Since 1959

Atomically Precise Clusters: New Advancements

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Department of Chemistry, Purdue University, February 1, 2024

CHEMICAL REVIEWS

Review

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

Indranath Chakraborty† and Thalappil Pradeep*

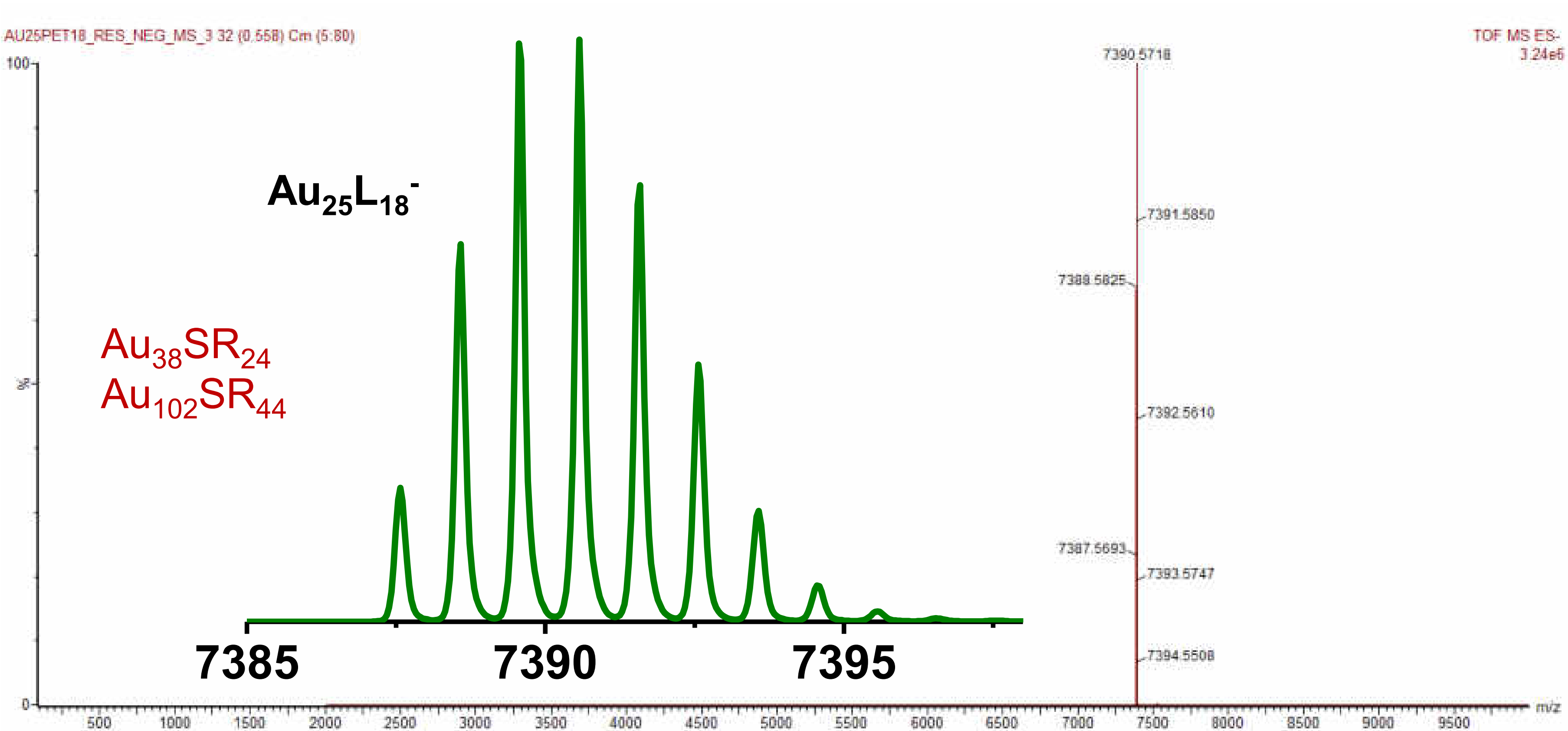
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Ⓢ *Supporting Information*

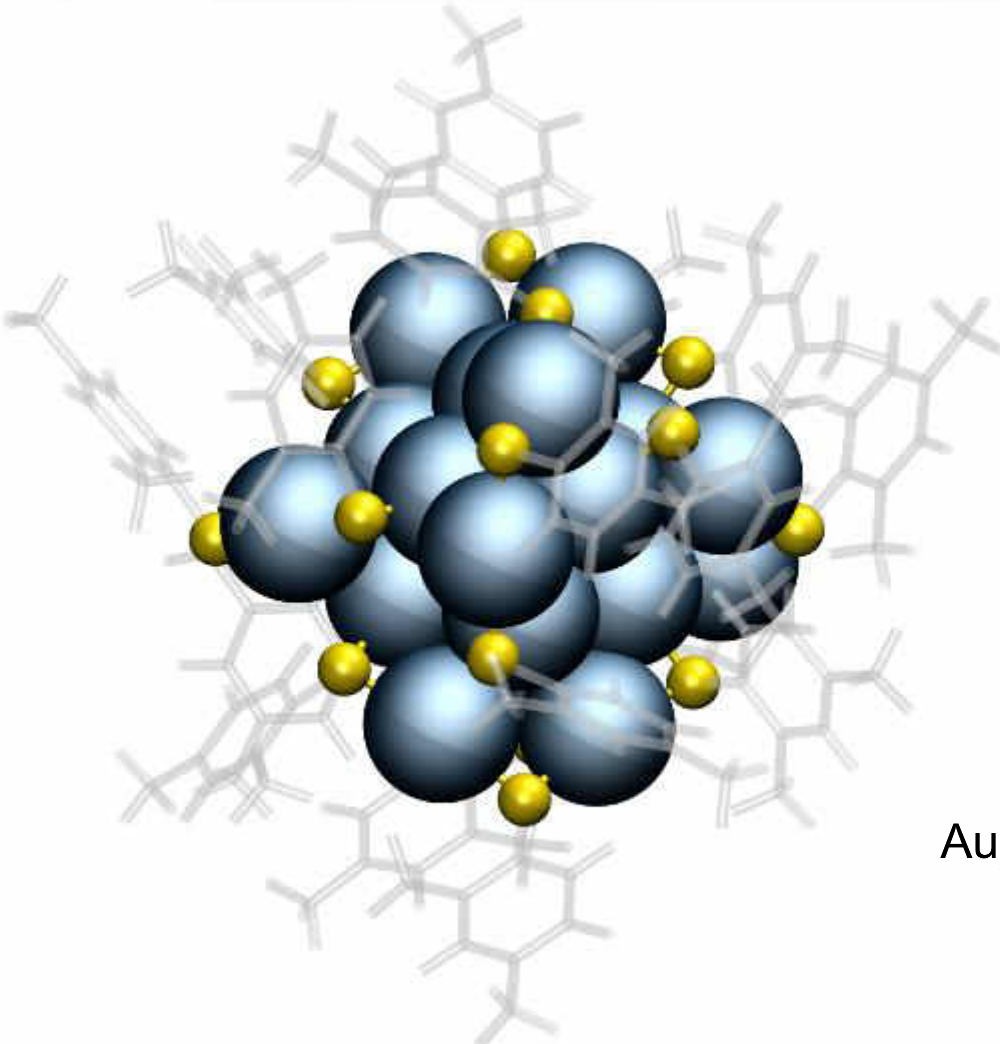
ABSTRACT: Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{102}(SR)_{44}$ as well as $Ag_{25}(SR)_{18}$, $Ag_{29}(S_2R)_{12}$, and $Ag_{44}(SR)_{30}$ (often with a few counterions to compensate charges) are known now. They can be made reproducibly with robust synthetic protocols, resulting in colored solutions, yielding powders or diffractable crystals. They are distinctly different from nanoparticles in their spectroscopic properties such as optical absorption and emission, showing well-defined features, just like molecules. They show isotopically resolved molecular ion peaks in mass spectra and provide diverse information when examined through multiple instrumental methods. Most important of these properties is luminescence, often in the visible−near-infrared window, useful in biological applications. Luminescence in the visible region, especially by clusters protected with proteins, with a large Stokes shift, has been used for various sensing applications, down to a few tens of molecules/ions, in air and water. Catalytic properties of clusters, especially oxidation of organic substrates, have been examined. Materials science of these systems presents numerous possibilities and is fast evolving. Computational insights have given reasons for their stability and unusual properties. The molecular nature of these materials is unequivocally manifested in a few recent studies such as intercluster reactions forming precise clusters. These systems manifest properties of the core, of the ligand shell, as well as that of the integrated system. They are better described as protected molecules or *aspicules*, where *aspis* means shield and *cules* refers to molecules, implying that they are "shielded molecules". In order to understand their diverse properties, a nomenclature has been introduced with which it is possible to draw their structures with positional labels on paper, with some training. Research in this area is captured here, based on the publications available up to December 2016.

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

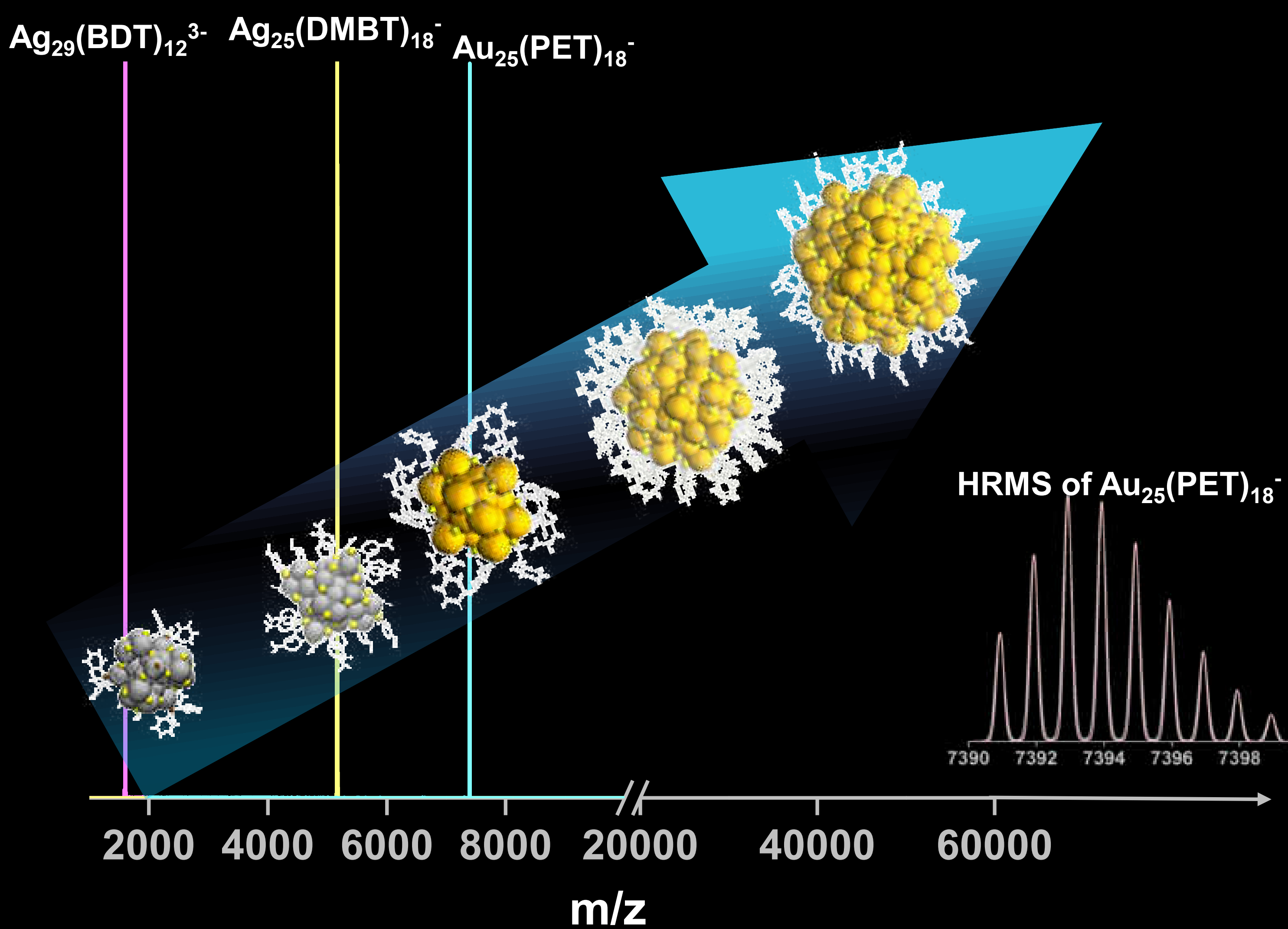
Molecular formula, Molecular weight



New molecules

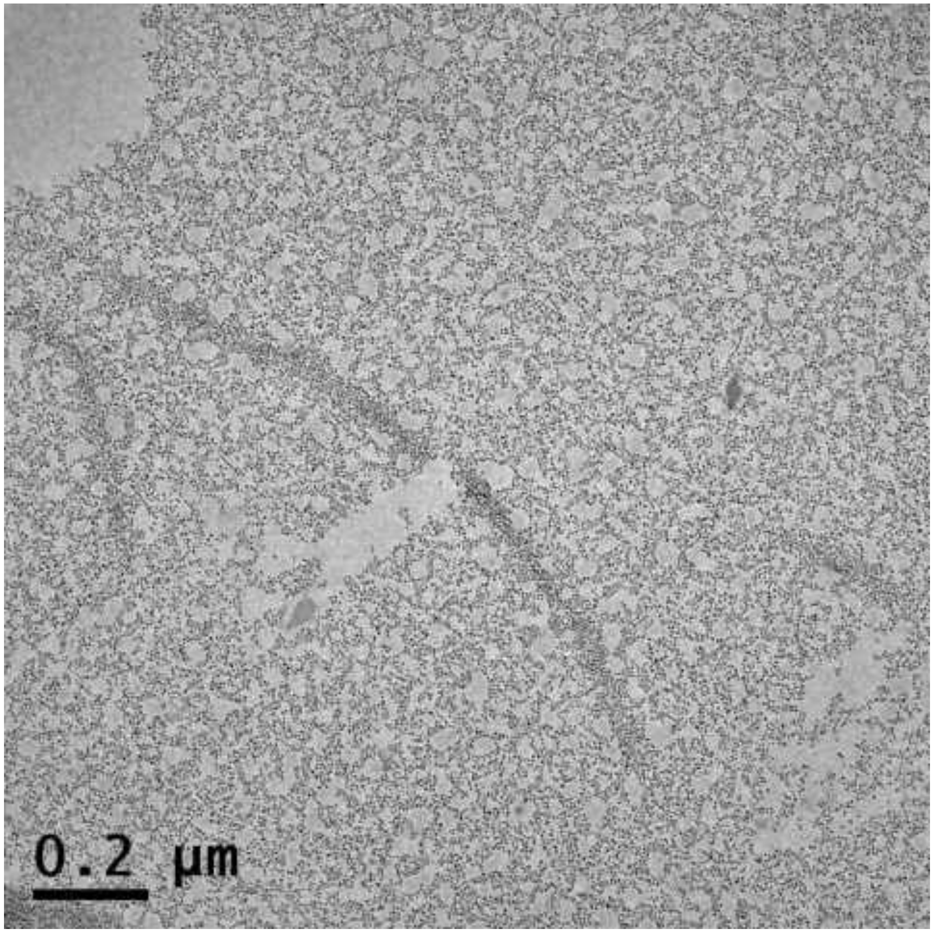


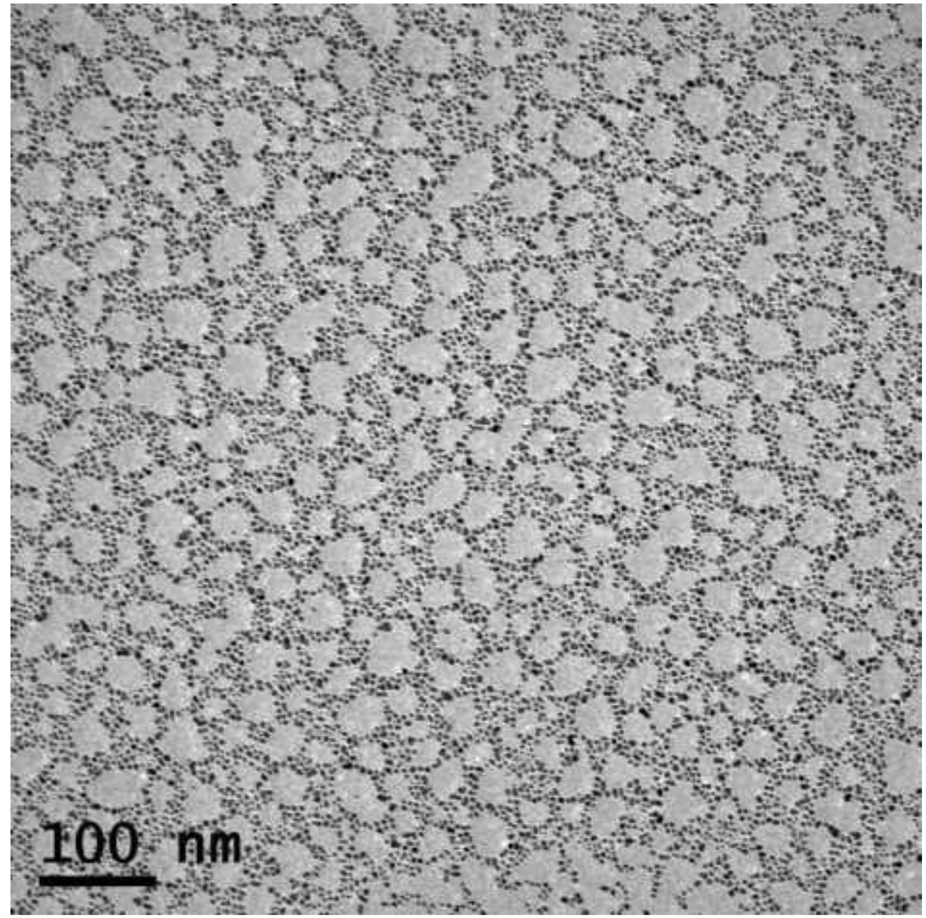
$Au_{25}, Ag_{25}, Ag_{29}$



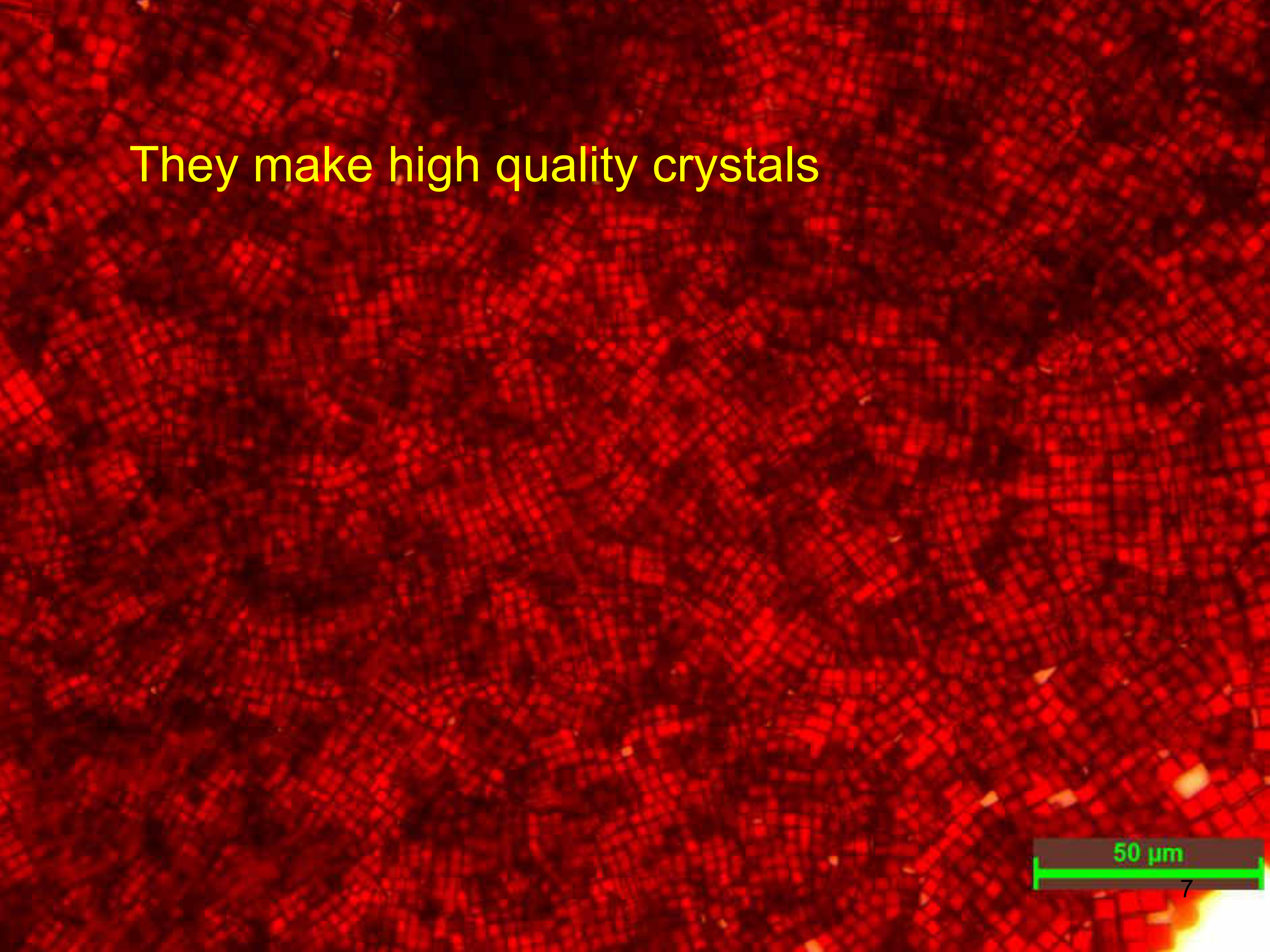
$Ag_{29}(BDT)_{12}^{3-}$
$Ag_{25}(DMBT)_{18}^{-}$
$Au_{25}(PET)_{18}^{-}$
HRMS of $Au_{25}(PET)_{18}^{-}$
7390
7392
7394
7396
7398
2000
4000
6000
8000
20000
40000
60000
m/z

TEM images of Au_{25} and Au_{144}

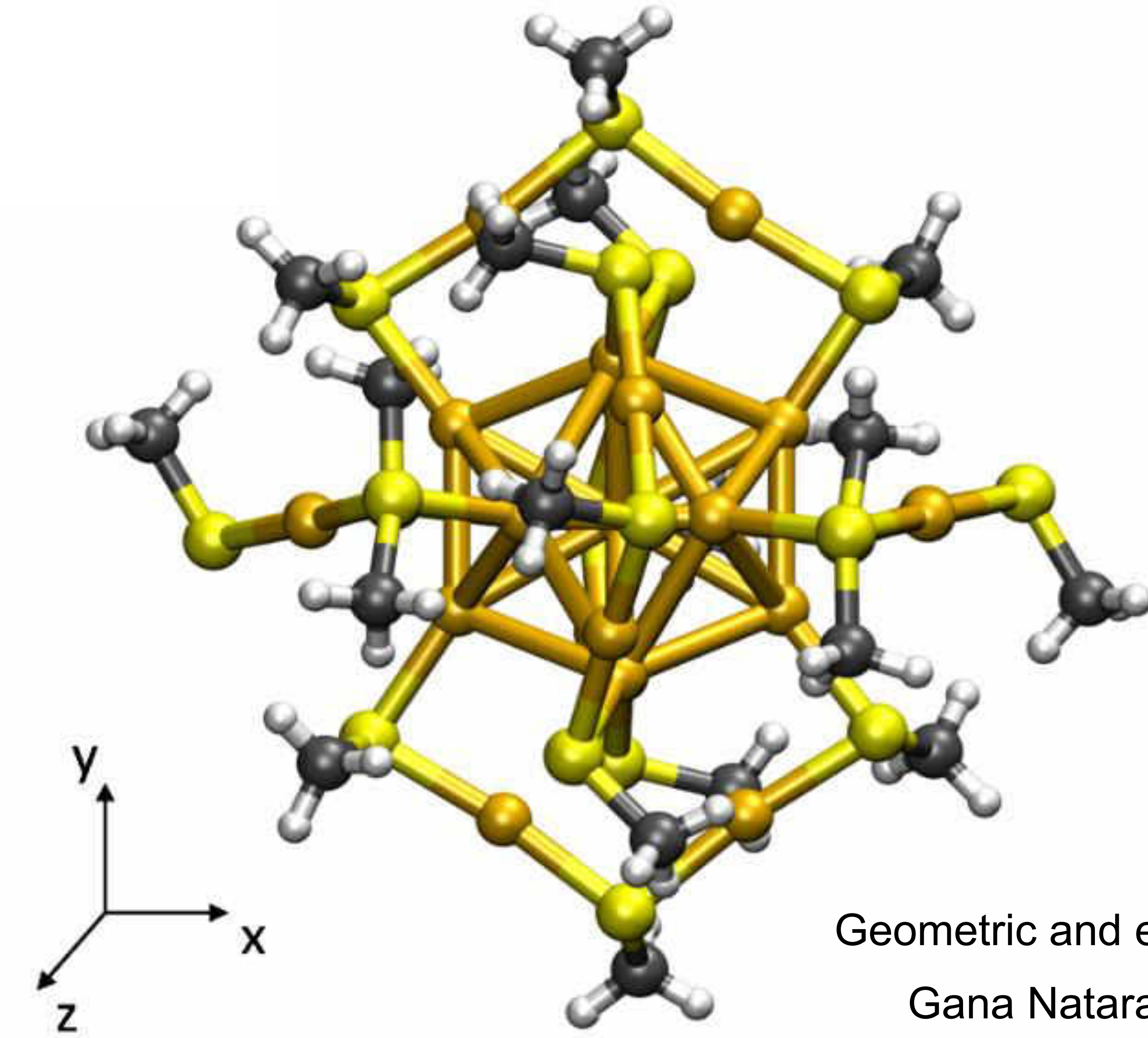




They make high quality crystals



Molecular structure



Molecular materials

ACCOUNTS of chemical research

Article

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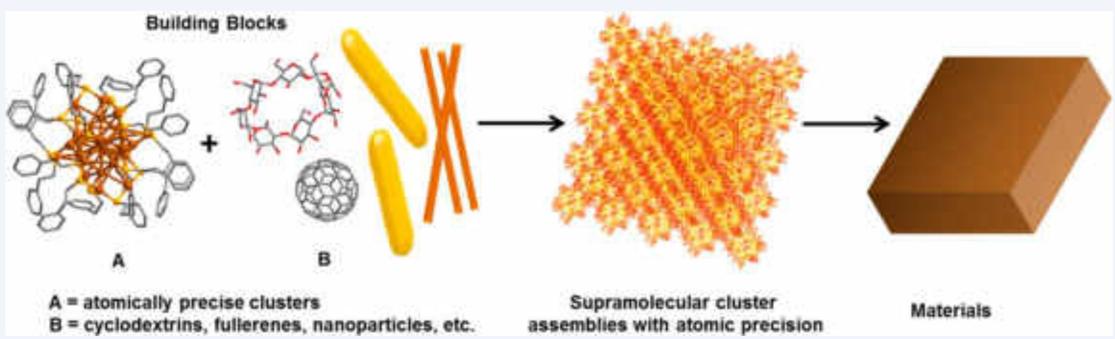
Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

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

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



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	256.32×10^{-6} K^{-1}
Thermal Conductivity, 25°C	0.608 W/m.K

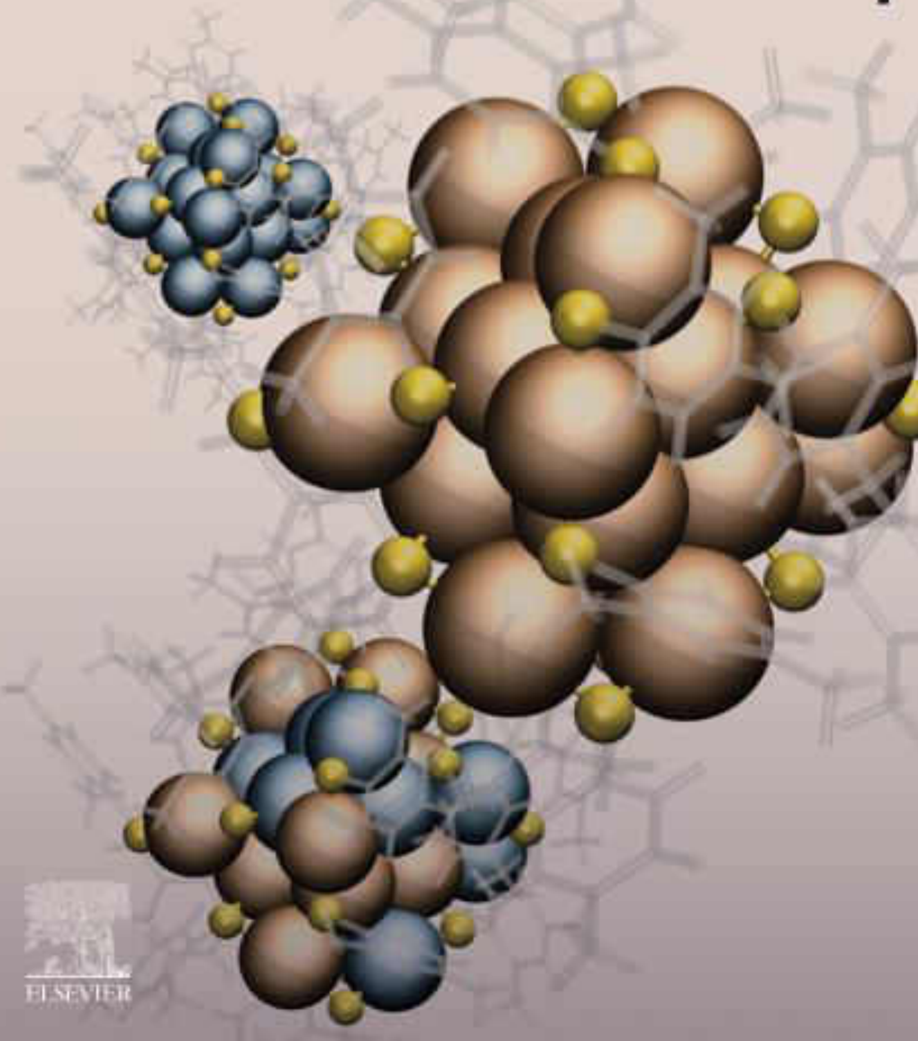
Molecular formula
Molecular weight
Molecular structure
Molecular absorption and emission
Molecular reactions
Molecular assembly
Molecular co-crystals

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
pubs.acs.org/JACS

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

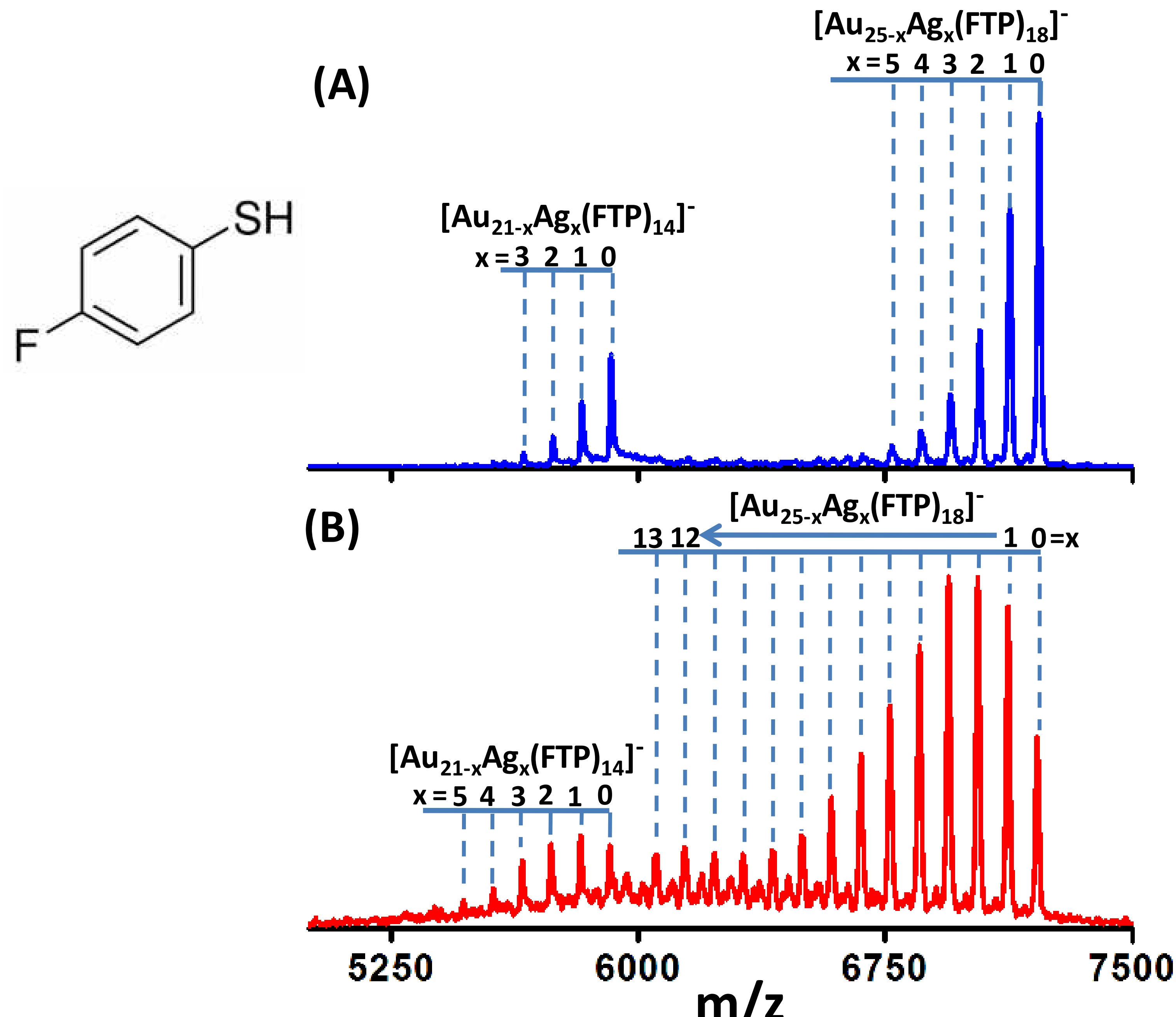
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep[*]

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

Supporting Information

A + B → C + D

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



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)

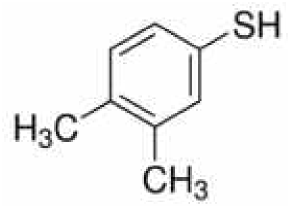
	Locations of Au in $Au_xAg_{44-x}(SR)_{30}$			
Location of Ag in $Au_{25-x}Ag_x(SR)_{18}$	**I**	**D_{cv}**	**D_{cf}**	**S**
C	-0.015	+0.564	+0.388	+0.226
I	-0.486	+0.093	-0.083	-0.245
S	-0.276	+0.303	+0.127	-0.035

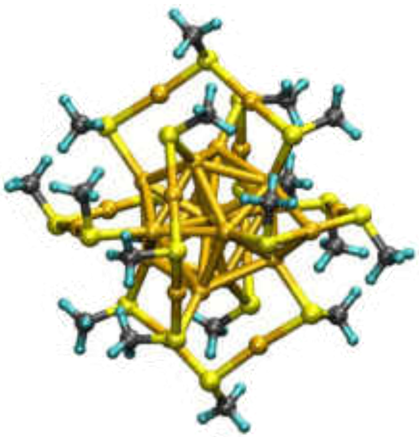
Ag_{25}-Au_{25} experiments

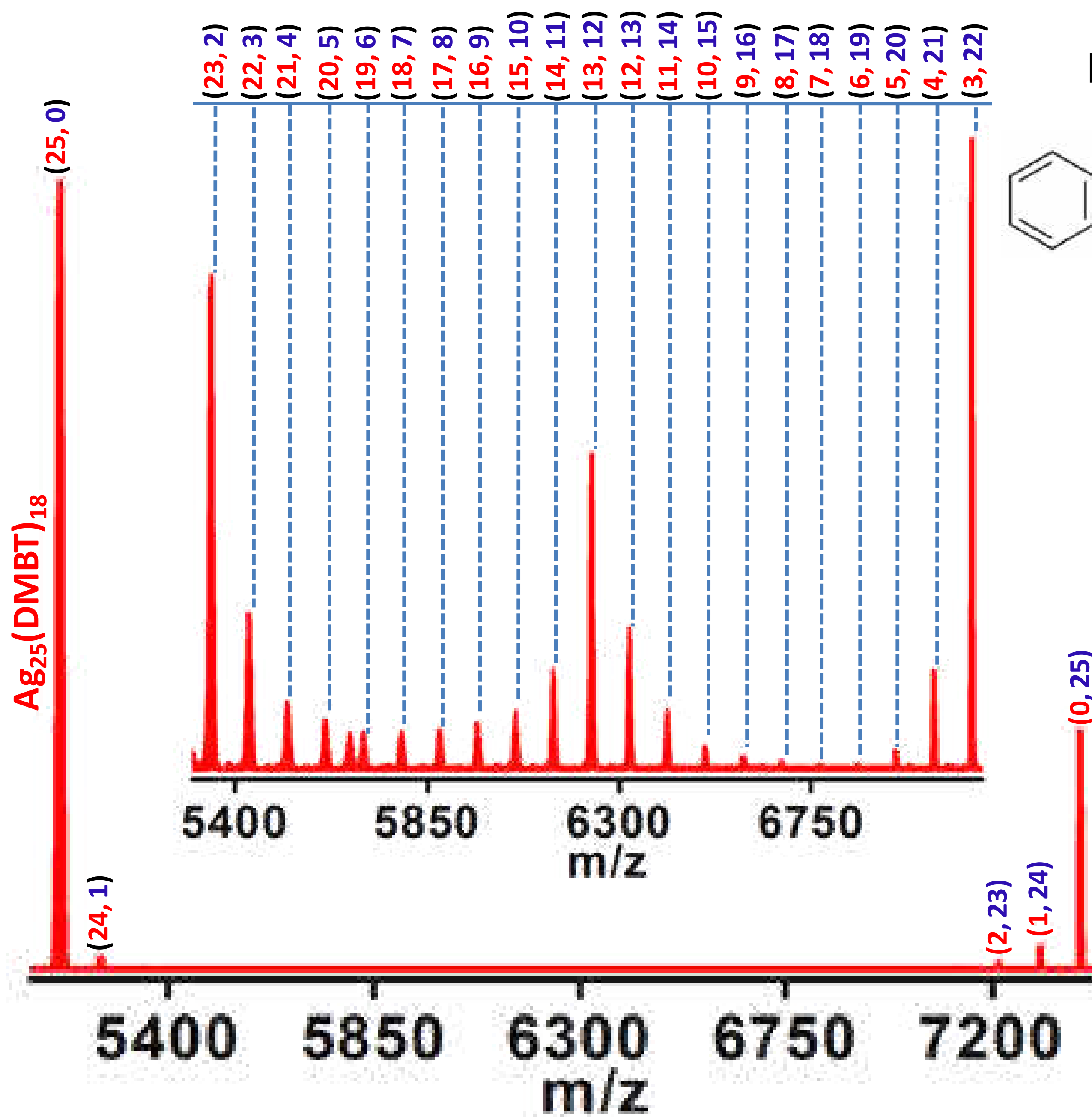
K. R. Krishnadas et al. *Nature Commun.* 2016

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

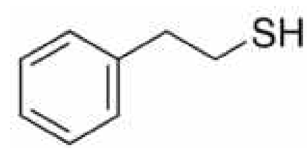
DMBT



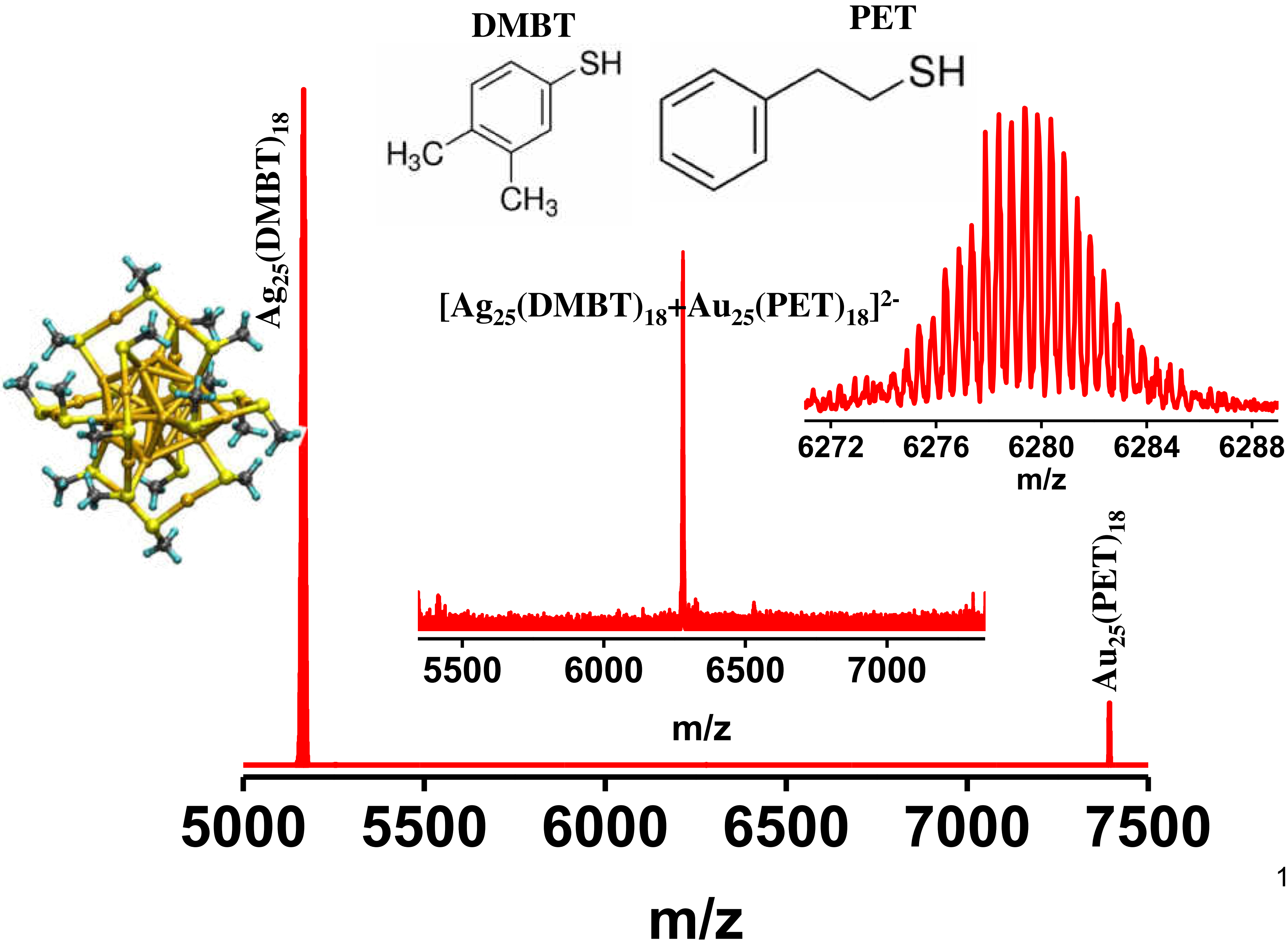




PET

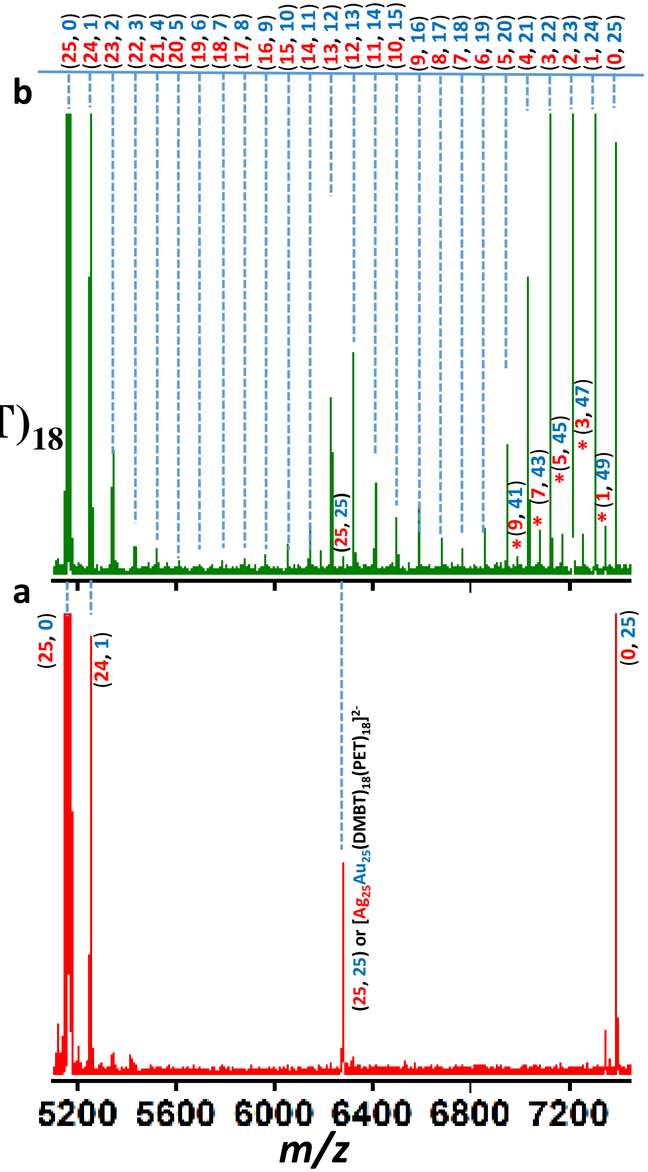


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

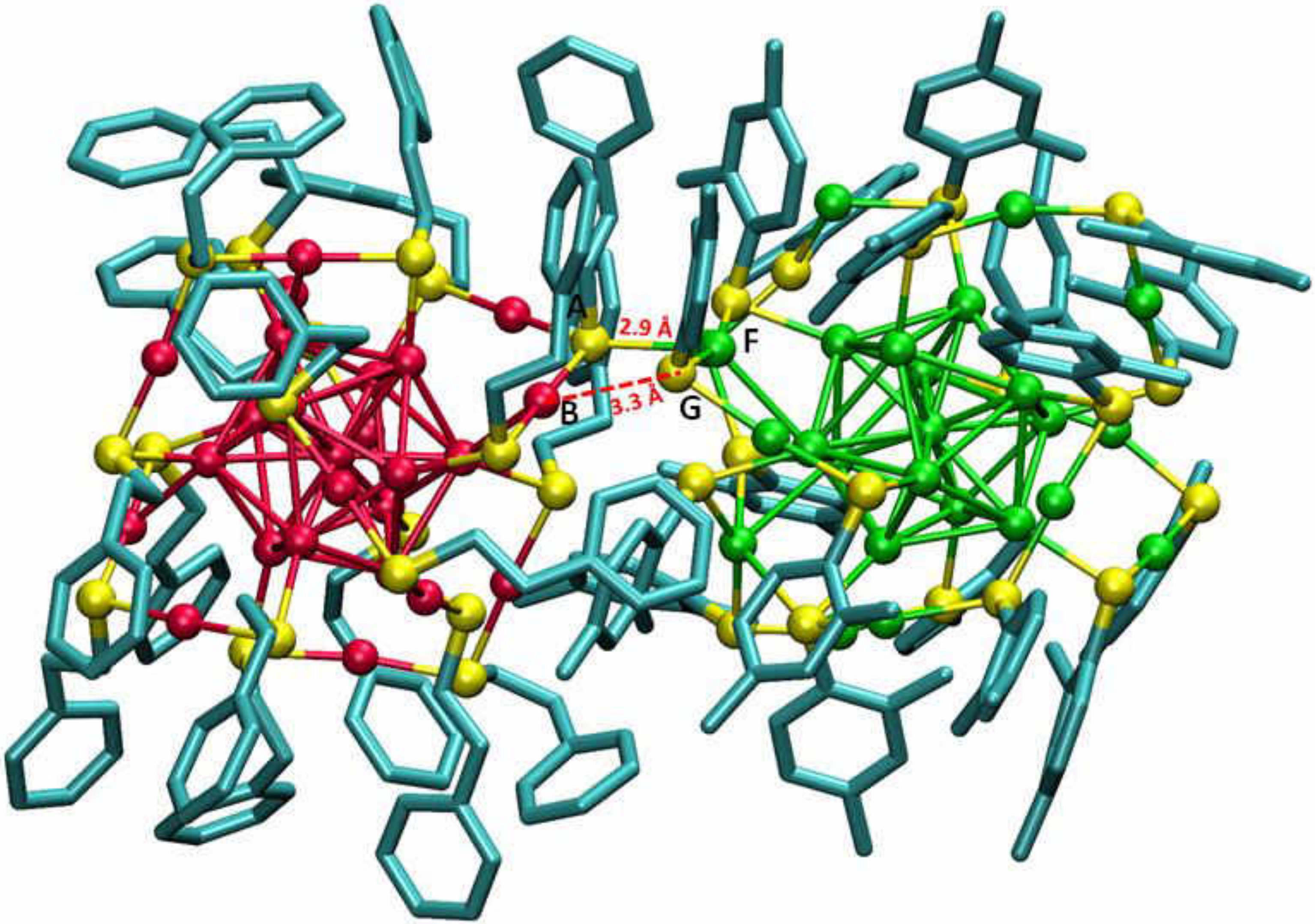
$Ag_{25}(DMBT)_{18}:Au_{25}(PET)_{18}$
0.3:1.0

