Now in the 58th year

Reactions between nanoparticles

T. Pradeep
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Founder
InnoNano Research Pvt. Ltd.
An IIT Madras Incubated Company

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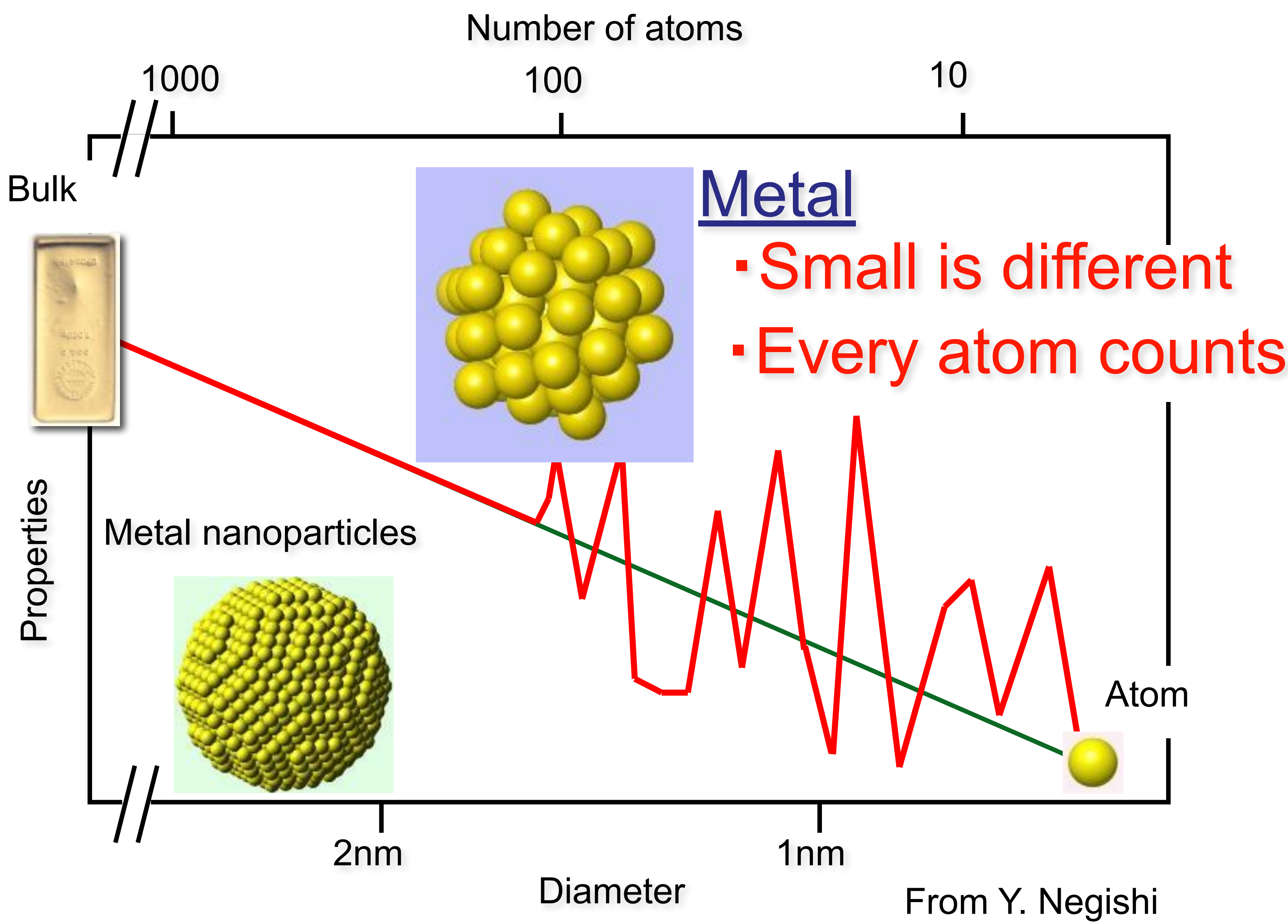
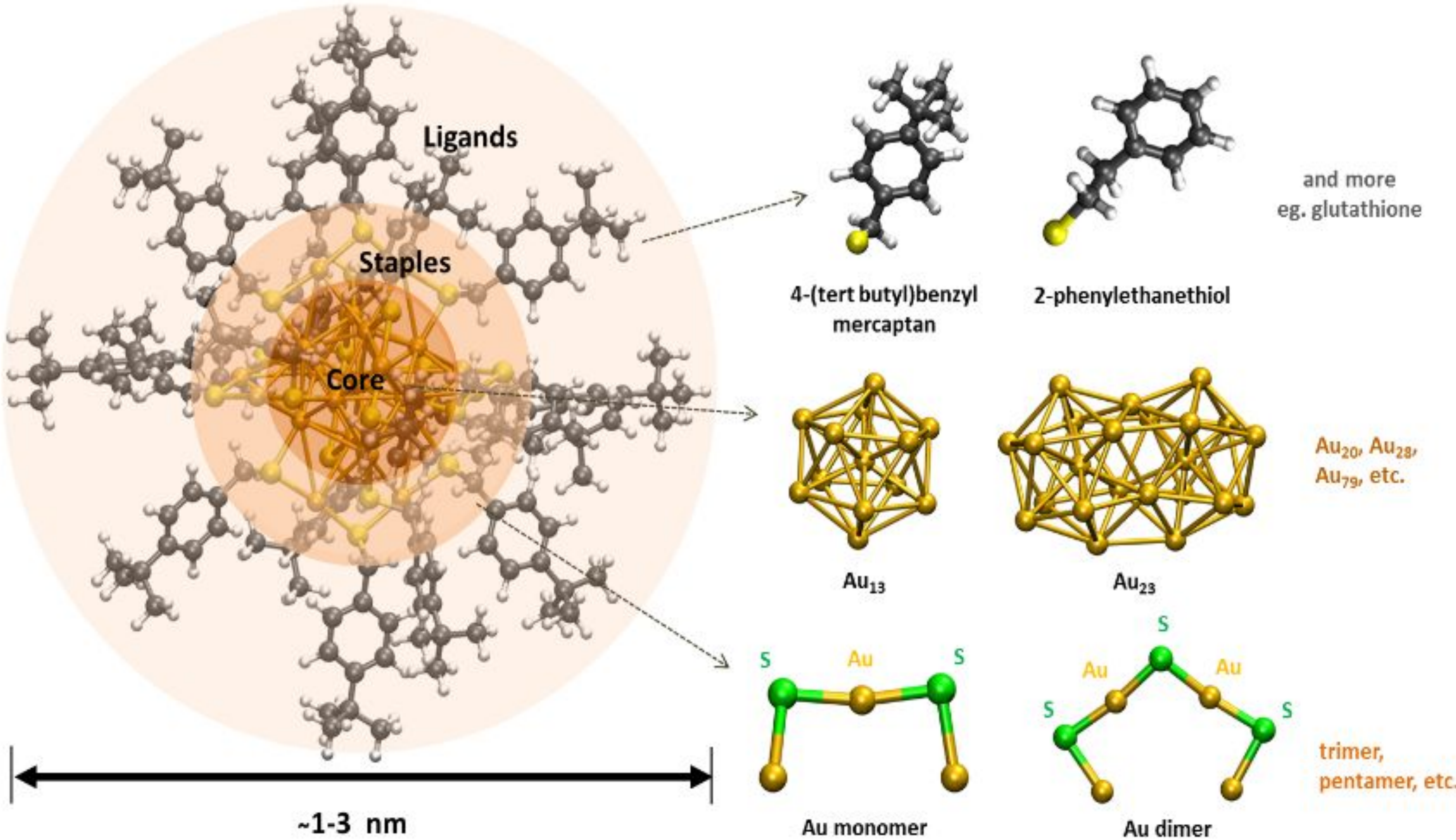
An IIT Madras incubated company

Associate Editor
ACS Sustainable Chemistry & Engineering

International Conference on Emerging Frontiers in Chemical Sciences
Farook College, September 23-25, 2017



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


Ligands
Staples
Core
~1-3 nm
4-(tert butyl)benzyl mercaptan
2-phenylethanethiol
and more
eg. glutathione
Au_{13}
Au_{23}
Au_{20}, Au_{28}, Au_{79}, etc.
S
Au
S
Au monomer
S
Au
Au
S
S
Au dimer
trimer, pentamer, etc.

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

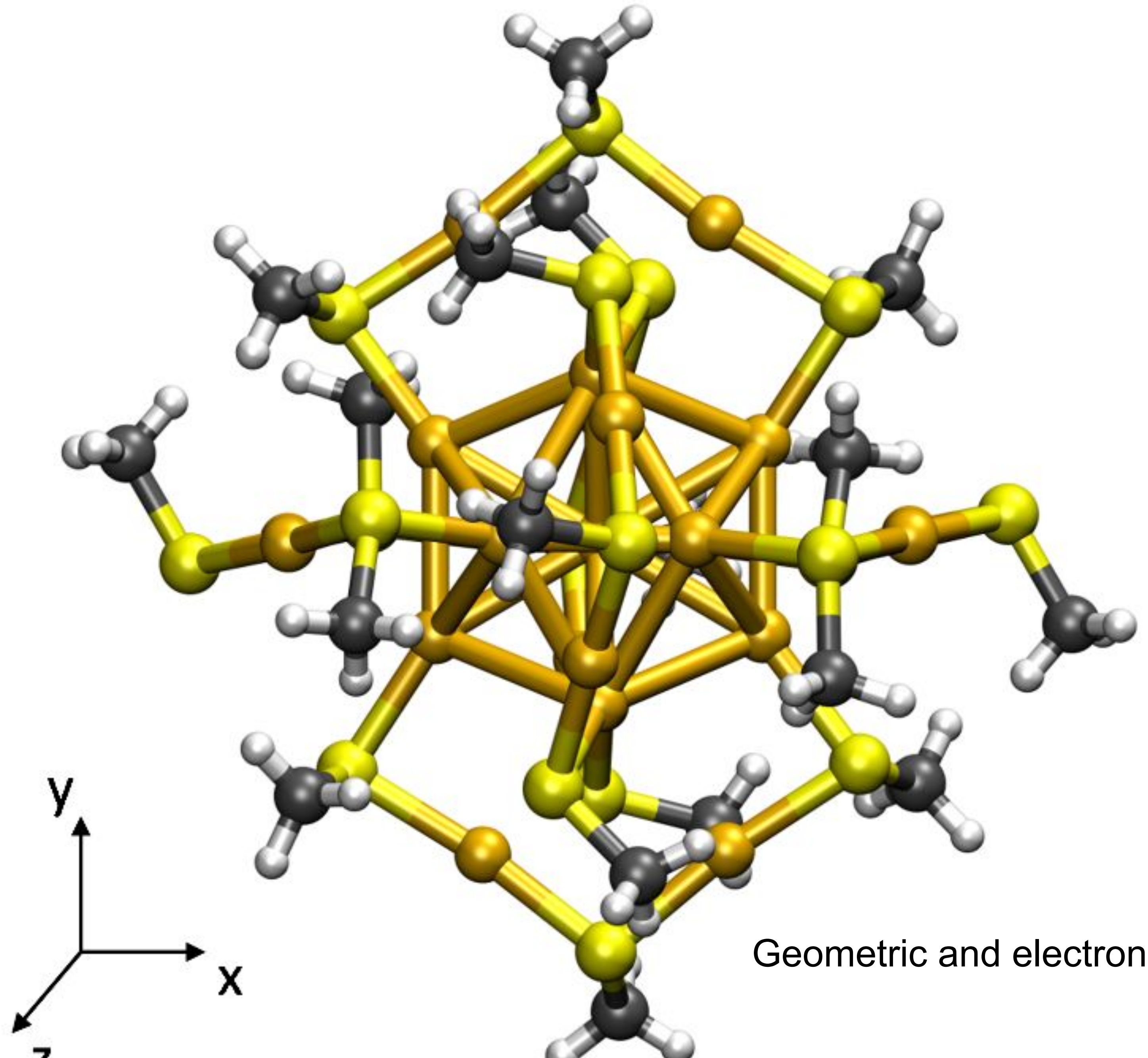
ABSTRACT: Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{102}(SR)_{44}$ as well as $Ag_{25}(SR)_{18}$, $Ag_{29}(S_2R)_{12}$, 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, …

