Centre of Excellence
on
Molecular Materials and Functions

The big idea

A centre with global visibility on molecular matter focusing on atomically precise clusters and gas hydrates

Cutting edge science in respective areas, best people across the world, state-of-the-art resources, involvement of next generation

Centre of Excellence
on
Molecular Materials and Functions

Thalappil Pradeep
Institute Professor, IIT Madras
with

Pulikkel M. Ajayan[$,#,%] (Rice University, USA)
Tomas Base[%] (Institute of Inorganic Chemistry, Czech Republic)
R.G. Cooks[$,#,%] (Purdue University, USA)
Stefanie Dehnen (Philipps-Universität Marburg, Germany)
Pijush Ghosh[%] (IIT Madras, India)
Sundargopal Ghosh[%] (IIT Madras, India)
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Tatsuya Tsukuda[%] (Univ. of Tokyo, Japan)
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Robert L. Whetten[%] (NAU, USA)
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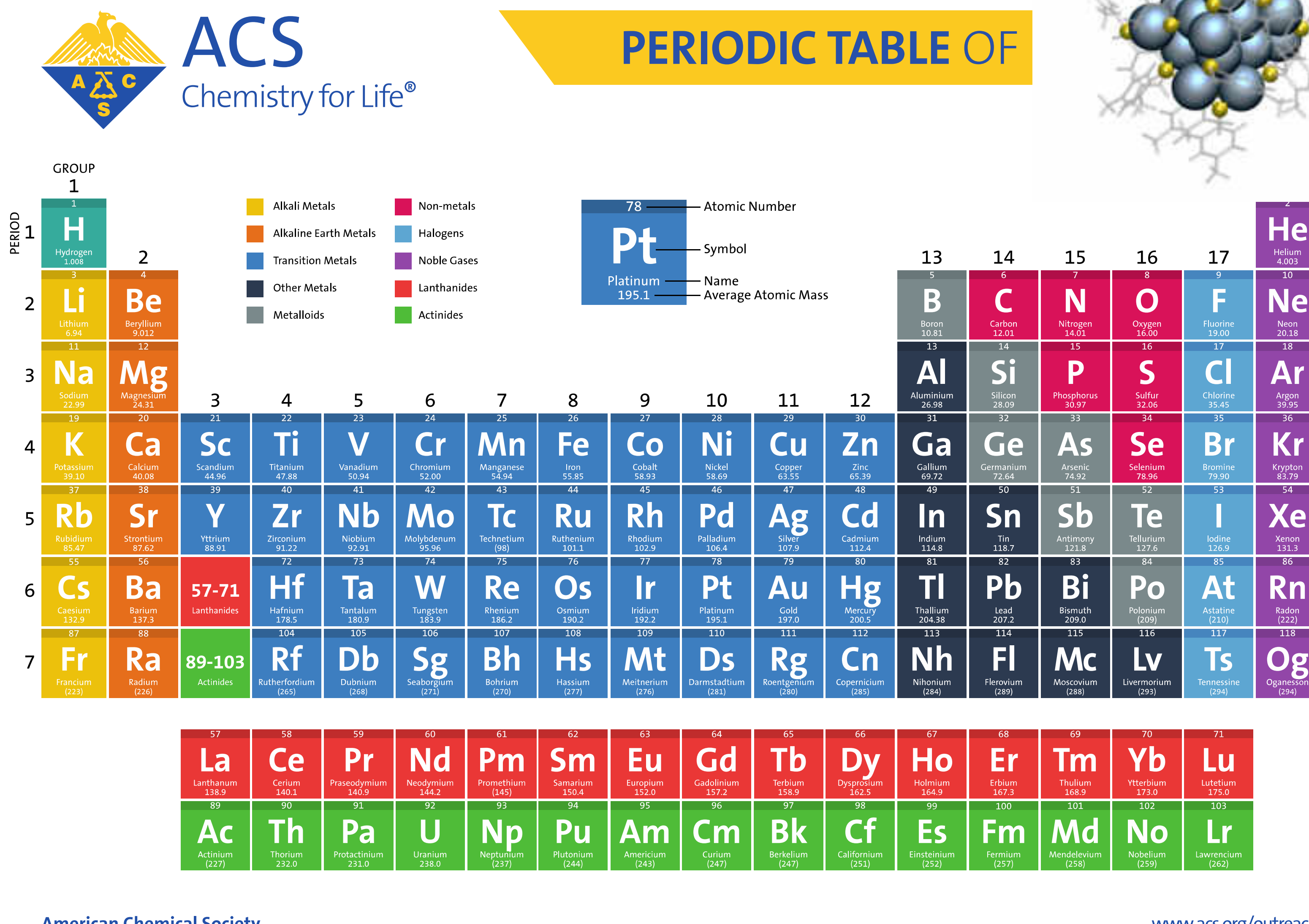
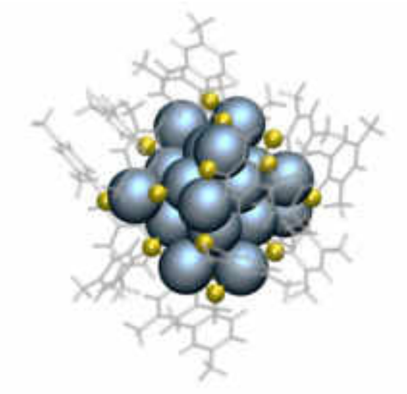
Vimal Edachery (IIT Madras, India)

[#]VAJRA faculty [%]Collaborator with joint papers
[$]Distinguished Professor of IIT Madras

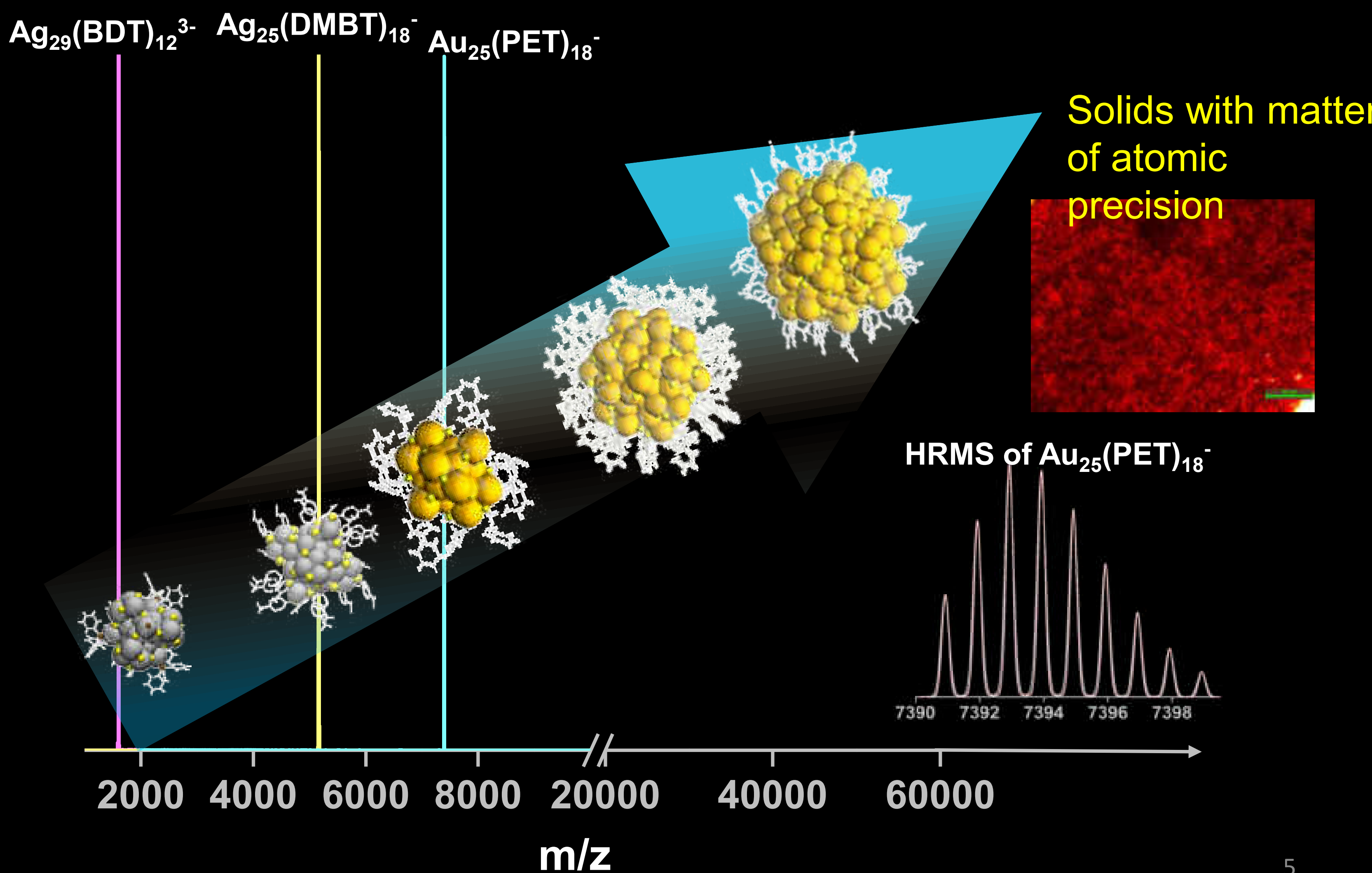
pCOE Lecture series on Molecular Materials and Functions

Can we create materials of atomic precision across the periodic table?





Origin of metallicity - Molecular metals, magnets, applications, ...



