



Since 1959

Nanoparticles with atomic precision

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InnoNano Research Pvt. Ltd.
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VayuJAL Technologies Pvt. Ltd.
Aqueasy Innovations Pvt. Ltd.
Hydromaterials Pvt. Ltd.

Professor-in-charge



International Centre for Clean Water



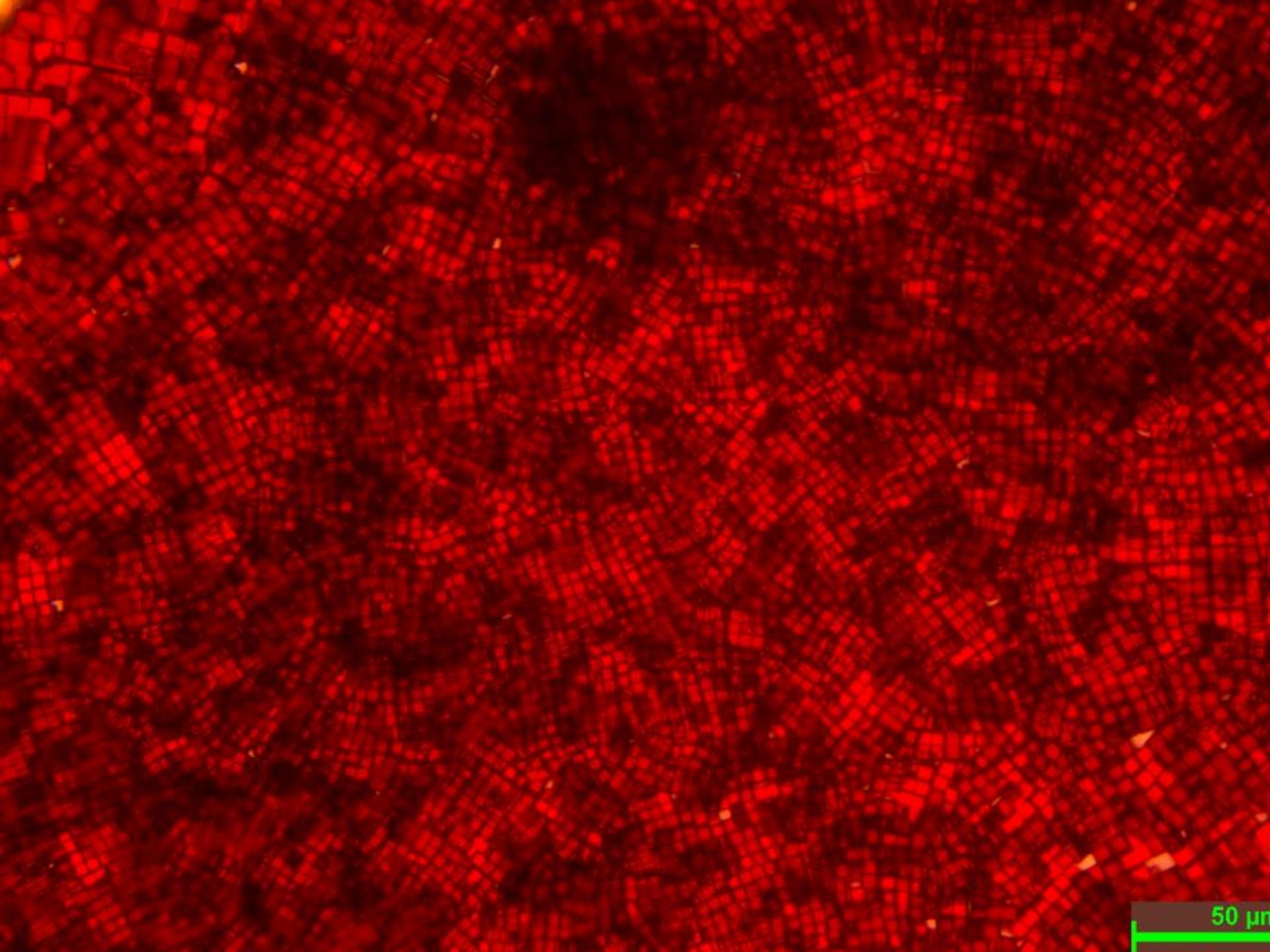
international conference on advances in chemistry with specific reference to catalysis, sensors, drug delivery and energy materials (icacsem – 2020), University of Madras, january 9-10, 2020

AU25PET18_RES_NEG_MS_3 32 (0.558) Cm (5:80)

TOF MS ES-
3.24e6

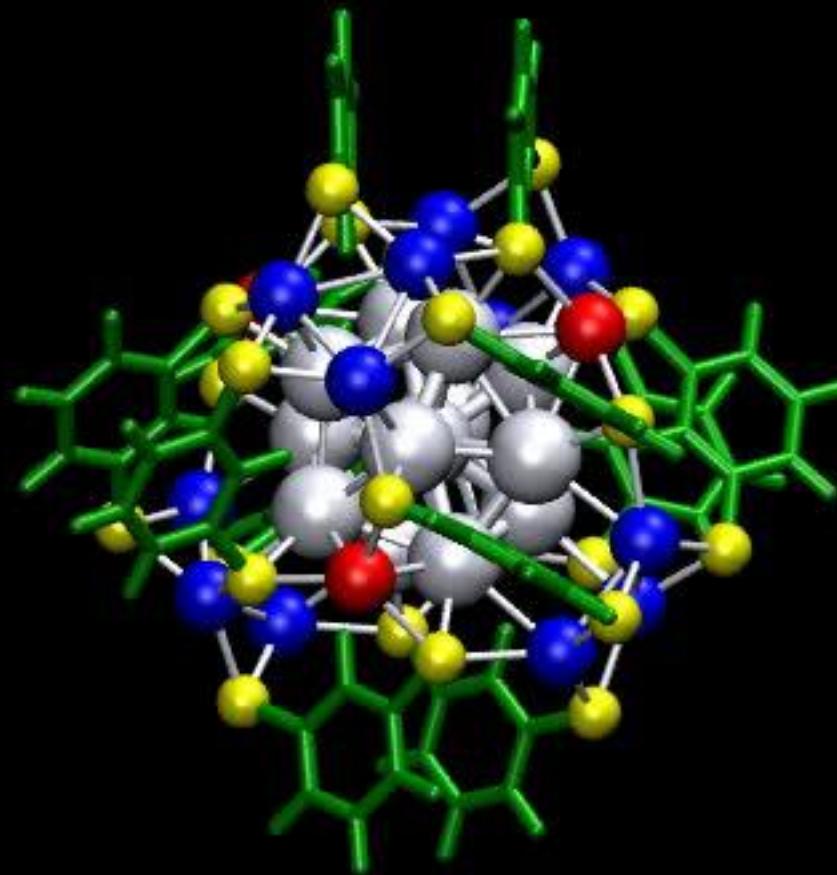
Au₂₅L₁₈



A micrograph showing a dense, red, textured surface, likely a biological tissue or a synthetic material. The texture consists of small, roughly square, red elements of varying sizes, creating a mottled appearance. A prominent, darker, elongated feature runs diagonally across the center of the image. In the bottom right corner, there is a scale bar consisting of a green horizontal line with a black rectangle at its end. The text "50 μm" is written in white within this scale bar.

50 μ m

Clusters



Science of nanomaterials has advanced tremendously in the recent past.

2019

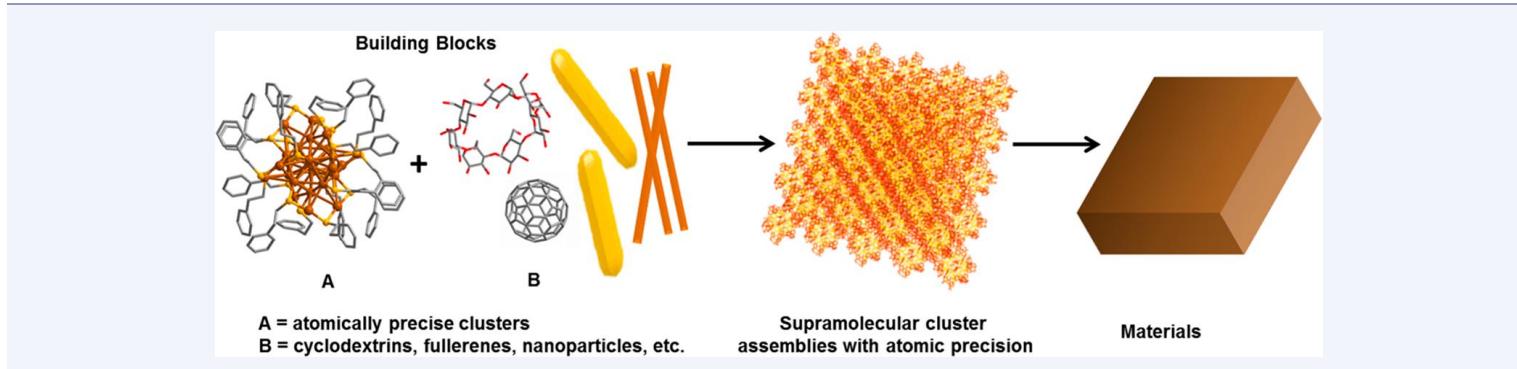
¹ Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

²

⁴ Papri Chakraborty, Abhijit Nag, Amrita Chakraborty, and Thalappil Pradeep*⁵

⁵ DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of

⁶ Technology Madras, Chennai 600 036, India



Contents

The subject area of clusters

New science in synthesis, properties - functionalisation

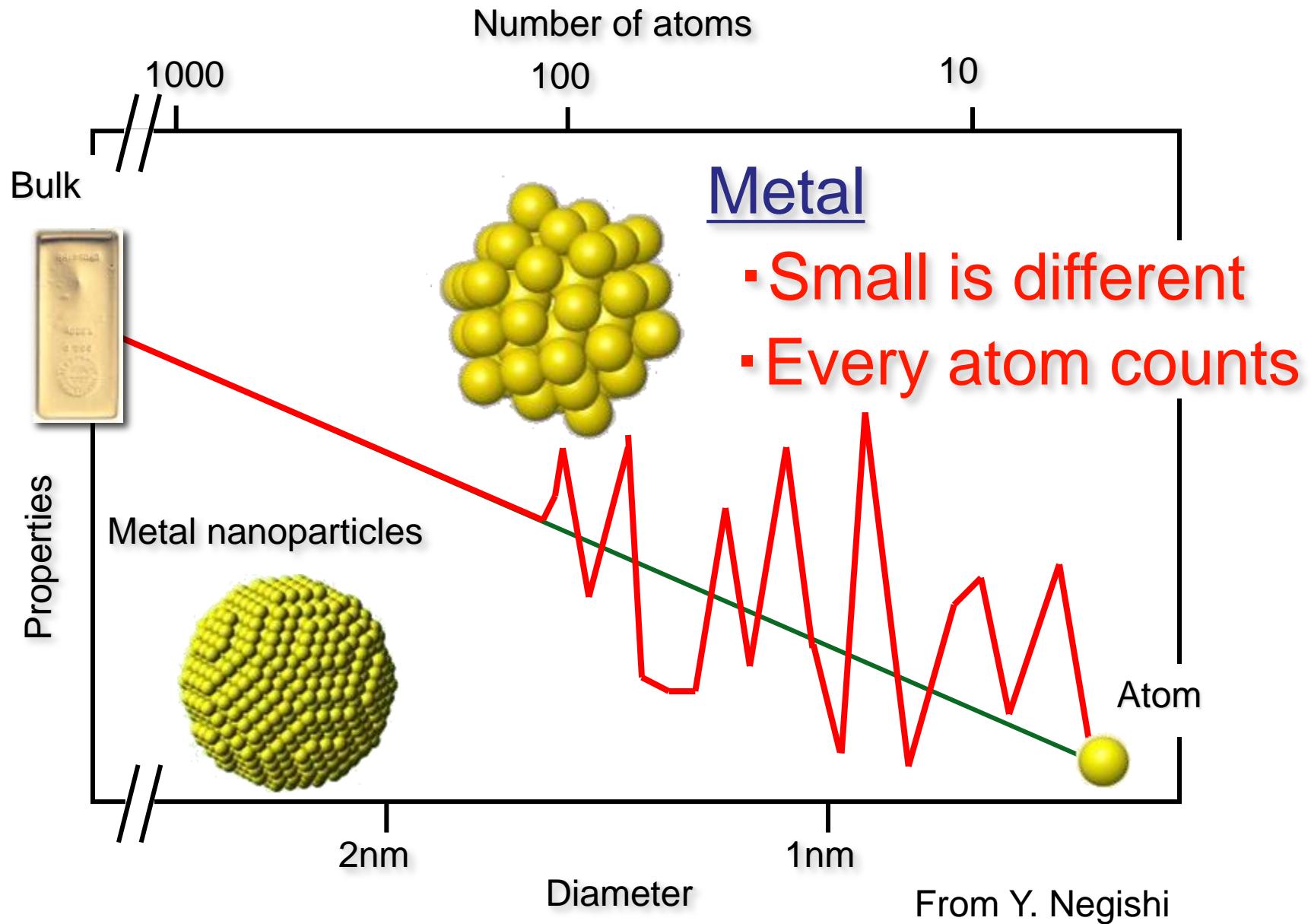
Reactions between clusters

Borromean structures of clusters

Supramolecular science of clusters

Applications

Future directions



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

Indranath Chakraborty[†]  and Thalappil Pradeep^{*} 

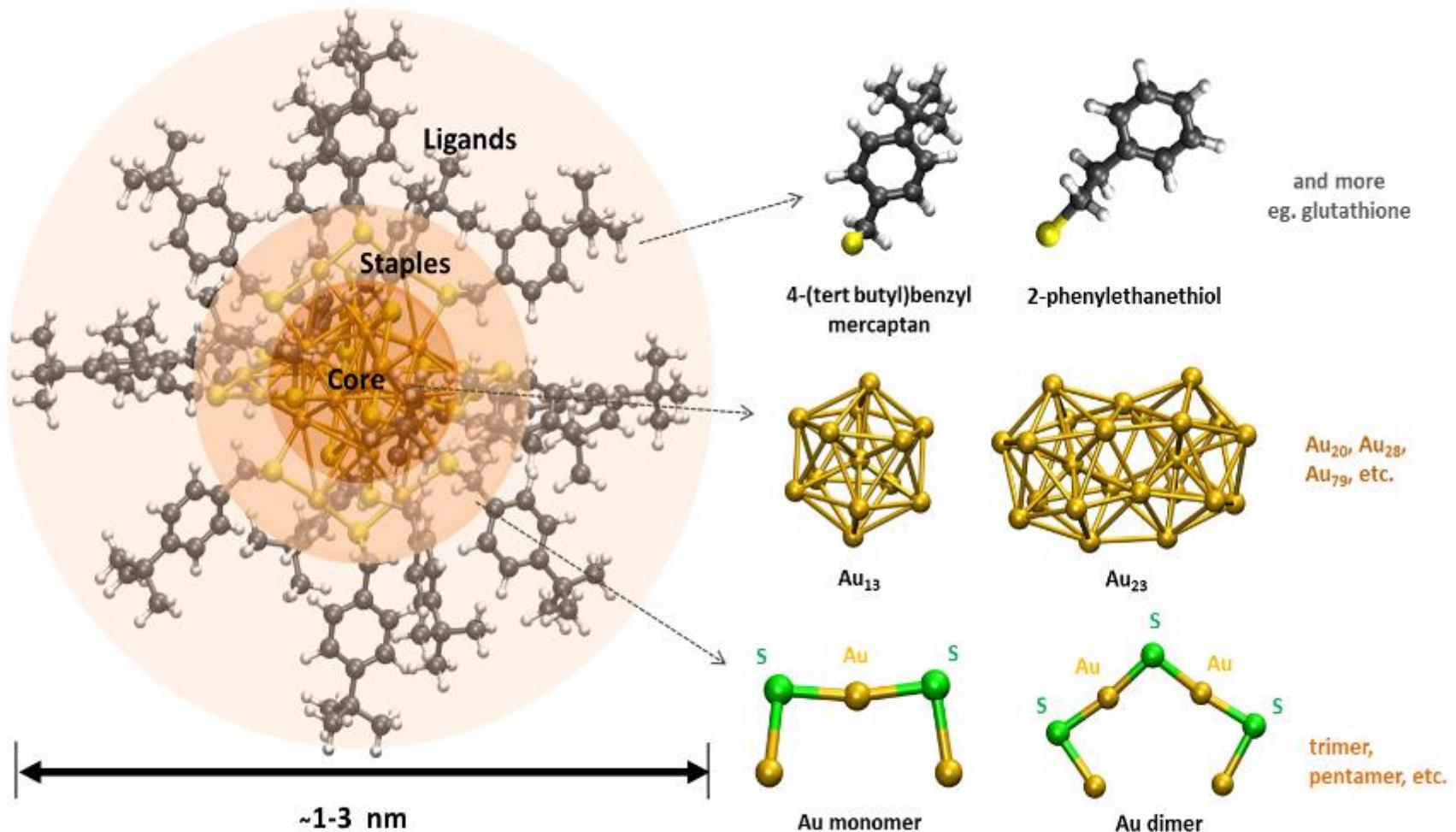
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

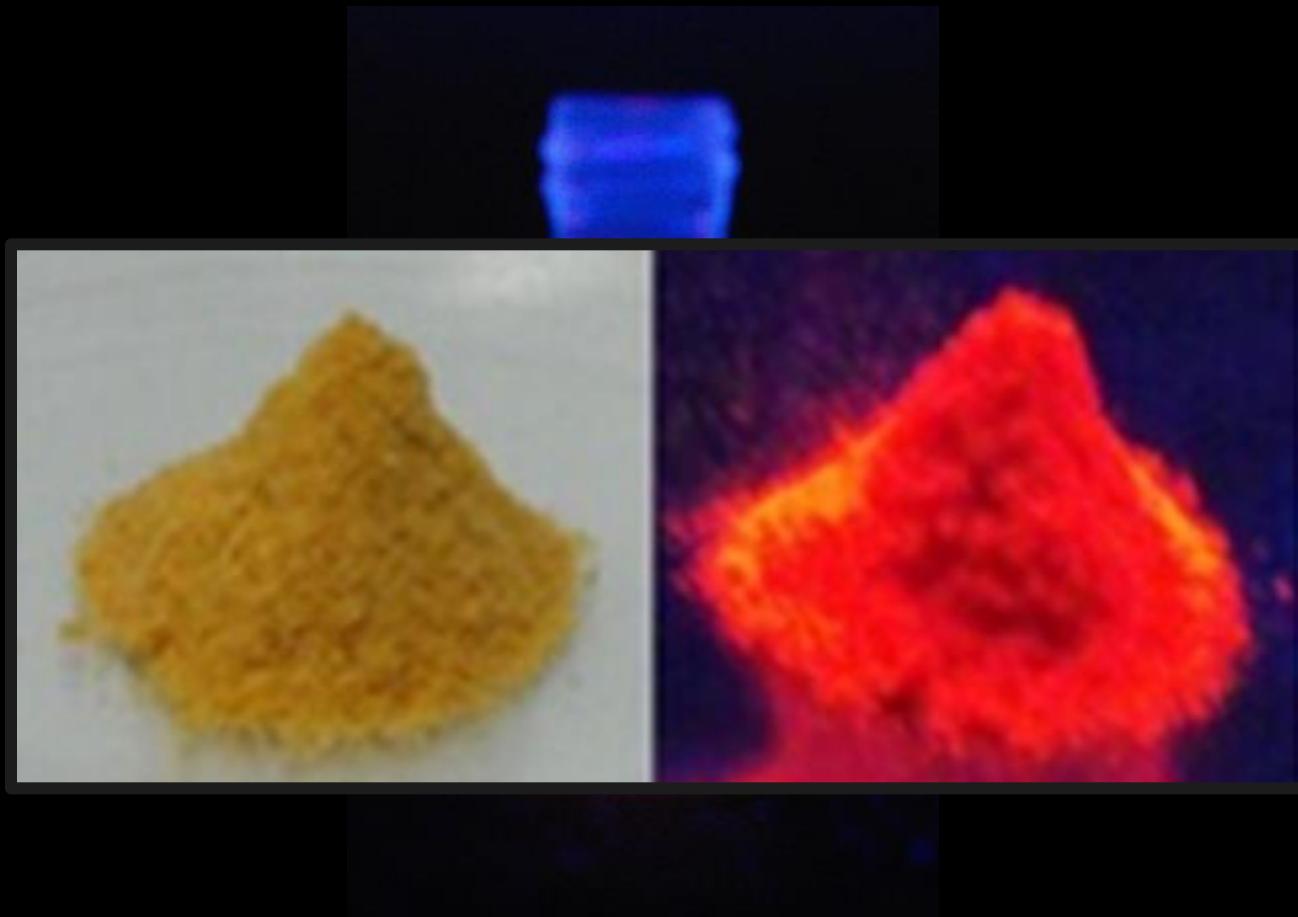
 Supporting Information

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 $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$, 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.

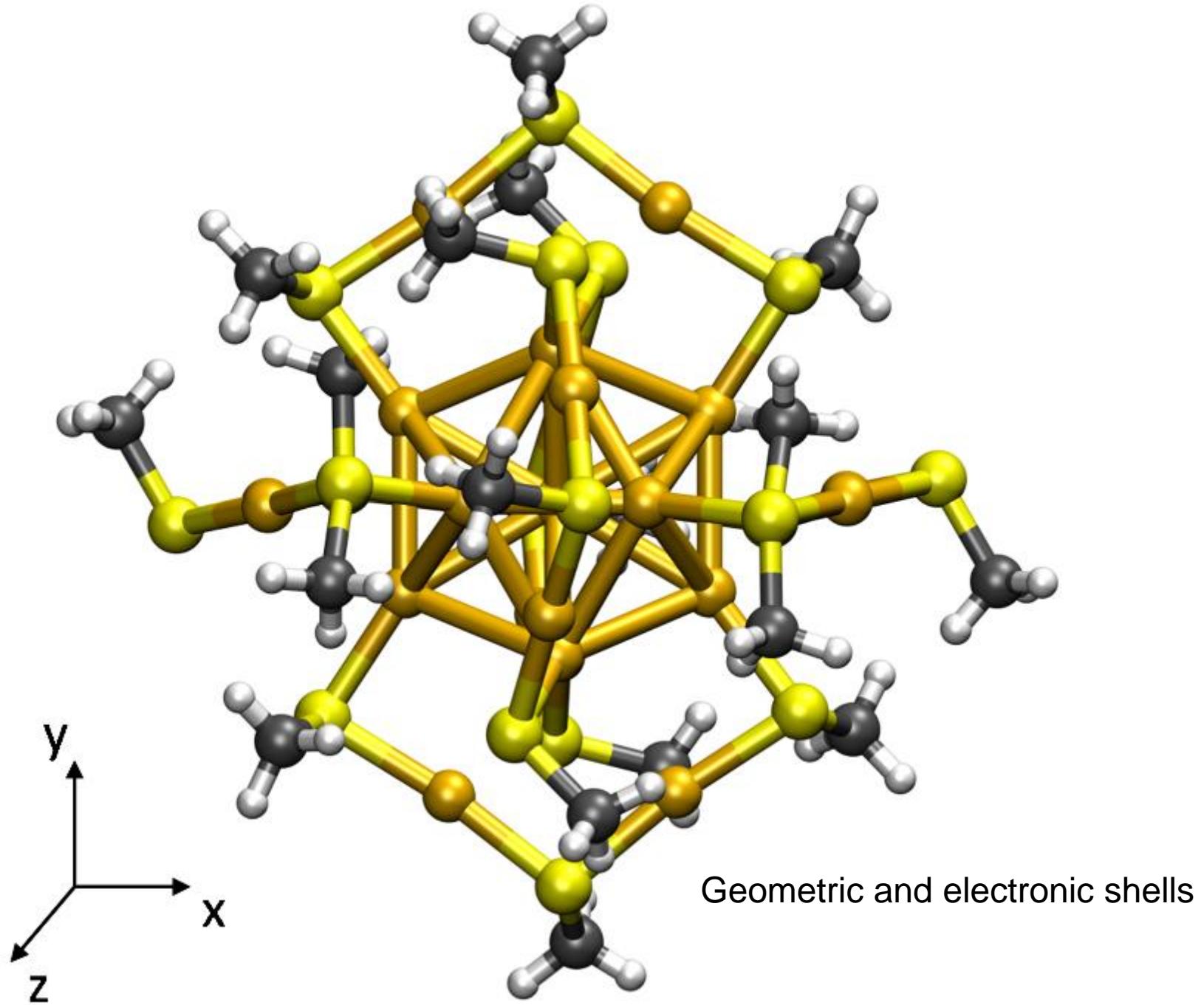


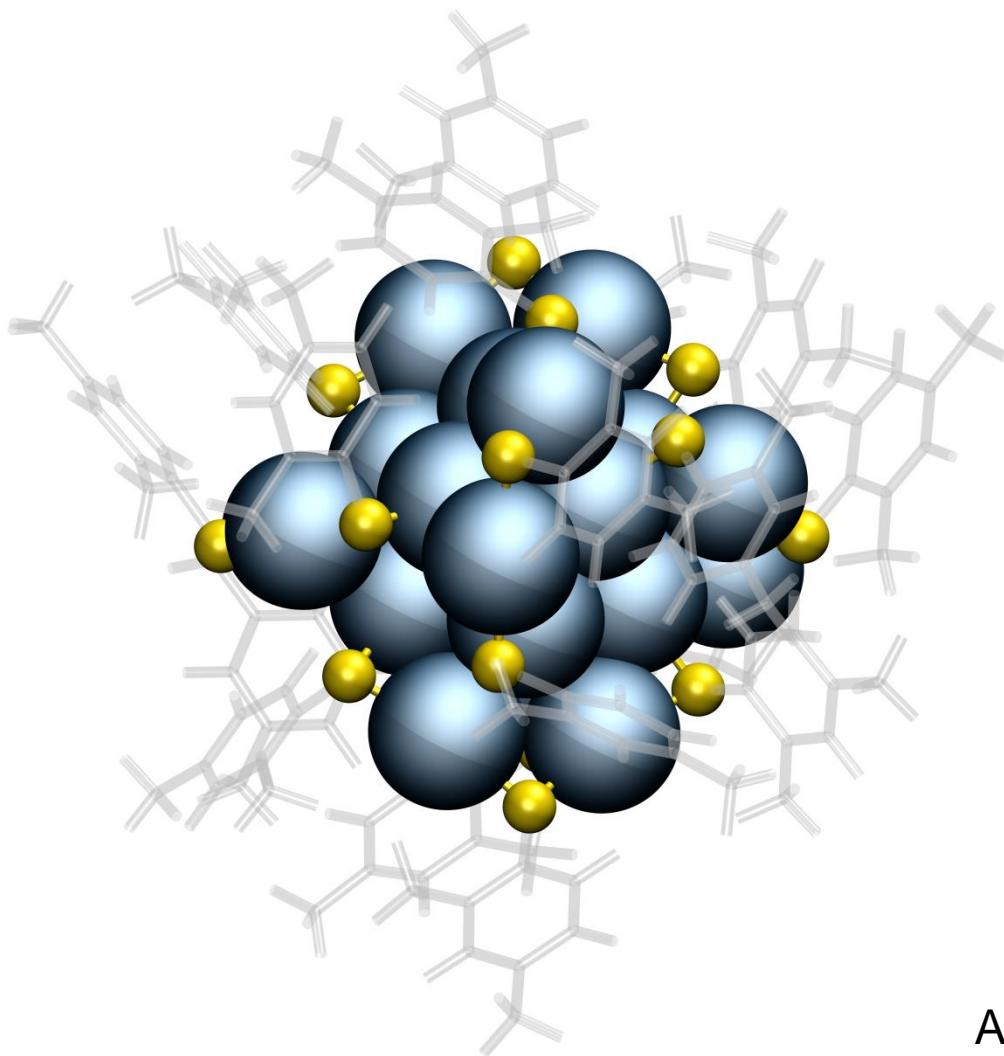
Also the pioneering work of R. W. Murray, Robert L. Whetten, Uzi Landman, Tatuya Tsukuda, Yuichi Negishi, Hannu Hakkinen, R. Jin, Nanfeng Zheng, Terry Bigioni, Osman Bakr, Kornberg, Jianping Xie, C. M. Aikens, Thomas Buergi, Amala Dass, A. W. Castleman Jr., H. Schmidbauer, ...



