Now in the 60^{th} year

Nanoparticles are Molecules

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Co-founder

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

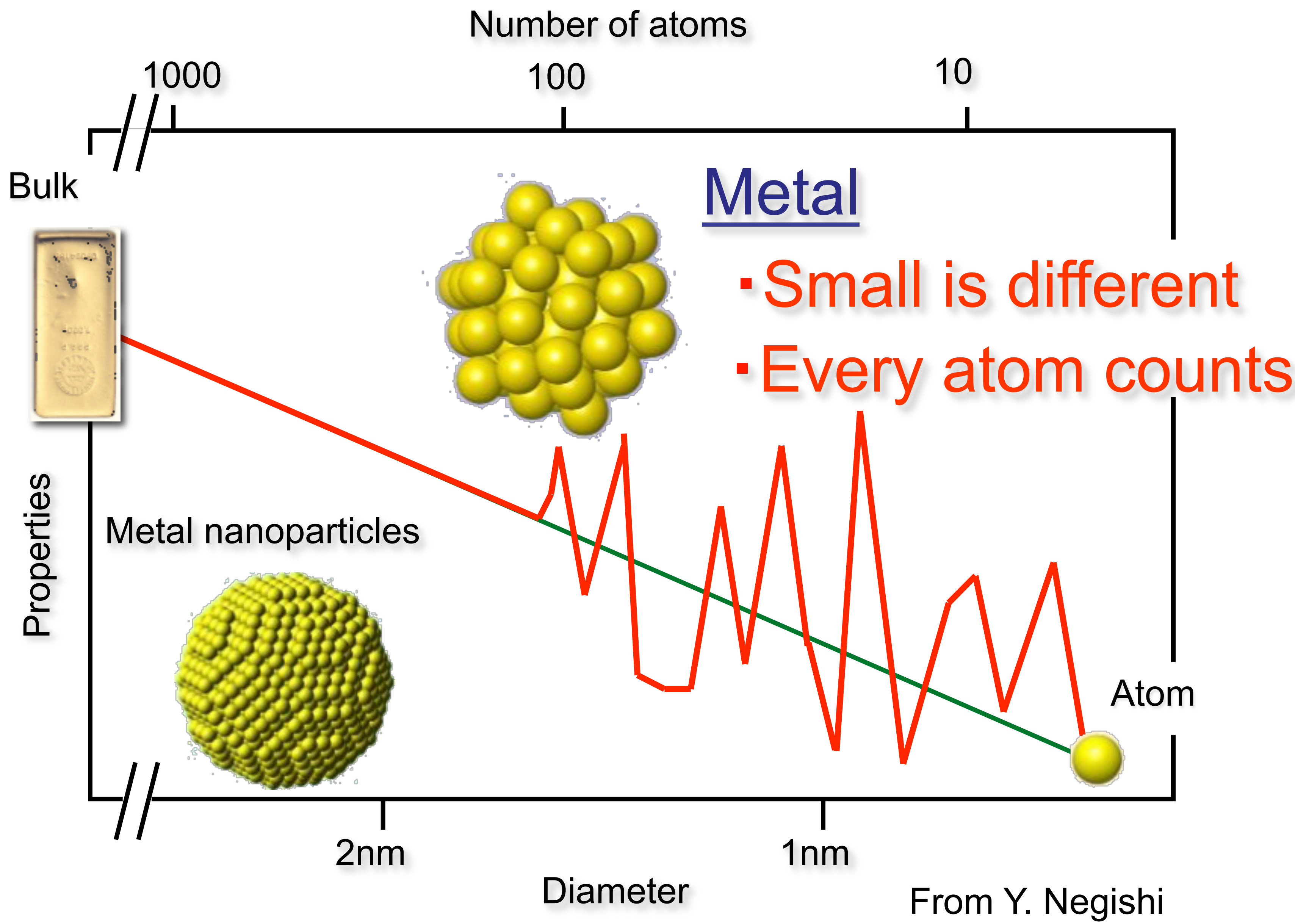
Professor-in-charge

International Centre for Clean Water

Associate Editor

ACS Sustainable Chemistry & Engineering

ISMAS 2019, BARC, Mumbai, November 27-30, 2019


Number of atoms
1000
100
10
Bulk
Metal
·Small is different
·Every atom counts
Properties
Metal nanoparticles
Atom
2nm
1nm
Diameter
From Y. Negishi

CHEMICAL REVIEWS

Review

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

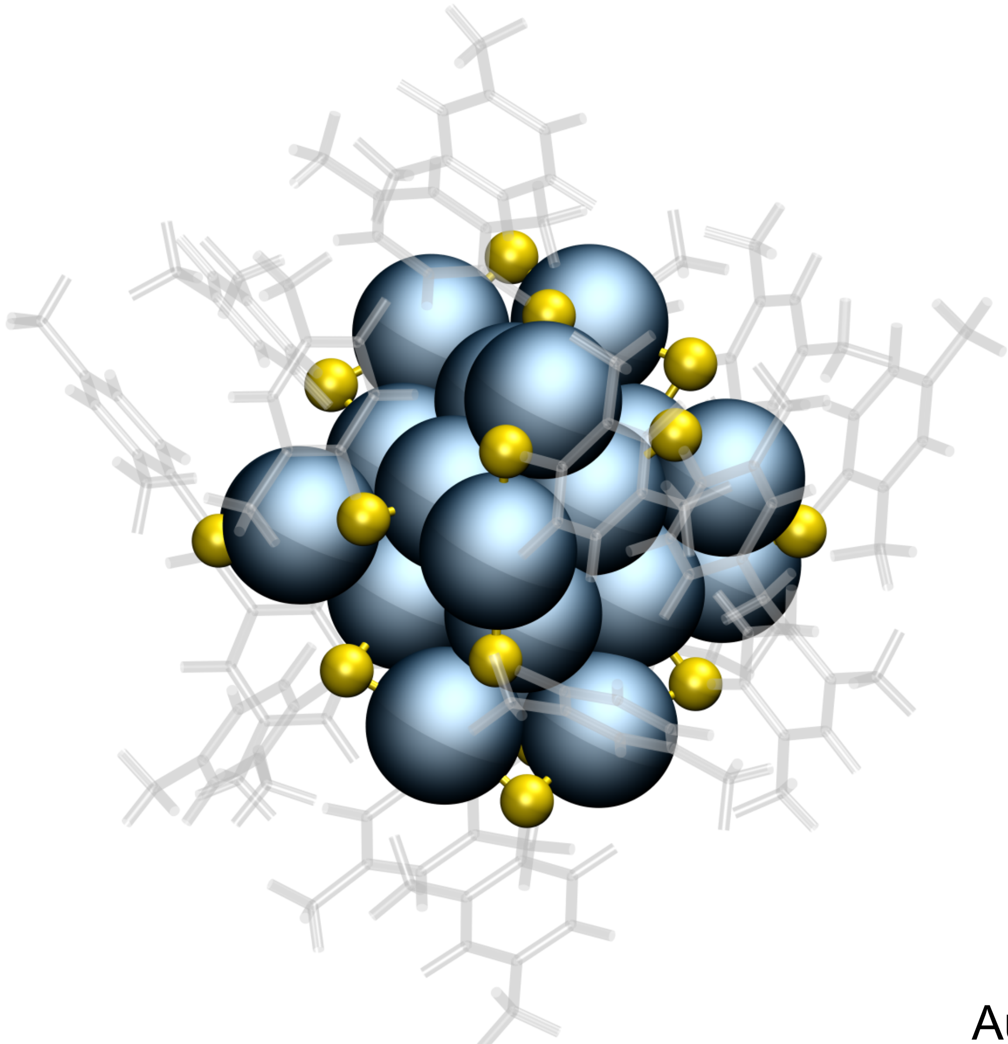
Indranath Chakraborty[†] and Thalappil Pradeep*