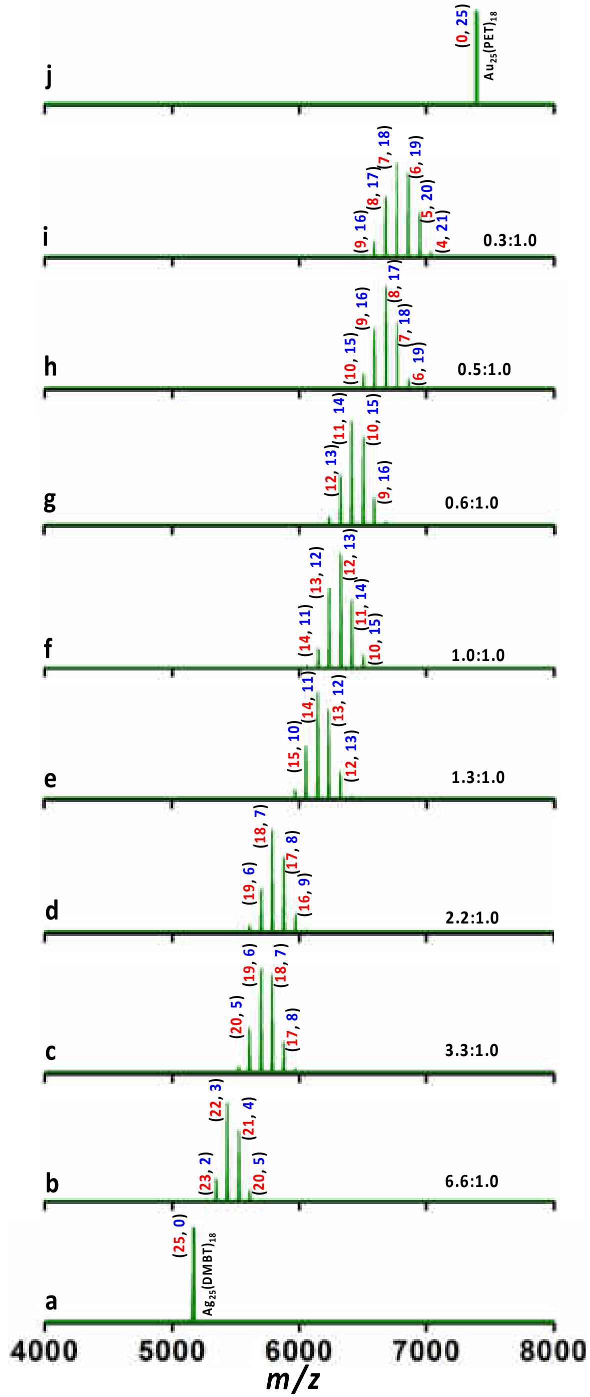


within 5 min

within 2 min

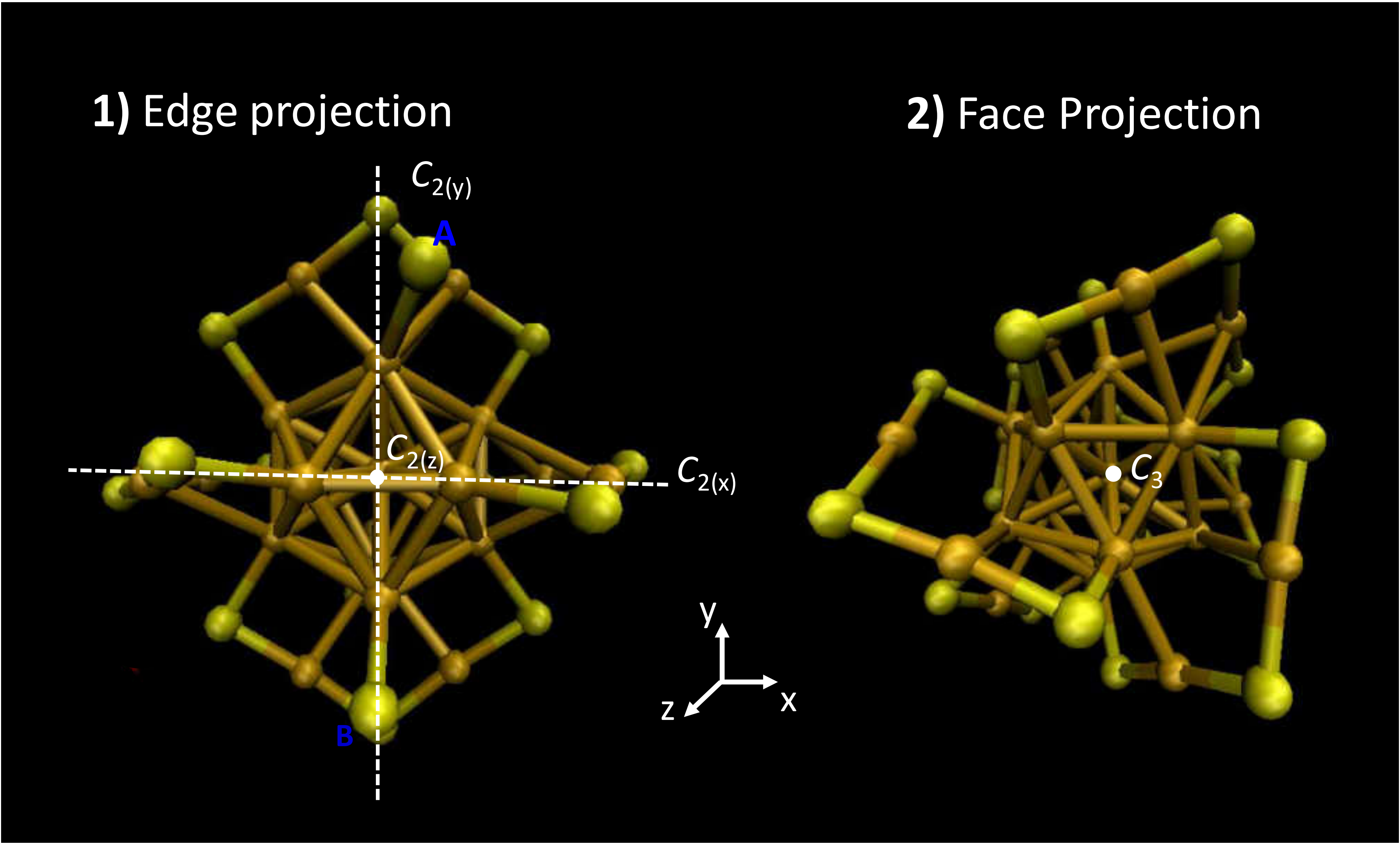
Optimized structure of $[Ag_{25}Au_{25}(DMBT)_{18}(PET)_{18}]^{2-}$

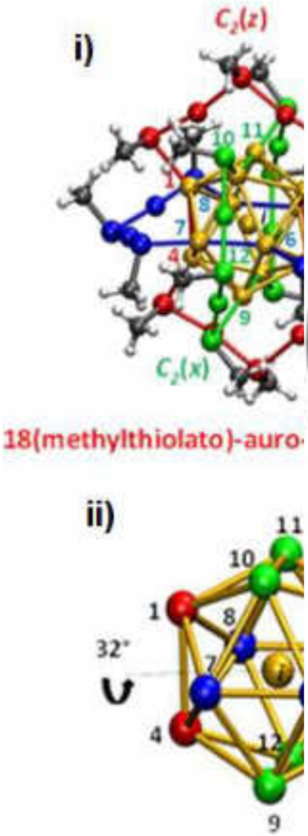


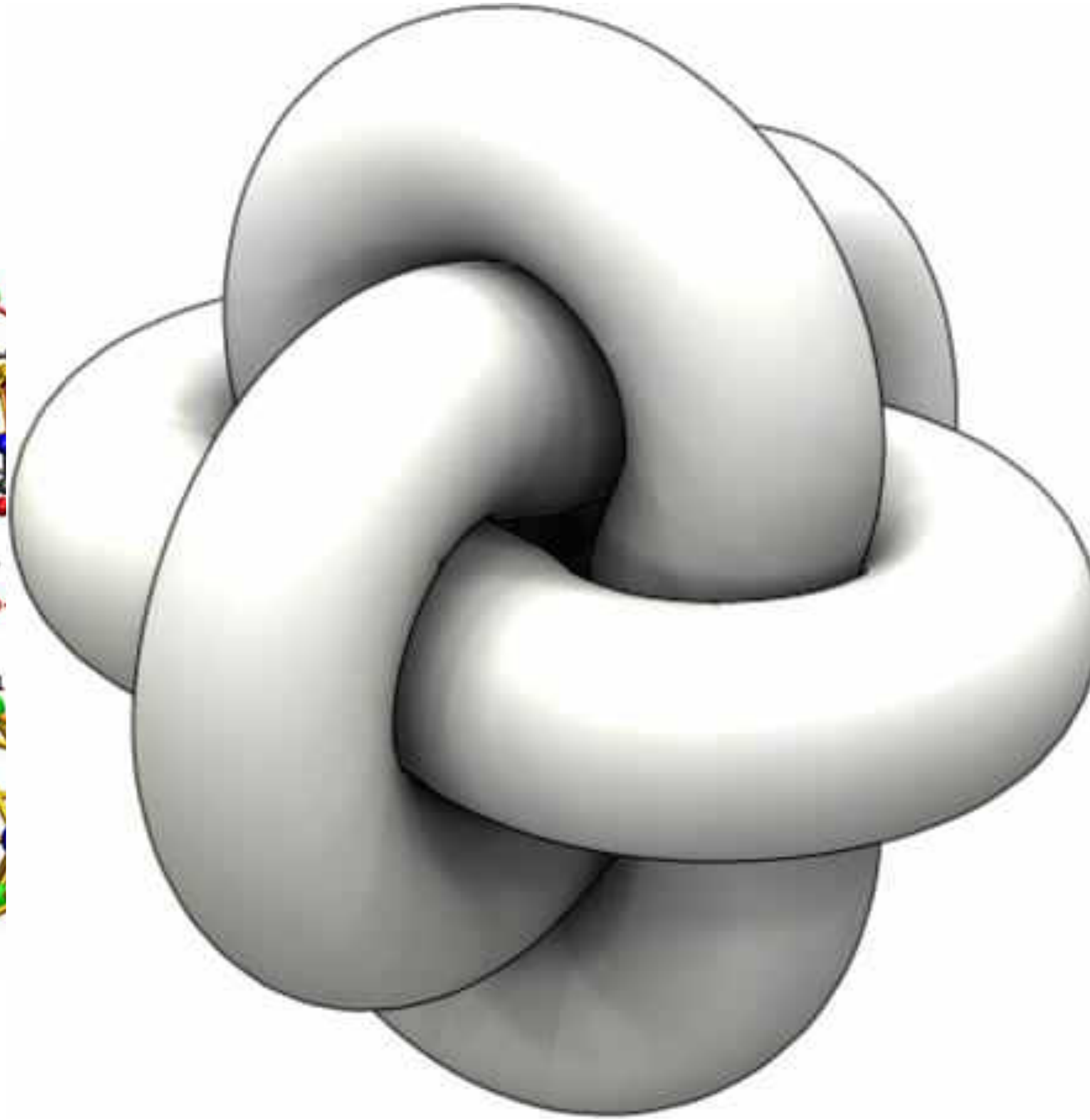

j
(0, 25)
Au25(PET)18
i
(9, 16)
(8, 17)
(7, 18)
(6, 19)
(5, 20)
(4, 21)
0.3:1.0
h
(10, 15)
(9, 16)
(8, 17)
(7, 18)
(6, 19)
0.5:1.0
g
(12, 13)
(11, 14)
(10, 15)
(9, 16)
0.6:1.0
f
(14, 11)
(13, 12)
(12, 13)
(11, 14)
(10, 15)
1.0:1.0
e
(15, 10)
(14, 11)
(13, 12)
(12, 13)
1.3:1.0
d
(19, 6)
(18, 7)
(17, 8)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

How do we comprehend this?

Nomenclature


1) Edge projection
2) Face Projection
$C_{2(y)}$
A
$C_{2(z)}$
$C_{2(x)}$
B
y
x
z
C_3





Gana Natarajan et. al. *JPC C* 2015

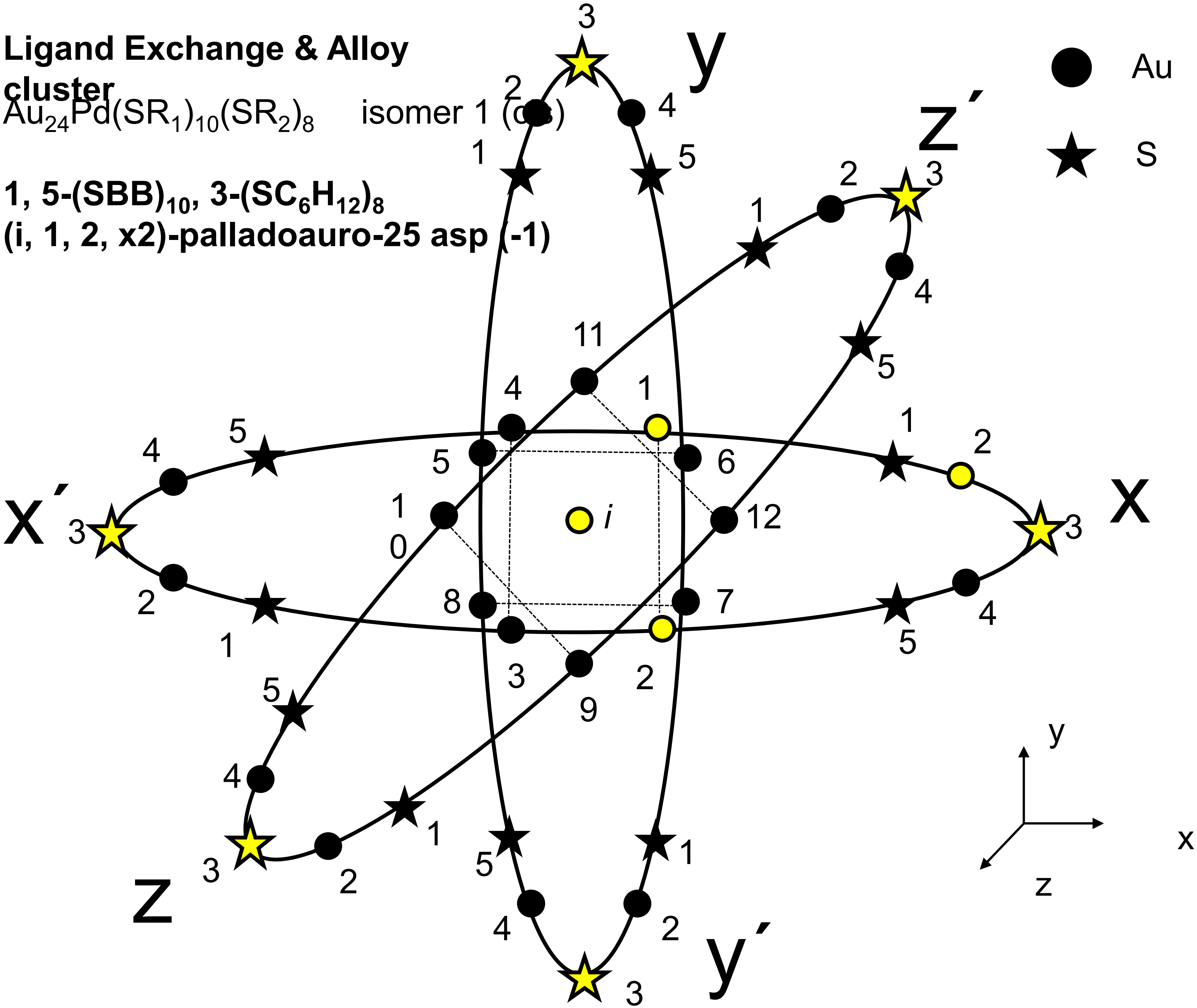
Aspicules

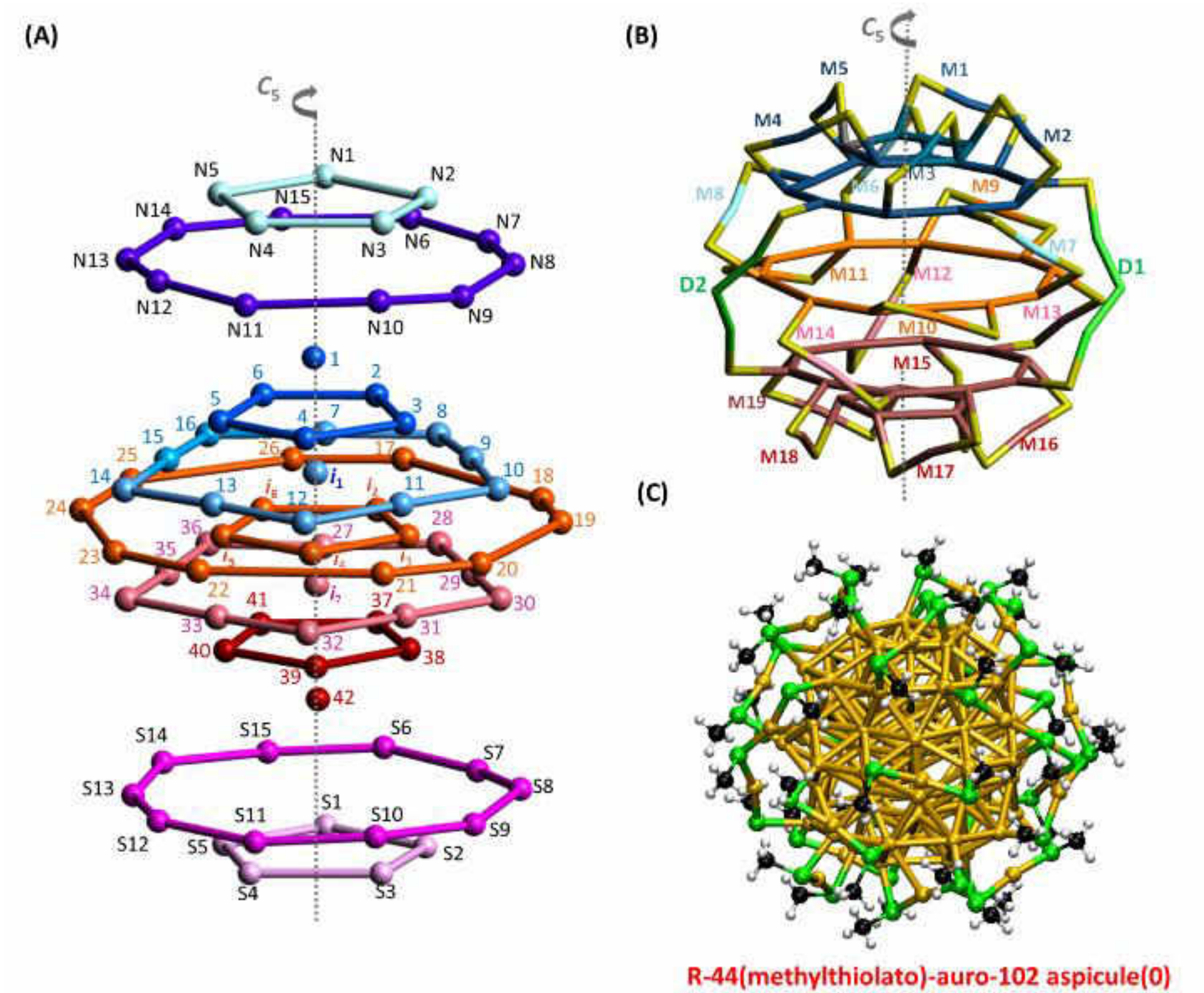
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule(1-)

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-$(SMe)_{44}$-auro-102 aspicule**(**0**)** and L-$(SMe)_{44}$-auro-102 aspicule**(**0**)** [28]

ACCOUNTS
of chemical research

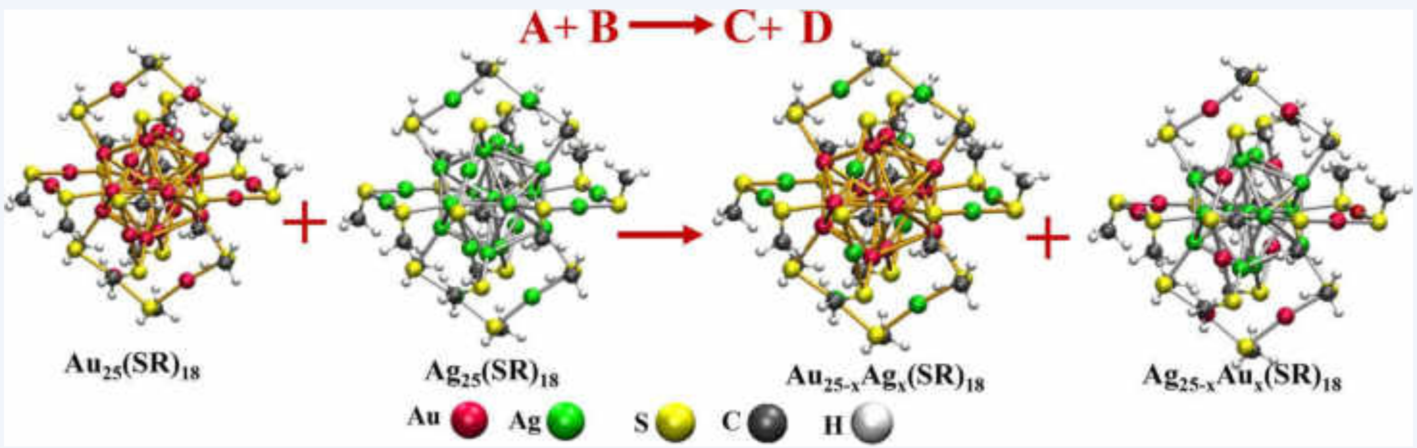
Article

pubs.acs.org/accounts

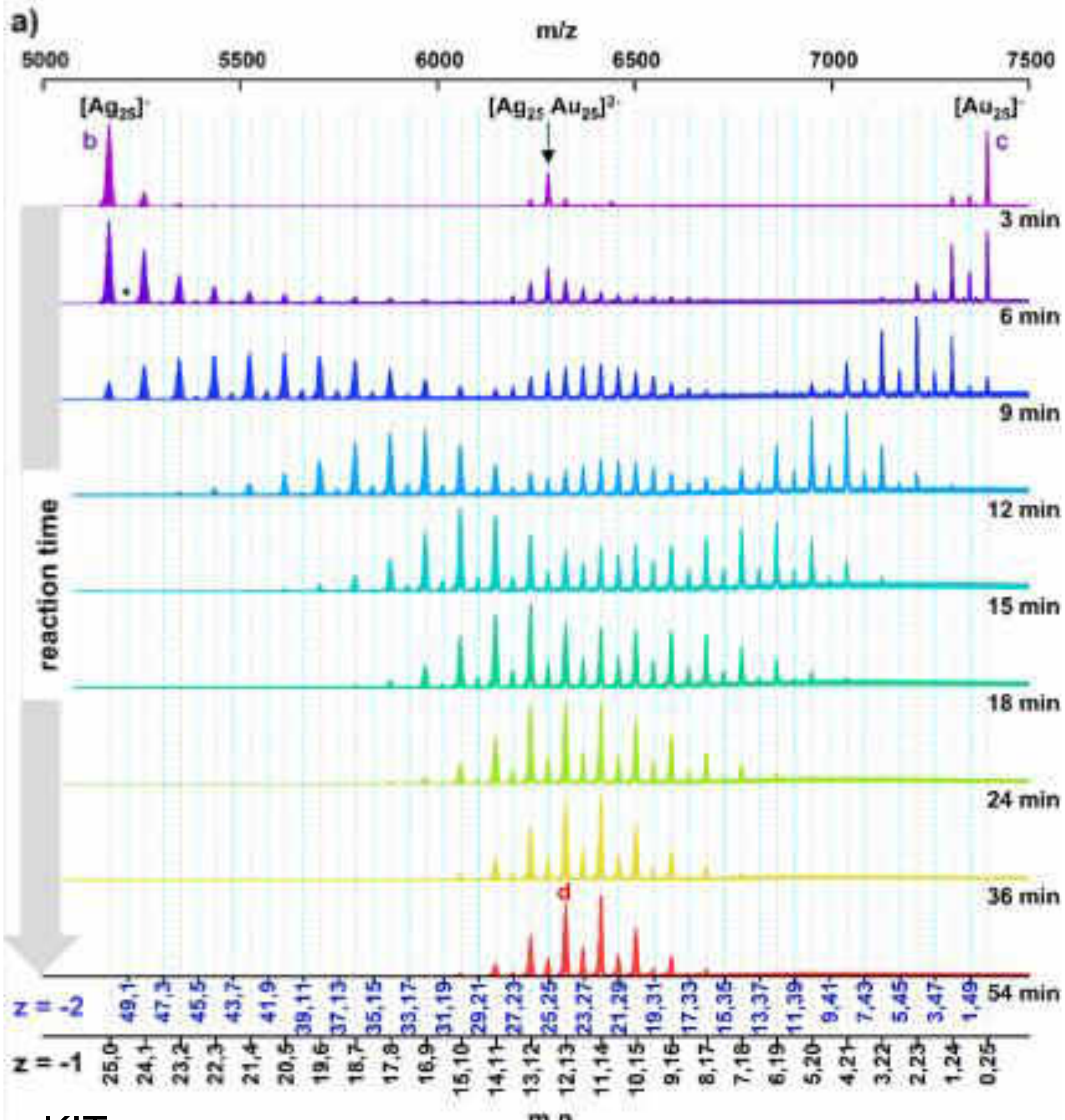
Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

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

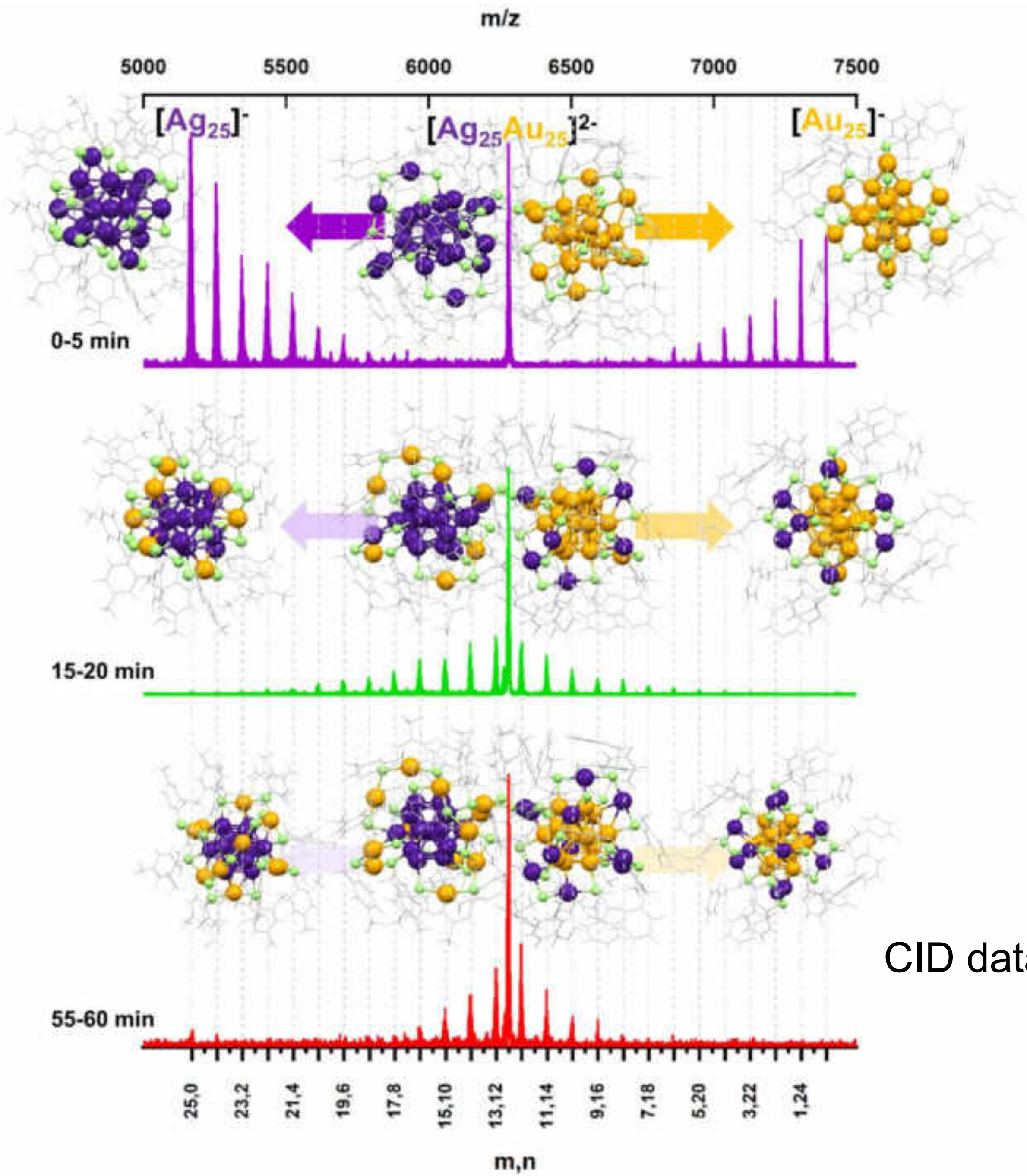


CONSPECTUS: Nanoparticles exhibit a rich variety in terms of structure, composition, and properties. However, reactions between them remain largely unexplored. In this *Account*, we discuss an emerging aspect of nanomaterials chemistry, namely, interparticle reactions in solution phase, similar to reactions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



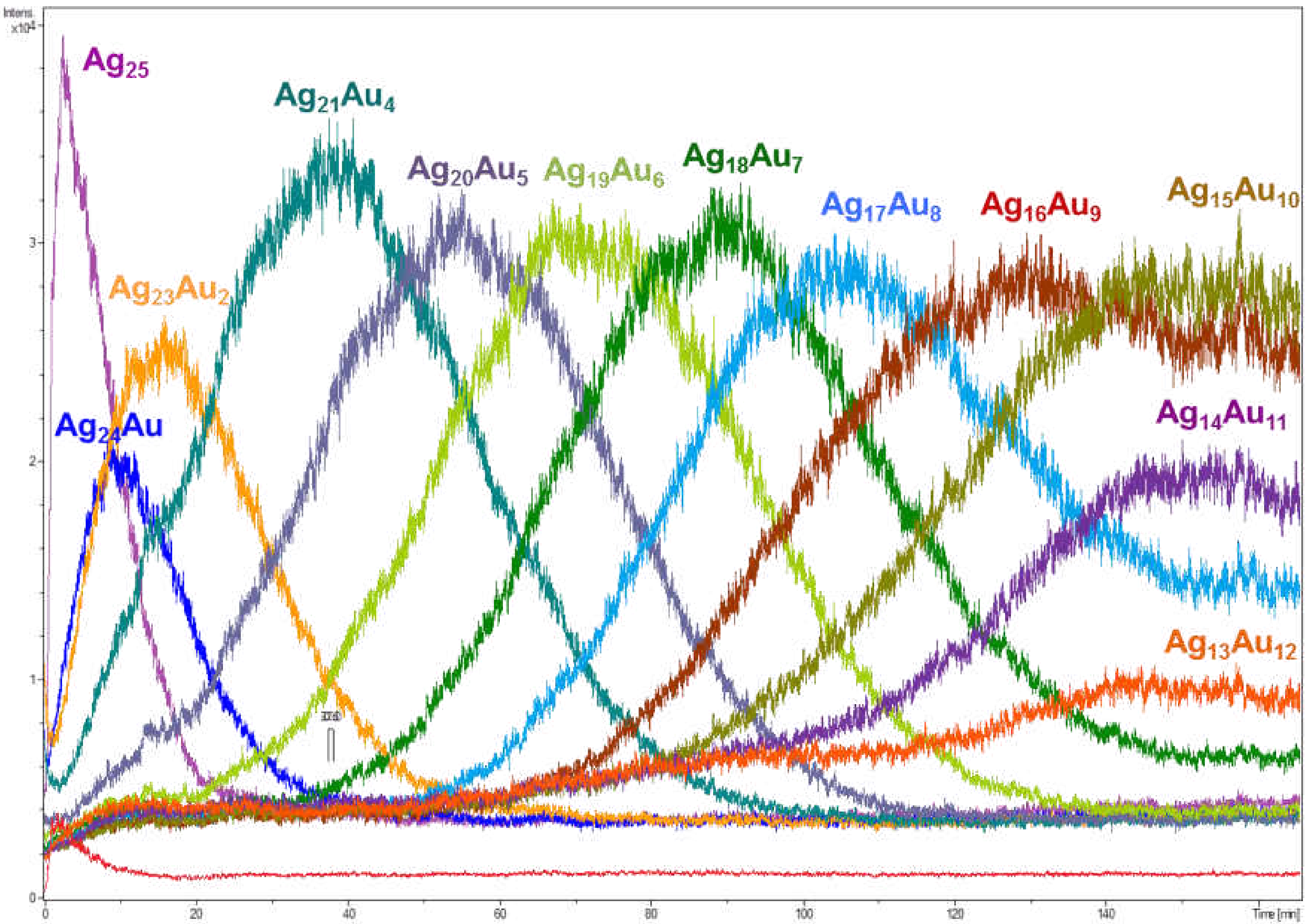
Manfred Kappes, KIT

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



CID data of $[Au25Ag25]^{2-}$

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



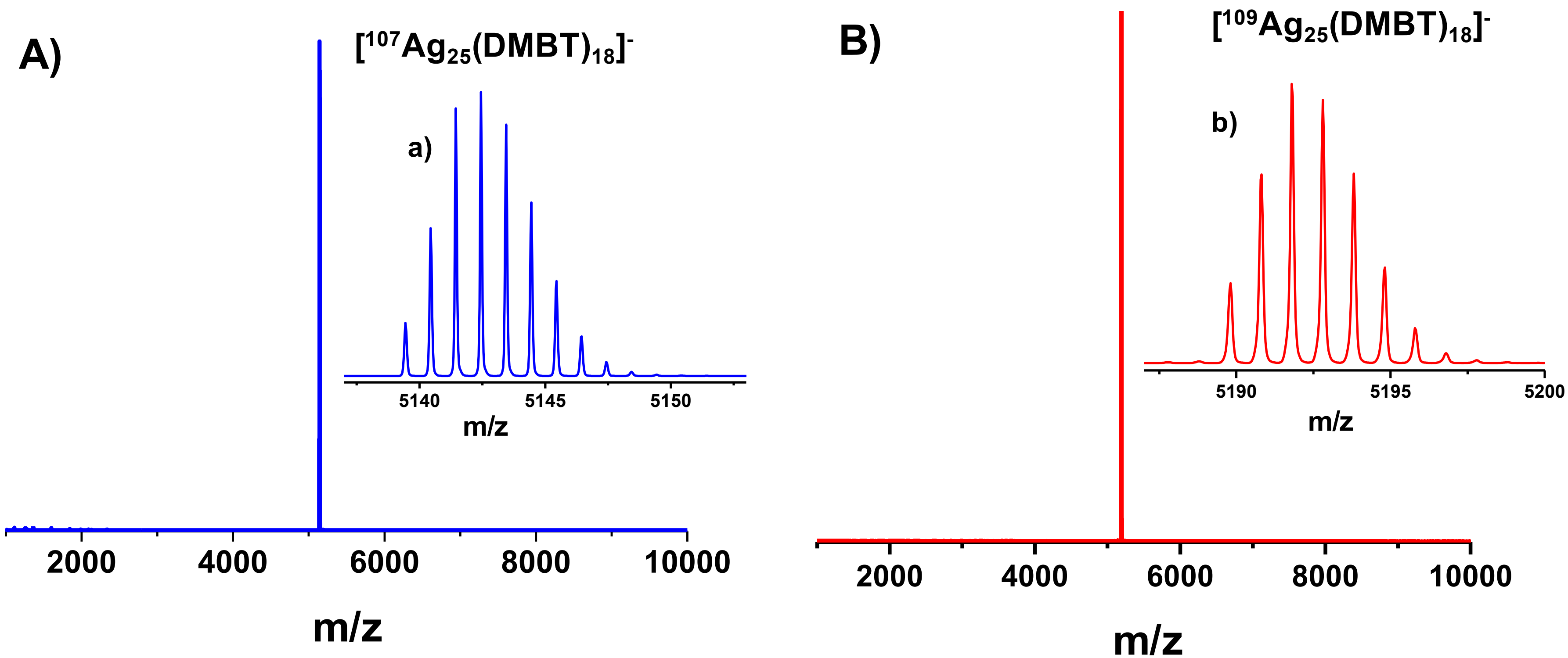
SCIENCE ADVANCES | RESEARCH ARTICLE

CONDENSED MATTER PHYSICS

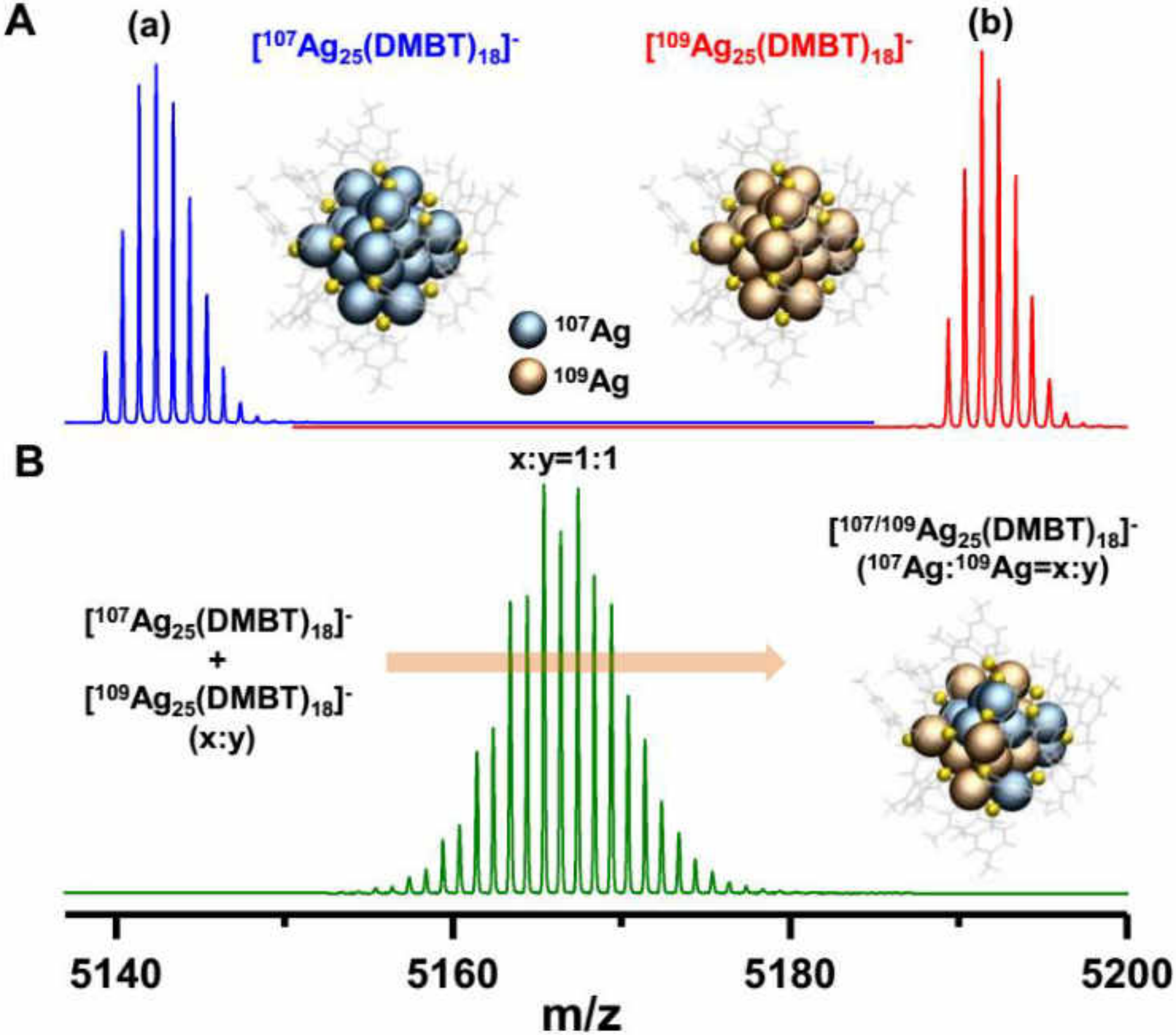
Rapid isotopic exchange in nanoparticles

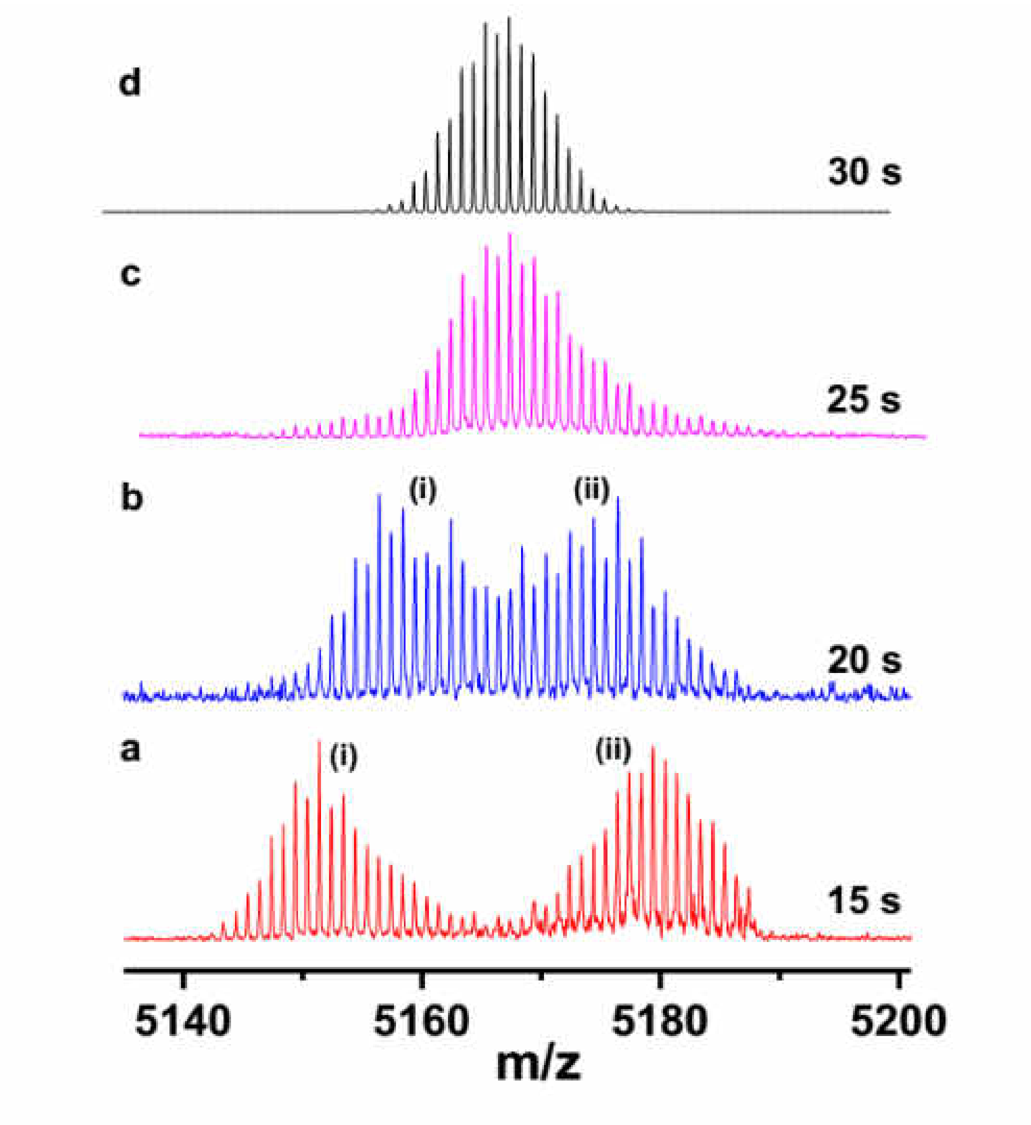
Papri Chakraborty[1], Abhijit Nag[1], Ganapati Natarajan[1], Nayanika Bandyopadhyay[1], Ganesan Paramasivam[1], Manoj Kumar Panwar[1], Jaydeb Chakrabarti[2], Thalappil Pradeep[1]*

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.

