Since 1959

Atom dynamics in nanoparticles

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Lecture 9

FS-CHM 2022 IISER Thiruvananthapuram, April 8-10, 2022

CHEMICAL REVIEWS

Review

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

Indranath Chakraborty[†] and Thalappil Pradeep[*]

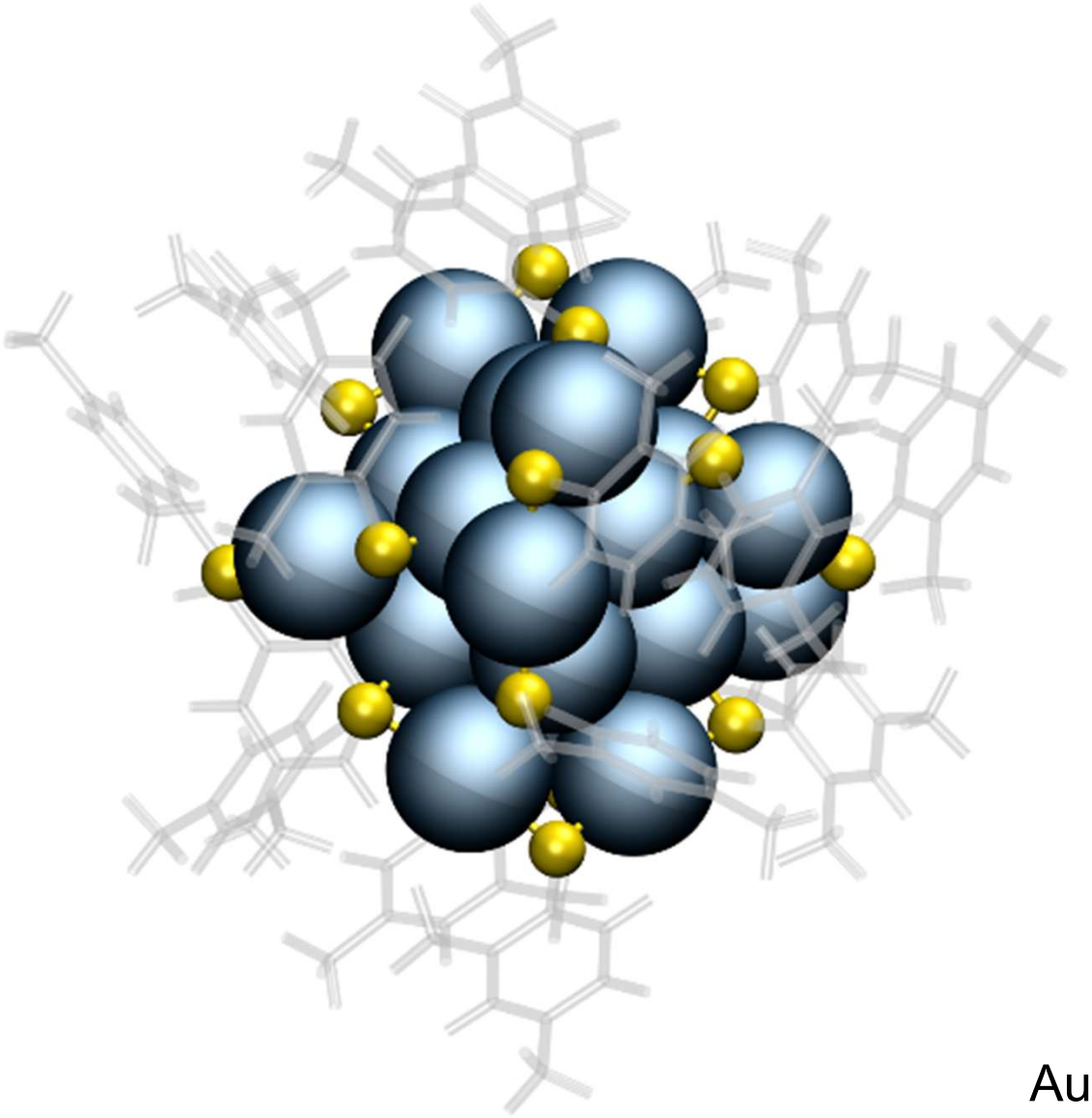
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Supporting Information

Citations: >1100

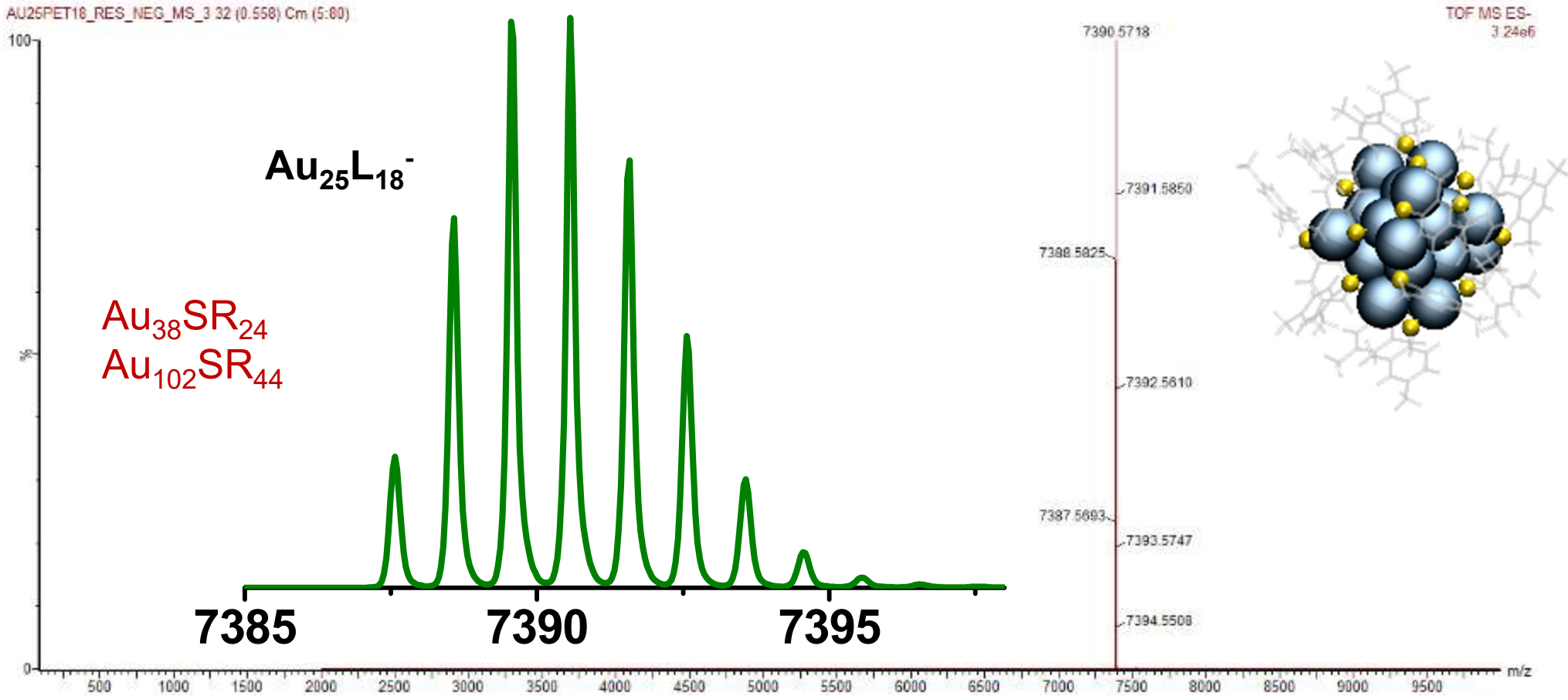
ABSTRACT: Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{102}(SR)_{44}$ as well as $Ag_{25}(SR)_{18}$, $Ag_{29}(S_2R)_{12}$, 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, Rongchao Jin, Nanfeng Zheng, Terry Bigioni, Osman Bakr, Kornberg, Jianping Xie, C. M. Aikens, Thomas Buergi, Amala Dass, Ackerson, De-en Jiang, …. A. W. Castleman Jr., H. Schmidbauer, …