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

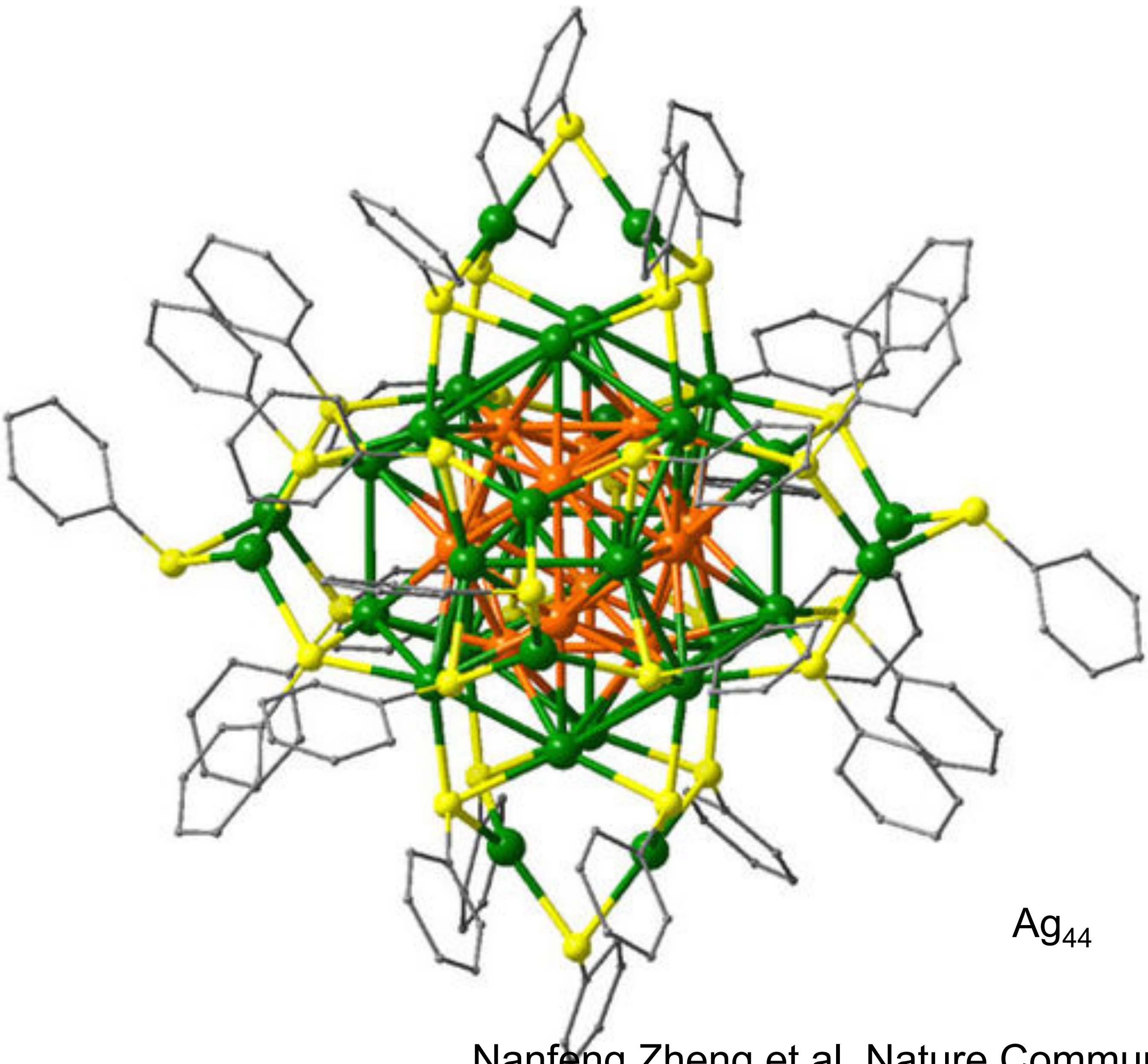
Supporting Information

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

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

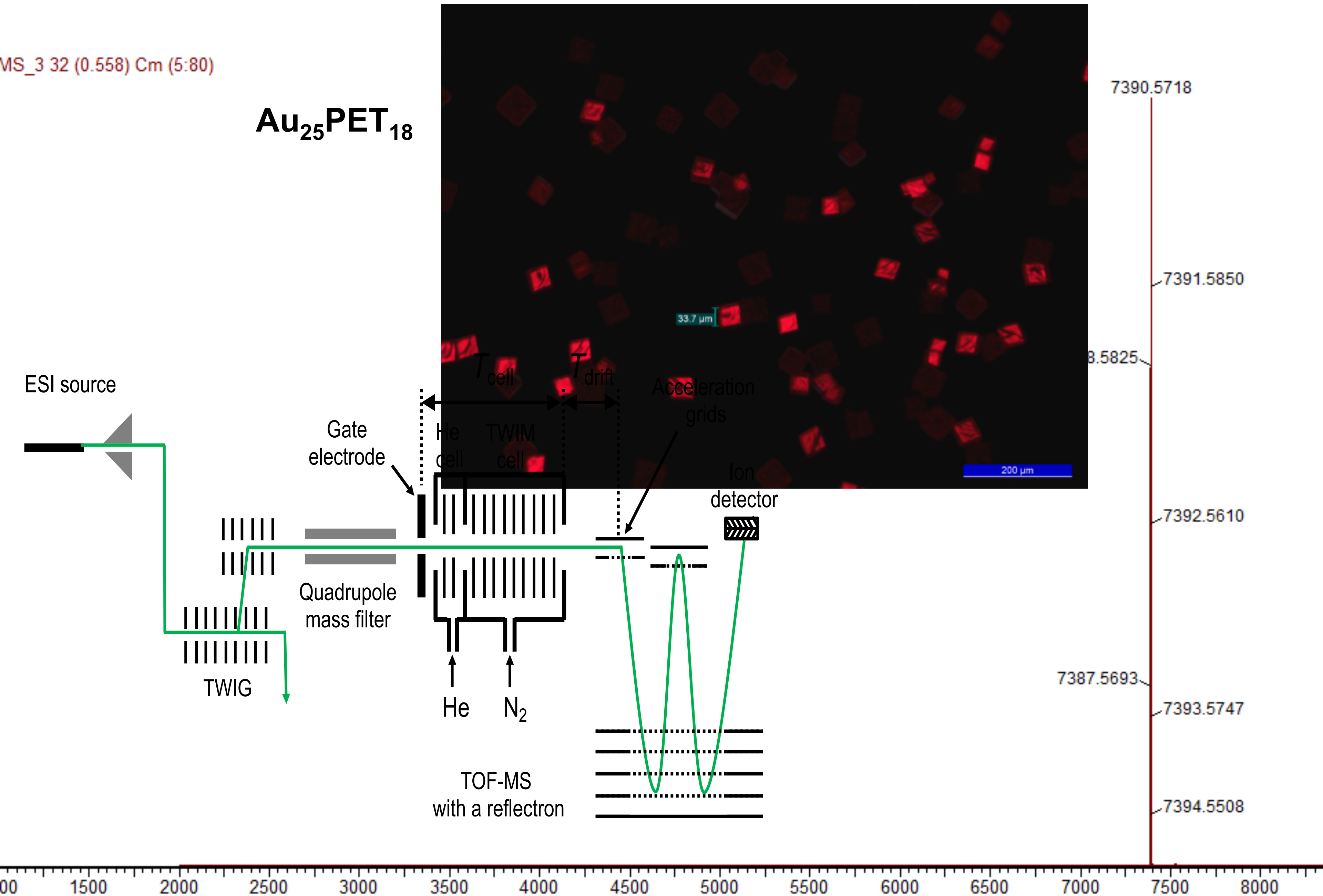


Au_{25}, Ag_{25}

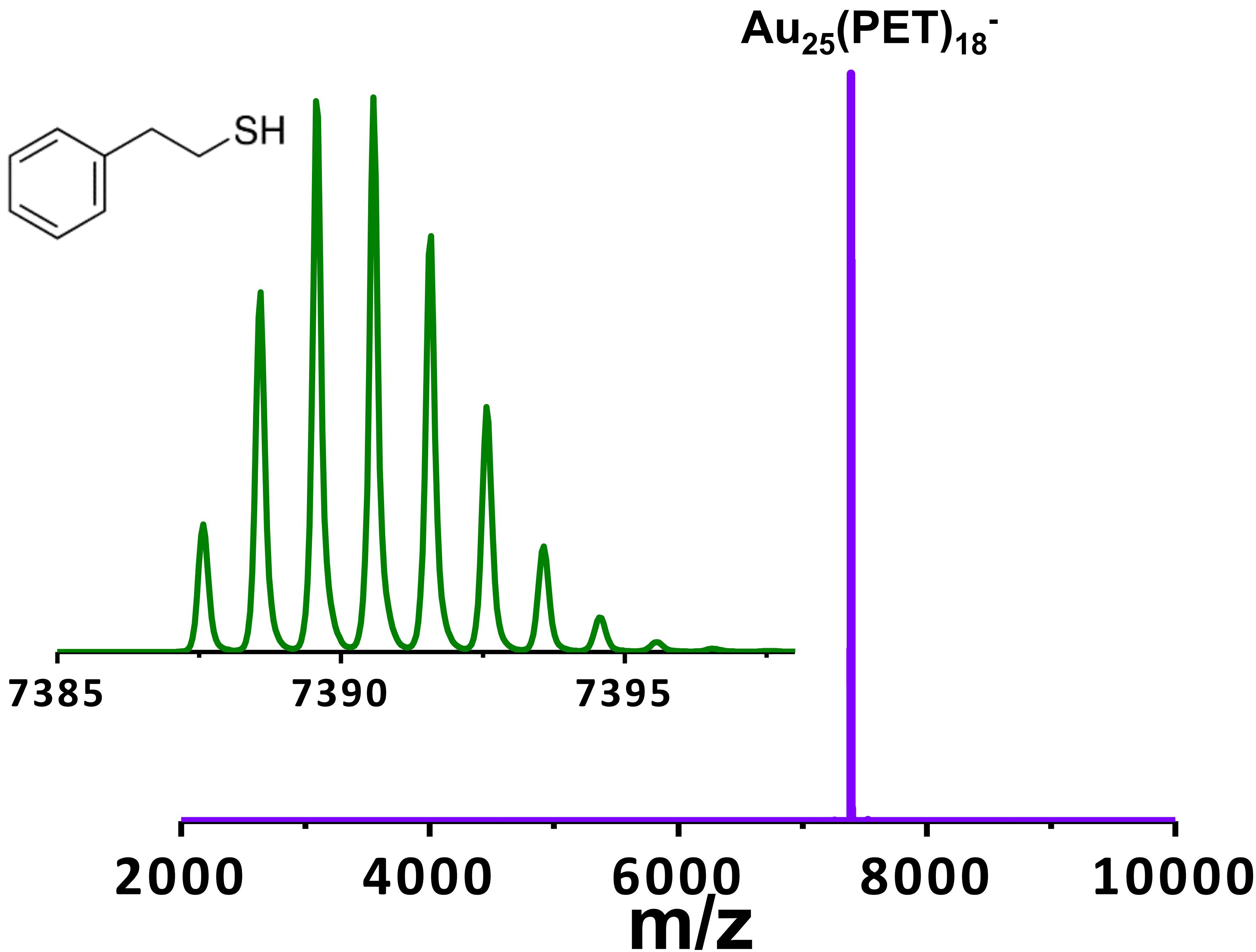


Ag_{44}

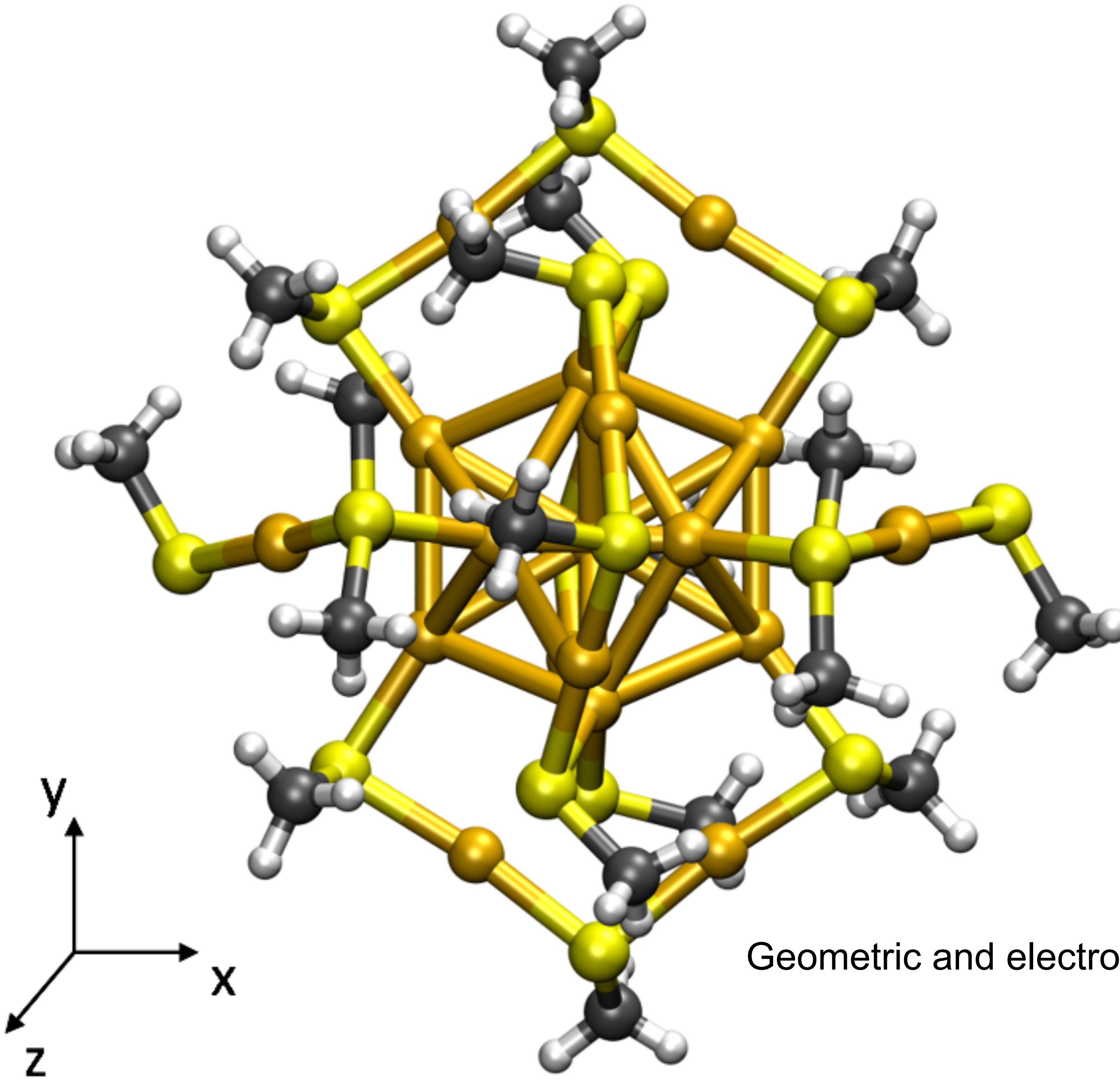
Nanfeng Zheng et al. Nature Communications, 2013
Terry Bigioni et al. Nature 2013



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



$Au_{25}(PET)_{18}^{-}$
SH
7385
7390
7395
2000
4000
6000
8000
10000
m/z



Geometric and electronic shells

Chemistry of clusters

Reactions of clusters

Reactions <u>between</u> clusters

Inter-cluster reactions

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

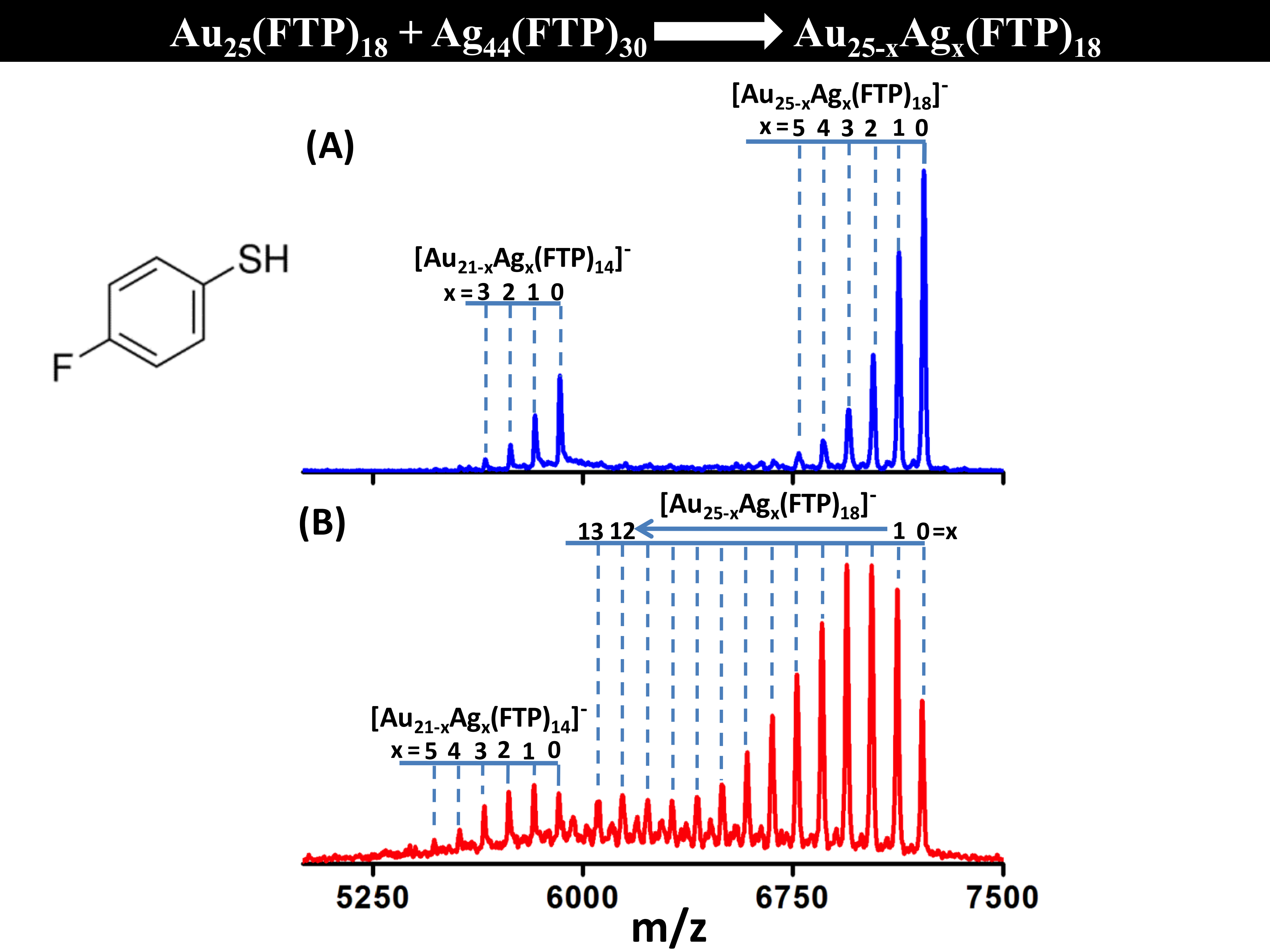
Intercluster Reactions between $Au_{25}(SR)_{18}$ and $Ag_{44}(SR)_{30}$

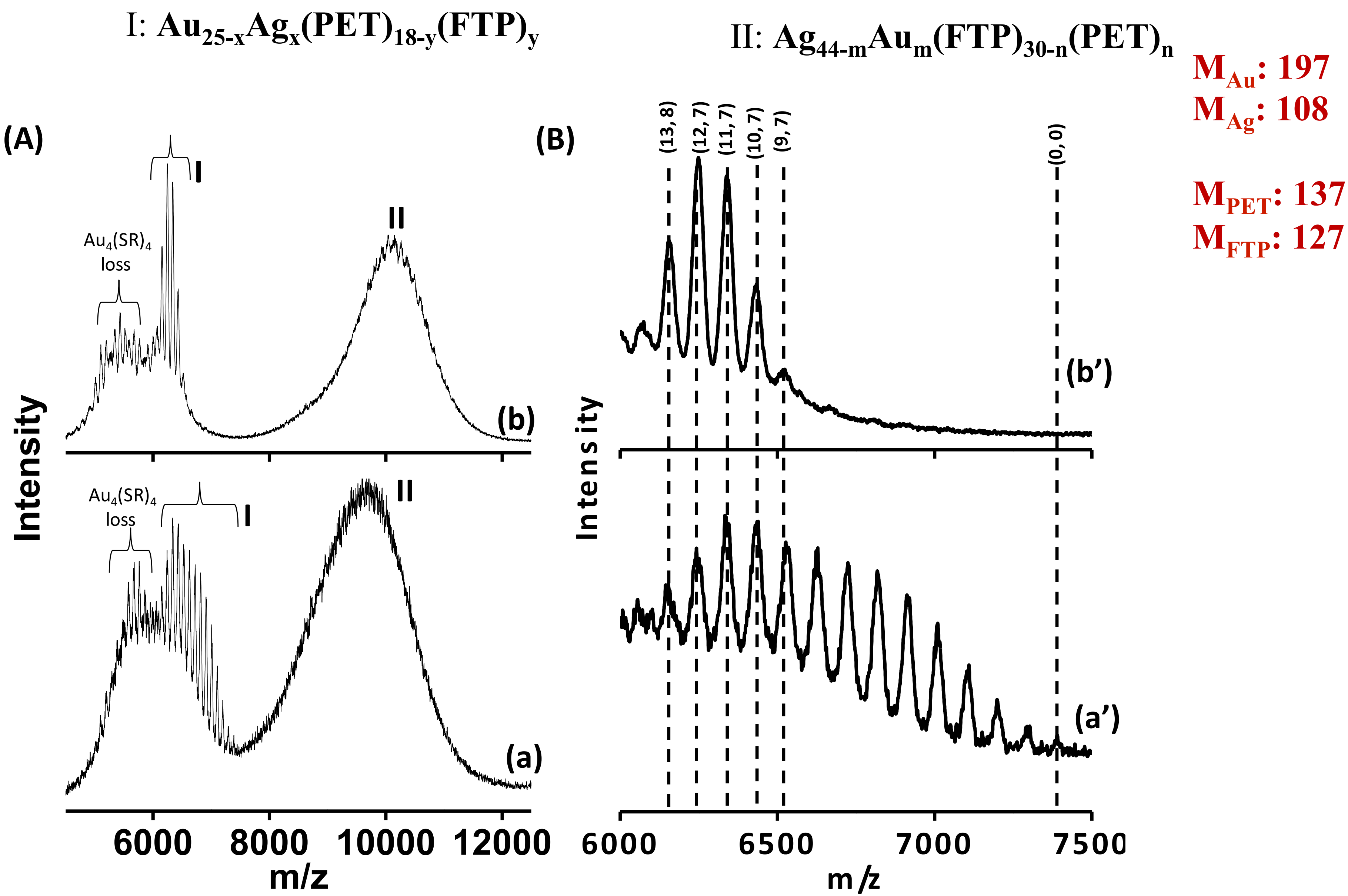
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

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

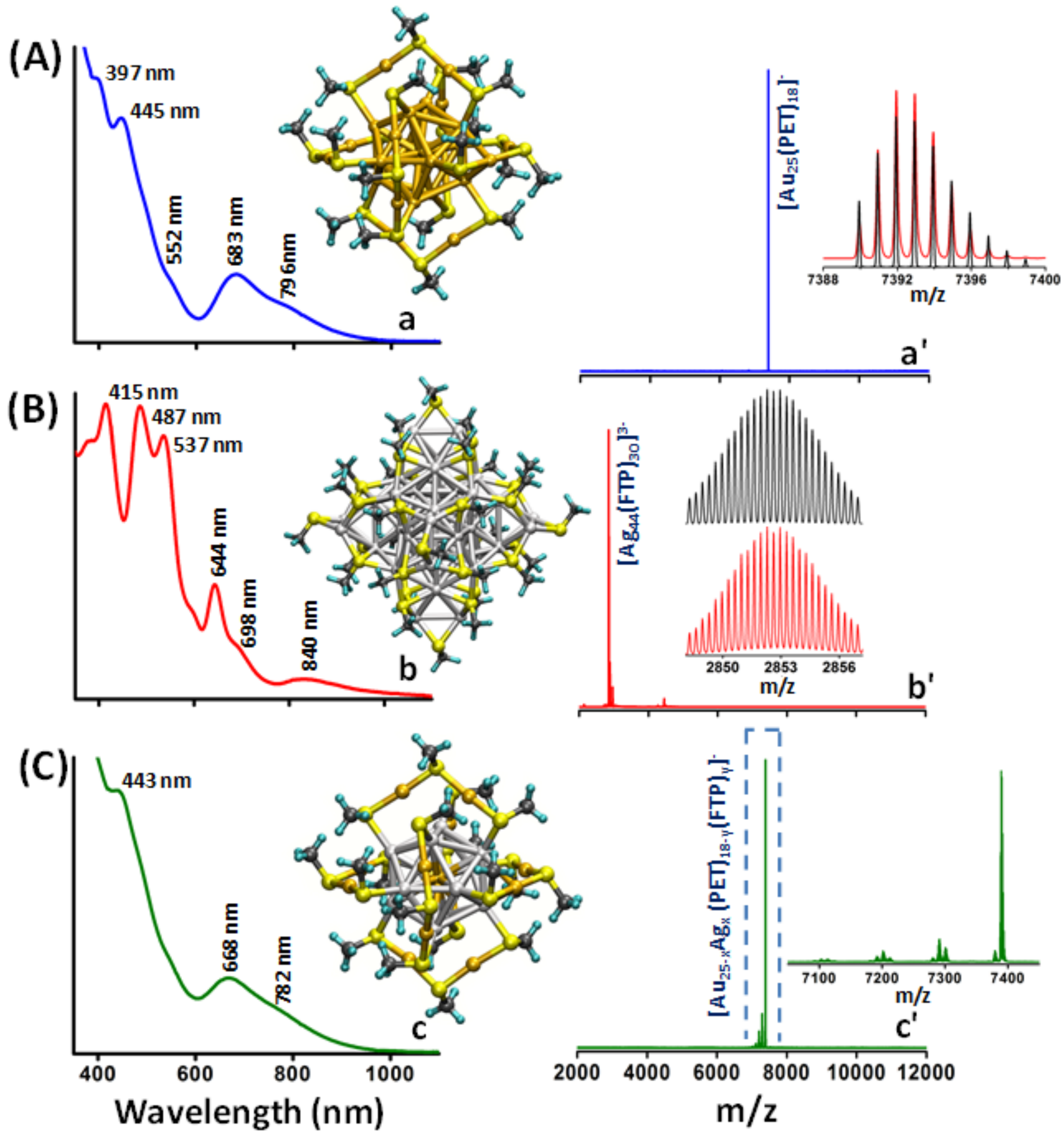
Supporting Information

$$A + B \rightarrow C + D$$


Au25(FTP)18 + Ag44(FTP)30 → Au25-xAgx(FTP)18
SH
F
(A)
[Au21-xAgx(FTP)14]-
x = 3 2 1 0
[Au25-xAgx(FTP)18]-
x = 5 4 3 2 1 0
(B)
[Au25-xAgx(FTP)18]-
13 12 1 0=x
[Au21-xAgx(FTP)14]-
x = 5 4 3 2 1 0
5250
6000
6750
7500
m/z



I: $Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y$
II: $Ag_{44-m}Au_m(FTP)_{30-n}(PET)_n$
M_{Au}: 197
M_{Ag}: 108
M_{PET}: 137
M_{FTP}: 127
(A)
(B)
$Au_4(SR)_4$ 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

