Now in the 60th year

Nanoparticles with atomic precision

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InnoDI Water Technologies Pvt. Ltd.
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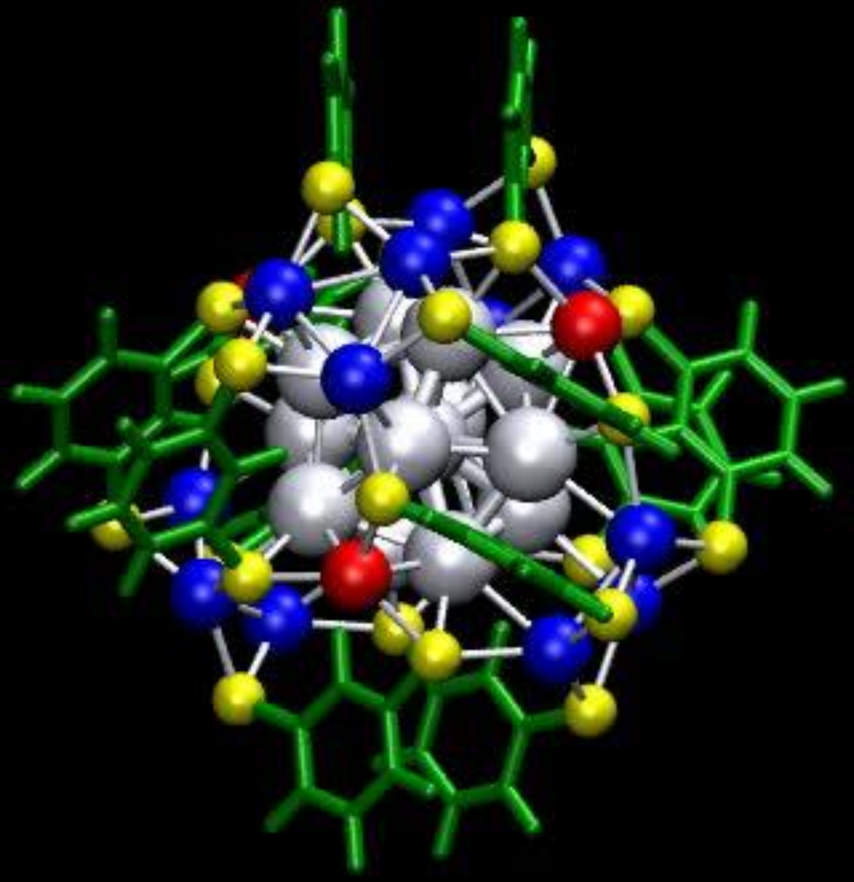
Thematic Unit of Excellence

Saint-Gobain Research India, IIT Madras Research Park, July 23, 2019

Clusters



Science of nanomaterials has advanced tremendously in the recent past.

2019

ACCOUNTS of chemical research

Article

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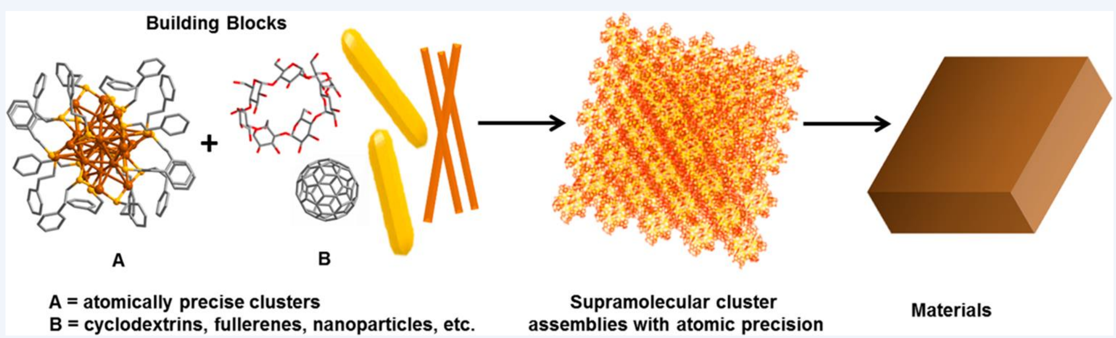
Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

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

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



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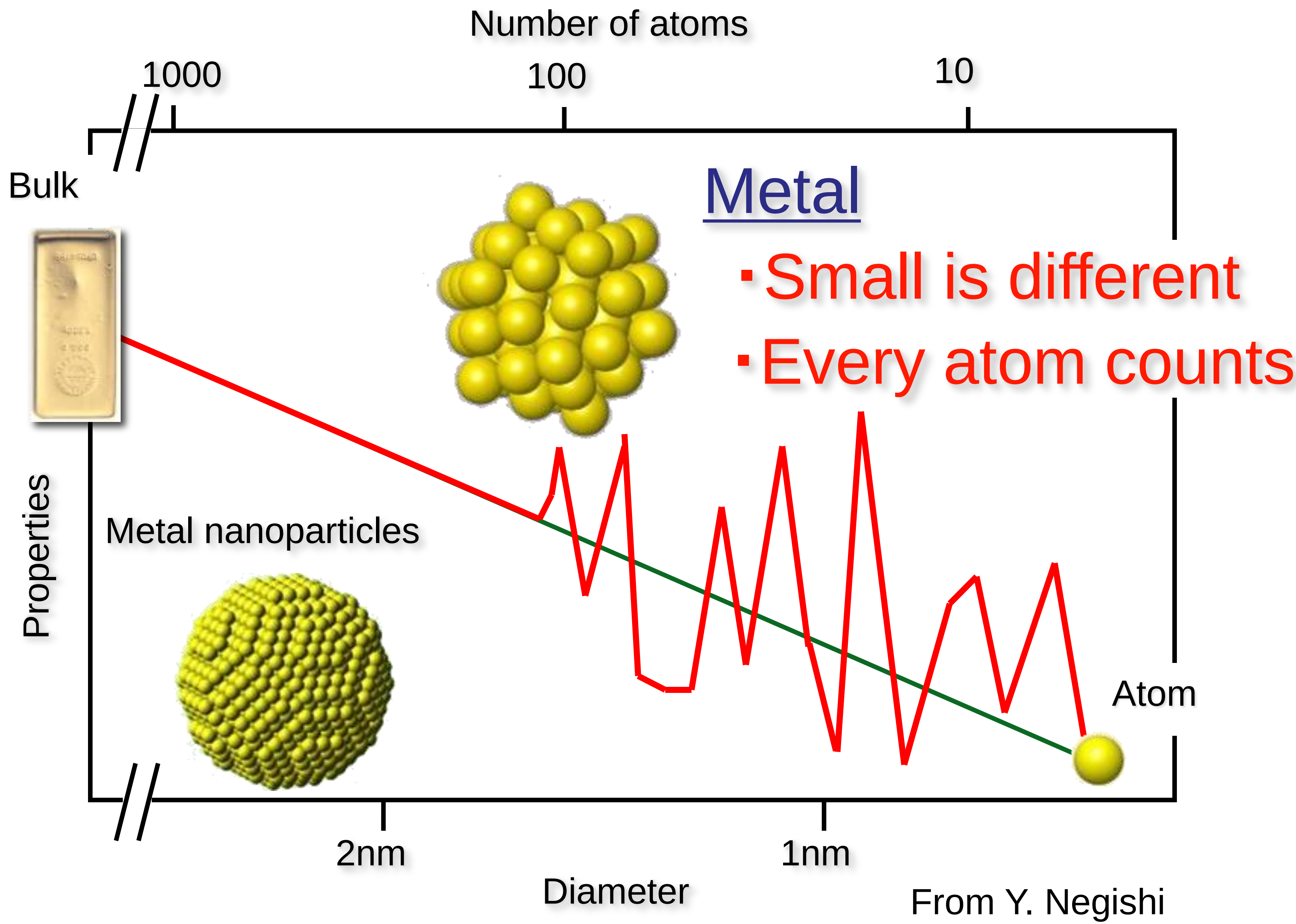
New science in synthesis, properties
Reactions between clusters
Borromean structures of clusters
Supramolecular science of clusters
Applications
Future directions


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

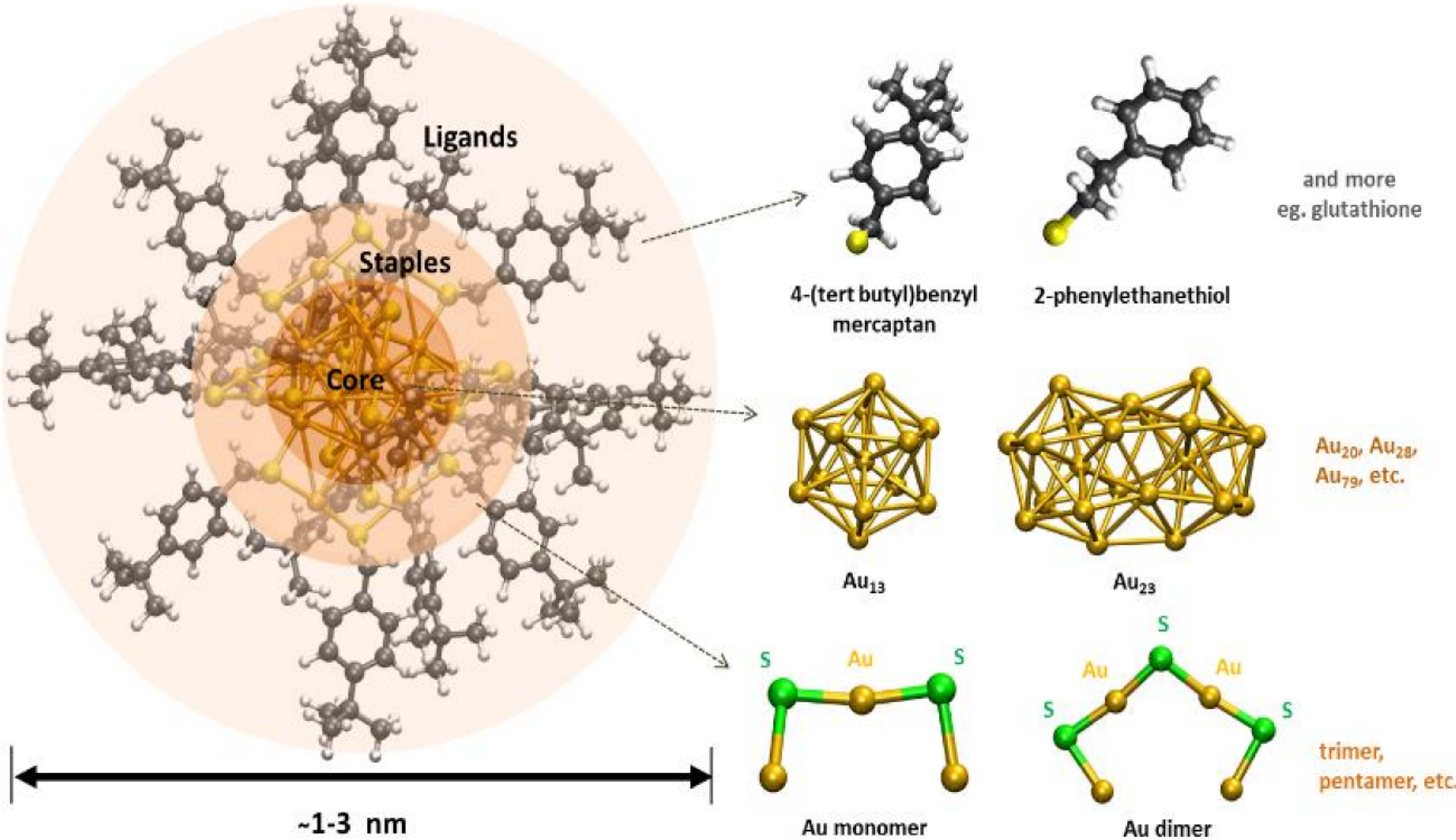
Indranath Chakraborty[†] and Thalappil Pradeep[*]

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

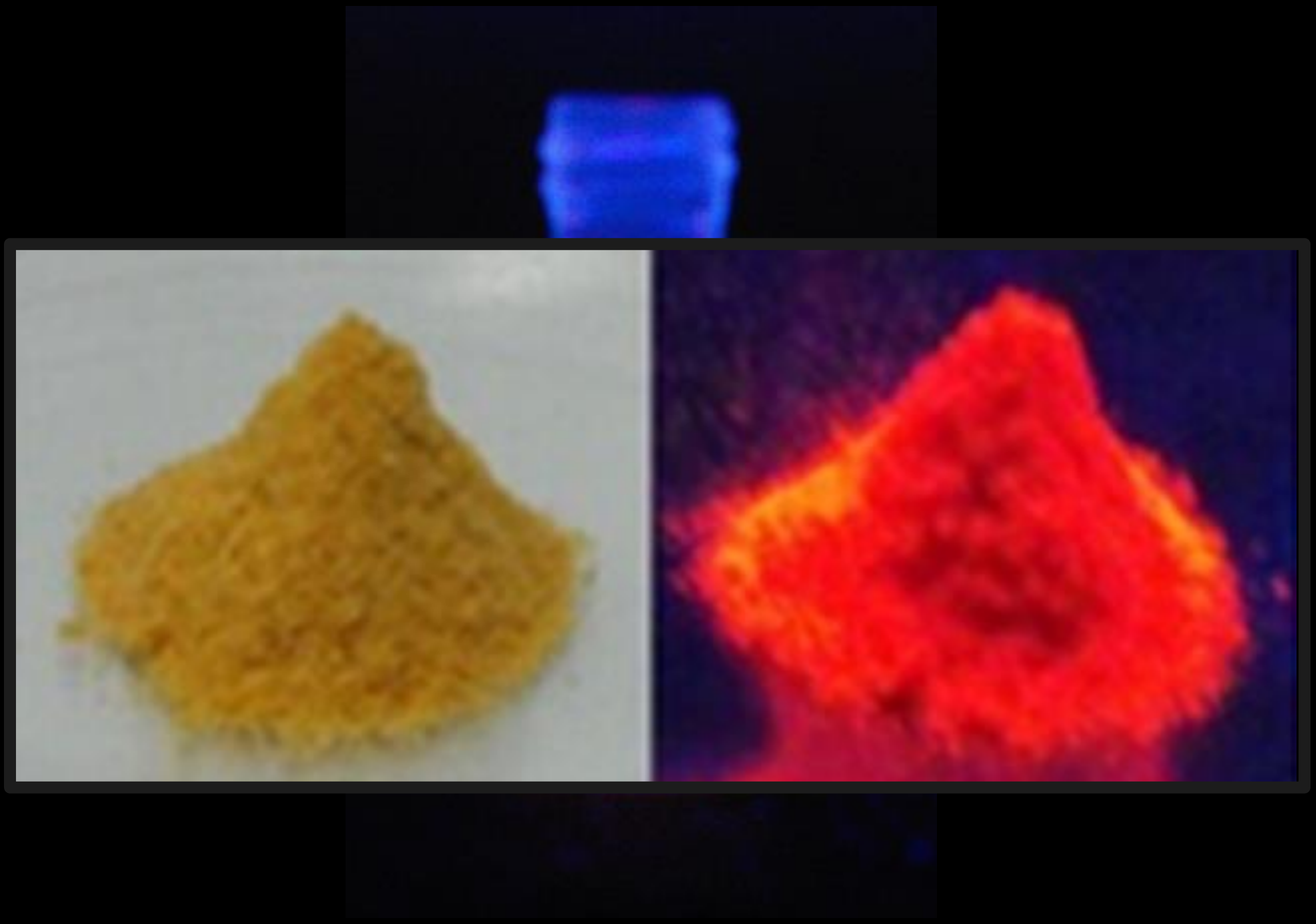
Supporting Information

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.

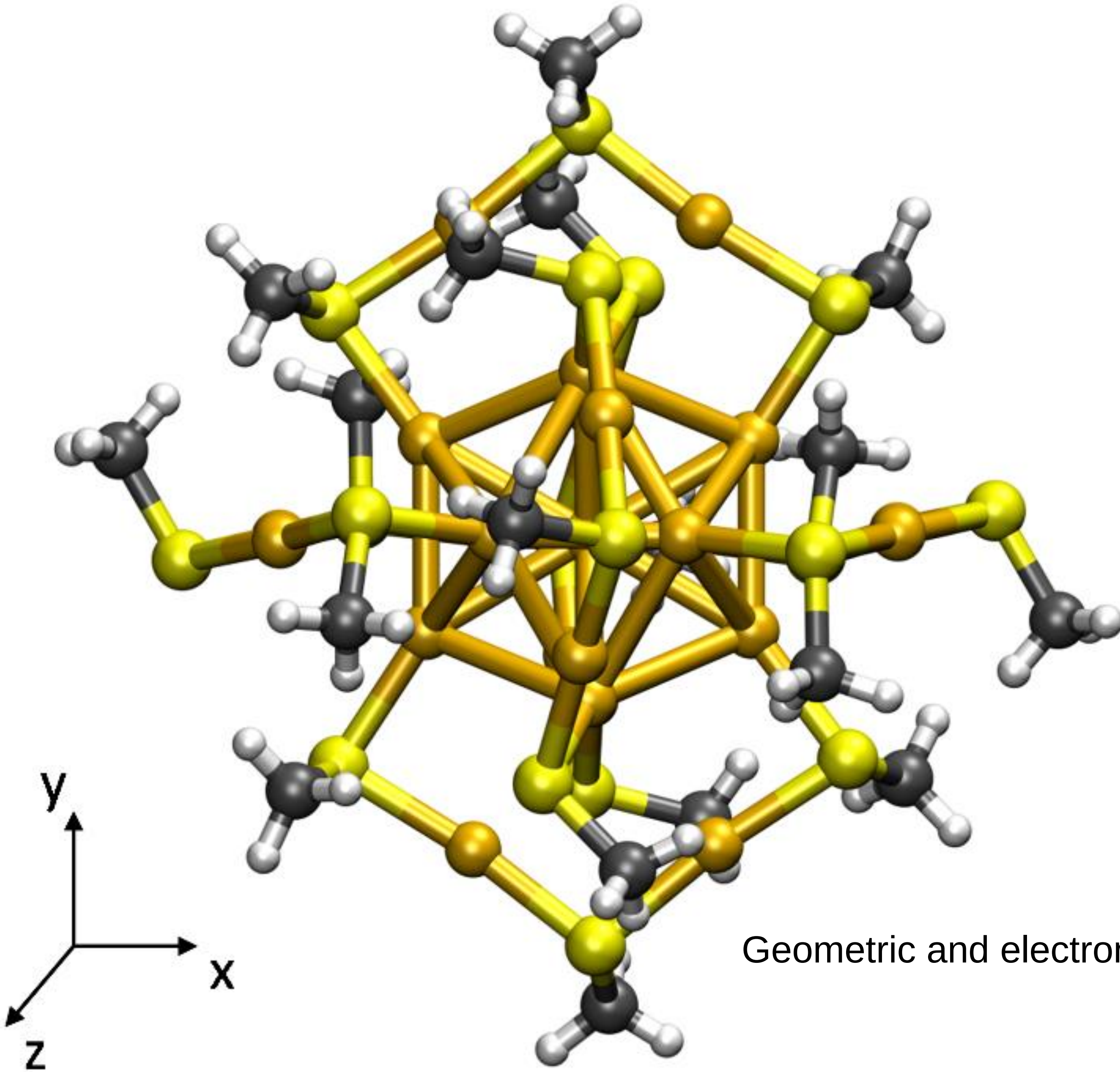
Also the pioneering work of R. W. Murray, Robert L. Whetten, Uzi Landman, Tatuya Tsukuda, Yuichi Negishi, Hannu Hakkinen, R. Jin, Nanfeng Zheng, Terry Bigioni, Osman Bakr, Kornberg, Jianping Xie, C. M. Aikens, Thomas Buergi, Amala Dass, …. A. W. Castleman Jr., H. Schmidbauer, …



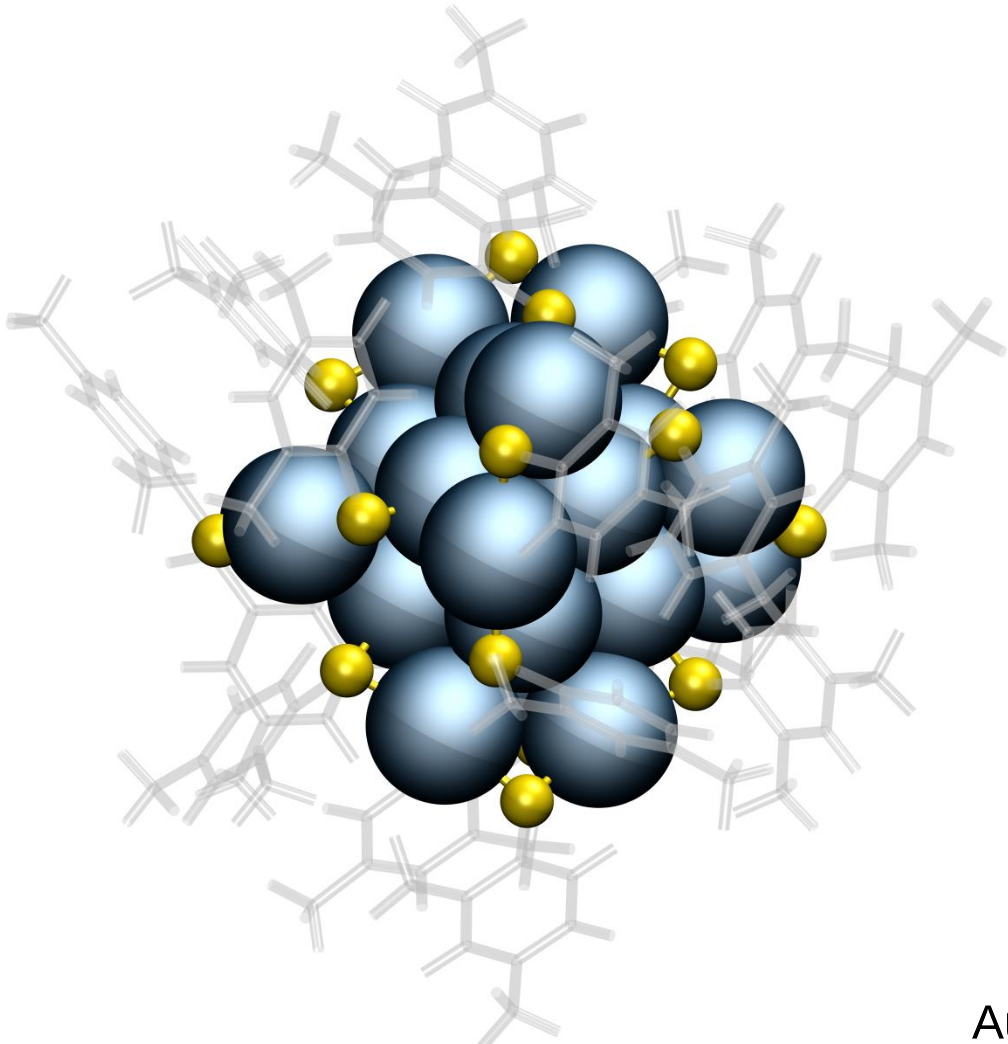
Ligands
Staples
Core
~1-3 nm
4-(tert butyl)benzyl mercaptan
2-phenylethanethiol
and more
eg. glutathione
Au13
Au23
Au20, Au28,
Au79, etc.
S
Au
S
Au monomer
S
Au
Au
S
S
Au dimer
trimer,
pentamer, etc.



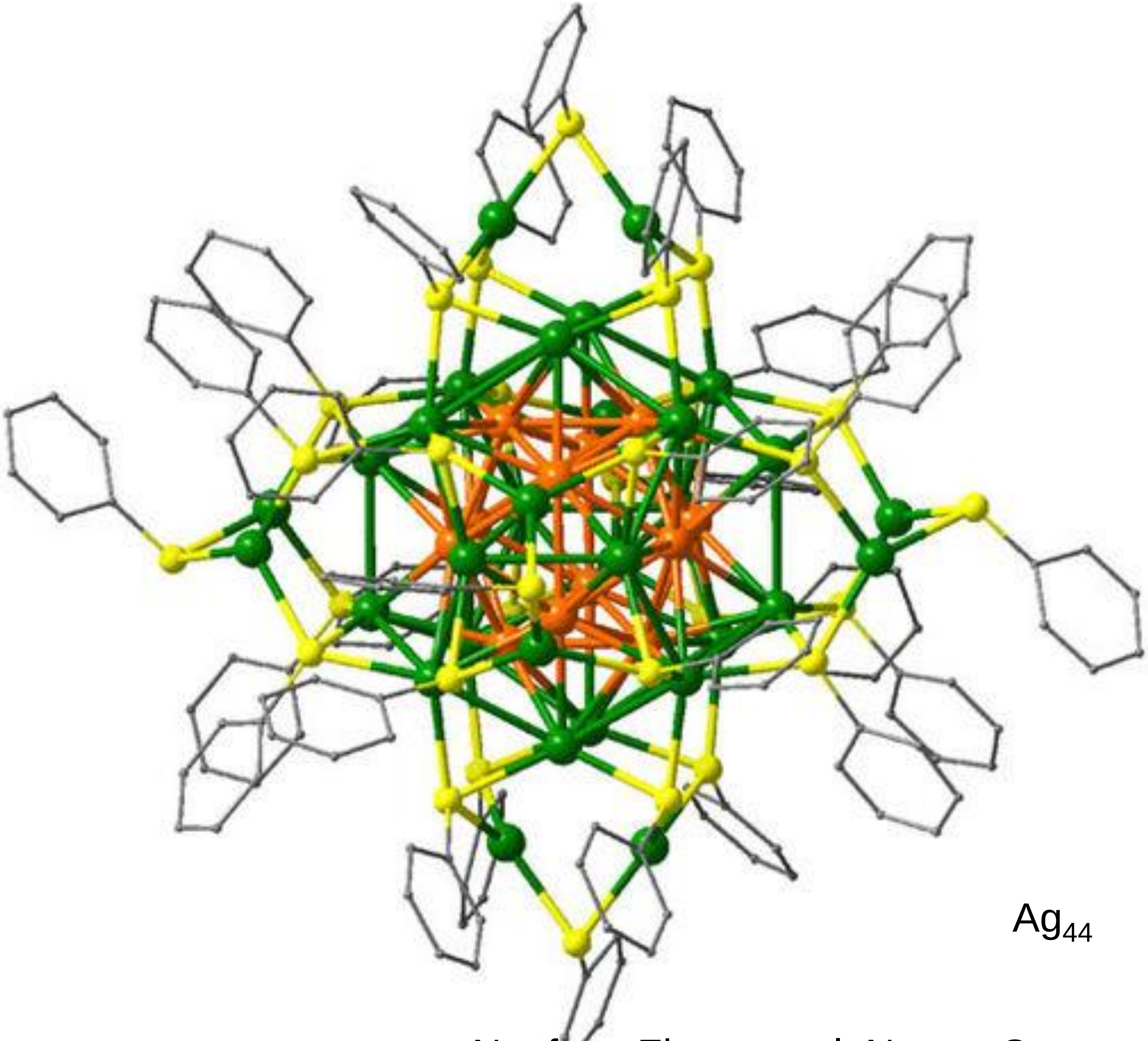
Shibhu, Habeeb, Uday, Kamalesh, Lourdu, Ammu, Ananya, Indranath, Atanu, Krishnadas, Shridevi, Papri, Esma, Debasmita, Abhijit, Amrita, Jyoti, Sugi, Bodi, Paulami, ….



Geometric and electronic shells

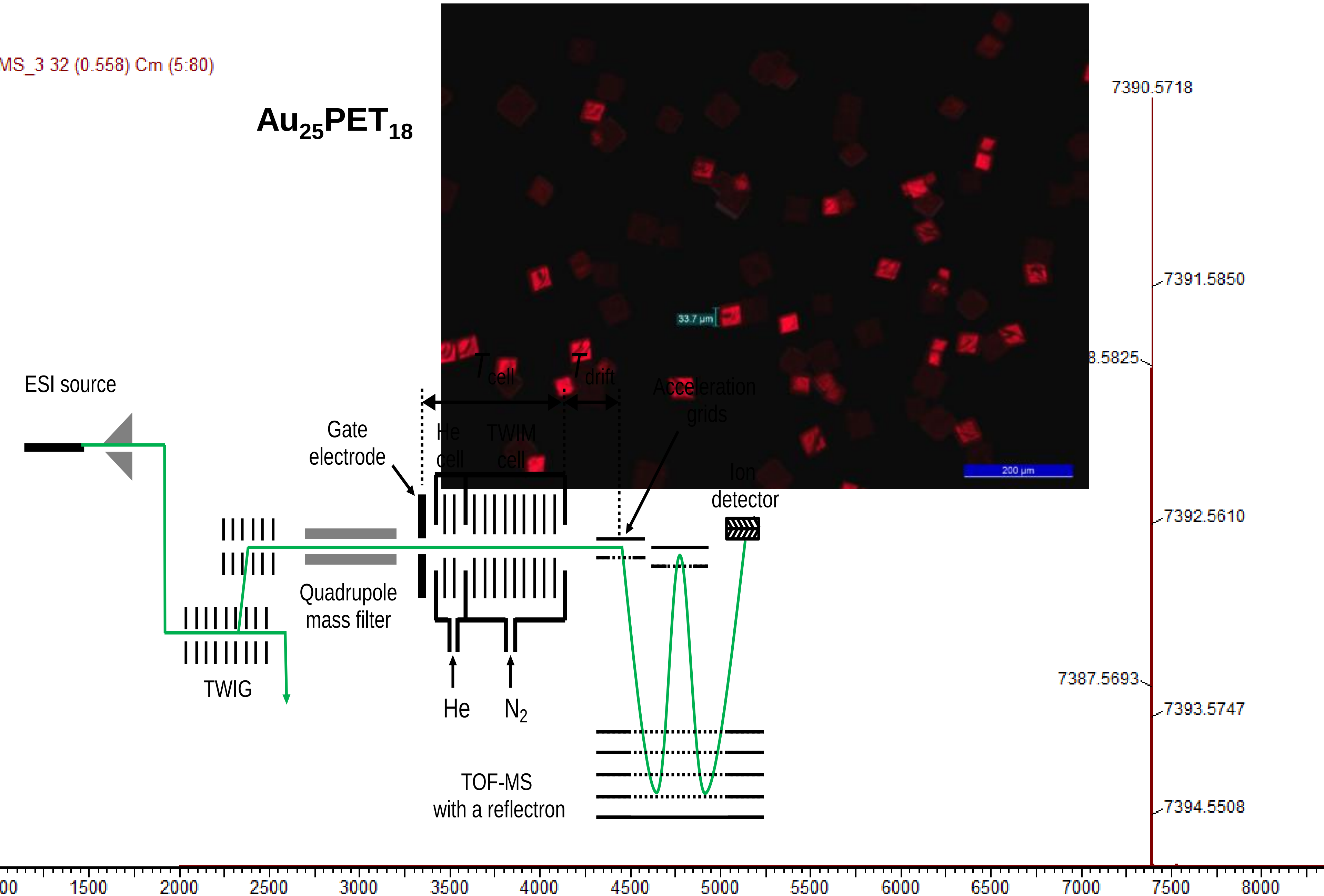


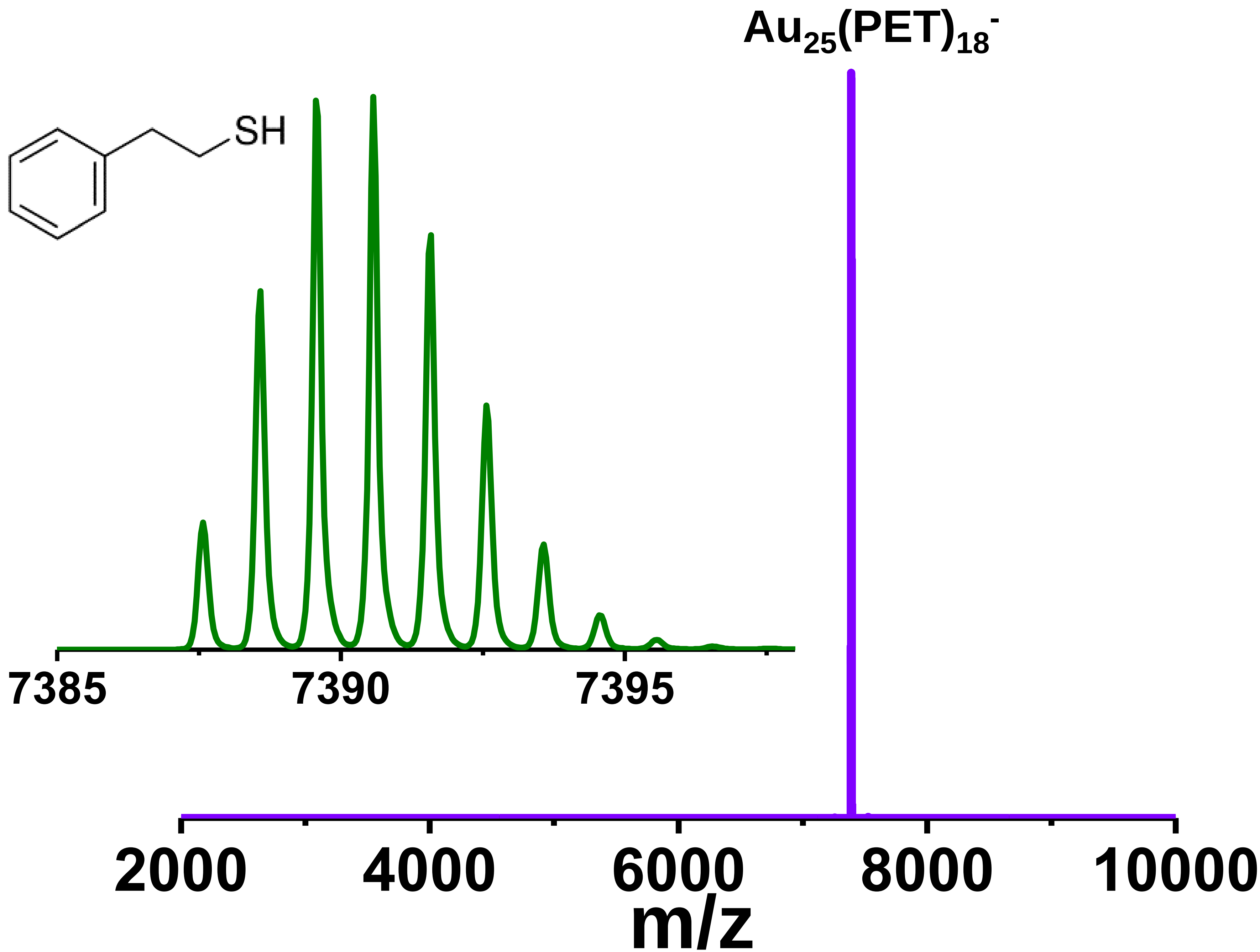
Au_{25}, Ag_{25}

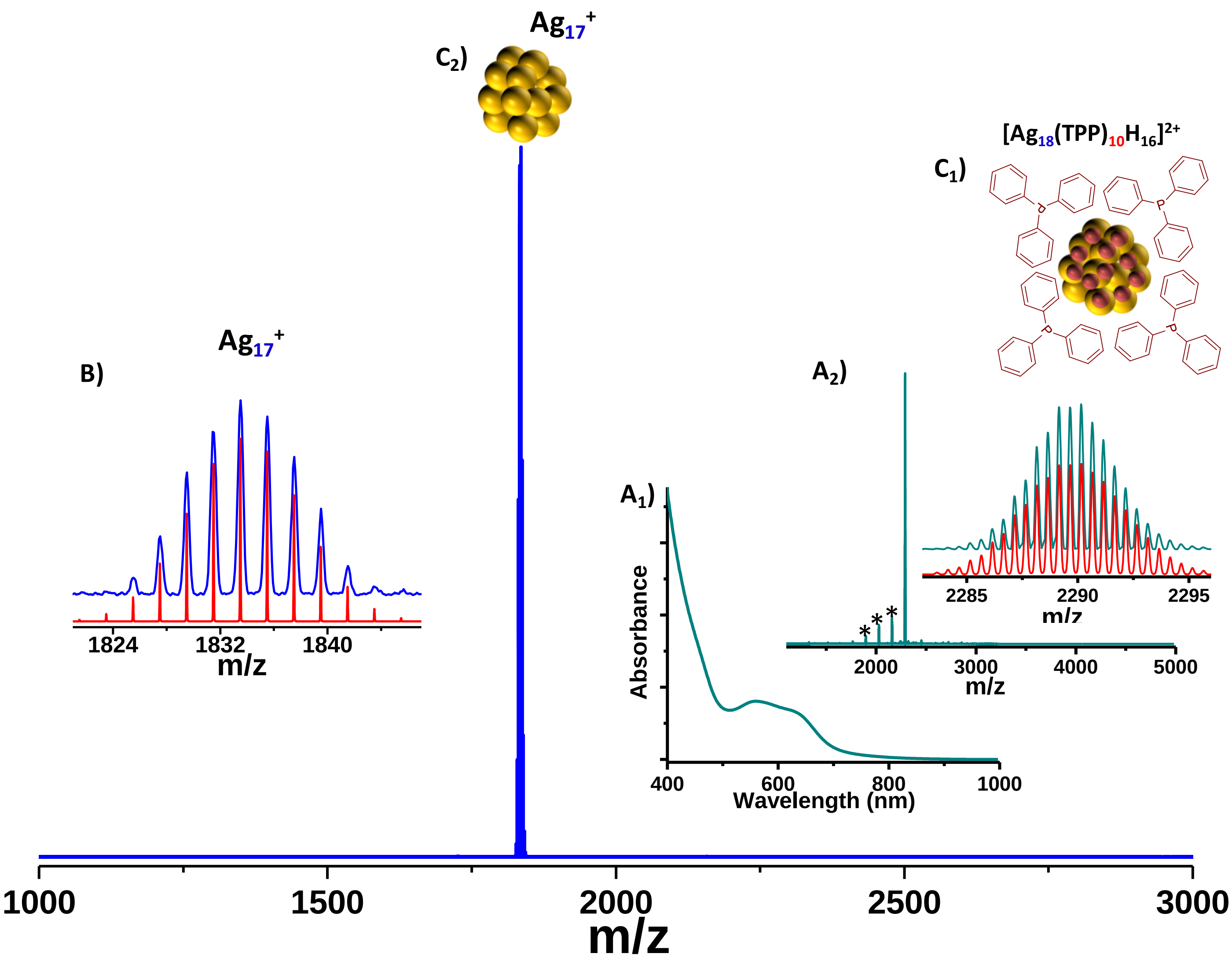


Ag_{44}

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
T cell
T drift
He cell
TWIM cell
Acceleration grids
Ion detector
Quadrupole mass filter
TWIG
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

Structure of a Thiol Monolayer–Protected Gold Nanoparticle at 1.1 Å Resolution

Pablo D. Jadzinsky,[1,2]* Guillermo Calero,[1]* Christopher J. Ackerson,[1]† David A. Bushnell,[1] Roger D. Kornberg[1]‡

Structural information on nanometer-sized gold particles has been limited, due in part to the problem of preparing homogeneous material. Here we report the crystallization and x-ray structure determination of a *p*-mercaptobenzoic acid (p-MBA)–protected gold nanoparticle, which comprises 102 gold atoms and 44 p-MBAs. The central gold atoms are packed in a Marks decahedron, surrounded by additional layers of gold atoms in unanticipated geometries. The p-MBAs interact not only with the gold but also with one another, forming a rigid surface layer. The particles are chiral, with the two enantiomers alternating in the crystal lattice. The discrete nature of the particle may be explained by the closing of a 58-electron shell.

