Carboranethiols

Versatile Ligand Platform for Atomically Precise Clusters

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FAROOK COLLEGE AUTONOMOUS

Co-founder

InnoNano Research Pvt. Ltd.
InnoDI Water Technologies Pvt. Ltd.
VayuJAL Technologies Pvt. Ltd.
Aqueasy Innovations Pvt. Ltd.
Hydromaterials Pvt. Ltd.
EyeNetAqua Pvt. Ltd.
Deepspectrum Analytics Pvt. Ltd.

Professor-in-charge

ICCW
International Centre for Clean Water

RESEARCH GROUP

THEMATIC UNIT OF EXCELLENCE

We supply arsenic-free water to 1.3 million people every day.

Our technologies provide clean water to 13 million people.

Advanced materials for clean water

PNAS PNAS

Biopolymer-reinforced synthetic granular nanocomposites for affordable point-of-use water purification

Mohan Udhaya Sankar[1], Sahaja Aigal[1], Shihabudheen M. Maliyekkal[1], Amrita Chaudhary, Anshup, Avula Anil Kumar, Kamalesh Chaudhari, and Thalappil Pradeep[2]

Unit of Nanoscience and Thematic Unit of Excell

dras, Chennai 600 036, India

Edited by Eric Hoek, University of California, Los

ceived for review November 21, 2012)

Creation of affordable materials for constan water is one of the most promising ways to drinking water for all. Combining the ca composites to scavenge toxic species suc other contaminants along with the above affordable, all-inclusive drinking water pu without electricity. The critical problem i synthesis of stable materials that can rel uously in the presence of complex spe drinking water that deposit and cause s surfaces. Here we show that such consta be synthesized in a simple and effective fas out the use of electrical power. The nano sand-like properties, such as higher shear st forms. These materials have been used to water purifier to deliver clean drinking wat ily. The ability to prepare nanostructure ambient temperature has wide relevanc water purification.

lable; and (*c*) continued retention
ıtrix is difficult.
a unique family of nanocrystalline
granular composite materials pre-
re through an aqueous route. The
osition is attributed to abundant -O-
chitosan, which help in the crys-
de and also ensure strong covalent
rface to the matrix. X-ray photo-
nfirms that the composition is rich
Using hyperspectral imaging, the
ing in the water was confirmed.
reactivate the silver nanoparticle
antimicrobial activity in drinking
tes have been developed that can
in water. We demonstrate an af-
rice based on such composites de-
undergoing field trials in India, as
ead eradication of the waterborne

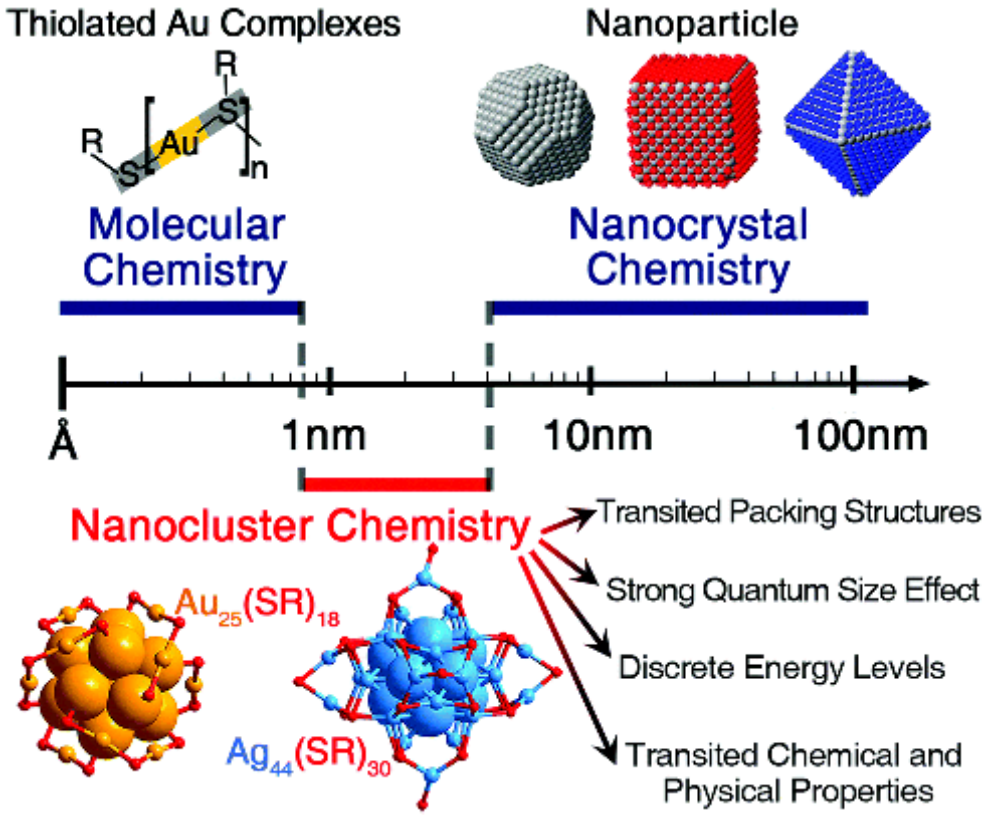
hybrid | green | appropriate technology | frugal science | developing world

disease burden.

Results and Discussion

M. Udhaya Sankar, et. al. *Proc. Natl. Acad. Sci.,* 110 (2013) 8459-8464.

Clusters



Jin, R. *et al., Chem. Soc. Rev.* **2020**, *49*, 6443-6514.

CHEMICAL REVIEWS
Review
pubs.acs.org/CR

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

Indranath Chakraborty[†] and Thalappil Pradeep[*]

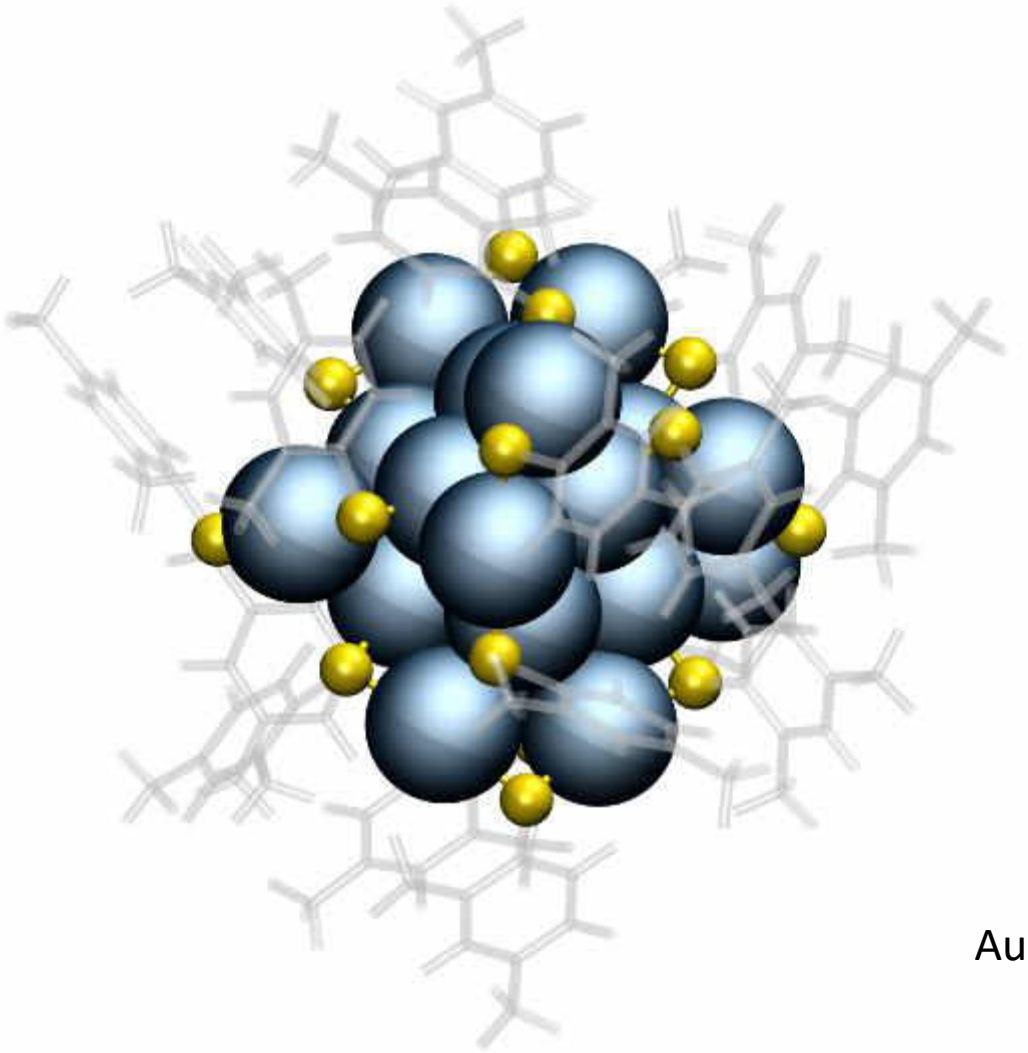
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Supporting Information

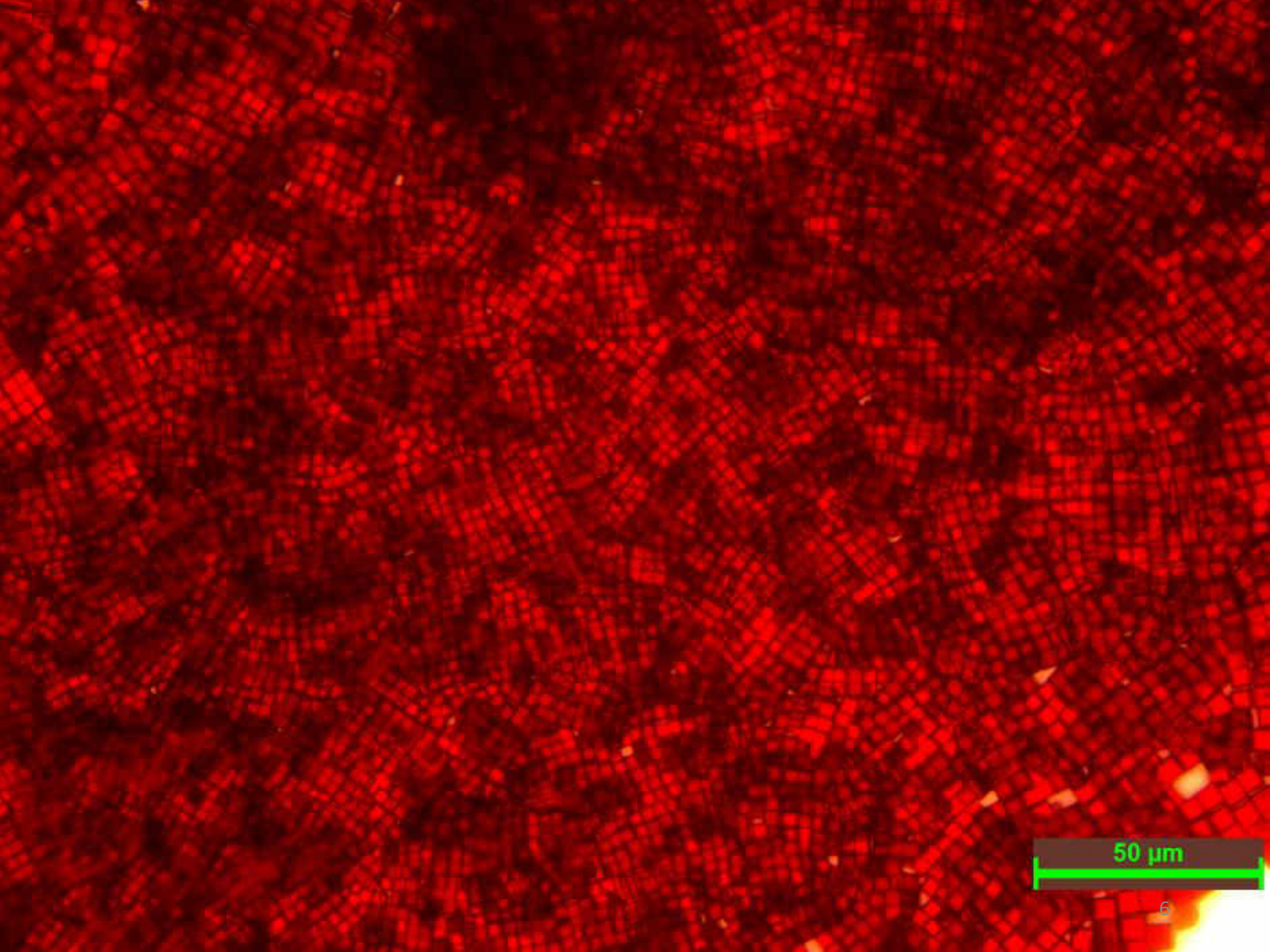
ABSTRACT: Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{102}(SR)_{44}$ as well as $Ag_{25}(SR)_{18}$,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

I. Chakraborty and T. Pradeep, *Chem. Rev.*, 2017, 117, 8208-8271.

New molecules



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


50 µm

Molecular materials

ACCOUNTS of chemical research

Article

Cite This: *Acc. Chem. Res.* 2019, 52, 2–11

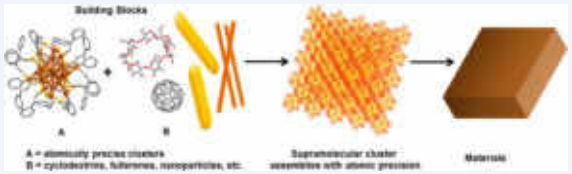
pubs.acs.org/accounts

Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

Published as part of the Accounts of Chemical Research special issue "Toward Atomic Precision in Nanoscience".

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

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



ACCOUNTS of chemical research

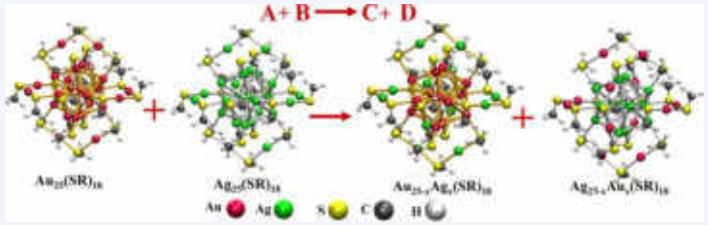
Article

pubs.acs.org/accounts

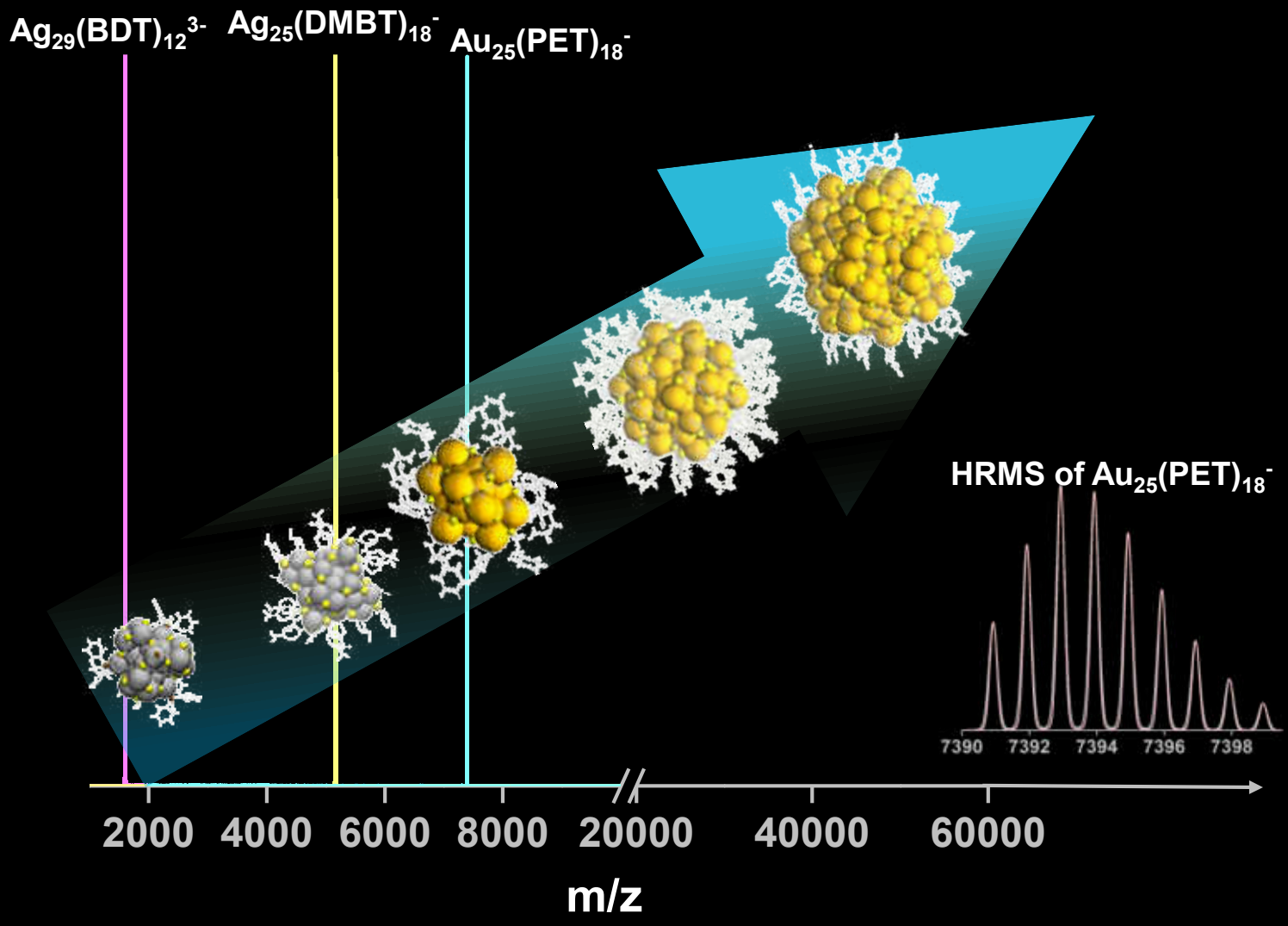
Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

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



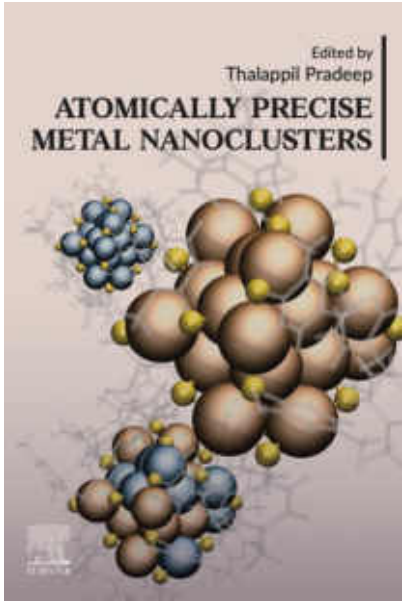
Acc. Chem. Res., 2017, 2019

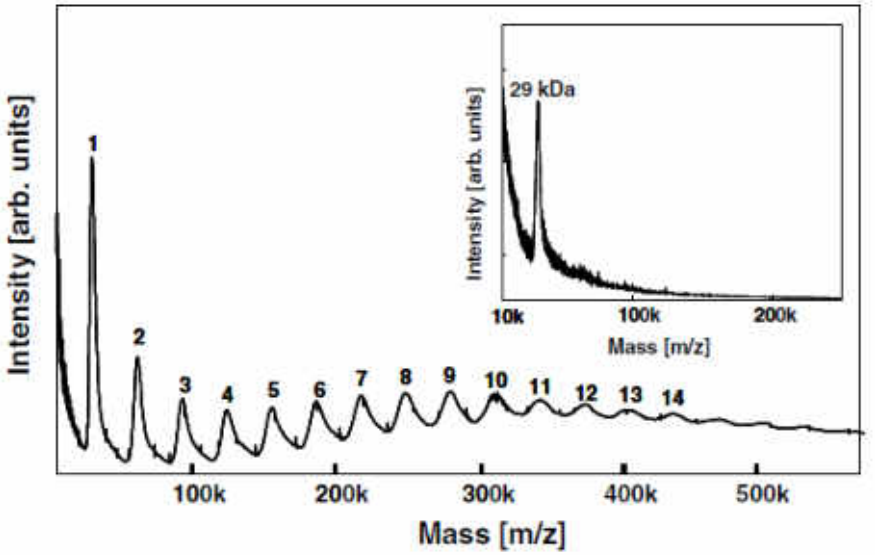

$Ag_{29}(BDT)_{12}^{3-}$
$Ag_{25}(DMBT)_{18}^{-}$
$Au_{25}(PET)_{18}^{-}$
HRMS of $Au_{25}(PET)_{18}^{-}$
7390
7392
7394
7396
7398
2000
4000
6000
8000
20000
40000
60000
m/z

345 structures!

Alkane- and arene- thiols are great, but…

Clusters are hard to crystallise, except in some cases
Thermal stability is limited
Applications are limited

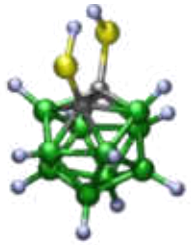




Jobin et al. *Chem. Phys. Lett.* 2004, 390,181

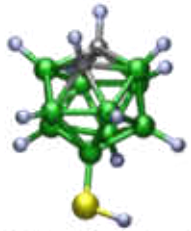
Building Blocks: Carborane Thiols

1,2-$C_2B_{10}H_{12}$

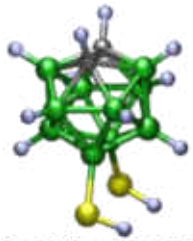


1,2-$(HS)_2$-1,2-$C_2B_{10}H_{10}$

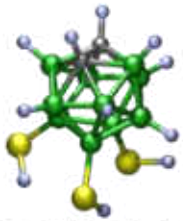
1-HS-1,2-$C_2B_{10}H_{11}$



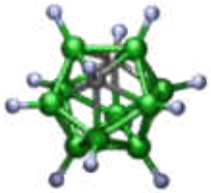
9-HS-1,2-$C_2B_{10}H_{11}$



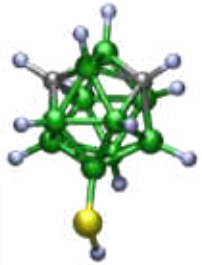
9,12-$(HS)_2$-1,2-$C_2B_{10}H_{10}$



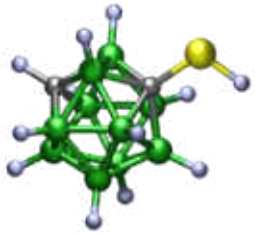
8,9,12-$(HS)_3$-1,2-$C_2B_{10}H_9$



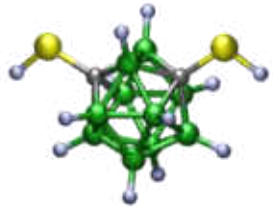
1,7-$C_2B_{10}H_{12}$



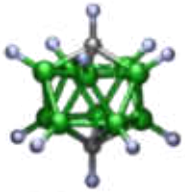
9-HS-1,7-$C_2B_{10}H_{11}$



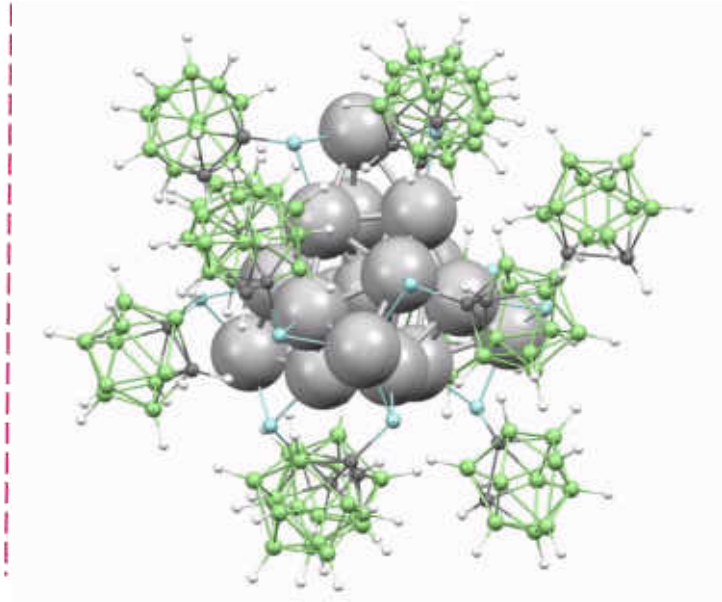
1-HS-1,7-$C_2B_{10}H_{11}$

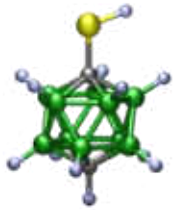


1,7-$(HS)_2$-1,7-$C_2B_{10}H_{10}$

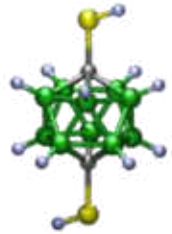


1,12-$C_2B_{10}H_{12}$



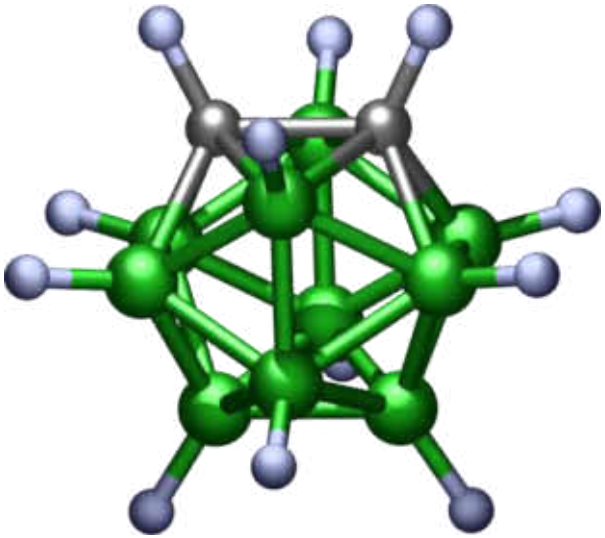


1-HS-1,12-$C_2B_{10}H_{11}$

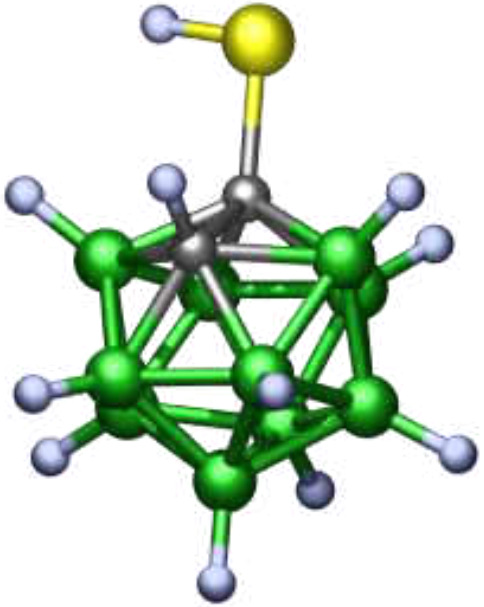


1,12-$(HS)_2$-1,12-$C_2B_{10}H_{10}$

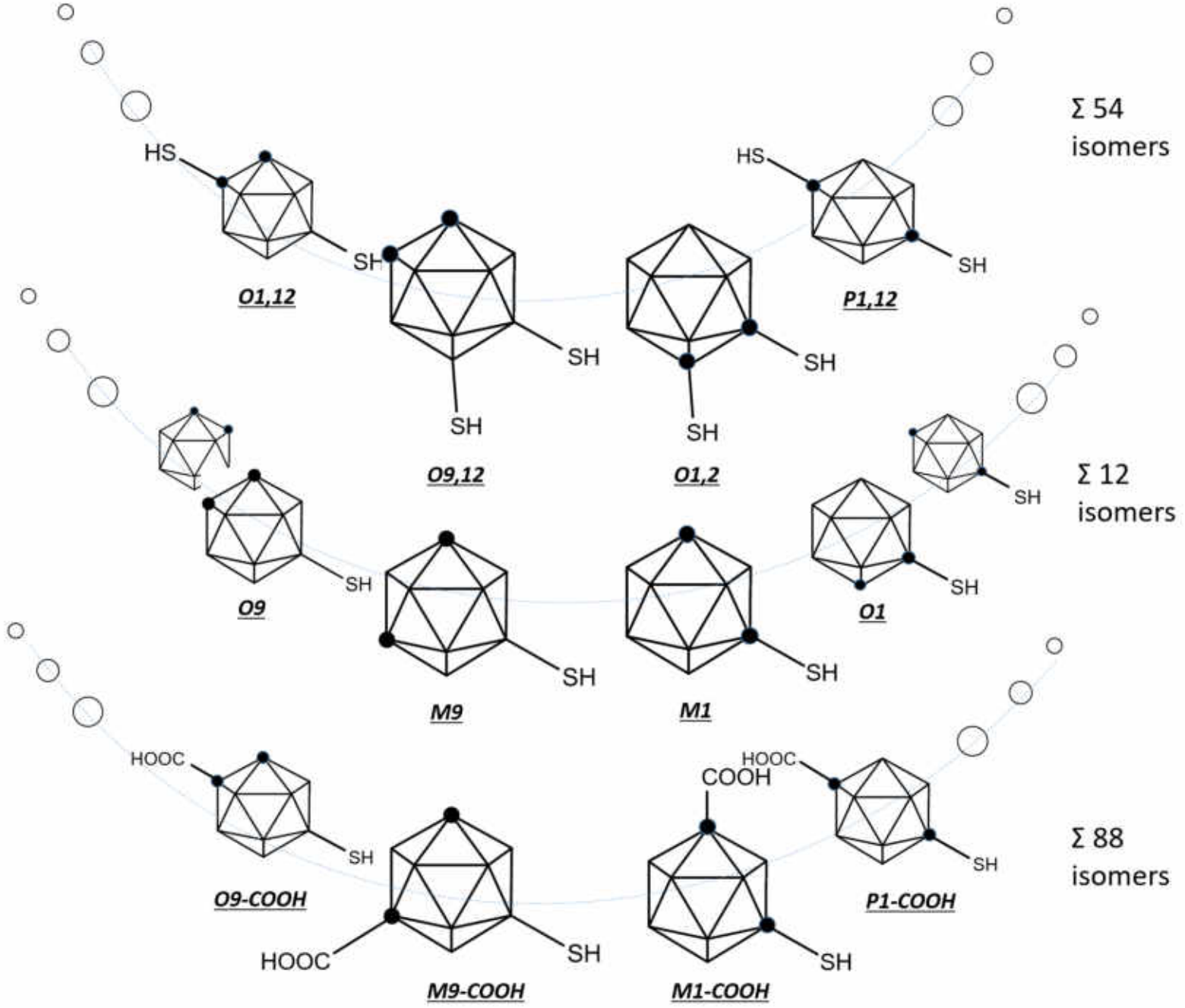
About the Ligand



1,2-$C_2B_{10}H_{12}$



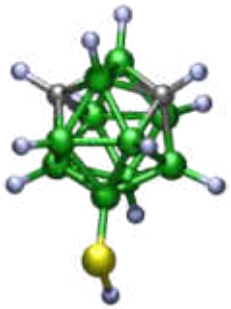
1-HS-1,2-$C_2B_{10}H_{11}$


HS
SH
SH
SH
O1,12
HS
SH
SH
SH
P1,12
Σ 54
isomers
SH
SH
O9,12
SH
SH
O1,2
SH
SH
O9
SH
SH
O1
Σ 12
isomers
SH
SH
M9
SH
SH
M1
HOOC
SH
HOOC
SH
O9-COOH
HOOC
COOH
SH
SH
P1-COOH
Σ 88
isomers
HOOC
SH
SH
M9-COOH
COOH
SH
SH
M1-COOH

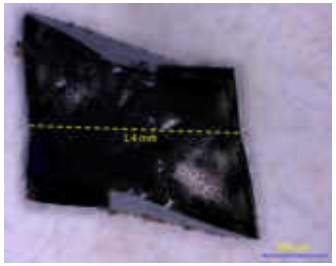
Cu_4 Ag_{14} Ag_{21} Ag_{42}

Propeller shaped $[Ag_{21}(m_9\text{-}CBT)_{12}(TPP)_2]$ Nanocluster

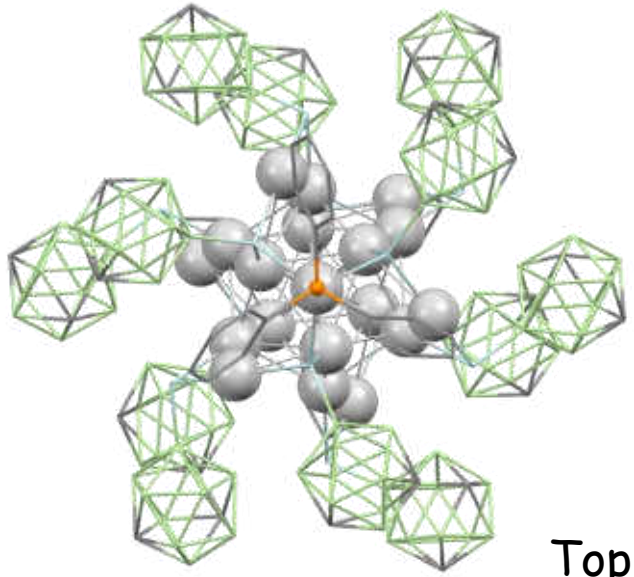
Ligand:



