Now in the 60th year

Atomically precise noble metal nanoparticles

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8th ChinaNANO, Beijing, August 17-19, 2019

2019

ACCOUNTS of chemical research

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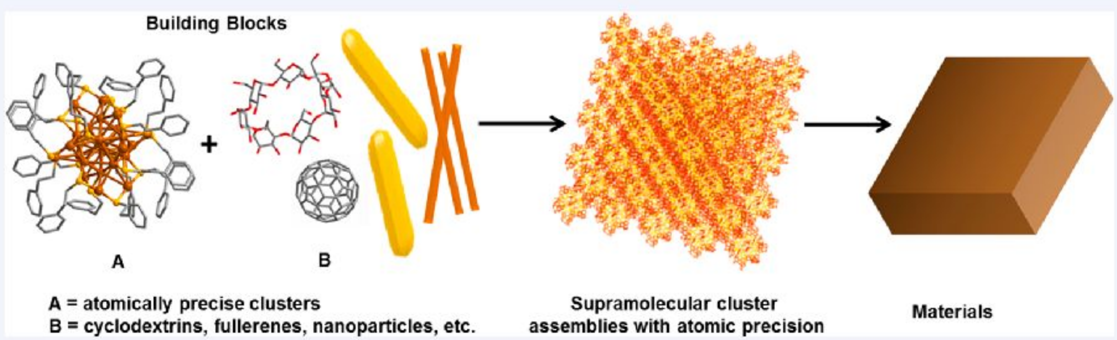
1 # Approaching Materials with Atomic Precision Using Supramolecular
2 # Cluster Assemblies

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



Contents

CHEMICAL REVIEWS

Review

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

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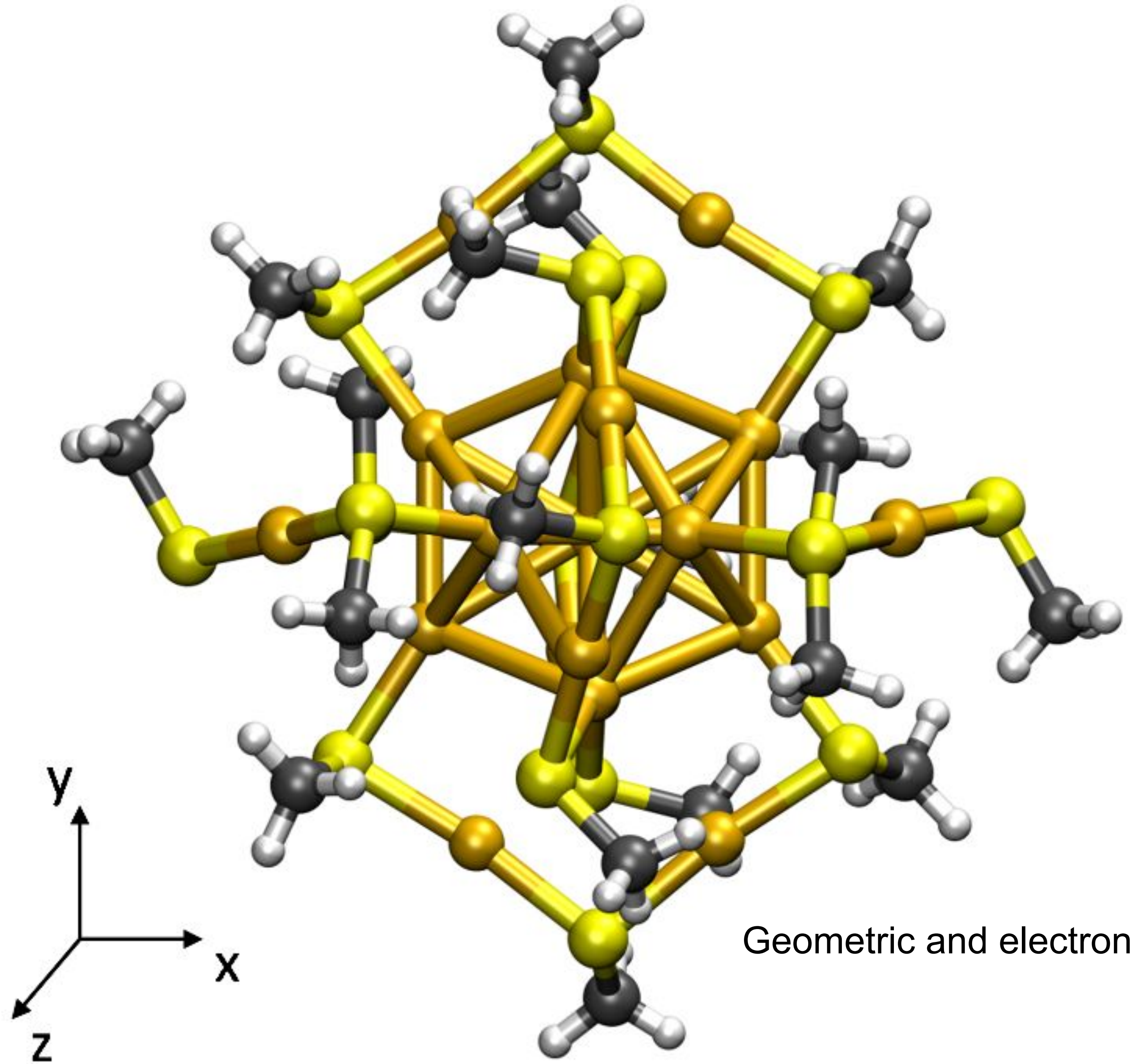
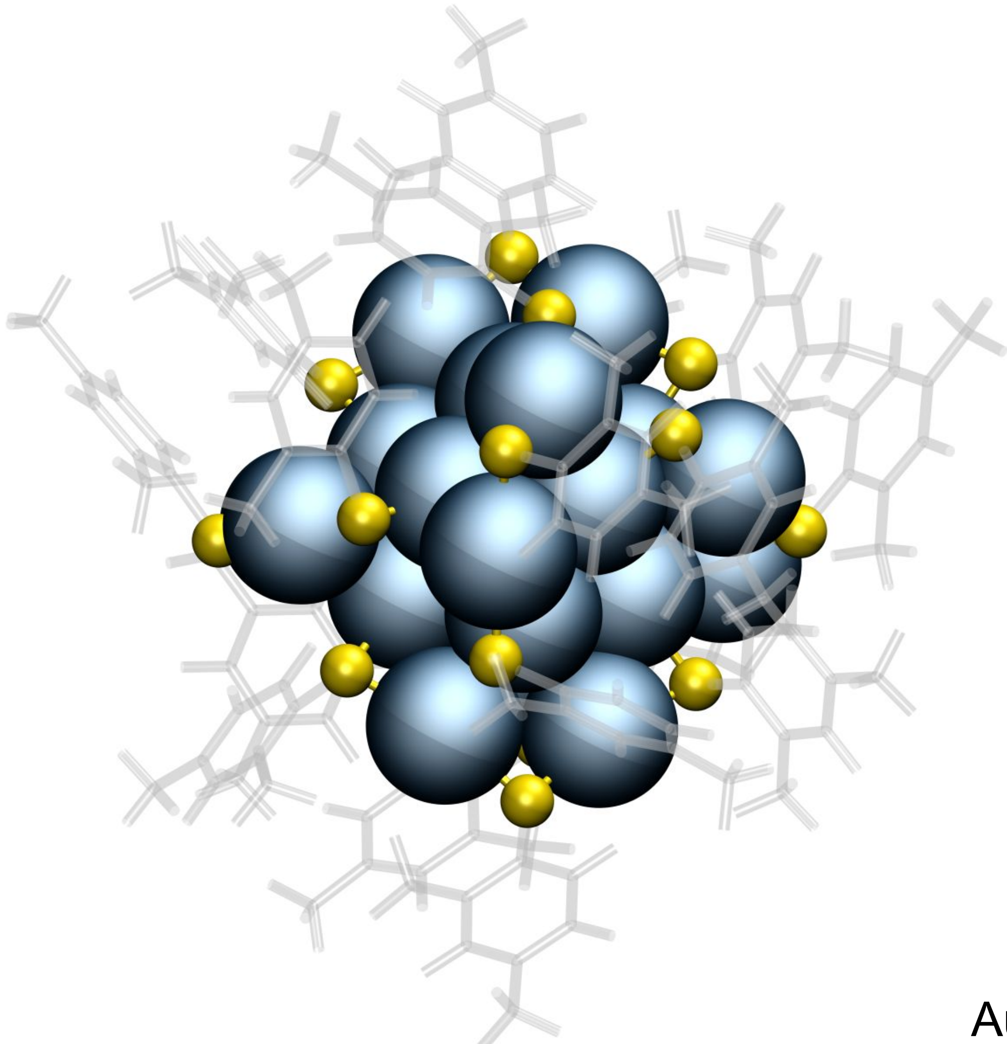
Supporting Information

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.

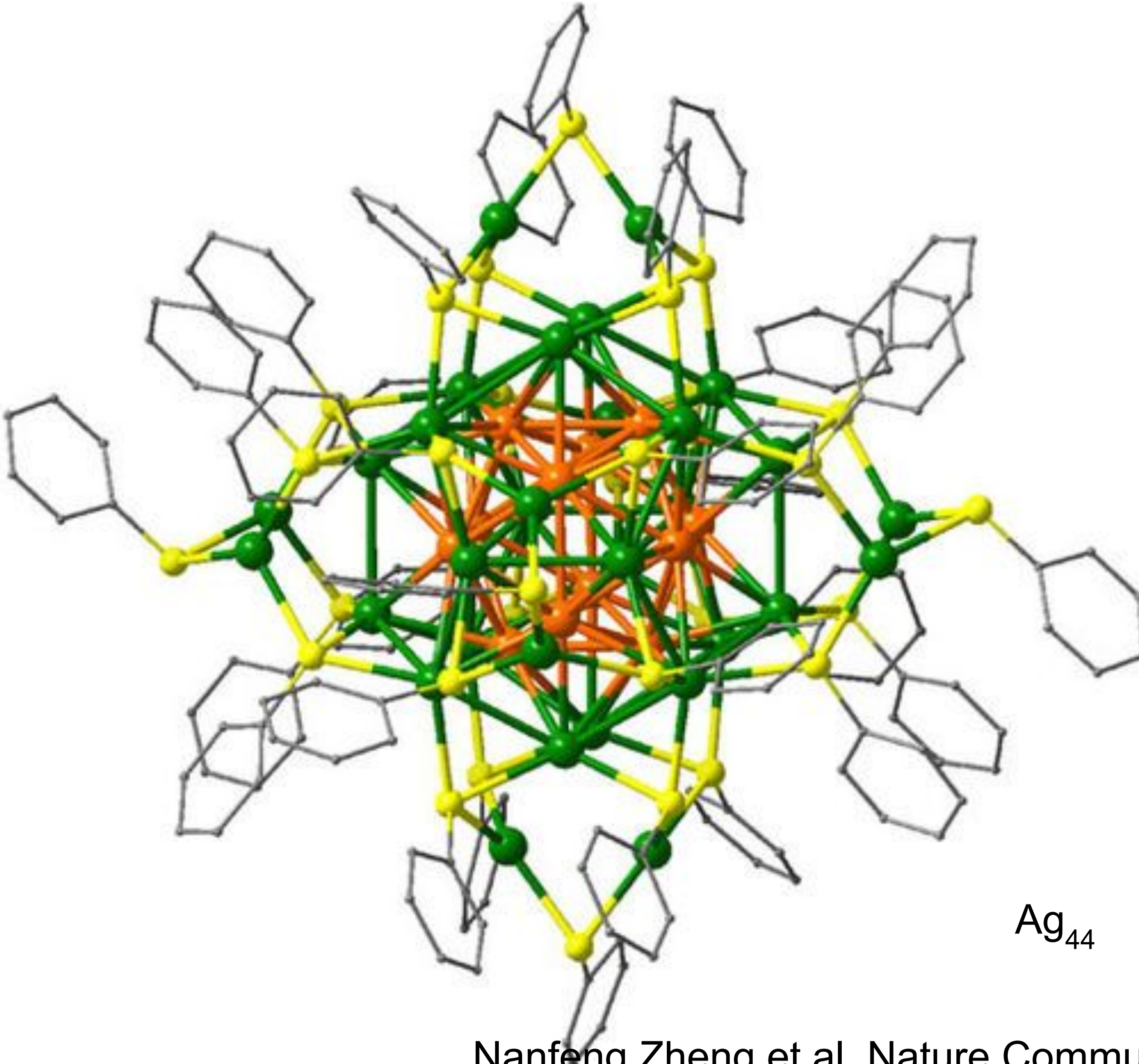
Also the pioneering work of R. W. Murray, Robert L. Whetten, Uzi Landman, Tatuya Tsukuda, Yuichi Negishi, Hannu Hakkinen, R. Jin, Nanfeng Zheng, Terry Bigioni, Osman Bakr, Kornberg, Jianping Xie, C. M. Aikens, Thomas Buergi, Quanming Wang, Amala Dass, …. A. W. Castleman Jr., H. Schmidbauer, …



