Carboranethiols

Versatile Ligand Platform for Atomically Precise Clusters

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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

International Centre for Clean Water

Clathrate Hydrates in UHV

ACCOUNTS of chemical research

Article

Formation and Transformation of Clathrate Hydrates under Interstellar Conditions

Jyotirmoy Ghosh, Gaurav Vishwakarma, Rajnish Kumar,* and Thalappil Pradeep*

Cite This: https://doi.org/10.1021/acs.accounts.3c00317 Read Online

Clathrate hydrates in interstellar environment

Jyotirmoy Ghosh[a], Rabin Rajan J. Methikkalam[a,1], Radha Gobinda Bhuin[a,2], Gopi Ragupathy[a], Nilesh Choudhary[b], Rajnish Kumar[b,3], and Thalappil Pradeep[a,3]

[a]Department of Science and Technology (DST) Unit of Nanoscience and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India; and [b]Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, India

Edited by Francois Forget, Laboratoire de Météorologie Dynamique, Paris, France, and accepted by Editorial Board Member Jean Jouzel December 10, 2018 (received for review August 18, 2018)

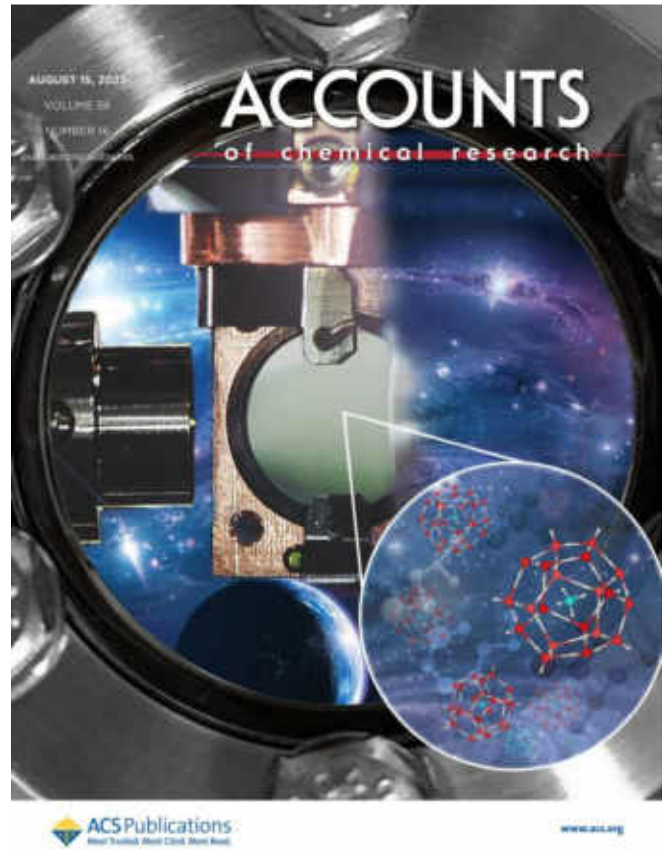
Clathrate hydrates (CHs) are ubiquitous in earth under high-pressure conditions, but their existence in the interstellar medium (ISM) remains unknown. Here, we report experimental observations of the formation of methane and carbon dioxide hydrates in an environment analogous to ISM. Thermal treatment of solid methane and carbon dioxide–water mixture in ultrahigh vacuum of the order of 10^{-10} mbar for extended periods led to the formation of CHs at 30 and 10 K, respectively. High molecular mobility and H bonding play important roles in the entrapment of gases in the in situ formed 5^{12} CH cages. This finding implies that CHs can exist in extreme low-pressure environments present in the ISM. These hydrates in ISM, subjected to various chemical processes, may act as sources for relevant prebiotic molecules.

CO_2, or other volatile gases in cold interstellar clouds or in comets could possibly be explained by the existence of such hydrates in gas-forming regions of the interstellar space (10, 12). Irradiation or annealing leads to the chemical evolution of ice in ISM, forming new species (13). CHs could be one such new chemical system in the ISM, which may be subjected to additional processing.

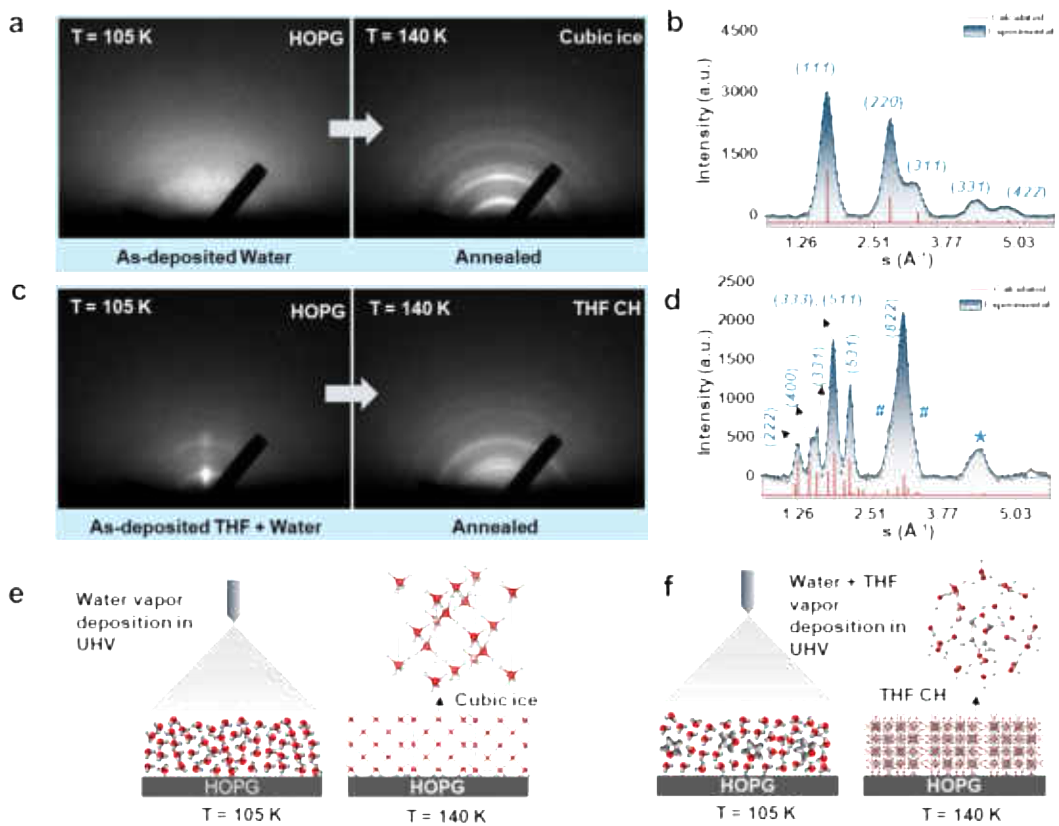
Results and Discussion

Fig. 1*A* displays time-dependent reflection absorption infrared (RAIR) spectra of 300 monolayers (MLs; 1 monolayer is equivalent to $\sim 1.0 \times 10^{15}$ molecules · cm^{-2}) of a codeposited mixture (1:1) of CH_4 and water at the C–H antisymmetric stretching region at three different temperatures (10, 20, and

1526–1531 | PNAS | January 29, 2019 | vol. 116 | no. 5

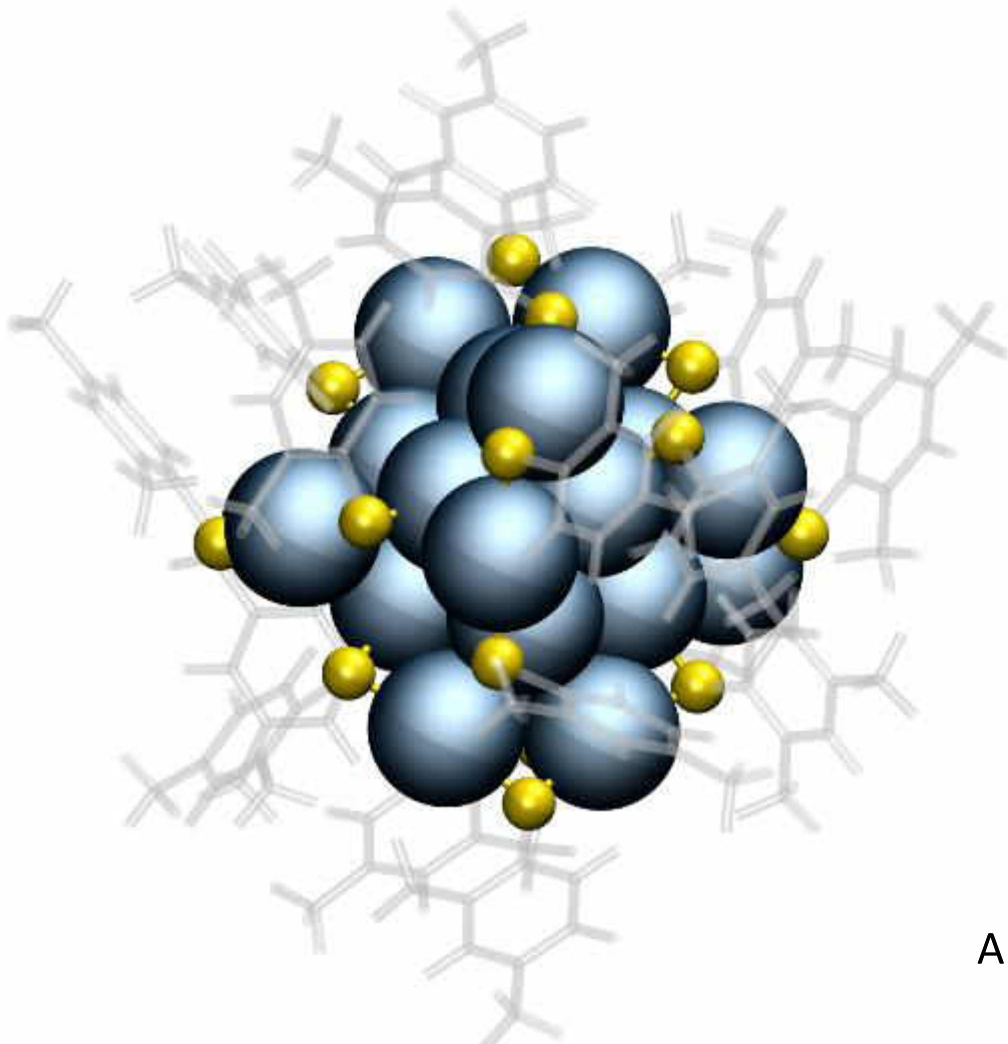


Structure of Clathrate Hydrates – Electron Diffraction

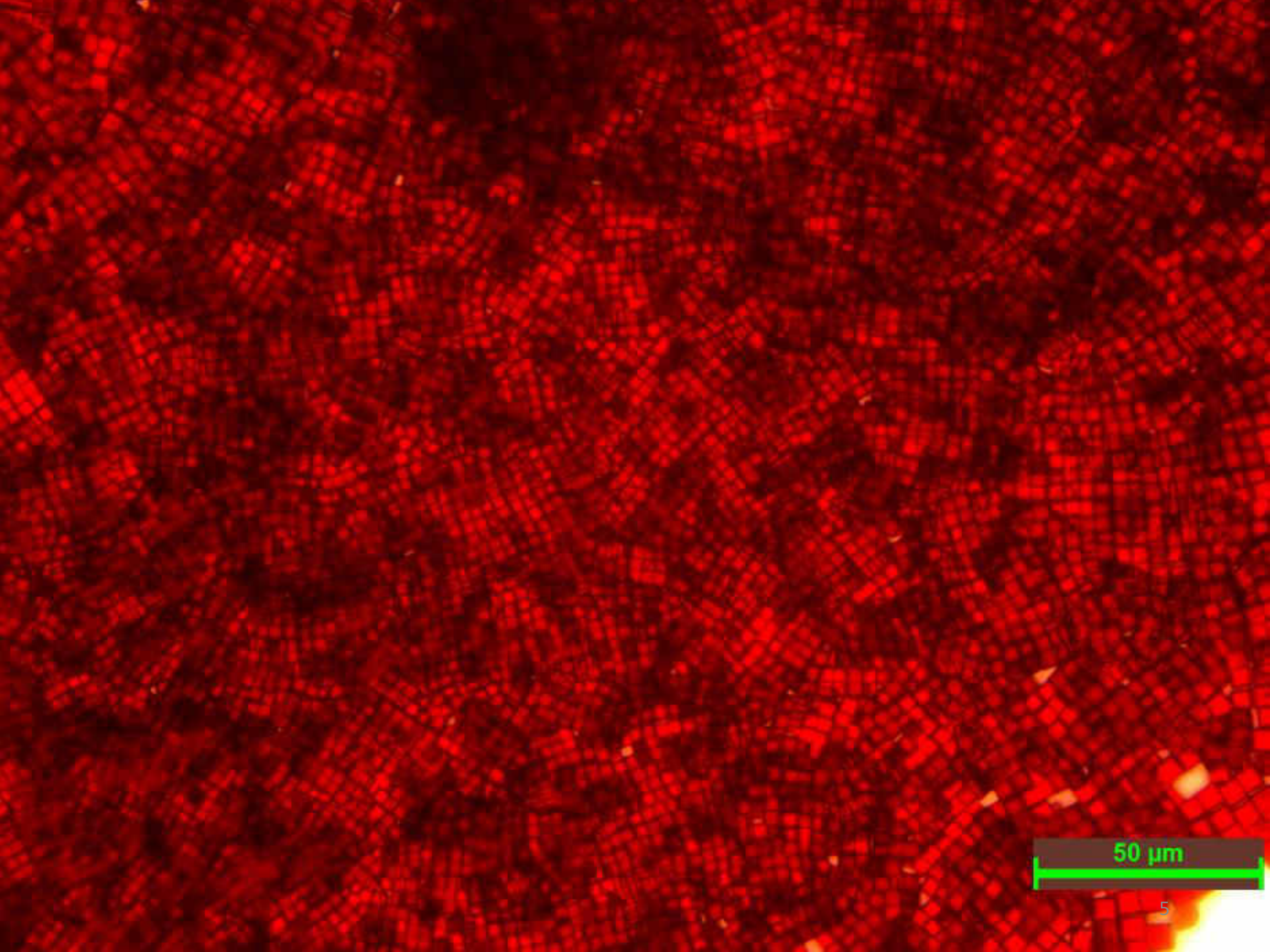


Bijesh Malla, et. al, J. Phys. Chem. Lett. 2024 (in press)

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

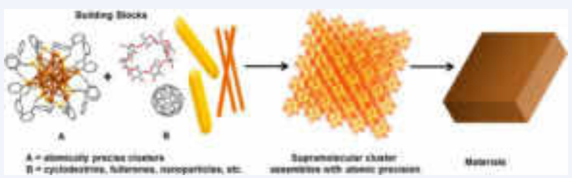
pubs.acs.org/accounts

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

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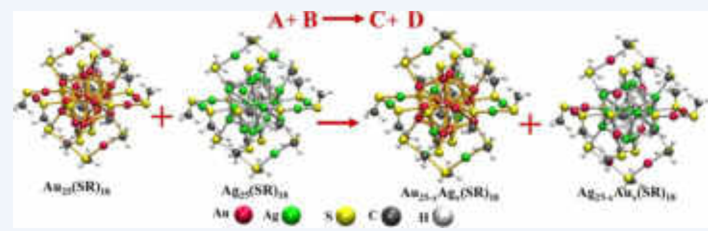
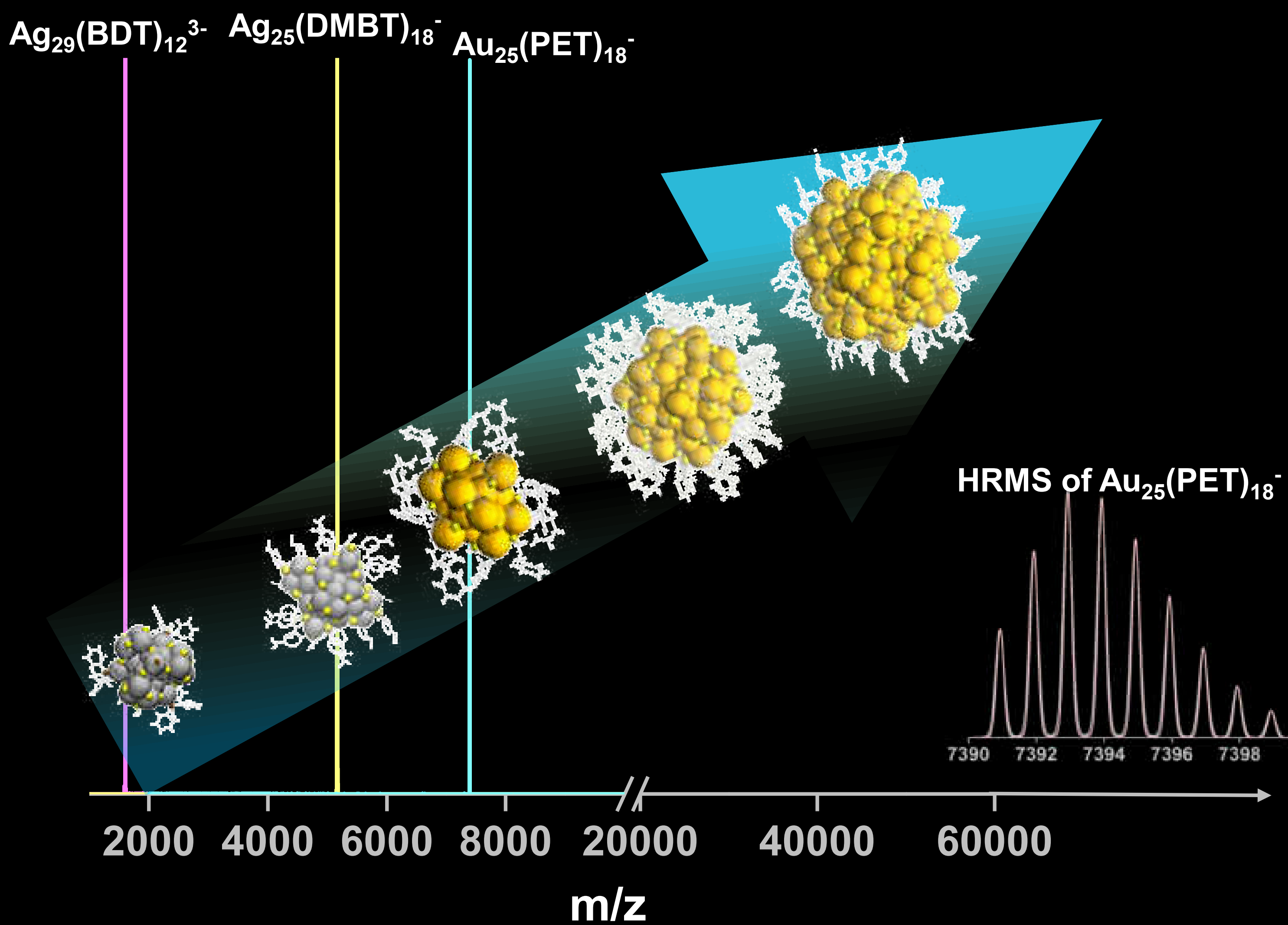
Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry

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

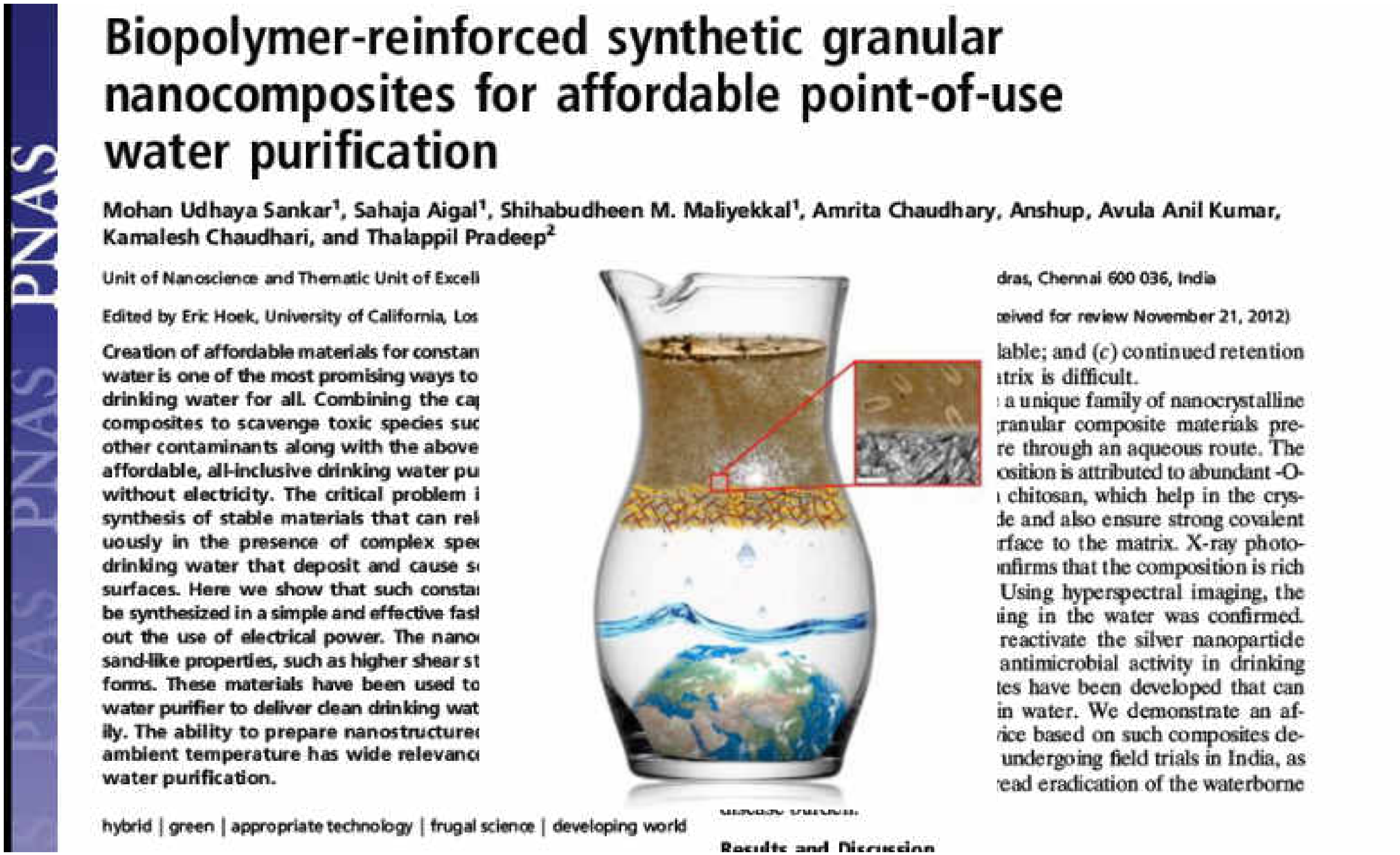
Department of Chemistry, DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE) Indian Institute of Technology Madras, Chennai 600 036, India



T. Pradeep et. al., *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

Advanced materials for clean water



PNAS 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.

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

lable; and (*c*) continued retention
atrix 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-
vice based on such composites de-
undergoing field trials in India, as
ead eradication of the waterborne

Results and Discussion

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

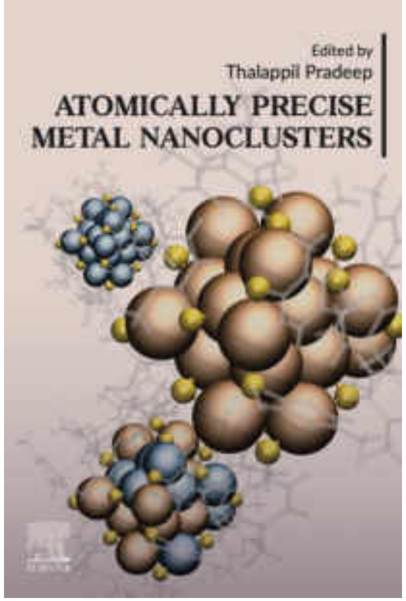
We supply arsenic-free water to 1.3 million people every day.

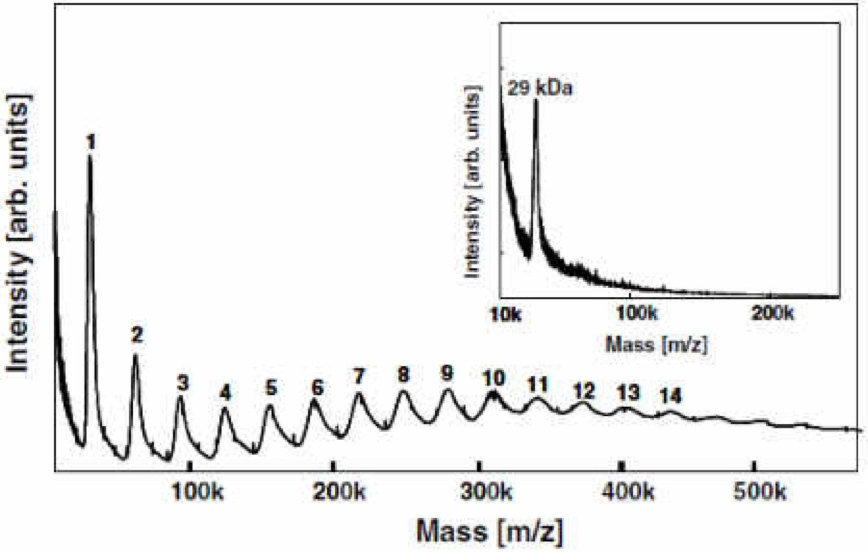
Our technologies provide clean water to 13 million people.

345 structures!

