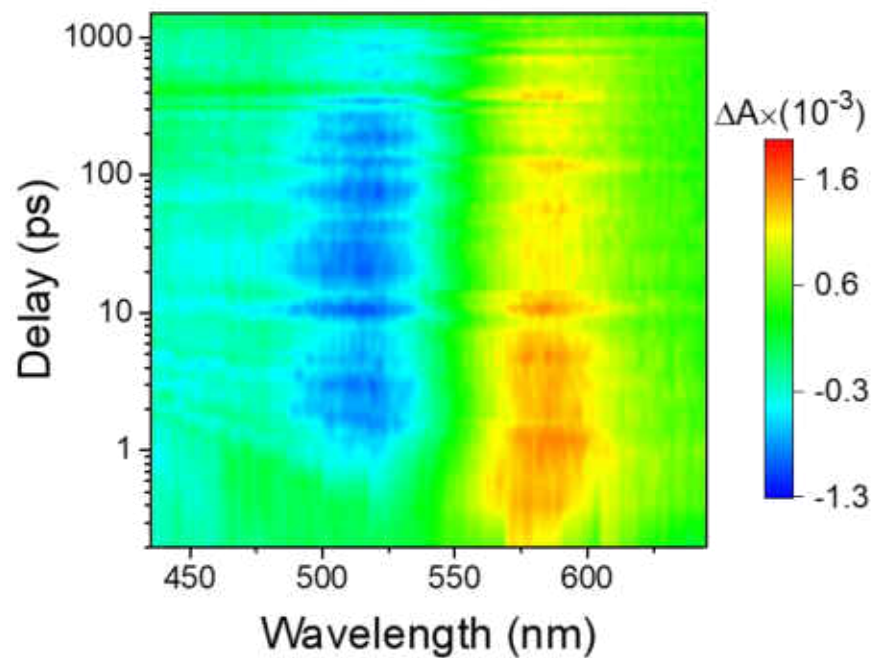
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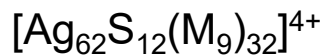
[Application Information](#)

Collaborators: Tatsuya Tsukuda, Keisaku Kimura, Yuichi Negishi, Ozi Landman, Rob Whetten, Hannu Hakkinen, Robin Ras, Manfred Kappes, Horst Hahn, Tomas Base, Nonappa, Shiv Khanna, Umesh Waghmare, Chandrabhas Narayana, Giridhar U. Kulkarni, Reji Philip, Vivek Polshettiwar, R. Mukhopadhyay, K. V. Adarsh, Biswarup Pathak, Chaitanya Sharma Yamijala

Thank you all

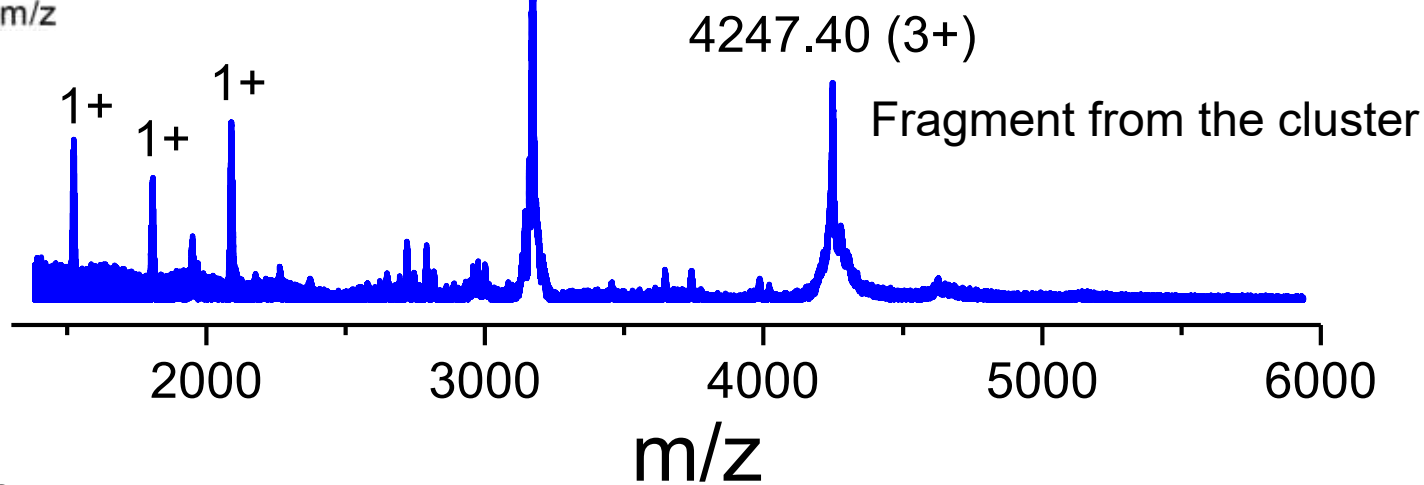
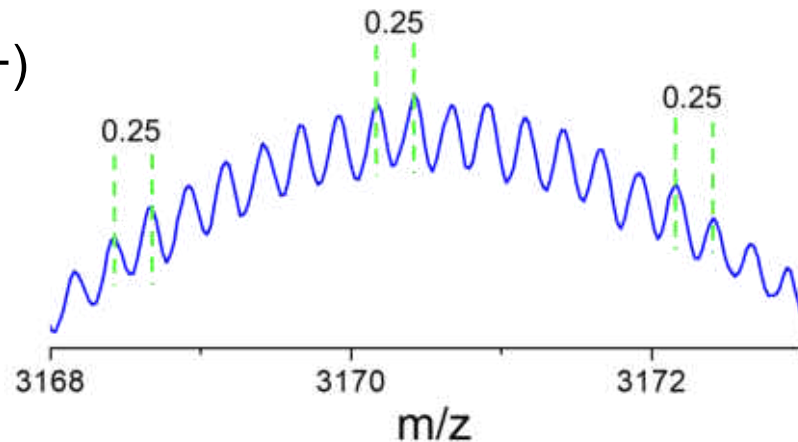
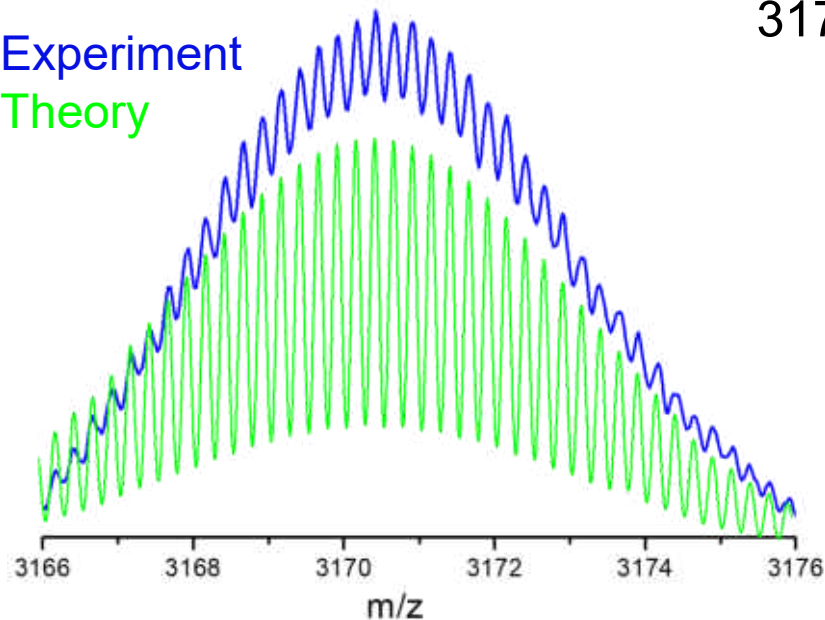


Mass spectrum of the cluster



Experiment

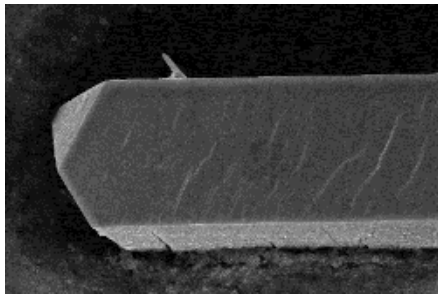
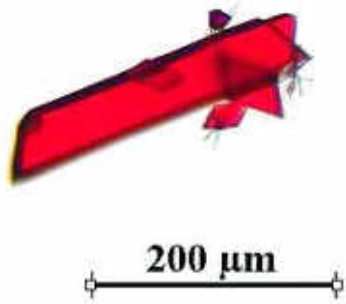
Theory



MS/MS was done

Polymorphic crystals

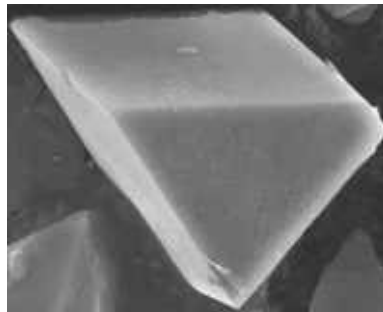
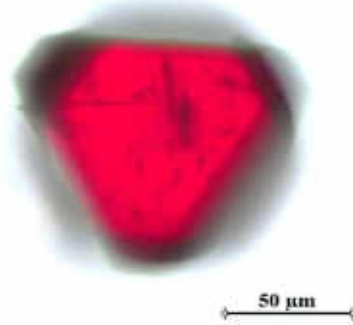
Type A:



Hexagonal

$a = 25.004 \text{ \AA}$
 $b = 26.666 \text{ \AA}$
 $c = 124.542 \text{ \AA}$
 $\alpha = 91.185^\circ$
 $\beta = 92.169^\circ$
 $\gamma = 117.904^\circ$
Volume = $73207 \text{ \AA}^3$

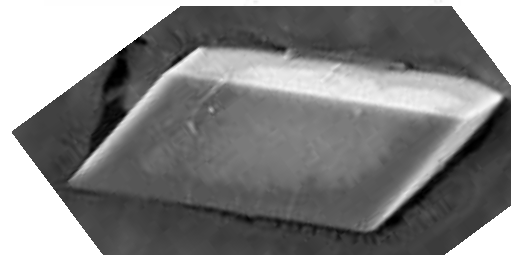
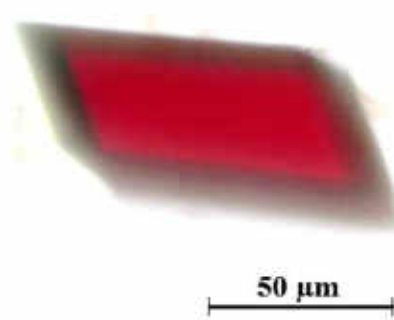
Type B:



Tetragonal

$a = 24.890 \text{ \AA}$
 $b = 35.704 \text{ \AA}$
 $c = 25.059 \text{ \AA}$
 $\alpha = 90^\circ$
 $\beta = 92^\circ$
 $\gamma = 90^\circ$
Volume = $22247 \text{ \AA}^3$

