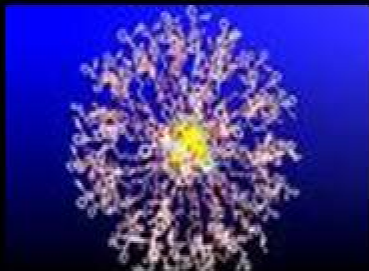
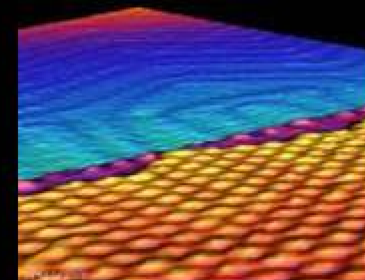
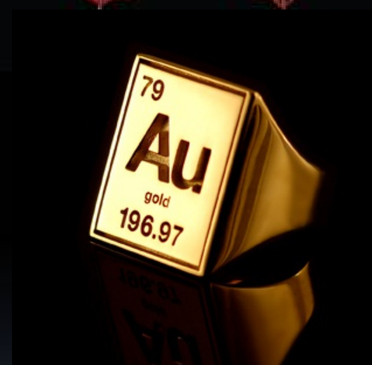
The Different Colors of Gold







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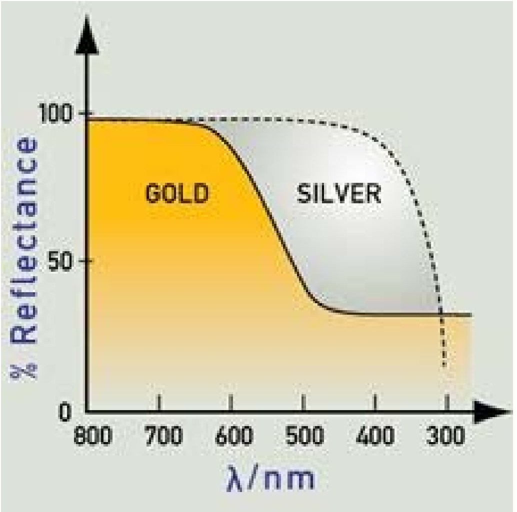
PSG College September 25, 2009



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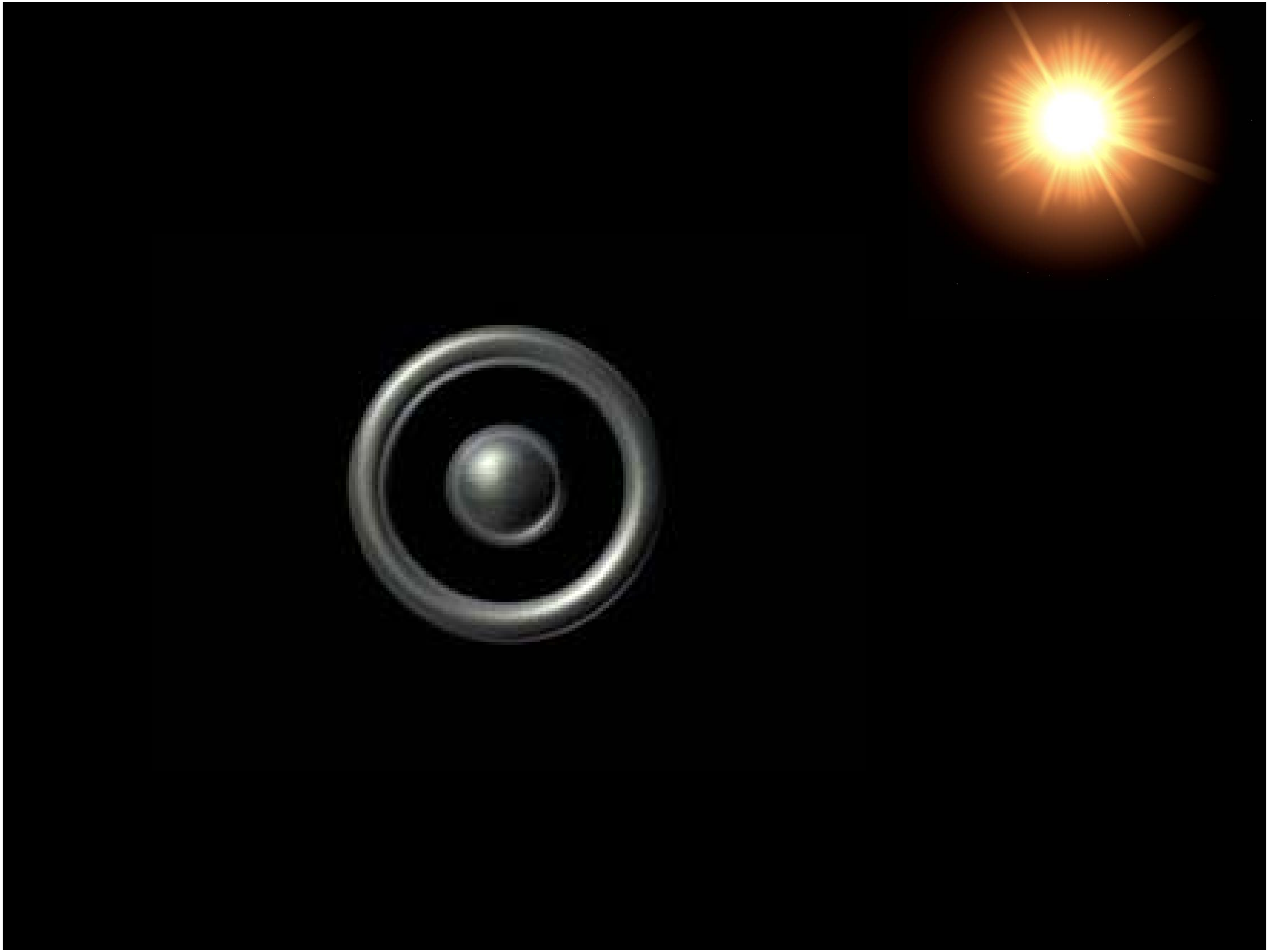


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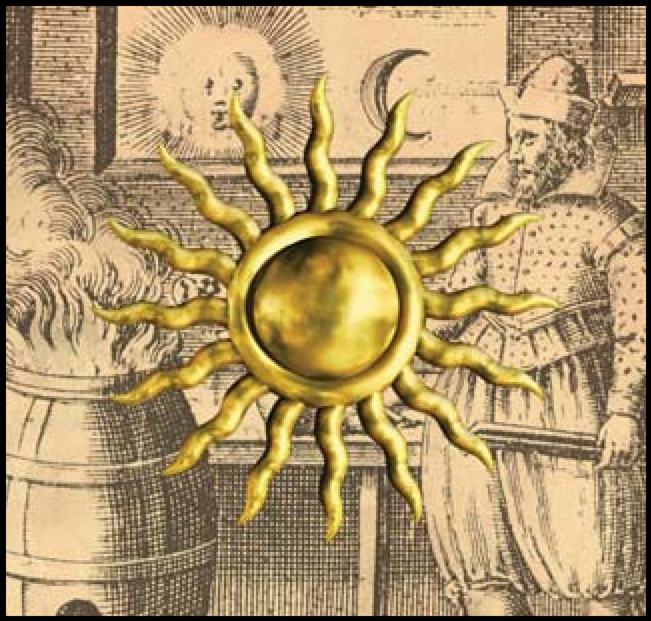
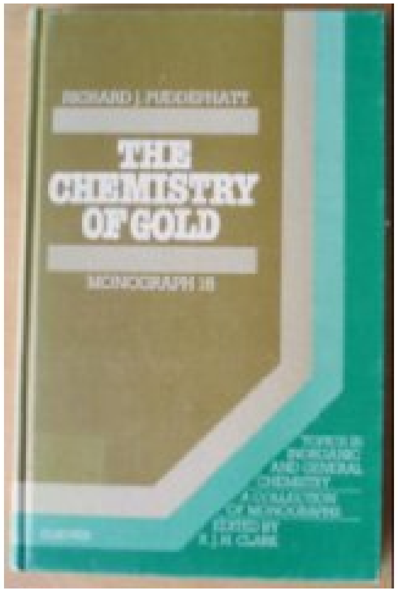
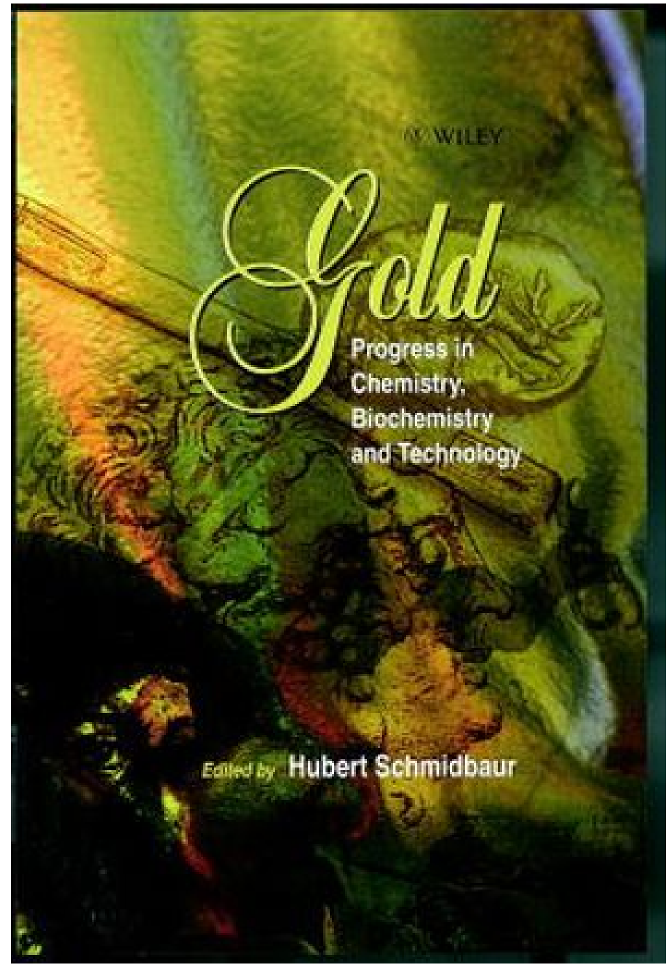


Gold was fascinating for many alchemists.
Copyright Murray Robertson.

Alchemy!

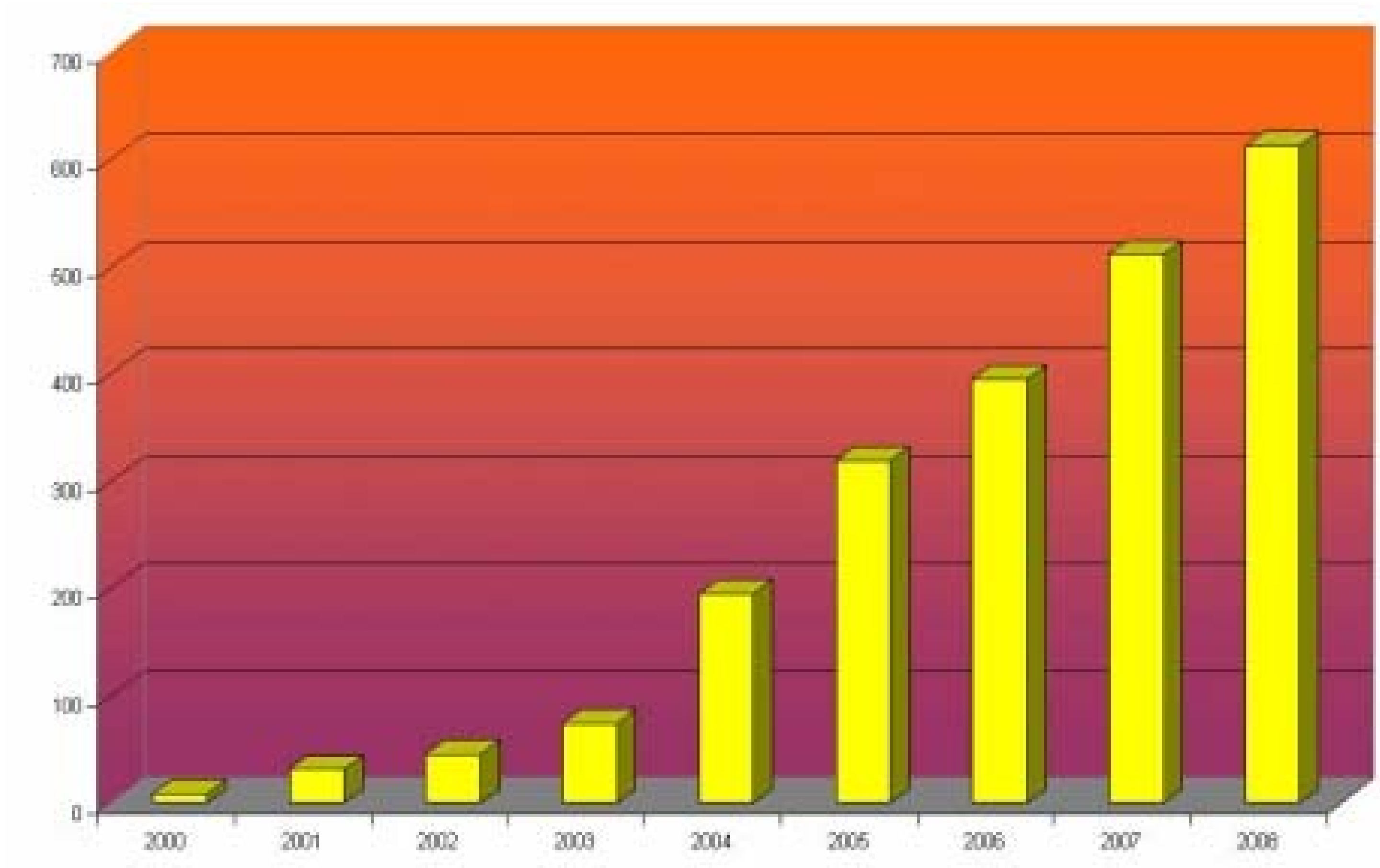


Hardcover: 274 pages
Publisher: Elsevier Science Ltd (June 1978)
Language: English
ISBN-10: 0444416242
ISBN-13: 978-0444416247

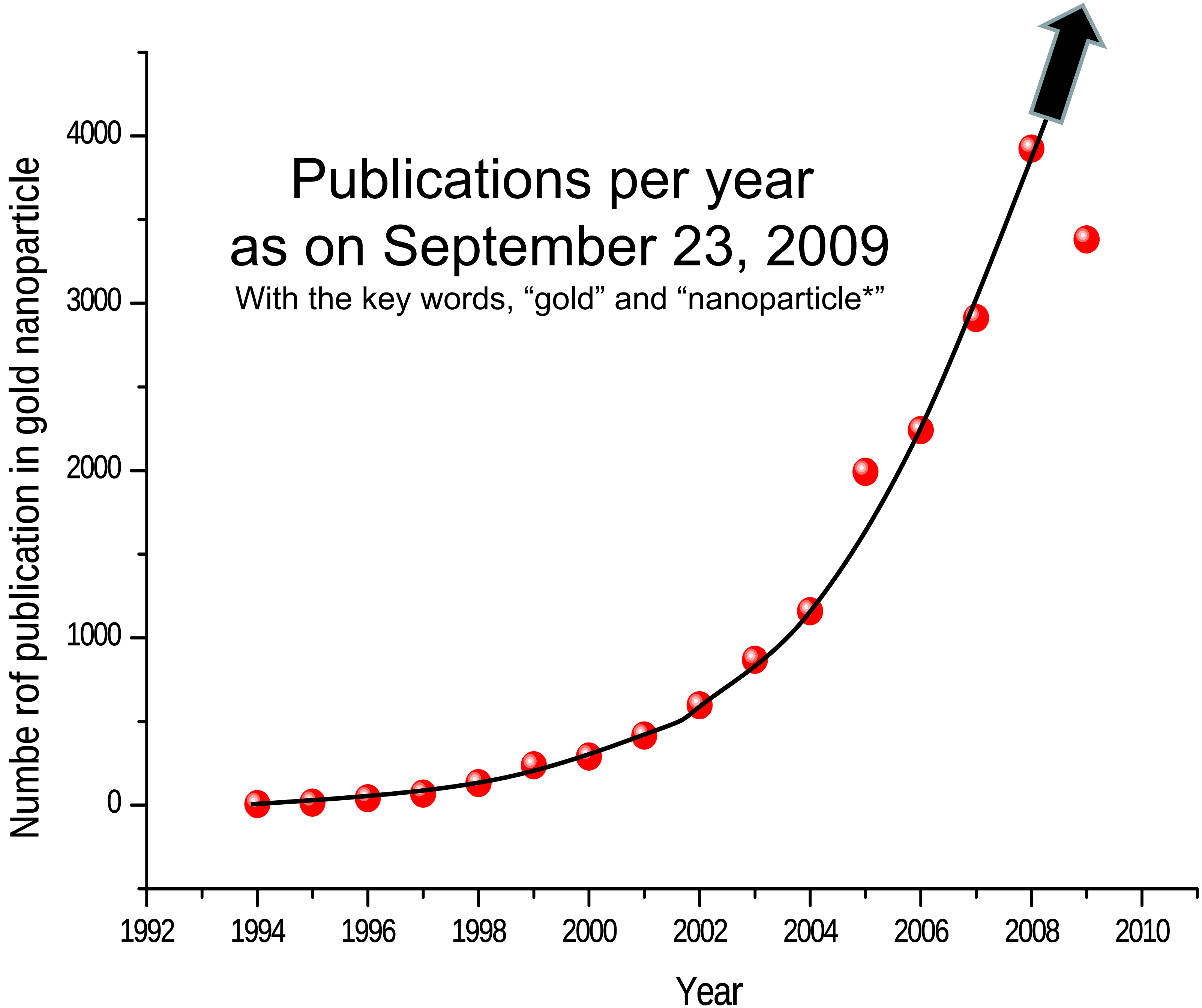


Gold Chemistry
ISBN: 978-0-471-97369-0
Hardcover
908 pages
March 1999

GOLD-CATALYSIS



Number of papers published per year after the discovery of gold catalysis.


Publications per year
as on September 23, 2009
With the key words, “gold” and “nanoparticle*”
Numbe rof publication in gold nanoparticle
0
1000
2000
3000
4000
1992
1994
1996
1998
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2004
2006
2008
2010
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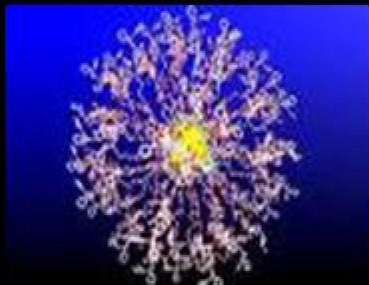
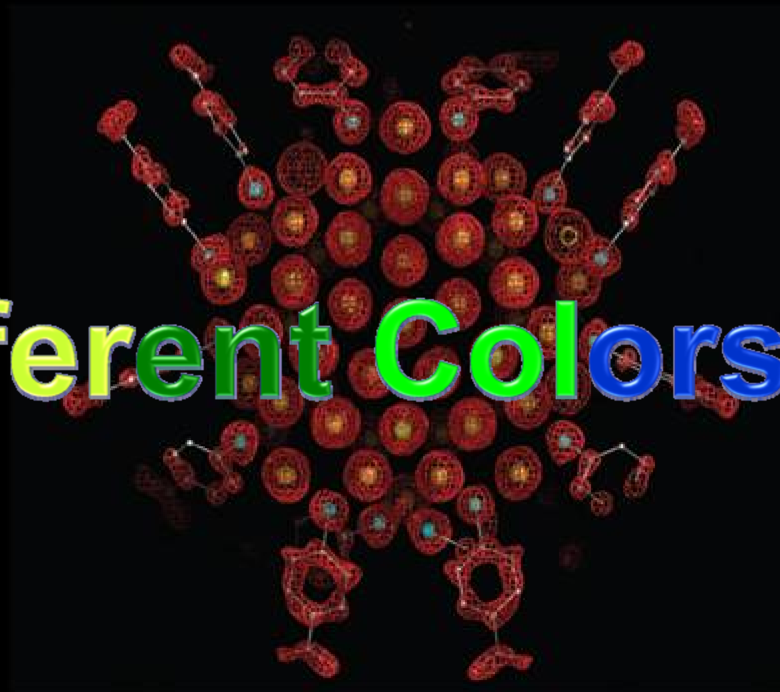
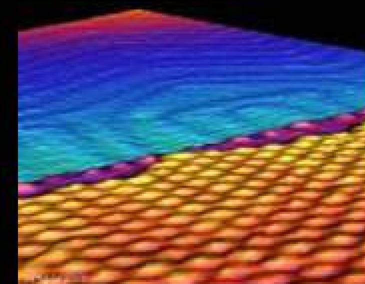




The Different Colors of Gold



Revisiting gold molecules in the era of nanotechnology

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Shaastra 2009 September 24, 2009

The gold that is not GOLD!

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R. V. Omkumar, RGCB, Tiruvananthapuram

Nano Mission, Department of Science and Technology

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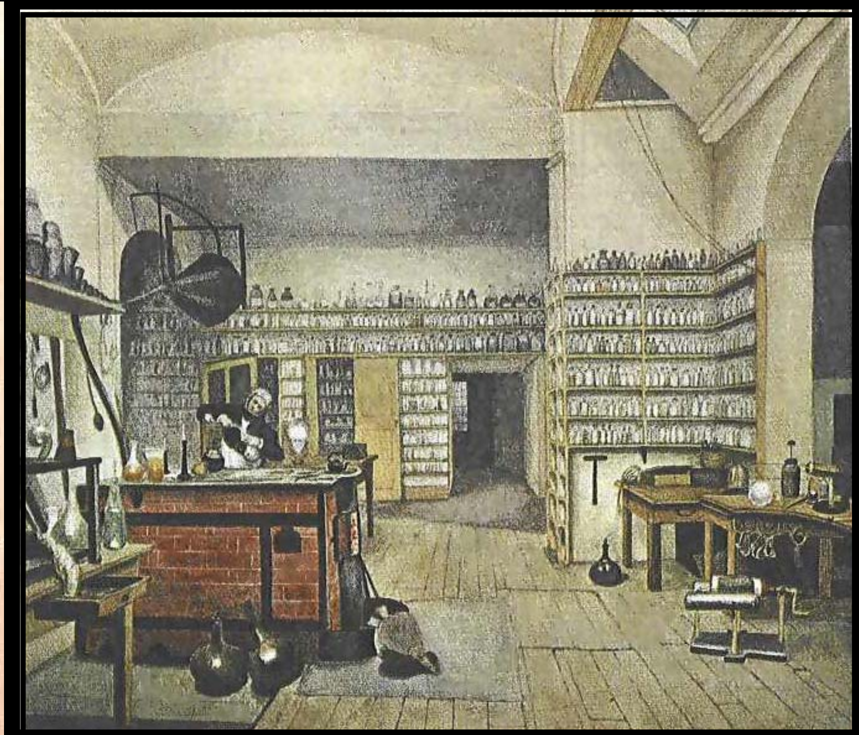
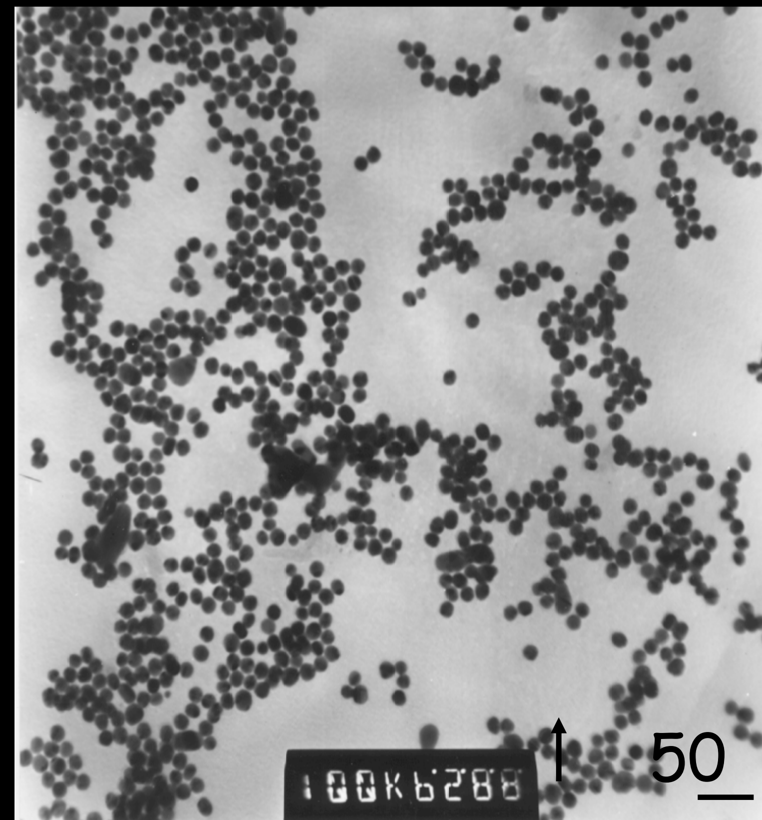


Faraday in his laboratory
Royal Institution



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 regards the action of light, and where they recur with other forms of gold, may be accepted as proof that

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 deflagrations by the voltaic battery lead to the same conclusion.

"The *gold 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
of evidence for their metallic nature. When
to chemical agents, both the thick and the
s have the same relations as pure metallic

ay 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."

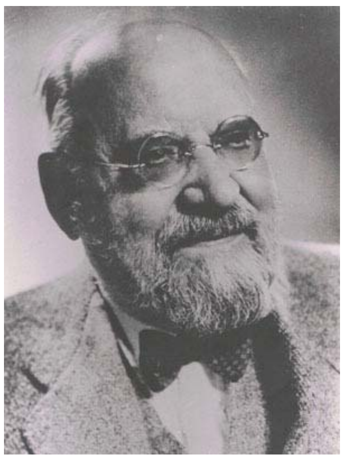
…they are simply cases of pure gold in a divided state; yet I have come to that conclusion, and believe that the differently-coloured fluids and particles are quite analogous….

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

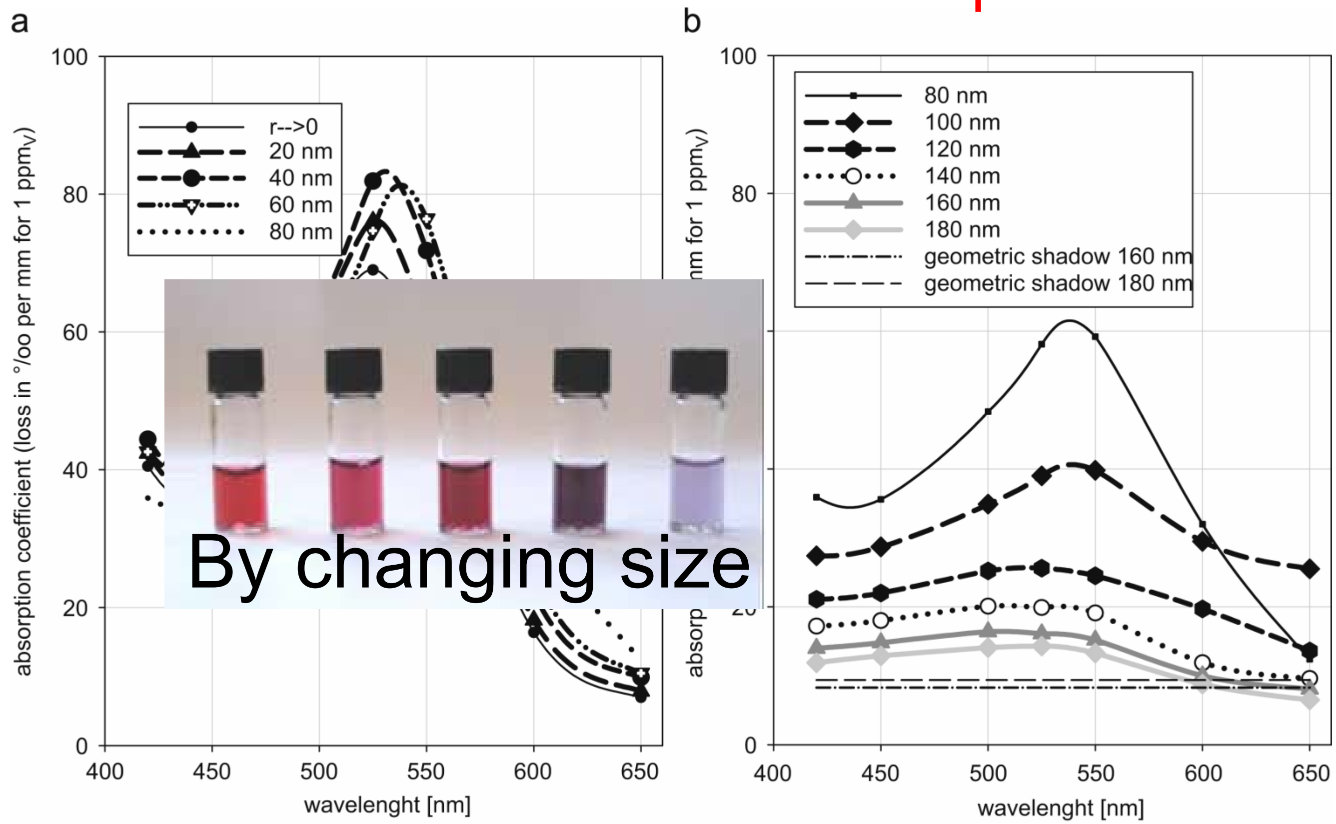
Gustav Mie (1868 - 1957)

1905

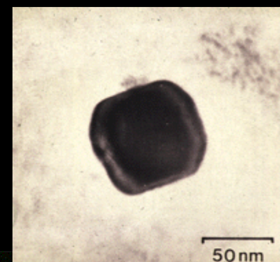
1940



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 .



Silicon dioxide in Lycurgus cup = 73%
Silicon dioxide in Modern Glass = 70%
Sodium oxide in Lycurgus cup = 14%
Sodium oxide in Modern Glass = 15%
Calcium oxide in Lycurgus cup = 7%
Calcium oxide in Modern Glass = 10%

So why is it coloured? The glass contains very small amounts of gold (about 40 parts per million) and silver (about 300 parts per million)

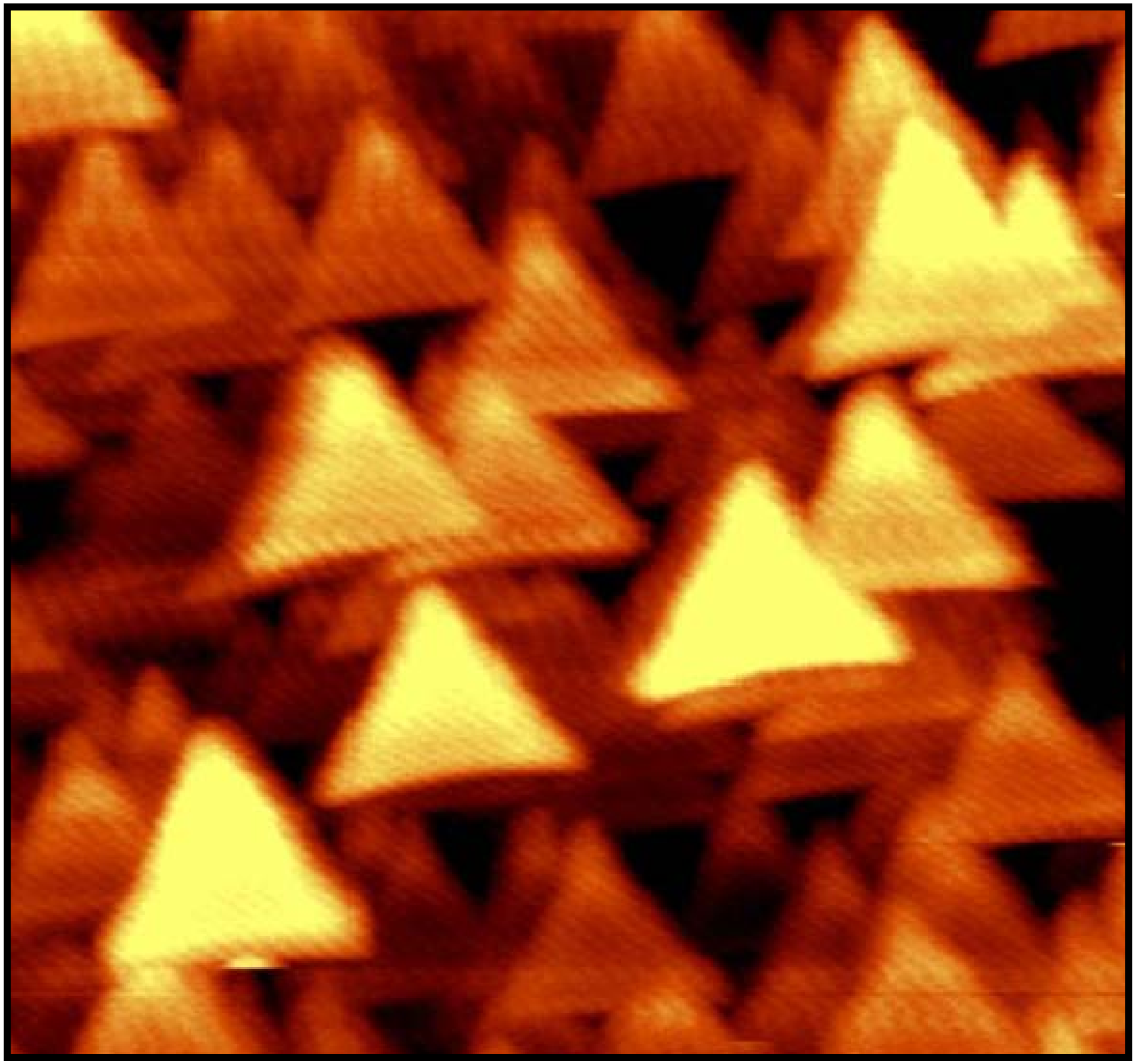
Lycurgus cup; in transmitting light (left) and in reflected light (right). From the site, http://www.thebritishmuseum.ac.uk.

Colours by changing shape

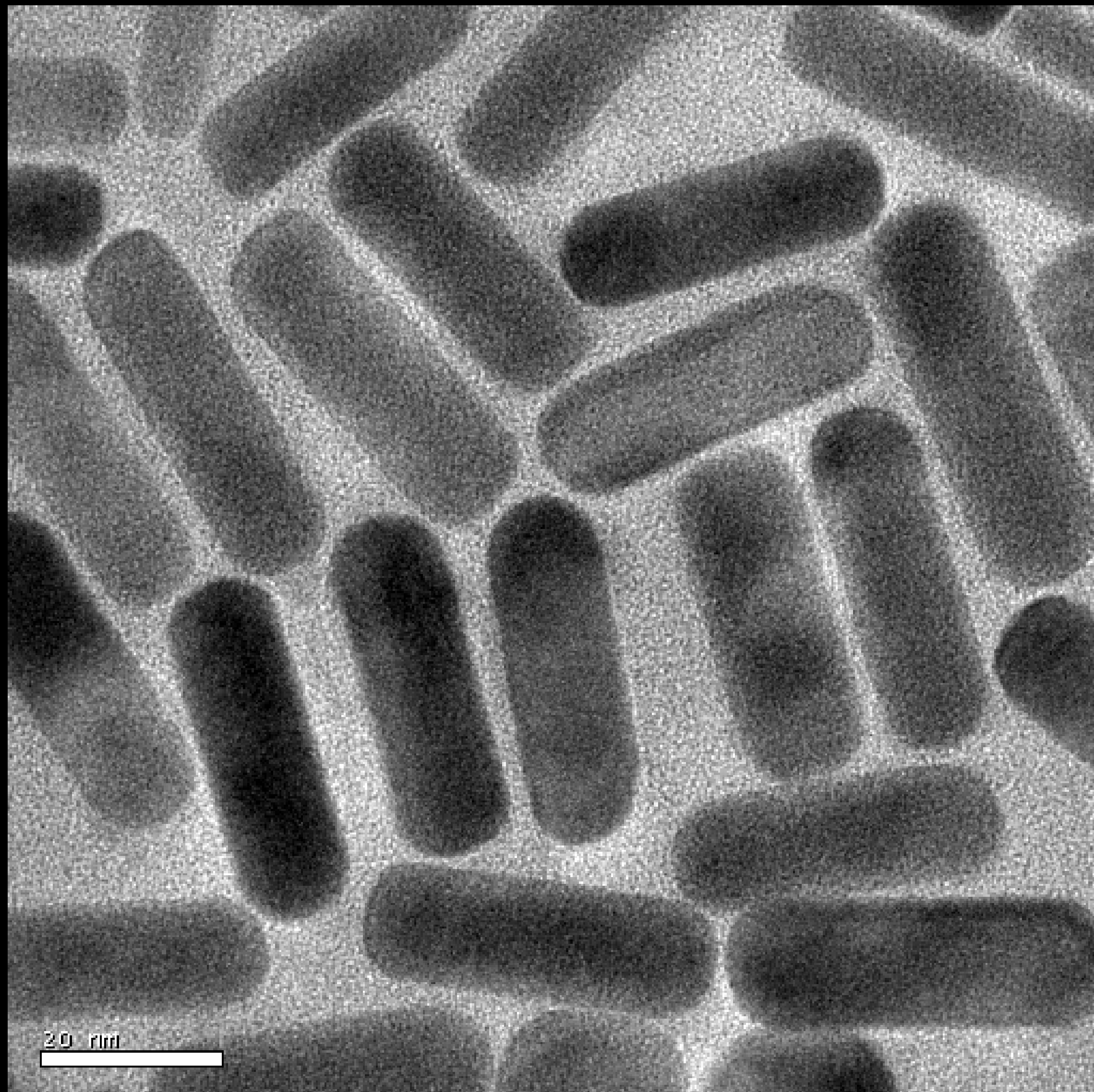
Shells

Gold shells. Nanoshells designed to absorb various wavelengths of light (the six vials on the right), including infrared (vial at far right) compared to gold colloid (far left). Used with permission from www.ece.rice.edu/people/faculty/halas.

