

Luminescent gold molecules

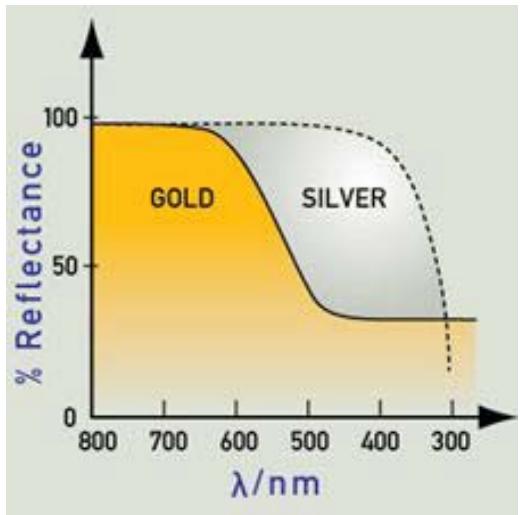
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Chennai 600 036

<http://www.dstuns.iitm.ac.in/prof-pradeep-group.php>

Au_{25} , Au_{23} , Au_{22} , Au_8 and Ag_8

IIT Delhi February 9, 2010



http://www.webexhibits.org/causesofcolor/9.html&usg=__eazWHmio6ubJtFEG_T6NScyGsc=&h=306&w=300&sz=9&hl=en&start=1&um=1&tbnid=g_xdRB5Fe6C6XM:&tbnh=117&tbnw=115&prev=/images%3Fq%3Dgold%2Bnanoparticles%2Bcolor%26hl%3Den%26sa%3DG%26um%3D1



Acknowledgements

M.A. Habeeb Muhammad

E.S. Shibu

Udayabhaskar Rao Tummu

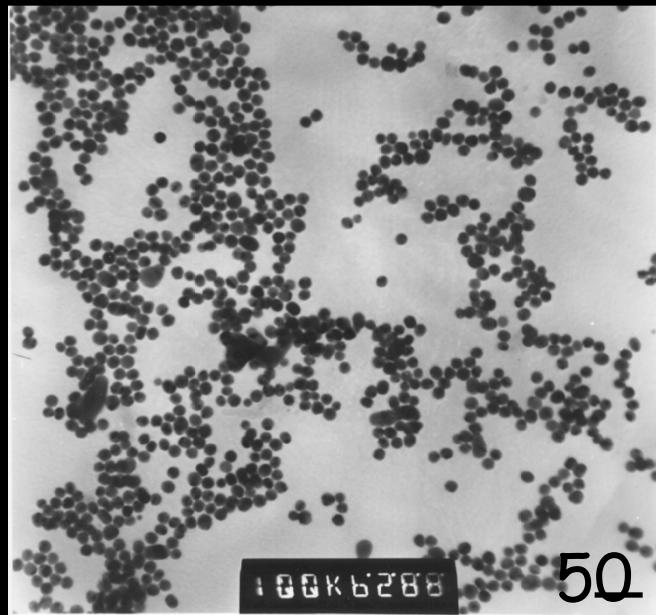
K.V. Mrudula

T. Tsukuda, IMS, Okazaki

S.K. Pal, SNBS, Kolkata

G.U. Kulkarni, JNCASR, Bangalore

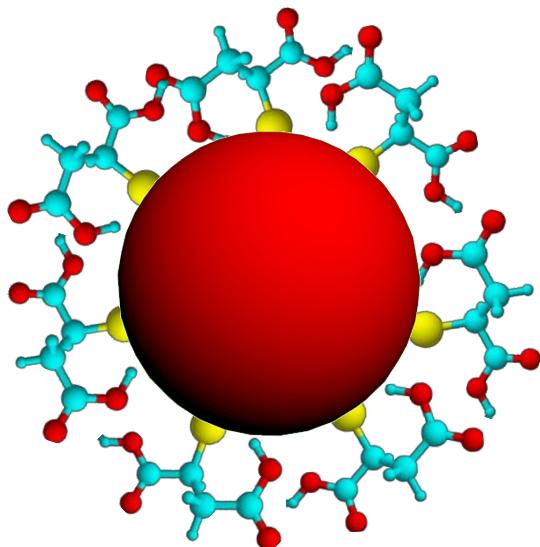
Nano Mission, Department of Science and Technology