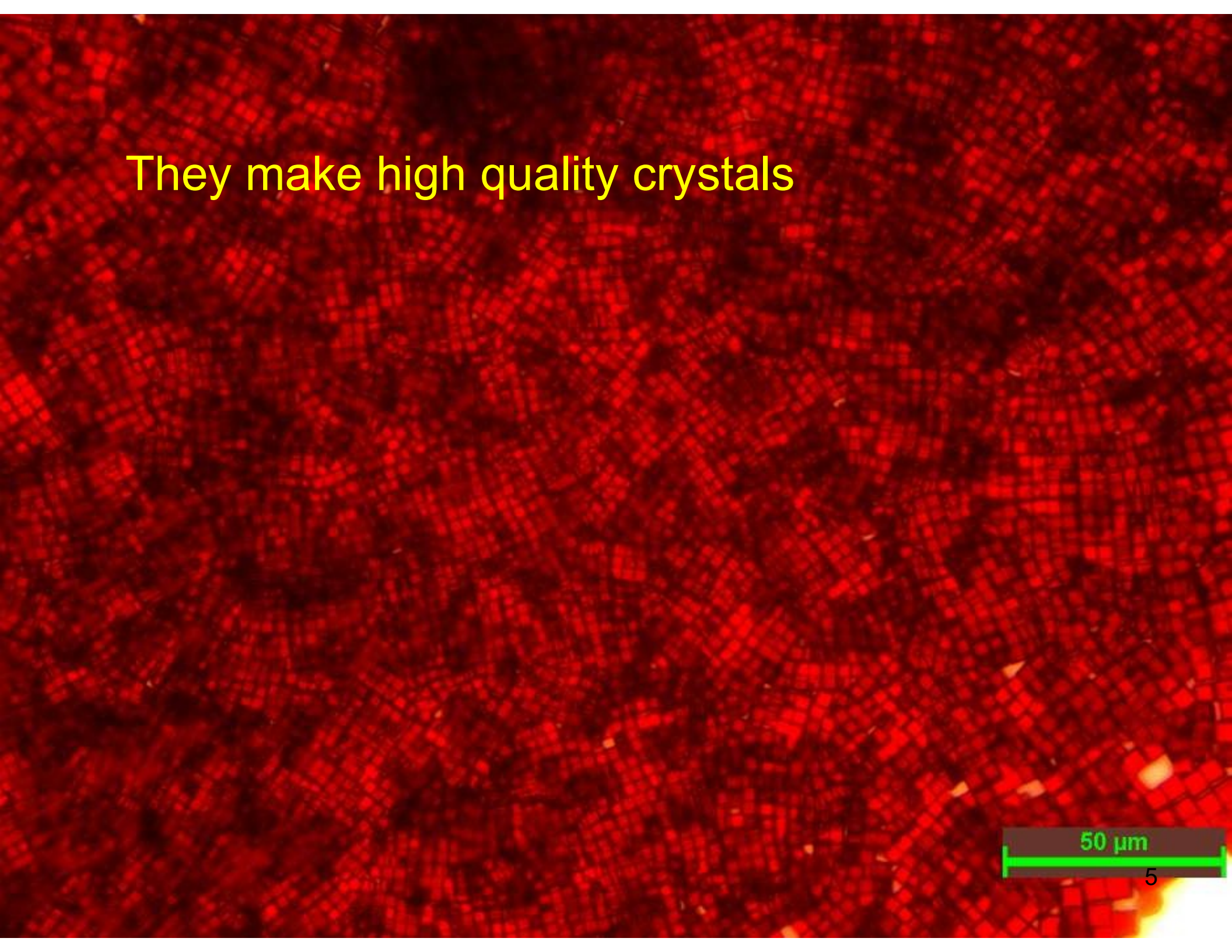


$Au_{25}, Ag_{25}, Ag_{29}$

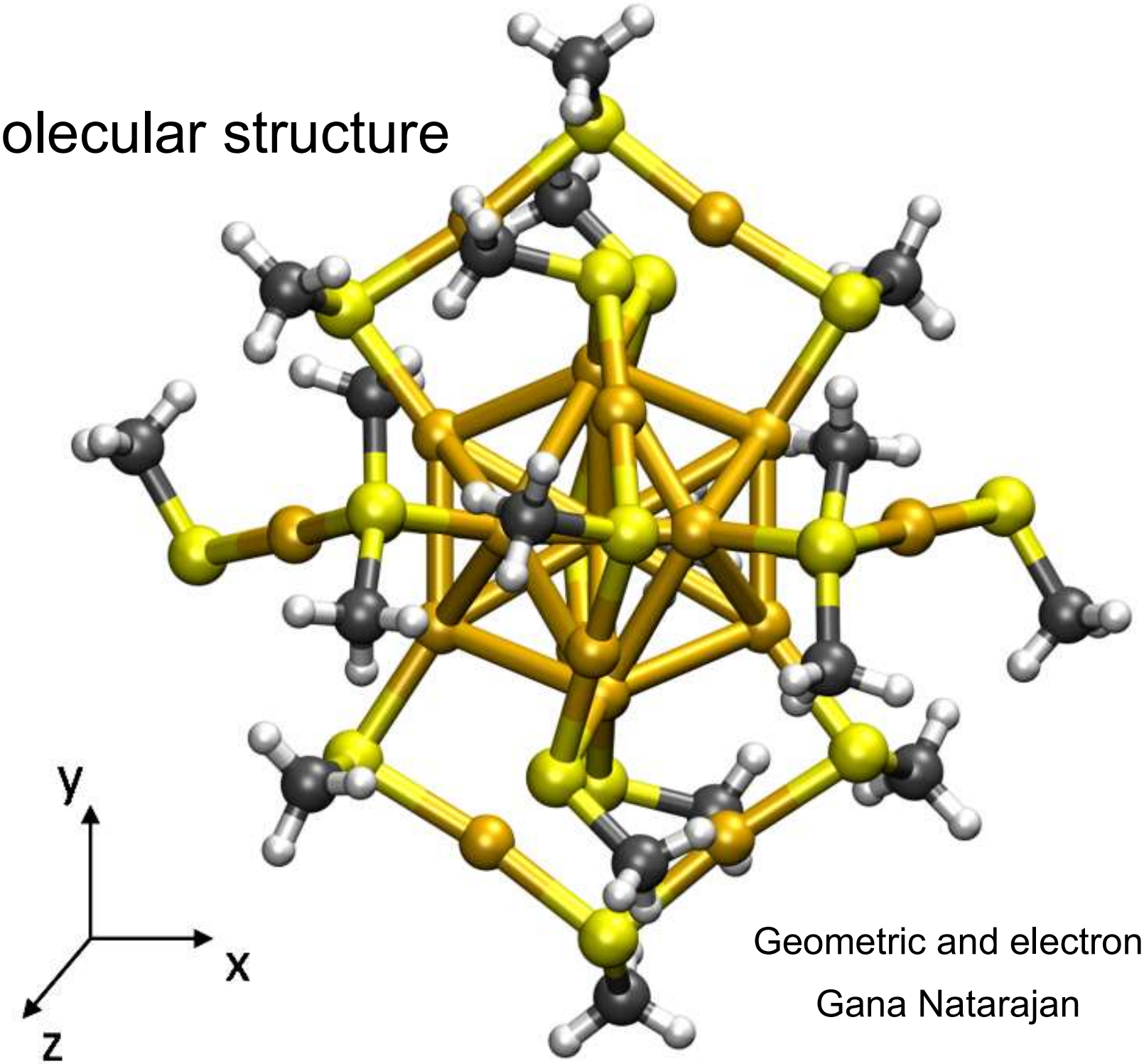
Molecular formula, Molecular weight



They make high quality crystals

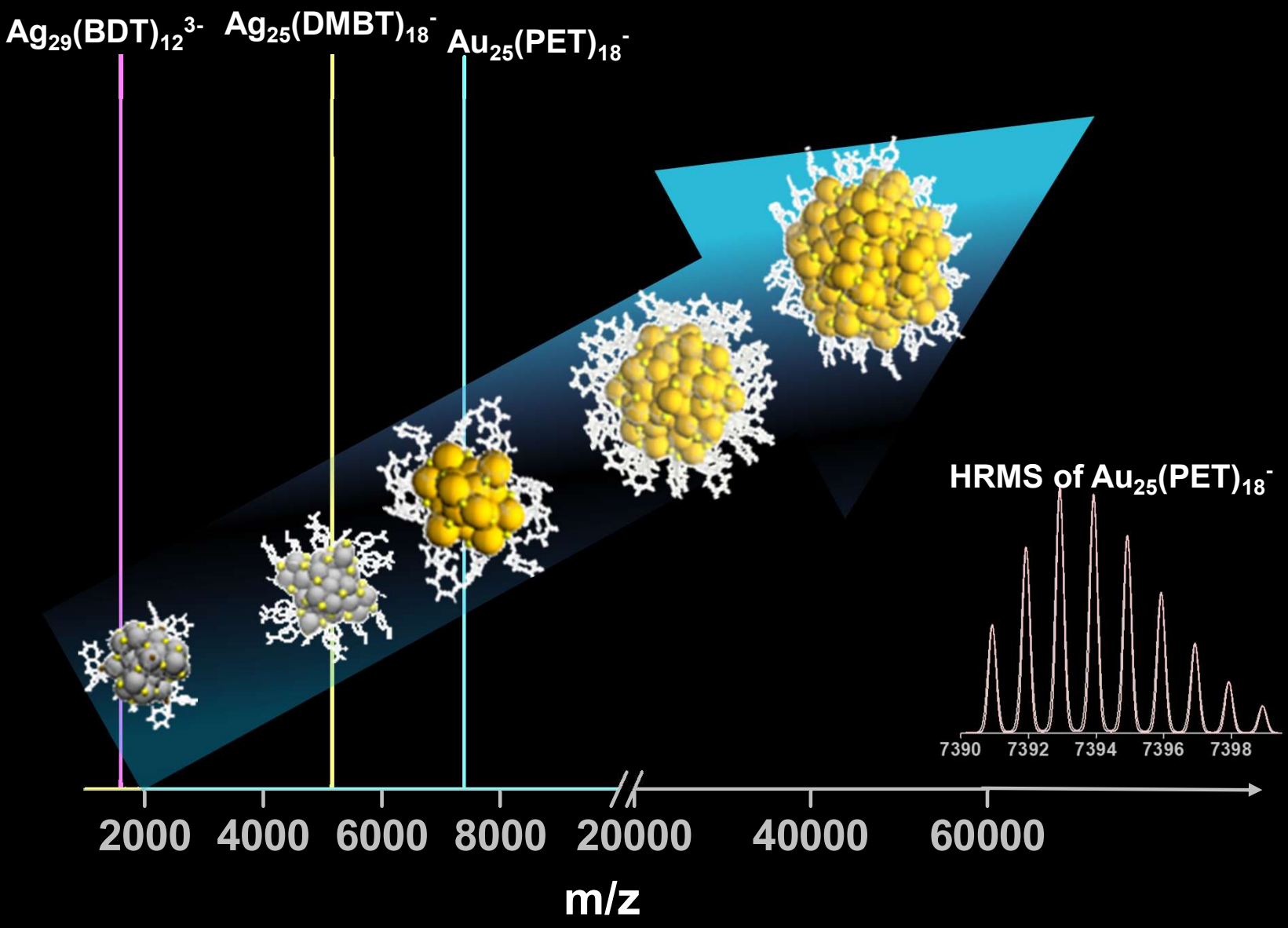


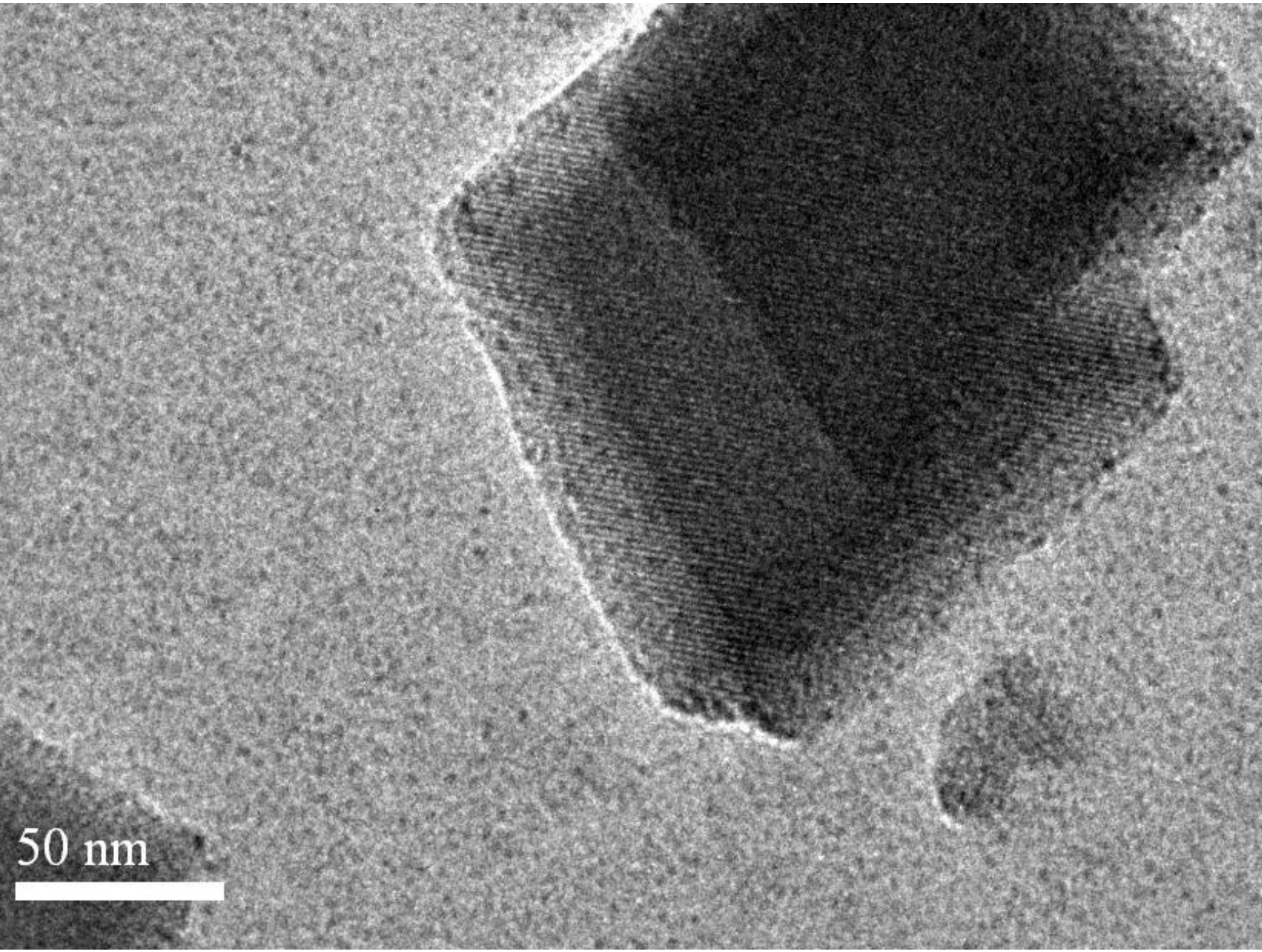
Molecular structure

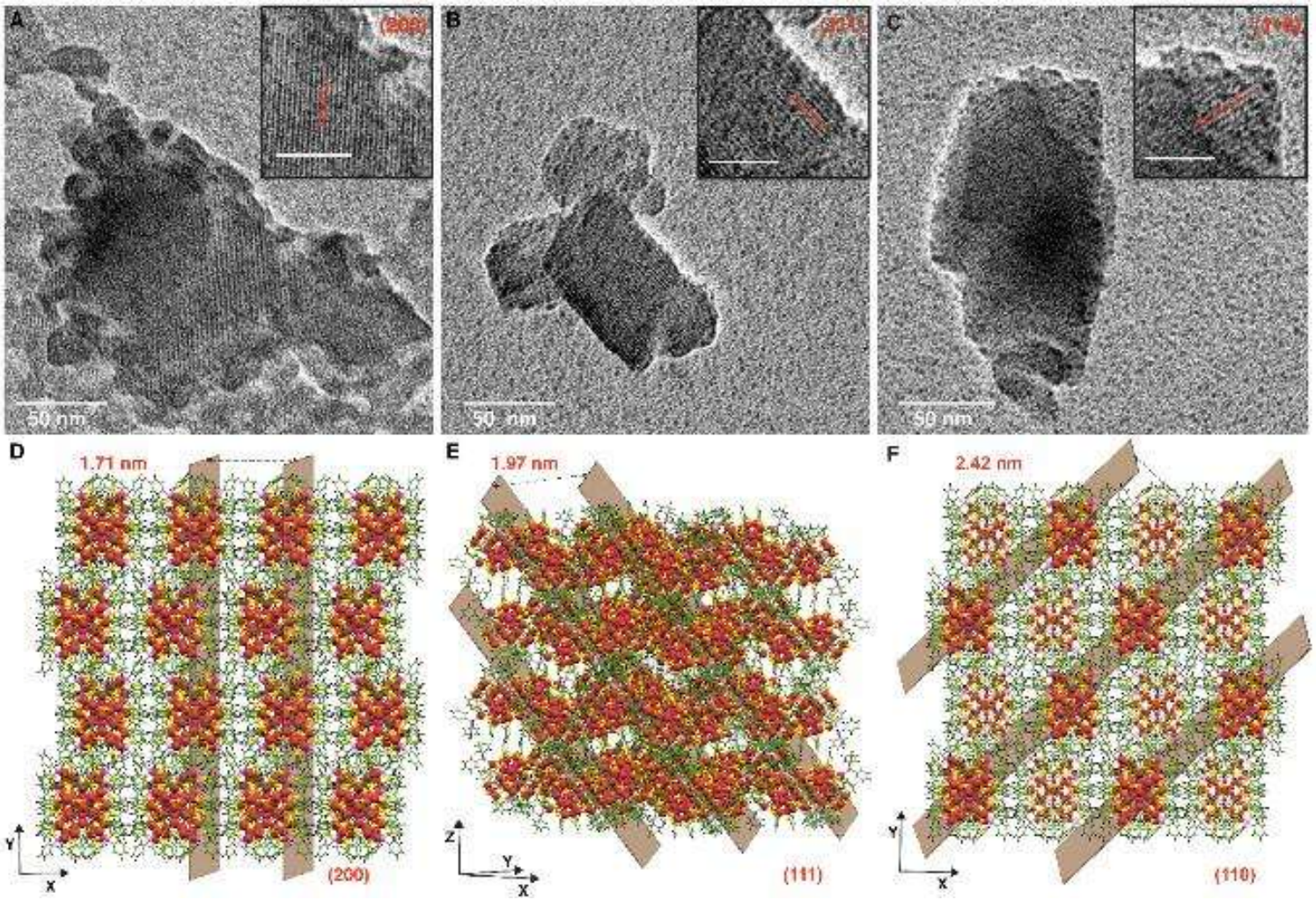


Molecules and their properties

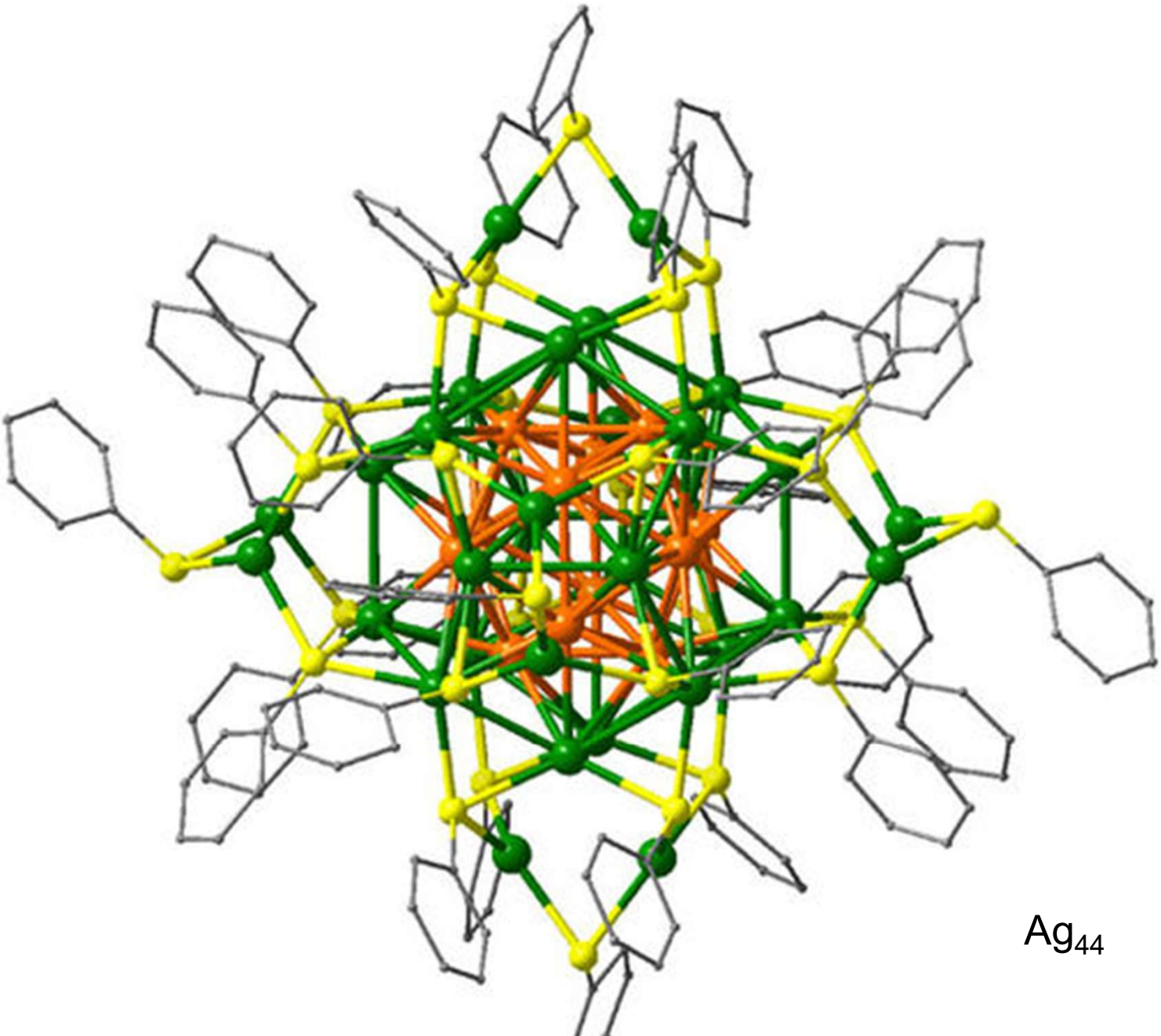
Chemical formula	H_2O
Molecular weight	18.0148
Critical temperature	373.91°C
Critical pressure	22.05 MPa
Critical density	315.0 kg/m^3
Triple point temperature	0.01°C
Triple point pressure	615.066 Pa
Normal boiling point	100.0°C
Normal freezing point	0.0°C
Density of ice at normal melting point	918.0 kg/m^3
Maximum density, 3.98°C	999.973 kg/m^3
Viscosity, 25°C	0.889 mN s/m^2
Surface tension, 25°C	72 mN/m
Heat Capacity, 25°C	4.1796 kJ/kg.K
Enthalpy of vaporisation, 100°C	2,257.7 kJ/kg
Enthalpy of fusion, 0°C	333.8 kJ/kg
Velocity of sound, 0°C	1.403 km/s
Dielectric constant, 25°C	78.40
Electrical conductivity, 25°C	8 μS/m
Refractive index, 25°C	1.333
Liquid compressibility, 10°C	480. × 10^{-12}m^2/N
Coefficient of thermal expansion, 25°C	256.32 × 10^{-6} K^{-1}
Thermal Conductivity, 25°C	0.608 W/m.K


$Ag_{29}(BDT)_{12}^{3-}$
$Ag_{25}(DMBT)_{18}^{-}$
$Au_{25}(PET)_{18}^{-}$
HRMS of $Au_{25}(PET)_{18}^{-}$
7390
7392
7394
7396
7398
2000
4000
6000
8000
20000
40000
60000
m/z


50 nm



Ananthu Mahendranath et al. Chem.Comm.2021



Ag_{44}

Nanfeng Zheng et al. *Nature Communications* 1 2013
Terry Bigioni et al. *Nature* 2013

Molecular reactions

Reactions on clusters

Reactions between clusters

Inter-cluster reactions

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

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

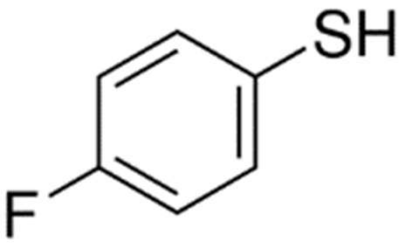
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,† Ganapati Natarajan, and Thalappil Pradeep*