Colours by changing shape



Sajanlal



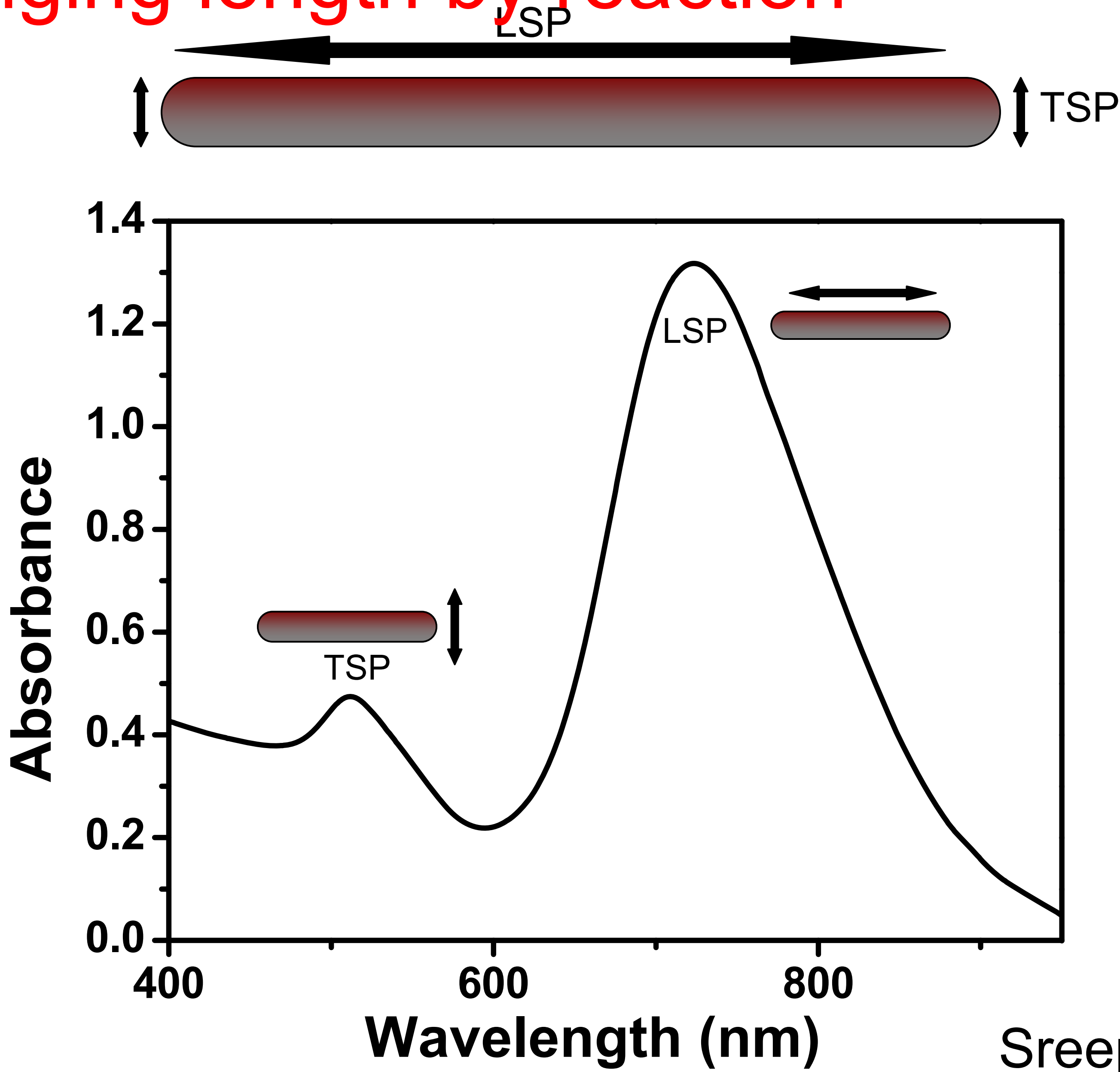
Samal

Materials are needed for chemistry

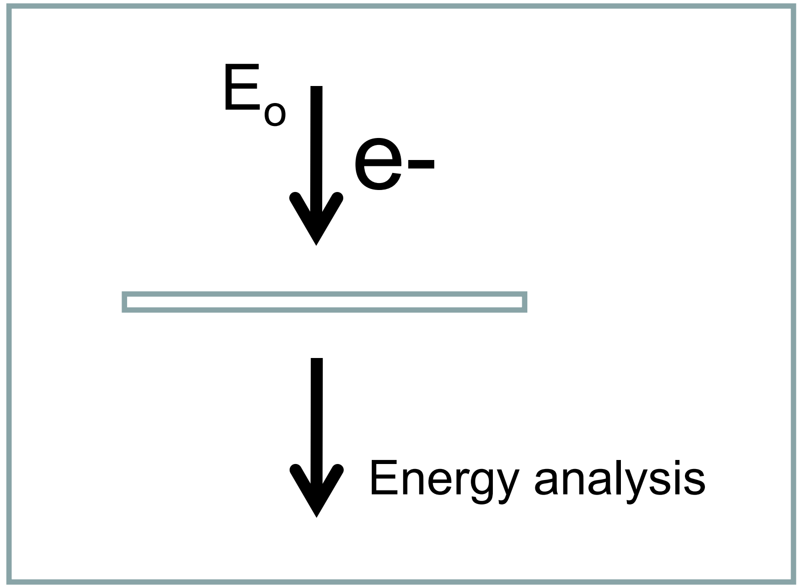
Nanorod Solution

Nanorod Powder

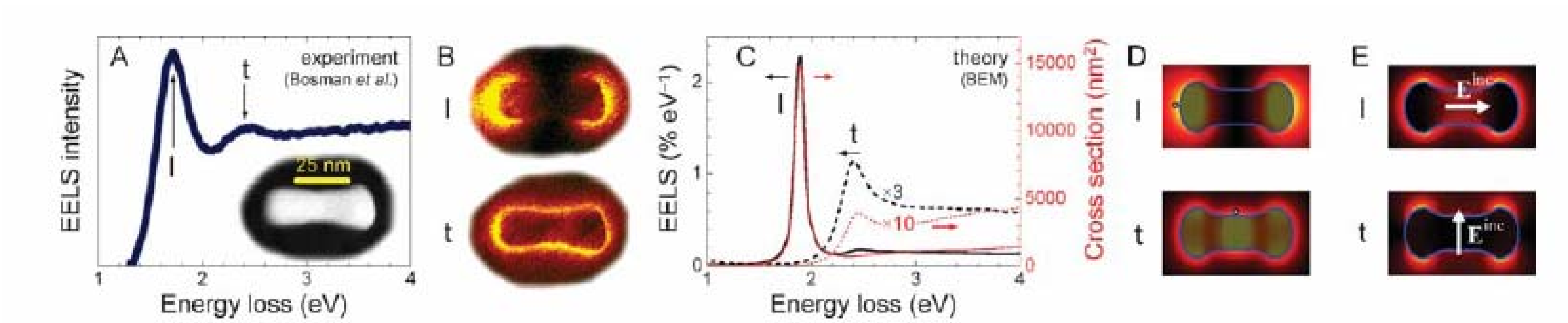
Changing length by reaction



Sreeprasad



EELS

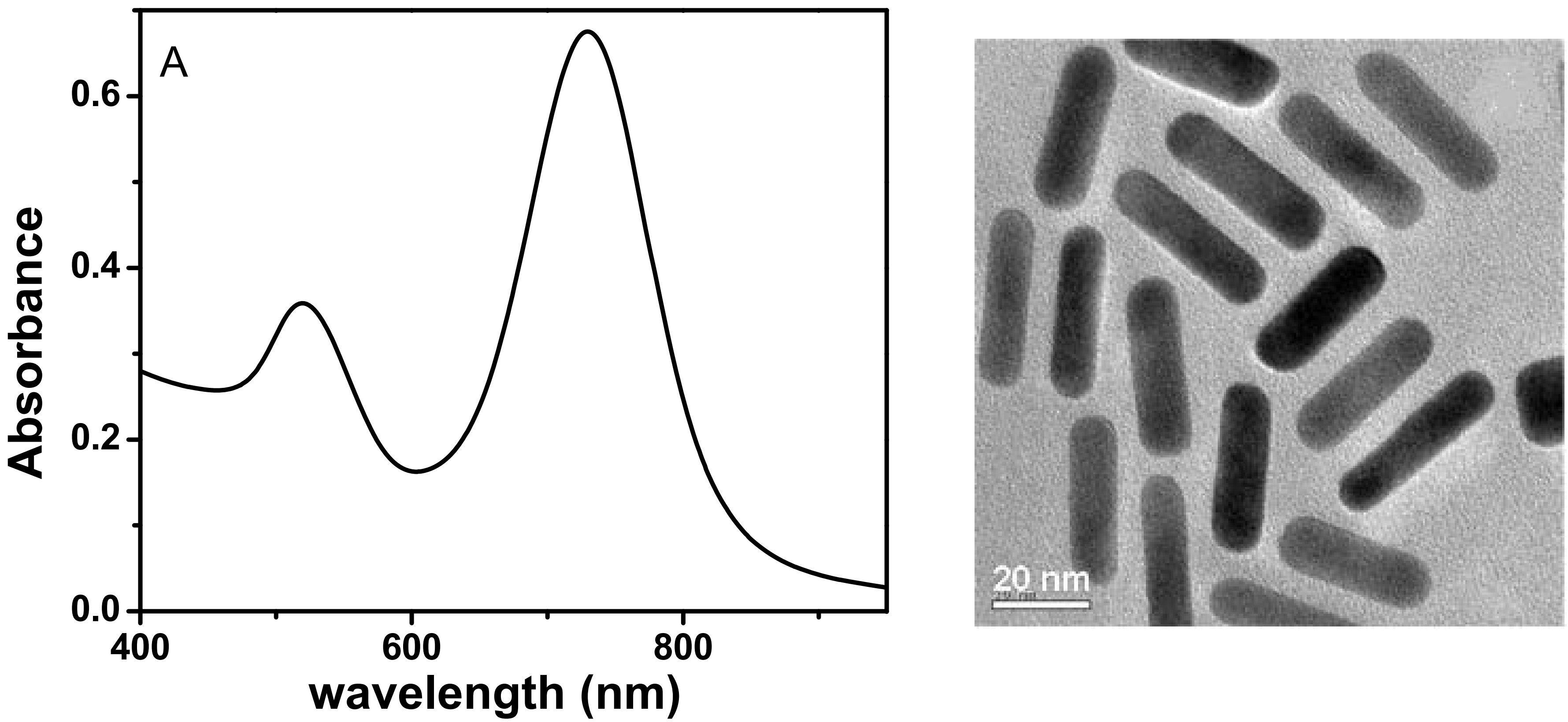


M. Bosman, V. J. Keast, M. Watanabe, A. I. Maaroof, M. B. Cortie, Nanotechnology, 2007, 18, 165505.

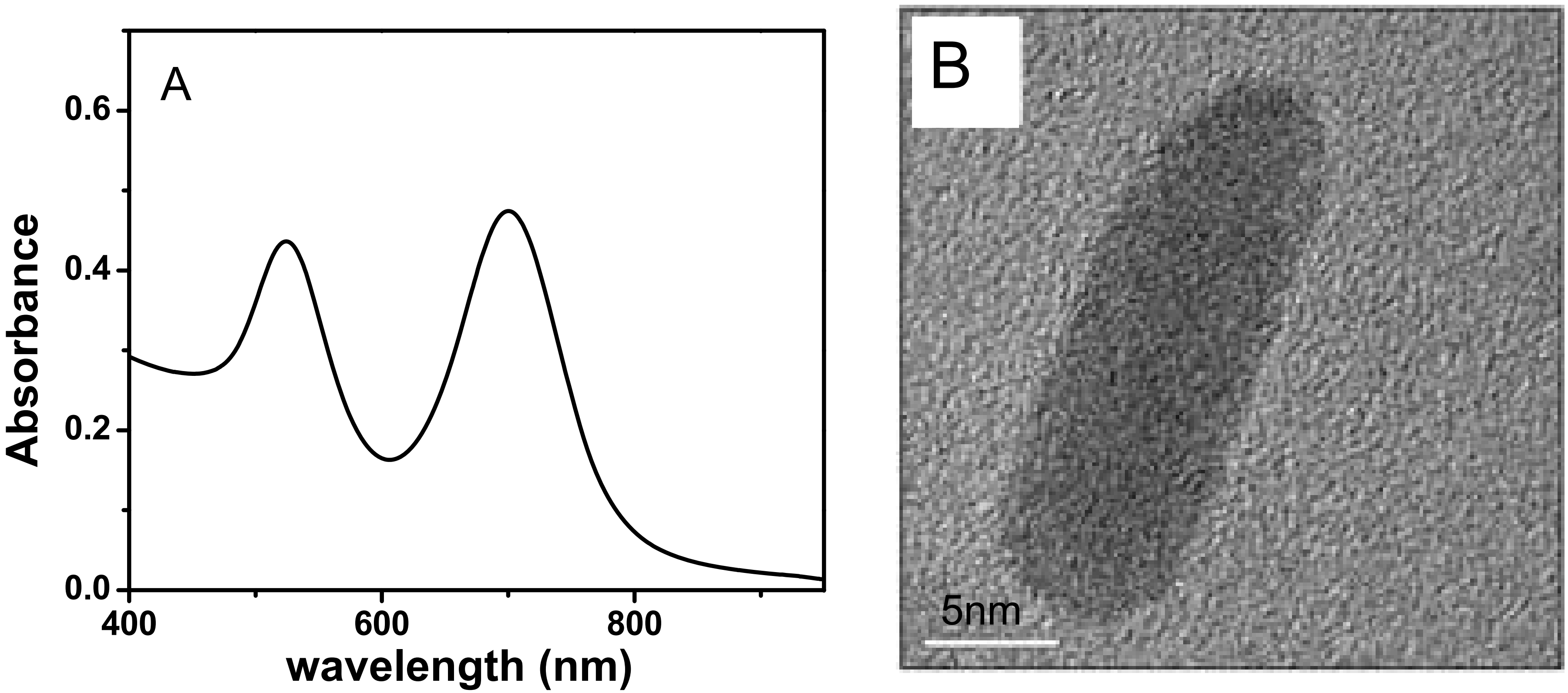

Electron Microscopy (HRTEM) of Nanomaterials

The reaction

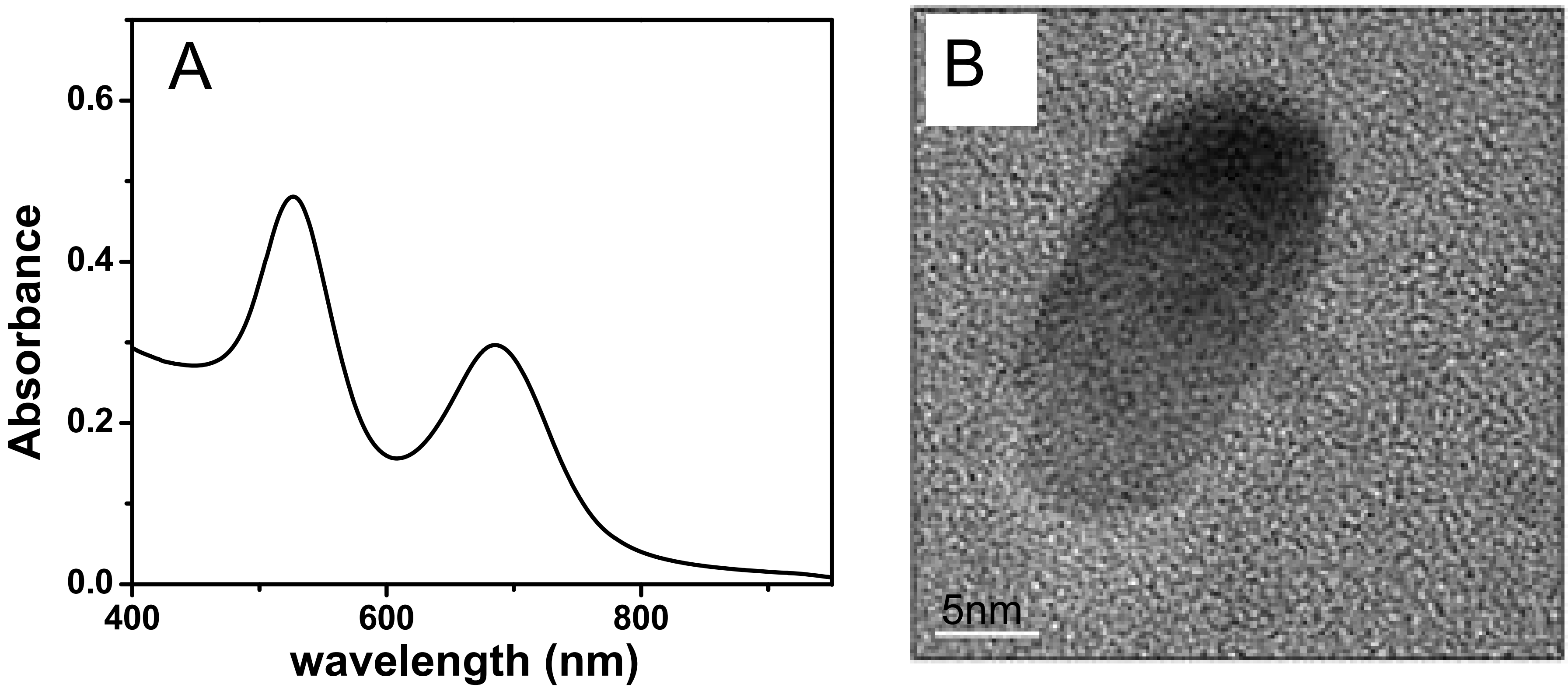
$$\xrightarrow[CuCl_2]{70\ ^oC}\ t$$



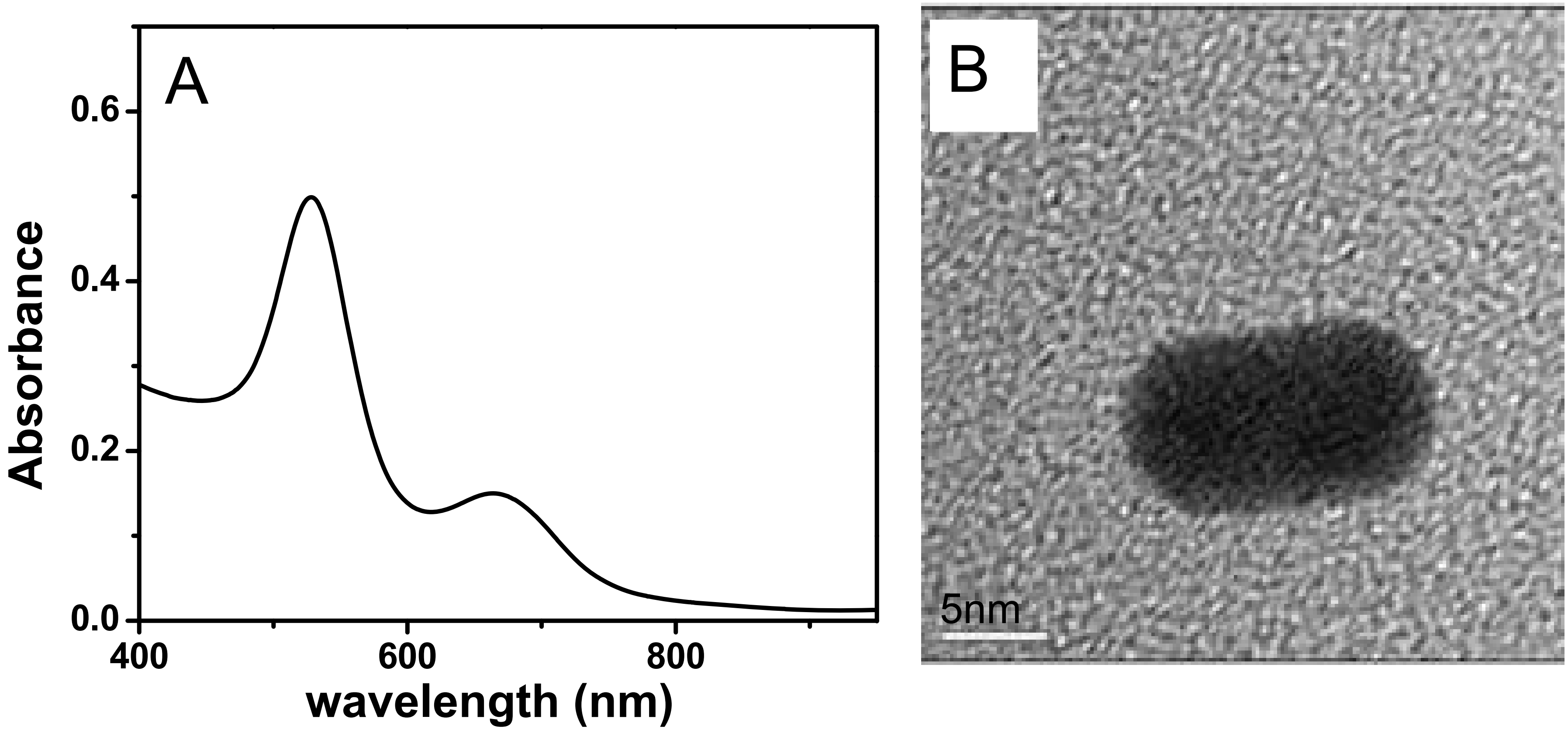
(A)UV-visible spectrum of the starting nanorod and (B) TEM image



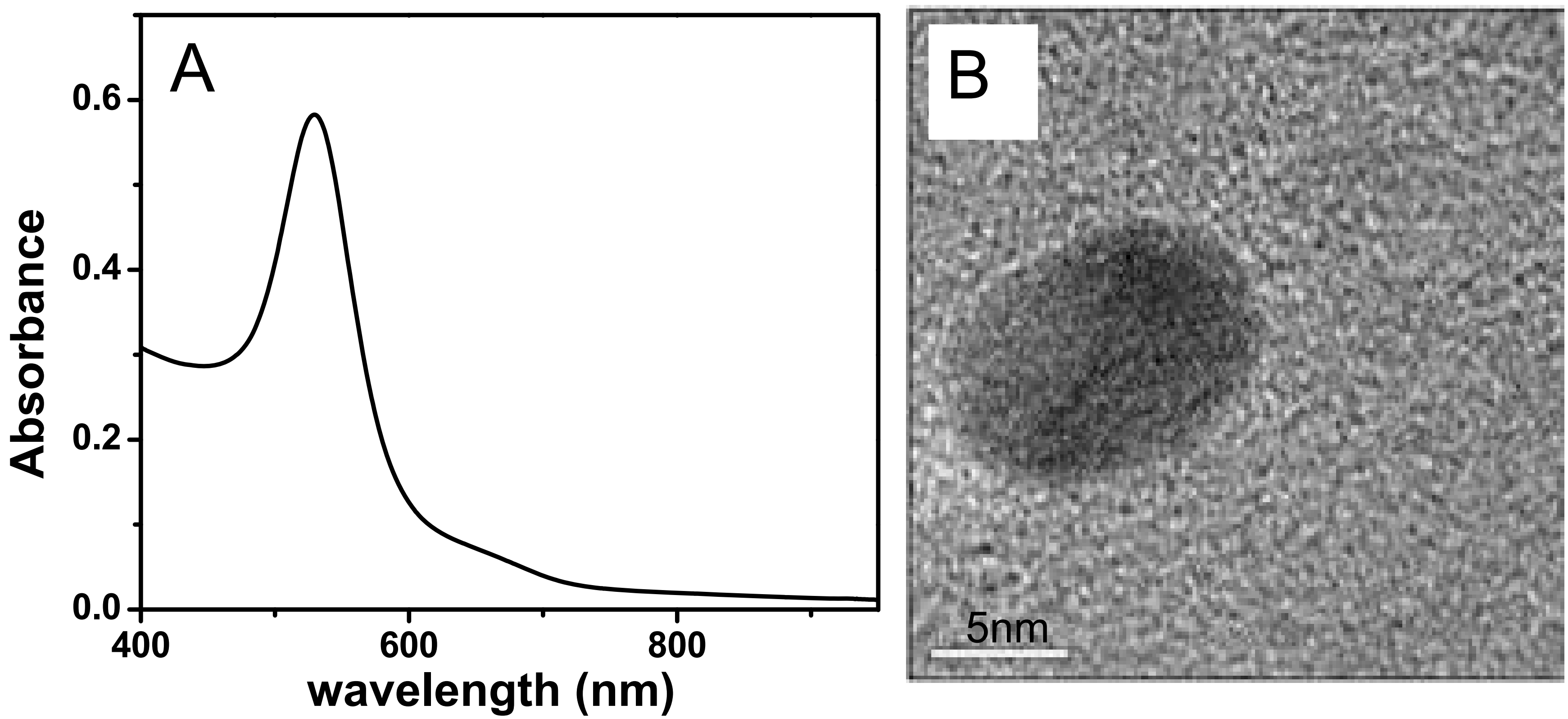
(A) UV-visible spectrum acquired after 1 h of reaction between gold nanorods and $CuCl_2$. TEM taken from the same sample.



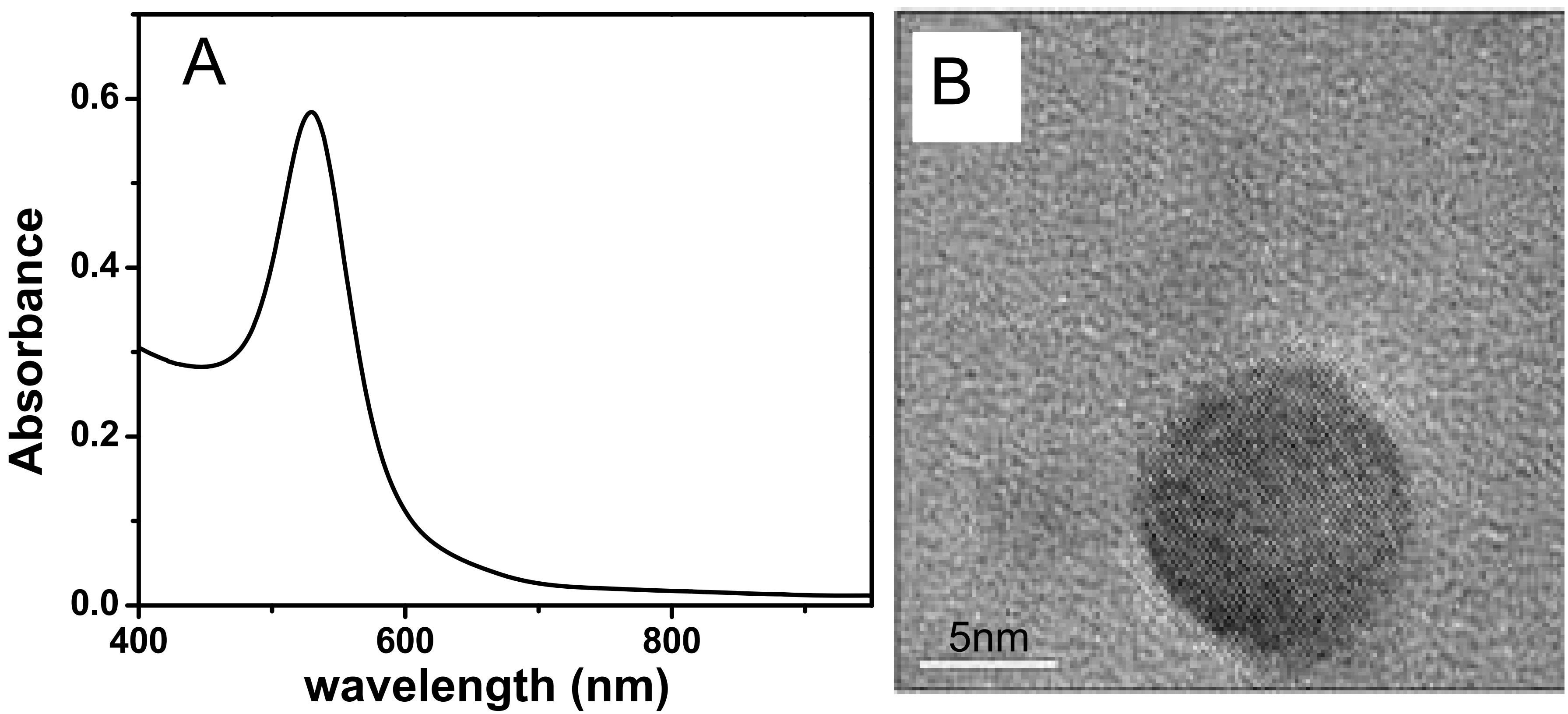
(A) UV-visible spectrum acquired after 2 h of reaction between gold nanorods and $CuCl_2$. TEM taken from the same sample.



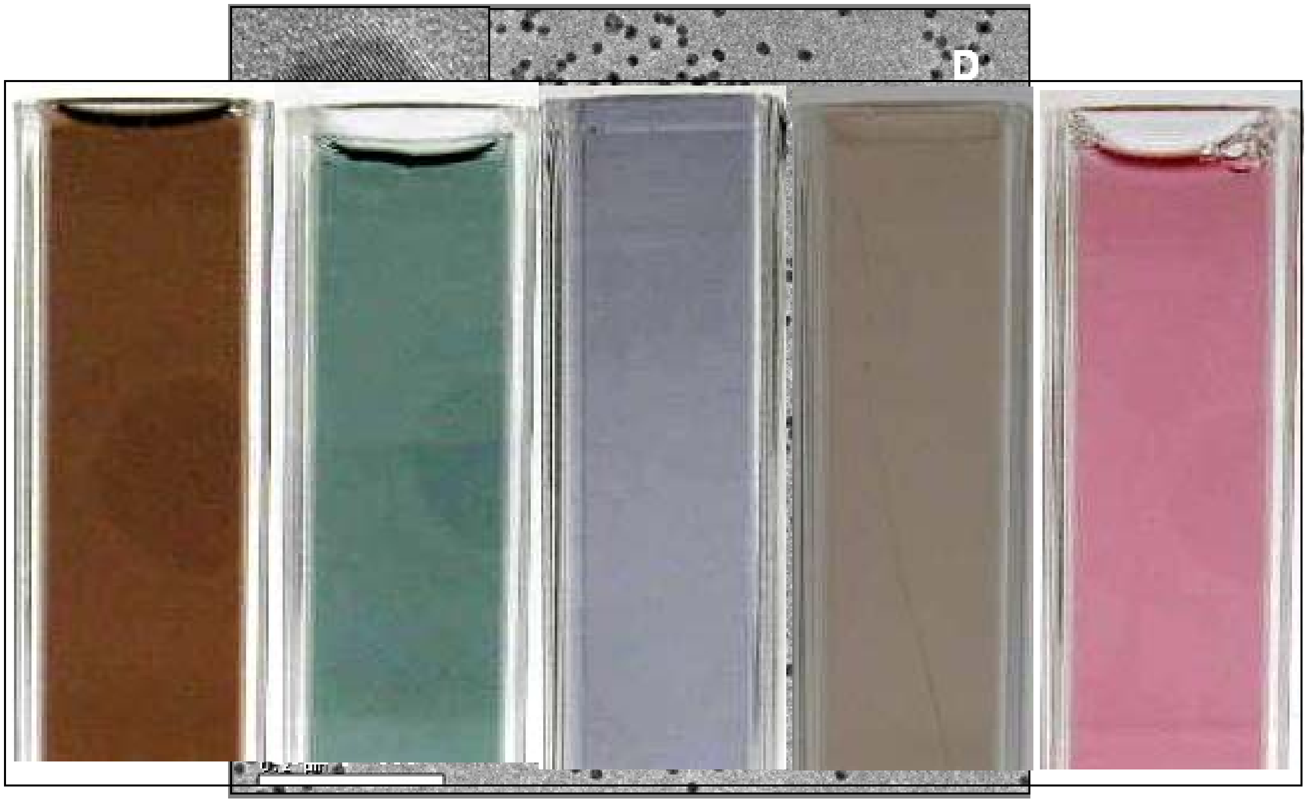
(A) UV-visible spectrum acquired after 3h of reaction between gold nanorods and $CuCl_2$. TEM taken from the same sample.



(A) UV-visible spectrum acquired after 4h of reaction between gold nanorods and $CuCl_2$. TEM taken from the same sample.

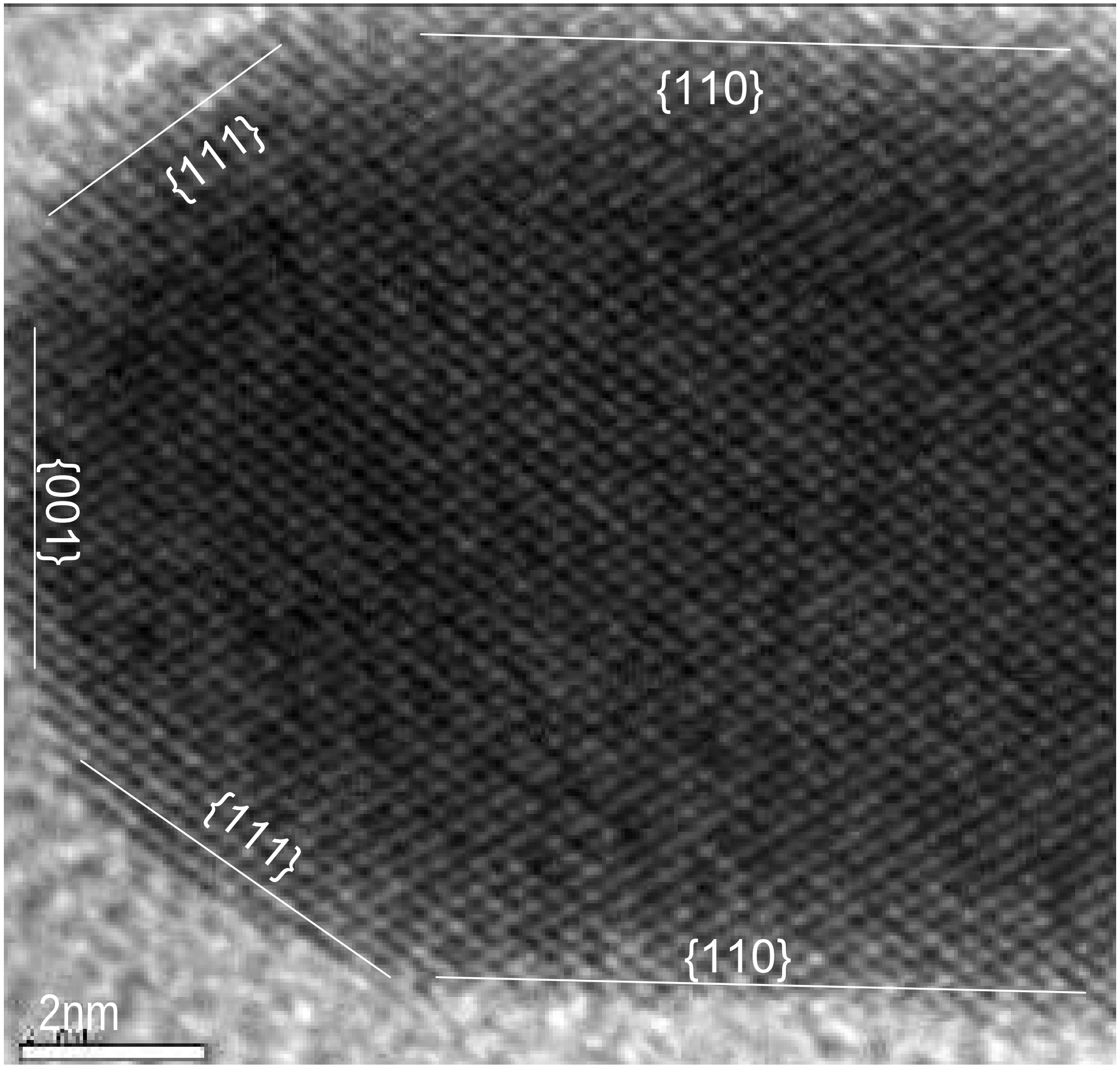


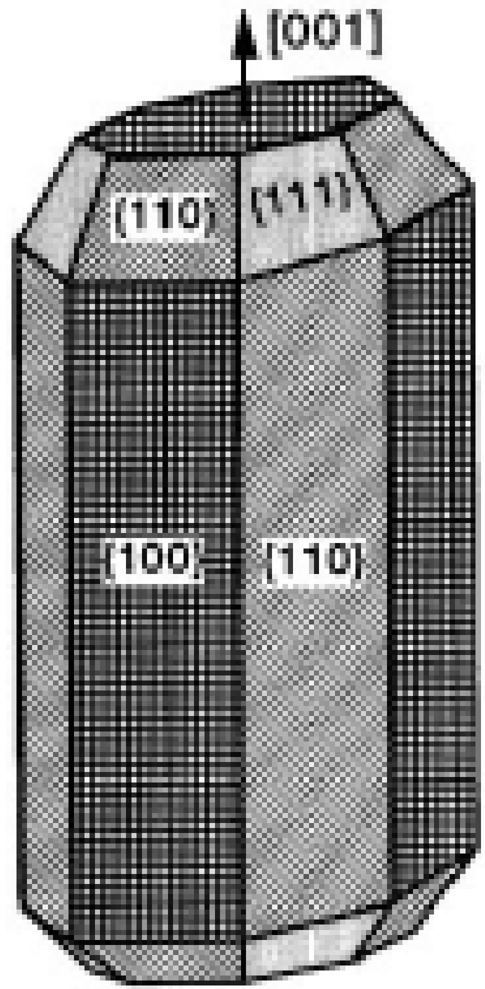
(A) UV-visible spectrum acquired after 5h of reaction between gold nanorods and $CuCl_2$. TEM taken from the same sample.



Any shape can be prepared by arresting the reaction

Why should the rod do that?





A structural model of the Au nanorod.

Wang, Z. L.; Mohamed, M. B.; Link, S.; El-Sayed, M. A. *Surf.Sci*. 1999, *440*, L809.

