



Now in the 65th year

Thalappil Pradeep

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InnoDI Water Technologies Pvt. Ltd.

VayuJAL Technologies Pvt. Ltd.

Aqueasy Innovations Pvt. Ltd.

Hydromaterials Pvt. Ltd.

EyeNe

Associate Editor
Spectrum Innovations Pvt. Ltd.



Sustainable
Resource Management

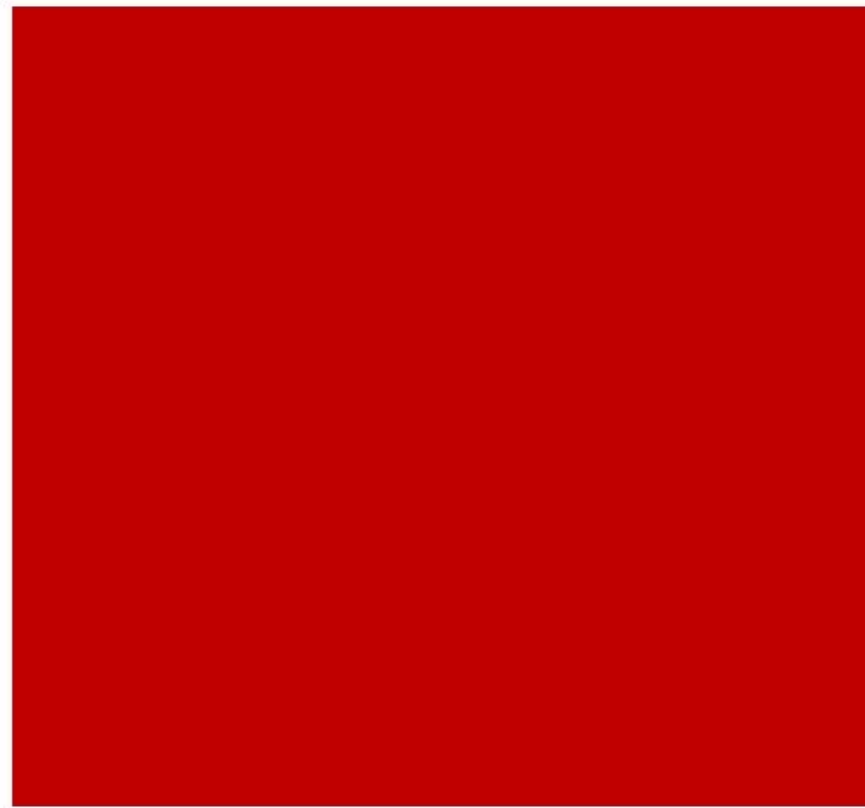
Professor-in-charge



International Centre for Clean Water



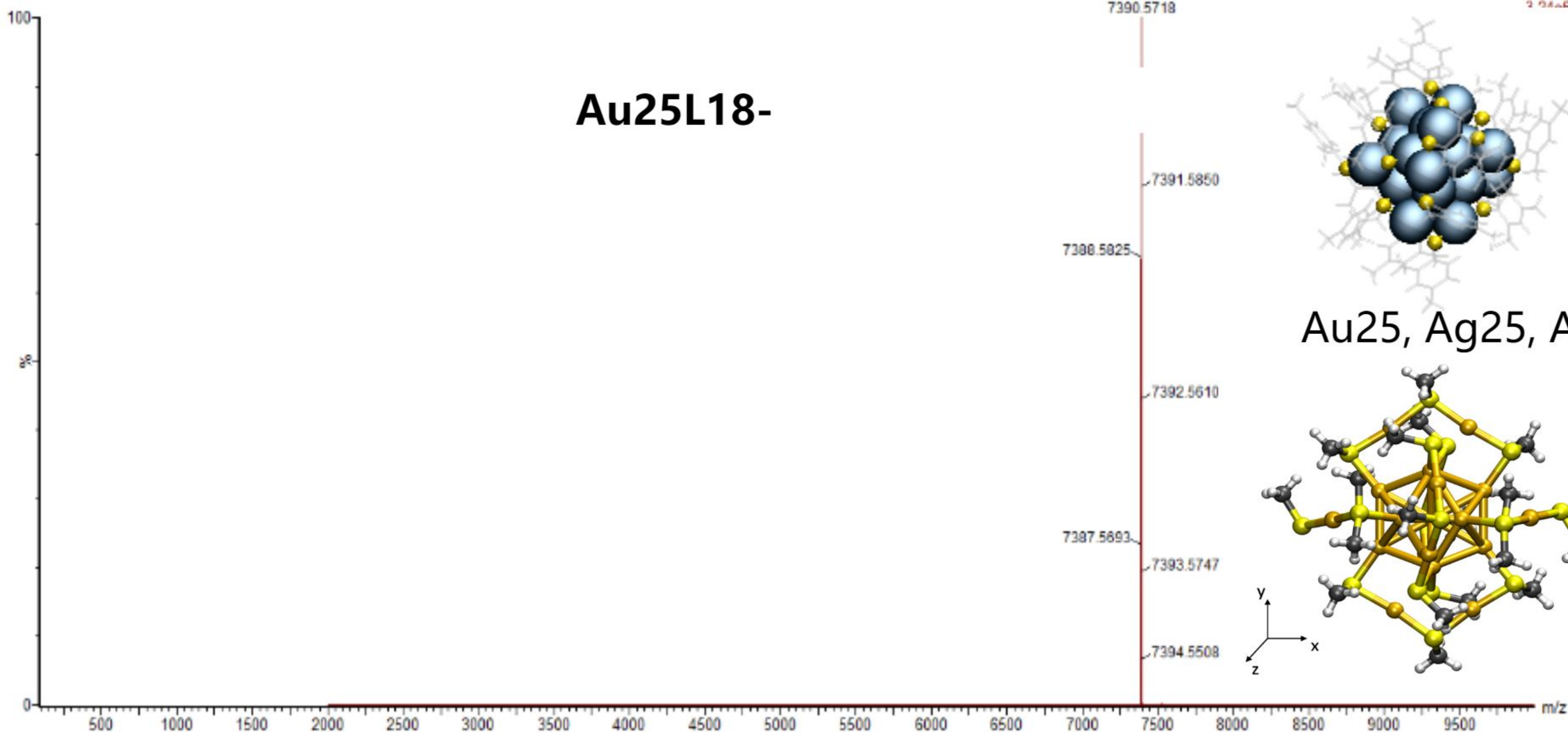
Gas phase



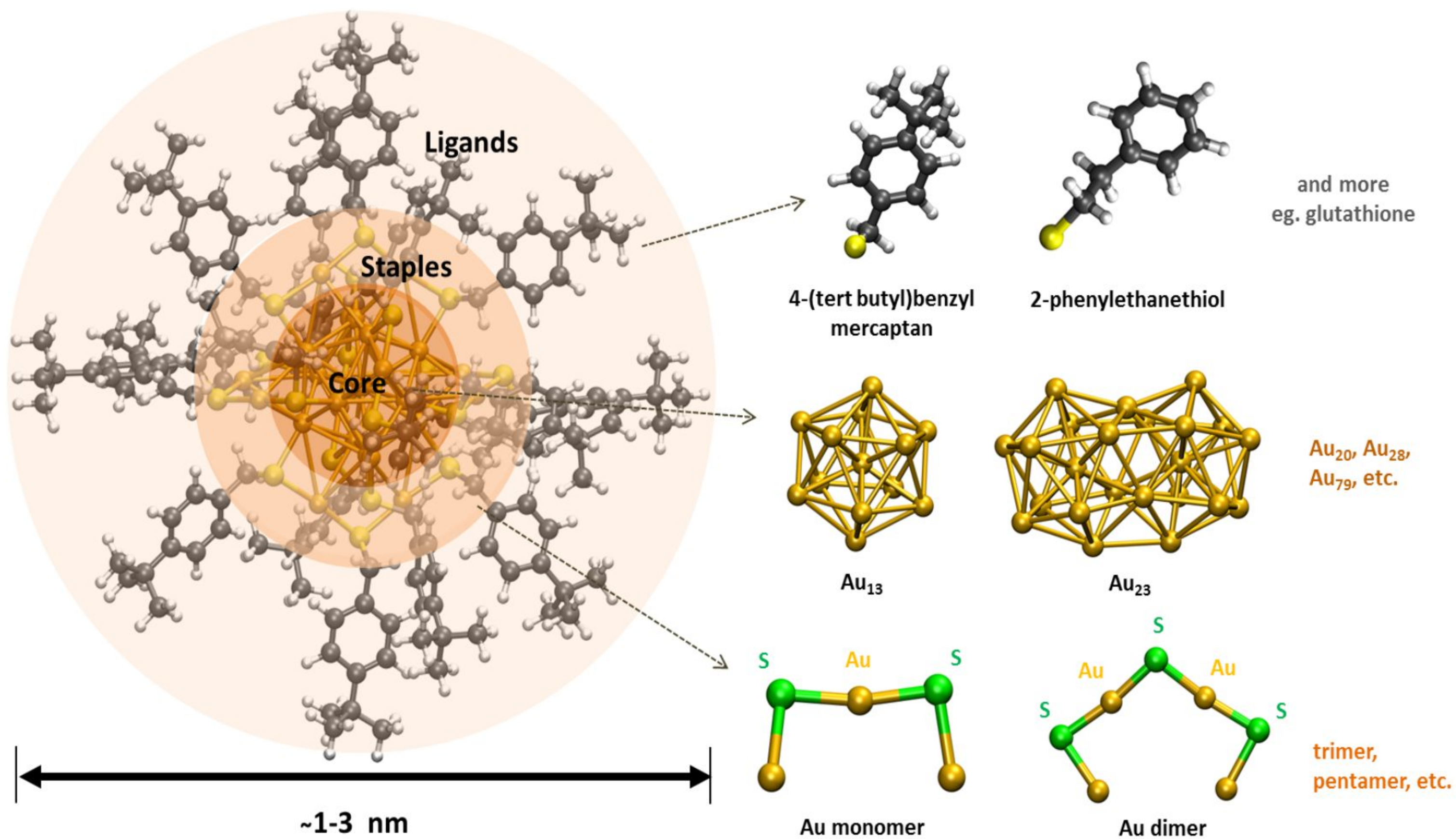


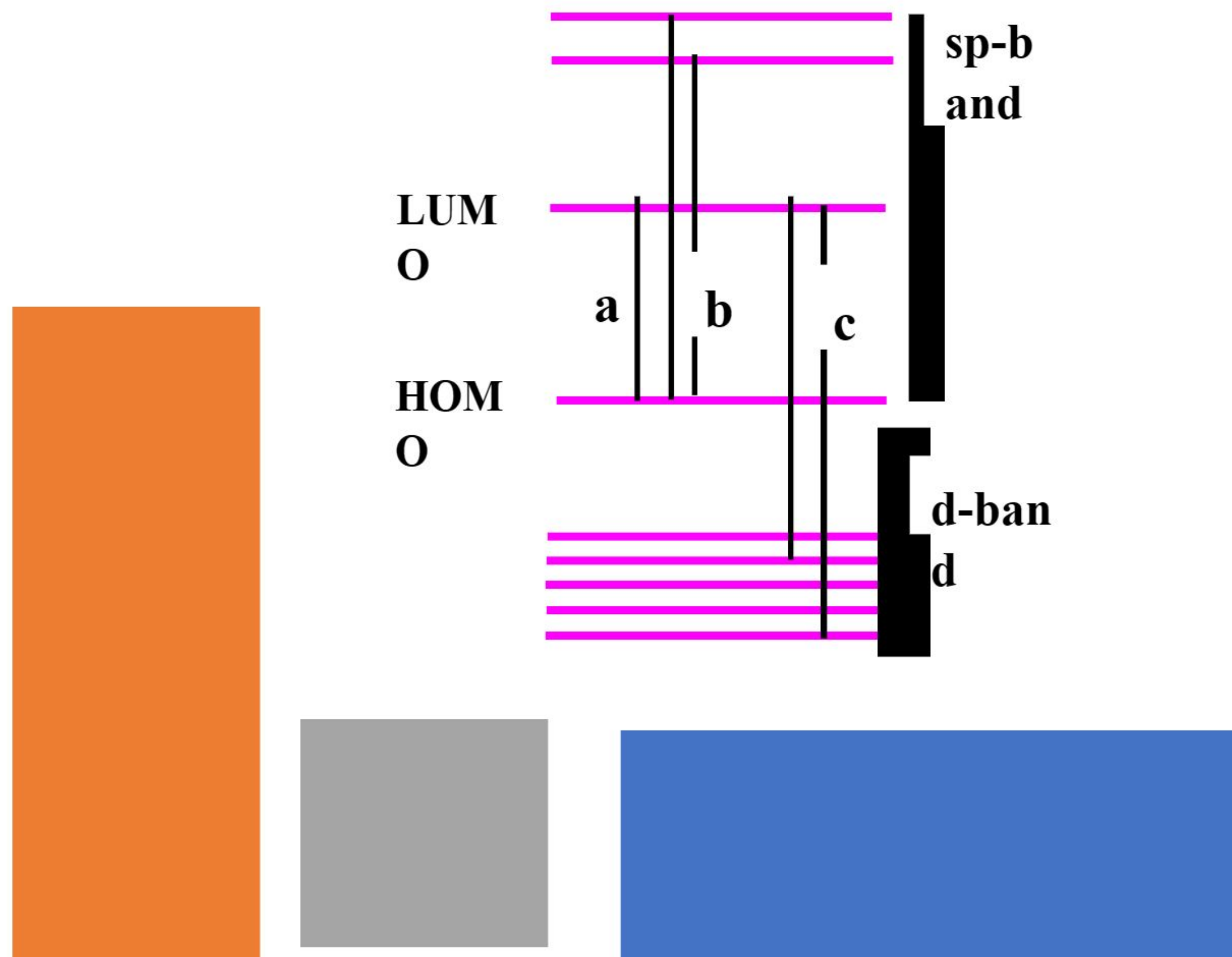
Atomically precise metal clusters as materials

AU25PET18_RES_NEG_MS_3 32 (0.558) Cm (5:80)



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





With Tatsuya Tsuku
da

Evolution of noble metal clusters

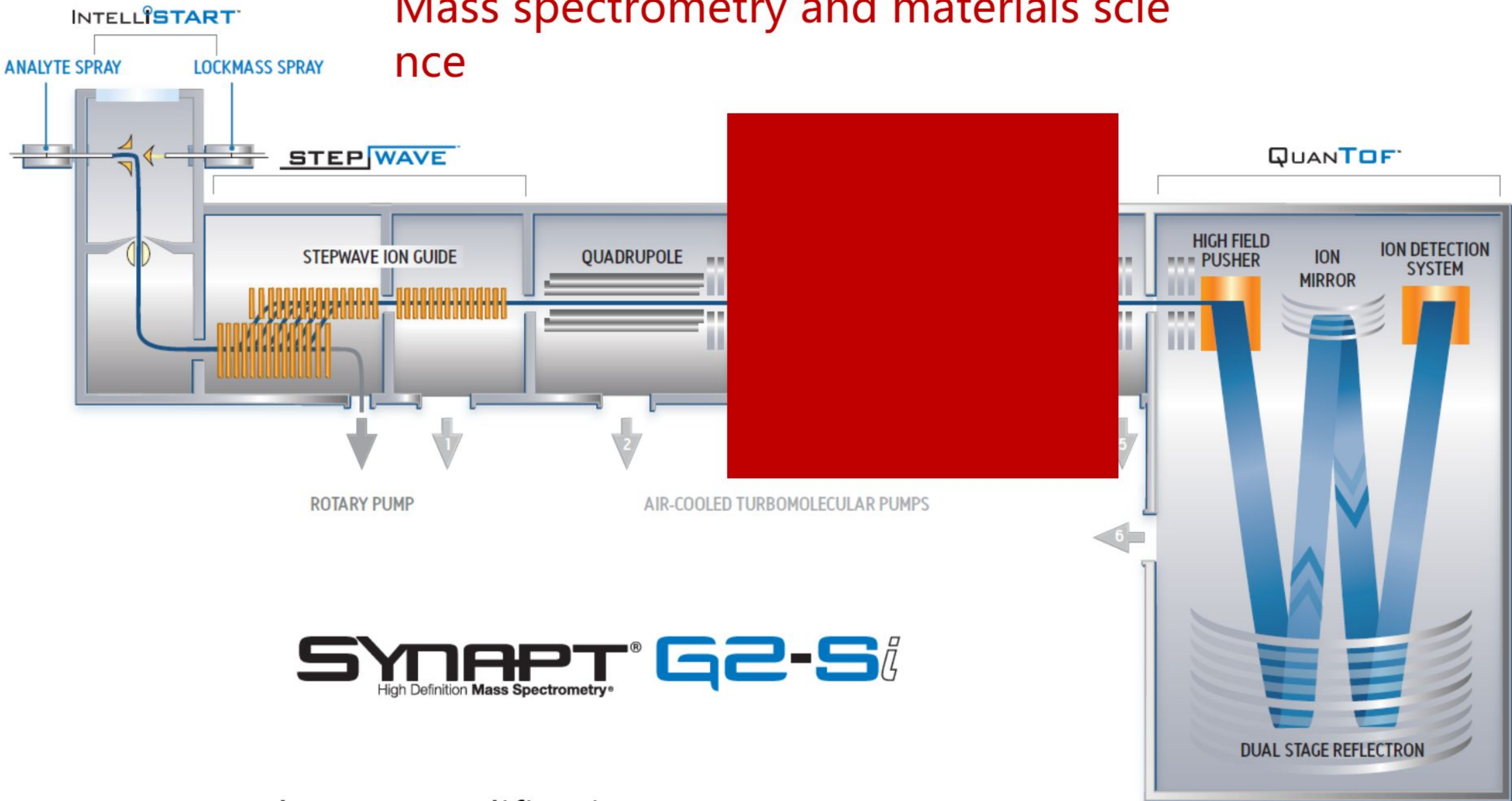
Citations: >200

0

Also the pioneering work of R. W. Murray, Robert L. Whetten, Uzi Landman, Tatuya Tsukuda, Yuichi Negishi, Hannu Hakkinen,

Rongchao Jin, Nanfeng Zheng, Terry Bigioni, Osman Bakr, Kornberg, Jianping Xie, C. M. Aikens, Thomas Buergi, Amala Dass, Ackerson, De-en Jiang, A. W. Castleman Jr., H. Schmidbauer, Robin Ras, Olli Ikkala

Mass spectrometry and materials science

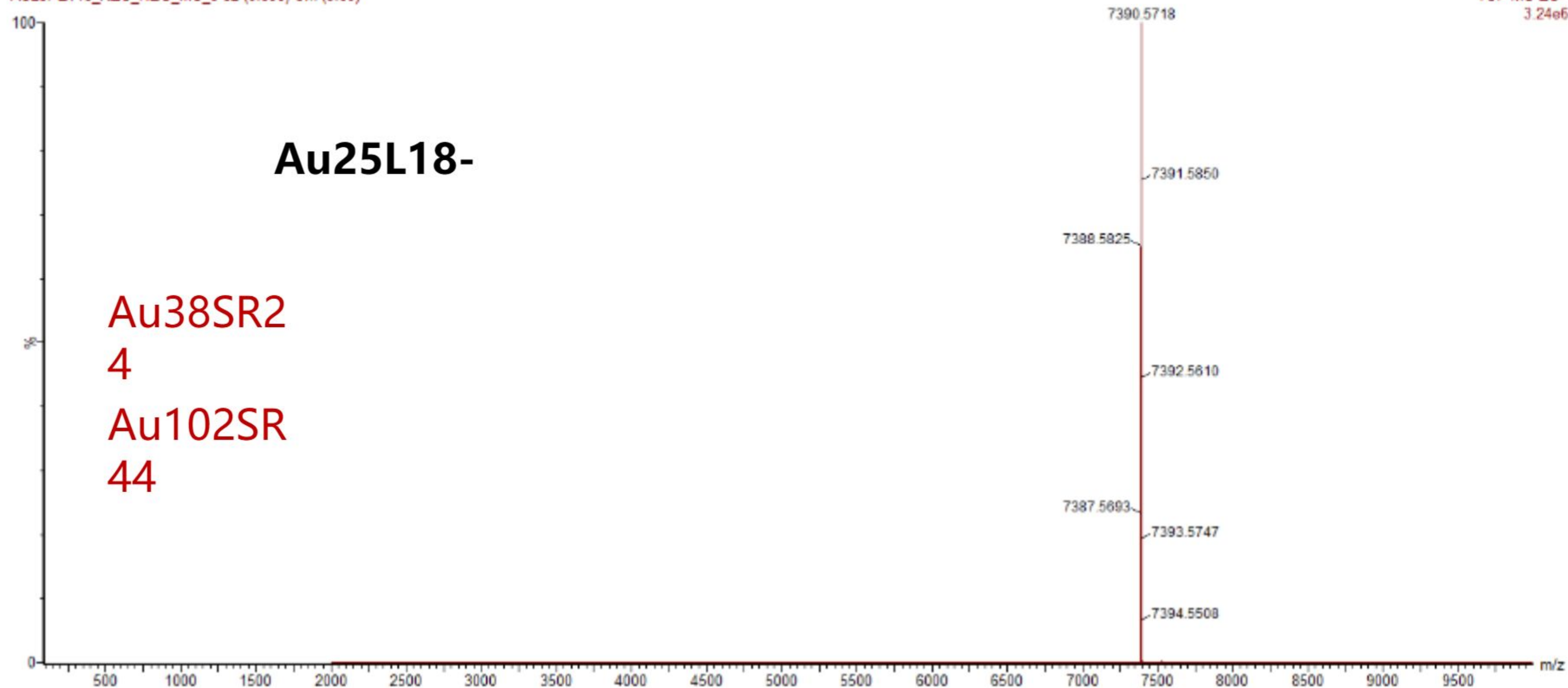


...and many modifications

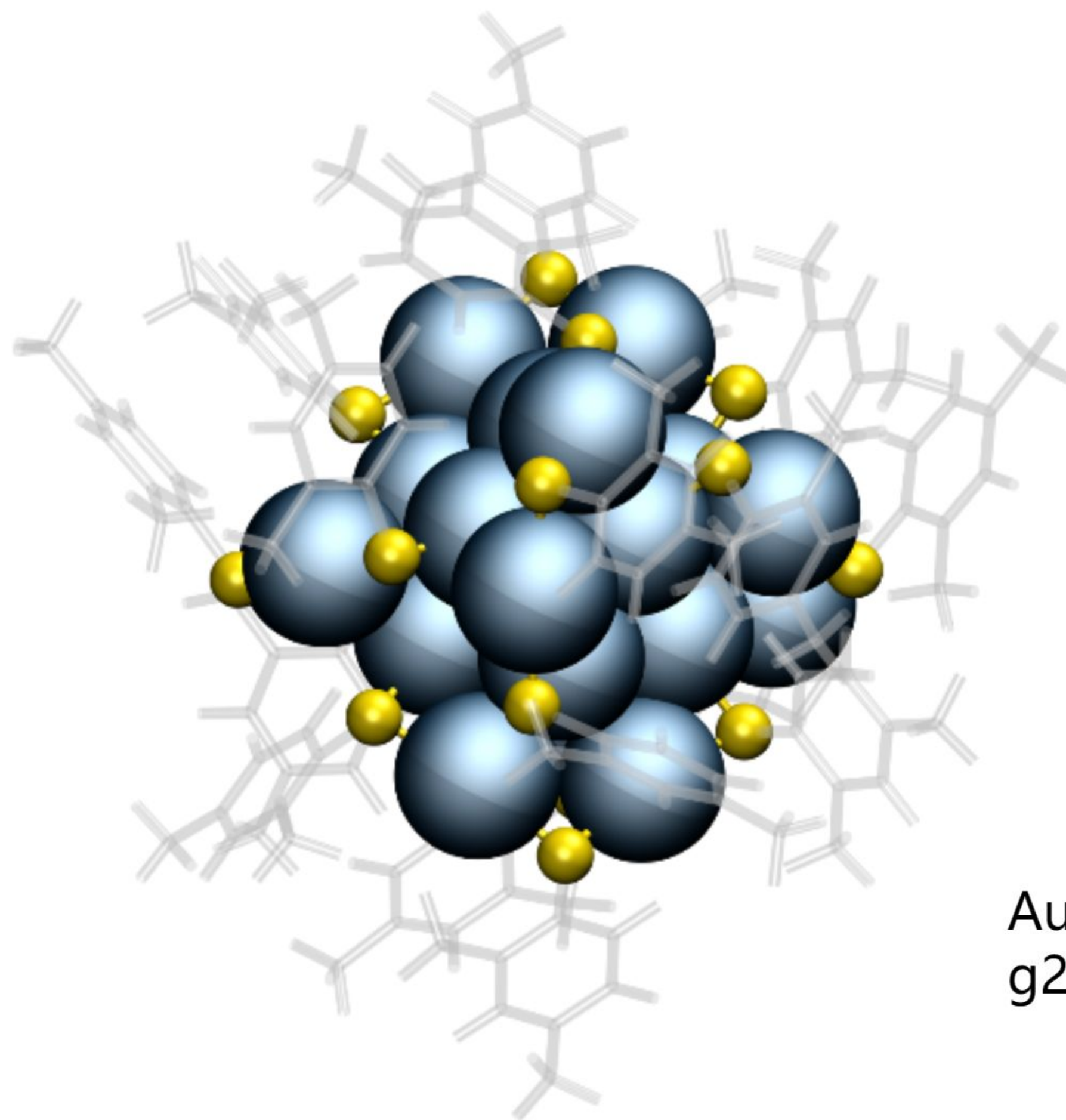
Molecular formula, Molecular weight

AU25PET18_RES_NEG_MS_3 32 (0.558) Cm (5:80)

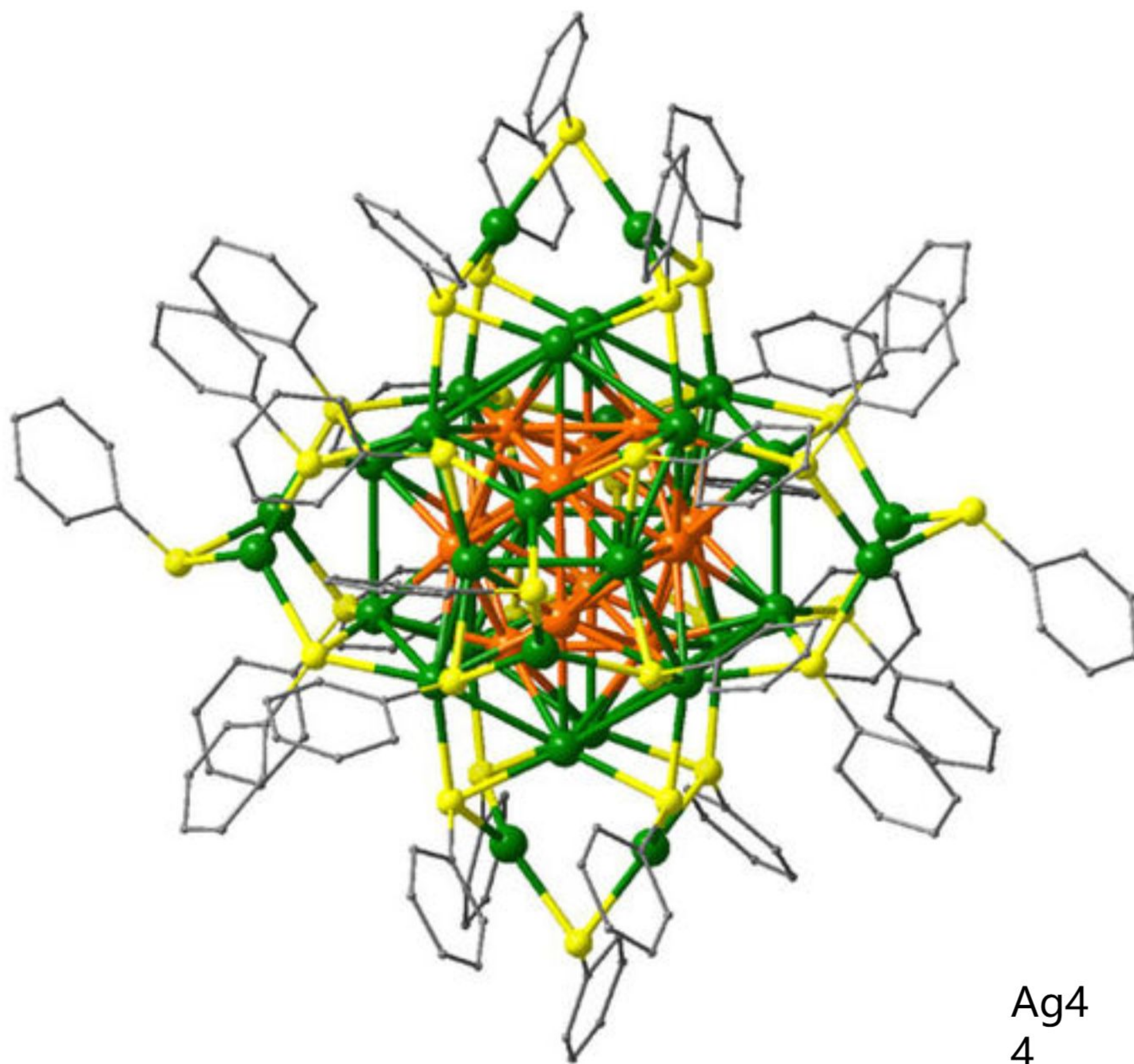
TOF MS ES-
3.24e6



New molecule s

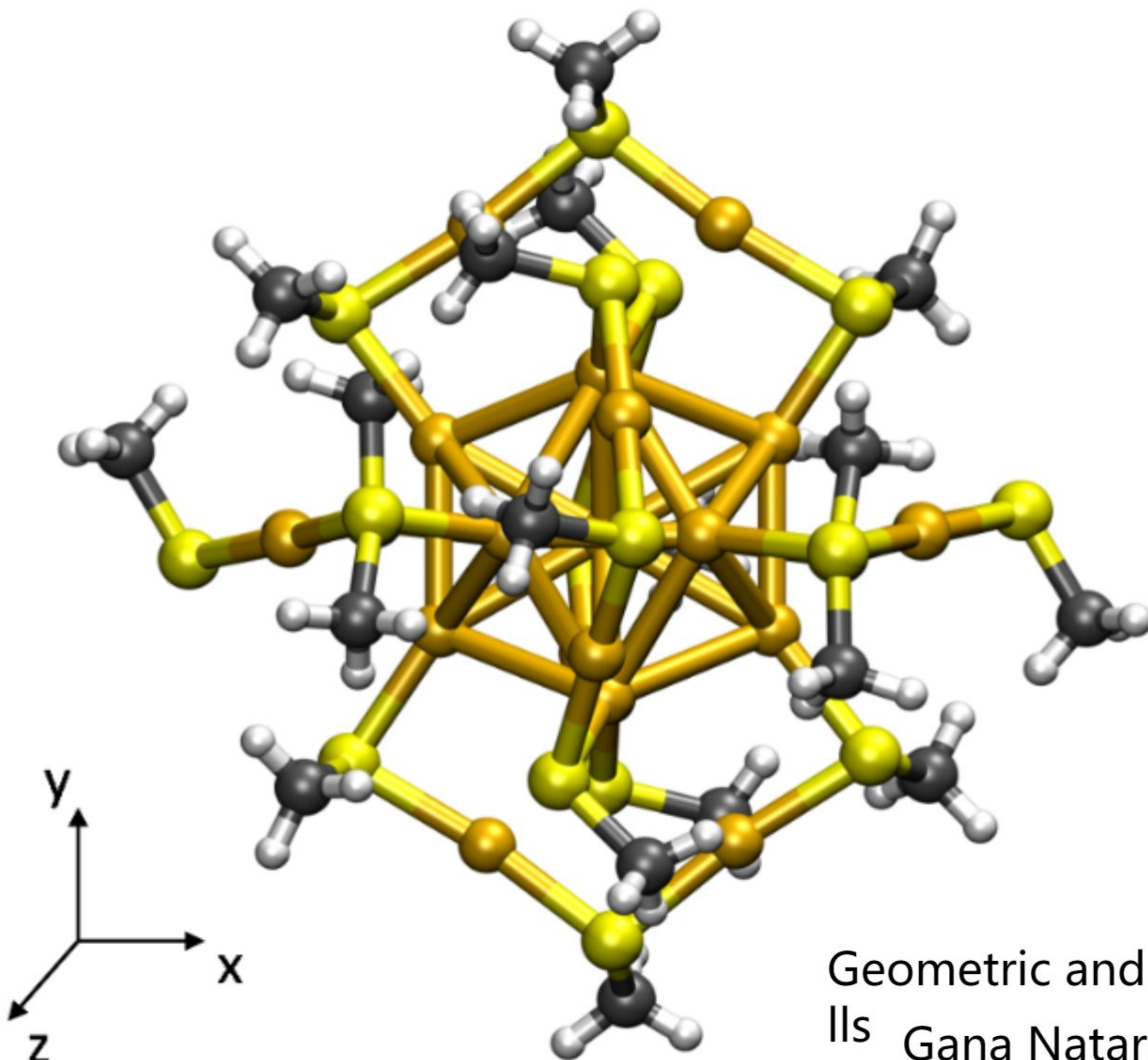


Au₂₅, Ag₂₅, A
g₂₉

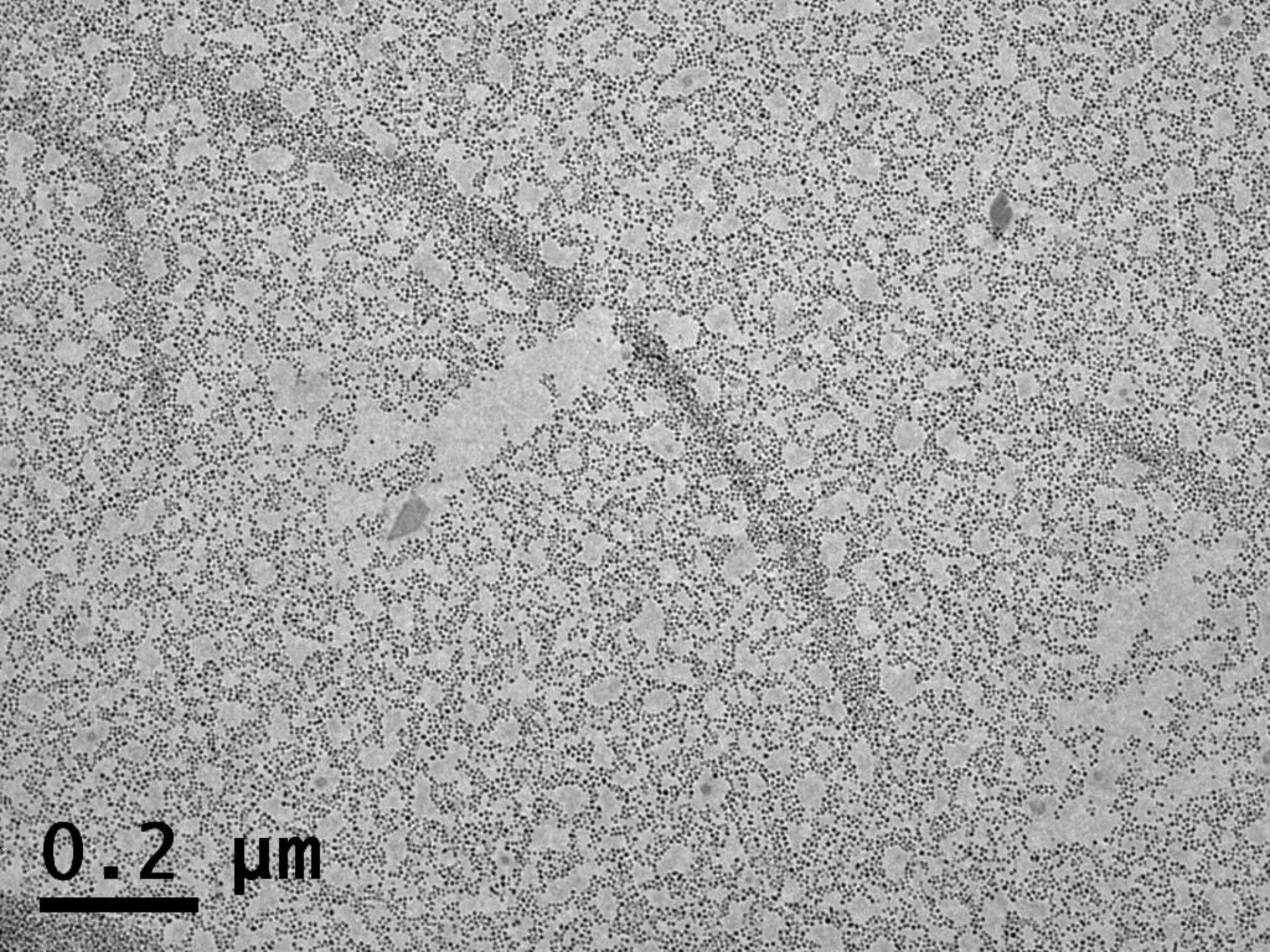


Nanfeng Zheng et al. *Nature Communications*, 2
013

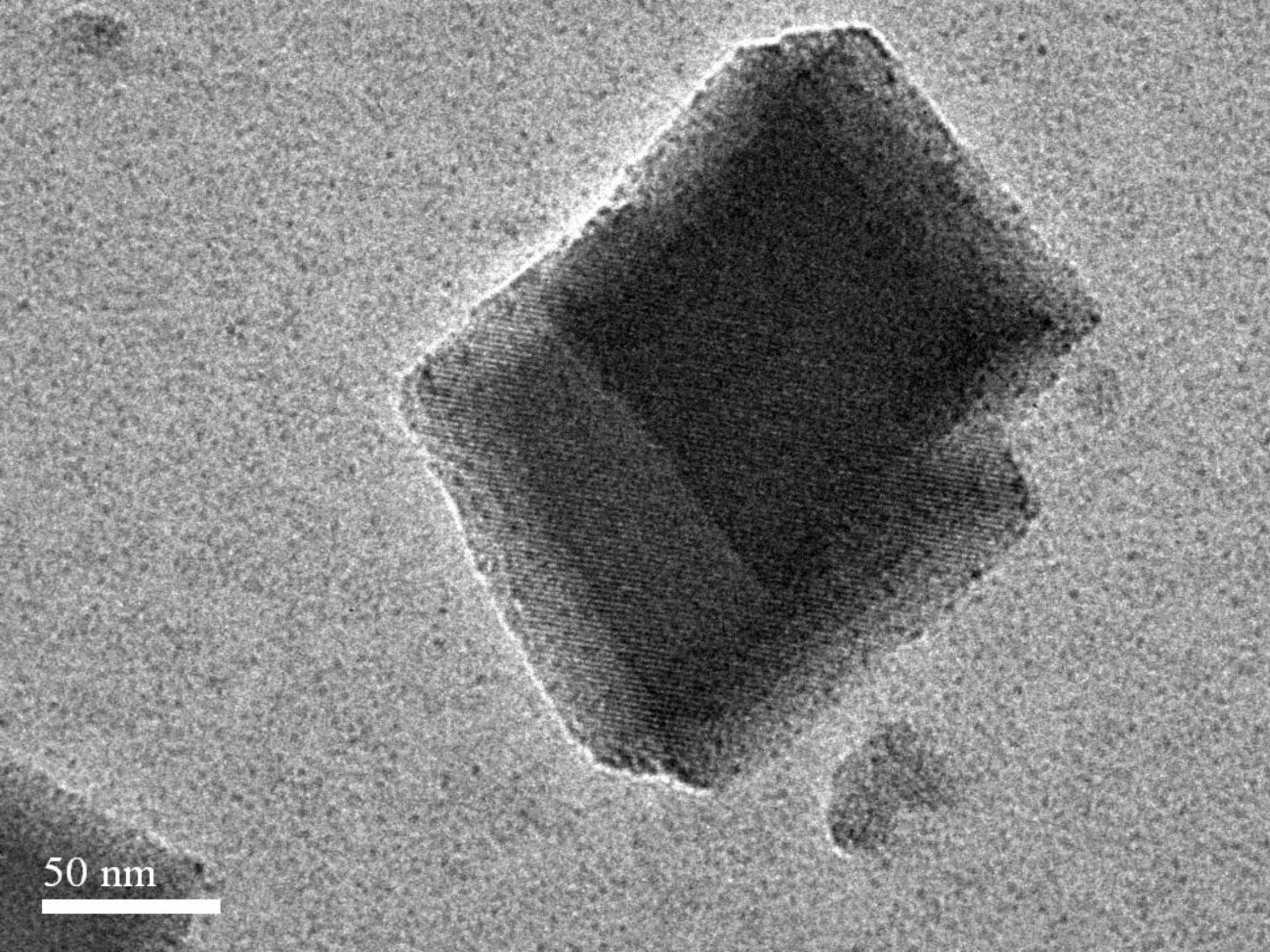
Molecular structure



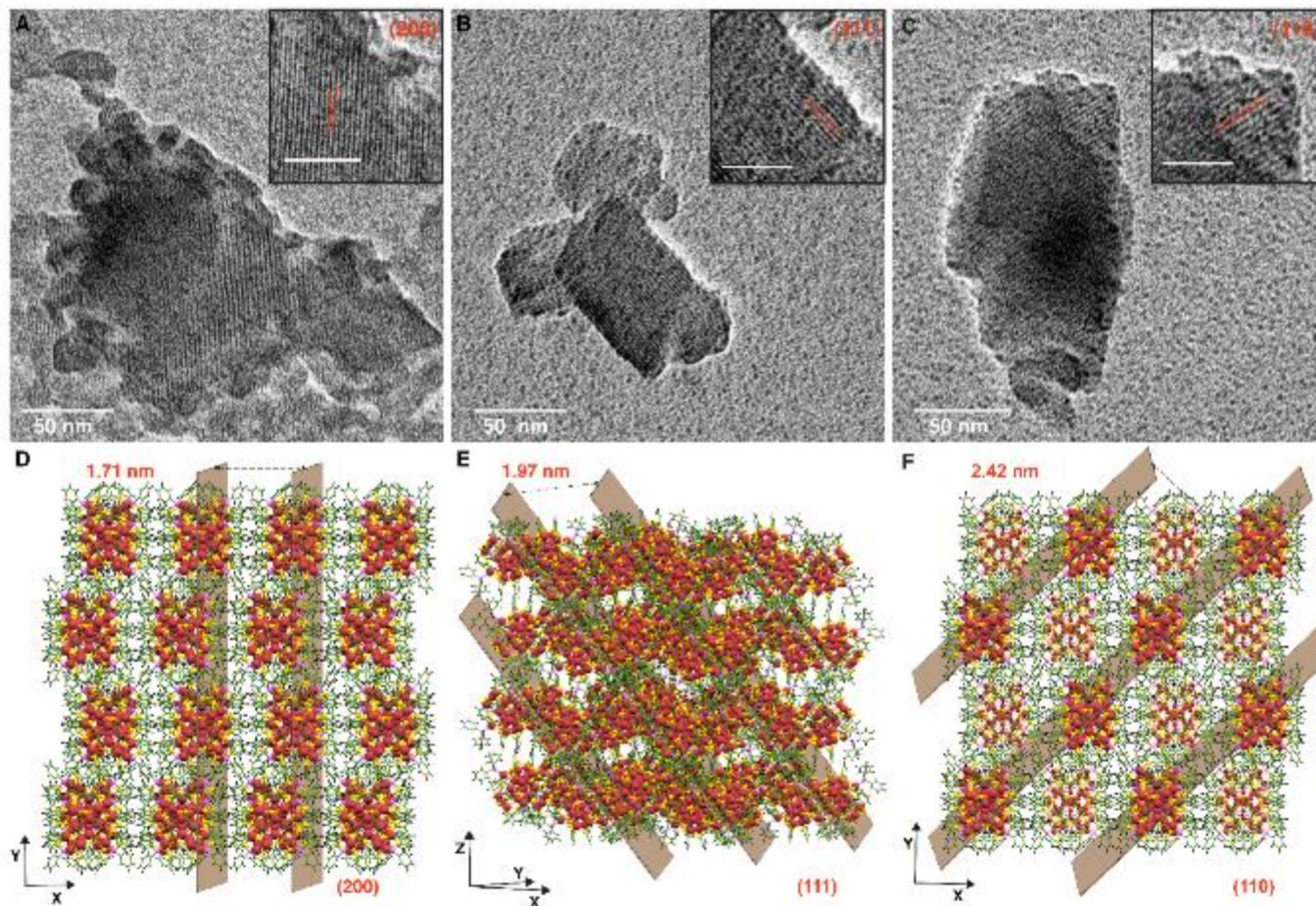
Geometric and electronic she
lls Gana Nataraja
n