CHEMICAL REVIEWS

Review

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

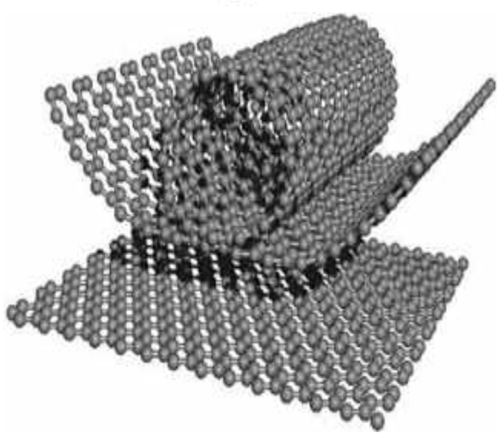
Indranath Chakraborty[†] and Thalappil Pradeep*

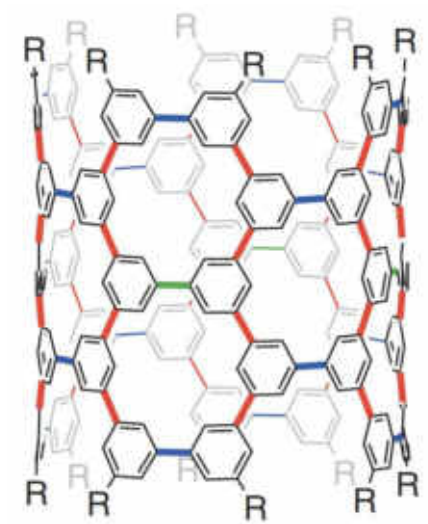
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

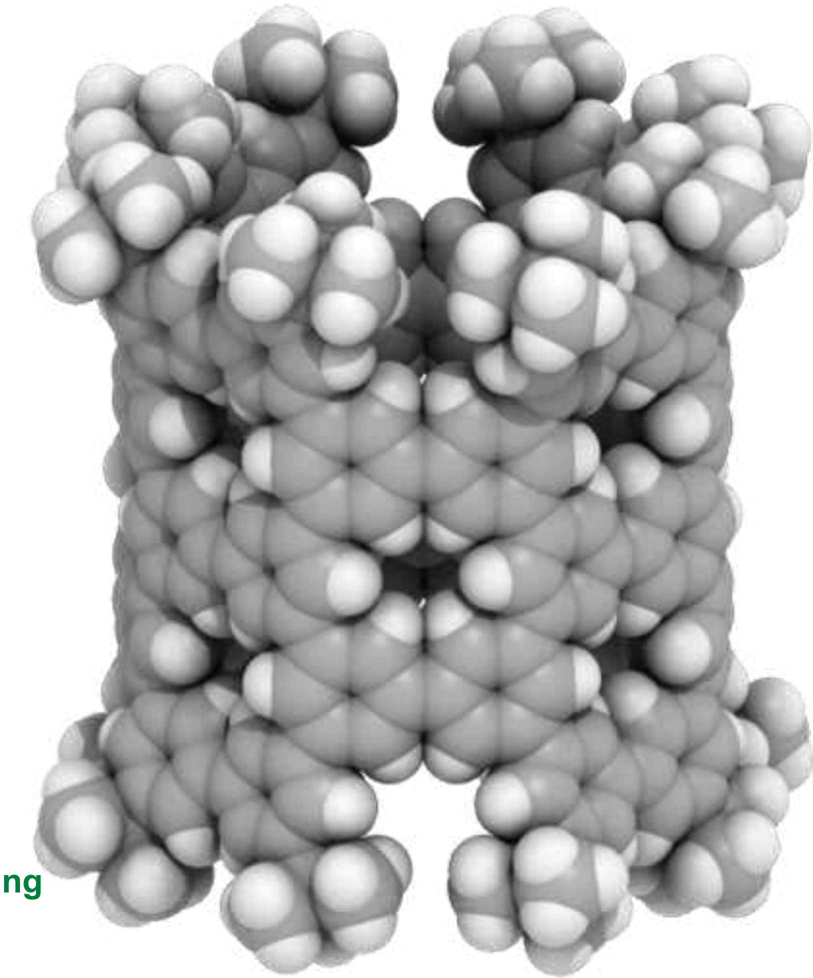
Supporting Information

ABSTRACT: Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{102}(SR)_{44}$ as well as $Ag_{25}(SR)_{18}$, $Ag_{29}(S_2R)_{12}$, and $Ag_{44}(SR)_{30}$ (often with a few counterions to compensate charges) are known now. They can be made reproducibly with robust synthetic protocols, resulting in colored solutions, yielding powders or diffractable crystals. They are distinctly different from nanoparticles in their spectroscopic properties such as optical absorption and emission, showing well-defined features, just like molecules. They show isotopically resolved molecular ion peaks in mass spectra and provide diverse information when examined through multiple instrumental methods. Most important of these properties is luminescence, often in the visible−near-infrared window, useful in biological applications. Luminescence in the visible region, especially by clusters protected with proteins, with a large Stokes shift, has been used for various sensing applications, down to a few tens of molecules/ions, in air and water. Catalytic properties of clusters, especially oxidation of organic substrates, have been examined. Materials science of these systems presents numerous possibilities and is fast evolving. Computational insights have given reasons for their stability and unusual properties. The molecular nature of these materials is unequivocally manifested in a few recent studies such as intercluster reactions forming precise clusters. These systems manifest properties of the core, of the ligand shell, as well as that of the integrated system. They are better described as protected molecules or *aspicules*, where *aspis* means shield and *cules* refers to molecules, implying that they are "shielded molecules". In order to understand their diverse properties, a nomenclature has been introduced with which it is possible to draw their structures with positional labels on paper, with some training. Research in this area is captured here, based on the publications available up to December 2016.

Phenine nanotube (pNT)