Geometric and electronic shells

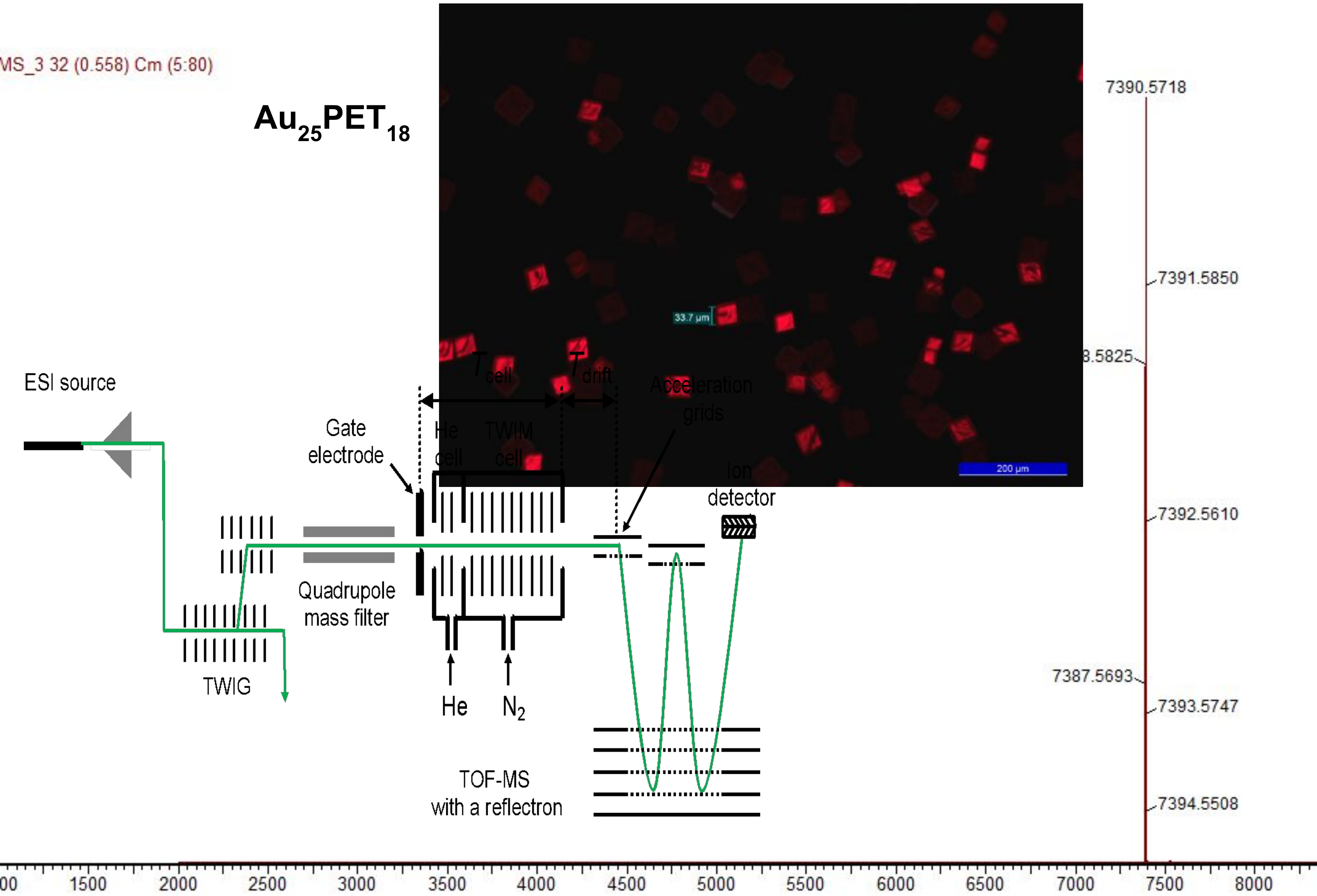


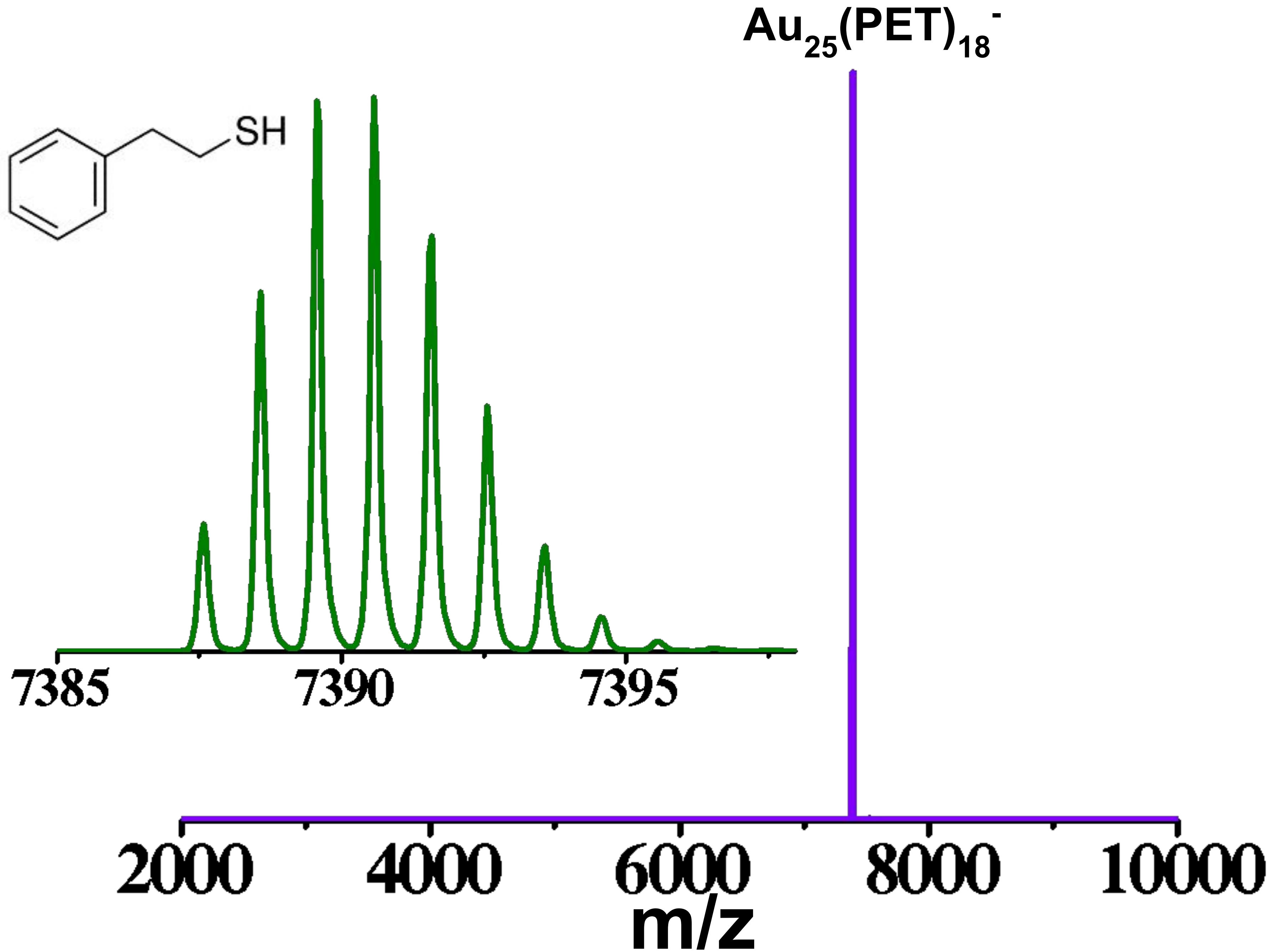
Au_{25}, Ag_{25}

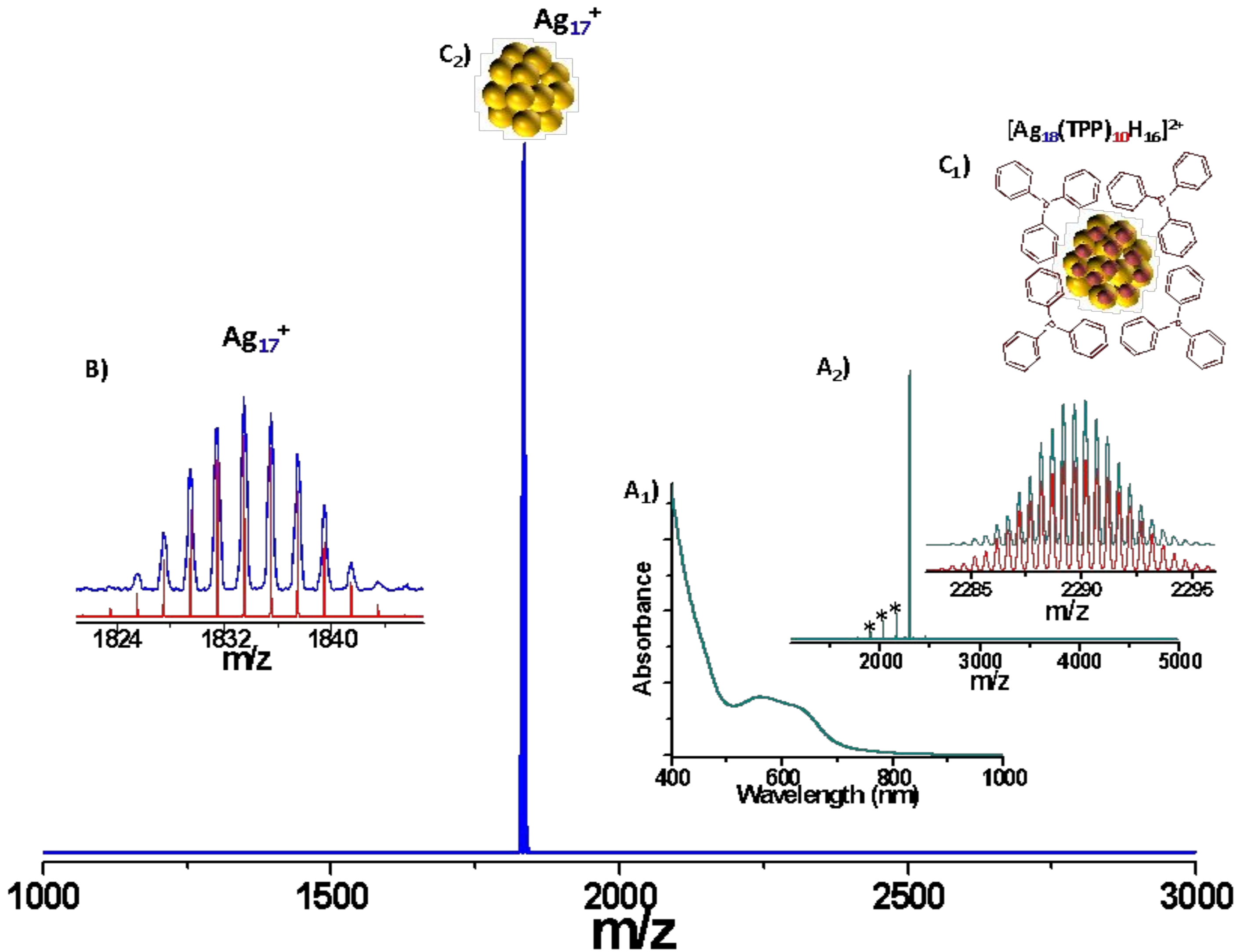


Ag_{44}

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

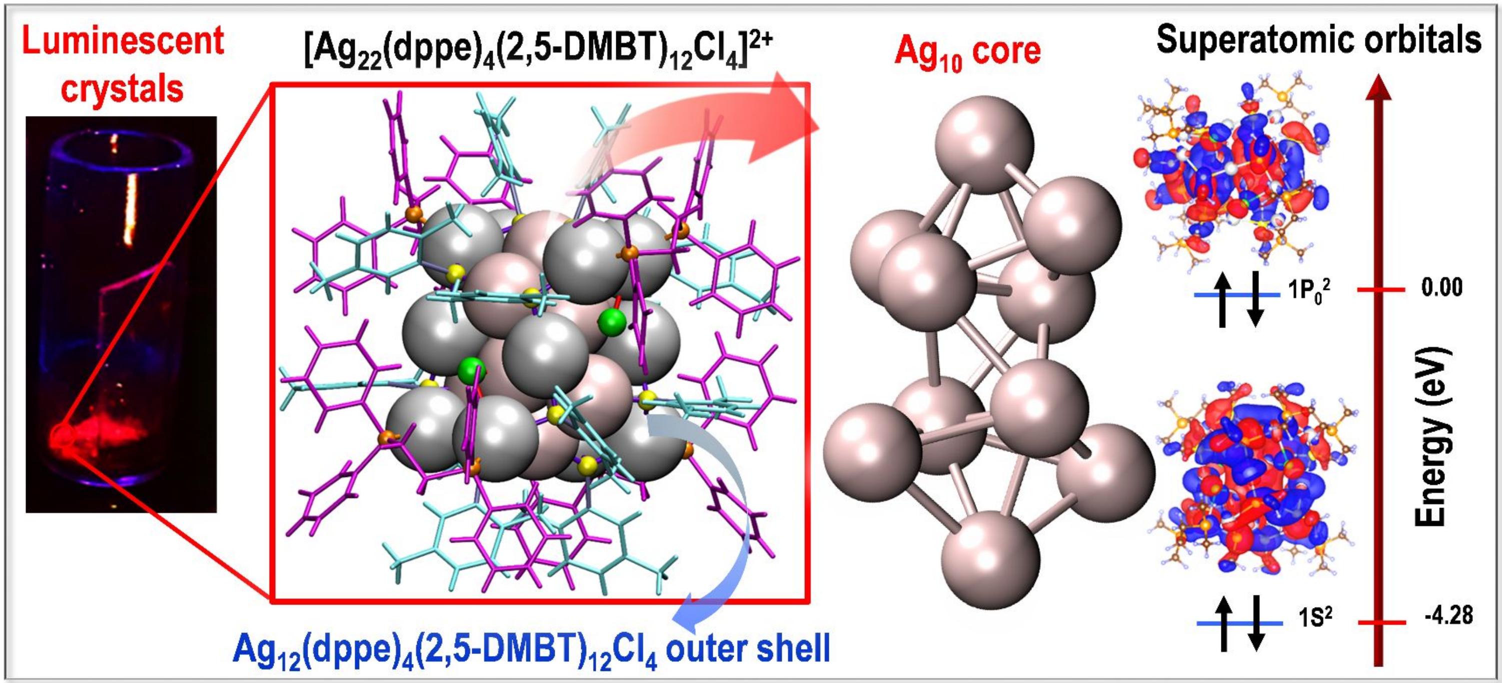

MS_3 32 (0.558) Cm (5:80)
Au25PET18
7390.5718
7391.5850
8.5825
7392.5610
7387.5693
7393.5747
7394.5508
00
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500
8000
33.7 µm
200 µm
ESI source
Gate electrode
He cell
TWIM cell
T cell
T drift
Acceleration grids
Ion detector
TWIG
Quadrupole mass filter
He
N2
TOF-MS with a reflectron


Au25(PET)18-
SH
7385
7390
7395
2000
4000
6000
8000
10000
m/z

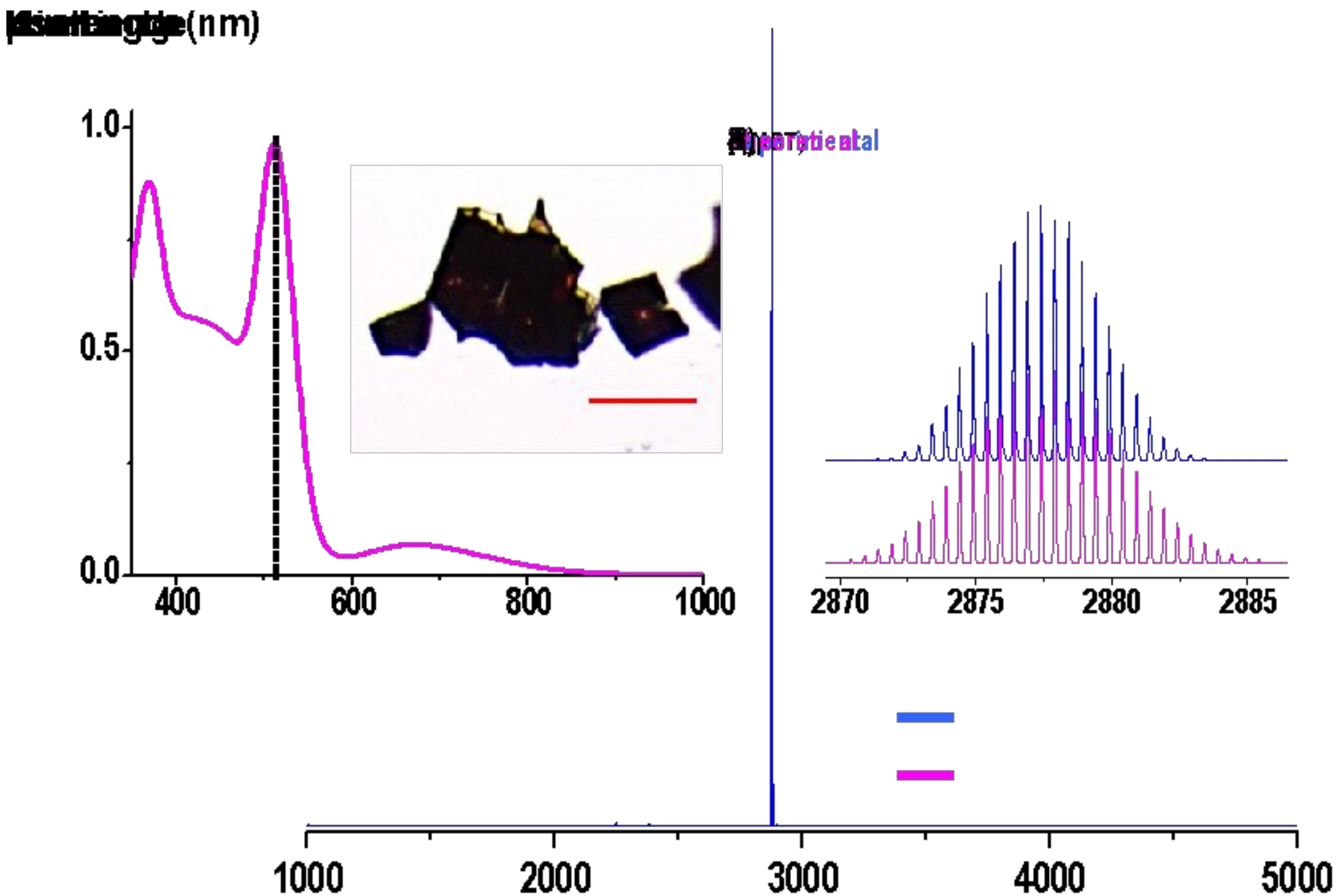


Atanu Ghosh, et. al., ACS Nano 2017

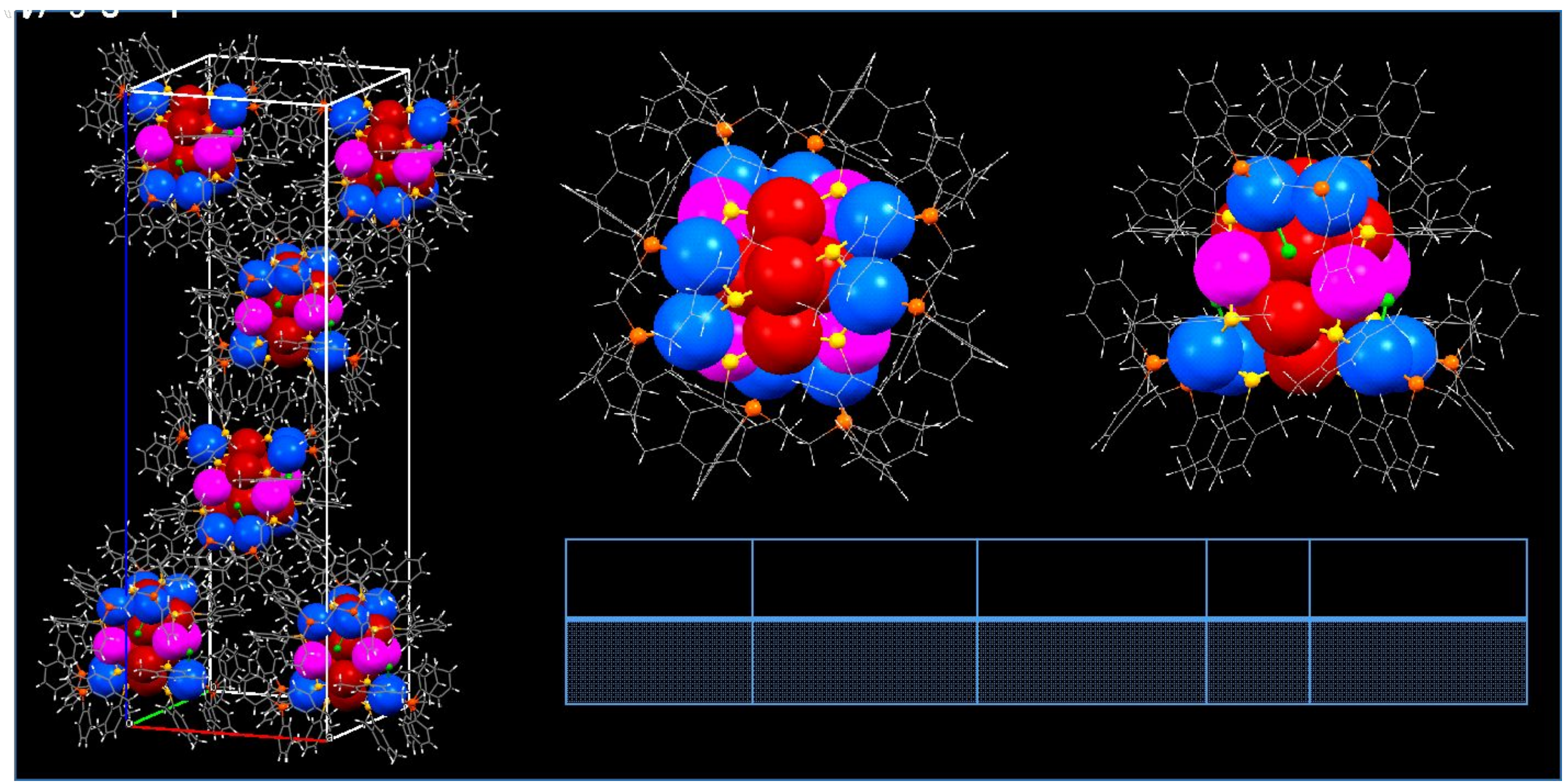
Ag_{10} Core in an Ag_{12} Shell: A Four-Electron Superatom



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}.



The overall structure of Ag_{22}: A) Unit cell with a tetragonal arrangement; B) top view; C) side view. Labels: red, blue and pink = Ag, yellow = S, orange = P, green = Cl, gray = C and white = H.

Chemistry of clusters

Reactions of clusters

Reactions between clusters

Inter-cluster reactions

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

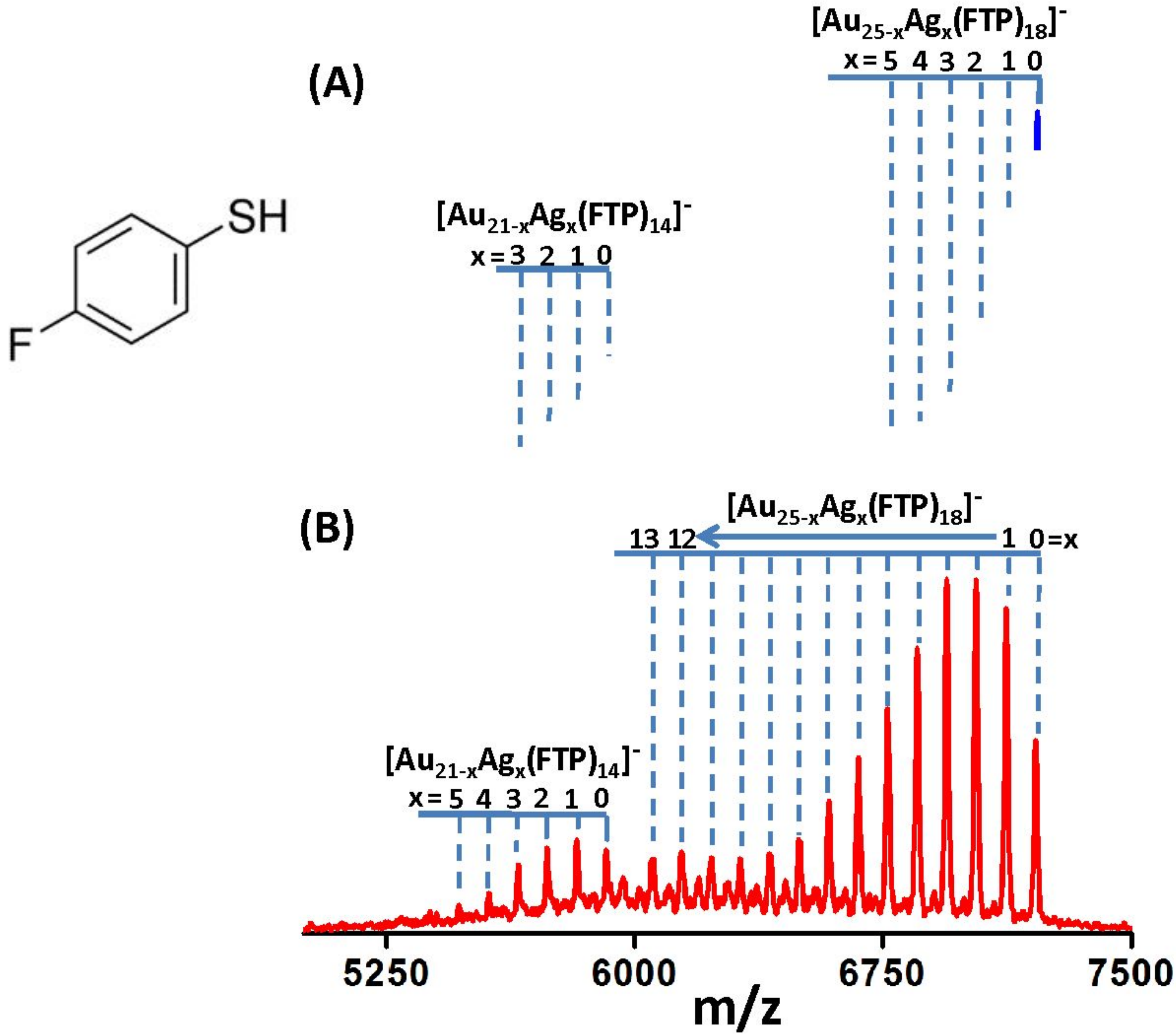
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

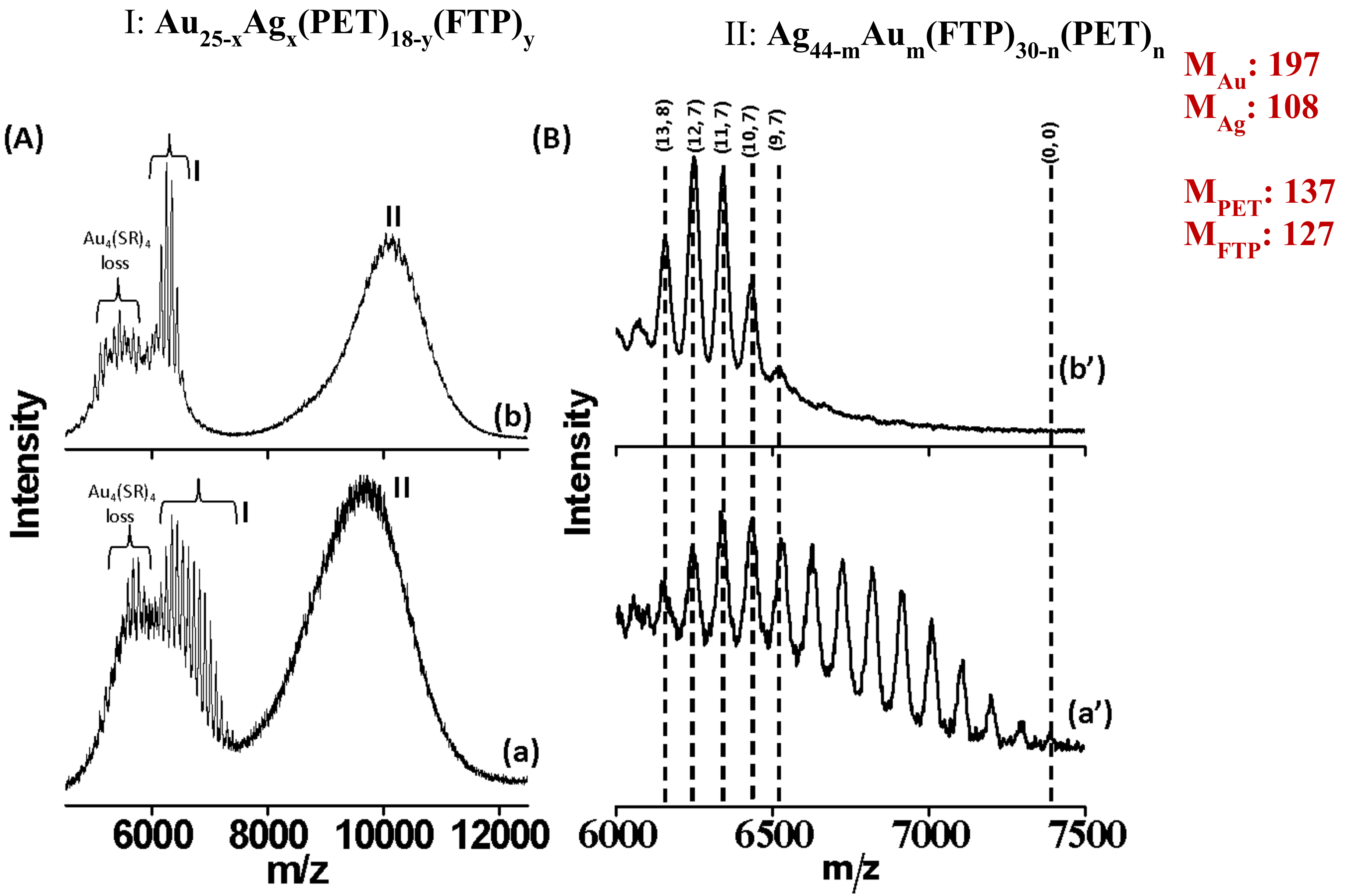
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India

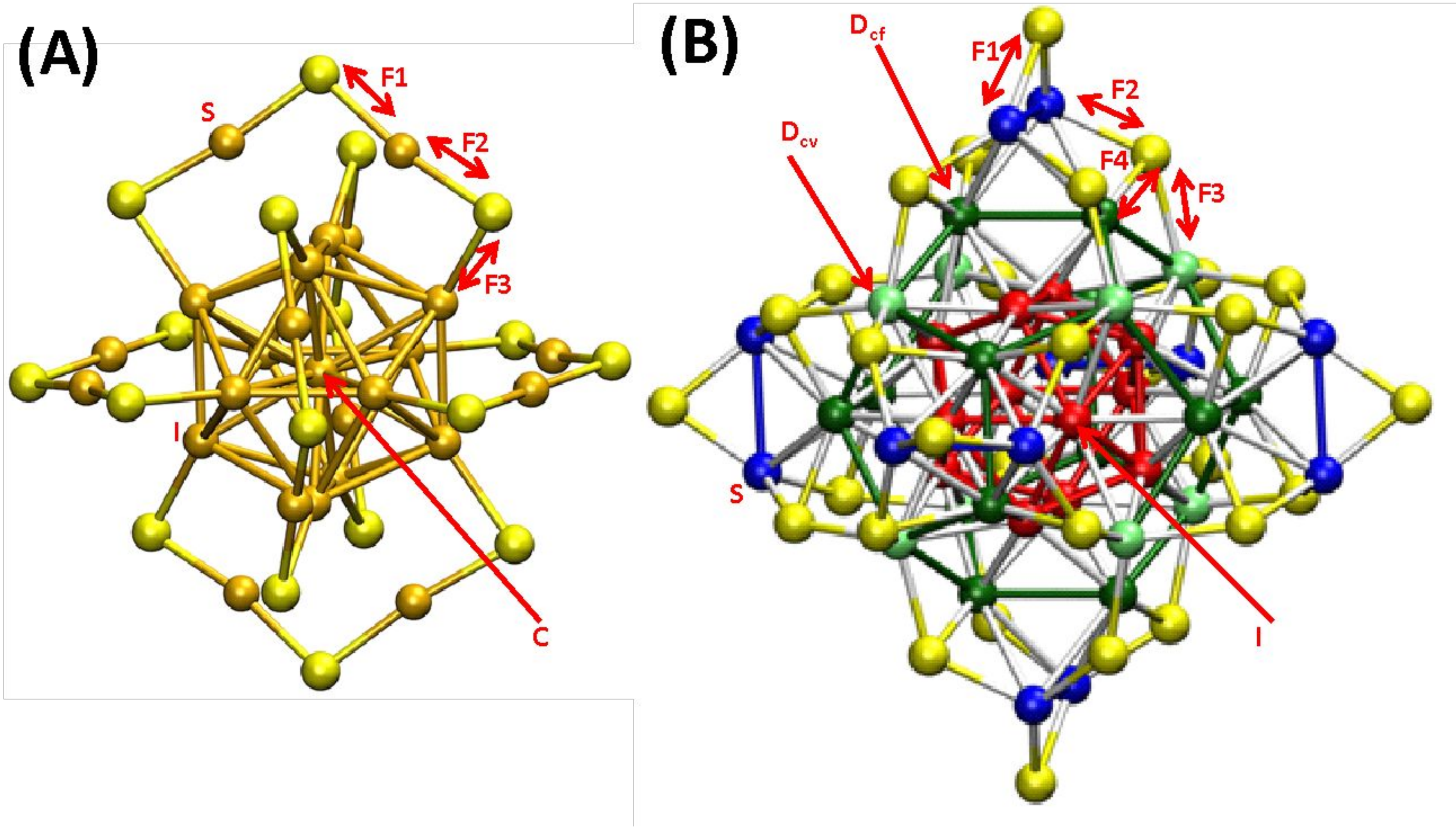
Supporting Information

A + B □ C + D

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




I: Au25-xAgx(PET)18-y(FTP)y
II: Ag44-mAum(FTP)30-n(PET)n
MAu: 197
MAg: 108
MPET: 137
MFTP: 127
(A)
(B)
Au4(SR)4 loss
I
II
(b)
(a)
Intensity
6000
8000
10000
12000
m/z
(13,8)
(12,7)
(11,7)
(10,7)
(9,7)
(0,0)
(b')
(a')
6500
7000
7500