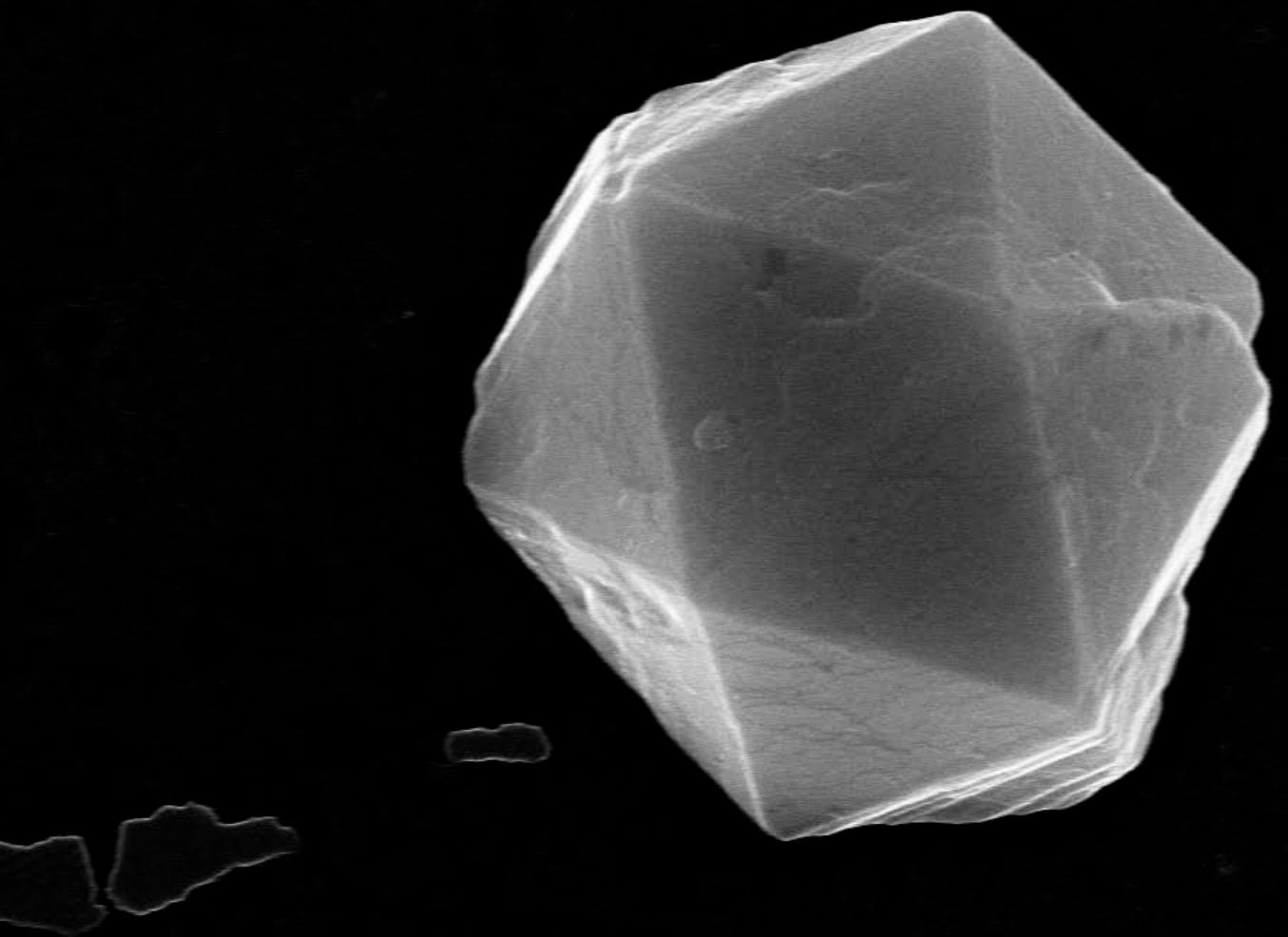
Faraday's gold preserved in Royal Institution. From the site,
<http://www.rigb.org/rimain/heritage/faradapage.jsp>

Monolayer Protected Metal Nanoparticles

Monolayer Protected Clusters (MPCs)