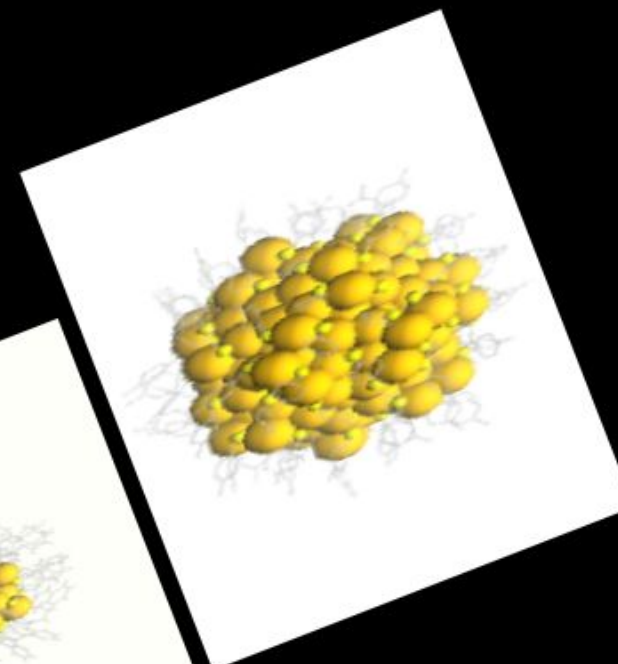
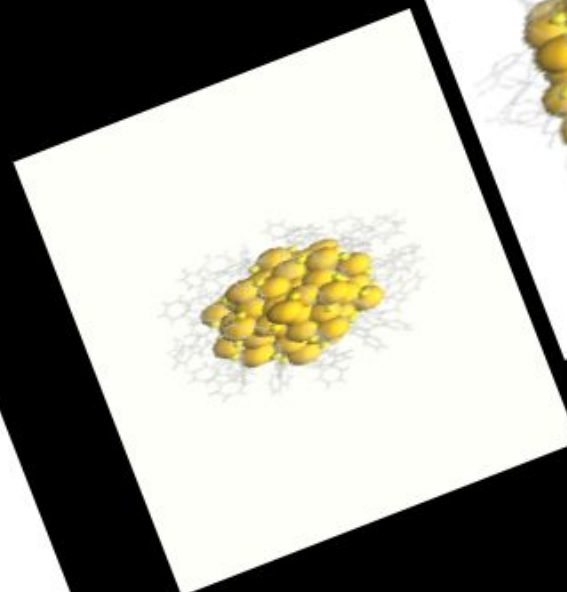
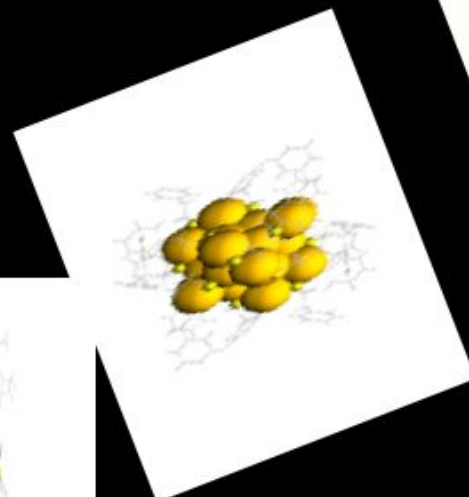
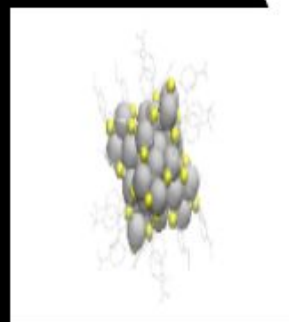
0.2 μm



50 nm



Ag₂₉(BDT)₁₂₃Ag₂₅(DMBT)₁₈ Au₂₅(PET)₁₈
 - 8- -



HRMS of Au₂₅(PET)₁₈
 -

m/z

Molecular materials

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	611.657 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

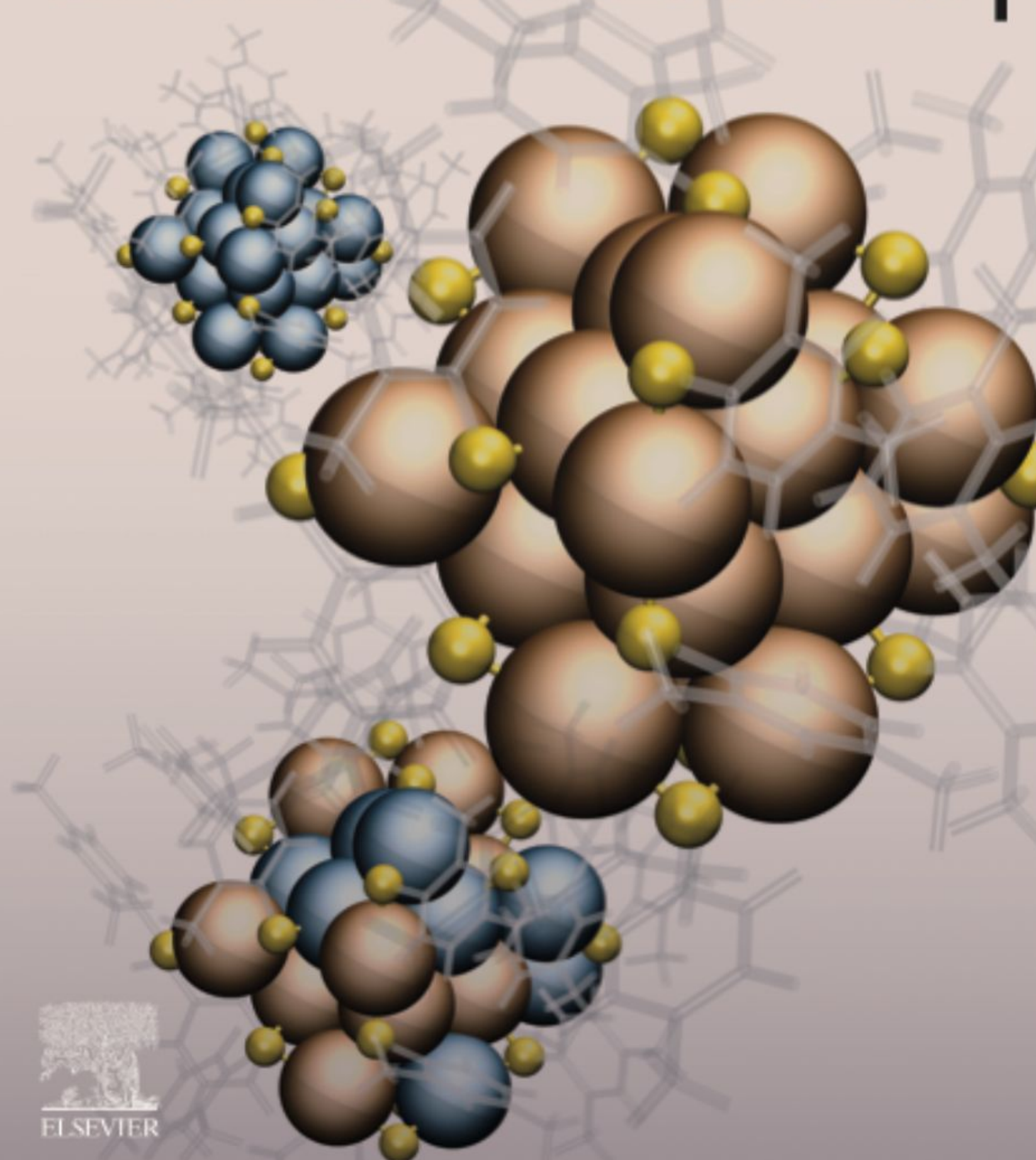
Molecular formula
 Molecular weight
 Molecular structure
 Molecular absorption and emission
 Molecular reactions
 Molecular assembly
 Molecular co-crystals

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

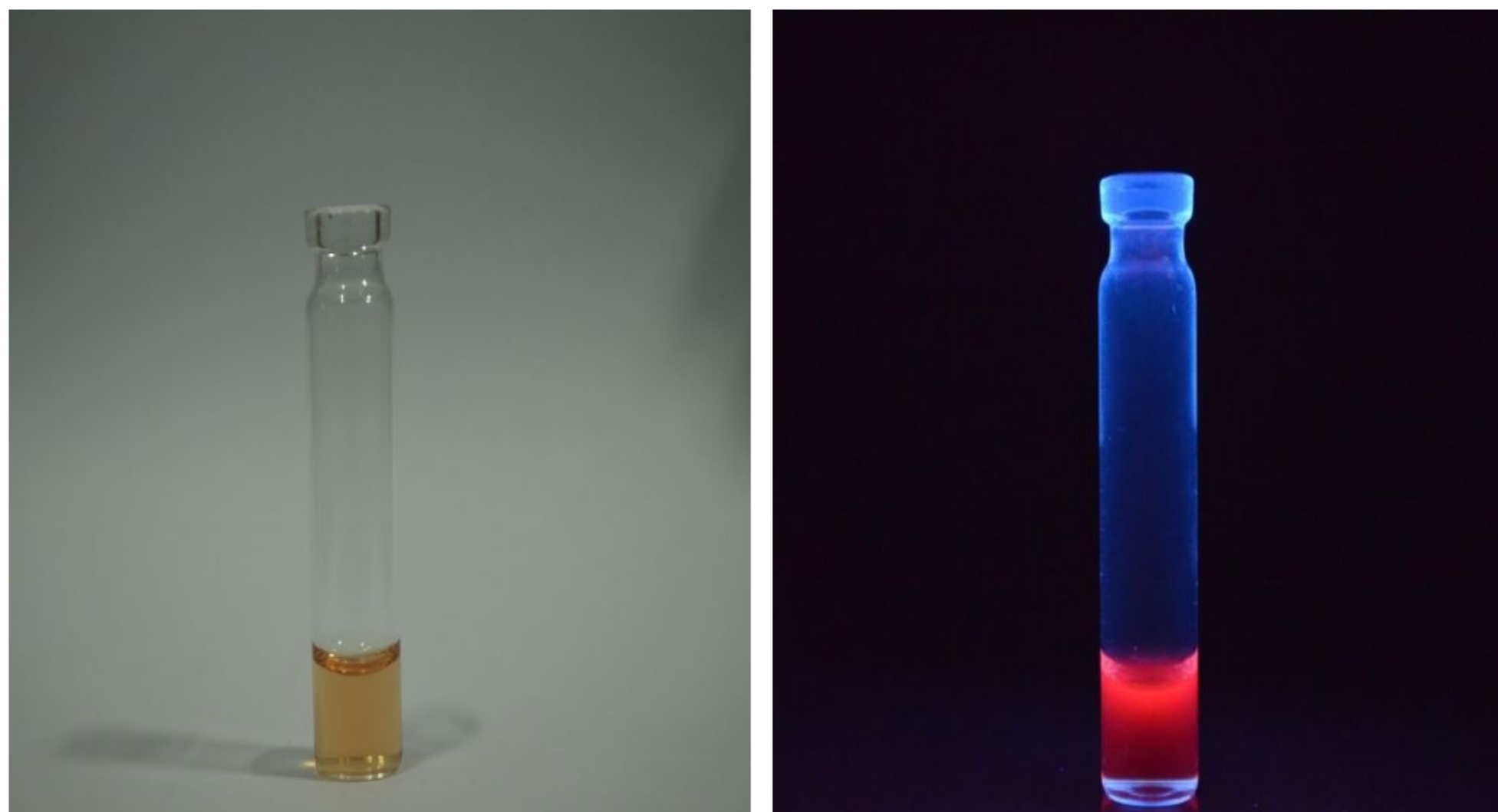
Future?

Edited by
Thalappil Pradeep

ATOMICALLY PRECISE METAL NANOCCLUSERS



Molecular reactions



Reactions on clusters

Reactions between clusters

Inter-cluster reactions



Article

pubs.acs.org/JACS

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

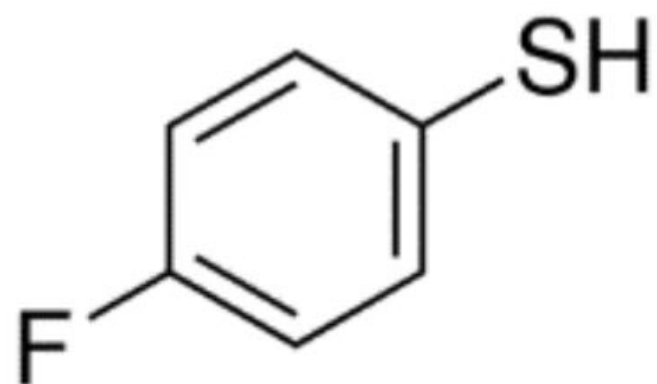
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

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



Au₂₅(FTP)₁₈ + Ag₄₄(FTP)₃₀  Au_{25-x}Ag_x(FTP)₁₈



Energies for the substitution reaction of (A) Au in Ag₄₄(SR)₃₀, (B) Ag in Au₂₅(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

Ag₂₅-Au₂₅ experiments

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

DMBT

PE
T

[Ag₂₅(DMBT)₁₈+Au₂₅(PET)₁₈]²⁻

DMBT

**PE
T**

**Ag₂₅(DMBT)
18**

[Ag₂₅(DMBT)₁₈+Au₂₅(PET)₁₈]²⁻

**Au₂₅(PET)
18**

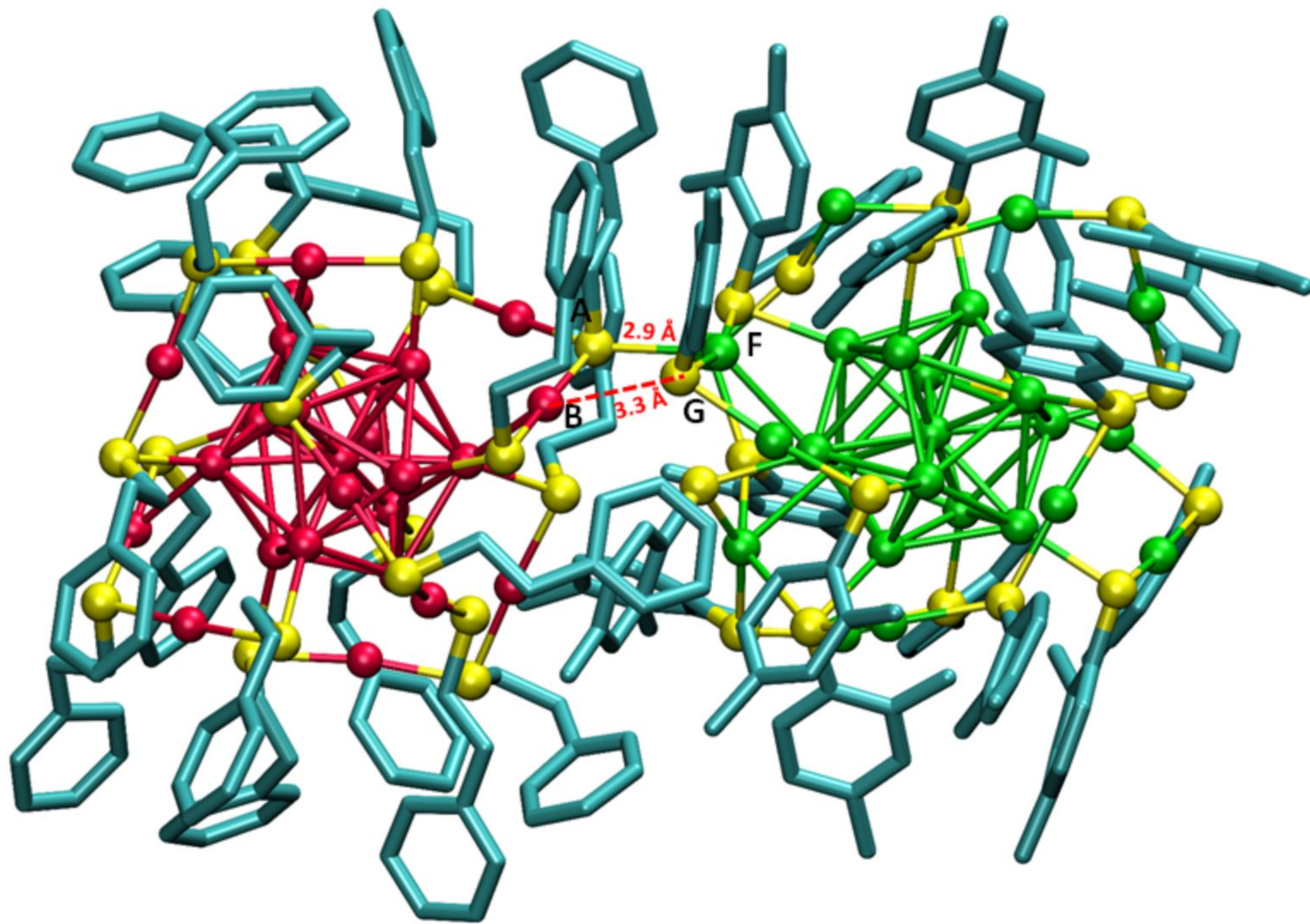
Evolution of alloy clusters from the dianionic adduct, [Ag₂₅Au₂₅(DMBT)₁₈(PET)₁₈]²⁻

within 5 min

Ag₂₅(DMBT)₁₈:Au₂₅(PET)₁₈
0.3:1.0

within 2 min

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

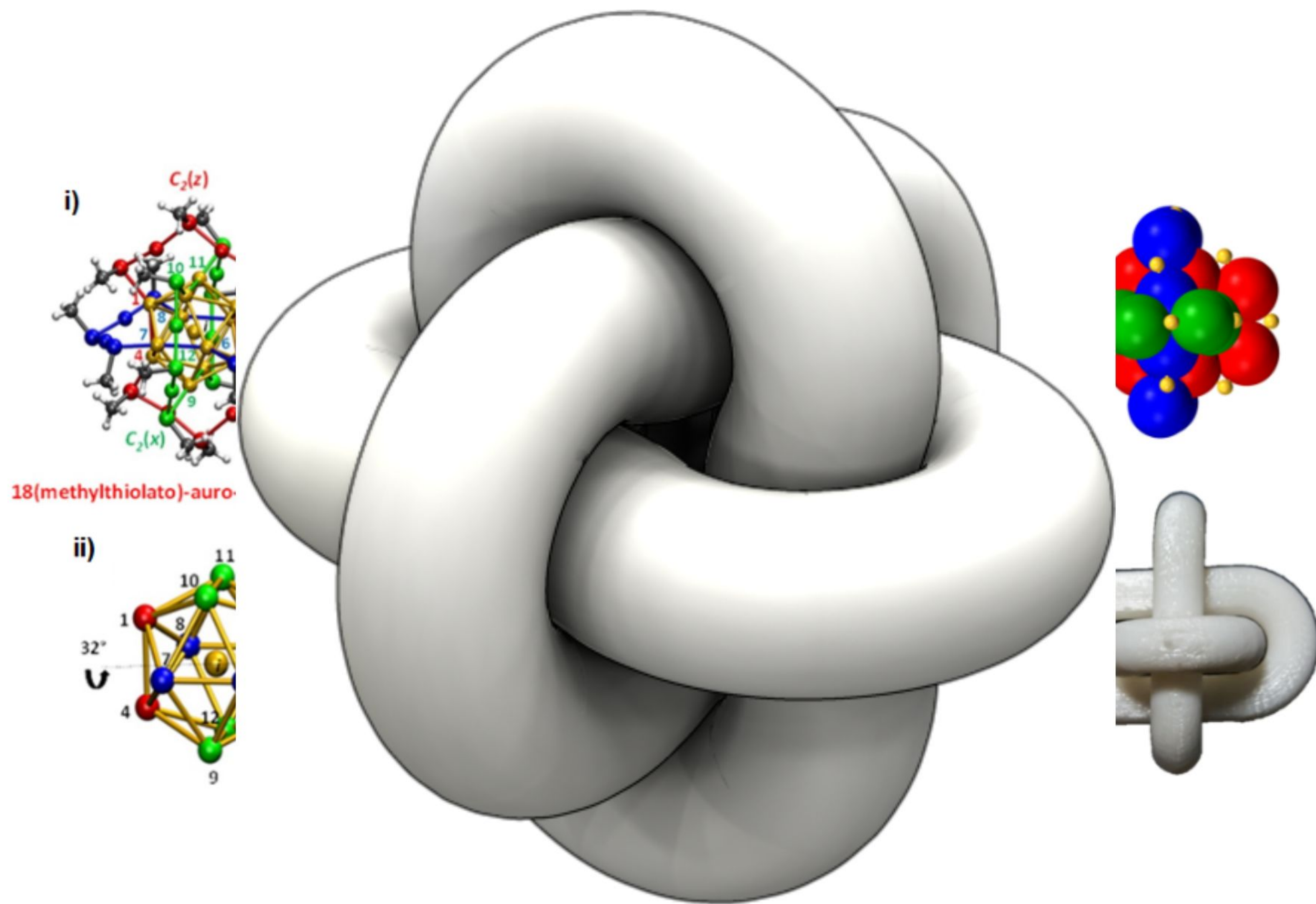


How do we comprehend th

is?

Nomenclatu

re



Aspicule
s

(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-)

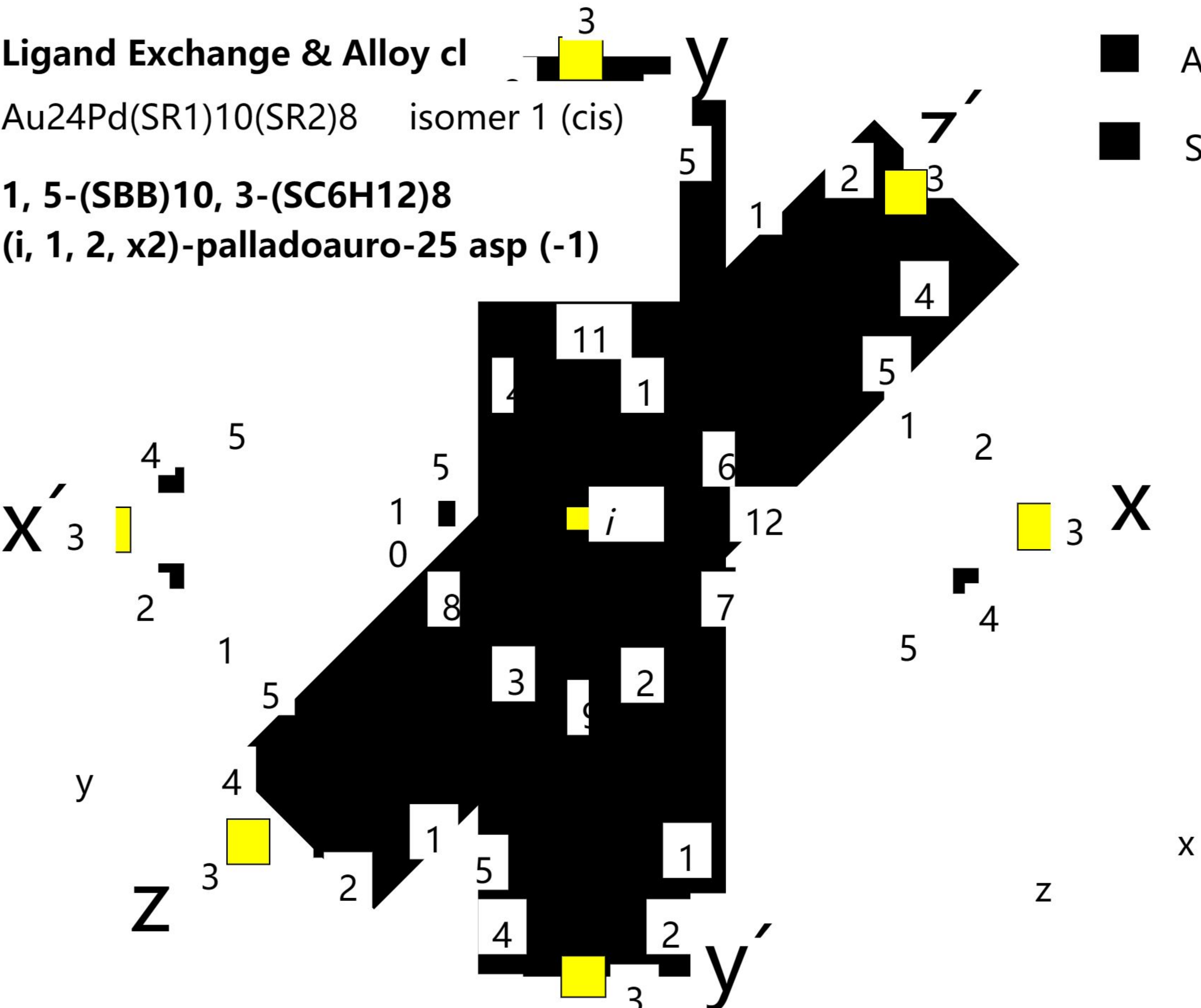
Ligand Exchange & Alloy cl

Au24Pd(SR1)10(SR2)8 isomer 1 (cis)

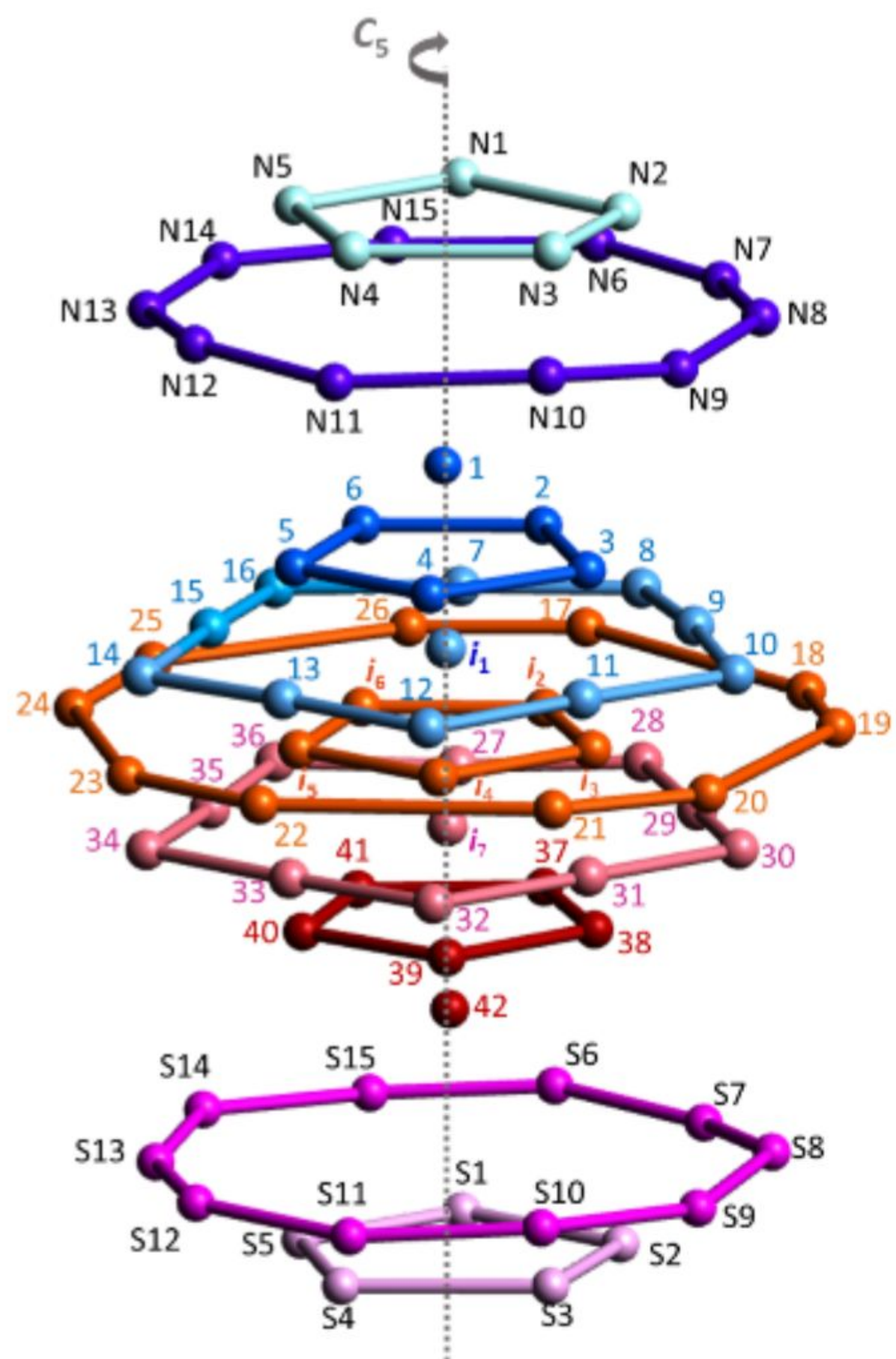
1, 5-(SBB)10, 3-(SC6H12)8
(i, 1, 2, x2)-palladoauro-25 asp (-1)

Au

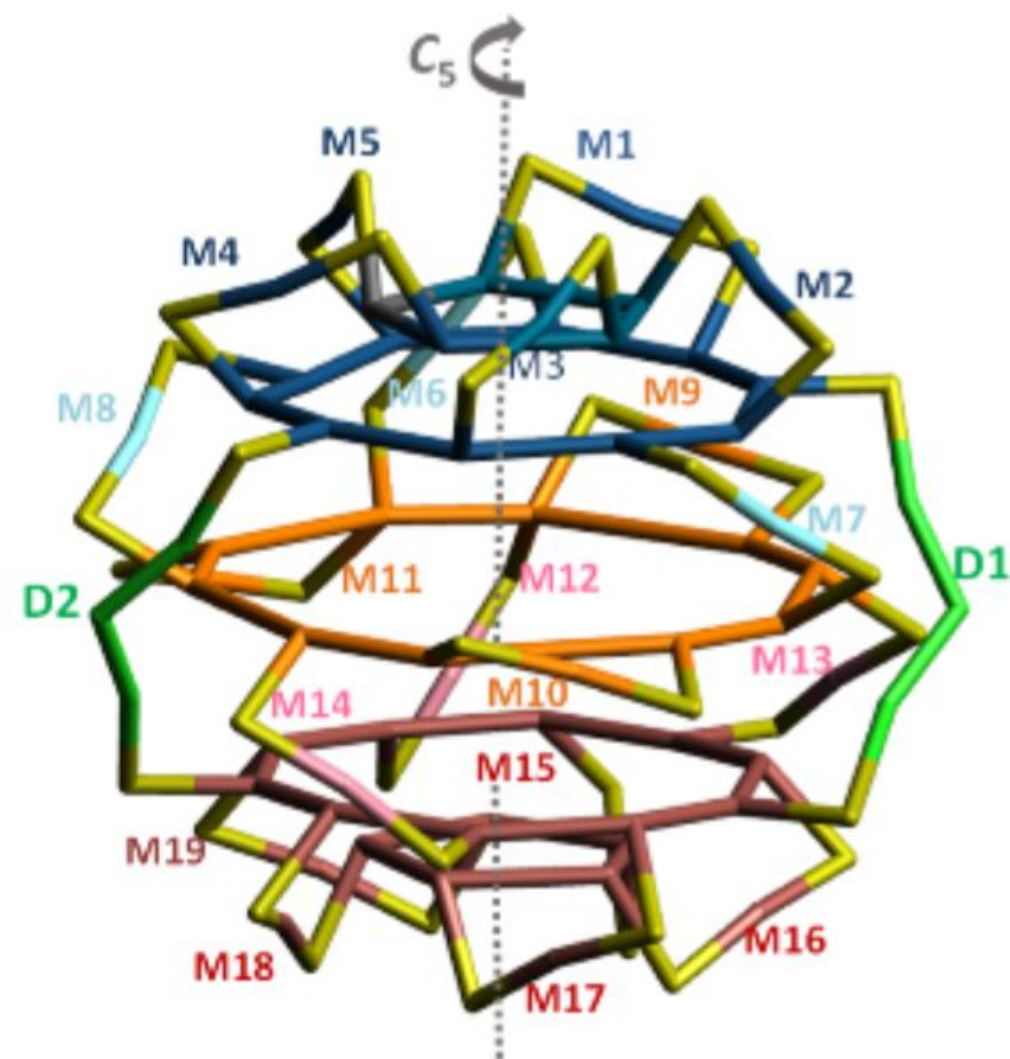
S



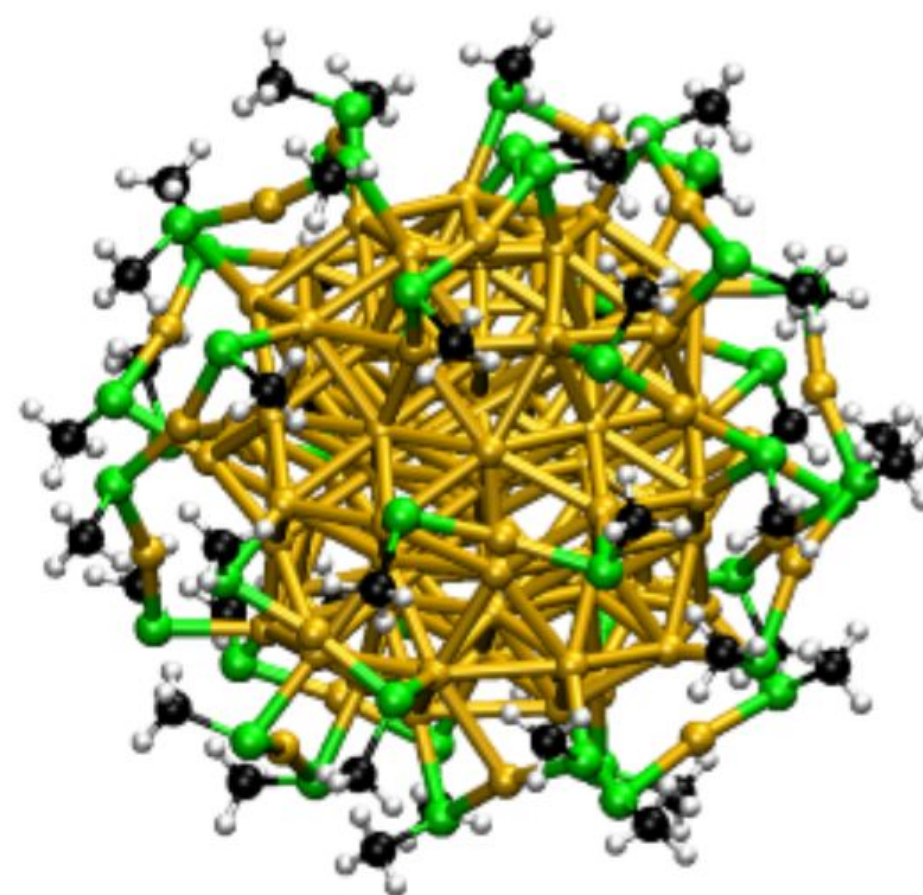
(A)



(B)

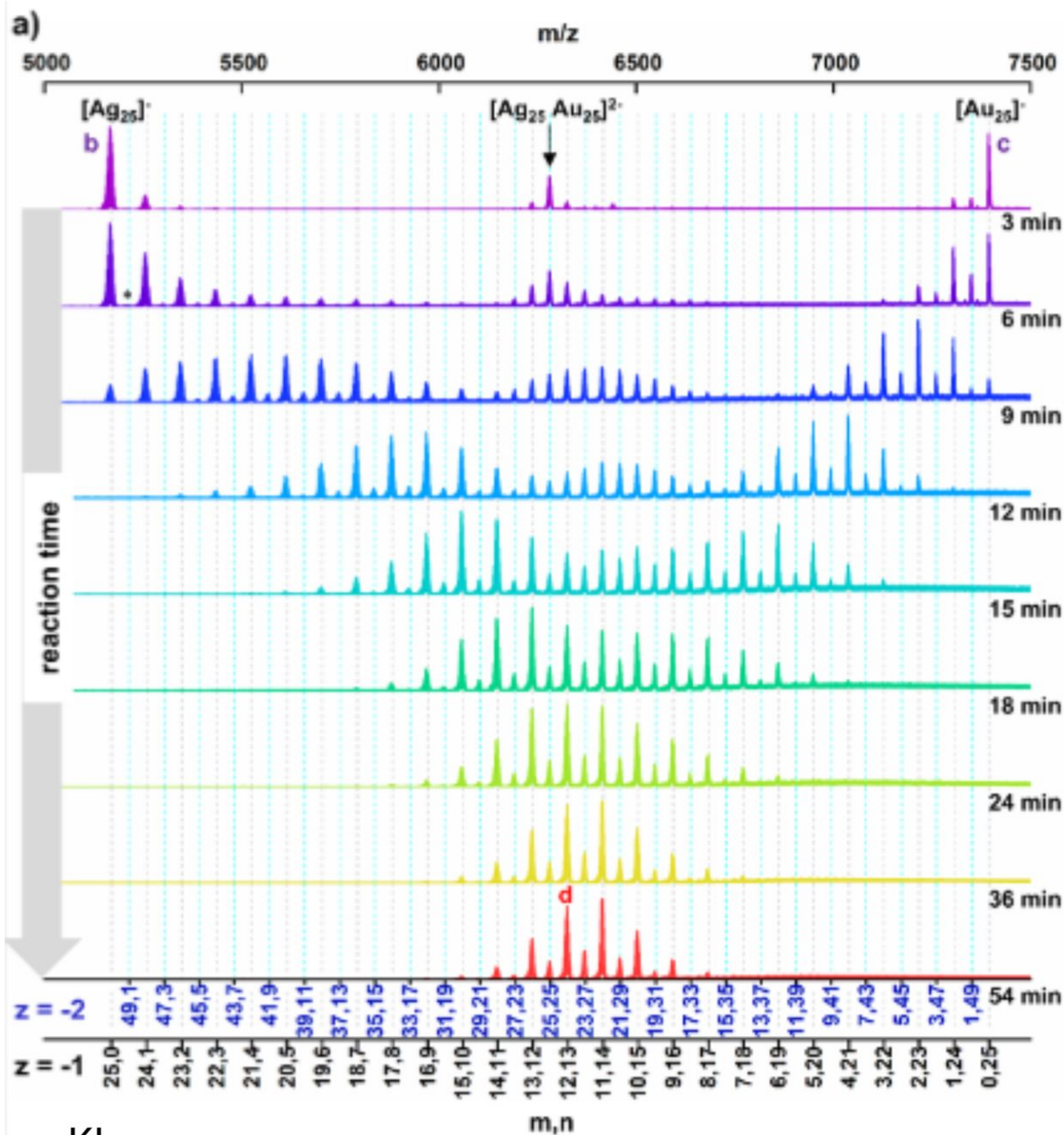


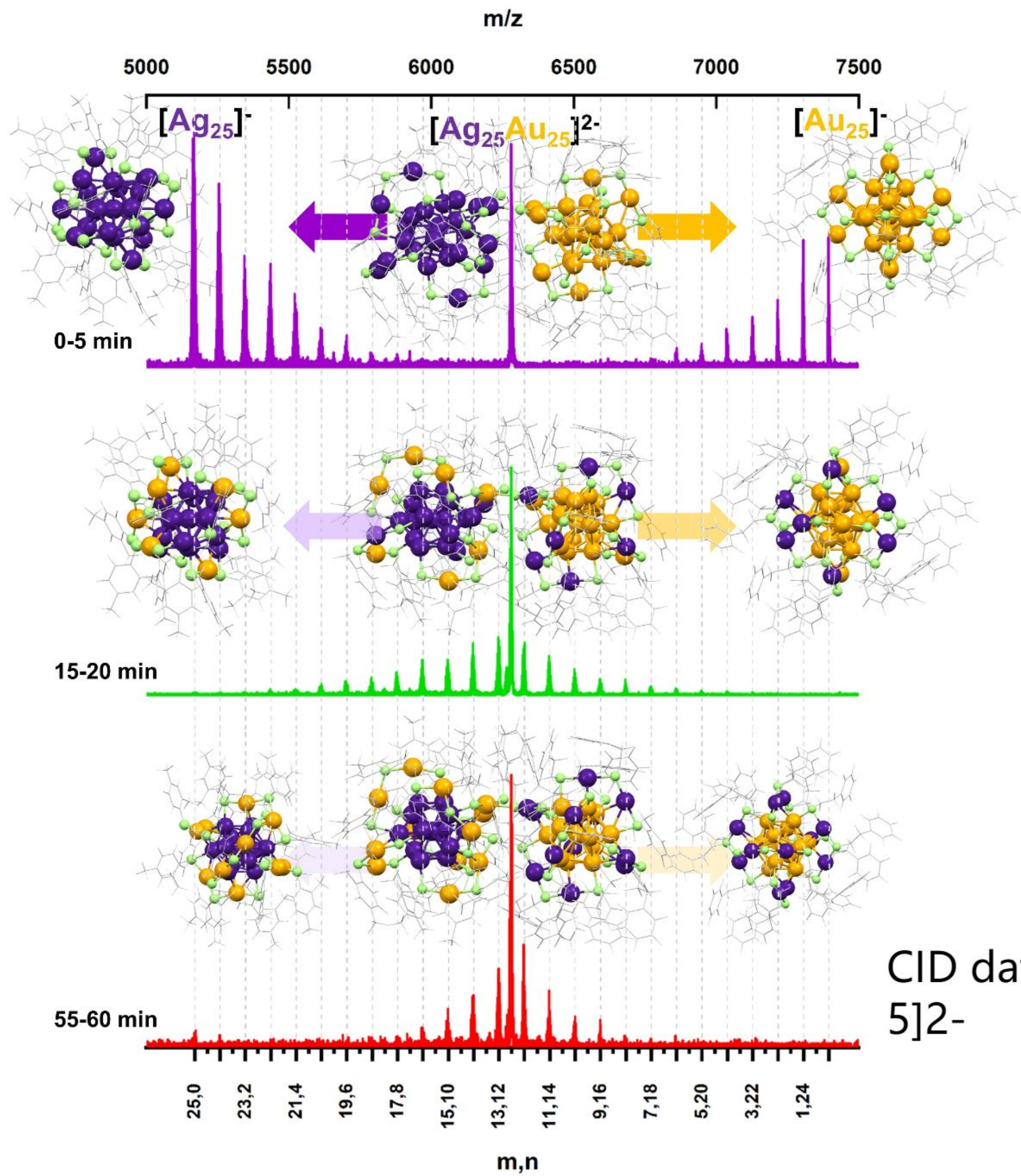
(C)



