

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)

Horst Hahn^{\$,#,%} (KIT, Germany)

Hannu Häkkinen[%] (University in
Jyväskylä, Finland)

Manfred Kappes^{\$,#,%} (KIT, Germany)

Rajnish Kumar[%] (IIT Madras, India)

Praveen Linga^{#,%} (NUS, Singapore)

Shobhana Narasimhan (JNCASR, India)

Robin Ras[%] (Aalto University, Finland)

Kunnikuruva Sooraj (IIT Madras, Chennai)

Thangavelu Palaniselvam (IIT Madras, India)

Tiju Thomas[%] (IIT Madras, India)

Tatsuya Tsukuda[%] (Univ. of Tokyo, Japan)

Umesh Waghmare[%] (JNCASR, India)

Robert L. Whetten[%] (NAU, USA)

Jianping Xie (NUS, Singapore)

Chaitanya Sharma Yamijala (IIT Madras, India)

Vimal Edachery (IIT Madras, India)

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

pCOE Lecture series on Molecular Materials and Functions

pCOE on Molecular Materials and Functions Lecture Series

Starts on February 11, 2022

Click on the photo to reach the website of the speakers.

 Prof. T. Pradeep IIT Madras, India November 5, 2022	 Prof. Takashi Nishikubo The University of Tokyo, Japan February 25, 2022	 Prof. Shengping Wu NUS, Singapore March 26, 2022	
 Prof. David S. Hughes HCCS, India July 25, 2022	 Prof. Graham Ojeda Portland University, USA June 14, 2022	 Prof. Prabodh M. Sanyal IISc Bangalore, India May 27, 2022	 Prof. Robert Wharmby Stanford University, USA April 28, 2022
 Prof. Madhavan Narayanan IIT Madras, India August 26, 2022	 Prof. Steve Hahn KIT, Germany September 22, 2022	 Prof. Praveen Singh IIT Madras, India October 26, 2022	 Prof. Harish Hachhikar University of Illinois at Chicago, USA November 10, 2022
 Prof. Rishi Rao IIT Bombay, India March 24, 2022	 Prof. Anandharaj Govind IIT Madras, India February 24, 2022	 Prof. Manfred Fugere KIT, Germany January 27, 2022	 Prof. Ravi Kumar IIT Madras, India February 26, 2022
 Prof. Pabitra Ghosh IIT Madras, India April 24, 2022	 Prof. Suresh Babu The College of William & Mary, USA May 26, 2022	Platform: 	

Platform:

(Click the icon to join the meeting)
06:30 PM to 07:30 PM
(IST)

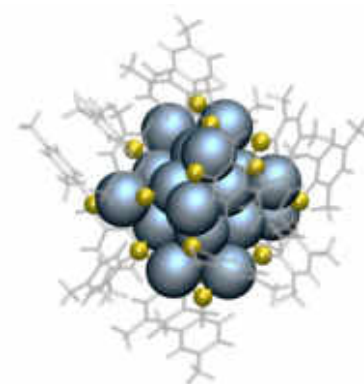
 Lecturer on "Molecular Materials and Functions" Lecture 1 12-02-2022 06:30 PM to 07:30 PM Zoom	 Lecturer on "Molecular Materials and Functions" Lecture 2 21-02-2022 06:30 PM to 07:30 PM Zoom	 Lecturer on "Molecular Materials and Functions" Lecture 3 28-02-2022 06:30 PM to 07:30 PM Zoom	 Lecturer on "Molecular Materials and Functions" Lecture 4 07-03-2022 06:30 PM to 07:30 PM Zoom	 Lecturer on "Molecular Materials and Functions" Lecture 5 14-03-2022 06:30 PM to 07:30 PM Zoom
---	---	--	---	---

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



ACS
Chemistry for Life®

PERIODIC TABLE OF



GROUP																							
1																		2					
PERIOD	1	H Hydrogen 1.008																	He Helium 4.003				
	2	Li Lithium 6.94	Be Beryllium 9.012															B Boron 10.81	C Carbon 12.01	N Nitrogen 14.01	O Oxygen 16.00	F Fluorine 19.00	Ne Neon 20.18
	3	Na Sodium 22.99	Mg Magnesium 24.31															Al Aluminium 26.98	Si Silicon 28.09	P Phosphorus 30.97	S Sulfur 32.06	Cl Chlorine 35.45	Ar Argon 39.95
	4	K Potassium 39.10	Ca Calcium 40.08	Sc Scandium 44.96	Ti Titanium 47.88	V Vanadium 50.94	Cr Chromium 52.00	Mn Manganese 54.94	Fe Iron 55.85	Co Cobalt 58.93	Ni Nickel 58.69	Cu Copper 63.55	Zn Zinc 65.39	Ga Gallium 69.72	Ge Germanium 72.64	As Arsenic 74.92	Se Selenium 78.96	Br Bromine 79.90	Kr Krypton 83.79				
	5	Rb Rubidium 85.47	Sr Strontium 87.62	Y Yttrium 88.91	Zr Zirconium 91.22	Nb Niobium 92.91	Mo Molybdenum 95.96	Tc Technetium (98)	Ru Ruthenium 101.1	Rh Rhodium 102.9	Pd Palladium 106.4	Ag Silver 107.9	Cd Cadmium 112.4	In Indium 114.8	Sn Tin 118.7	Sb Antimony 121.8	Te Tellurium 127.6	I Iodine 126.9	Xe Xenon 131.3				
	6	Cs Caesium 132.9	Ba Barium 137.3	57-71 Lanthanides	Hf Hafnium 178.5	Ta Tantalum 180.9	W Tungsten 183.9	Re Rhenium 186.2	Os Osmium 190.2	Ir Iridium 192.2	Pt Platinum 195.1	Au Gold 197.0	Hg Mercury 200.5	Tl Thallium 204.38	Pb Lead 207.2	Bi Bismuth 209.0	Po Polonium (209)	At Astatine (210)	Rn Radon (222)				
	7	Fr Francium (223)	Ra Radium (226)	89-103 Actinides	Rf Rutherfordium (261)	Db Dubnium (268)	Sg Seaborgium (271)	Bh Bohrium (270)	Hs Hassium (277)	Mt Meitnerium (276)	Ds Darmstadtium (281)	Rg Roentgenium (280)	Cn Copernicium (285)	Nh Nihonium (284)	Fl Flerovium (289)	Mc Moscovium (288)	Lv Livermorium (293)	Ts Tennessine (294)	Og Oganesson (294)				

Alkali Metals

Alkaline Earth Metals

Transition Metals

Other Metals

Metalloids

Non-metals

Halogens

Noble Gases

Lanthanides

Actinides

78

Pt

Platinum

195.1

Atomic Number

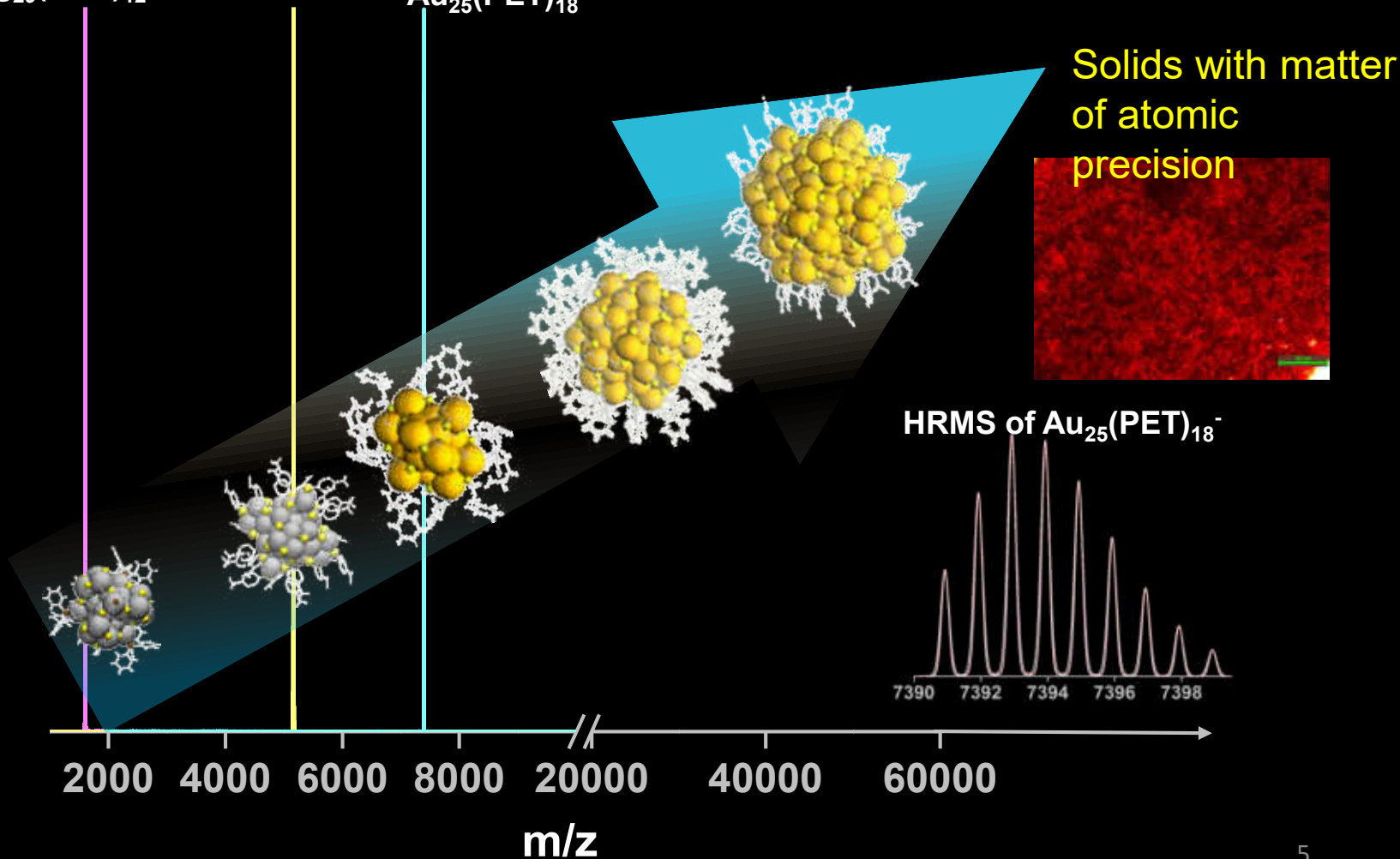
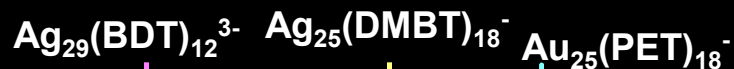
Symbol