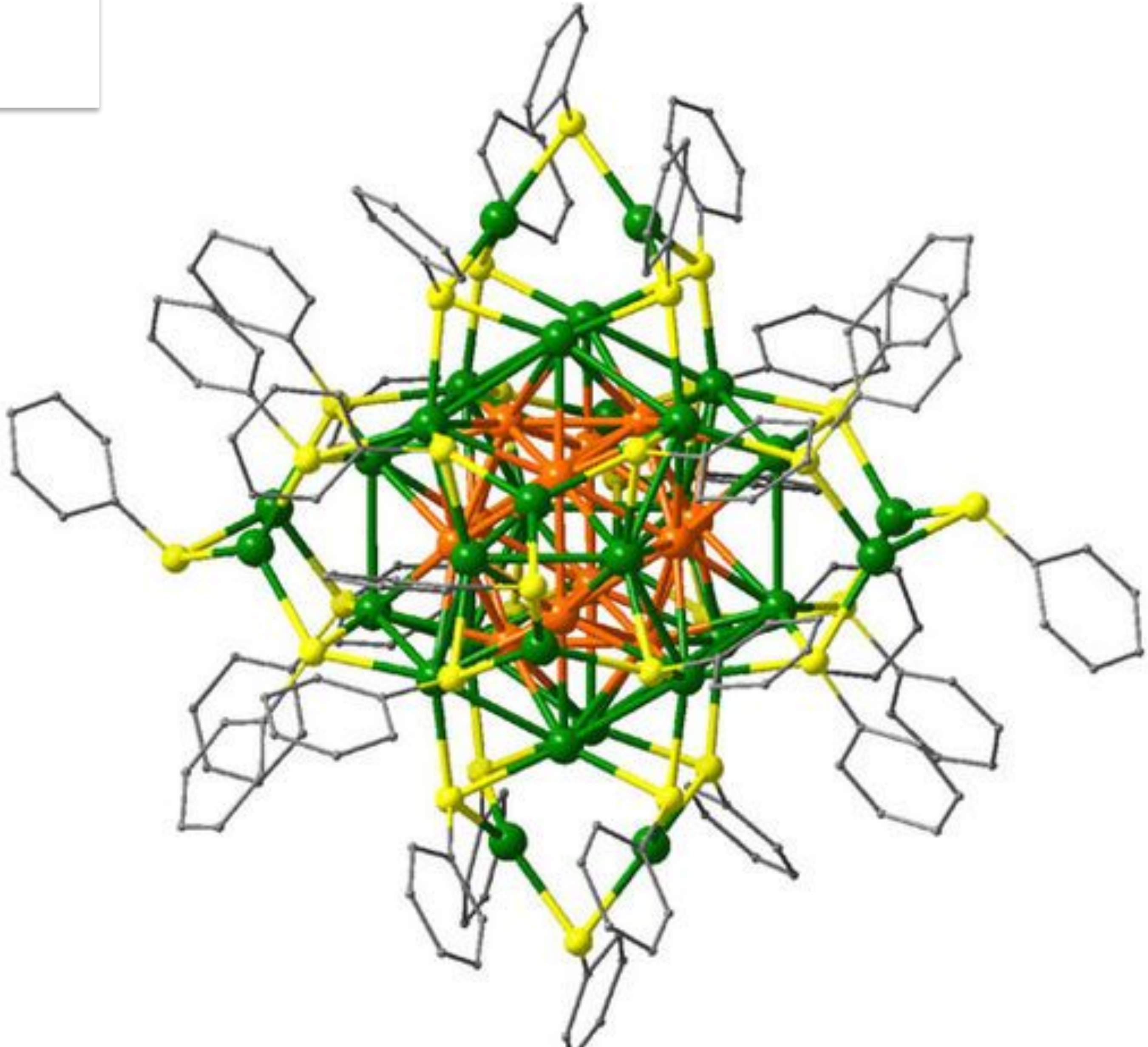
Chemistry of clusters

Reactions of clusters

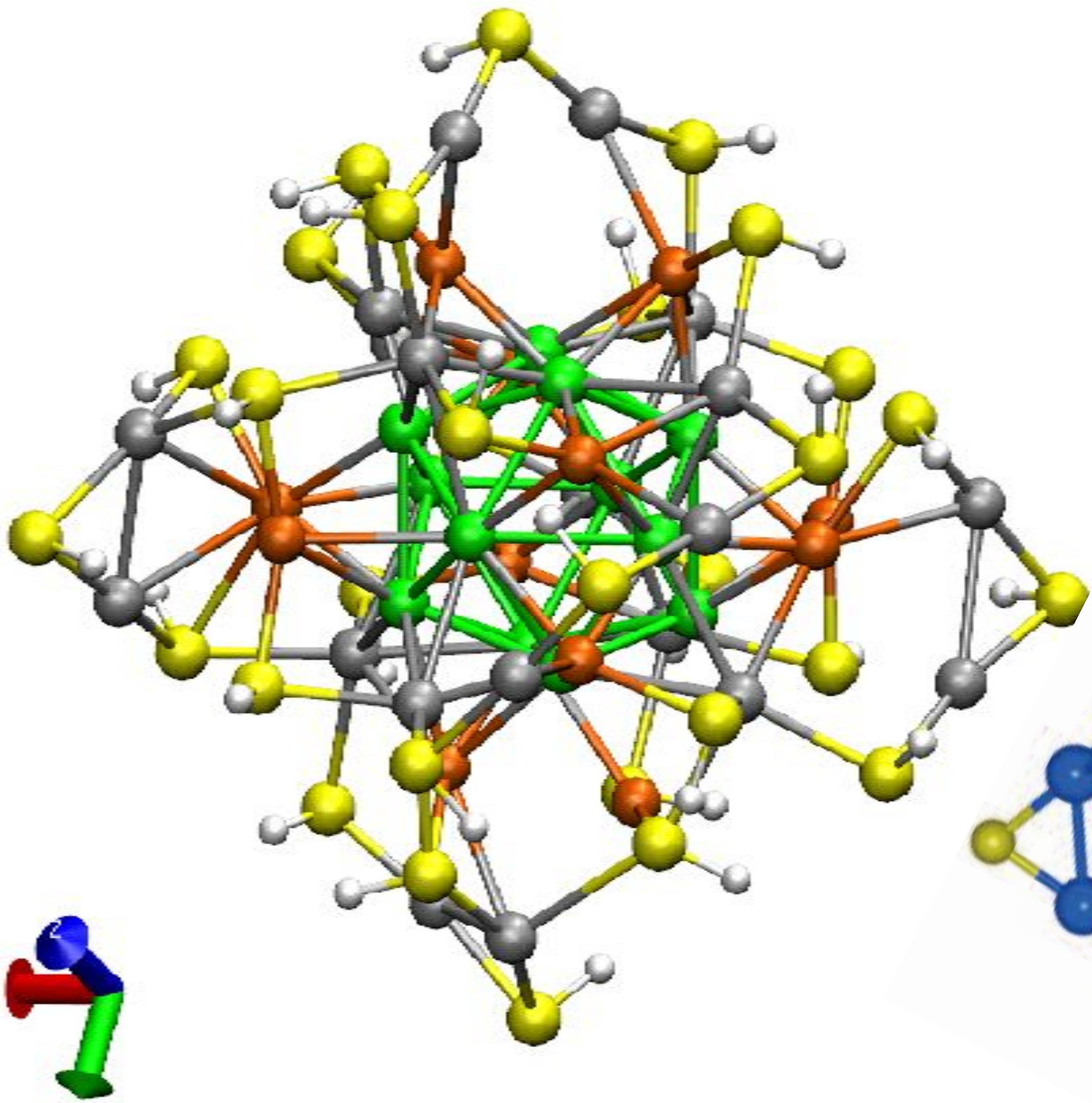
Reactions between clusters

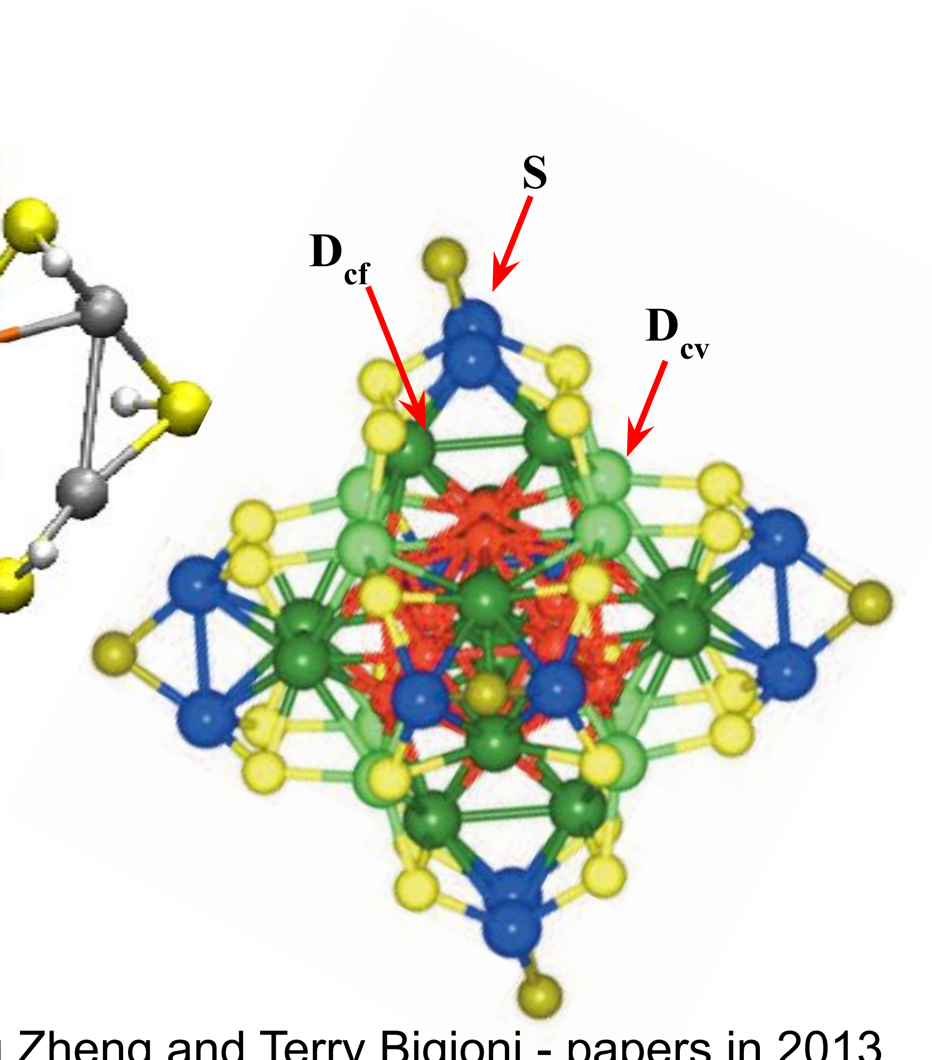


Geometric and electronic shells

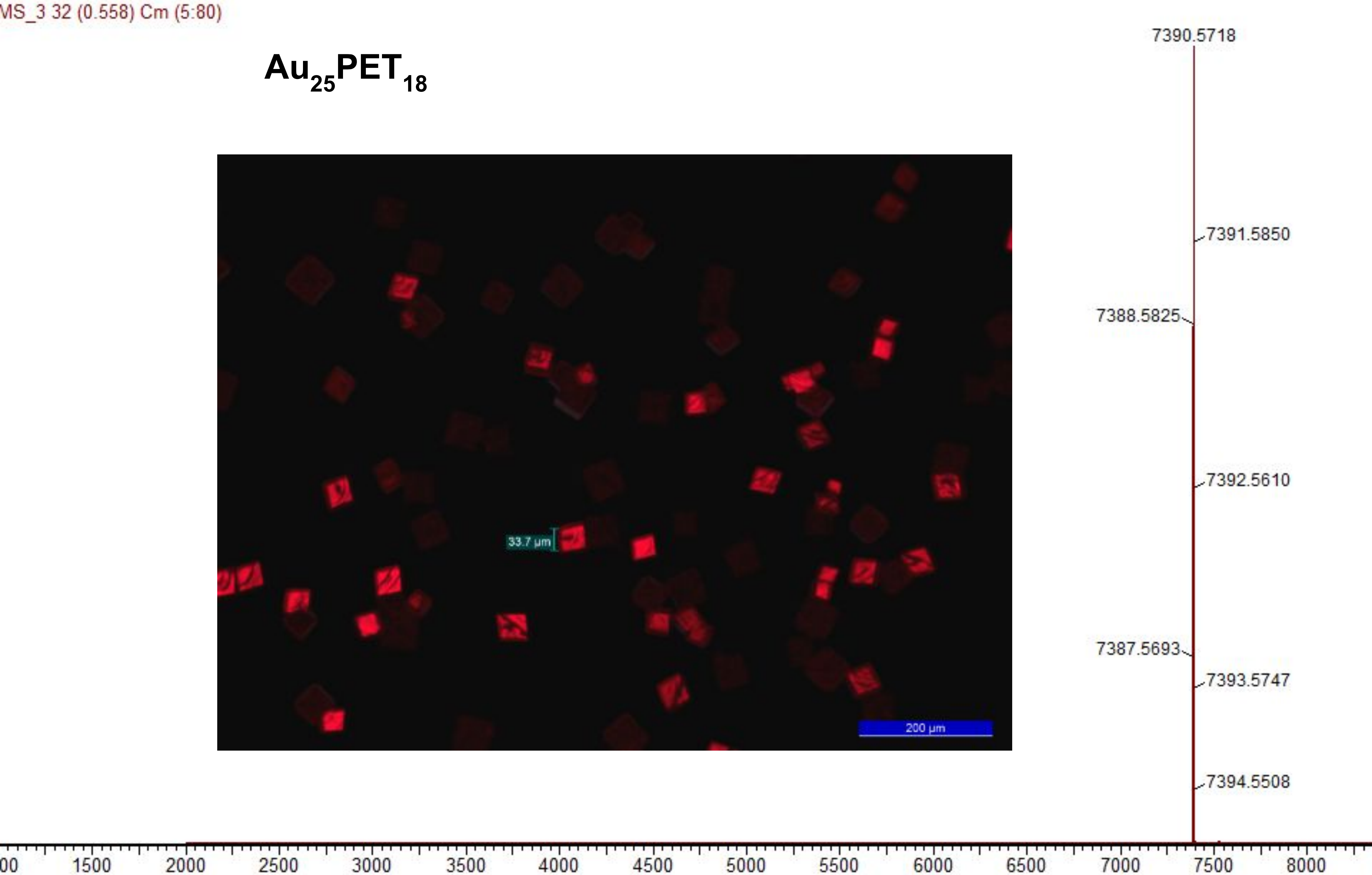


Nanfeng Zheng et al. Nature Communications, 2013

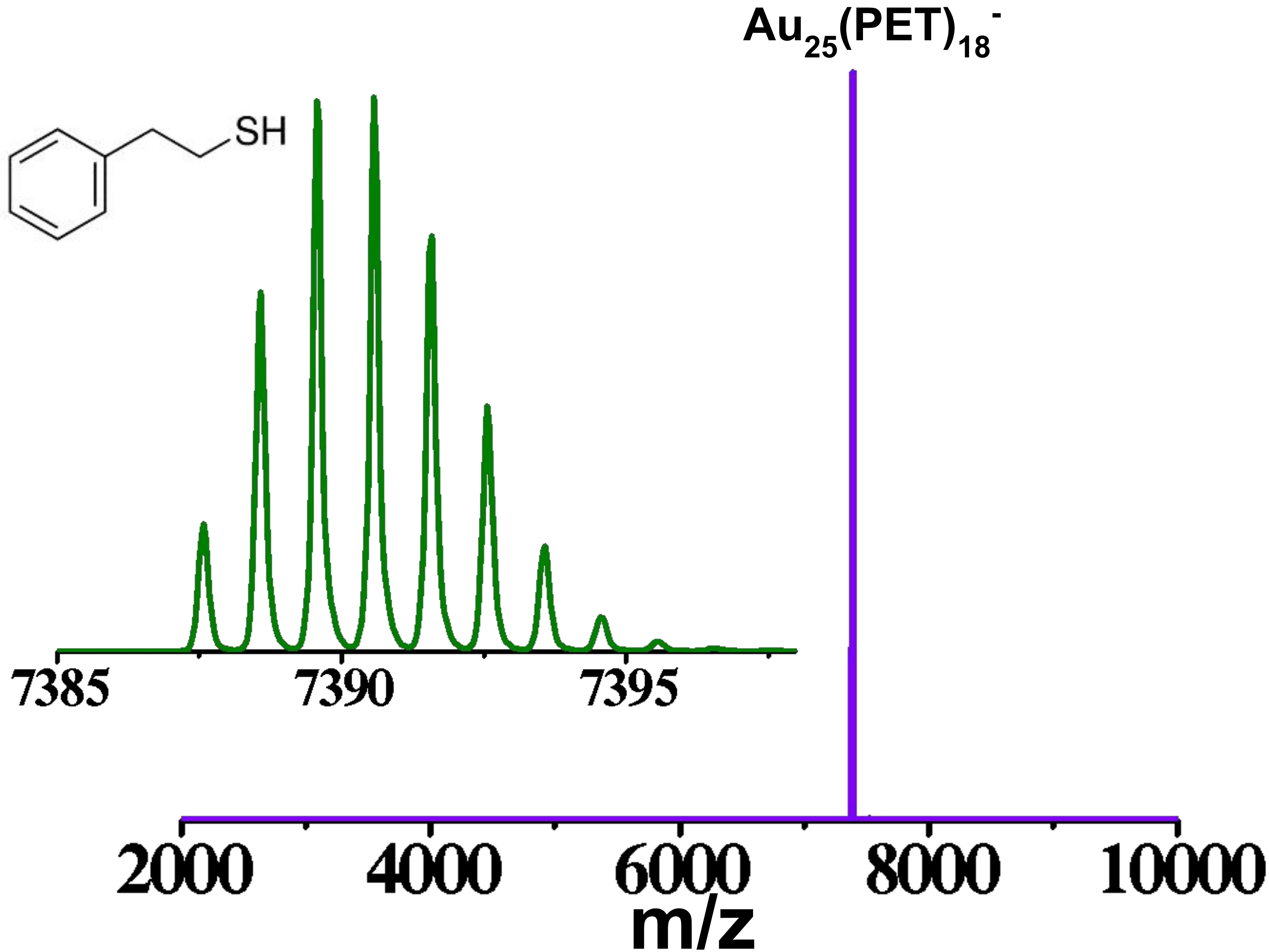




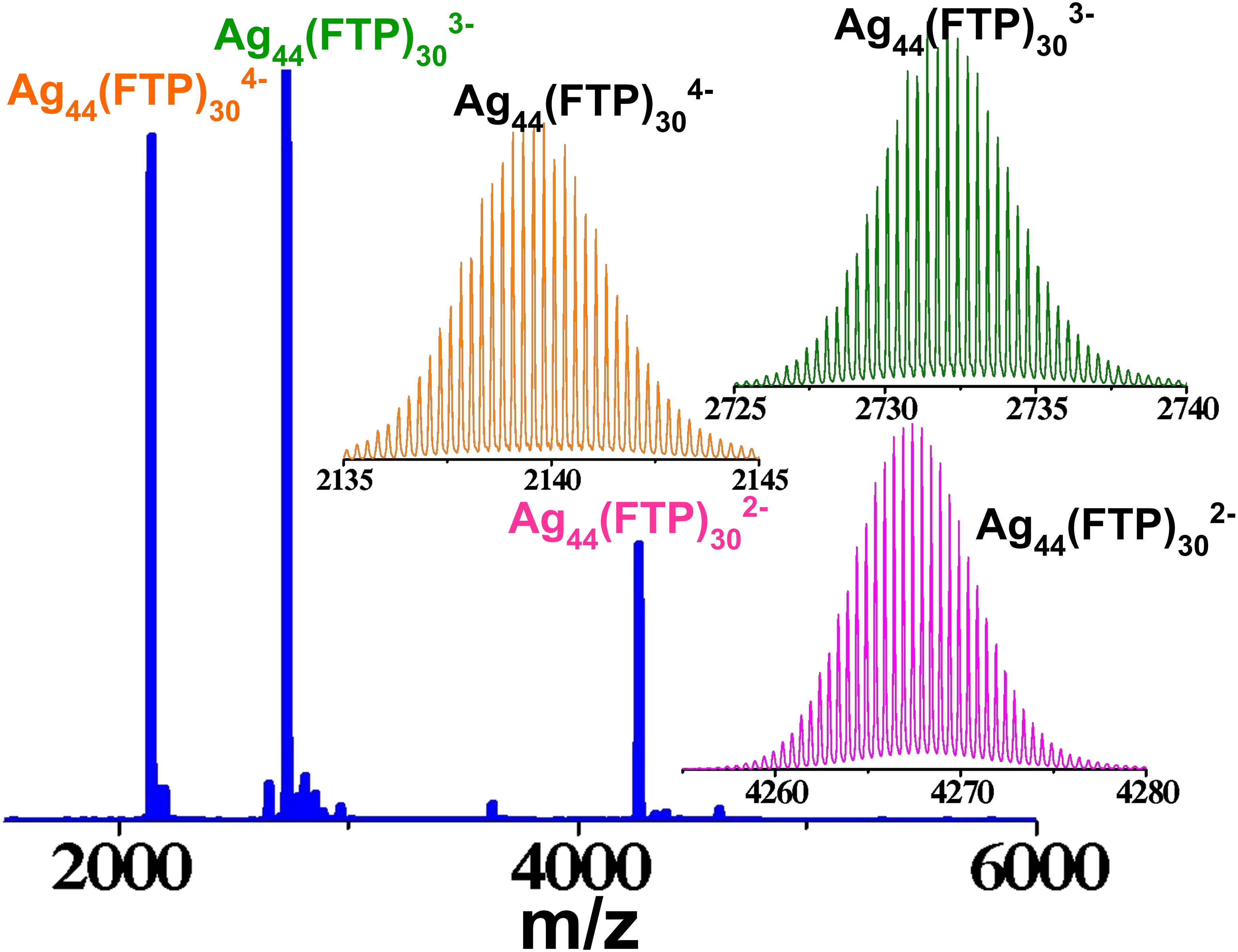
$Ag_{44}SR_{30}$ – Nanfeng Zheng and Terry Bigioni - papers in 2013



MS_3 32 (0.558) Cm (5:80)
Au25PET18
7390.5718
7391.5850
7388.5825
7392.5610
7387.5693
7393.5747
7394.5508
33.7 µm
200 µm
00
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500
8000



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



Ag44(FTP)30 3-
Ag44(FTP)30 4-
Ag44(FTP)30 4-
Ag44(FTP)30 3-
2725
2730
2735
2740
2135
2140
2145
Ag44(FTP)30 2-
Ag44(FTP)30 2-
4260
4270
4280
2000
4000
6000
m/z

Inter-cluster reactions

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

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

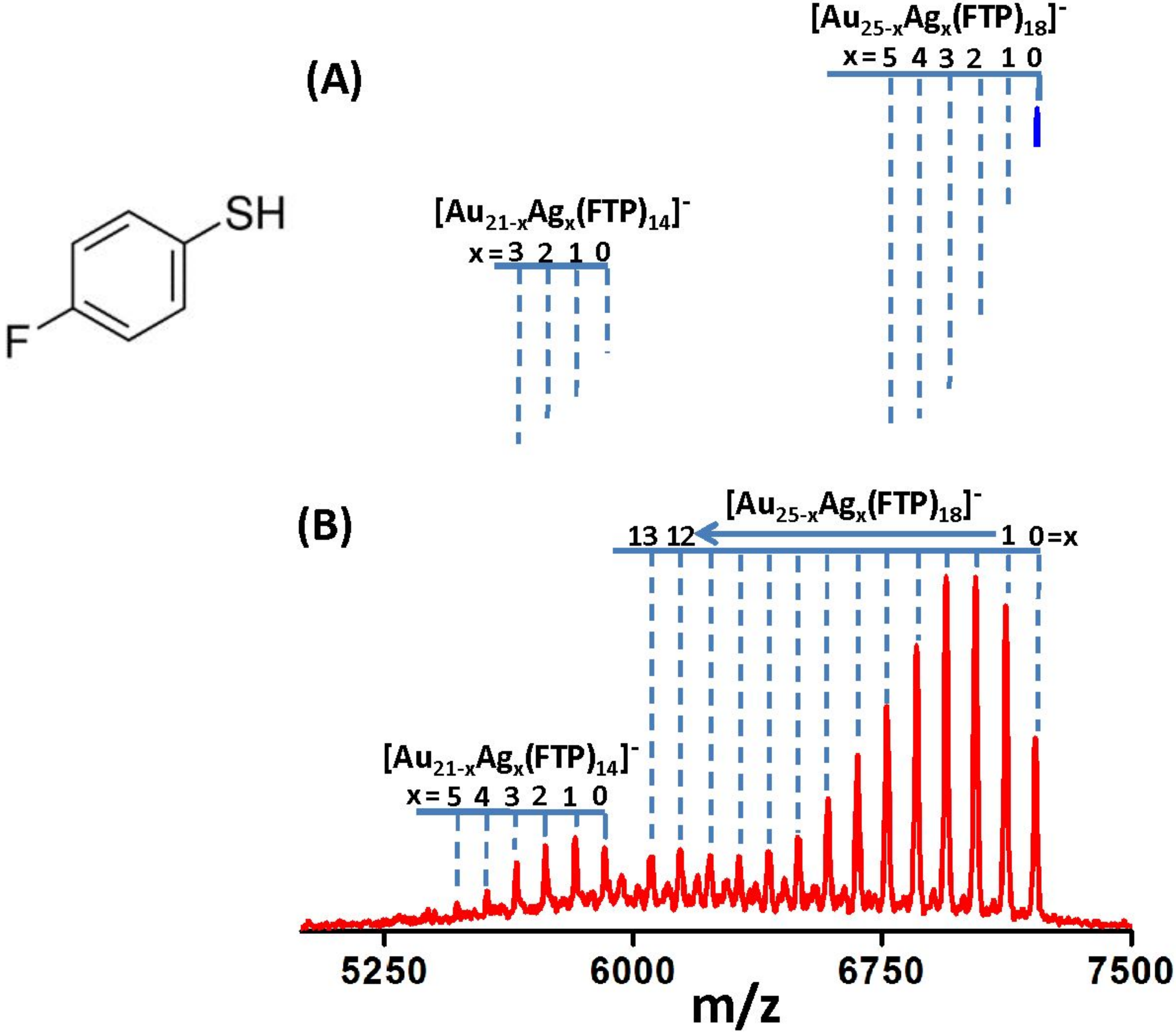
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

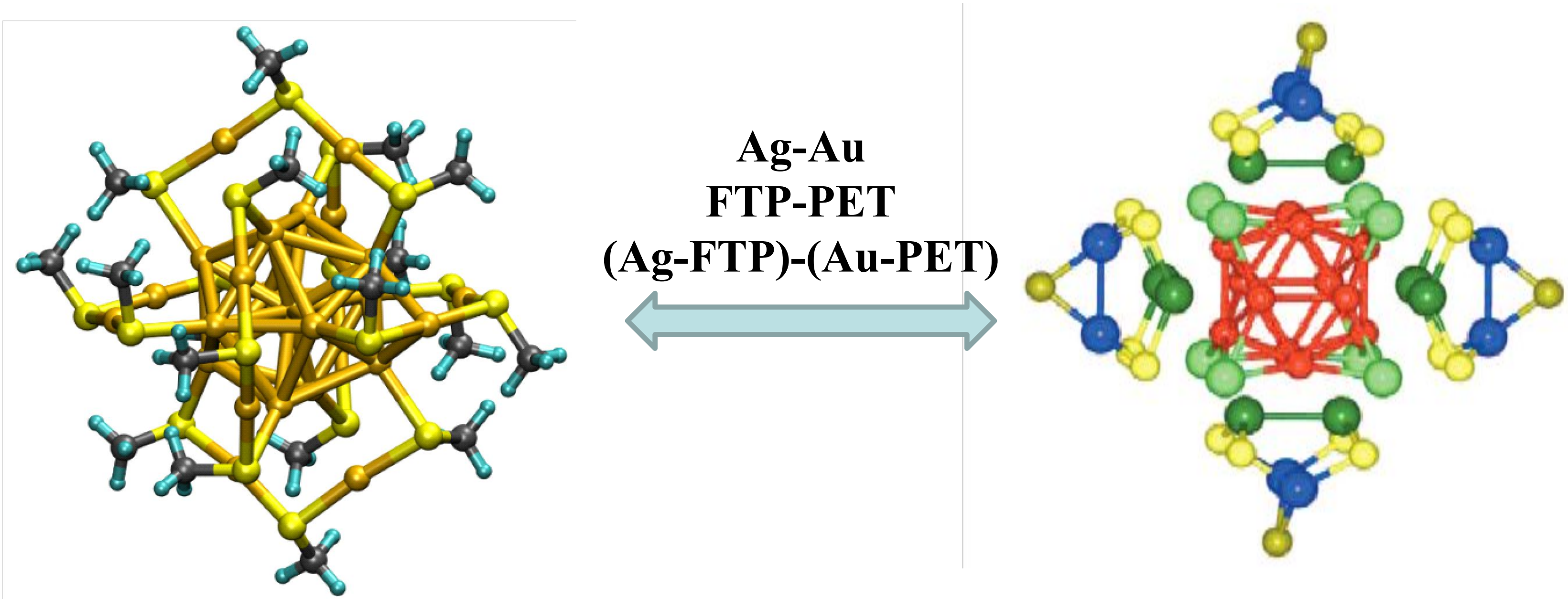
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India

Supporting Information

A + B → C + D

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





$$Au_{25}(PET)_{18} + Ag_{44}(FTP)_{30} \Rightarrow Au_{25-x}Ag_{x}(PET)_{18-y}(FTP)_{y} + Ag_{44-m}Au_{m}(FTP)_{30-n}(PET)_{n}$$

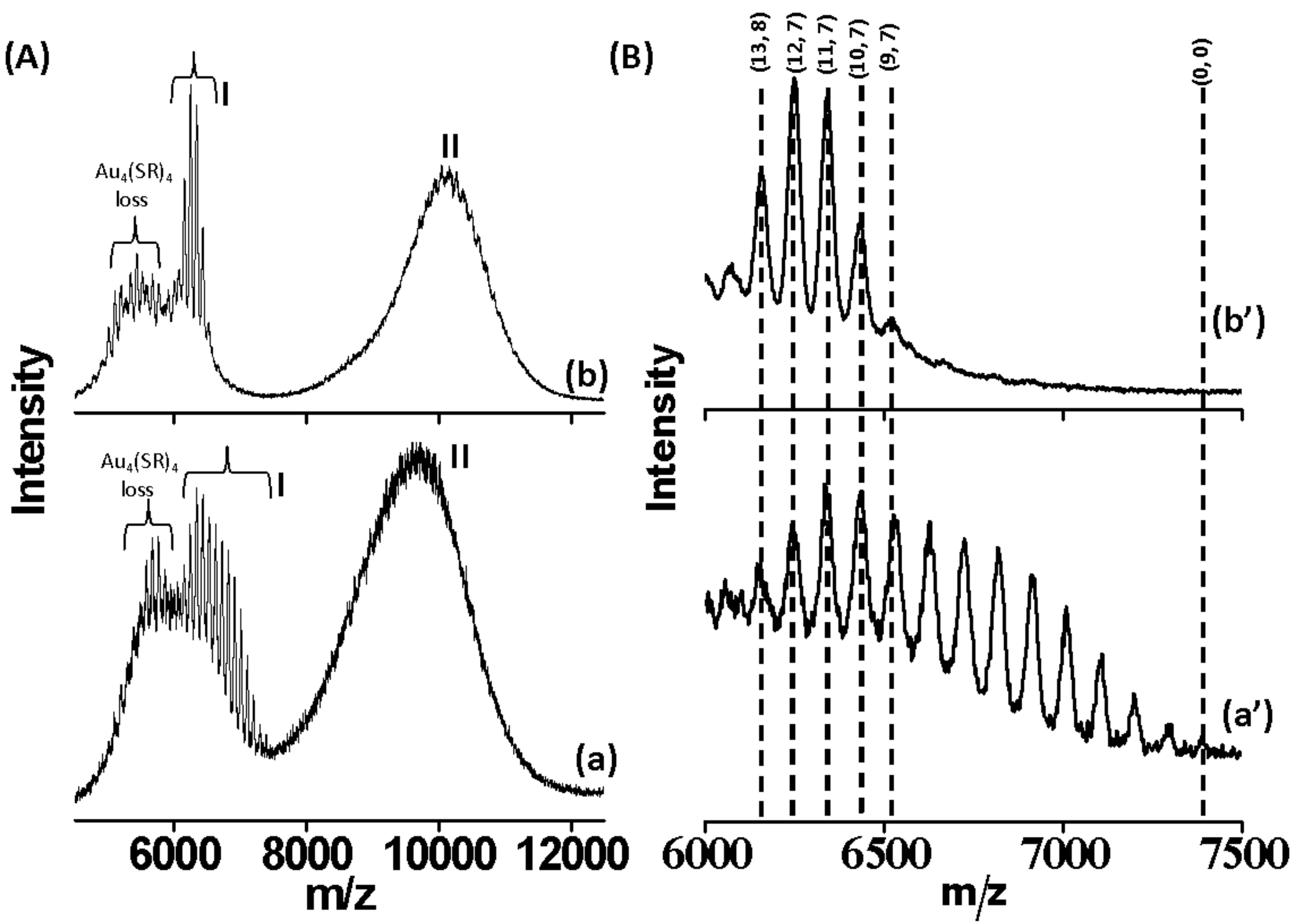
$$Au_{25}(FTP)_{18} + Ag_{44}(FTP)_{30} \Rightarrow Au_{25-x}Ag_{x}(FTP)_{18} + Ag_{44-m}Au_{m}(FTP)_{30}$$

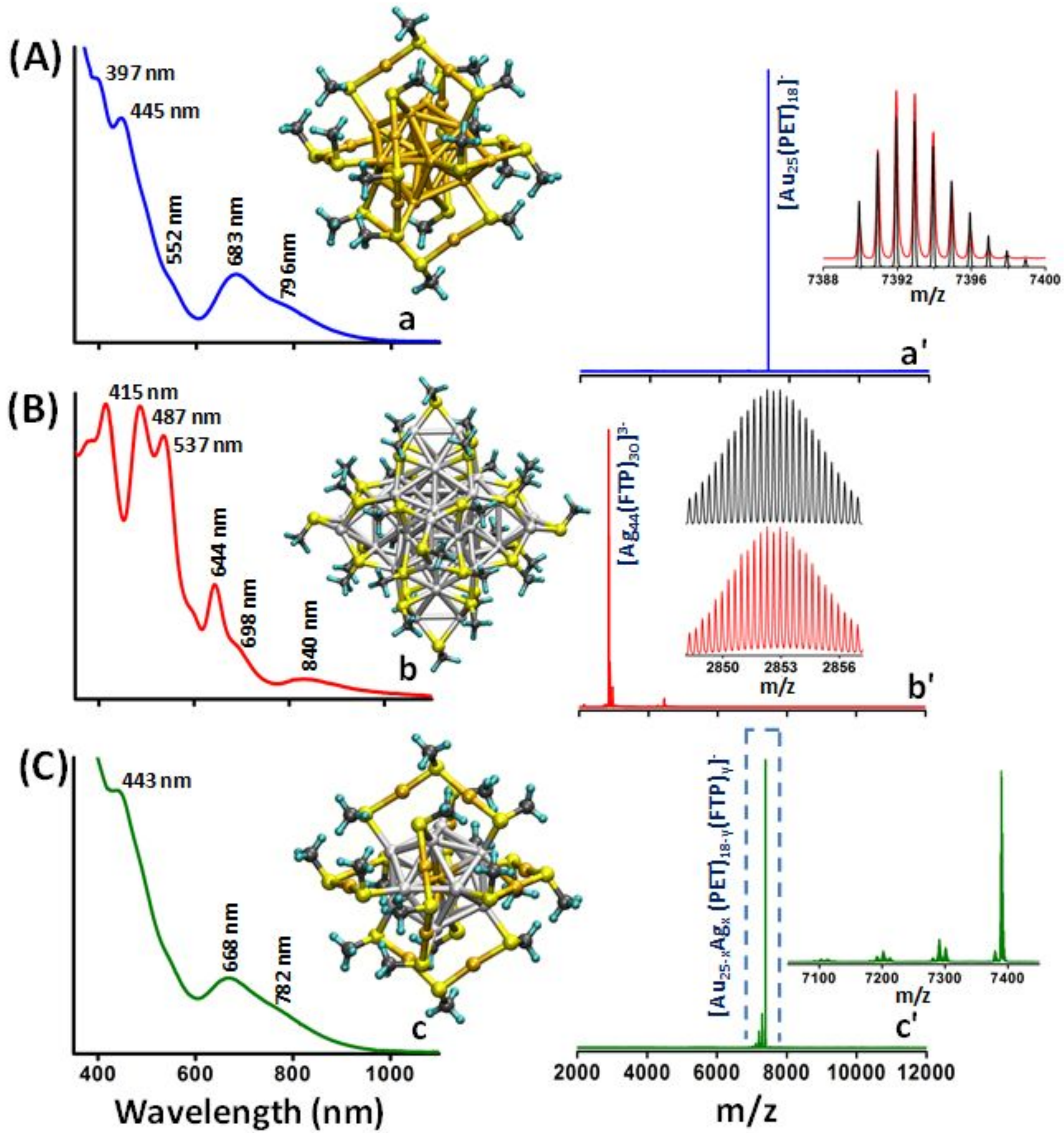
I: $Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y$