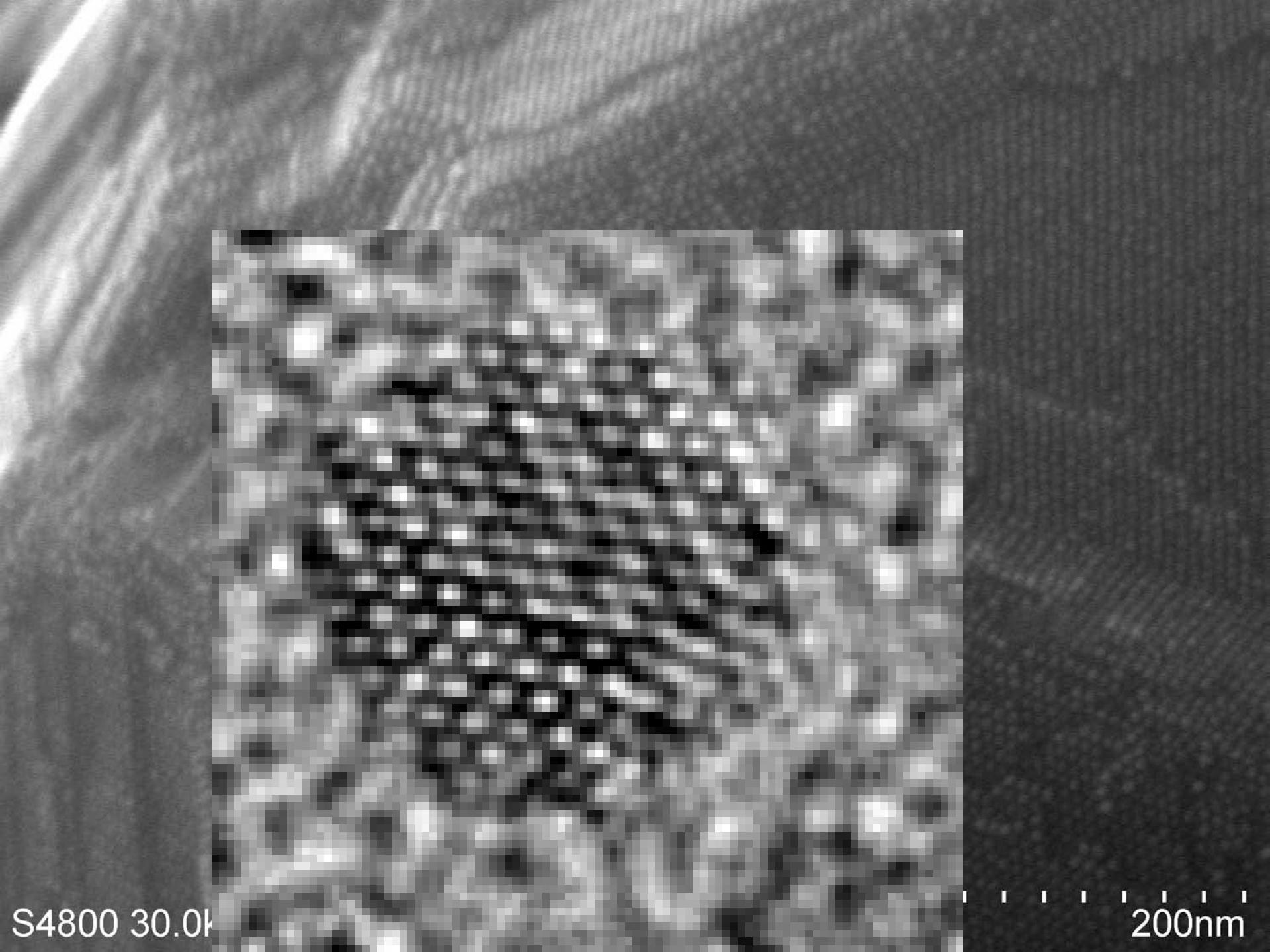


Synthesis of thiol-derivatised gold nanoparticles in a two-phase Liquid–Liquid system, Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *Chem. Commun.* **1994**, 801.



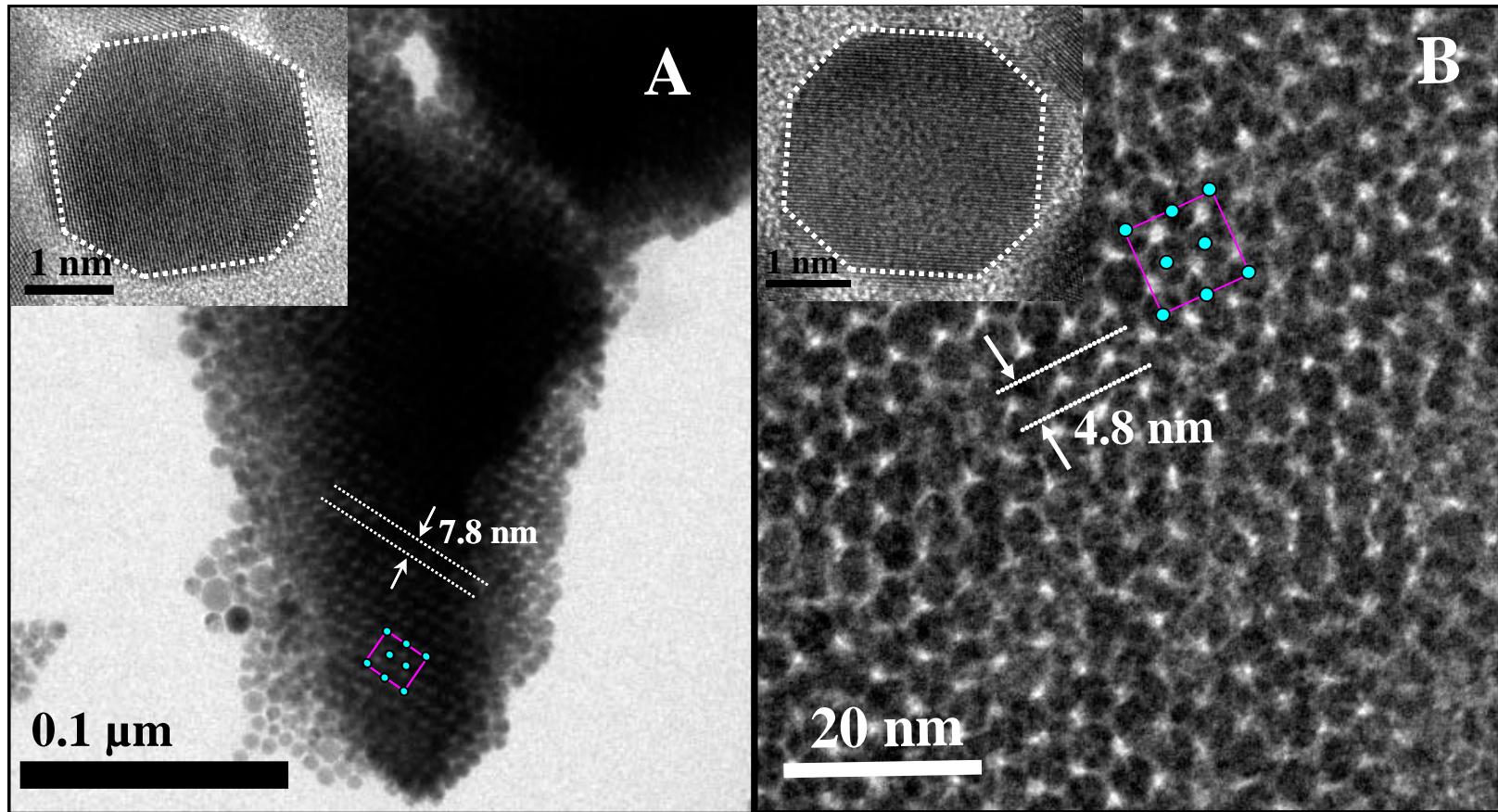
S4800 30.0kV 8.3mm x13.0k SE(U,LA0)