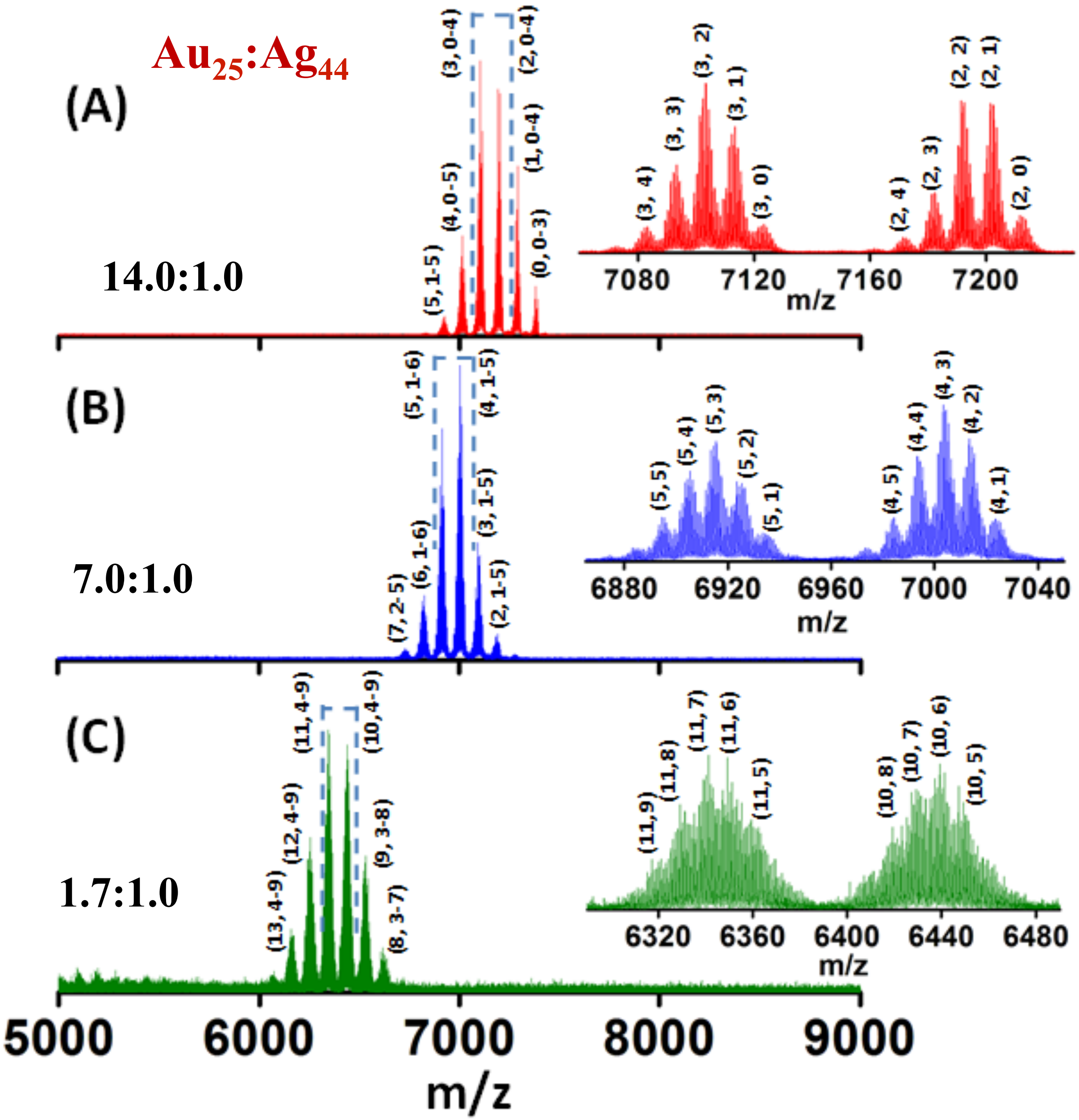


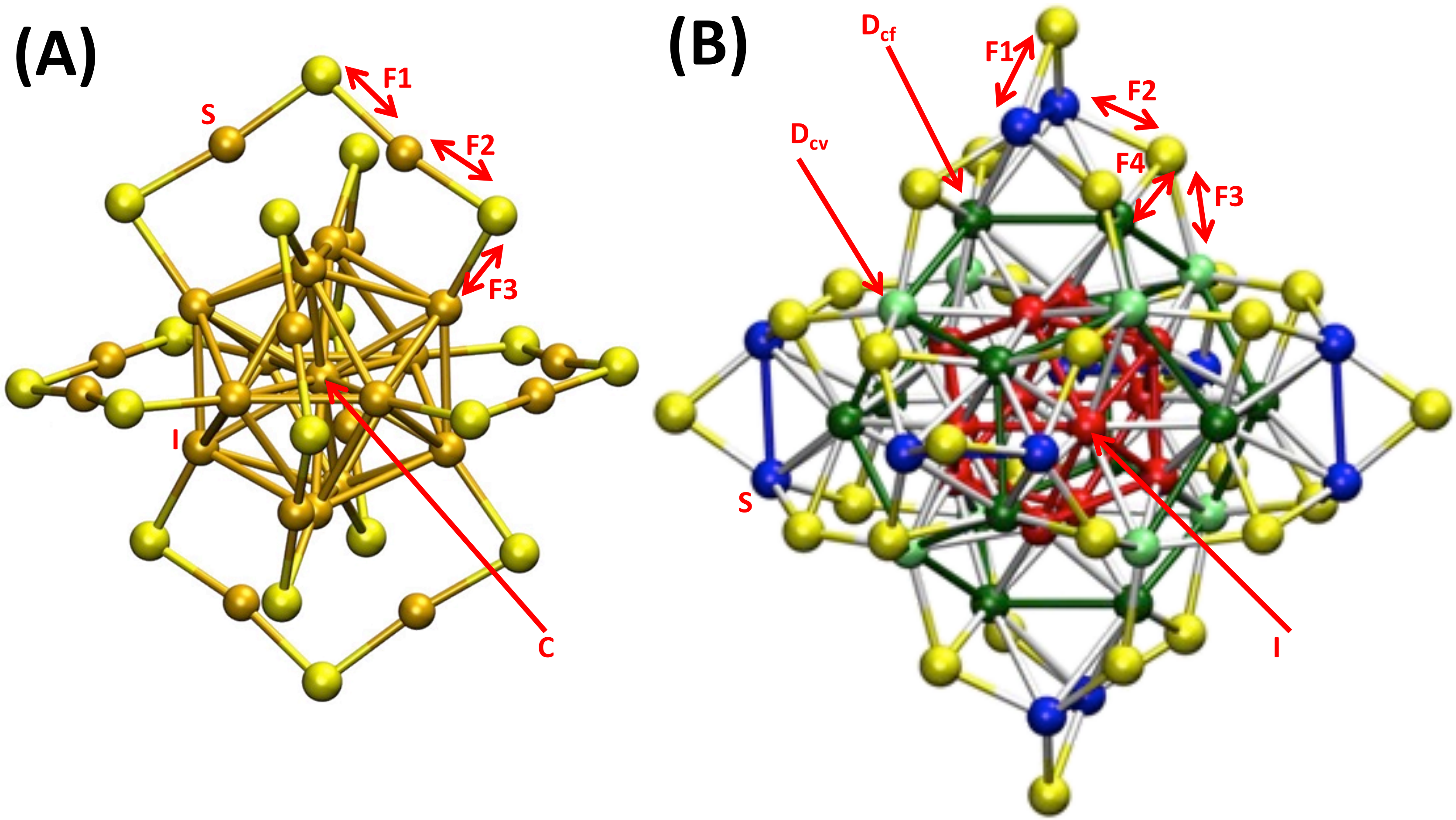
(A)
397 nm
445 nm
552 nm
683 nm
796nm
a
[Au25(PET)18]-
7388
7392
7396
7400
m/z
a'
(B)
415 nm
487 nm
537 nm
644 nm
698 nm
840 nm
b
[Ag44(FTP)30]3-
2850
2853
2856
m/z
b'
(C)
443 nm
668 nm
782 nm
c
[Au25-xAgx(PET)18-y(FTP)y]-
7100
7200
7300
7400
m/z
c'
400
600
800
1000
Wavelength (nm)
2000
4000
6000
8000
10000
12000
m/z

$Au_{25}(PET)_{18} + Ag_{44}(FTP)_{30} \longrightarrow Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y;\ x=0\text{-}13$

M_{Au}: 197
M_{Ag}: 108

M_{PET}: 137
M_{FTP}: 127





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

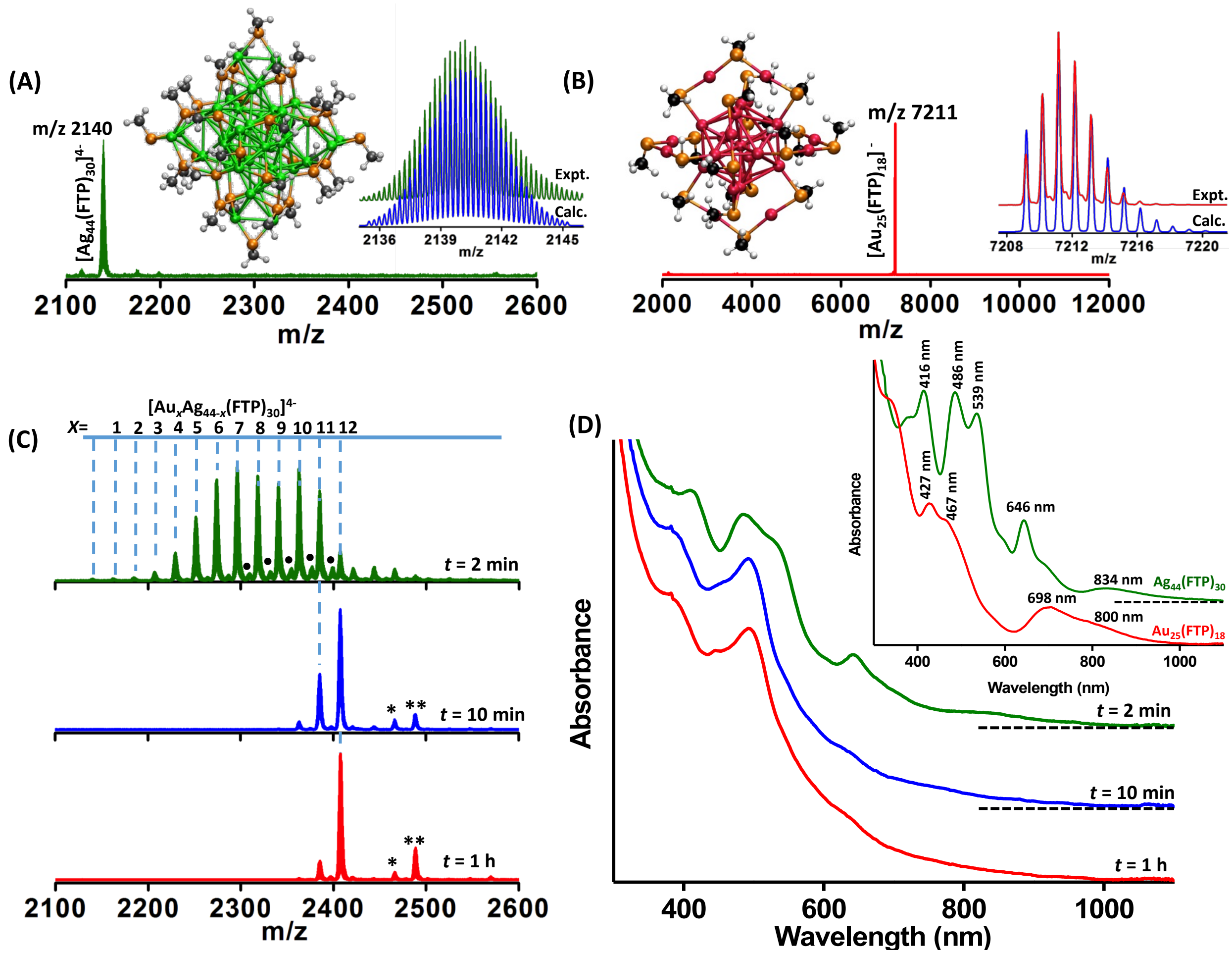
(B)

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

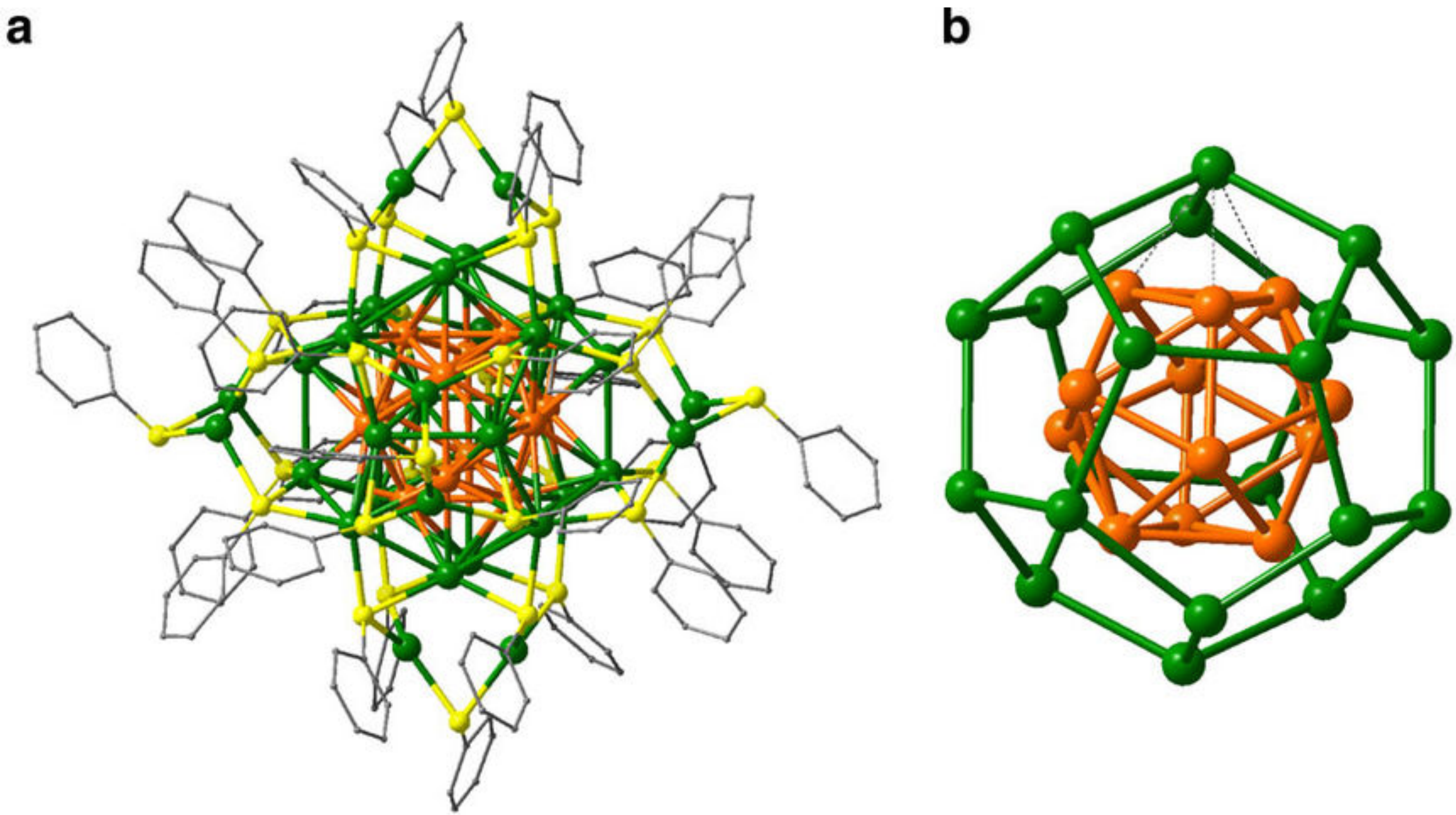
(C)