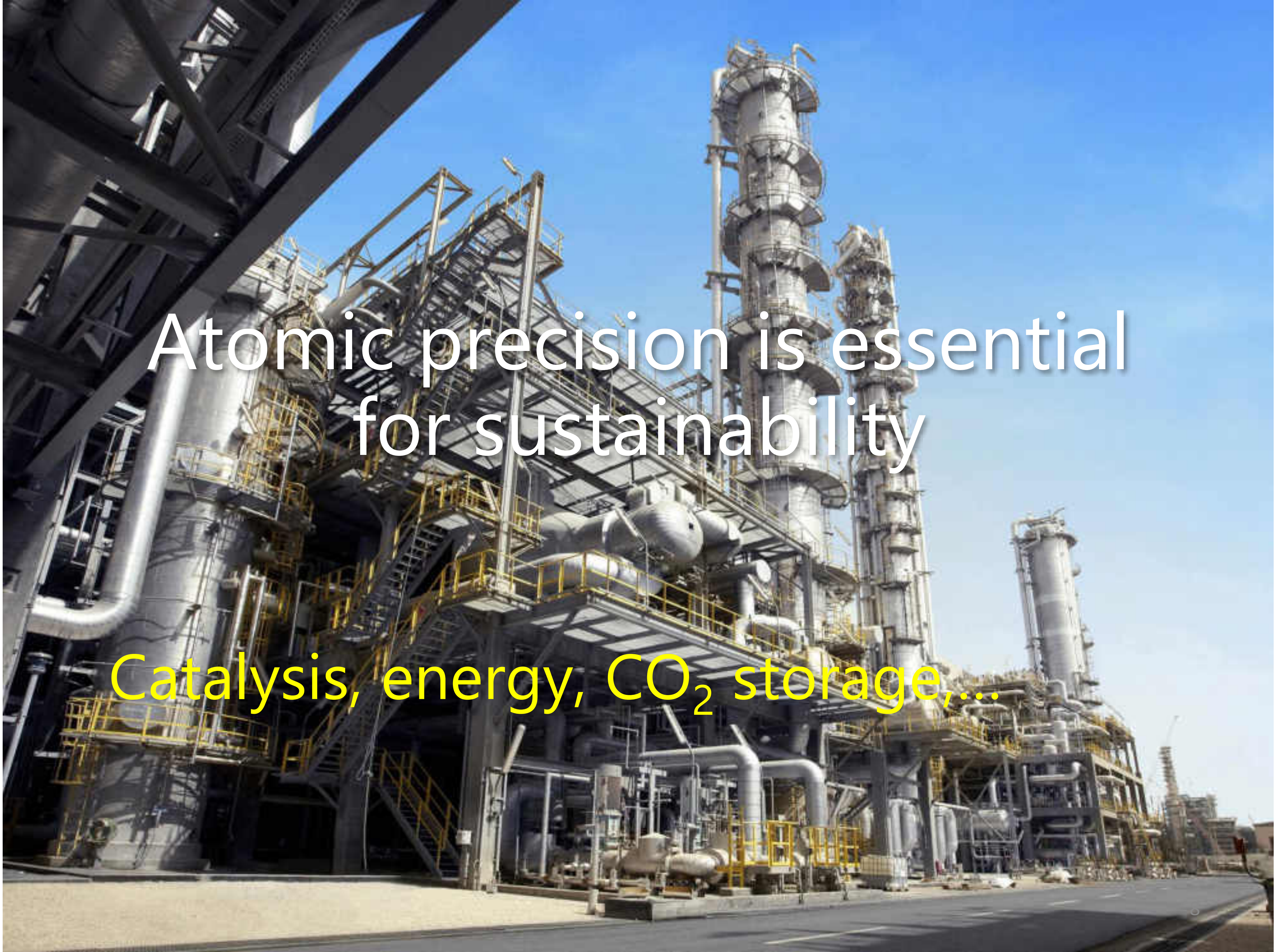




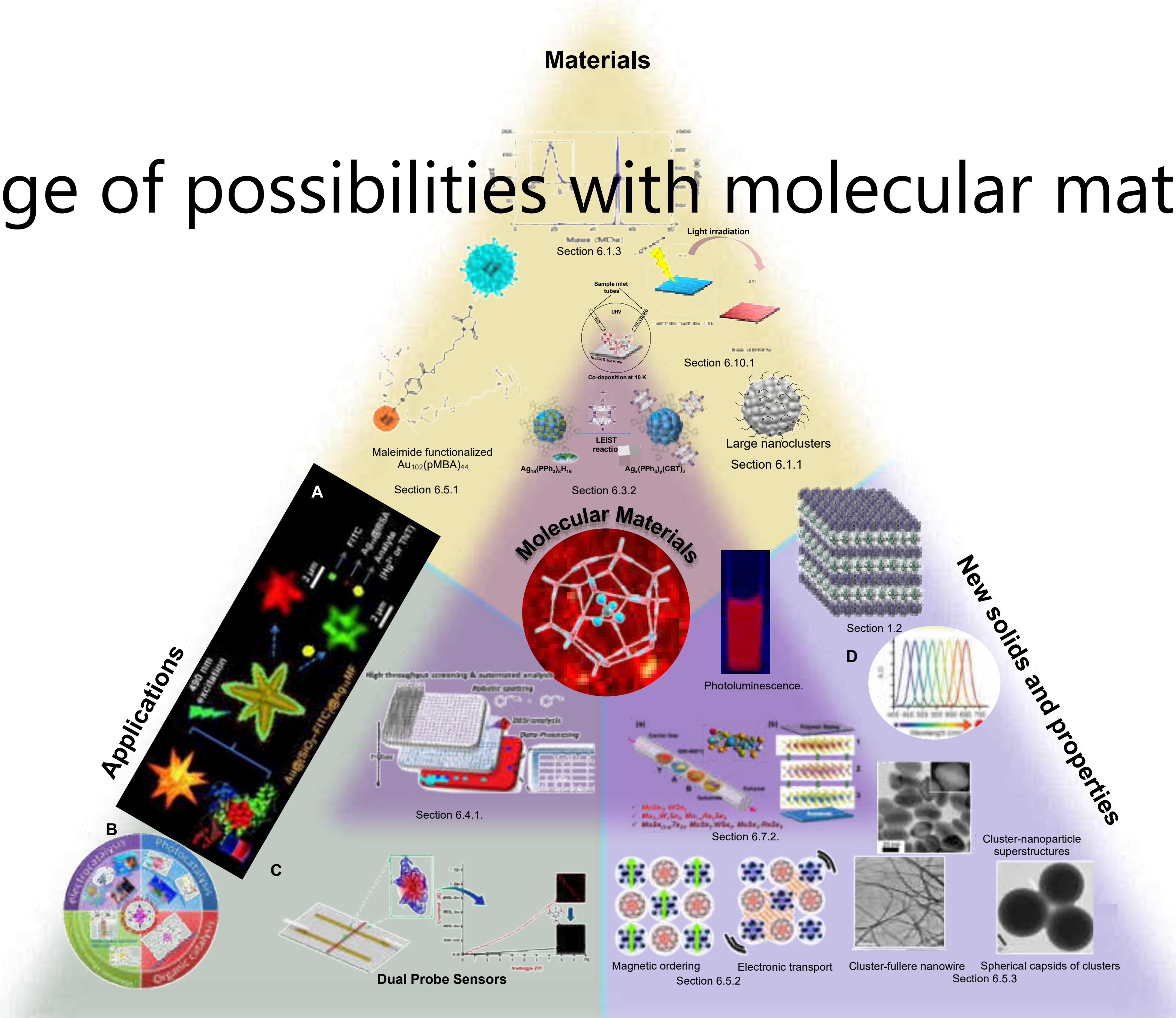


— Yamamoto coupling
— Suzuki-Miyaura coupling
— **Bäurle/Yamago/Isobe coupling**

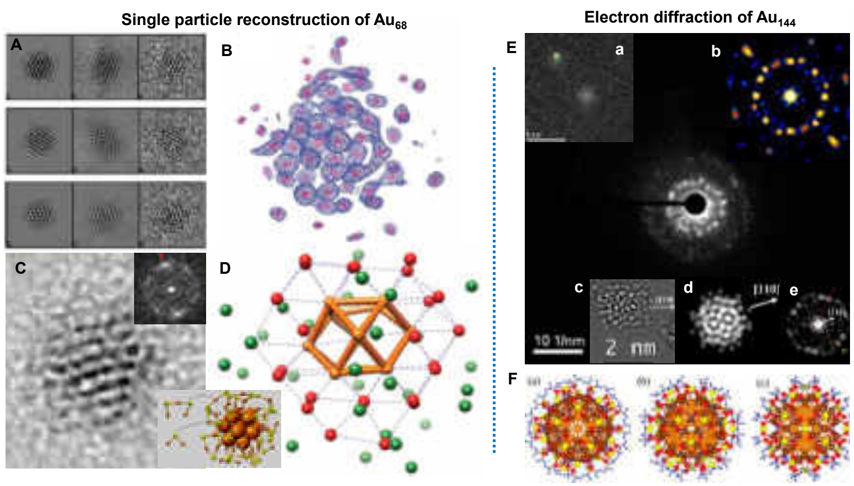
H. Isobe *et al*. *Science* **2019**, *363*, 151


Atomic precision is essential for sustainability
Catalysis, energy, CO_2 storage,...

Range of possibilities with molecular materials

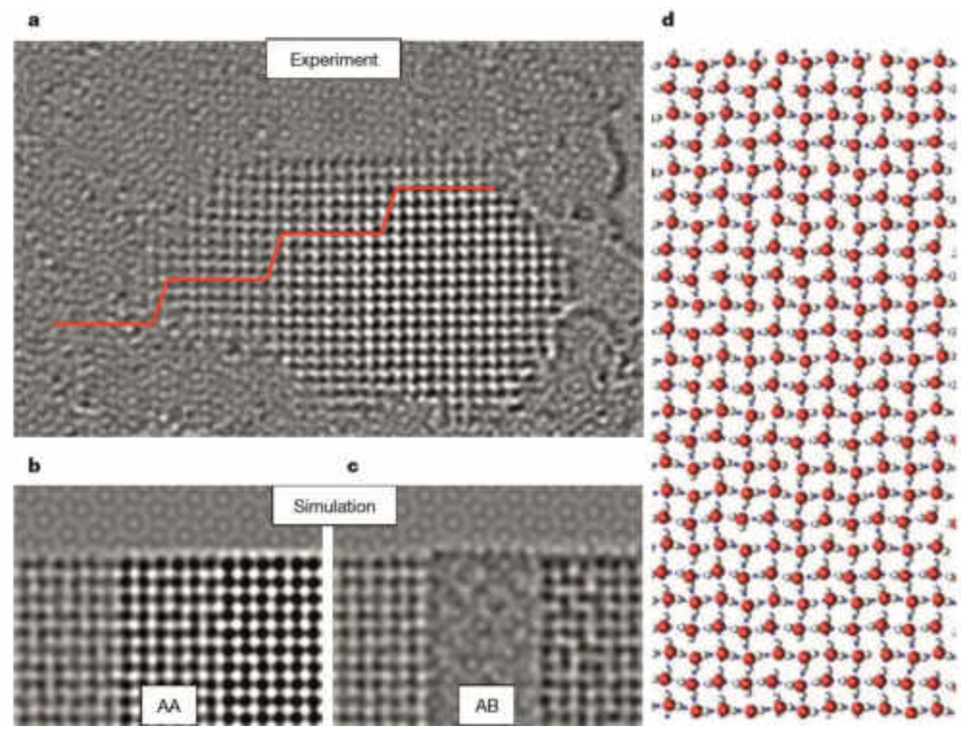


Observing molecular matter at atomic resolution – Advanced tools are essential



Azubel, M.; …… Tsukuda, T.; Häkkinen, H.; Kornberg, R. D., *Science* **2014,** *345* (6199), 909.

