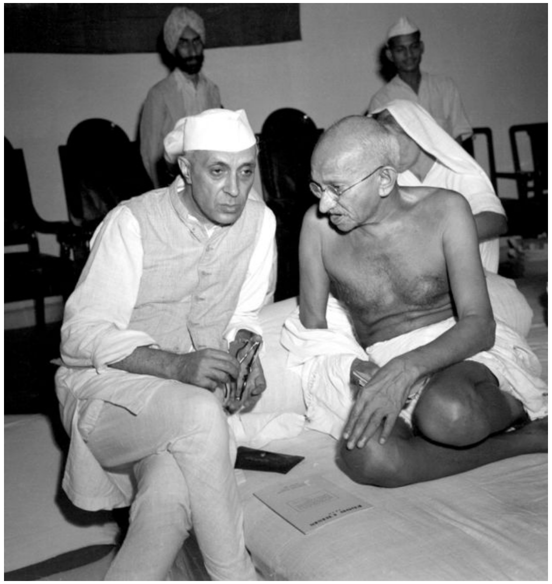
Now in the 57th year

Inter-cluster 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

pradeep@iitm.ac.in

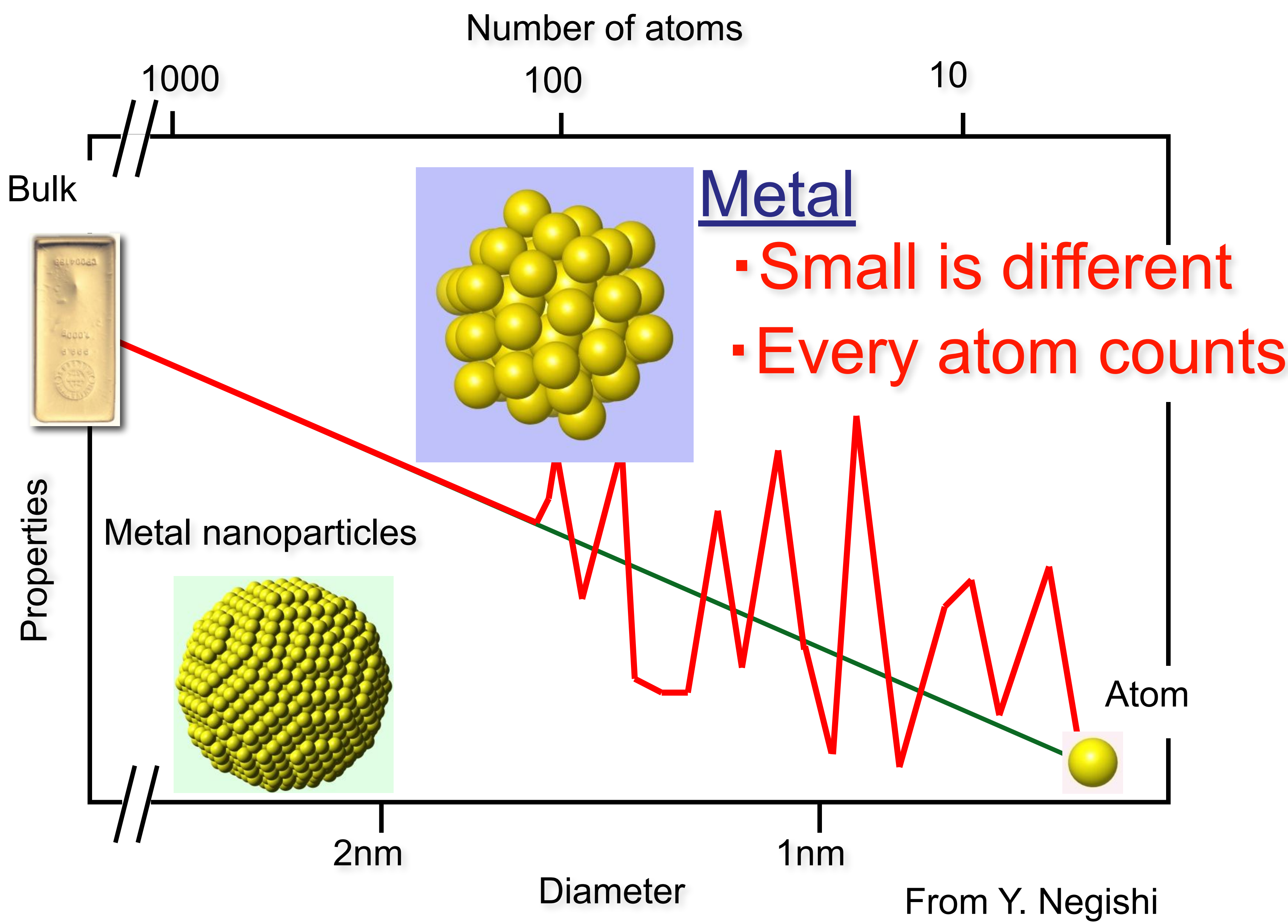


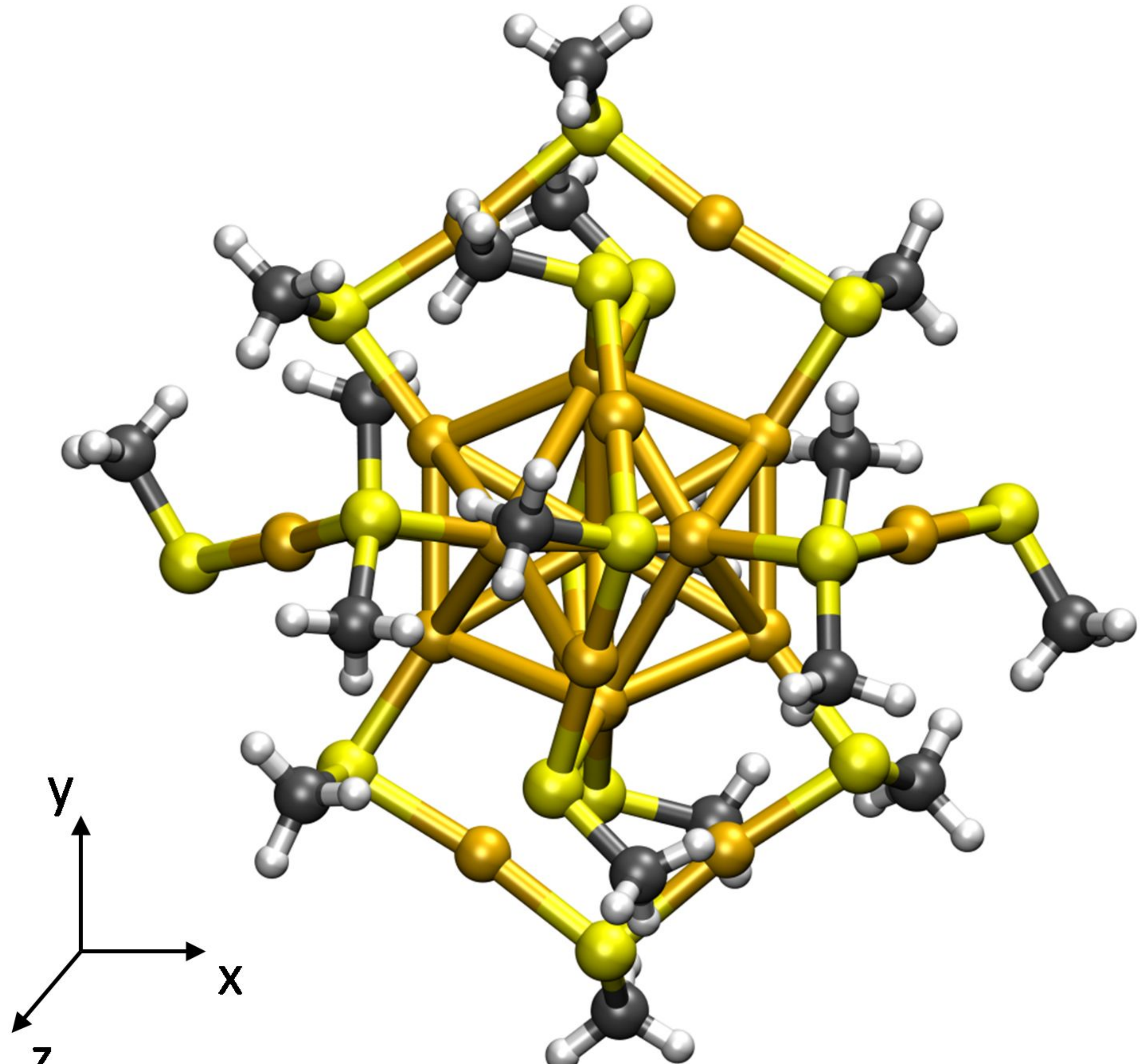
Founder
InnoNano Research Pvt. Ltd.
An IIT Madras Incubated Company

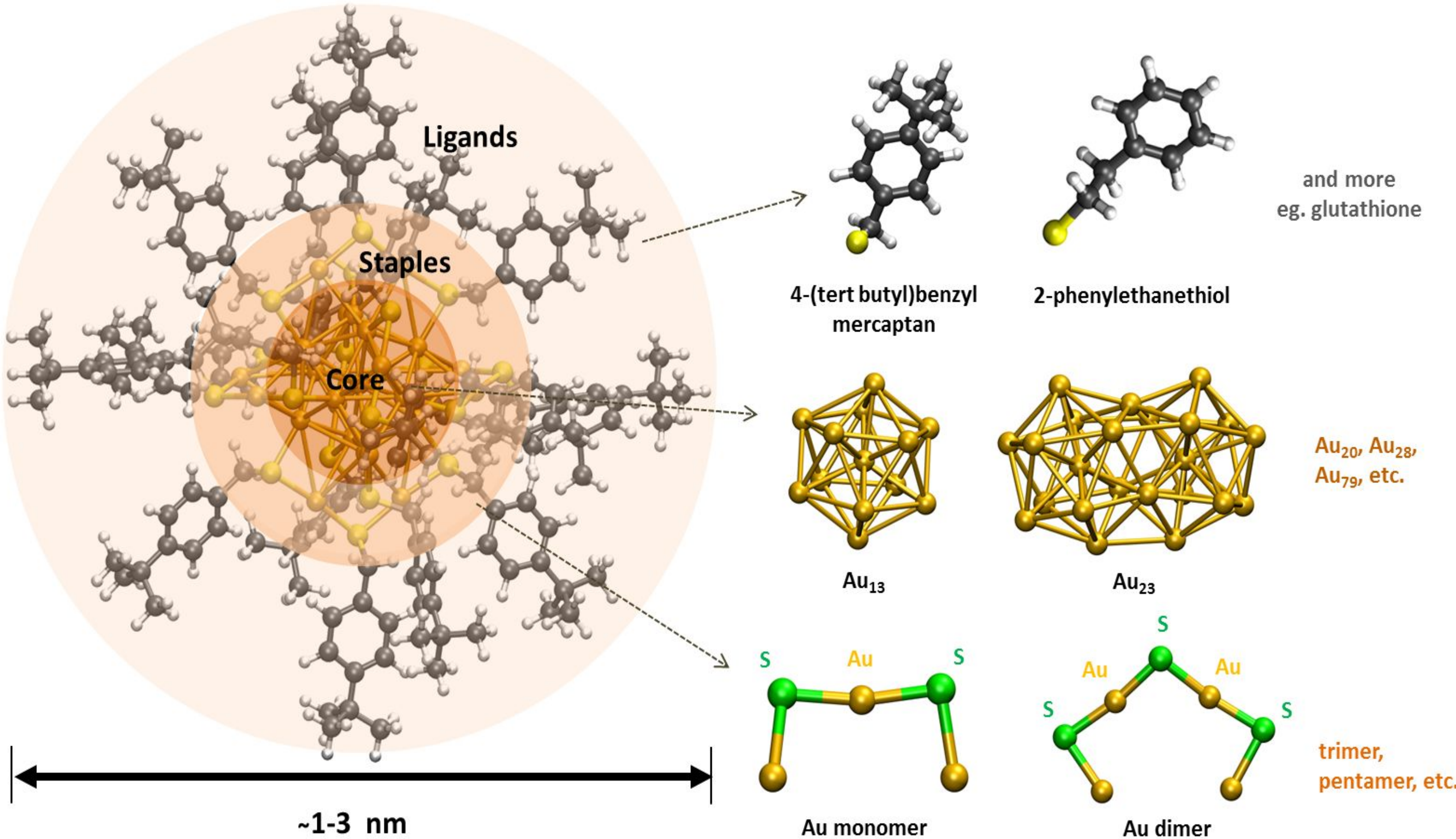
An IIT Madras incubated company

Associate Editor
ACS Sustainable Chemistry & Engineering

Nano-Scaled Systems for Energy Harvesting, VIT University, February 1, 2016

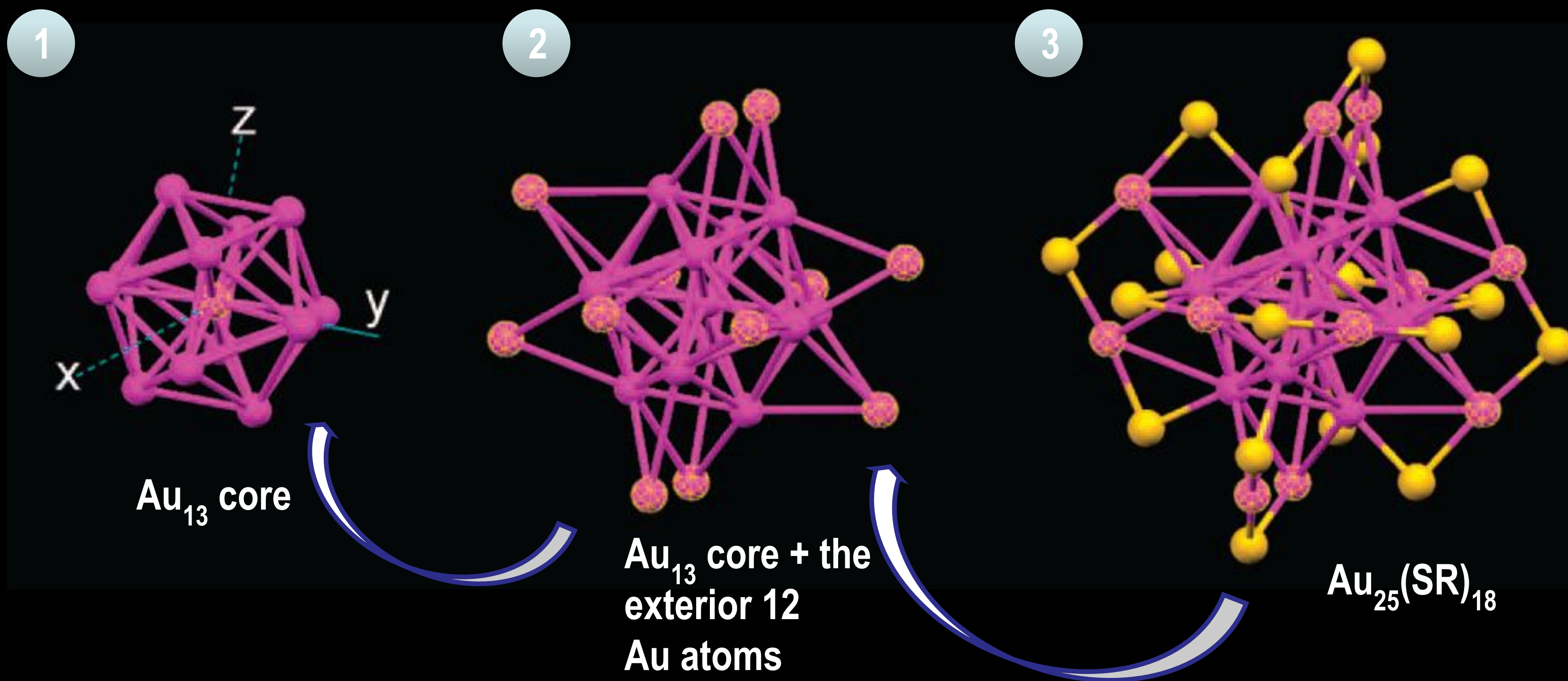

Number of atoms
1000
100
10
Bulk
Metal
・Small is different
・Every atom counts
Properties
Metal nanoparticles
Atom
2nm
1nm
Diameter
From Y. Negishi


y
x
z


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.

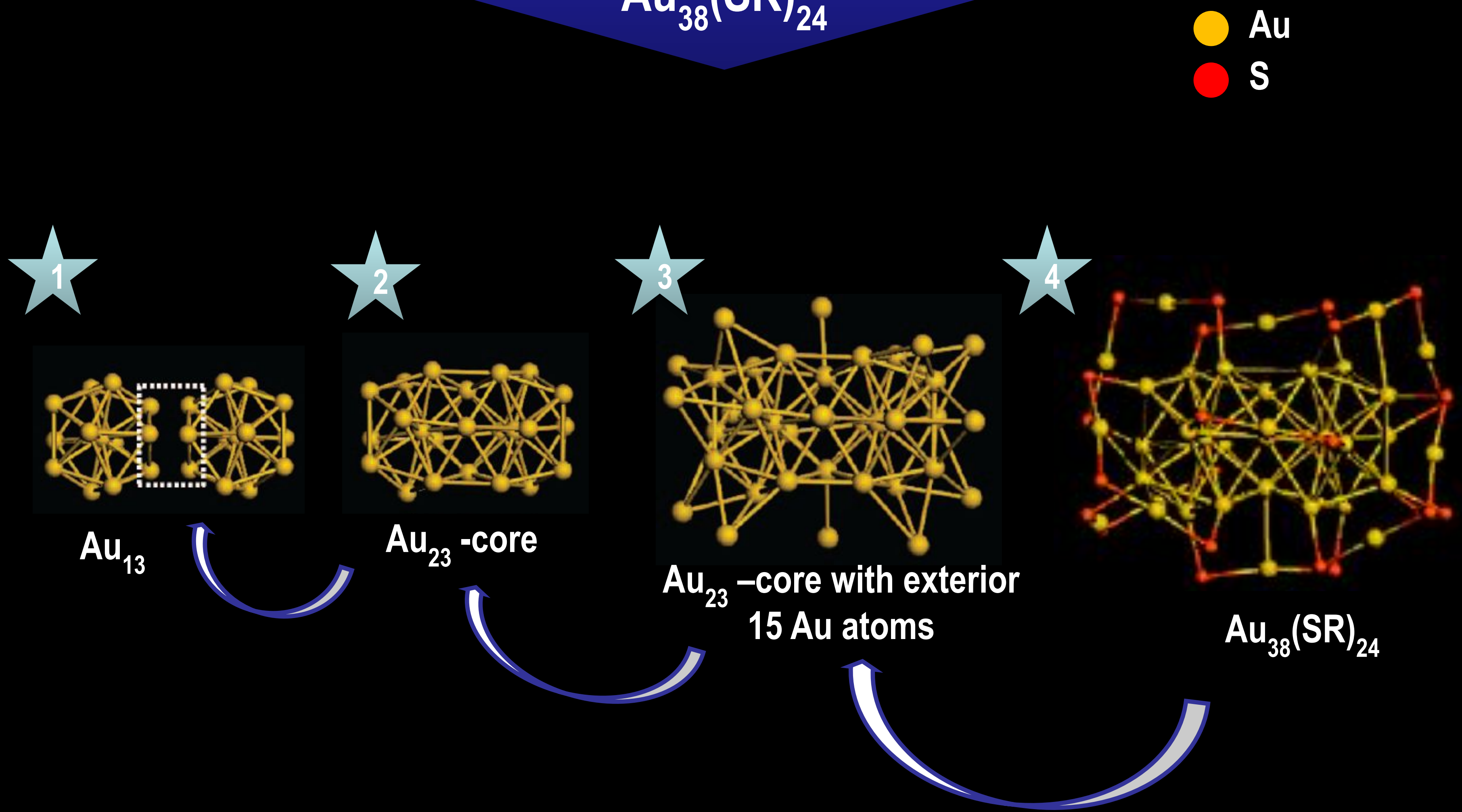
$Au_{25}(SR)_{18}$

Au
S



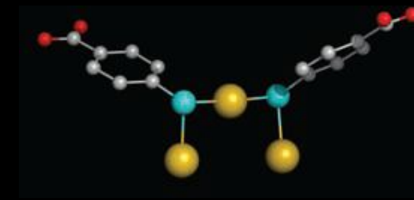
Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. *J. Am. Chem. Soc.* **2008**, *130*, 5883-5885.

$Au_{38}(SR)_{24}$



Pei, Y.; Gao, Y.; Zeng, X. C. *J. Am. Chem. Soc.* **2008**, *130*, 7830-7832.

$Au_{102}(p\text{-}MBA)_{44}$



2 p-MBA with 3 Au atoms

1

Axis

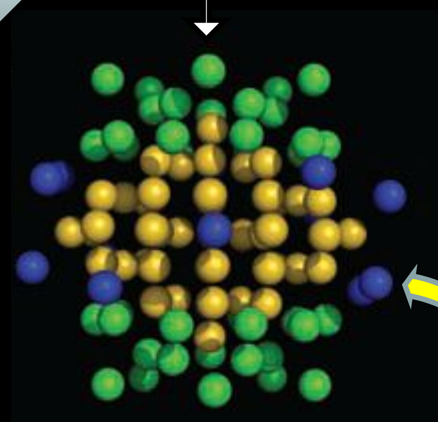
Marks decahedral (40 atoms)

Along the axis 4 Au atoms
(total 49 atoms)

Core

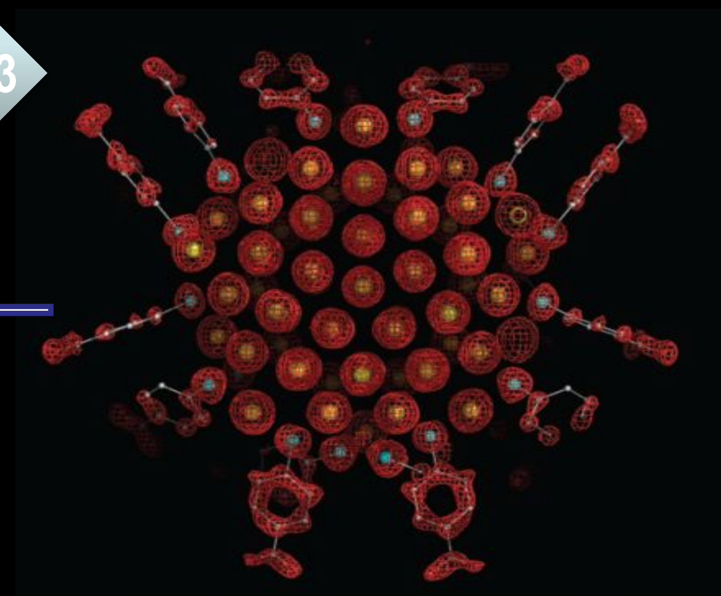
2

Two 20-atom caps
(total 89 atoms)



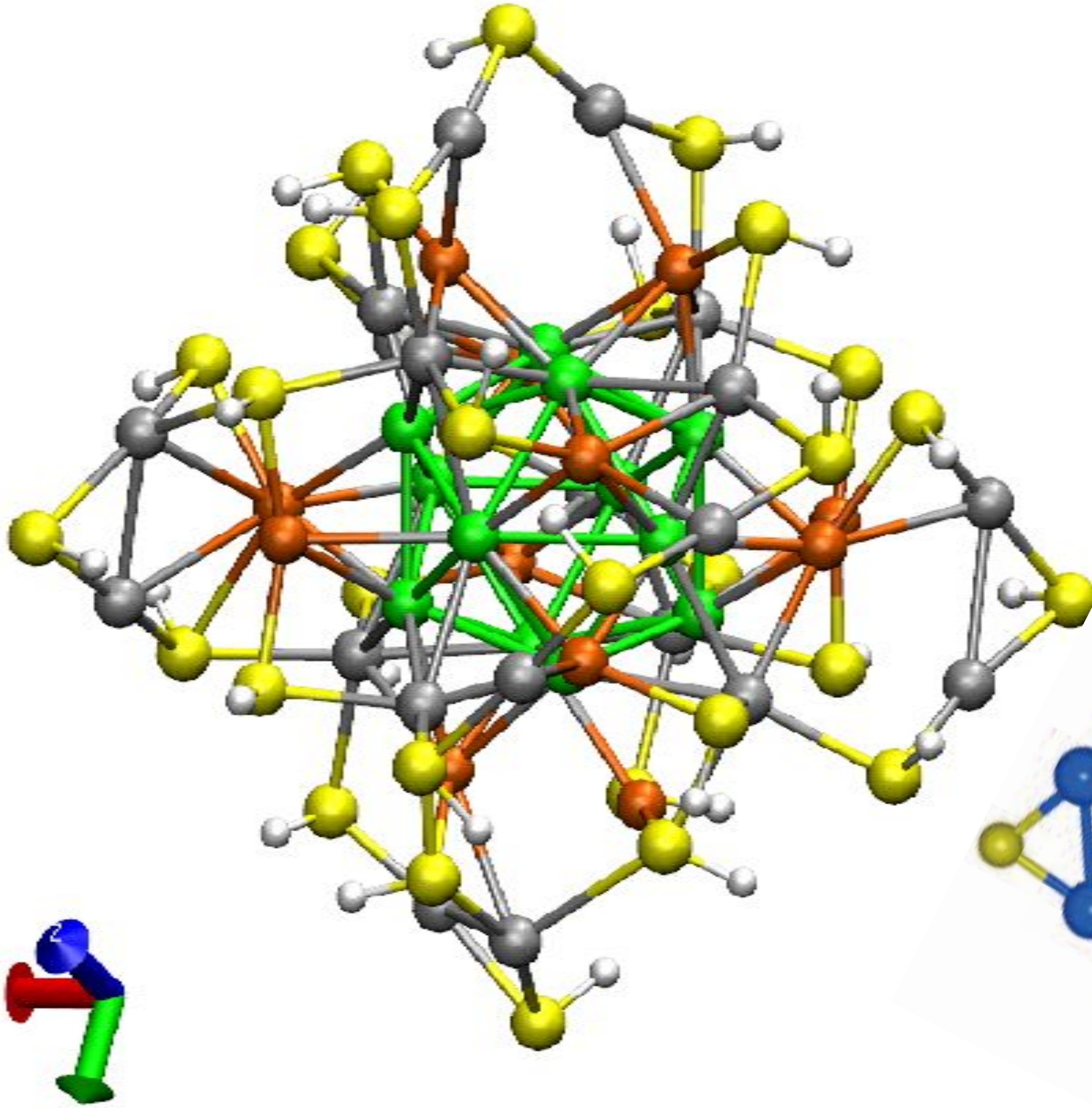
13-atom band
(total 102 atoms)

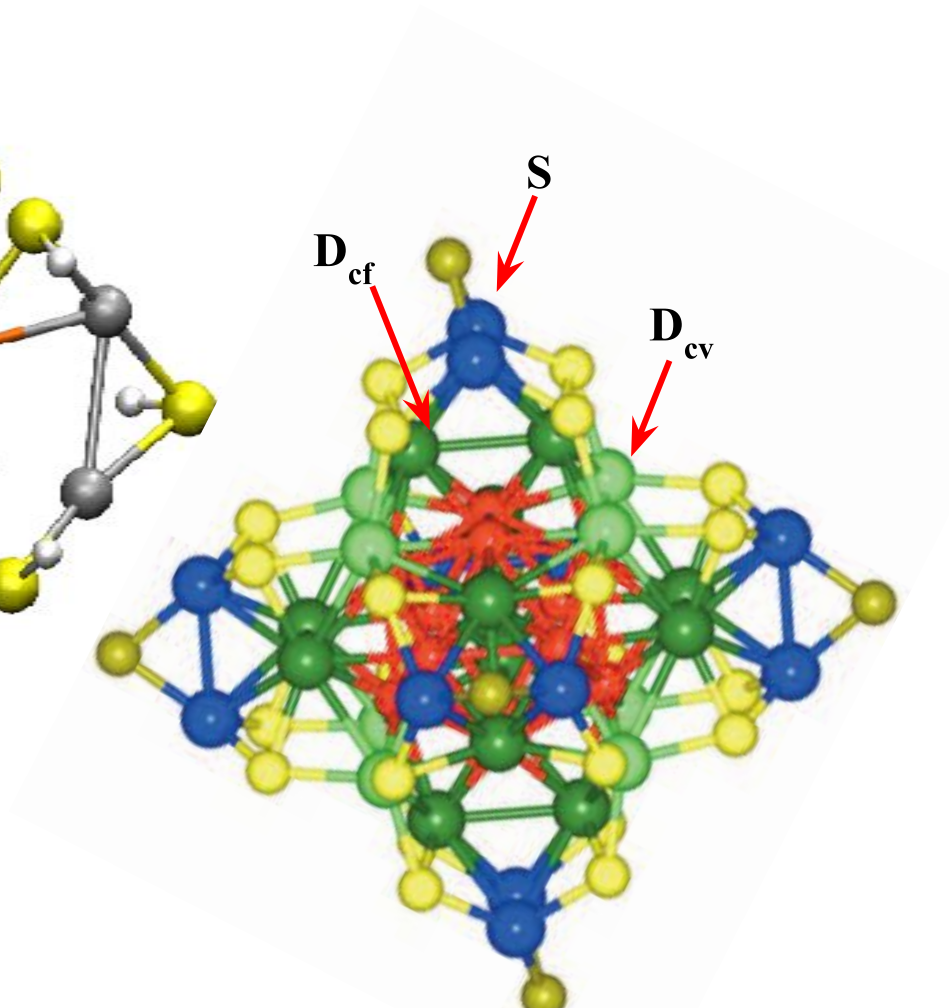
3



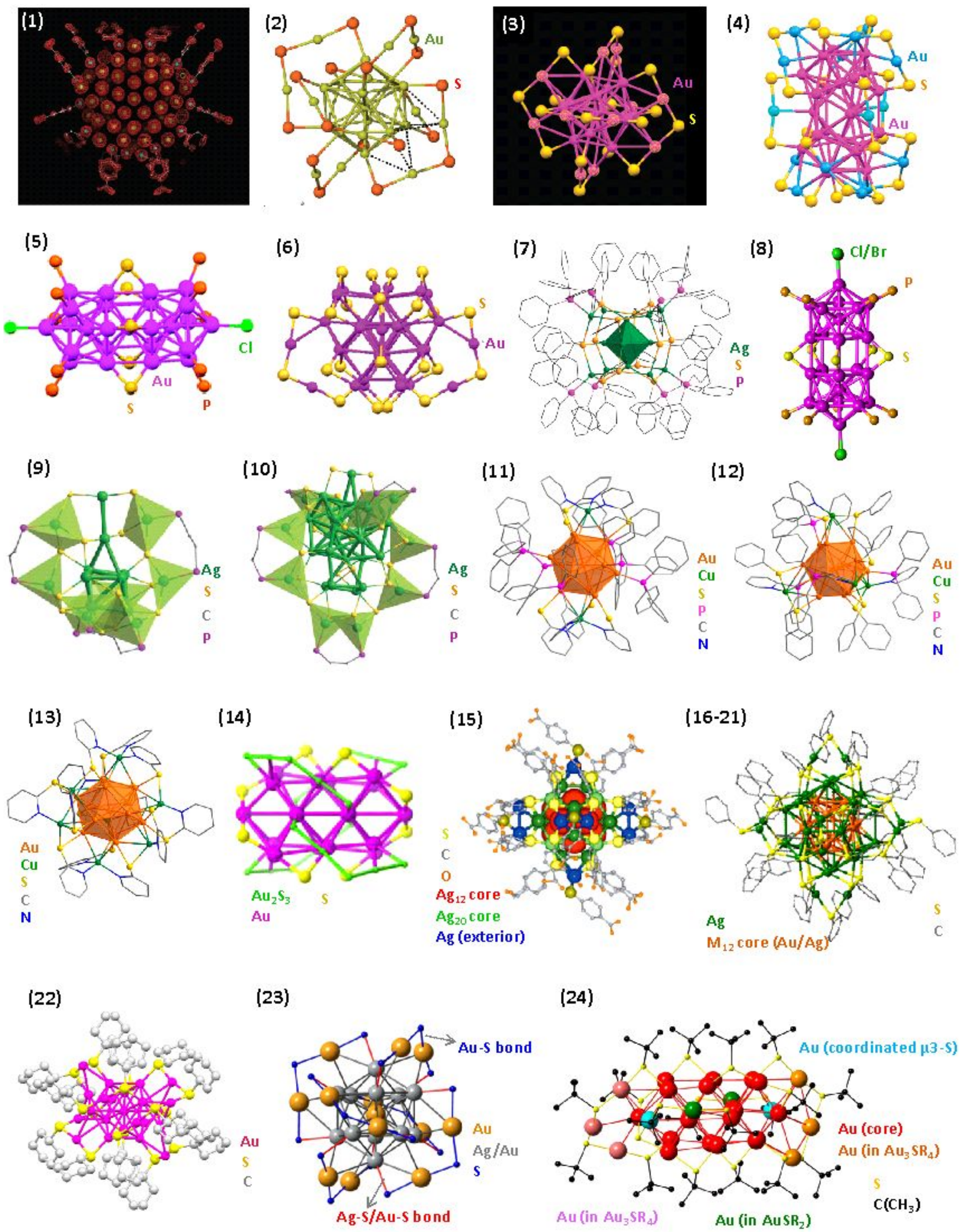
$Au_{102}(p\text{-}MBA)_{44}$

Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. *Science* **2007**, *19*, 430–433.



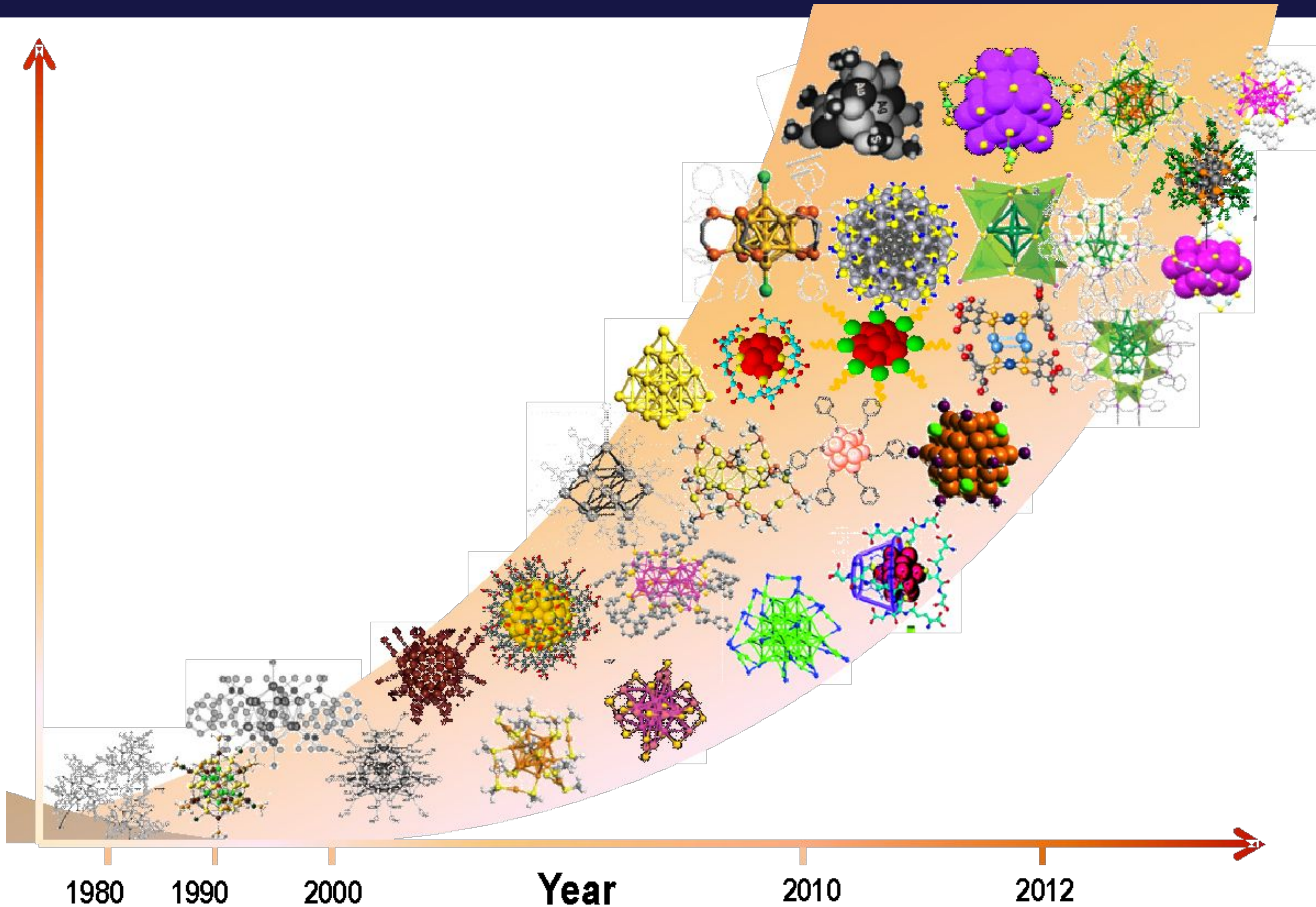


$Ag_{44}SR_{30}$ – Nanfeng Zheng and Terry Bigioni



Ammu Mathew and T. Pradeep, Particle, 2014

Evolution of noble metal clusters



I. Chakraborty et al, to appear in *Chem. Rev.* 2016

Evolving Science

Part I Cluster chemistry is getting increasingly complex

- Ligand exchange
- Isomers
- Alloys
- Supramolecular chemistry

Part II Are there pointers?

- Specific examples

Part III How do we understand these systems?