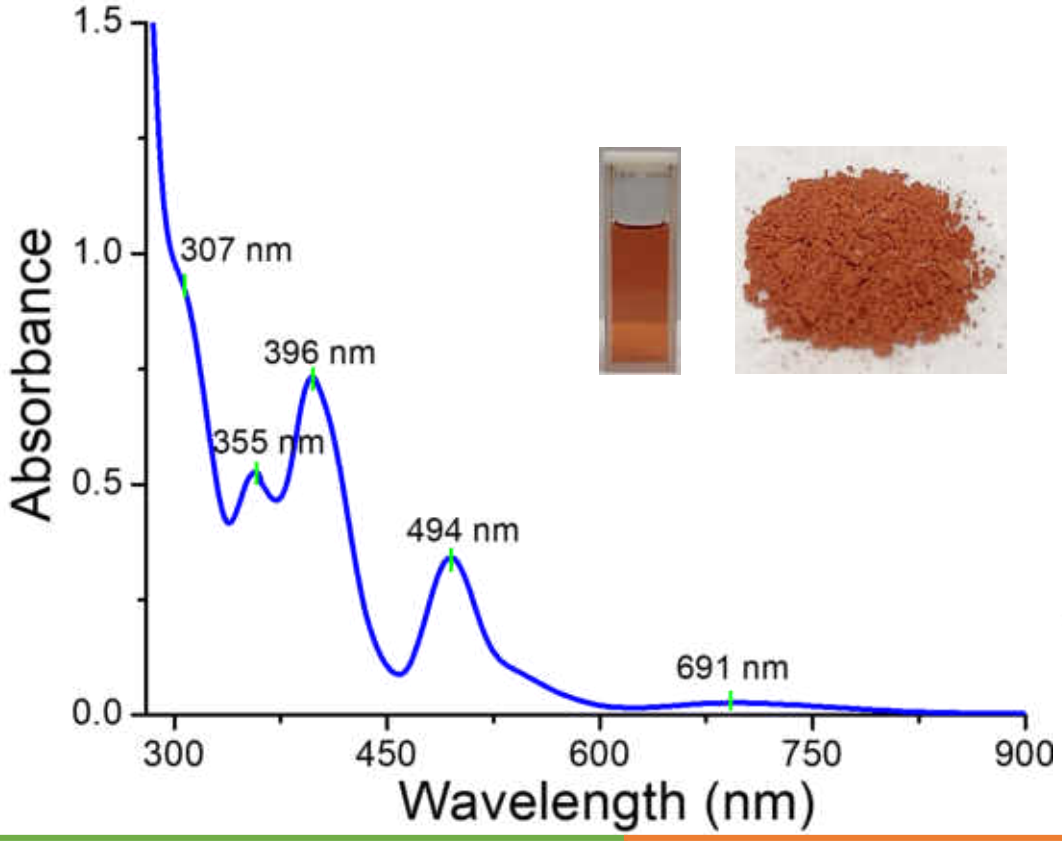
9-HS-1,7-$C_2B_{10}H_{11}$

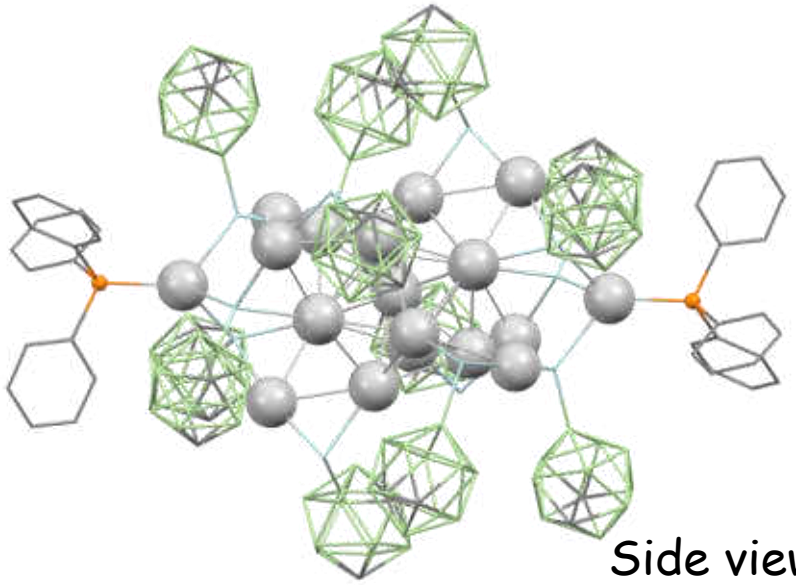


Crystal



Top view

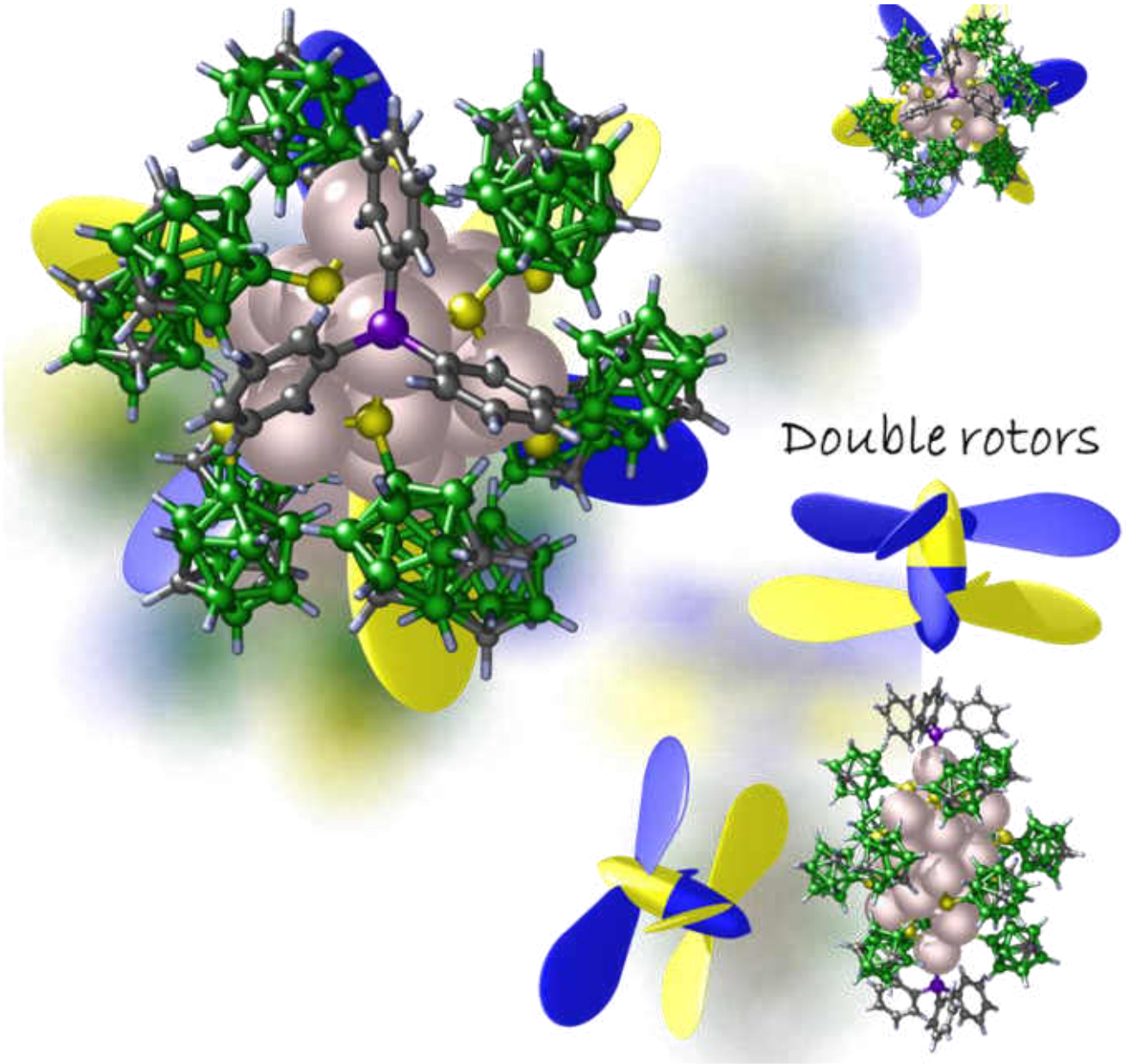




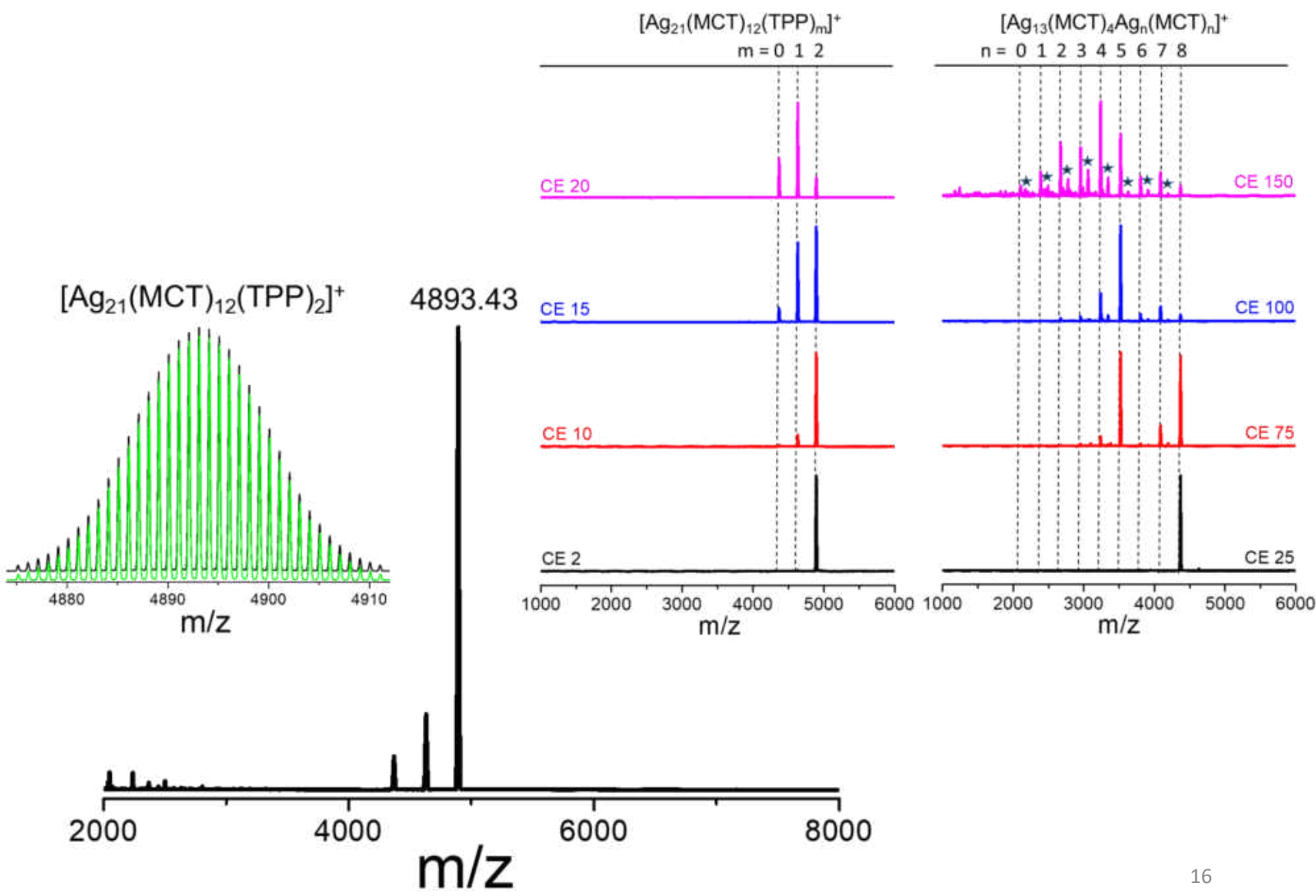
Side view

Jana *et al.*, *Inorg. Chem.*, **2022**, 61, 23, 8593-8603

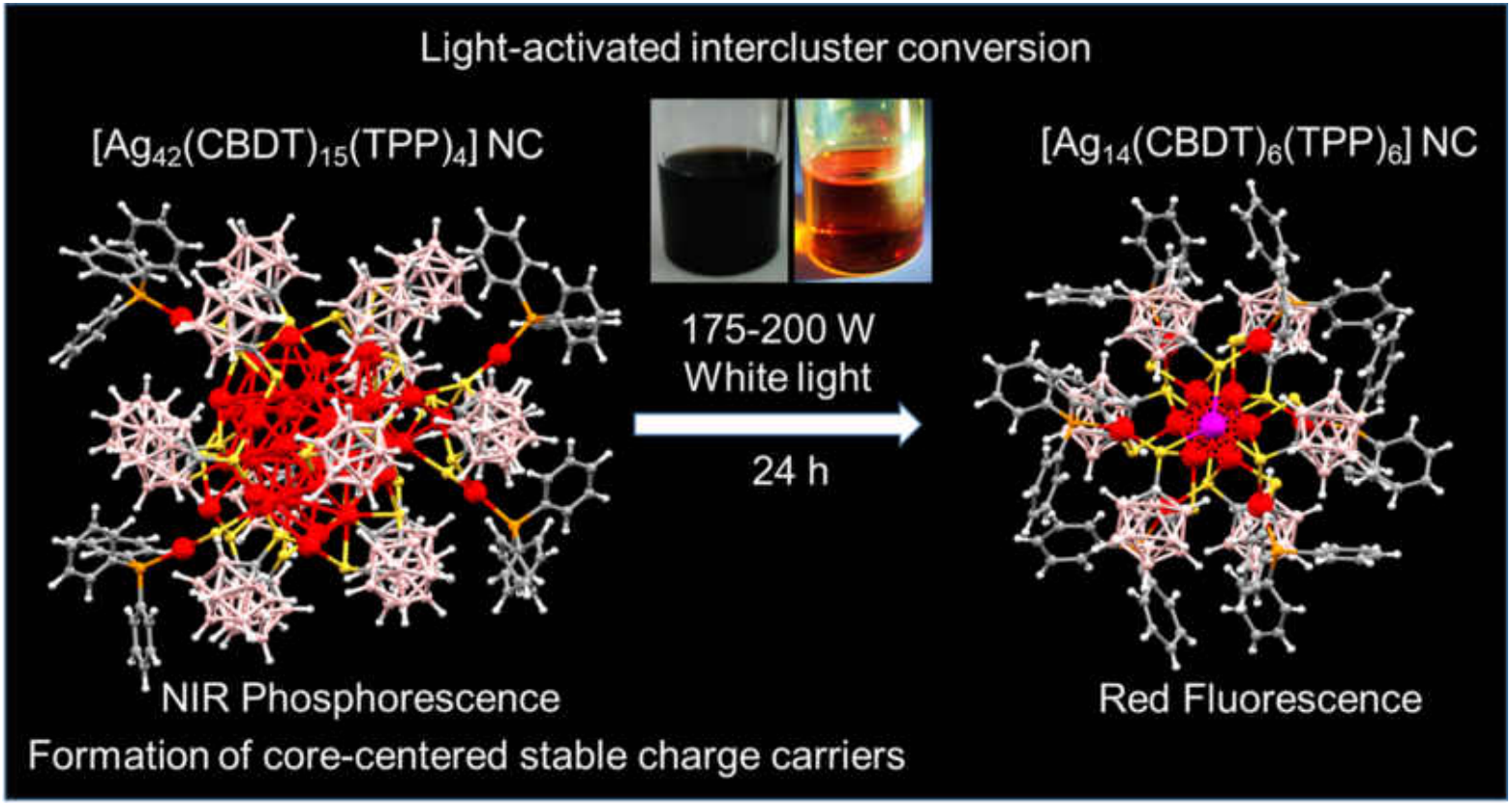
Propeller shaped $[Ag_{21}(m_9\text{-}CBT)_{12}(TPP)_2]$ Nanocluster



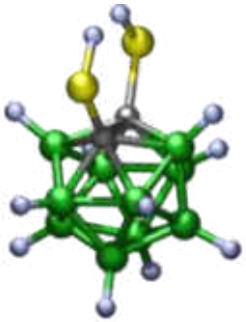
Mass spectrometric characterization



Light-activated Conversion of Carborane Thiol Appended Silver Nanocluster



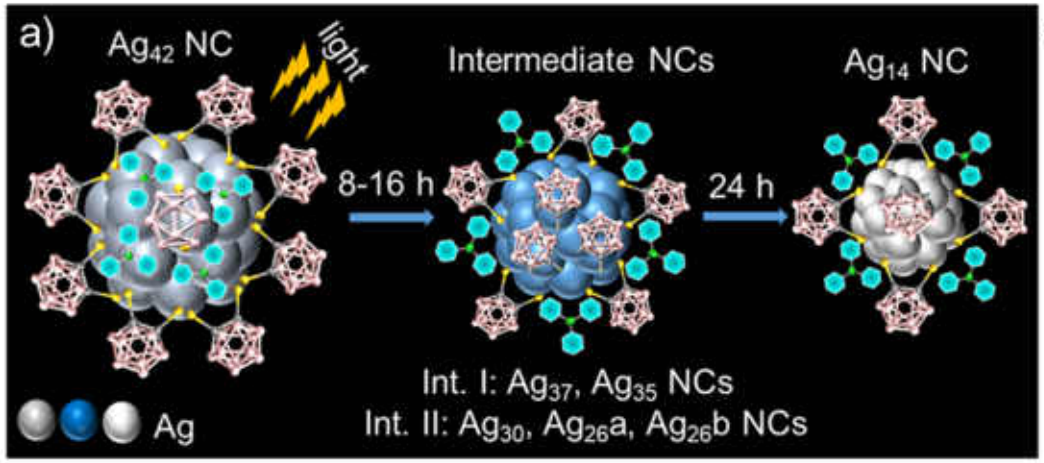
Ligand:

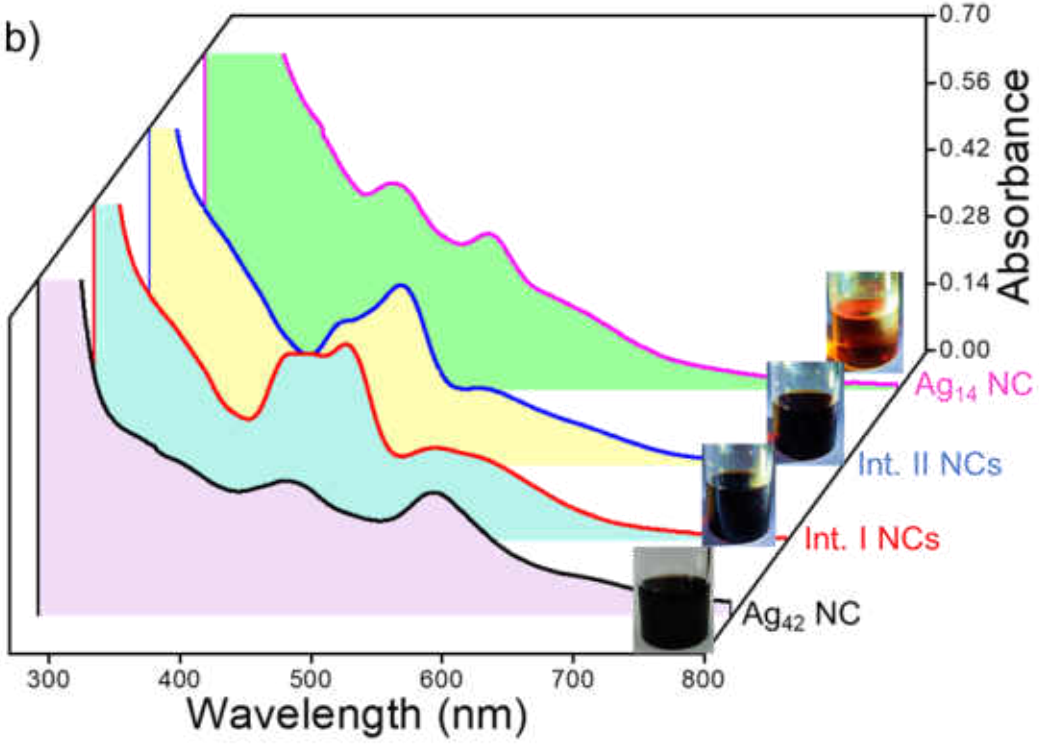


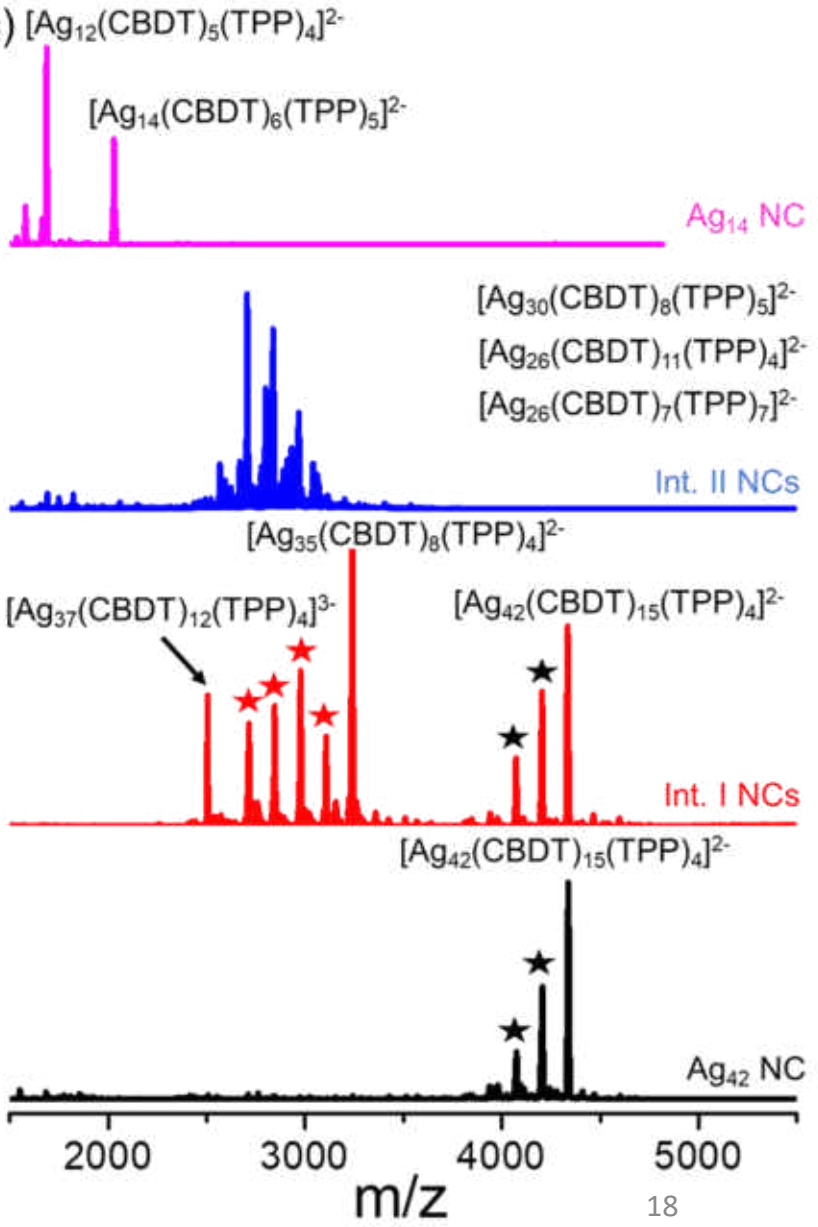
$1,2\text{-}(HS)_2\text{-}1,2\text{-}C_2B_{10}H_1$

Jana et. al, *ACS Nano* 2021, 15, 10, 15781–15793

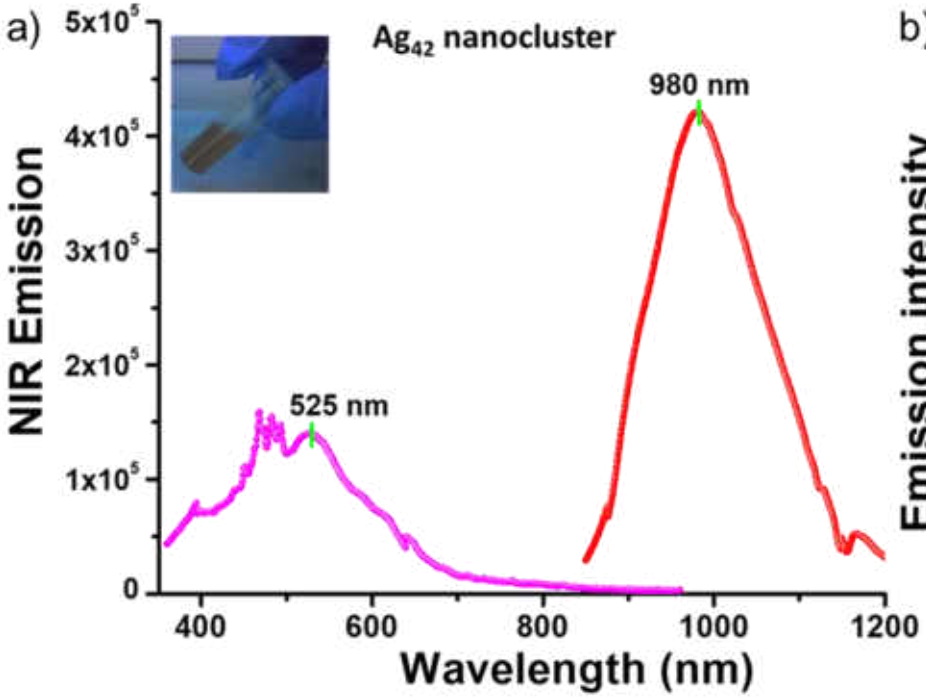
Light-activated Intercluster Conversion

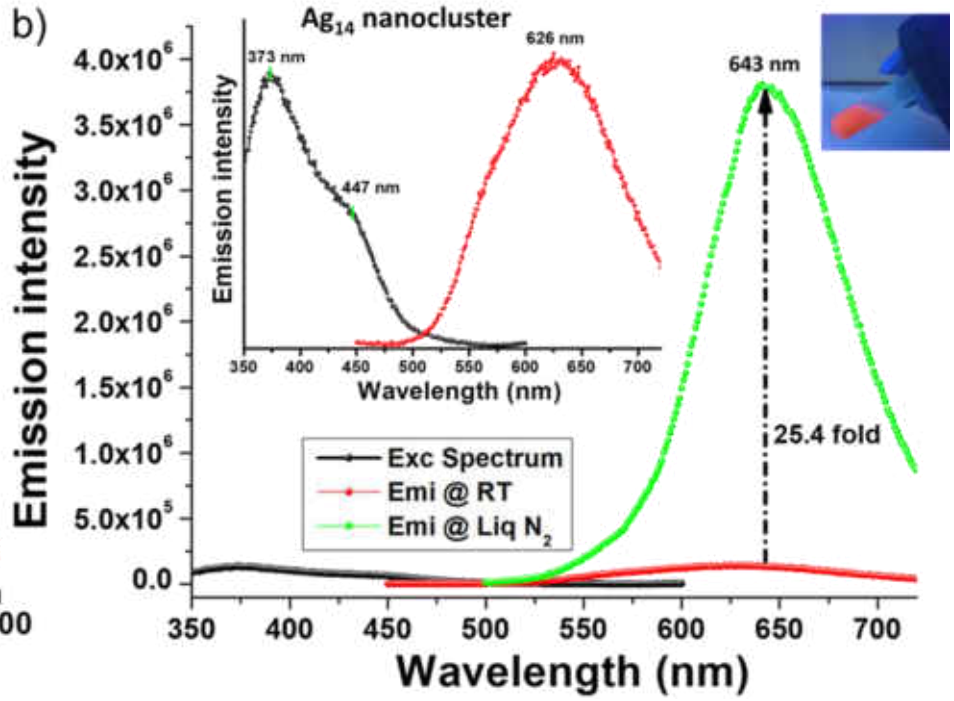




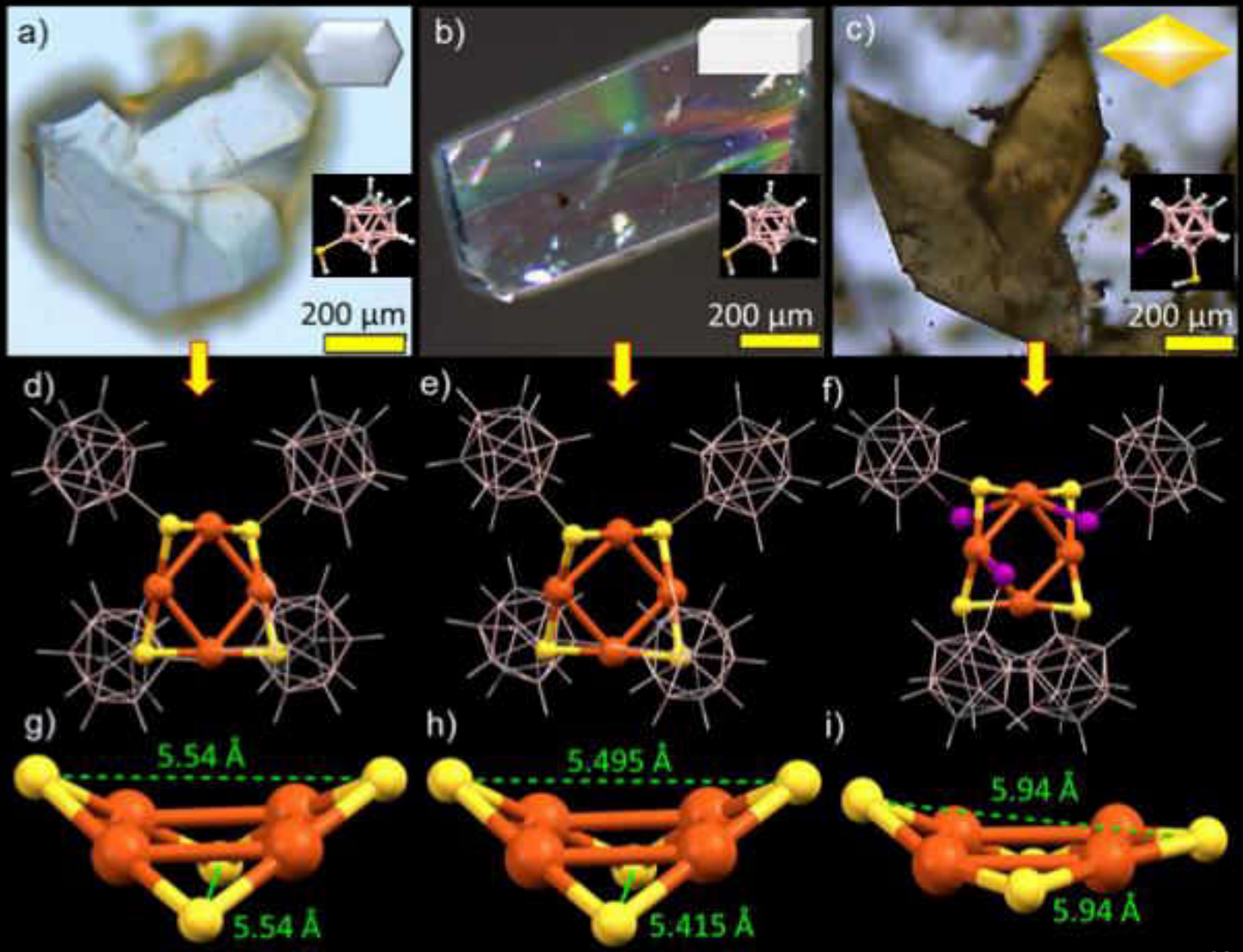


Photoluminescence Properties



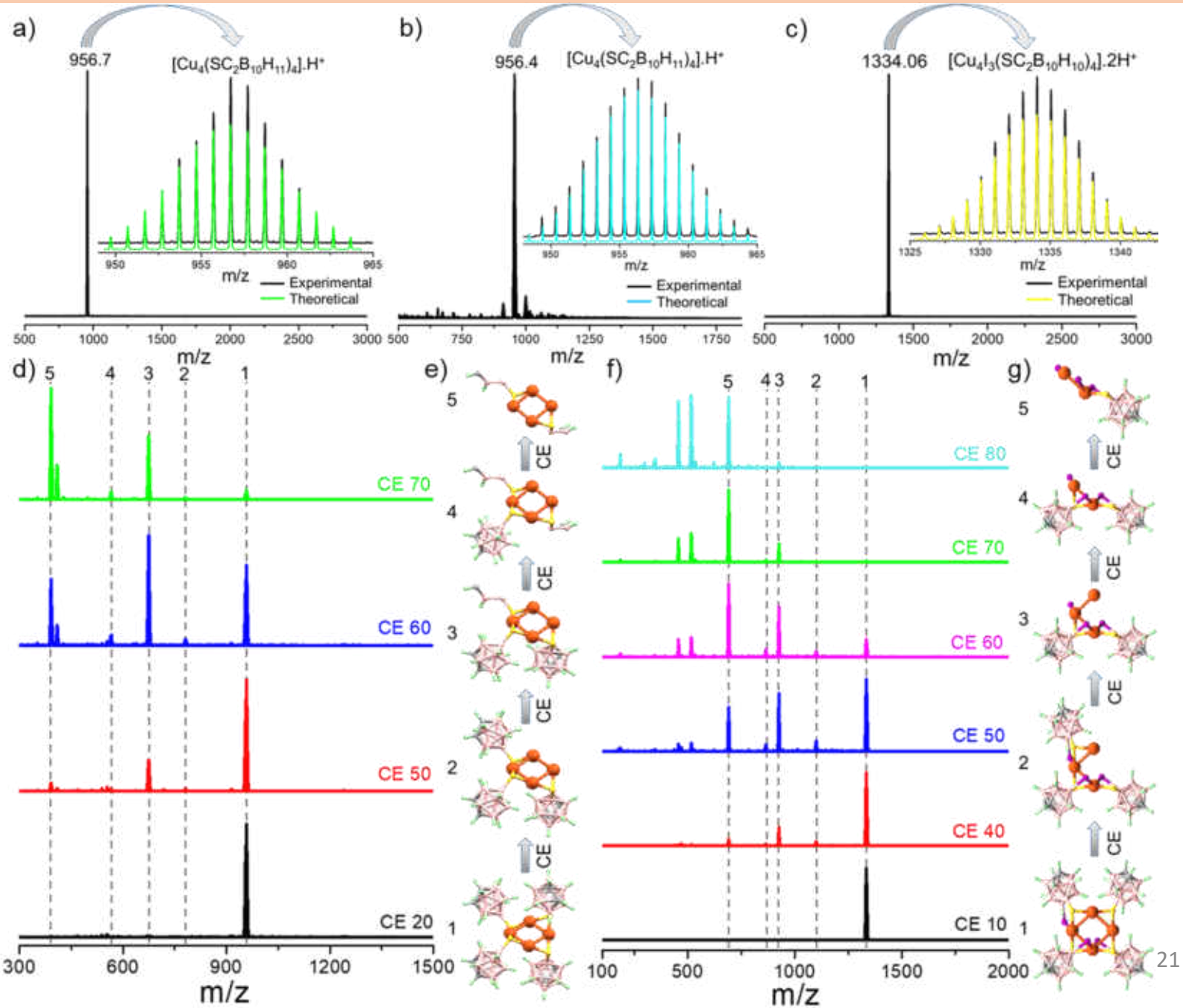


Multicolor Phosphorescence of Tetranuclear Copper Nanoclusters

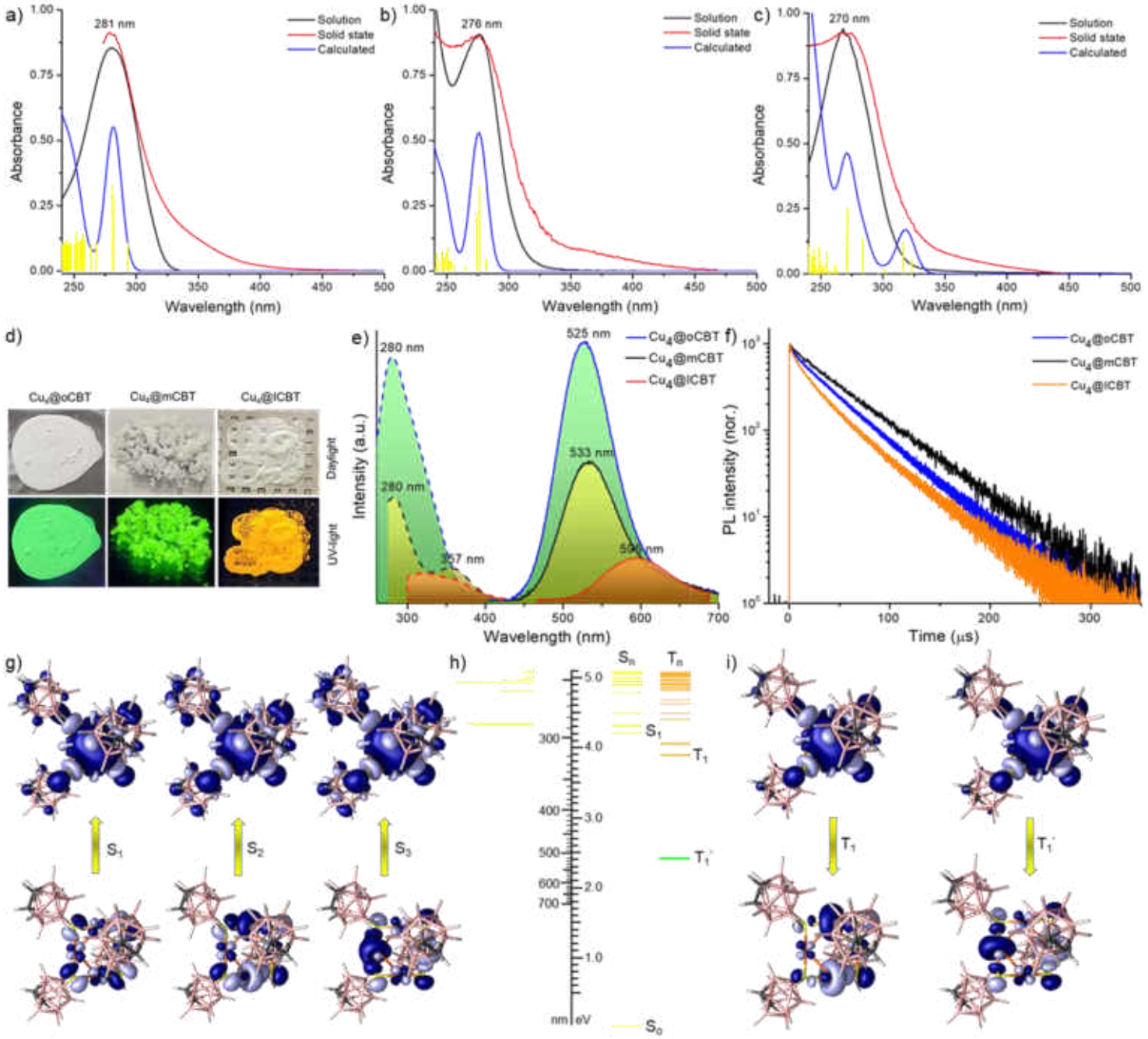


Jana *et al.*, *Chem. Sci.*, 2023, 14, 1613-1626.