Nanometer-size metal particles are of fundamental interest for their chemical and quantum electronic properties and of practical interest for many potential applications (*1*, *2*). With the development of facile routes of synthesis (*3*), gold nanoparticles coated with surface thiol layers have been studied in most detail. The particles are typically heterogeneous as synthesized, and though their size distribution may be narrowed by fractionation or other means (*4*–*9*), no atomically monodisperse preparation has been reported, and no atomic structure has been obtained. Electron microscopy (EM) (*10*, *11*), powder x-ray diffraction (PXRD) (*12*), and theoretical studies have led to the idea of Marks decahedral (MD) and truncated octahedral geometries of the metal core, with crystalline packing and {111} faces (*13*). According to this idea, discrete core sizes represent "magic numbers" of gold atoms, arising from closed geometric shells (*14*). Alternatives of amorphous (*15*), molten, or quasimolten (*16*) cores have also been proposed. The structure of the surface thiol layer is similarly obscure. The nature of the gold-sulfur interaction (*17*), the fate of the sulfhydryl proton (*18*), and the conformation of the organic moiety all remain to be determined. The thiols are

[1]Department of Structural Biology, Stanford University School of Medicine, Stanford, CA 94305, USA. [2]Department of Applied Physics, Stanford University, Stanford, CA 94305, USA.

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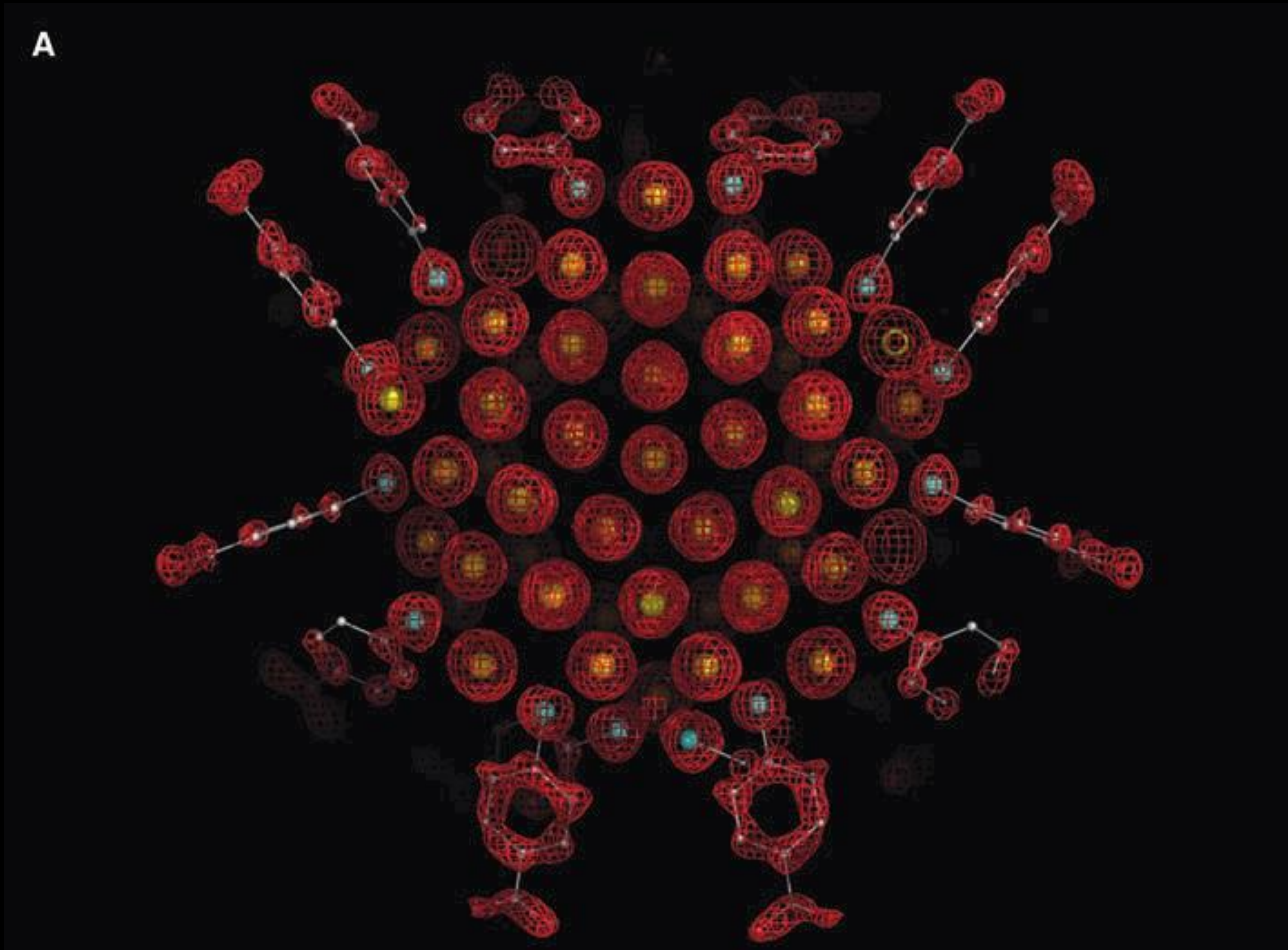
†Present address: Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA.
‡To whom correspondence should be addressed. E-mail: kornberg@stanford.edu


A

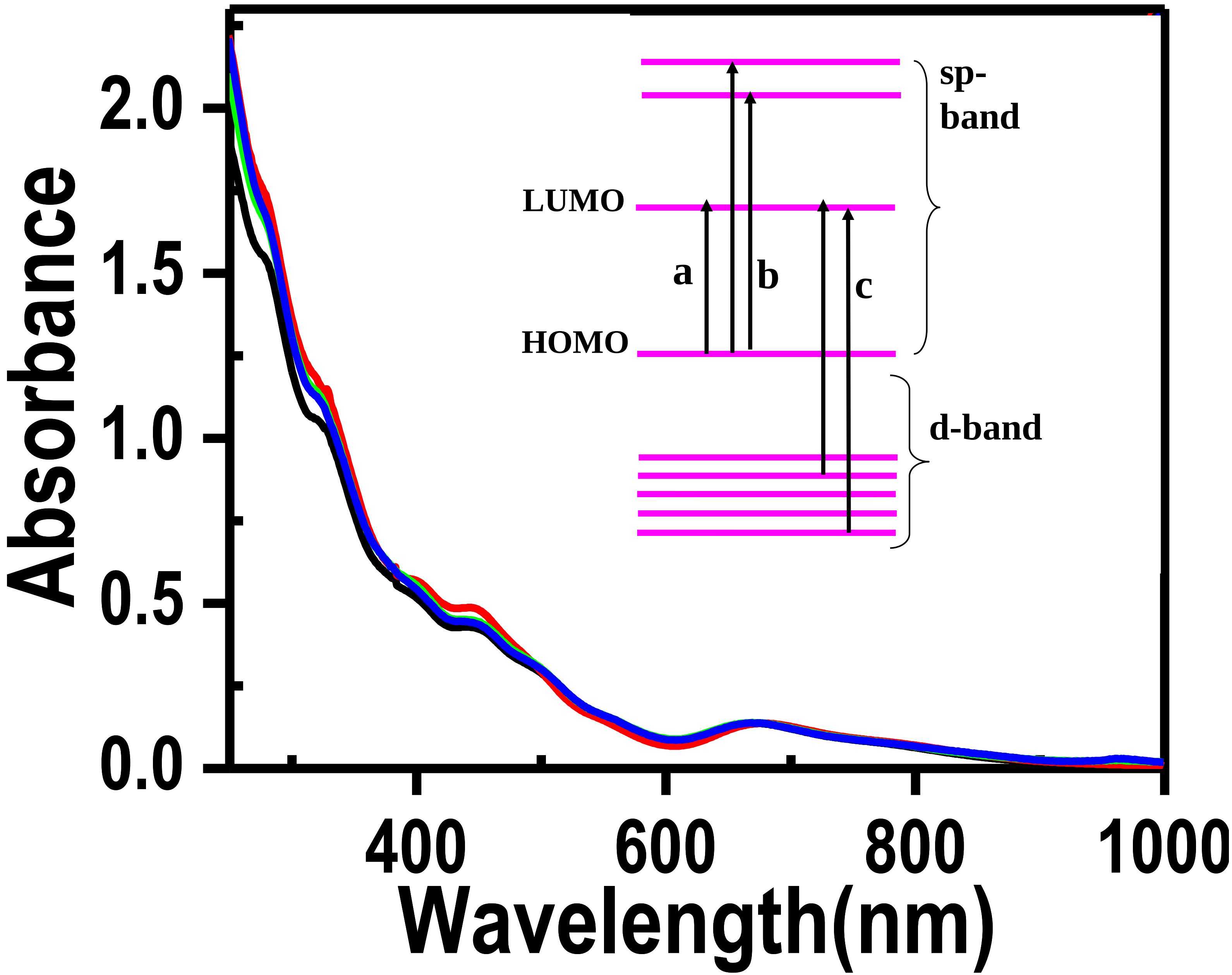
$Au_{25}SG_{18}$

Synthesis: Au_{25} clusters can be preferentially populated by dissociative excitation of larger precursors

Direct synthesis from mixture of particles

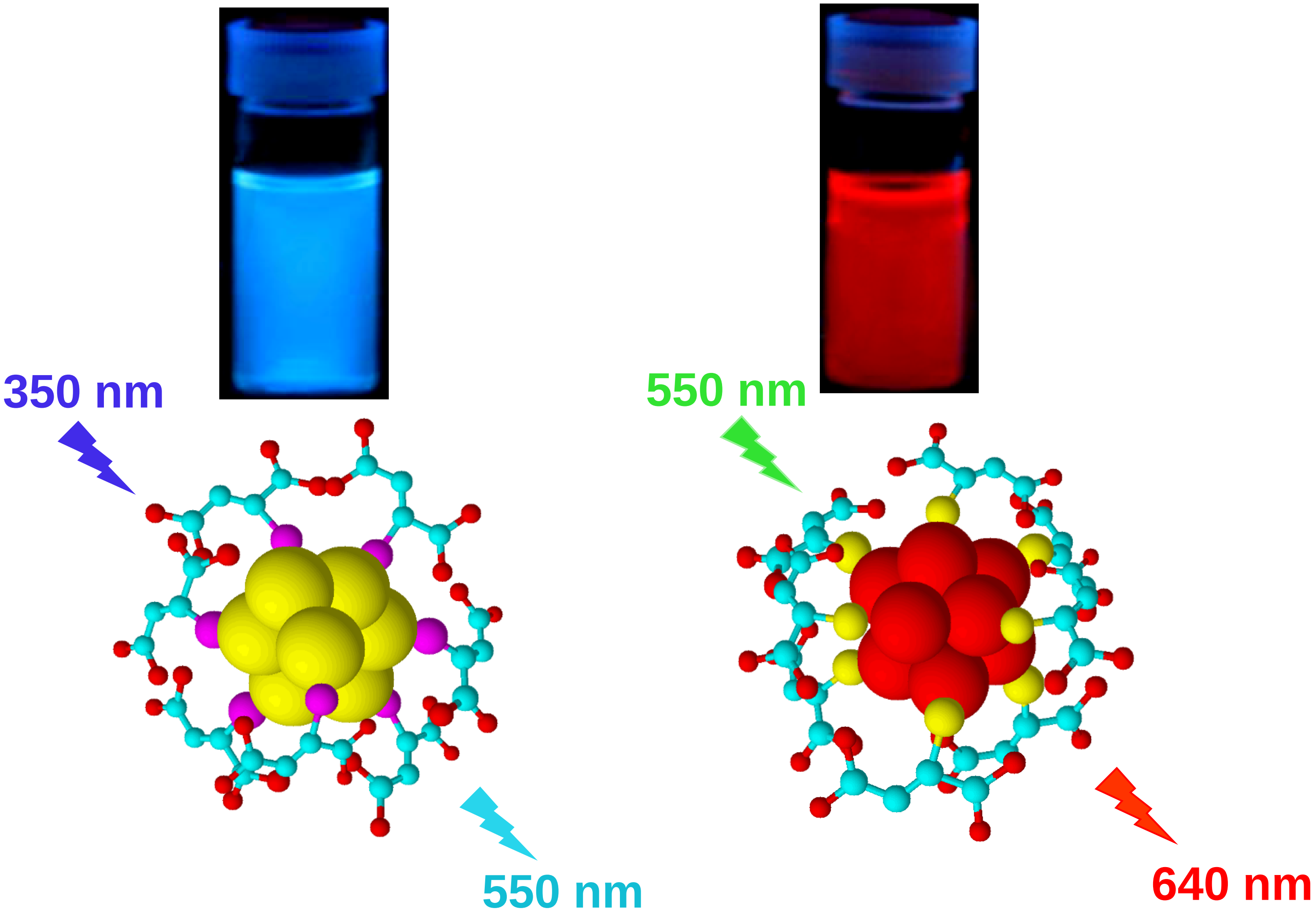
Scheme showing the synthesis of $Au_{25}SG_{18}$ clusters

E. S. Shibu et al. J. Phys. Chem. C. 2008



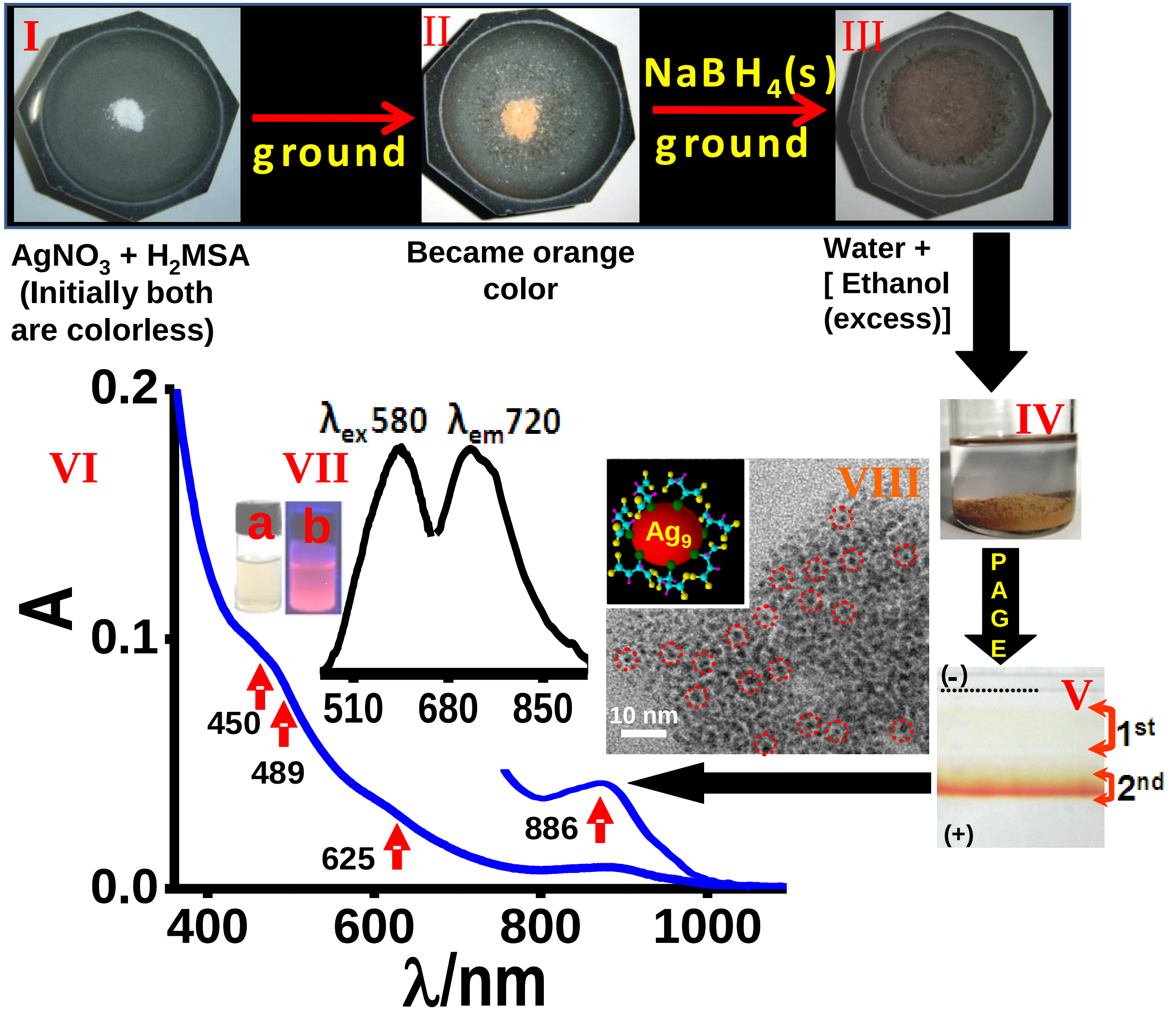
sp-
band
LUMO
a
b
c
HOMO
d-band
2.0
1.5
1.0
0.5
0.0
Absorbance
400
600
800
1000
Wavelength(nm)

Silver clusters - interfacial etching



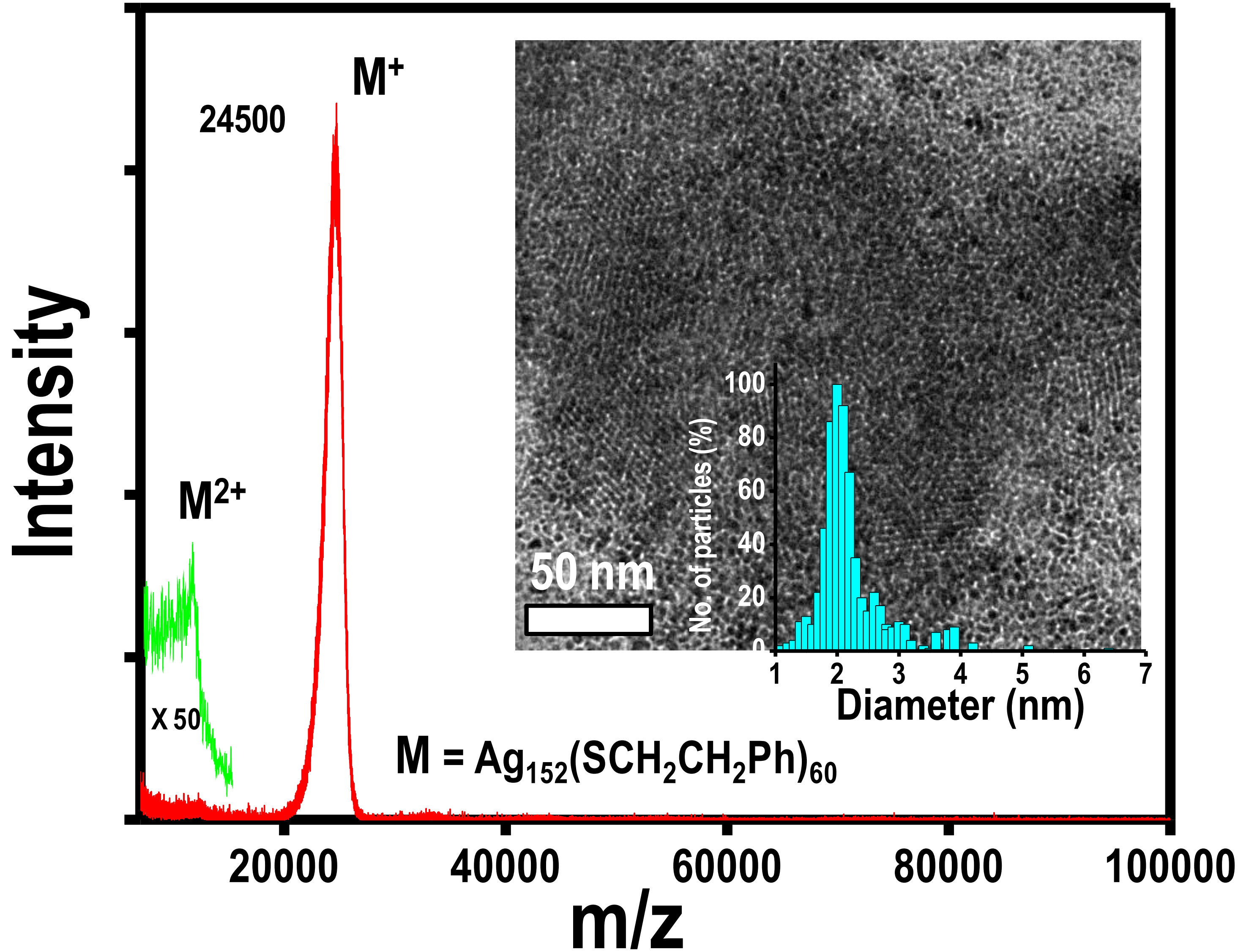
TUB Rao and T Pradeep, Angew. Chem. Int. Ed. 49 (2010) 3925-3929(2010).

Ag_9MSA_7 - solid state synthesis

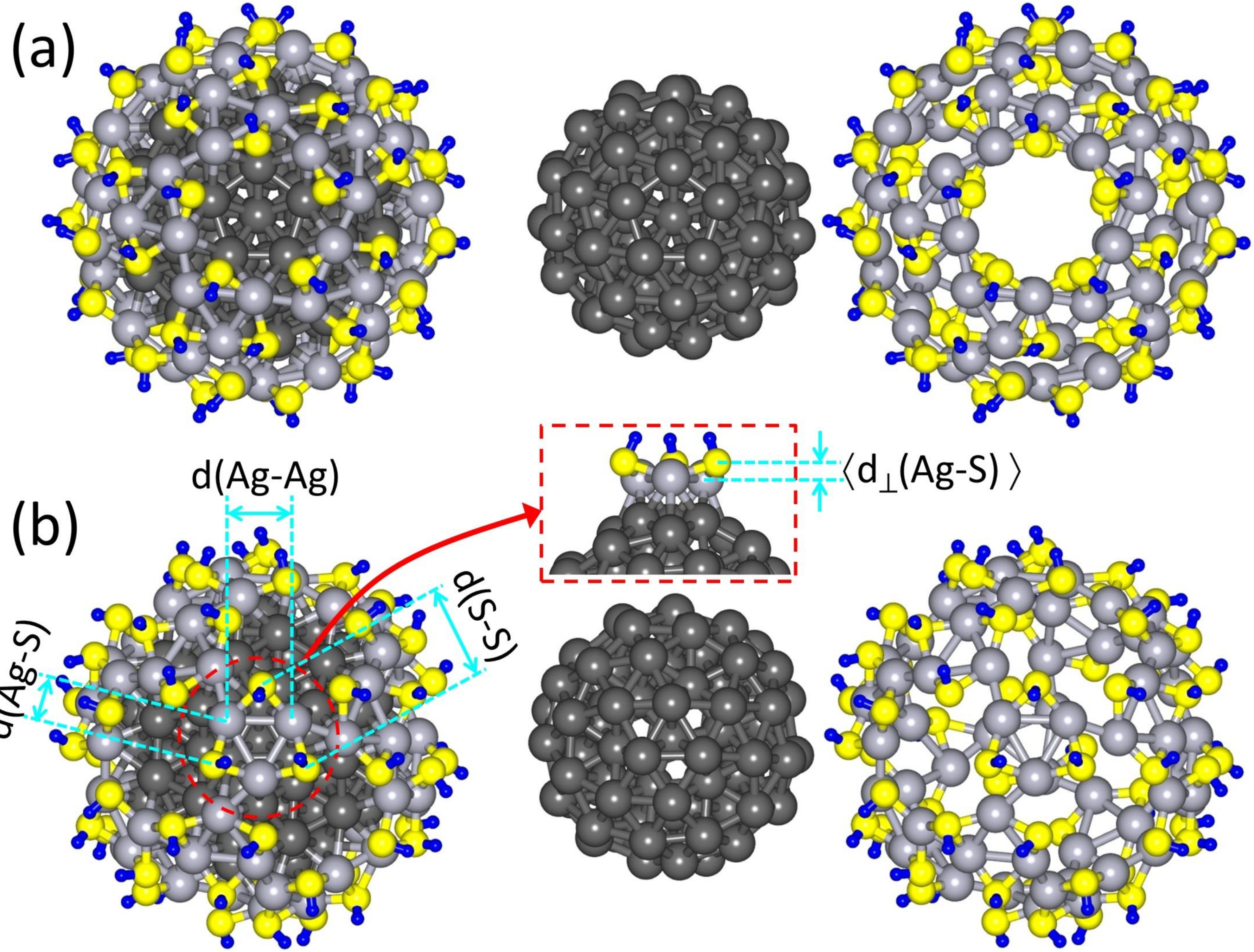


TUB Rao and T Pradeep, J. Am. Chem. Soc. 132 (2010) 16304-16307.

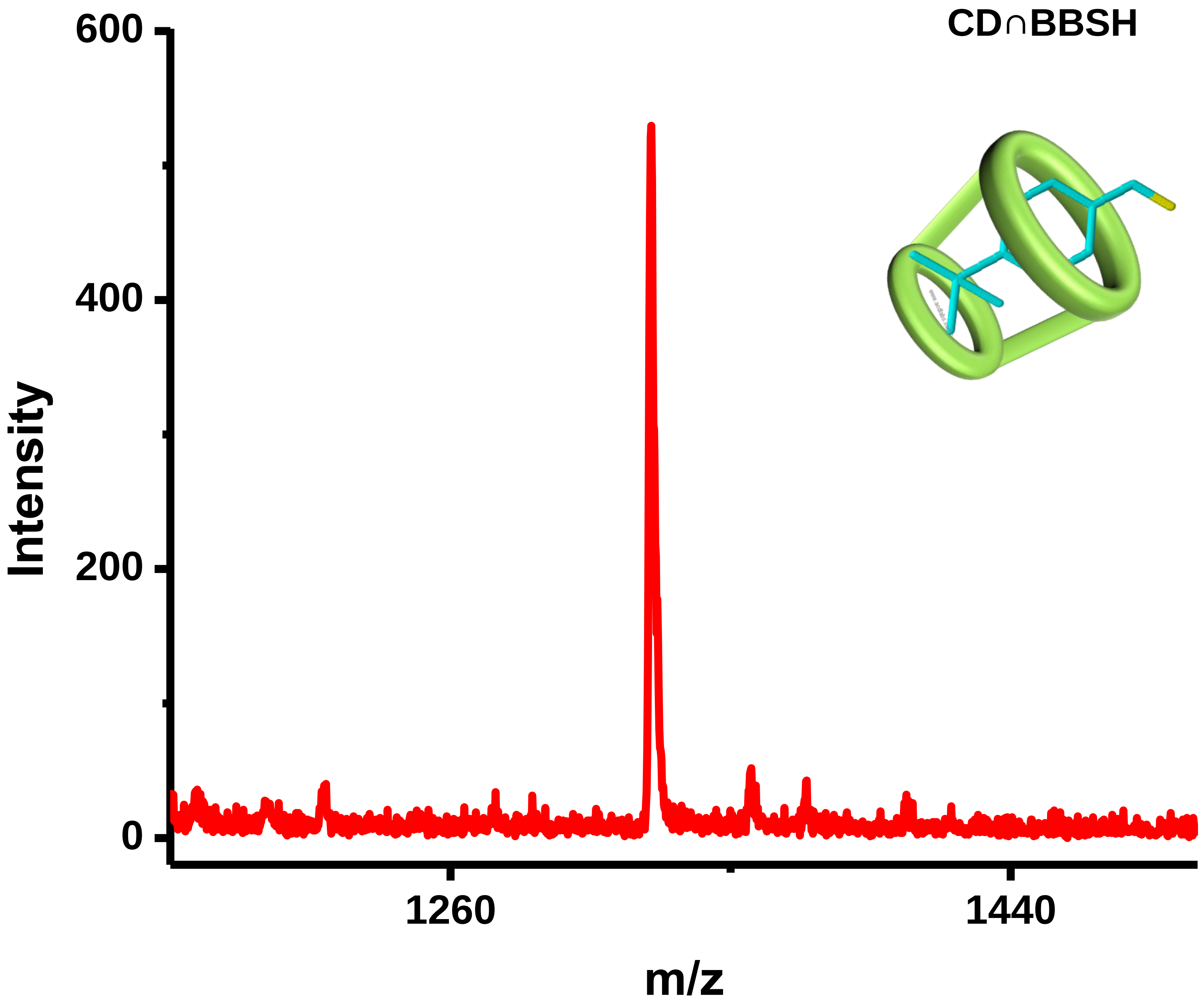
$Ag_{152}PET_{60}$



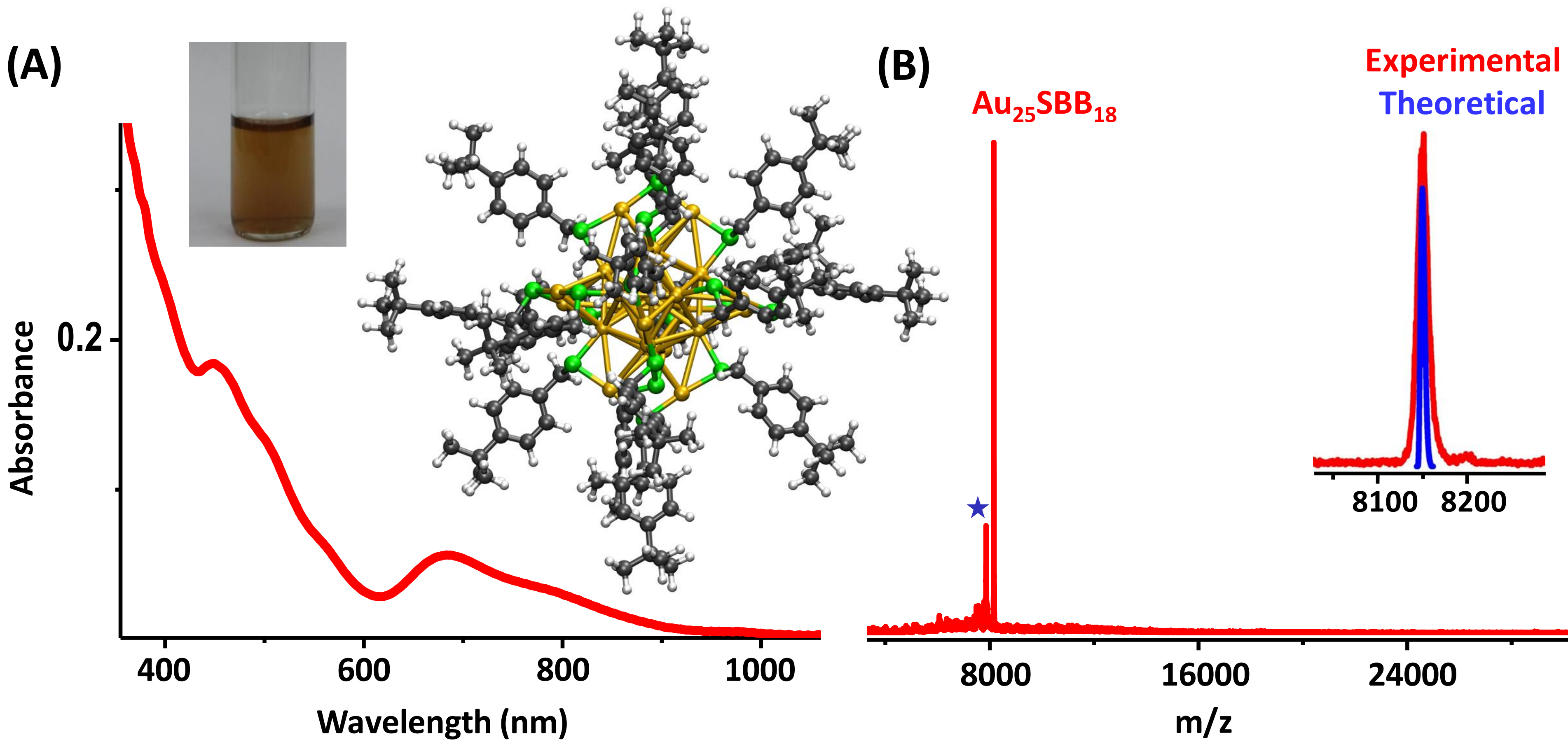
Indranath Chakraborty, et al. Nano Lett. 2012 With Uzi Landman and Rob Whetten


(a)
(b)
d(Ag-Ag)
d(Ag-S)
d(S-S)
⟨$d_{\perp}$(Ag-S)⟩

Positive mode MALDI MS of BBSH∩CD complex

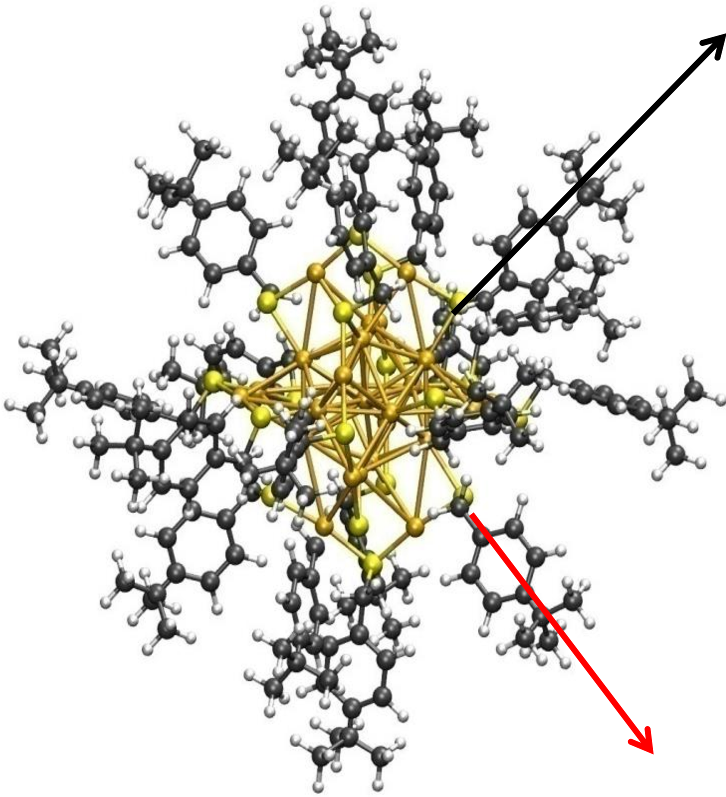


$Au_{25}SBB_{18}$



Ammu Mathew et al. ACS Nano 2014.

