ISMPC 2024

Carboranethiols: Versatile Ligands for Atomically Precise Clusters

Thalappil Pradeep

Institute Professor, IIT Madras

https://pradeepresearch.org/

pradeep@iitm.ac.in

Professor-in-charge

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.

International Centre for Clean Water

ISMPC 2024, Penn State, College Station, June 12, 2024

Thank you…

- Ken Knappenberger (Pennsylvania State University)klk260@psu.edu
- Ben Lear (Pennsylvania State University)bul14@psu.edu
- Christine Aikens (Kansas State University)cmaikens@ksu.edu
- Chris Ackerson (Colorado State University)Chris.Ackerson@colostate.edu
- Rongchao Jin (Carnegie Mellon University)rongchao@andrew.cmu.edu

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

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scientific conference focused on advancing the frontiers of science through the presentation of cutting-edge and unpublished research, prioritizing time for discussion after each talk and fostering informal interactions among scientists of all career stages.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)

Collaborators



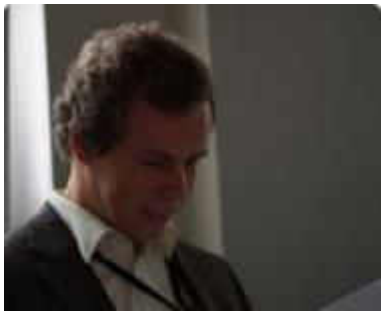



Tatsuya Tsukuda
Keisaku Kimura Yuichi Negishi
Uzi Landman Hannu Hakkinen Rob Whetten

Shiv Khanna

Robin Ras

Nonappa



Tomas Base

Manfred Kappes

Olli Ikkala

Horst Hahn

Biswarup Pathak

K. V. Adarsh

G. U. Kulkarni

Vivek Polshettiwar

Molecular materials

ACCOUNTS of chemical research

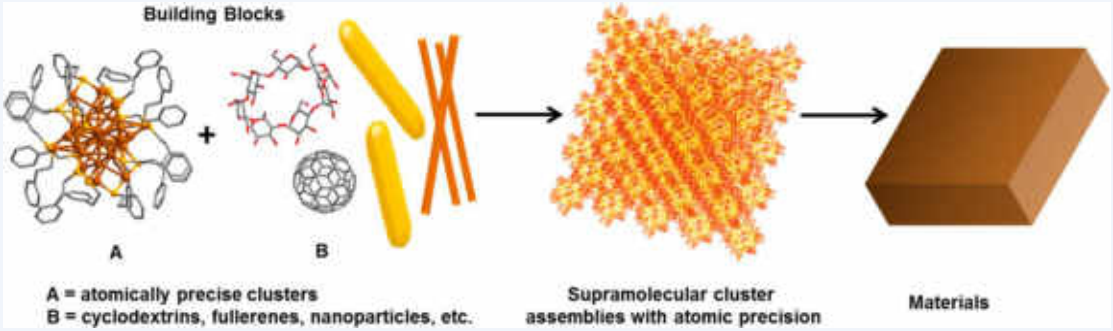
Article

pubs.acs.org/accounts

Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

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

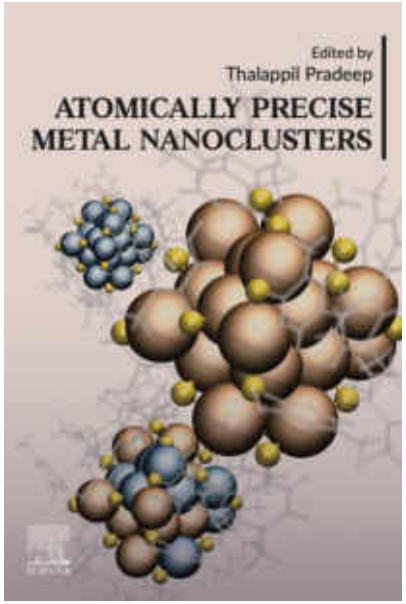
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

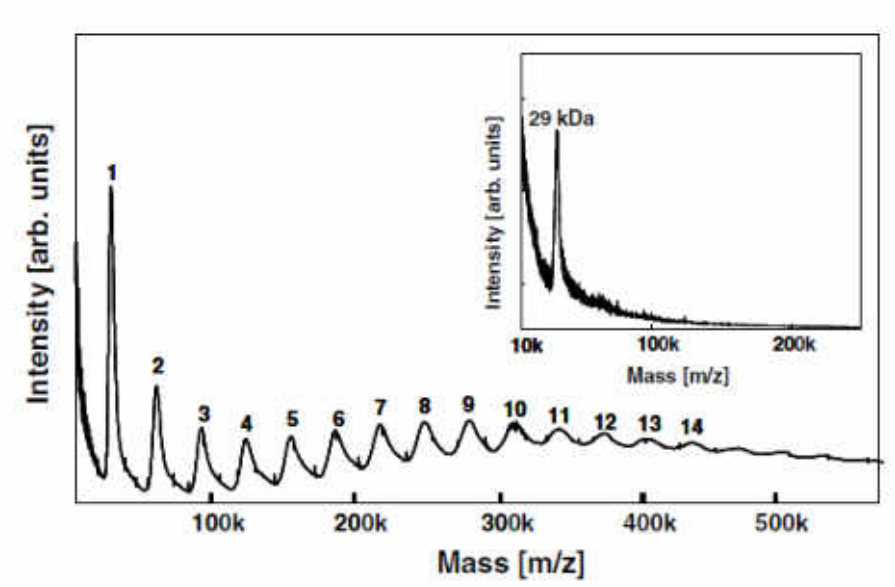


345 structures!

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

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.

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

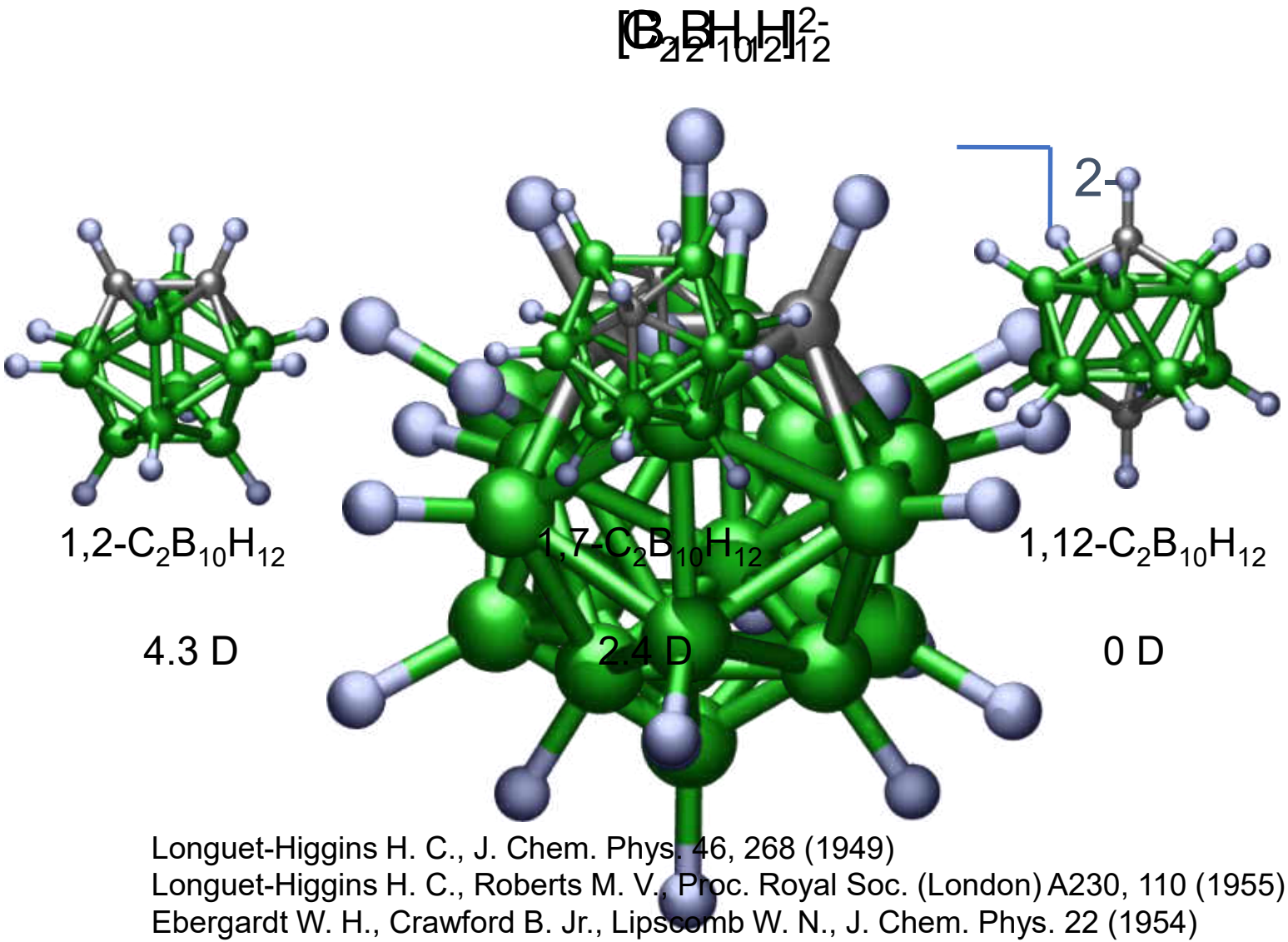
hybrid | green | appropriate technology | frugal science | developing world

disease burden.

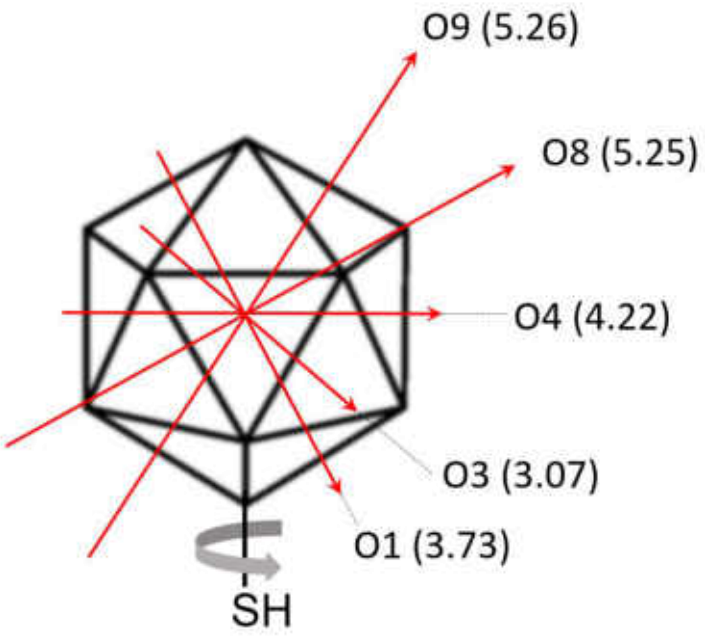
Results and Discussion

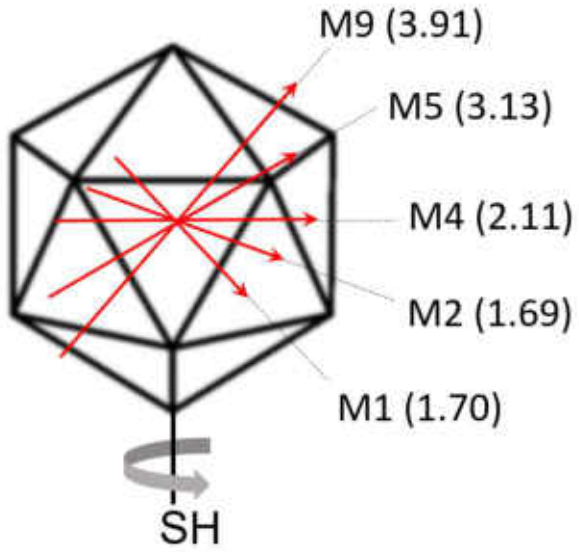
M. Udhaya Sankar, et. al. *Proc. Natl. Acad. Sci.,* 110 (2013) 8459-8464.

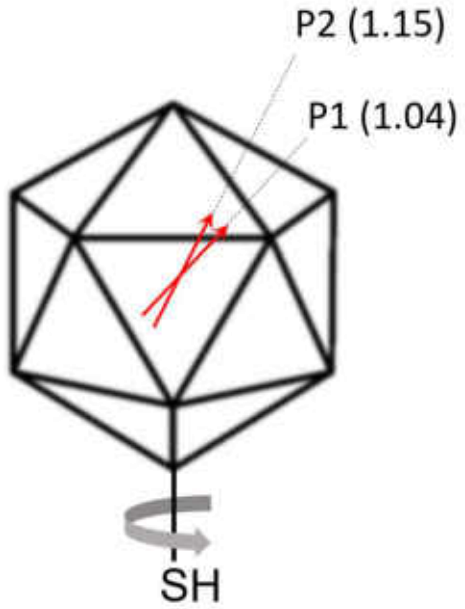

We supply arsenic-free water to 1.3 million people every day.

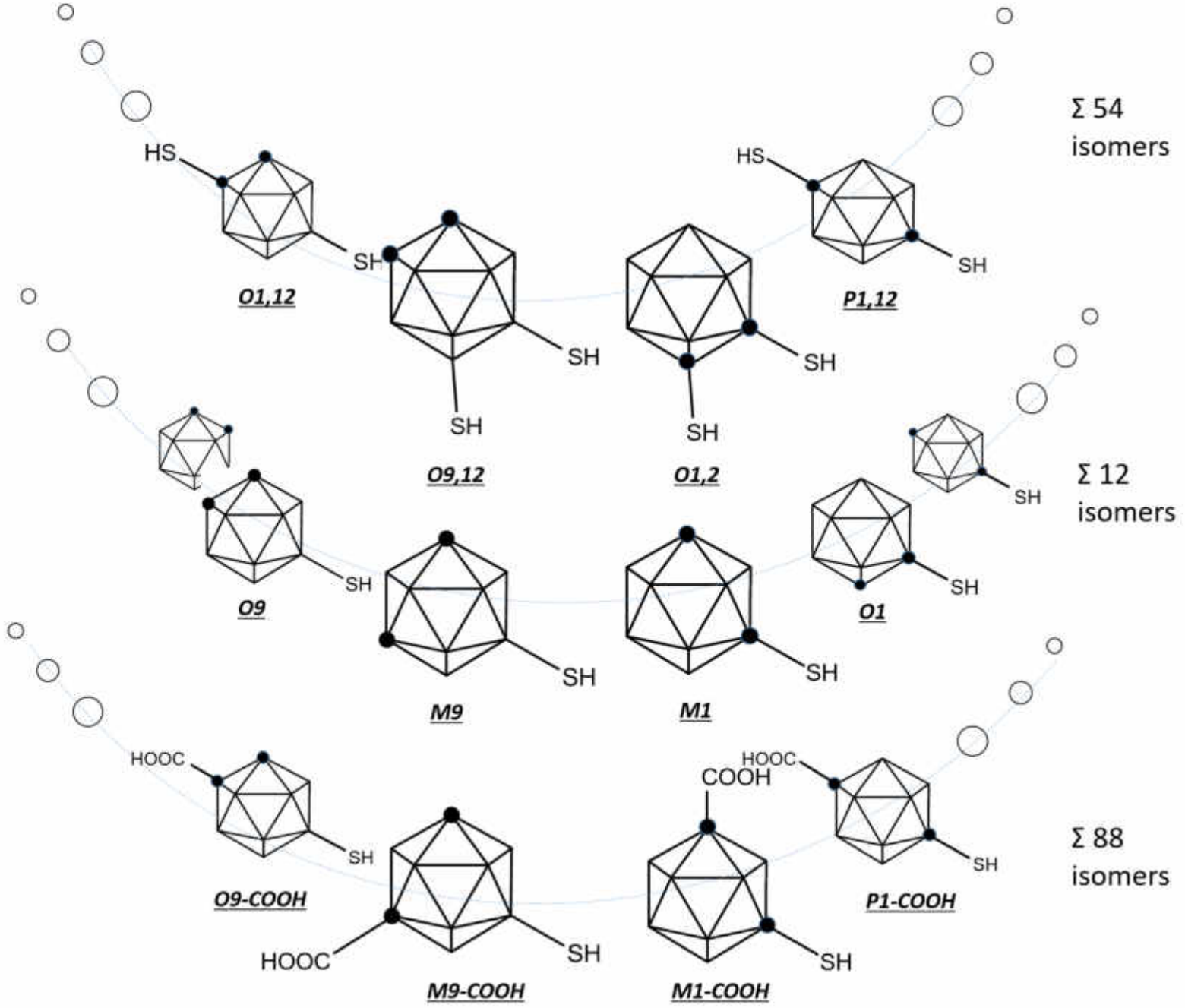


Longuet-Higgins H. C., J. Chem. Phys. 46, 268 (1949)
Longuet-Higgins H. C., Roberts M. V., Proc. Royal Soc. (London) A230, 110 (1955)
Ebergardt W. H., Crawford B. Jr., Lipscomb W. N., J. Chem. Phys. 22 (1954)
Greenwood N. N., Earnshaw A. Chemistry of elements, Pergamon Press, London, 1984.