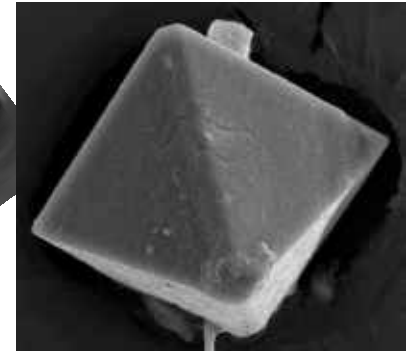
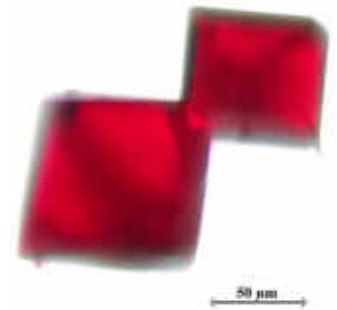
Type C



Triclinic

$a = 25.03 \text{ \AA}$
 $b = 26.69 \text{ \AA}$
 $c = 43.30 \text{ \AA}$
 $\alpha = 76^\circ$
 $\beta = 75^\circ$
 $\gamma = 62^\circ$
Volume = $24944 \text{ \AA}^3$

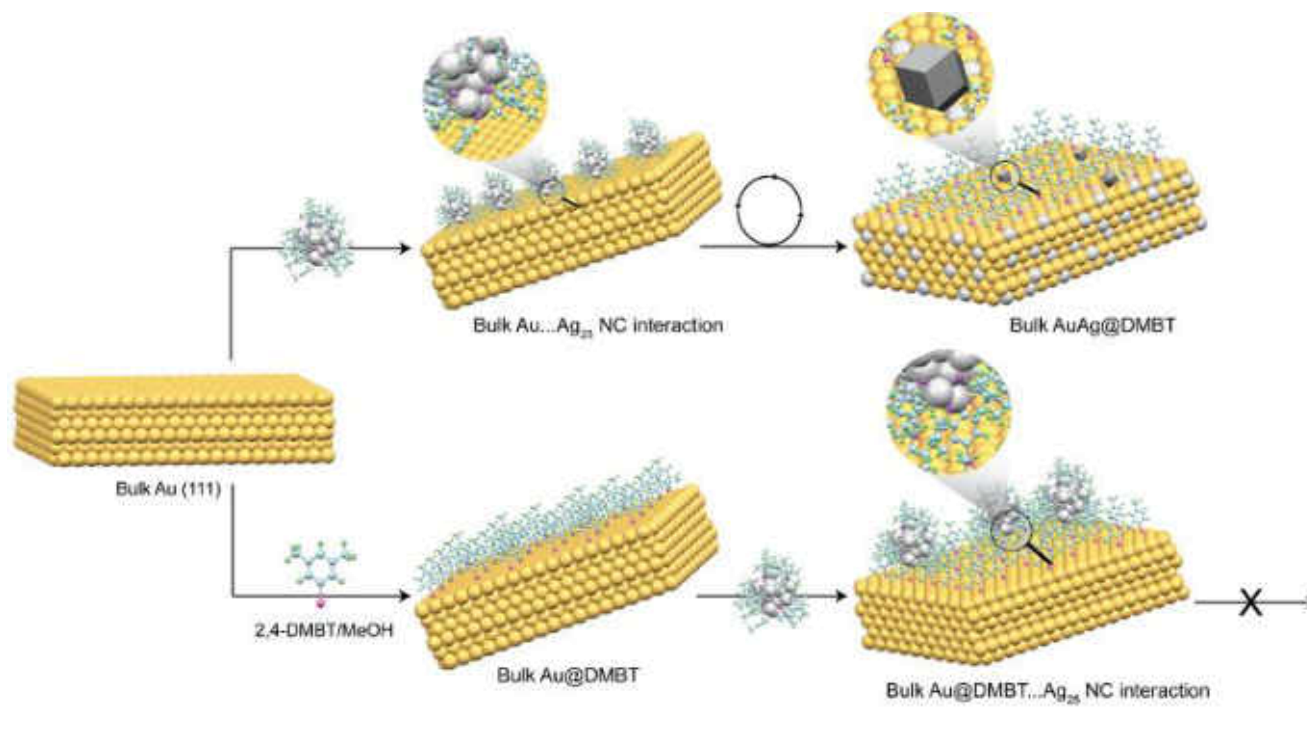
Type D

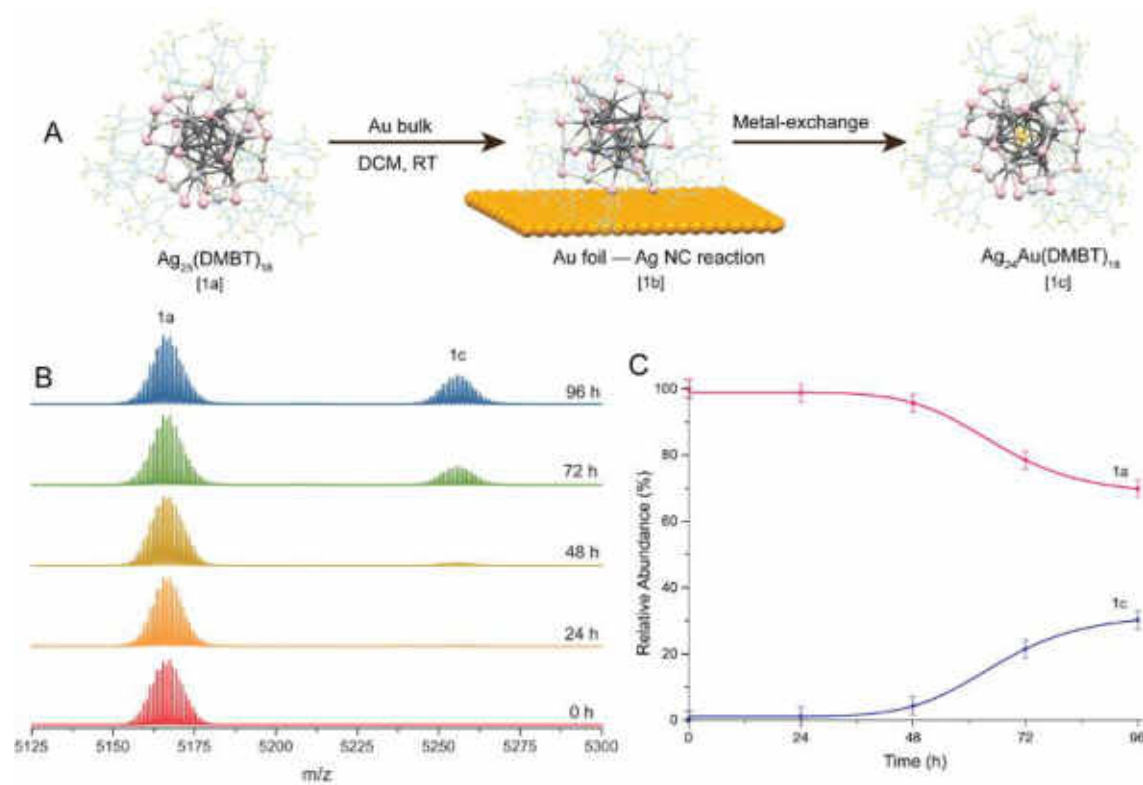


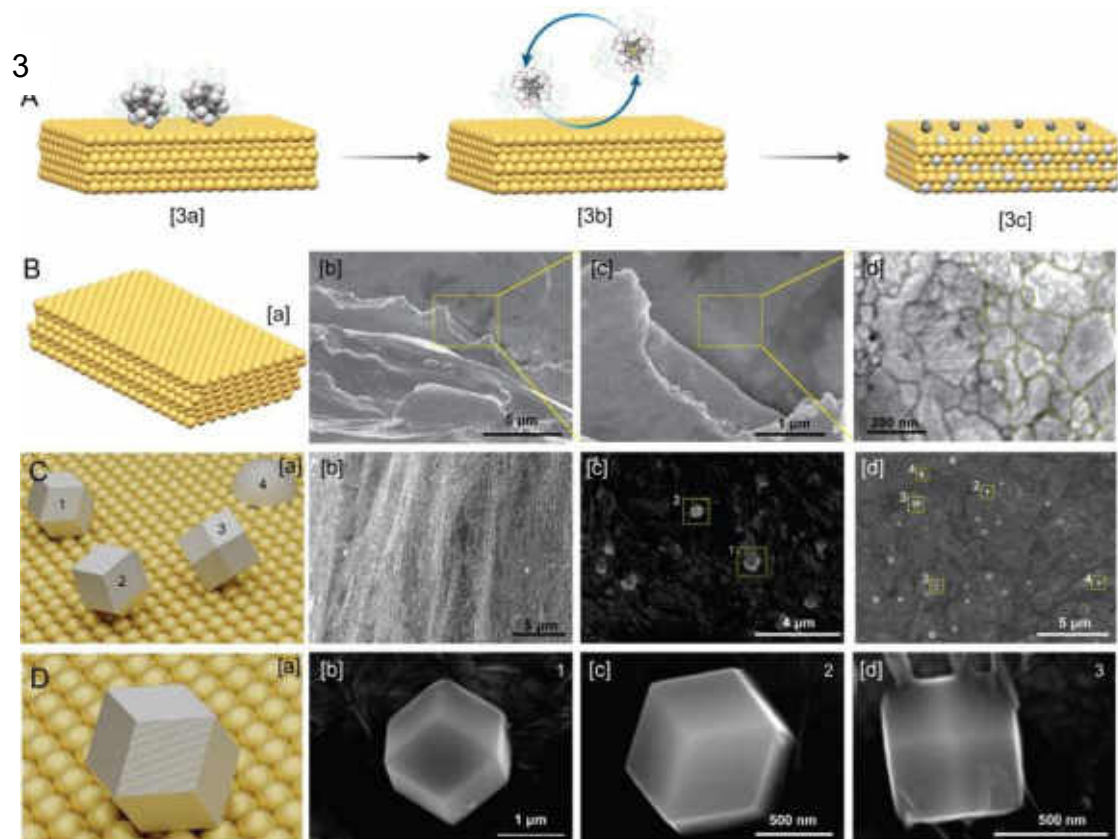
Cubic

$a = 35.42 \text{ \AA}$
 $b = 35.52$
 $c = 35.45$
 $\alpha = 90^\circ$
 $\beta = 89.90^\circ$
 $\gamma = 90^\circ$
Volume = $44599 \text{ \AA}^3$