Alkane- and arene- thiols are great, but…

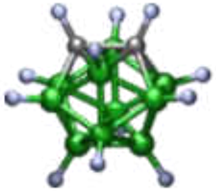
Clusters are hard to crystallise, except in some cases
Thermal stability is limited
Applications are limited



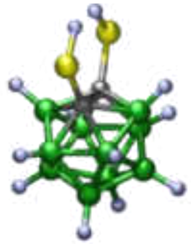


Jobin et al. *Chem. Phys. Lett.* 2004, 390,181

Building Blocks: Carborane Thiols

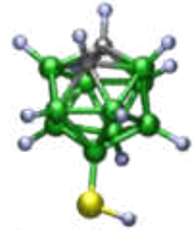


1,2-$C_2B_{10}H_{12}$

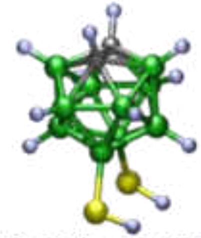


1,2-$(HS)_2$-1,2-$C_2B_{10}H_{10}$

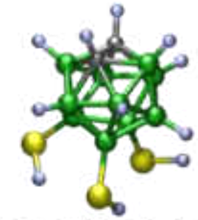
1-HS-1,2-$C_2B_{10}H_{11}$



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

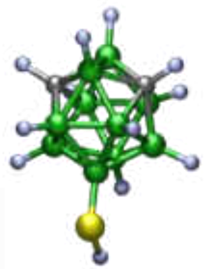


9,12-$(HS)_2$-1,2-$C_2B_{10}H_{10}$



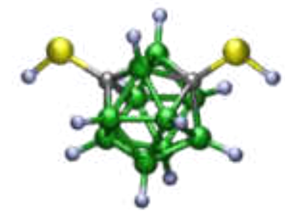
8,9,12-$(HS)_3$-1,2-$C_2B_{10}H_9$

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

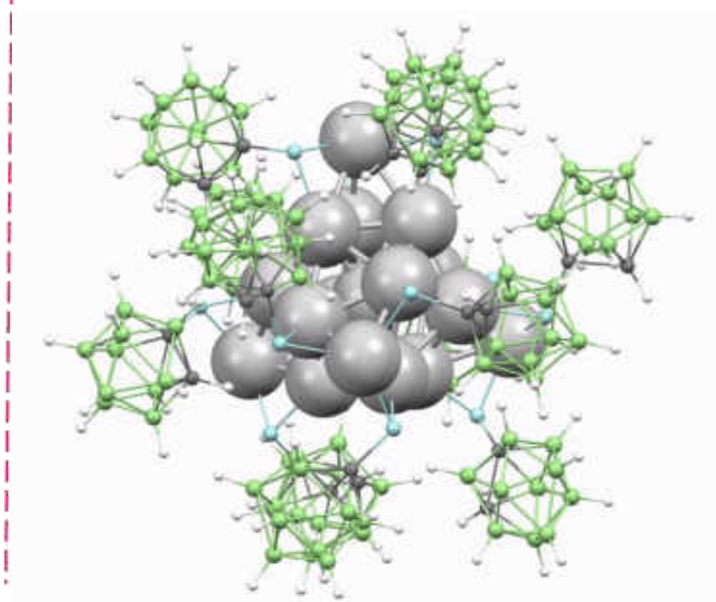


9-HS-1,7-$C_2B_{10}H_{11}$

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

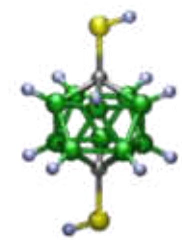


1,7-$(HS)_2$-1,7-$C_2B_{10}H_{10}$



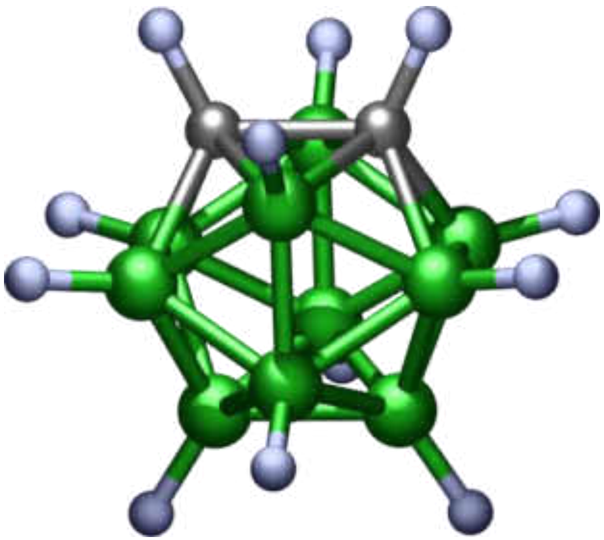
1,12-$C_2B_{10}H_{12}$

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

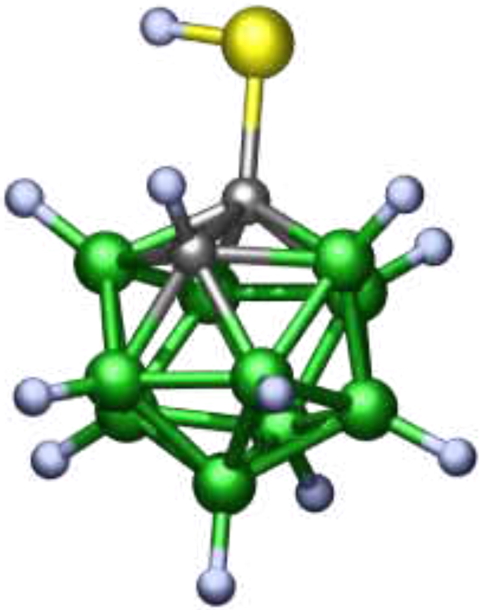


1,12-$(HS)_2$-1,12-$C_2B_{10}H_{10}$

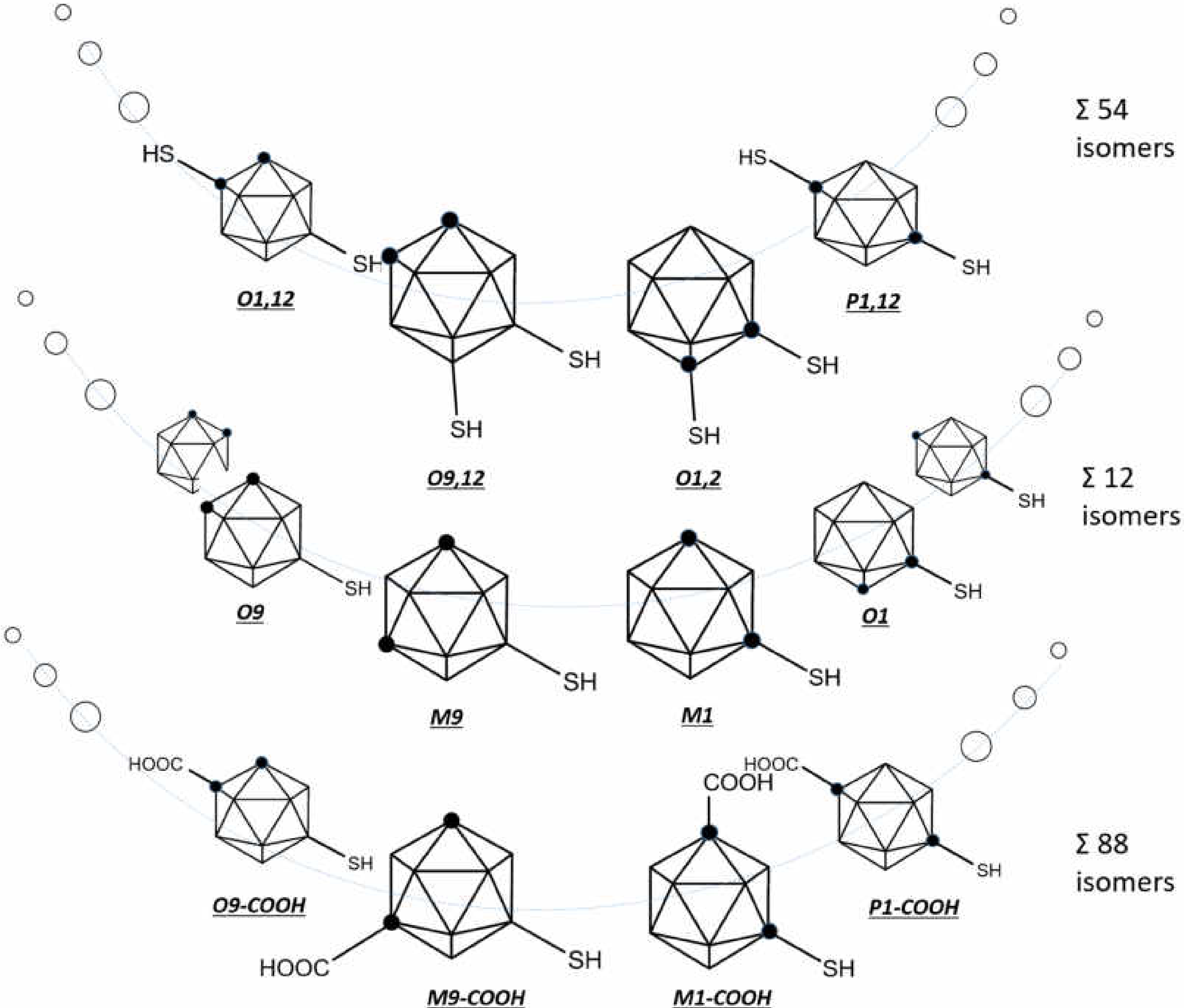
About the Ligand



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



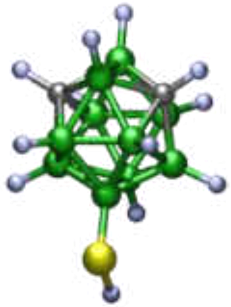
$1\text{-}HS\text{-}1,2\text{-}C_2B_{10}H_{11}$


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

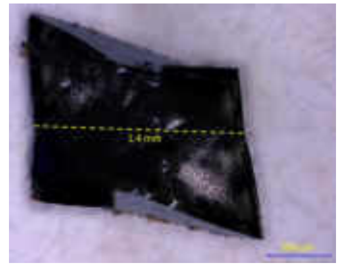
Cu_4 Ag_{14} Ag_{21} Ag_{42}

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

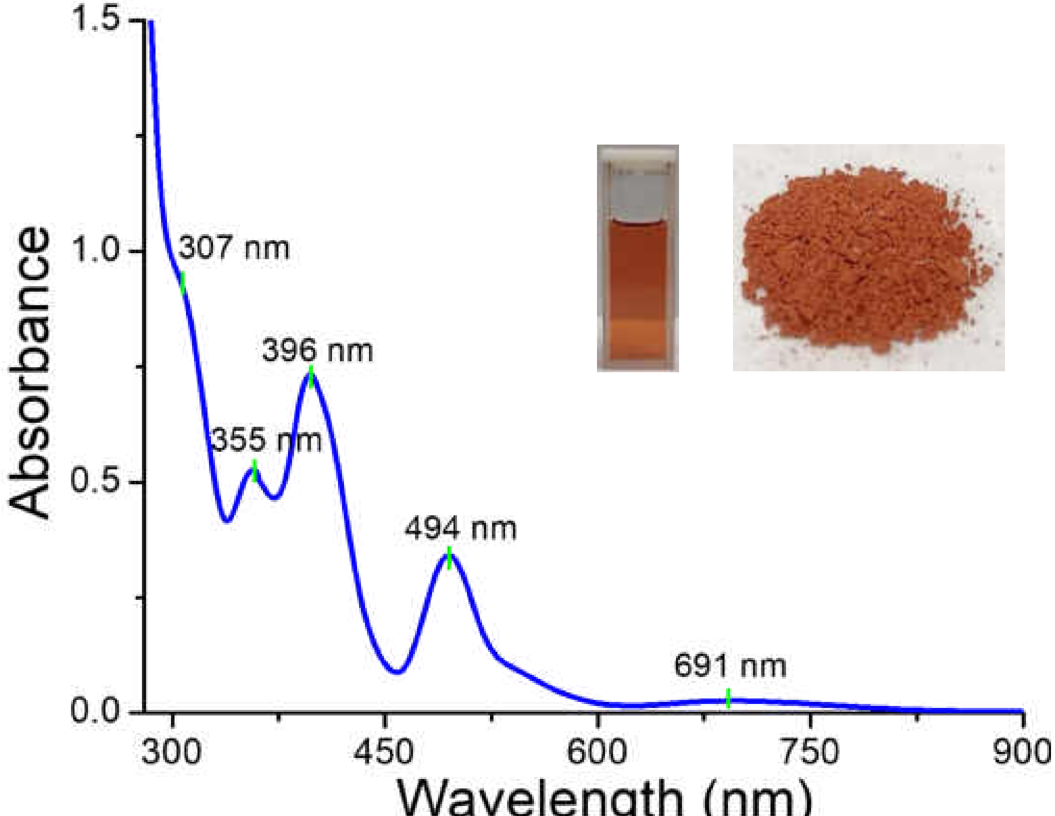
Ligand:

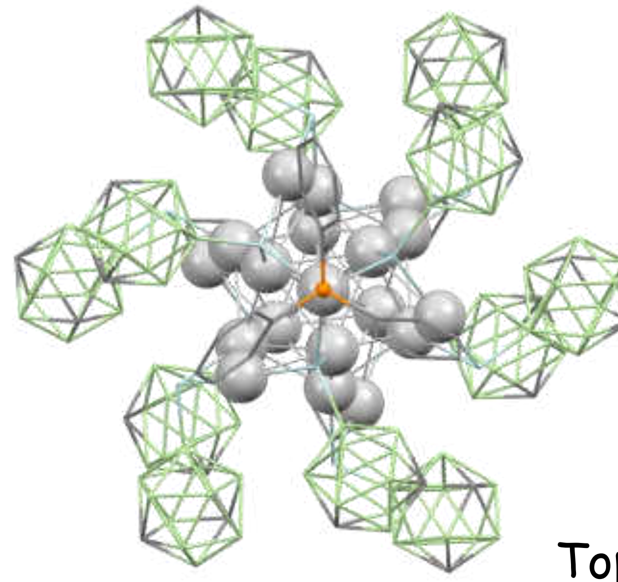


9-HS-1,7-$C_2B_{10}H_{11}$

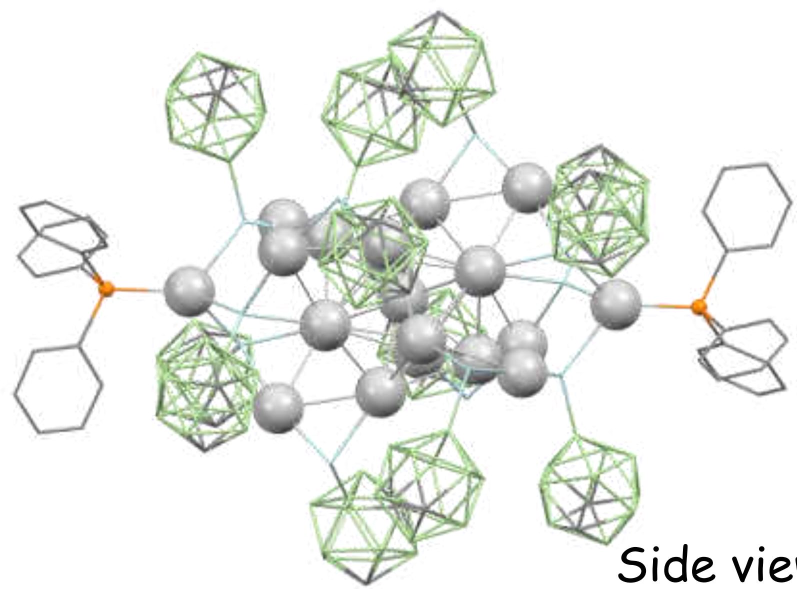


Crystal





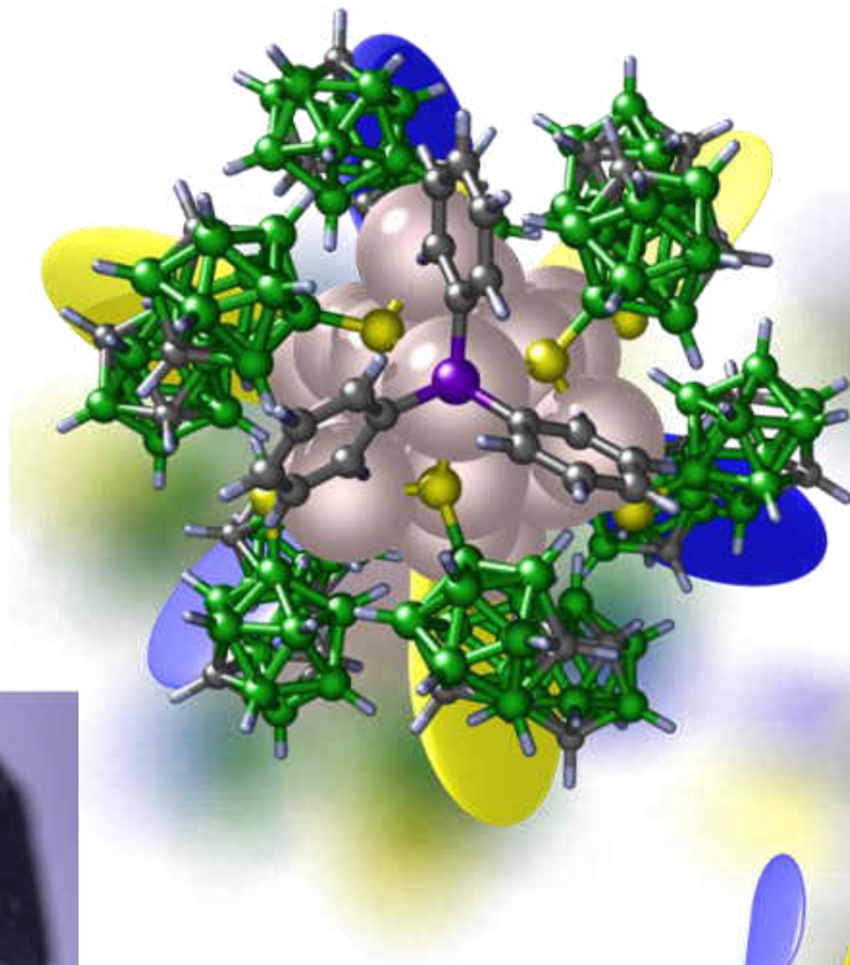
Top view

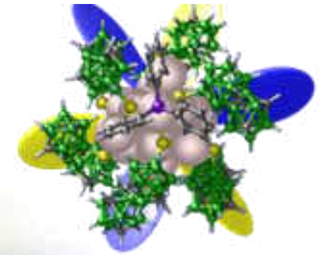


Side view

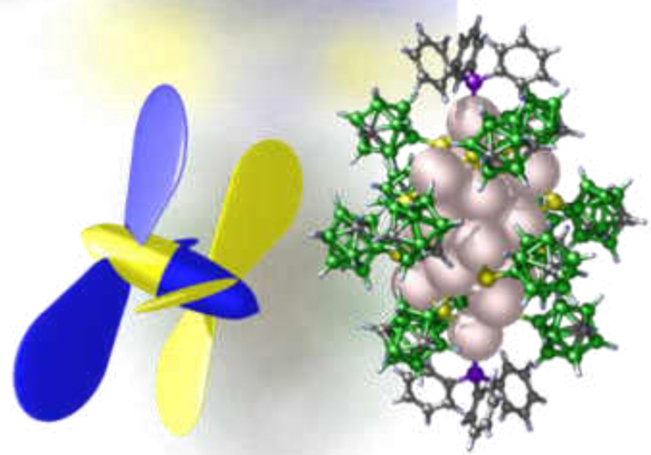
Jana *et al.*, *Inorg. Chem.*, **2022**, 61, 23, 8593-8603

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

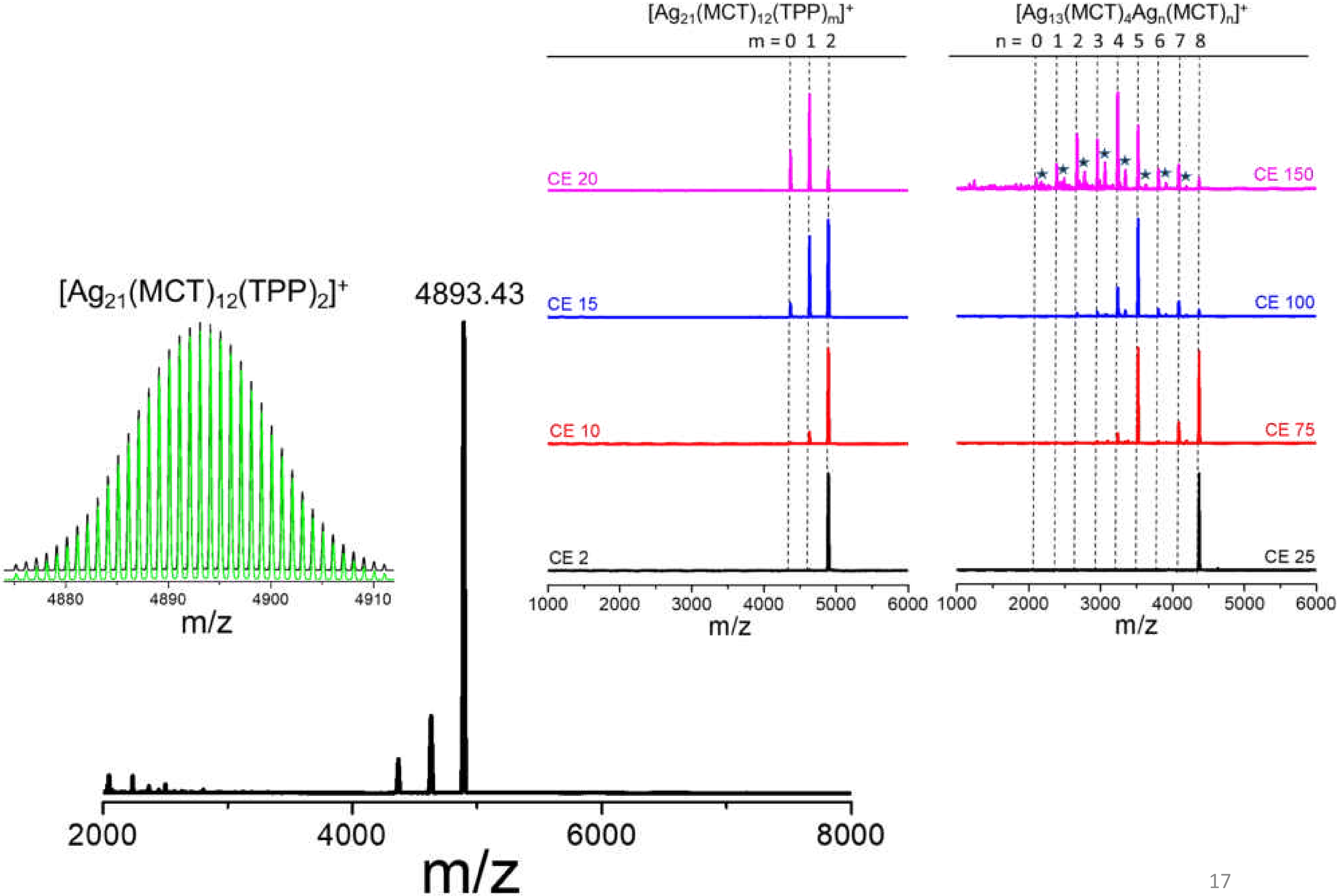


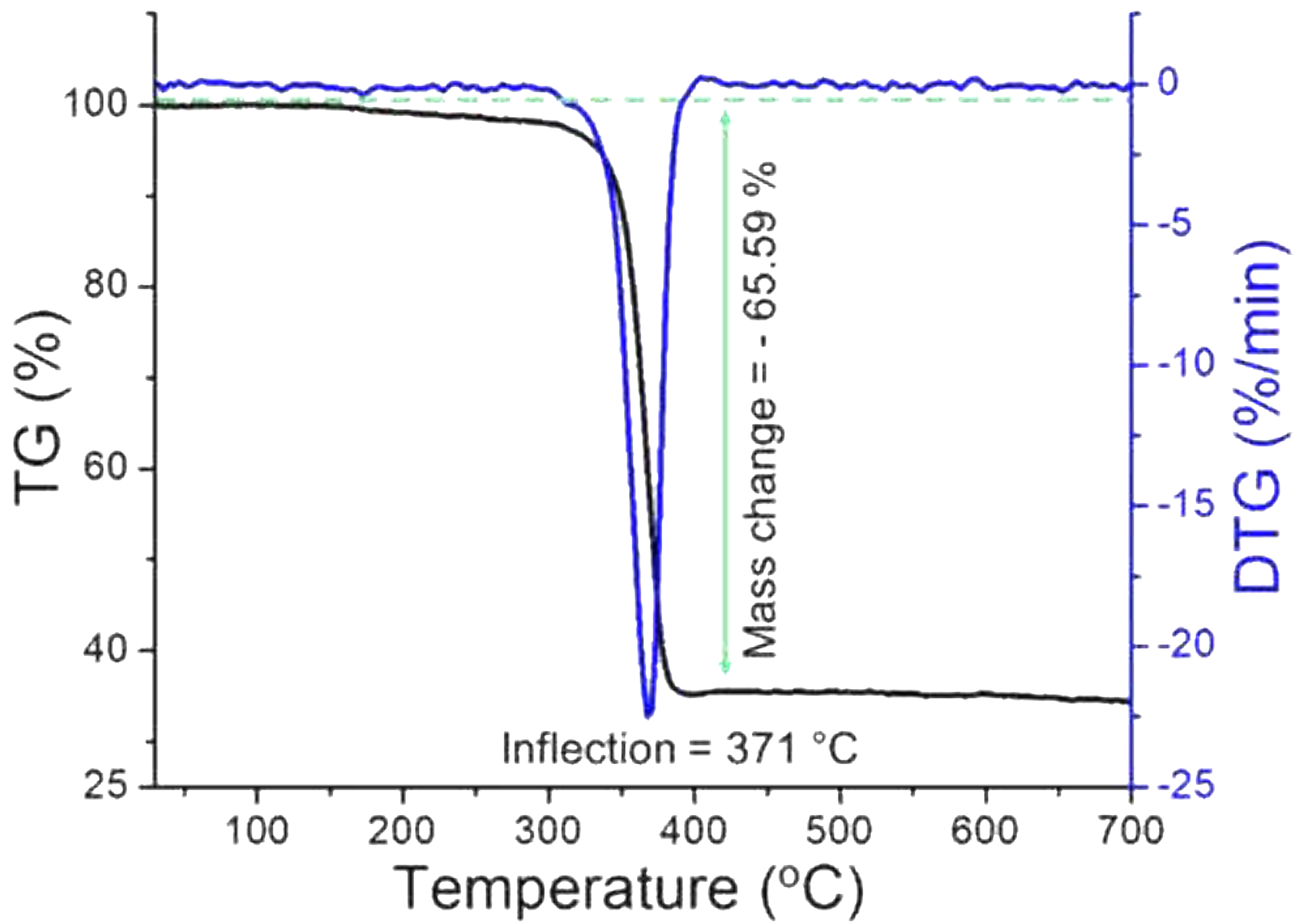


Double rotors



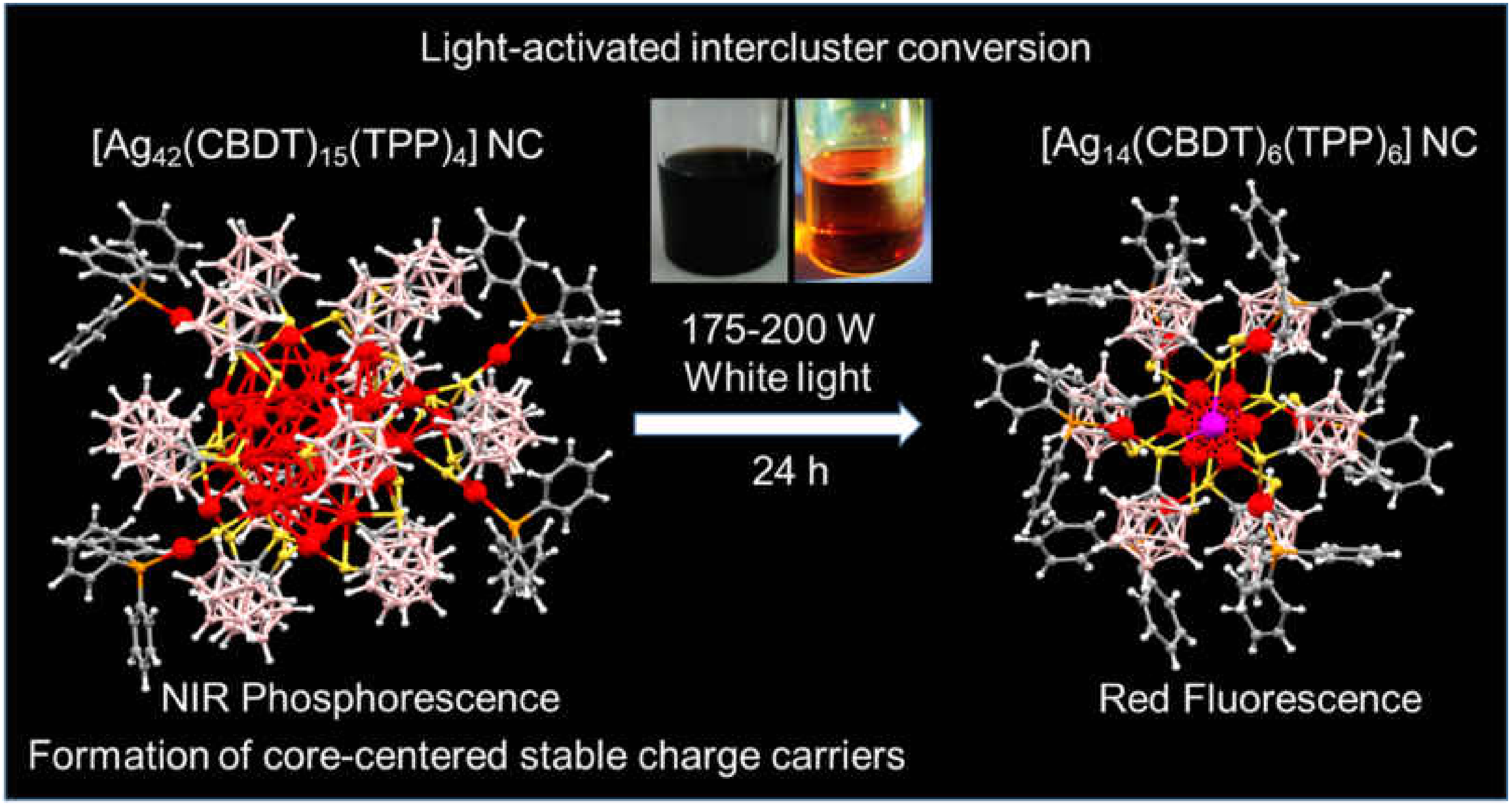
Mass spectrometric characterization



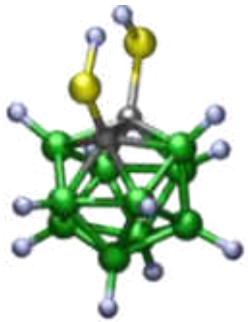


TG (%)
DTG (%/min)
Temperature (°C)
Mass change = - 65.59 %
Inflection = 371 °C
100
80
60
40
25
0
-5
-10
-15
-20
-25
100
200
300
400
500
600
700