C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

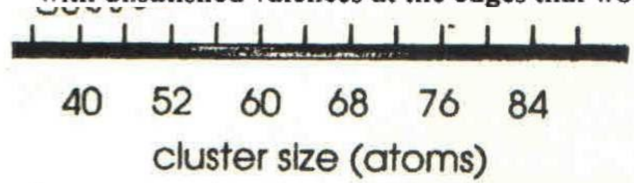
Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

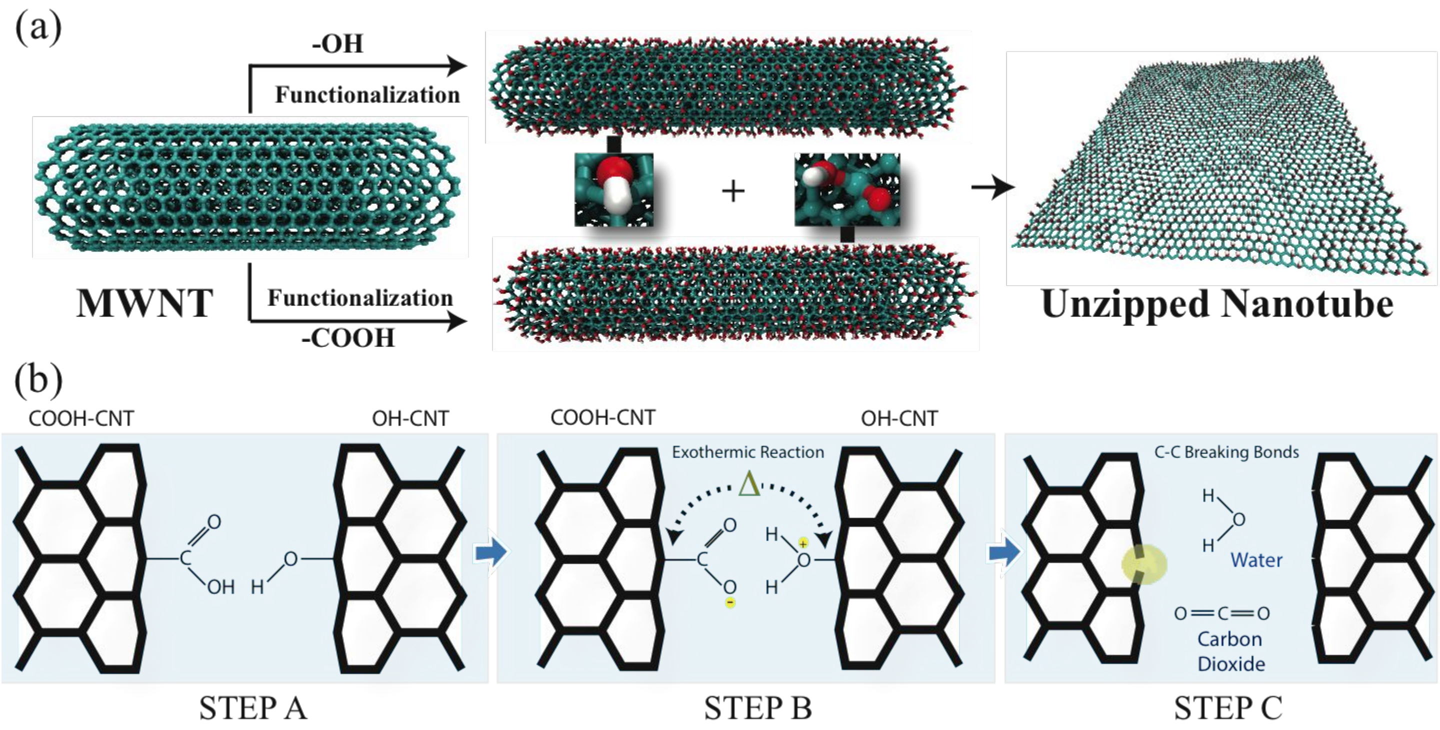
Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise



Grinding nanotubes



M. A. Kabbani *et al.* Nat. Comm. 6 (2015) 7291

With P. M. Ajayan

Part I

THE JOURNAL OF PHYSICAL CHEMISTRY Letters
Perspective
pubs.acs.org/JPCL

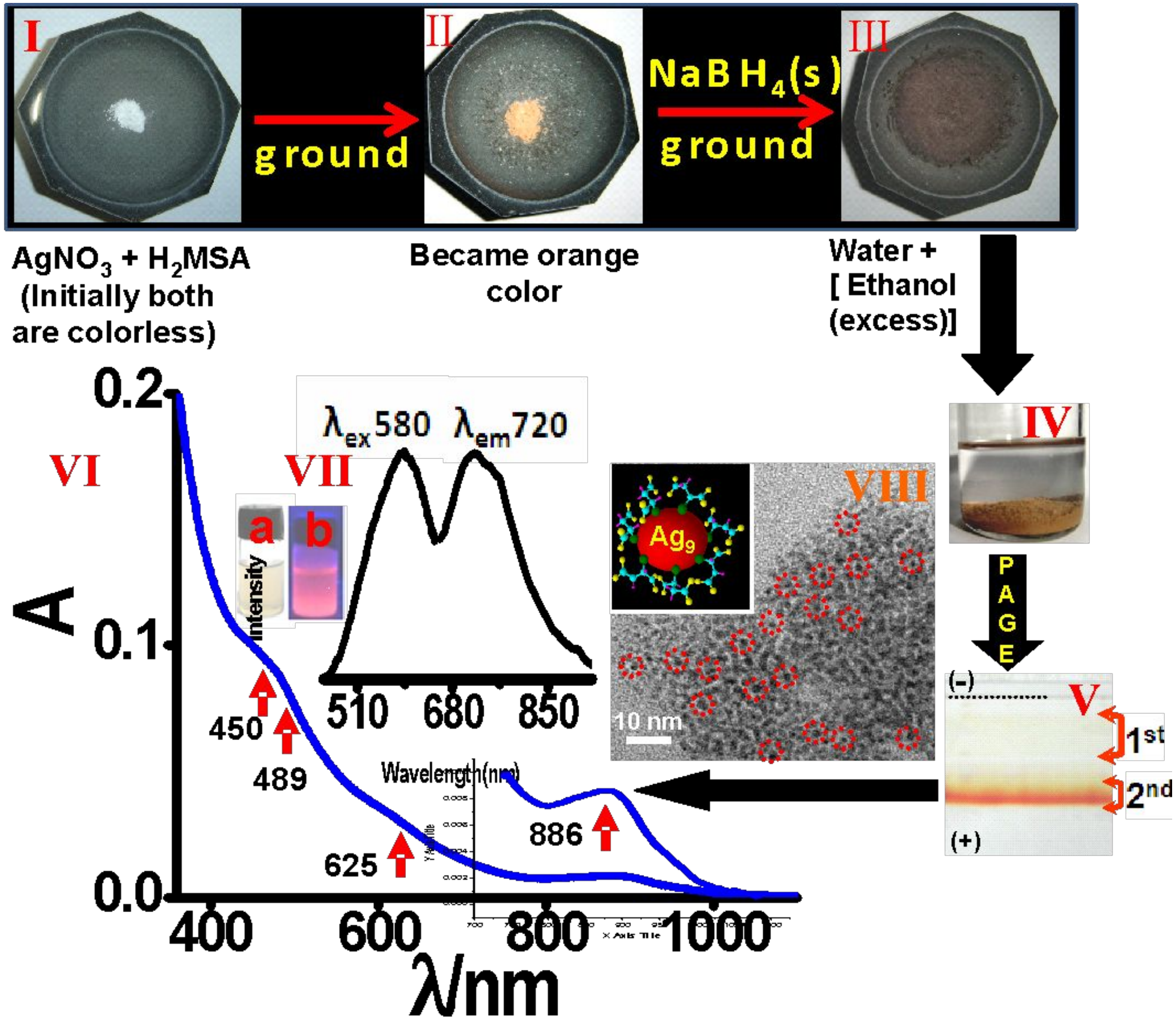
New Protocols for the Synthesis of Stable Ag and Au Nanocluster Molecules

T. Udayabhaskararao and T. Pradeep*

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

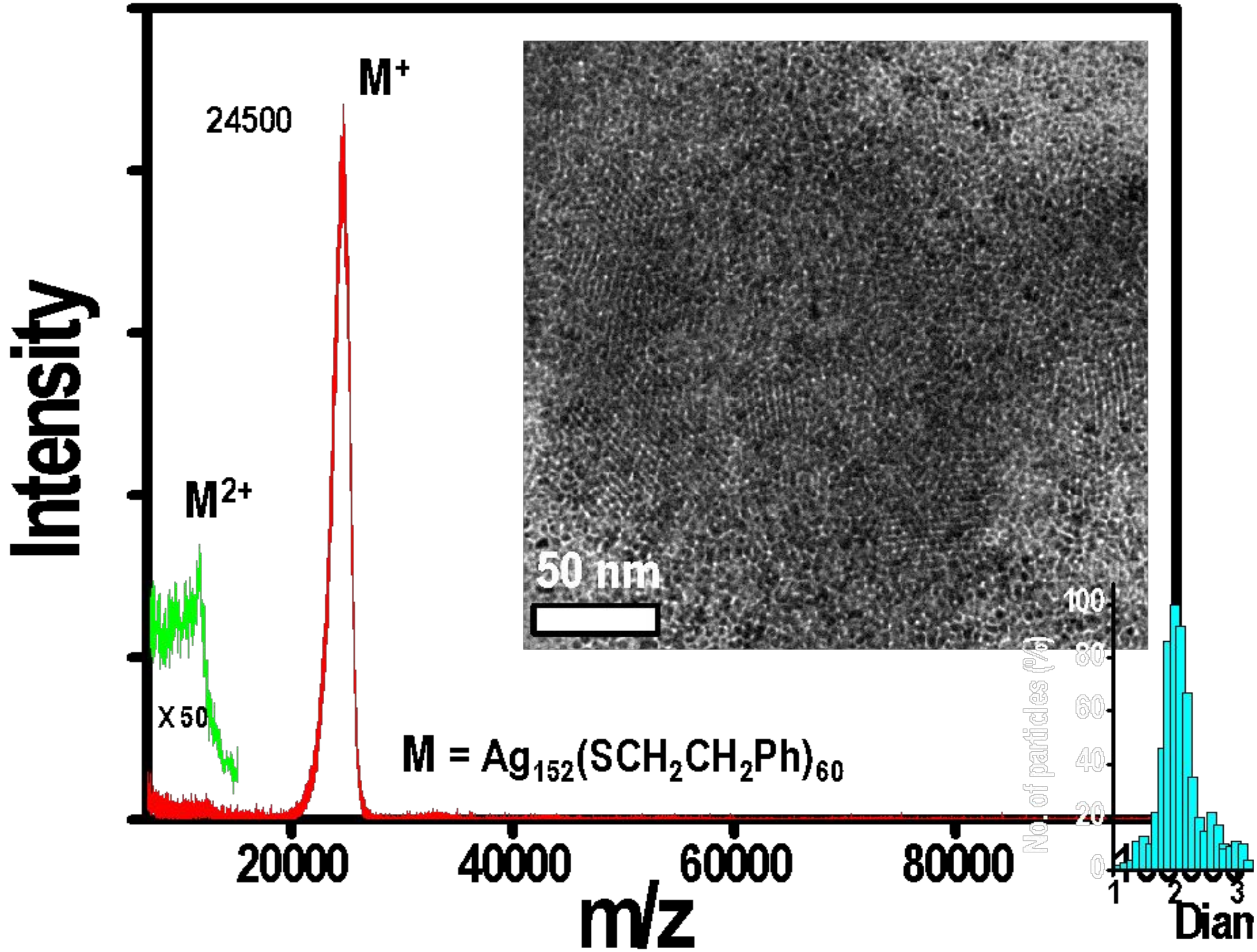
ABSTRACT: "Catching" metals in the nonmetallic form in solution, as they grow to bulk, is one of the most exciting areas of contemporary materials research. A new kind of stabilization to catch the nonmetallic form of noble metals with small thiols has evolved as an exciting area of synthesis during the past decade. Gold clusters stay in the frontline of this research, yielding new "molecules" composed of a few to several hundreds of atoms. By taking guidelines from gold cluster research, various new protocols for silver nanoclusters were developed. In this Perspective, we highlight the recent advances on the synthesis of atomically precise silver, gold, and their alloy clusters with a special emphasis on silver. As a result of intense efforts of the recent past, clusters such as $Ag_{7,8}(SR)_{7,8}$, $Ag_7(-S-R-S-)_4$, $Ag_9(SR)_7$, $Ag_{32}(SR)_{19}$, $Ag_{44}(SR)_{30}$, $Ag_{140}(SR)_{53}$, $Ag_{280}(SR)_{140}$, and $Ag_{152}(SR)_{60}$ (SR and S−R−S refer to thiolate and dithiolate ligands, respectively) were added to the literature. Moreover, "silver-covered" and "gold-covered" alloy clusters have also been synthesized. Early reports of the crystallization of such clusters are available. Several of these clusters are shown to act as sensors, catalysts, and pesticide degradation agents, which suggests that these materials may find applications in daily life in the foreseeable future.

Ag_9MSA_7 - solid state synthesis



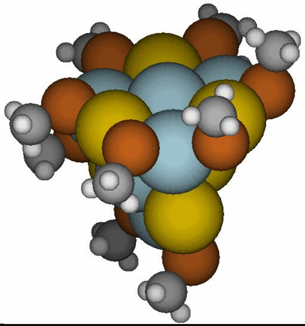
TUB Rao and T Pradeep, J. Am. Chem. Soc. 132 (2010) 16304-16307.

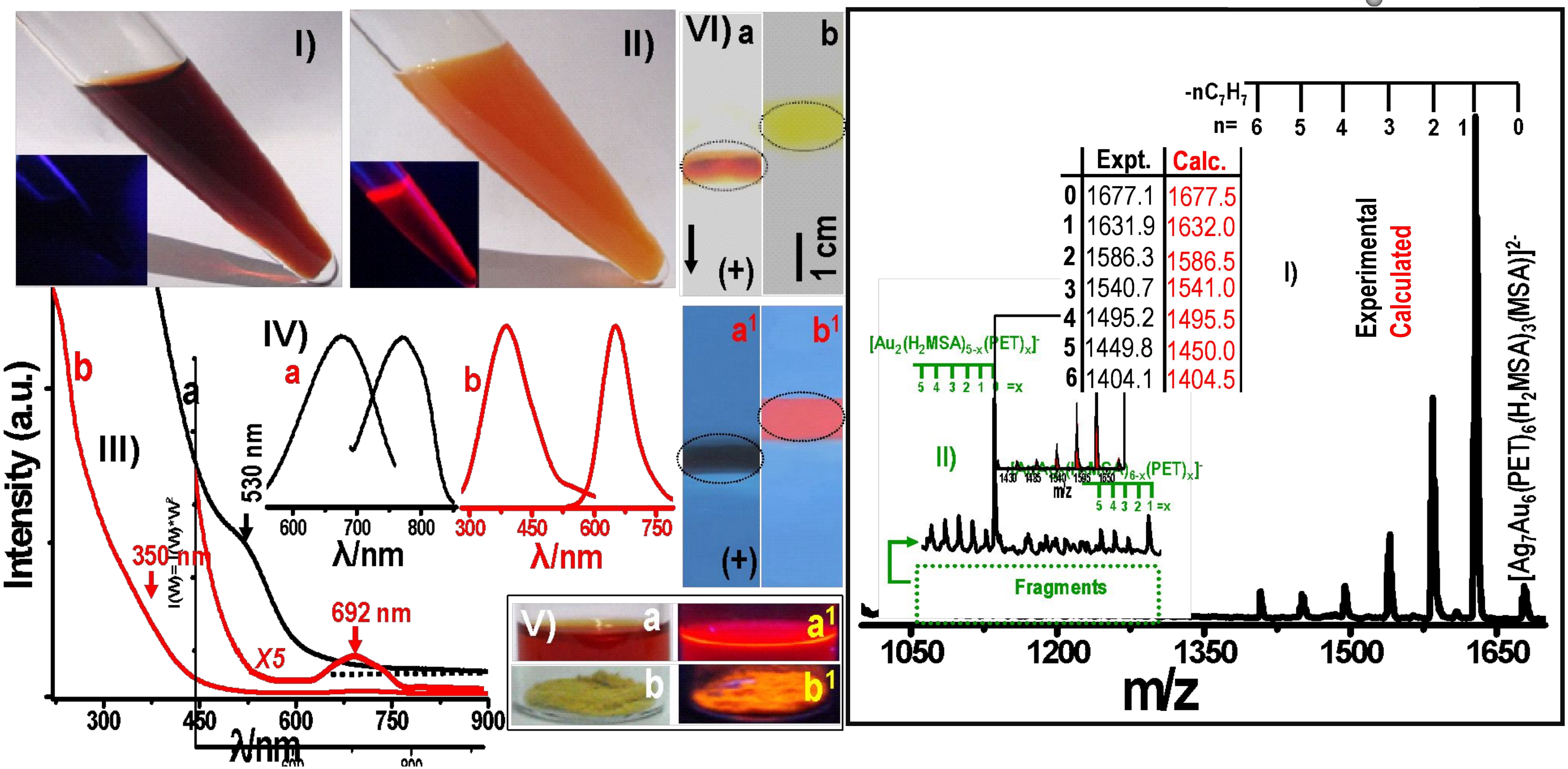
$Ag_{152}PET_{60}$



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

Ag_7Au_6 – 13 atom alloy cluster

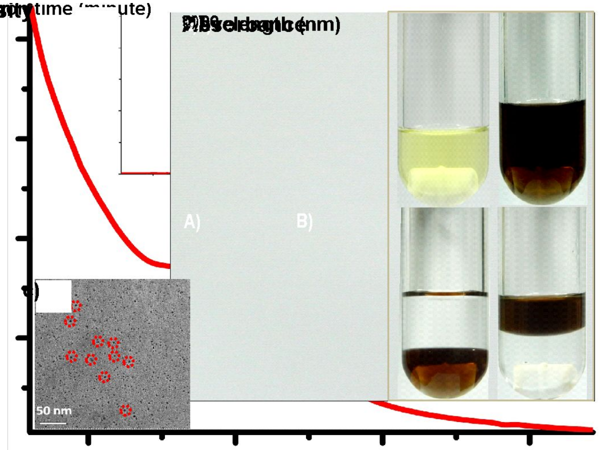


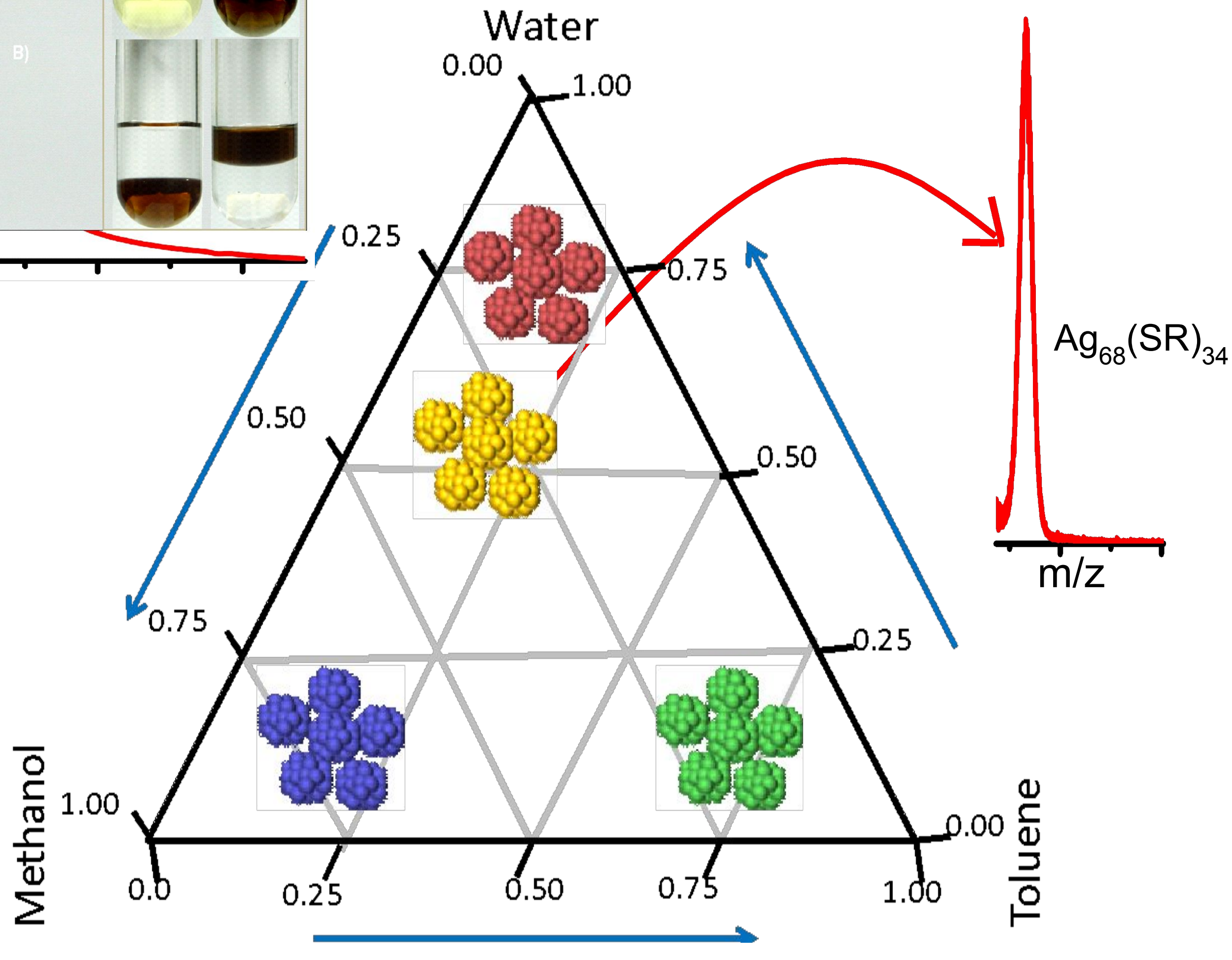


T. U. B. Rao et al. Angew. Chem. Int. Ed. 2012

Hot article

Three phase synthesis





$Ag_{68}SR_{34}$

Atanu Ghosh and T. Pradeep, Eur. J. Inorg. Chem. 2014

Available online at www.sciencedirect.com

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Chemical Physics Letters 390 (2004) 181–185

CHEMICAL PHYSICS LETTERS

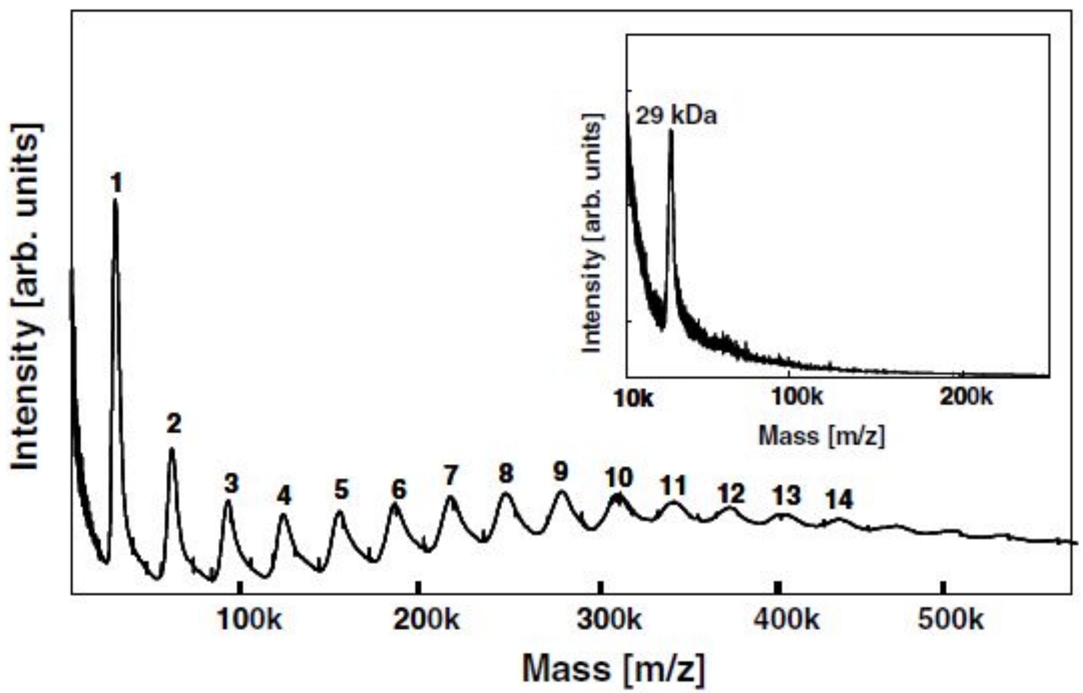
www.elsevier.com/locate/cplett

Gas phase aggregates of protected clusters

Jobin Cyriac, V.R. Rajeev Kumar, T. Pradeep *

Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras, Chennai 600 036, India

Received 30 January 2004; in final form 2 April 2004
Available online 27 April 2004



Jobin *et al. Chem. Phys. Lett.* 2004, *390*,181

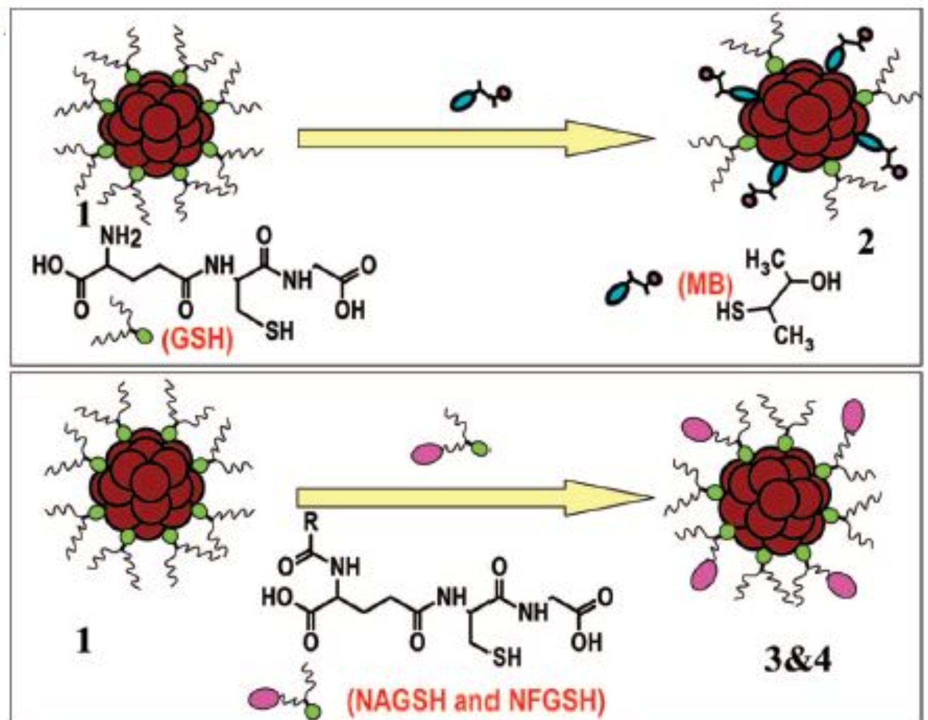
J. Phys. Chem. C **2008,** *112,* 12168–12176

Ligand Exchange of $Au_{25}SG_{18}$ Leading to Functionalized Gold Clusters: Spectroscopy, Kinetics, and Luminescence

E. S. Shibu,[†] M. A. Habeeb Muhammed,[†] T. Tsukuda,[‡] and T. Pradeep[*,†]

DST Unit on Nanoscience (DST UNS), Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Madras, Chennai 600 036, India and Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Received: January 18, 2008;

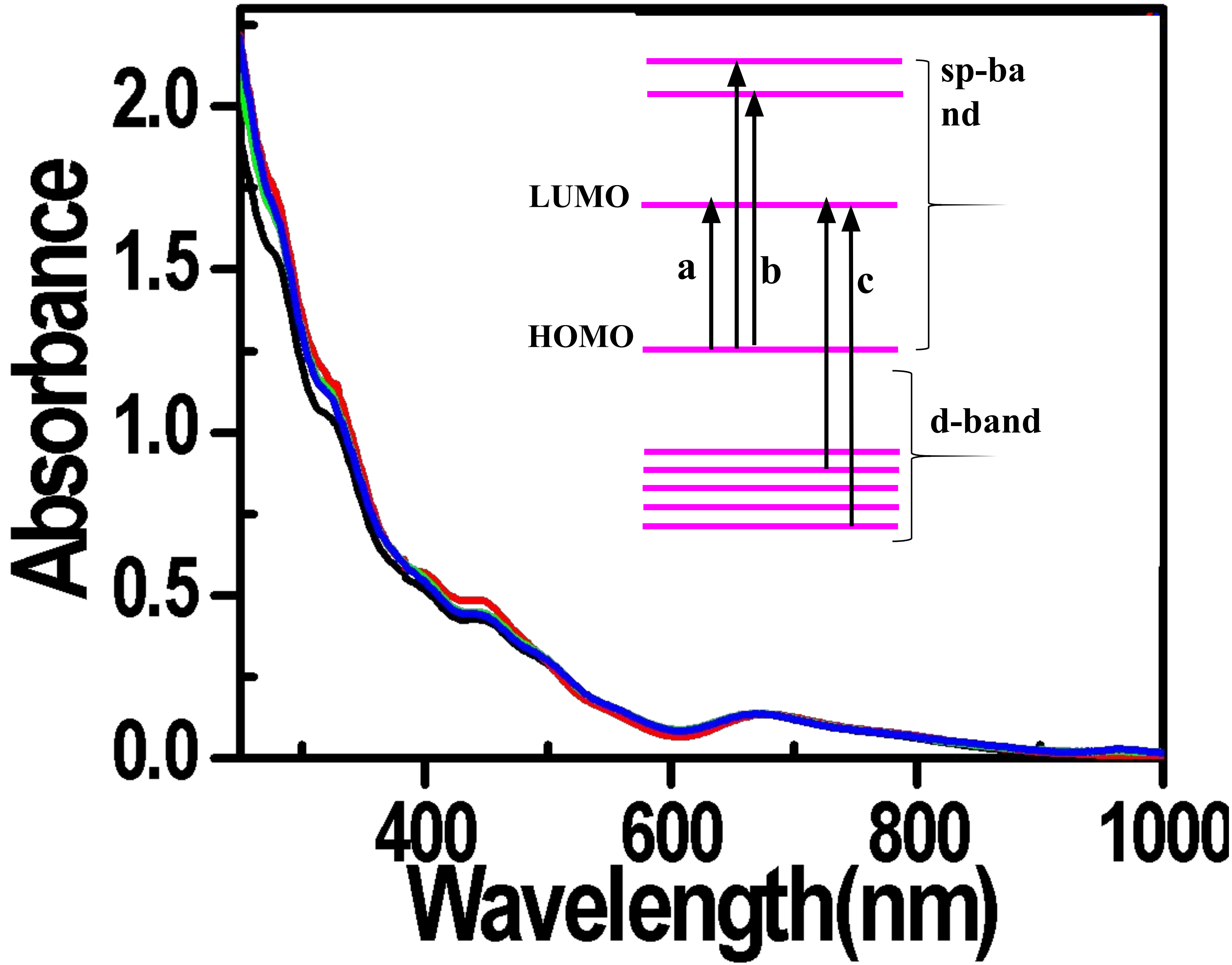


With Tatsuya Tsukuda

$Au_{25}SG_{18}$

Direct synthesis from mixture of particles

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



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

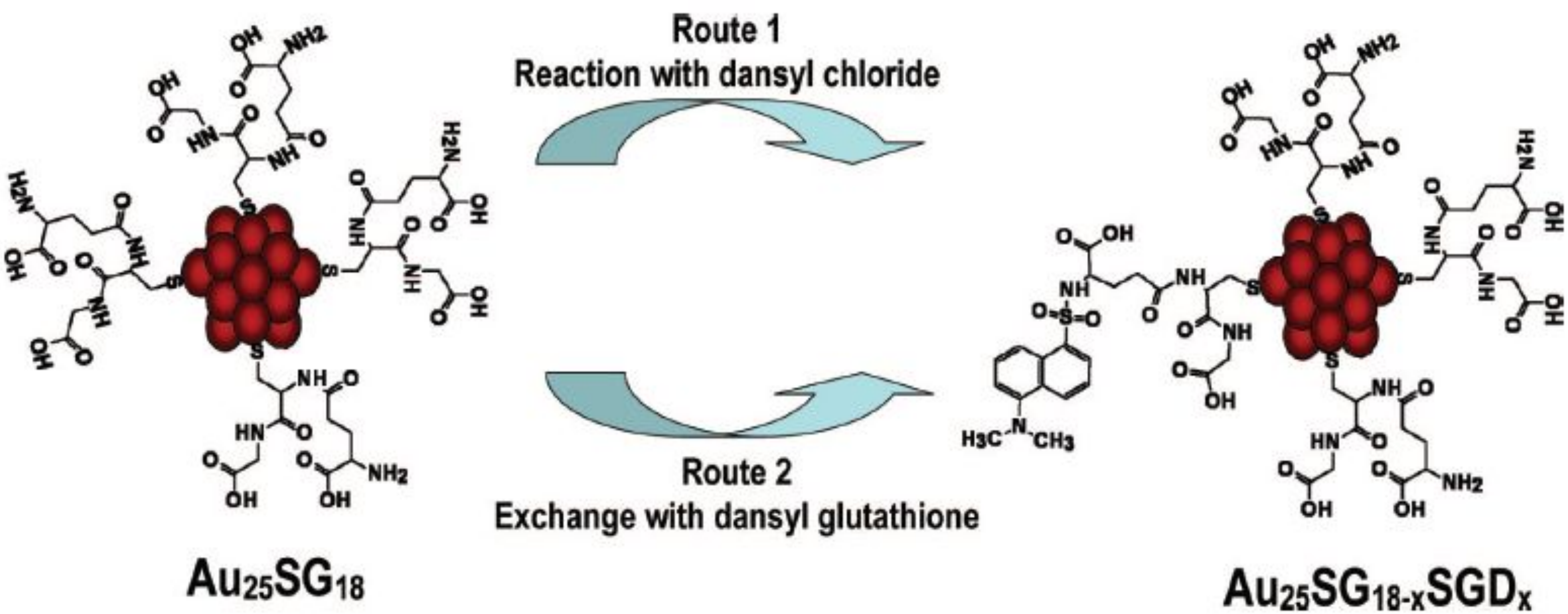
Quantum Clusters of Gold Exhibiting FRET

M. A. Habeeb Muhammed,[†] Ajay Kumar Shaw,[‡] Samir Kumar Pal,[*,‡] and T. Pradeep[*,†]

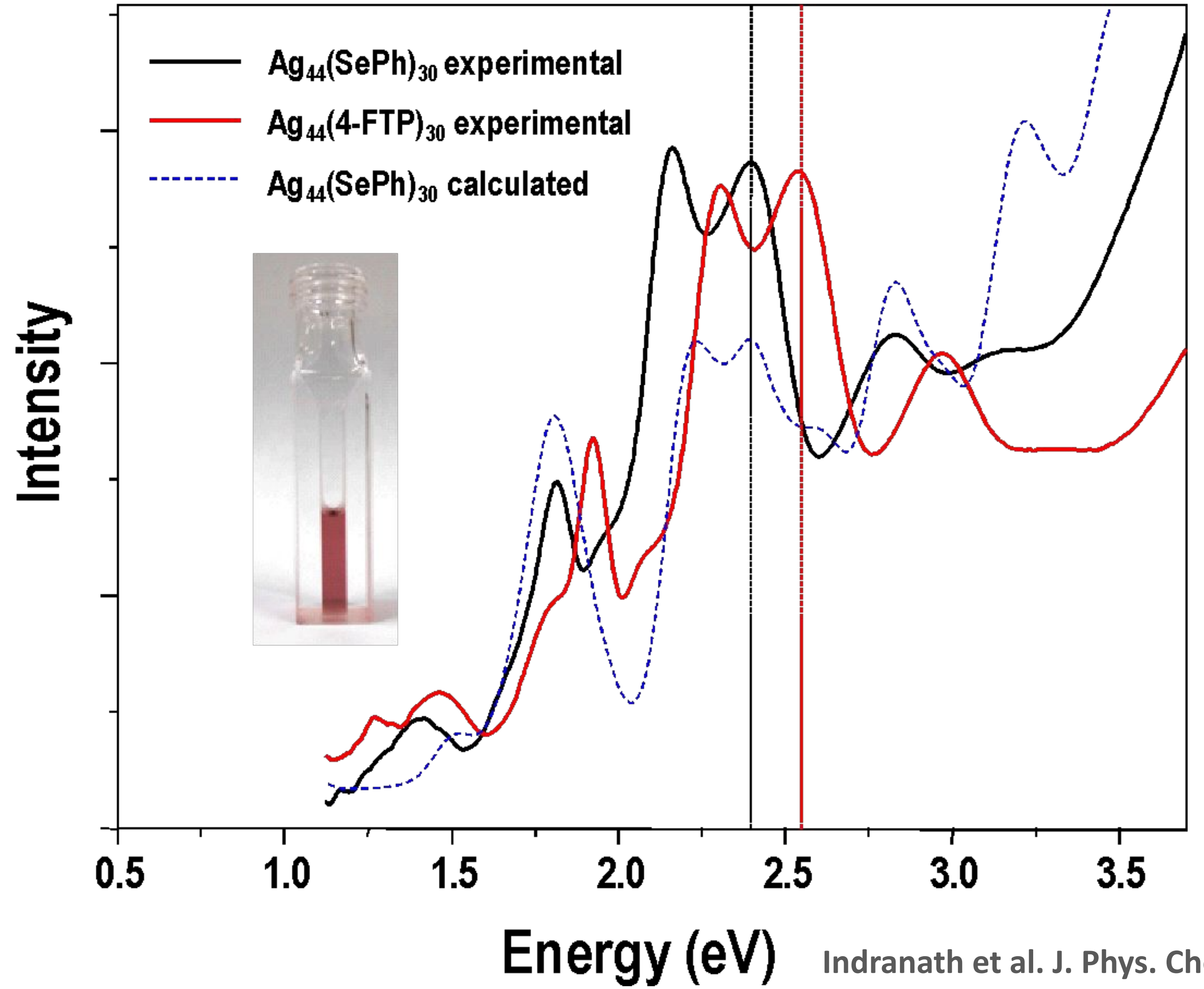
DST Unit on Nanoscience, Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras, Chennai 600 036, India, and Unit for Nanoscience and Technology, Department of Chemical, Biological and Macromolecular Sciences, Satyendra Nath Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700 098, India