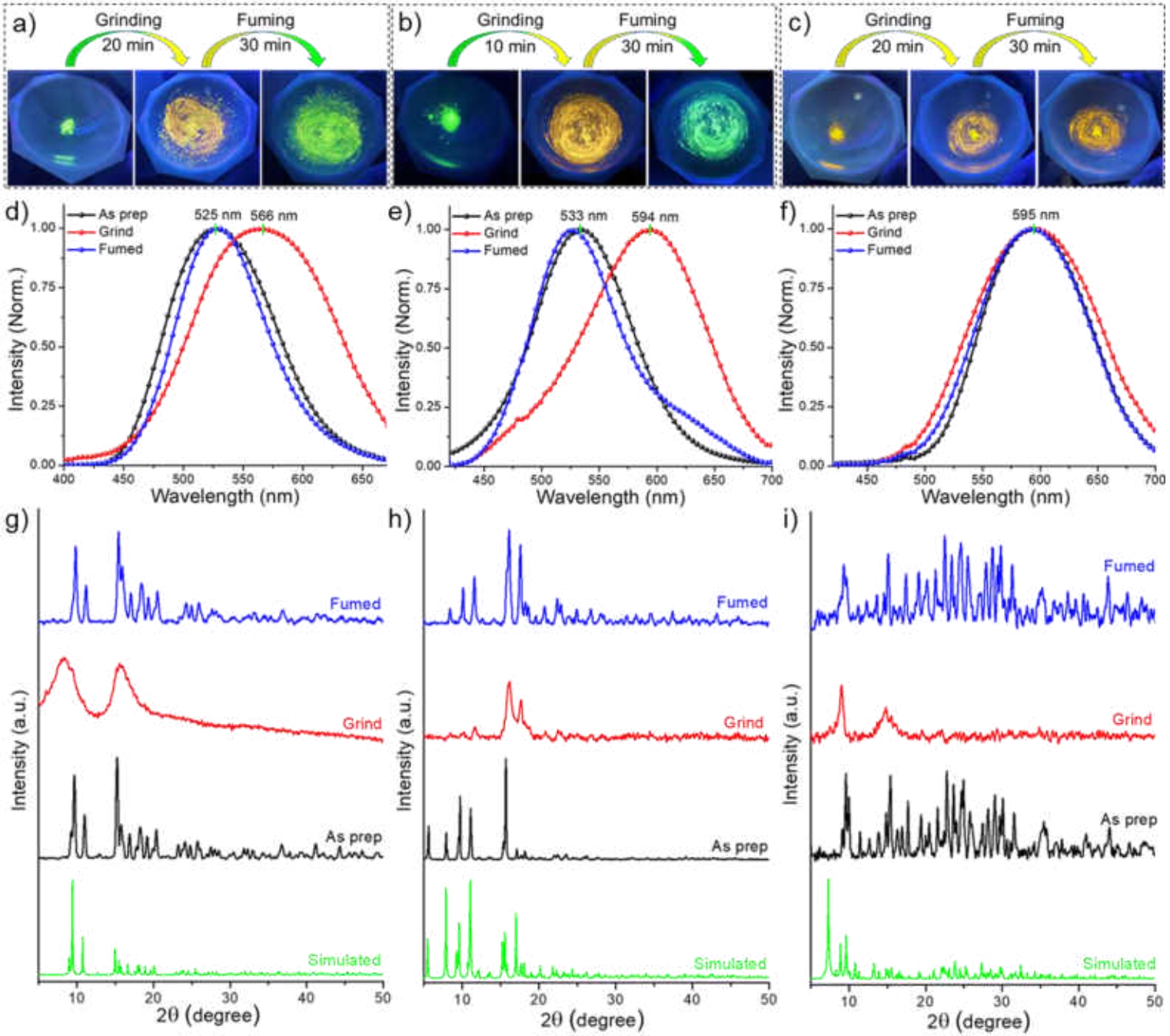
Mass spectrometric studies



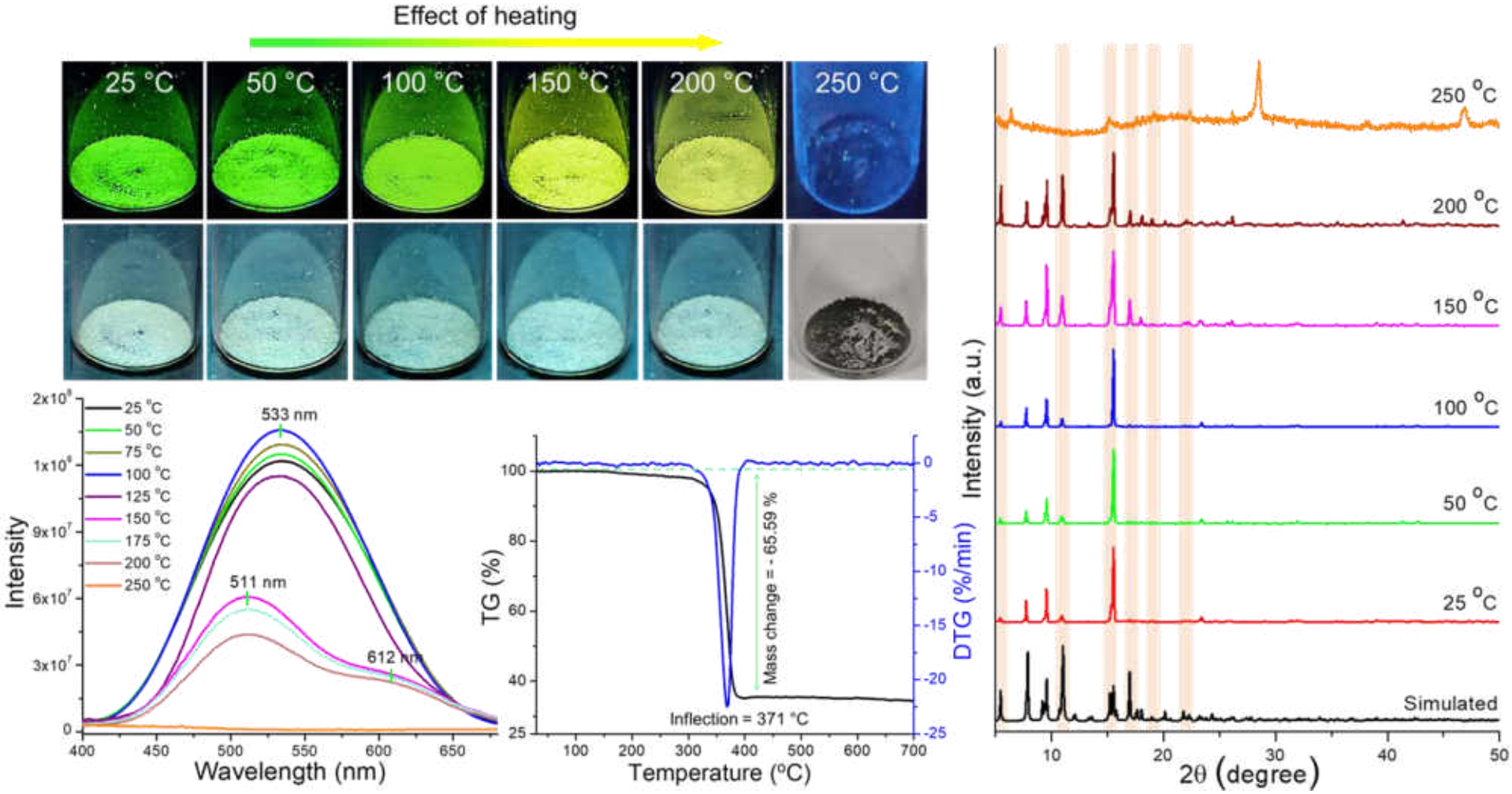
Photophysical properties



Mechanoresponsive properties



Thermoresponsive properties



Dynamics in clusters

Reactions

Isotope exchange

Positional dynamics

Inter-cluster reactions

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

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

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Supporting Information

$A + B \rightarrow C + D$

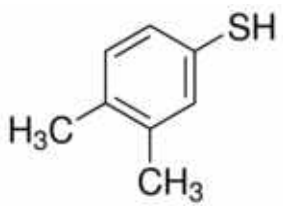
K. R. Krishnadas, et. al., *JACS*, 2016

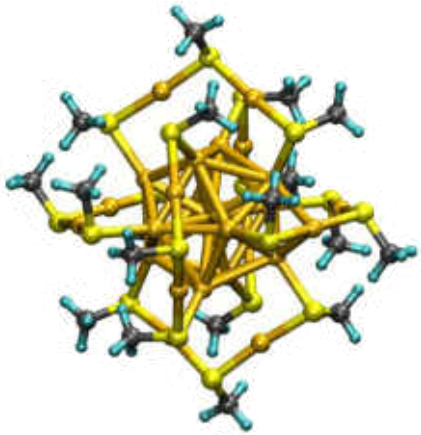
Ag_{25}-Au_{25} experiments

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

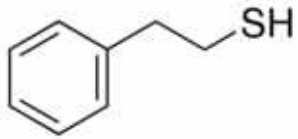
Reaction between $Au_{25}(PET)_{18}$ and $Ag_{25}(DMBT)_{18}$

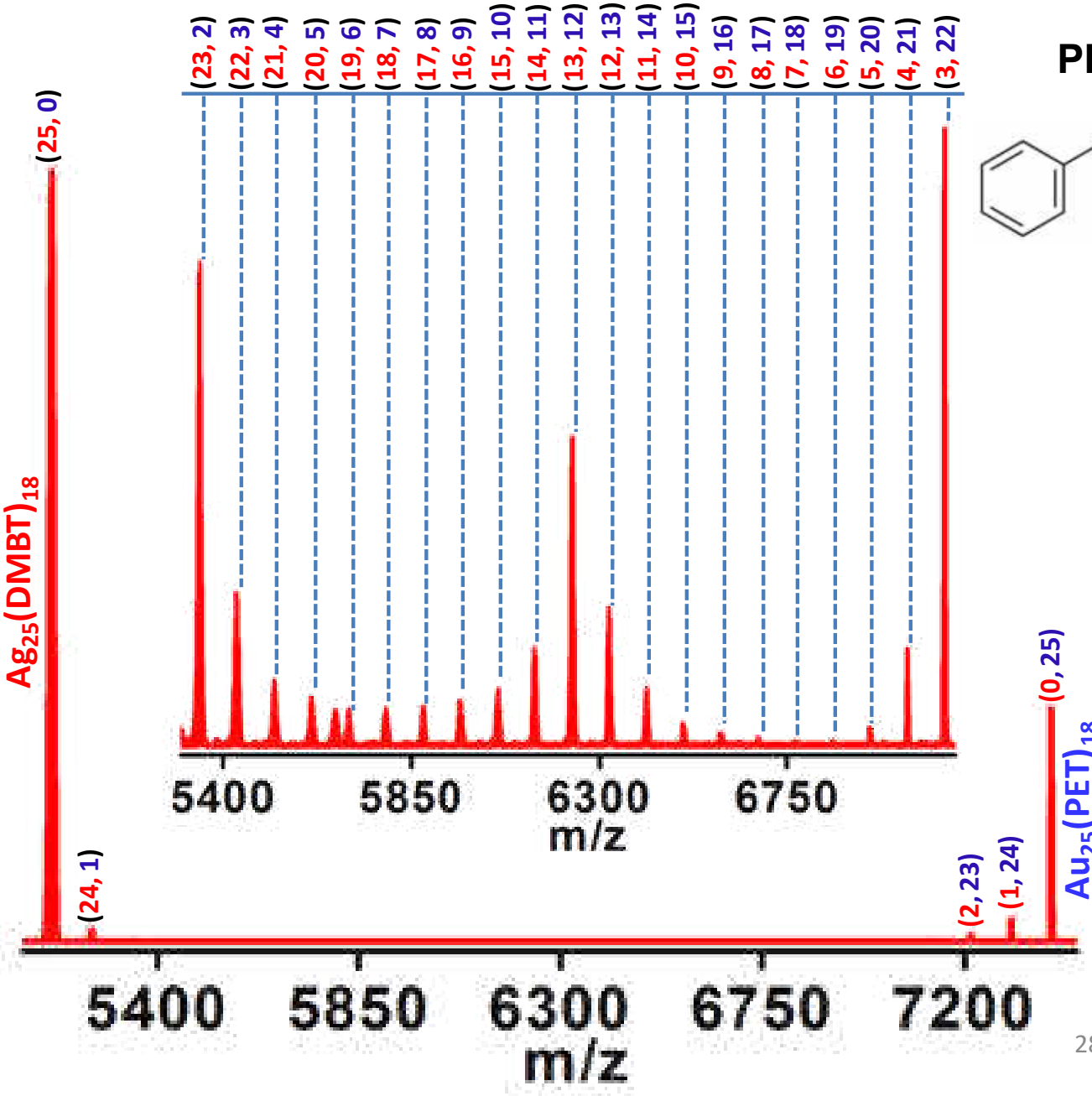
DMBT



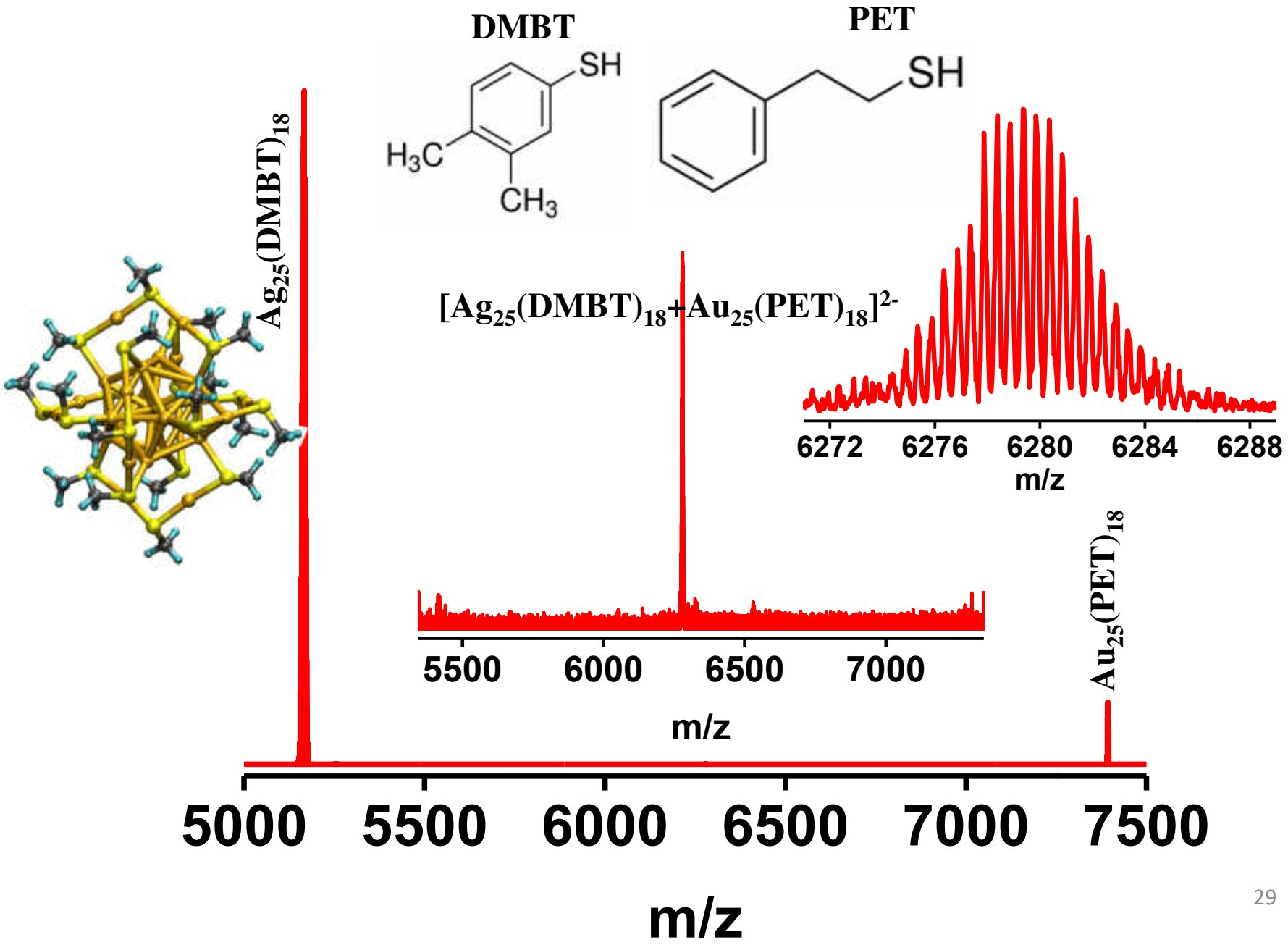


PET

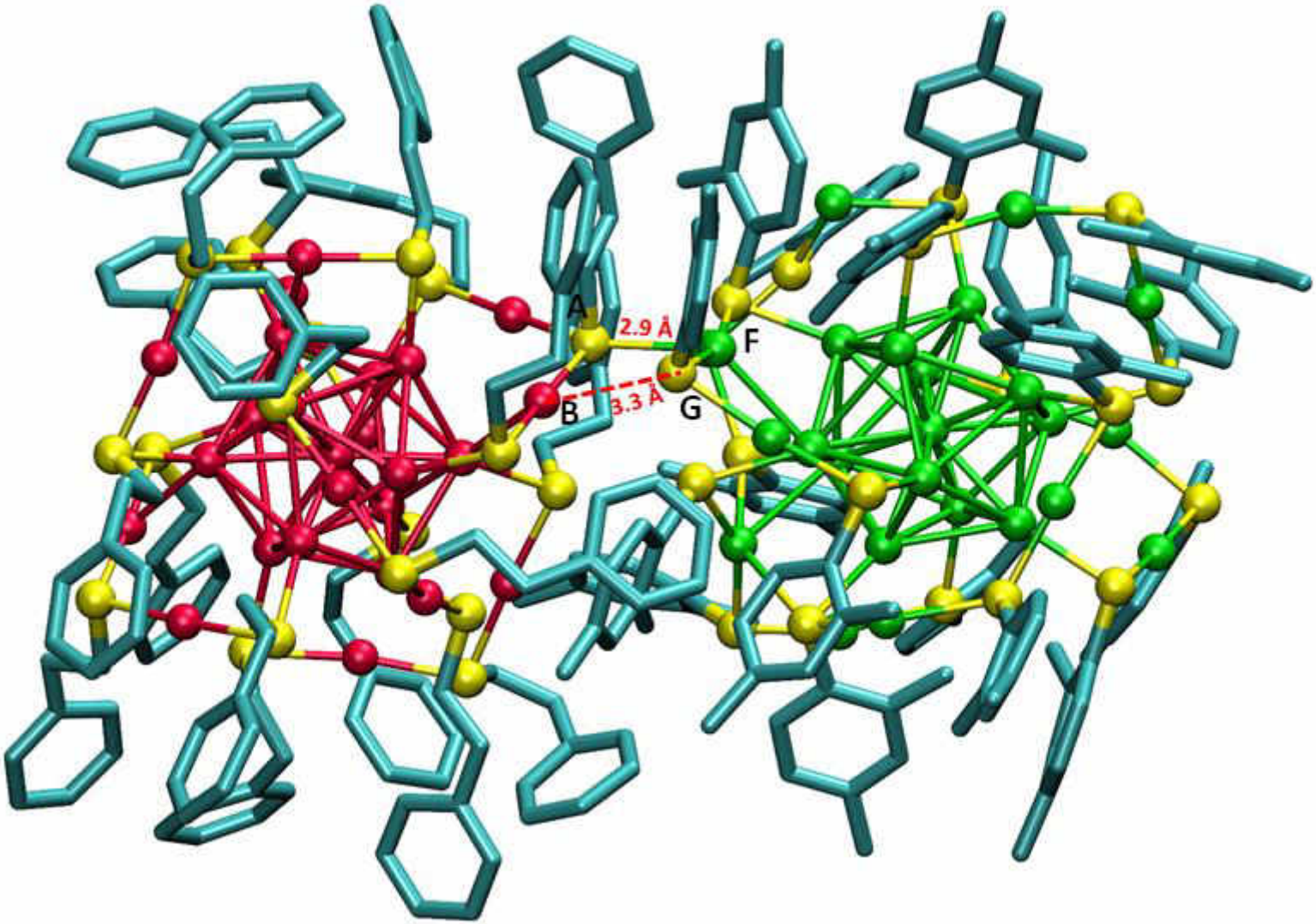


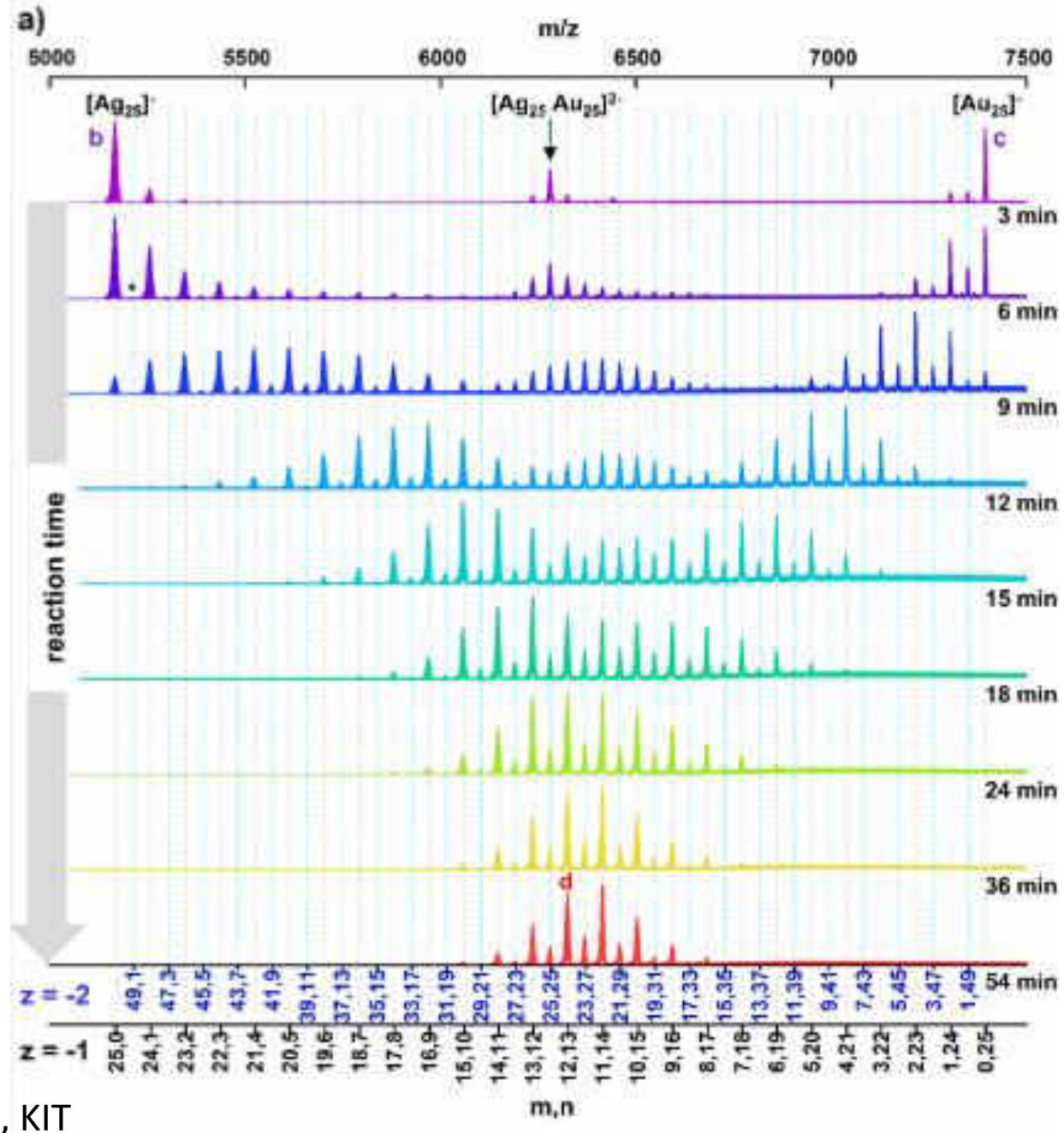


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

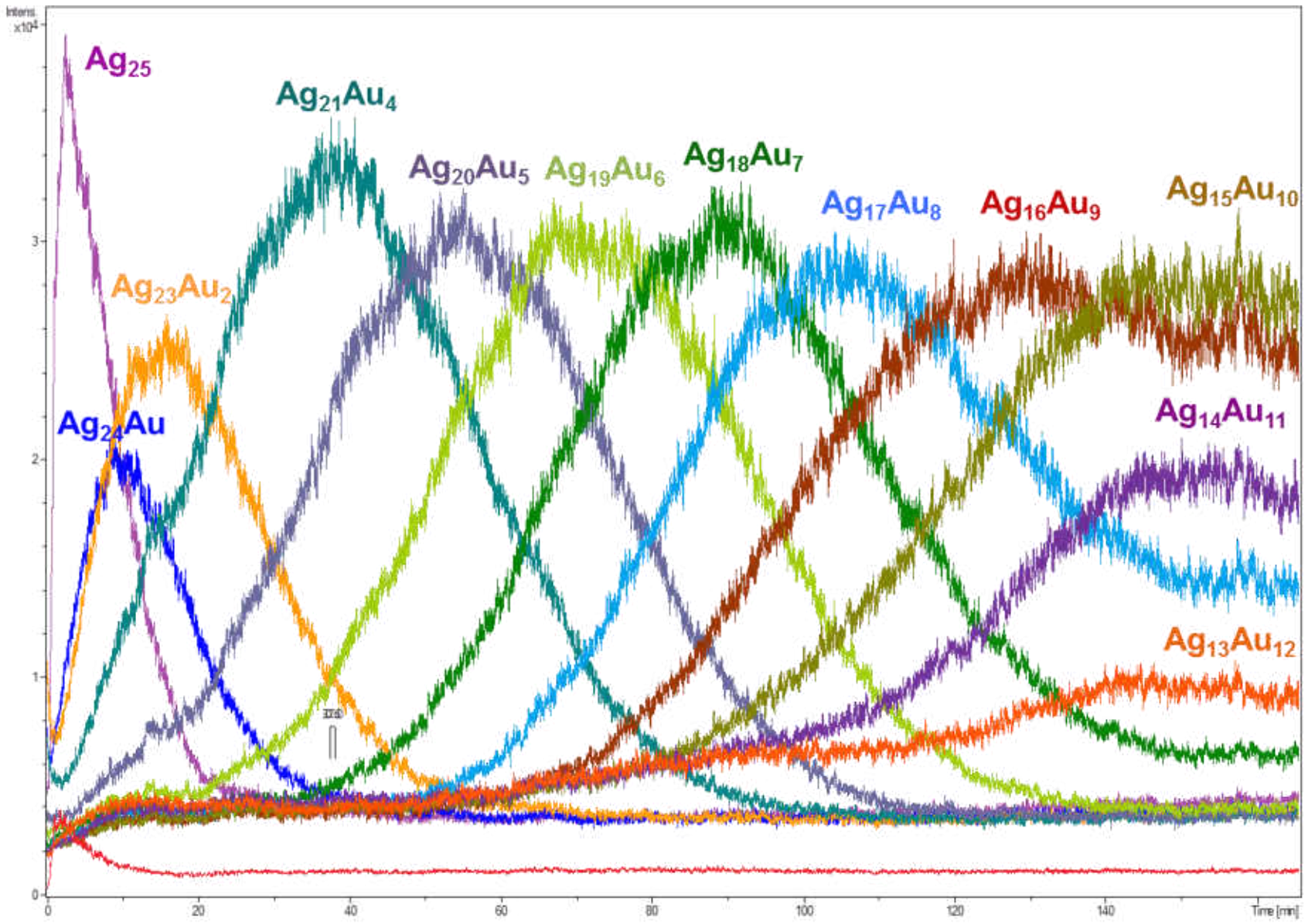




Manfred Kappes, KIT

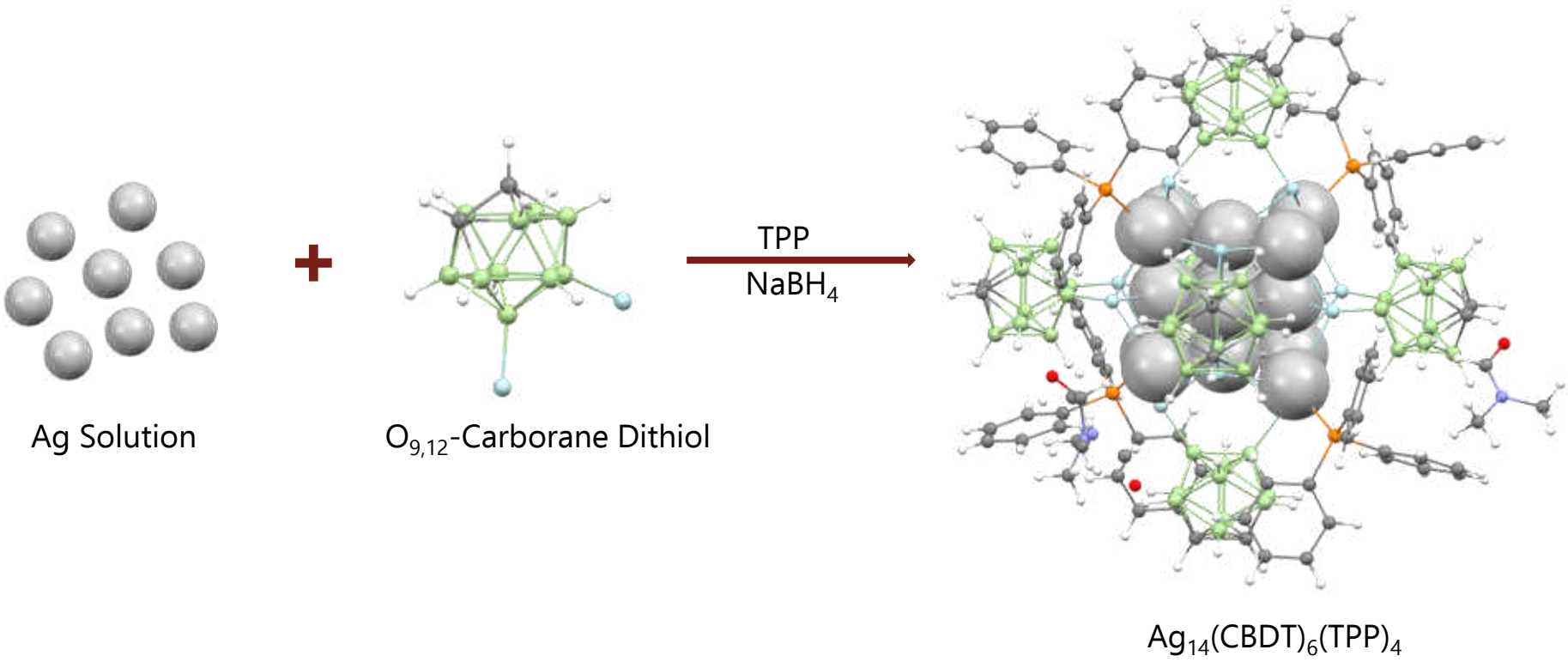
M. Neumaier, A. Baksi, et. al., *JACS* 2021

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



Modulation by Site-specific Positioning of Triphenylphosphine in $Ag_{14}(CBDT)_6(TPP)_4$ Nanoclusters