O9 (5.26)
O8 (5.25)
O4 (4.22)
O3 (3.07)
O1 (3.73)
SH

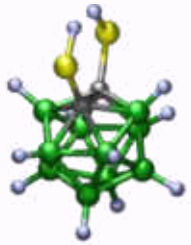

M9 (3.91)
M5 (3.13)
M4 (2.11)
M2 (1.69)
M1 (1.70)
SH


P2 (1.15)
P1 (1.04)
SH


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

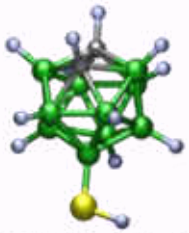
Building blocks: Carborane-thiol

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

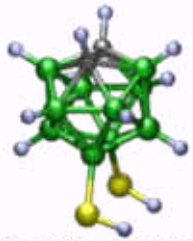


$1,2\text{-}(HS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$

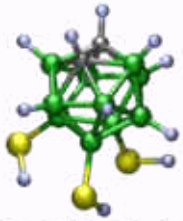
$1\text{-}HS\text{-}1,2\text{-}C_2B_{10}H_{11}$



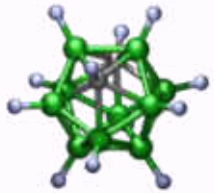
$9\text{-}HS\text{-}1,2\text{-}C_2B_{10}H_{11}$



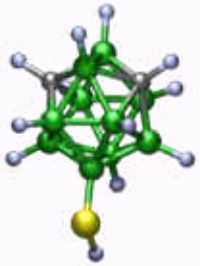
$9,12\text{-}(HS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$



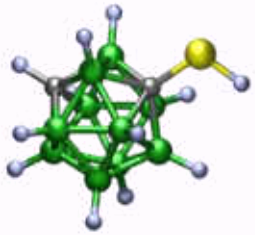
$8,9,12\text{-}(HS)_3\text{-}1,2\text{-}C_2B_{10}H_9$



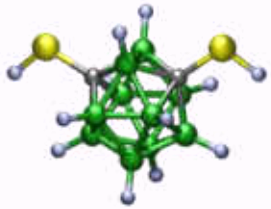
$1,7\text{-}C_2B_{10}H_{12}$



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

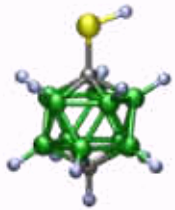


$1\text{-}HS\text{-}1,7\text{-}C_2B_{10}H_{11}$

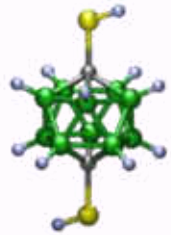


$1,7\text{-}(HS)_2\text{-}1,7\text{-}C_2B_{10}H_{10}$

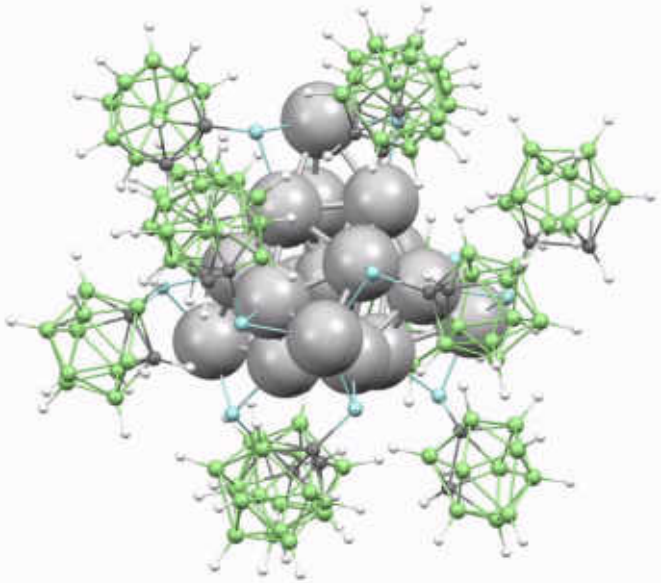
$1,12\text{-}C_2B_{10}H_{12}$



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



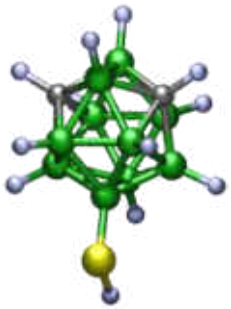
$1,12\text{-}(HS)_2\text{-}1,12\text{-}C_2B_{10}H_{10}$



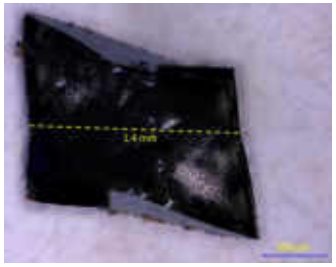
Clustering of clusters

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

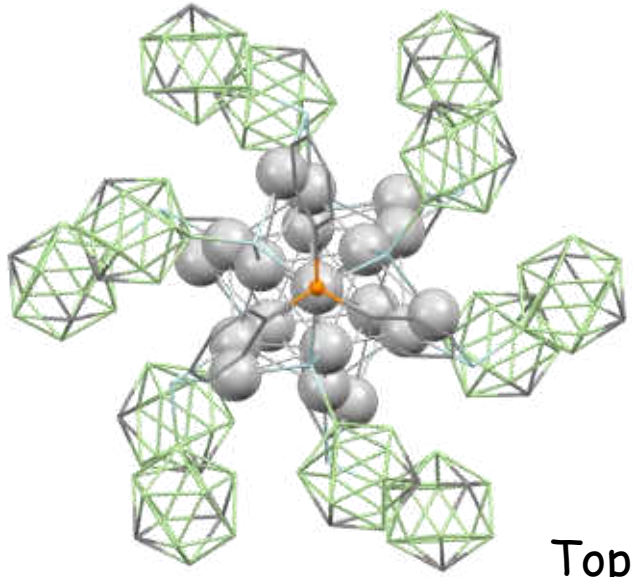
Ligand:



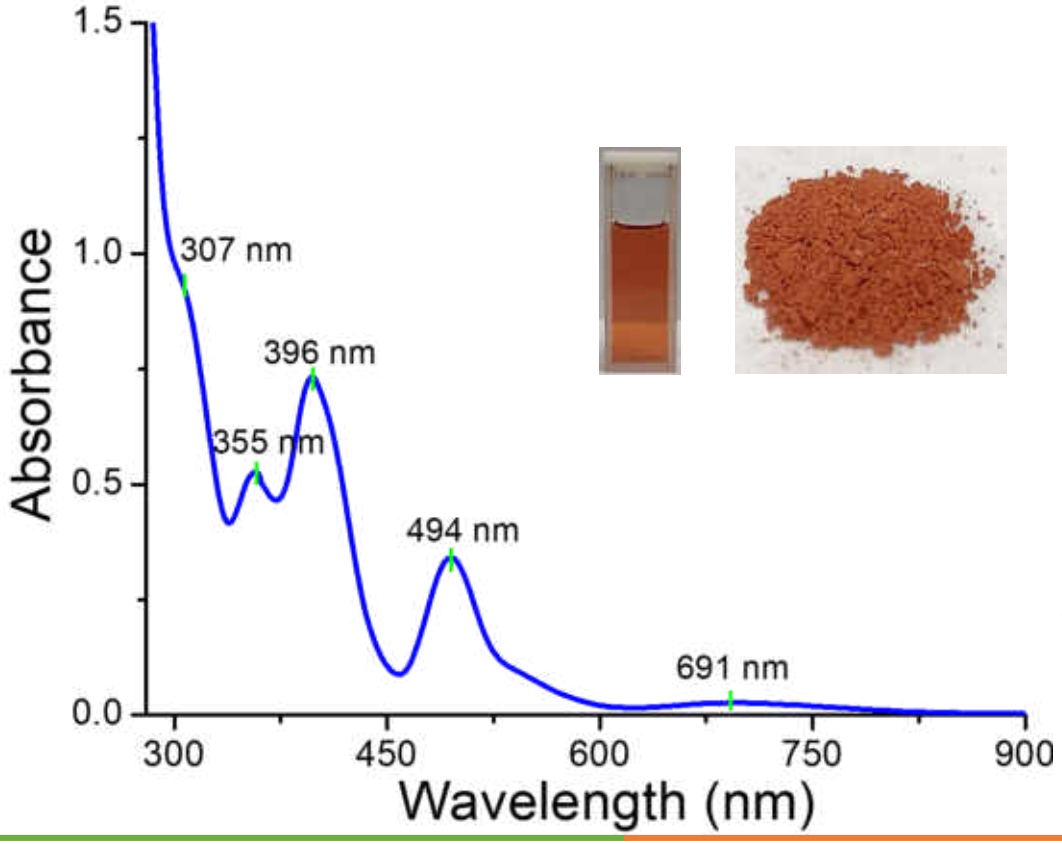
9-HS-1,7-$C_2B_{10}H_{11}$

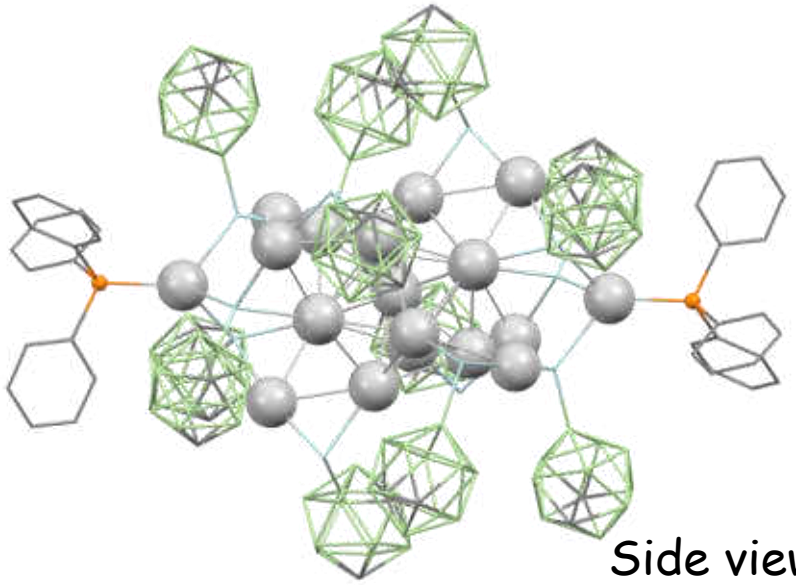


Crystal



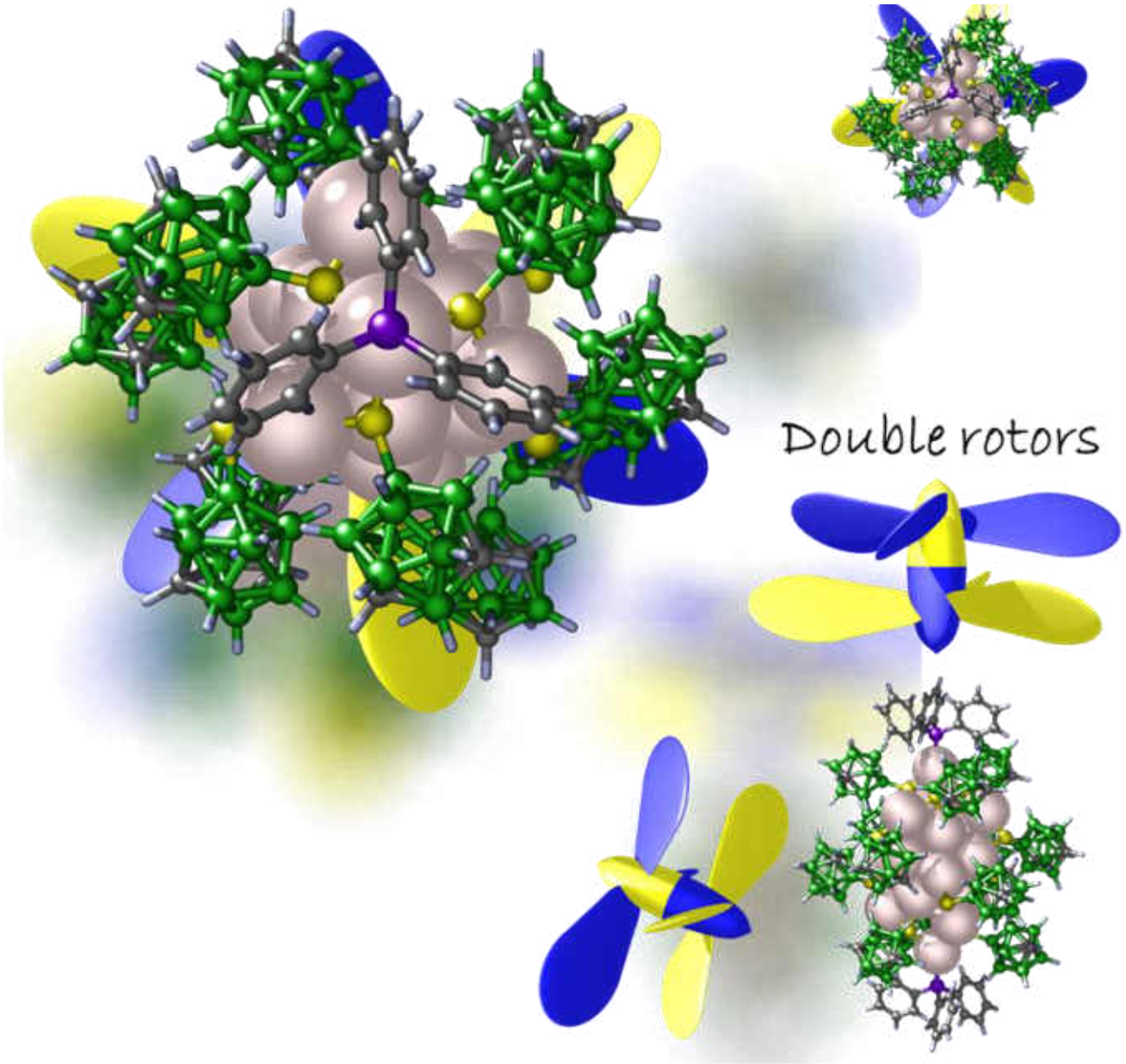
Top view



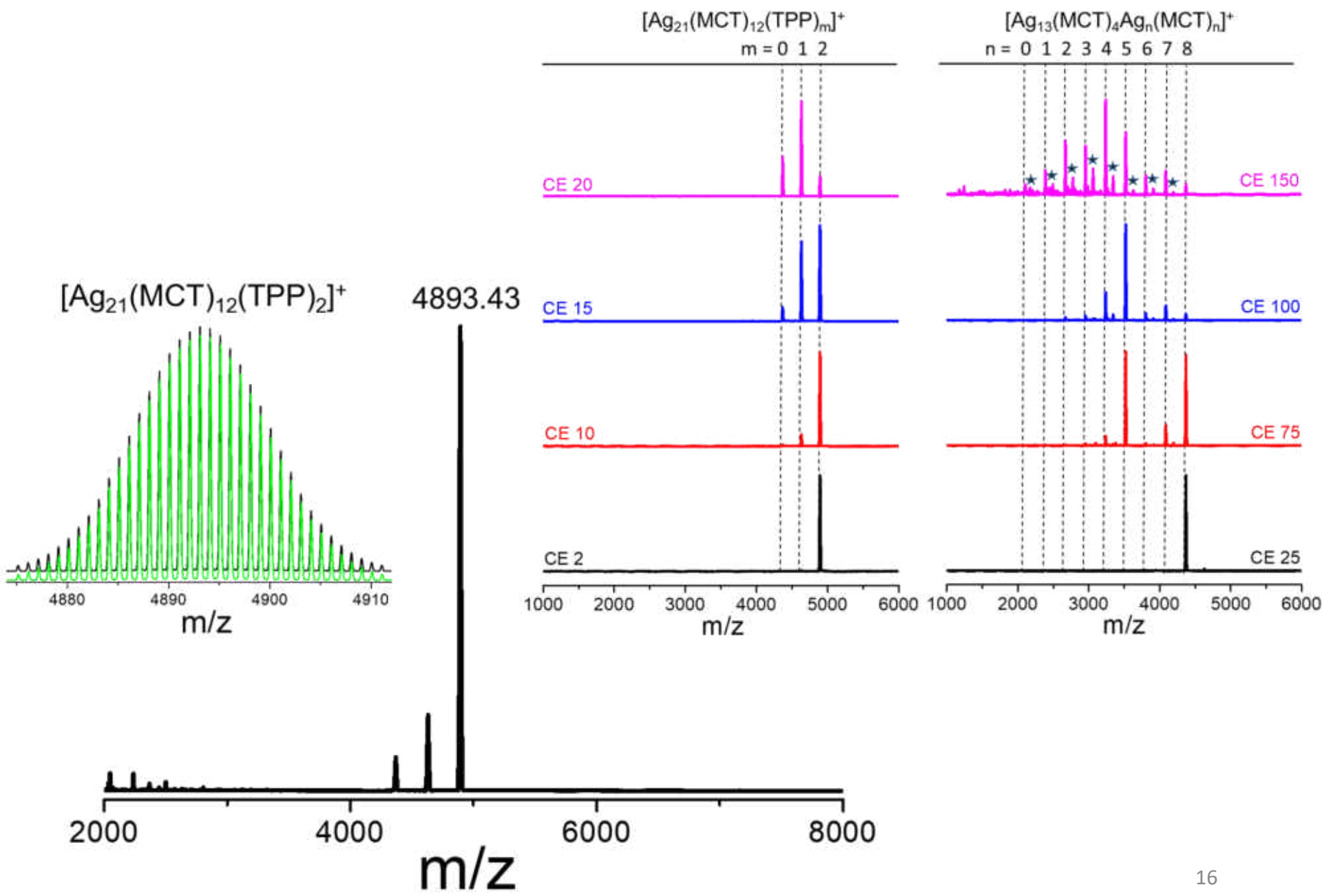


Side view

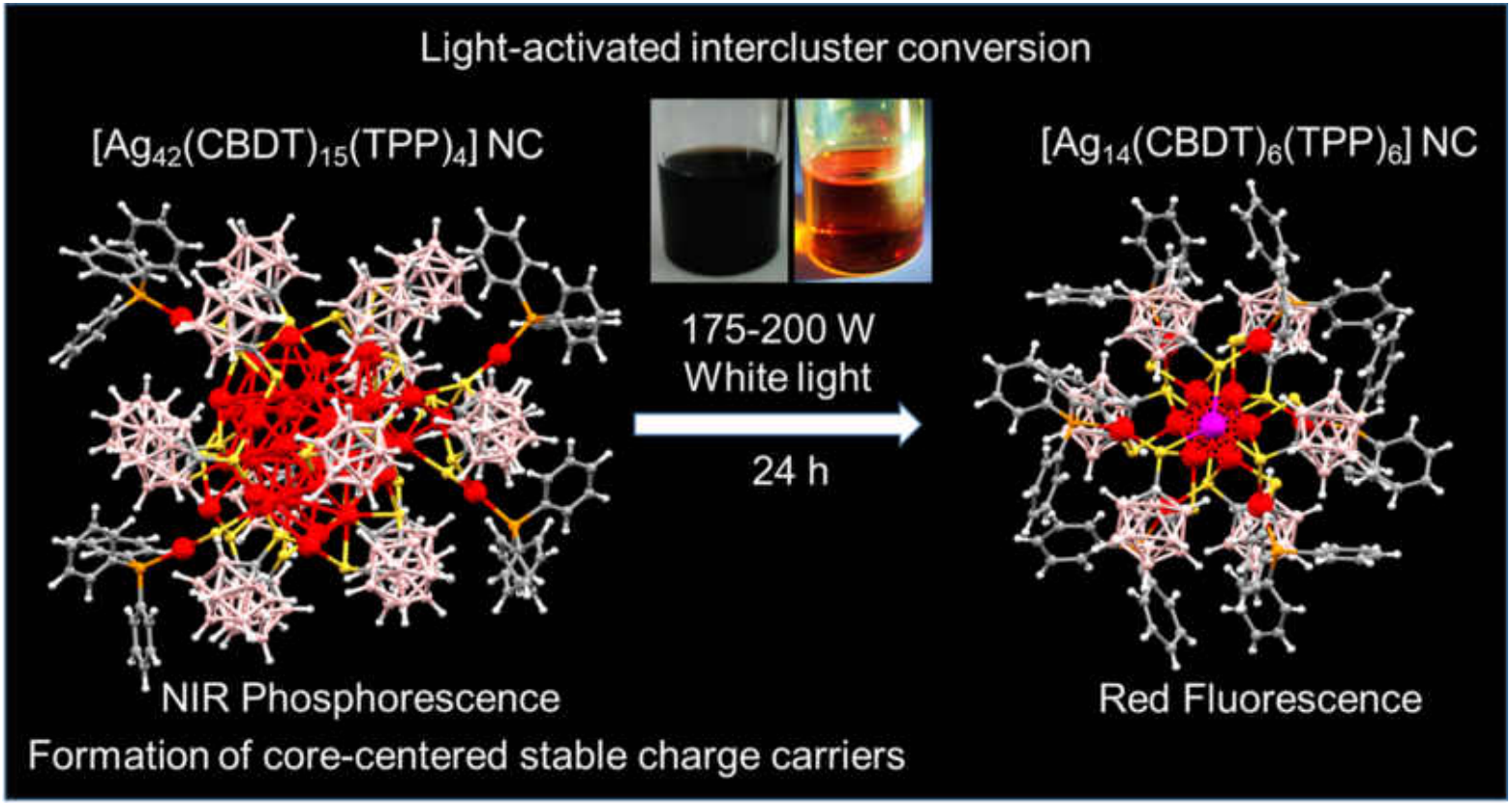
Propeller shaped $[Ag_{21}(m_9\text{-}CBT)_{12}(TPP)_2]$ Nanocluster