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

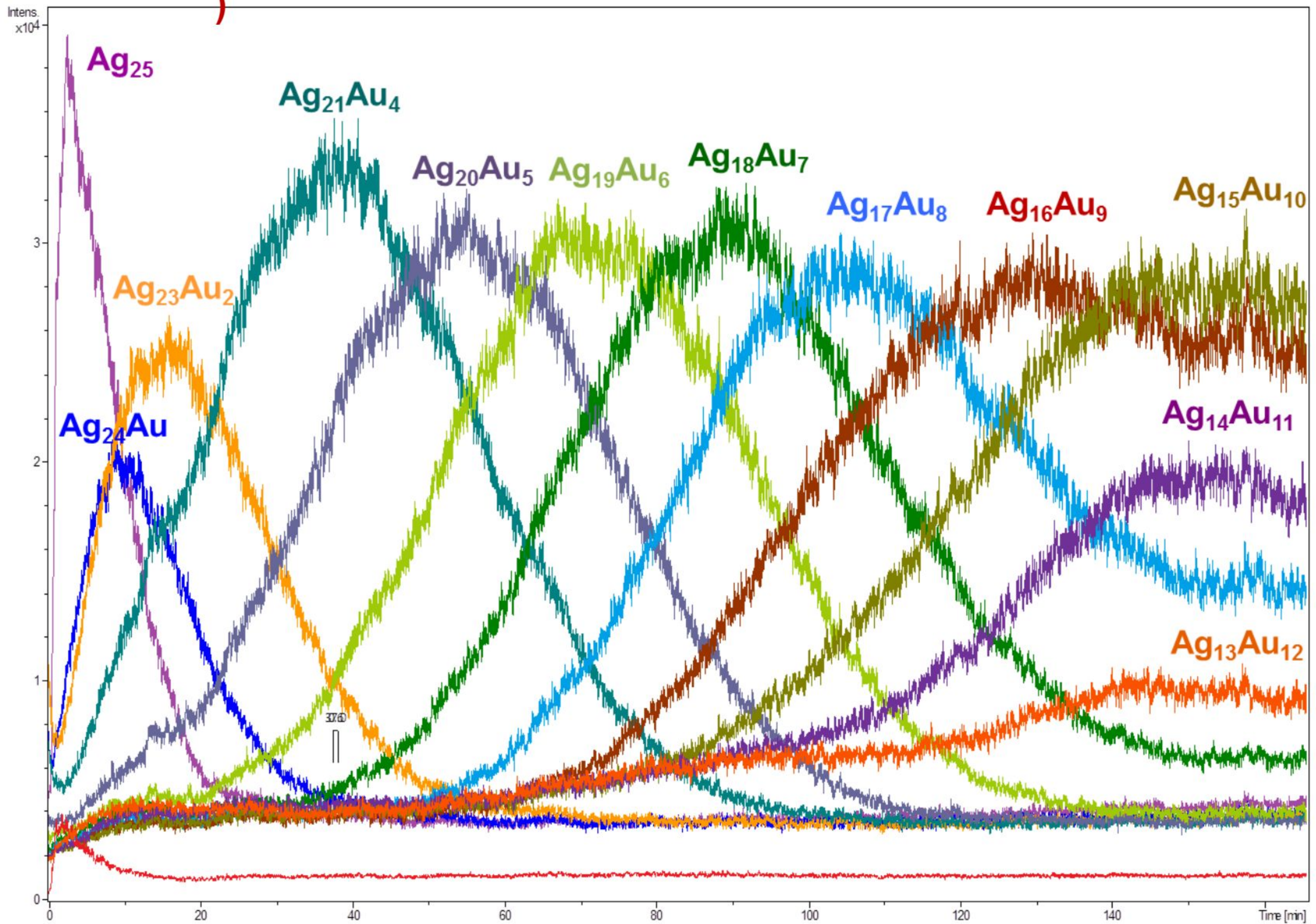
R-(SMe)₄₄-auro-102 aspicule(0) and L-(SMe)₄₄-auro-102 aspicule(0)





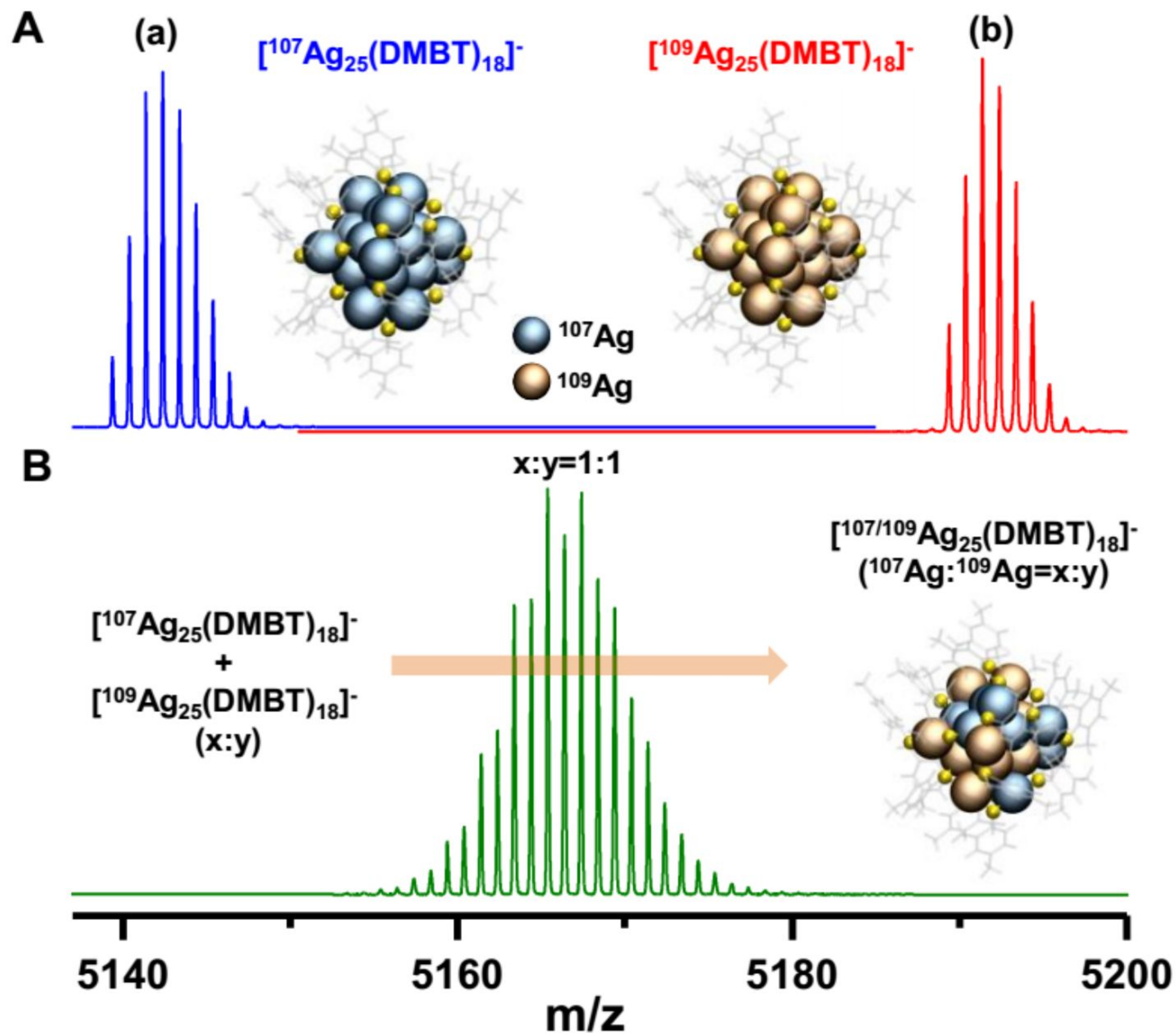
CID data of $[Au_{25}Ag_{25}]^{2-}$

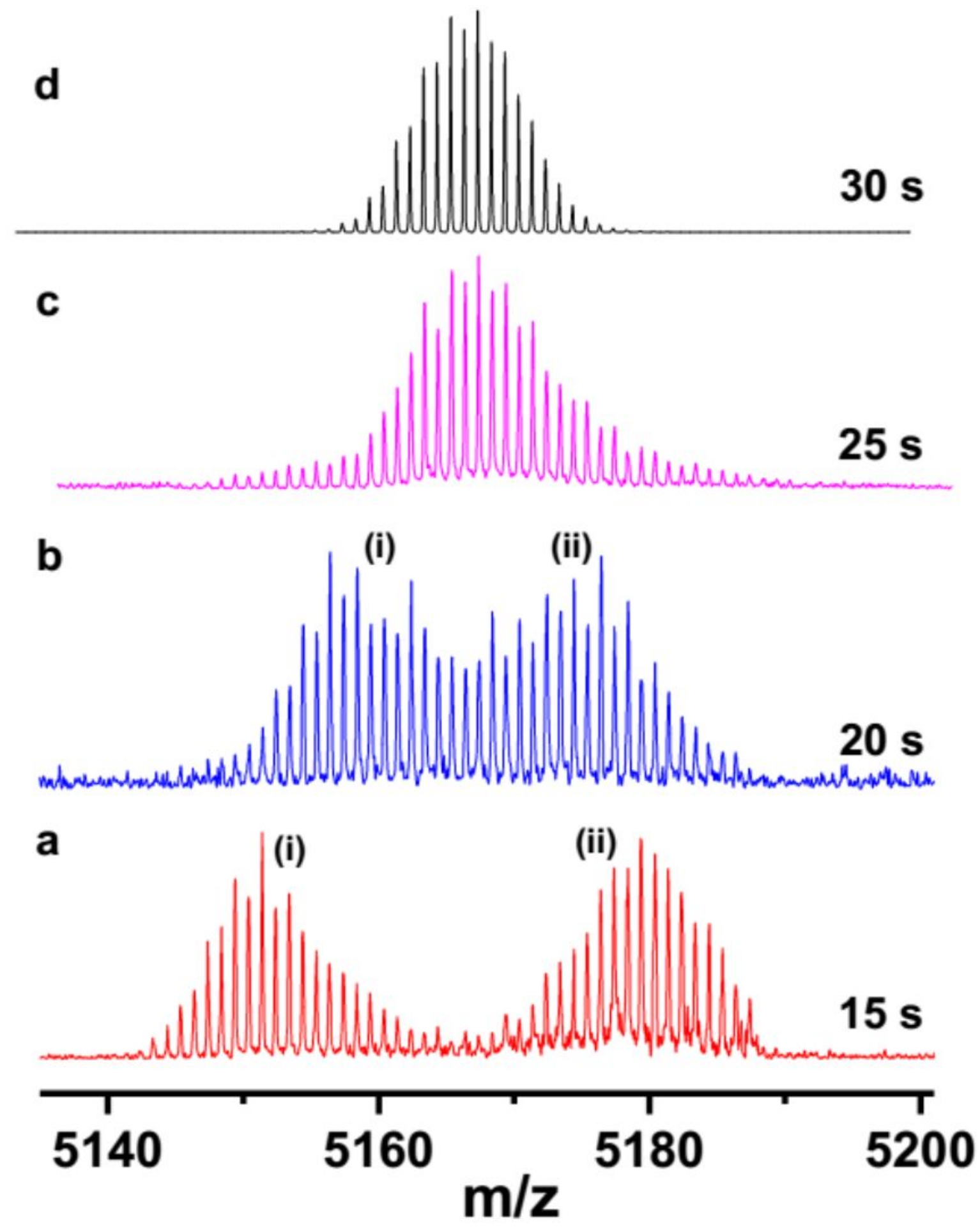
Kinetics of the exchange (monitored on the Ag25 side)

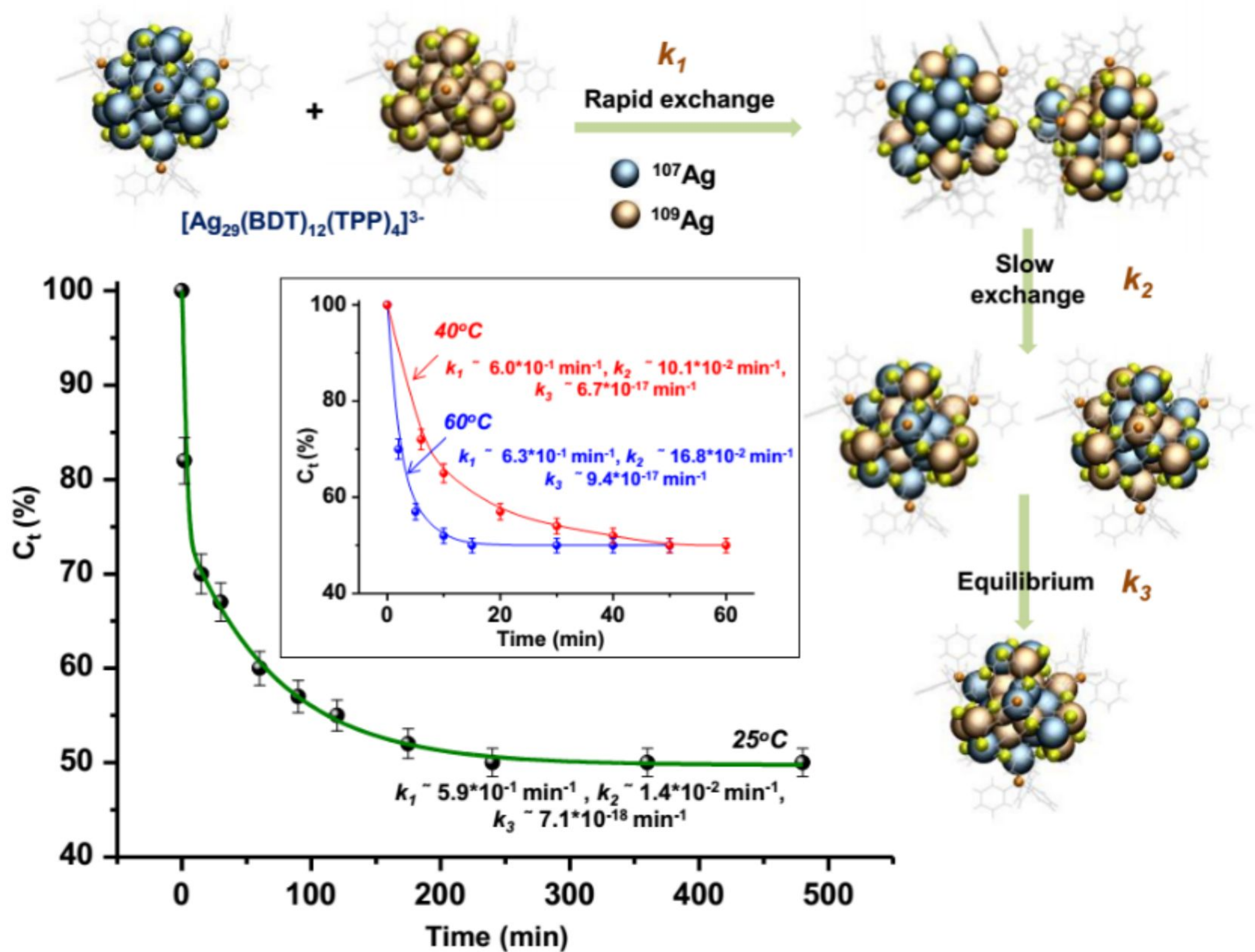




ESI MS of **A)** $^{107}\text{Ag}_{25}(\text{DMBT})_{18}$ and **B)** $^{109}\text{Ag}_{25}(\text{DMBT})_{18}$. Insets shows the respective isotope patterns.

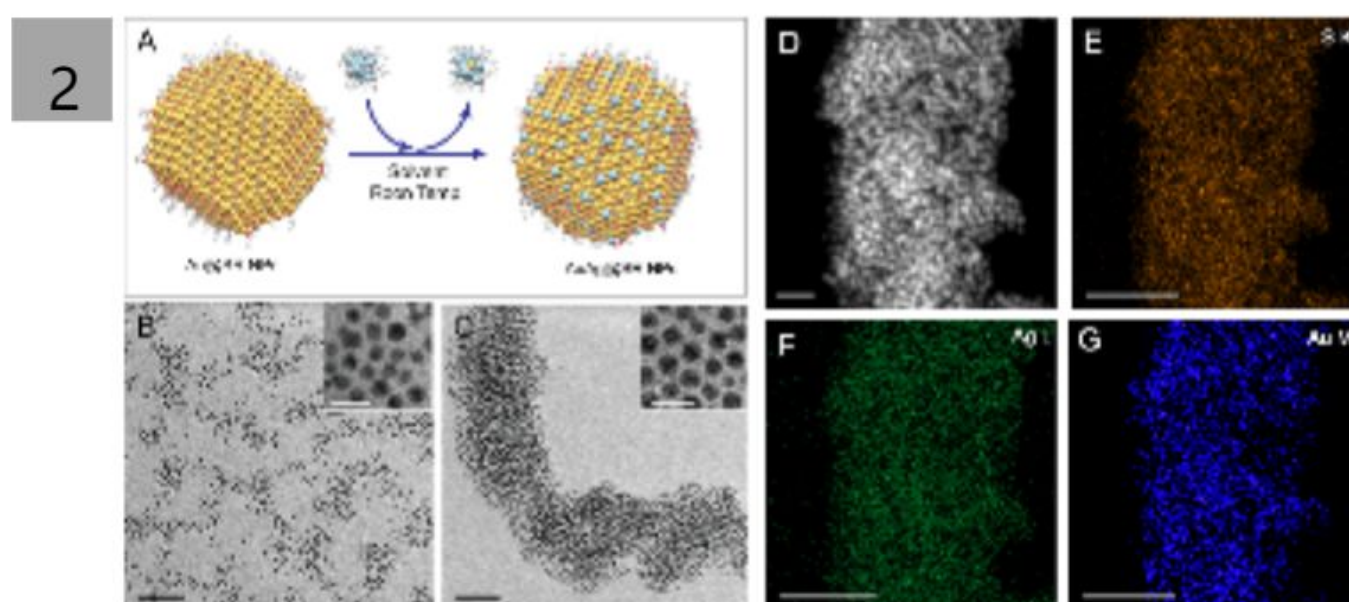
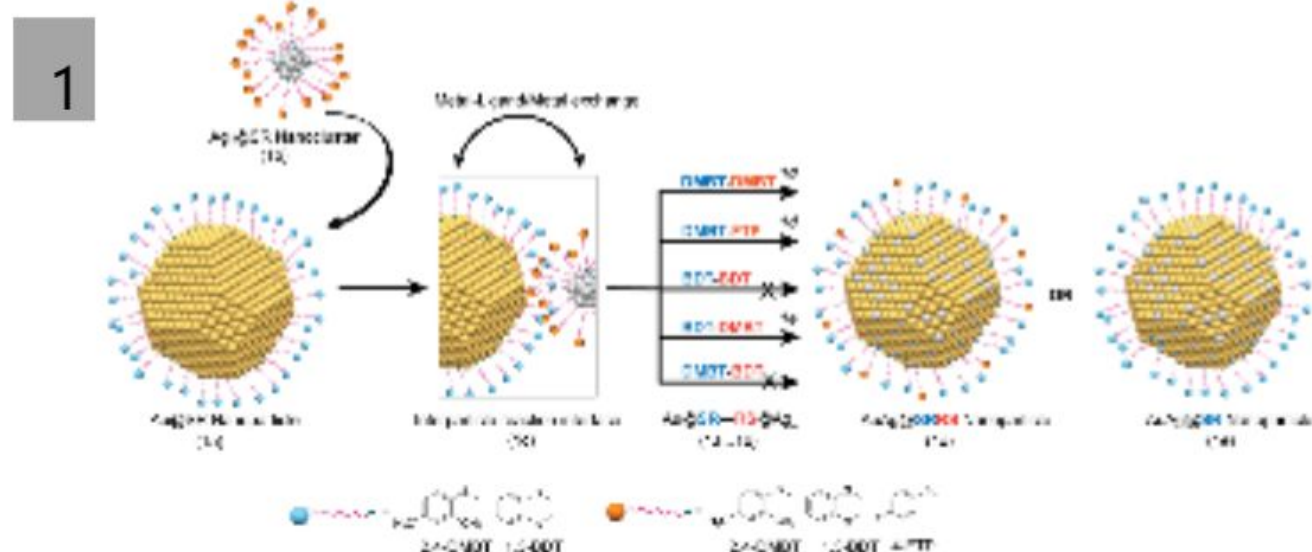




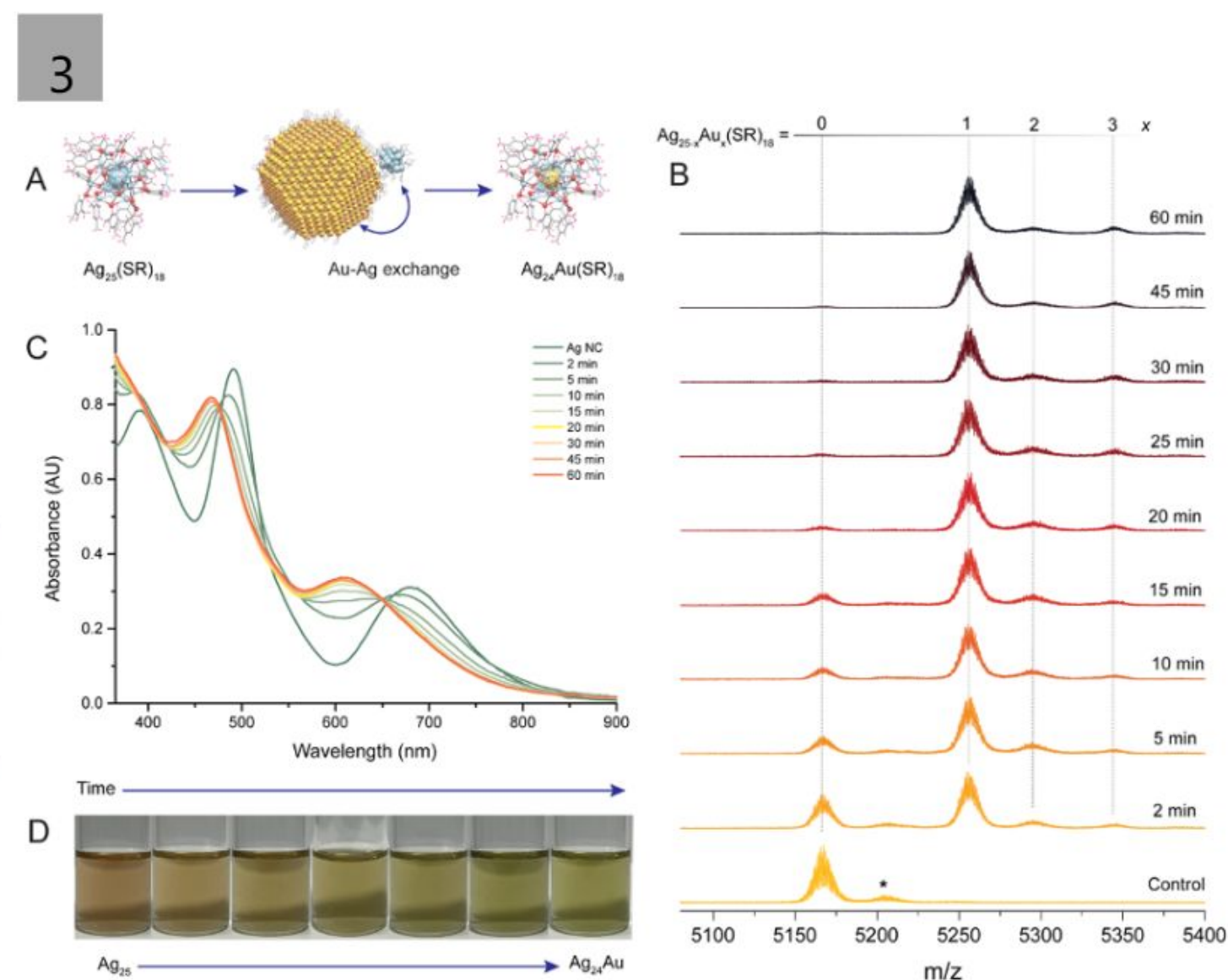


Can clusters react with nanoparticles?

Ag₂₅ with Au nanoparticles



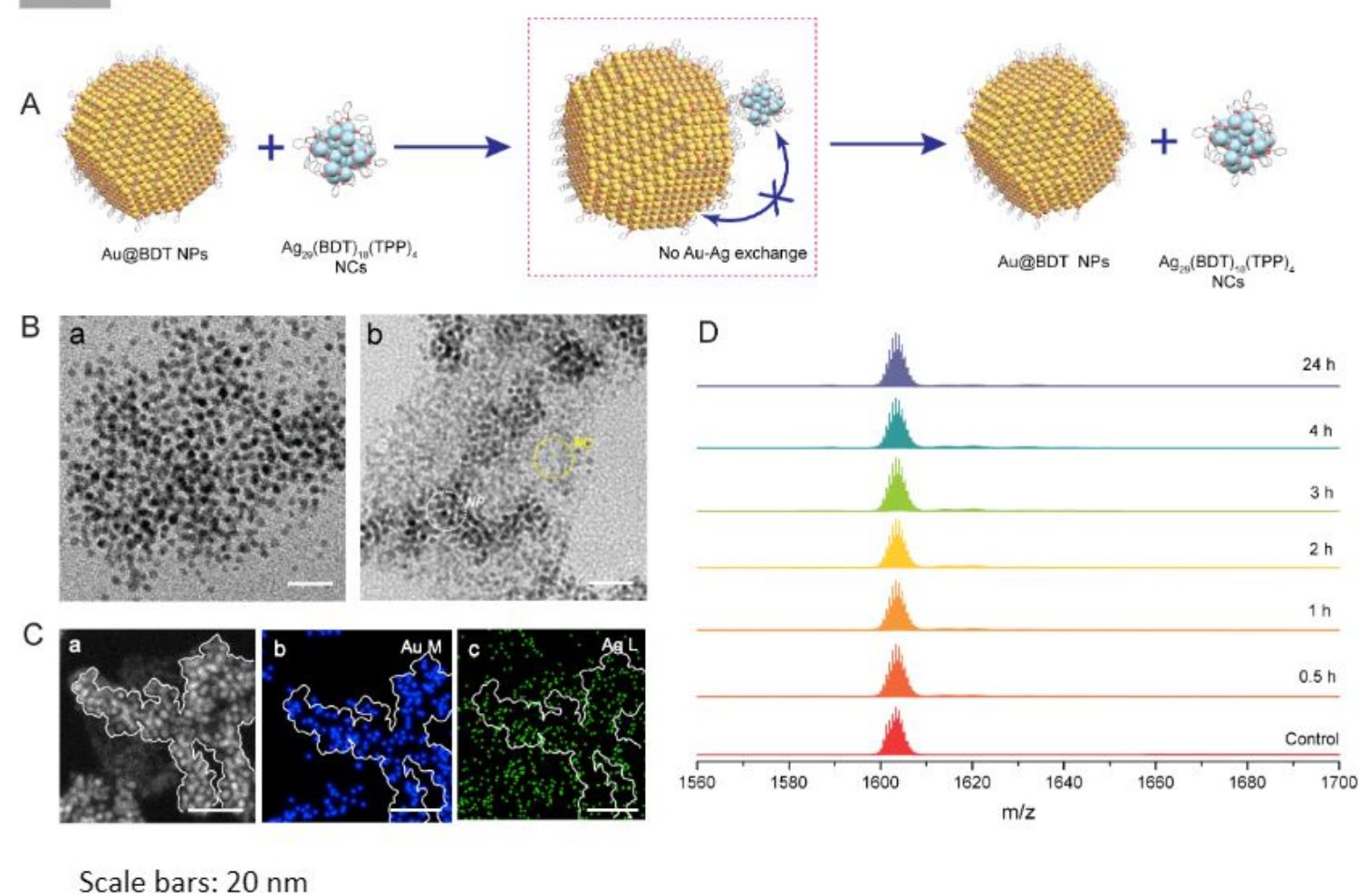
Scale bars: 50 nm (B-G) and 10 nm (insets of B and C).