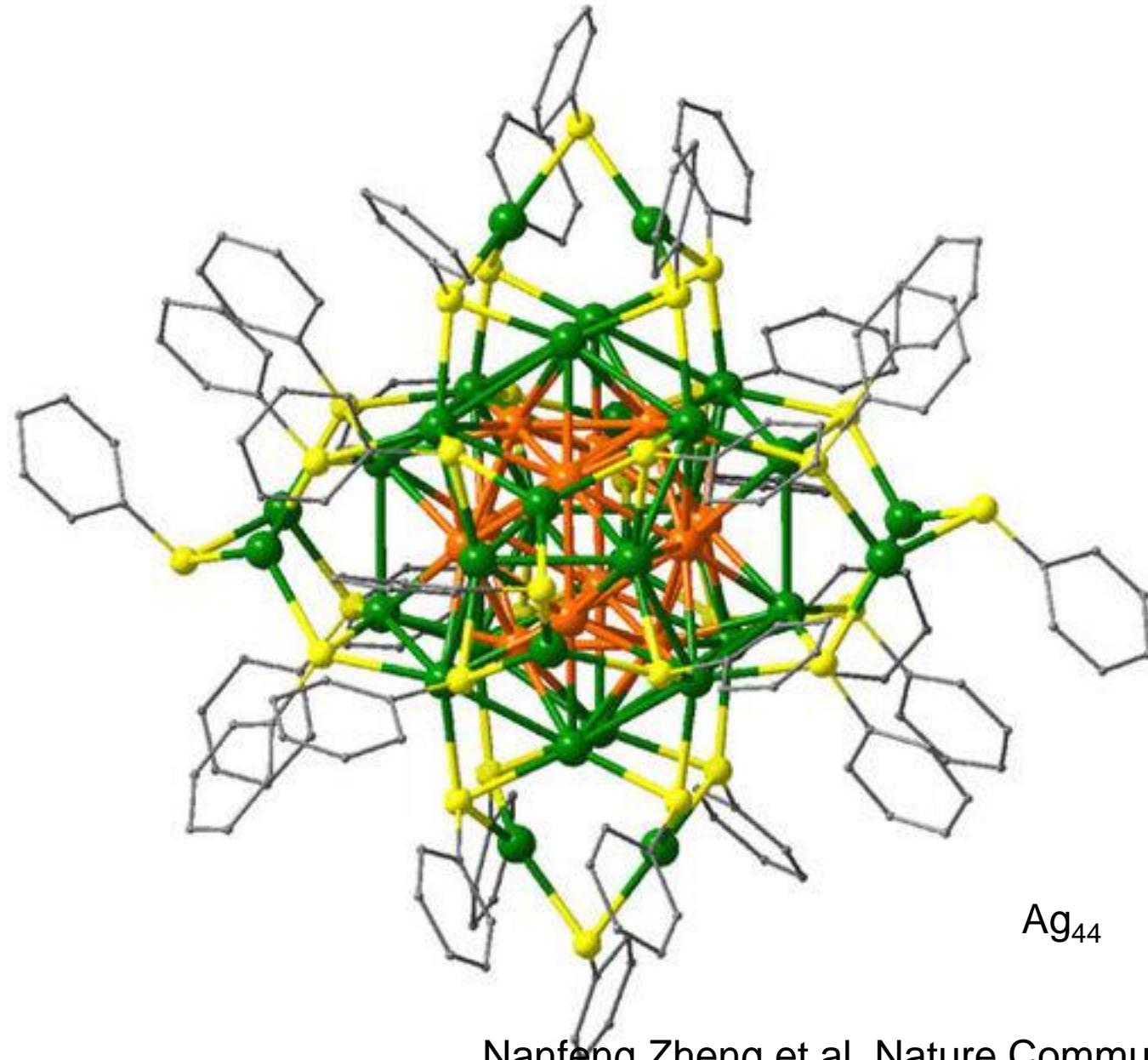


Shibhu, Habeeb, Uday, Kamalesh, Lourdu, Ammu, Ananya, Indranath, Atanu, Krishnadas, Shridevi, Manju, Papri, Esma, Debasmita, Abhijit, Amrita, Jyoti, Sugi, Bodi, Paulami, Jayoti,Gana Natarajan, P. Ganesn, Karteeek, ...



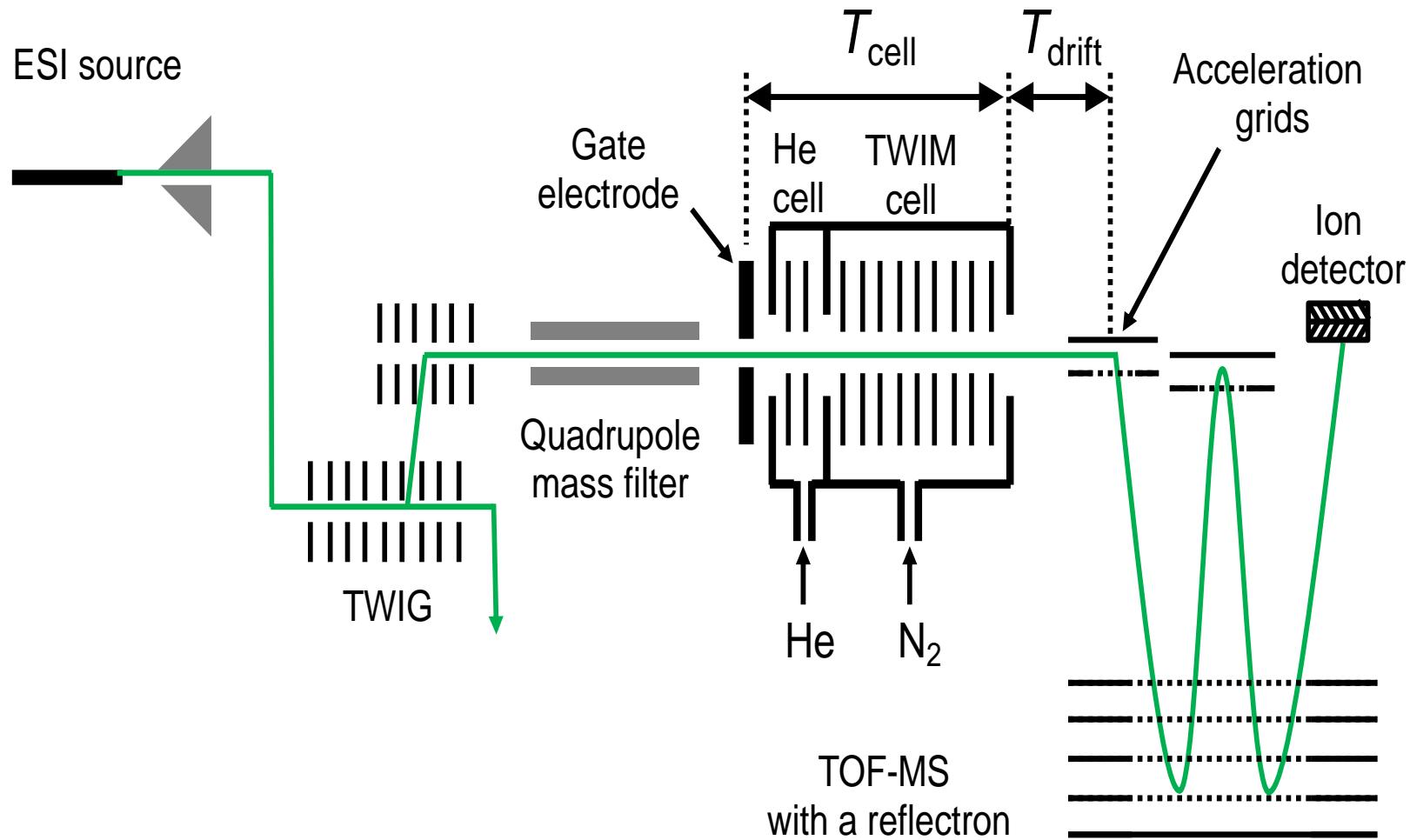


$\text{Au}_{25}, \text{Ag}_{25}$

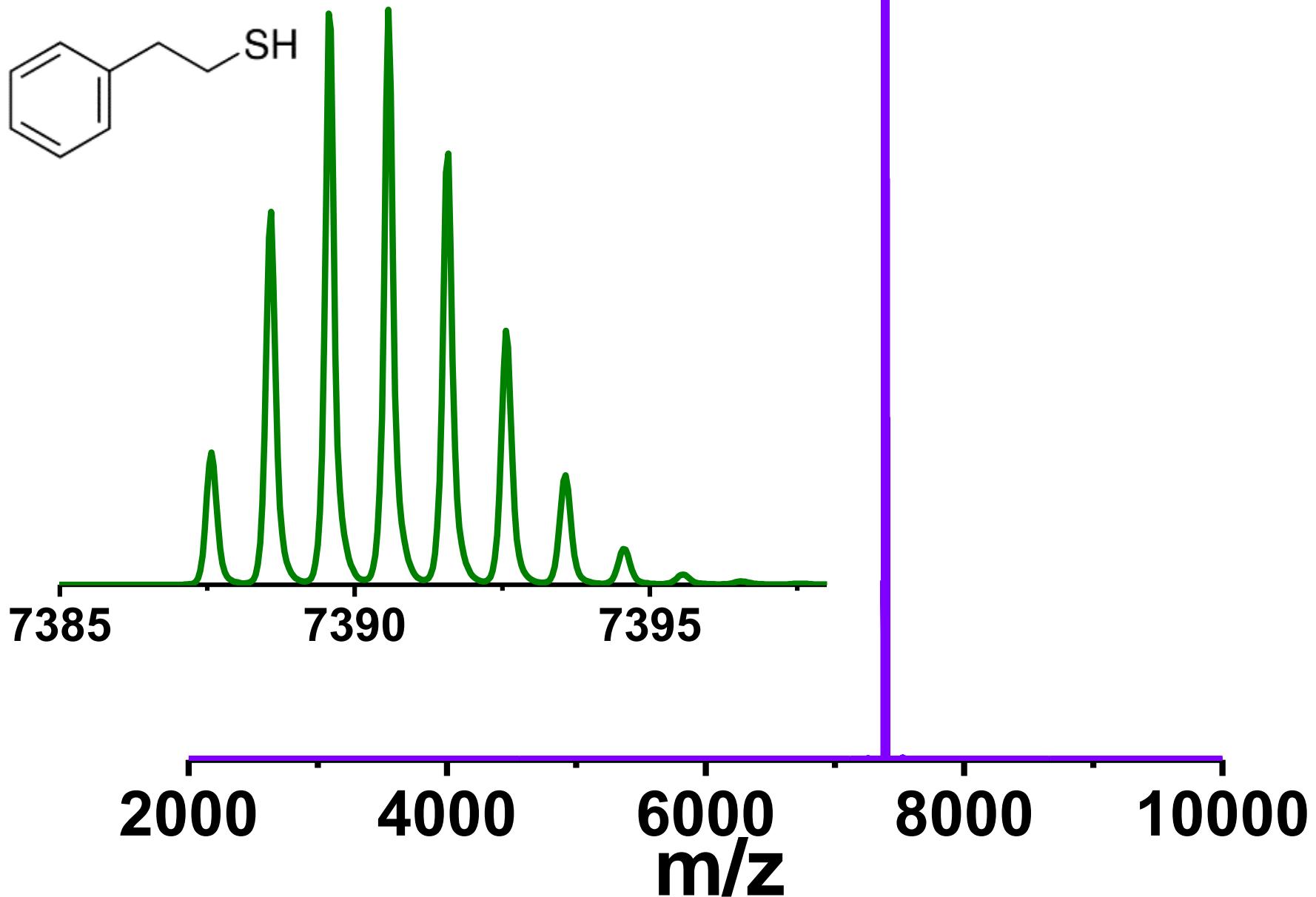
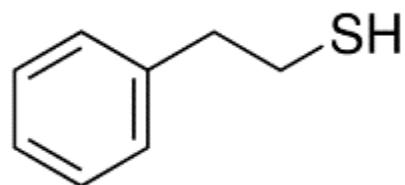


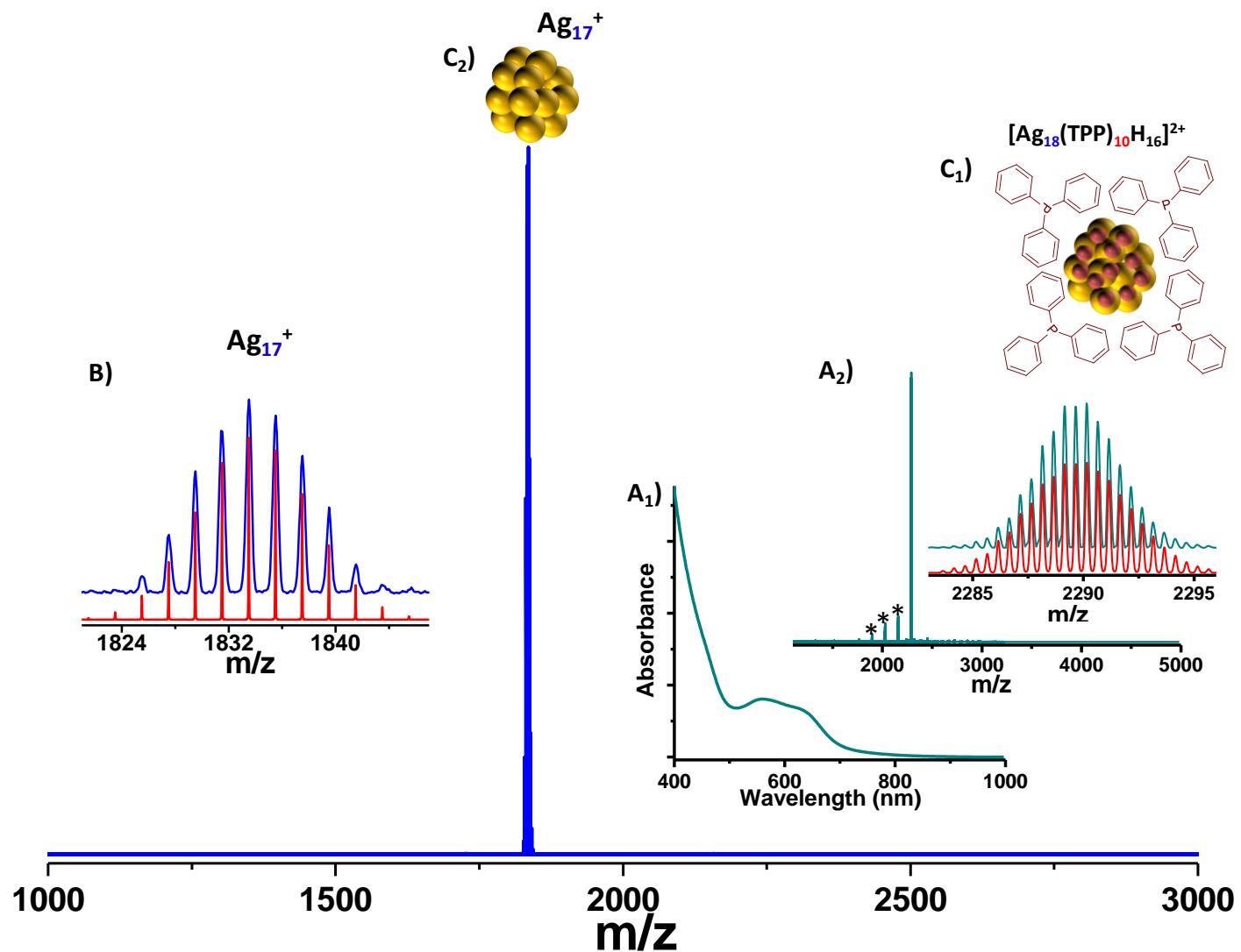
Nanfeng Zheng et al. Nature Communications, 2013
Terry Bigioni et al. Nature 2013

Au₂₅PET₁₈

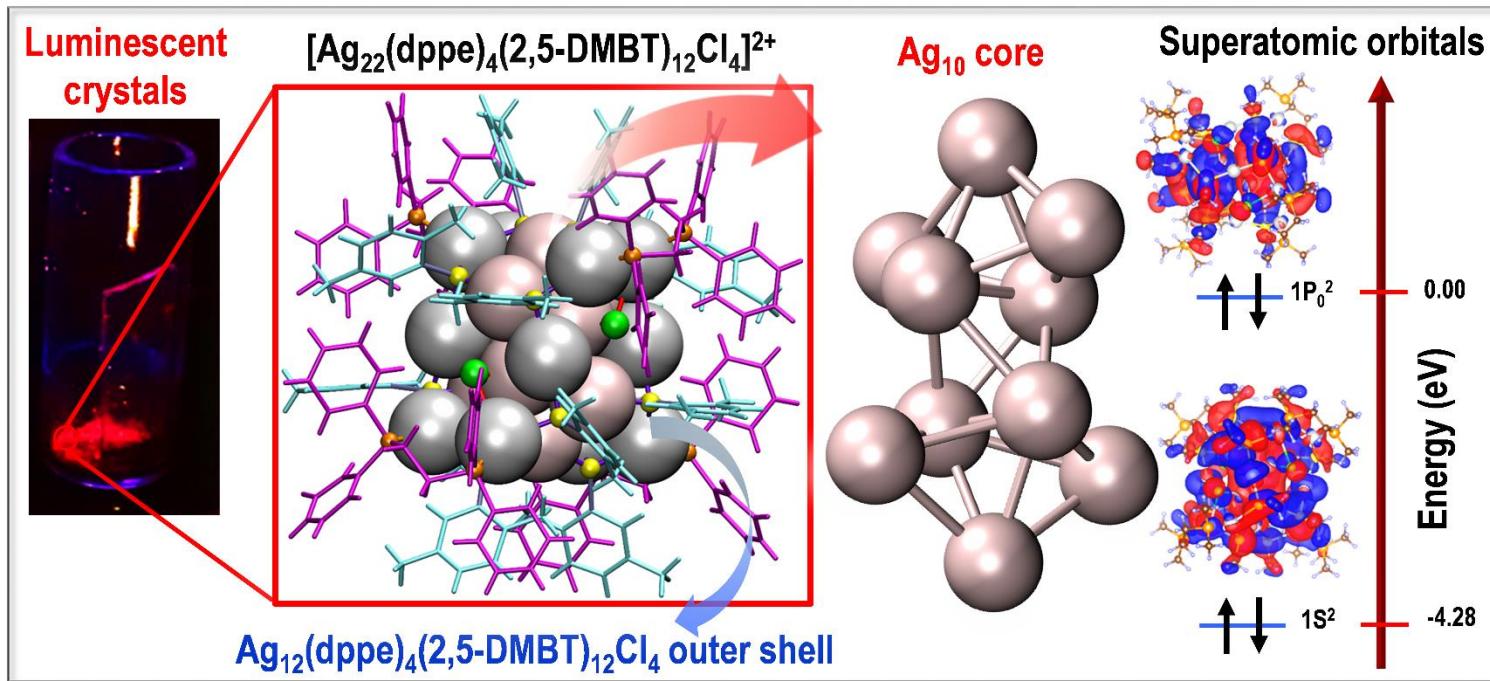


$\text{Au}_{25}(\text{PET})_{18}^-$

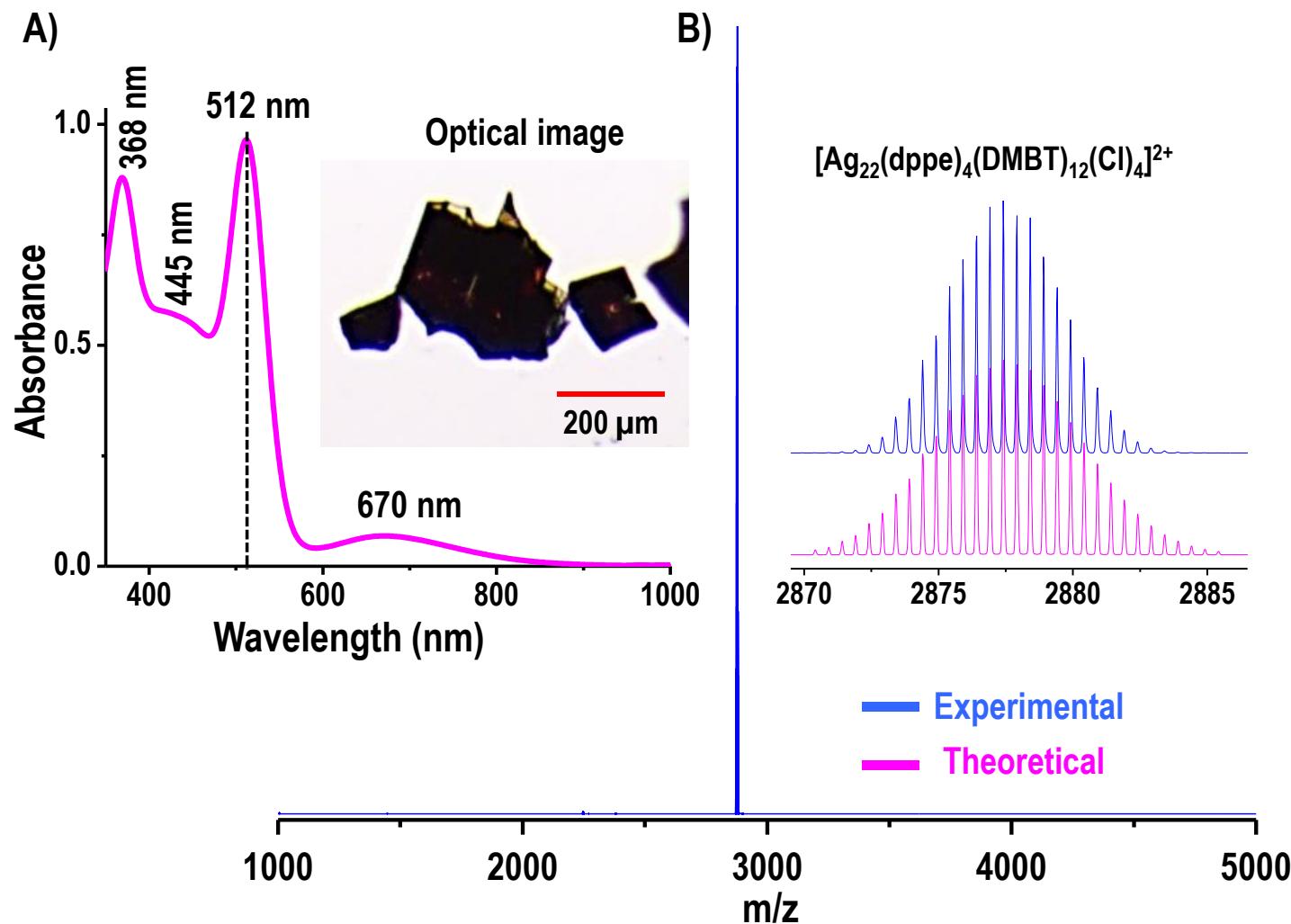




Ag_{10} Core in an Ag_{12} Shell: A Four-Electron Superatom



Esma Khatun, et. al., ACS Nano, 2019



(A) Optical absorption spectrum of Ag_{22} . Inset: image of single crystals under a microscope. (B) HRESI MS of I which displays a peak at ~ 2876 m/z. Inset: Comparison of the theoretical and the experimental isotopic distributions of Ag_{22} .

Chemistry of clusters



Reactions of 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*

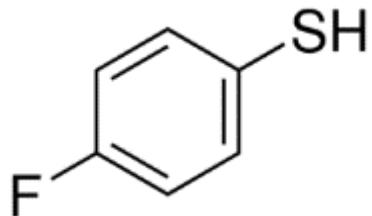
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India

Supporting Information





(A)



$[\text{Au}_{21-x}\text{Ag}_x(\text{FTP})_{14}]^-$
 $x = 3 \ 2 \ 1 \ 0$

$[\text{Au}_{25-x}\text{Ag}_x(\text{FTP})_{18}]^-$
 $x = 5 \ 4 \ 3 \ 2 \ 1 \ 0$

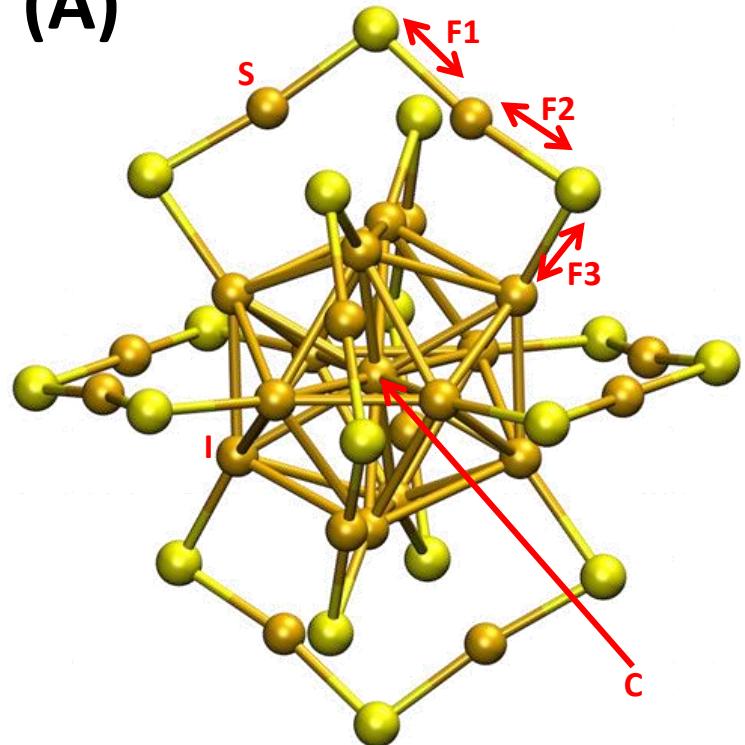
(B)

$[\text{Au}_{25-x}\text{Ag}_x(\text{FTP})_{18}]^-$
13 12 ← 1 0 = x

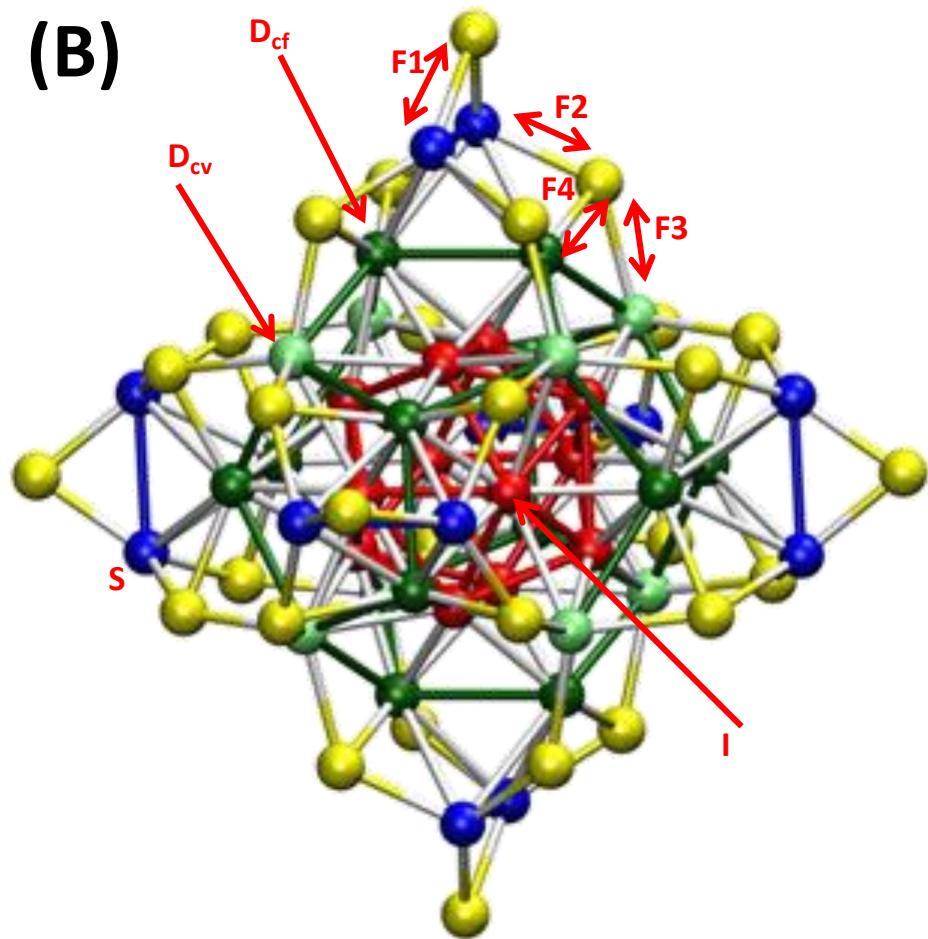
$[\text{Au}_{21-x}\text{Ag}_x(\text{FTP})_{14}]^-$
 $x = 5 \ 4 \ 3 \ 2 \ 1 \ 0$