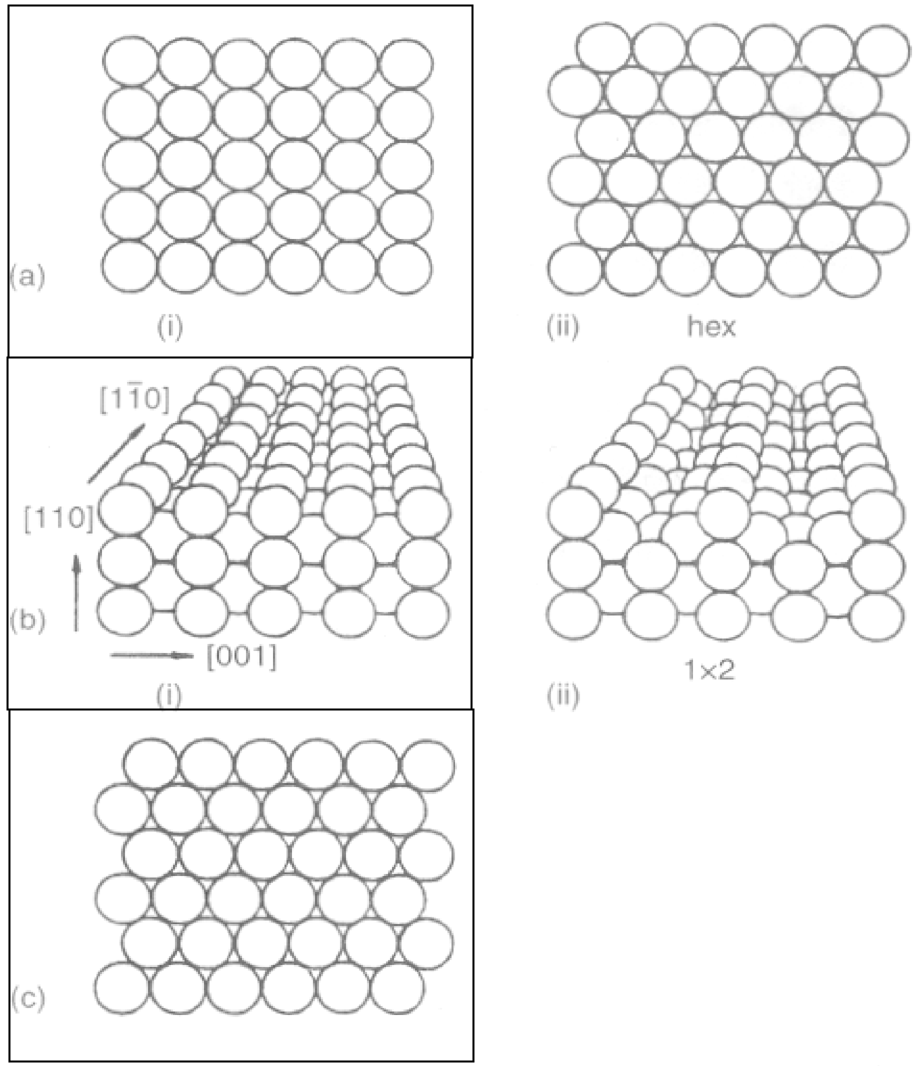
Reconstruction

Surface Energies

(100) — 0.66 J m^{-2}

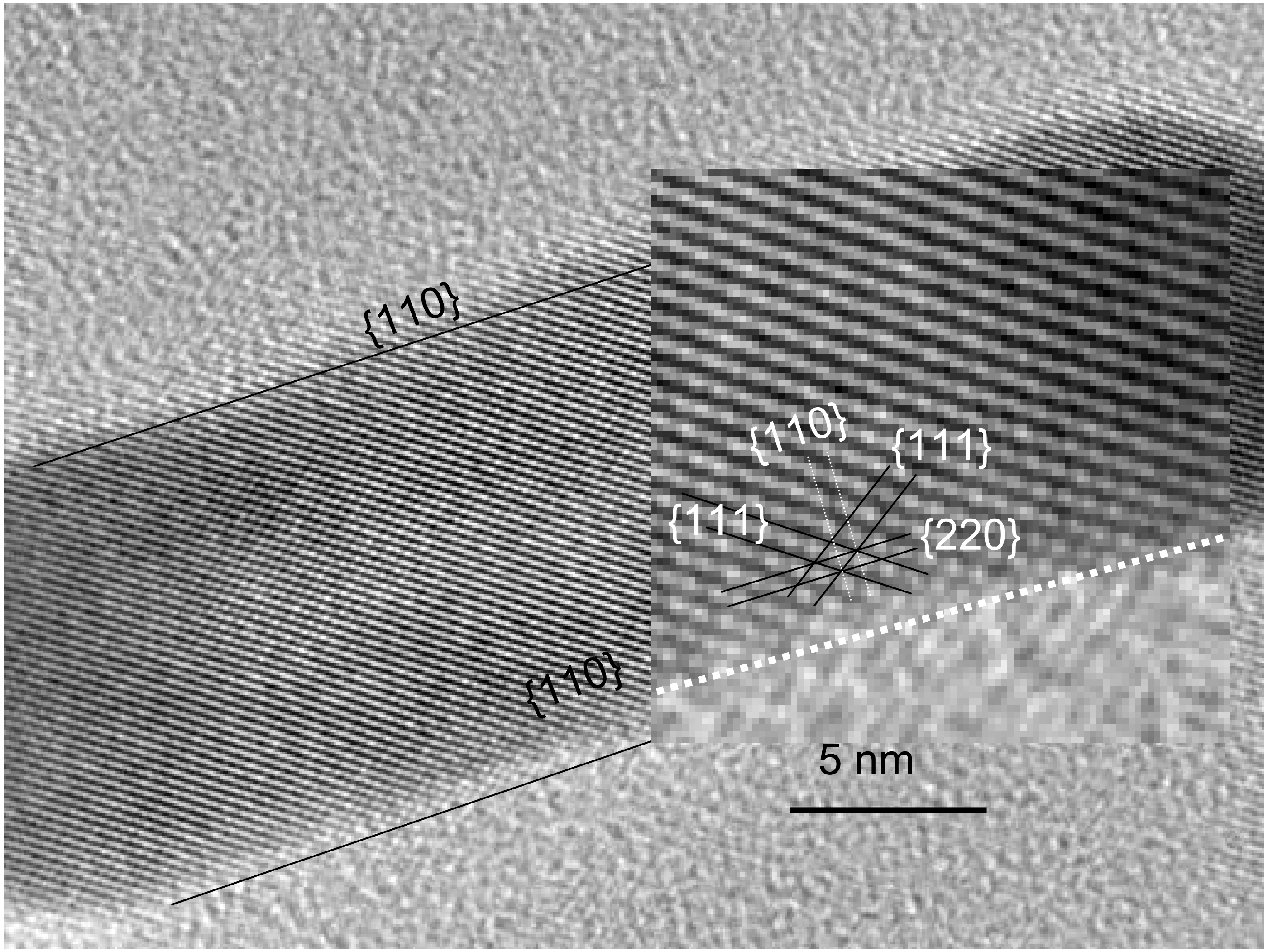
(110) — 0.70 J m^{-2}

(111) — 0.58 J m^{-2}

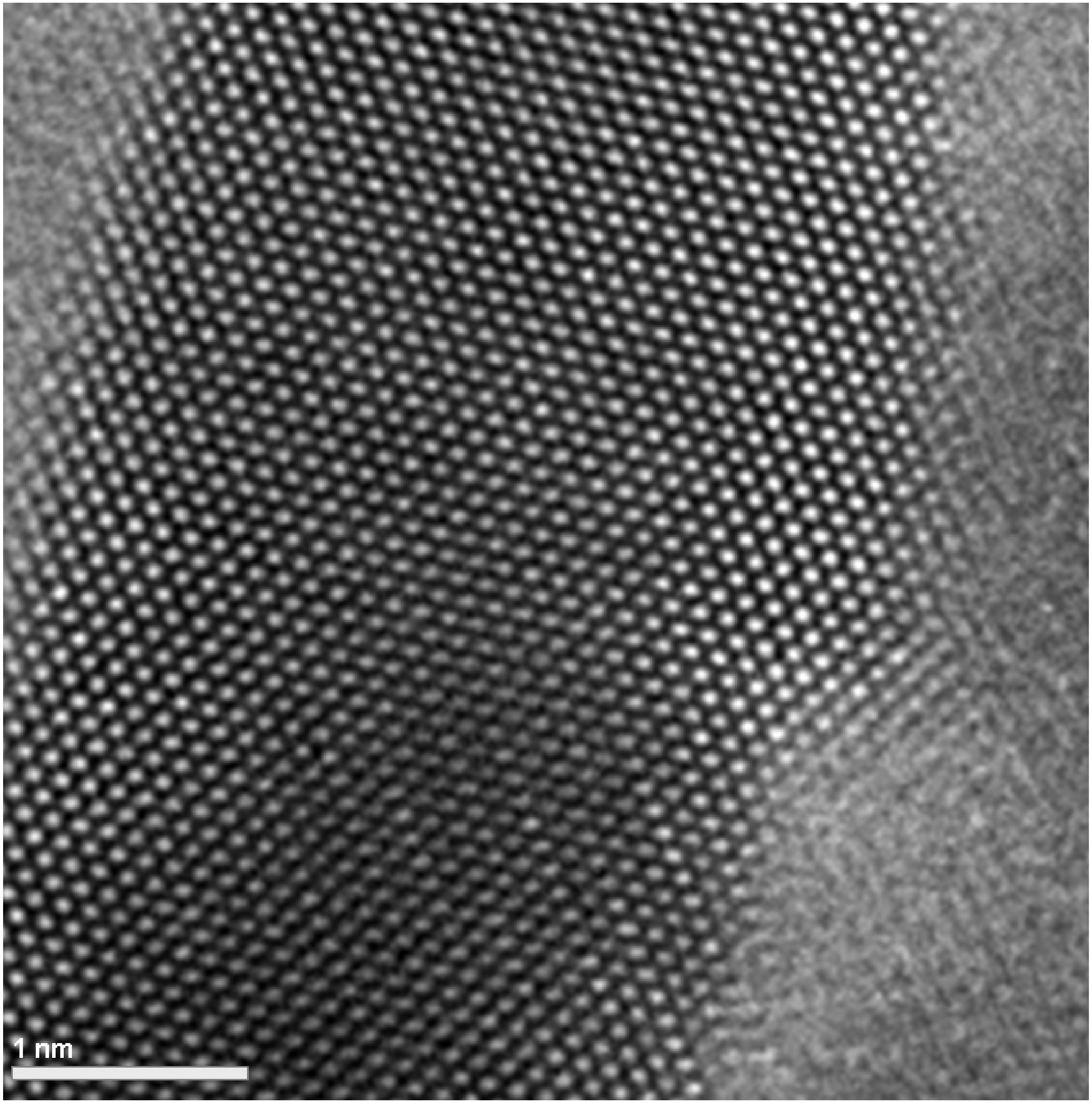


planes

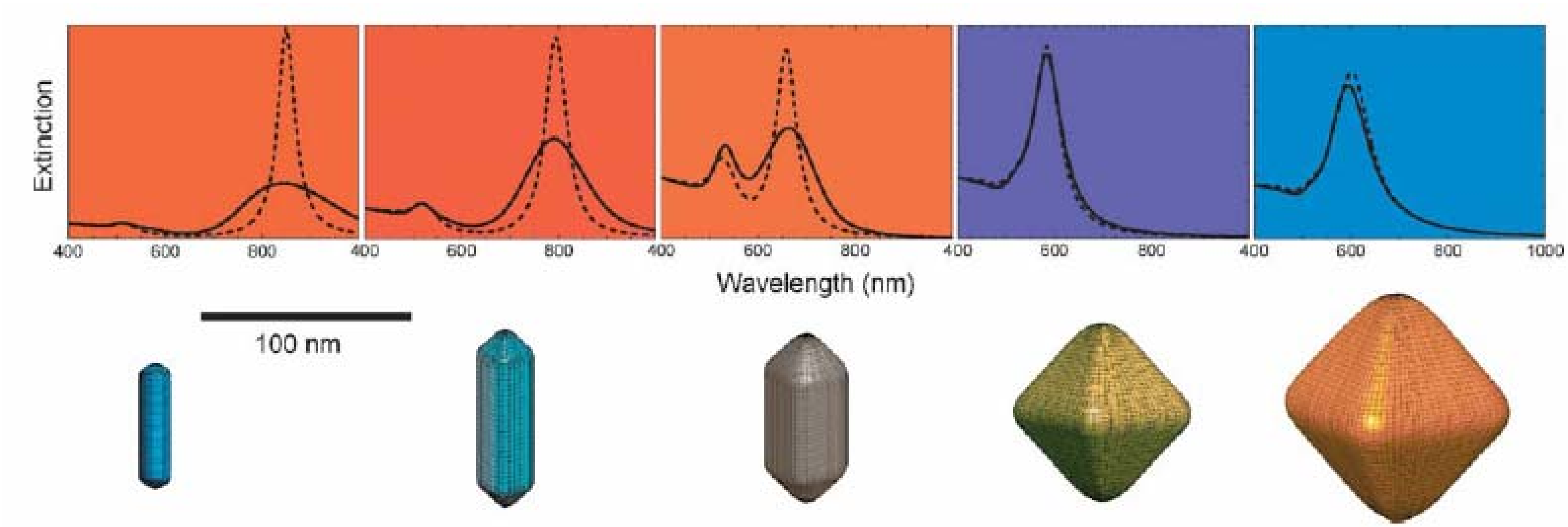
(a) Todd, B. D.; Lynden-Bell, R. M. *Surf. Sci.* 1993, *281*, 191. (b) Uppenbrink, J.; Johnston, R. L.; Murrell, J. N. *Surf. Sci.* 1994, *304*, 223.



{110}
{110}
{111}
{111}
{110}
{220}
5 nm

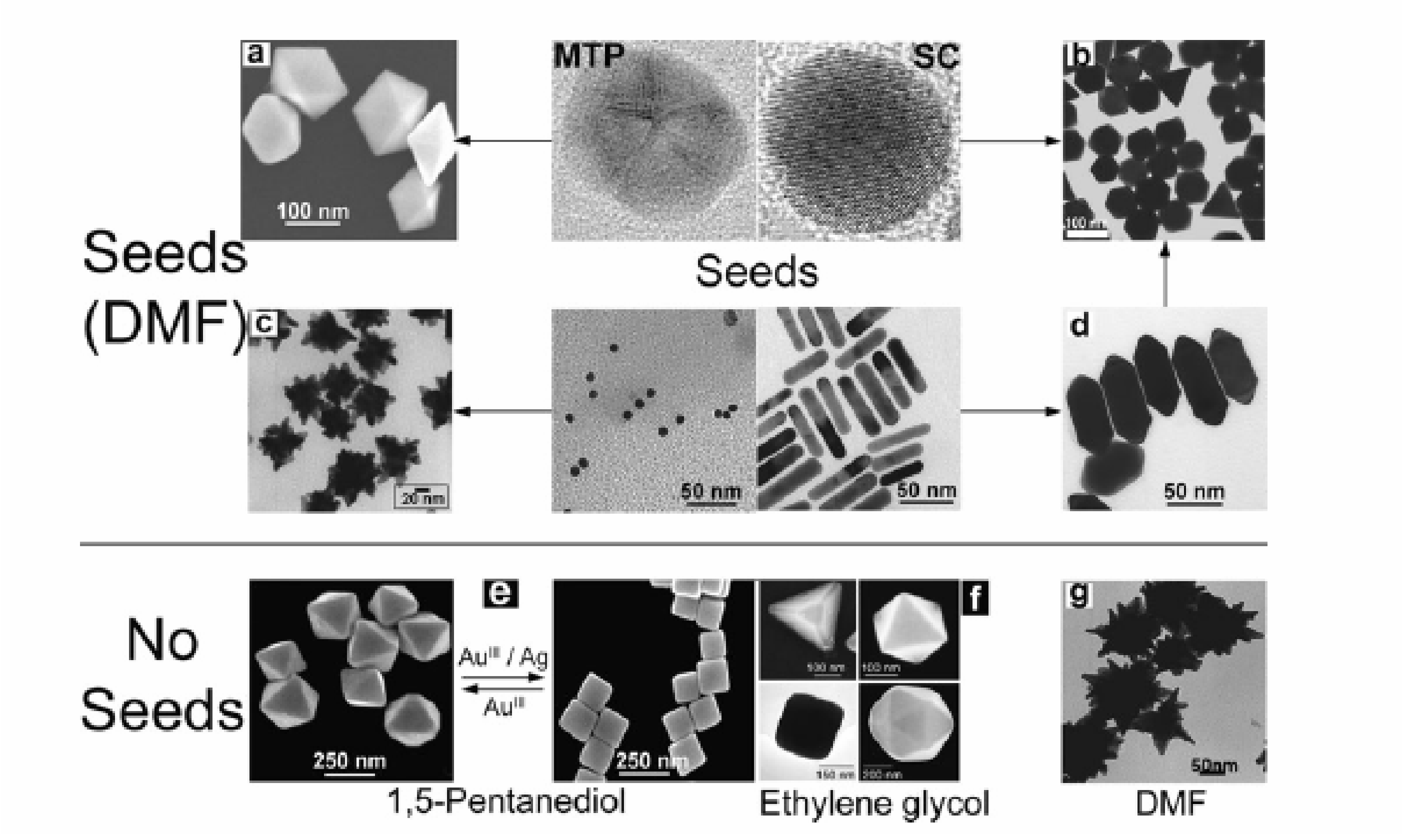

1 nm

Colours with octahedra



E. Carbo-Argibay, B. Rodriguez-Gonzalez, J. Pacifico, I. Pastoriza-Santos, L. M. Liz-Marzan, Angew. Chem. Int. Ed. 2007, 46, 8983.

Colours by assorted shapes

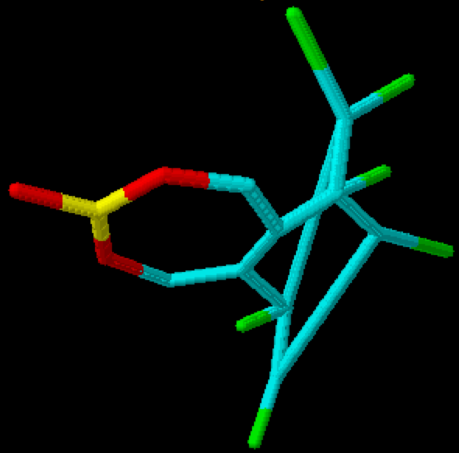


M. Grzelczak, J. Perez-Juste, P. Mulvaney and L. M. Liz-Marzan, Chem. Soc. Rev. 2008, 37, 1783-1791.

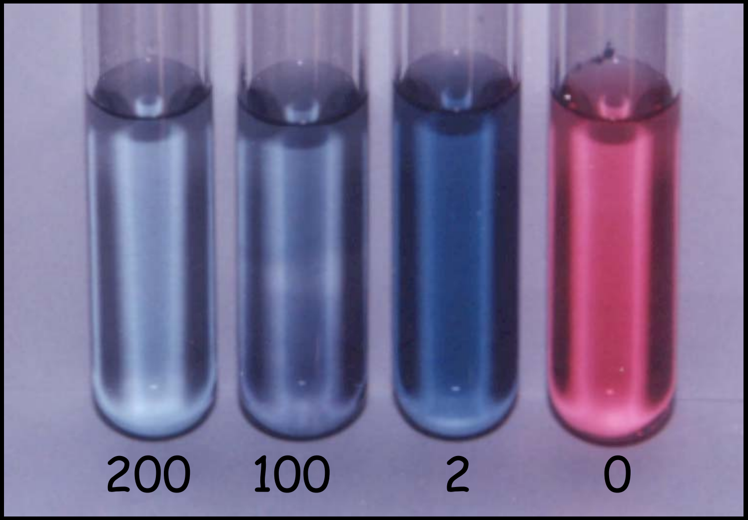
Colour by surface modification

Color of gold nanoparticles with endosulfan

Example



Endosulfan

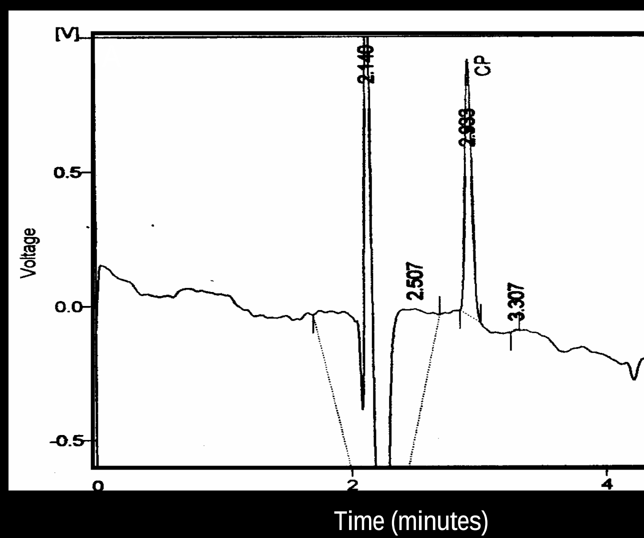


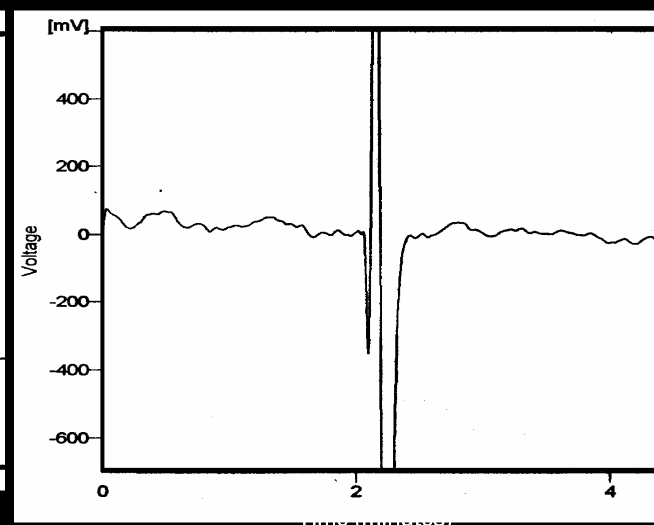
Endosulfan concentration in ppm

Color changes with pesticide concentration
Good response at lower concentrations
Down to 0.1 ppm
Adsorbed pesticides can be removed from solution

J. Environ. Monitoring. 2003

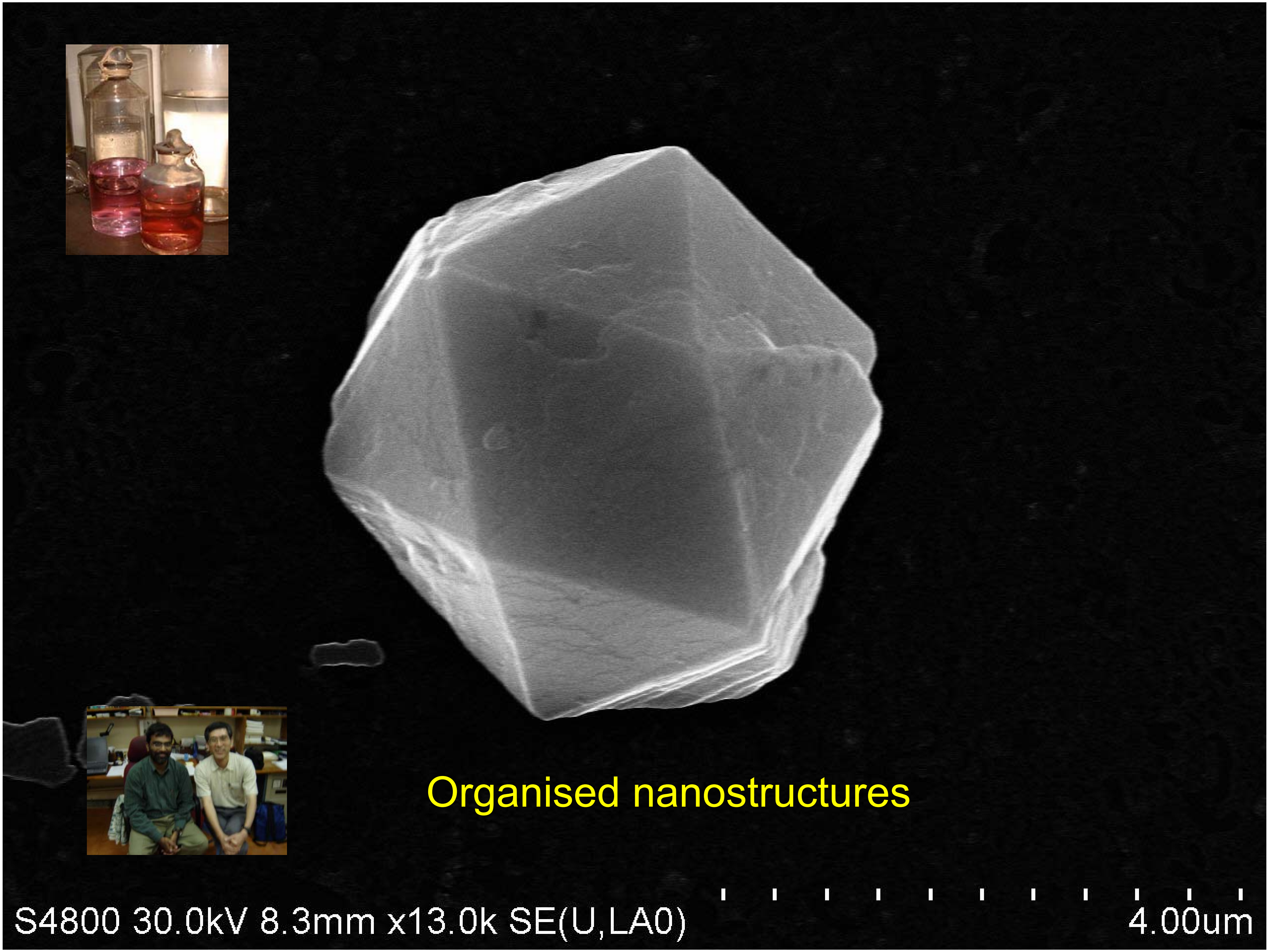
Pesticide removal from drinking water

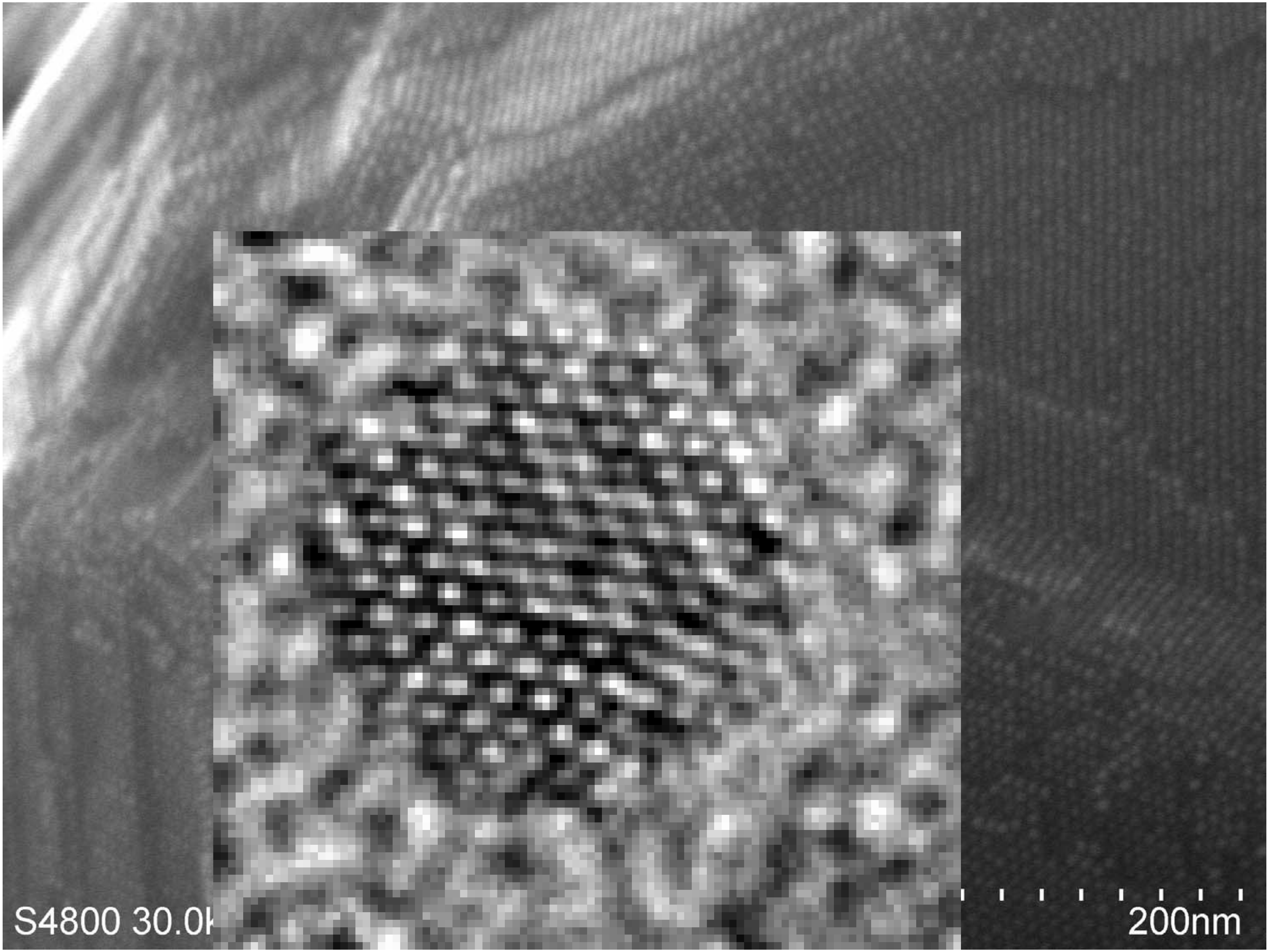




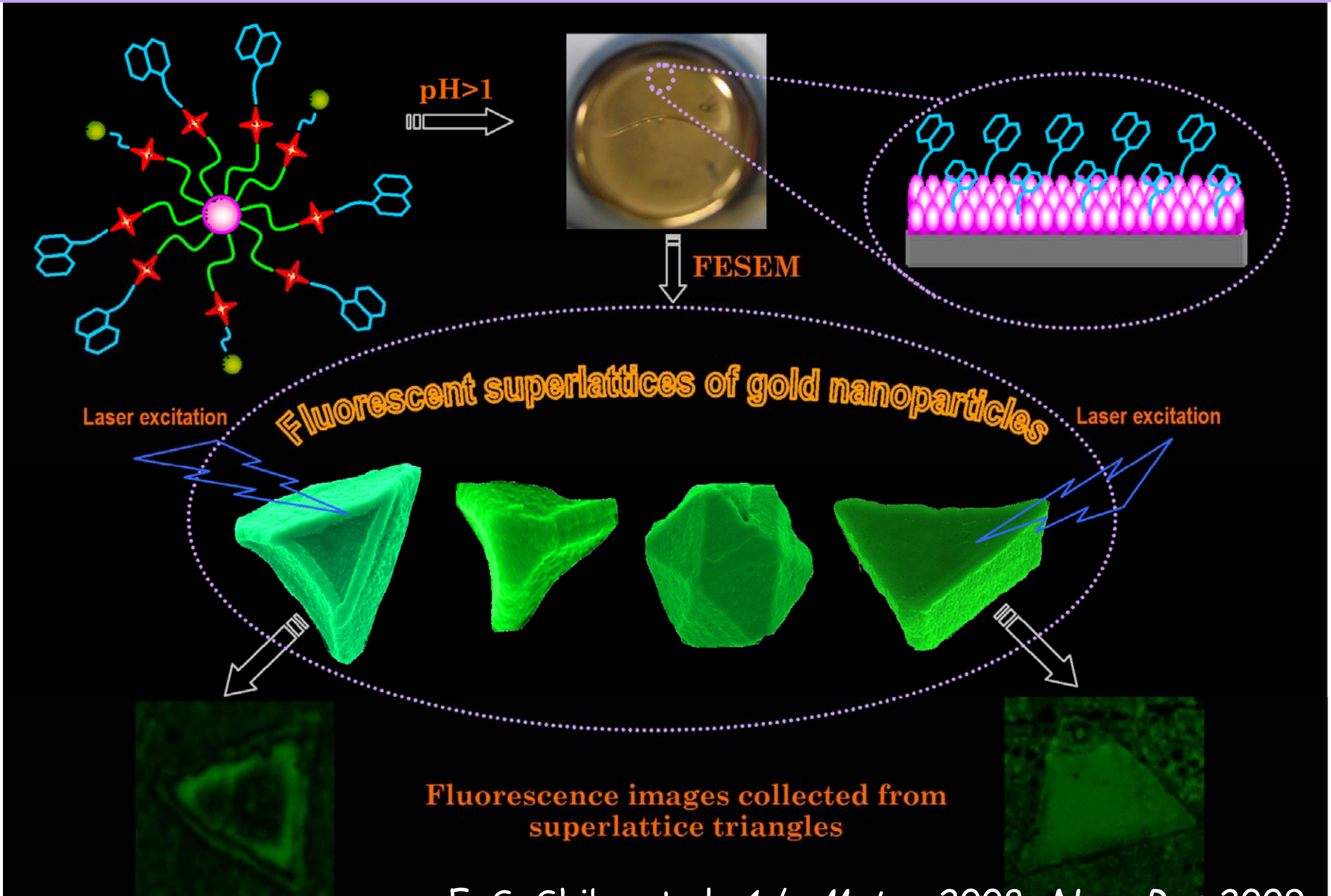
Indian patent granted
PCT application filed
Technology transferred
Product is in the market


HEATING VESSEL
2007 1 16


Organised nanostructures
S4800 30.0kV 8.3mm x13.0k SE(U,LA0)
4.00um

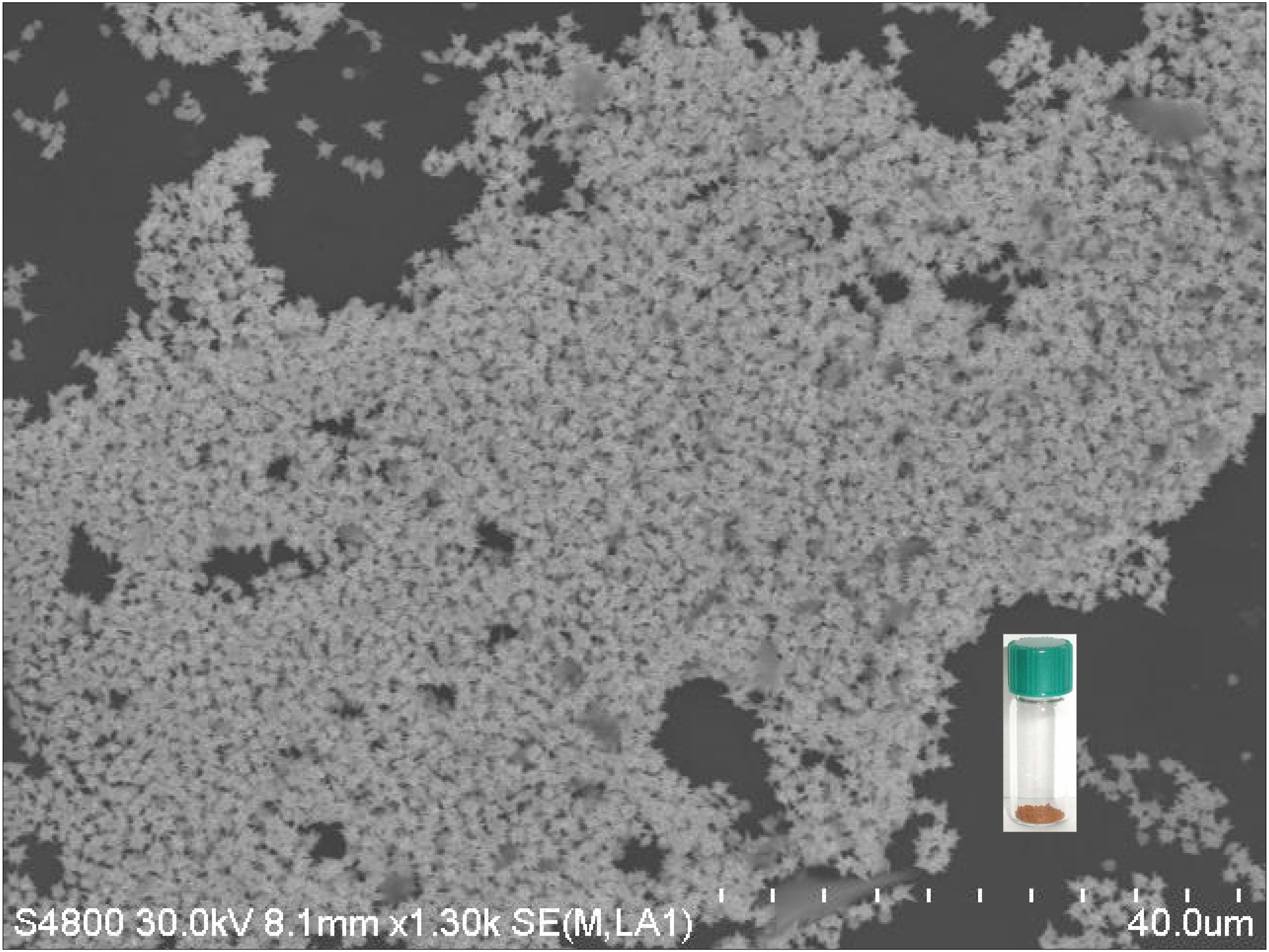

S4800 30.0k
200nm

Colours by organisation



E. S. Shibu et al. *Adv. Mater.* 2008; *Nano Res.* 2009


Mesoflowers
Sajanlalal and Pradeep – *Nano Res.* 2009


S4800 30.0kV 8.1mm x1.30k SE(M,LA1)
40.0um

First report- catalysis by gold nanoparticle

M. HARUTA

JOURNAL OF CATALYSIS 115, 301–309 (1989)

Gold Catalysts Prepared by Coprecipitation for Low-Temperature Oxidation of Hydrogen and of Carbon Monoxide

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*Government Industrial Research Institute of Osaka, Midorigaoka 1, Ikeda 563, Japan; †Kishida Chemicals Company, Ltd., Joshoji-machi, Kadoma 571, Japan; and ‡Research Development Corporation of Japan, Science Building, 5-2 Nagata-cho 2-chome, Tokyo 100, Japan

Received October 7, 1987; revised June 6, 1988

Novel gold catalysts were prepared by coprecipitation from an aqueous solution of $HAuCl_4$ and the nitrates of various transition metals. Calcination of the coprecipitates in air at 400°C produced ultrafine gold particles smaller than 10 nm which were uniformly dispersed on the transition metal oxides. Among them, Au/α-Fe_2O_3, Au/Co_3O_4, and Au/NiO were highly active for H_2 and CO oxidation, showing markedly enhanced catalytic activities due to the combined effect of gold and the transition metal oxides. For the oxidation of CO they were active even at a temperature as low as −70°C.

INTRODUCTION

During the course of an investigation into new oxide catalysts useful for the low-temperature catalytic combustion of hydrogen (*1–4*), it became evident that the catalytic activities of transition metal oxides for hydrogen oxidation had a volcano-like relation with the heat of formation of oxides per gram-atom of oxygen (*5*). The volcano relation indicates that the formation of metal–oxygen (*M*–O) bonds is rate determining for the oxides of Ag and Au, which are located on the left side, while the breaking of *M*–O bonds is the slow step for the other metal oxides located on the right side. Therefore, an attempt was made to develop composite oxides of Ag with the 3*d* transition metals, for which an enhancement in both catalytic activity and thermal stability was expected.

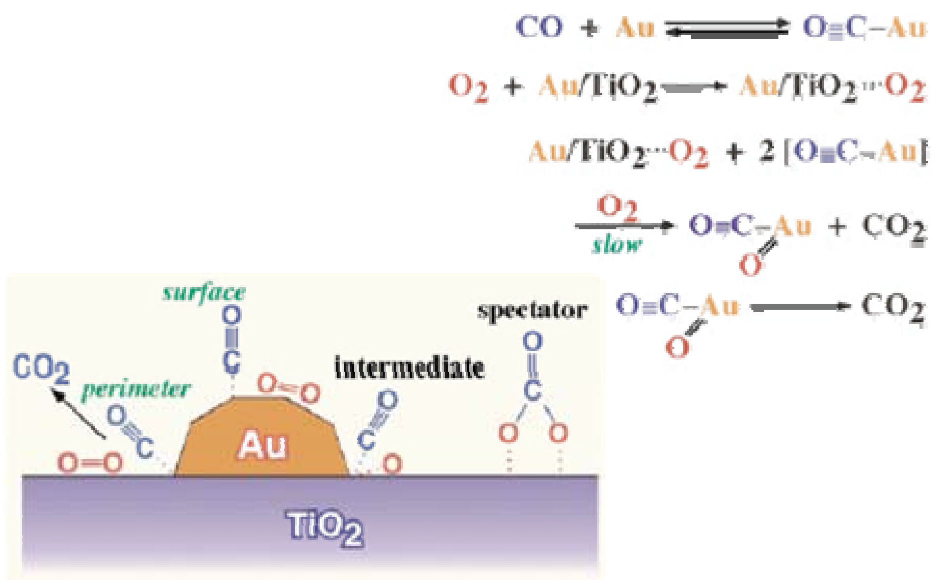
Our earlier paper (*5*) reported that an appreciable enhancement in catalytic activity was, in fact, achieved in some composite oxides of silver with 3*d* transition metals which were prepared by coprecipitation. Specifically, a mixed oxide composed of Co, Mn, and Ag (20 : 4 : 1 in atom ratio) was both thermally stable and highly active for the oxidation of H_2 and CO. The successful results obtained for these composite oxides of silver led us to expect that a significant enhancement in catalytic activity might also be exhibited by composites of gold and the other metal oxides. The present investigation into gold-based oxide catalysts was undertaken to test this hypothesis.

Previous work on gold catalysts has been reviewed by several authors (*6–10*). All the gold catalysts investigated so far are gold supported on inactive ceramic oxides, such as SiO_2 (*11–17*), Al_2O_3 (*14–16, 18*), MgO (*15–17, 19*), and TiO_2 (*20*), or unsupported gold filaments (*21*), powder (*22, 23*), sponges (*24*), filings (*25*), and gauze (*26*).

The chemical reactivity of gold catalysts has been studied for the oxidation by oxygen or nitrogen oxides of CO (*11, 22, 24, 26*) and H_2 (*12, 15, 17, 21–23*), selective oxidation of organic compounds by nitrogen dioxide (*13*), hydrogenation of alkenes (*7*), and so on. However, the conventional gold catalysts prepared by impregnation have been reported to be usually far less active than platinum-group metal catalysts, although they are superior in selectivity for only a few reactions such as the oxidation

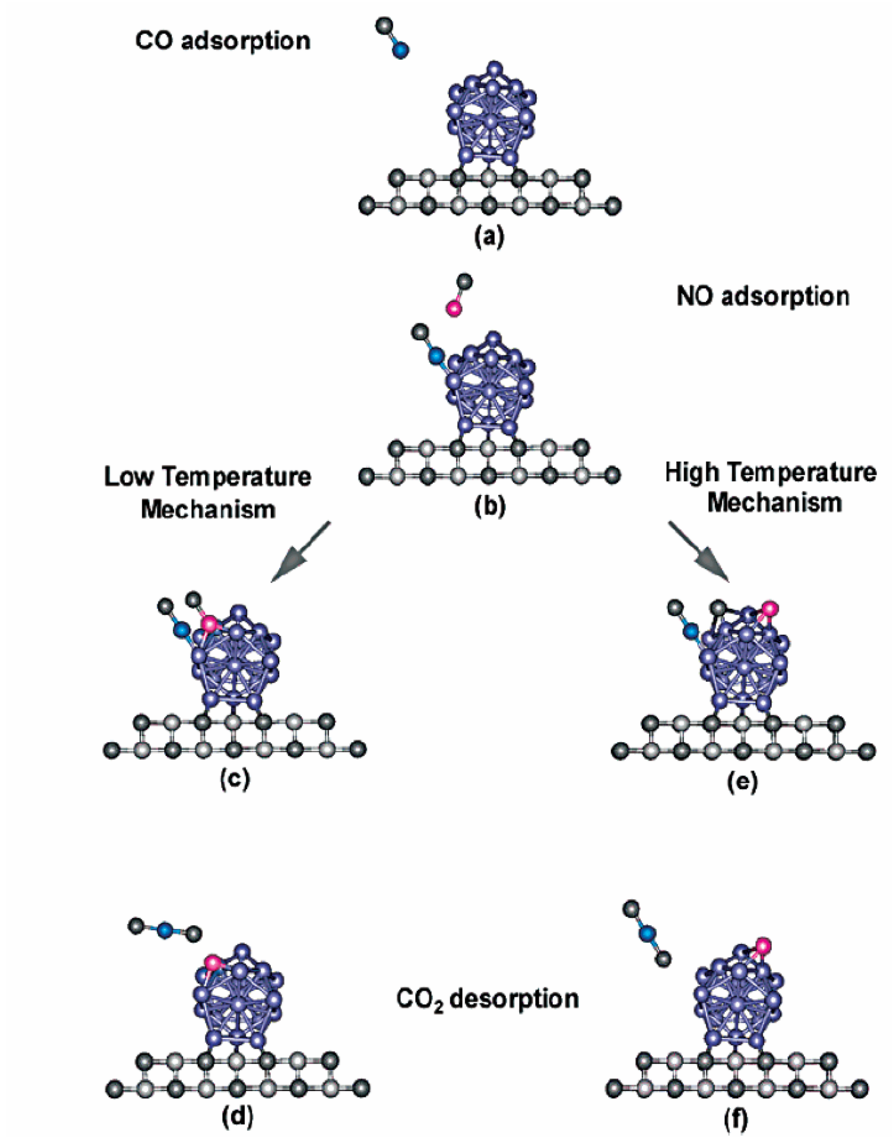
[1] Present address: NEC Corp., Miyazaki 4, Miyamae, Kawasaki 213, Japan.