(A)
S
F1
F2
F3
I
C
(B)
D_{cf}
D_{cv}
F1
F2
F4
F3
S
I

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

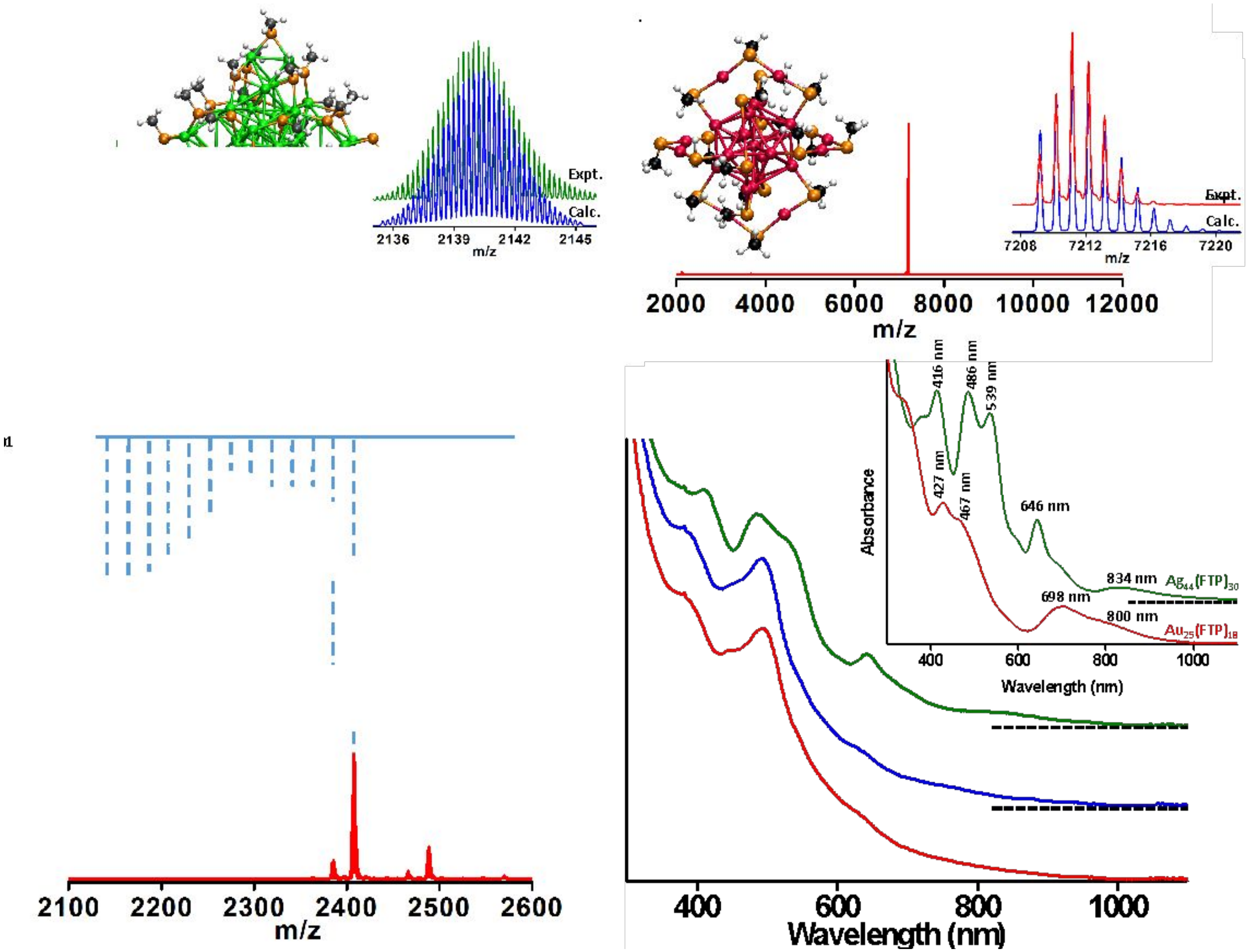
(B)

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

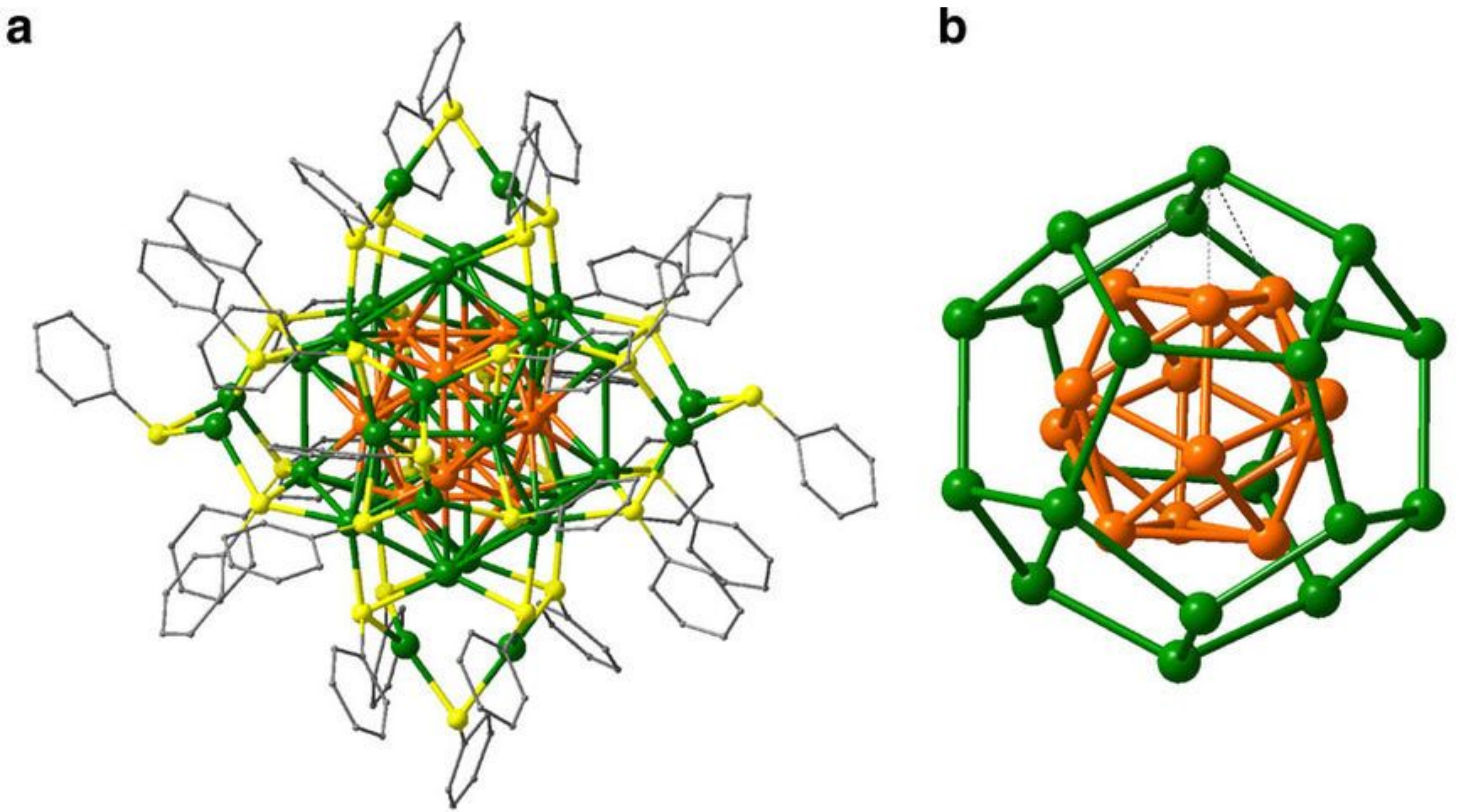
(C)

Location of Ag in $Au_{25-x}Ag_x(SR)_{18}$	Locations of Au in $Au_xAg_{44-x}(SR)_{30}$: 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

Shell closure in intercluster reactions



Krishnadas et al., ACS Nano 2017

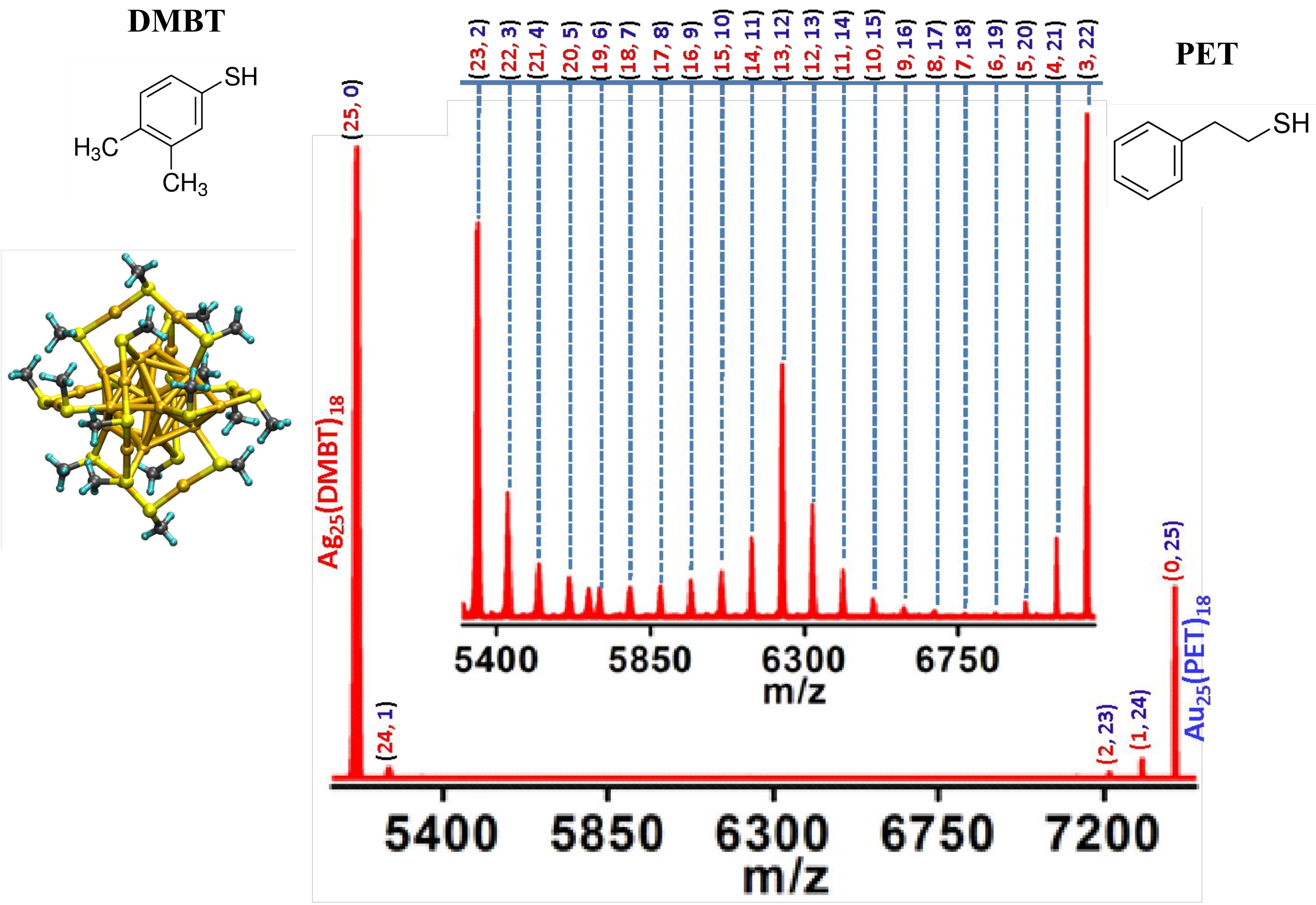


Nanfeng Zheng et al. Nature Communications, 2013

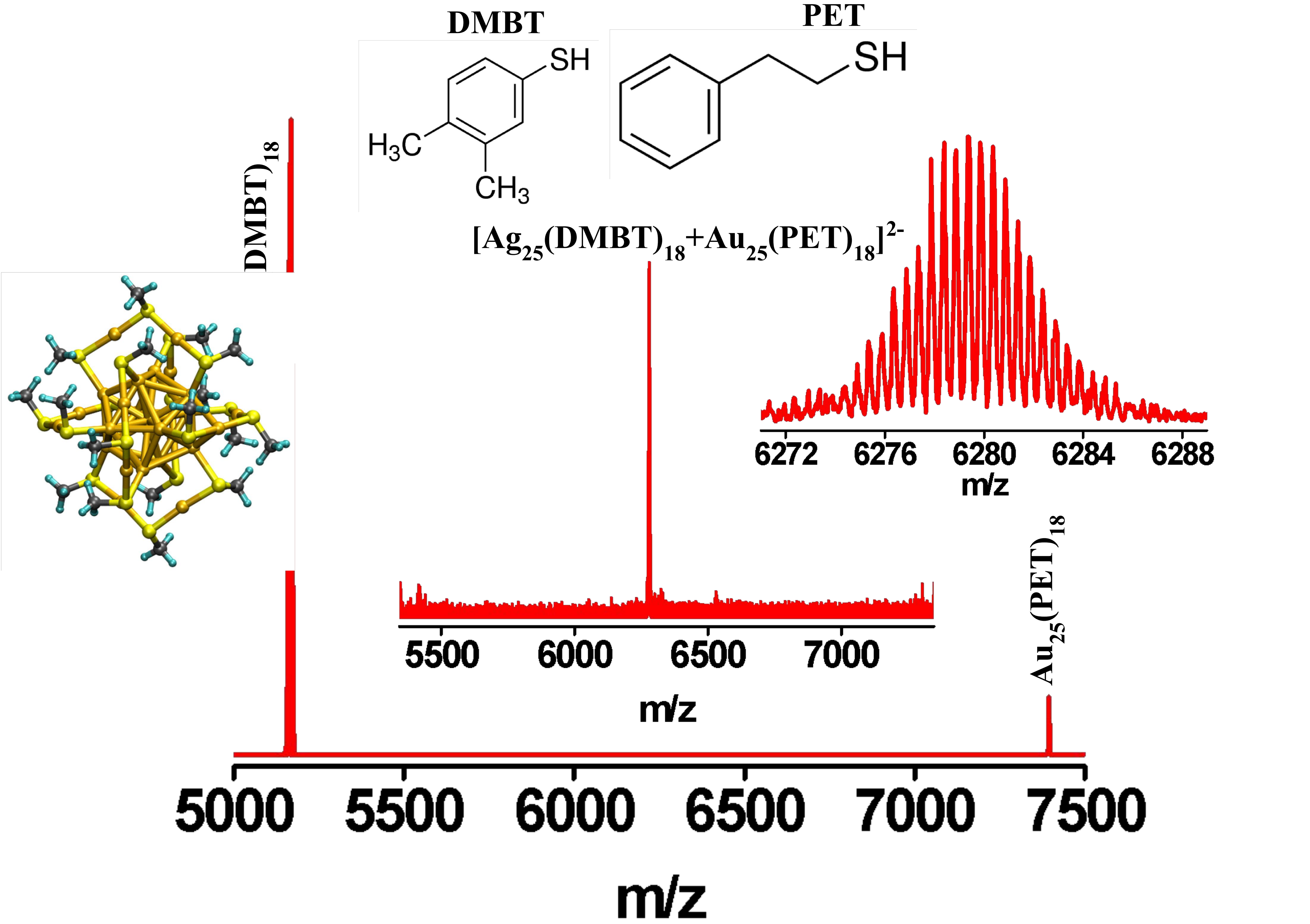
Ag_{25}-Au_{25} experiments

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

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

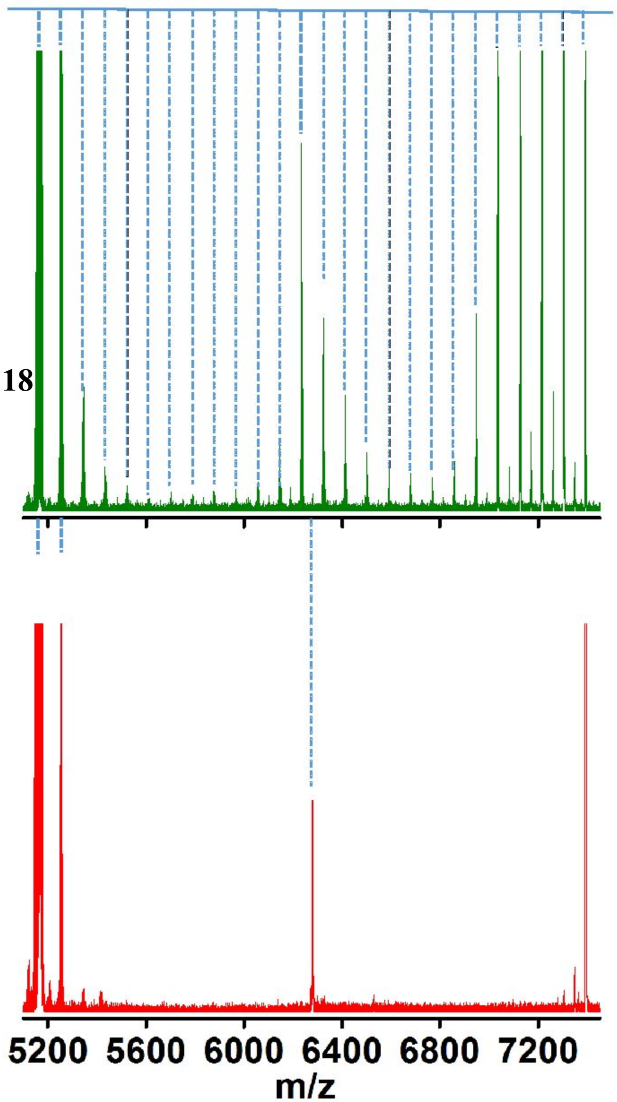


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

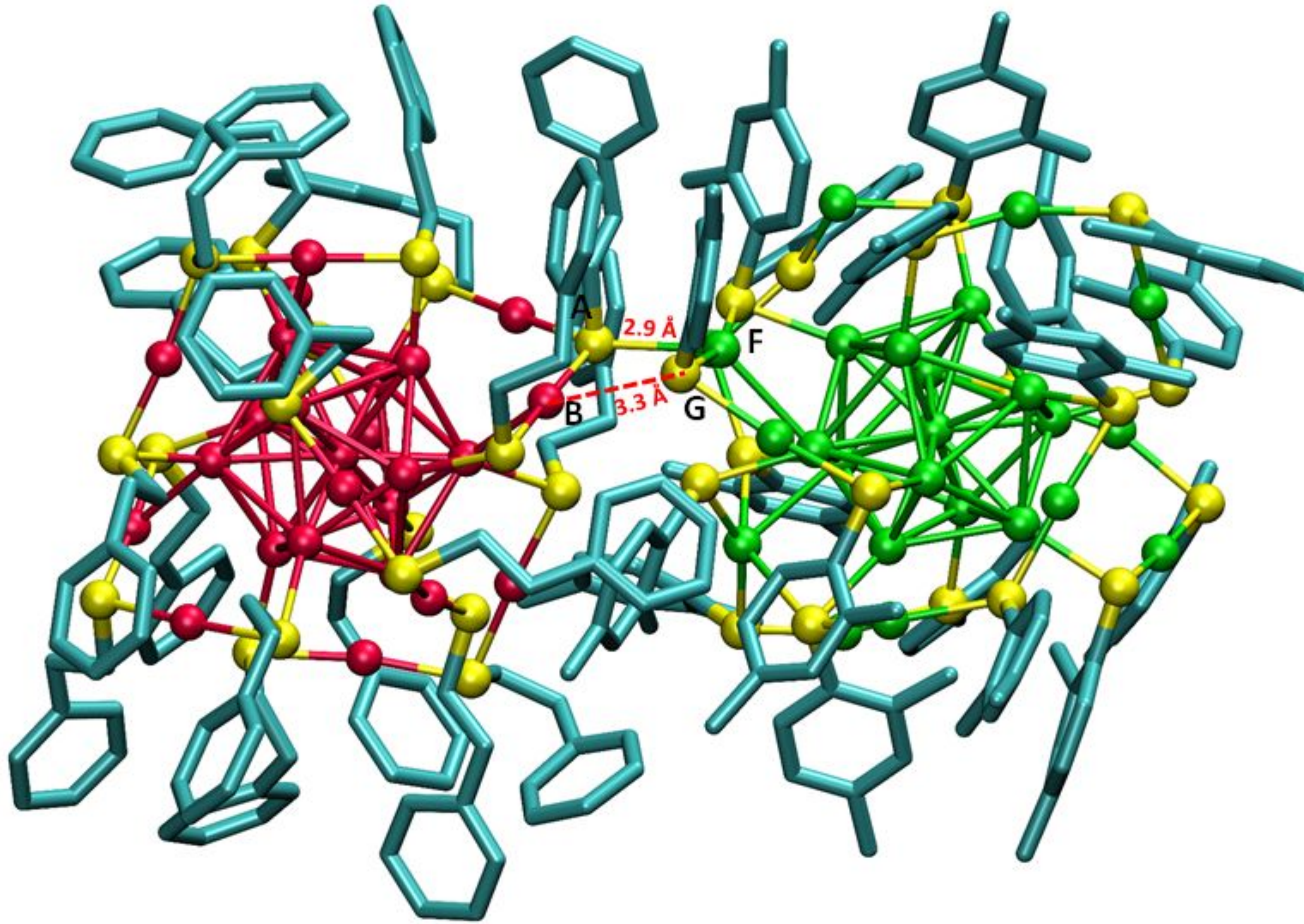
$Ag_{25}(DMBT)_{18}$:$Au_{25}(PET)_{18}$
0.3:1.0