Light-activated Conversion of Carborane Thiol Appended Silver Nanocluster



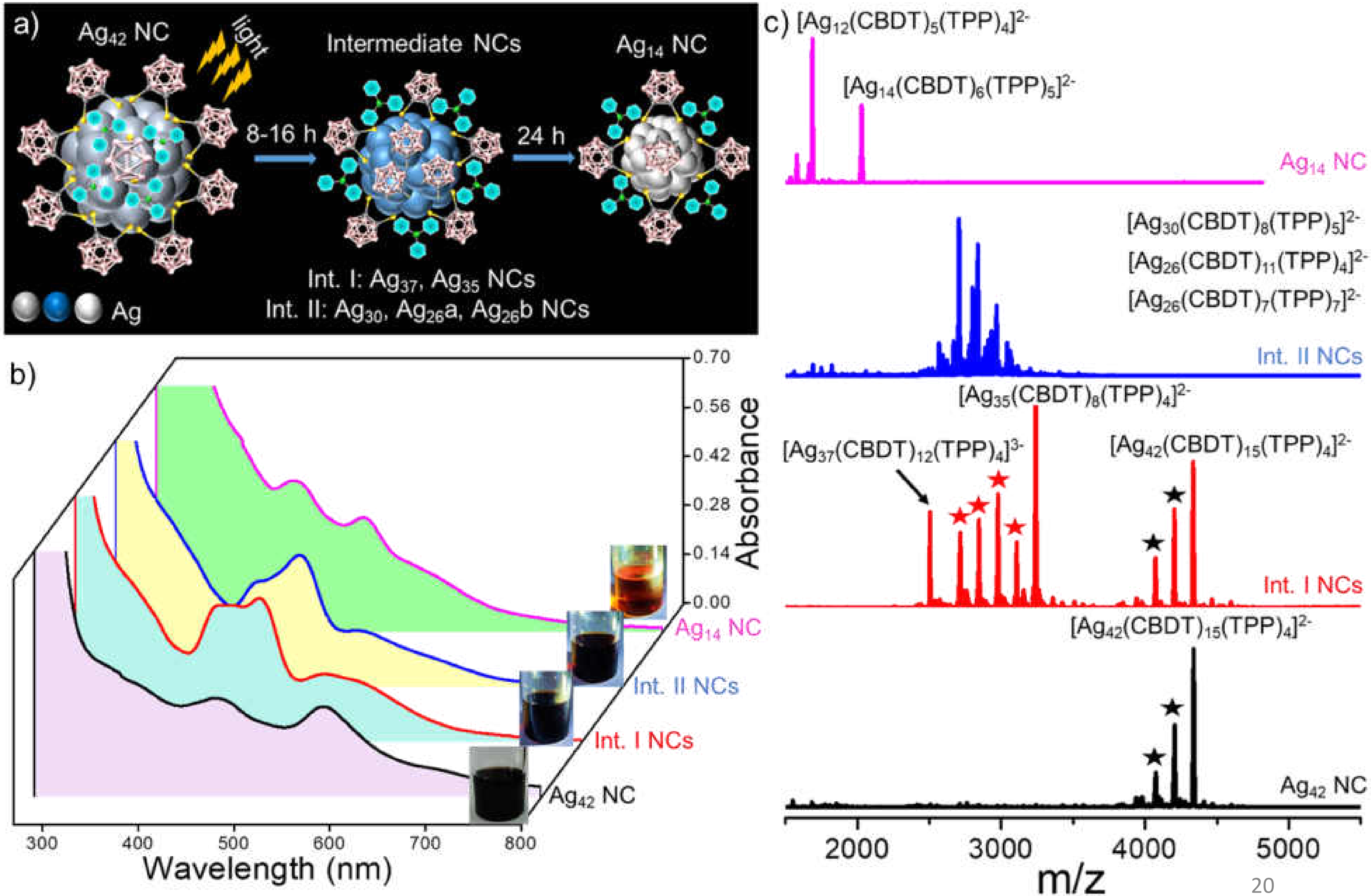
Ligand:



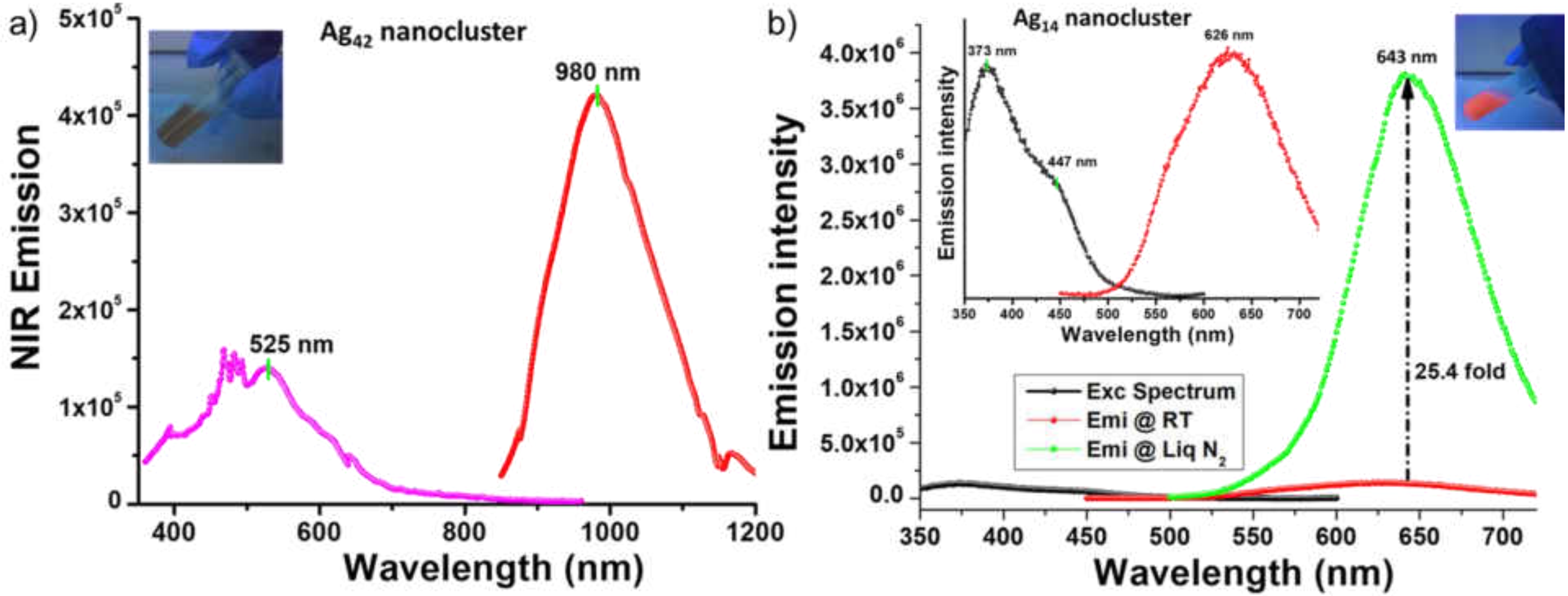
$1,2\text{-}(HS)_2\text{-}1,2\text{-}C_2B_{10}H_1$

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

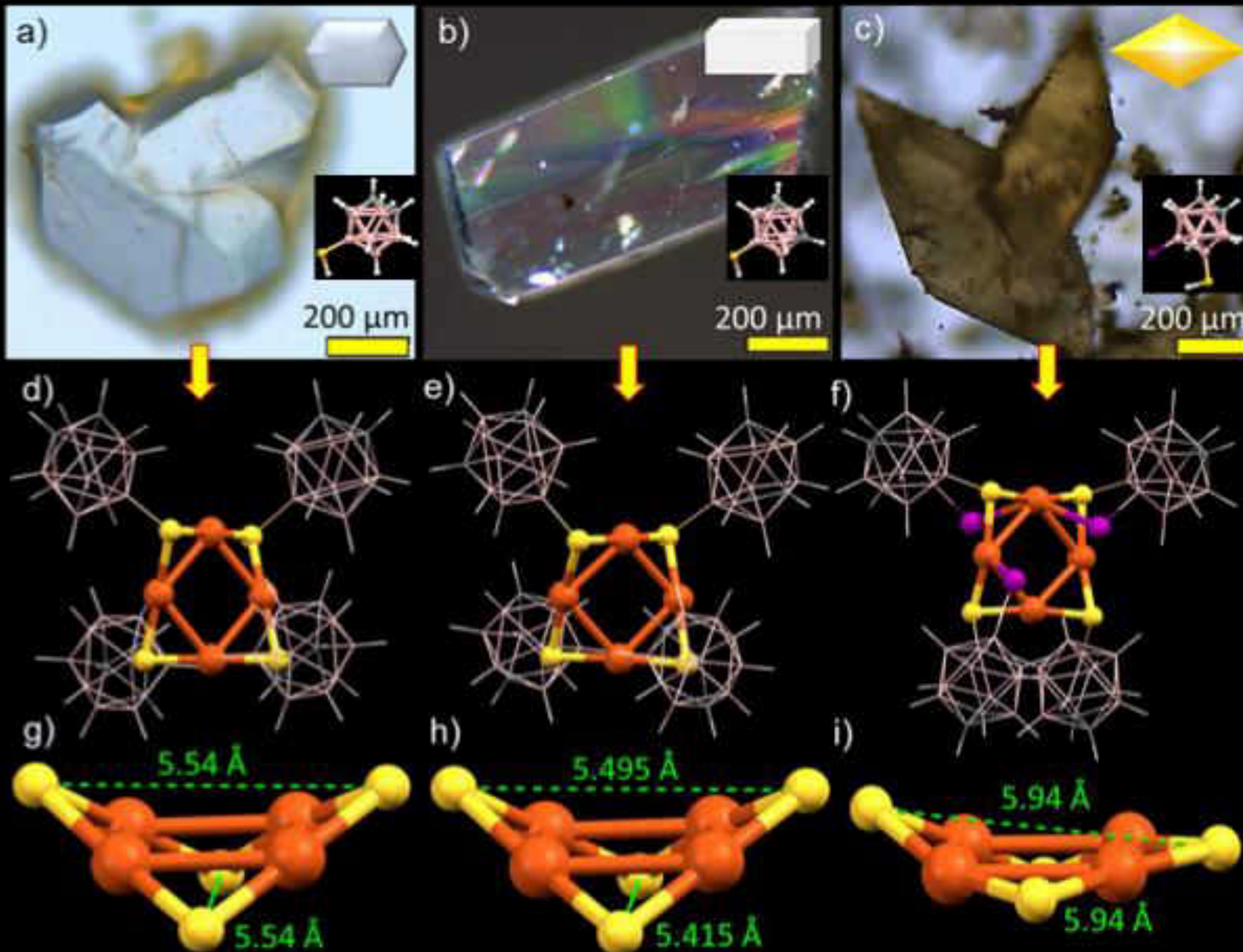
Light-activated Intercluster Conversion



Photoluminescence Properties

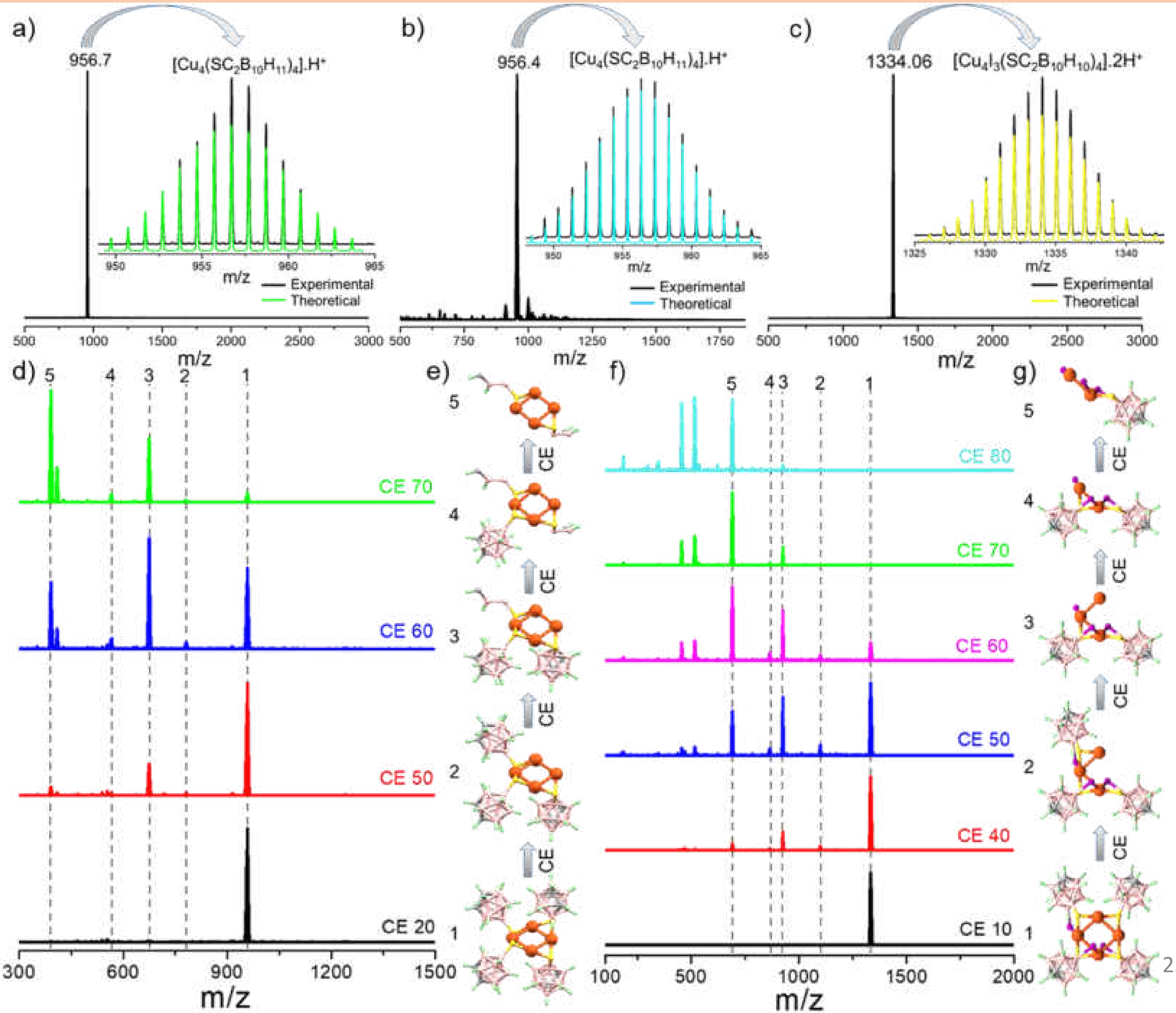


Multicolor Phosphorescence of Tetranuclear Copper Nanoclusters

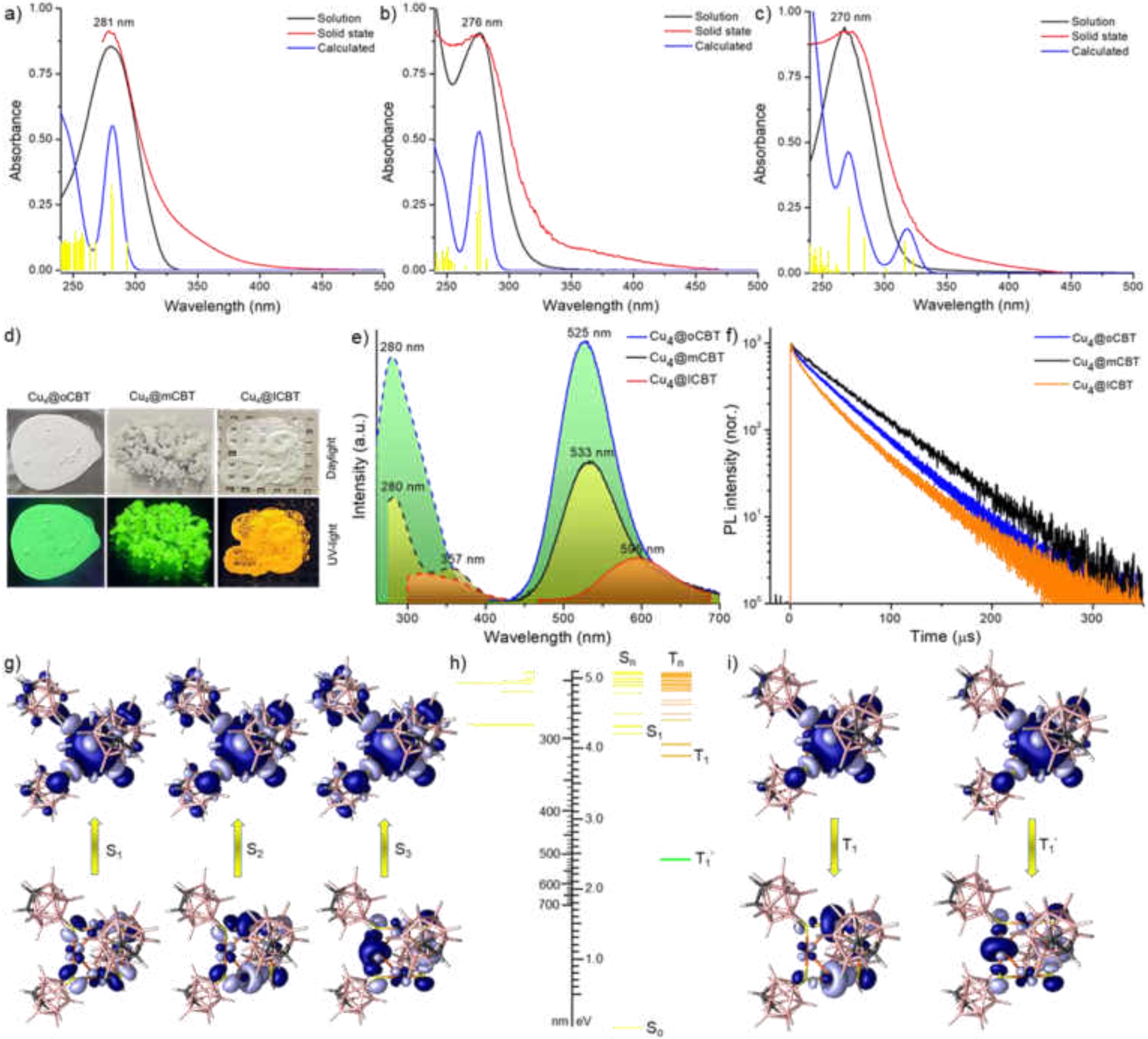


Jana *et al.*, *Chem. Sci.*, 2023, 14, 1613-1626.