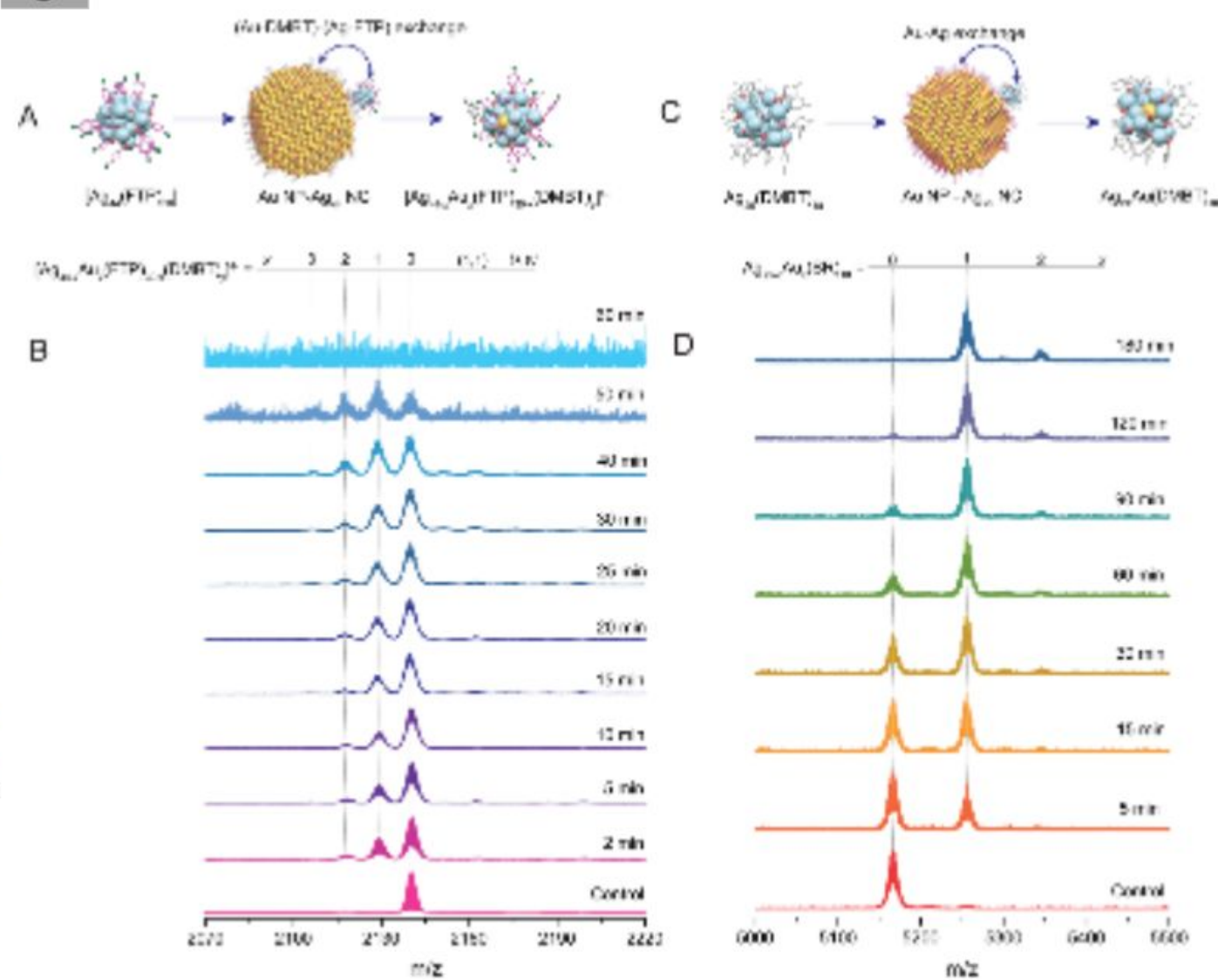
Paulami Bose, et al. *Chem. Mat.* 202

Interface controls the reaction

4

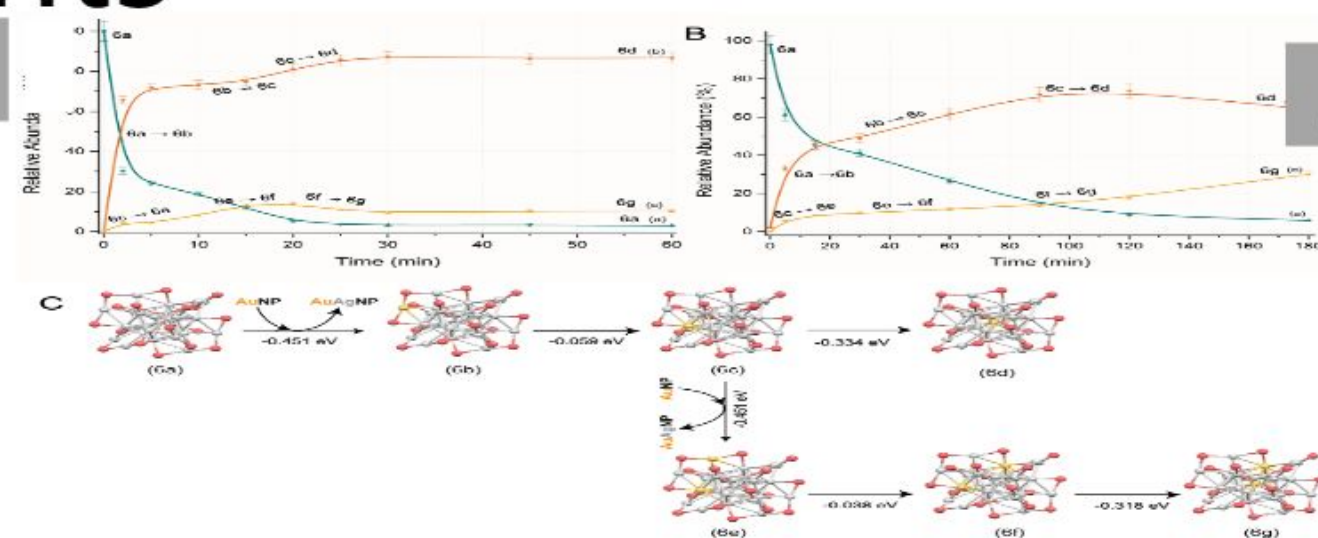


5

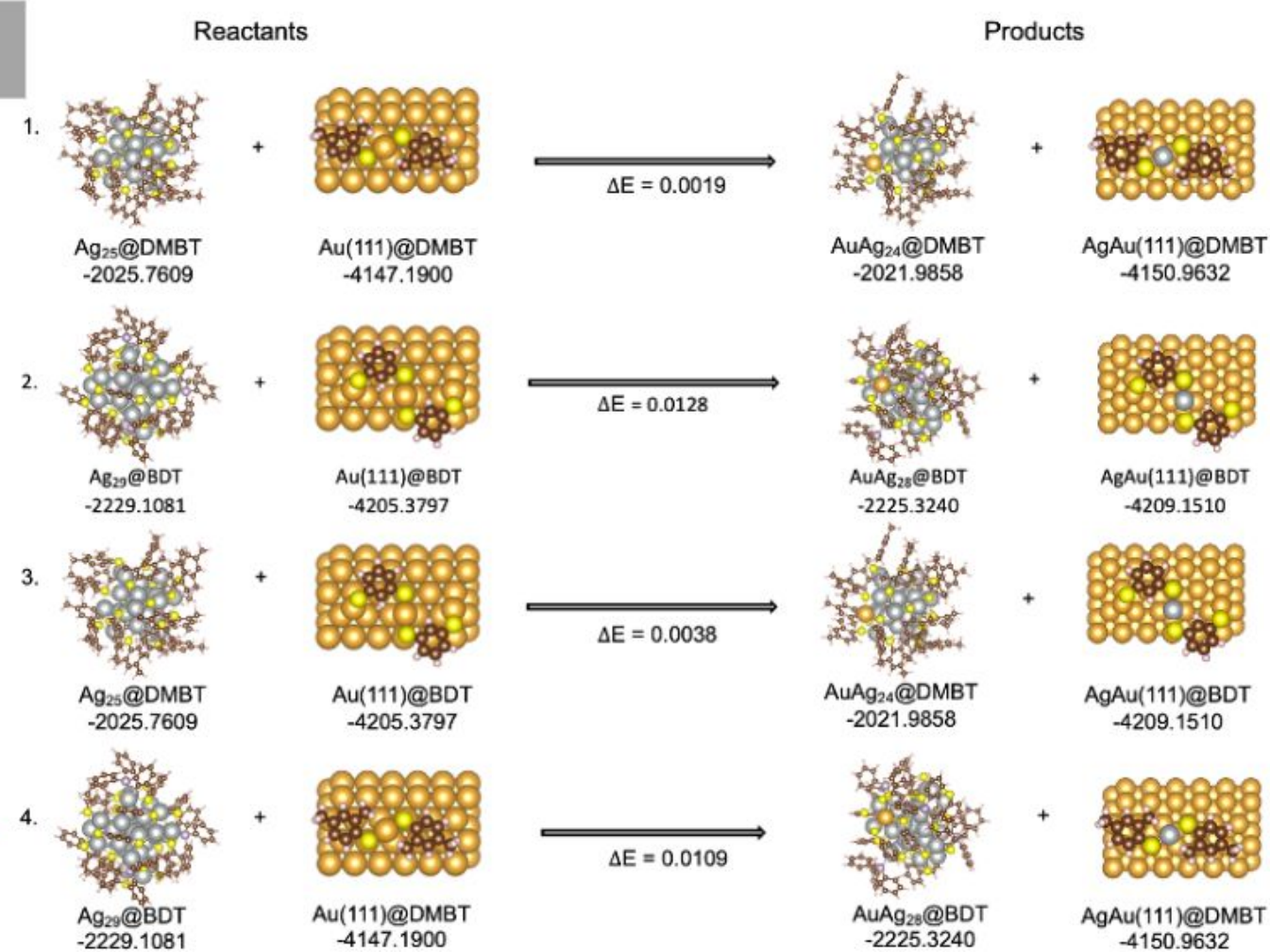


Computational insights

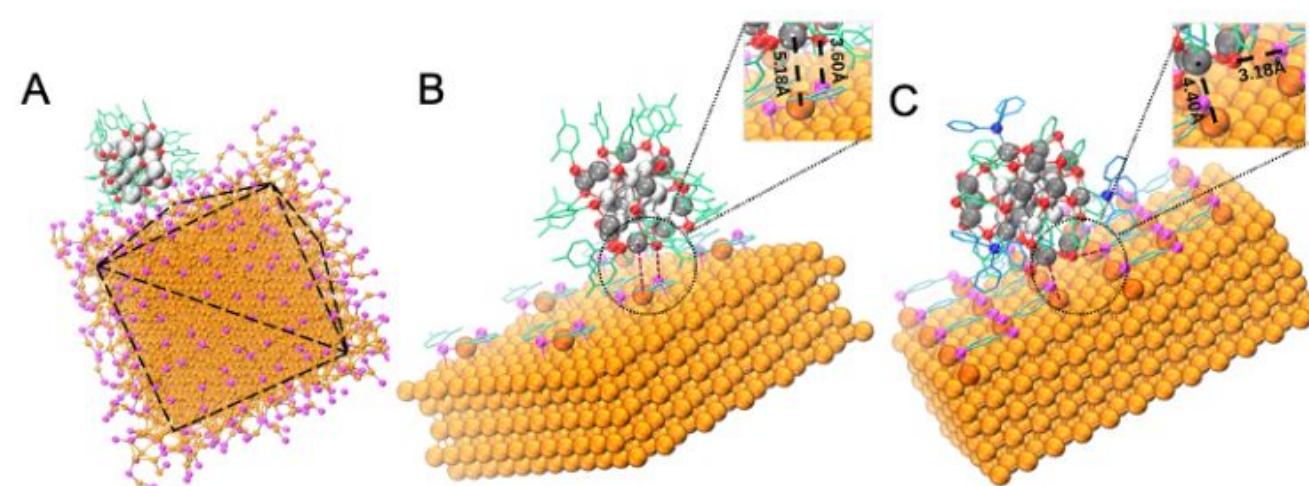
6



8



7



Reactions and new materials

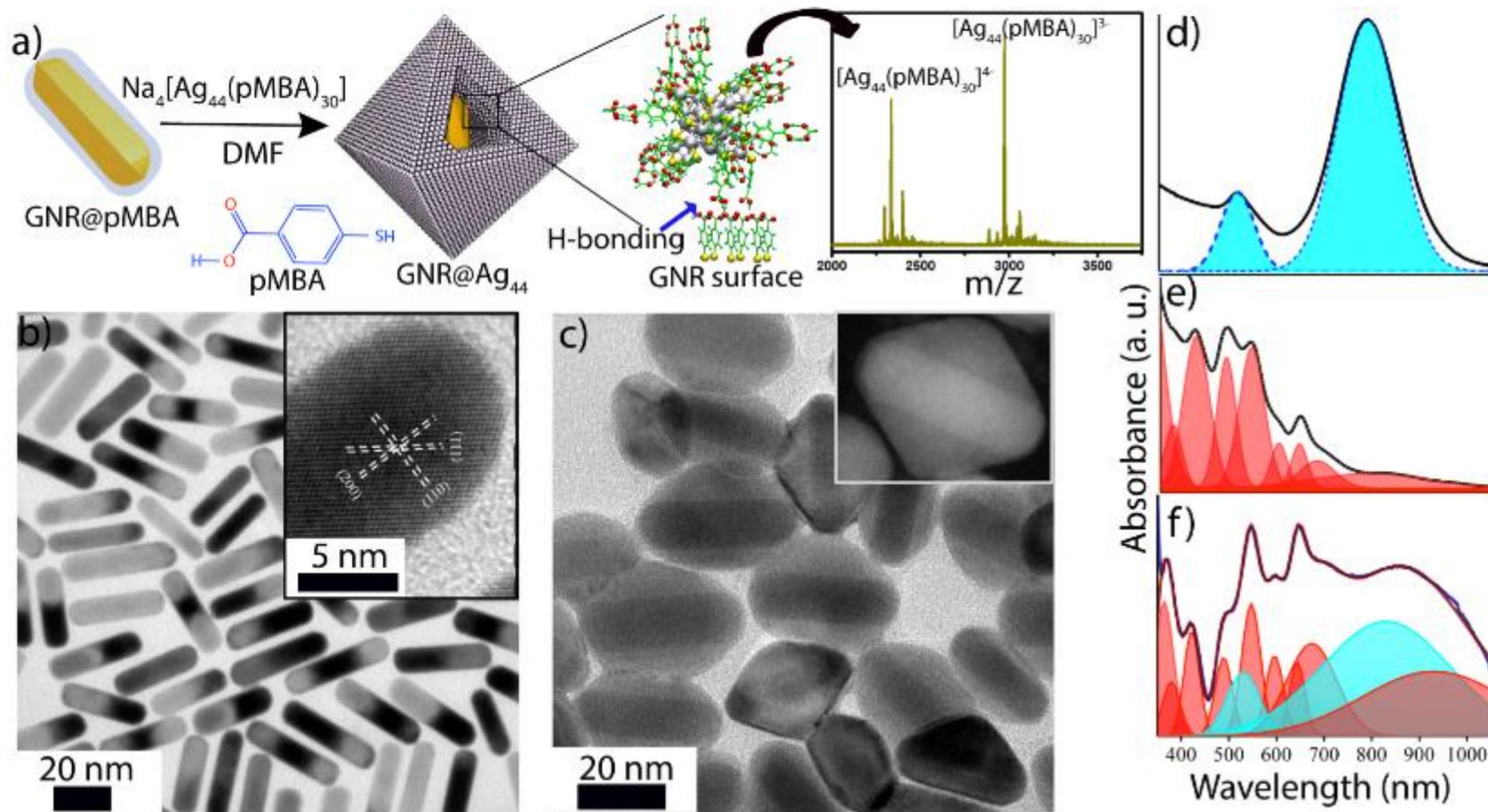
Reactions leading to co-crystals

Supramolecular chemistry

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

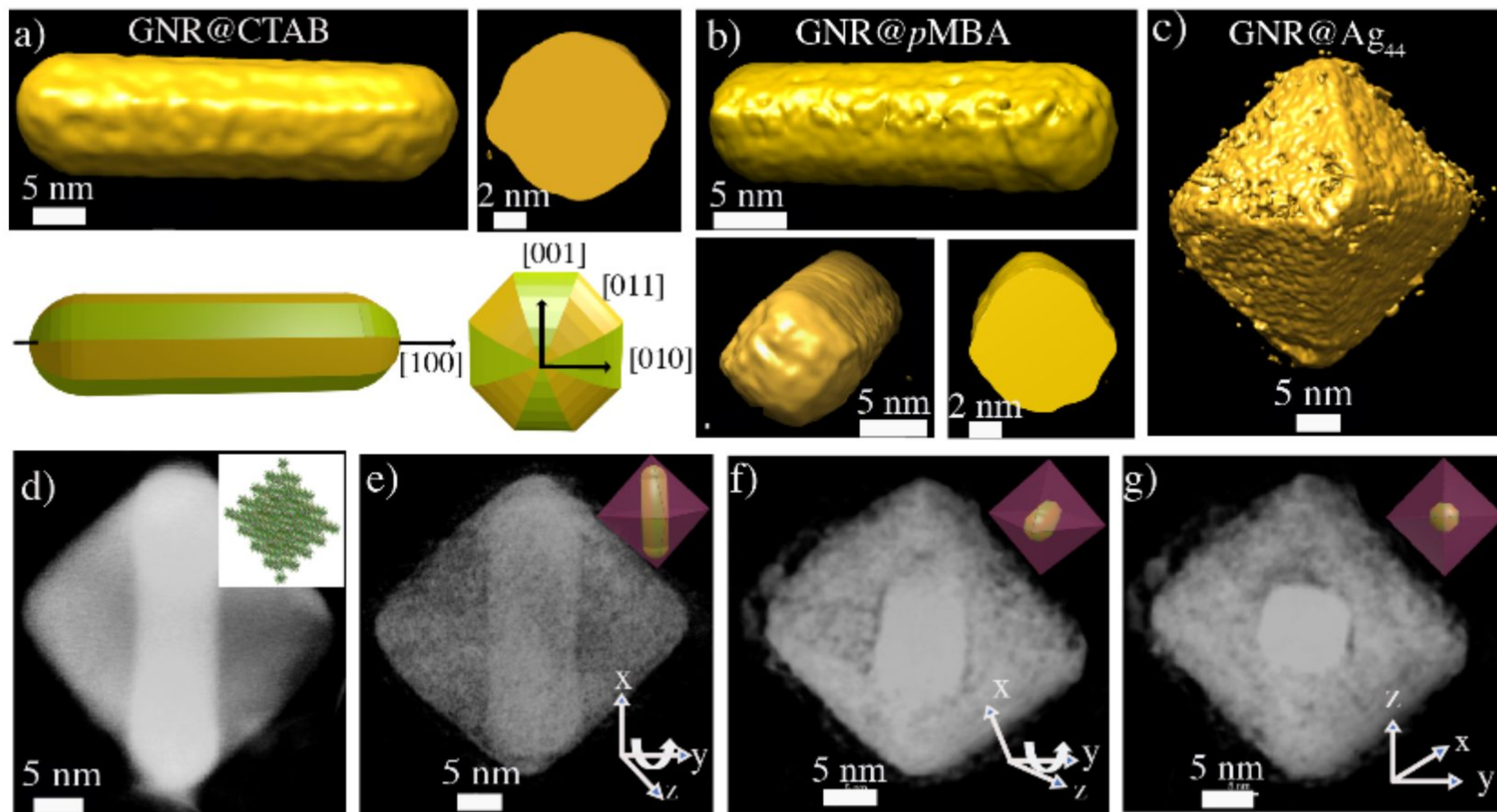
Assemblies and superstructure s

Atomically precise nanocluster assemblies encapsulating plasmonic gold nanorods

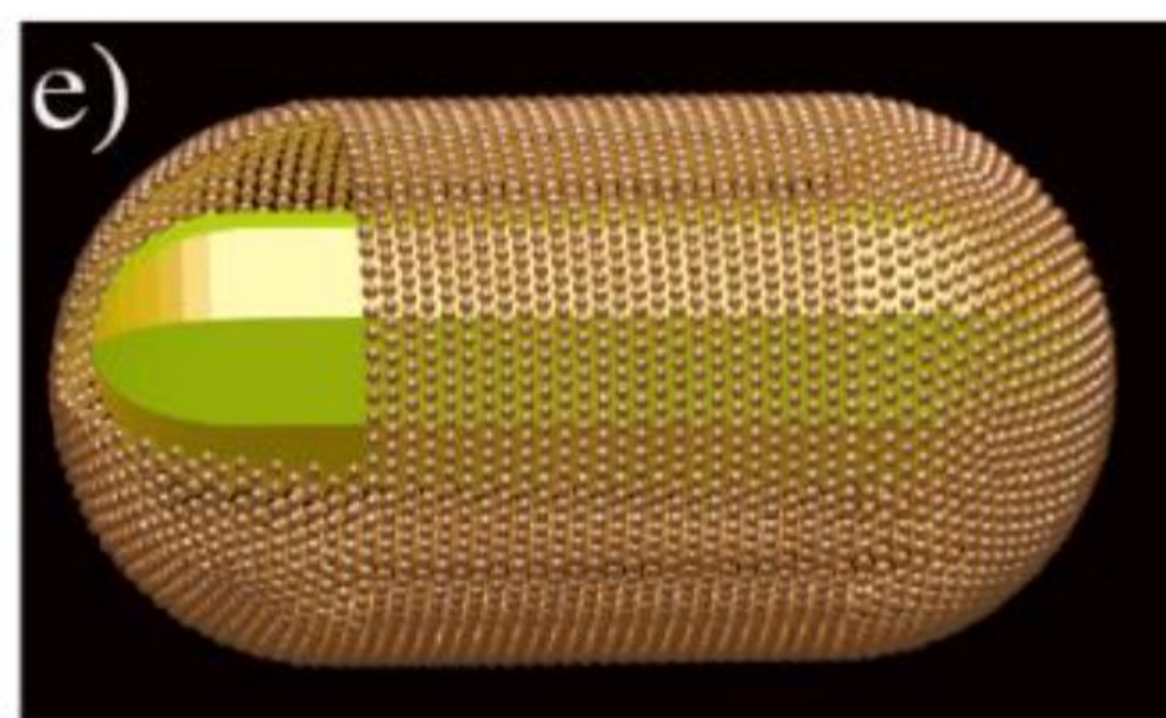
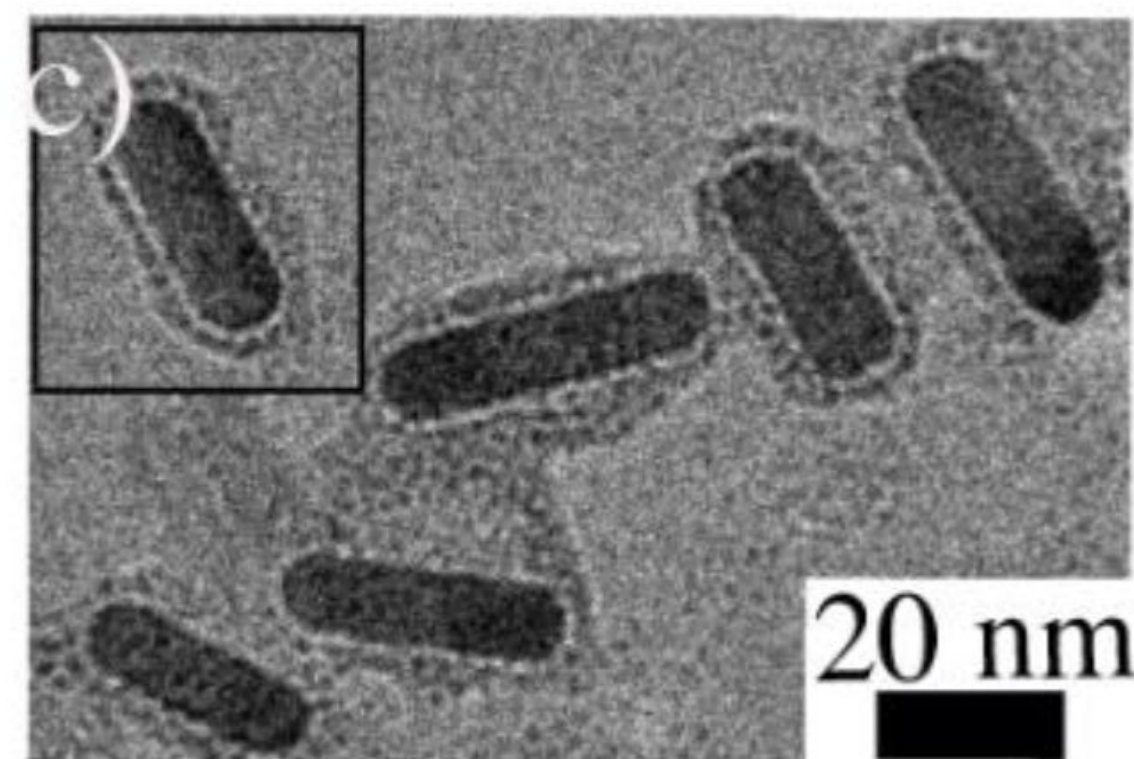
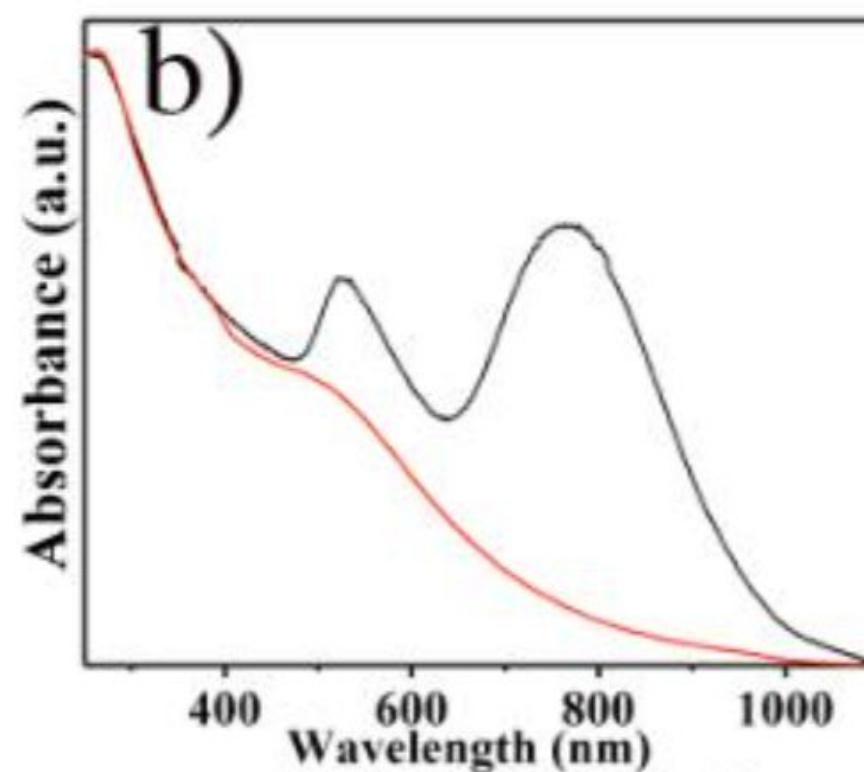
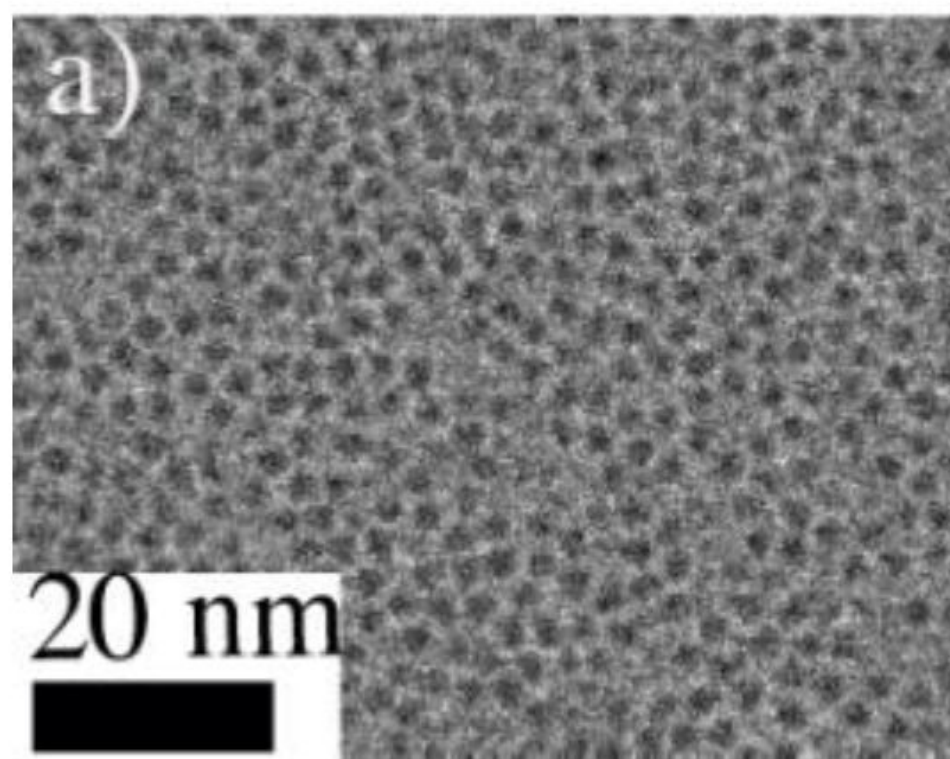


Chakraborty, A. et al., *Angew. Chem. Int. Ed.* **2018**, 57, 6522–6526.

3D morphological analysis



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



Co-crystal

s

Ag40 and Ag46 with the same
shell

Isomerism in supramolecular adducts

A)

Ag₂₉BDT12 = X β-cyclodextrin = CD

X∩CD13-

Calculated
Experimental

X∩CD23-

a)

X∩CD13- X∩CD33-

m/z

X3-

X∩CD43-

b)

CD-

X∩CD53-

X∩CD63-

X∩CD13-

m/z

a) **XnCD33-**
Isomer 1 613.0 Å² Isomer 2 628.0 Å²

d) **XnCD63-**
903.0 Å²

b) **XnCD23-**
Isomer 1 526.0 Å² Isomer 2 540.0 Å²

e) **XnCD53-**
812.0 Å²

c) **XnCD13-**
438.0 Å²

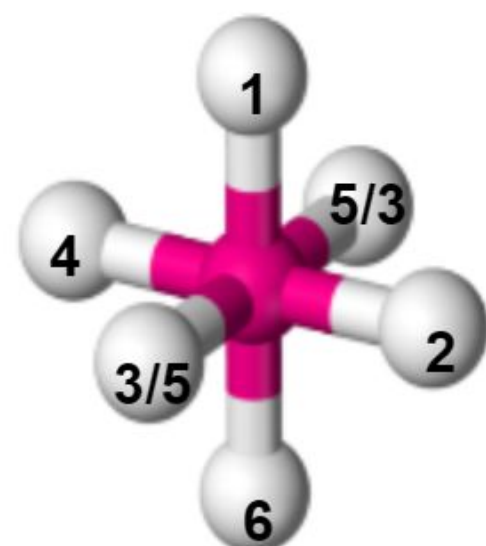
f) **XnCD43-**
Isomer 1 705.0 Å² Isomer 2 724.0 Å²

Drift time (ms)

Drift time (ms)

A)

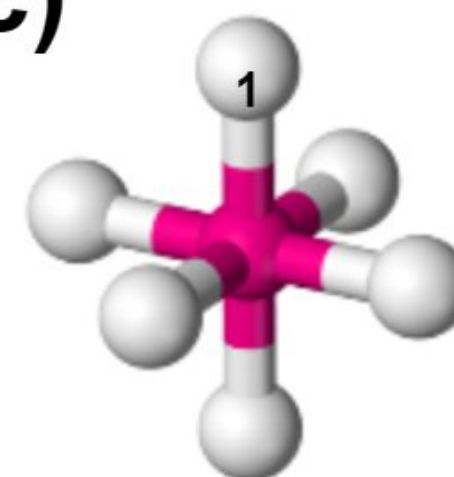
a)



b)

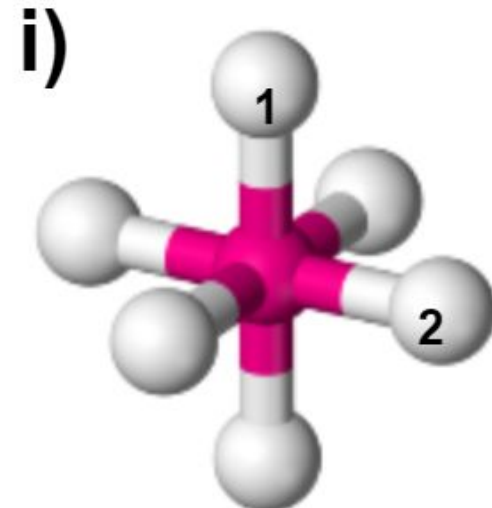


c)



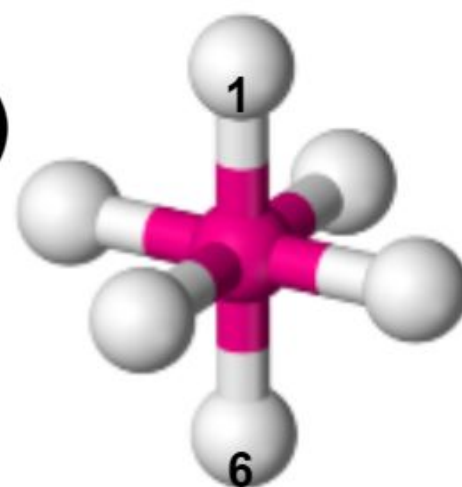
B)

a)



C-Ag29(BDT)12 $\cap$ CD2

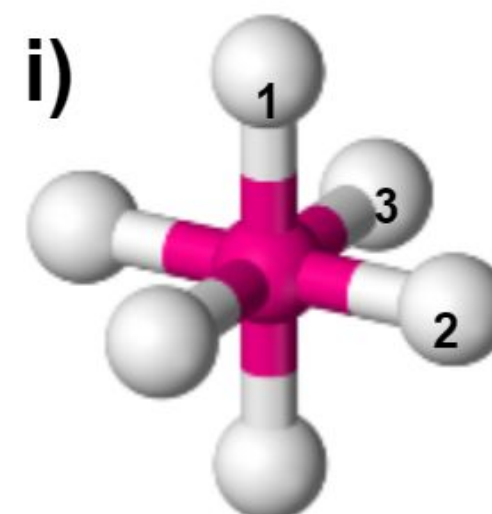
ii)



T-Ag29(BDT)12 $\cap$ CD2

b)

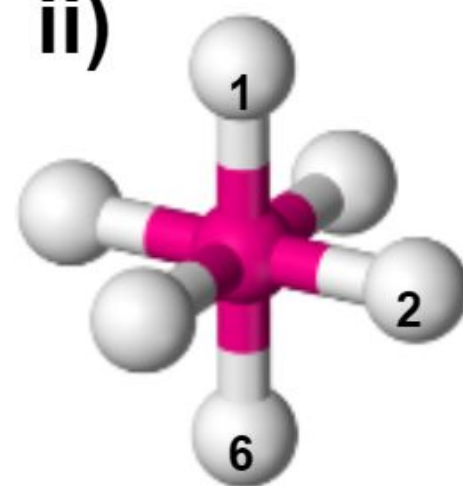
i)



C-Ag29(BDT)12 $\cap$ CD3

Cis = C
Trans = T

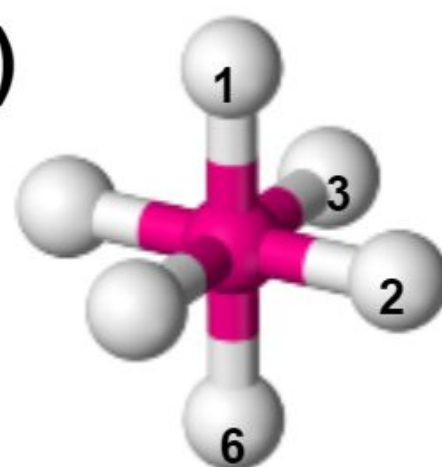
ii)



T-Ag29(BDT)12 $\cap$ CD3

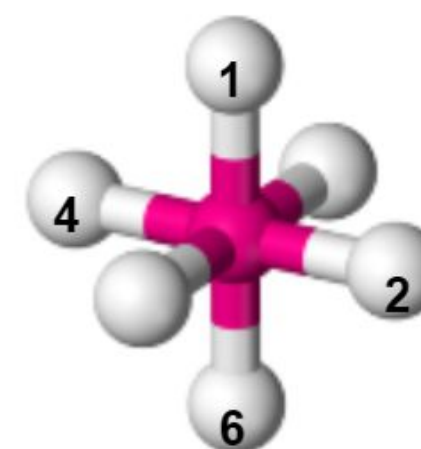
c)

i)



C-Ag29(BDT)12 $\cap$ CD4

ii)



T-Ag29(BDT)12 $\cap$ CD4

Where are they taking us to?

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

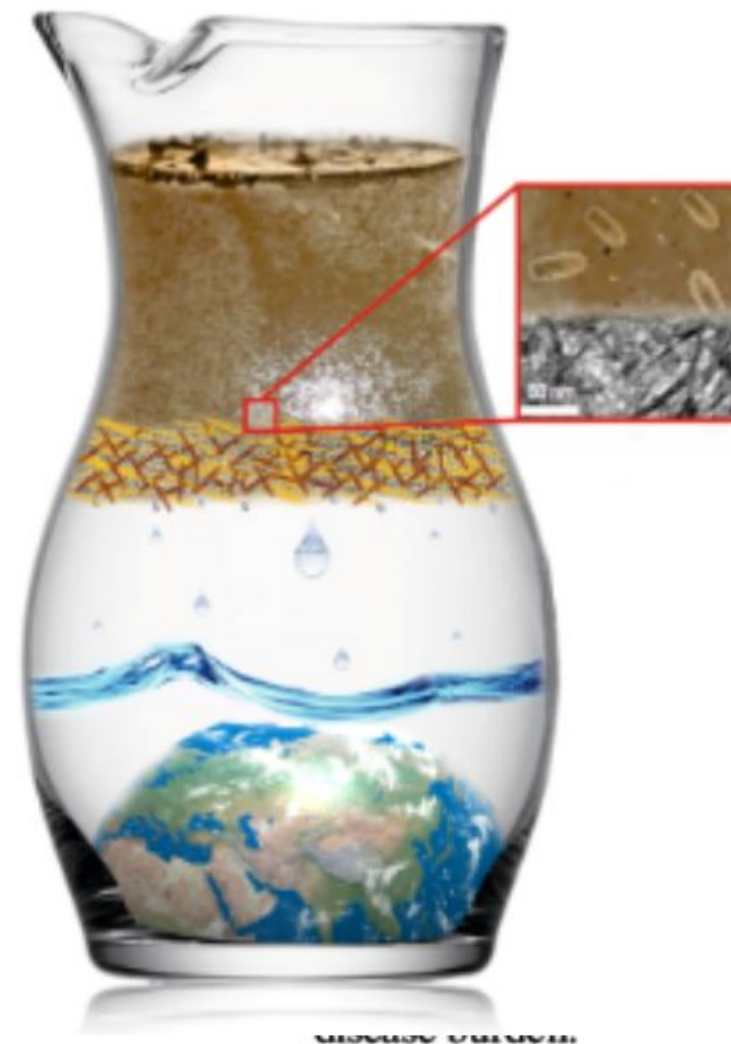
Mohan Udhaya Sankar¹, Sahaja Aigal¹, Shihabudheen M. Maliyekkal¹, Amrita Chaudhary, Anshup, Avula Anil Kumar, Kamalesh Chaudhari, and Thalappil Pradeep²

Unit of Nanoscience and Thematic Unit of Ex

Edited by Eric Hoek, University of California,

Creation of affordable materials for clean drinking water is one of the most promising ways to ensure drinking water for all. Combining the composites to scavenge toxic species and other contaminants along with the ability to produce affordable, all-inclusive drinking water without electricity. The critical problem is the synthesis of stable materials that can function in the presence of complex contaminants in drinking water that deposit and clog filter surfaces. Here we show that such composites can be synthesized in a simple and effective way without the use of electrical power. The nanocomposites have sand-like properties, such as higher shear modulus and stability. These materials have been used in a water purifier to deliver clean drinking water. The ability to prepare nanostructures at ambient temperature has wide relevance for water purification.

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



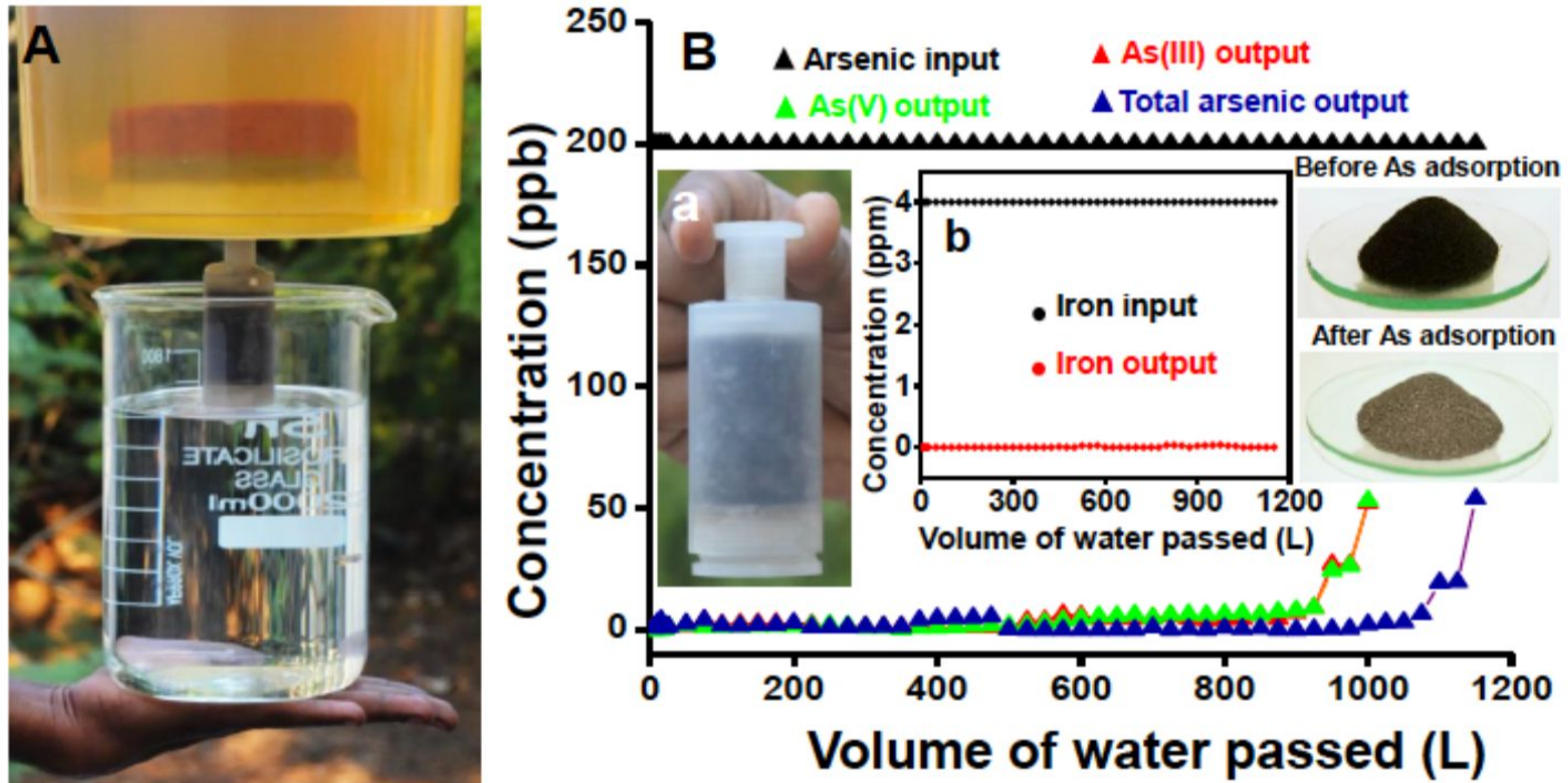
Madras, Chennai 600 036, India

(received for review November 21, 2012)

available; and (c) continued retention matrix is difficult. We create a unique family of nanocrystalline granular composite materials prepared through an aqueous route. The composition is attributed to abundant -OH 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 leaching 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

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

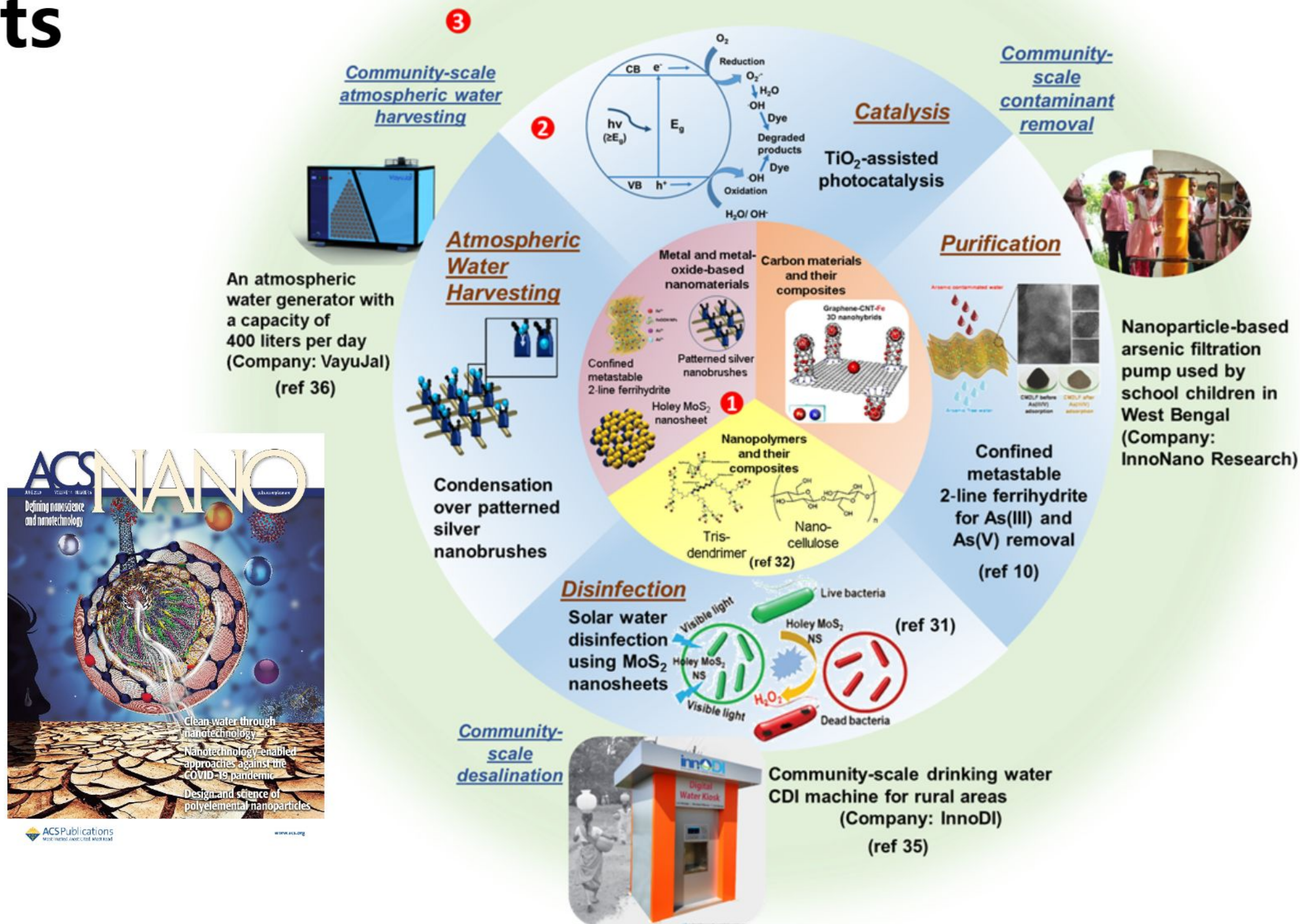




We developed environmentally friendly water positive nanoscale materials for affordable, sustainable and rapid removal of arsenic from drinking water.

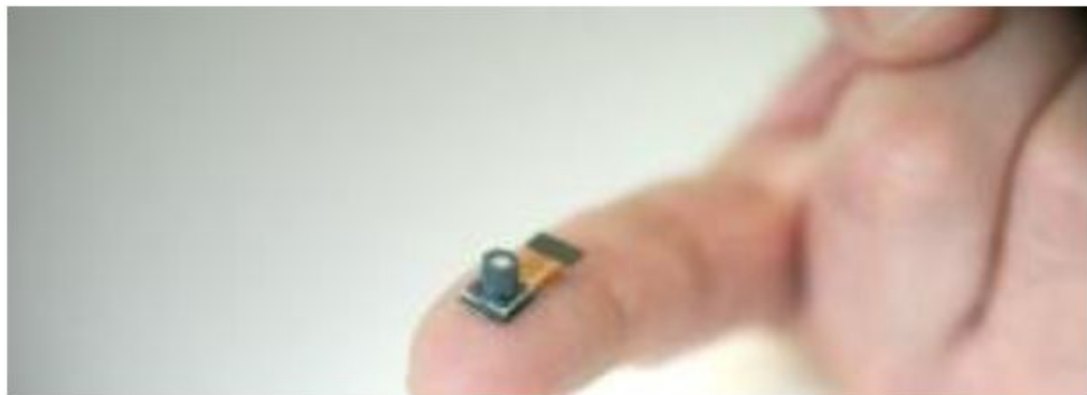
There are over 1700 community installations across the country, serving 1.3 million people with arsenic and iron-free water every day.