Received: May 24, 2008; Revised Manuscript Received: June 25, 2008

SCHEME 1: Approaches Used for Functionalization of Dansyl Chromophore on the Au_{25} Cluster

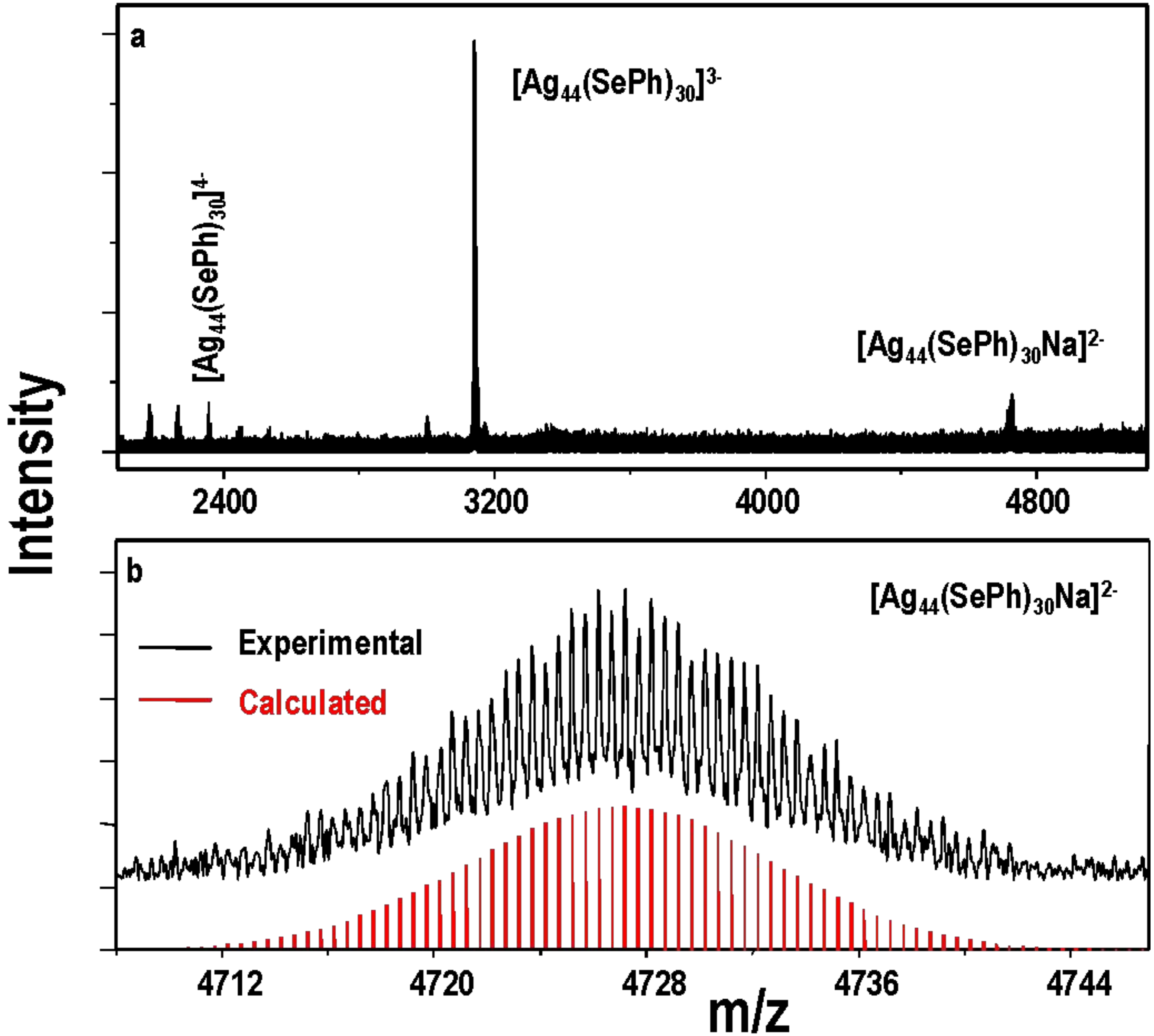


$Ag_{44}SePh_{30}$

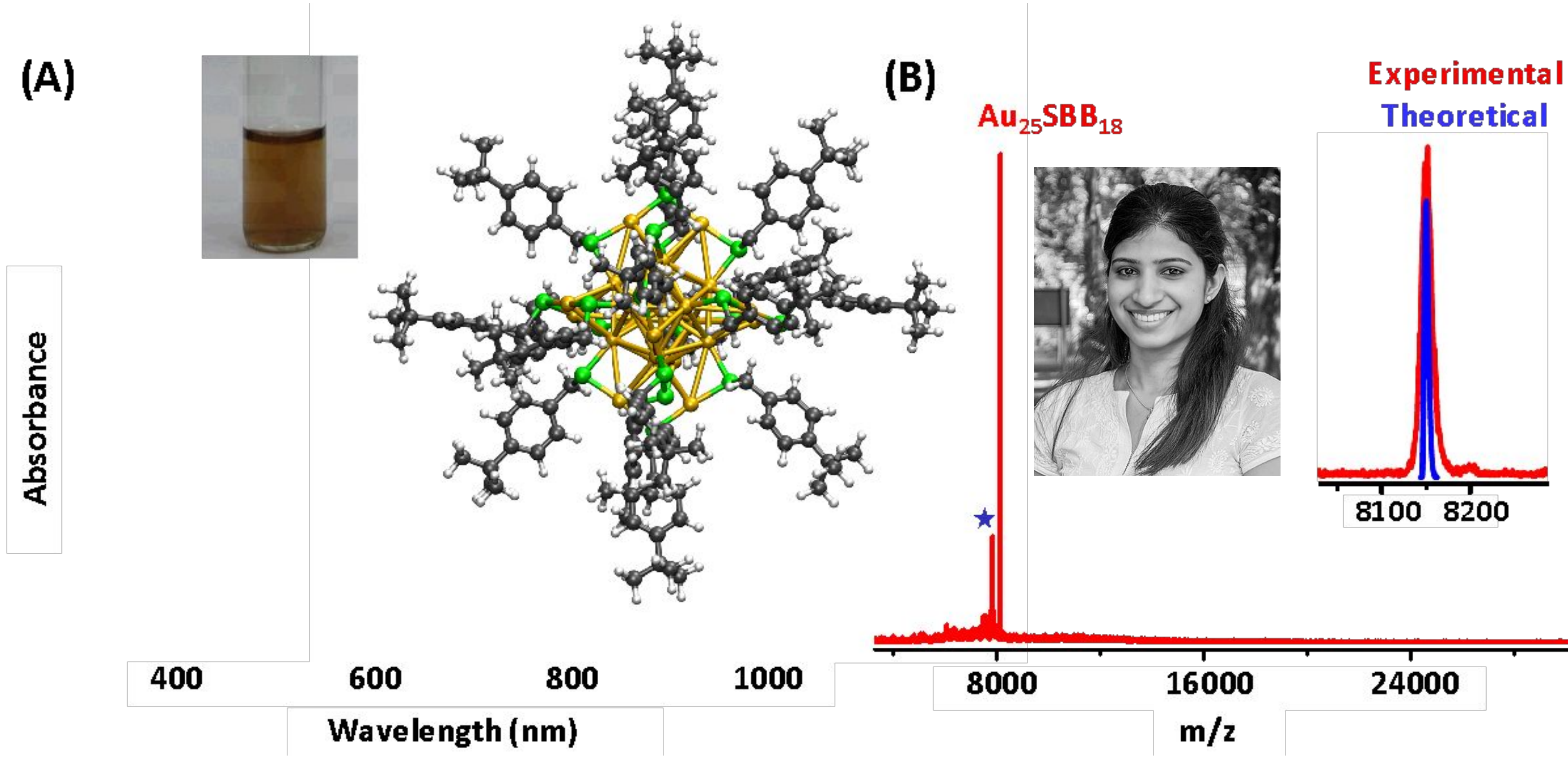


Indranath et al. J. Phys. Chem. Lett. 2013

With Lars Gell, Hannu Hakkinen, Wataru Kurashige, Y. Negishi



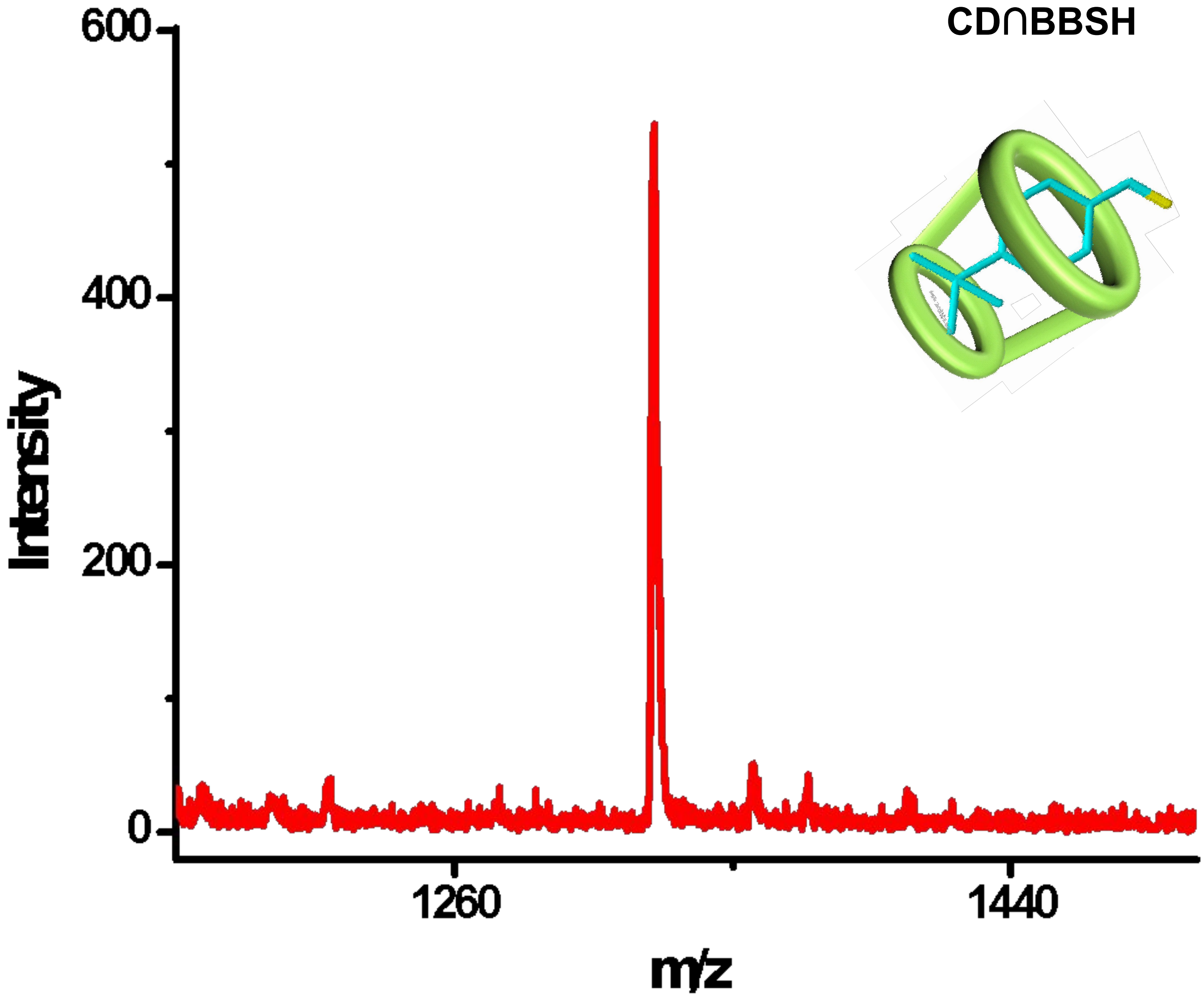
Intensity
a
[Ag44(SePh)30]3-
[Ag44(SePh)30]4-
[Ag44(SePh)30Na]2-
2400
3200
4000
4800
b
[Ag44(SePh)30Na]2-
Experimental
Calculated
4712
4720
4728
4736
4744
m/z



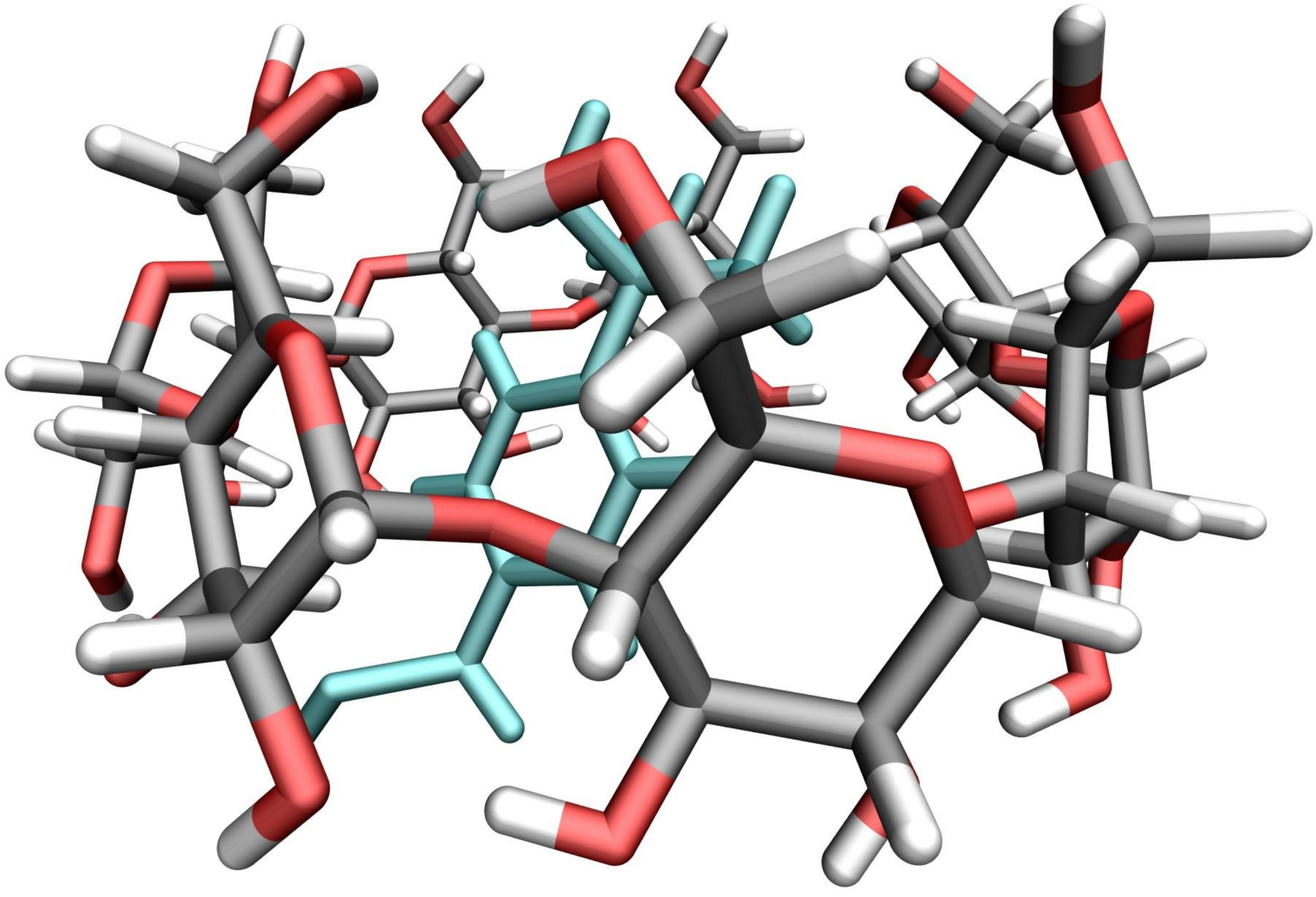
Ammu Mathew et al. ACS Nano 2014.

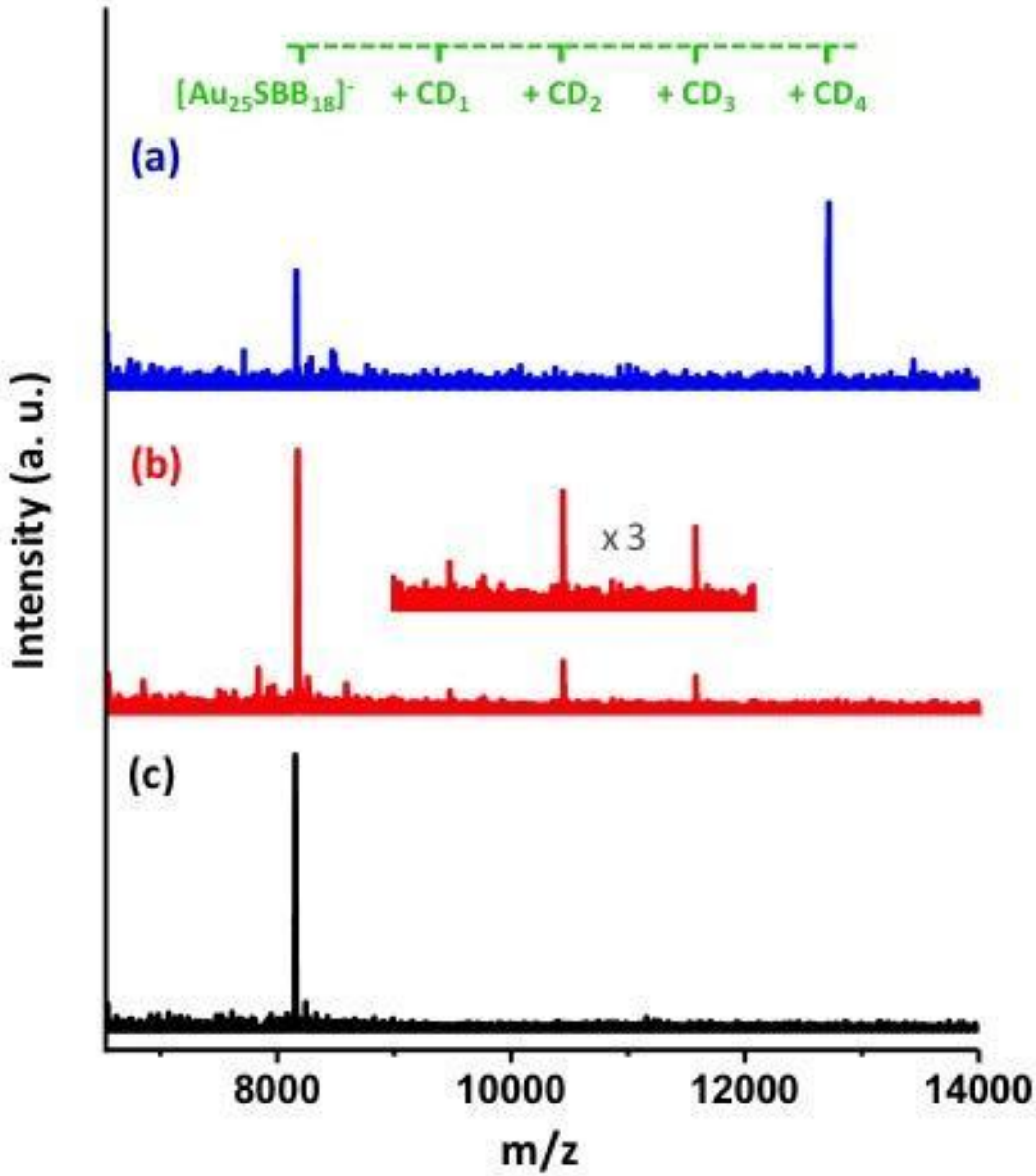
With Lauri Lehtovaara, Hannu H.kkinen

Positive mode MALDI of BBSH∩CD complex

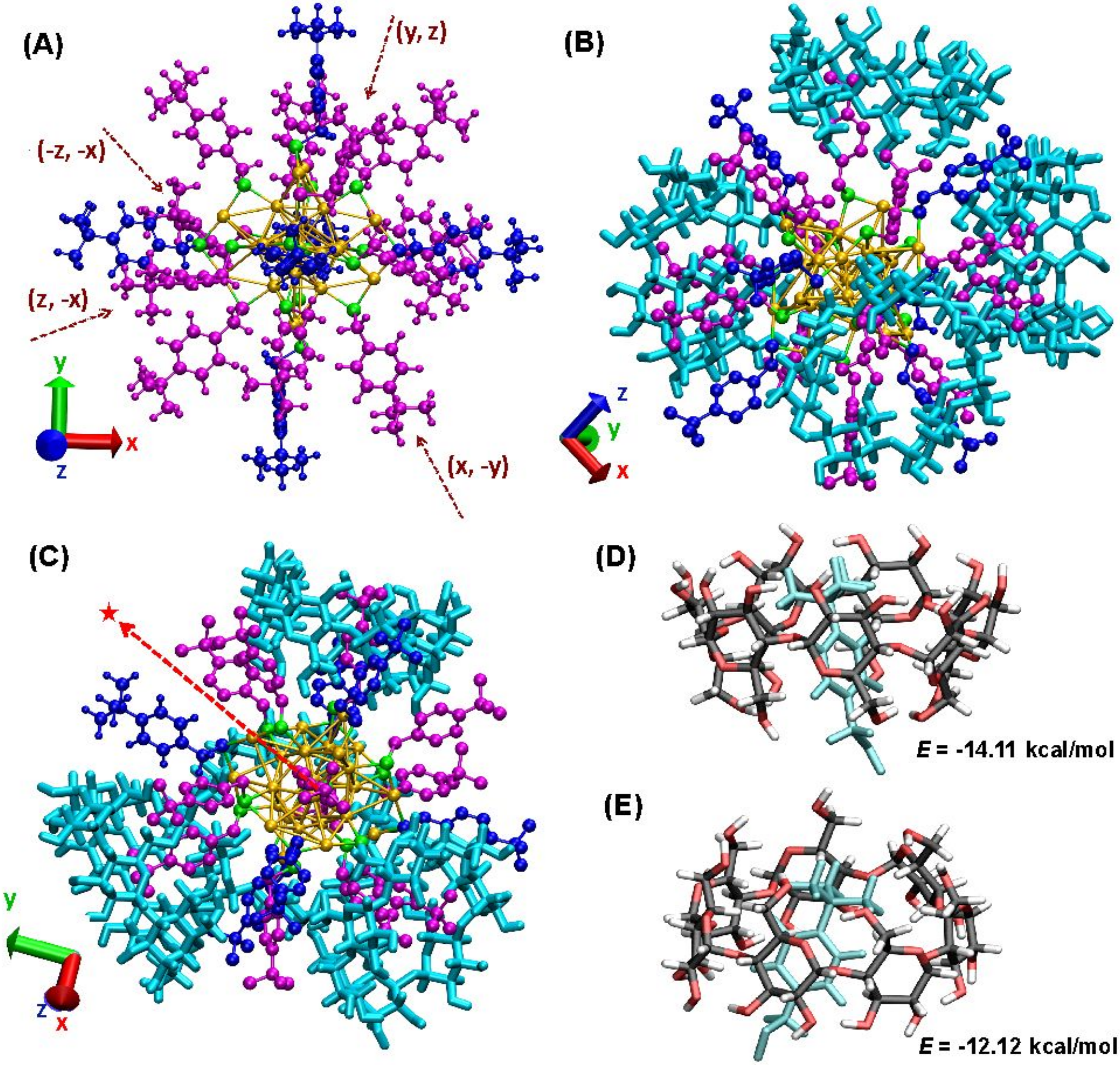


β-CD/BBSH



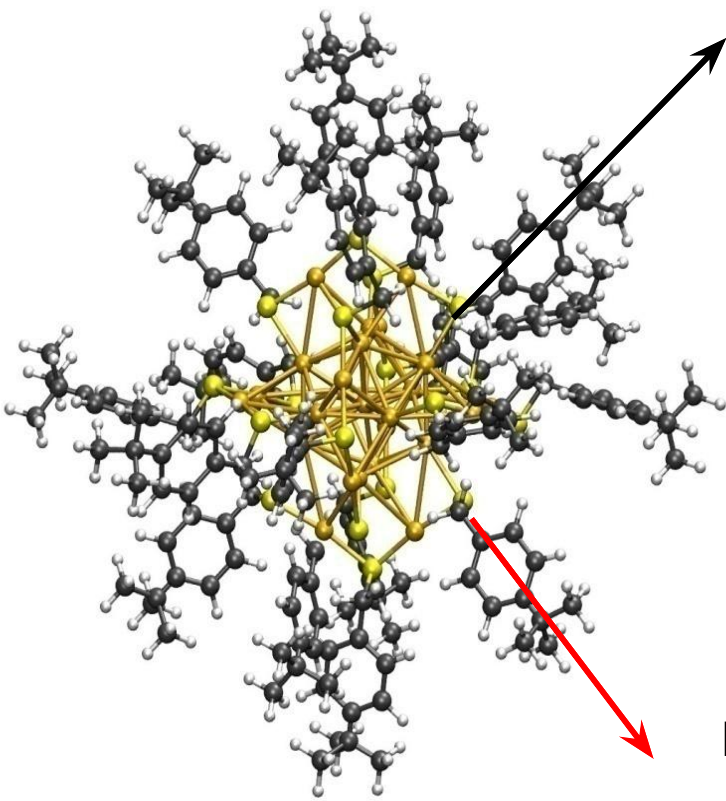


[Au25SBB18]-
+ CD1
+ CD2
+ CD3
+ CD4
(a)
(b)
x 3
(c)
Intensity (a. u.)
8000
10000
12000
14000
m/z



(A)
(y, z)
(-z, -x)
(z, -x)
(x, -y)
y
x
z
(B)
z
y
x
(C)
y
z
x
(D)
E = -14.11 kcal/mol
(E)
E = -12.12 kcal/mol

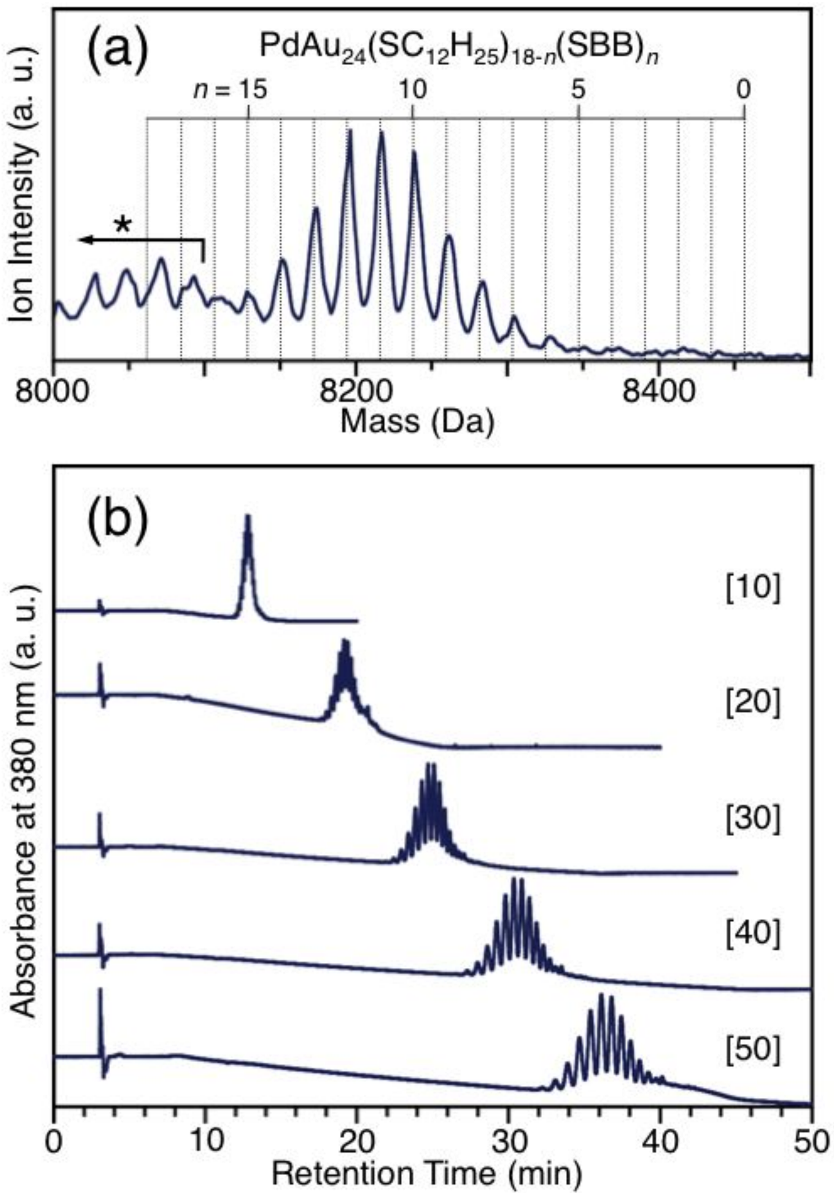
Substitution chemistry of clusters



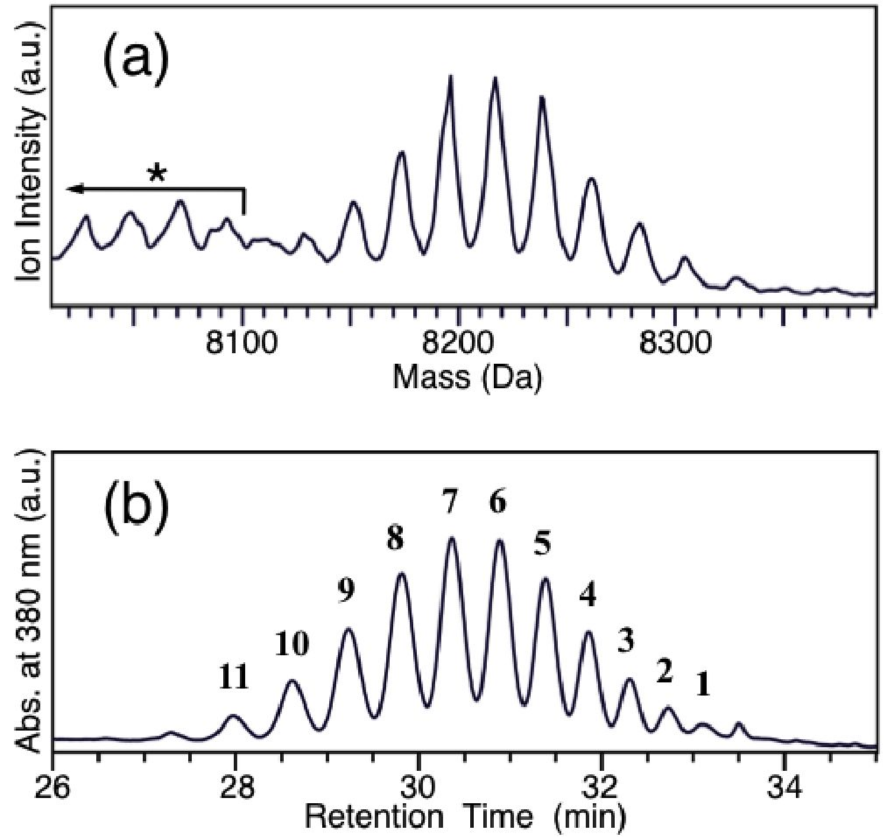
Mixed functionalised clusters

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

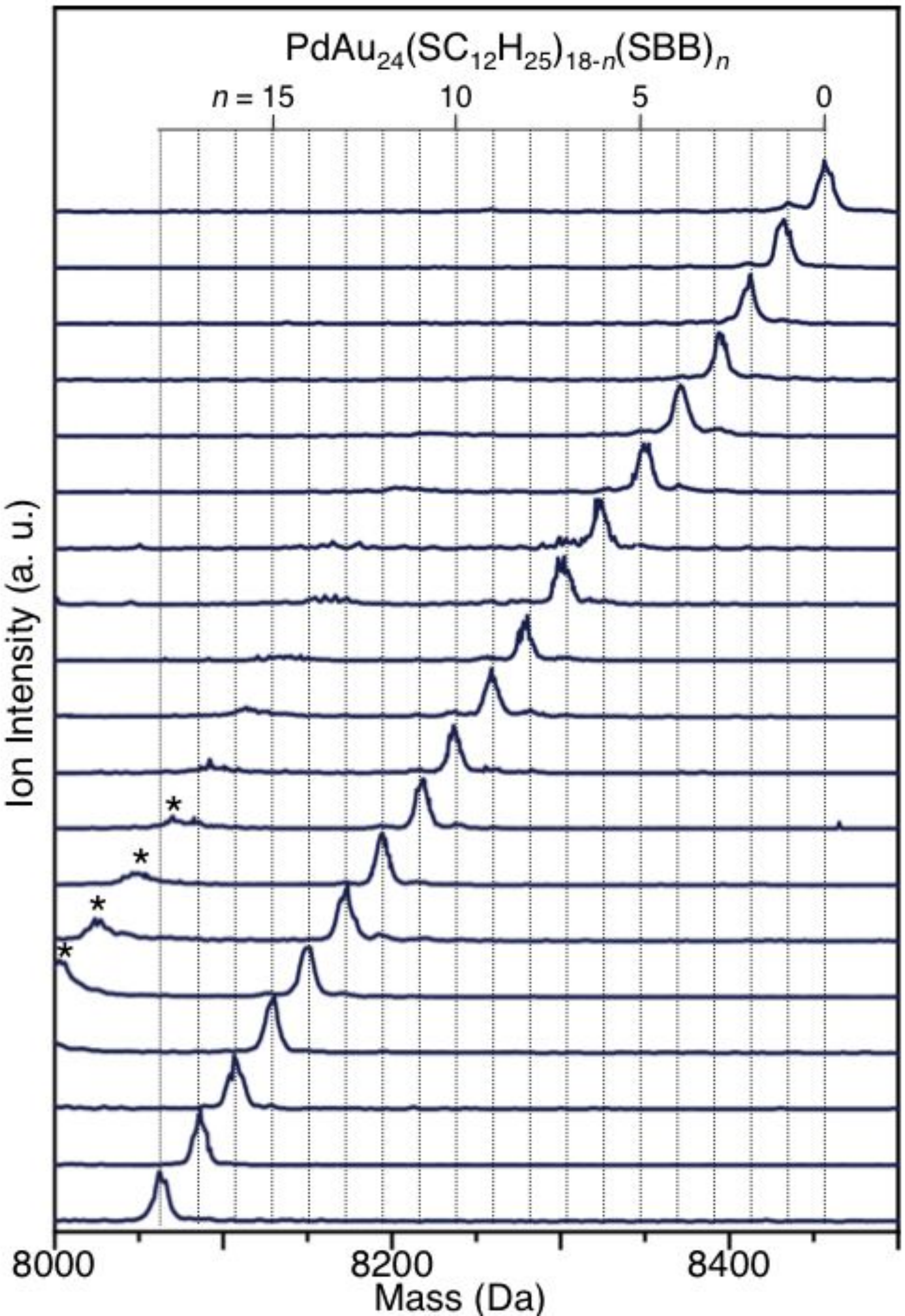
Separation of precise compositions of noble metal clusters protected with mixed ligands



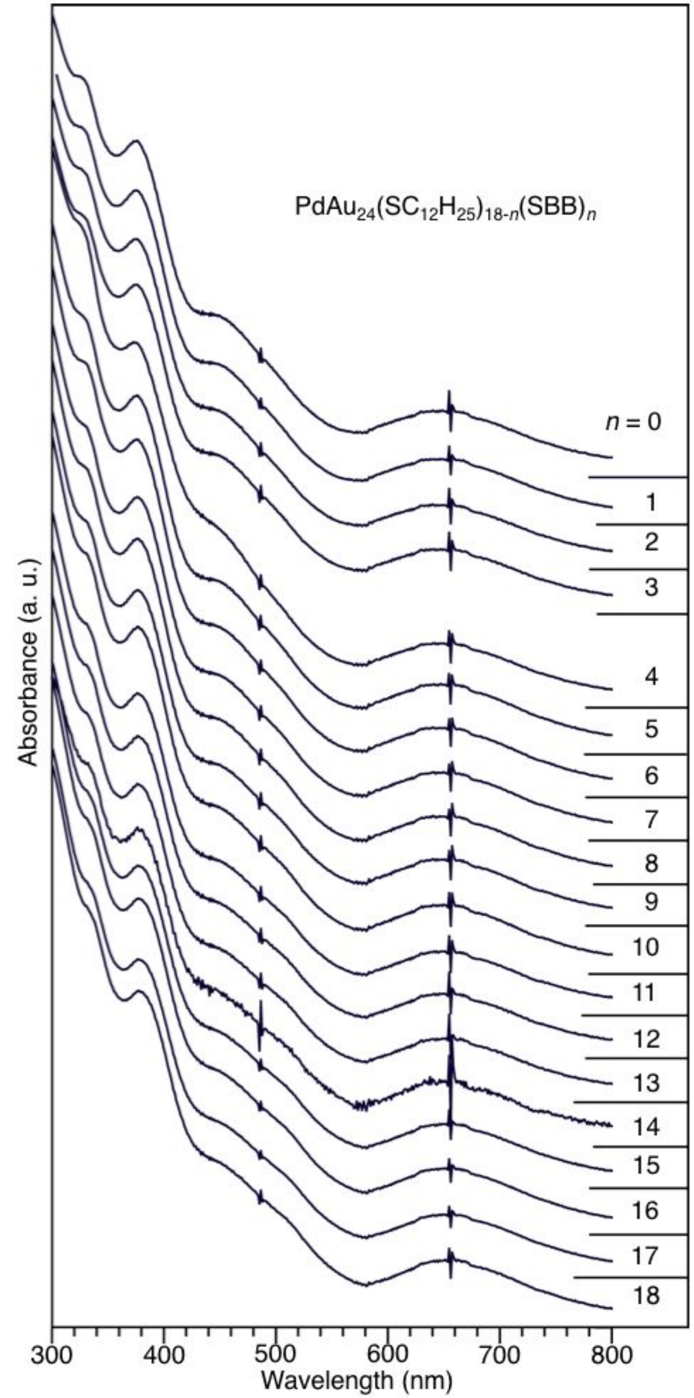
Ligand exchange chemistry – Substitution chemistry