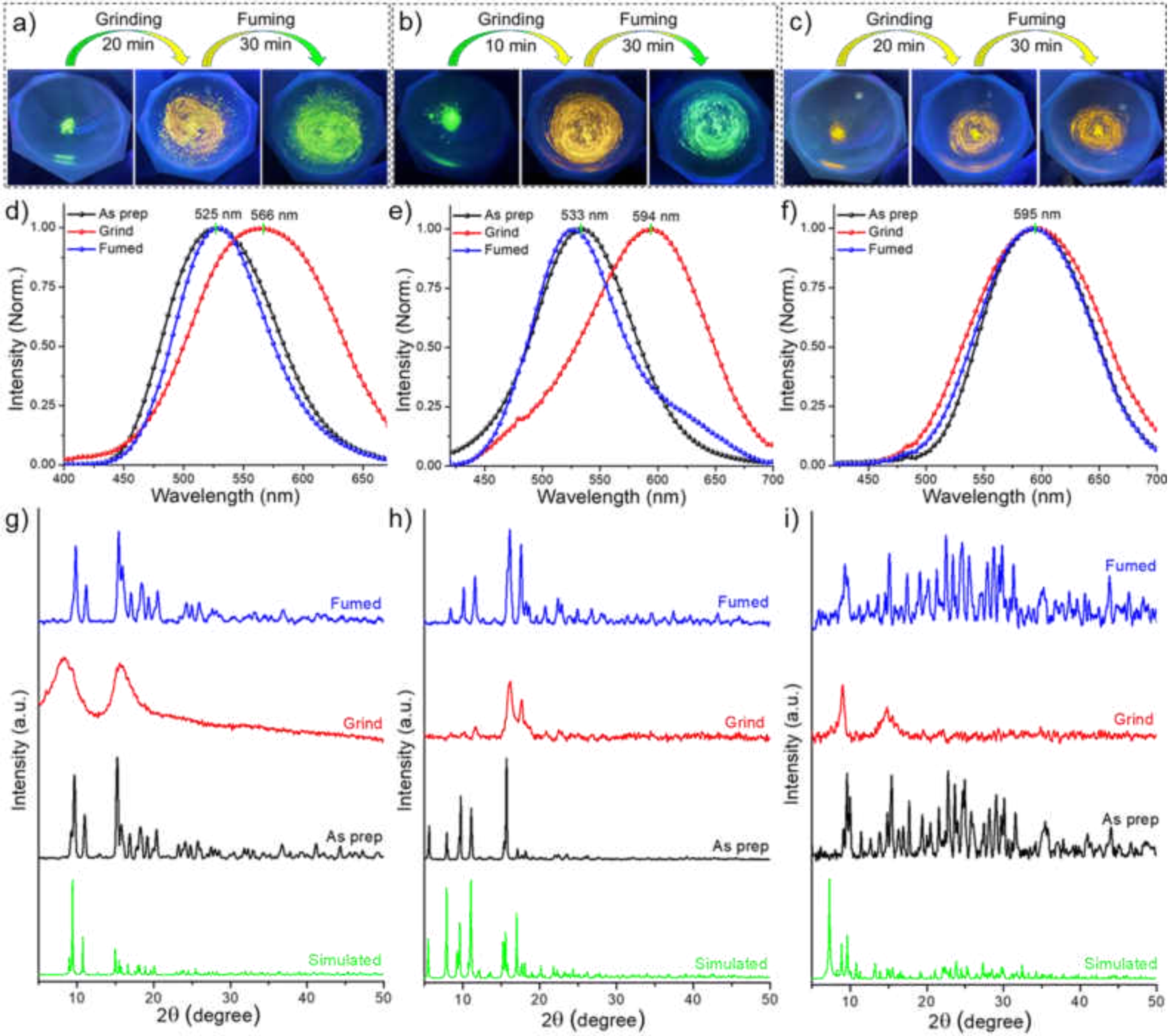
Mass spectrometric studies



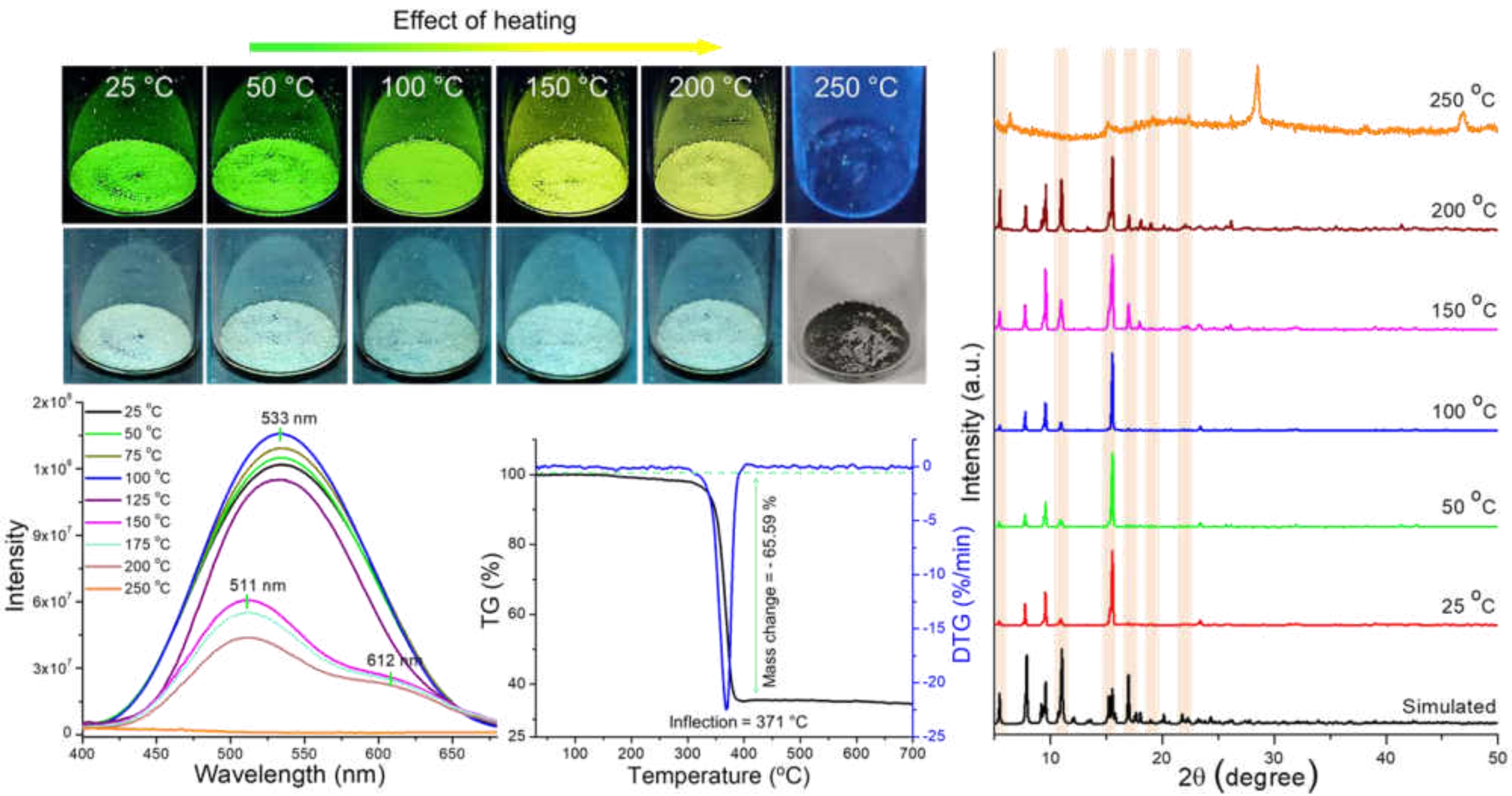
Photophysical properties



Mechanoresponsive properties



Thermoresponsive properties



Dynamics in clusters

Reactions
Isotope exchange
Positional dynamics

Inter-cluster reactions

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

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

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

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

Supporting Information

A + B → C + D

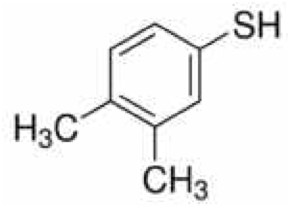
K. R. Krishnadas, et. al., *JACS*, 2016

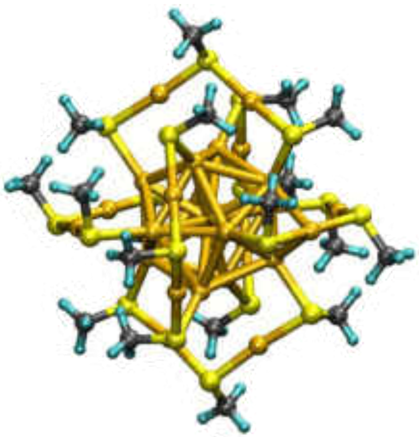
Ag_{25}-Au_{25} experiments

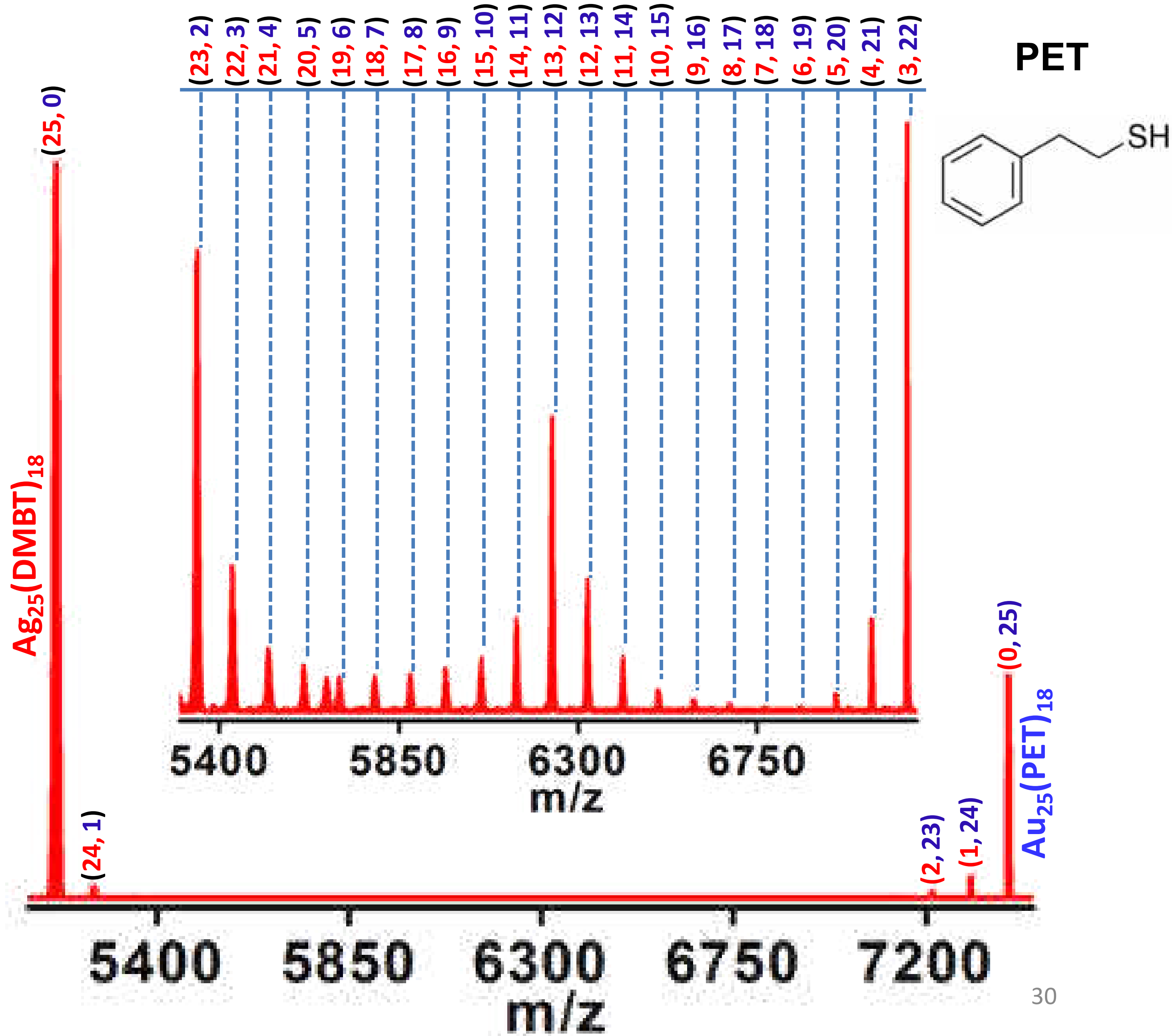
K. R. Krishnadas et al. *Nature Commun.* 2016

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

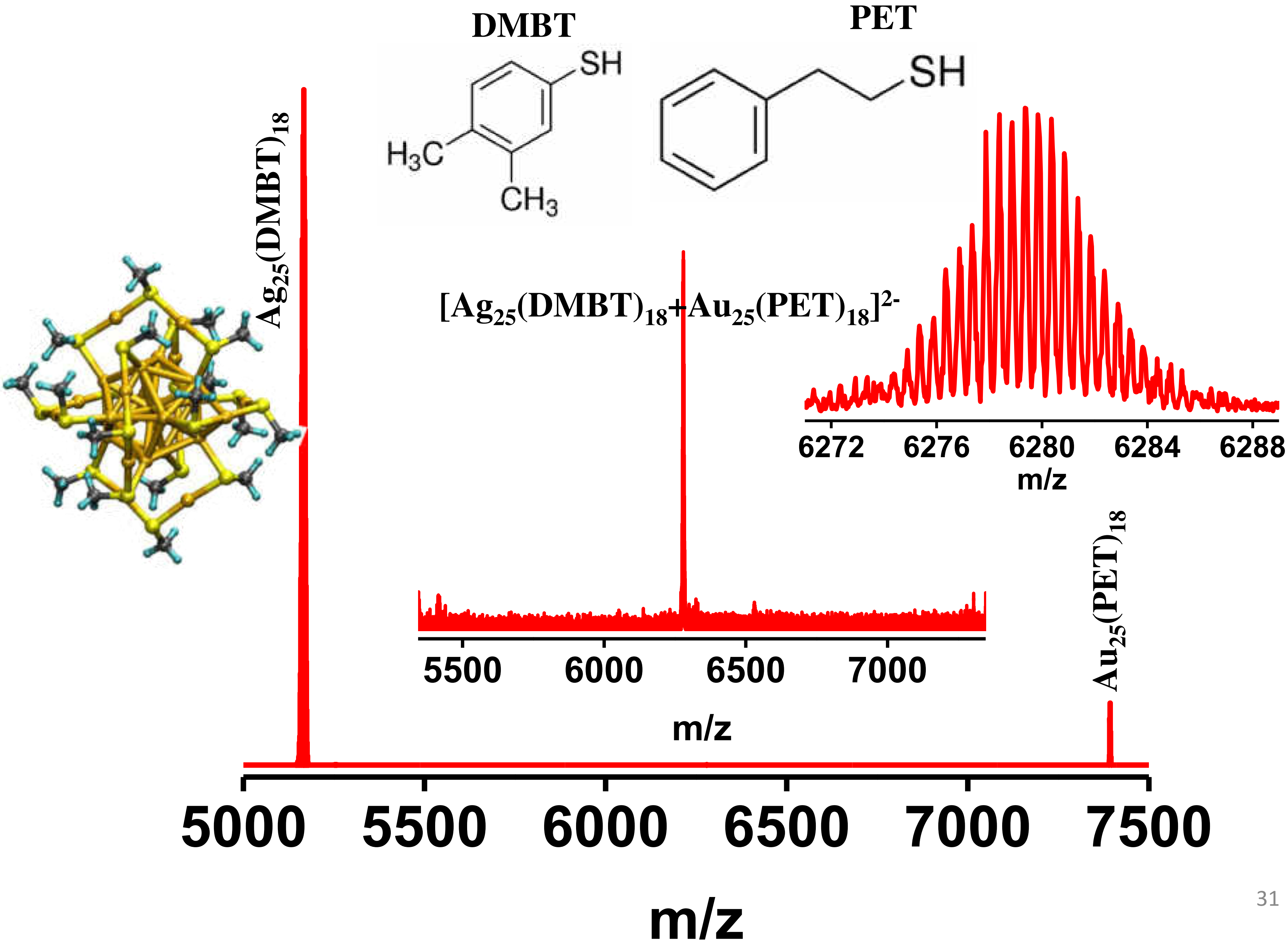
DMBT



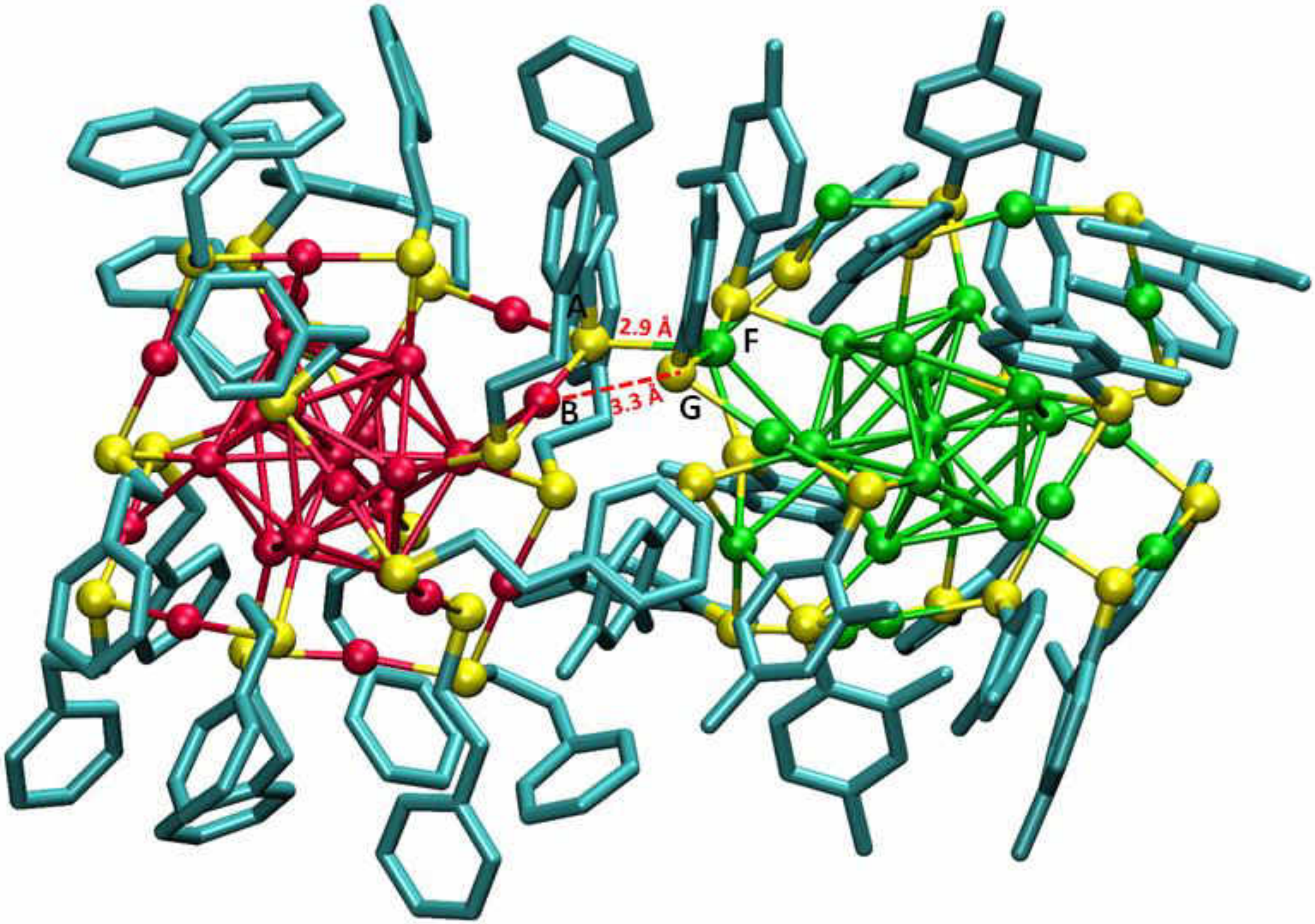


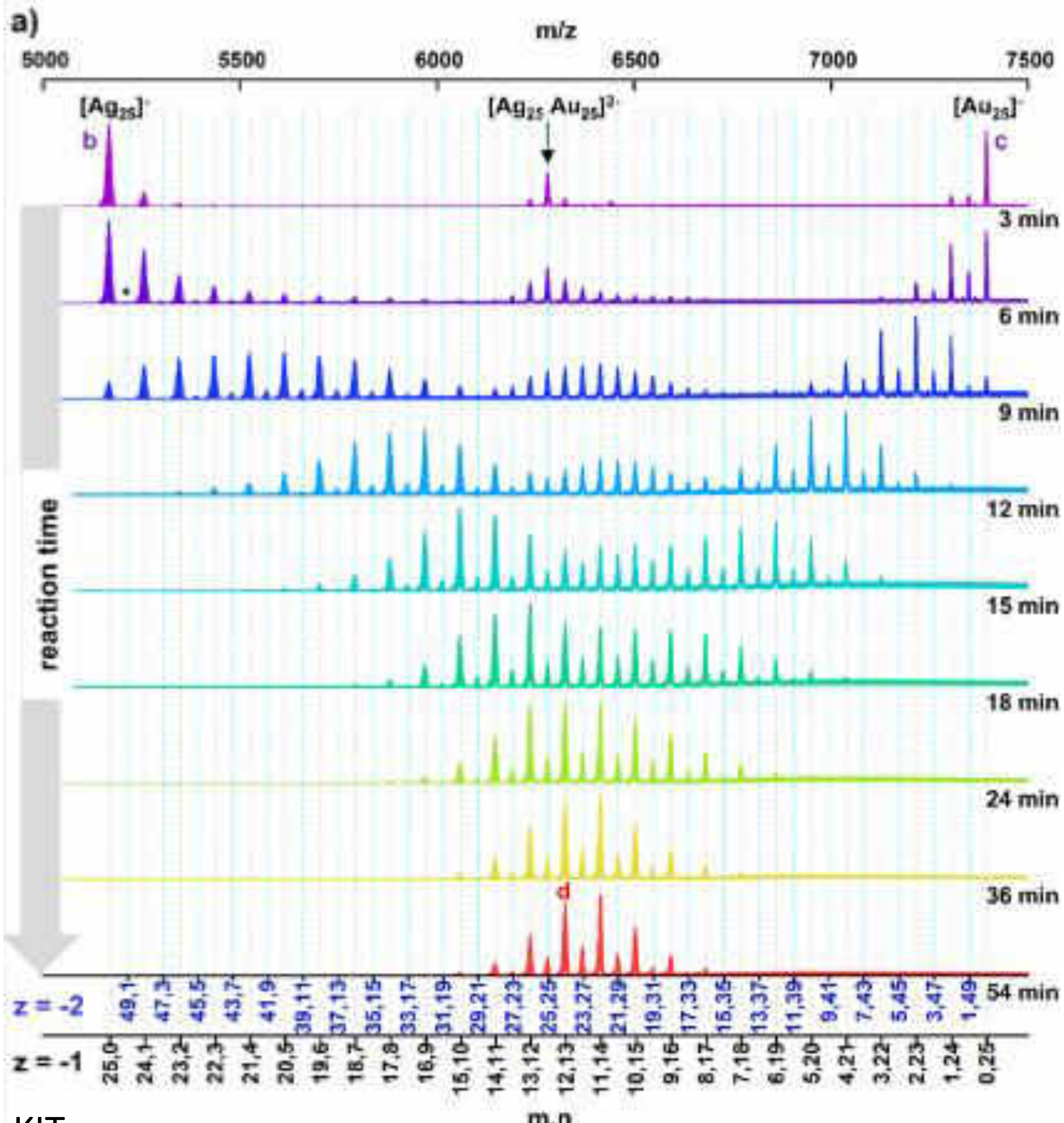


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



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

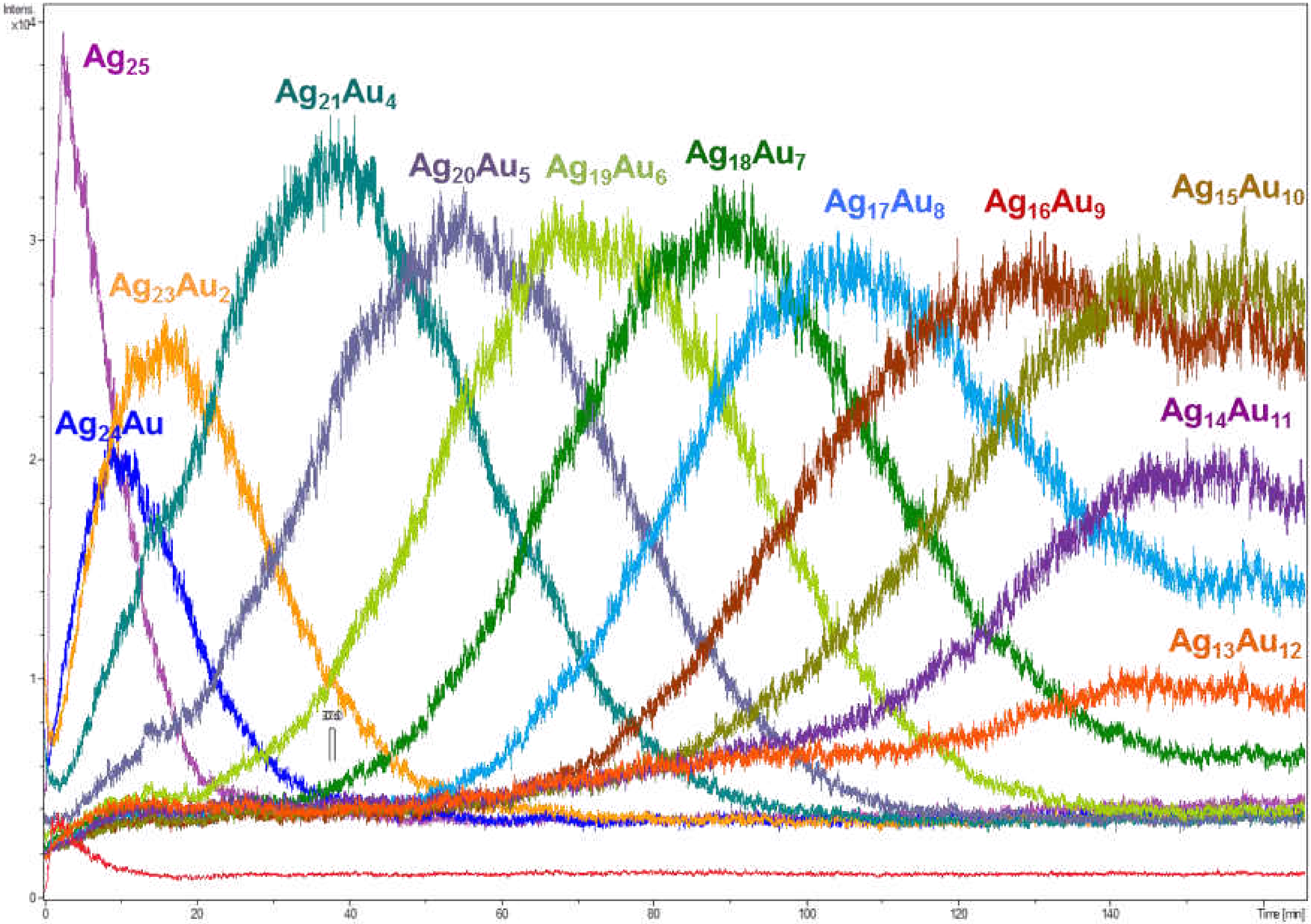




Manfred Kappes, KIT

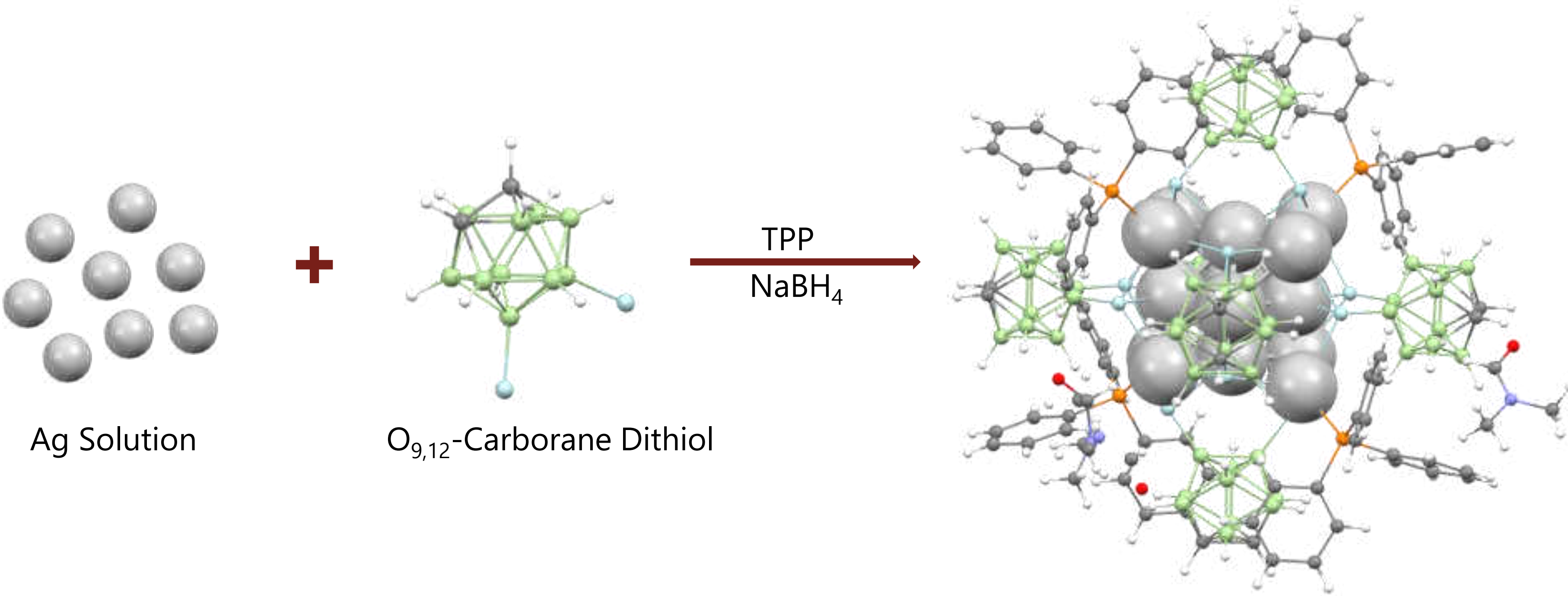
M. Neumaier, A. Baksi, et. al., *JACS* 2021