Synthesis Schematic of $Ag_{14}(CBDT)_6(TPP)_4$ Nanocluster

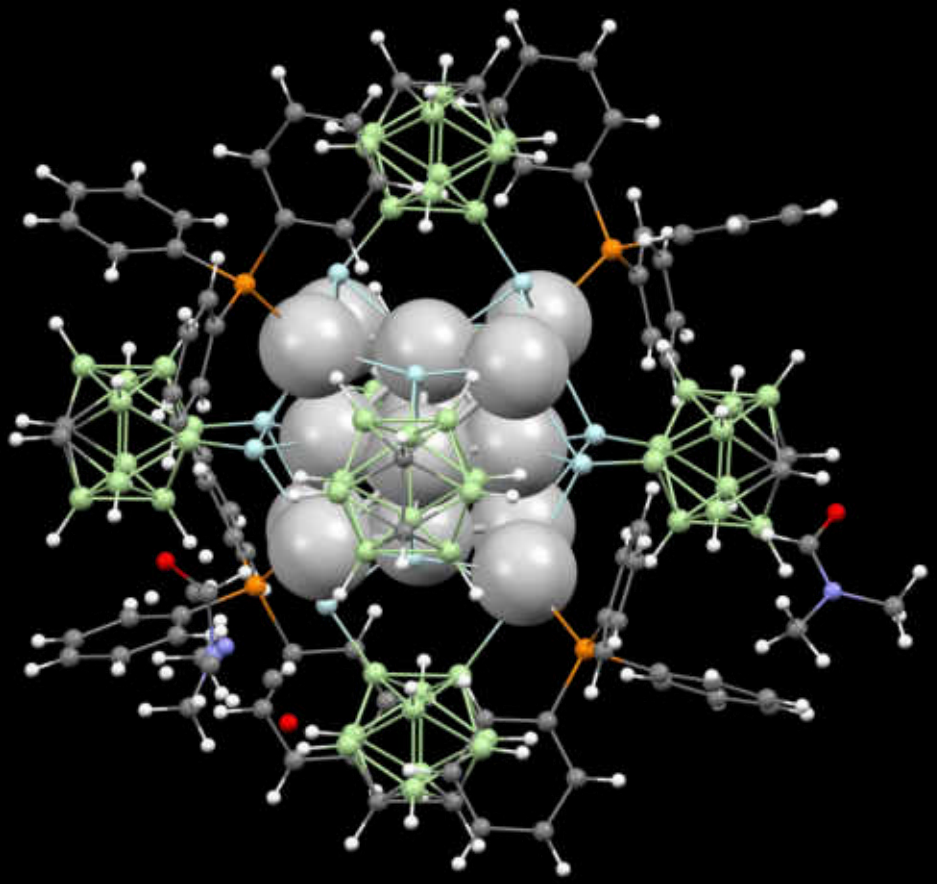


Vivek Yadav, et. al., Unpublished

Crystallization

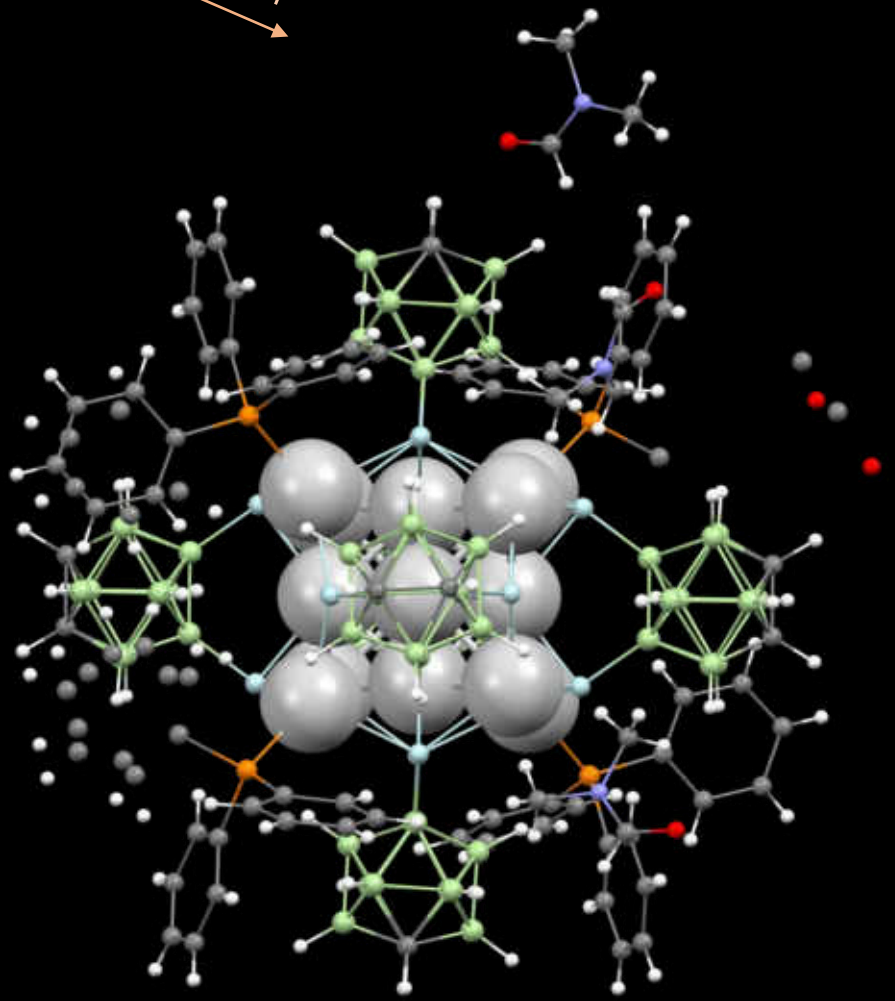
Without MeOH

With MeOH



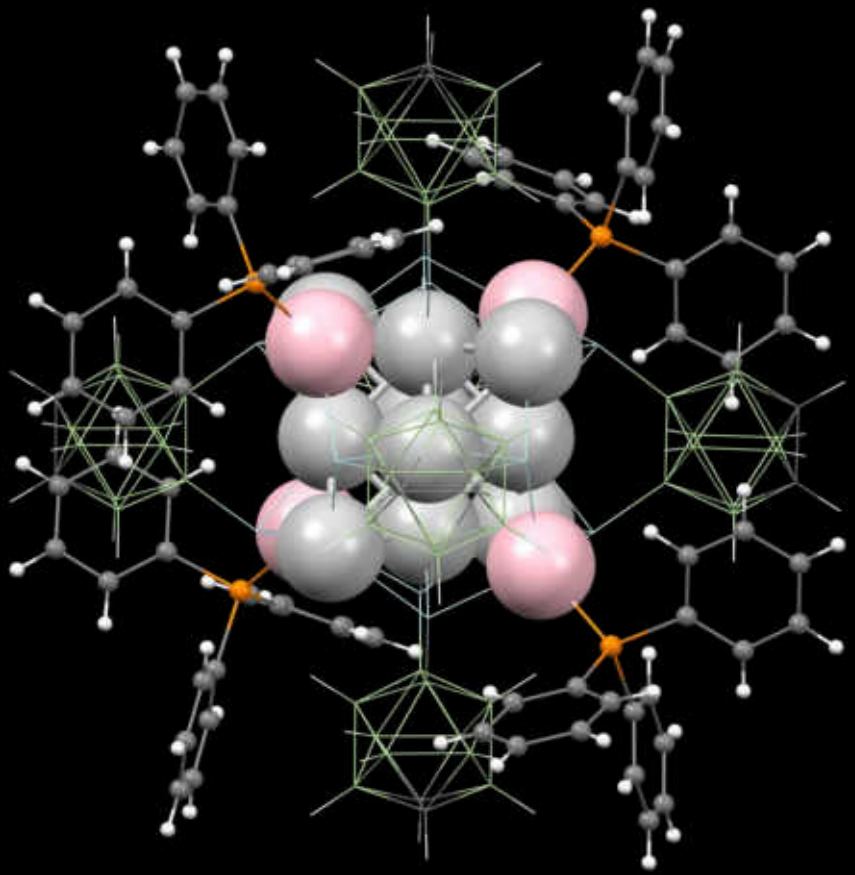
$Ag_{14}(CBDT)_6(TPP)_4$

Tetrahedral TPP

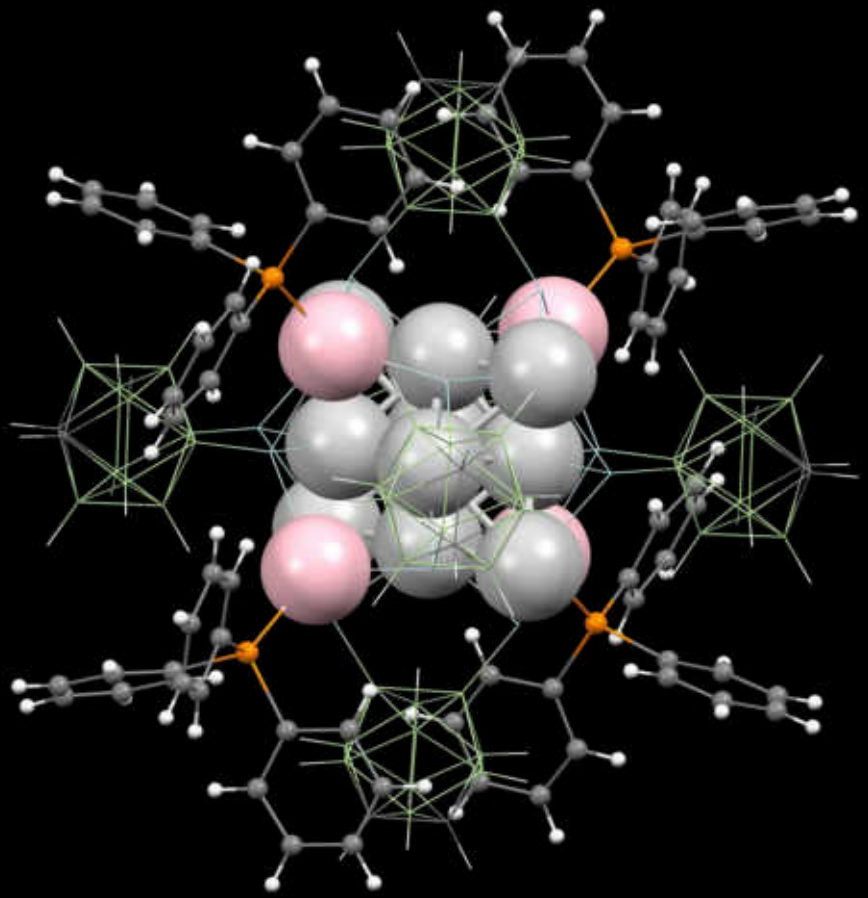


$Ag_{14}(CBDT)_6(TPP)_4$

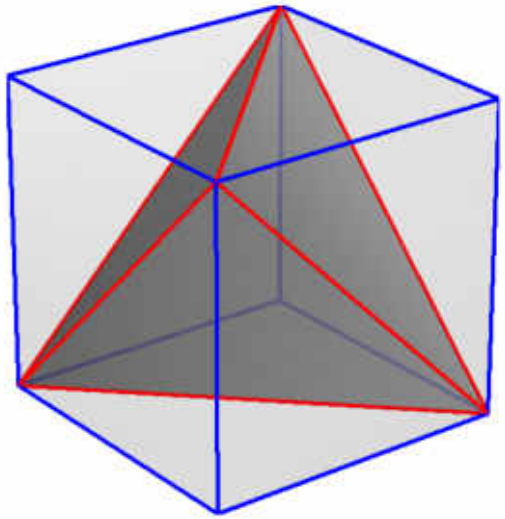
Square Planar TPP

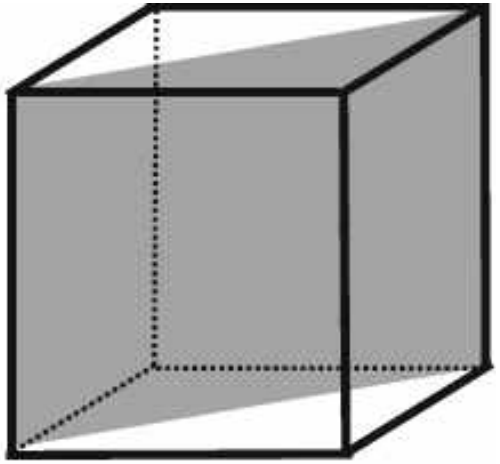


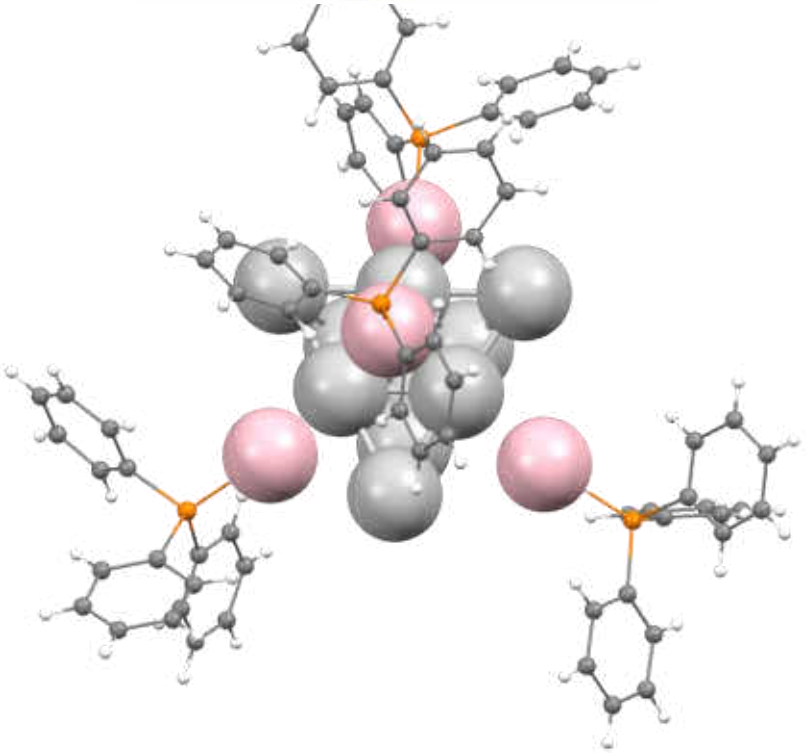
Tetrahedral TPP



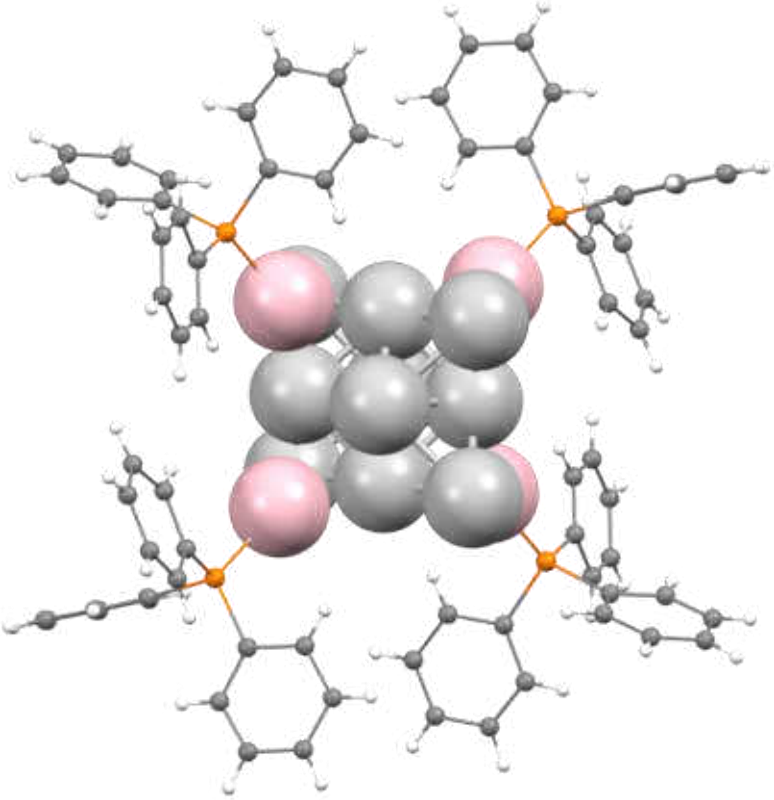
Square Planar TPP





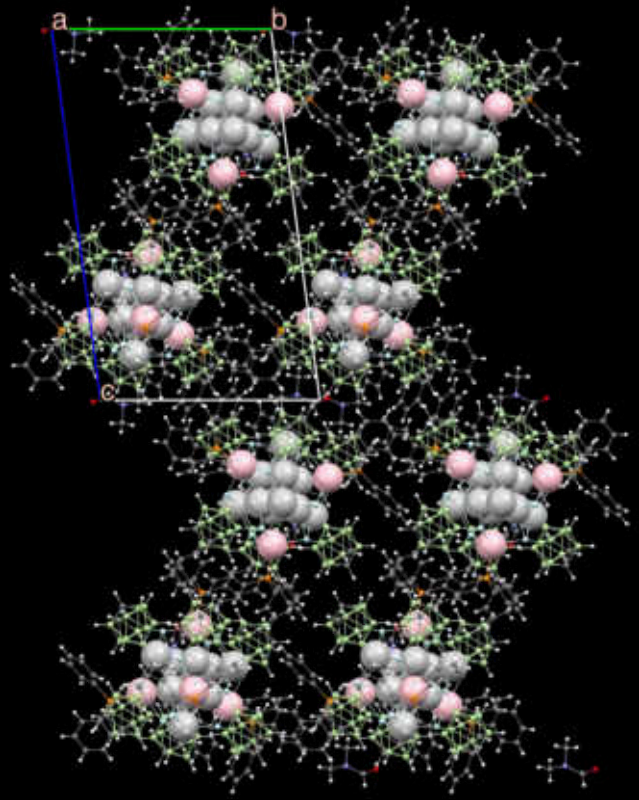


Tetrahedral TPP

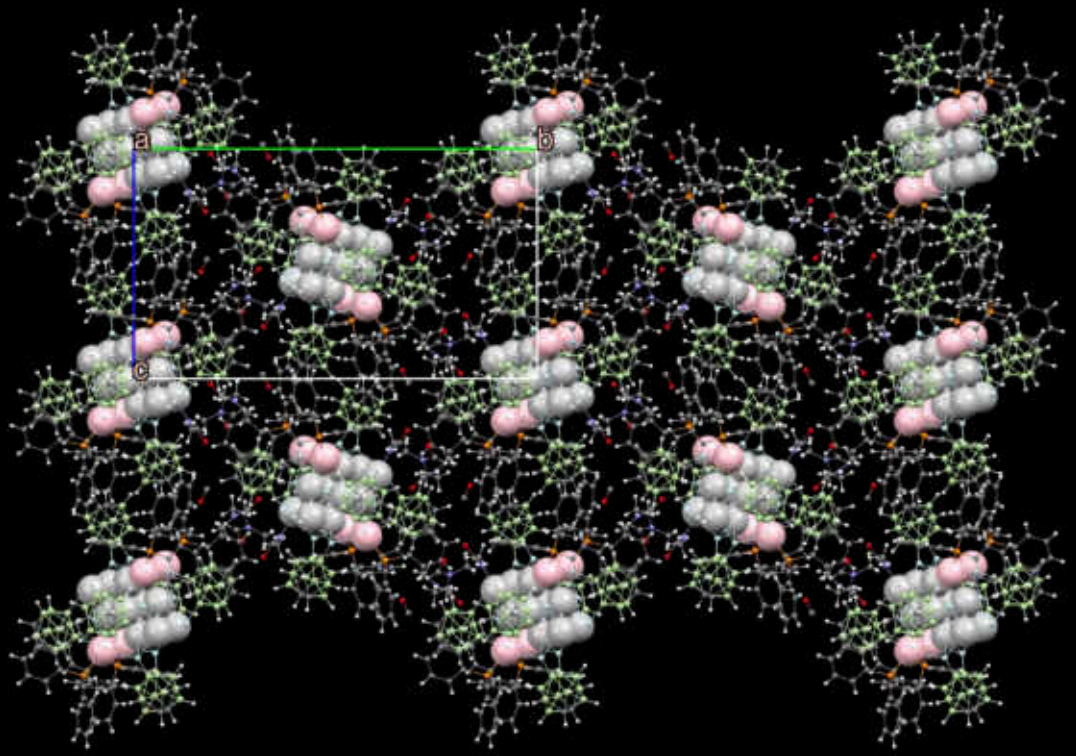


Square Planar TPP

Packing of Ag_{14} $(CBDT)_6$ $(TPP)_4$



Tetrahedral TPP

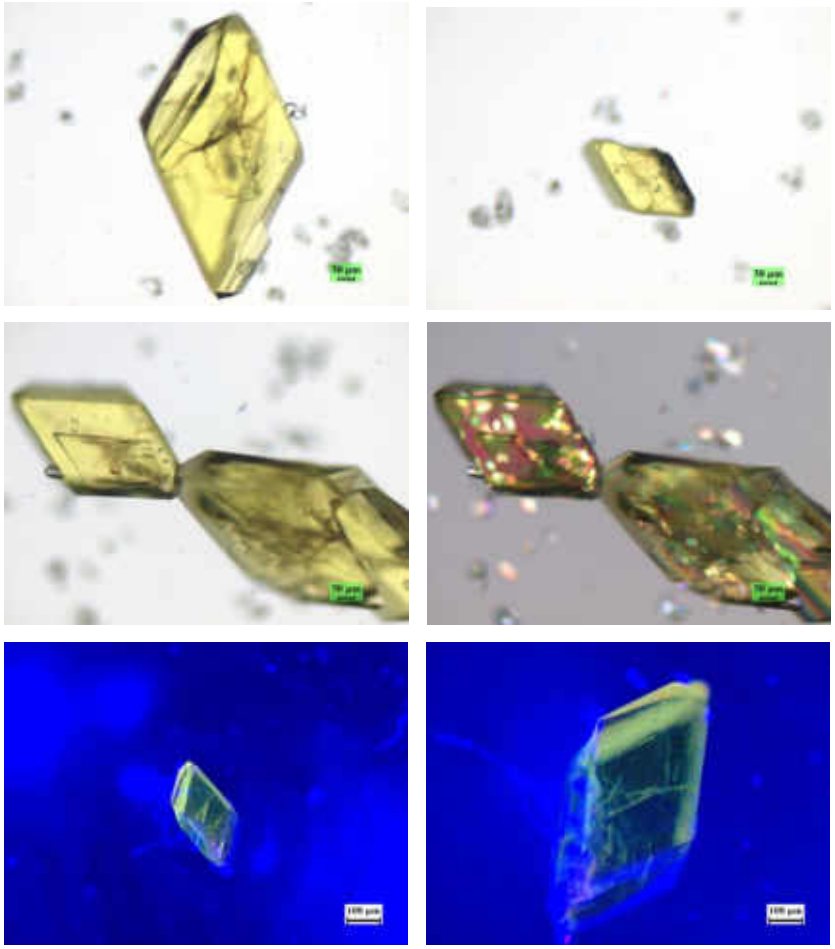


Square Planar TPP

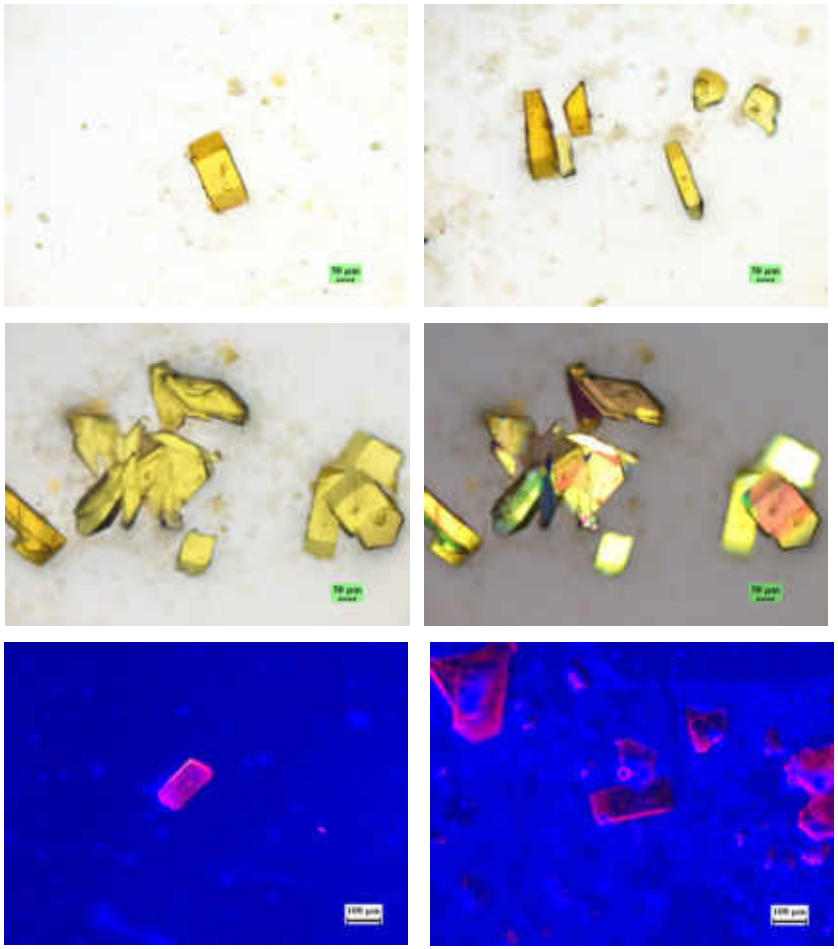
Crystal system - Triclinic
Space group - P -1
Volume - 8176.8(13) Å3
Z - 2

Crystal system - Monoclinic
Space group - P 21/c
Volume - 8703.8(5) Å3
Z - 2

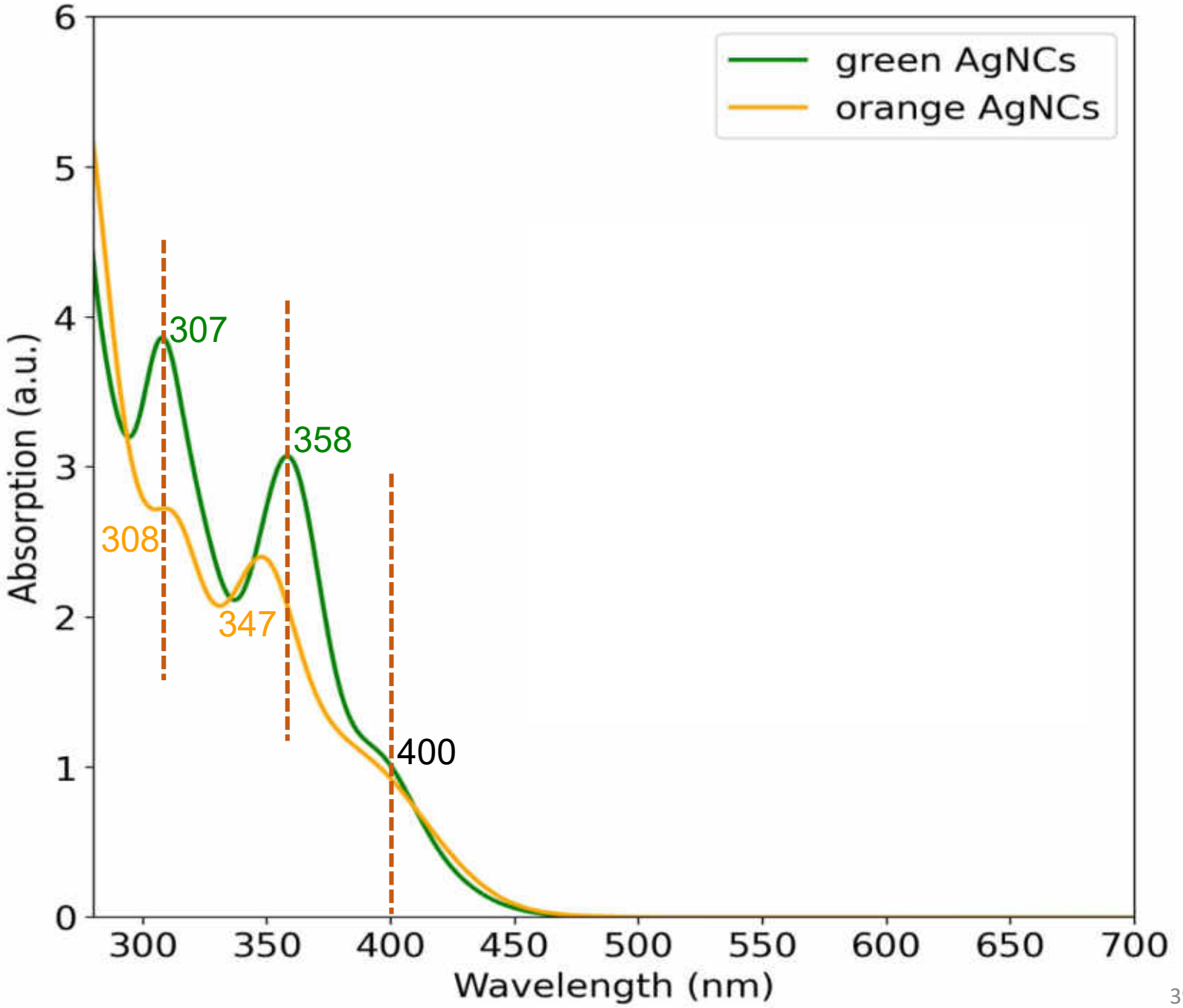
Luminescence of crystals of $Ag_{14}(CBDT)_6(TPP)_4$



Tetrahedral TPP



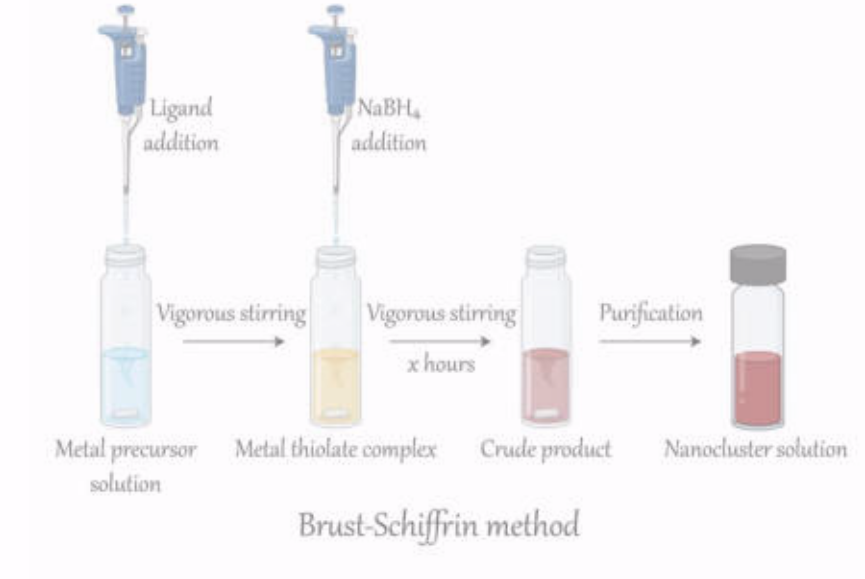
Square Planar TPP

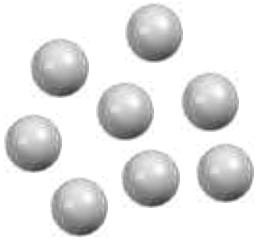

green AgNCs
orange AgNCs
Absorption (a.u.)
Wavelength (nm)
307
358
308
347
400
0
1
2
3
4
5
6
300
350
400
450
500
550
600
650
700