With Niihori and Negishi, Tokyo University of Science

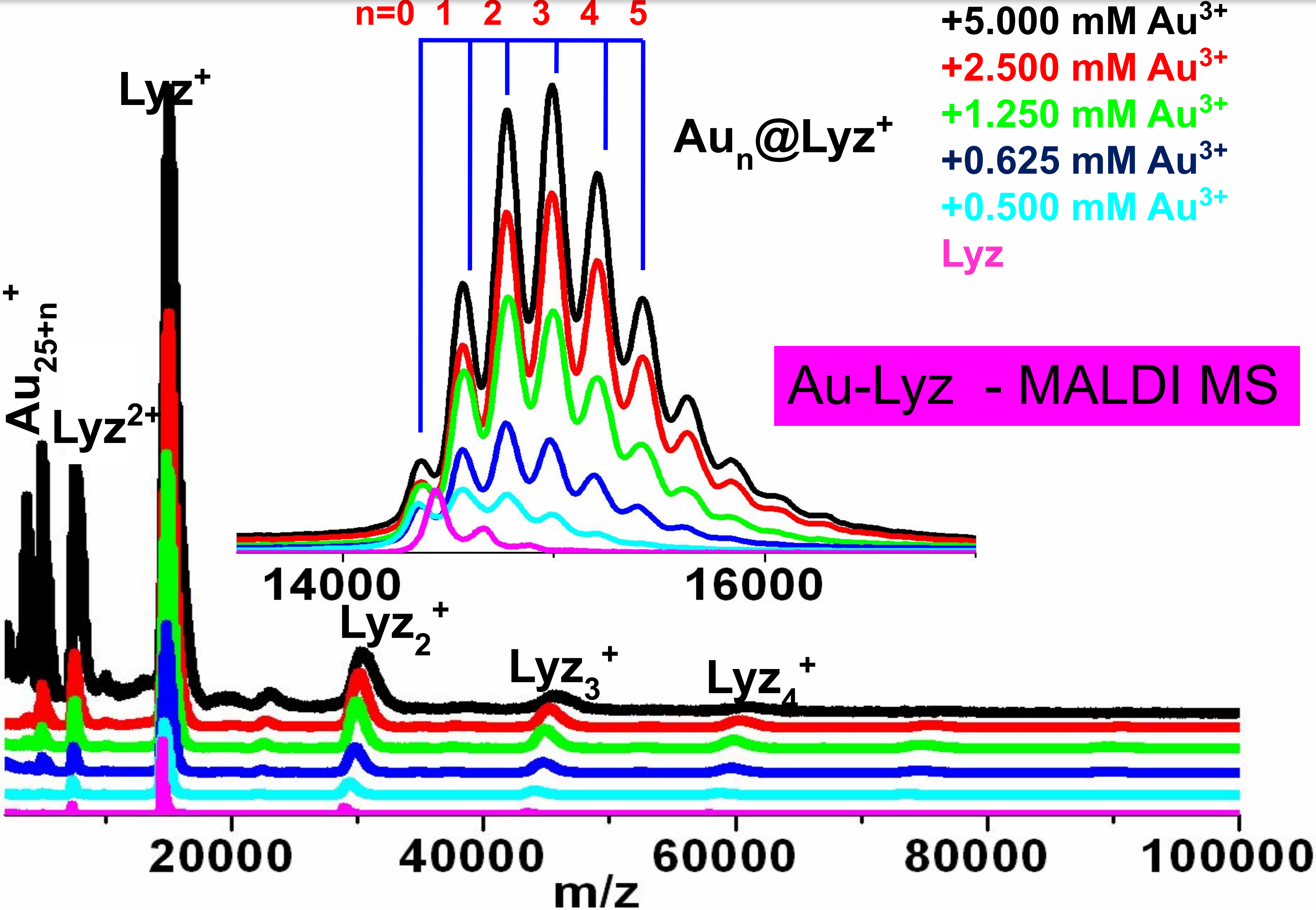


$PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$
n = 15
10
5
0
Ion Intensity (a. u.)
*
*
*
*
8000
8200
8400
Mass (Da)

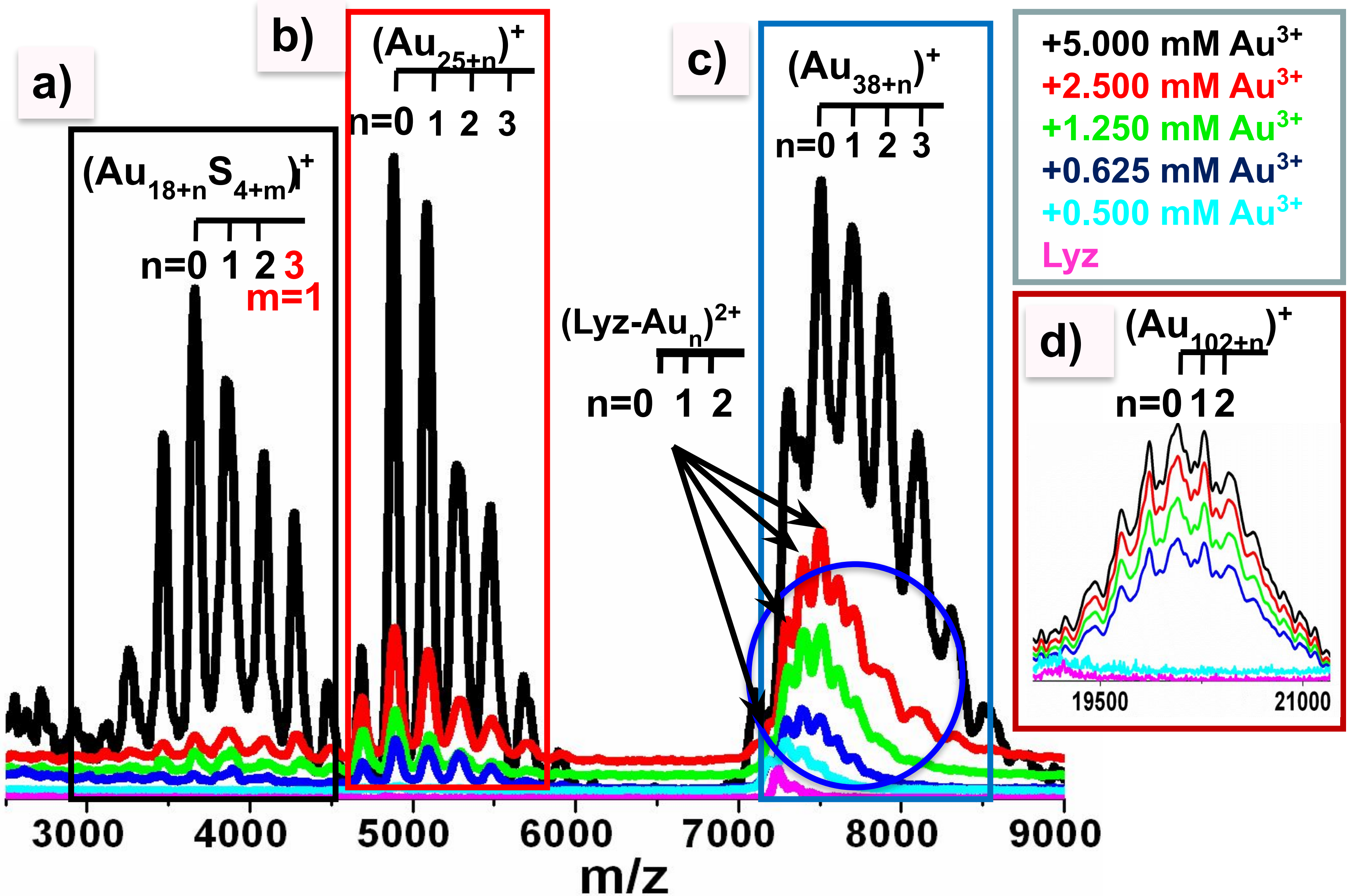


$PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$
n = 0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Absorbance (a. u.)
300
400
500
600
700
800
Wavelength (nm)

Unprotected clusters from protein templates

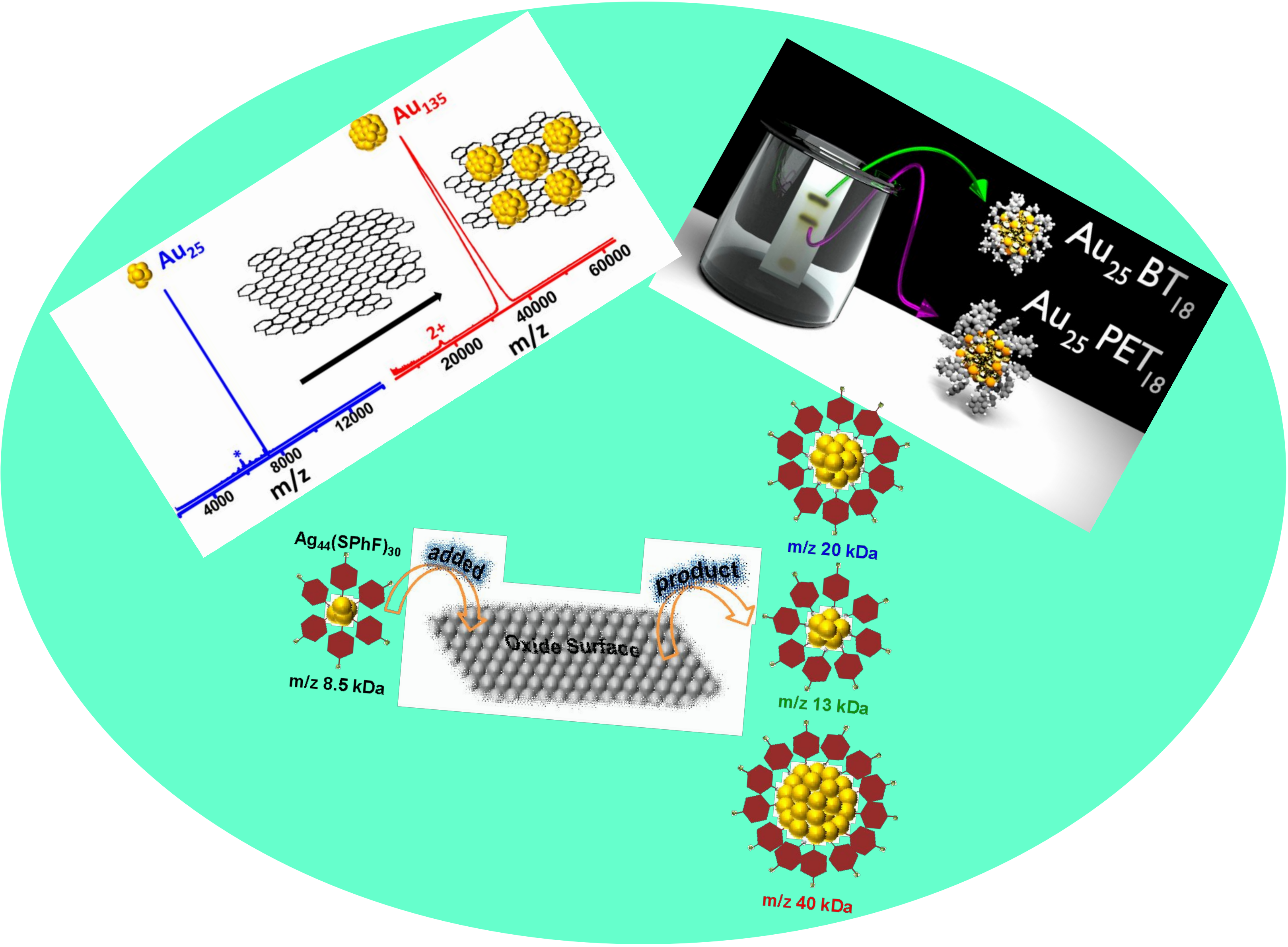


A. Baksi, T. Pradeep, B. Yoon, C. Yannouleas and U.Landman, ChemPhysChem, 14 (2013) 1272-1282.

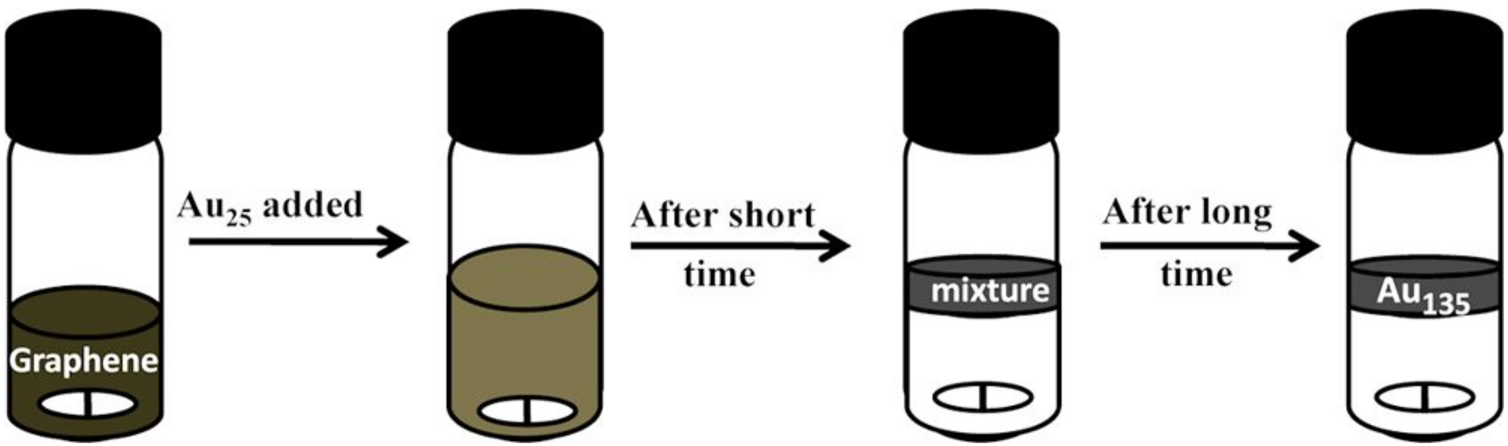

a)
b)
c)
d)
$(Au_{18+n}S_{4+m})^+$
n=0 1 2 3
m=1
$(Au_{25+n})^+$
n=0 1 2 3
$(Au_{38+n})^+$
n=0 1 2 3
$(Lyz\text{-}Au_n)^{2+}$
n=0 1 2
$(Au_{102+n})^+$
n=0 1 2
+5.000 mM Au^{3+}
+2.500 mM Au^{3+}
+1.250 mM Au^{3+}
+0.625 mM Au^{3+}
+0.500 mM Au^{3+}
Lyz
3000
4000
5000
6000
7000
8000
9000
m/z
19500
21000

Part II
Some Pointers

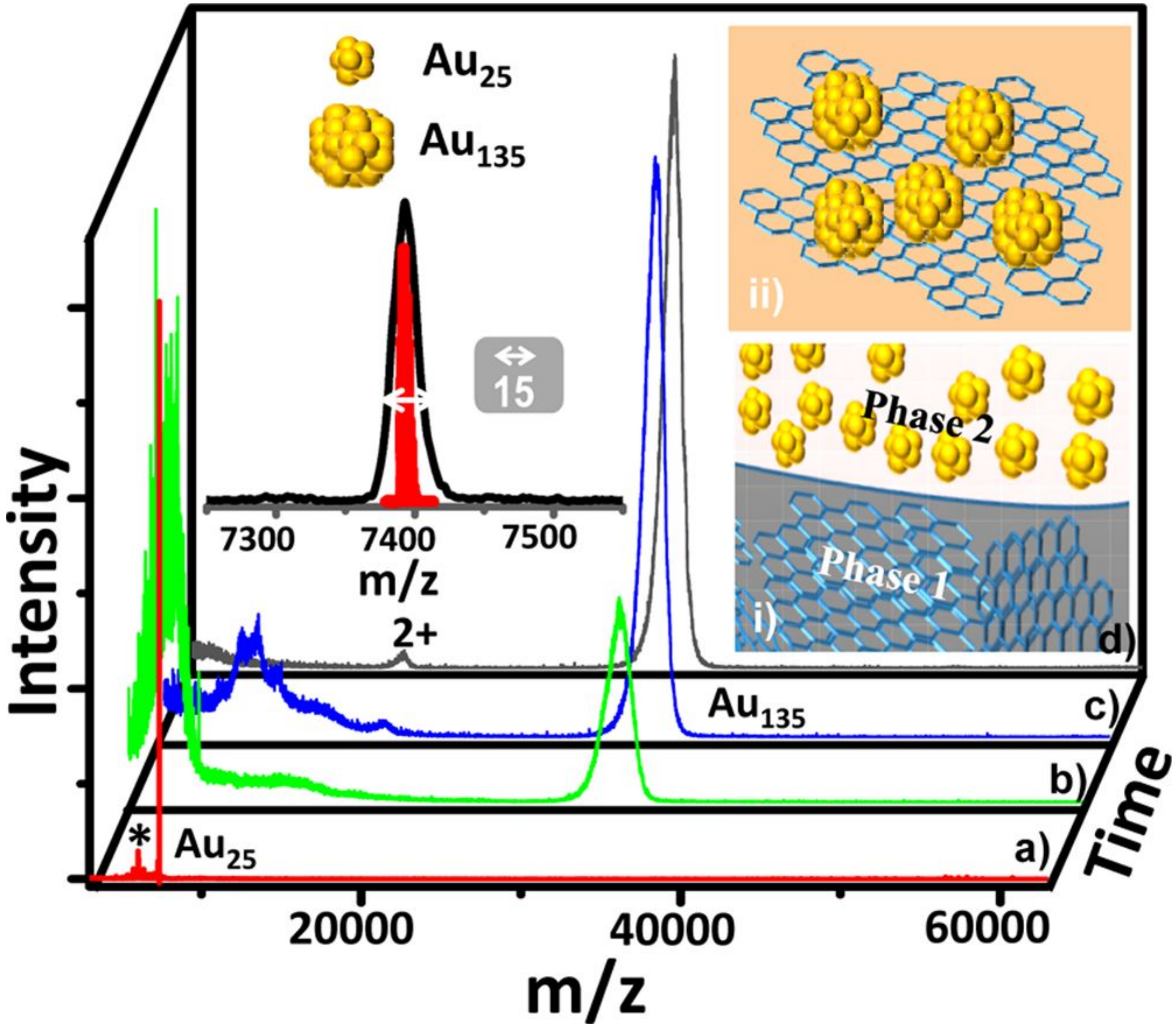
Noble Metal Clusters Over Oxides: Aggregation, Separation and Reaction



Coalescence of Atomically Precise Clusters on Graphenic Surfaces

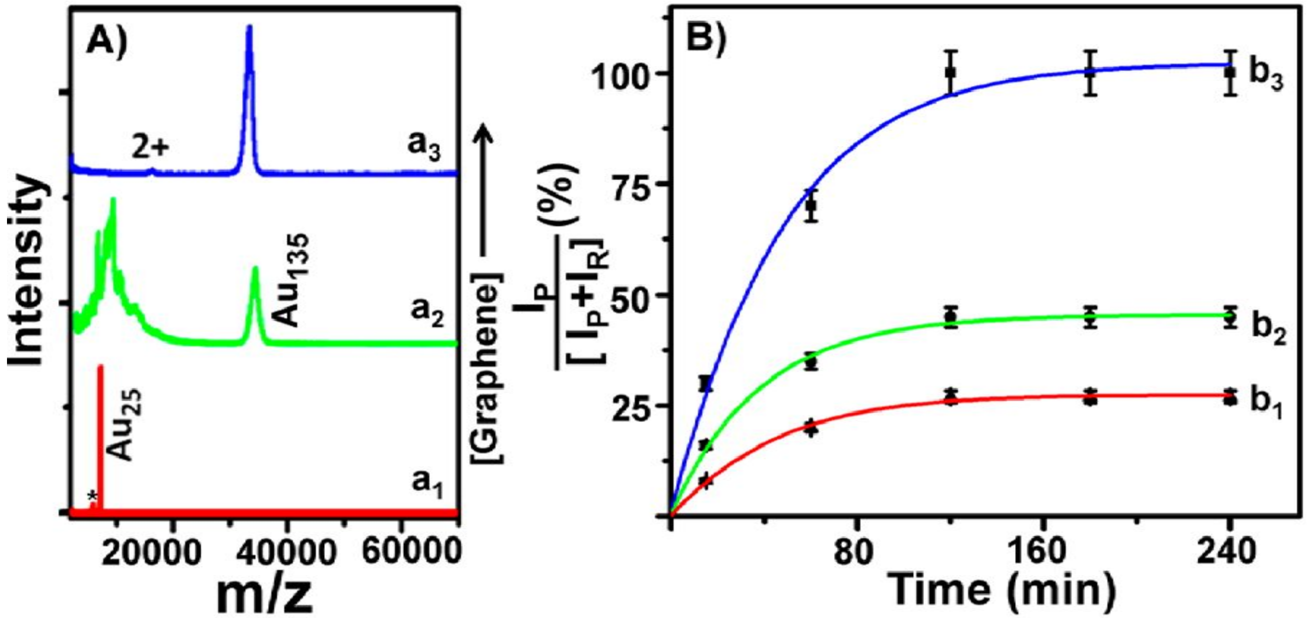


Schematic of the reaction

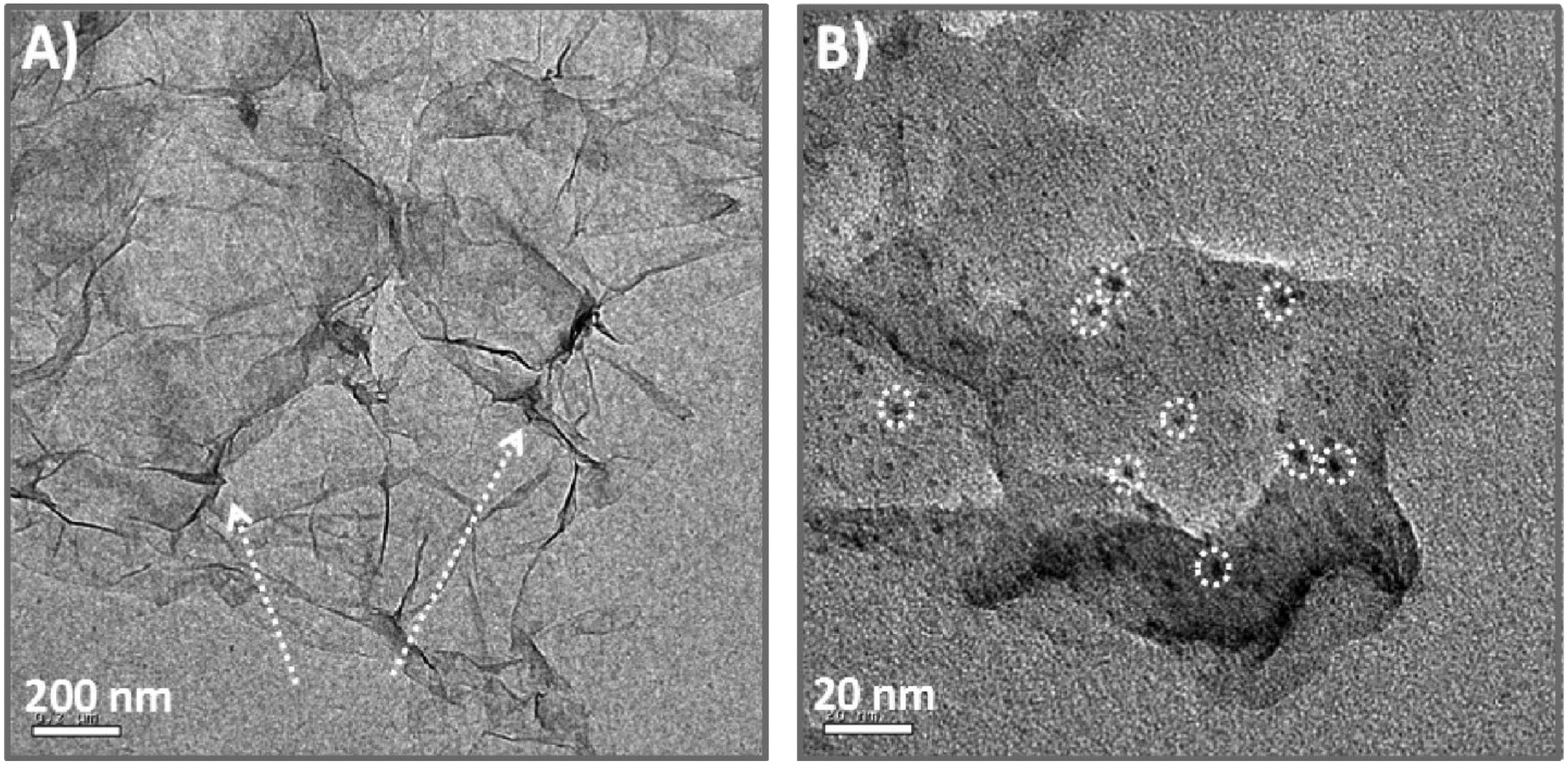


Time dependent MALDI MS study of the conversion of Au_{25}.

Ghosh, A.; Pradeep, T.; Chakrabarti, J. *J. Phys. Chem. C* **2014**, *118,* 13959.



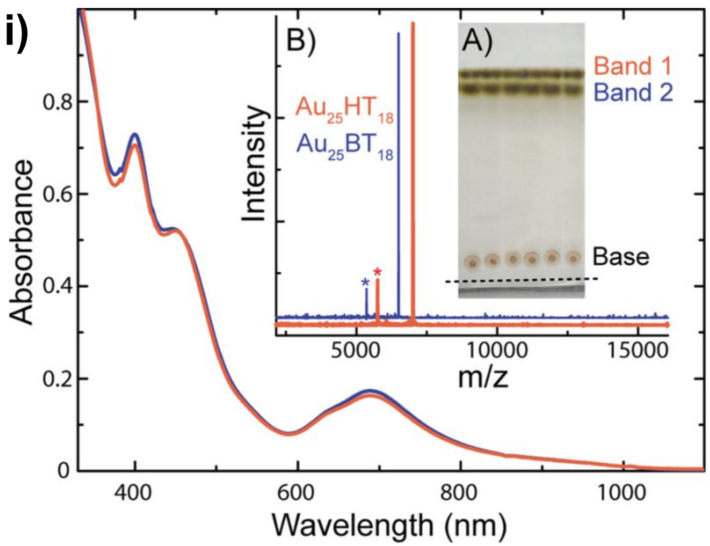
MALDI MS spectra with increasing graphene concentration for a constant Au_{25} concentration. (a_2) Data at lower concentration (0.005 wt %) of graphene where complete conversion of Au_{25} to Au_{135} has not taken place. It shows some peaks at lower mass. (a3) At higher concentration (0.01 wt %) of graphene, complete conversion to Au_{135} has happened. Both the spectra were collected after 180 min of mixing the reactants. (B) Time dependent conversion of Au_{25} for a fixed graphene concentration at different Au_{25} concentrations. IP and IR represent the intensity of Au_{135} and Au_{25} in the MALDI MS spectra. Traces b_1, b_2, and b_3 represent final concentrations of Au_{25} in solutions (3.17, 1.68, and 0.87 μM, respectively).



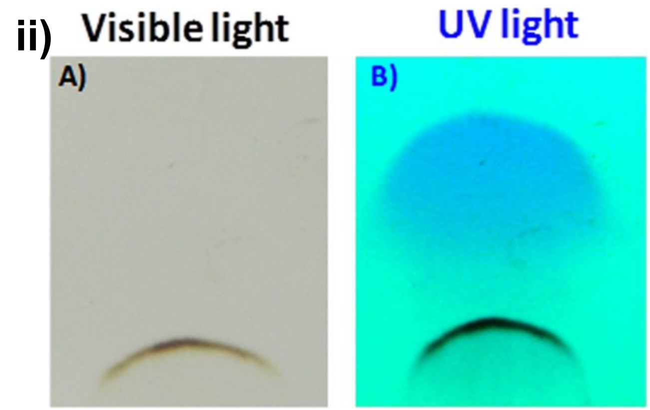
(A) TEM image of chemically synthesized graphene alone. The nanometer thin folding (marked) indicates that the sheets imaged contain two-three layers of chemically synthesized graphene. (B) Image of graphene surface containing clusters (Au_{135}). Some clusters are marked with circles. Outside the graphene surface, there was no cluster. It proves that the conversion happened only on graphene surfaces. Number of folding has decreased significantly in panel B.

Clusters on surfaces

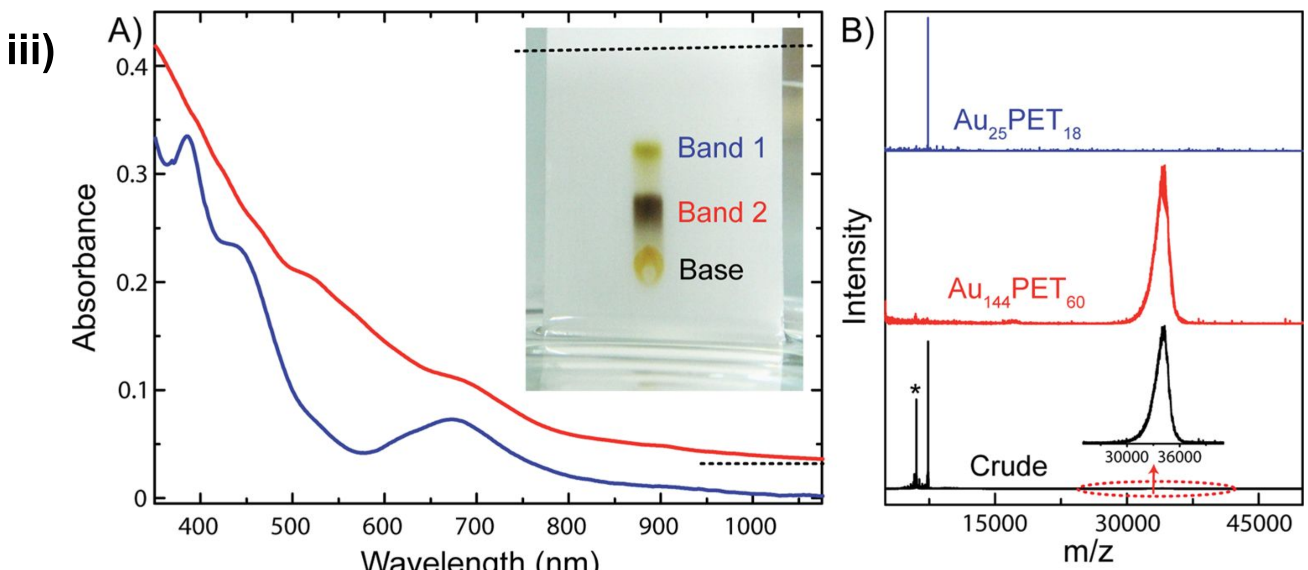
Simple and Efficient Separation of Atomically Precise Noble Metal Clusters



Separation of HT and BT protected Au_{25}



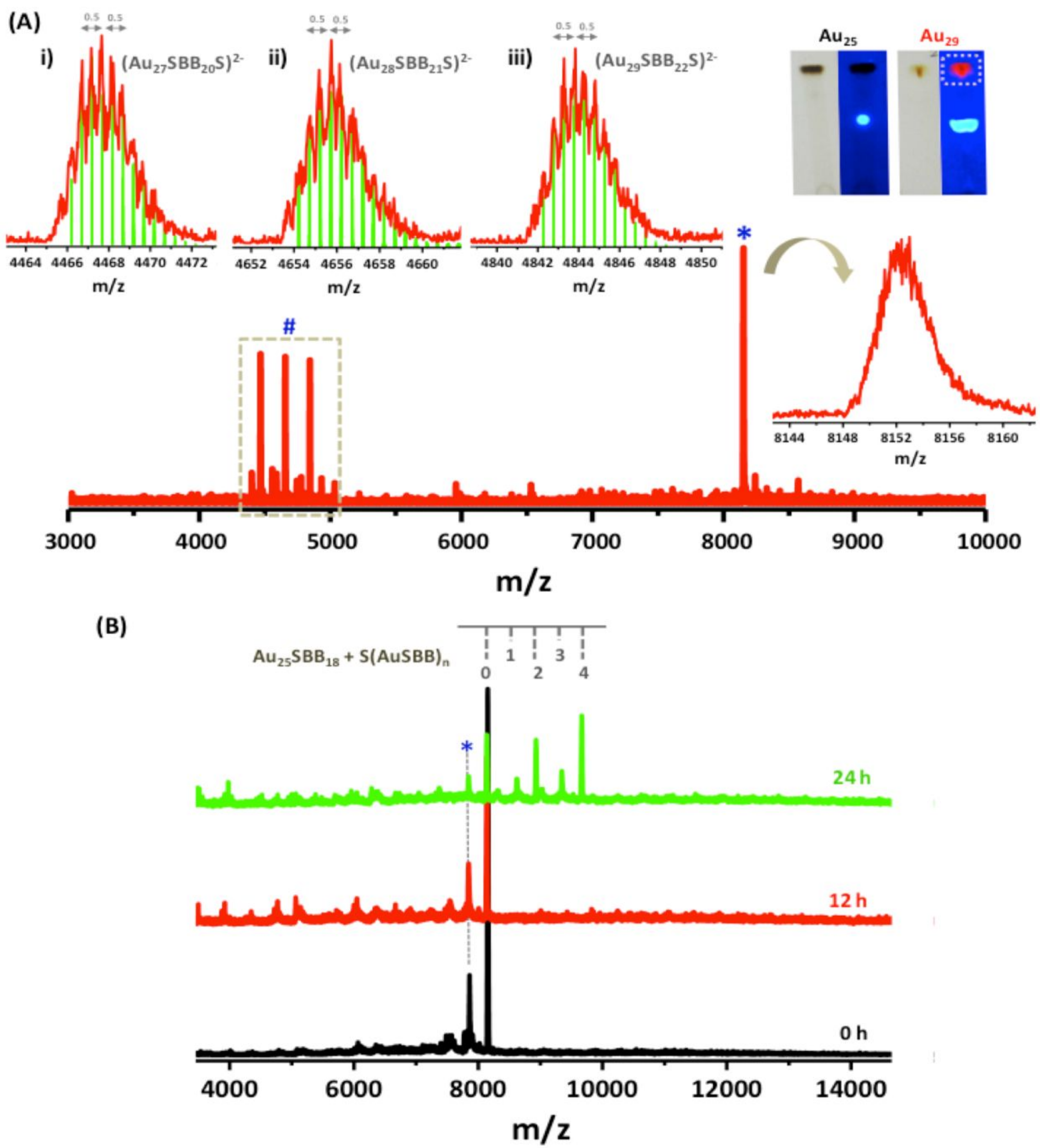
Removal of excess thiol



Separation of $Au_{25}PET_{18}$ and $Au_{144}PET_{60}$

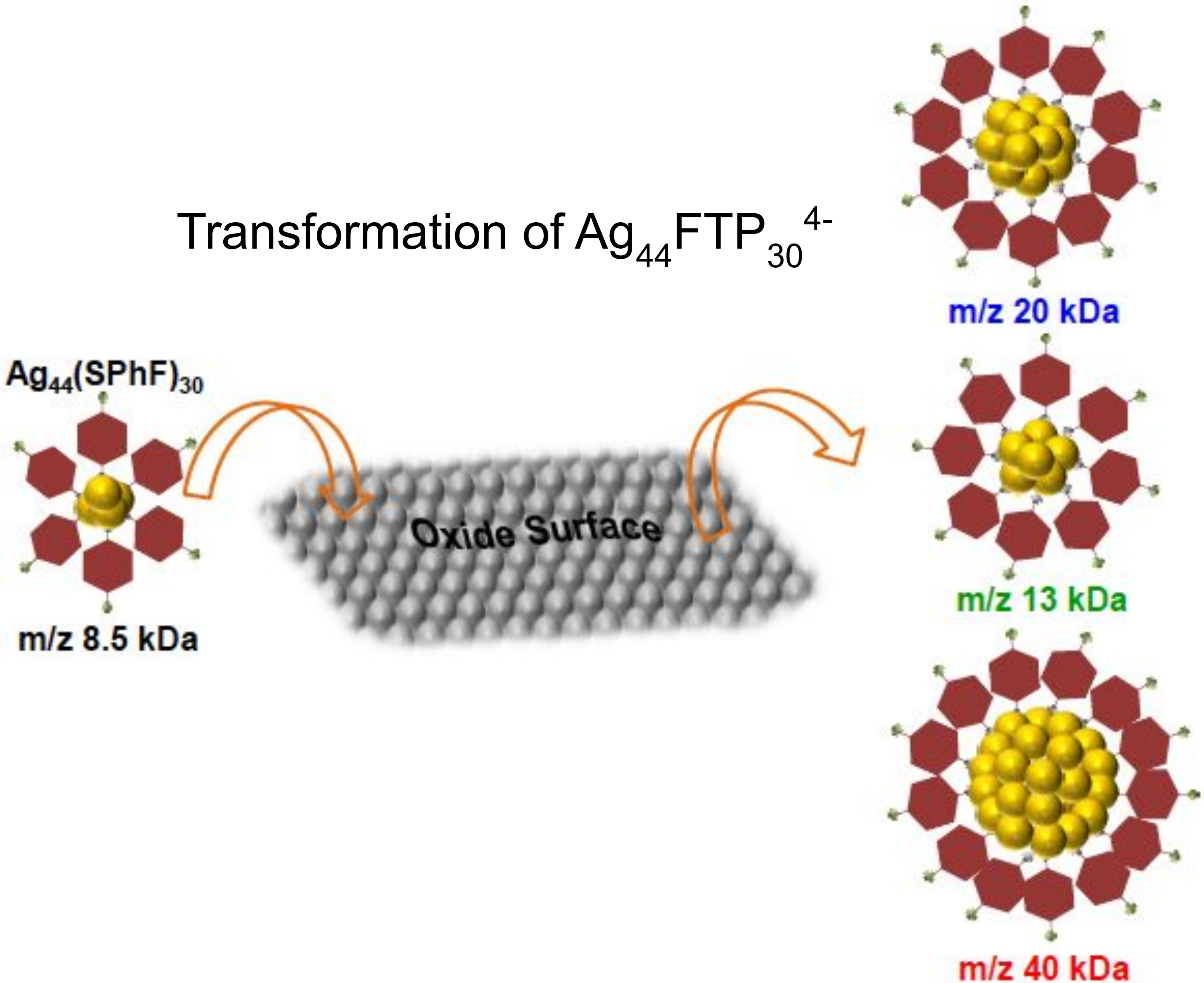
With Robin Ras

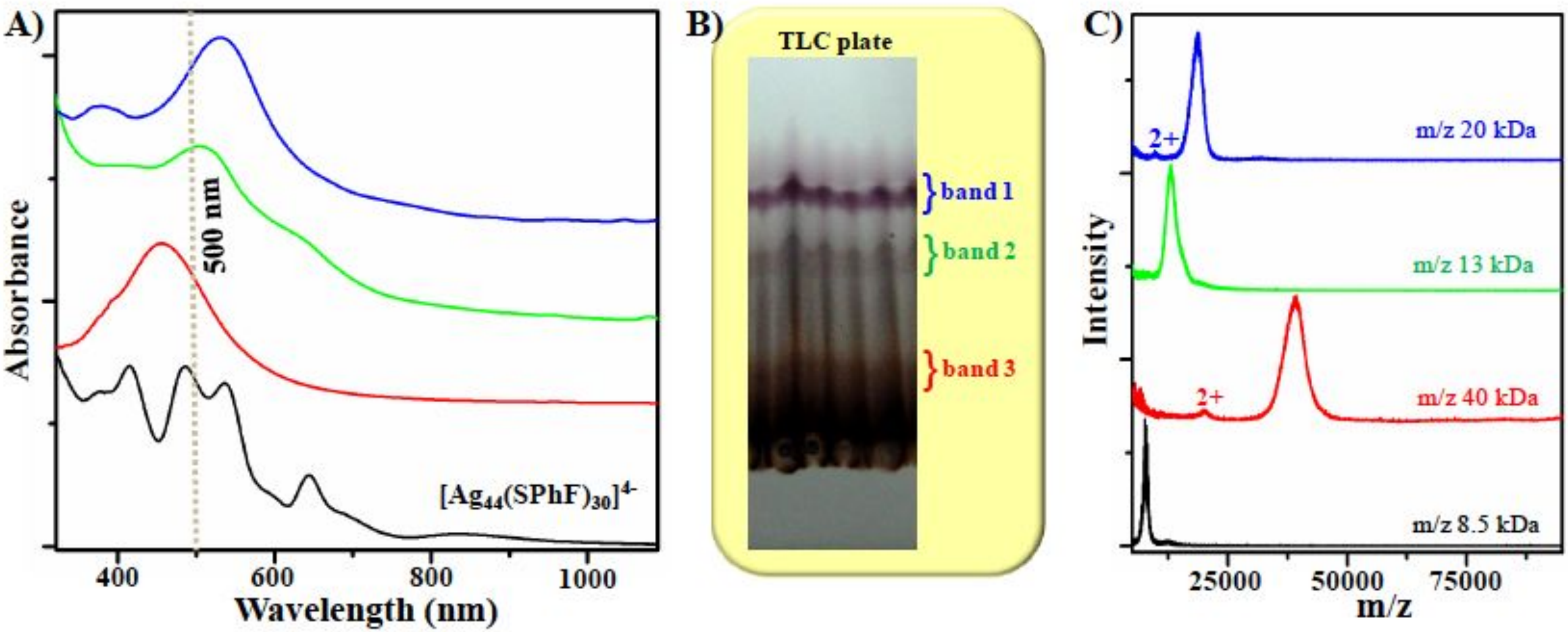
Ghosh, A.; Hassinen, J.; Pulkkinen, P.; Tenhu, H.; Ras, R. H. A.; Pradeep, T. *Anal. Chem.* **2014,** *86*, 12185.