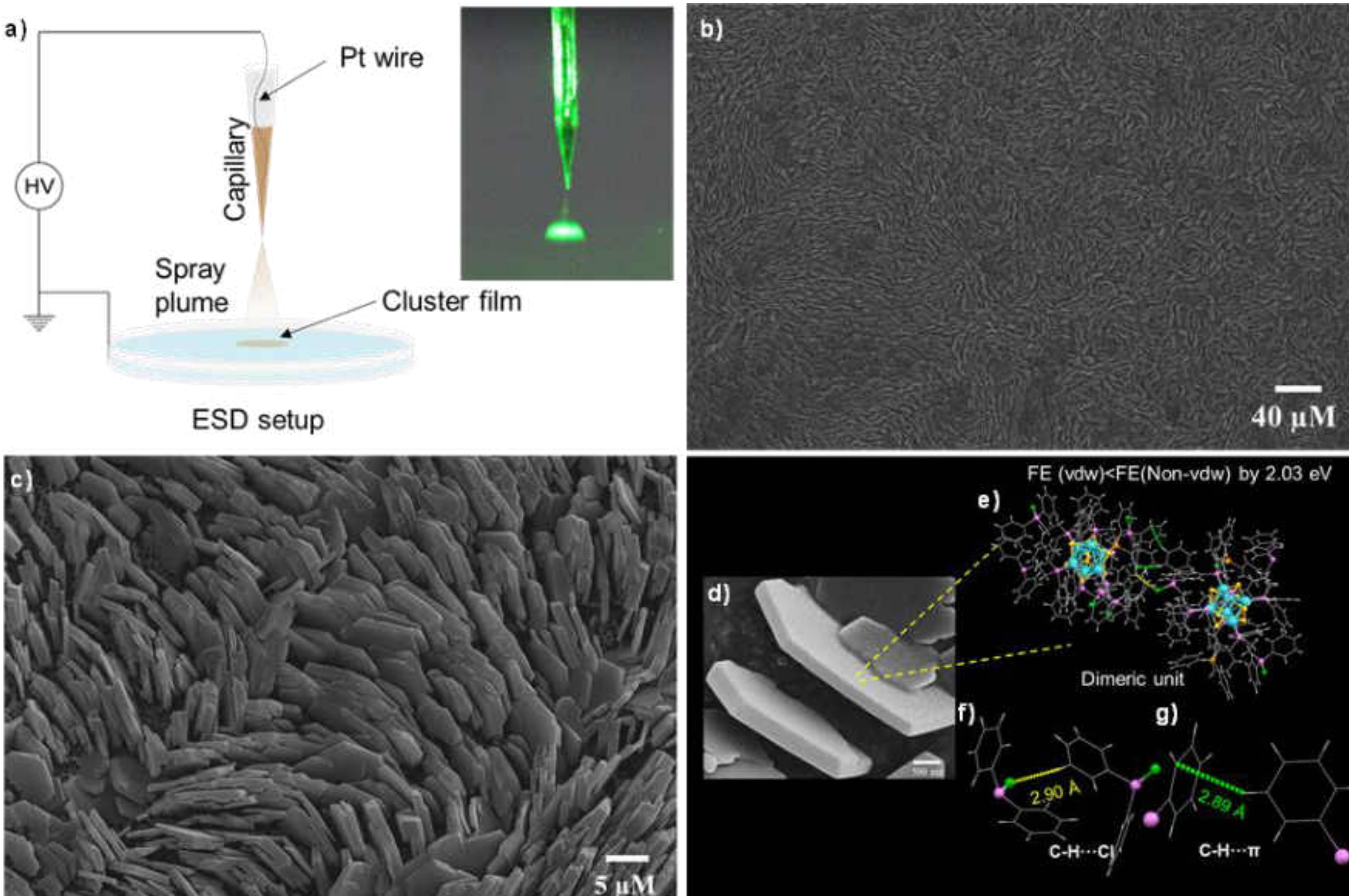
Bahena, D.; ….Whetten, R. L.; Landman, U.; Jose-Yacaman, M., *The Journal of Physical Chemistry Letters* **2013,** *4* (6), 975-981.



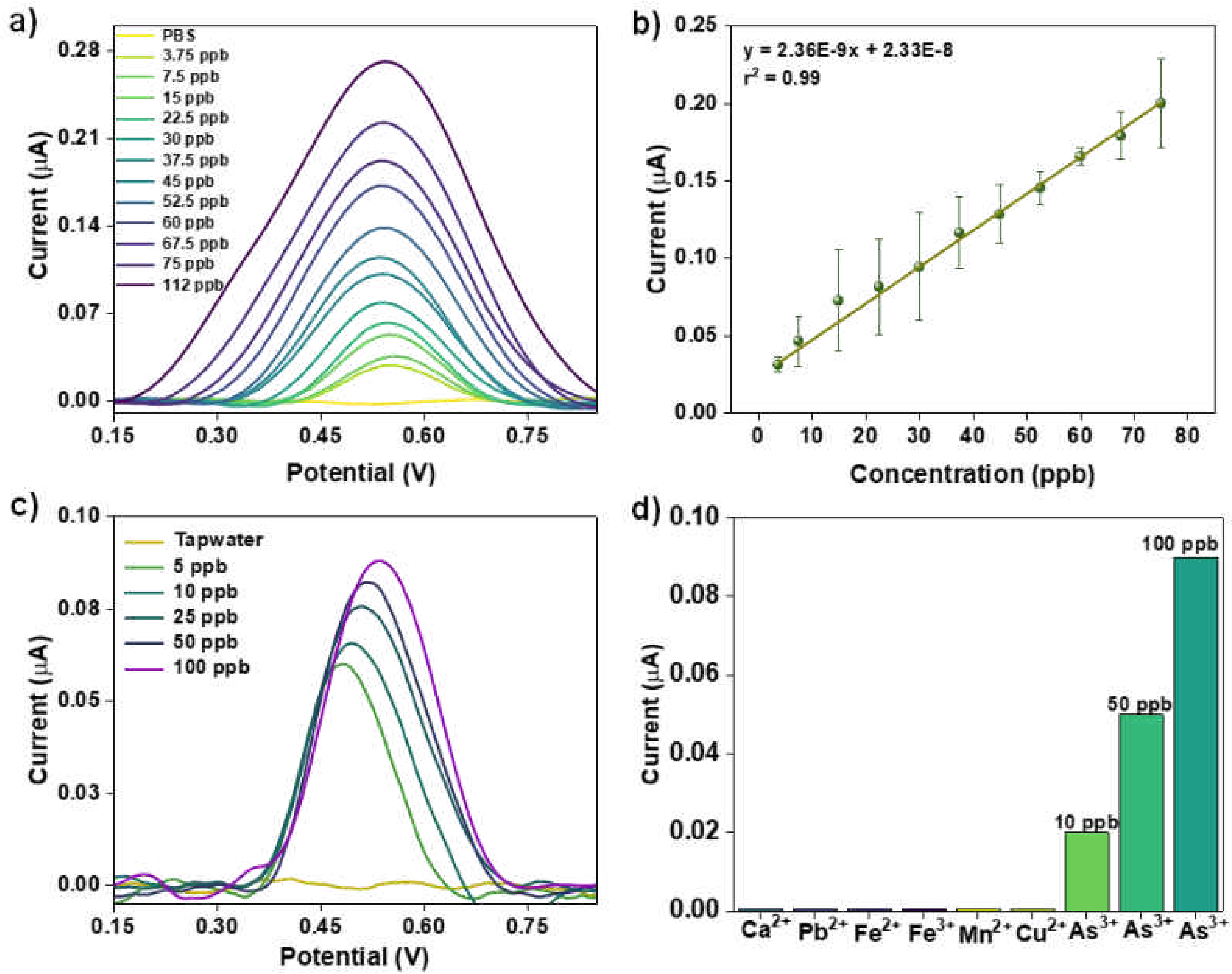
Algara-Siller, G.; Lehtinen, O.; Wang, F. C.; Nair, R. R.; Kaiser, U.; Wu, H. A.; Geim, A. K.; Grigorieva, I. V., Square ice in graphene nanocapillaries. *Nature* **2015,** *519* (7544), 443-445.

Every molecular matter will be understood tomorrow with detailed structure using cryo-EM

