Luminescent molecular clusters of noble metals

T. Pradeep

Quantum clusters: Au_{25}, Au_{23}, Au_{22}, Au_{8}, Ag_{8}, Ag_{9}, Ag_{25}

Department of Chemistry
Indian Institute of Technology Madras
Chennai – 600 036
http://www.dstuns.iitm.ac.in/prof-pradeep-group.php

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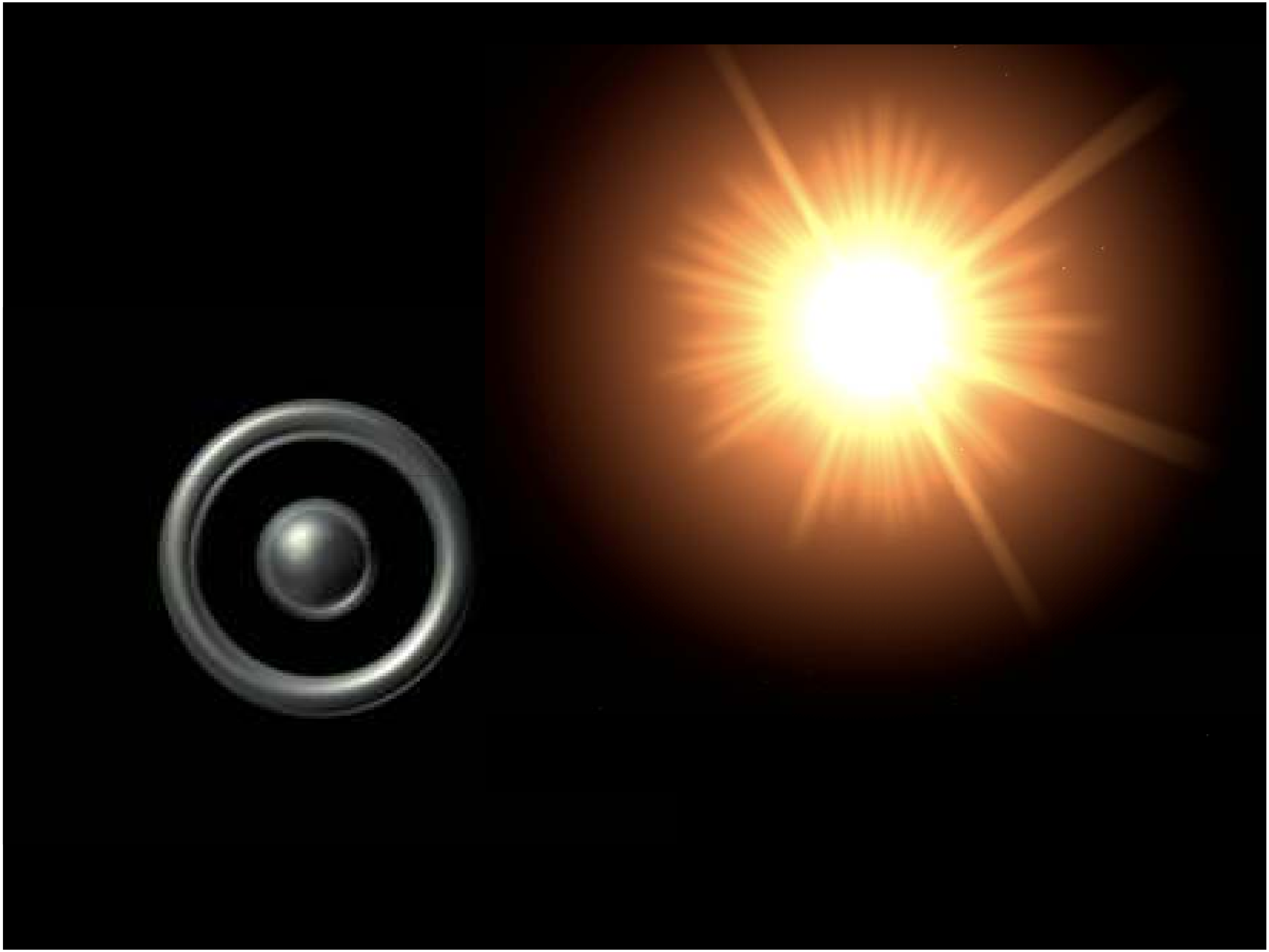
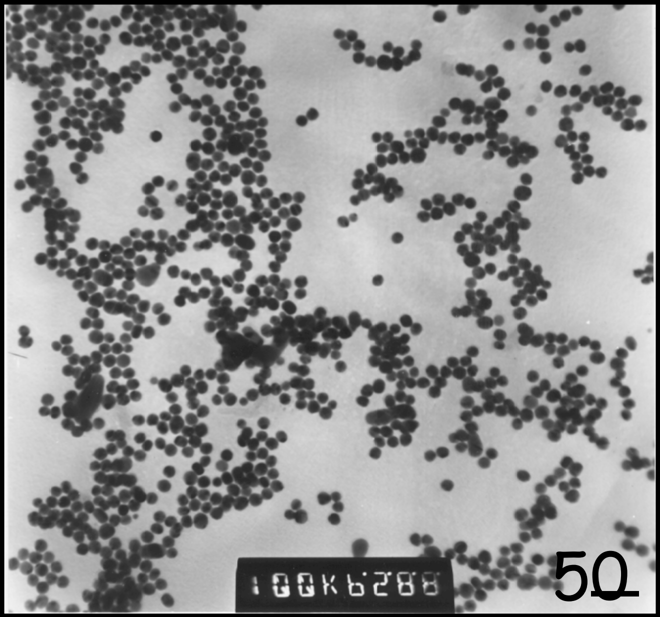