II: $Ag_{44-m}Au_m(FTP)_{30-n}(PET)_n$

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

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



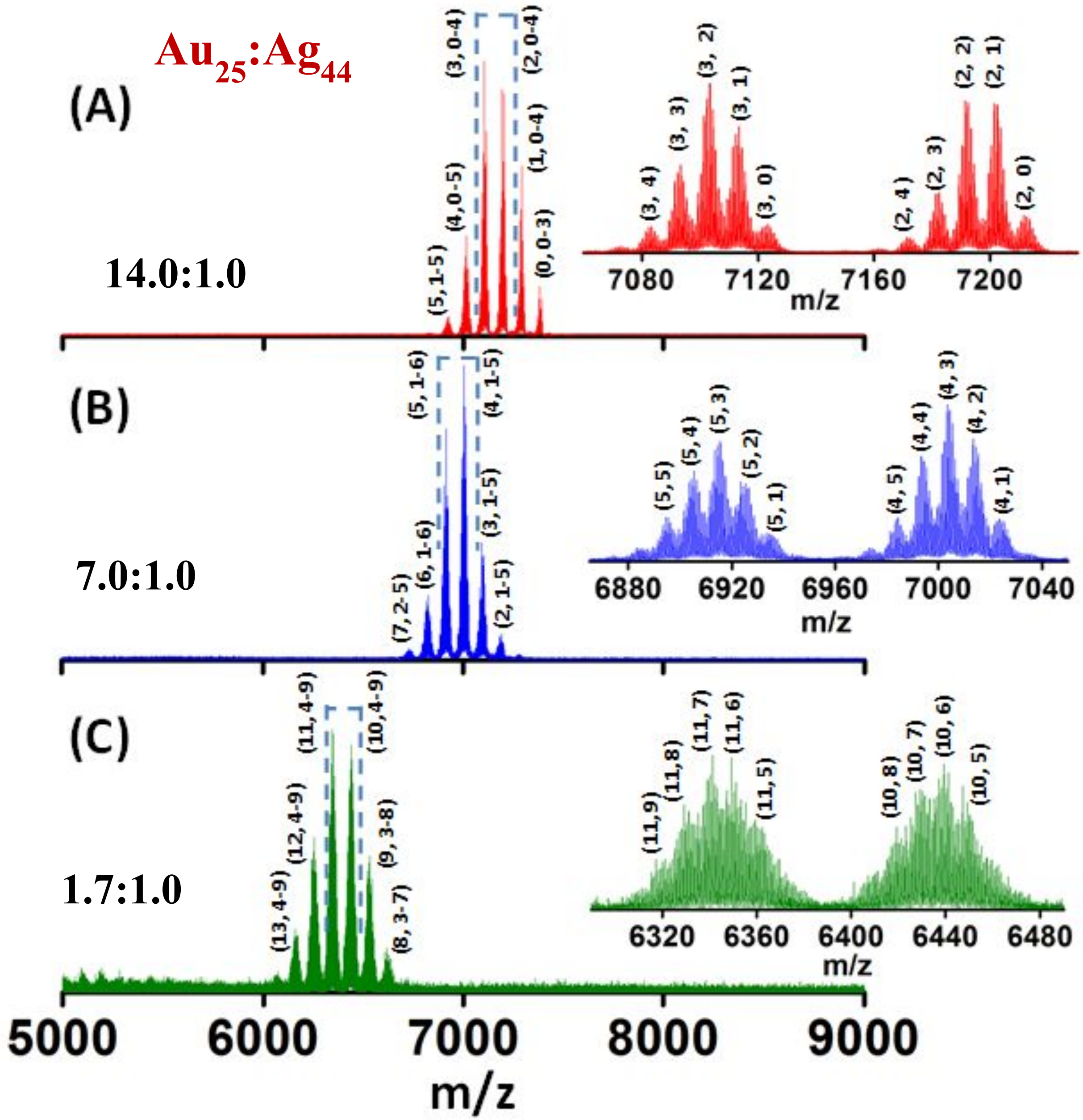


(A)
397 nm
445 nm
552 nm
683 nm
796nm
a
$[Au_{25}(PET)_{18}]^-$
7388
7392
7396
7400
m/z
a'
(B)
415 nm
487 nm
537 nm
644 nm
698 nm
840 nm
b
$[Ag_{44}(FTP)_{30}]^{3-}$
2850
2853
2856
m/z
b'
(C)
443 nm
668 nm
782 nm
c
$[Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y]^-$
7100
7200
7300
7400
m/z
c'
400
600
800
1000
Wavelength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

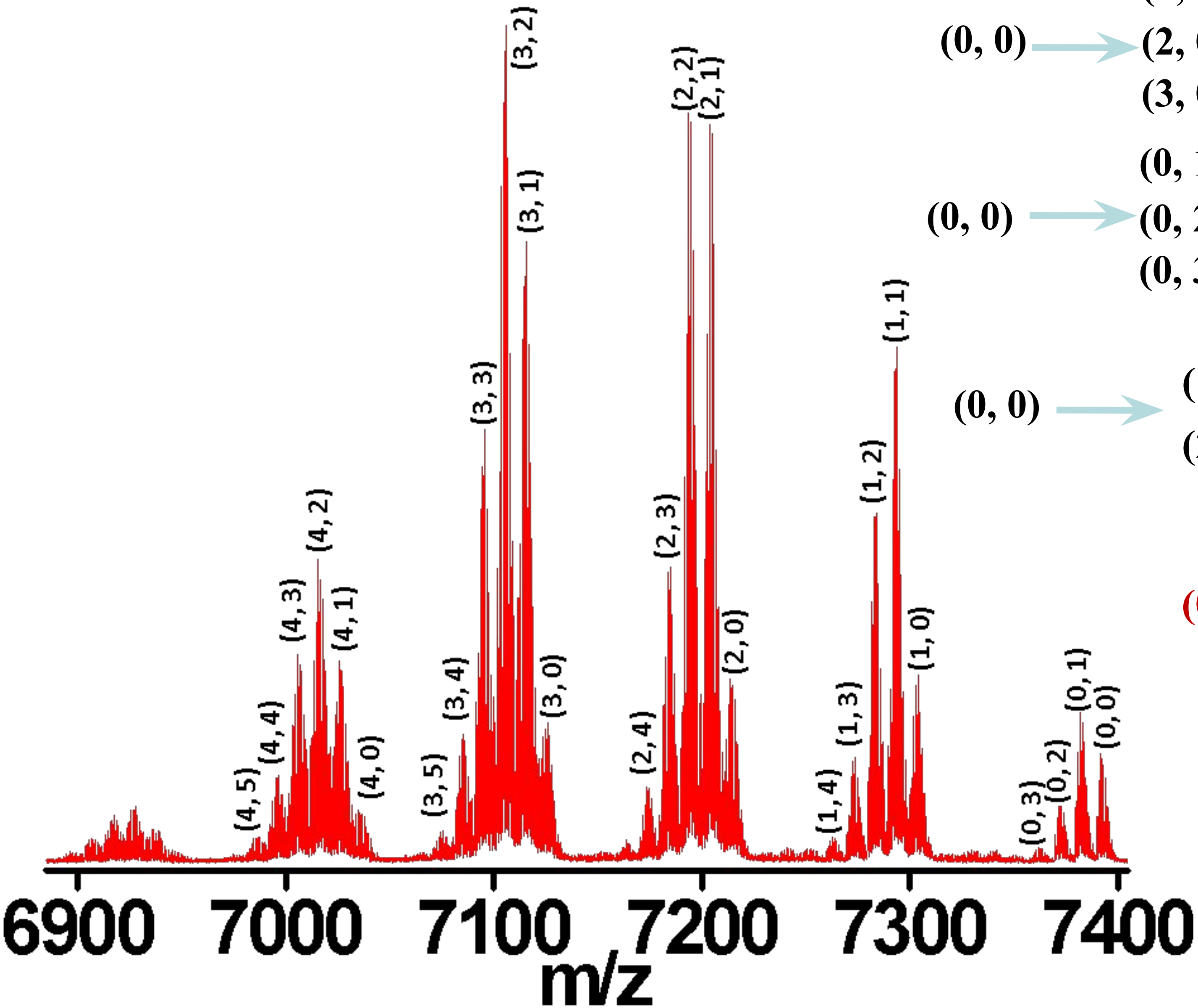
$Au_{25}(PET)_{18} + Ag_{44}(FTP)_{30} \longrightarrow Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y$; x=0-13

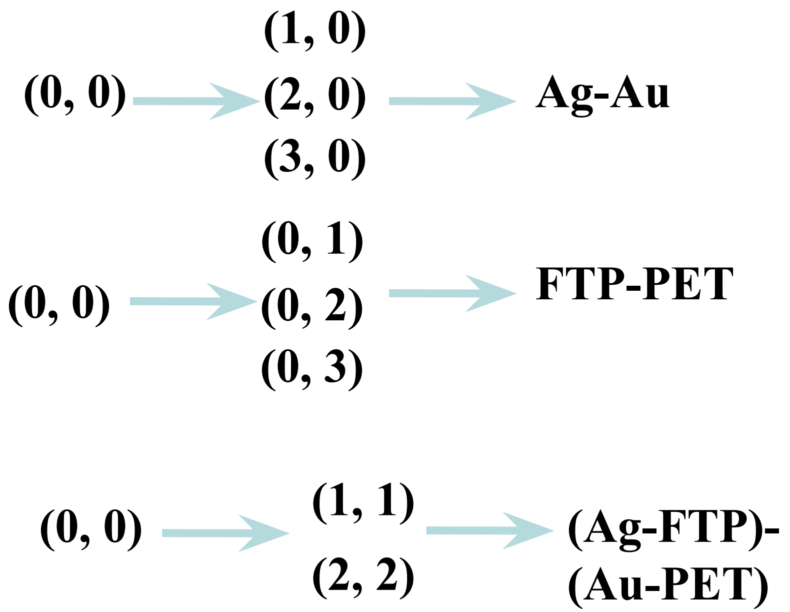
M_{Au}: 197
M_{Ag}: 108

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

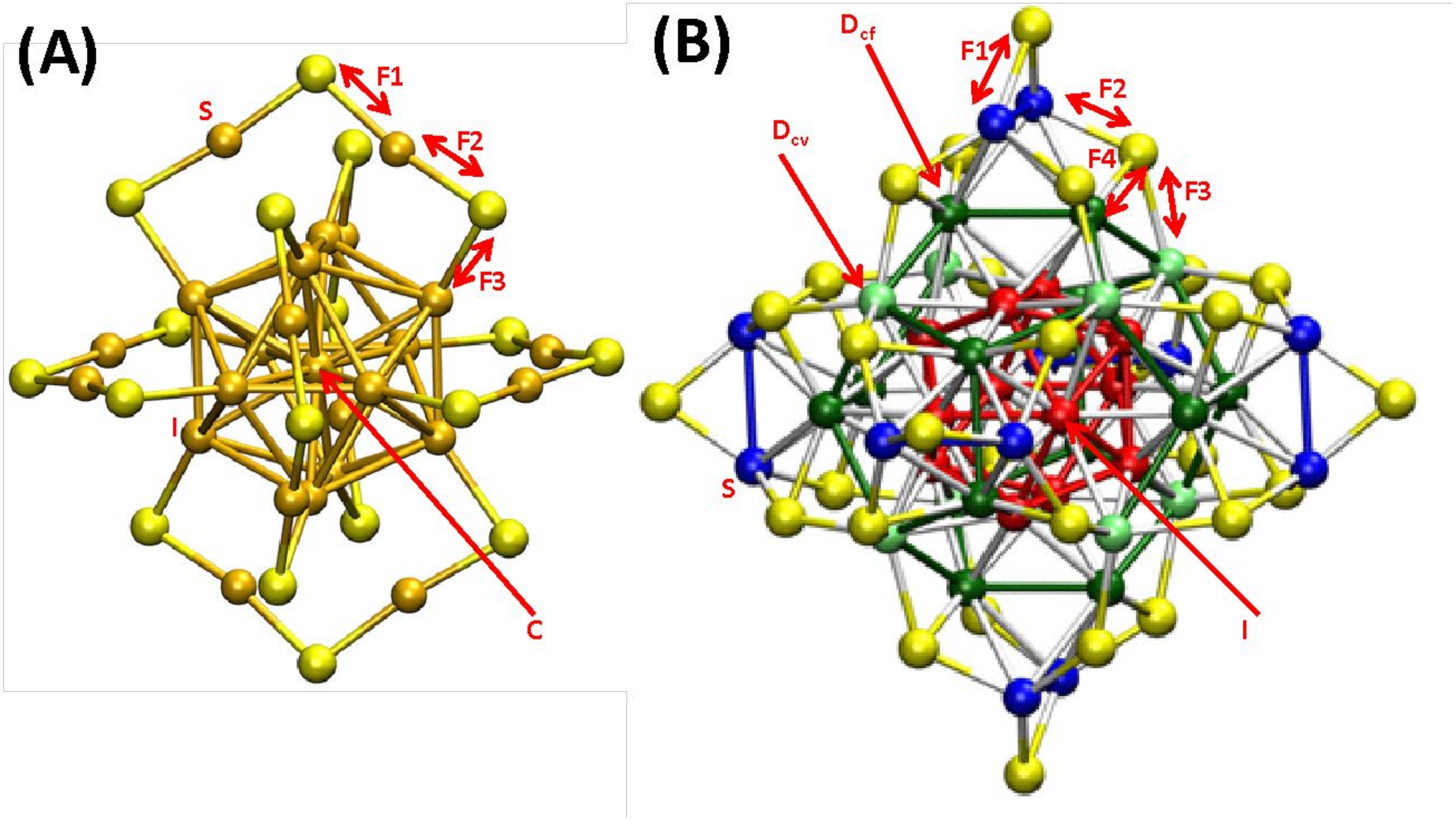


$Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y$: A closer view





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


(A)
S
F1
F2
F3
I
C
(B)
D_cf
F1
F2
D_cv
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

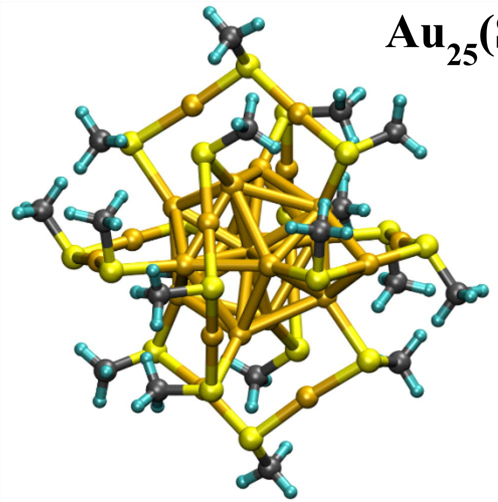
(B)

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

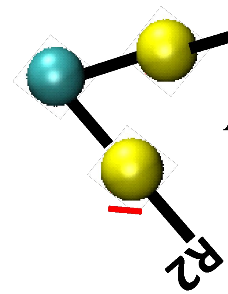
(C)

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

Schematic of the reaction mechanism for Ag-SR/Au-SR substitution

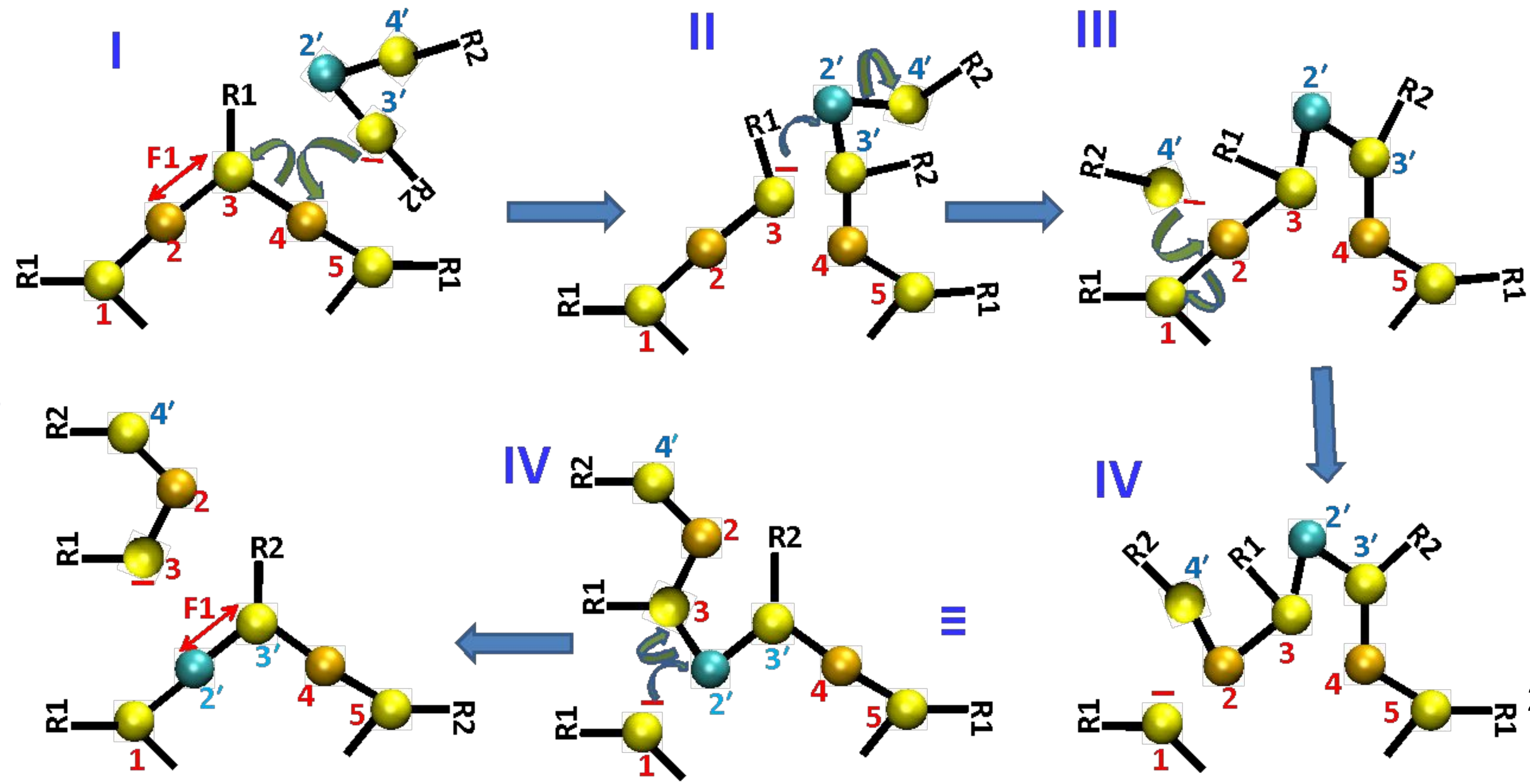


$Au_{25}(SR1)_{18}$

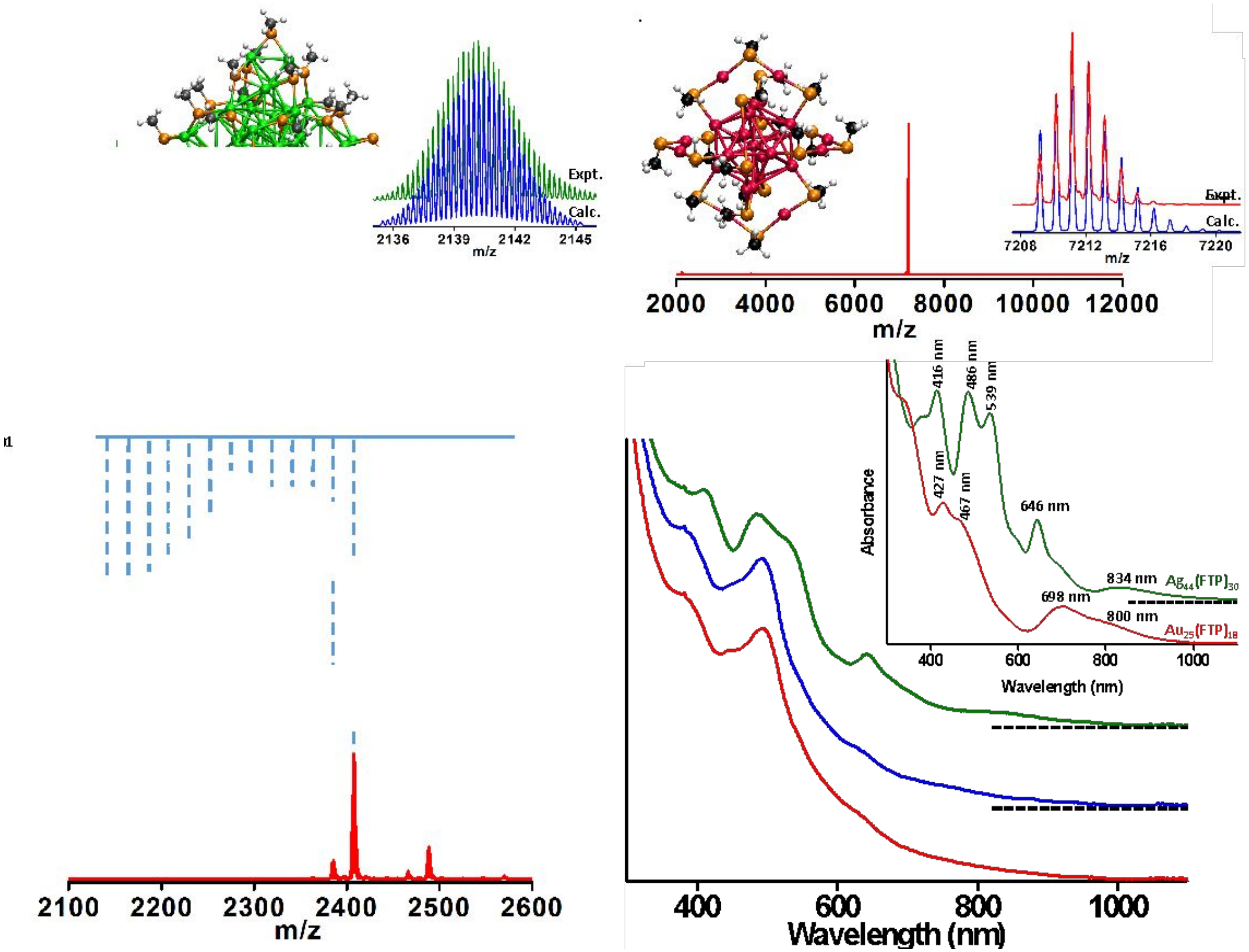


$Ag(SR2)_2$

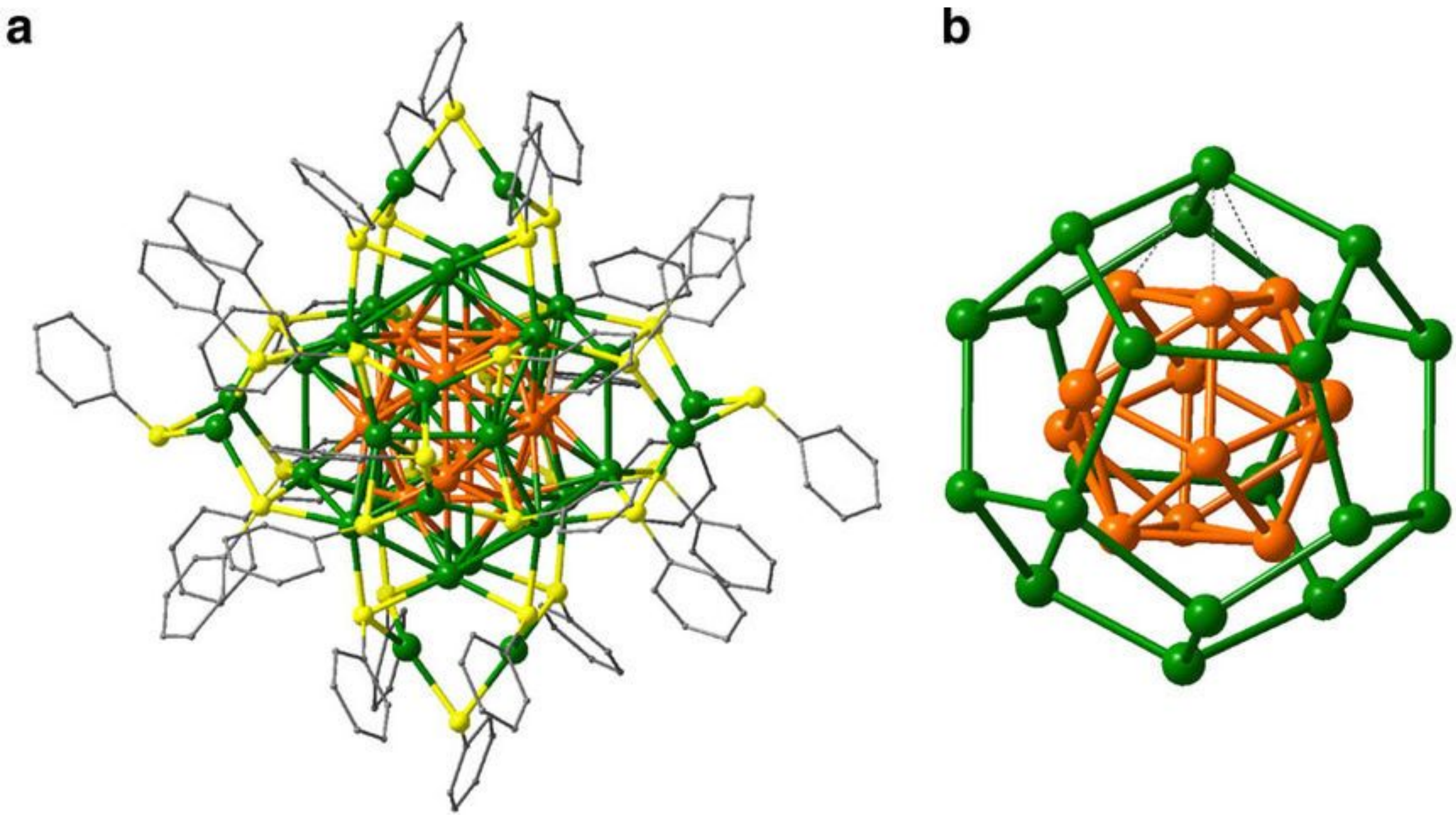
(A)