Ag_{17} $AuAg_{16}$ $Ag_{13}Cu_4$ $AuAg_{12}Cu_4$

Vivek Yadav, et. al., *Nature Communications*, Revised and submitted

Synthesis Schematic of $[Ag_{17}(o_1\text{-CBT})_{12}]^{3-}$ Nanocluster



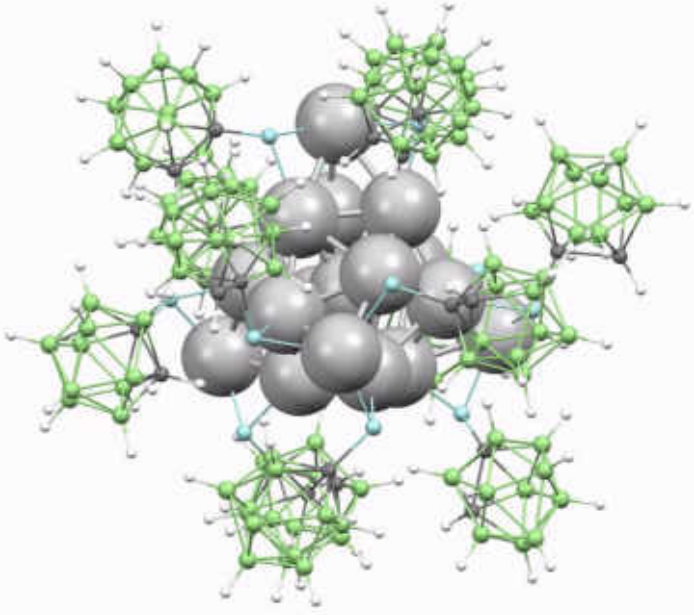


Ag Solution

+

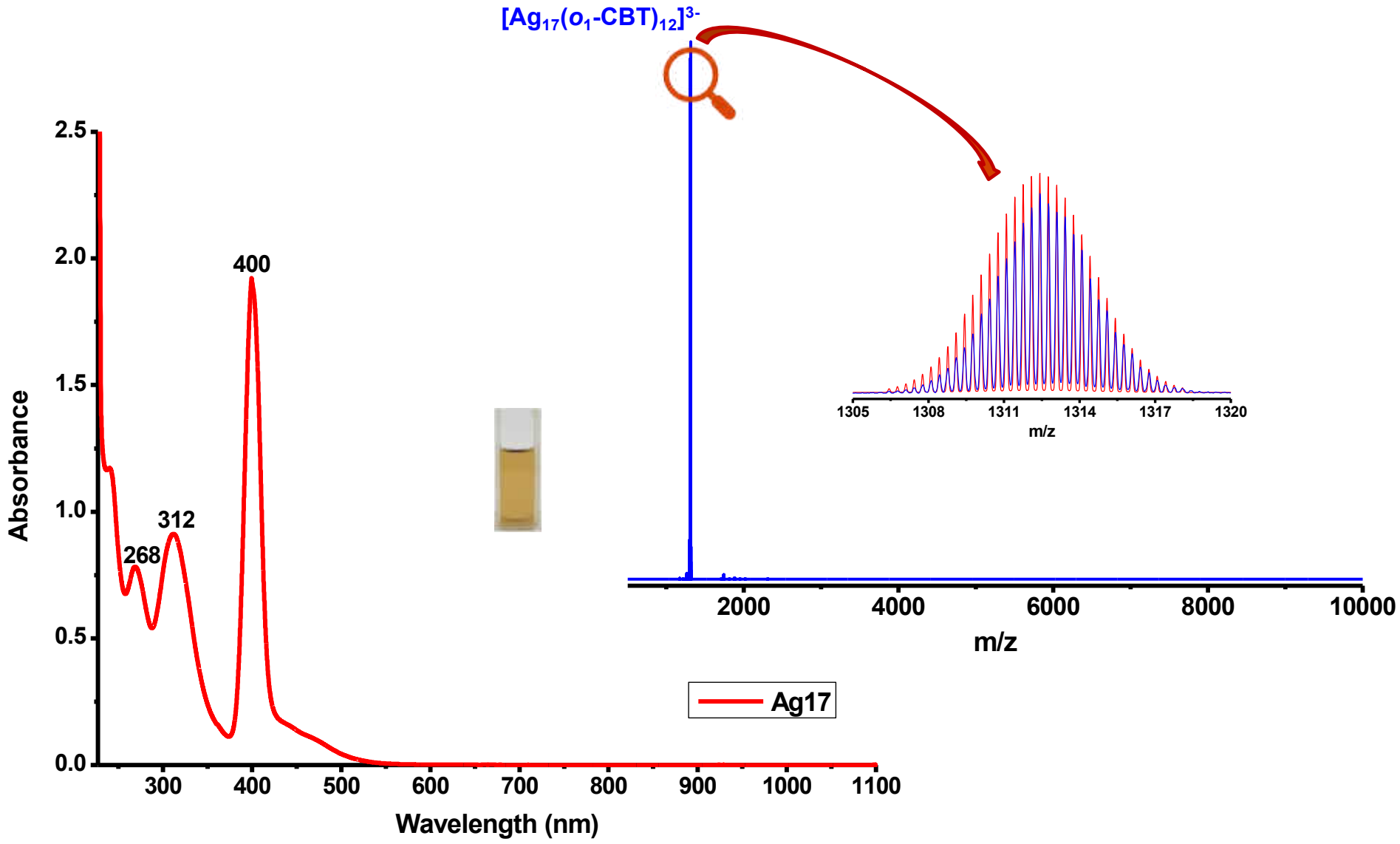
o_1-Carborane Thiol

$NaBH_4$

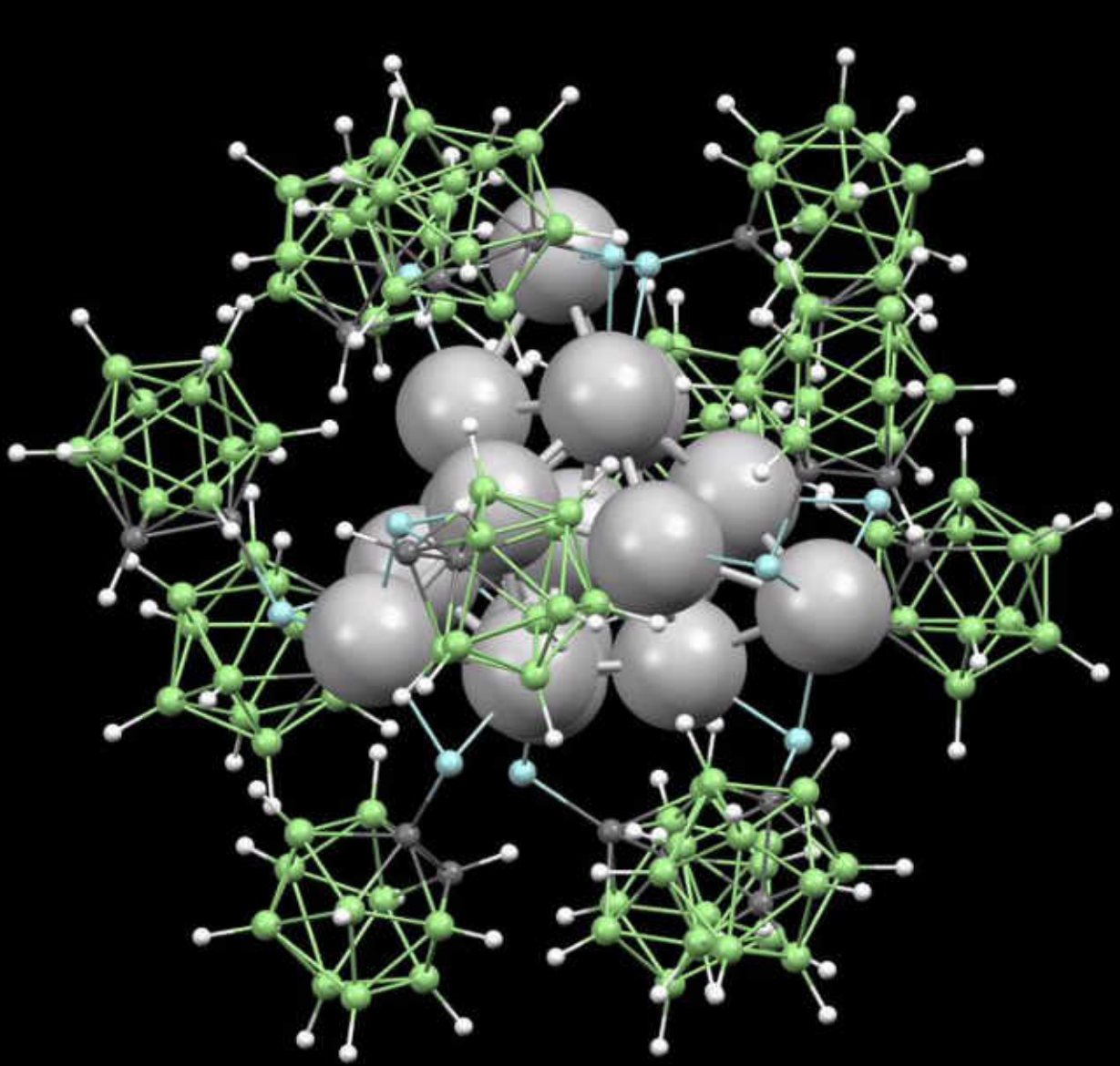


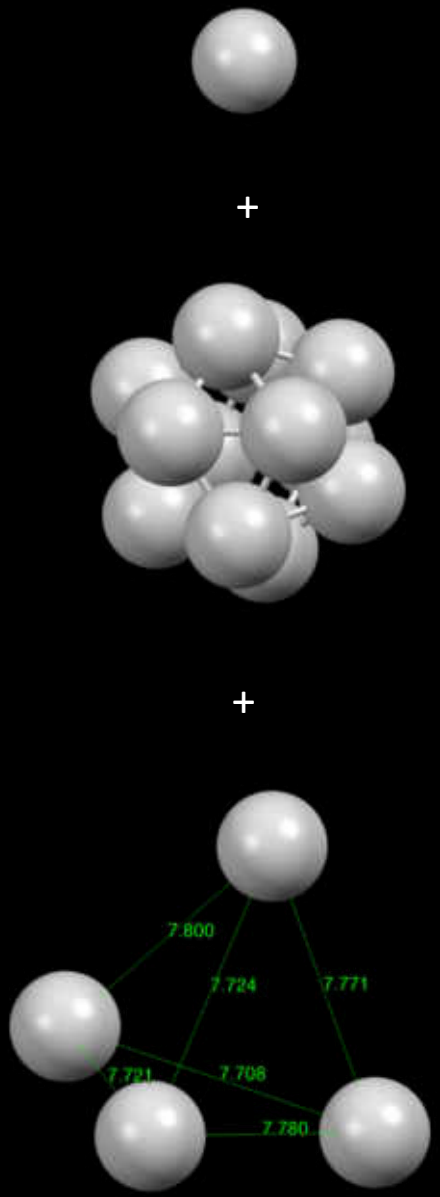
$[Ag_{17}(o_1\text{-CBT})_{12}]^{3-}$

Characterisation of $[Ag_{17}(o_1\text{-CBT})_{12}]^{3-}$ Nanocluster

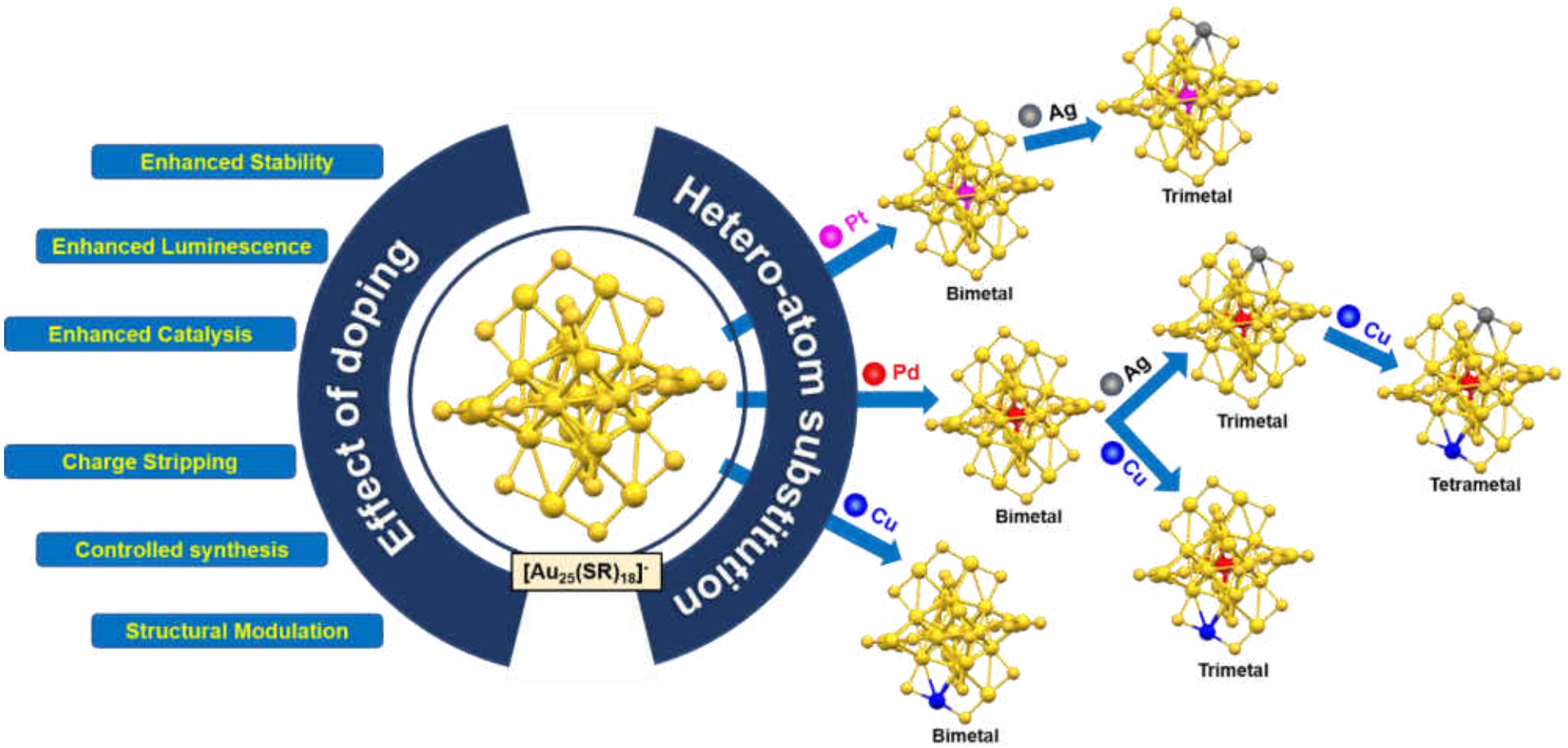


Structure of $[Ag_{17}(o_1\text{-}CBT)_{12}]^{3-}$ Nanocluster

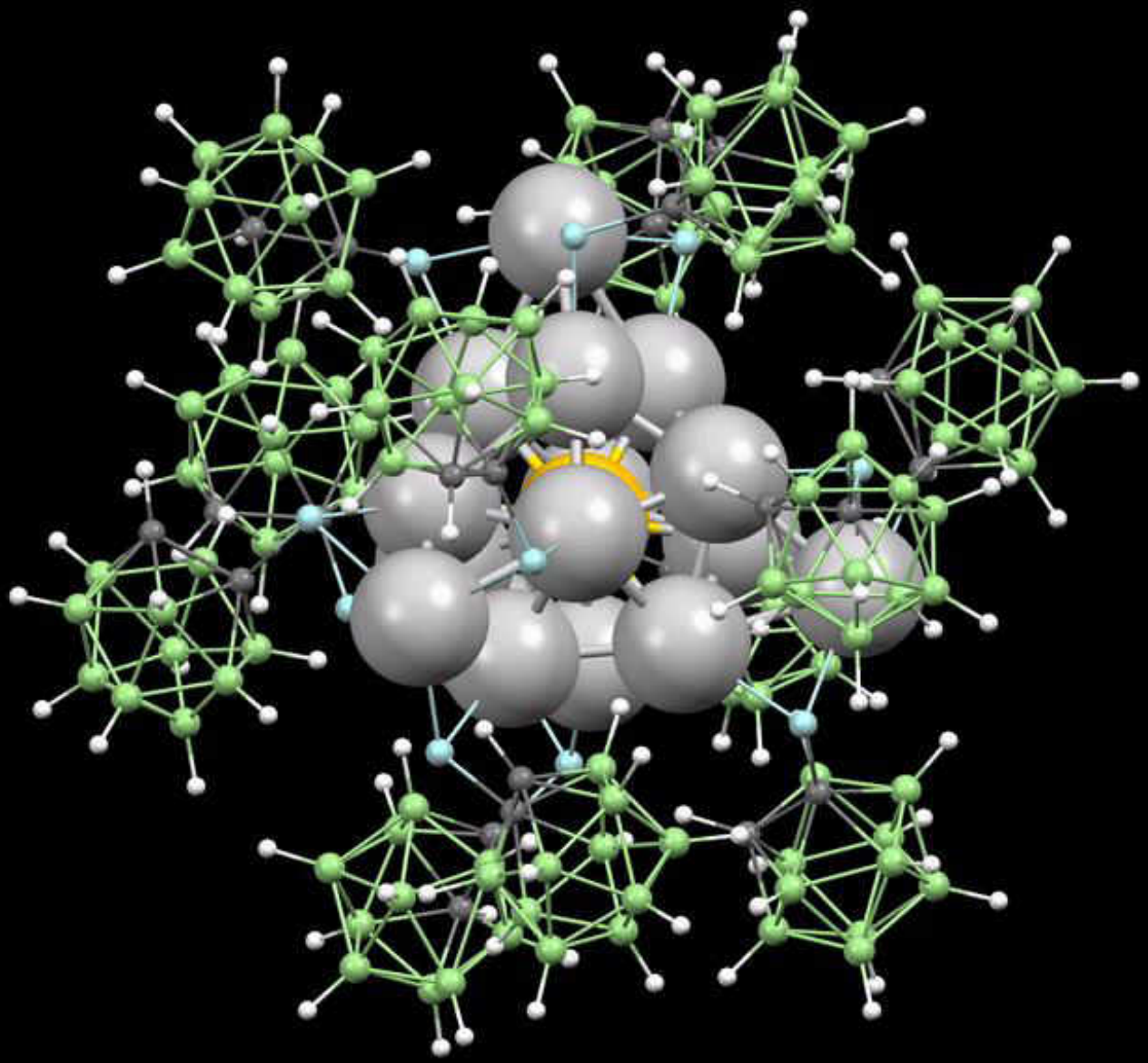




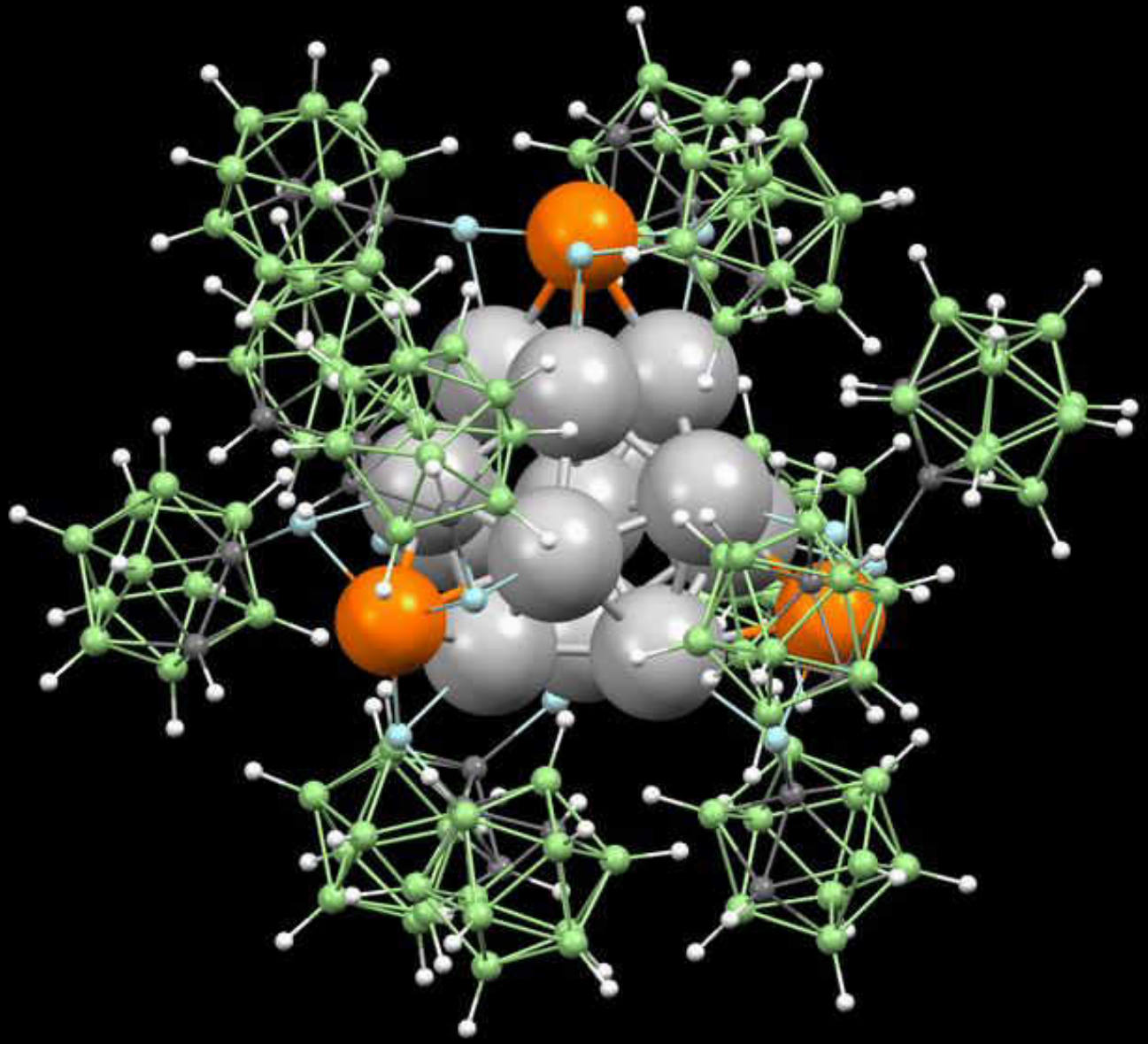
Alloying of Nanoclusters: The Work Plan



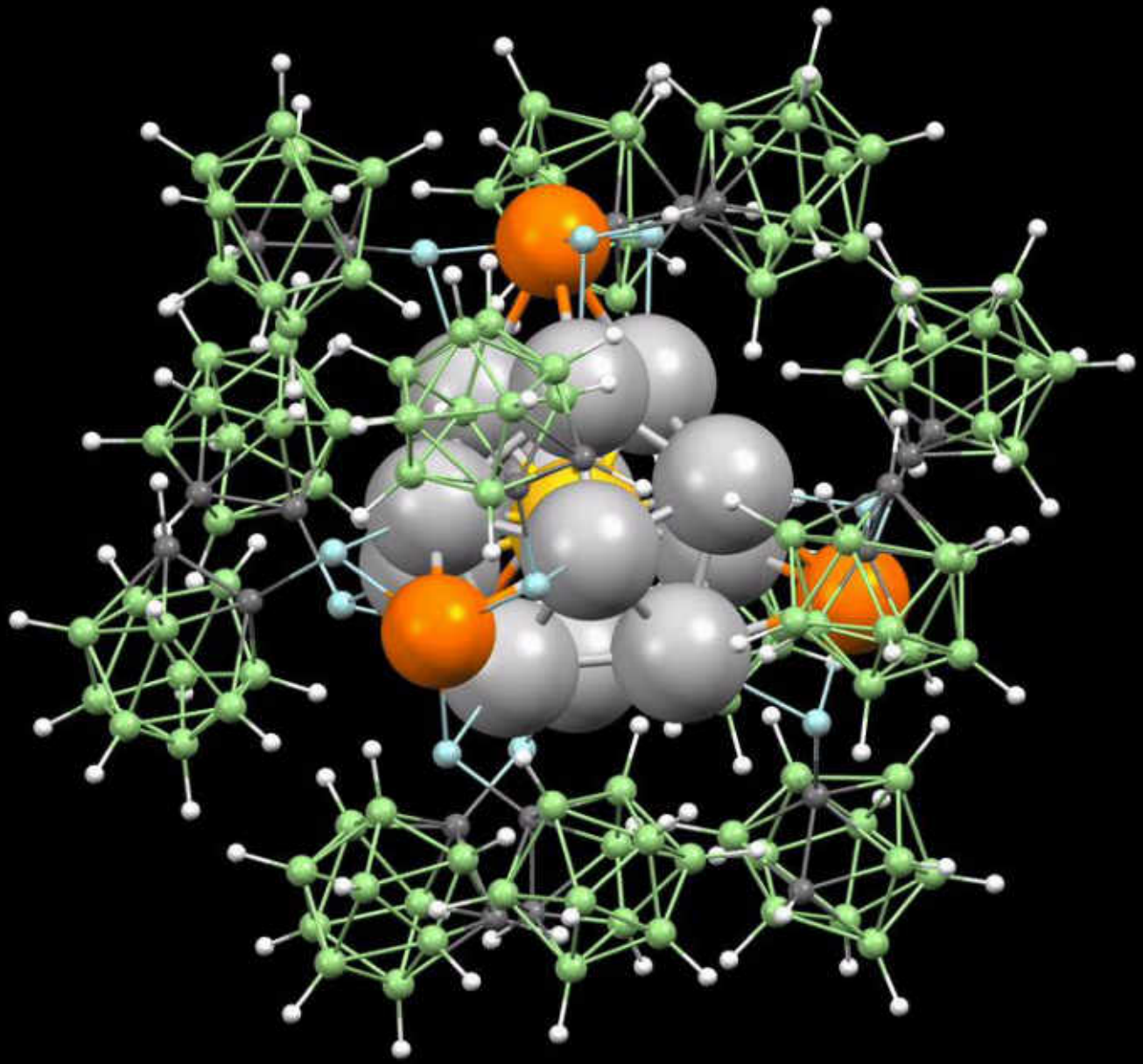
Structure of $AuAg_{16}$ Nanocluster



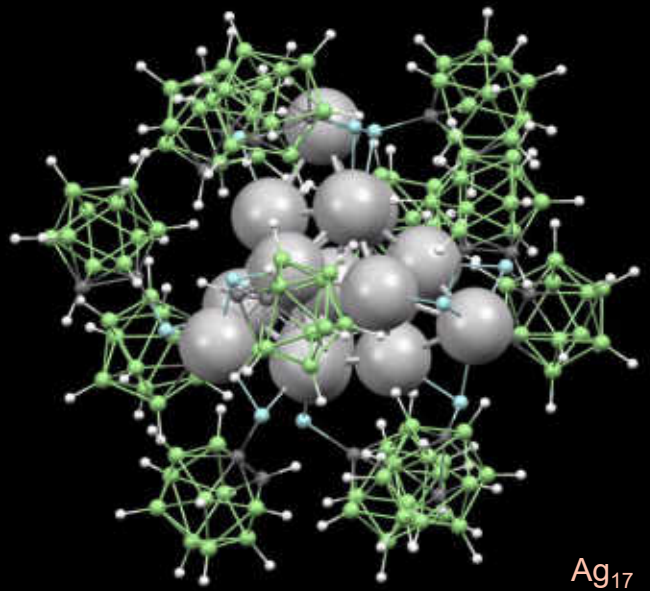
Structure of $Ag_{13}Cu_4$ Nanocluster



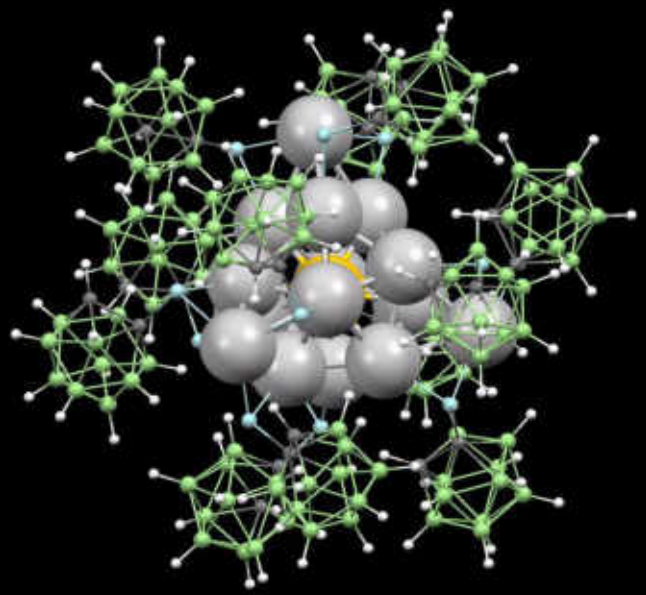
Structure of $AuAg_{12}Cu_4$ Nanocluster



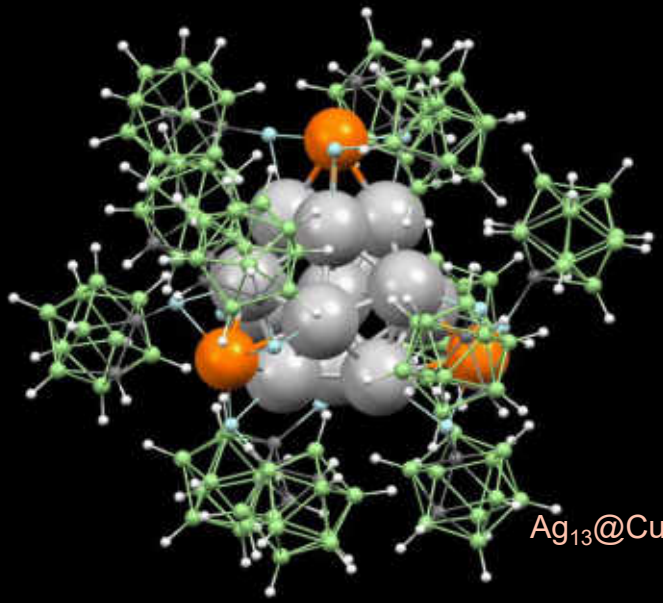
Structure of M_{17} Nanoclusters



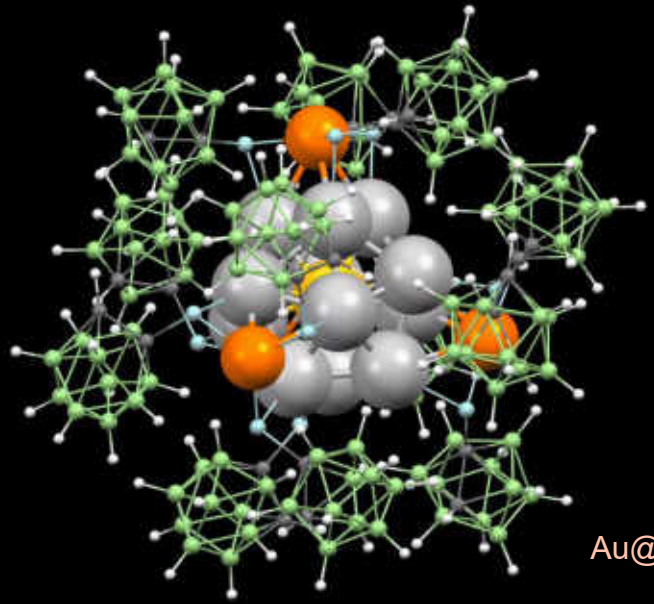
Ag_{17}



$Au@Ag_{16}$

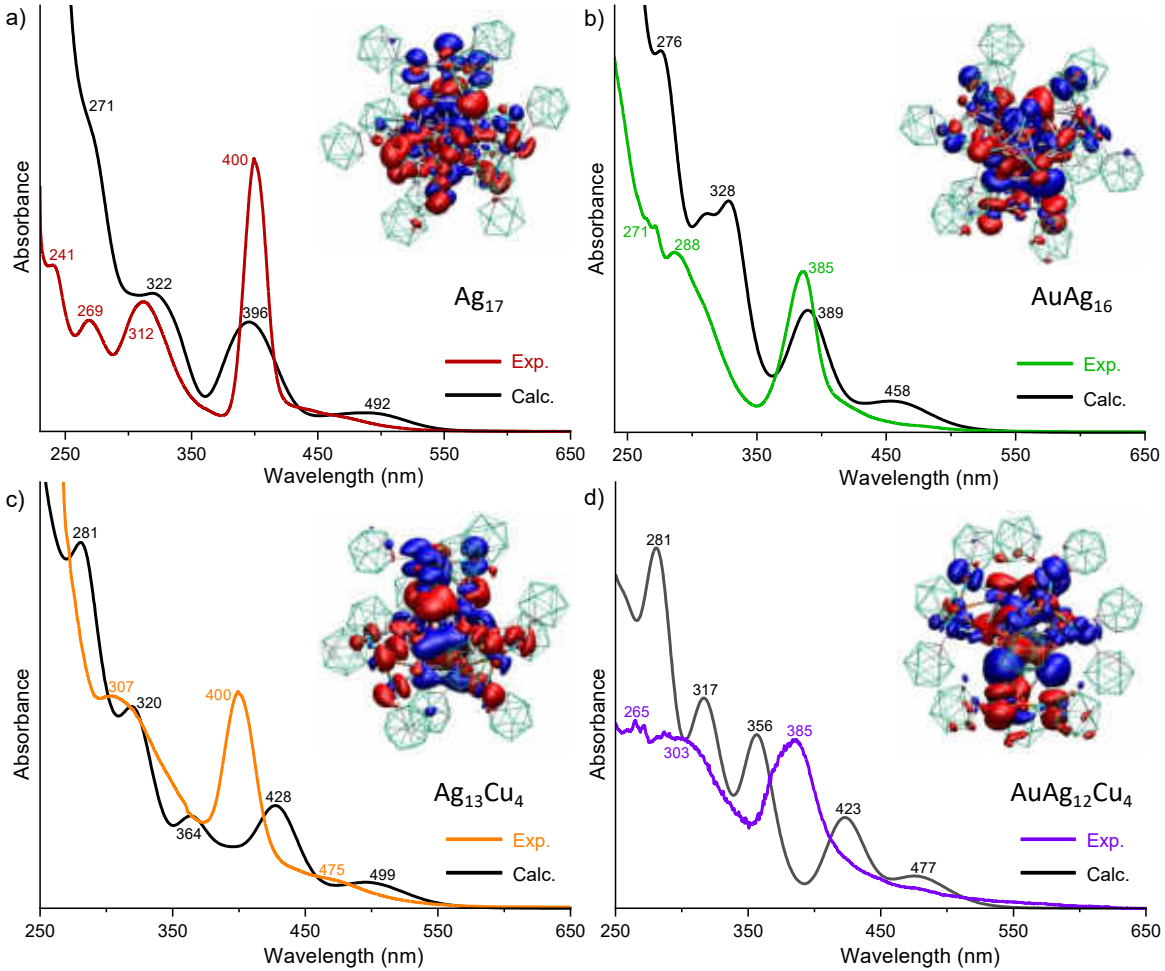


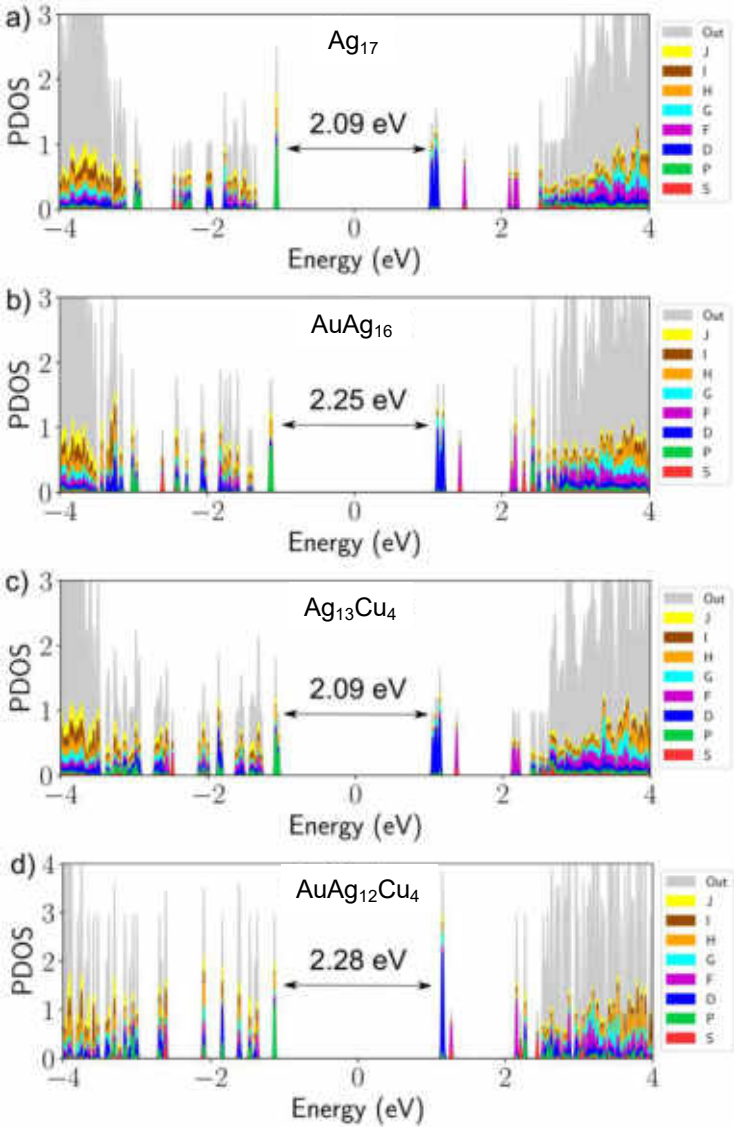
$Ag_{13}@Cu_4$



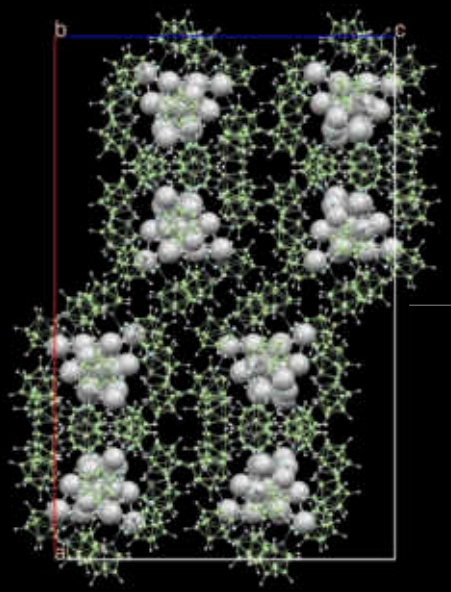
$Au@Ag_{12}@Cu_4$

Theoretical Understanding



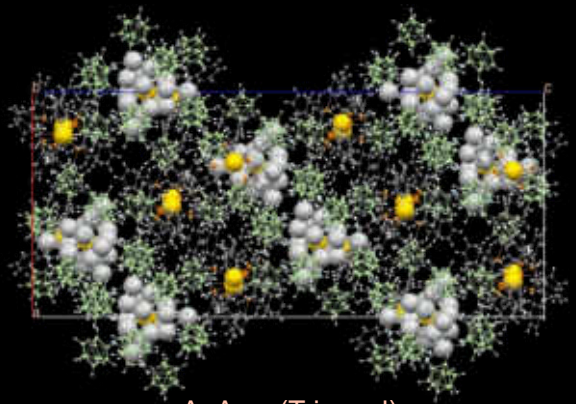


Packing of M_{17} Nanoclusters

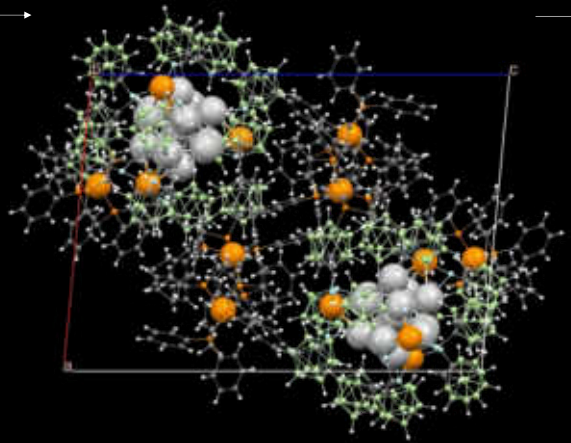


Ag_{17} (Orthorombic)