New applications – impossible in the past

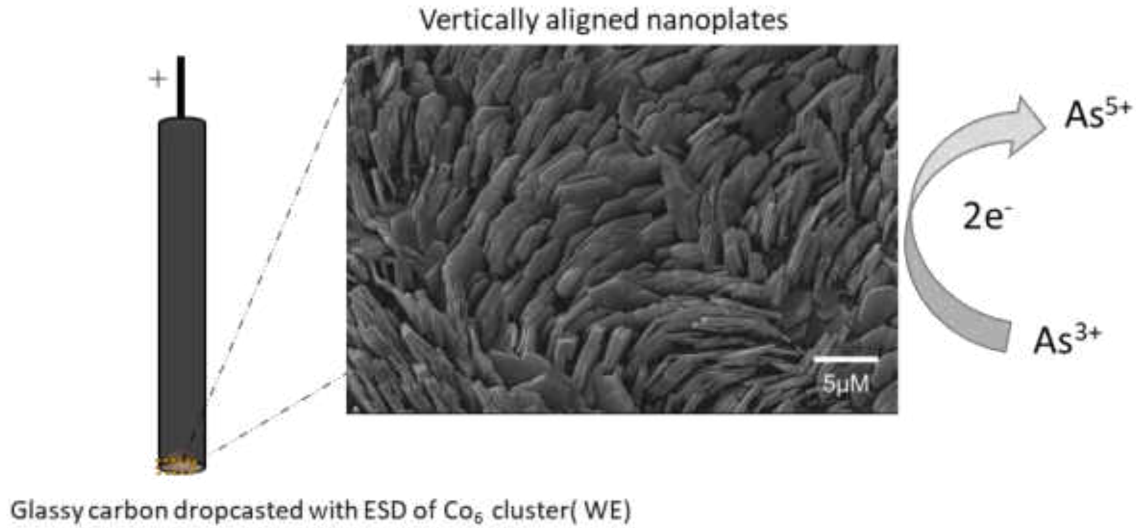


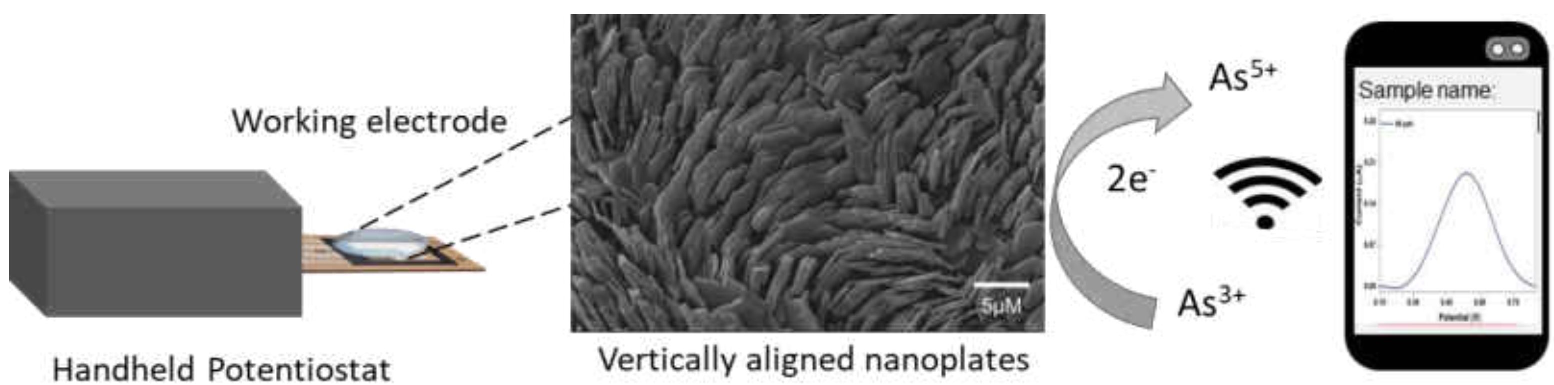
Sensing



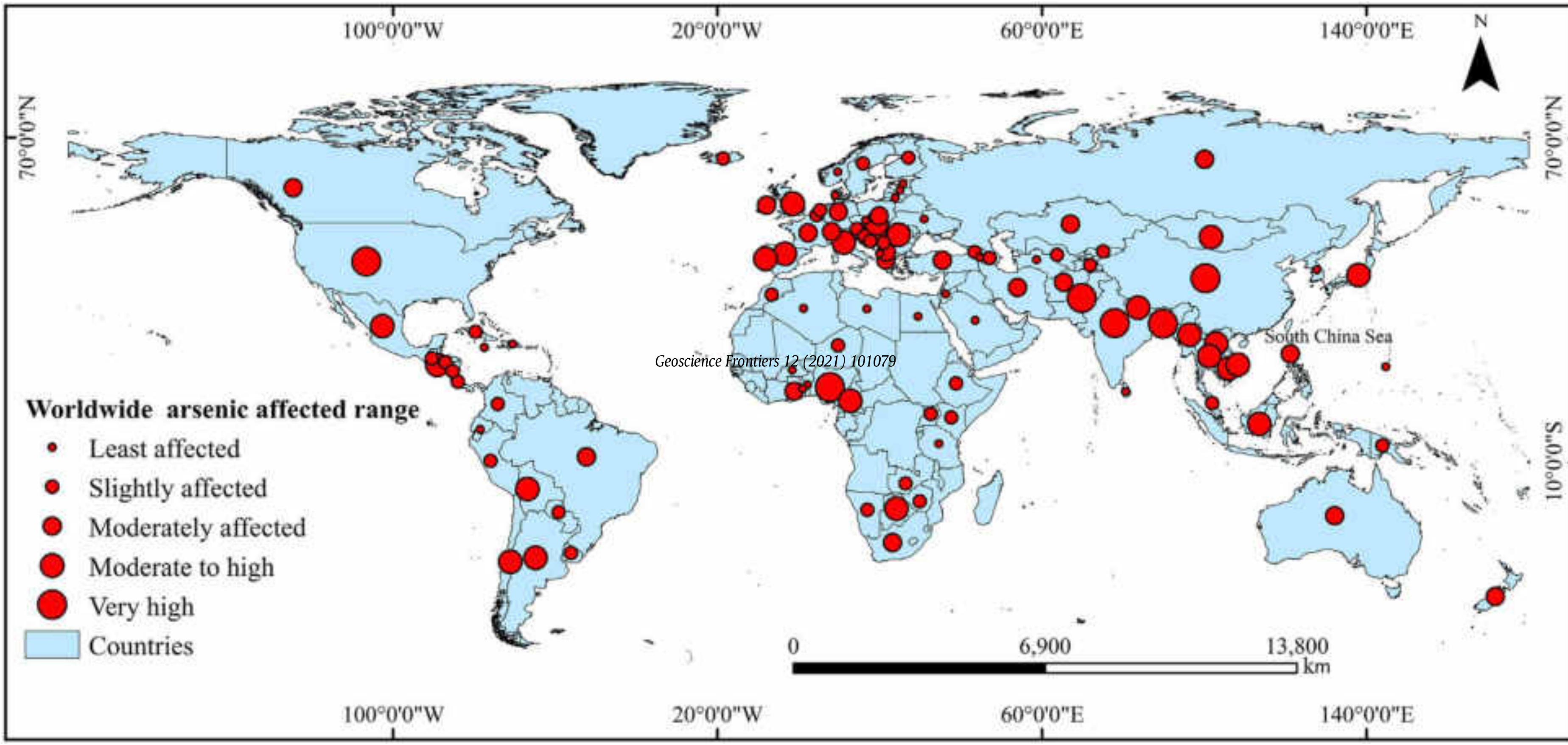
a)
PBS
3.75 ppb
7.5 ppb
15 ppb
22.5 ppb
30 ppb
37.5 ppb
45 ppb
52.5 ppb
60 ppb
67.5 ppb
75 ppb
112 ppb
Current (μA)
Potential (V)
b)
y = 2.36E-9x + 2.33E-8
r^2 = 0.99
Current (μA)
Concentration (ppb)
c)
Tapwater
5 ppb
10 ppb
25 ppb
50 ppb
100 ppb
Current (μA)
Potential (V)
d)
100 ppb
50 ppb
10 ppb
Current (μA)
Ca^{2+} Pb^{2+} Fe^{2+} Fe^{3+} Mn^{2+} Cu^{2+} As^{3+} As^{3+} As^{3+}

A problem on the ground can be solved



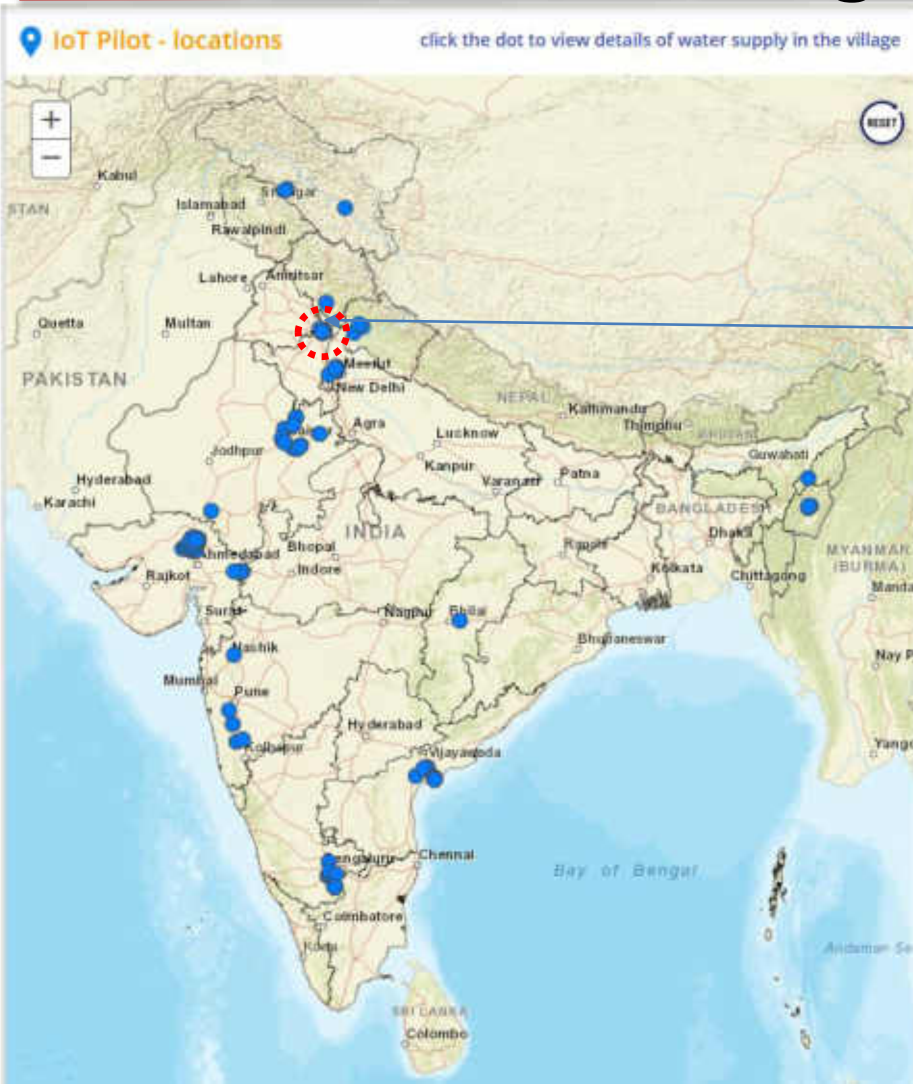


Arsenic poisoning across the world



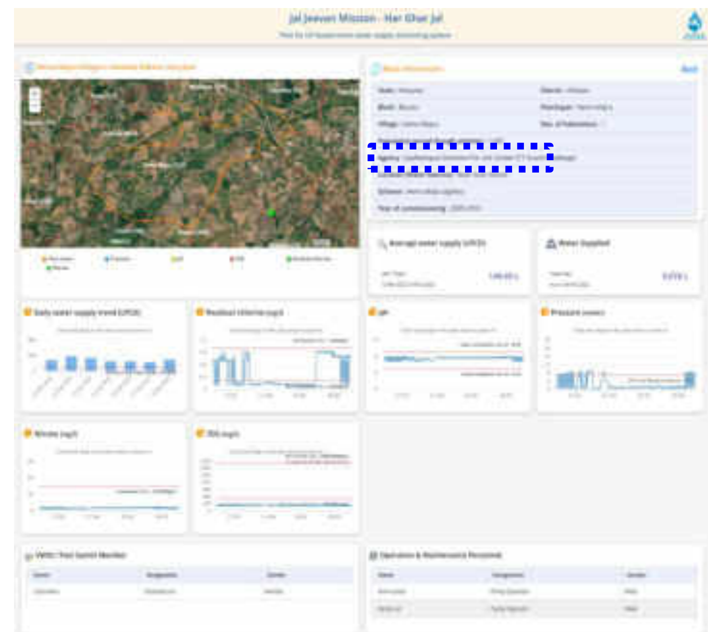
E. Shaji, M. Santosh, K. V. Sarath, Pranav Prakash, V. Deepch and B. V. Divya, Geoscience Frontiers, 12 (2021) 101079.