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

Shell closure in intercluster reactions



Krishnadas et al., ACS Nano 2017

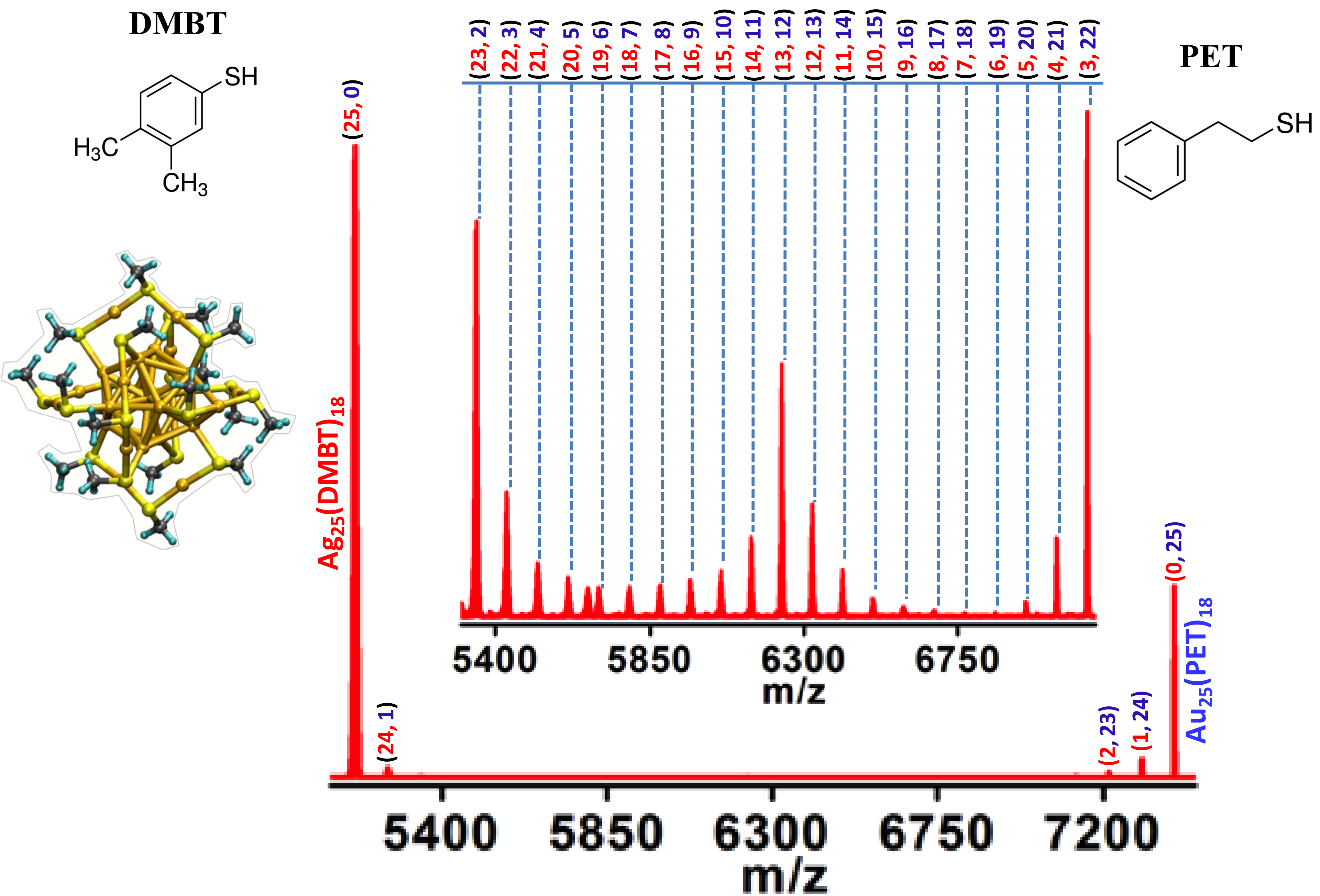


Nanfeng Zheng et al. Nature Communications, 2013

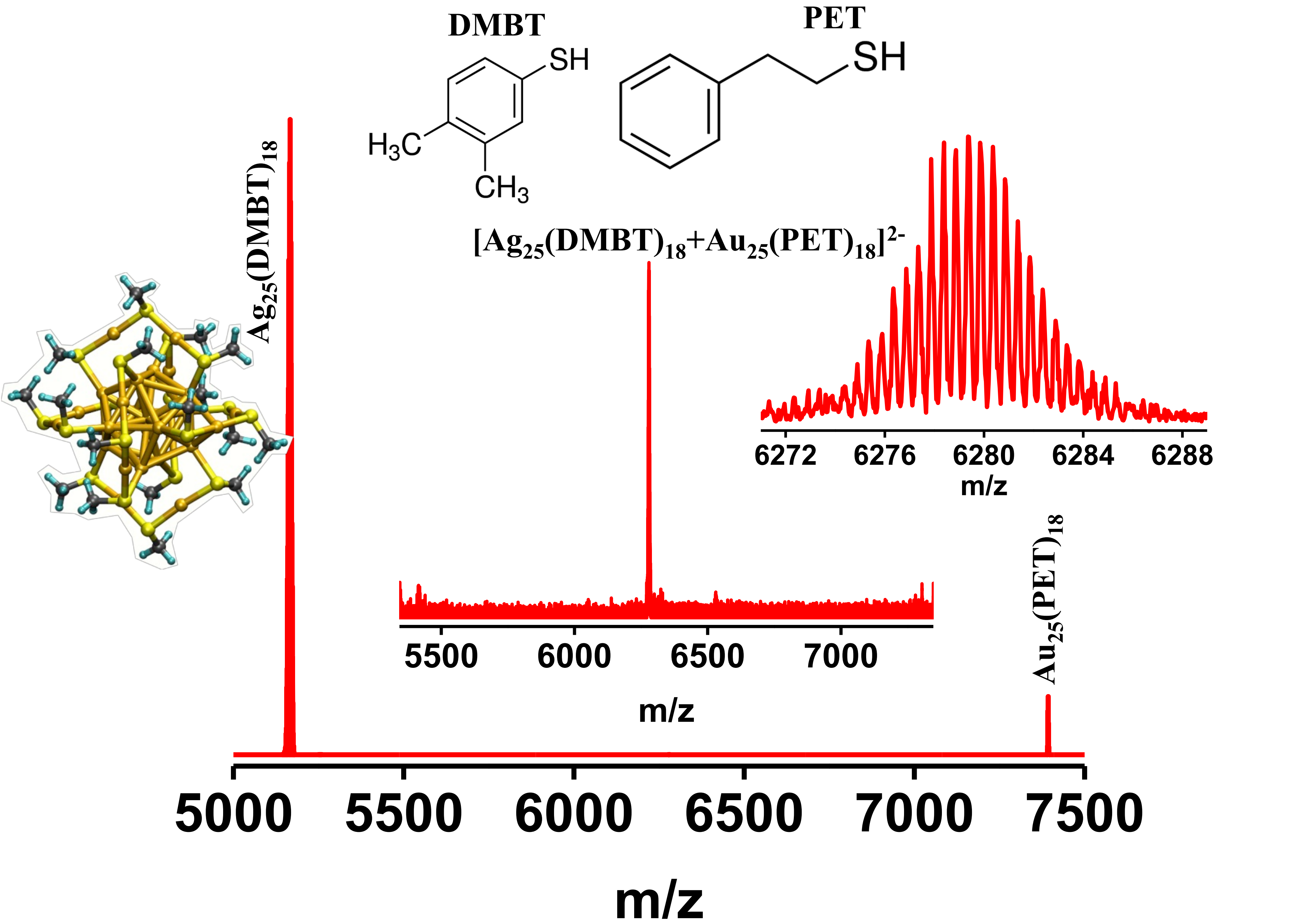
Ag_{25}-Au_{25} experiments

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

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

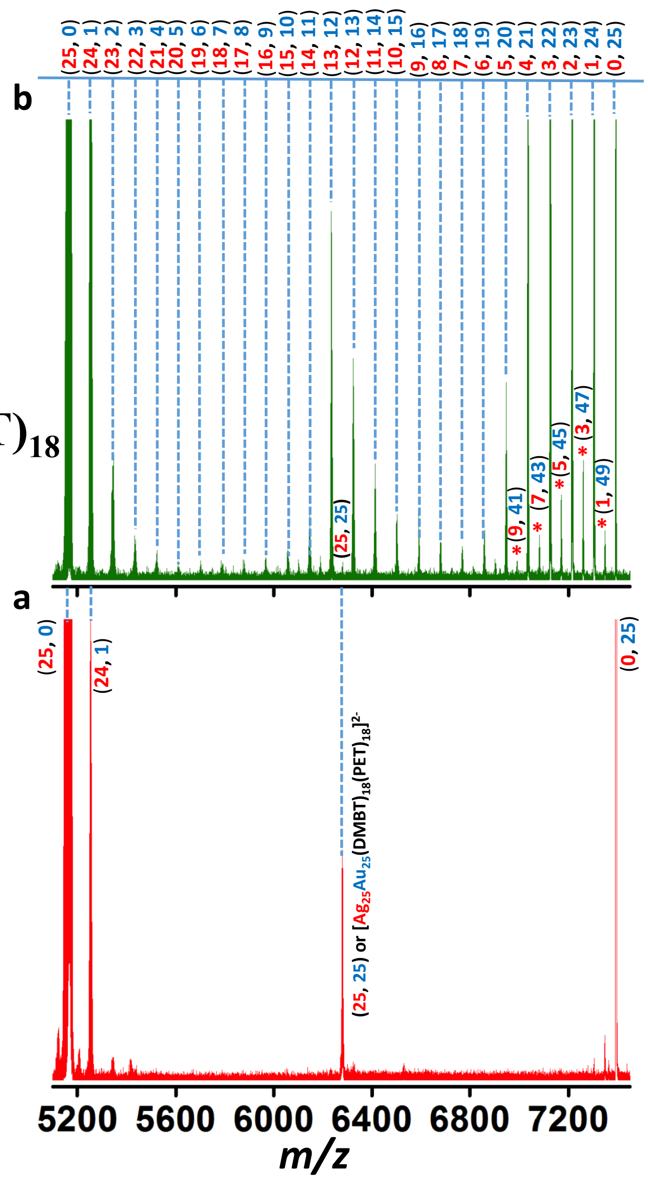


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

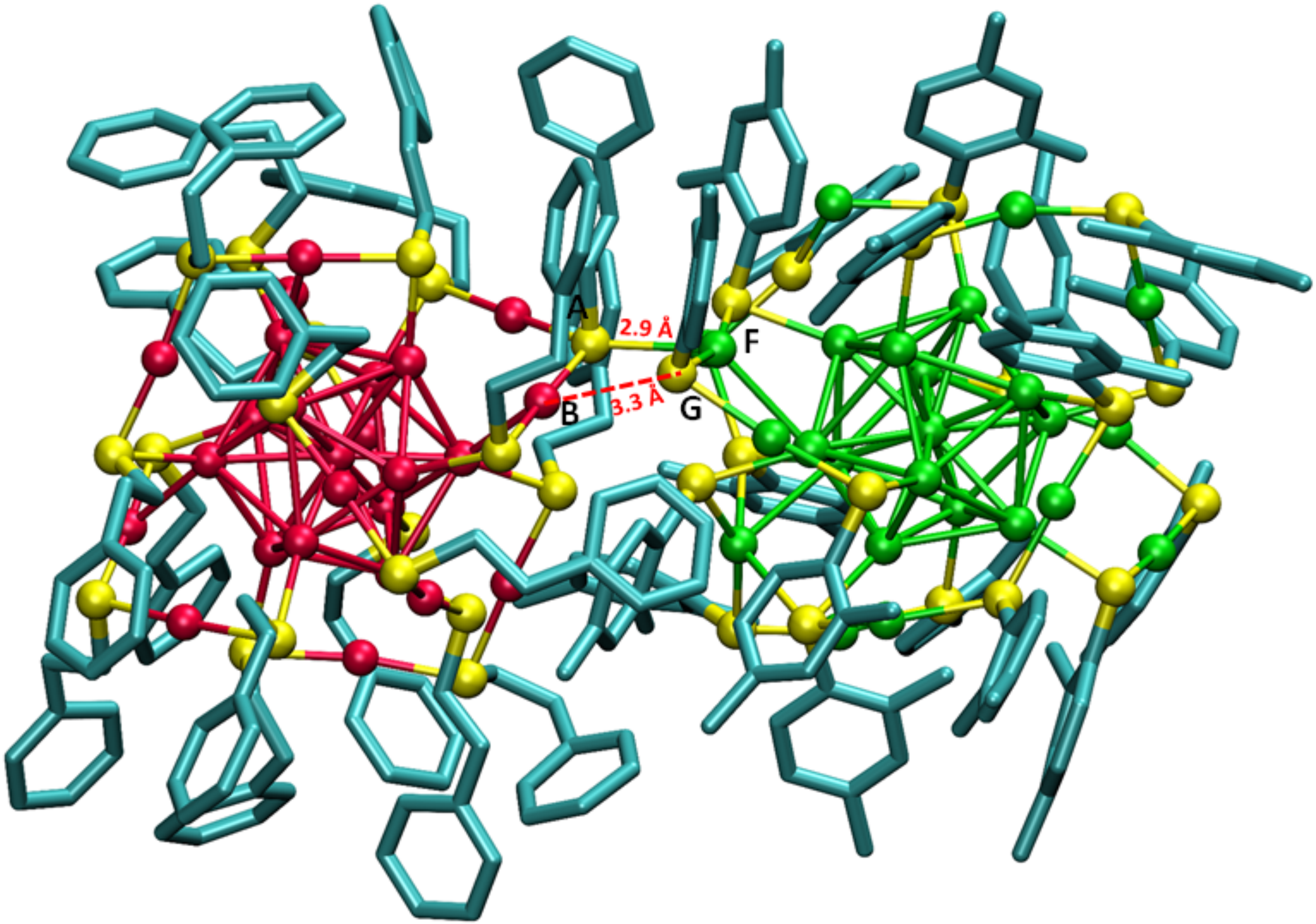
$Ag_{25}(DMBT)_{18}$:$Au_{25}(PET)_{18}$
0.3:1.0

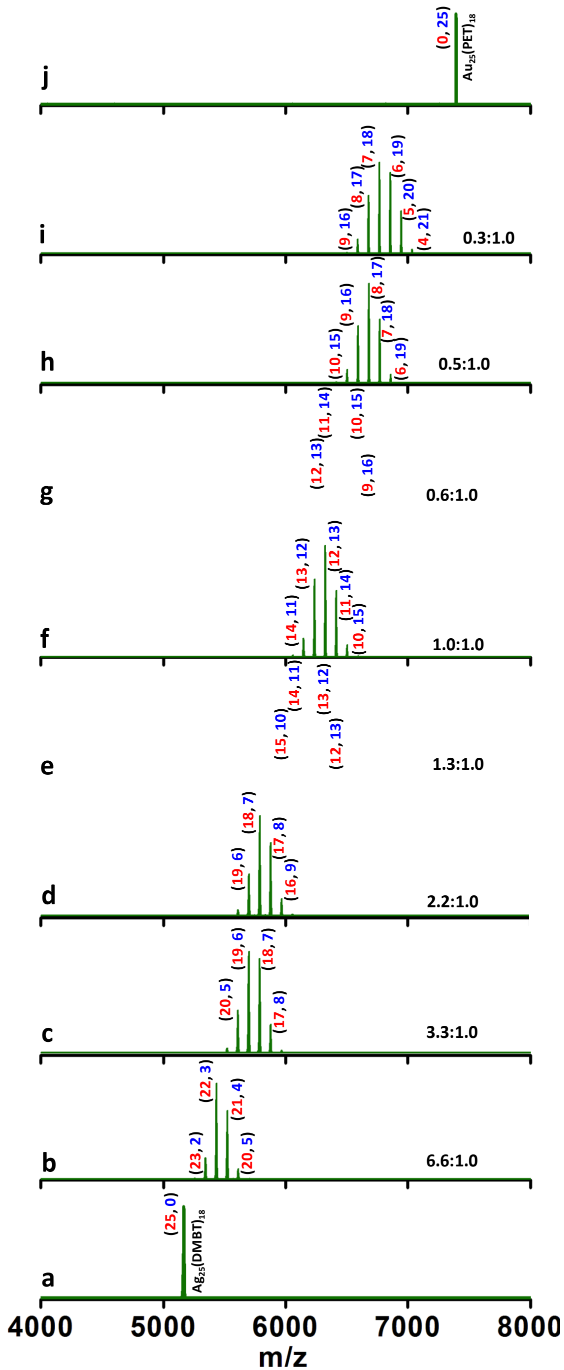


within 5 min

within 2 min

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

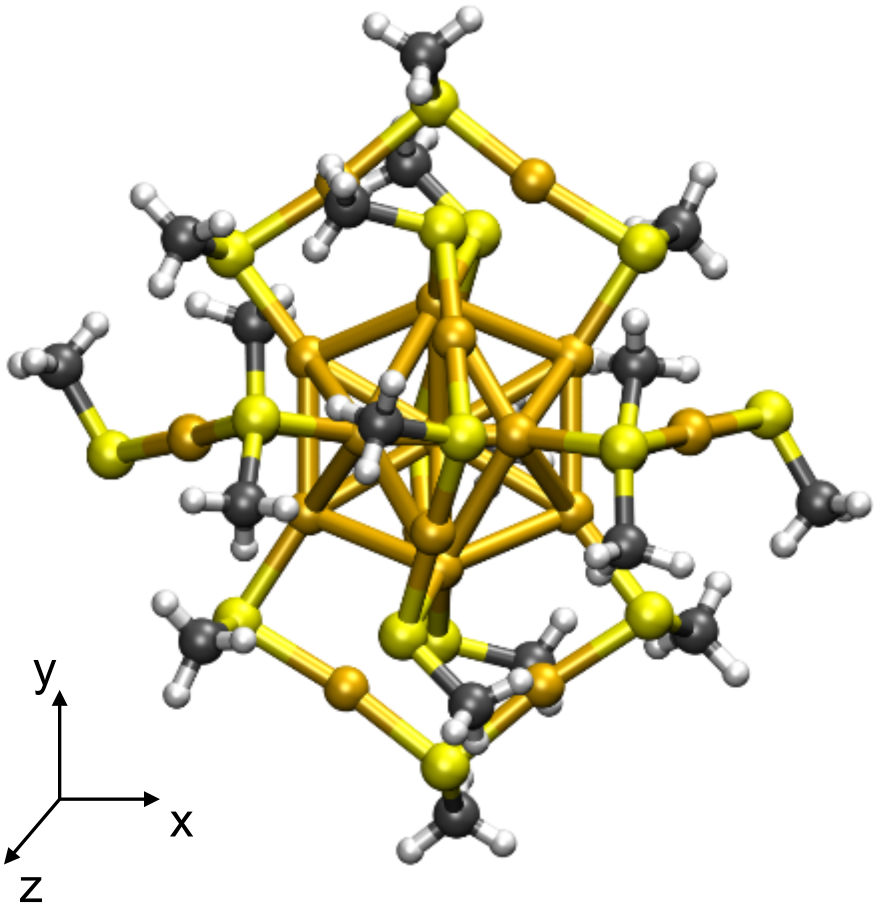


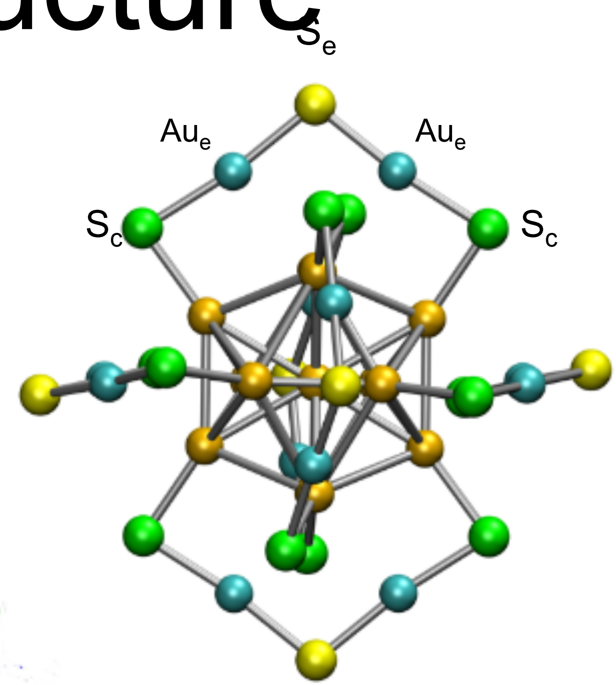


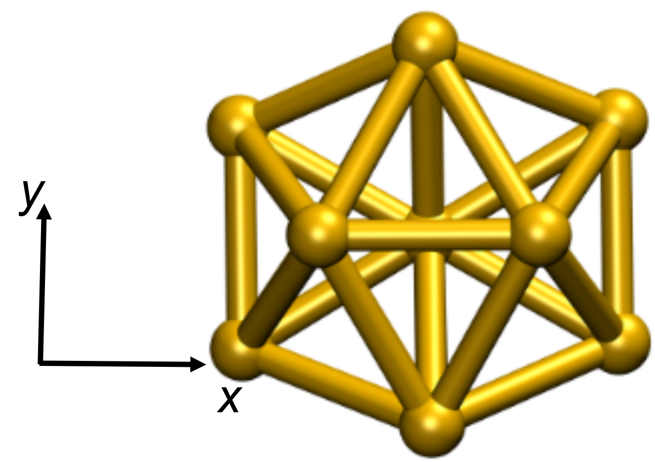
j
(0, 25)
Au25(PET)18
i
(9, 16)
(8, 17)
(7, 18)
(6, 19)
(5, 20)
(4, 21)
0.3:1.0
h
(10, 15)
(9, 16)
(8, 17)
(7, 18)
(6, 19)
0.5:1.0
g
(12, 13)
(11, 14)
(10, 15)
(9, 16)
0.6:1.0
f
(14, 11)
(13, 12)
(12, 13)
(11, 14)
(10, 15)
1.0:1.0
e
(15, 10)
(14, 11)
(13, 12)
(12, 13)
1.3:1.0
d
(19, 6)
(18, 7)
(17, 8)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

How do we comprehend this?