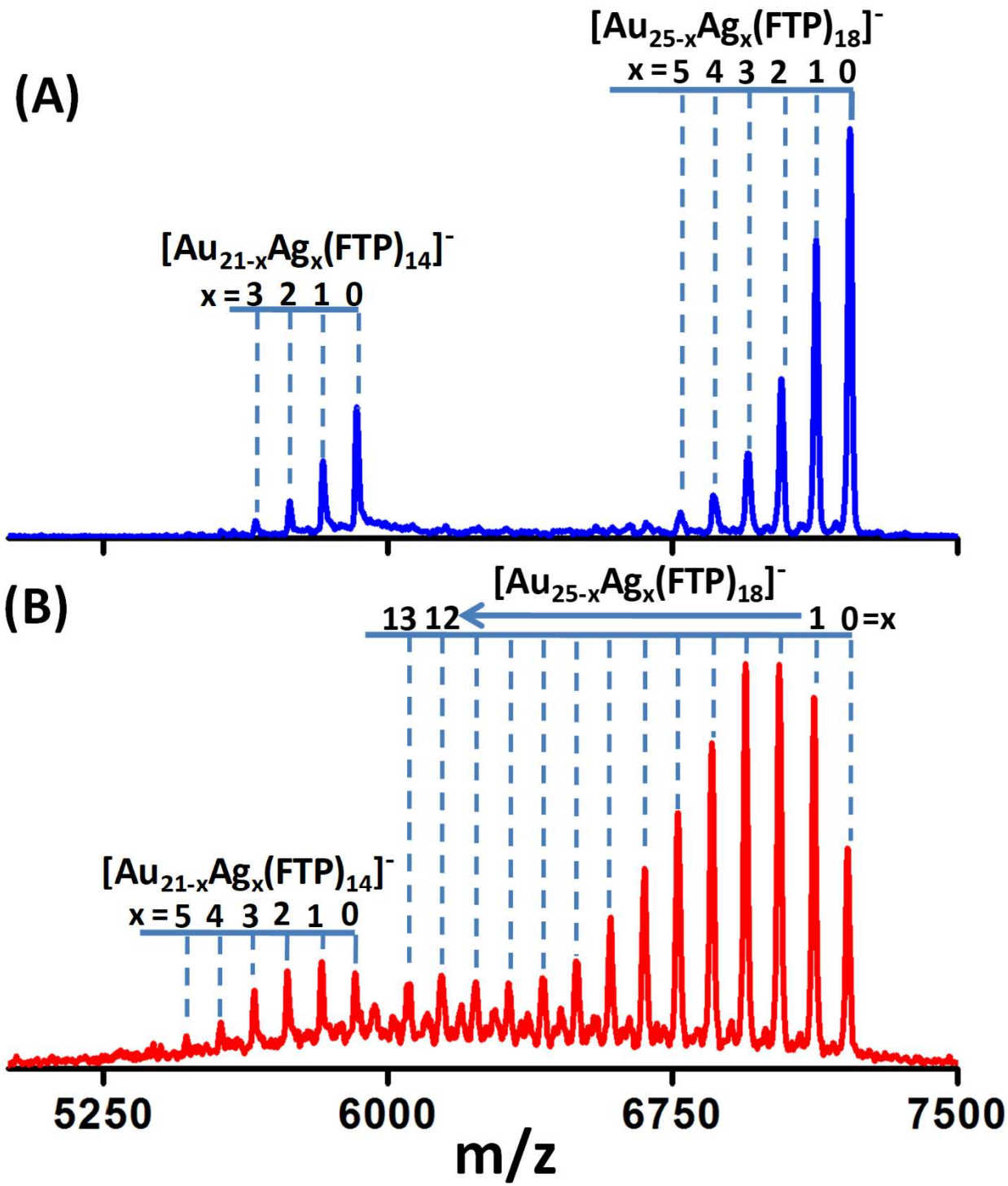
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India

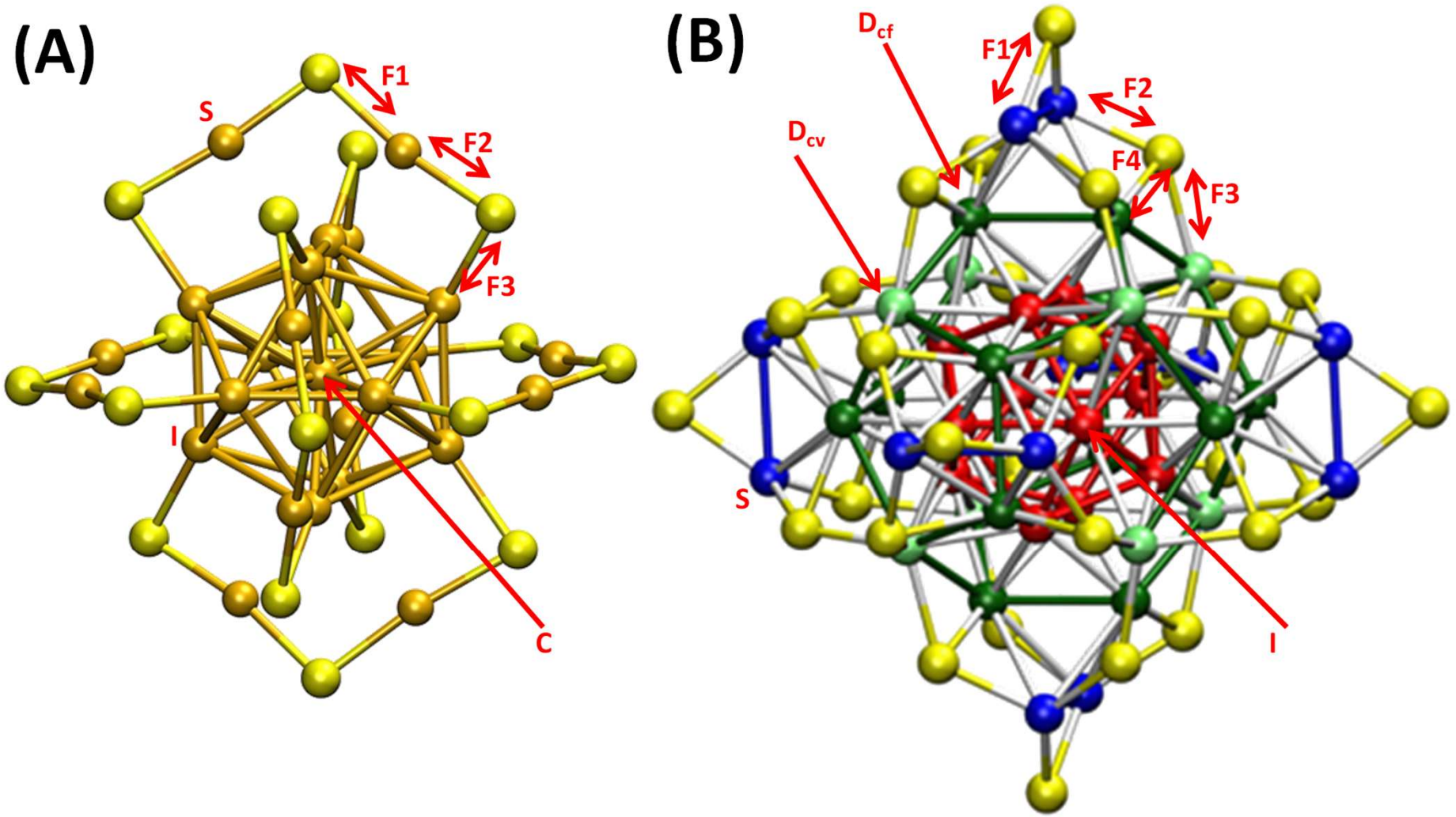
Supporting Information

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

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






(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)

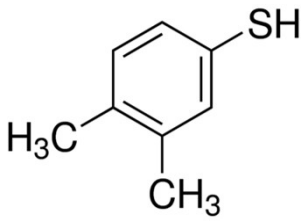
Location of Ag in $Au_{25-x}Ag_x(SR)_{18}$	Locations of Au in $Au_xAg_{44-x}(SR)_{30}$			
	I	D_{cv}	D_{cf}	S
C	-0.015	+0.564	+0.388	+0.226
I	-0.486	+0.093	-0.083	-0.245
S	-0.276	+0.303	+0.127	-0.035

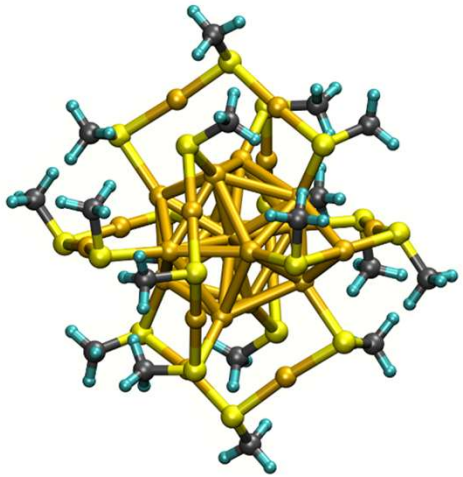
Ag_{25}-Au_{25} experiments

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

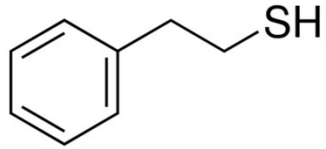
Reaction between $Au_{25}(PET)_{18}$ and $Ag_{25}(DMBT)_{18}$