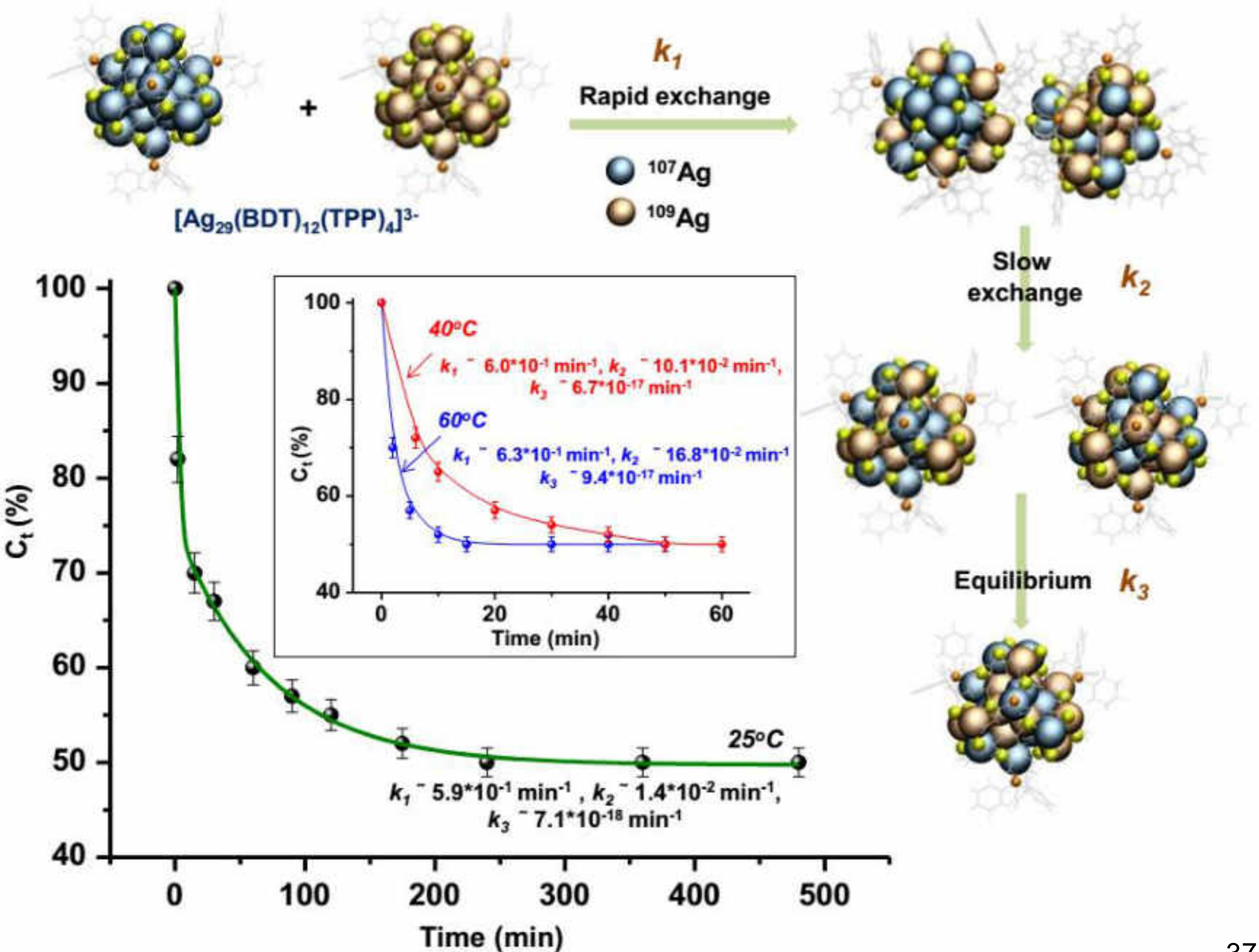


ESI MS of **A)** $^{107}Ag_{25}(DMBT)_{18}$ and **B)**$^{109}Ag_{25}(DMBT)_{18}$. Insets shows the respective isotope patterns.


A
(a)
[107Ag25(DMBT)18]-
[109Ag25(DMBT)18]-
(b)
107Ag
109Ag
B
x:y=1:1
[107/109Ag25(DMBT)18]-
(107Ag:109Ag=x:y)
[107Ag25(DMBT)18]-
+
[109Ag25(DMBT)18]-
(x:y)
5140
5160
5180
5200
m/z



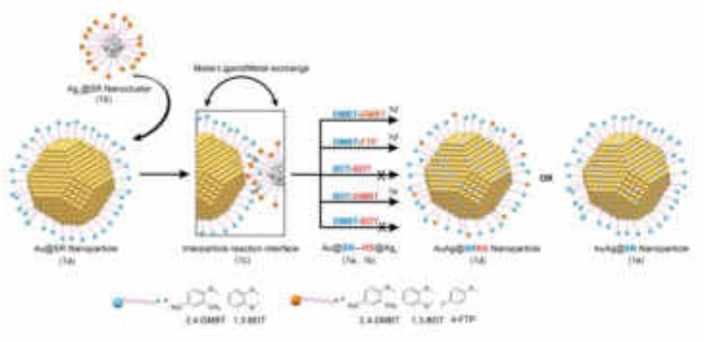
Papri Chakraborty, et. al. *Science Advances* 2019


[Ag29(BDT)12(TPP)4]3-
+
k1
Rapid exchange
107Ag
109Ag
Slow exchange
k2
Equilibrium
k3
Ct (%)
Time (min)
40°C
k1 ~ 6.0*10-1 min-1, k2 ~ 10.1*10-2 min-1,
k3 ~ 6.7*10-17 min-1
60°C
k1 ~ 6.3*10-1 min-1, k2 ~ 16.8*10-2 min-1
k3 ~ 9.4*10-17 min-1
25°C
k1 ~ 5.9*10-1 min-1 , k2 ~ 1.4*10-2 min-1,
k3 ~ 7.1*10-18 min-1

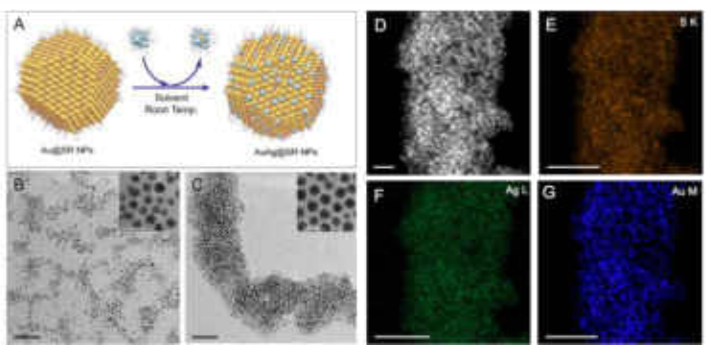
Can clusters react with nanoparticles?

Ag_{25} with Au nanoparticles

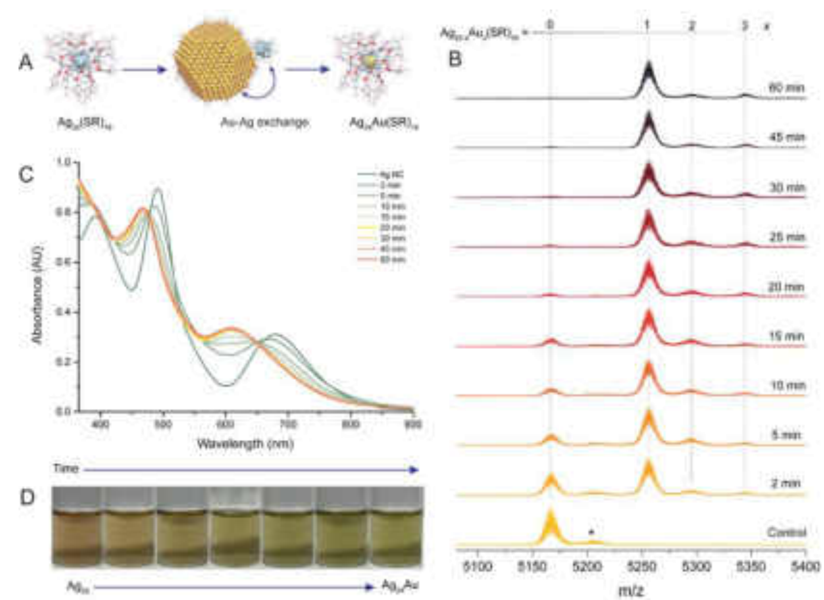
1



2



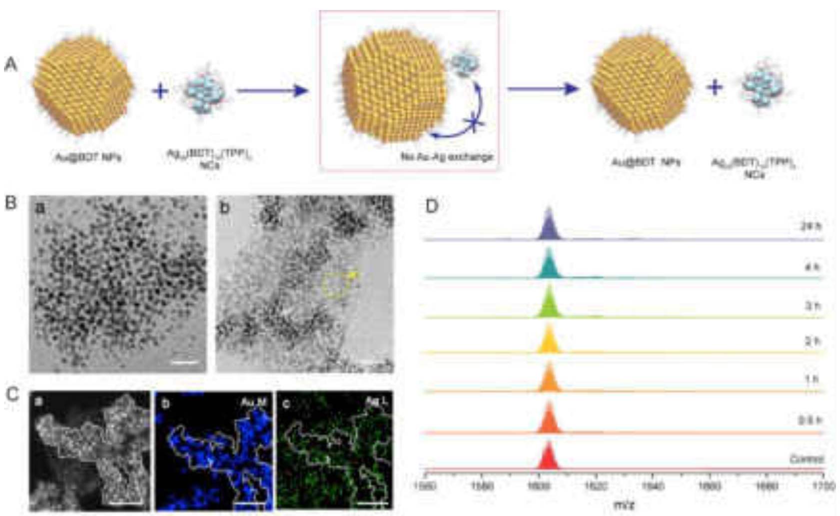
3



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

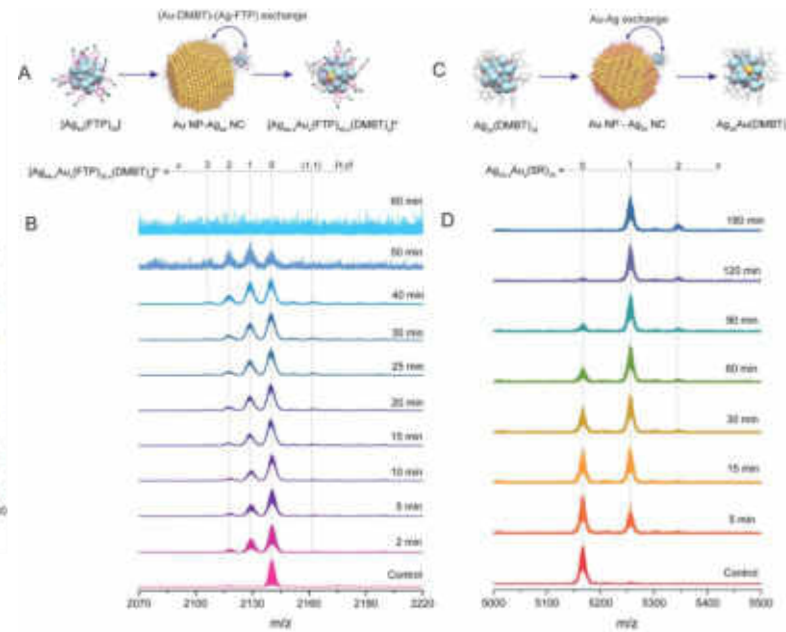
Interface controls the reaction

4



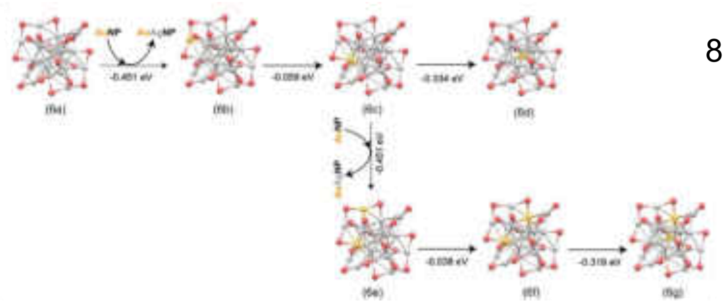
Scale bars: 20 nm

5

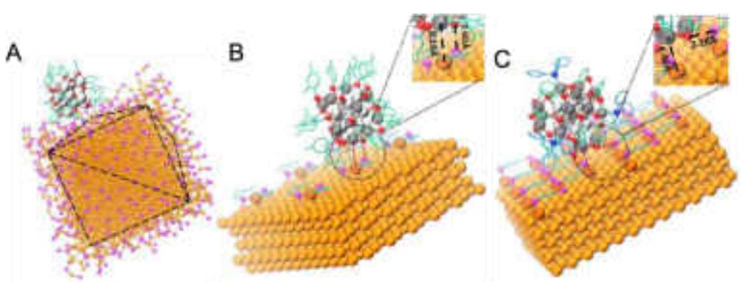


Computational insights

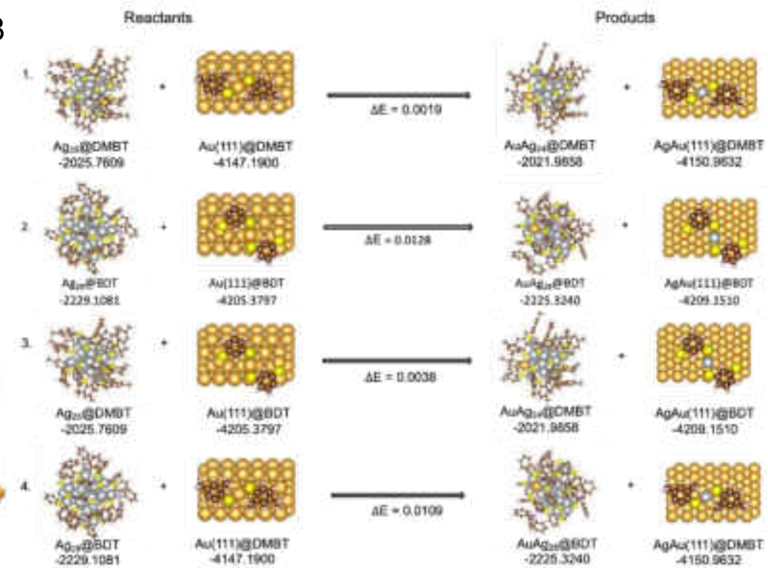
6



7



8



Reactions and new materials

CHEMISTRY OF MATERIALS

Article

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

pubs.acs.org/cm

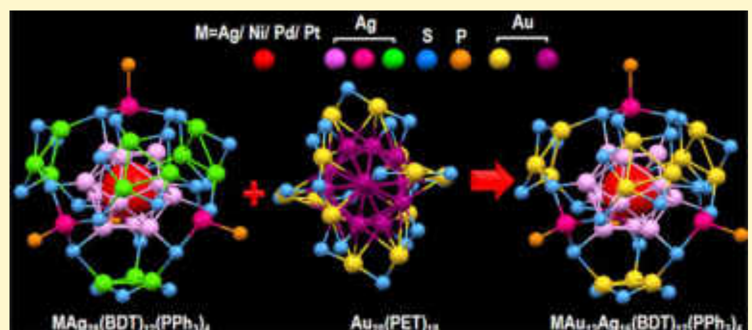
Interclusterreactions Resulting in Silver-Rich Trimetallic Nanoclusters

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

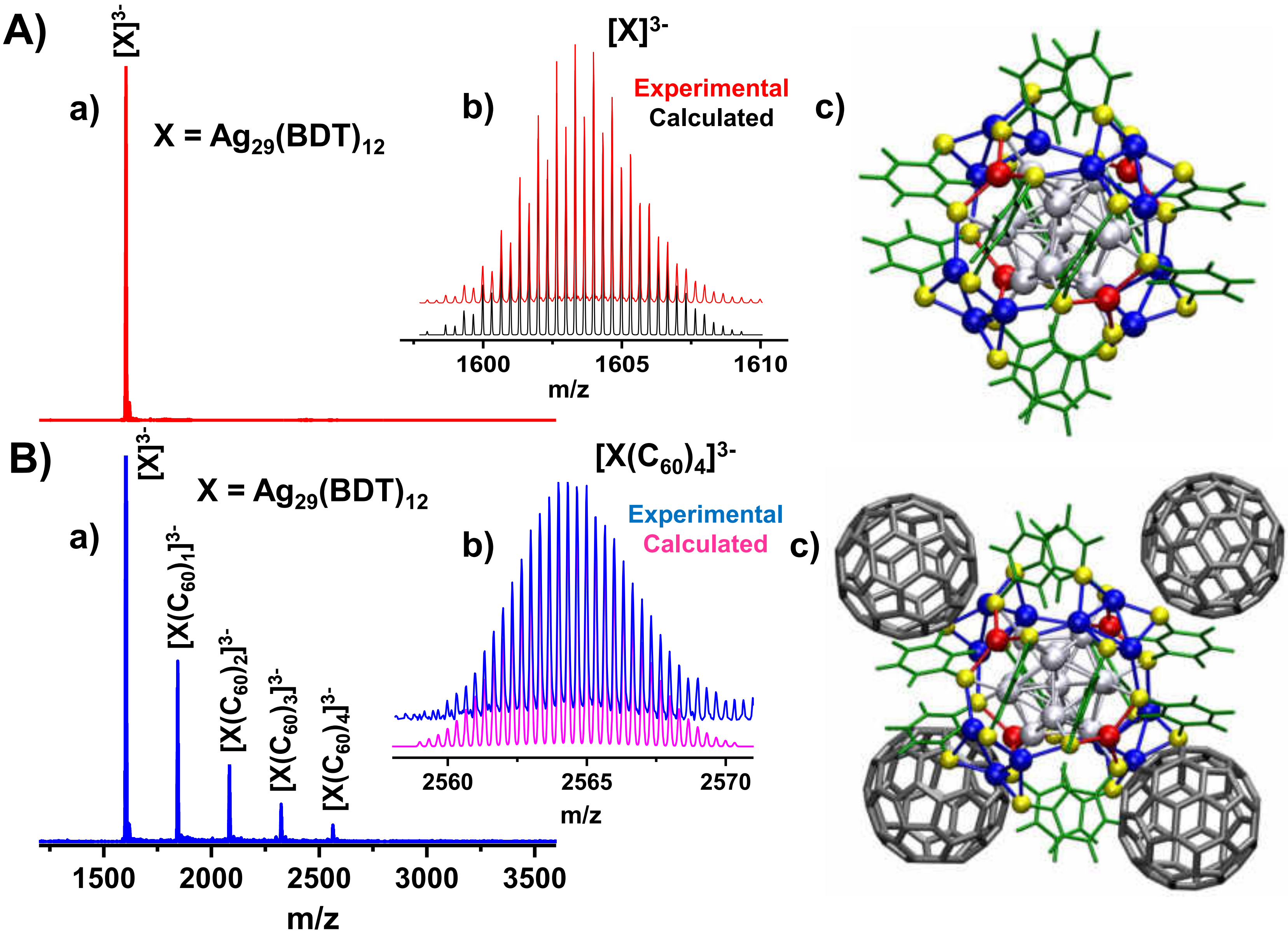


Figure 1. **A)** **(a)** Full range ESI MS, **(b)** experimental and calculated isotope patterns and **(c)** DFT optimized structure of $[Ag_{29}(BDT)_{12}]^{3-}$ cluster. **B)** **(a)** ESI MS of $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (n=1-4) complexes, **(b)** experimental and calculated isotope patterns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

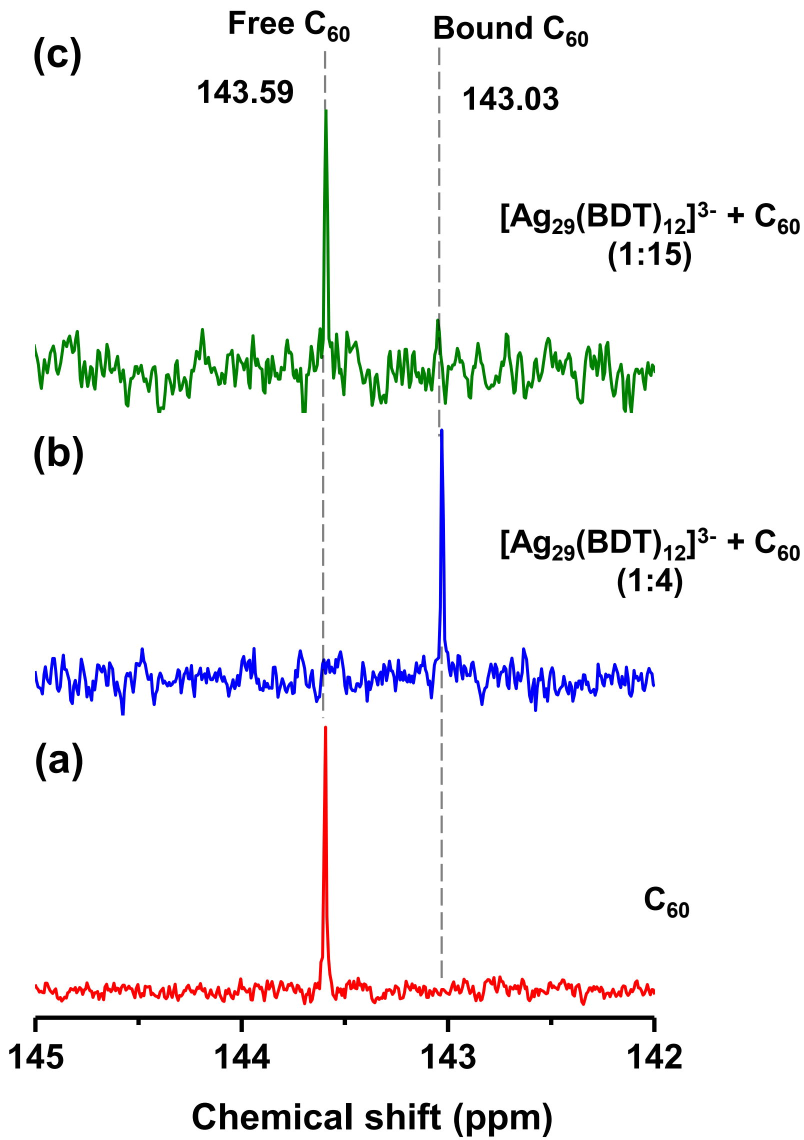
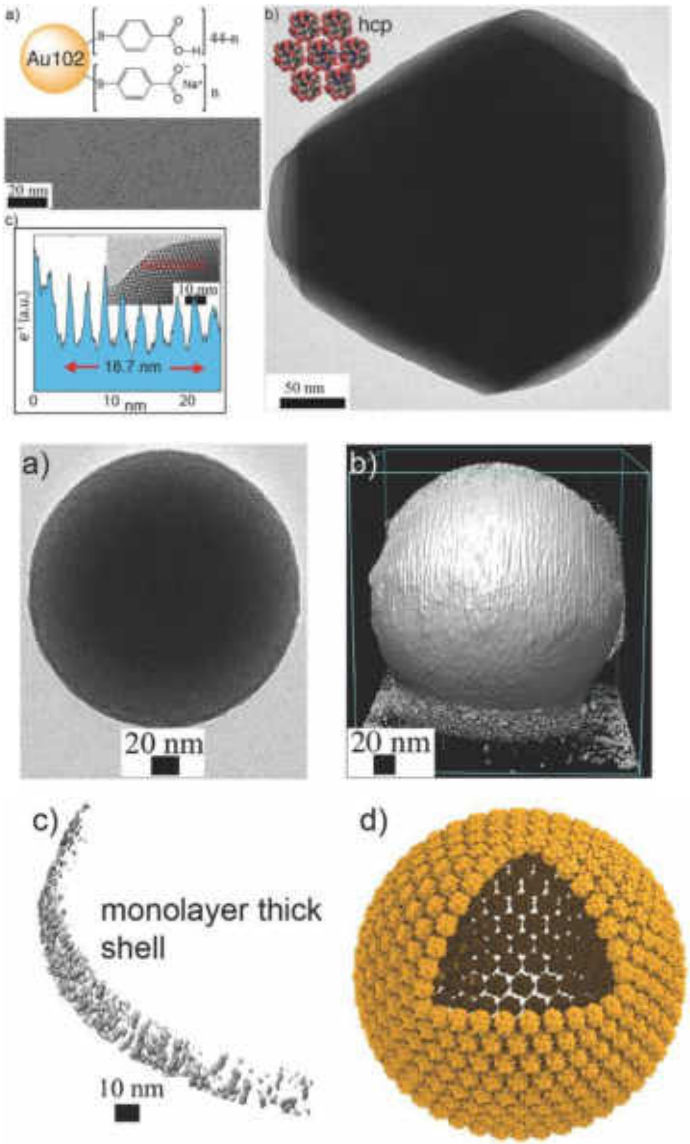
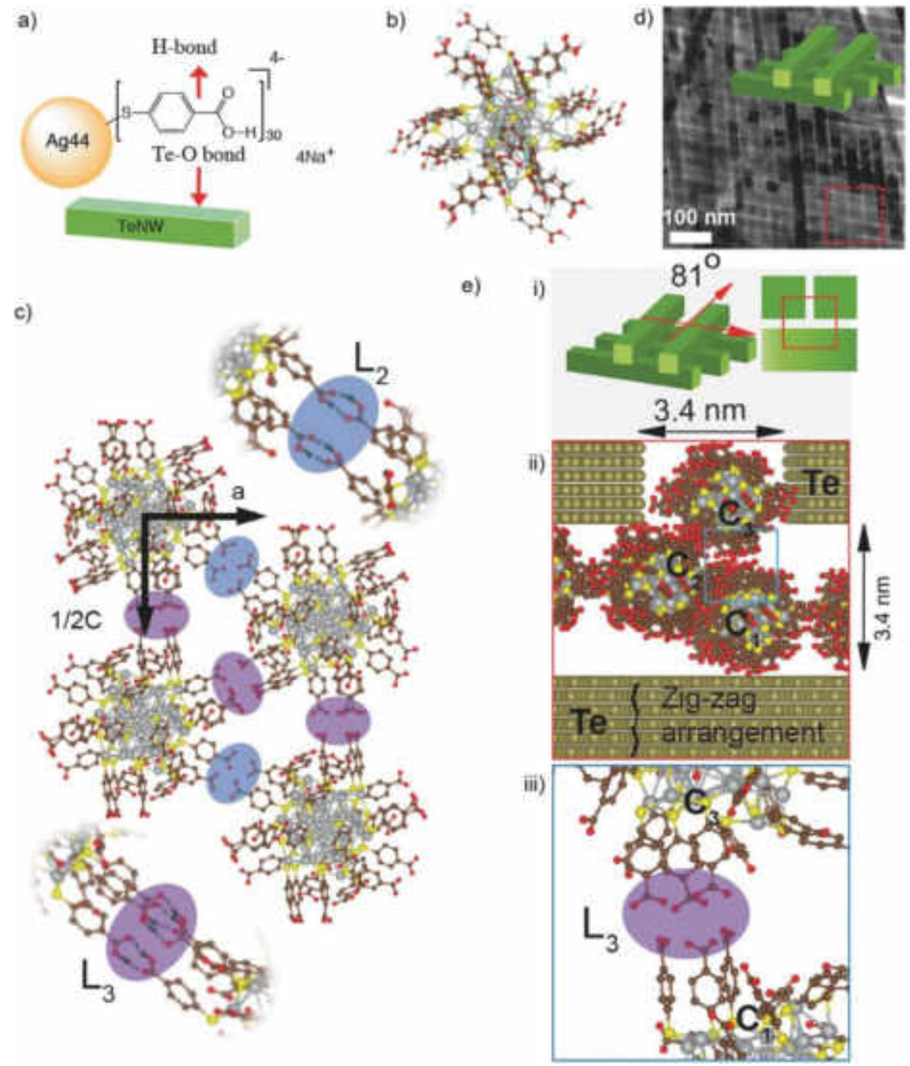


Figure 3. NMR of **(a)** C_{60} showing peak at 143.59 ppm, **(b)** the adducts at a cluster:fullerene molar ratio of 1:4 showing peak at 143.03 ppm for the C_{60} molecules in bound state and **(c)** the adducts at an excess concentration of C_{60} (cluster:fullerene molar ratio of 1:15) showing a predominant peak for free C_{60} (143.59 ppm) and a less intense peak for bound C_{60} (143.03 ppm).

Assemblies and superstructures

Nanoclusters in colloidal assemblies

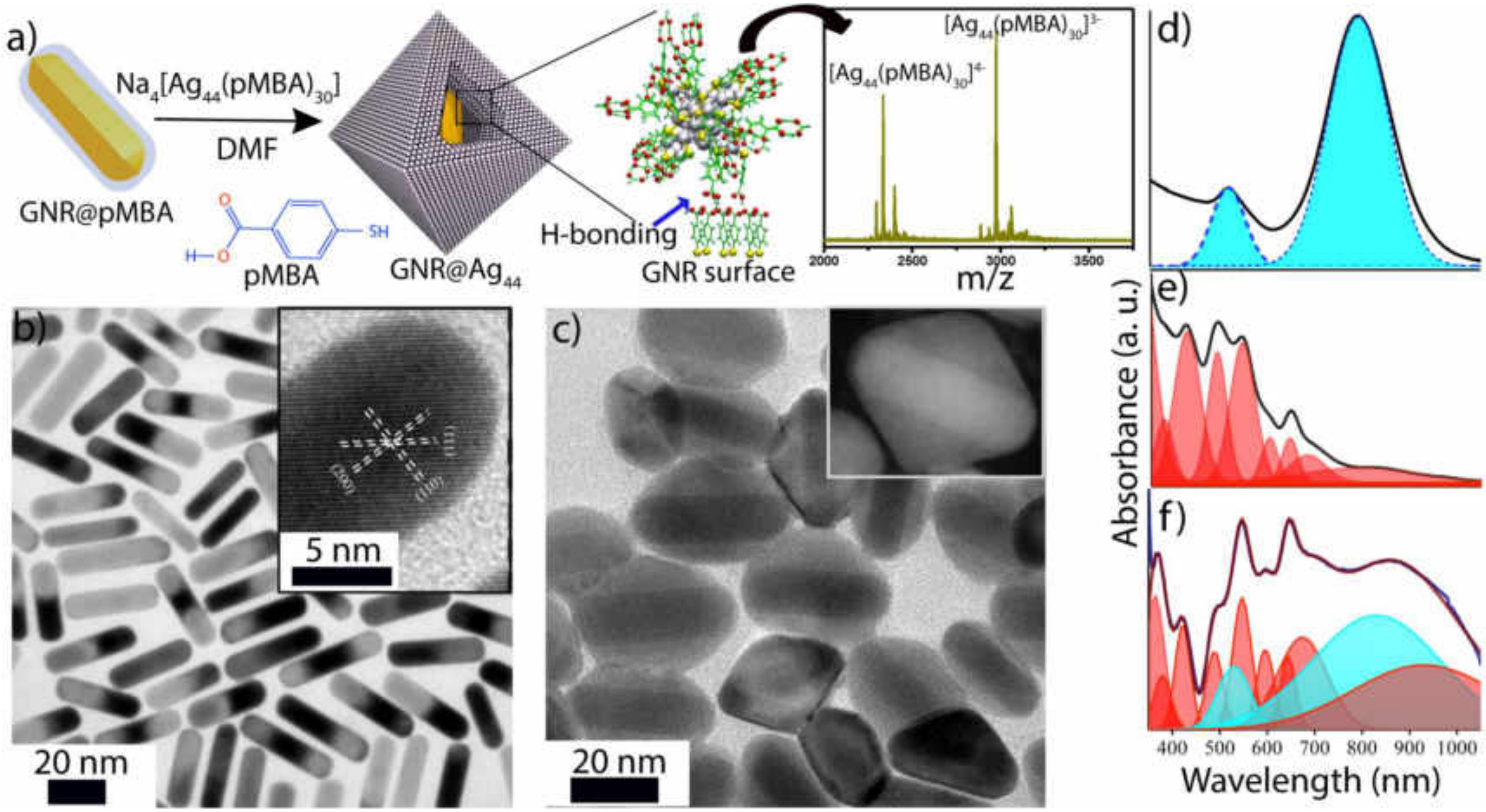




Som, A. et al., *Adv. Mater.* **2016**, *28*, 2827–2833

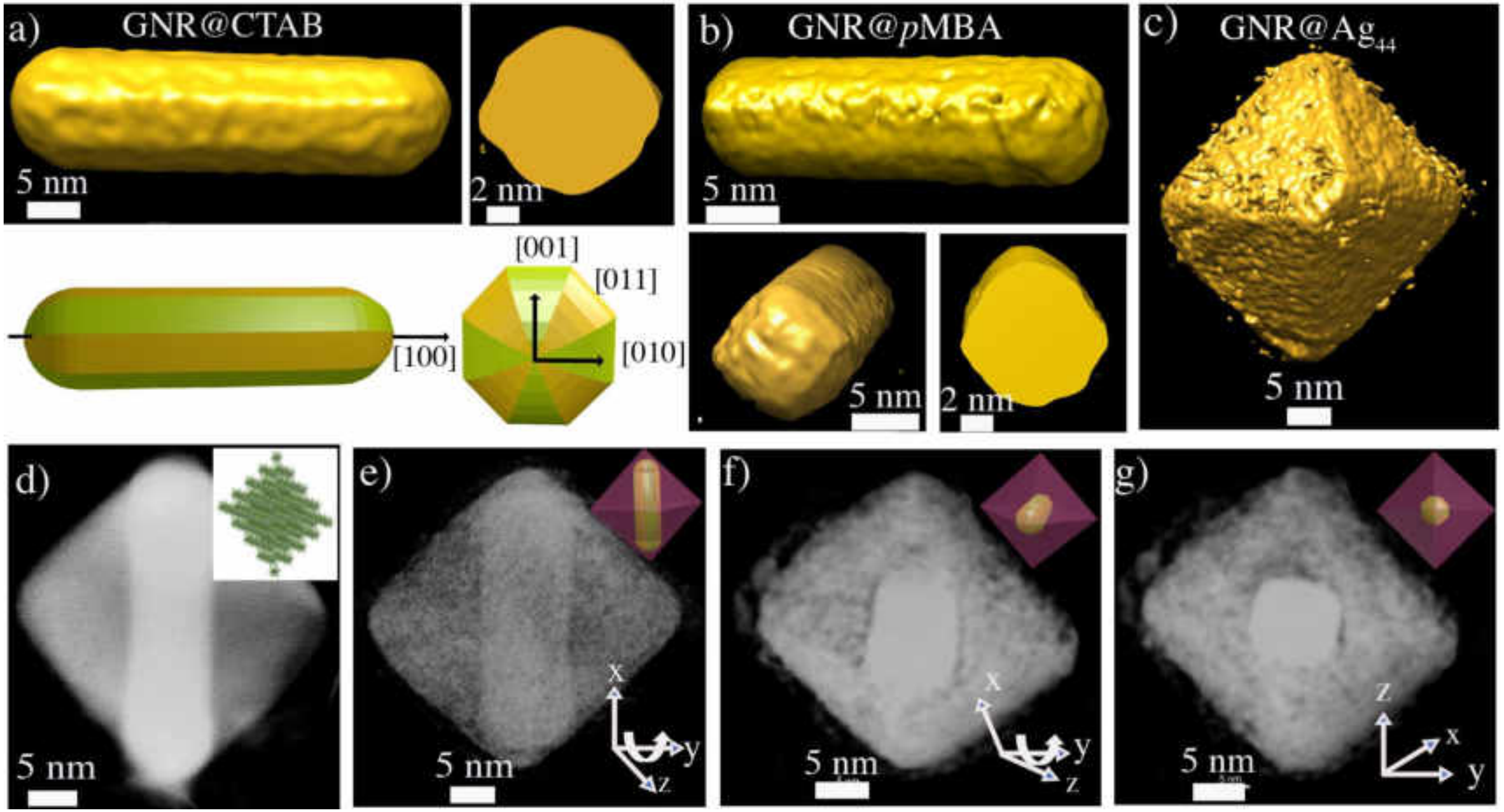
Nonappa et al., *Angew. Chem. Int. Ed.* **2016**, *55*, 16035–16038.

Atomically precise nanocluster assemblies encapsulating plasmonic gold nanorods

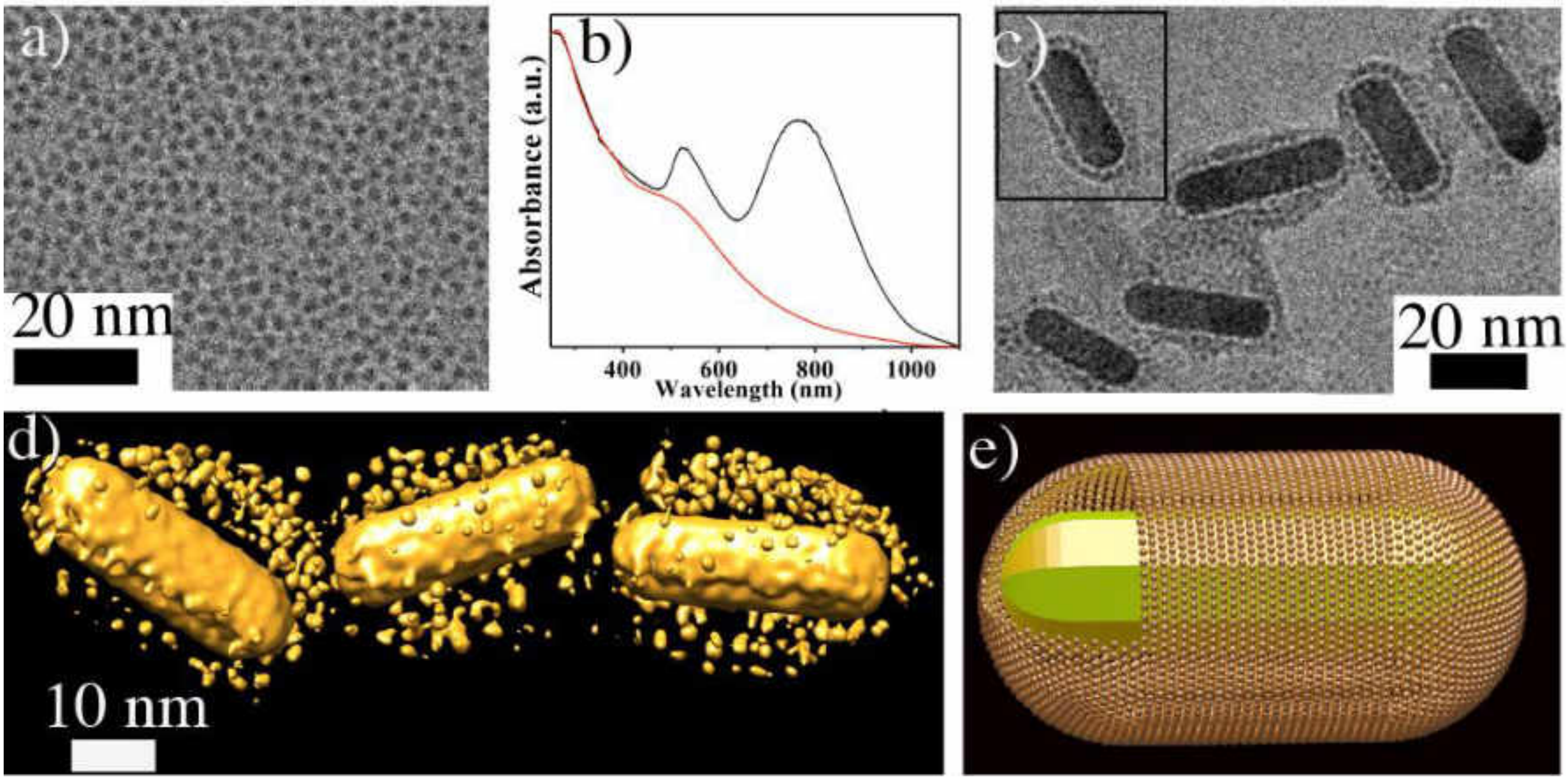


Chakraborty, A. et al., *Angew. Chem. Int. Ed.* **2018,** *57*, 6522–6526.