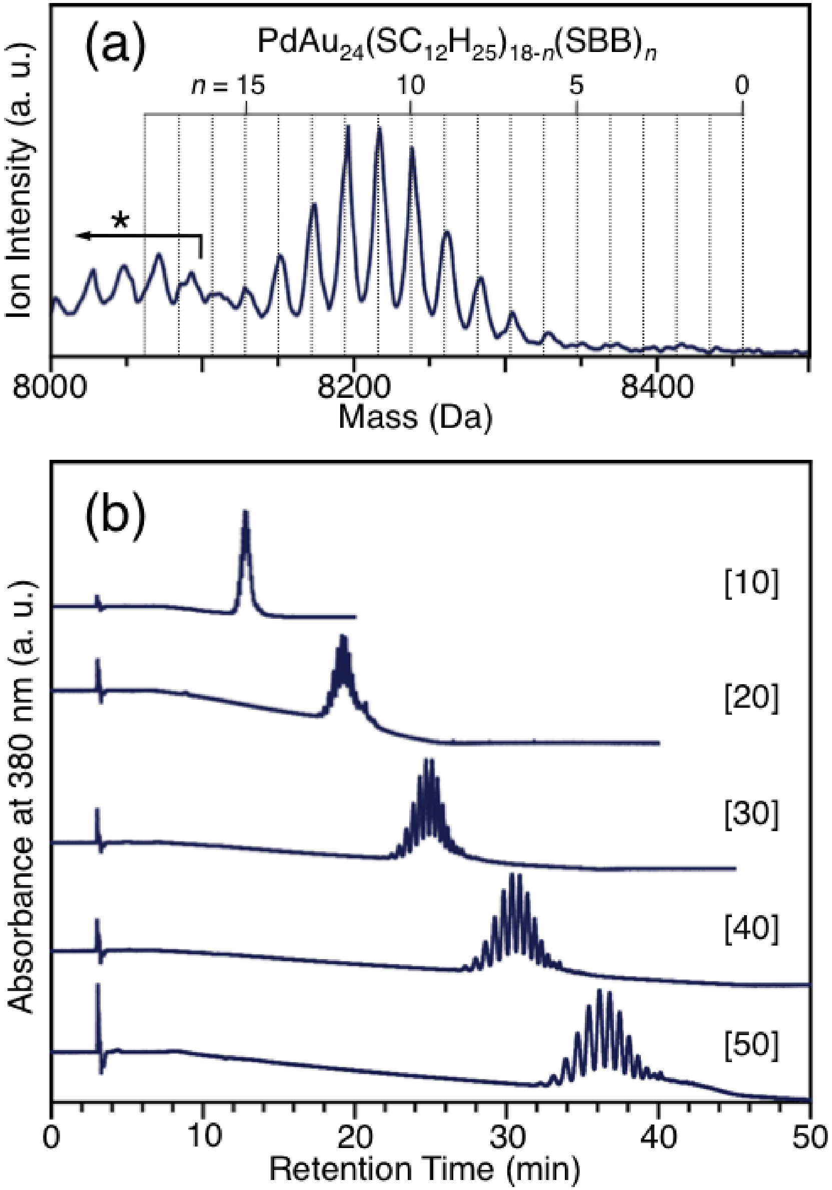
Substitution chemistry of clusters



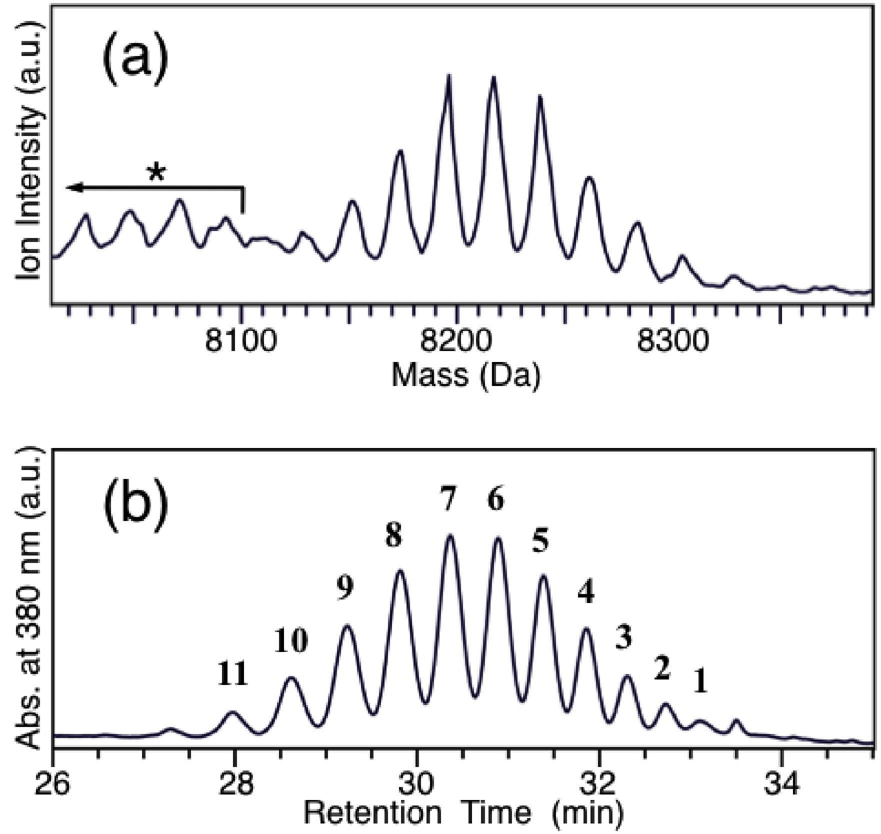
Mixed functionalised clusters

Yoshiki Niihori, Miku Matsuzaki, T. Pradeep and Yuichi Negishi, J. Am. Chem. Soc., 135 (2013) 4946-4949

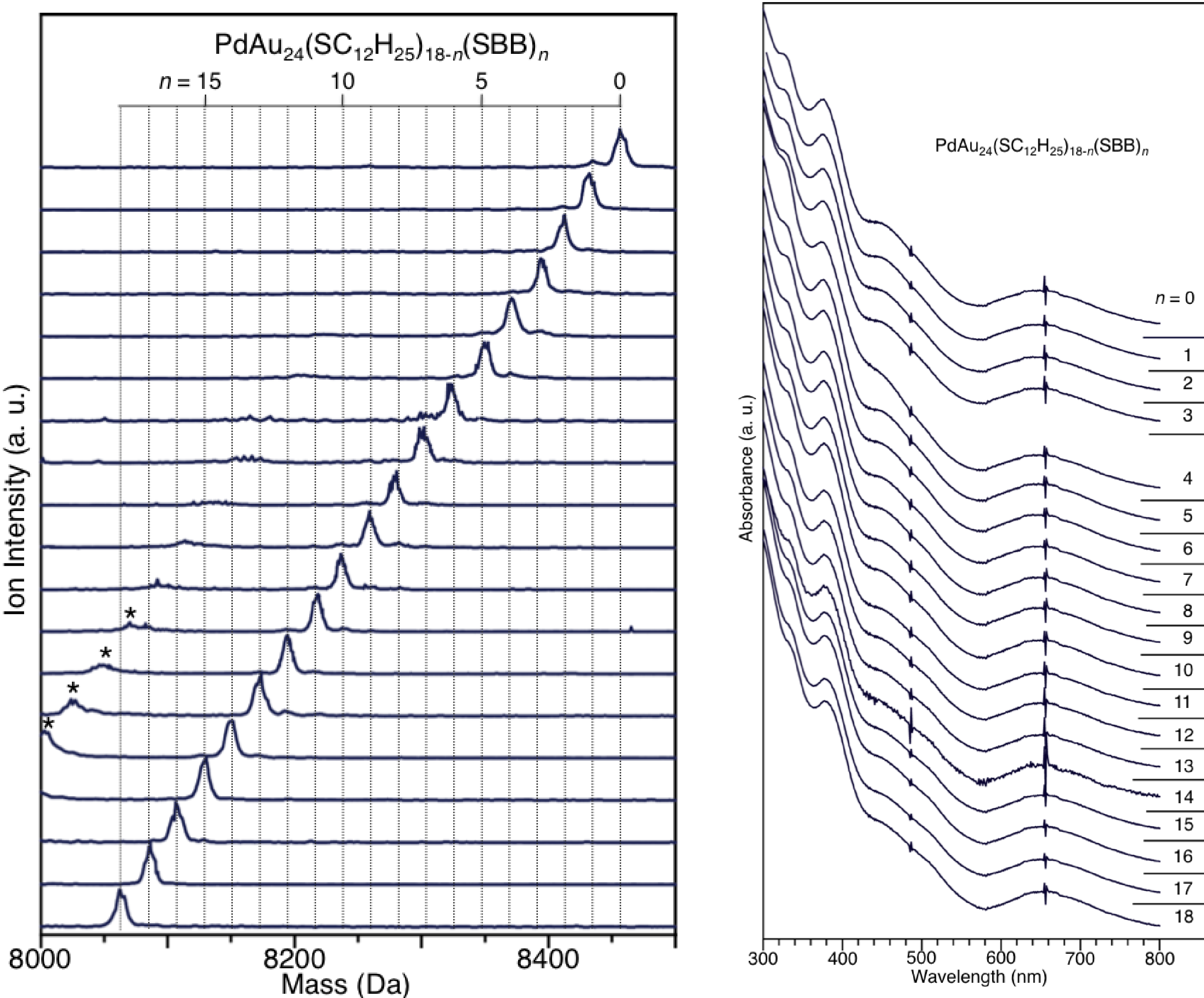
Separation of precise compositions of noble metal clusters protected with mixed ligands

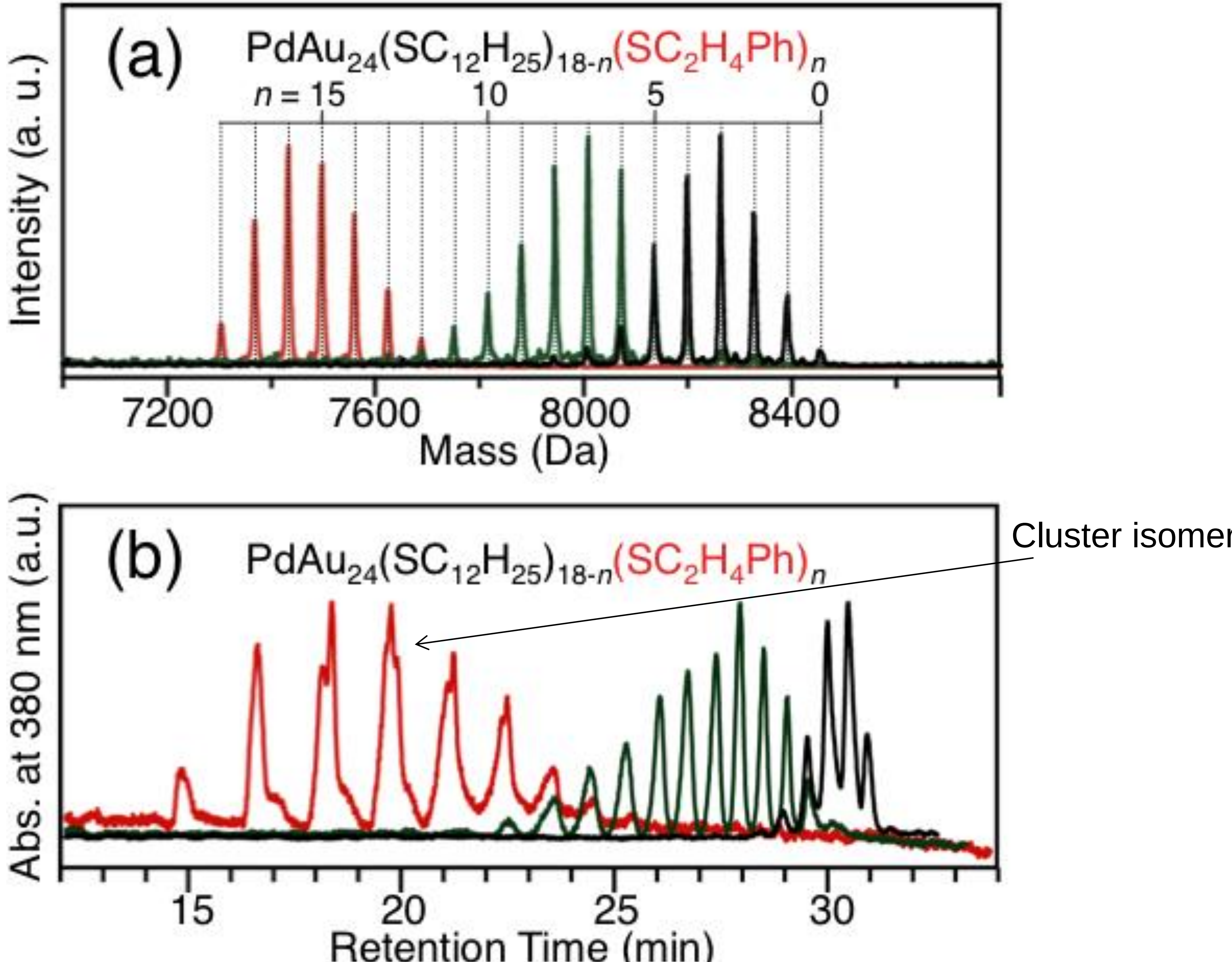


Ligand exchange chemistry – Substitution chemistry



With Niihori and Negishi, Tokyo University of Science

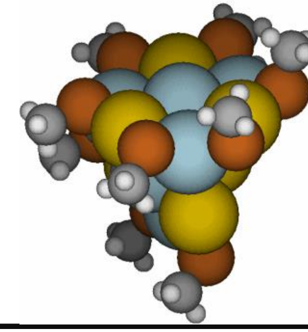

PdAu24(SC12H25)18-n(SBB)n
n = 15
10
5
0
Ion Intensity (a. u.)
8000
8200
8400
Mass (Da)
PdAu24(SC12H25)18-n(SBB)n
n = 0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Absorbance (a. u.)
300
400
500
600
700
800
Wavelength (nm)

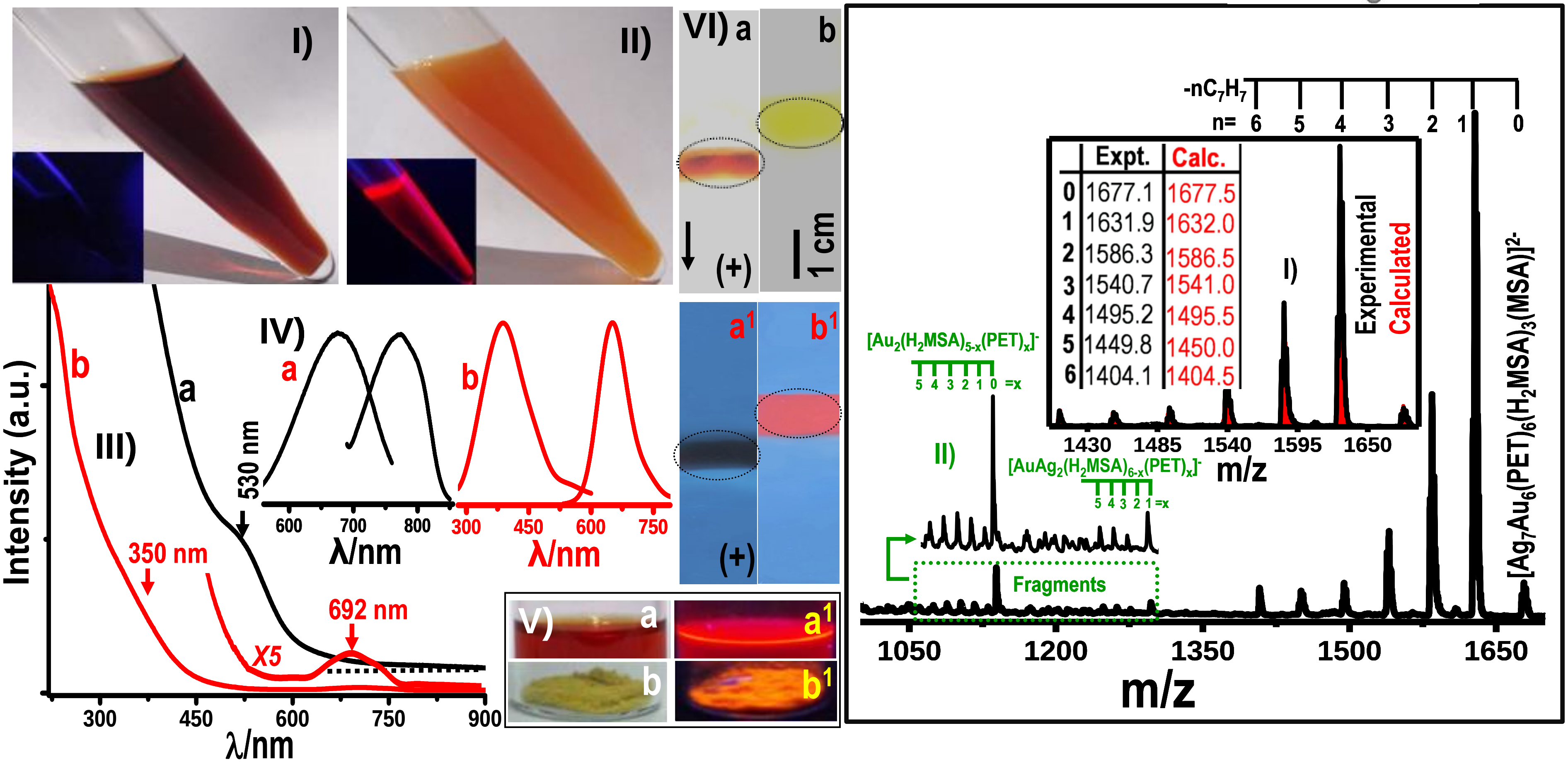


(a)
$PdAu_{24}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$
n = 15
10
5
0
Intensity (a. u.)
7200
7600
8000
8400
Mass (Da)
(b)
$PdAu_{24}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$
Cluster isomer
Abs. at 380 nm (a.u.)
15
20
25
30
Retention Time (min)

Cluster alloys

Ag_7Au_6 – 13 atom alloy cluster

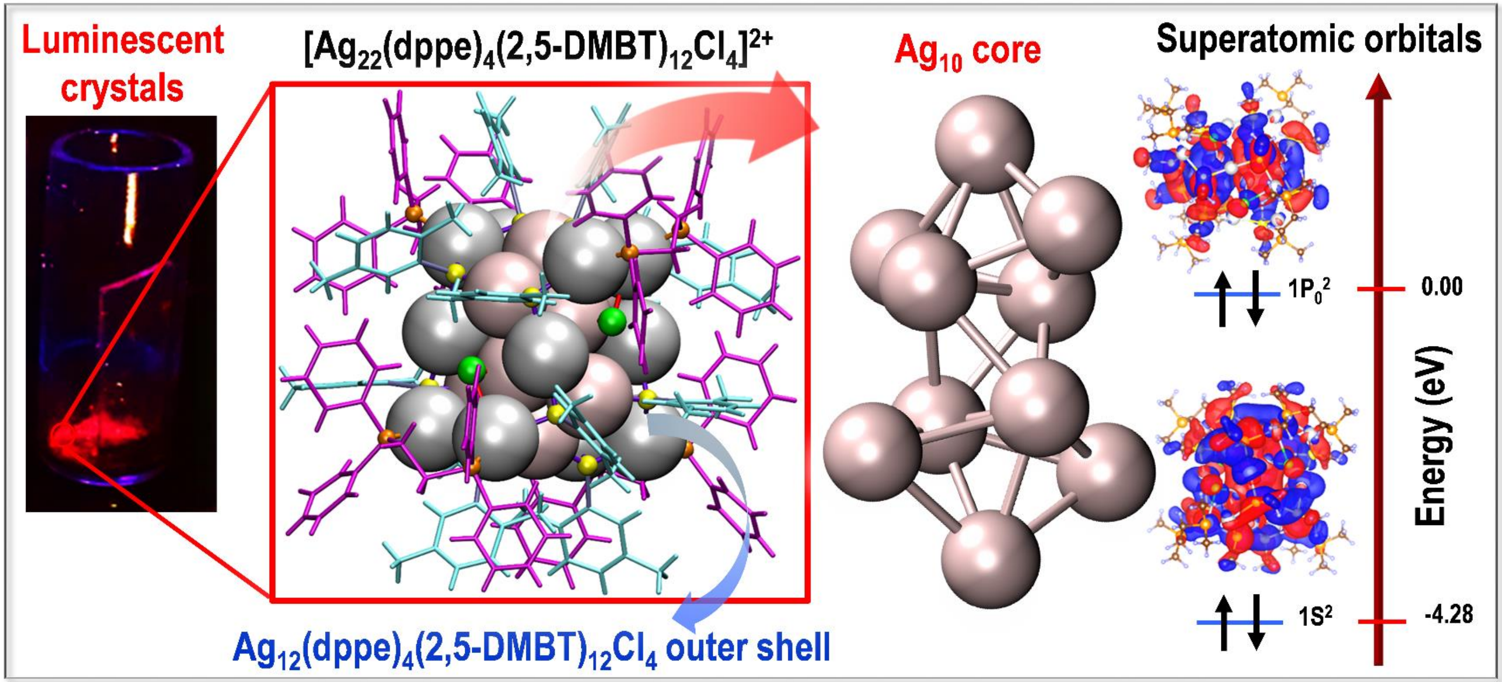




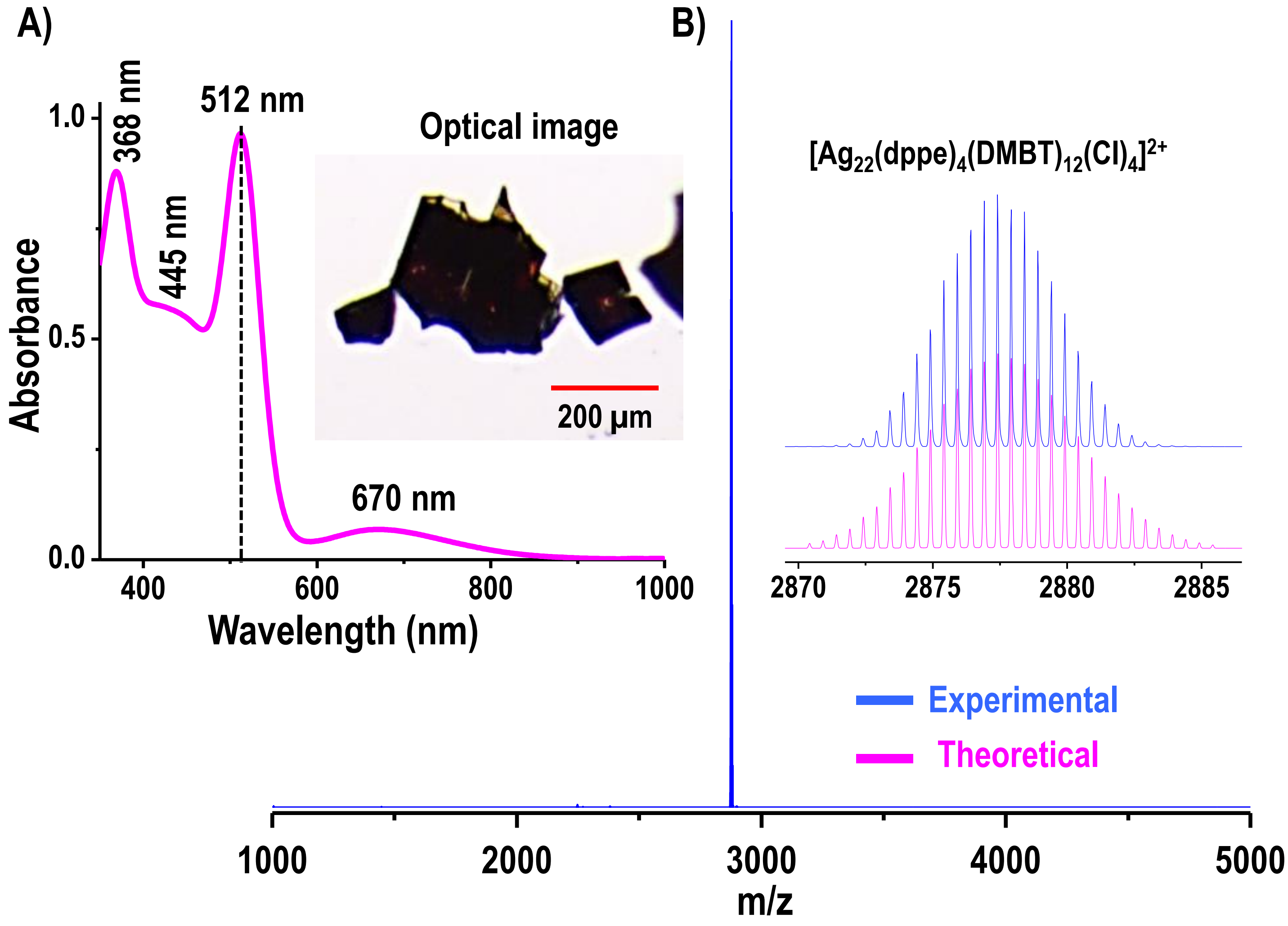
T. U. B. Rao et al. Angew. Chem. Int. Ed. 2012

Hot article

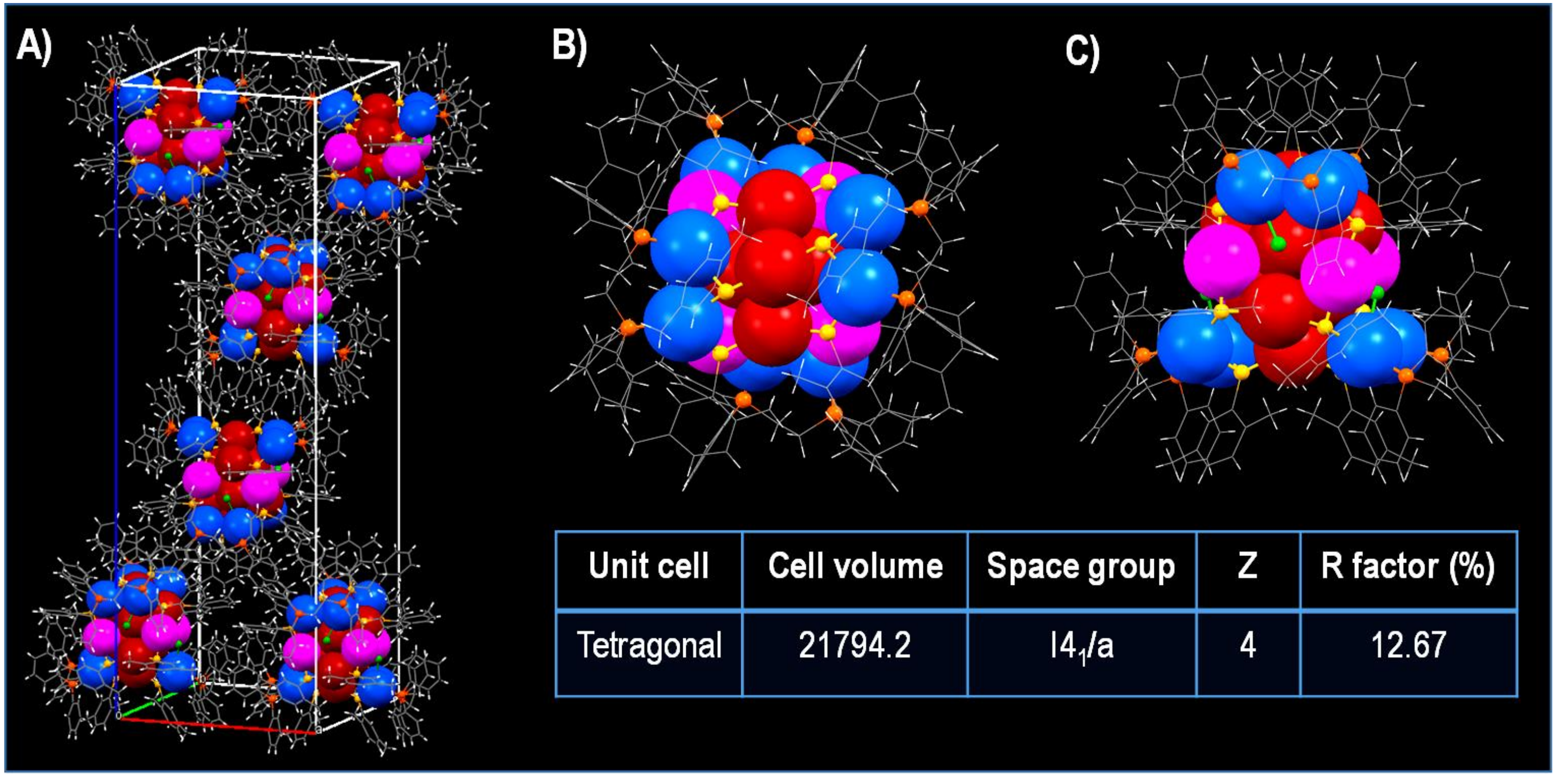
Ag_{10} Core in an Ag_{12} Shell: A Four-Electron Superatom



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

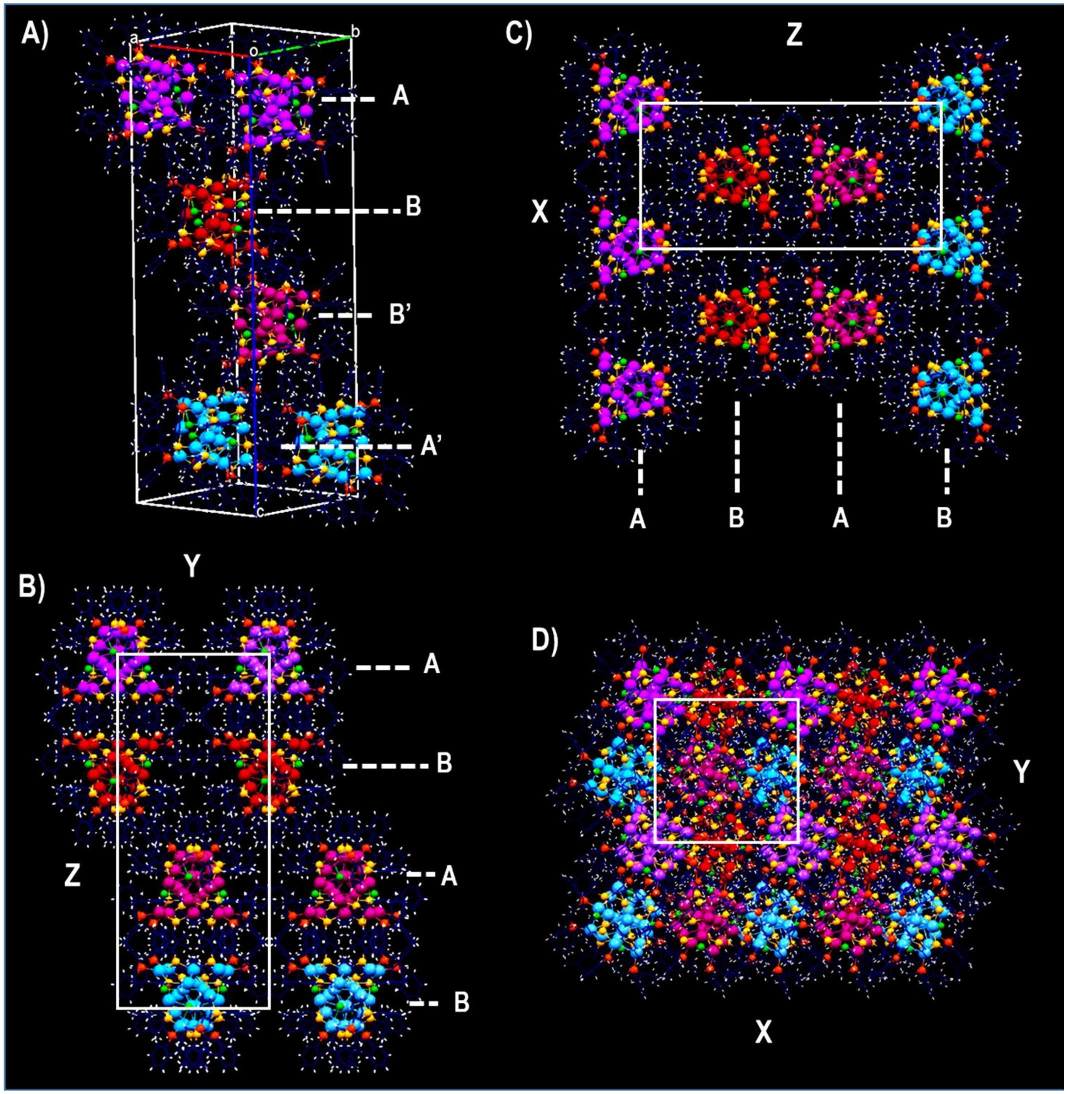


(A) Optical absorption spectrum of Ag_{22}. Inset: image of single crystals under a microscope. (B) HRESI MS of I which displays a peak at ~2876 m/z. Inset: Comparison of the theoretical and the experimental isotopic distributions of Ag_{22}.



Unit cell	Cell volume	Space group	Z	R factor (%)
Tetragonal	21794.2	$I4_1/a$	4	12.67

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.



Packing diagram of Ag_{22}: (A) Organization of clusters in a unit cell; (B) and (C) Packing diagrams along X and Y-axes, respectively display rectangular 2D lattice; (D) Packing diagram along Z-axis presents square 2D lattice.

Chemistry of clusters

Reactions of clusters

Reactions <u>between</u> clusters

Inter-cluster reactions

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

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

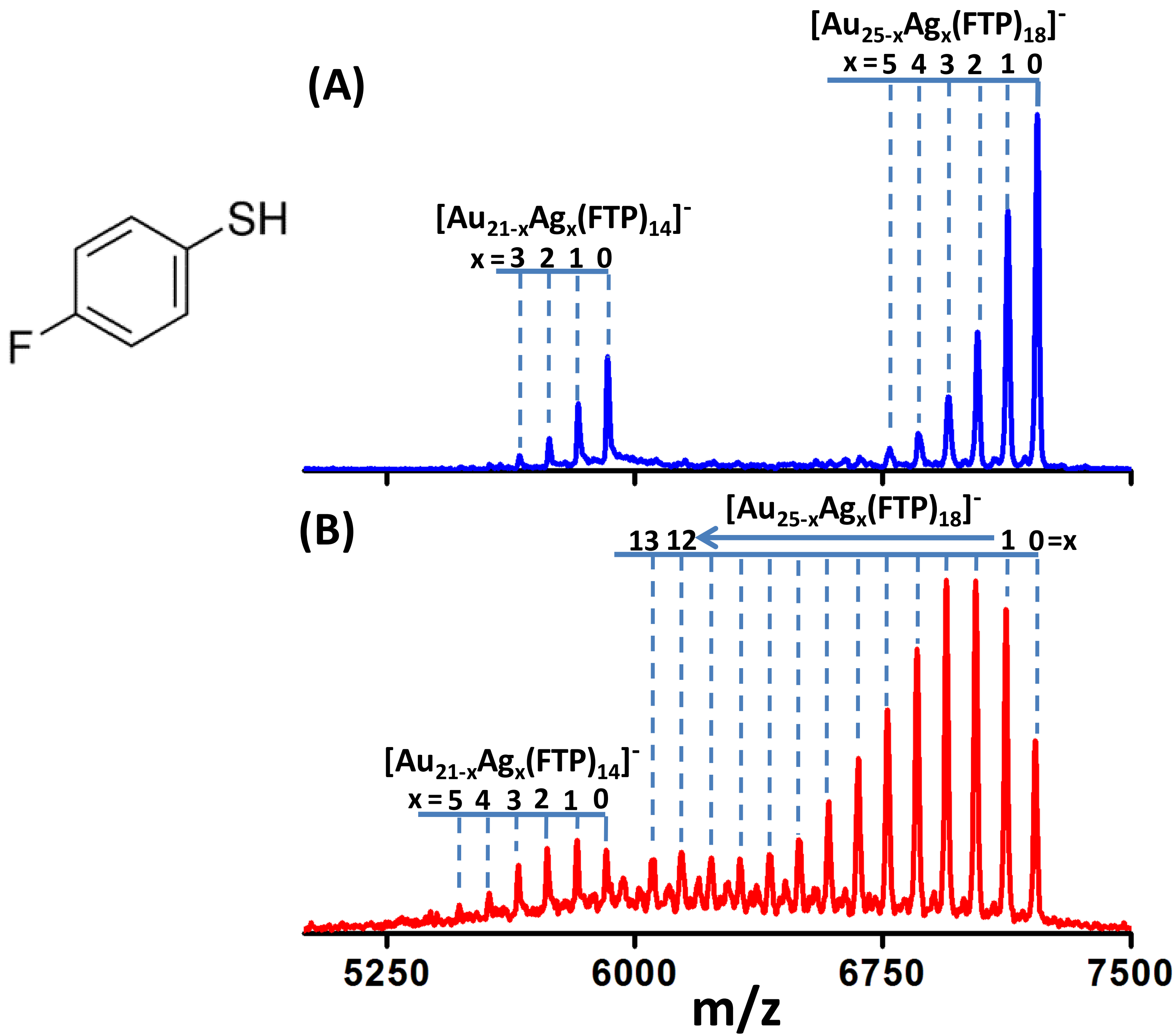
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

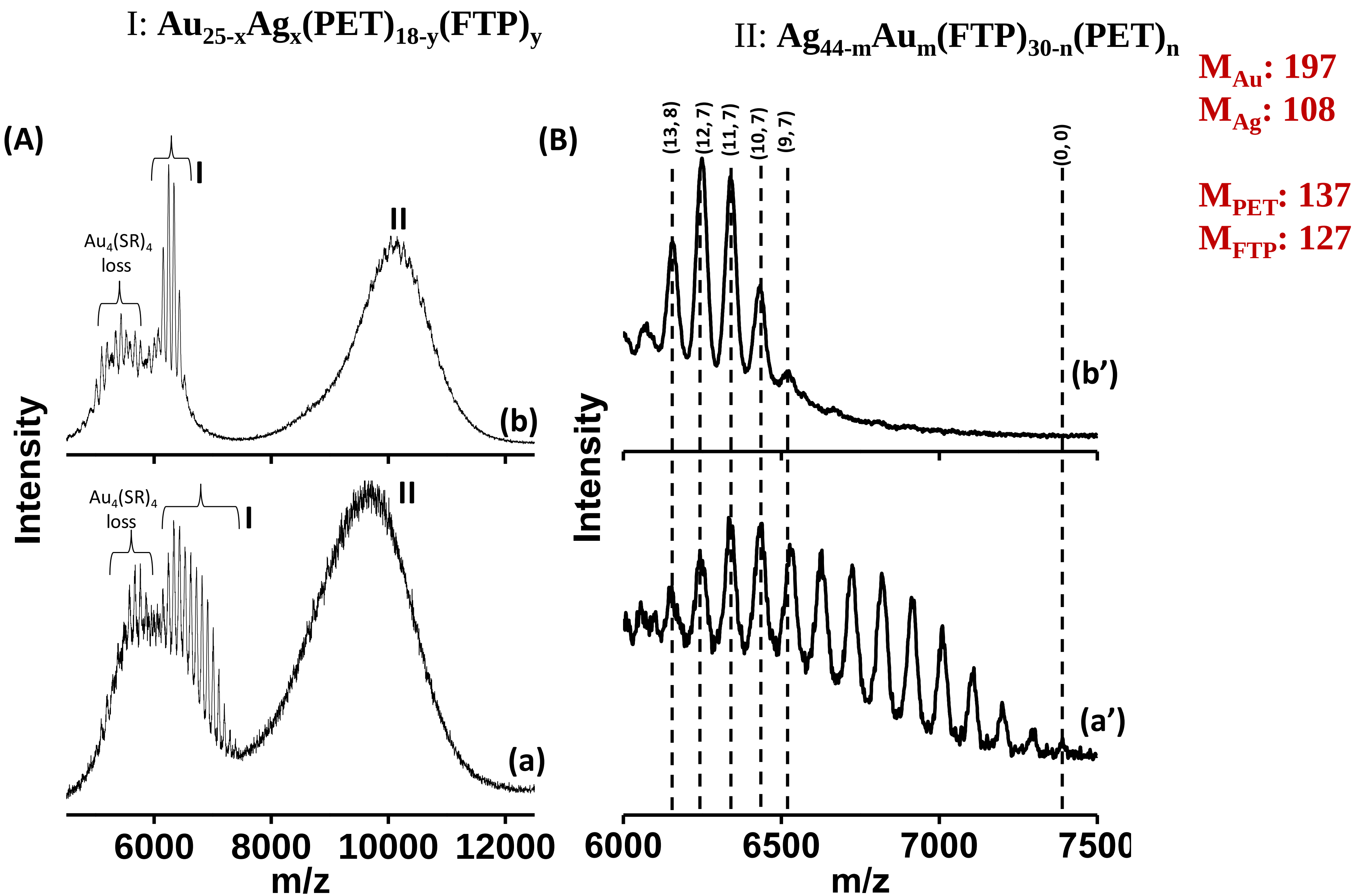
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India