Name

Average Atomic Mass

57 La Lanthanum 138.9	58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (145)	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
89 Ac Actinium (227)	90 Th Thorium 232.0	91 Pa Protactinium 231.0	92 U Uranium 238.0	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

Origin of metallicity - Molecular metals, magnets, applications,



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

Indranath Chakraborty[†] and Thalappil Pradeep^{*†}

Scopus 1341 citations

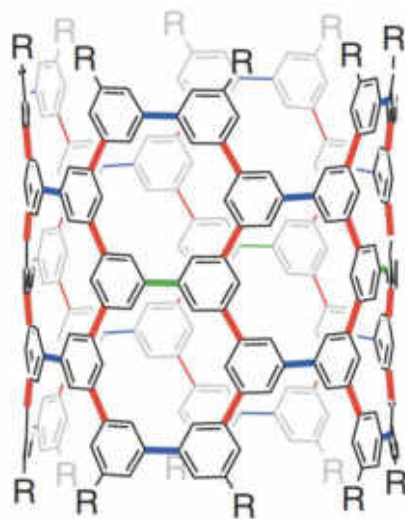
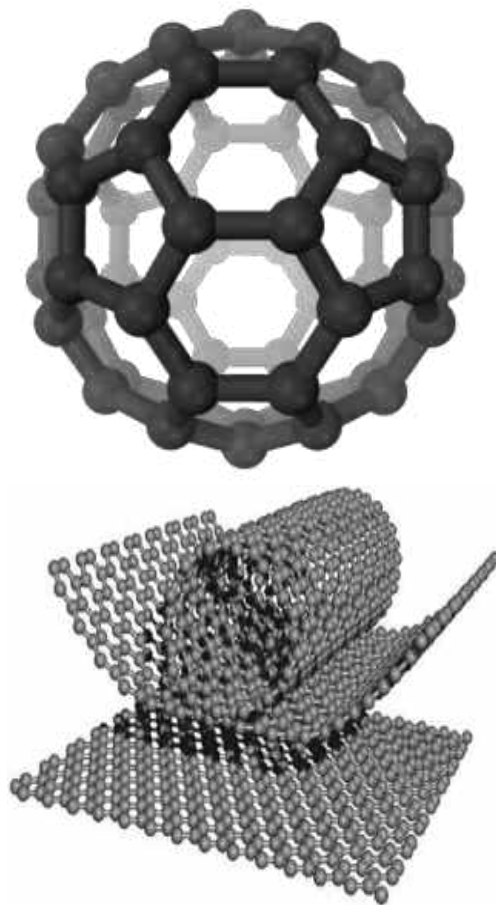
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

S Supporting Information

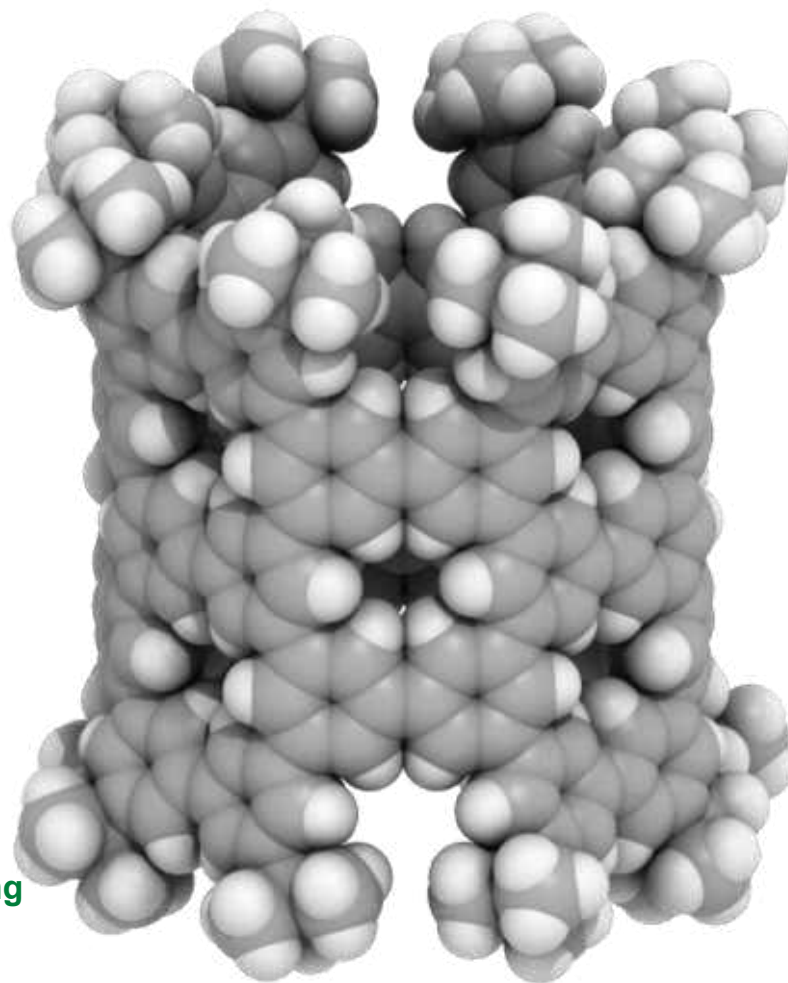
ABSTRACT: Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$, and $\text{Au}_{102}(\text{SR})_{44}$ as well as $\text{Ag}_{25}(\text{SR})_{18}$, $\text{Ag}_{29}(\text{S}_2\text{R})_{12}$, and $\text{Ag}_{44}(\text{SR})_{30}$ (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.

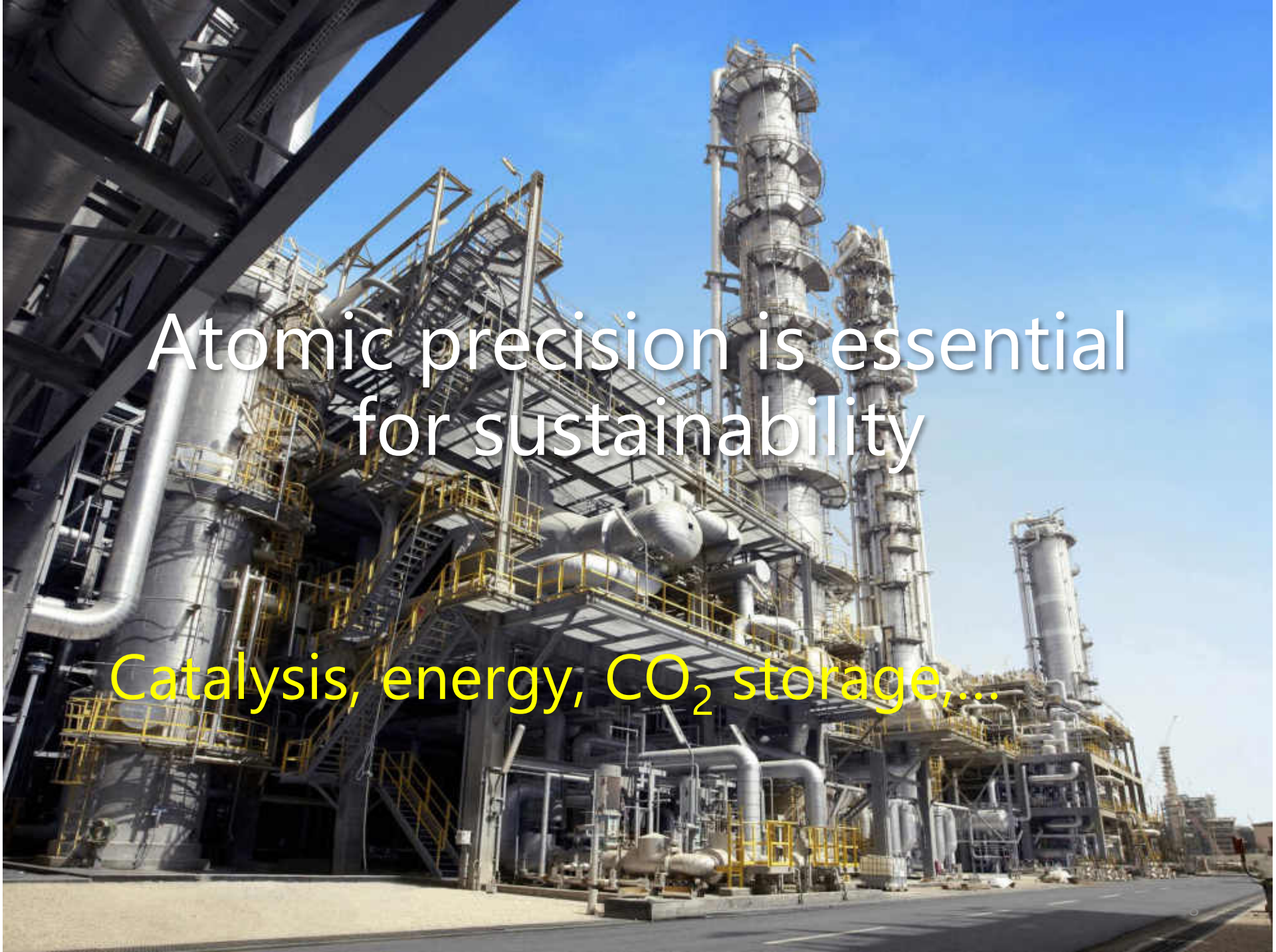


Phenine nanotube (pNT)