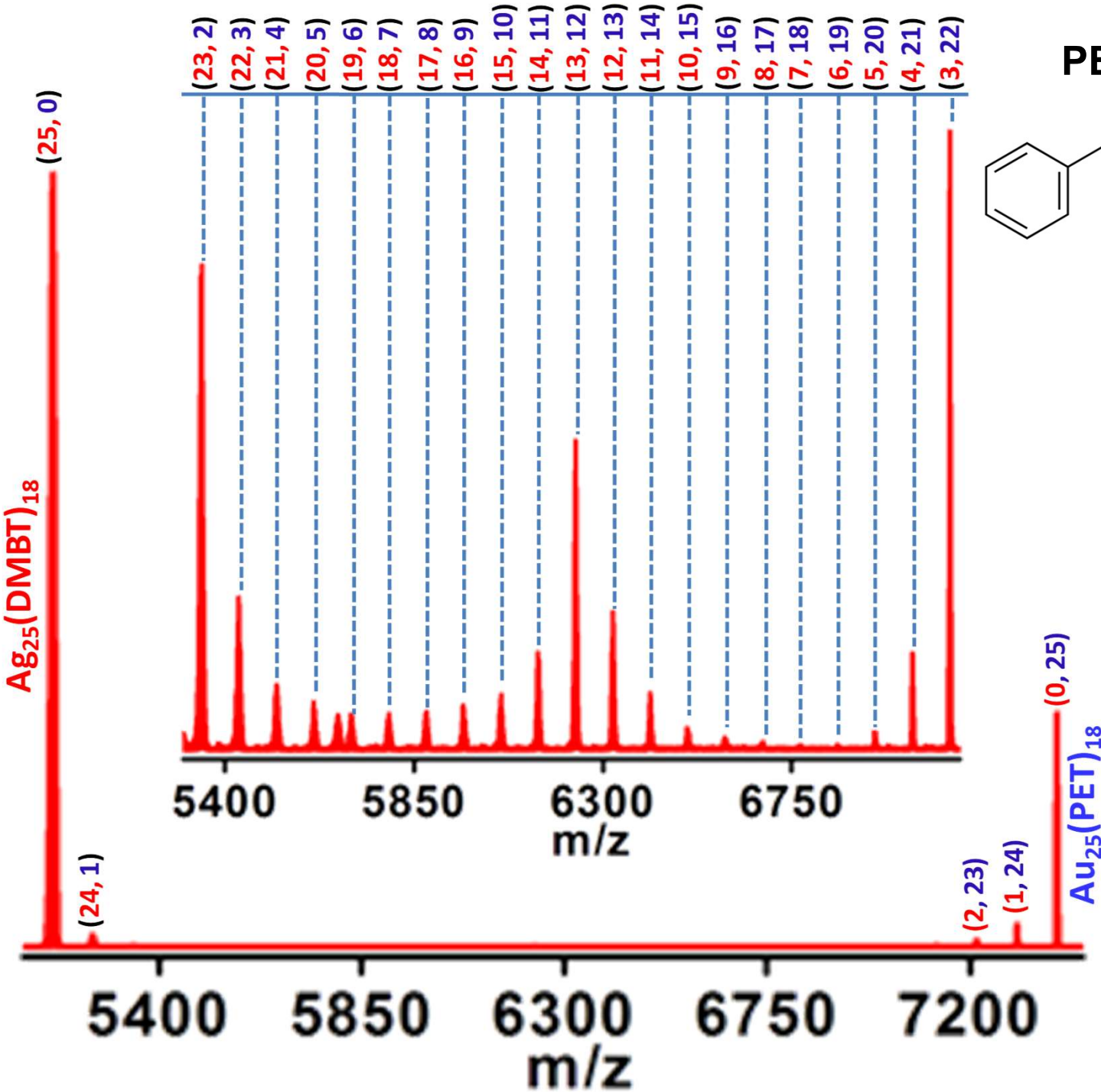
DMBT



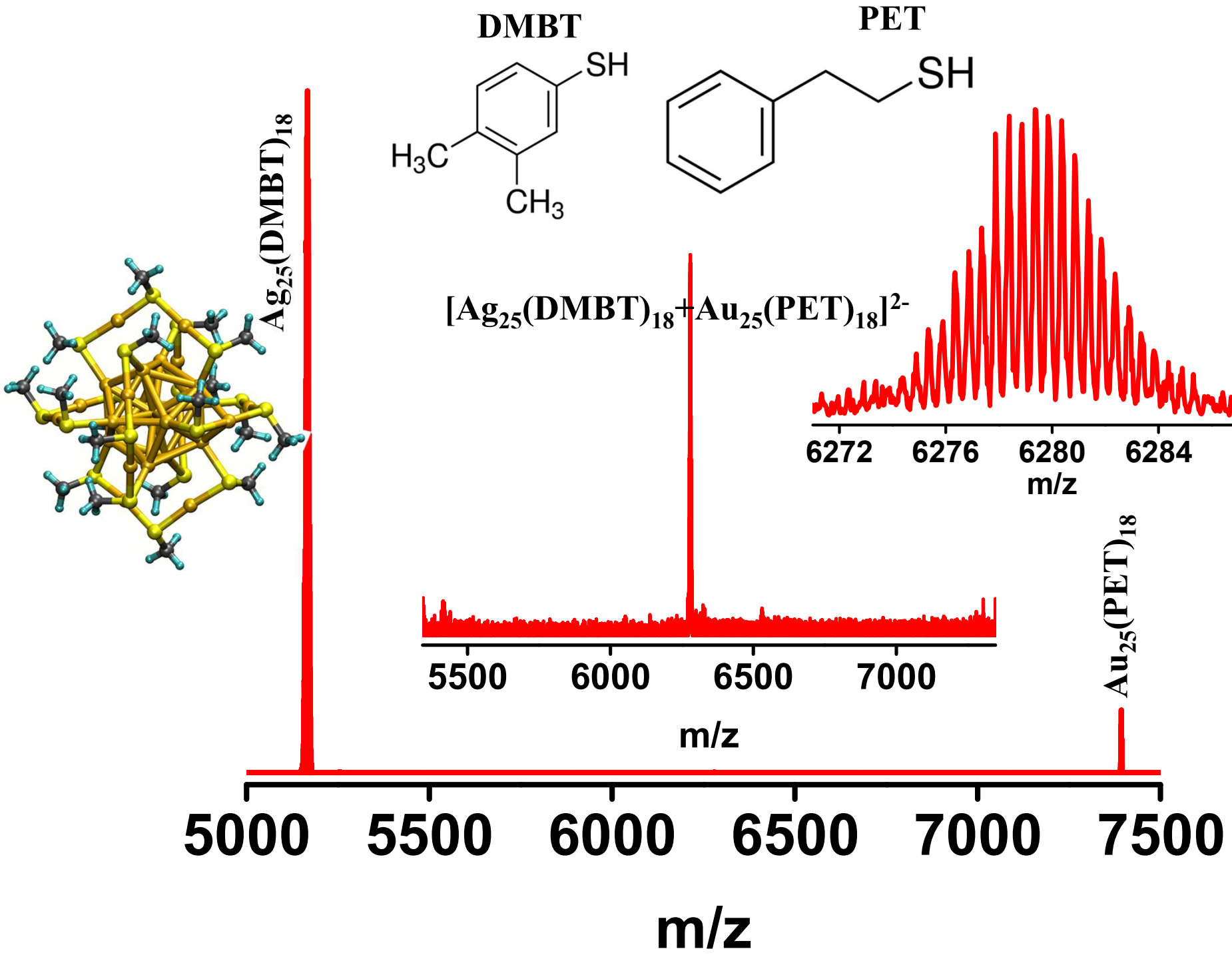


PET



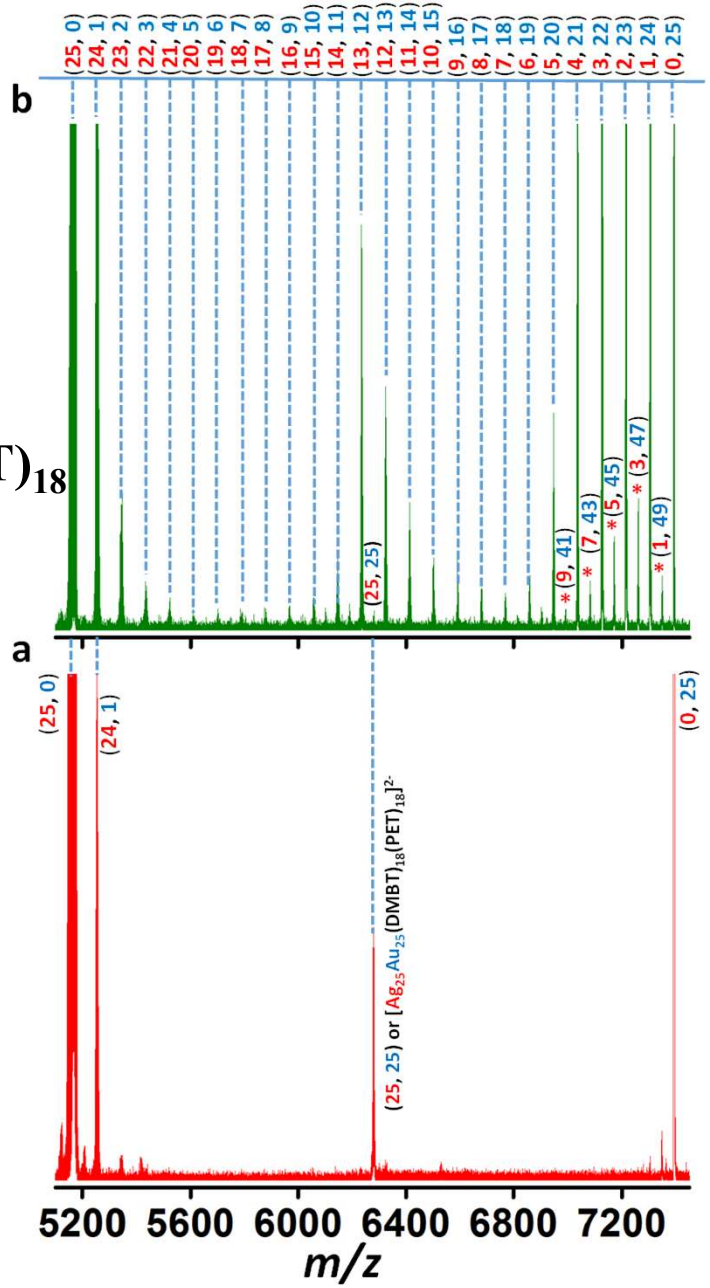


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

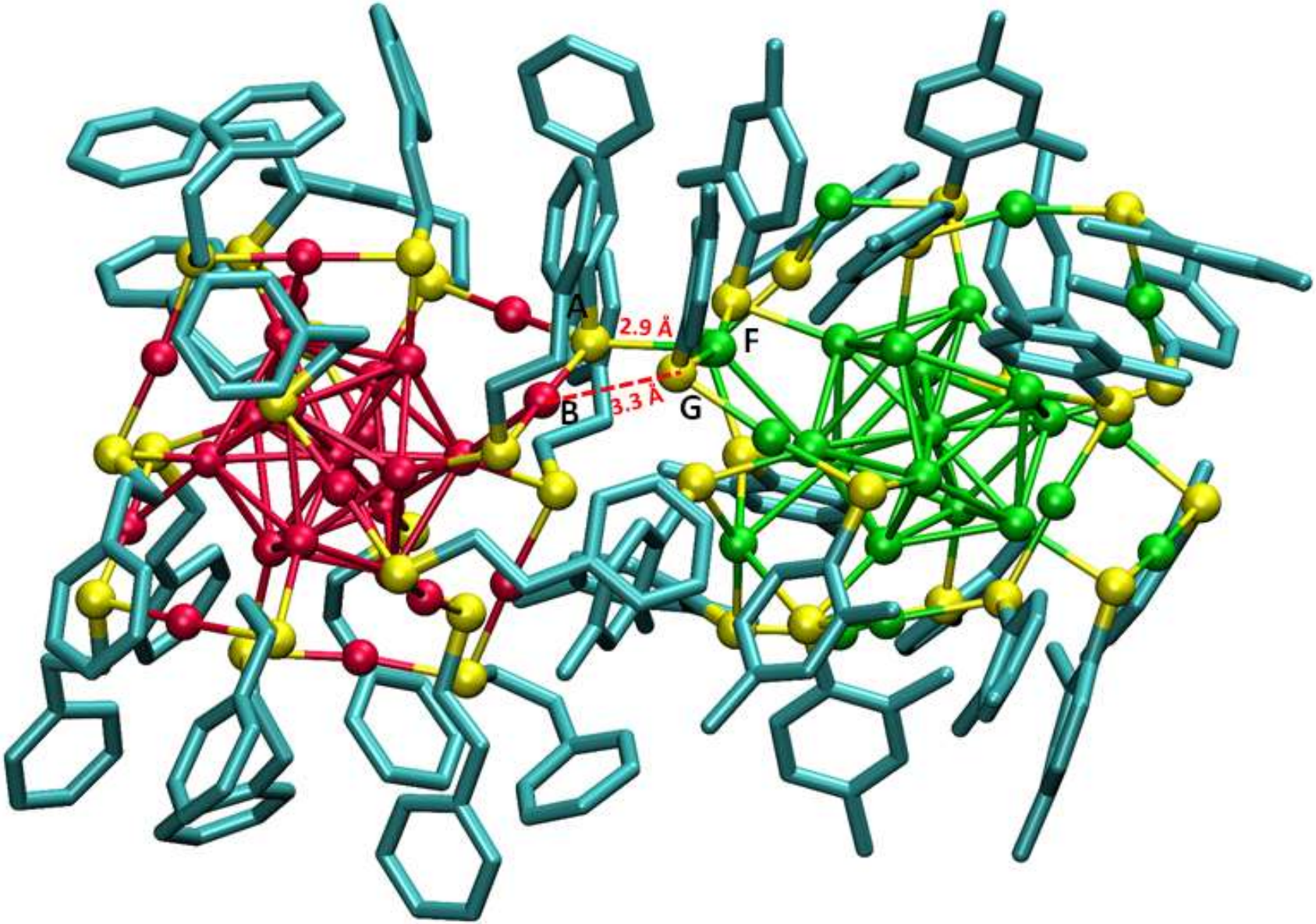
$Ag_{25}(DMBT)_{18}$:$Au_{25}(PET)_{18}$
0.3:1.0

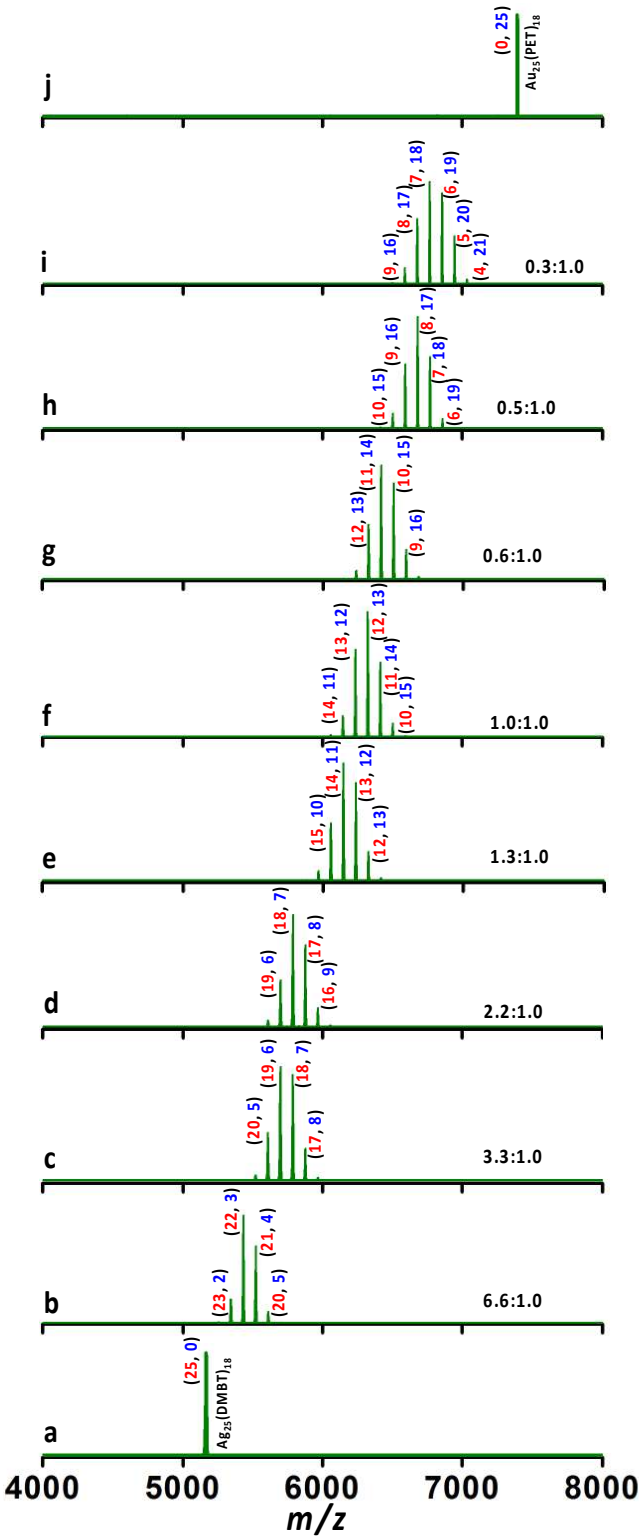


within 5 min

within 2 min

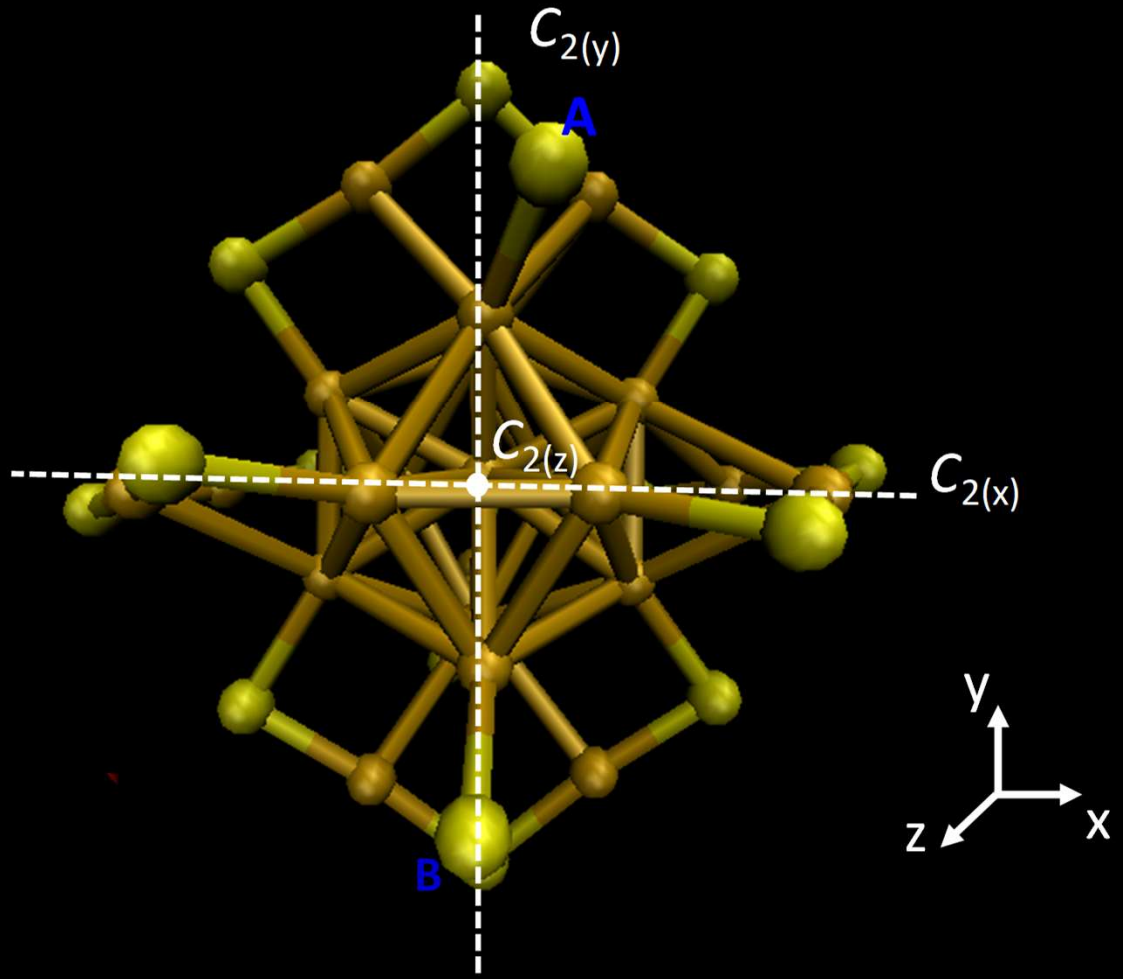
Optimized structure of $[Ag_{25}Au_{25}(DMBT)_{18}(PET)_{18}]^{2-}$



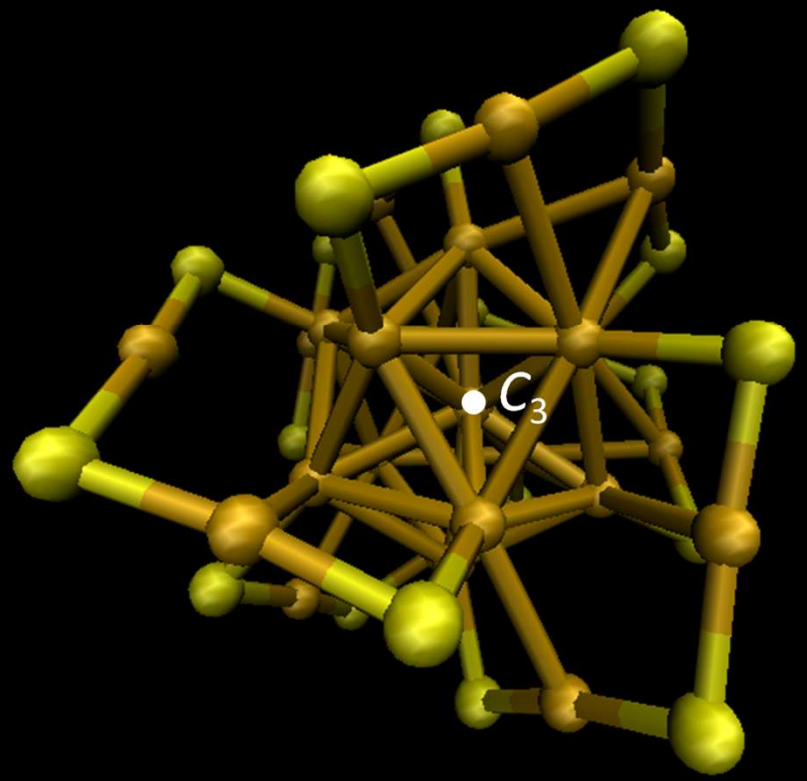

j
(0, 25)
Au25(PET)18
i
0.3:1.0
(9, 16)
(8, 17)
(7, 18)
(6, 19)
(5, 20)
(4, 21)
h
0.5:1.0
(10, 15)
(9, 16)
(8, 17)
(7, 18)
(6, 19)
g
0.6:1.0
(12, 13)
(11, 14)
(10, 15)
(9, 16)
f
1.0:1.0
(14, 11)
(13, 12)
(12, 13)
(11, 14)
(10, 15)
e
1.3:1.0
(15, 10)
(14, 11)
(13, 12)
(12, 13)
d
2.2:1.0
(19, 6)
(18, 7)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

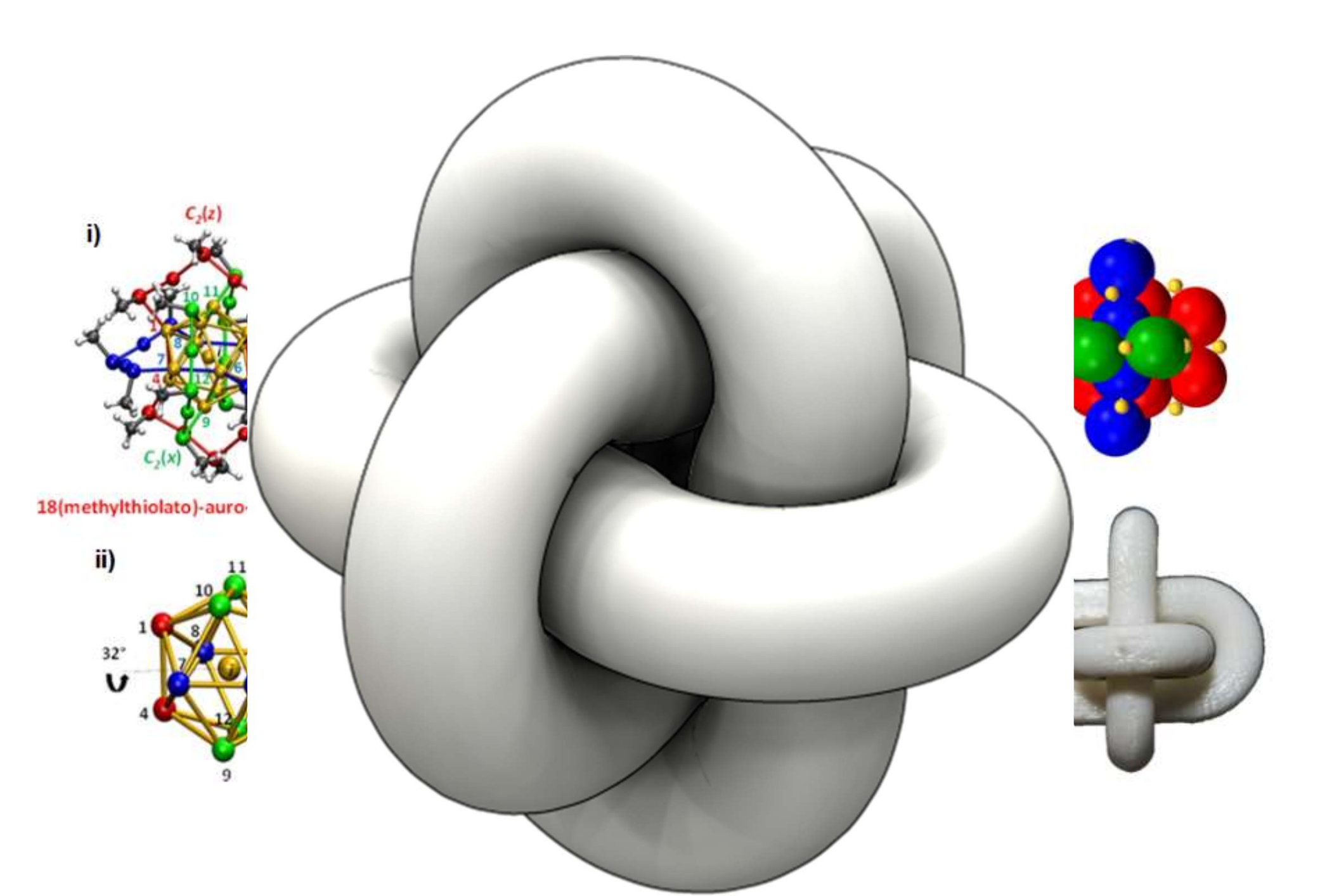
How do we comprehend this?