Bimetallic

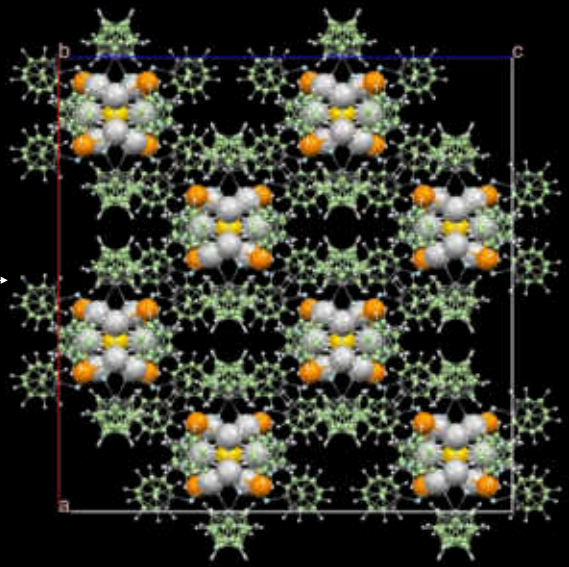


$AuAg_{16}$ (Trigonal)



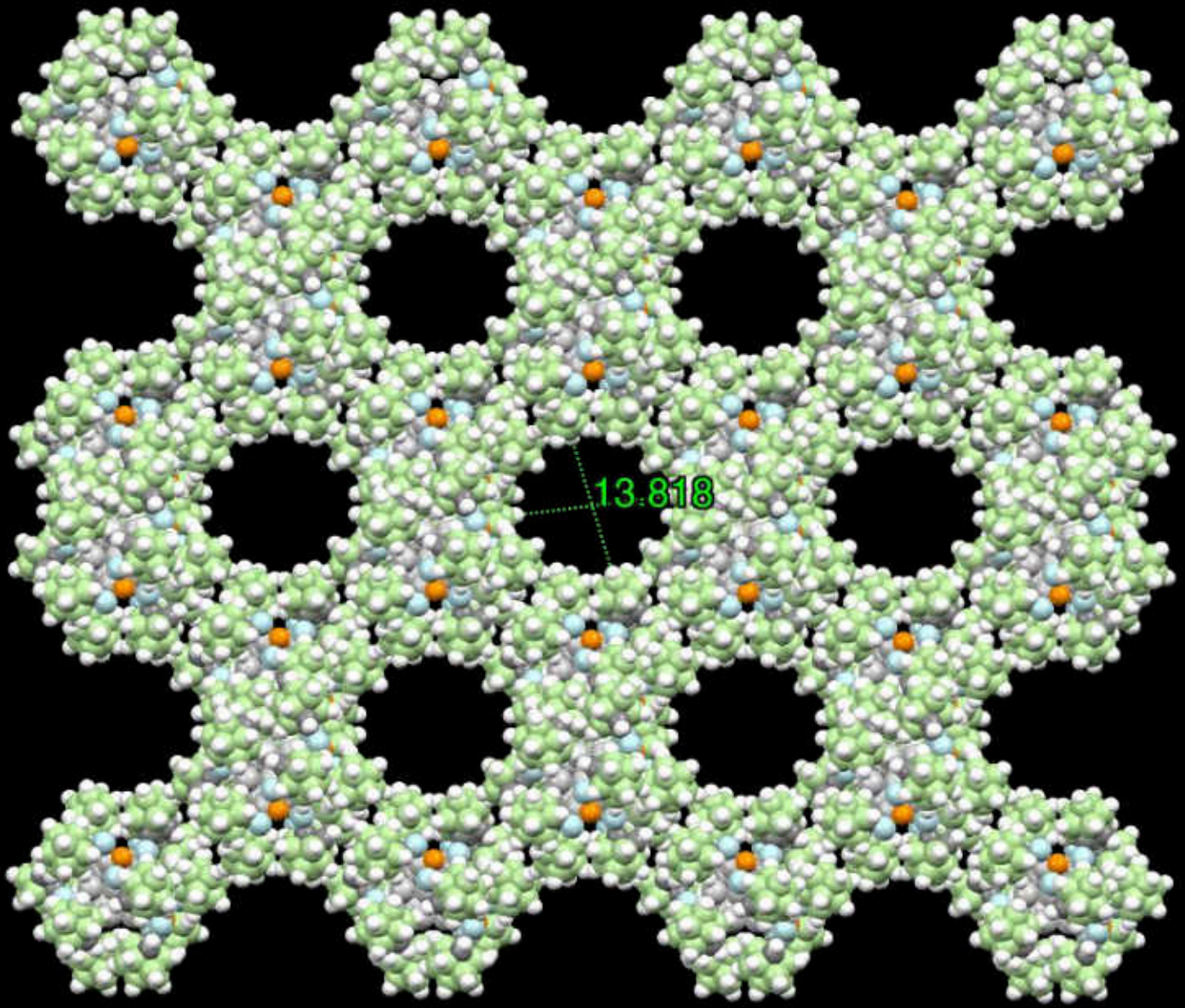
$Ag_{13}Cu_4$ (Triclinic)

Trimetallic

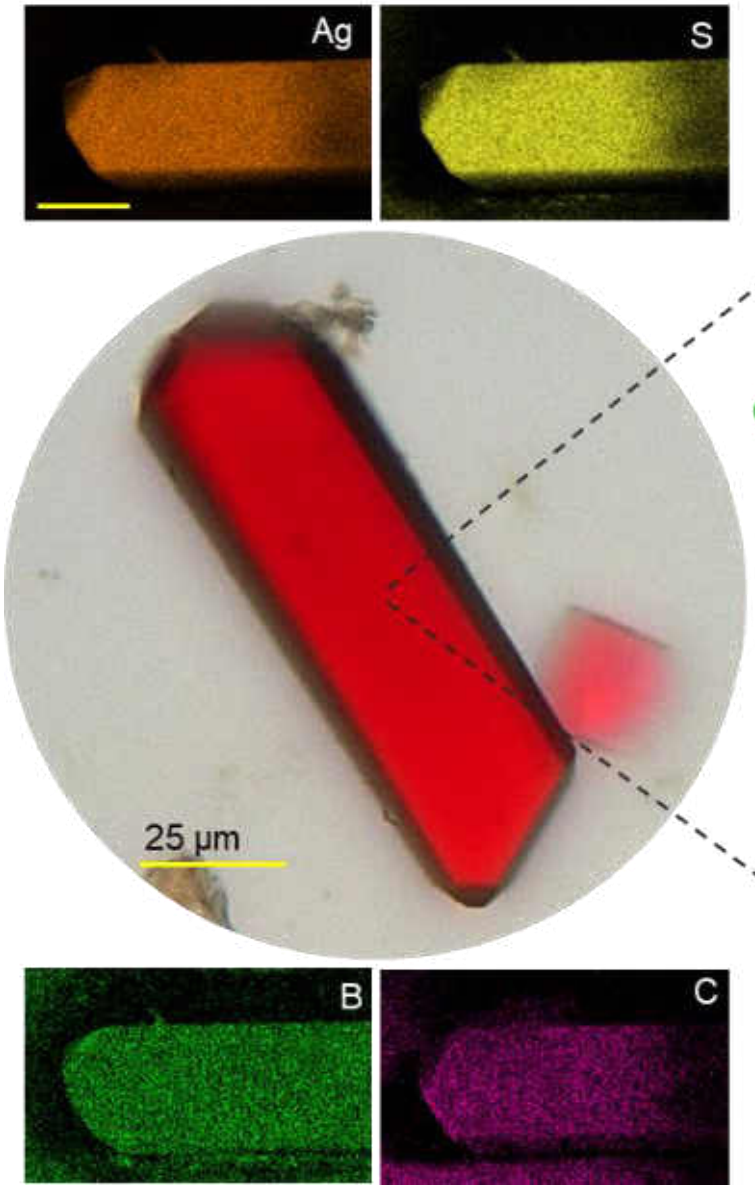


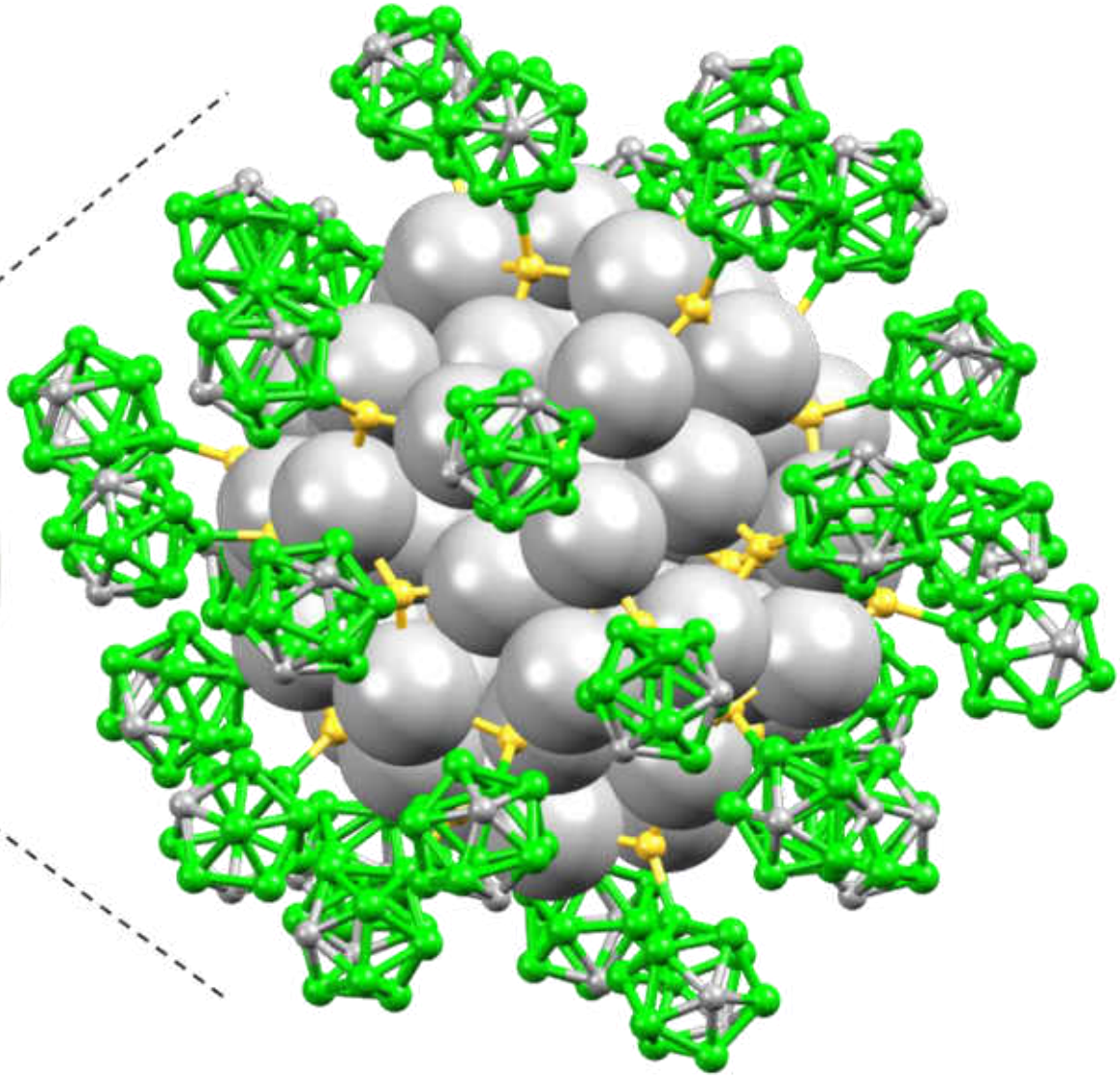
$AuAg_{12}Cu_4$ (Cubic)

Structural Pores of $AuAg_{12}Cu_4$ Nanoclusters



$[Ag_{62}S_{12}(CBT)_{32}]$ Nanocluster

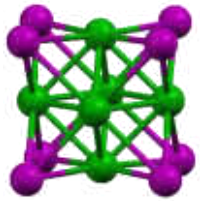




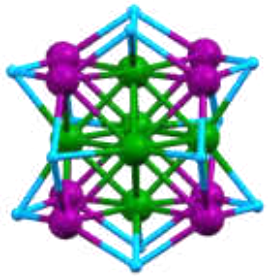
Largest molecule with carboranes so far……

Jana *et al.*, manuscript under preparation

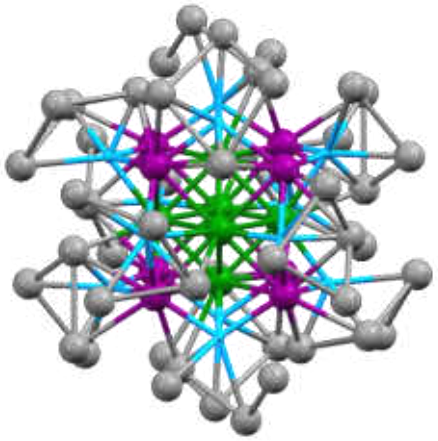
Structural anatomy of $[Ag_{62}S_{12}(CBT)_{32}]$ Nanocluster



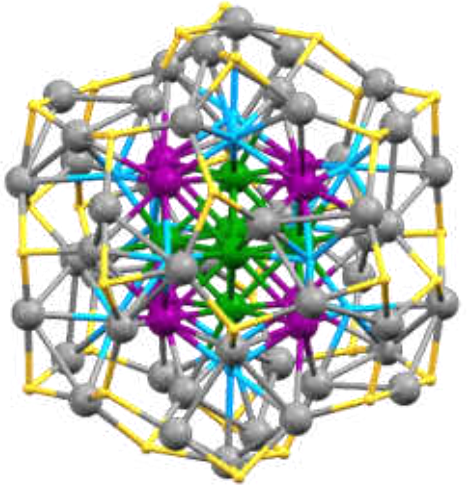
$Ag_6@Ag_8$



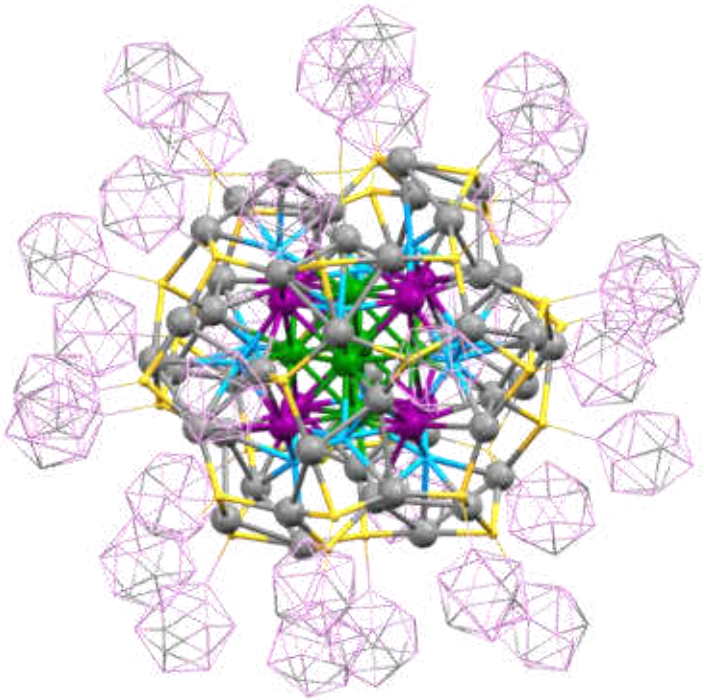
$Ag_6@Ag_8S_{12}$



$Ag_6@Ag_8S_{12}@Ag_{48}$

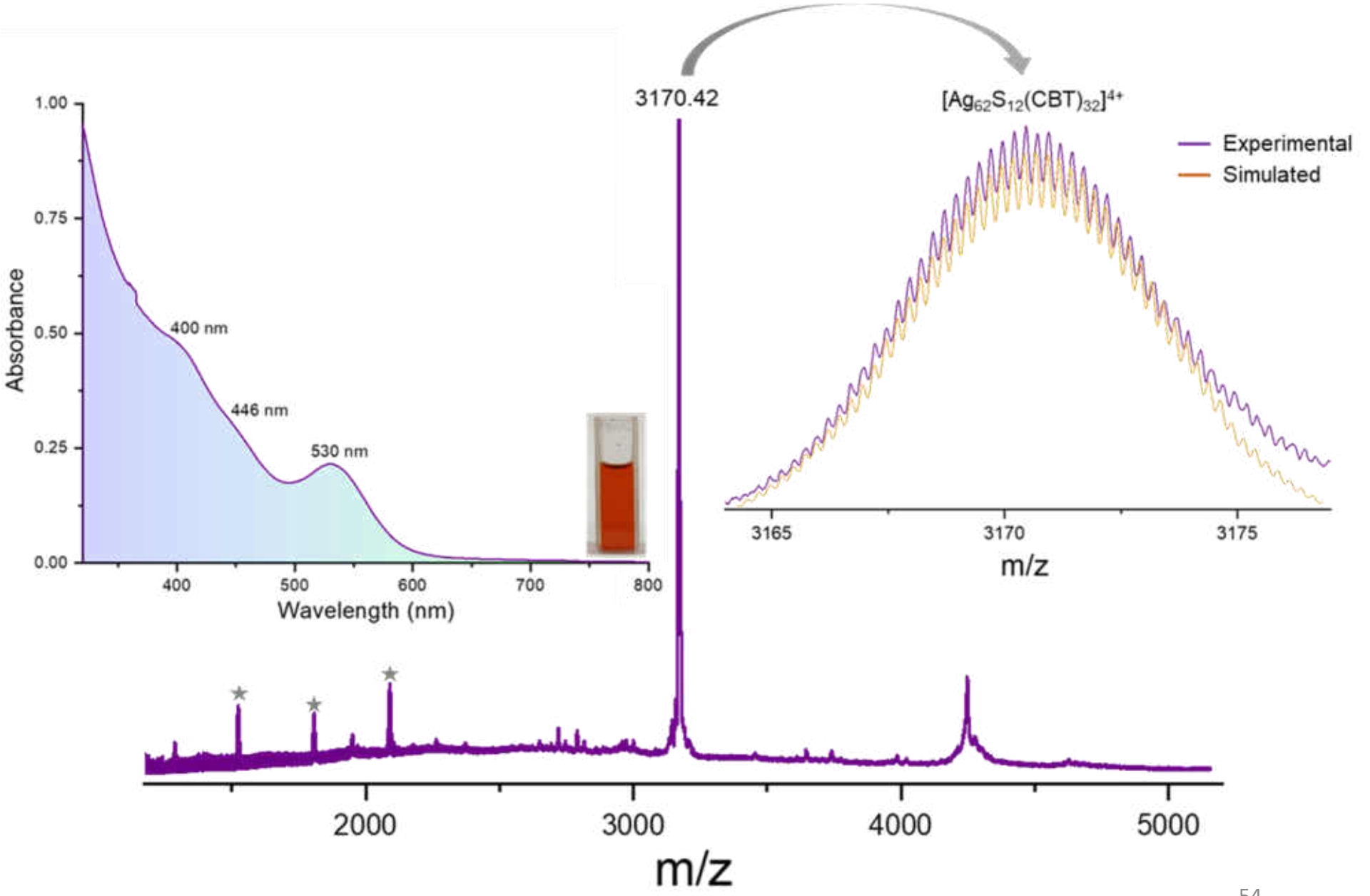


$Ag_6@Ag_8S_{12}@Ag_{48}S_{32}$



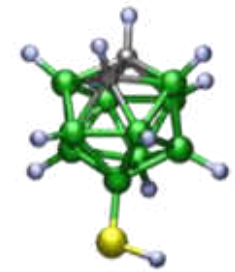
$Ag_6@Ag_8S_{12}@Ag_{48}S_{32}(CB)_{32}$

Characterization of Ag_{62} cluster

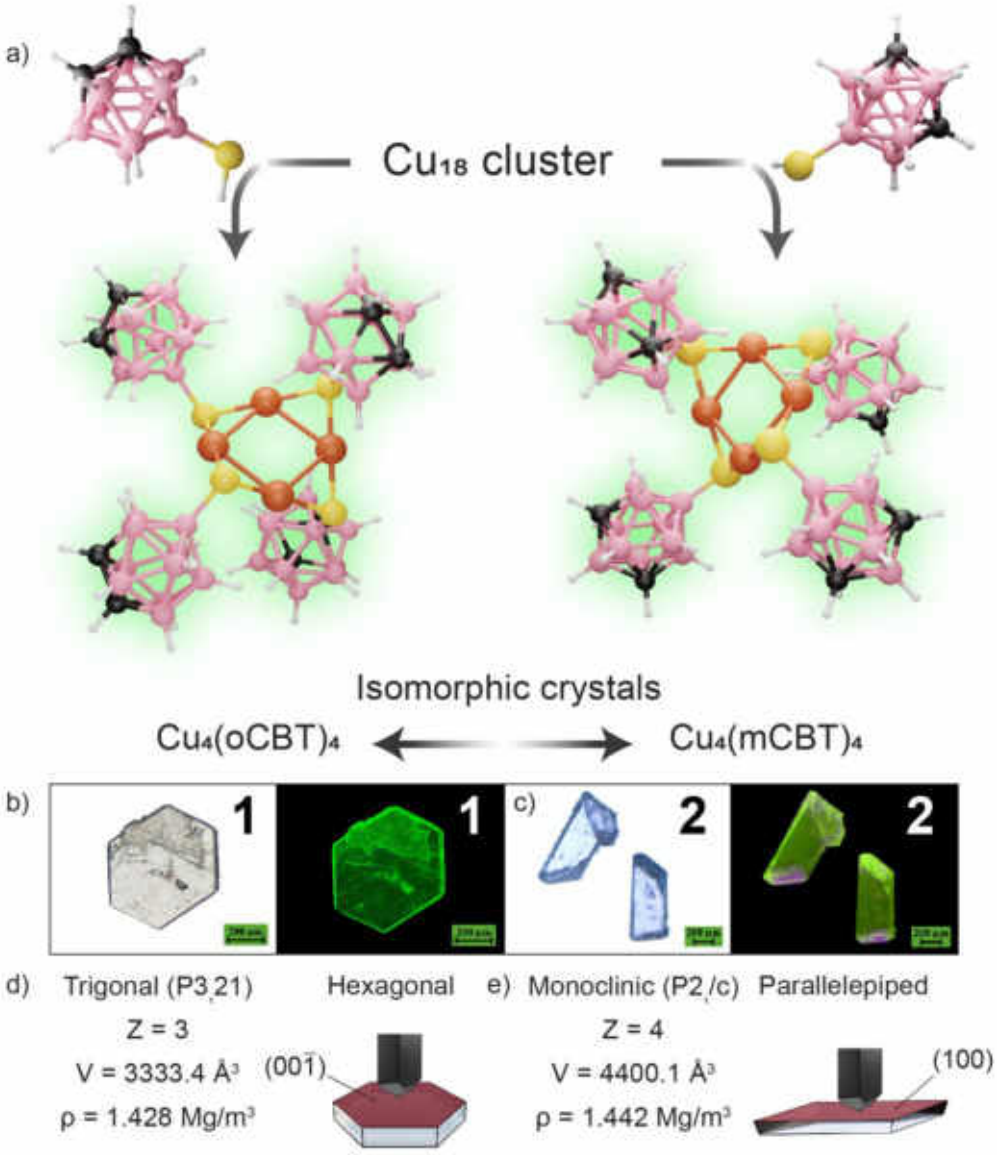


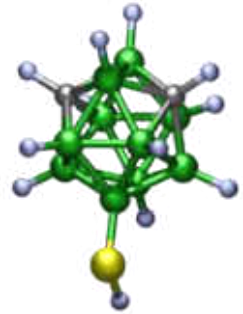
Properties

Nanomechanical Properties of Cu_4 Nanoclusters



9-HS-1,2-$C_2B_{10}H_{11}$

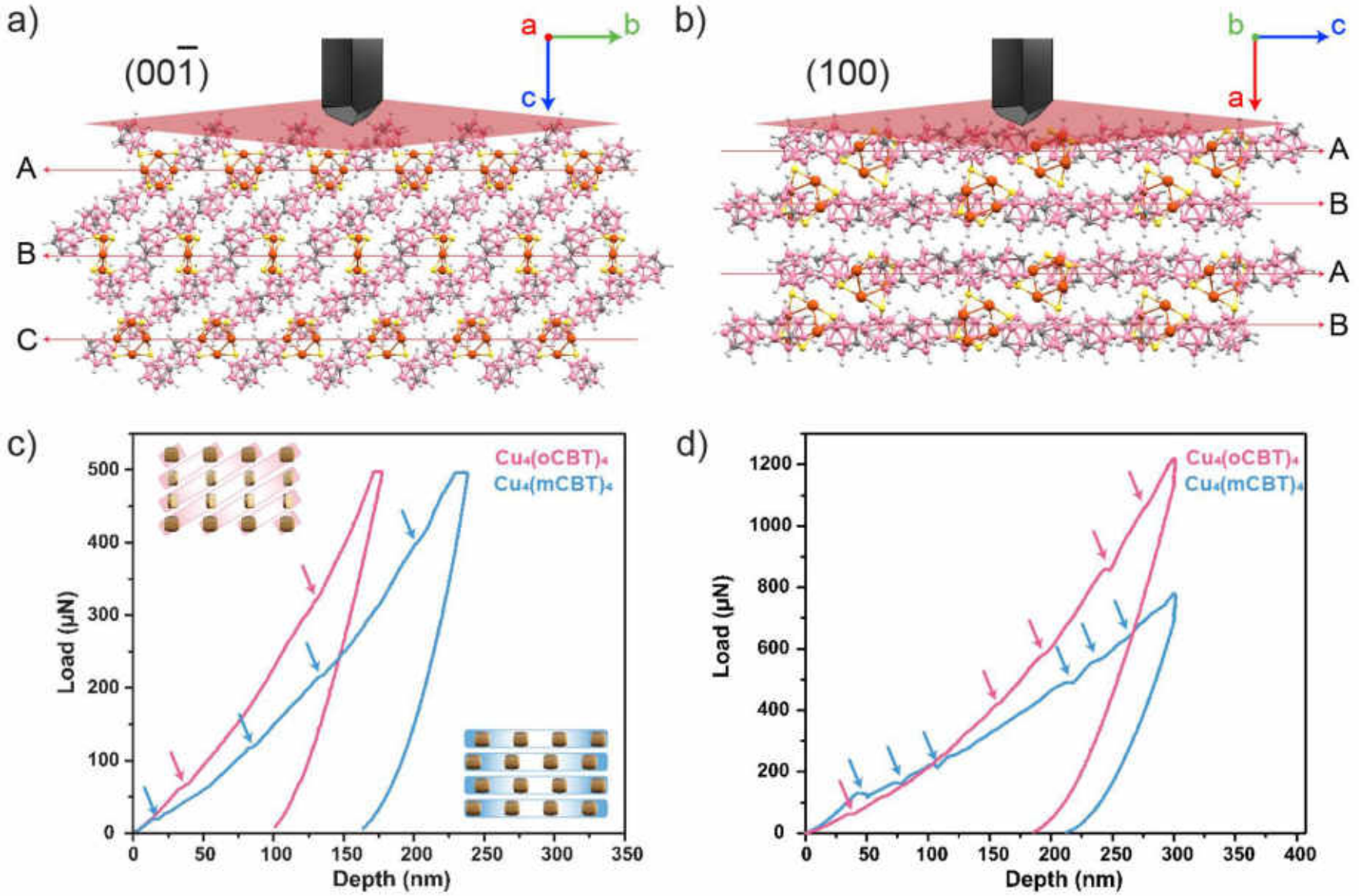




9-HS-1,7-$C_2B_{10}H_{11}$

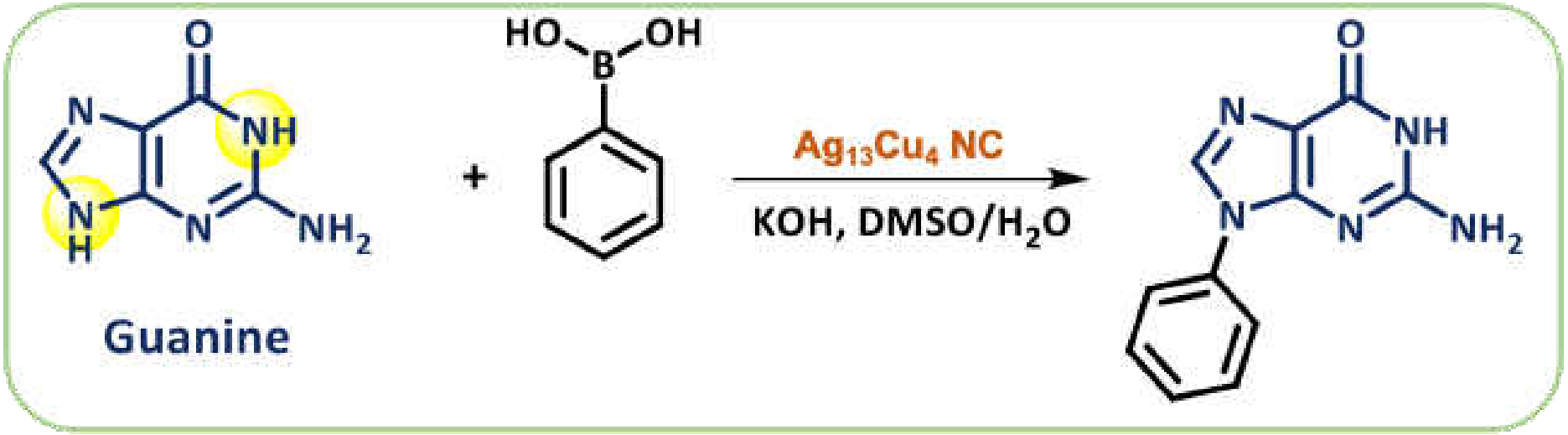
Amoghavasha Ramachandra Kini, et. al., *Chem. Mater.*, Revised (submitted)

Nanomechanical Properties of Cu_4 Nanoclusters



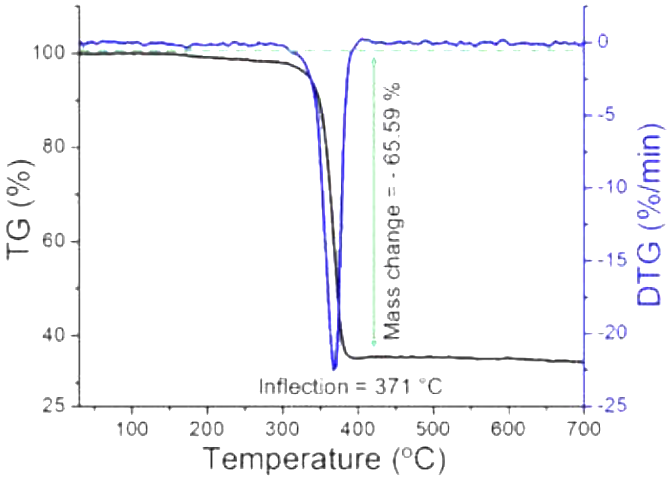
Catalysis by $Ag_{13}Cu_4$ Nanoclusters

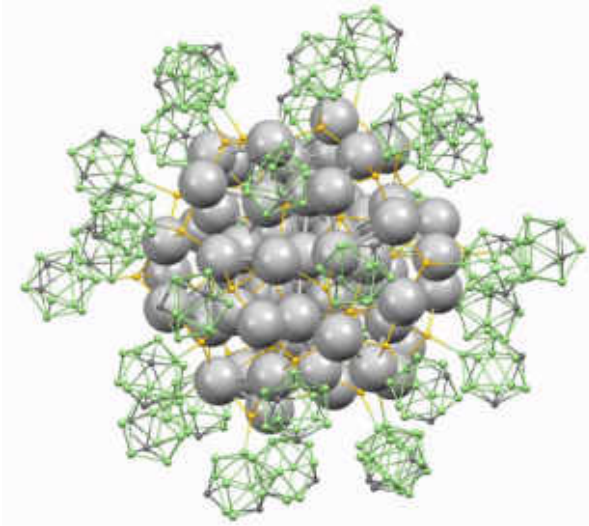
- **Direct N^9-arylation of Guanine with Phenylboronic Acid Catalyzed by Cu-doped Silver Nanocluster**



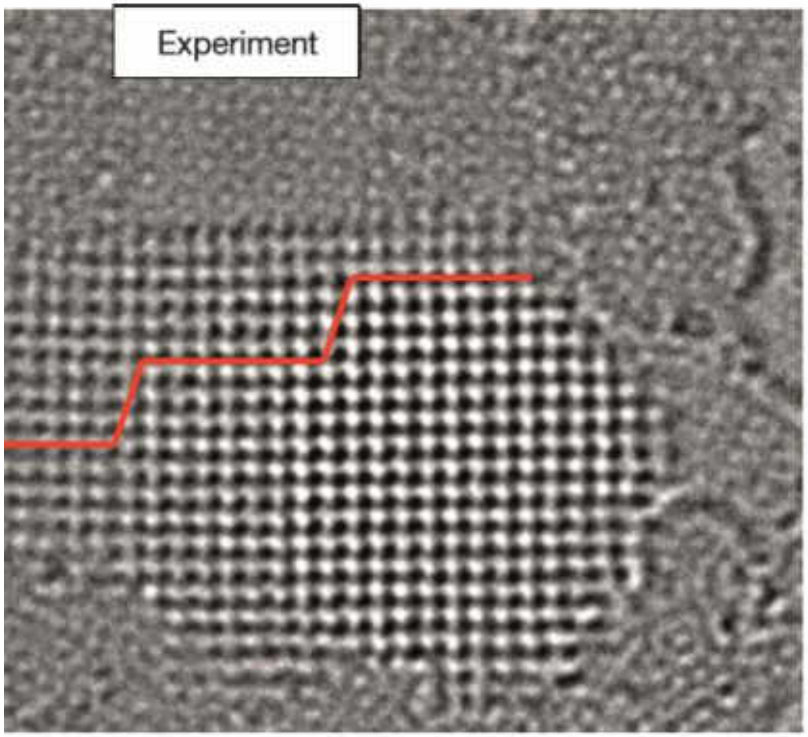
Summary

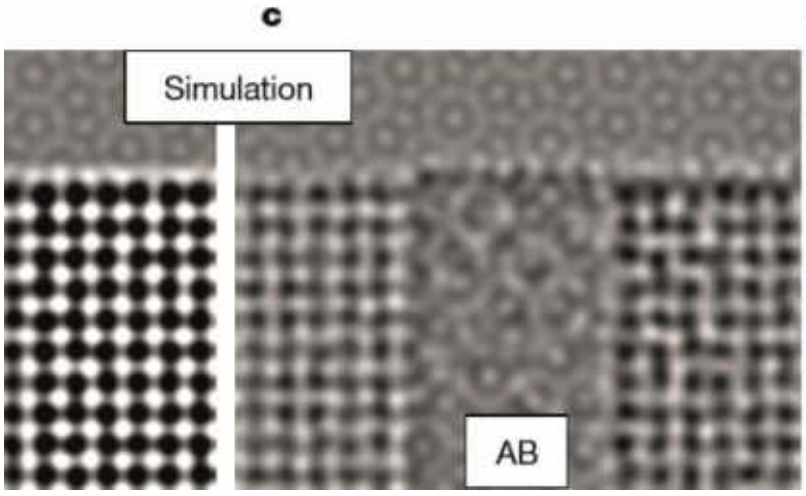
- Carborane protected nanoclusters are versatile.
- Clusters are thermally stable up to 400°C.
- Comparatively larger crystals are available for experiments.
- Nuclearity up to Ag_{62} is now known.
- Need to explore new properties – electrical and thermal conductivity
- Limitation: Need to expand to Au clusters; beyond the reports on Au_{28} and Au_{23}.