A. Mathew et al. Nanoscale, 2015

Transformation of $Ag_{44}FTP_{30}^{4-}$





A)
500 nm
Absorbance
Wavelength (nm)
400
600
800
1000
[Ag44(SPhF)30]4-
B)
TLC plate
band 1
band 2
band 3
C)
Intensity
m/z
2+
m/z 20 kDa
m/z 13 kDa
2+
m/z 40 kDa
m/z 8.5 kDa
25000
50000
75000

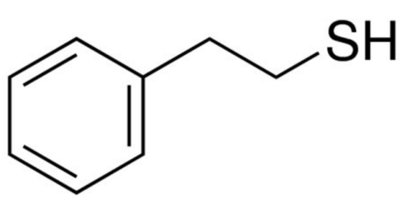
Inter cluster exchange reaction between $Au_{25}(SR)_{18}$ with $Ag_{44}(SR)_{30}$

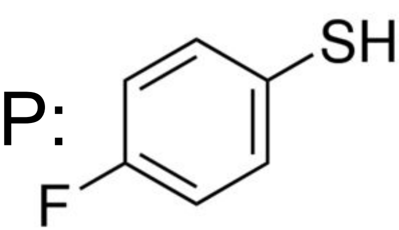
$$Au_{25}(PET)_{18} + Ag_{44}(FTP)_{30} \Rightarrow Au_{25-x}Ag_{x}(PET)_{18-y}(FTP)_{y} + Ag_{m}Au_{n}(PET)_{m'}(FTP)_{n'}$$

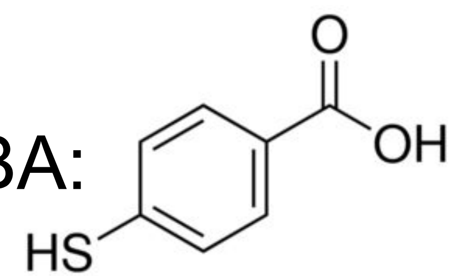
$$Au_{25}(FTP)_{18} + Ag_{44}(FTP)_{30} \Rightarrow Au_{25-x}Ag_{x}(FTP)_{18} + Ag_{m}Au_{n}(FTP)_{n'}$$

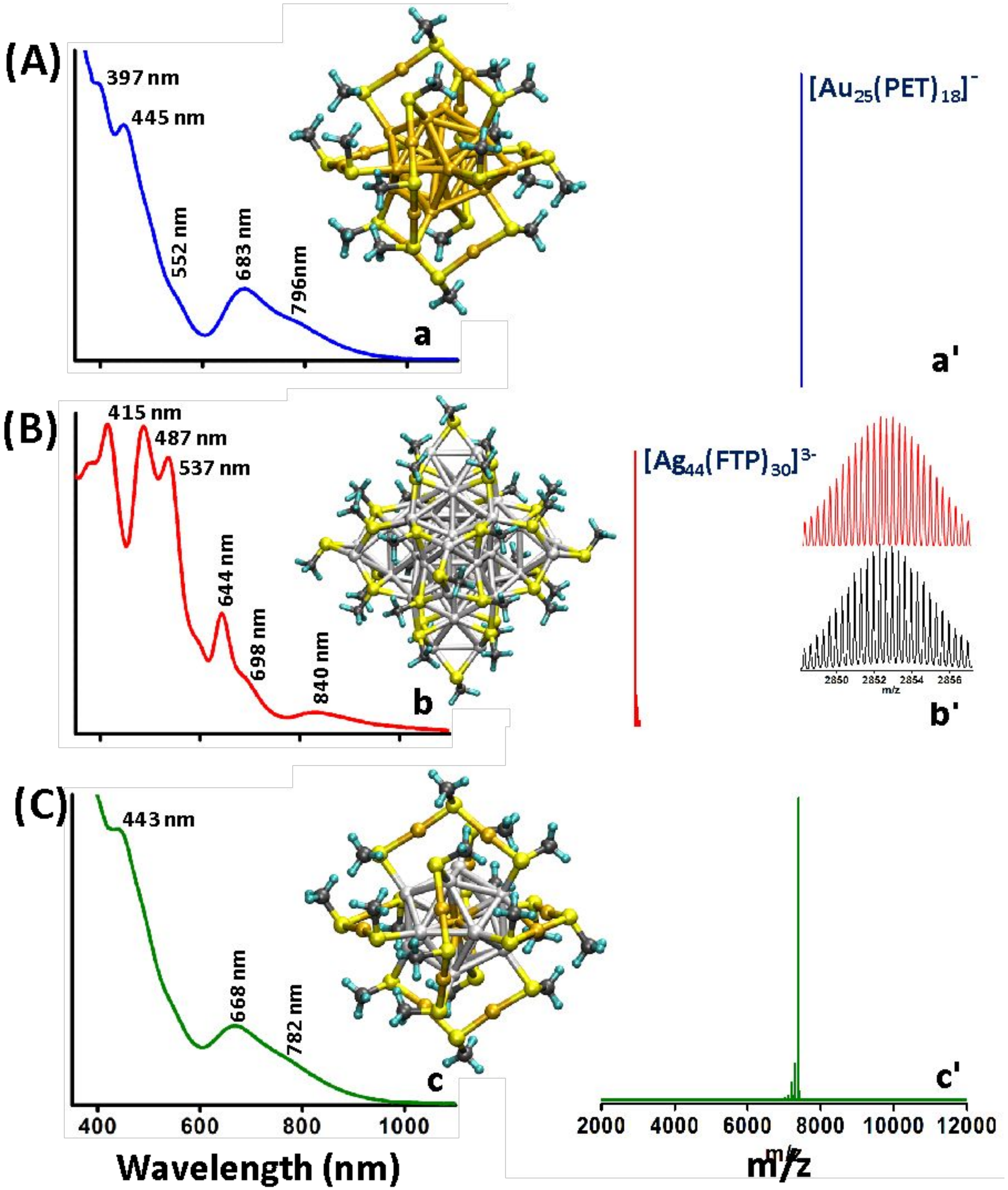
Clusters tried: $Au_{25}(PET)_{18}$
$Au_{25}(FTP)_{18}$
$Au_{25}(nBuS)_{18}$

$Ag_{44}(FTP)_{30}$
$Ag_{152}(PET)_{60}$

PET:


FTP:


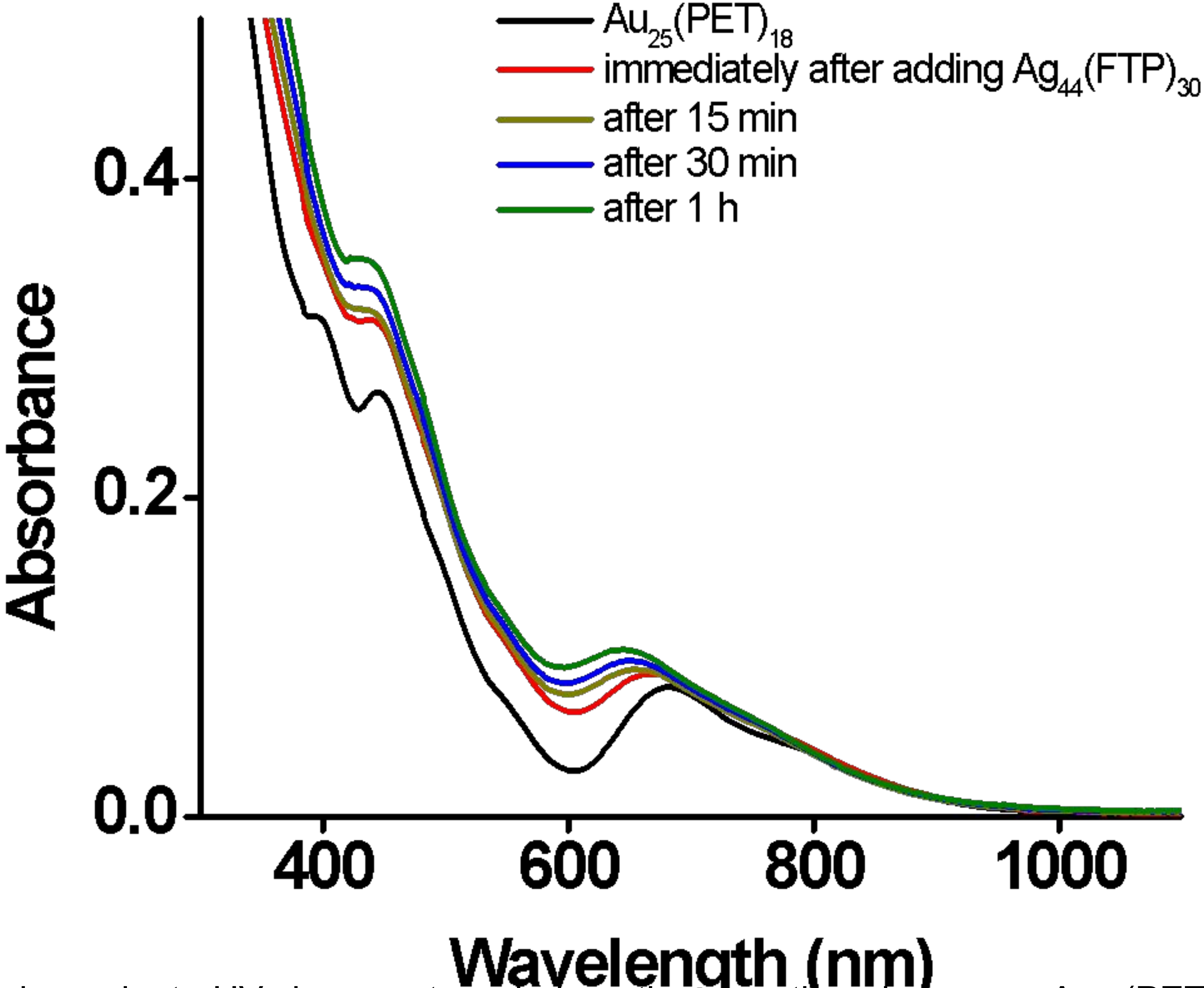
MBA:




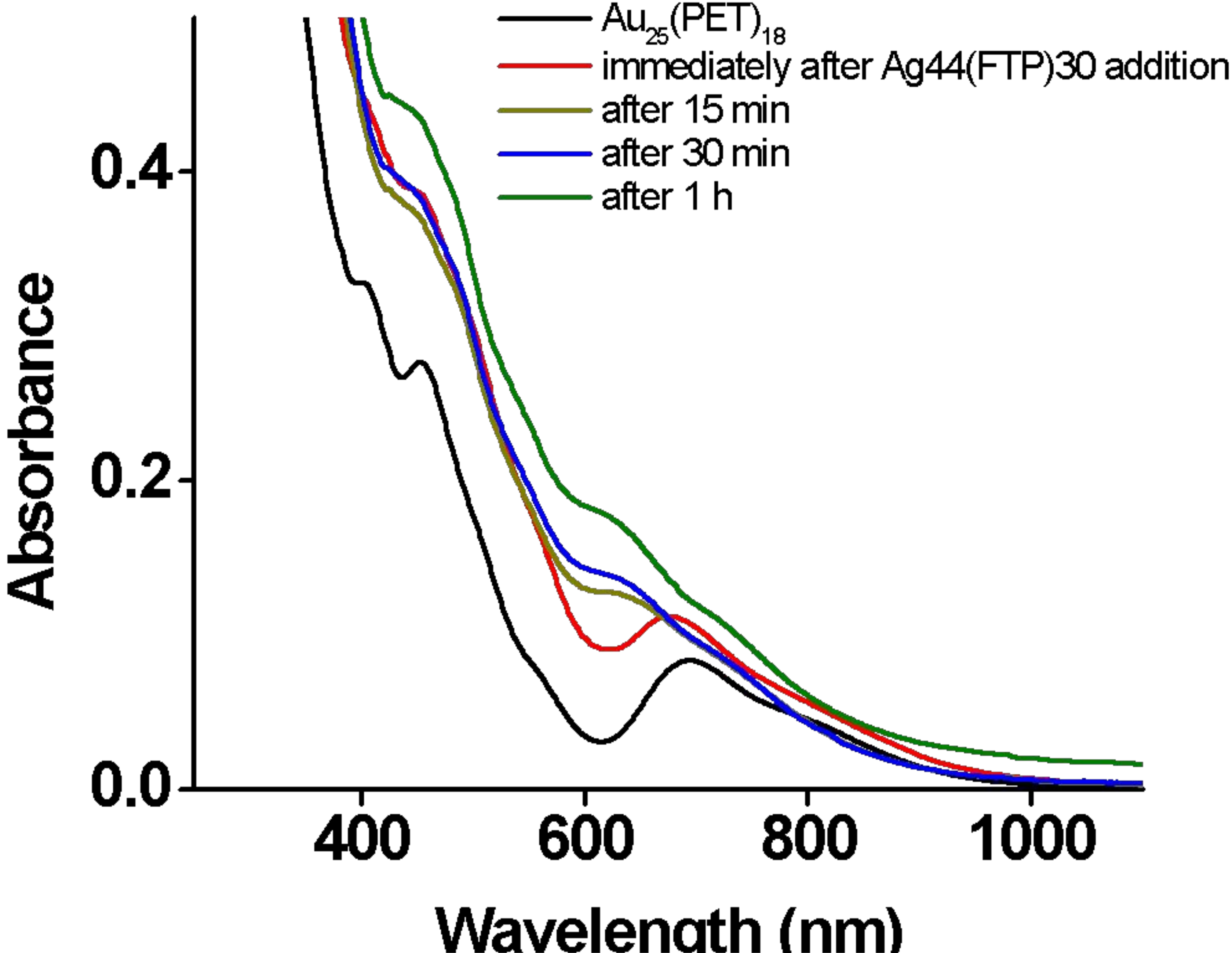
A + B □ C + D

$Au_{25}(PET)_{18} + Ag_{44}(FTP)_{30}$

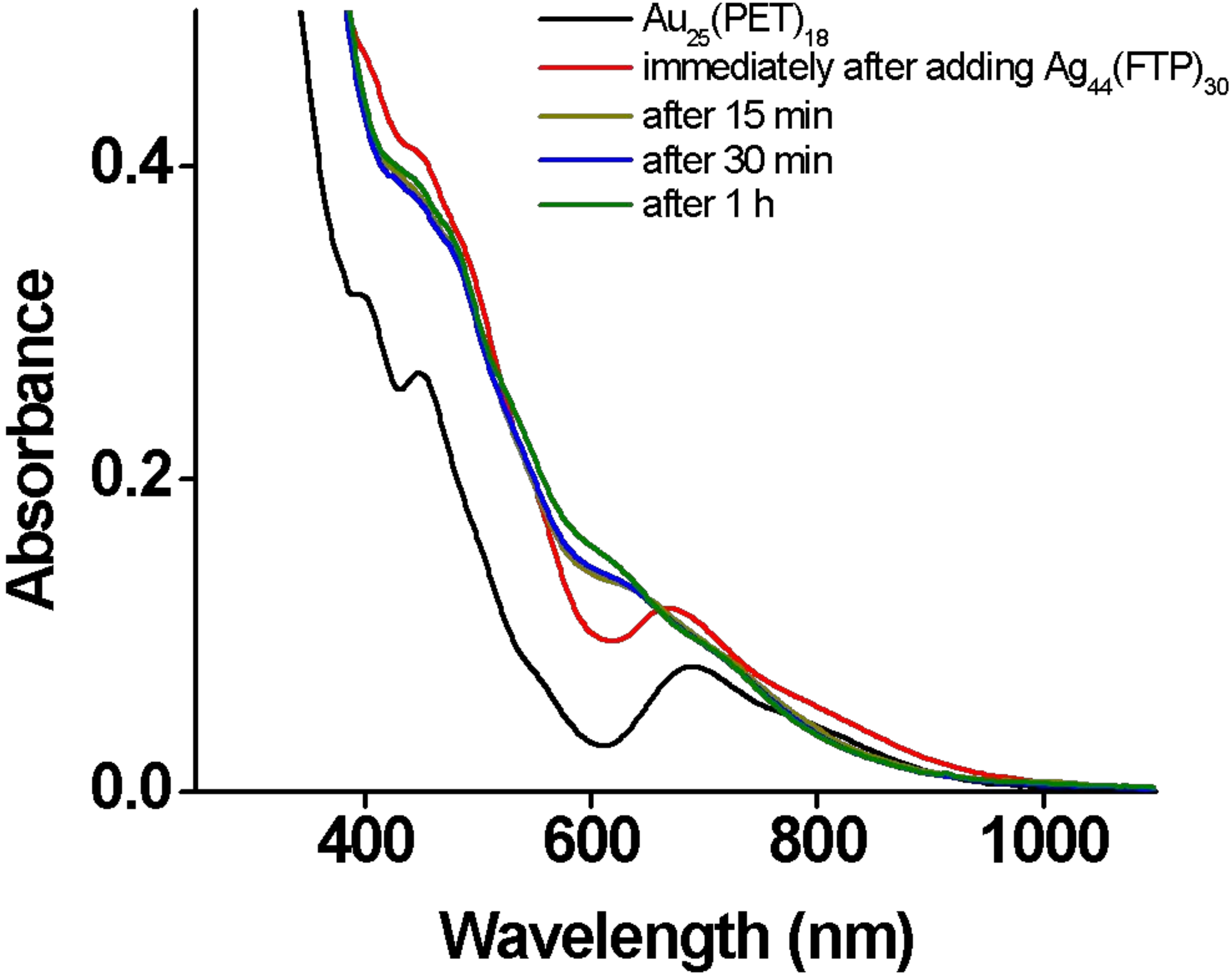
K. R. Krishnadas et al. JACS 2016



Time-dependent UV-vis spectra during the reaction between $Au_{25}(PET)_{18}$ and $Ag_{44}(FTP)_{30}$ clusters at a ratio (Au_{25}:Ag_{44}) of 14:1.



Time-dependent UV-vis spectra during the reaction between $Au_{25}(PET)_{18}$ and $Ag_{44}(FTP)_{30}$ clusters at a ratio (Au_{25}:Ag_{44}) of 7:1.



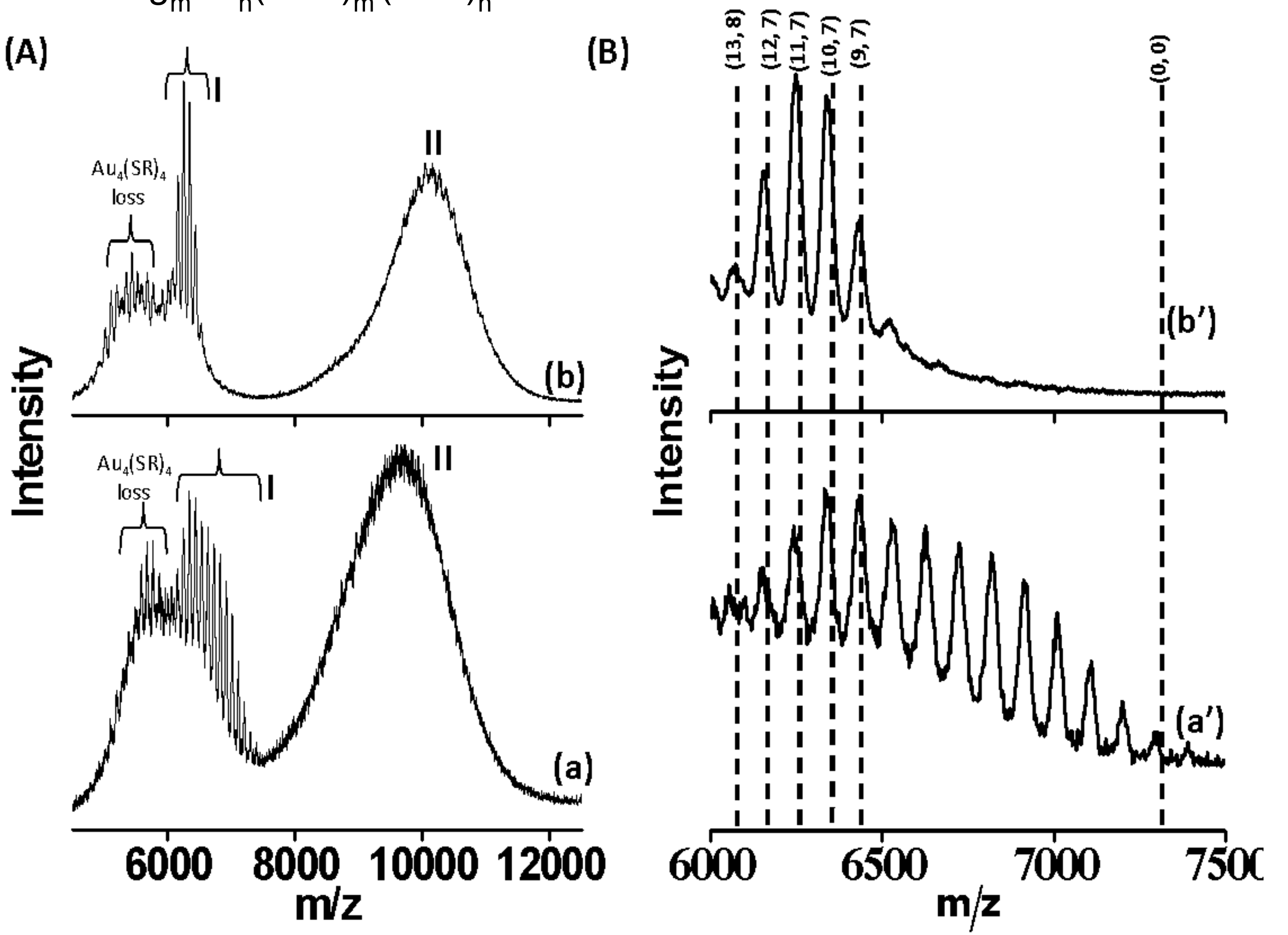
Time-dependent UV-vis spectra during the reaction between $Au_{25}(PET)_{18}$ and $Ag_{44}(FTP)_{30}$ clusters at a ratio (Au_{25}:Ag_{44}) of 1.7:1.

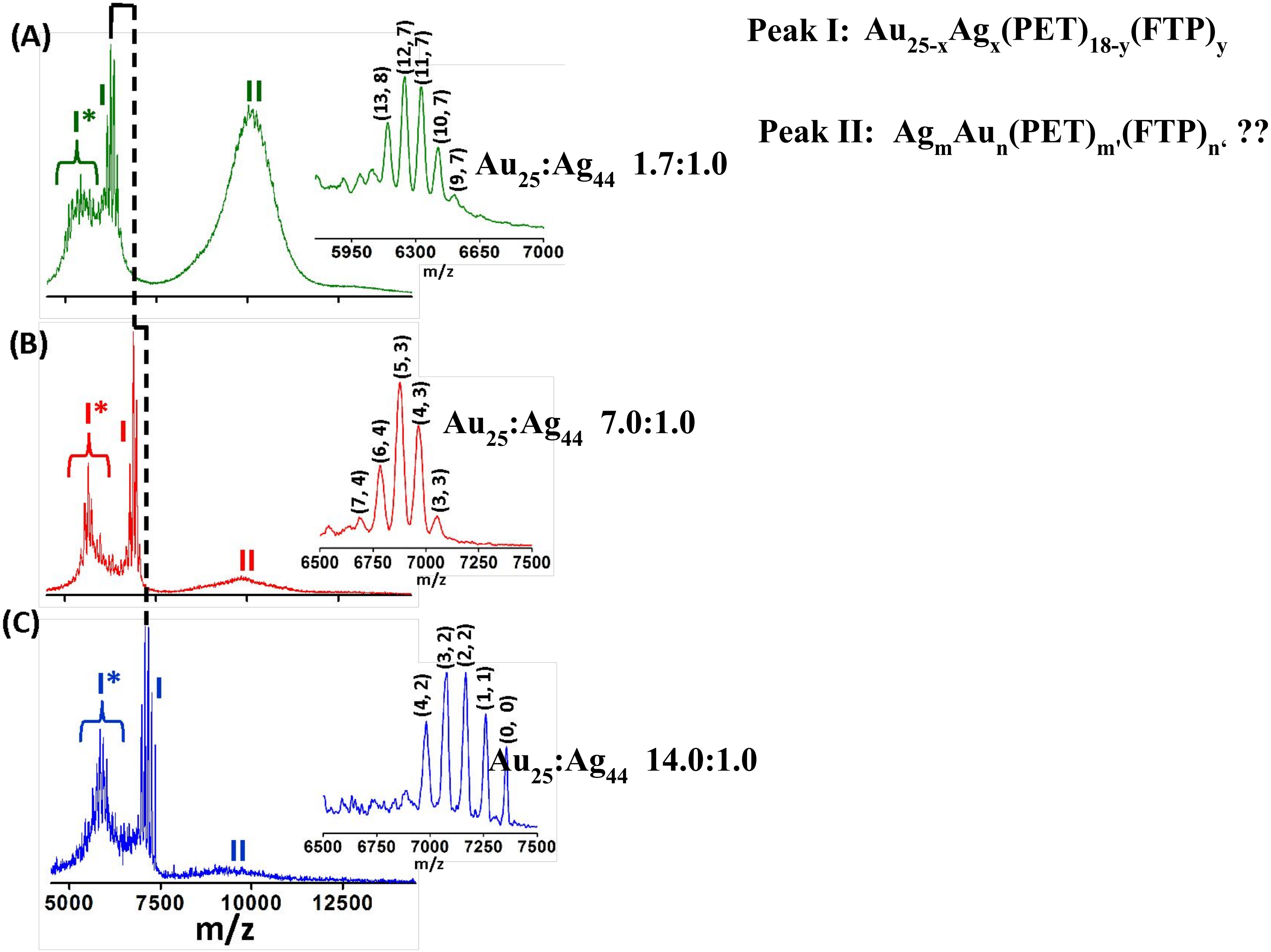
Peak I: $Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y$

A: immediately after mixing

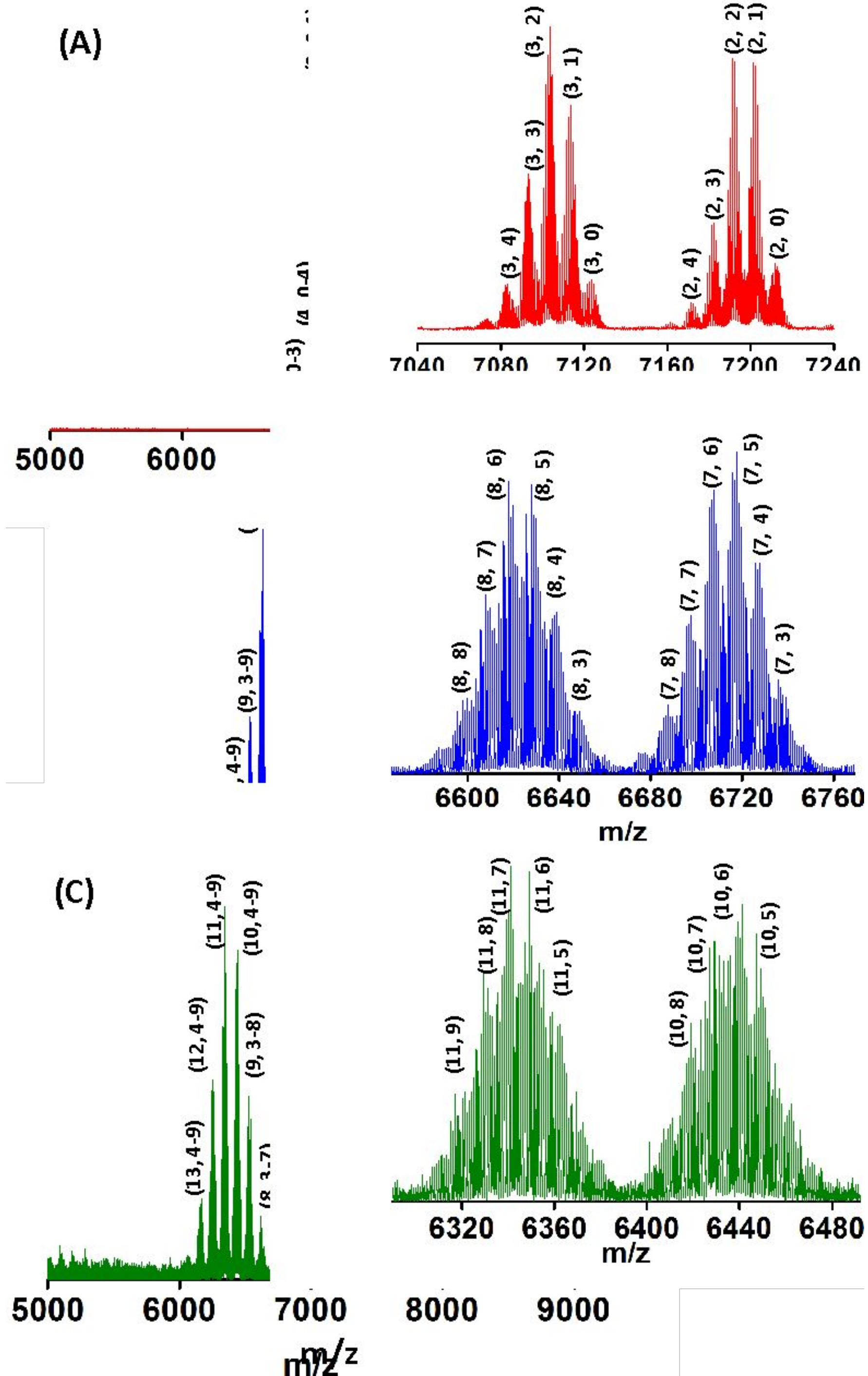
B: 1h after mixing

Peak II: $Ag_mAu_n(PET)_{m'}(FTP)_{n'}$??