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



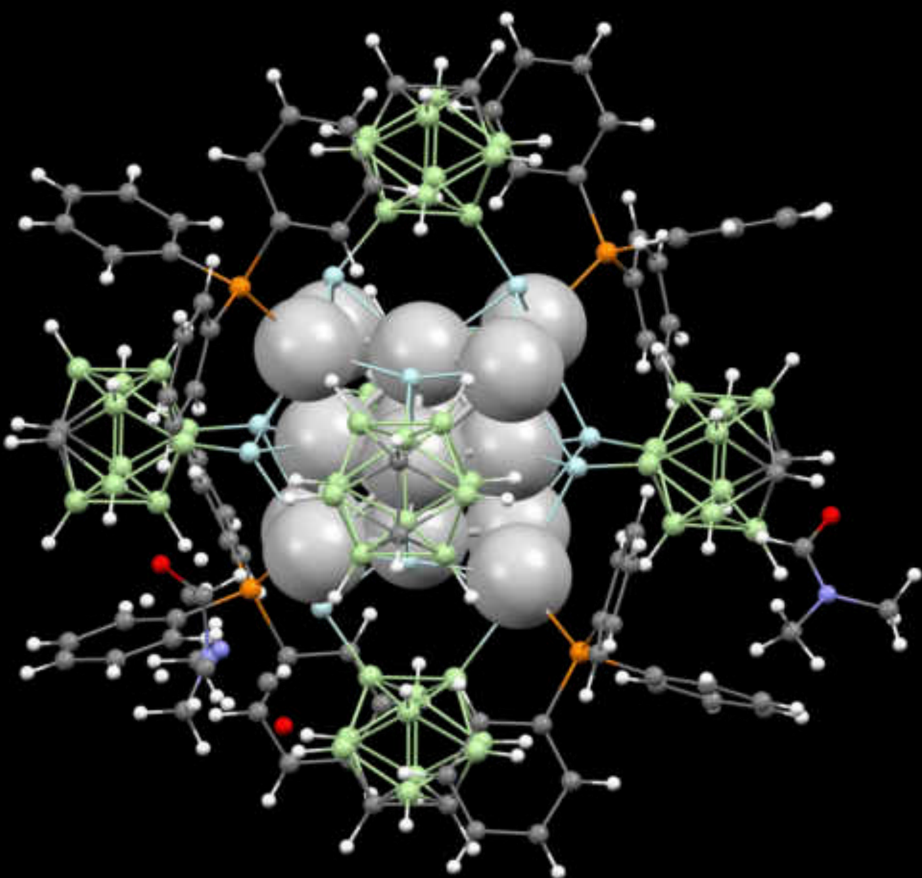
$Ag_{14}(CBDT)_6(TPP)_4$

Vivek Yadav, et. al., Unpublished

Crystallization

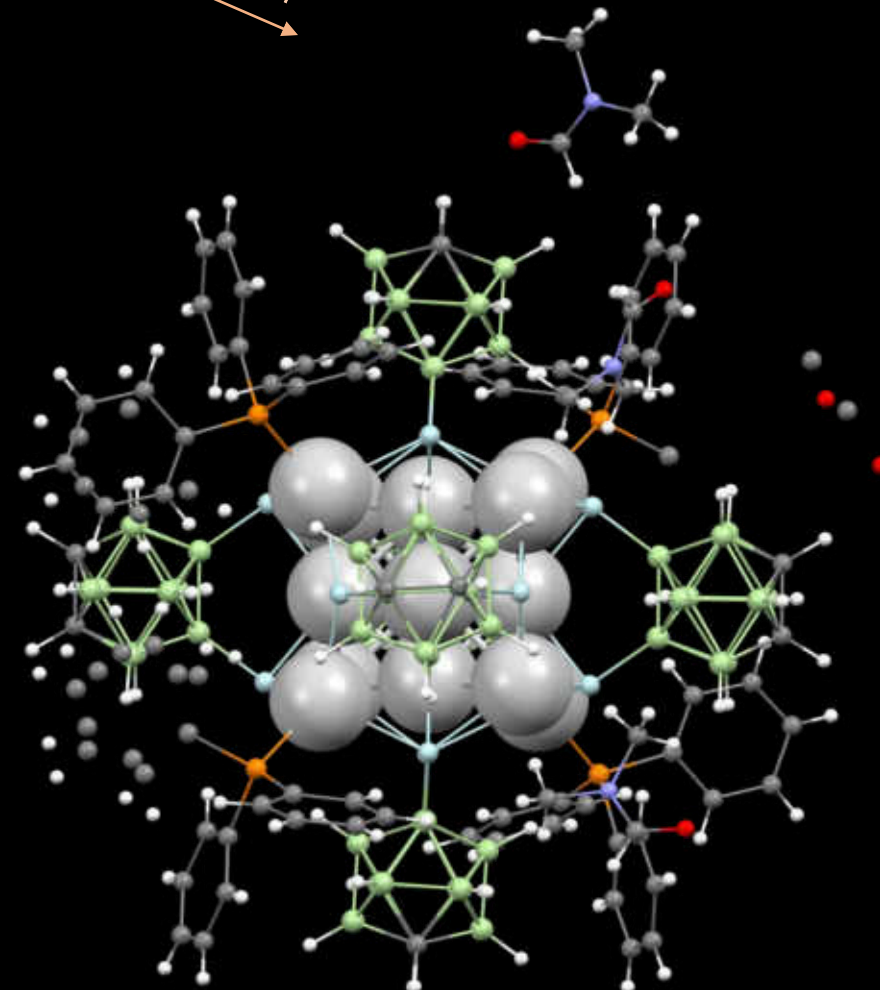
Without MeOH

With MeOH



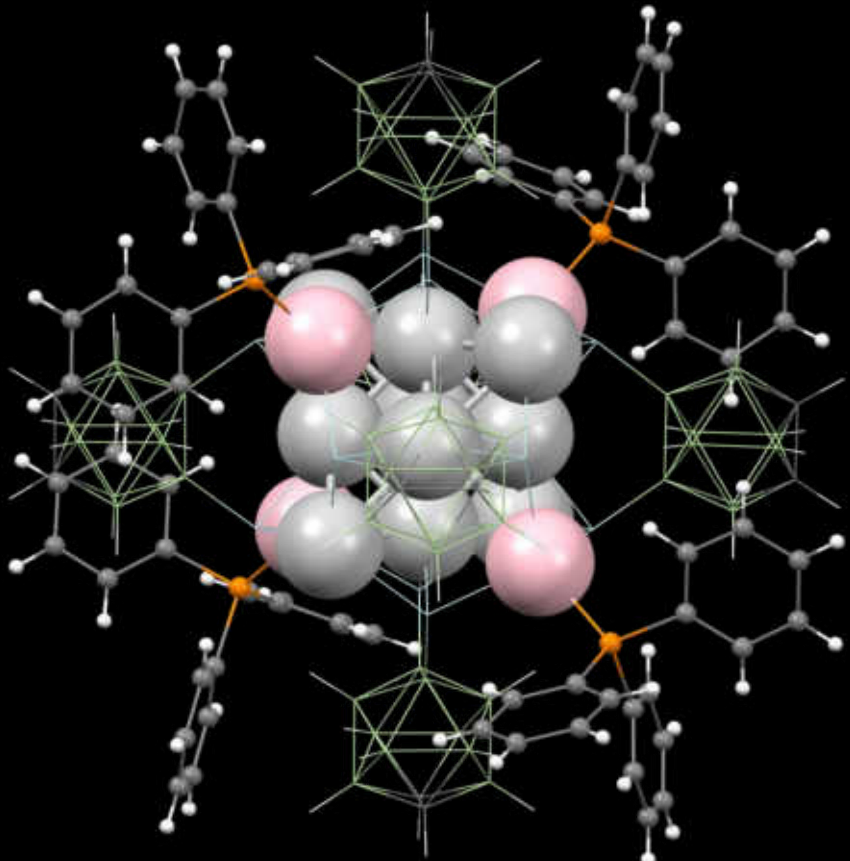
Ag_{14} $(CBDT)_6$ $(TPP)_4$

Tetrahedral TPP

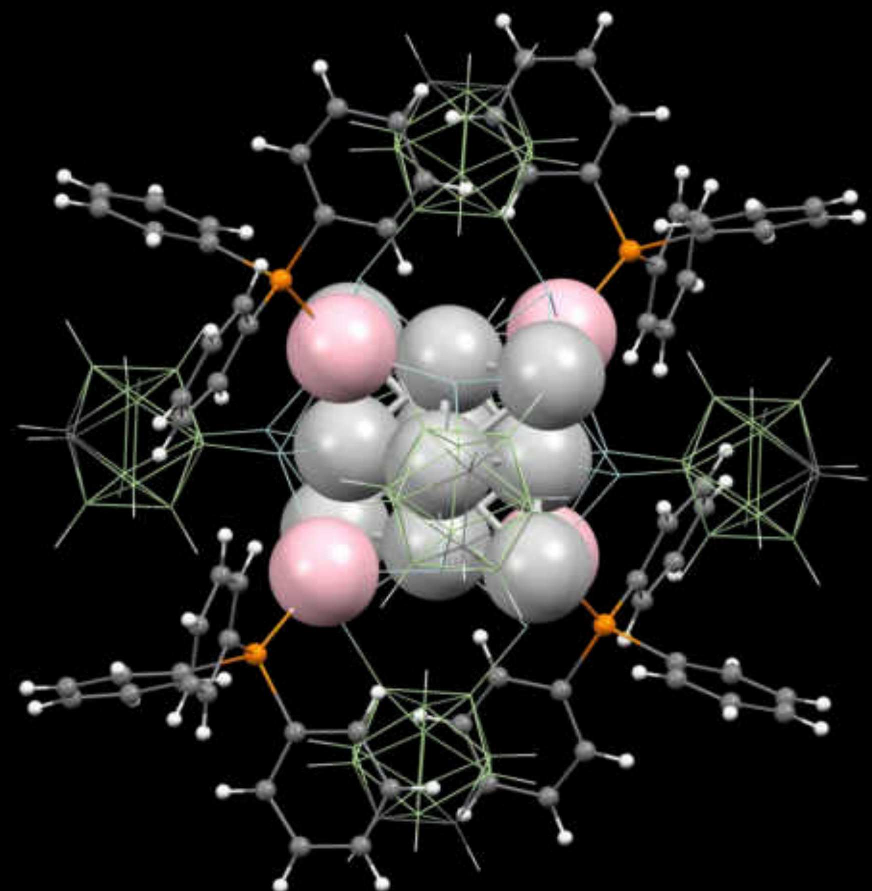


Ag_{14} $(CBDT)_6$ $(TPP)_4$

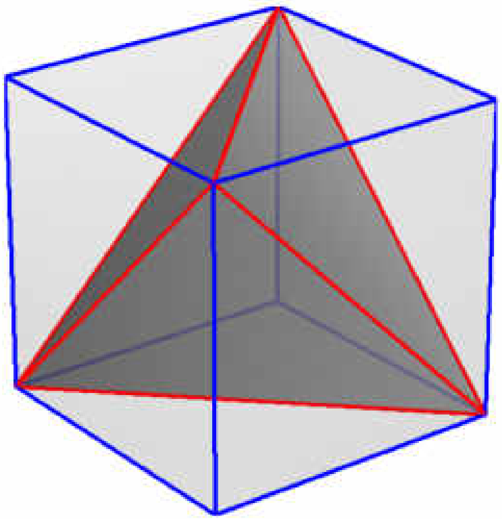
Square Planar TPP

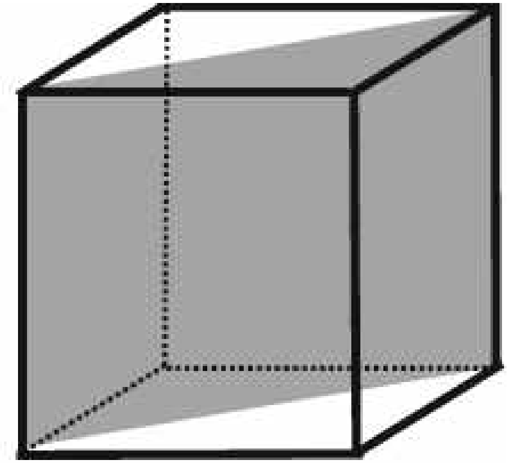


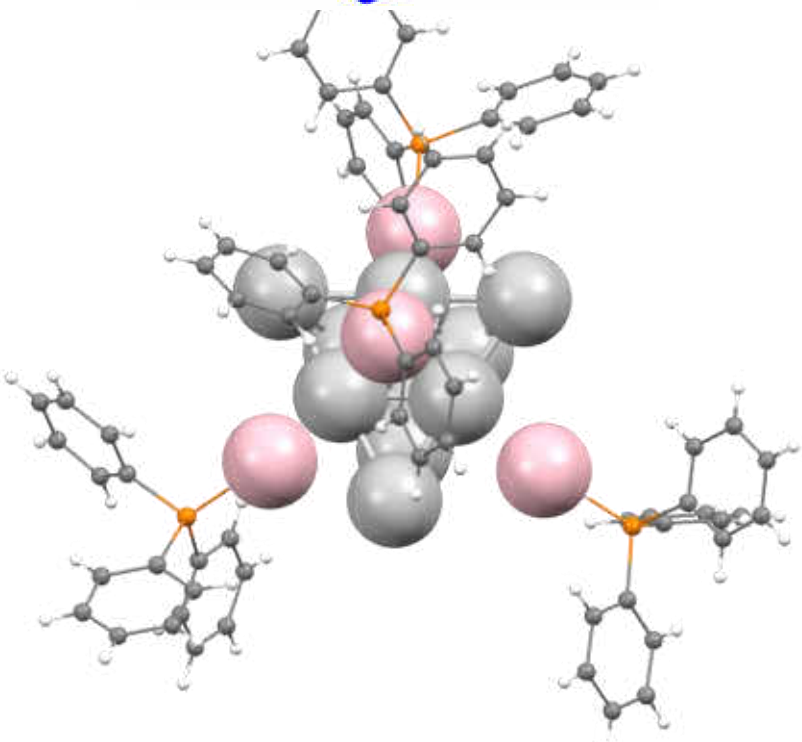
Tetrahedral TPP



Square Planar TPP







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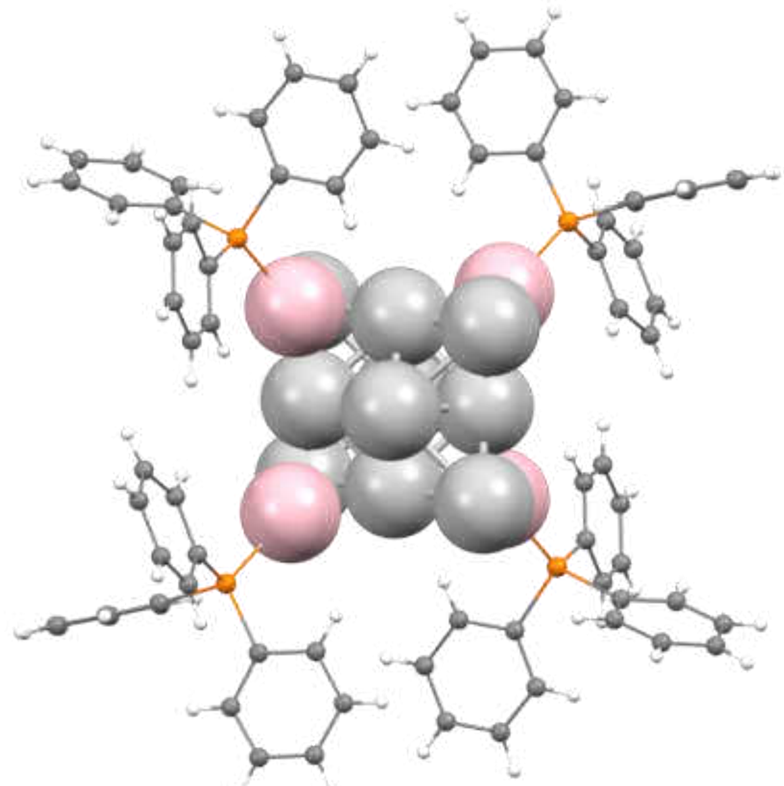
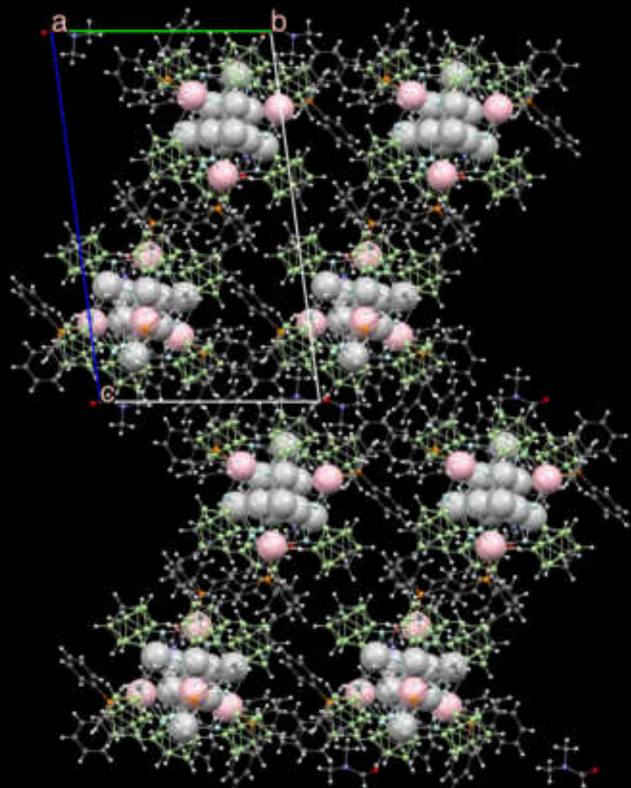
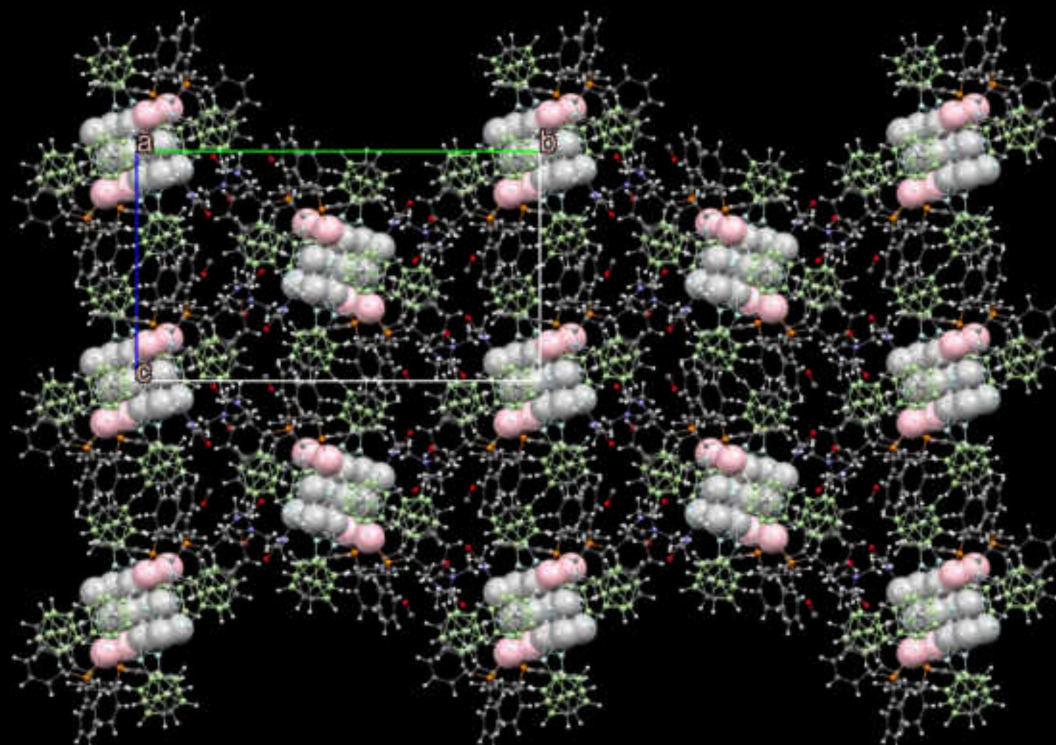


Square Planar TPP

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



Tetrahedral TPP

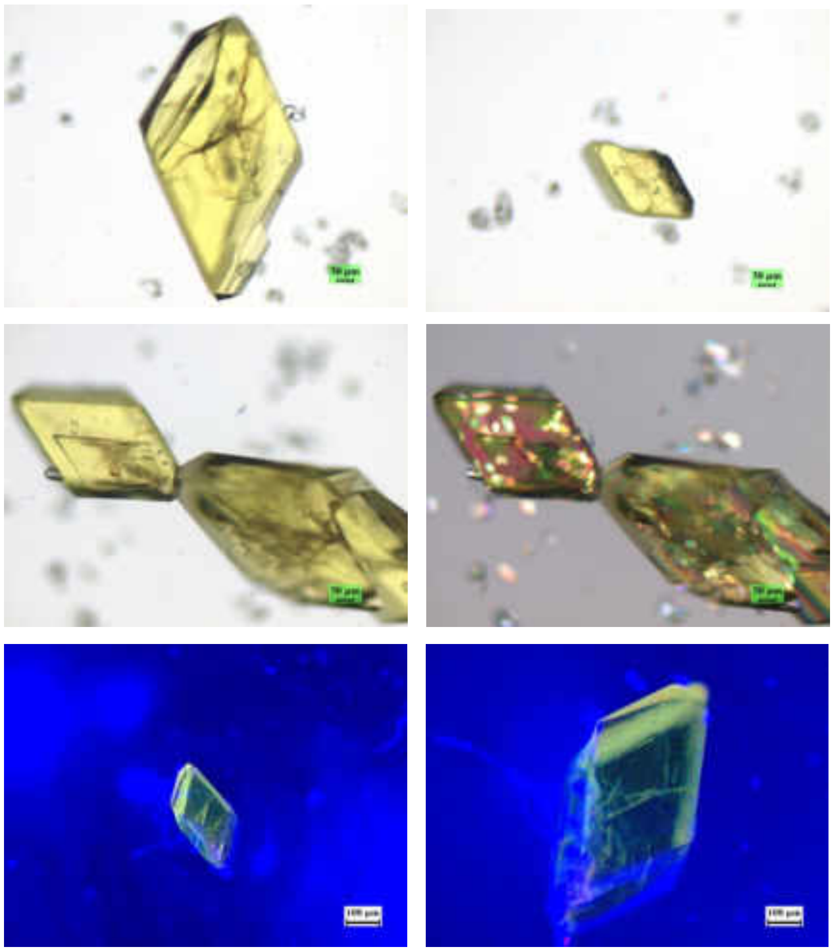


Square Planar TPP

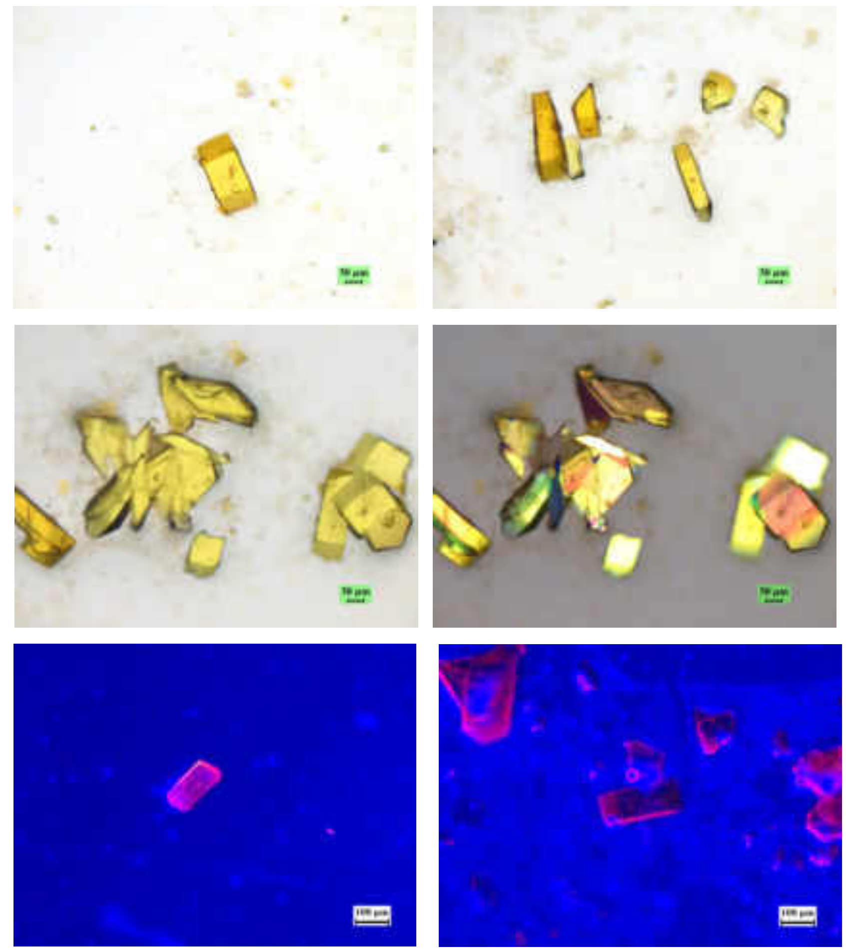
Crystal system - Triclinic
Space group - P -1
Volume - 8176.8(13) Å3
Z - 2

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

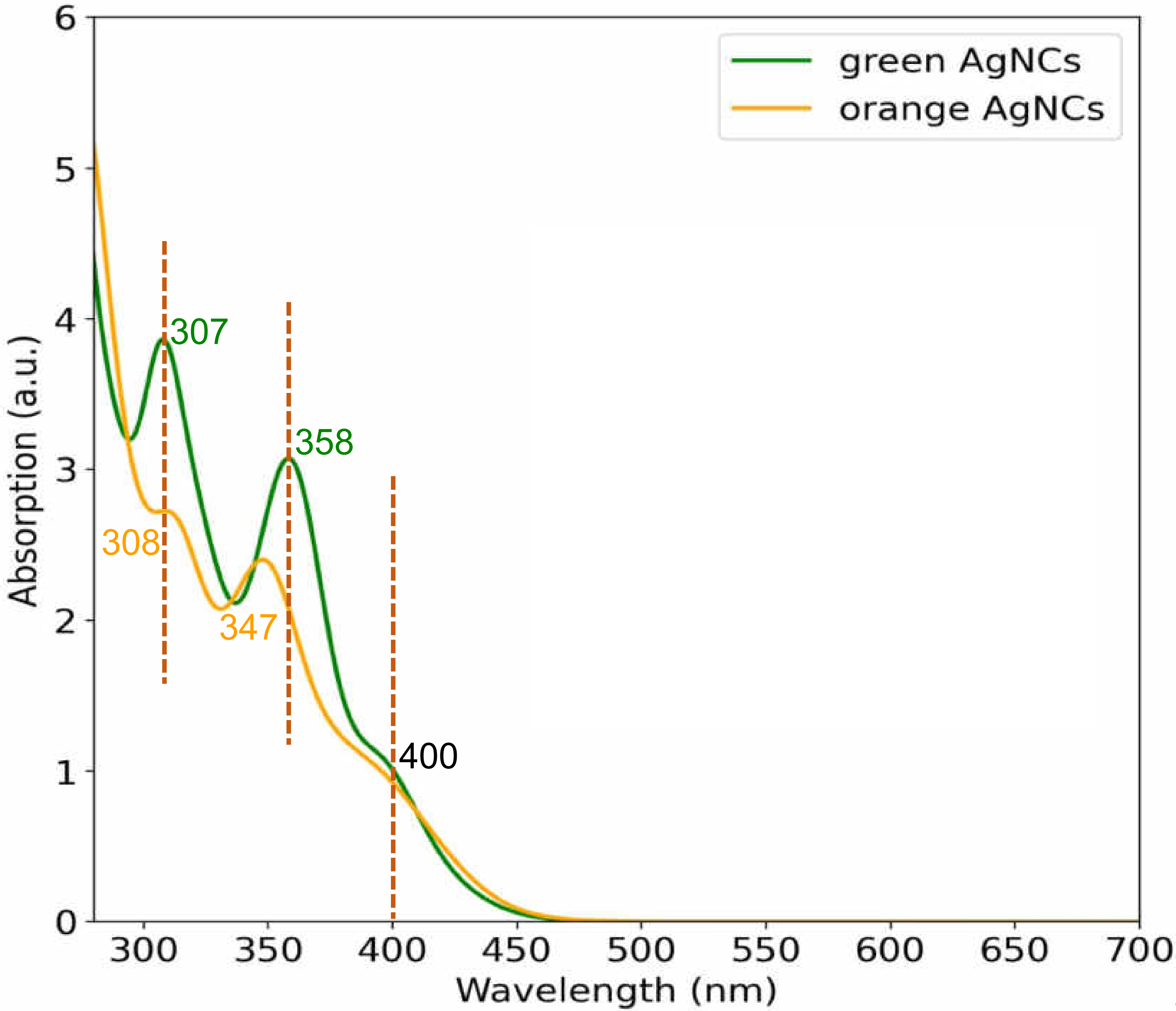
Luminescence of crystals of $Ag_{14}(CBDT)_6(TPP)_4$



Tetrahedral TPP



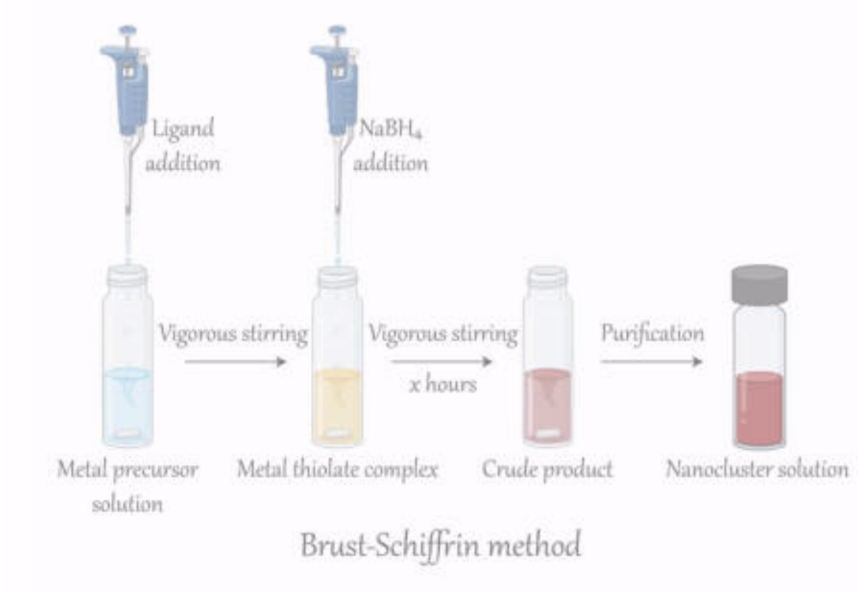
Square Planar TPP

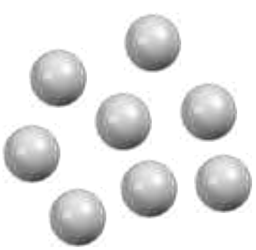

6
5
4
3
2
1
0
Absorption (a.u.)
300
350
400
450
500
550
600
650
700
Wavelength (nm)
green AgNCs
orange AgNCs
307
358
308
347
400