Ball and stick structure



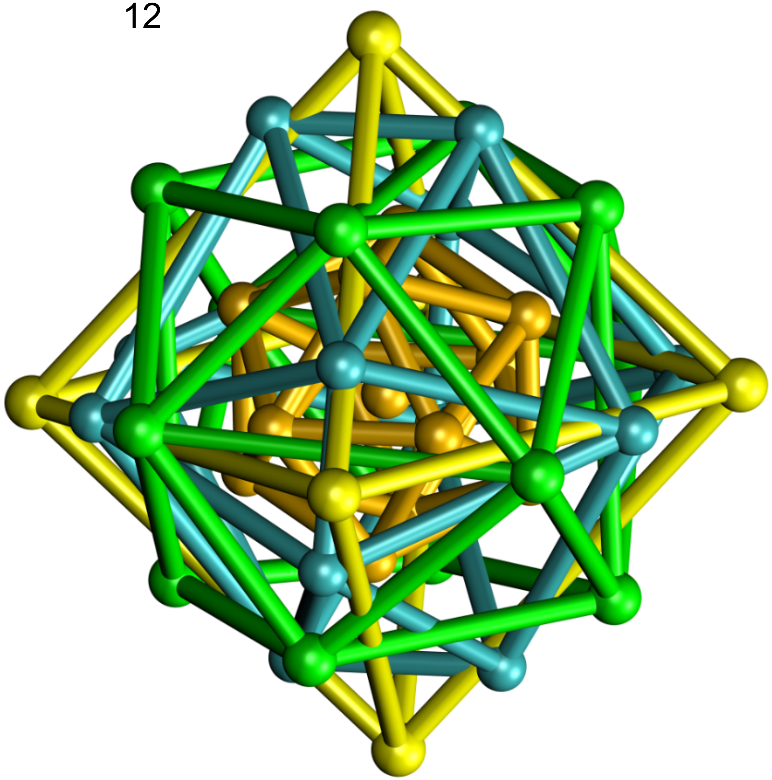




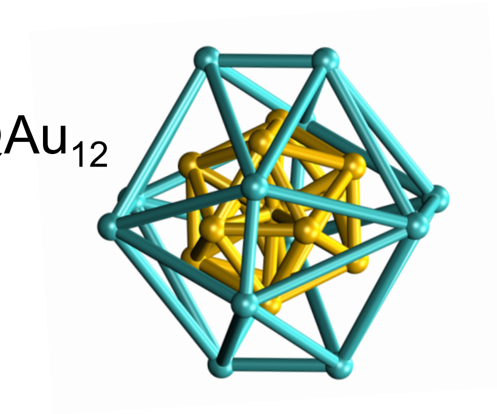
A view of gold methly thiolate [25]aspicule ($Au_{25}(SMe)_{18}$). Gold atoms colored gold, sulfur atoms by yellow, carbon dark gray, hydrogen atoms as white and (b) with the gold and sulfur atoms alone .