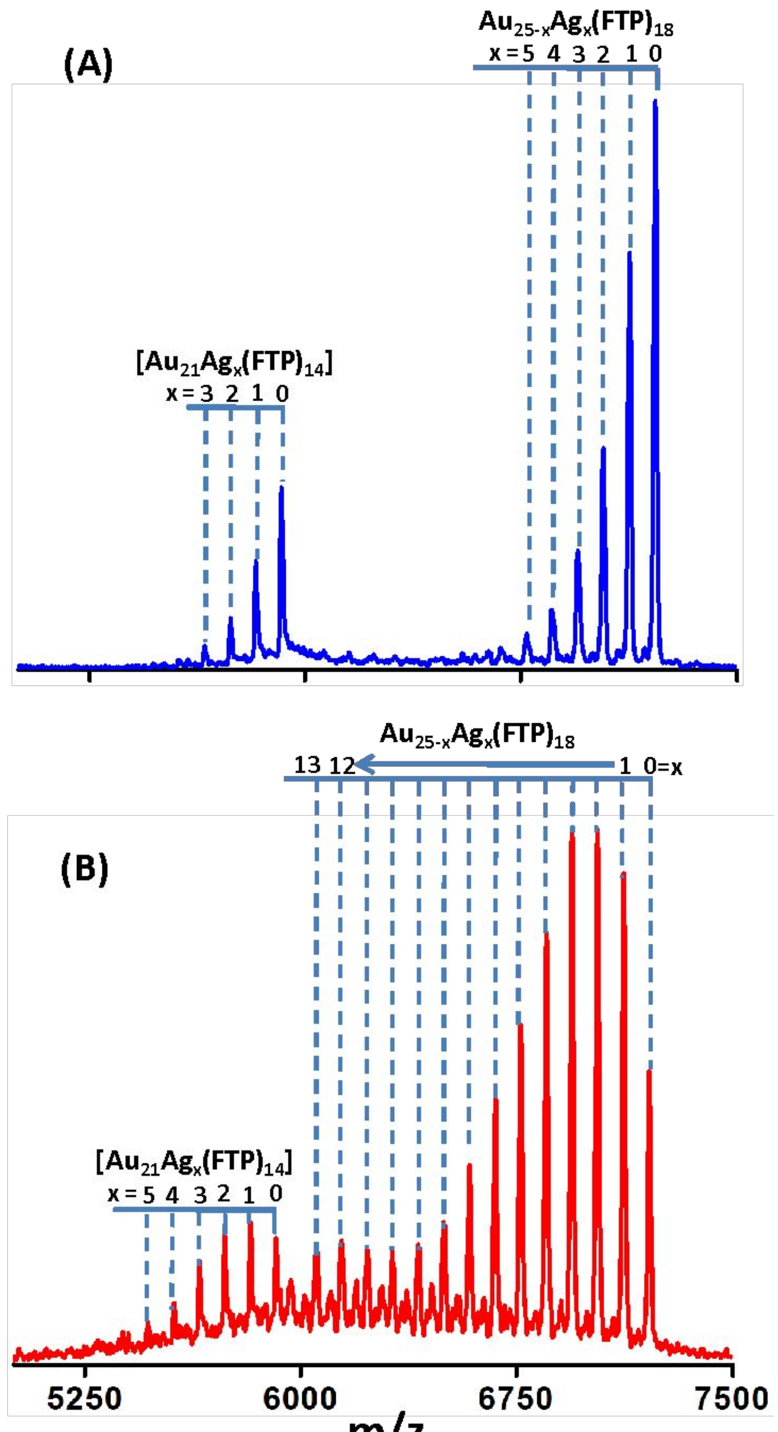




Peak I: $Au_{25-x}Ag_x(PET)_{18-y}(FTP)_y$
Peak II: $Ag_mAu_n(PET)_{m'}(FTP)_{n'}$??
(A)
I*
I
II
(13, 8)
(12, 7)
(11, 7)
(10, 7)
(9, 7)
5950
6300
6650
7000
m/z
Au_{25}:Ag_{44} 1.7:1.0
(B)
I*
I
II
(7, 4)
(6, 4)
(5, 3)
(4, 3)
(3, 3)
6500
6750
7000
7250
7500
m/z
Au_{25}:Ag_{44} 7.0:1.0
(C)
I*
I
II
(4, 2)
(3, 2)
(2, 2)
(1, 1)
(0, 0)
6500
6750
7000
7250
7500
m/z
Au_{25}:Ag_{44} 14.0:1.0
5000
7500
10000
12500
m/z



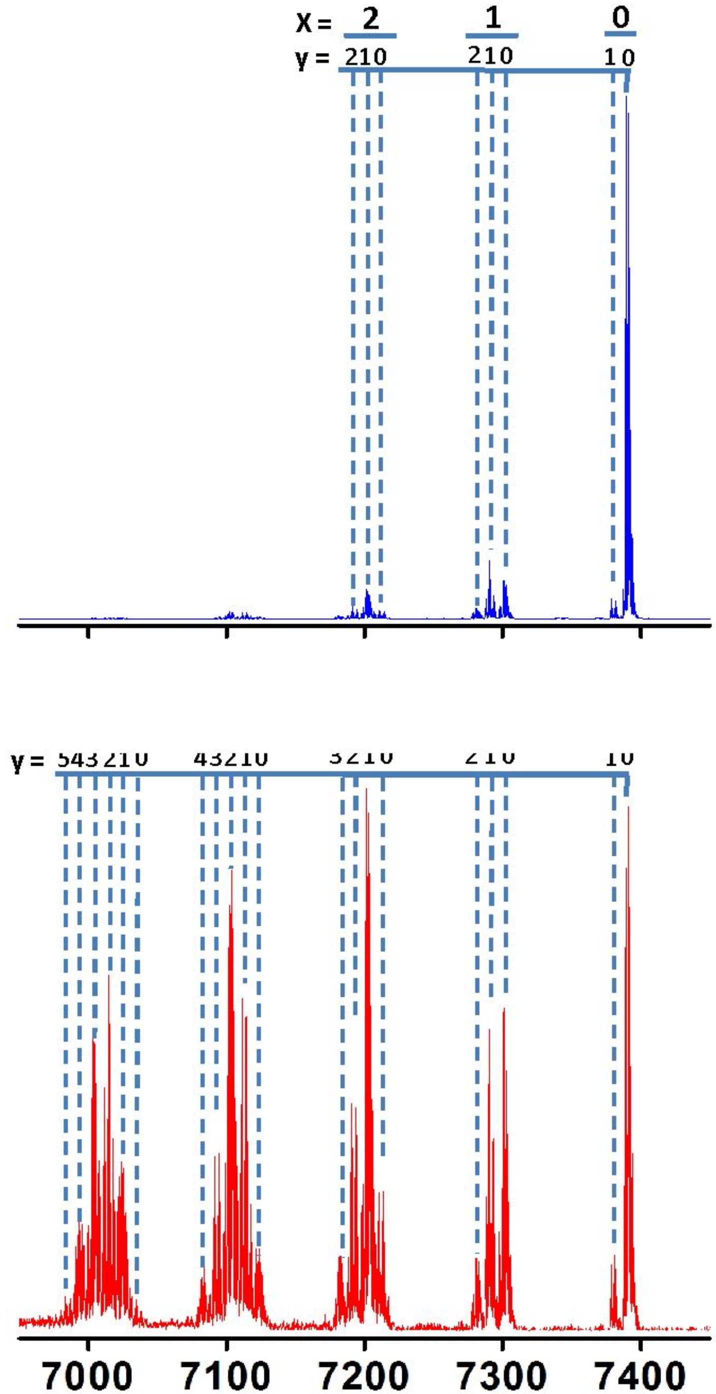
(A)
(3, 2)
(3, 1)
(3, 3)
(3, 4)
(3, 0)
(2, 2)
(2, 1)
(2, 3)
(2, 4)
(2, 0)
7040
7080
7120
7160
7200
7240
5000
6000
(8, 6)
(8, 5)
(8, 7)
(8, 4)
(8, 8)
(8, 3)
(7, 6)
(7, 5)
(7, 4)
(7, 7)
(7, 8)
(7, 3)
(9, 3-9)
6600
6640
6680
6720
6760
m/z
(C)
(11, 4-9)
(10, 4-9)
(12, 4-9)
(9, 3-8)
(13, 4-9)
(11, 7)
(11, 6)
(11, 8)
(11, 5)
(11, 9)
(10, 6)
(10, 7)
(10, 5)
(10, 8)
6320
6360
6400
6440
6480
m/z
5000
6000
7000
8000
9000
m/z



$$Au_{25}(FTP)_{18} + Ag_{44}(FTP)_{30}$$

$$\Downarrow$$

$$Au_{25-x}Ag_x(FTP)_{18} + Ag_mAu_n(FTP)_{n'}$$



X = 2 1 0
y = 210 210 10
y = 543210 43210 3210 210 10
7000 7100 7200 7300 7400

What does it mean?

Two kinds of chemistry

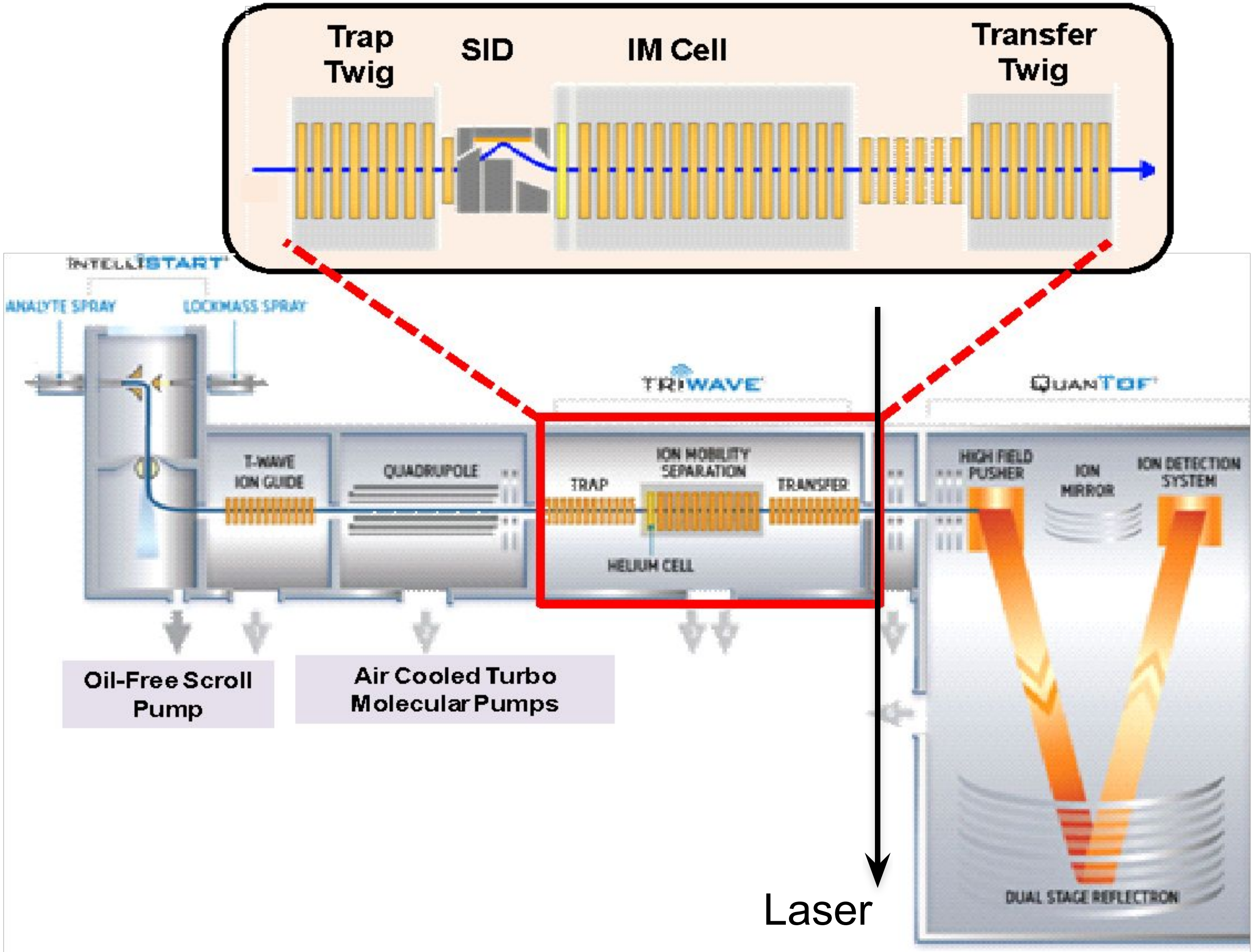
Substitution, exchange, conjugation, supramolecular, etc. chemistry

and

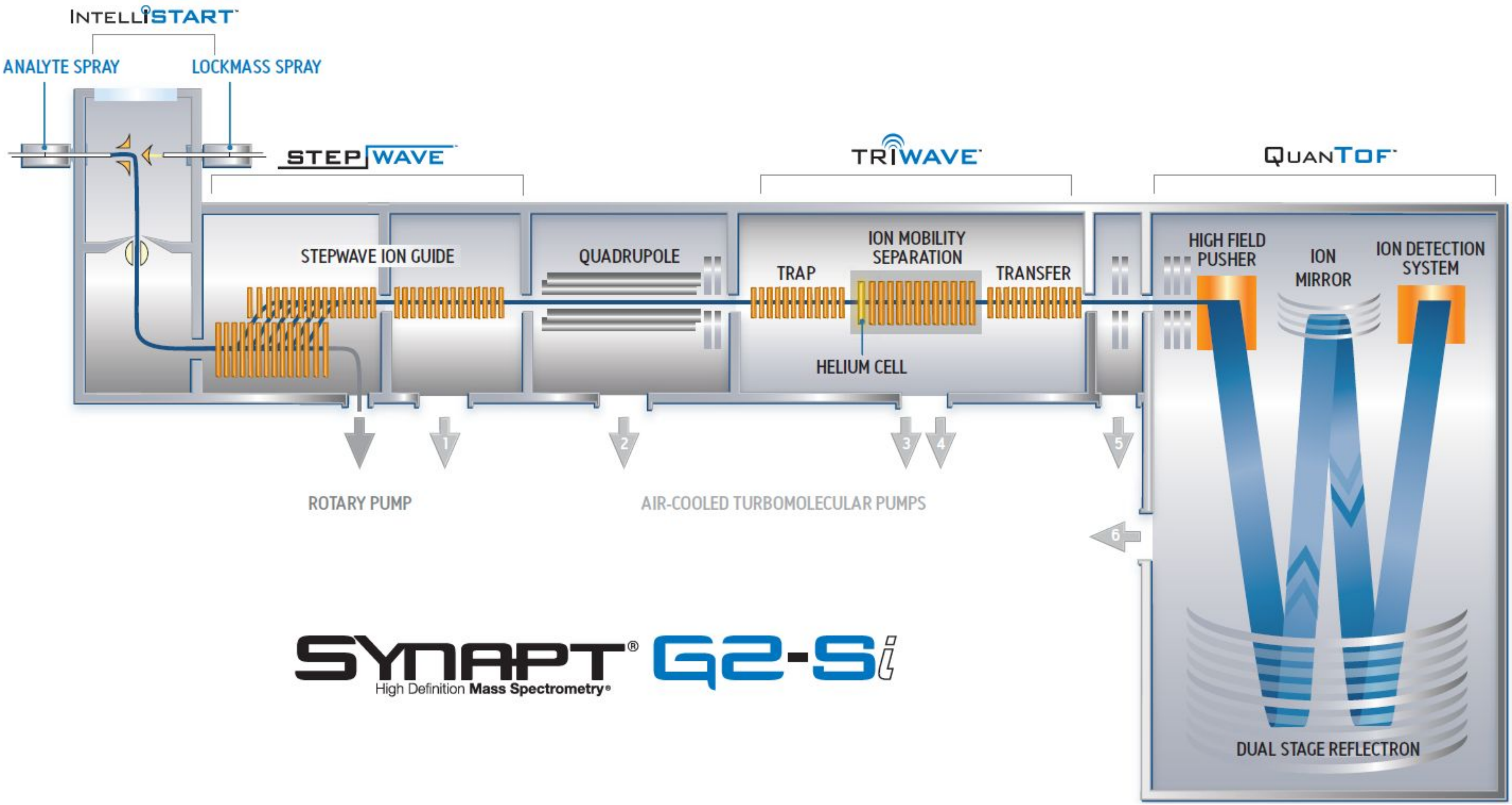
Cluster chemistry

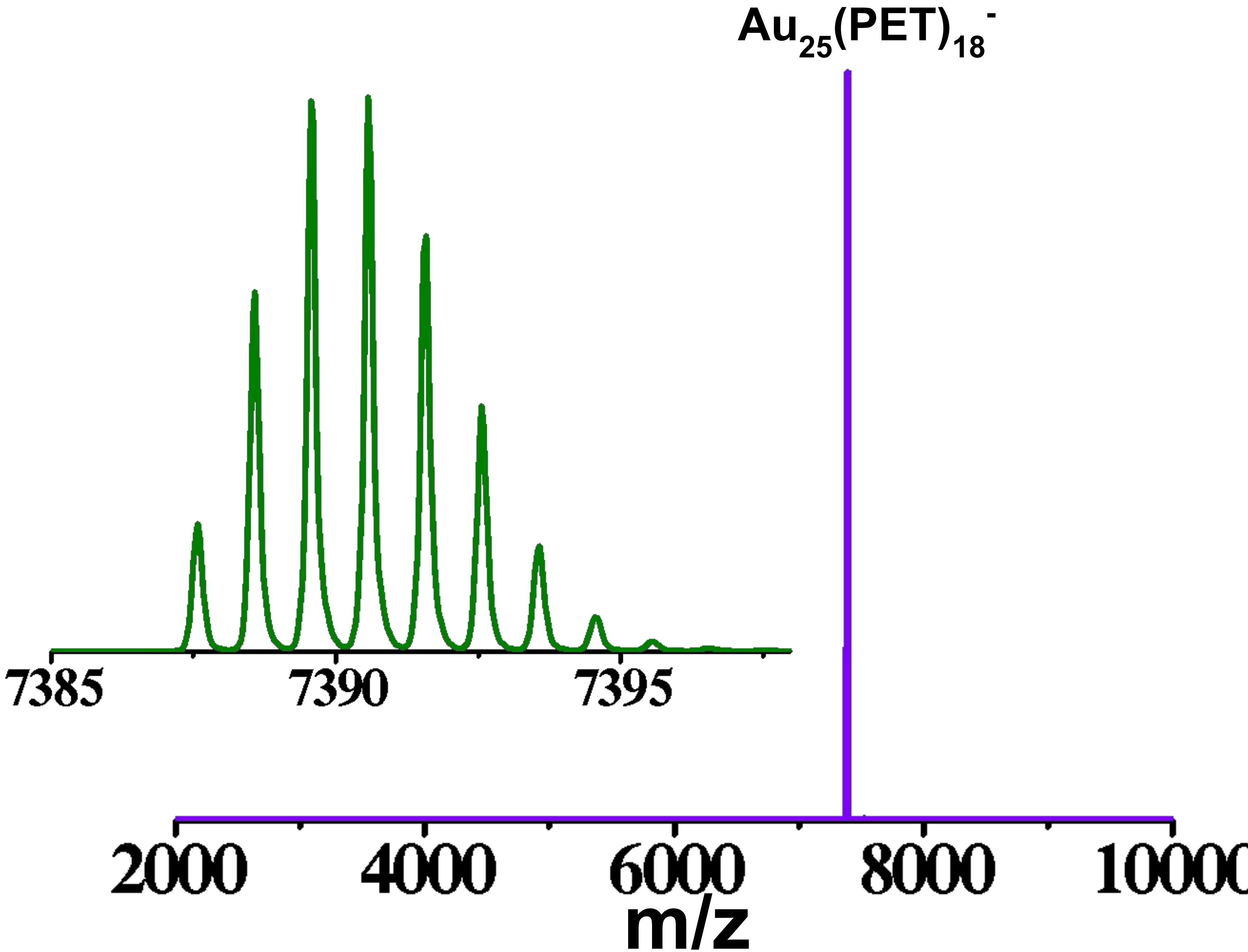
Graphene reaction
    No intermediates were prominent.
On oxide surfaces
    13 kDa, ~Ag_{80}, n = 34?
    20 kDa, ~Ag_{120}, n = 58?
Cluster coalescence

Unique inter-cluster reactions, simultaneous transformations

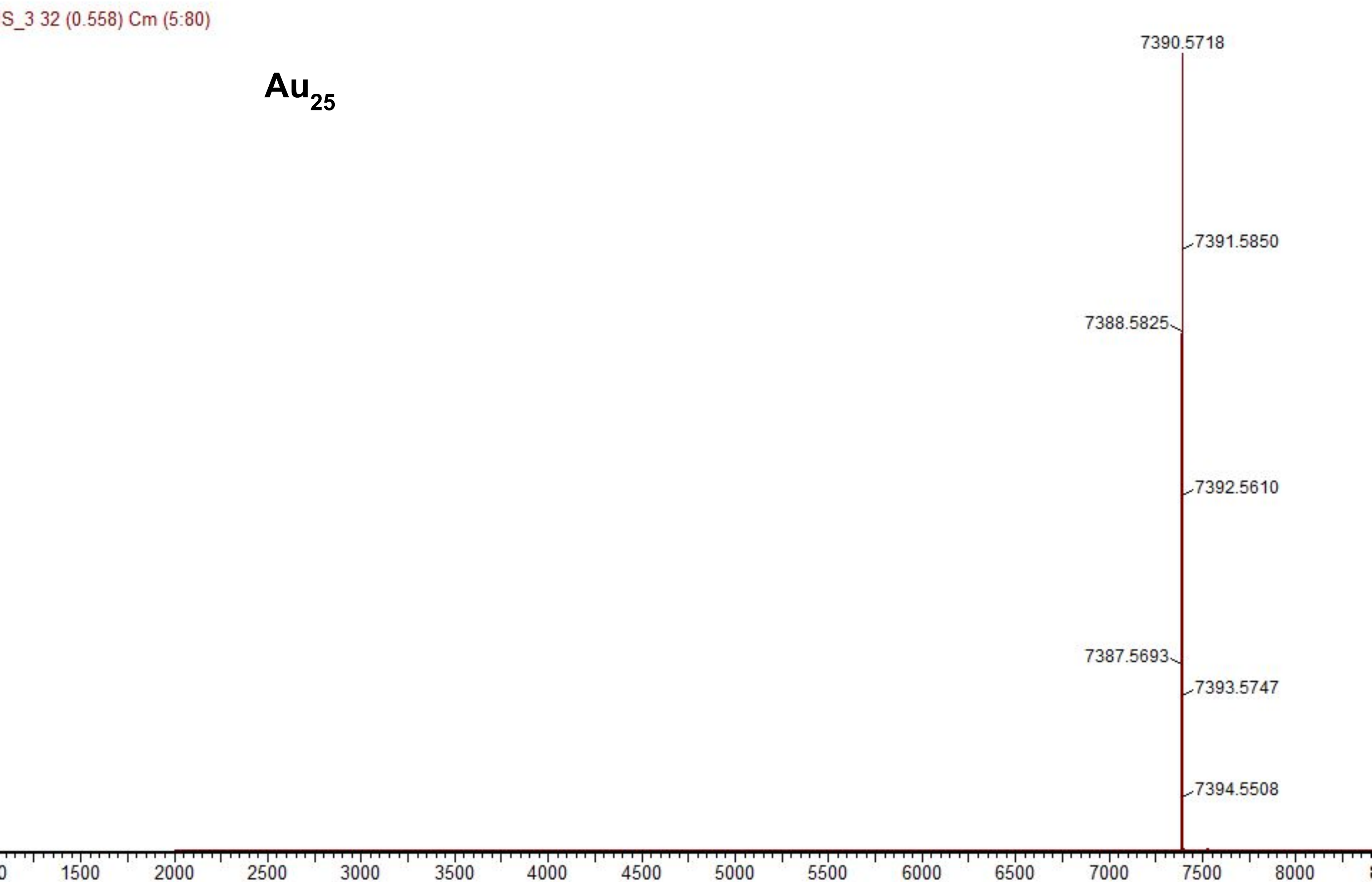


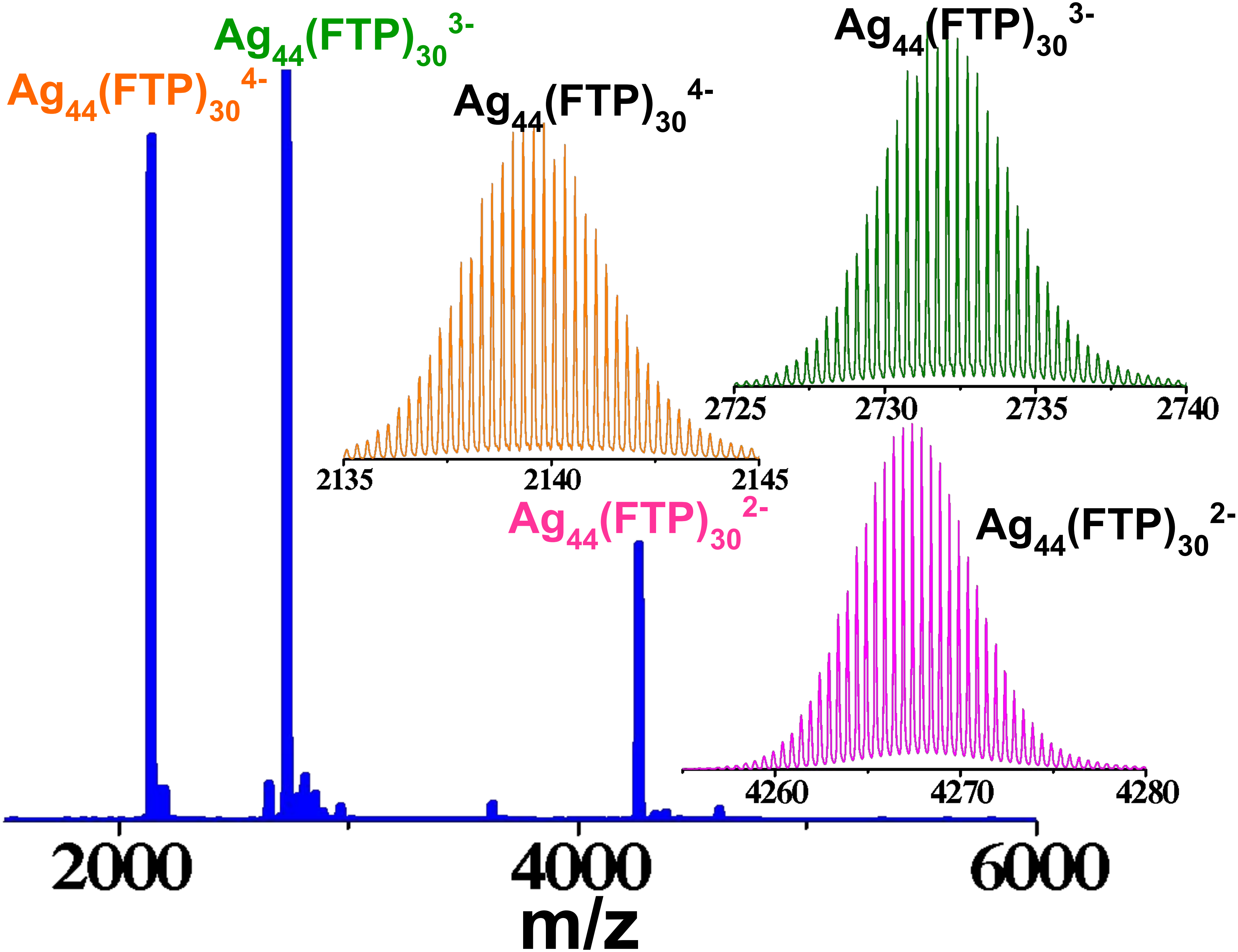
SID incorporation was introduced by Wysocki *et al. Angew. Chem. Int. Ed.* **2012,** *51* (18), 4336-4339.


INTELLISTART
ANALYTE SPRAY
LOCKMASS SPRAY
STEPWAVE
TRIWAVE
QUANTOF
STEPWAVE ION GUIDE
QUADRUPOLE
ION MOBILITY SEPARATION
TRAP
TRANSFER
HELIUM CELL
HIGH FIELD PUSHER
ION MIRROR
ION DETECTION SYSTEM
1
2
3
4
5
6
ROTARY PUMP
AIR-COOLED TURBOMOLECULAR PUMPS
DUAL STAGE REFLECTRON
SYNAPT® G2-Si
High Definition Mass Spectrometry®



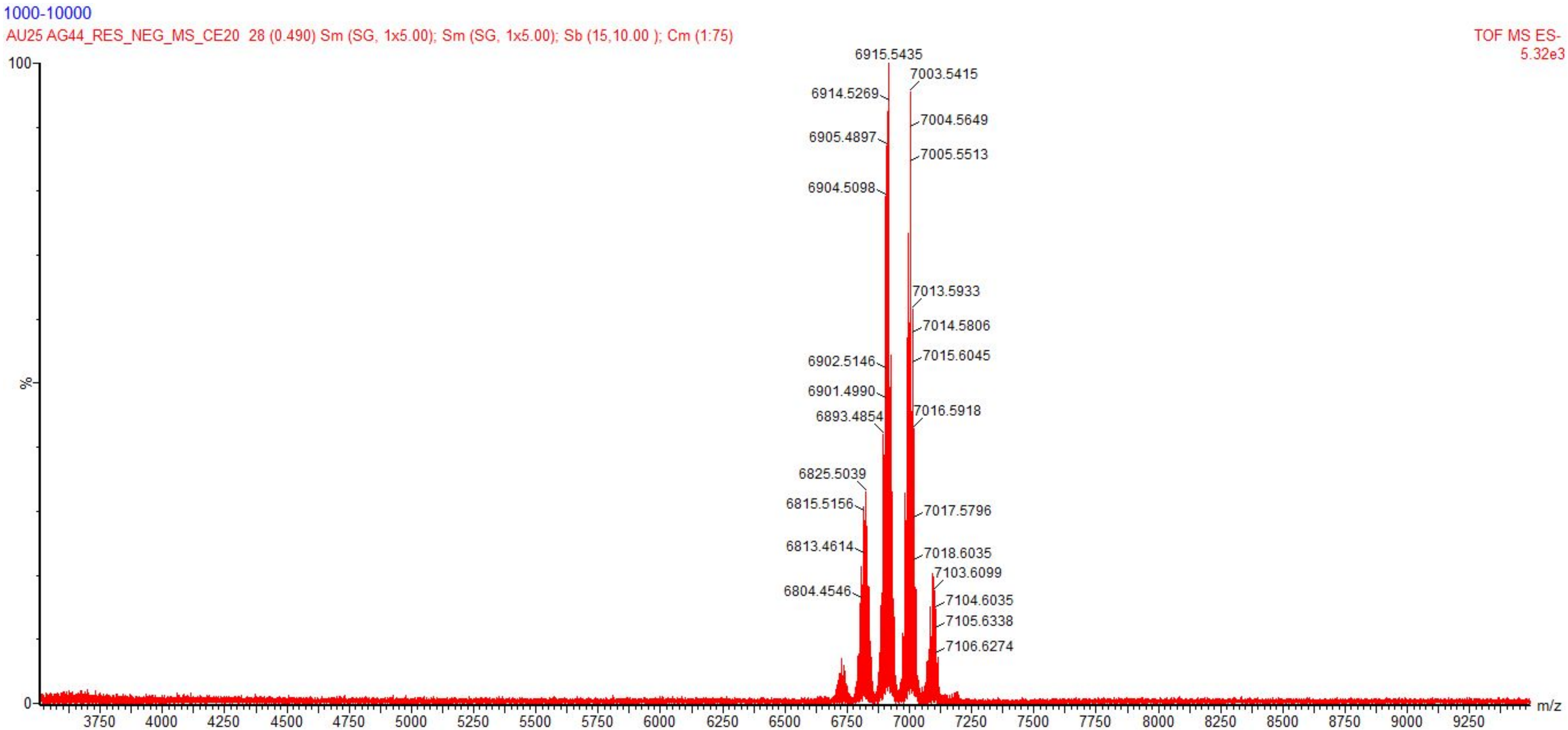
Au$_{25}$(PET)$_{18}^{-}$
7385
7390
7395
2000
4000
6000
8000
10000
m/z

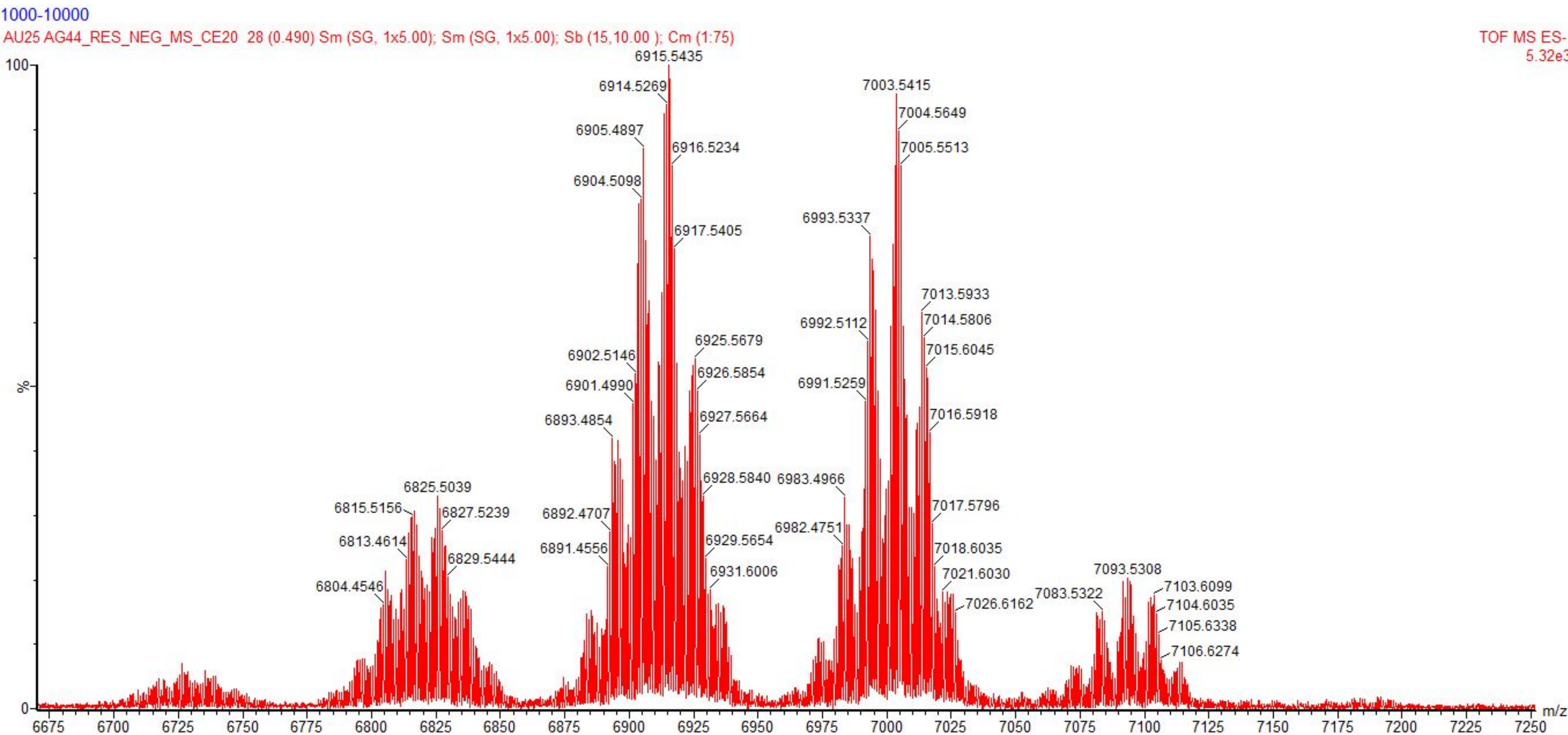

S_3 32 (0.558) Cm (5:80)
Au25
7390.5718
7391.5850
7388.5825
7392.5610
7387.5693
7393.5747
7394.5508
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500
8000



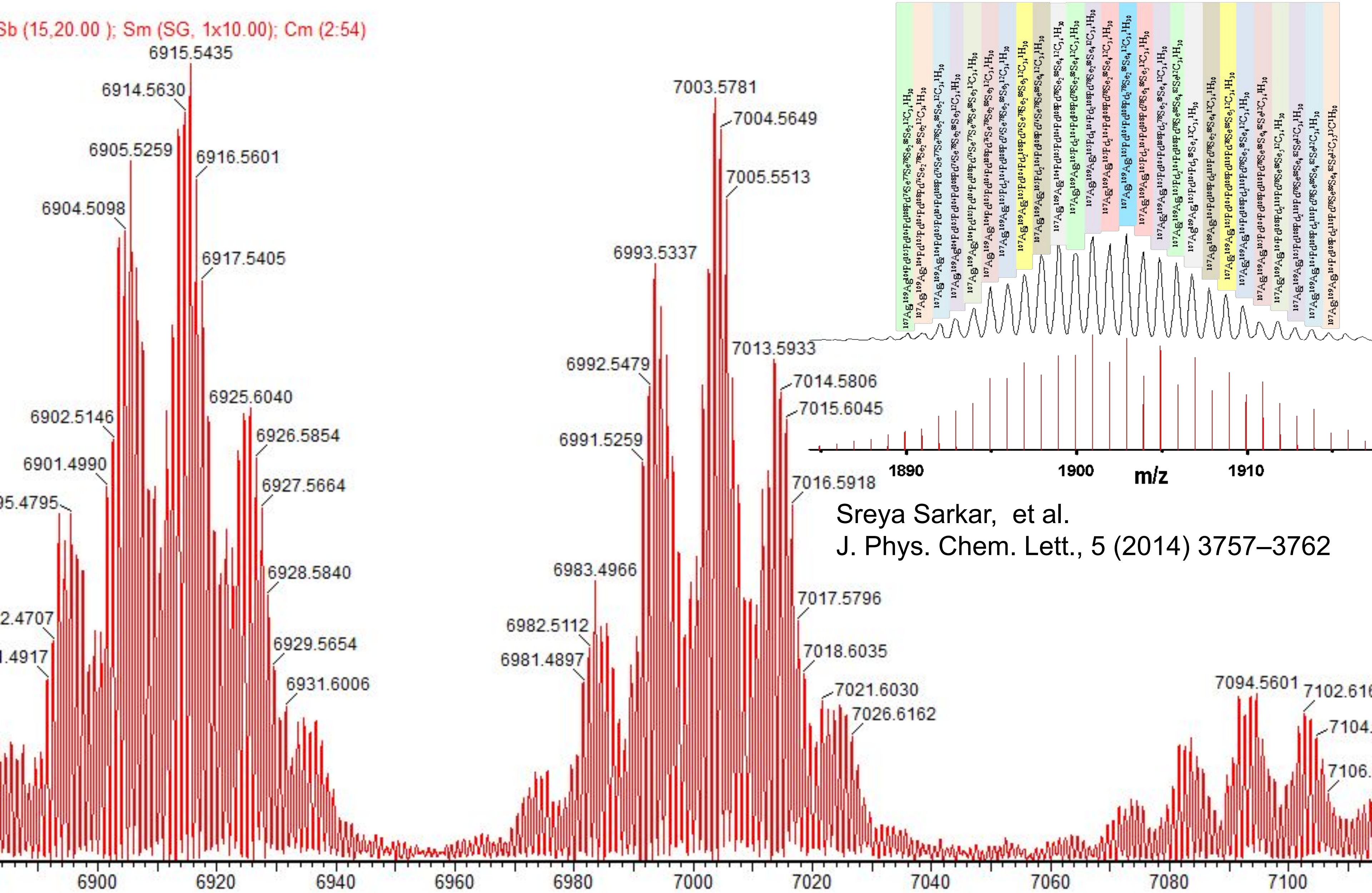
Ag44(FTP)30 3-
Ag44(FTP)30 4-
Ag44(FTP)30 4-
Ag44(FTP)30 3-
2725
2730
2735
2740
2135
2140
2145
Ag44(FTP)30 2-
Ag44(FTP)30 2-
4260
4270
4280
2000
4000
6000
m/z

Reaction between Au_{25} and Ag_{44}





1000-10000
AU25 AG44_RES_NEG_MS_CE20 28 (0.490) Sm (SG, 1x5.00); Sm (SG, 1x5.00); Sb (15,10.00); Cm (1:75)
TOF MS ES-
5.32e3
100
%
0
6915.5435
6914.5269
6905.4897
6916.5234
6904.5098
6917.5405
6902.5146
6901.4990
6925.5679
6926.5854
6927.5664
6893.4854
6928.5840
6892.4707
6891.4556
6929.5654
6931.6006
6825.5039
6815.5156
6827.5239
6813.4614
6829.5444
6804.4546
7003.5415
7004.5649
7005.5513
6993.5337
7013.5933
6992.5112
7014.5806
7015.6045
6991.5259
7016.5918
6983.4966
7017.5796
6982.4751
7018.6035
7021.6030
7026.6162
7093.5308
7083.5322
7103.6099
7104.6035
7105.6338
7106.6274
6675
6700
6725
6750
6775
6800
6825
6850
6875
6900
6925
6950
6975
7000
7025
7050
7075
7100
7125
7150
7175
7200
7225
7250
m/z



Sreya Sarkar, et al.
J. Phys. Chem. Lett., 5 (2014) 3757–3762

Evolving Science

- Cluster science is getting increasingly complex
  Ligand exchange
  Isomers
  Alloys
  Supramolecular chemistry

- How do we comprehend them?