Supporting Information

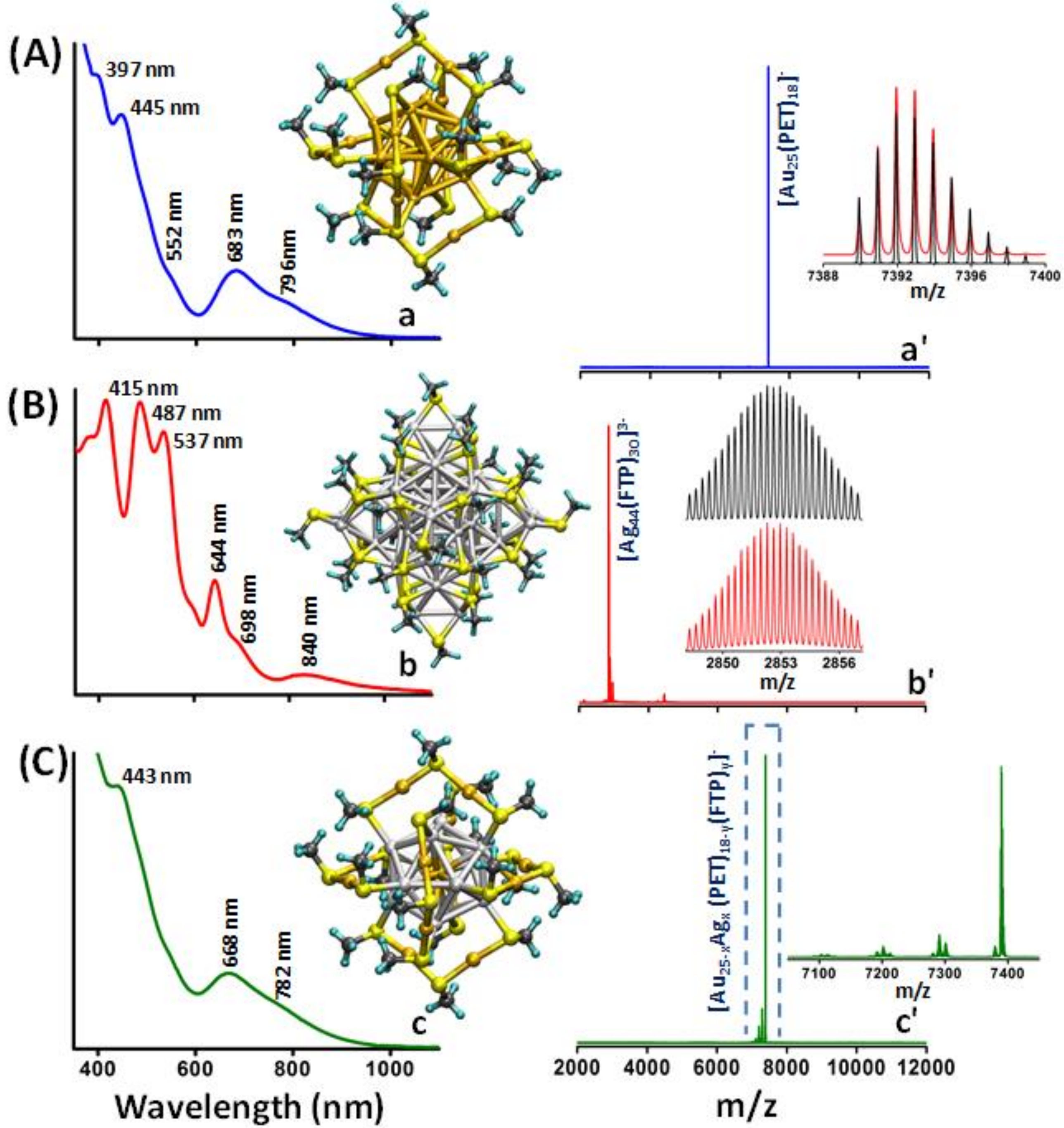
$$A + B \rightarrow C + D$$

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





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')
6000
6500
7000
7500

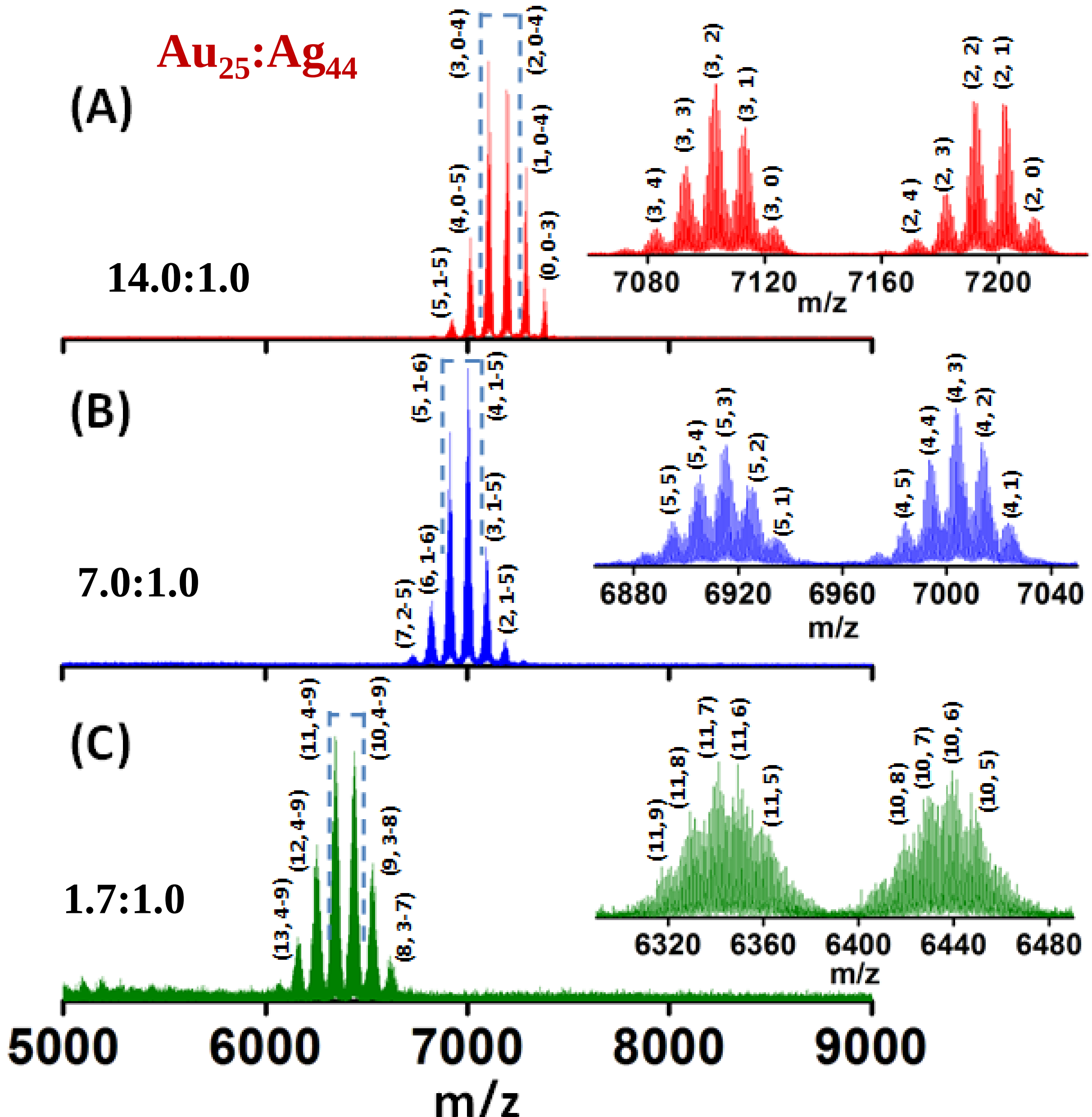


(A)
397 nm
445 nm
552 nm
683 nm
796nm
a
$[Au_{25}(PET)_{18}]^-$
7388
7392
7396
7400
m/z
a'
(B)
415 nm
487 nm
537 nm
644 nm
698 nm
840 nm
b
$[Ag_{44}(FTP)_{30}]^{3-}$
2850
2853
2856
m/z
b'
(C)
443 nm
668 nm
782 nm
c
$[Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y]^-$
7100
7200
7300
7400
m/z
c'
400
600
800
1000
Wavelength (nm)
2000
4000
6000
8000
10000
12000
m/z

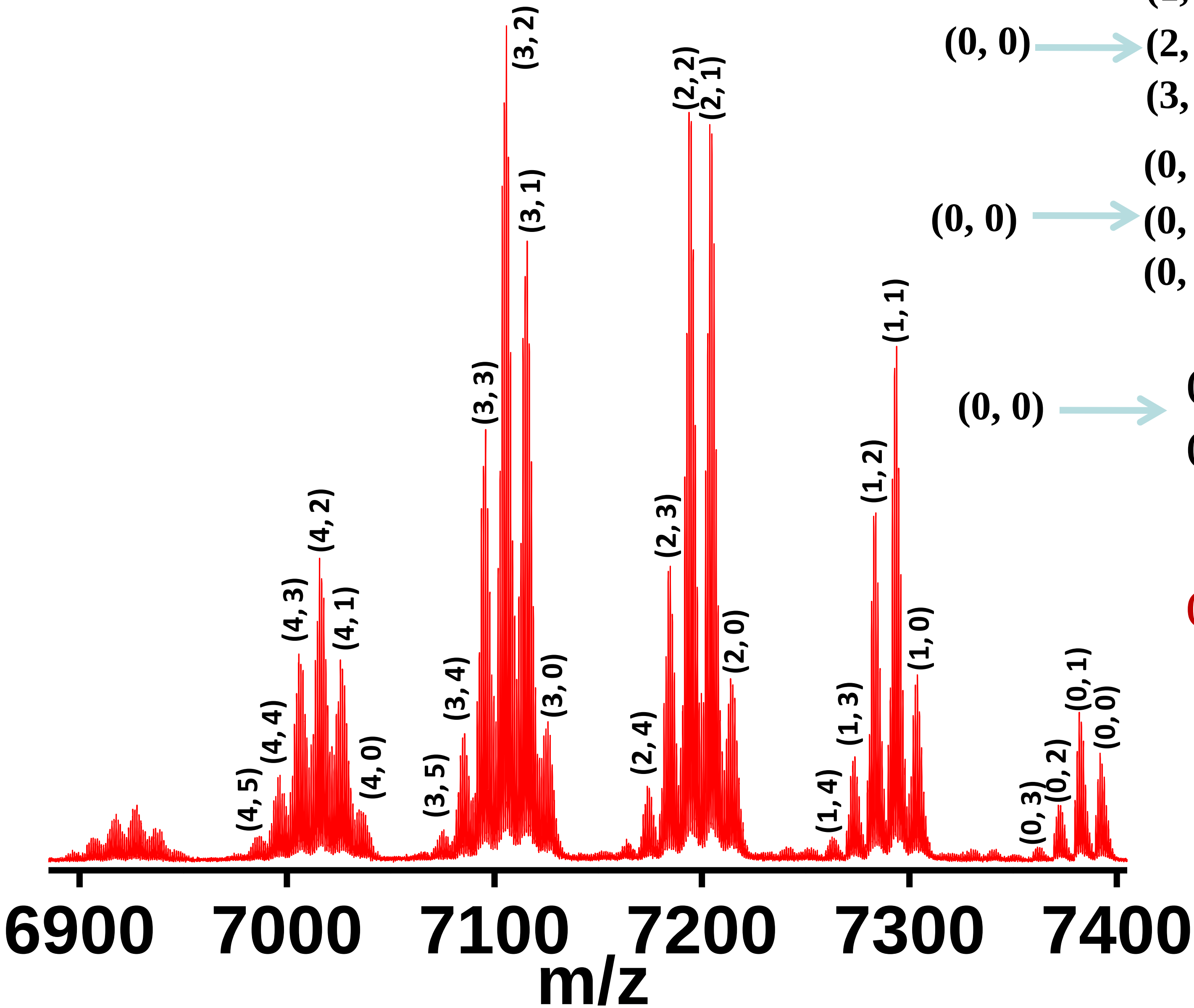
$Au_{25}(PET)_{18} + Ag_{44}(FTP)_{30} \longrightarrow Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y;\ x=0\text{-}13$

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

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



$Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y$: A closer view

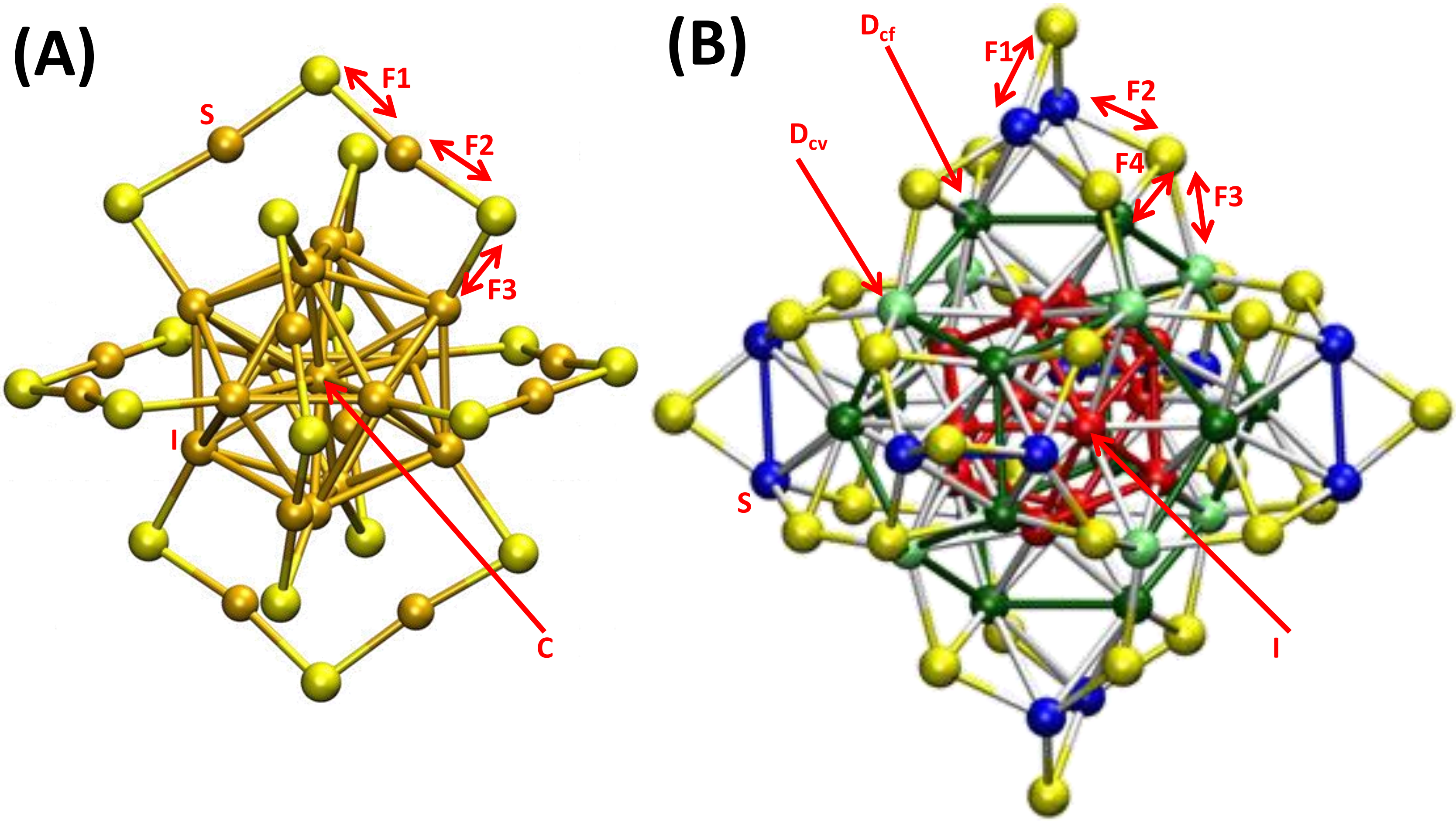


(0, 0) → (1, 0), (2, 0), (3, 0) → Ag-Au

(0, 0) → (0, 1), (0, 2), (0, 3) → FTP-PET

(0, 0) → (1, 1), (2, 2) → (Ag-FTP)-(Au-PET)

(0, 0) = $Au_{25}(PET)_{18}$



(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

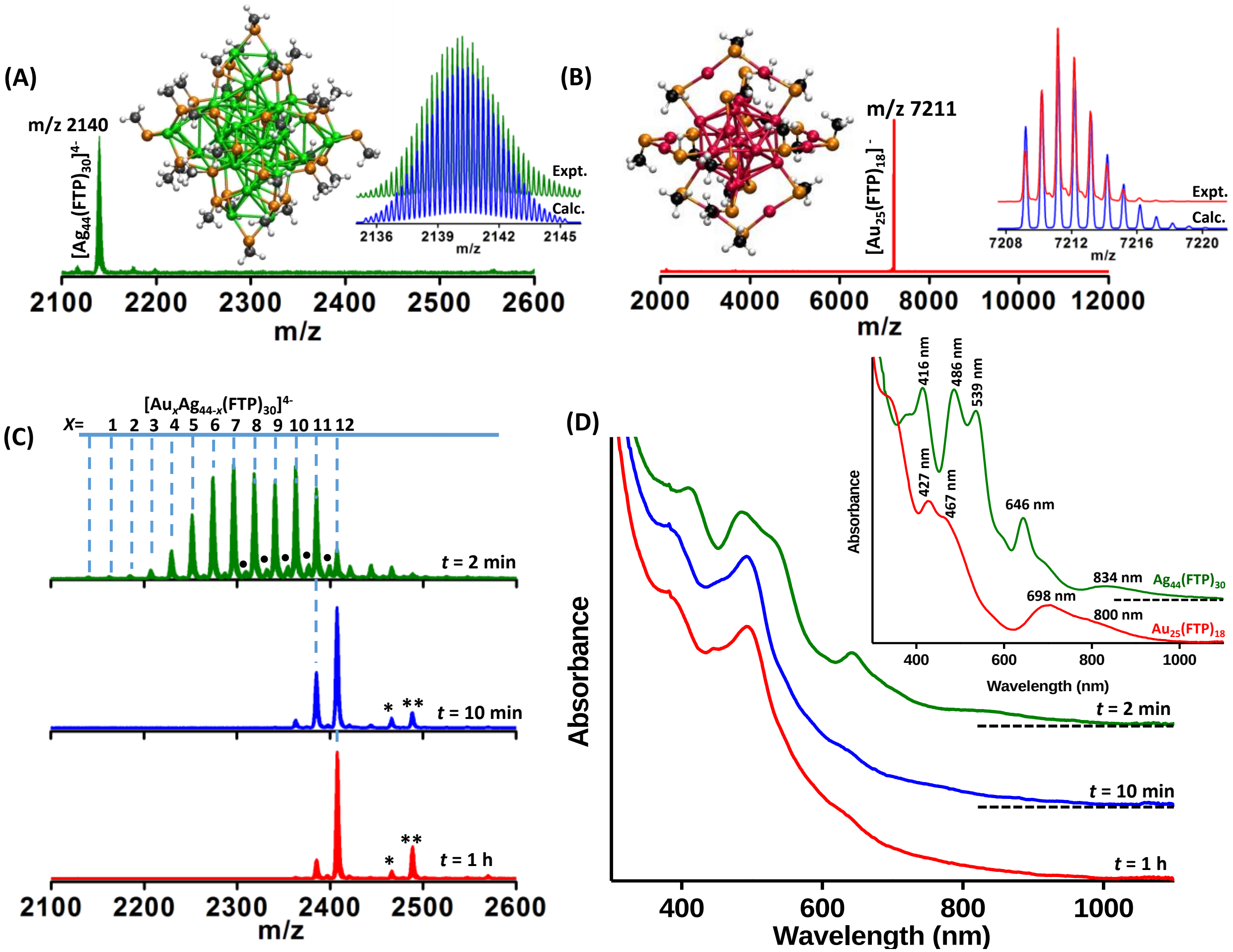
(B)

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

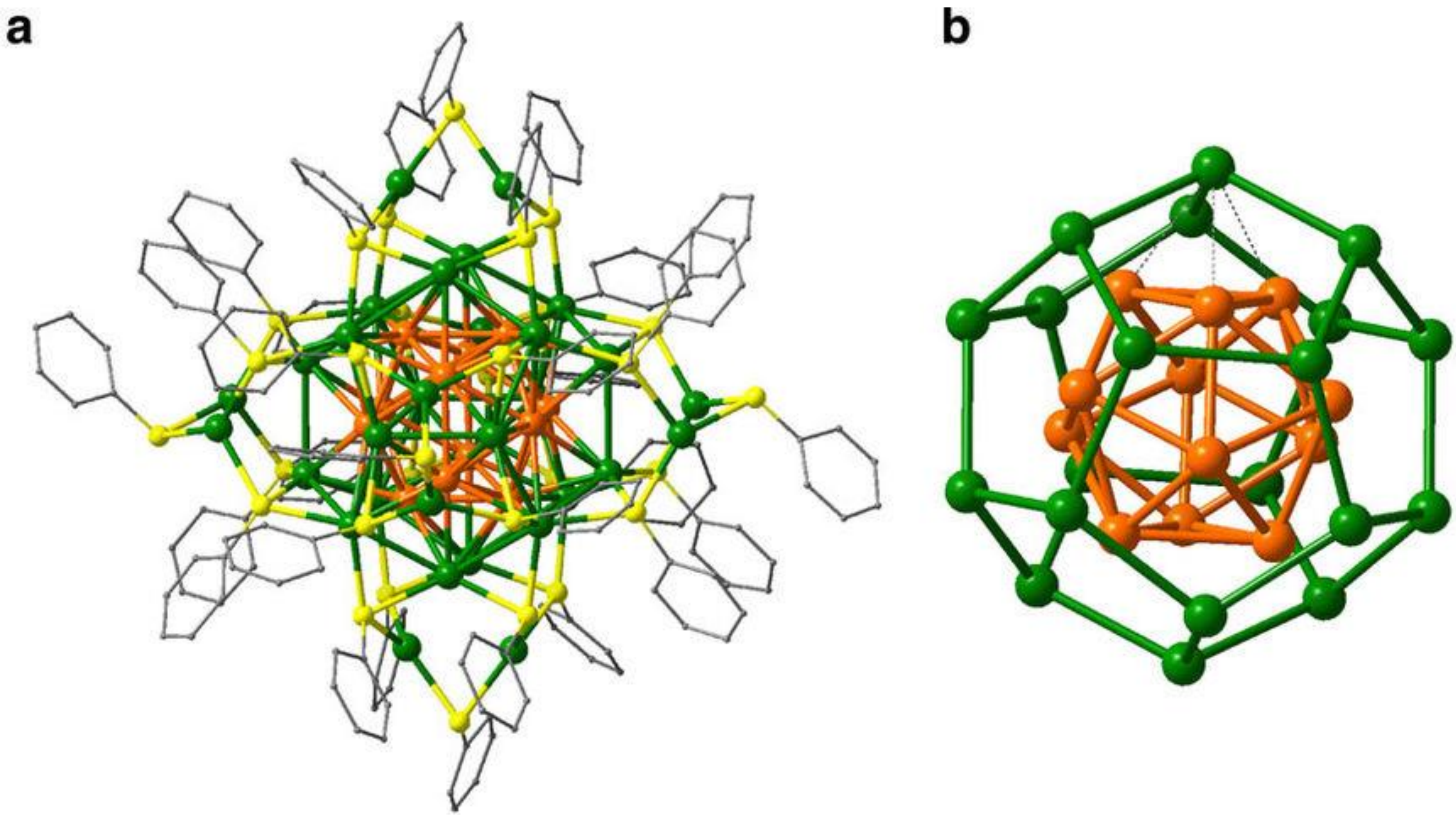
(C)

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

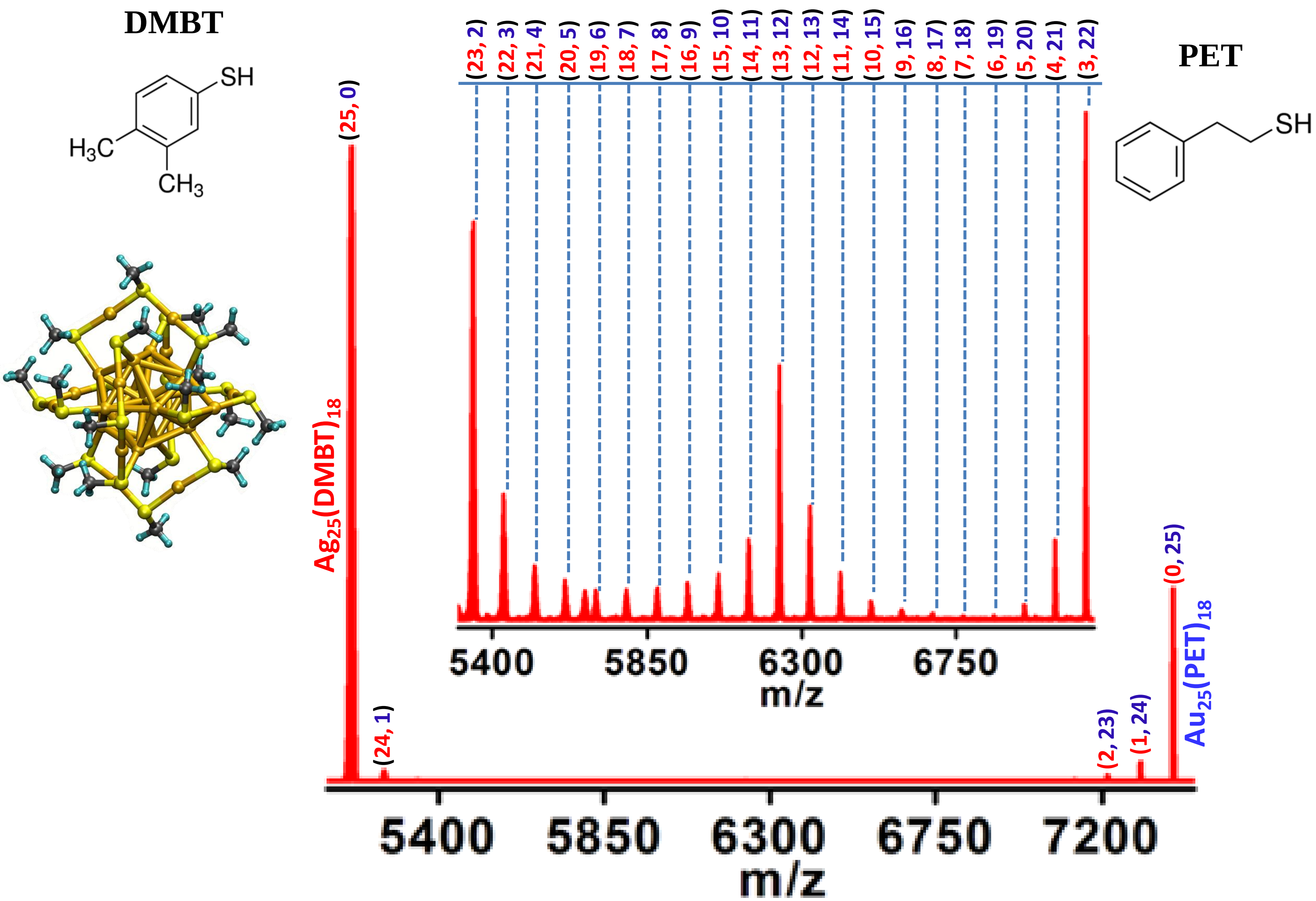


Nanfeng Zheng et al. Nature Communications, 2013

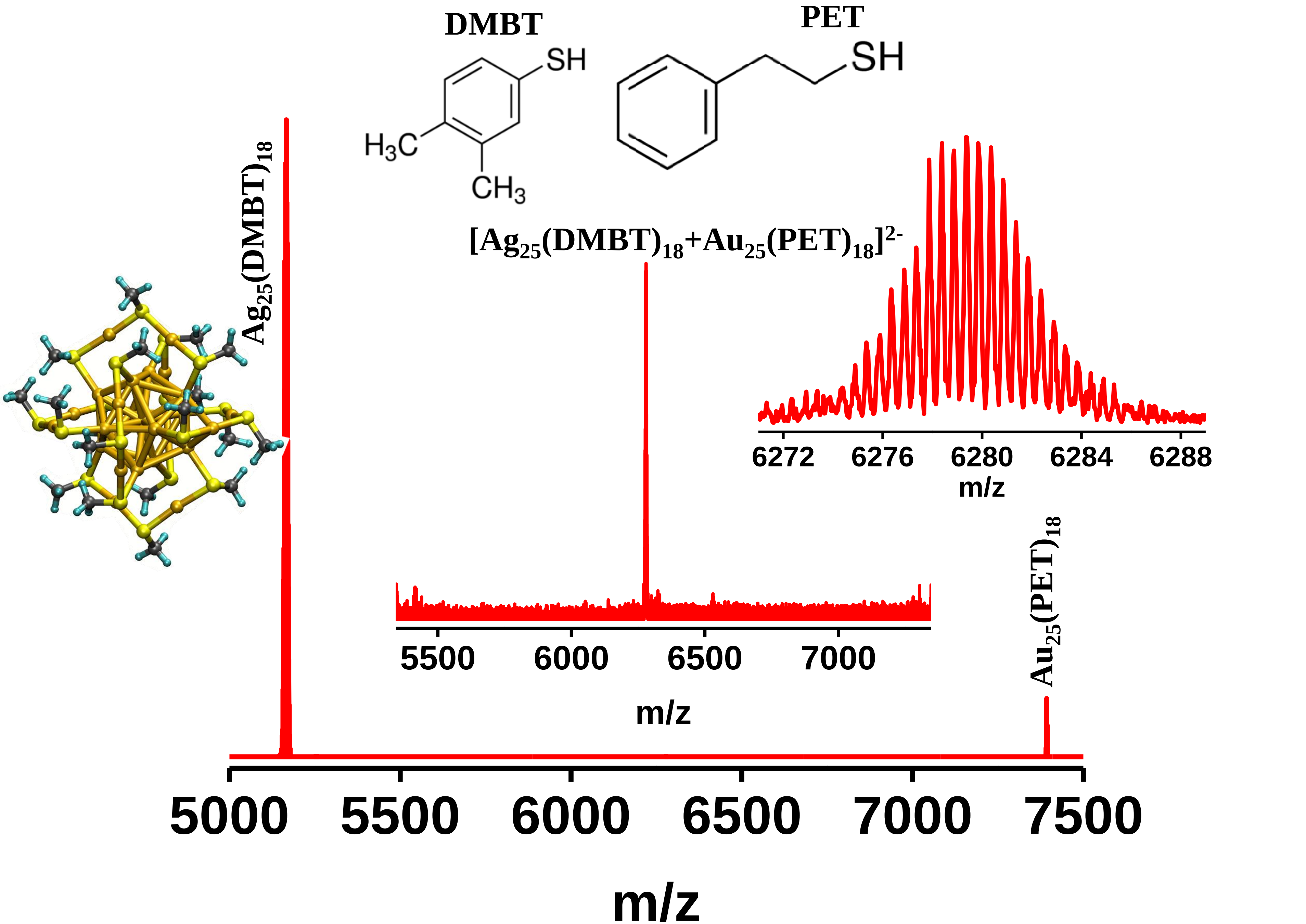
Ag_{25}-Au_{25} experiments

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

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

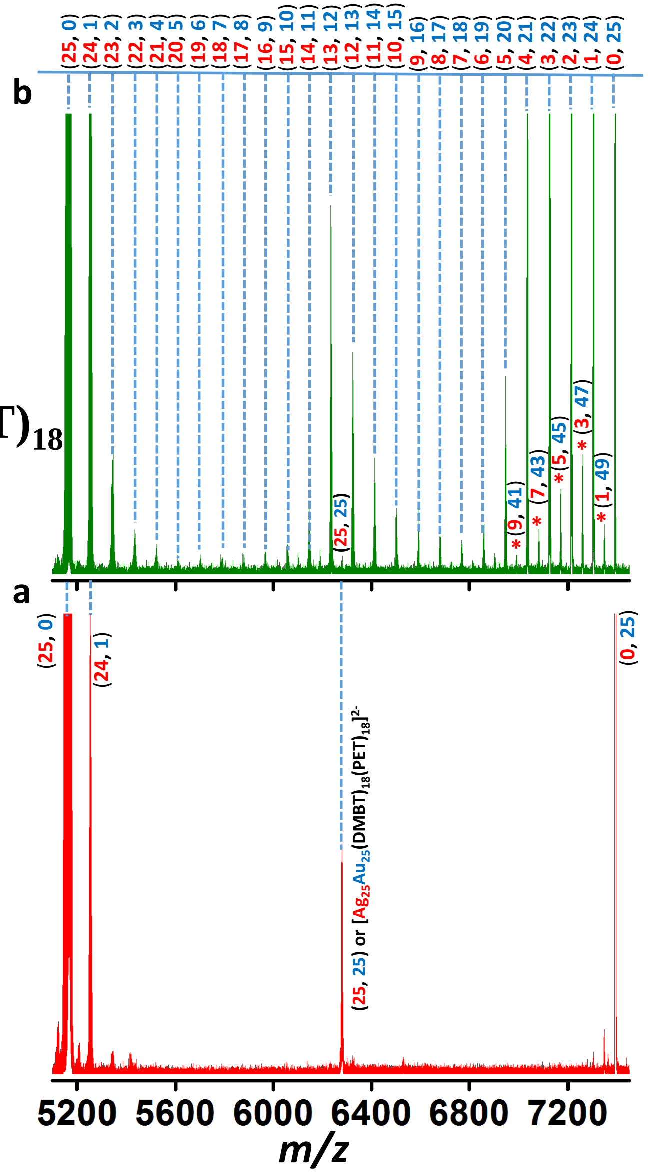


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

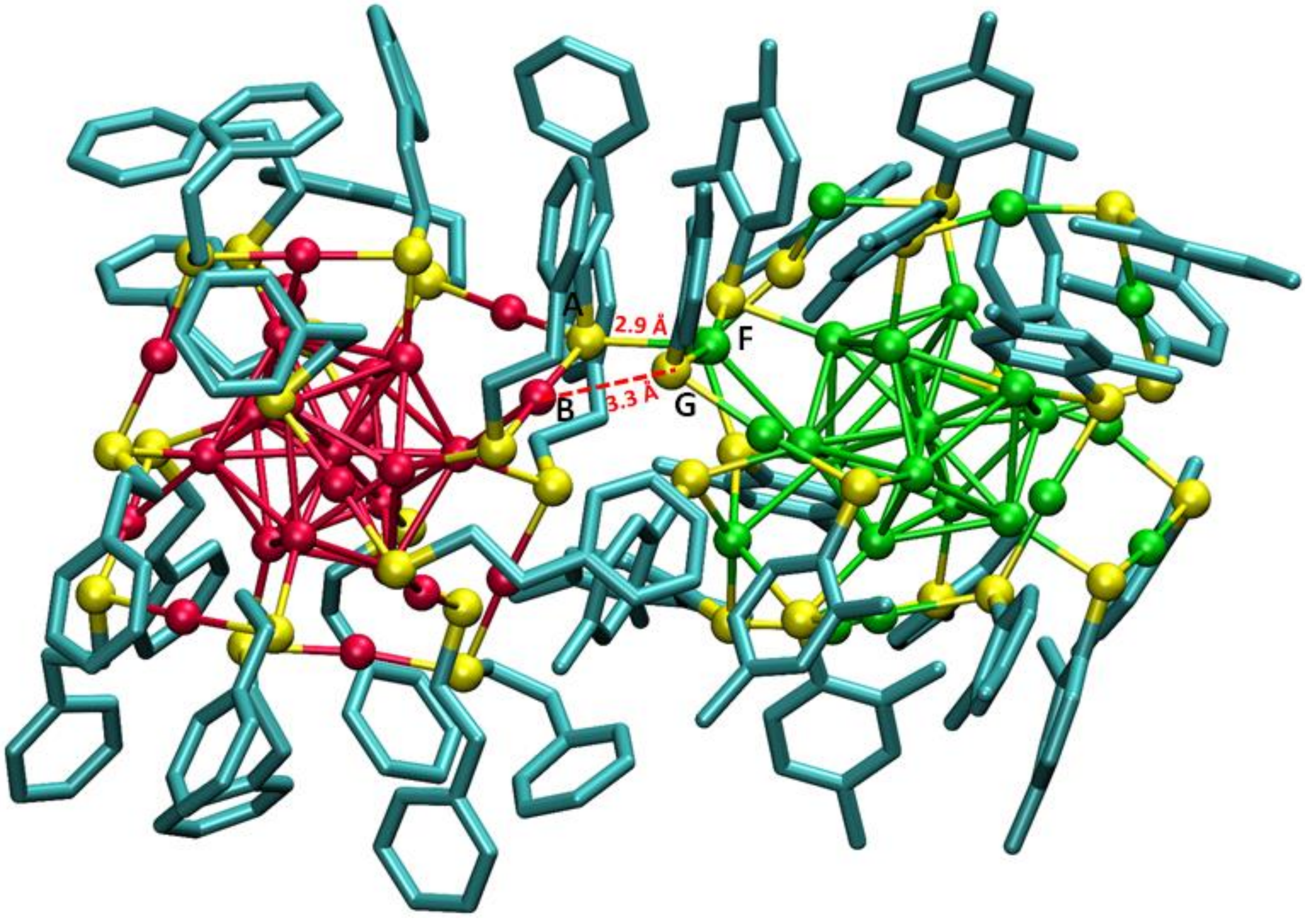
$Ag_{25}(DMBT)_{18}$:$Au_{25}(PET)_{18}$
0.3:1.0