Faraday's gold preserved in Royal Institution. From the site, http://www.rigb.org/rimain/heritage/faradaypage.jsp

"With regard to *gold-leaf* no question respecting its metallic nature can arise, but it offers evidence reaching to the other preparations. The green colour conferred by pressure, and the removal of this colour by heat, evidently belong to it as a metal; these effects are very striking and important as

…they are simply cases of pure gold in a divided state;
…….the differently-coloured fluids and particles are quite analogous….

the same whatever the atmosphere surrounding them at the time, or whatever the substance on which they are deposited. They have all the chemical reactions of gold, being so finely divided, insoluble in the fluids that refuse to act on the massive metal, and soluble in those that dissolve it, producing the same result. Heat makes these divided particles assume a ruby tint, yet such heat is not likely to take away their metallic character, and when heated they still act with chemical agents as gold. Pressure then confers the green colour, which heat takes away, and pressure reconfers. All these changes occur with particles attached to the substances which support them by the slightest possible mechanical force, just enough indeed to prevent their coalescence and to keep them apart and in place, and yet offering no resistance to any chemical action of test agents, as the acids, &c., not allowing any supposition of chemical action between them and the body supporting them. Still this gold, unexceptionable as to metallic state, presents different colours when viewed by transmitted light. Ruby, green, violet, blue, &c., occur, and the mere degree of division appears to be the determining cause of many of these colours. The …ons by the voltaic battery lead to the same …n.

…*old films* produced by phosphorus have every … belonging to the metallic state. When …ey are in colour, lustre, weight, &c., equal …af, but in the unpressed state, their trans… …lour is generally grey, or violet-grey. The …on of their lustre and colour is gradual from …est to the thinnest, and the same is generally …thick films are gradually thinned and dis… …hilst floating on solvents; the thick and the …s must both be accepted as having the same amount of evidence for their metallic nature. When subjected to chemical agents, both the thick and the thin films have the same relations as pure metallic gold.

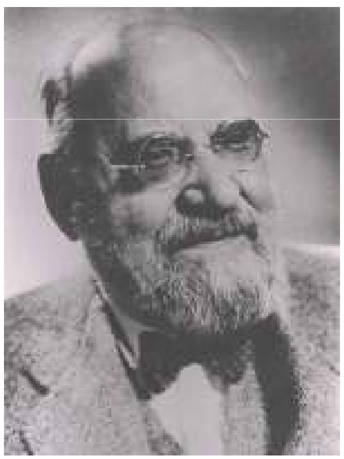
"It may be thought that the *fluid preparations* present more difficulty to the admission, that they are simply cases for pure gold in a divided state; yet I have come to that conclusion, and believe that the differently-coloured fluids and particles are quite analogous to those that occur in the deflagrations and the films. In the first place they are produced as the films are, except that the particles are separated under the surface and out of the contact of the air; still, when produced in sufficient quantity against the side of the containing vessel to form an adhering film, that film has every character of lustre, colour, &c., in the parts differing in thickness, that a film formed at the surface has."

Experimental Relations of Gold (and Other Metals) to Light, M. Faraday, Philos. Trans. R. Soc. London, 1857, **147, 145**

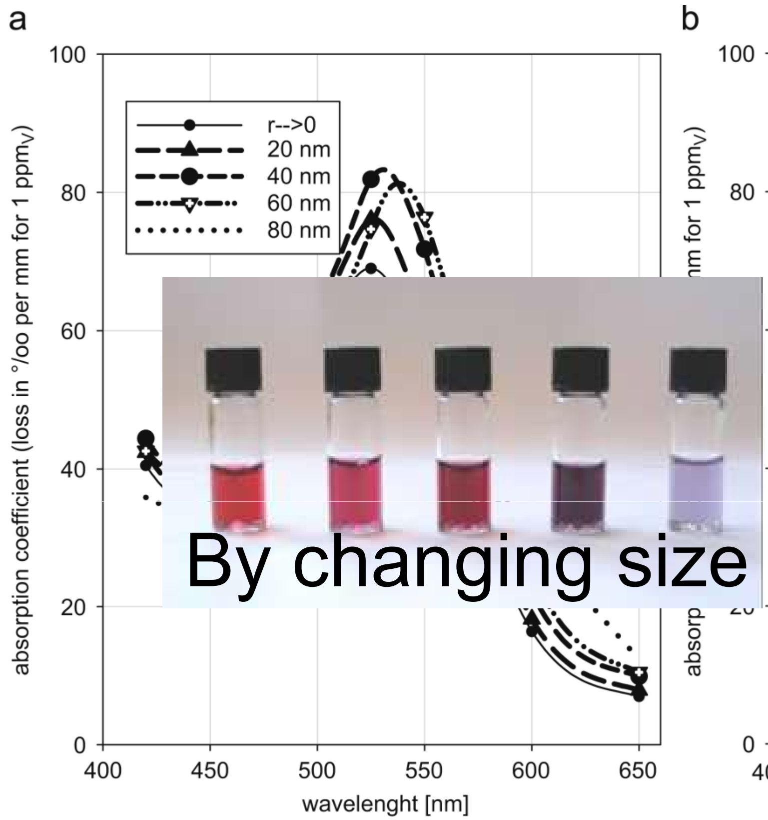
Gustav Mie (1868 - 1957)