1) Edge projection



2) Face Projection





Gana Natarajan et. al. *JPC C* 2015

Aspicules

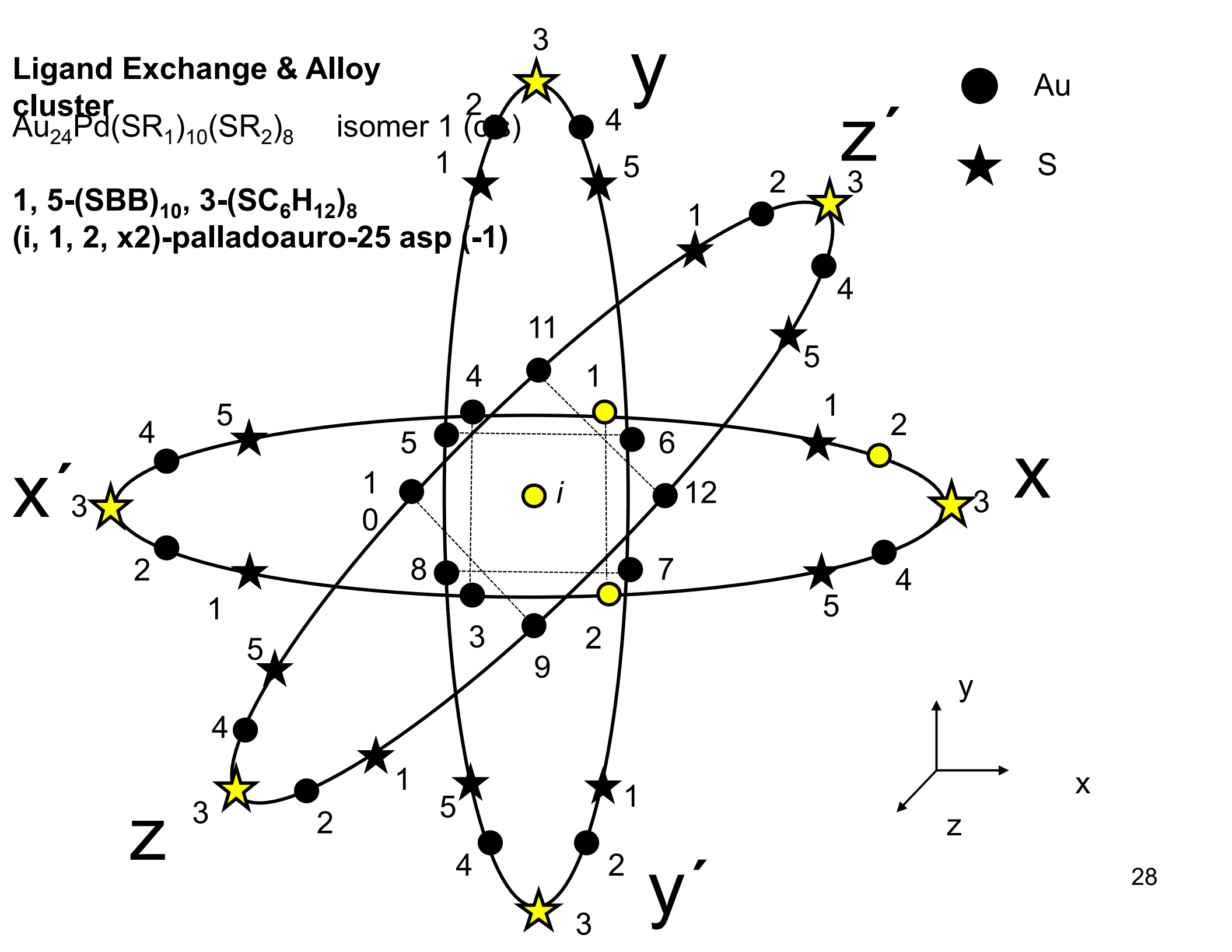
(D1-3,D2-3)-di(2-phenylethylthiolato),16(methylthiolato)-auro-25 aspicule(1-)
(D1-3,D2-3)-$(PET)_2$,$(SMe)_{16}$-auro-25 aspicule(1-)

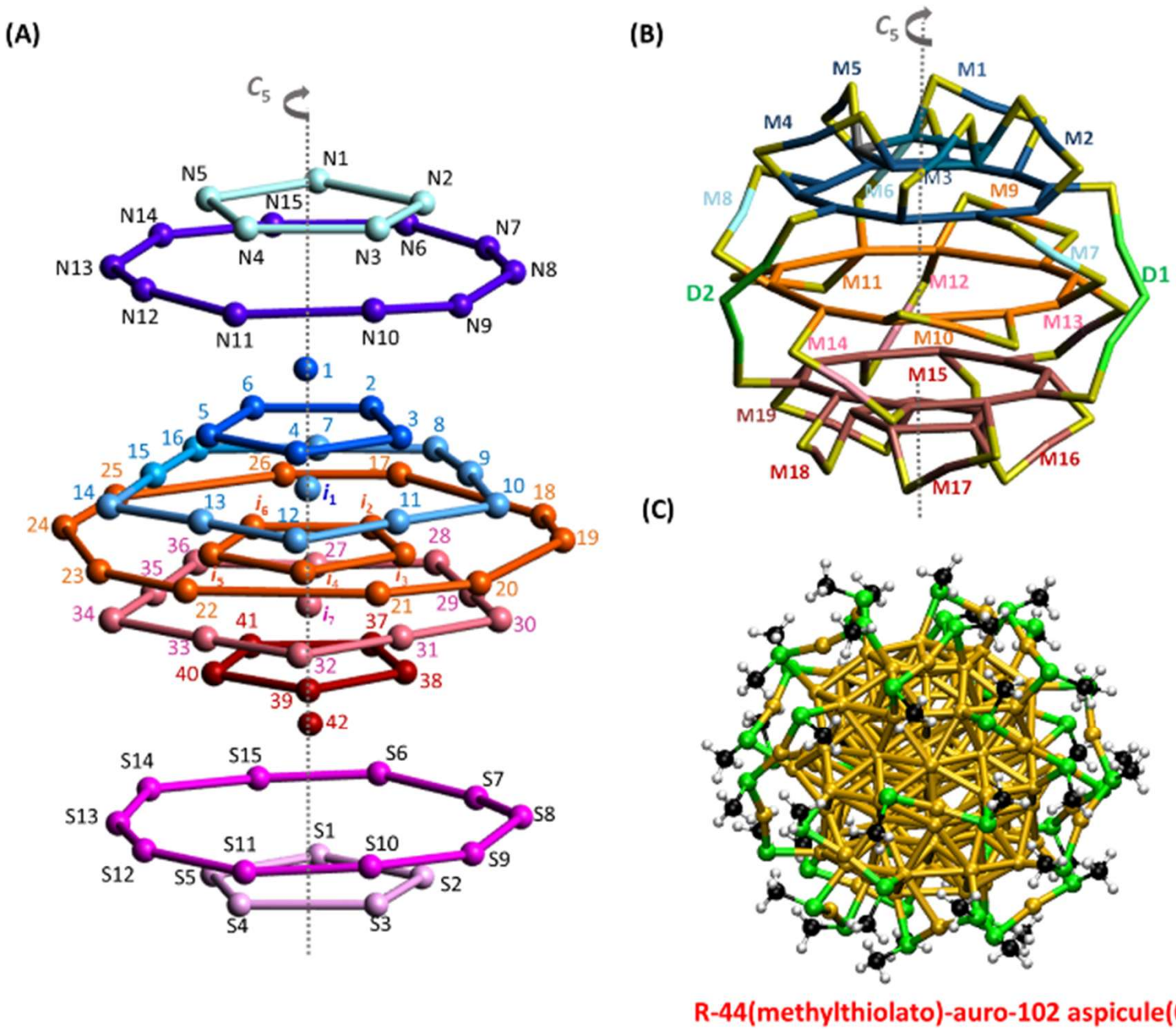
Ligand Exchange & Alloy cluster

$Au_{24}Pd(SR_1)_{10}(SR_2)_8$ 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)** [29]

ACCOUNTS of chemical research

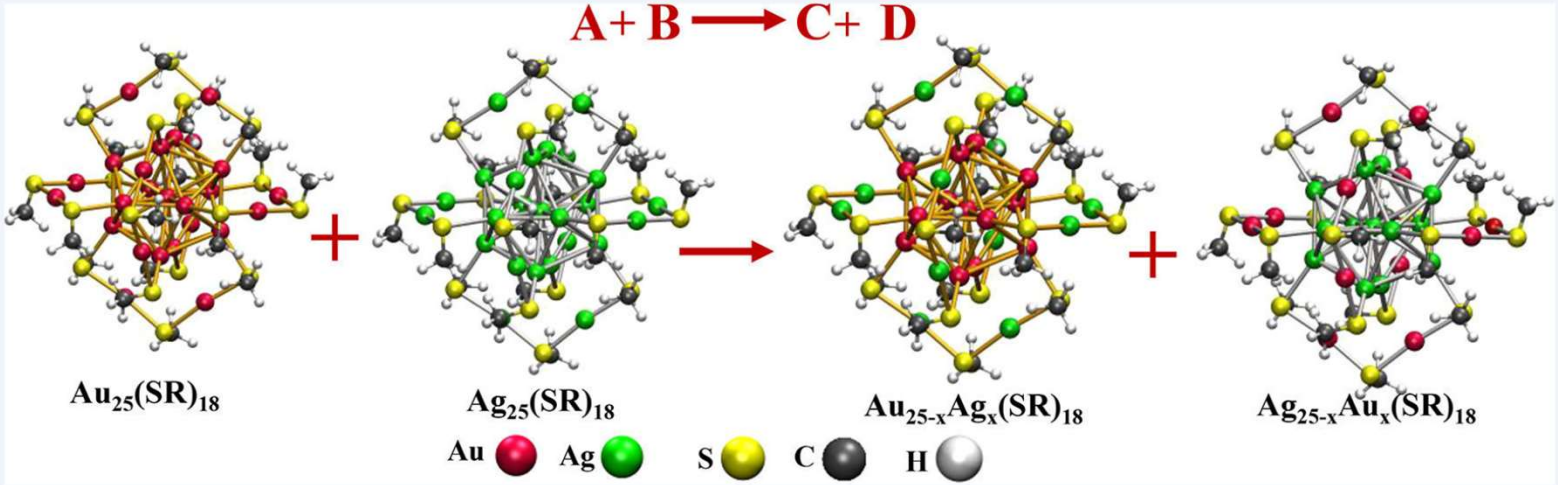
Article

pubs.acs.org/accounts

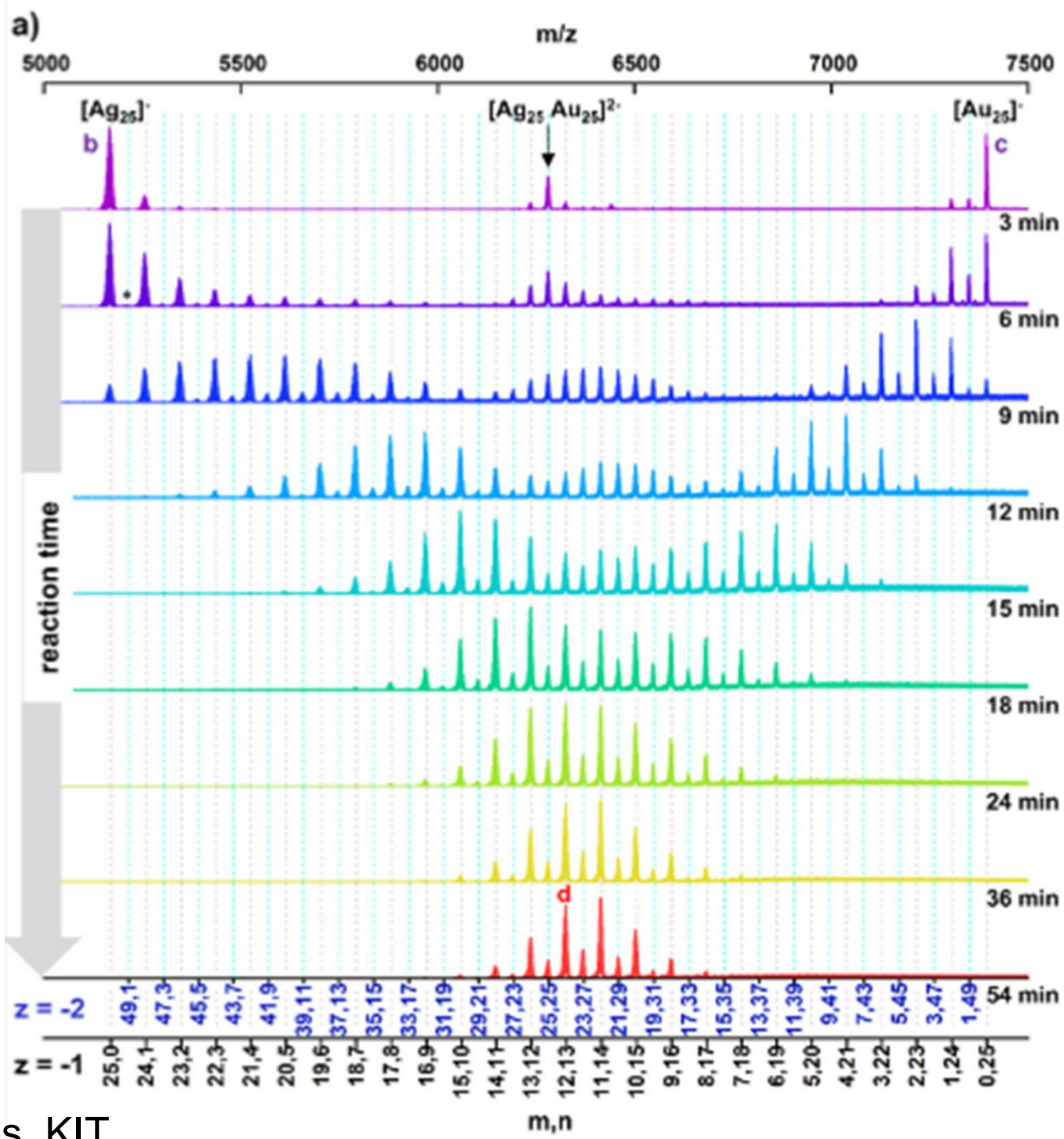
Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