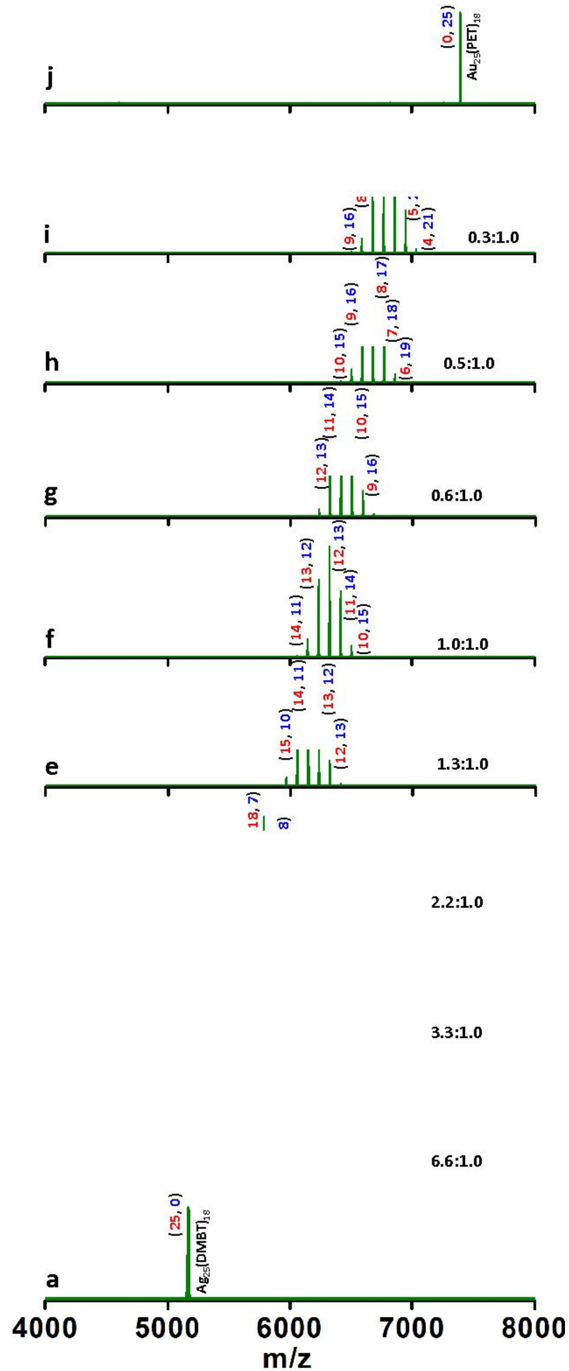


within 5 min

within 2 min

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

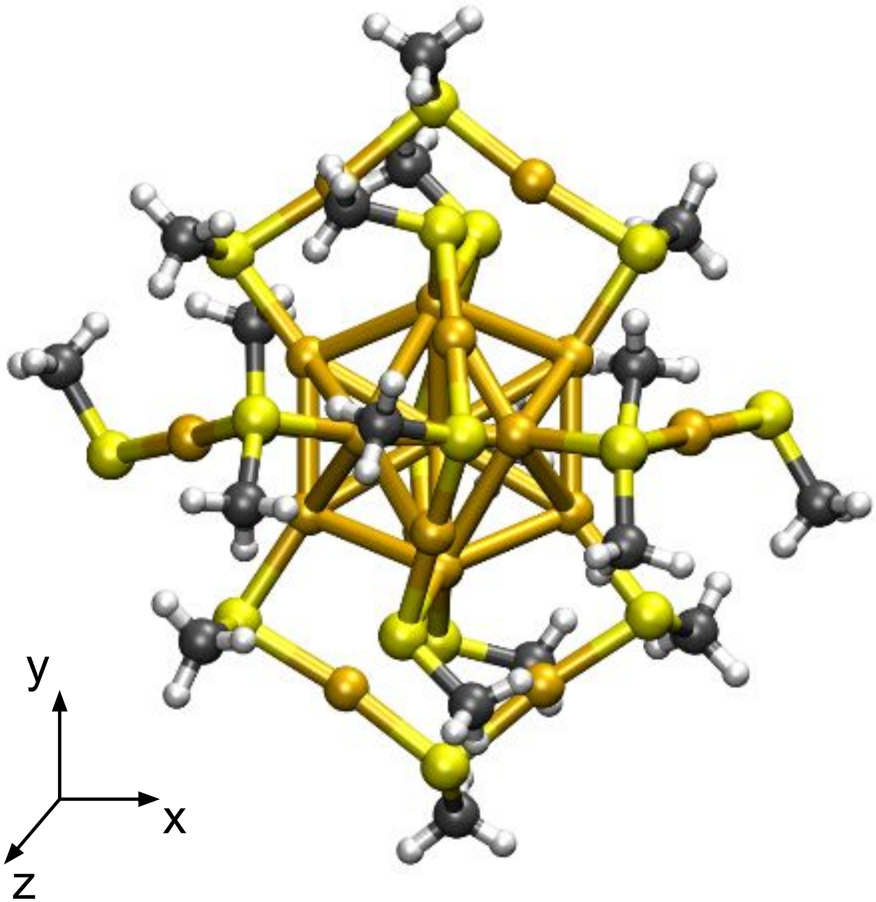


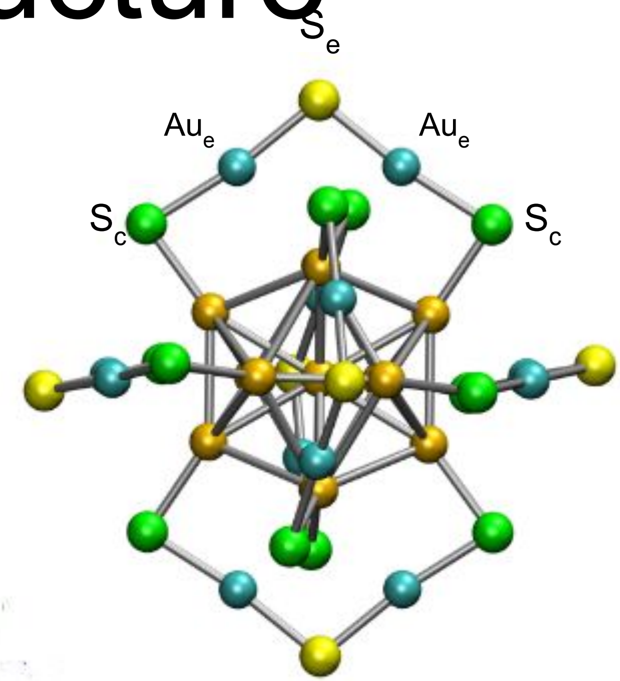


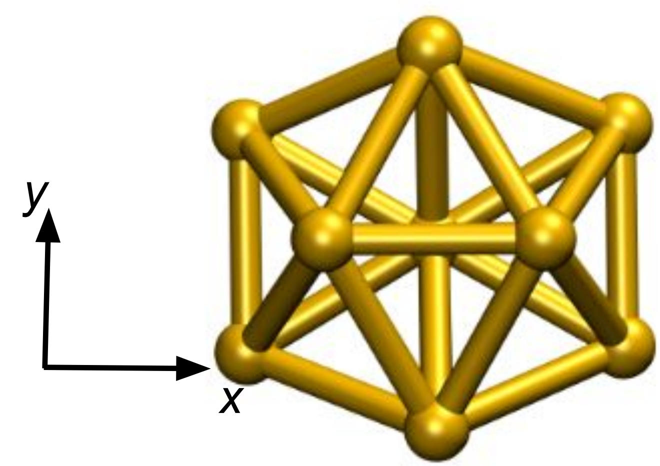
j
(0, 25)
$Au_{25}(PET)_{18}$
i
(9, 16)
(4, 21)
0.3:1.0
h
(10, 15)
(9, 16)
(8, 17)
(7, 18)
(6, 19)
0.5:1.0
g
(12, 13)
(11, 14)
(10, 15)
(9, 16)
0.6:1.0
f
(14, 11)
(13, 12)
(12, 13)
(11, 14)
(10, 15)
1.0:1.0
e
(15, 10)
(14, 11)
(13, 12)
(12, 13)
1.3:1.0
2.2:1.0
3.3:1.0
6.6:1.0
a
(25, 0)
$Ag_{25}(DMBT)_{18}$
4000
5000
6000
7000
8000
m/z

How do we comprehend this?

Ball and stick structure



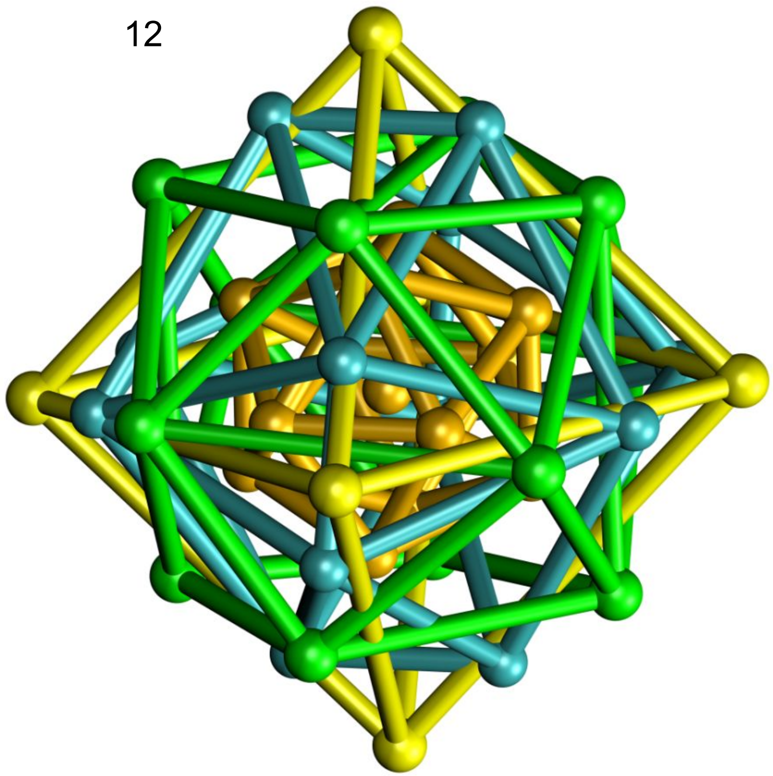




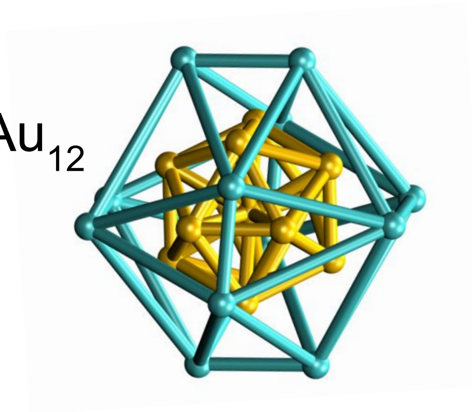
A view of gold methly thiolate [25]aspicule ($Au_{25}(SMe)_{18}$). Gold atoms colored gold, sulfur atoms by yellow, carbon dark gray, hydrogen atoms as white and (b) with the gold and sulfur atoms alone .

Shell Structure

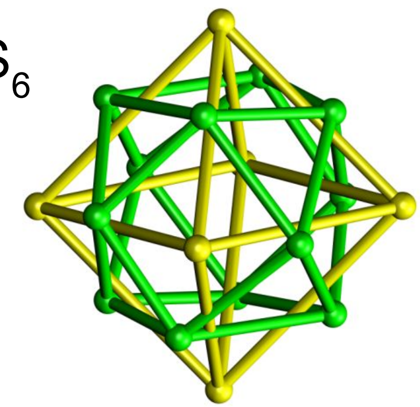
(a) $Au@Au_{12}@Au_{12}@S_6@S_{12}$



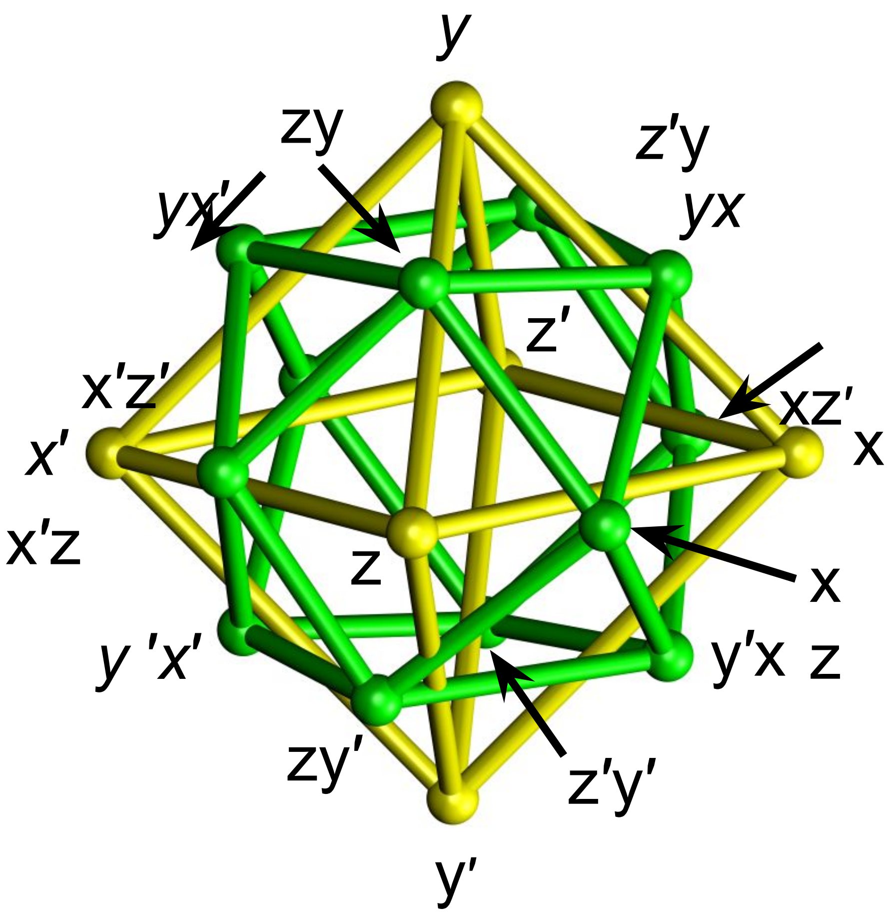
(b) $Au_{12}@Au_{12}$

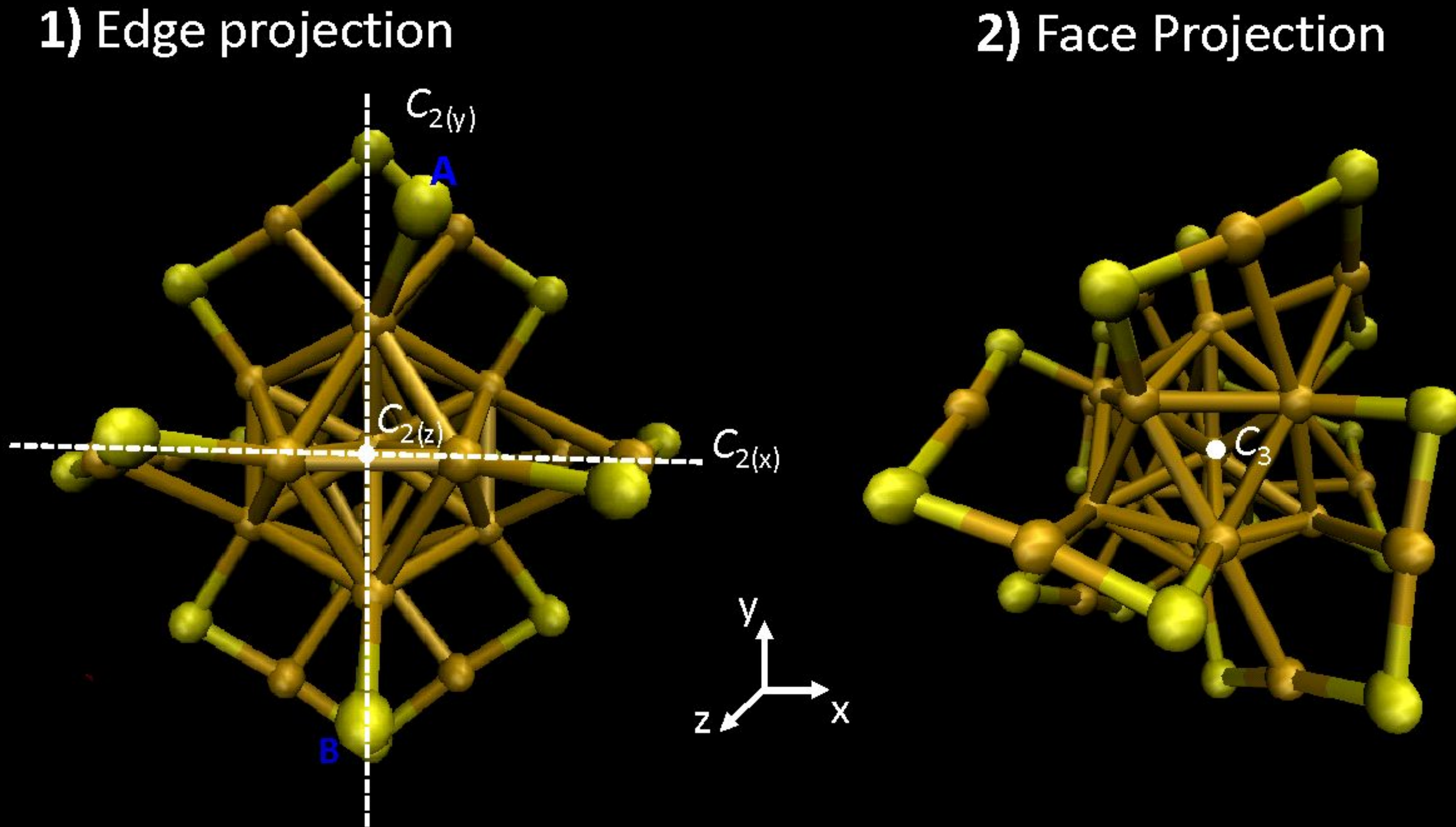


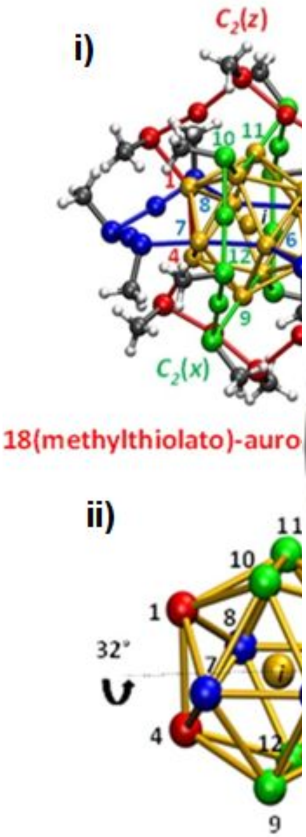
(c) $S_{12}@S_6$

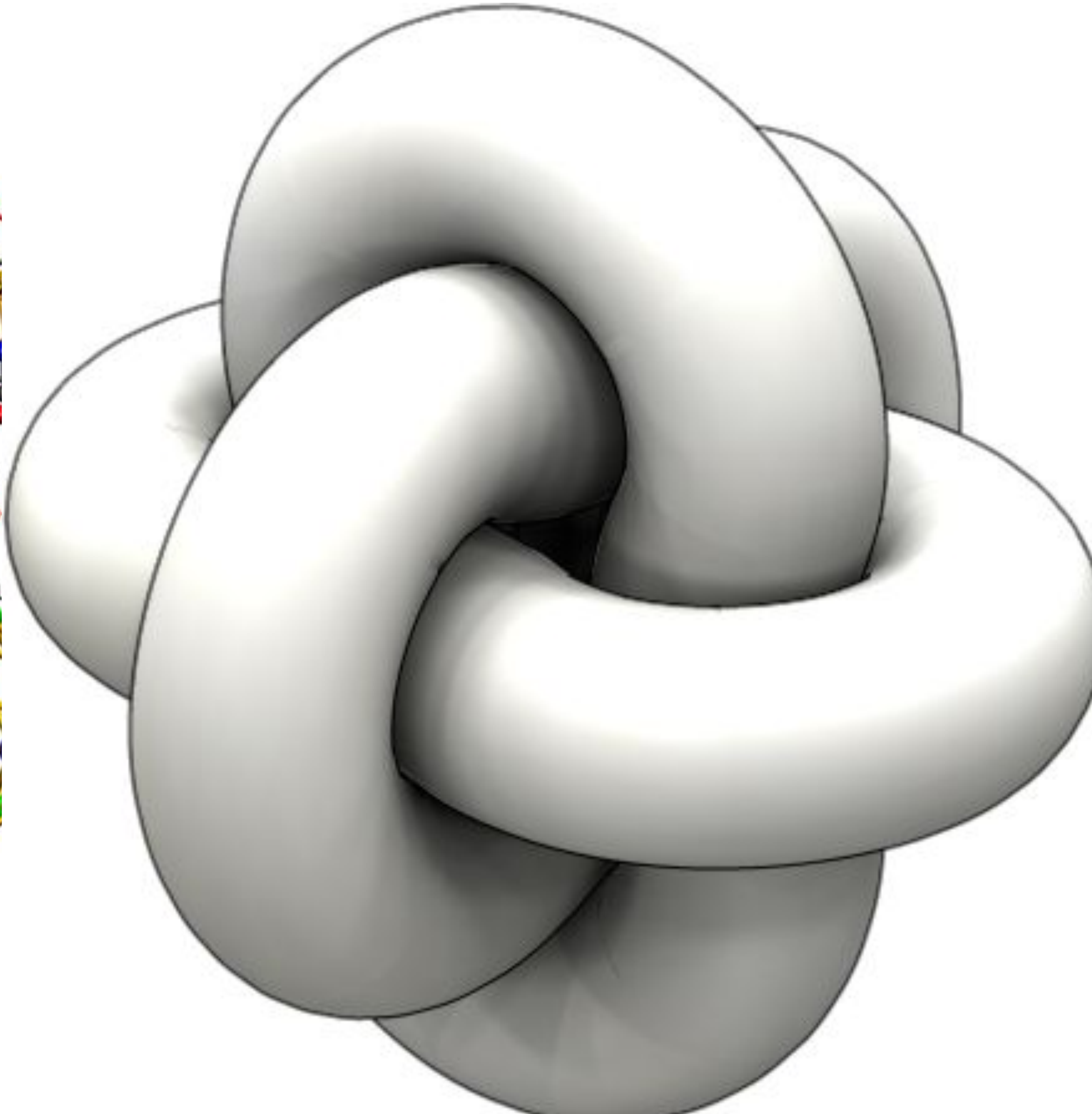


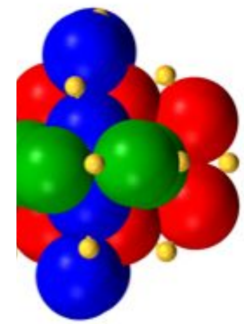
Terminologies




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


i)
$C_2(z)$
10
11
1
8
7
6
4
12
9
$C_2(x)$
18(methylthiolato)-auro
ii)
11
10
1
8
32°
7
4
12
9