Shell closure in intercluster reactions

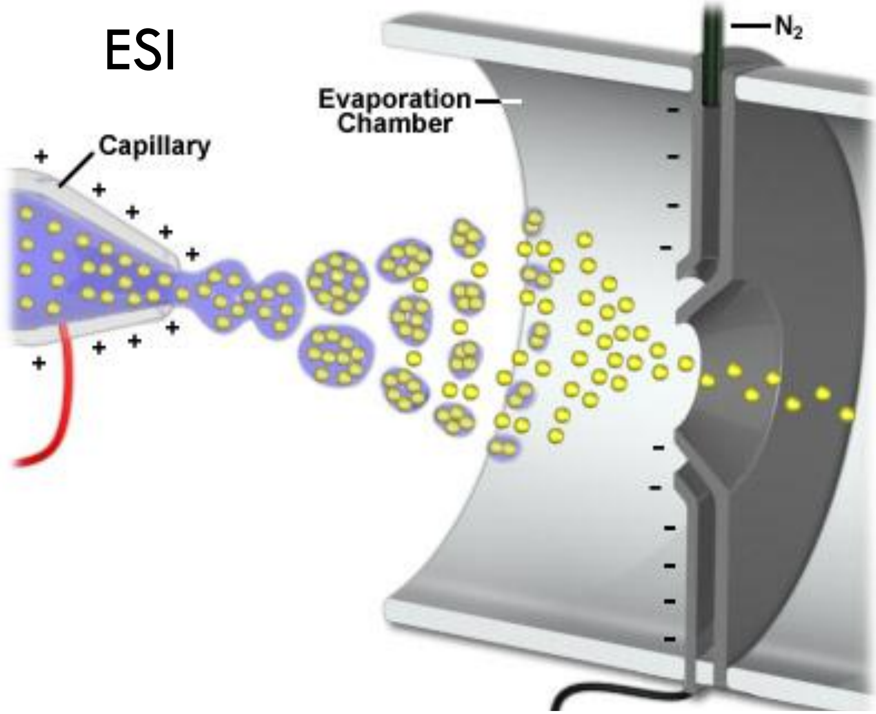


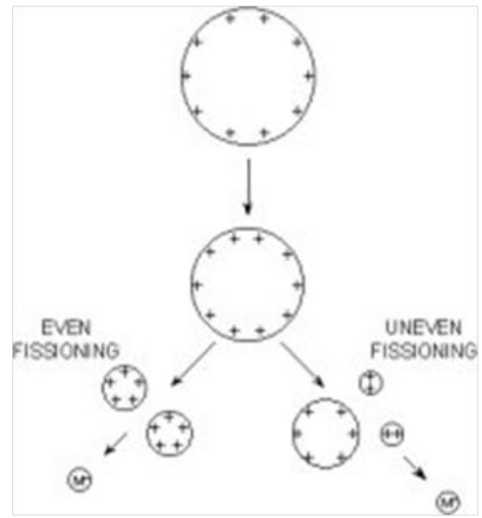
Krishnadas et al., ACS Nano 2017



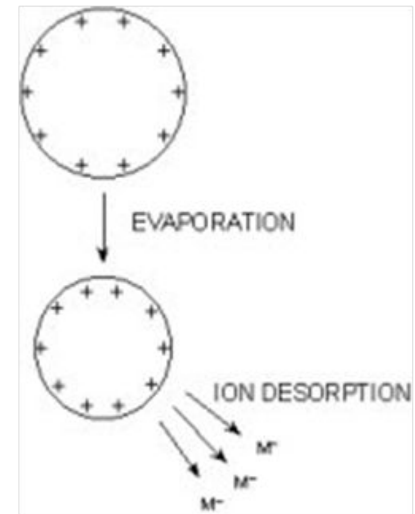
Nanfeng Zheng et al. Nature Communications, 2013

ESI



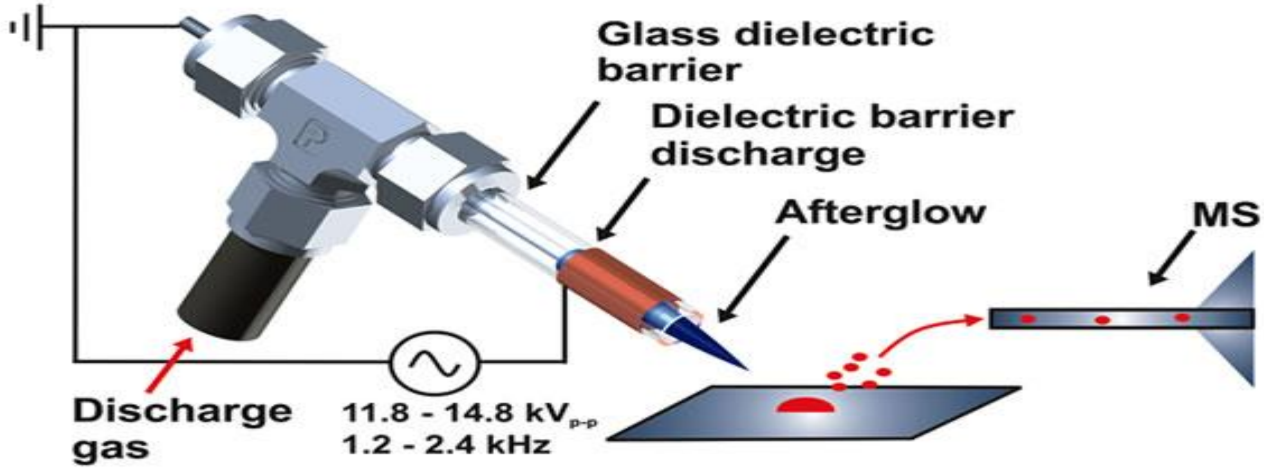


Charge Residue Model

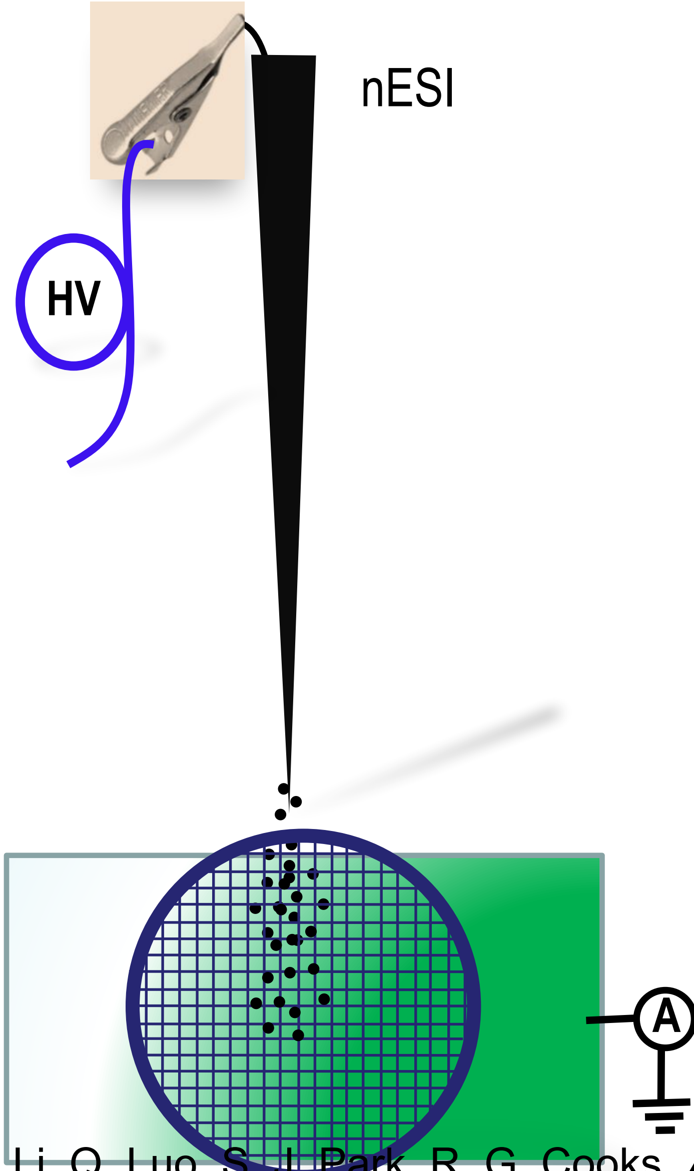


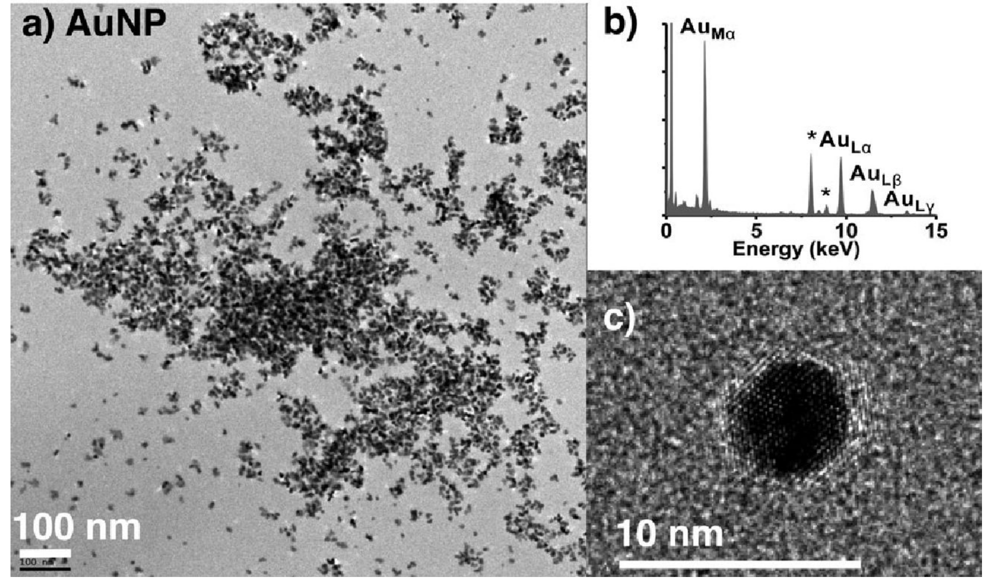
Ion Desorption Model

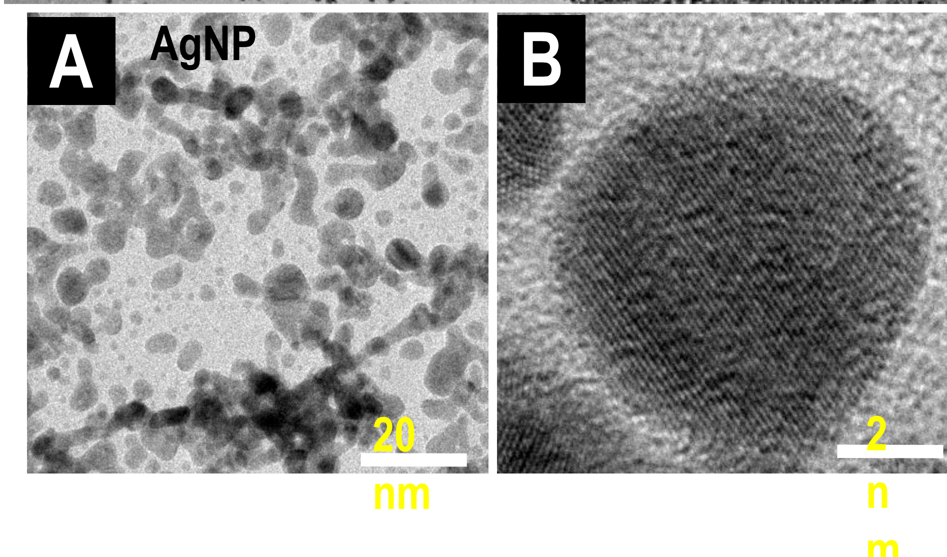
DESI



Z. Takats, J. M. Wiseman, B. Gologan, R. G. Cooks, *Science* **2004**, *306*, 471-473.

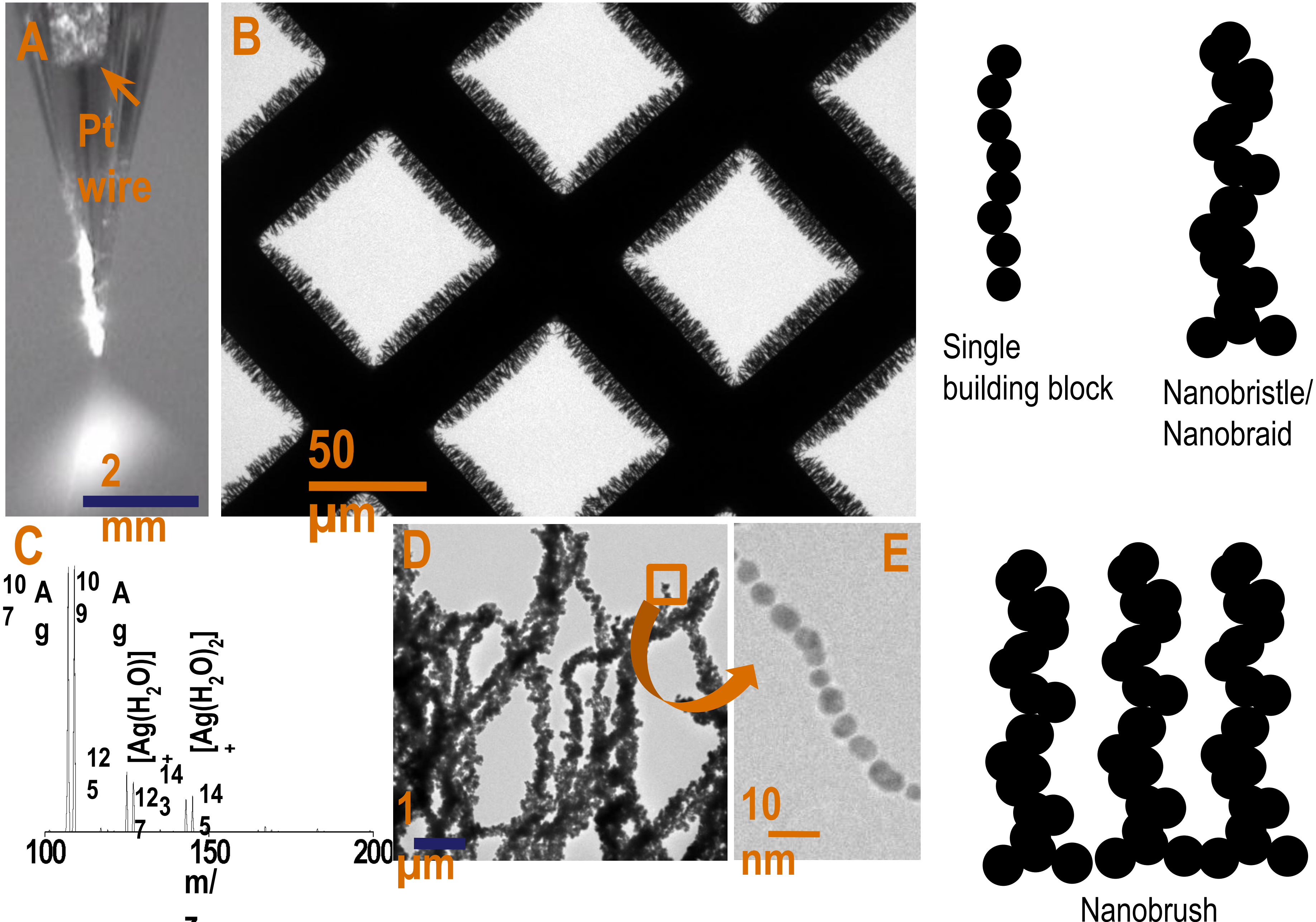






A. Li, Q. Luo, S. J. Park, R. G. Cooks, *Angew. Chem. In. Ed.* **2014**, 53, 3147 –3150.

A. Li, Z. Baird, S. Bag, D. Sarkar, A. Prabhath, T. Pradeep, R. G. Cooks, *Angew. Chem. In. Ed.* **2014**, *53*, 12528-12531.

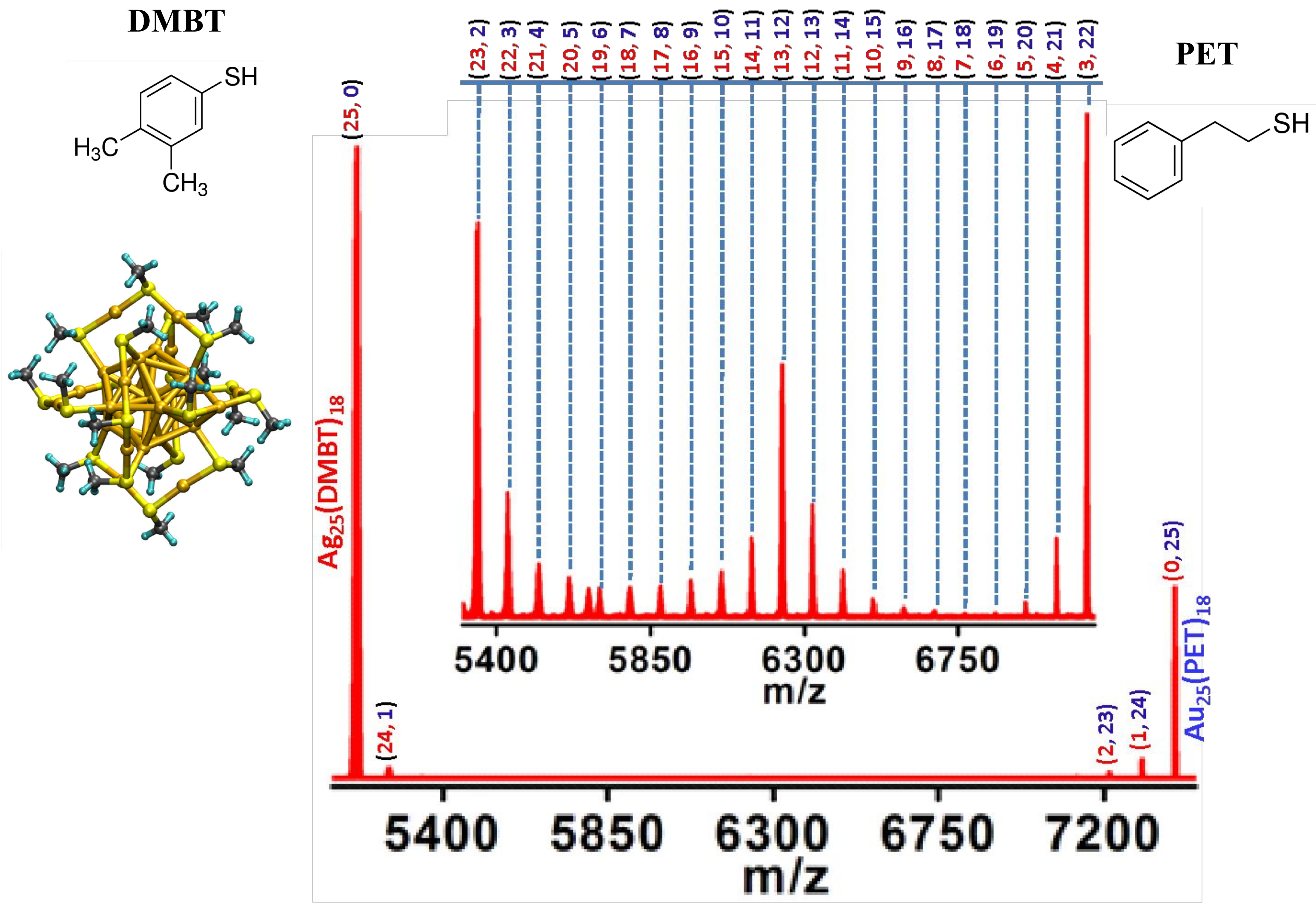


D. Sarkar, M. K. Mahitha, A. Som, A. Li, M. Wleklinski, R. G. Cooks, T. Pradeep, *Adv. Mater.* **2016**, *28*, 2223-2228.

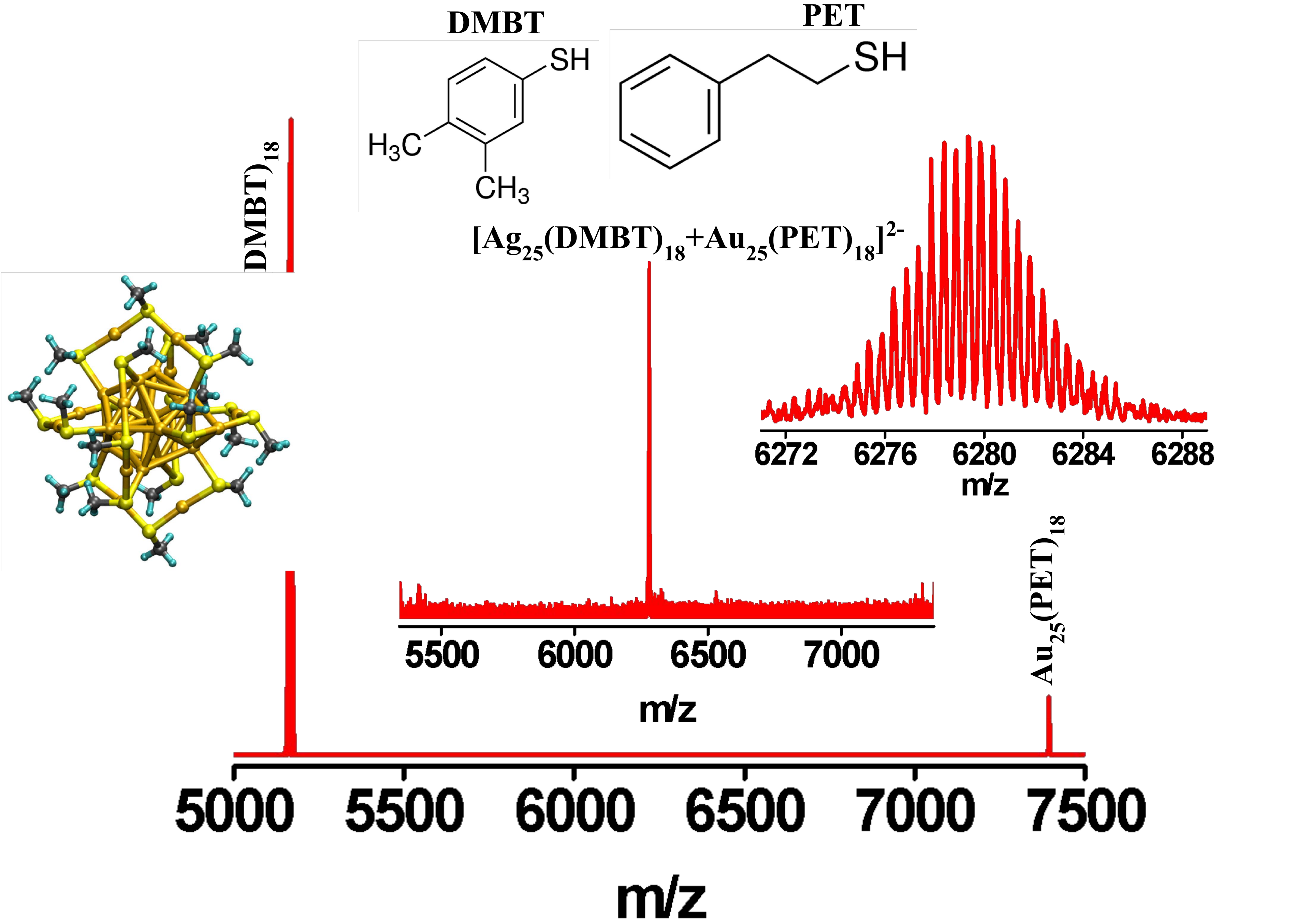
Ag_{25}-Au_{25} experiments

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

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

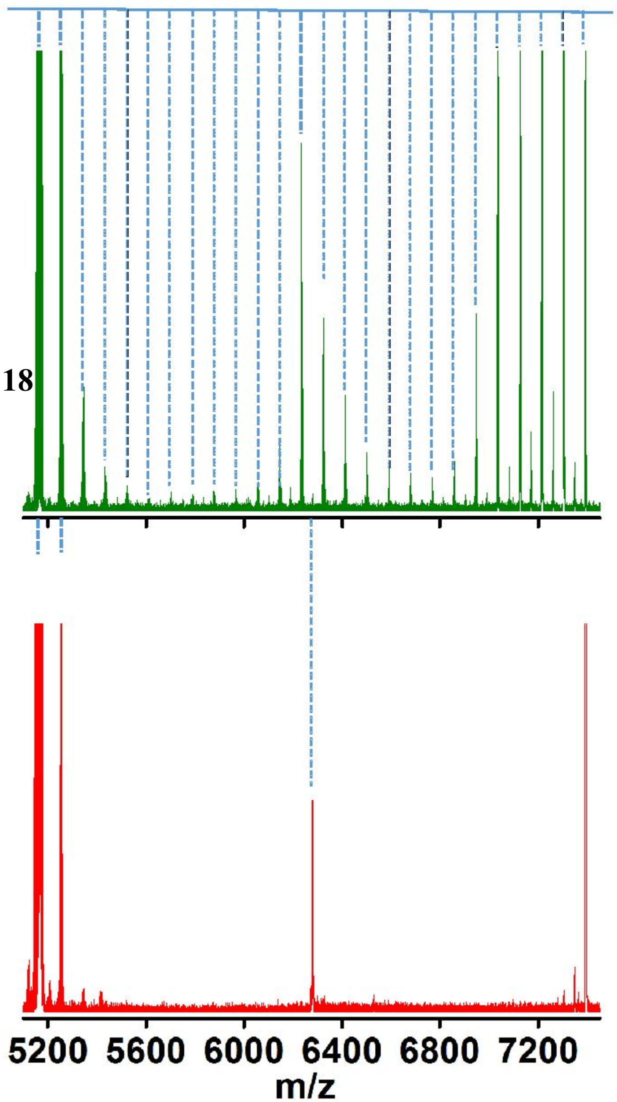


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

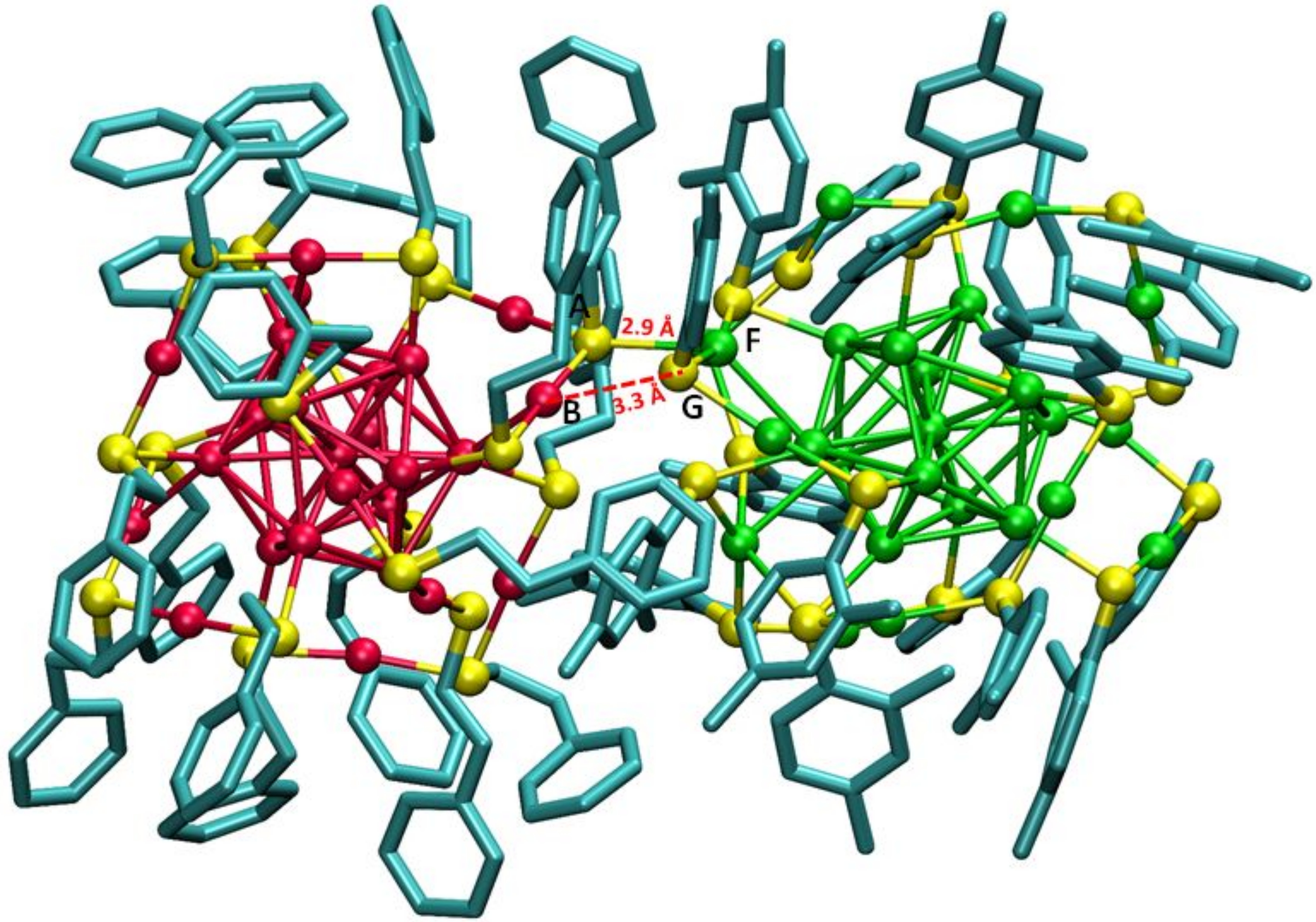
$Ag_{25}(DMBT)_{18}:Au_{25}(PET)_{18}$
0.3:1.0