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

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

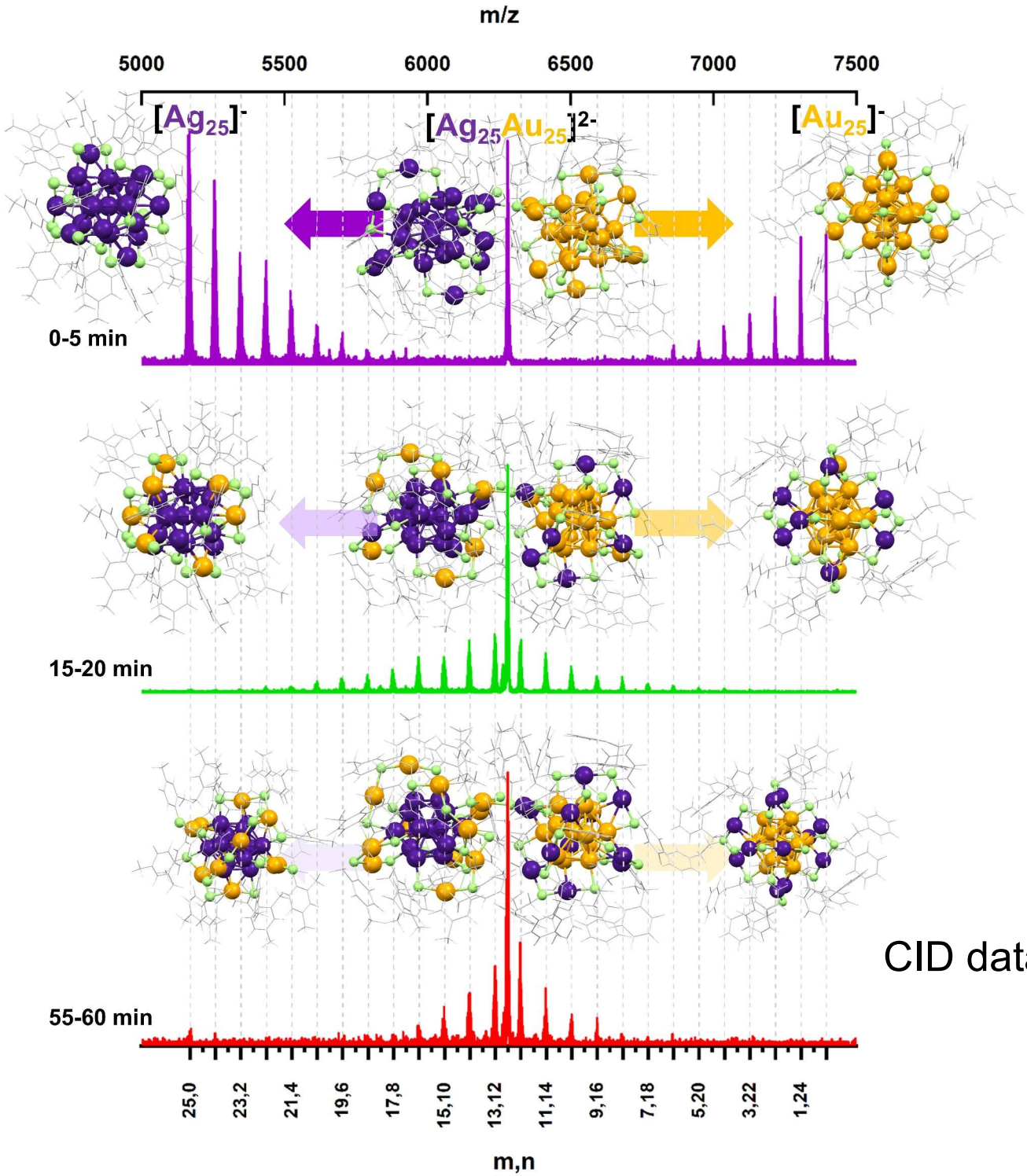


CONSPECTUS: Nanoparticles exhibit a rich variety in terms of structure, composition, and properties. However, reactions between them remain largely unexplored. In this *Account*, we discuss an emerging aspect of nanomaterials chemistry, namely, interparticle reactions in solution phase, similar to reactions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



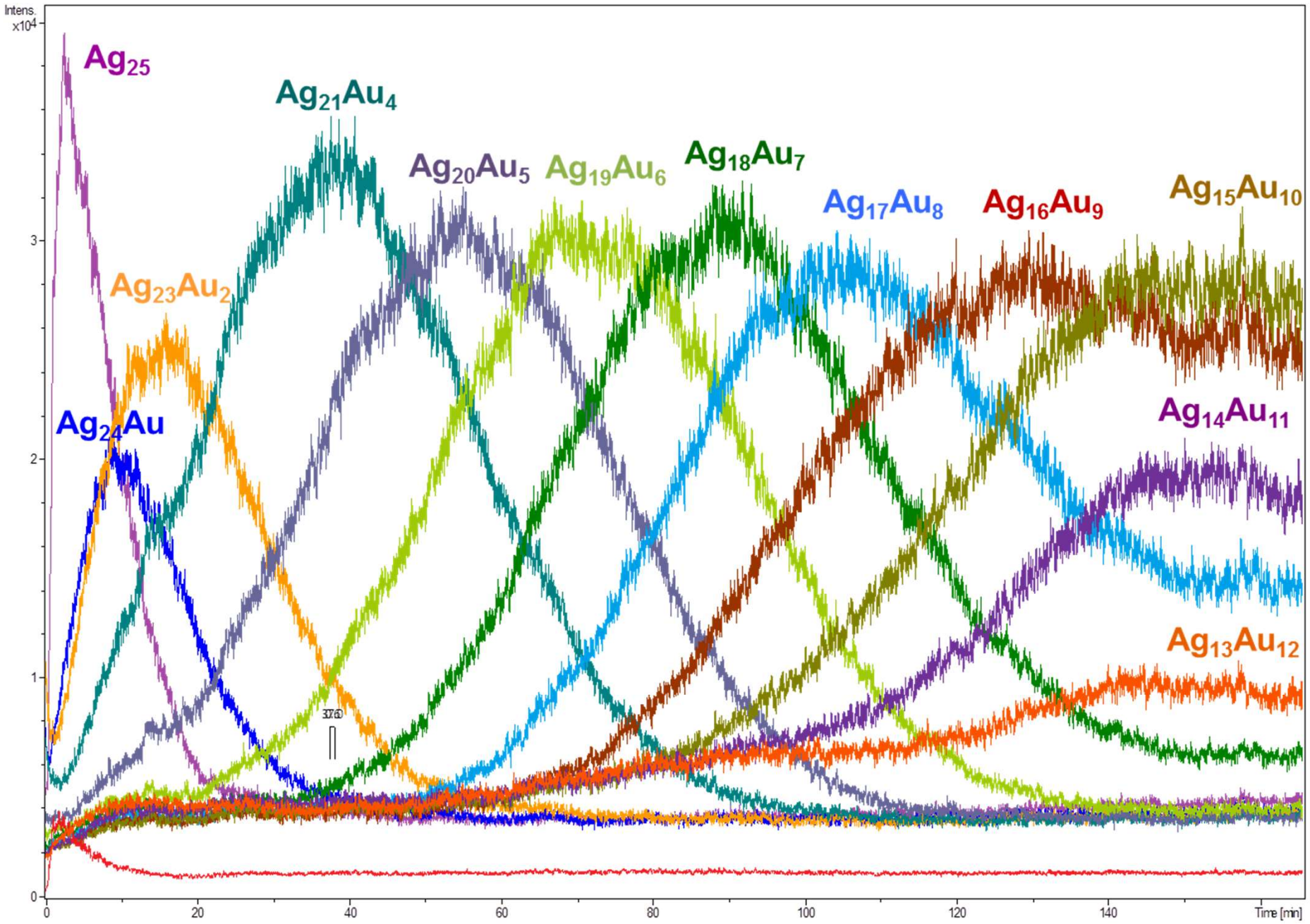
Manfred Kappes, KIT

M. Neumaier, A. Baksi, et. al., *JACS* 2021



CID data of $[Au25Ag25]^{2-}$

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



Expanding reactions

CHEMISTRY OF MATERIALS

Article

Cite This: *Chem. Mater.* 2020, 32, 611−619

pubs.acs.org/cm

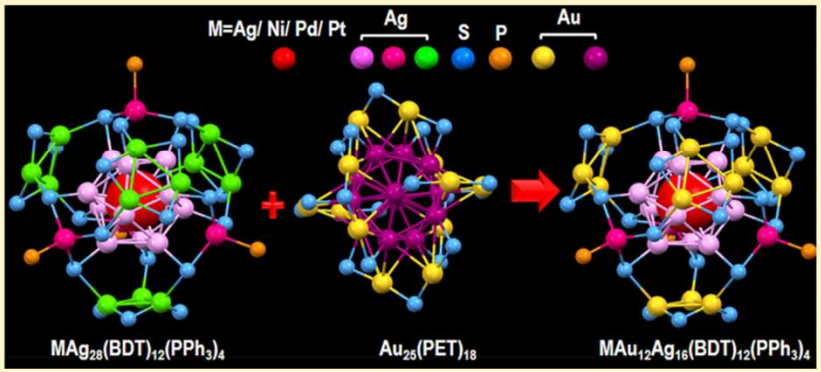
Intercluster Reactions Resulting in Silver-Rich Trimetallic Nanoclusters

Esma Khatun, Papri Chakraborty, Betsy Rachel Jacob, Ganesan Paramasivam, Mohammad Bodiuzzaman, Wakeel Ahmed Dar, and Thalappil Pradeep*

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

Supporting Information

ABSTRACT: Herein, we present an intercluster reaction leading to new trimetallic nanoclusters (NCs) using bimetallic and monometallic NCs as reactants. Dithiol protected bimetallic $MAg_{28}(BDT)_{12}(PPh_3)_4$ (BDT = 1,3-benzenedithiol and M = Ni, Pd, or Pt) and monothiol protected $Au_{25}(PET)_{18}$ (PET = 2-phenylethanethiol) were used as model NCs. A mixture of trimetallic $MAu_xAg_{28-x}(BDT)_{12}(PPh_3)_4$ (x = 1−12) and bimetallic $Ag_xAu_{25-x}(PET)_{18}$ (x = 1−7) NCs were formed during the reaction as understood from time-dependent electrospray ionization mass spectrometry (ESI MS). Detailed studies of intercluster reaction between $Ag_{29}(BDT)_{12}(PPh_3)_4$ and $Au_{25}(PET)_{18}$ were also performed. Although both $MAg_{28}(BDT)_{12}(PPh_3)_4$ (M = Ag, Ni, Pd, or Pt) and $Au_{25}(PET)_{18}$ contain 13 atoms icosahedral core, only a maximum of 12 Au doped NCs were formed for the former as a major product and not the 13 Au doped one, unlike the previous reports of intercluster reaction. The transfer of Ni, Pd, or Pt atom from the center of icosahedron of $MAg_{28}(BDT)_{12}(PPh_3)_4$ to $Au_{25}(PET)_{18}$ was not observed, which suggests that the central atom is not involved in the reaction. Density functional theory (DFT) calculations were performed to know structures



Interparticle Reactions Forming Product Co-Crystals

ACS NANO

Cite This: *ACS Nano* 2019, 13, 13365−13373

www.acsnano.org

ARTICLE

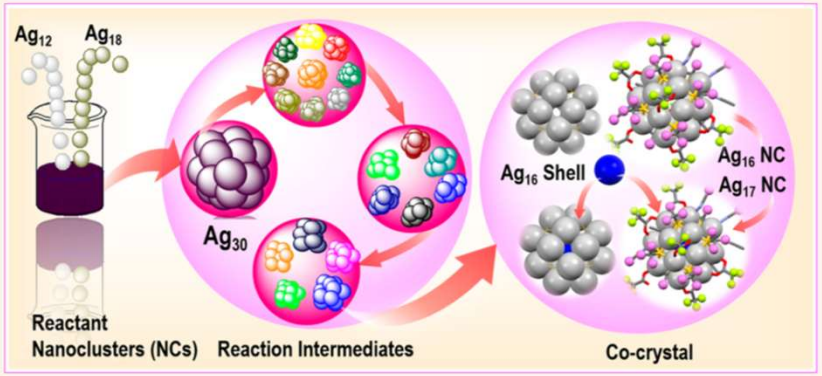
Interparticle Reactions between Silver Nanoclusters Leading to Product Cocrystals by Selective Cocrystallization

Wakeel Ahmed Dar,[†] Mohammad Bodiuzzaman,[†] Debasmita Ghosh, Ganesan Paramasivam, Esma Khatun, Korath Shivan Sugi, and Thalappil Pradeep*

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

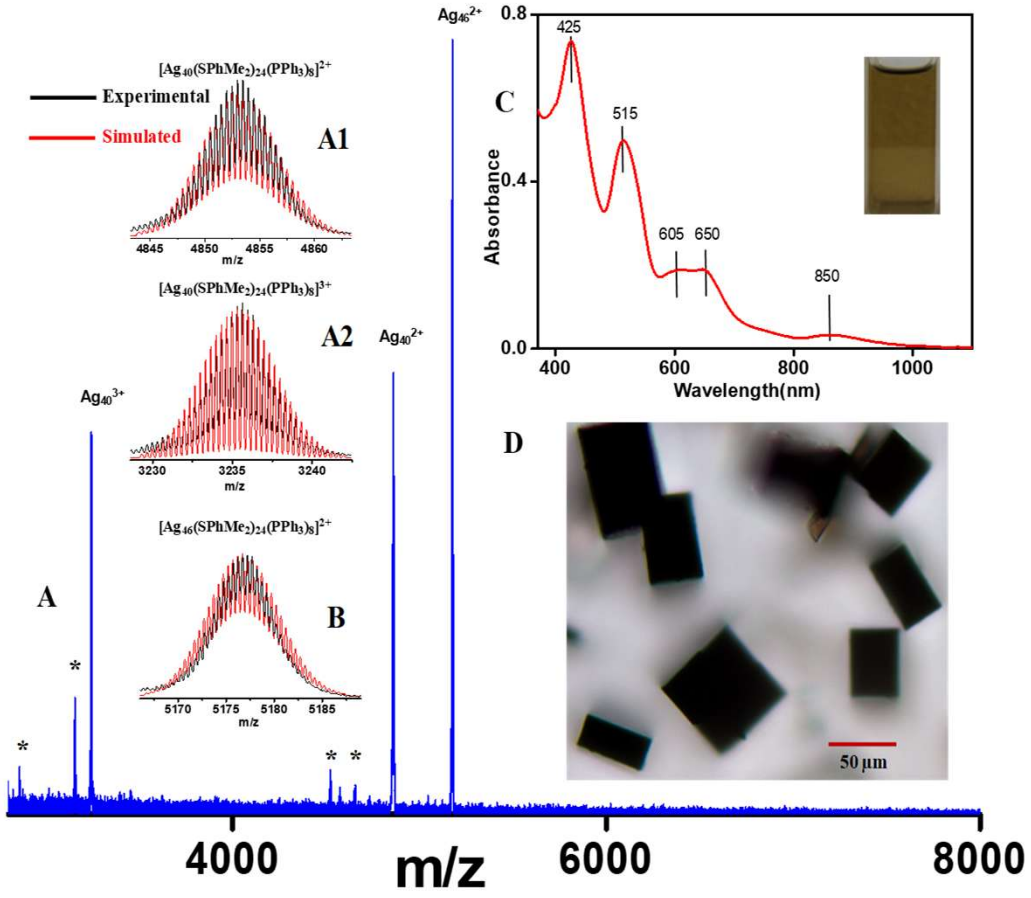
Supporting Information

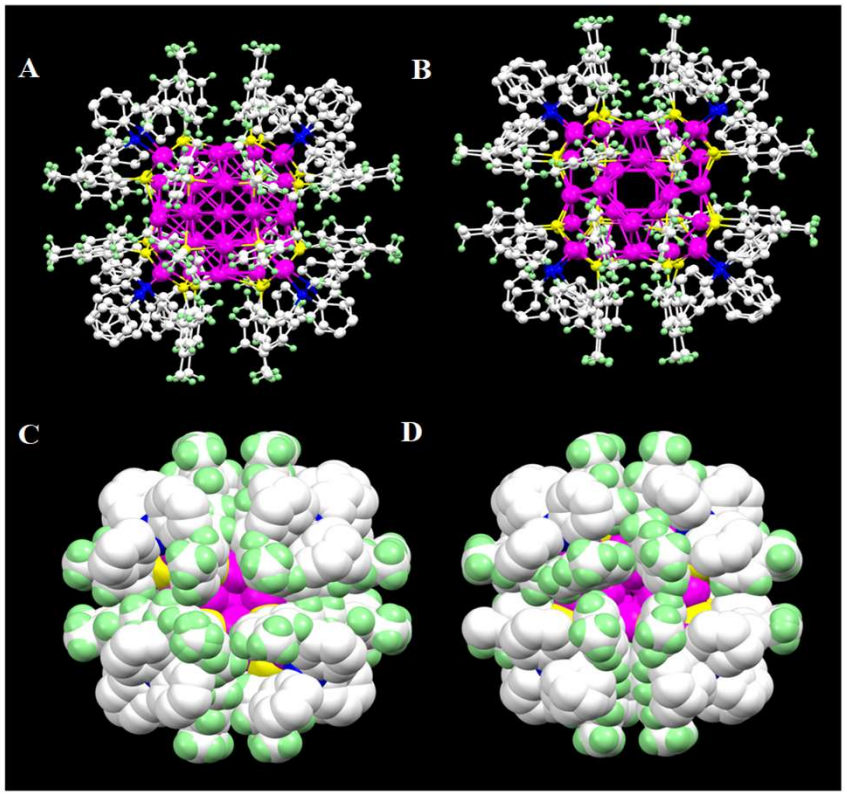
ABSTRACT: We present an example of an interparticle reaction between atomically precise nanoclusters (NCs) of the *same* metal, resulting in entirely different clusters. In detail, the clusters $[Ag_{12}(TBT)_8(TFA)_5(CH_3CN)]^+$ (TBT = *tert*-butylthiolate, TFA = trifluoroacetate, CH_3CN = acetonitrile) and $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ (TPP = triphenylphosphine) abbreviated as Ag_{12} and Ag_{18}, respectively, react leading to $[Ag_{16}(TBT)_8(TFA)_7(CH_3CN)_3Cl]^+$ and $[Ag_{17}(TBT)_8(TFA)_7(CH_3CN)_3Cl]^+$, abbreviated as Ag_{16} and Ag_{17}, respectively. The two product NCs crystallize together as both possess the same metal chalcogenolate



Co-crystals

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





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

Atom transfer dynamics

They are indeed molecules!

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.