C C. 2015

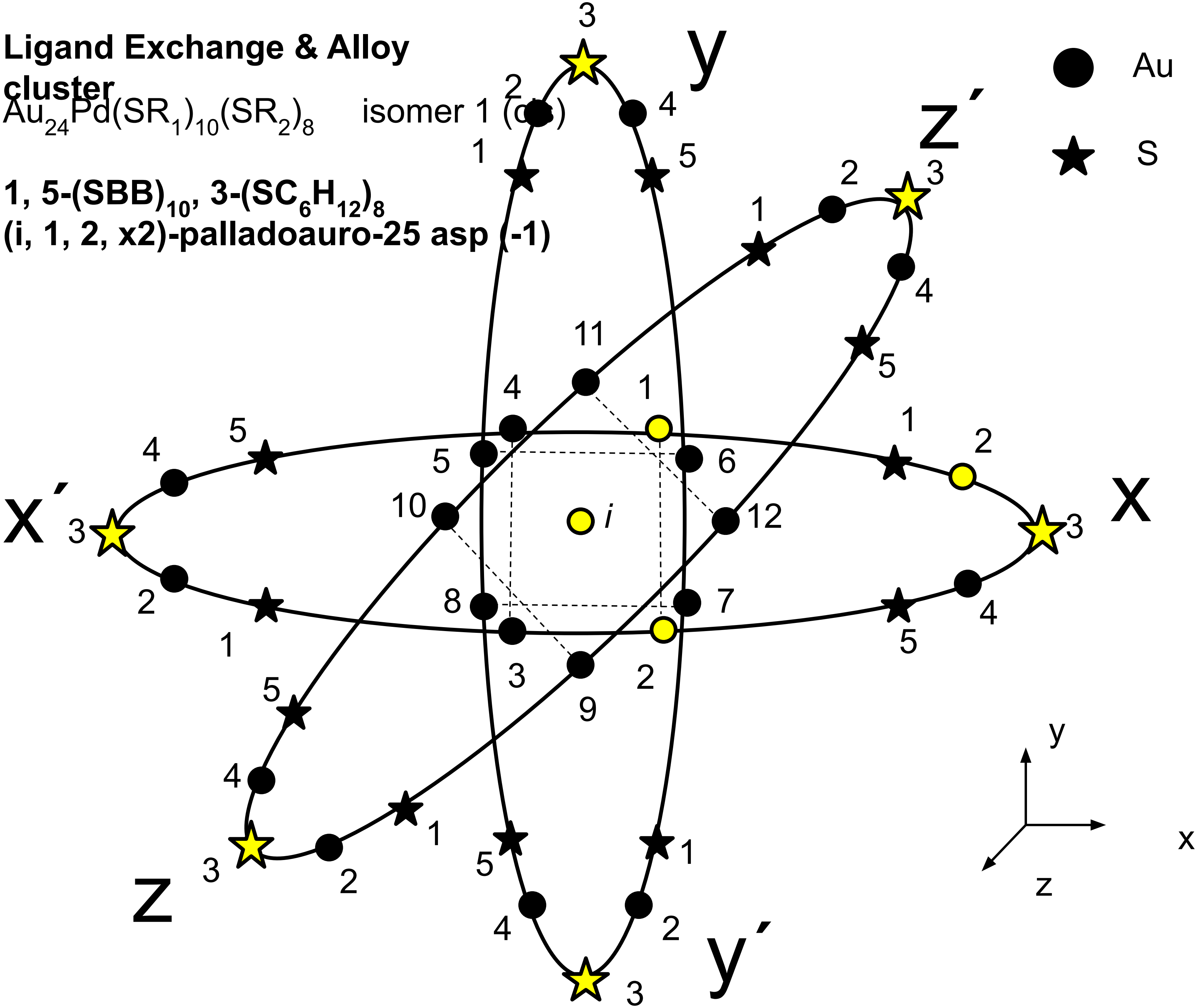
Aspicules

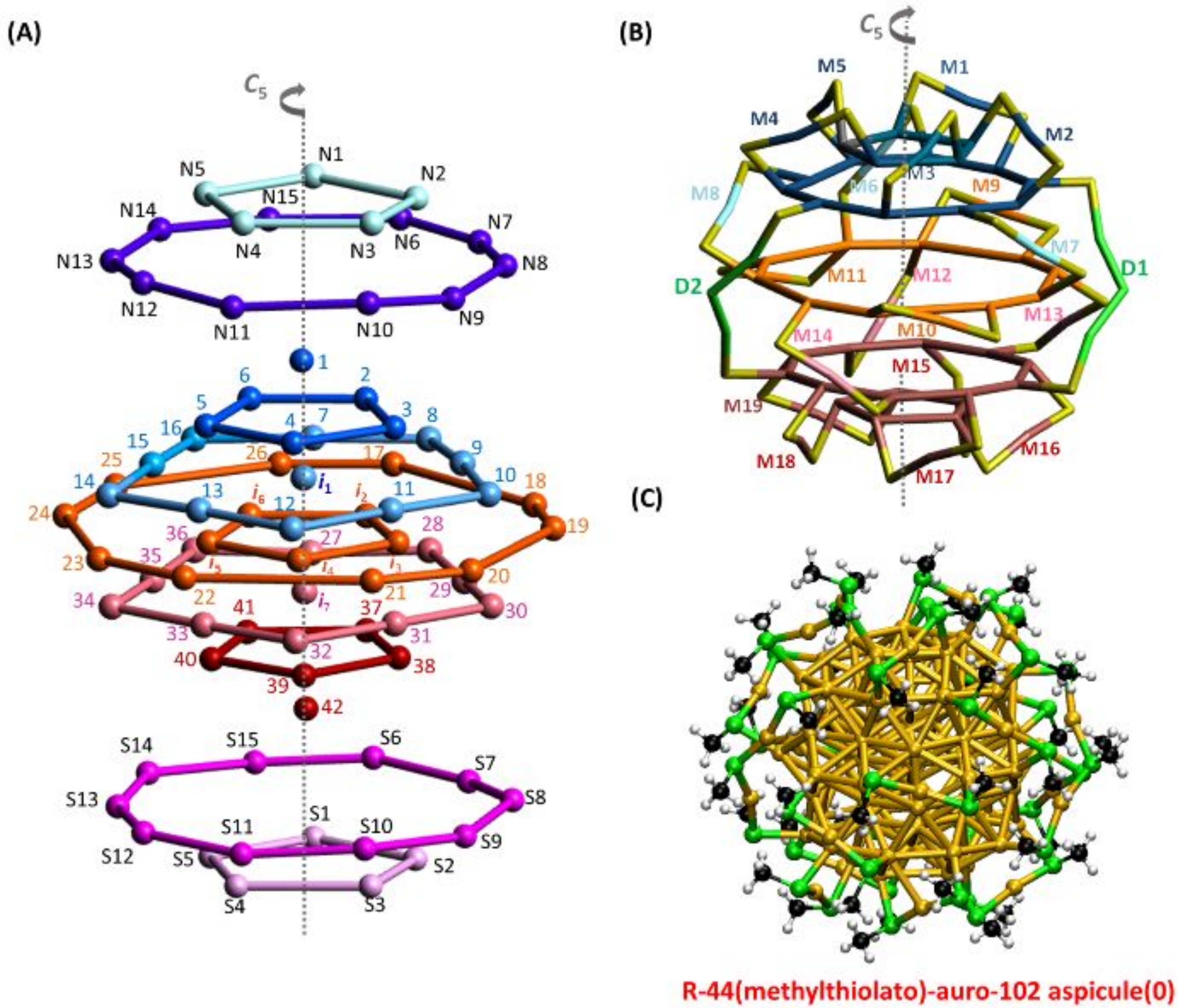
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule(1-)

Ligand Exchange & Alloy cluster

$Au_{24}Pd(SR_1)_{10}(SR_2)_8$ isomer 1 (cis)

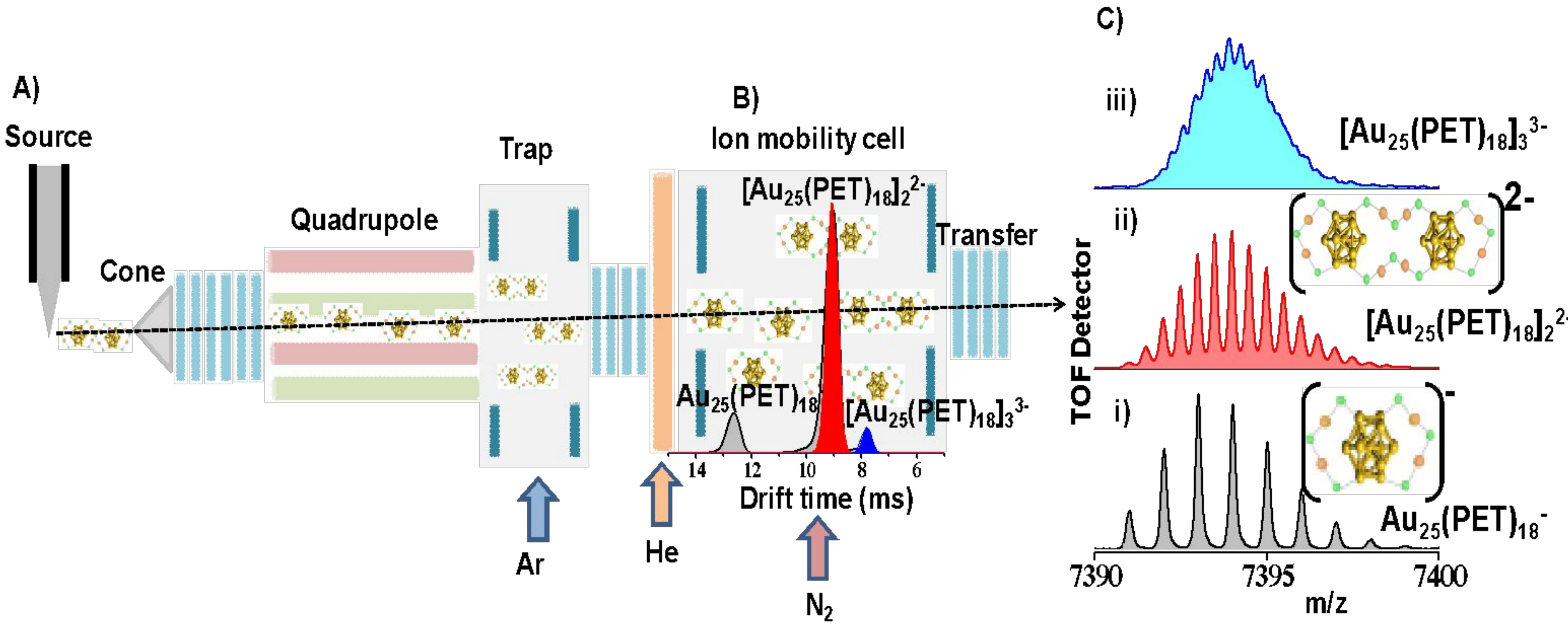
1, 5-$(SBB)_{10}$, 3-$(SC_6H_{12})_8$
(i, 1, 2, x2)-palladoauro-25 asp (-1)





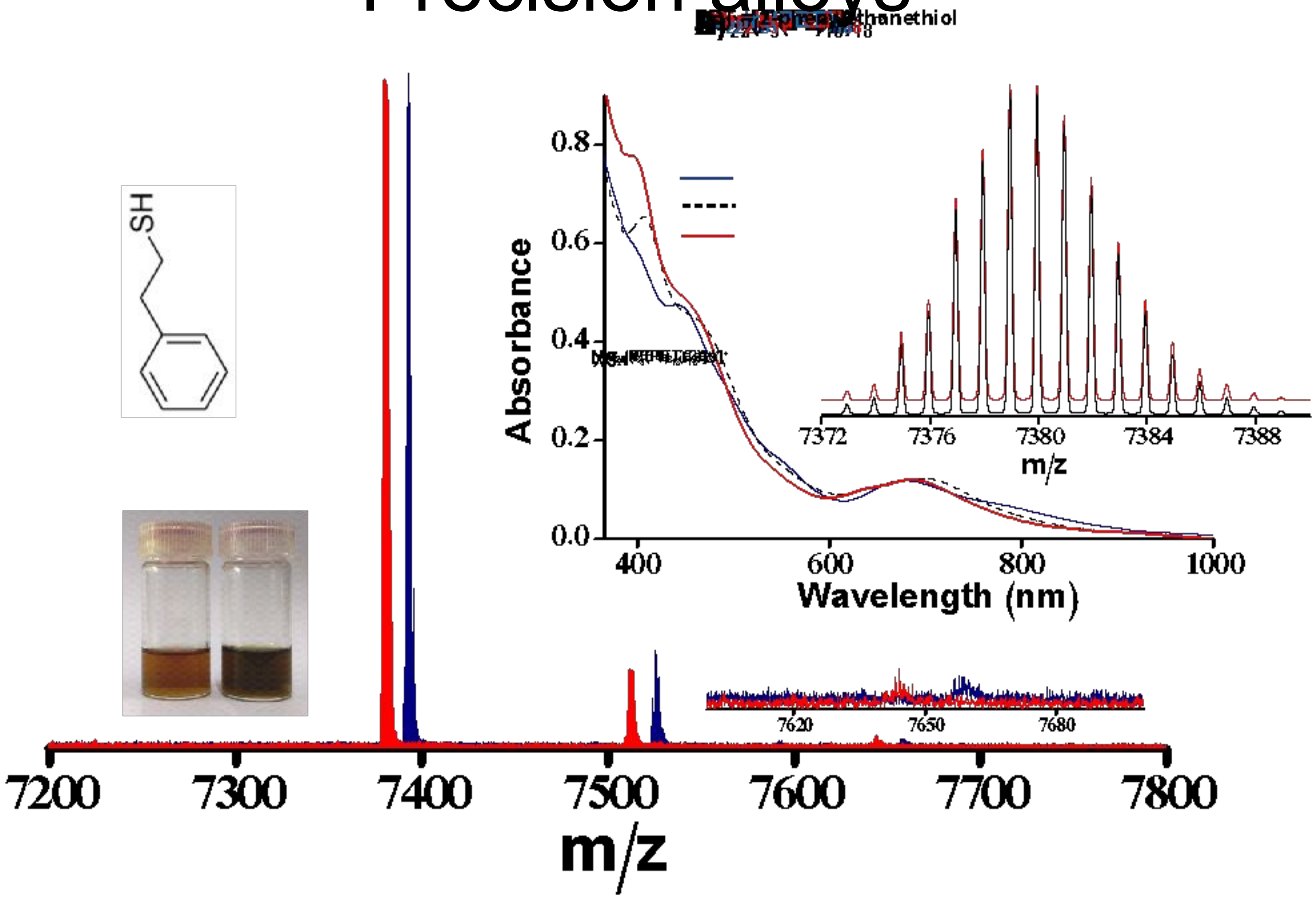
R-$(SMe)_{44}$-auro-102 aspicule**(**0**)** and L-$(SMe)_{44}$-auro-102 aspicule**(**0**)**

Cluster dimers



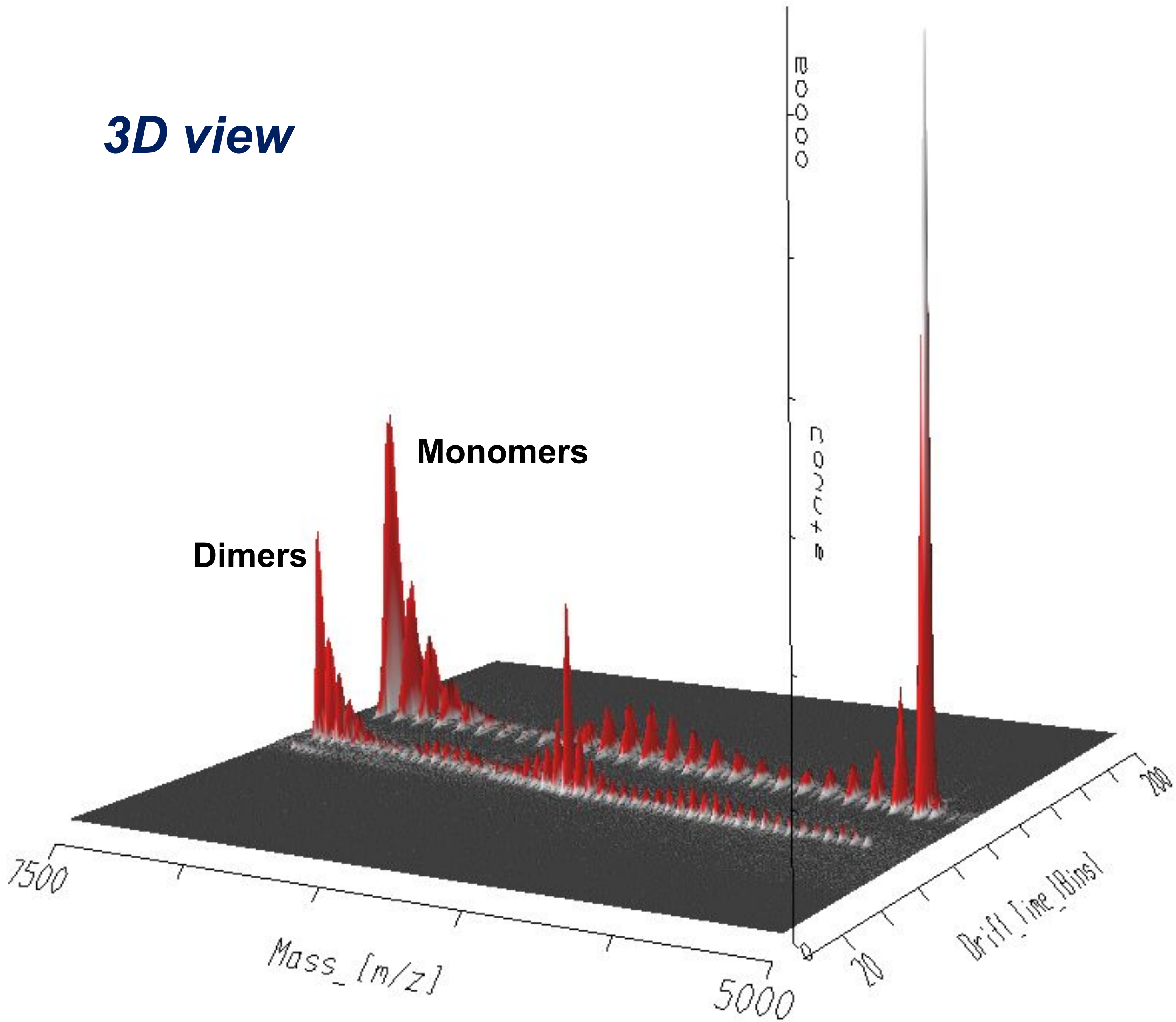
Ananya Baksi et al. Chem. Commun. 2016

Precision alloys

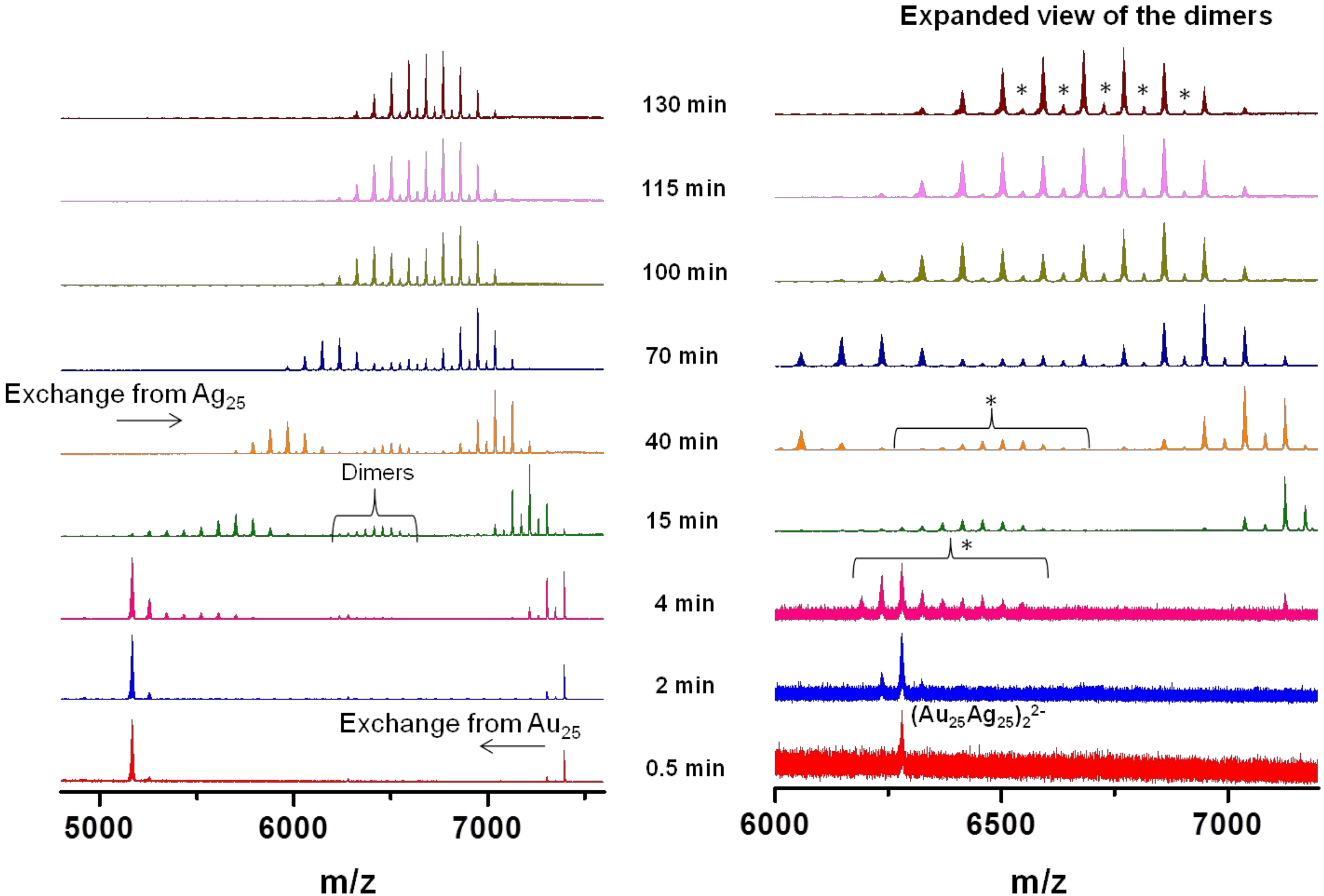


Shridevi Bhat et. al. J. Phys. Chem. Lett. (2017)