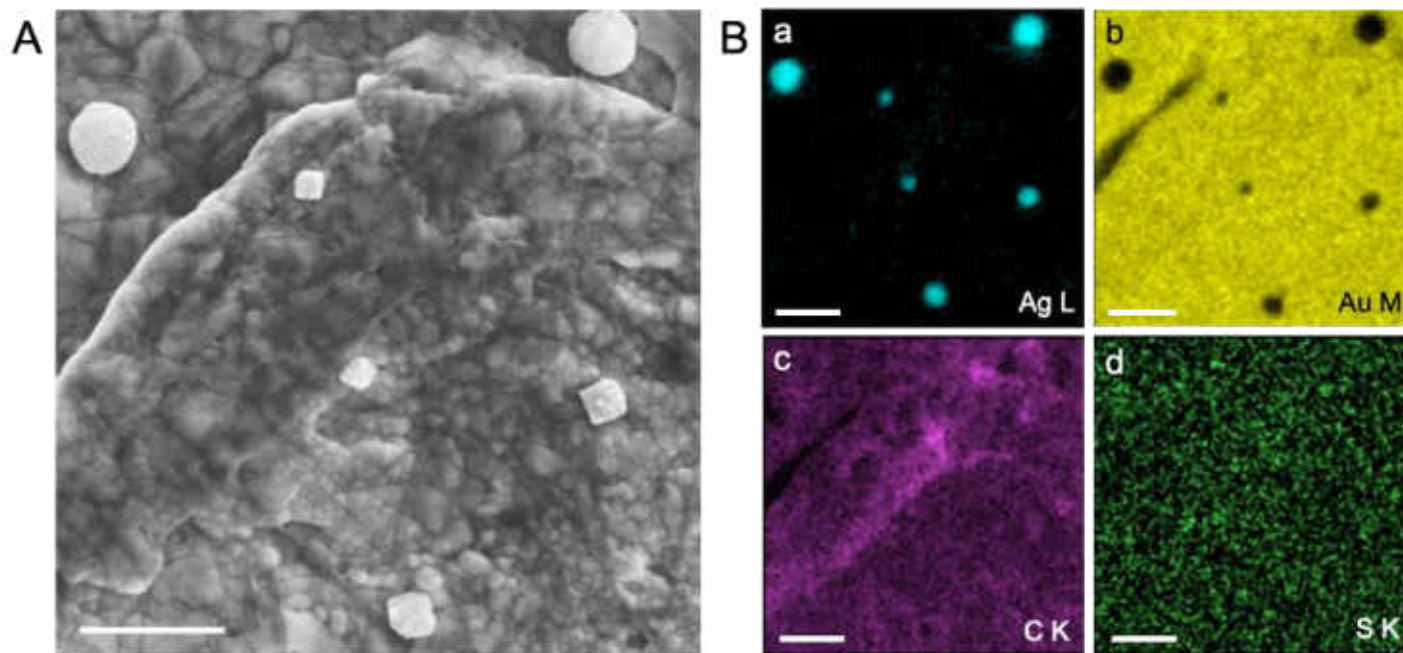
Reactions with bulk gold







Composition of microstructures



Scale bars: 1 μm

Collaborators



Robin Ras



Nonappa



Mauri Kostainen



Manfred Kappes



Olli Ikkala

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



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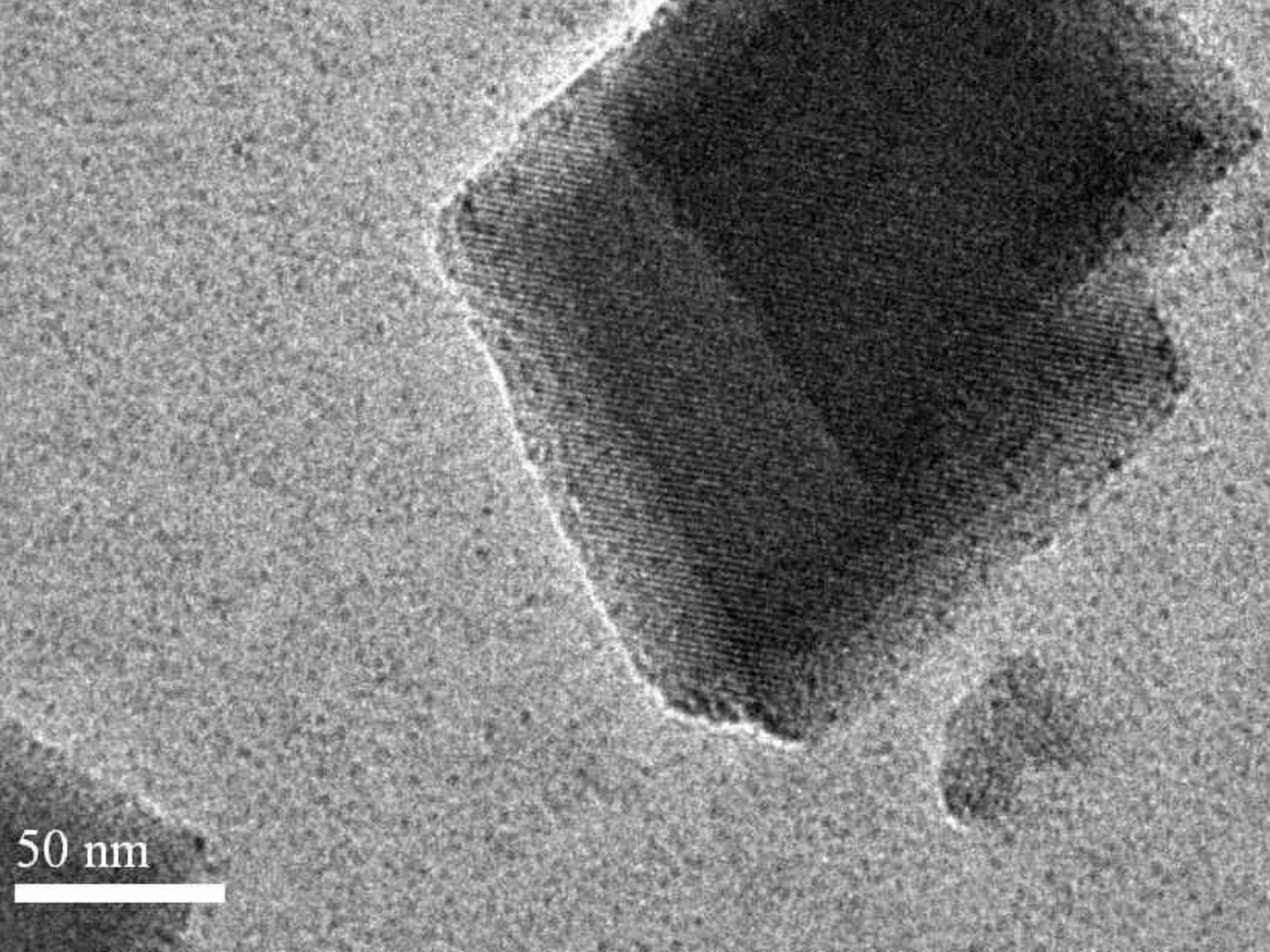
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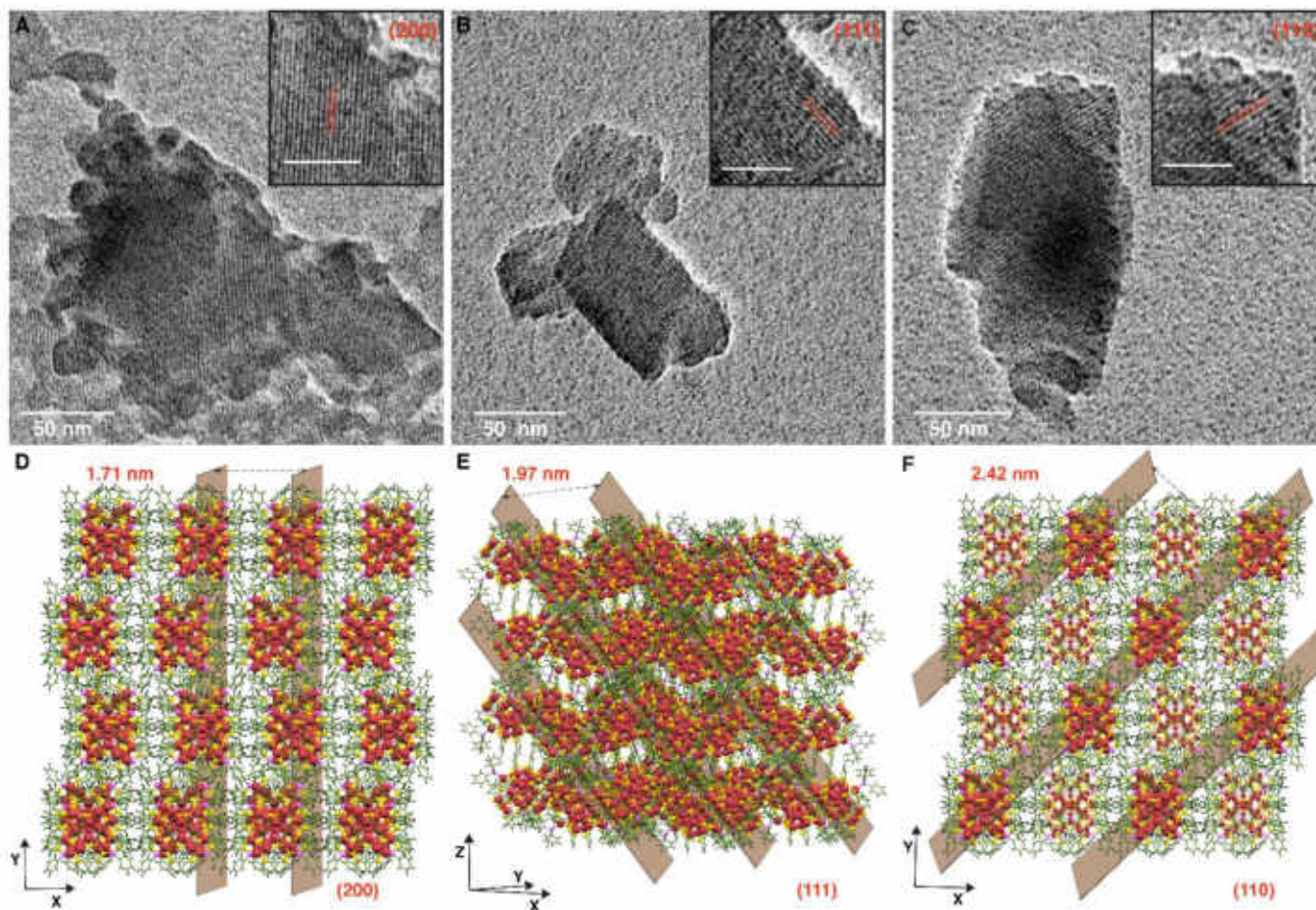
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Notes Comments