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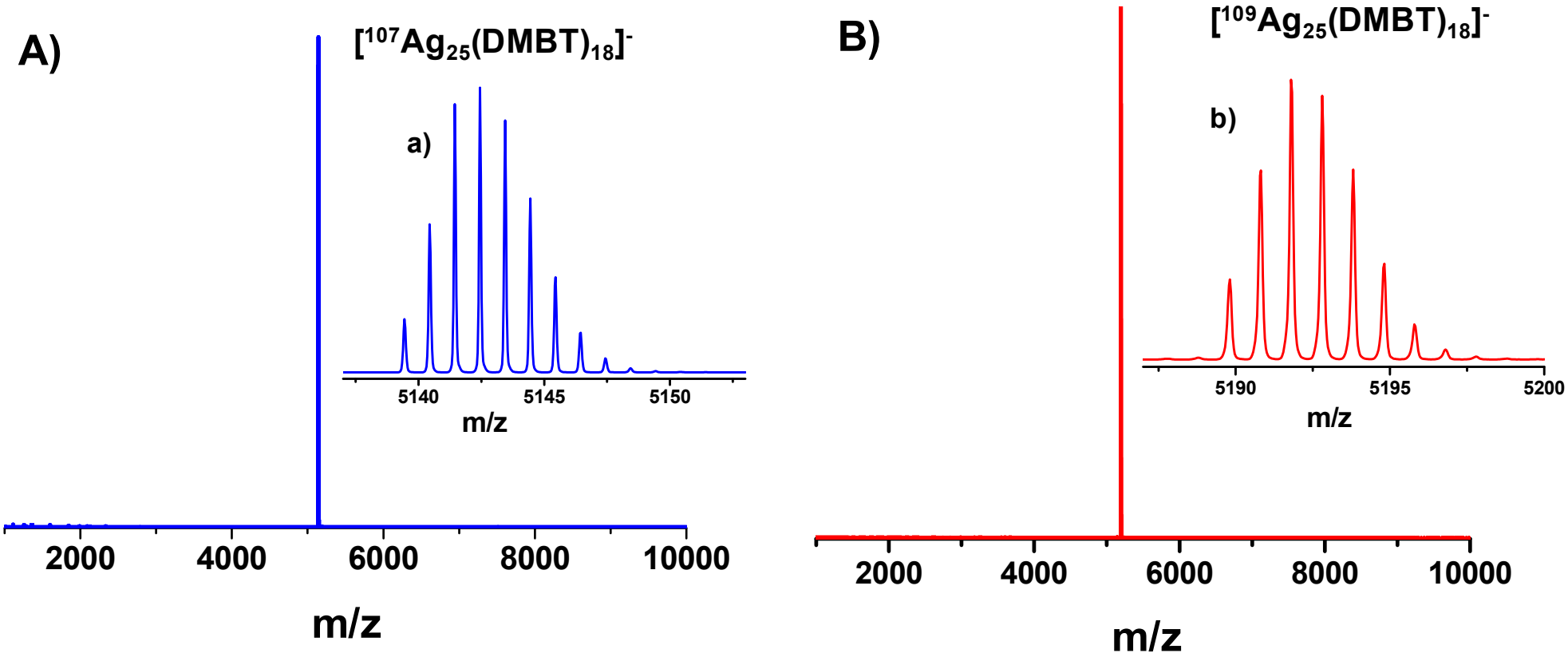
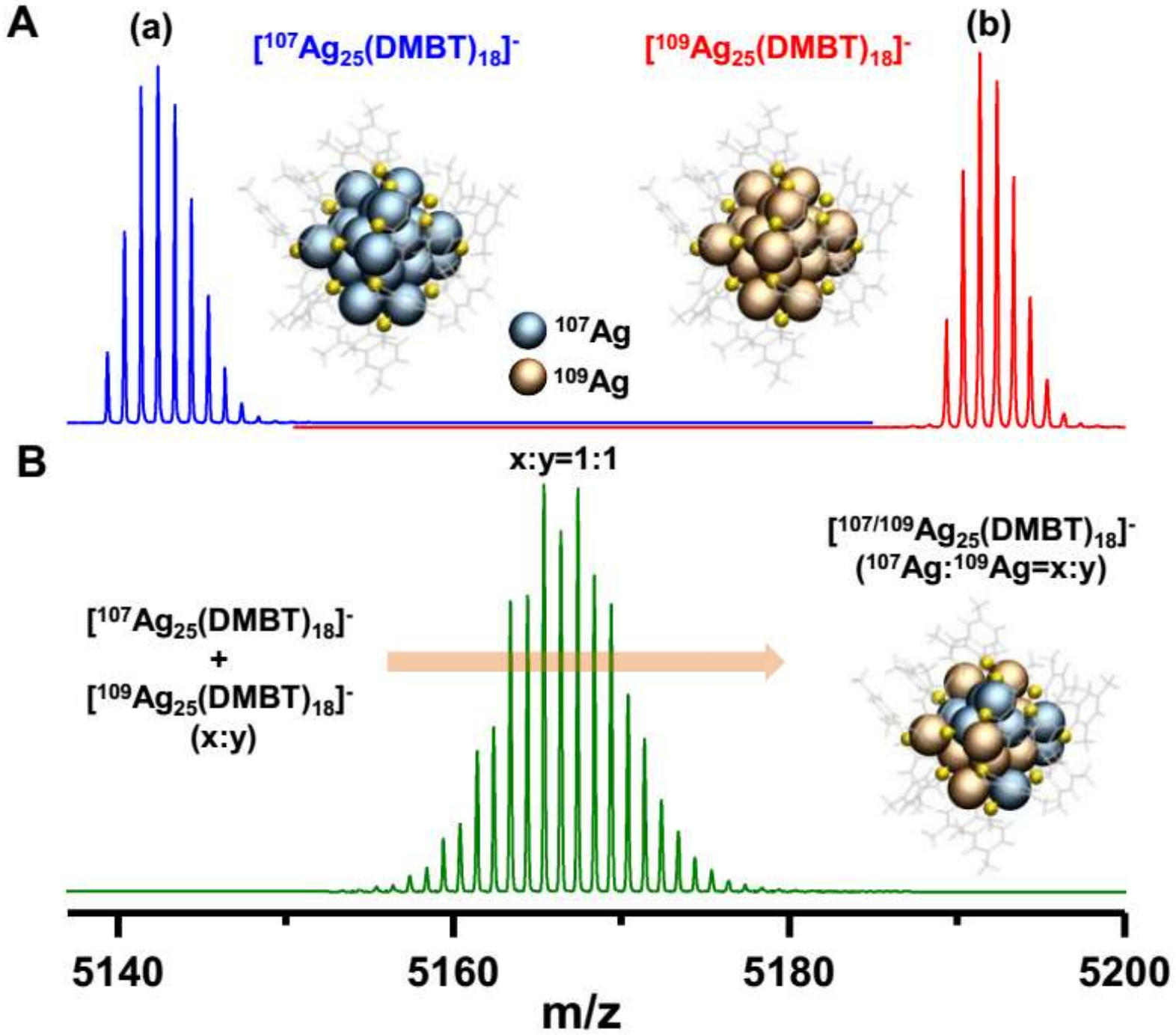
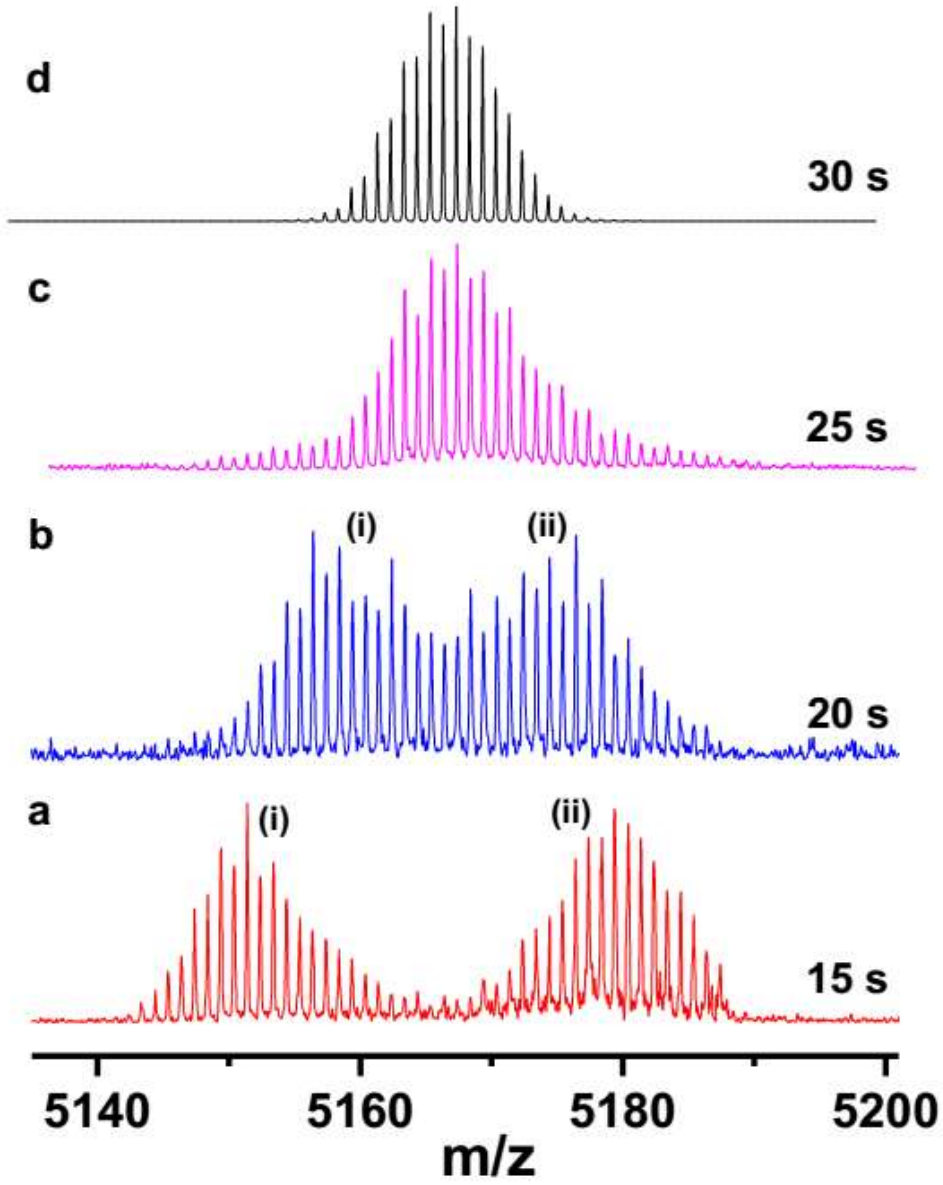
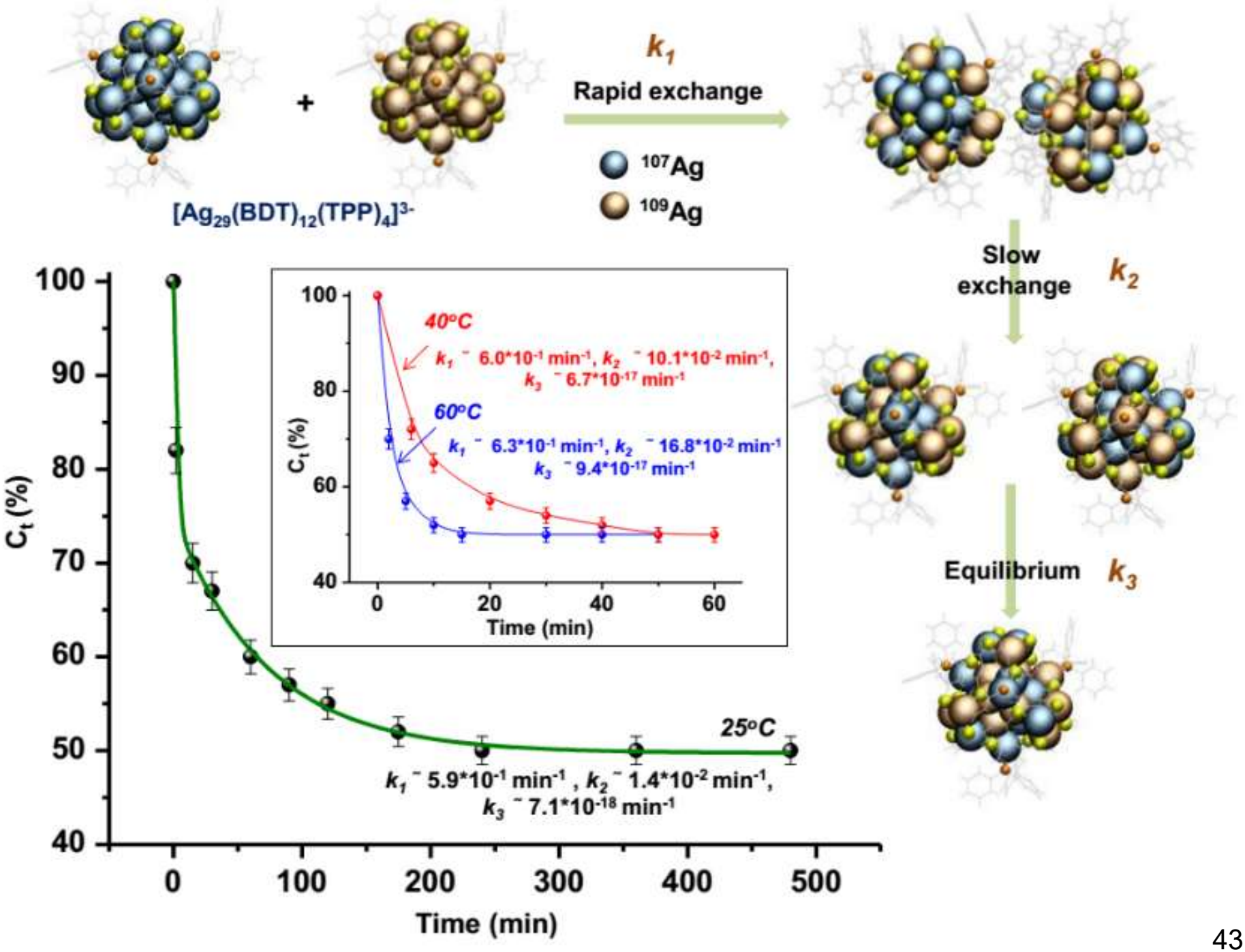


ESI MS of **A)** $^{107}Ag_{25}(DMBT)_{18}$ and **B)** $^{109}Ag_{25}(DMBT)_{18}$. Insets shows the respective isotope patterns.

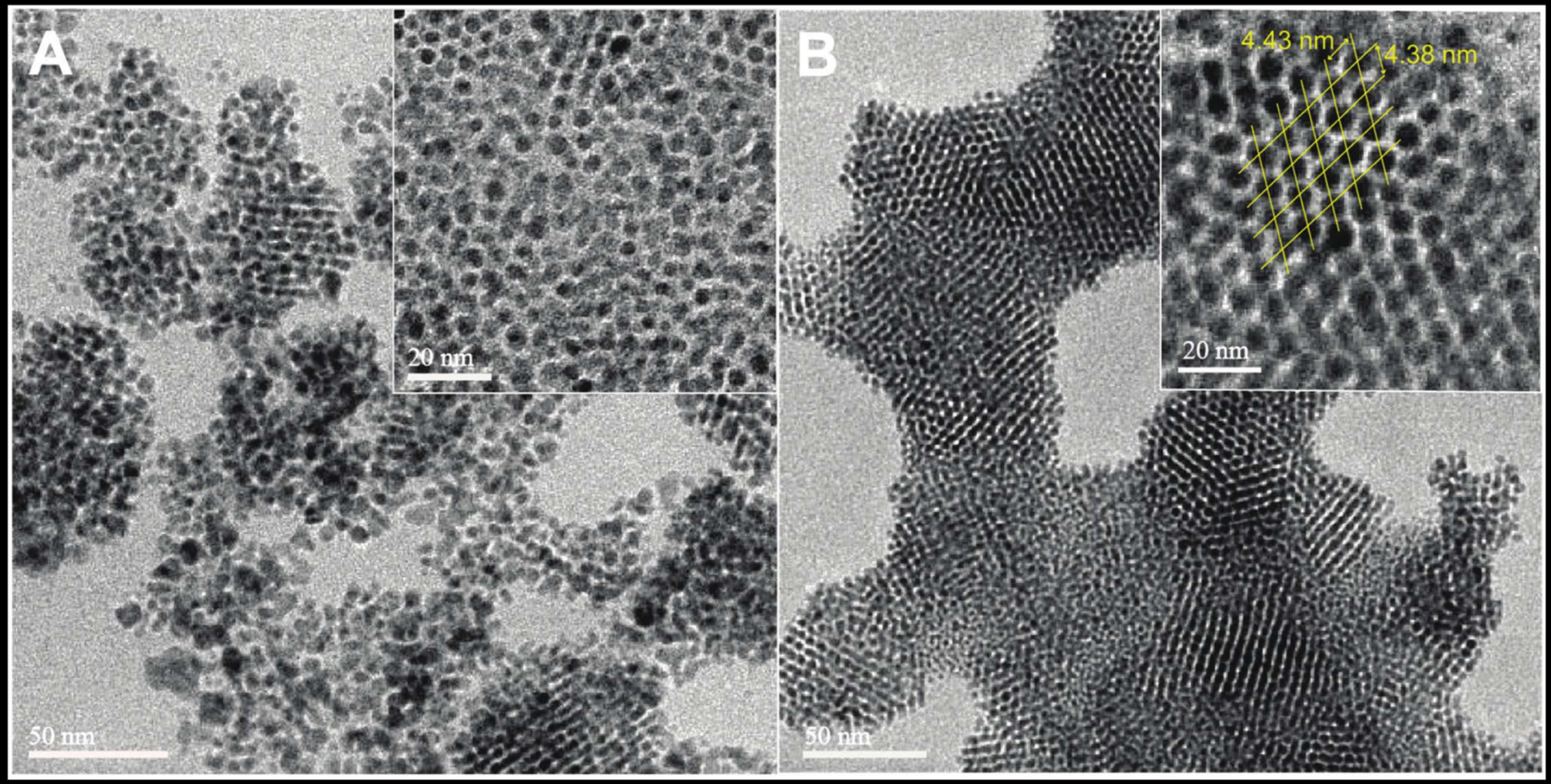

A
(a)
[107Ag25(DMBT)18]-
[109Ag25(DMBT)18]-
(b)
107Ag
109Ag
B
x:y=1:1
[107/109Ag25(DMBT)18]-
(107Ag:109Ag=x:y)
[107Ag25(DMBT)18]-
+
[109Ag25(DMBT)18]-
(x:y)
5140
5160
5180
5200
m/z