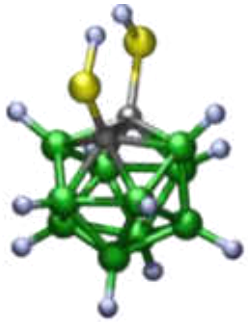
Mass spectrometric characterization



Light-activated Conversion of Carborane Thiol Appended Silver Nanocluster



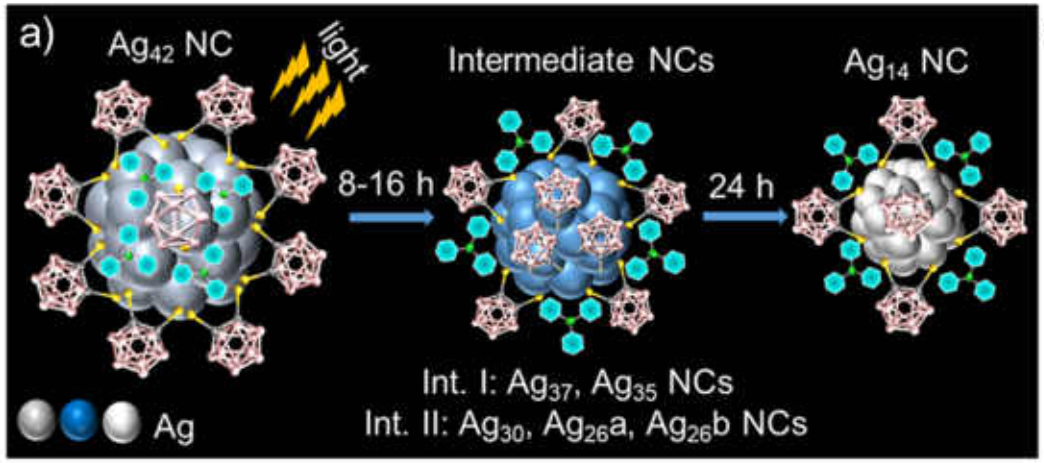
Ligand:

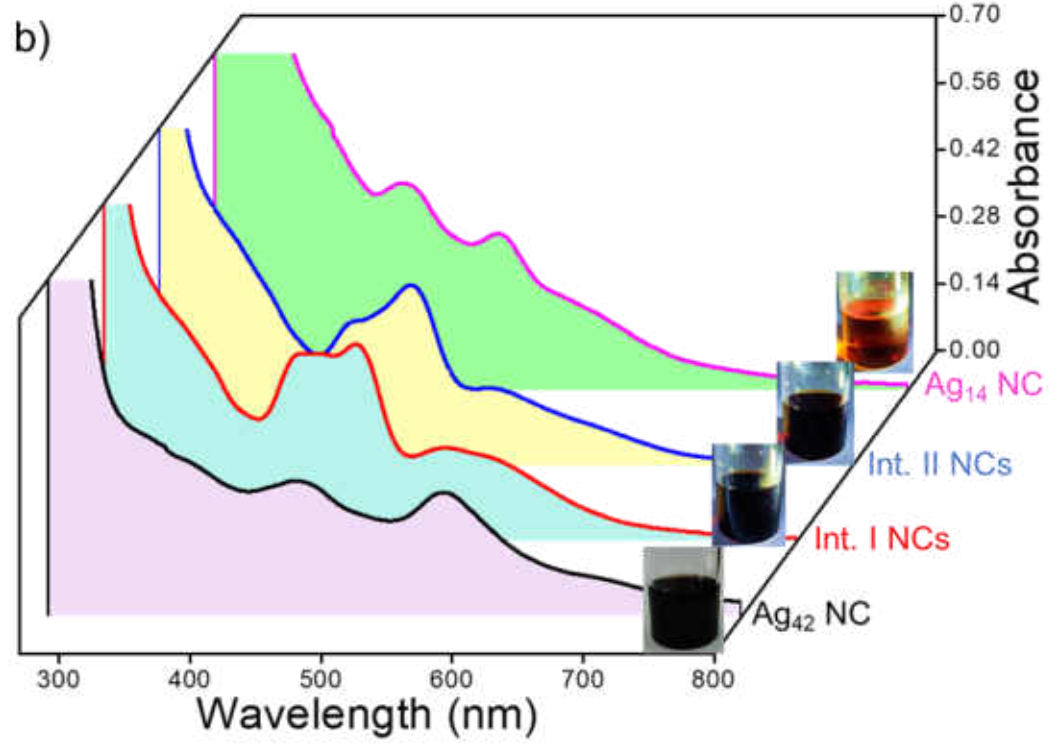


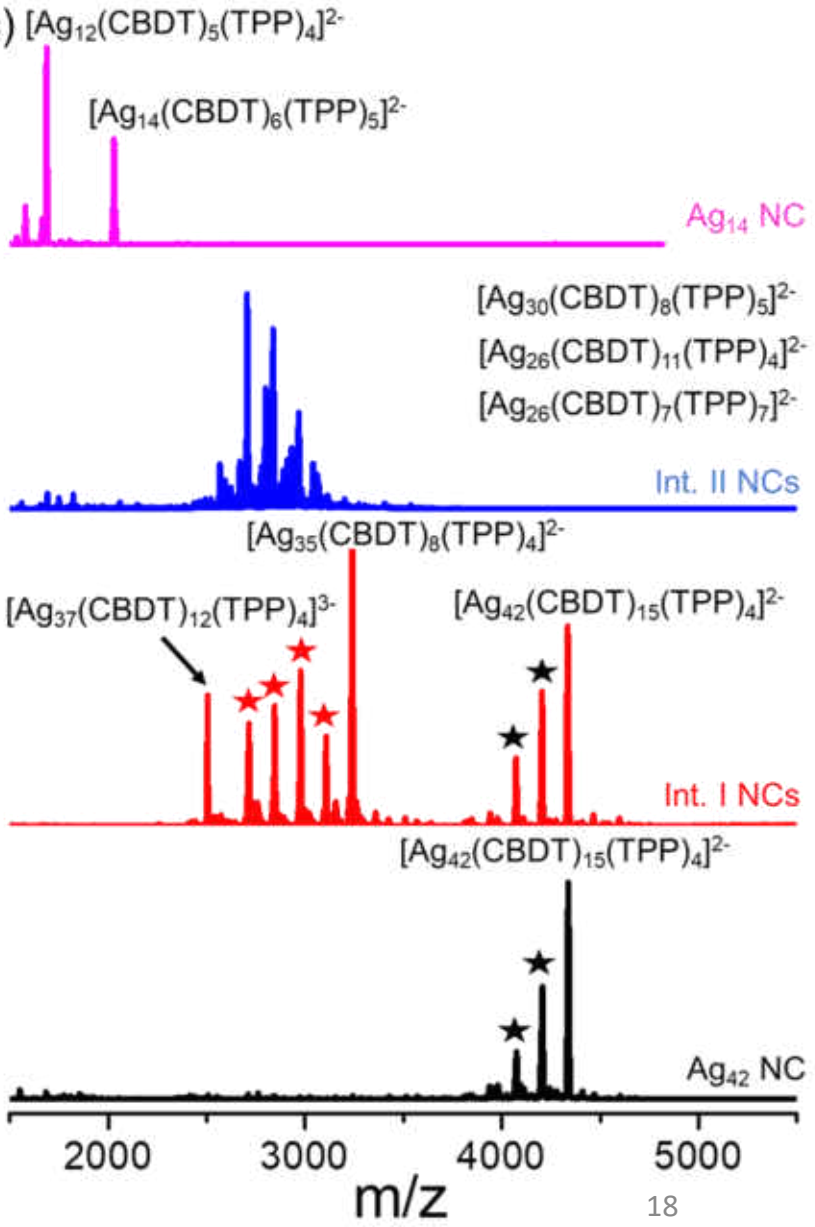
$1,2\text{-}(HS)_2\text{-}1,2\text{-}C_2B_{10}H_1$