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



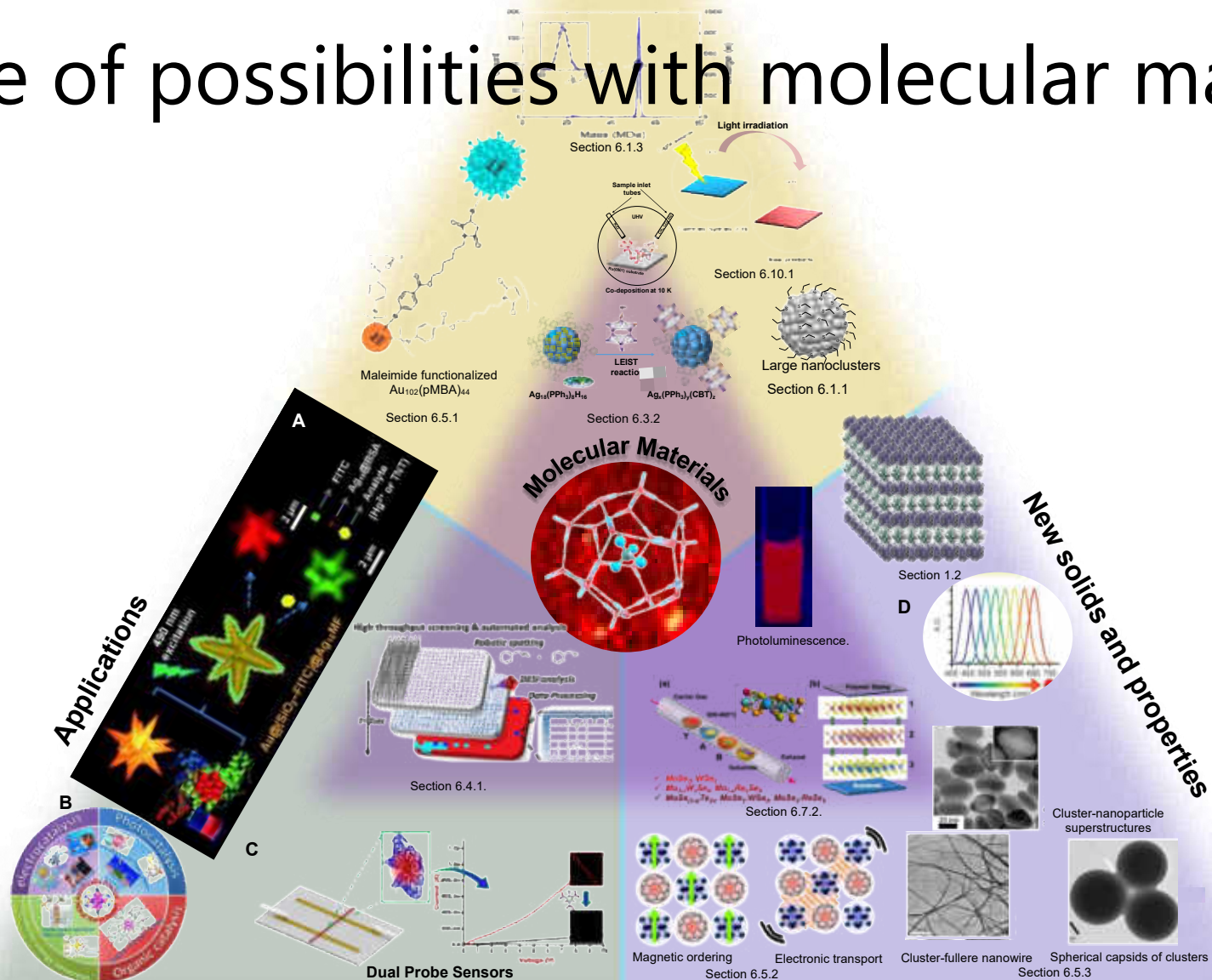
A photograph of a large industrial facility, likely a refinery or chemical plant. The image shows several tall, cylindrical distillation columns with multiple trays and ladders. A complex network of pipes, valves, and structural steel supports the equipment. Yellow safety railings are visible on the platforms. The sky is clear and blue. The overall scene conveys a sense of large-scale industrial operations.

Atomic precision is essential
for sustainability

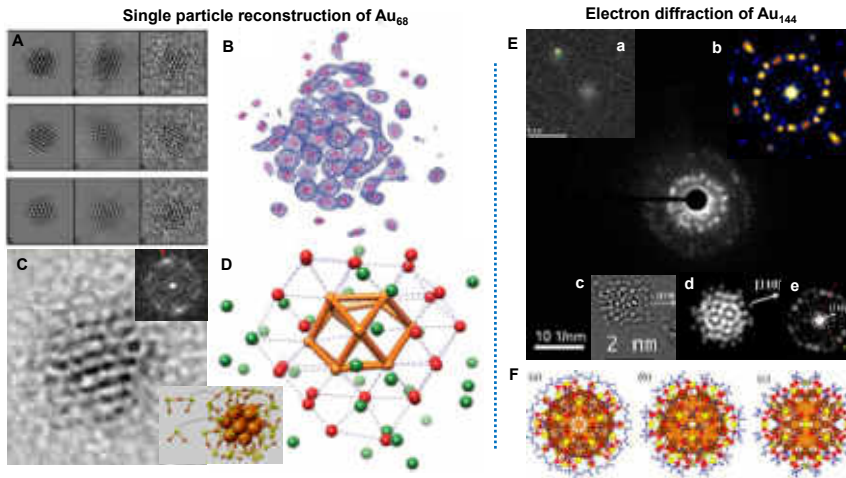
Catalysis, energy, CO₂ storage,...