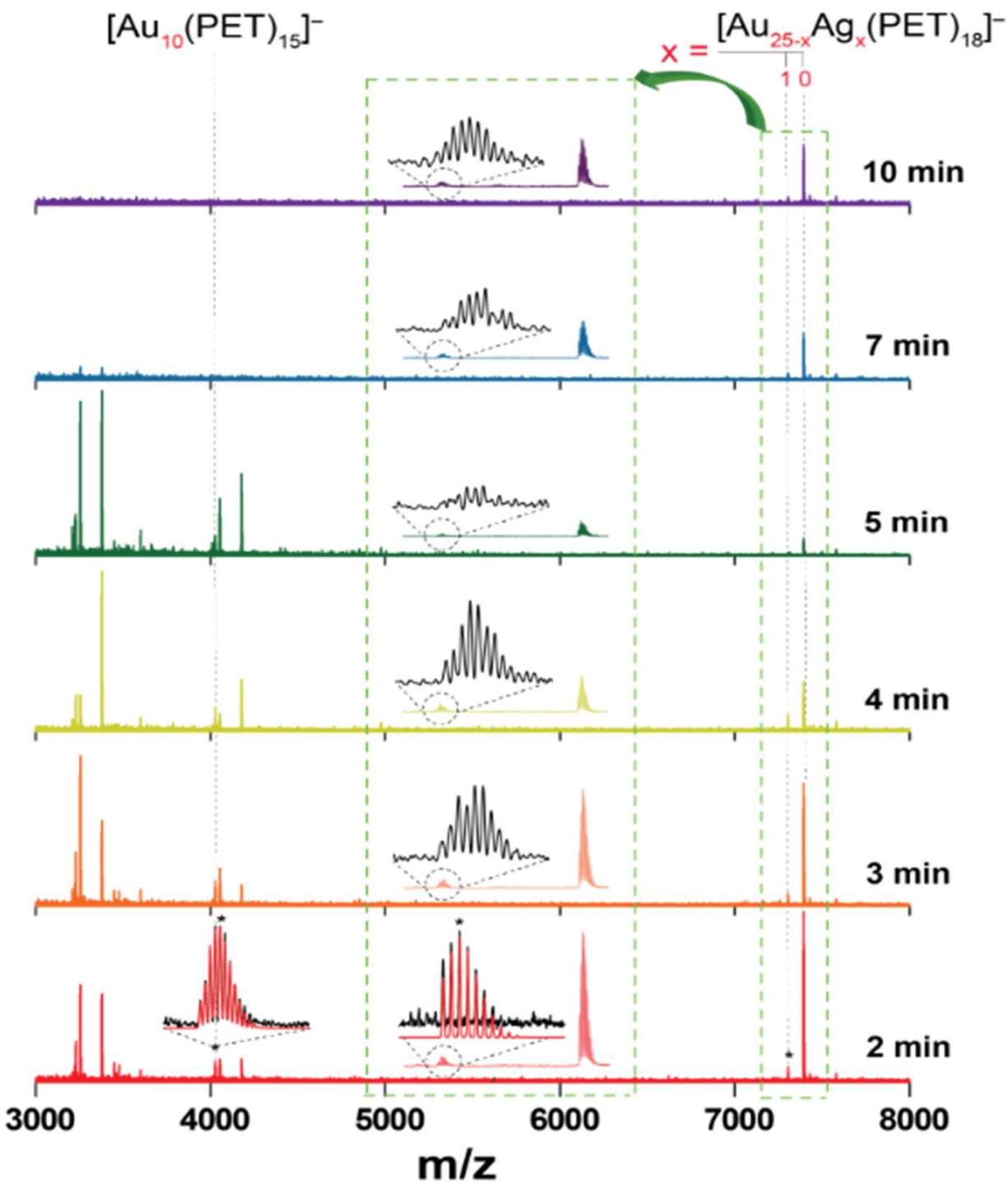
Papri Chakraborty, et. al. *Science Advances* 2019

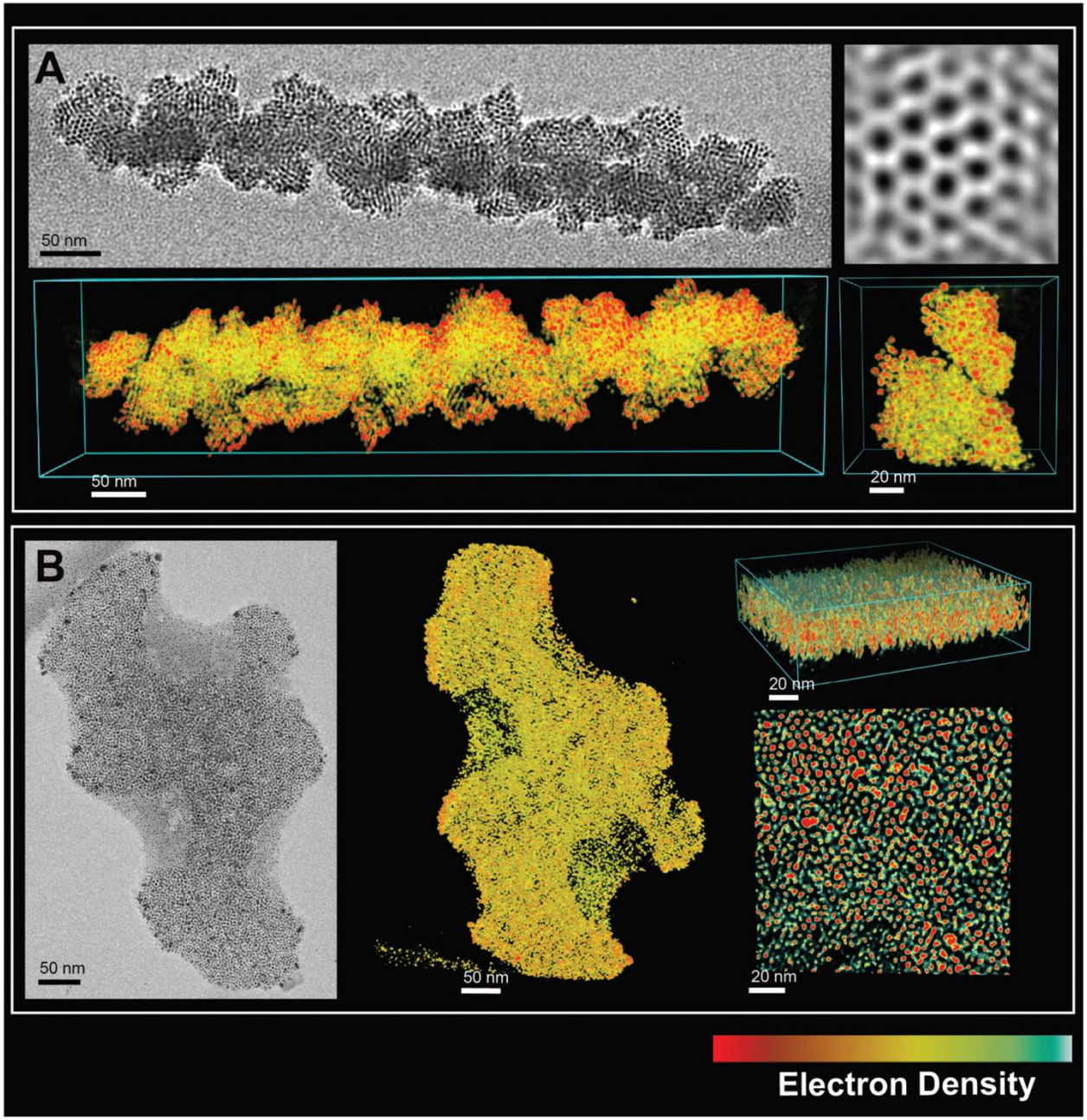

k_1
Rapid exchange
^{107}Ag
^{109}Ag
$[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$
Slow exchange
k_2
Equilibrium
k_3
C_t (%)
Time (min)
25°C
k_1 ~ 5.9*10^{-1} min^{-1} , k_2 ~ 1.4*10^{-2} min^{-1},
k_3 ~ 7.1*10^{-18} min^{-1}
40°C
k_1 ~ 6.0*10^{-1} min^{-1}, k_2 ~ 10.1*10^{-2} min^{-1},
k_3 ~ 6.7*10^{-17} min^{-1}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

Can clusters react with nanoparticles?

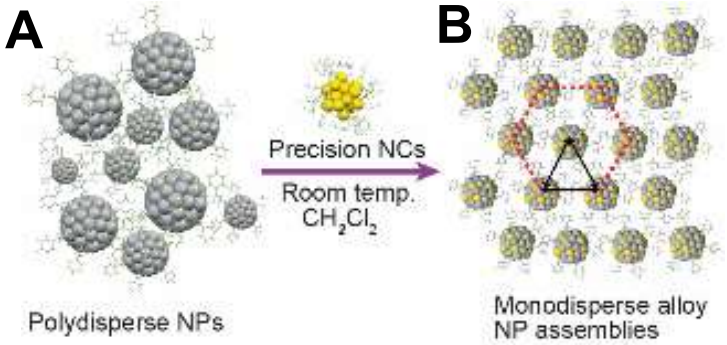


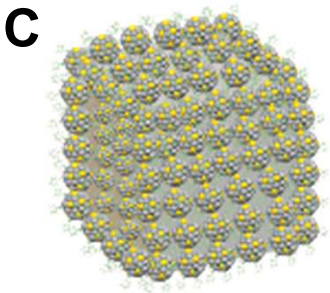
Paulami Bose et al. *Nanoscale* 2020


[Au10(PET)15]−
[Au25-xAgx(PET)18]−
x = 10
10 min
7 min
5 min
4 min
3 min
2 min
3000
4000
5000
6000
7000
8000
m/z

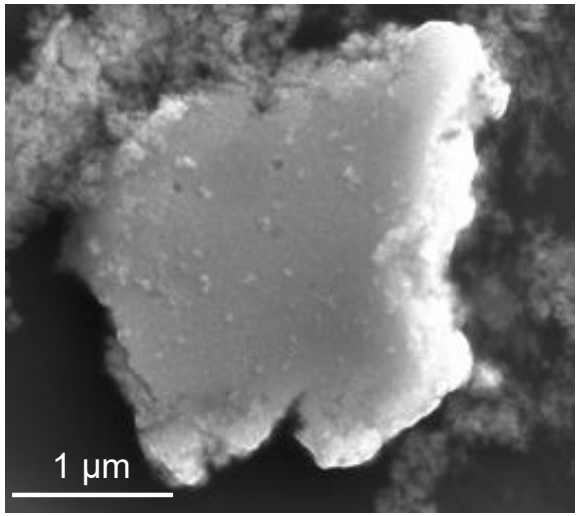

A
50 nm
50 nm
20 nm
B
50 nm
50 nm
20 nm
20 nm
Electron Density

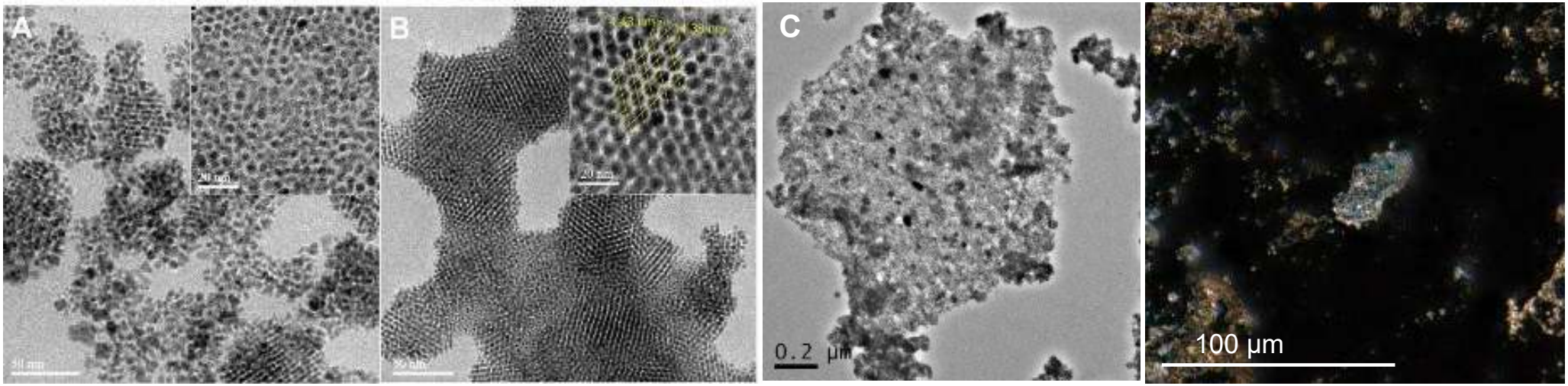
Interparticle reactions routed crystallization of nanoparticles





Colloidal crystal





Paulami Bose et al. Unpublished

Outlook

2019

ACCOUNTS of chemical research

Article

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Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

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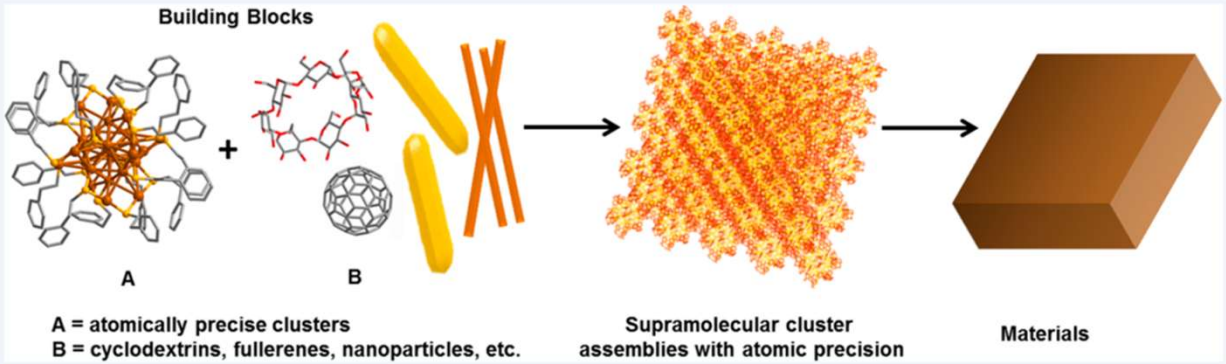

Molecules and their properties

Chemical formula	H_2O
Molecular weight	18.0148
Critical temperature	373.91°C
Critical pressure	22.05 MPa
Critical density	315.0 kg/m^3
Triple point temperature	0.01°C
Triple point pressure	615.066 Pa
Normal boiling point	100.0°C
Normal freezing point	0.0°C
Density of ice at normal melting point	918.0 kg/m^3
Maximum density, 3.98°C	999.973 kg/m^3
Viscosity, 25°C	0.889 mN s/m^2
Surface tension, 25°C	72 mN/m
Heat Capacity, 25°C	4.1796 kJ/kg.K
Enthalpy of vaporisation, 100°C	2,257.7 kJ/kg
Enthalpy of fusion, 0°C	333.8 kJ/kg
Velocity of sound, 0°C	1.403 km/s
Dielectric constant, 25°C	78.40
Electrical conductivity, 25°C	8 μS/m
Refractive index, 25°C	1.333
Liquid compressibility, 10°C	480. × 10^{-12}m^2/N
Coefficient of thermal expansion, 25°C	256.32 × 10^{-6} K^{-1}
Thermal Conductivity, 25°C	0.608 W/m.K

Molecular formula
Molecular weight
Molecular structure
Molecular absorption and emission
Molecular reactions
Molecular assembly
Molecular co-crystals

Phases - phase transitions
Physical properties
Electrical, magnetic
Mechanical properties
Electrochemical properties

Future?

Department of Science and Technology

Collaborators: Tatsuya Tsukuda, Keisaku Kimura, Yuichi Negishi, Uzi Landman, Rob Whetten, Hannu Hakkinen, Robin Ras, Manfred Kappes, Horst Hahn, Tomas Base, Shiv Khanna, Umesh Waghmare, Chandrabhas Narayana, Giridhar U. Kulkarni, Reji Philip, Vivek Polshettiwar, R. Mukhopadhay

Thank you all