India's water is being monitored

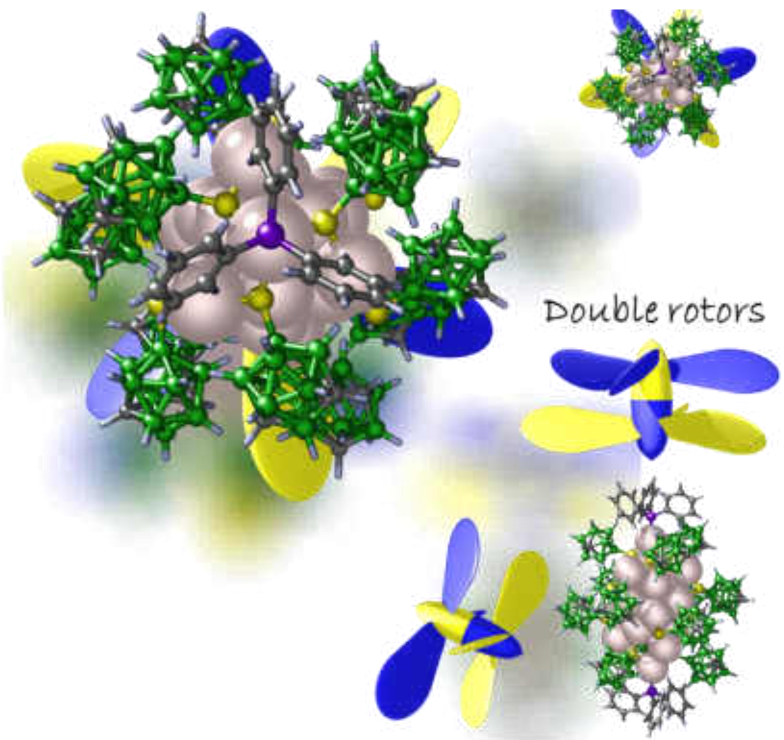


IITM/IISc

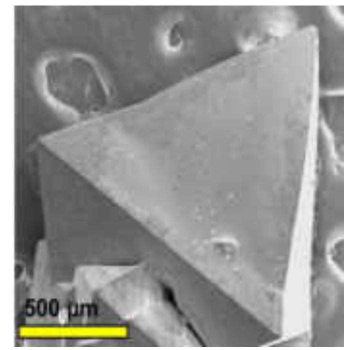
Installations made by four companies

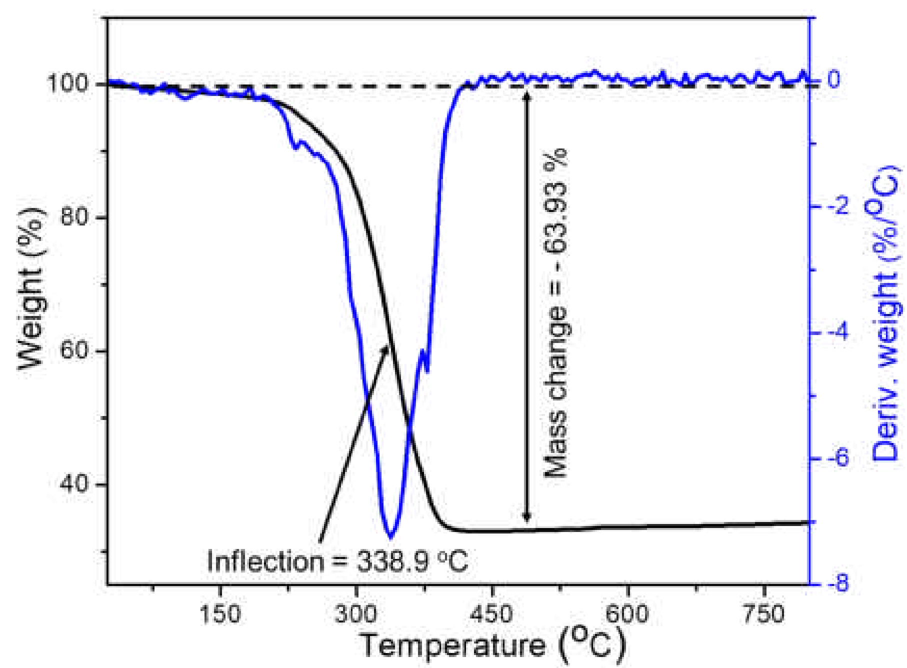


Limitations of atomically precise are addressed – Thermal

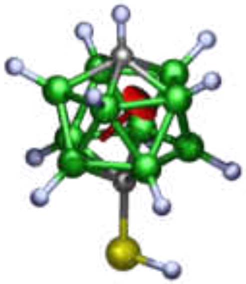


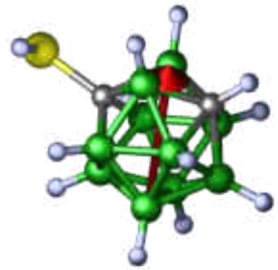
With Tomas Base

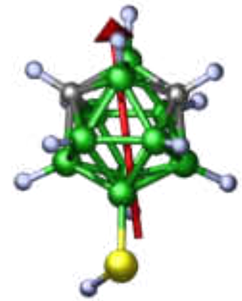


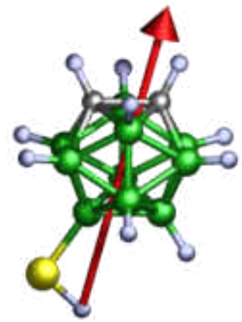


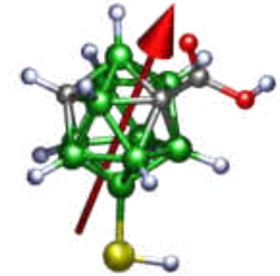
New materials and new properties

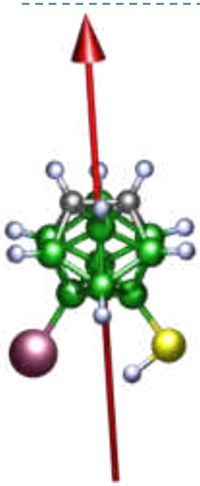

p1-CBT

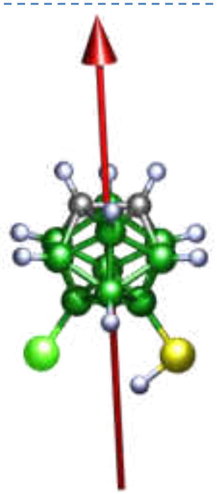

m1-CBT

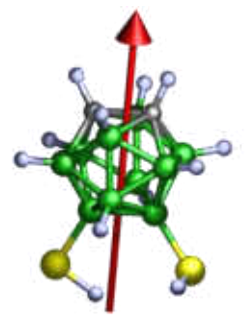

m9-CBT

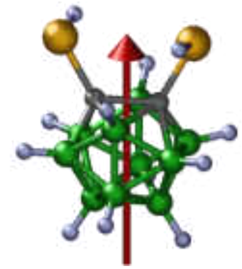

o9-CBT

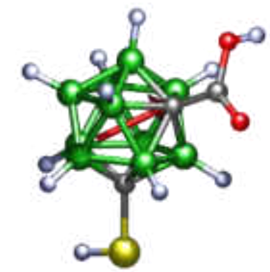

1-COOH-9-SH-1,7-CBT
(M9-COOH)