Shell Structure

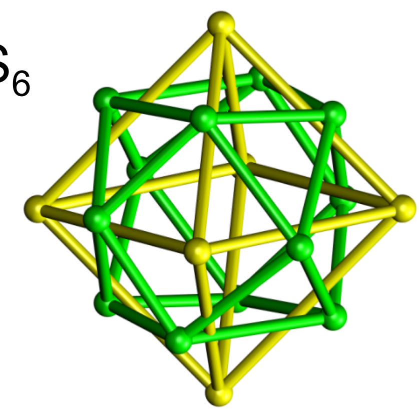
(a) $Au@Au_{12}@Au_{12}@S_6@S_{12}$



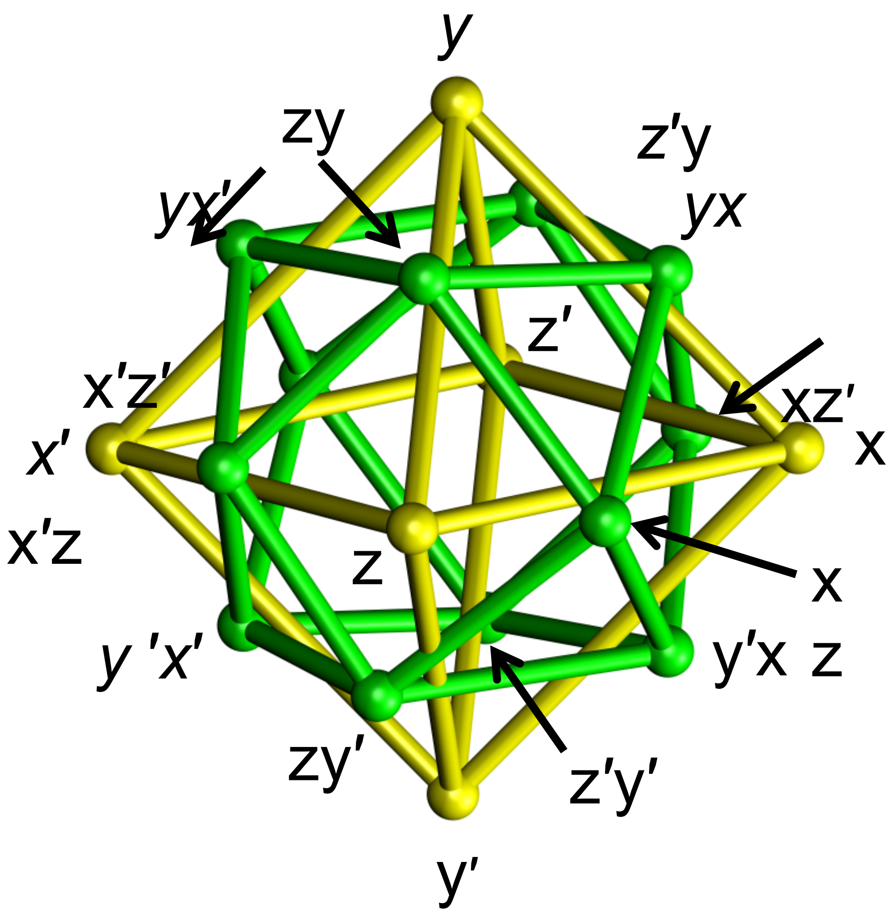
(b) $Au_{12}@Au_{12}$



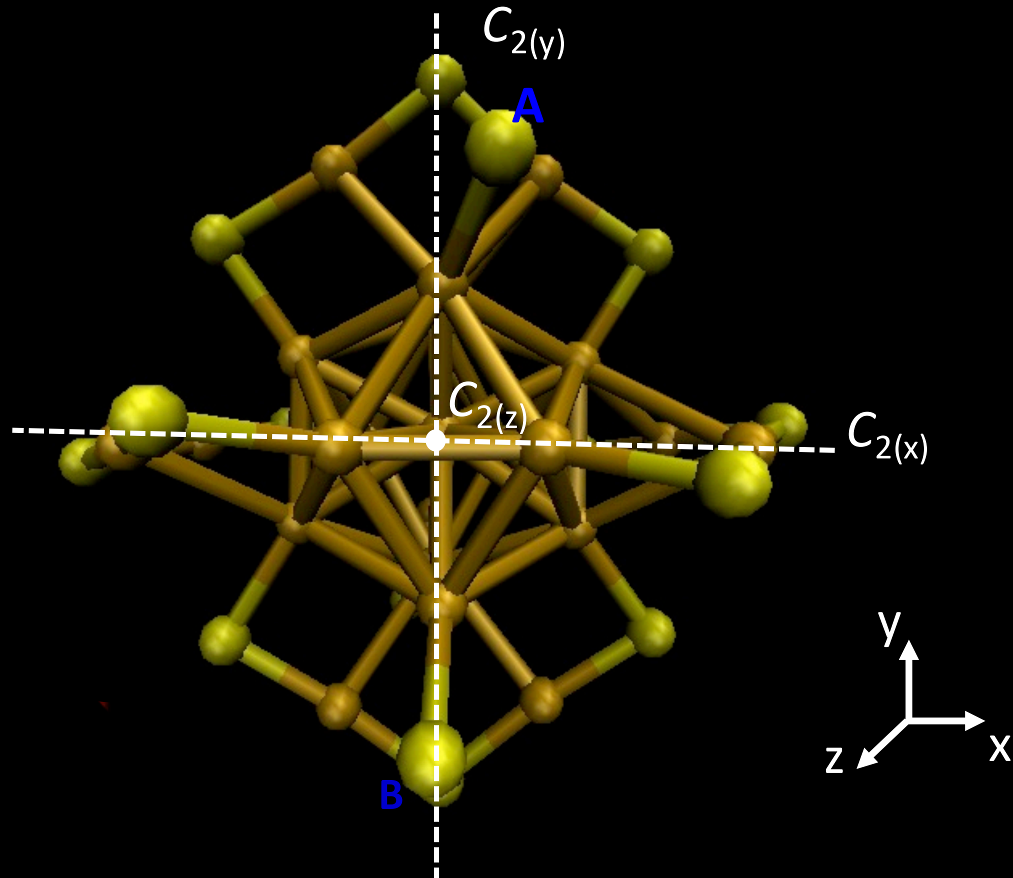
(c) $S_{12}@S_6$



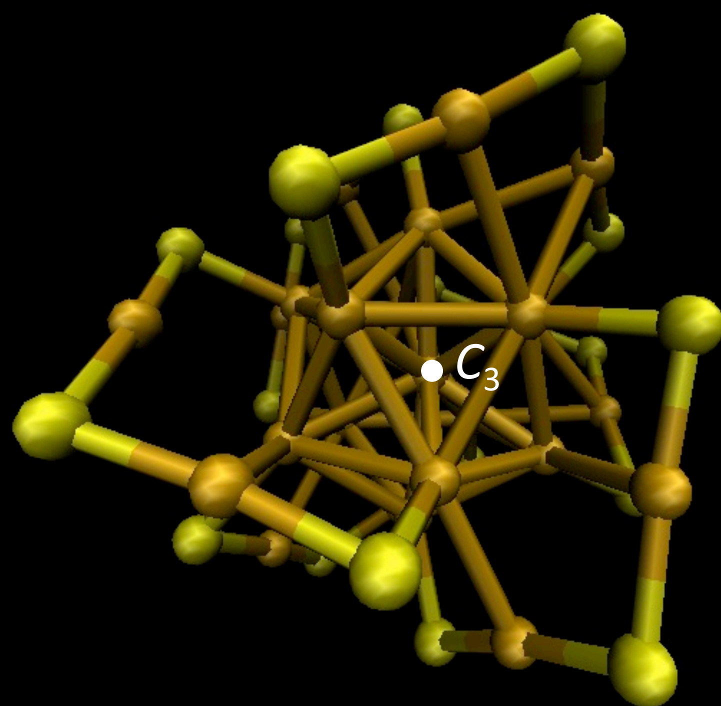
Terminologies

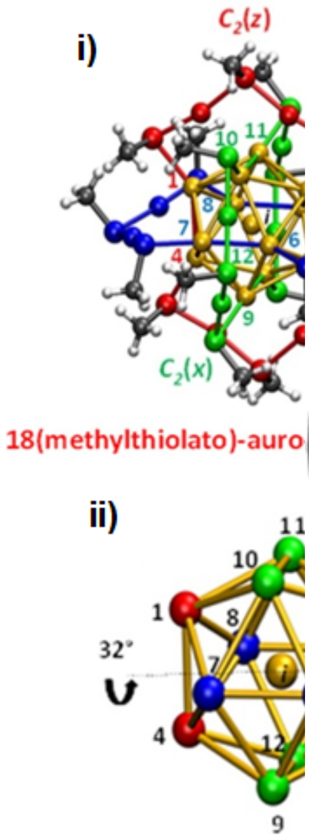


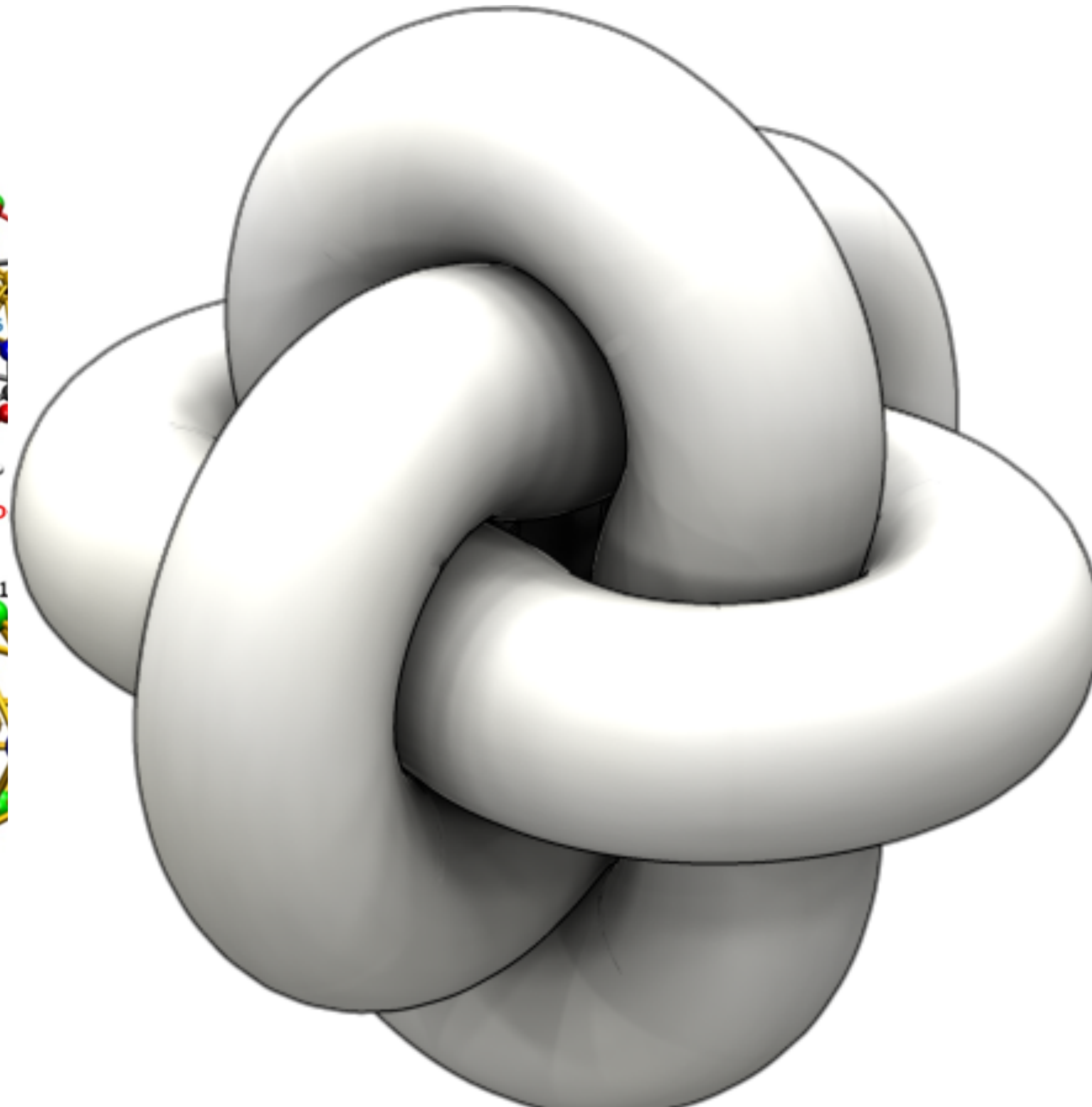
1) Edge projection

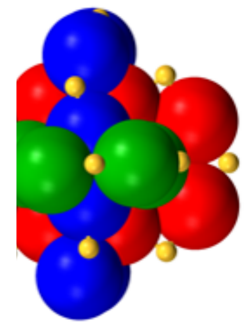


2) Face Projection









PC C. 2015

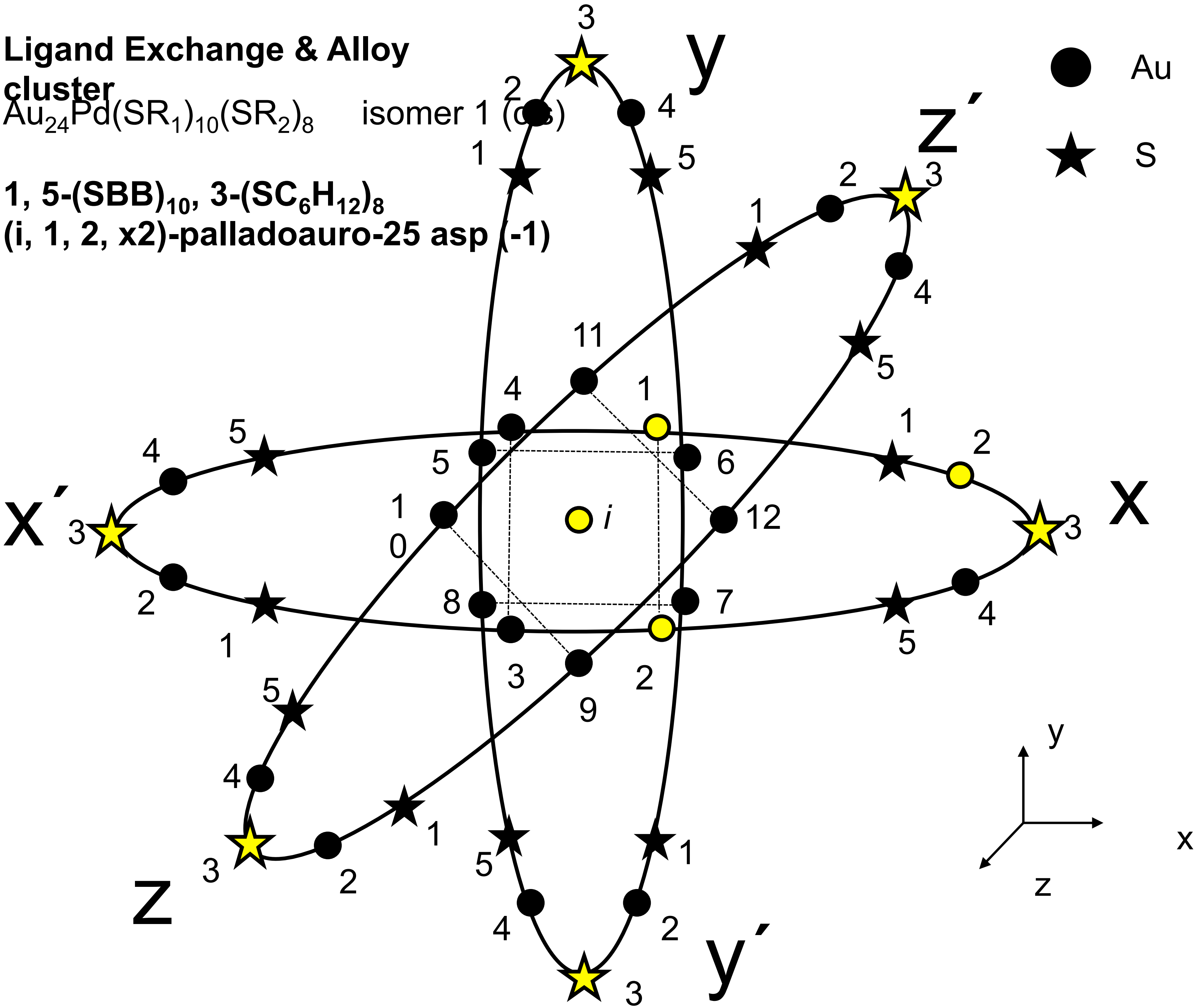
Aspicules

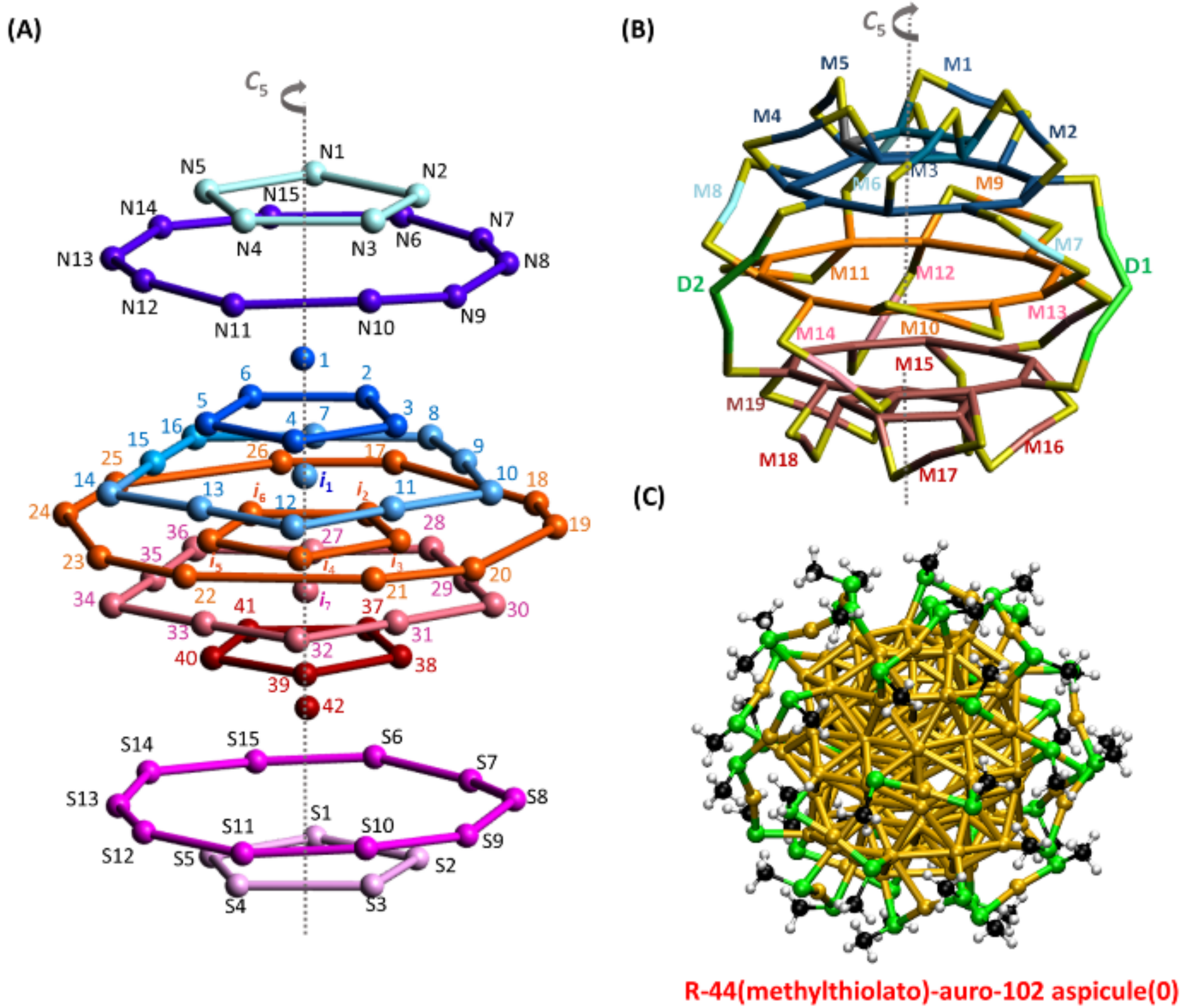
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule(1-)

Ligand Exchange & Alloy cluster

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

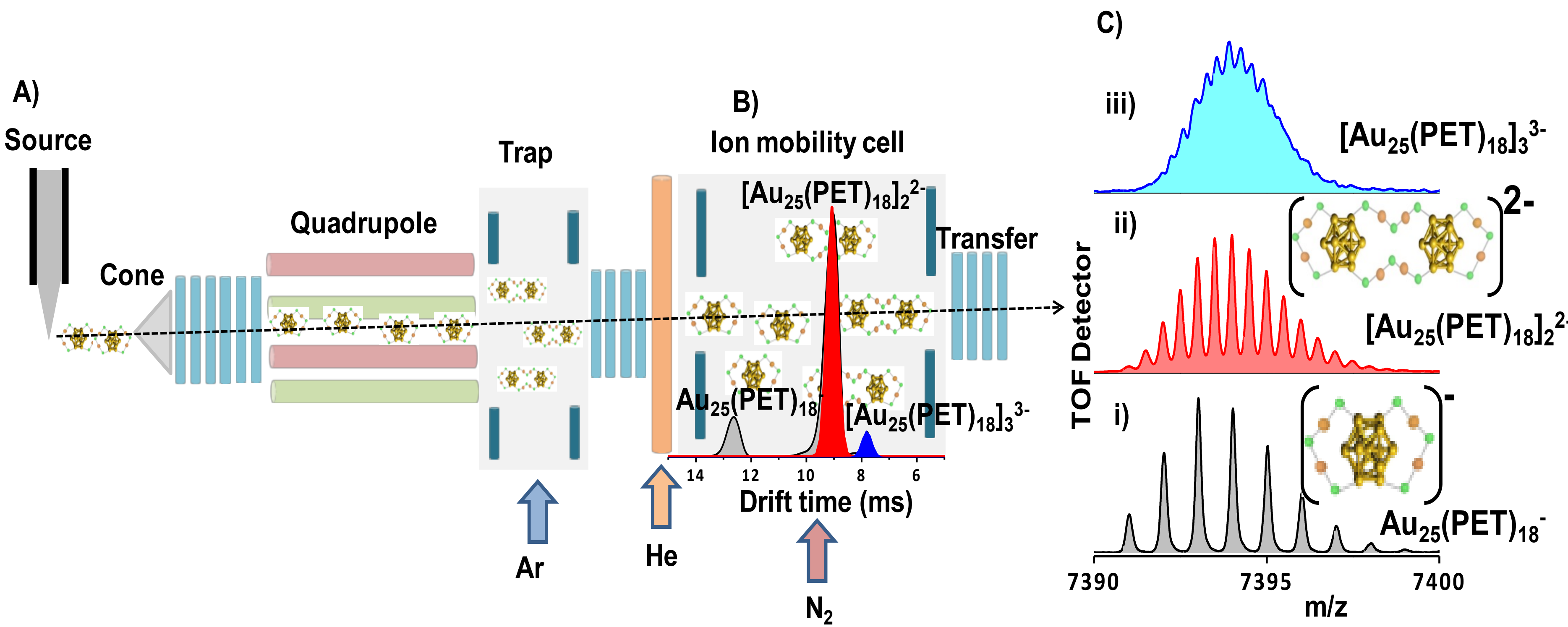
1, 5-$(SBB)_{10}$, 3-$(SC_6H_{12})_8$
(i, 1, 2, x2)-palladoauro-25 asp (-1)





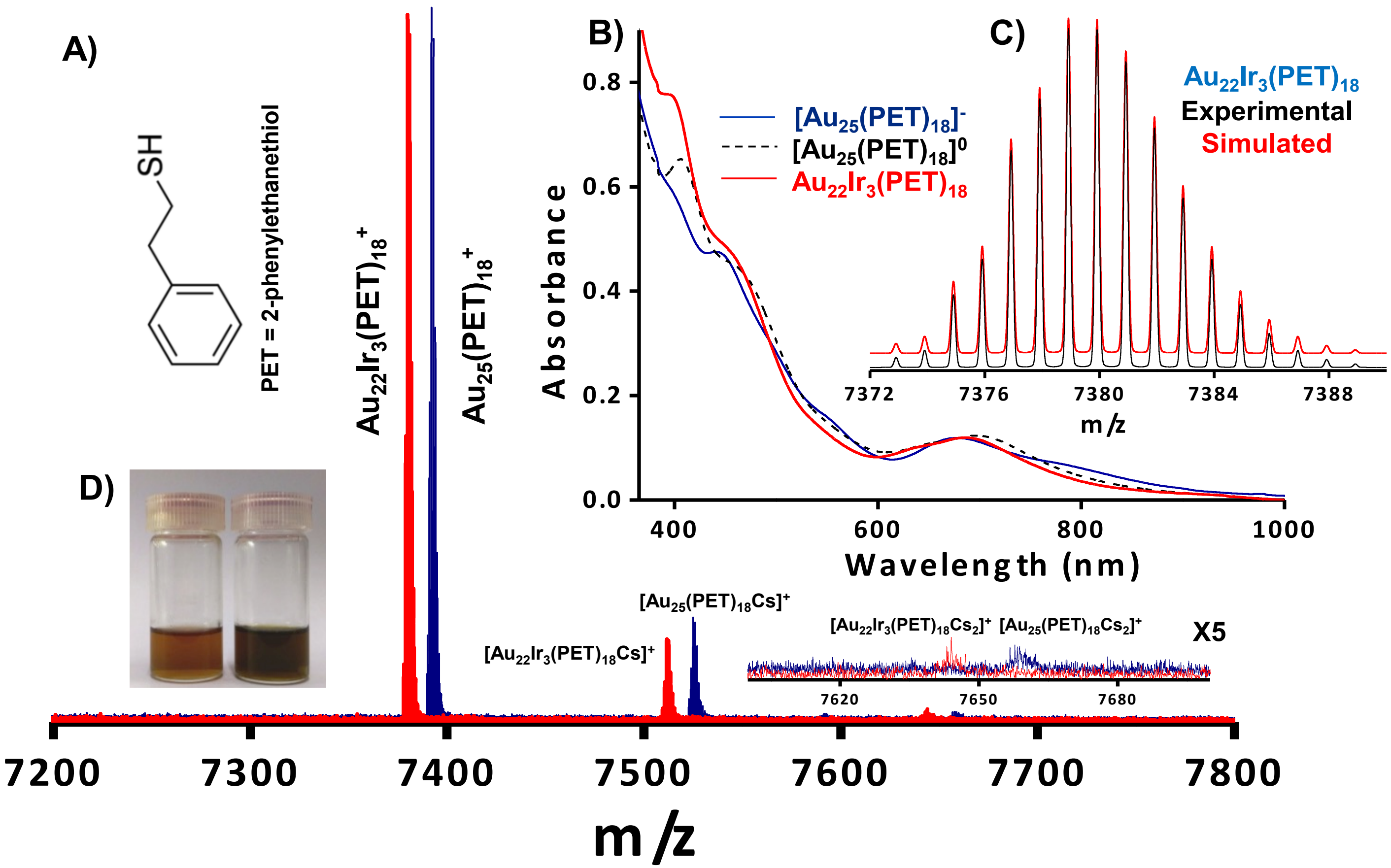
R-$(SMe)_{44}$-auro-102 aspicule**(**0**)** and L-$(SMe)_{44}$-auro-102 aspicule**(**0**)**

Cluster dimers



Ananya Baksi et al. Chem. Commun. 2016

Precision alloys



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

ACCOUNTS of chemical research

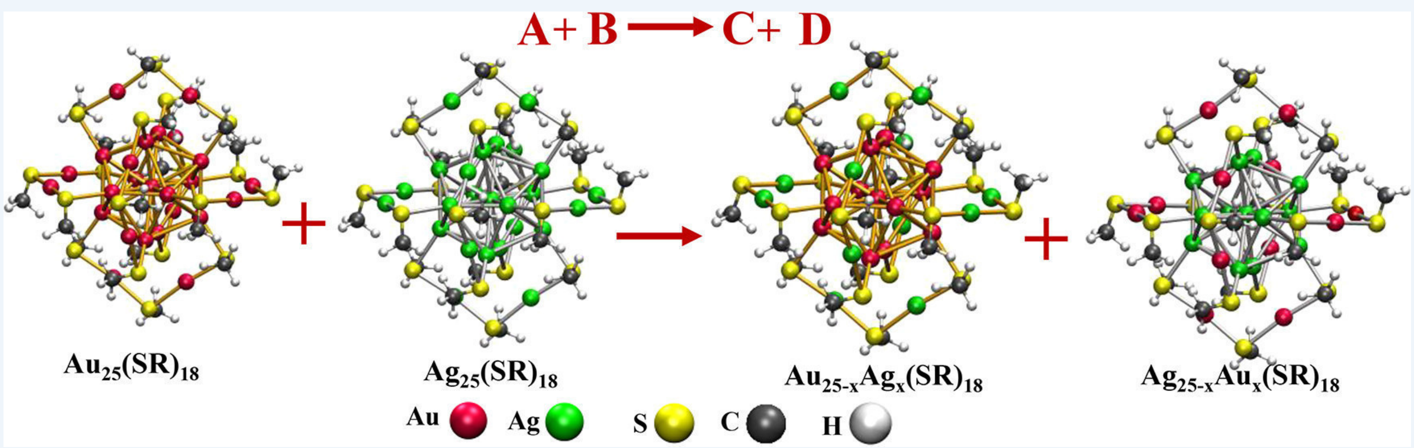
Article

pubs.acs.org/accounts

Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

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

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



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

Cluster dynamics

They are indeed molecules!

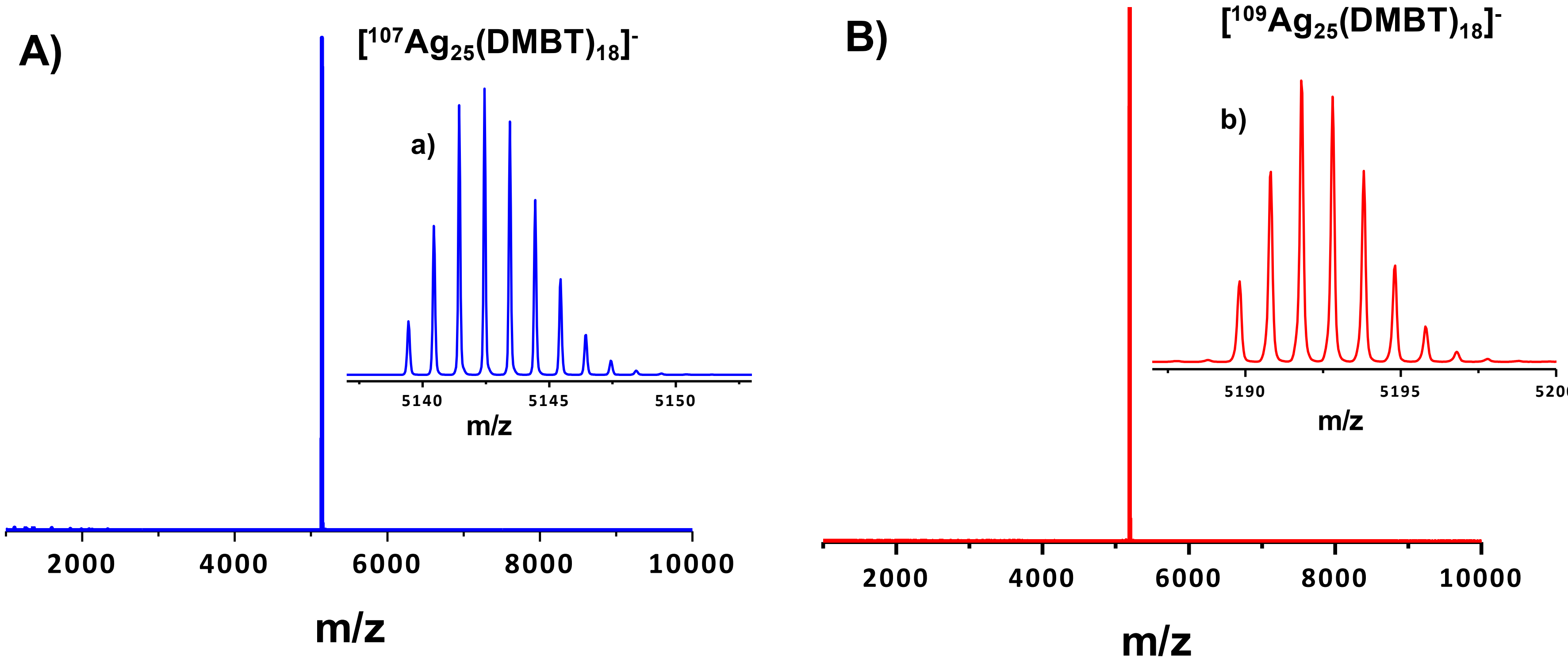
K. R. Krishnadas, et al. Acc. Chem. Res. 2017