5250 6000 6750 7500
 m/z

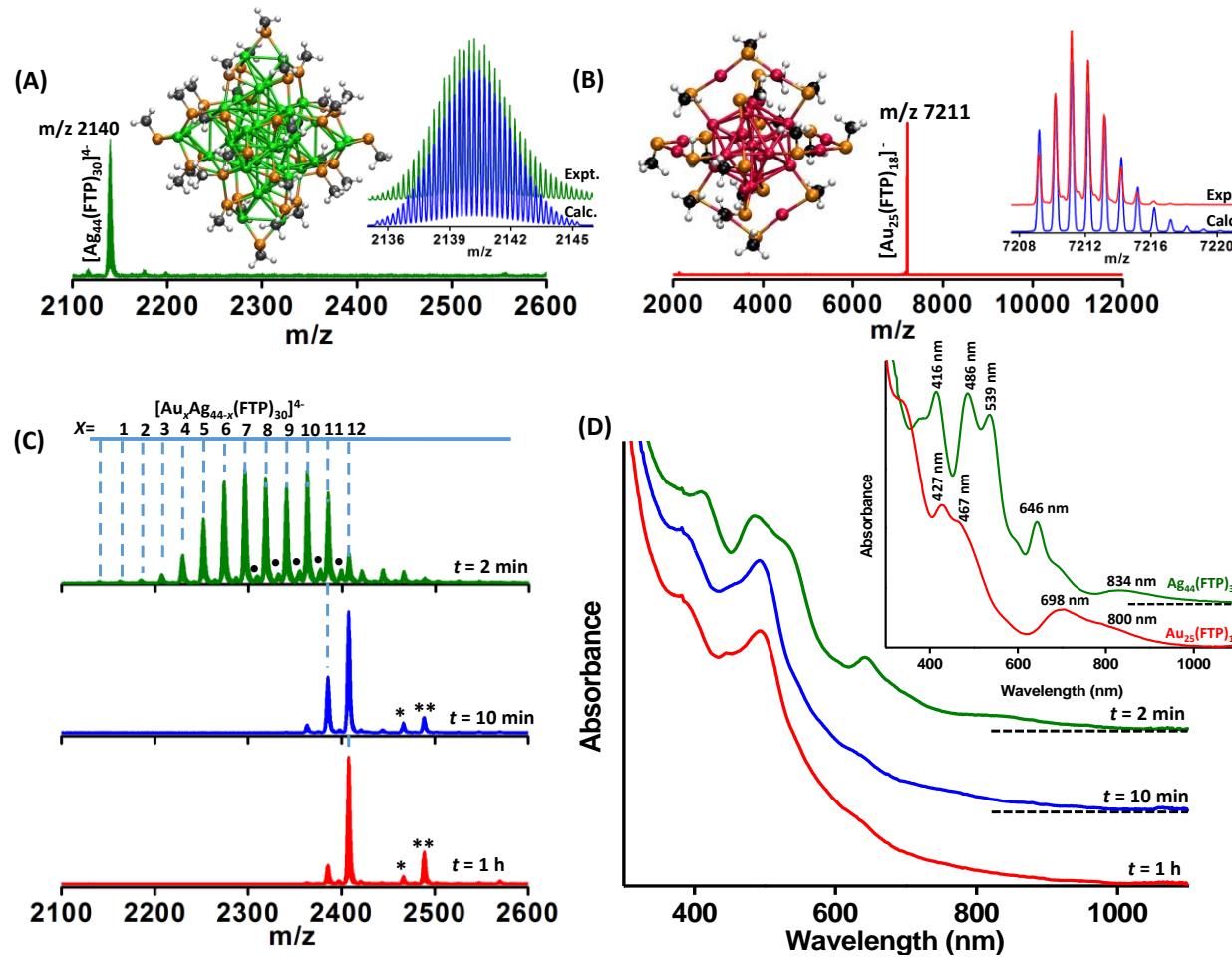
(A)

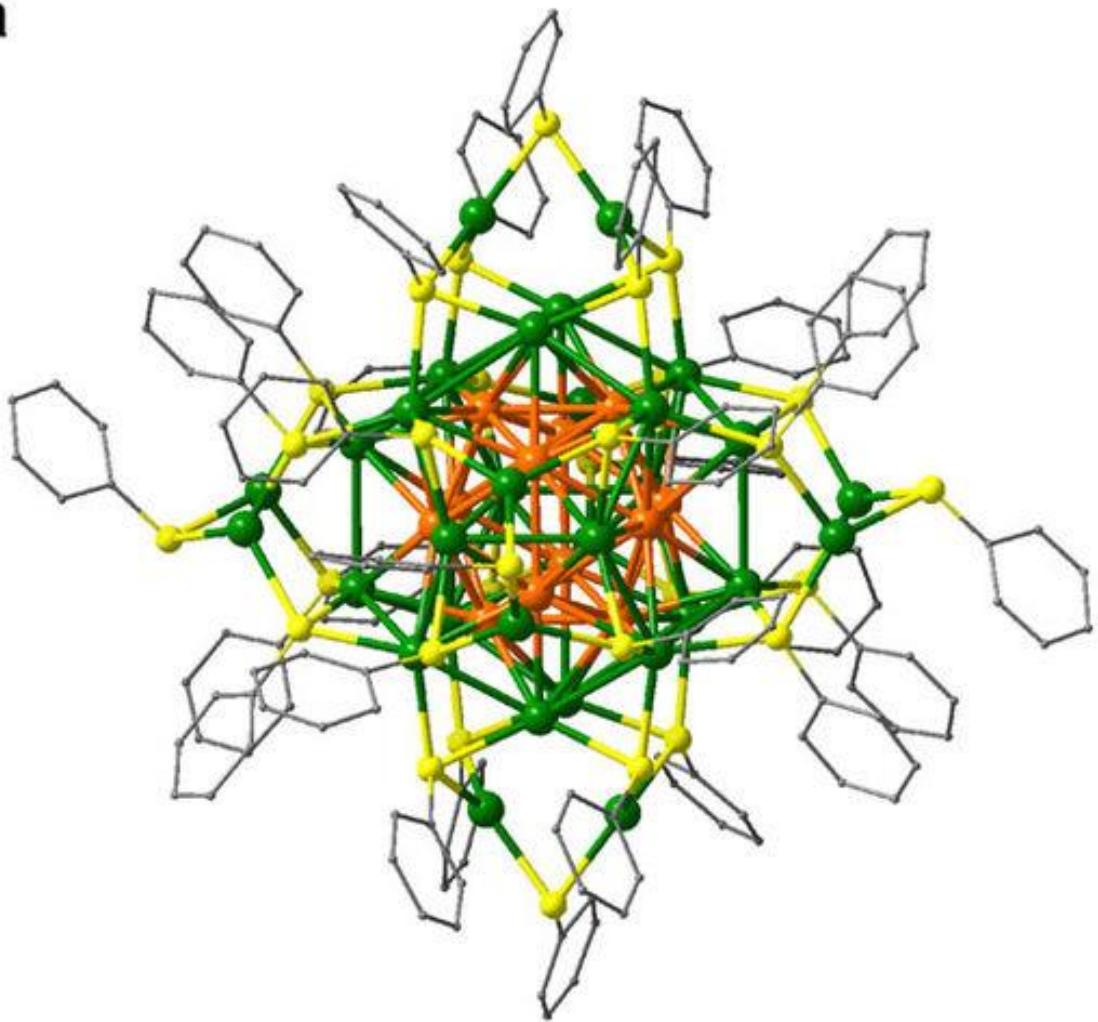
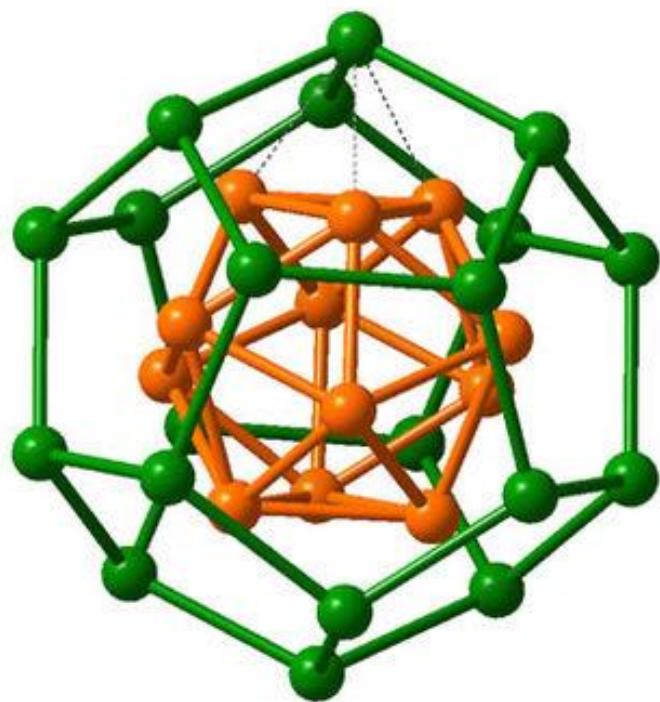


(B)



Shell closure in intercluster reactions

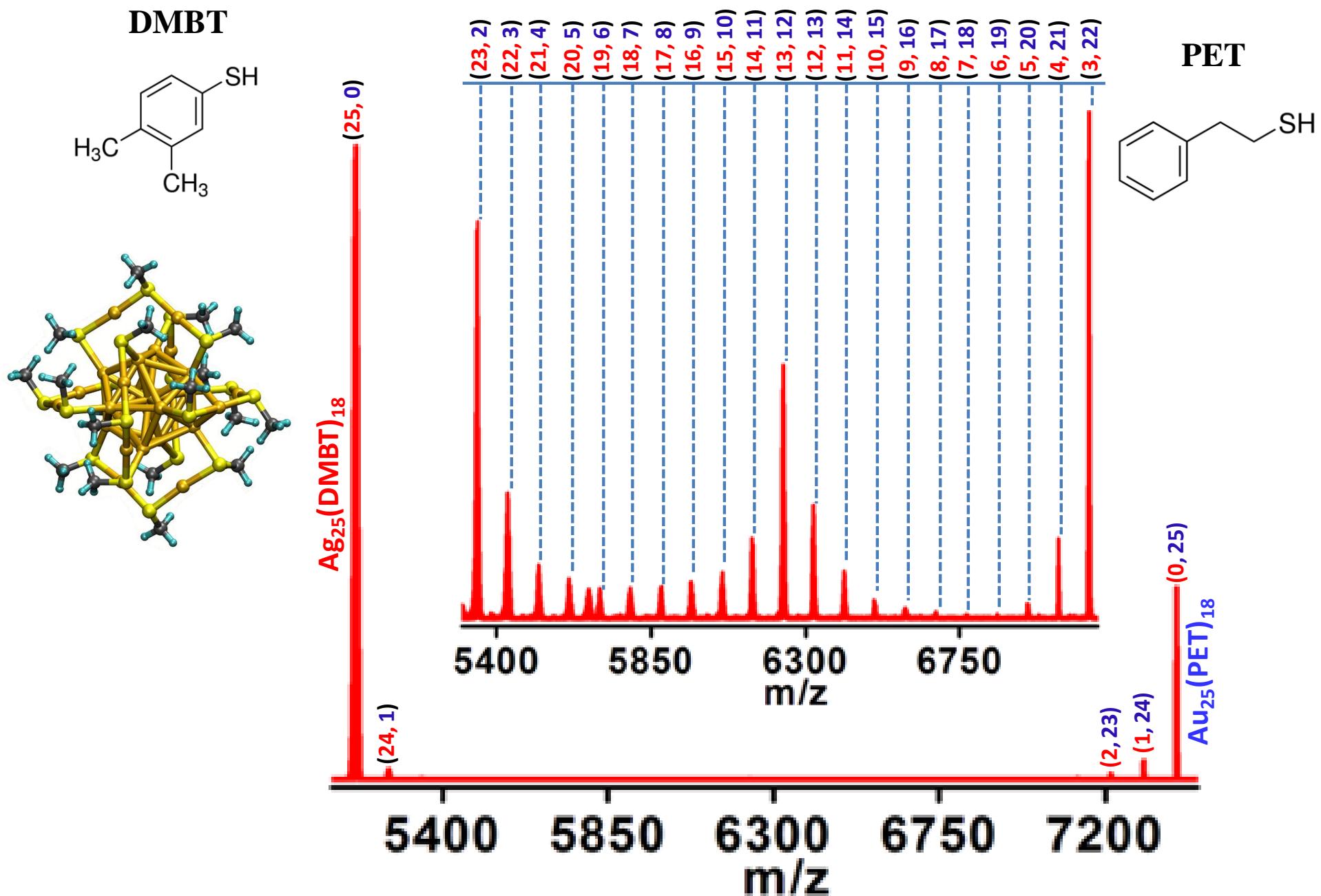


a**b**

Ag₂₅-Au₂₅ experiments

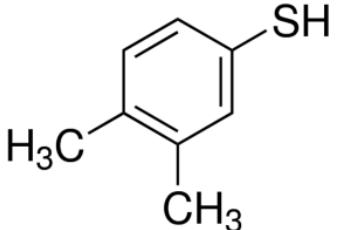
K. R. Krishnadas et al. Nature Commun. 2016

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

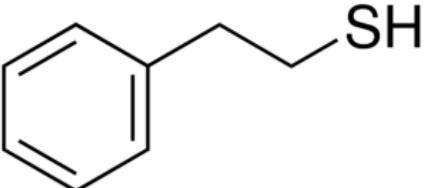


$[\text{Ag}_{25}(\text{DMBT})_{18} + \text{Au}_{25}(\text{PET})_{18}]^{2-}$

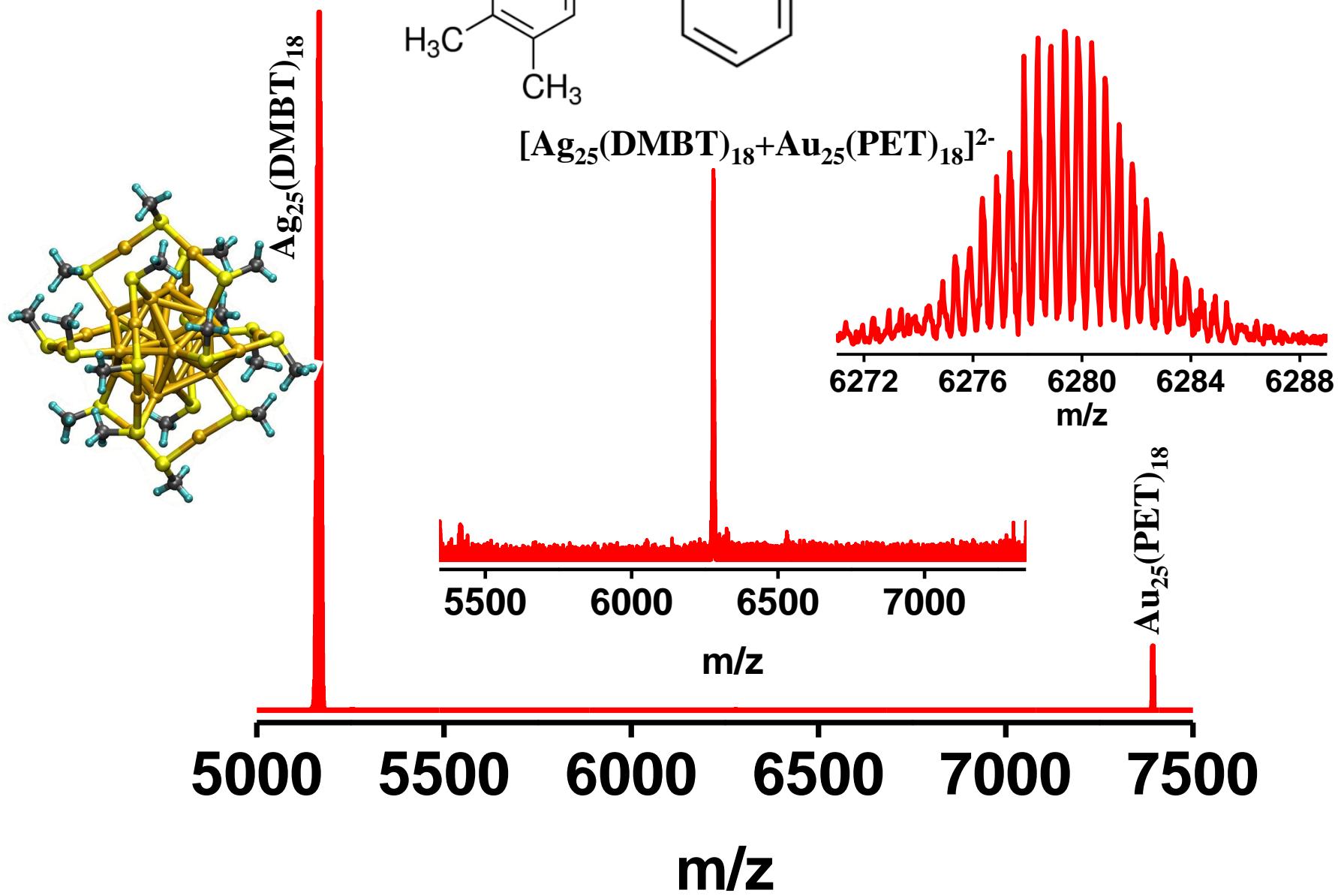
DMBT



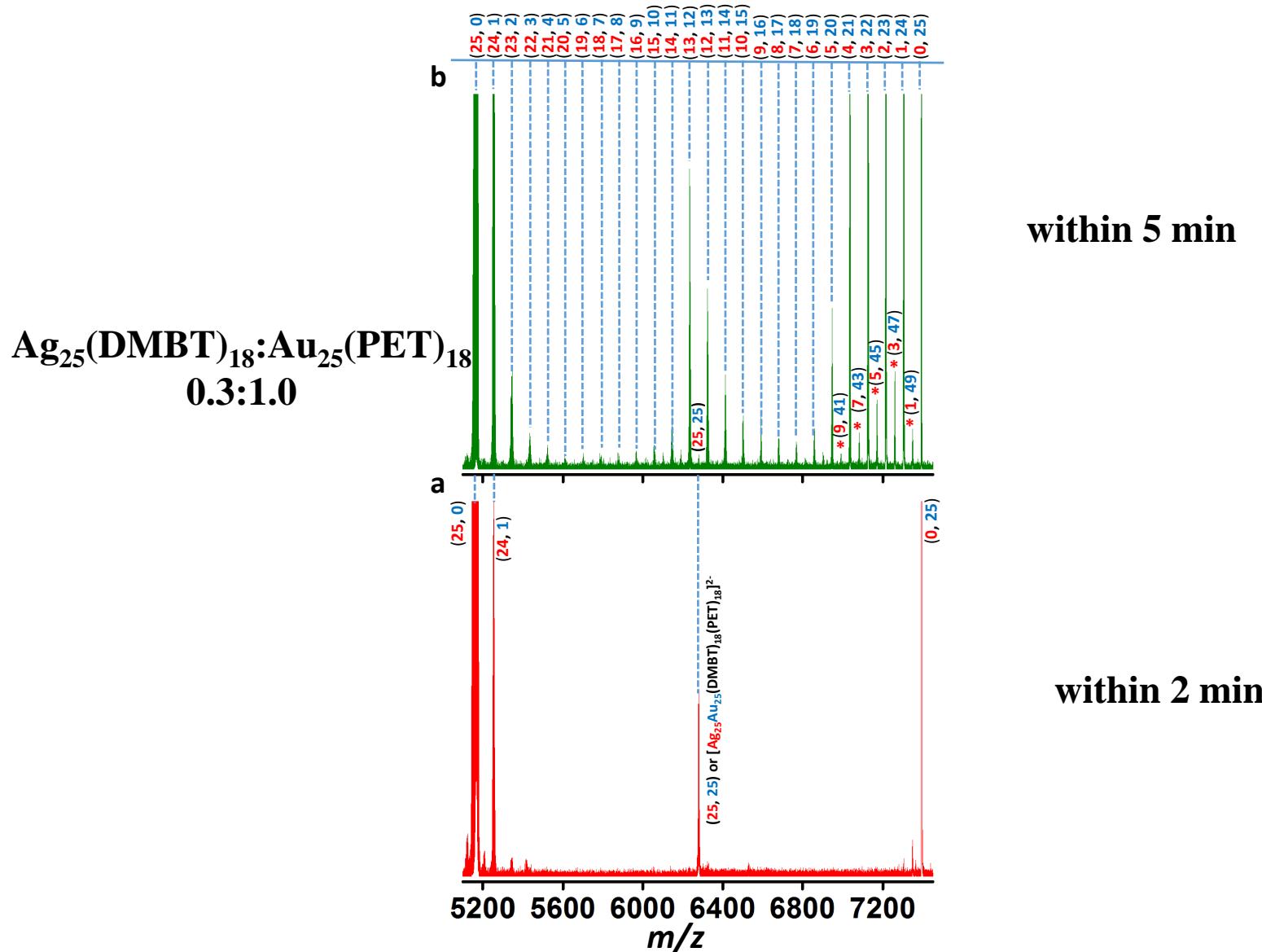
PET



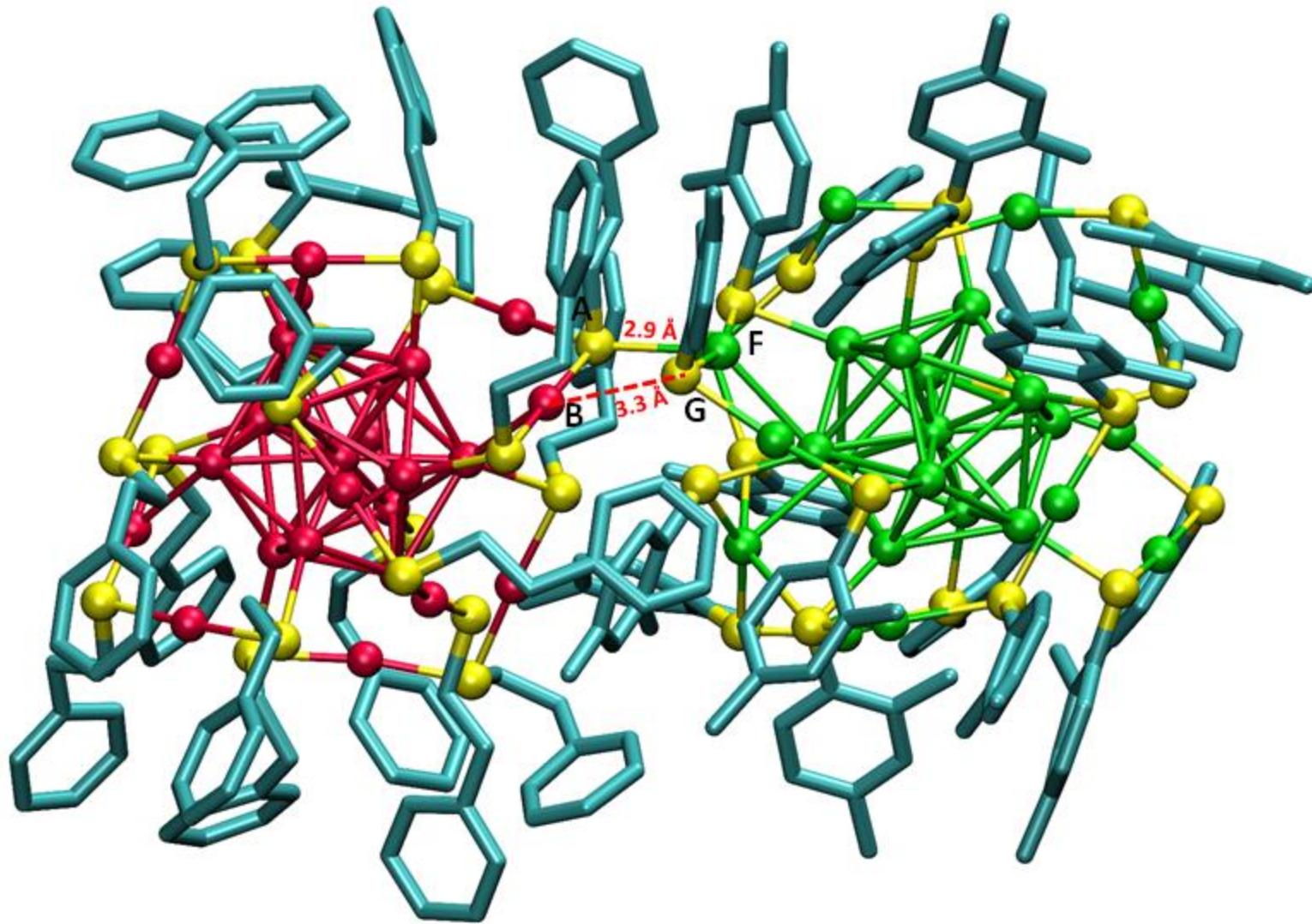
$[\text{Ag}_{25}(\text{DMBT})_{18} + \text{Au}_{25}(\text{PET})_{18}]^{2-}$

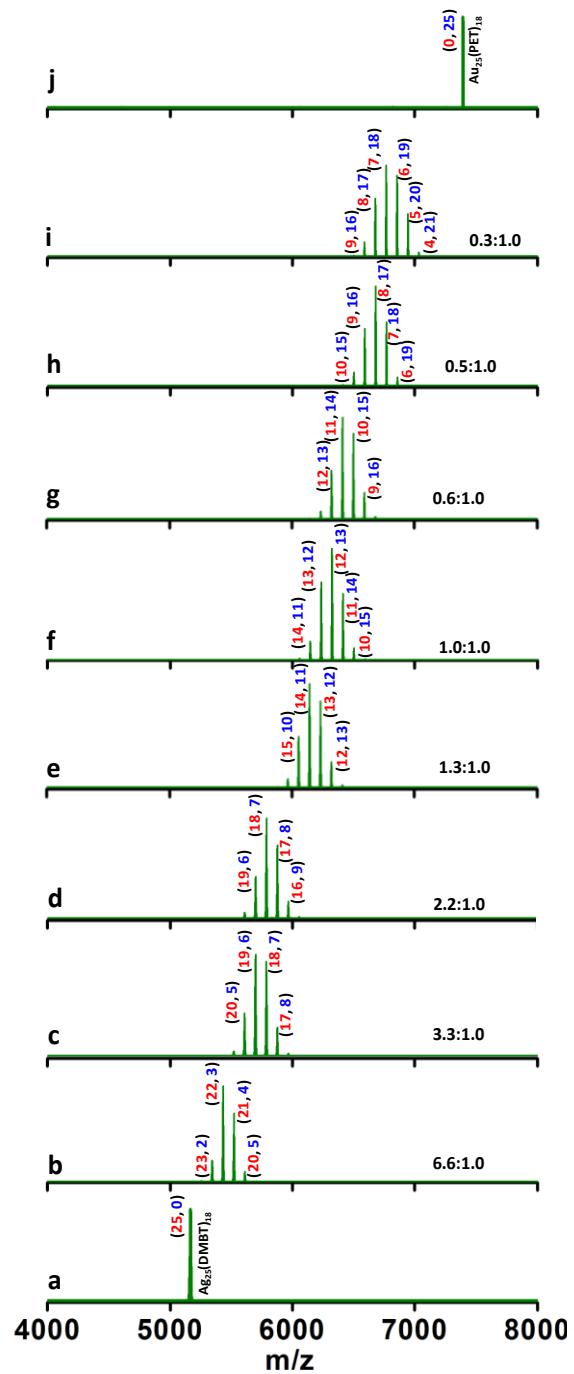


Evolution of alloy clusters from the dianionic adduct, [Ag₂₅Au₂₅(DMBT)₁₈(PET)₁₈]²⁻



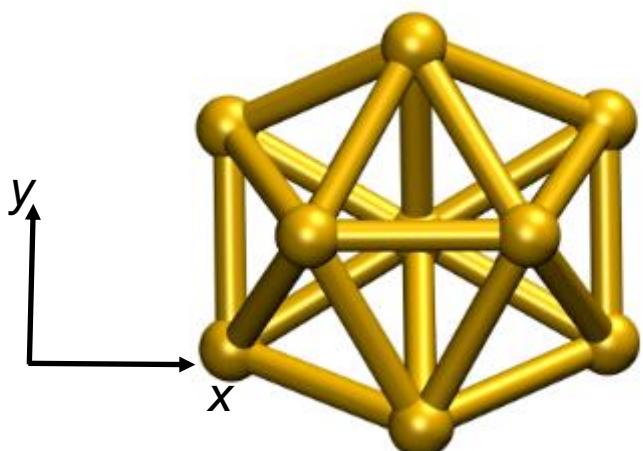
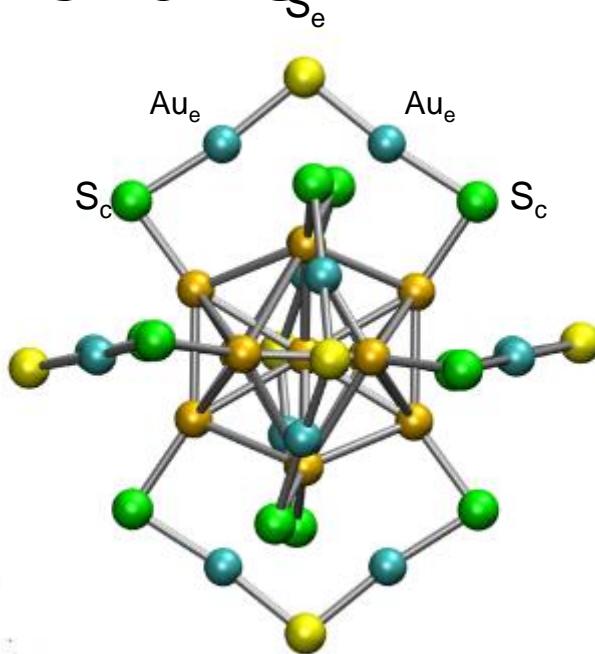
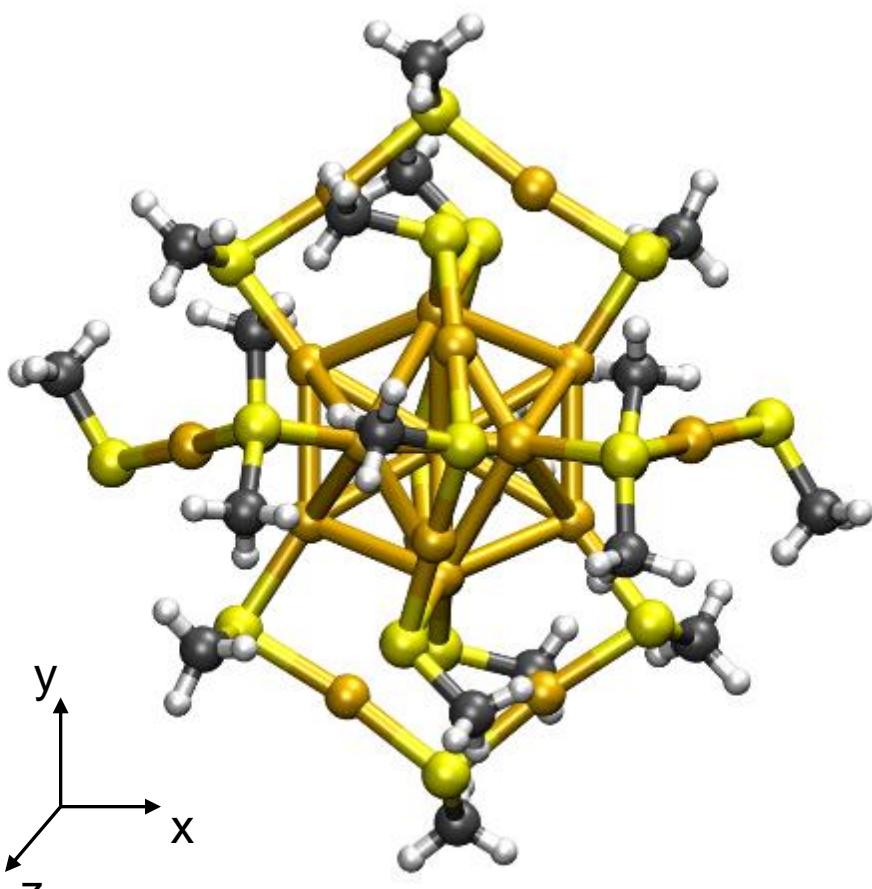
DFT-optimized structure of $[\text{Ag}_{25}\text{Au}_{25}(\text{DMBT})_{18}(\text{PET})_{18}]^{2-}$





How do we comprehend this?