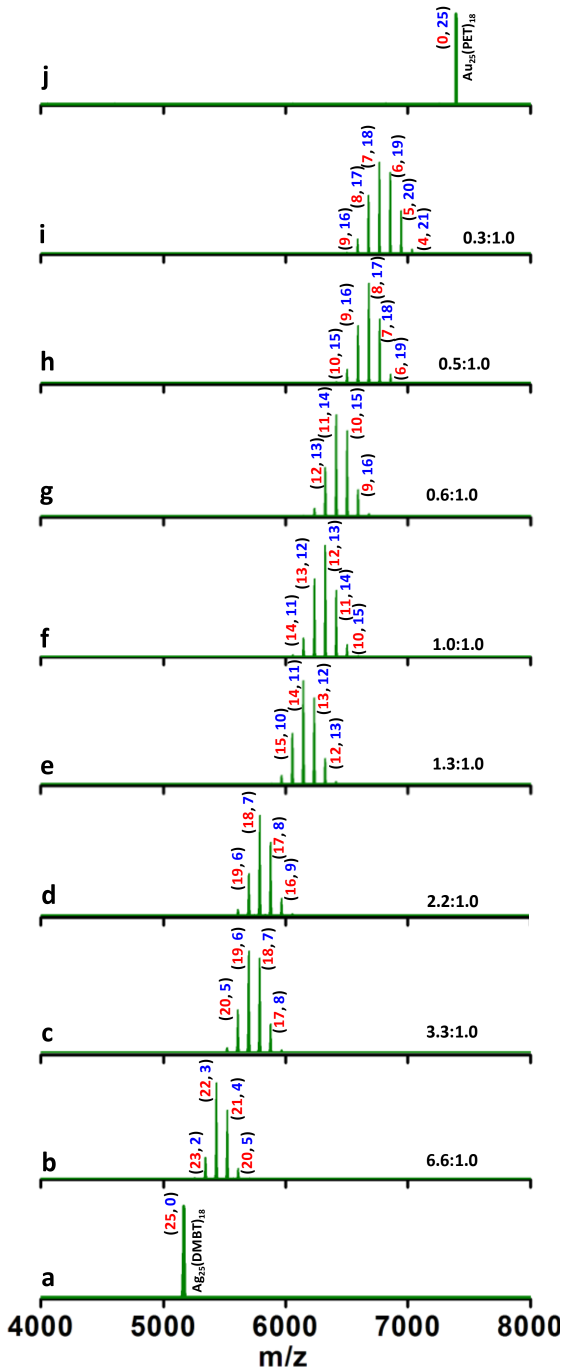


within 5 min

within 2 min

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

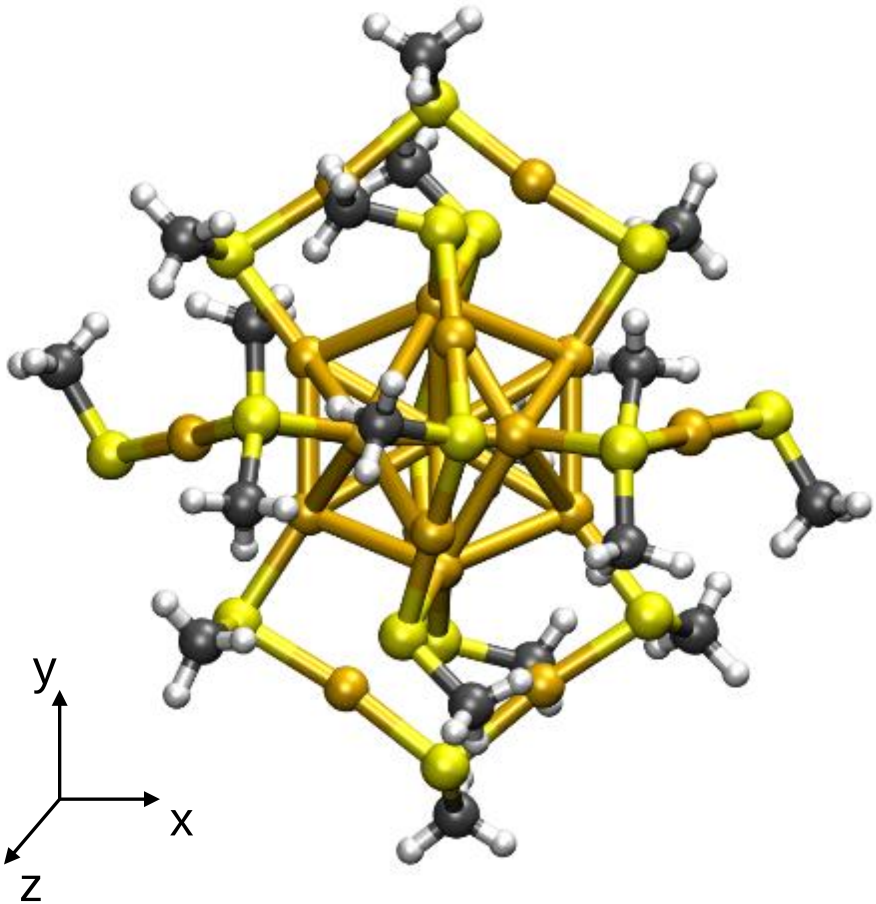


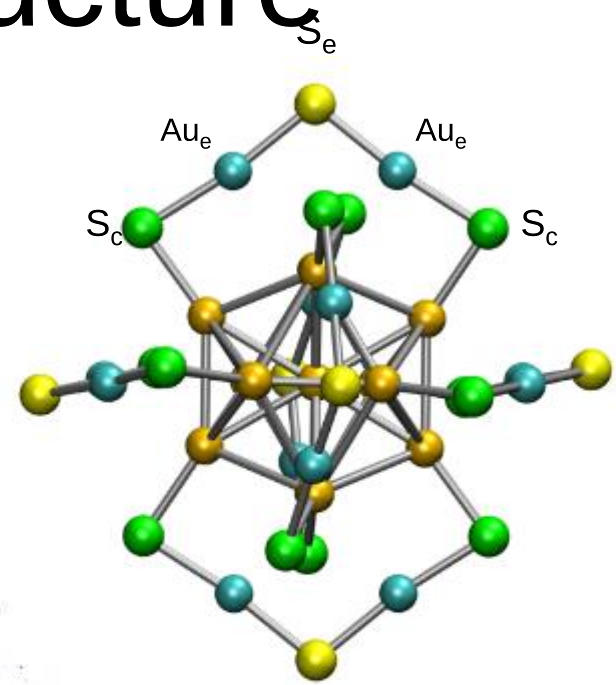


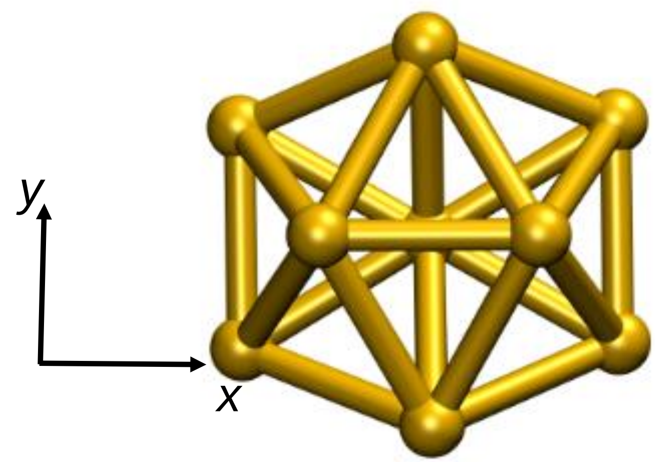
j
(0, 25)
Au25(PET)18
i
(9, 16)
(8, 17)
(7, 18)
(6, 19)
(5, 20)
(4, 21)
0.3:1.0
h
(10, 15)
(9, 16)
(8, 17)
(7, 18)
(6, 19)
0.5:1.0
g
(12, 13)
(11, 14)
(10, 15)
(9, 16)
0.6:1.0
f
(14, 11)
(13, 12)
(12, 13)
(11, 14)
(10, 15)
1.0:1.0
e
(15, 10)
(14, 11)
(13, 12)
(12, 13)
1.3:1.0
d
(19, 6)
(18, 7)
(17, 8)
(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



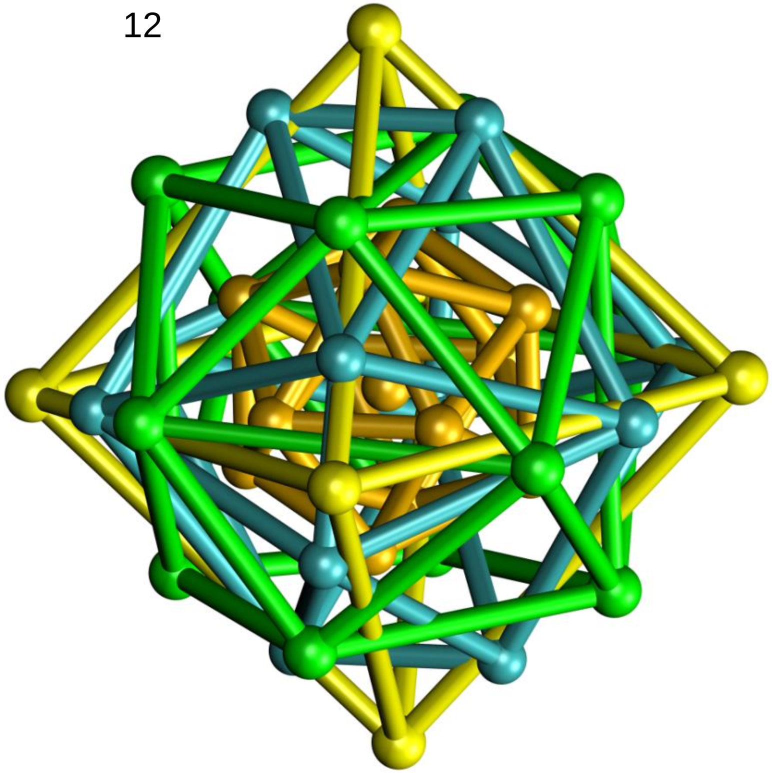




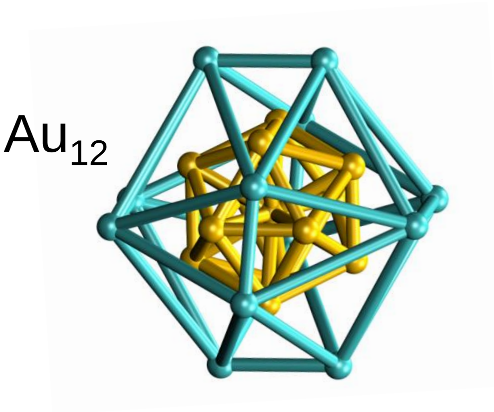
A view of gold methly thiolate [25]aspicule ($Au_{25}(SMe)_{18}$). Gold atoms colored gold, sulfur atoms by yellow, carbon dark gray, hydrogen atoms as white and (b) with the gold and sulfur atoms alone .

Shell Structure

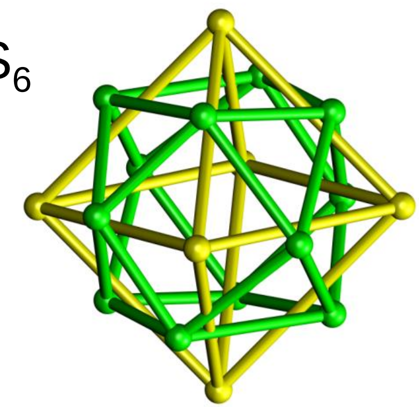
(a) $Au@Au_{12}@Au_{12}@S_6@S_{12}$



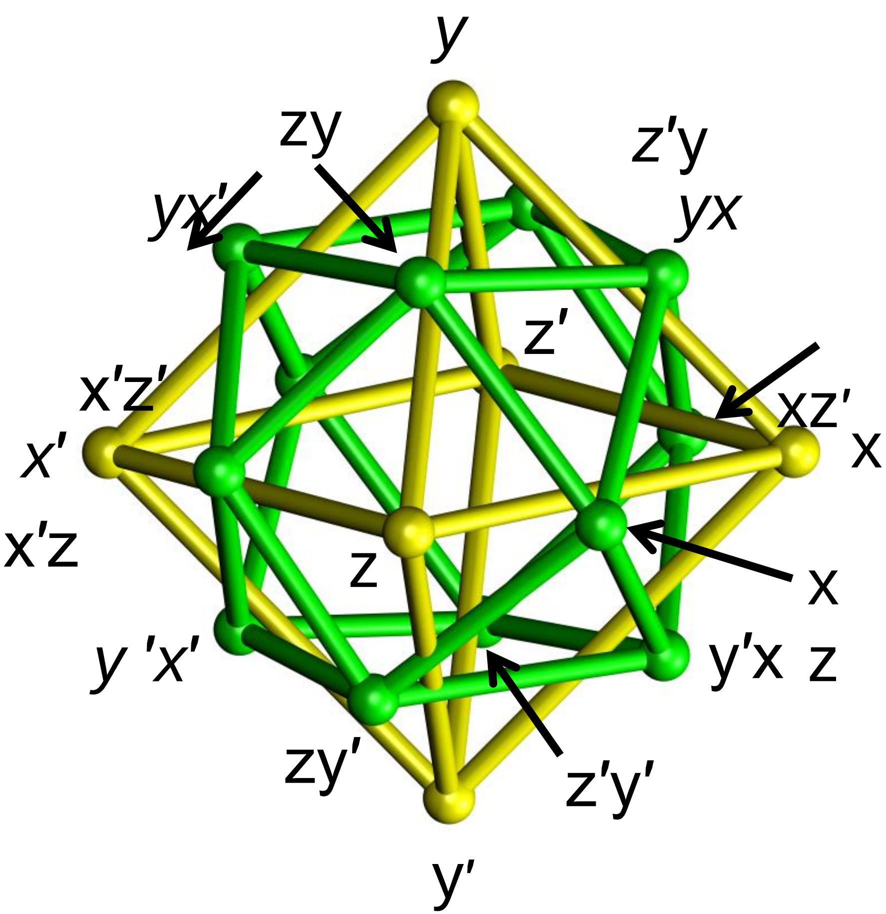
(b) $Au_{12}@Au_{12}$



(c) $S_{12}@S_6$

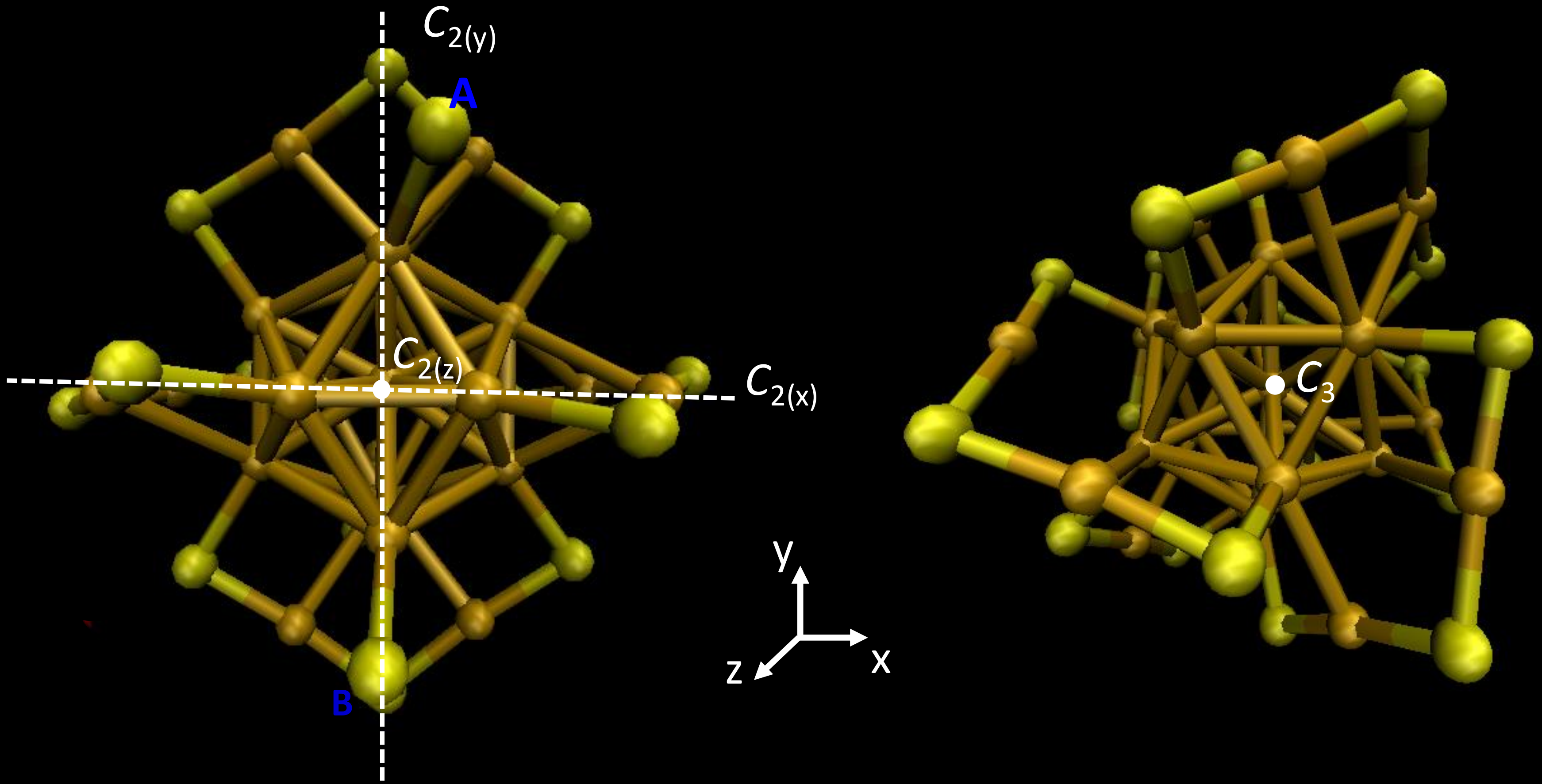


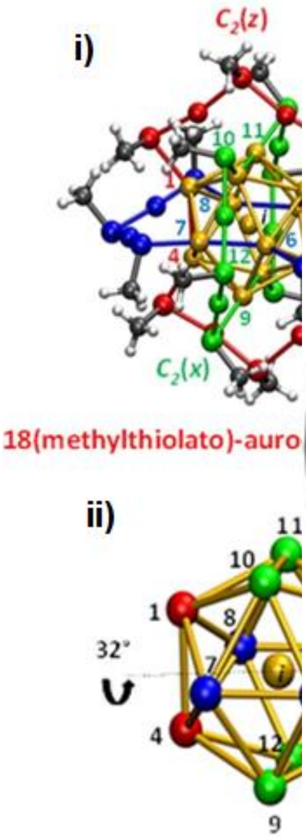
Terminologies

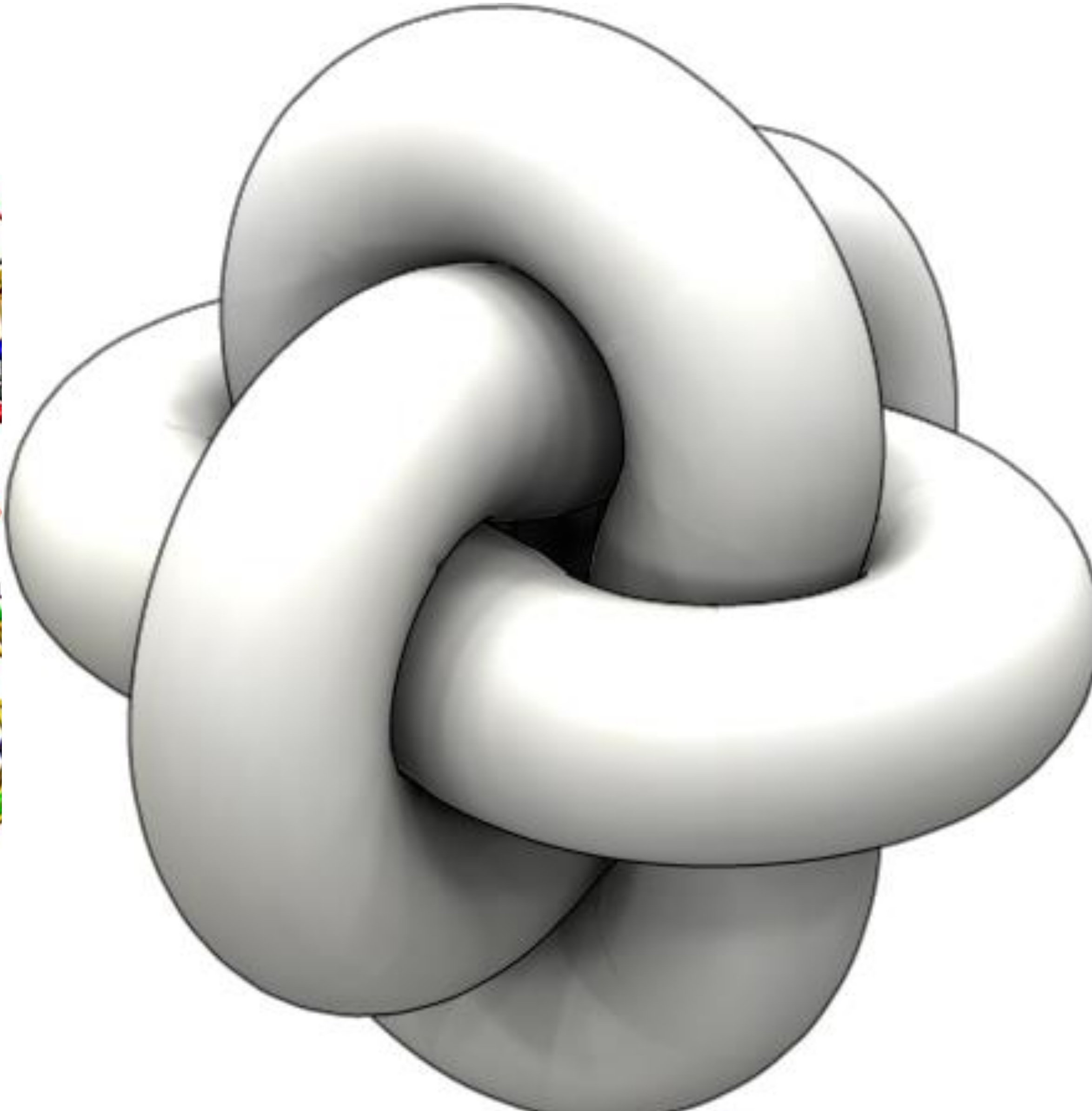


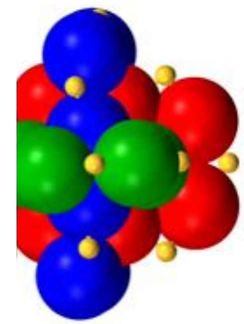
1) Edge projection

2) Face Projection









PC C. 2015

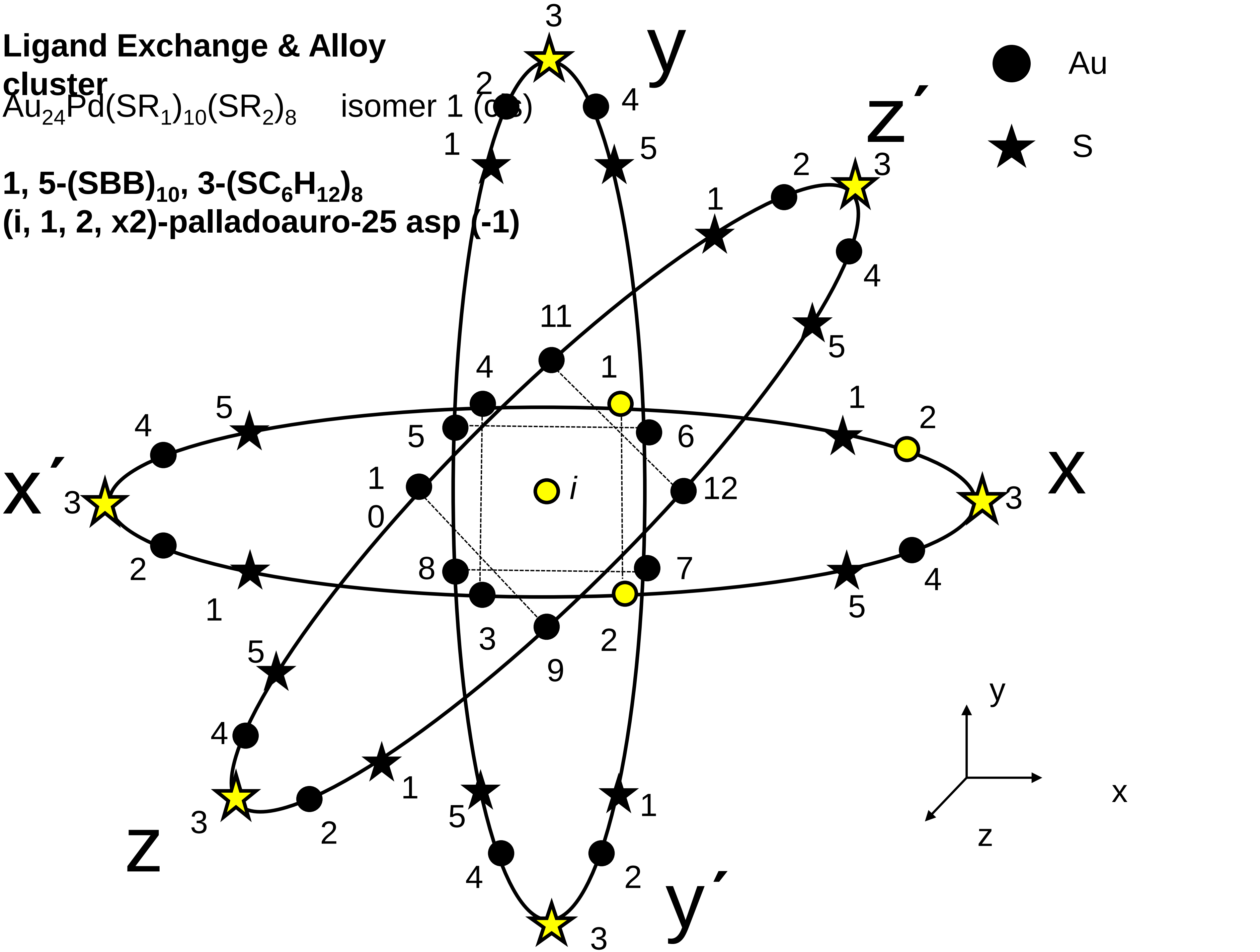
Aspicules

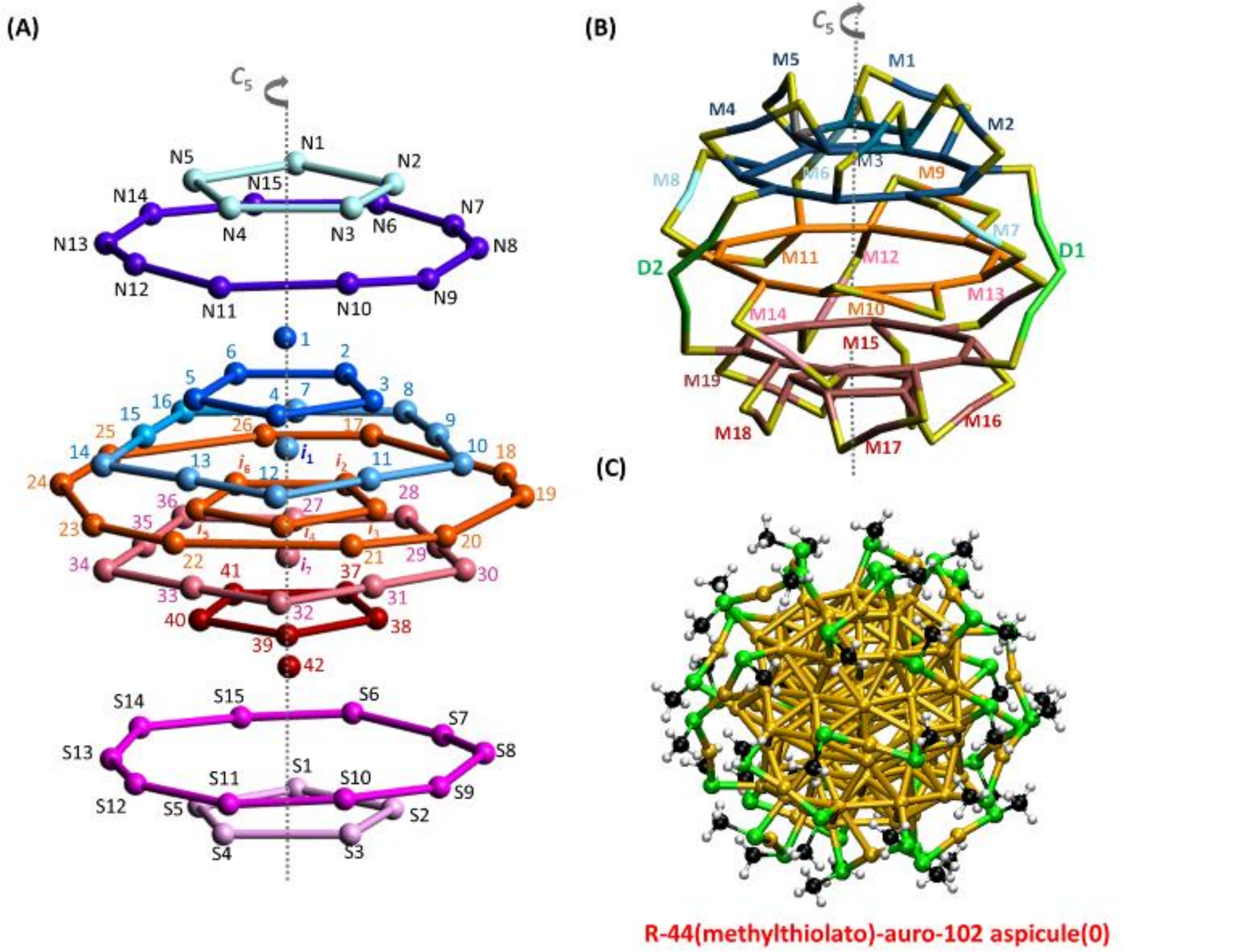
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule(1-)

Ligand Exchange & Alloy cluster

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

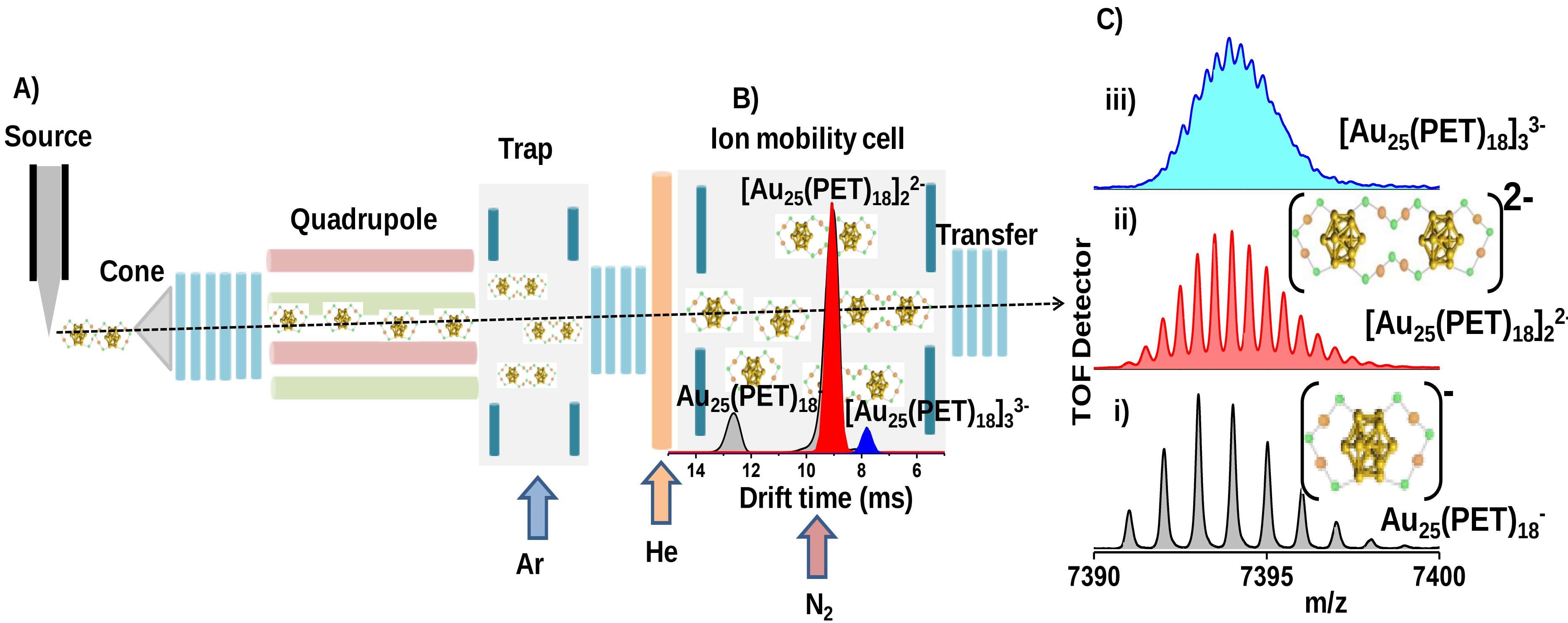
1, 5-$(SBB)_{10}$, 3-$(SC_6H_{12})_8$
(i, 1, 2, x2)-palladoauro-25 asp (-1)





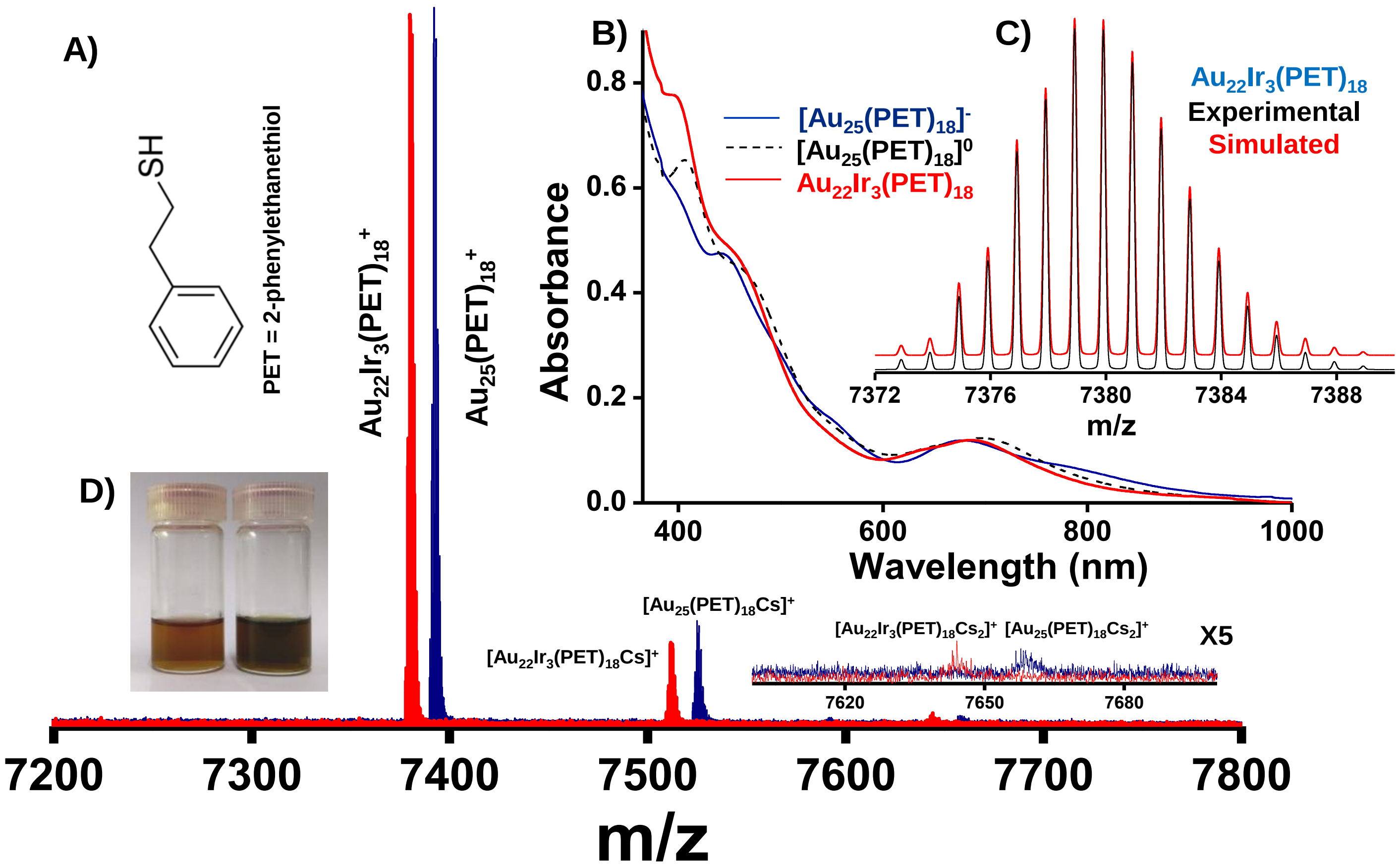
R-$(SMe)_{44}$-auro-102 aspicule**(**0**)** and L-$(SMe)_{44}$-auro-102 aspicule**(**0**)**

Cluster dimers



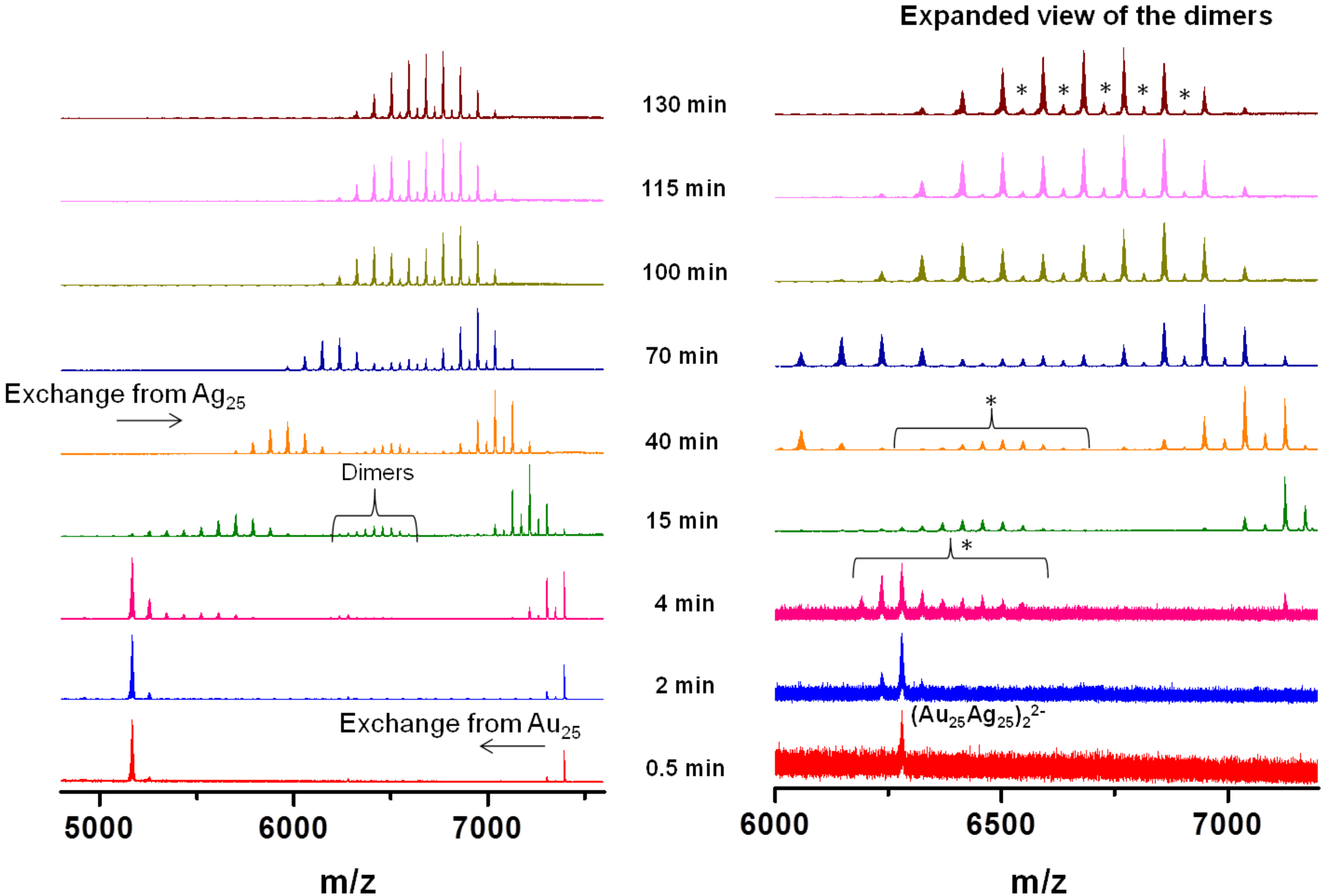
Ananya Baksi et al. Chem. Commun. 2016

Precision alloys

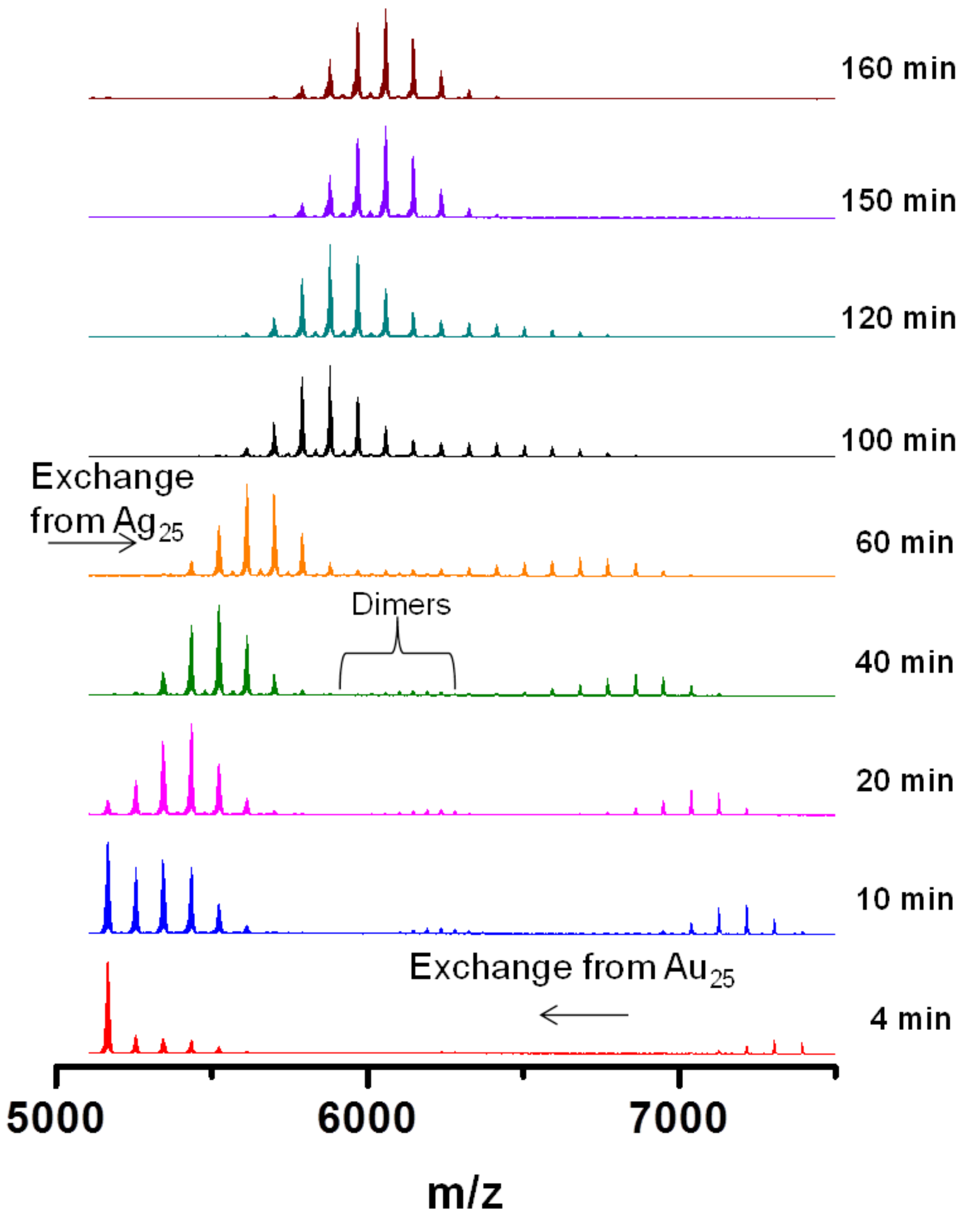


Shridevi Bhat et. al. J. Phys. Chem. Lett. (2017)