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

Vivek Yadav, et. al., *Nature Communications*, In Press

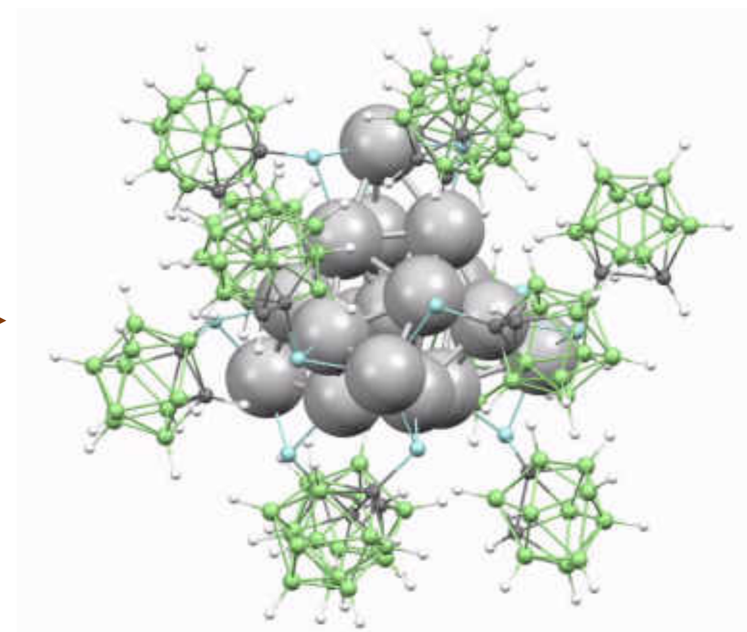
Synthesis Schematic of $[Ag_{17}(o_1\text{-}CBT)_{12}]^{3-}$ Nanocluster