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

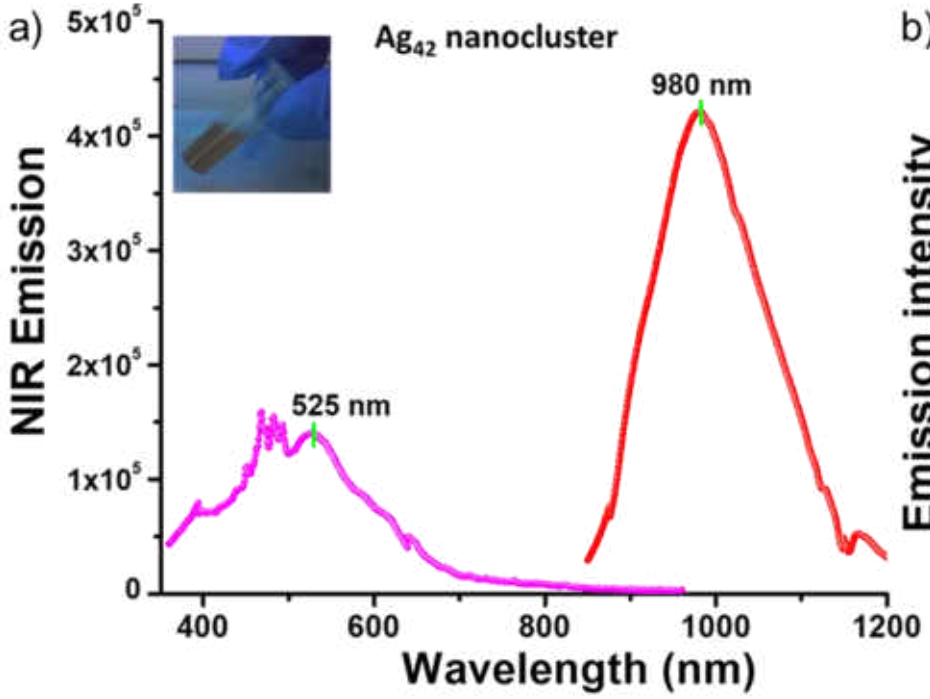
Light-activated Intercluster Conversion

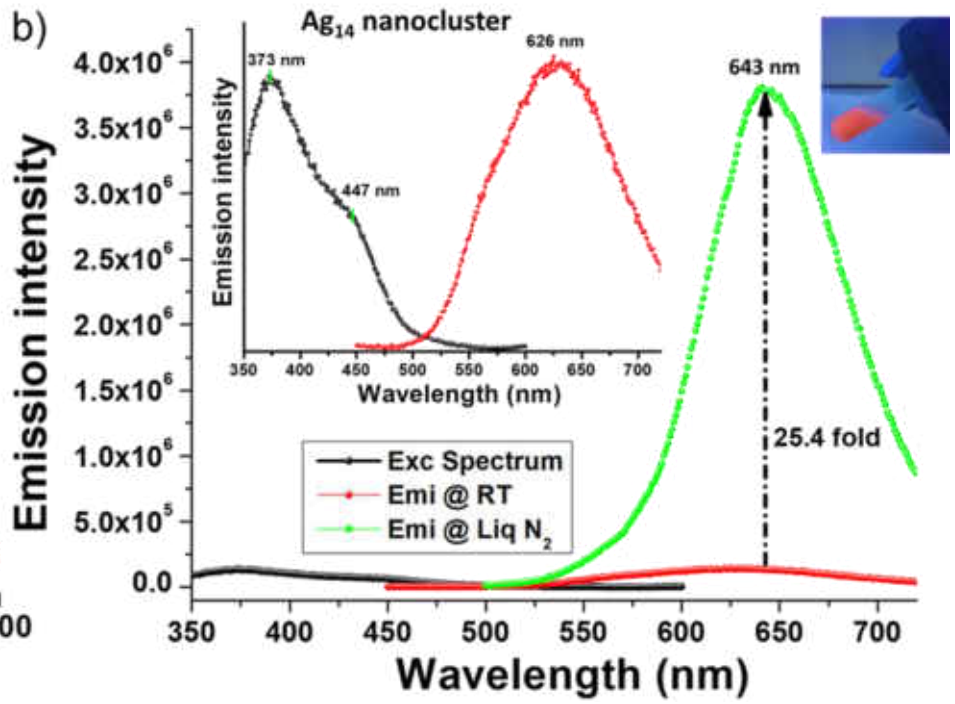




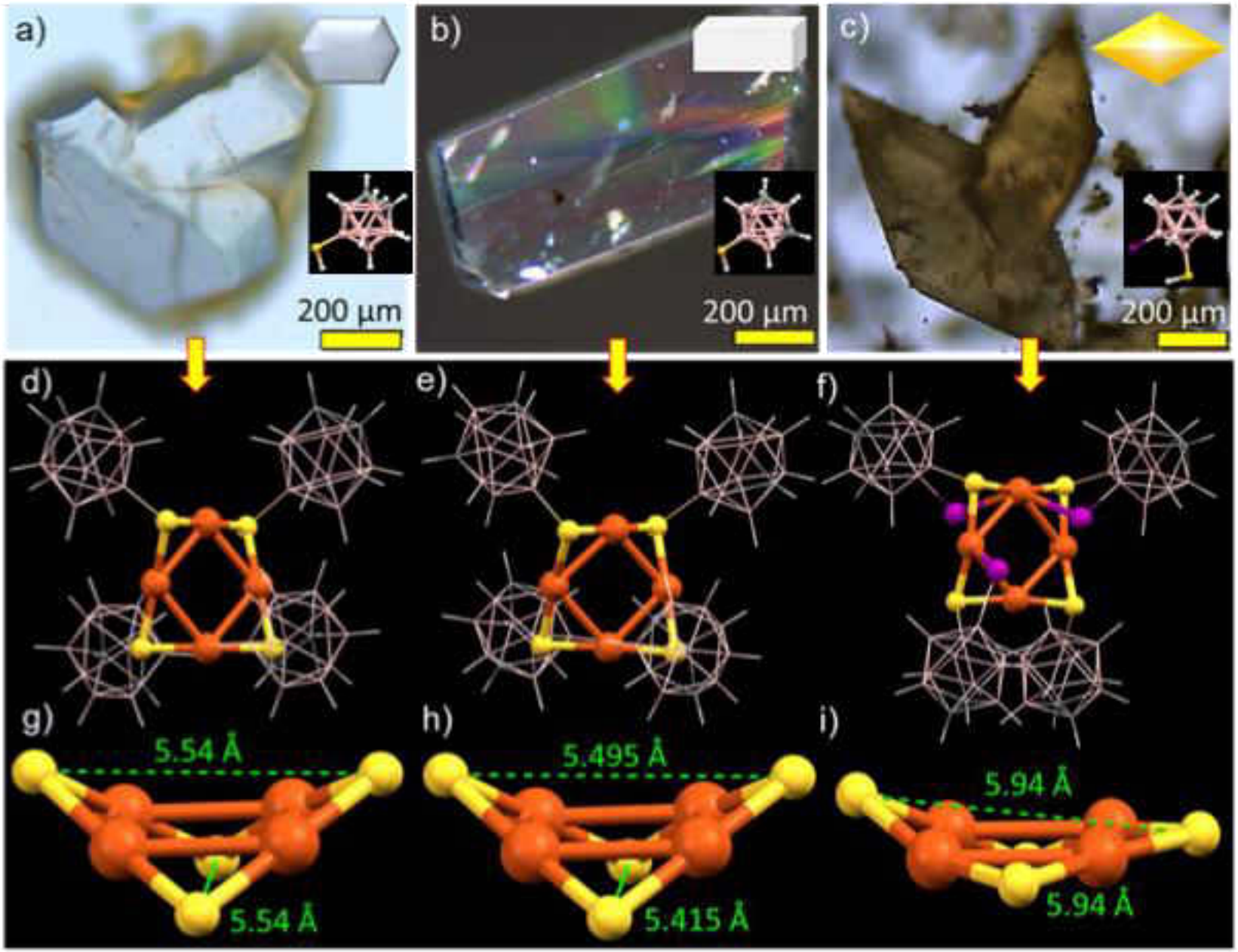


Photoluminescence Properties



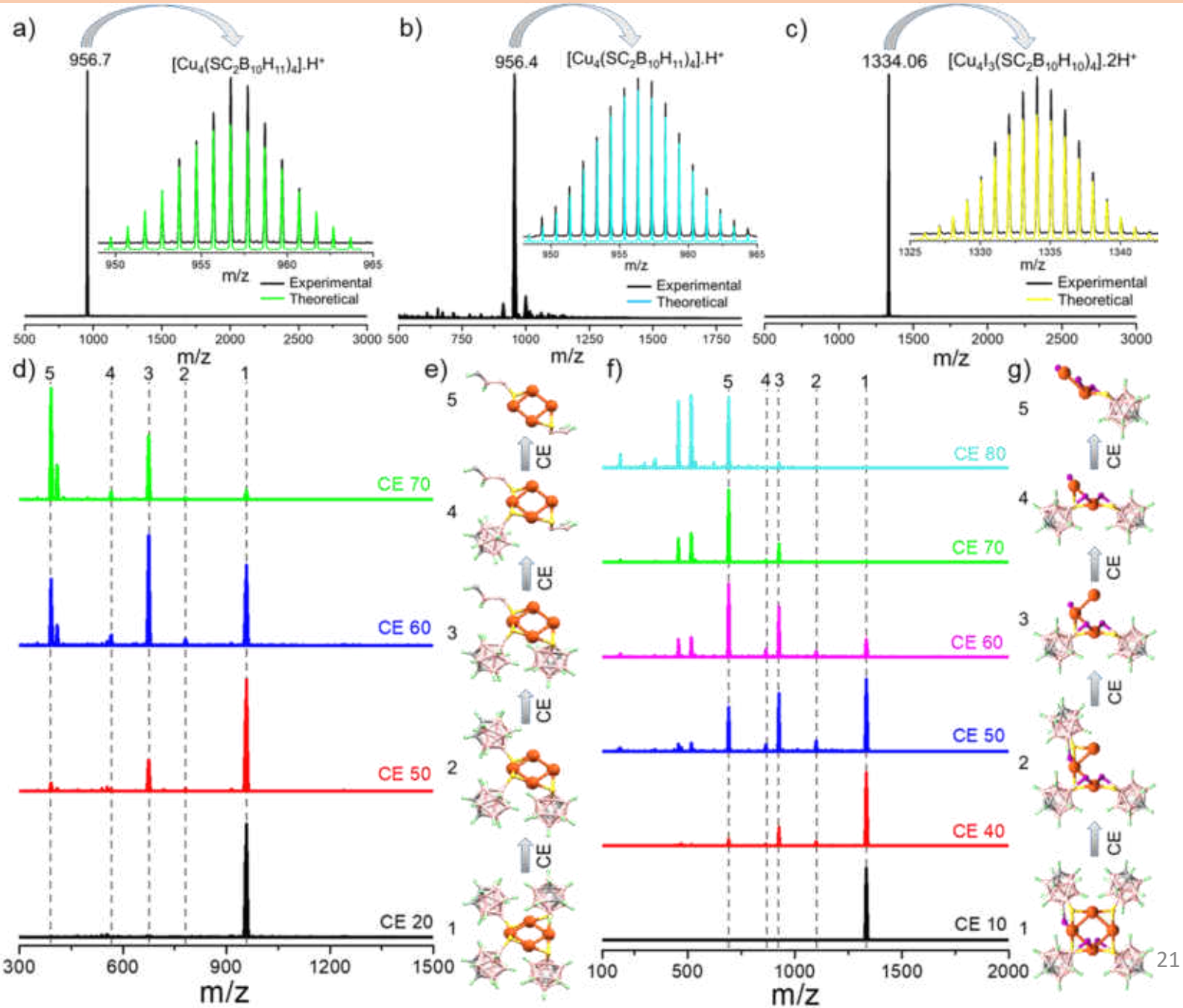


Multicolor Phosphorescence of Tetranuclear Copper Nanoclusters

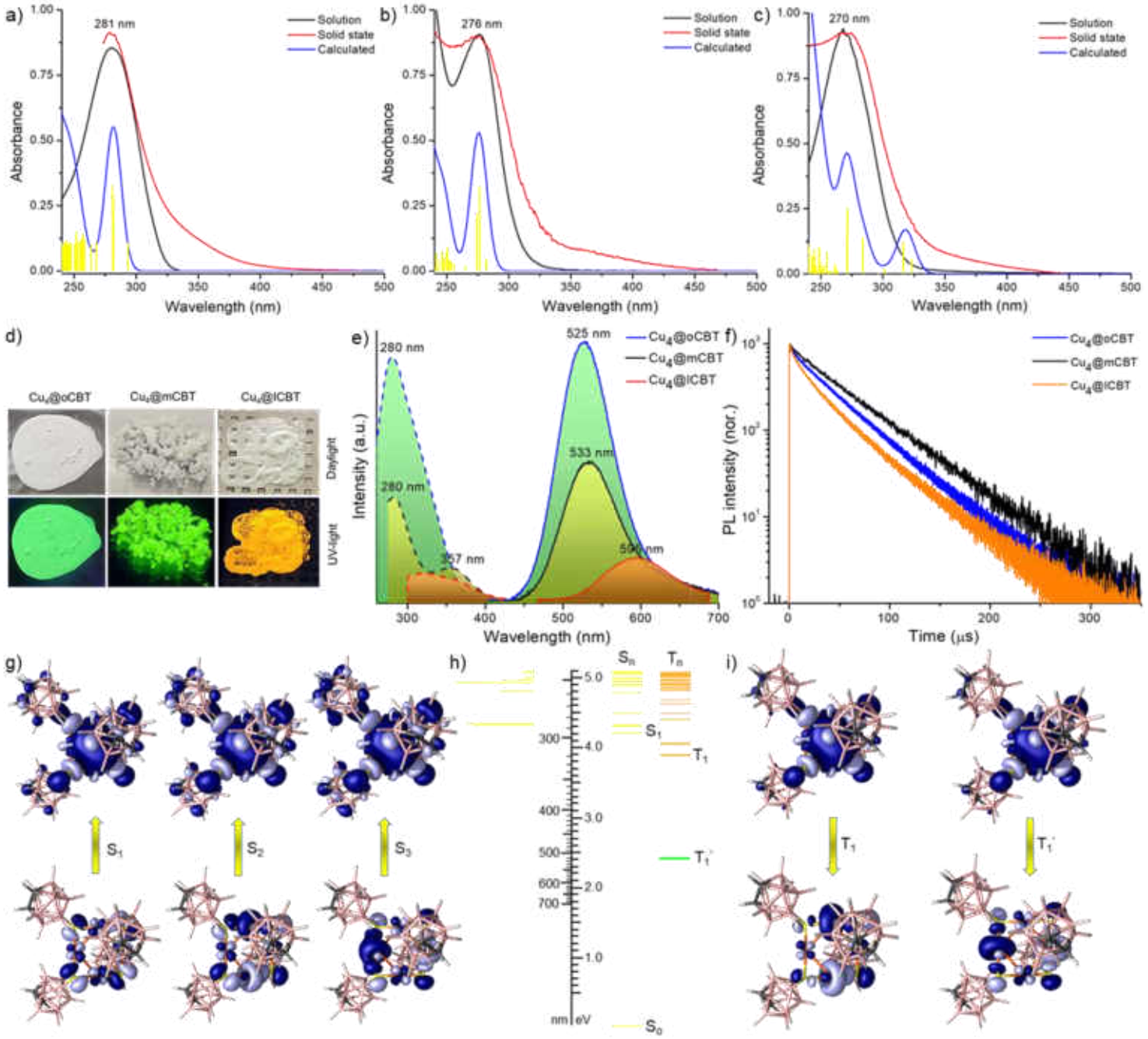


Jana *et al.*, Chem. Sci., 2023, 14, 1613-1626.

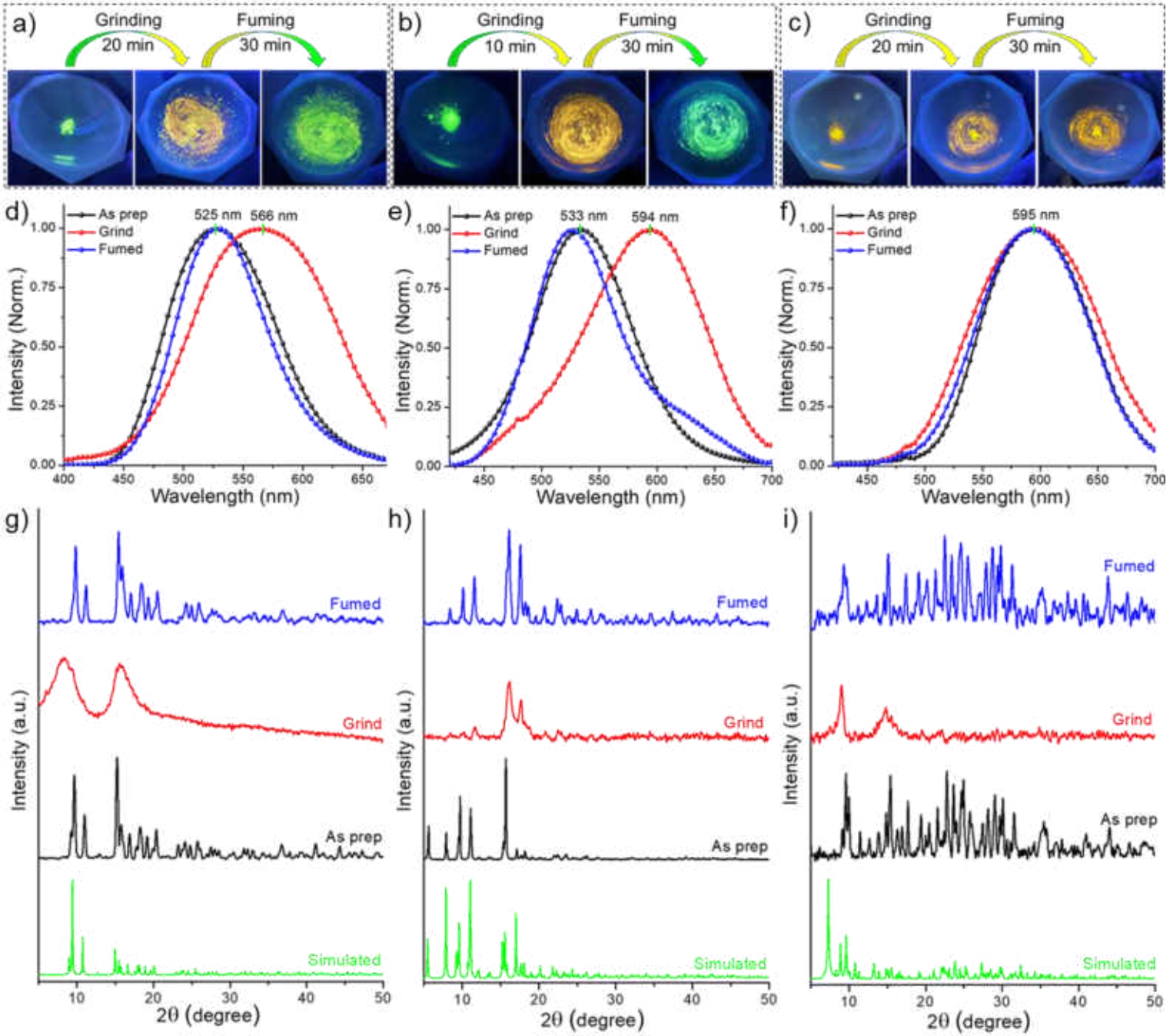
Mass spectrometric studies



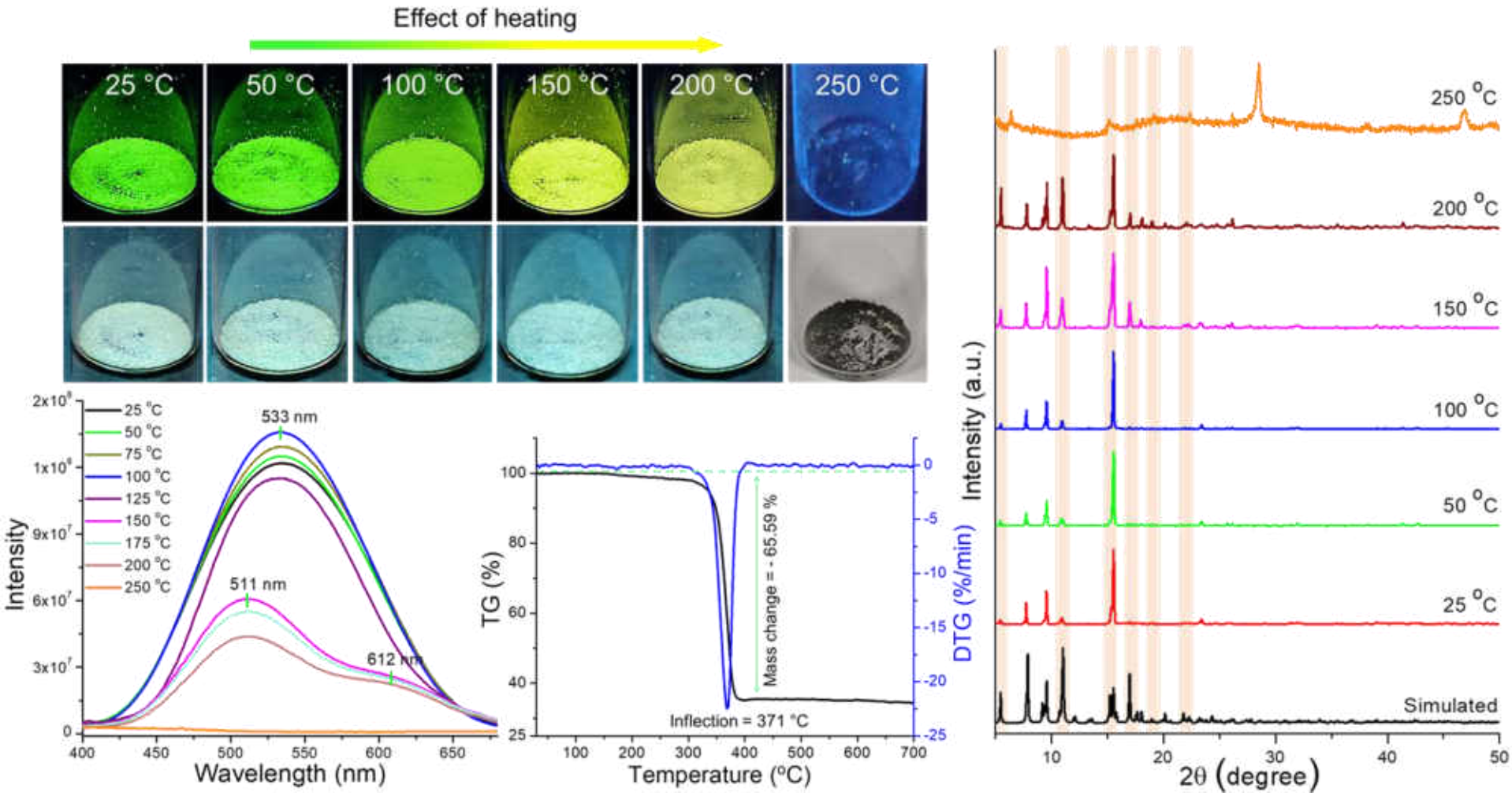
Photophysical properties



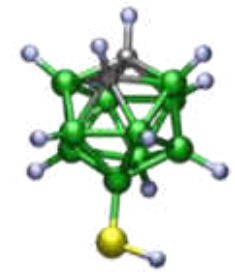
Mechanoresponsive properties



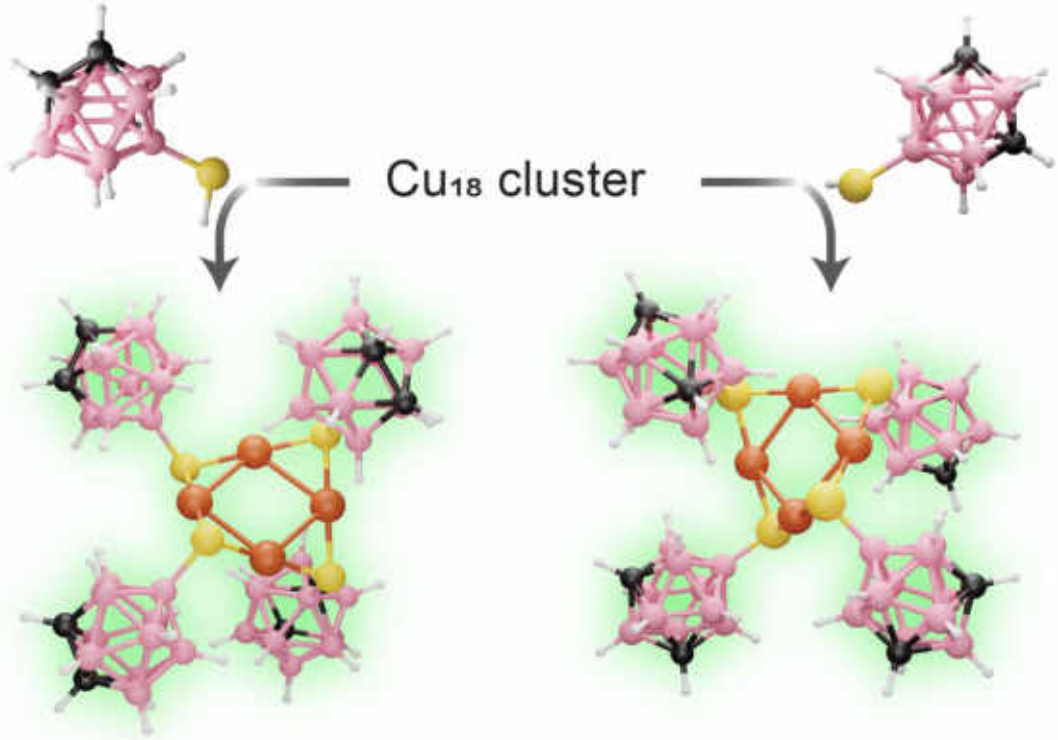
Thermoresponsive properties

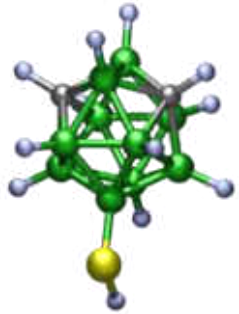


Nanomechanical Properties of Cu_4 Nanoclusters



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

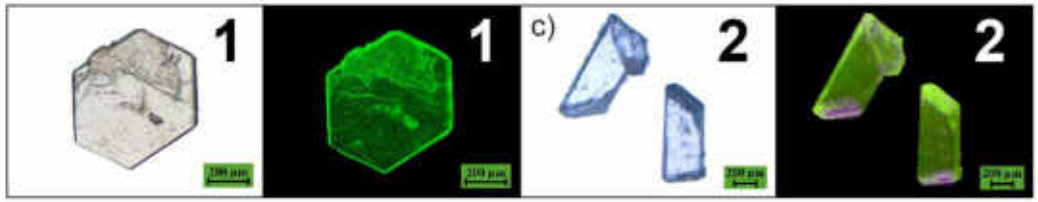




9-HS-1,7-$C_2B_{10}H_{11}$

Isomorphic crystals

$Cu_4(oCBT)_4$ ⟷ $Cu_4(mCBT)_4$

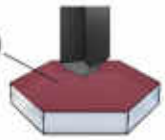


d) Trigonal ($P3_121$)