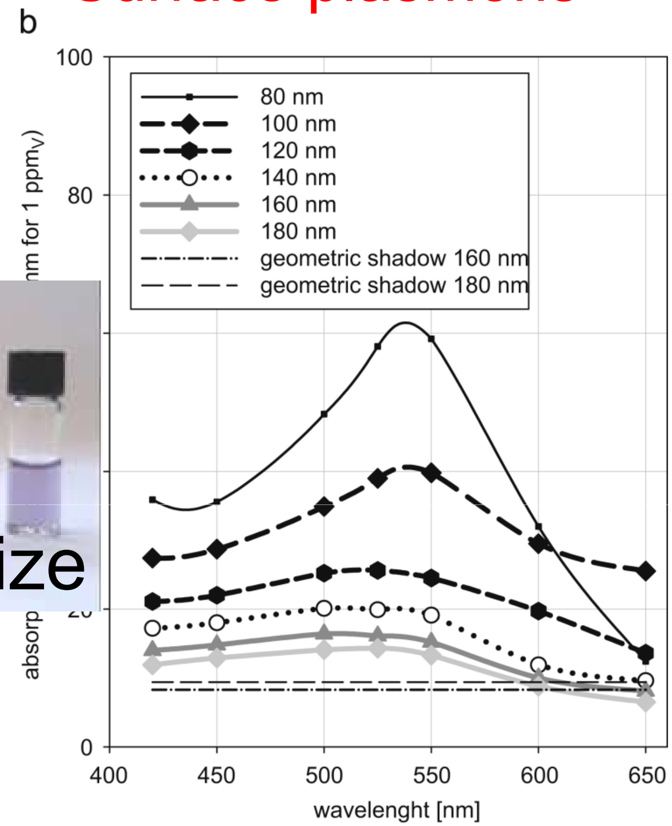
1905

1940

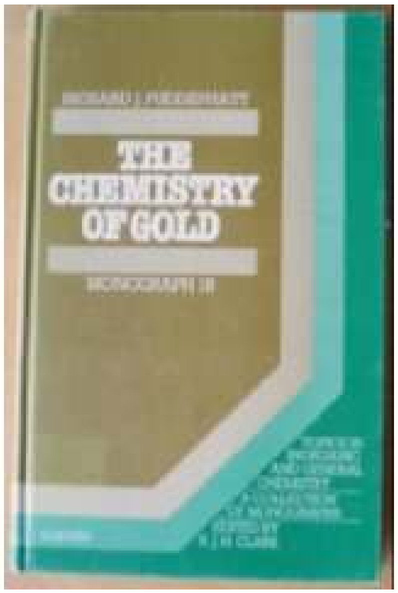


Surface plasmons





Mie G. Beiträge zur Optik trüber Medien speziell kolloidaler Goldlösungen (contributions to the optics of diffuse media, especially colloid metal solutions). Ann Phys 1908;25:377–445. This paper, including an English translation, as well as other historic papers on light scattering and absorption can be found at www.iwt-bremen.de/vt/laser/wriedt/index_ns.html .



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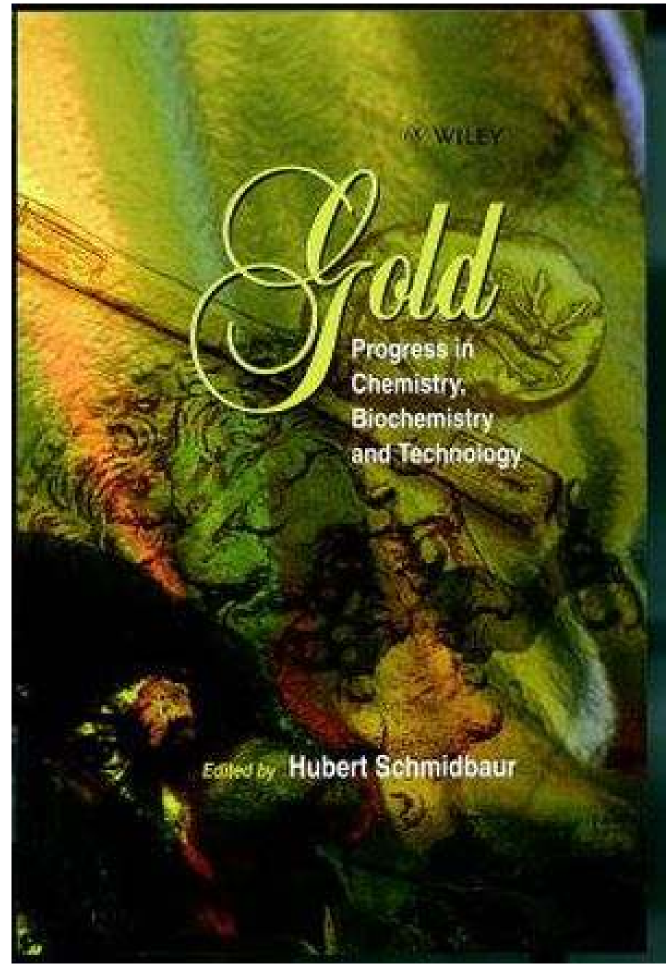