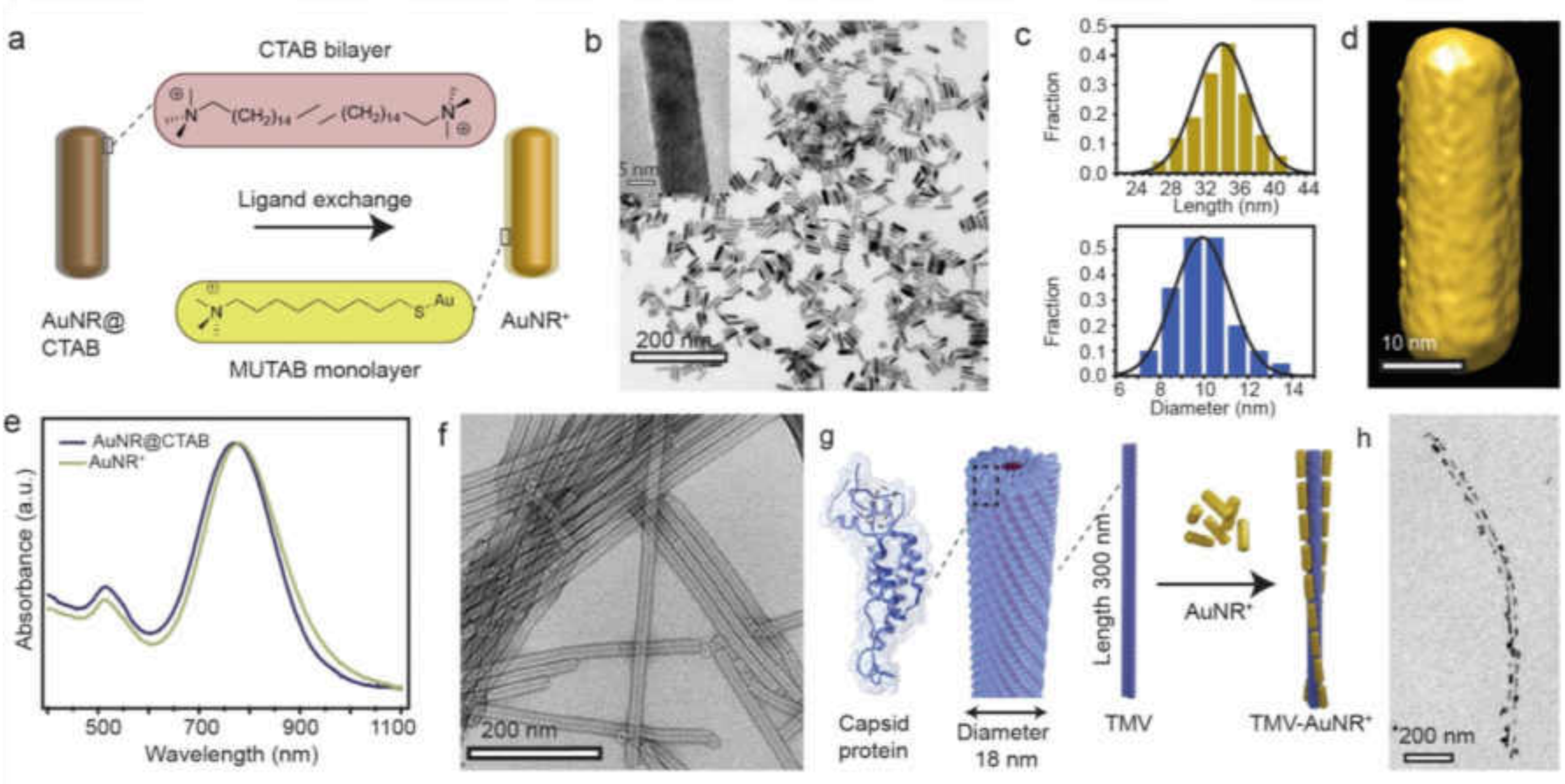
3D morphological analysis



Works for $Au_{250}(pMBA)_n$ and aqueous solvent



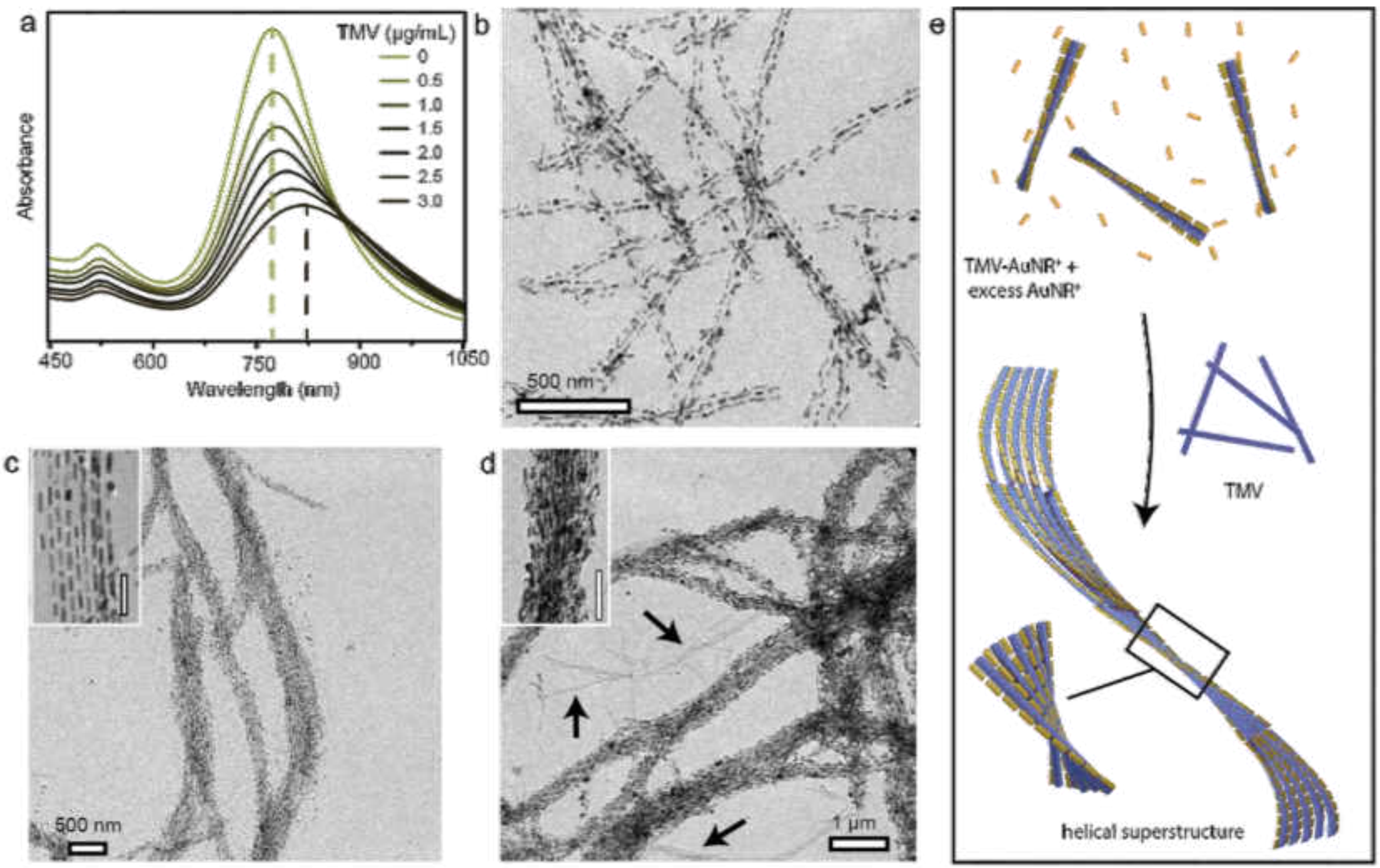
Near-infrared chiral plasmonic microwires through precision assembly of gold nanorods on soft biotemplates



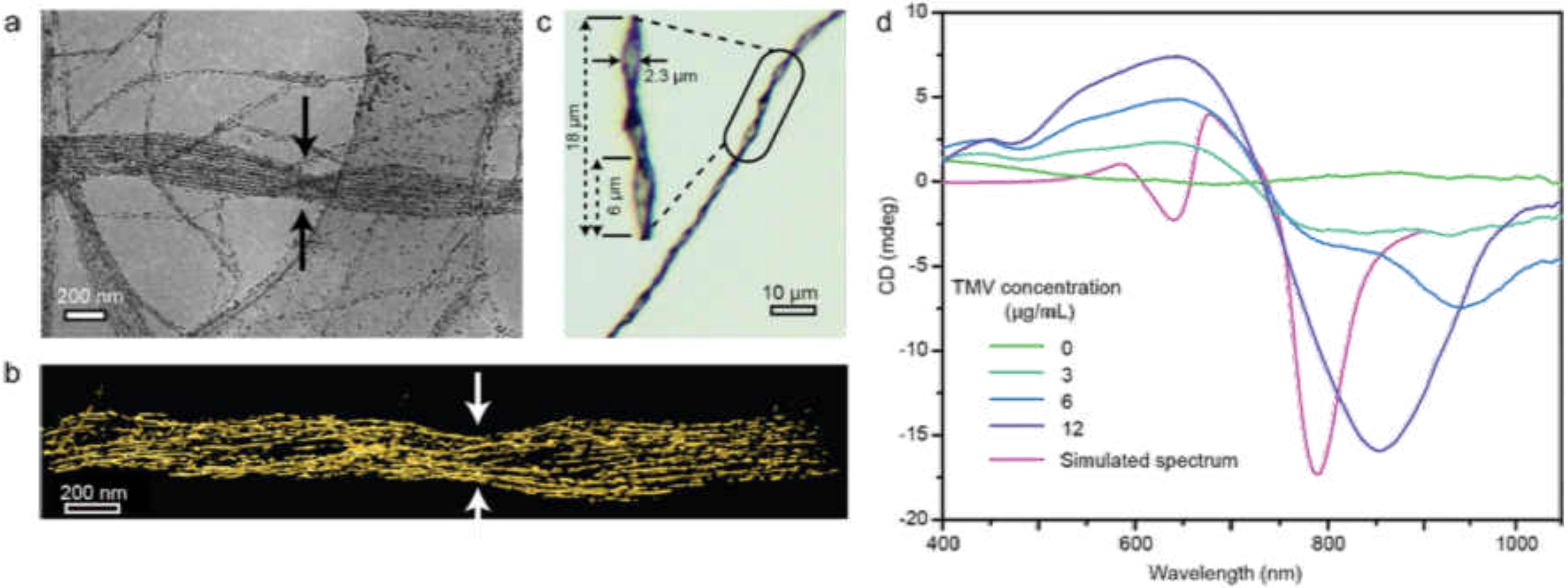
Chakraborty, A. et al., *J. Phys. Chem. C* **2021**, *125*, 3256−3267.

With Nonappa, Mauri A. Kostiainen and Robin H. A. Ras

Long-range assembly

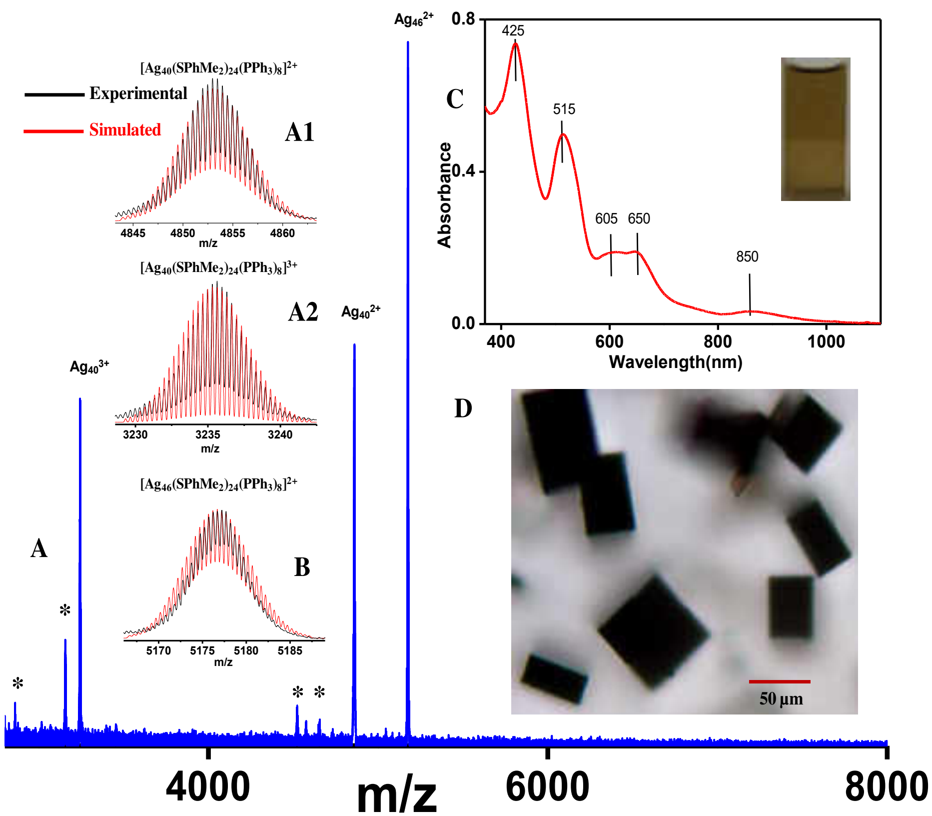


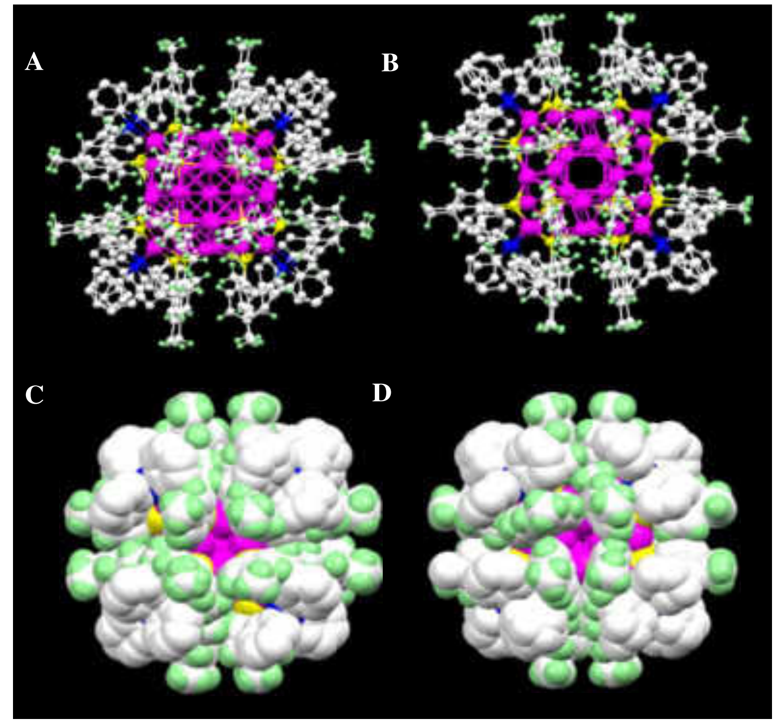
NIR chirality



Co-crystals

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

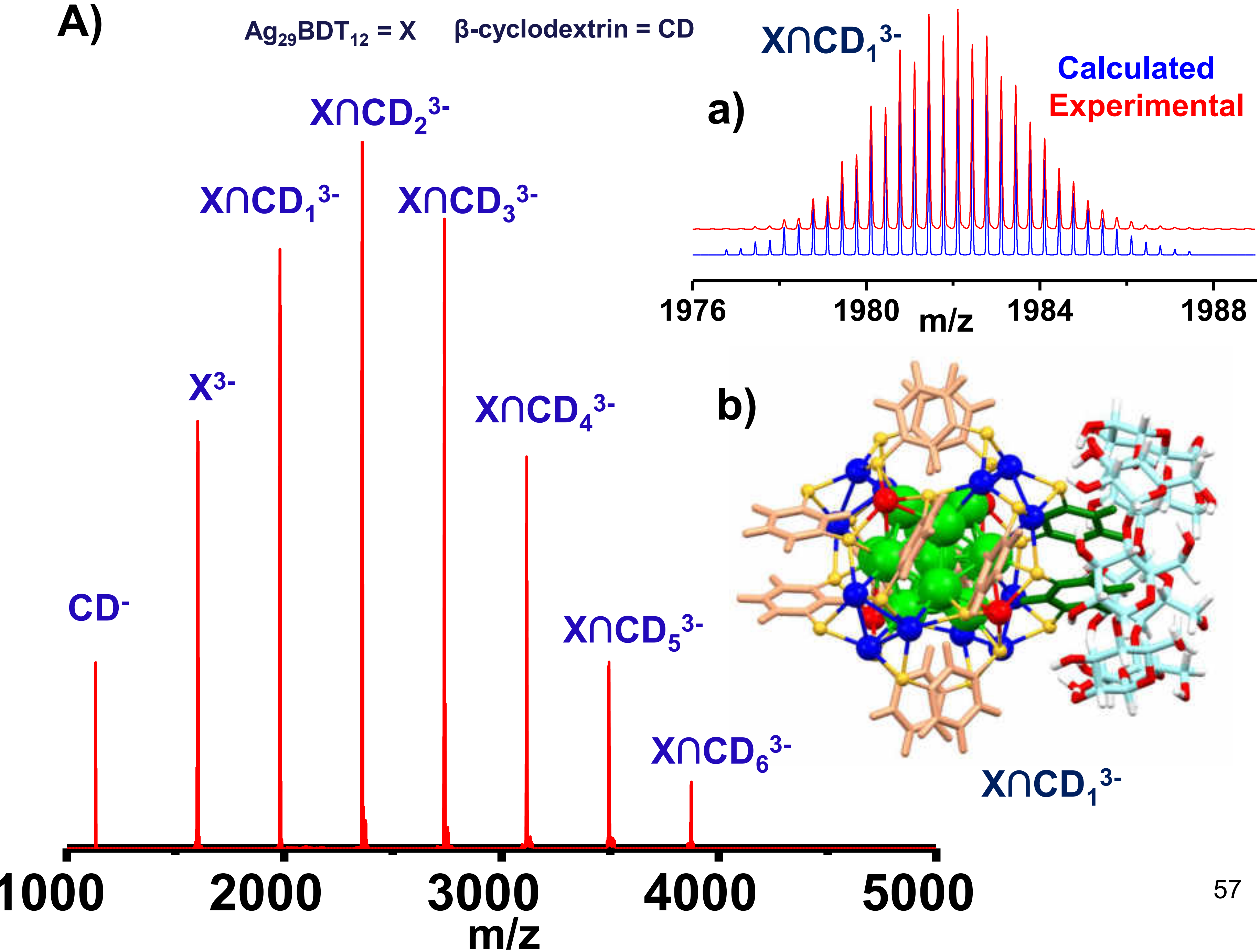


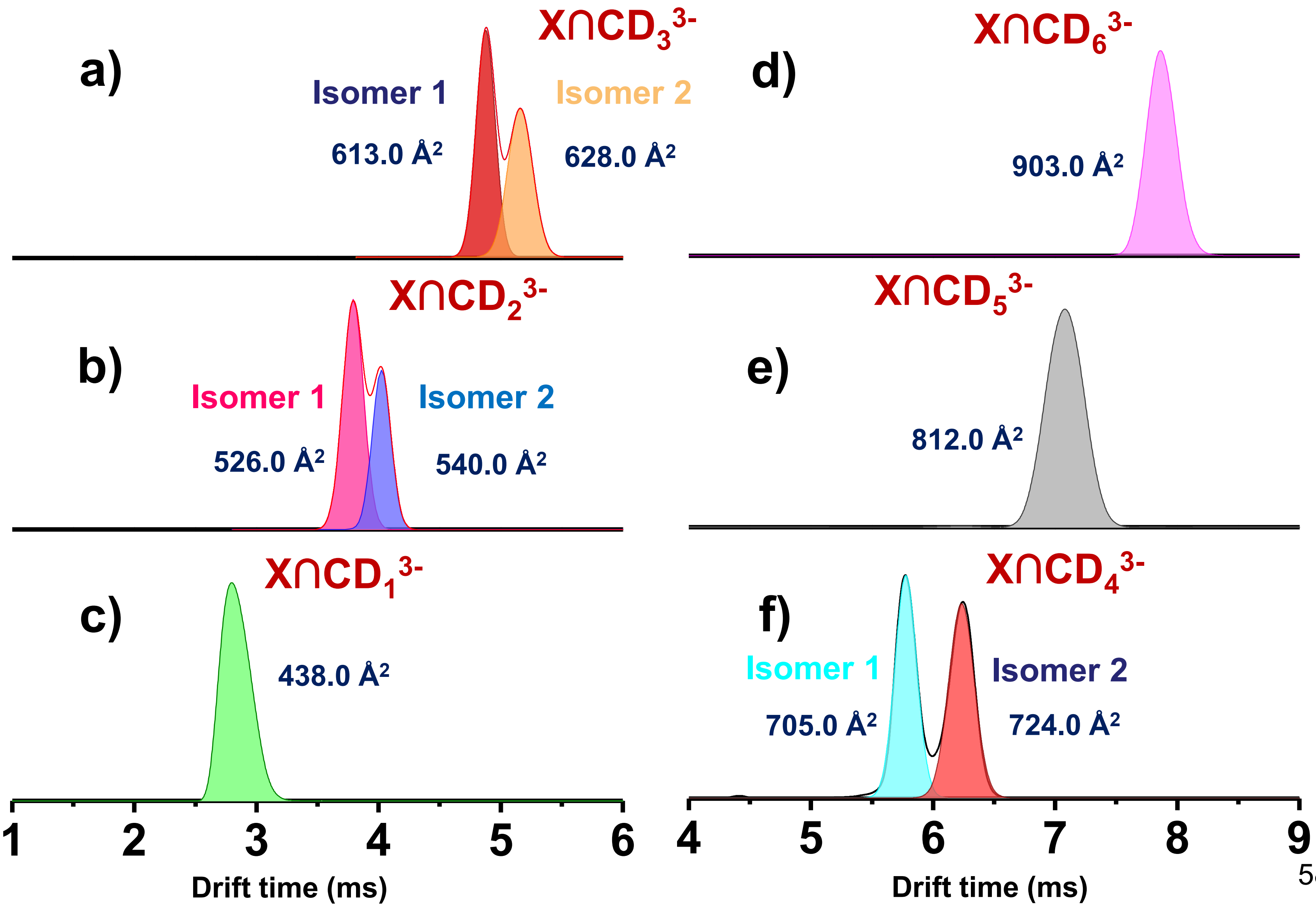


M. Bodiuzzaman, et. al. *Angew. Chem. Int. Ed.* **2018**

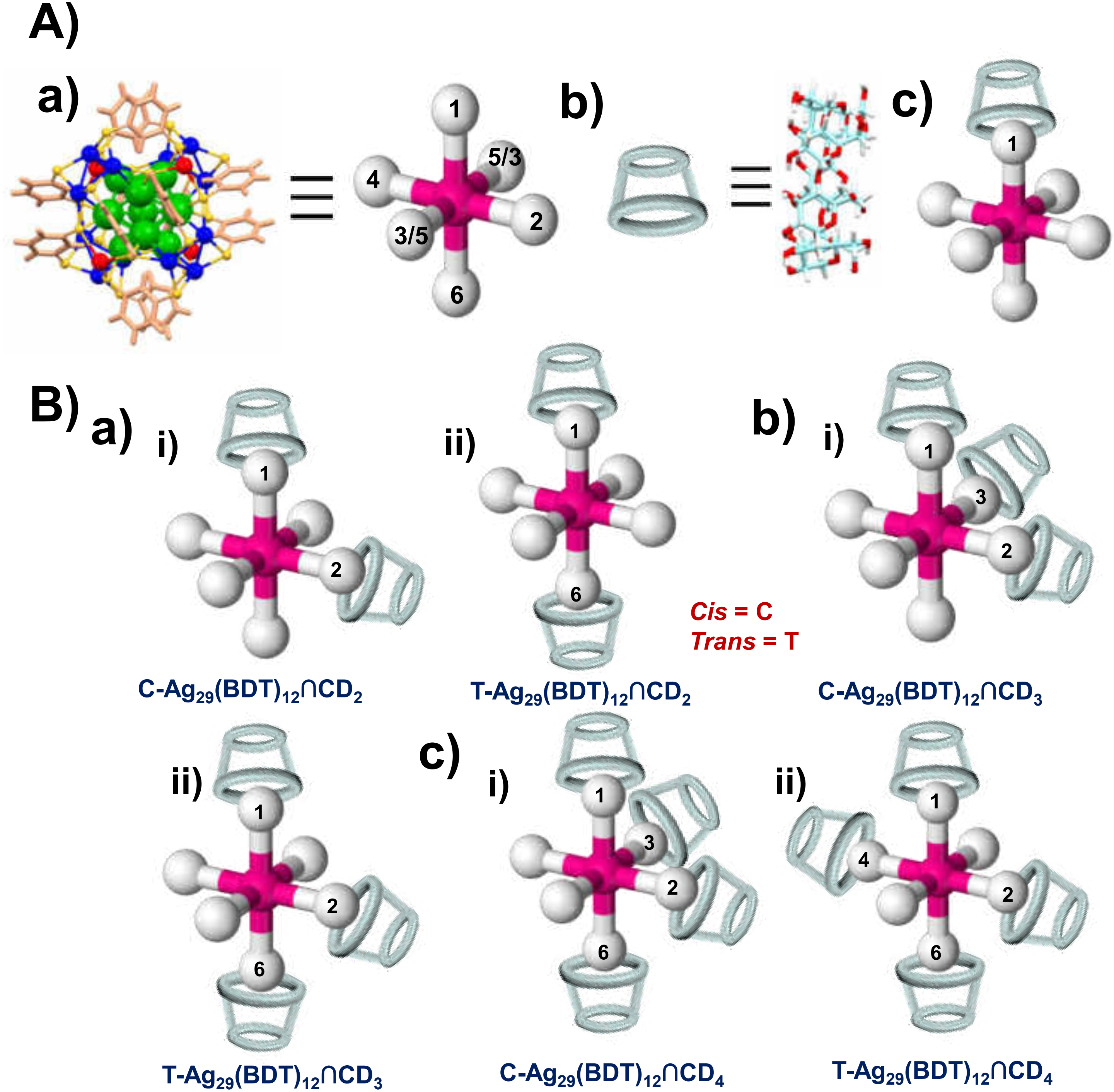
Isomerism in supramolcular adducts

Abhijit Nag, et al. *JACS* 2018


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



a)
X∩CD$_3^{3-}$
Isomer 1
613.0 Å^2
Isomer 2
628.0 Å^2
b)
X∩CD$_2^{3-}$
Isomer 1
526.0 Å^2
Isomer 2
540.0 Å^2
c)
X∩CD$_1^{3-}$
438.0 Å^2
1 2 3 4 5 6
Drift time (ms)
d)
X∩CD$_6^{3-}$
903.0 Å^2
e)
X∩CD$_5^{3-}$
812.0 Å^2
f)
X∩CD$_4^{3-}$
Isomer 1
705.0 Å^2
Isomer 2
724.0 Å^2
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-$Ag_{29}(BDT)_{12}{\cap}CD_2$
T-$Ag_{29}(BDT)_{12}{\cap}CD_2$
C-$Ag_{29}(BDT)_{12}{\cap}CD_3$
ii)
1
2
6
c)
i)
1
3
2
6
ii)
1
4
2
6
T-$Ag_{29}(BDT)_{12}{\cap}CD_3$
C-$Ag_{29}(BDT)_{12}{\cap}CD_4$
T-$Ag_{29}(BDT)_{12}{\cap}CD_4$

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

Edited by Eric Hoek, University of California,

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

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

Madras, Chennai 600 036, India

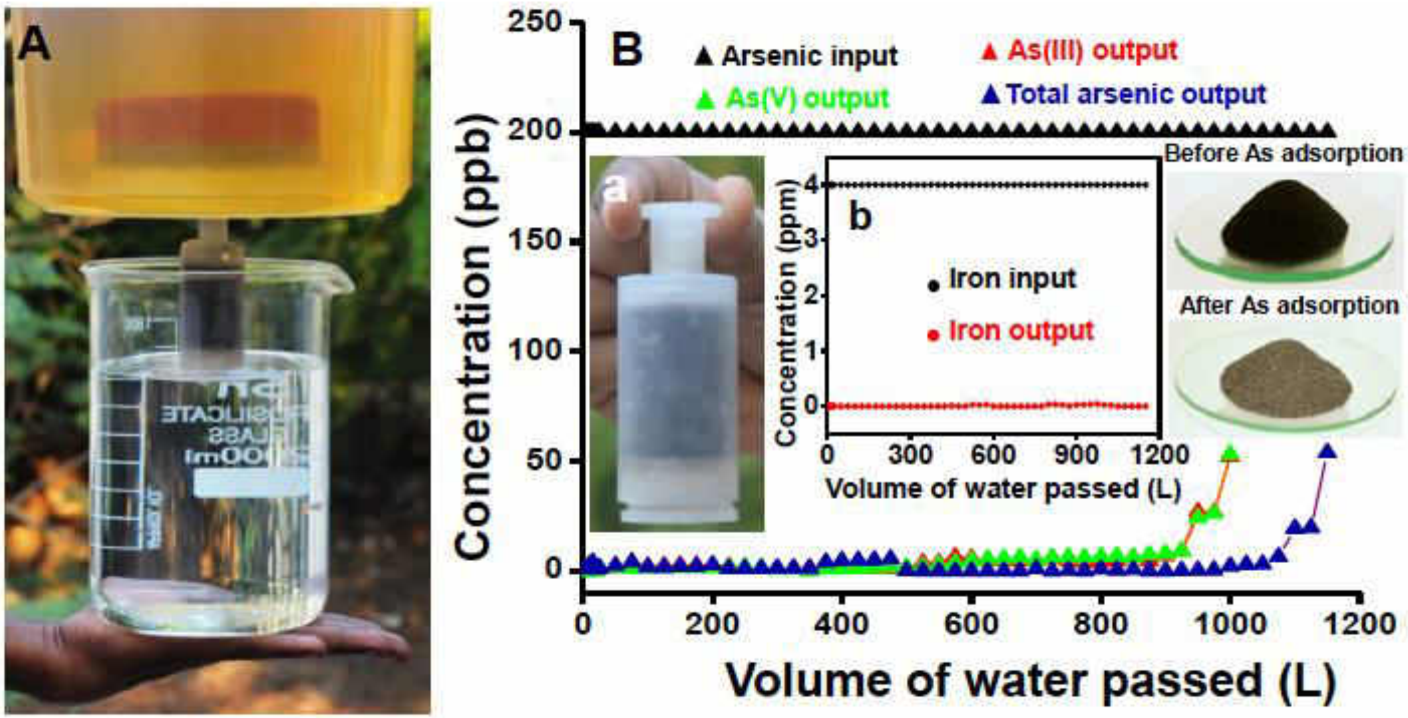
(received for review November 21, 2012)

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-
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.

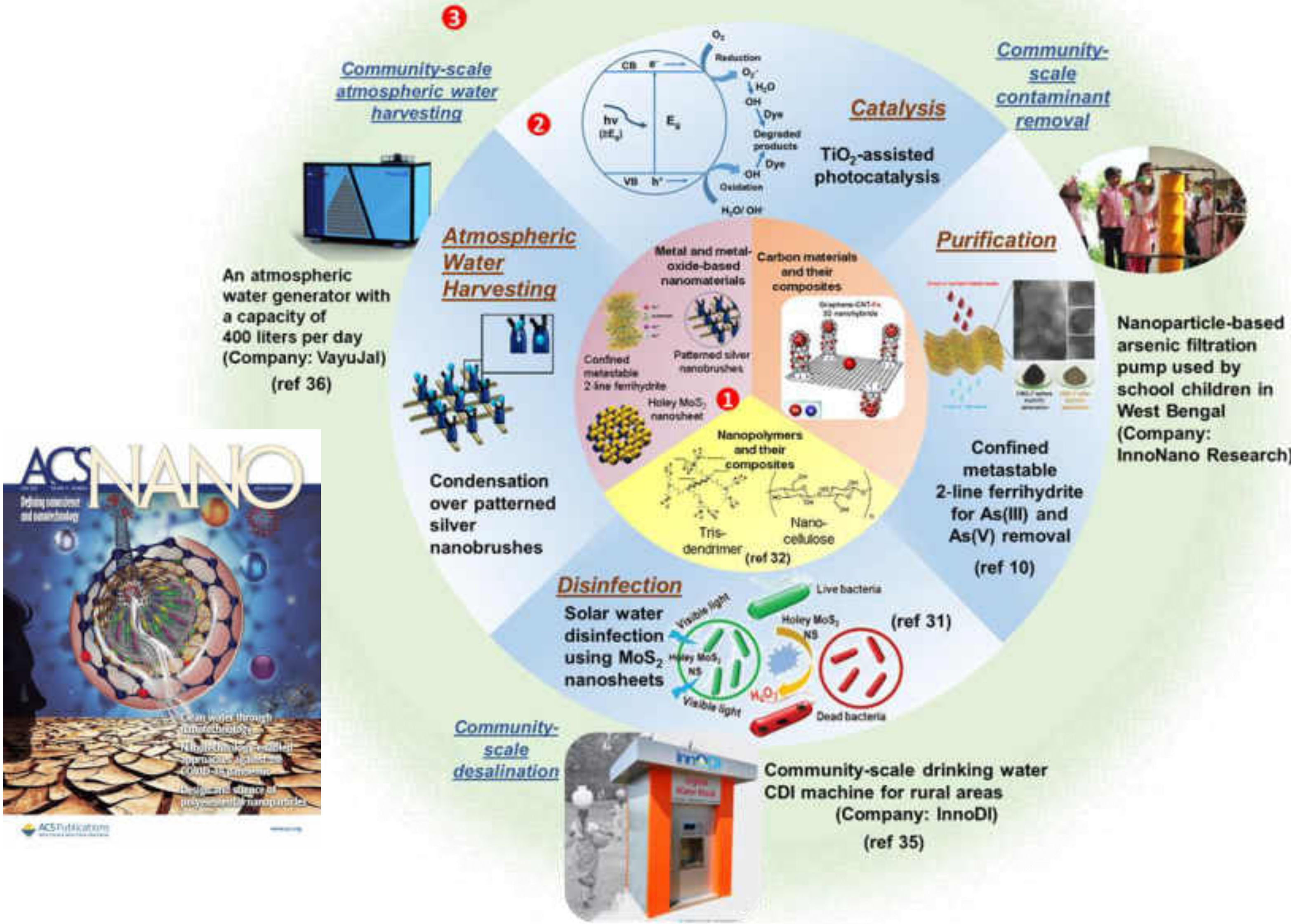
Safety of spent media, TCLP

Clean water for everyone

ACS Sustainable Chemistry & Engineering Editorial, December 2016

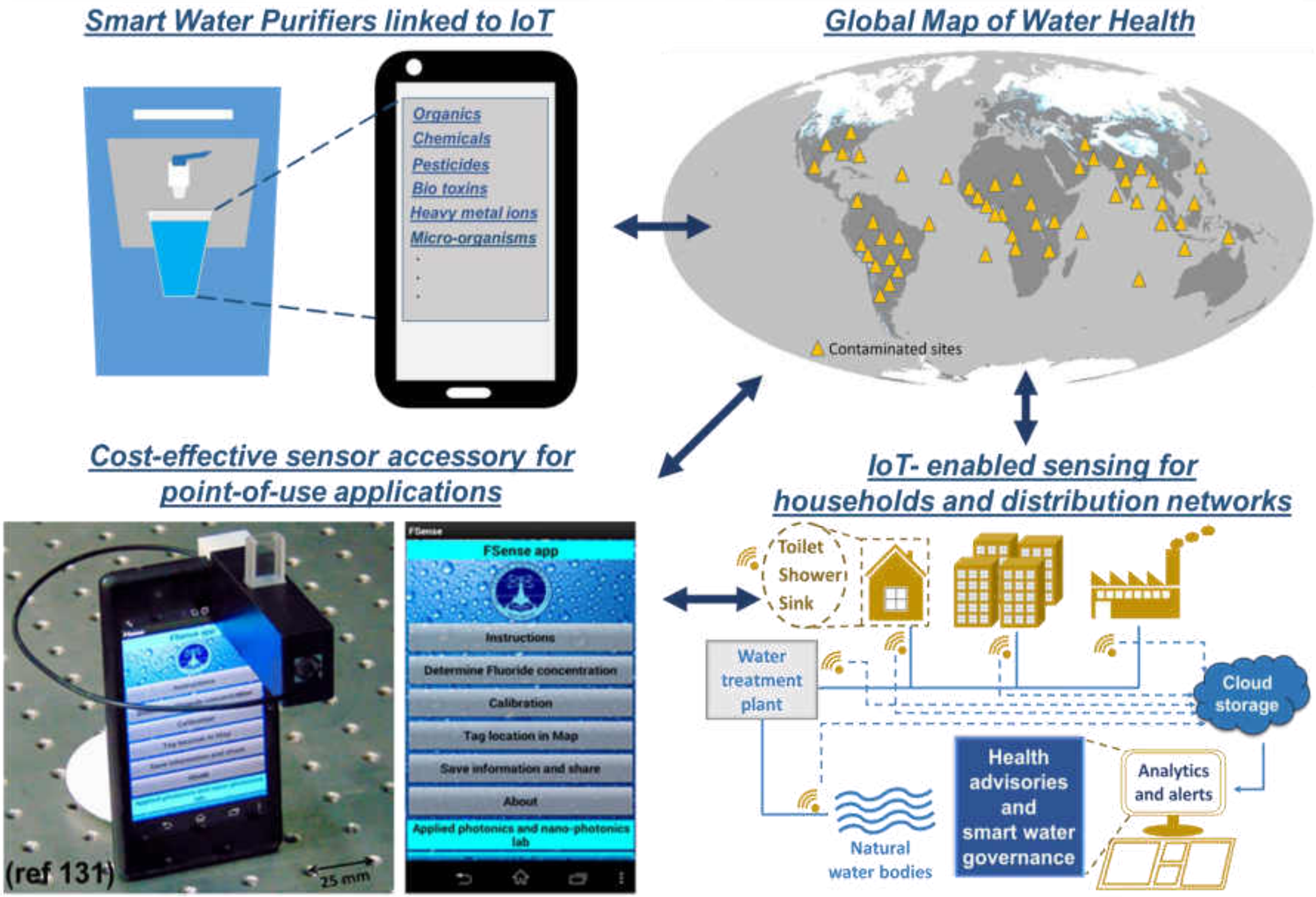

We developed environmentally friendly water positive nanoscale materials for affordable, sustainable and rapid removal of arsenic from drinking water.
There are over 1700 community installations across the country, serving 1.3 million people with arsenic and iron-free water every day.