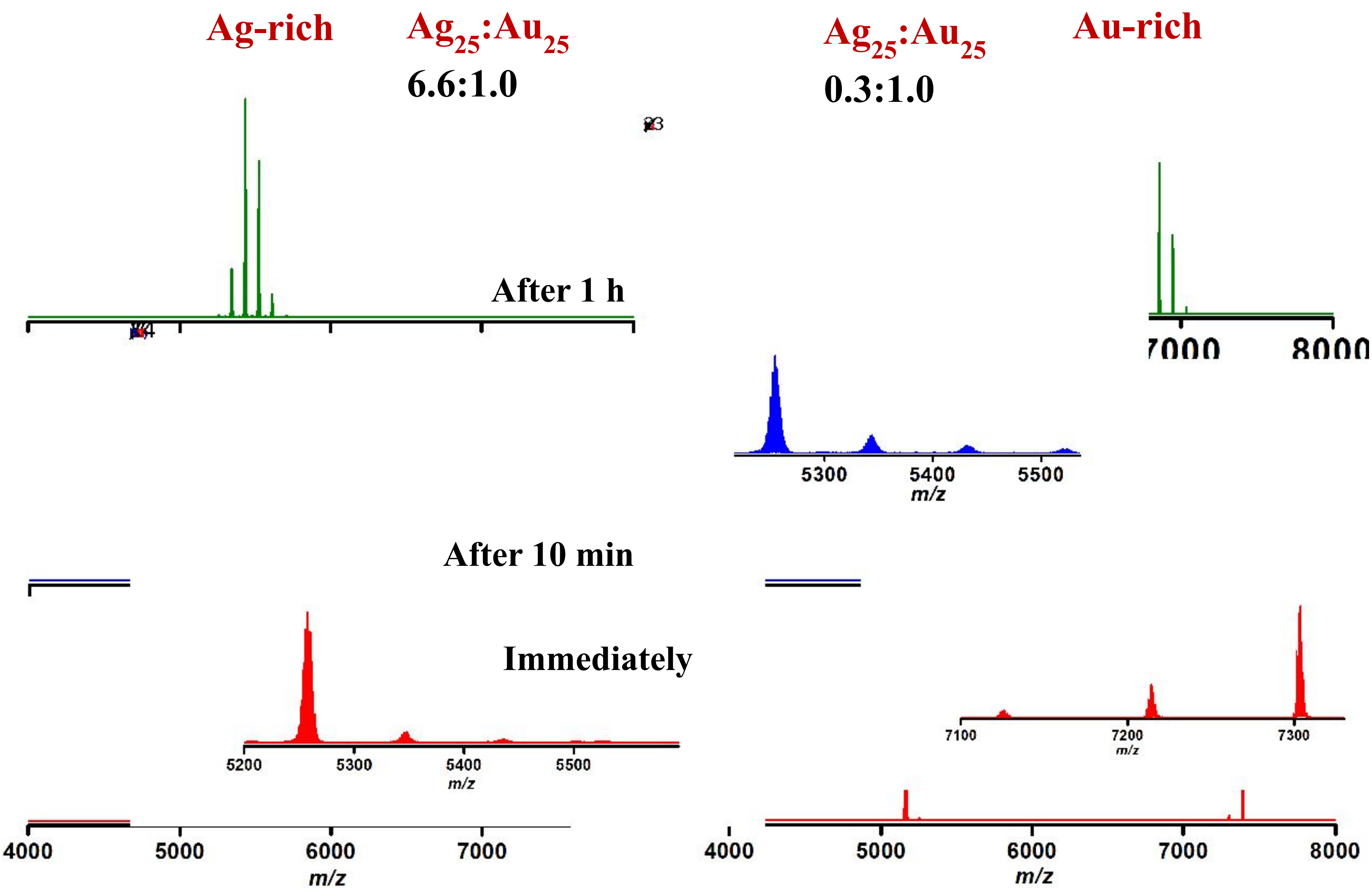
within 5 min

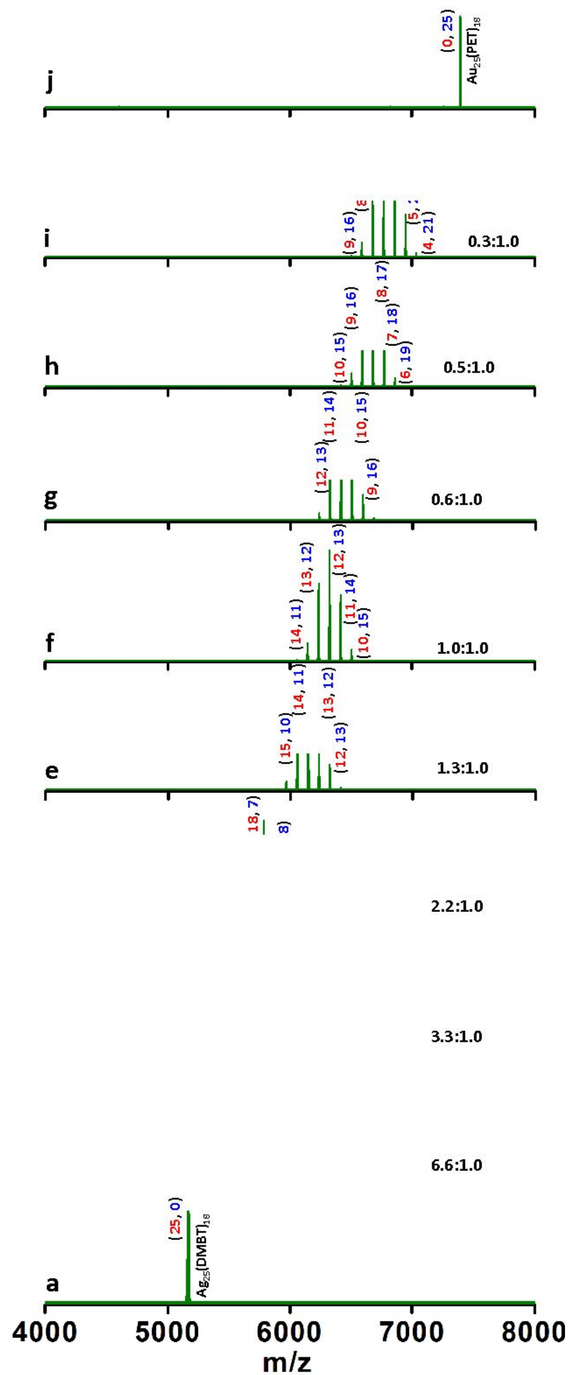
within 2 min

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



Formation of Ag-rich or Au-rich $Ag_mAu_n(SR)_{18}$ (m+n=25) clusters





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

Calculated energies for the substitution reaction (ΔE_s) of Au in $Ag_{25}(DMBT)_{18}$ (a), Ag in $Au_{25}(PET)_{18}$ (b) and the overall reaction energies (c), in meV, as a function of their positions in the product clusters, $Ag_{24}Au_1(DMBT)_{18}$ and $Au_{24}Ag_1(PET)_{18}$.

a

Location of Au in $Ag_{24}Au(DMBT)_{18}$	ΔE_s/meV
Centre of icosahedron (C)	-904
Icosahedron (I)	-540
Staple (S)	-578

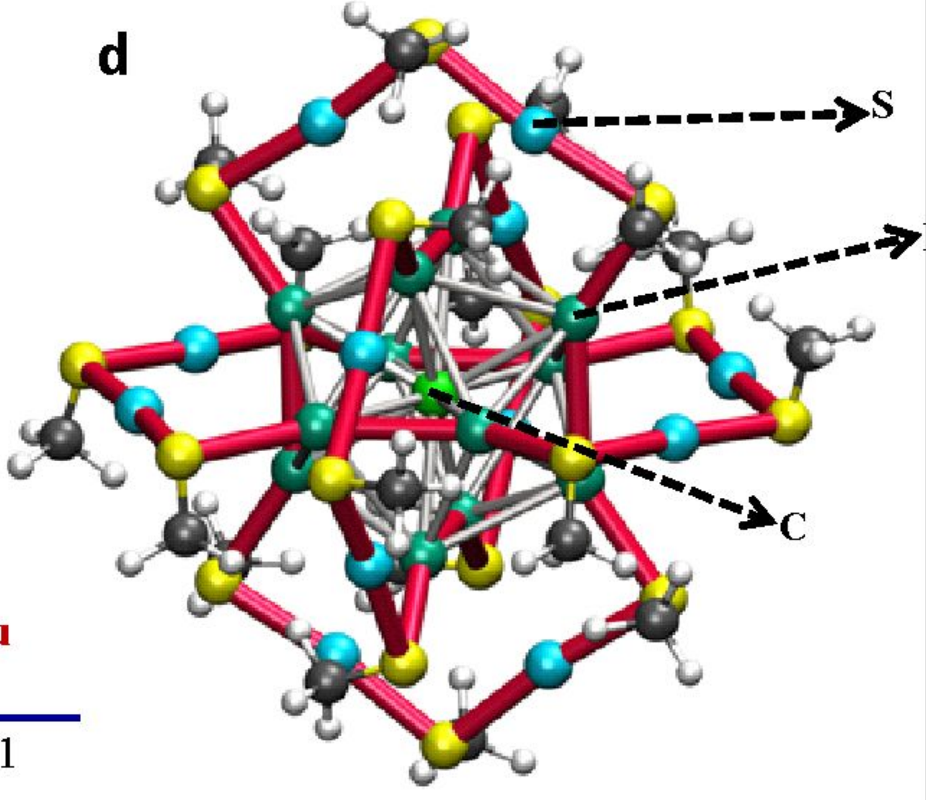
b

Location of Ag in $Au_{24}Ag(PET)_{18}$	ΔE_s/meV
Centre of icosahedron (C)	+396
Icosahedron (I)	-44
Staple (S)	+224

c

Location of Ag in $Au_{24}Ag$	Location of Au in $Ag_{24}Au$		
	C	I	S
C	-507	-143	-181
I	-948	-584	-622
S	-679	-315	-354

d

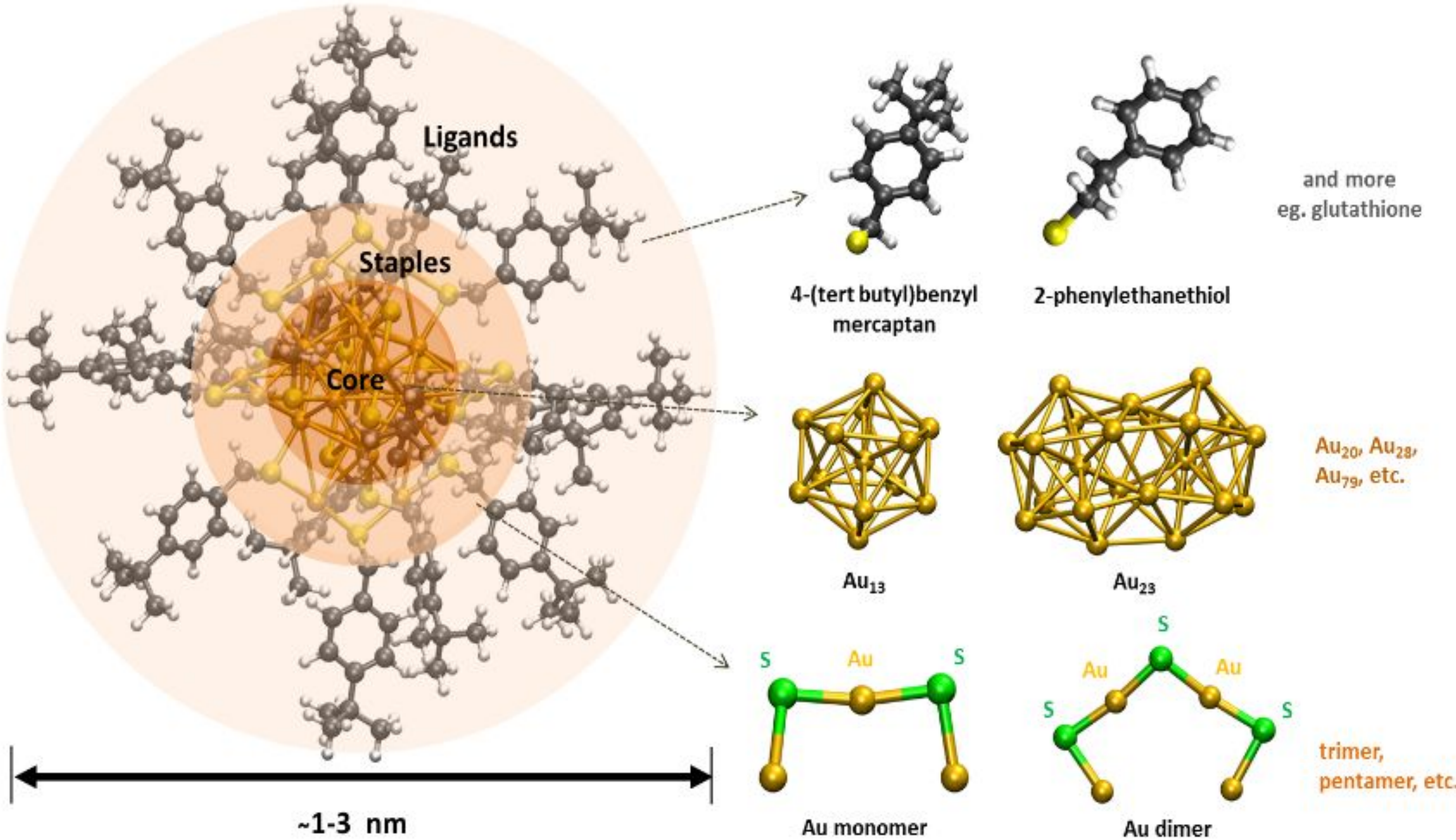


How do we comprehend this?

Structure and name

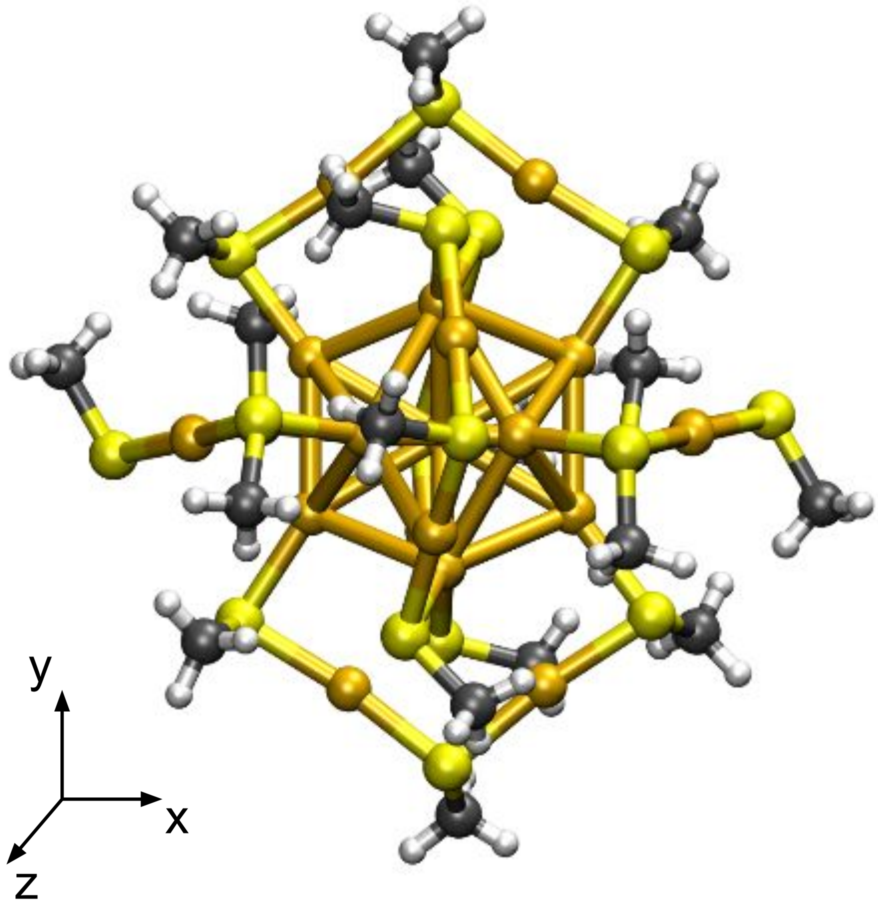
- Current names
  - $Au_{25}(SR)_{18}$, $Au_{25}(SR)_{18}$, Au@R, or just Au_{25}
  - $Au_{25-m}\,Pd_m(SR1)_{18-n}(SR2)_n$
- Complexity: eg. Isomers and chirality
- => Nomenclature
  - Organic, inorganic, etc.
  - Fullerenes
  - Boranes

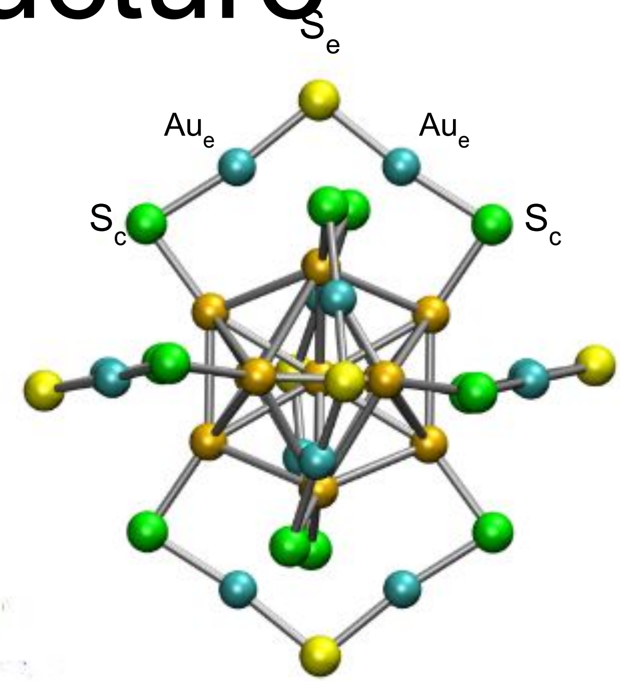
What are these materials?



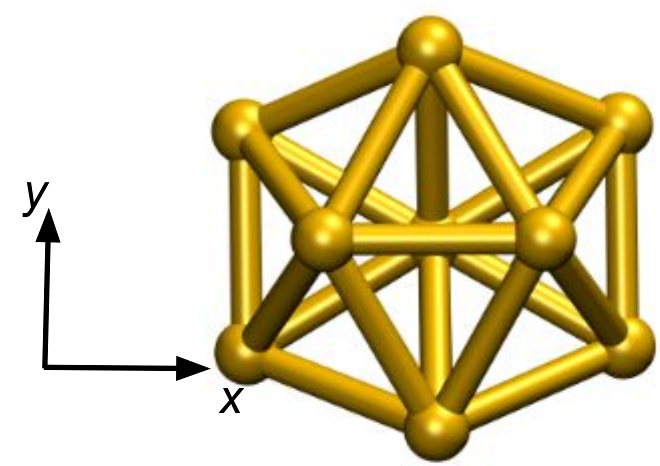
Aspicules

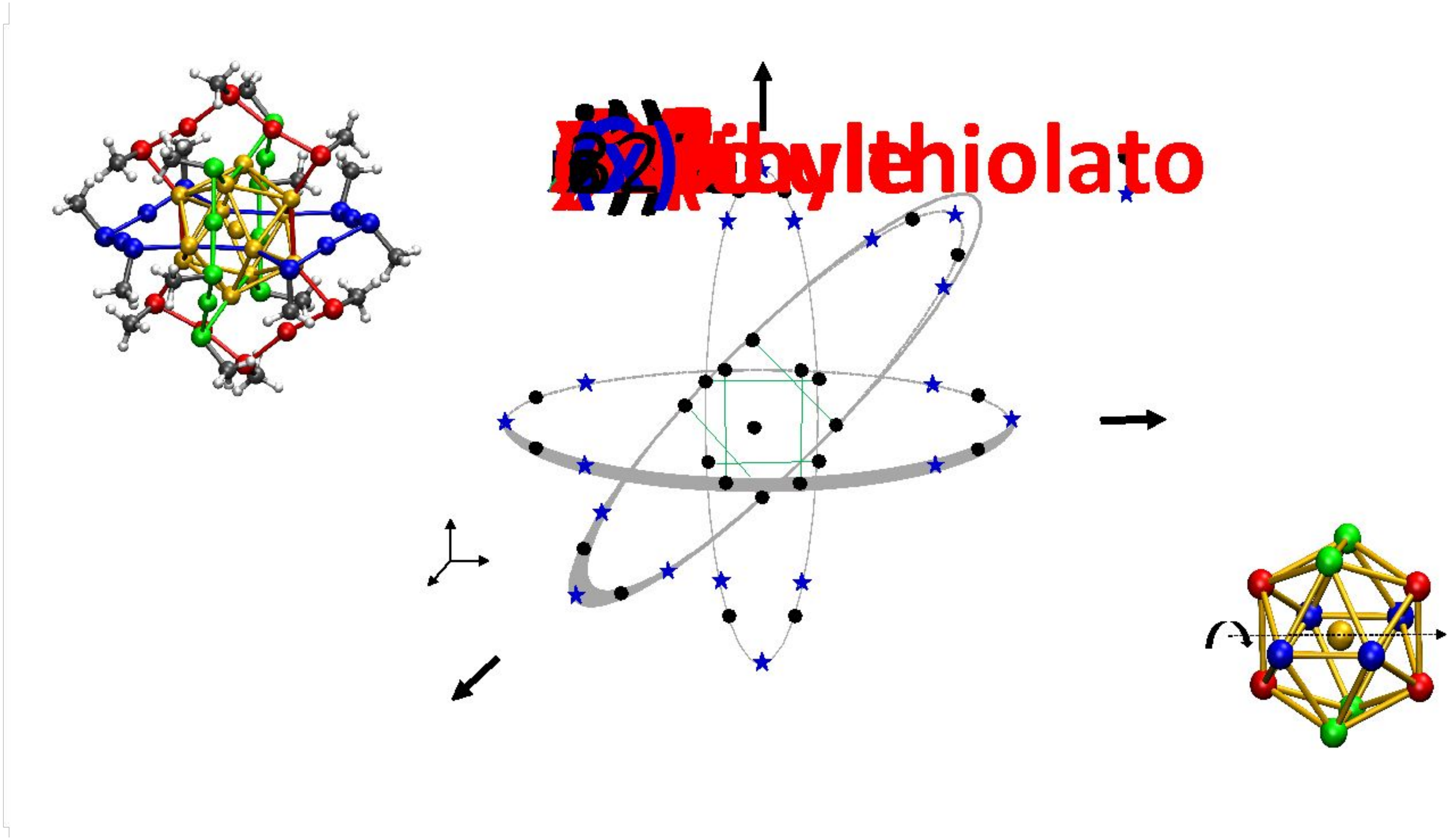
Ball and stick structure





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 .