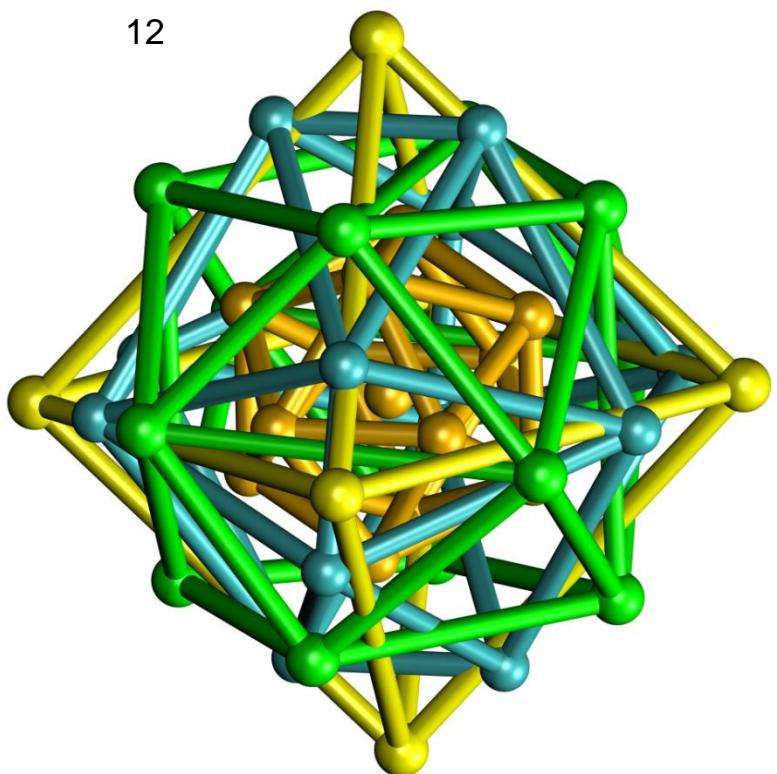
Ball and stick structure



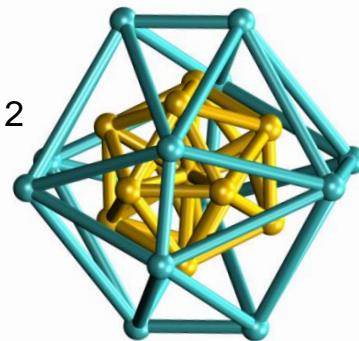
A view of gold methyl thiolate [25]aspicule ($\text{Au}_{25}(\text{SMe})_{18}$).
Gold atoms colored gold, sulfur atoms by yellow, carbon
dark gray, hydrogen atoms as white and (b) with the gold and
sulfur atoms alone .

Shell Structure

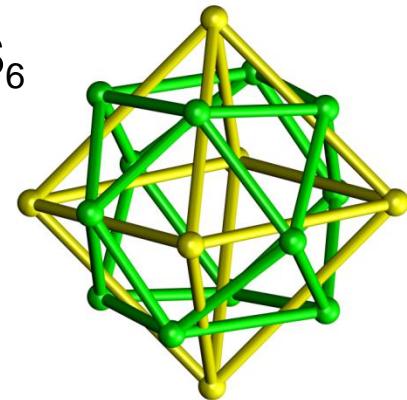
(a) $\text{Au}@\text{Au}_{12}@\text{Au}_{12}@\text{S}_6@\text{S}$



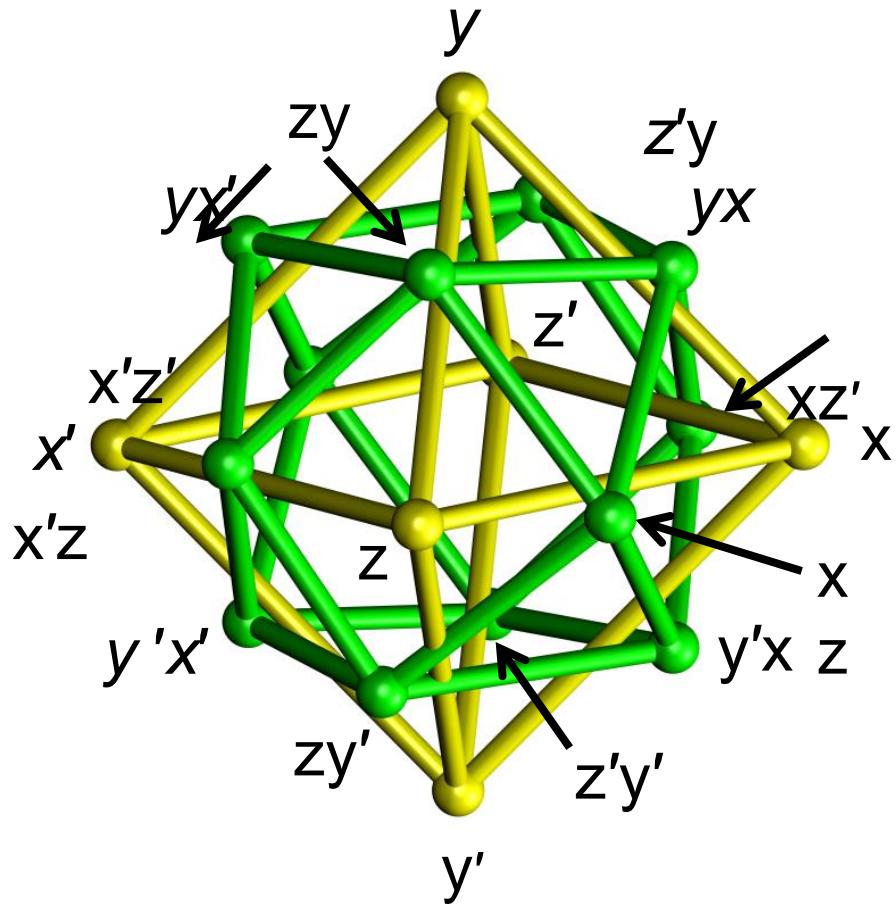
(b) $\text{Au}_{12}@\text{Au}_{12}$



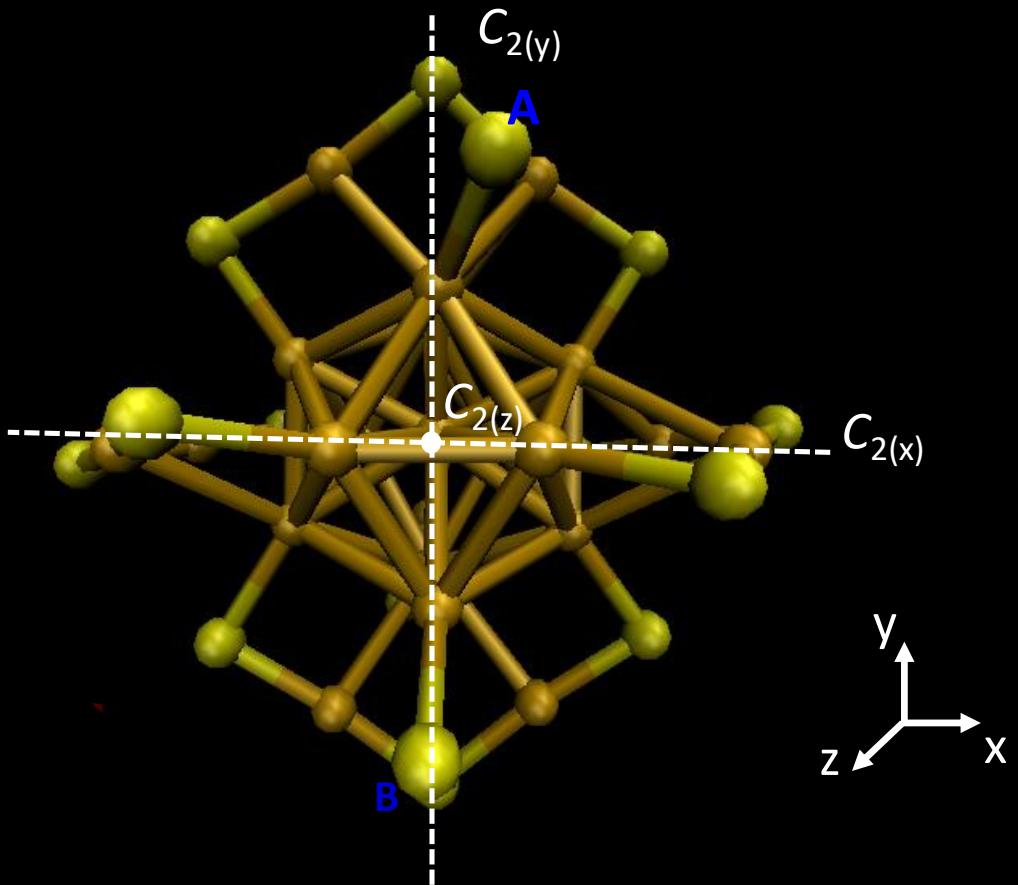
(c) $\text{S}_{12}@\text{S}_6$



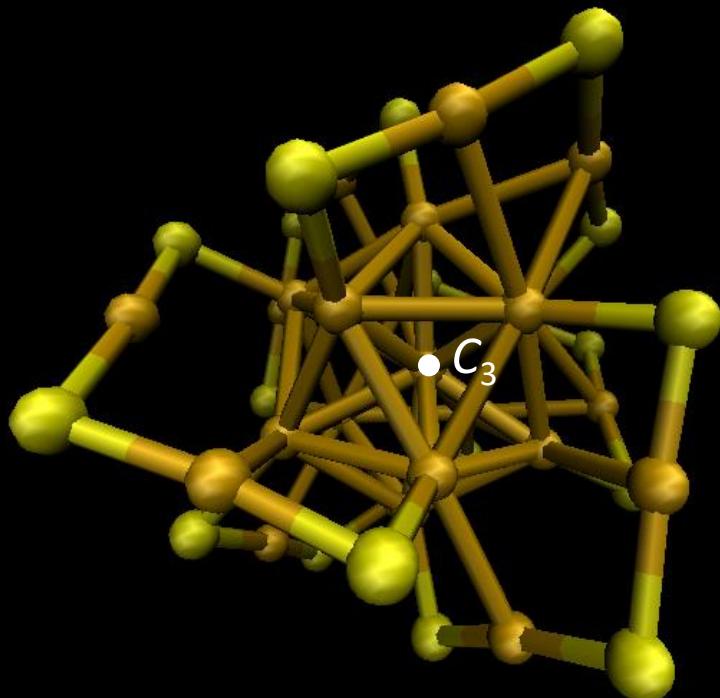
Terminologies

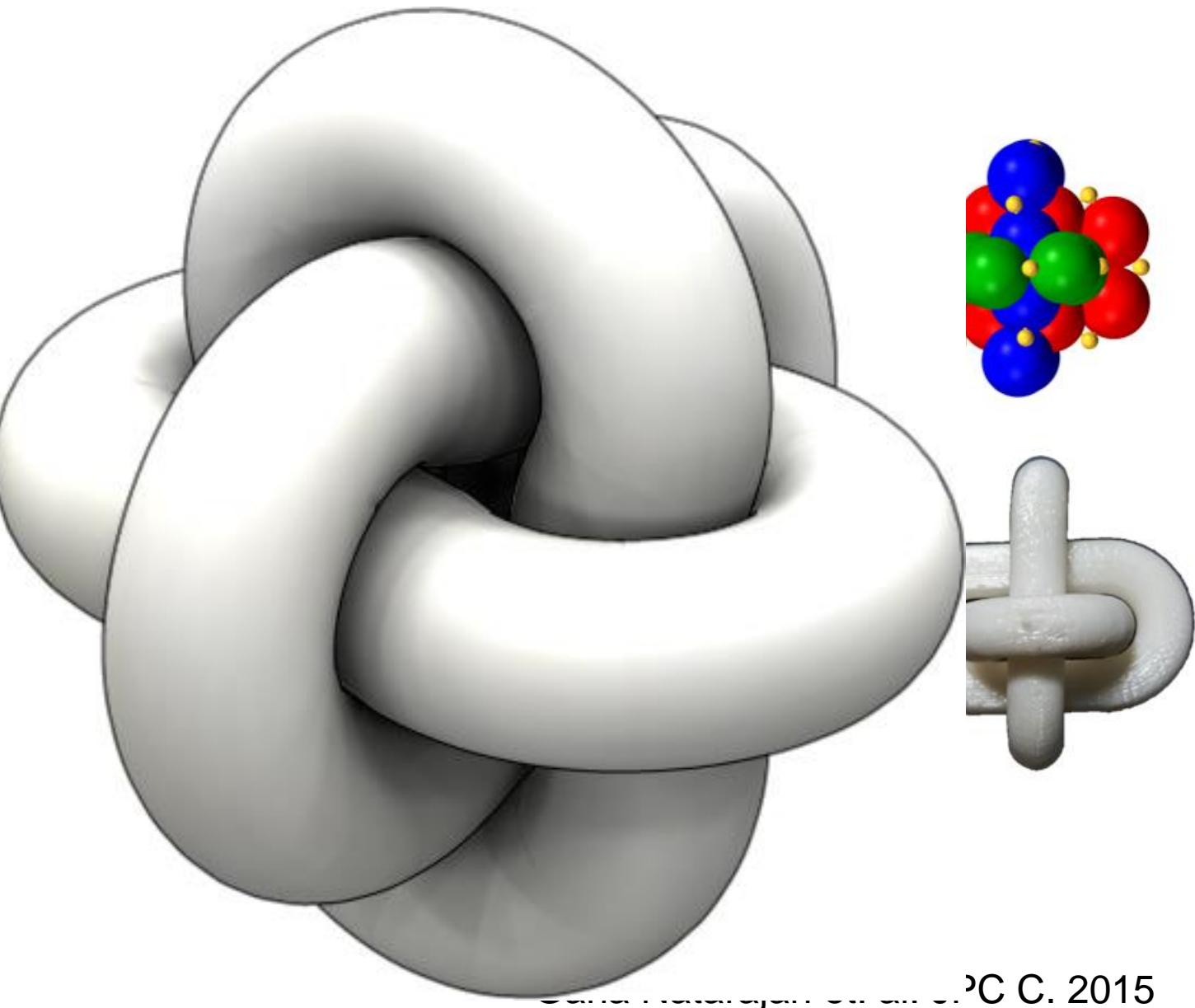
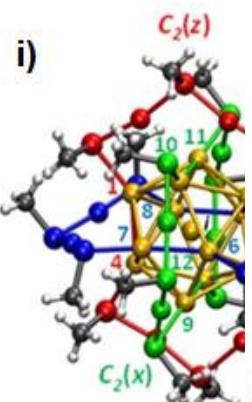


1) Edge projection



2) Face Projection





Aspicules

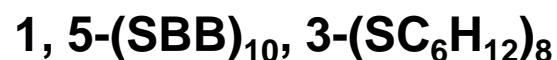
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-(PET)₂,(SMe)₁₆-auro-25 aspicule(1-)

Ligand Exchange & Alloy

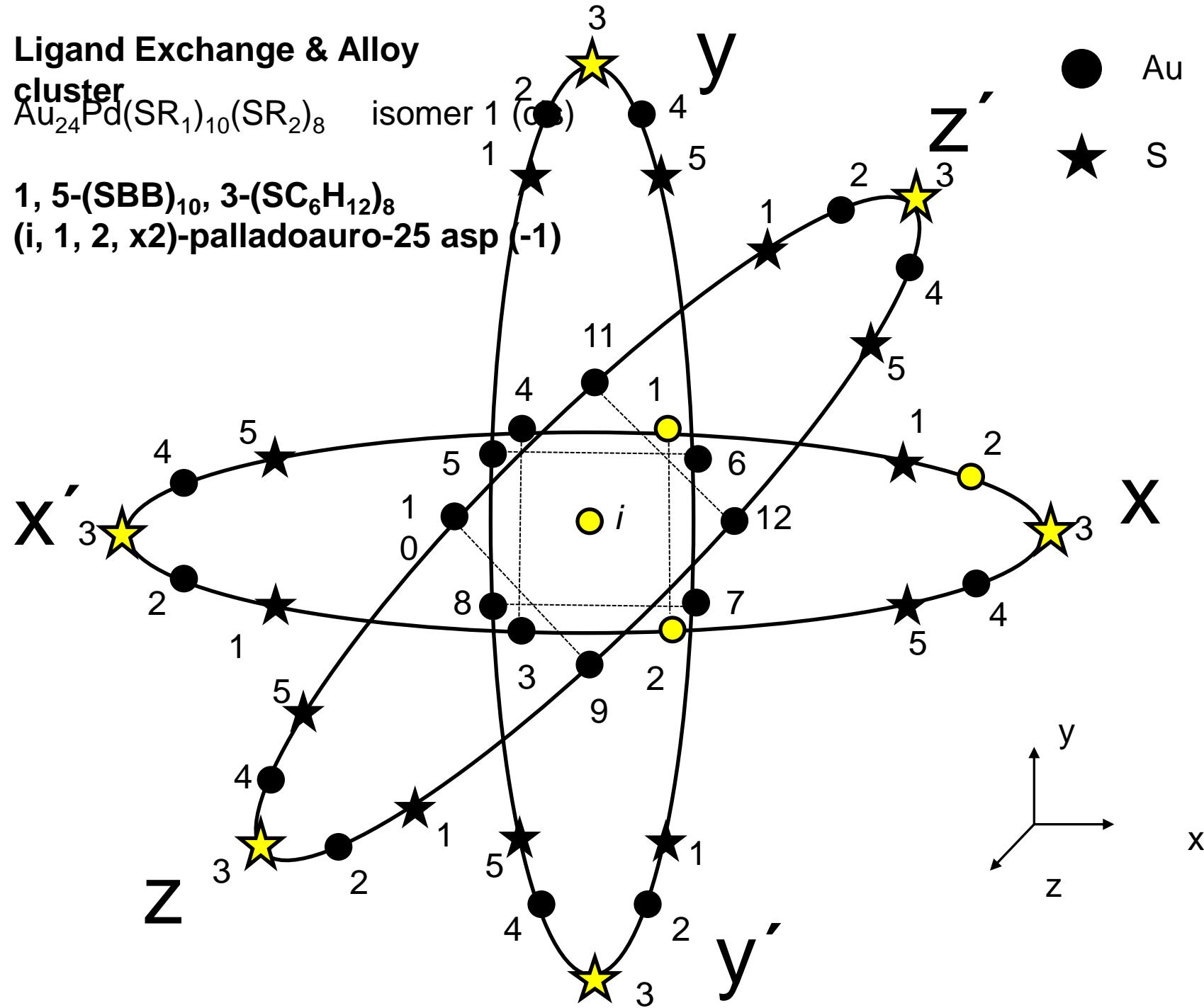
cluster



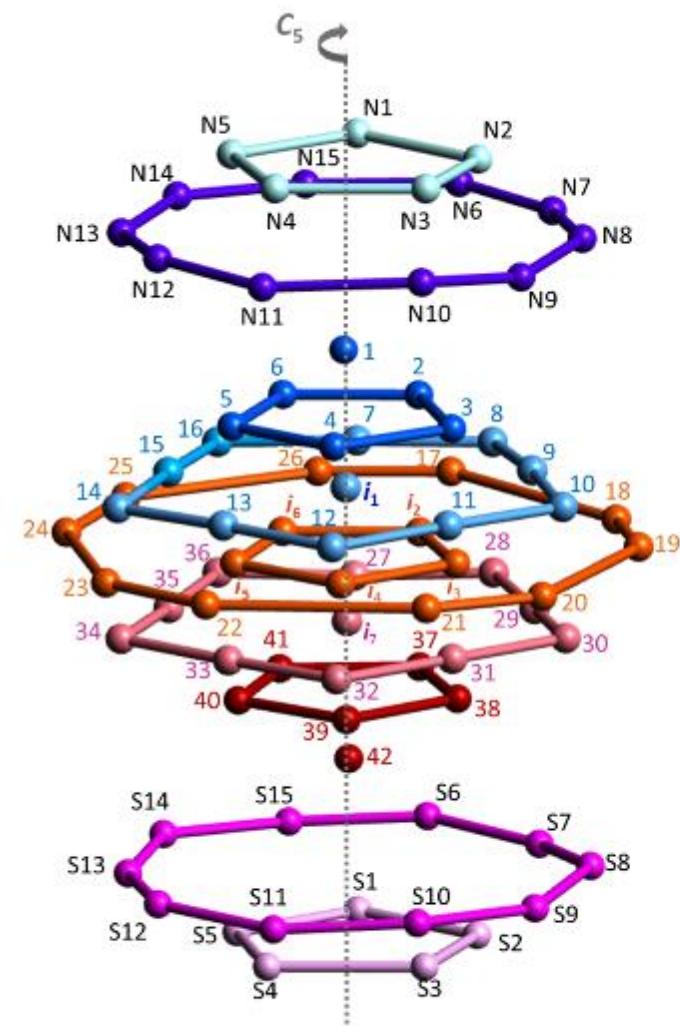
isomer 1



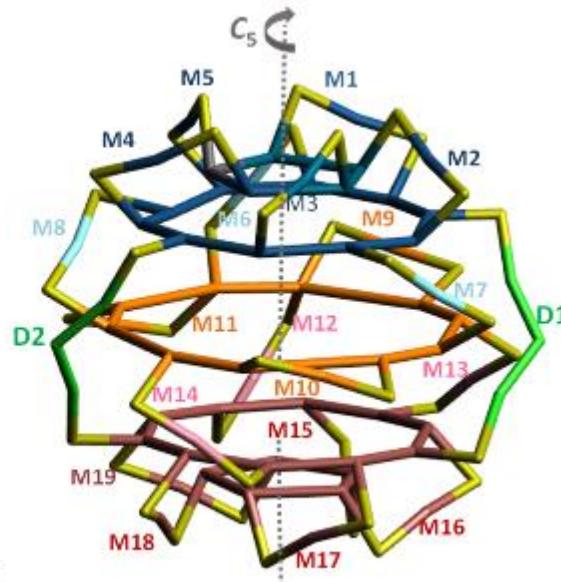
(i, 1, 2, x2)-palladoauro-25 asp (-1)



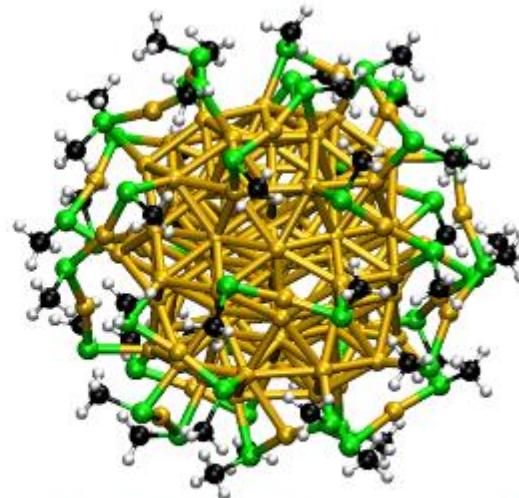
(A)



(B)



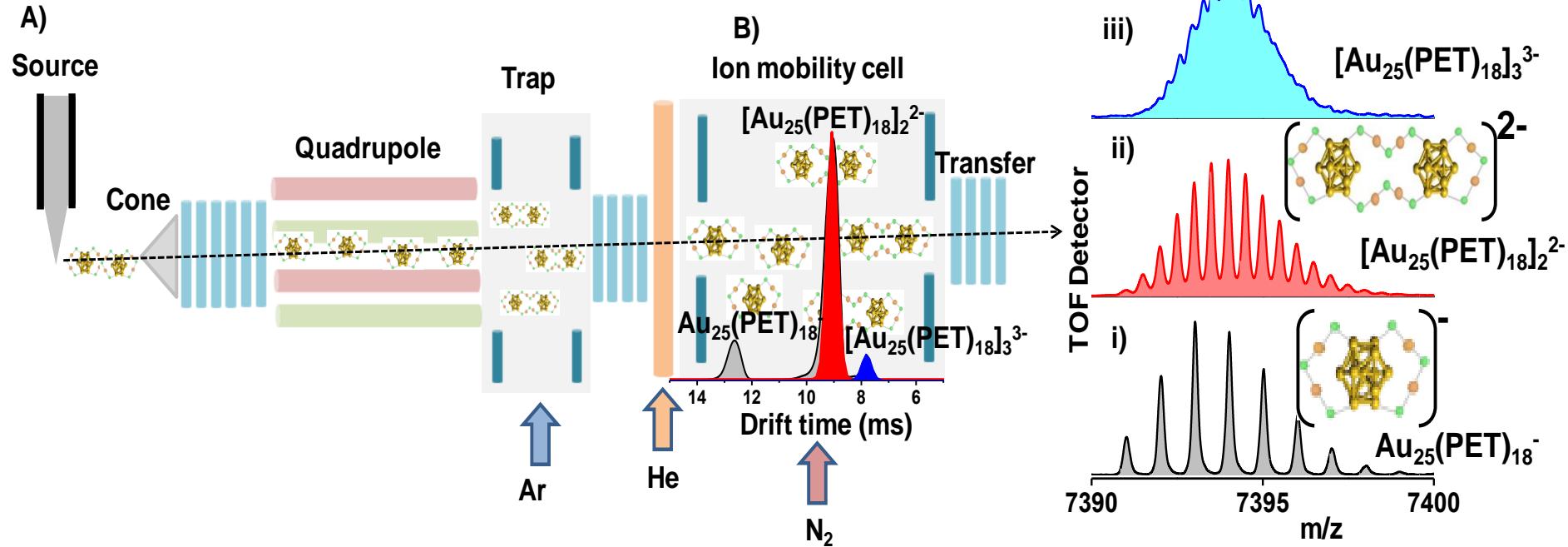
(C)