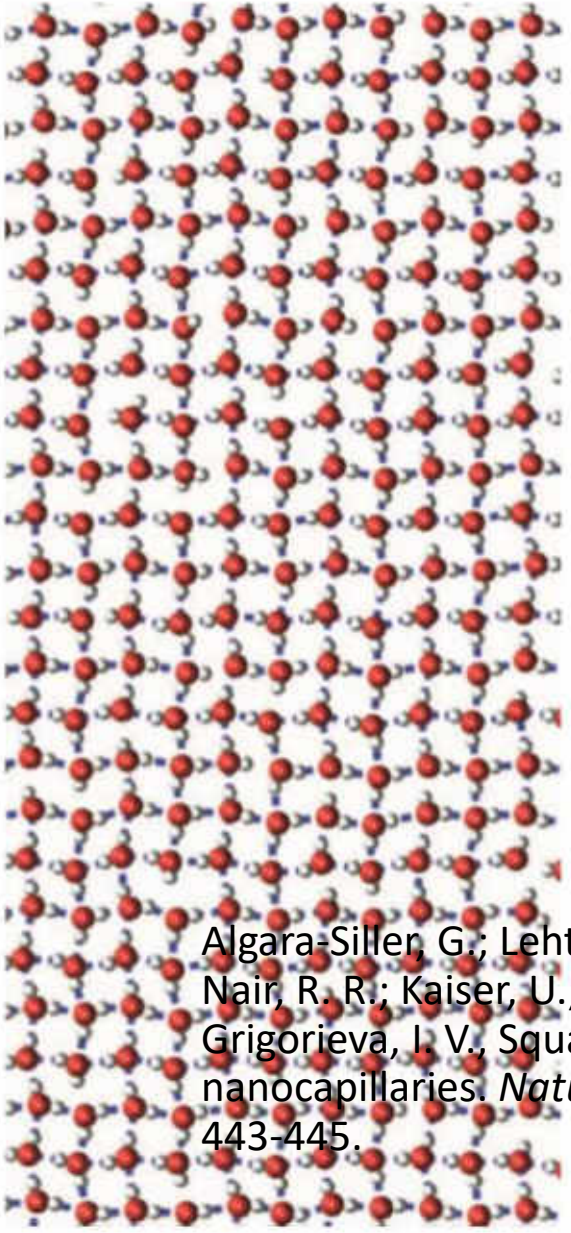




Observing Molecules



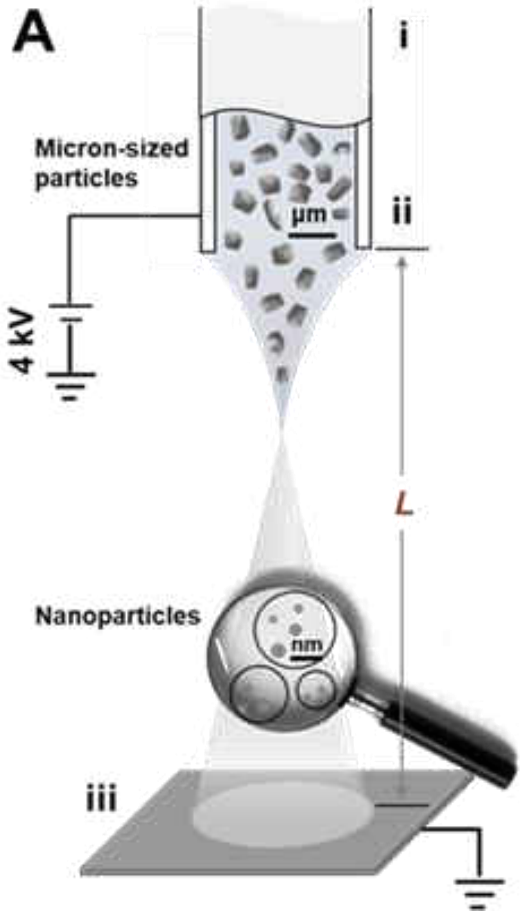


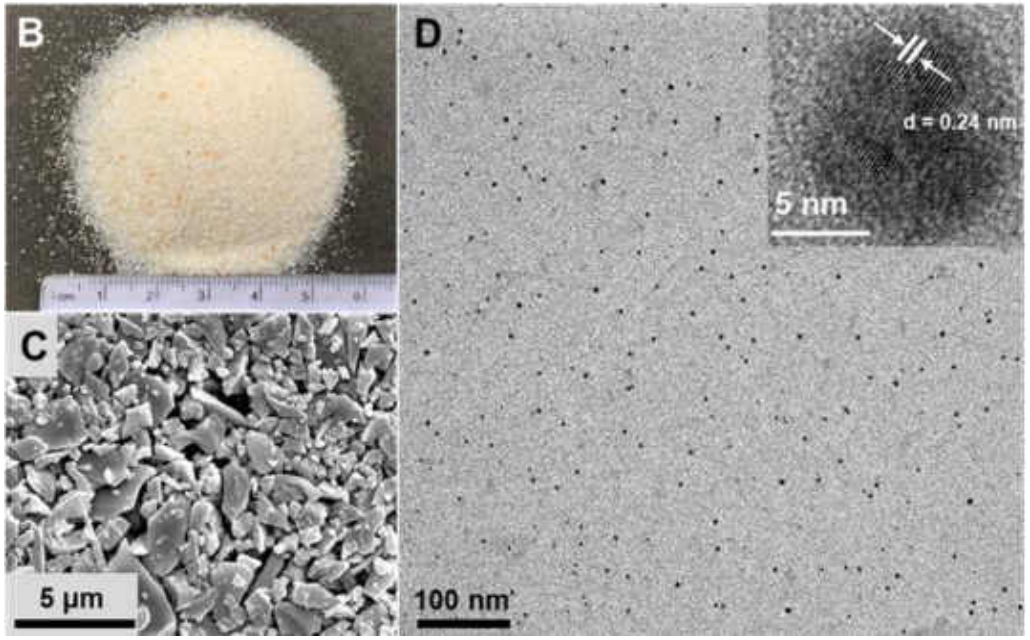


Algara-Siller, G.; Lehtinen, O.; Wang, F. C.; Nair, R. R.; Kaiser, U.; Wu, H. A.; Geim, A. K.; Grigorieva, I. V., Square ice in graphene nanocapillaries. *Nature* **2015,** *519* (7544), 443-445.

Weathering of Minerals in Microdroplets

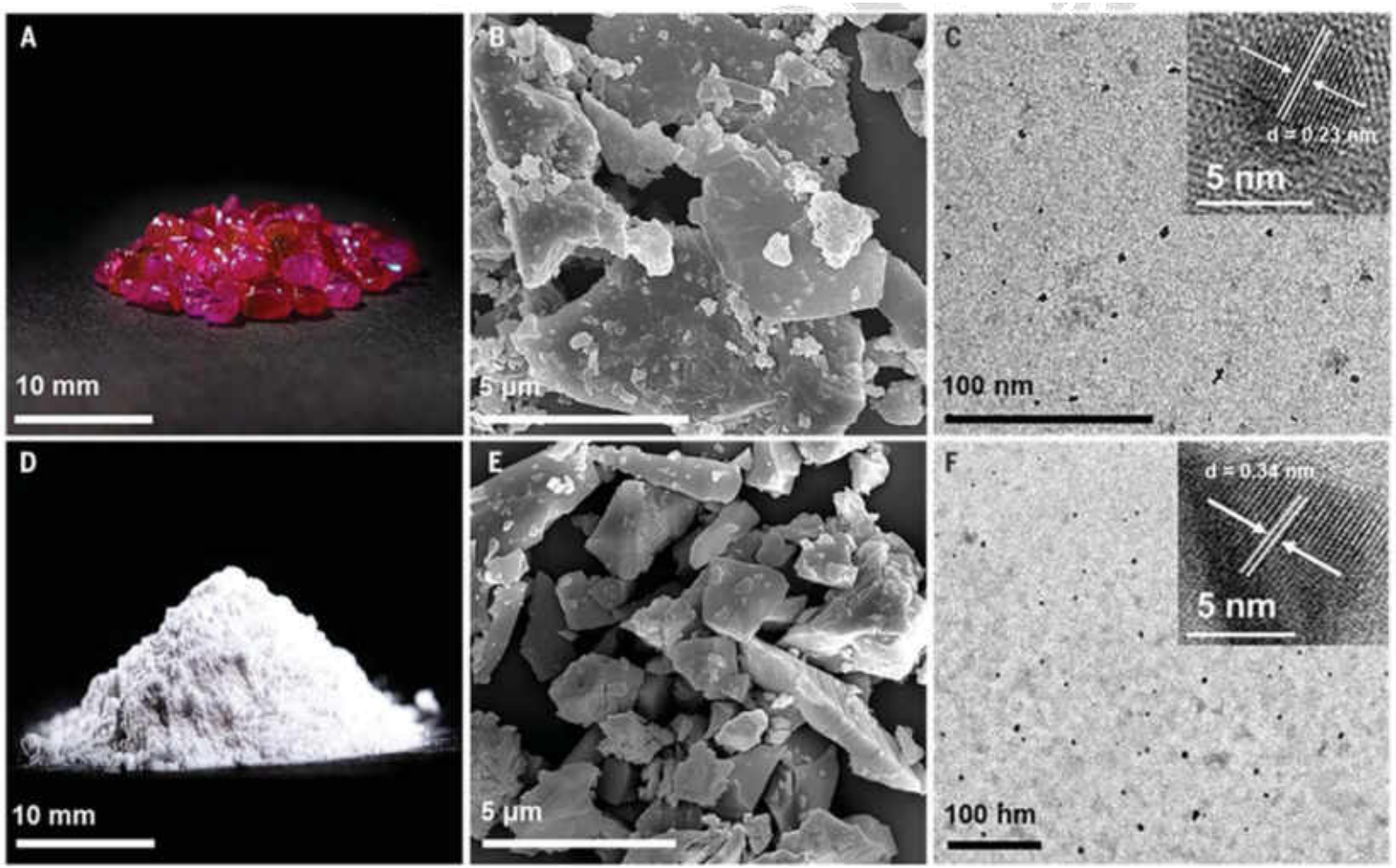
Spontaneous Weathering of Natural Minerals in Charged Water Microdroplets Forms Nanomaterials



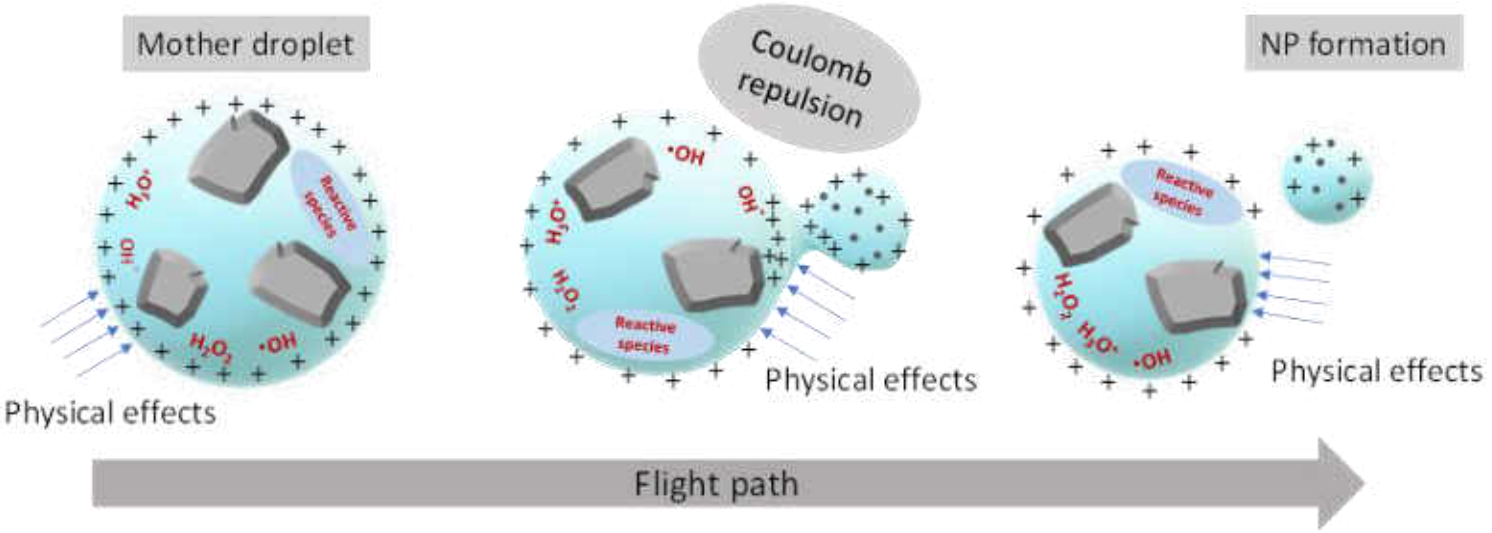


Spoorthi, et. al., *Science*, 384 (2024) 1012-1017.

Ruby, Fused Alumina



Mechanism of nanoparticle formation



Collaborators

Pictures of Arijit, Vivek, Amogh and Deepak

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Institute of Inorganic Chemistry

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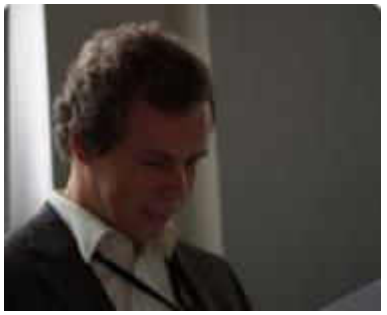
Keisaku Kimura Yuichi Negishi
Uzi Landman Hannu Hakkinen Rob Whetten

Shiv Khanna

Robin Ras

Nonappa



Tomas Base

Manfred Kappes

Olli Ikkala

Horst Hahn

Biswarup Pathak

K. V. Adarsh

G. U. Kulkarni

Vivek Polshettiwar

Noble Metal Nanoparticles

Gordon Research Conference

June 17 - 22, 2012

Chair
Michael J. Natan

Vice Chair
Francesco Stellacci

Mount Holyoke College
50 College Street
South Hadley, Massachusetts,
United States

Venue and Travel Information

7:30 pm - 9:30 pm	**Clusters**
	Discussion Leader: **Royce Murray** (University of North Carolina)
7:30 pm - 7:40 pm	**Royce Murray** (University of North Carolina) "Session Introduction"
7:40 pm - 8:05 pm	**Tatsuya Tsukuda** (Hokkaido University) "Gold cluster compounds: from isolation to controlled synthesis"
8:05 pm - 8:20 pm	Discussion
8:20 pm - 8:40 pm	**Olga Lopez-Acevedo** (Aalto University) "Simulation of protected and stabilized metal cluster electronic properties"
8:40 pm - 8:50 pm	Discussion
8:50 pm - 9:15 pm	**Thalappil Pradeep** (Indian Institute of Technology) "Au_{25}, Au_{38} and Au_{102}: Naked cores of stable noble metal clusters derived from protein templates"
9:15 pm - 9:30 pm	Discussion

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GRC

Atomically Precise Nanochemistry

Gordon Research Conference

Diversity, Symmetry and Functions of Molecular Materials

February 4 - 9, 2024

Chairs
Thalappil Pradeep and Stefanie S. Dehnen

Vice Chairs
Stacy Copp and Hannu Häkkinen

Contact Chairs

Grand Galvez
2024 Seawall Boulevard
Galveston, Texas, United States

Venue and Travel Information

Conference Description

The Atomically Precise Nanochemistry GRC is a premier, international scientific conference focused on advancing the frontiers of science through the presentation of cutting-edge and unpublished research, prioritizing time for discussion after each talk and fostering informal interactions among scientists of all career stages. The conference program includes a diverse range of speakers

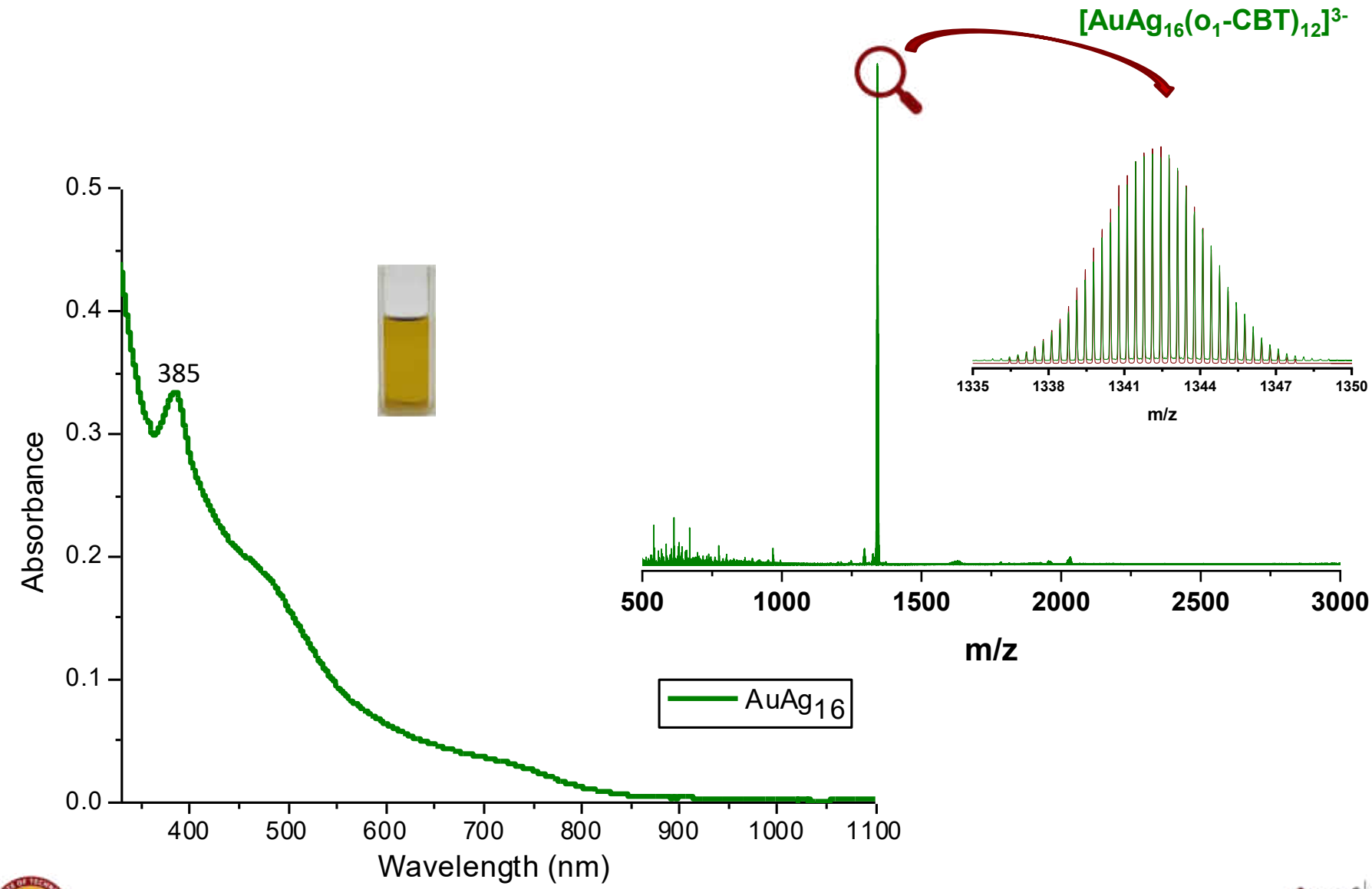
Conference Links

» Conference History
» Atomically Precise Nanochemistry (GRS)

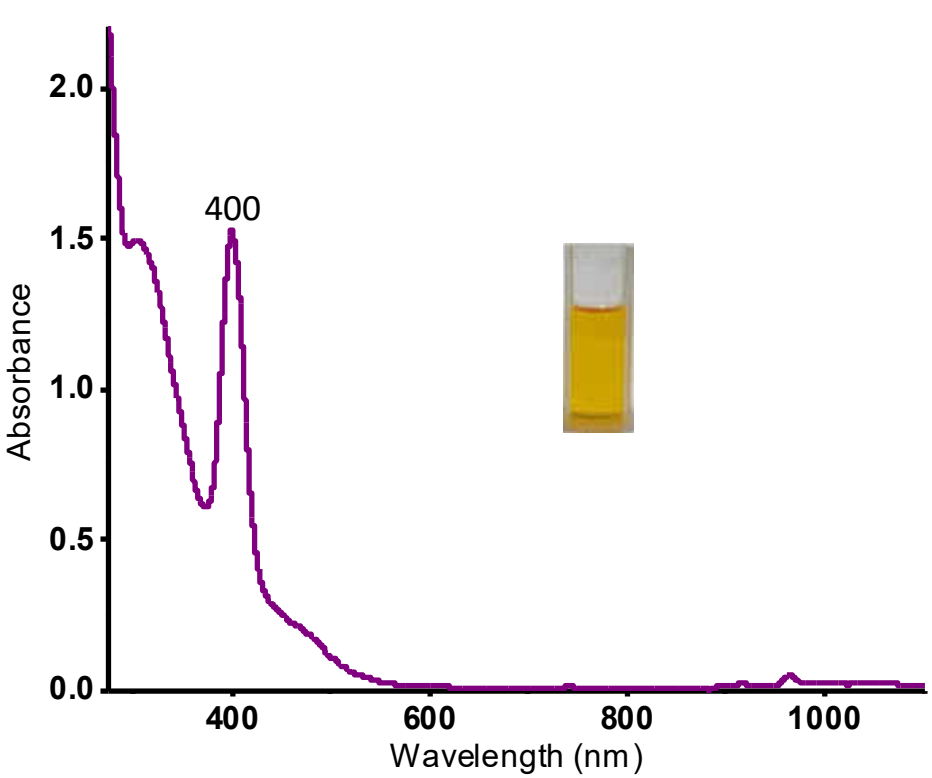
Pradeep Research Group

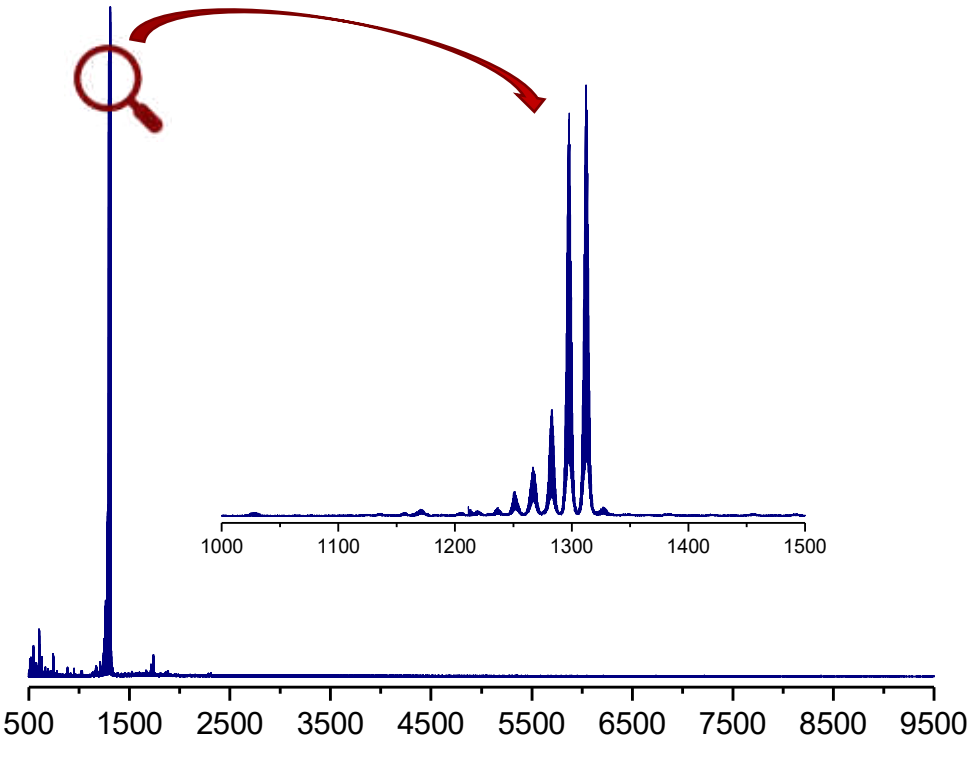
सत्यमेव जयते
Department of Science & Technology
Government of india