Materials

Range of possibilities with molecular materials

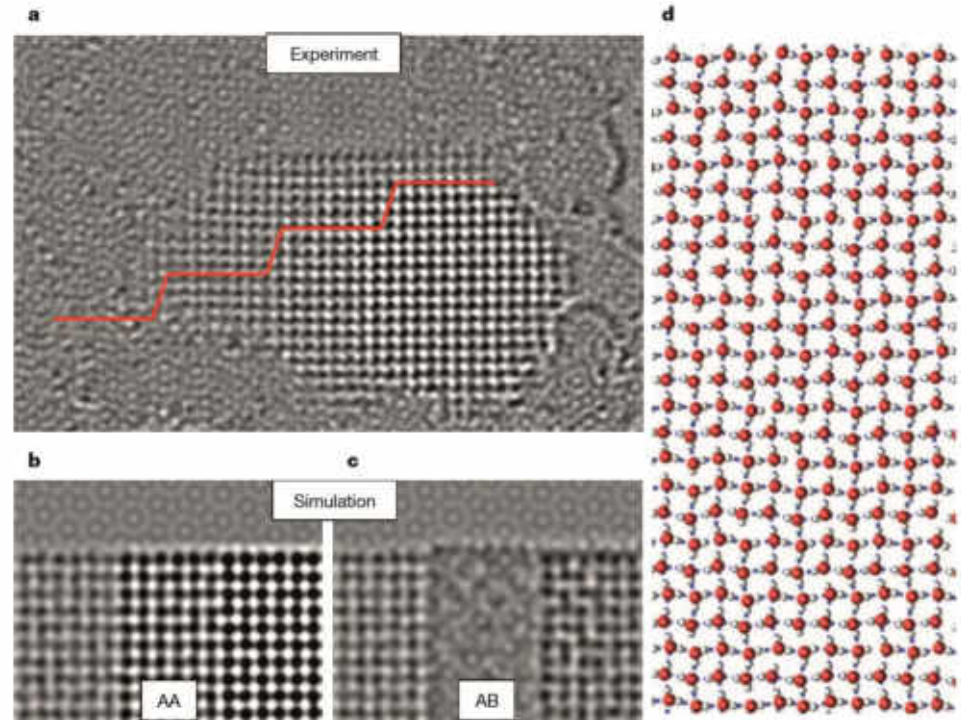


Observing molecular matter at atomic resolution – Advanced tools are essential



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

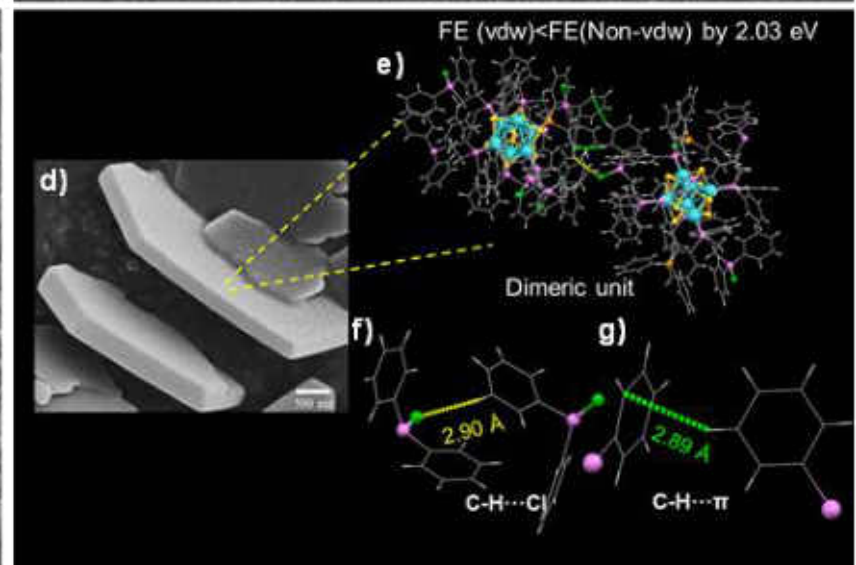
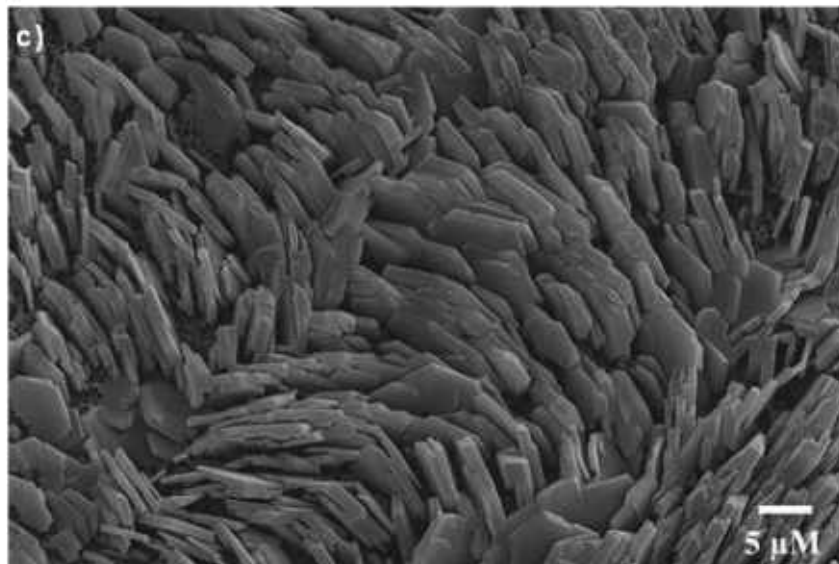
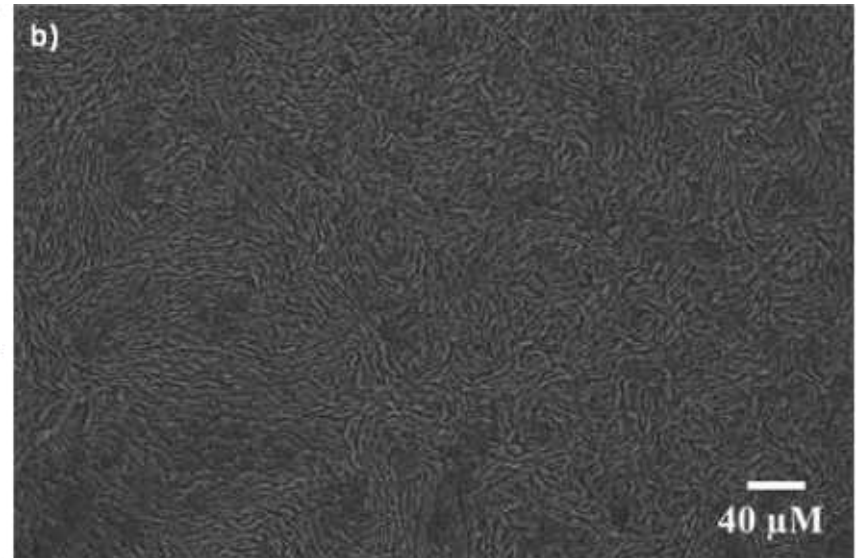
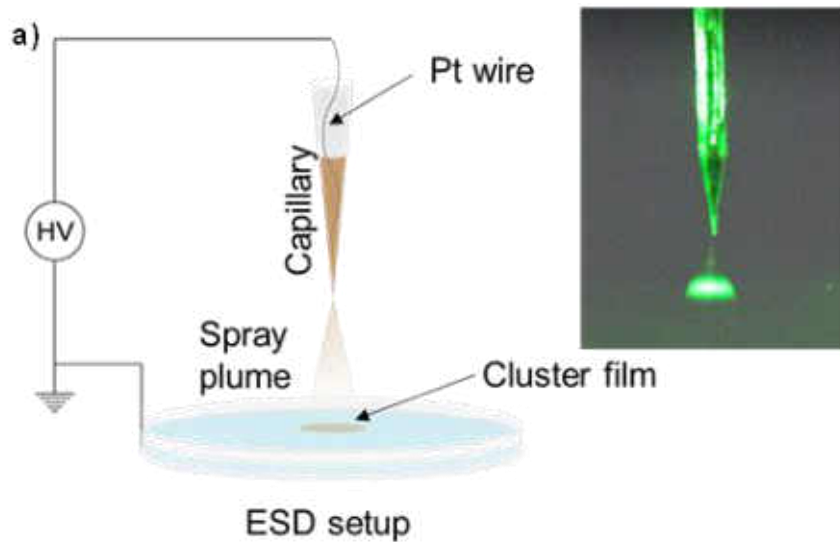
Bahena, D.;Whetten, R. L.; Landman, U.; Jose-Yacamán, M., *The Journal of Physical Chemistry Letters* **2013**, 4 (6), 975-981.



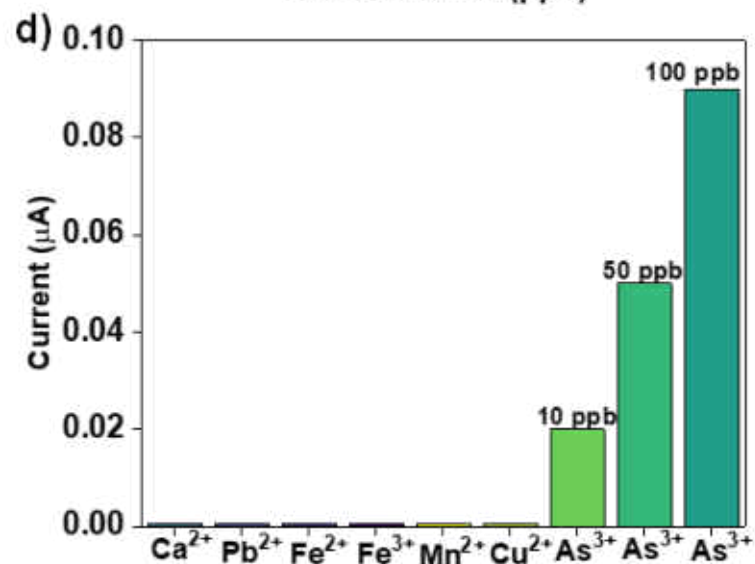
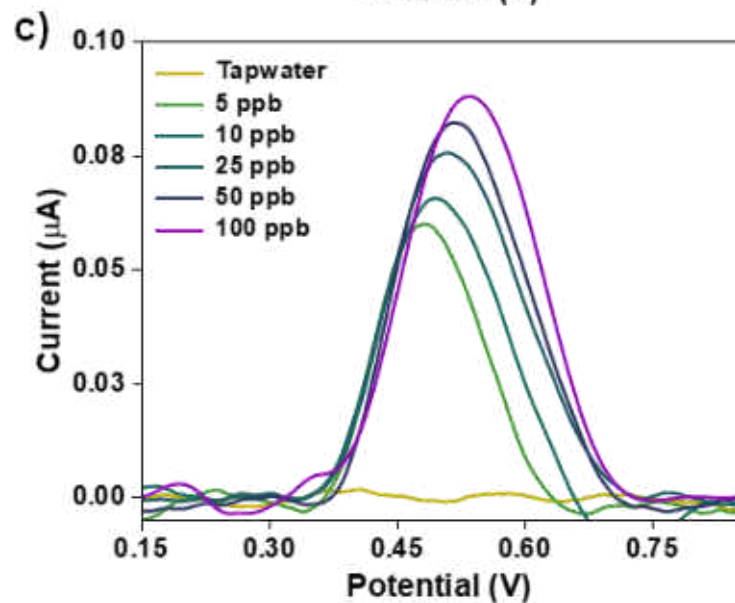
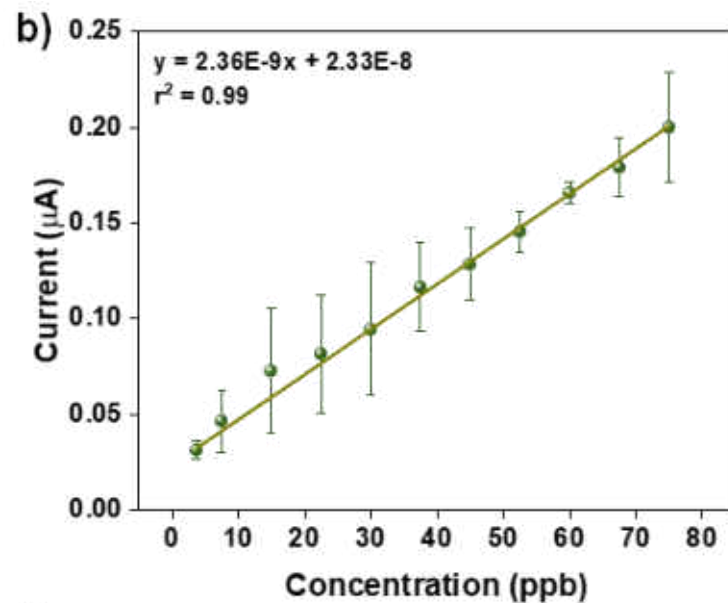
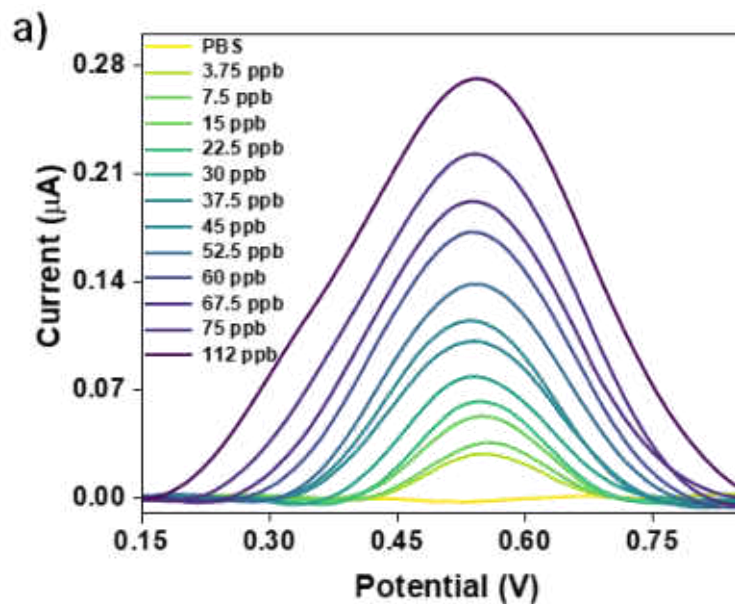
Algara-Siller, G.; Lehtinen, O.; Wang, F. C.; Nair, R. R.; Kaiser, U.; Wu, H. A.; Geim, A. K.; Grigorieva, I. V., Square ice in graphene nanocapillaries. *Nature* **2015**, 519 (7544), 443-445.