50 nm



Ananthu Mahendranath et al. Chem.Comm.2021

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

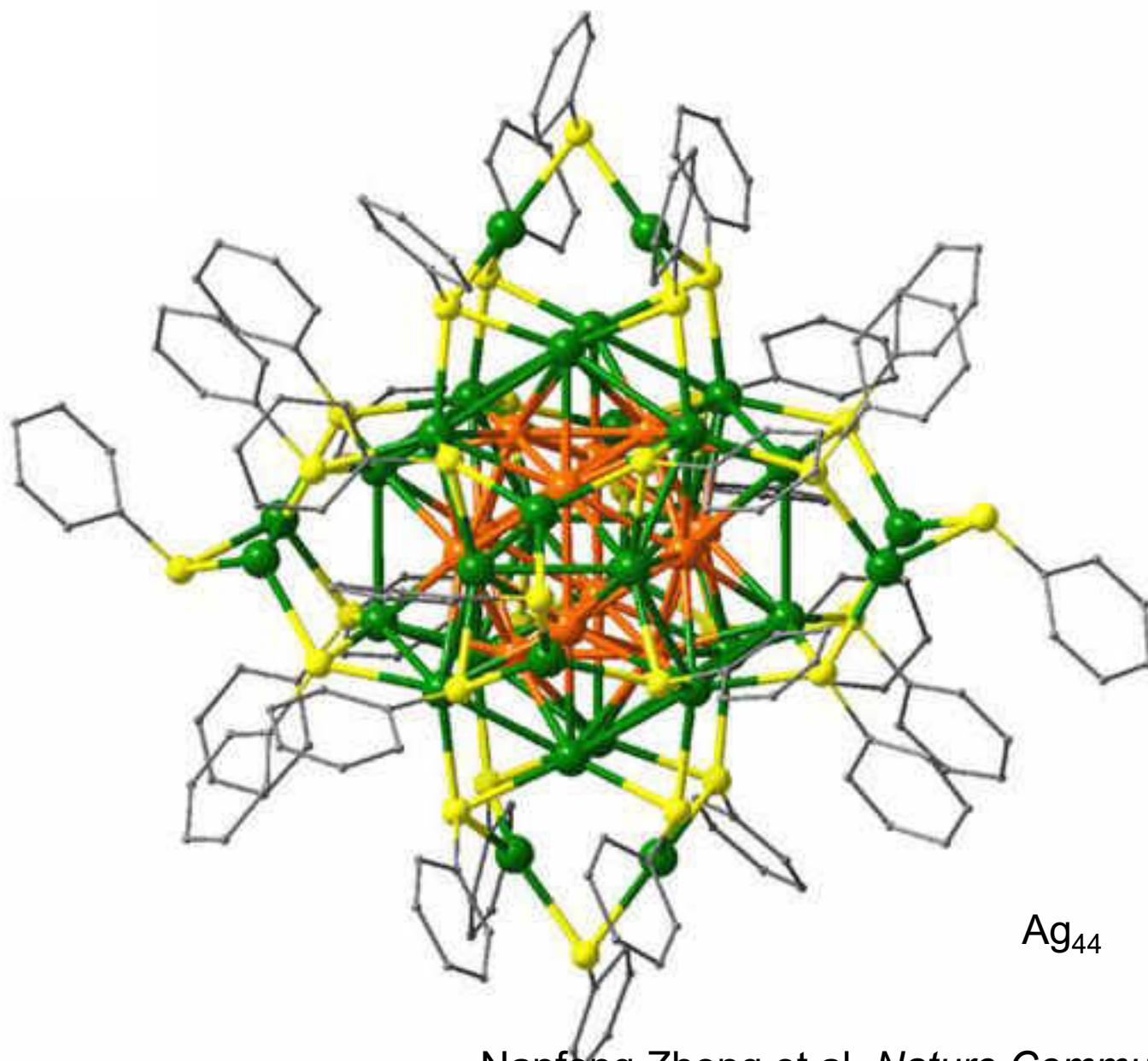
Physical properties

Electrical, magnetic

Mechanical properties

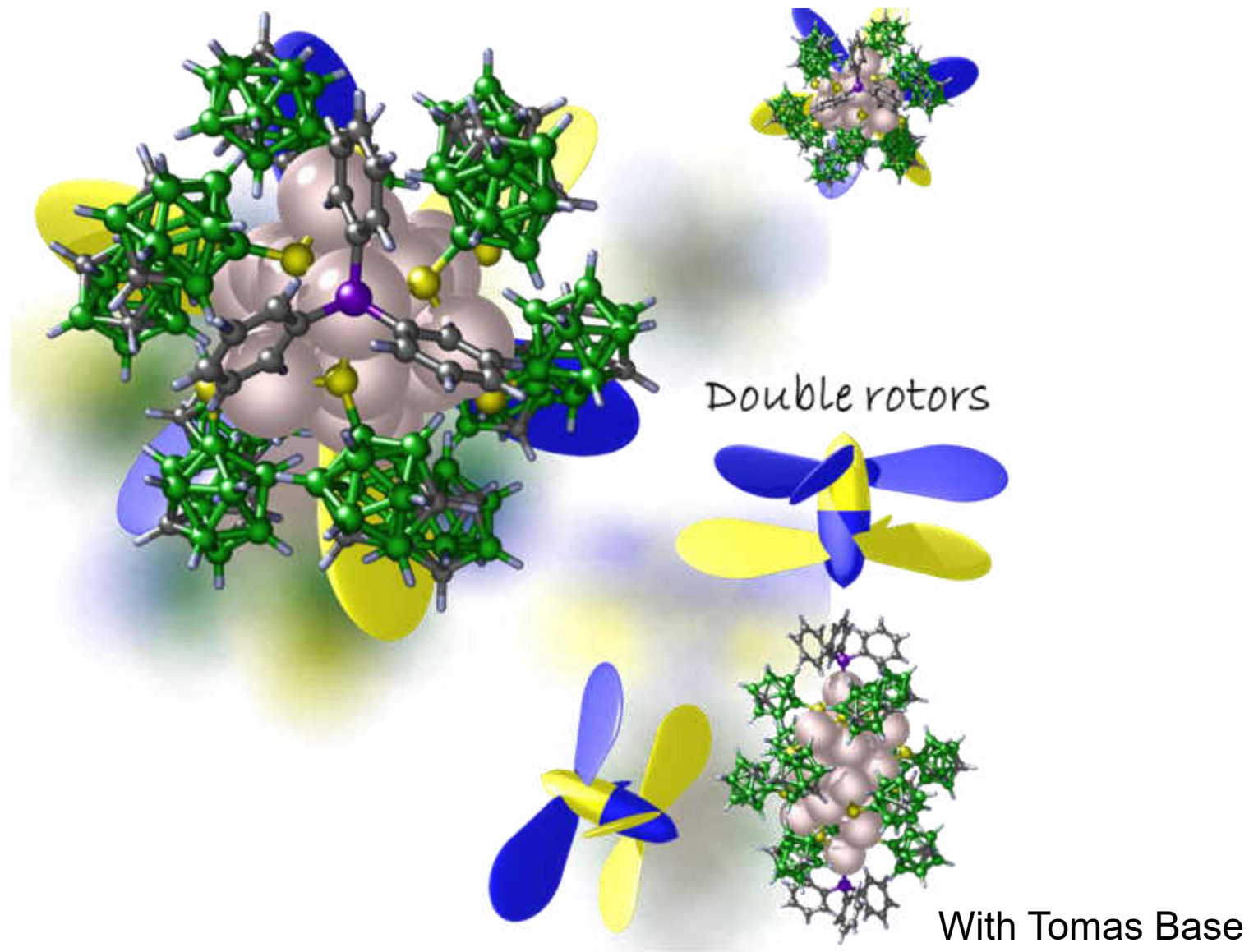
Electrochemical properties

Future?

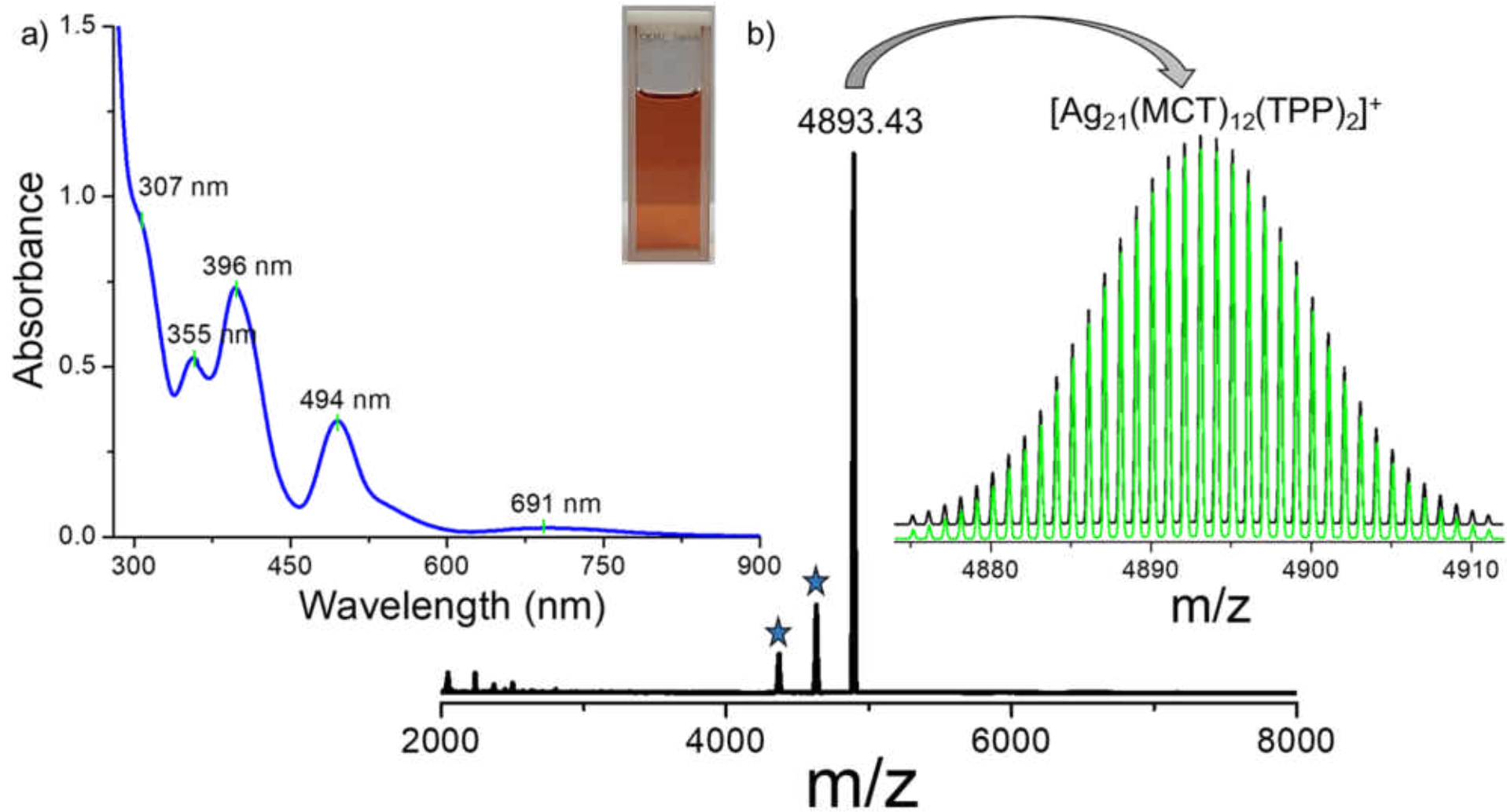


Nanfeng Zheng et al. *Nature Communications*, 2013
Terry Bigioni et al. *Nature* 2013