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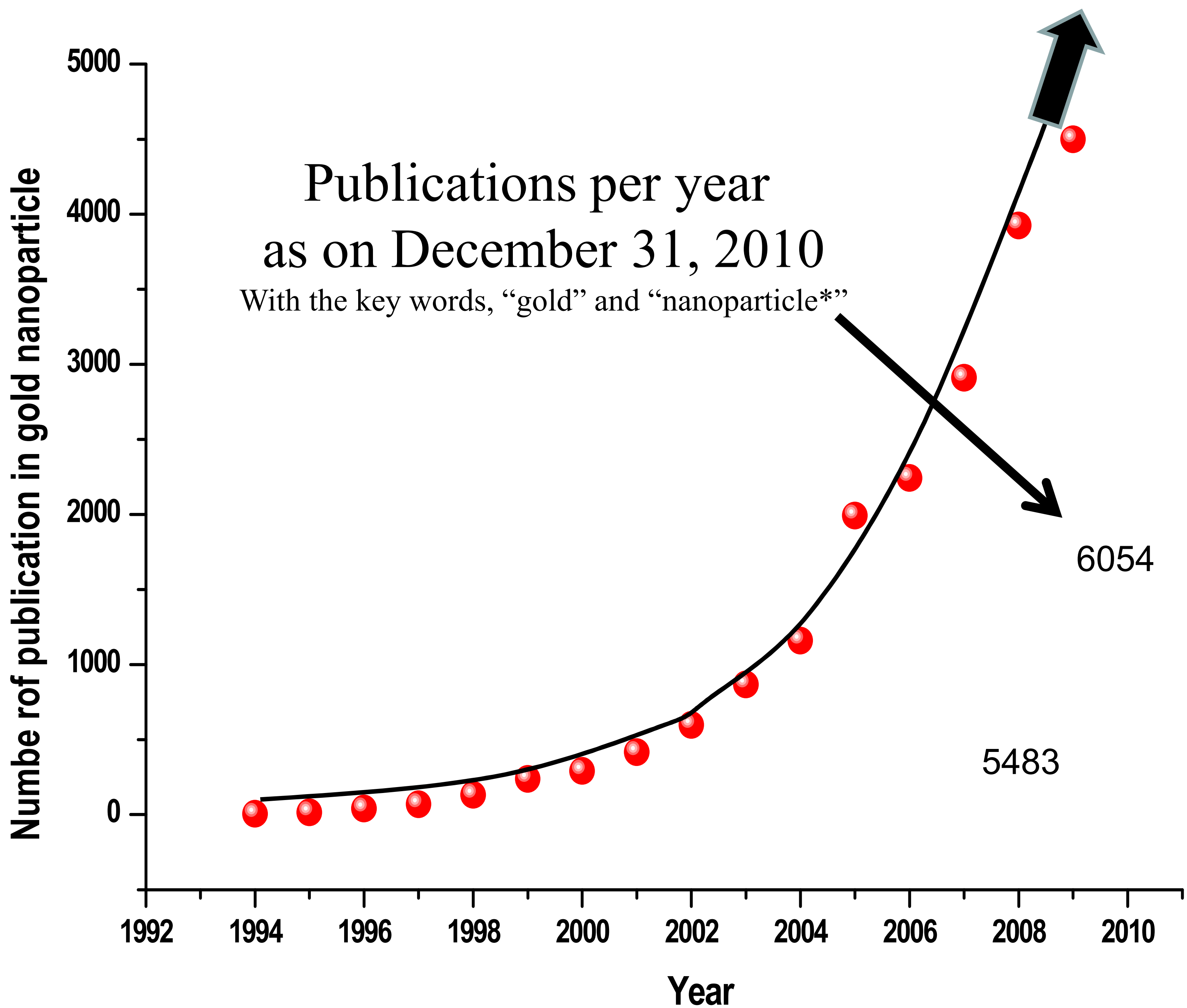
Publications per year
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With the key words, "gold" and "nanoparticle*"
6054
5483
Numbe rof publication in gold nanoparticle
Year
0
1000
2000
3000
4000
5000
1992
1994
1996
1998
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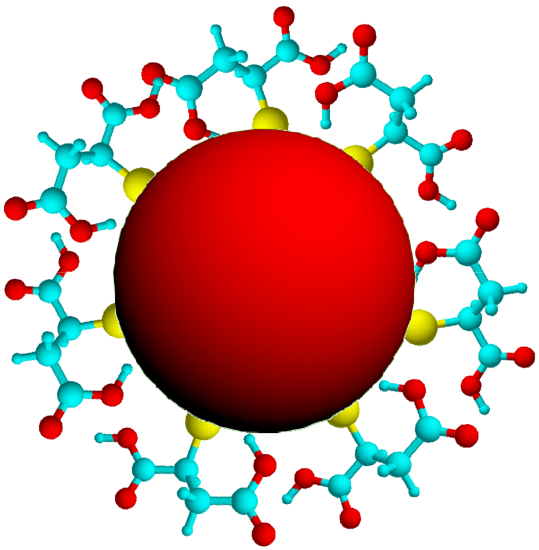
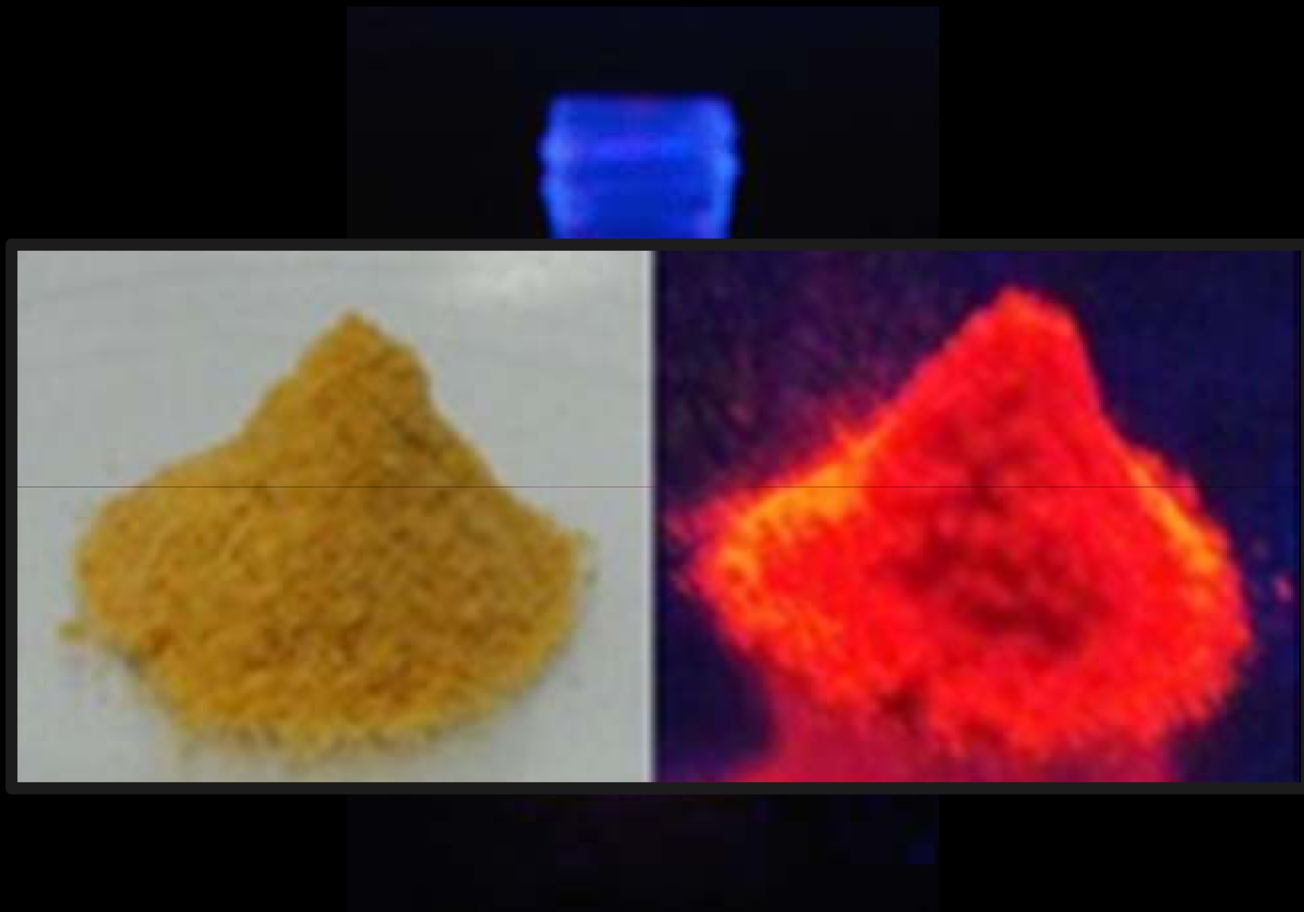
Monolayer Protected Metal Nanoparticles