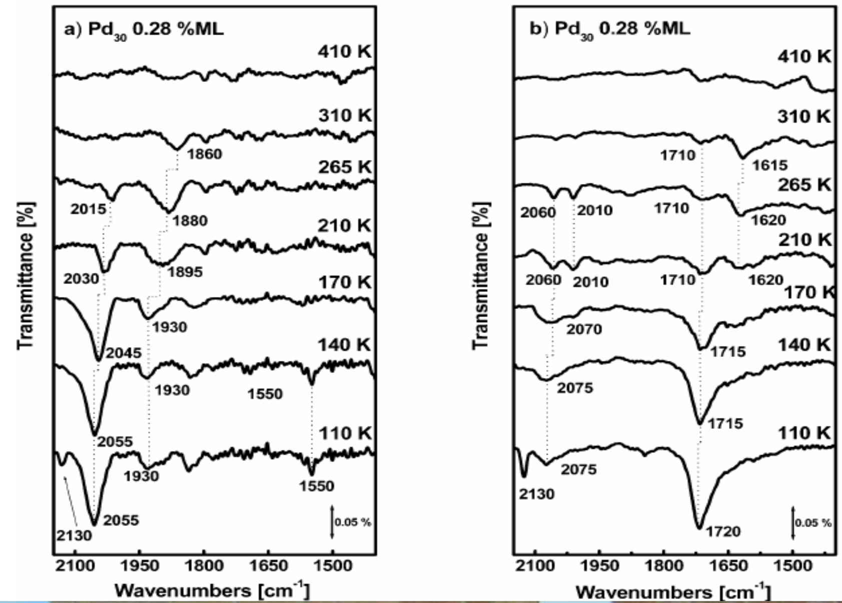
0021-9517/89 $3.00



Schematic representation for CO oxidation pathways over Au/TiO2.

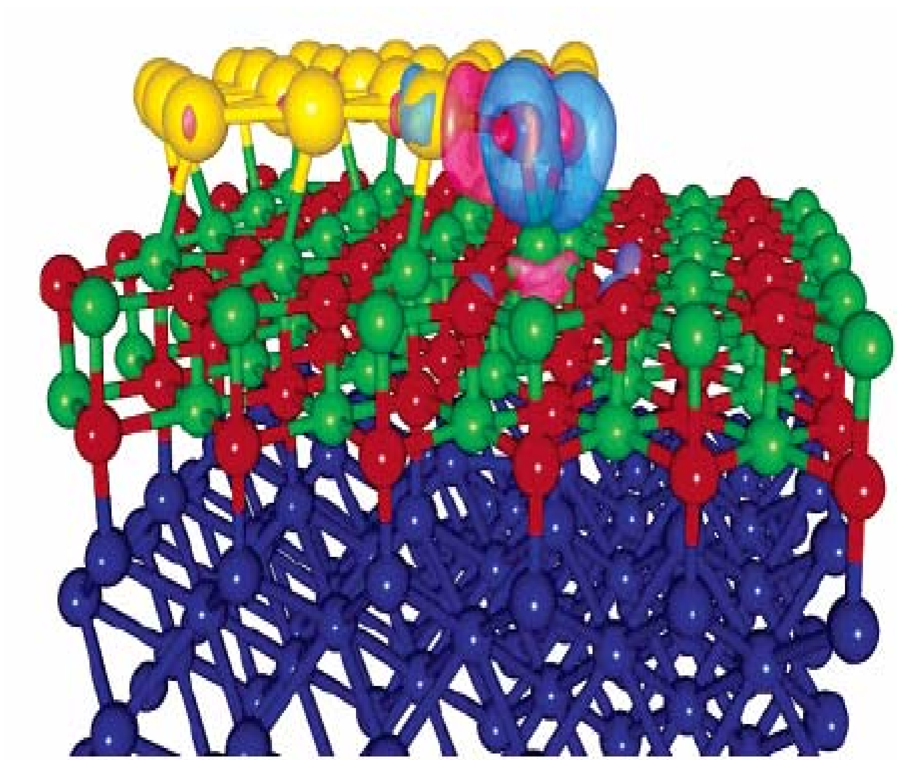
M. Haruta. When Gold Is Not Noble: Catalysis by Nanoparticles. *Chem. Rec*. **2003**, *3*, 75.

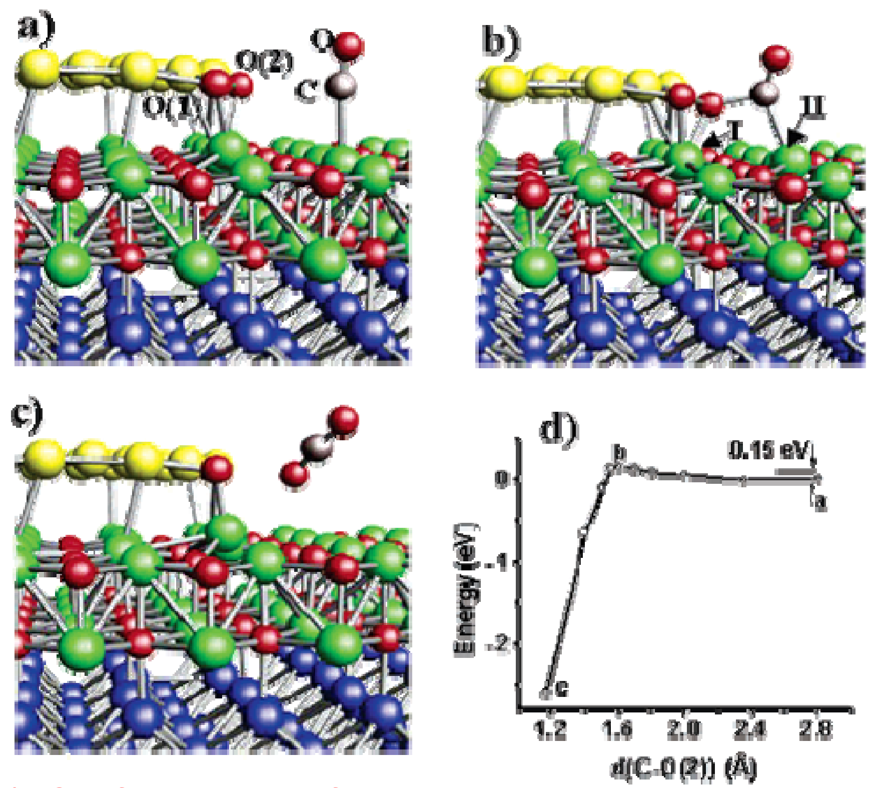




IR-spectra of 13CO and 15NO adsorbed on Pd30 (Figure 3a/b) and Pd8 (Figure 3c/d) clusters. Figure 3a/c shows the spectra if 13CO was predosed for both cluster sizes. Figure 3b/d shows the spectra if 15NO was predosed. All of the spectra were taken at 90 K after annealing the cluster samples to the indicated temperatures.

Wörz, A. S.; Judai, K.; Abbet, S.; Heiz, U. Cluster Size-Dependent Mechanisms of the CO + NO Reaction on Small Pdn (n e 30) Clusters on Oxide Surfaces. *J. Am. Chem. Soc.* **2003**, *125*, 7964.





Two-dimensional Au20 island (yellow on line) adsorbs on a two layer MgO film (O atoms in red and Mg in green) supported on Mo(100) (blue on line), with a coadsorbed O2 molecule. Superimposed we show an isosurface of the excess electronic charge (light blue on line) illustrating activation of the adsorbed molecule through population of the antibonding $2\pi^*$ *orbital.*

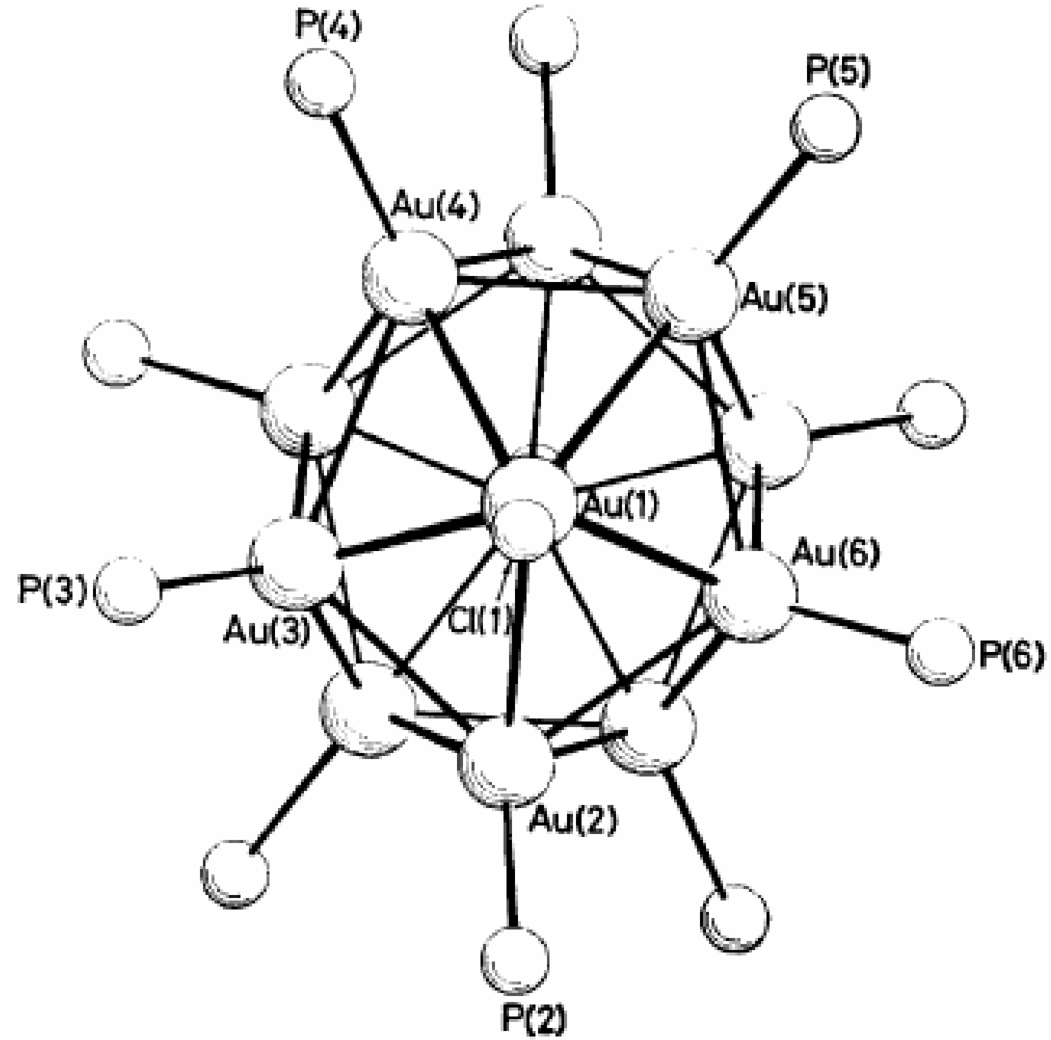
(a-c) Configurations of the two-dimensional Au20 island
shown in
same as in
Figure 1)
ked O(1) and
O(2)) and
a) the initial
optimized
Å, *d(C-O(2)))*
2.85 Å; (b
-neighbor Mg
atoms are
d(O(1)-O(2)))
1.55 Å, d(
d(C-Mg(II)))
2.30 Å;
rmation and
desorption
along the C-

O(2) reaction coordinate, with the zero of the energy scale taken for configuration a. The sharp drop past the barrier top corresponds to CO2 formation.

Zhang, C.; Yoon, B.; Landman, U. Predicted Oxidation of CO Catalyzed by Au Nanoclusters on a Thin Defect-Free MgO Film Supported on a Mo(100) Surface . *J. Am. Chem. Soc.* **2007**, *129*, 2228.

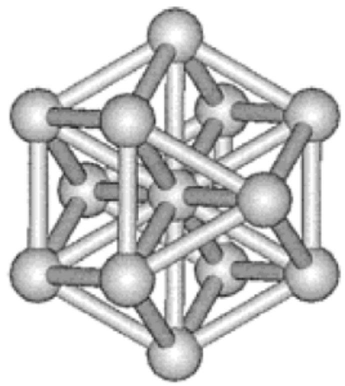
Au_{13}

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

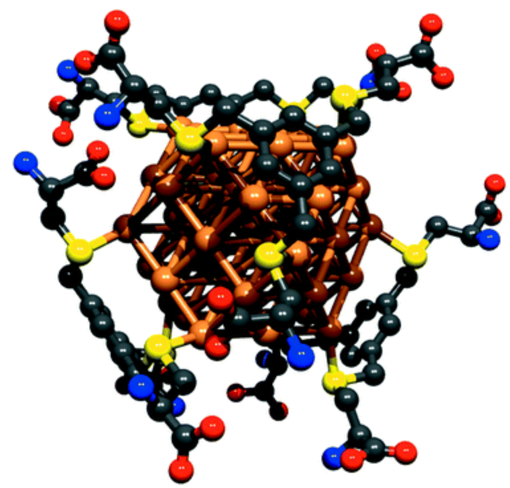


Briant, C. E.; Theobald, B. R. C.; White, J. W.; Bell, L. K.; Mingos, D. M. P.; Welch, A. J. Synthesis and x-ray structural characterization of the centered icosahedral gold cluster compound $[Au_{13}(PPhMe_2)_{10}Cl_2](PF_6)_3$; the realization of a theoretical prediction. *J. C. S. Chem. Comm*. **1981**, *5*, 201.

Gold clusters



Au_{13}



Au_{55}

- **Au_{55} $[P(C_6H_5)_3]_{12}Cl_6$ - a gold cluster of unusual size,** Schmid, G.; Pfeil, R.; Boese, R.; Brandermann, F.; Meyer, S.; Calis, G. H. M.; Van der Velden.; Jan W. A. *Chemische Berichte* **1981**, *114*, 3634.
- **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.
- **Synthesis of water-soluble undecagold cluster compounds of potential importance in electron microscopic and other studies in biological systems**, Bartlett, P. A.; Bauer, B.; Singer, S. *J. Am. Chem. Soc.* **1978**, *100*, 5085.

Magic clusters

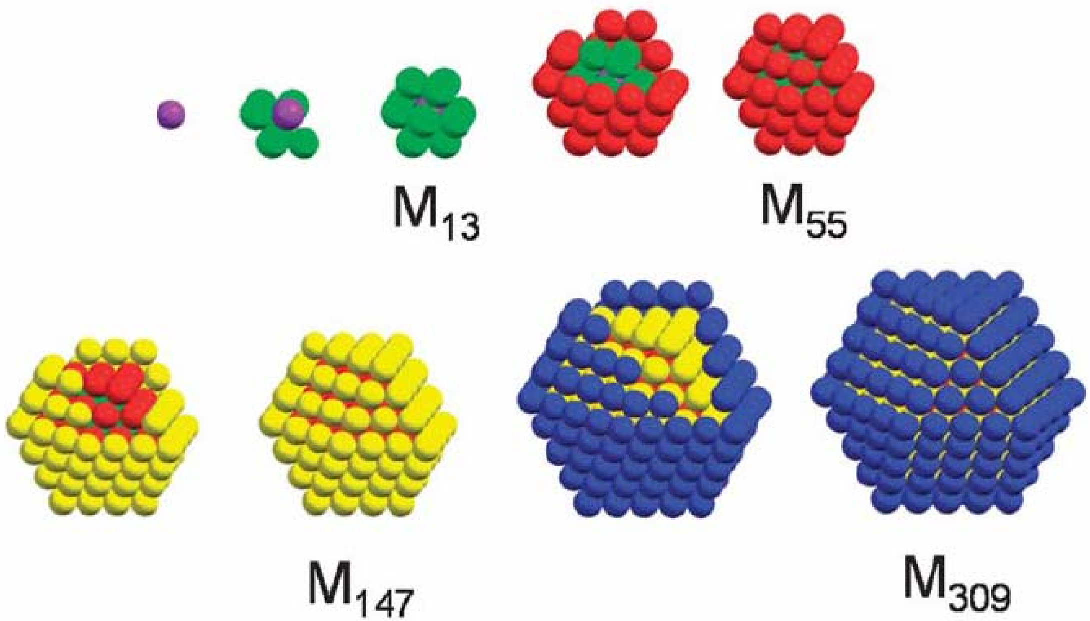
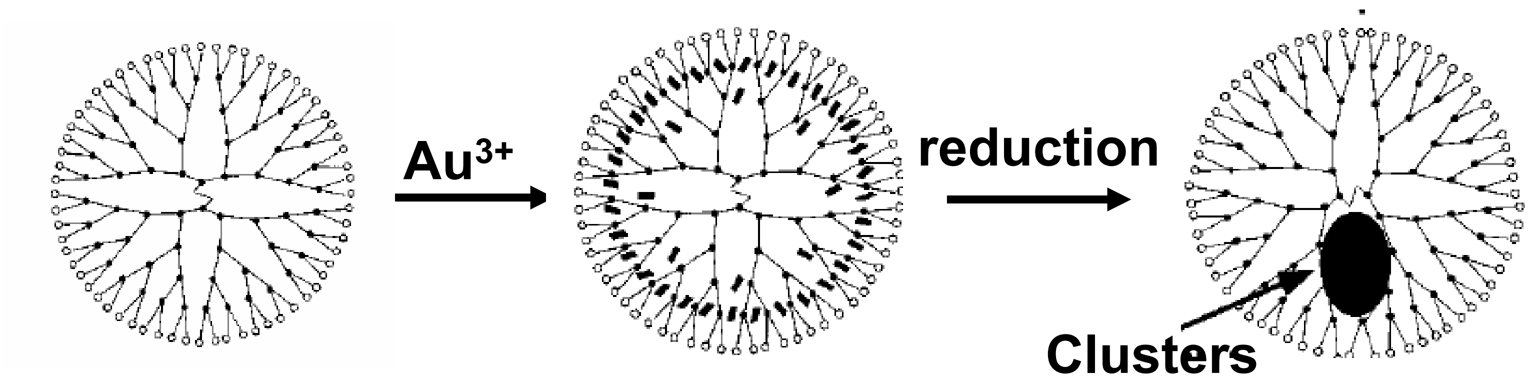
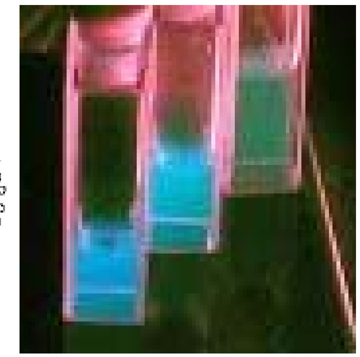


Fig. 1 Organization of full-shell clusters: a first single atom (purple) is surrounded by 12 others (green) to give a one-shell cluster M_{13}. 42 atoms (red) can be densely packed on the 12 green atoms ending with the M_{55} two-shell cluster, followed by 92 atoms (yellow) and 162 atoms (blue) to give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

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

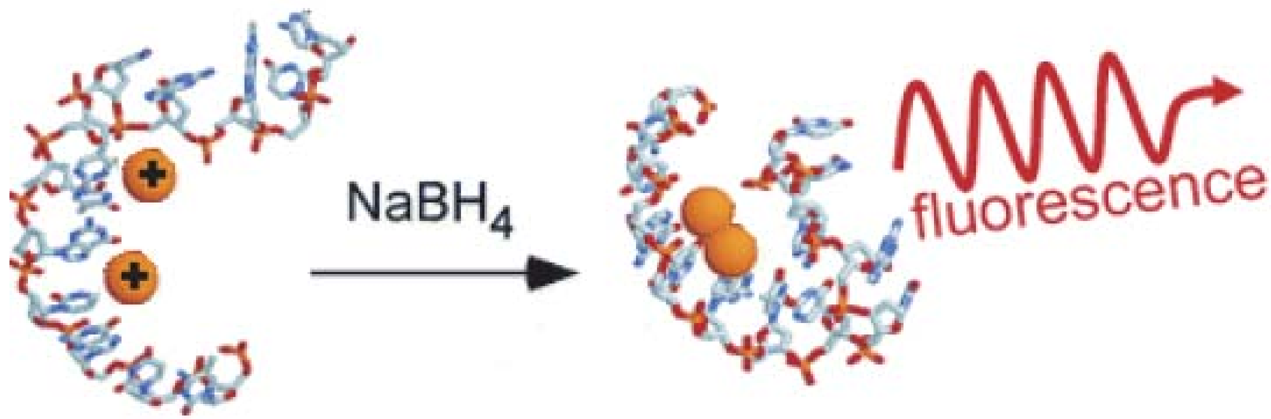
Dendrimer encapsulated clusters



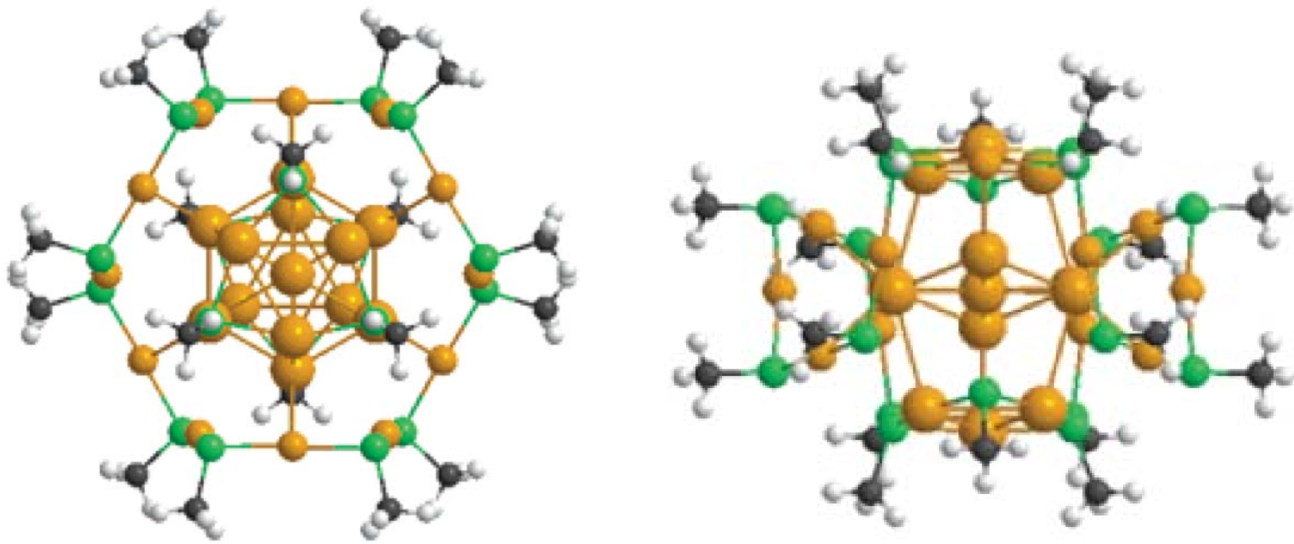


- **High quantum yield blue emission from water-soluble Au_8 nanodots**, Zheng, J.; Petty, J. T.; Dickson, R. M. *J. Am. Chem. Soc***.** **2003**, *125*, 7780.
- **Highly fluorescent, water-soluble, size-tunable gold quantum dots,** Zheng, J.; Zhang, C. W.; Dickson, R. M. *Phys. Rev. Lett*. **2004**, *93*, 077402.
- **Highly fluorescent noble-metal quantum dots**, Zheng, J.; Nicovich, P. R.; Dickson, R. M. *Annu. Rev. Phys. Chem.* **2007**, *58*, 409.
- **Etching colloidal gold nanocrystals with hyperbranched and multivalent polymers: A new route to fluorescent and water-soluble atomic clusters**, Duan, H.; Nie, S. *J. Am. Chem. Soc*. **2007**, *129*, 2412.

DNA encapsulated clusters



DNA-Templated Ag Nanocluster Formation, Petty, J. T.; Zheng, J.; Hud, N. V.; Dickson, R. M. *J. Am. Chem. Soc*. **2004**, *126*, 5207.

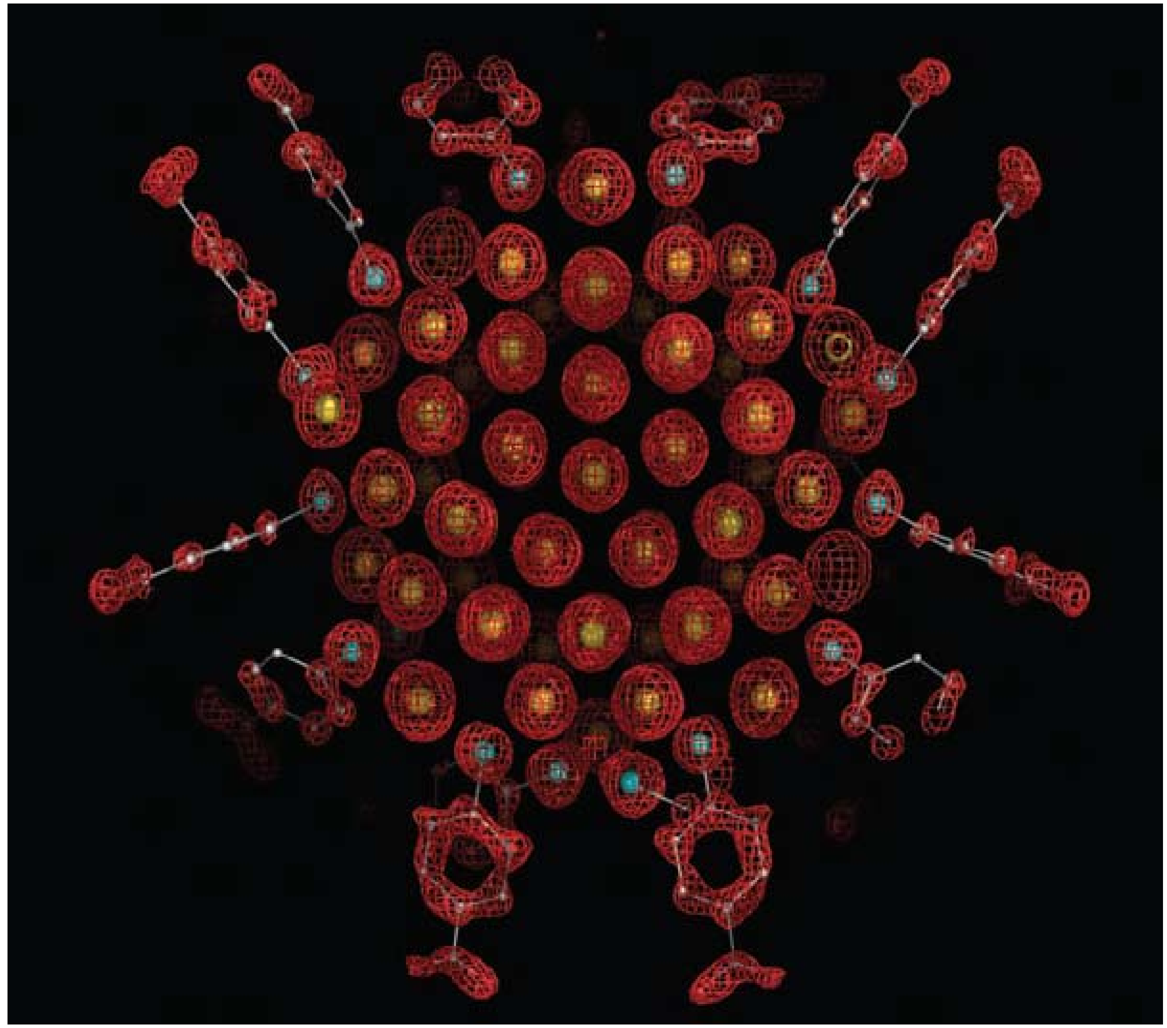


Top and side view of $[Au_{25}(SCH_3)_{18}]^+$

Theoretical Investigation of Optimized Structures of Thiolated Gold Cluster $[Au_{25}(SCH_3)_{18}]^+$, Iwasa, T.; Nobusada, K. *J. Phys. Chem. C* **2007**, *111*, 45.

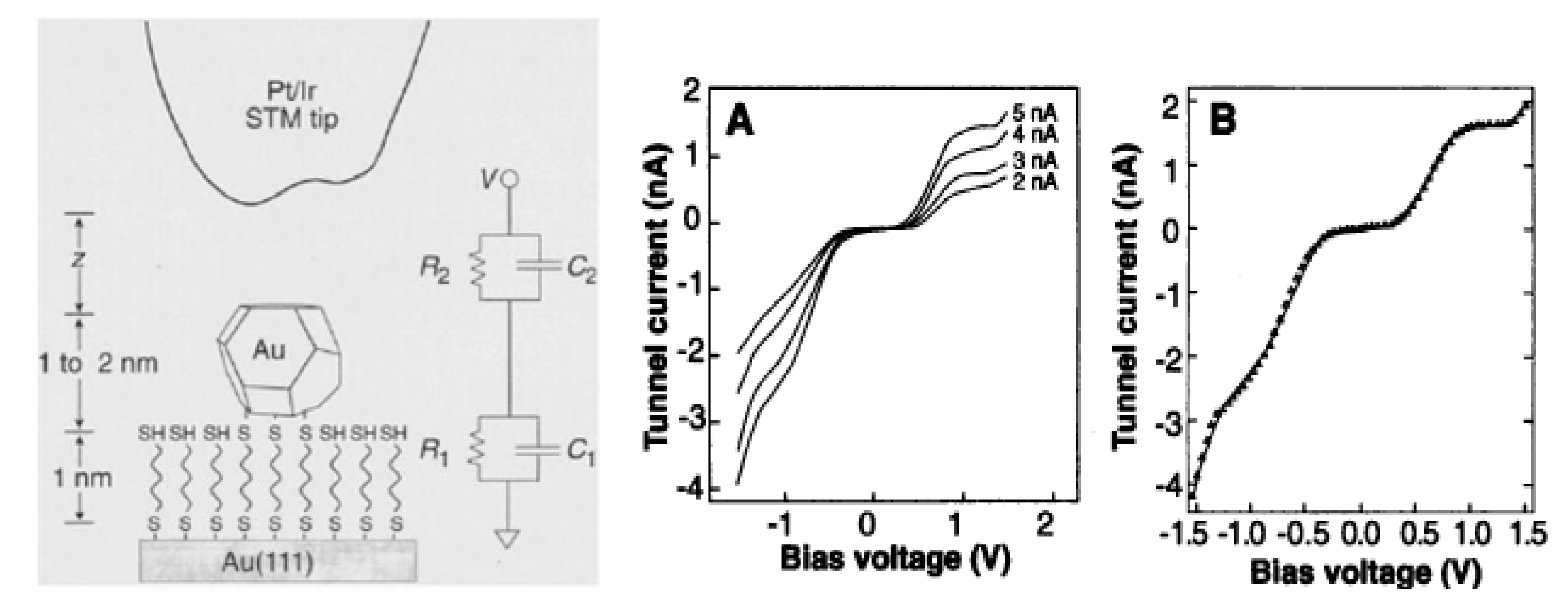
Au_{102}

Au_{102}(p-MBA)$_{44}$

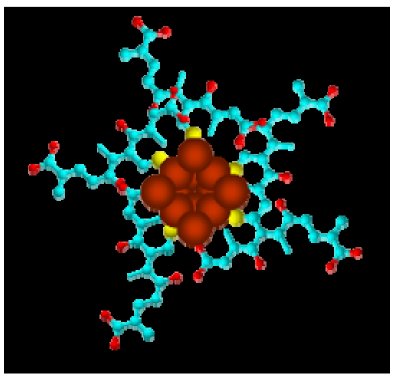


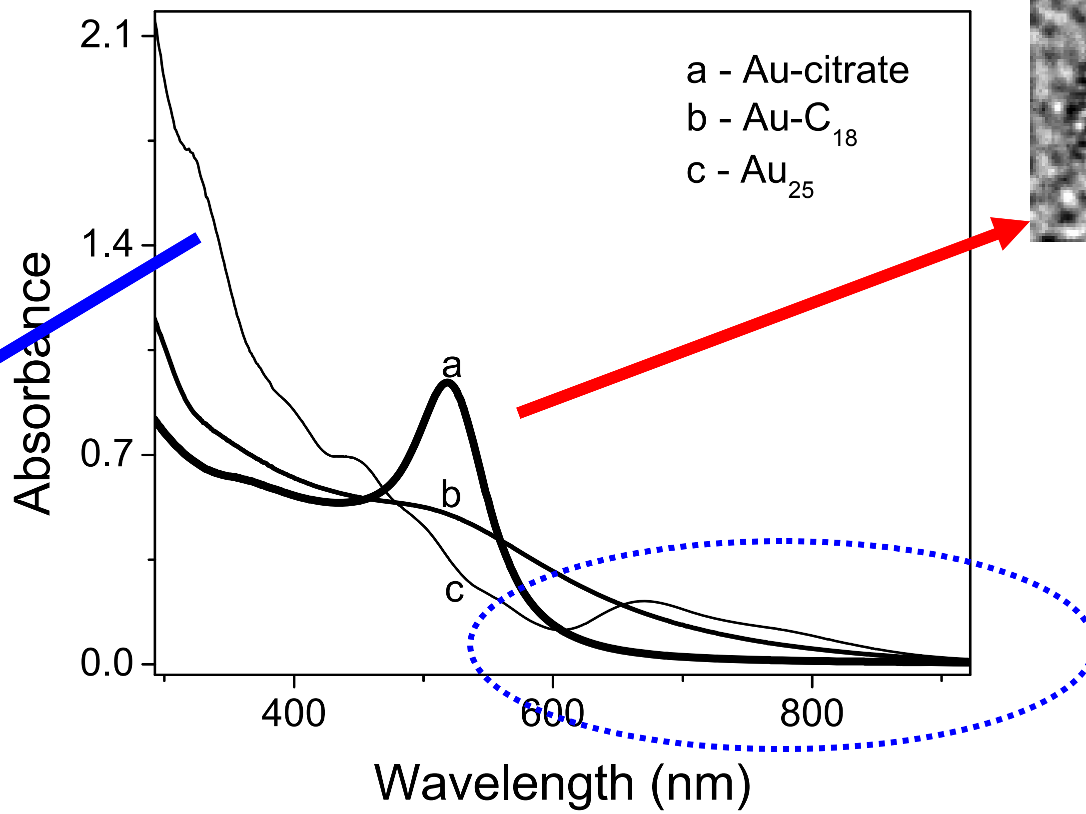
Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a Thiol Monolayer–Protected Gold Nanoparticle at 1.1 Å Resolution *Science* **2007**, *318*, 430.

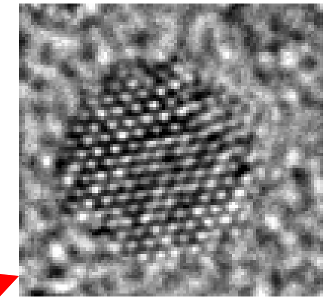
Coulomb staircase

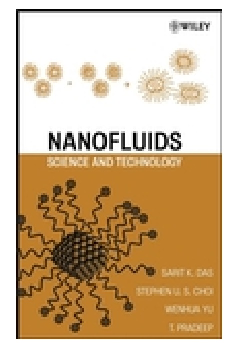


Andres, R. P. Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mohoney, W.; Osifchin, R. G.; Reifenberger, O. R. Coulomb staircase at room temperature in a self-assembled molecular nanostructure. *Science* **1996**, *272*, 1323.







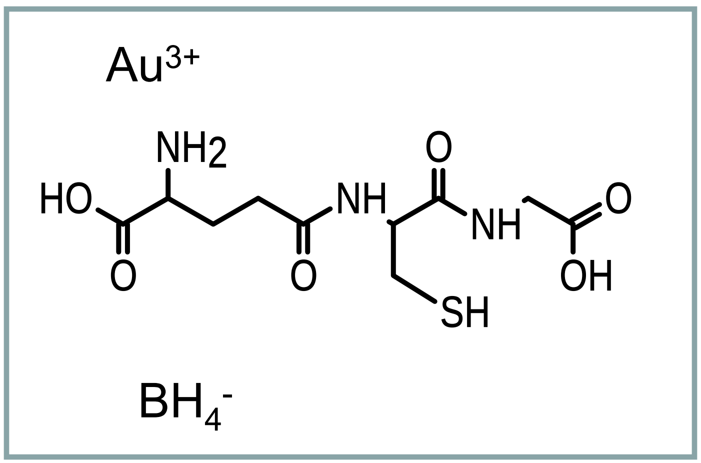


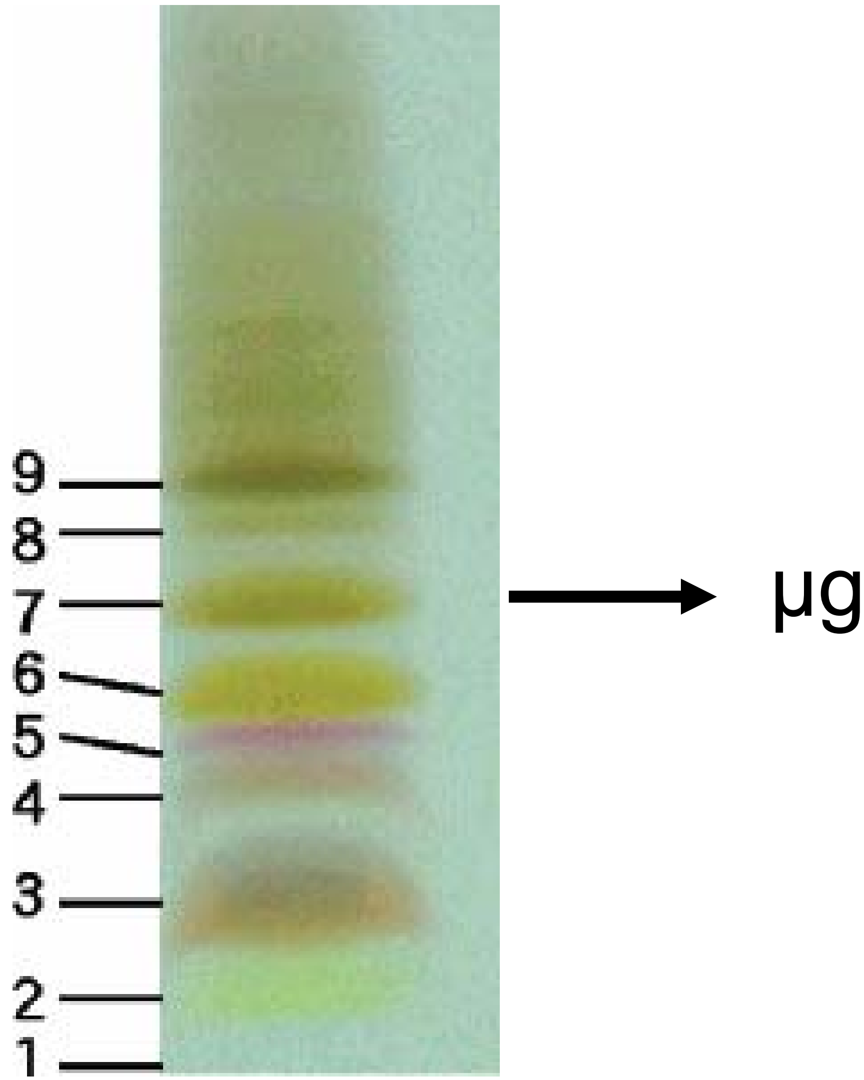
Optical absorption (extinction) spectrum of (a) 15 nm gold particles in aqueous solution (labeled Au@citrate). The spectrum of (b) 3 nm particles in toluene is also shown. See the broadening of the plasmon feature. The spectrum of (c) Au_{25} in water. In this, there is no plasmon excitation and all the features are due to molecular absorptions of the cluster.

Das, Choi, Yu and Pradeep, *Nanofluids*, John Wiley, New York, 2008

Polyacrylamide gel electrophoresis (PAGE)

How to make them?

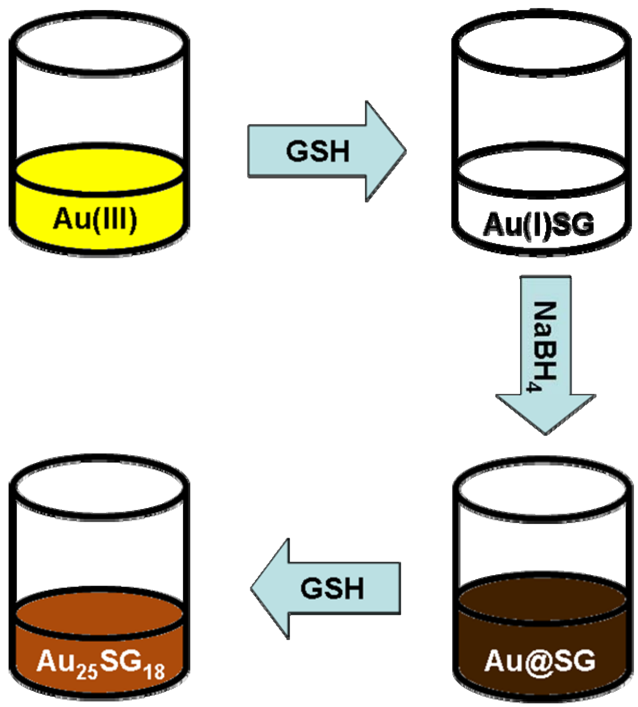




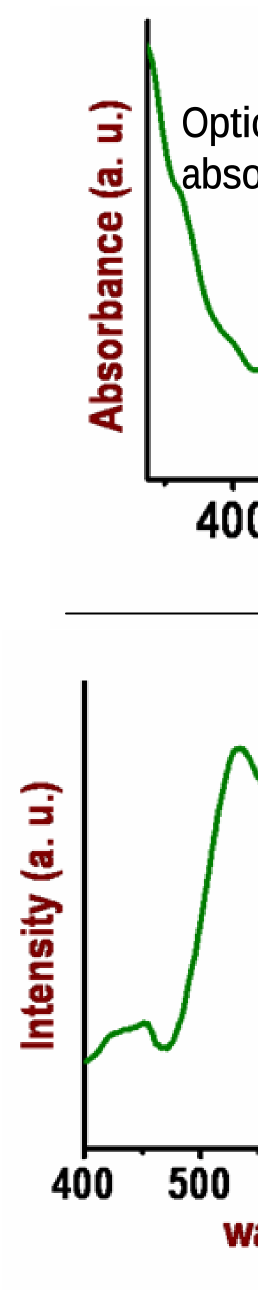
Negishi, Y.; Nobusada, K.; and Tsukuda, T. Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)-Thiolate Complexes and Thiolate-Protected Gold Nanocrystals. *J. Am. Chem. Soc*. 2005, *127*, 5261-70.