9-I-12-SH-o1-CBT


9-Cl-12-SH-o1-CBT


9,12-$(HS)_2$-1,2-CBDT


o-1,2-$(SeH)_2$-oCBDT

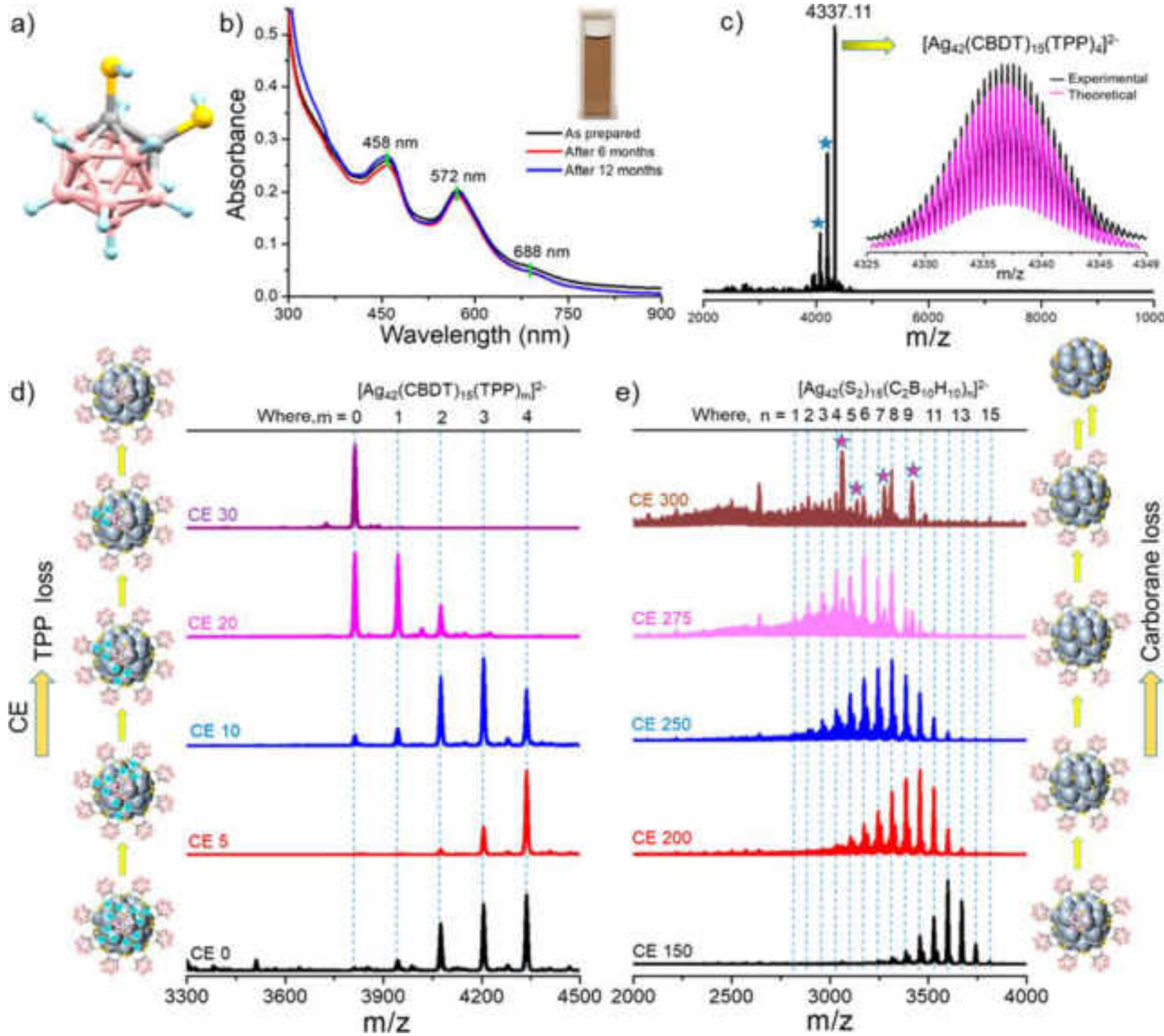

1-COOH-7-SH-1,7-CBT
(M1-COOH)

Global expertise on such ligands

The Czech Academy of Sciences
Institute of Inorganic Chemistry

A glimpse of our collaborative work

Stable cluster materials

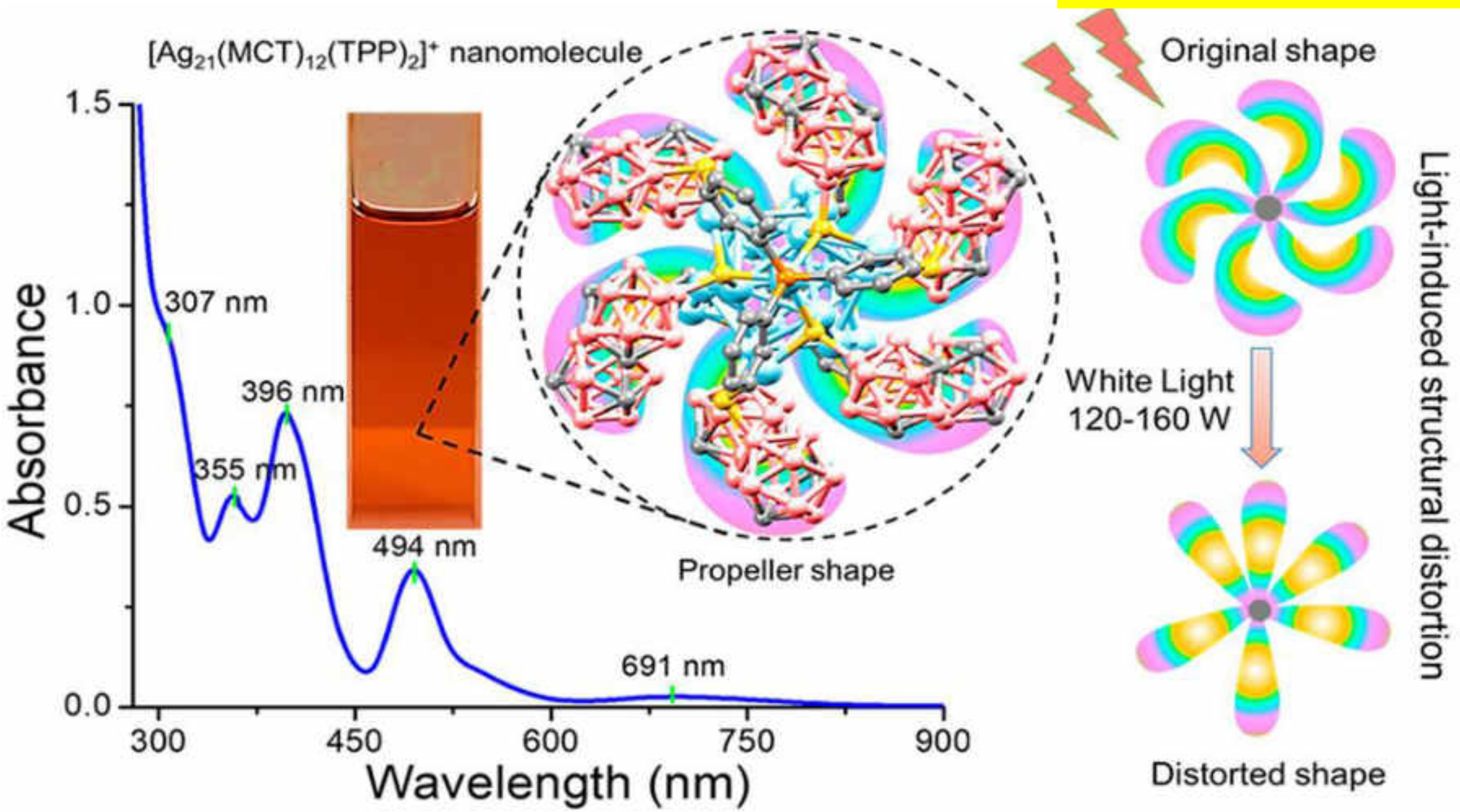


Synthesis and characterization of Ag_{42} NC. (a) Molecular structure of the *ortho*-carborane 1,2-dithiol ligand. (b) Time-dependent UV–vis absorption spectra of Ag_{42} NC in DCM indicating its stability. (c) Full range negative ion-mode ESI-MS spectrum of Ag_{42} NC. Features marked * are due to ligand losses. (d) Systematic losses of four TPP were observed from the peak at m/s 4337.11 with a charge state of 2– up to a collision energy (CE) of 30. (e) Fourteen sequential mass losses of carborane ($C_2B_{10}H_{10}$, M 142) units, along with a few silver sulfide loss peaks (marked as ☆).

Jana, A. et al. *ACS Nano.* **2021,** *15*, 15781-15793

Stable cluster materials

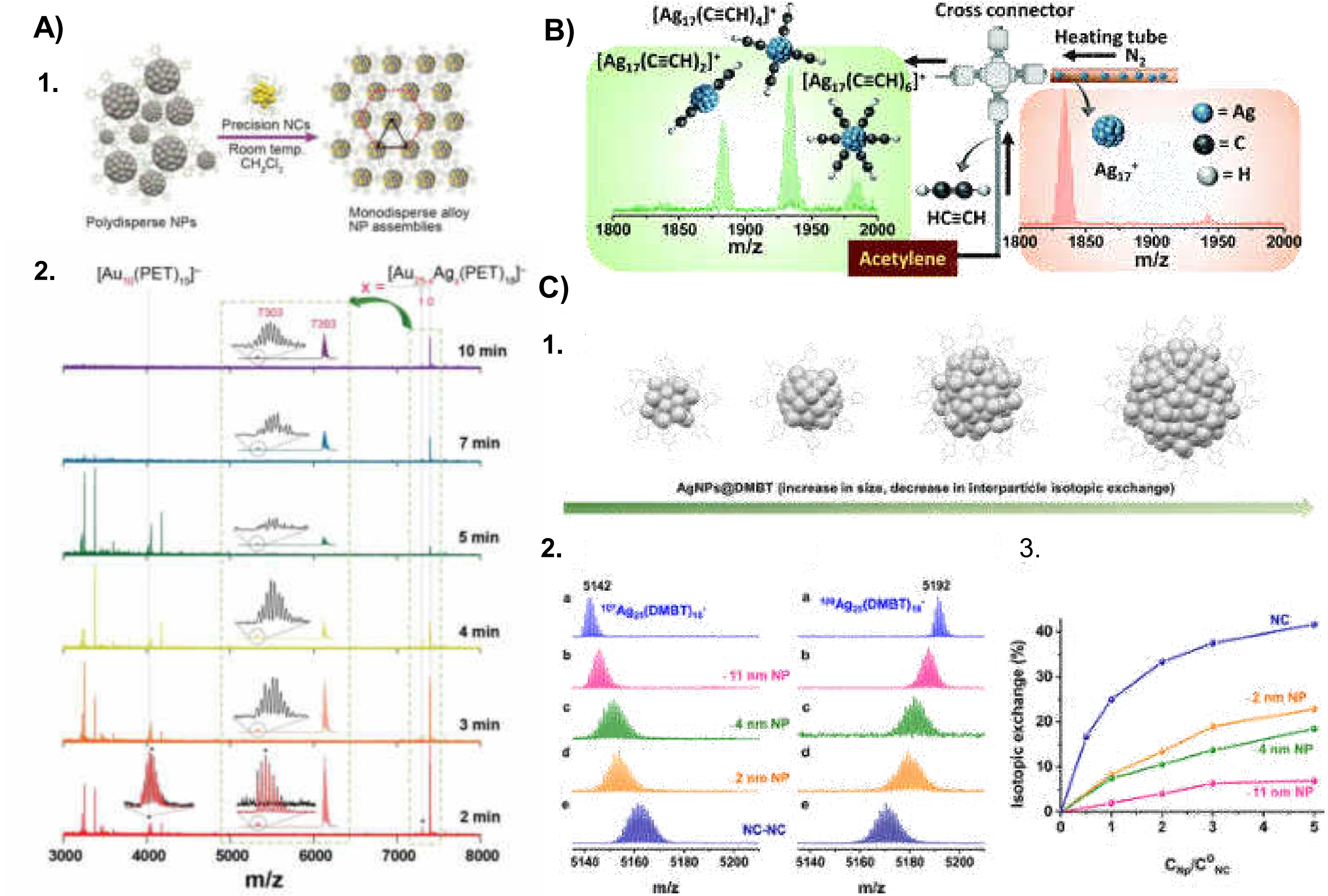
Chiral metals



Propeller-shaped Ag_{21} nanomolecule with six rotary arms made of carboranes.