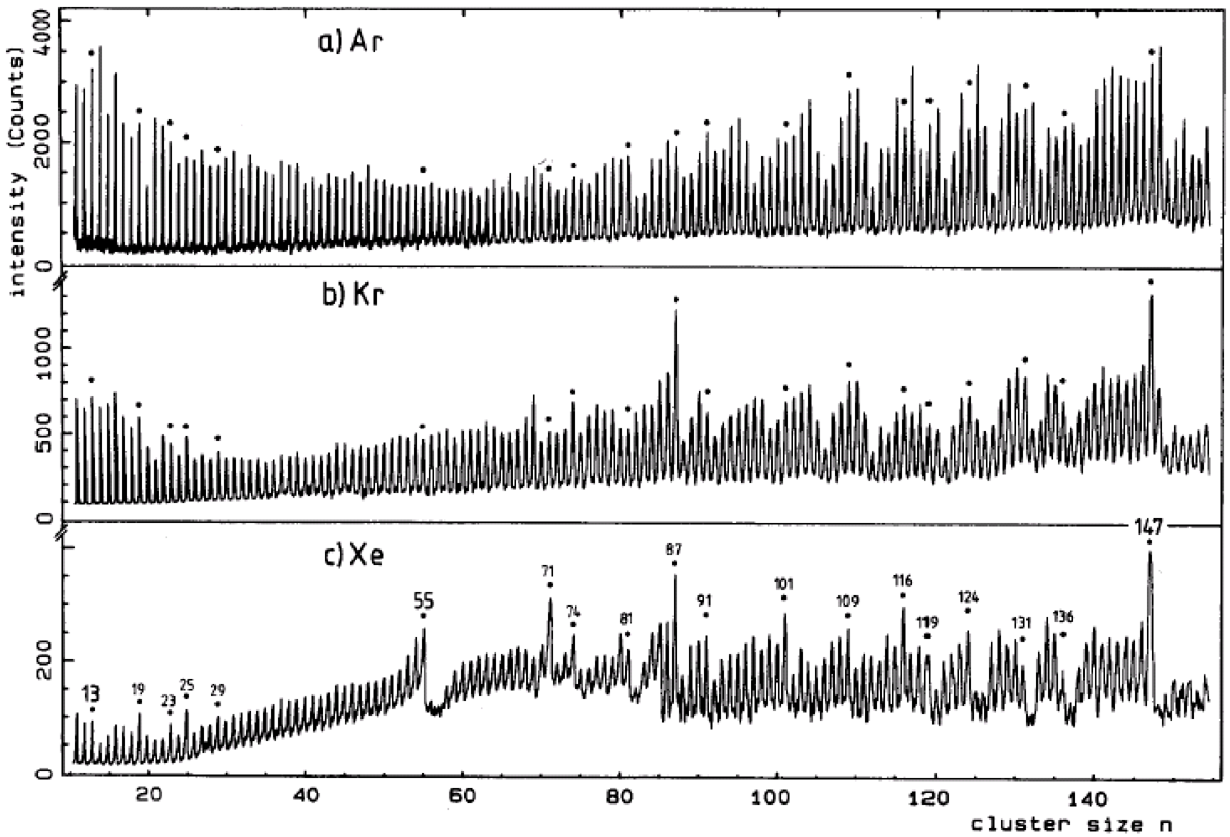
Monolayer Protected Clusters (MPCs)