Z = 3

V = 3333.4 Å^3

ρ = 1.428 Mg/m^3



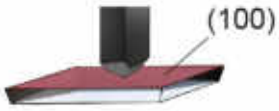
Hexagonal

e) Monoclinic ($P2_1/c$)

Z = 4

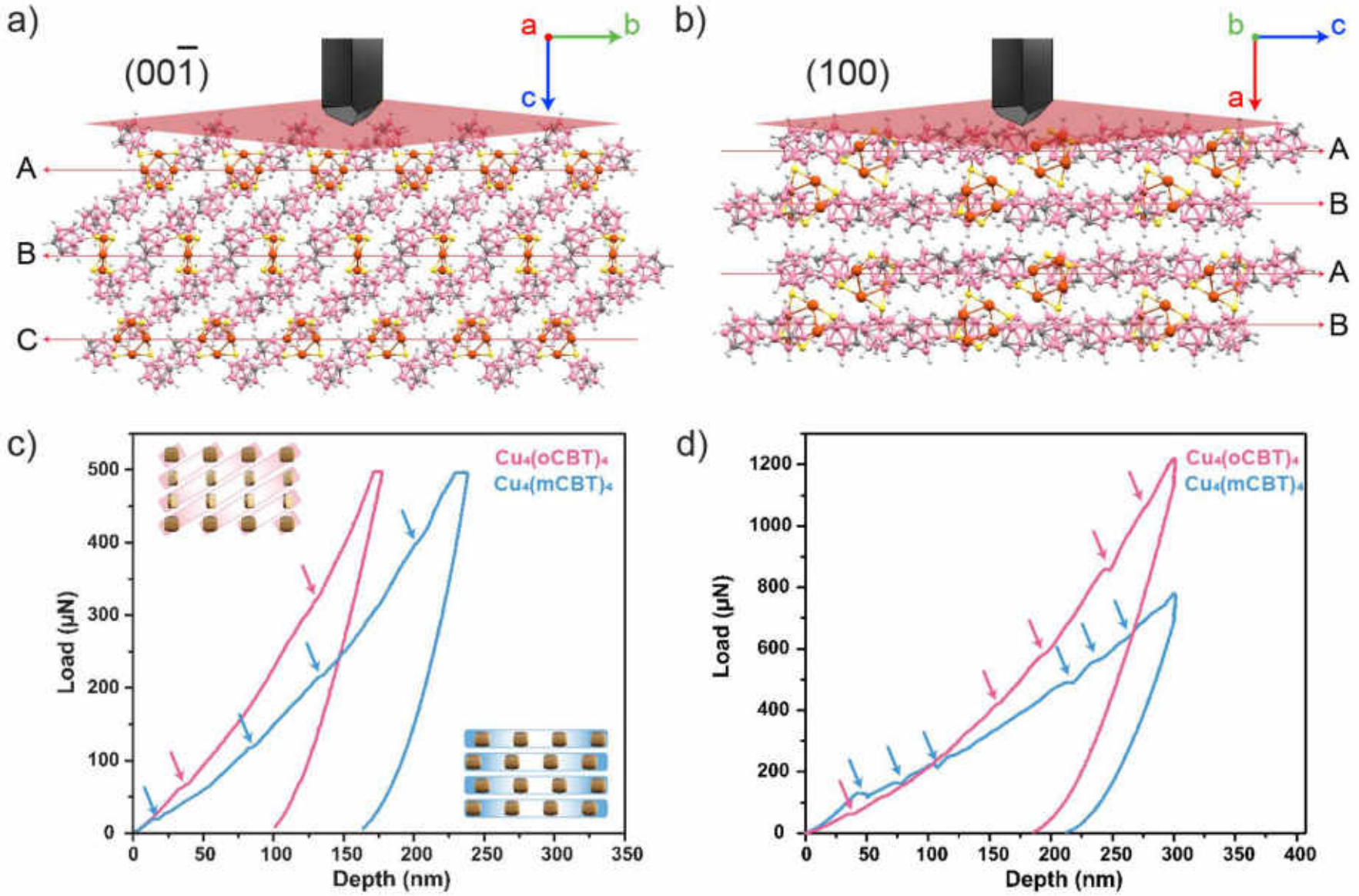
V = 4400.1 Å^3

ρ = 1.442 Mg/m^3

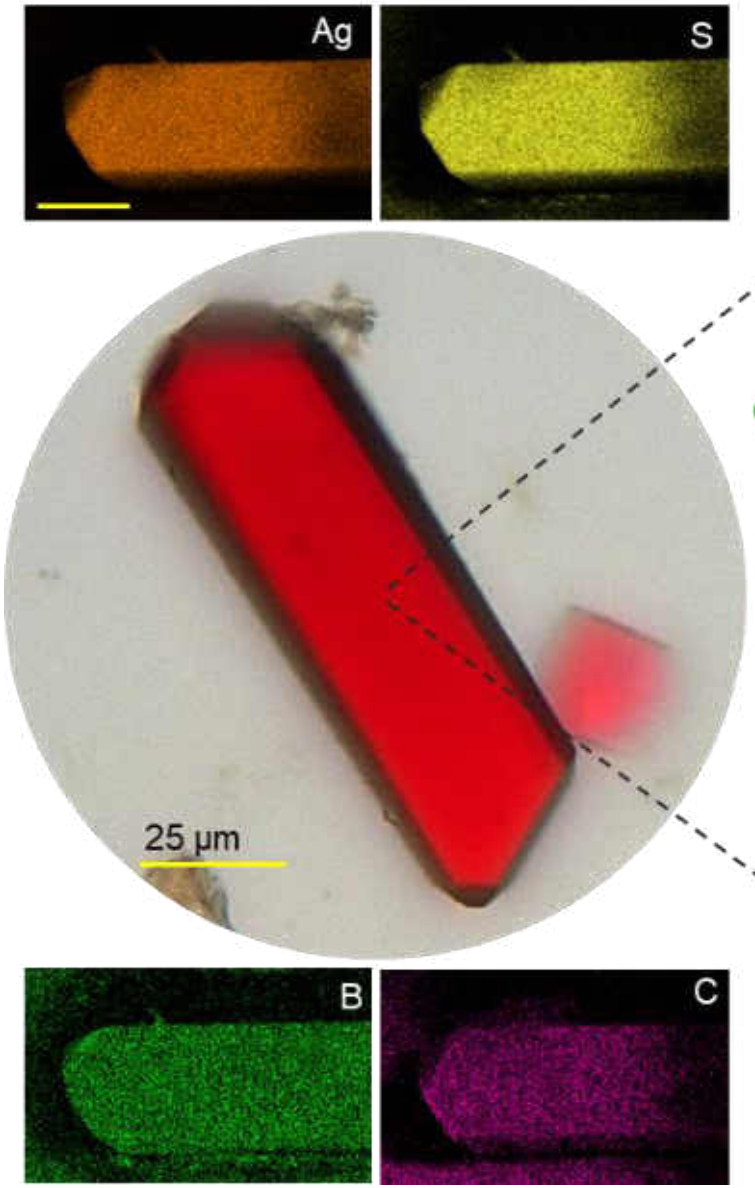


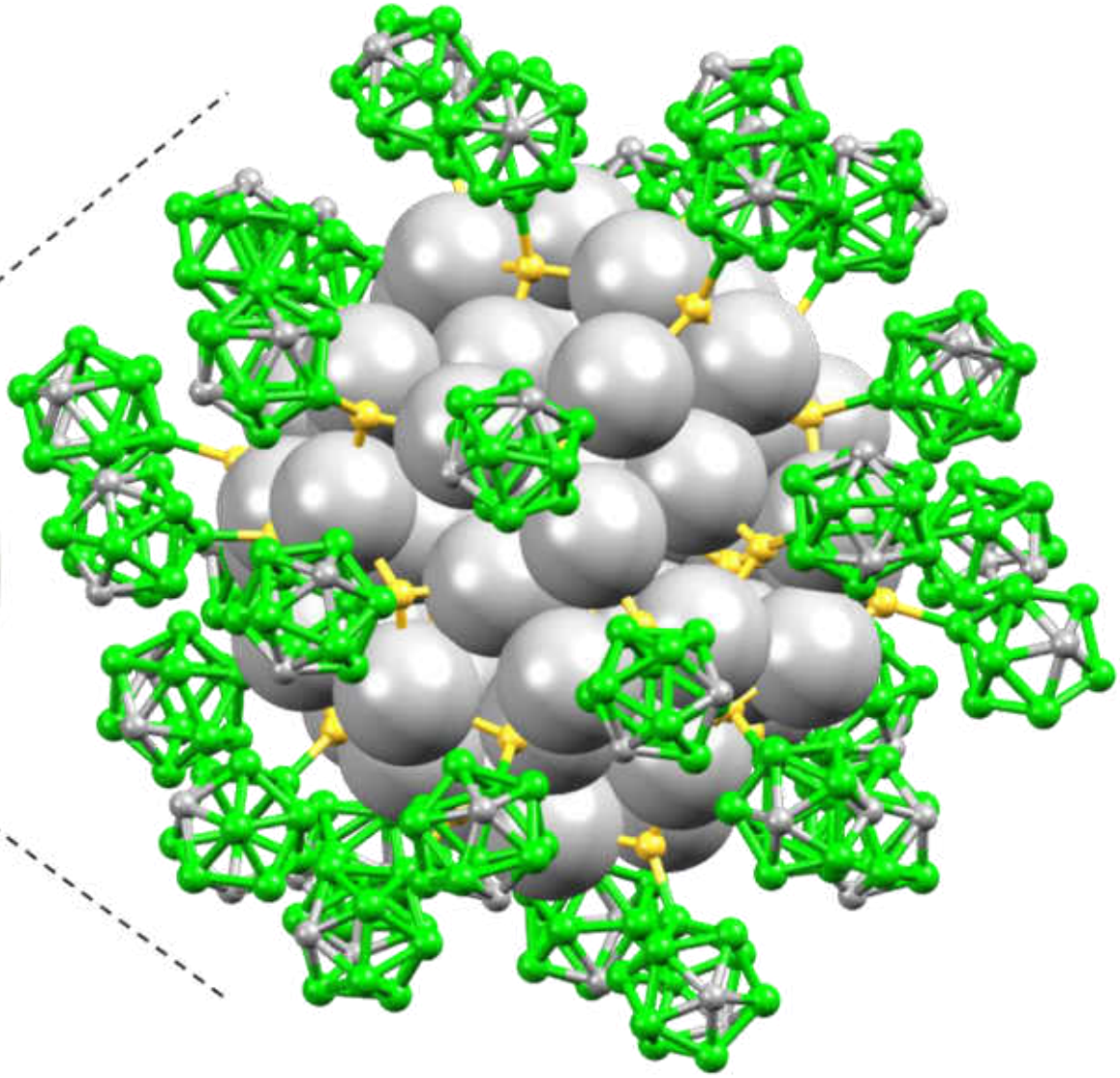
Parallelepiped

Nanomechanical Properties of Cu_4 Nanoclusters



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

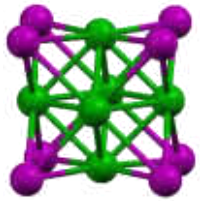




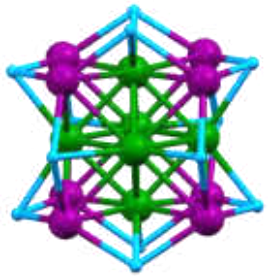
Largest molecule with carboranes so far……

Jana *et al.*, manuscript under preparation

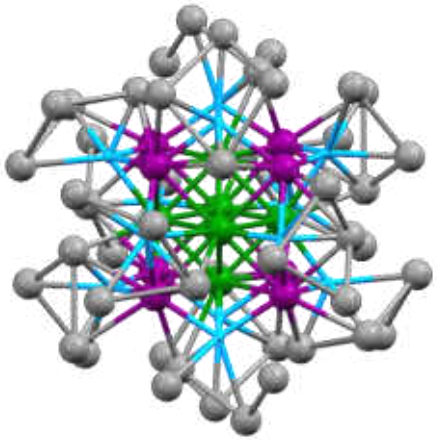
Structural anatomy of $[Ag_{62}S_{12}(CBT)_{32}]$ Nanocluster