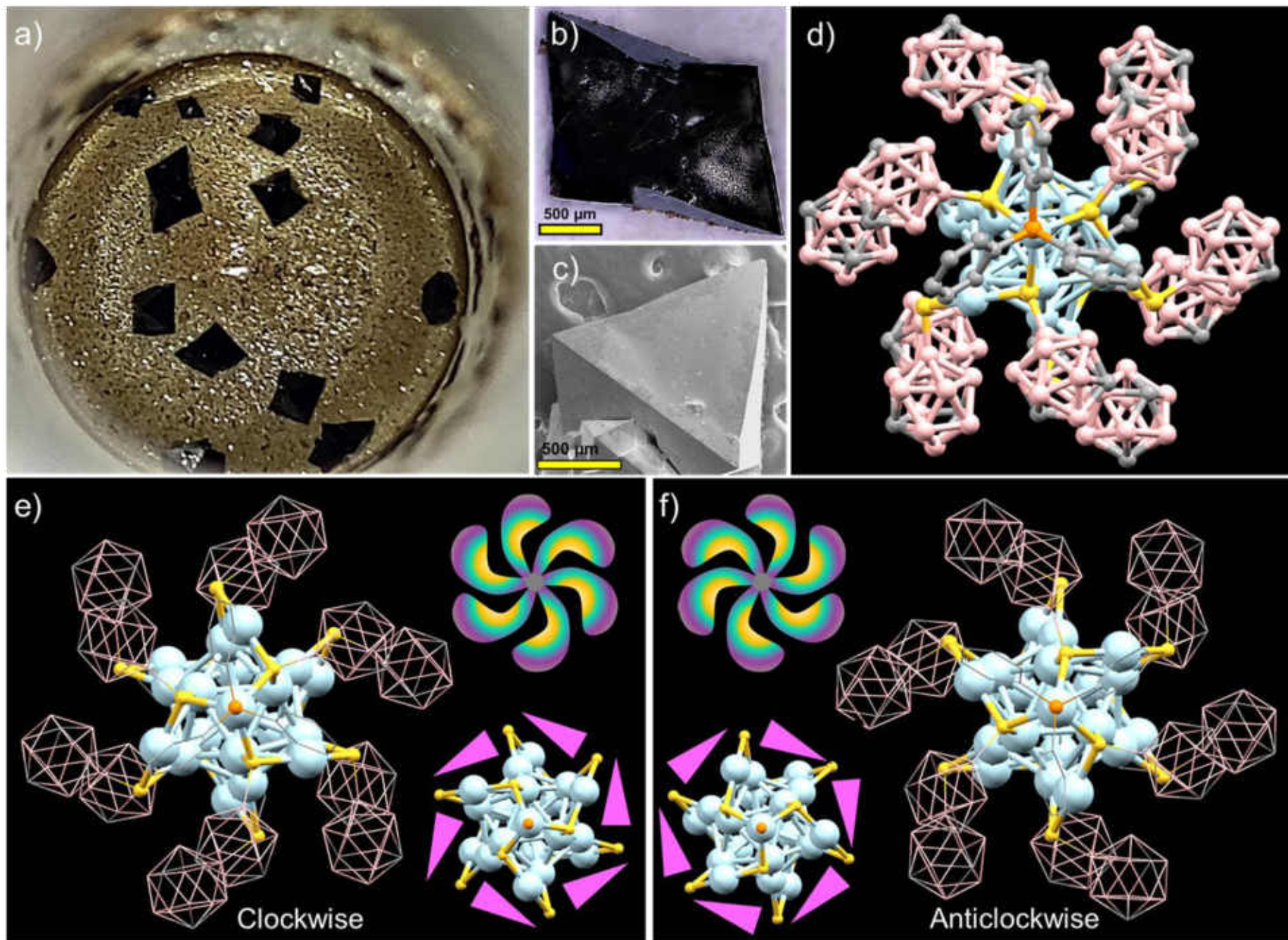
Carborane-thiol protected propeller-shaped photoresponsive silver nanomolecule