N. Sandhyarani and T. Pradeep, *Int. Rev. Phys. Chem.* **2003**



Gas phase cluster spectroscopy



Mass spectra of positively charged Ar, Kr, Xe clusters, W. Miehle, O. Kandler, T. Leisner, and O. Echt. (**1989**) *J. Chem. Phys.*, 91, 5940.

Magic clusters

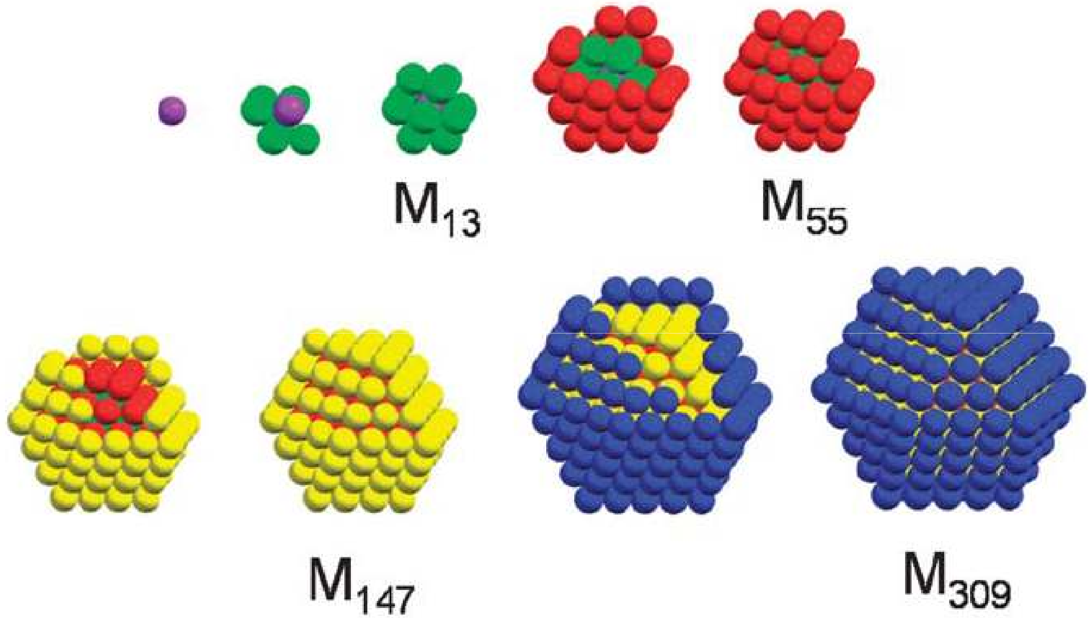
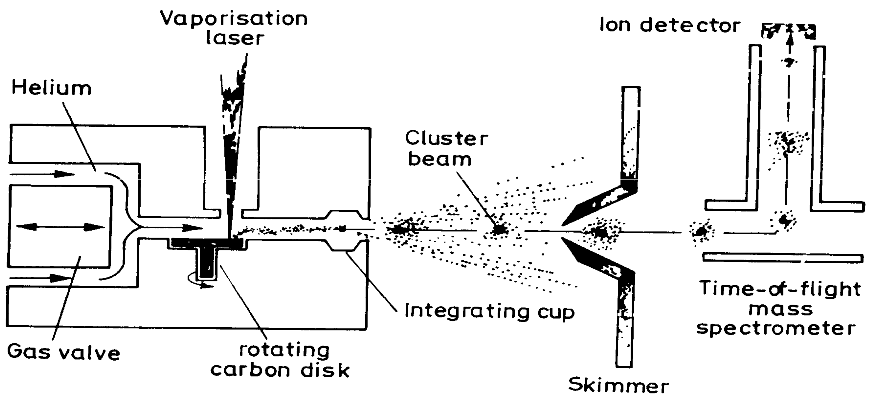
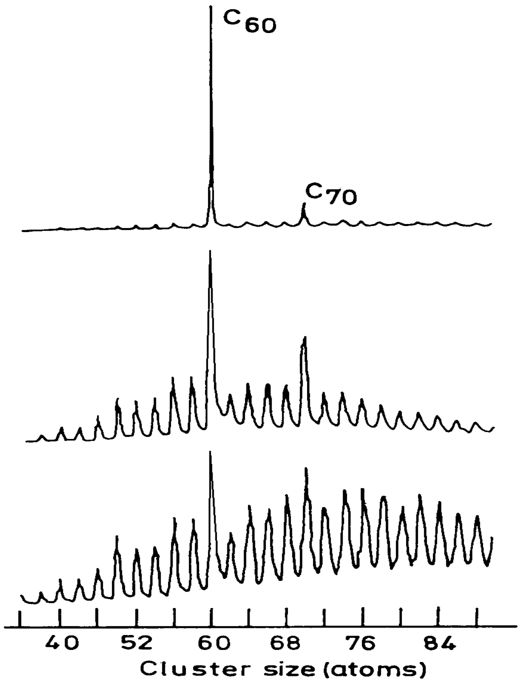