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

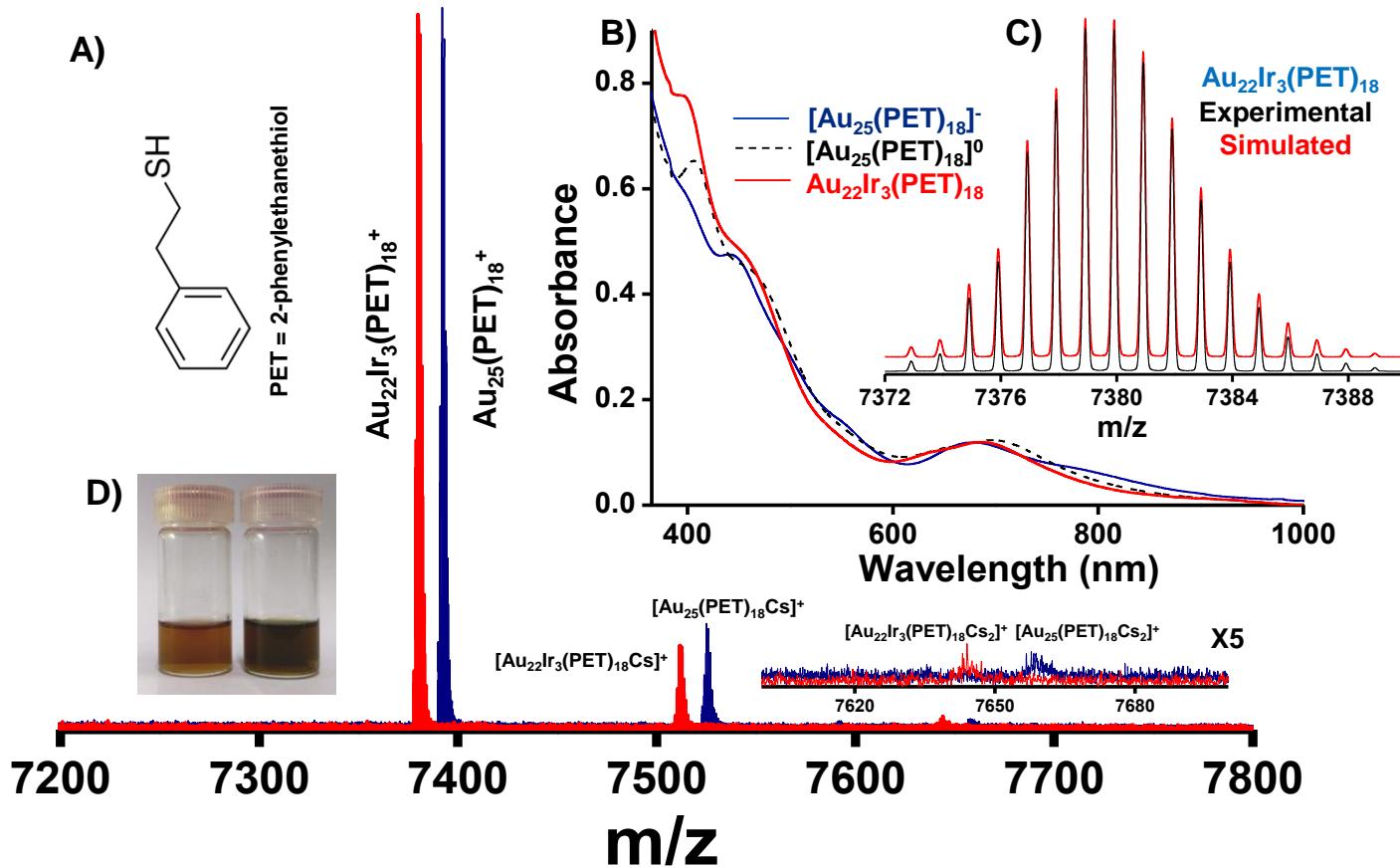
R-(SMe)₄₄-auro-102 aspicule(0) and L-(SMe)₄₄-auro-102 aspicule(0)

Cluster dimers

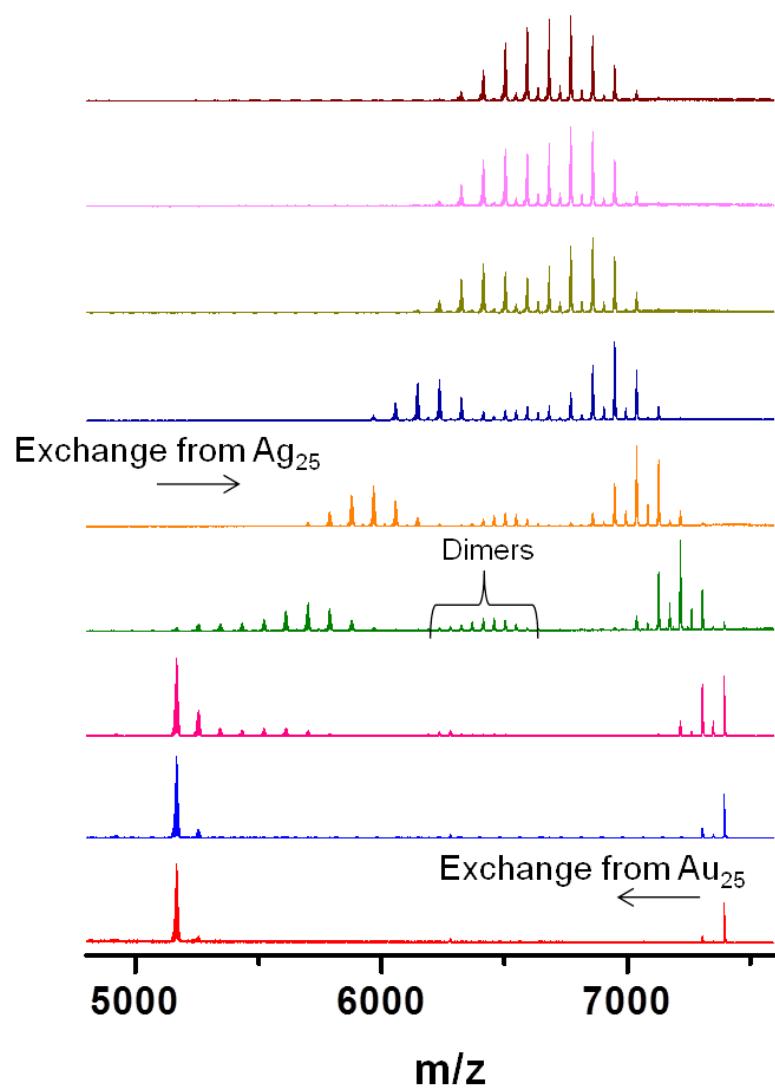


Ananya Baksi et al. Chem. Commun. 2016

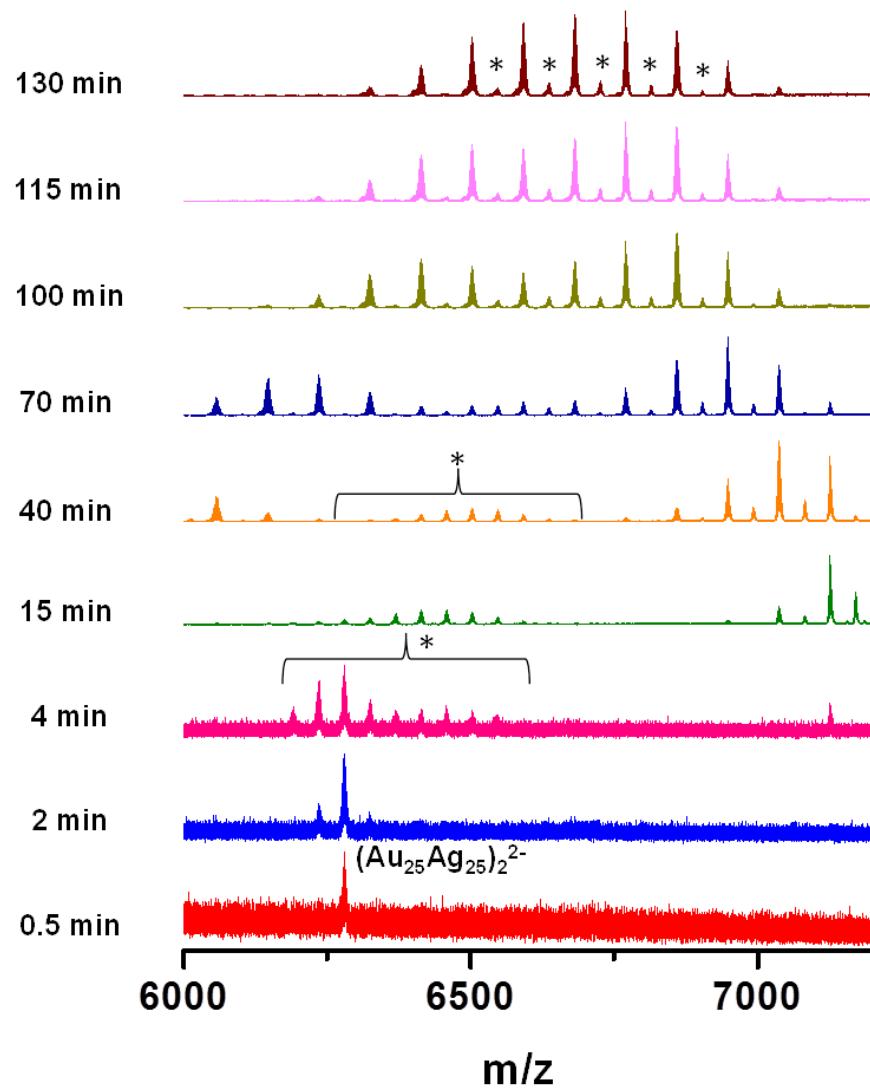
Precision alloys



ESI MS of the reaction mixture

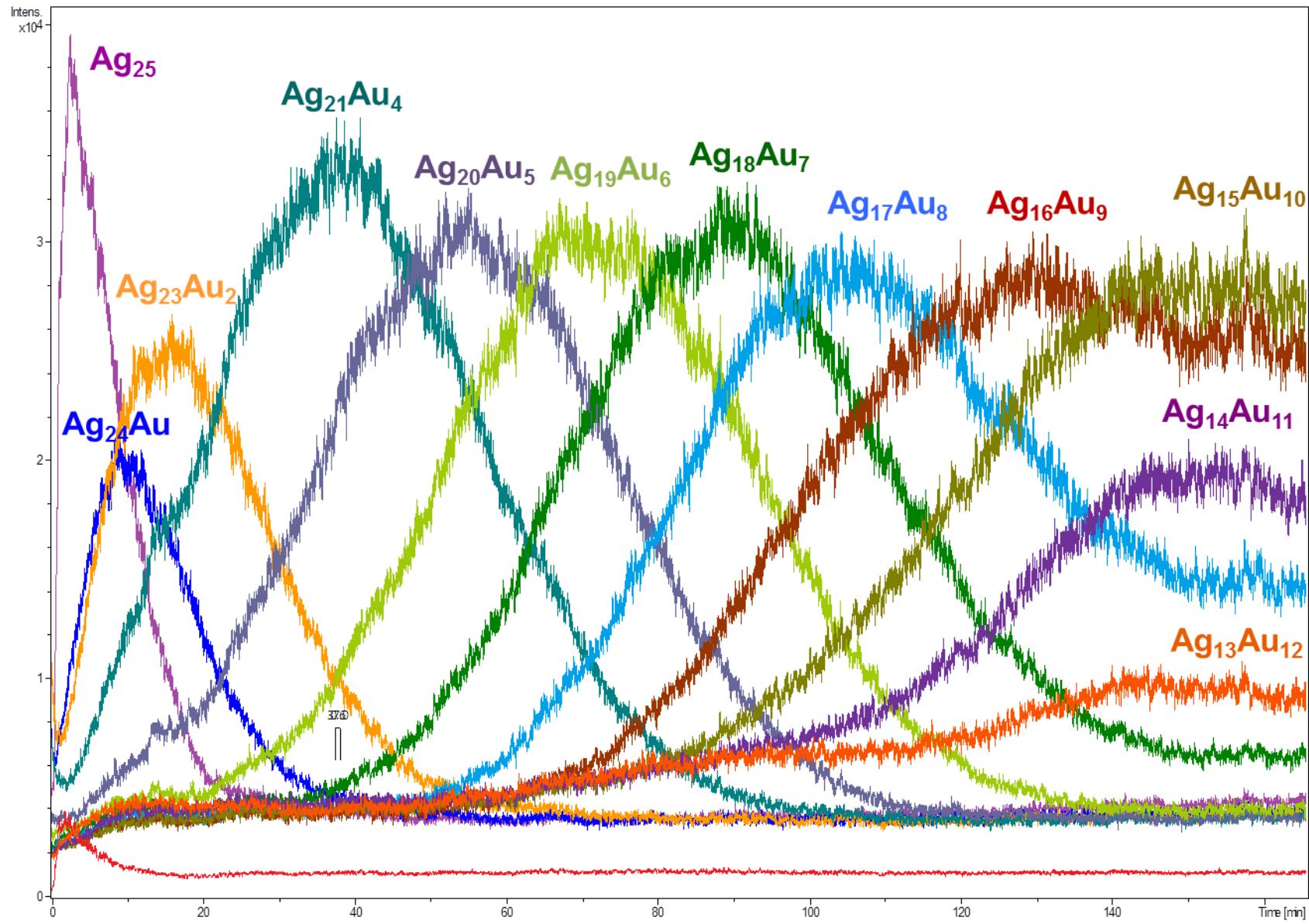


Expanded view of the dimers



* peaks for the dimers (at higher time, the monomeric peaks due to Au-Ag exchange also arise). Au_{25} was kept in excess.

Kinetics of the exchange (monitored on the Ag₂₅ side)



Cluster dynamics

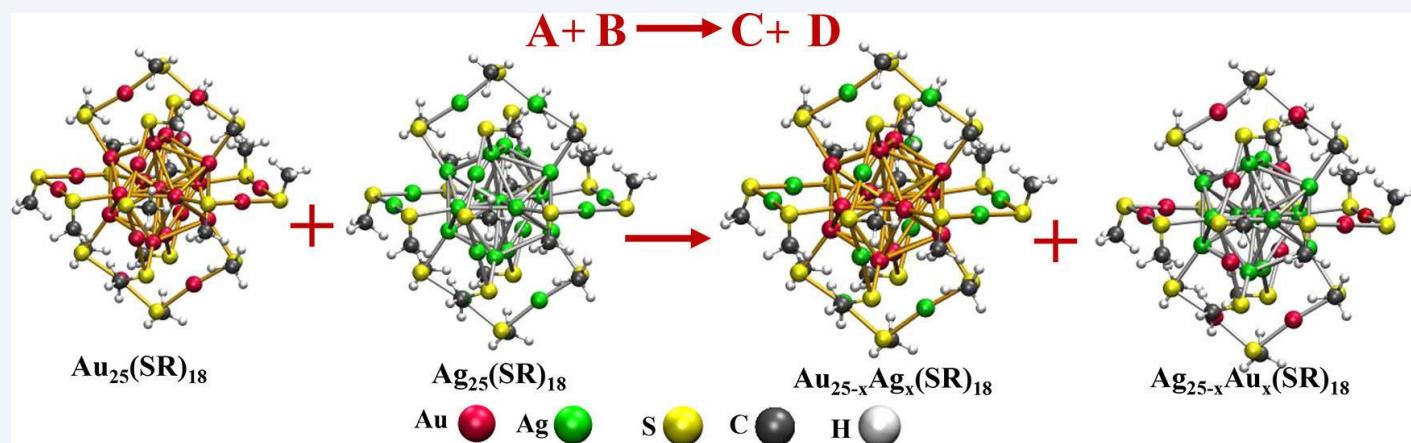


They are indeed molecules!

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.

CONDENSED MATTER PHYSICS

Rapid isotopic exchange in nanoparticles

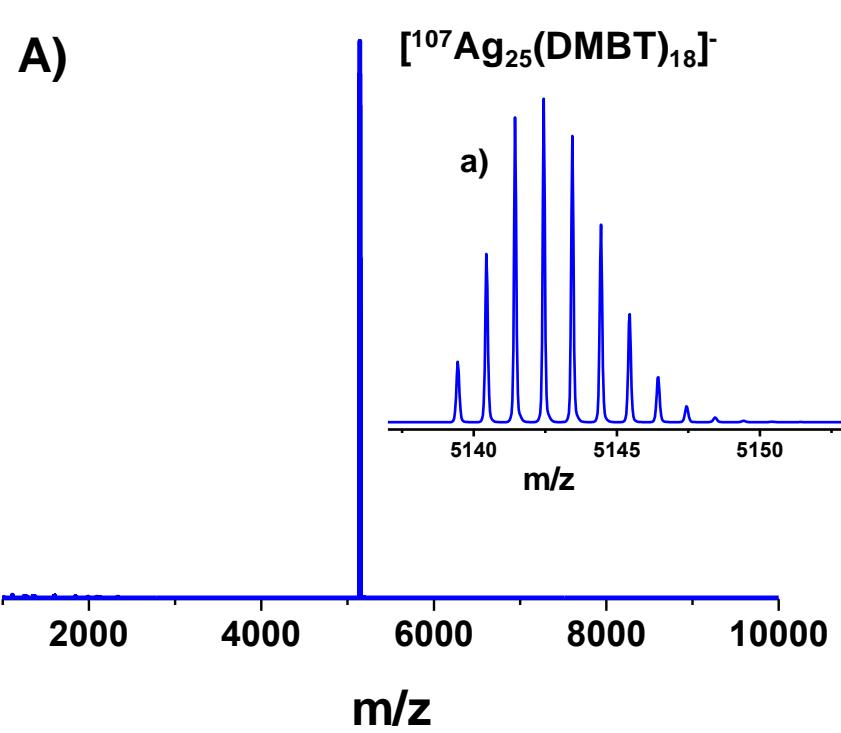
Papri Chakraborty¹, Abhijit Nag¹, Ganapati Natarajan¹, Nayanika Bandyopadhyay¹,
Ganesan Paramasivam¹, Manoj Kumar Panwar¹, Jaydeb Chakrabarti², Thalappil Pradeep^{1*}

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.

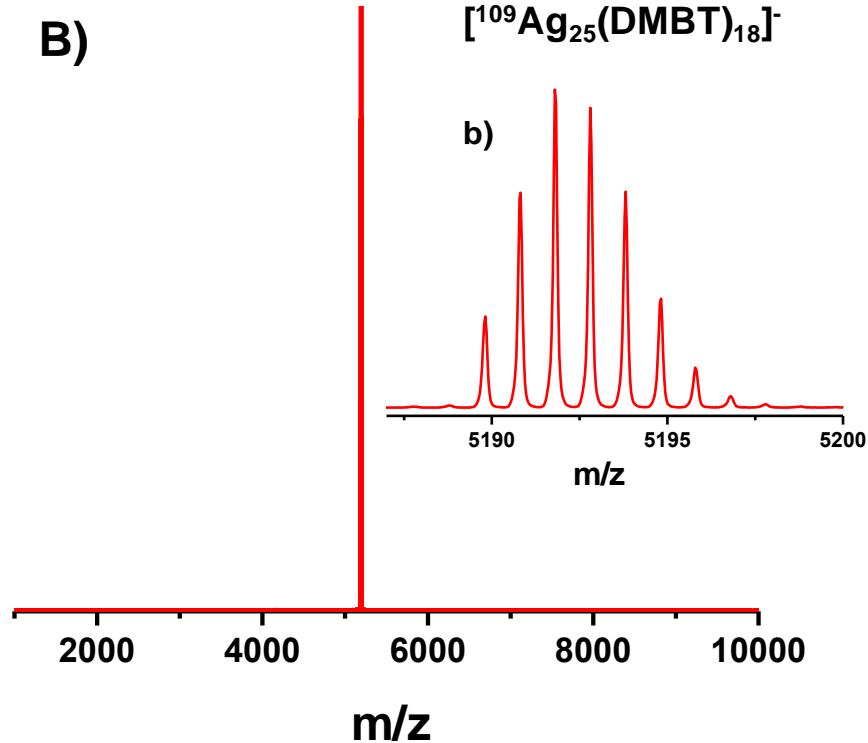
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A)

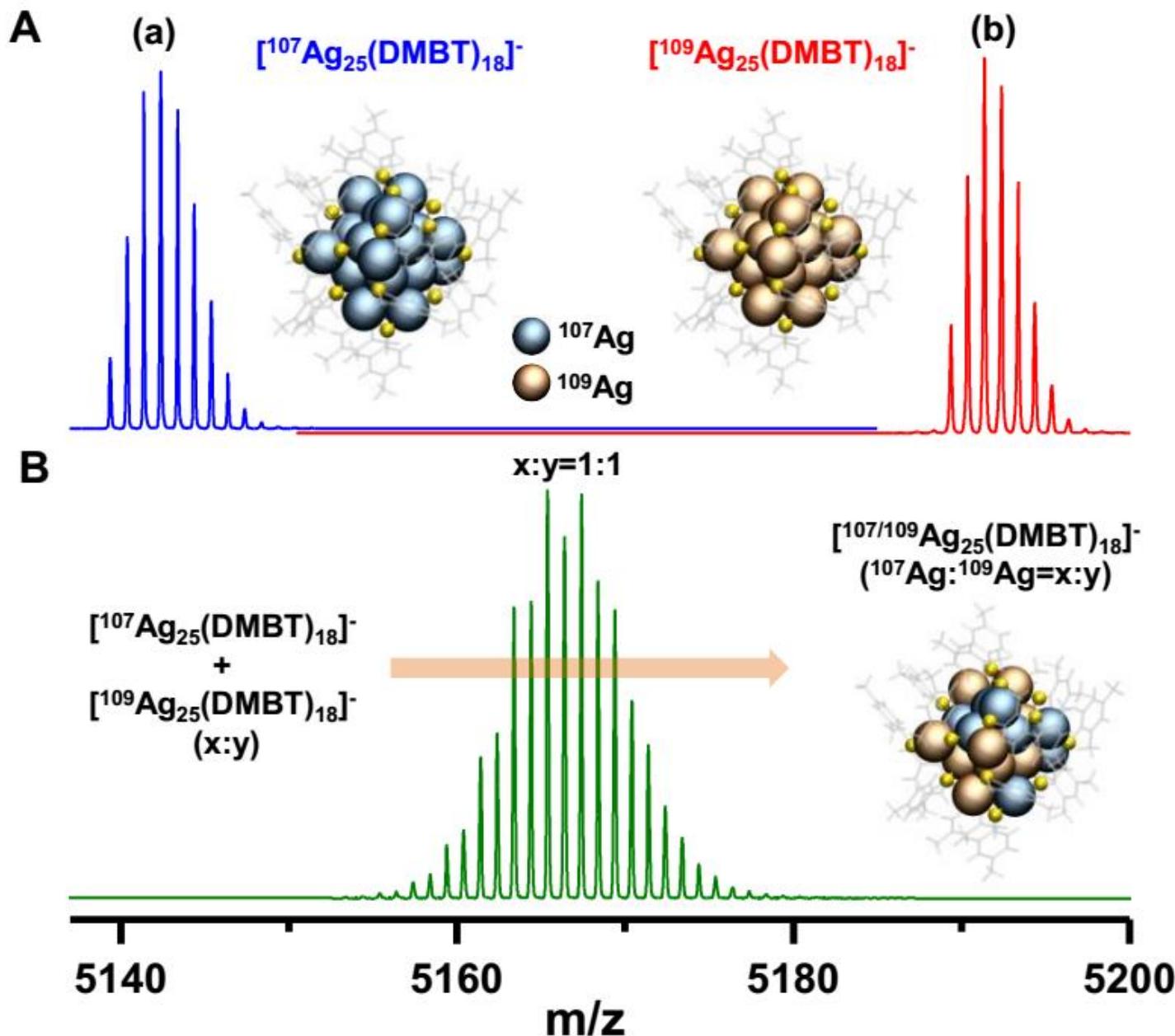
a)

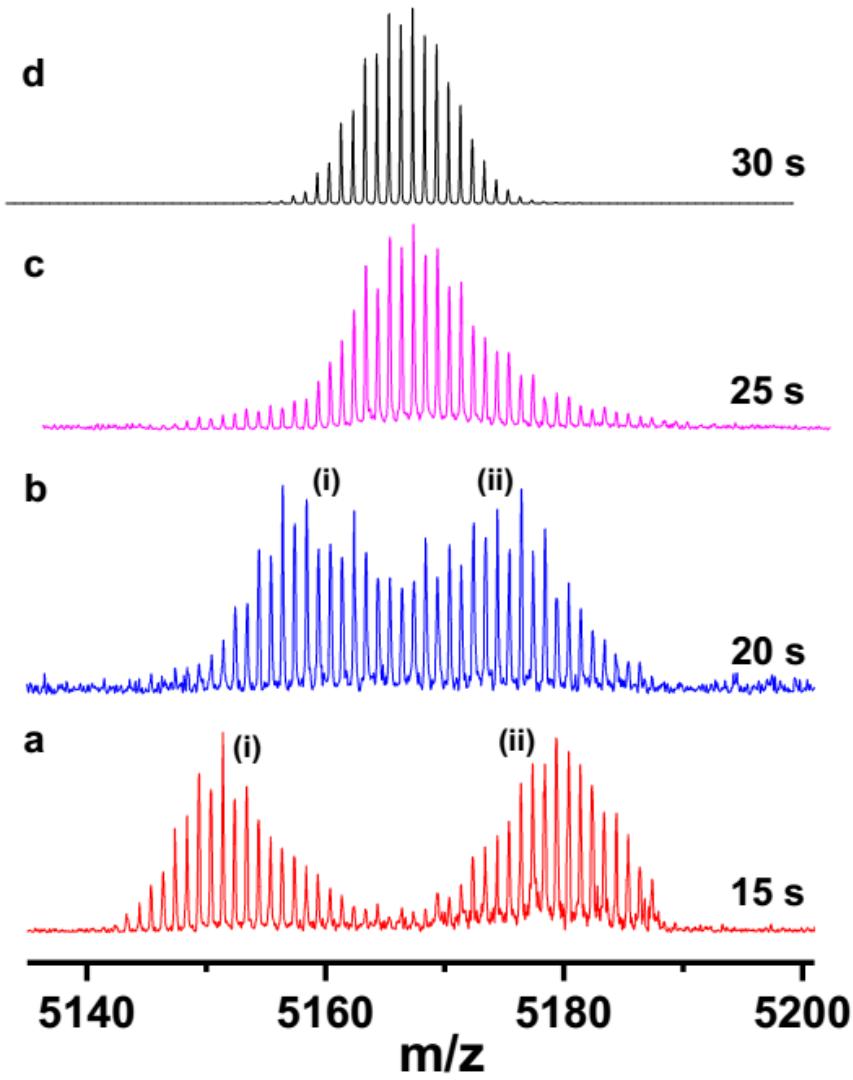
**B)**

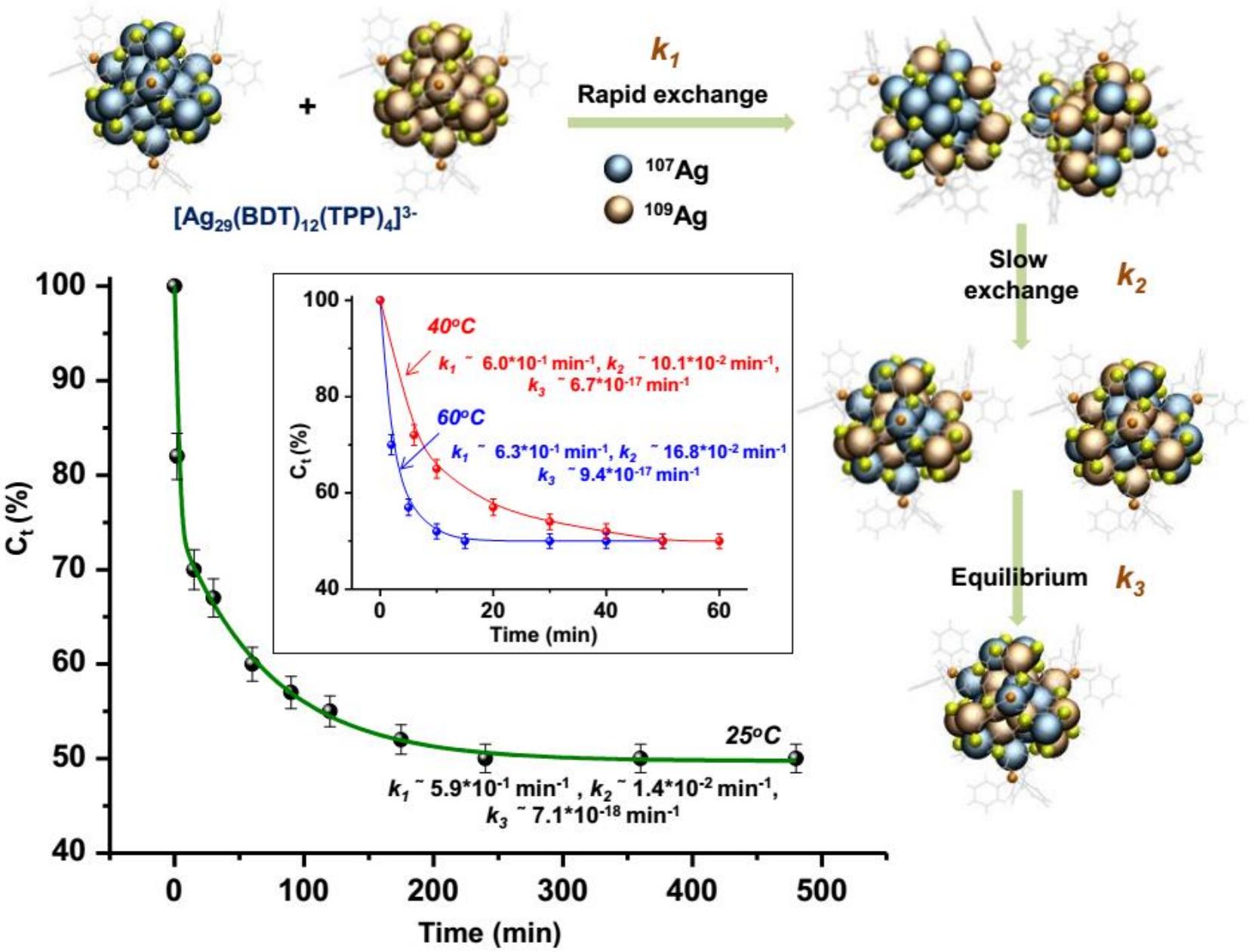
b)



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.