4.00μm

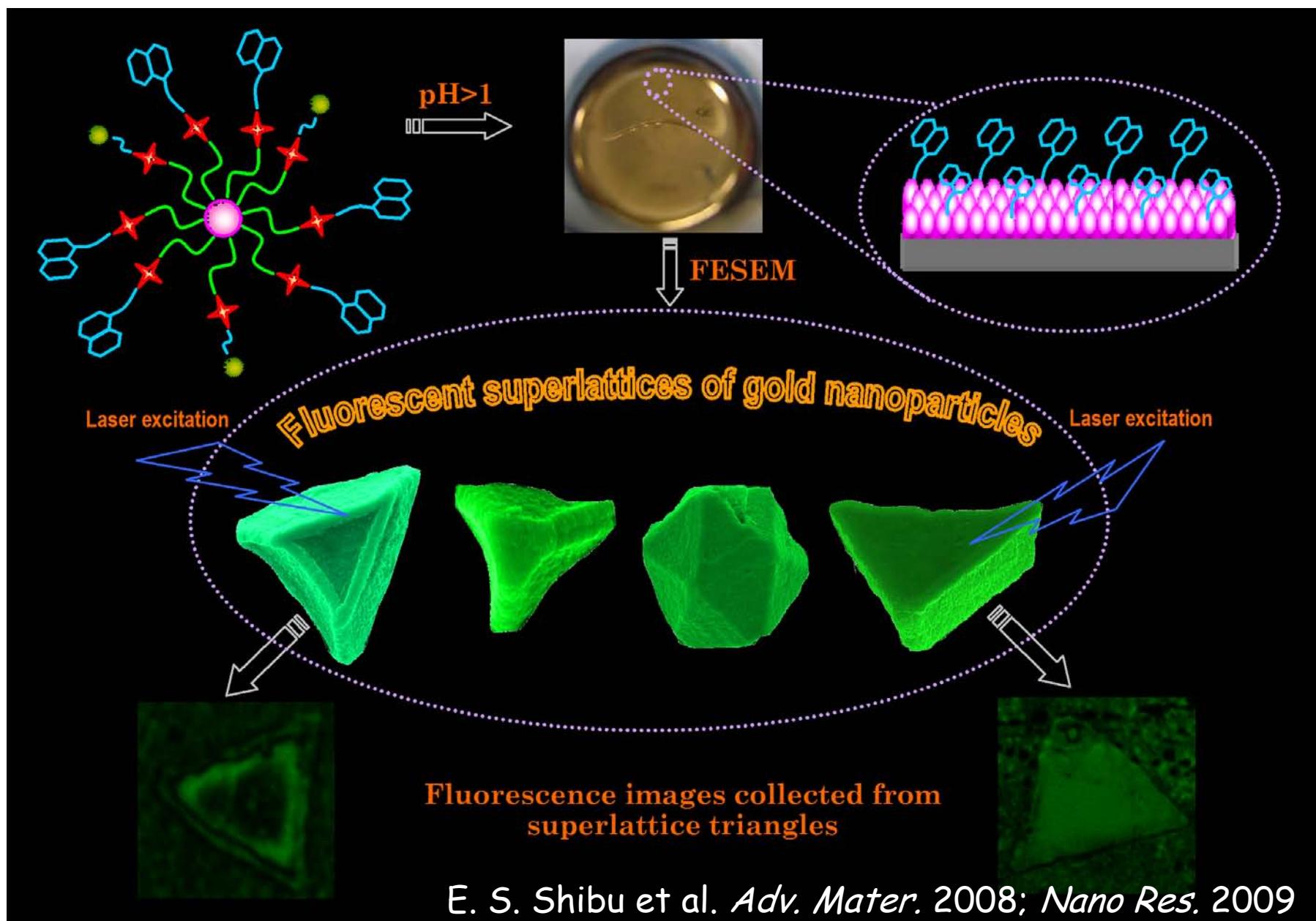


S4800 30.0k

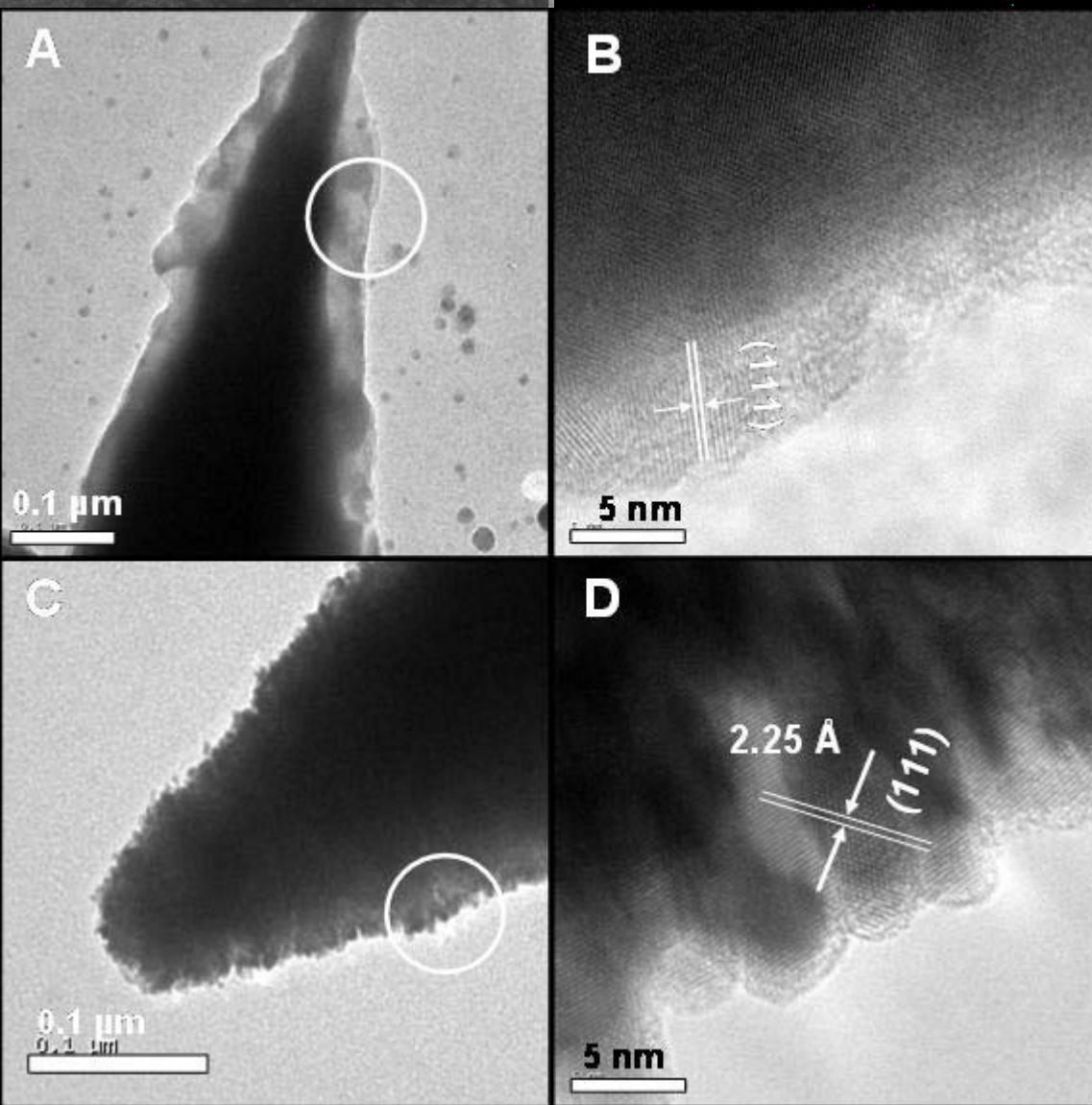
200nm



Fluorescent superlattices



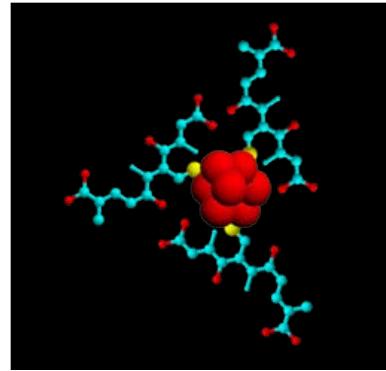
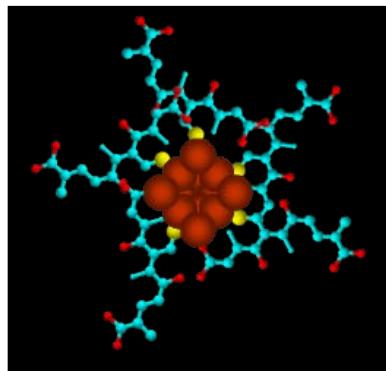
New materials