Fig. 1 Organization of full-shell clusters: a first single atom (purple) is surrounded by 12 others (green) to give a one-shell cluster M_{13}. 42 atoms (red) can be densely packed on the 12 green atoms ending with the M_{55} two-shell cluster, followed by 92 atoms (yellow) and 162 atoms (blue) to give M_{147} and M_{309}, respectively.

From Gunter Schmidt, *Chem. Soc. Rev.* **2008**, *37*, 1909–1930

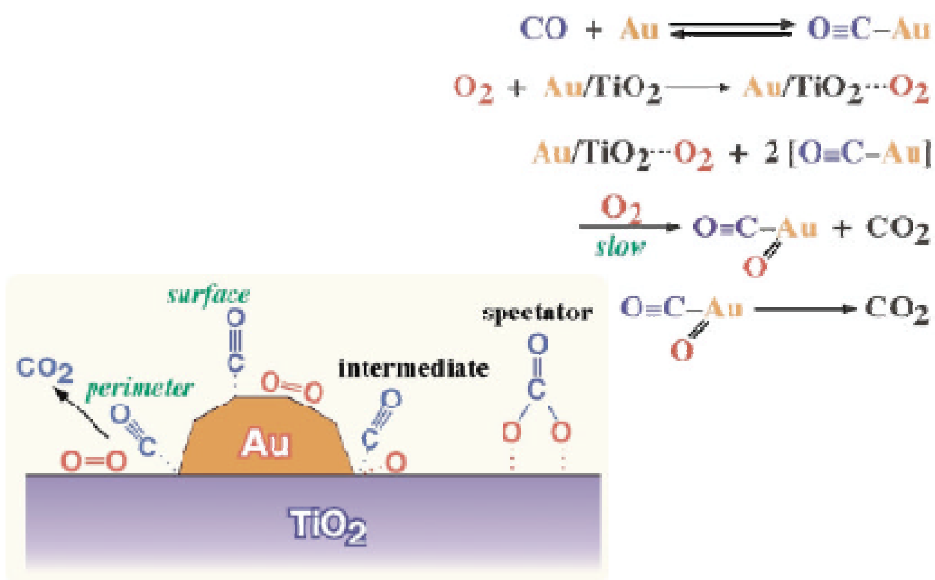
Laser desorption mass spectrometry





Smalley et al. Nature 1985

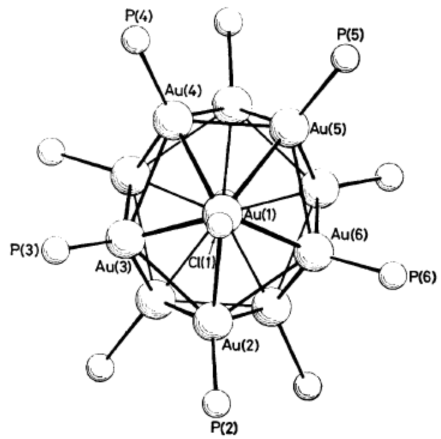
Supported gold clusters in catalysis



Schematic representation for CO oxidation pathways over Au/TiO2.