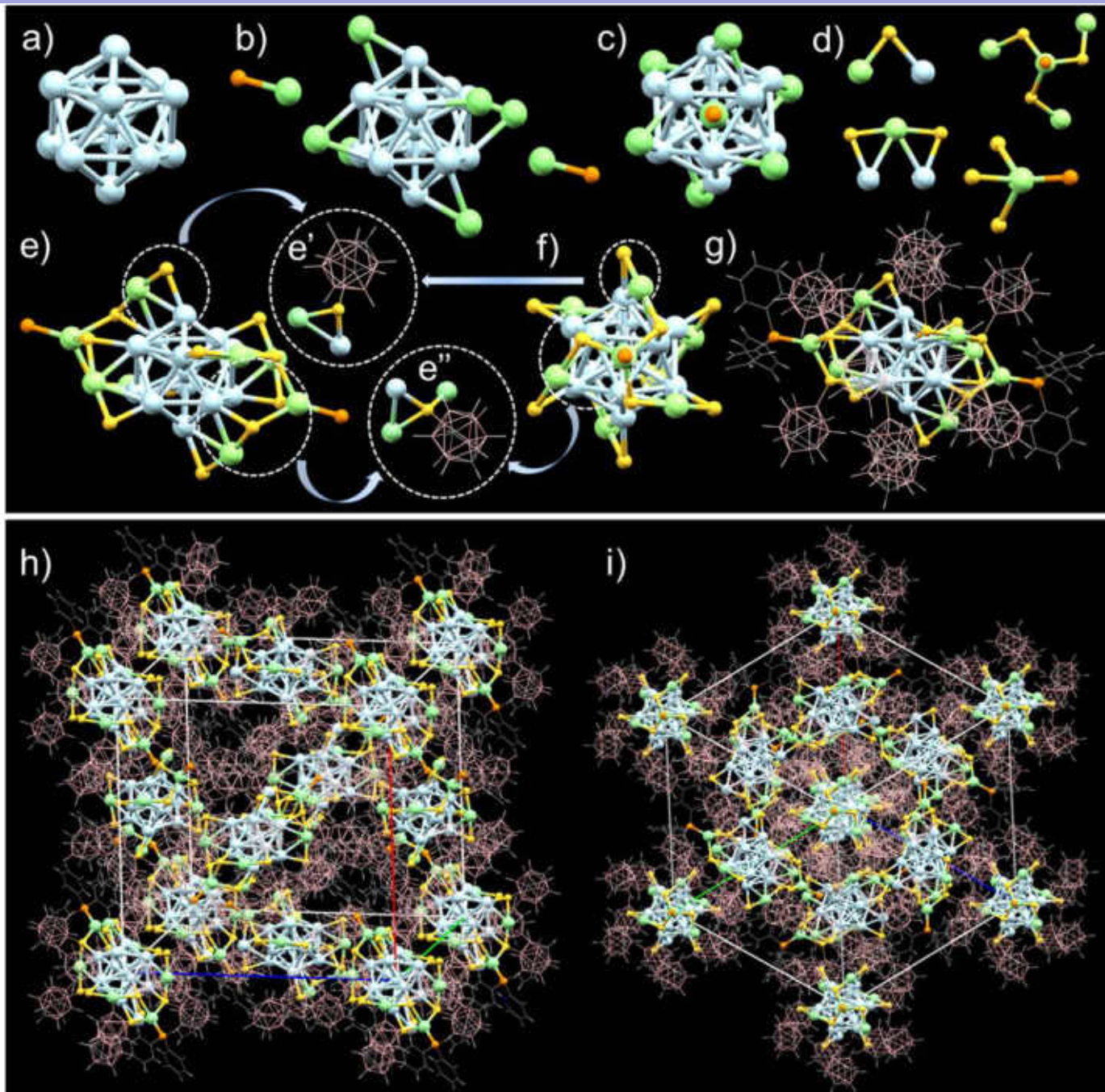
Characterization of Ag₂₁

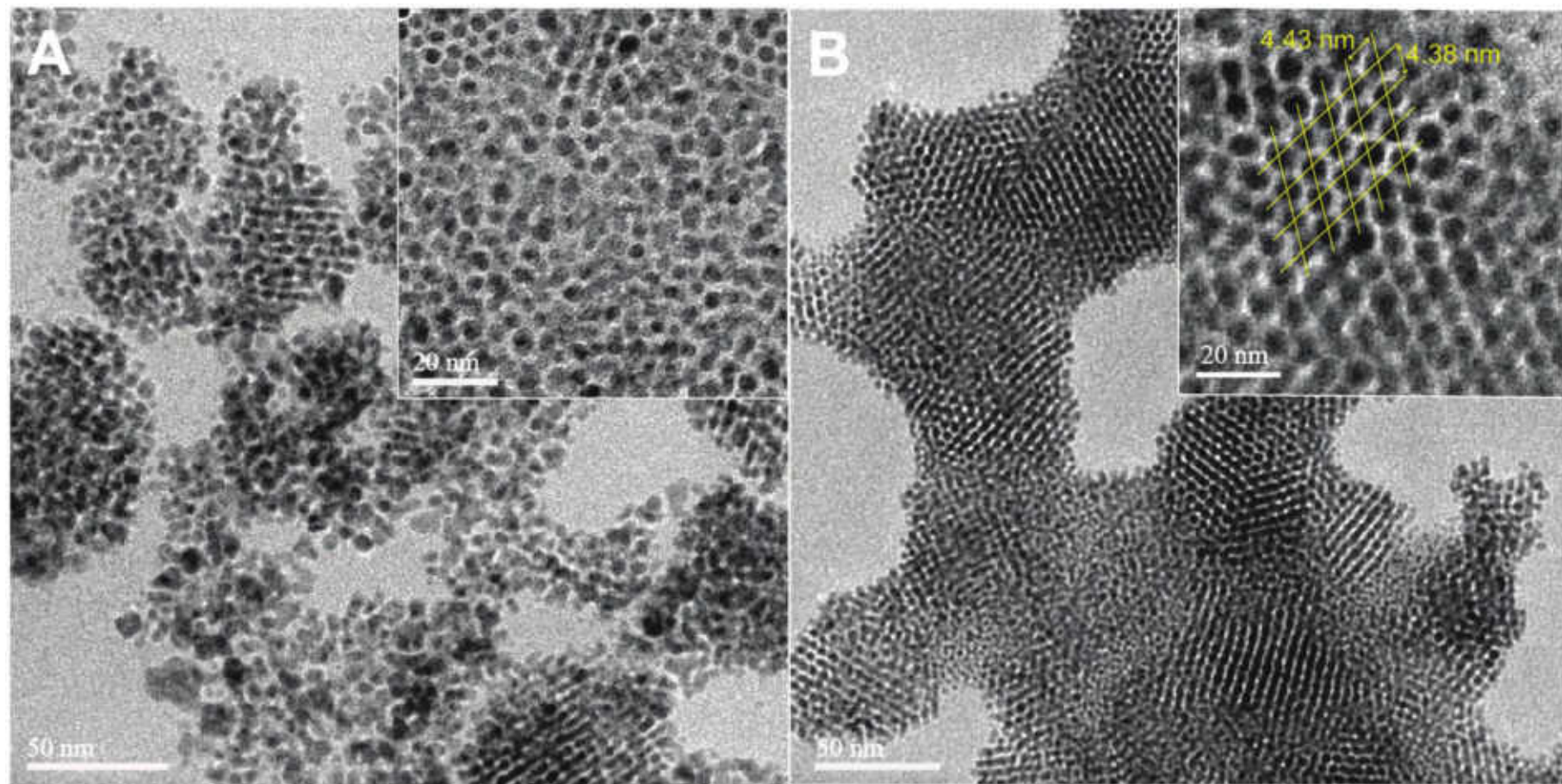


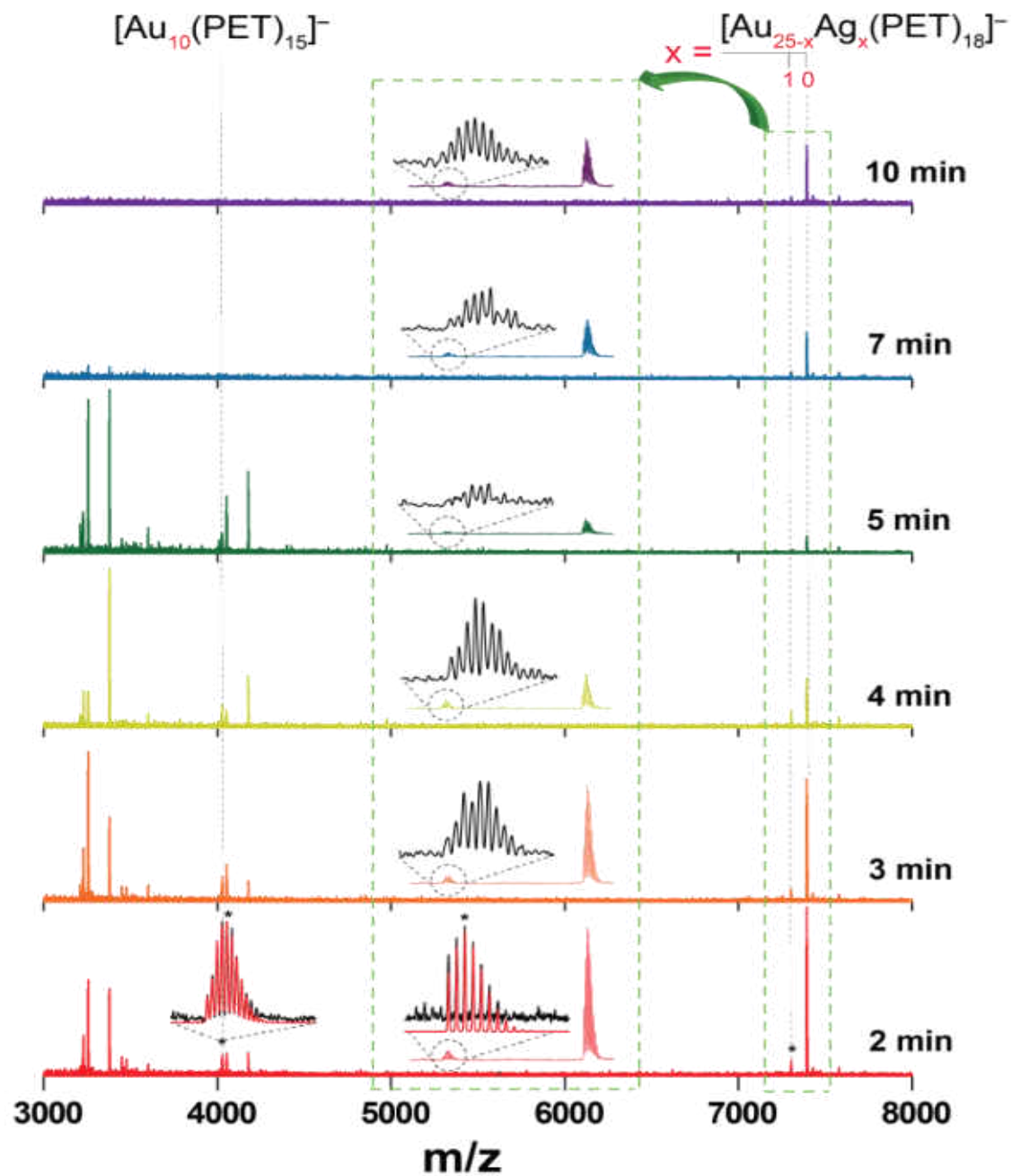
Structural details of Ag_{21}

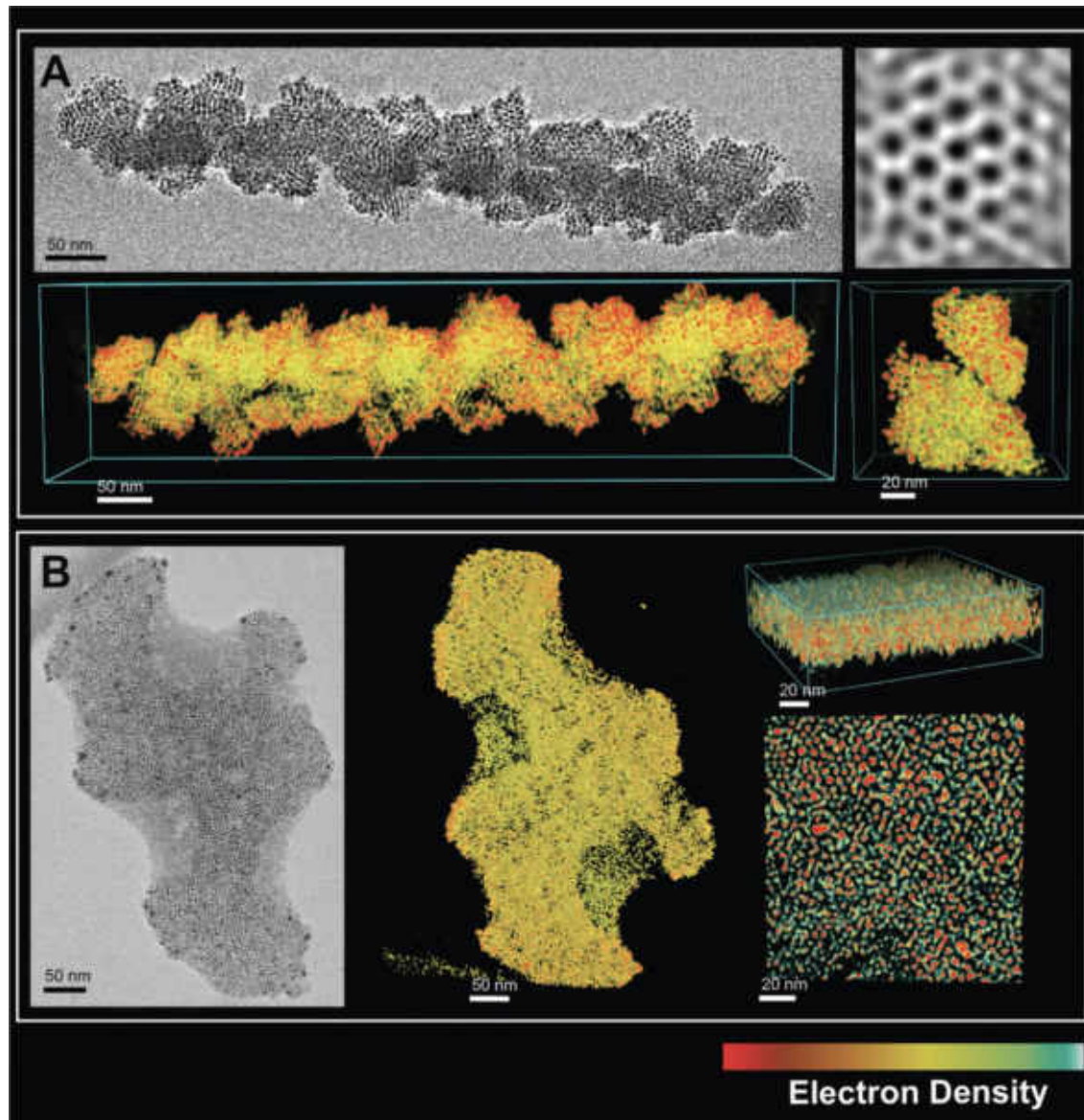


Structural details of Ag_{21}

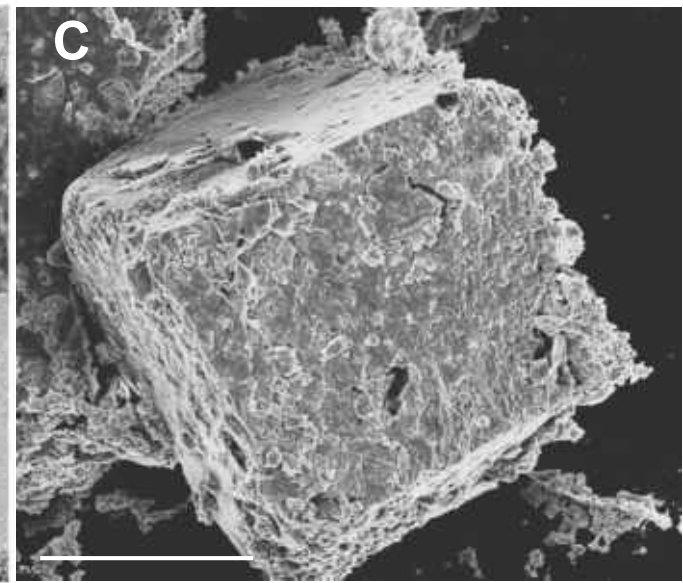
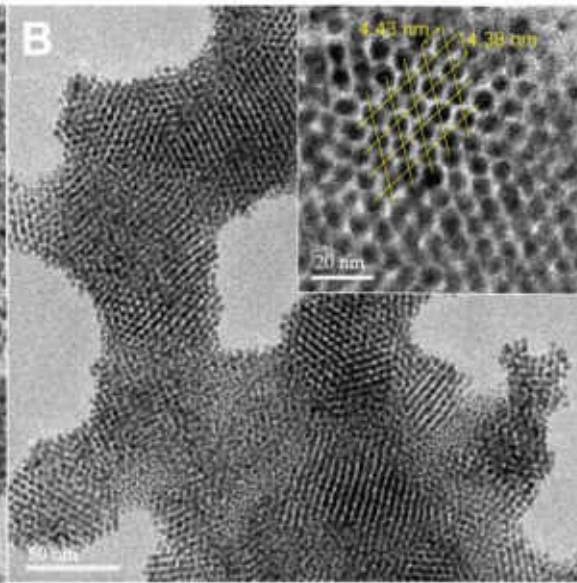
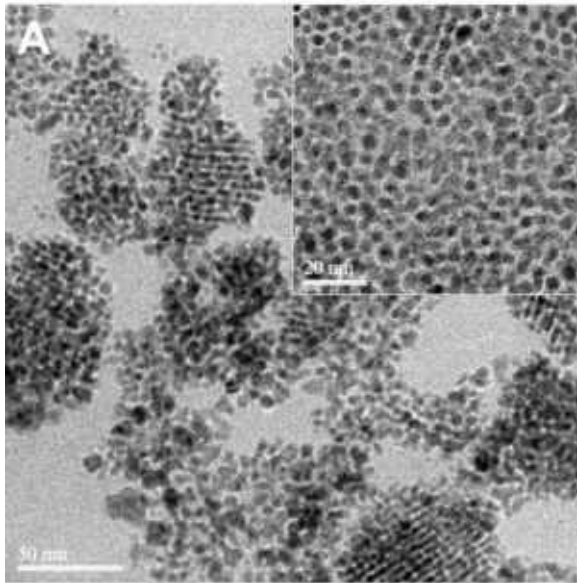
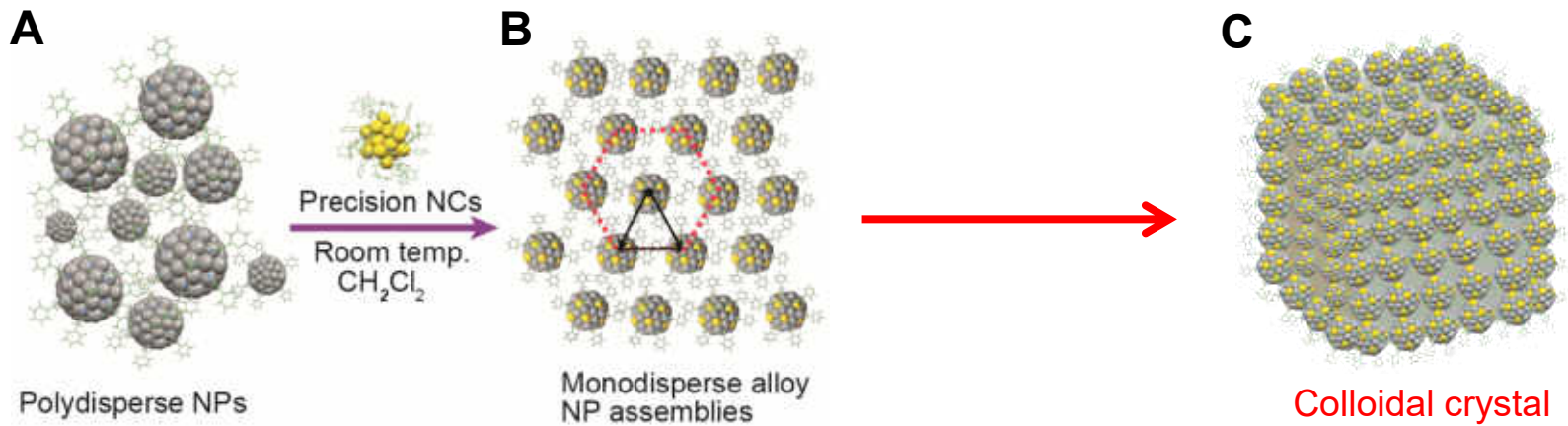