- We need to name them - uniquely

Structure and name

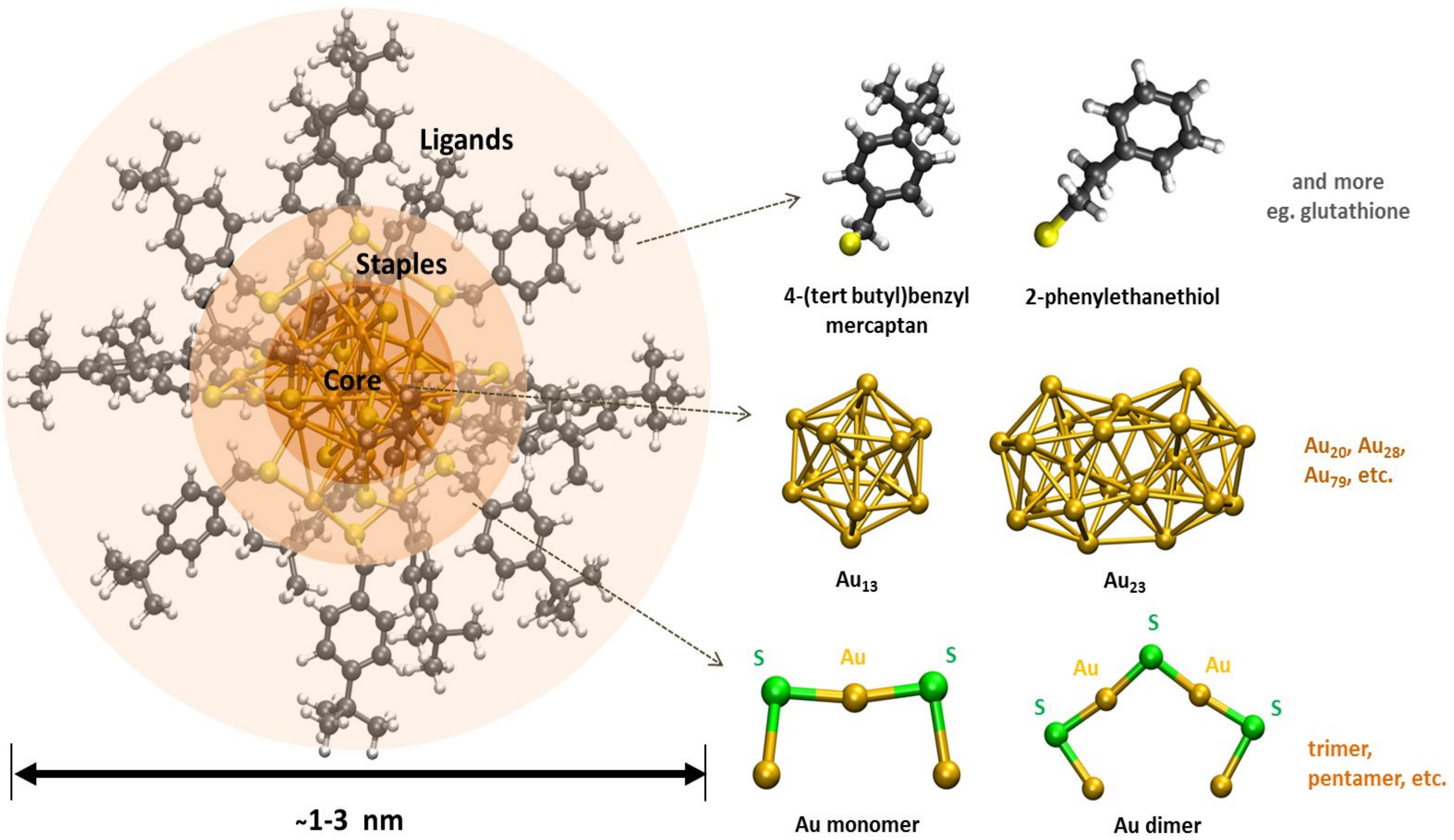
- Current names
  - $Au_{25}(SR)_{18}$, $Au_{25}(SR)_{18}$, Au@R, or just Au_{25}
  - $Au_{25-m}\ Pd_m(SR1)_{18-n}(SR2)_n$
- Complexity: eg. Isomers and chirality
- => Nomenclature
  - Organic, inorganic, etc.
  - Fullerenes
  - Boranes

What does it contain?

- We need:
  1. Diagram of the molecule with labels

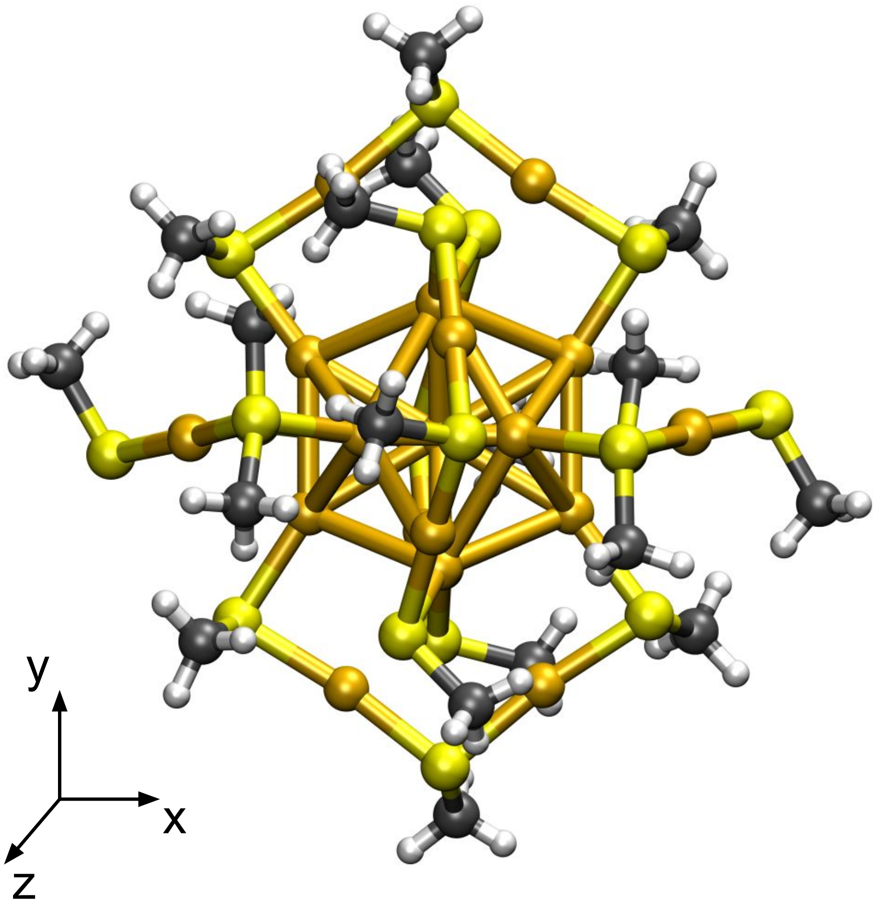
  2. Naming scheme
     1. Flexible
     2. Unique
     3. Structural details

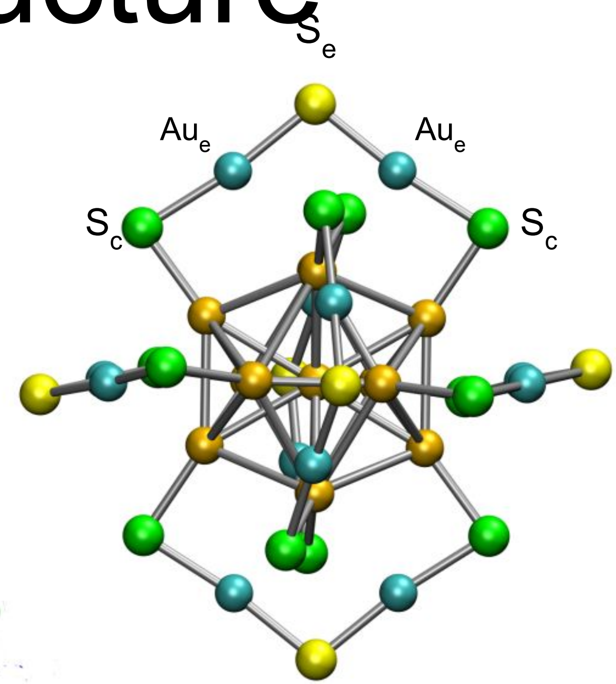
What are these materials?

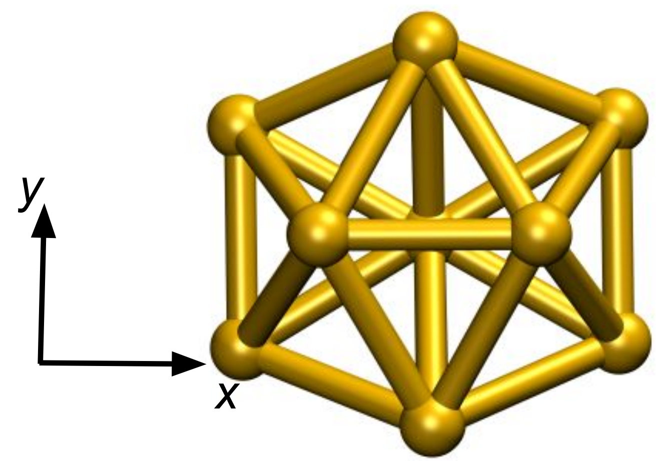


Aspicules

Ball and stick structure



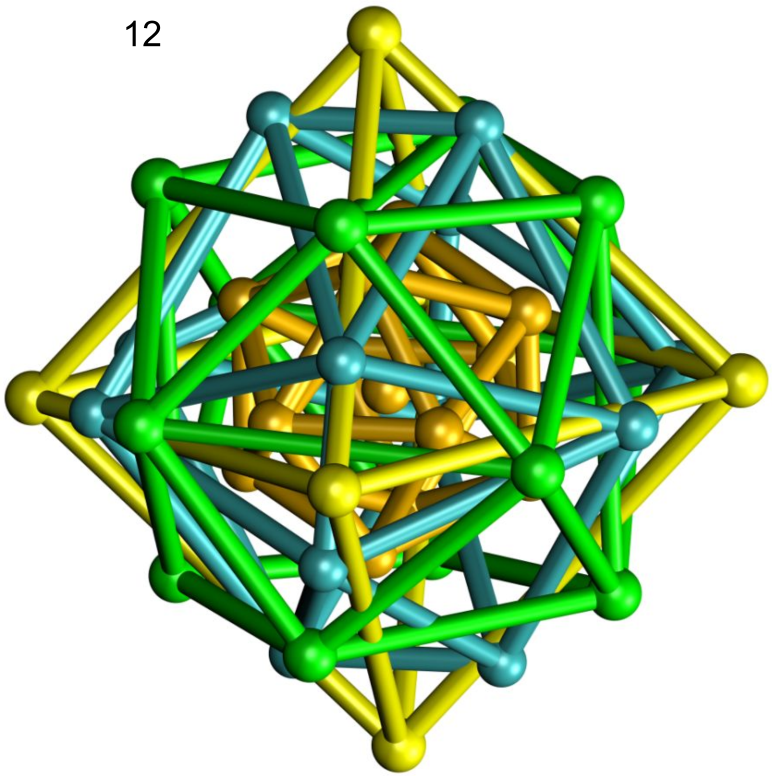




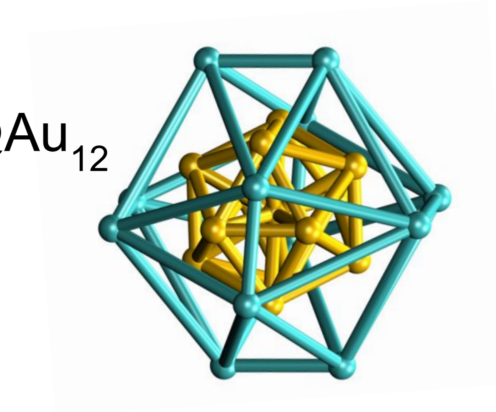
A view of gold methly thiolate [25]aspicule ($Au_{25}(SMe)_{18}$). Gold atoms colored gold, sulfur atoms by yellow, carbon dark gray, hydrogen atoms as white and (b) with the gold and sulfur atoms alone .

Shell Structure

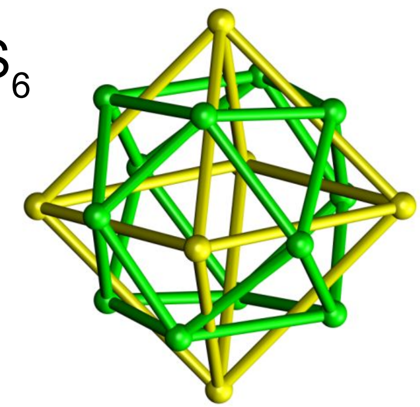
(a) $Au@Au_{12}@Au_{12}@S_6@S_{12}$



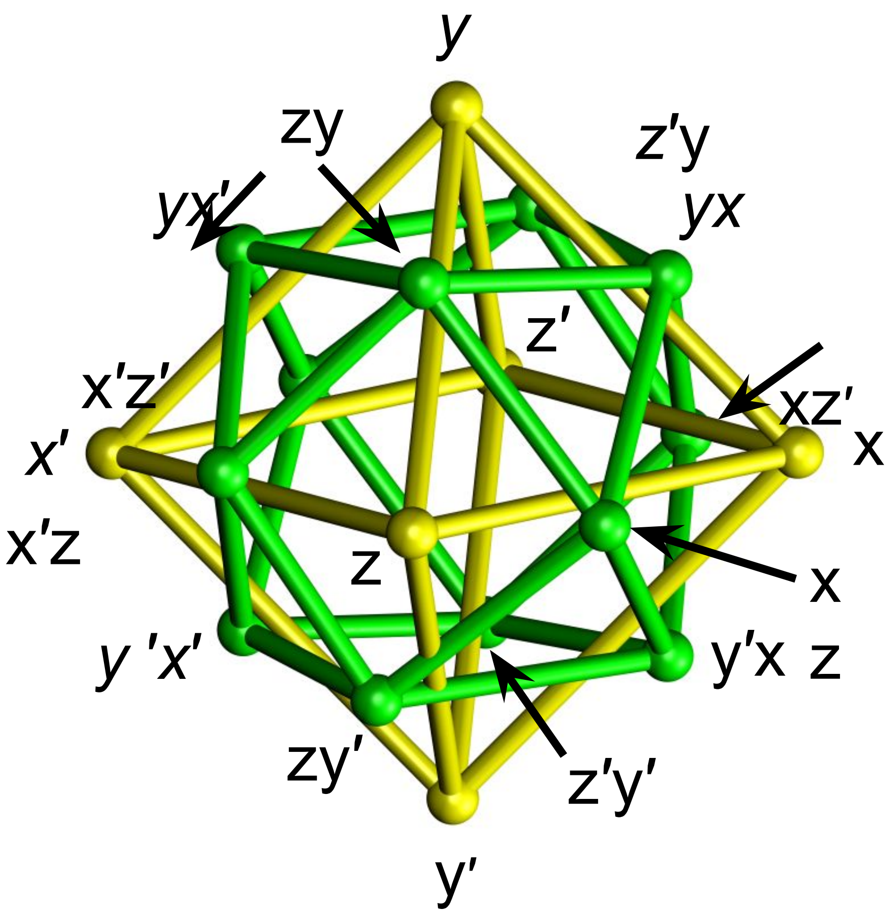
(b) $Au_{12}@Au_{12}$

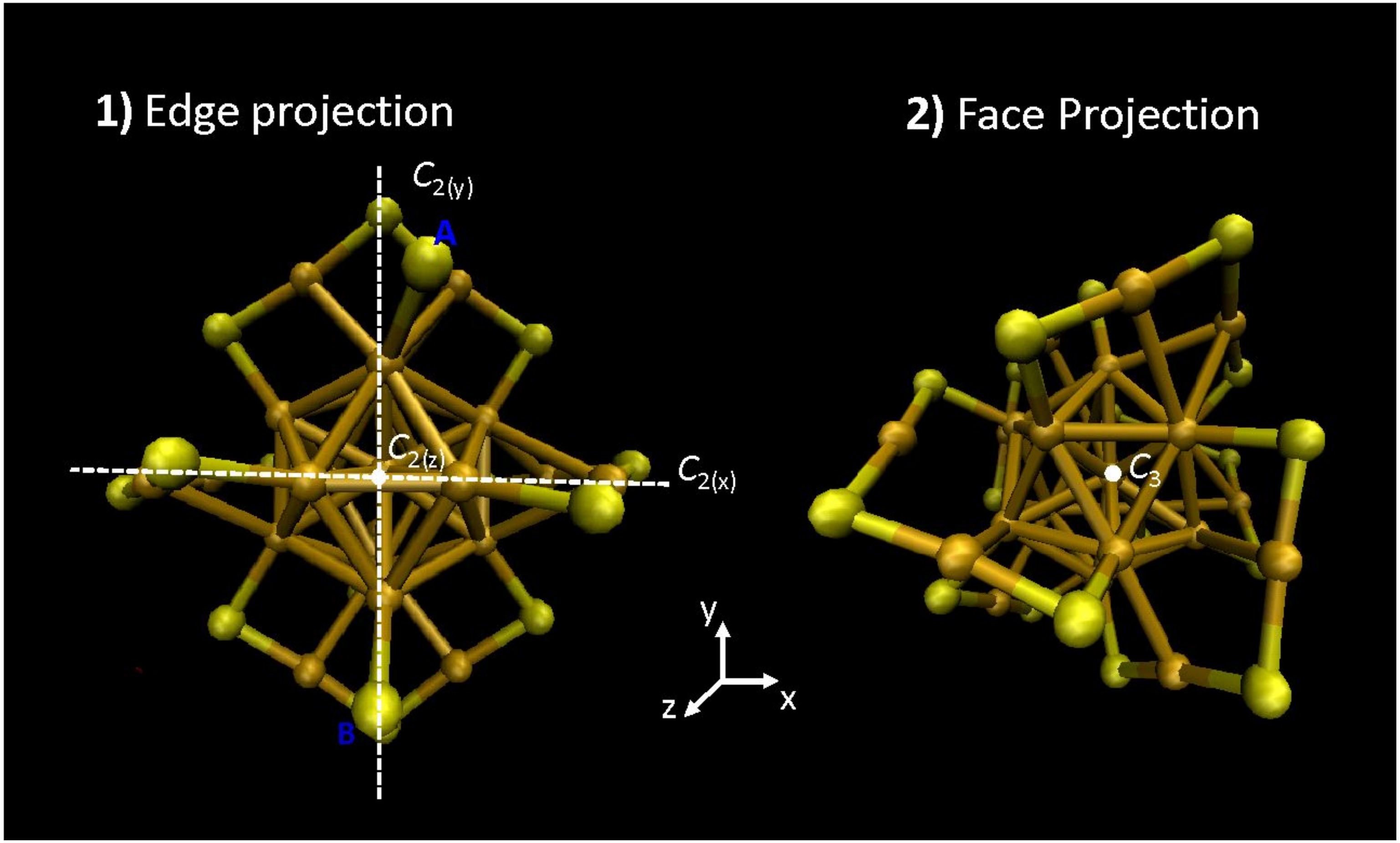


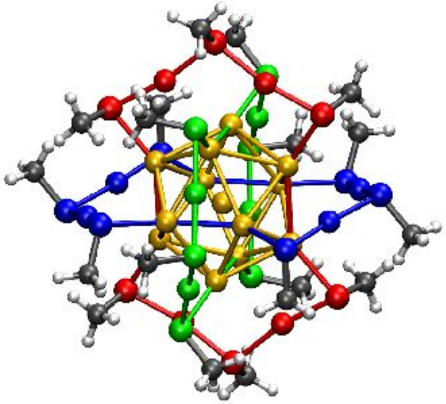
(c) $S_{12}@S_6$

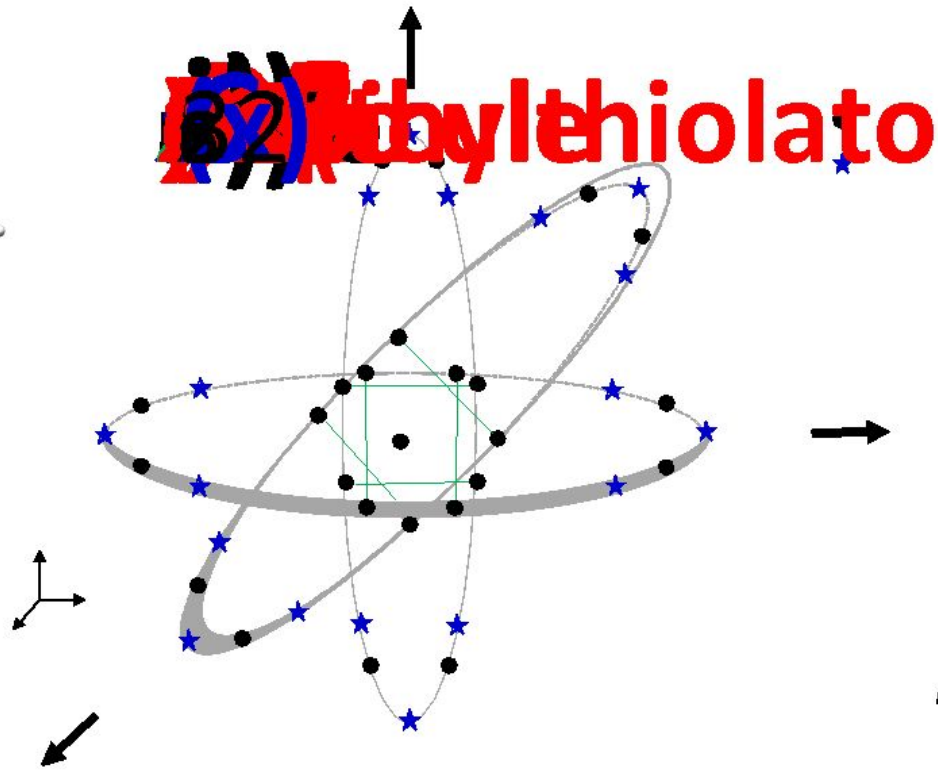


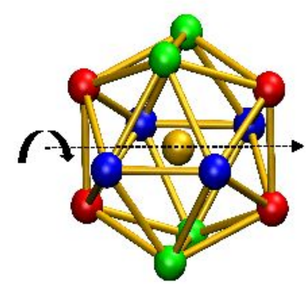
Terminologies




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

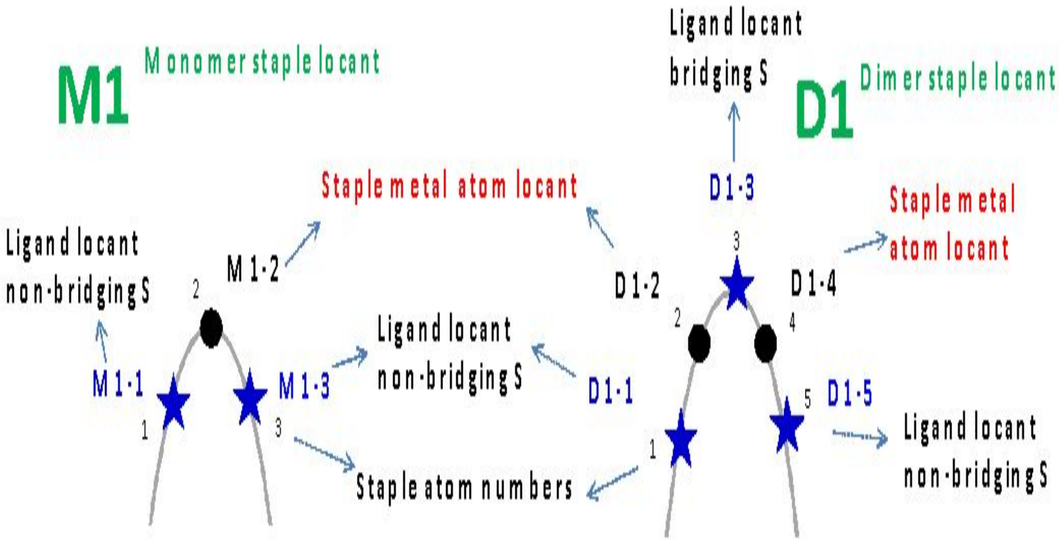


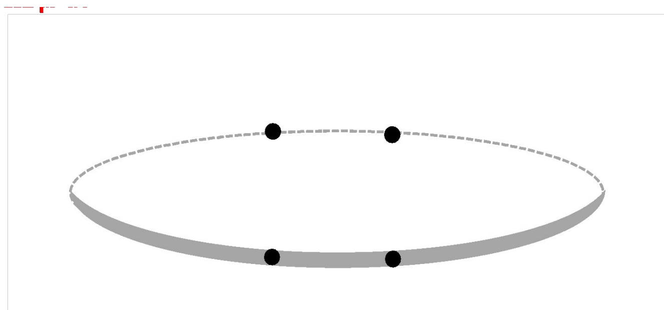


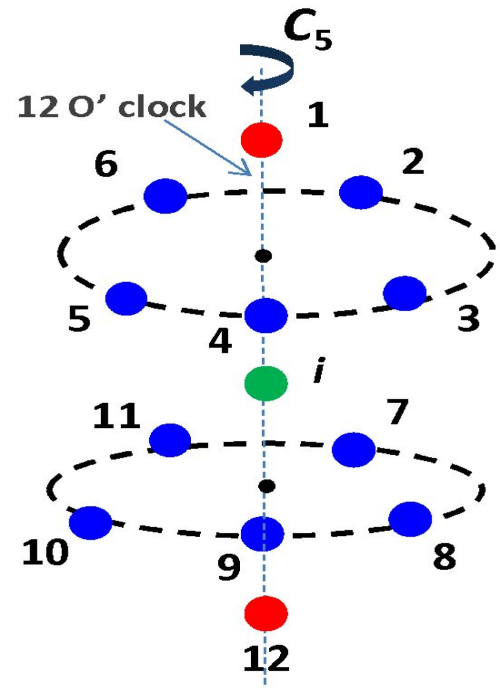


18(methylthiolato)-auro-25
aspicule(1-)

Gana Natarajan et. al. JPC C. 2015


M1
Monomer staple locant
Ligand locant
bridging S
D1
Dimer staple locant
Staple metal atom locant
D1-3
Staple metal
atom locant
Ligand locant
non-bridging S
M1-2
D1-2
D1-4
M1-1
M1-3
Ligand locant
non-bridging S
D1-1
D1-5
Ligand locant
non-bridging S
Staple atom numbers
1
2
3
4
5




C_5
12 O' clock
1
2
3
4
5
6
i
7
8
9
10
11
12

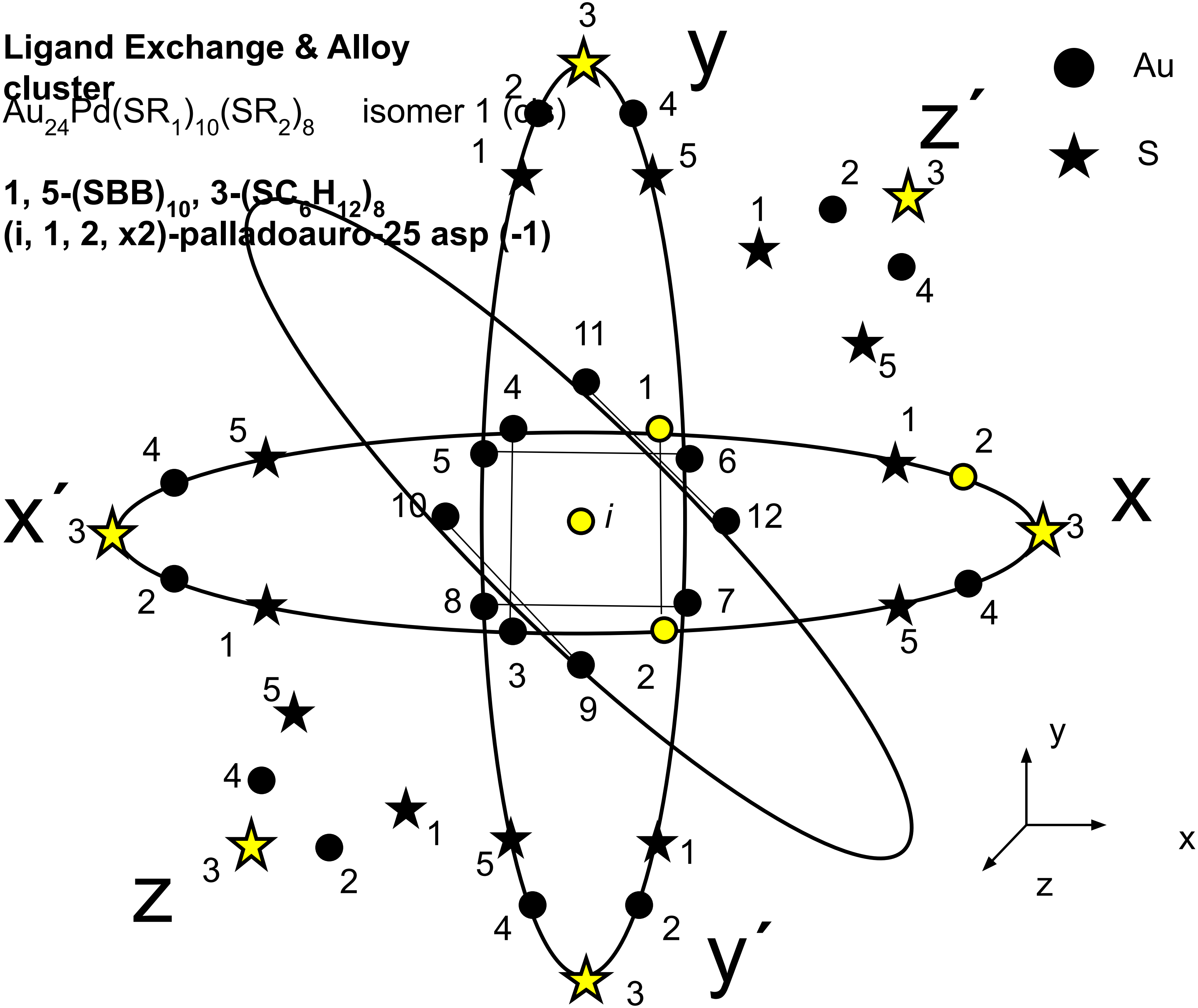
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)

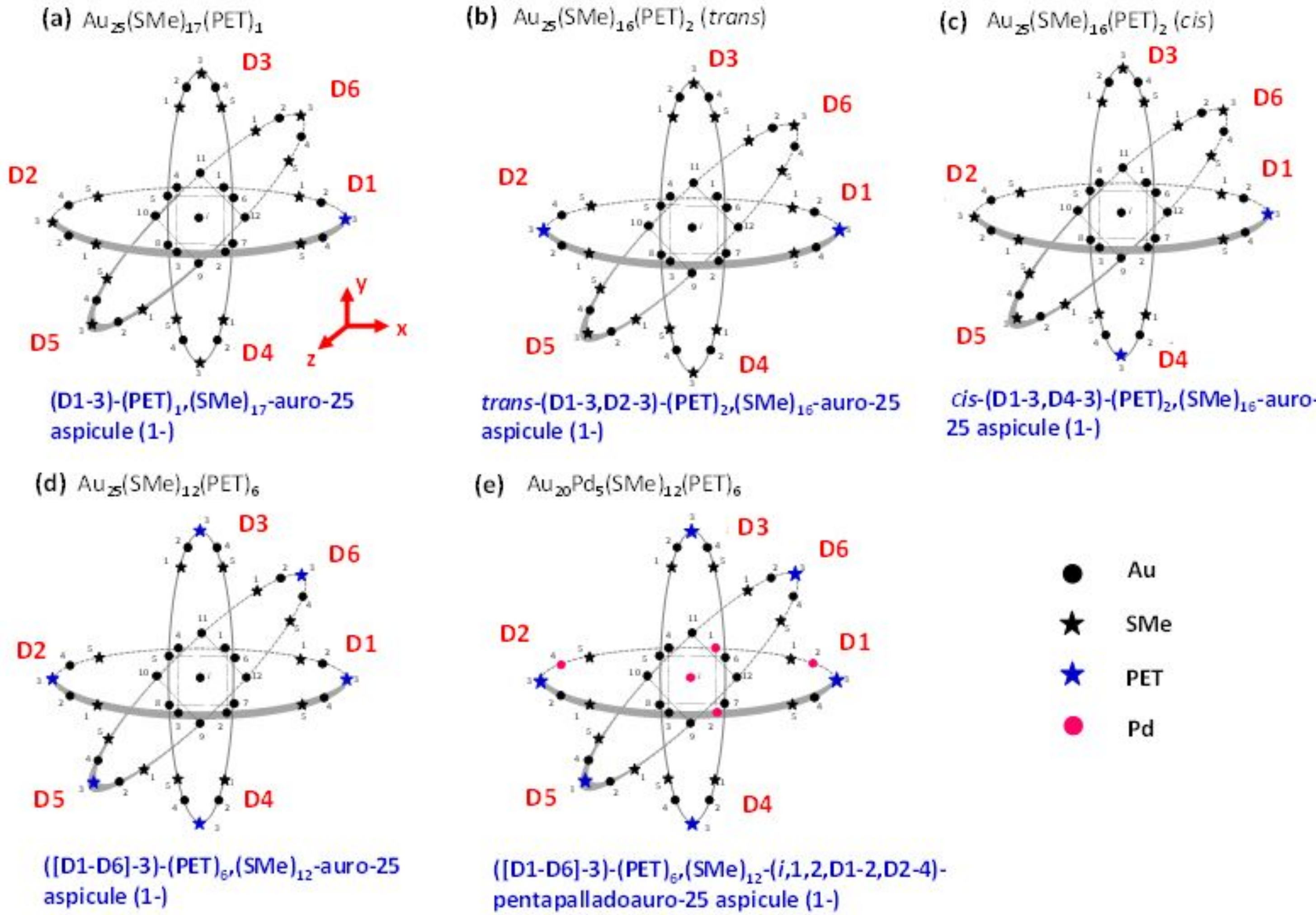
(D1-3,D2-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule(1-)