+

$\xrightarrow{NaBH_4}$

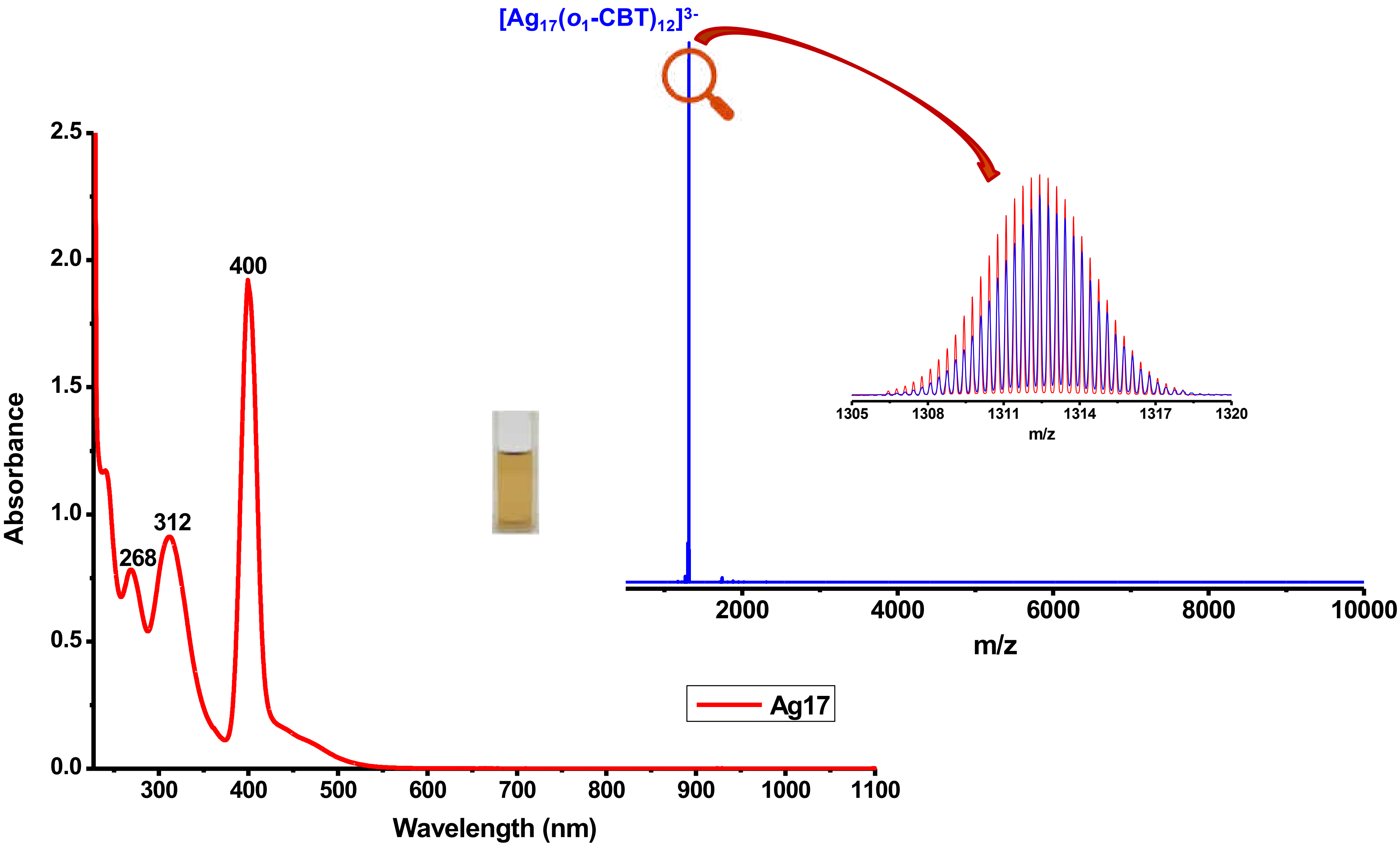


Ag Solution

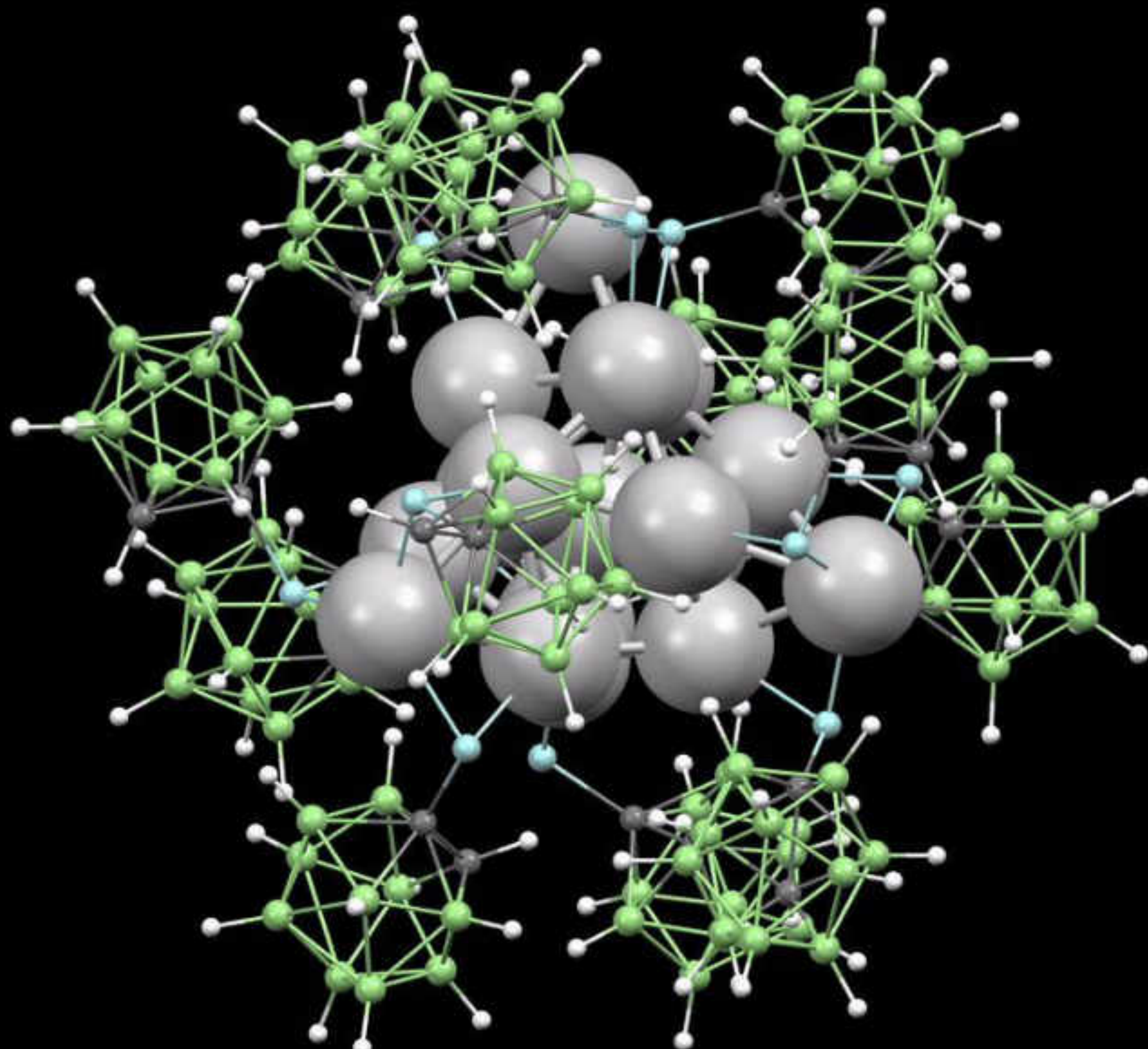
o_1-Carborane Thiol

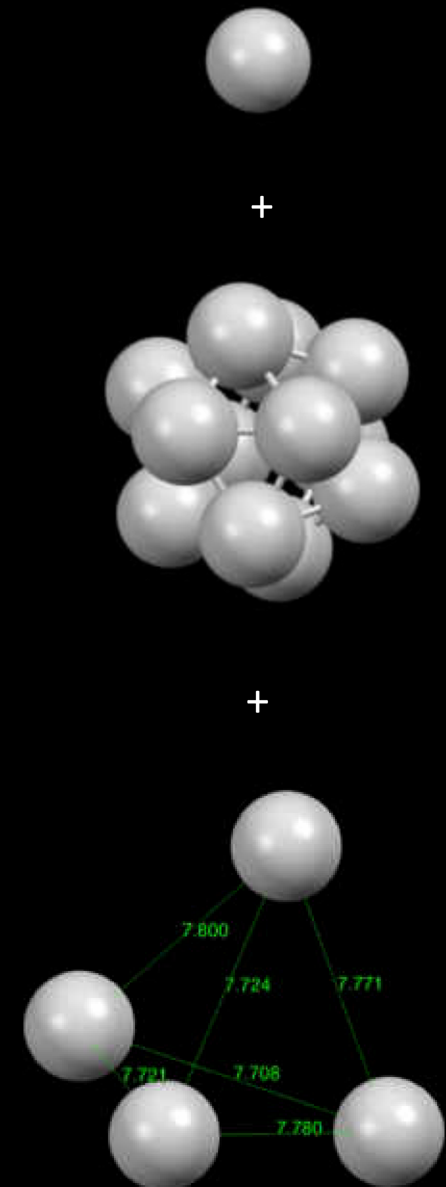
$[Ag_{17}(o_1\text{-}CBT)_{12}]^{3-}$

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

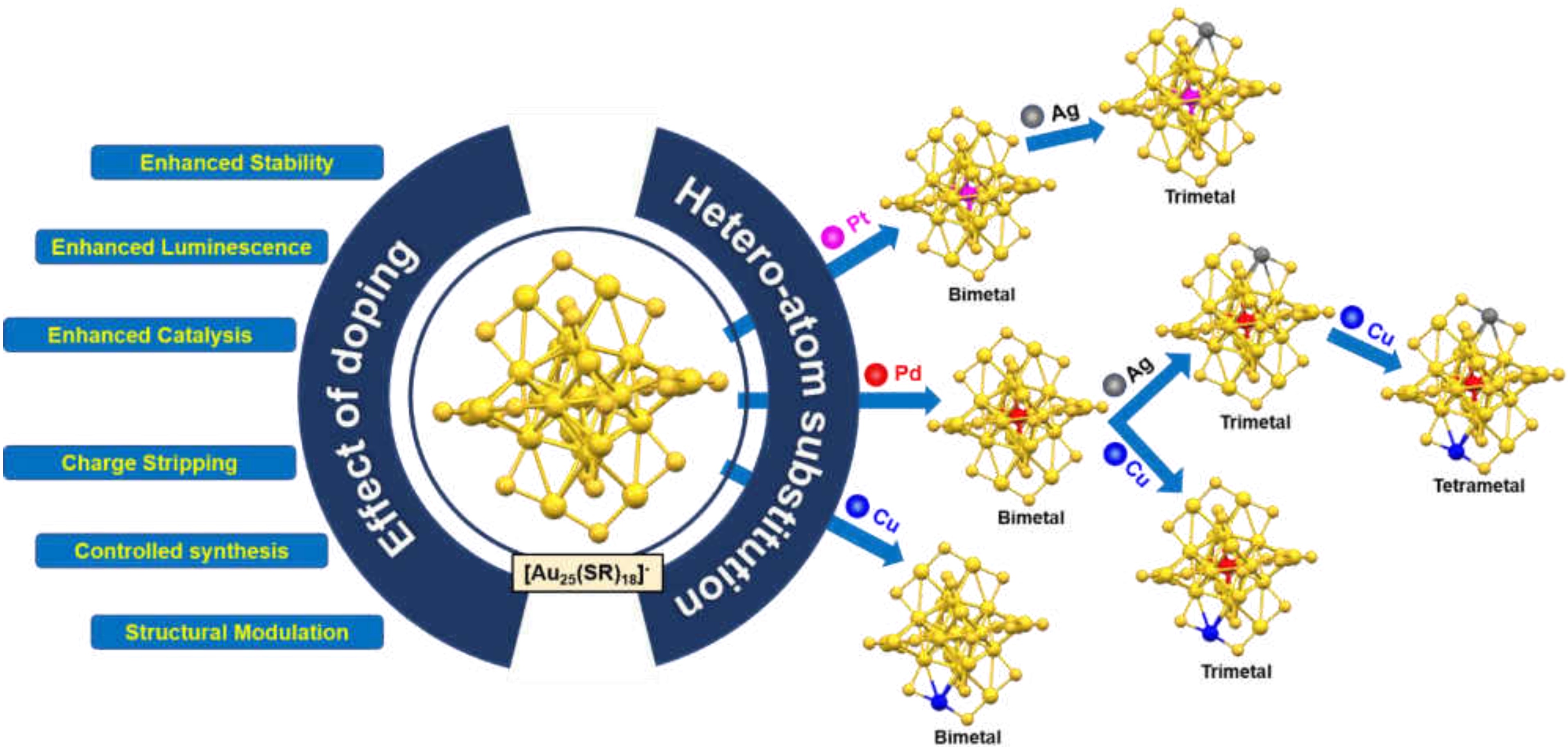


Structure of $[Ag_{17}(o_1\text{-}CBT)_{12}]^{3-}$ Nanocluster

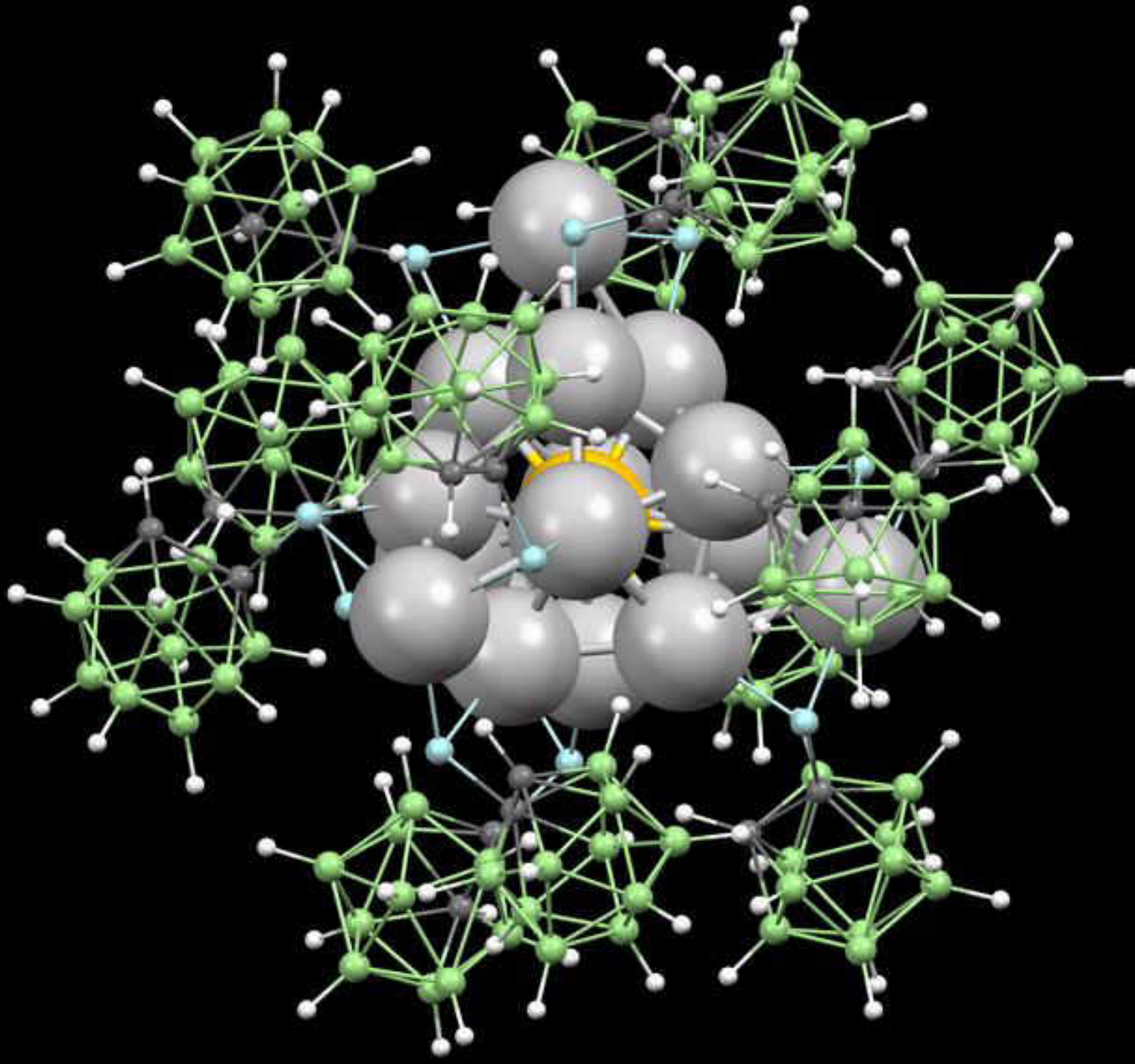




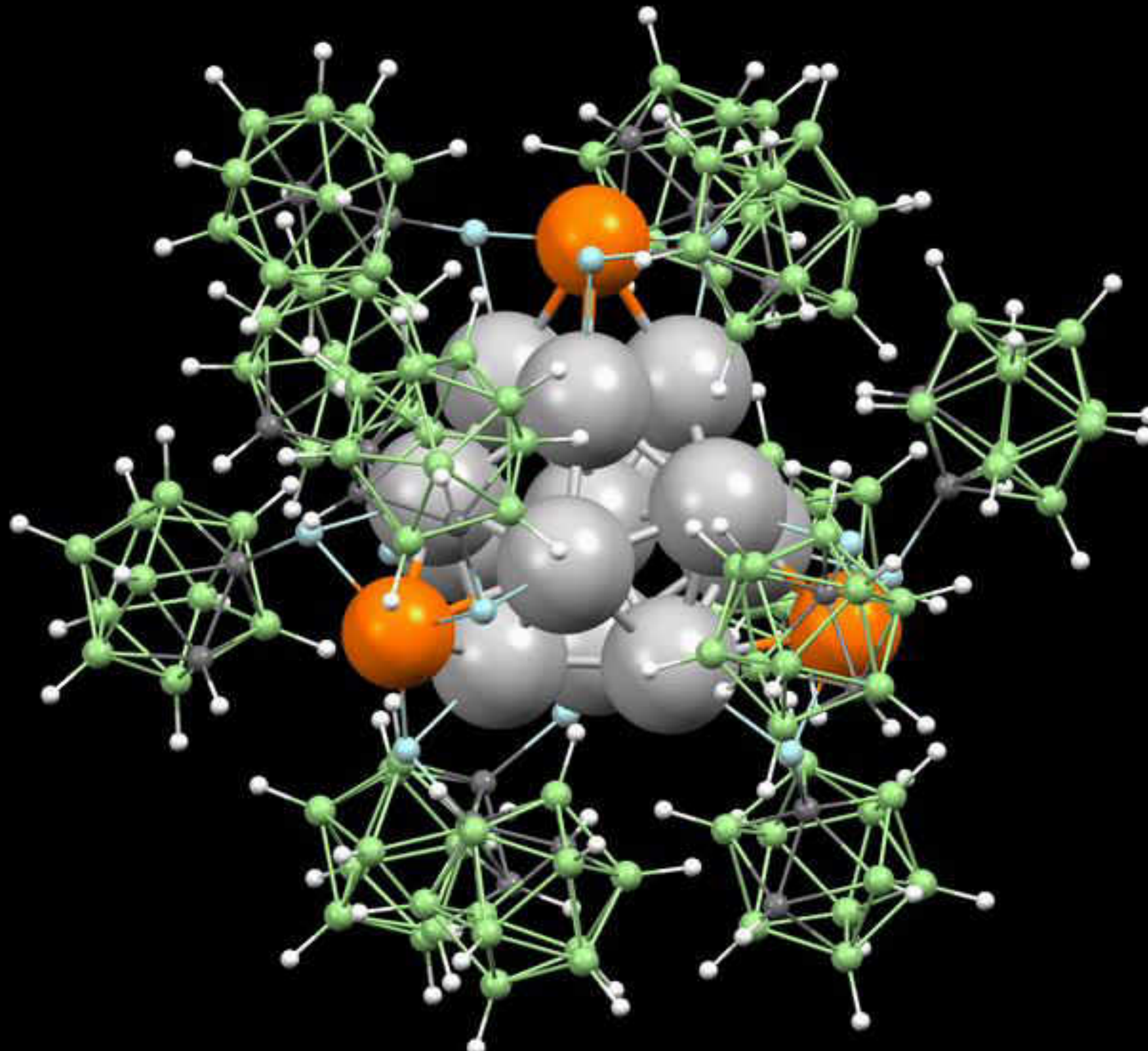
Alloying of Nanoclusters: The Work Plan



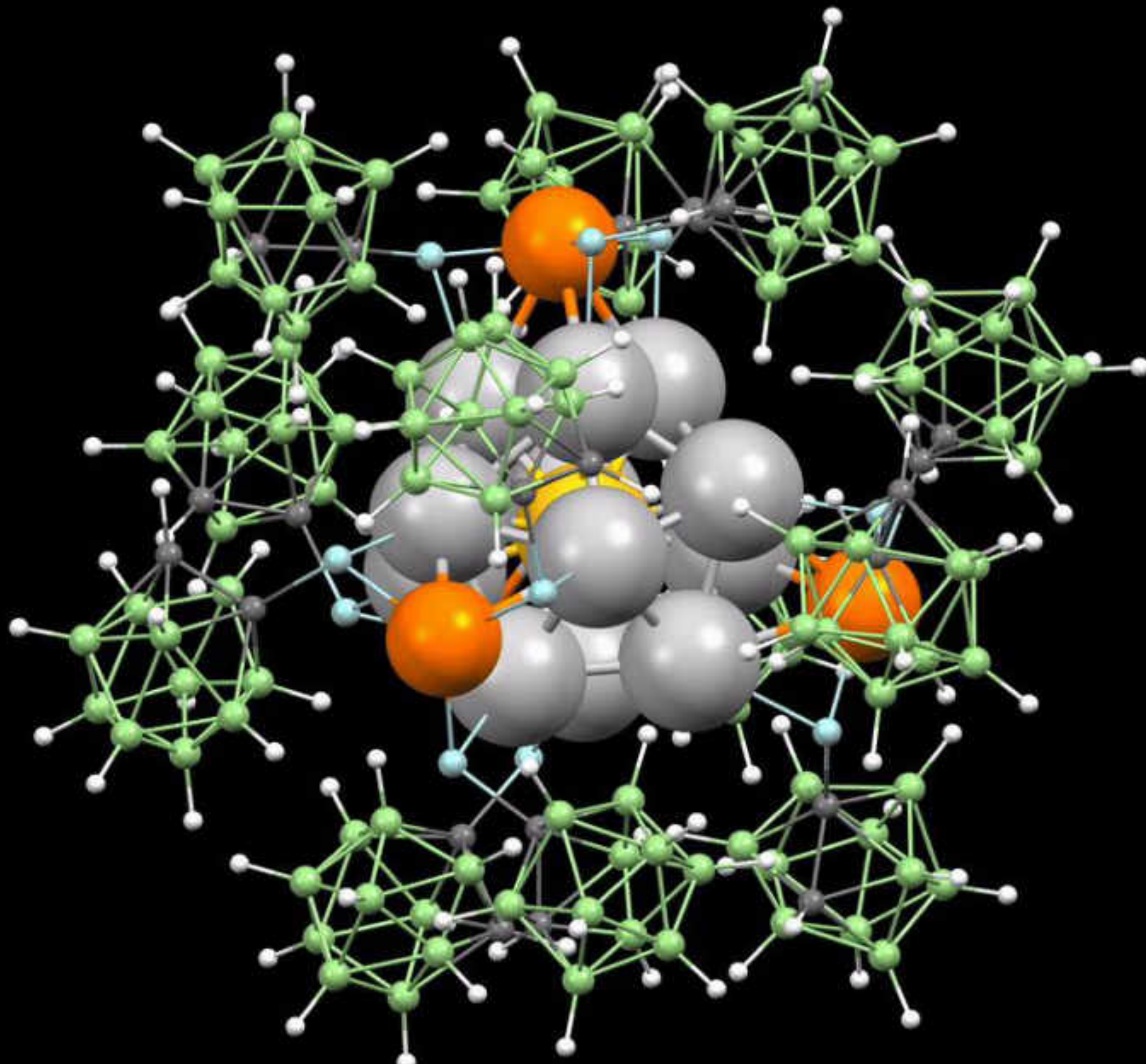
Structure of $AuAg_{16}$ Nanocluster



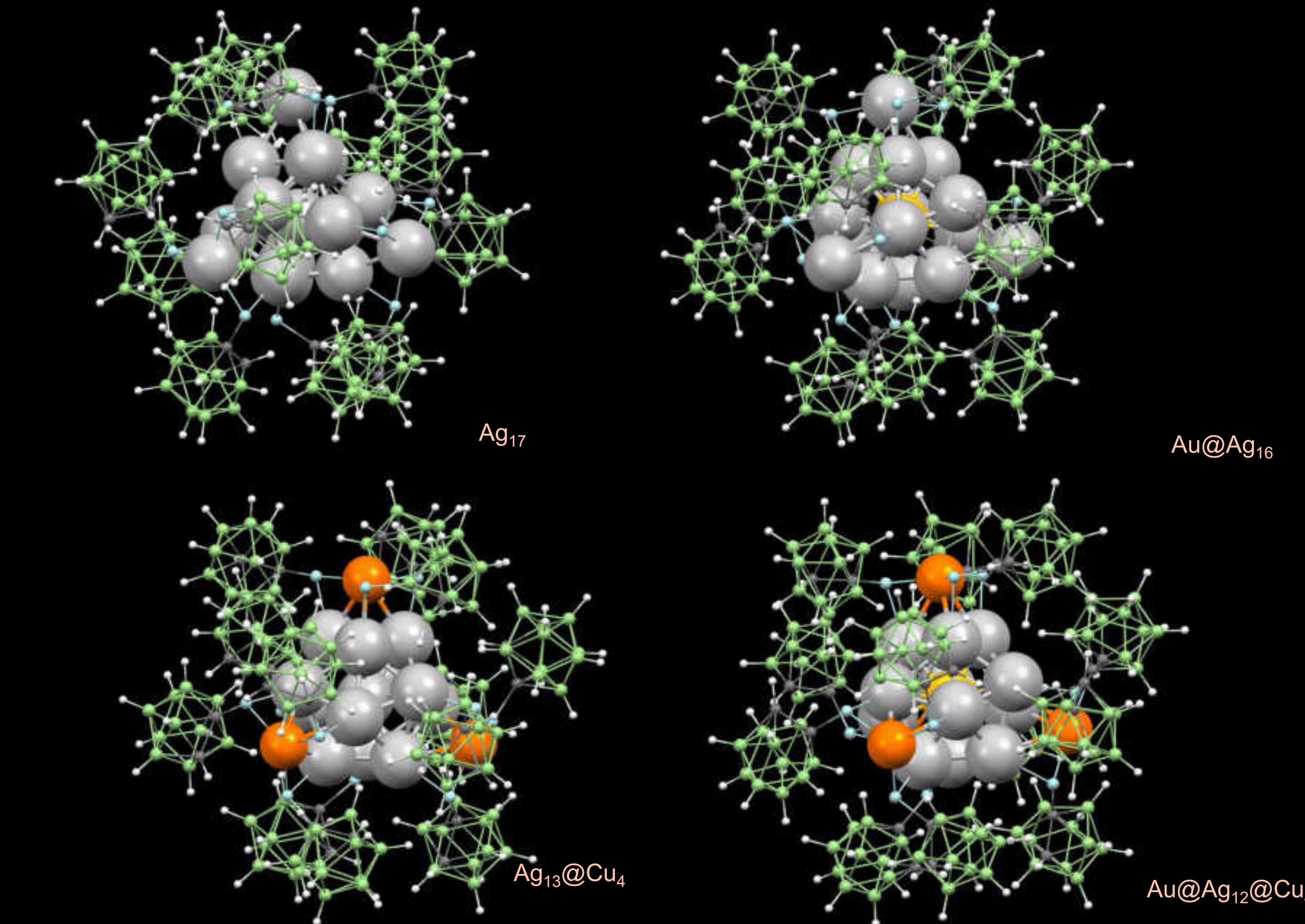
Structure of $Ag_{13}Cu_4$ Nanocluster



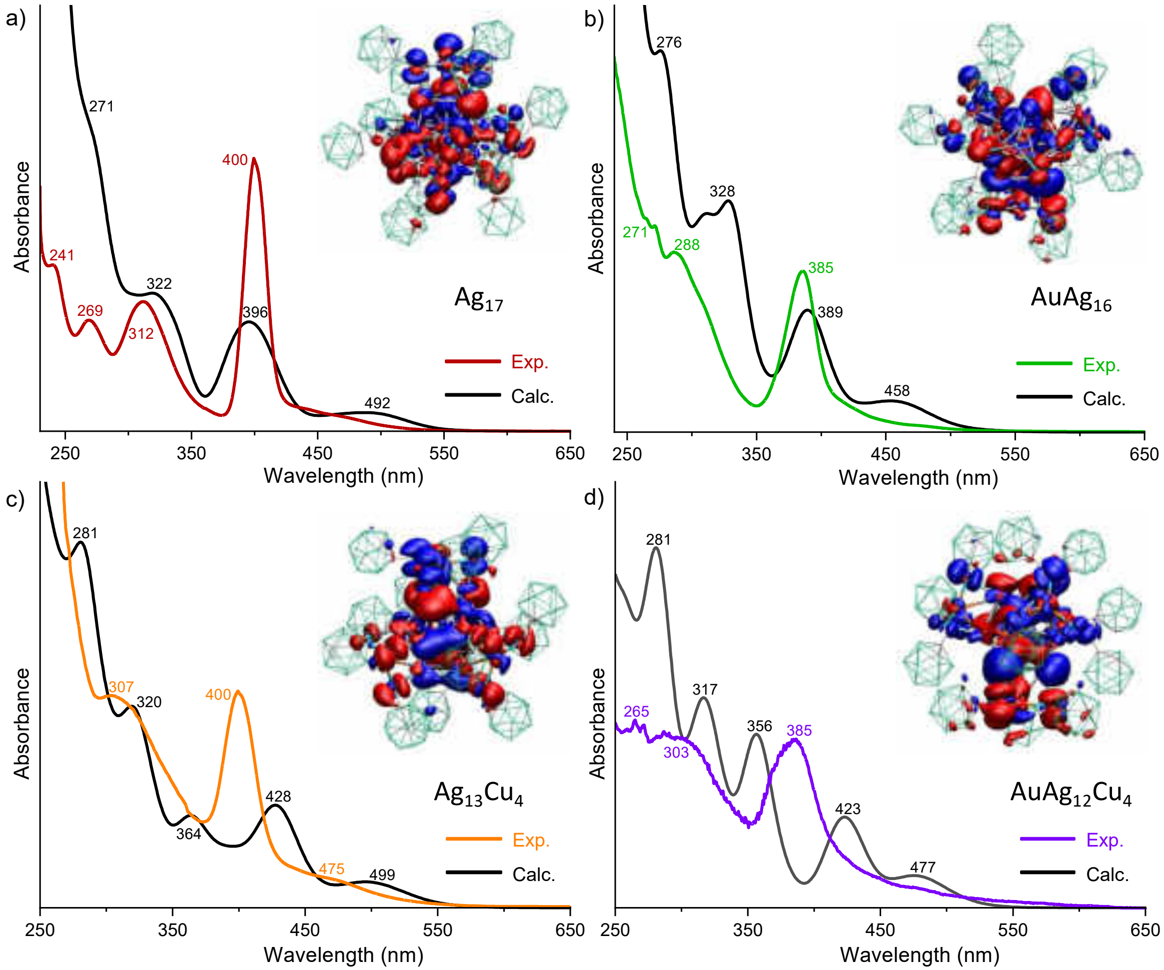
Structure of $AuAg_{12}Cu_4$ Nanocluster

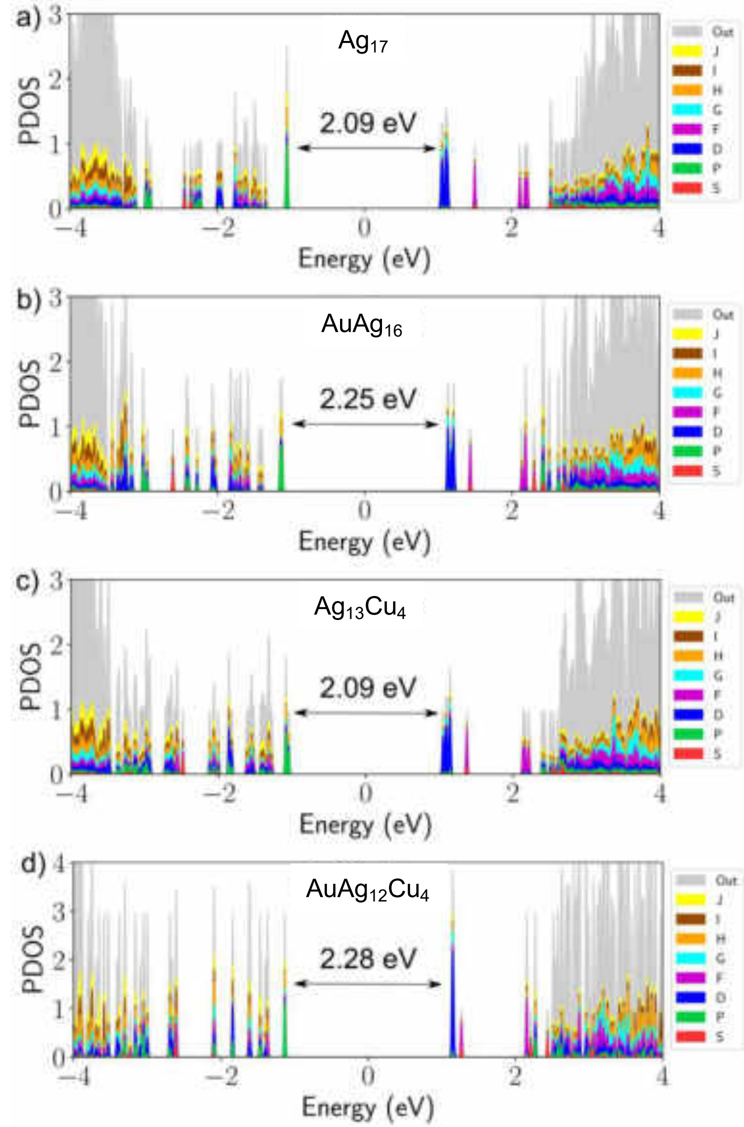


Structure of M_{17} Nanoclusters

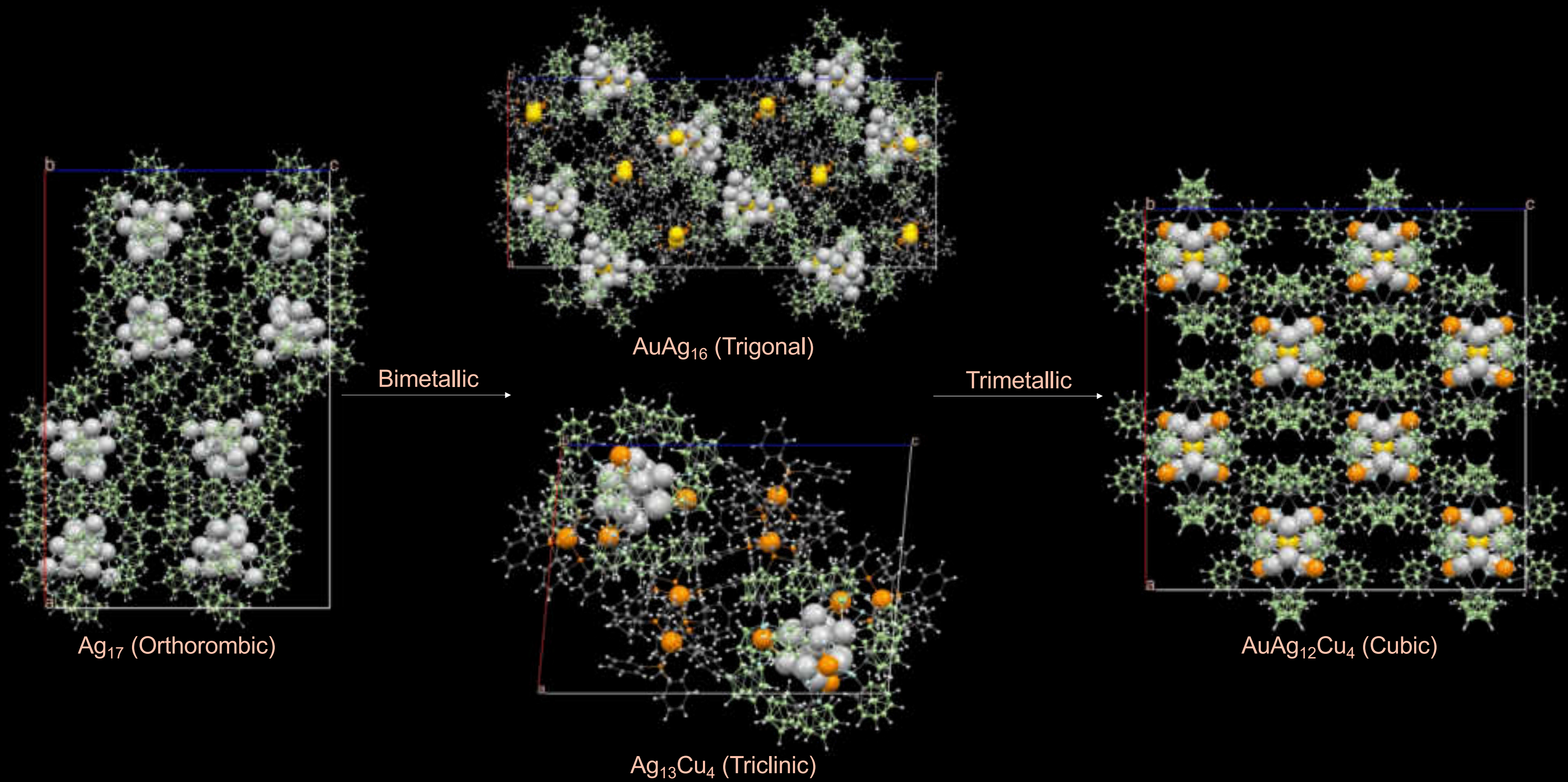


Theoretical Understanding

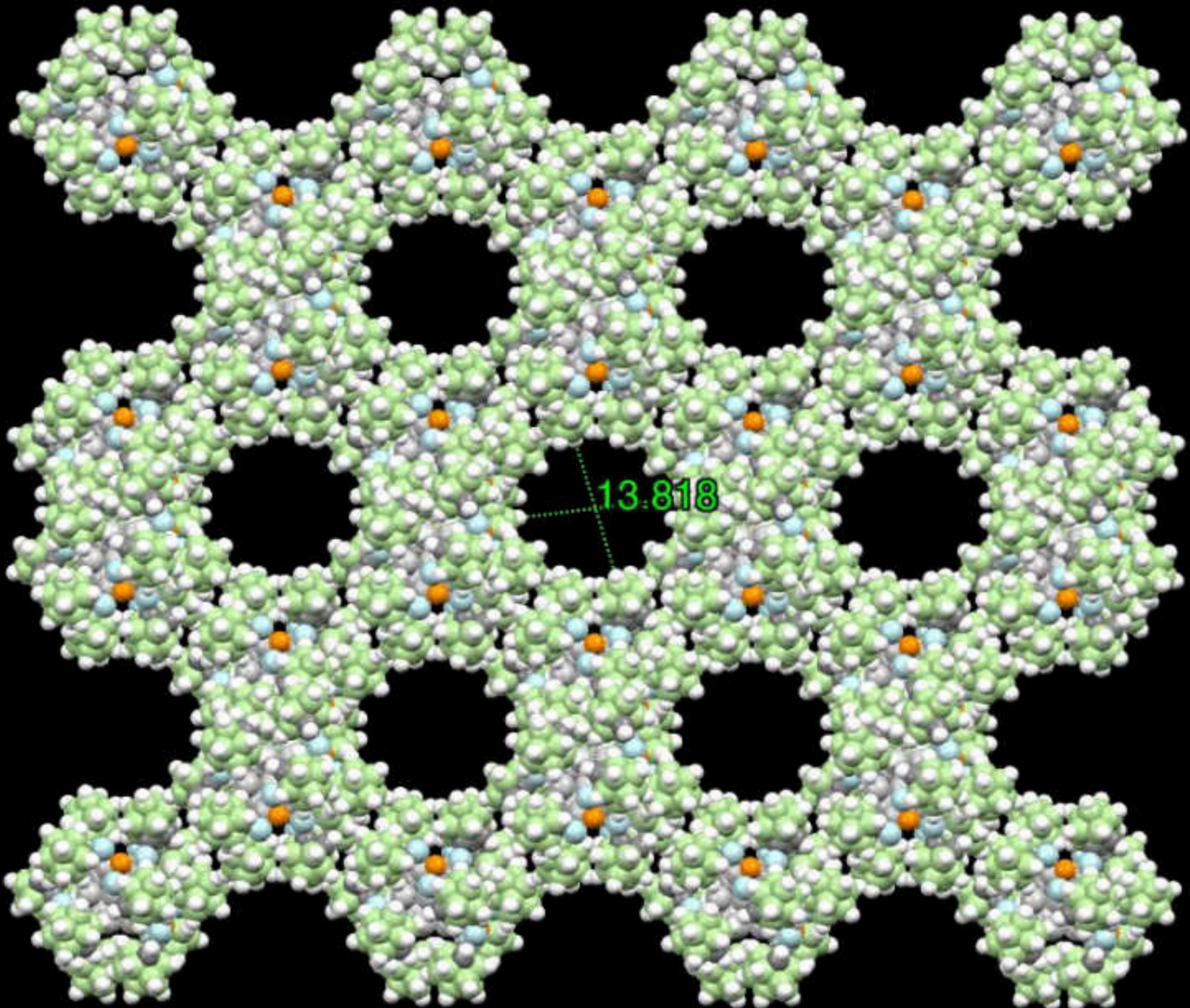




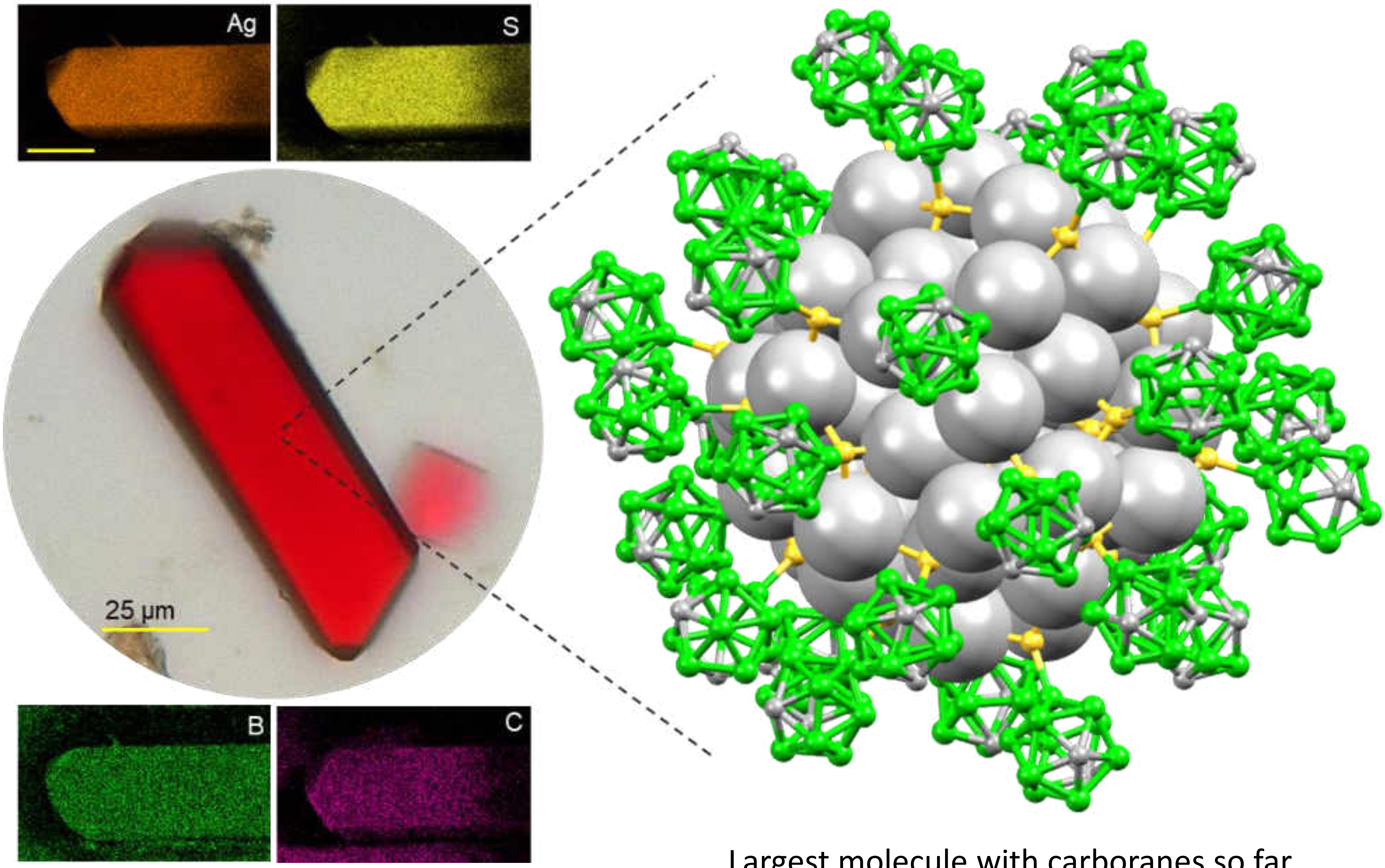
Packing of M_{17} Nanoclusters



Structural Pores of $AuAg_{12}Cu_4$ Nanoclusters



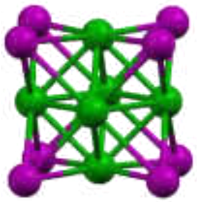
[$Ag_{62}S_{12}(CBT)_{32}$] Nanocluster



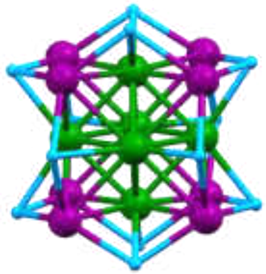
Largest molecule with carboranes so far……

Jana *et al.*, manuscript under preparation

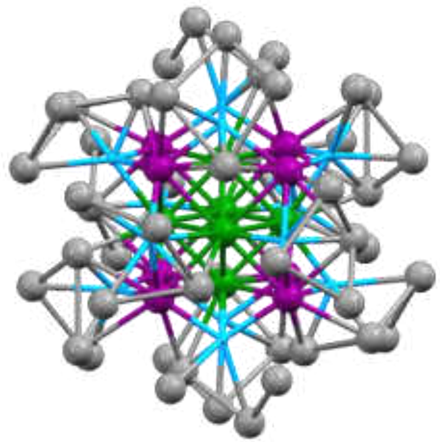
Structural anatomy of $[Ag_{62}S_{12}(CBT)_{32}]$ Nanocluster