Evolution of materials to products



Smart water purifiers and big data

Sensors and new opportunities



Water quality measurement – In the pipe line

Cluster-based metal ion sensing

Decrease in the absorption of Au15 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 Hg₂

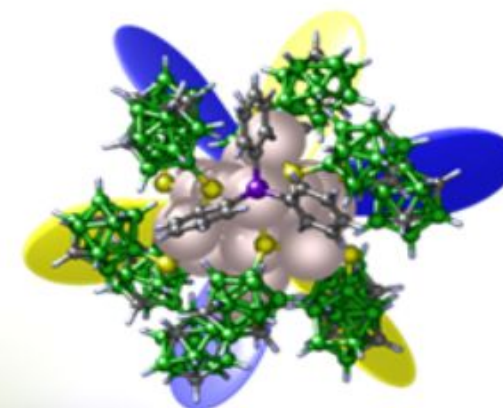
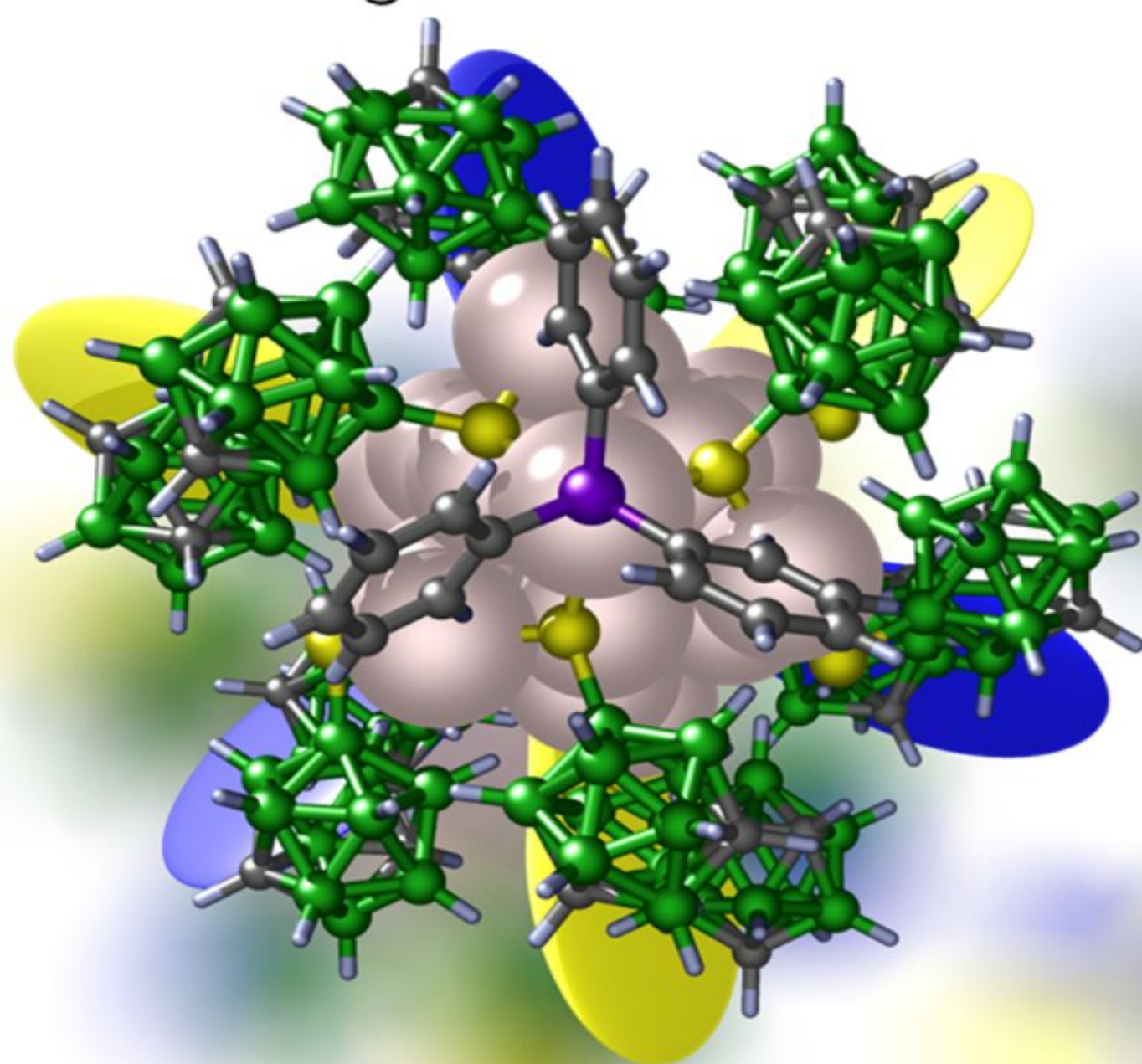
+

Mercury quenching experiment using nanofiber

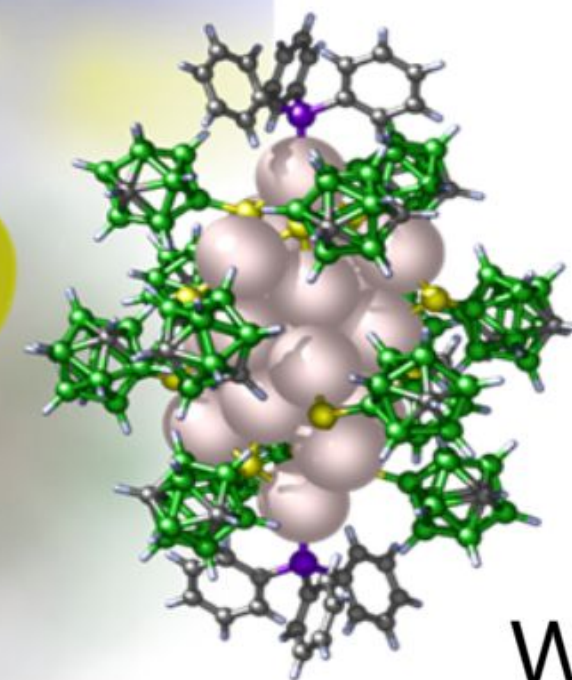
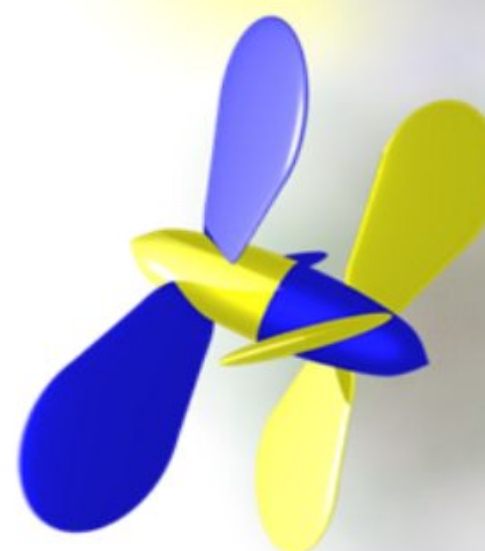


Carborane-thiol protected silver nanomolecule

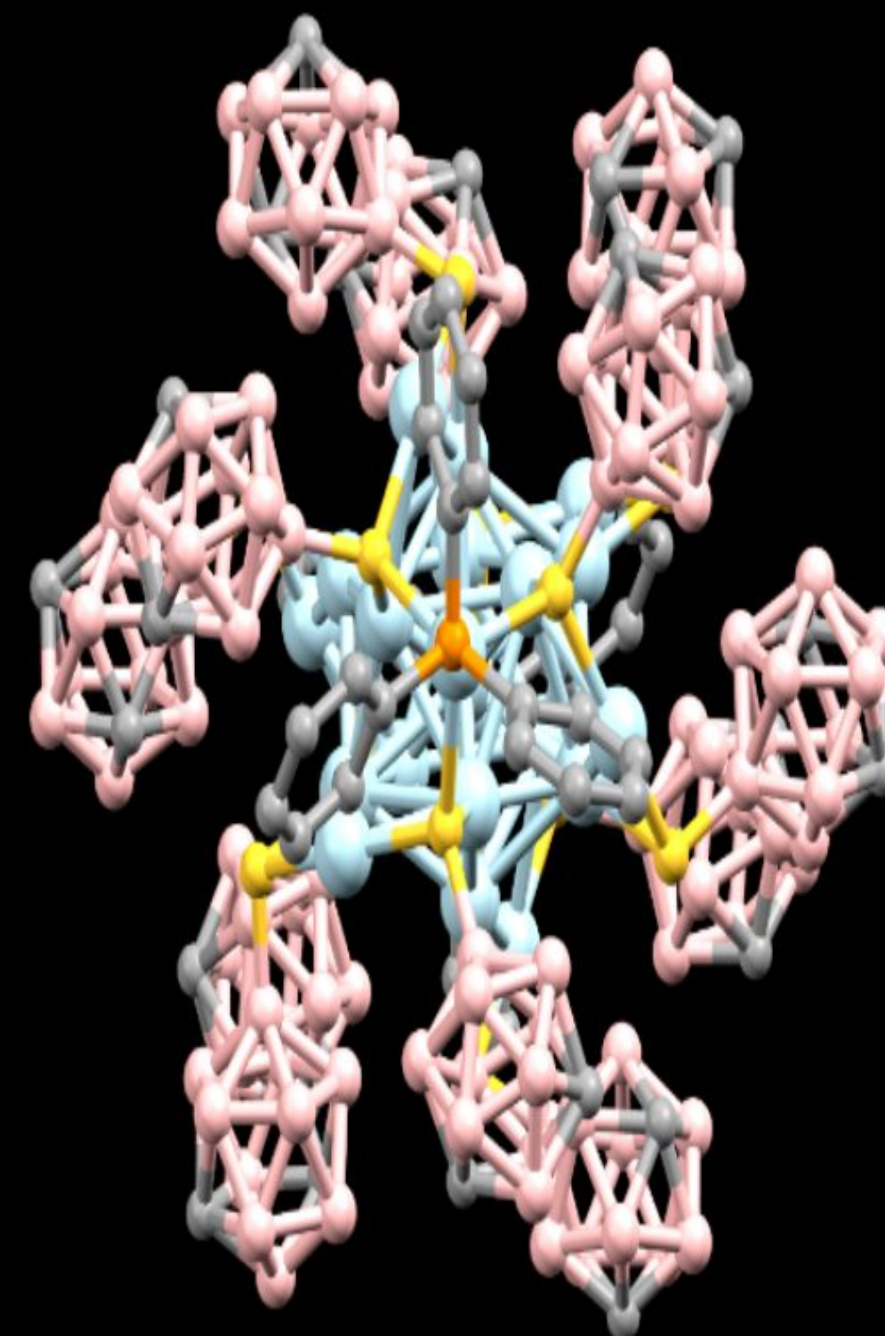
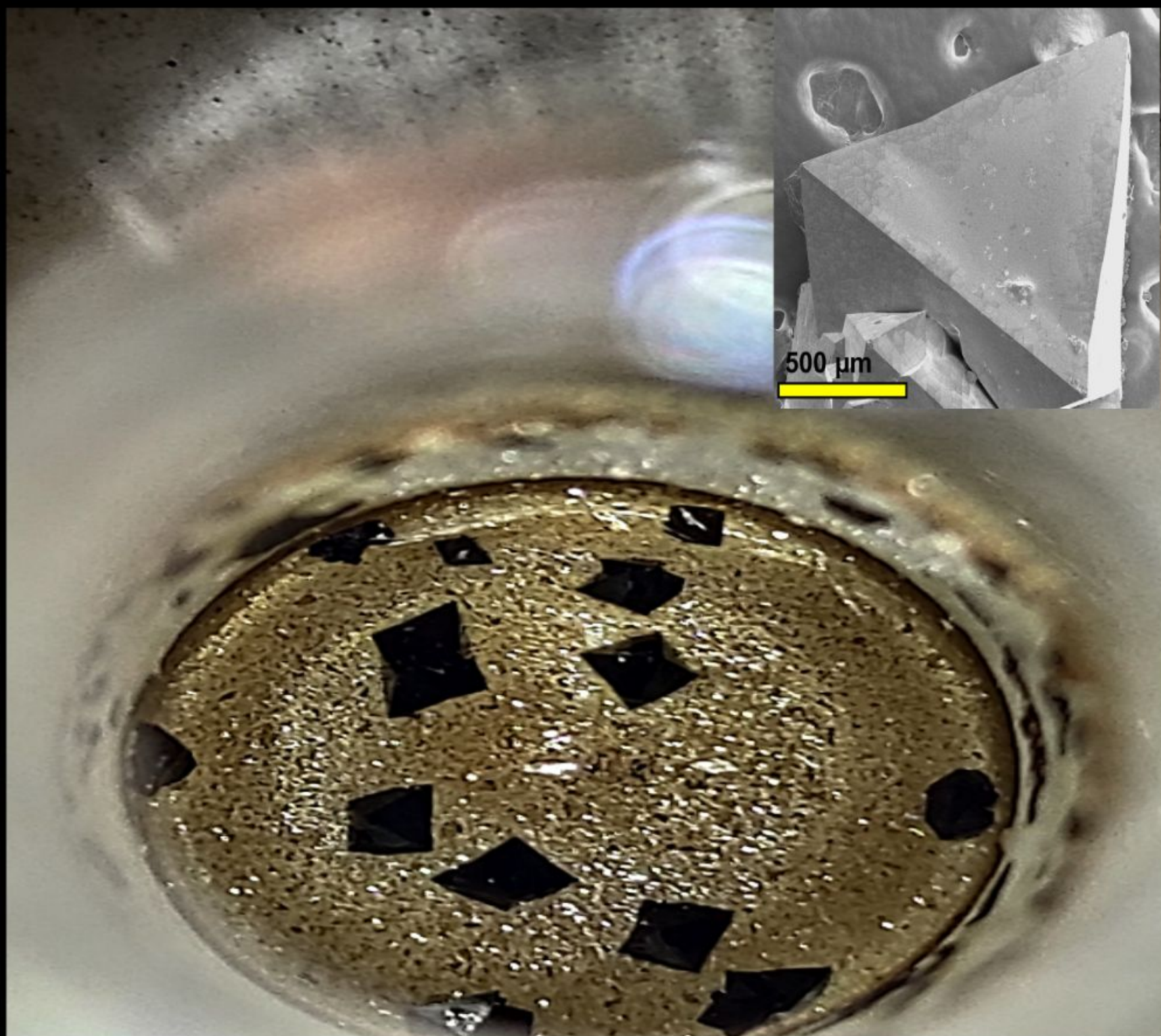
Rotary nanomolecule



Double rotors

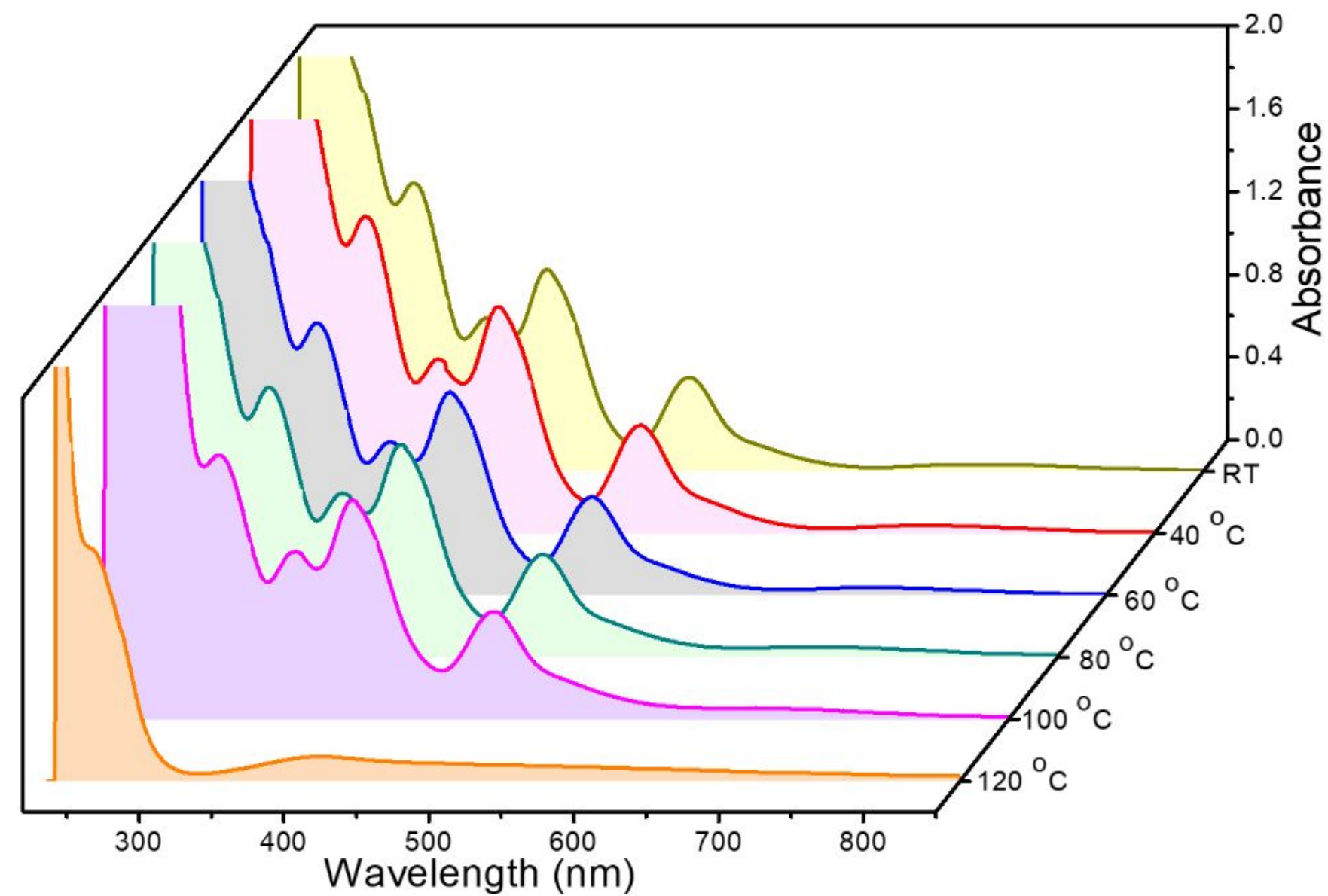
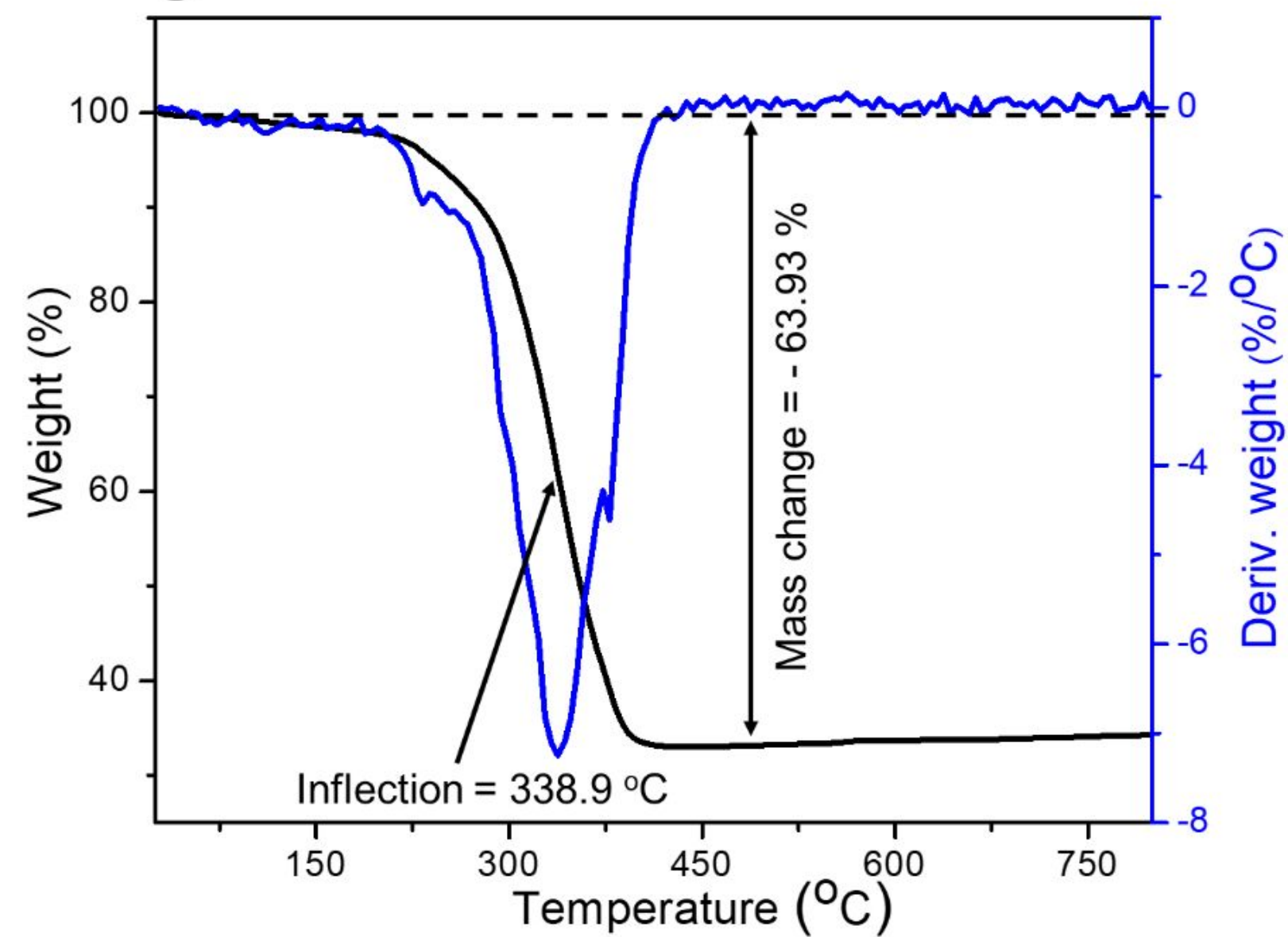


With Tomas Bas
e



Thermal stability

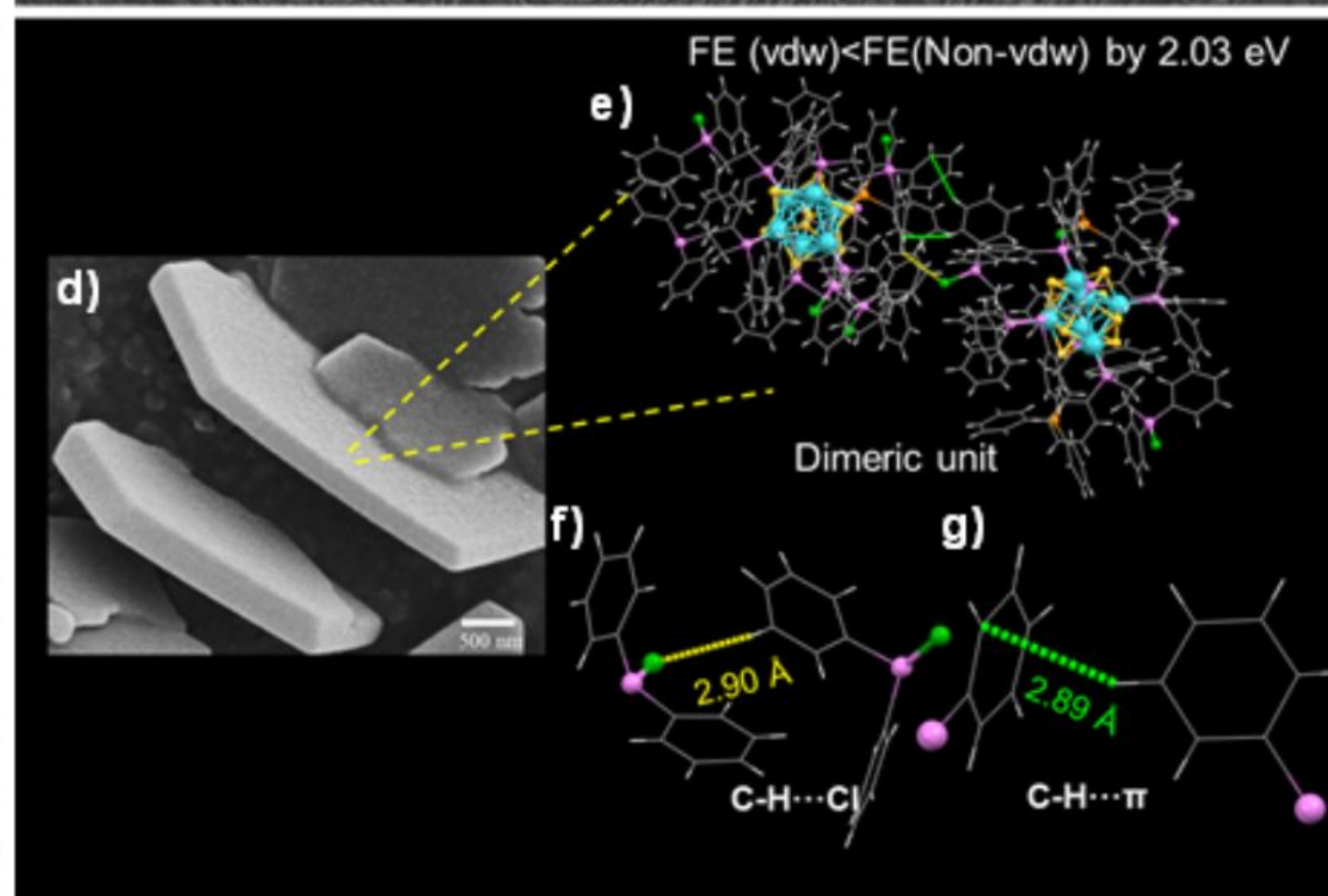
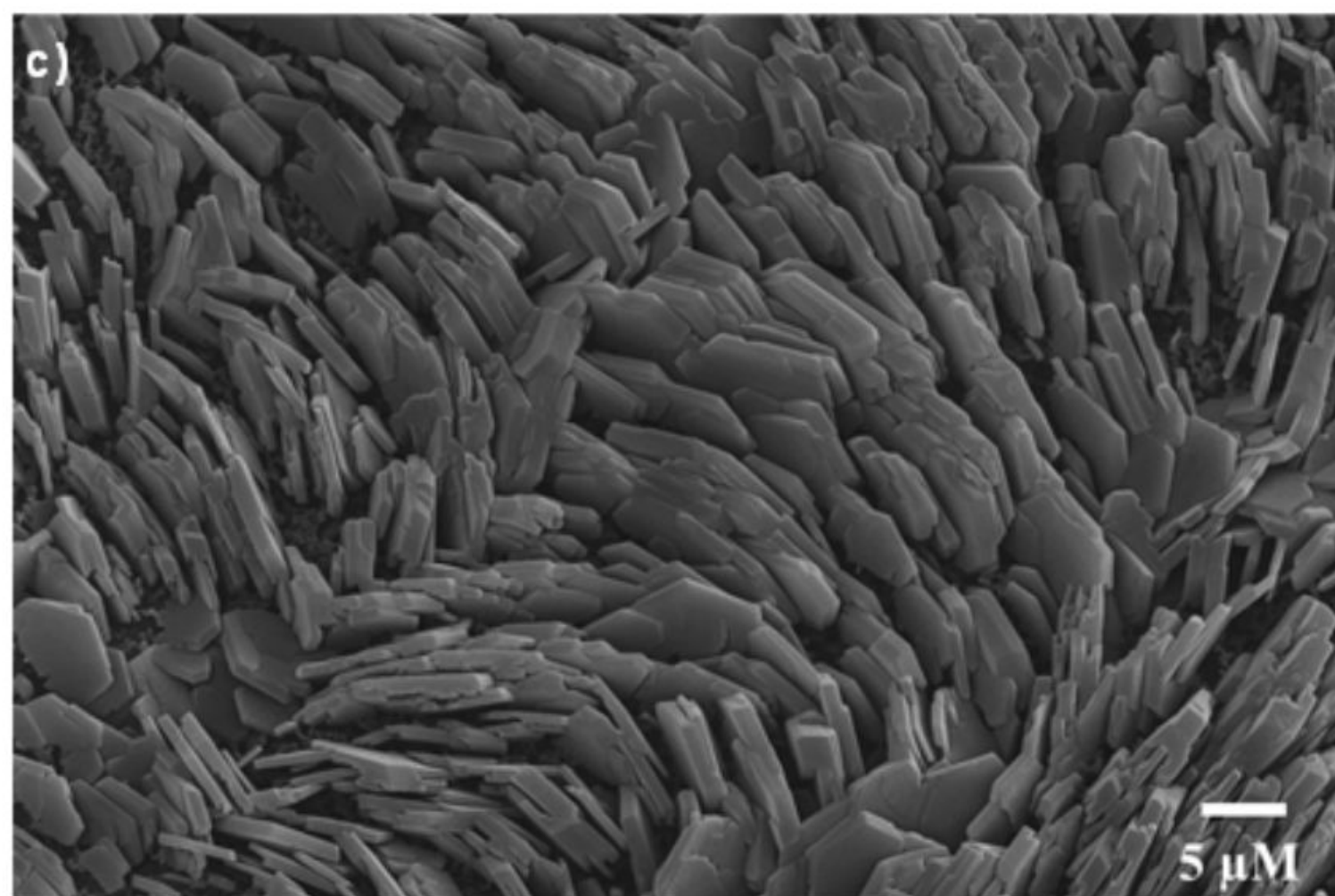
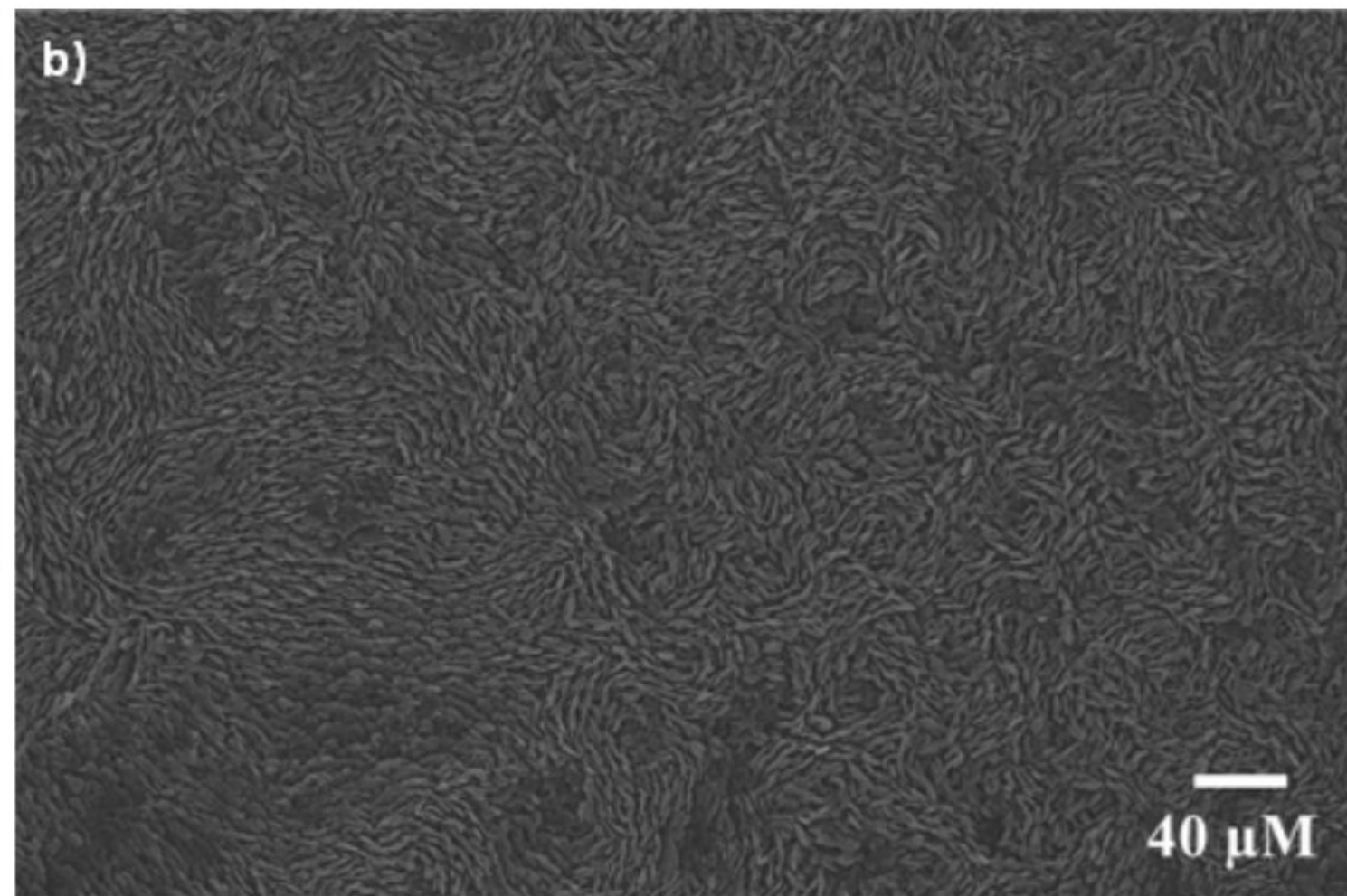
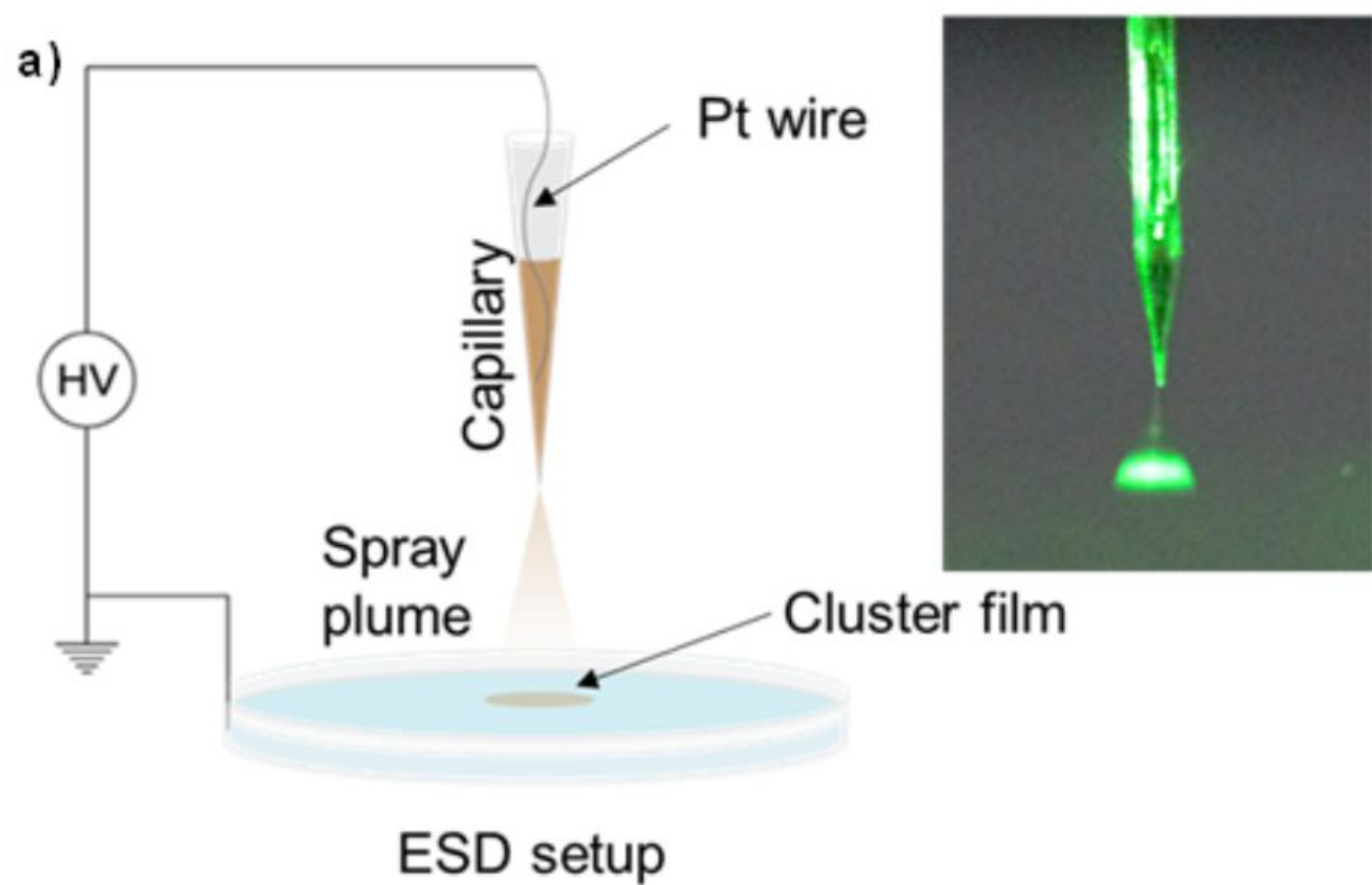
y



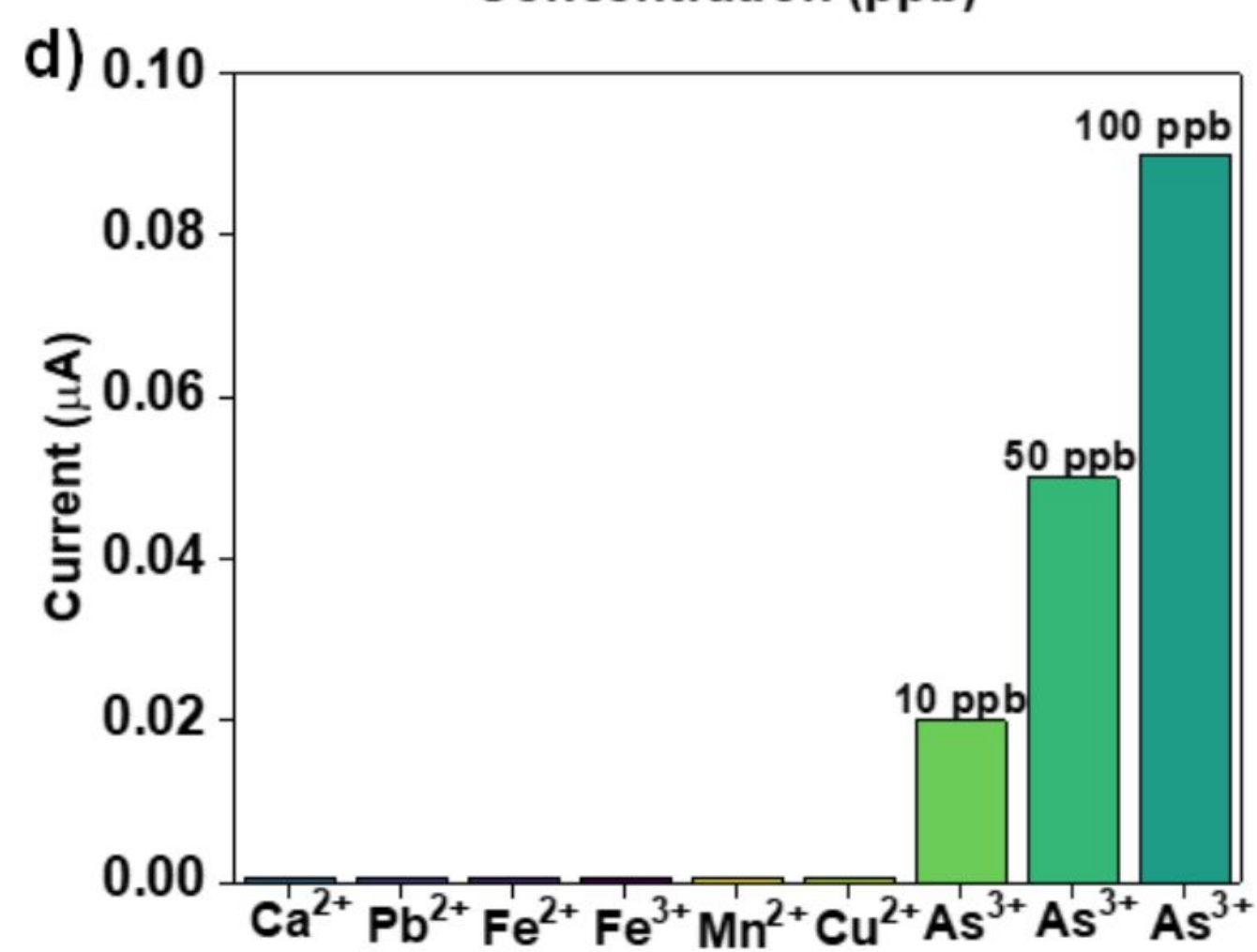
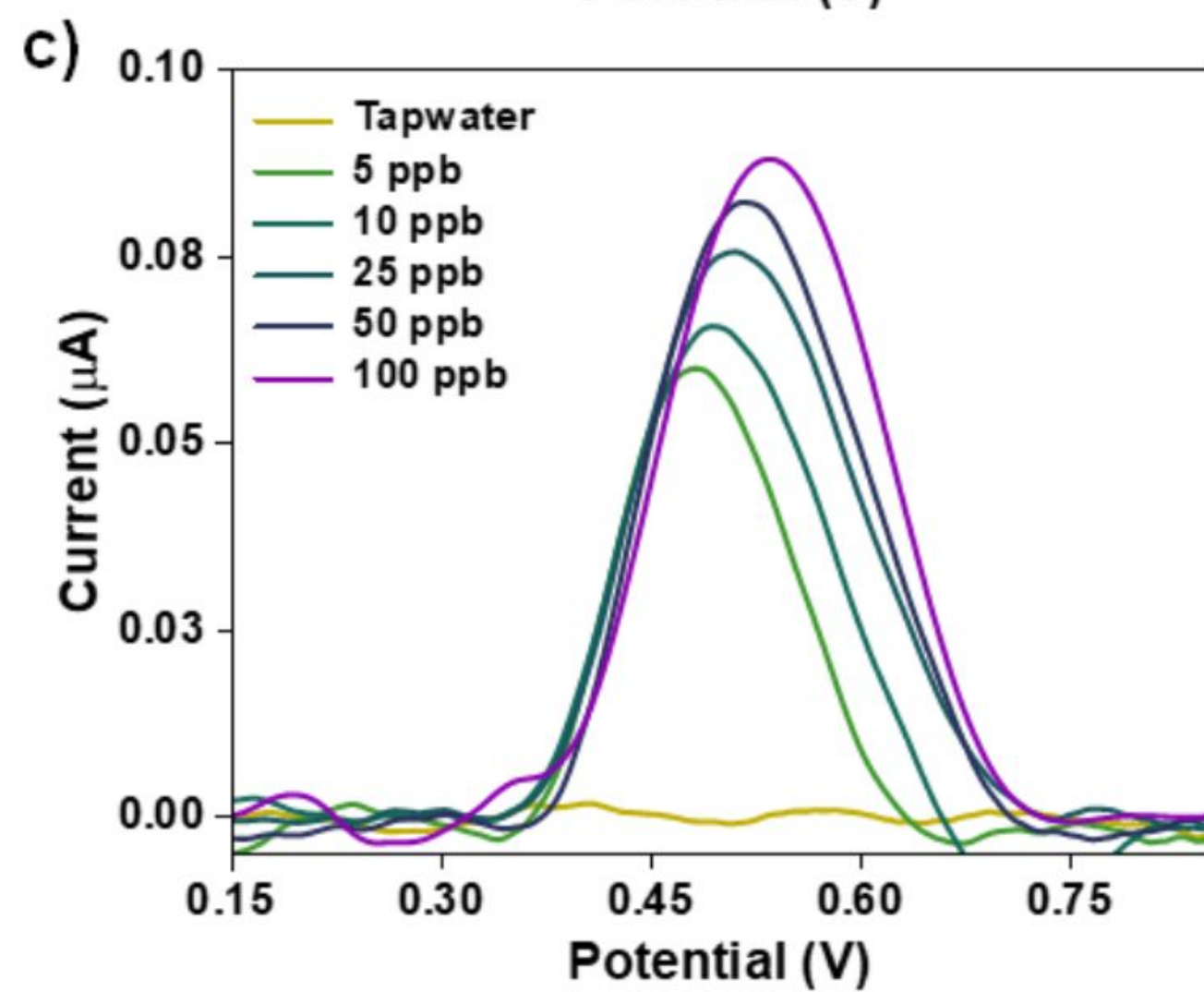
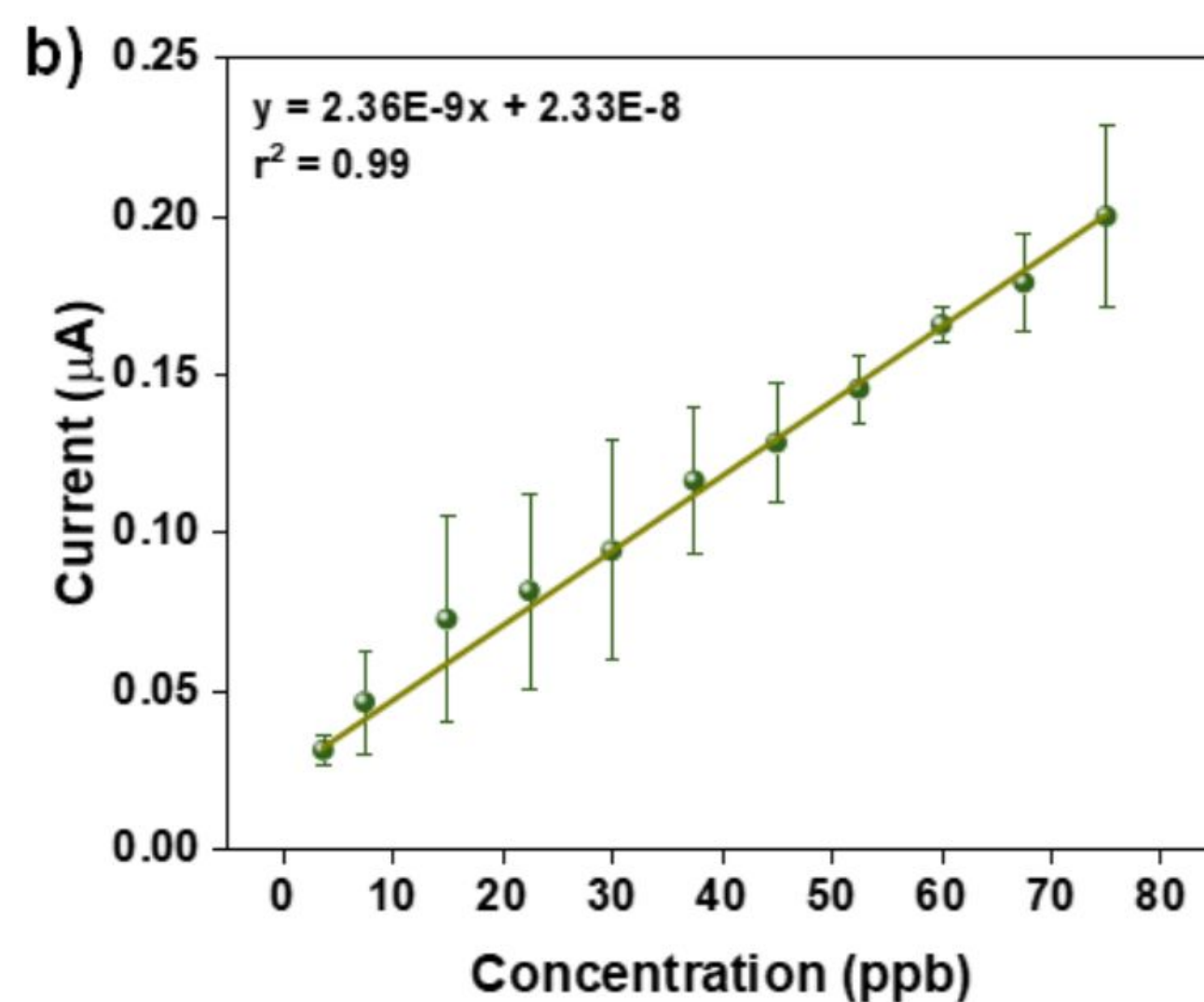
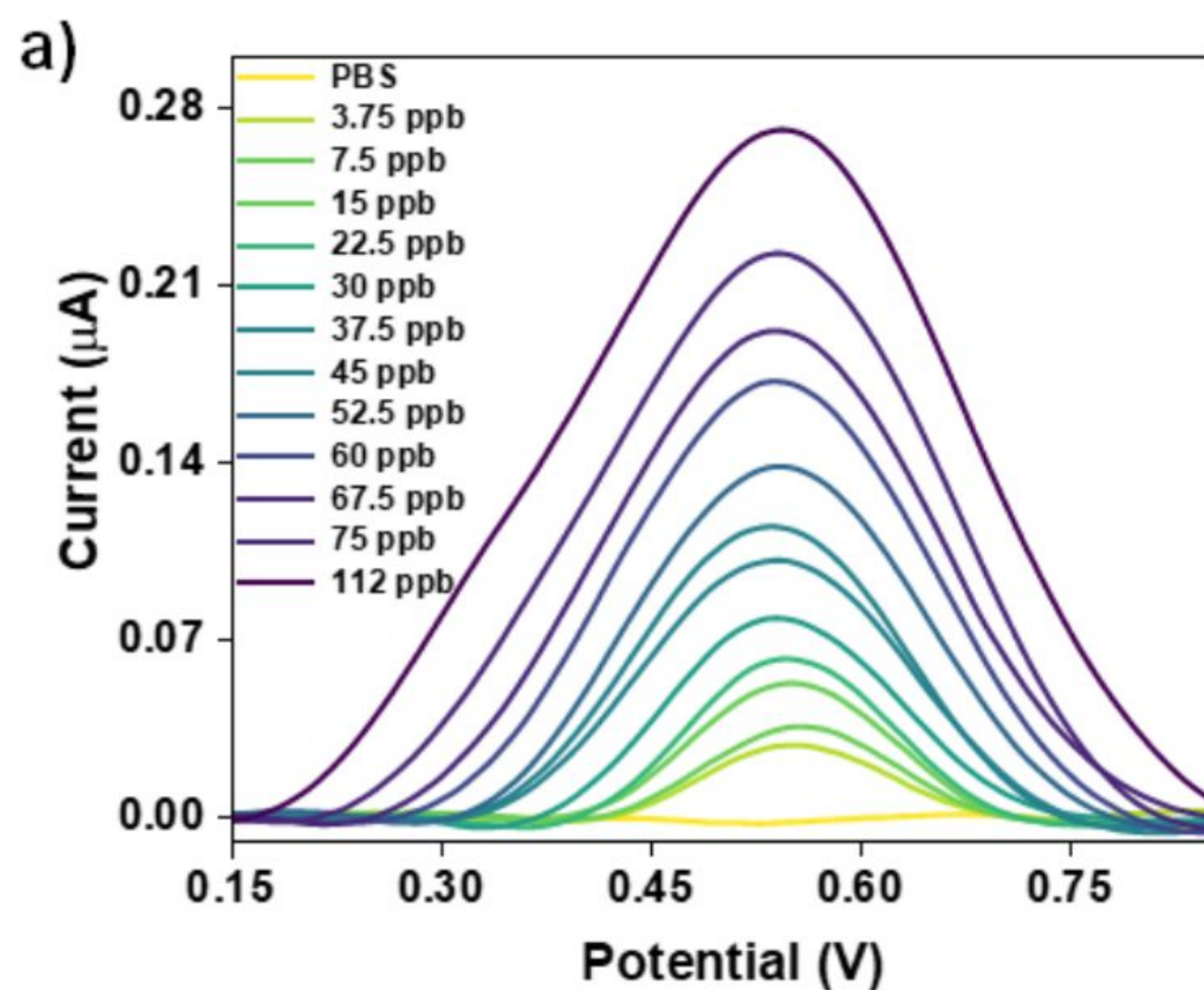
New electrodes - Aligned nanoplates of Co₆S₈