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

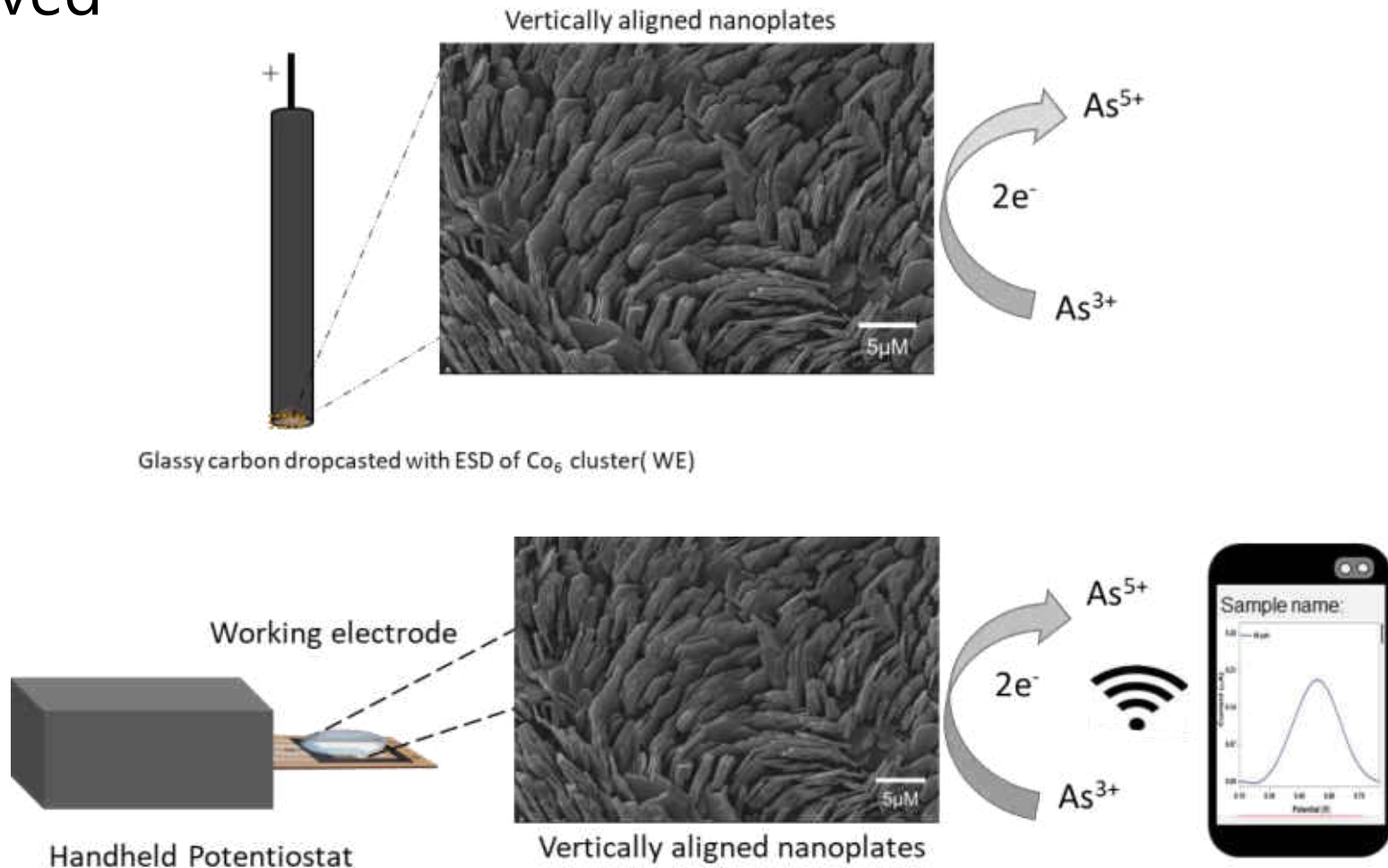
New applications – impossible in the past