ESI MS of the reaction mixture

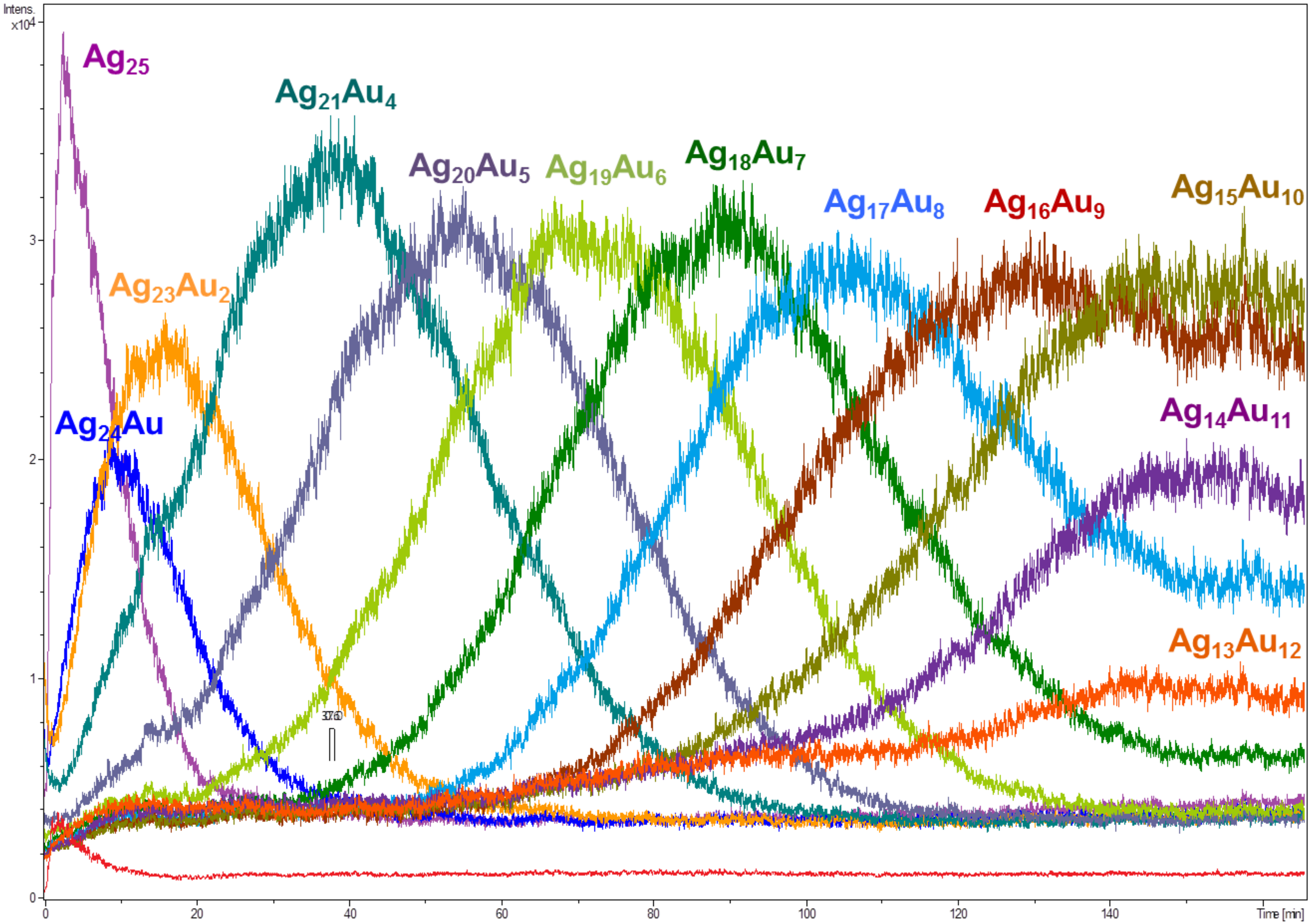


* peaks for the dimers (at higher time, the monomeric peaks due to Au-Ag exchange also arise). Au_{25} was kept in excess.



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

Article

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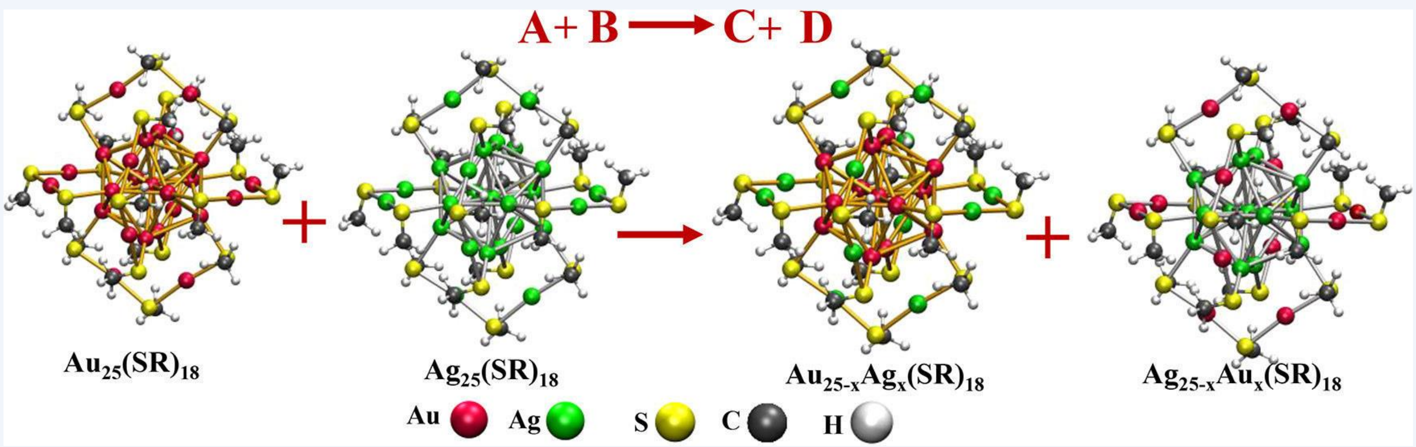
Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

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.

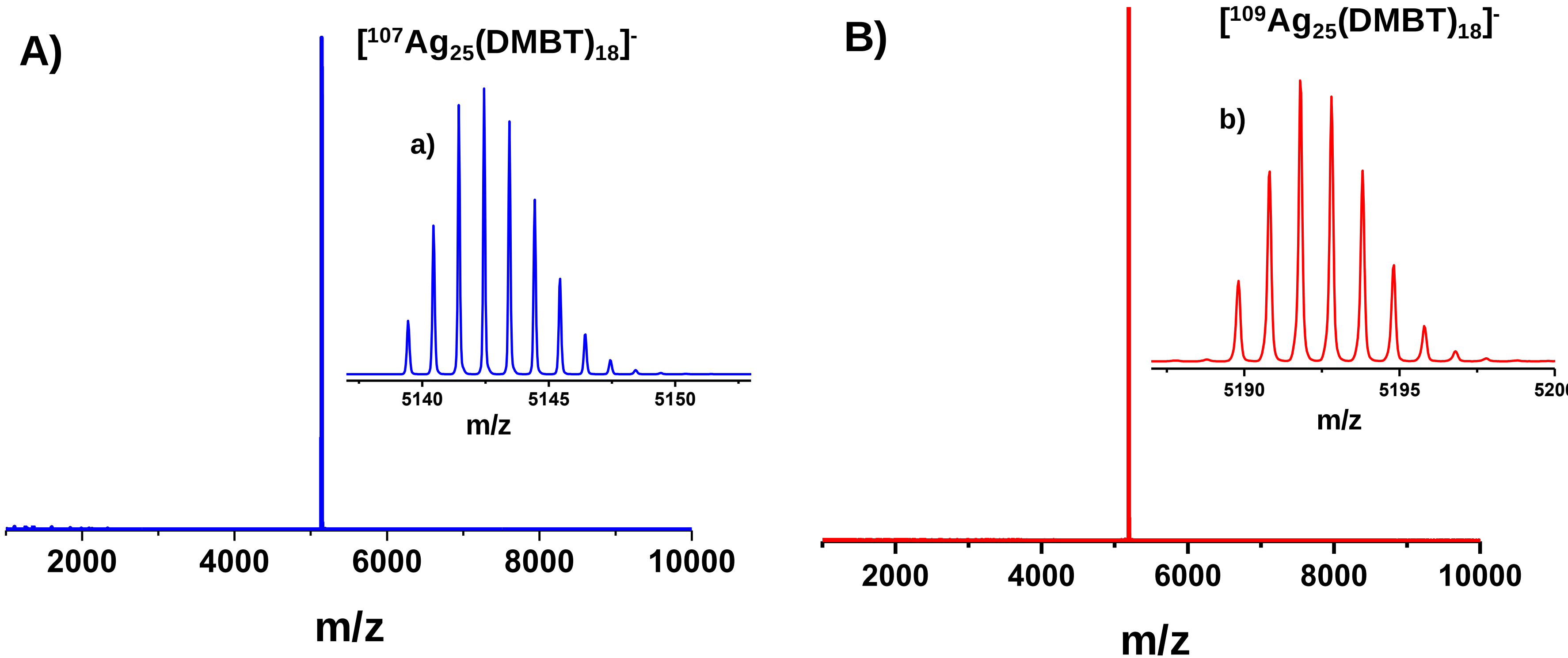
SCIENCE ADVANCES | RESEARCH ARTICLE

CONDENSED MATTER PHYSICS

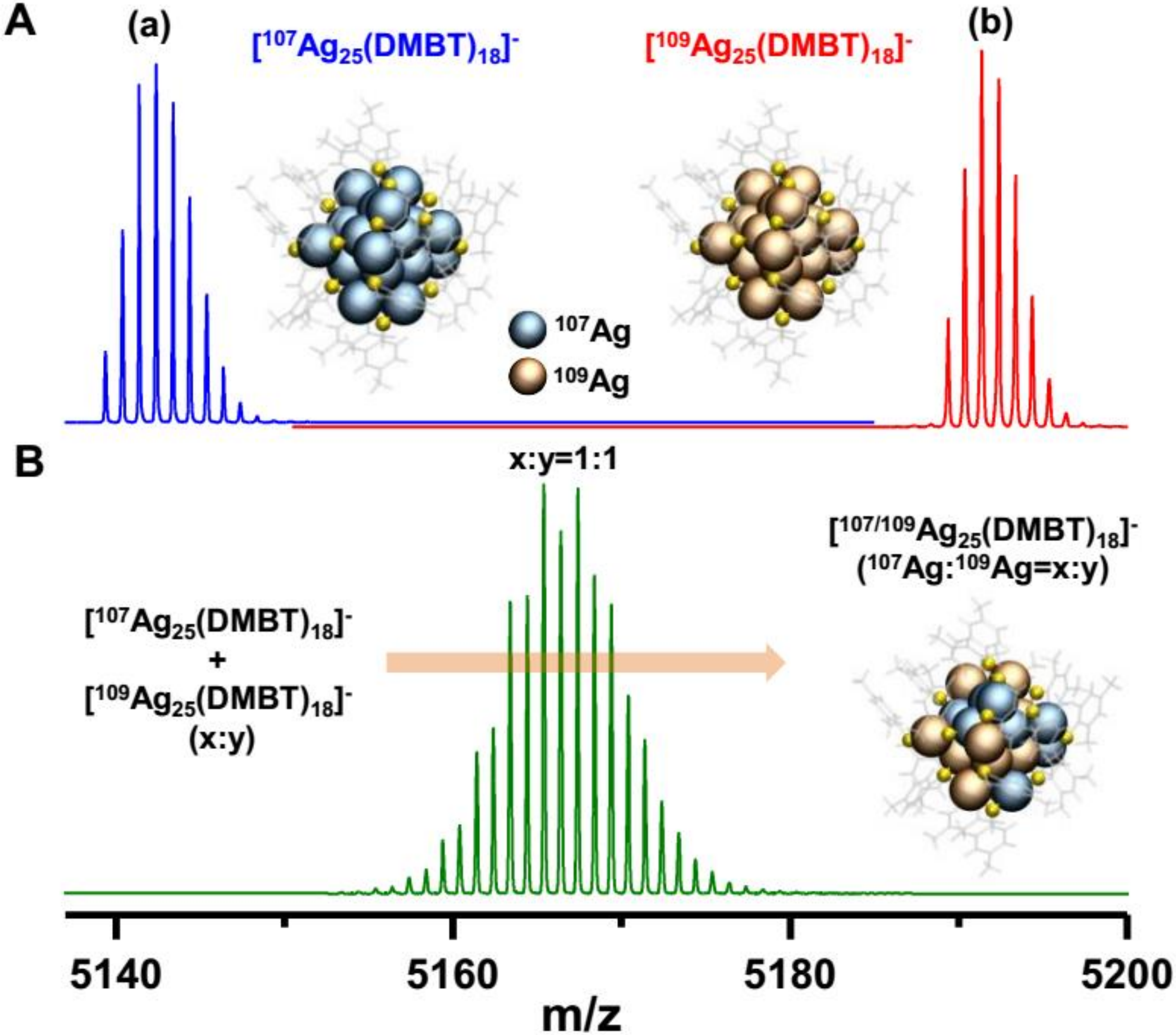
Rapid isotopic exchange in nanoparticles

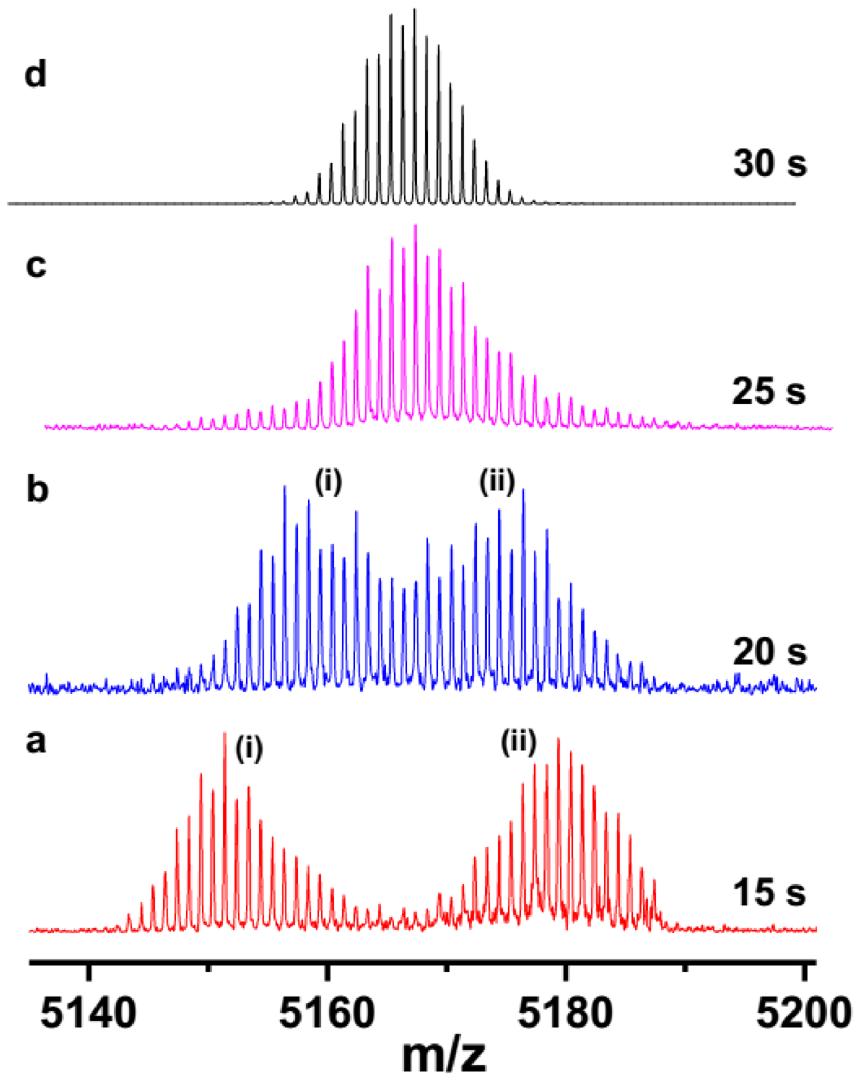
Papri Chakraborty[1], Abhijit Nag[1], Ganapati Natarajan[1], Nayanika Bandyopadhyay[1], Ganesan Paramasivam[1], Manoj Kumar Panwar[1], Jaydeb Chakrabarti[2], Thalappil Pradeep[1]*

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.

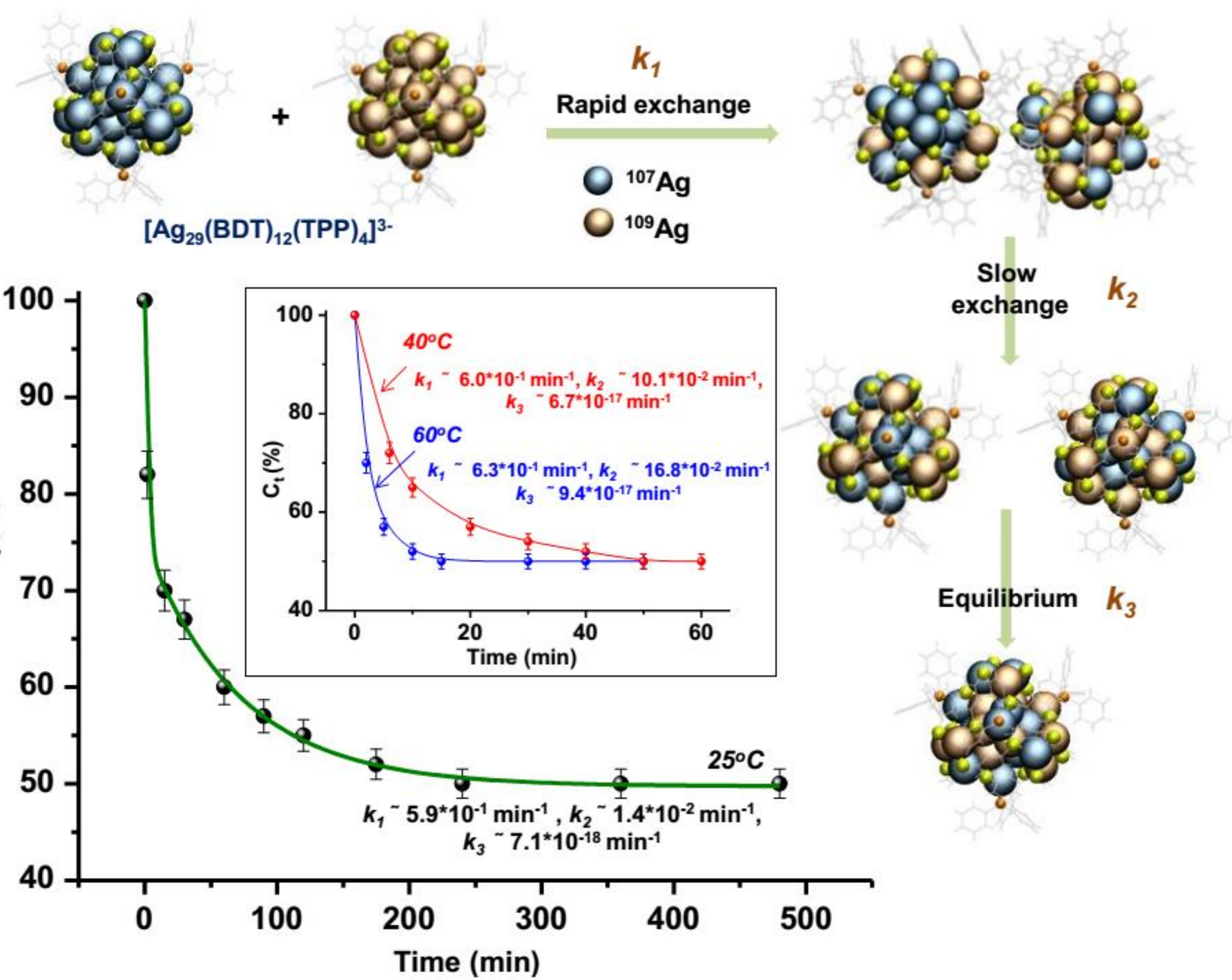


ESI MS of **A)** $^{107}Ag_{25}(DMBT)_{18}$ and **B)**$^{109}Ag_{25}(DMBT)_{18}$. Insets shows the respective isotope patterns.


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

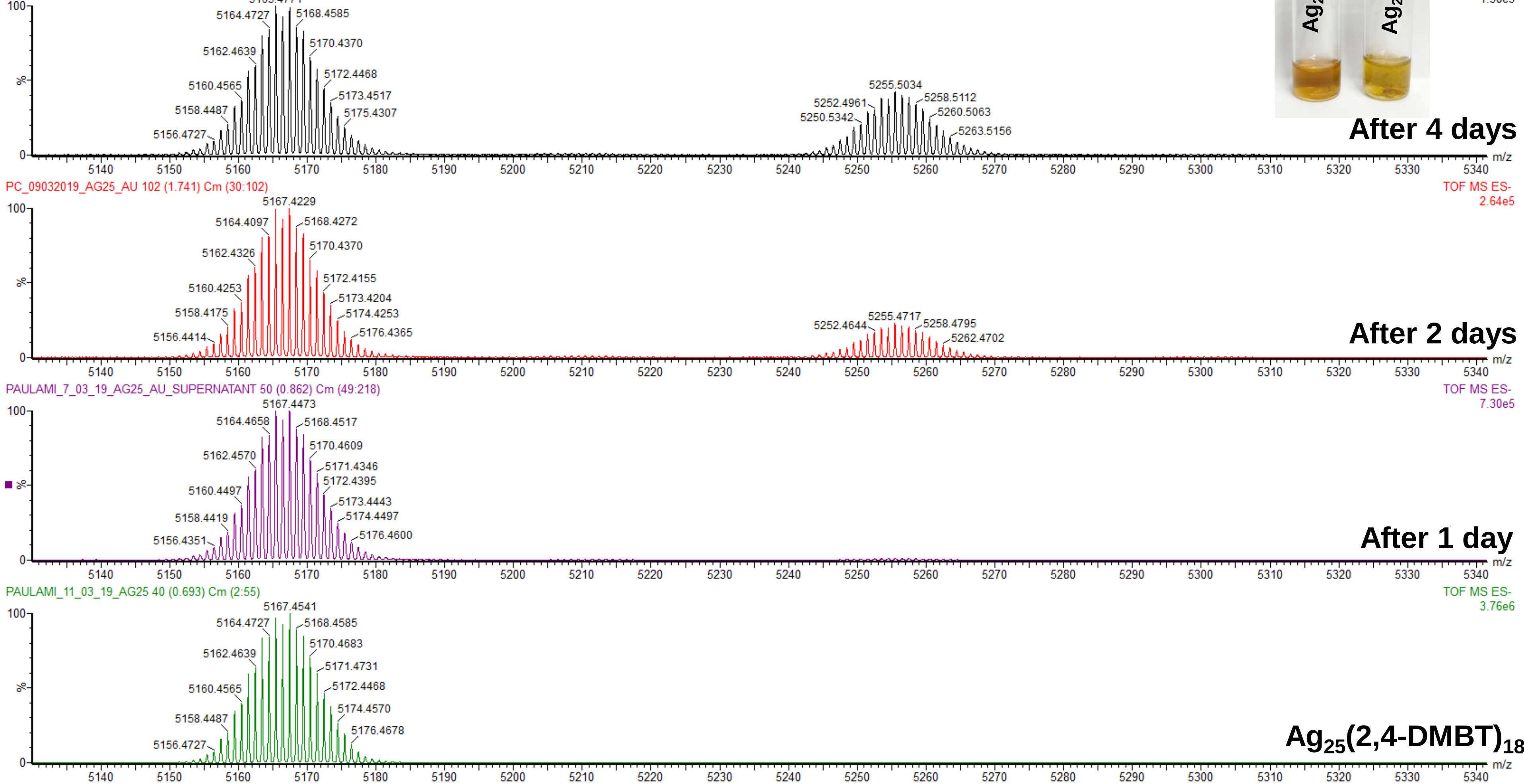


Papri Chakraborty, et. al. Science Advances 2018



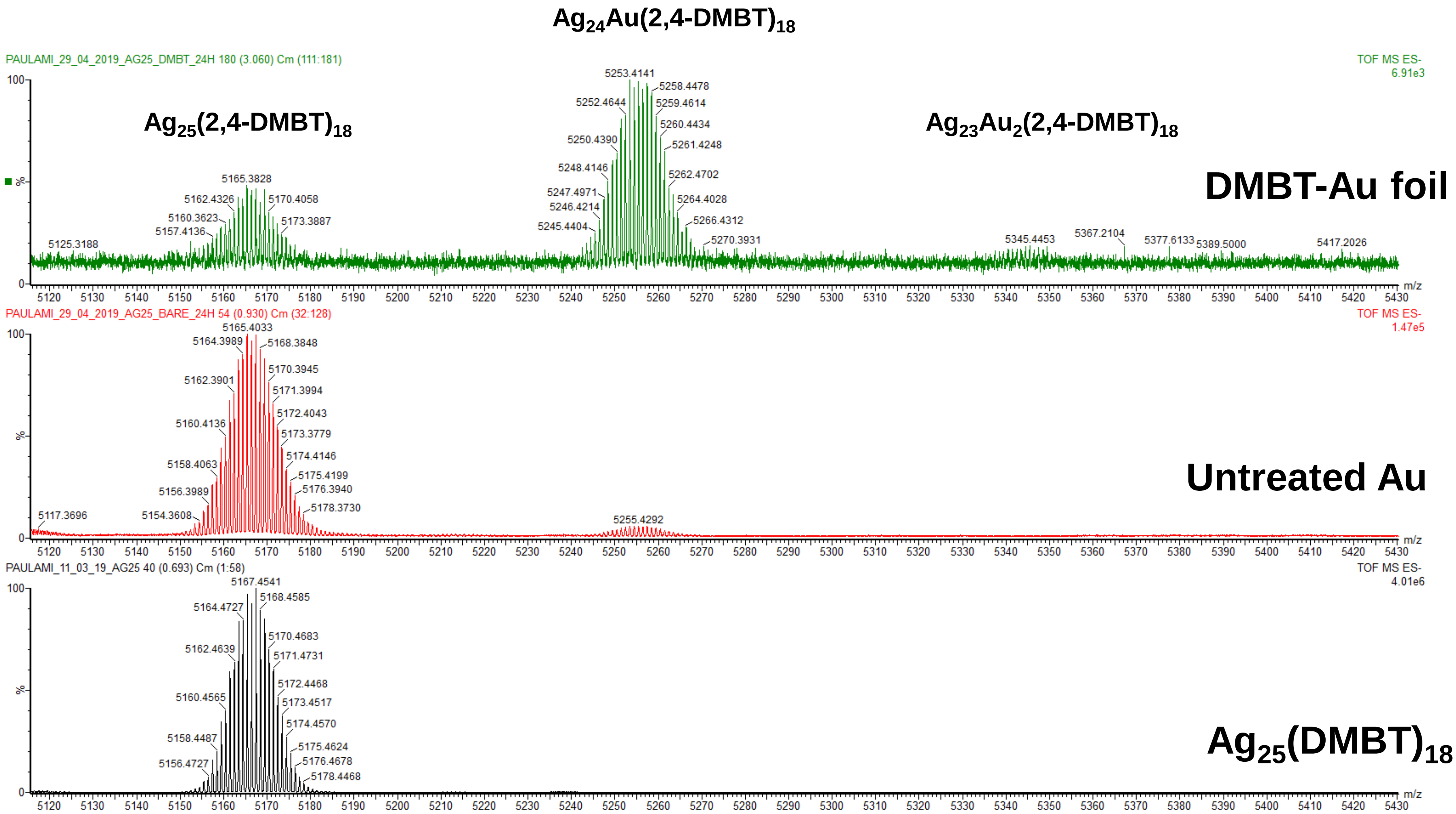
k_1
Rapid exchange
^{107}Ag
^{109}Ag
$[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$
Slow exchange
k_2
Equilibrium
k_3
40°C
k_1 ~ 6.0*10^-1 min^-1, k_2 ~ 10.1*10^-2 min^-1, k_3 ~ 6.7*10^-17 min^-1
60°C
k_1 ~ 6.3*10^-1 min^-1, k_2 ~ 16.8*10^-2 min^-1, k_3 ~ 9.4*10^-17 min^-1
C_t (%)
Time (min)
25°C
k_1 ~ 5.9*10^-1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

Ag25 reacts with Untreated-Pure Au foil (24



$Ag_{25}(2,4\text{-}DMBT)_{18}$ $Ag_{24}Au(2,4\text{-}DMBT)_{18}$

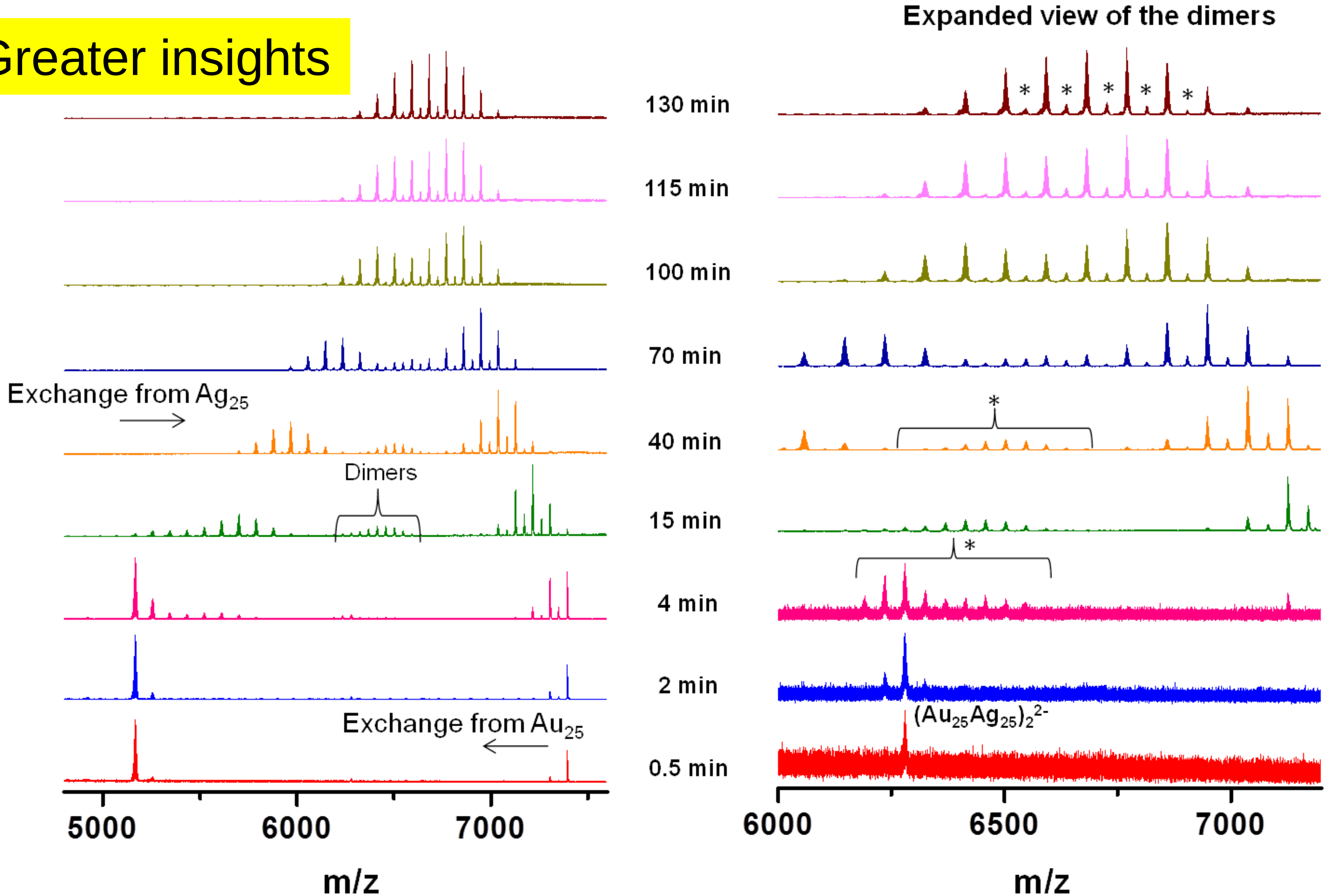
Ag25 reacts with 22 Carat Au foil after 24 hours (200 rpm)



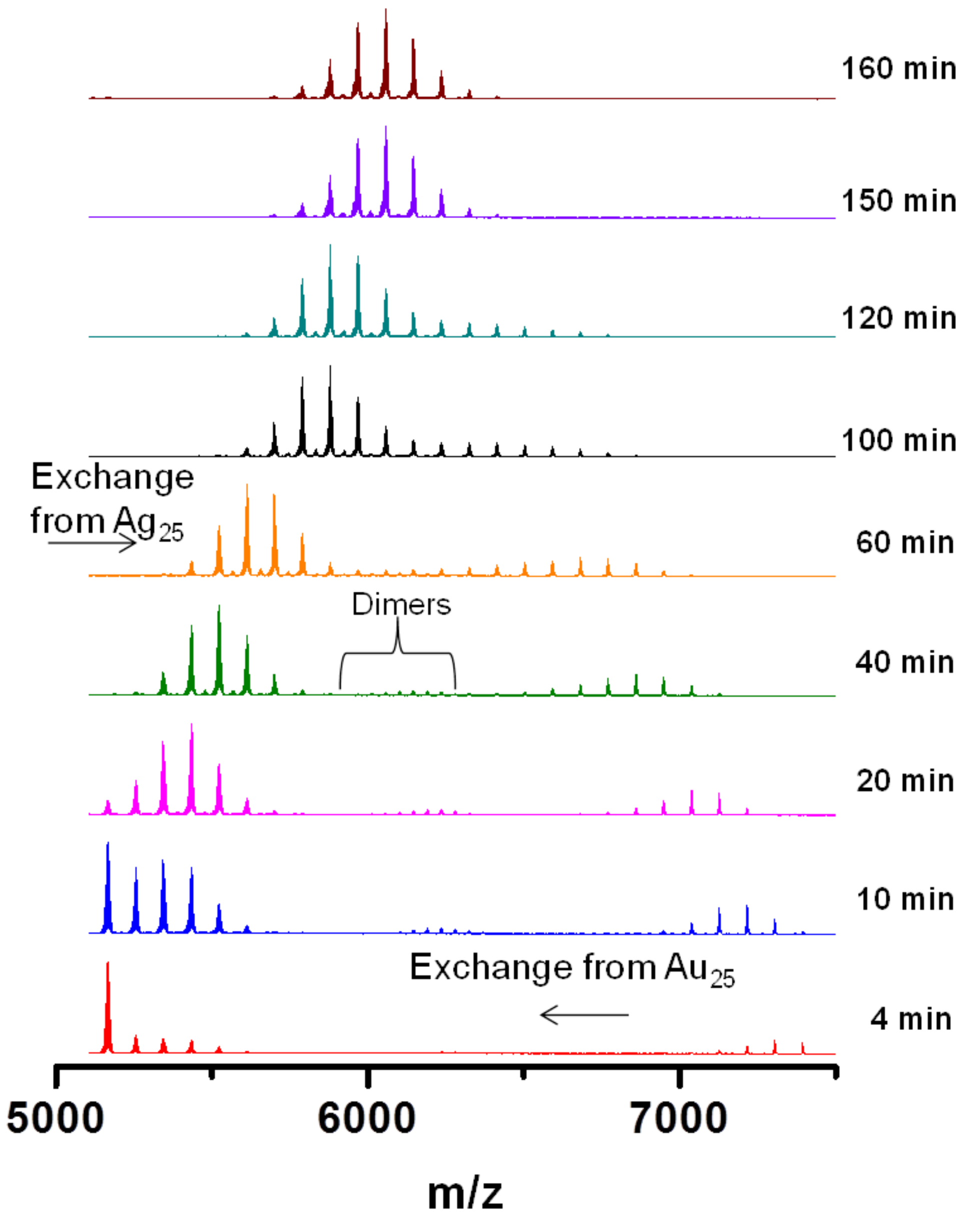
Unpublished

ESI MS of the reaction mixture

Greater insights

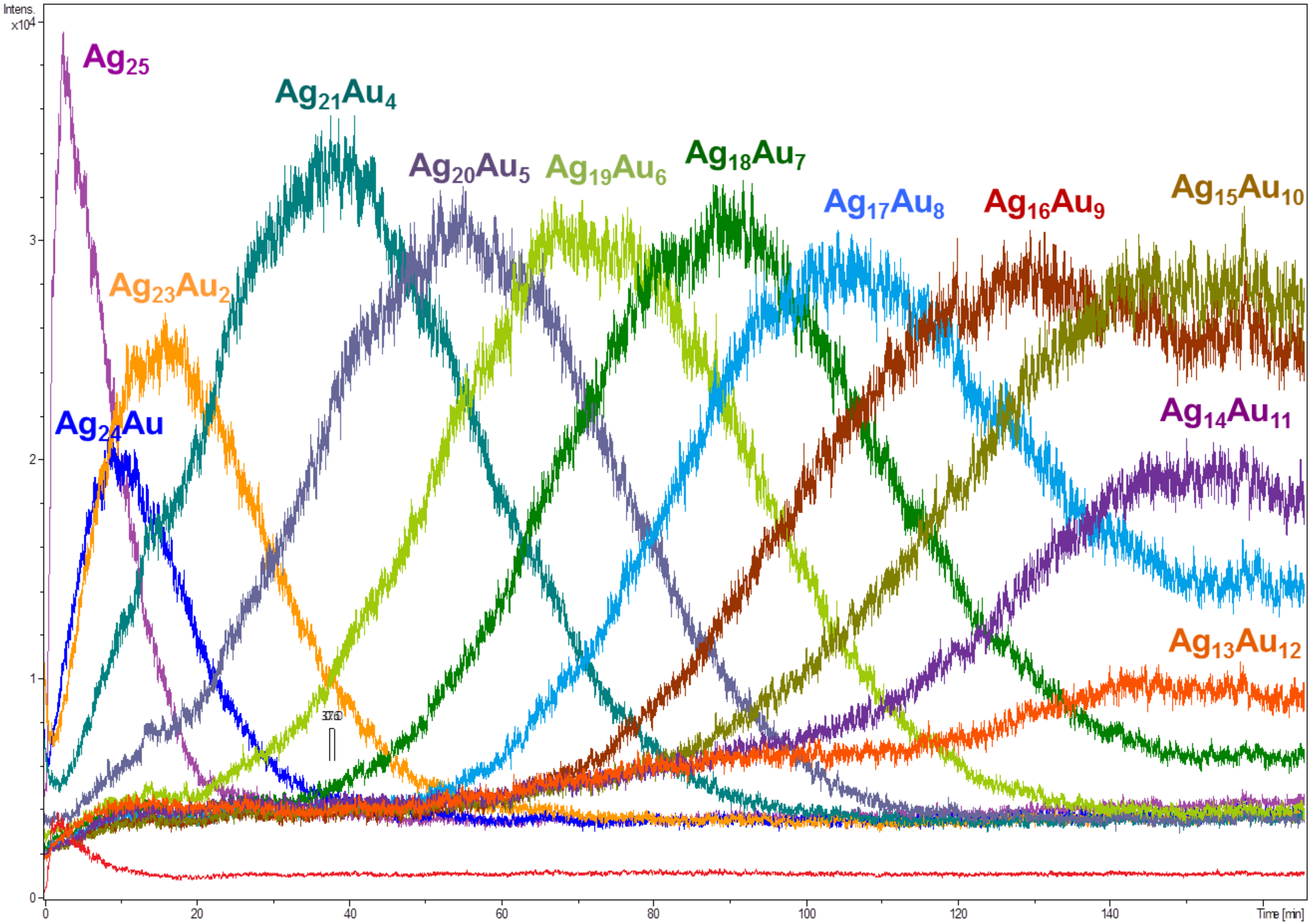


* peaks for the dimers (at higher time, the monomeric peaks due to Au-Ag exchange also arise). Au_{25} was kept in excess.