Evolution of materials to products



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

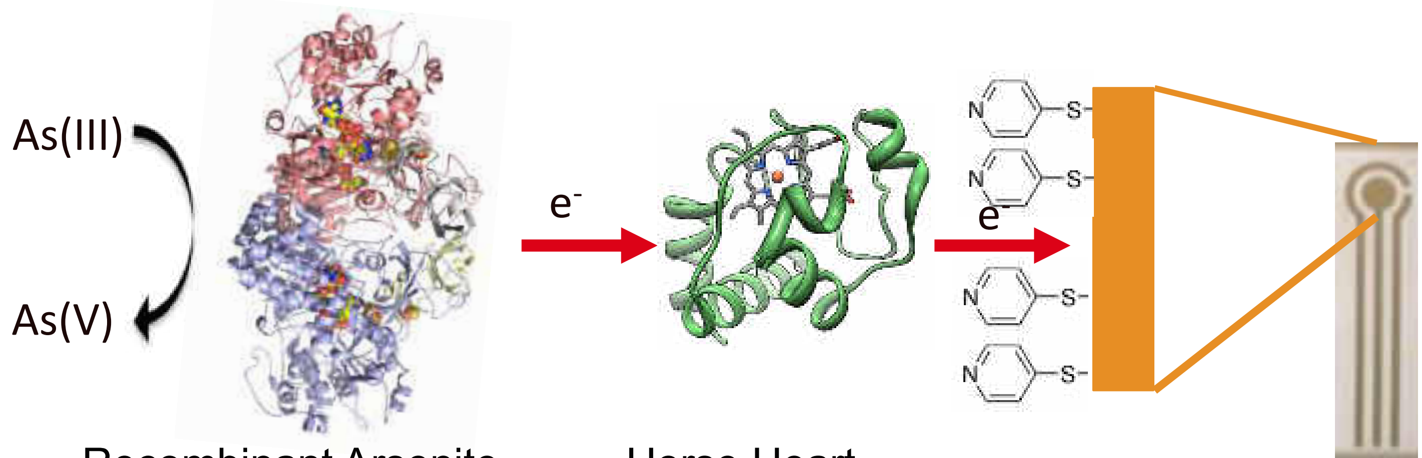
Smart water purifiers and big data



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

Biosensor Design

1st Generation Design (Mediated Electrochemistry)



Buffer: pH 7-8

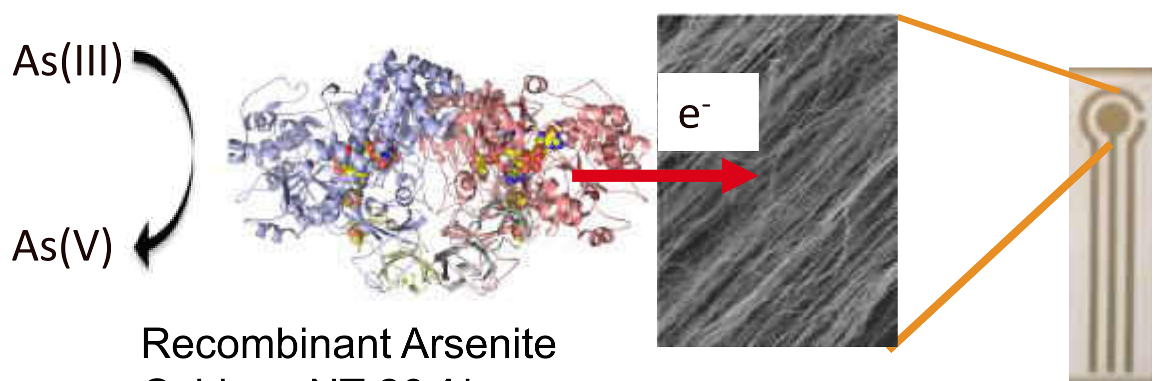
Recombinant Arsenite Oxidase NT-26 Aio

Horse Heart Cytochrome C

Aldrithiol

Low-cost Gold sputtered thin film on PET substrate

2nd Generation Design (Direct Electron Transfer)

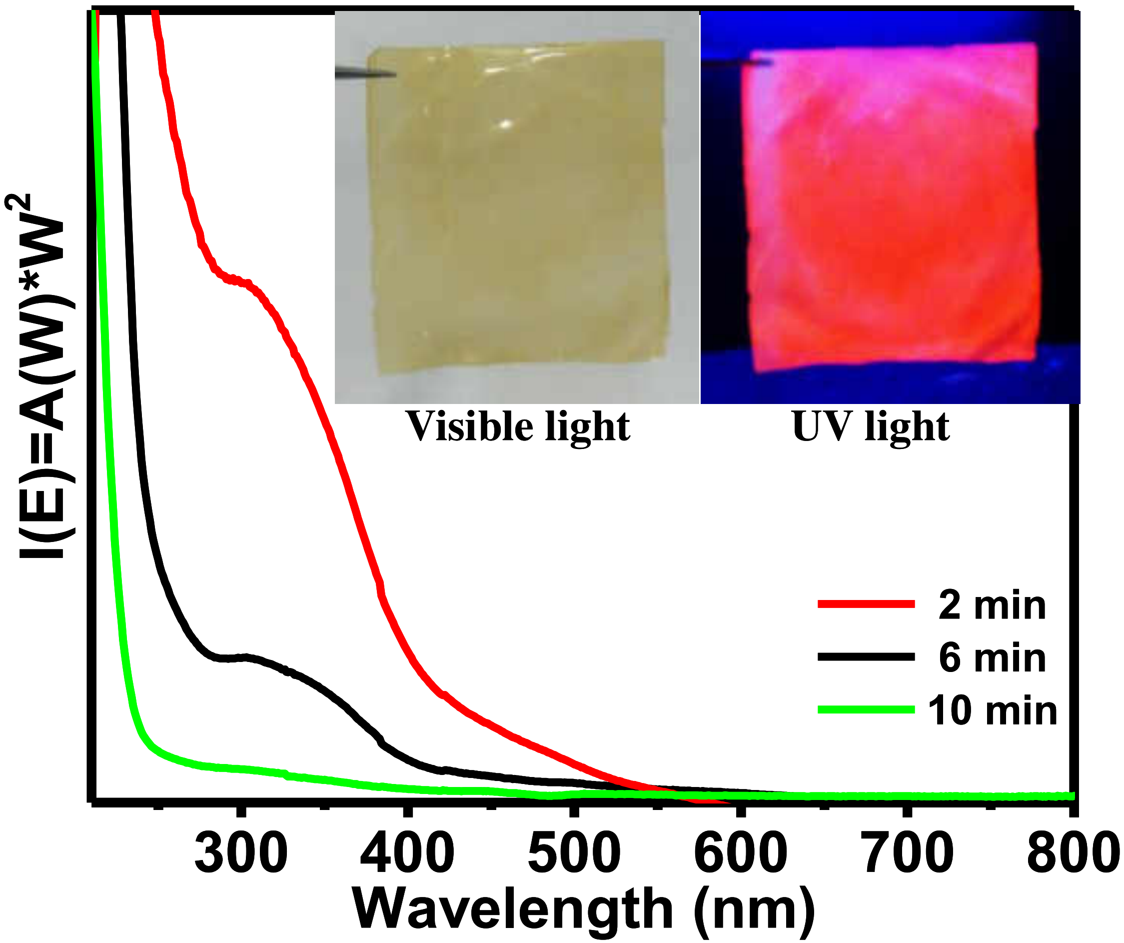


Recombinant Arsenite Oxidase NT-26 Aio

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

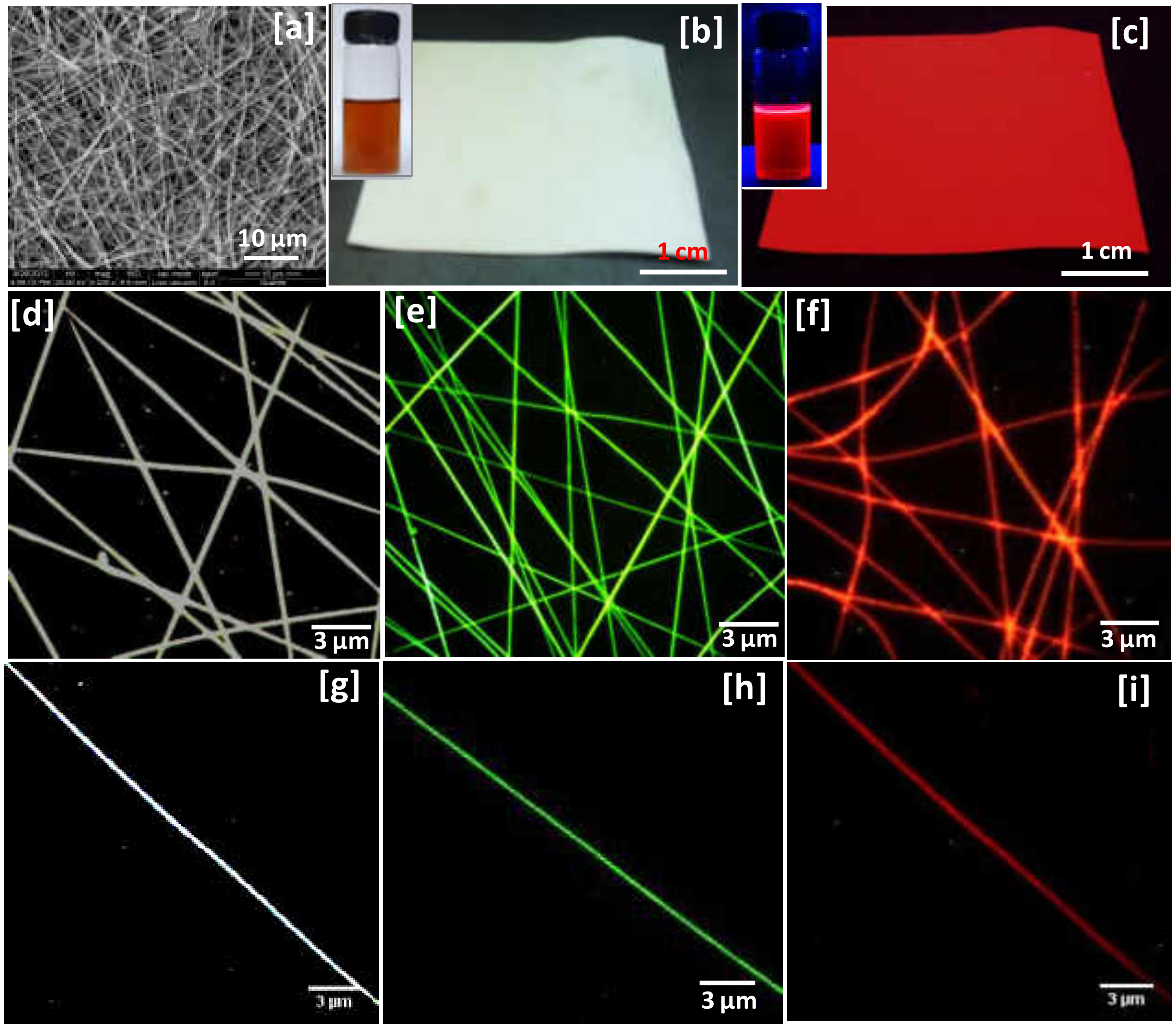
Bio-nano Consulting & Imperial College, London

Cluster-based metal ion sensing



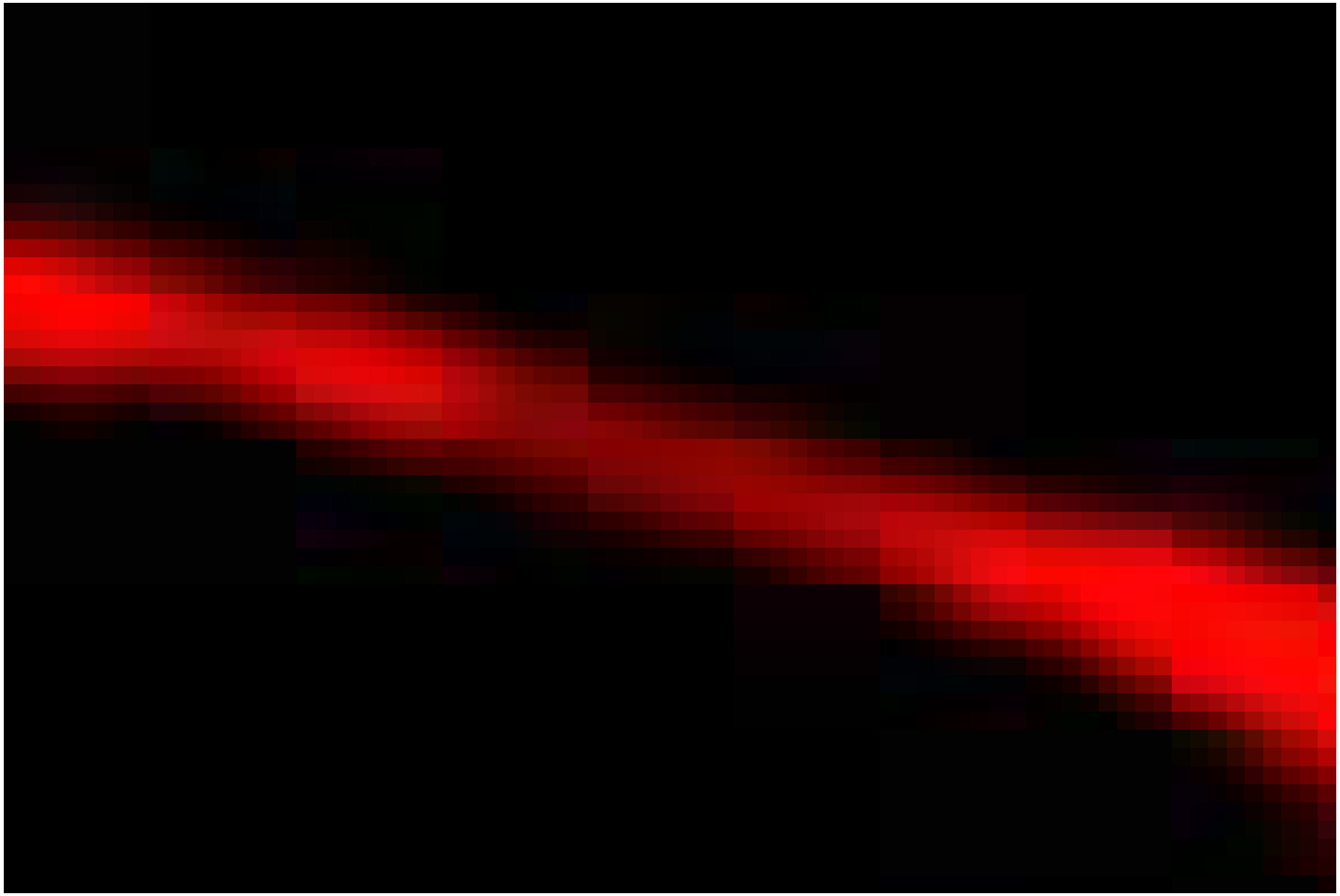
Decrease in the absorption of Au_{15} as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

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

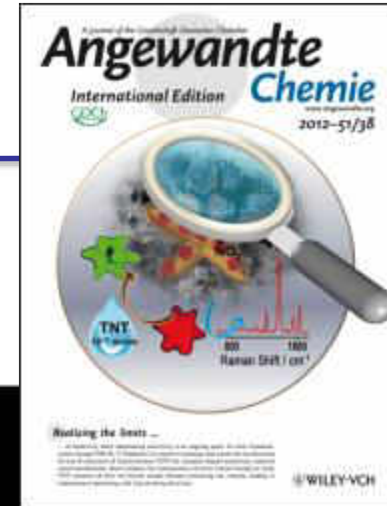


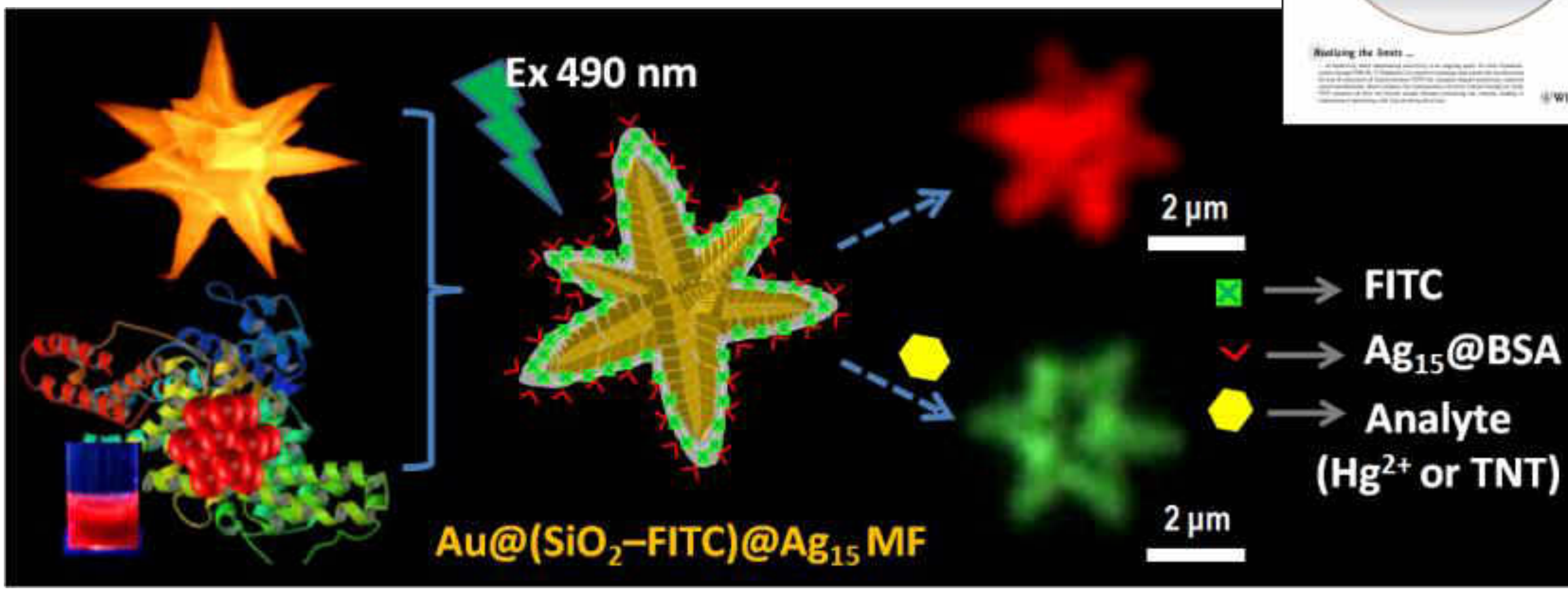
Atanu Ghosh et al. Anal. Chem. 2014.

Mercury quenching experiment using nanofiber



Sub-zeptomolar detection





Featured in:

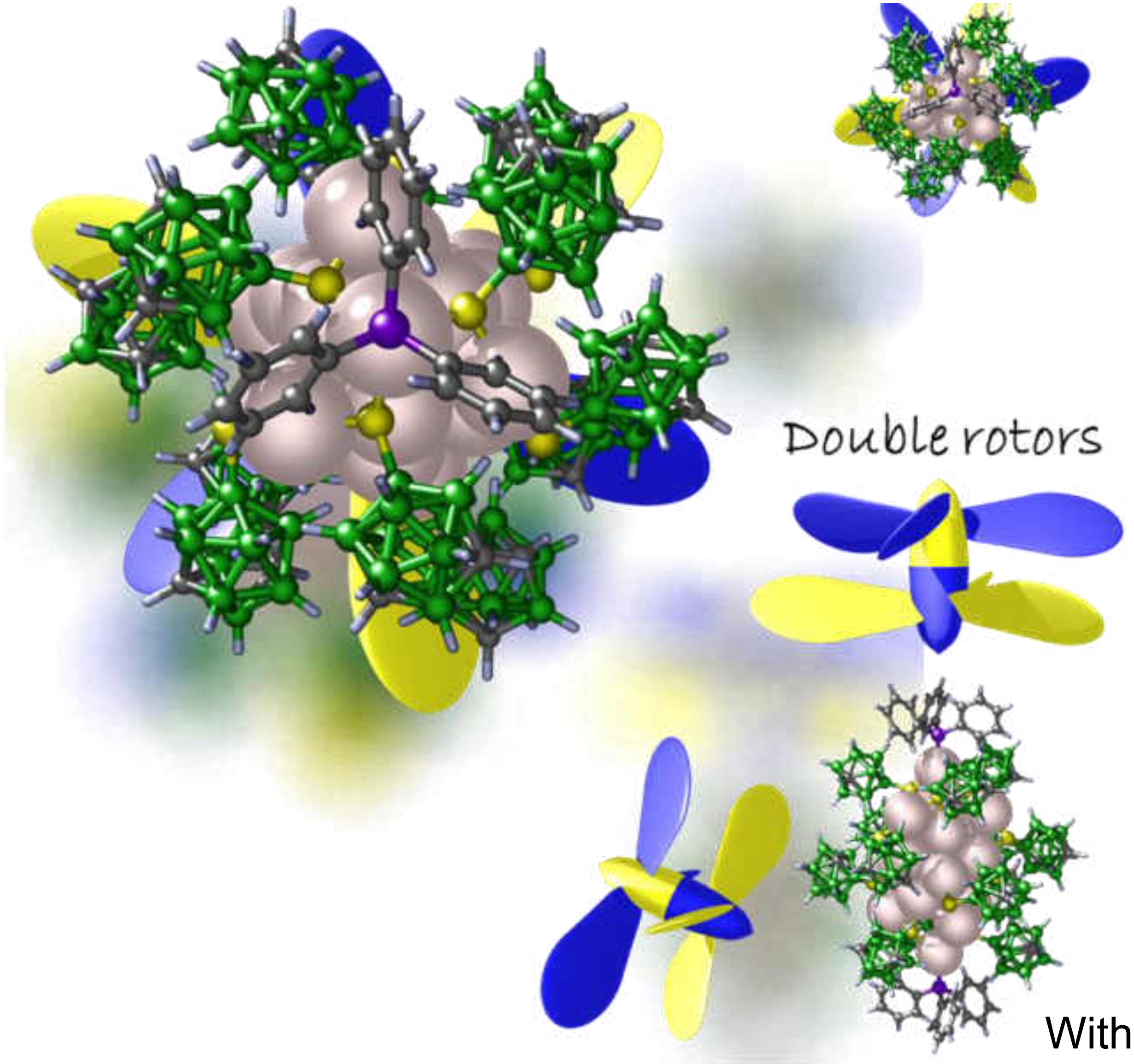
The Hindu, Telegraph, Times of India, etc.

C&E News

and many others

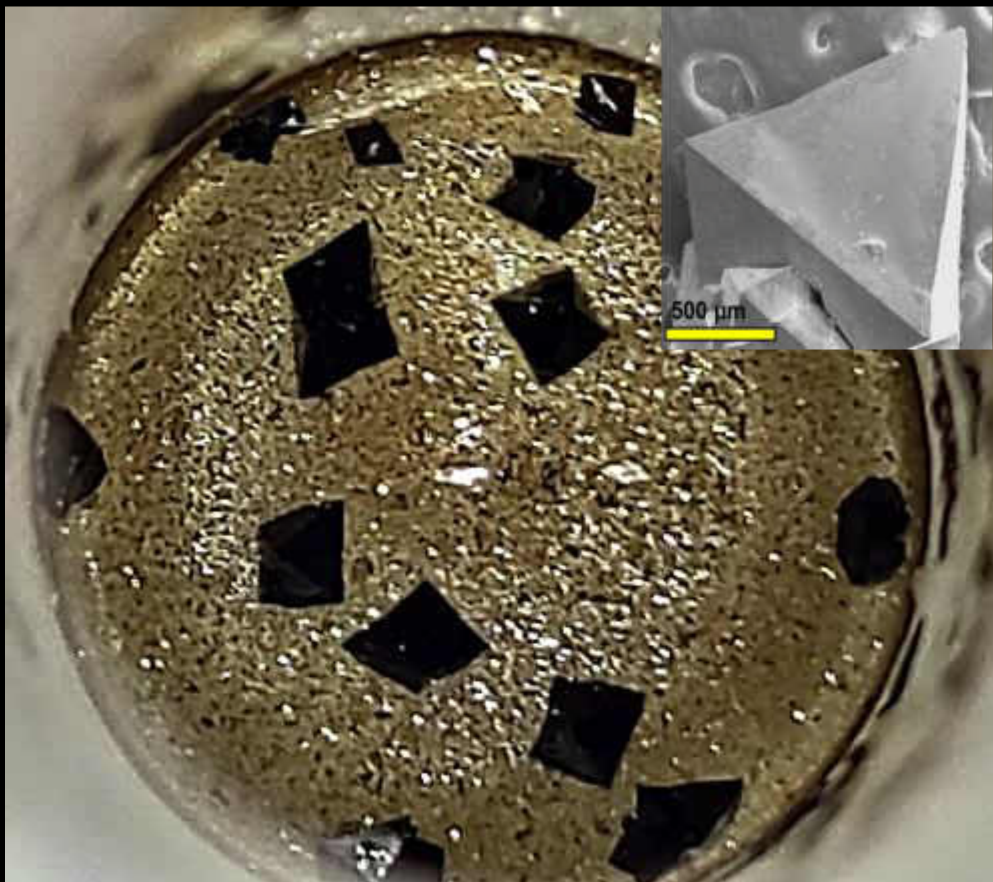
Ammu Mathew, et al. Angew. Chem. Int. Ed. 2012

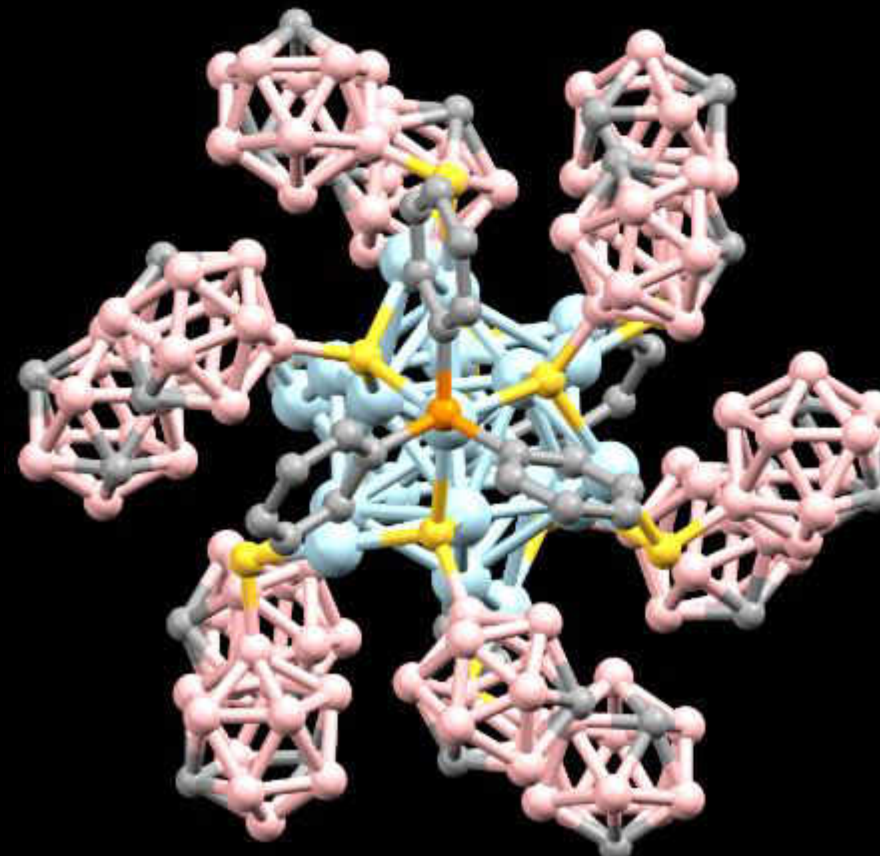
Carborane-thiol protected silver nanomolecule



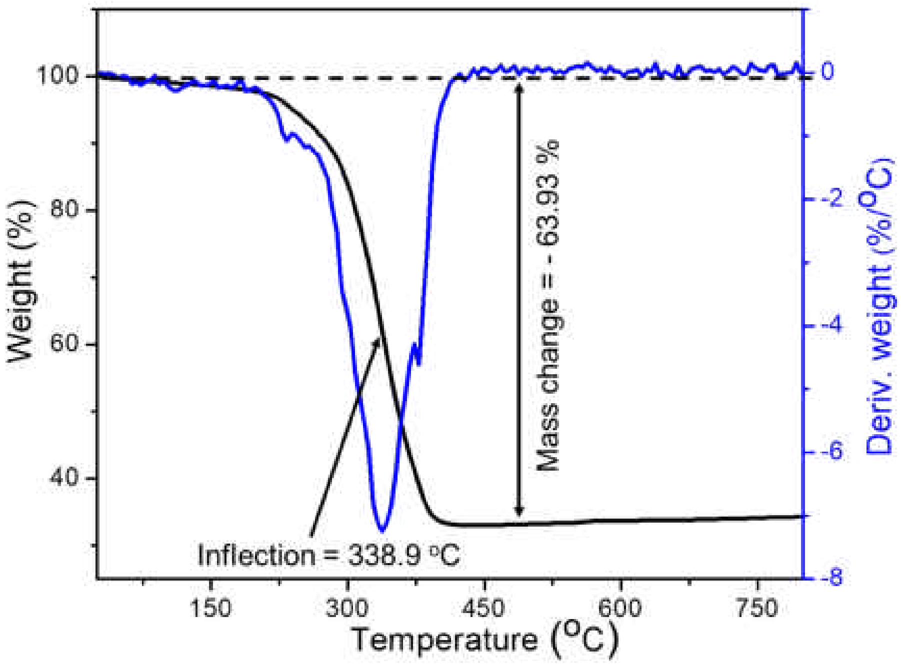
With Tomas Base

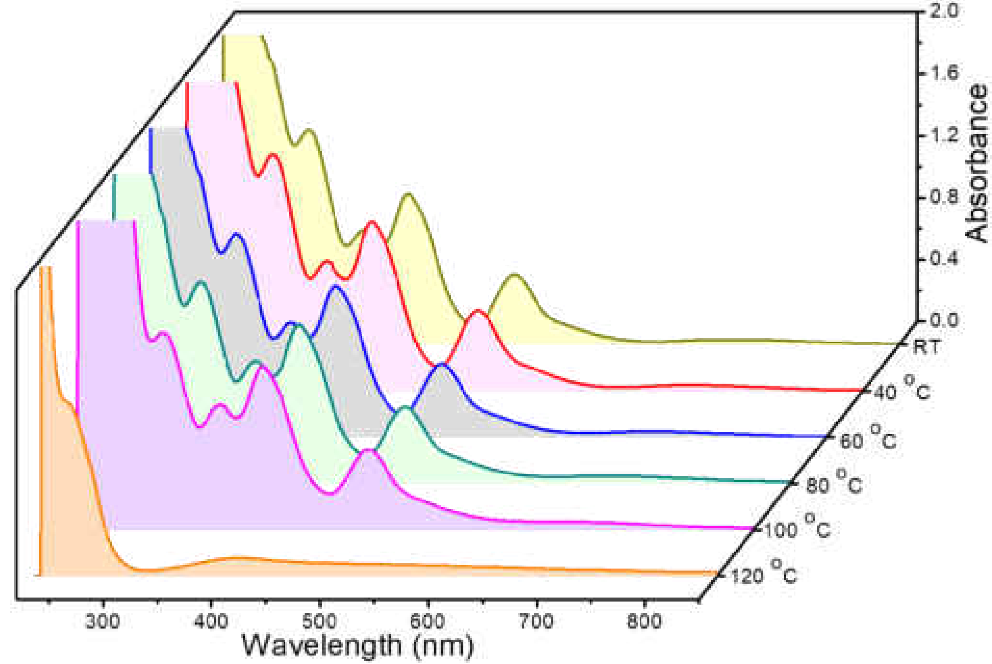
Jana *et*. *al*, Inorganic Chemistry (2022)


500 µm



Thermal stability

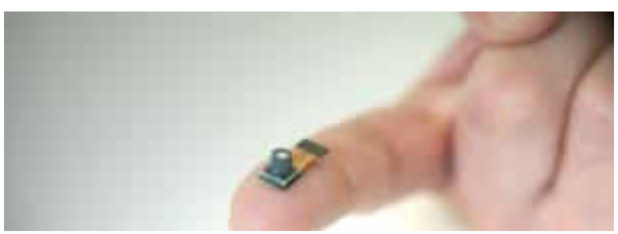




Sensors and new opportunities

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

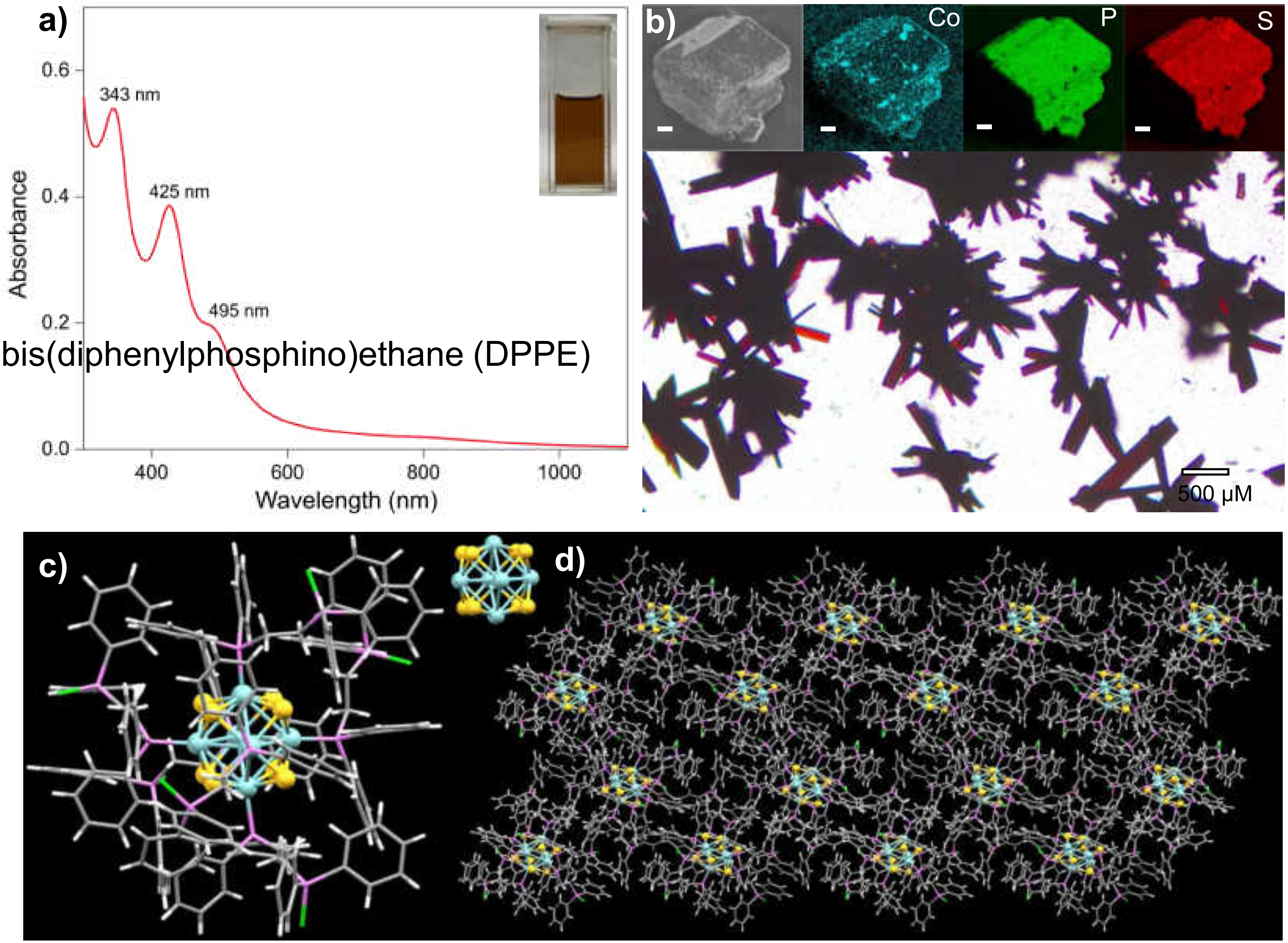
Ultra compact Low Cost Spectral Sensor Module
~ Billions units (? 2027)



Water quality measurement – In the pipeline

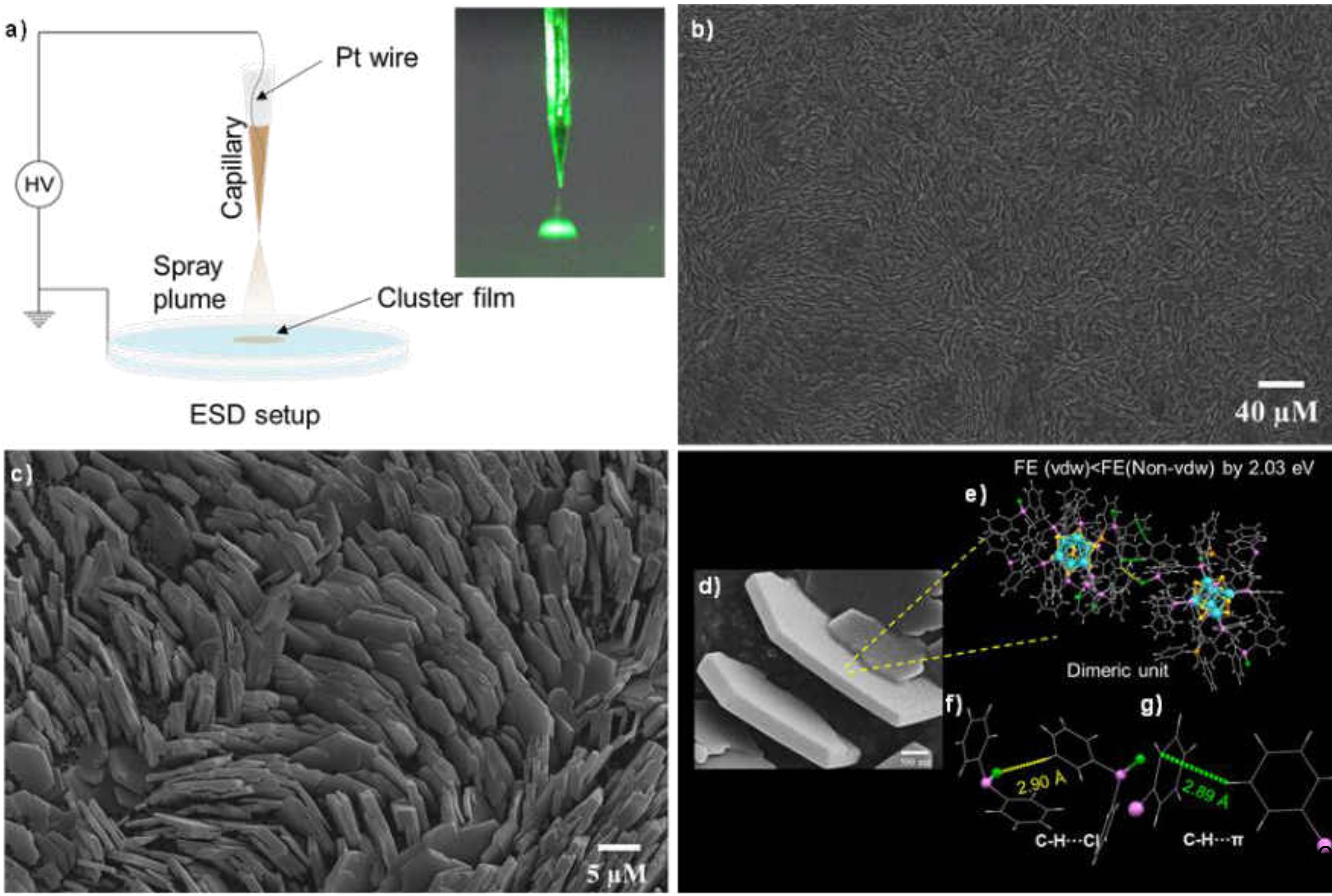
nanoλ

New electrodes - Aligned nanoplates of Co_6S_8

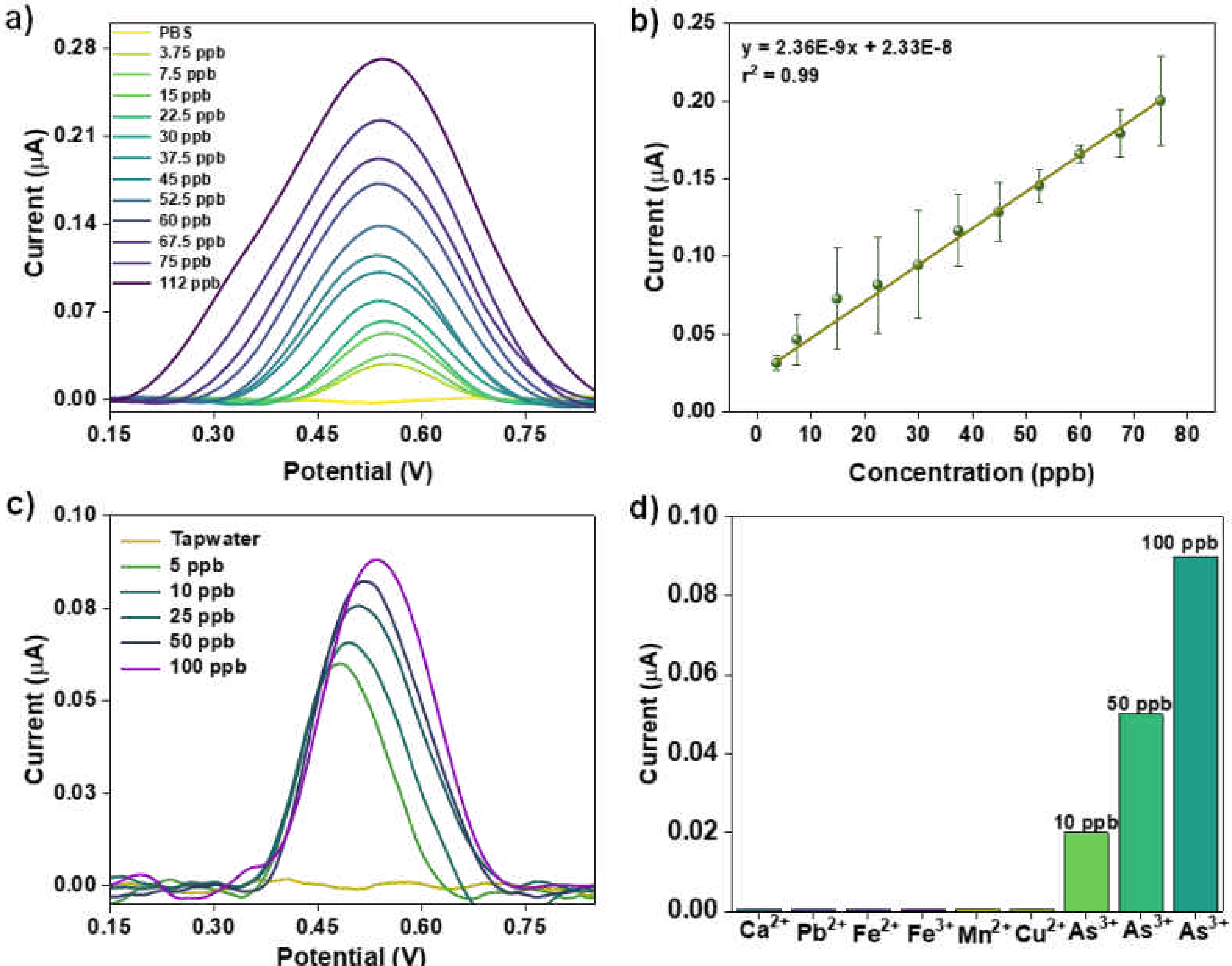


1,2-bis(diphenylphosphino)ethane (DPPE)

Electrospray deposition

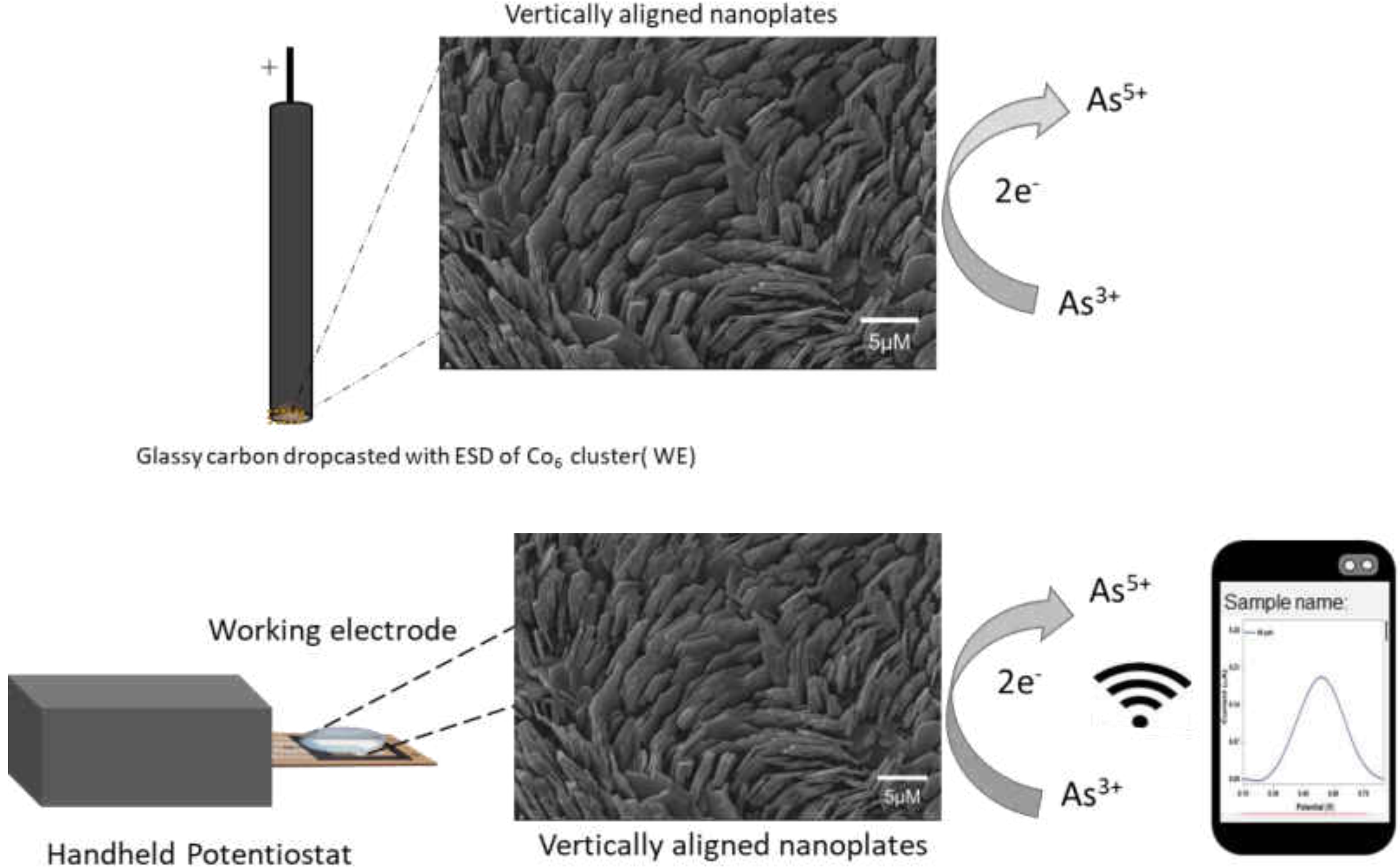


Sensing



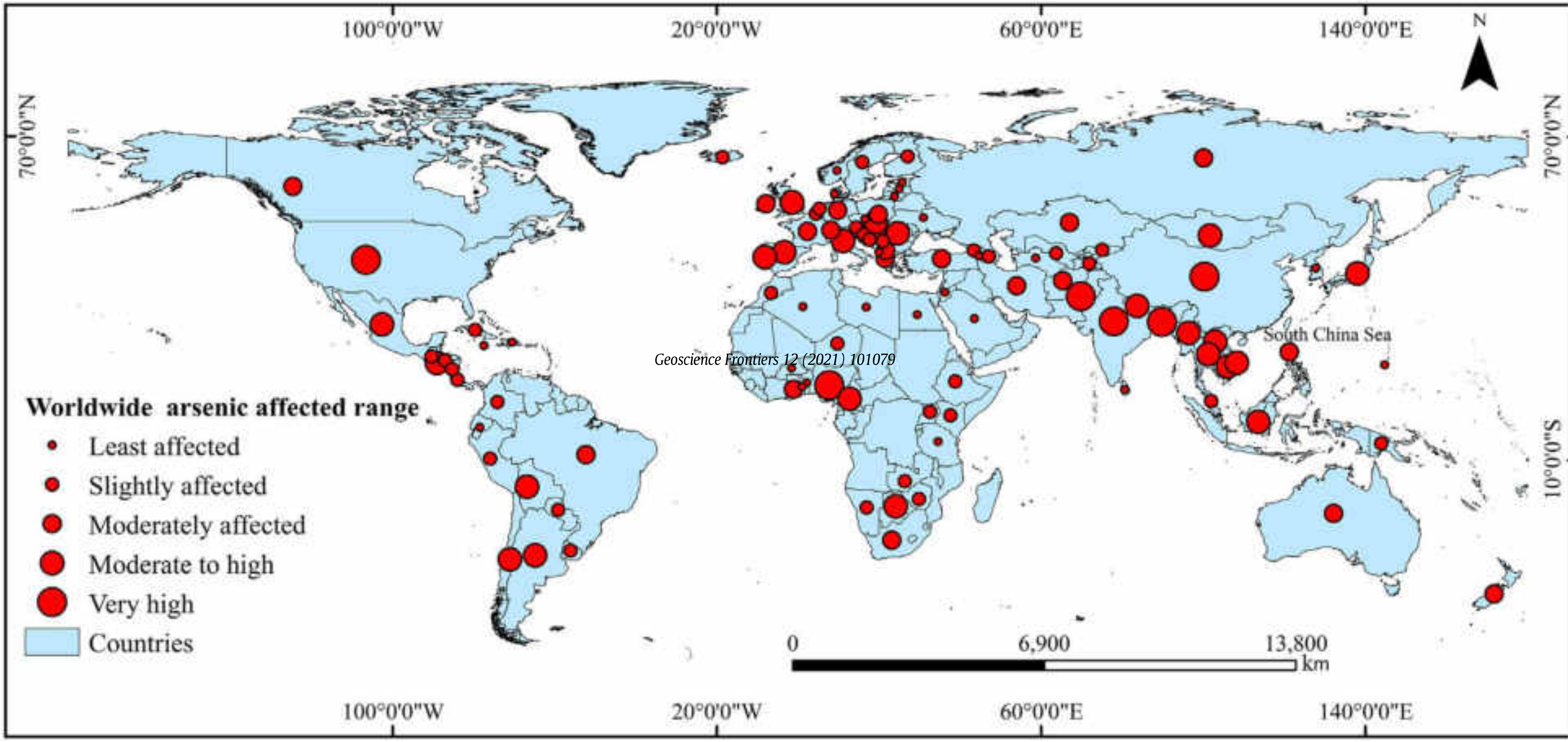
a)
PBS
3.75 ppb
7.5 ppb
15 ppb
22.5 ppb
30 ppb
37.5 ppb
45 ppb
52.5 ppb
60 ppb
67.5 ppb
75 ppb
112 ppb
Current (μA)
0.00
0.07
0.14
0.21
0.28
0.15
0.30
0.45
0.60
0.75
Potential (V)
b)
y = 2.36E-9x + 2.33E-8
r² = 0.99
Current (μA)
0.00
0.05
0.10
0.15
0.20
0.25
0
10
20
30
40
50
60
70
80
Concentration (ppb)
c)
Tapwater
5 ppb
10 ppb
25 ppb
50 ppb
100 ppb
Current (μA)
0.00
0.03
0.05
0.08
0.10
0.15
0.30
0.45
0.60
0.75
Potential (V)
d)
Current (μA)
0.00
0.02
0.04
0.06
0.08
0.10
10 ppb
50 ppb
100 ppb
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