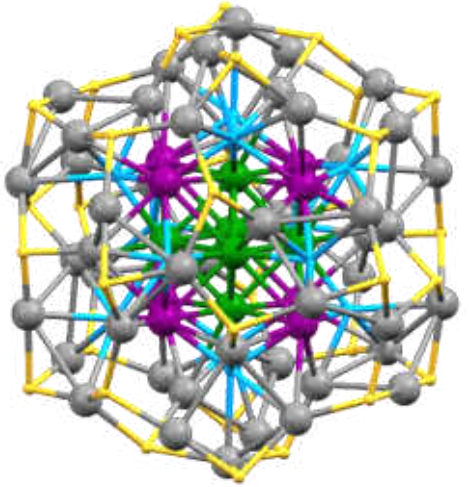
$Ag_6@Ag_8$



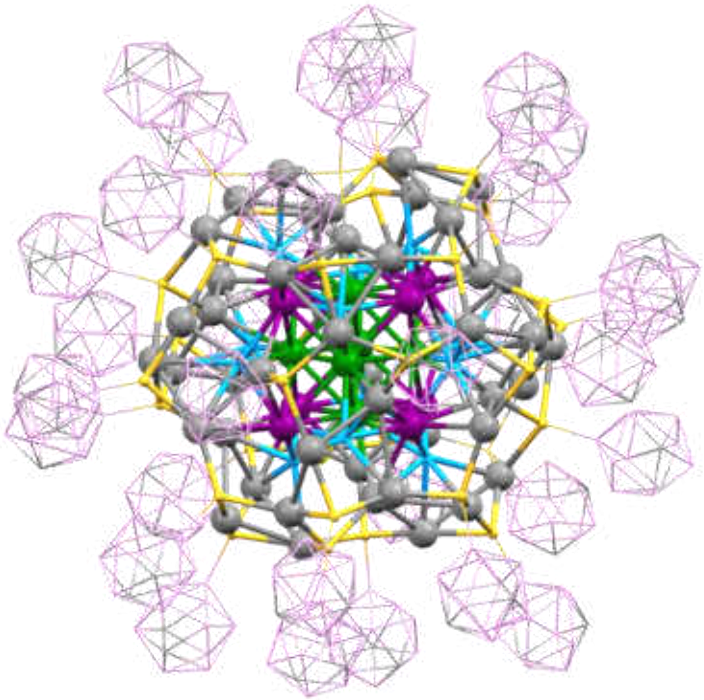
$Ag_6@Ag_8S_{12}$



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

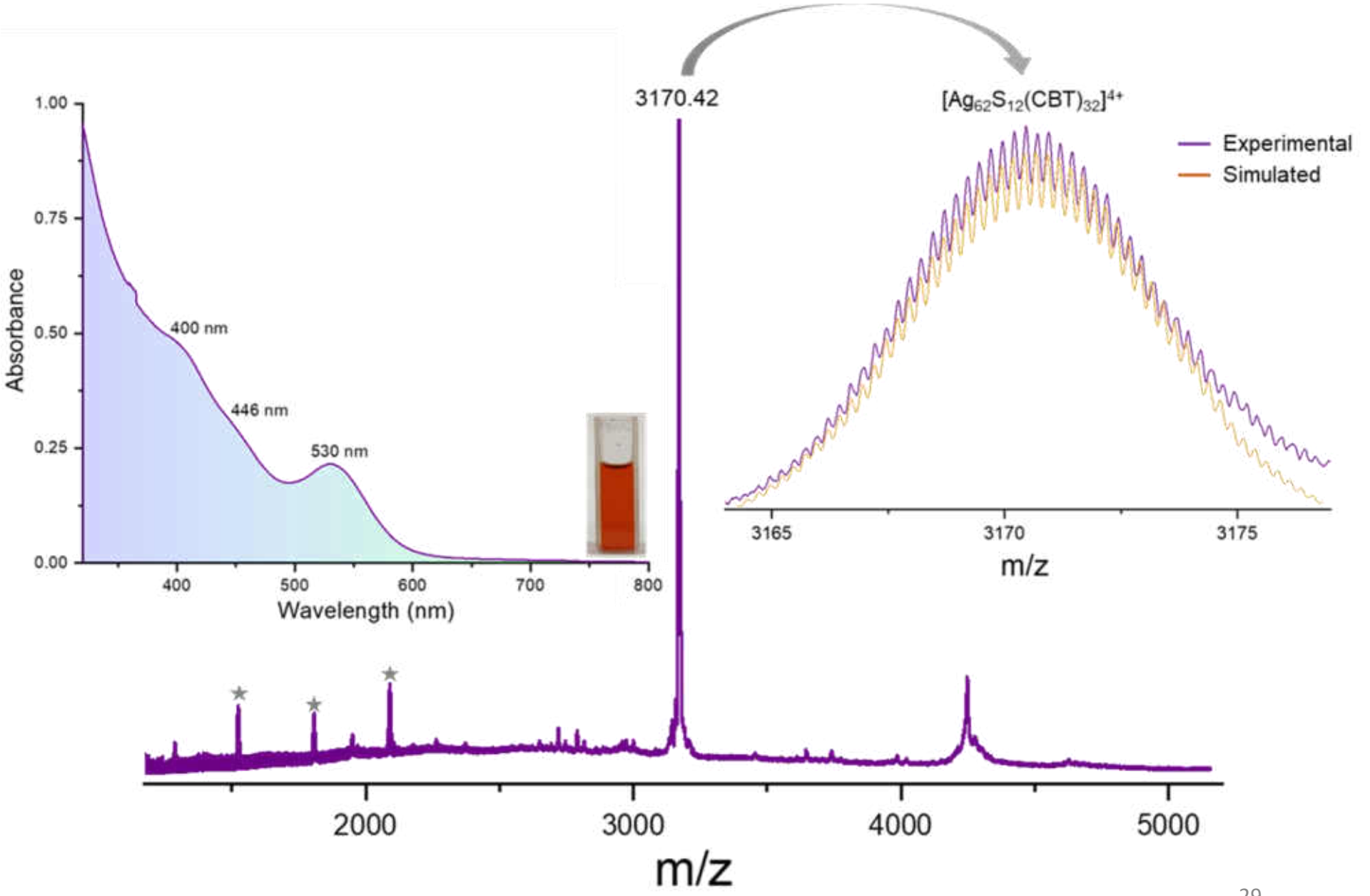


$Ag_6@Ag_8S_{12}@Ag_{48}S_{32}$

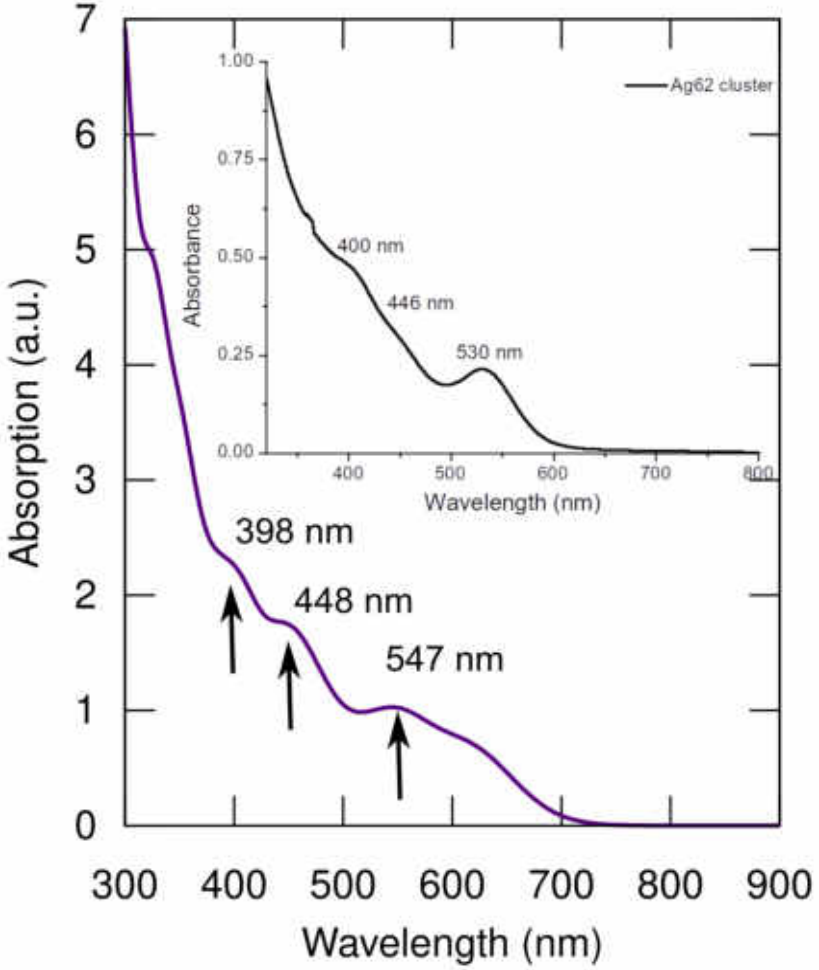


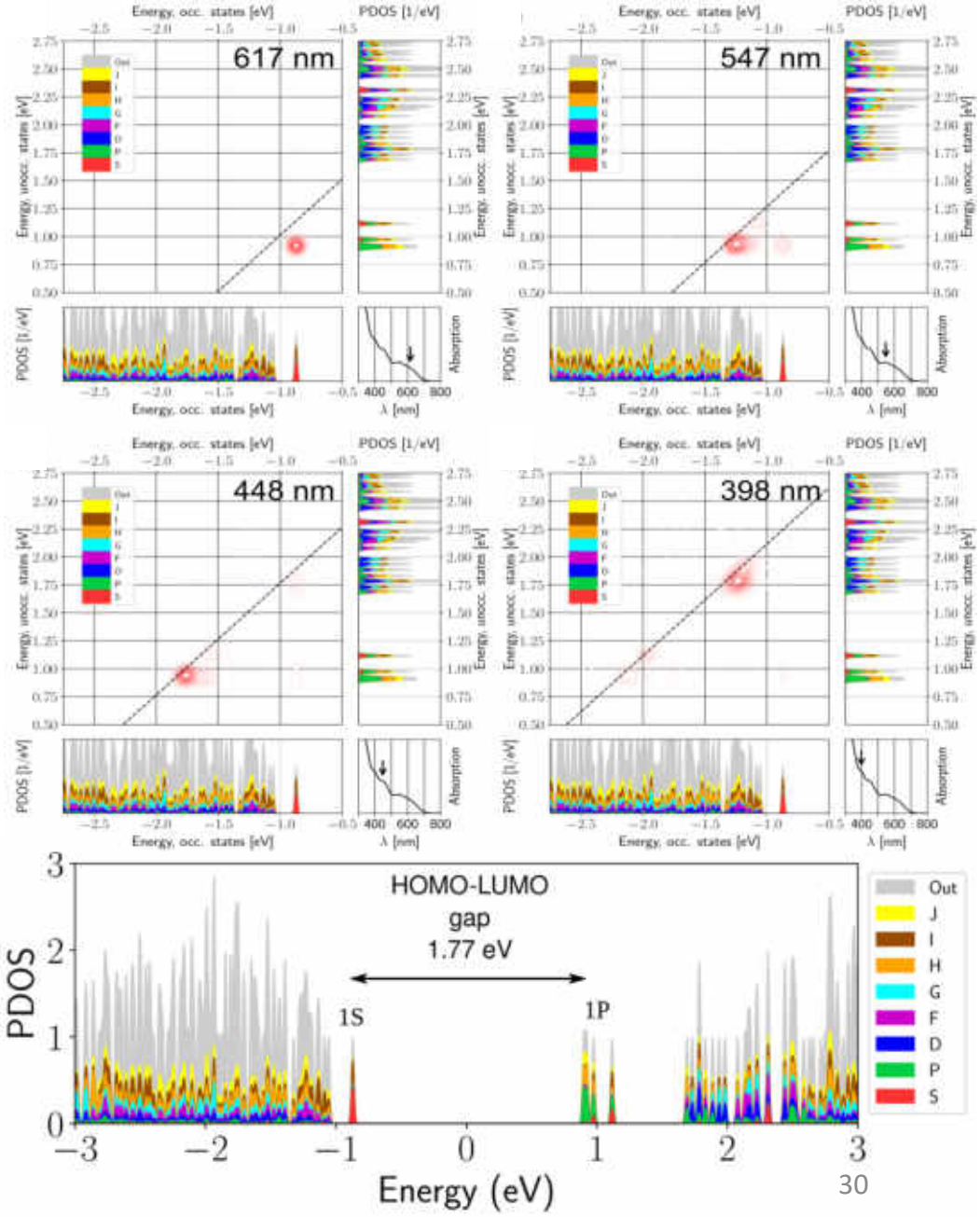
$Ag_6@Ag_8S_{12}@Ag_{48}S_{32}(CB)_{32}$

Characterization of Ag_{62} cluster



Theoretical understanding of electronic energy levels

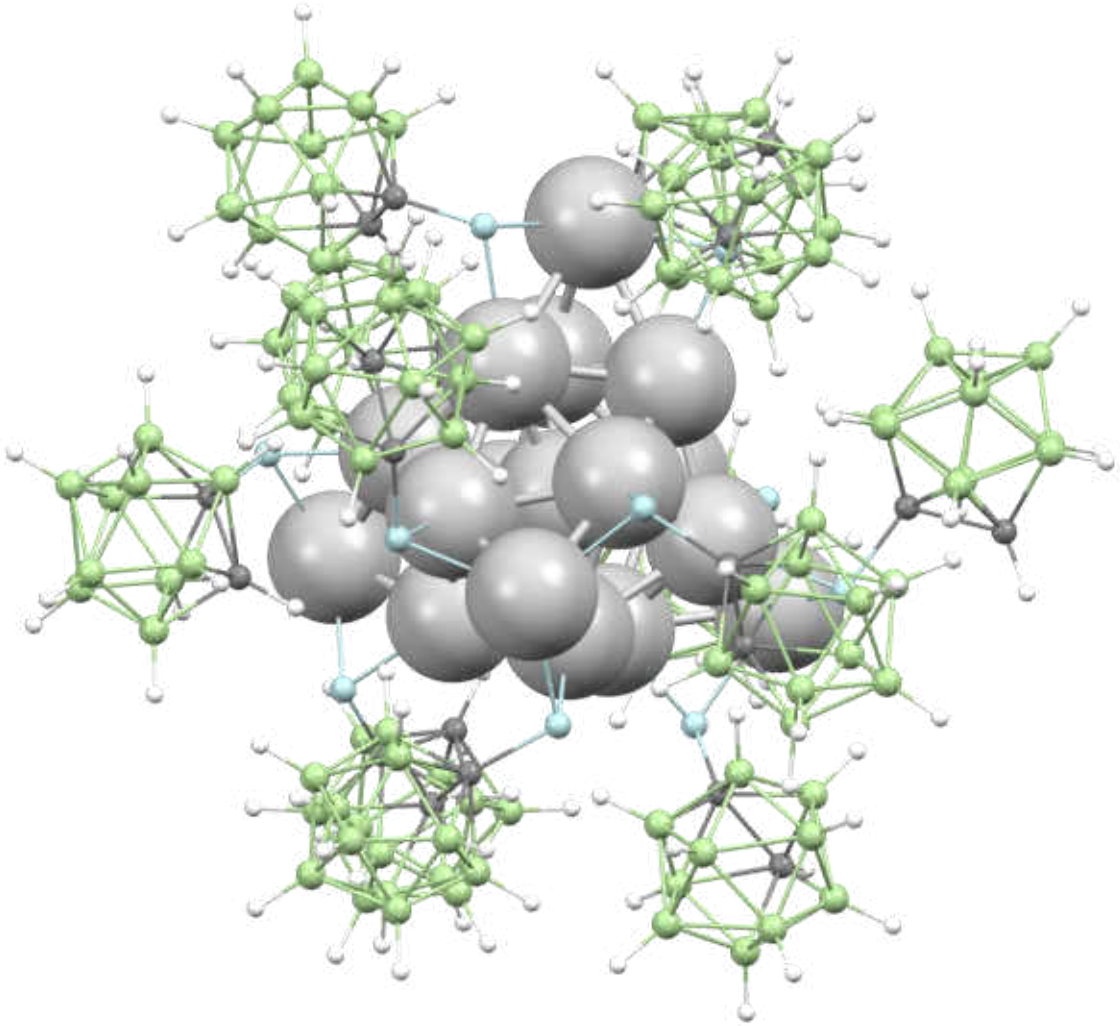




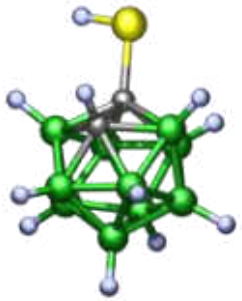
Credit: Dr. Sami, Prof. Häkkinen

Carboranethiol-protected Ag_{17}, $AuAg_{16}$, $Ag_{13}Cu_4$ and $AuAg_{12}Cu_4$ nanoclusters

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

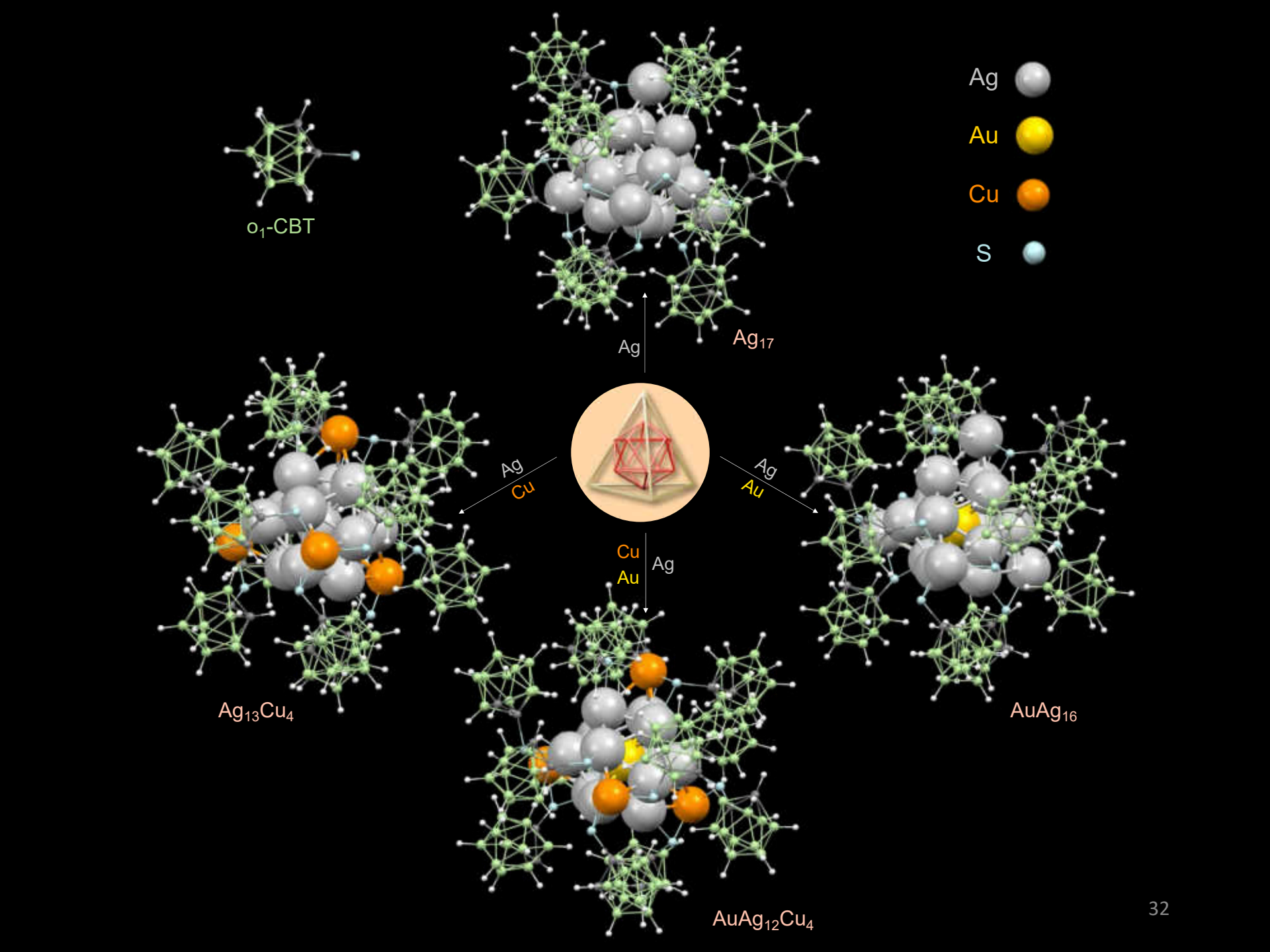


Ligand:



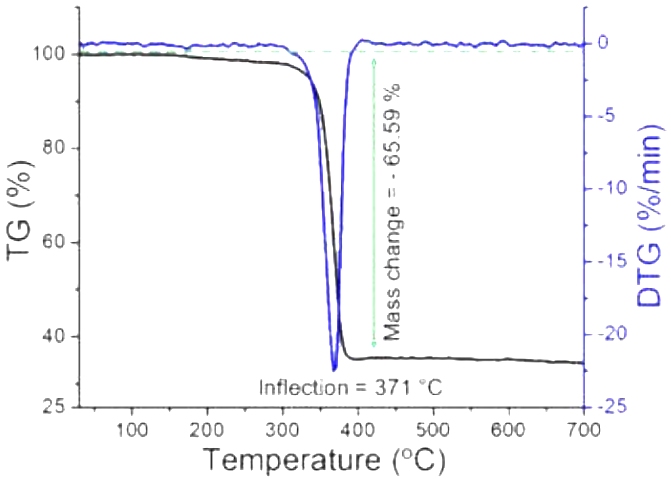
1-HS-1,2-$C_2B_{10}H_{11}$

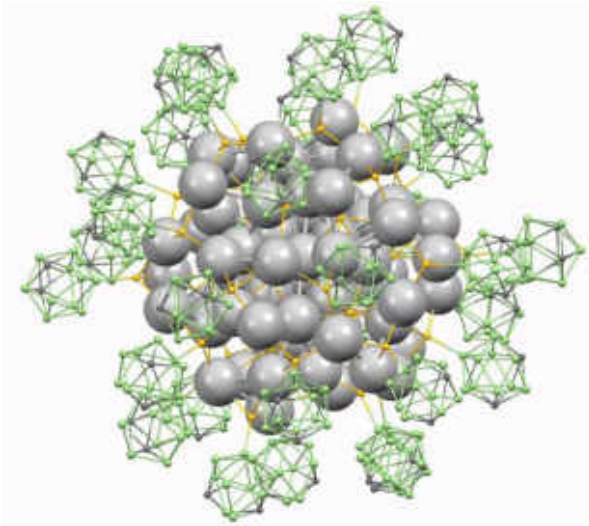
Yadav *et al.*, manuscript under preparation