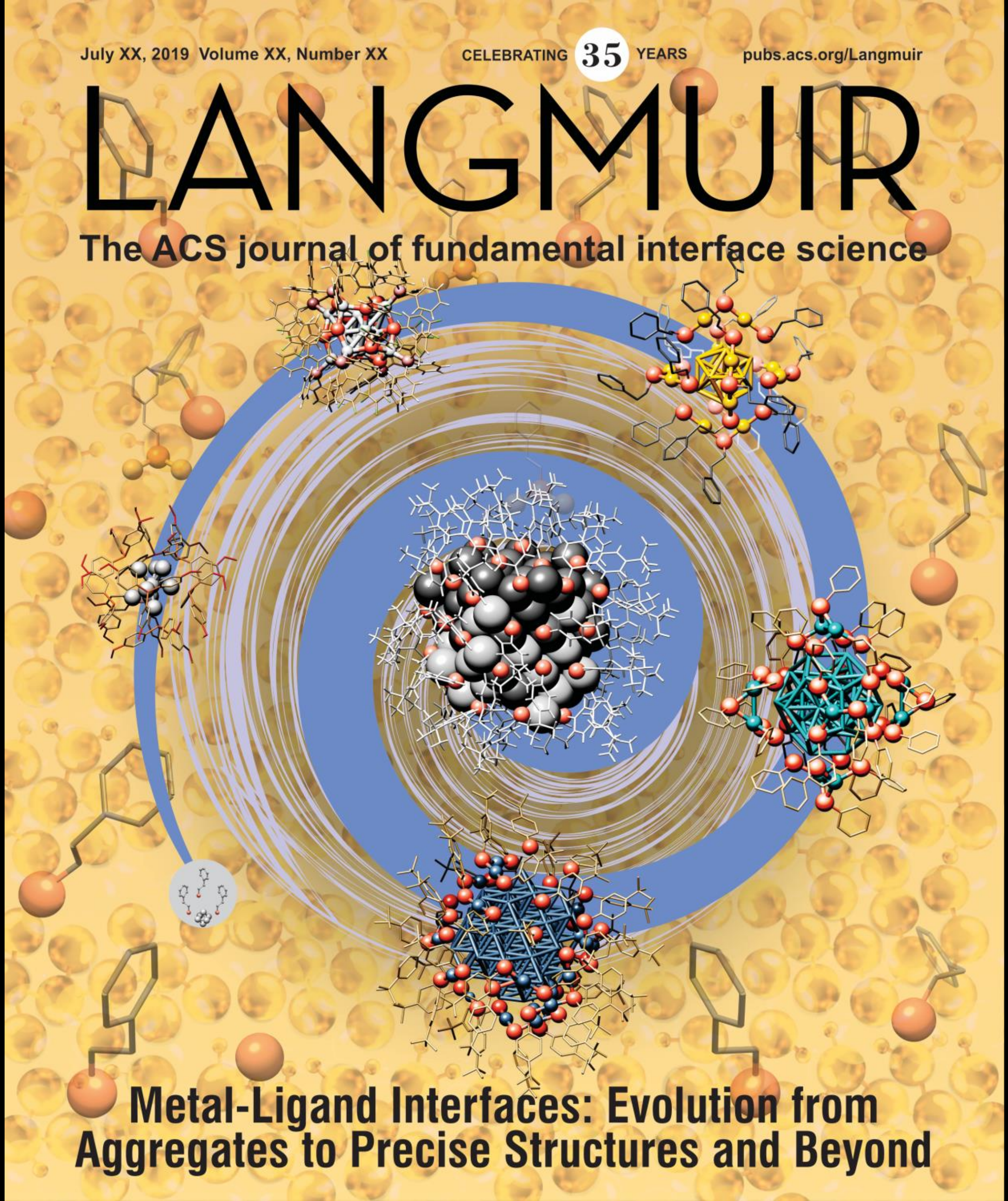


Molar ratio of two clusters= 1:1

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



With Manfred Kappes and Horst Hahn


July XX, 2019 Volume XX, Number XX
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The ACS journal of fundamental interface science
Metal-Ligand Interfaces: Evolution from Aggregates to Precise Structures and Beyond

To appear

Supramolecular chemistry

Papri Chakraborty, et,. al. ACS Nano 2018

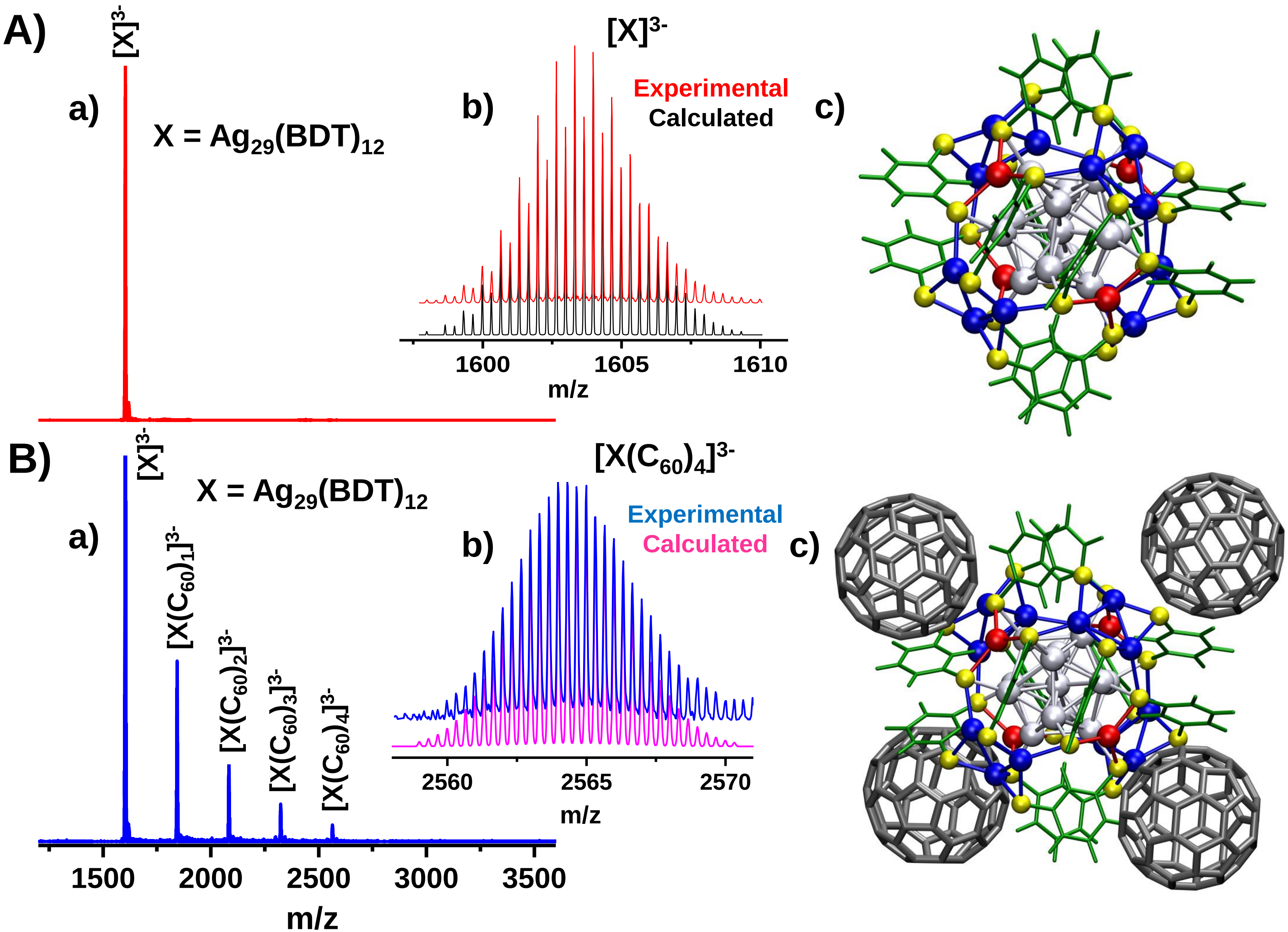


Figure 1. A) (a) Full range ESI MS, **(b)** experimental and calculated isotope patterns and **(c)** DFT optimized structure of $[Ag_{29}(BDT)_{12}]^{3-}$ cluster. **B) (a)** ESI MS of $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (n=1-4) complexes, **(b)** experimental and calculated isotope patterns of $[Ag_{29}(BDT)_{12}(C_{60})_4]^{3-}$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

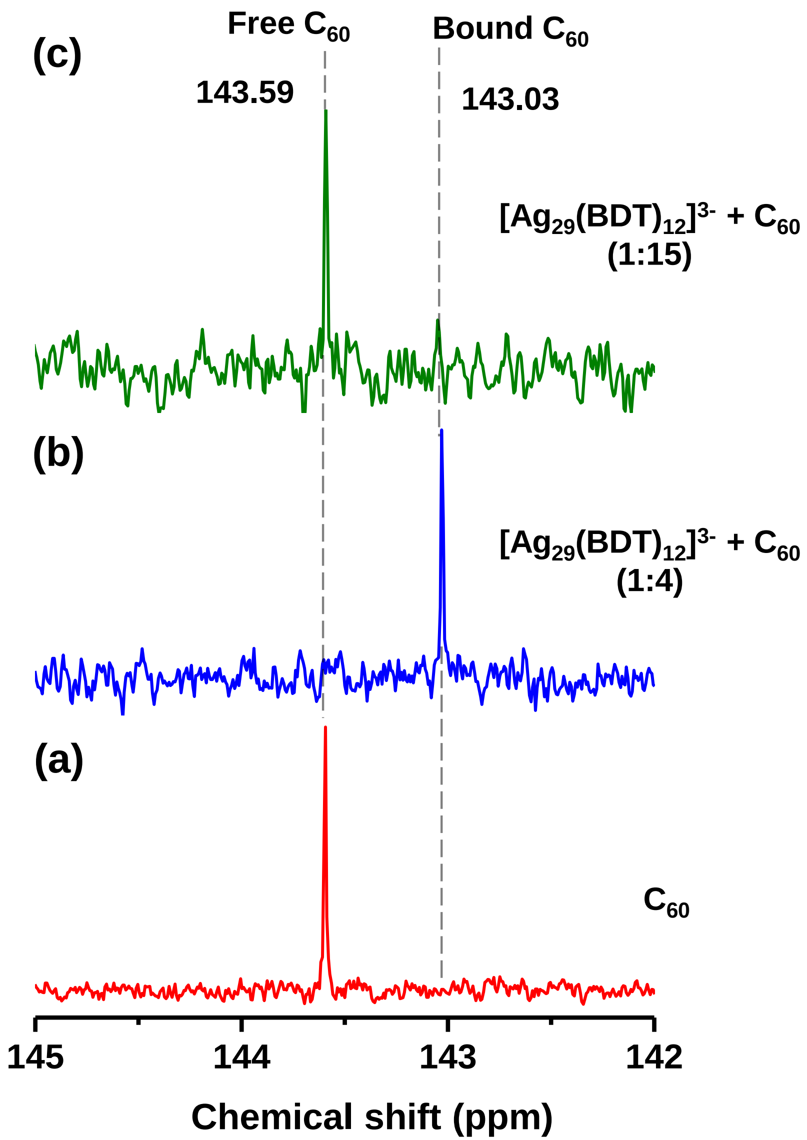
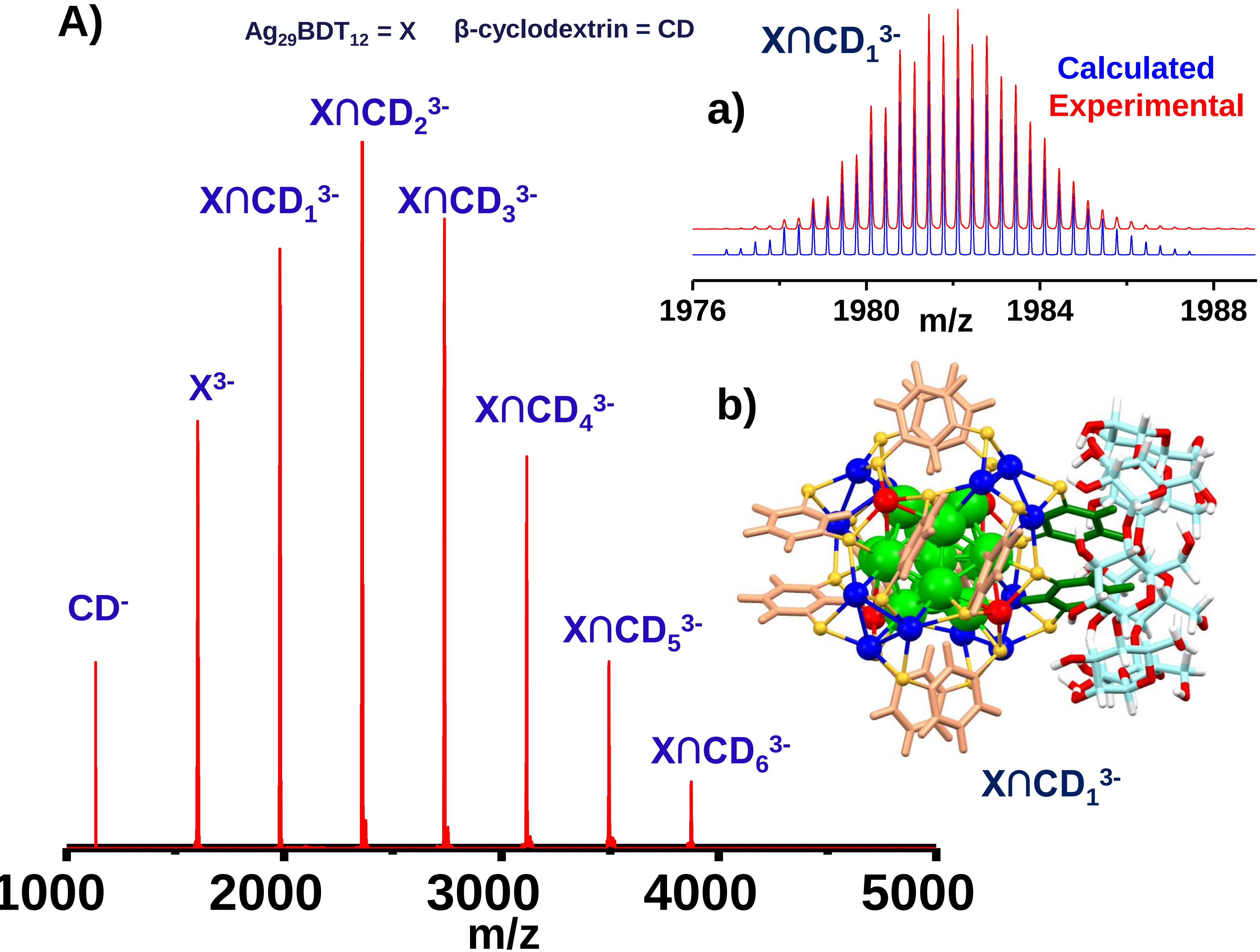


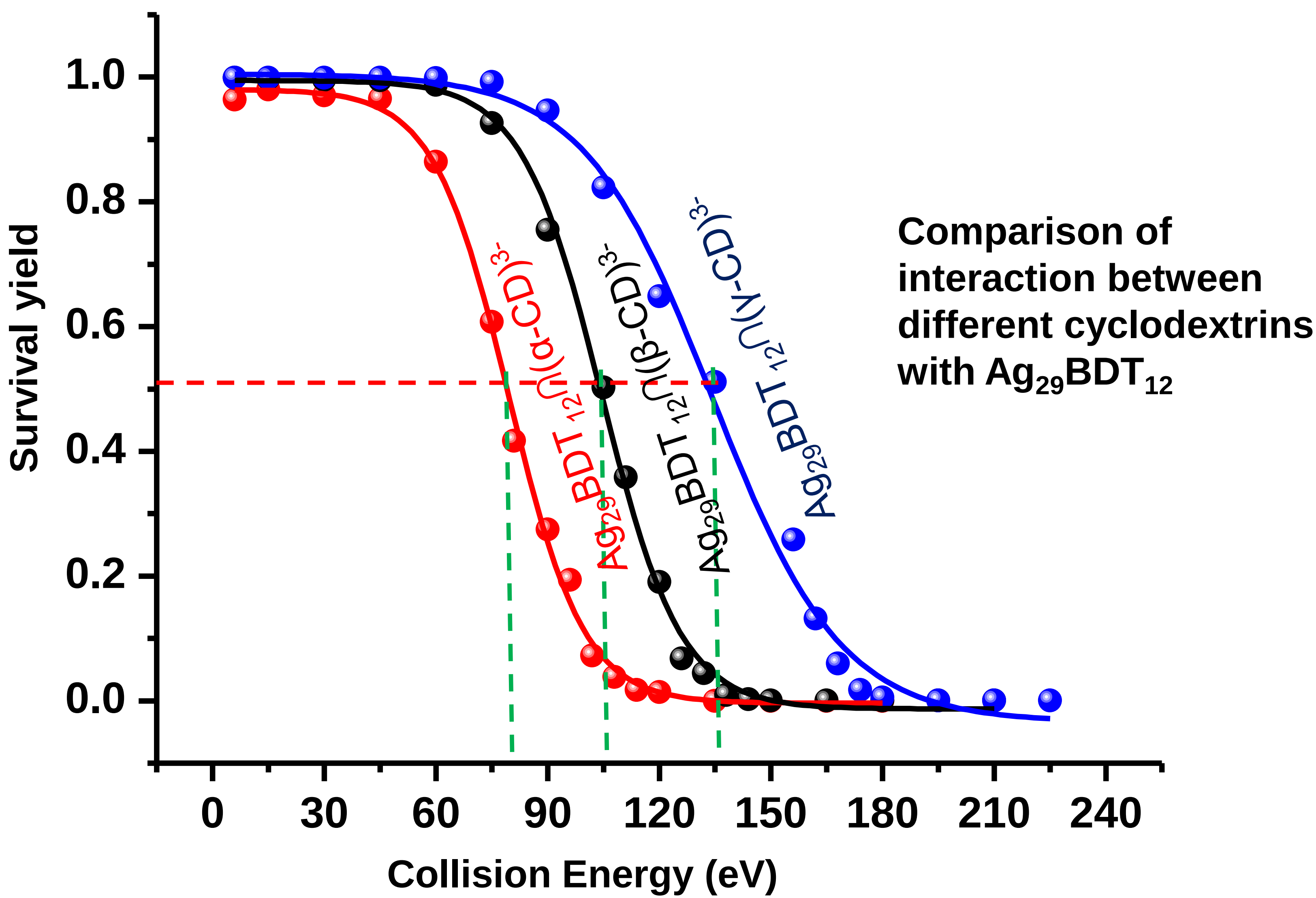
Figure 3. NMR of **(a)** C_{60} showing peak at 143.59 ppm, **(b)** the adducts at a cluster:fullerene molar ratio of 1:4 showing peak at 143.03 ppm for the C_{60} molecules in bound state and **(c)** the adducts at an excess concentration of C_{60} (cluster:fullerene molar ratio of 1:15) showing a predominant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

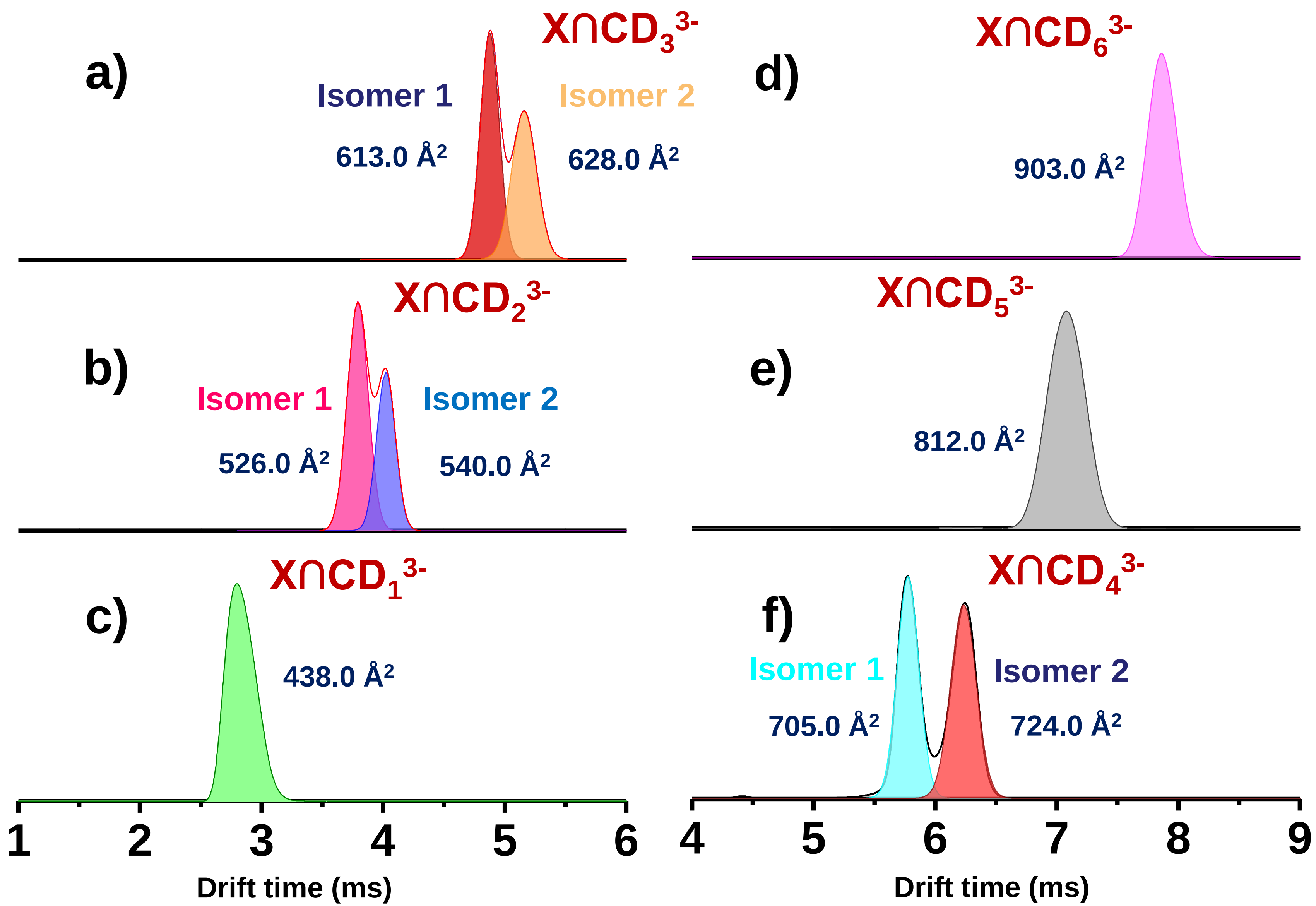
Isomerism in supramolcular adducts

Abhijit Nag, et al. JACS 2018

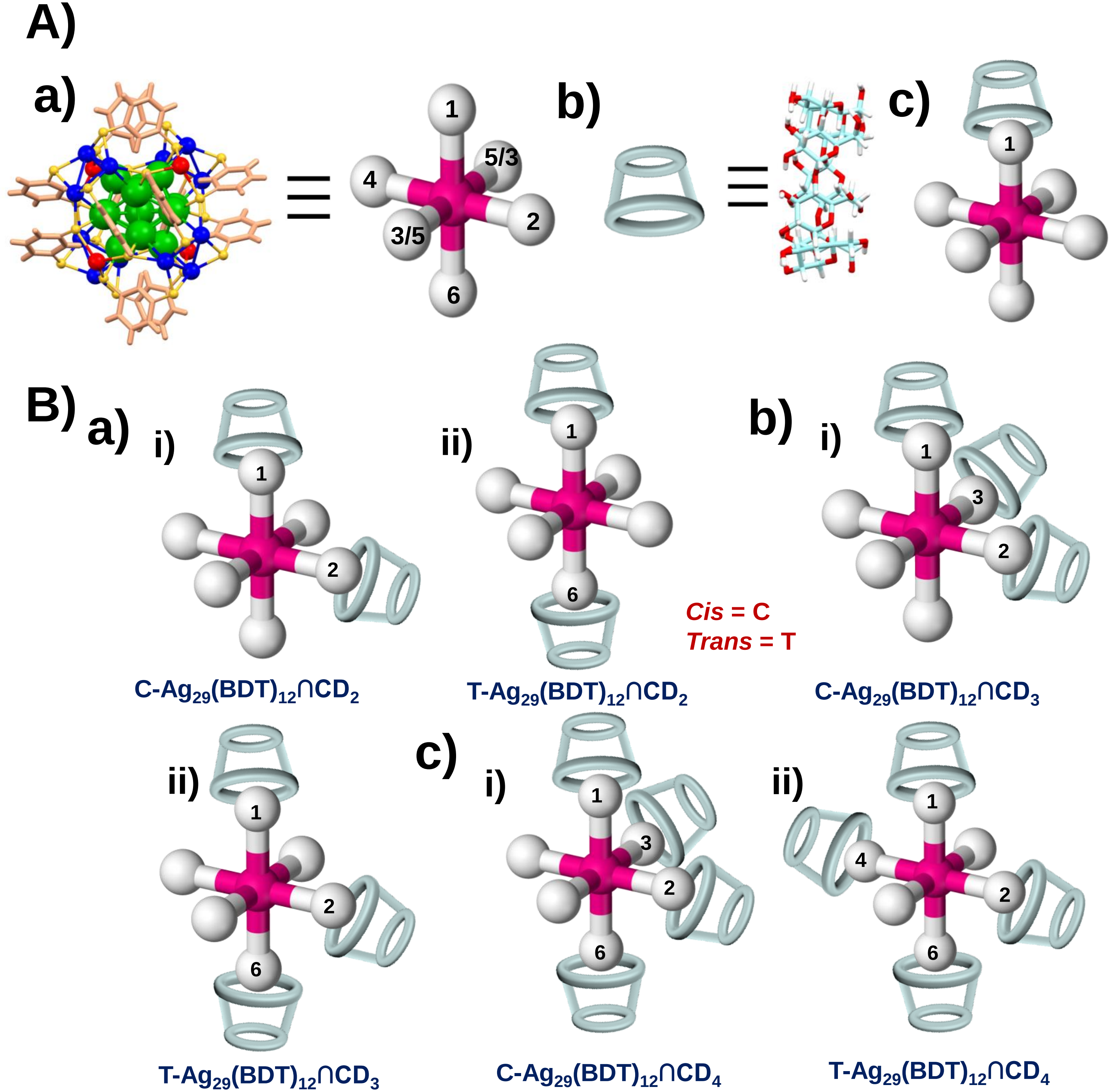

A)
Ag29BDT12 = X
β-cyclodextrin = CD
X∩CD2 3-
X∩CD1 3-
X∩CD3 3-
X3-
X∩CD4 3-
CD-
X∩CD5 3-
X∩CD6 3-
1000
2000
3000
4000
5000
m/z
X∩CD1 3-
a)
Calculated
Experimental
1976
1980
1984
1988
m/z
b)
X∩CD1 3-

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

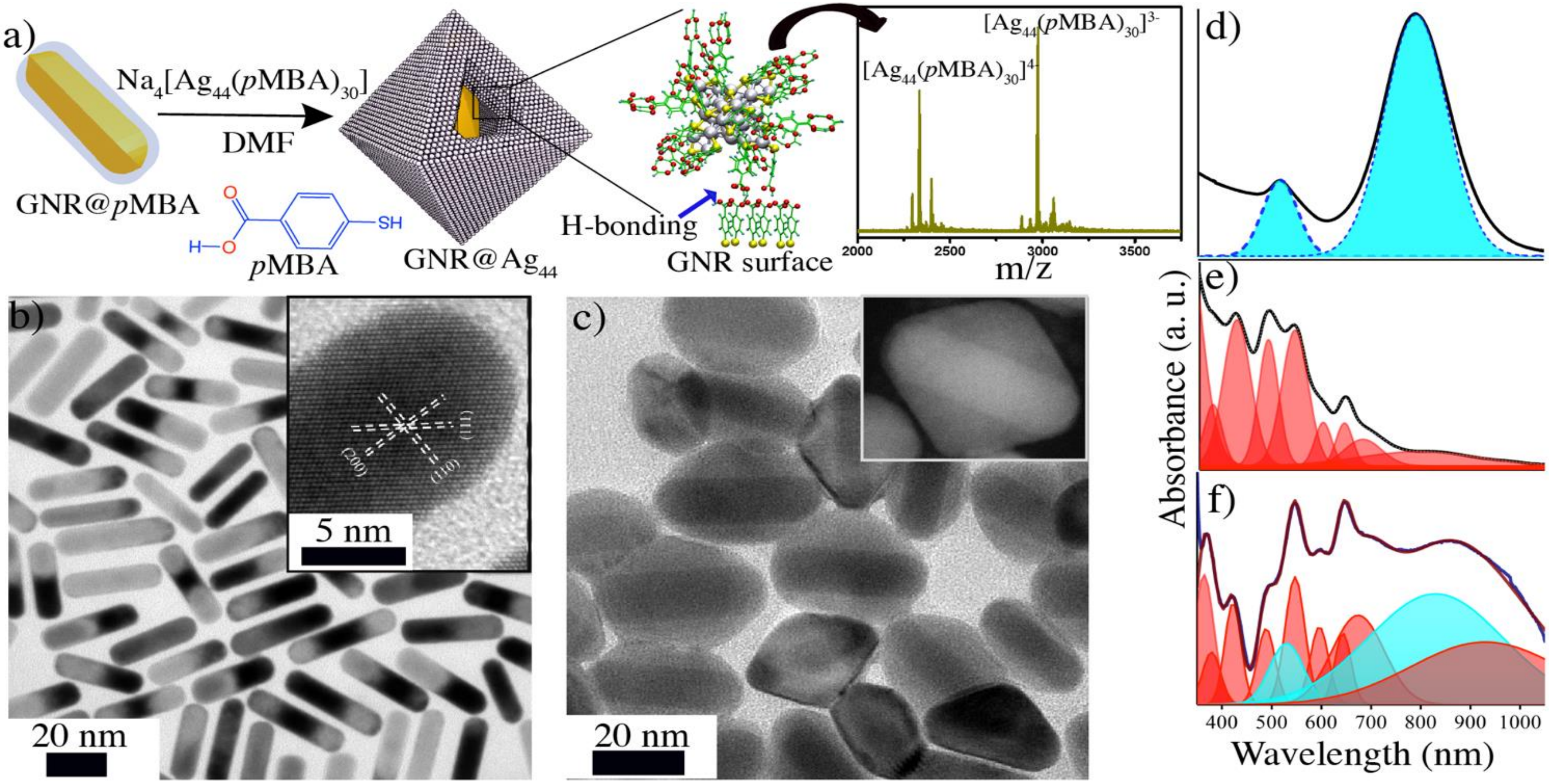




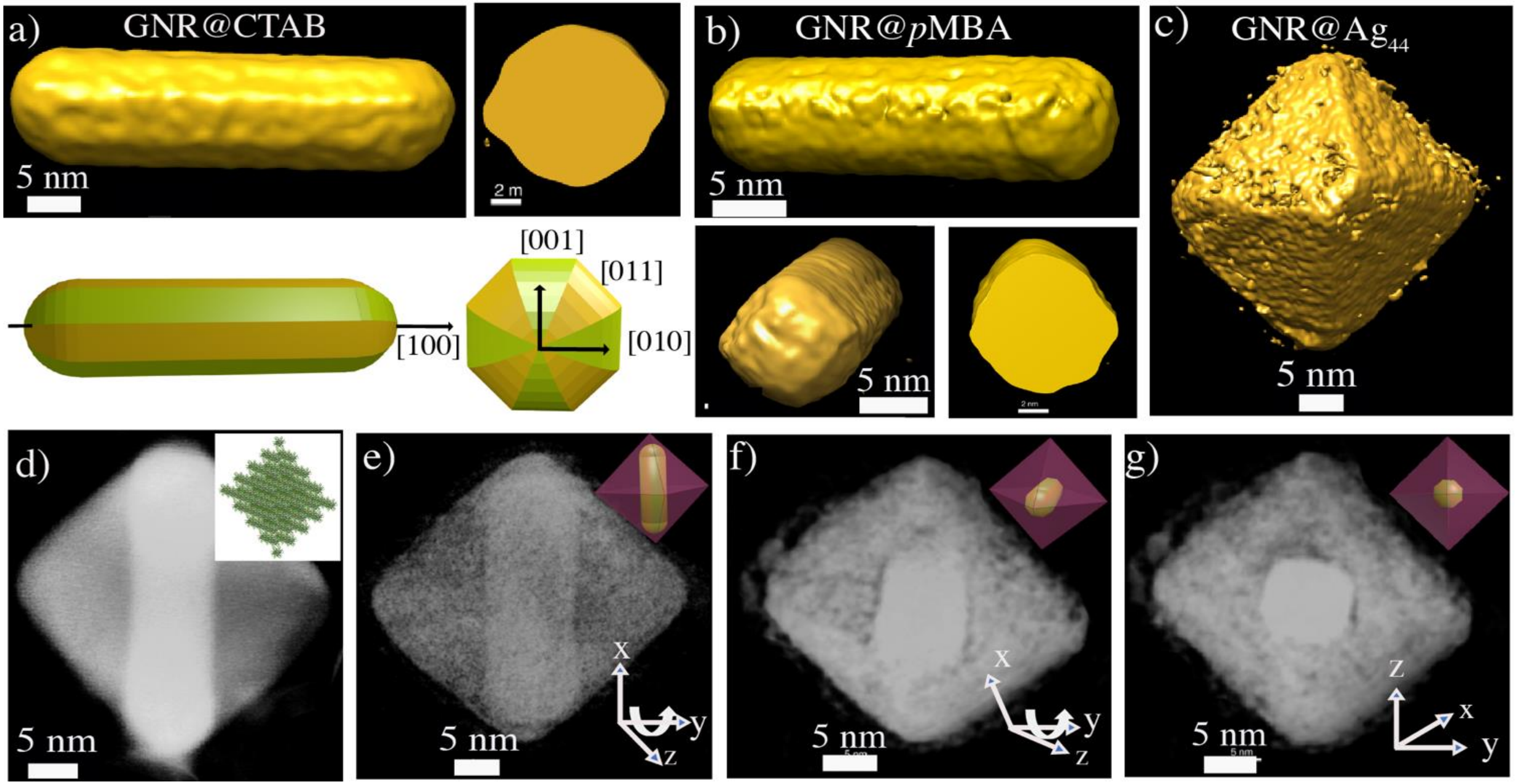
a)
X∩CD$_3^{3-}$
Isomer 1
613.0 Å²
Isomer 2
628.0 Å²
b)
X∩CD$_2^{3-}$
Isomer 1
526.0 Å²
Isomer 2
540.0 Å²
c)
X∩CD$_1^{3-}$
438.0 Å²
1
2
3
4
5
6
Drift time (ms)
d)
X∩CD$_6^{3-}$
903.0 Å²
e)
X∩CD$_5^{3-}$
812.0 Å²
f)
X∩CD$_4^{3-}$
Isomer 1
705.0 Å²
Isomer 2
724.0 Å²
4
5
6
7
8
9
Drift time (ms)