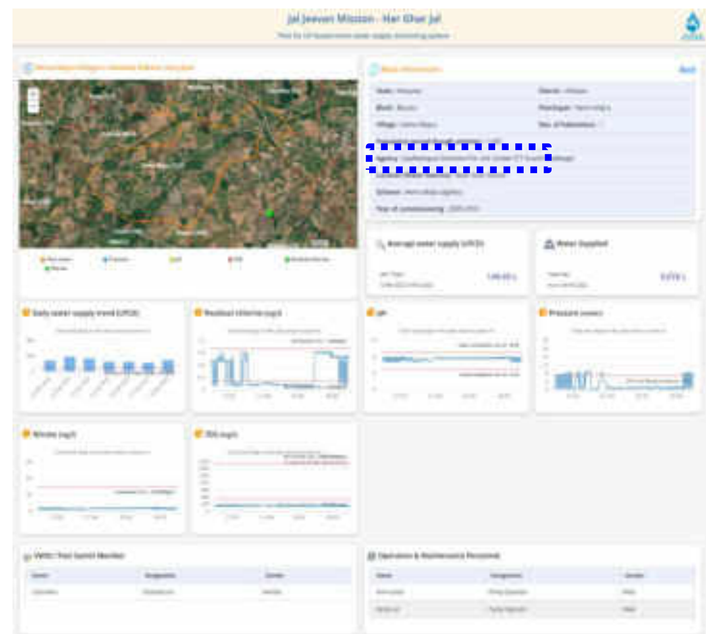


E. Shaji, M. Santosh, K. V. Sarath, Pranav Prakash, V. Deepch and B. V. Divya, Geoscience Frontiers, 12 (2021) 101079.

India’s water is being monitored

IITM/IISc

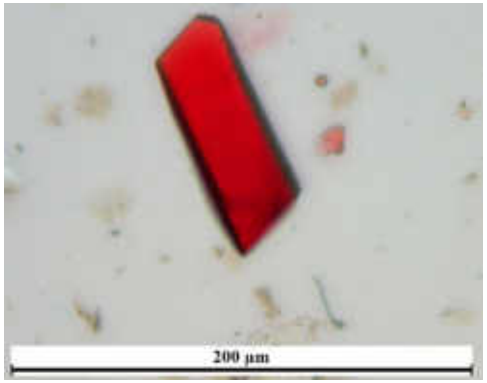
Installations made by four companies



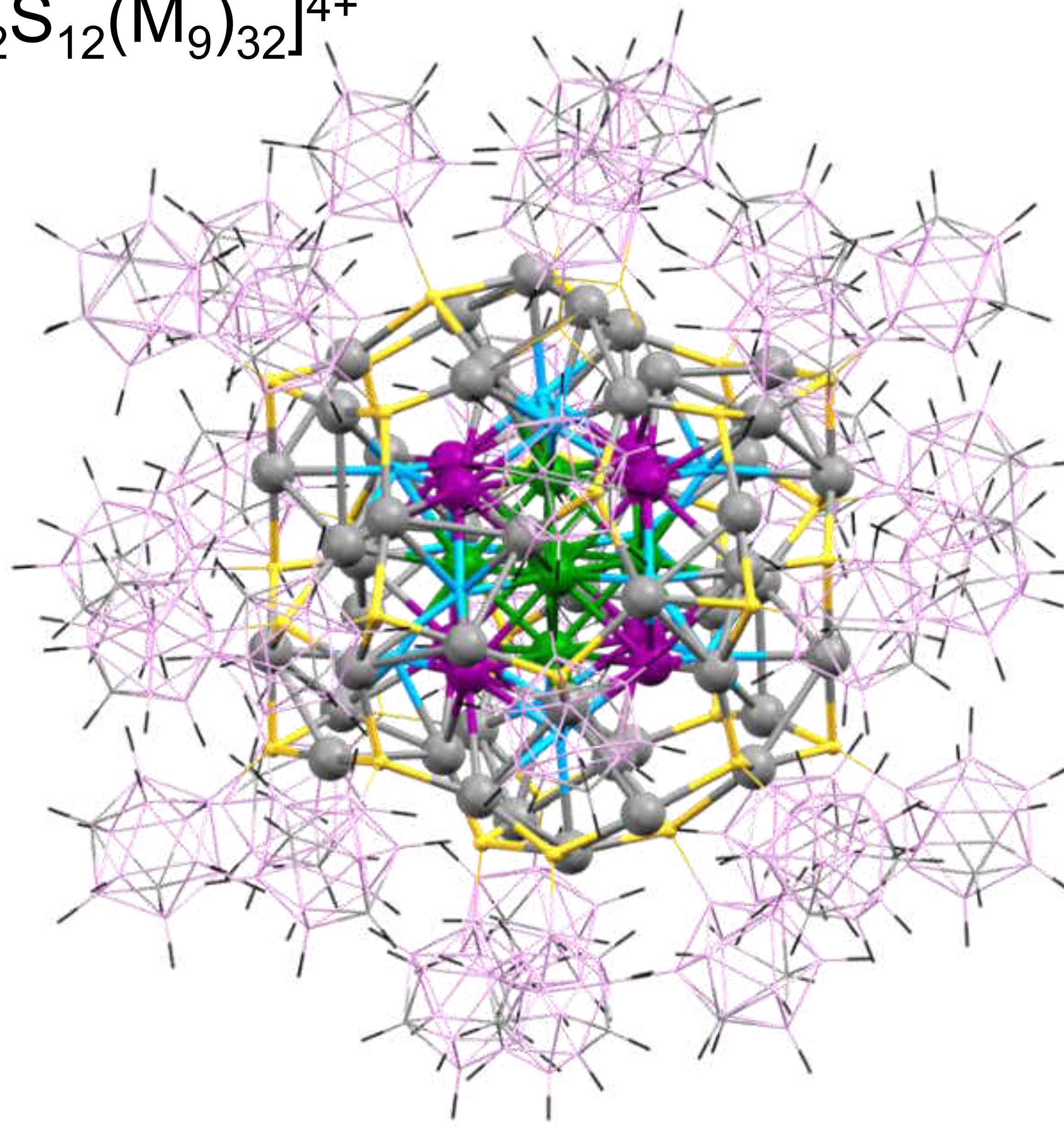
International Centre for Clean Water

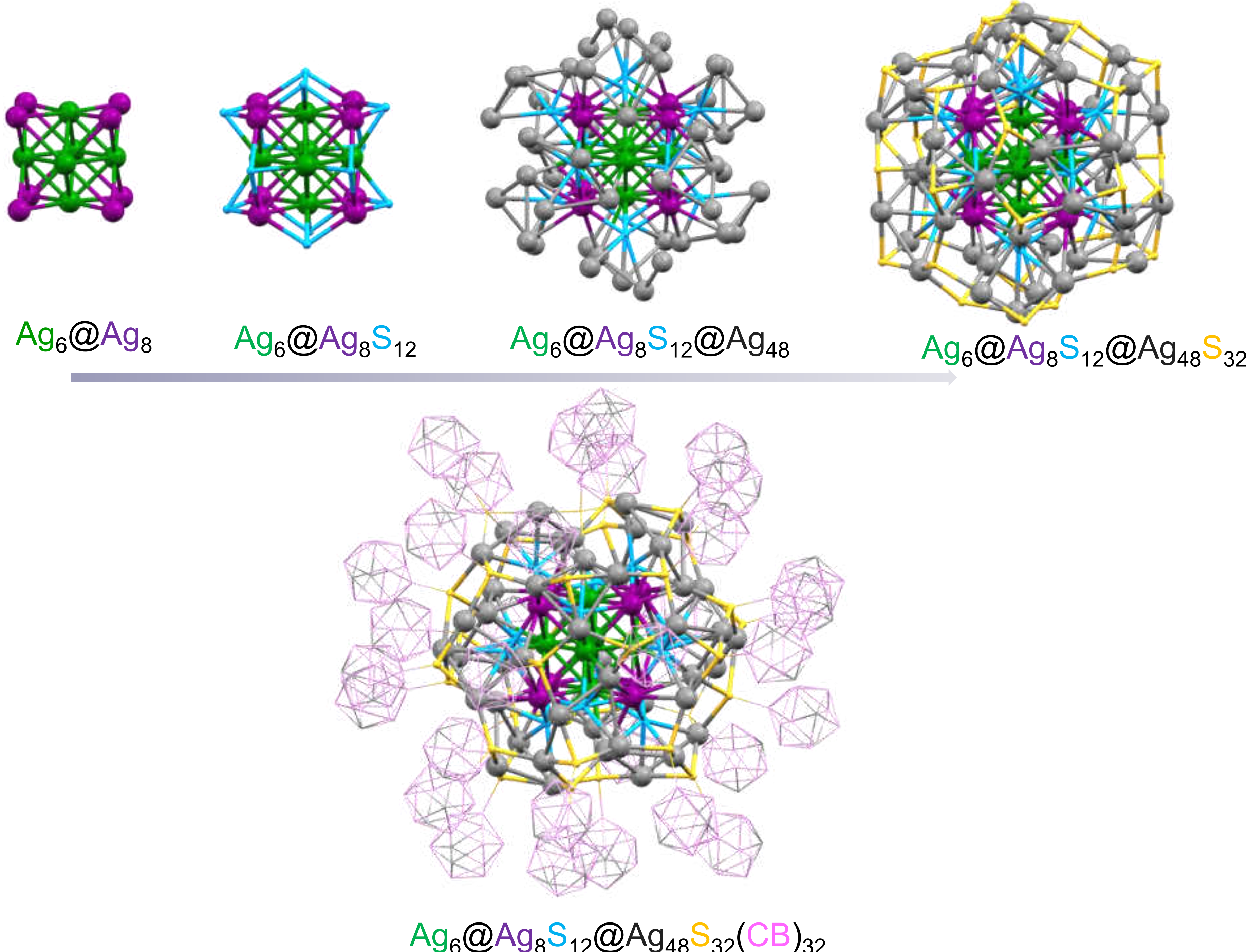
Very new science

Unprecedented Polymorphism in Carborane-thiol Protected 2e-superatomic Spherical $[Ag_{62}S_{12}(M_9)_{32}]^{4+}$ Nanocluster

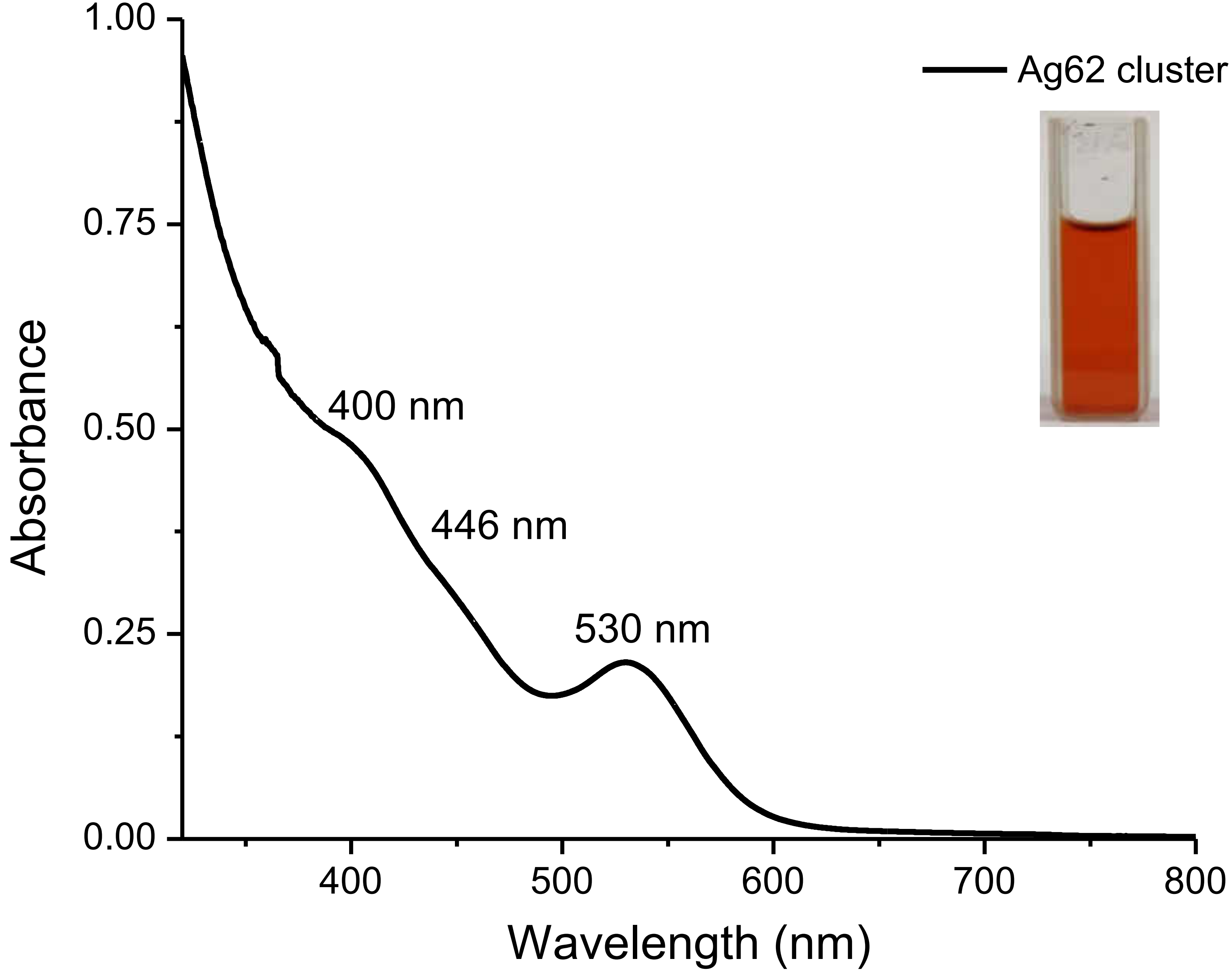


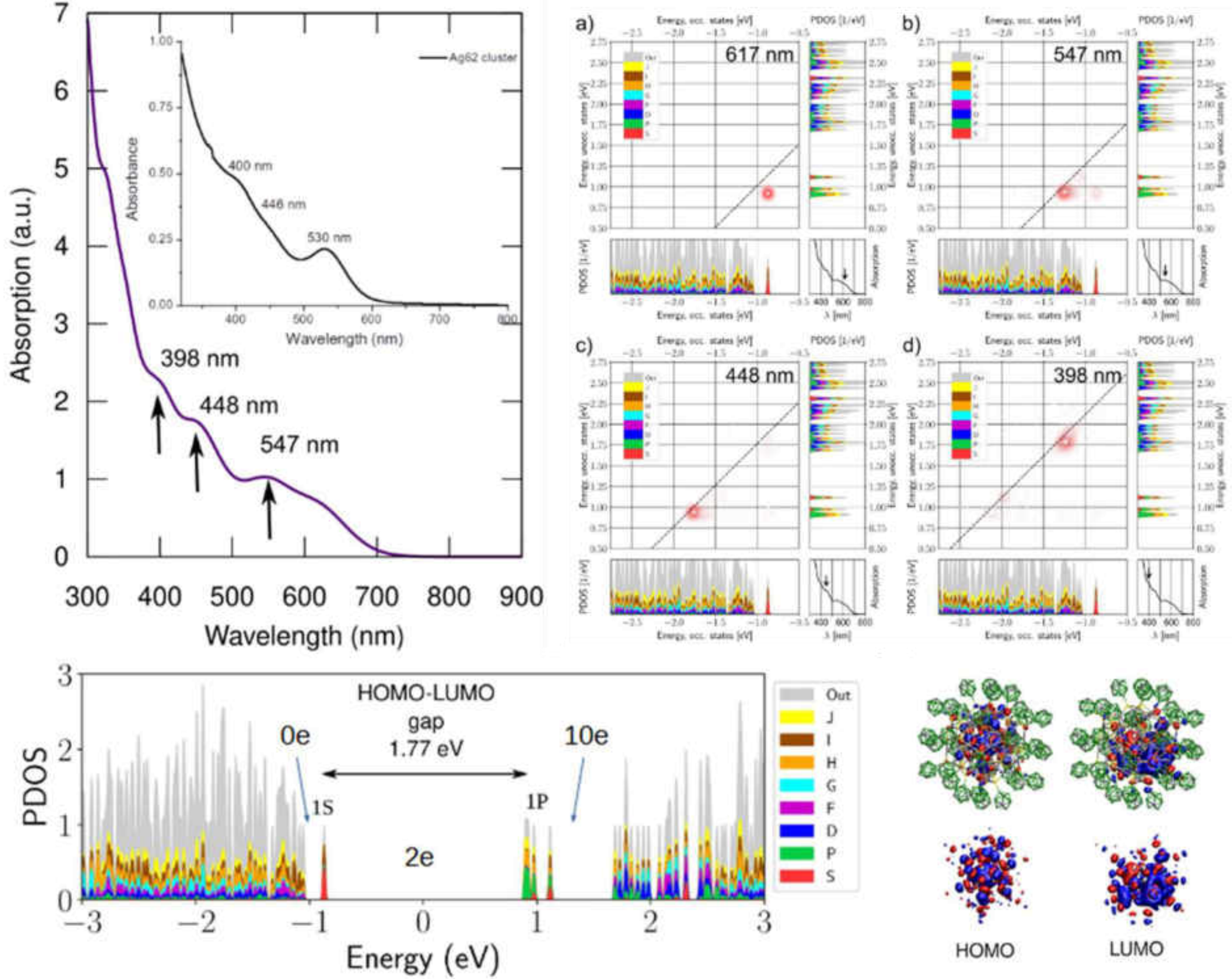
$[Ag_{62}S_{12}(M_9)_{32}]^{4+}$




$Ag_6@Ag_8$
$Ag_6@Ag_8S_{12}$
$Ag_6@Ag_8S_{12}@Ag_{48}$
$Ag_6@Ag_8S_{12}@Ag_{48}S_{32}$
$Ag_6@Ag_8S_{12}@Ag_{48}S_{32}(CB)_{32}$

Absorption spectrum

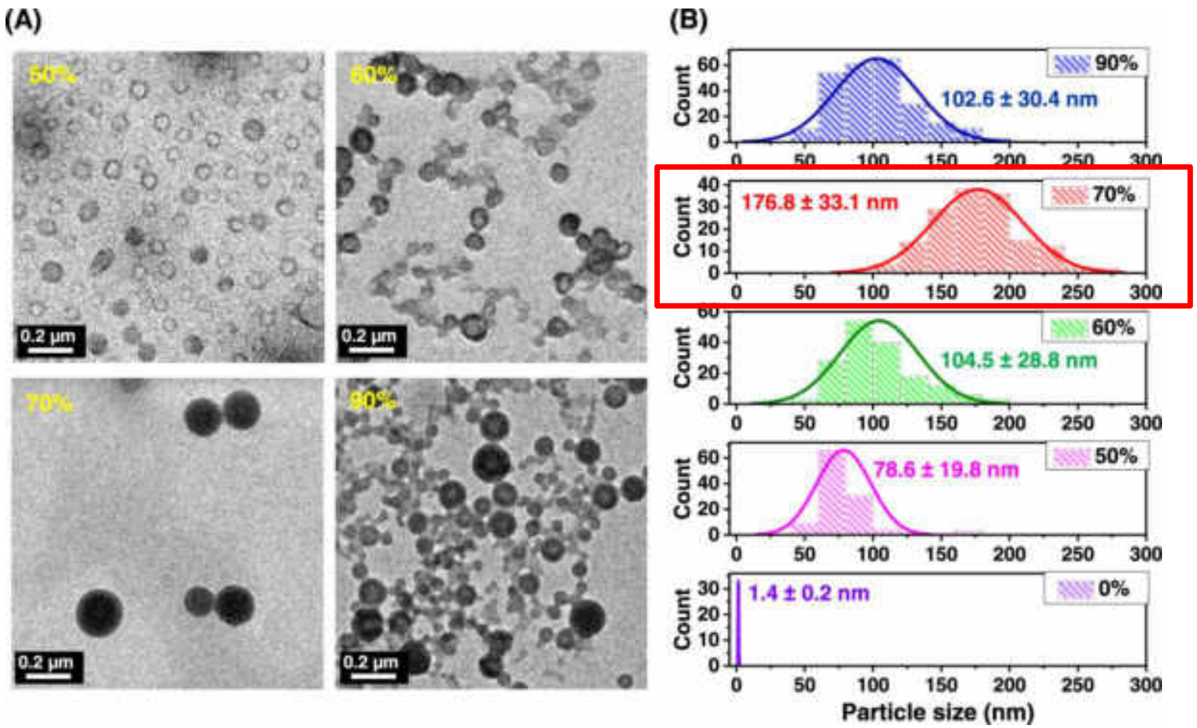




Absorption (a.u.)
Wavelength (nm)
398 nm
448 nm
547 nm
Absorbance
Wavelength (nm)
Ag62 cluster
400 nm
446 nm
530 nm
a)
617 nm
b)
547 nm
c)
448 nm
d)
398 nm
Energy, occ. states [eV]
Energy, unocc. states [eV]
PDOS [1/eV]
Absorption
λ [nm]
PDOS
Energy (eV)
HOMO-LUMO
gap
1.77 eV
0e
10e
1S
1P
2e
Out
J
I
H
G
F
D
P
S
HOMO
LUMO

Cluster aggregates

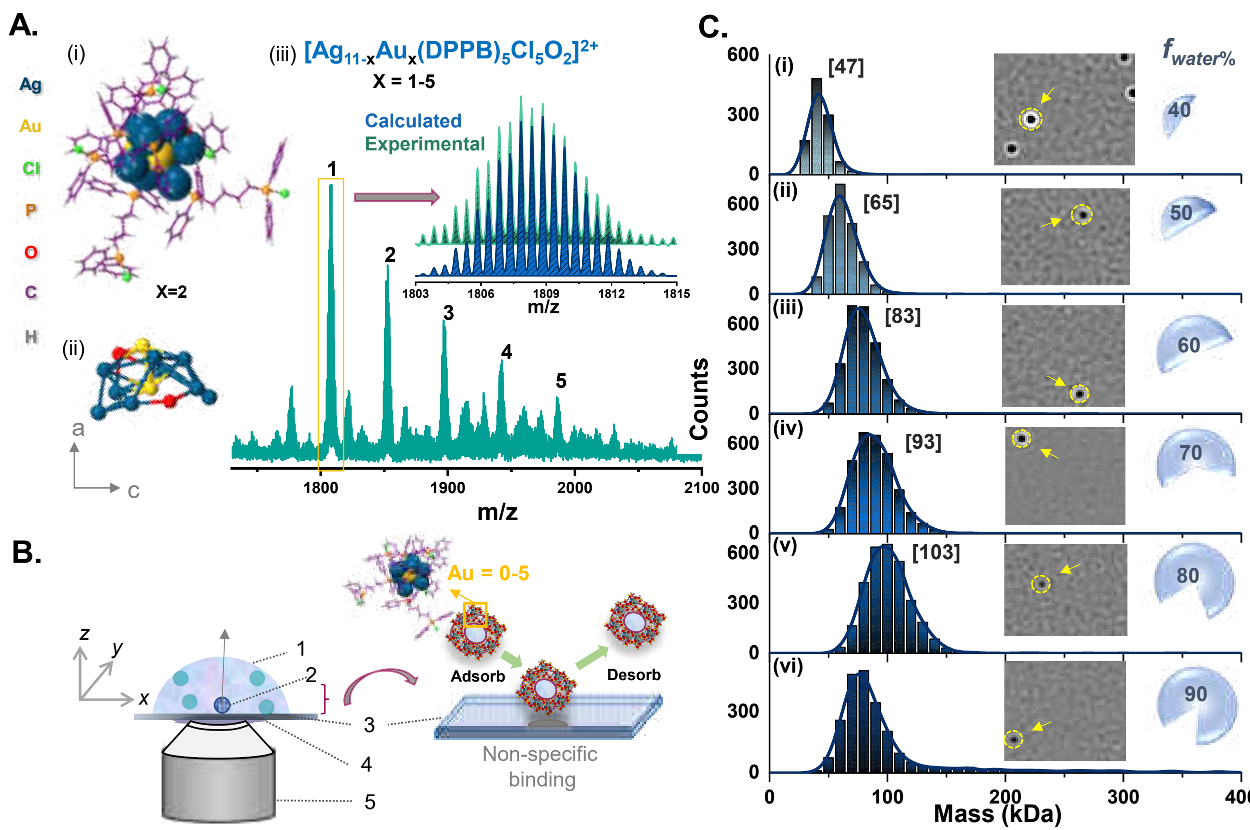
$[Ag_{11-x}Au_x(DPPB)_5Cl_5O_2]$
Dynamic light scattering



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

Madhuri Jash, et. al., Chem. Mater., 35 (2023) 313-326

Mass photometry

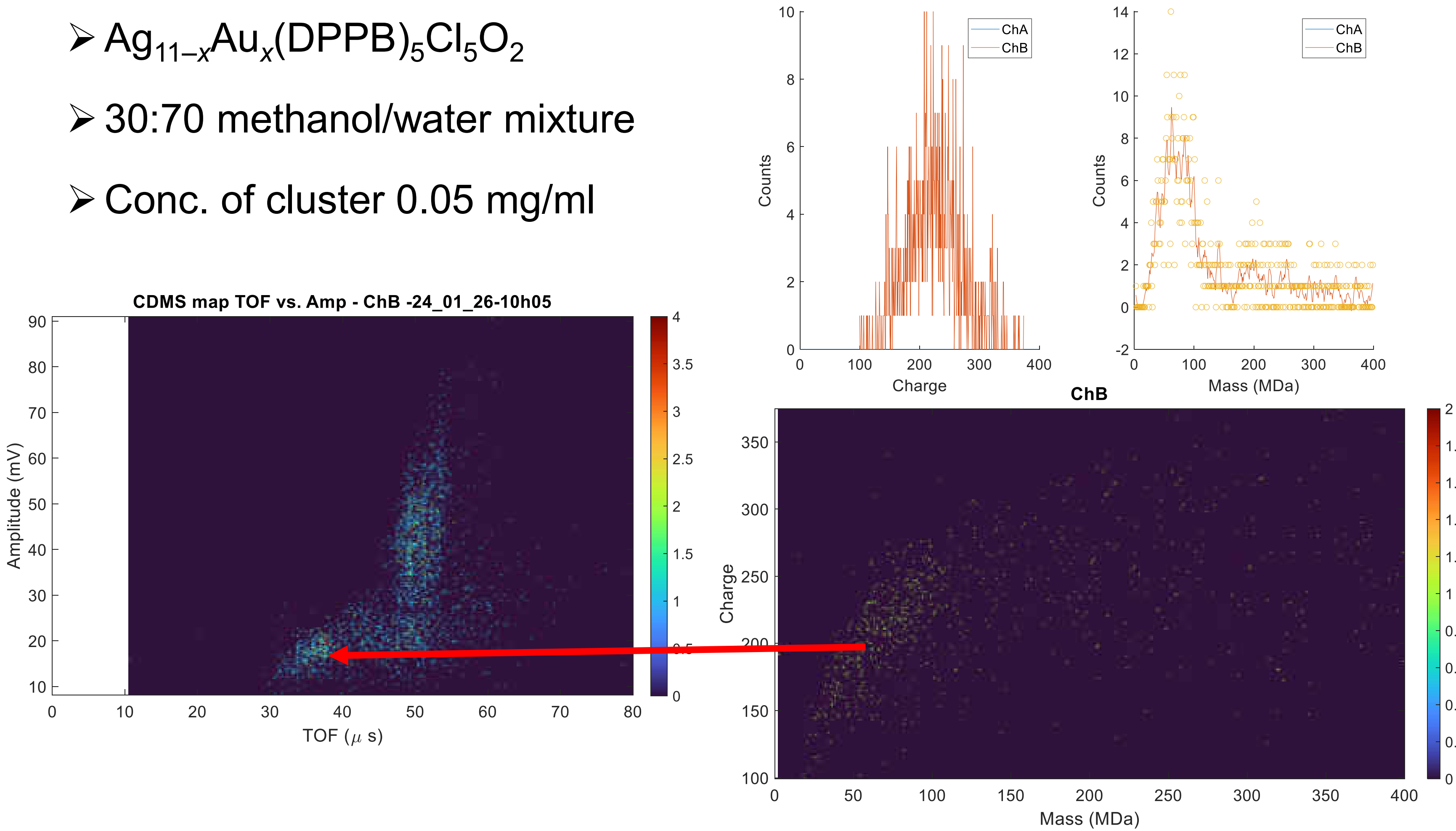


A (i) Calculated structure (x = 2), (ii) the metal, Ag11-xAux, core (x = 2), and (iii) ESI MS of $[Ag_{11-x}Au_x(DPPB)_5Cl_5O_2]^{2+}$ (x = 1-5) nanoclusters. In inset, calculated isotopic distribution is stacked with the experimental one. B. Concept and experimental implementation of MP. Parts in the 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. Mav are shown on the spectra as [xx]. The photographs of single-particle binding events on the glass-sol interface during each set of measurements is shown. The corresponding $f_{water\%}$ of solvent mixture is labelled on each histogram.

With Vicki Wysocki

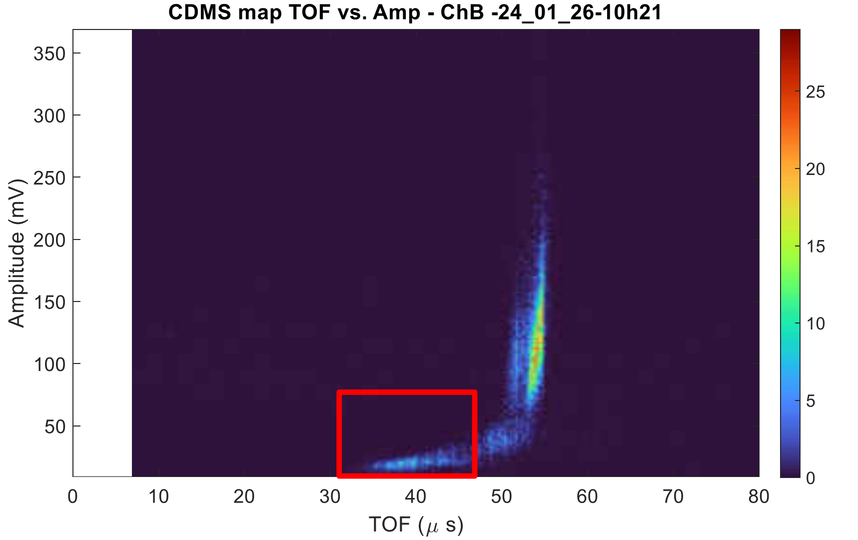
CDMS

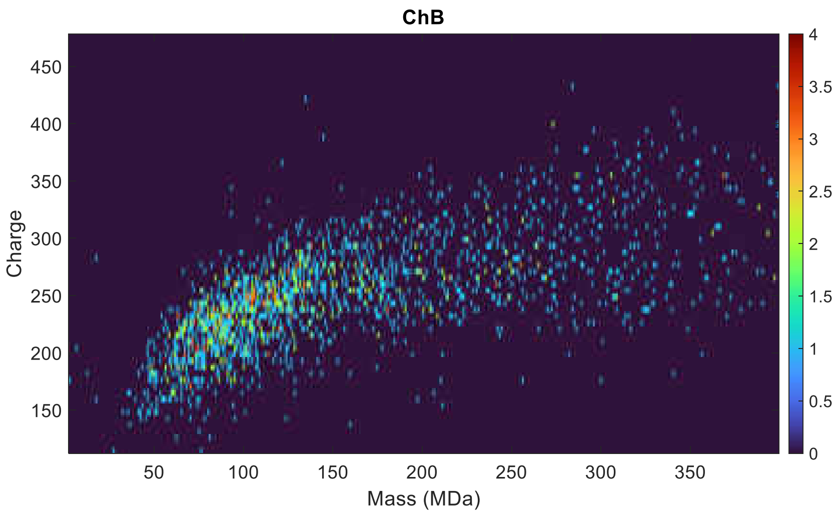
- $Ag_{11-x}Au_x(DPPB)_5Cl_5O_2$
- 30:70 methanol/water mixture
- Conc. of cluster 0.05 mg/ml

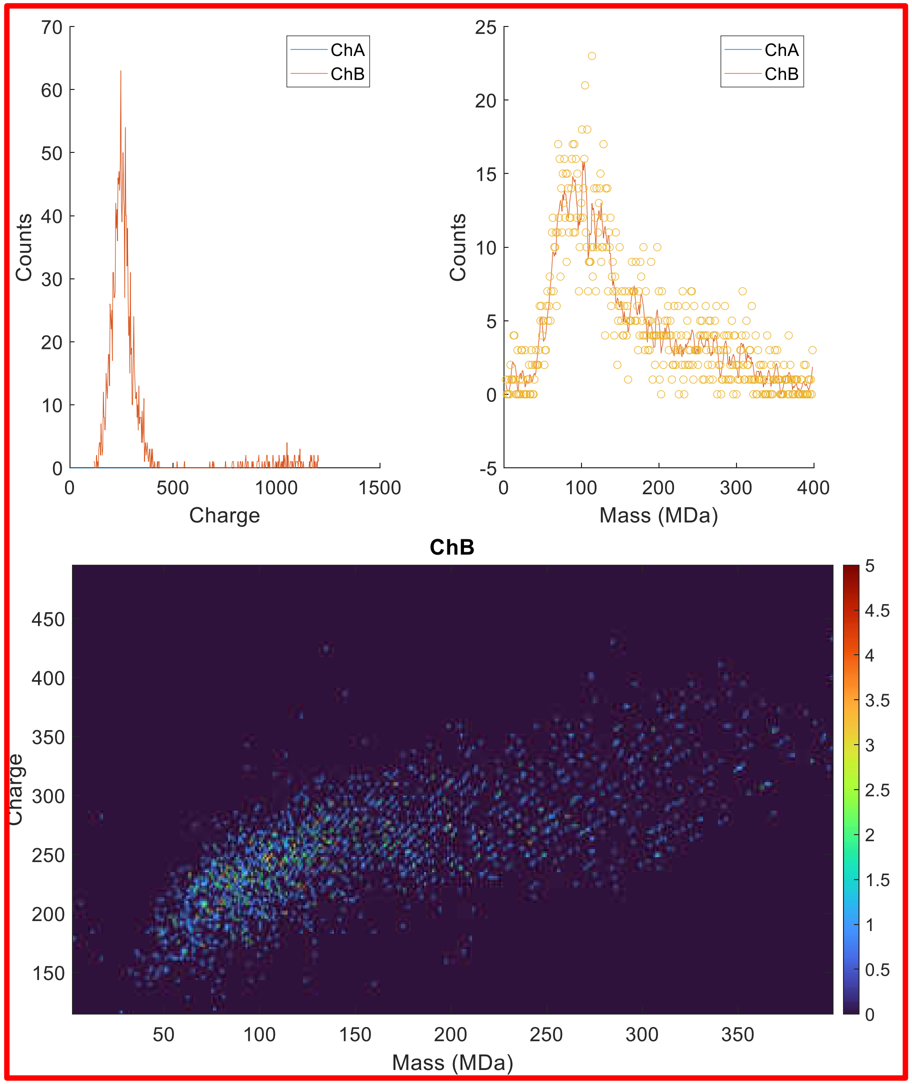


With Antoine Rodolphe, Lyon

Plasmonic nanoparticles







Molecular materials

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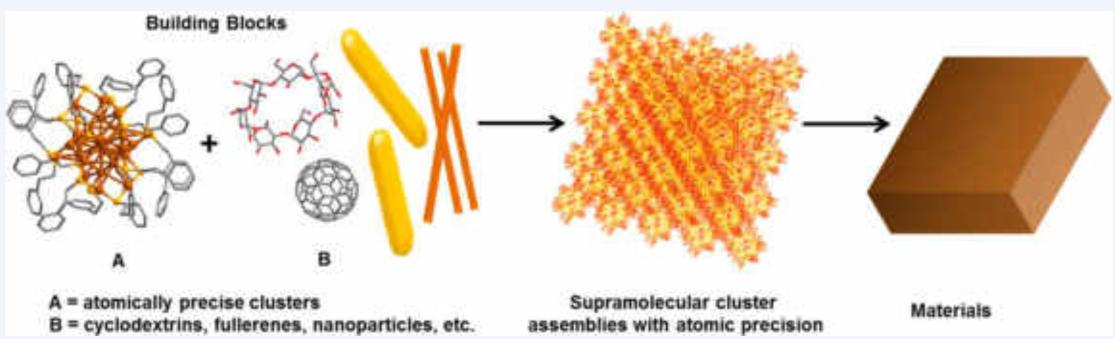
Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

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







Robin Ras


Nonappa


Tomas Base


Manfred Kappes


Olli Ikkala


Horst Hahn

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

Shiv Khanna

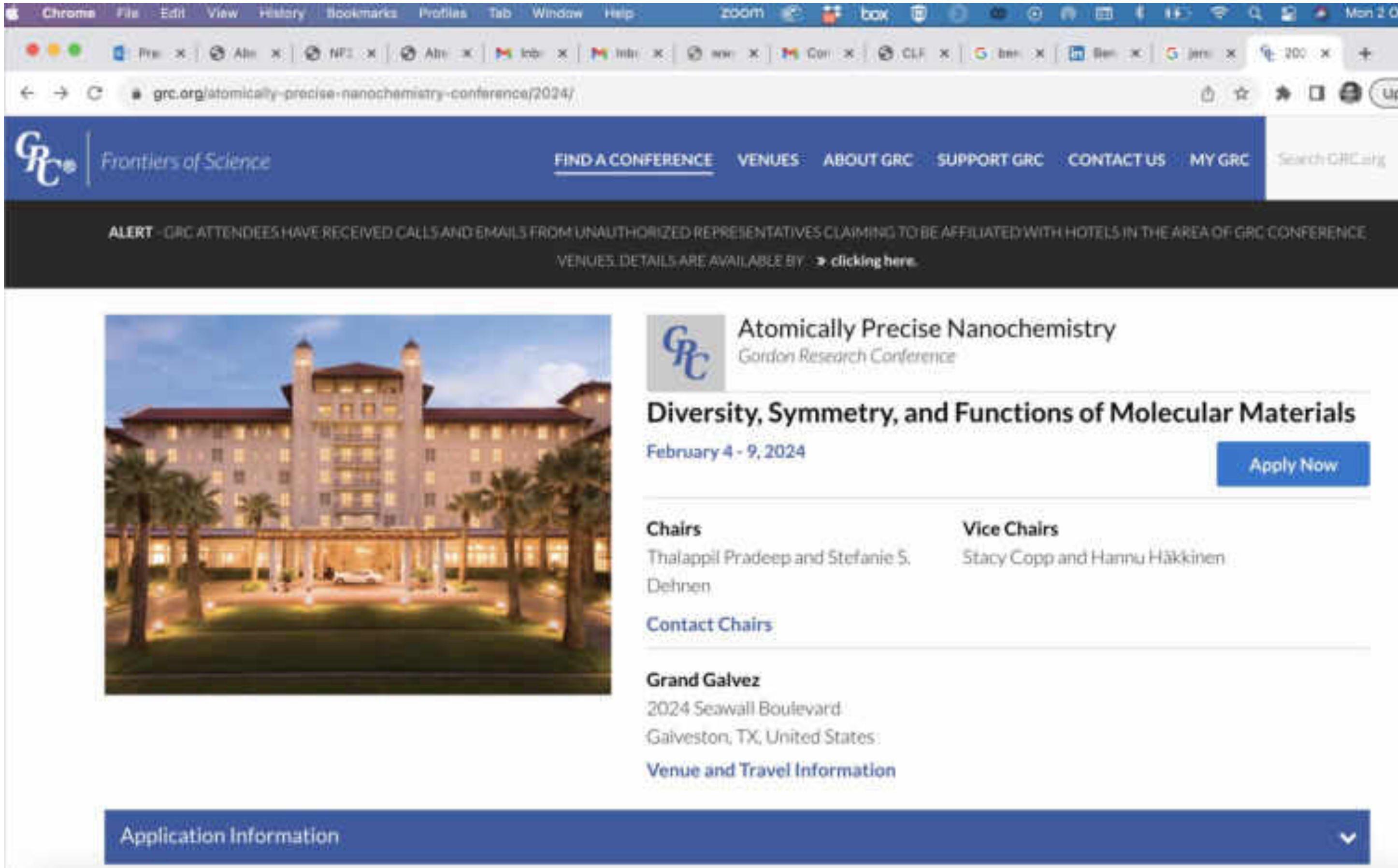

Biswarup Pathak


K. V. Adarsh


G. U. Kulkarni

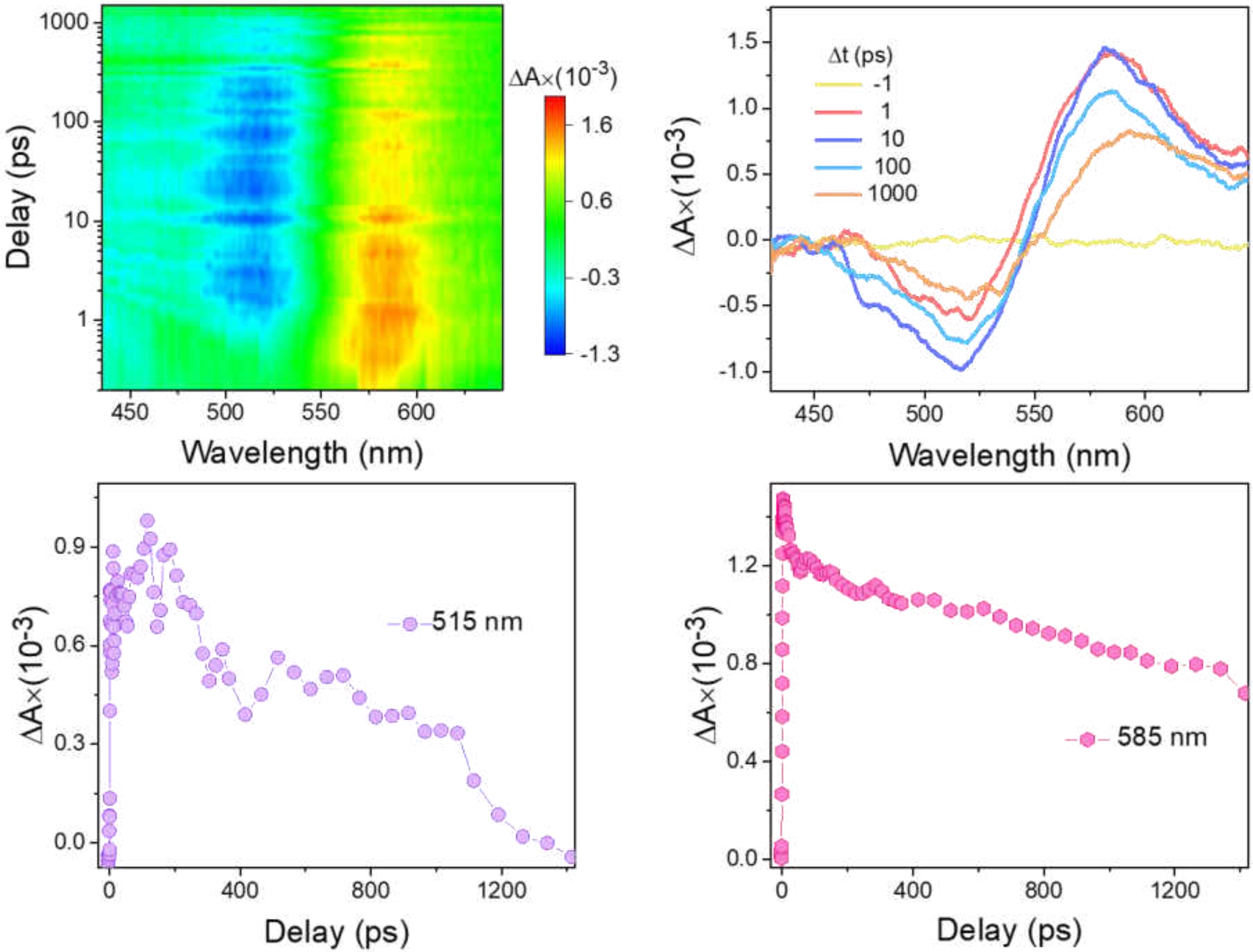

Vivek Polshettiwar


thermo scientific



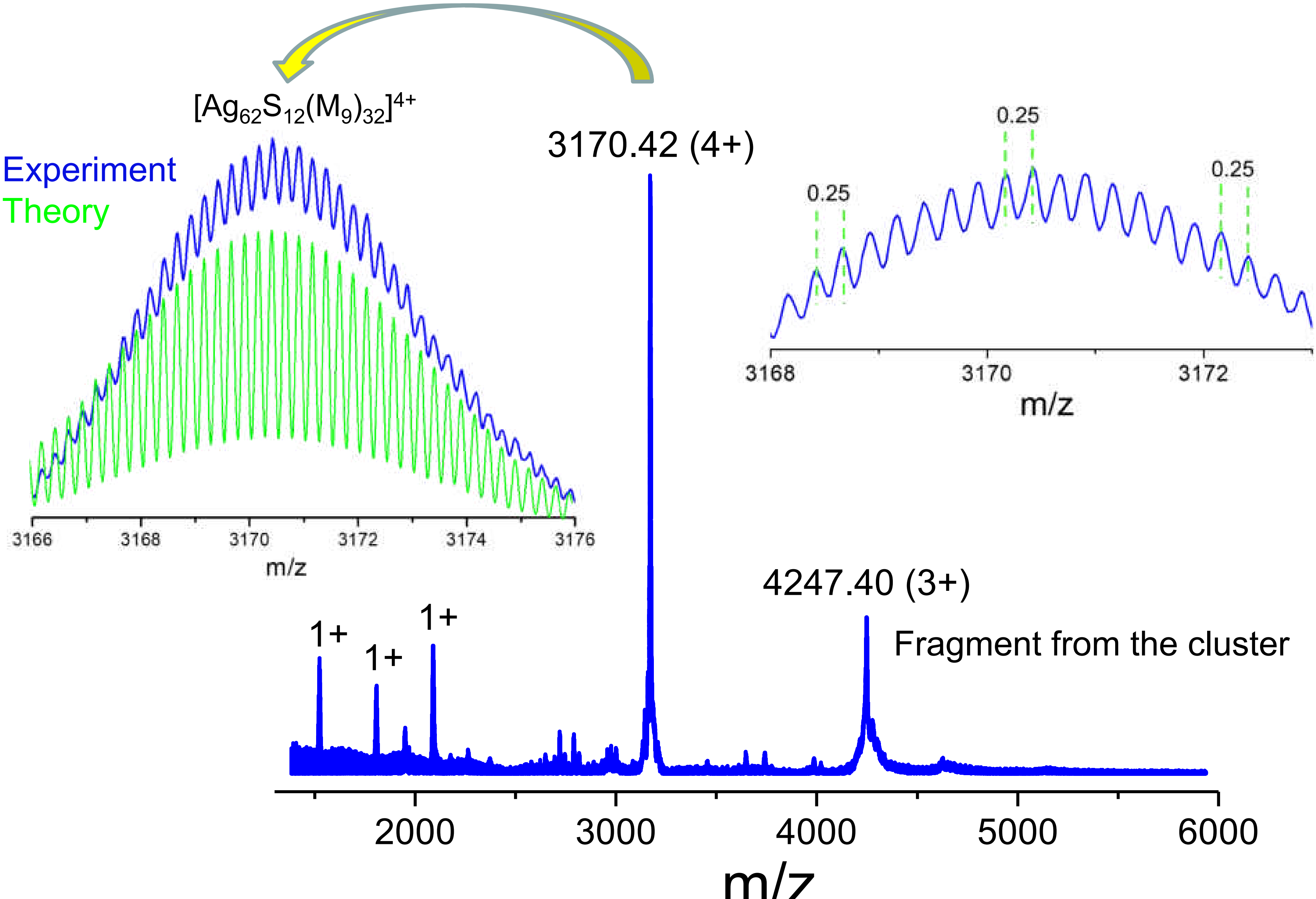
Collaborators: Tatsuya Tsukuda, Keisaku Kimura, Yuichi Negishi, Uzi Landman, Rob Whetten, Hannu Hakkinen, Robin Ras, Manfred Kappes, Horst Hahn, Tomas Base, Nonappa, Shiv Khanna, Umesh Waghmare, Chandrabhas Narayana, Giridhar U. Kulkarni, Reji Philip, Vivek Polshettiwar, R. Mukhopadhay, K. V. Adarsh,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