Supramolecular chemistry

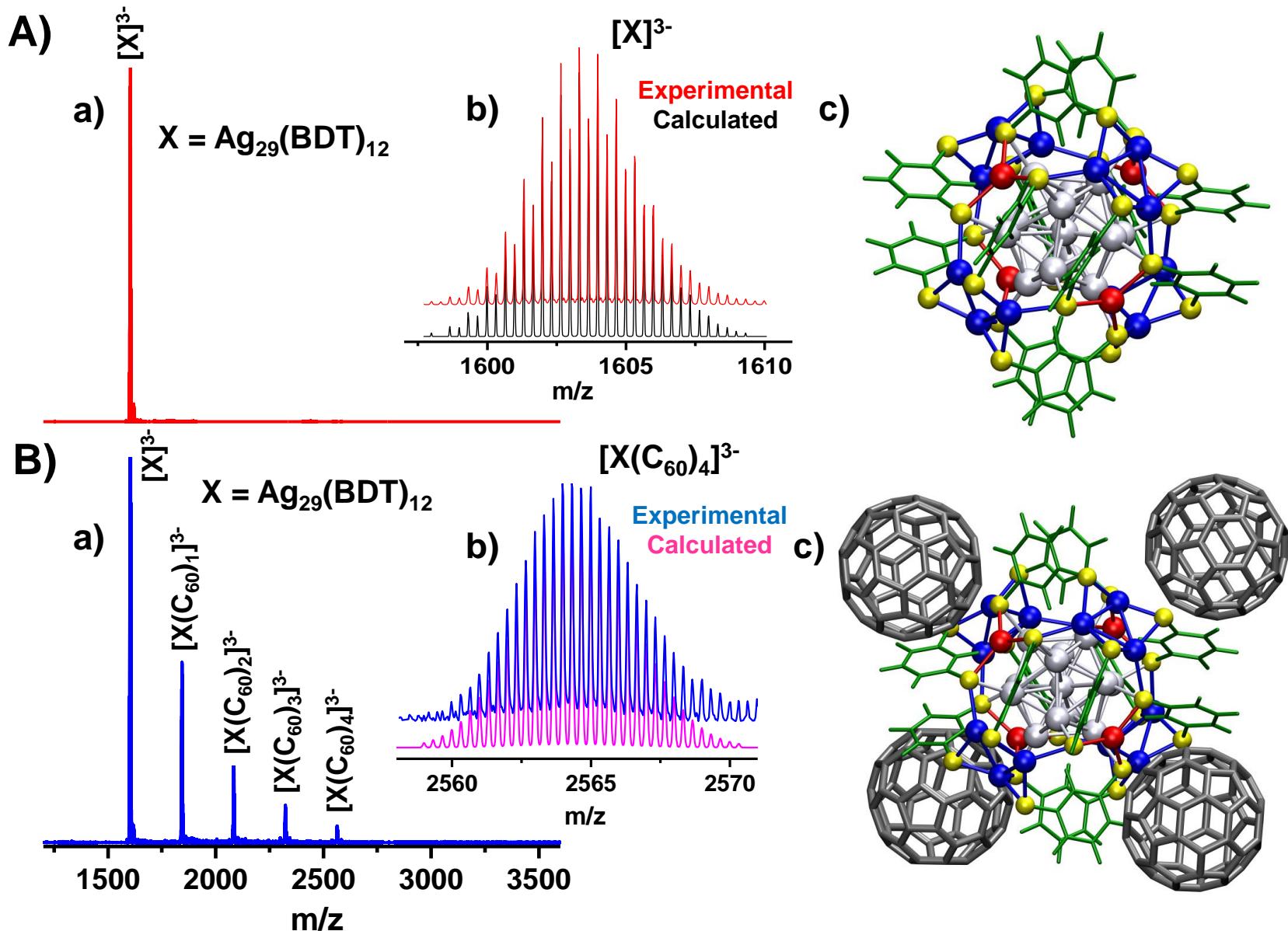


Figure 1. **A)** (a) Full range ESI MS, (b) experimental and calculated isotope patterns and (c) DFT optimized structure of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ cluster. **B)** (a) ESI MS of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{C}_{60})_n]^{3-}$ ($n=1-4$) complexes, (b) experimental and calculated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

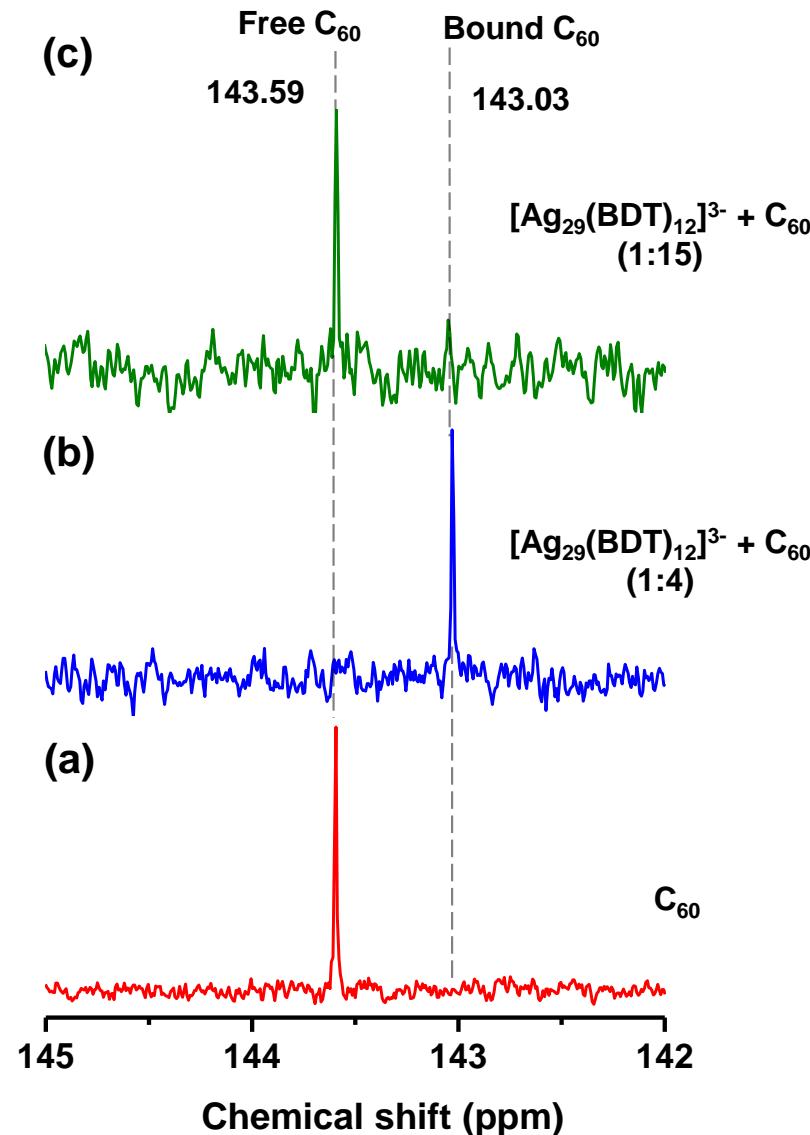
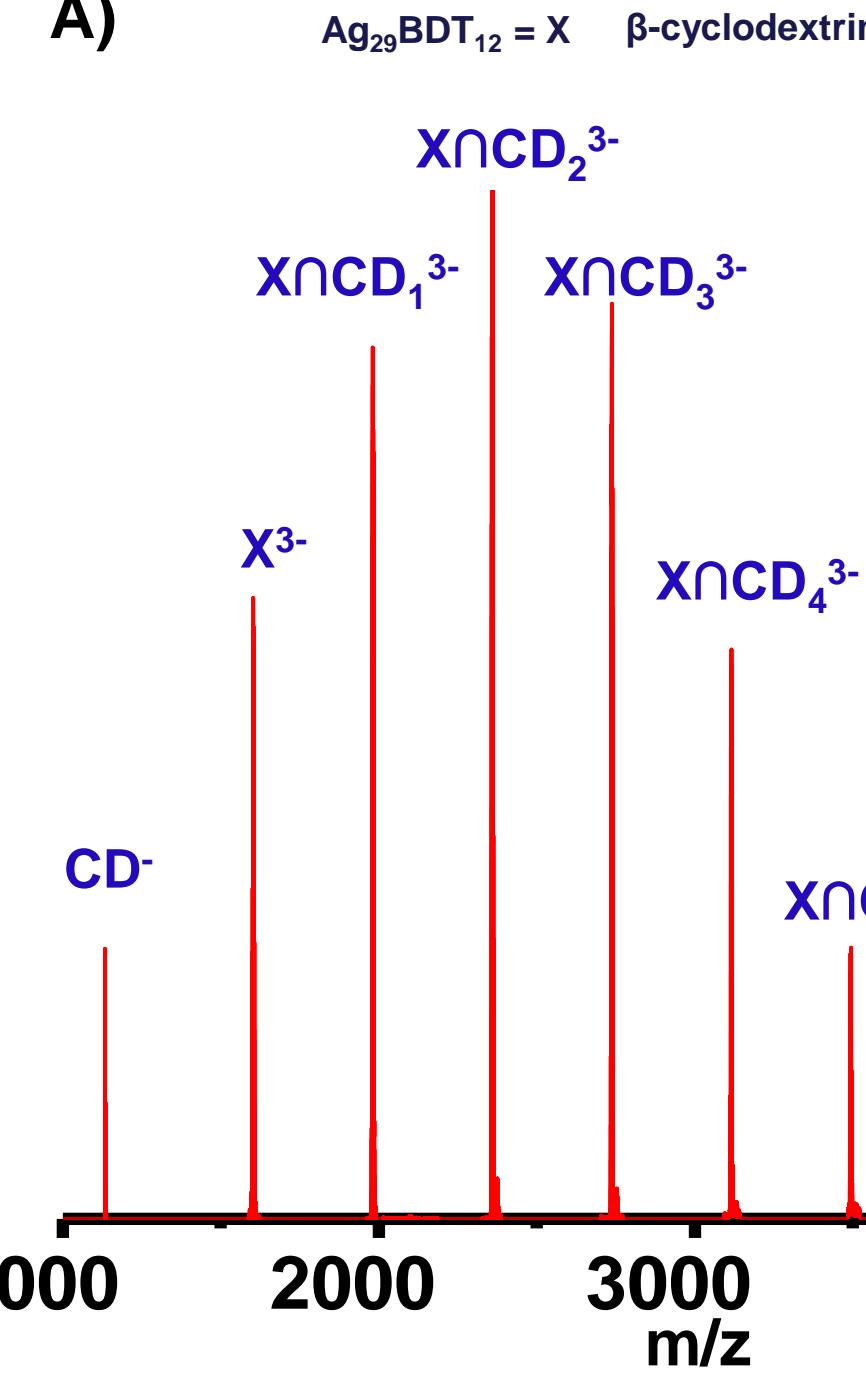
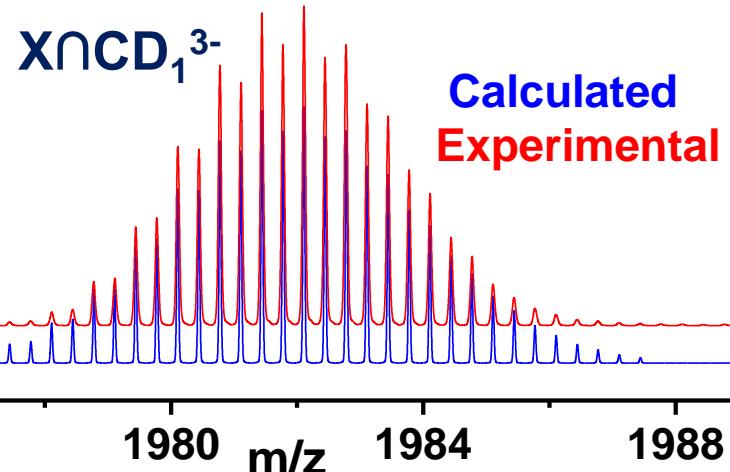
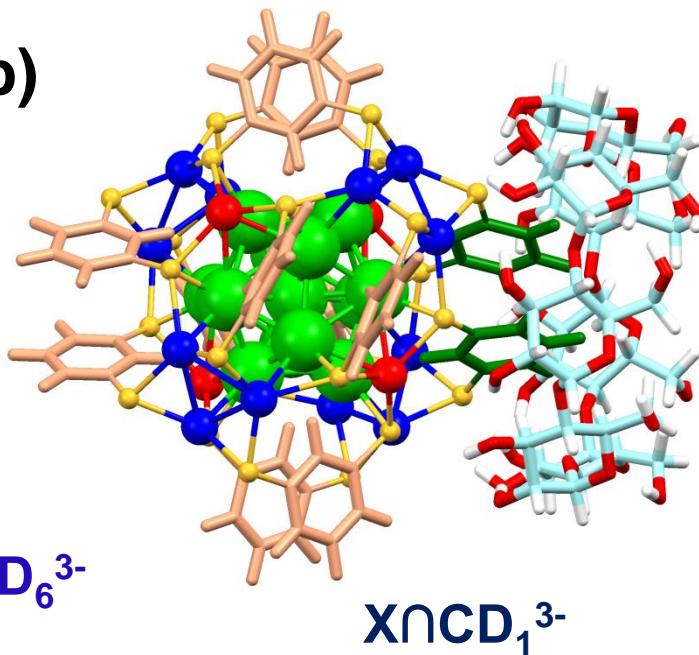


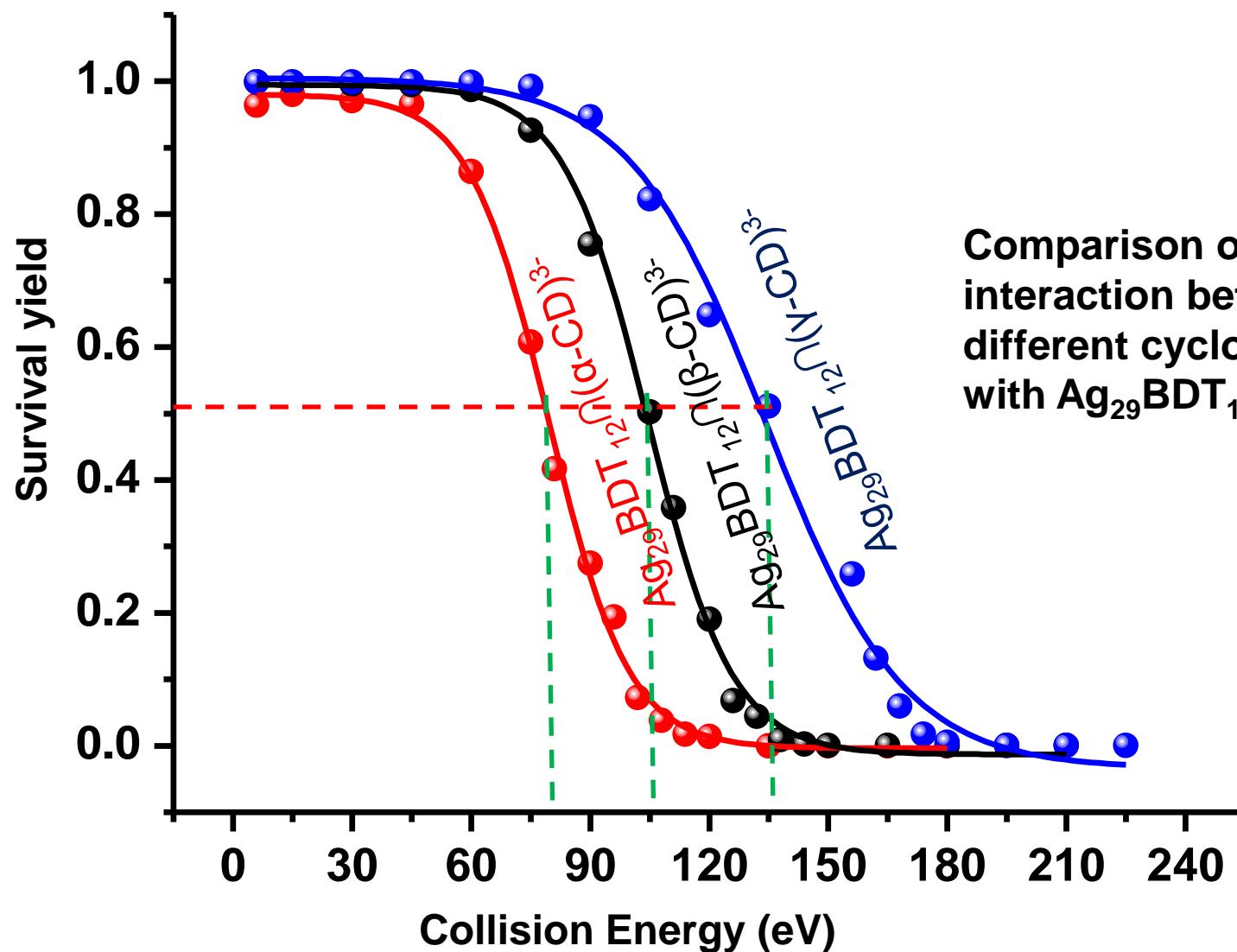
Figure 3. NMR of (a) C_{60} showing peak at 143.59 ppm, (b) the adducts at a cluster:fullerene molar ratio of 1:4 showing peak at 143.03 ppm for the C_{60} molecules in bound state and (c) the adducts at an excess concentration of C_{60} (cluster:fullerene molar ratio of 1:15) showing a predominant peak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

Isomerism in supramolecular adducts

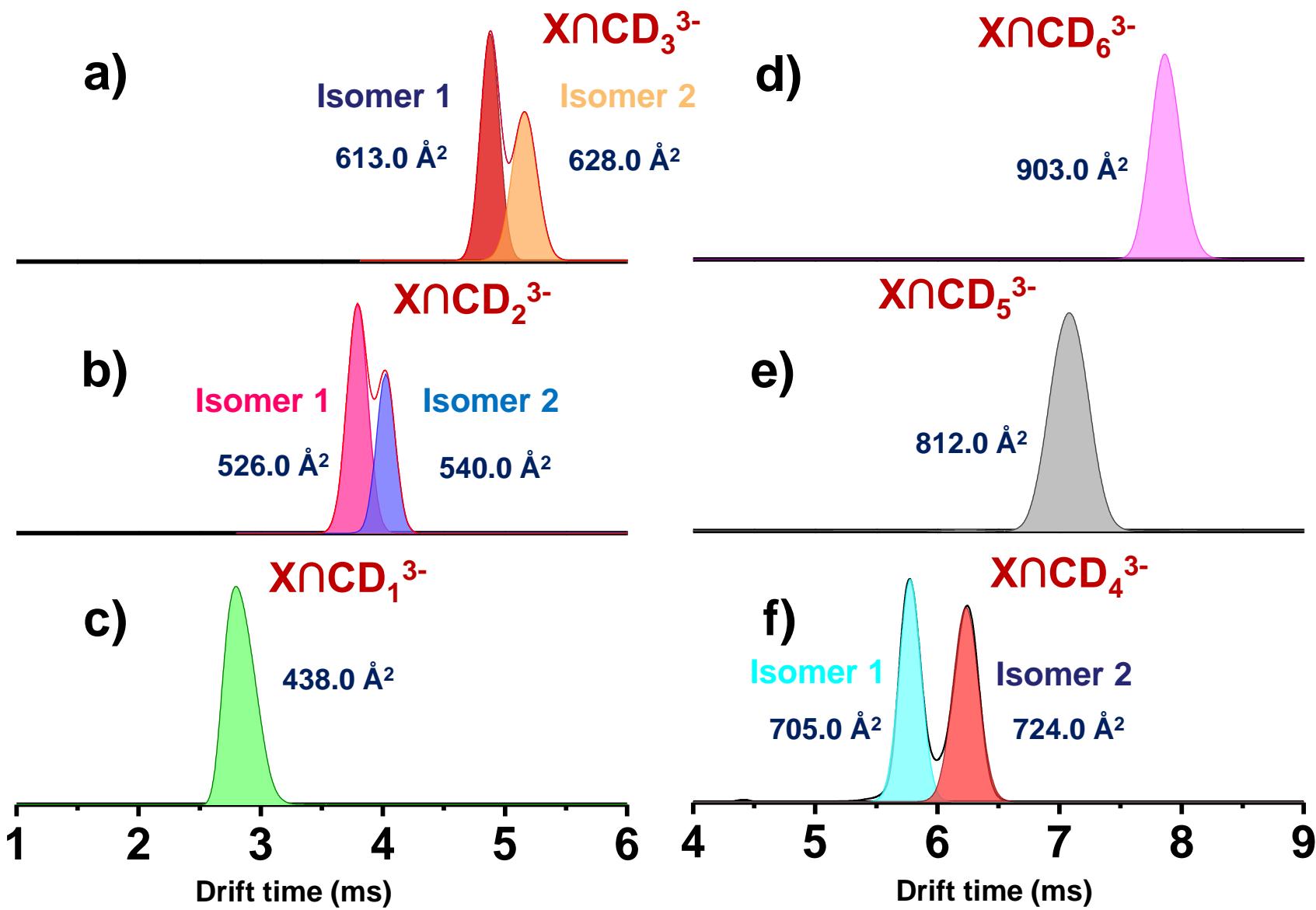
Abhijit Nag, et al. JACS 2018

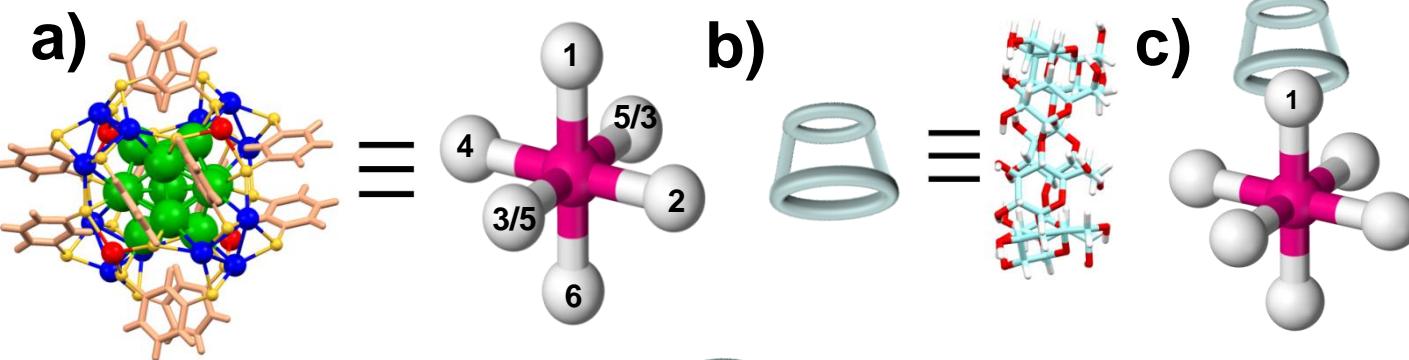
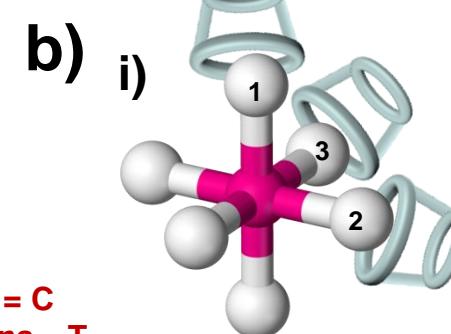
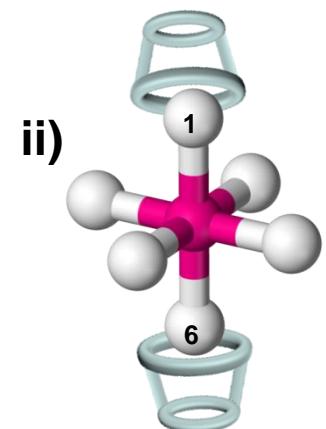
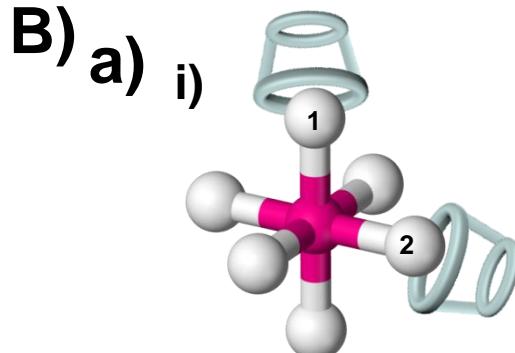
A)**a)****b)**

Energy Resolved Fragmentation of $\text{Ag}_{29}\text{BDT}_{12} \cap (\text{X-CD})^{3-}$



Comparison of
interaction between
different cyclodextrins
with $\text{Ag}_{29}\text{BDT}_{12}$



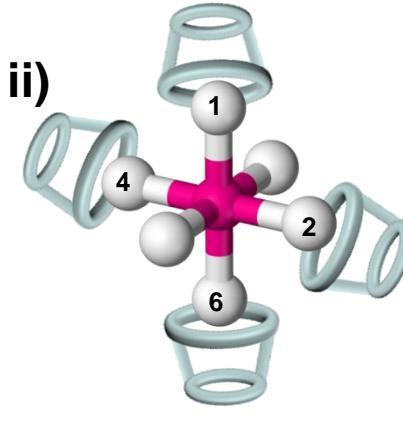
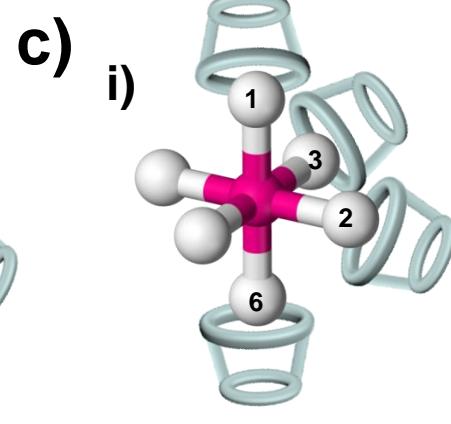
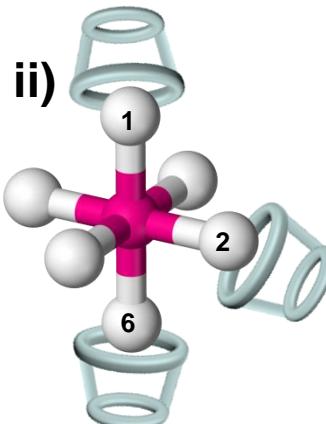
A)**B)**