18(methylthiolato)-auro-25
aspicule(1-)

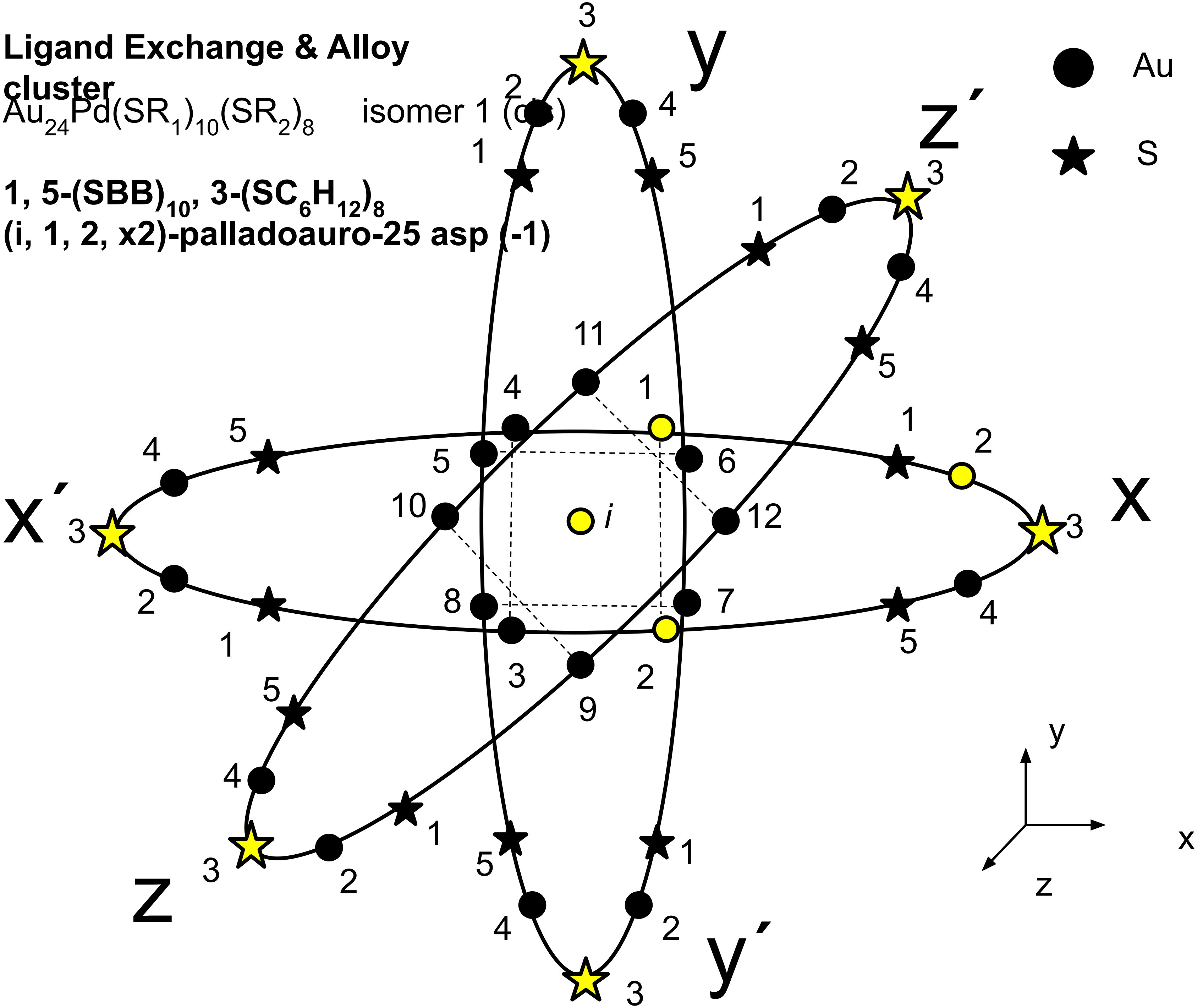
Gana Natarajan et. al. JPC C. 2015

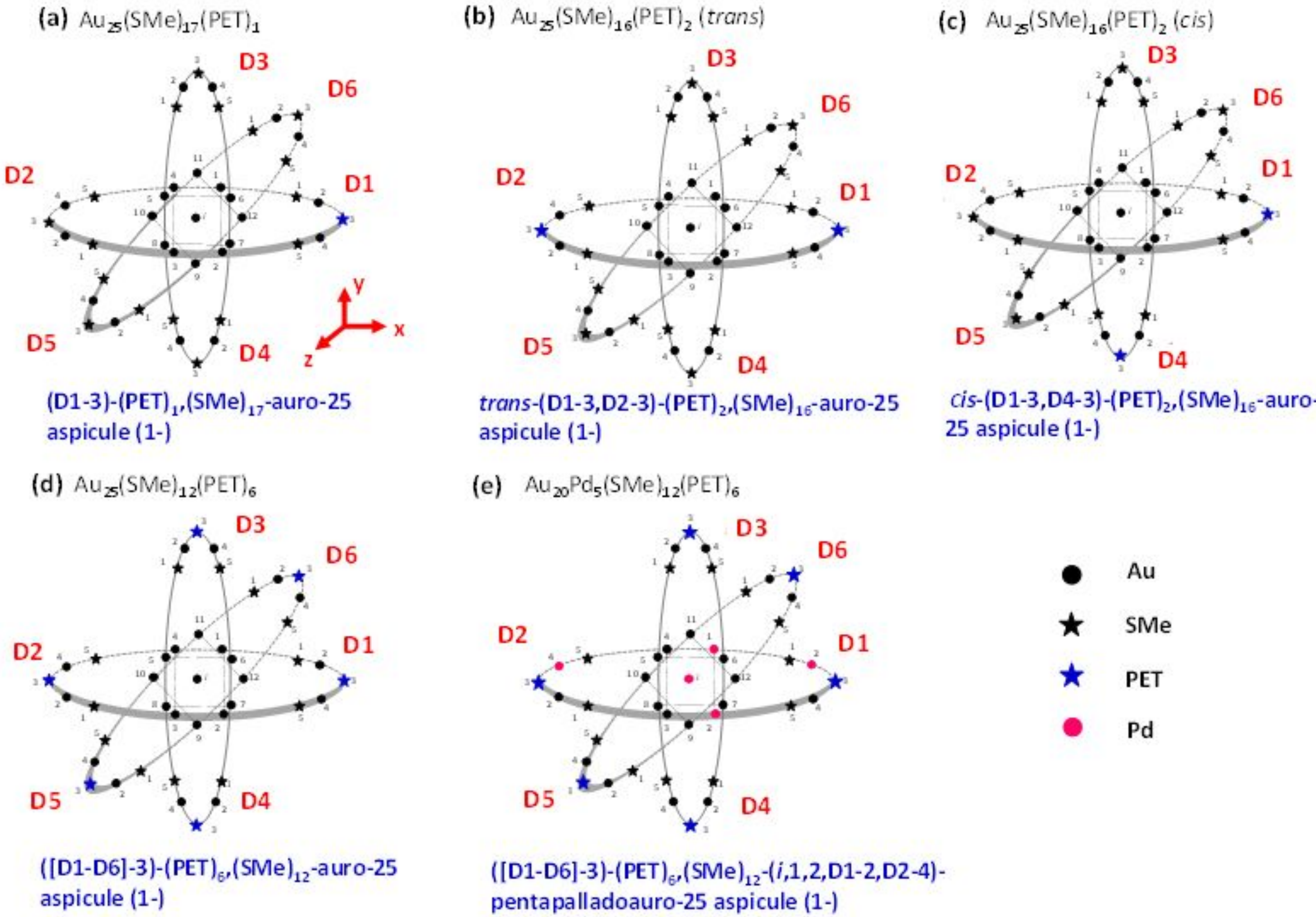
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule(1-)

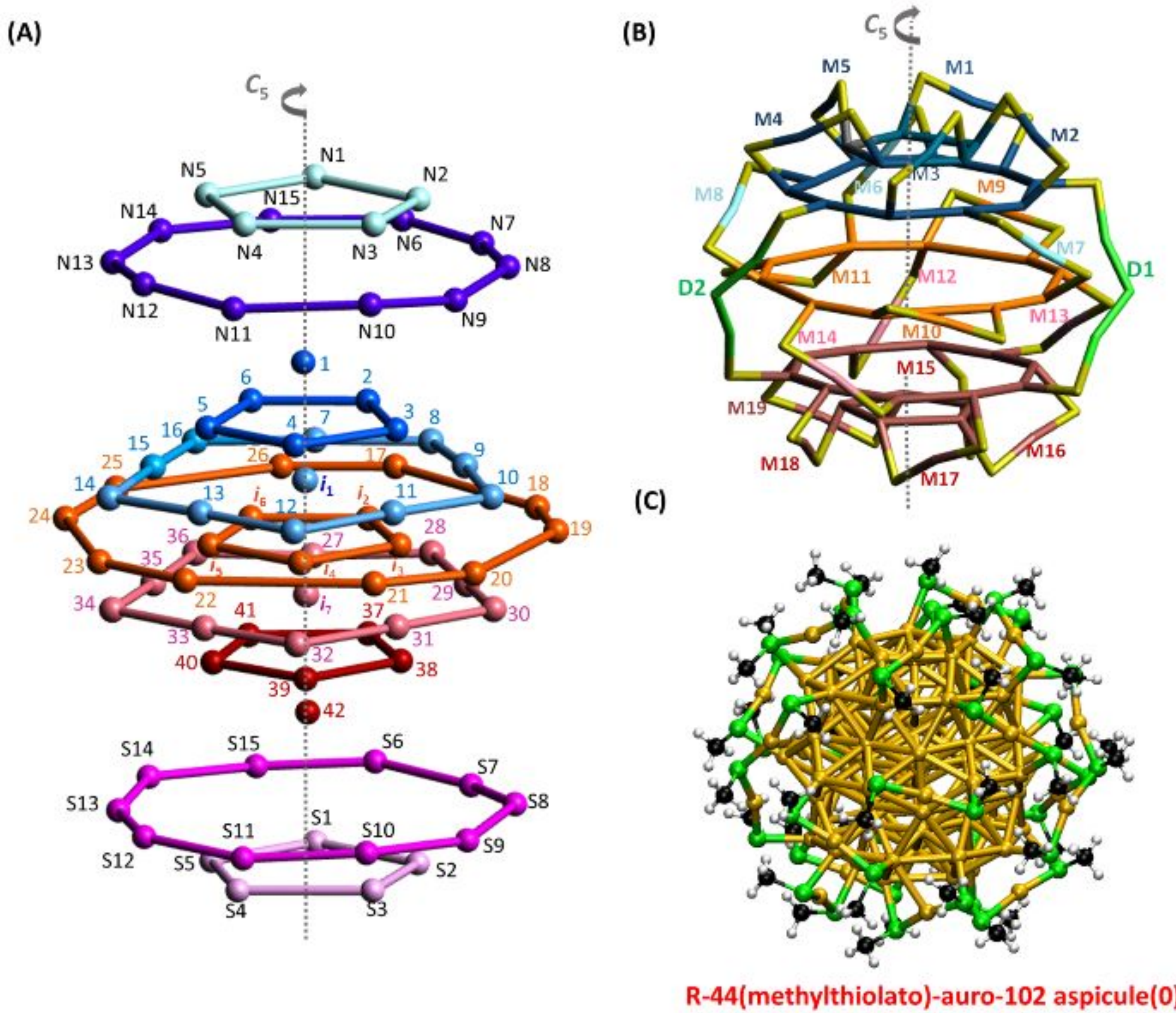
Ligand Exchange & Alloy cluster

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

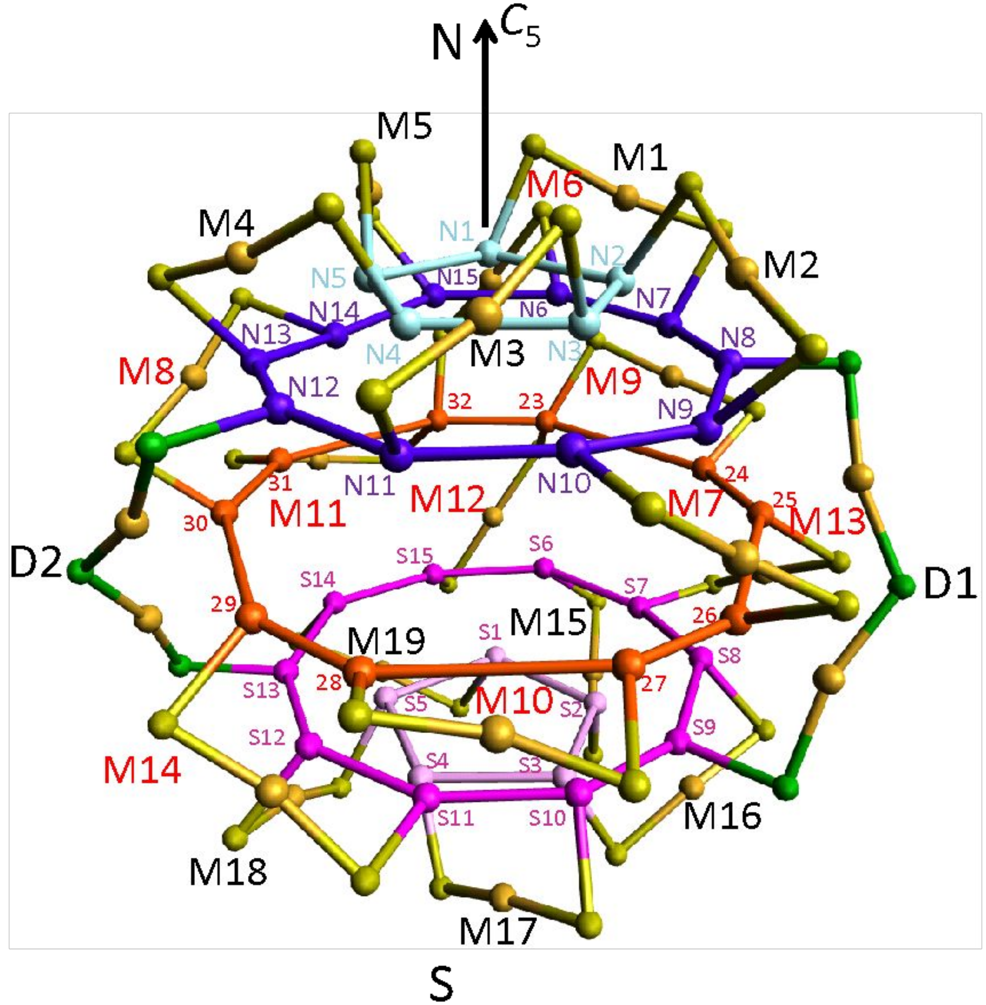
1, 5-$(SBB)_{10}$, 3-$(SC_6H_{12})_8$
(i, 1, 2, x2)-palladoauro-25 asp (-1)




(a) $Au_{25}(SMe)_{17}(PET)_1$
D1
D2
D3
D4
D5
D6
y
x
z
(D1-3)-$(PET)_1$,$(SMe)_{17}$-auro-25 aspicule (1-)
(b) $Au_{25}(SMe)_{16}(PET)_2$ (*trans*)
trans-(D1-3,D2-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule (1-)
(c) $Au_{25}(SMe)_{16}(PET)_2$ (*cis*)
cis-(D1-3,D4-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule (1-)
(d) $Au_{25}(SMe)_{12}(PET)_6$
([D1-D6]-3)-$(PET)_6$,$(SMe)_{12}$-auro-25 aspicule (1-)
(e) $Au_{20}Pd_5(SMe)_{12}(PET)_6$
([D1-D6]-3)-$(PET)_6$,$(SMe)_{12}$-(*i*,1,2,D1-2,D2-4)-pentapalladoauro-25 aspicule (1-)
Au
SMe
PET
Pd



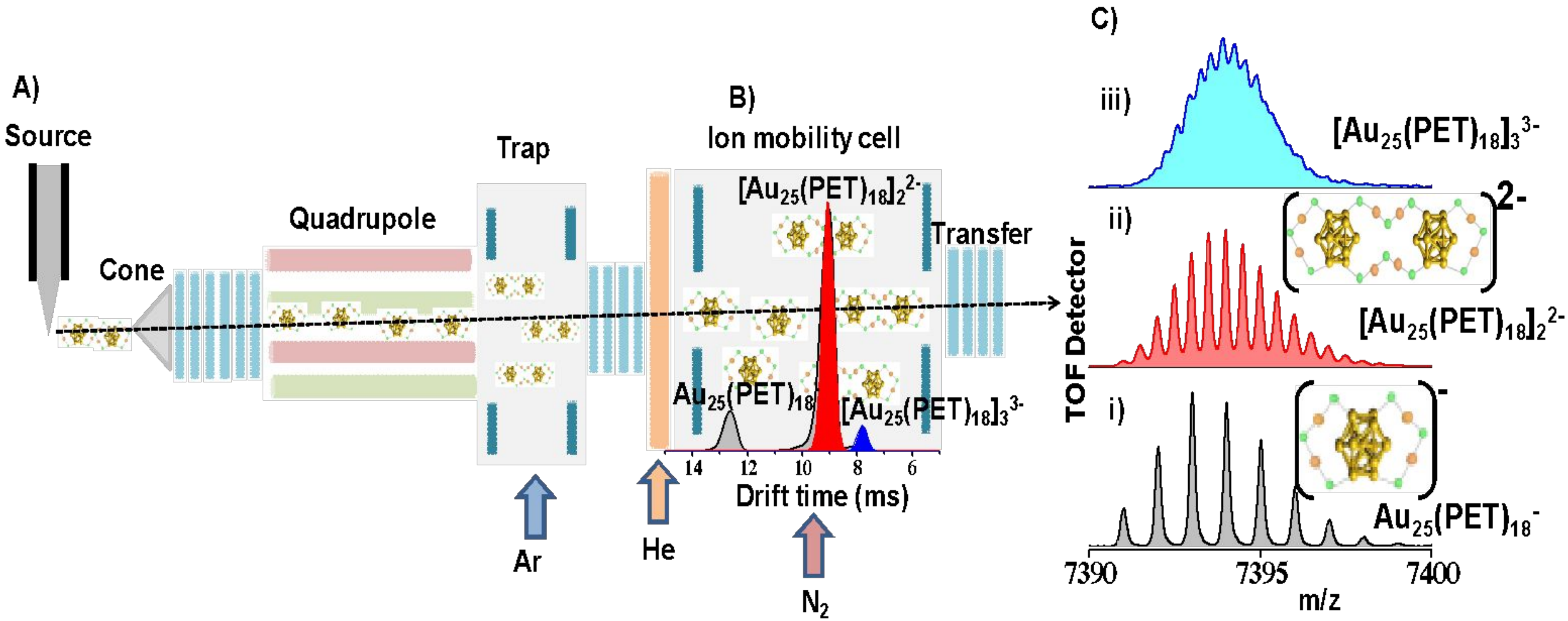
R-(SMe)$_{44}$-auro-102 aspicule**(**0**)** and L-(SMe)$_{44}$-auro-102 aspicule**(**0**)**


N
C_5
M5
M1
M6
M4
N1
N2
M2
N5
N15
N7
N14
N6
N8
N13
N4
M3
N3
M8
N12
32
23
M9
N9
31
24
N11
N10
25
M11
M12
M7
M13
30
S15
S6
D2
S14
S7
D1
29
S1
M15
26
M19
S8
S13
28
S5
M10
S2
27
S12
S9
M14
S4
S3
S11
S10
M16
M18
M17
S

Compact aspicule structural names for Au_{25}, Au_{38} and Au_{102} aspicules and one modification of each.

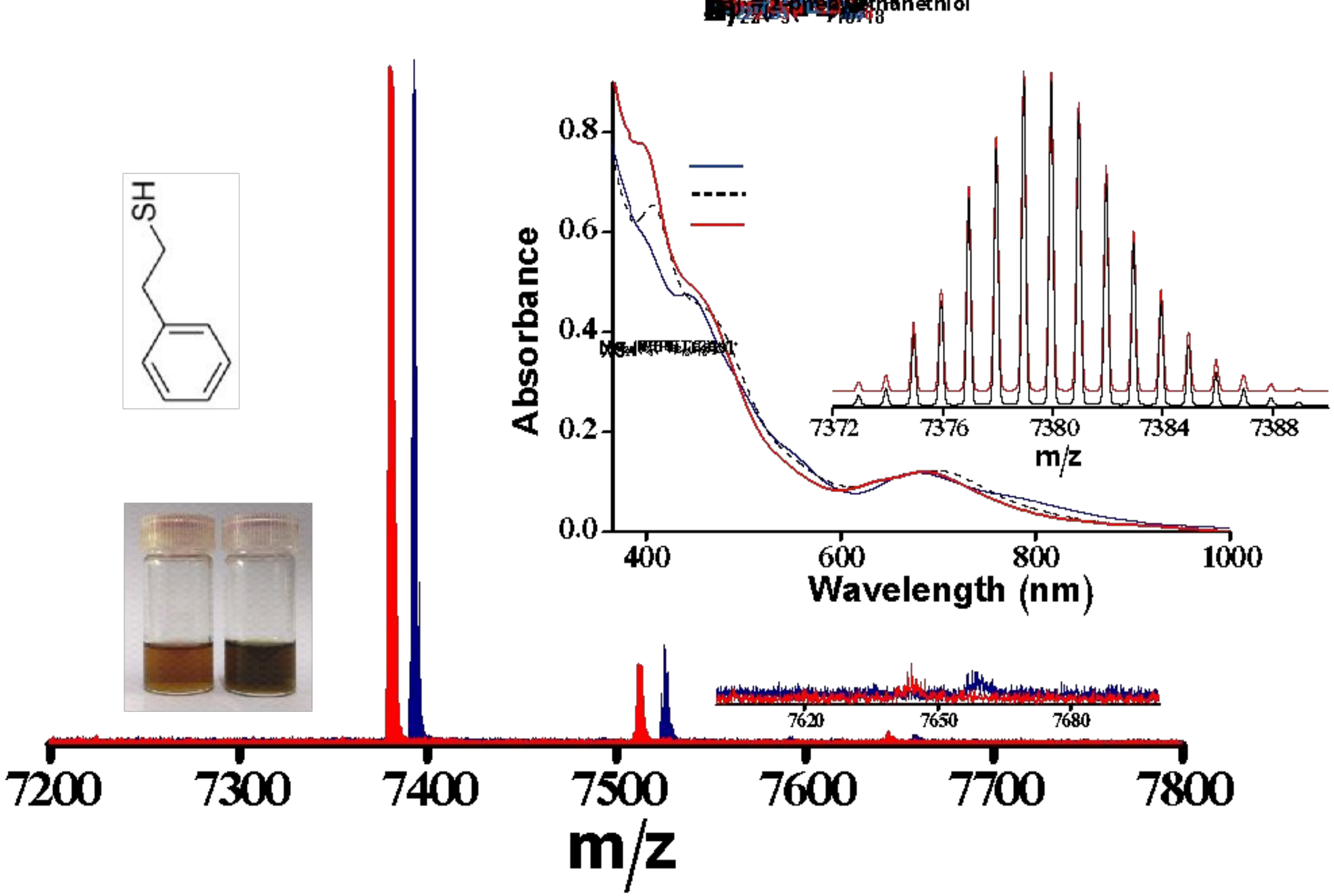
Formula Name/substituent positions	Compact Aspicule Structural Name	Aspicule name
$Au_{25}(SMe)_{18}$	[D1-D6]-[1, 3, 5-Me-Au_2S_3]$_6$ *I-i*-auro-25 aspicule (1-)	$(SMe)_{18}$ auro-25 (1-)
$Au_{23}Pd_2(SMe)_{16}(SPET)_2$ Two Pd in the core. Two PET at the bridging ligands	D1, D2-[1, 3, 5-Me-$AuPdS_3$]$_2$, [D3-D6]-[1,3,5-Me-Au_2S_3]$_4$ *I-(i,2)*-dipalladoauro-25 aspicule (1-)	(D1-3, D2-3)-$(SPET)_2$, $(SMe)_{16}$ (*i*, 2)-dipalladoauro-25 (1-)
$Au_{38}(SMe)_{24}$	[D1-D6]-[1, 3, 5-Me-Au_2S_3]$_6$, [M1-M3]-[1, 3-Me-AuS_2]$_2$ *BI*-(i_1, i_2)-auro-38 aspicule (0)	$(SMe)_{24}$ (i_1, i_2)-auro-38 aspicule (0)
$Au_{36}Pd_2(SMe)_{22}(SPET)_2$ Two Pd atoms in interstials. Two PET ligands in dimer staples	D1, D2- [3-PET, 1,5-Me-Au_2S_3]$_2$, [D3-D6]-[1, 3, 5-Me-Au_2S_3]$_4$, [M1-M3]-[1, 3 -Me-AuS_2]$_3$ *BI*-(i_1, i_2)-dipalladoauro-38 aspicule (0)	(D1-3, D2-3, M1-1, M2-3)-$(SPET)_4$, $(SMe)_{20}$ (i_1, i_2)-dipalladoauro-38 aspicule (0)
$Au_{102}(SMe)_{44}$	[M1-M19]-[1, 3-Me-AuS_2]$_{19}$, D1, D2-[1, 3-Me-Au_2S_3]$_2$ *MD_{49}@(N-RID_{15},S-RID_{15})*-auro-102 aspicule (0)	$(SMe)_{44}$ auro-102 aspicule (0)
$Au_{100}Pd_2(SMe)_{40}(SPET)_4$ Two Pd atoms in the MD core. Two PET ligands at bridging ligands of the dimer staples and two on differnt monomer staples.	M1-[1-PET, 3-Me-AuS_2], M2-[3-PET, 1-Me-AuS_2], [M3-M19]-[1,3-Me-AuS_2]$_{17}$, D1, D2-[3-PET, 1, 5-Me-Au_2S_3]$_2$ *MD_{49}@(N-RID_{15},S-RID_{15})*-(1, 49)-dipalladoauro-102 aspicule (0)	(D1-3, D2-3, M1-1, M2-3)-$(SPET)_4$, $(SMe)_{40}$ (1,49)-dipalladoauro-102 aspicule (0)