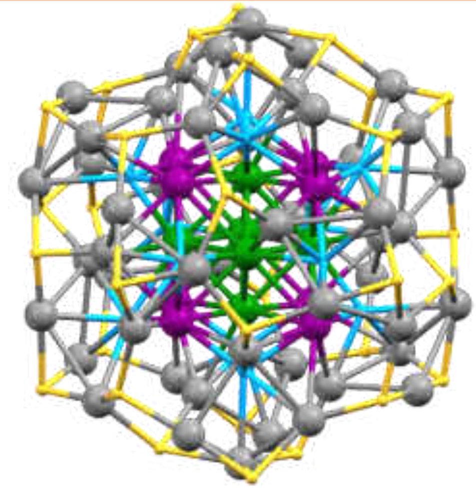
$Ag_6@Ag_8$



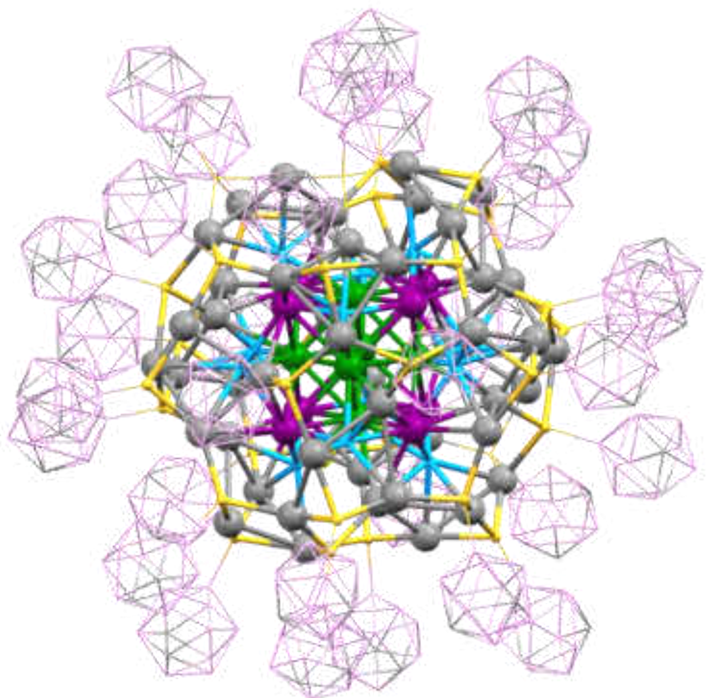
$Ag_6@Ag_8S_{12}$



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

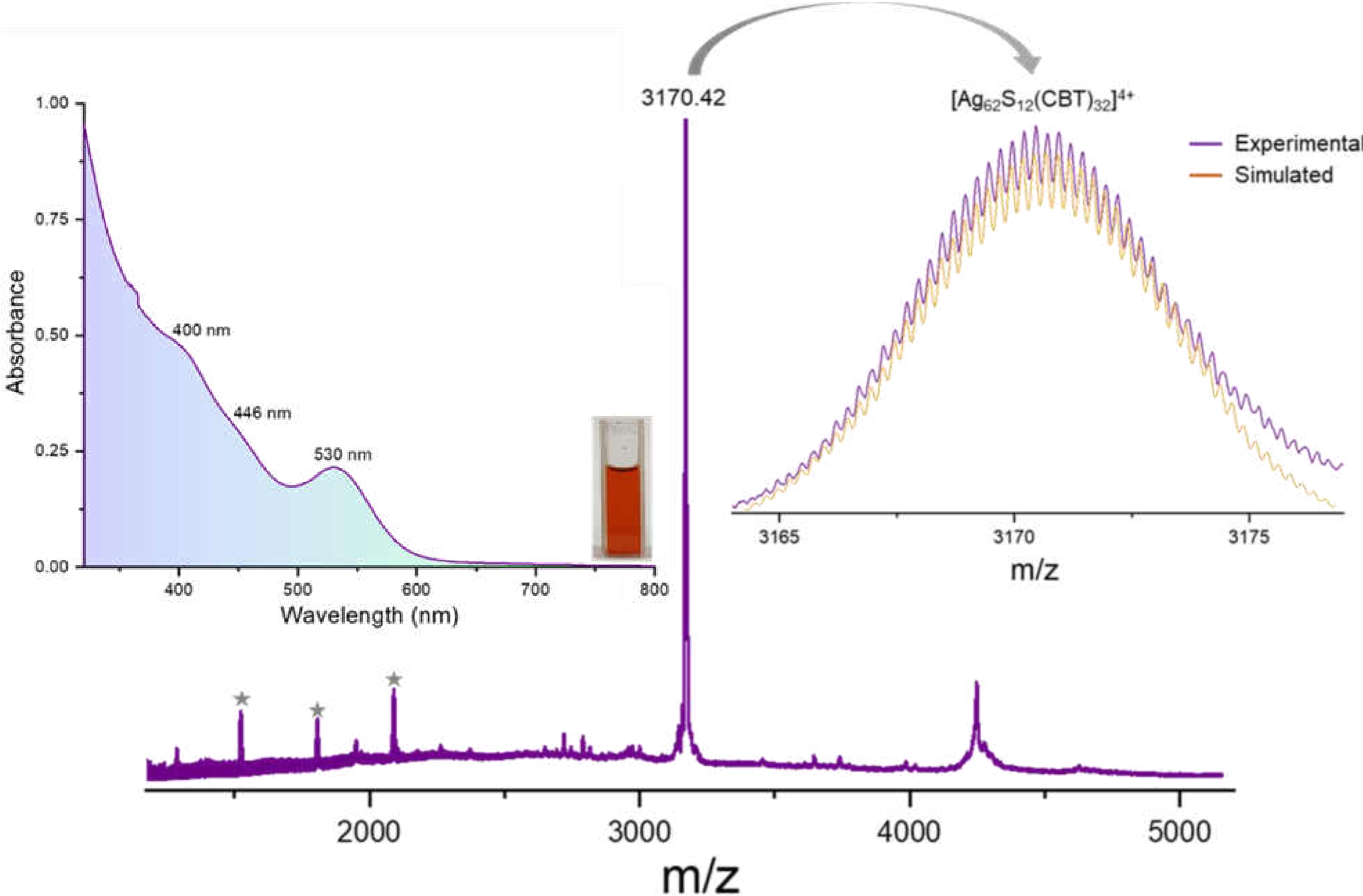


$Ag_6@Ag_8S_{12}@Ag_{48}S_{32}$



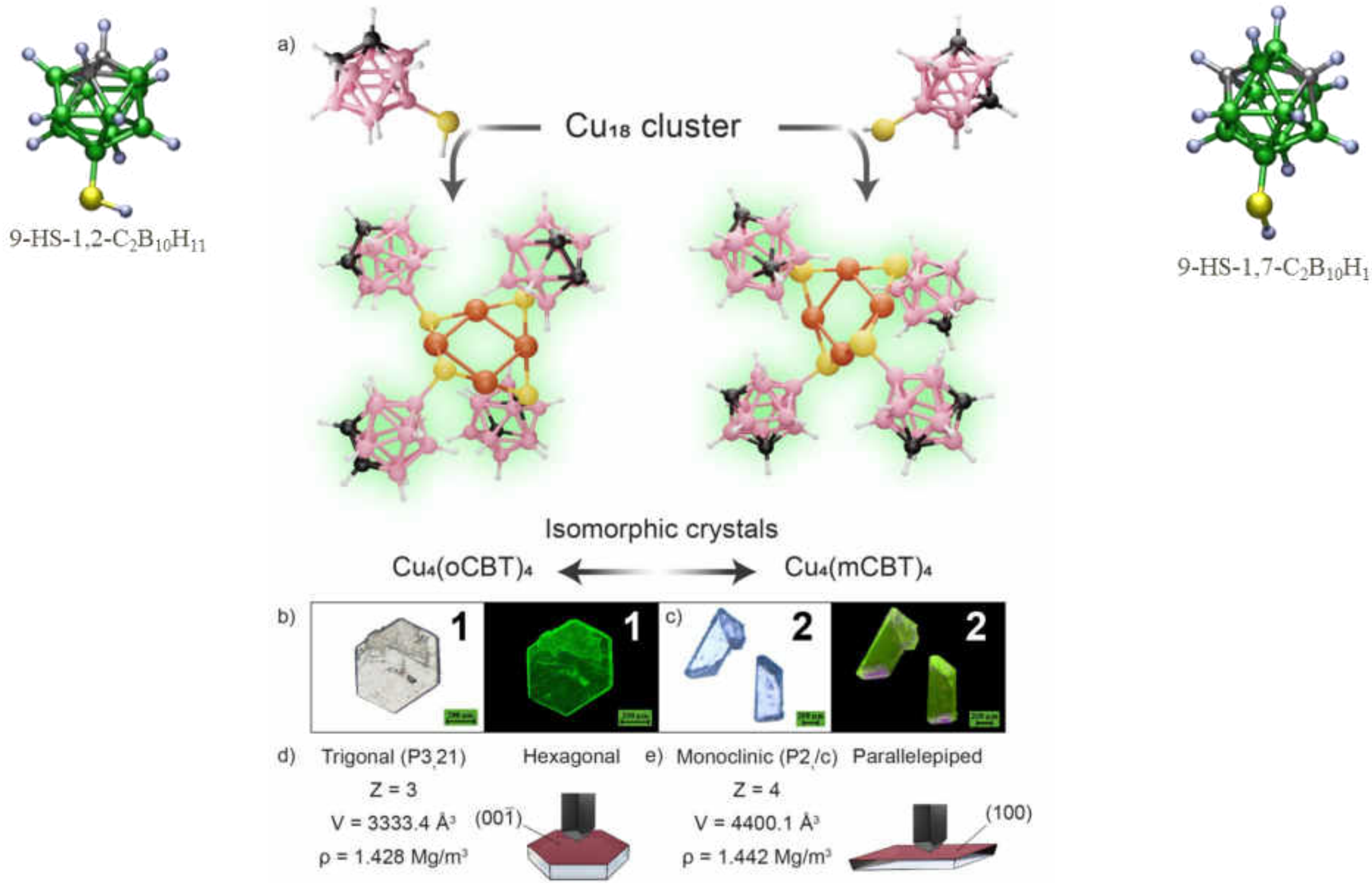
$Ag_6@Ag_8S_{12}@Ag_{48}S_{32}(CB)_{32}$

Characterization of Ag_{62} cluster



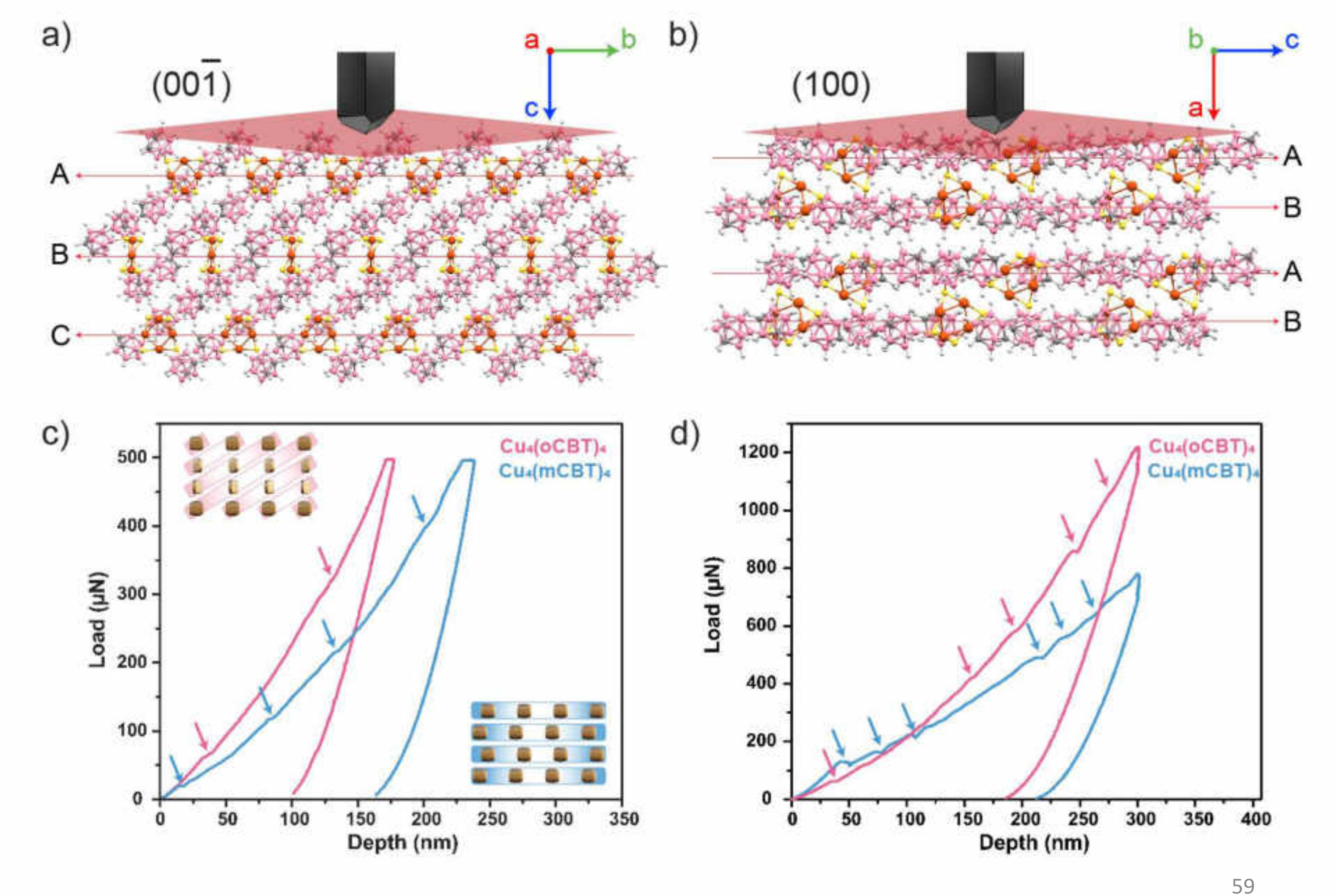
Properties

Nanomechanical Properties of Cu_4 Nanoclusters



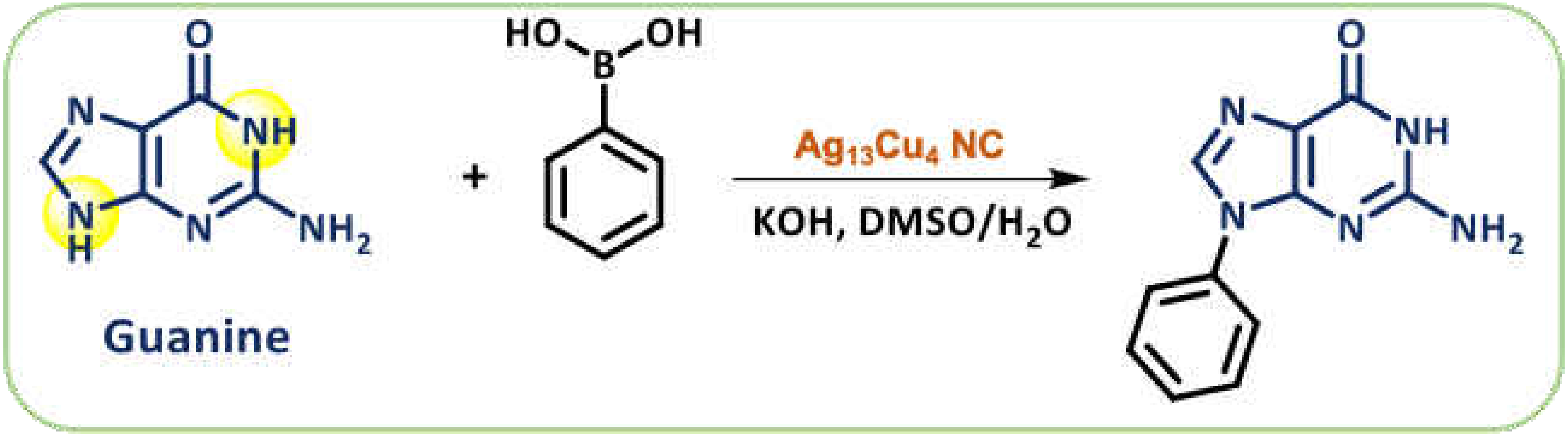
Amoghavasha Ramachandra Kini, et. al., *Chem. Mater.*, Revised (submitted)

Nanomechanical Properties of Cu_4 Nanoclusters



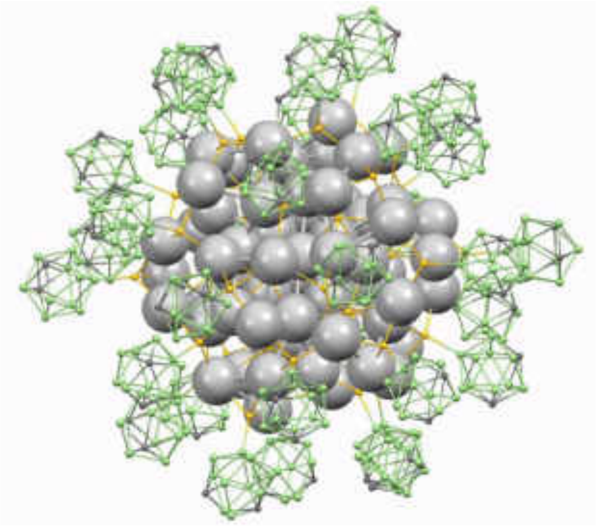
Catalysis by $Ag_{13}Cu_4$ Nanoclusters

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

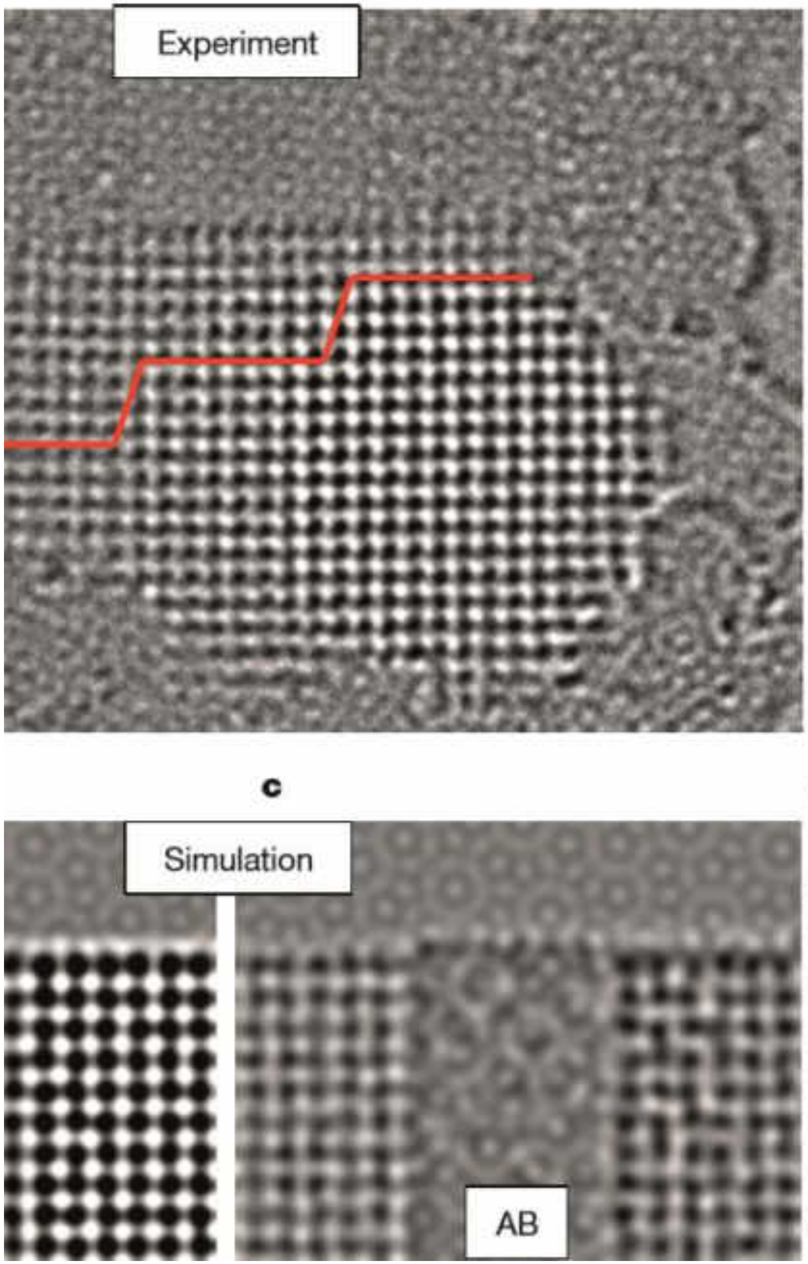


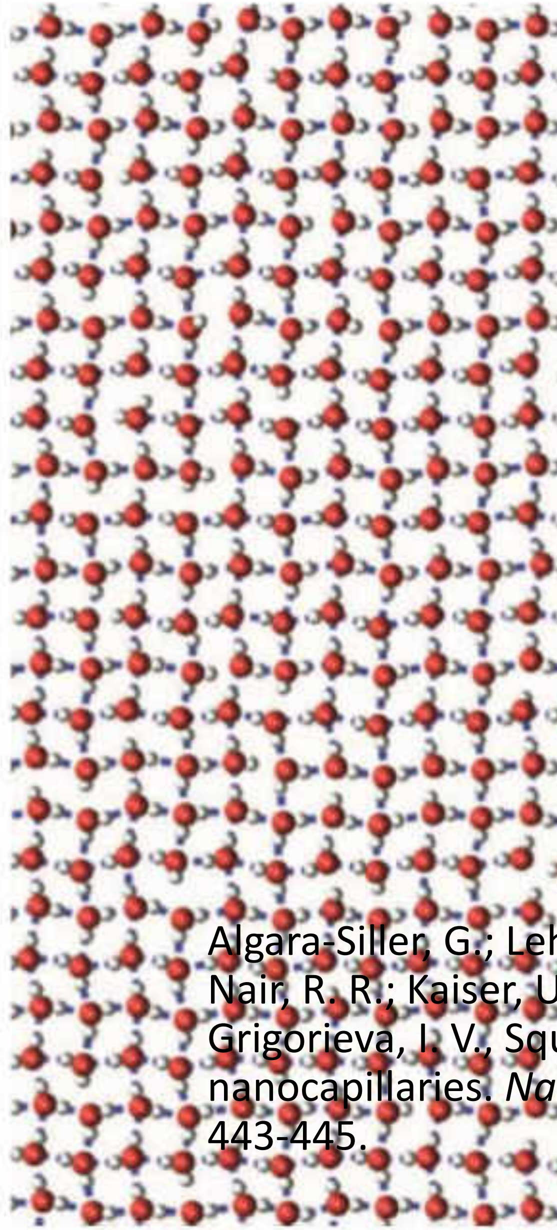
Summary

- 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}.



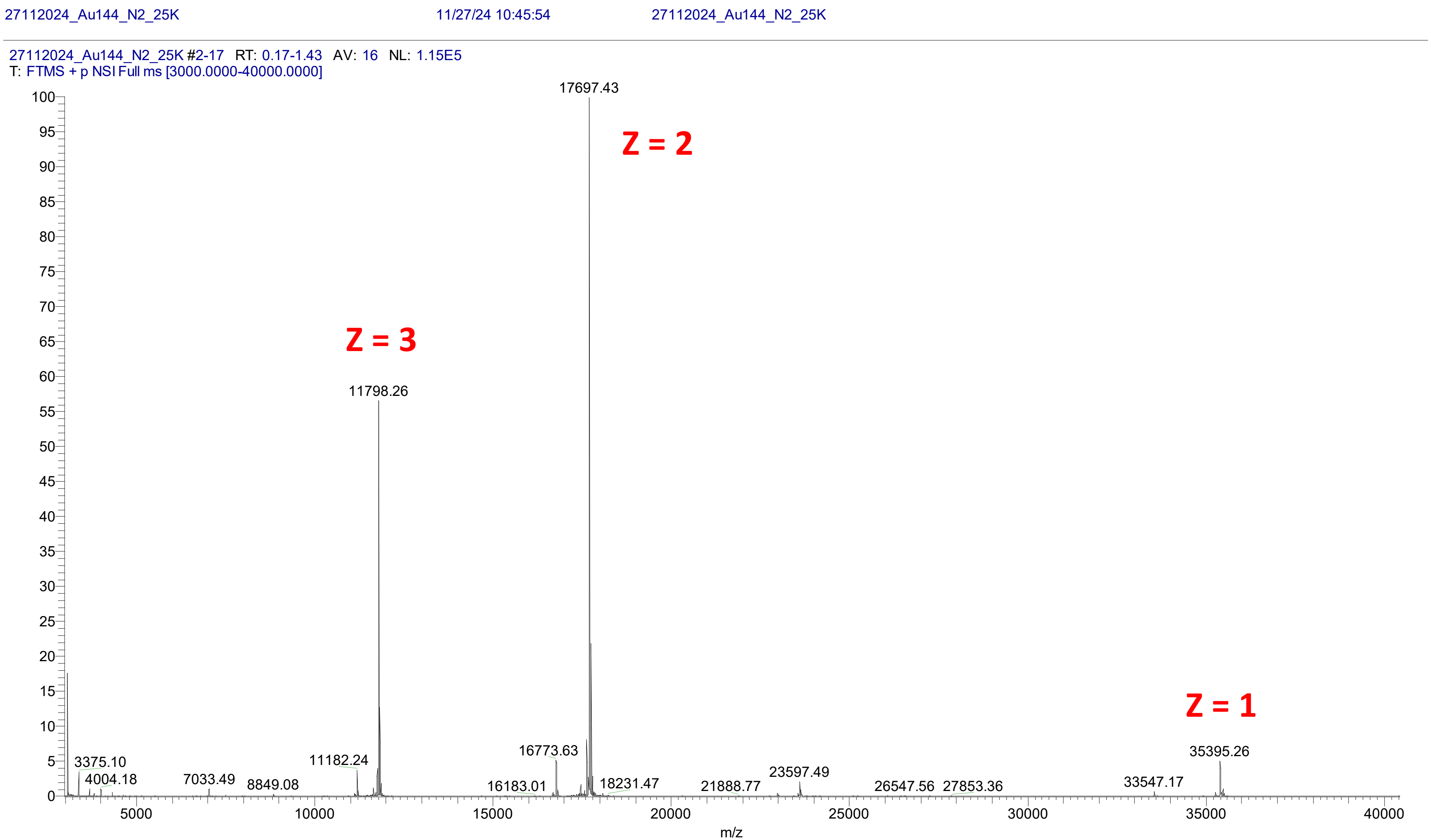
Observing Molecules



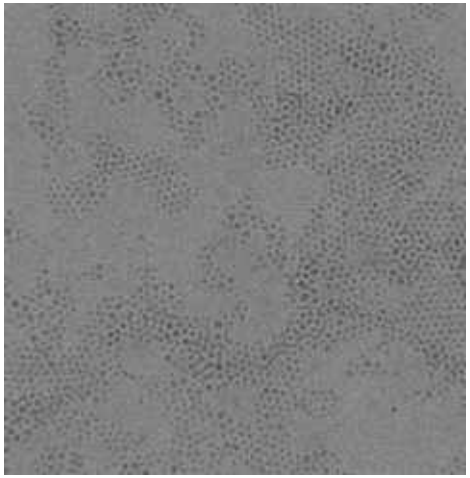


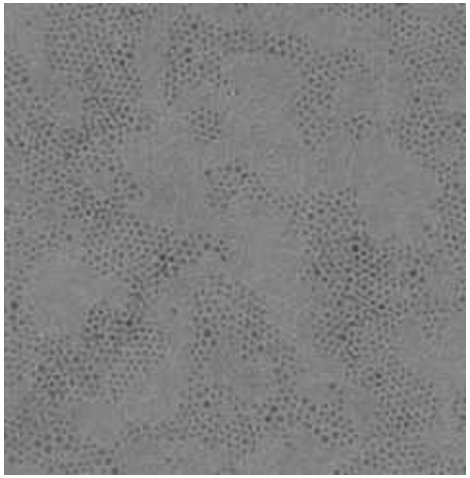
Algara-Siller, G.; Lehtinen, O.; Wang, F. C.; Nair, R. R.; Kaiser, U.; Wu, H. A.; Geim, A. K.; Grigorieva, I. V., Square ice in graphene nanocapillaries. *Nature* **2015,** *519* (7544), 443-445.

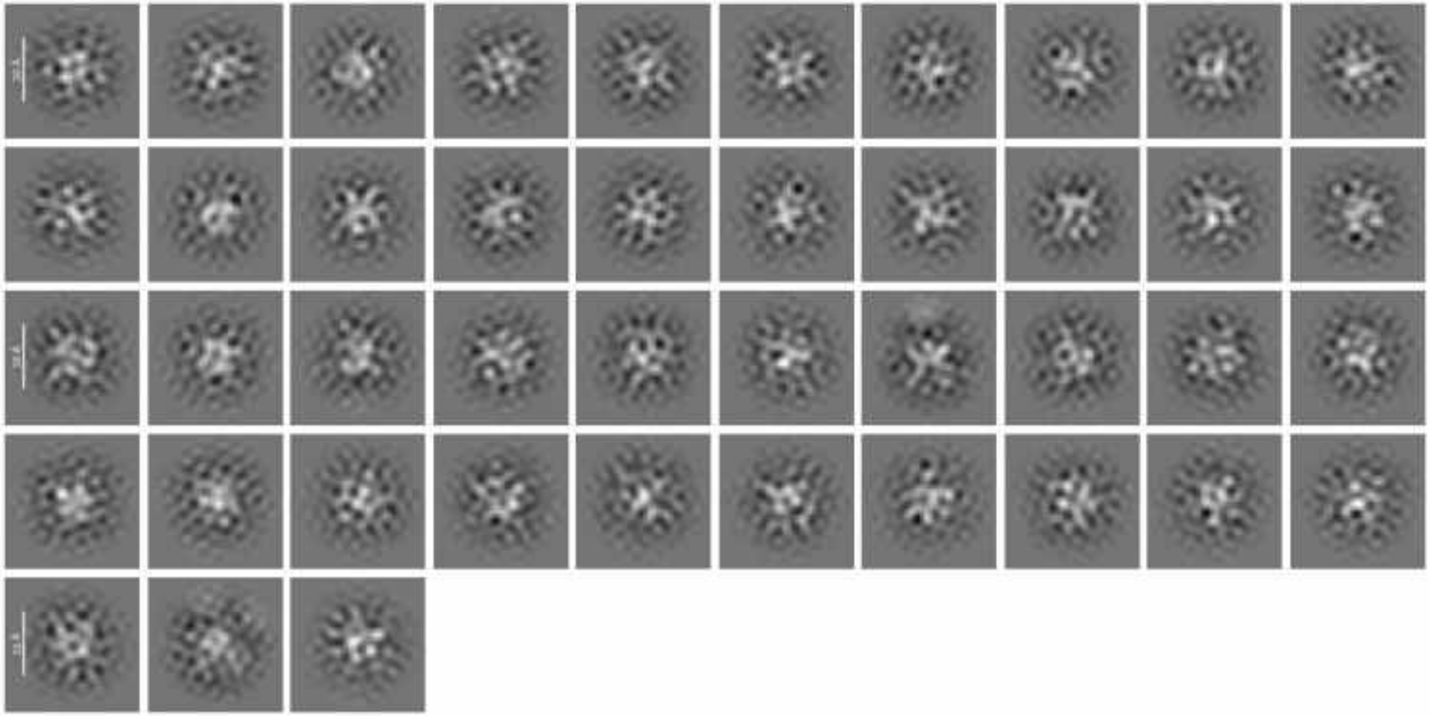
ESI-MS of $Au_{144}(HT)_{60}$



2D classification images







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Whetten

Shiv Khanna

Biswarup Pathak

K. V. Adarsh

G. U. Kulkarni

Vivek Polshettiwar

Pradeep Research Group

सत्यमेव जयते

Department of Science & Technology
Government of india