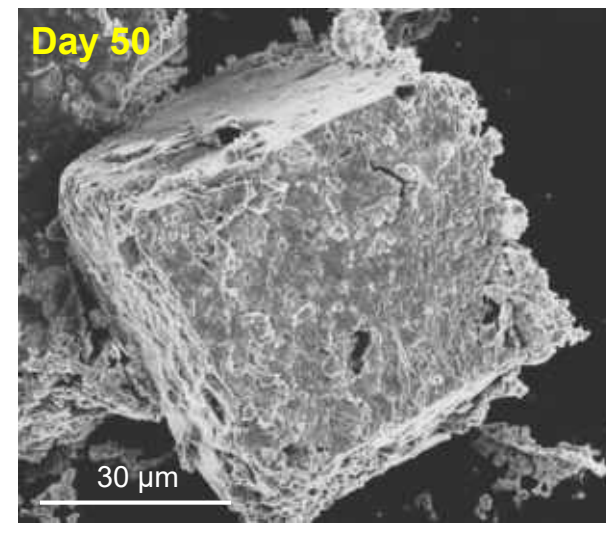
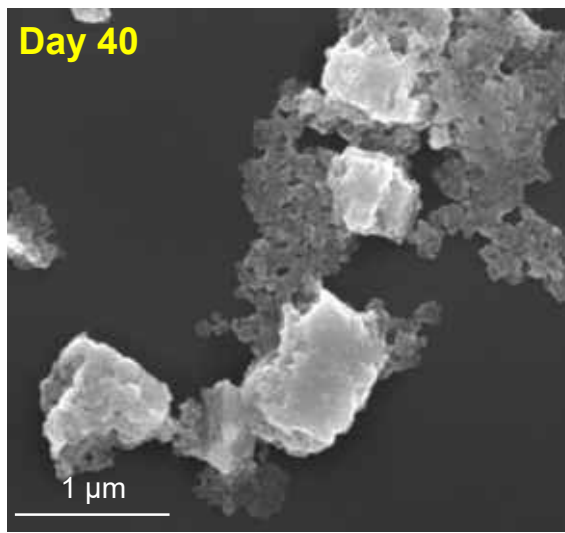
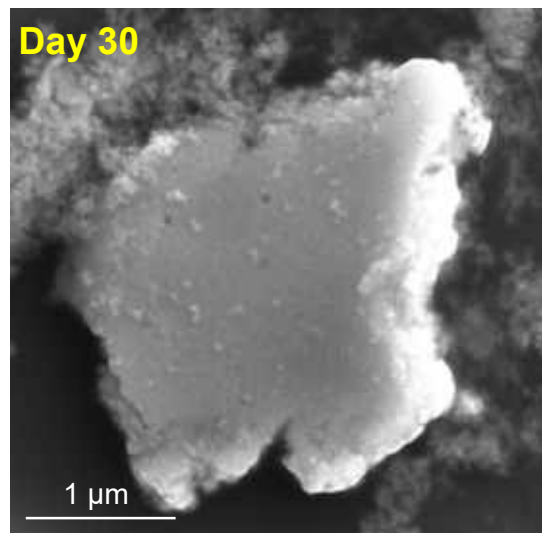
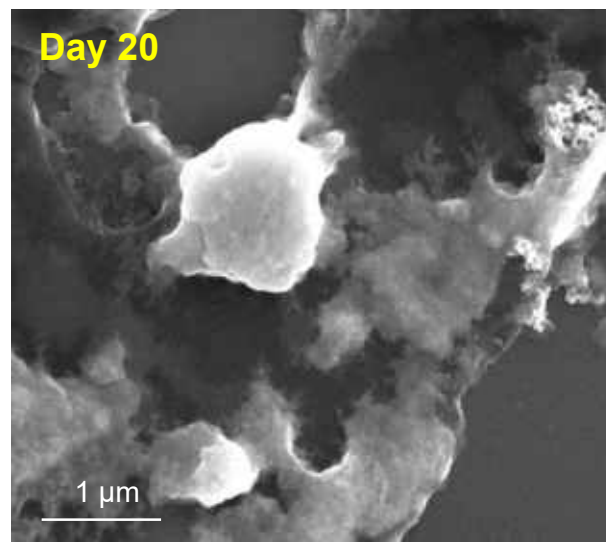
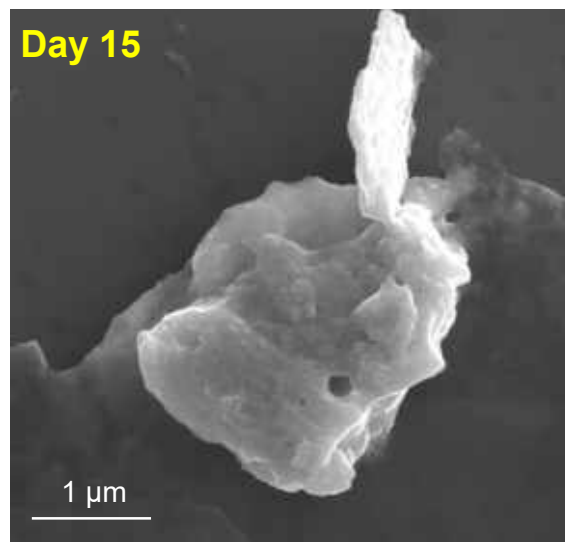
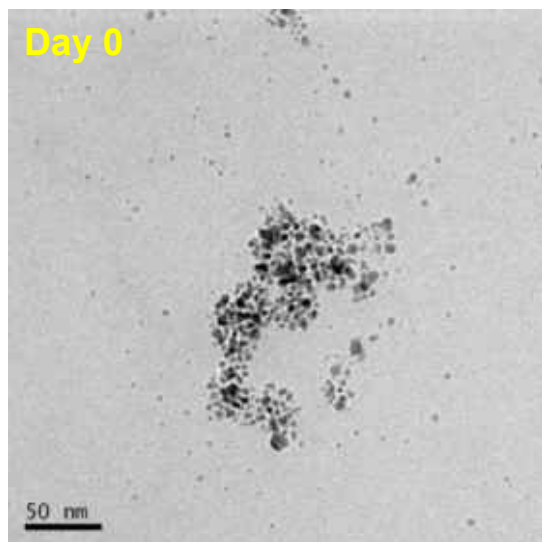