*Cis = C
Trans = T*

$\text{C-Ag}_{29}(\text{BDT})_{12} \cap \text{CD}_2$

$\text{T-Ag}_{29}(\text{BDT})_{12} \cap \text{CD}_2$

$\text{C-Ag}_{29}(\text{BDT})_{12} \cap \text{CD}_3$



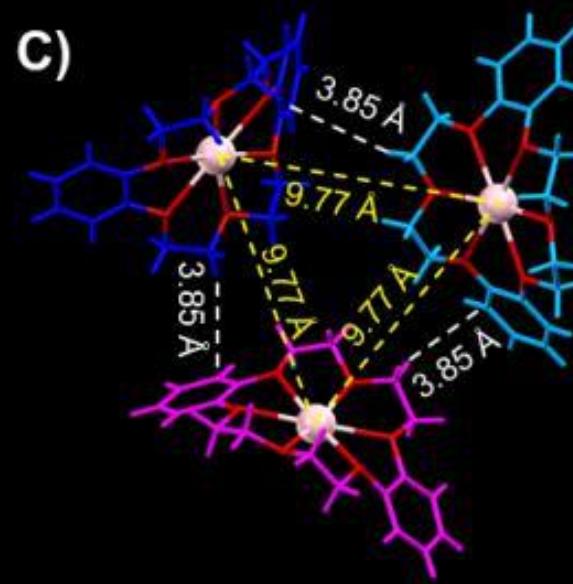
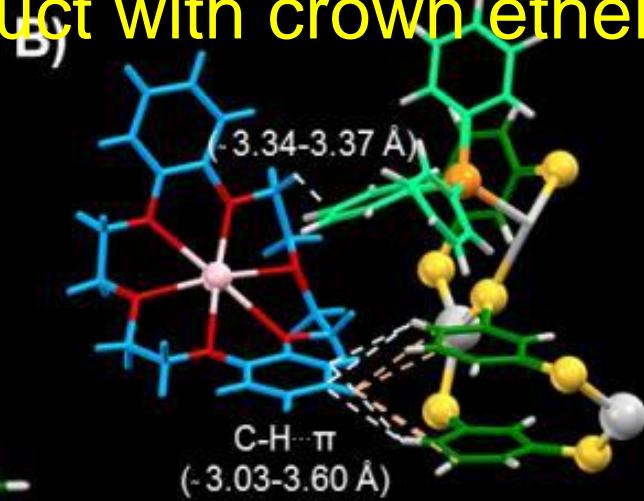
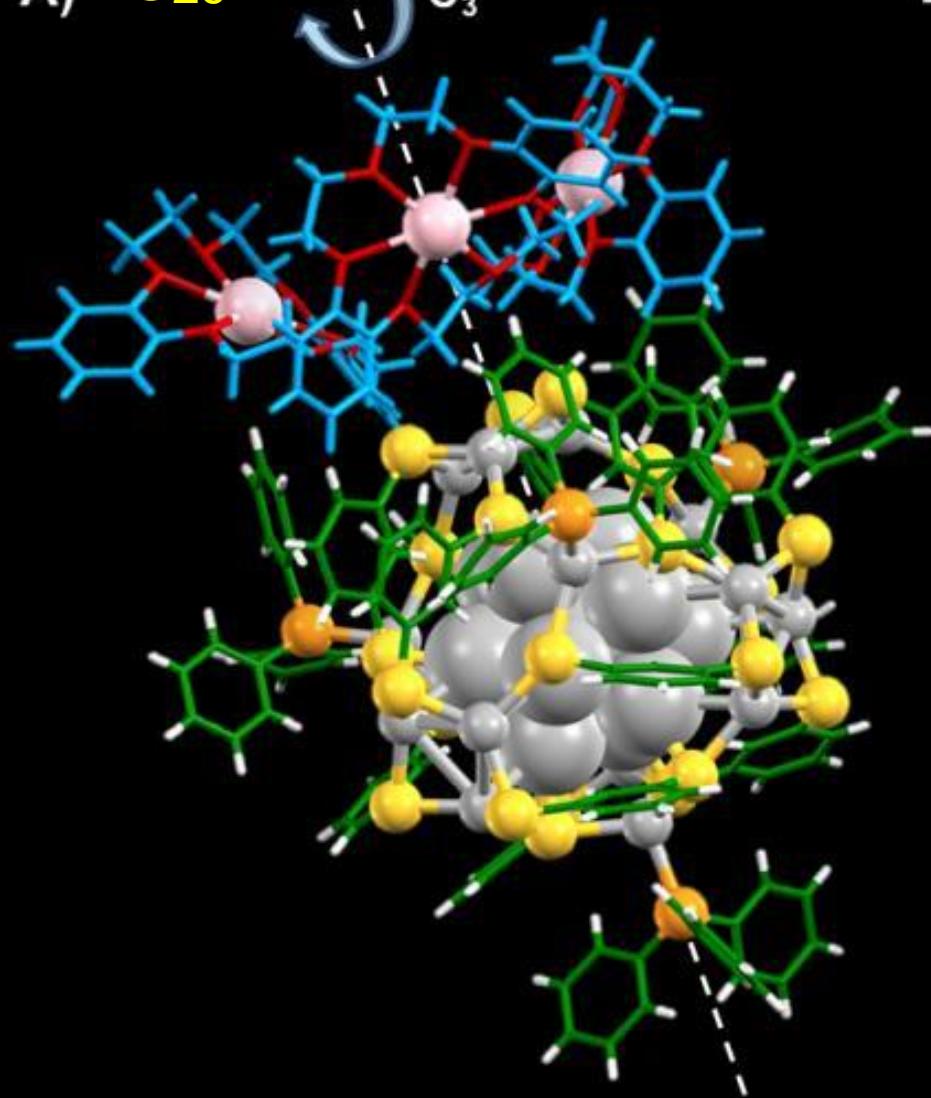
$\text{T-Ag}_{29}(\text{BDT})_{12} \cap \text{CD}_3$

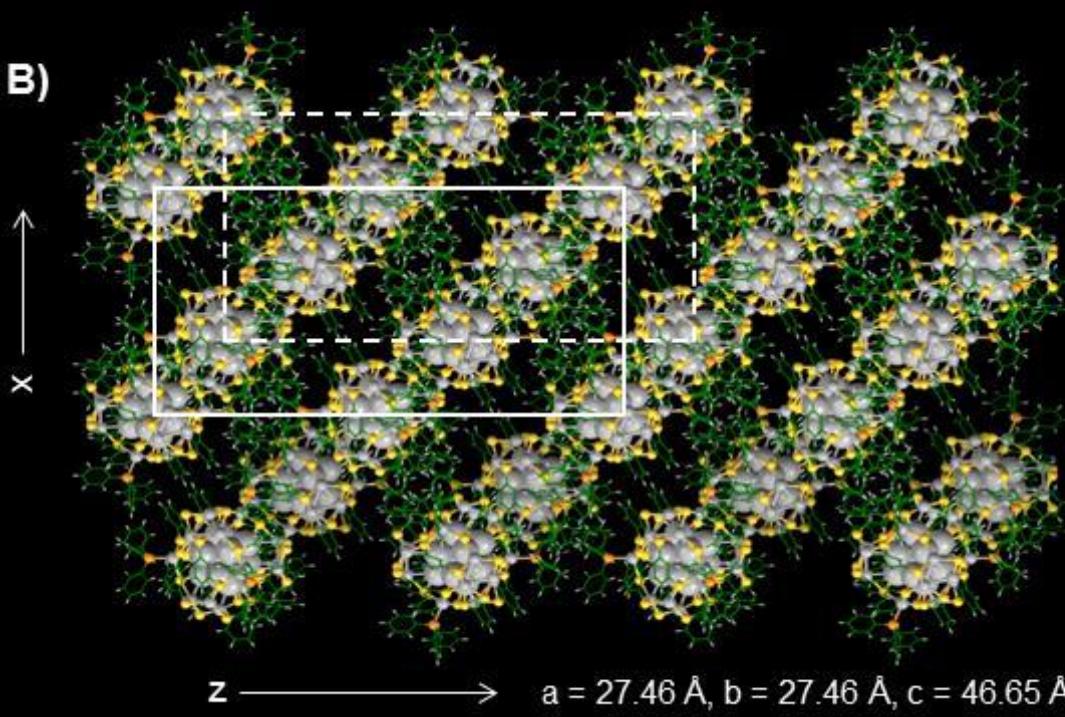
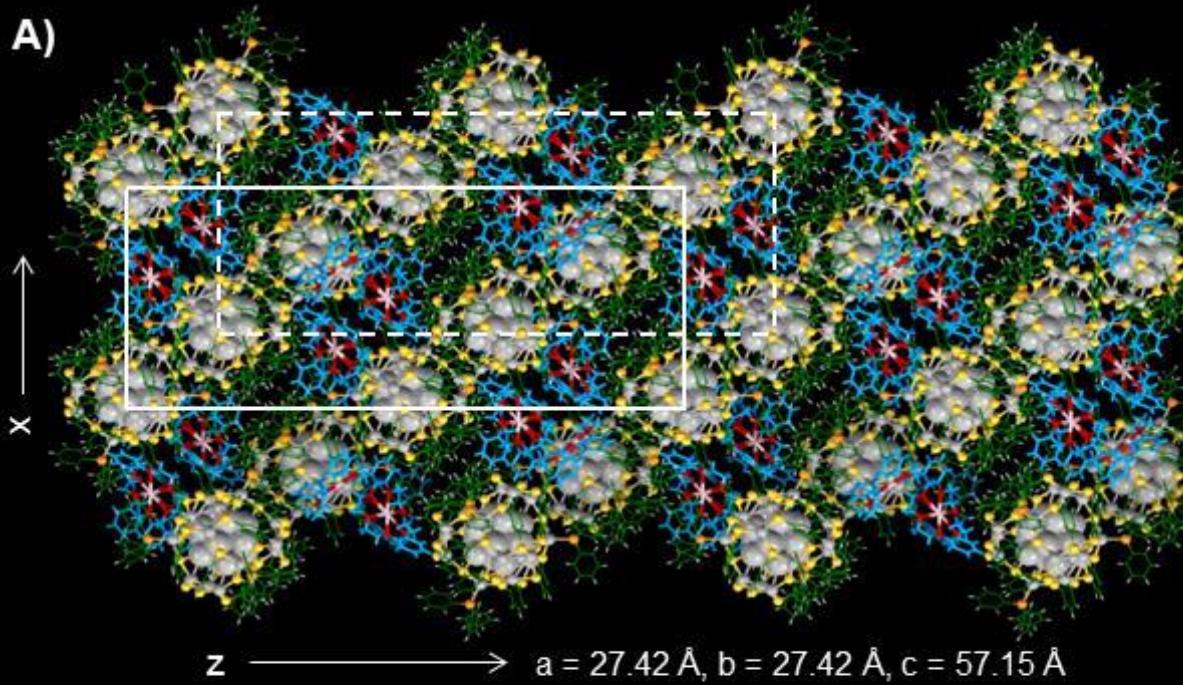
$\text{C-Ag}_{29}(\text{BDT})_{12} \cap \text{CD}_4$

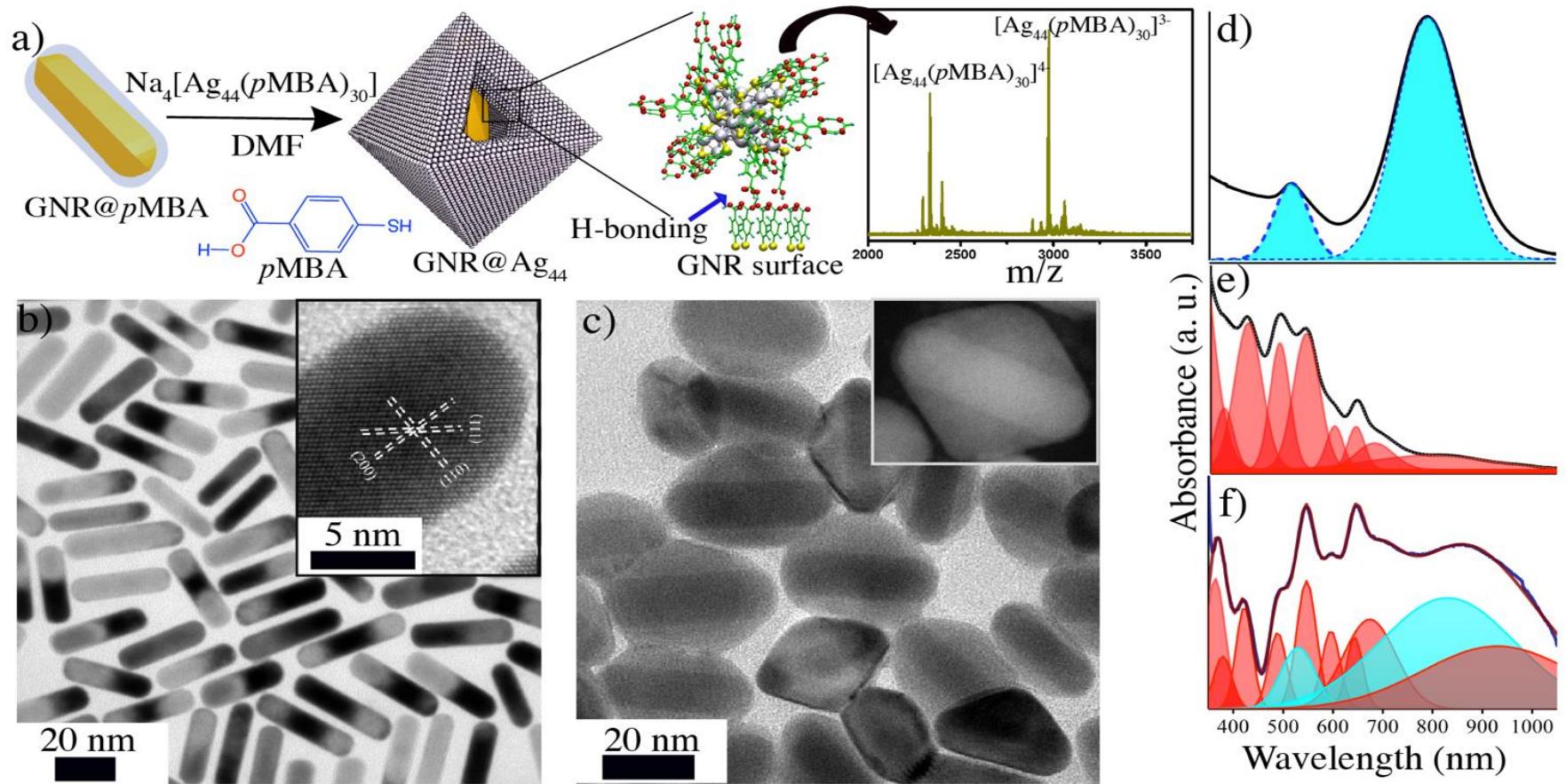
$\text{T-Ag}_{29}(\text{BDT})_{12} \cap \text{CD}_4$

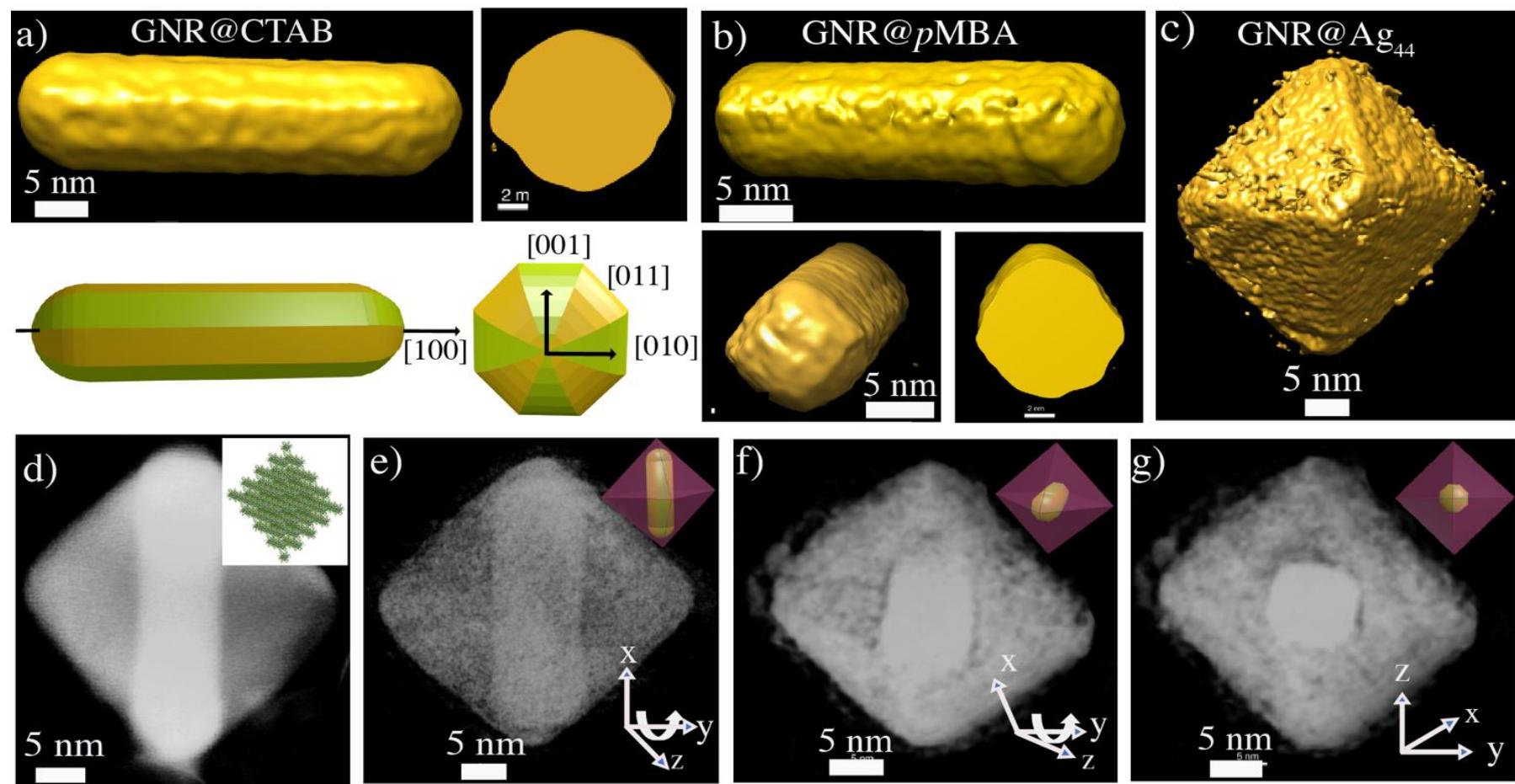
Assemblies and superstructures

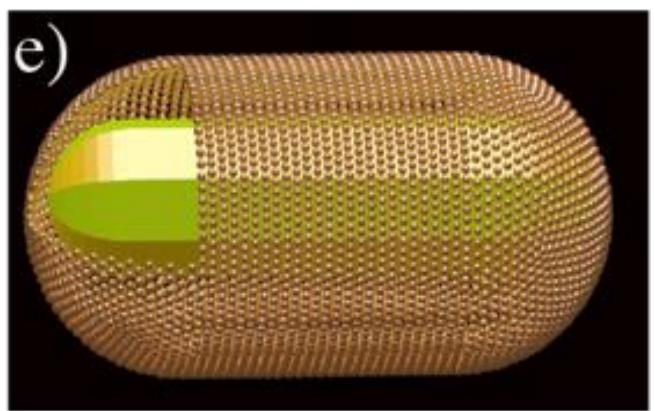
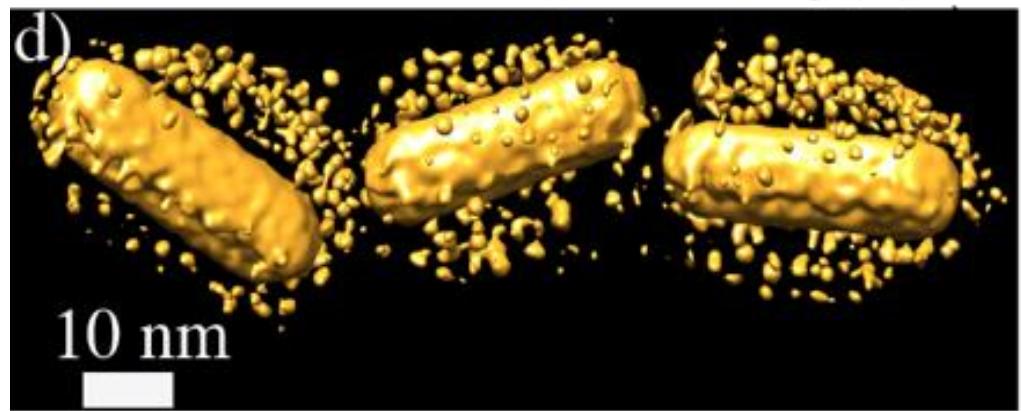
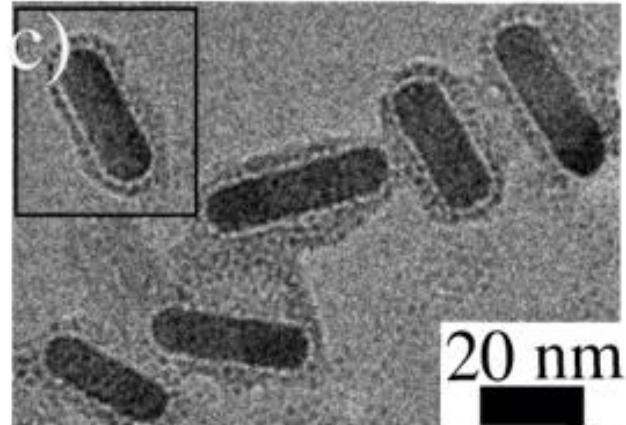
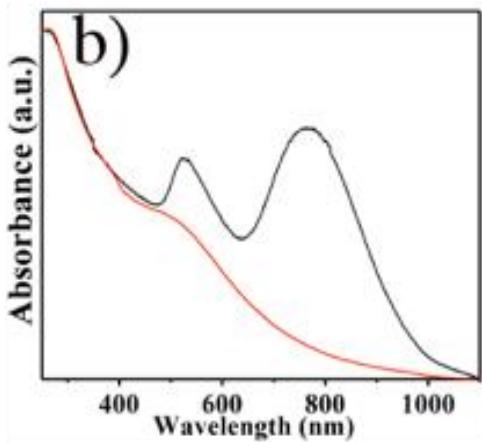
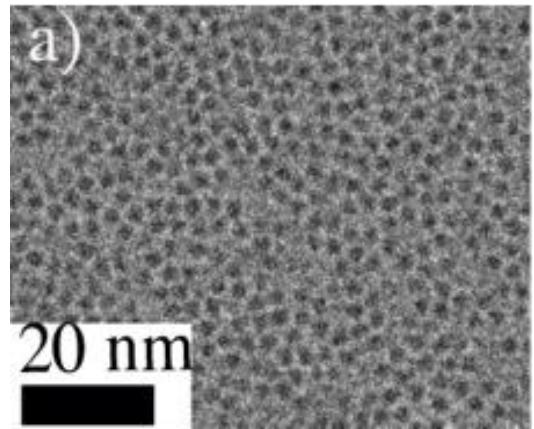
A) Ag_{29} supramolecular adduct with crown ether



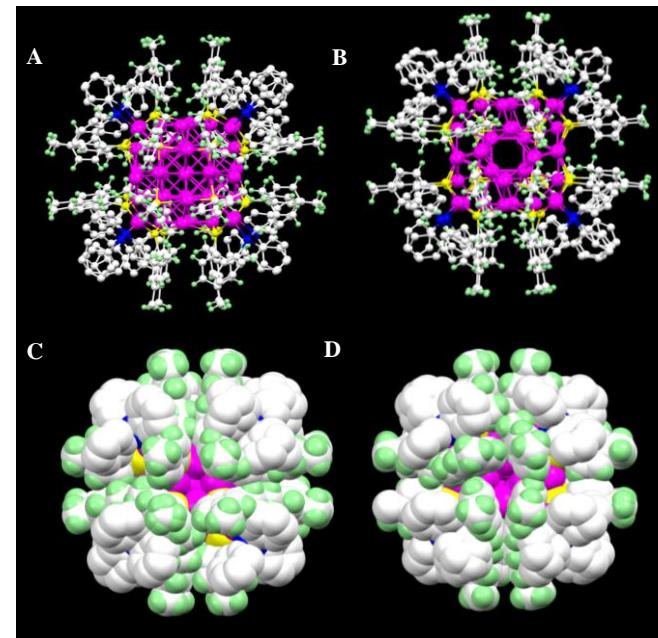
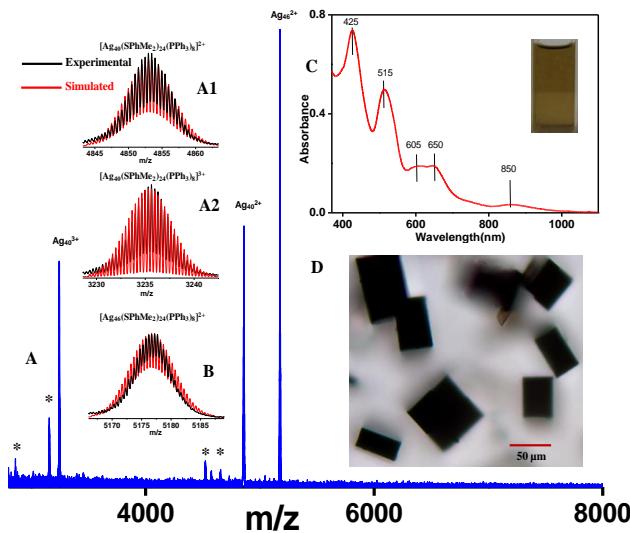