CONDENSED MATTER PHYSICS

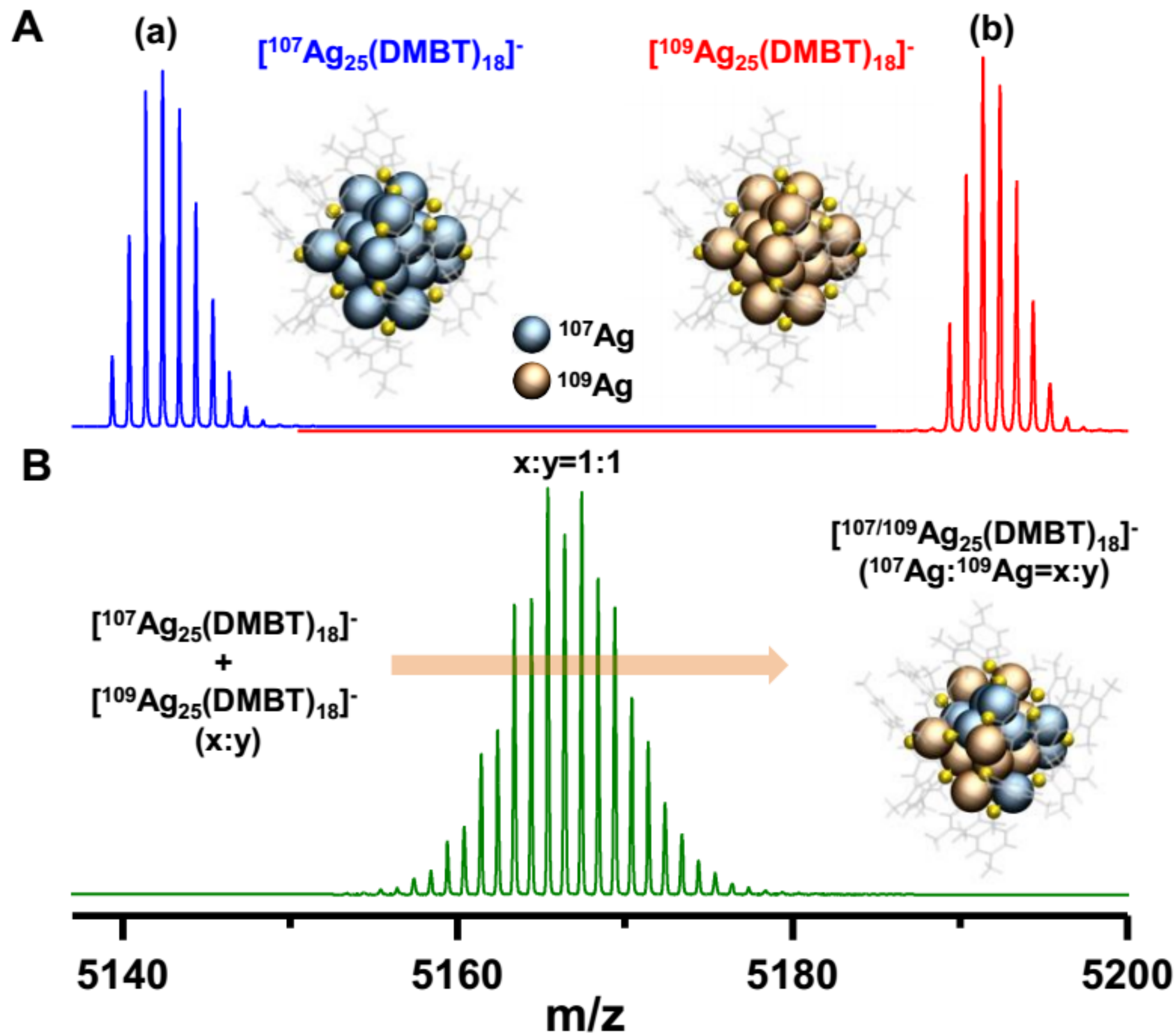
Rapid isotopic exchange in nanoparticles

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]*

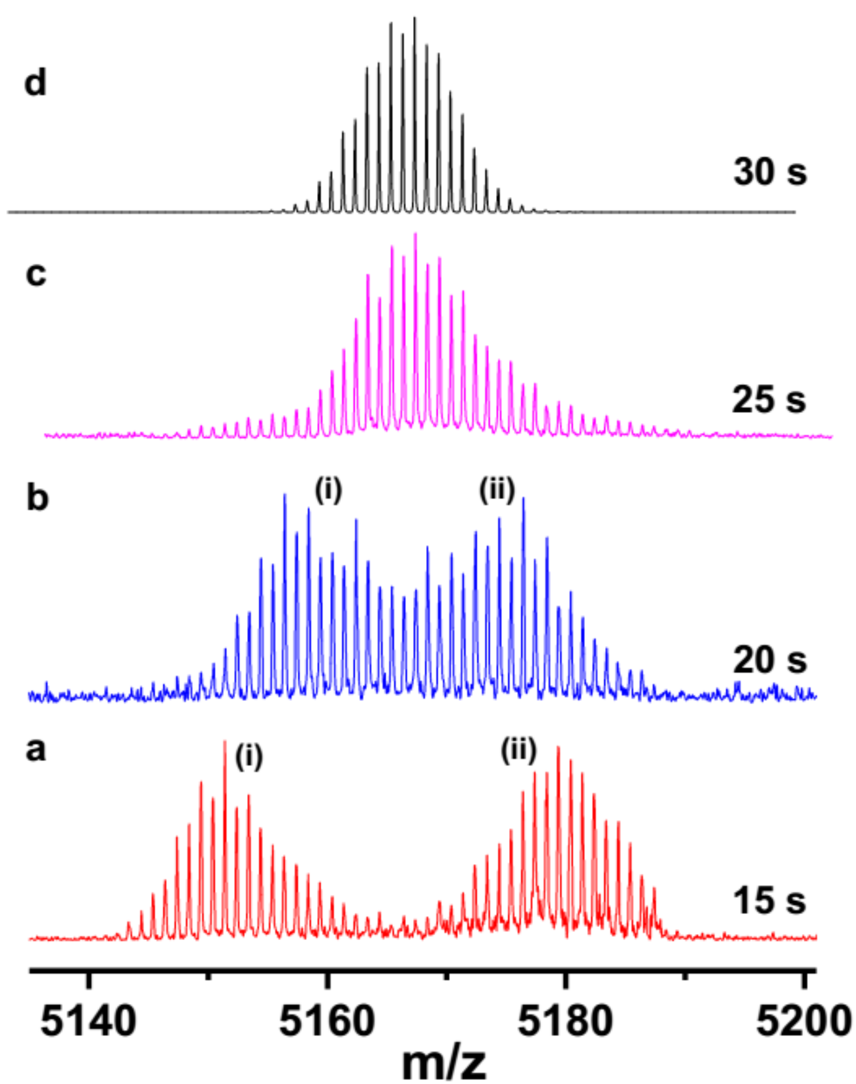
Rapid solution-state exchange dynamics in nanoscale pieces of matter is revealed, taking isotopically pure atomically precise clusters as examples. As two isotopically pure silver clusters made of ^{107}Ag and ^{109}Ag are mixed, an isotopically mixed cluster of the same entity results, similar to the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



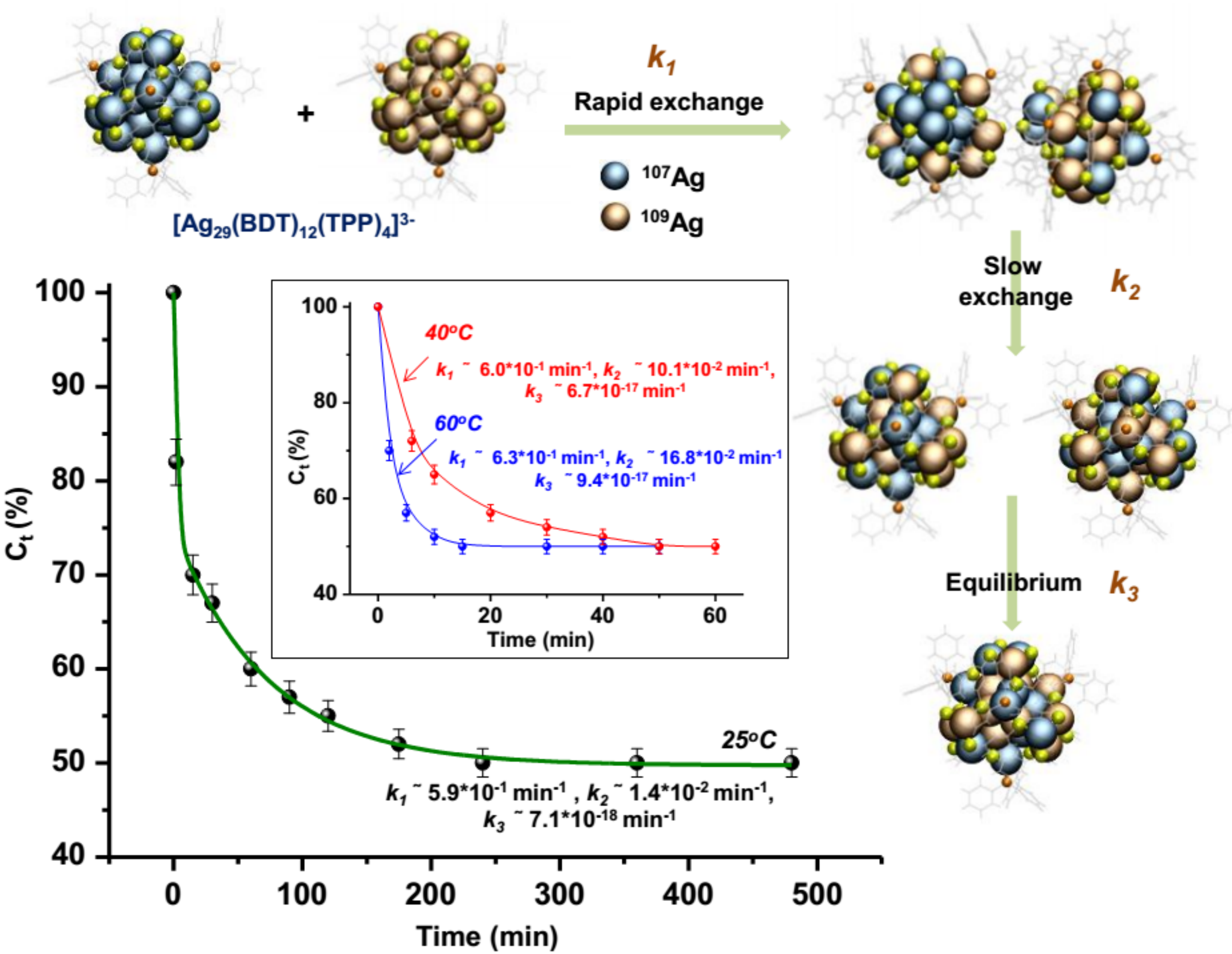
ESI MS of **A)** $^{107}Ag_{25}(DMBT)_{18}$ and **B)**$^{109}Ag_{25}(DMBT)_{18}$. Insets shows the respective isotope patterns.

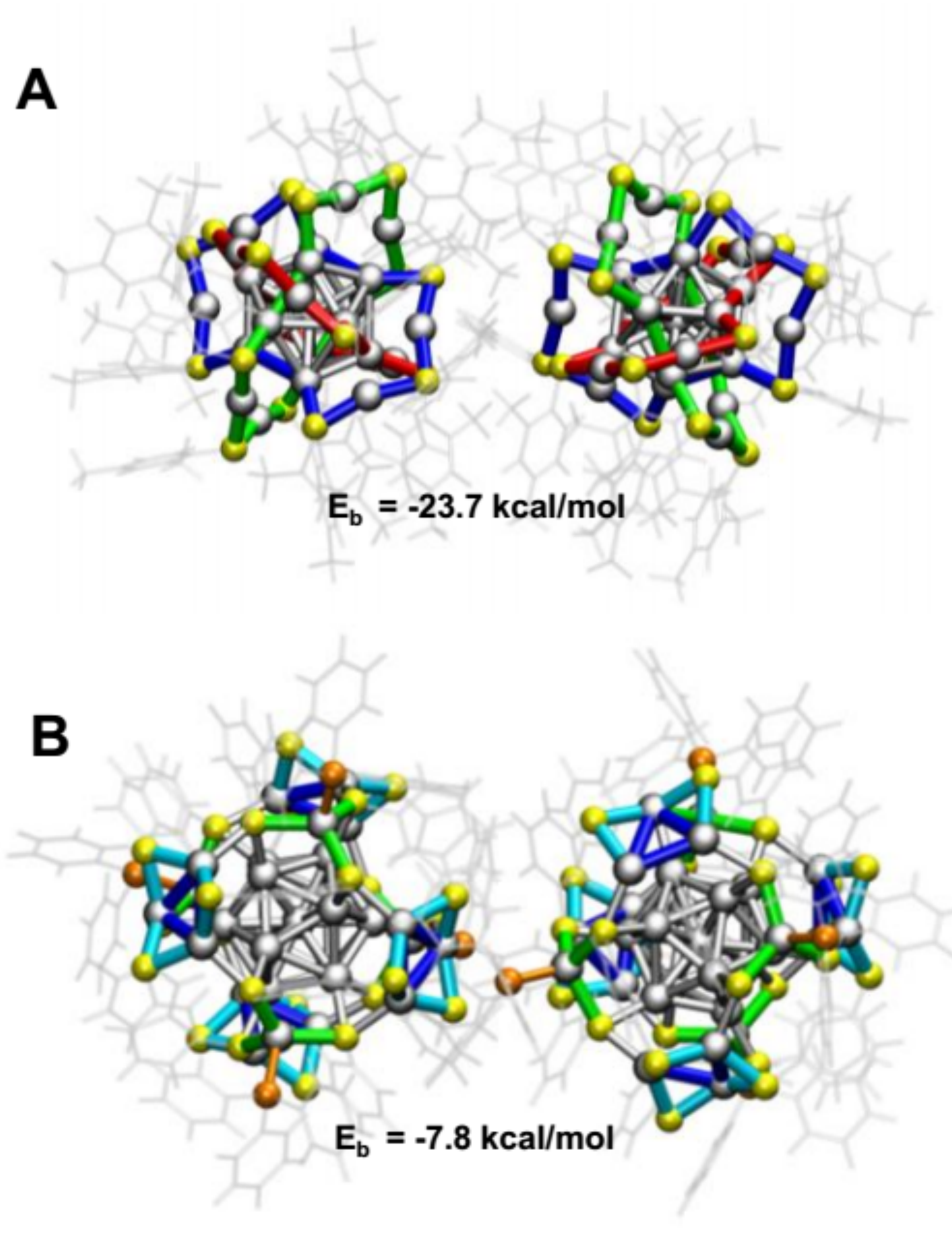


A
(a)
[^{107}Ag$_{25}$(DMBT)$_{18}$]$^-$
[^{109}Ag$_{25}$(DMBT)$_{18}$]$^-$
(b)
^{107}Ag
^{109}Ag
B
x:y=1:1
[$^{107/109}$Ag$_{25}$(DMBT)$_{18}$]$^-$
(^{107}Ag:^{109}Ag=x:y)
[^{107}Ag$_{25}$(DMBT)$_{18}$]$^-$
+
[^{109}Ag$_{25}$(DMBT)$_{18}$]$^-$
(x:y)
5140
5160
5180
5200
m/z