Incorporation of Au in Ag_{17}

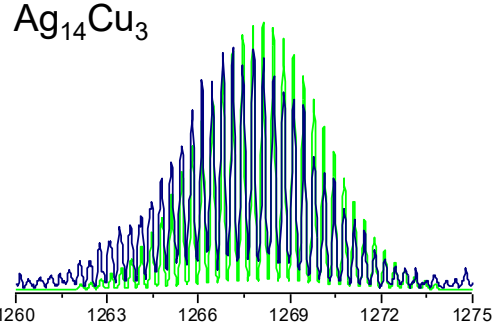


Incorporation of Cu in Ag_{17}

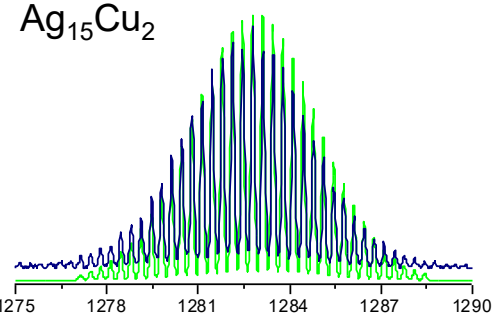




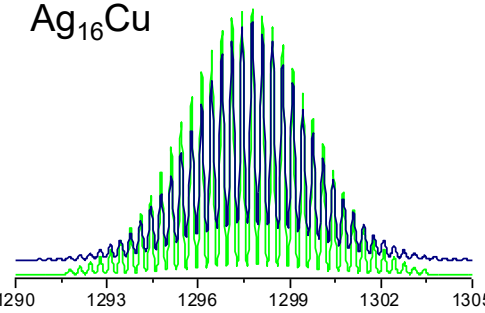
$Ag_{14}Cu_3$



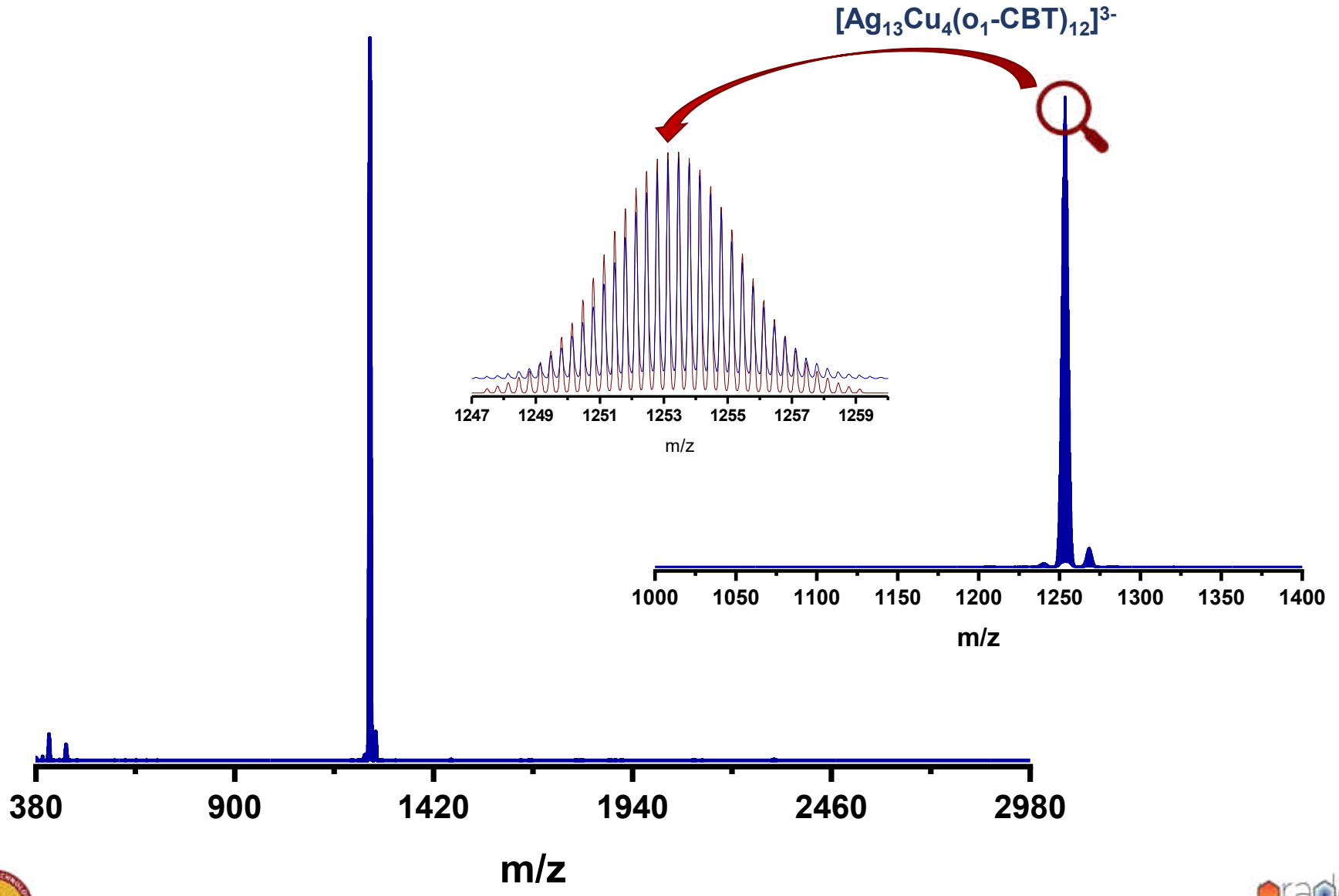
$Ag_{15}Cu_2$



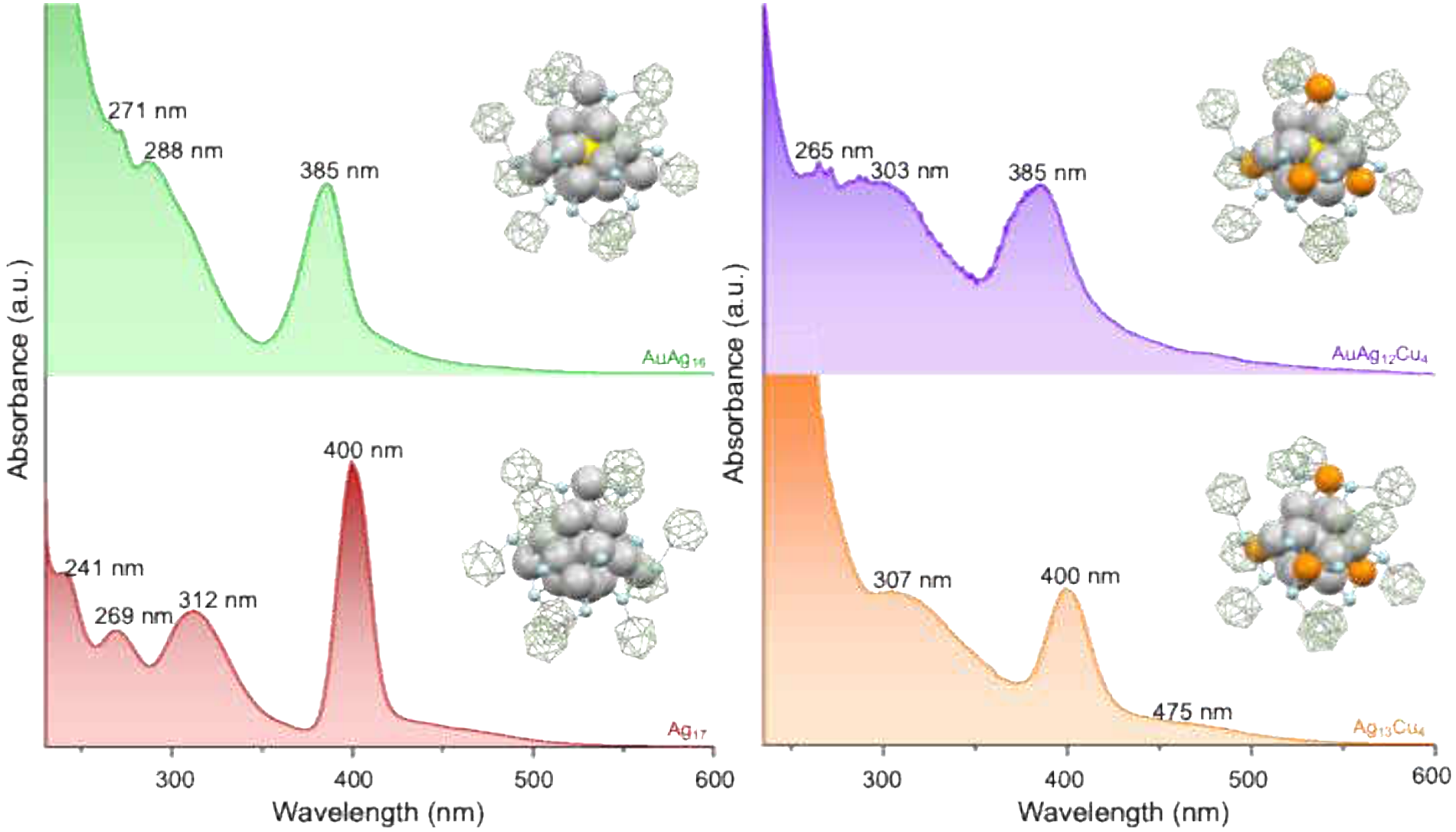
$Ag_{16}Cu$



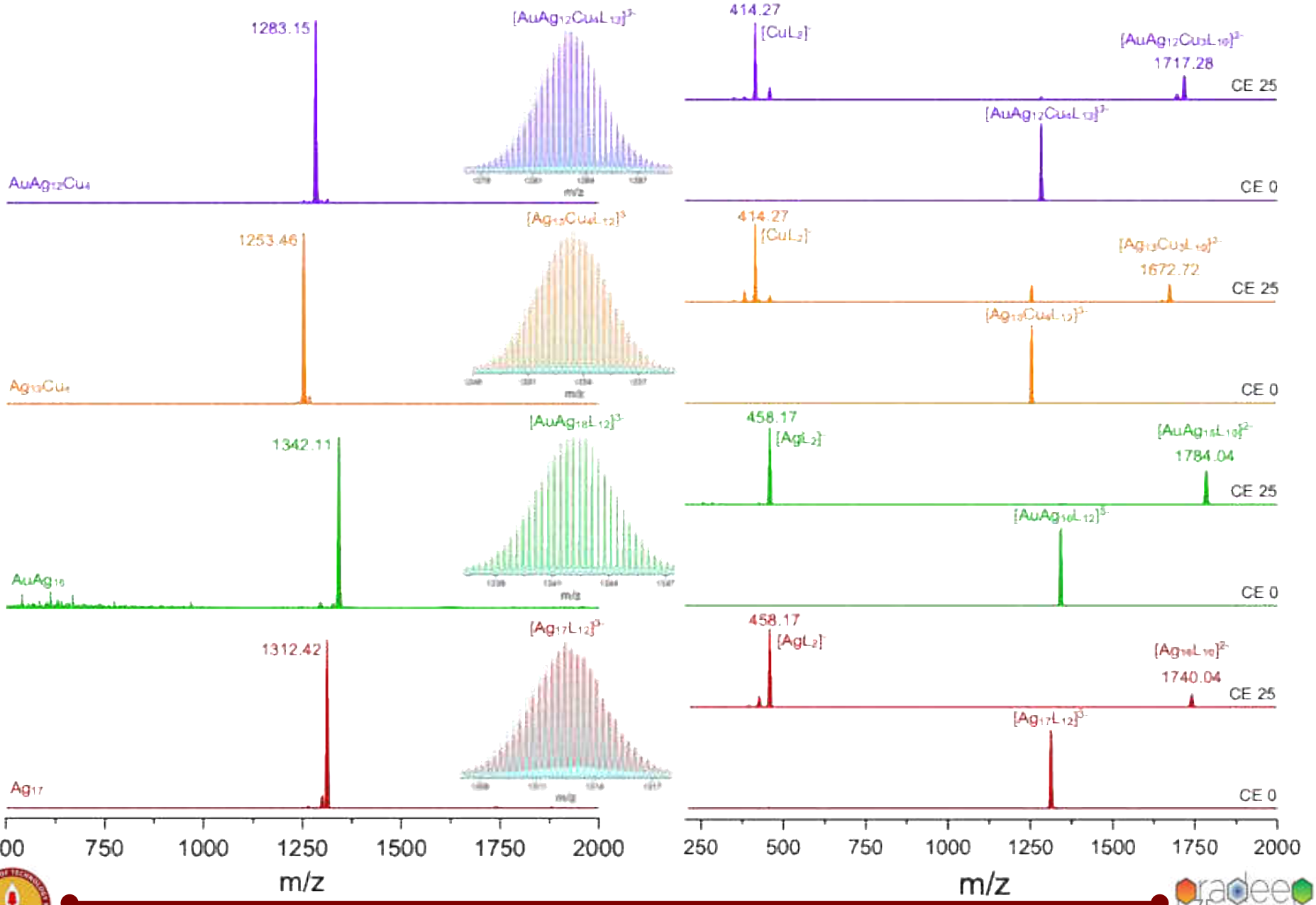
Incorporation of Cu in Ag_{17}



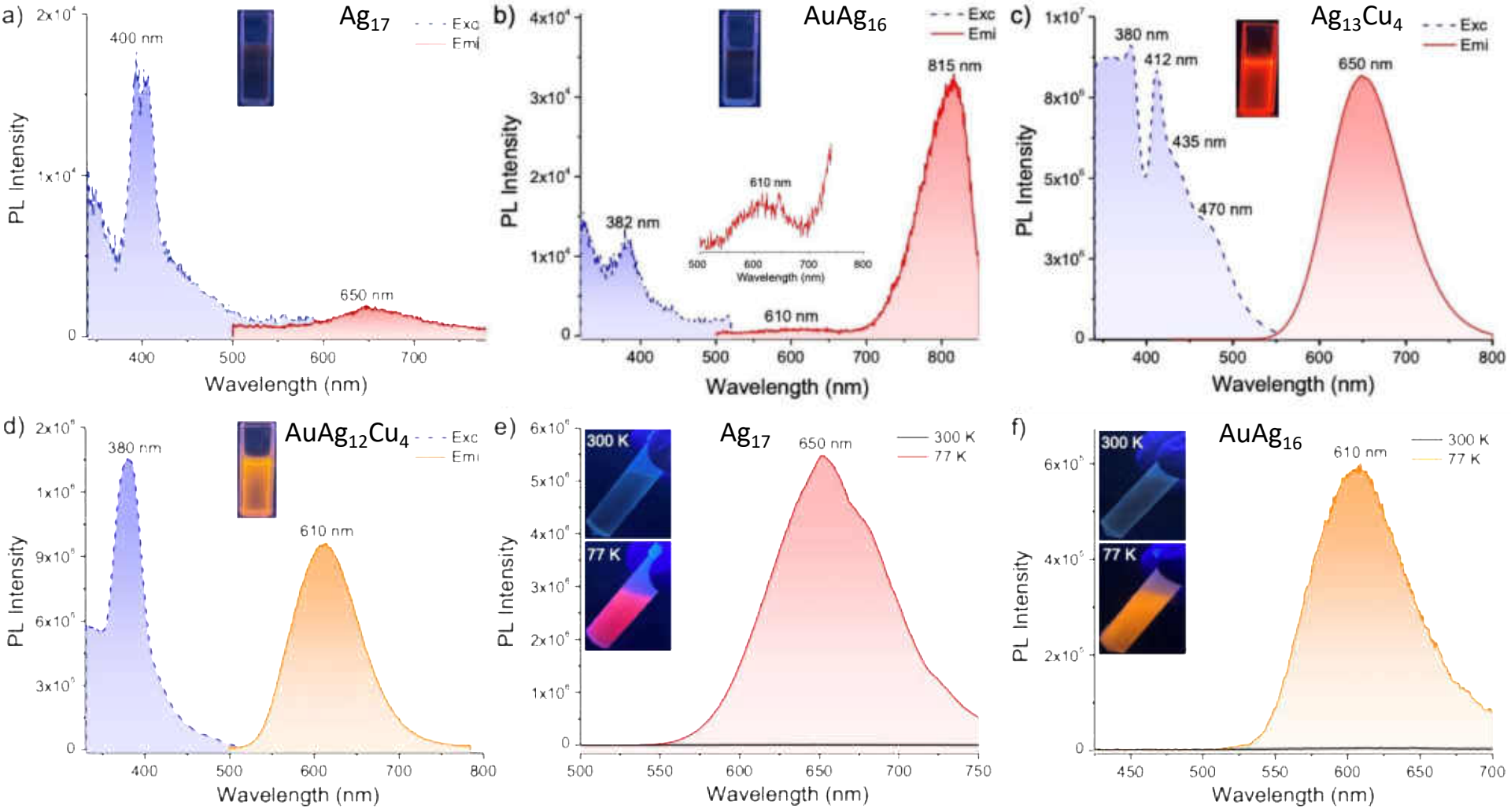
UV-Vis of M_{17} Nanoclusters



Mass Spec of M_{17} Nanoclusters

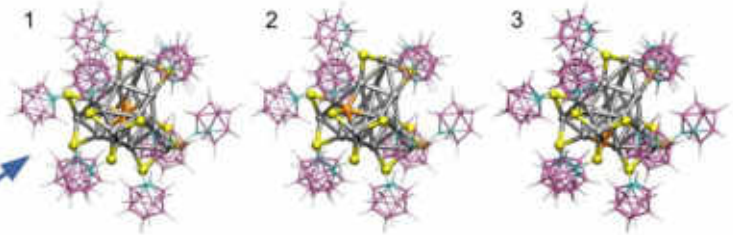


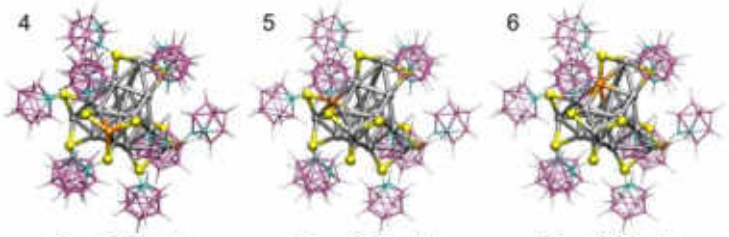
Photoluminescence of M_{17} Nanoclusters



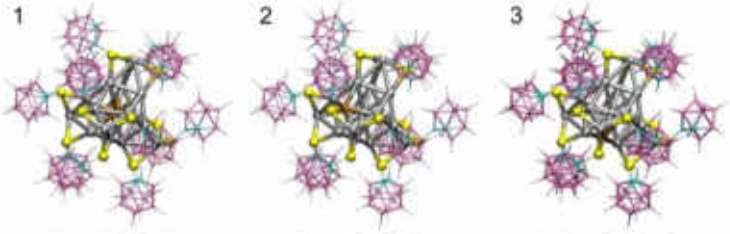
Theoretical Understanding

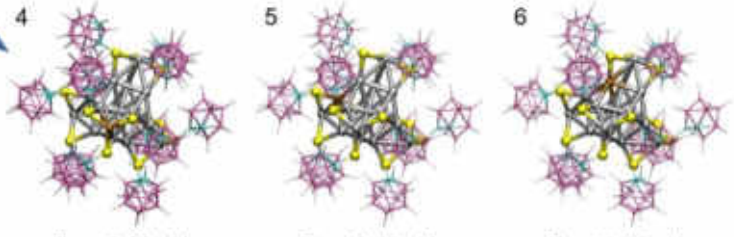
Energetically best doping position for Au is in the center of the metal core.

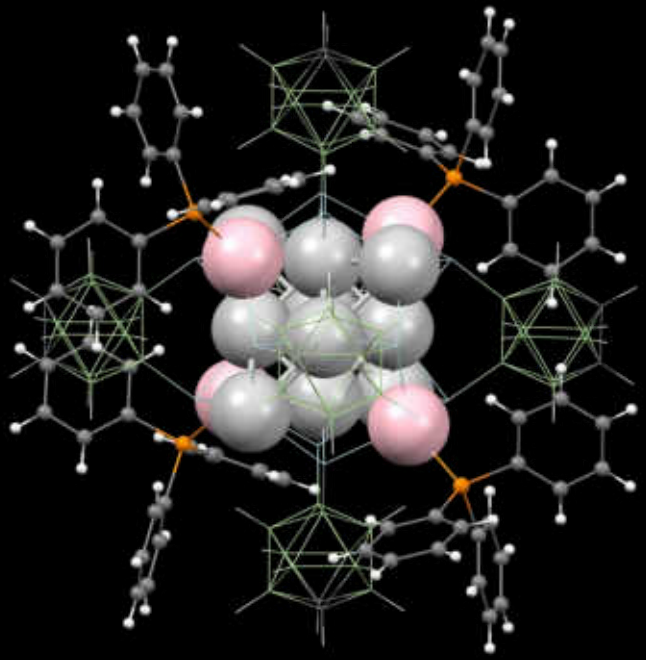


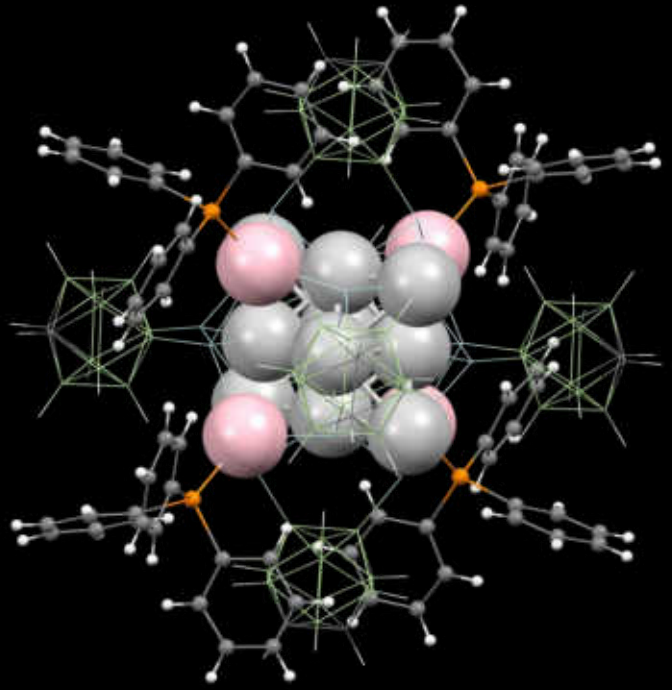


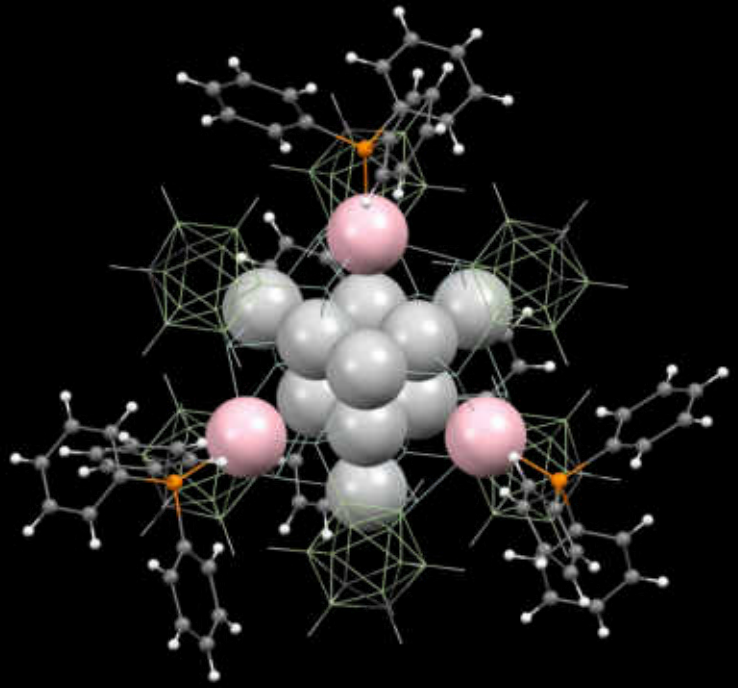
Energetically best doping position for Cu is at the metal-ligand interface, in the $Cu(SR)_3$ units.

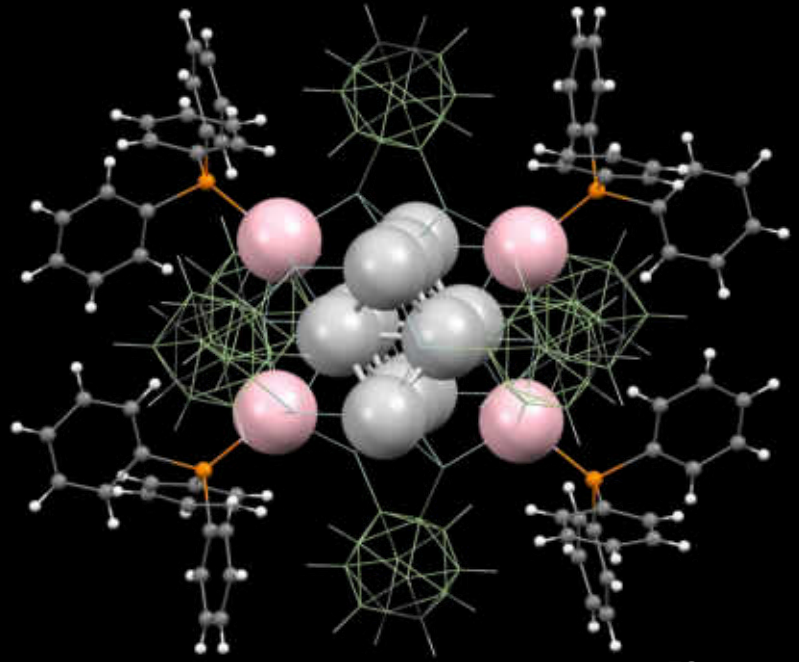






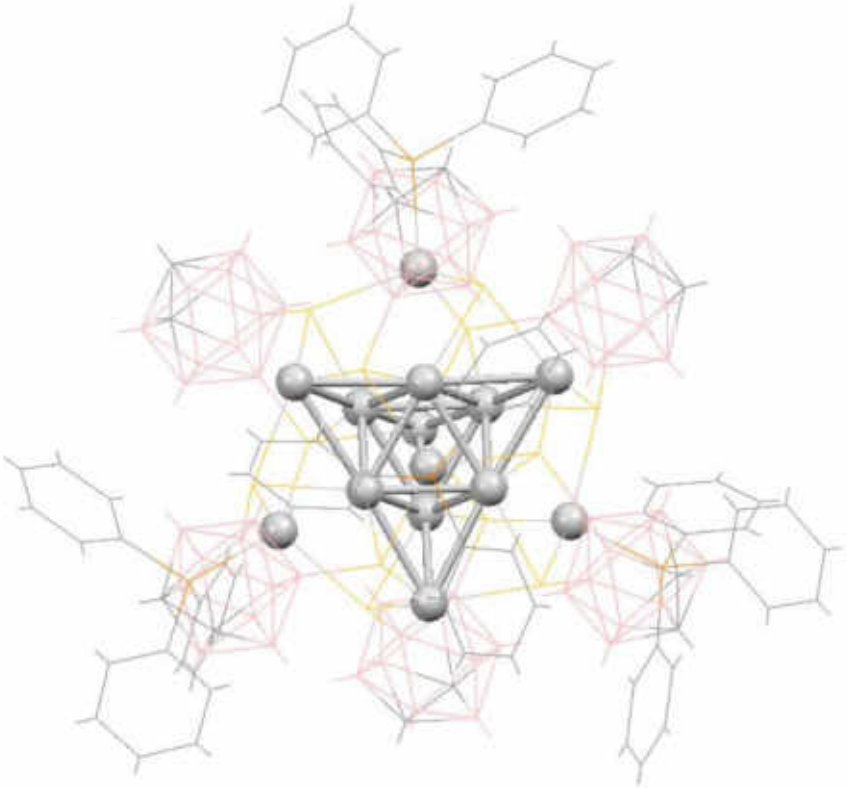






Tetrahedral TPP

Square Planar TPP



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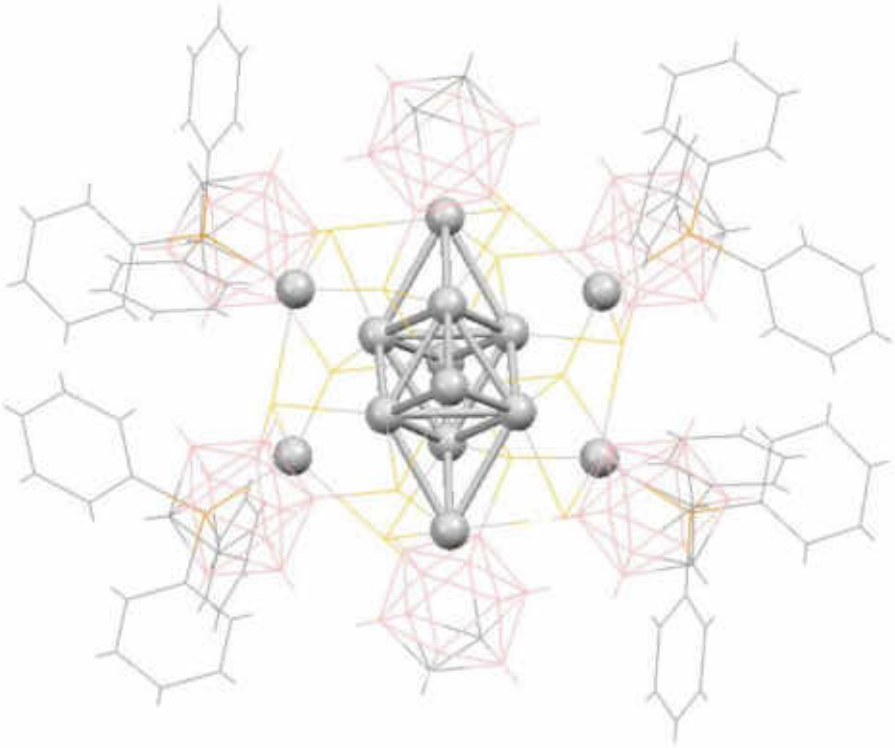
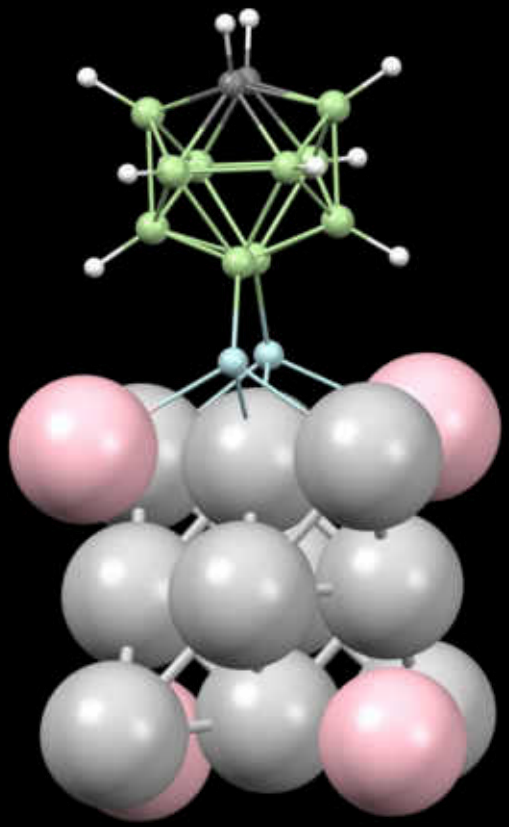


Square Planar TPP

Bonding of CBDT to Metal Core



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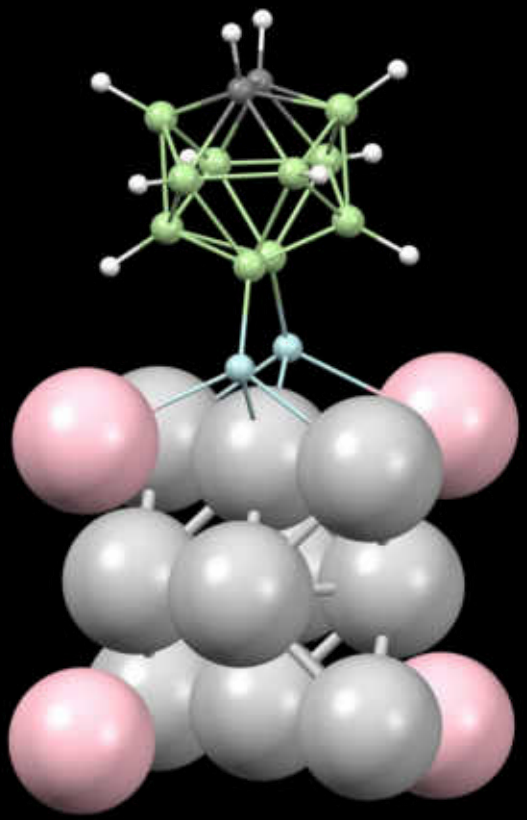
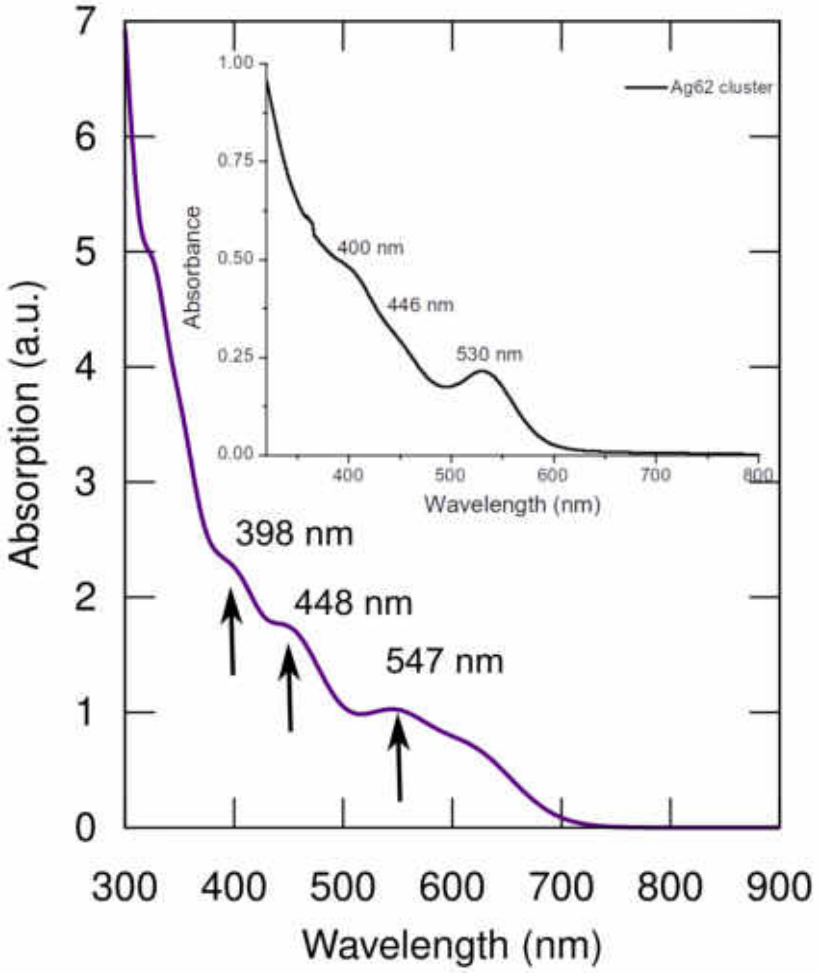
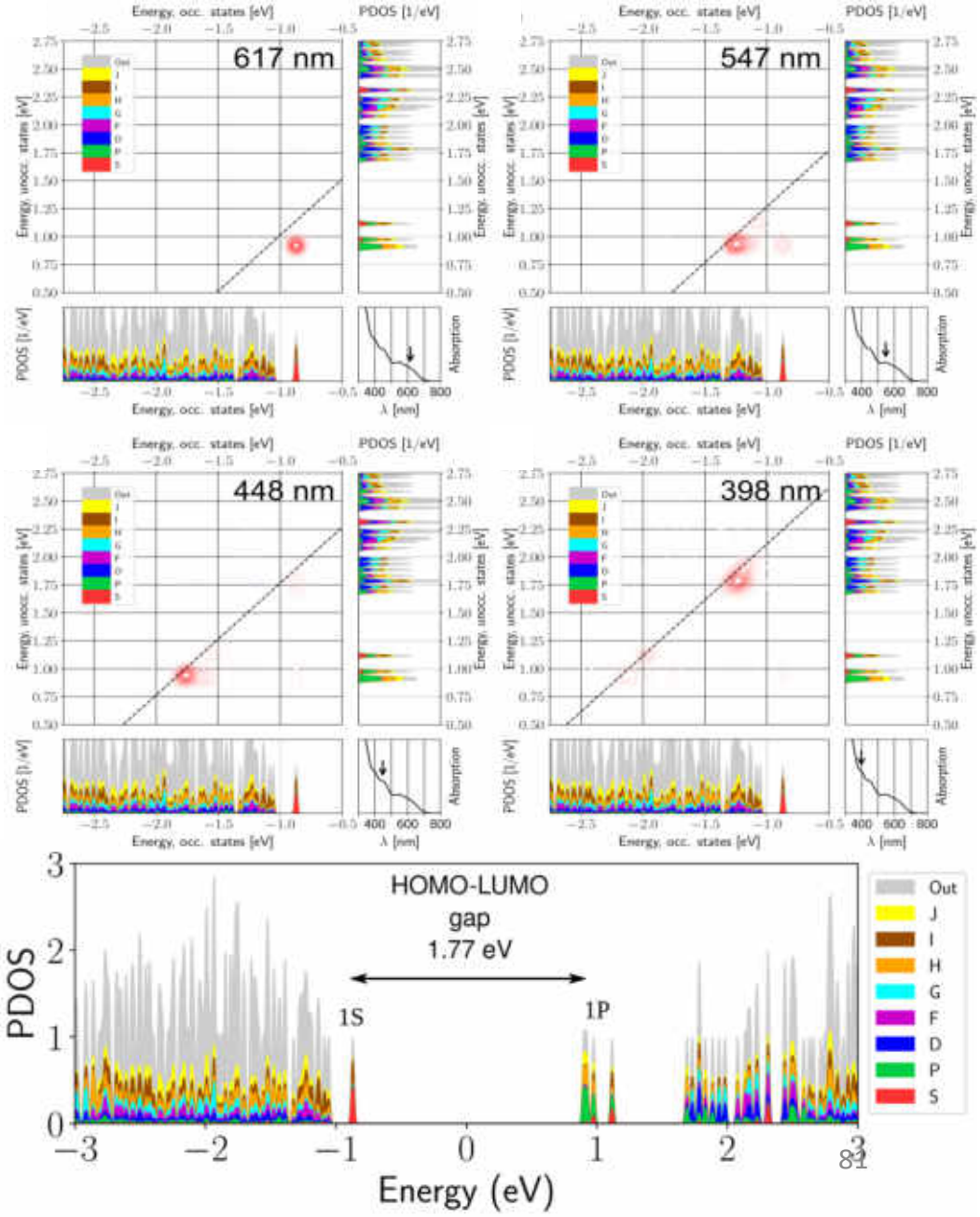


Square Planar TPP

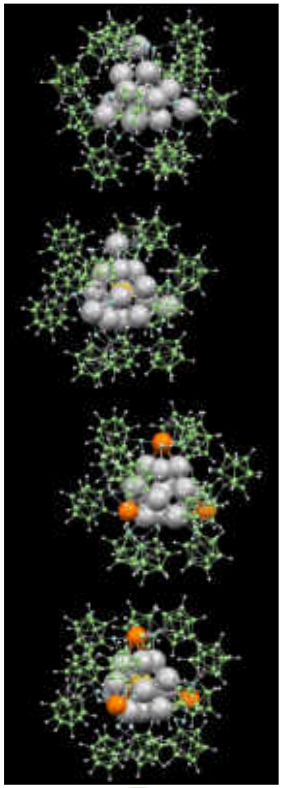
Theoretical understanding of electronic energy levels





Credit: Dr. Sami, Prof. Hannu Häkkinen

Summary and Takeaway



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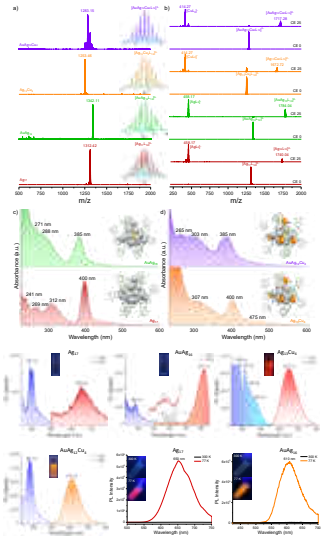
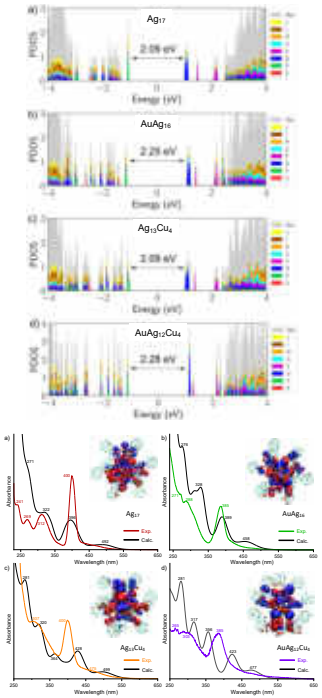


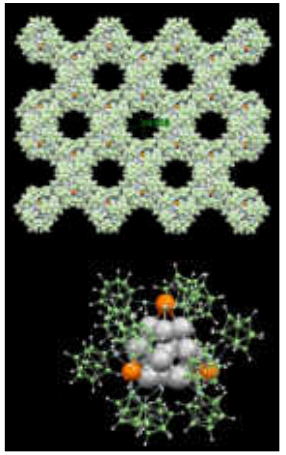
2

Characterization & Properties



3

Theoretical Understanding



4

Future Prospectives

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