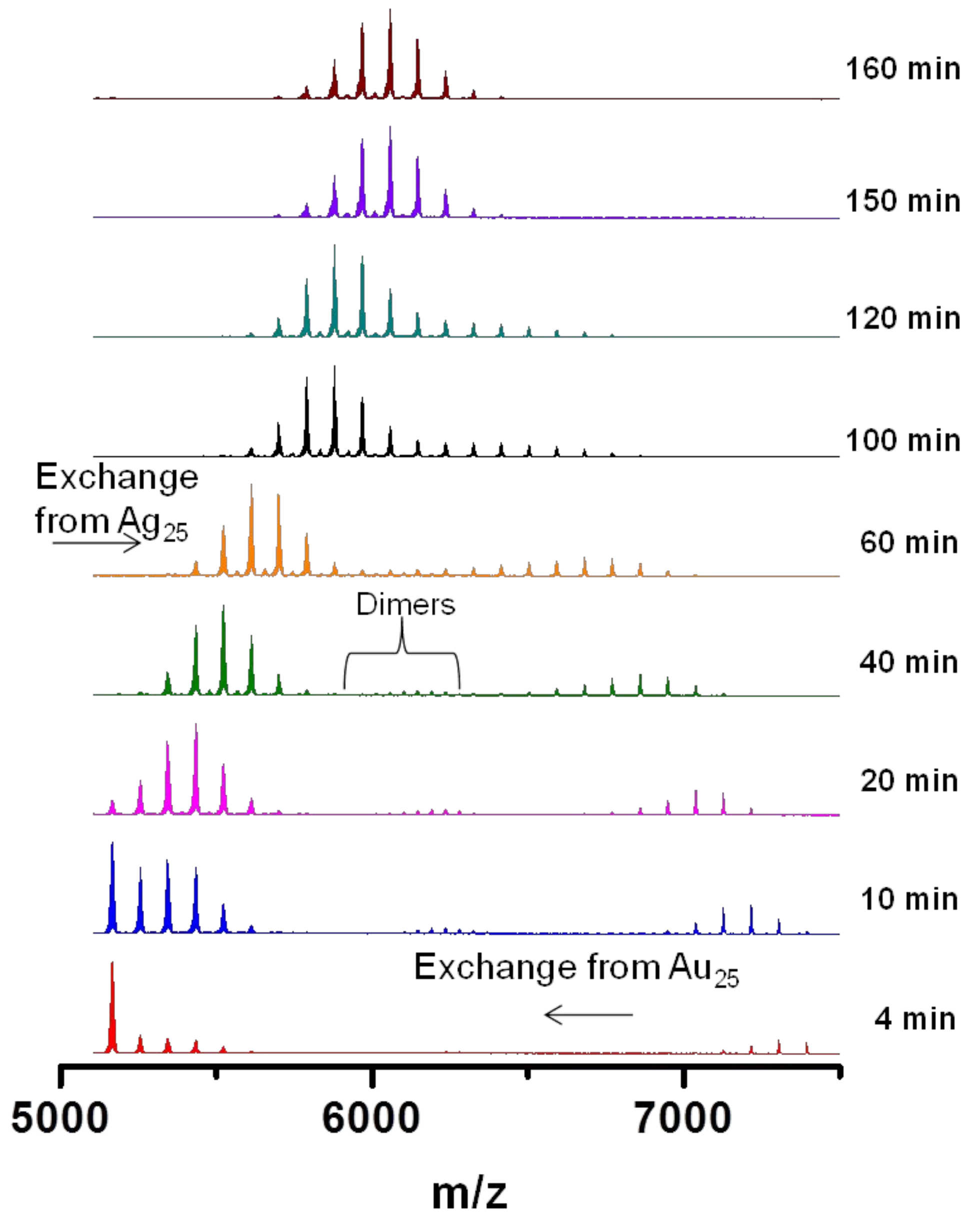
3D view



ESI MS of the reaction mixture

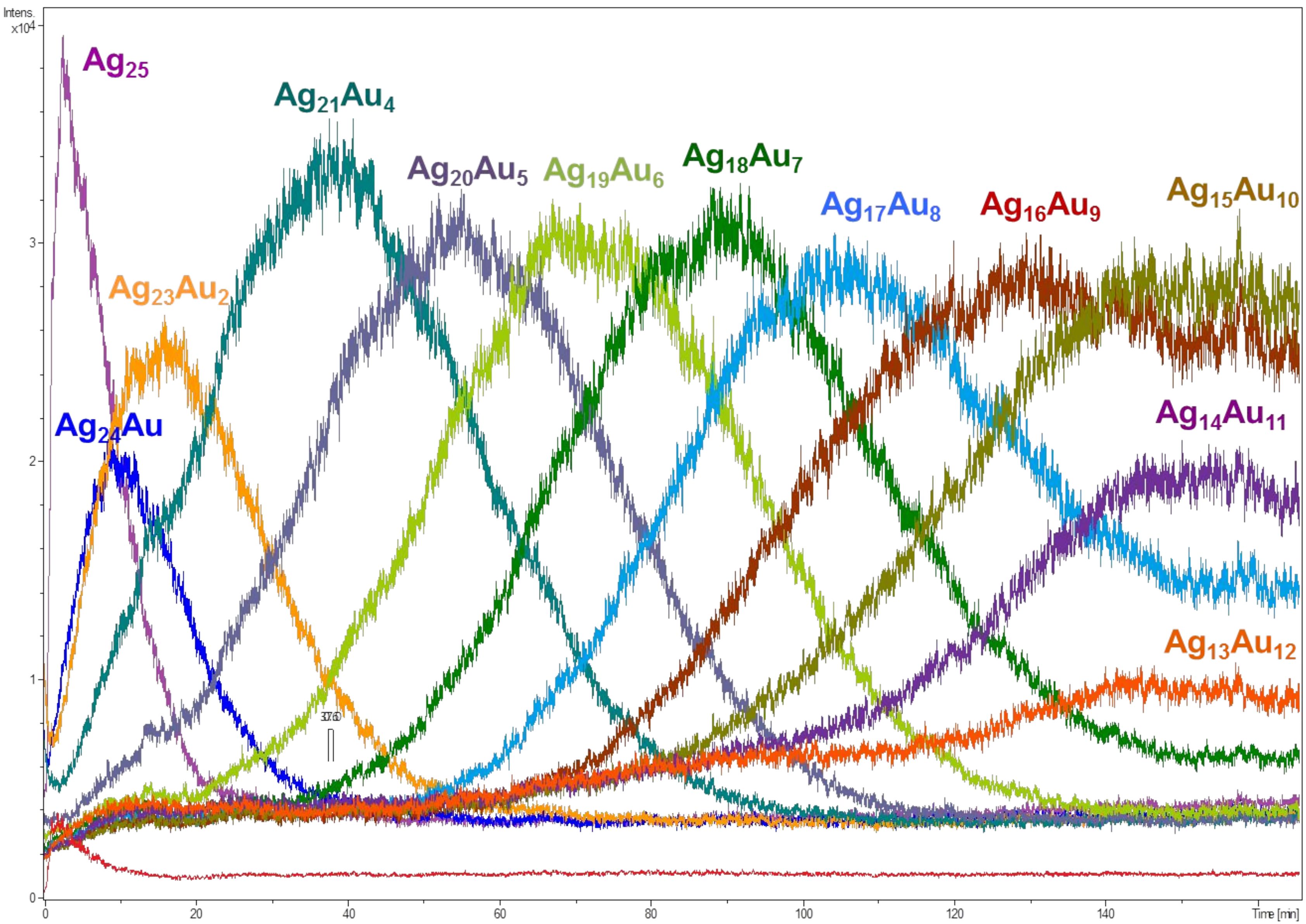


* peaks for the dimers (at higher time, the monomeric peaks due to Au-Ag exchange also arise). Au_{25} was kept in excess.



Molar ratio of two clusters= 1:1

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



Cluster dynamics

They are indeed molecules!

K. R. Krishnadas, et al. Acc. Chem. Res. 2017

ACCOUNTS of chemical research

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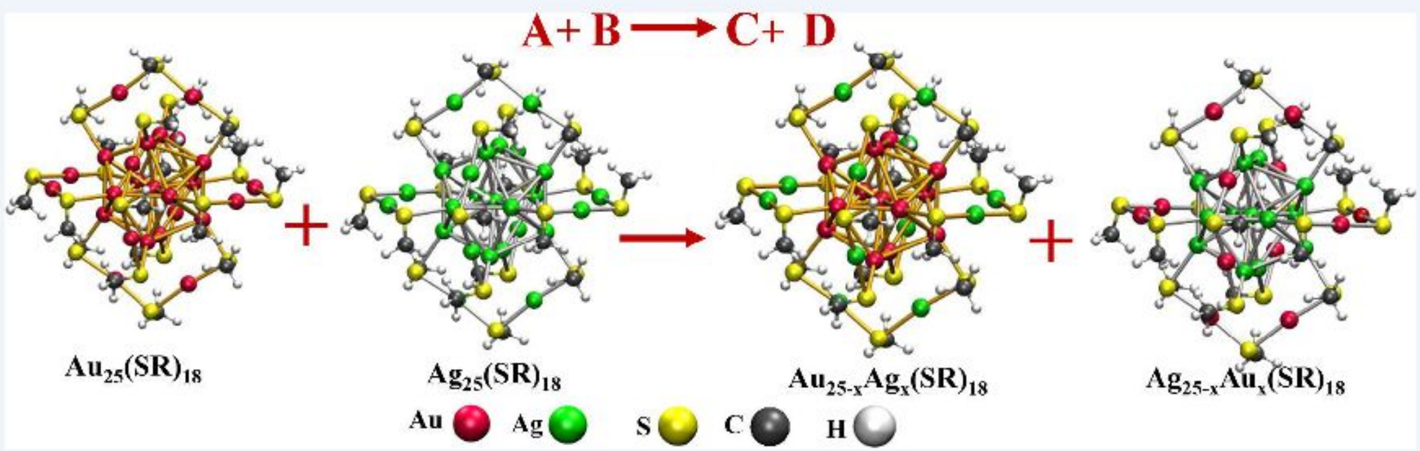
Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

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.

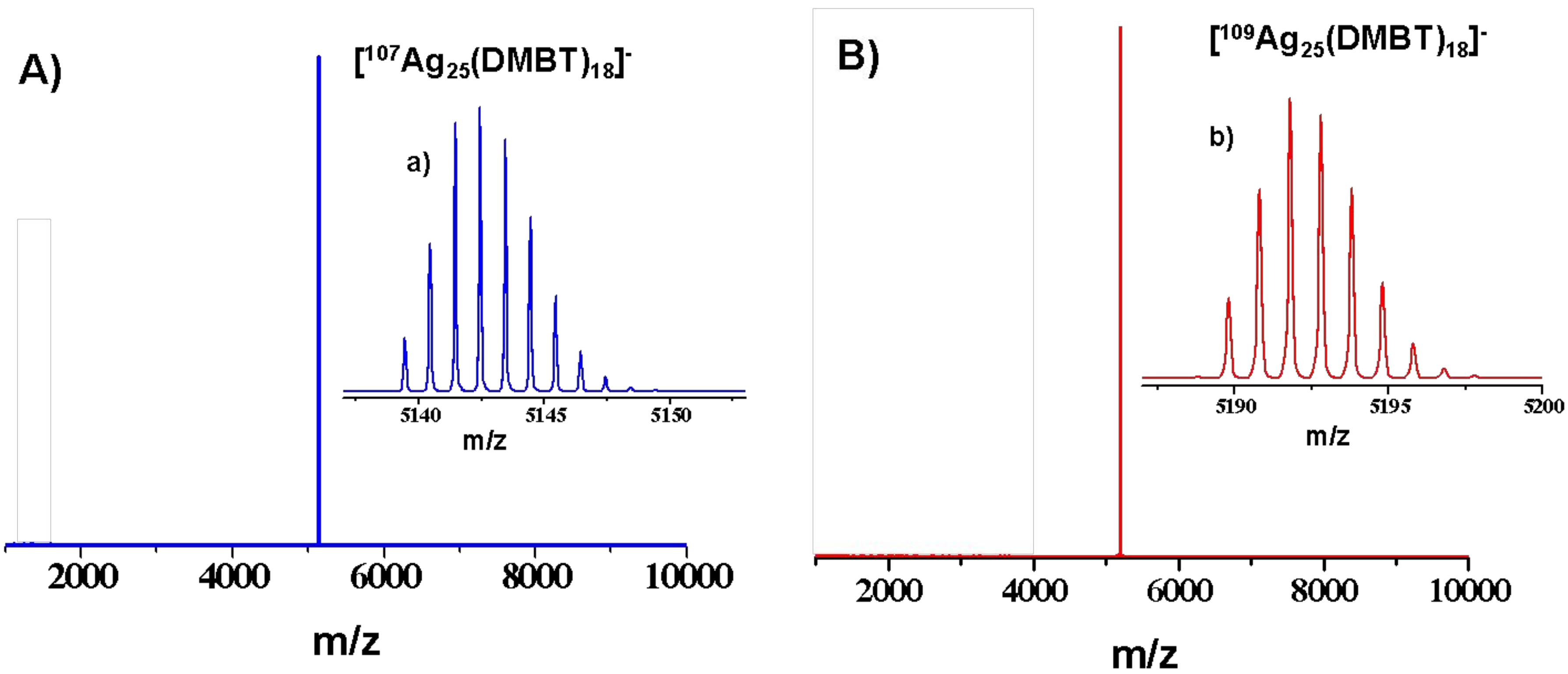
SCIENCE ADVANCES | RESEARCH ARTICLE

CONDENSED MATTER PHYSICS

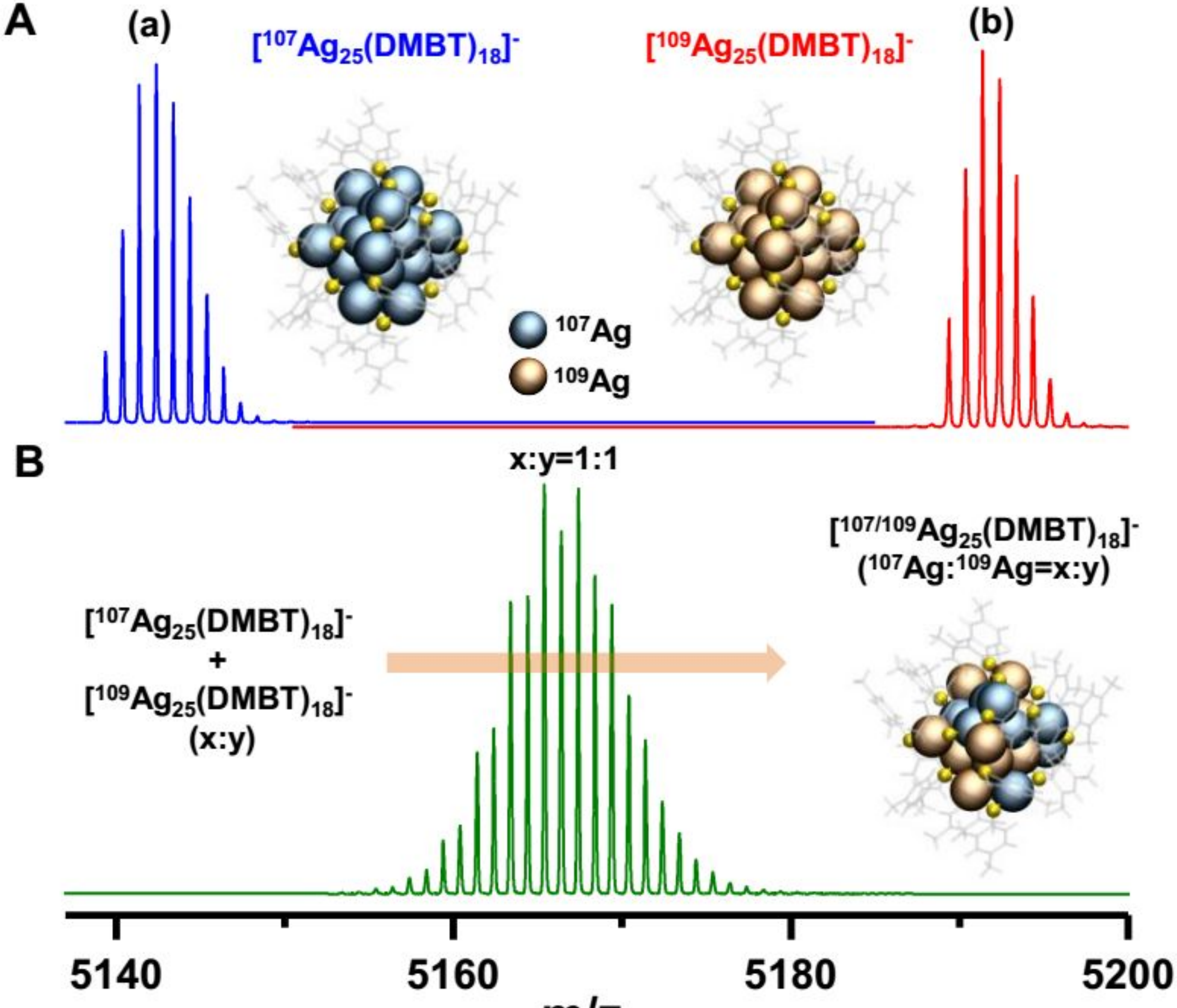
Rapid isotopic exchange in nanoparticles

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]*

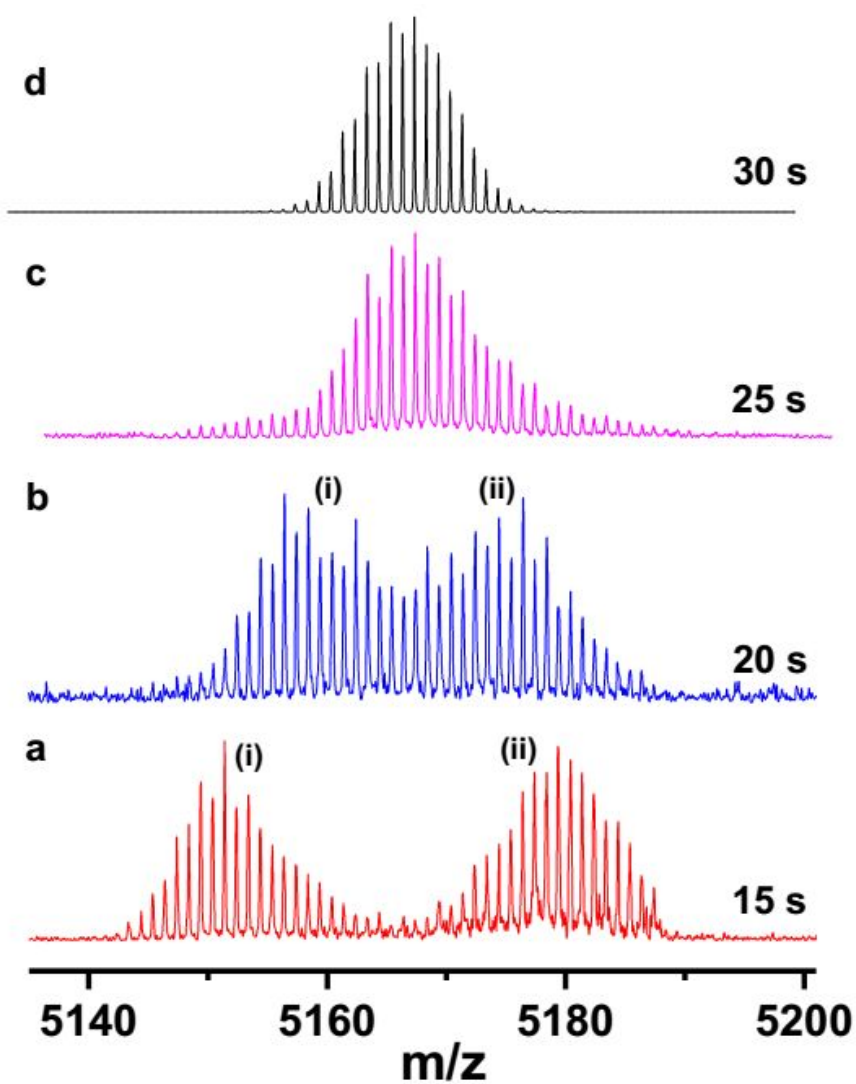
Rapid solution-state exchange dynamics in nanoscale pieces of matter is revealed, taking isotopically pure atomically precise clusters as examples. As two isotopically pure silver clusters made of ^{107}Ag and ^{109}Ag are mixed, an isotopically mixed cluster of the same entity results, similar to the 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.



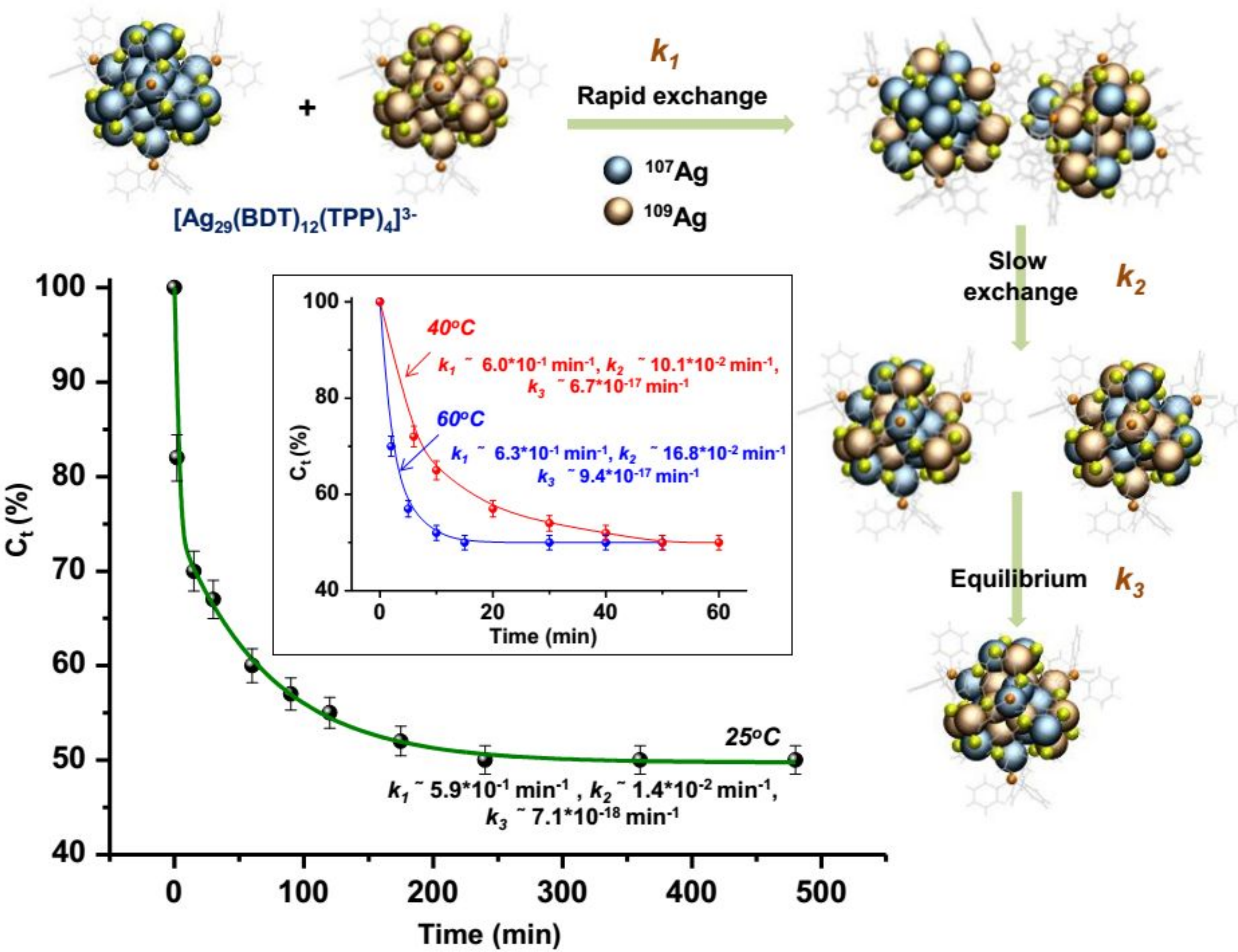
ESI MS of **A)** $^{107}Ag_{25}(DMBT)_{18}$ and **B)**$^{109}Ag_{25}(DMBT)_{18}$. Insets shows the respective isotope patterns.