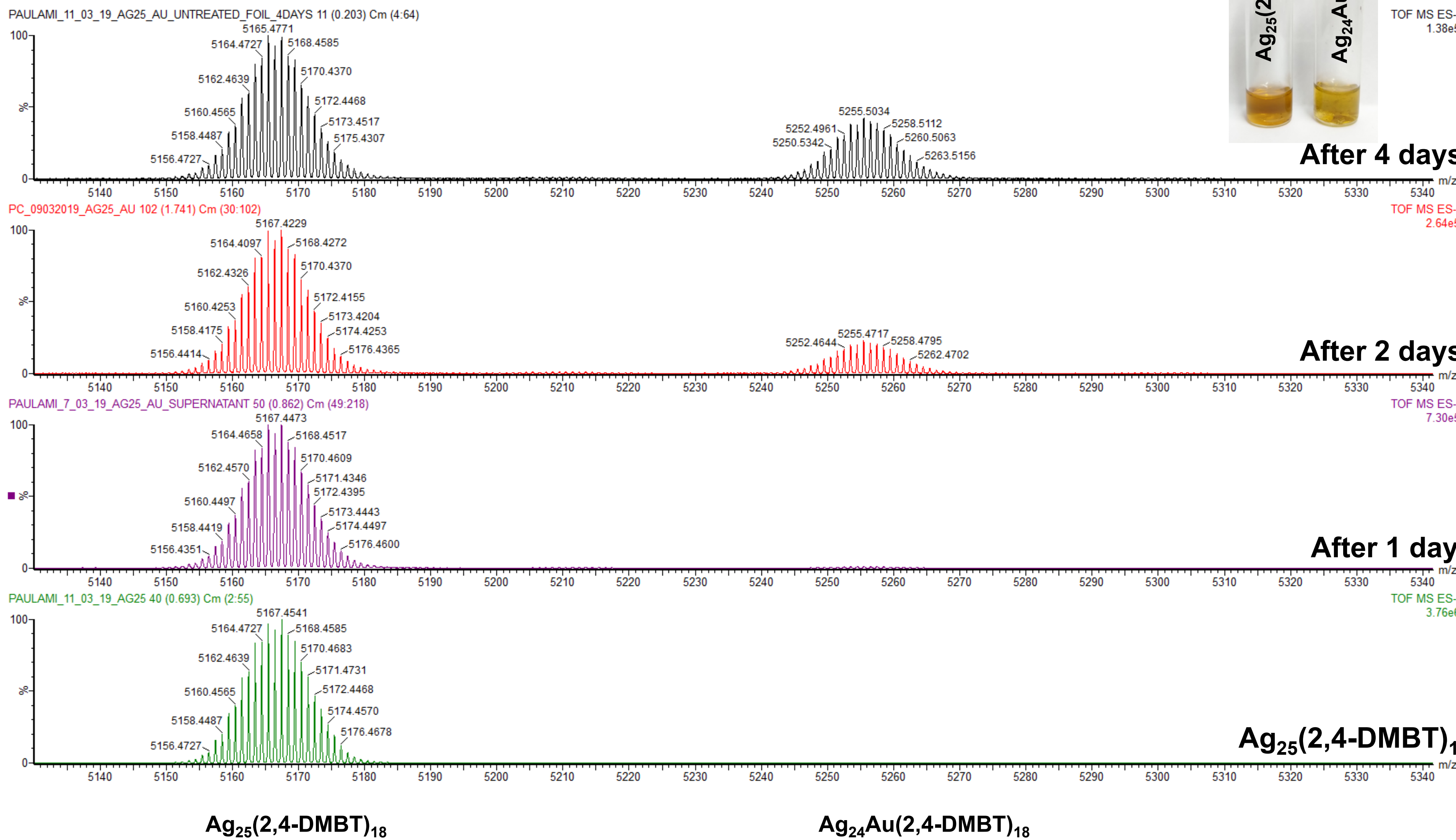


Papri Chakraborty, et. al. Science Advances 2018

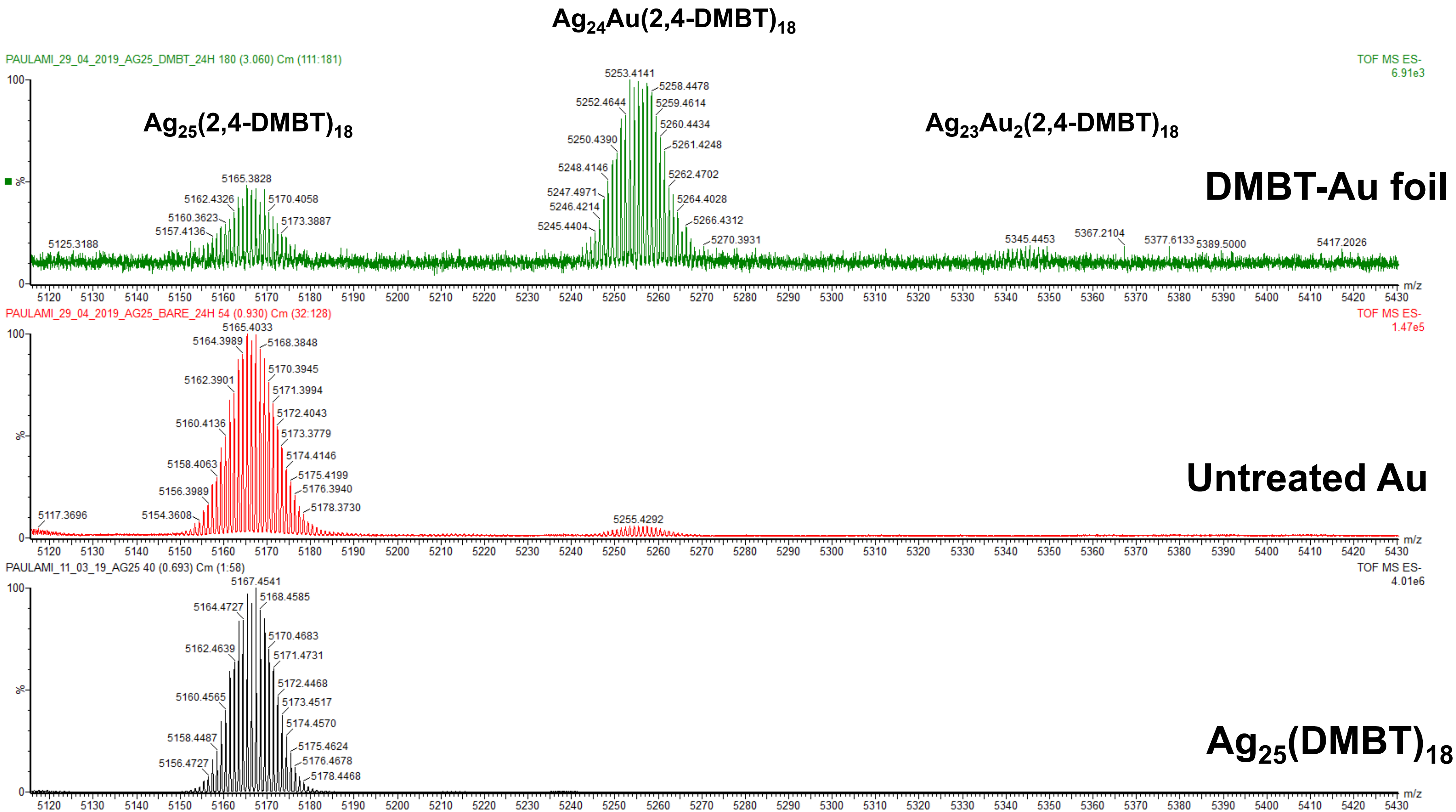

[Ag29(BDT)12(TPP)4]3-
k1
Rapid exchange
107Ag
109Ag
Slow exchange
k2
Equilibrium
k3
40oC
k1 ~ 6.0*10-1 min-1, k2 ~ 10.1*10-2 min-1,
k3 ~ 6.7*10-17 min-1
60oC
k1 ~ 6.3*10-1 min-1, k2 ~ 16.8*10-2 min-1
k3 ~ 9.4*10-17 min-1
Ct (%)
Time (min)
25oC
k1 ~ 5.9*10-1 min-1 , k2 ~ 1.4*10-2 min-1,
k3 ~ 7.1*10-18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


A
E_b = -23.7 kcal/mol
B
E_b = -7.8 kcal/mol

Ag25 reacts with Untreated-Pure Au foil (24



Ag25 reacts with 22 Carat Au foil after 24 hours (200 rpm)



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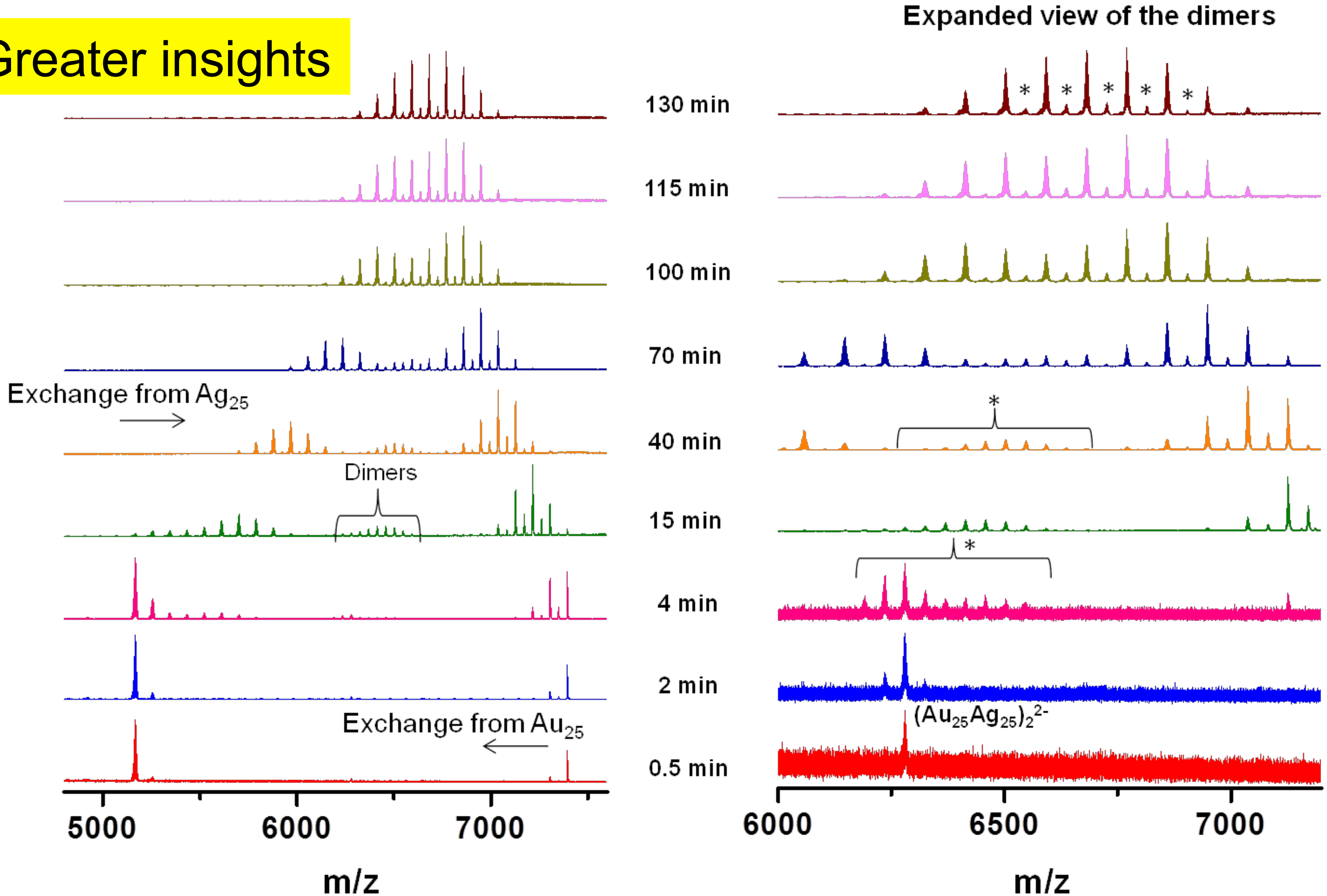
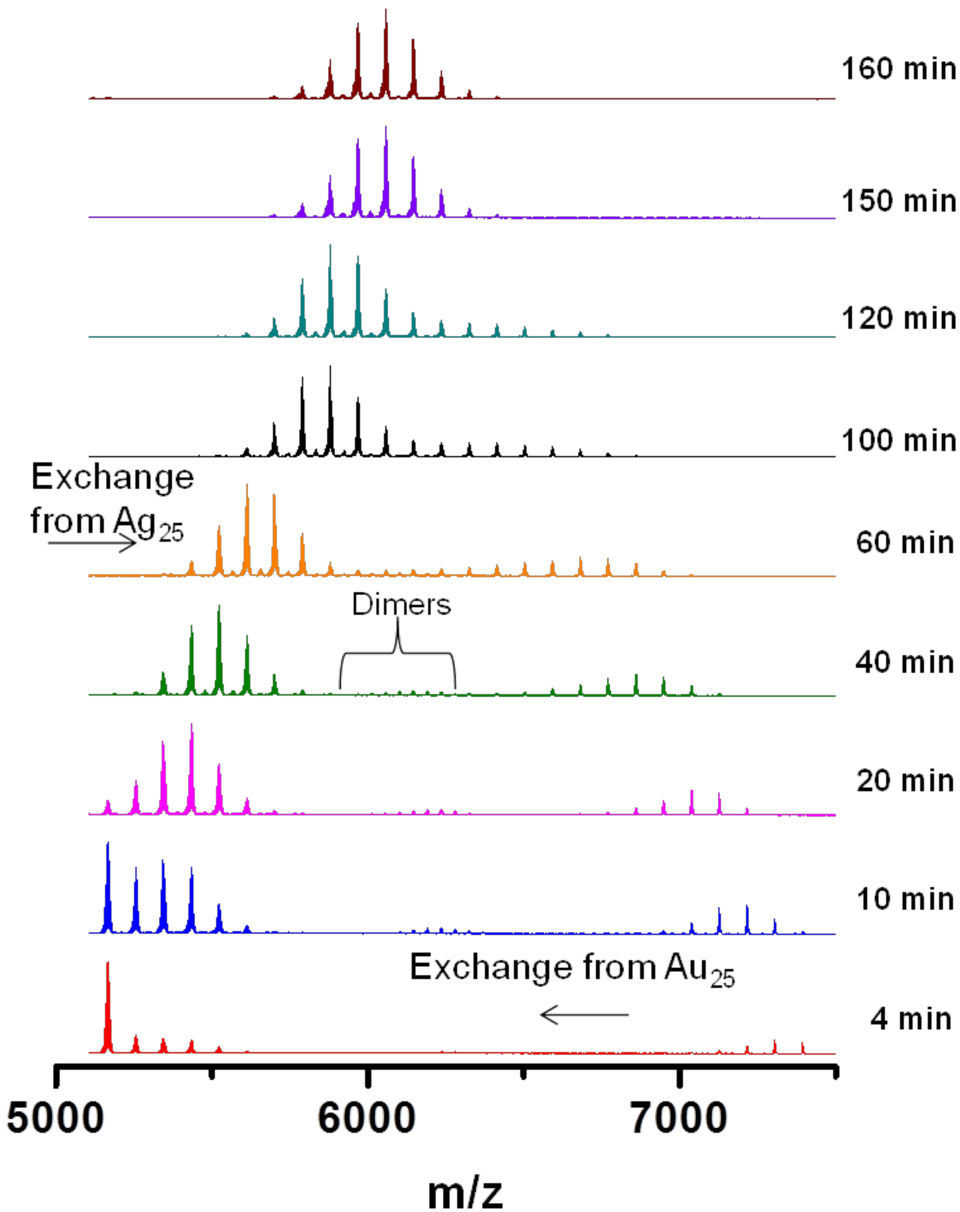
ESI MS of the reaction mixture

Greater insights

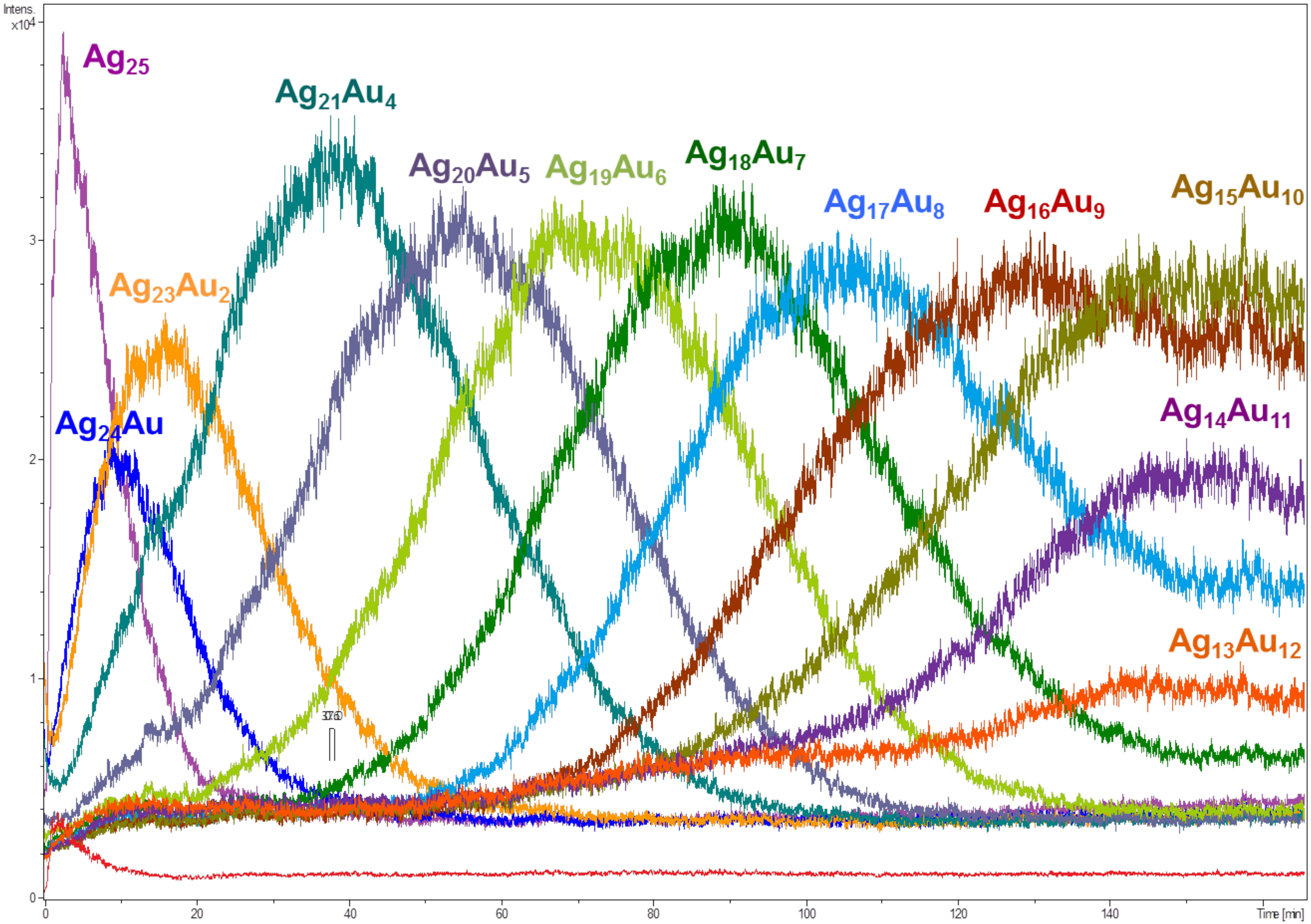


* peaks for the dimers (at higher time, the monomeric peaks due to Au-Ag exchange also arise). Au_{25} was kept in excess.



Molar ratio of two clusters= 1:1

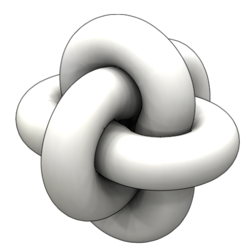
Kinetics of the exchange (monitored on the Ag_{25} side)



With Manfred Kappes and Horst Hahn

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
- Clusters are indeed molecules
- New materials are coming!



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Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

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

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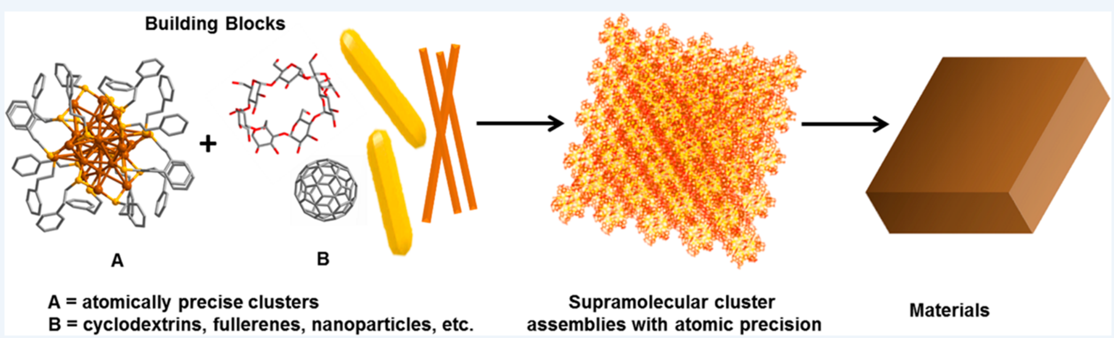
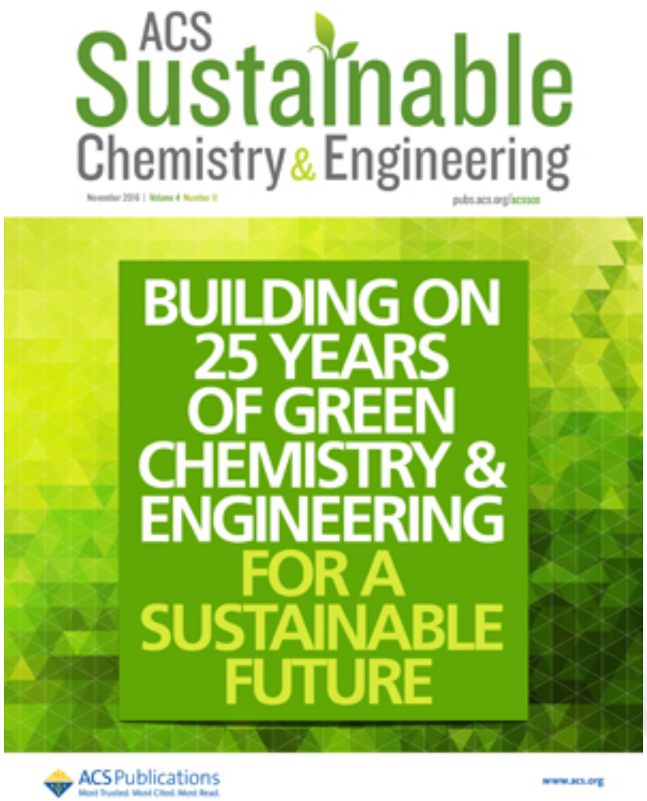


Clean water through advanced materials

Where there is clean water, there is hope.


iitmadras.
27/11/19 07:06

A Leader in Advancing Green Chemistry & Green Engineering Concepts



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Thank you