Ag
Au
Cu
S
o1-CBT
Ag17
Ag
Ag
Cu
Ag
Au
Cu
Au
Ag
Ag13Cu4
AuAg16
AuAg12Cu4

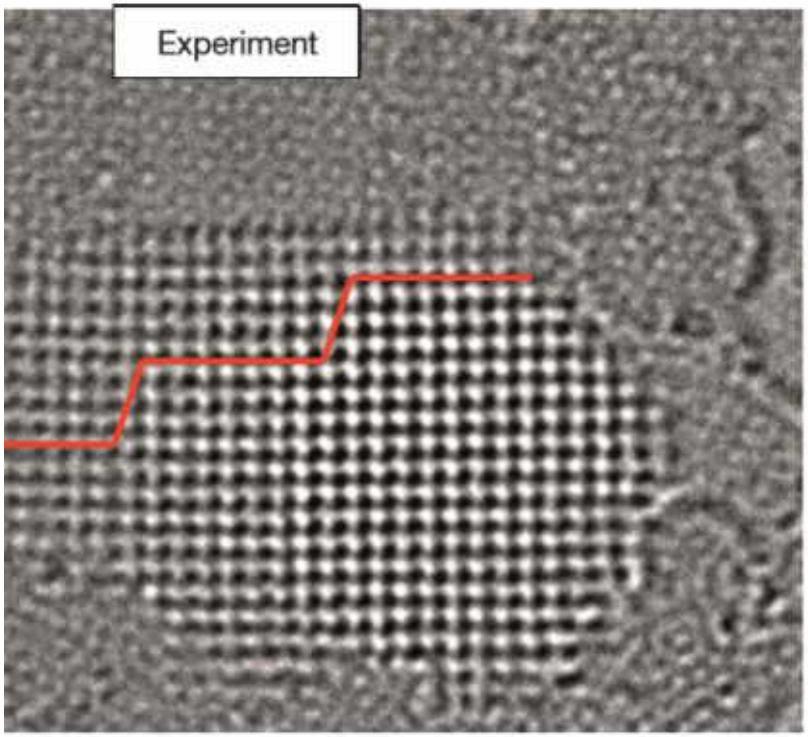
Summary

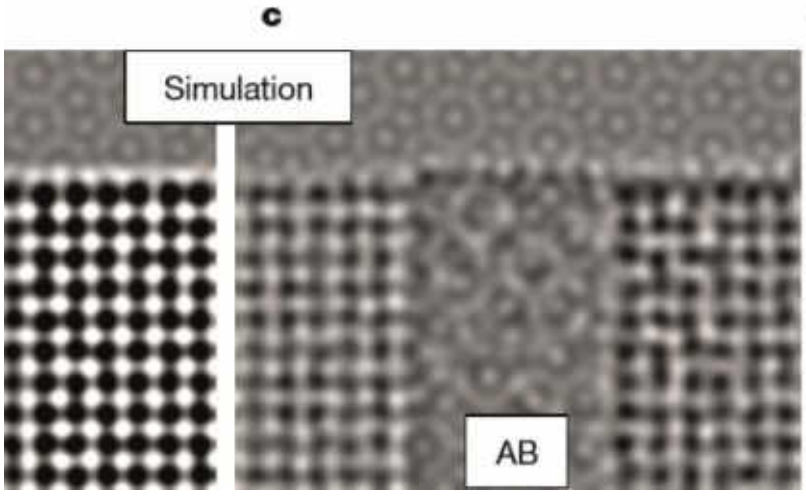
- Carborane protected nanoclusters are versatile.
- Clusters are thermally stable up to 400°C.
- Comparatively larger crystals are available for experiments.
- Nuclearity up to Ag_{62} is now known.
- Need to explore new properties – electrical and thermal conductivity
- Limitation: Need to expand to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

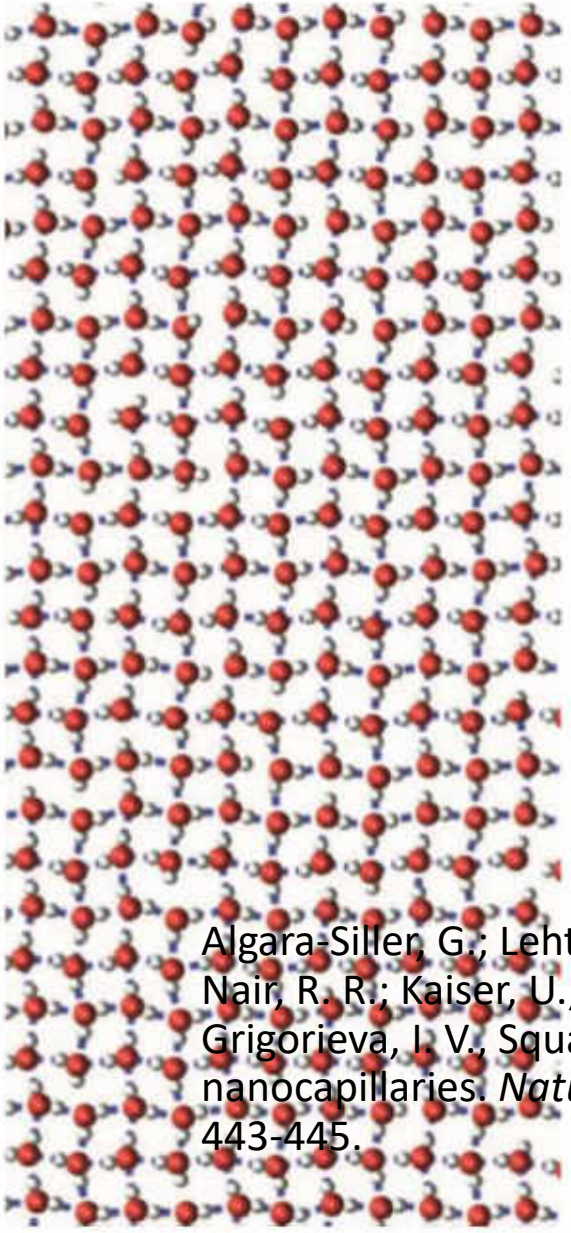




Observing Molecules







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

Volume 13
Number 45
7 December 2022
Pages 13251–13634

Chemical Science

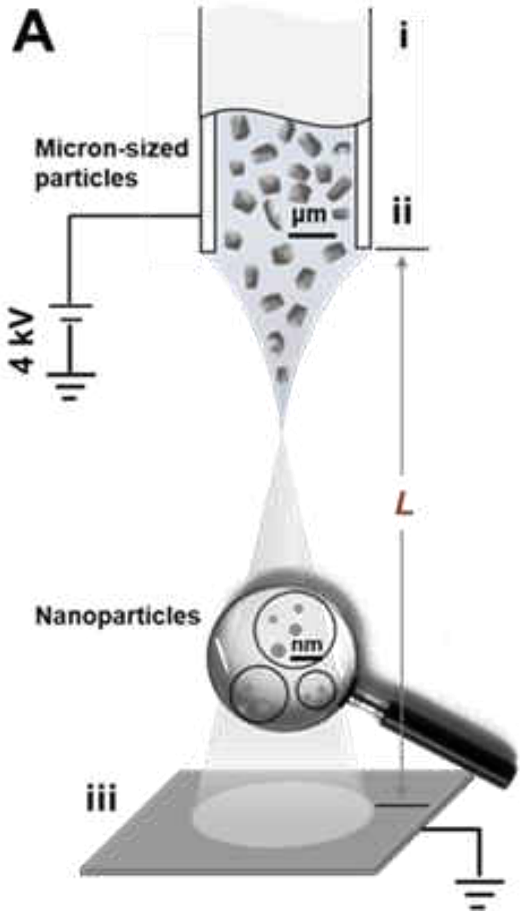
rsc.li/chemical-science

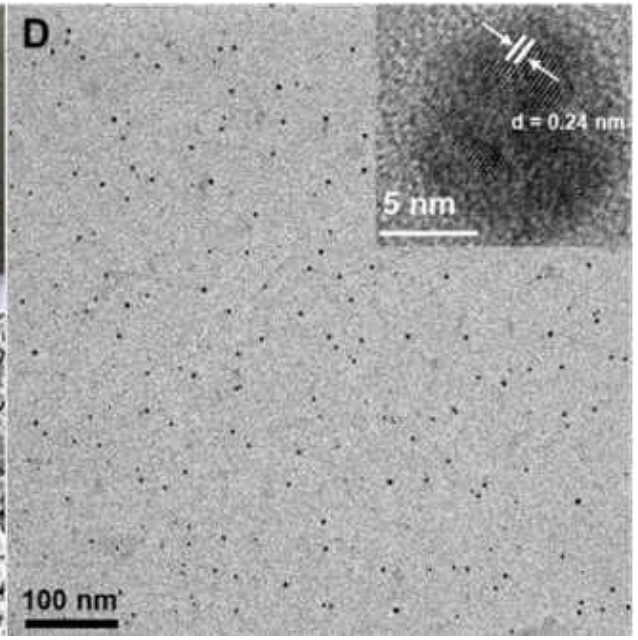
ISSN 2041-6539

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE
Thalappil Pradeep *et al.*
Spatial reorganization of analytes in charged aqueous microdroplets

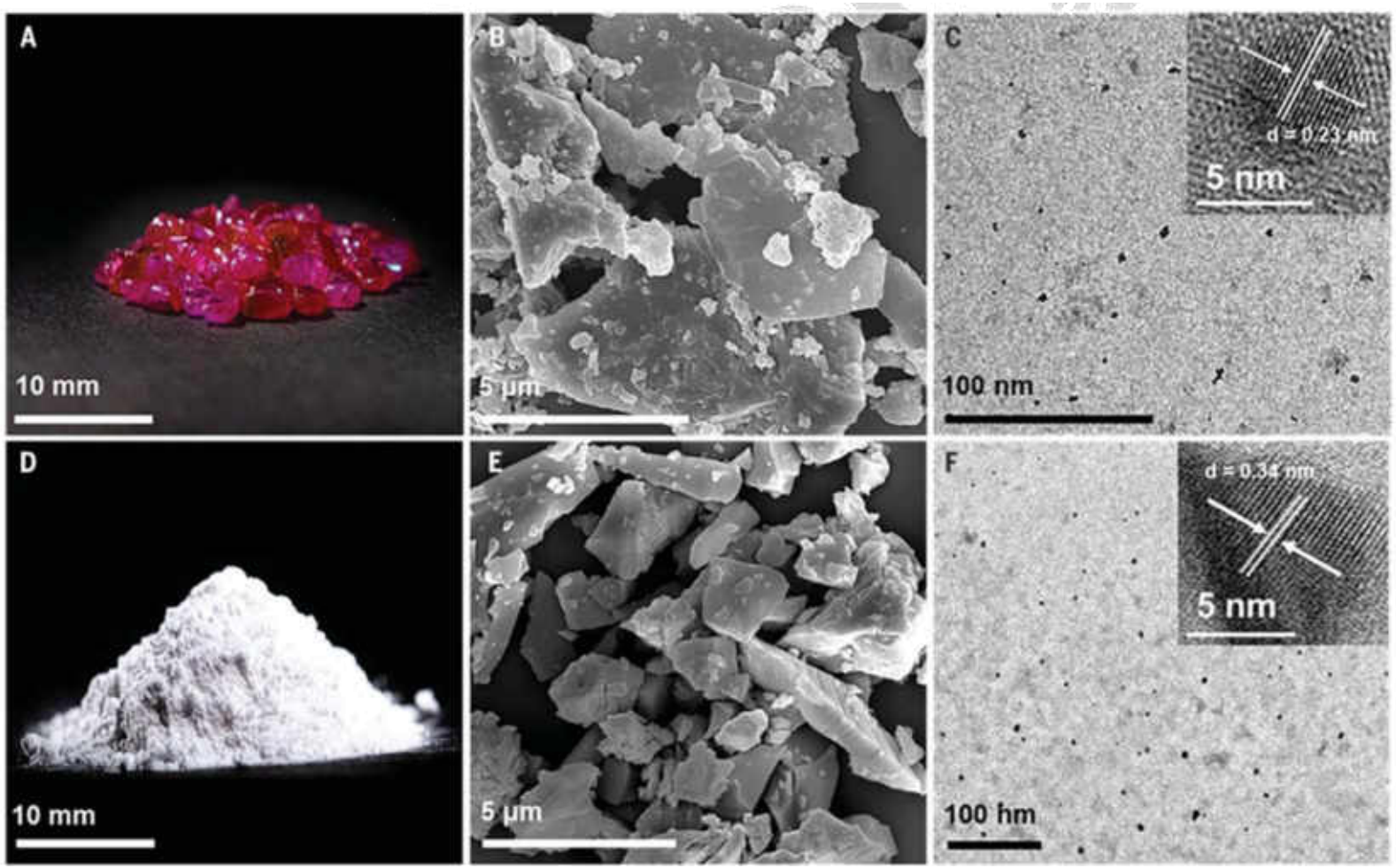
Spontaneous Weathering of Natural Minerals in Charged Water Microdroplets Forms Nanomaterials





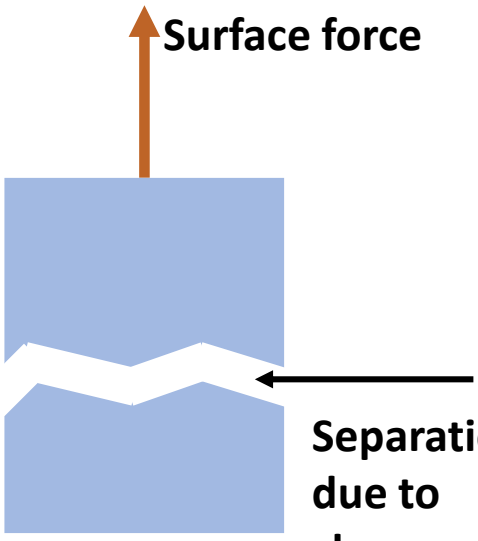
Spoorthi, et. al., *Science*, 384 (2024) 1012-1017.