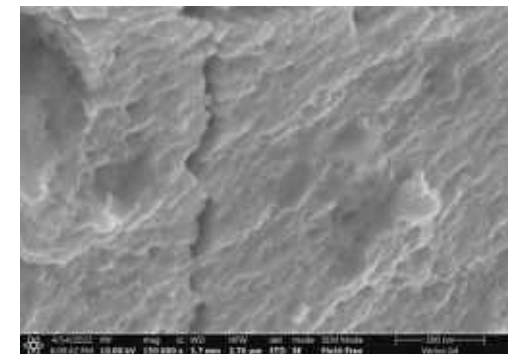
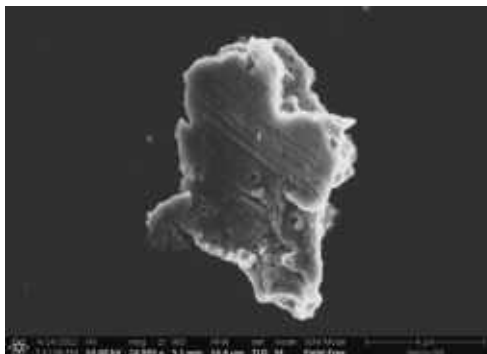
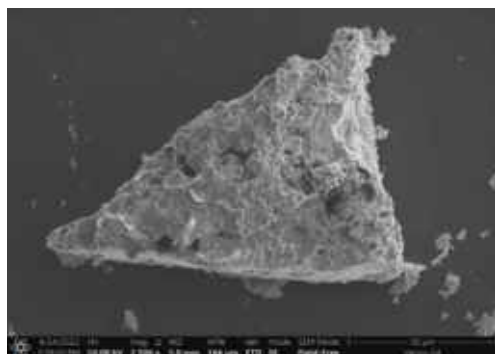
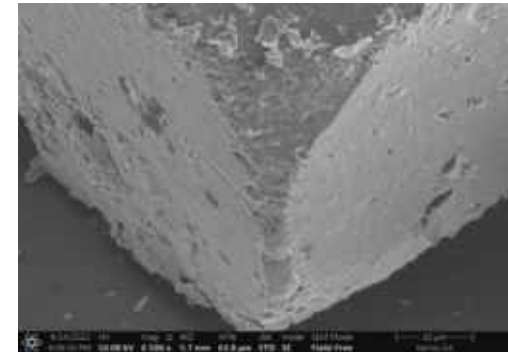
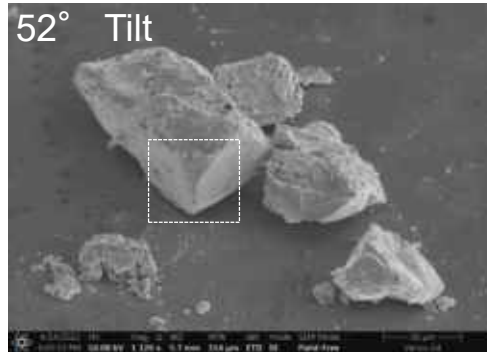
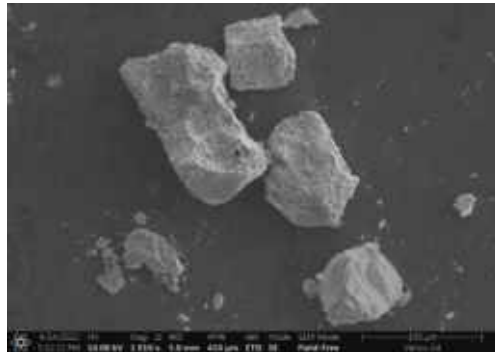
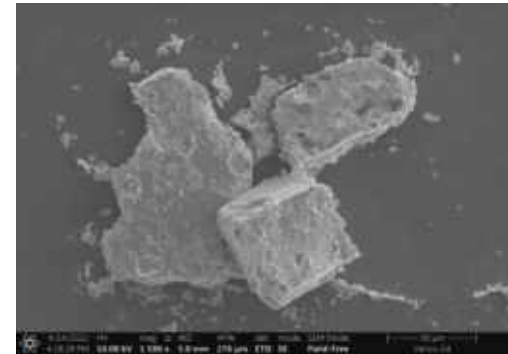
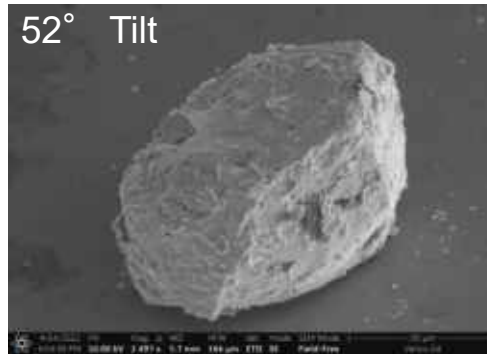
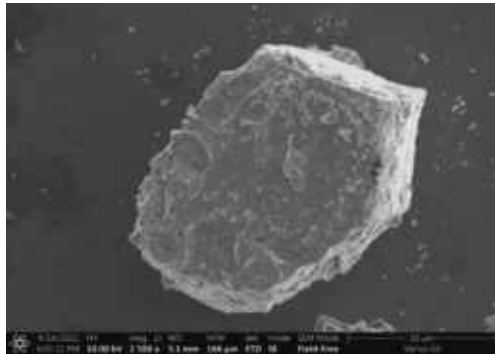
Crystallization of AgAu NP



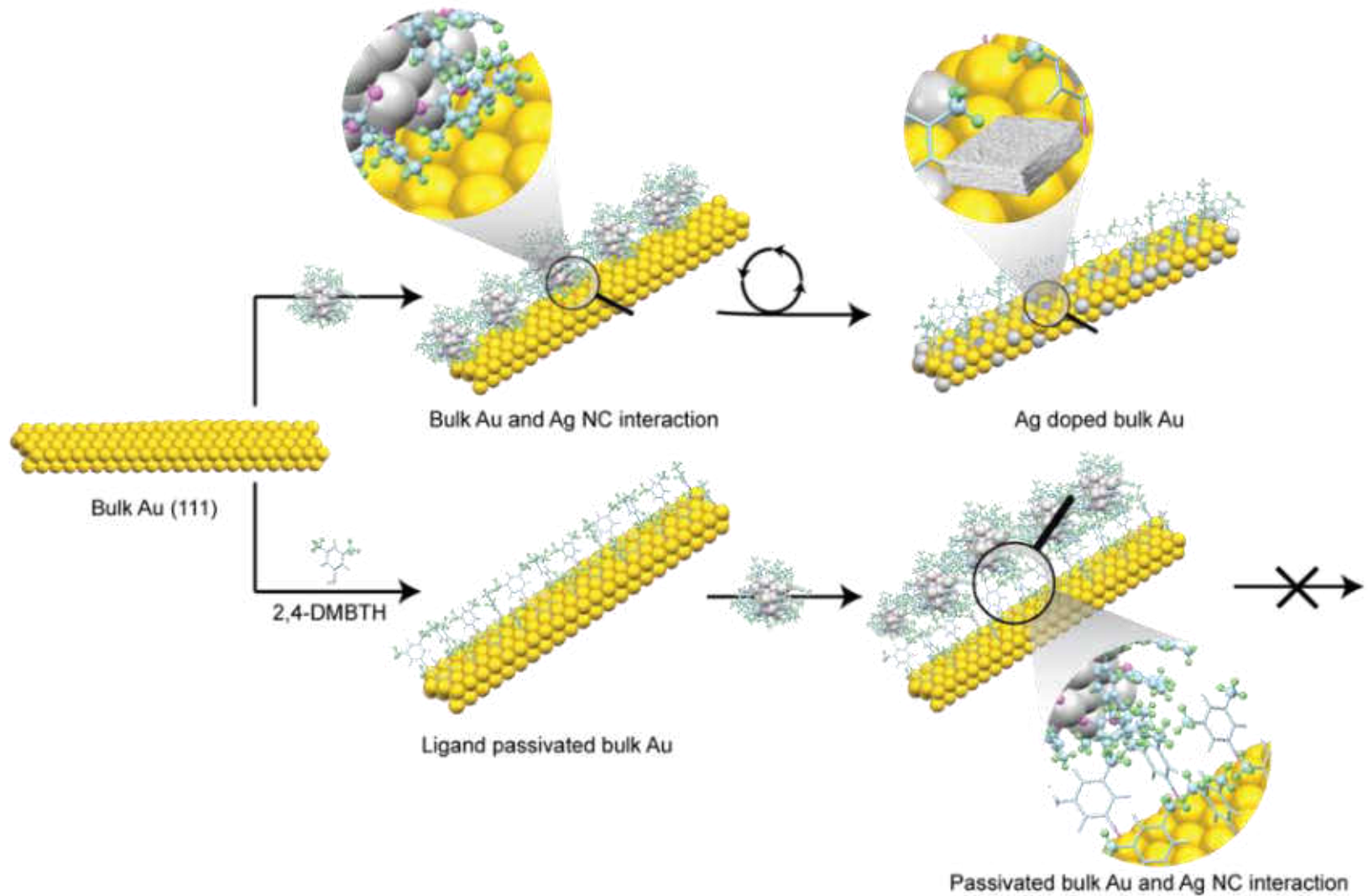
Transformation of colloidal particles in solution



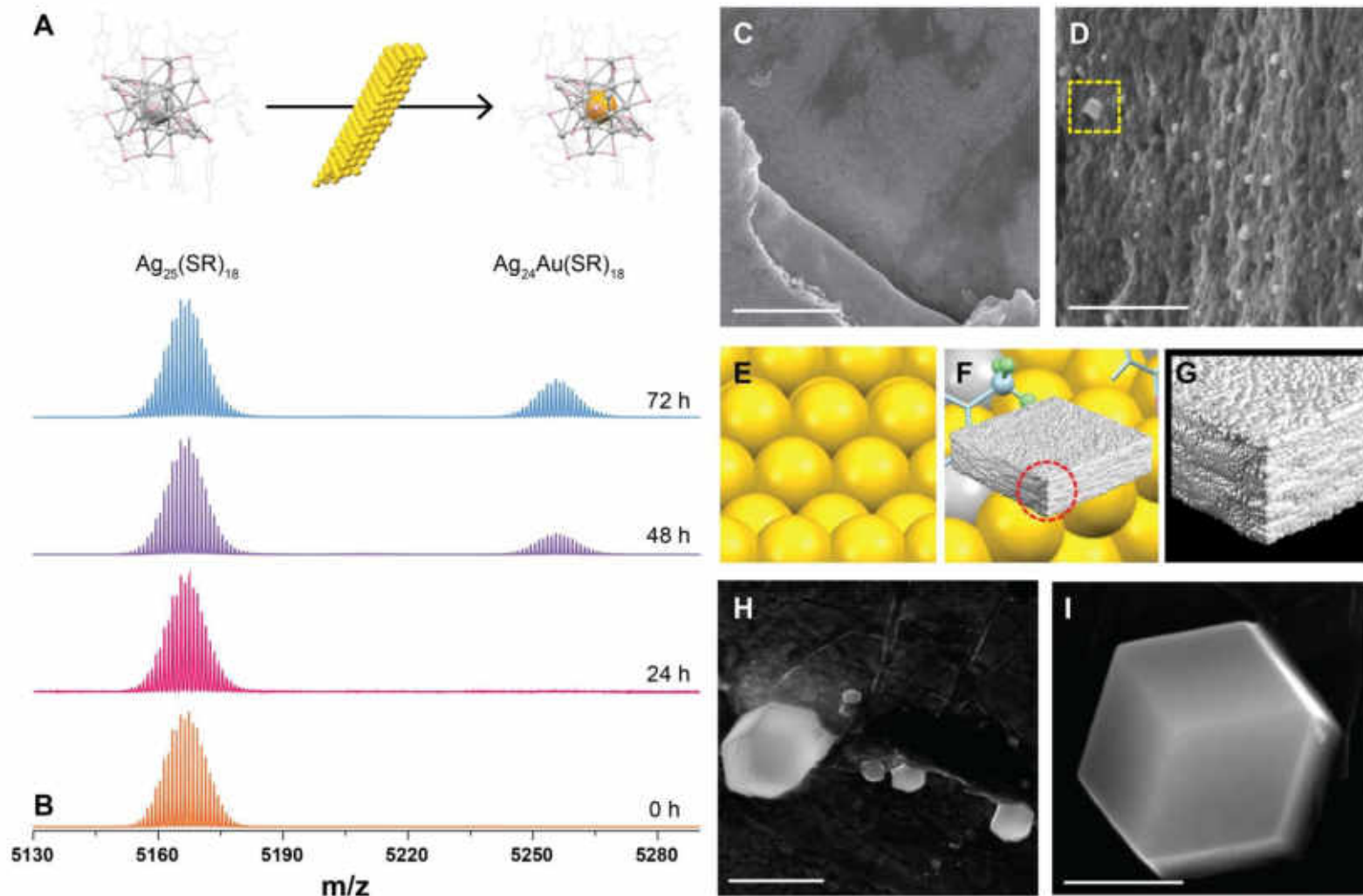
Crystals imaged after 50 days



Bulk Au—Ag NC reaction



Characterization of reaction products



Isotopic exchange