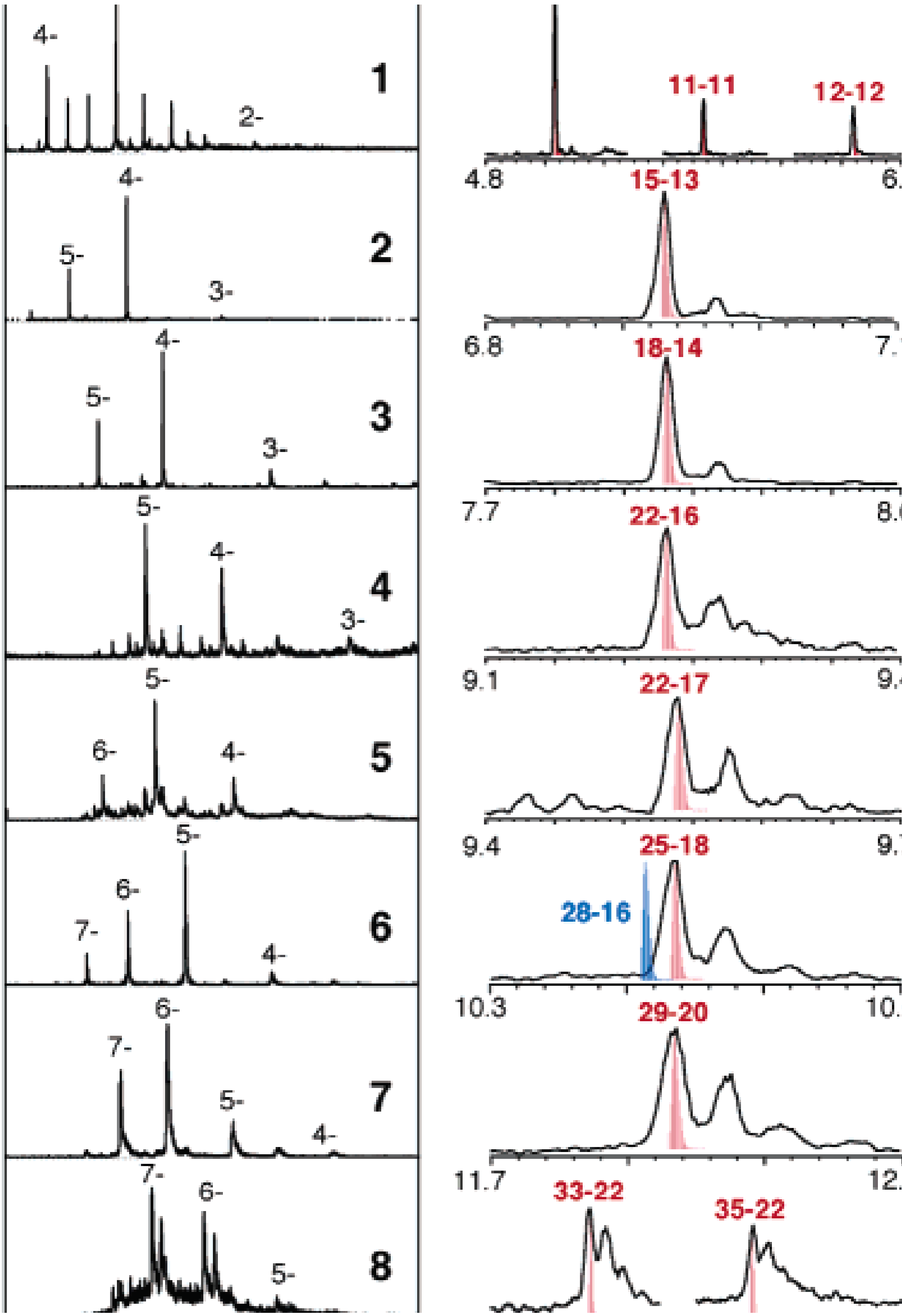
$Au_{25}SG_{18}$

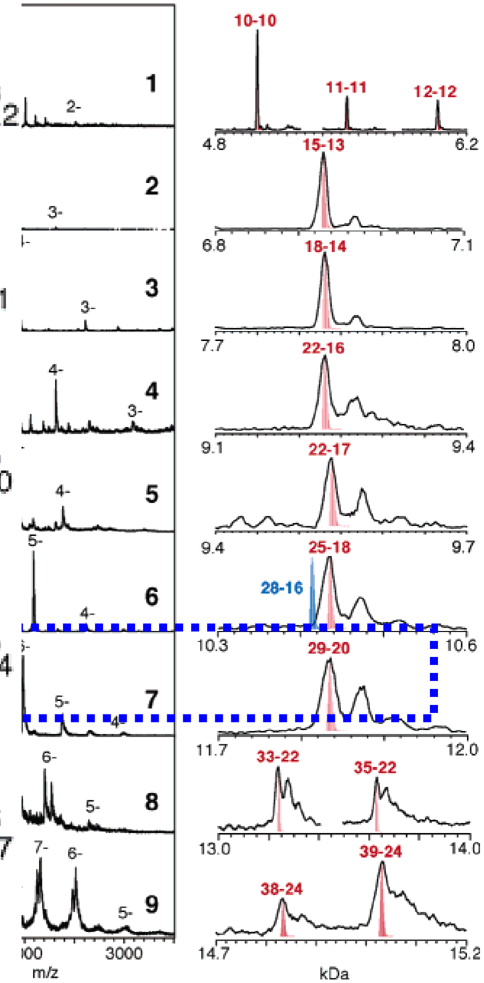
Synthesis: Au_{25} clusters can be preferentially populated by dissociative excitation of larger precursors



Scheme showing the synthesis of $Au_{25}SG_{18}$ clusters



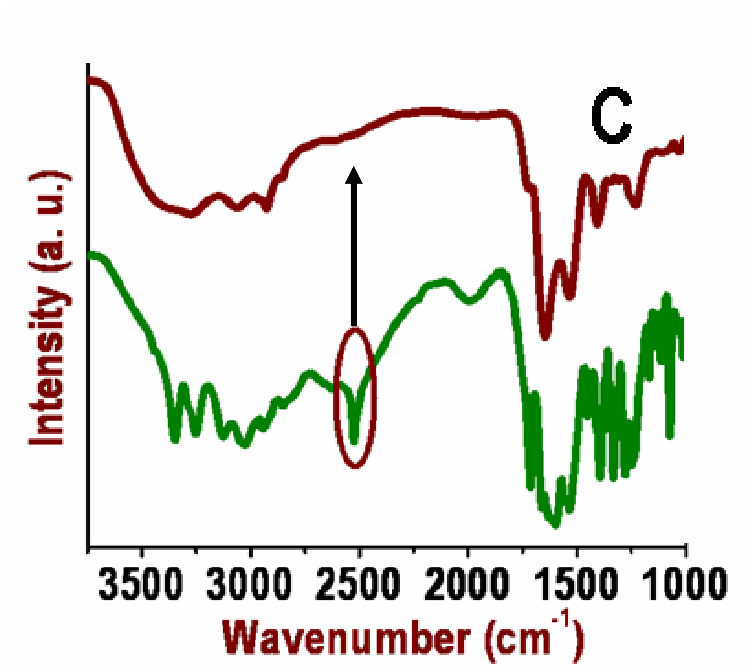


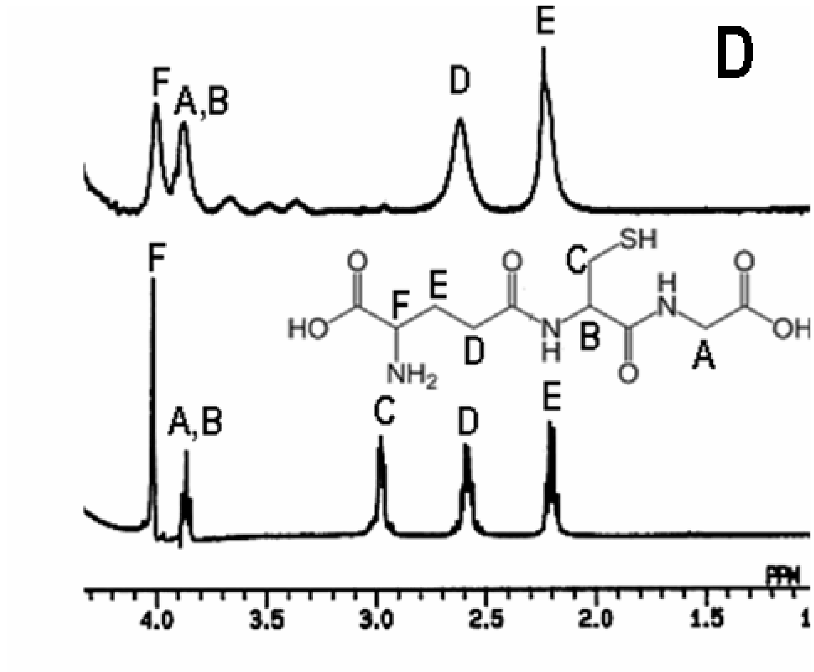


da et. al. JACS 2005

excitation
d 700 nm,

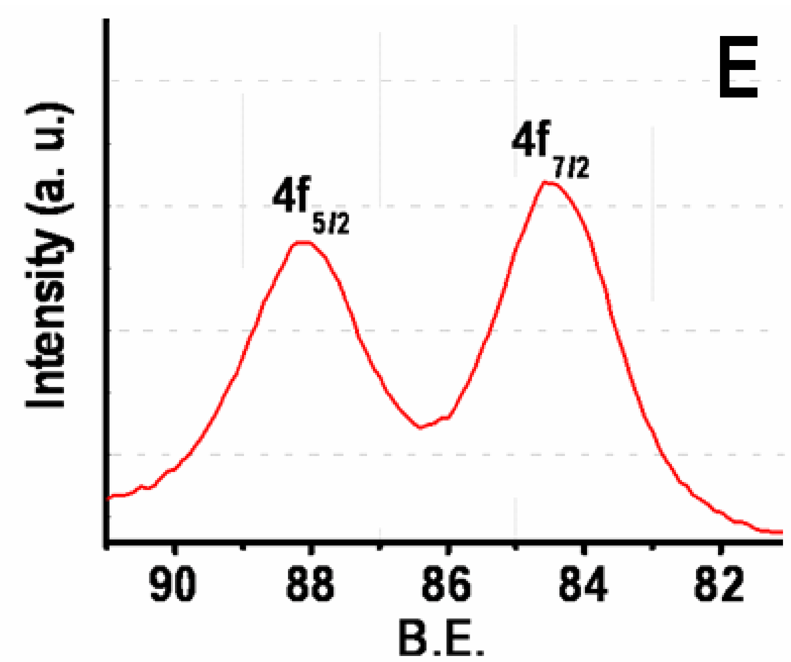
Q-Trap ESI Mass Spectrometer



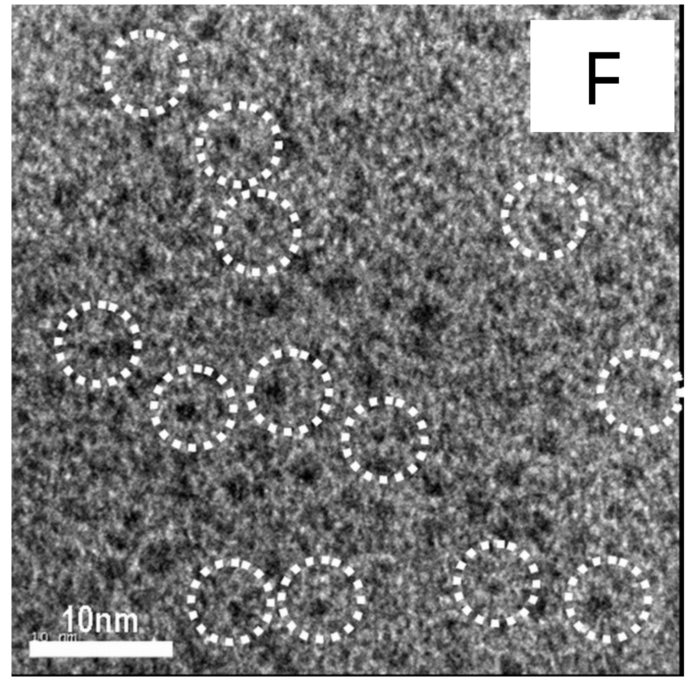


FTIR spectrum: The peak at 2526 cm^{-1} of glutathione due to –SH stretching frequency is absent in IR spectrum of Au_{25} suggesting the ligand binding on cluster surface.

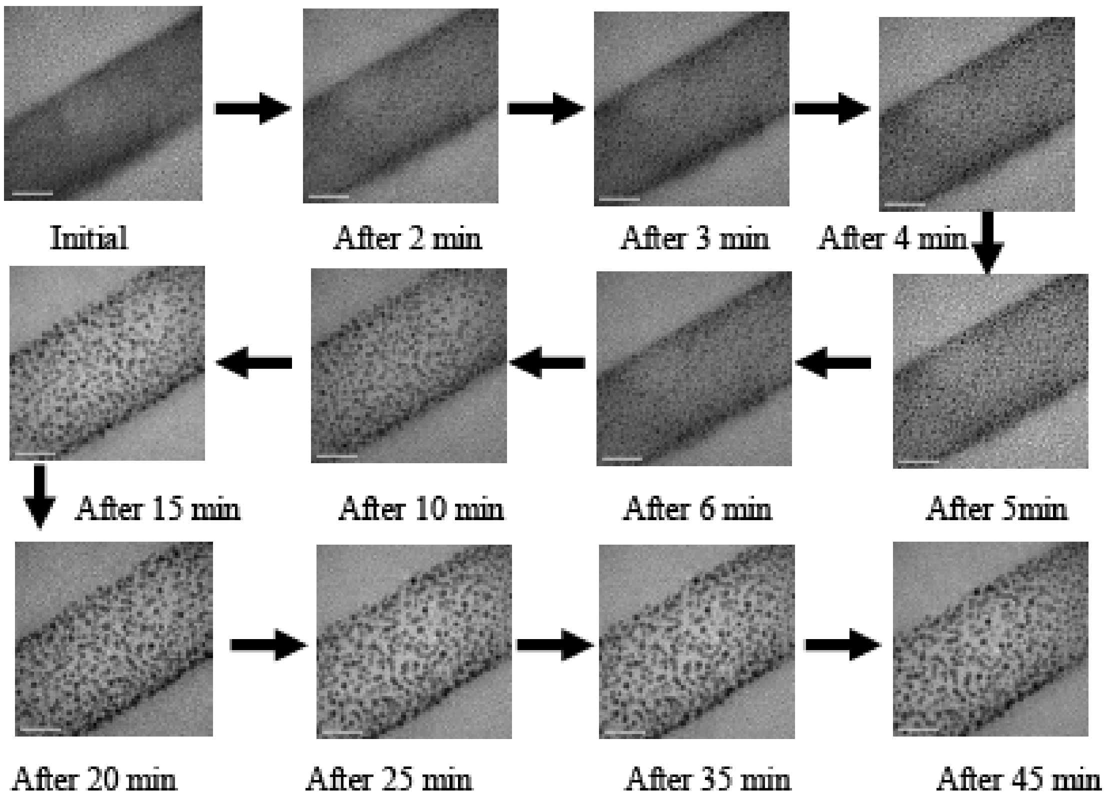
1H NMR spectrum: There is one-to-one correspondence between the two spectra, except that the **β**CH_2 resonance (labeled as C) disappears completely in the cluster which is expected as it is close to the cluster surface. All the observed resonances have been broadened in view of their faster relaxation and non-uniform distribution of ligands.

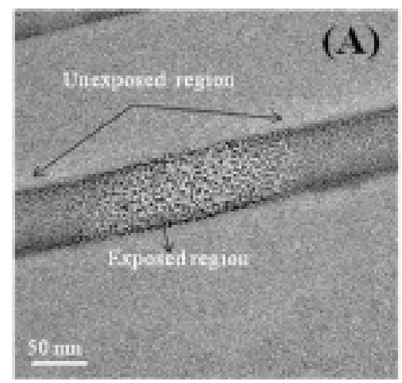


XPS spectrum



TEM image: The clusters are seen only faintly since the size is ~1 nm. Some of the individual clusters are shown by circles. There are also cluster aggregates which upon extended electron beam irradiation fuse to form bigger particles

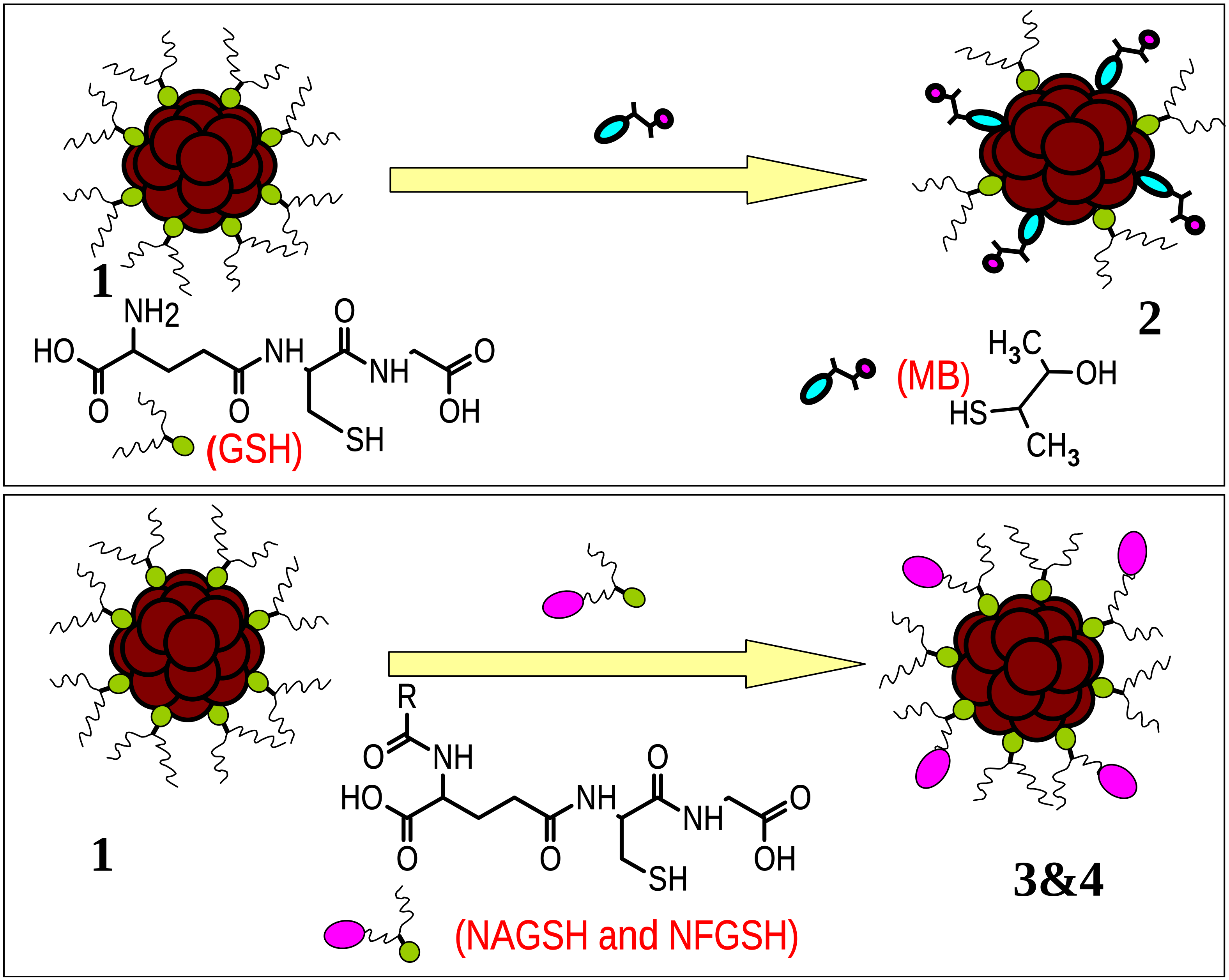


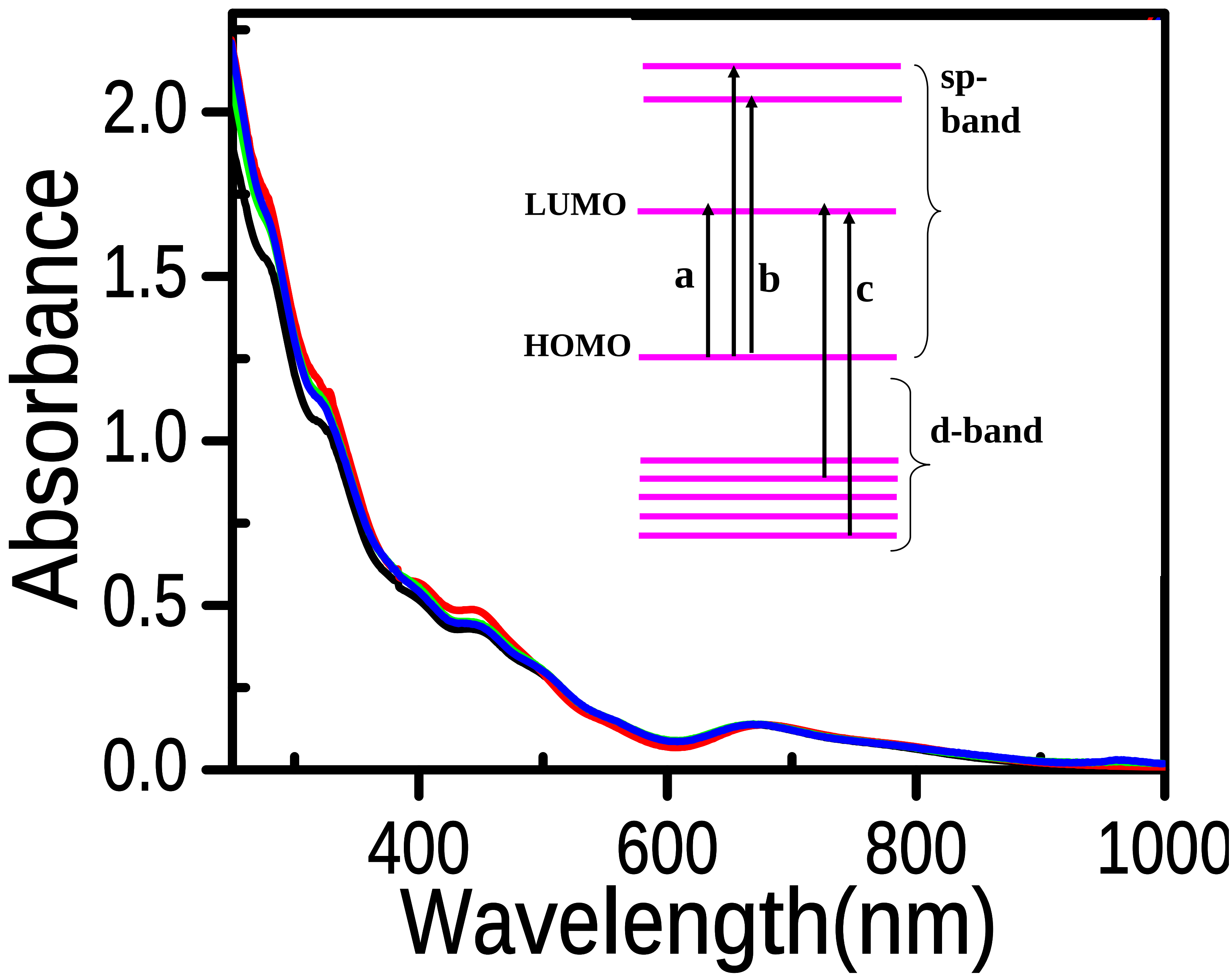


With Arindam Banerjee

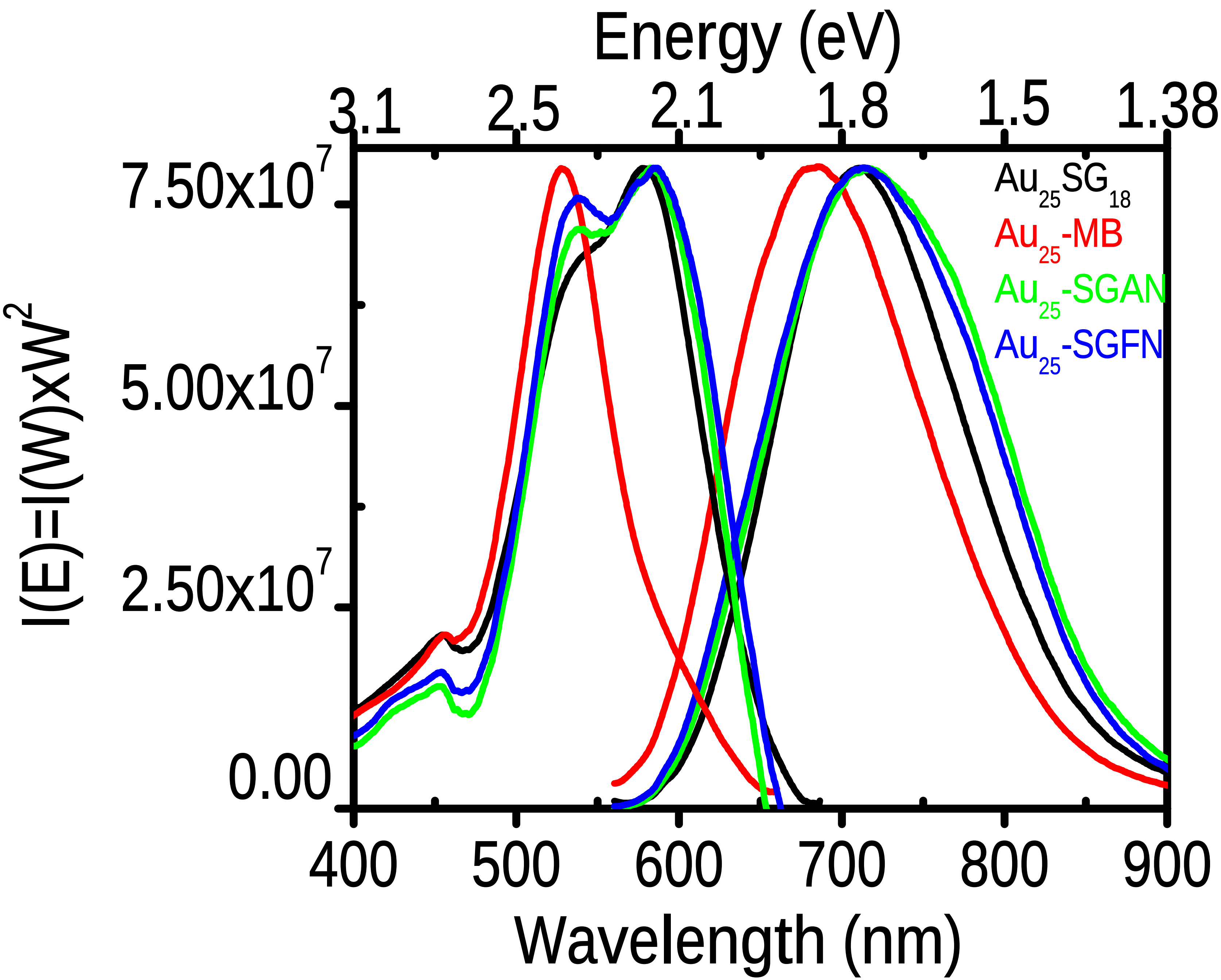
Perumal et al. J. Mater. Chem. (In Press)

Ligand exchange of Au_{25}



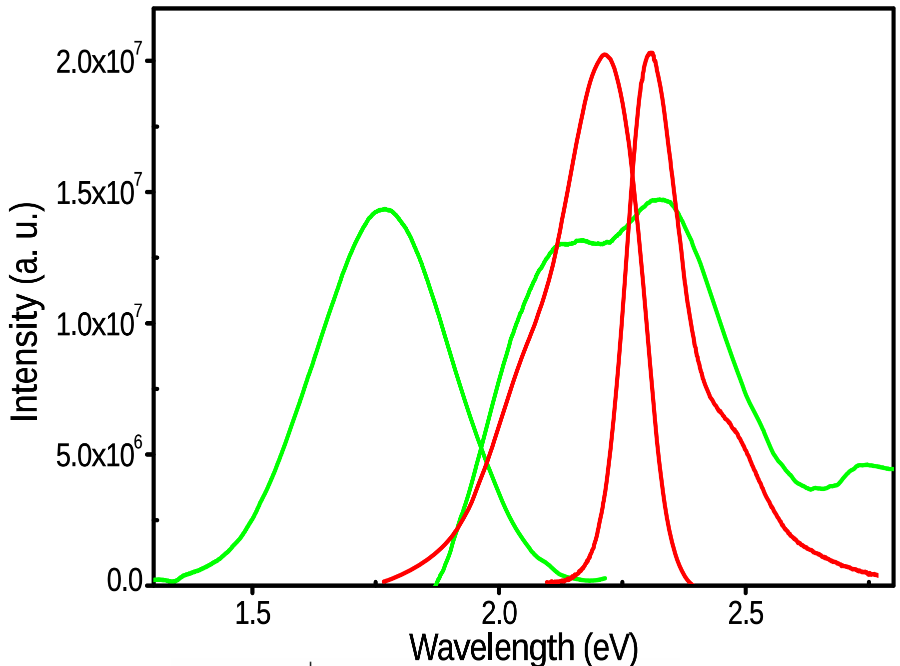


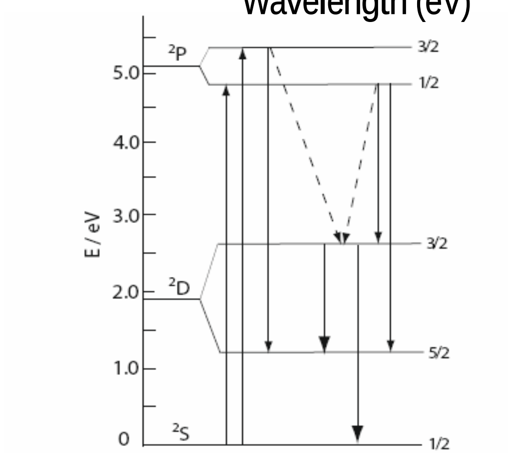
Shibu *et al. J. Phys. Chem. C* 2008

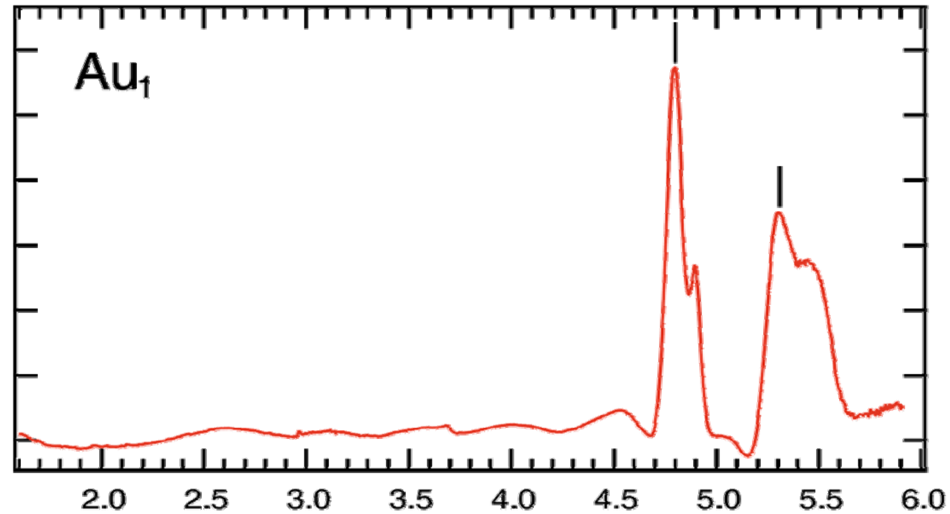


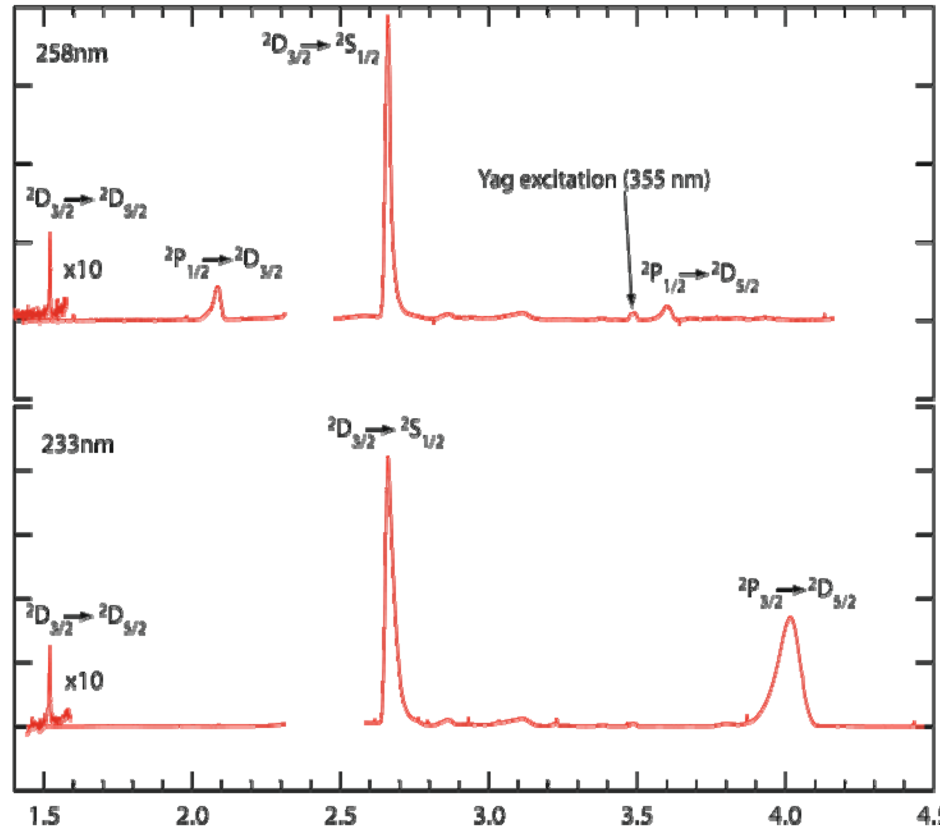
Energy (eV)
3.1
2.5
2.1
1.8
1.5
1.38
7.50x10^7
5.00x10^7
2.50x10^7
0.00
I(E)=I(W)xW^2
Au25SG18
Au25-MB
Au25-SGAN
Au25-SGFN
400
500
600
700
800
900
Wavelength (nm)

<u>Fluorescence : A comprehensive study between organic dye, gold atoms and molecular clusters of gold</u>









Lecoultrea, S.; Rydlo, A.; F´elixb, C.; Harbich, W. Eur. Phys. J. D (2009) DOI: 10.1140/epjd/e2008-00290-0

Cluster	Q.Yield
$Au_{10}(SG)_{10}$ $Au_{11}(SG)_{11}$ $Au_{11}(SG)_{11}$	$1*10^{-4}$
$Au_{15}(SG)_{13}$	$2*10^{-4}$
$Au_{18}(SG)_{14}$	$4*10^{-3}$
$Au_{22}(SG)_{16}$	$4*10^{-3}$
$Au_{22}(SG)_{17}$	$2*10^{-3}$
$Au_{25}(SG)_{18}$	$1.9*10^{-3}$
$Au_{29}(SG)_{20}$	$3*10^{-3}$
$Au_{33}(SG)_{22}$ $Au_{35}(SG)_{22}$	$2*10^{-3}$
$Au_{38}(SG)_{24}$, $Au_{39}(SG)_{24}$	$2*10^{-3}$
Gold nanoparticles	$1*10^{-10}$

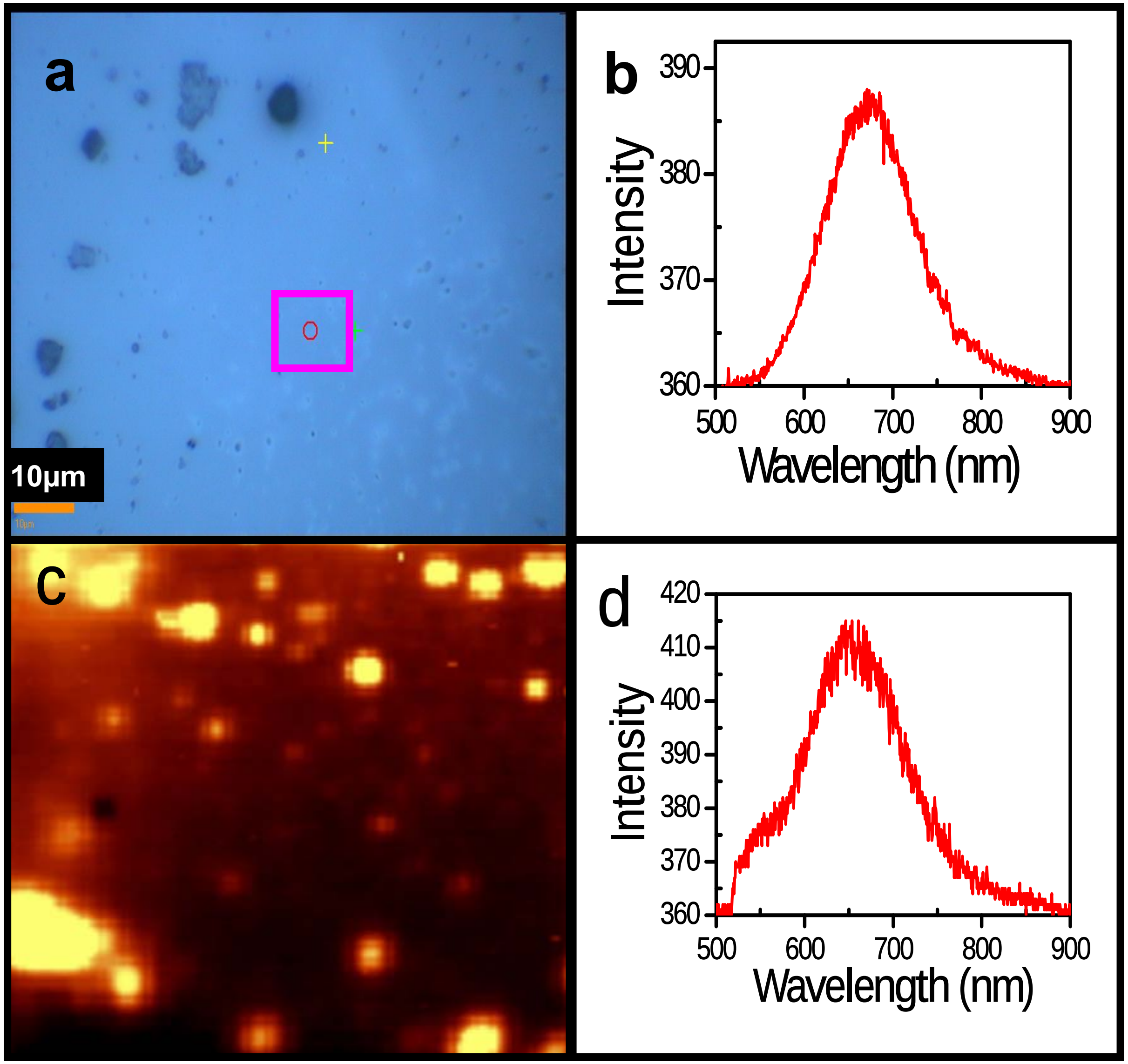
Negishi, Y.; Nobusada, K.; Tsukuda, T. J. Am. Chem. Soc. 2005, 127, 5261.