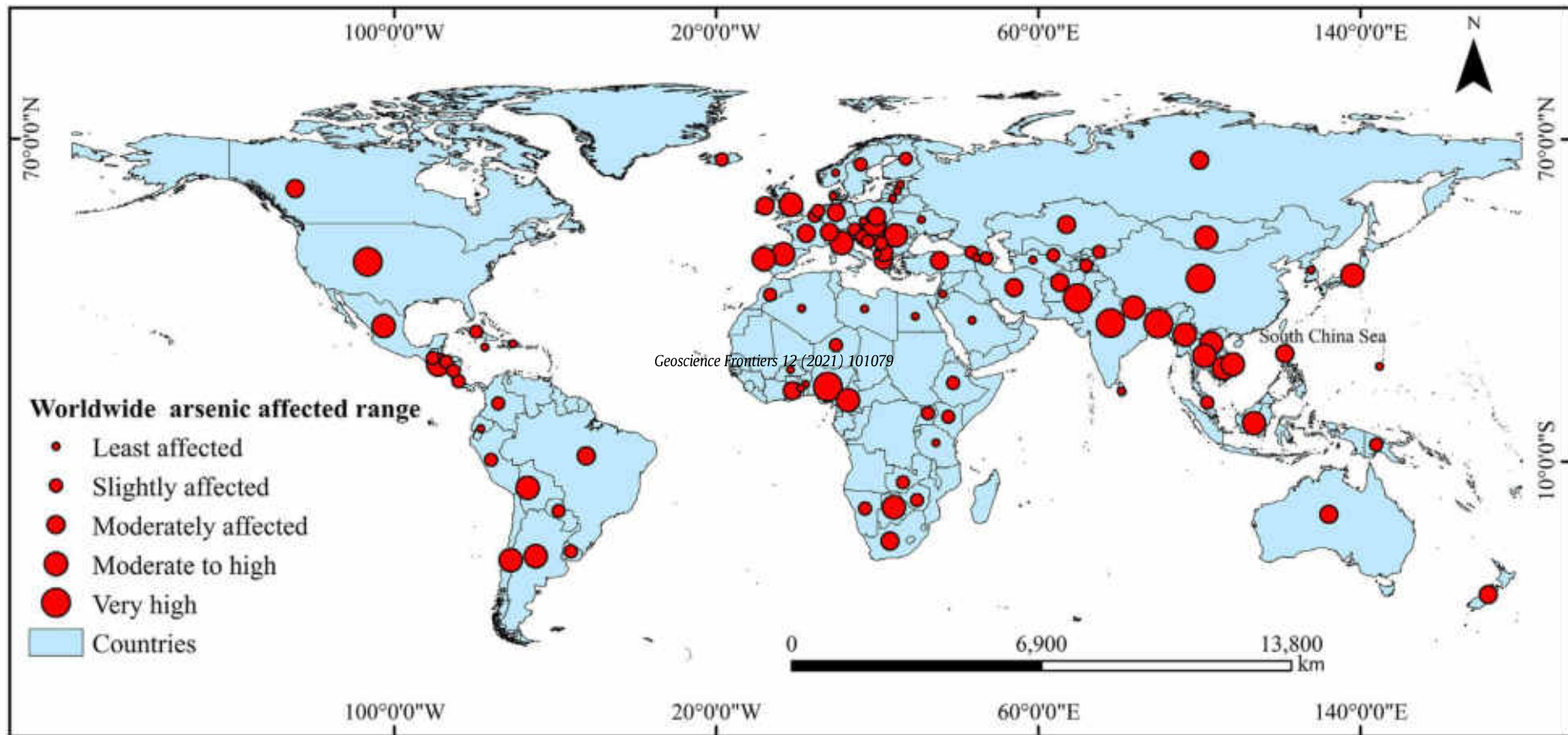
Sensing



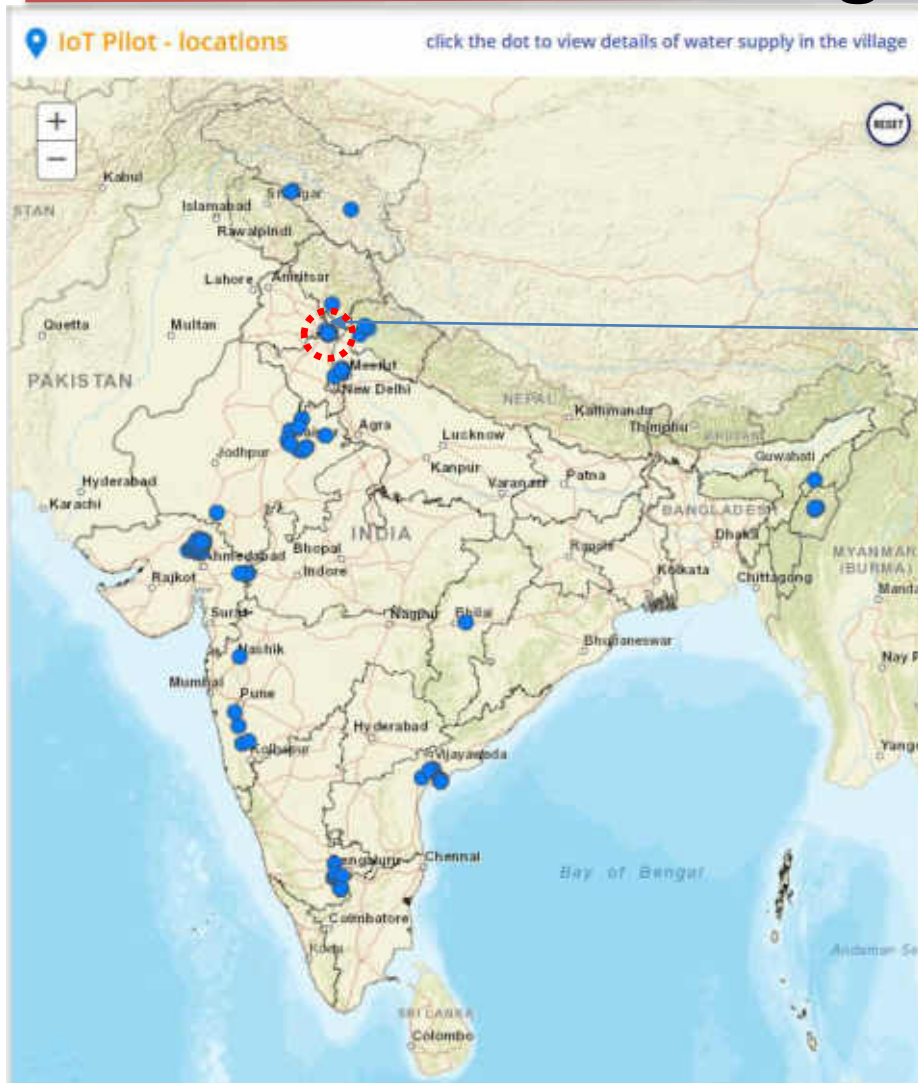
A problem on the ground can be solved



Arsenic poisoning across the world

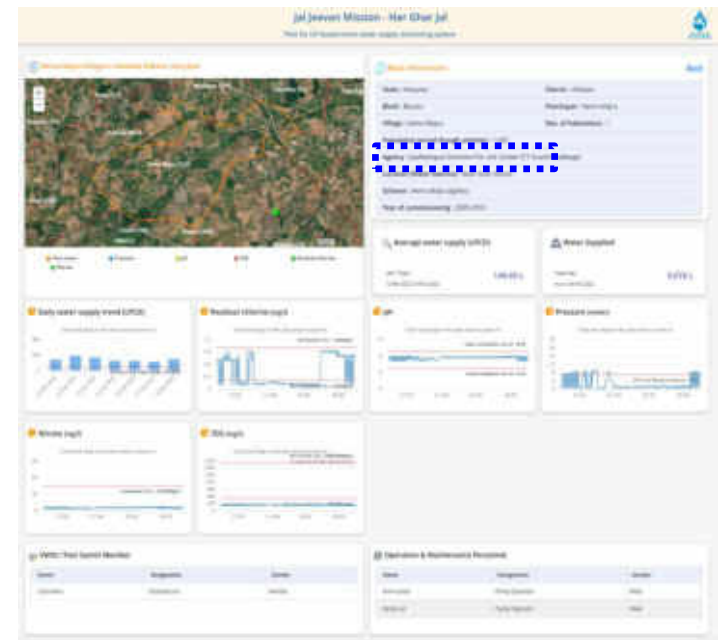


India's water is being monitored

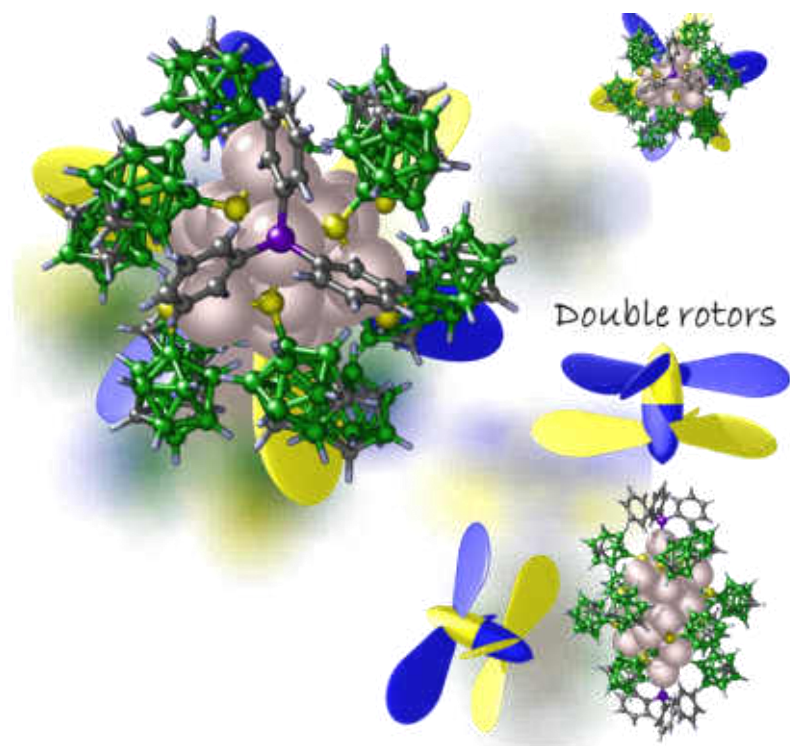


IITM/IISc

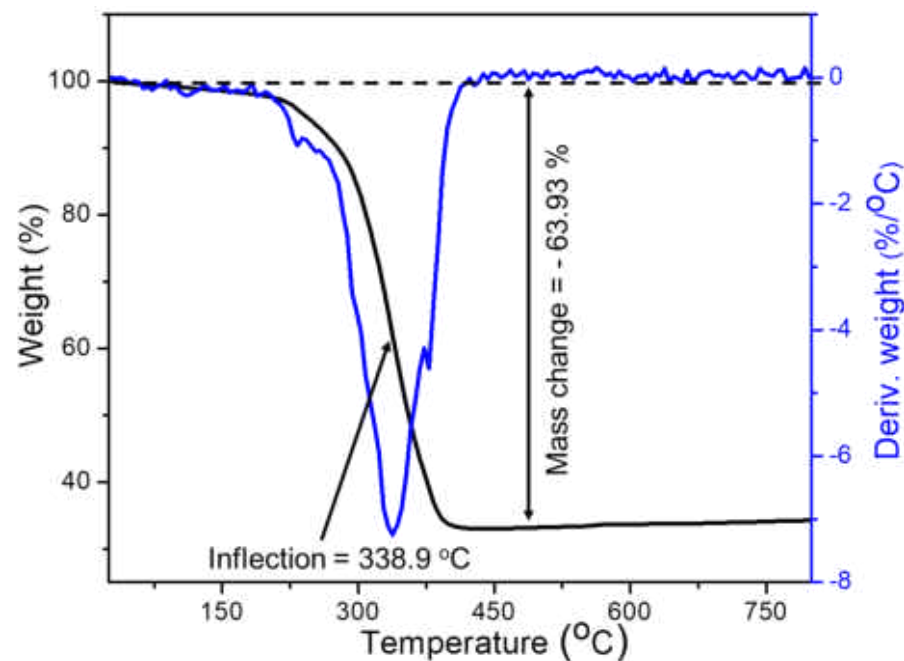
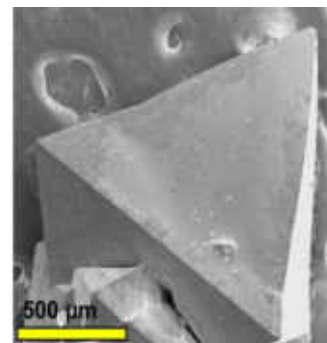
Installations made by four companies



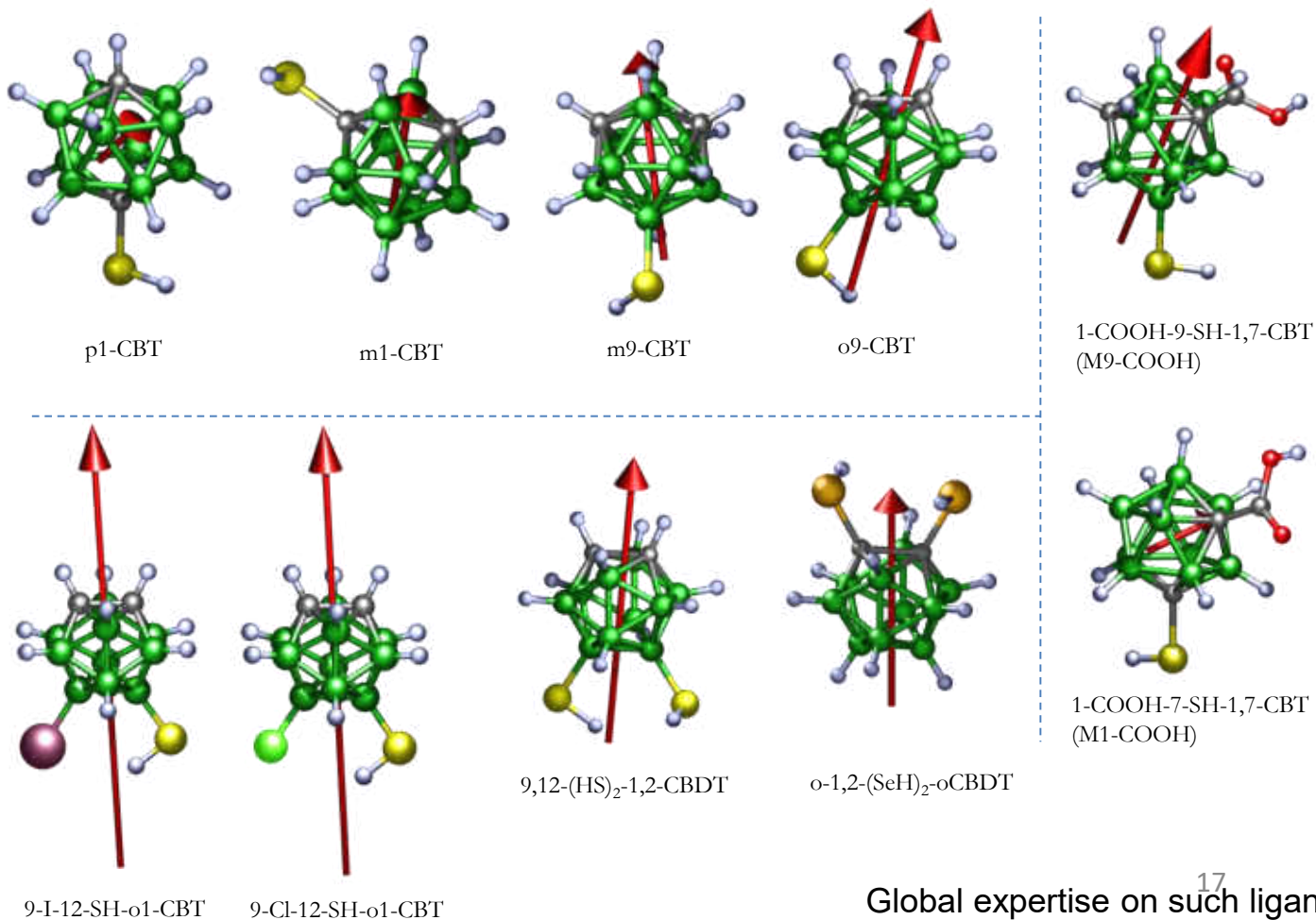
Limitations of atomically precise are addressed – Thermal