A
(a)
[$^{107}Ag_{25}(DMBT)_{18}]^-$
[$^{109}Ag_{25}(DMBT)_{18}]^-$
(b)
^{107}Ag
^{109}Ag
B
x:y=1:1
$[^{107/109}Ag_{25}(DMBT)_{18}]^-$
$(^{107}Ag:^{109}Ag=x:y)$
$[^{107}Ag_{25}(DMBT)_{18}]^-$
+
$[^{109}Ag_{25}(DMBT)_{18}]^-$
(x:y)
5140
5160
5180
5200
m/z



Papri Chakraborty, et. al. Science Advances 2018



$[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$
+
k_1
Rapid exchange
^{107}Ag
^{109}Ag
Slow exchange
k_2
Equilibrium
k_3
C_t (%)
Time (min)
25°C
k_1 ~ 5.9*10^{-1} min^{-1} , k_2 ~ 1.4*10^{-2} min^{-1},
k_3 ~ 7.1*10^{-18} min^{-1}
40°C
k_1 ~ 6.0*10^{-1} min^{-1}, k_2 ~ 10.1*10^{-2} min^{-1},
k_3 ~ 6.7*10^{-17} min^{-1}
60°C
k_1 ~ 6.3*10^{-1} min^{-1}, k_2 ~ 16.8*10^{-2} min^{-1}
k_3 ~ 9.4*10^{-17} min^{-1}

Supramolecular chemistry

Papri Chakraborty, et,. al. ACS Nano 2018

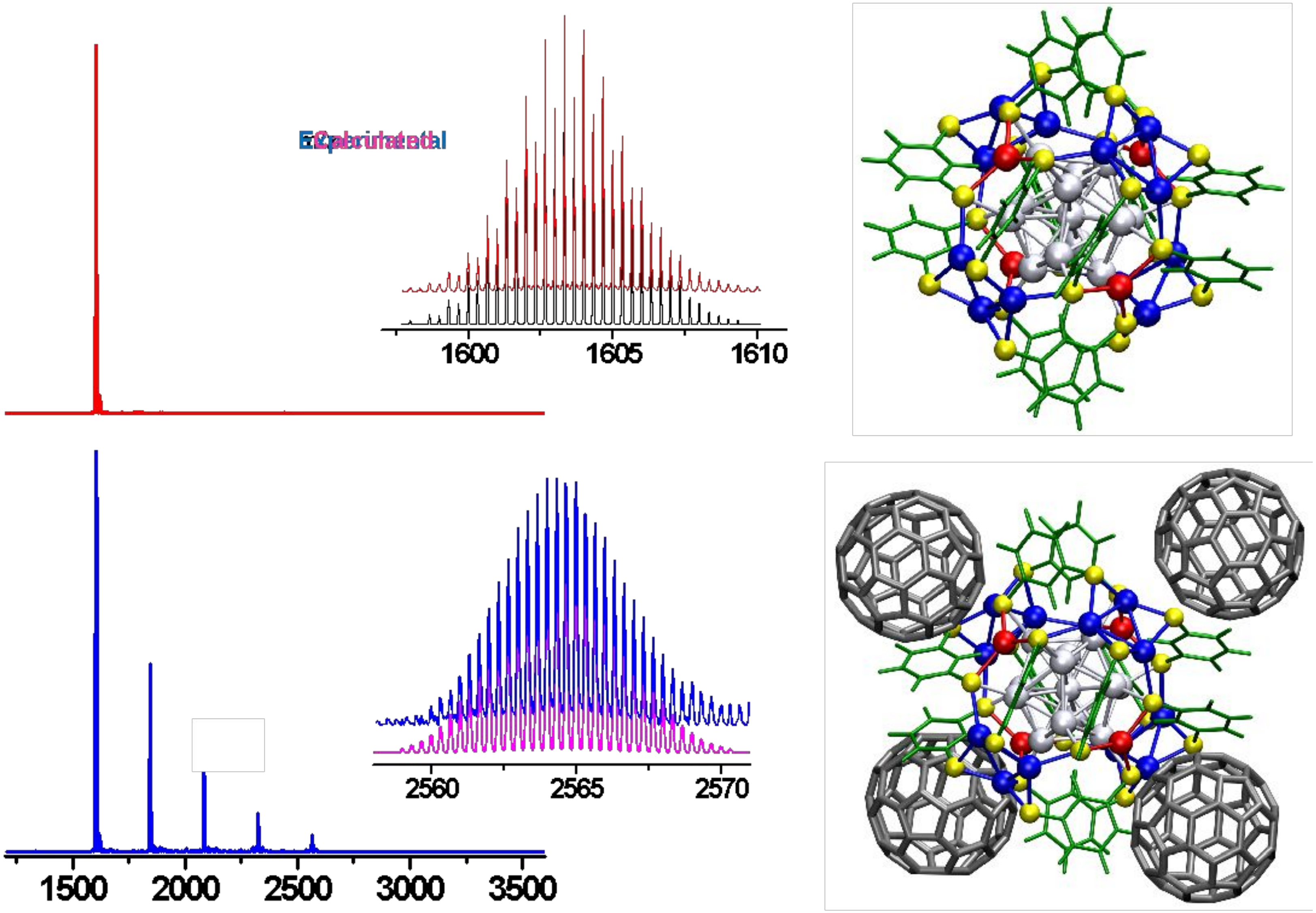


Figure 1. A) (a) Full range ESI MS, **(b)** experimental and calculated isotope patterns and **(c)** DFT optimized structure of $[Ag_{29}(BDT)_{12}]^{3-}$ cluster. **B) (a)** ESI MS of $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (n=1-4) complexes, **(b)** experimental and calculated isotope patterns of $[Ag_{29}(BDT)_{12}(C_{60})_4]^{3-}$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

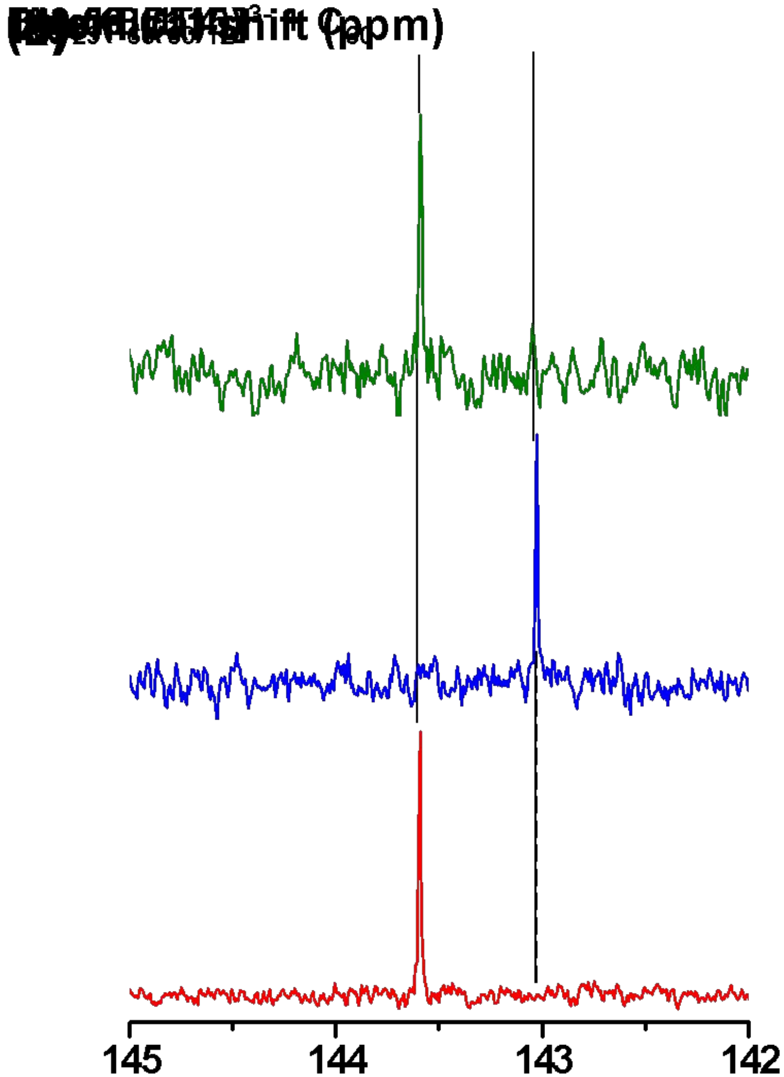
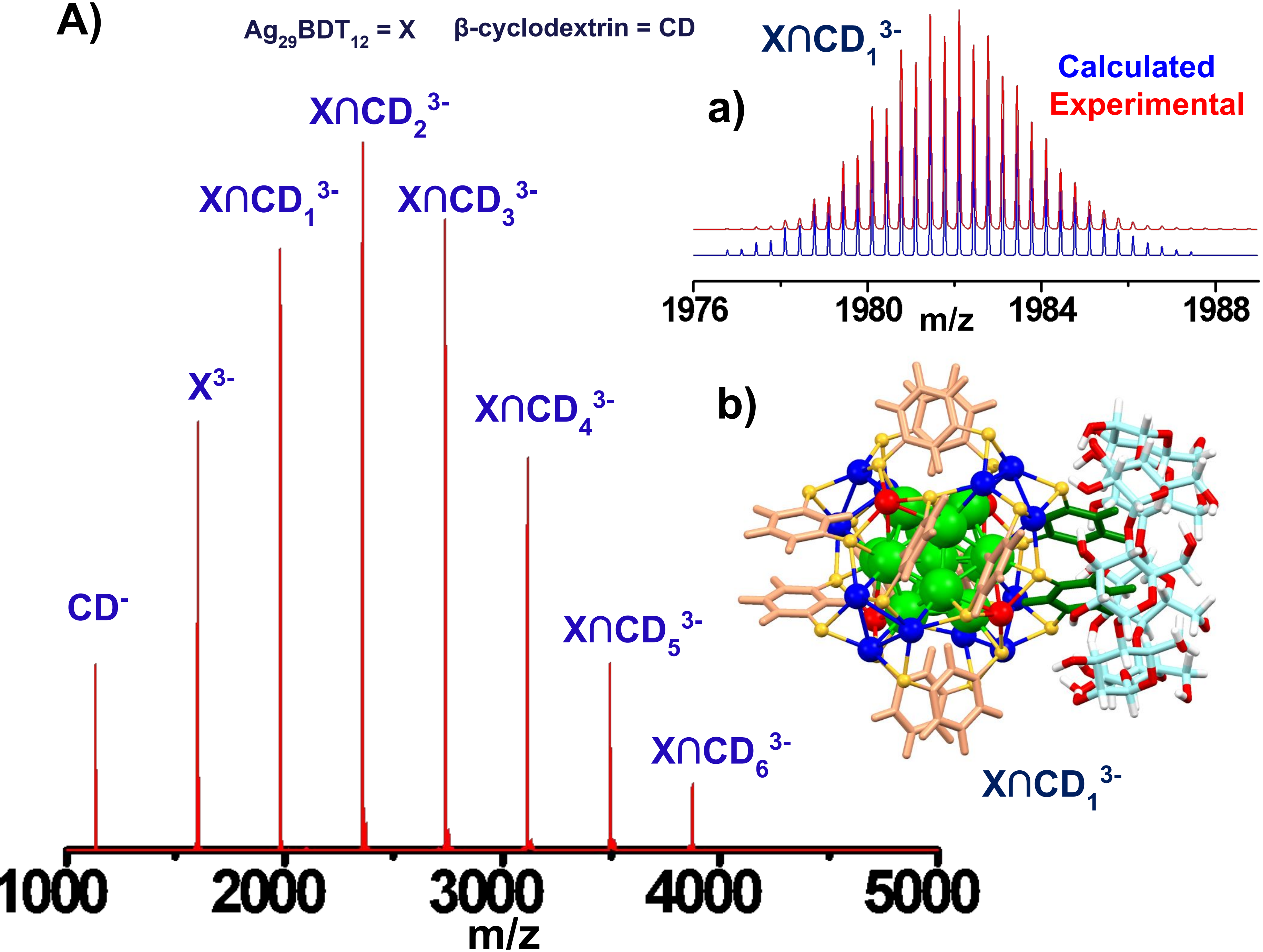


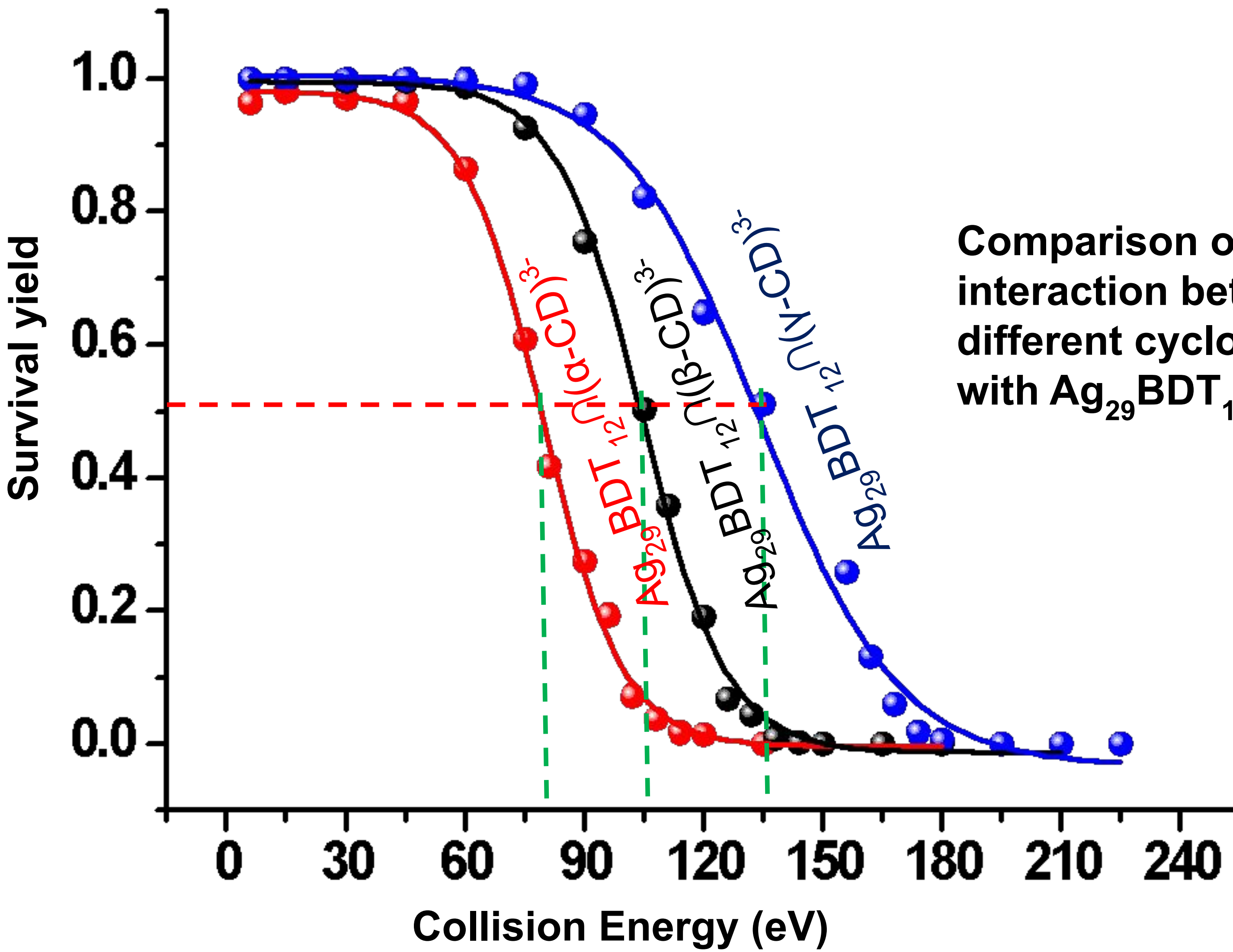
Figure 3. NMR of **(a)** C_{60} showing peak at 143.59 ppm, **(b)** the adducts at a cluster:fullerene molar ratio of 1:4 showing peak at 143.03 ppm for the C_{60} molecules in bound state and **(c)** the adducts at an excess concentration of C_{60} (cluster:fullerene molar ratio of 1:15) showing a predominant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

Isomerism in supramolcular adducts

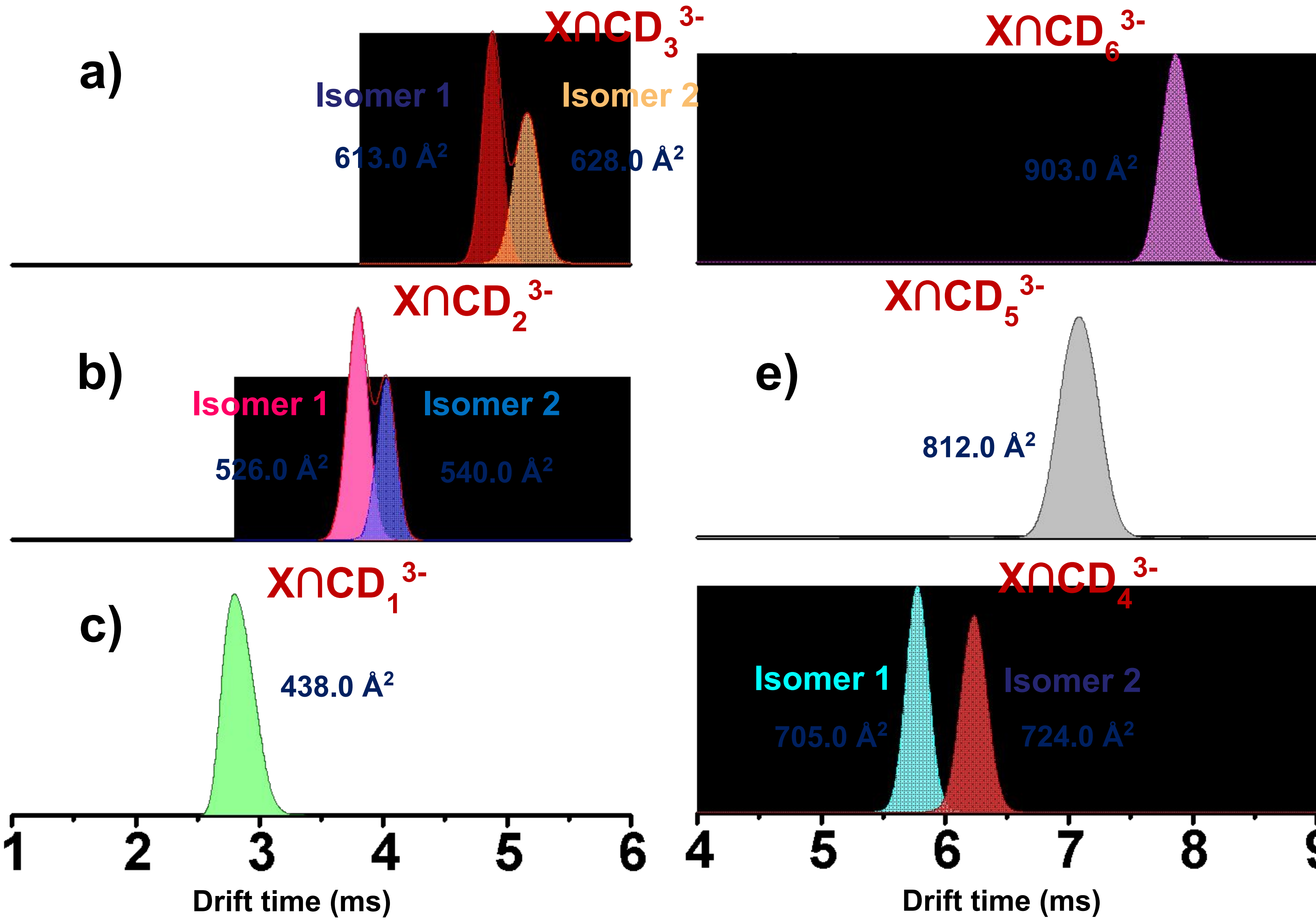
Abhijit Nag, et al. JACS 2018


A)
Ag29BDT12 = X β-cyclodextrin = CD
CD-
X3-
X∩CD1 3-
X∩CD2 3-
X∩CD3 3-
X∩CD4 3-
X∩CD5 3-
X∩CD6 3-
1000 2000 3000 4000 5000
m/z
a)
X∩CD1 3-
Calculated
Experimental
1976 1980 1984 1988
m/z
b)
X∩CD1 3-

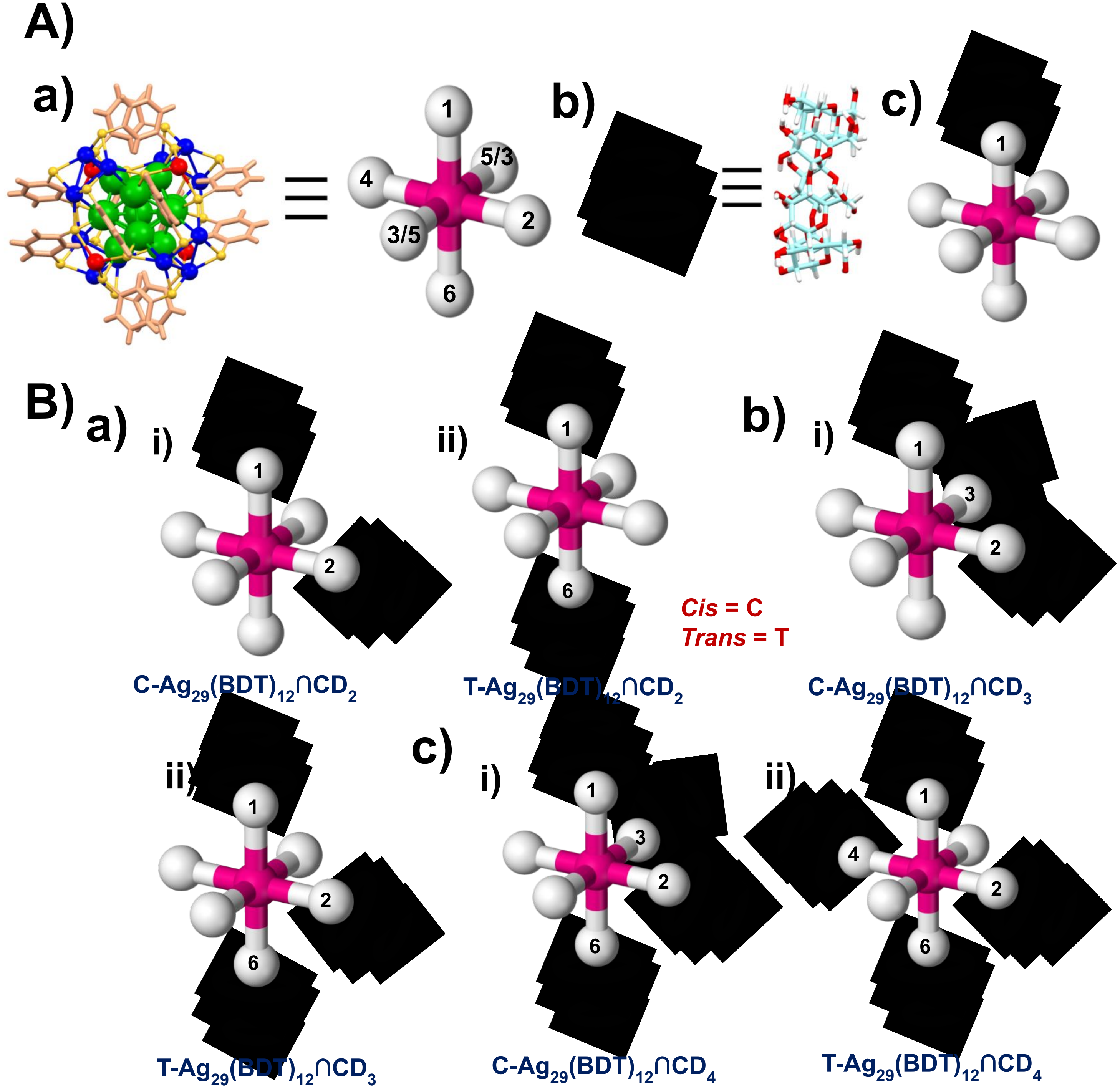
Energy Resolved Fragmentation of $Ag_{29}BDT_{12}\cap(X\text{-}CD)^{3-}$