Thank you all



Delay (ps)
1000
100
10
1
450
500
550
600
Wavelength (nm)
ΔA×(10^-3)
1.6
0.6
-0.3
-1.3
Δt (ps)
-1
1
10
100
1000
1.5
1.0
0.5
0.0
-0.5
-1.0
ΔA×(10^-3)
515 nm
0.9
0.6
0.3
0.0
0
400
800
1200
Delay (ps)
585 nm
1.2
0.8
0.4

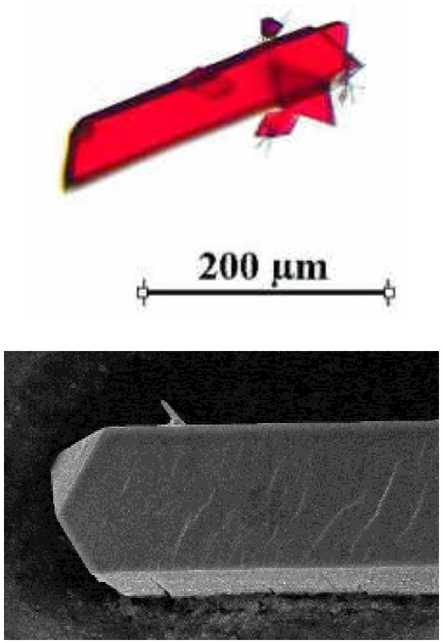
Mass spectrum of the cluster



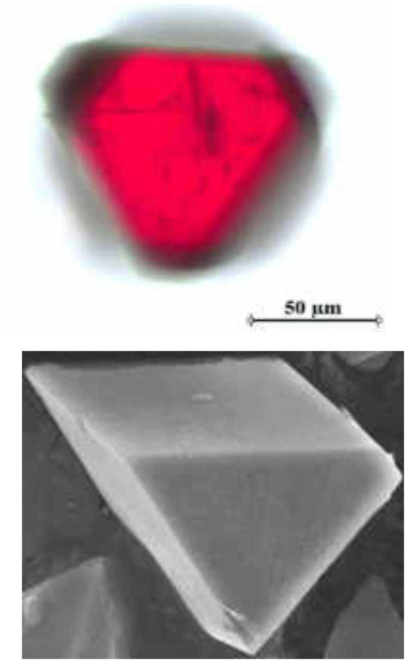
MS/MS was done

Polymorphic crystals

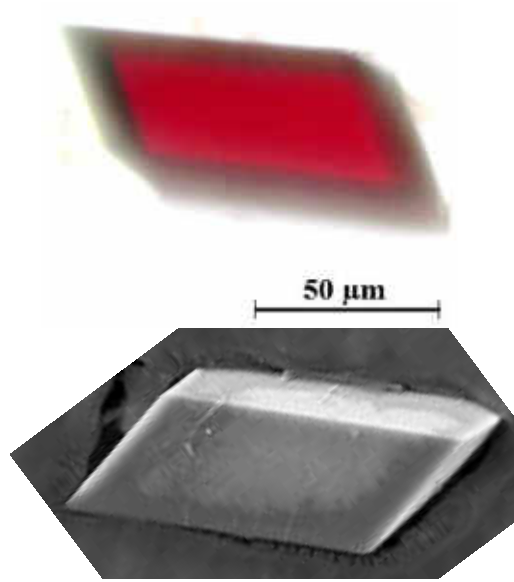
Type A:



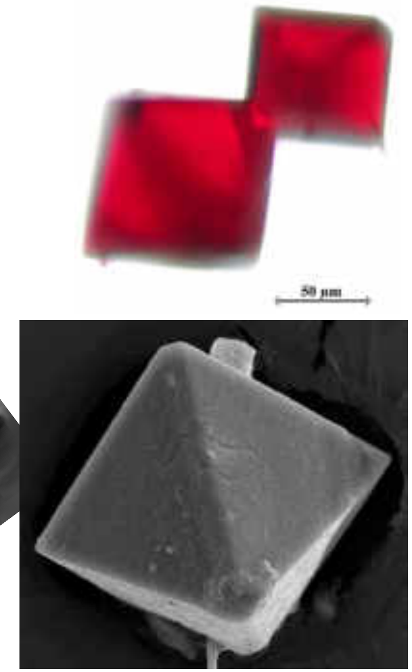
Type B:



Type C



Type D



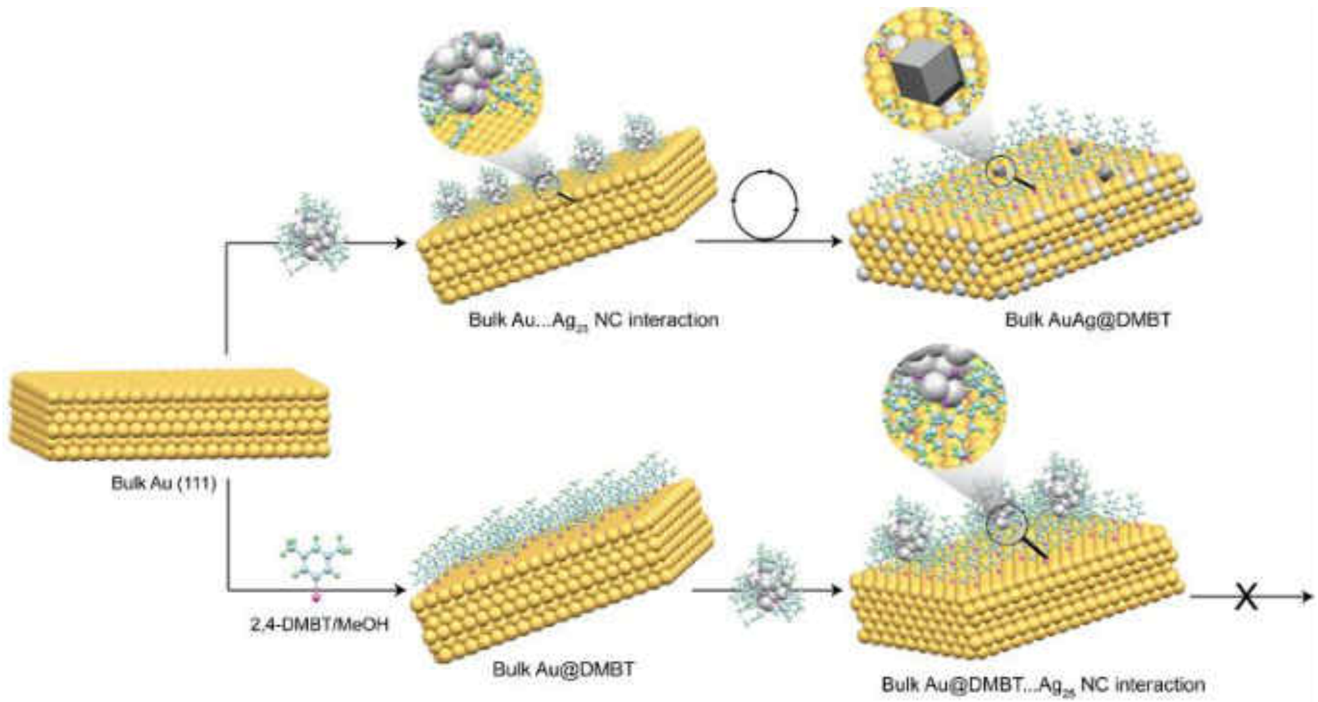
Hexagonal
a = 25.004 Å
b = 26.666 Å
c = 124.542 Å
α = 91.185°
β = 92.169°
γ = 117.904°
Volume = 73207 $Å^3$

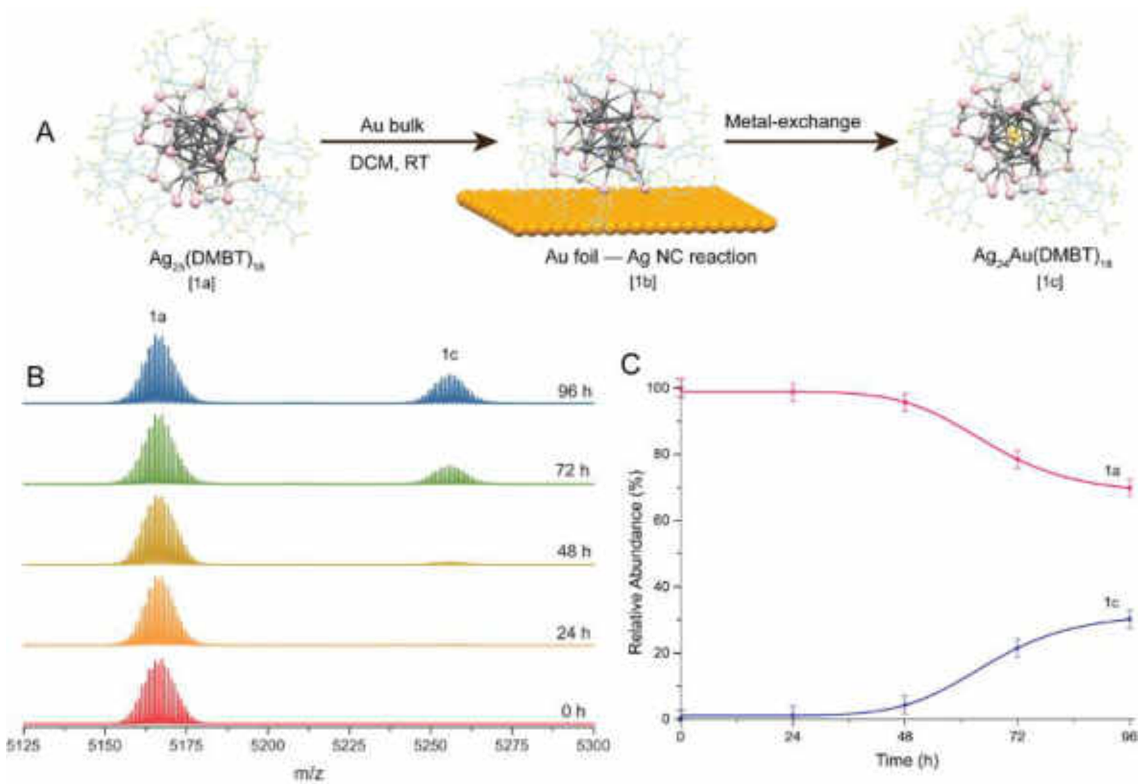
Tetragonal
a = 24.890 Å
b = 35.704 Å
c = 25.059 Å
α = 90°
β = 92°
γ = 90°
Volume = 22247 $Å^3$

Triclinic
a = 25.03 Å
b = 26.69 Å
c = 43.30 Å
α = 76°
β = 75°
γ = 62°
Volume = 24944 $Å^3$

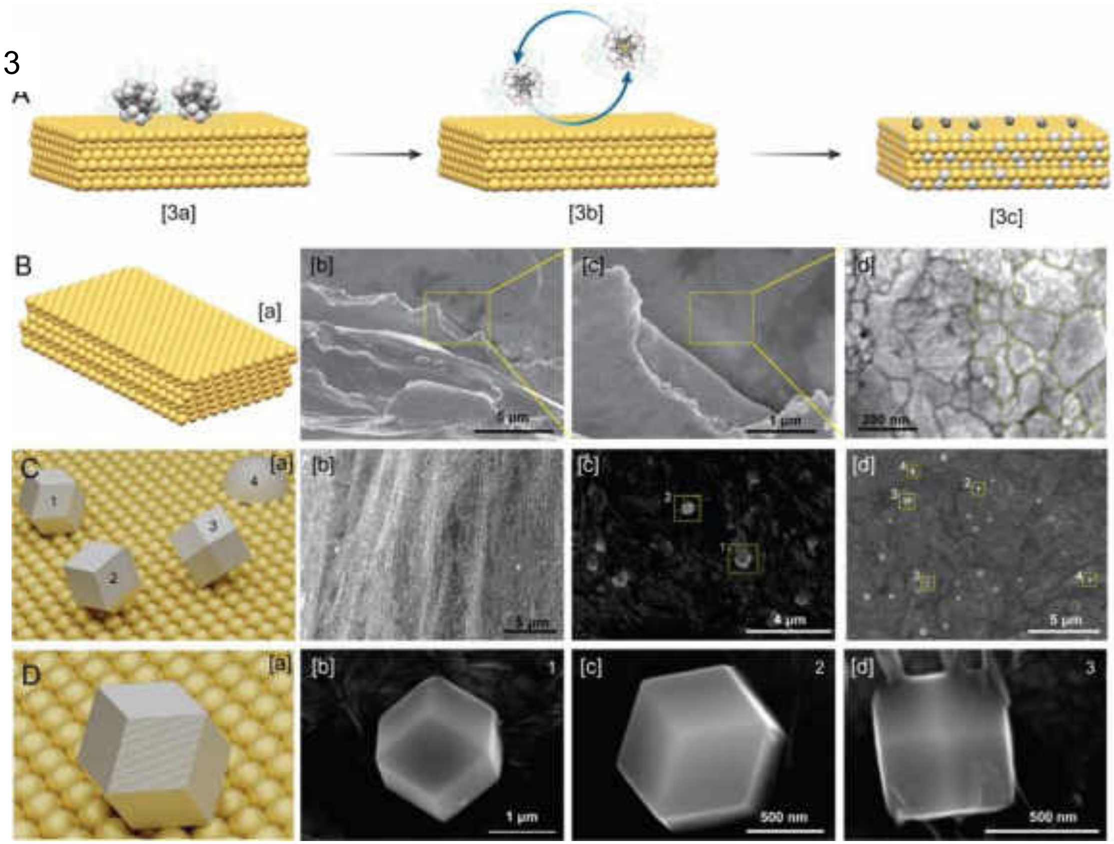
Cubic
a = 35.42 Å
b = 35.52
c = 35.45
α = 90°
β = 89.90°
γ = 90°
Volume = 44599 Å

Reactions with bulk gold

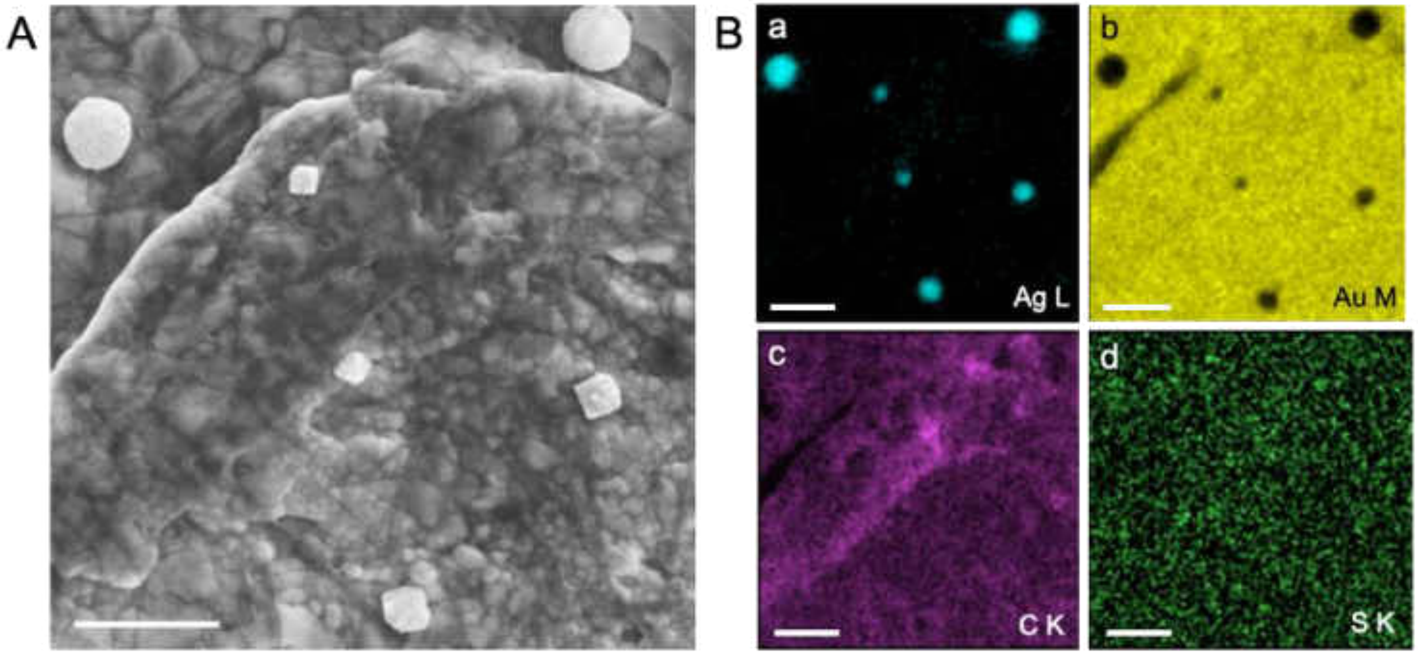



A
Au bulk
DCM, RT
Metal-exchange
Au foil — Ag NC reaction
[1a]
[1b]
[1c]
B
1a
1c
96 h
72 h
48 h
24 h
0 h
m/z
C
Relative Abundance (%)
Time (h)
1a
1c

3


A
[3a]
[3b]
[3c]
B
[a]
[b]
5 μm
[c]
1 μm
[d]
200 nm
C
[a]
[b]
5 μm
[c]
4 μm
[d]
5 μm
D
[a]
[b]
1 μm
[c]
500 nm
[d]
500 nm

Composition of microstructures



Scale bars: 1 µm

Collaborators

Robin Ras

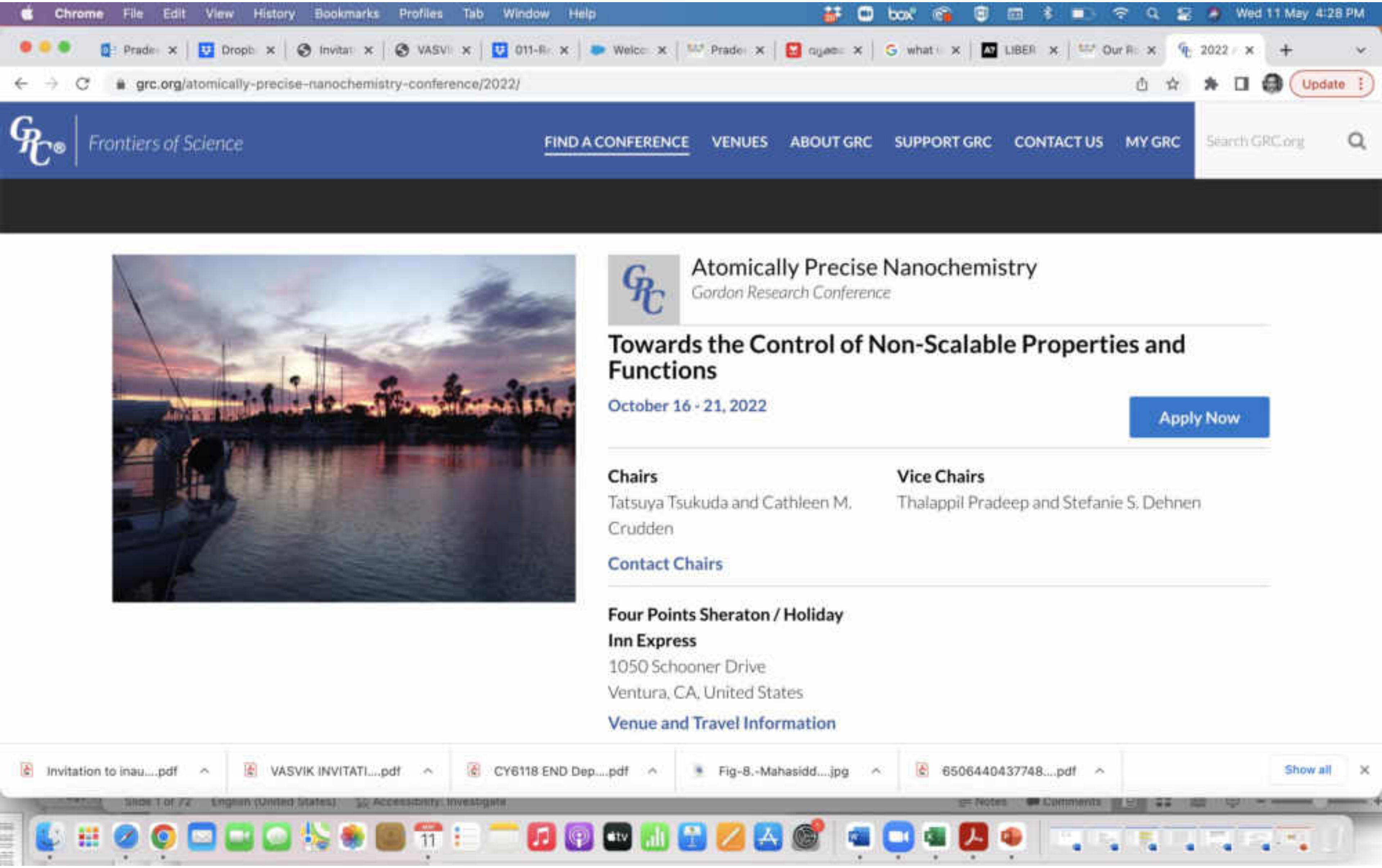
Nonappa

Mauri Kostiainen

Manfred Kappes

Olli Ikkala

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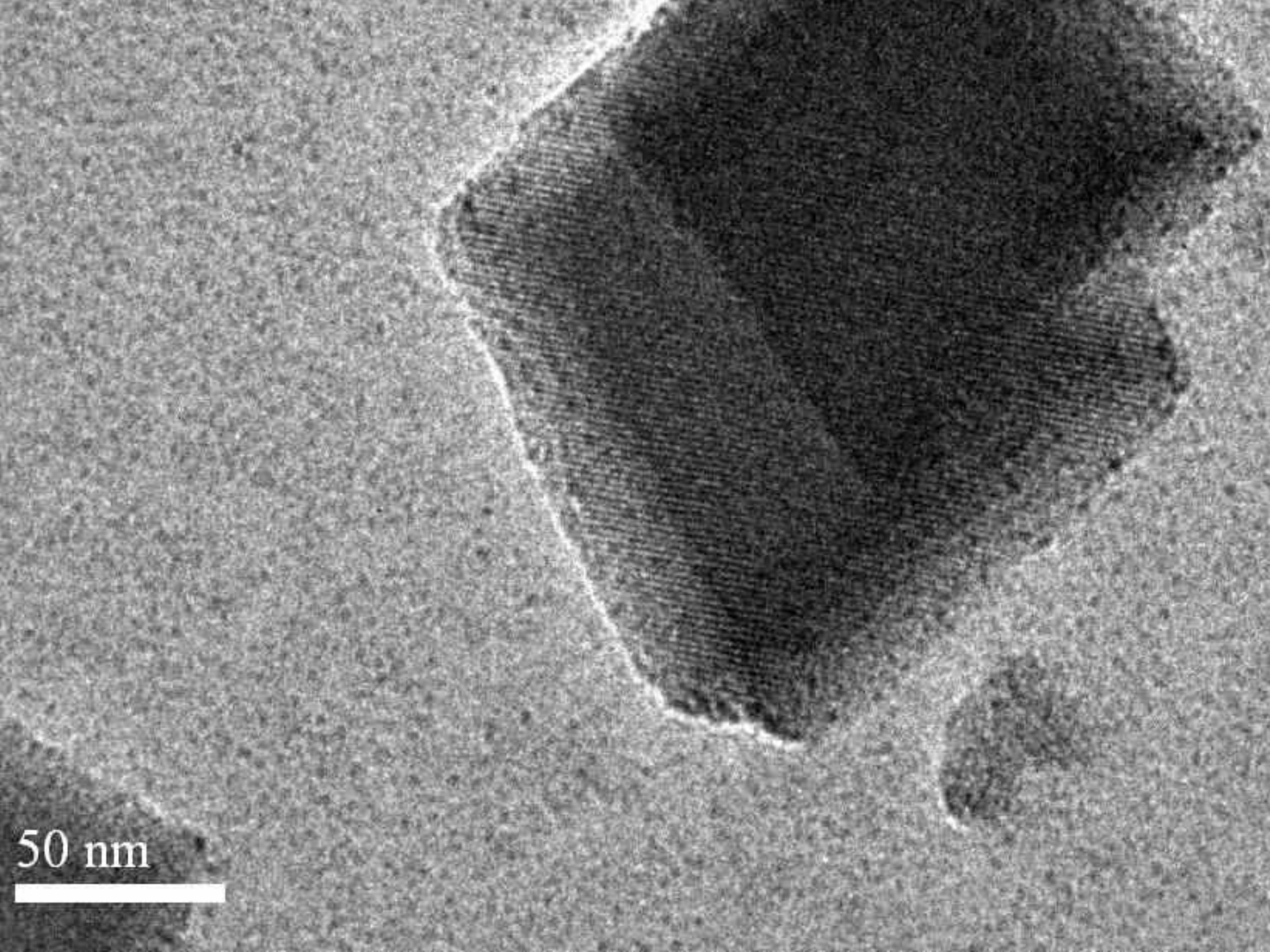
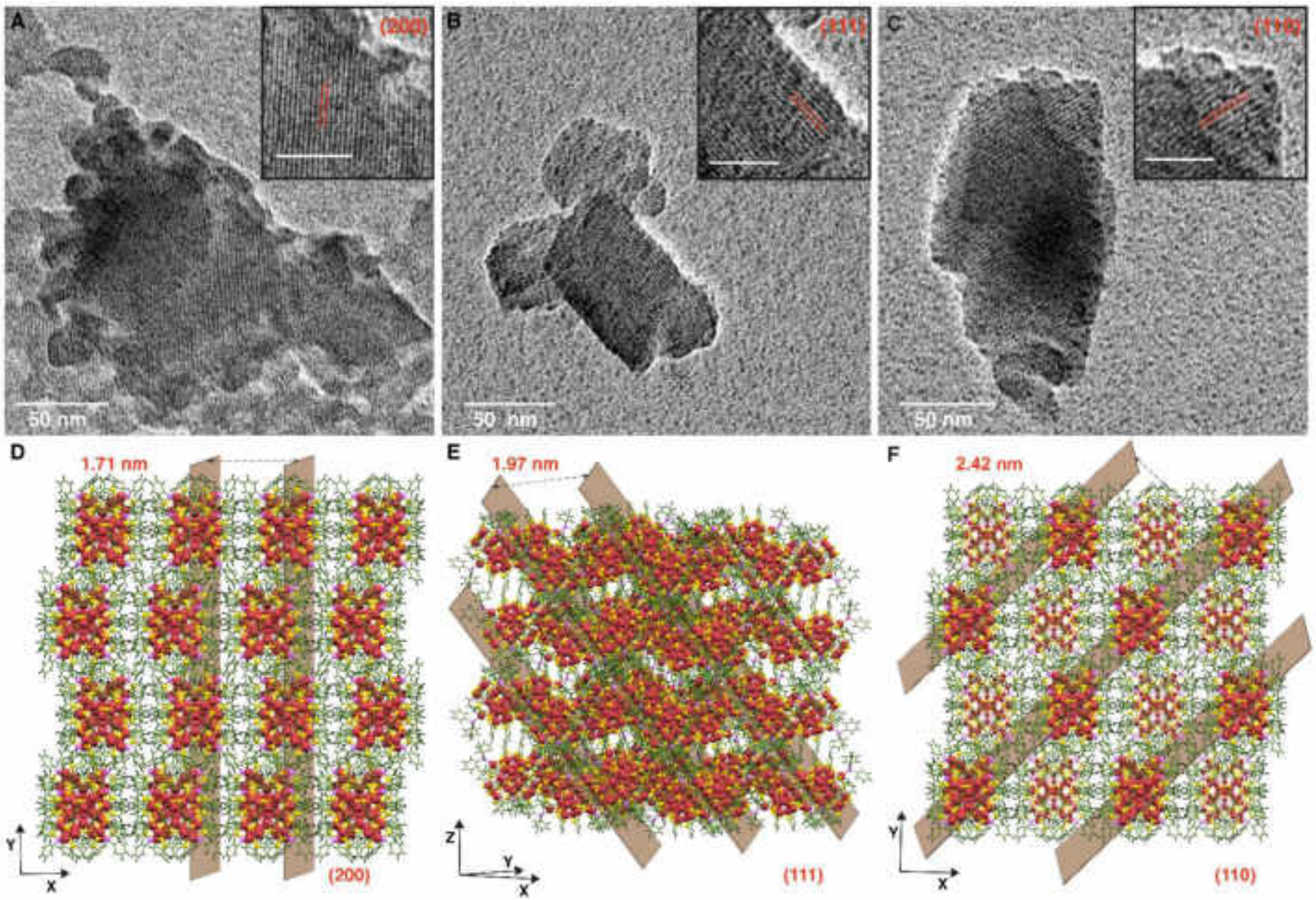

50 nm



Ananthu Mahendranath et al. Chem.Comm.2021

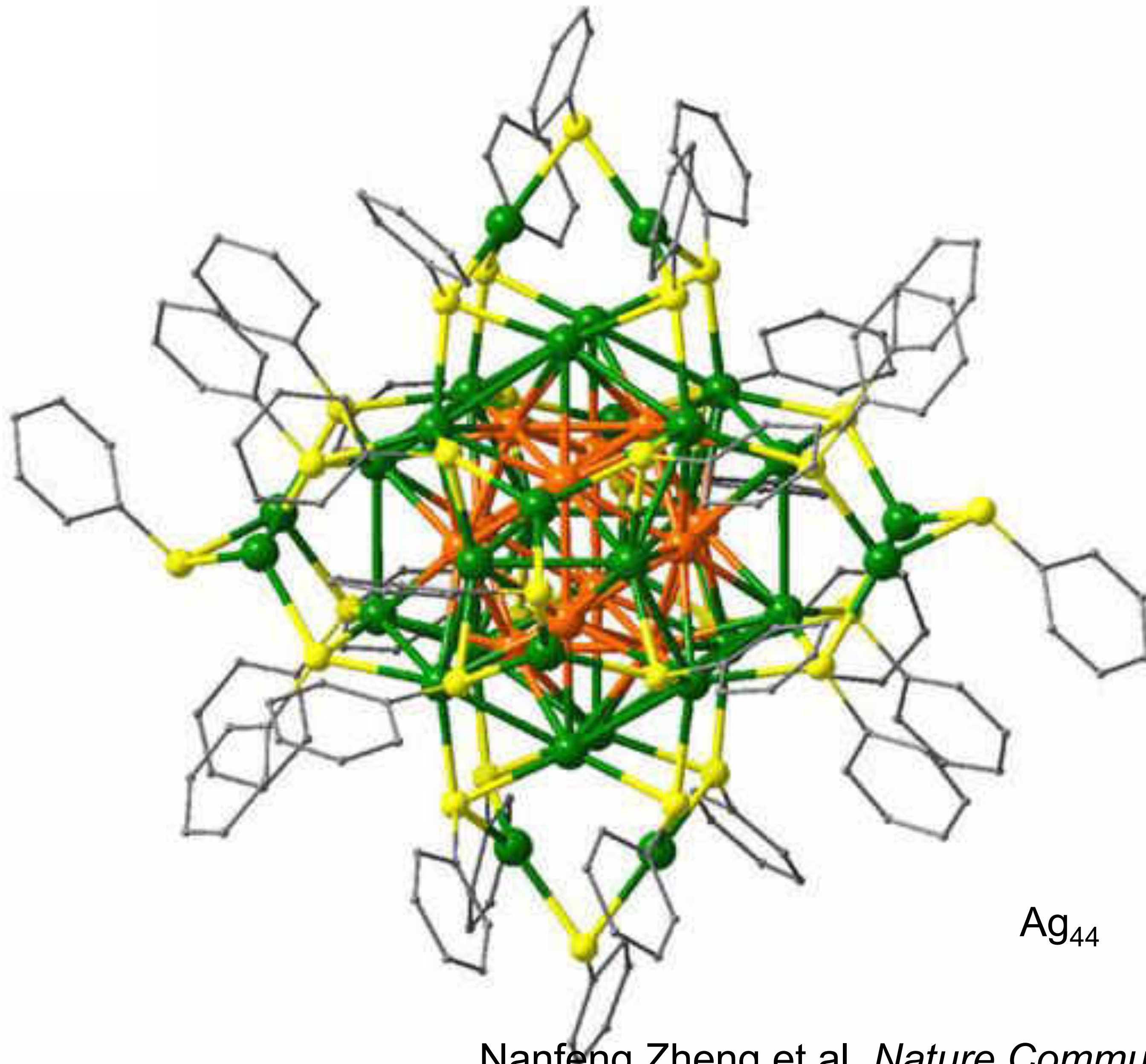
Molecules and their properties

Chemical formula	H_2O
Molecular weight	18.0148
Critical temperature	373.91°C
Critical pressure	22.05 MPa
Critical density	315.0 kg/m^3
Triple point temperature	0.01°C
Triple point pressure	615.066 Pa
Normal boiling point	100.0°C
Normal freezing point	0.0°C
Density of ice at normal melting point	918.0 kg/m^3
Maximum density, 3.98°C	999.973 kg/m^3
Viscosity, 25°C	0.889 mN s/m^2
Surface tension, 25°C	72 mN/m
Heat Capacity, 25°C	4.1796 kJ/kg.K
Enthalpy of vaporisation, 100°C	2,257.7 kJ/kg
Enthalpy of fusion, 0°C	333.8 kJ/kg
Velocity of sound, 0°C	1.403 km/s
Dielectric constant, 25°C	78.40
Electrical conductivity, 25°C	8 μS/m
Refractive index, 25°C	1.333
Liquid compressibility, 10°C	$480. \times 10^{-12} m^2/N$
Coefficient of thermal expansion, 25°C	$256.32 \times 10^{-6}\ K^{-1}$
Thermal Conductivity, 25°C	0.608 W/m.K

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

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

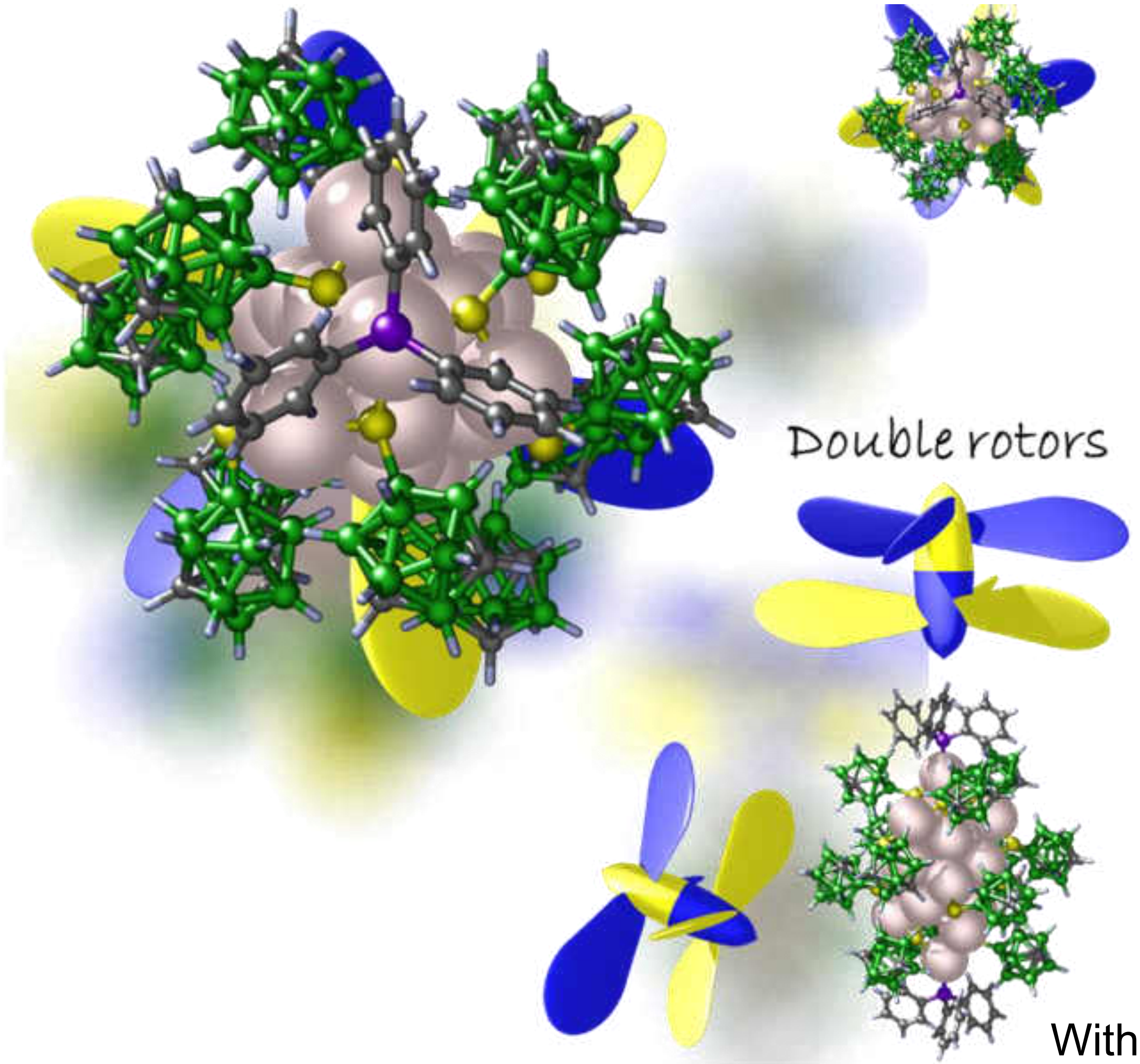
Future?