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

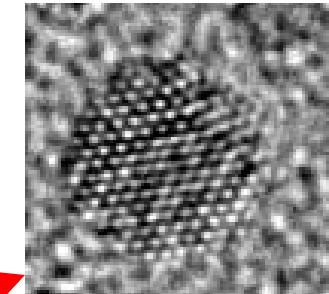
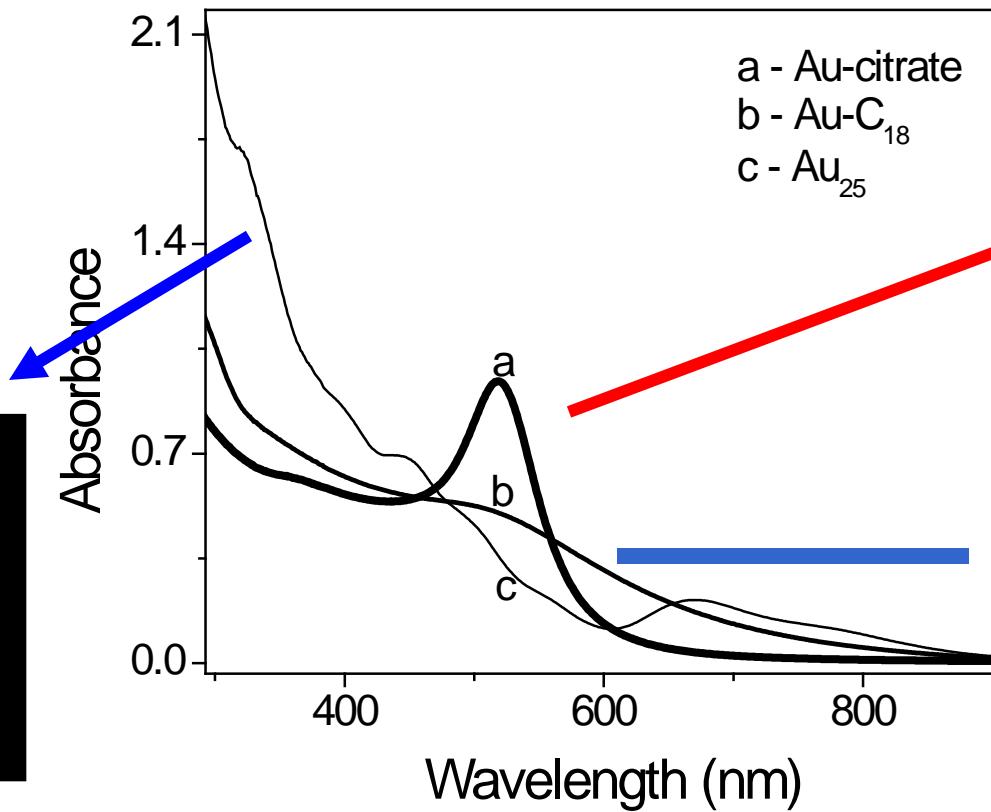
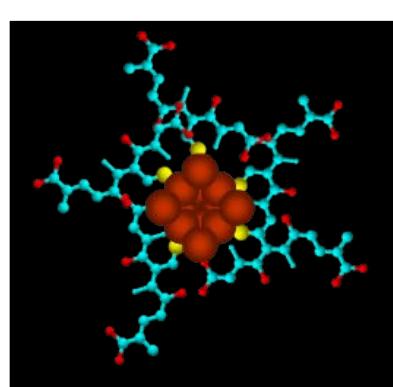
40.0 μm