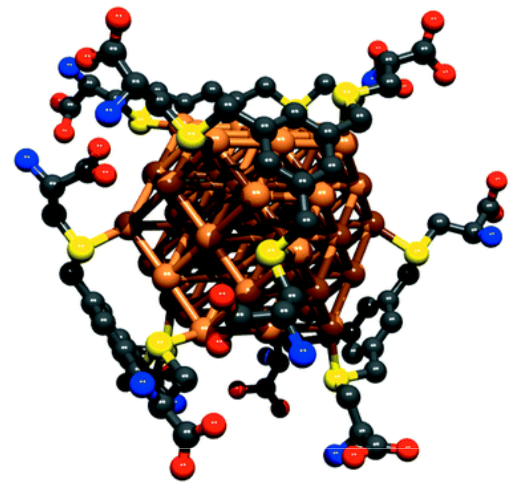
M. Haruta, When Gold Is Not Noble: Catalysis by Nanoparticles.

Gold clusters



Au_{13}

$[Au_{13}(PPhMe_2)_{10}C1_2]^{3+}$



Au_{55}

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- **Synthesis and x-ray structural characterization of the centered icosahedral gold cluster compound [Au_{13} $(PMe_2Ph)_{10}Cl_2](PF_6)_3$; the realization of a theoretical prediction,** Briant, C. E.; Theobald, B. R. C.; White, J. W.; Bell, L. K.; Mingos, D. M. P.; Welch, A. J. *Chem. Commun.* **1981**, *5*, 201.
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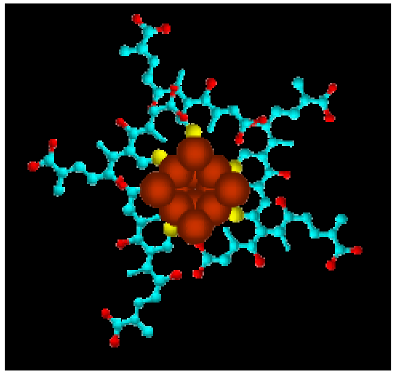
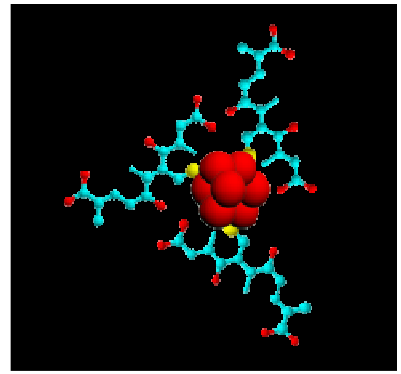
Molecular Clusters





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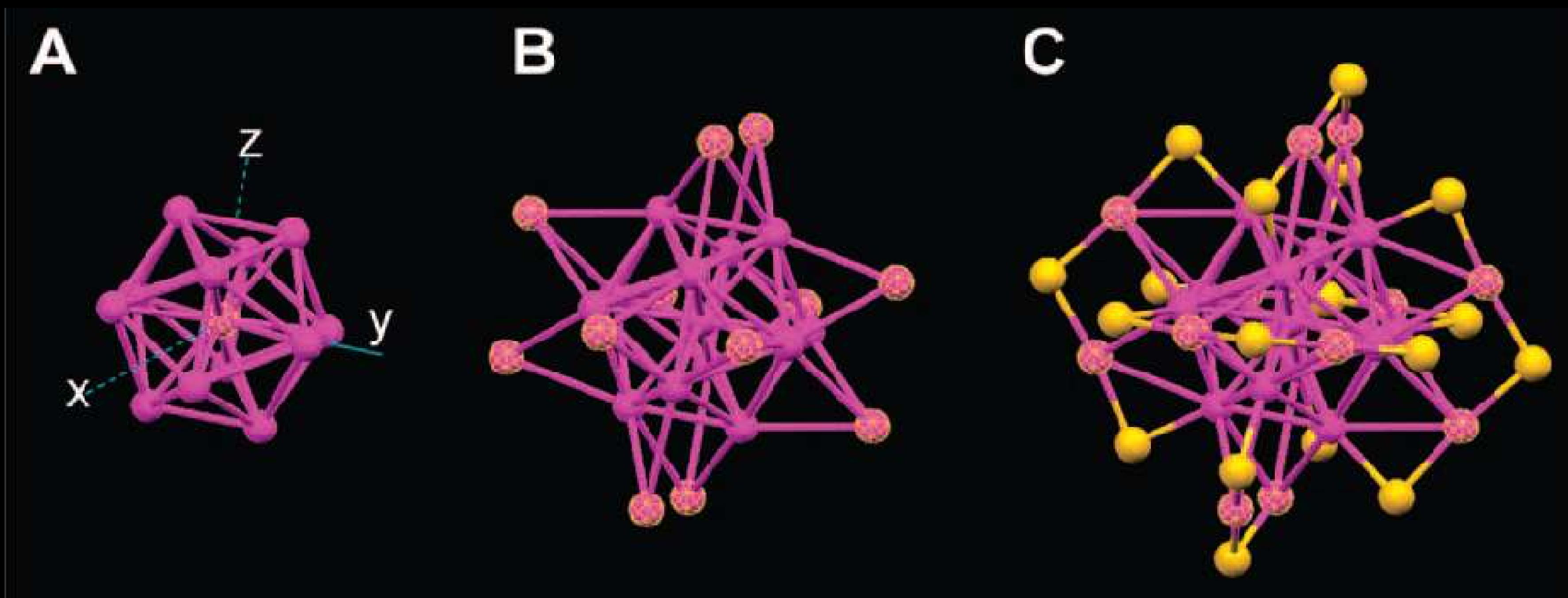
A
z
y
x
B
C

How to make them?