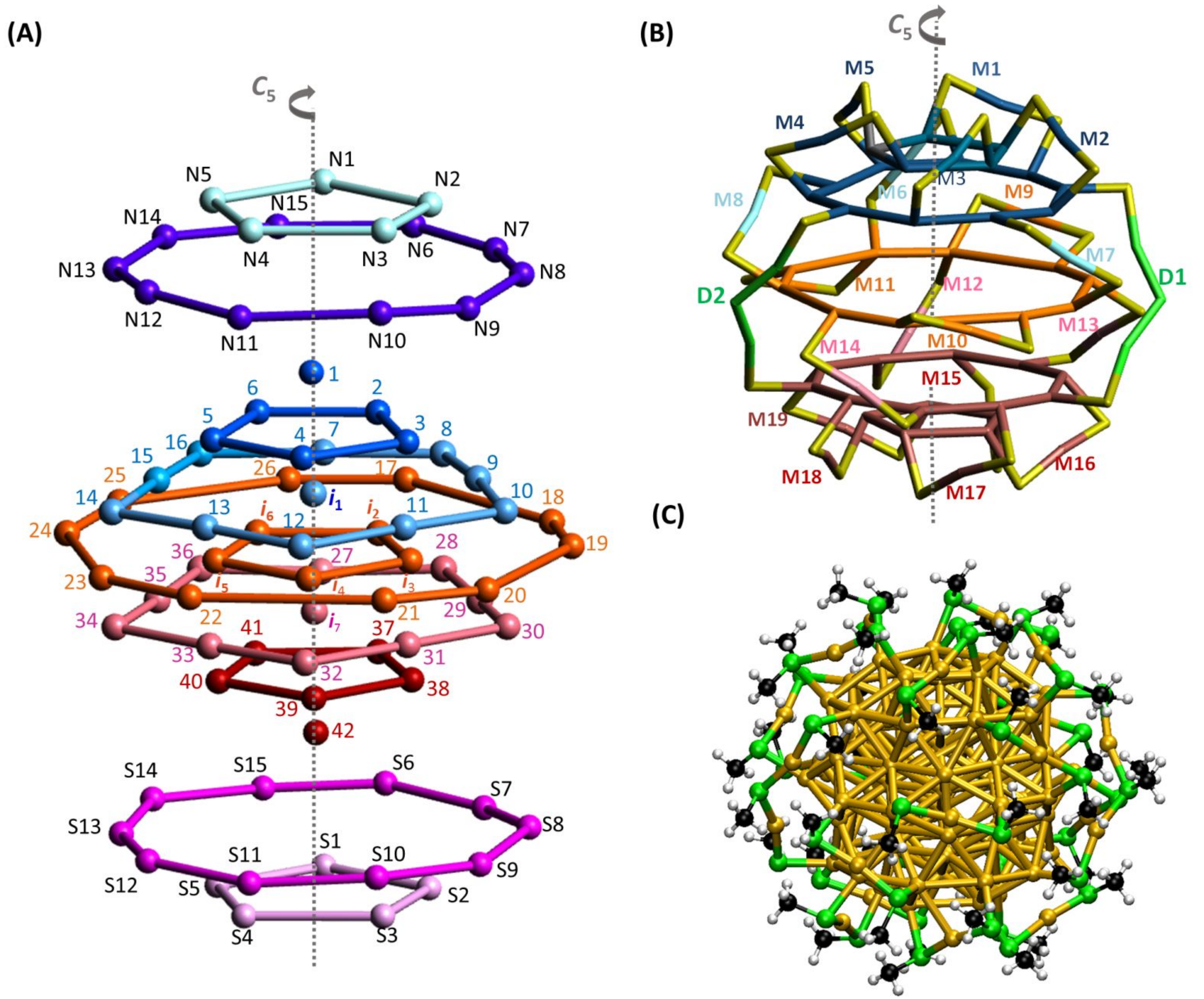
Ligand Exchange & Alloy cluster

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

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

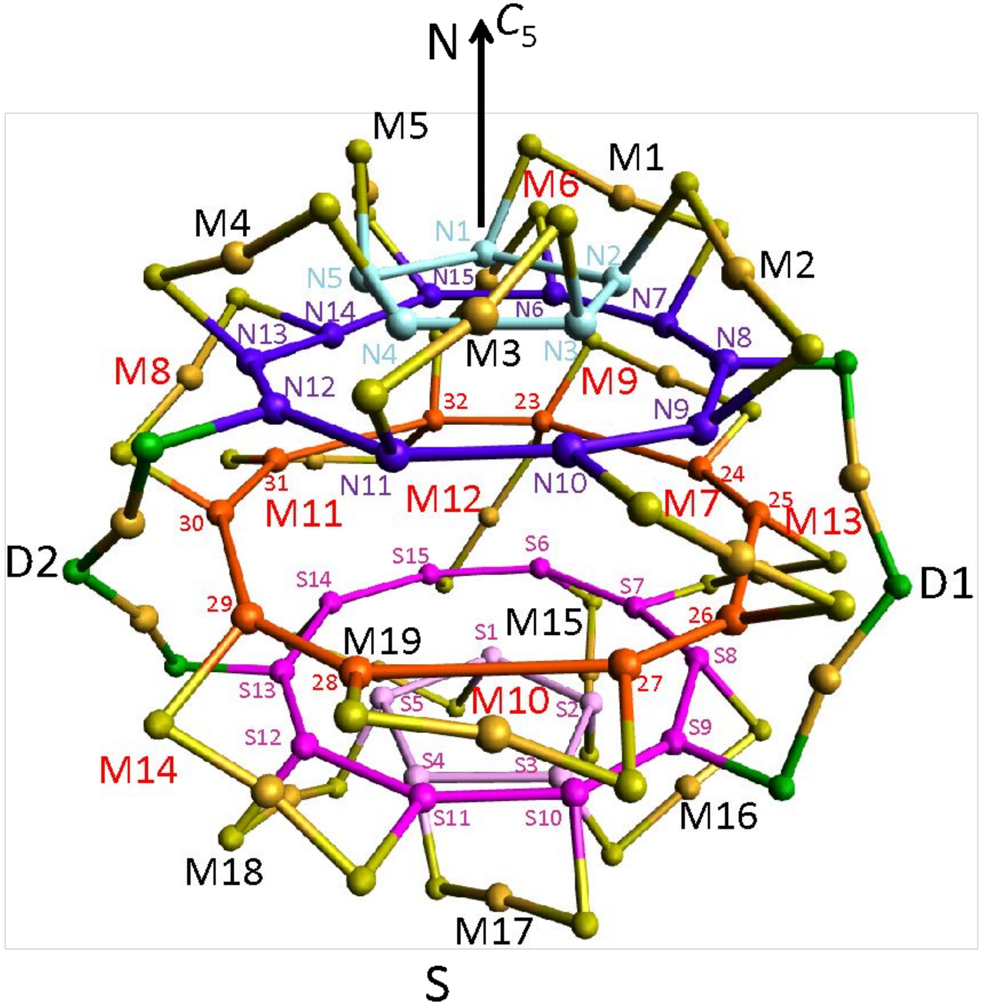



(a) Au25(SMe)17(PET)1
(D1-3)-(PET)1,(SMe)17-auro-25 aspicule (1-)
(b) Au25(SMe)16(PET)2 (trans)
trans-(D1-3,D2-3)-(PET)2,(SMe)16-auro-25 aspicule (1-)
(c) Au25(SMe)16(PET)2 (cis)
cis-(D1-3,D4-3)-(PET)2,(SMe)16-auro-25 aspicule (1-)
(d) Au25(SMe)12(PET)6
([D1-D6]-3)-(PET)6,(SMe)12-auro-25 aspicule (1-)
(e) Au20Pd5(SMe)12(PET)6
([D1-D6]-3)-(PET)6,(SMe)12-(i,1,2,D1-2,D2-4)-pentapalladoauro-25 aspicule (1-)
D1
D2
D3
D4
D5
D6
x
y
z
Au
SMe
PET
Pd



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

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



N
C_5
S
M1
M2
M3
M4
M5
M6
M7
M8
M9
M10
M11
M12
M13
M14
M15
M16
M17
M18
M19
D1
D2
N1
N2
N3
N4
N5
N6
N7
N8
N9
N10
N11
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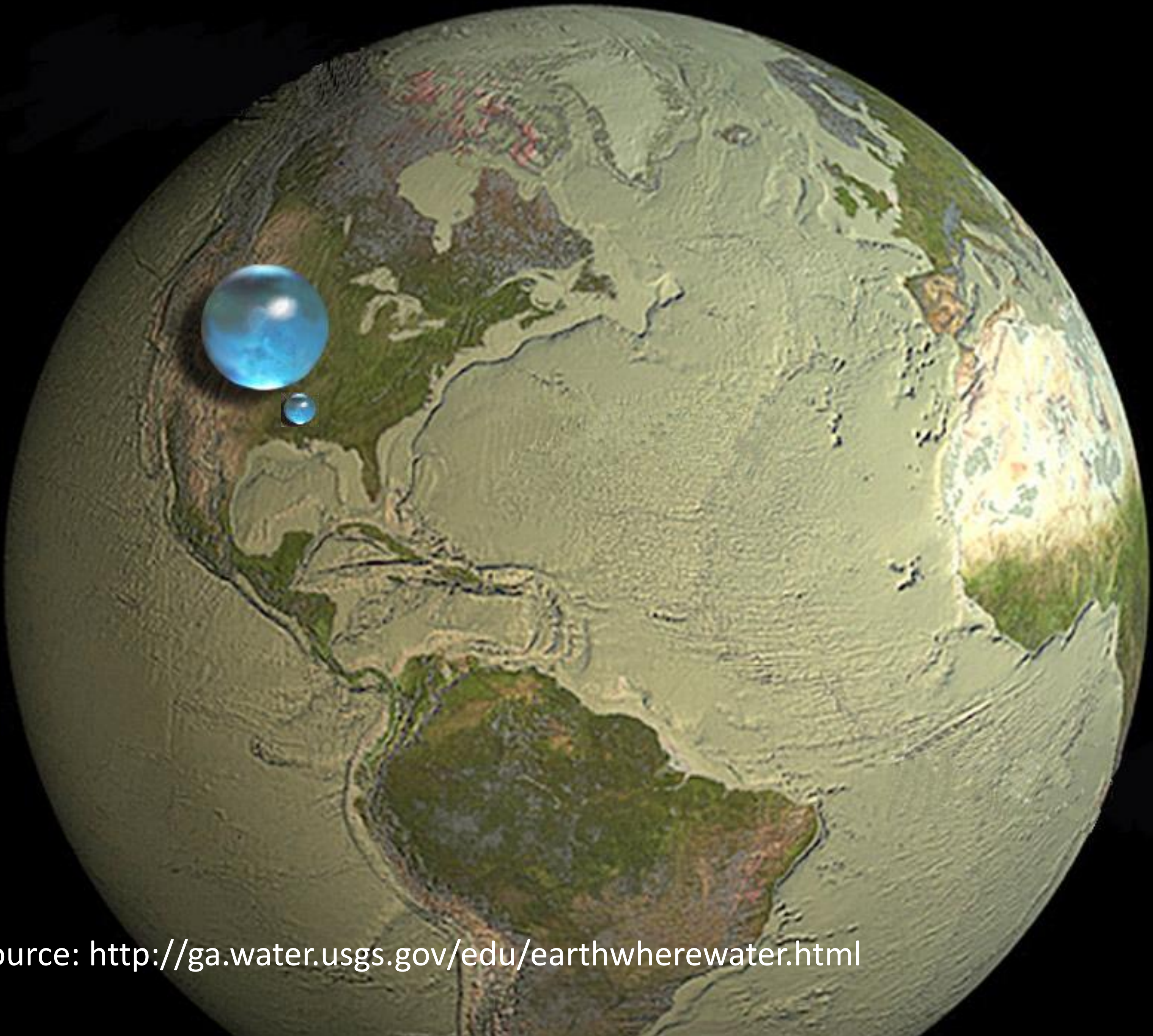
Compact aspicule structural names for Au_{25}, Au_{38} and Au_{102} aspicules and one modification of each.

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)

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

Formula Name	Aspicule Structural Name	Aspicule Name
$Au_{25}(SMe)_{18}$	[D1-D6]-(1,2 : 3,4 : 5,6 : 7,8 : 9,10)-[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 PET on the bridging ligands, and two Pd in the core.	[D1, D2]-(1,2 : 3,4)-[1, 3, 5-Me-$AuPdS_3$]$_2$, [D3-D6]-(5,6 : 7,8 : 9,10 : 11,12)-[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]-1,9 : 2,10 : 3,8 : 14,22 : 15,23-[1,3,5-Me-Au_2S_3]$_6$, [M1-M3]-4,18 : 5 19 : 6,20-[1,3-Me-AuS_2]$_3$*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 in interstials, Two PET in dimer staples	[D1, D2]-(1,9 : 2,10)-[3-PET, 1, 5-Me-Au_2S_3]$_2$, [D3-D6]-(3,8 : 14,22 : 15,23)- [1, 3, 5-Me-Au_2S_3]$_4$, [M1-M3]-4,18 : 5,19 : 6,20-[1, 3 -Me-AuS_2]$_3$ *BI*-(i_1, i_2)-dipalladoauro-38 aspicule (0)	(D1-3, D2-3, M1-1, M2-3)-$(SPET)_2$, $(SMe)_{22}$ (i_1, i_2)-dipalladoauro-38 aspicule (0)
$Au_{102}(SMe)_{44}$	[M1-M5]-(N1,N7 : N2:N9 : N3:N11 : N4:N13 : N5,N15), [M6-M8]-(N6,31: N10:26: N14,30)-[M9-M11]-(23,24 : 27,28 : 31,32)-[M12-M14]-(23,S15 : 25,S7 : 29,S1)-[M15-M19]-(S6,S2 : S8,S3 : S10,S4 : S12,S5 : S14,S1)-[1,3-Me-AuS_2]$_{19}$, [D1,D2]-(N8,S9 : N14,S13)-[1,3,5-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 in the MD core. Two PET ligands on bridging ligands of the dimer staples and two PET ligands on different positions of monomer staples.	[M1,M2]-(N1,N7 : N2:N9)-[5-PET, 1,3-Me-AuS_2]$_2$, [D1,D2]-(N8,S9 : N14,S13)-[5-PET, 1,3-Me-Au_2S_3]$_2$, [M3,M4,M5]-(N1,N7 : N2:N9 : N3:N11 : N4:N13 : N5,N15)-[M6,⋯,M8]-(N6,31: N10:26: N14,30)-[M9-M11]-(23,24 : 27,28 : 31,32)-[M12-M14]-(23,S15 : 25,S7 : 29,S1)-[M15-M19]-(S6,S2 : S8,S3 : S10,S4 : S12,S5 : S14,S1)-[1,3-Me-AuS_2]$_{17}$ *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)



Source: http://ga.water.usgs.gov/edu/earthwherewater.html

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Biopolymer-re
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water purifica

Mohan Udhaya Sankar[1], Saha
Kamalesh Chaudhari, and Tha

Unit of Nanoscience and Thematic Uni

Edited by Eric Hoek, University of Calif

**Creation of affordable materials fo
water is one of the most promising
drinking water for all. Combinin
composites to scavenge toxic sp
other contaminants along with th
affordable, all-inclusive drinking
without electricity. The critical p
synthesis of stable materials tha
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surfaces. Here we show that suc
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sand-like properties, such as highe
forms. These materials have been
water purifier to deliver clean drin
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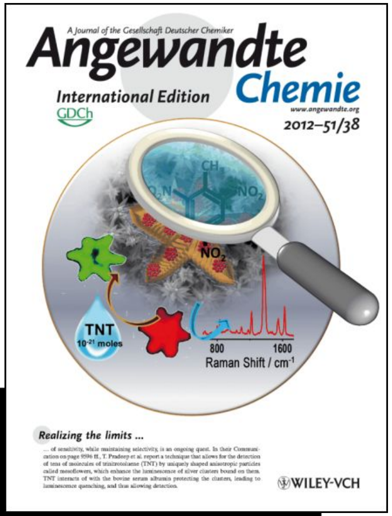
ambient temperature has wide
water purification.**

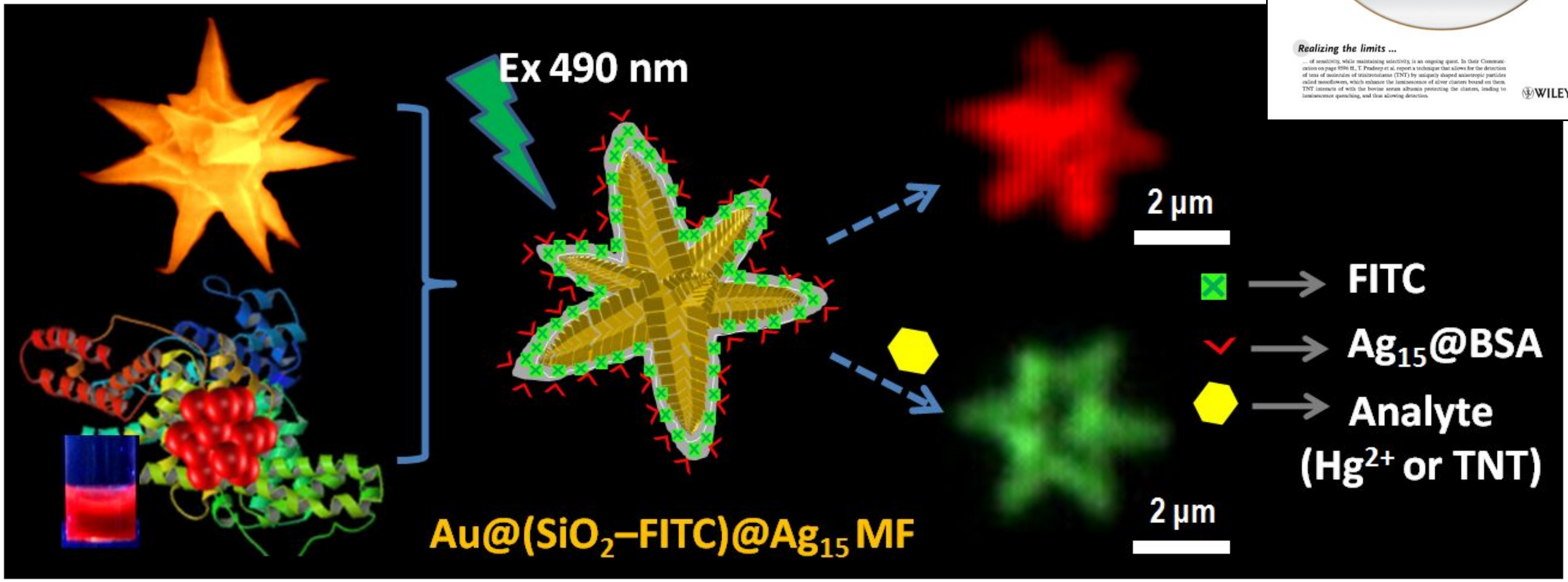
hybrid | green | appropriate technolog

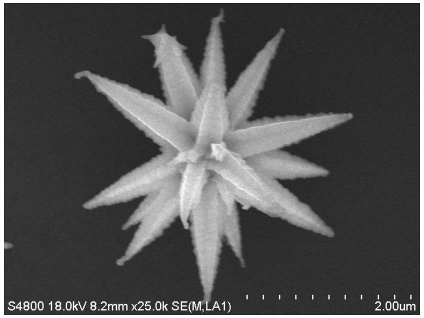
Work was featured in several journals

Nature Nanotechnology, July 2014 issue

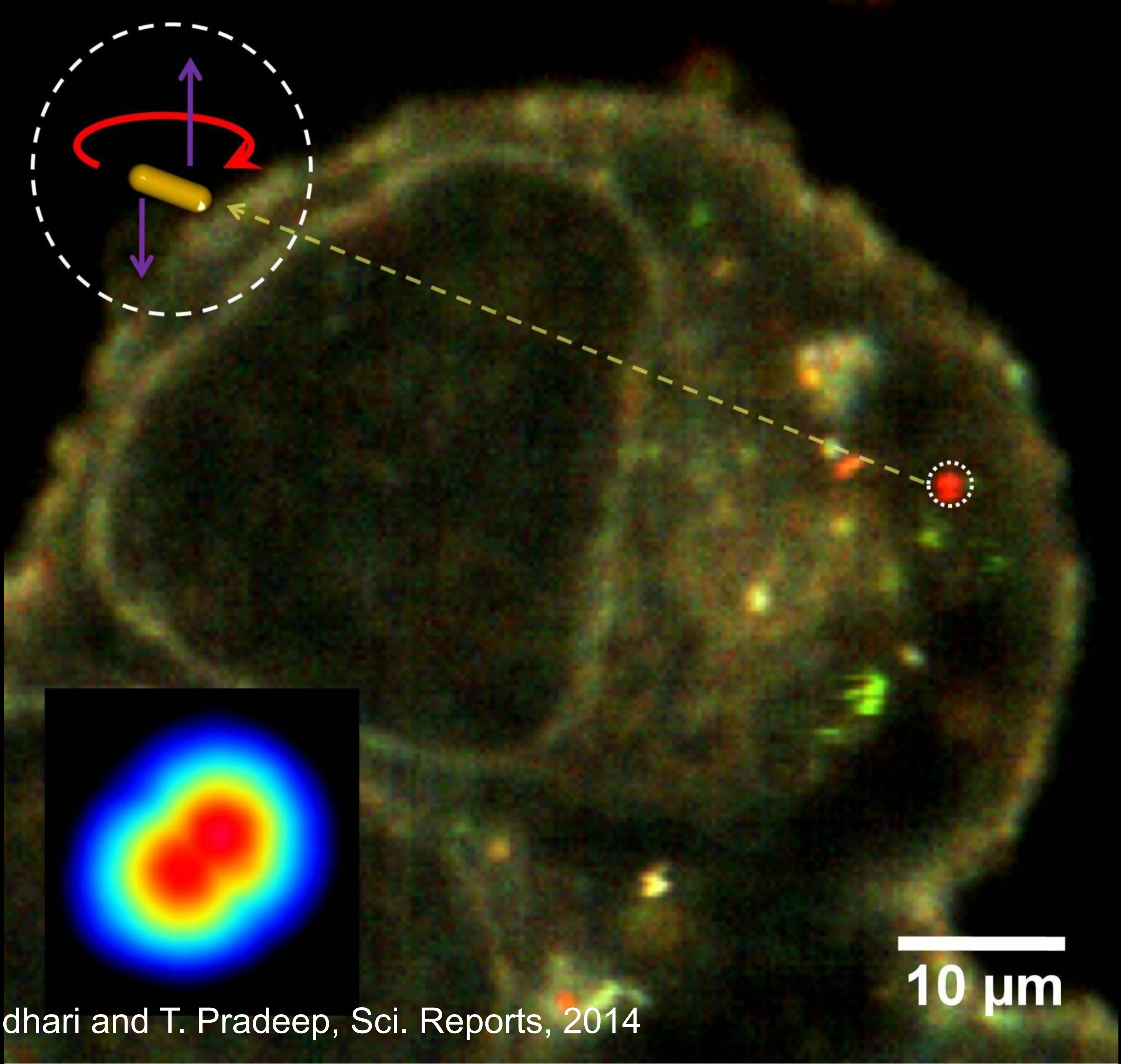
Sub-zeptomolar detection





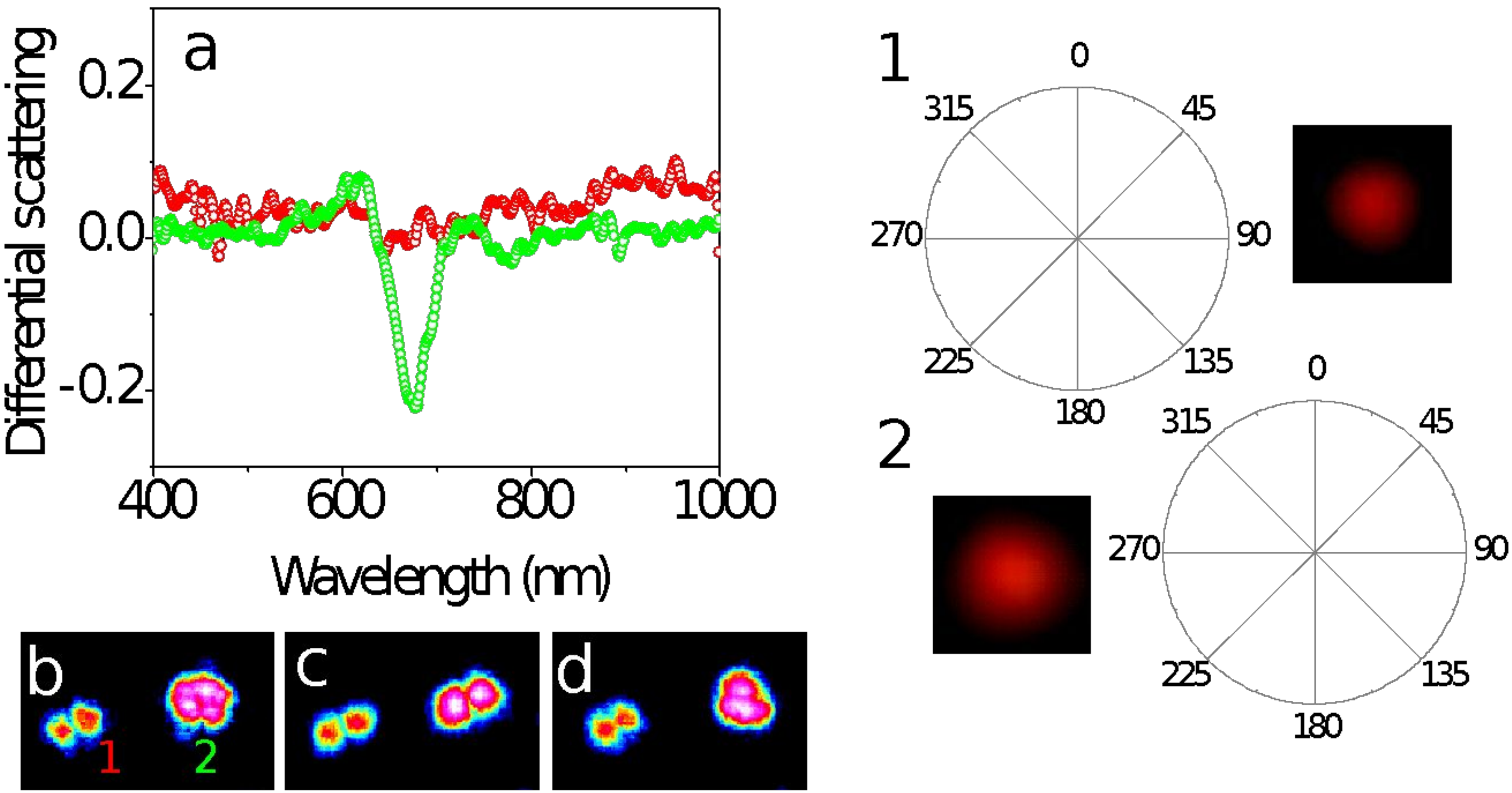


Ammu Mathew, et al. Angew. Chem. Int. Ed. 2012



K. Chaudhari and T. Pradeep, Sci. Reports, 2014

Optical rotation due to plasmonic chirality of GNR aggregates



Chaudhari, K.; Pradeep, T., Applied Physics Letters, 2014, 105, 049447.

Angewandte Chemie International Edition

DOI: 10.1002/anie.201311053

VIP **Mass Spectrometry** *Very Important Paper*

Molecular Ionization from Carbon Nanotube Paper**

*Rahul Narayanan, Depanjan Sarkar, R. Graham Cooks, and Thalappil Pradeep**

Dedicated to Professor C. N. R. Rao on the occasion of his 80th birthday.

Abstract: *Ambient ionization is achieved by spraying from a carbon nanotube (CNT)-impregnated paper surface under the influence of small voltages (≥3 V). Organic molecules give simple high-quality mass spectra without fragmentation in the positive or negative ion modes. Conventional field ionization is ruled out, and it appears that field emission of microdroplets occurs. Microscopic examination of the CNT paper confirms that the nanoscale features at the paper surface are responsible for the high electric fields. Raman spectra imply substantial current flows in the nanotubes. The performance of this analytical method was demonstrated for a range of volatile and nonvolatile compounds and a variety of matrices.*

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achieved from a s
tubes (CNTs) at a
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analytes, which ar
are detectable in s
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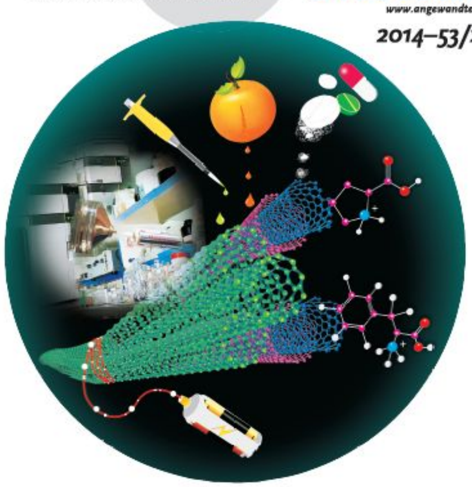
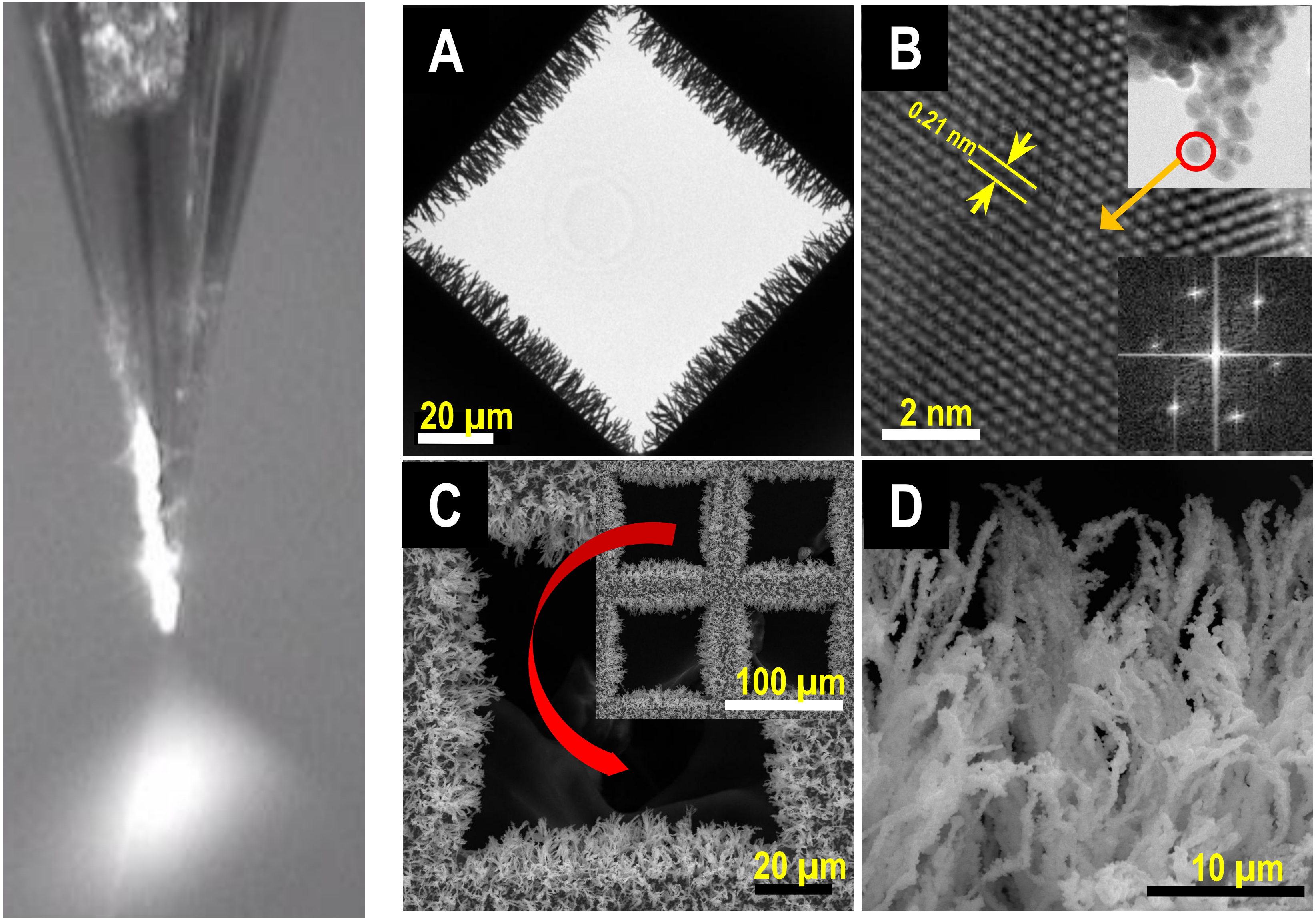
A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie International Edition
www.angewandte.org
2014–53/23



A piece of paper ...

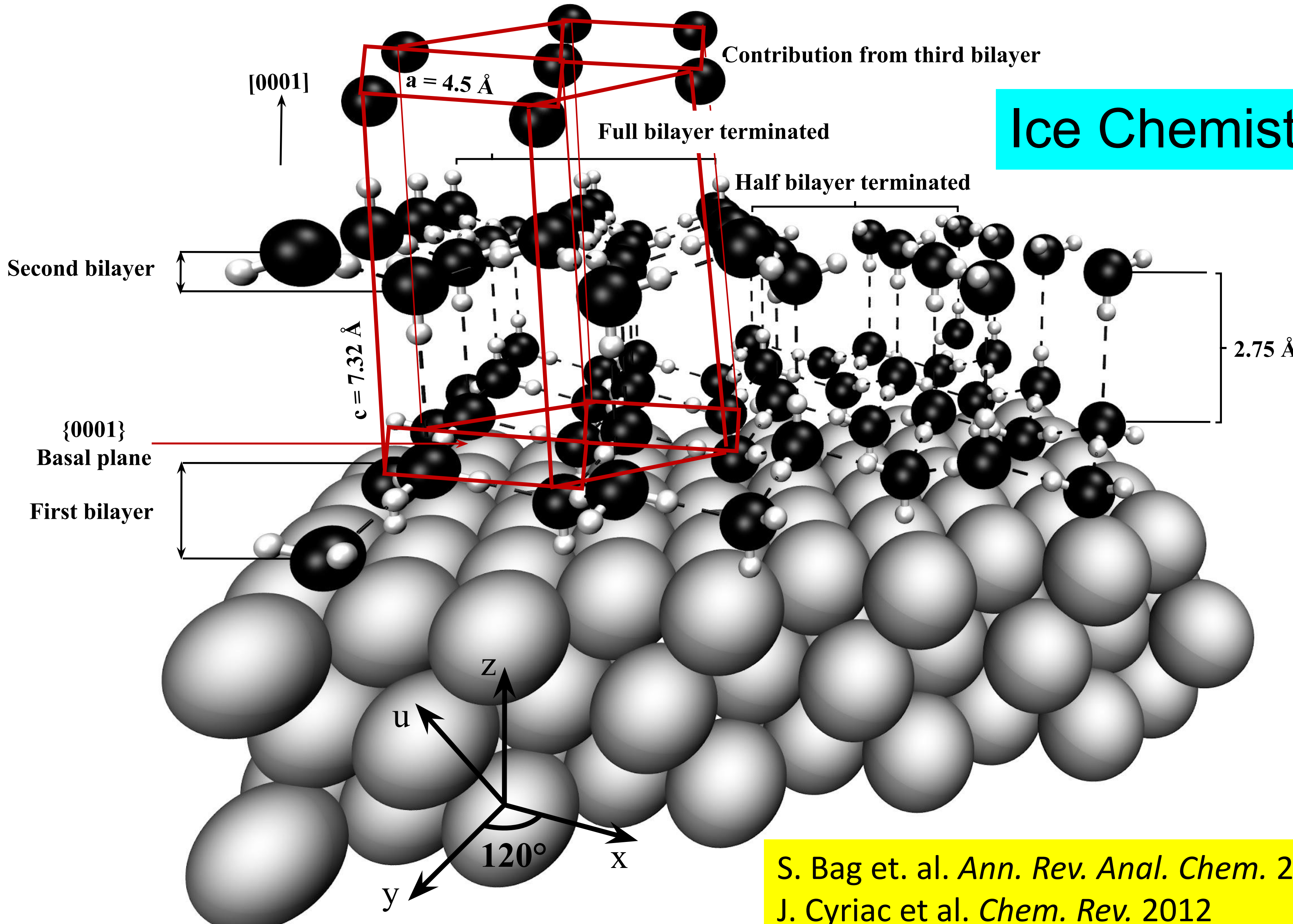
... that is impregnated with multi-walled or single-walled carbon nanotubes generates ions from diverse analytes at voltages as low as 3 V, as T. Pradeep et al. show in their Communication on page 5936 ff. This miniaturized ion source is held in front of a mass-spectrometer inlet to collect the mass spectrum. Common pesticides from the surface of an orange, active molecules from tablets, and a variety of analytes, such as amino acids, can been characterized.

WILEY-VCH



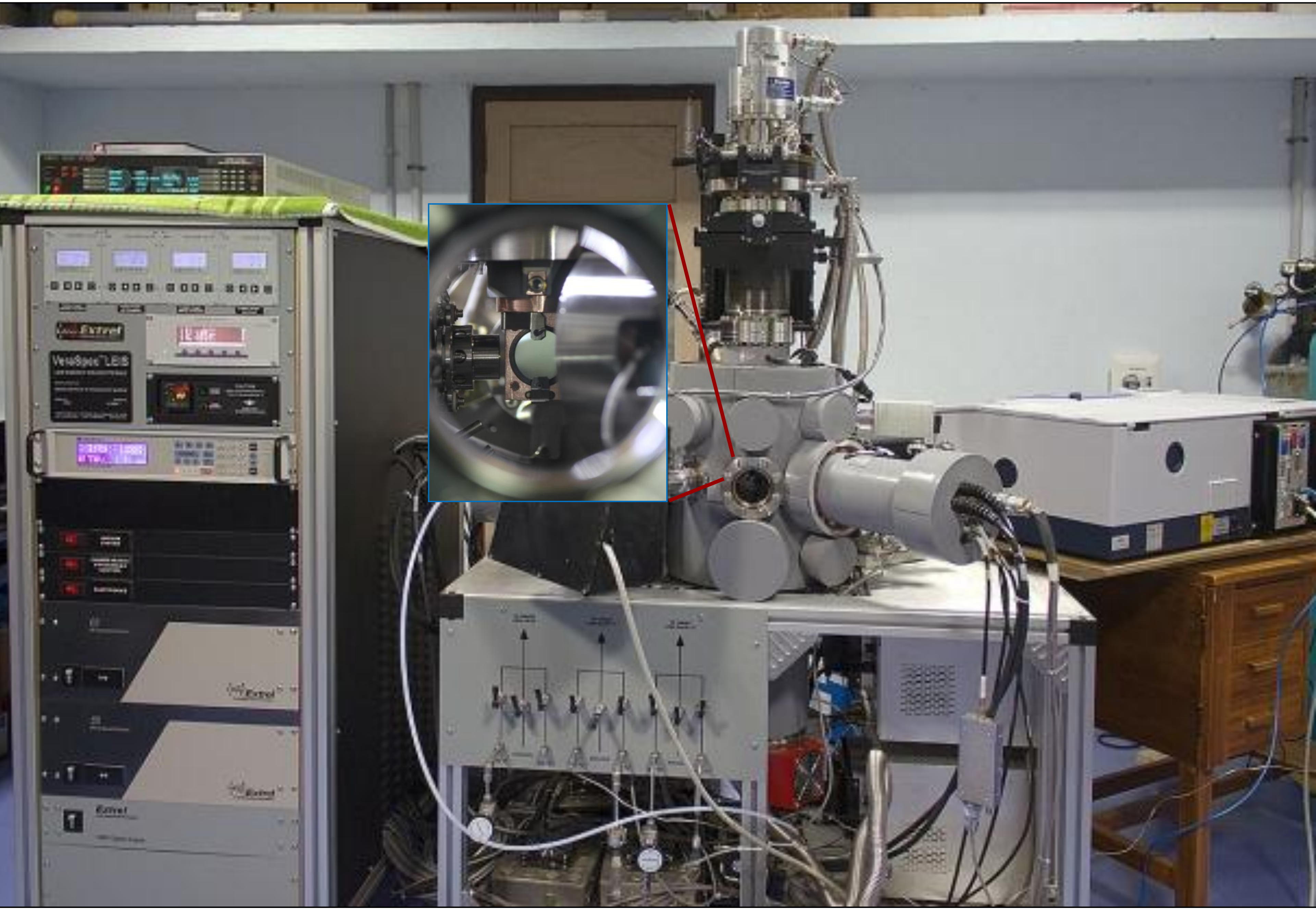
Depanjan Sarkar, et.al. Adv. Mater. 2016

Ice Chemistry



S. Bag et. al. *Ann. Rev. Anal. Chem.* 2013
J. Cyriac et al. *Chem. Rev.* 2012

A perspective view of Ih ice growth on a Ru(0001) substrate. The grey balls indicate the Ru atoms, the black balls represent the oxygen atoms and the white balls stands for the hydrogen atoms. Hydrogen bonds in the ice structure are shown by black dotted line in between the water molecules. The epitaxial growth of ice is shown.



Extrel

Summary

- New chemistry of clusters
- Borromean rings diagram of Au_{25}
- Understanding of the structures formed
- Nomenclature for Au_{25}, Au_{38}, Au_{102} and $Au_M(SR)_N$ to describe both structure and modifications


EDAX

Department of Science and Technology

Thank you