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

Cluster reactions

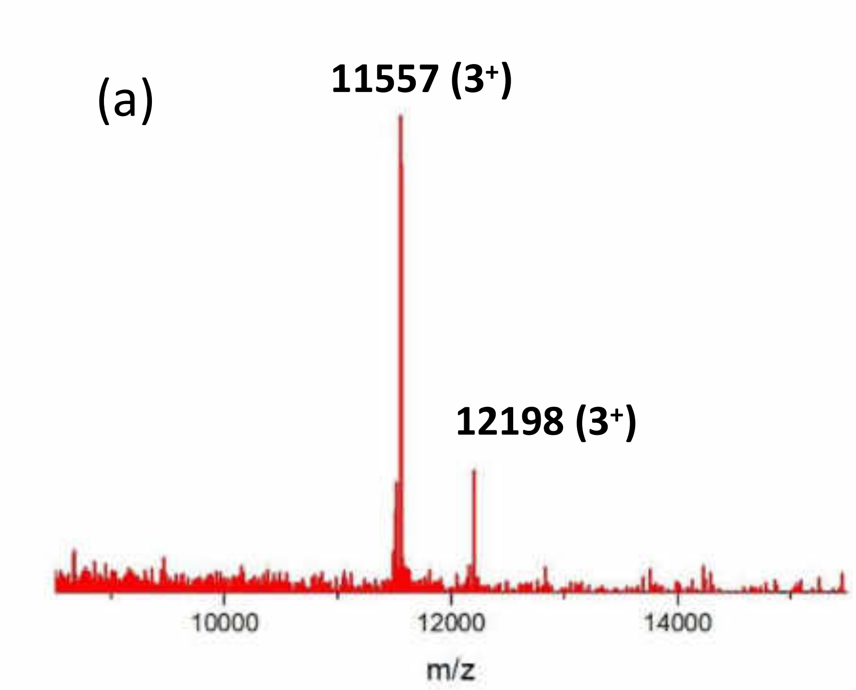


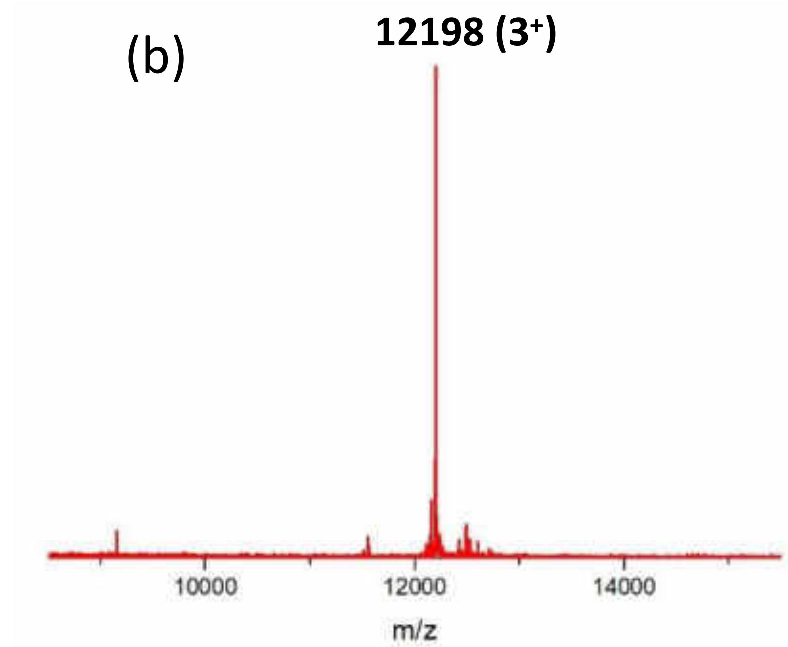
A) 1. Schematic representation of conversion of polydispersed NPs to monodispersed silver NPs. 2. Size-dependent reactivity monitored using ESI MS, keeping the reaction and mass spectrometric conditions constant. B) Schematic representation of formation of acetylide protected silver clusters in gas phase. C) 1. Schematic showing NPs of increasing sizes, 2. ESI MS of (a) parent isotopic NCs, $^{107}Ag_{25}(DMBT)_{18}^-$ and $^{109}Ag_{25}(DMBT)_{18}^-$, respectively, and products formed by the reaction of the isotopic NCs with (b) ~11, (c) ~4, (d) ~2 nm AgNPs, and (e) NC (made from naturally abundant Ag). (3.) Plot showing the extent of isotopic exchange (%) as a function of the ratio of the concentration of NPs (CNP) and concentration of isotopic NCs (CNCo) used in the NC–NP and NC–NC reactions.

Bose, P. et al. *Nanoscale* **2020, 12**, 22116-22128, Chakraborty, P. et al. *J. Phys. Chem. C* **2021**, 25(29), 16110-16117

Jash, M. et al. *Chem. Commun*. **2020**, 56, 15623-15626

Clusters beyond 100 atoms core

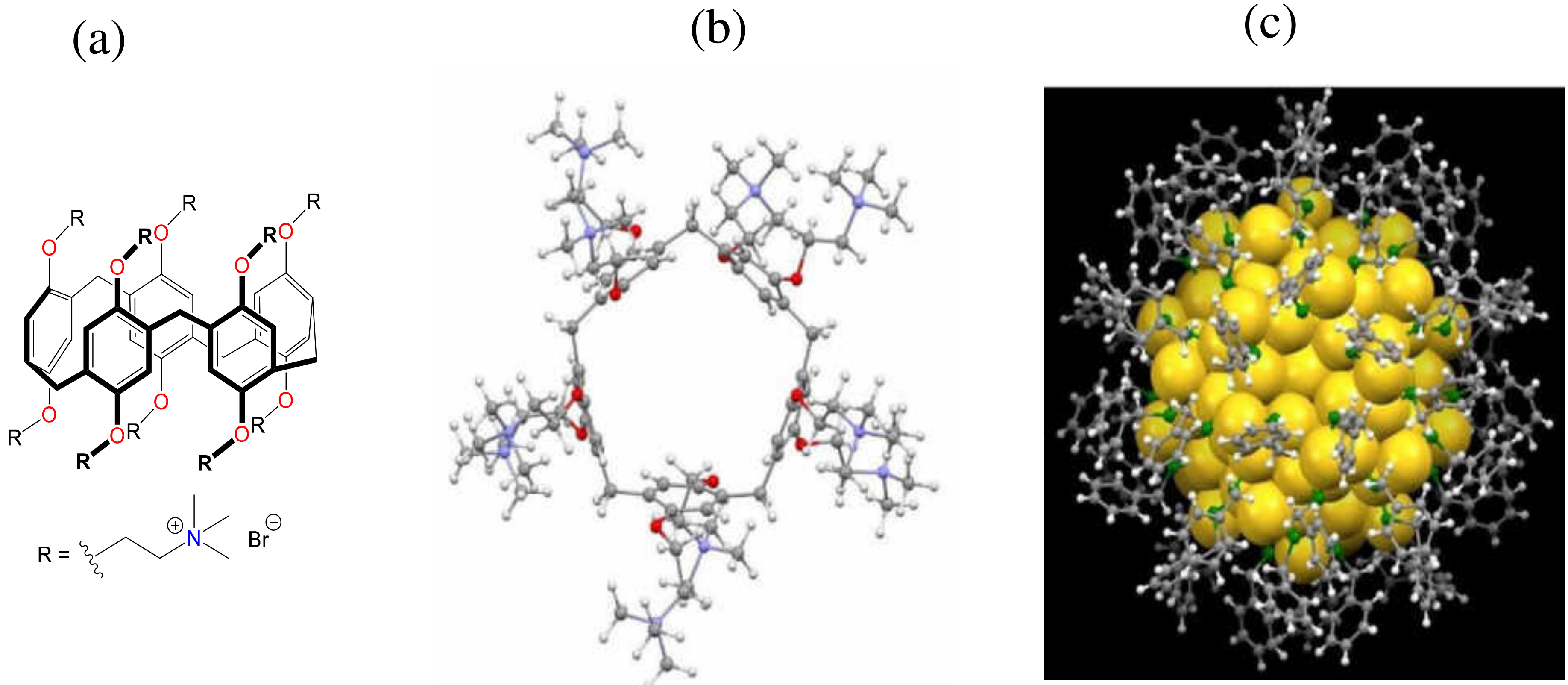




(a) Mass spectrum of a newly synthesised mixture of clusters composed of $Au_{144}(PET)_{60}$ and $Au_{137}(PET)_{56}$. The clusters have been separated with thin later chromatography.; (b) Mass spectrum of the separated $Au_{144}(PET)_{60}$ cluster.

Examples of science proposed

Enhanced ionization of plasmonic nanoparticles of >10000 atoms for mass spectrometric analysis



(a) Structure of Pillar-5-arene ligand; (b) Top view of Pillar-5-arene crystal structure; (c) Crystal structure of $Au_{144}(PET)_{60}$ nanocluster. R group is cationized, which will make the cluster as a whole charged.