Recently developed clusters using Au_{25} as precursor

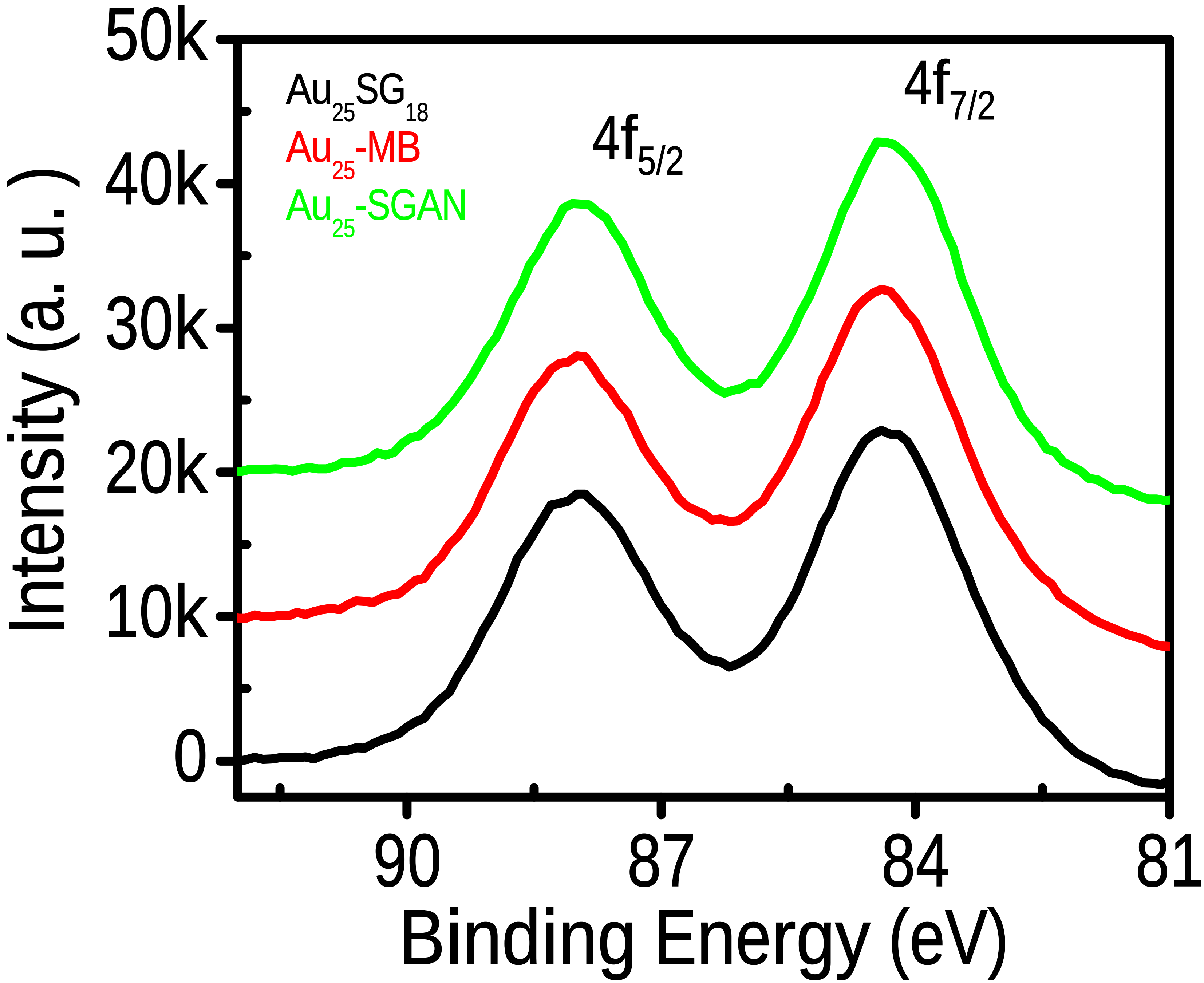
Precursor ⇒ Using other ligands

Cluster	Q. Yield
Au_{22}	$4.0*10^{-2}$
Au_{23}	$1.3*10^{-2}$
Au_{31}	$1.0*10^{-2}$
$Au_8(SG)_8$	$1.5*10^{-1}$

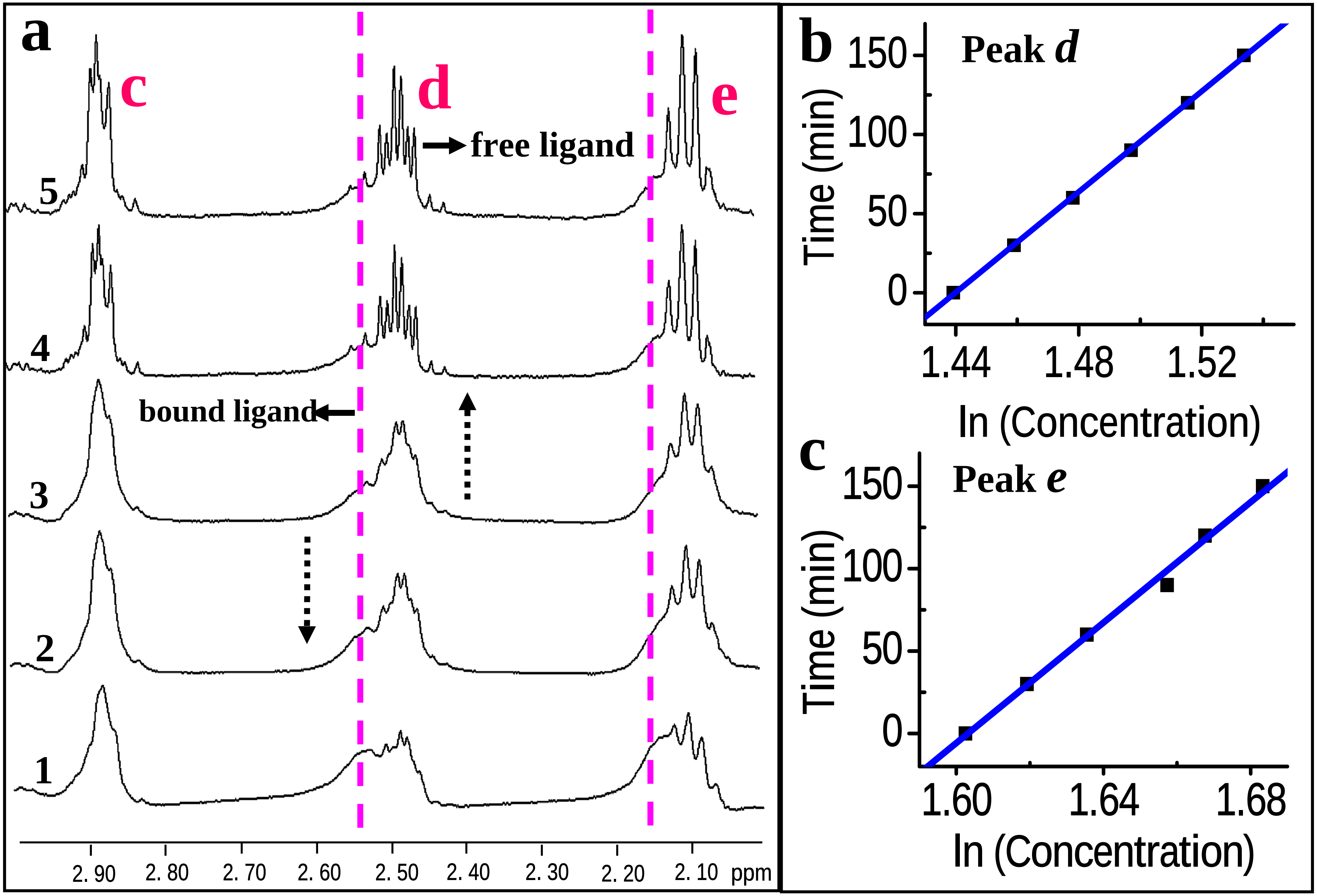
1. Nano Res., 1(2008) 333-340.
2. Chemistry A European Journal. (In Press).
3. ACS Applied Materials and Interfaces (in press)



a
10µm
b
Intensity
390
380
370
360
500
600
700
800
900
Wavelength (nm)
c
d
Intensity
420
410
400
390
380
370
360
500
600
700
800
900
Wavelength (nm)

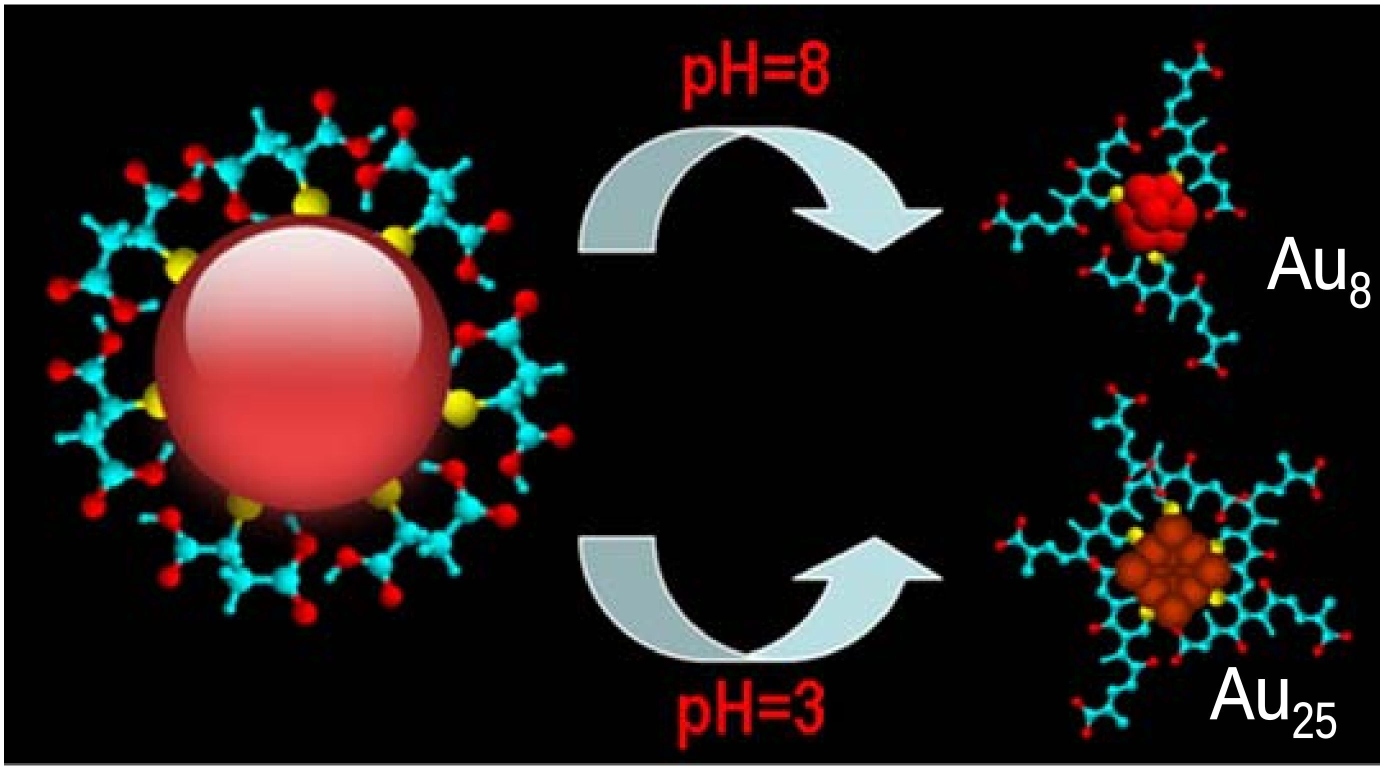


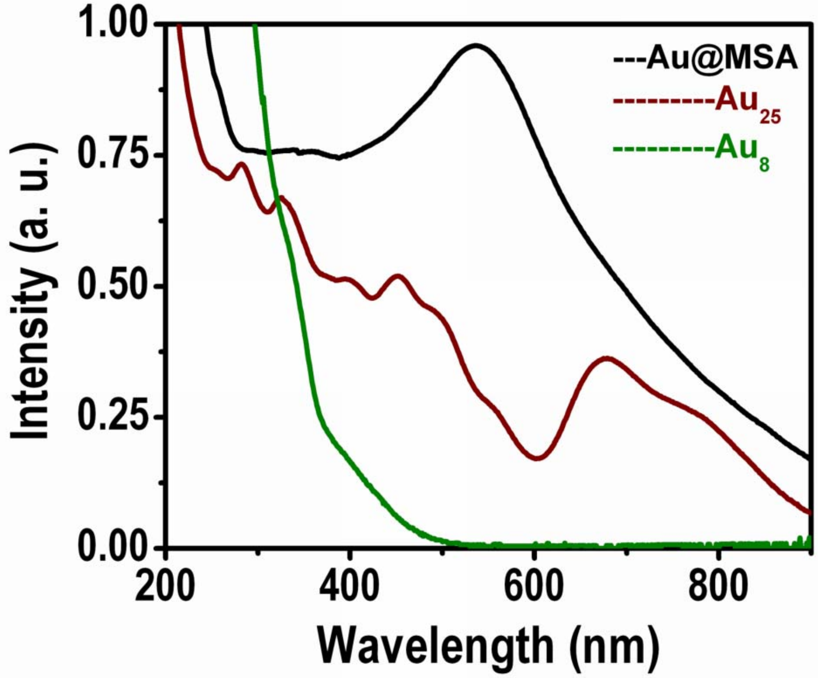
Au25SG18
Au25-MB
Au25-SGAN
4f5/2
4f7/2
50k
40k
30k
20k
10k
0
Intensity (a. u.)
90
87
84
81
Binding Energy (eV)



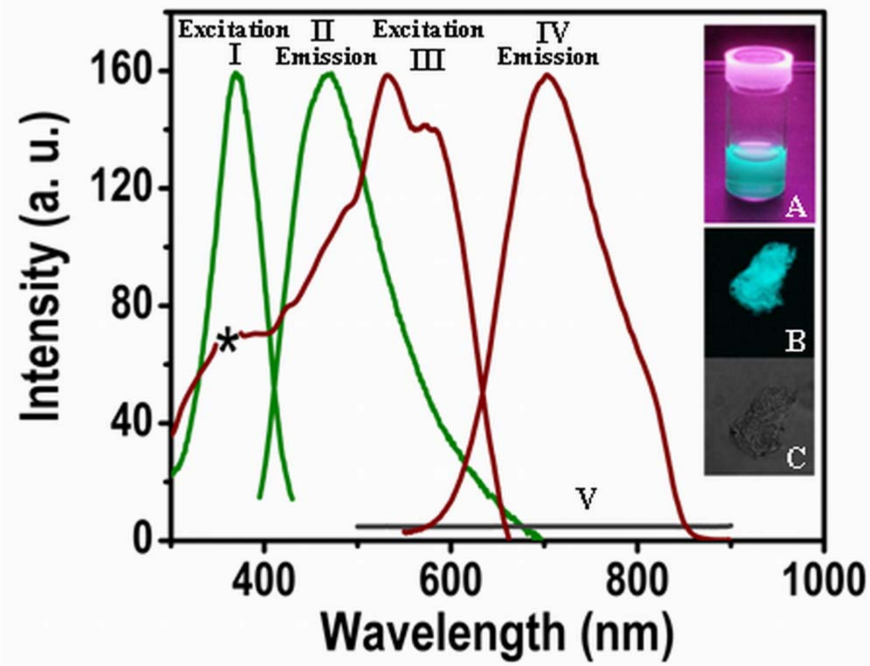
a
c
d
e
free ligand
bound ligand
5
4
3
2
1
2.90
2.80
2.70
2.60
2.50
2.40
2.30
2.20
2.10
ppm
b
Peak d
Time (min)
150
100
50
0
1.44
1.48
1.52
ln (Concentration)
c
Peak e
Time (min)
150
100
50
0
1.60
1.64
1.68
ln (Concentration)

Au_8SG_8



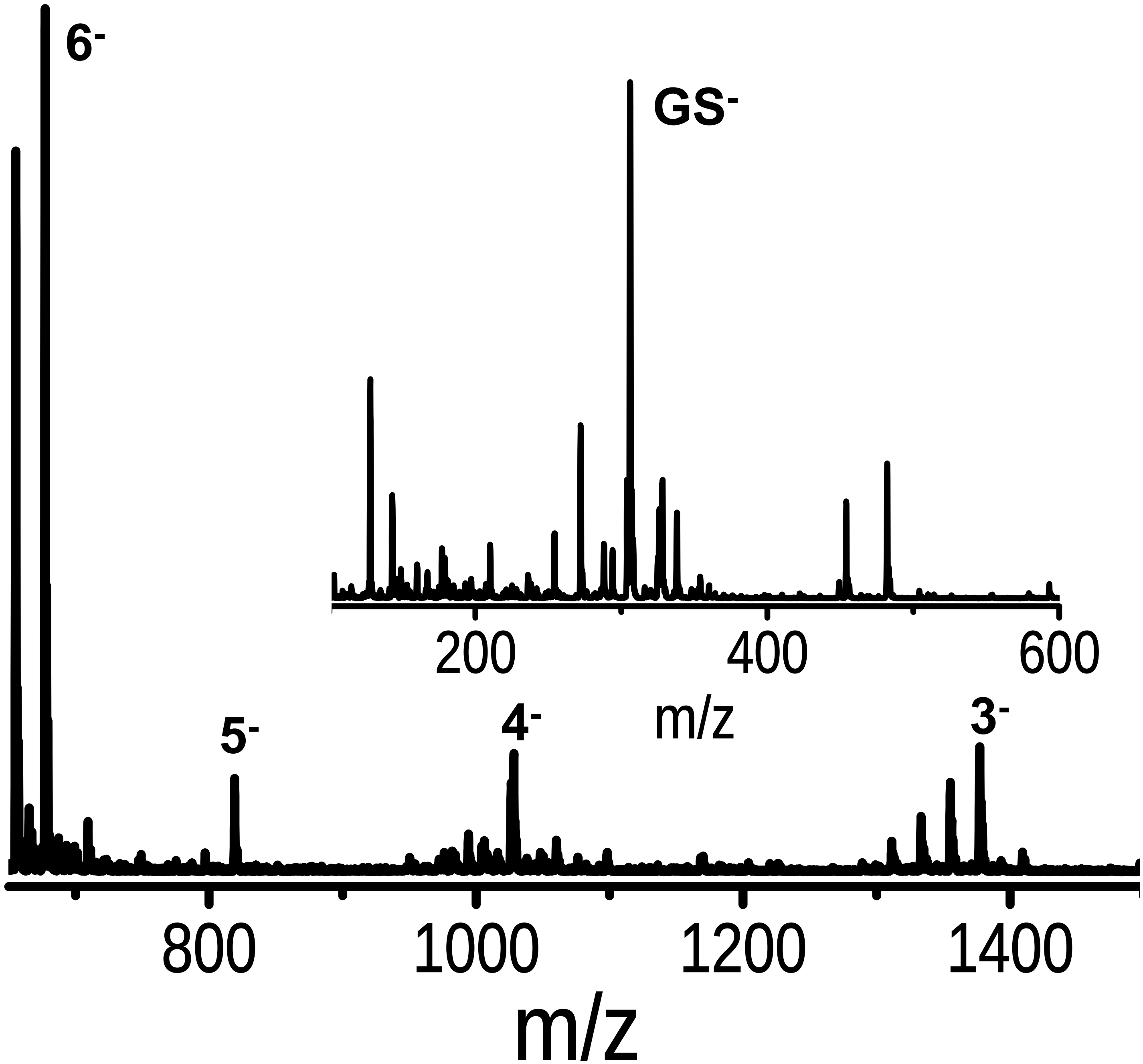


Comparison of the optical absorption profiles of Au@MSA, Au_{25} and Au_8.



Comparison of the photoluminescence profiles of the clusters with Au@MSA. Traces I and II are the excitation and emission spectra of Au_8, respectively. Traces III and IV are the excitation and emission spectra of Au_{25}, respectively and trace V is the emission spectrum of Au@MSA.

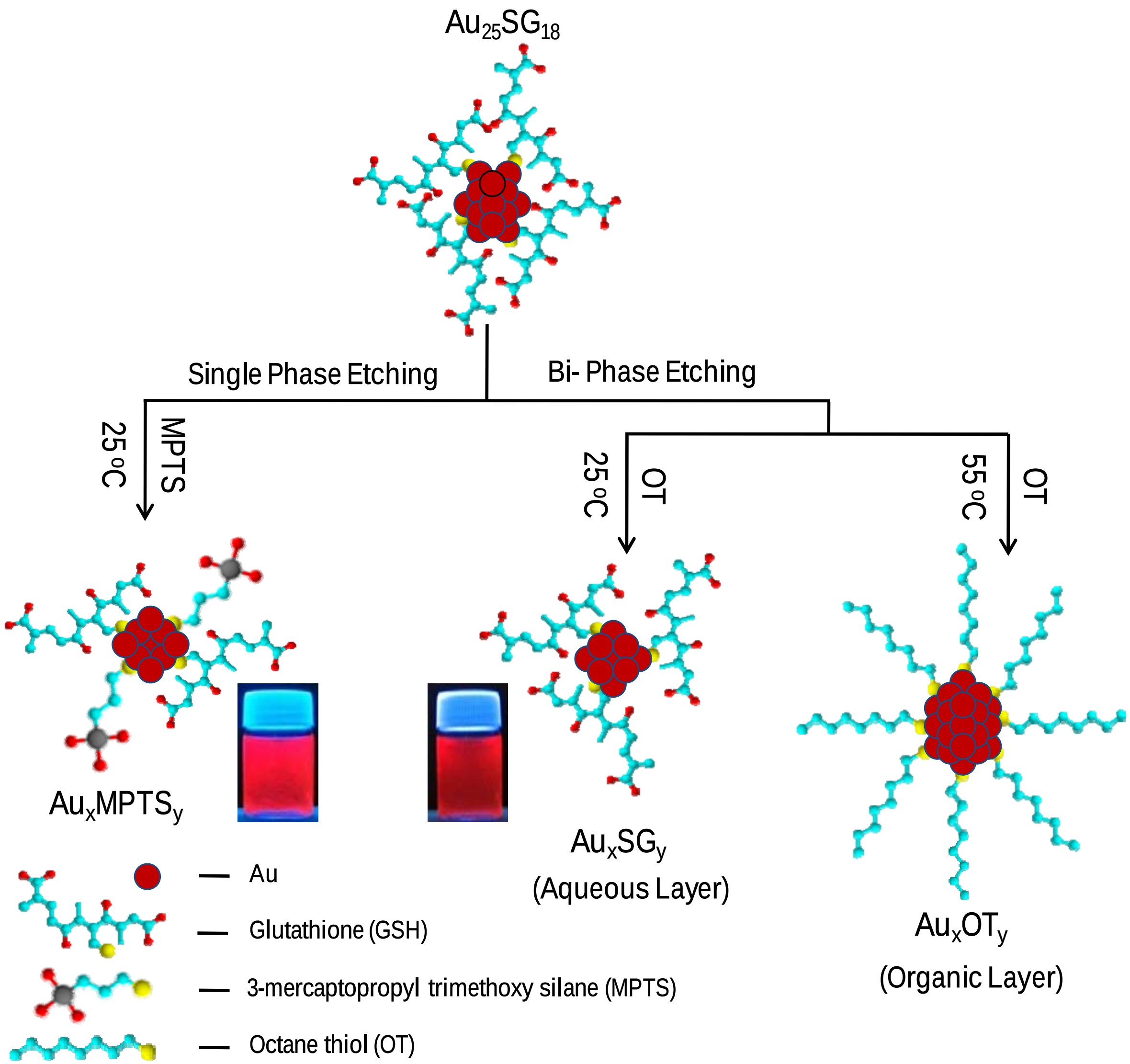
Habeeb Muhammed et al. *Nano Res.* 2008



Habeeb Muhammed, et. al. Unpublished

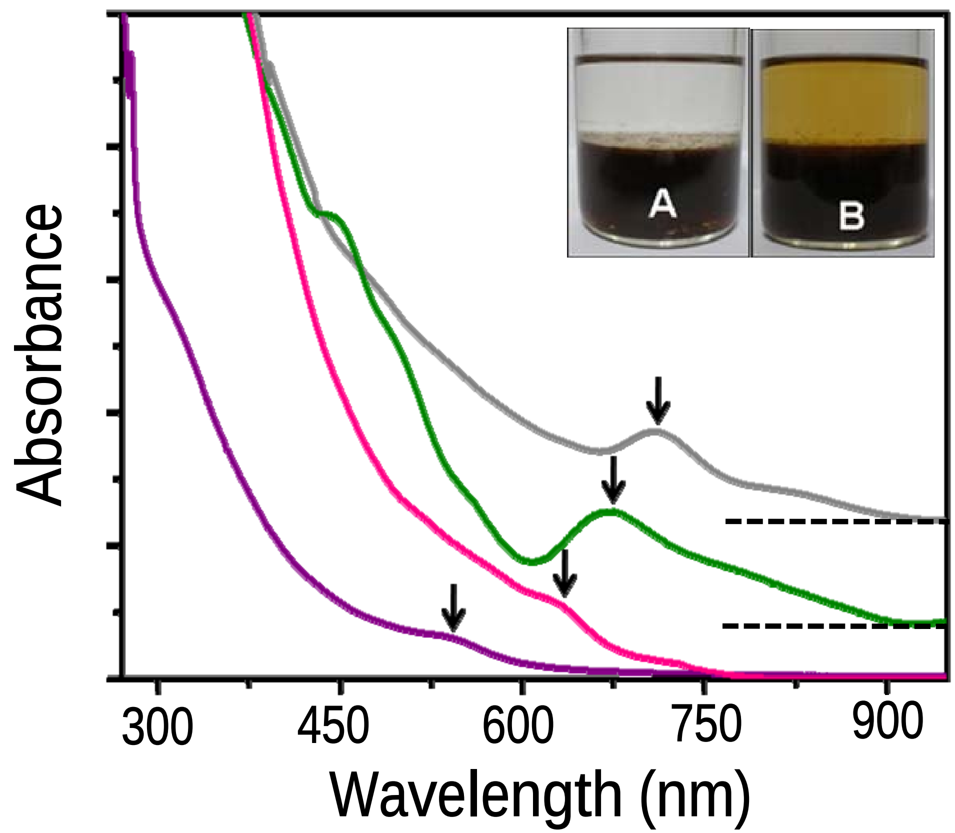
Clusters from clusters: Au_{25} to make other clusters

Schematic of the interfacial synthesis of red emitting clusters from $Au_{25}SG_{18}$.



Scheme 1. Formation of the three sub-nanoclusters from $Au_{25}SG_{18}$ by core etching by two routes. Photographs of the cluster aqueous solutions under UV light are also given.

Habeeb Muhammed et al. Chem. Eur. J. (2009)



Comparison of the optical absorption features of $Au_{25}SG_{18}$ (green trace) with Au_xOT_y (grey trace), Au_xSG_y (pink trace) and Au_xMPTS_y (purple trace). The arrows show the absorption peaks of the clusters due to intra band transitions. The spectra are shifted vertically for clarity. Dotted lines indicate the threshold of absorption. Inset shows the photographs (under white light) of the water-toluene bi-phasic mixture before (A) and after (B) reaction at 55 ºC (interfacial etching) for 1 h.

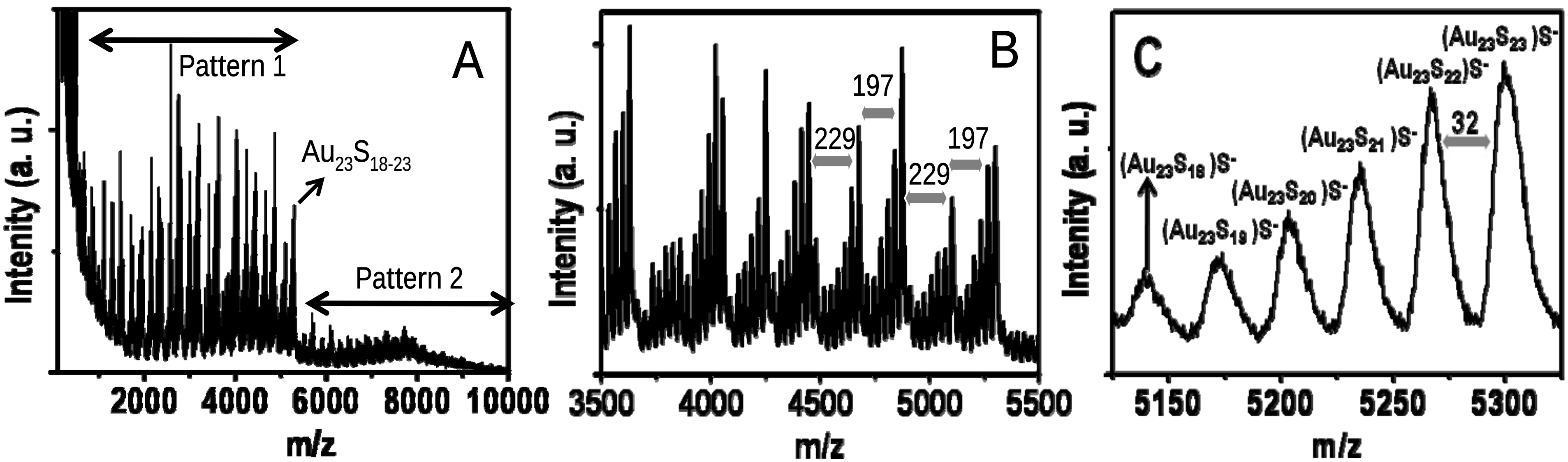
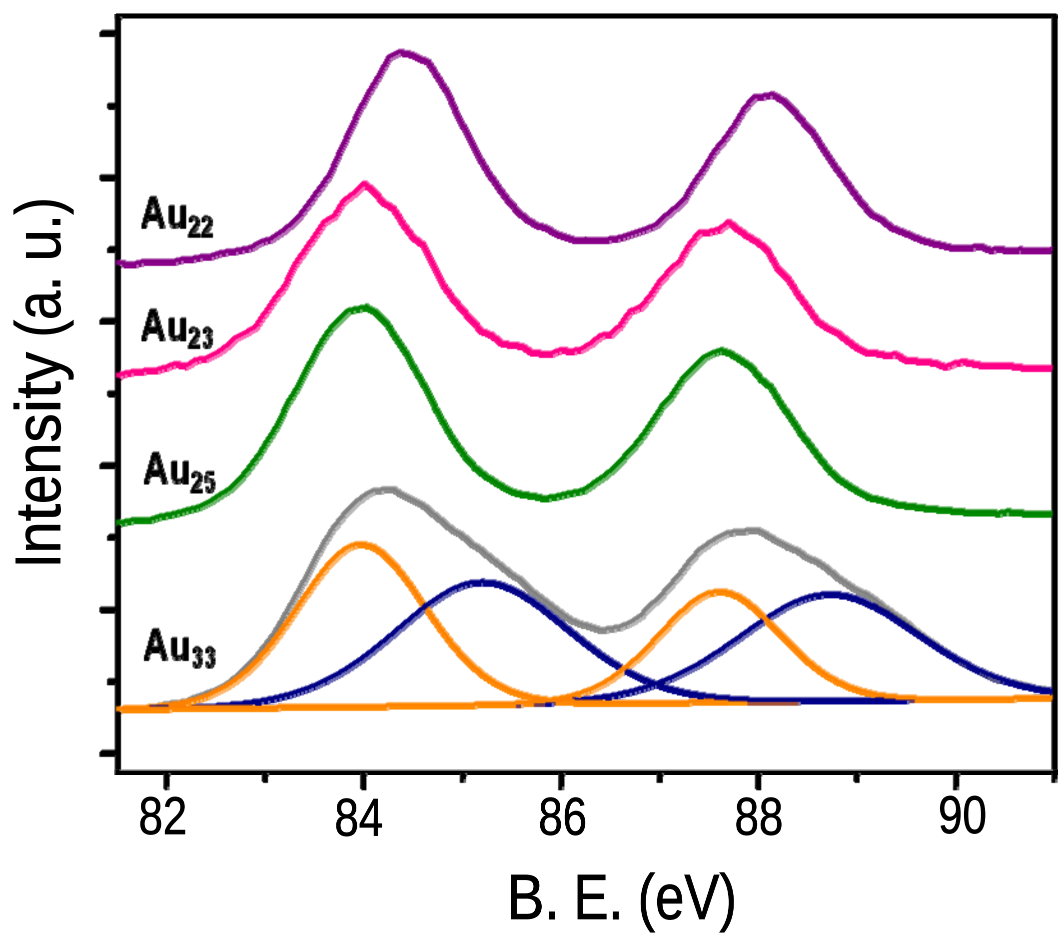
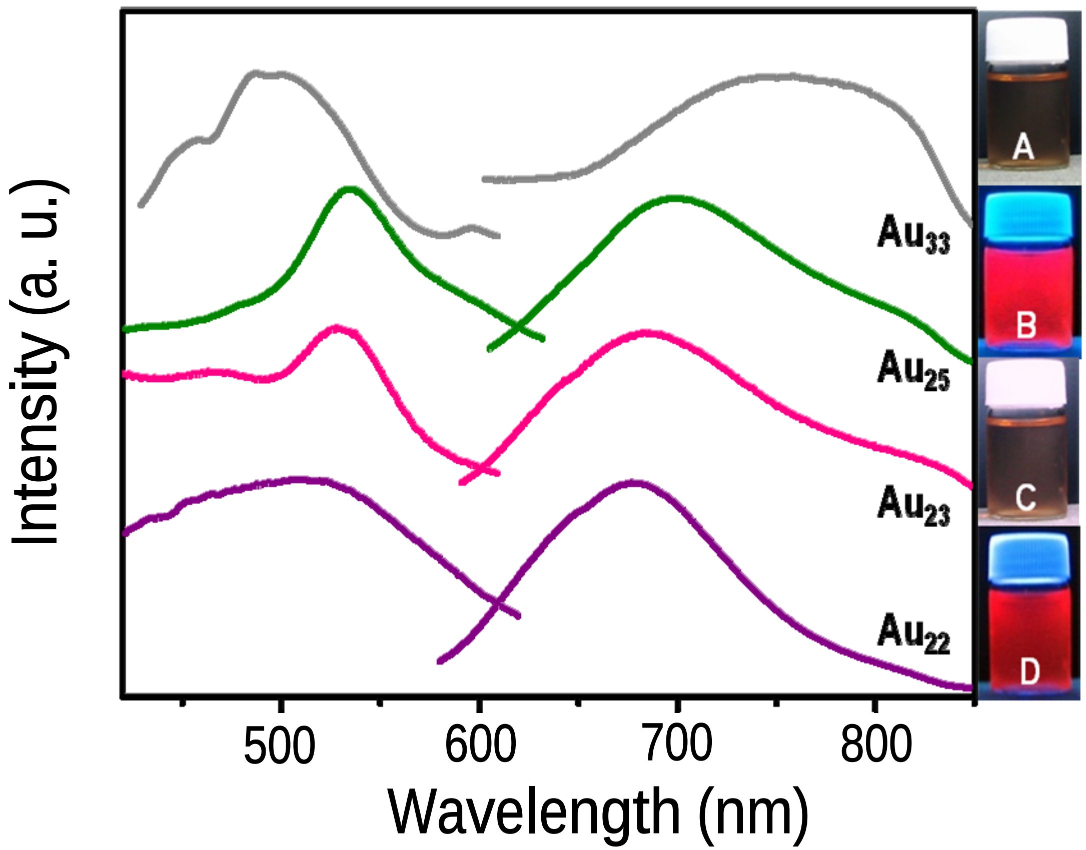


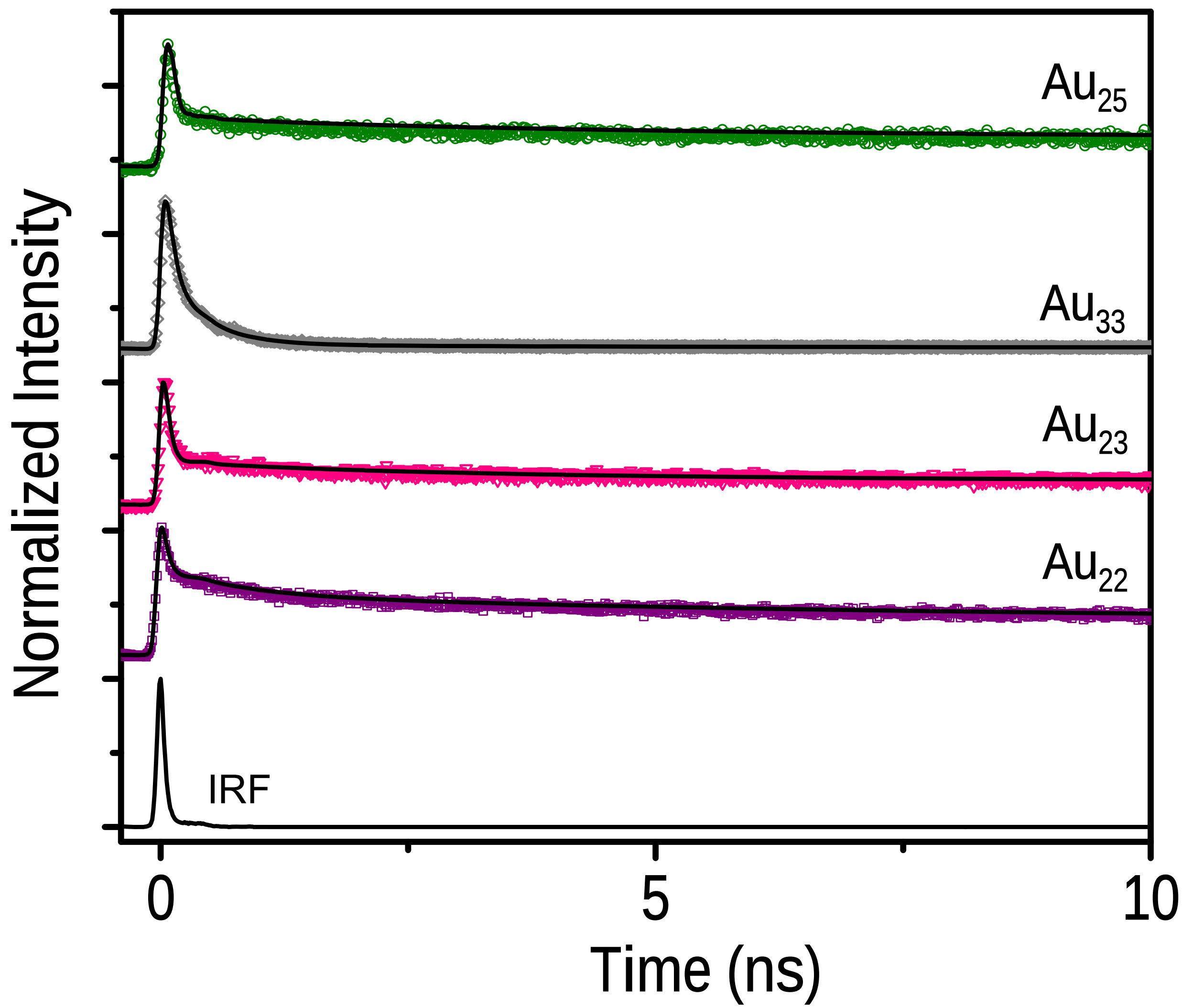
Figure 2. A) MALDI-MS of Au_xSG_y which shows bunch of peaks due to Au_mS_n clusters. B) A group of peaks with m/z spacing of 197 or 229 between the major peaks of the adjacent group of peaks. C) Expanded view of peaks due to $Au_{23}S_{18-23}$.