Comparison of interaction between different cyclodextrins with $Ag_{29}BDT_{12}$

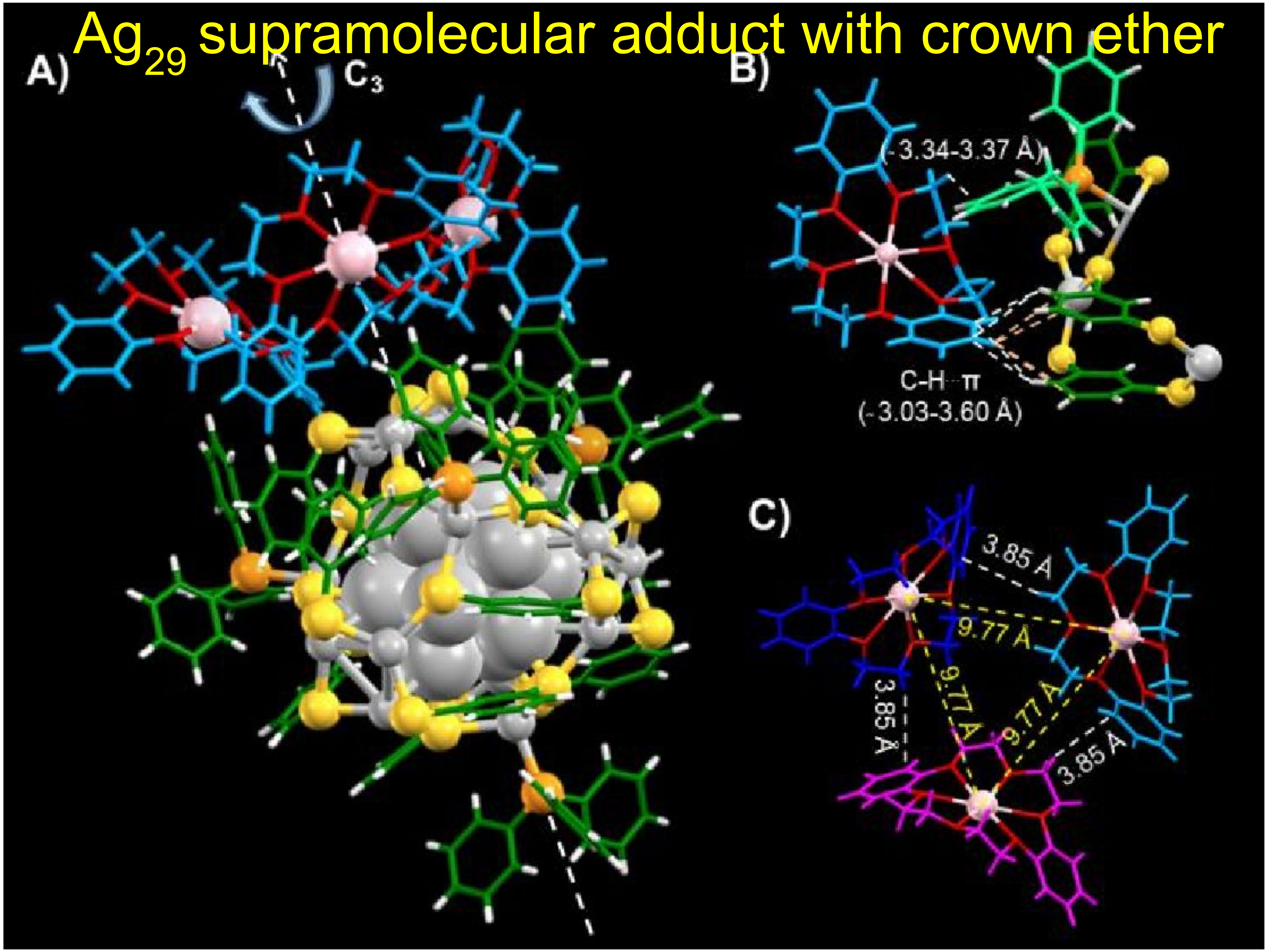


a)
X∩CD3 3-
Isomer 1
613.0 Å2
Isomer 2
628.0 Å2
b)
X∩CD2 3-
Isomer 1
526.0 Å2
Isomer 2
540.0 Å2
c)
X∩CD1 3-
438.0 Å2
1 2 3 4 5 6
Drift time (ms)
X∩CD6 3-
903.0 Å2
X∩CD5 3-
e)
812.0 Å2
X∩CD4 3-
Isomer 1
705.0 Å2
Isomer 2
724.0 Å2
4 5 6 7 8 9
Drift time (ms)

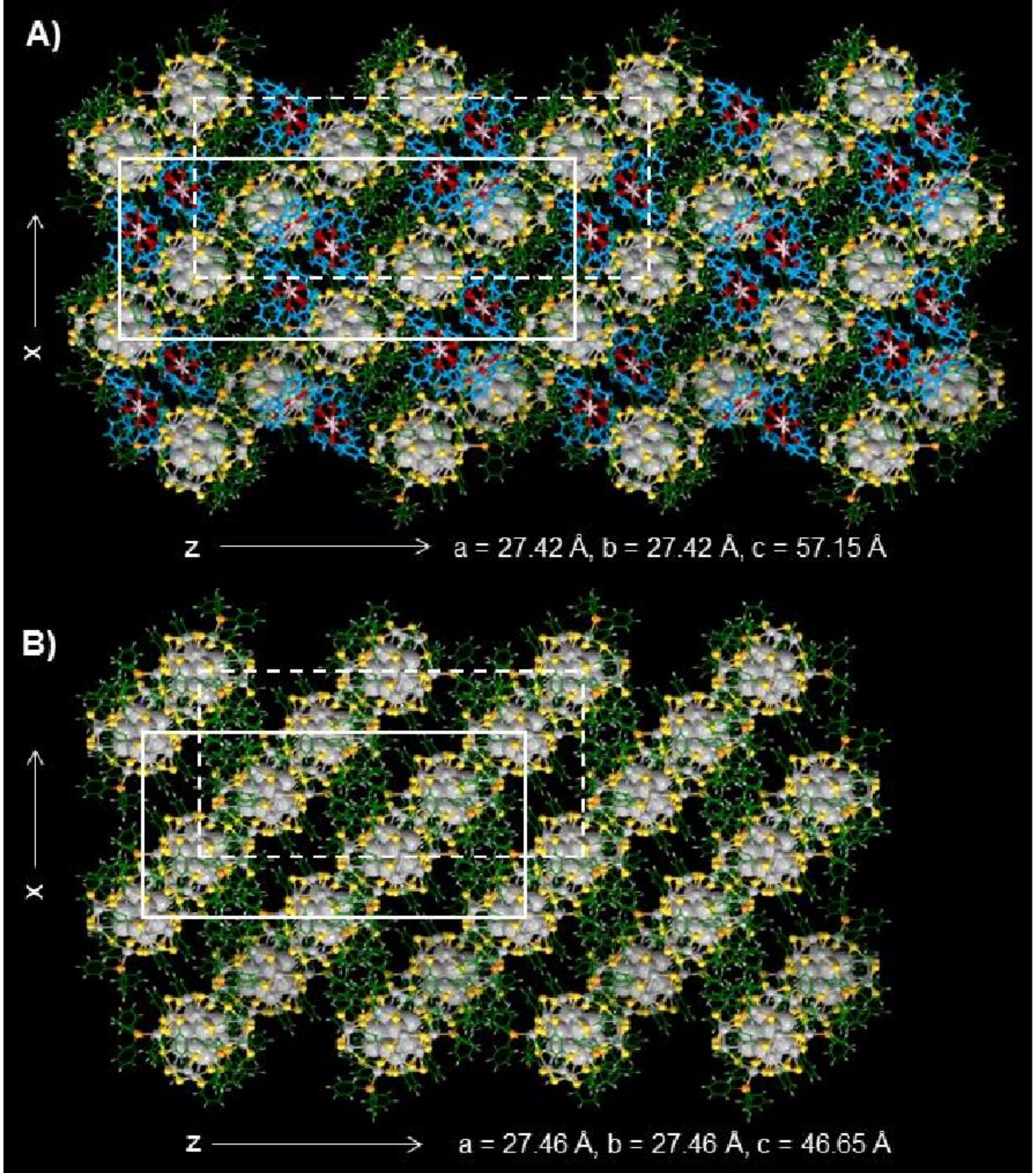

A)
a)
1
5/3
4
2
3/5
6
b)
c)
1
B)
a)
i)
1
2
$C\text{-}Ag_{29}(BDT)_{12} \cap CD_2$
ii)
1
6
$T\text{-}Ag_{29}(BDT)_{12} \cap CD_2$
Cis = C
Trans = T
b)
i)
1
3
2
$C\text{-}Ag_{29}(BDT)_{12} \cap CD_3$
ii)
1
2
6
$T\text{-}Ag_{29}(BDT)_{12} \cap CD_3$
c)
i)
1
3
2
6
$C\text{-}Ag_{29}(BDT)_{12} \cap CD_4$
ii)
1
4
2
6
$T\text{-}Ag_{29}(BDT)_{12} \cap CD_4$

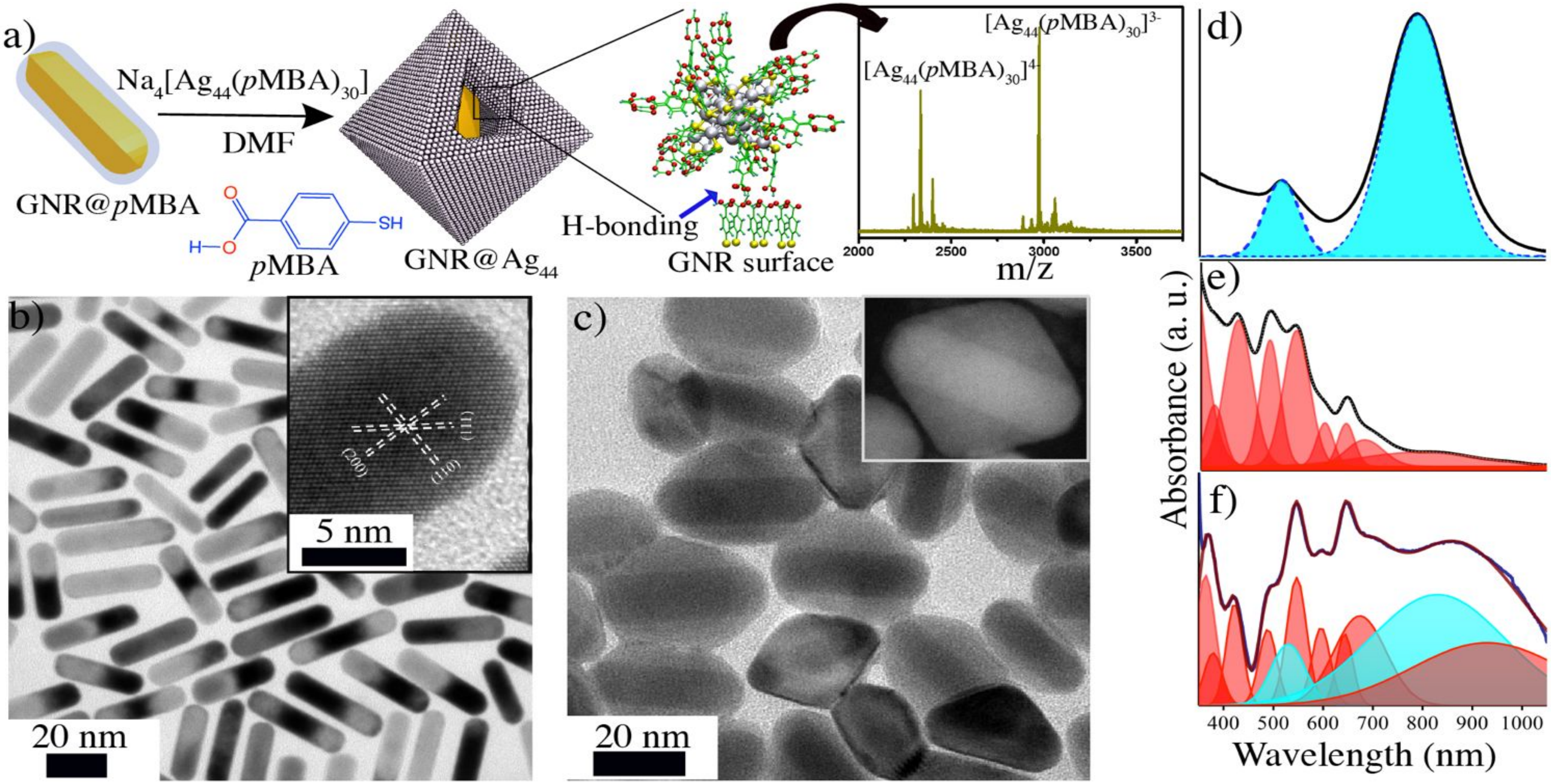
Assemblies and superstructures

Ag_{29} supramolecular adduct with crown ether

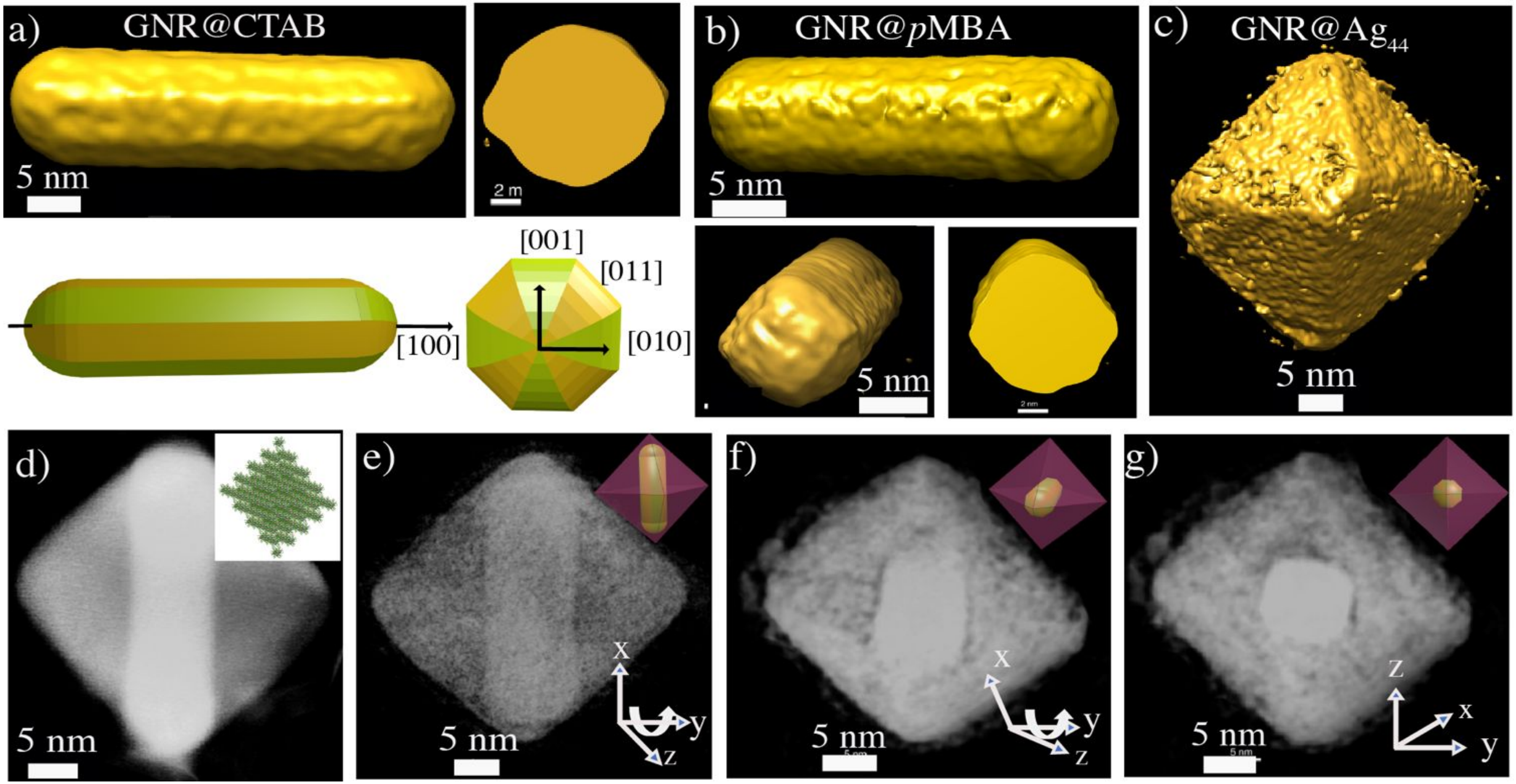


Papri Chakraborti, et. al., submitted

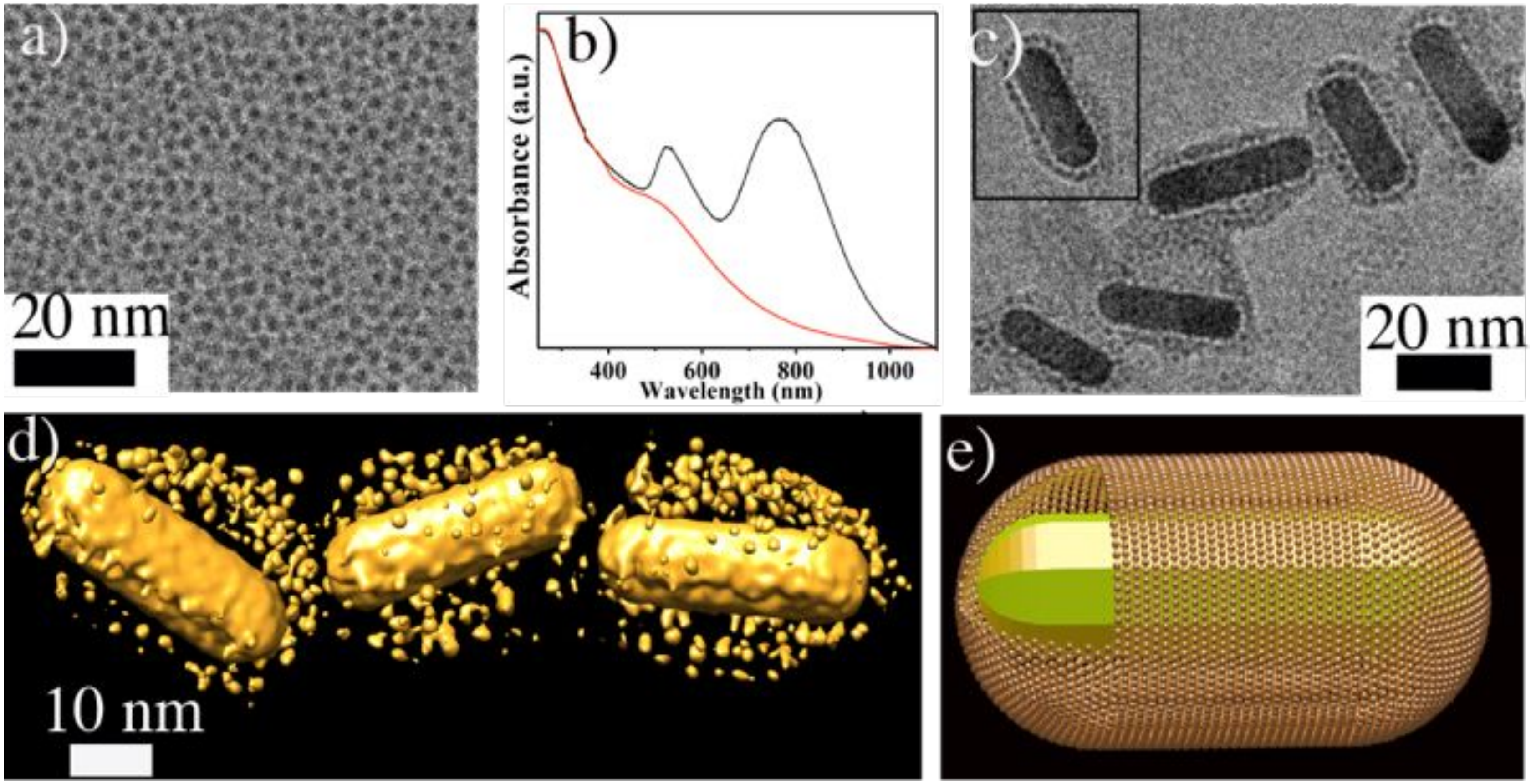

A)
x
z
a = 27.42 Å, b = 27.42 Å, c = 57.15 Å
B)
x
z
a = 27.46 Å, b = 27.46 Å, c = 46.65 Å



Amrita Chakraborty, et. al. Angew. Chem. 2018

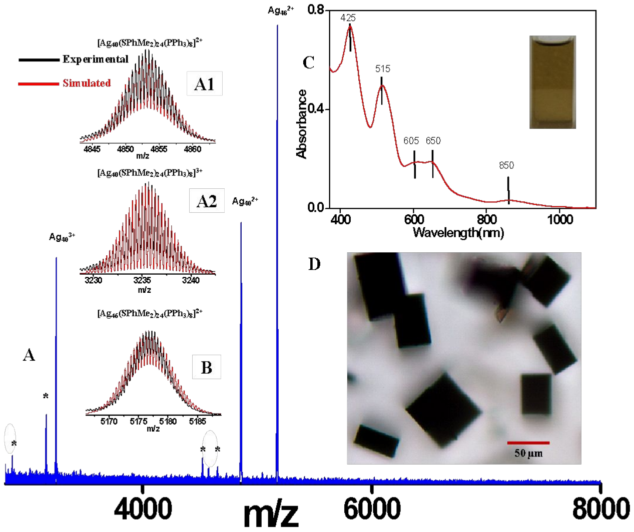


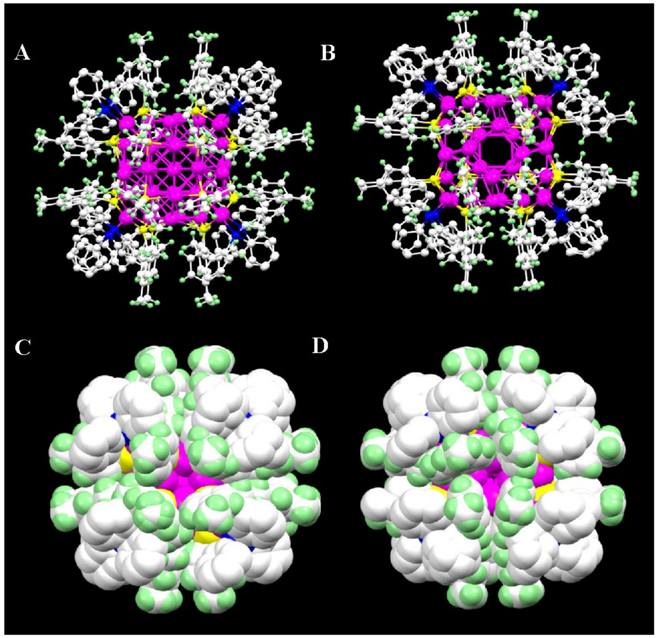
a)
GNR@CTAB
5 nm
2 m
[001]
[011]
[010]
[100]
b)
GNR@pMBA
5 nm
5 nm
2 nm
c)
GNR@Ag44
5 nm
d)
5 nm
e)
5 nm
x
y
z
f)
5 nm
x
y
z
g)
5 nm
z
x
y



a)
20 nm
b)
Absorbance (a.u.)
400
600
800
1000
Wavelength (nm)
c)
20 nm
d)
10 nm
e)

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





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

Sensors
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 !

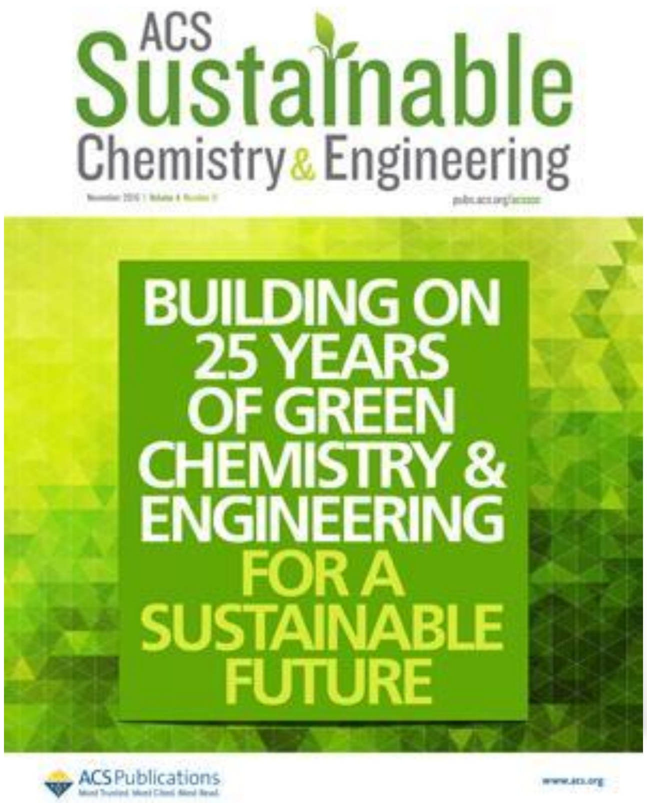
Clean water through advanced materials


iitmadras.

Department of Science and Technology

Thank you

A Leader in Advancing Green Chemistry & Green Engineering Concepts



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