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

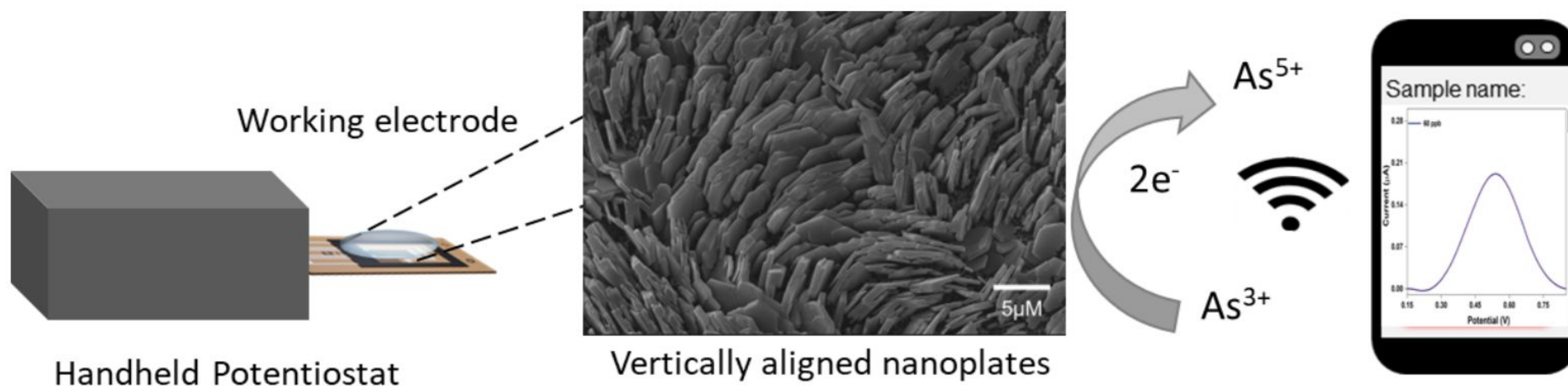
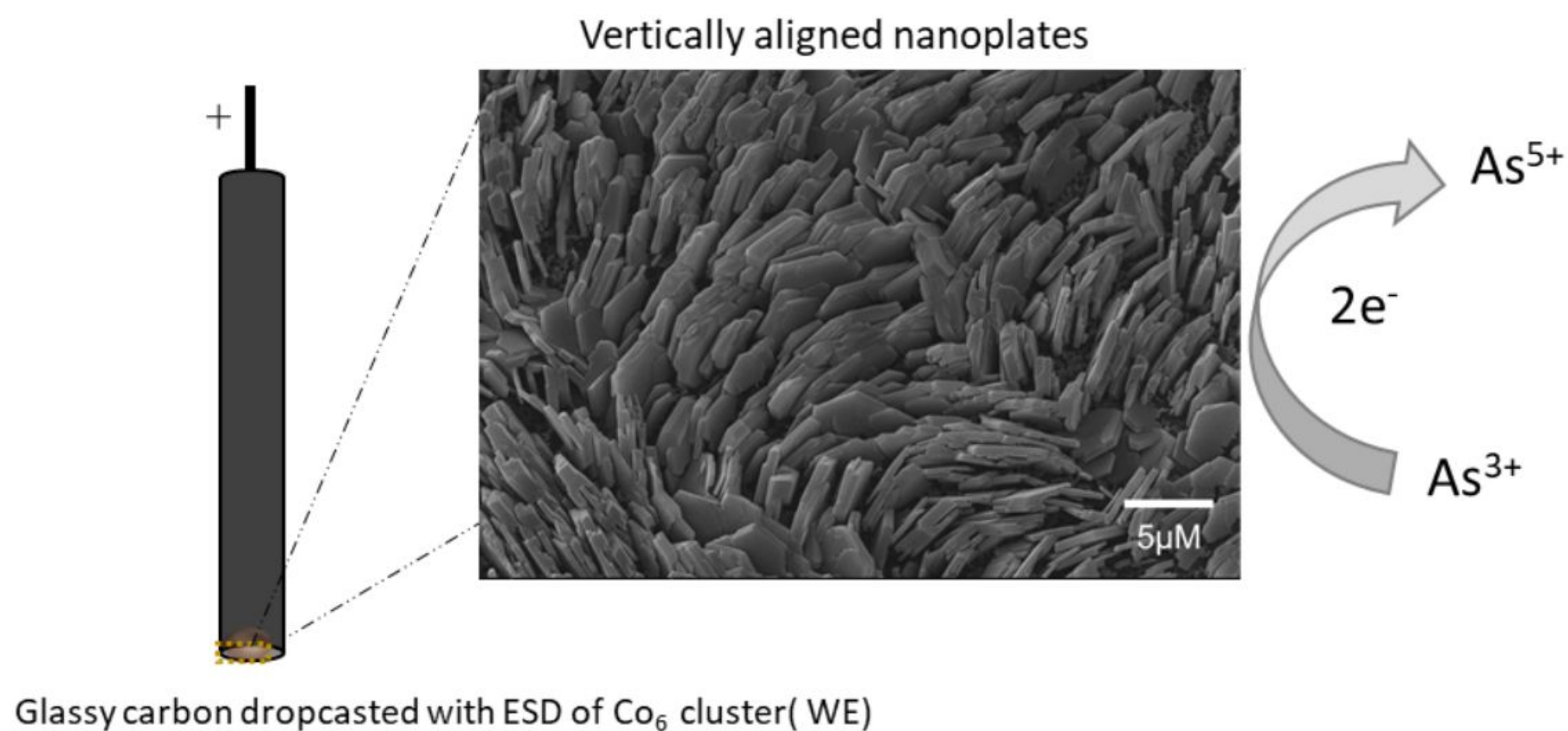
Electrospray deposition



Sensing

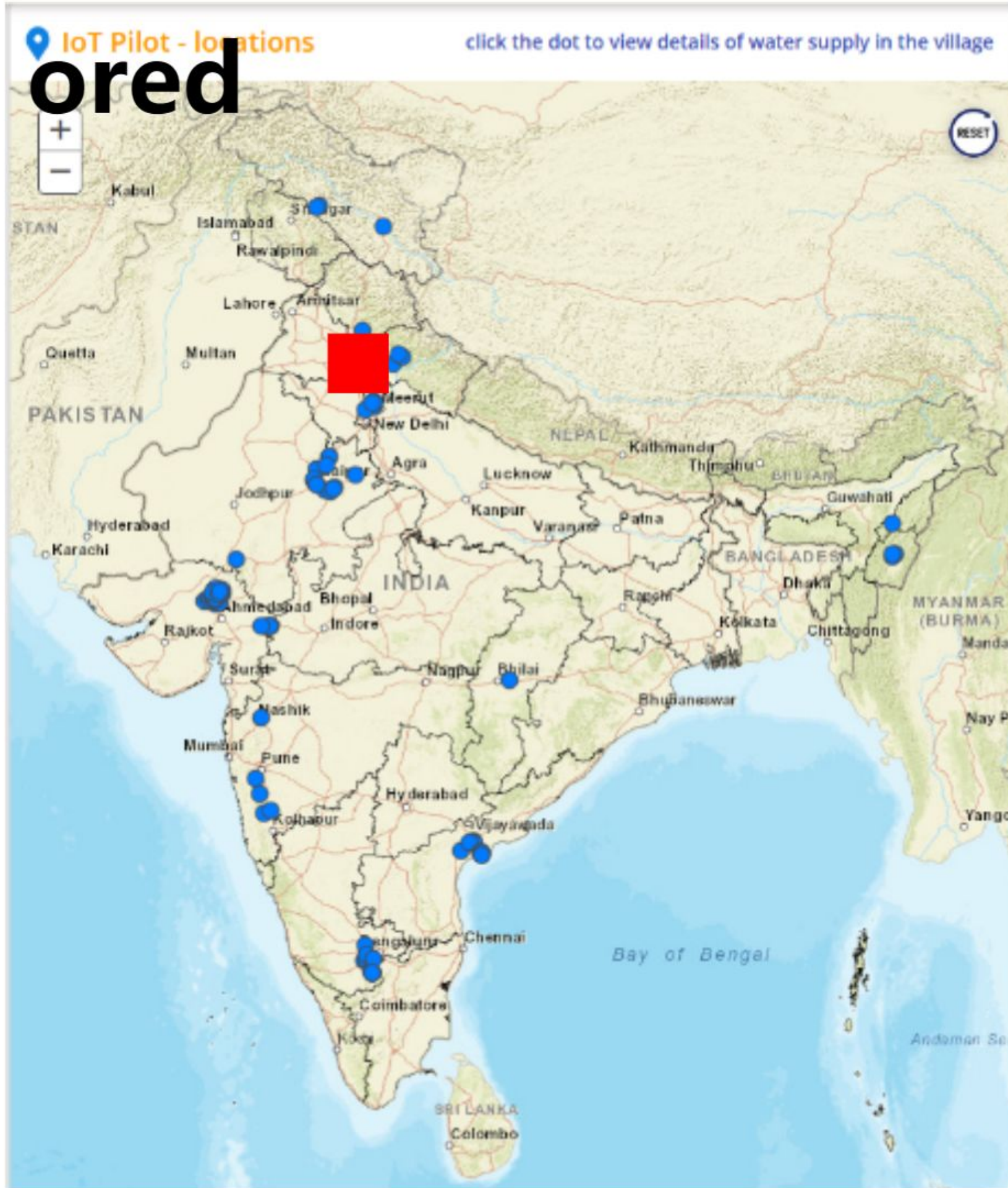


Working electrode



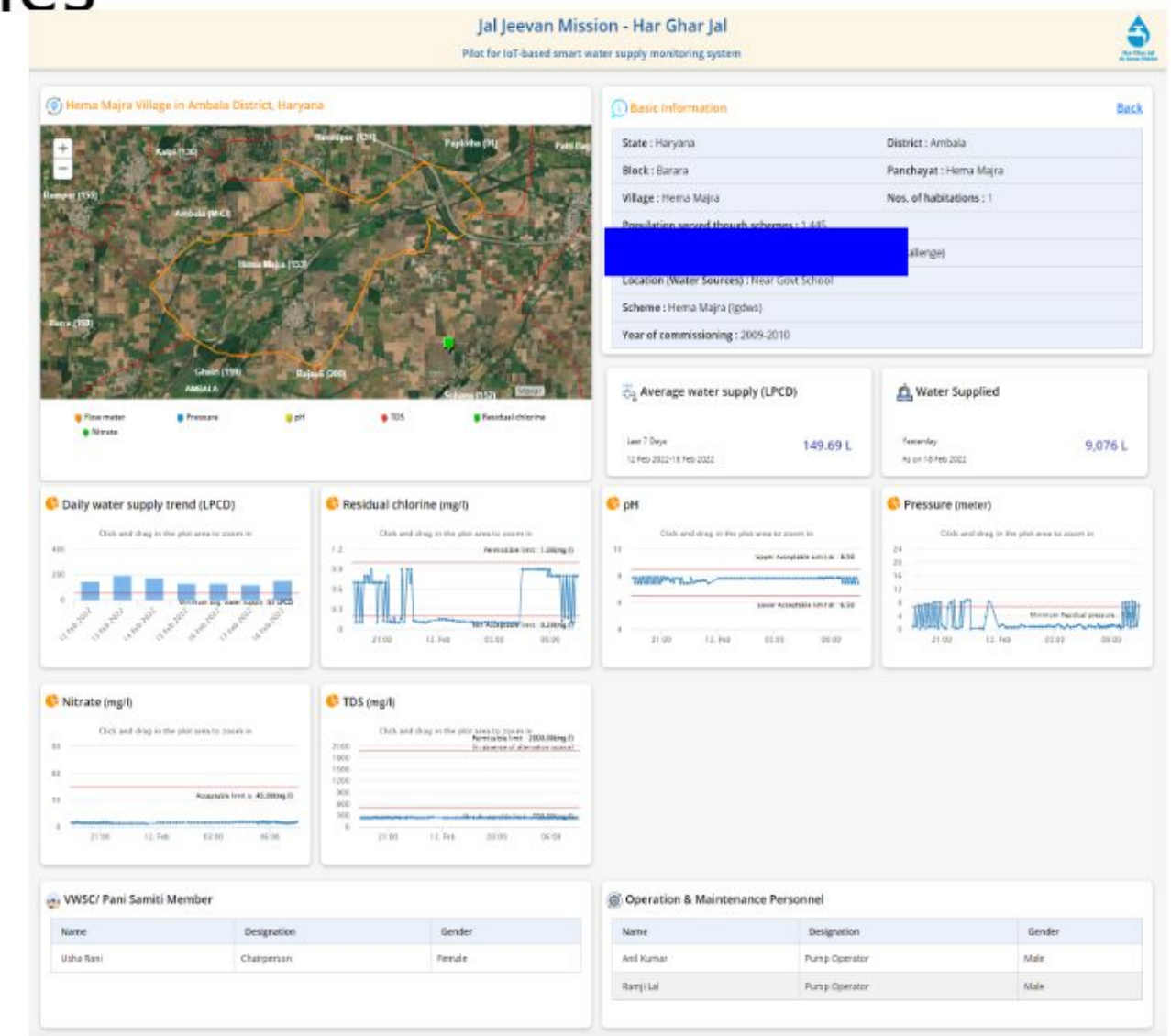
Arsenic poisoning across the world

India's water is being monitored



IITM/IIS

Installations made by four companies



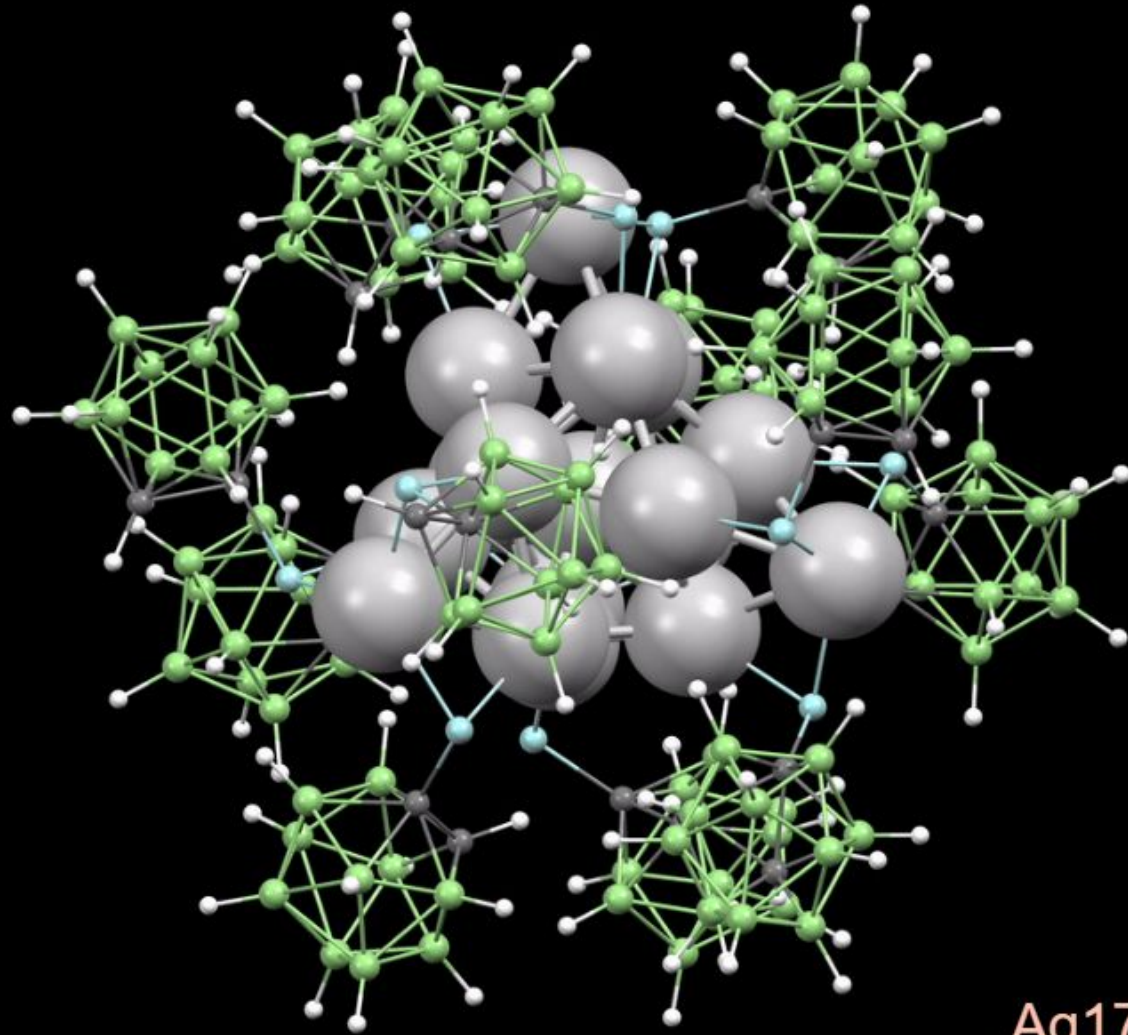
Ag₁₇

AuAg₁₆

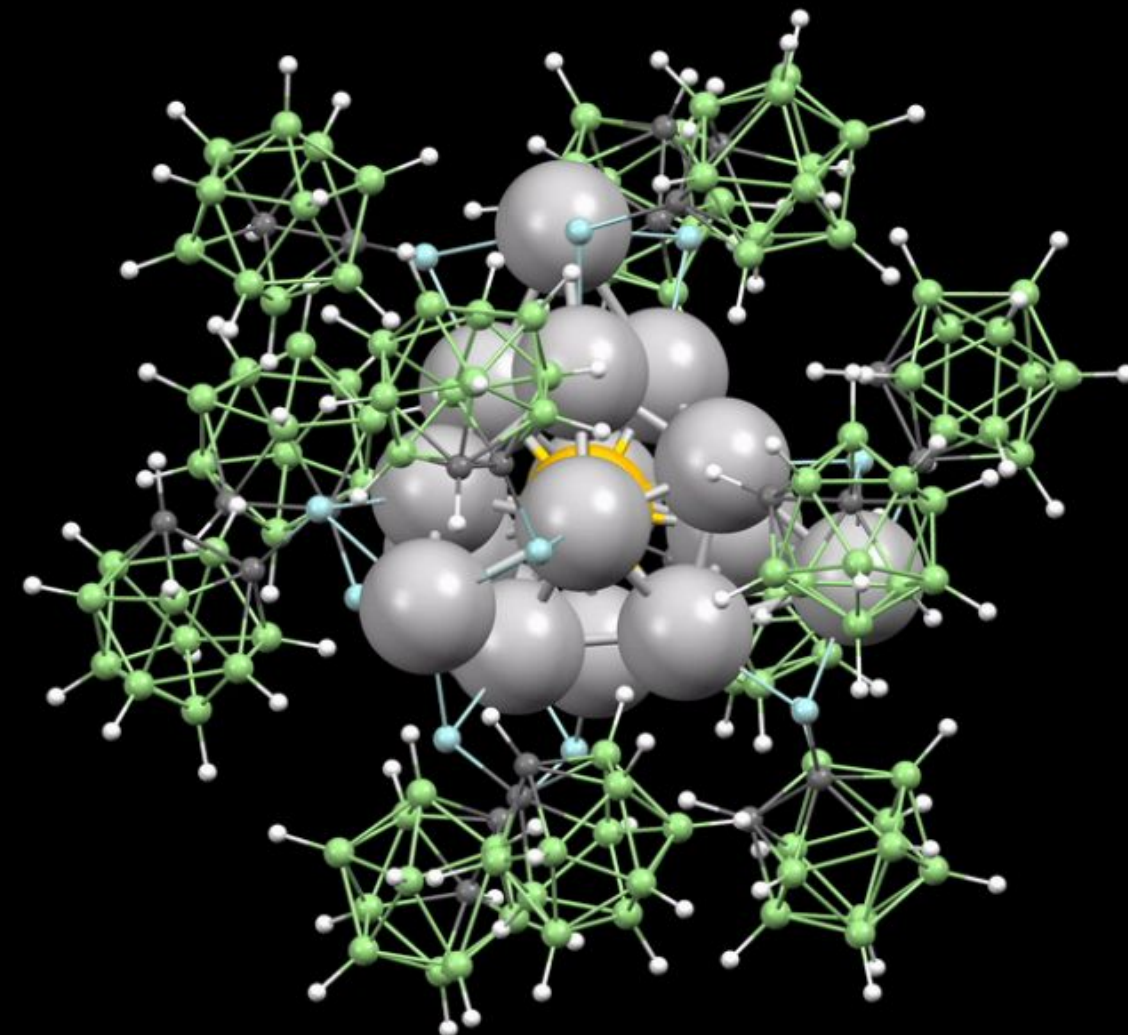
Ag₁₃Cu₄

AuAg₁₂Cu₄

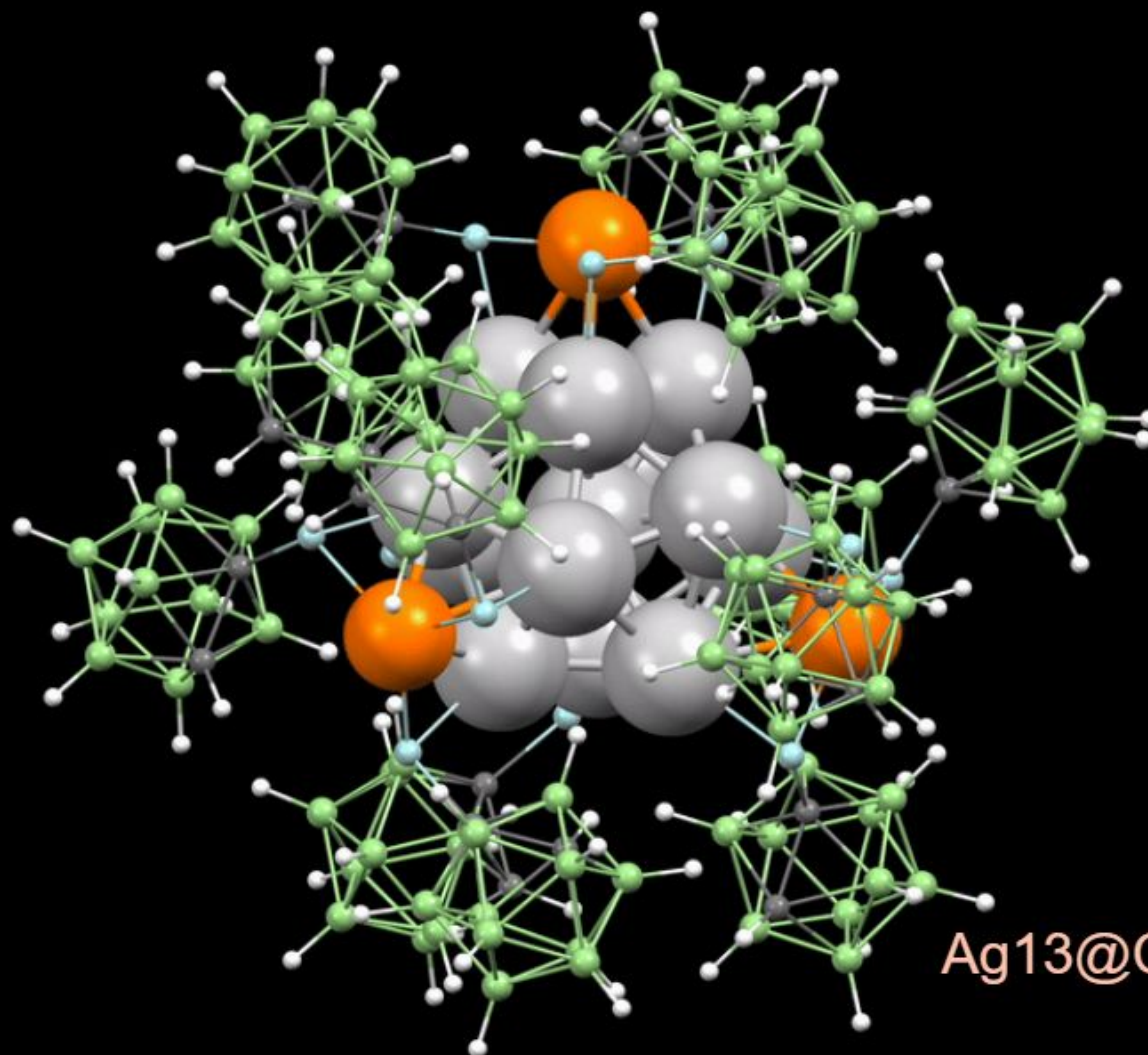
Structure of M17 Nanoclusters



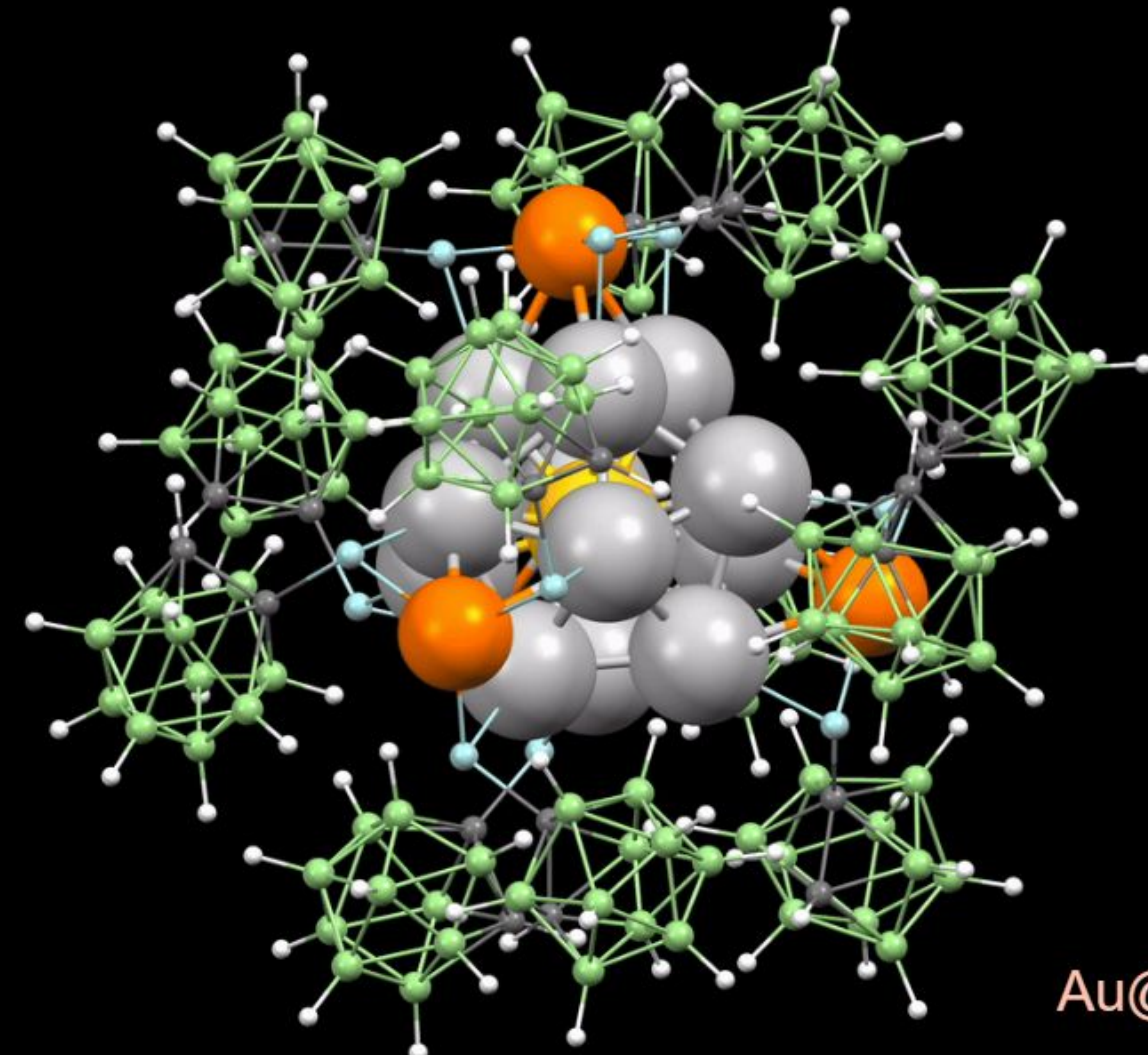
Ag₁₇



Au@Ag₁₆

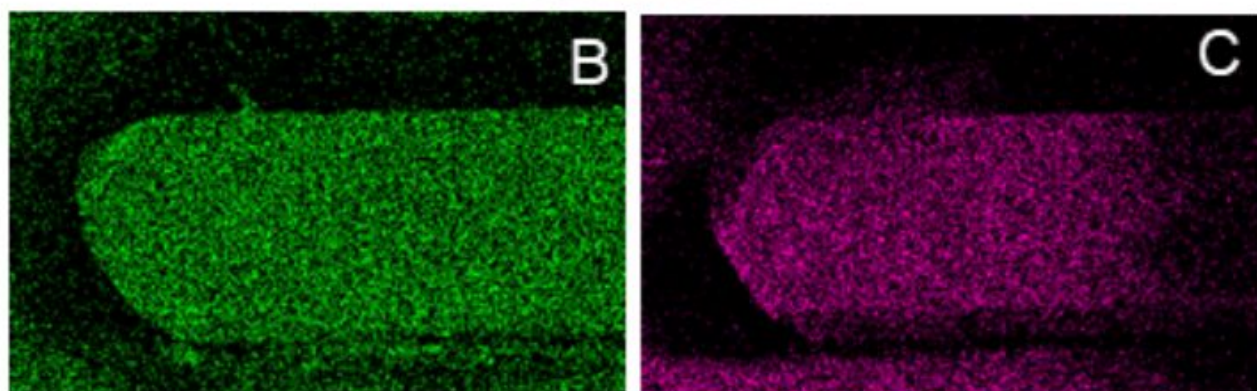
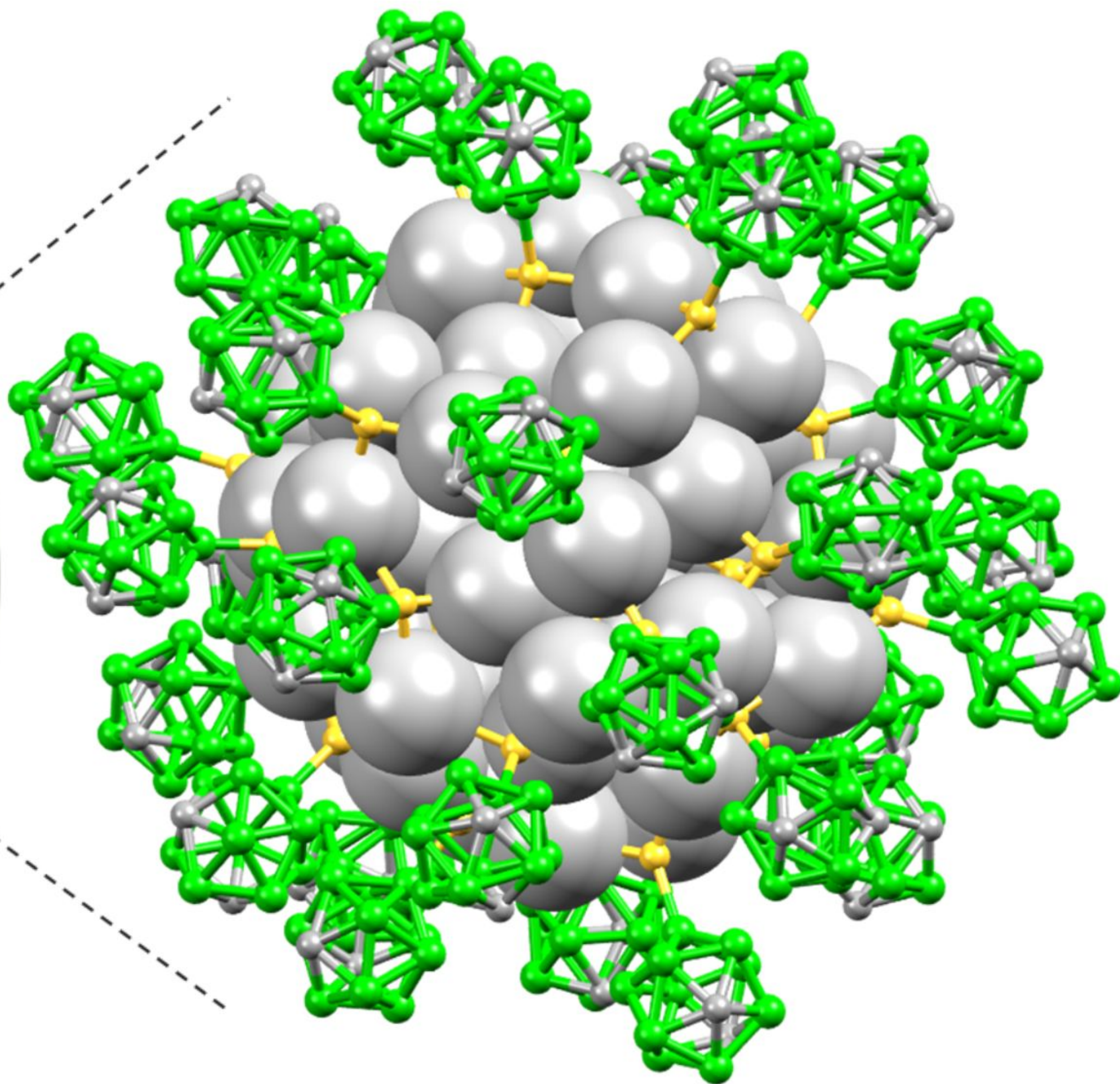
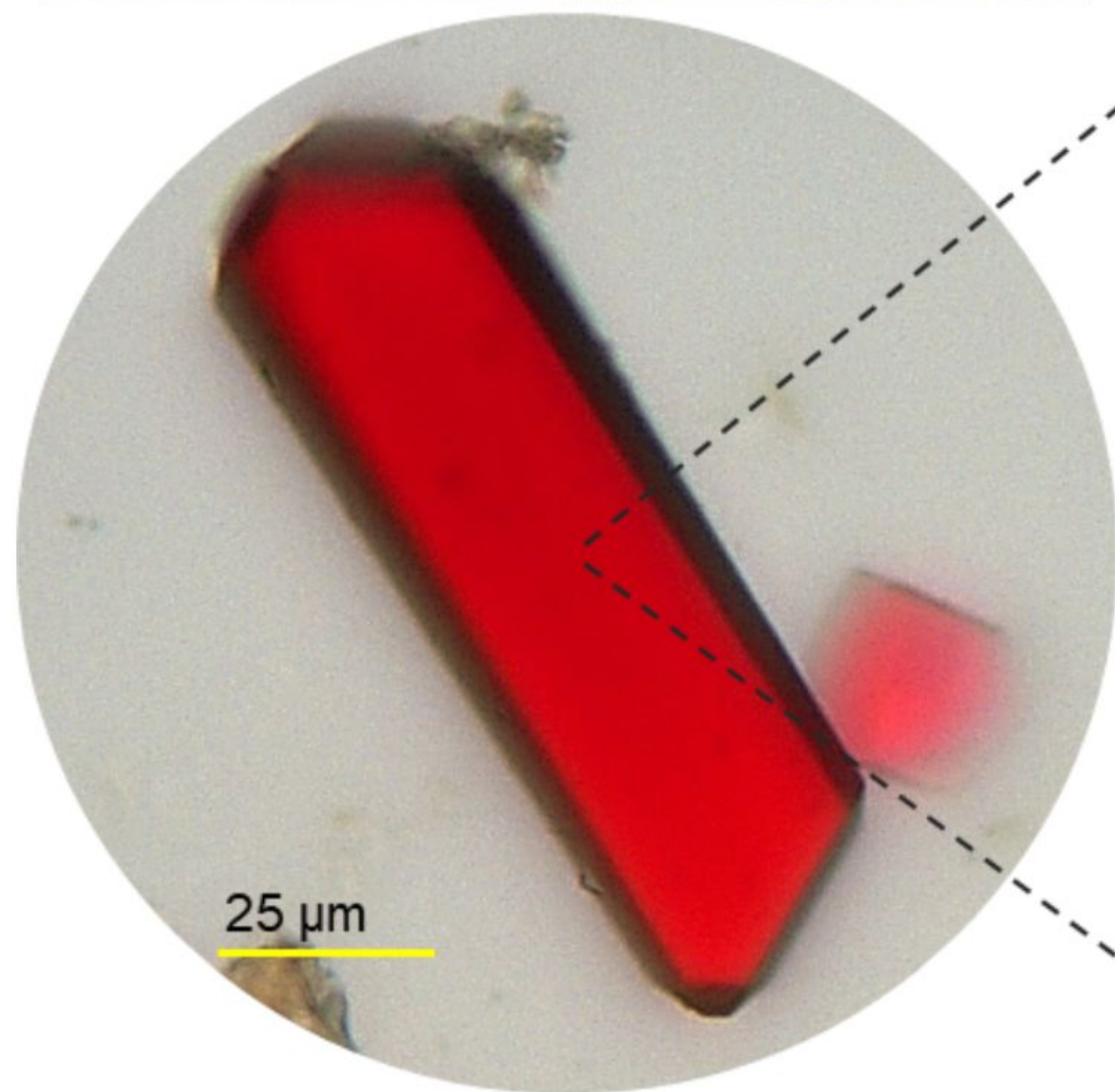
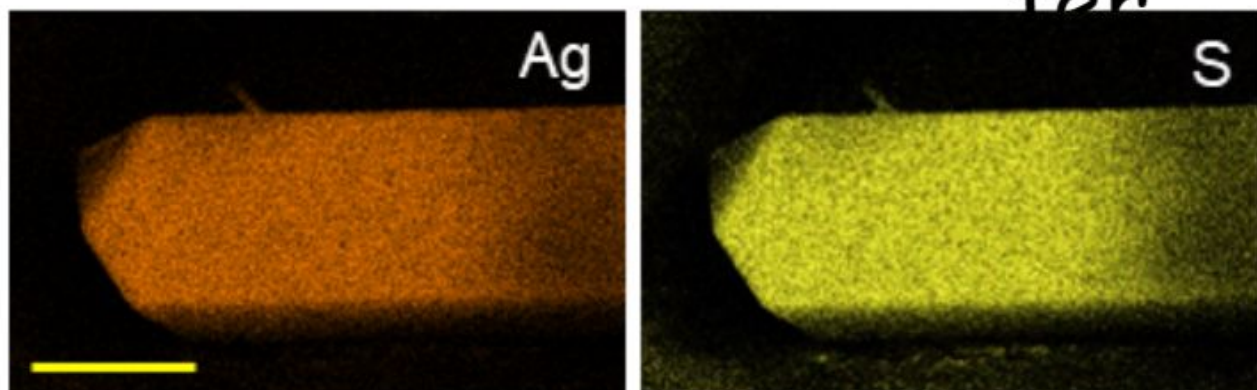


Ag₁₃@Cu₄



Au@Ag₁₂@Cu₄

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

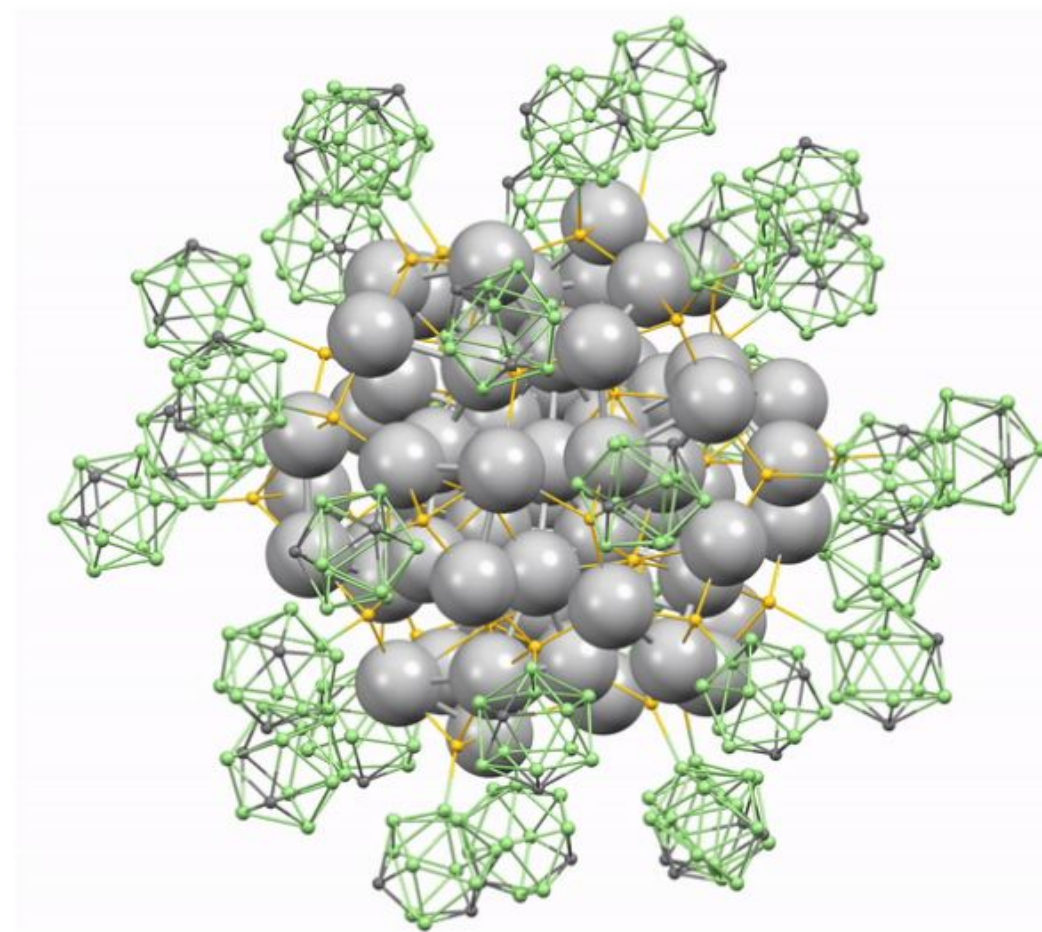


Largest molecule with carboranes so far.....