Ag_{44}

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

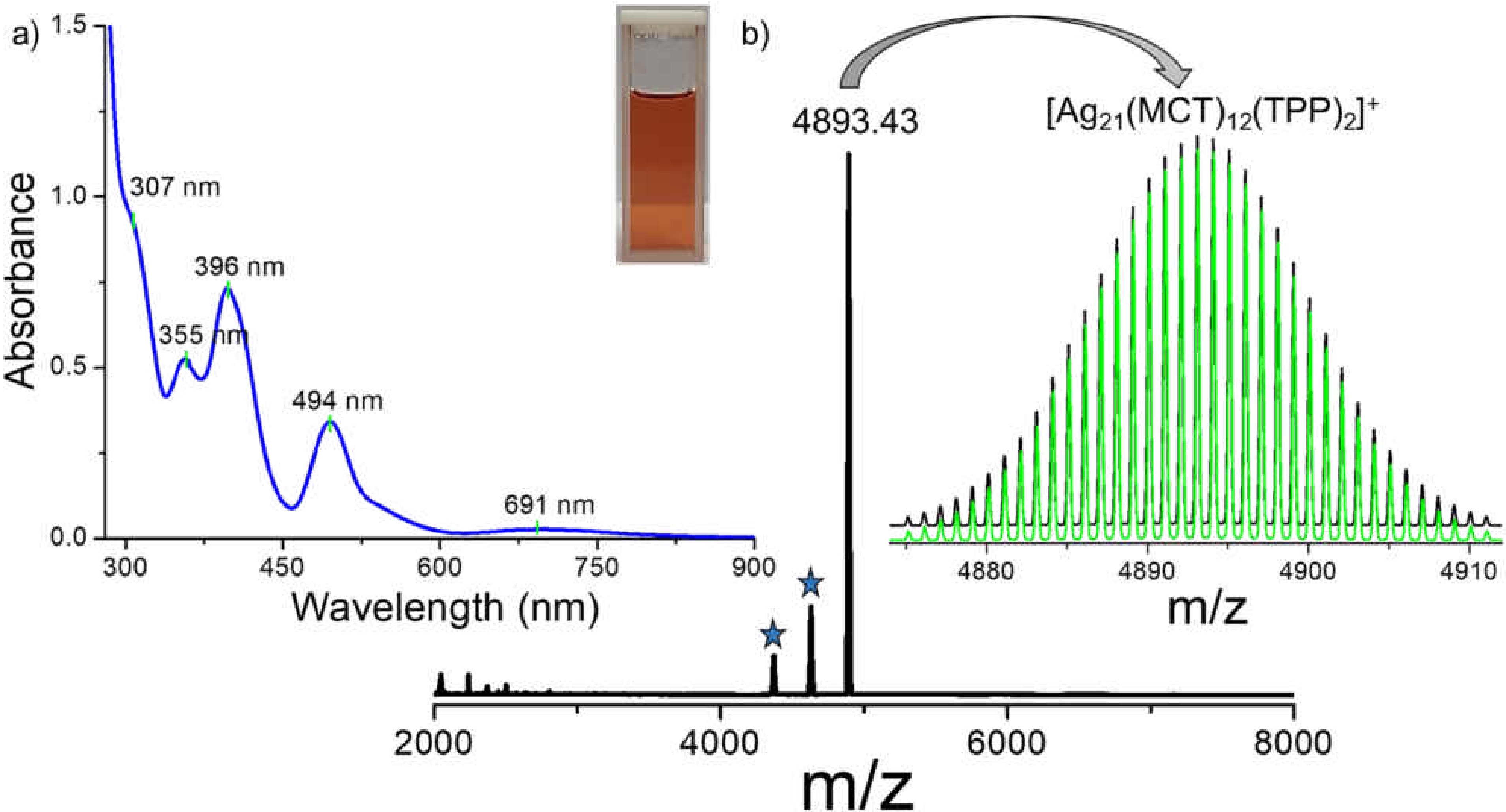
Carborane-thiol protected propeller-shaped photoresponsive silver nanomolecule



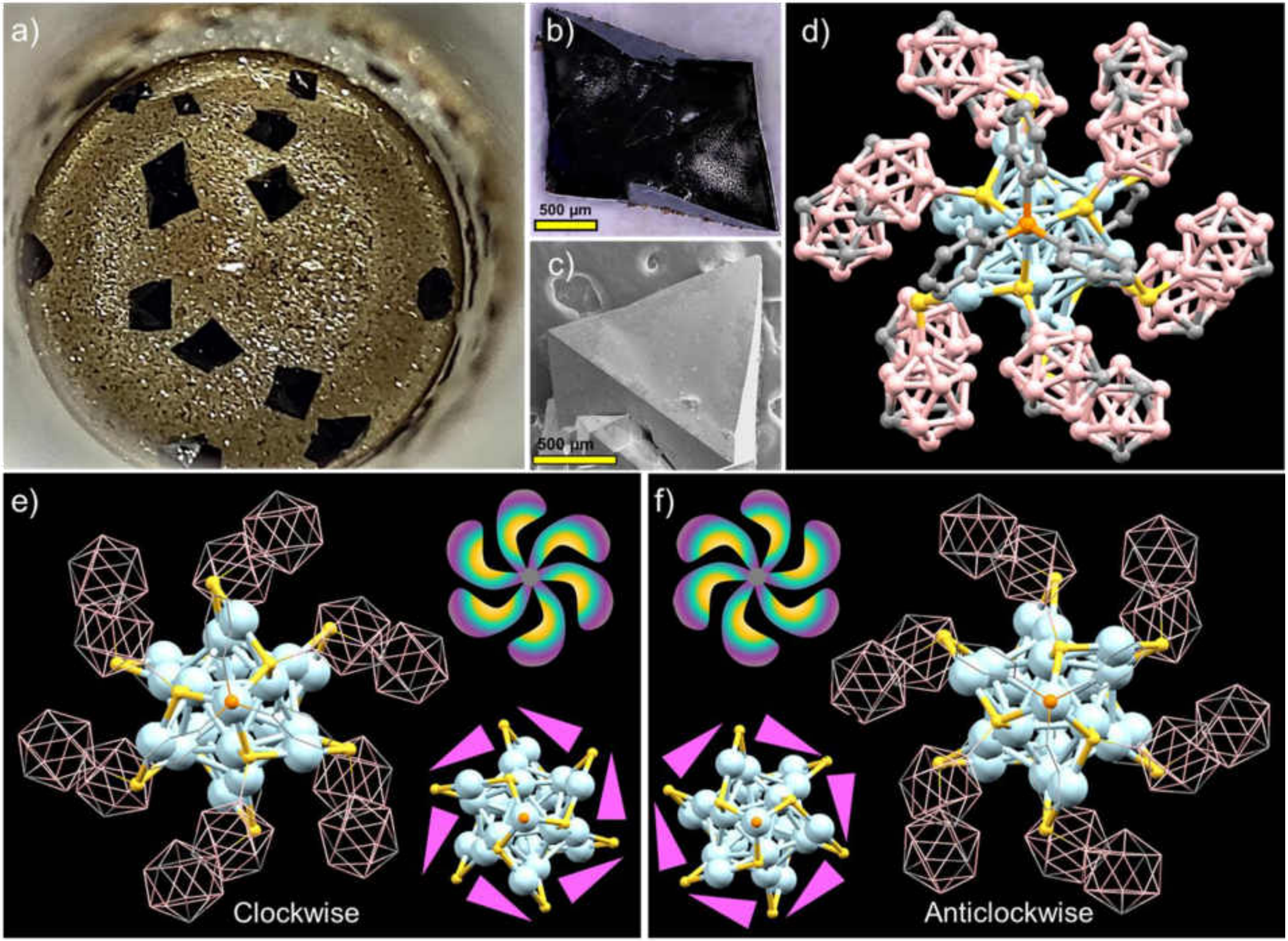
With Tomas Base

Jana *et. al*, Inorganic Chemistry (just accepted)

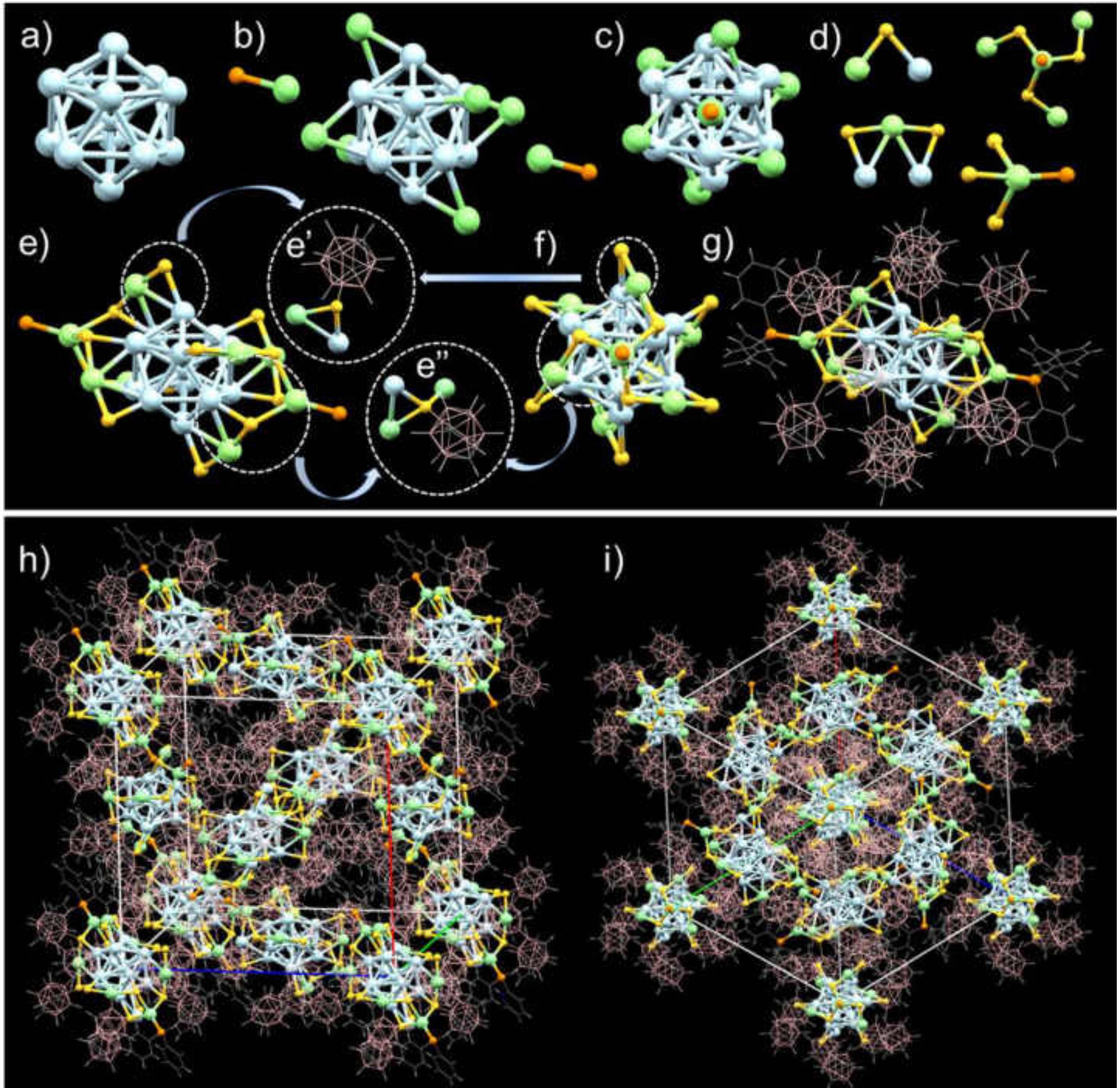
Characterization of Ag_{21}

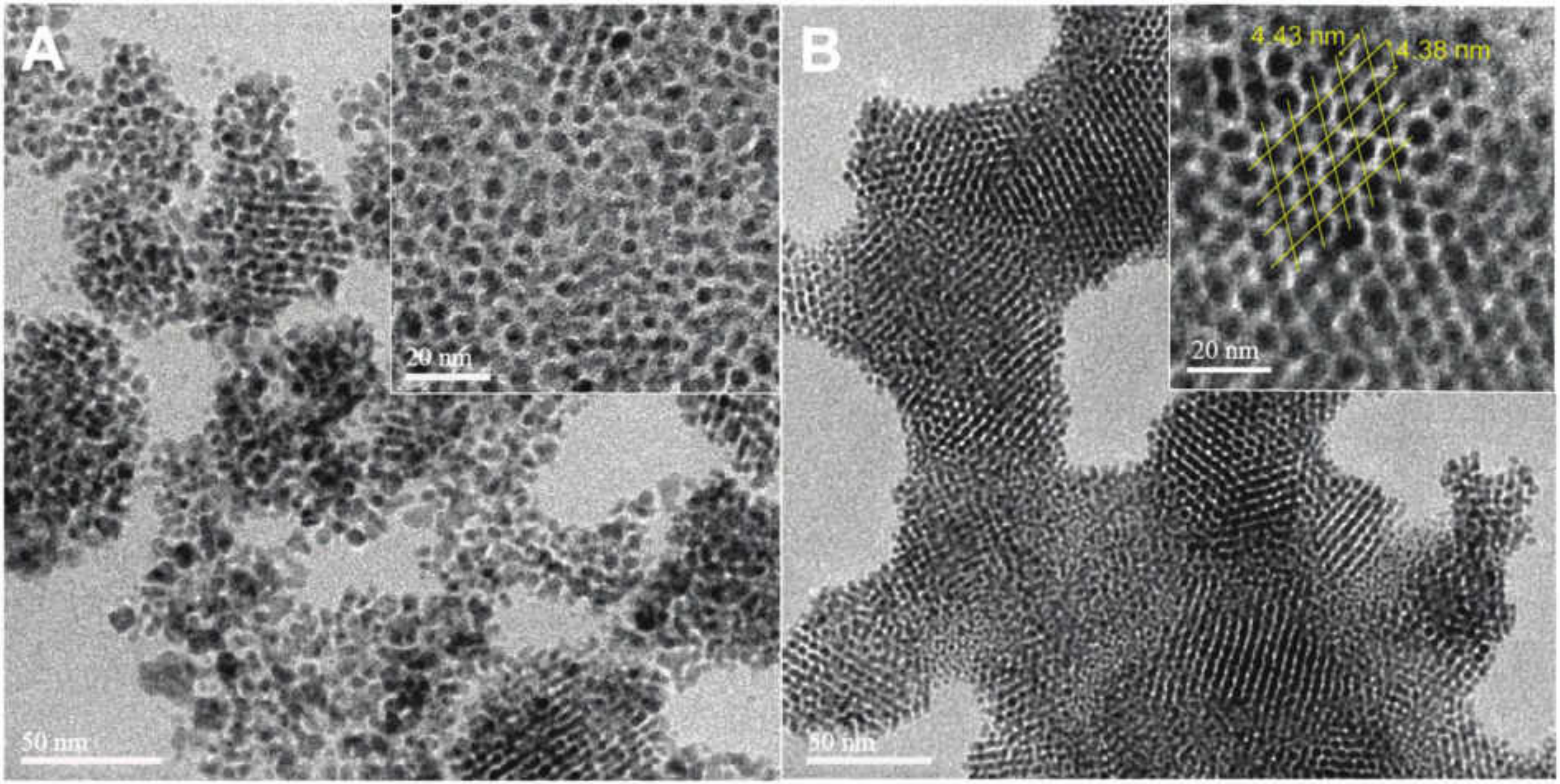


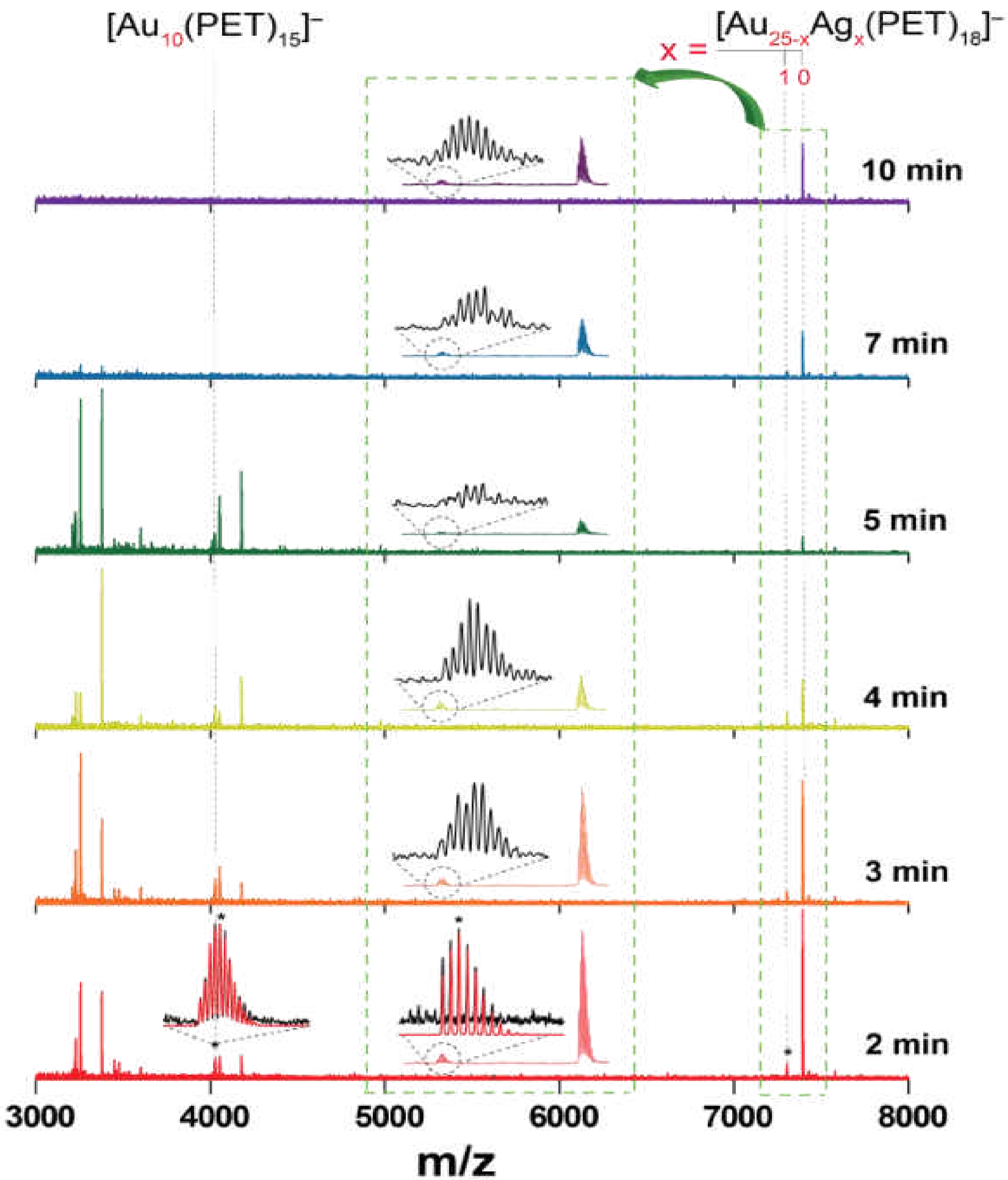
Structural details of Ag_{21}



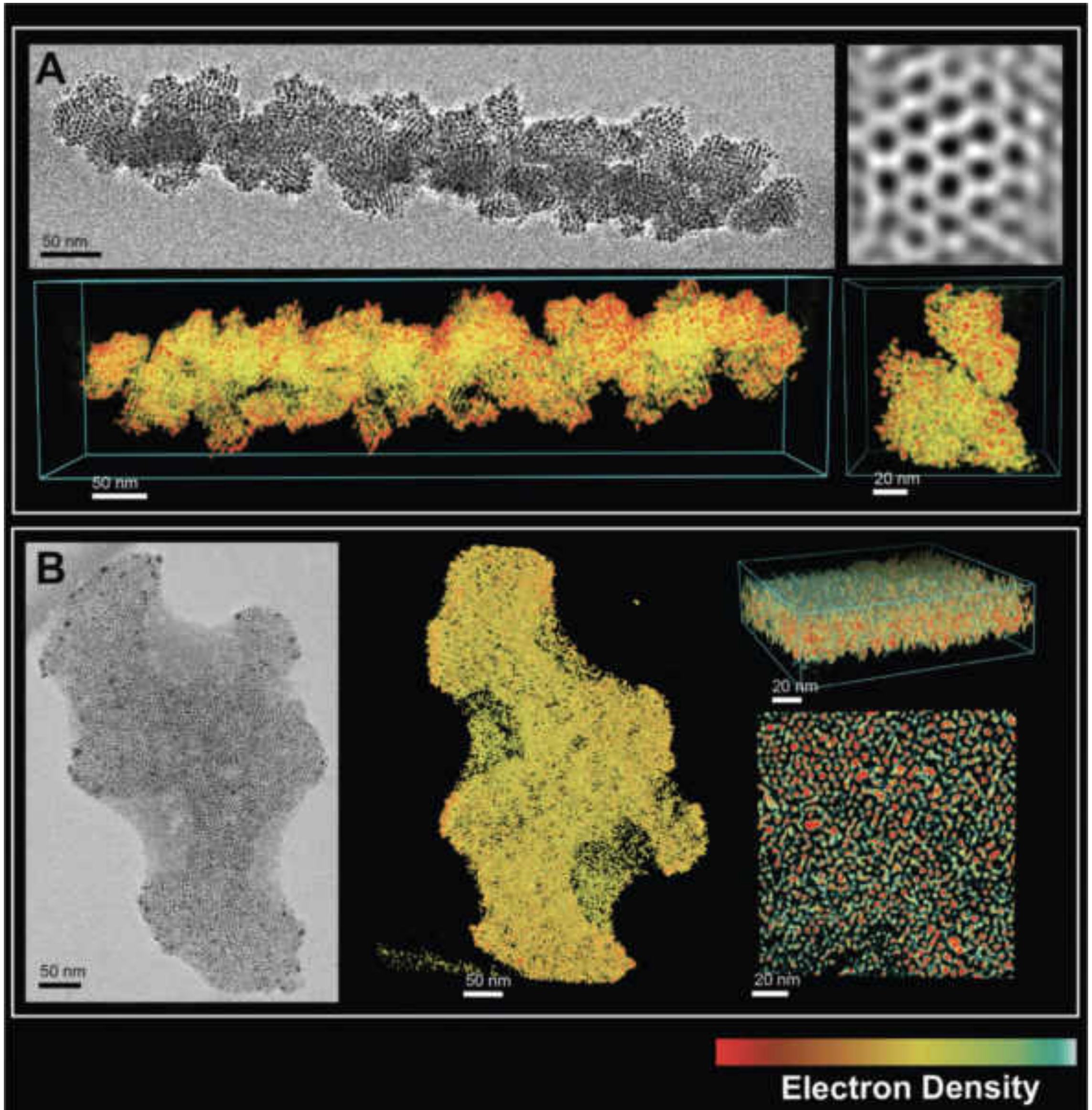
Structural details of Ag_{21}



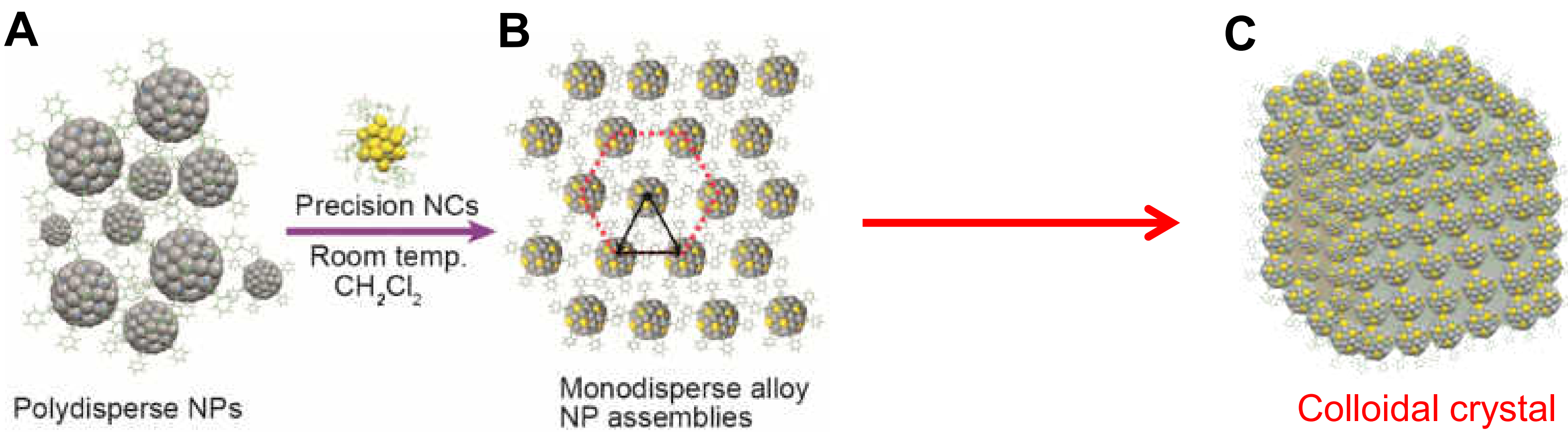

A
20 nm
50 nm
B
4.43 nm
4.38 nm
20 nm
50 nm

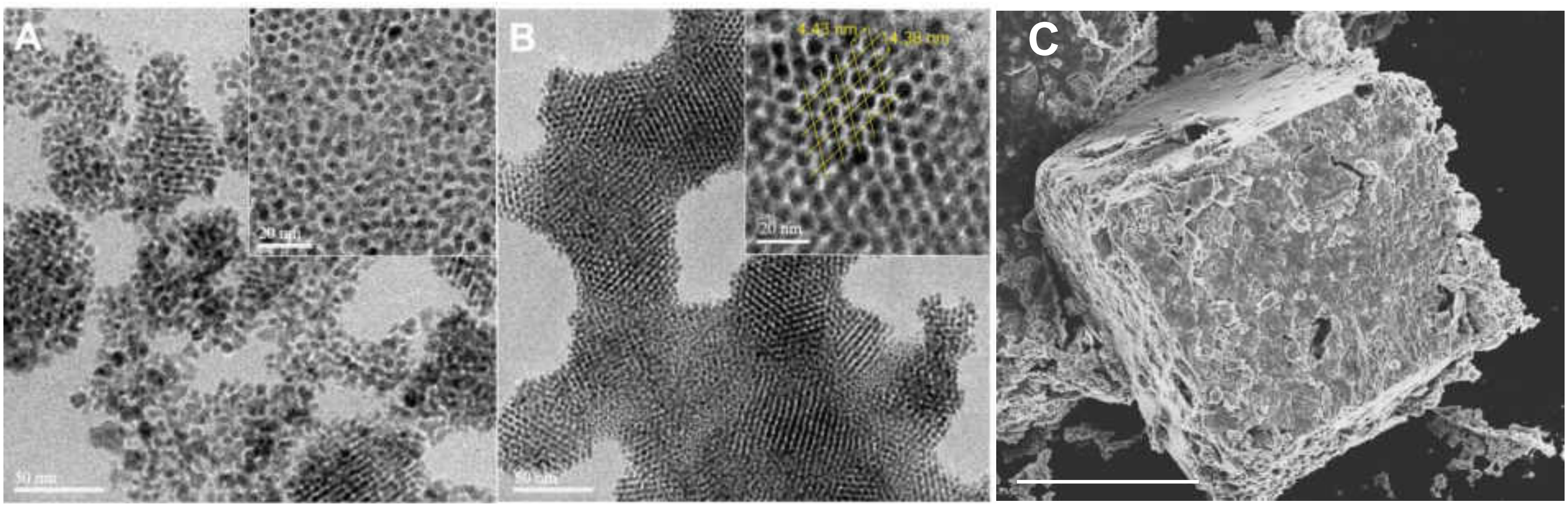


$[Au_{10}(PET)_{15}]^-$
$[Au_{25-x}Ag_x(PET)_{18}]^-$
x =
1 0
10 min
7 min
5 min
4 min
3 min
2 min
3000
4000
5000
6000
7000
8000
m/z

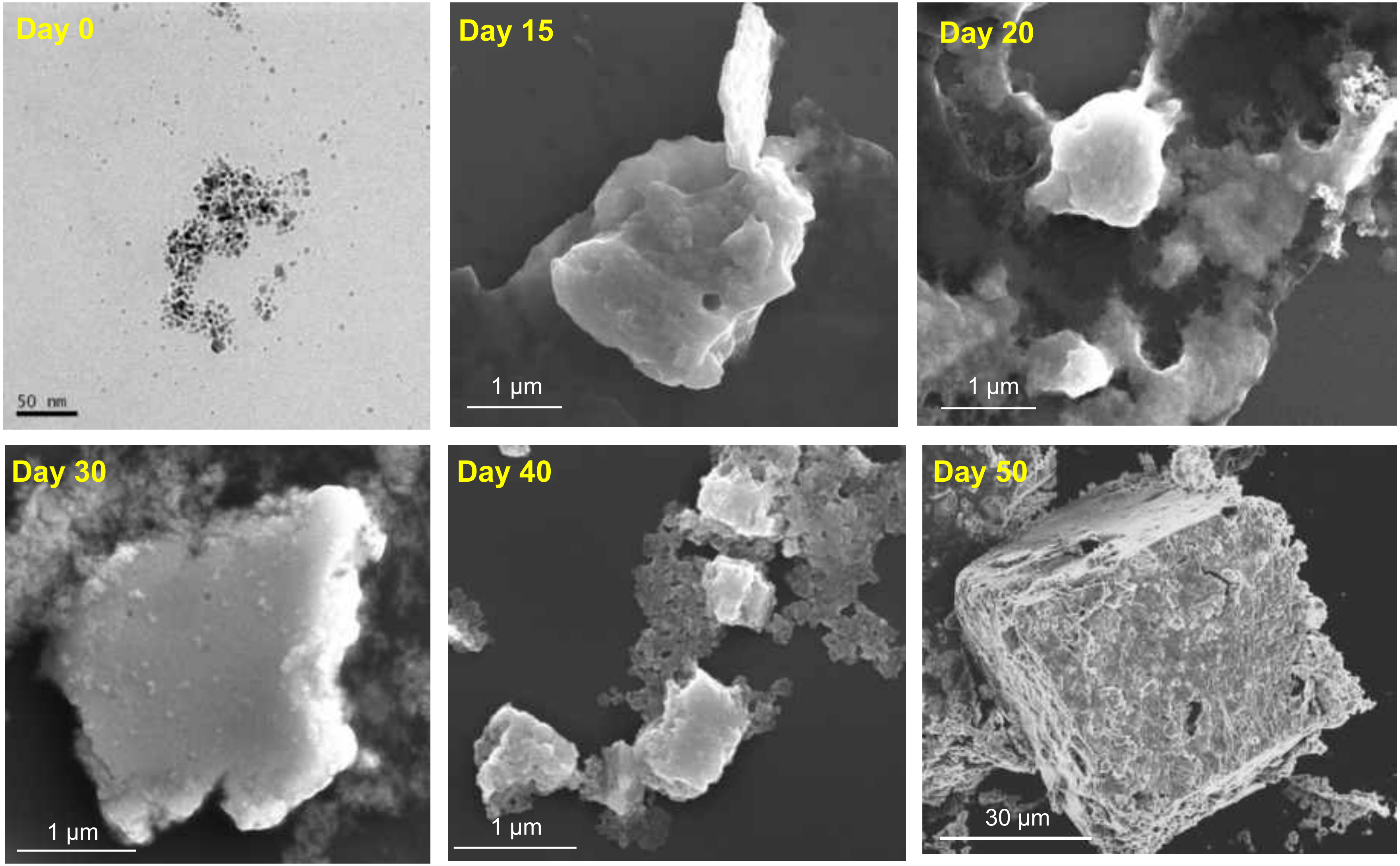

A
50 nm
50 nm
20 nm
B
50 nm
50 nm
20 nm
20 nm
Electron Density

Crystallization of AgAu NP

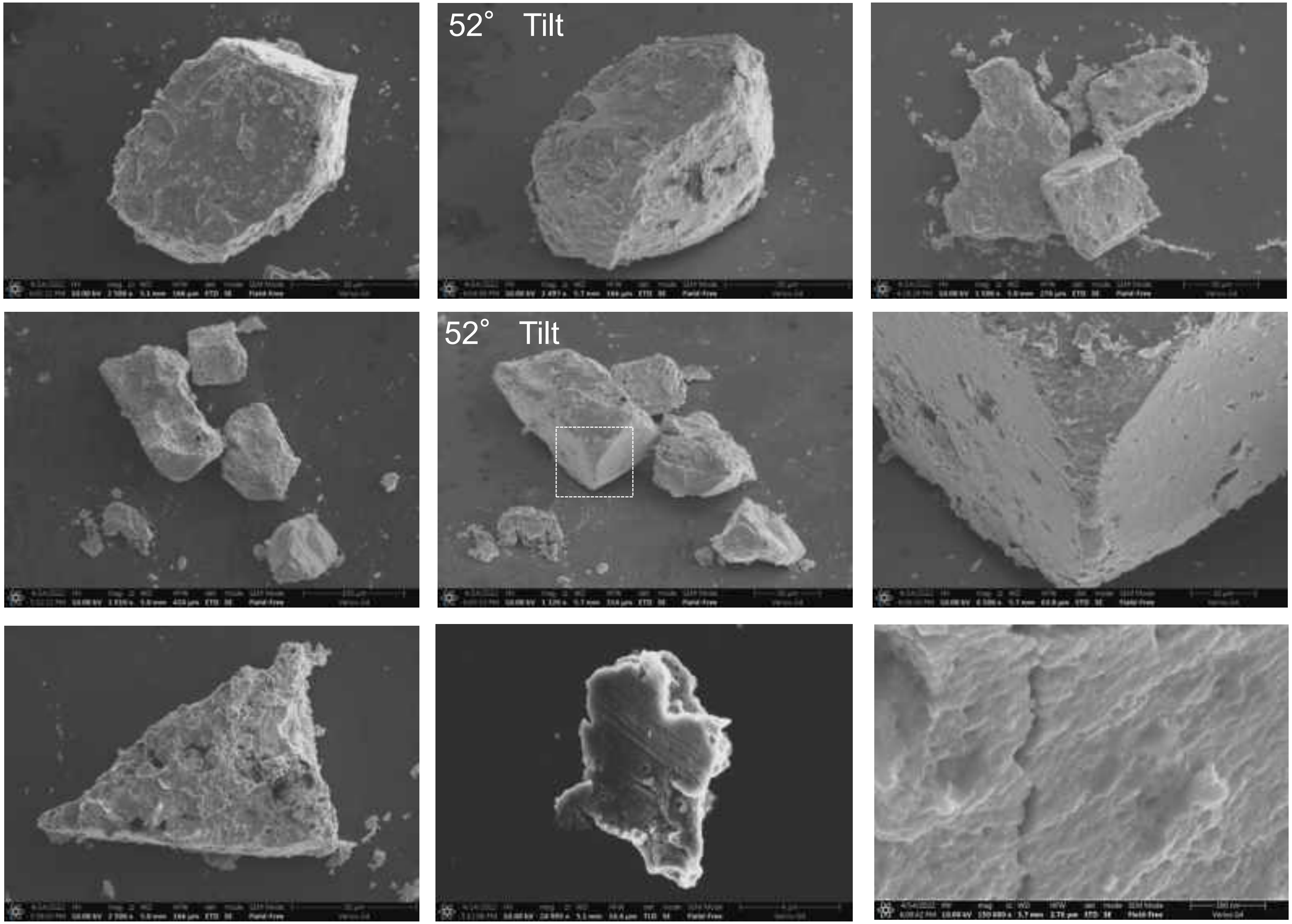




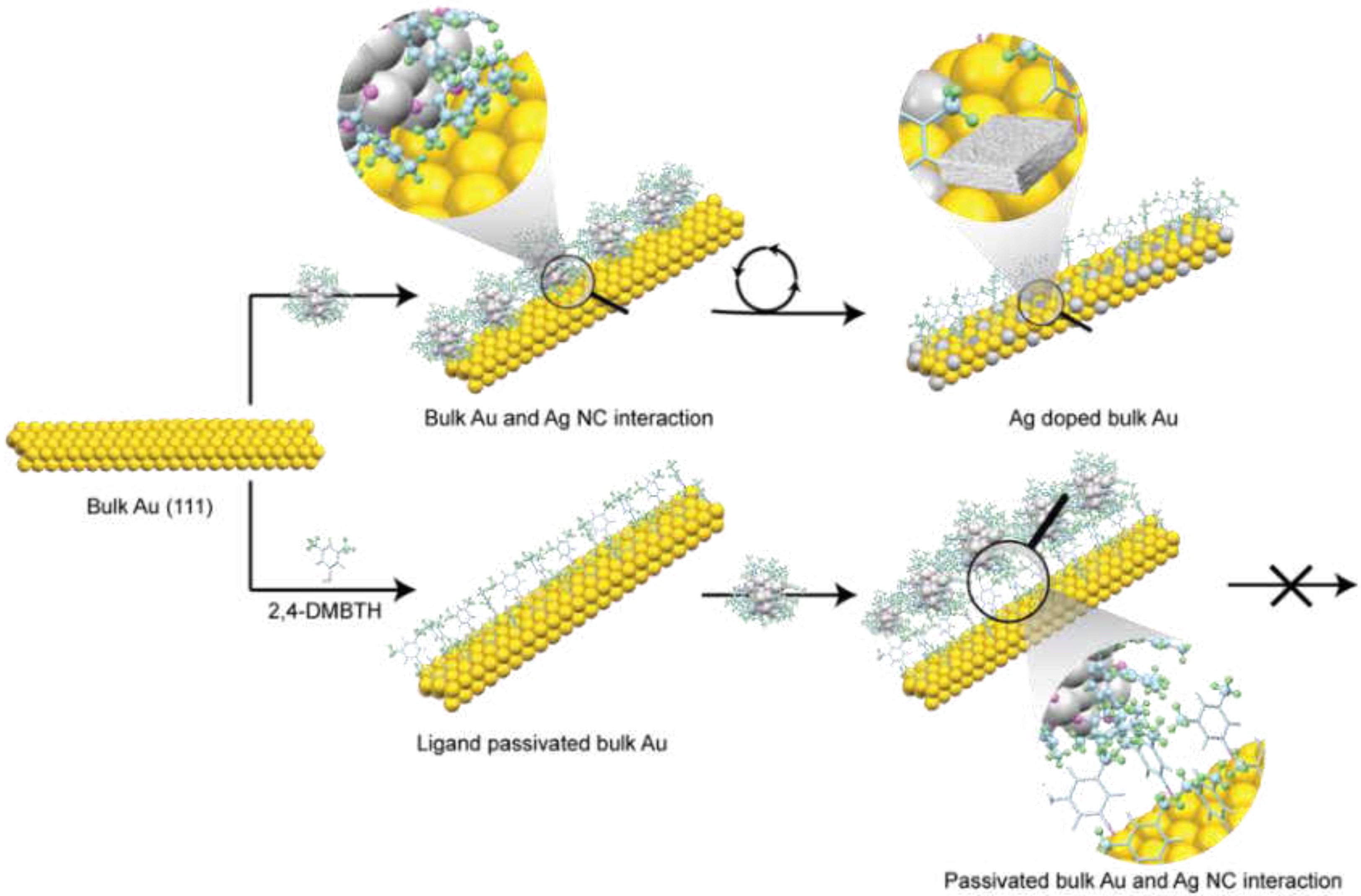
Transformation of colloidal particles in solution



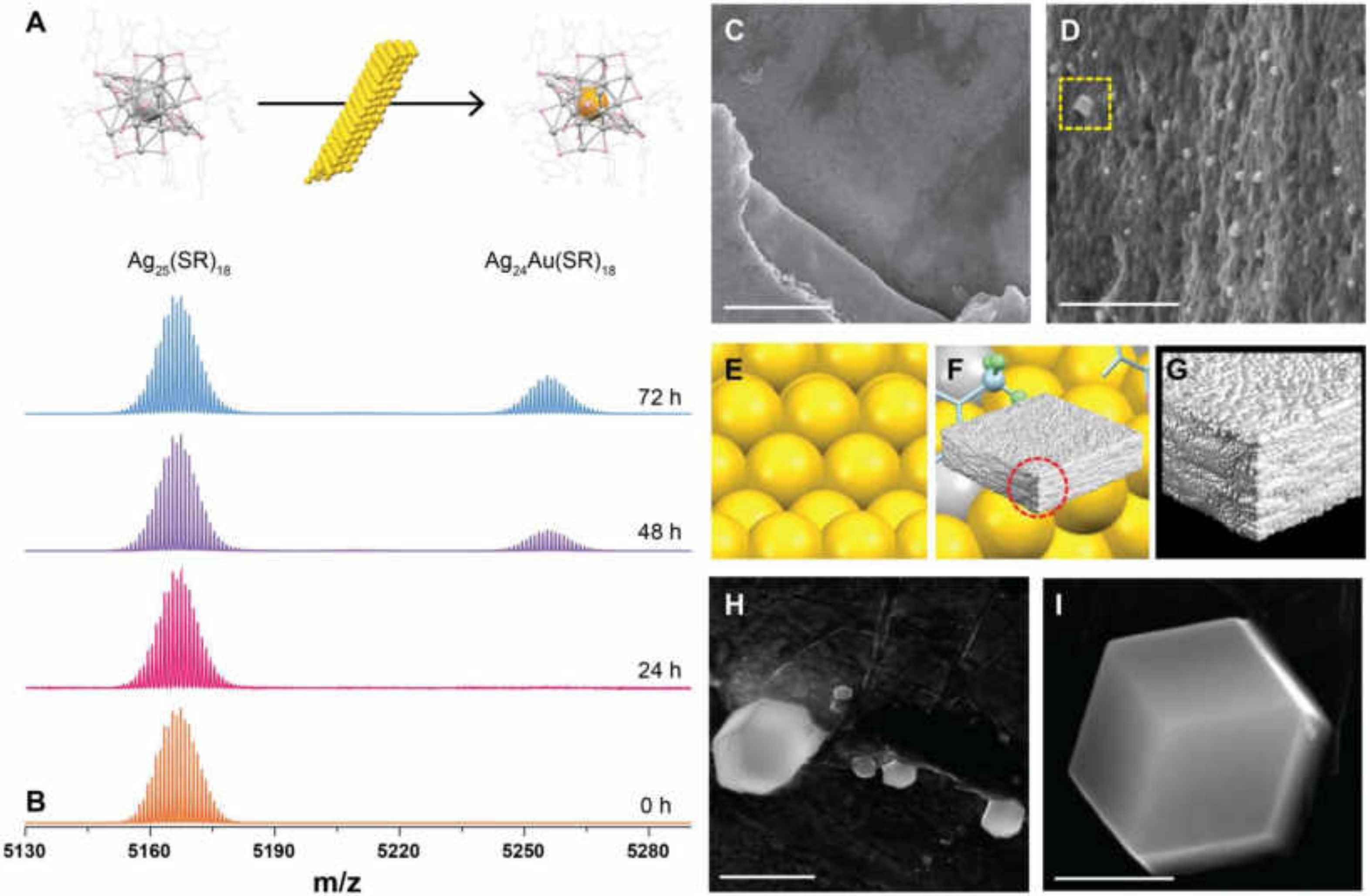
Crystals imaged after 50 days



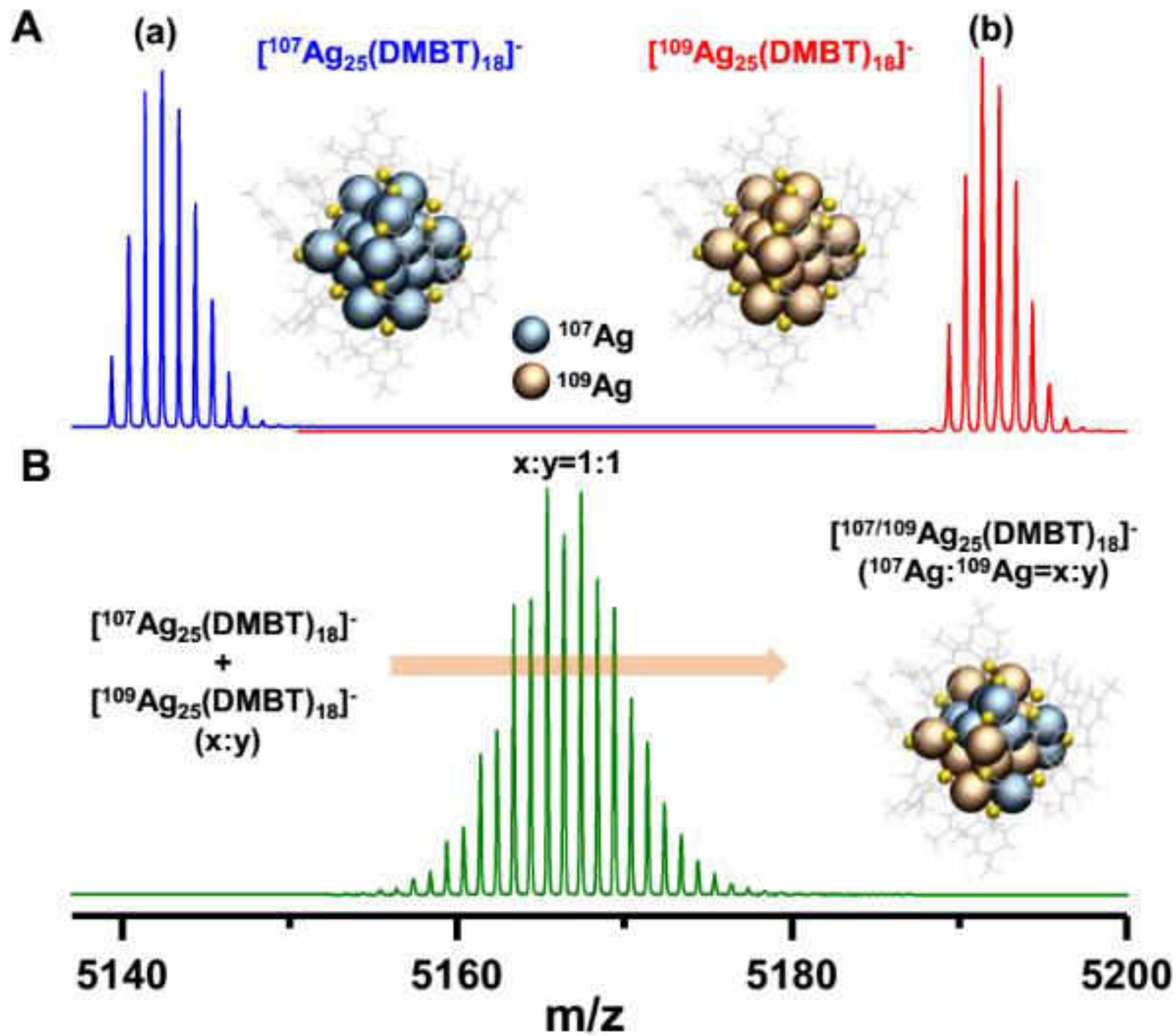
Bulk Au— Ag NC reaction



Characterization of reaction products



Isotopic exchange



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