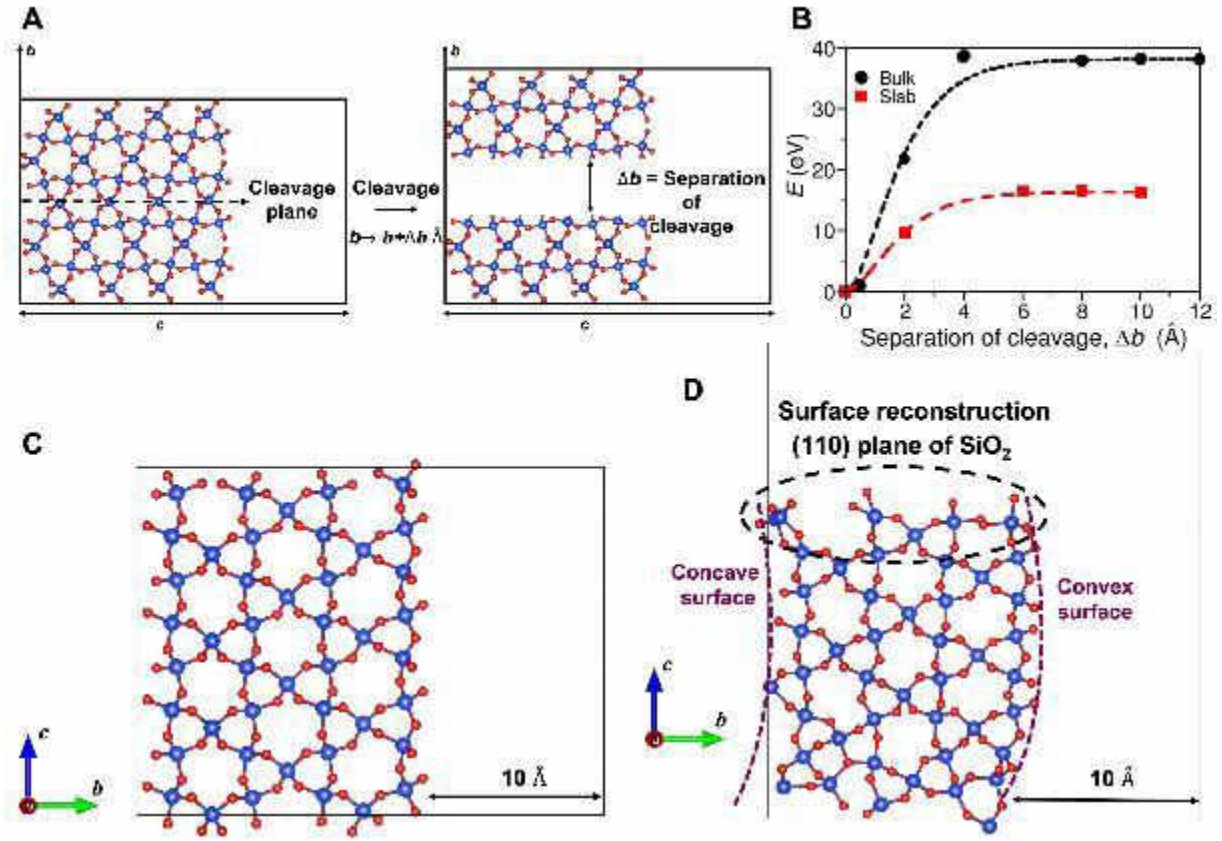
Ruby, Fused Alumina

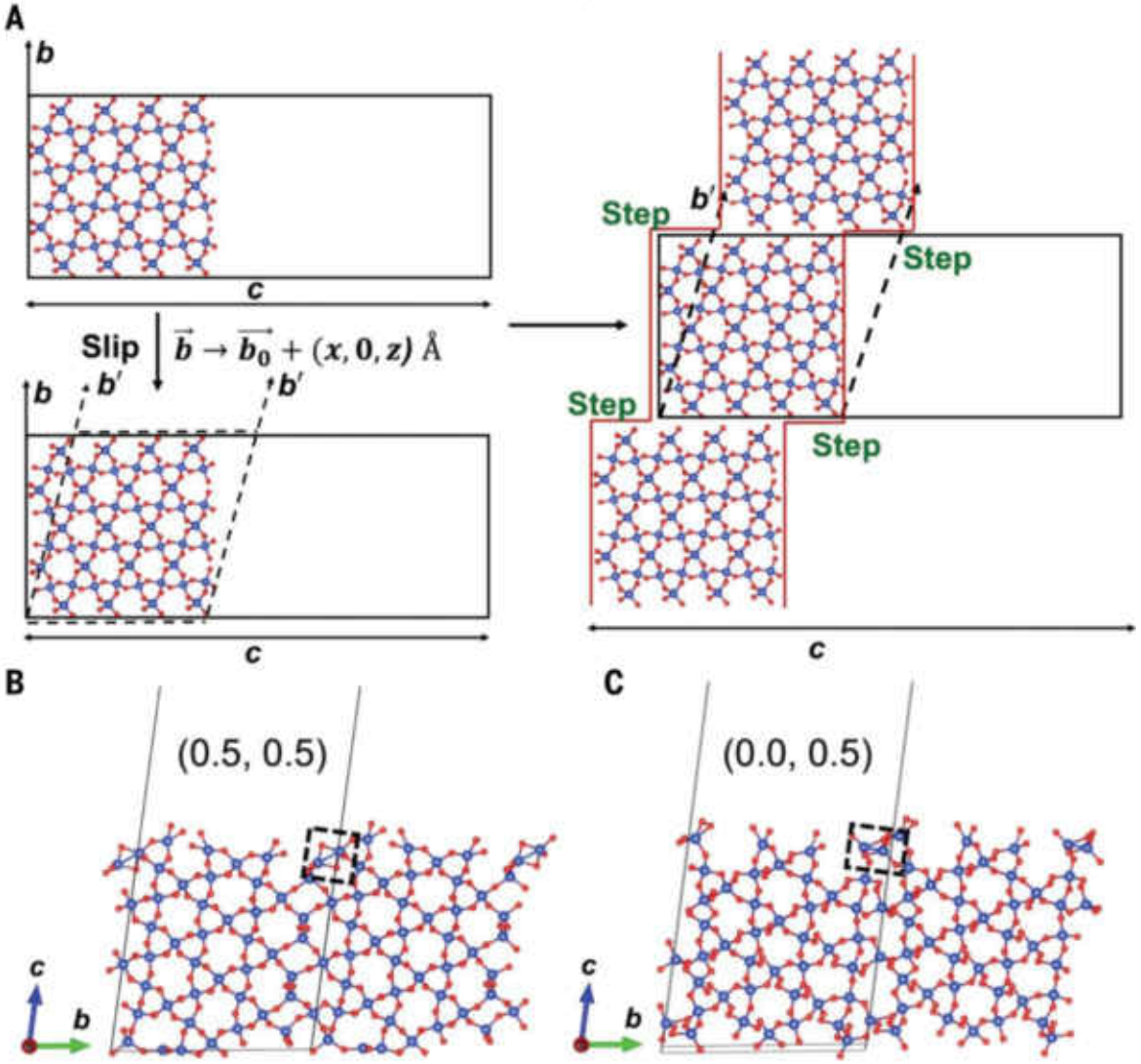


Mechanism: Cleavage

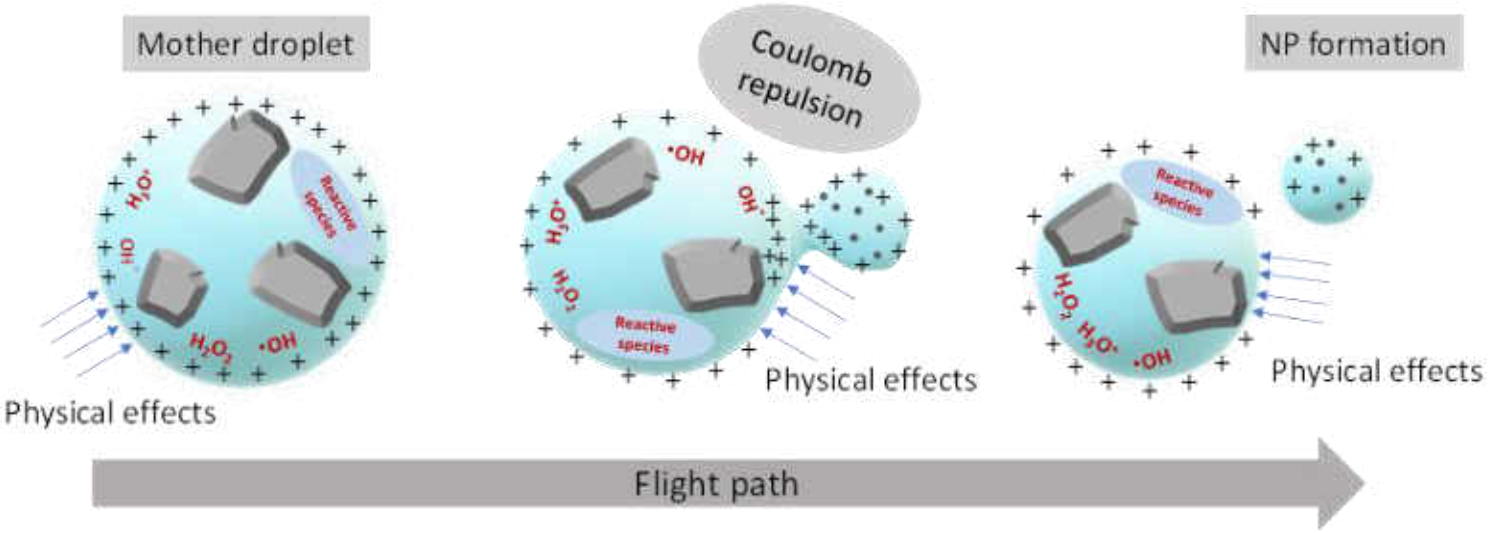
The process of cleavage and surface reconstruction visualized with first-principles simulations






A
b
c
Slip
$\vec{b} \rightarrow \overrightarrow{b_0} + (x, 0, z)$ Å
b
b′
b′
c
Step
b′
Step
Step
Step
c
B
(0.5, 0.5)
c
b
C
(0.0, 0.5)
c
b

Mechanism of nanoparticle formation



Collaborators

Dr. Tomas Base

The Czech Academy of Sciences

Institute of Inorganic Chemistry

Prof. Hannu Häkkinen

University of Jyväskylä, Finland

Prof. Manfred Kappes

Institute of Nanotechnology

Karlsruhe Institute of Technology (KIT)

Prof. Umesh V. Waghmare

JNCASR, Banglore, India

Prof. K. V. Adarsh

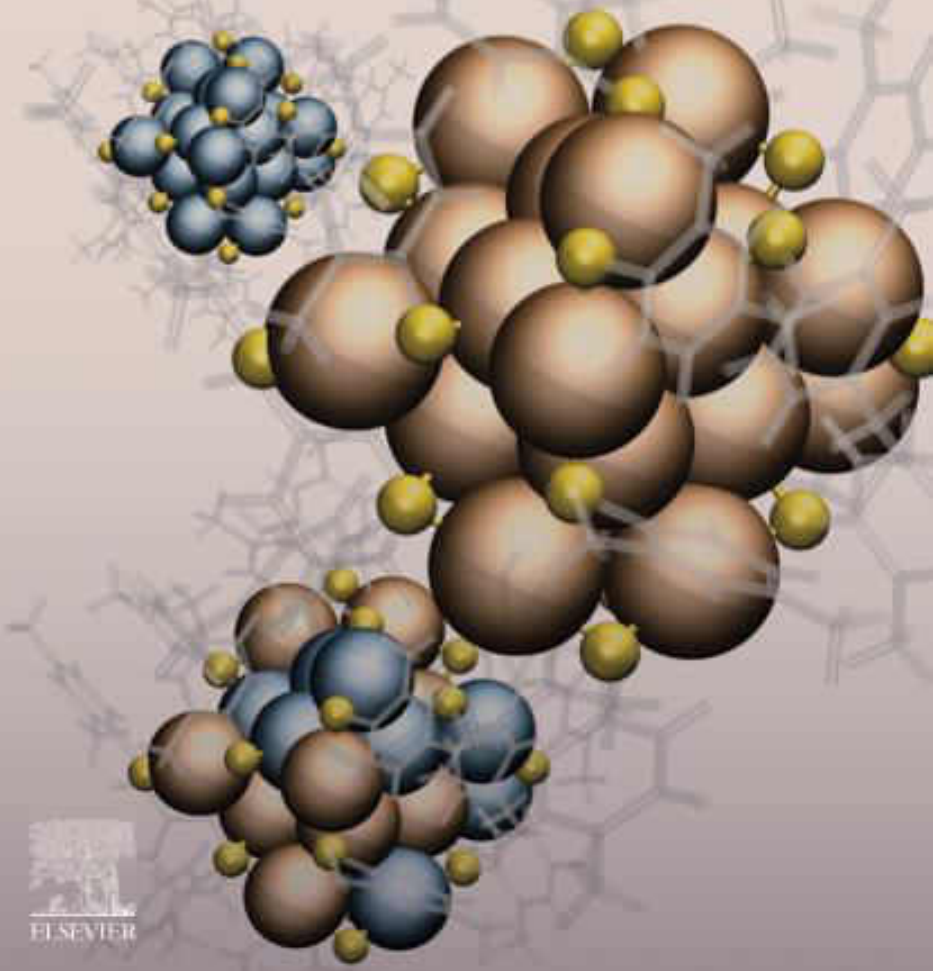
IISER Bhopal, India

Research Group

सत्यमेव जयते
Department of Science & Technology
Government of india

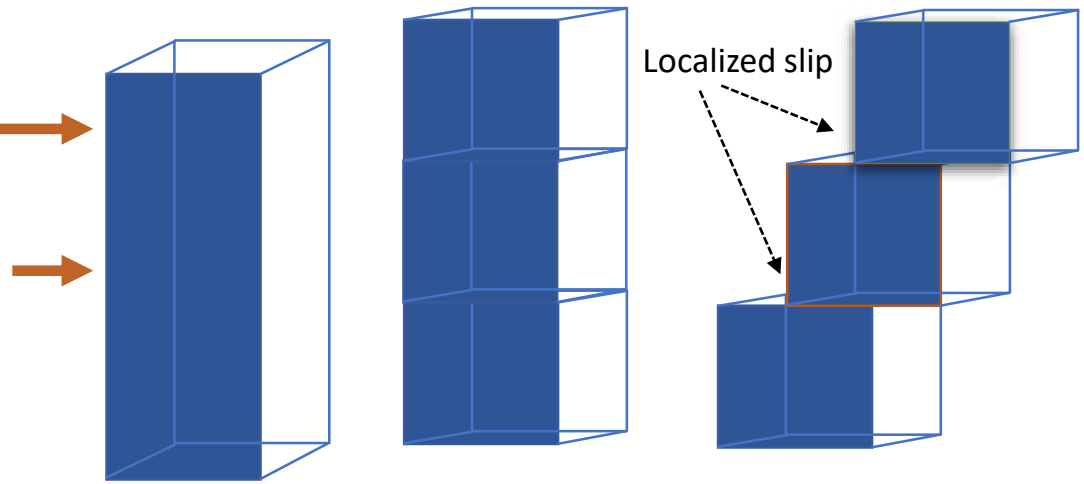
Edited by
Thalappil Pradeep

ATOMICALLY PRECISE METAL NANOCLUSTERS

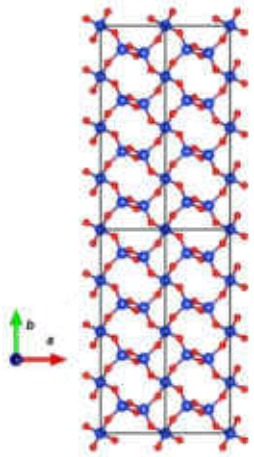


ELSEVIER

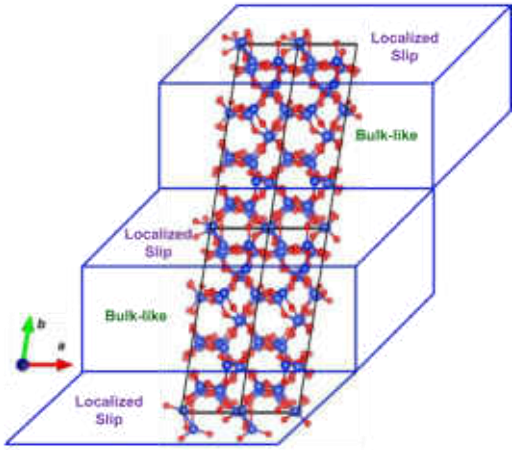
Mechanism: Slip



No slip



Slip



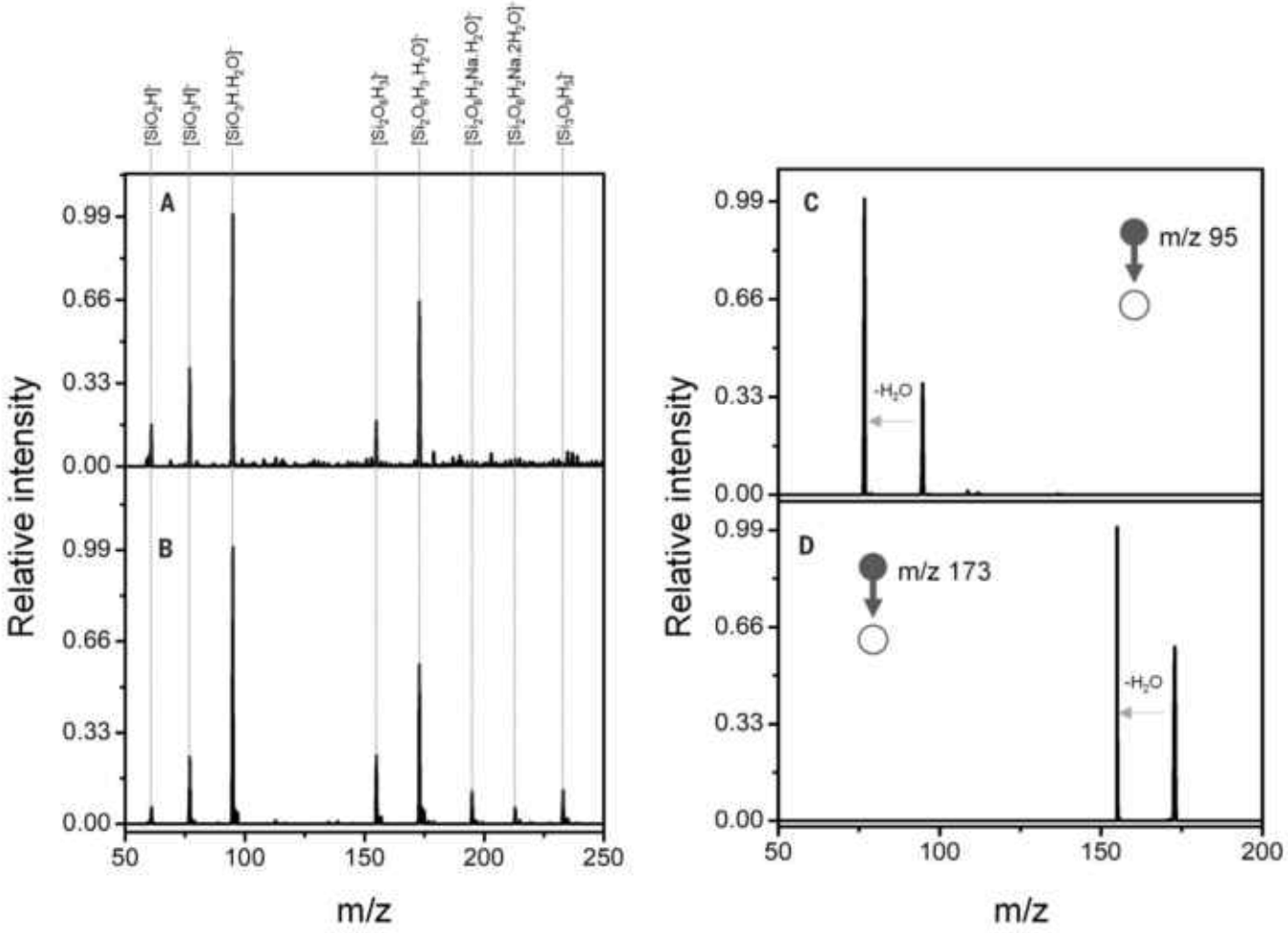
This instability leads to the formation of a stacking fault on the (010) plane, achieved with slip localized at (010) plane

Stacking fault

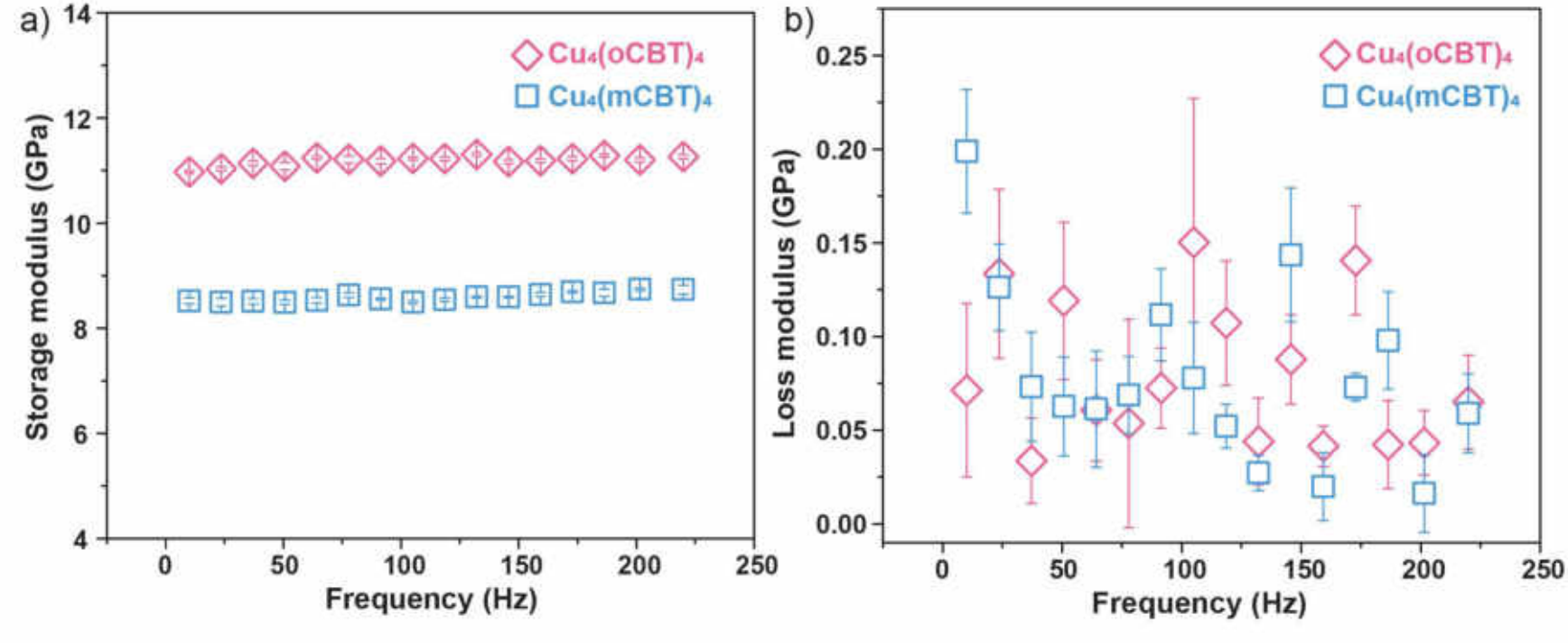
$$\vec{b} \rightarrow \overrightarrow{b_0} + (x, 0, z).$$

(x, $z \in [0,1]$) - fractional coordinates

Mass Spectrometry of the Fragments



Nanomechanical Properties of Cu_4 Nanoclusters



Suitable for vibration damping applications.

Nanomechanical Properties of Cu_4 Nanoclusters

Parameters	$Cu_4(oCBT)_4$	$Cu_4(mCBT)_4$
Density	1.428 g/cm^3	1.442 g/cm^3
E_{bare}	232 GPa	234 GPa
$E_{elastic}$	12.9 GPa	10.1 GPa
$E_{experimental}$	9.99 GPa	8.45 GPa

- $Cu_4(oCBT)_4$ is harder than $Cu_4(mCBT)_4$, even though it is less dense.
- Our material shows a significantly larger storage modulus and a lower loss modulus than silver nanoclusters, indicating superior mechanical strength.
- Such materials can be used in crystal optics, precision measurement instruments, mechanical resonators, and nanomechanical instruments, where damping of vibrations is essential.