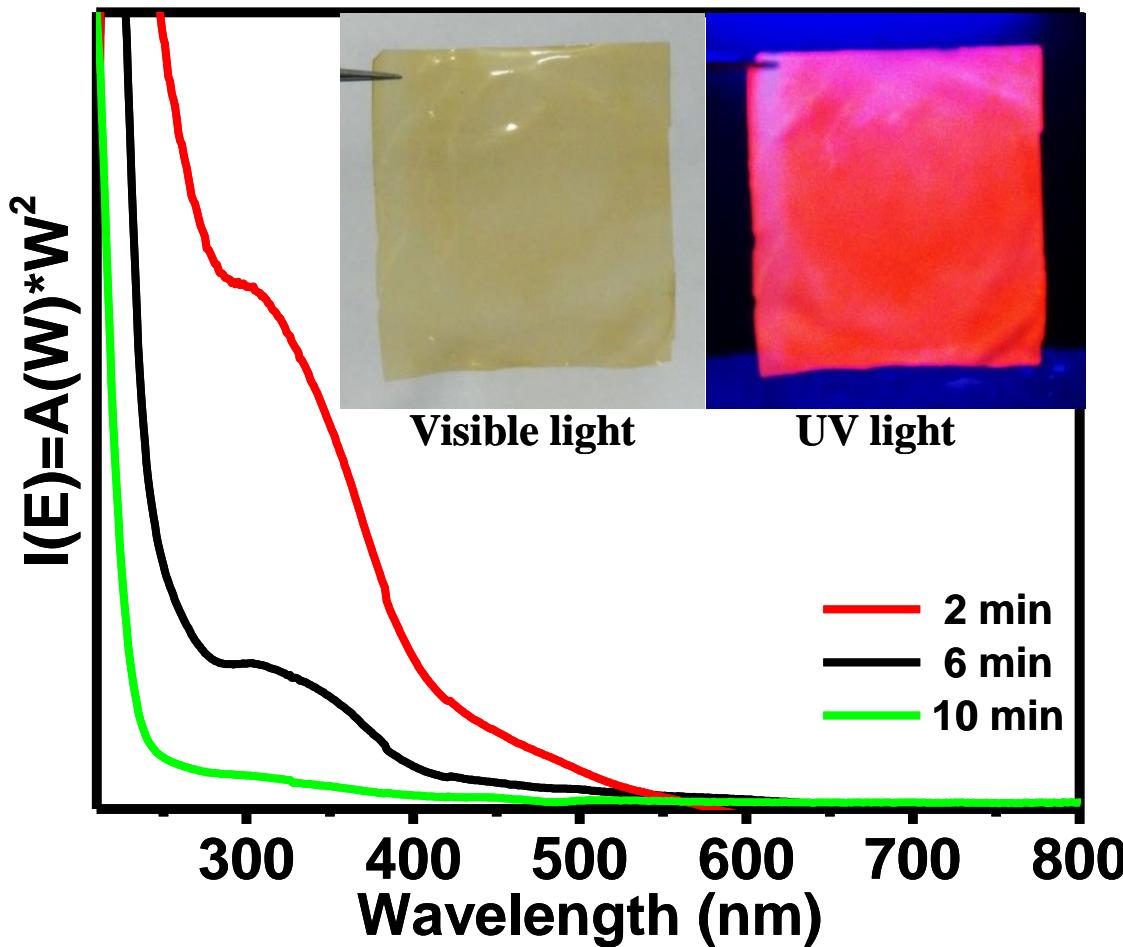
Ag_{40} and Ag_{46} with the same shell



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

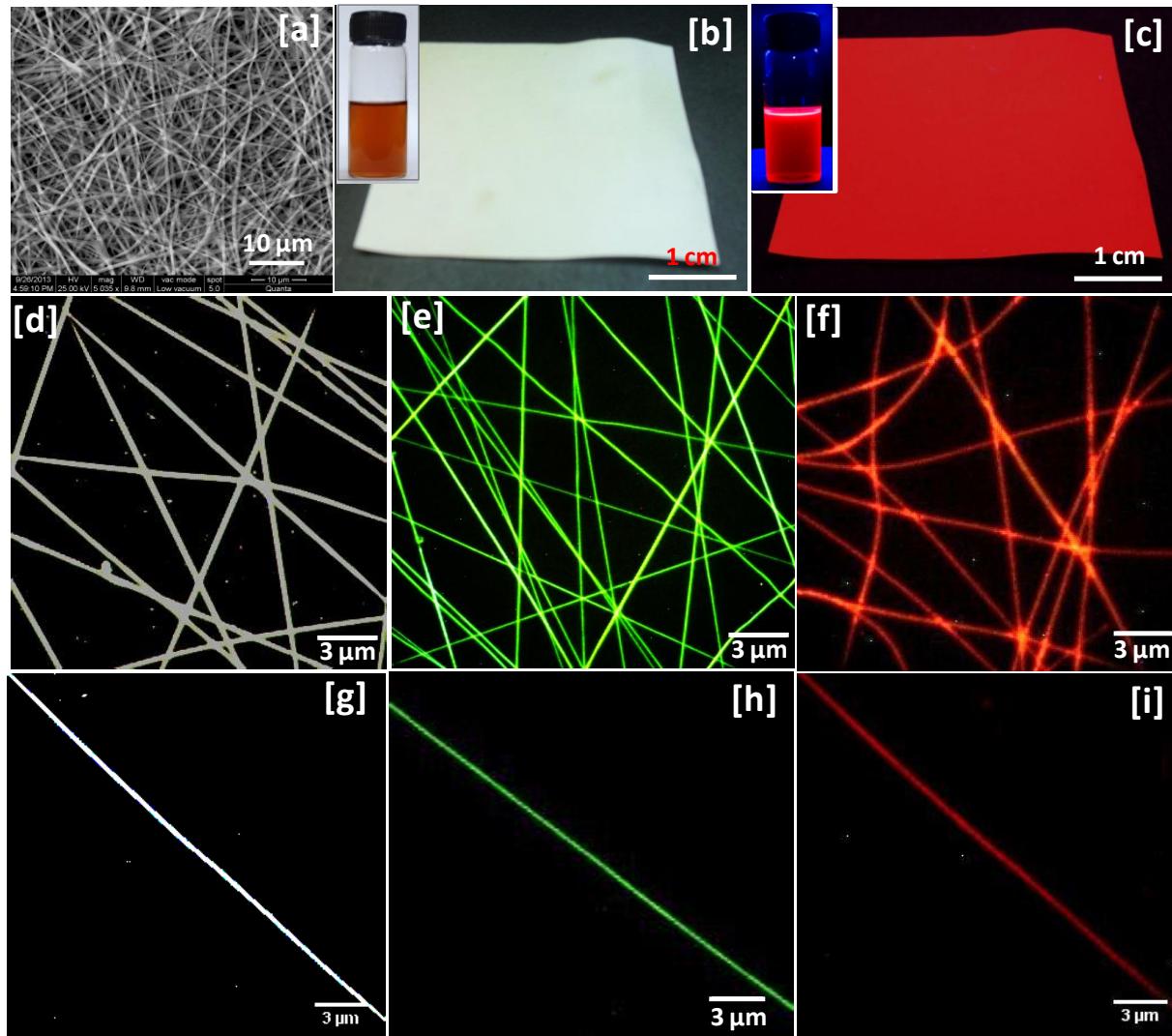
Sensors

Quantum cluster based metal ion sensing paper
Large area uniform illumination using quantum cluster

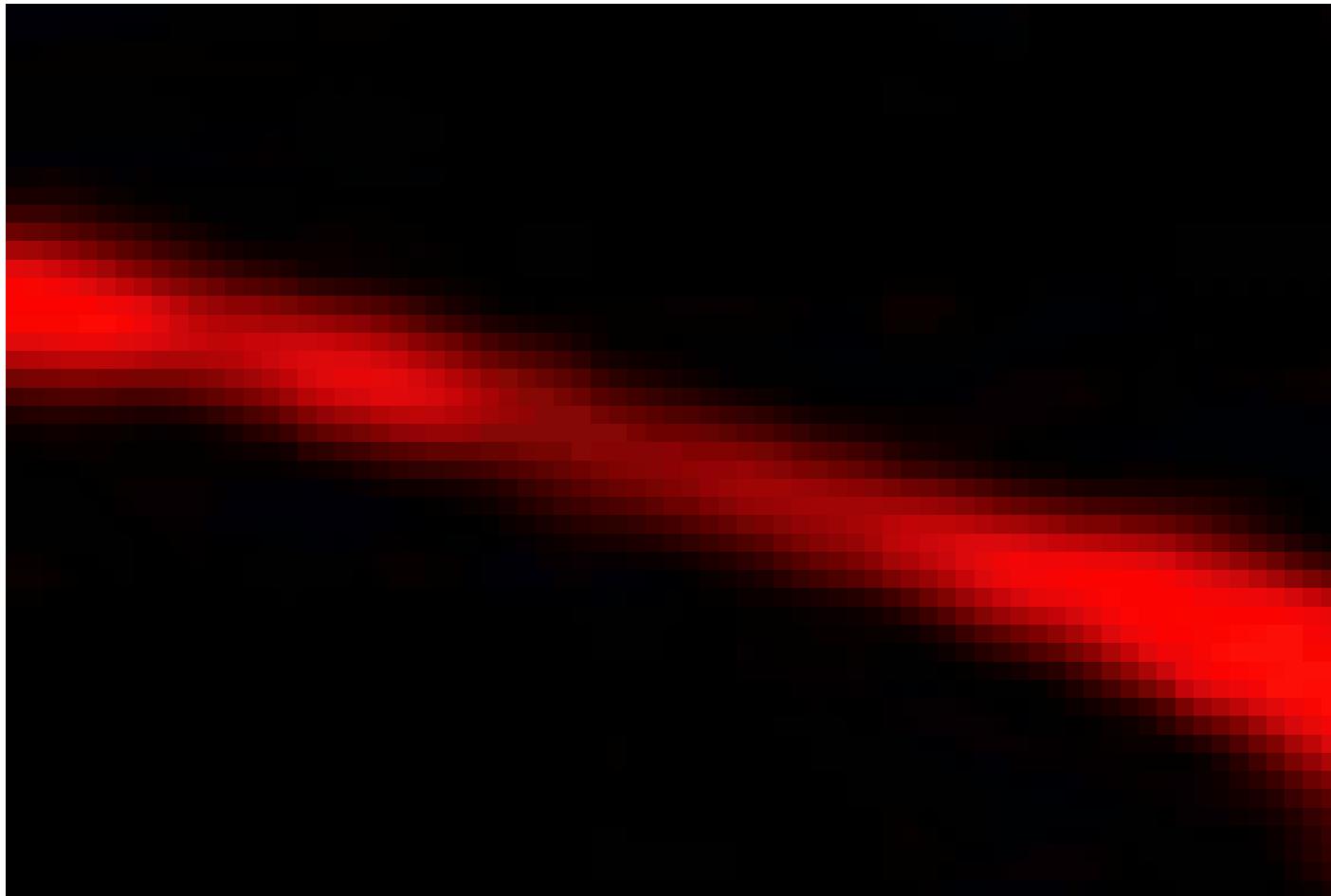


Decrease in the absorption of Au_{15} as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

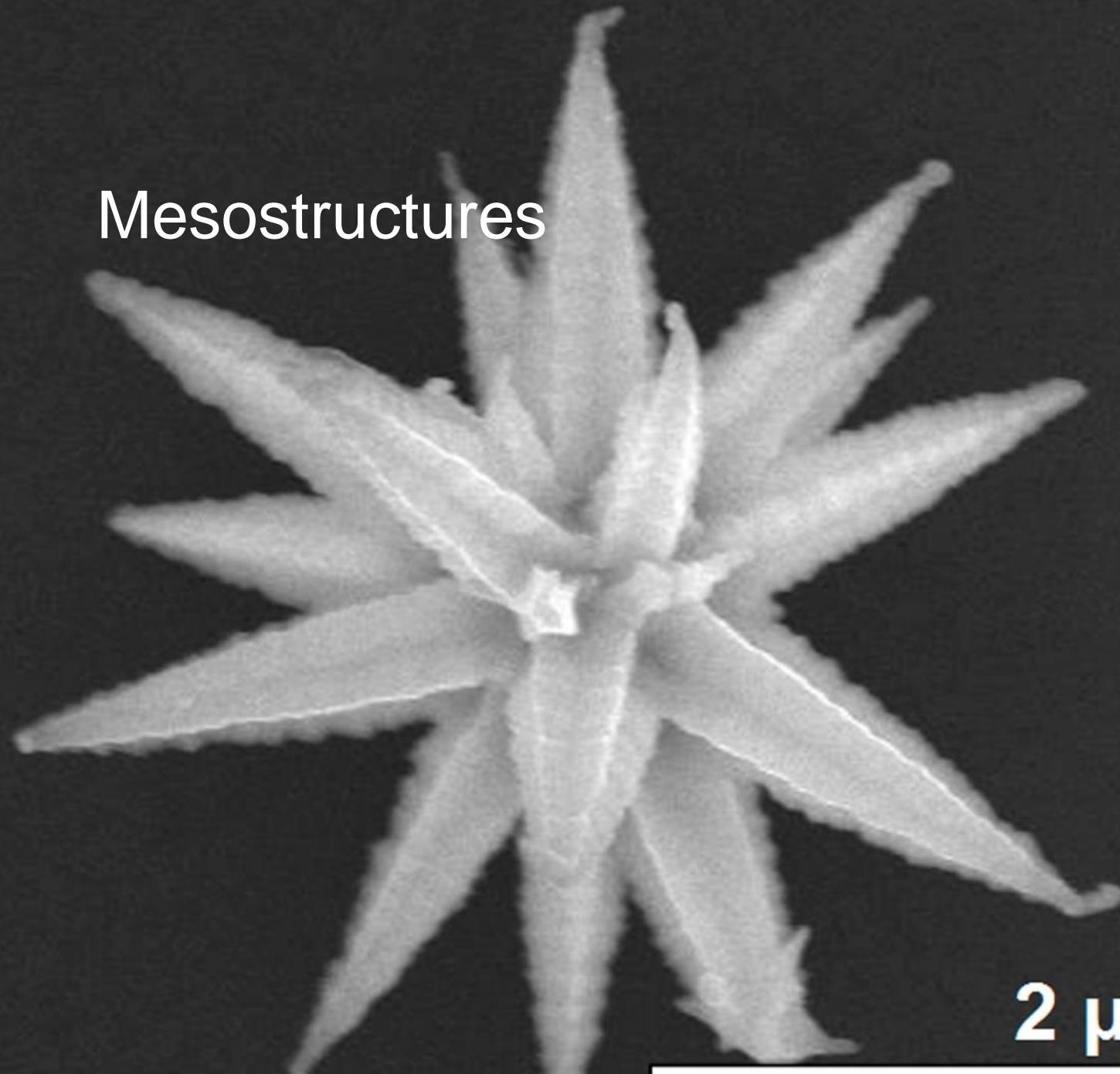
Approaching detection limits of tens of Hg²⁺



Video of mercury quenching experiment using the nanofiber

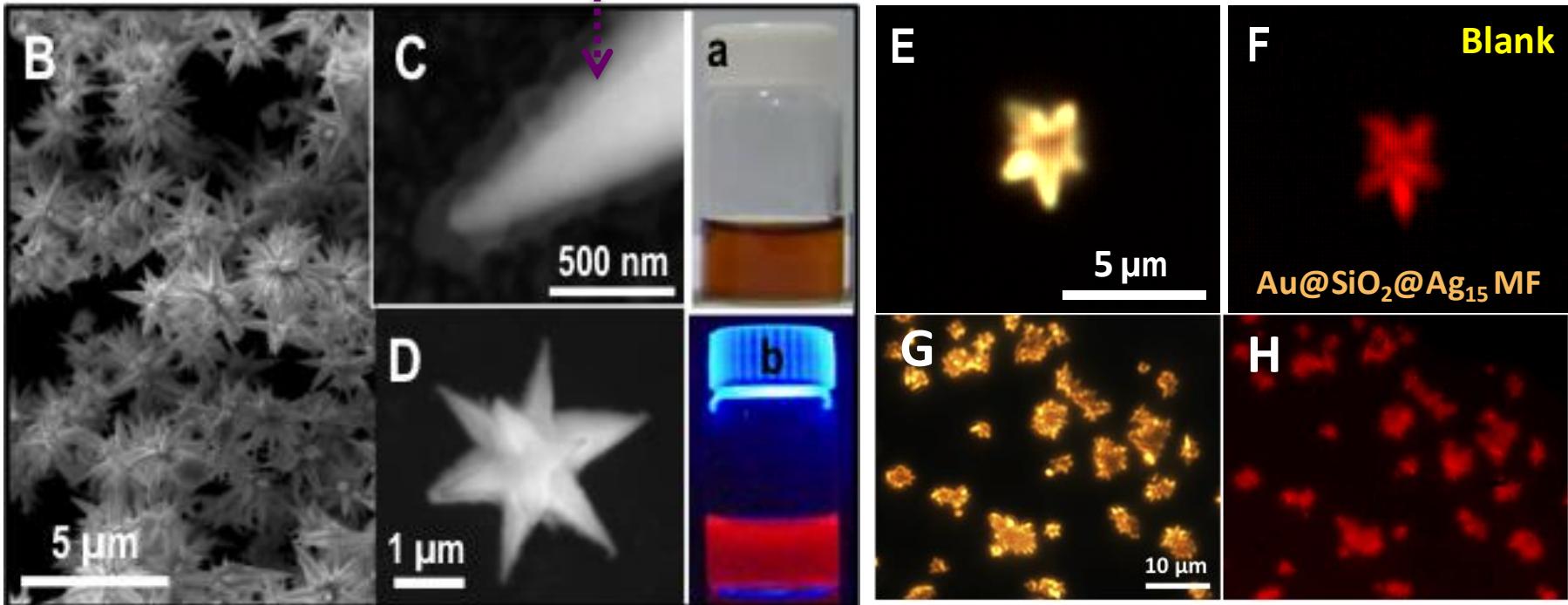
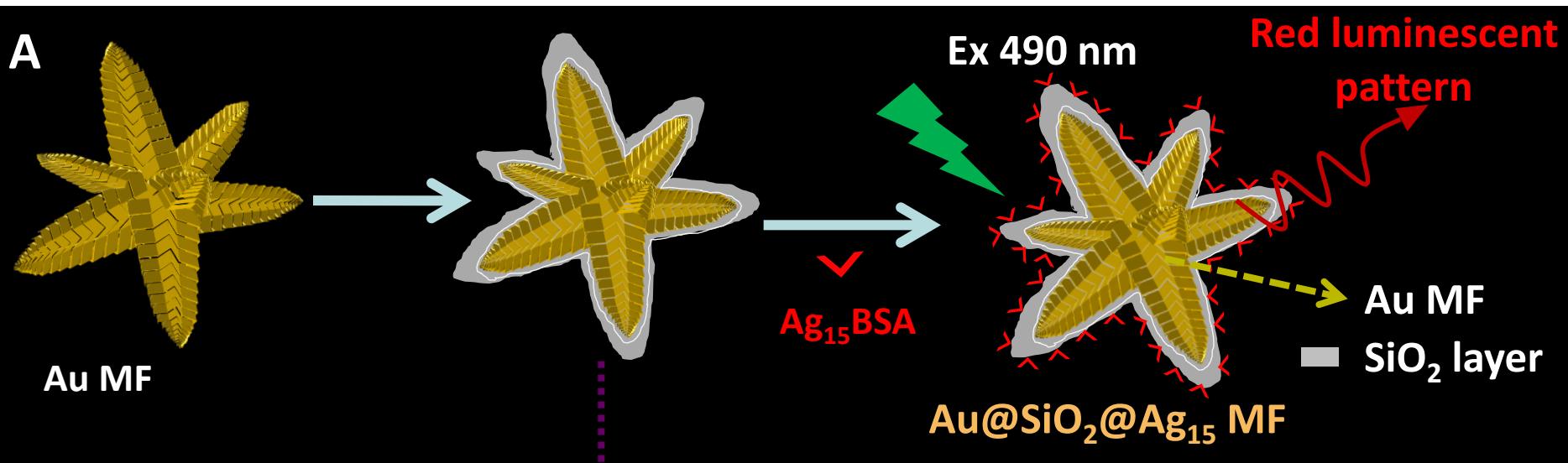


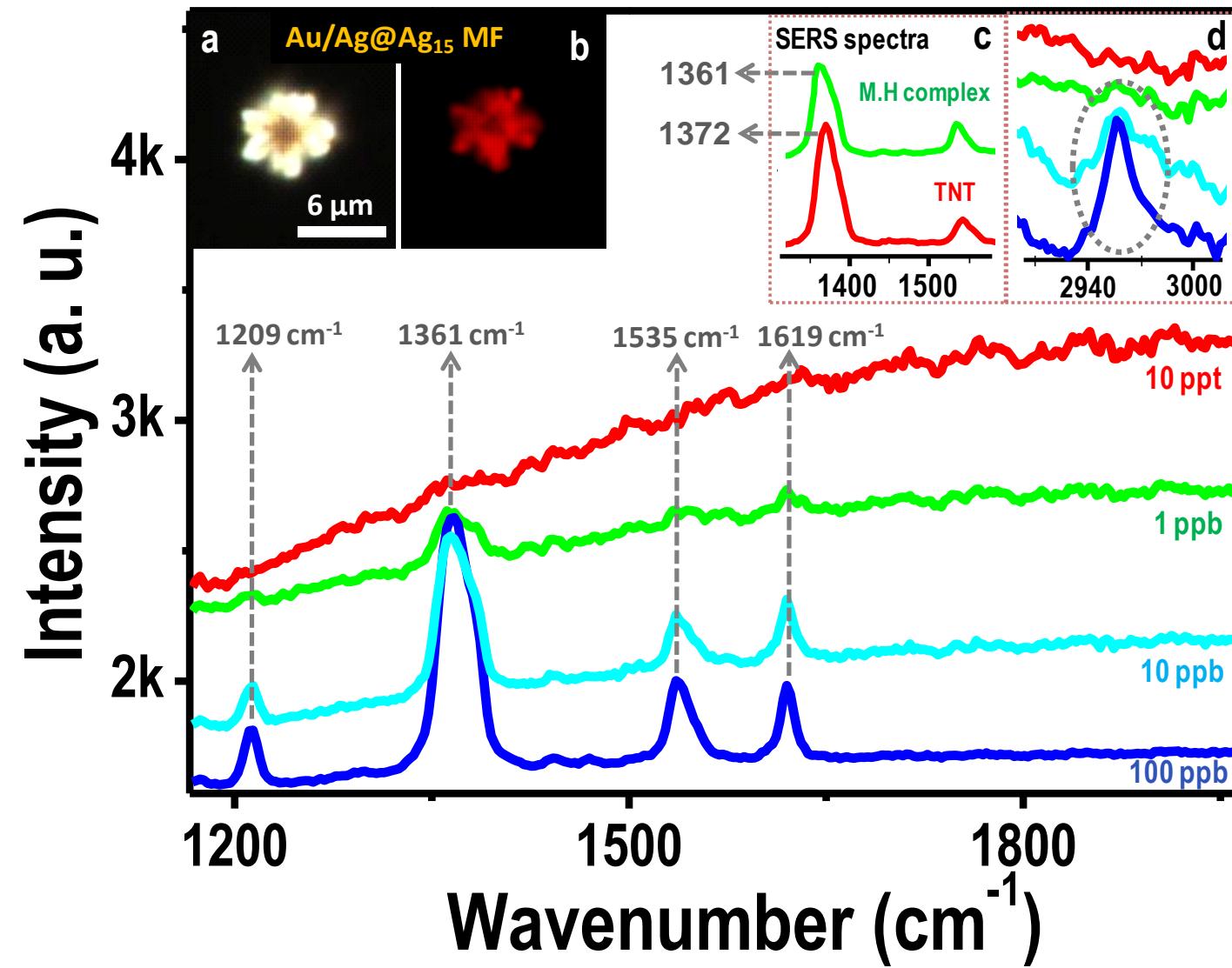
Mesostructures



2 μm

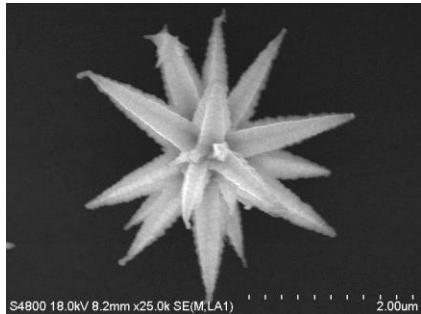
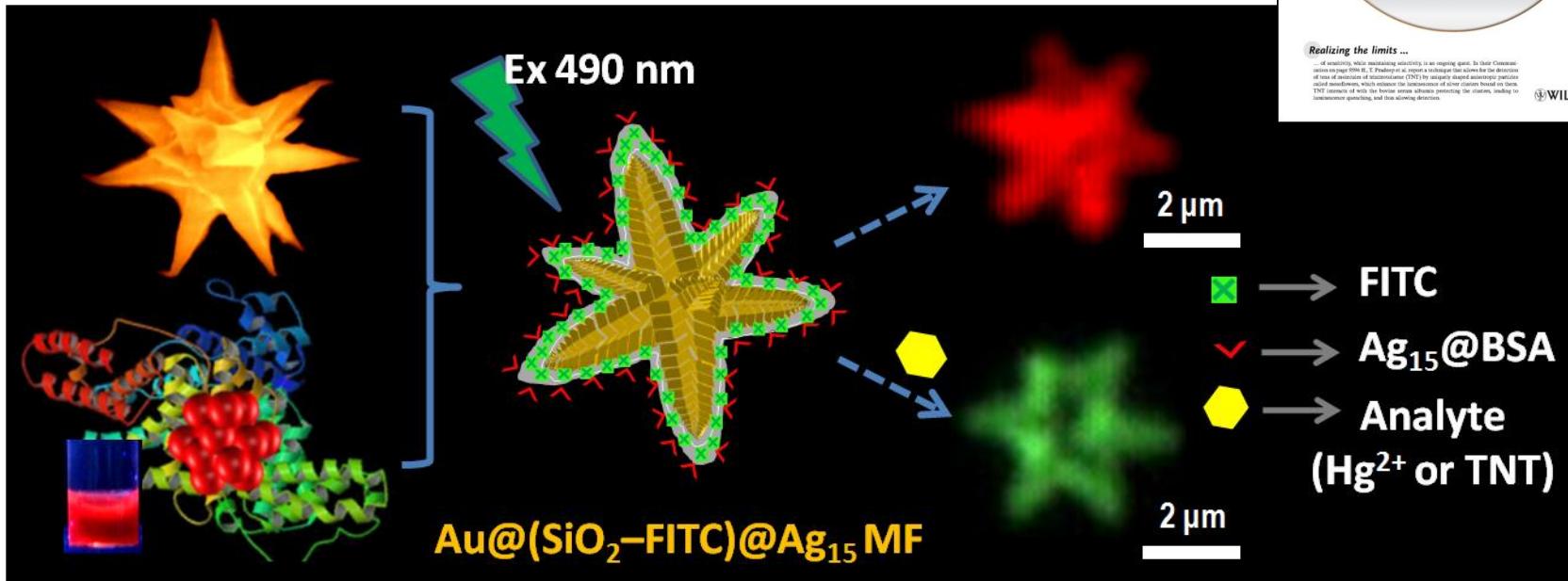
Designing a sensor





Raman spectra showing the gradual evolution of TNT features as the concentration of TNT added to Au/Ag@Ag₁₅ MFs (a and b) increases. (c) Comparison of the symmetric and asymmetric NO₂ stretching bands in the SERS spectra of TNT before (black) and after Meisenheimer complex formation (gray). (d) The gradual appearance of a Raman band at 2960 cm^{-1} .

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

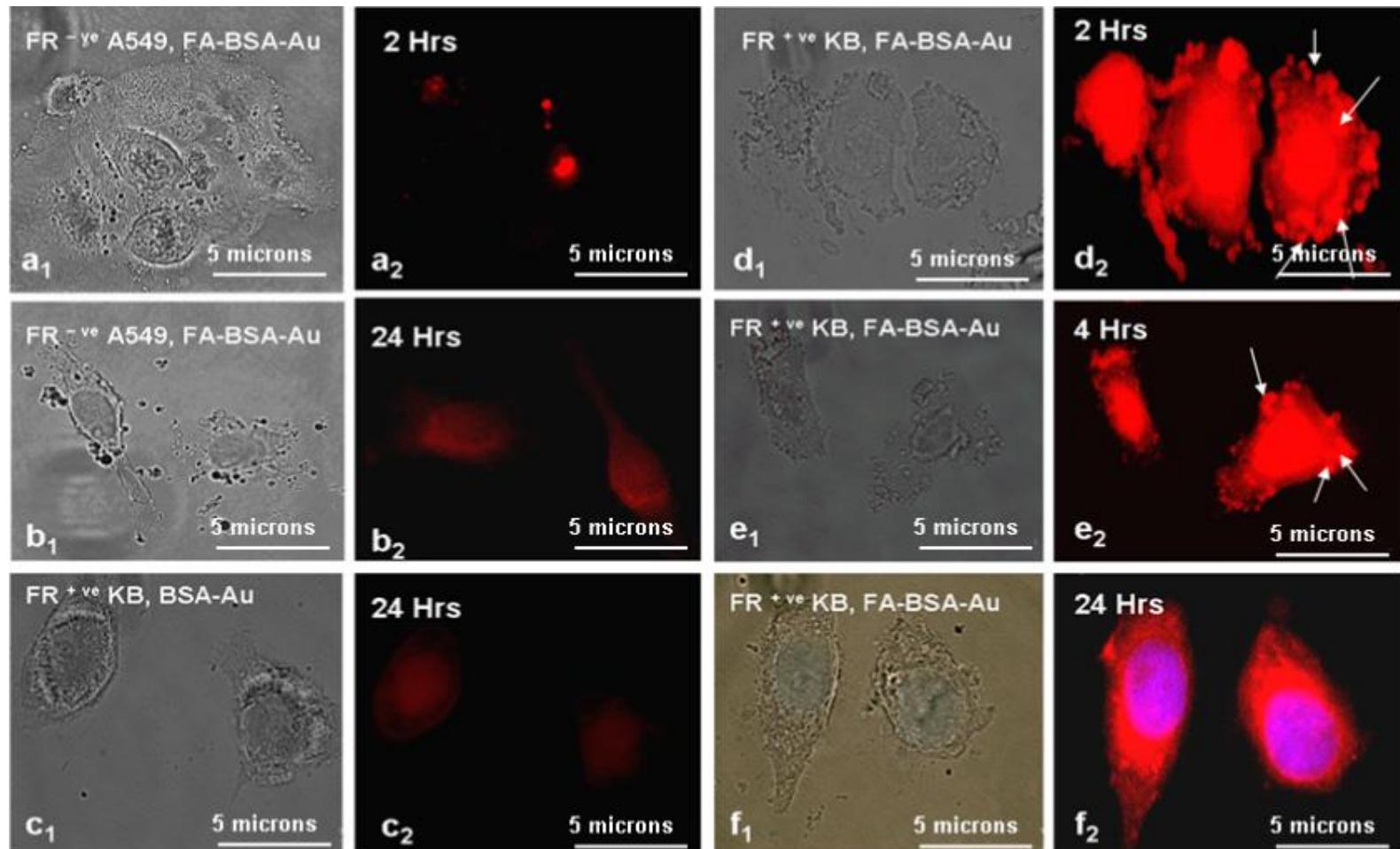


Figure 8. Fluorescent microscopic images showing interaction of Au–BSA–FA NCs with different types of cell lines: (a₁)–(a₂) FR^{−ve} lung carcinoma A549, (b₁)–(b₂) FR-depressed oral cell carcinoma, KB, (c₁)–(c₂) FR^{+ve} KB cells with unconjugated Au clusters, (d₁)–(d₂) FR^{+ve} KB cells with FA-conjugated Au clusters at 2 h, (e₁)–(e₂) 4 h and (f₁)–(f₂) 24 h of incubation.

Catalysis
Energy harvesting - Solar cells

Summary

- Atomically precise clusters is a new area of materials science
- Chemistry of these systems show new excitements
- Borromean ring diagram of clusters can be used to understand such reactions
- Their extremely fast solution state dynamics is a puzzle
- They show promising properties useful for applications
- Clusters are indeed molecules
- New materials are coming !

Clean water through advanced materials















Department of Science and Technology
Thank you