Molecular Clusters

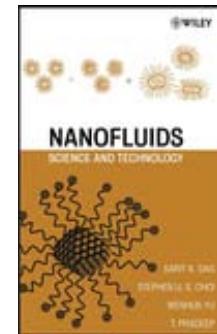


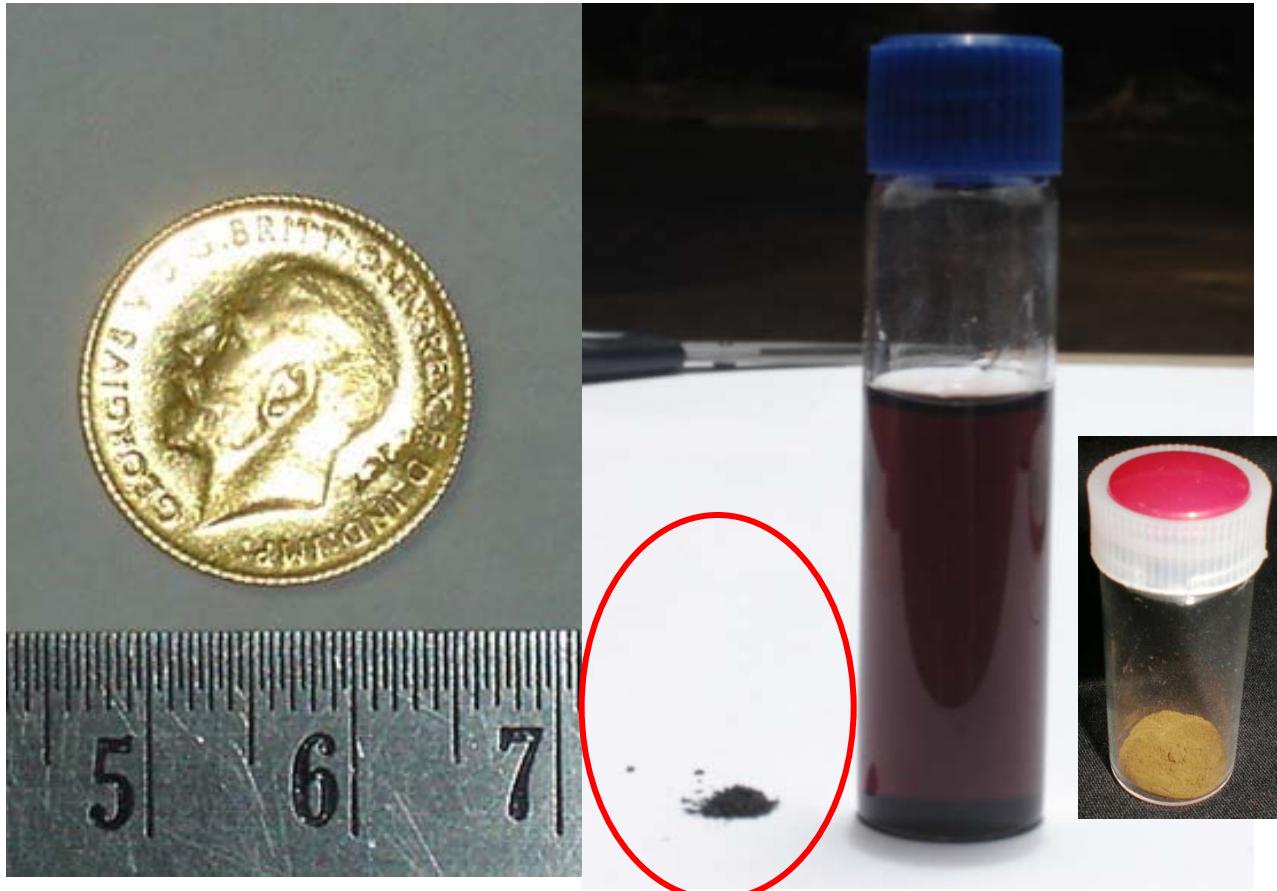
- **28 kDa Alkanethiolate-Protected Au Clusters Give Analogous Solution Electrochemistry and STM Coulomb Staircases**, Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khouri, J.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. *J. Am. Chem. Soc.* **1997**, *119*, 9279.
- **Isolation of Smaller Nanocrystal Au Molecules: Robust Quantum Effects in Optical Spectra**, Schaaff, T. G.; Shafiqullin, M. N.; Khouri, J. T.; Vezmar, I.; Whetten, R. L.; Cullen, W. G.; First, P. N.; Gutierrez-Wing, C.; Ascensio, J.; Jose-Yacaman, M. J. *J. Phys. Chem. B* **1997**, *101*, 7885.
- **Optical Absorption Spectra of Nanocrystal Gold Molecules**, Alvarez, M. M.; Khouri, J. T.; Schaaff, T. G.; Shafiqullin, M. N.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **1997**, *101*, 3706.

- **Isolation and Selected Properties of a 10.4 kDa Gold:Glutathione Cluster Compound**, Schaaff, T. G.; Knight, G.; Shafiqullin, M. N.; Borkman, R. F.; Whetten, R. L. *J. Phys. Chem. B* **1998**, *102*, 10643.
- **Controlled Etching of Au:SR Cluster Compounds**, Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **1999**, *103*, 9394.
- **Giant Gold-Glutathione Cluster Compounds: Intense Optical Activity in Metal-Based Transitions**, Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **2000**, *104*, 2630.
- **Near-Infrared Luminescence from Small Gold Nanocrystals**, Bigioni, T. P.; Whetten, R. L.; Dag, O. *J. Phys. Chem. B* **2000**, *104*, 6983.
- **Properties of a Ubiquitous 29 kDa Au:SR Cluster Compound**. Schaaff, T. G.; Shafiqullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **2001**, *105*, 8785.
- **Visible to Infrared Luminescence from a 28-Atom Gold Cluster**, Link, S.; Beeby, A.; FitzGerald, S.; El-Sayed, M. A.; Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **2002**, *106*, 3410.
- **All-Aromatic, Nanometer-Scale, Gold-Cluster Thiolate Complexes**, Price, R. C.; Whetten, R. L. *J. Am. Chem. Soc.* **2005**, *127*, 13750.

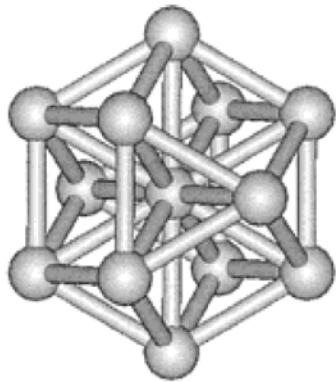


Optical absorption (extinction) spectrum of (a) 15 nm gold particles in aqueous solution (labeled Au@citrate). The spectrum of (b) 3 nm particles in toluene is also shown. See the broadening of the plasmon feature. The spectrum of (c) Au₂₅ in water. In this, there is no plasmon excitation and all the features are due to molecular absorptions of the cluster.