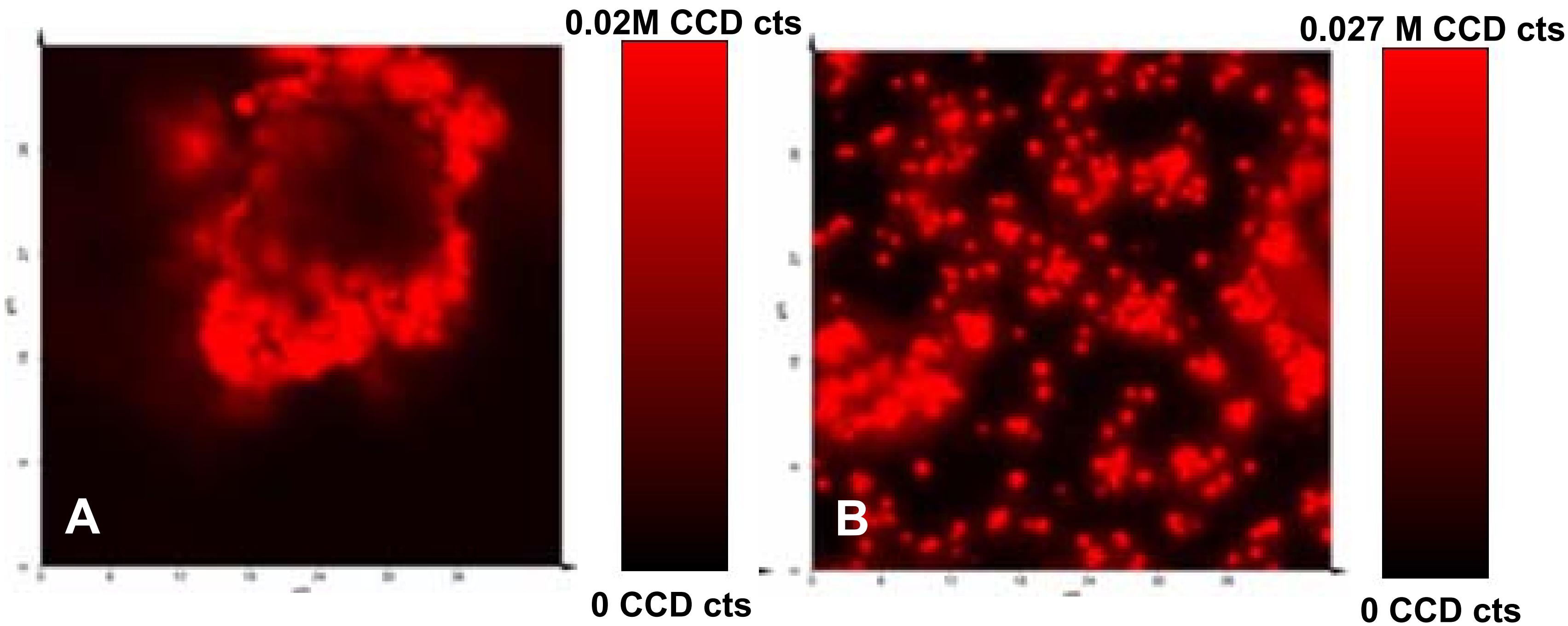
Comparison of the Au(4f) XPS spectra of Au_{22}, Au_{23} and Au_{33} along with parent Au_{25}.



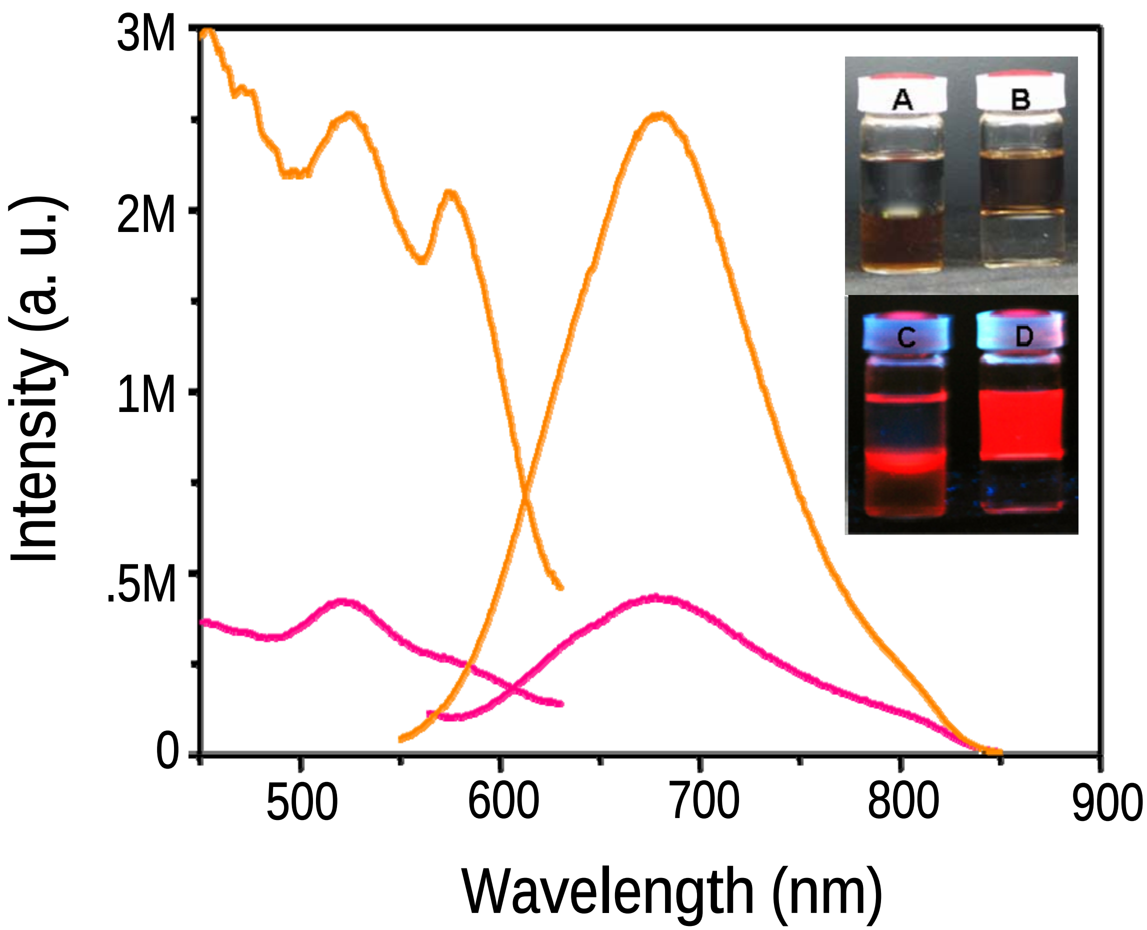
Comparison of the photoluminescence profiles of Au_{22}, Au_{23} and Au_{33} along with parent Au_{25}. Photographs of the aqueous solutions of Au_{22} and Au_{23} under white light (A and C, respectively) and UV light (B and D, respectively) are also given.



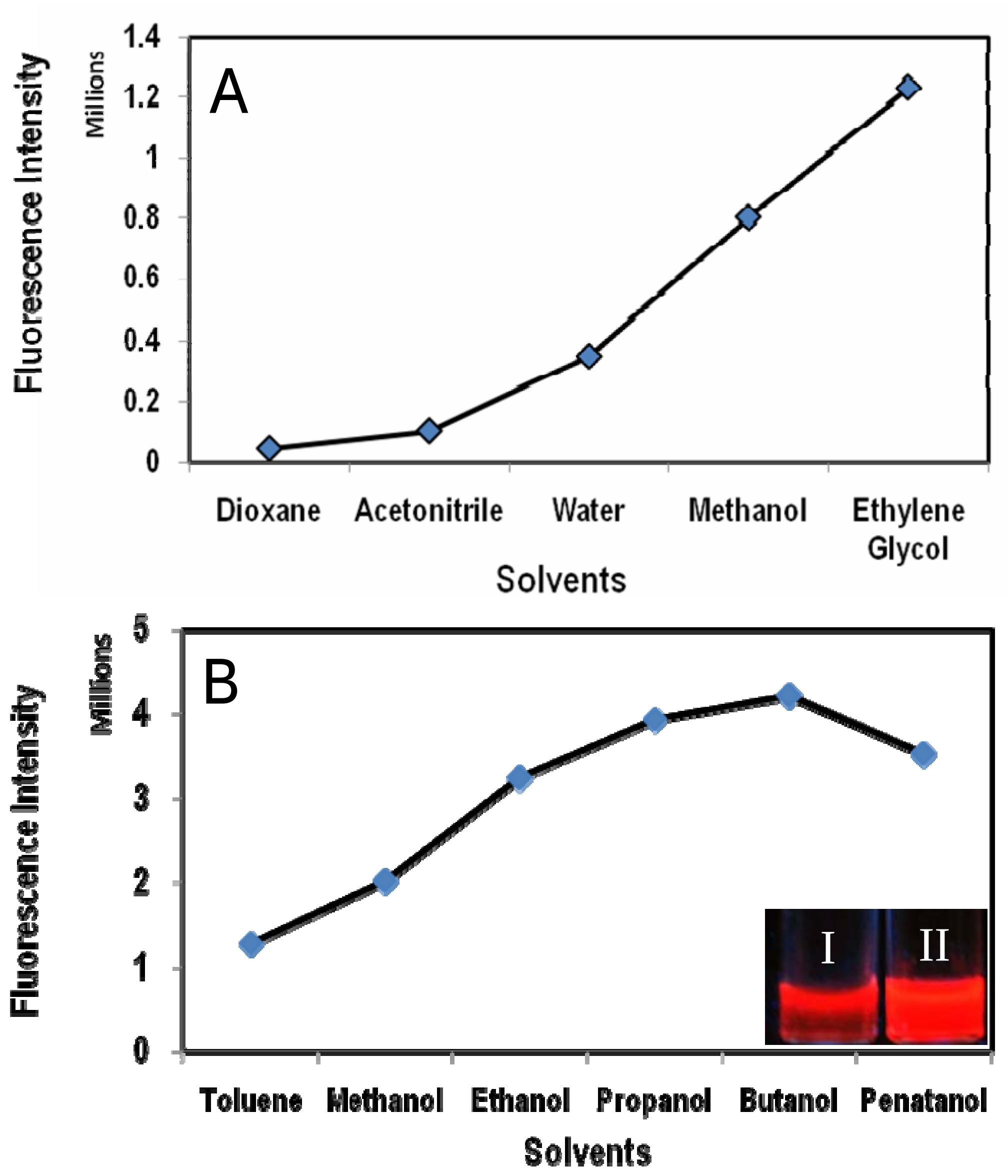
Fluorescence decay pattern of Au_{25}, Au_{33}, Au_{23}, and Au_{22} collected at 630 nm.



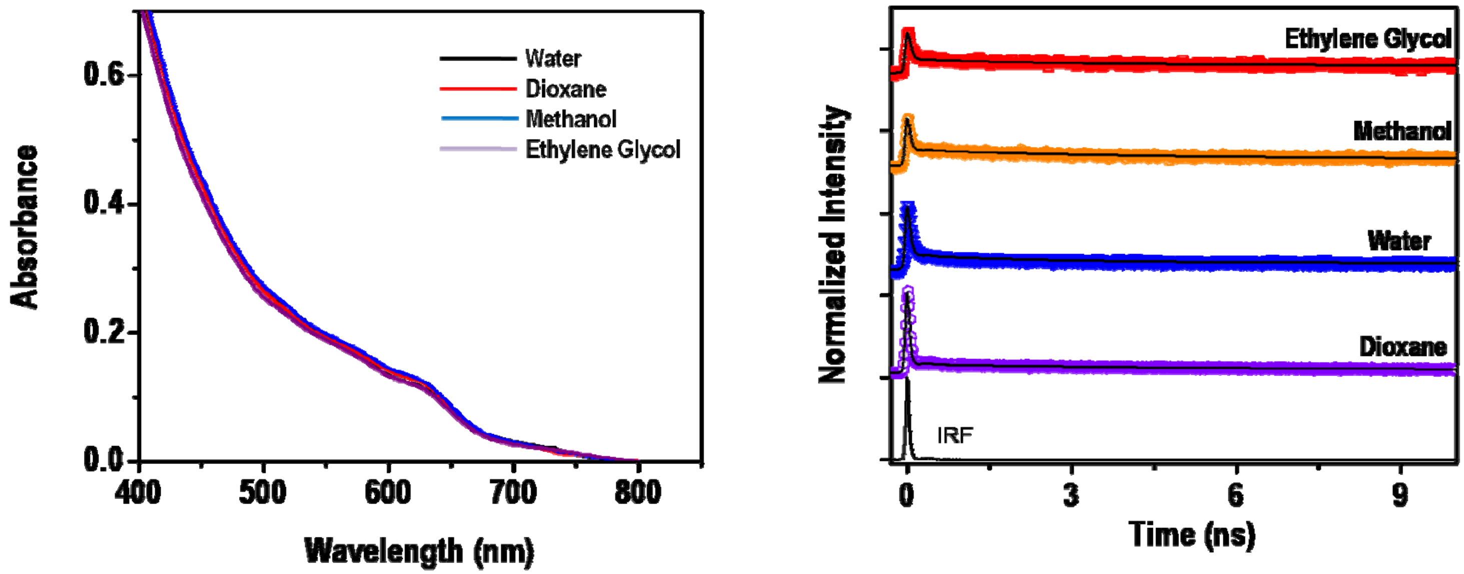
Inherent fluorescence image of Au_{22} (A) and Au_{23} (B) collected by the spectroscopic mapping at an excitation wavelength of 532 nm. Regions coded red represents the pixels where the signal (used for mapping) is a maximum, the minima being represented with black colors. The scan area was 40 μM x 40 μM.



Photoluminescene profile of Au_{23} cluster before (pink trace) and after (orange trace) phase transfer. Emission of the cluster enhances considerably after the phase transfer. Photographs of the aqueous-toluene mixture containing the cluster before and after phase transfer under white light (A and B, respectively) and UV light (C and D, respectively). In C, only the interface is illuminated as the UV is attenuated as the sample was irradiated from the top

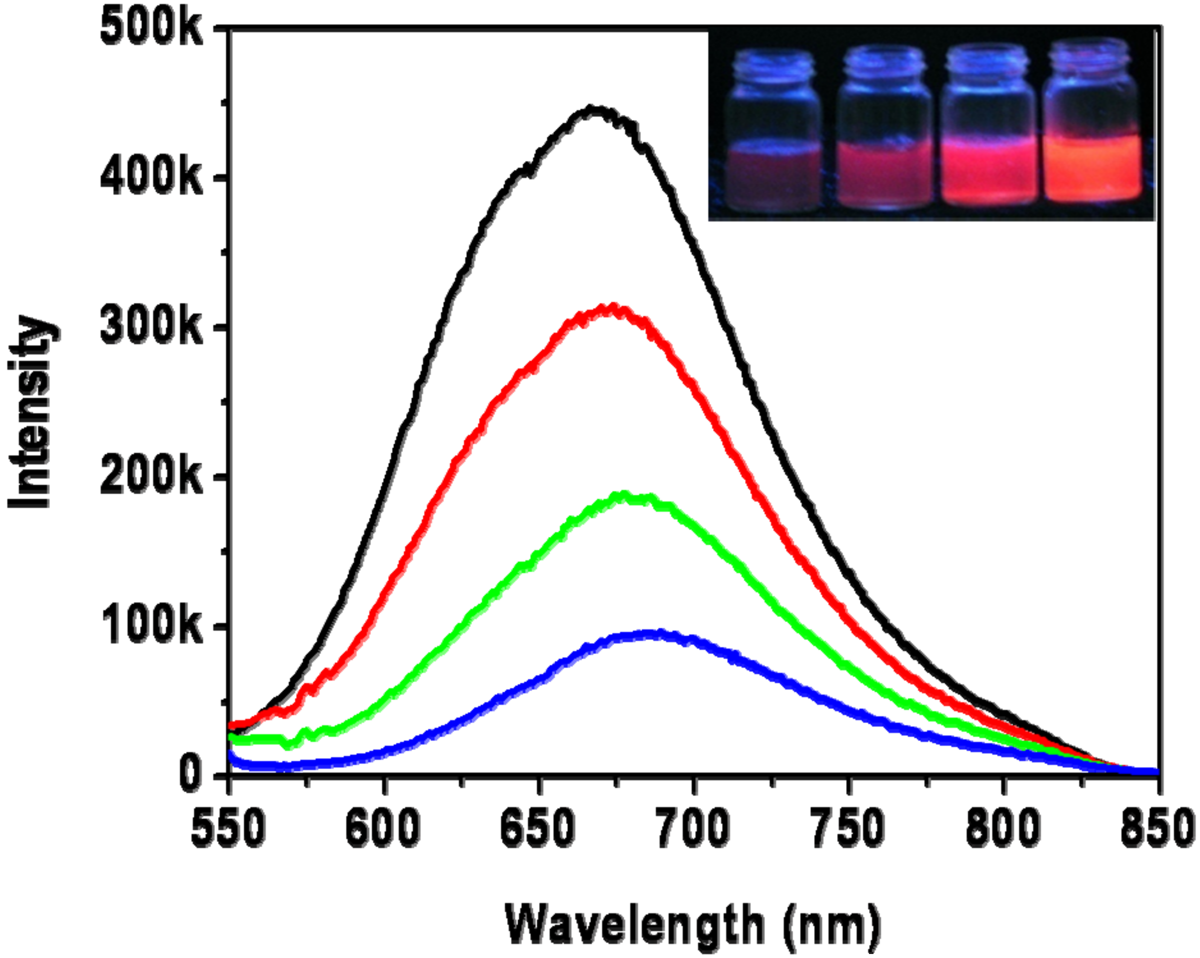


A) Solvent dependent fluorescence of 50 μM Au_{23} in ethylene glycol, methanol, water, acetonitrile and dioxane before phase transfer. B) Solvent dependent fluorescence of Au_{23} in methanol, ethanol, propanol, butanol and pentanol after phase transfer. Inset of B shows the photograph of phase transferred Au_{23} in toluene (I) and butanol (II) under UV light irradiation

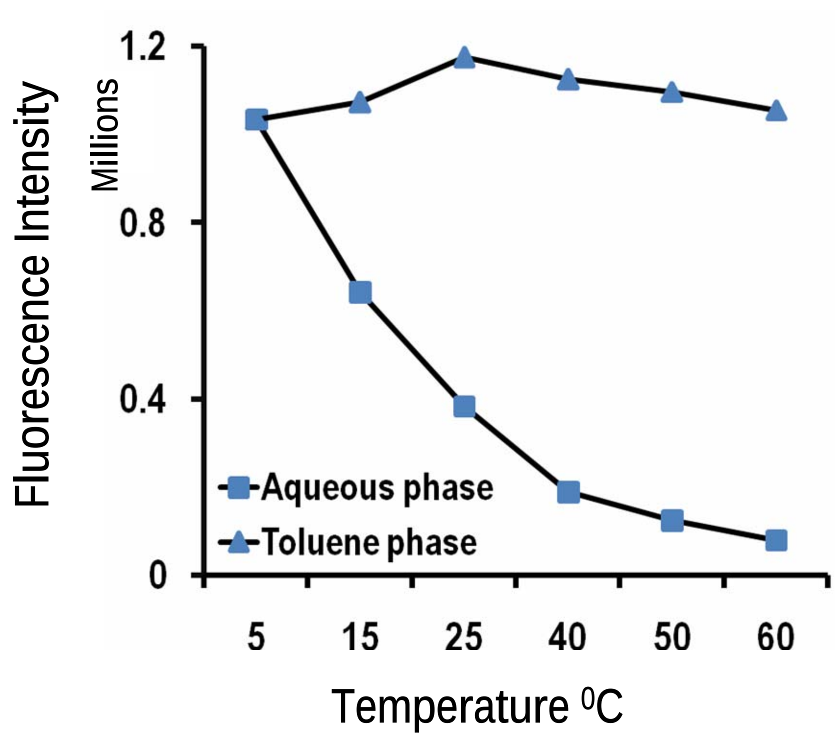


Solvent	τ_1(ps)	%	τ_2 (ns)	%	τ_3 (ns)	%
Ethylene Glycol	47	86.5	2.67	5.5	70.06	7.9
Methanol	36	87.6	3.27	5.8	62.91	6.6
Water	39	92.4	2.41	3.6	68.55	3.9
Dioxane	16	98.0	5.07	1.1	31.63	0.9

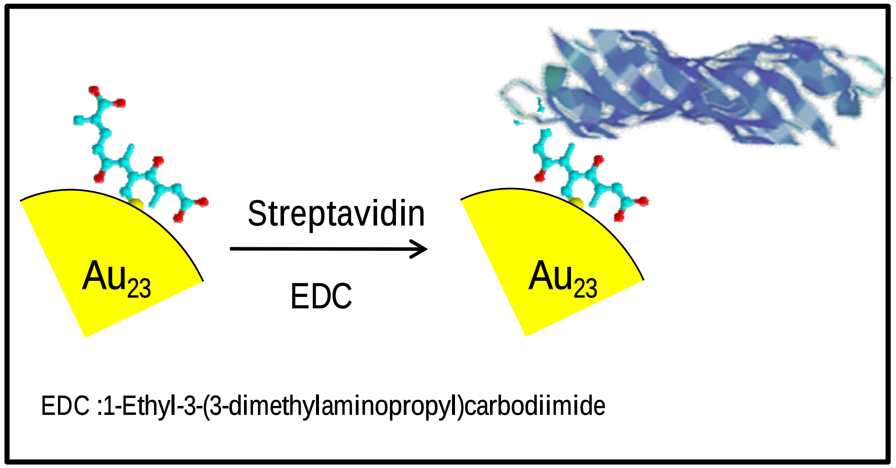
A) Optical absorption spectra of Au_{23} in dioxane, water, methanol and ethylene glycol. B) Fluorescence decay of Au collected at 630 nm in various solvents. Table tabulates the life time of the cluster in various solvents.



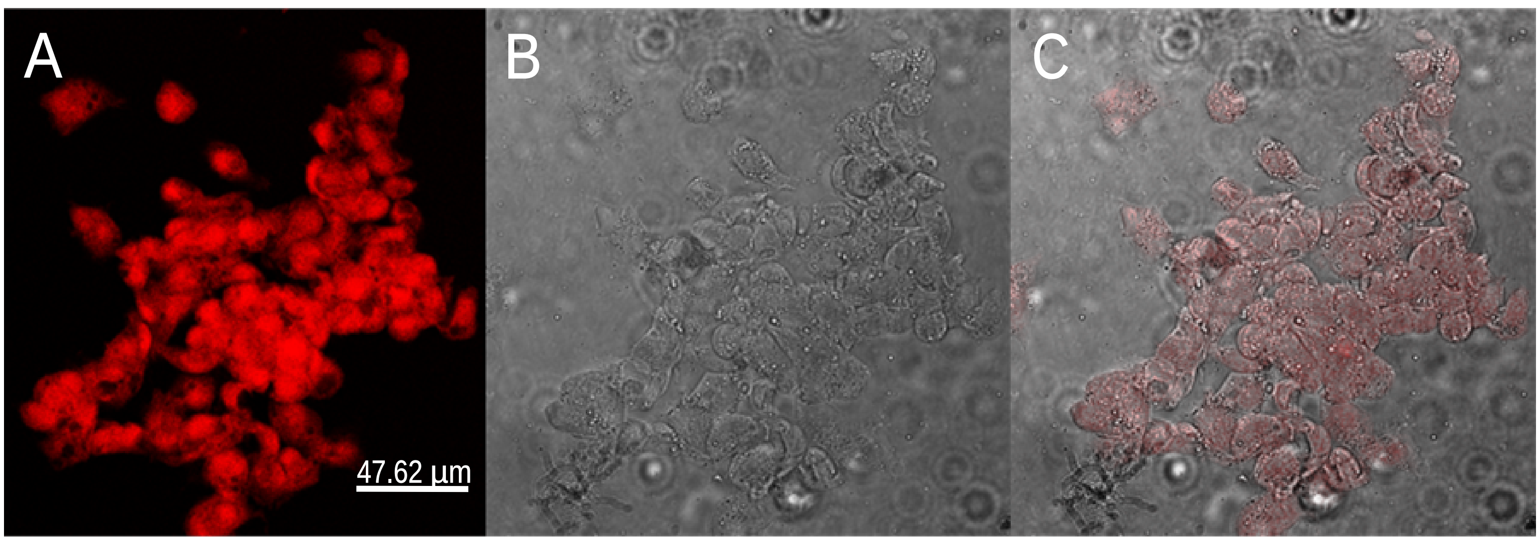
Plot of fluorescence intensity of Au_{23} cluster in water-DMSO mixture starting from pure water (blue line) to 1:1 (green line), 1:2 (red line) and 1:3 (black trace) water-DMSO mixtures. Inset shows the photographs of the corresponding solutions under UV light irradiation



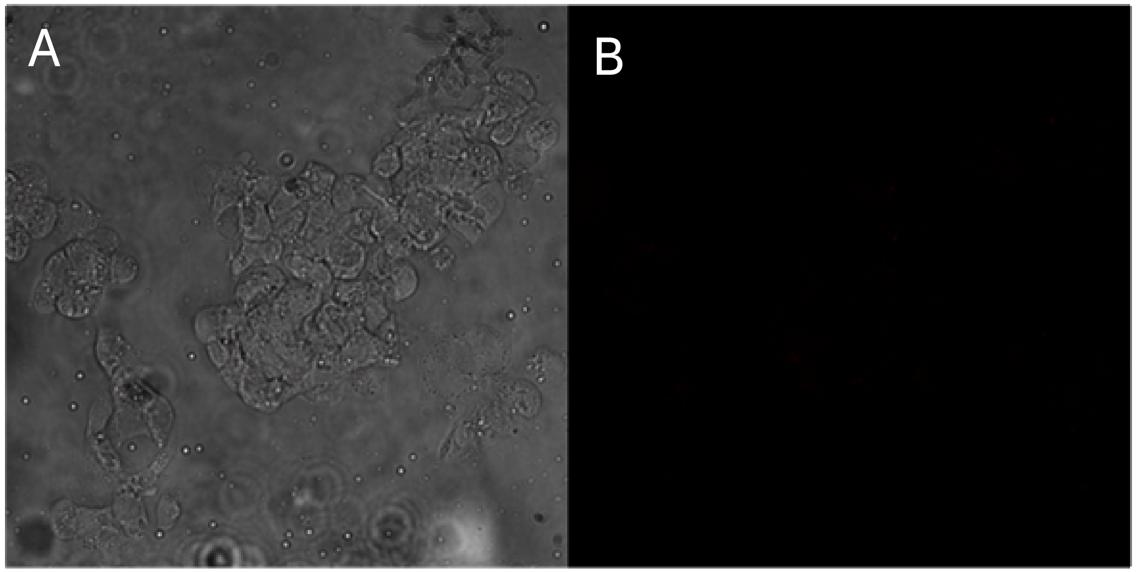
Plot of temperature *vs* fluorescence intensity of the cluster in the aqueous and toluene layers. While the intensity of emission of aqueous solution of Au_{23} decreases with increase in temperature, the emission intensity remains unaltered for phase transferred Au_{23}.



Schematic representation of the conjugation of streptavidin on $Au_{23}SG_{18}$ by EDC coupling.

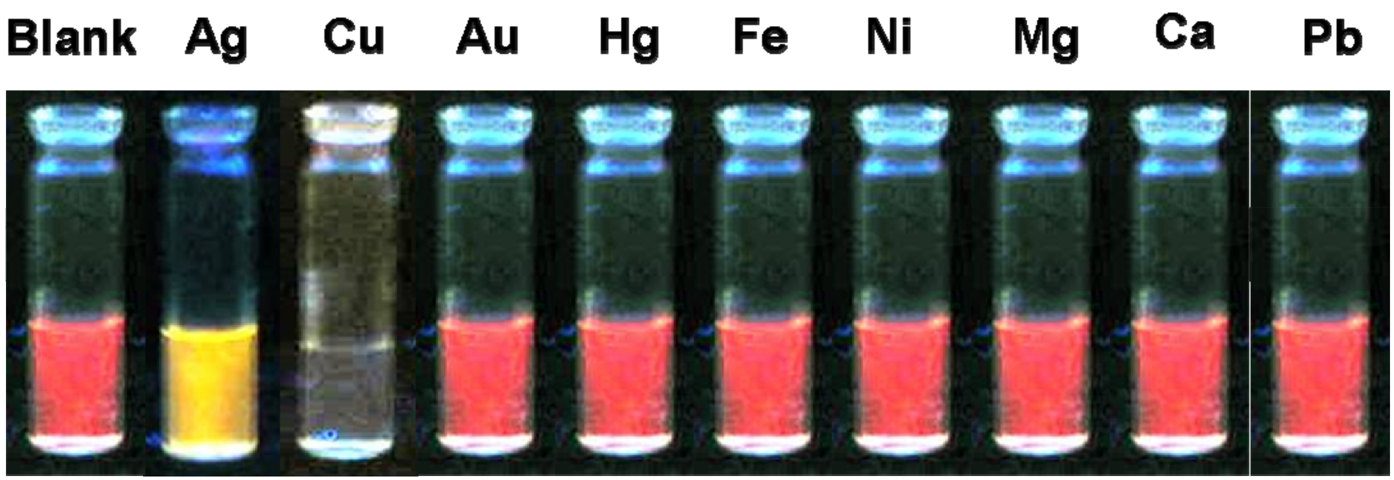


Fluorescence (A), bright field (B) and overlay of fluorescent and bright field images (C) of human hepatoma (HepG2) cells stained with streptavidin conjugated Au_{23}.



Bright field (A) and fluorescence (B) images of HepG2 cells stained with unconjugated Au_{23} clusters. No fluorescence was observed from the cells after washing

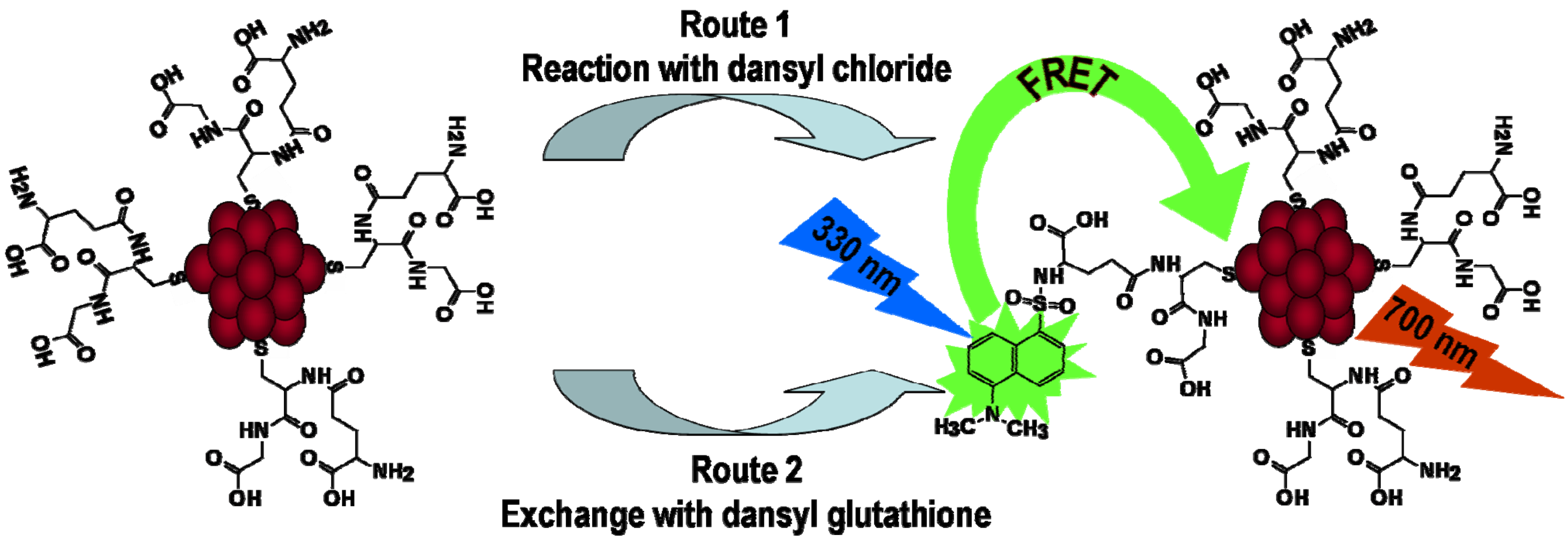
Clusters for metal ion detection



Water soluble red emitting clusters where treated with various metal ions with a final Concentration of 25 ppm. The emission was shifted to lower wavelength in case of silver ions and quenched completely in case of copper ions. The emission was an altered in case of other ions.

Habeeb Muhammed et al. Chem. Eur. J. (2009)

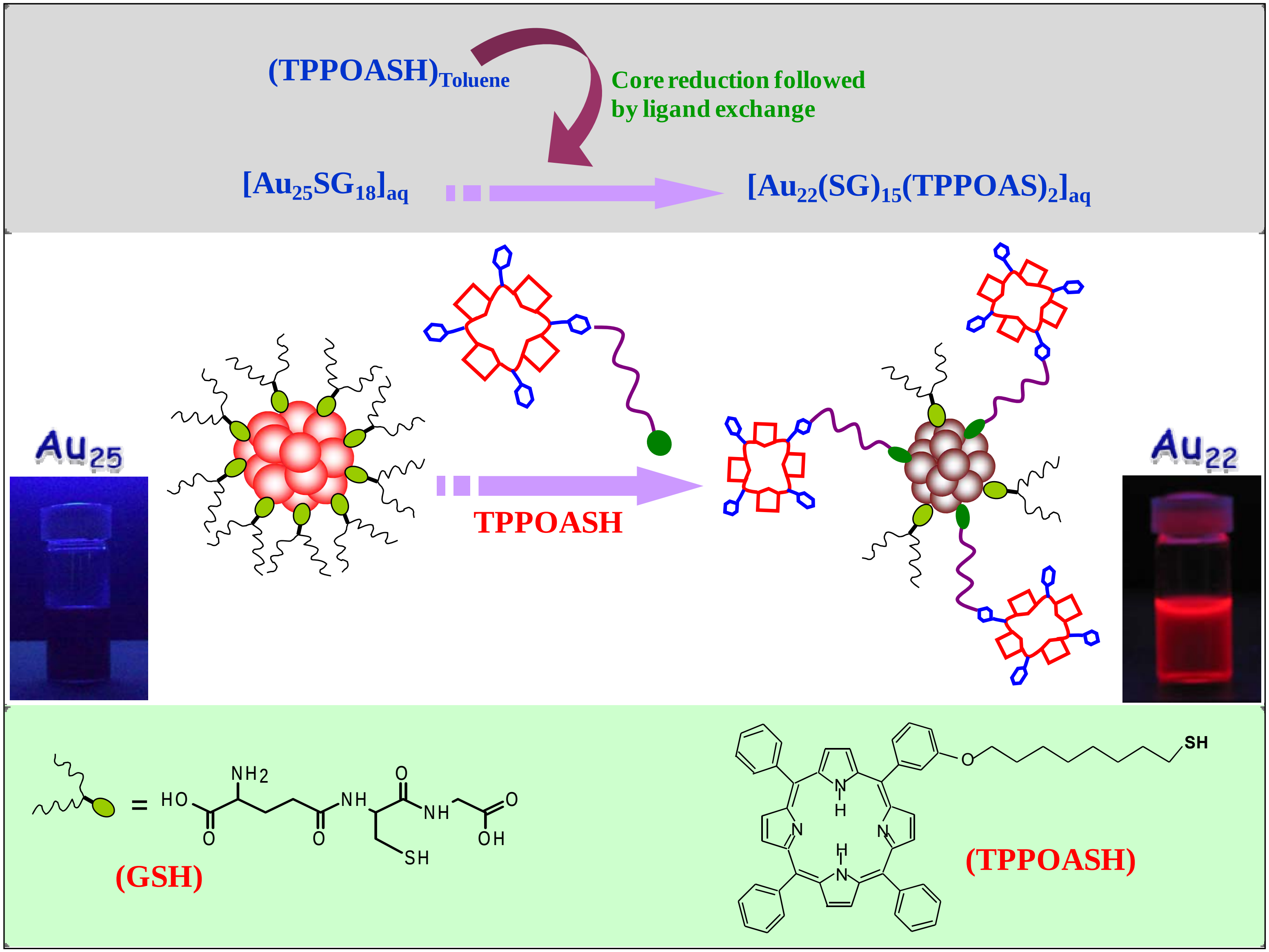
FRET between Au_{25} and Dansyl Chromophore



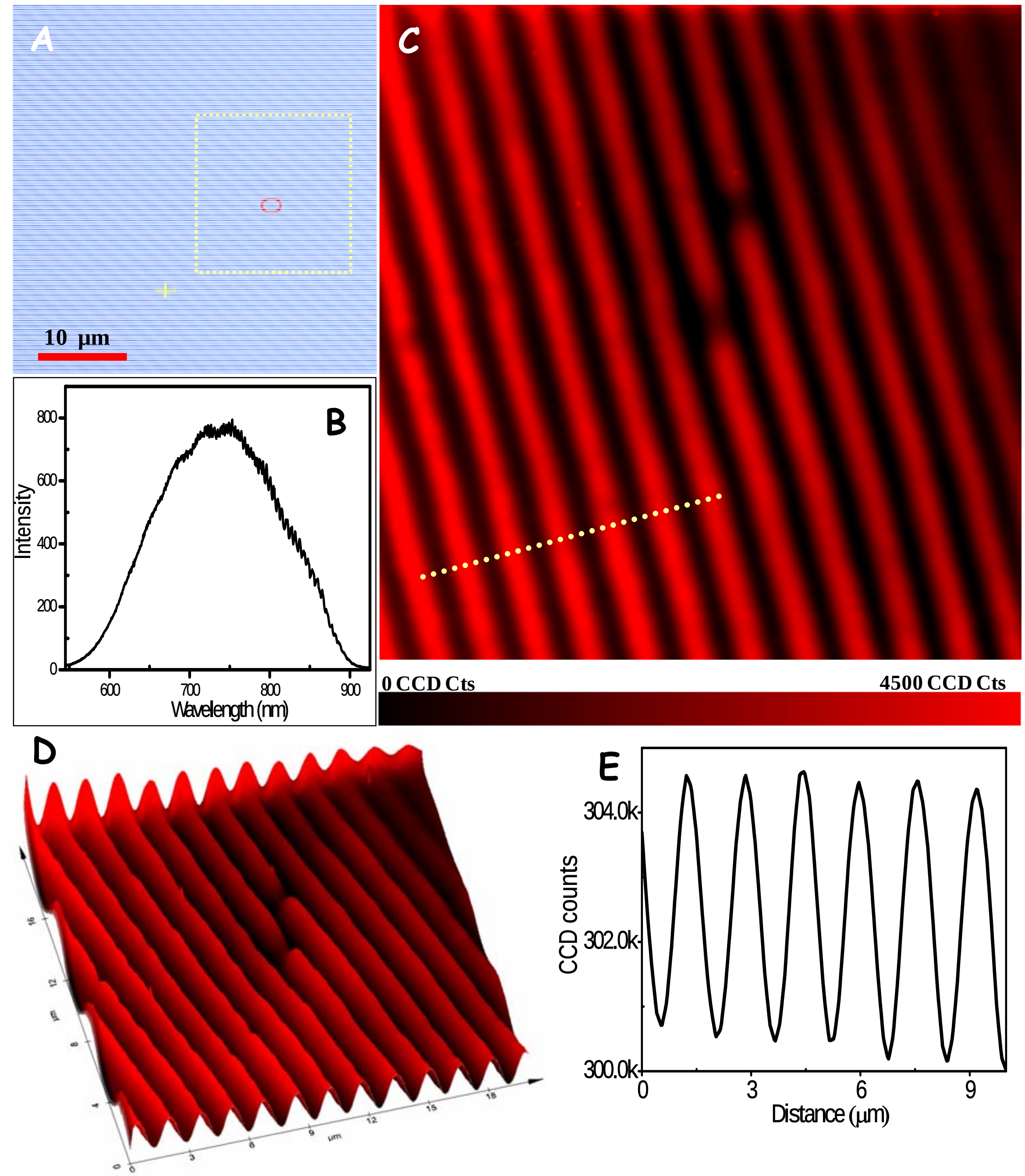
Approaches Used for the Functionalization of Dansyl Chromophore on the Au_{25} Cluster.