With Tomas Base



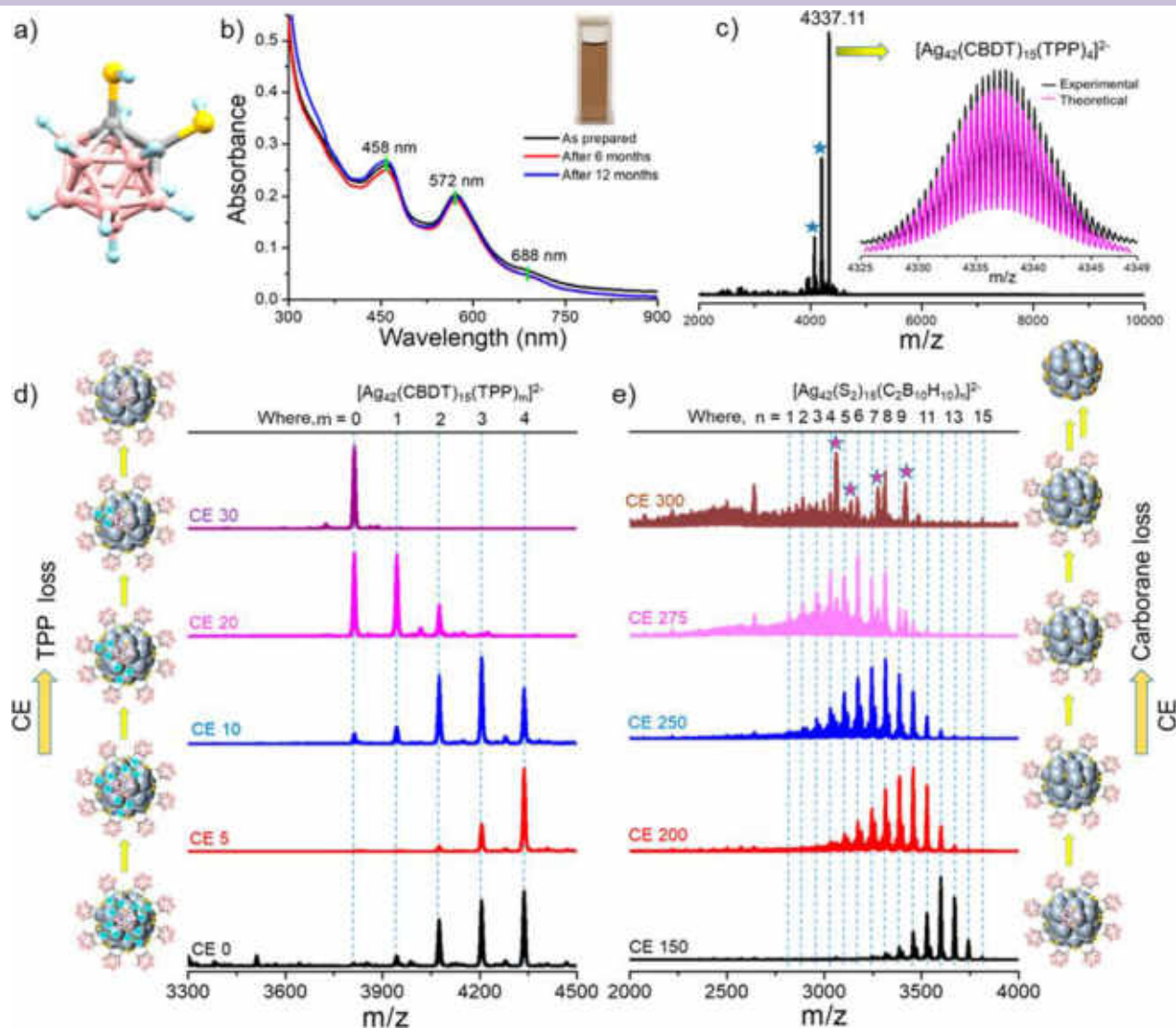
New materials and new properties



17
Global expertise on such ligands
The Czech Academy of Sciences
Institute of Inorganic Chemistry

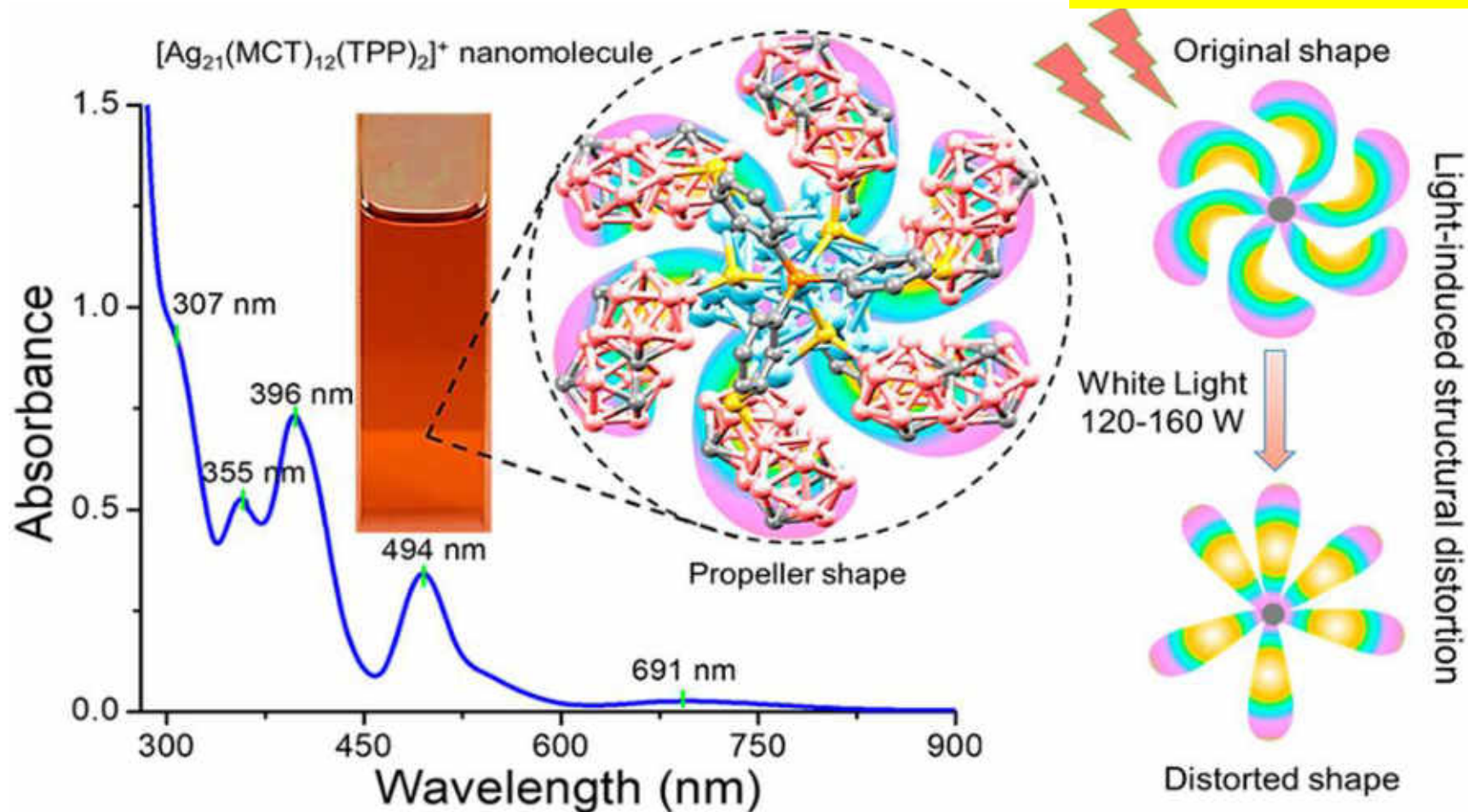
A glimpse of our collaborative work

Stable cluster materials



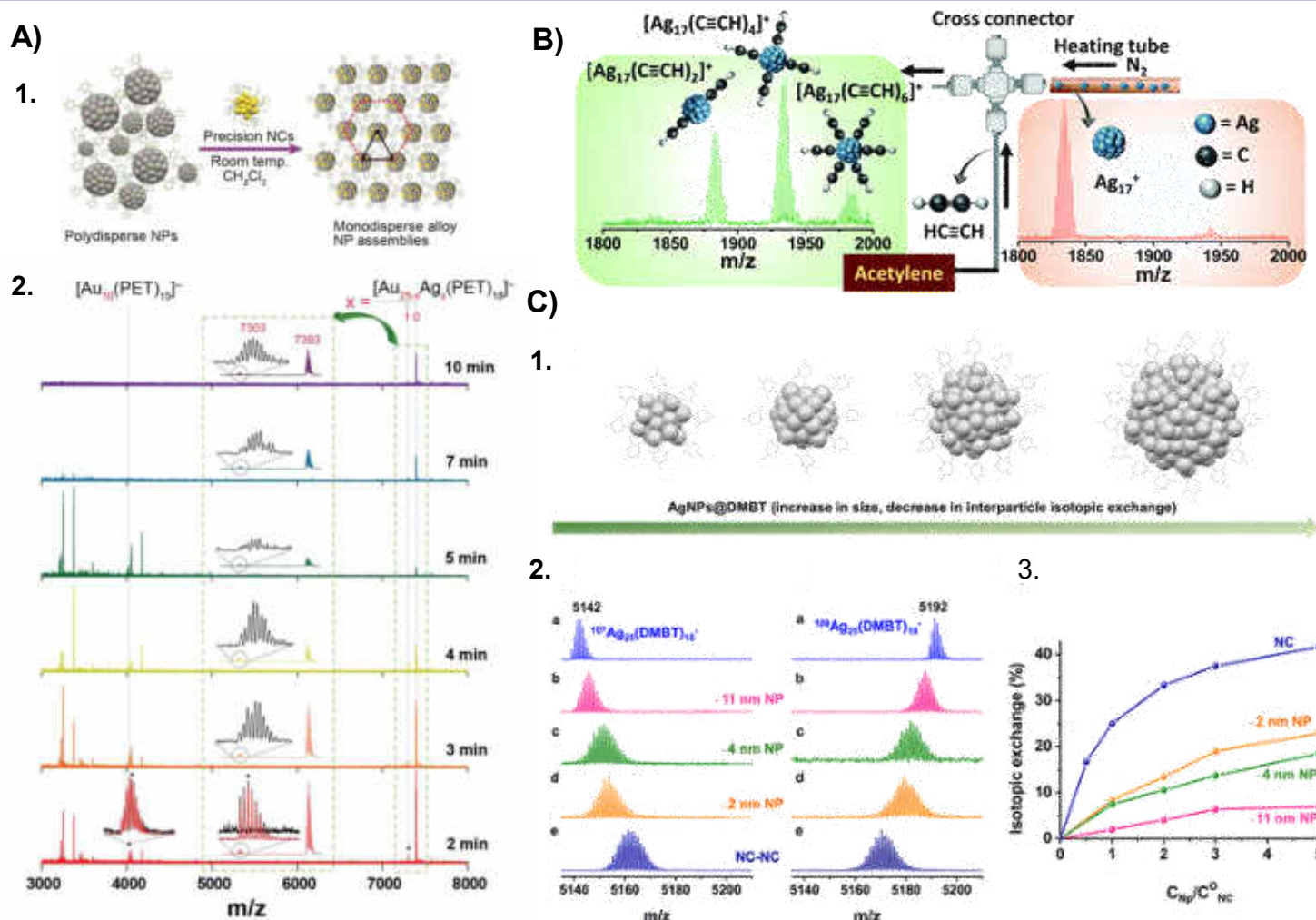
Synthesis and characterization of Ag_{42} NC. (a) Molecular structure of the *ortho*-carborane 1,2-dithiol ligand. (b) Time-dependent UV-vis absorption spectra of Ag_{42} NC in DCM indicating its stability. (c) Full range negative ion-mode ESI-MS spectrum of Ag_{42} NC. Features marked * are due to ligand losses. (d) Systematic losses of four TPP were observed from the peak at m/z 4337.11 with a charge state of 2- up to a collision energy (CE) of 30. (e) Fourteen sequential mass losses of carborane ($\text{C}_2\text{B}_{10}\text{H}_{10}$, M 142) units, along with a few silver sulfide loss peaks (marked as ☆).

Chiral metals



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

Cluster reactions

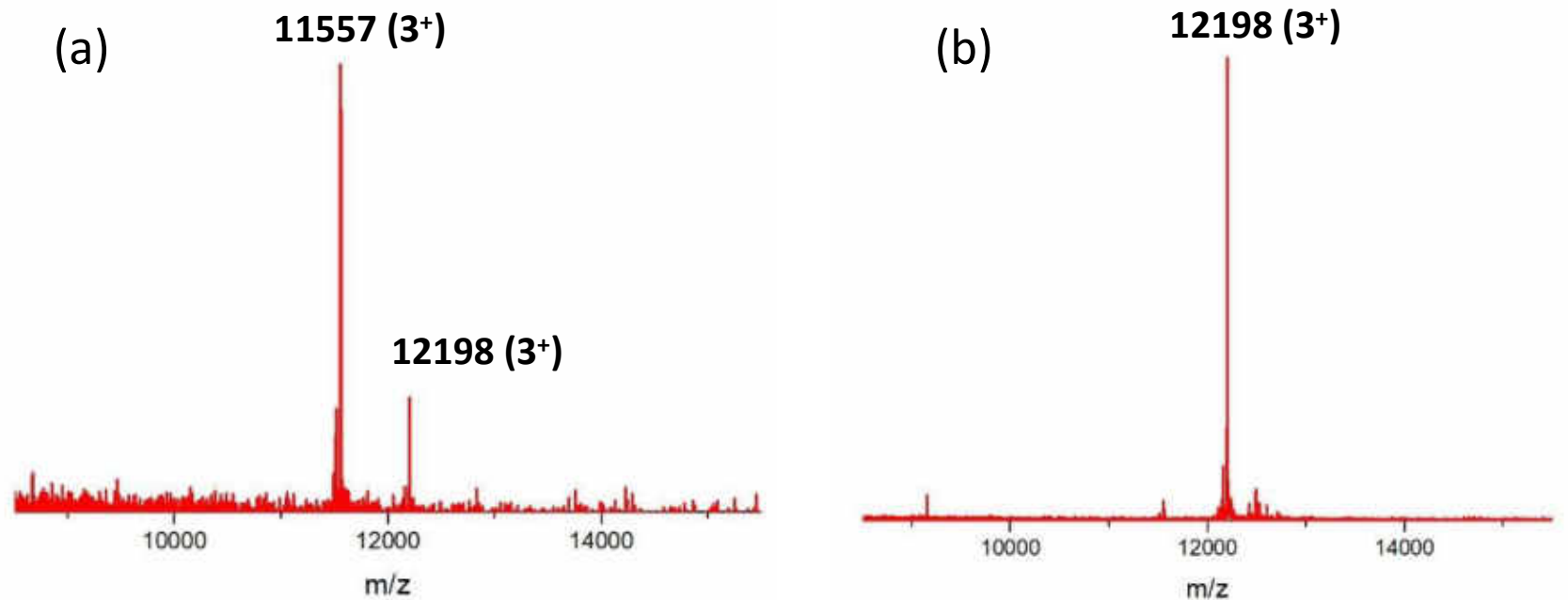