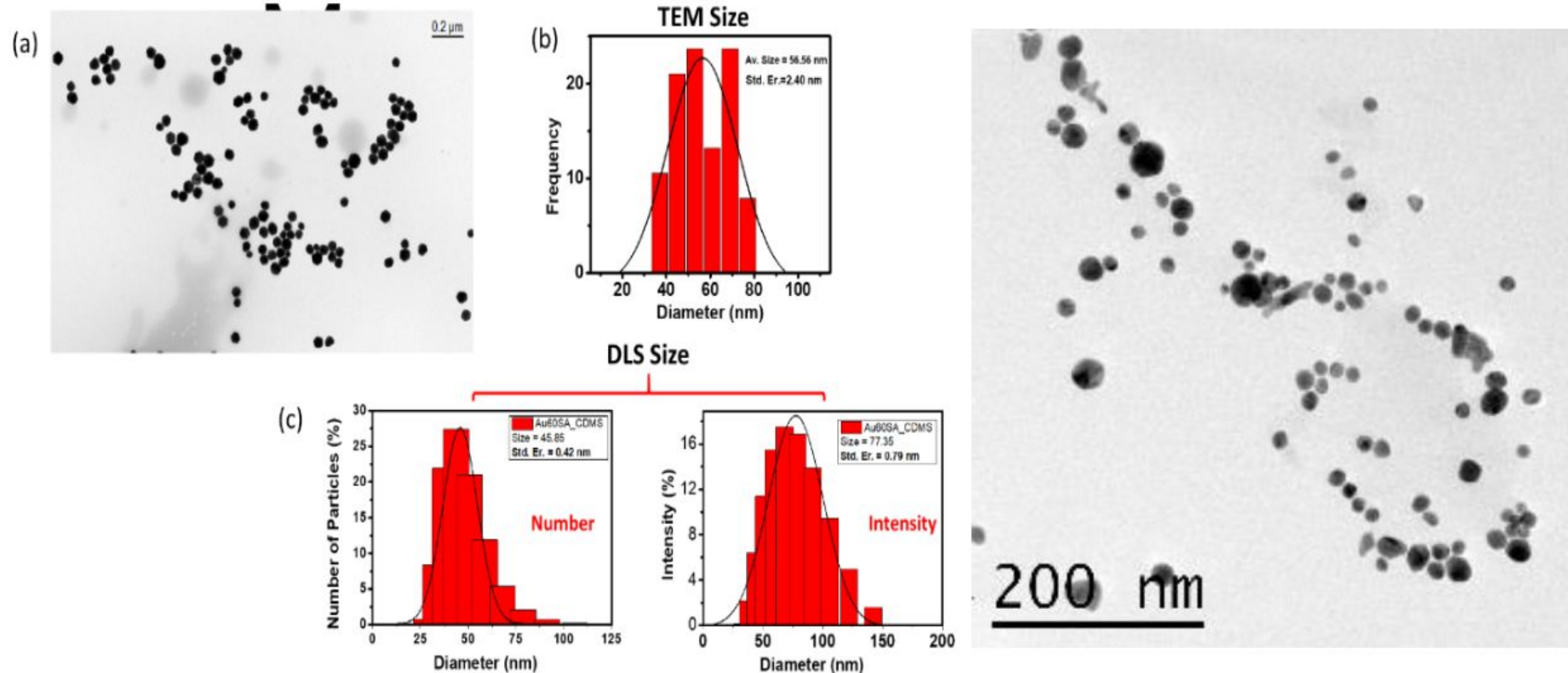
Jana *et al.*, Submitted

Summary

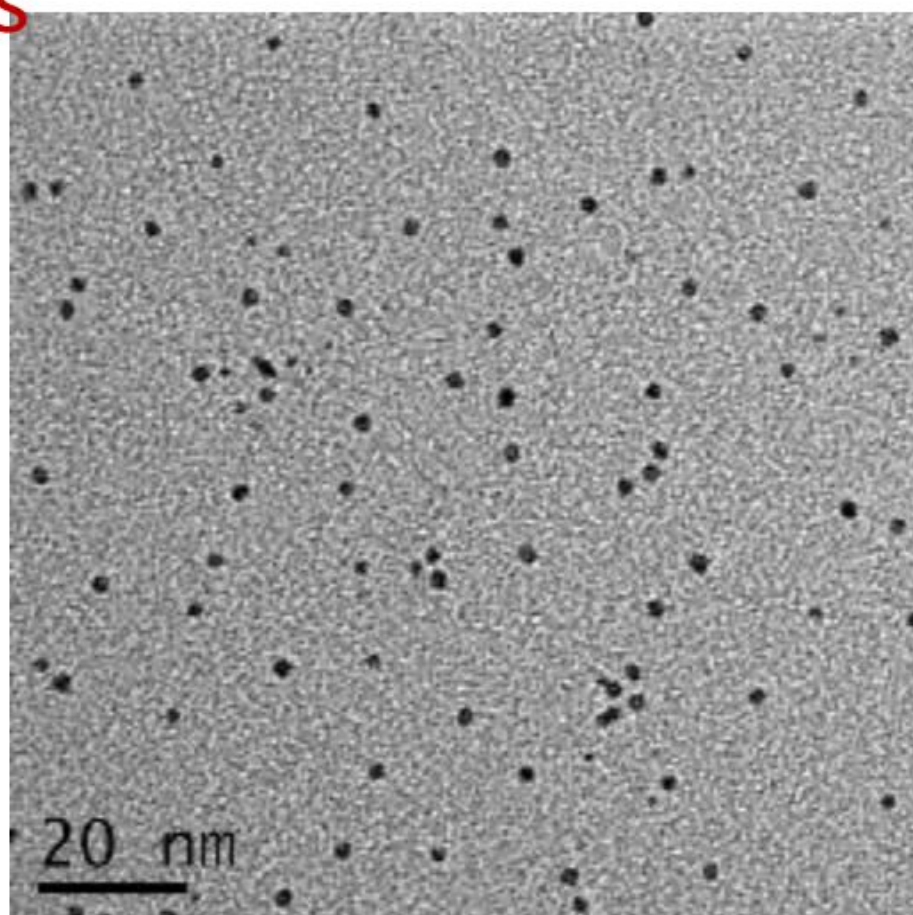
- Atomically precise clusters are a category of new materials
- They are molecules - properties, nomenclature,...
- Clusters are thermally stable up to 400°C.
- They exhibit useful applications
- Atomic precision across the periodic table
- An era cluster-based materials is being born



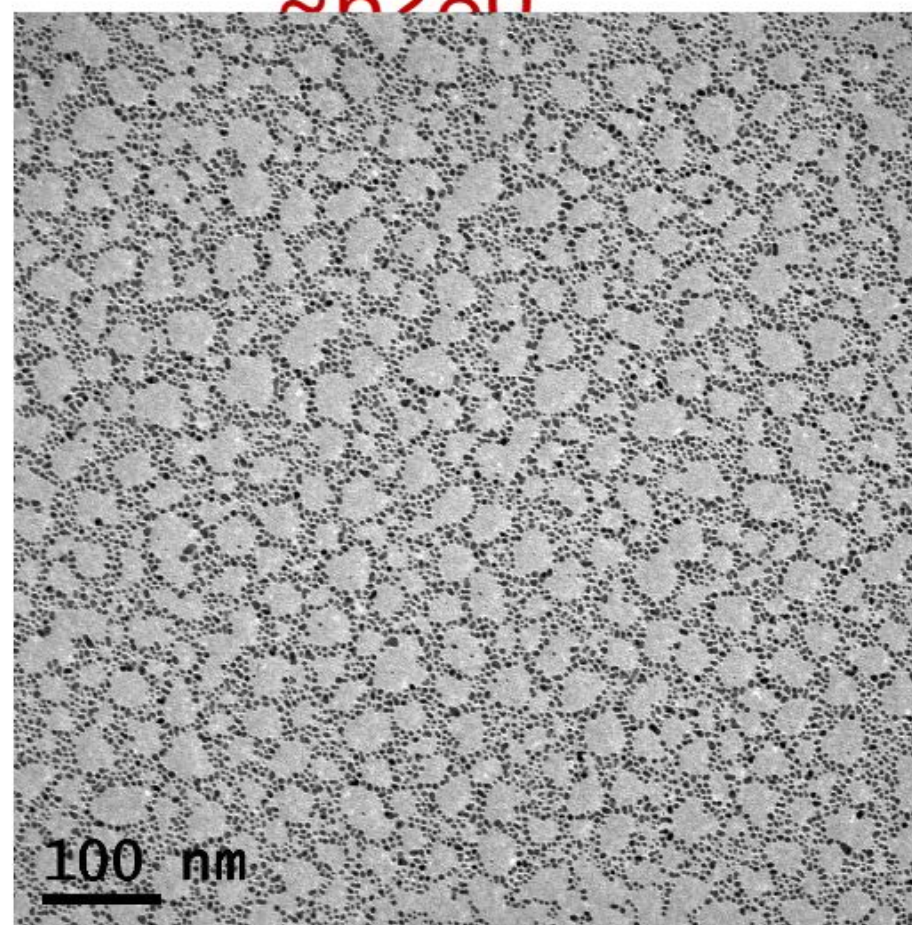
Larger clusters - TE



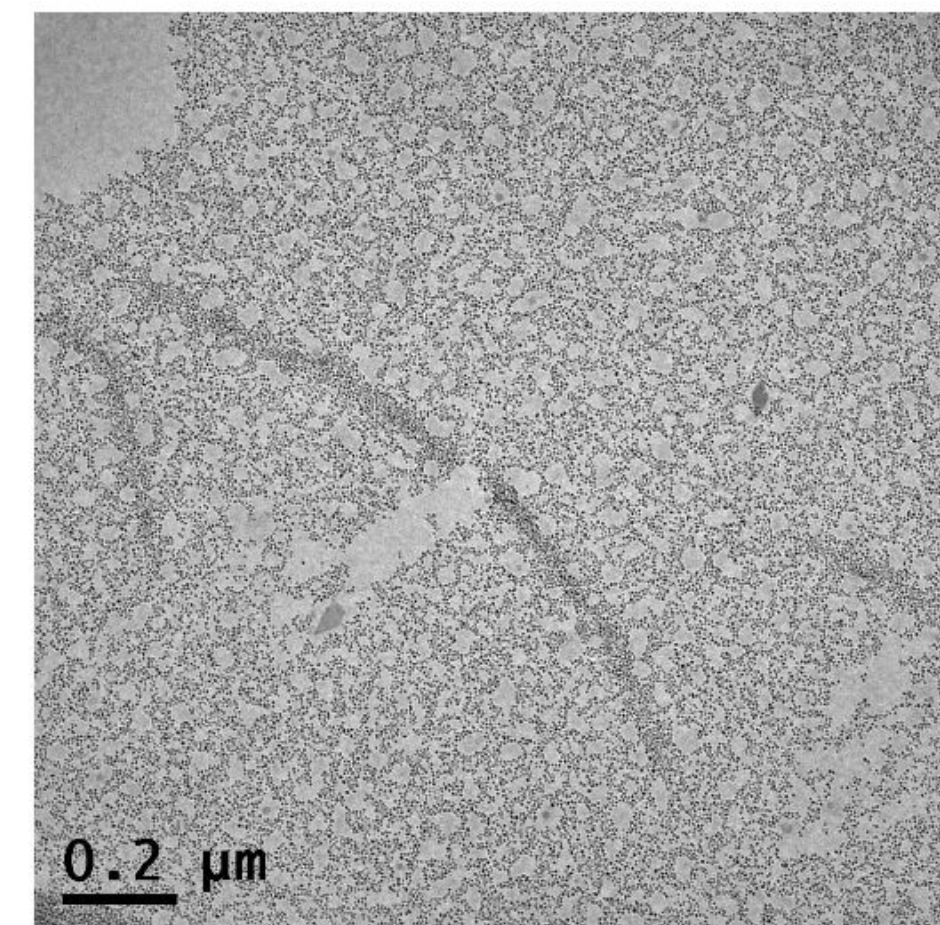
60 nm sized Au-citrate nanopartic Au~246000(MUTAB)
les ~6280



Au279(TBBT)84



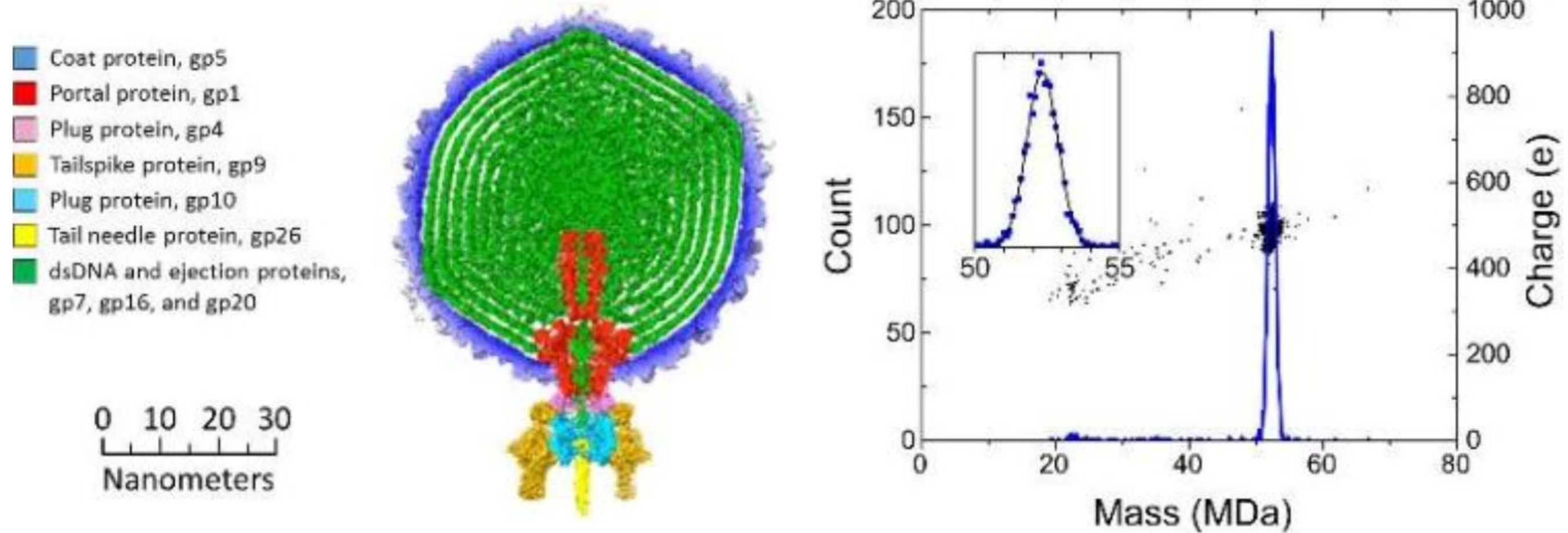
Au144(PET)60



Au25(PET)18

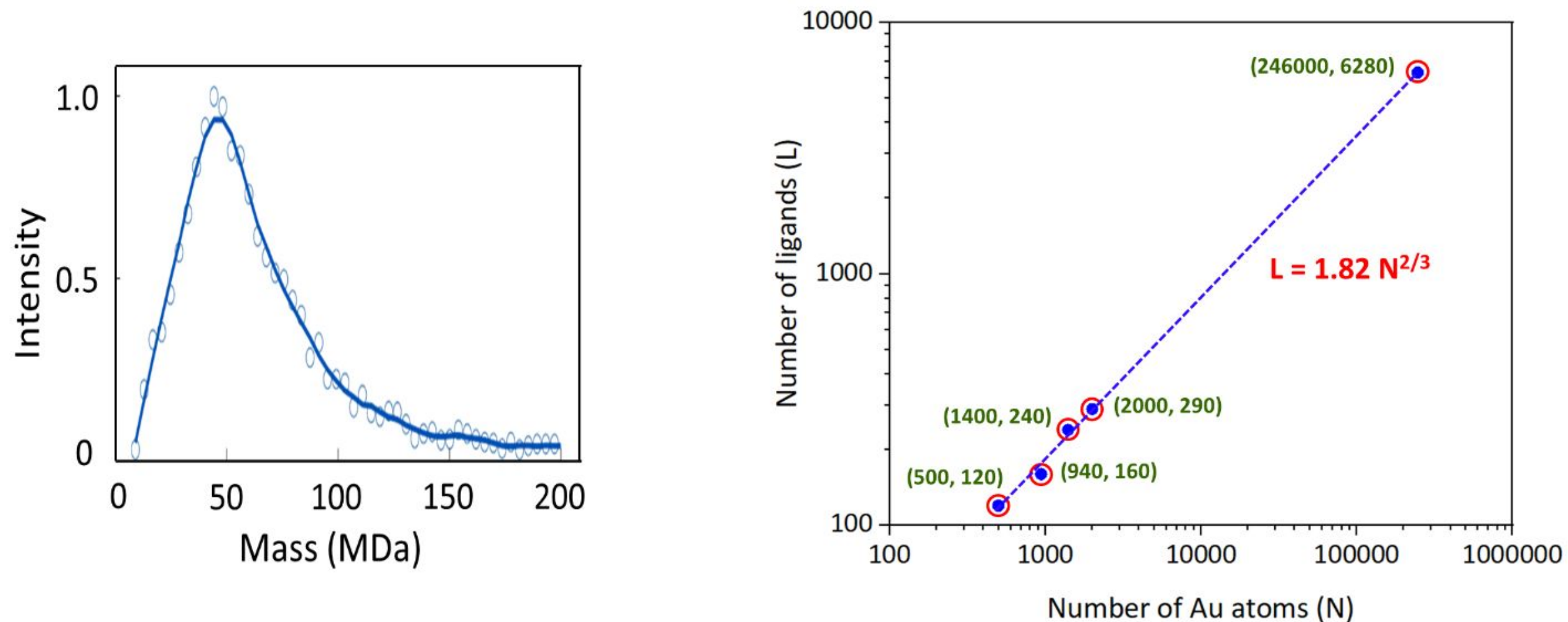
CDMS of viruses and nanoparticl

(a)



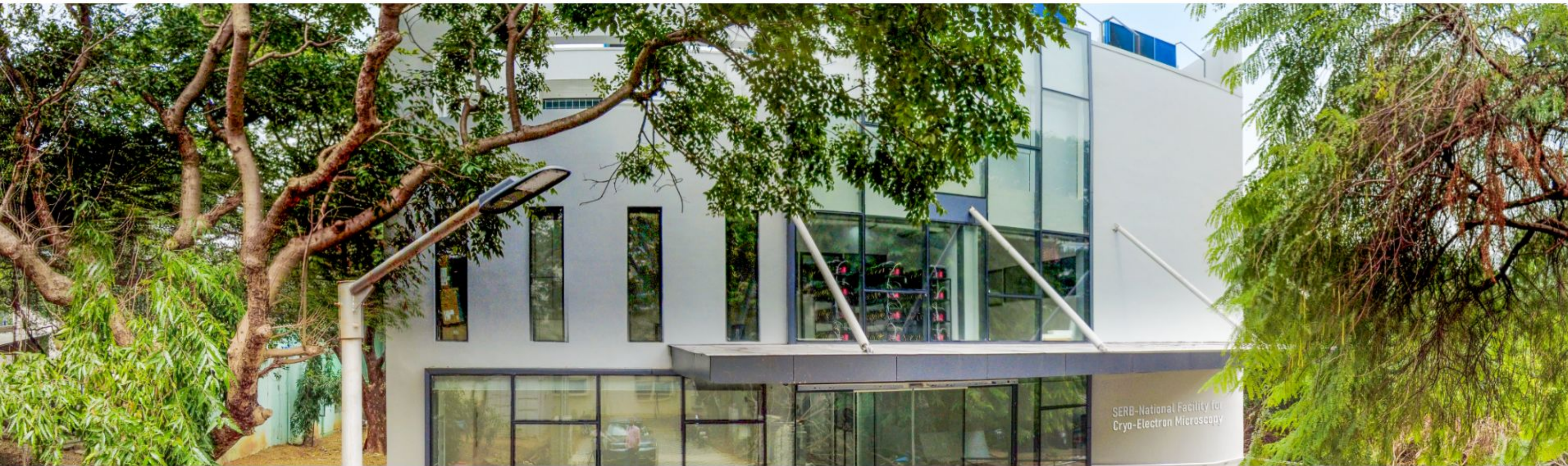
Keifer, D. Z.; Motwani, T.; Teschke, C. M.; Jarrold, M. F. Measurement of the Accurate Mass of a 50 MDa Infectious Virus. *Rapid Commun. Mass Spectrom.* **2016**, 30 (17), 1957–1962.

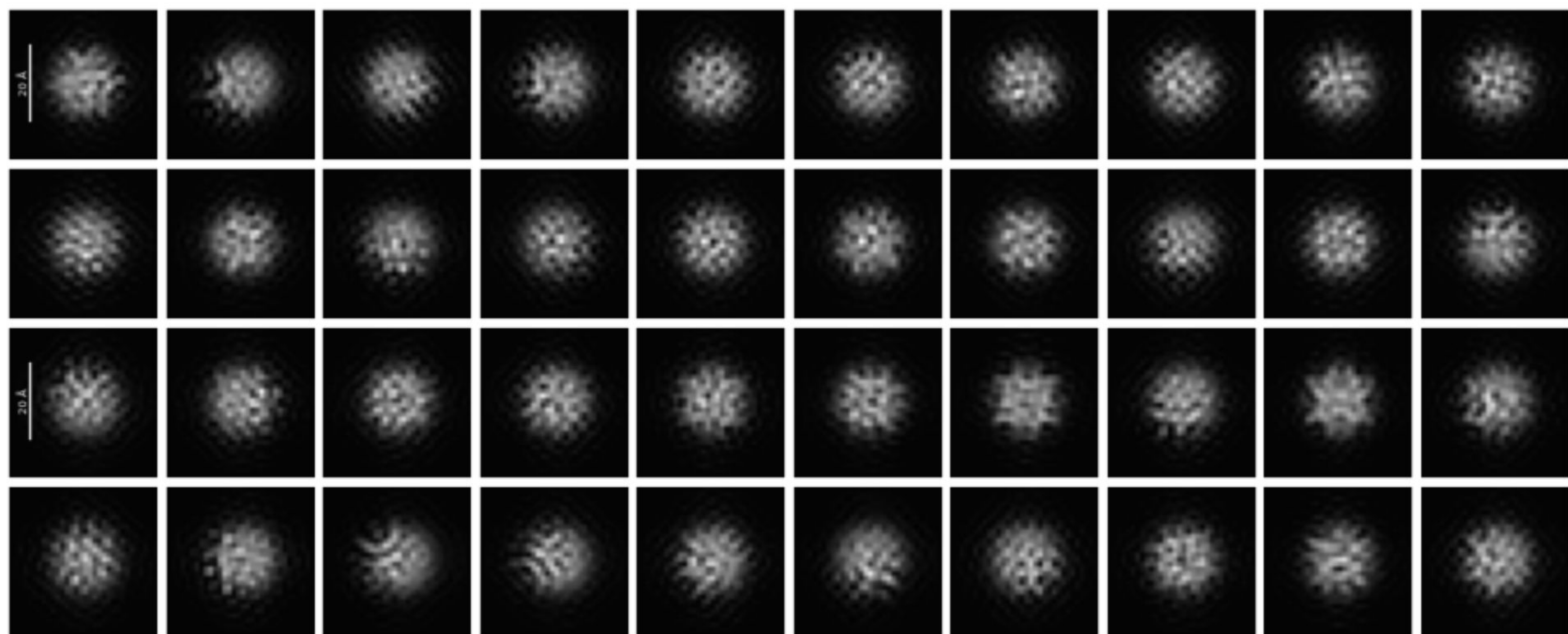
(b)



B. S. Sooraj, et. al. Revised and submitt

Resolving Structural Transitions through Microcrystal Electron Diffraction



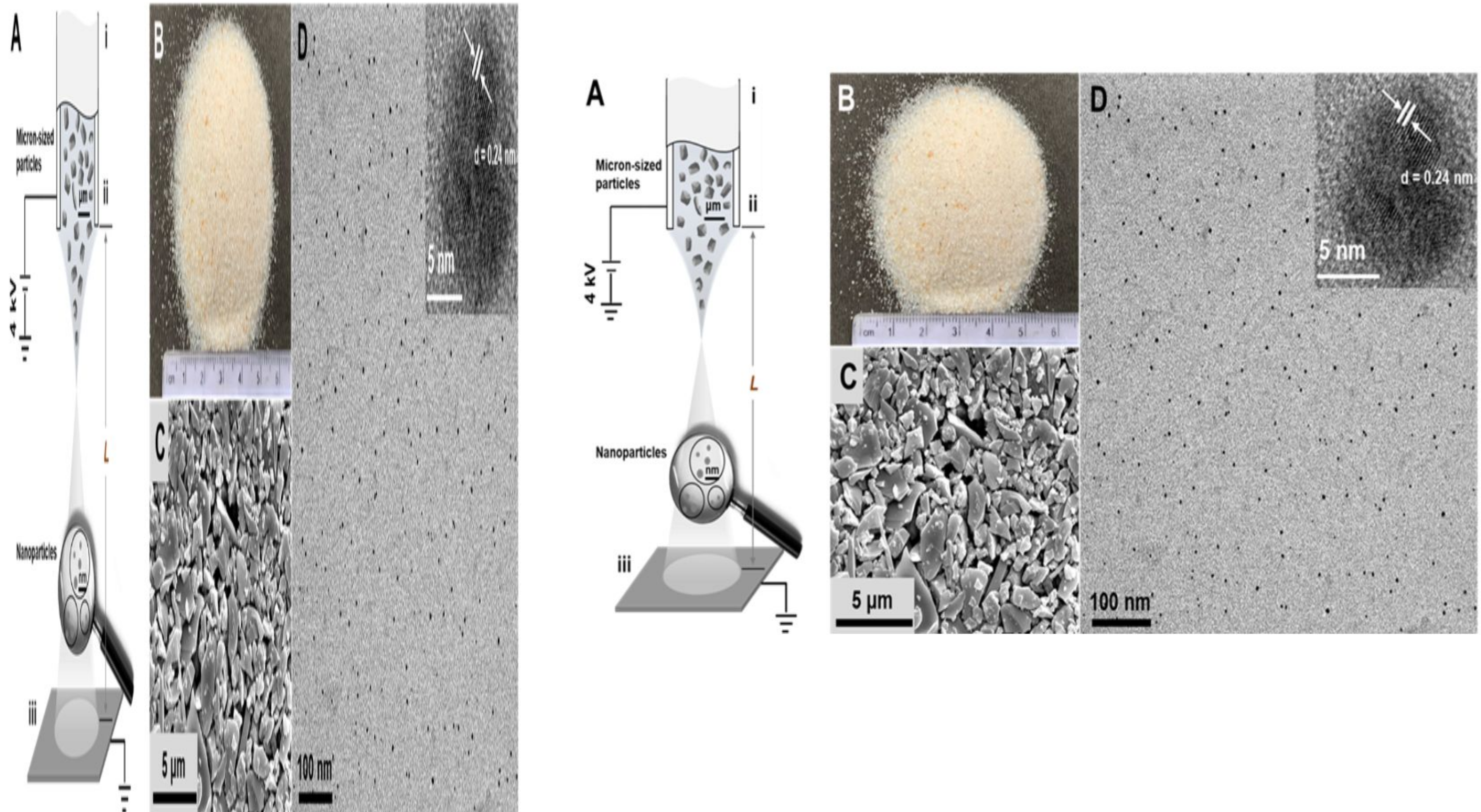


B. S. Sooraj, et. al. Unpublishe
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Weathering of Minerals in Microdroplets

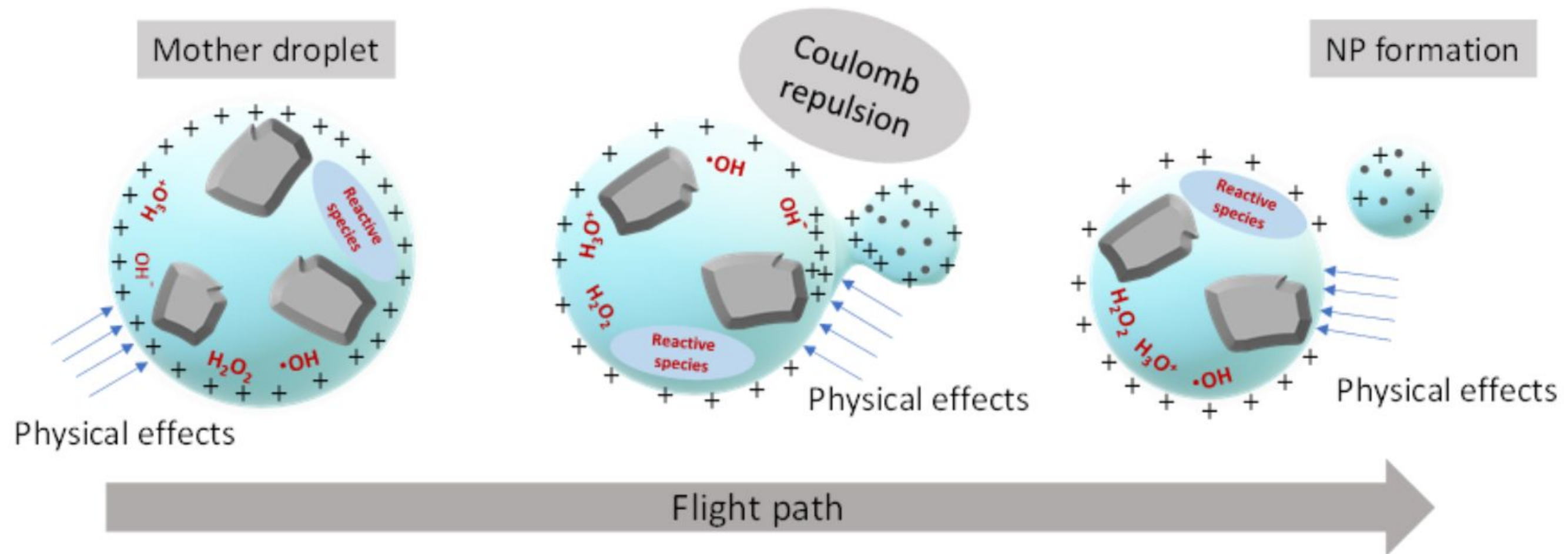


Spontaneous Weathering of Natural Minerals in Charged Water Microdroplets Forms Nanomaterials



Ruby, Fused Alumin
a

Mechanism of nanoparticle formation





International Centre for Clean Water

People's Water Data





Collaborator



Robin Ras

Nonappa

Tomas Bas
e



Manfred Kappes

Olli Ikkal
a

Horst Hah
n

Tatsuya Tsukuda
Keisaku Kimura
Yui Negishi
Uzi Landman
Hanu Hakkinen
Rob Whetten



Biswarup Patha K. V. Adars

G. U. Kulkarn

Vivek Polshettiwar

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

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

Funding: Department of Science and Technology, Government of India

Start-ups and partners:

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

MS Theses: Ananthu Mahendranath, Ramesh Kumar Soni

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



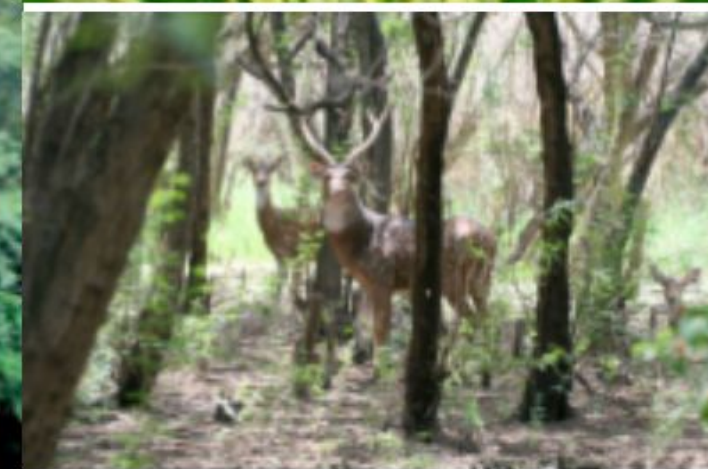
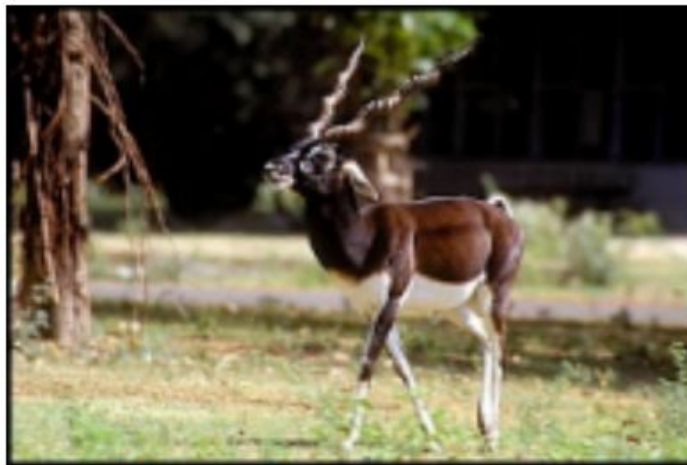
Department of Science and Technology, Government of India

Institute of Eminence

Many Outstanding Individuals



Indian Institute of Technology Madras



Associate Editor
Srinivasan Ramamurthi/V. Kamakoti

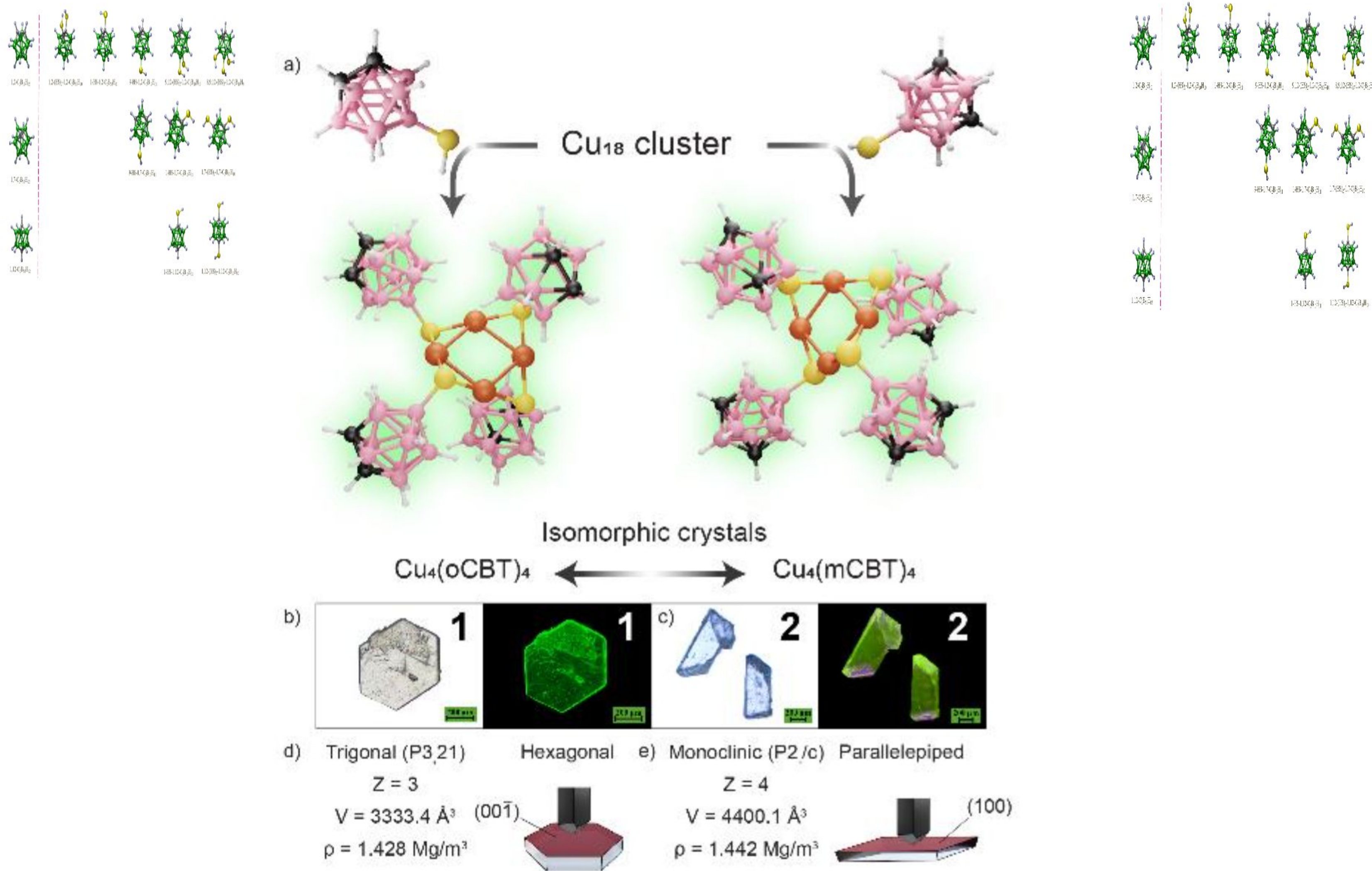
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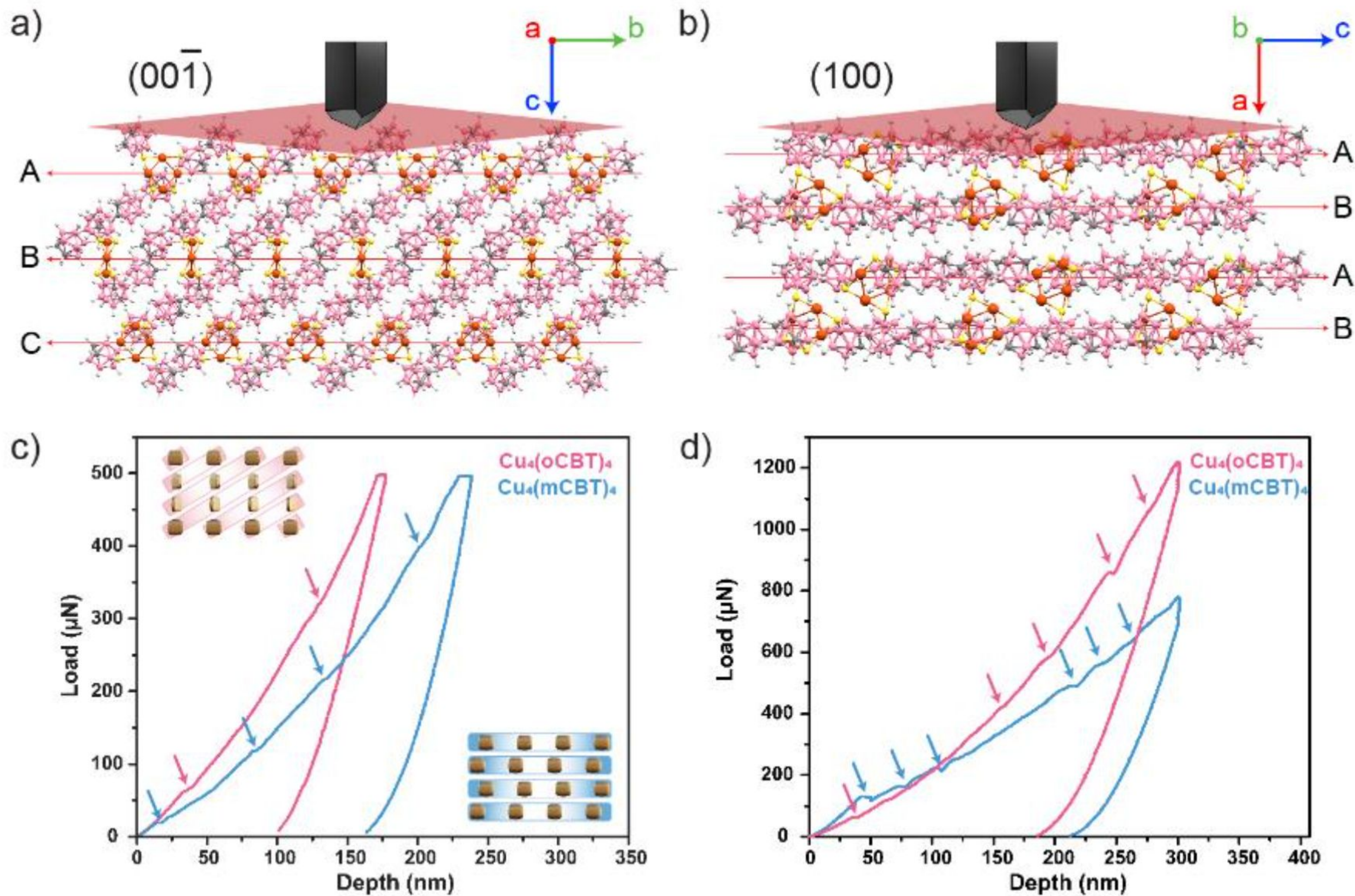
Manswita Mandal for help with the slides