Cluster dimers

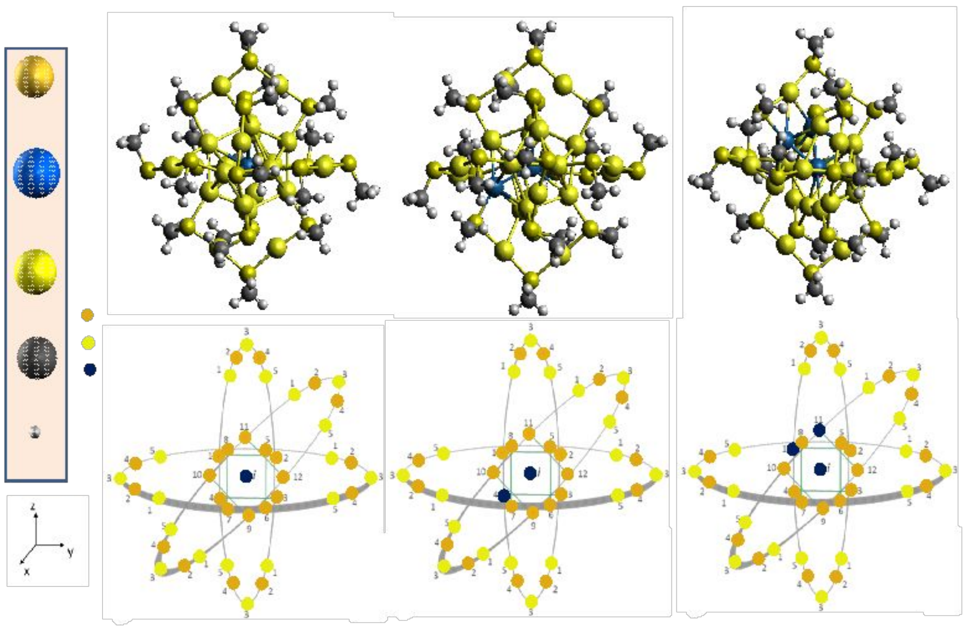


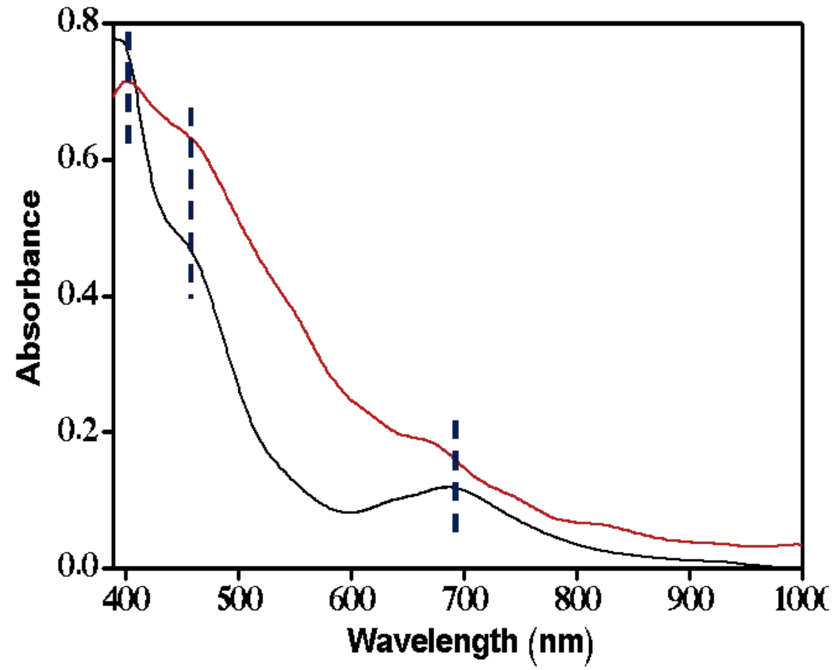
Ananya Baksi et al. Chem. Commun. 2016

Precision alloys



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





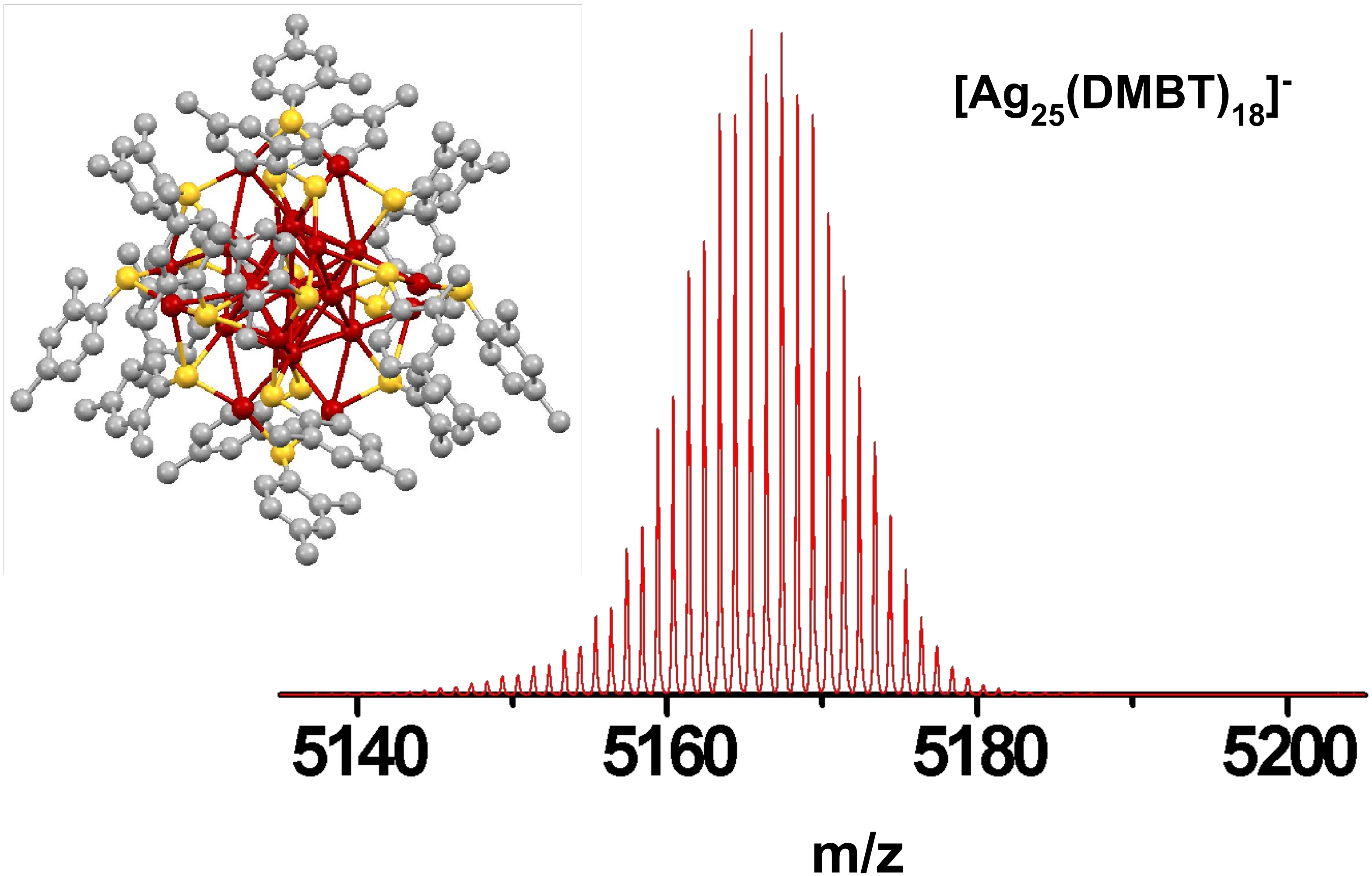
Absorbance
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
400
500
600
700
800
900
1000

Cluster dynamics

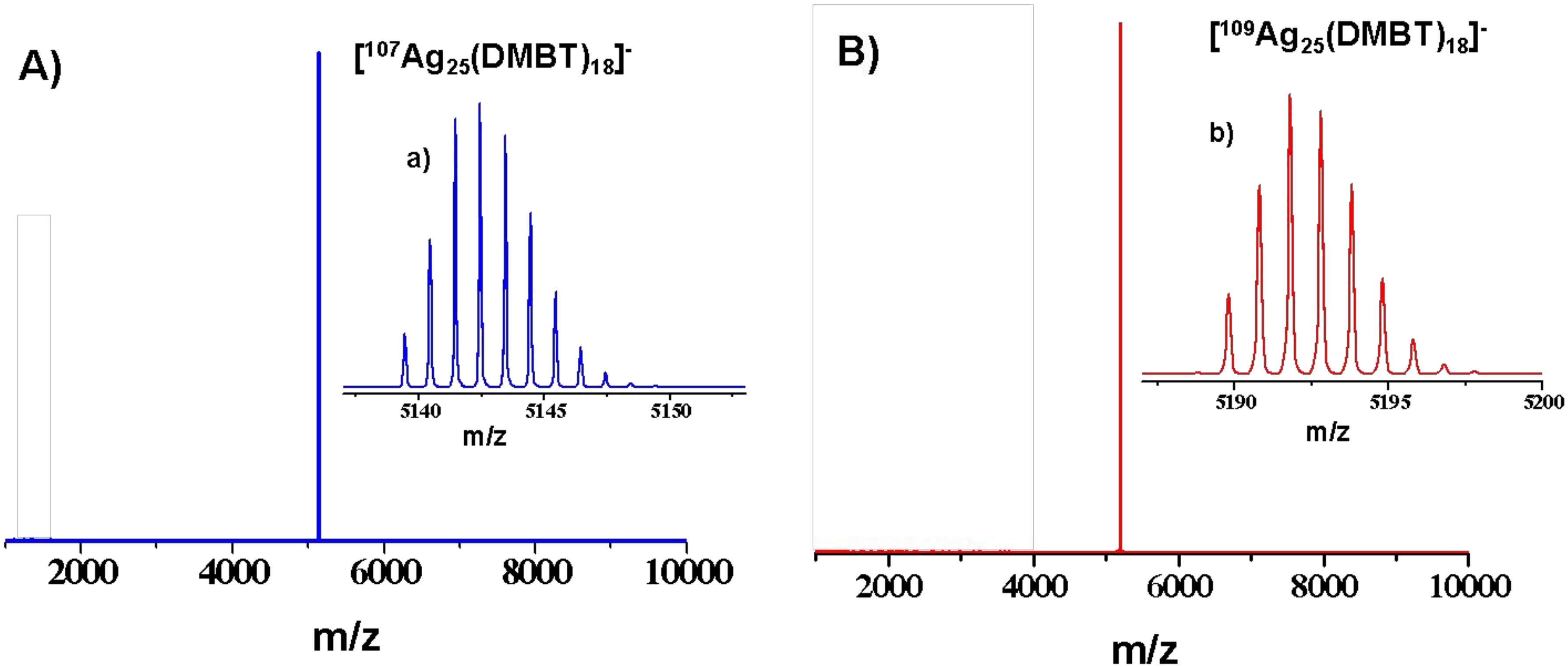
 

They are indeed molecules!

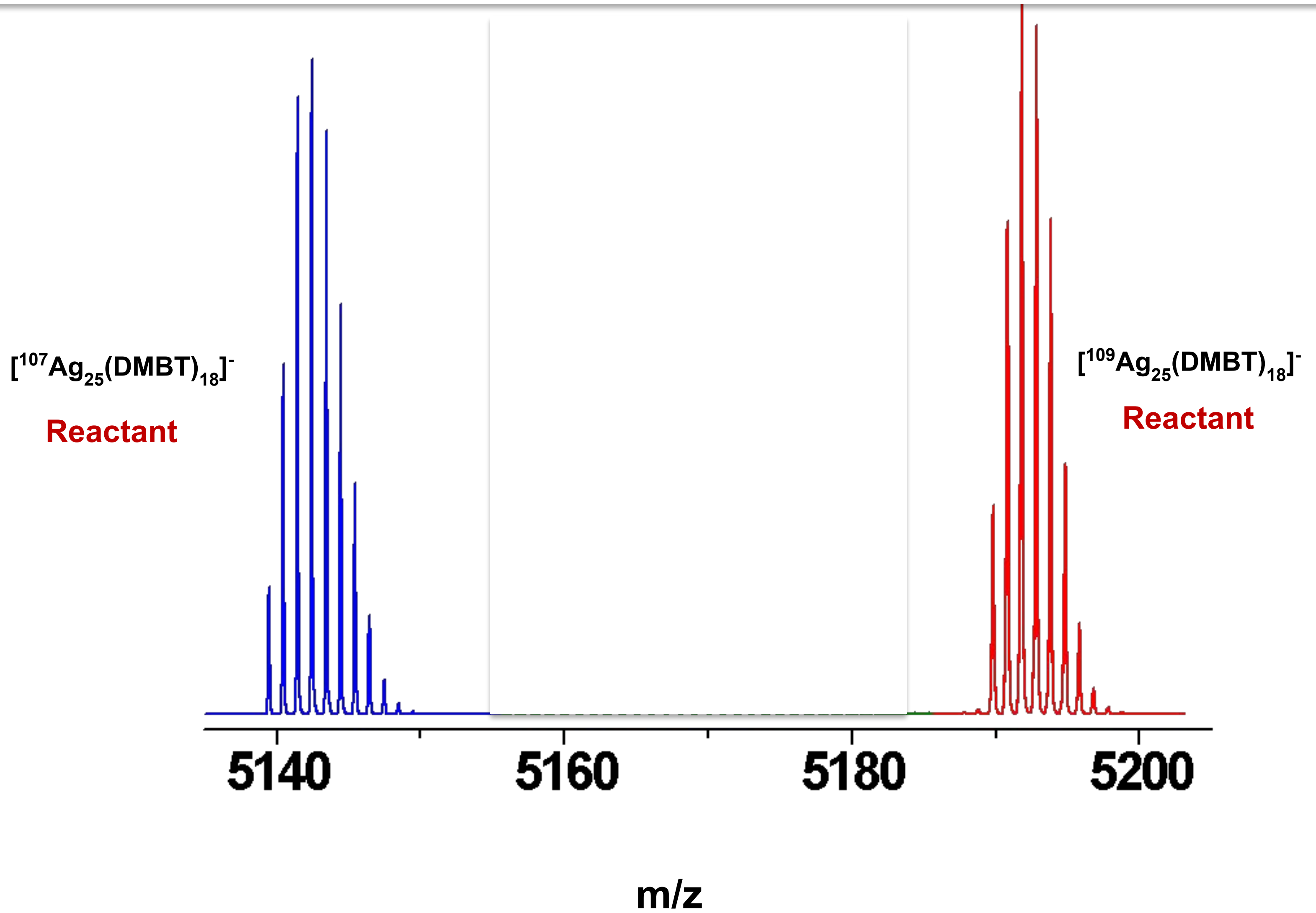
K. R. Krishnadas, et al. Acc. Chem. Res. 2017



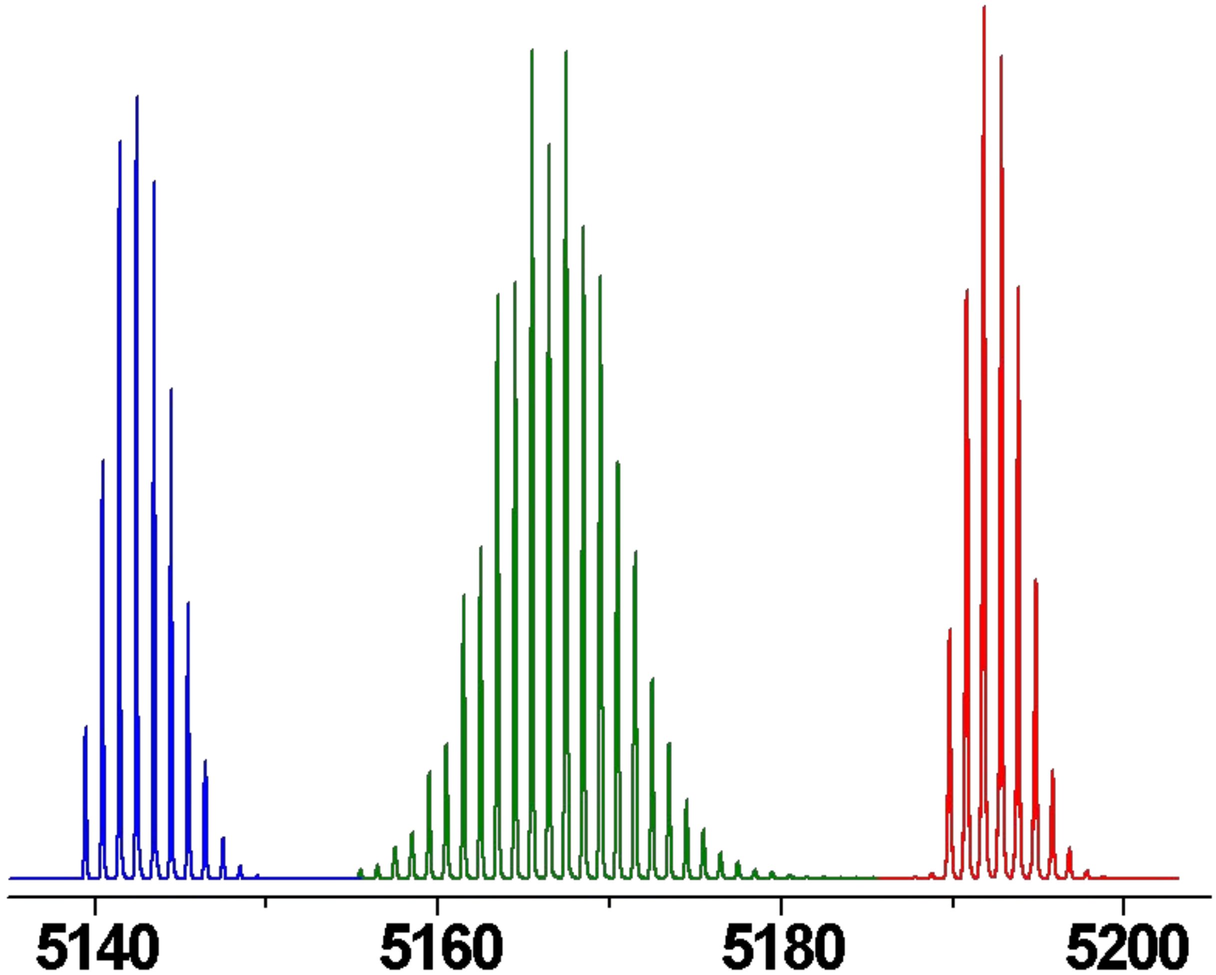
[Ag25(DMBT)18]-
5140
5160
5180
5200
m/z



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

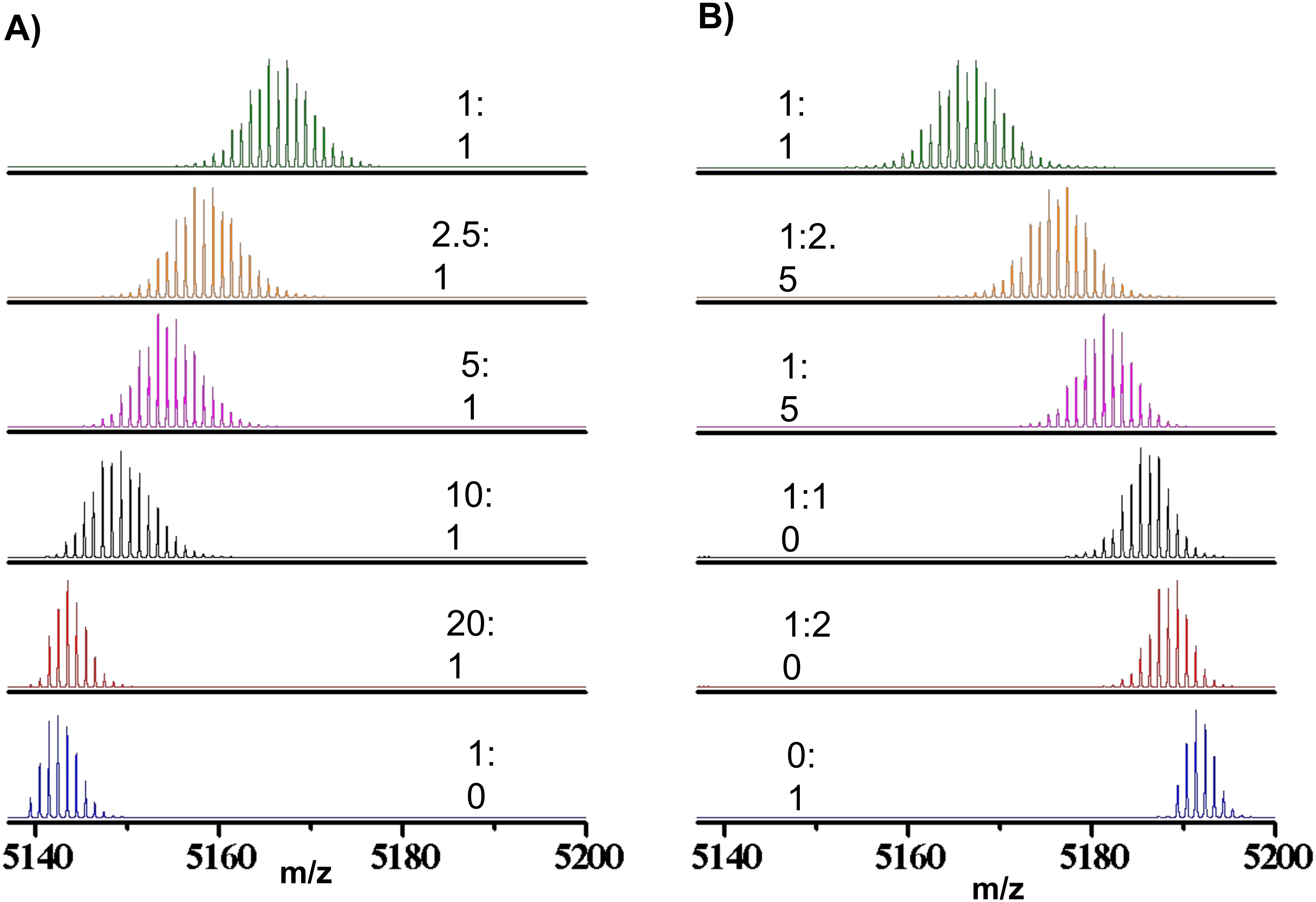


[$^{107}Ag_{25}(DMBT)_{18}]^-$
Reactant
[$^{109}Ag_{25}(DMBT)_{18}]^-$
Reactant
5140
5160
5180
5200
m/z

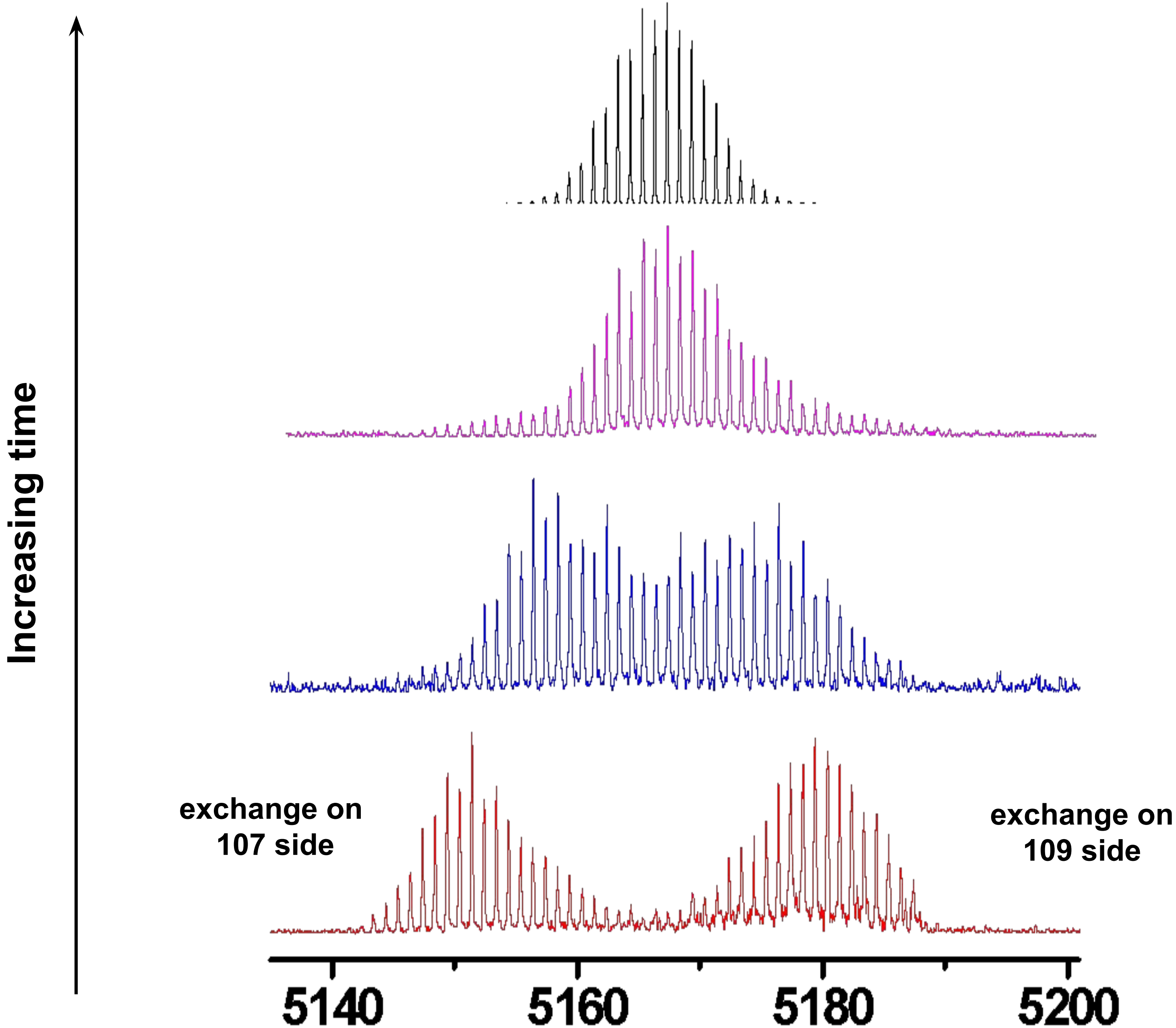


ESI showing the reaction product formed instantly on mixing the two isotopically pure clusters in 1:1 molar ratio. Reaction is instantaneous, no intermediates were detected at room temperature.