A) 1. Schematic representation of conversion of polydispersed NPs to monodispersed silver NPs. 2. Size-dependent reactivity monitored using ESI MS, keeping the reaction and mass spectrometric conditions constant. B) Schematic representation of formation of acetylide protected silver clusters in gas phase. C) 1. Schematic showing NPs of increasing sizes, 2. ESI MS of (a) parent isotopic NCs, $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^-$ and $^{109}\text{Ag}_{25}(\text{DMBT})_{18}^-$, 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 (C_{NP}) and concentration of isotopic NCs (C_{NC}) 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

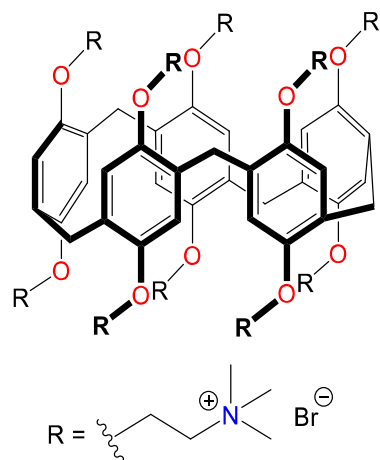


(a) Mass spectrum of a newly synthesised mixture of clusters composed of $\text{Au}_{144}(\text{PET})_{60}$ and $\text{Au}_{137}(\text{PET})_{56}$. The clusters have been separated with thin layer chromatography.; (b) Mass spectrum of the separated $\text{Au}_{144}(\text{PET})_{60}$ cluster.

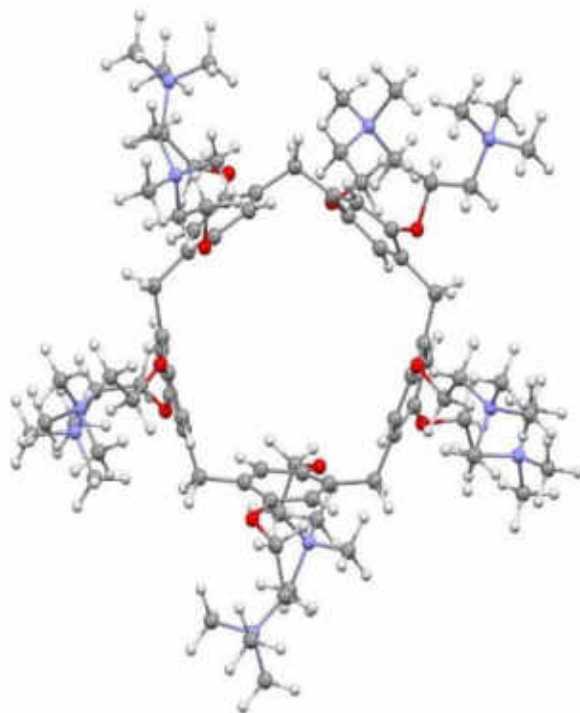
Examples of science proposed

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

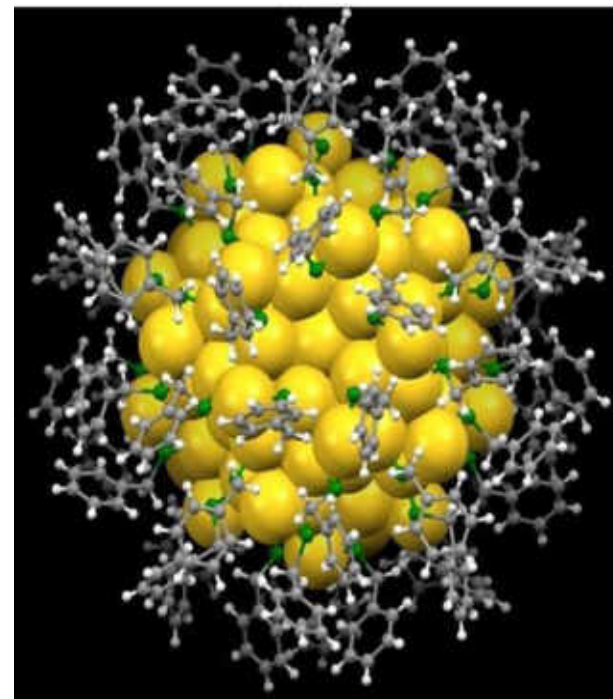
(a)



(b)



(c)



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