Habeeb Muhammed et al. *J. Phys. Chem. C* 2008

Cluster based patterns



With G. U. Kulkarni



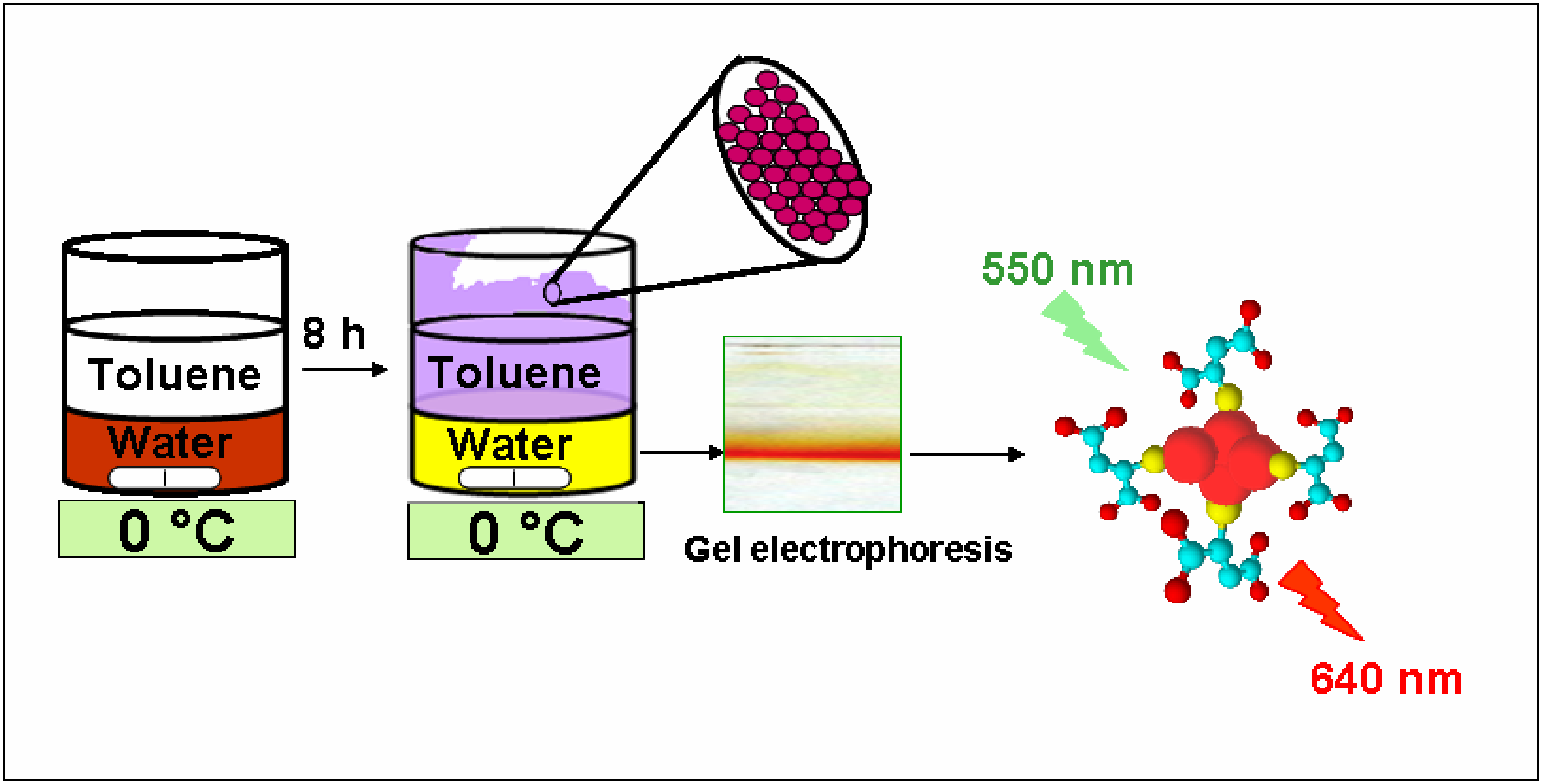
Shibu et al. ACS Applied Materials and Interfaces 2009 (in press)

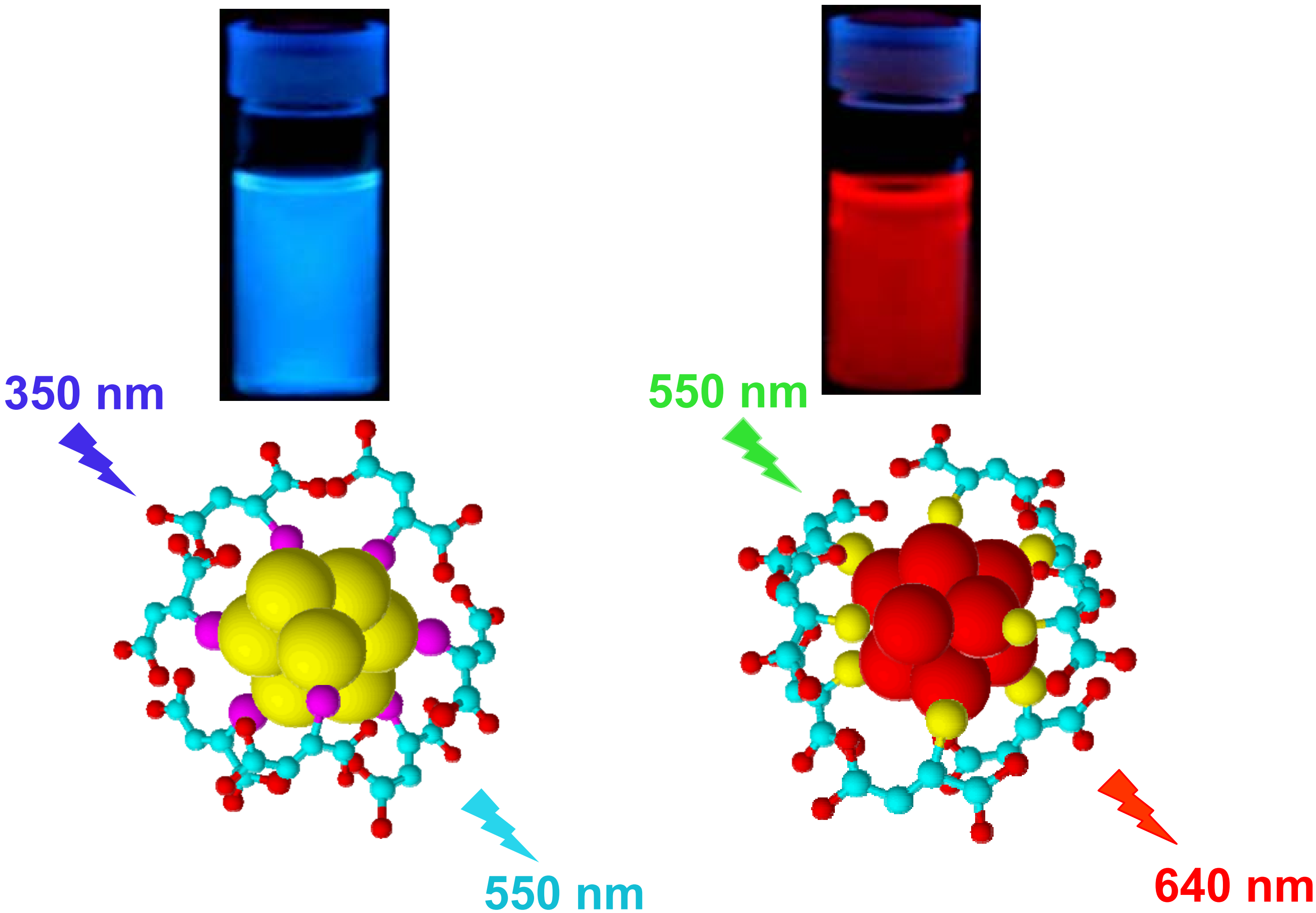
Size selected metal clusters

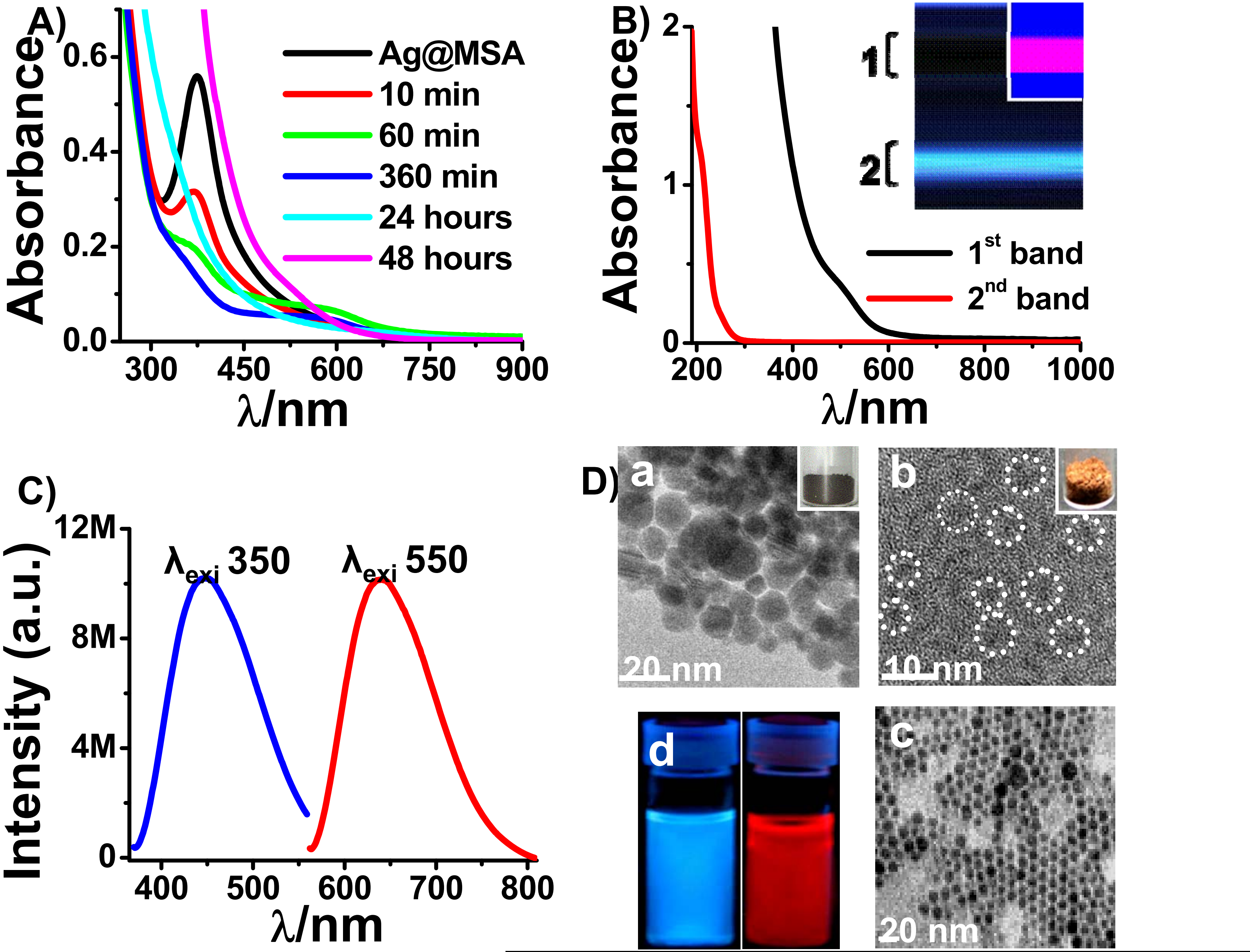
- The Optical Absorption Spectra of Small Silver Clusters (5-11) Embedded in Argon Matrices. Harbich, W.; Fedrigo, S.; Buttet, J. *Chem. Phys. Lett.* **1992,** *195,* 613
- Soft Landing and Fragmentation of Small Clusters Deposited in Noble-Gas Films. Harbich, W.; Fedrigo, S.; Buttet, J**.** *Phys. Rev. B* **1998,** *58*, 7428
- CO combustion on supported gold clusters. Arenz M, Landman U, Heiz U. *Chemphyschem* **2006,** *7*, 1871
- Low-temperature cluster catalysis. Judai, K.; Abbet, S.; Worz, A. S.; Heiz U.; Henry, C. R. *J Am. Chem. Soc.* **2004,** *126*, 2732
- The Reactivity of Gold and Platinum metals in their cluster phase. Heiz, U.; Sanchez,A.; Abbet, S. *Eur. Phys. J. D* **1999,** *9*,35
- When gold is not noble: Nanoscale gold catalysts. Sanchez A, Abbet S, Heiz U *J. Phys. Chem.* A. **1999,** *103*, 9573

Silver clusters

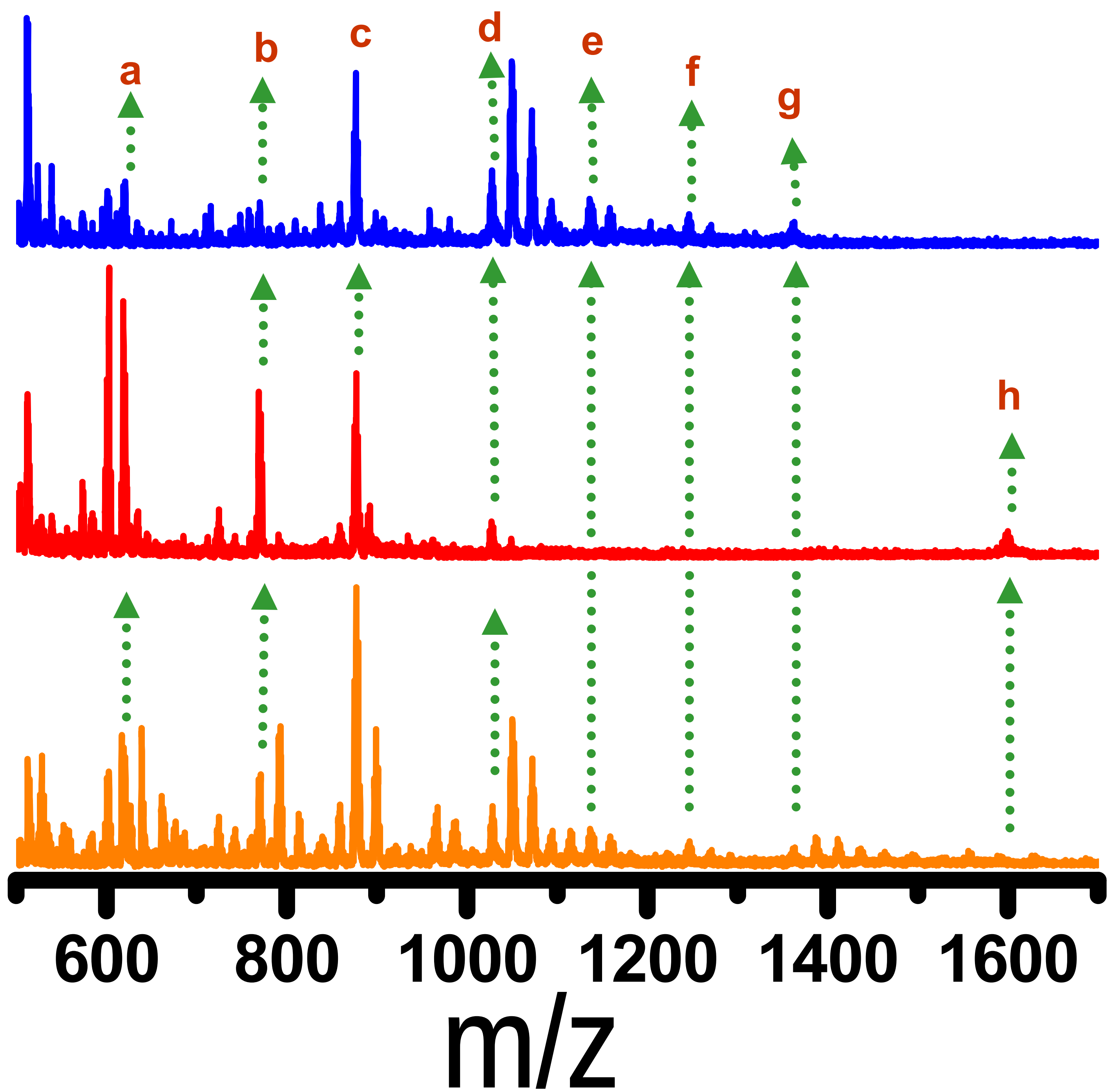
Interfacial etching



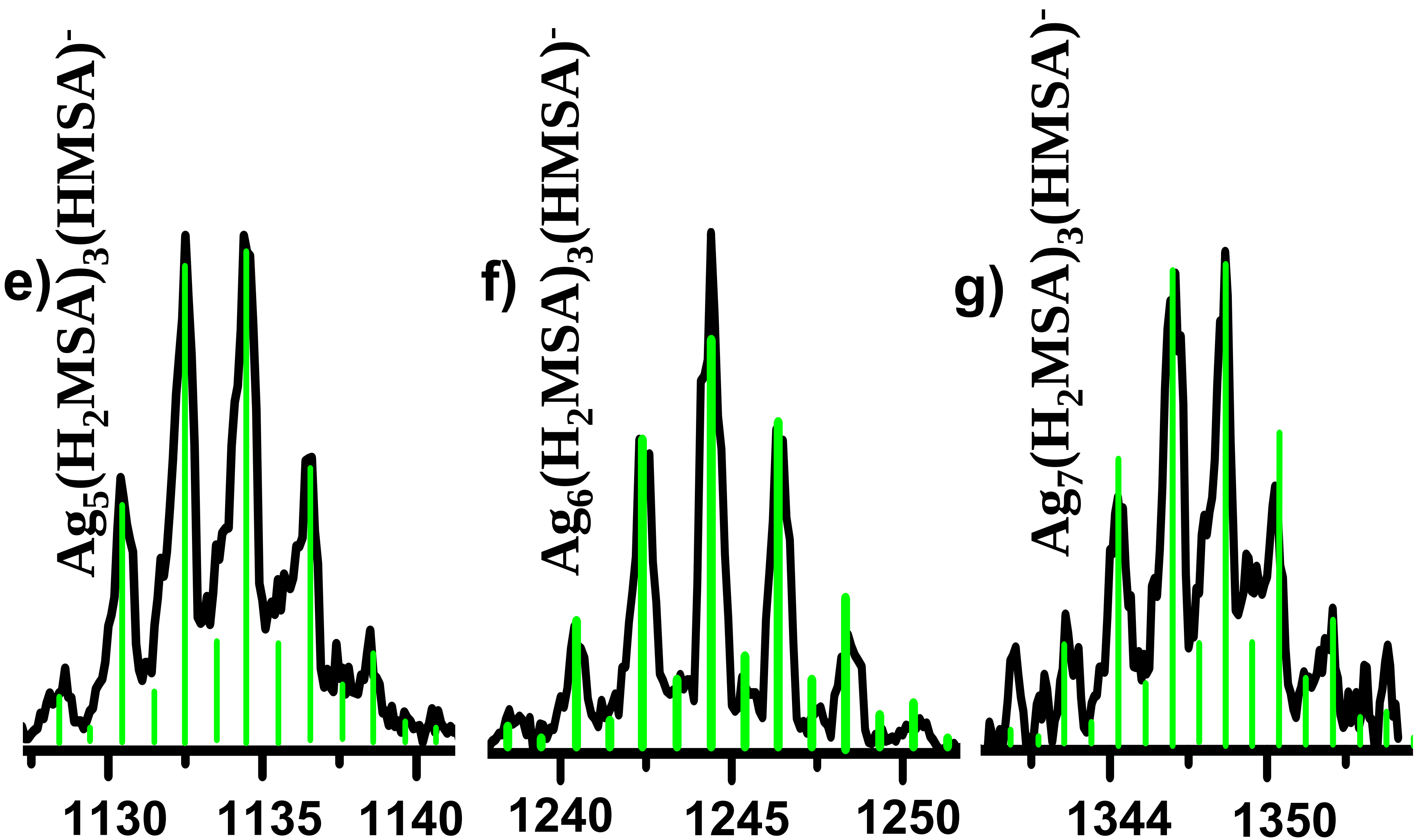

350 nm
550 nm
550 nm
640 nm



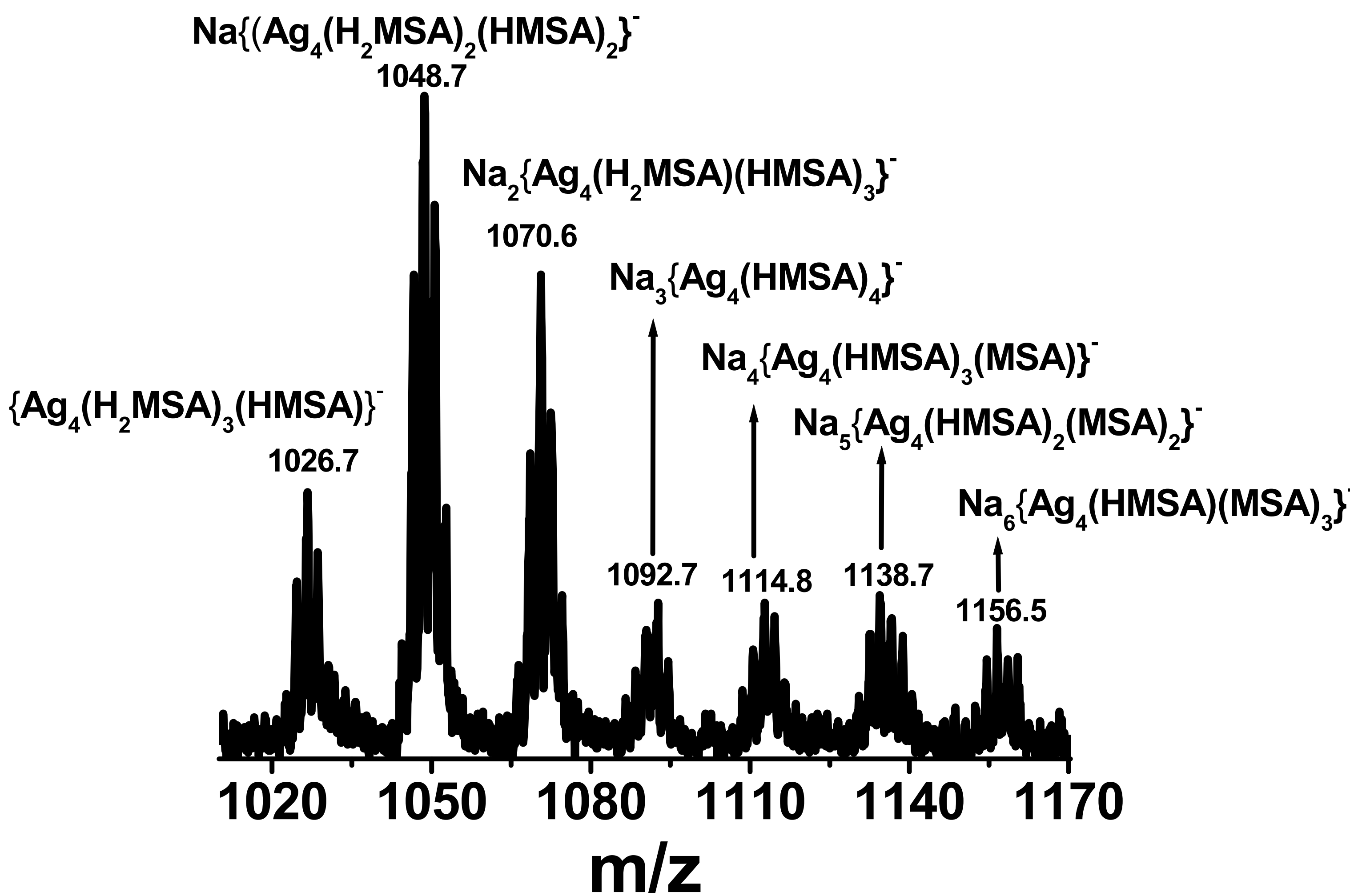
Udaybhaskar Rao and Pradeep, Submitted

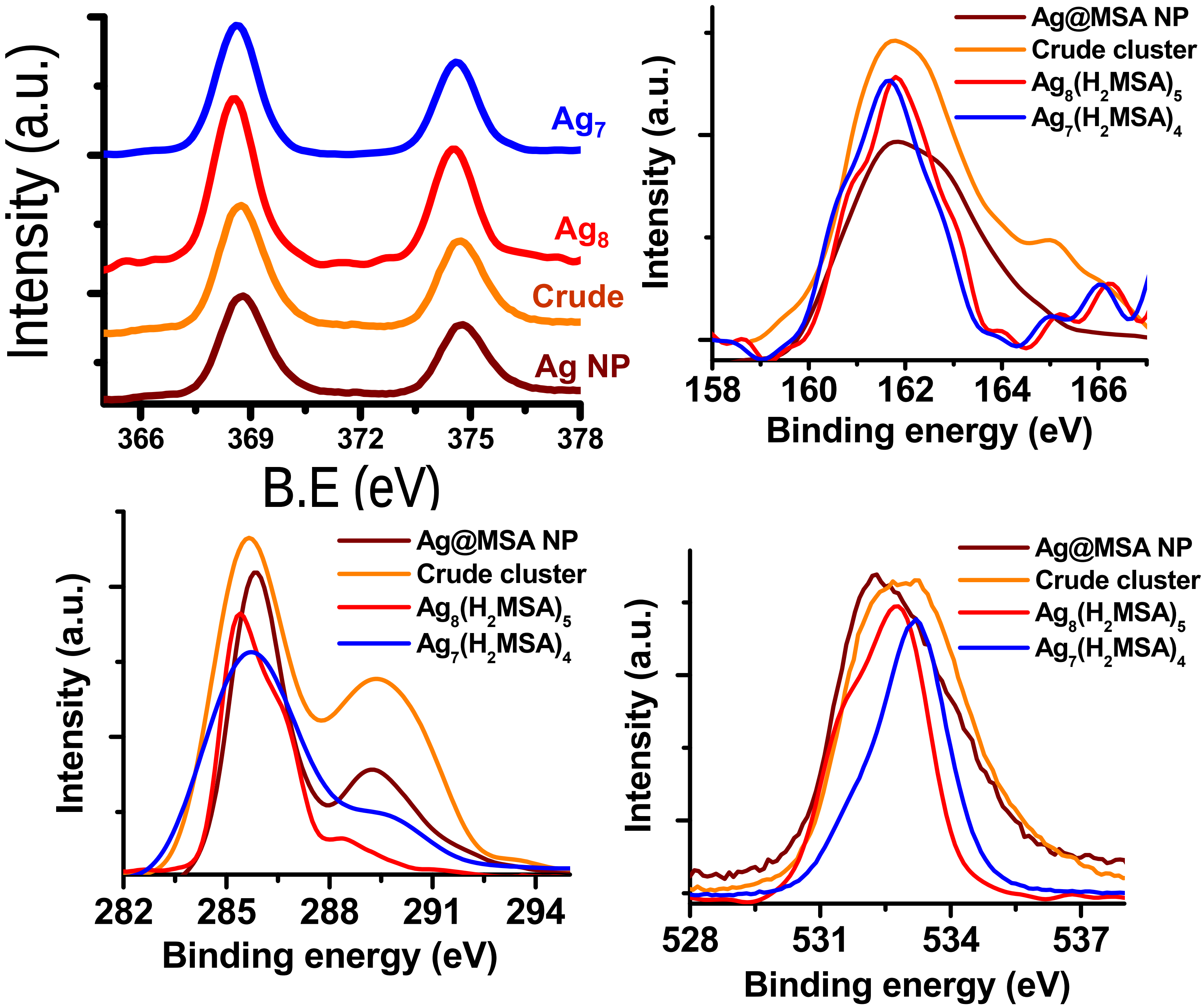


a
b
c
d
e
f
g
h
600
800
1000
1200
1400
1600
m/z

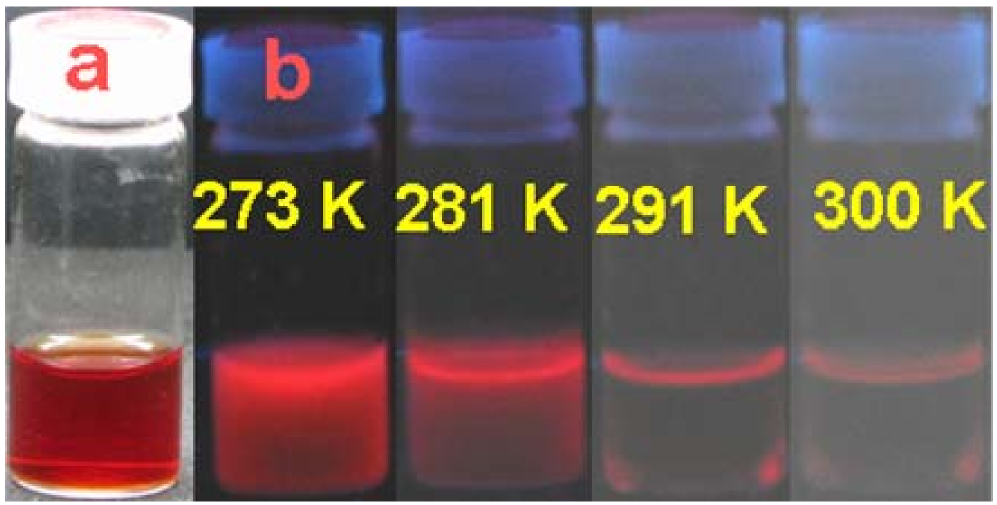


e)
$Ag_5(H_2MSA)_3(HMSA)^-$
1130
1135
1140
f)
$Ag_6(H_2MSA)_3(HMSA)^-$
1240
1245
1250
g)
$Ag_7(H_2MSA)_3(HMSA)^-$
1344
1350


Na{(Ag4(H2MSA)2(HMSA)2}-
1048.7
Na2{Ag4(H2MSA)(HMSA)3}-
1070.6
Na3{Ag4(HMSA)4}-
Na4{Ag4(HMSA)3(MSA)}-
{Ag4(H2MSA)3(HMSA)}-
1026.7
Na5{Ag4(HMSA)2(MSA)2}-
Na6{Ag4(HMSA)(MSA)3}-
1092.7
1114.8
1138.7
1156.5
1020
1050
1080
1110
1140
1170
m/z

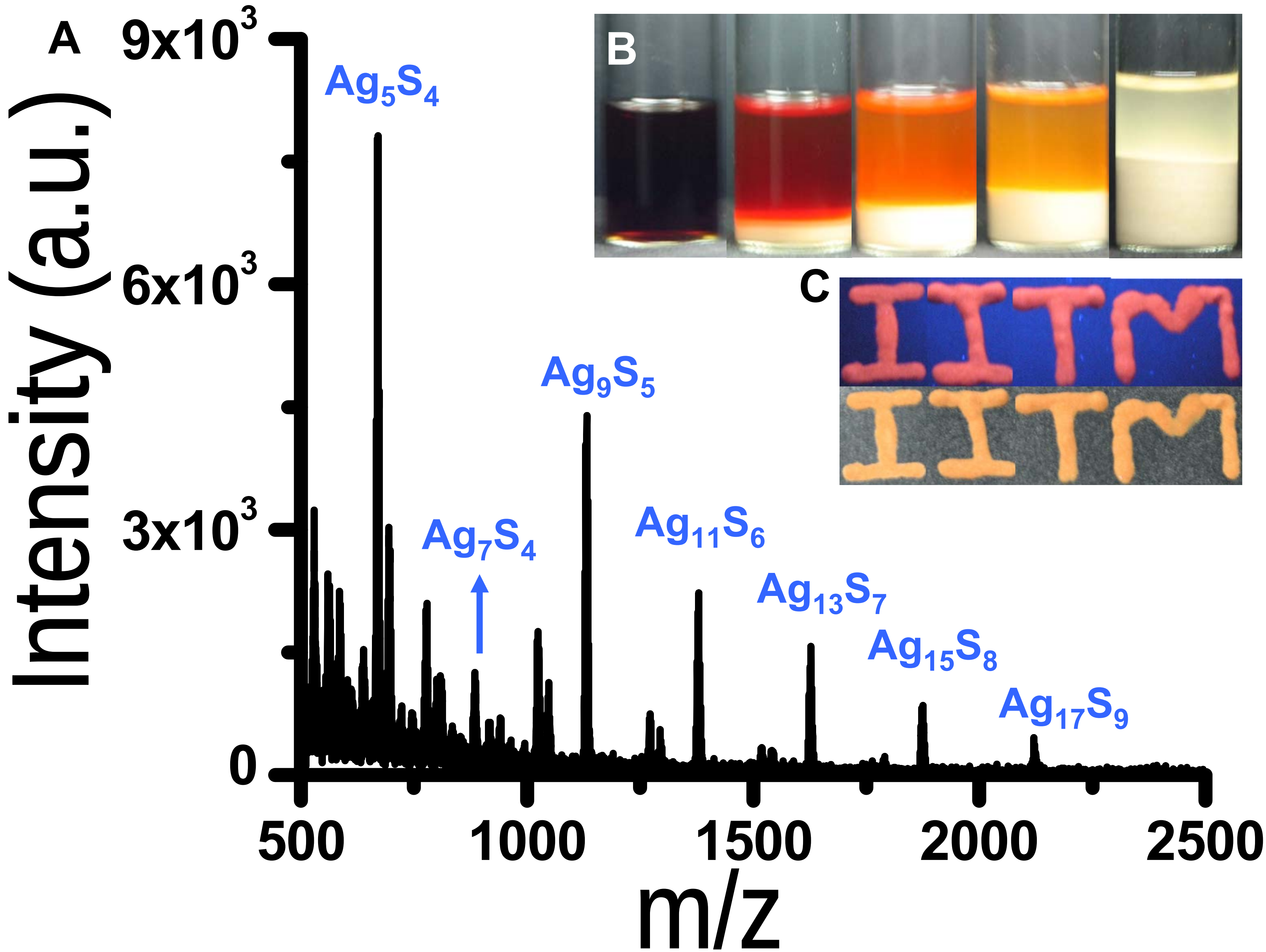


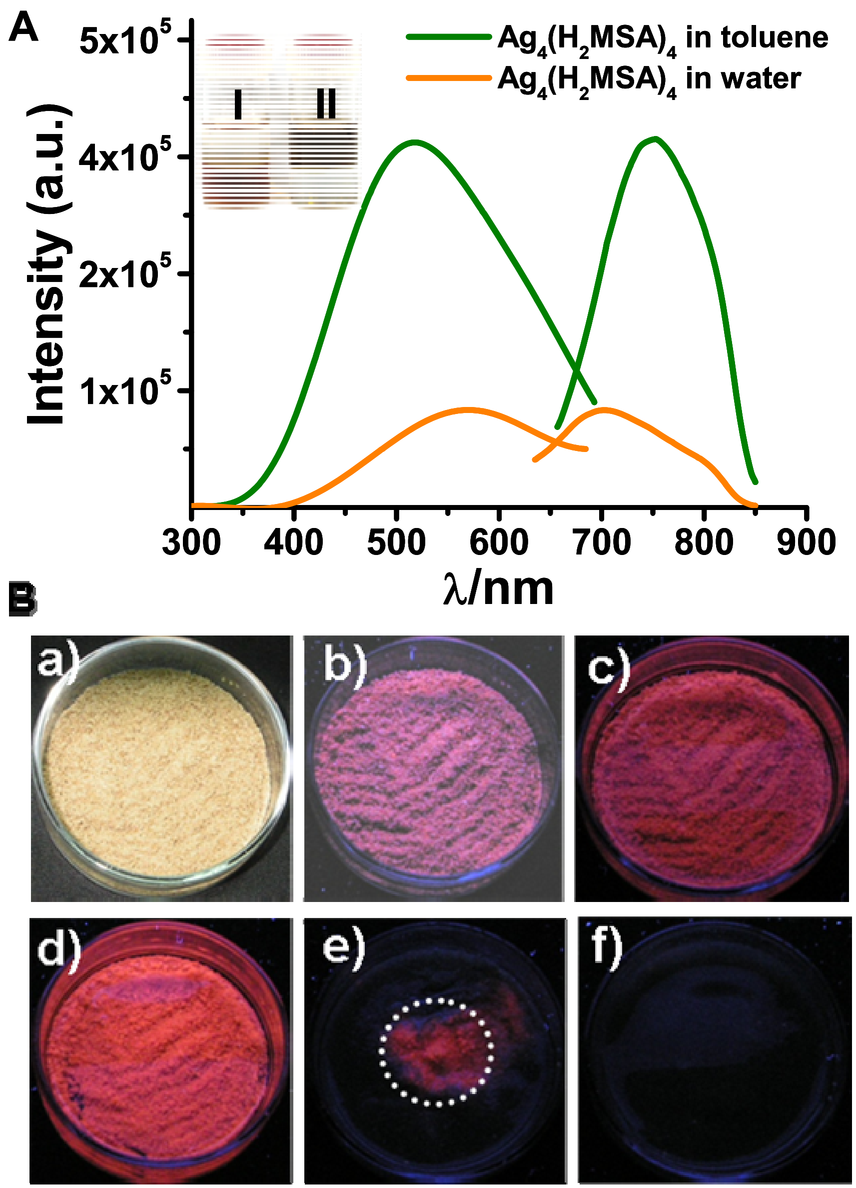
Intensity (a.u.)
Ag7
Ag8
Crude
Ag NP
366
369
372
375
378
B.E (eV)
Ag@MSA NP
Crude cluster
Ag8(H2MSA)5
Ag7(H2MSA)4
Intensity (a.u.)
158
160
162
164
166
Binding energy (eV)
Ag@MSA NP
Crude cluster
Ag8(H2MSA)5
Ag7(H2MSA)4
Intensity (a.u.)
282
285
288
291
294
Binding energy (eV)
Ag@MSA NP
Crude cluster
Ag8(H2MSA)5
Ag7(H2MSA)4
Intensity (a.u.)
528
531
534
537
Binding energy (eV)



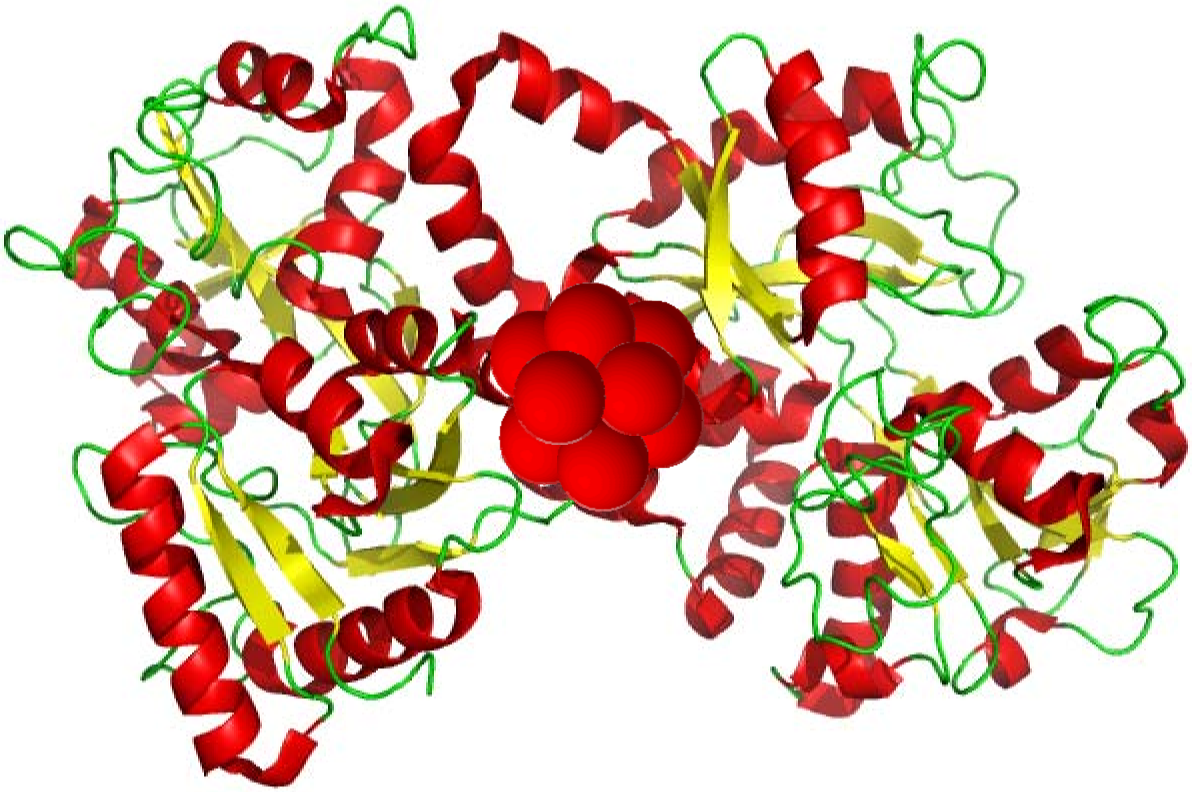
White light
RT

UV light **T →**


A
B
C
Intensity (a.u.)
m/z
9x10^3
6x10^3
3x10^3
0
500
1000
1500
2000
2500
Ag5S4
Ag7S4
Ag9S5
Ag11S6
Ag13S7
Ag15S8
Ag17S9
IITM
IITM


A
5x10^5
4x10^5
2x10^5
1x10^5
Intensity (a.u.)
I
II
Ag4(H2MSA)4 in toluene
Ag4(H2MSA)4 in water
300
400
500
600
700
800
900
λ/nm
B
a)
b)
c)
d)
e)
f)

Clusters in proteins

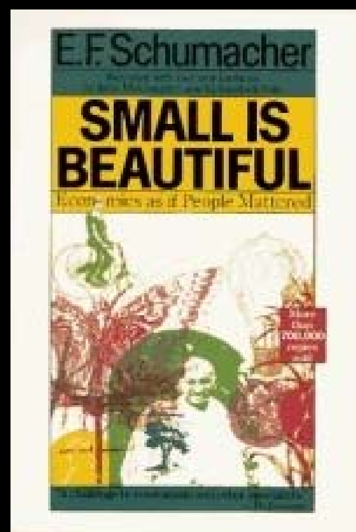


Lourdu Xavier

Nothing Gold Can Stay

Robert Frost (1923)

Nature’s first green is gold,
Her hardest hue to hold.
Her early leaf’s a flower;
But only so an hour.
Then leaf subsides to leaf.
So Eden sank to grief,
So dawn goes down to day.
Nothing gold can stay.



E. F. Schumacher

Nano Mission, Department of Science and Technology

IIT Madras

Thanks!