Properti
es

Nanomechanical Properties of Cu₄ Nanoclusters

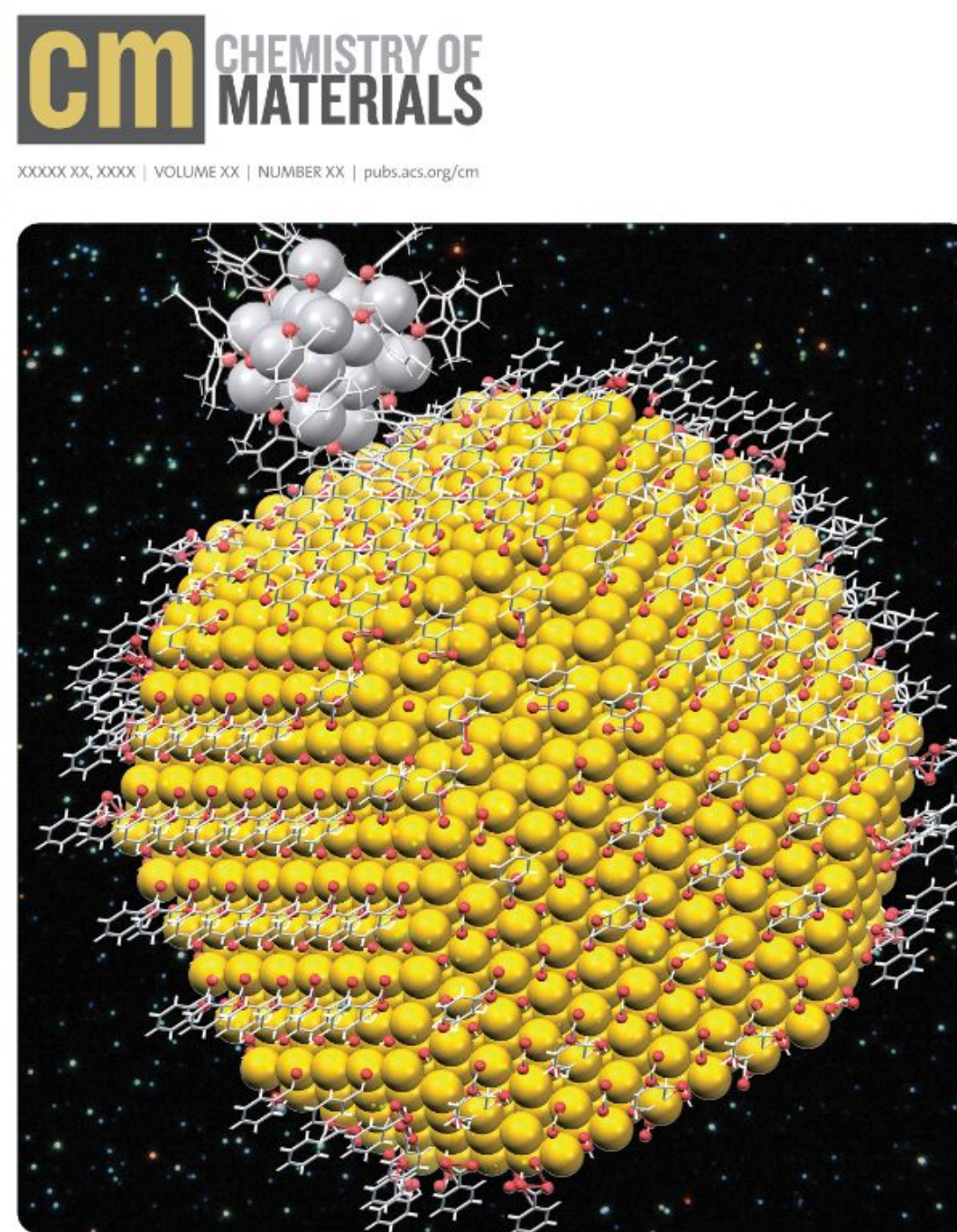
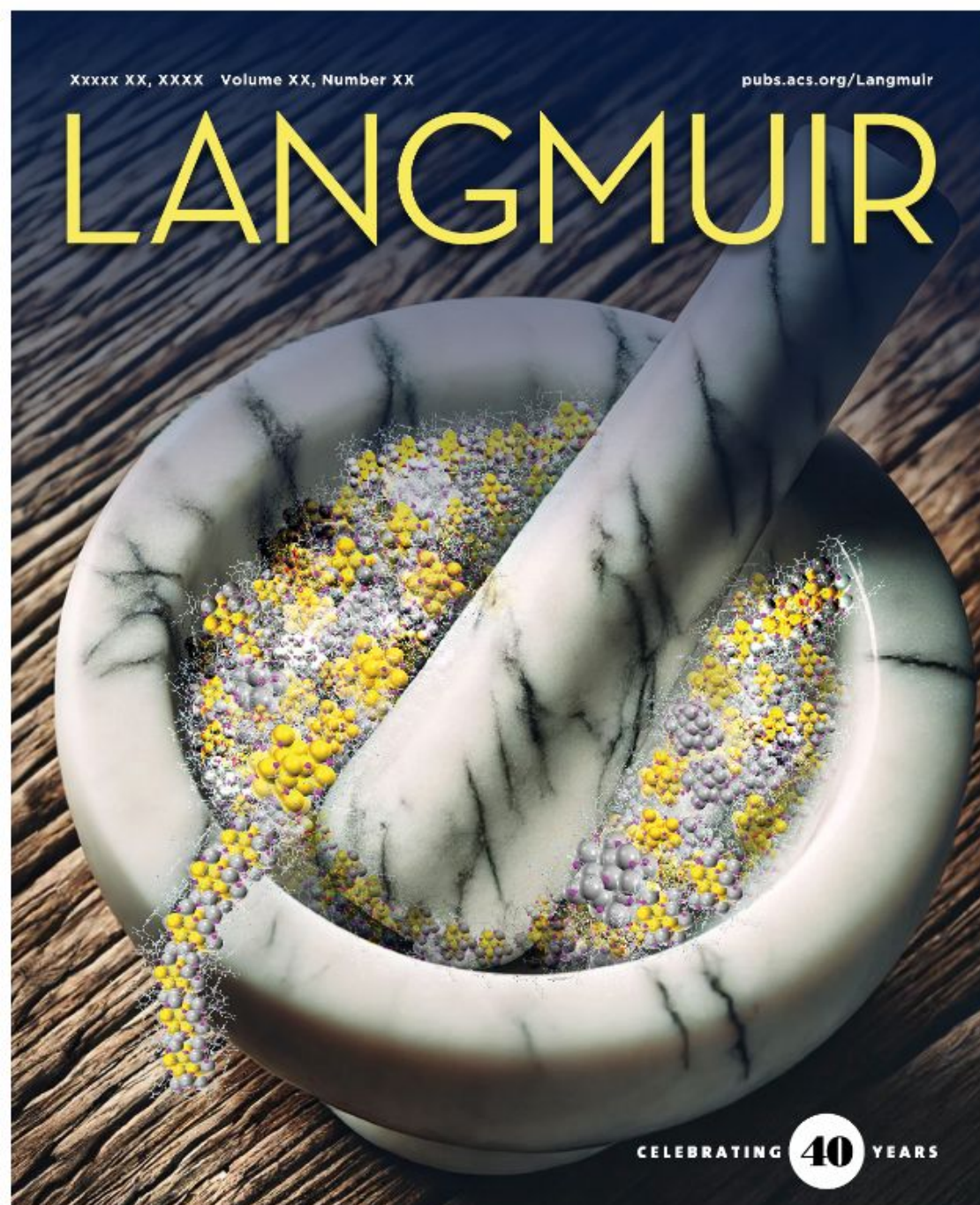


Nanomechanical Properties of Cu₄ Nanoclusters



Catalysis by Ag₁₃Cu₄ Nanoclusters

- ❖ Direct N9-arylation of Guanine with Phenylboronic Acid Catalyzed by Cu - doped Silver Nanocluster



Department of Science and Technology
Institute of Eminenc
e

Many Outstanding Individu
als

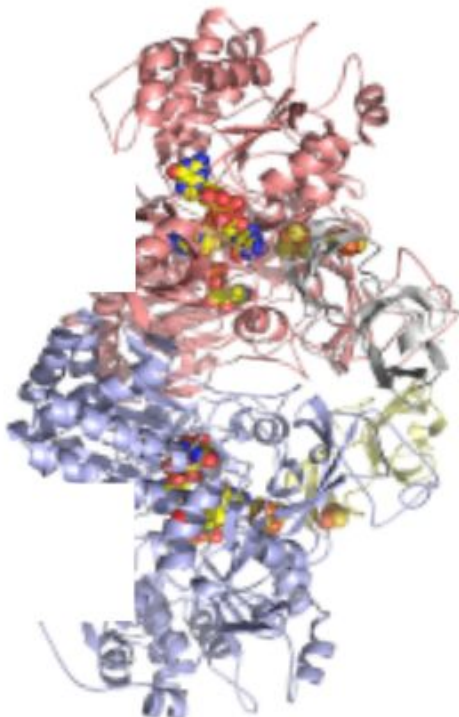
Biosensor Design

Enzyme immobilized on Electrode

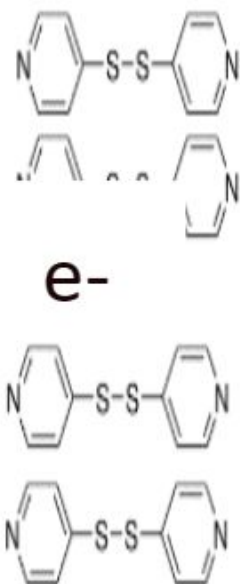
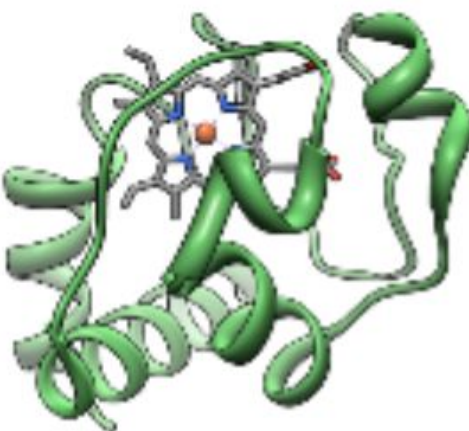
y)

As(III)

As(V)



e-



Aldrithiol



Buffer: pH 7-8

8

Recombinant Arsenite Oxidase NT-26 Aio

Horse Heart Cytochrome C

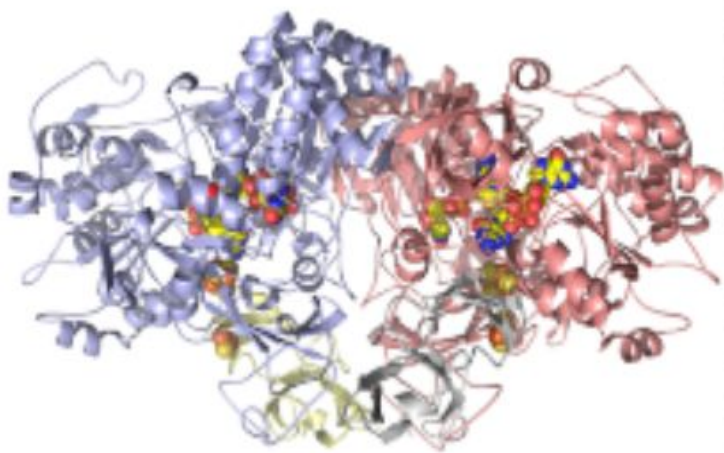
Low-cost Gold sputtered thin film on PET substrate

Enzyme immobilized on Electrode

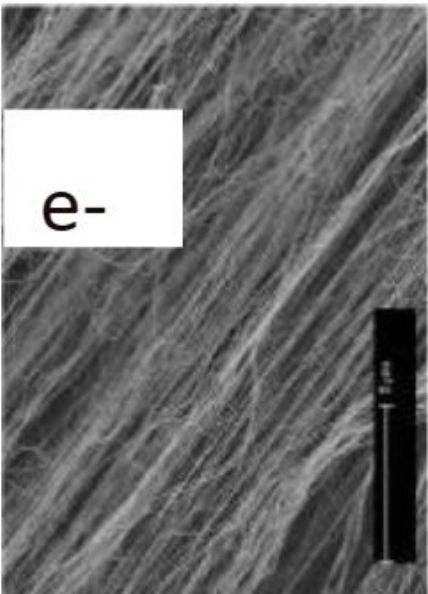
sfer)

As(III)

As(V)



e-

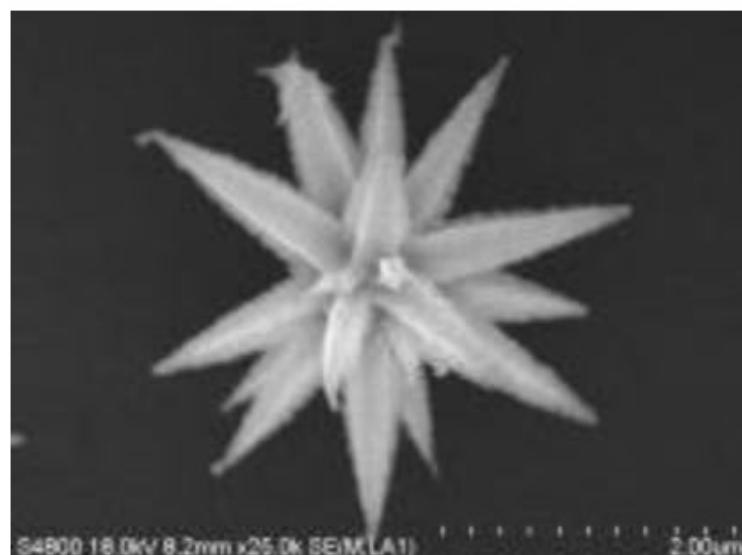
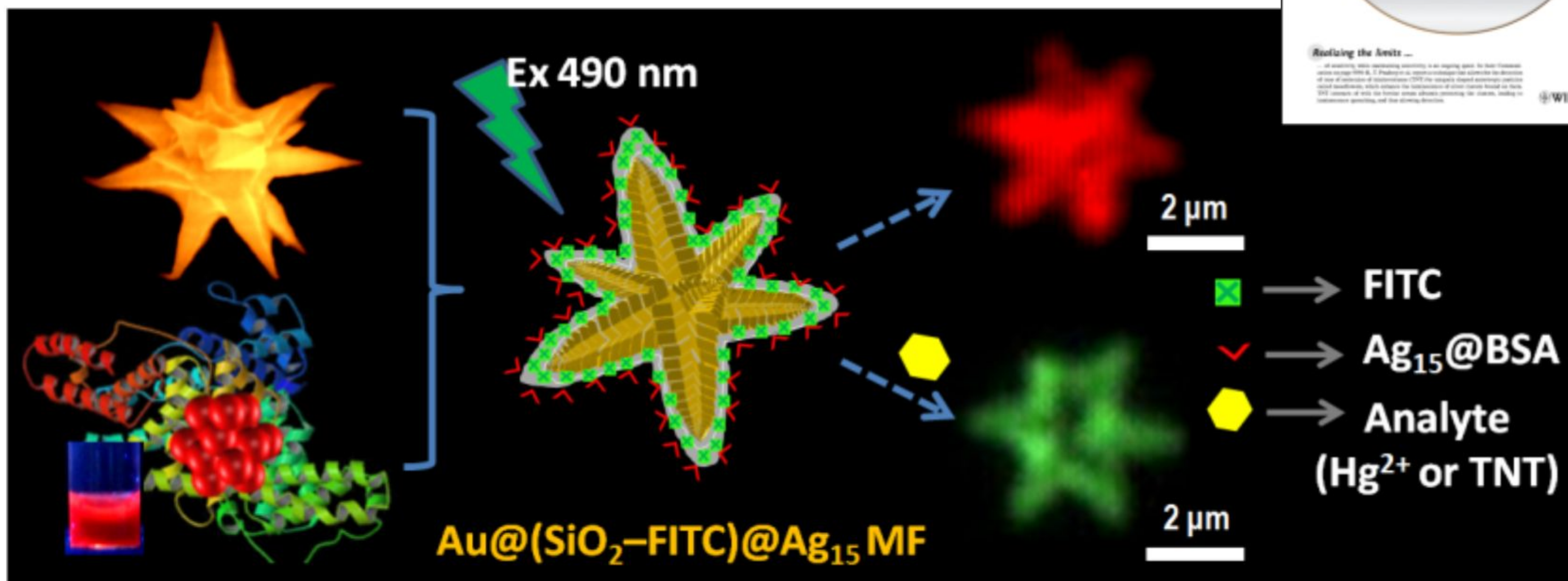
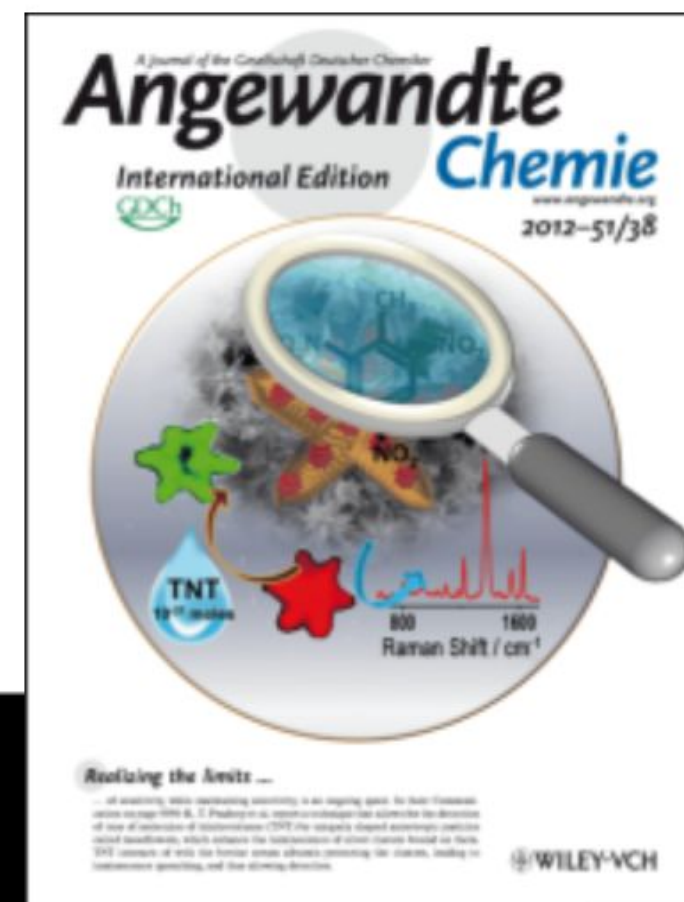


low-cost nanostructured electrodes which interact directly with enzyme (e.g. araphene or CNT).



Recombinant Arsenite Oxidase NT-26 Aio

Sub-zeptomolar detection



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

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

How do we know that they exist?

Charge detection
MS

Illustration of quantum dots

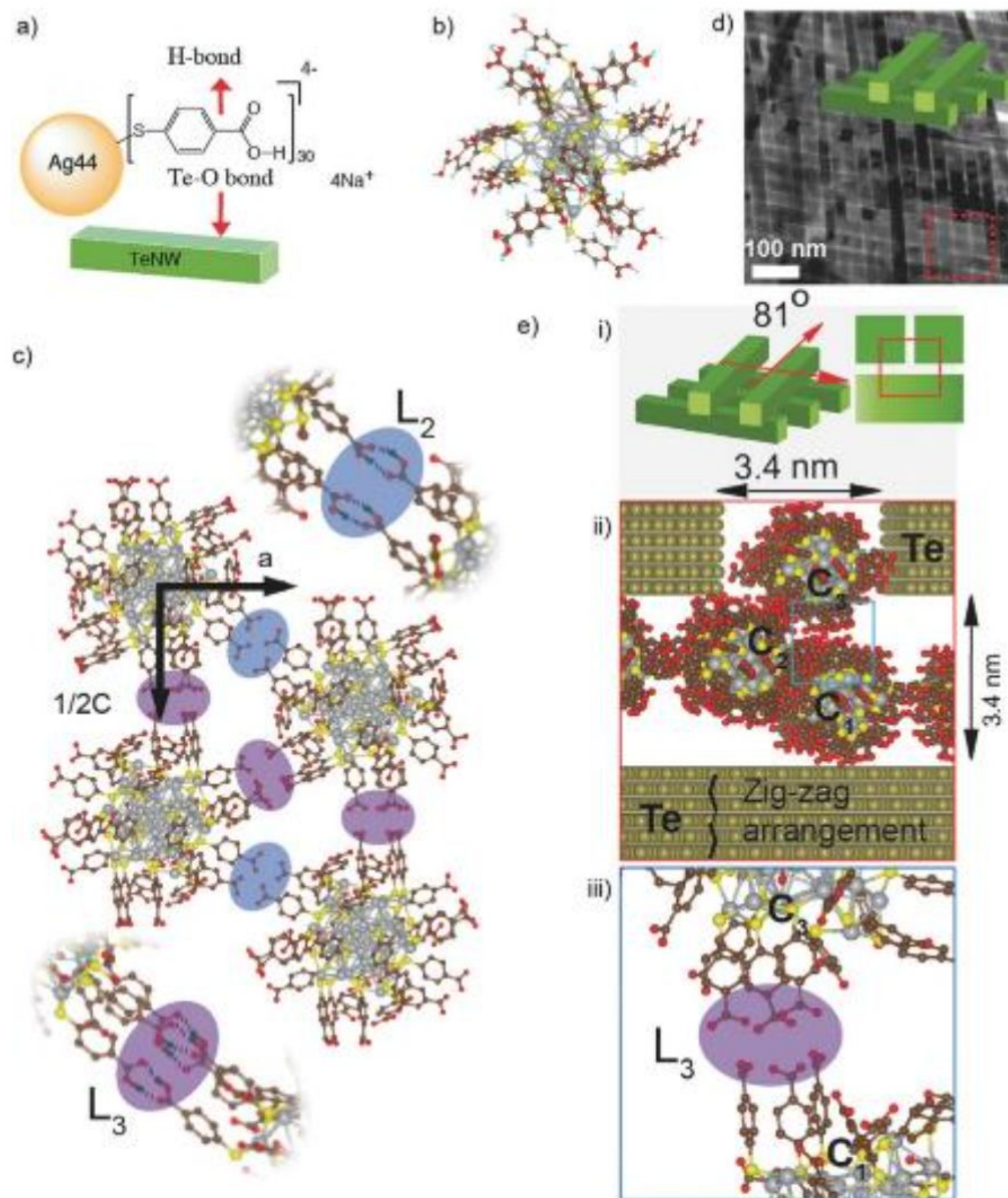
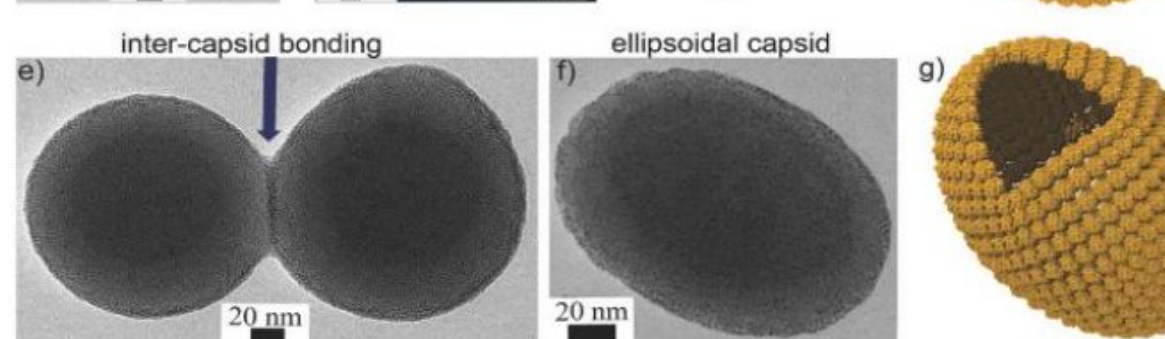
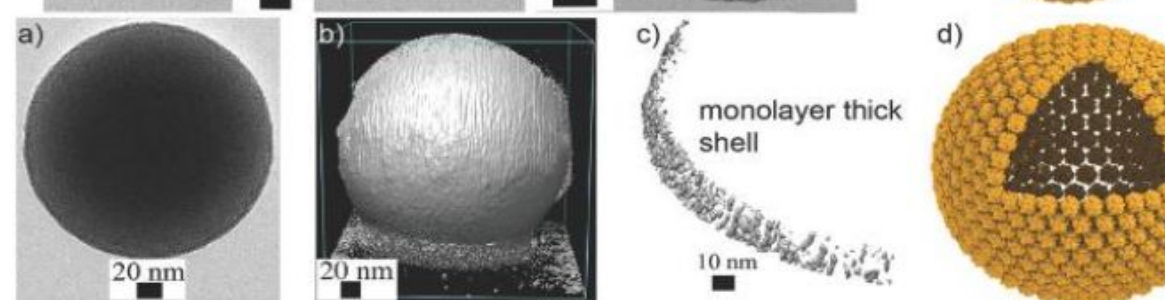
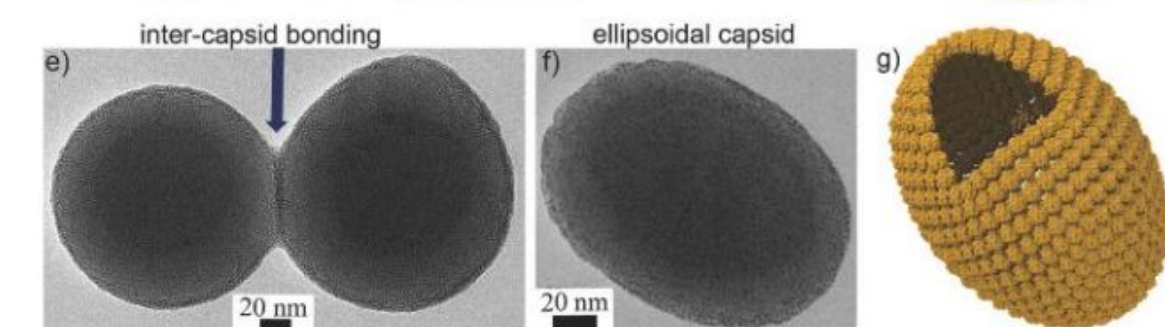
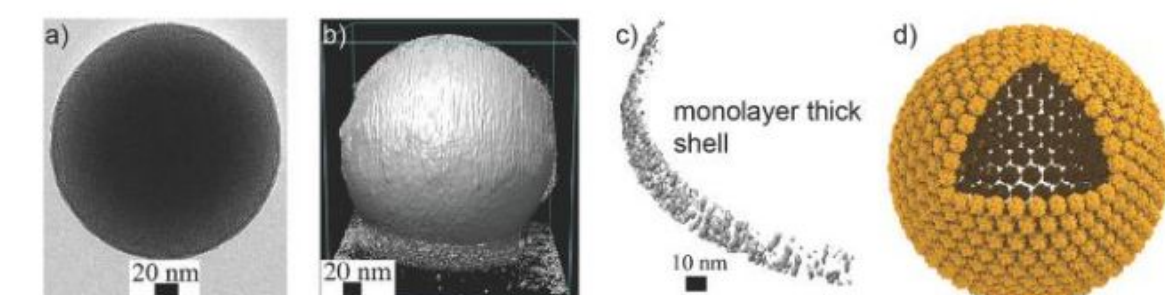
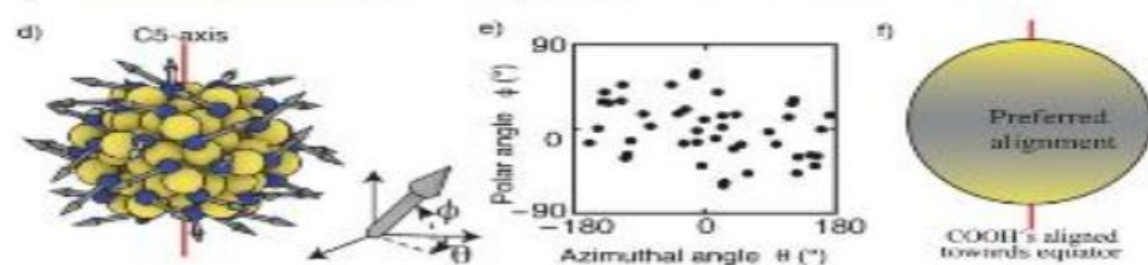
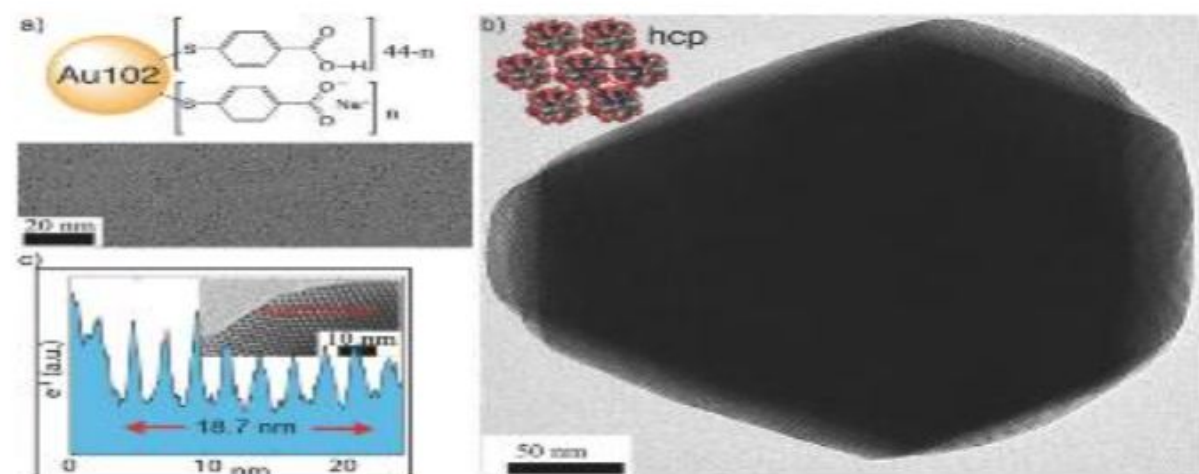
Left: transmission electron microscope image of a CdSe nanocrystal. Centre: Atomic structure of a nanocrystal. Right: Electronic states in a core-shell quantum dot, with the dot itself in the centre bracketed by a wide-bandgap shell.

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

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

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

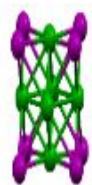
Nanoclusters in colloidal assemblies



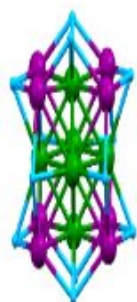
Som, A. et al., *Adv. Mater.* **2016**, 28, 2827–2833

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

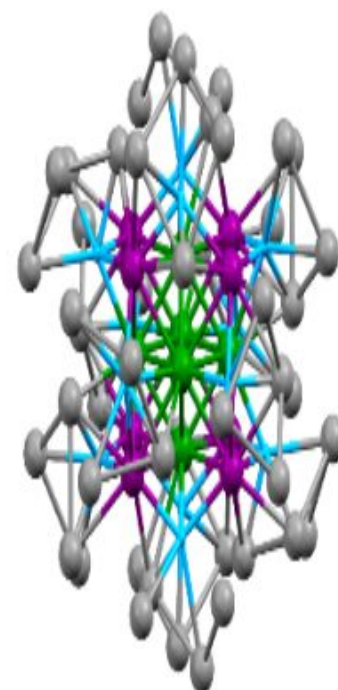
Structural anatomy of [Ag₆₂S₁₂(CBT)₃₂] Nanocluster



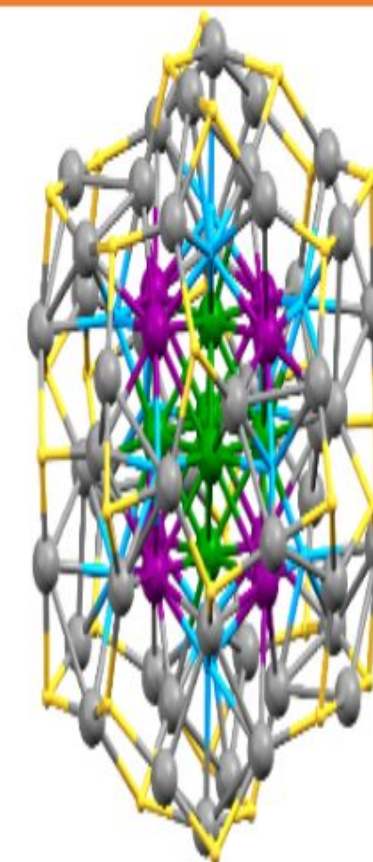
Ag₆@Ag₈



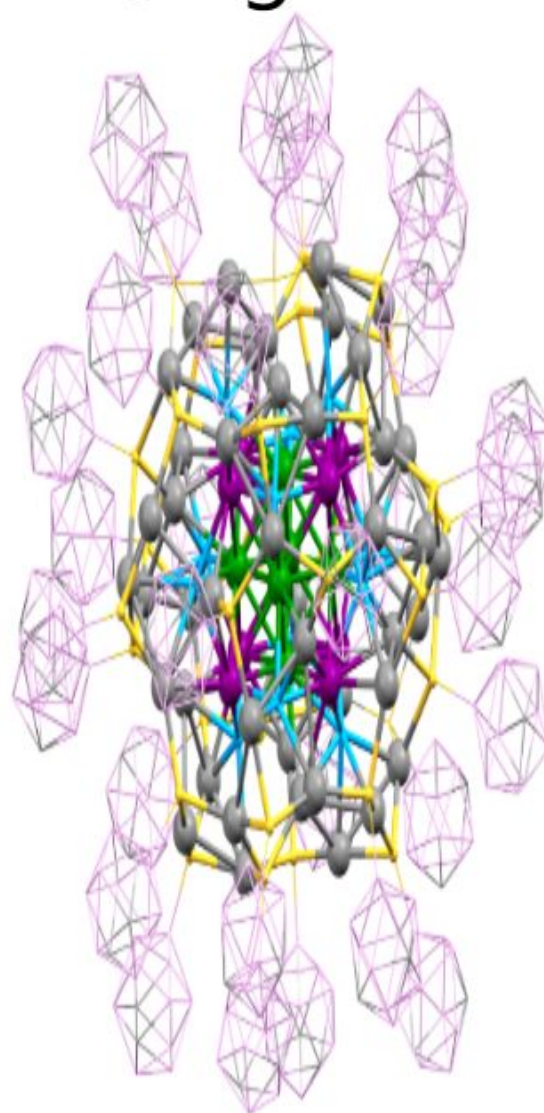
Ag₆@Ag₈S₁₂



Ag₆@Ag₈S₁₂@Ag₄₈



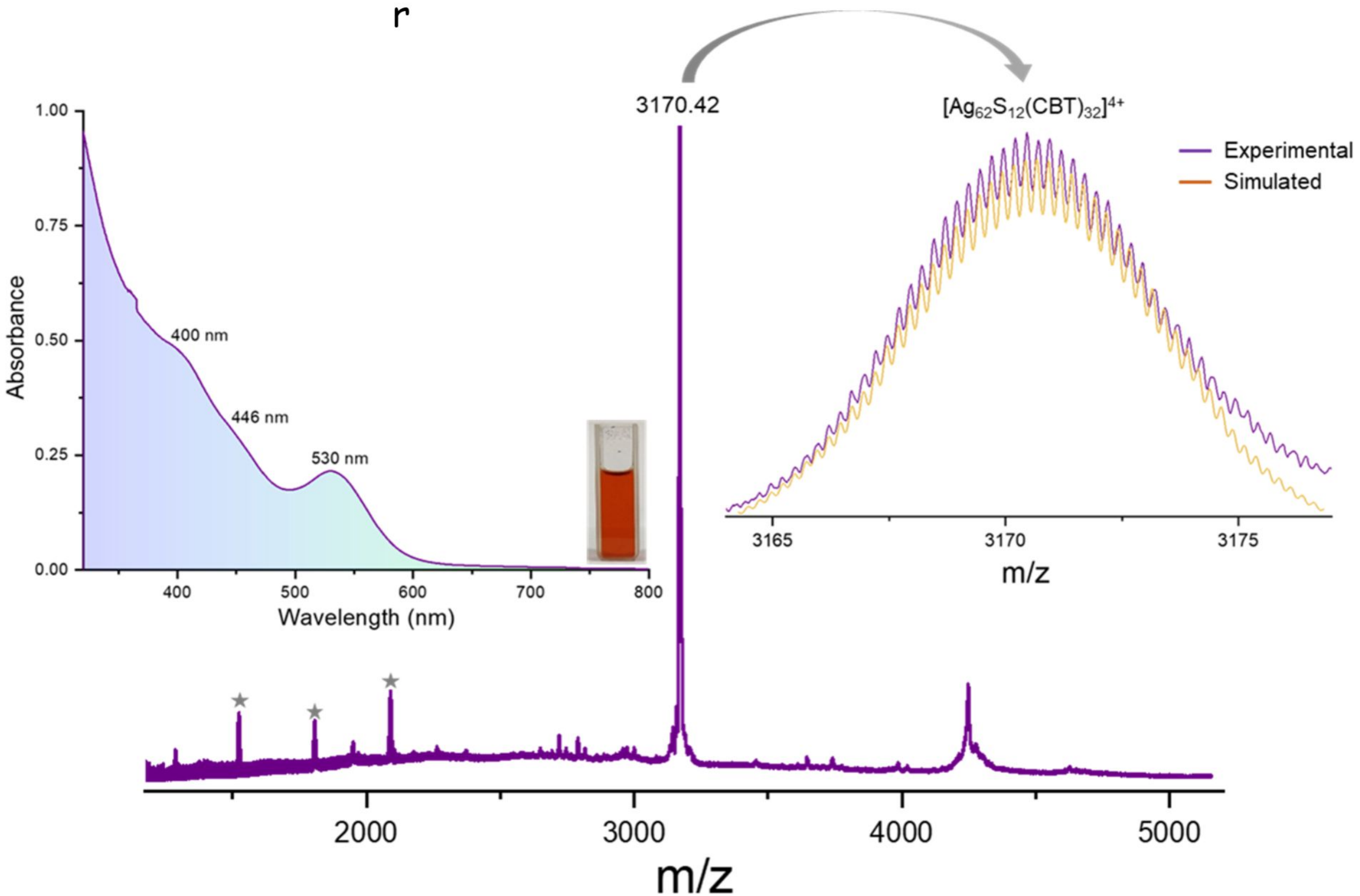
Ag₆@Ag₈S₁₂@Ag₄₈S₃₂



Ag₆@Ag₈S₁₂@Ag₄₈S₃

Characterization of Ag₆₂ cluster

r



Gas phase