A)
a)
1
5/3
4
2
3/5
6
b)
c)
1
B)
a)
i)
1
2
ii)
1
6
b)
i)
1
3
2
Cis = C
Trans = T
C-Ag29(BDT)12∩CD2
T-Ag29(BDT)12∩CD2
C-Ag29(BDT)12∩CD3
ii)
1
2
6
c)
i)
1
3
2
6
ii)
1
4
2
6
T-Ag29(BDT)12∩CD3
C-Ag29(BDT)12∩CD4
T-Ag29(BDT)12∩CD4

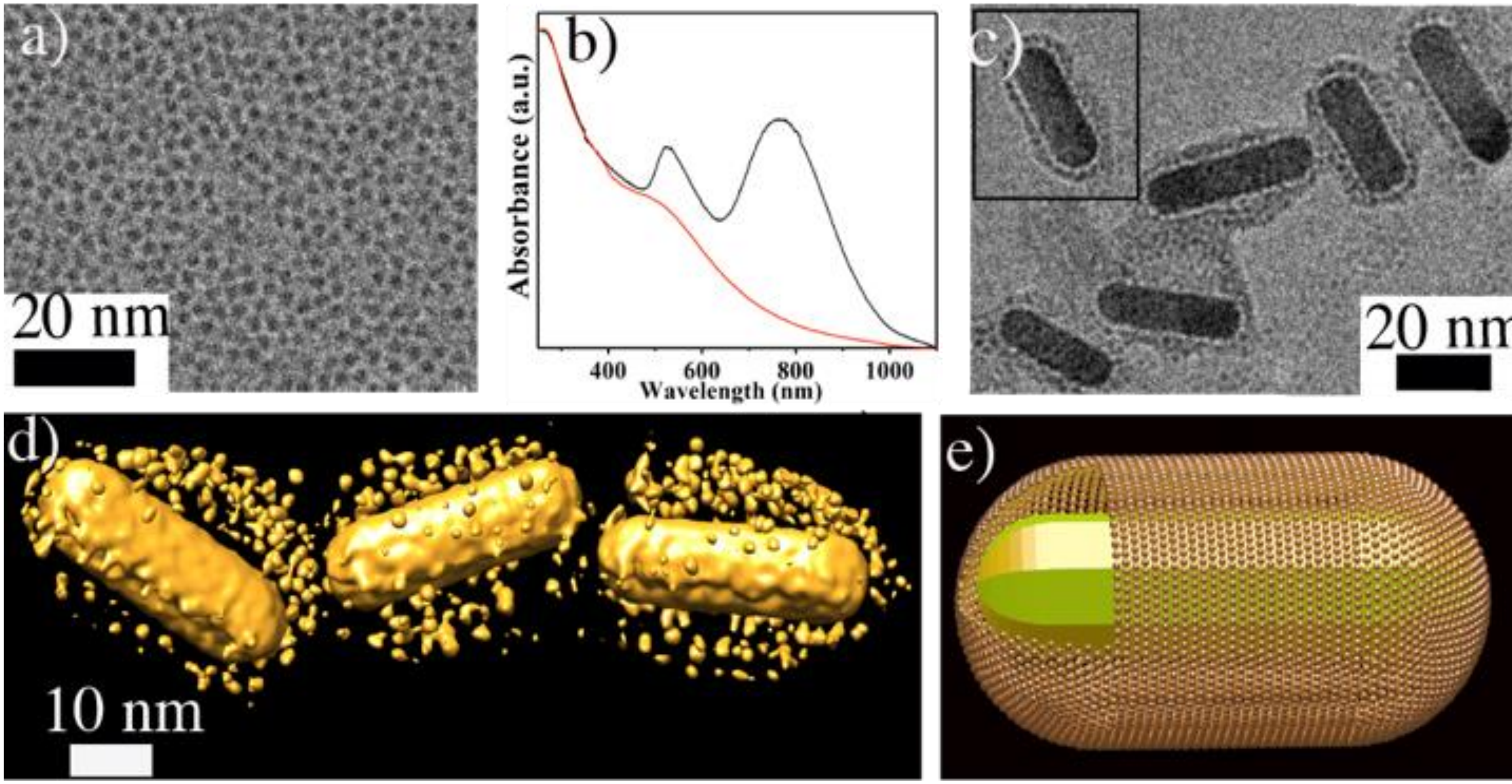
Assemblies and superstructures



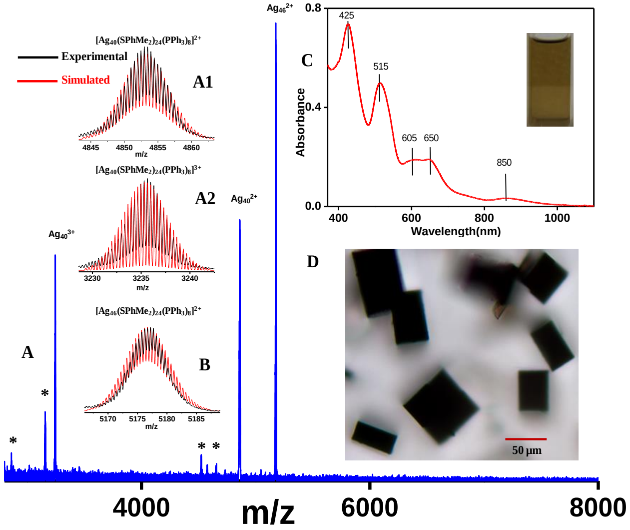
Amrita Chakraborty, et. al. Angew. Chem. 2018

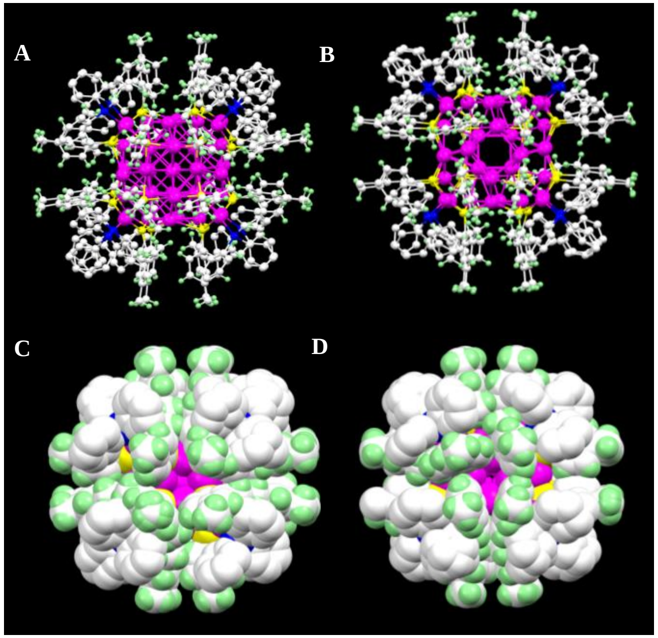


a)
GNR@CTAB
5 nm
2 m
[001]
[011]
[100]
[010]
b)
GNR@pMBA
5 nm
5 nm
2 nm
c)
GNR@Ag44
5 nm
d)
5 nm
e)
x
y
z
5 nm
f)
x
y
z
5 nm
g)
z
x
y
5 nm


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

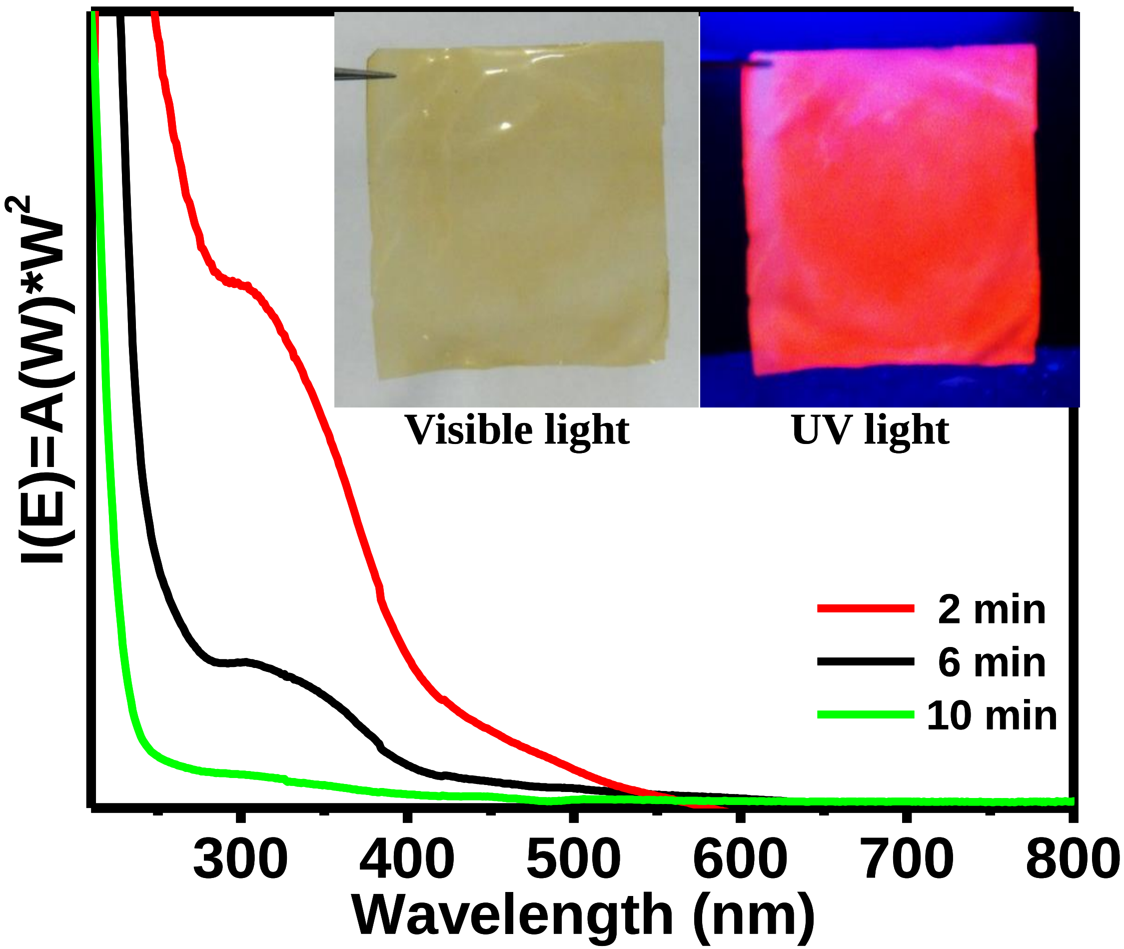




M. Bodiuzzaman, et. al. *Angew. Chem. Int. Ed.* **2018**

Sensors

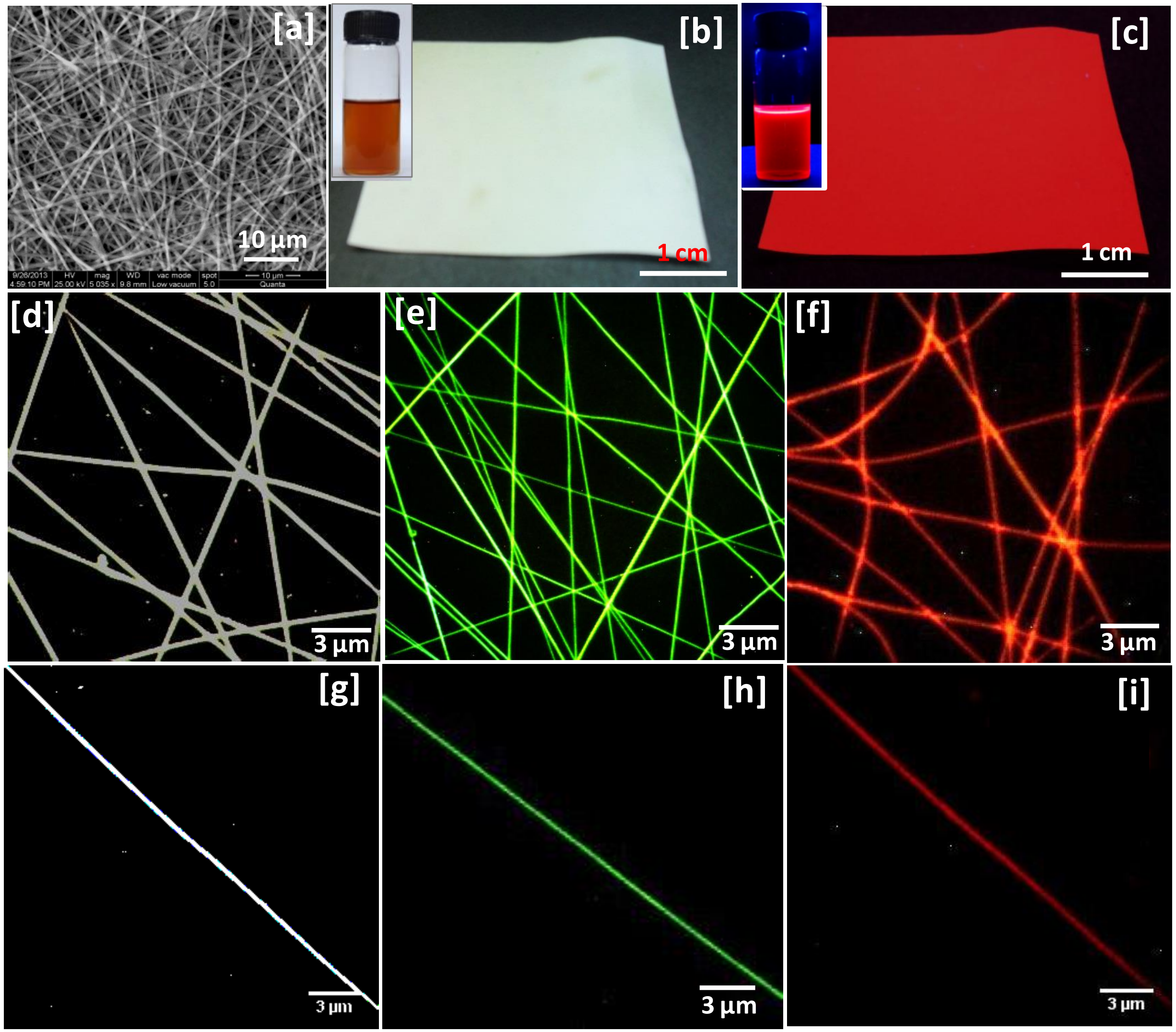
Quantum cluster based metal ion sensing paper
Large area uniform illumination using quantum cluster



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.

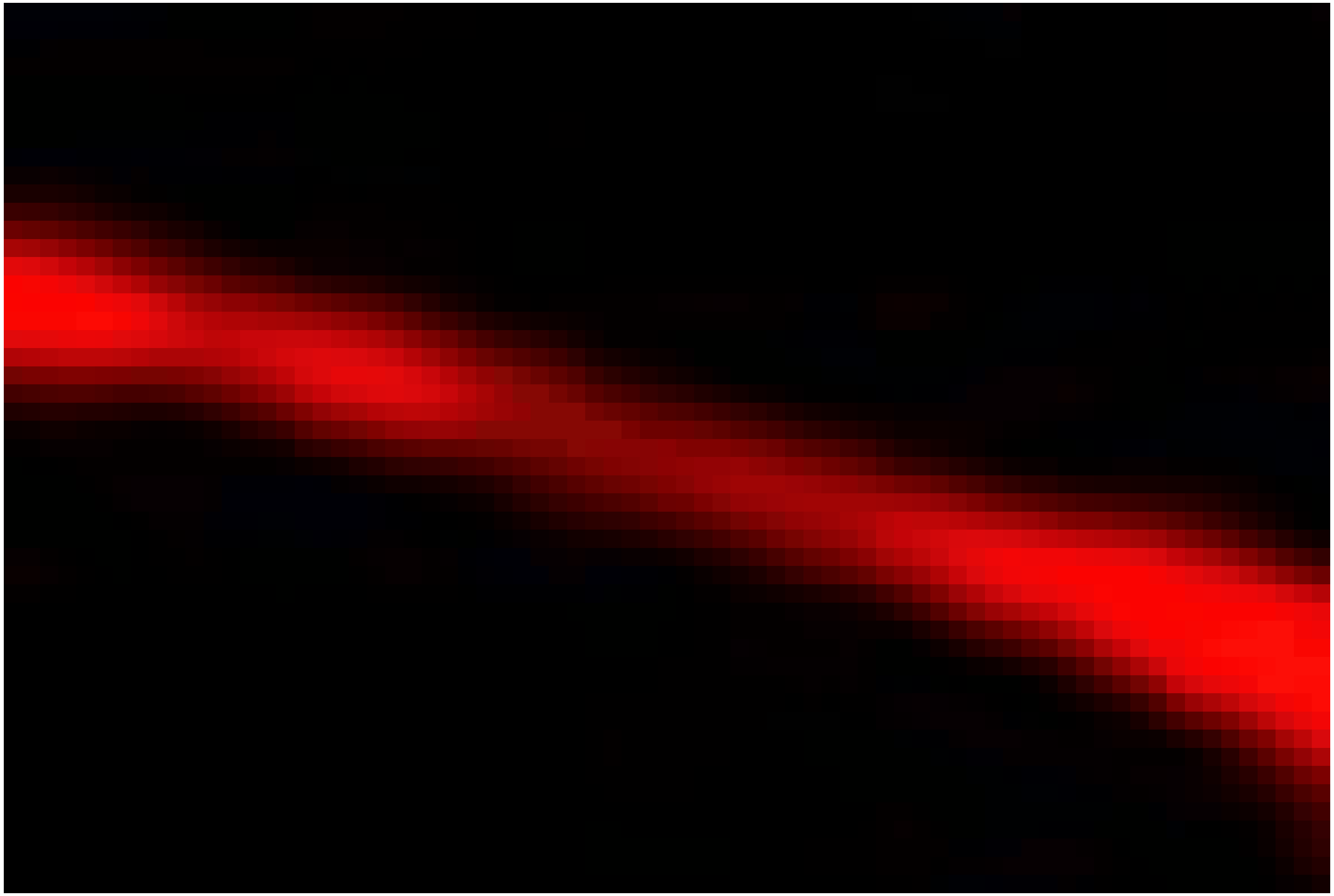
Anu George et al. *ACS Applied Materials & Interfaces*, 2012

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

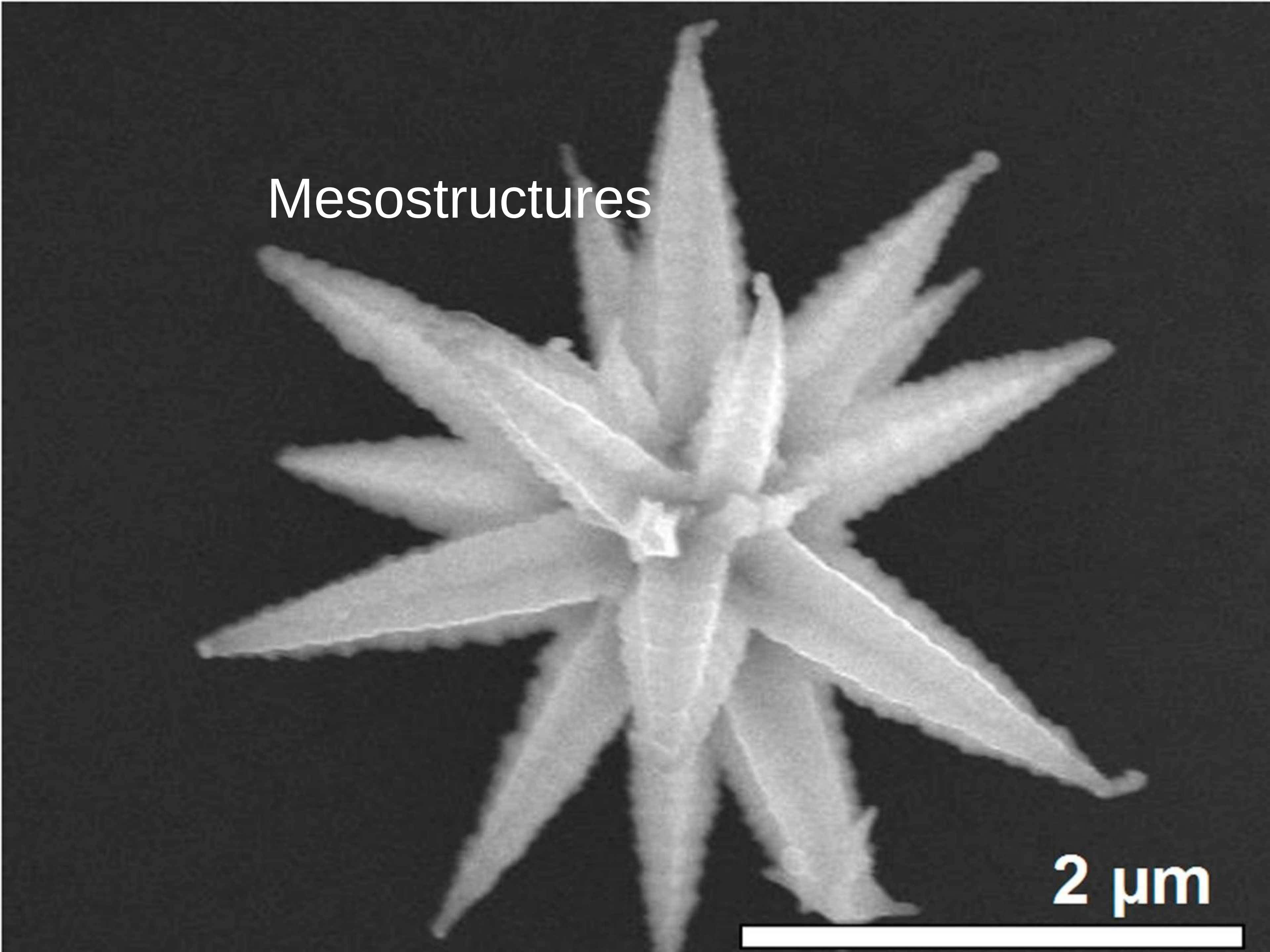


Atanu Ghosh et al. Anal. Chem. 2014.

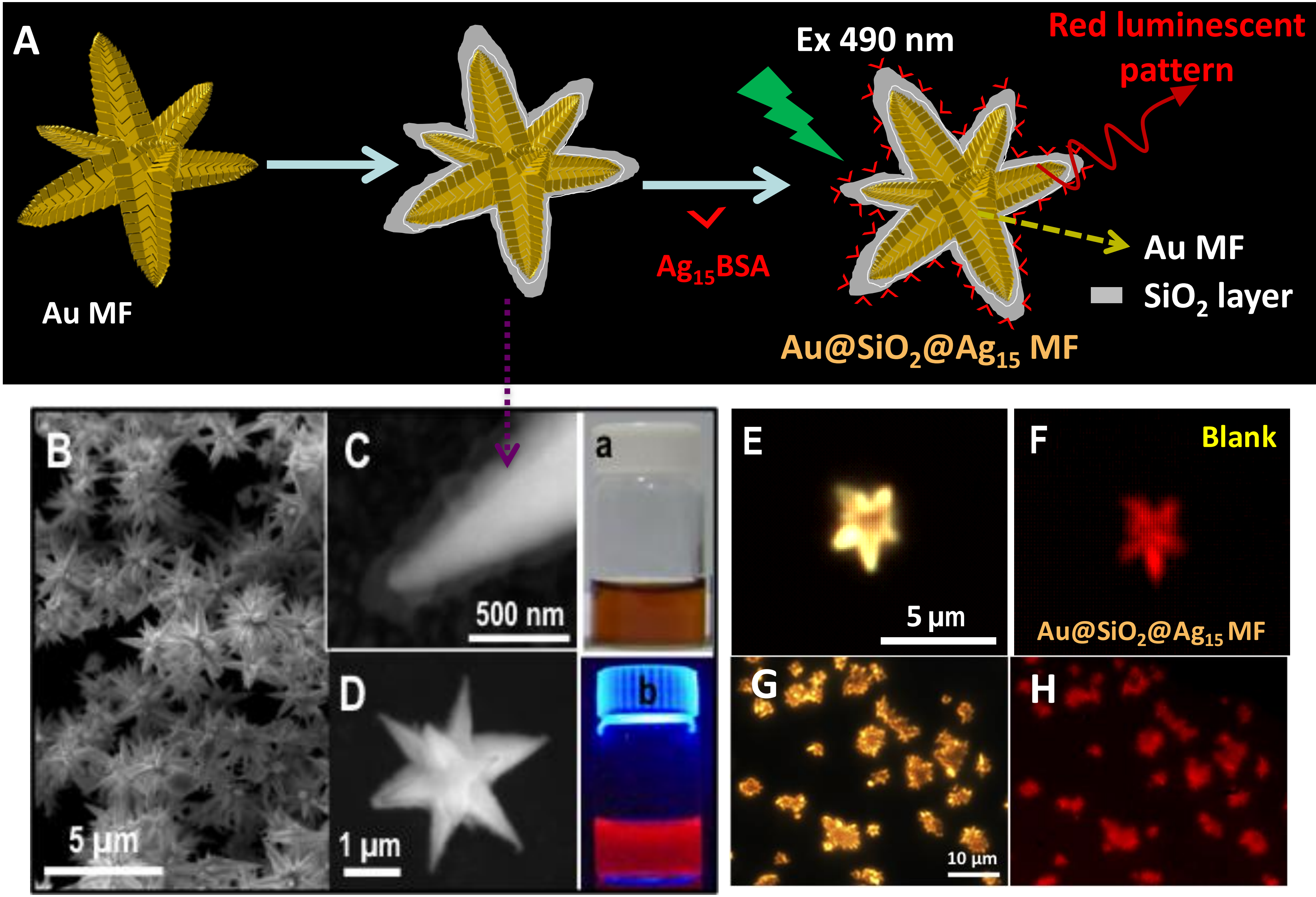
Video of mercury quenching experiment using the nanofiber

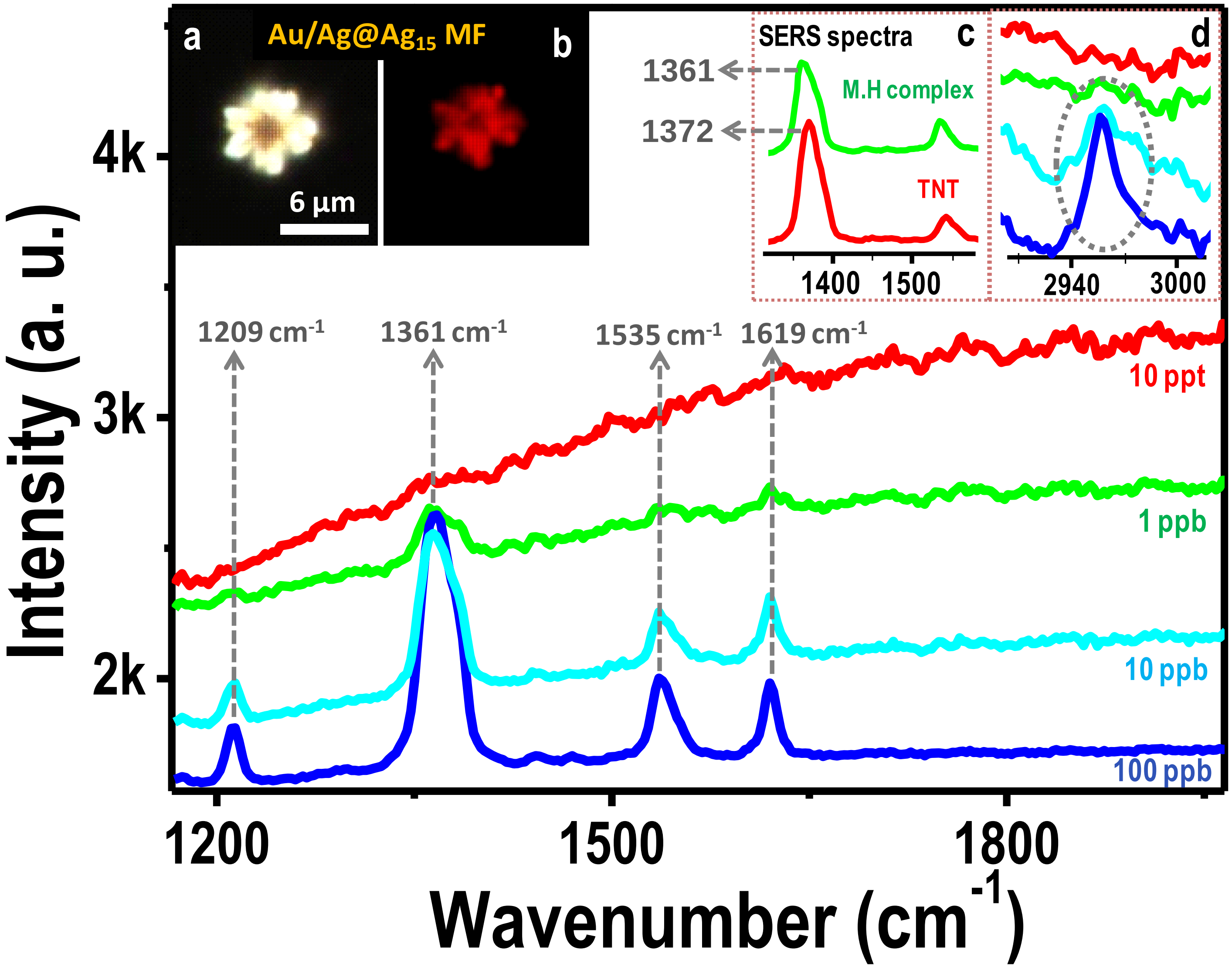


Mesostructures



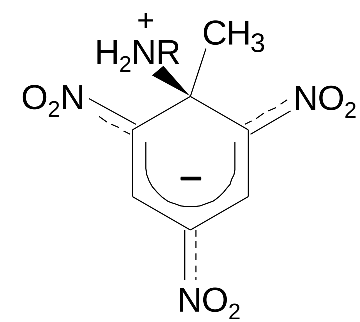
Designing a sensor





Meisenheimer complex

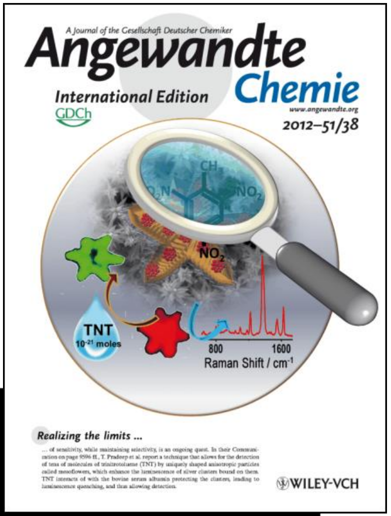
TNT

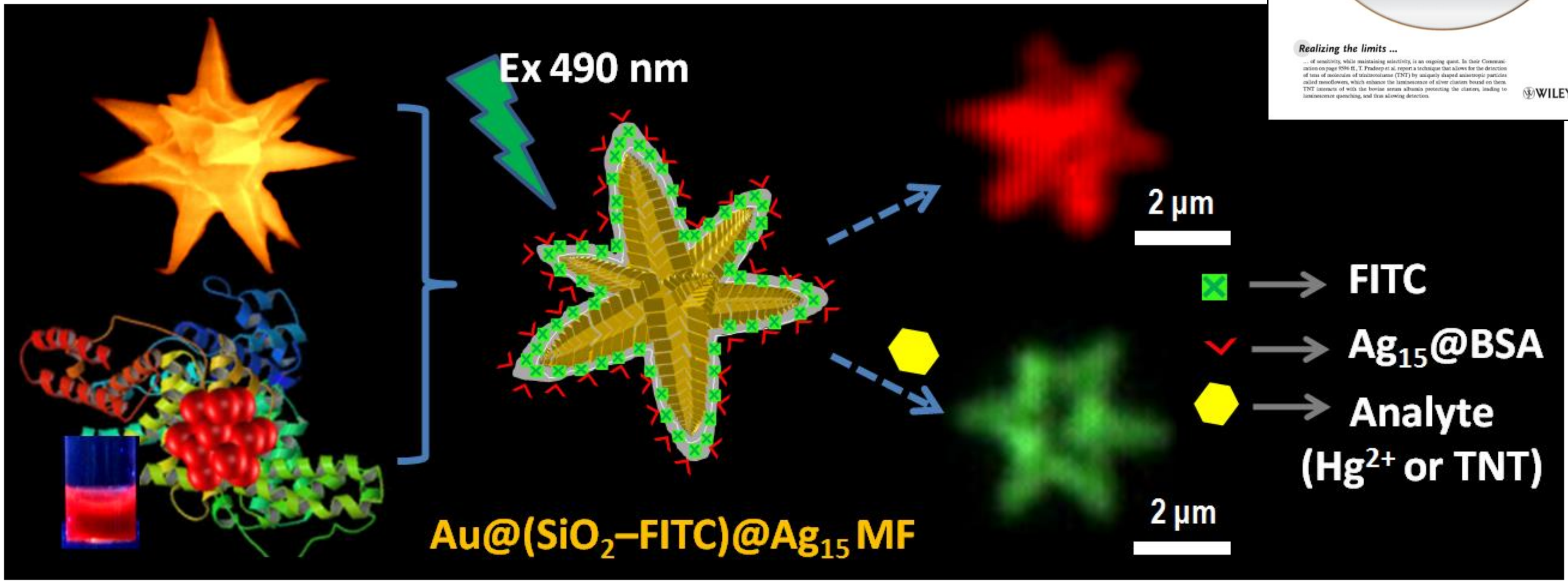


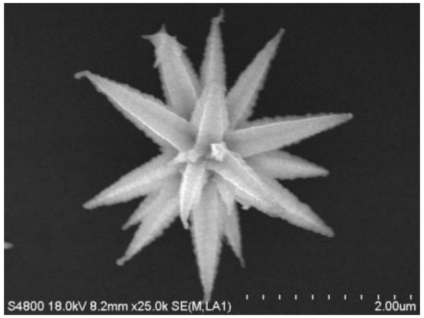
Meisenheimer complex is formed easily due to charge delocalization

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

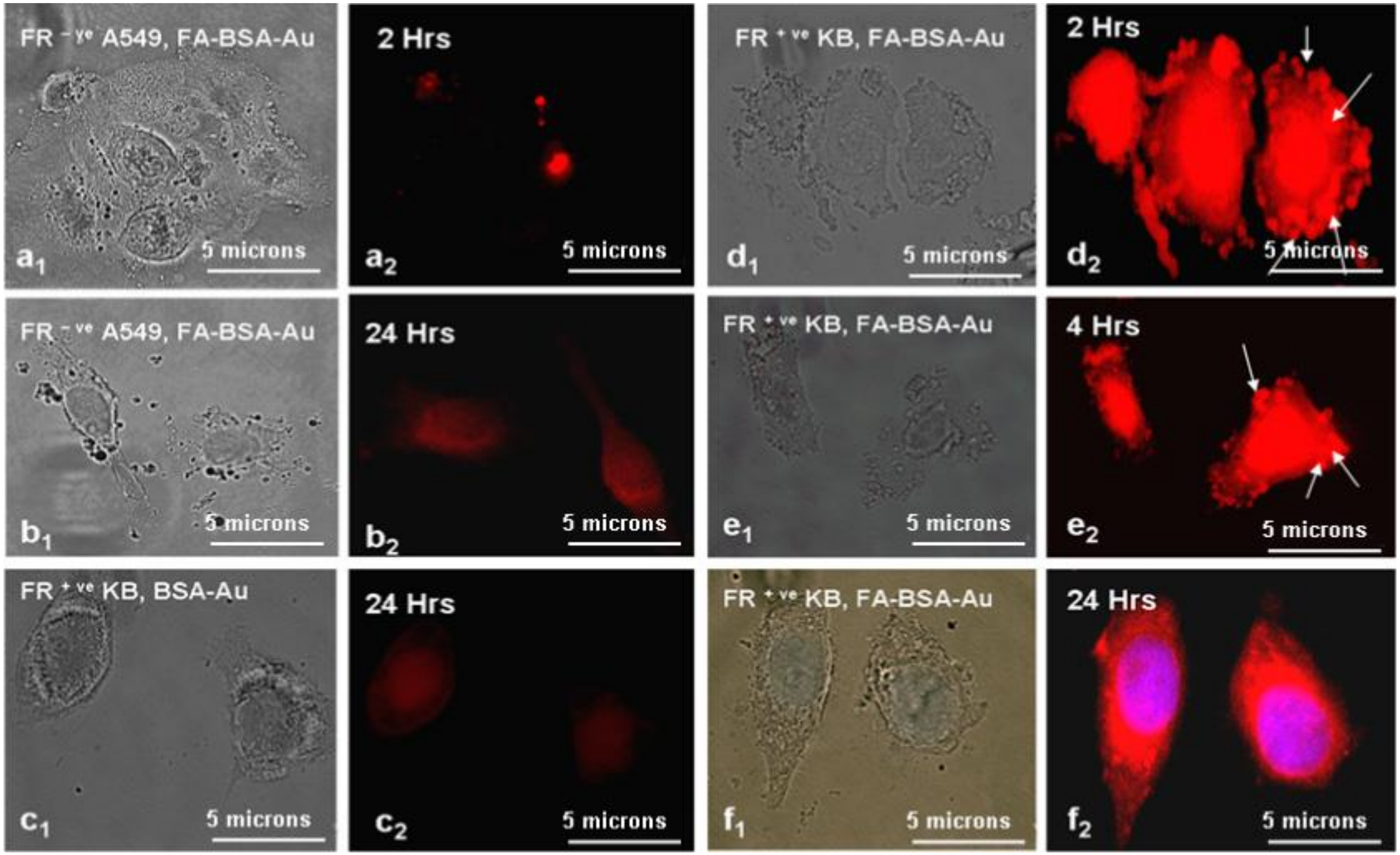


Figure 8. Fluorescent microscopic images showing interaction of Au–BSA–FA NCs with different types of cell lines: (a_1)–(a_2) FR^{-ve} lung carcinoma A549, (b_1)–(b_2) FR-depressed oral cell carcinoma, KB, (c_1)–(c_2) FR^{+ve} KB cells with unconjugated Au clusters, (d_1)–(d_2) FR^{+ve} KB cells with FA-conjugated Au clusters at 2 h, (e_1)–(e_2) 4 h and (f_1)–(f_2) 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


iitmadras.

Department of Science and Technology

Thank you