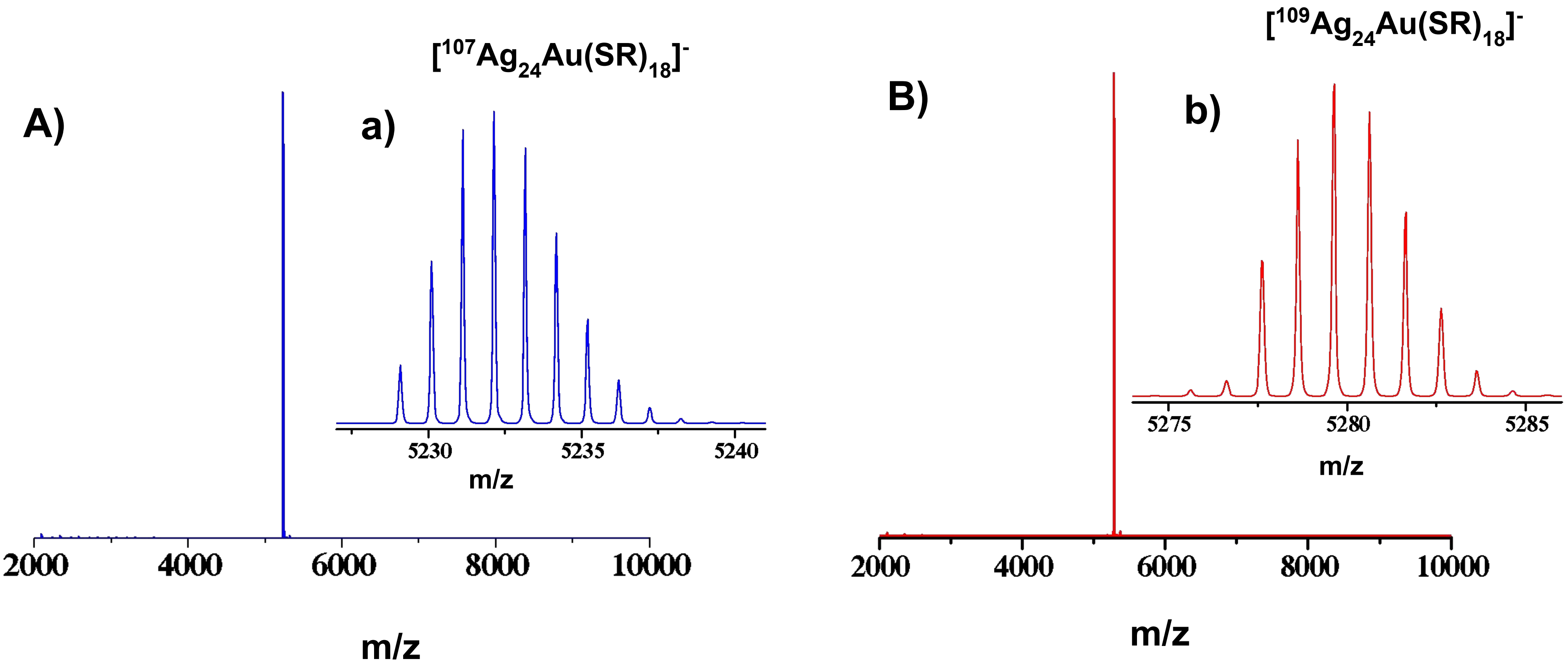
Papri Chakraborty et al. Unpublished.



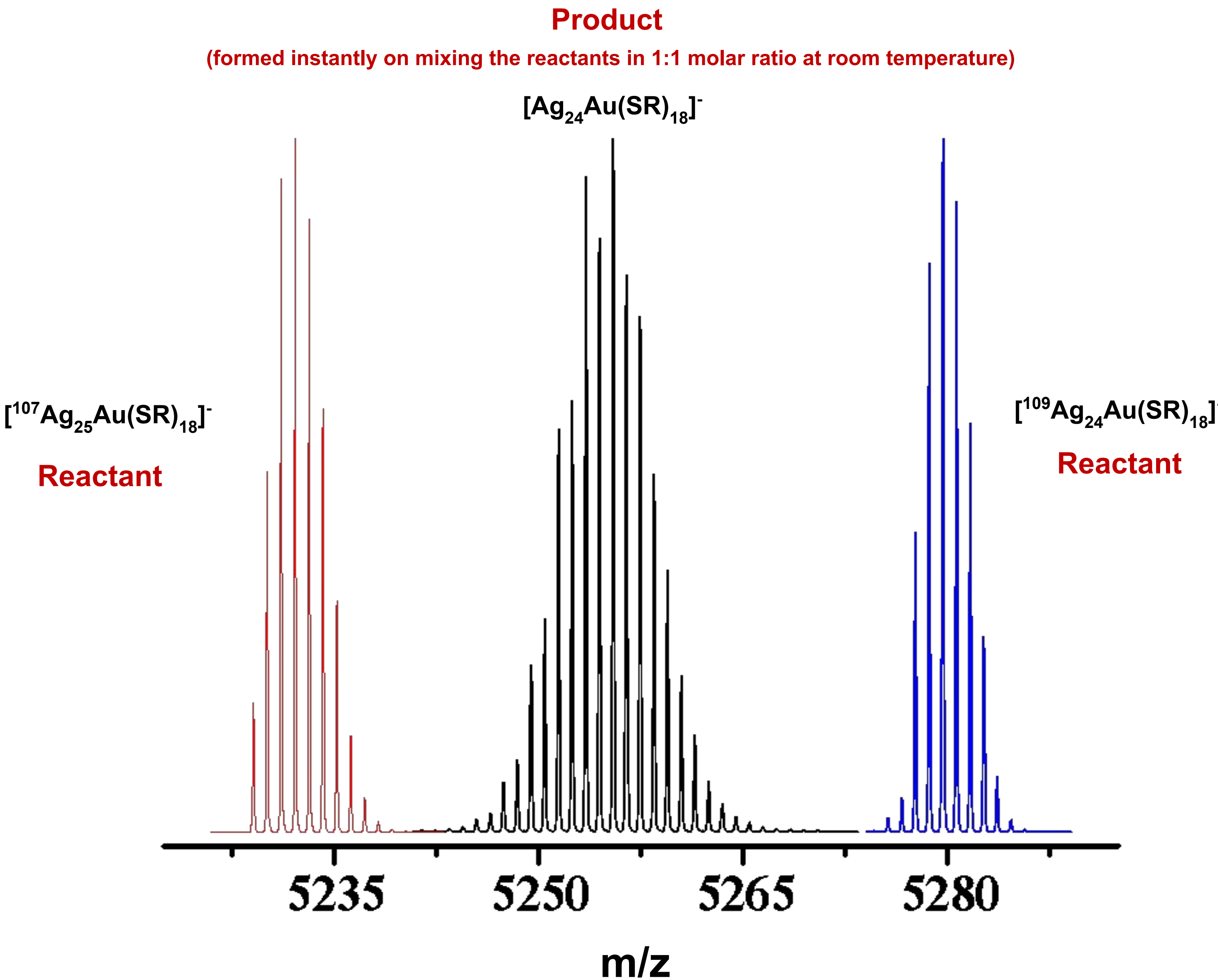
Reaction between the two isotopically pure clusters by controlling the molar ratio, $^{107}Ag_{25}(DMBT)_{18}$: $^{109}Ag_{25}(DMBT)_{18}$ molar ratio is indicated in the figure.



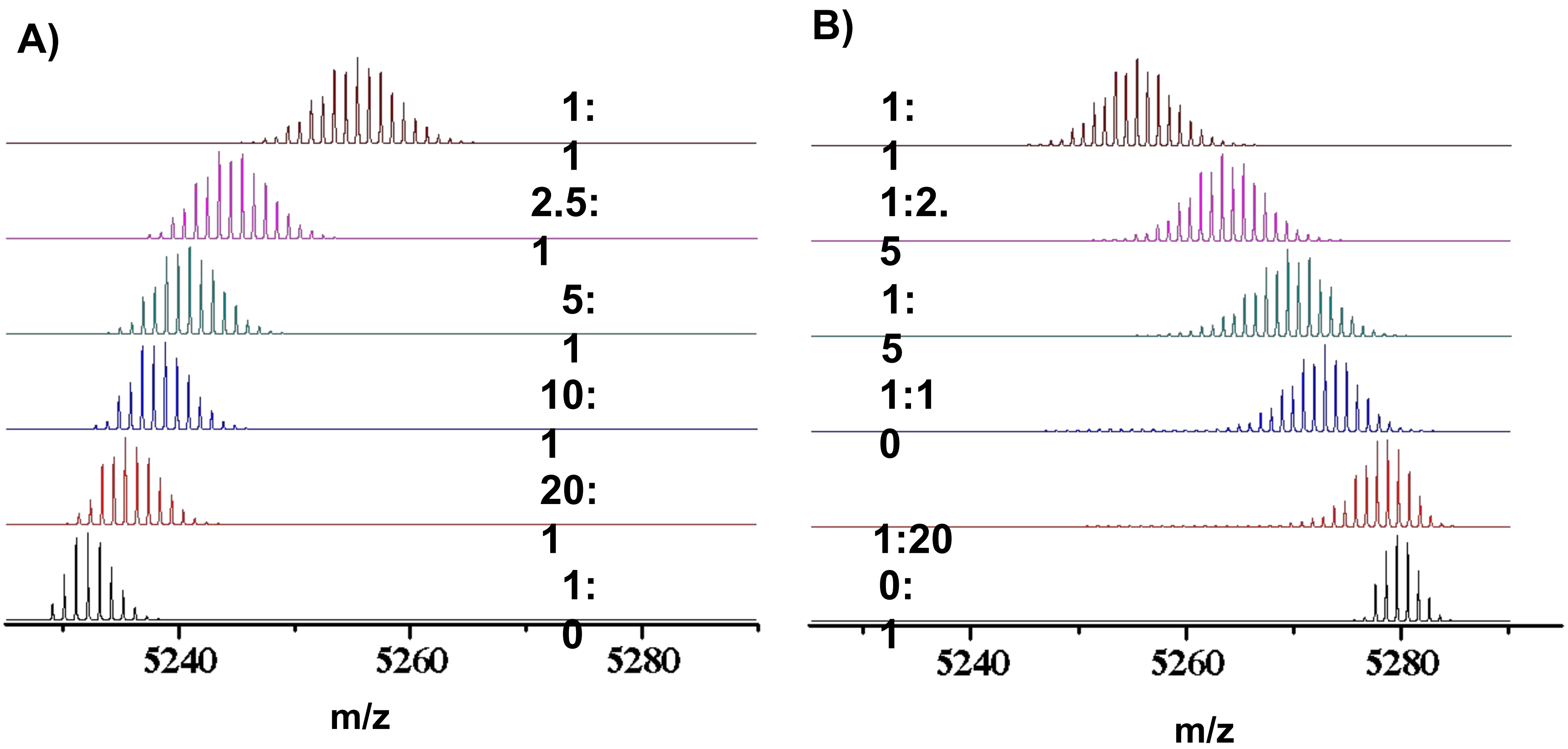
Reaction at 1:1 molar ratio of the two clusters at low temperature. Mixture comes towards natural abundance within 2-3 mins.



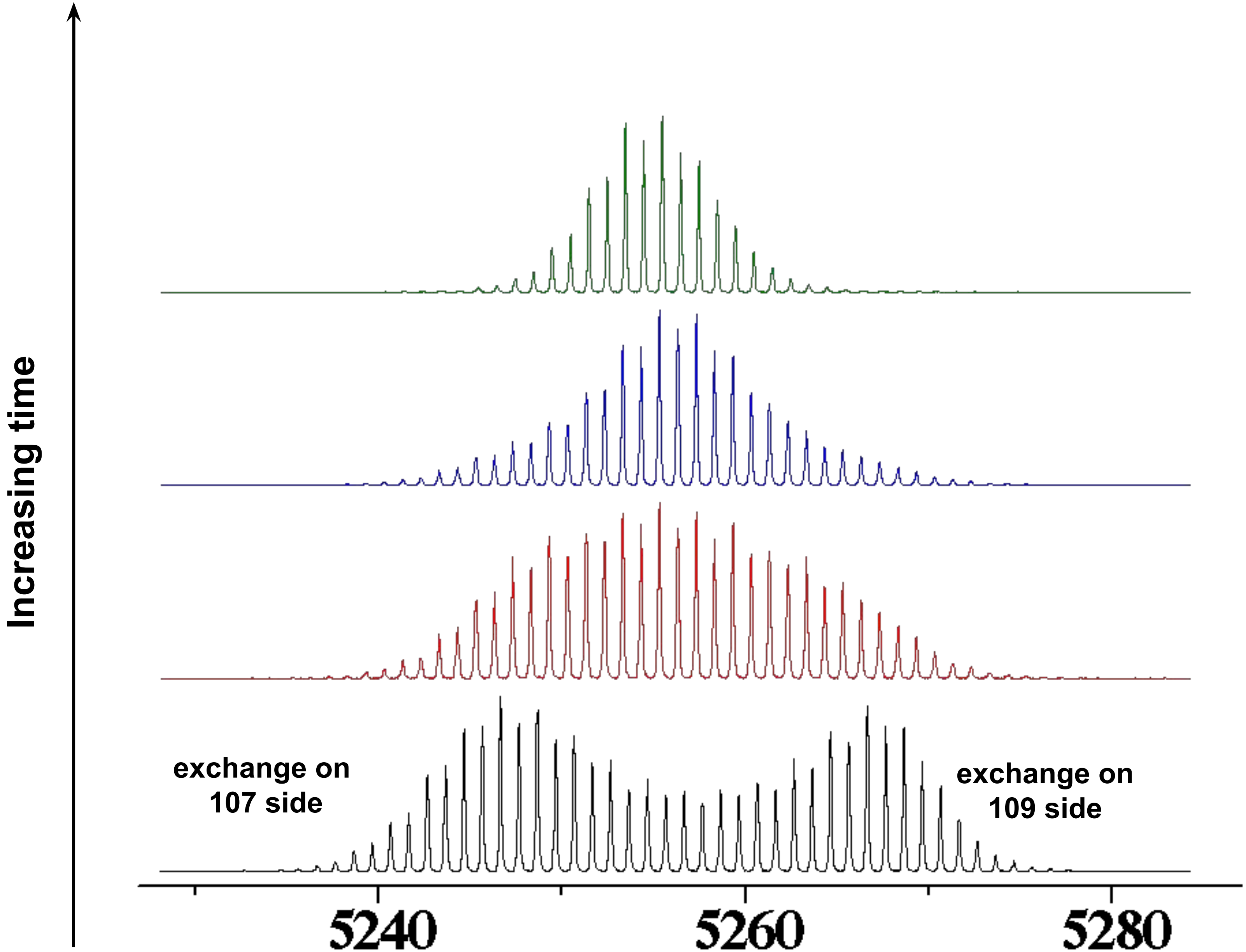
ESI MS of **A)** $^{107}Ag_{24}Au(SR)_{18}$ and **B)** $^{109}Ag_{24}Au(SR)_{18}$. Insets shows the respective isotope patterns.



ESI showing the reaction product formed instantly on mixing the two isotopically pure clusters in 1:1 molar ratio. Reaction is instantaneous, no intermediates were detected at room temperature.



Reaction between the two isotopically pure clusters by controlling the molar ratio, $^{107}Ag_{24}Au(SR)_{18}$: $^{109}Ag_{24}Au(SR)_{18}$ molar ratio is indicated in the figure.



Reaction at 1:1 molar ratio of the two clusters at low temperature. Mixture comes towards natural abundance within 2-3 mins.

Summary

- Reactions between atomically precise nanoparticles
- 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

Acknowledgements

K. R.Krishnadas
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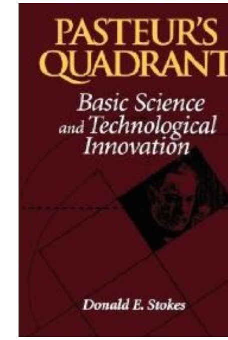
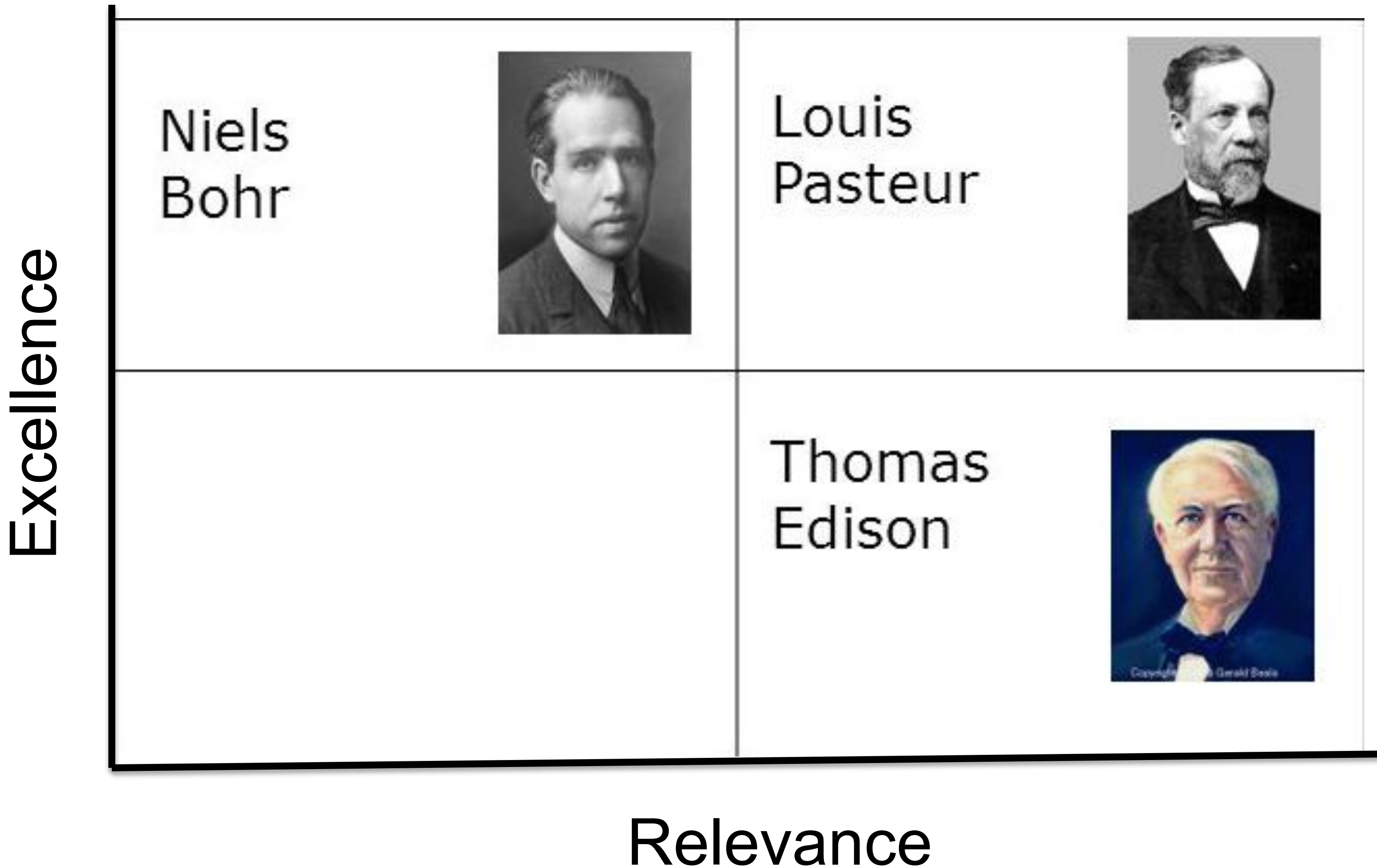
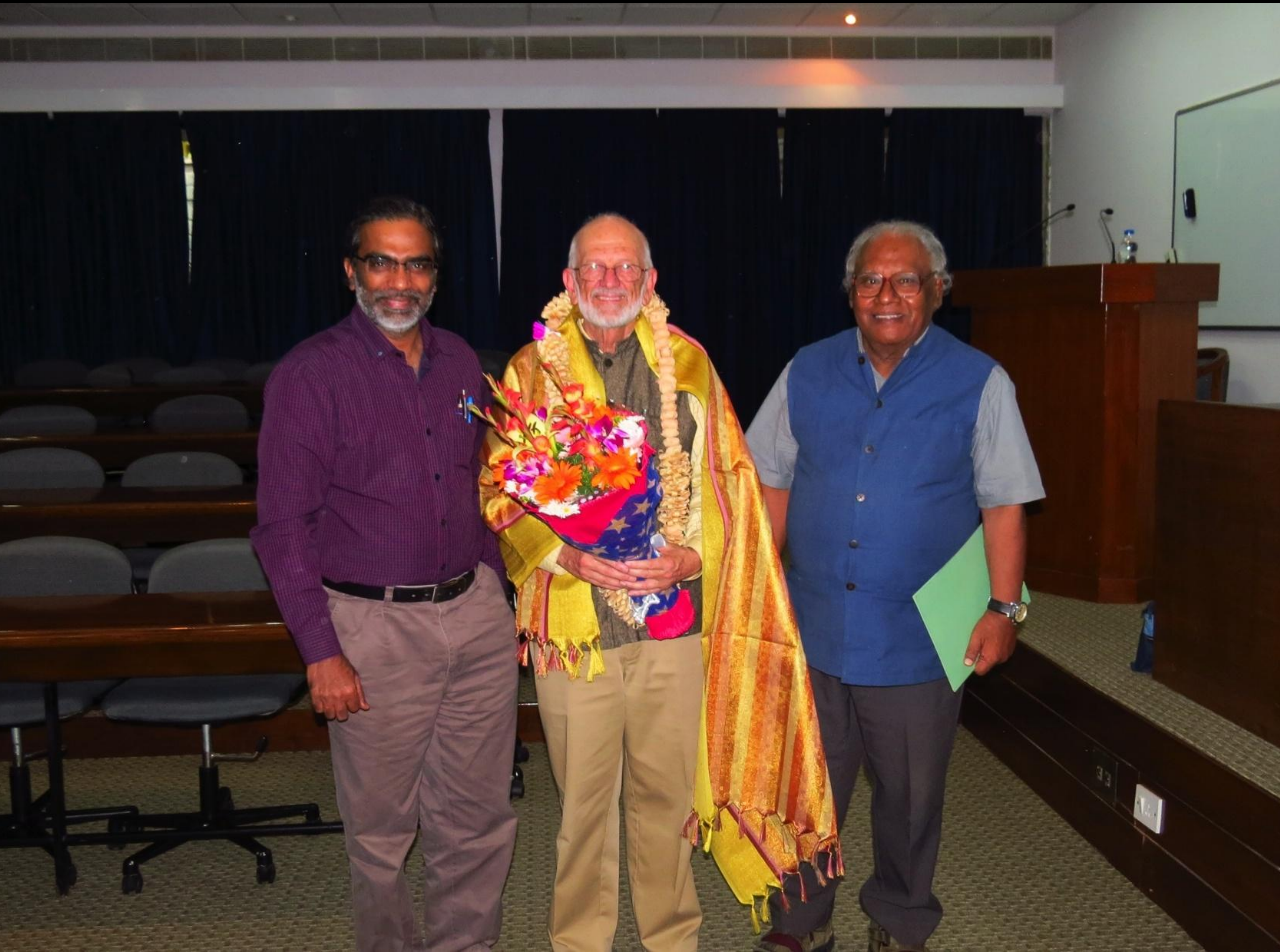
Shridevi Bhat, Madhuri Jash, Debasmita Ghosh, Papri Chabraborty,
Amrita Chakraborty, Esma Khatun, …


PASTEUR'S QUADRANT
Basic Science and Technological Innovation
Donald E. Stokes


Niels Bohr
Louis Pasteur
Thomas Edison
Excellence
Relevance

ACS Sustainable Chemistry & Engineering Editorial, December 2016

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Thank you