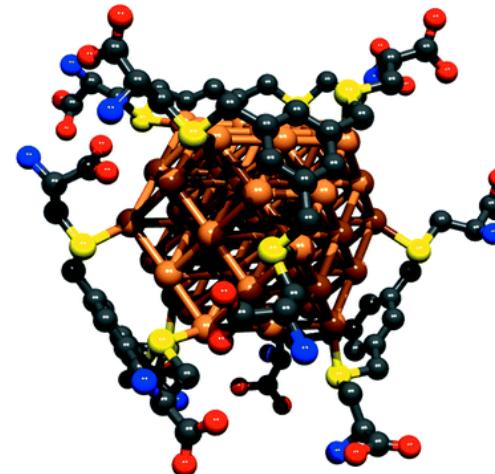




Phosphine Capped Gold Clusters



Au_{13}

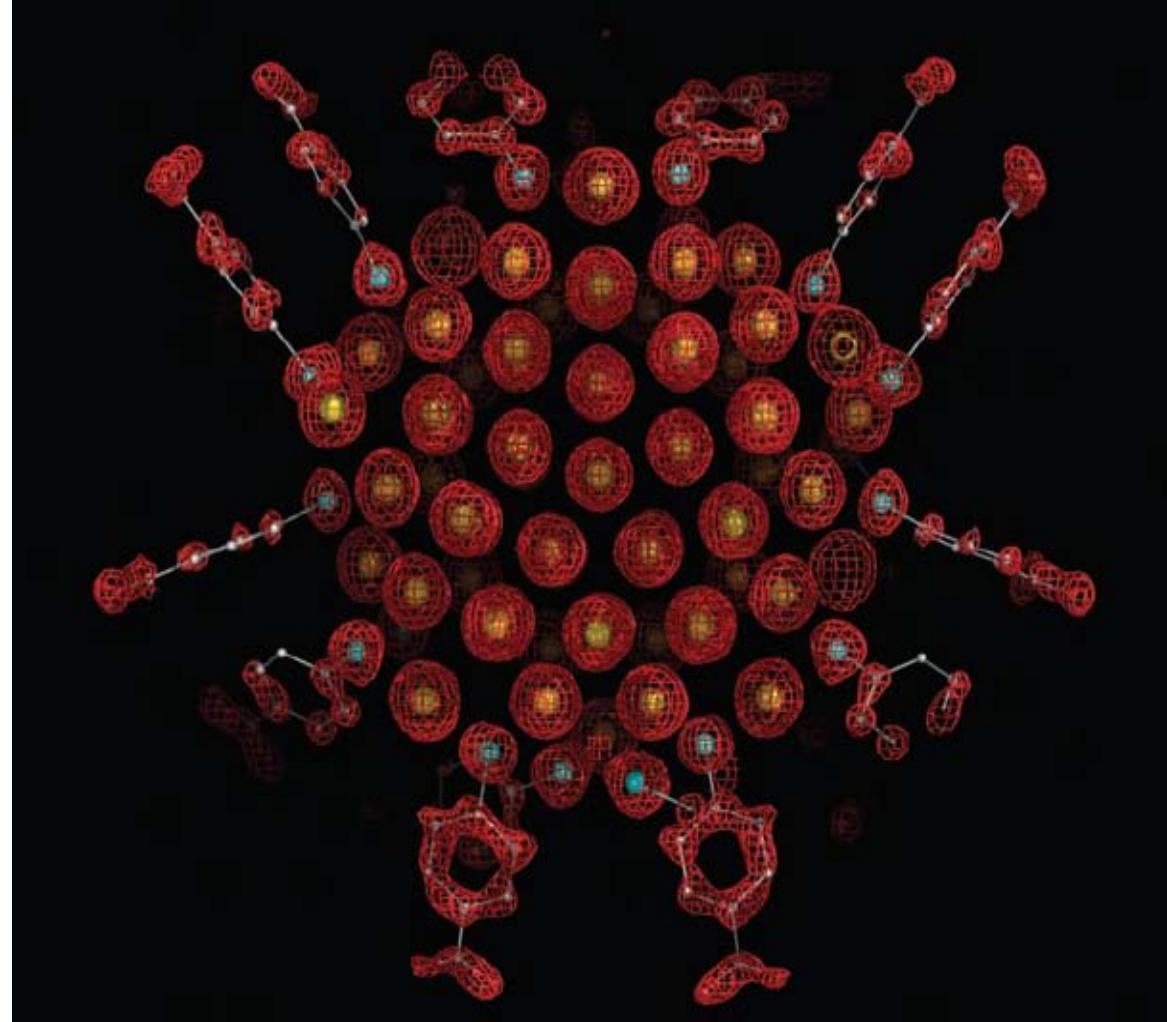


Au_{55}

- $\text{Au}_{55} [\text{P}(\text{C}_6\text{H}_5)_3]_{12}\text{Cl}_6$ - 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 $[\text{Au}_{13} (\text{PMe}_2\text{Ph})_{10}\text{Cl}_2](\text{PF}_6)_3$; 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.

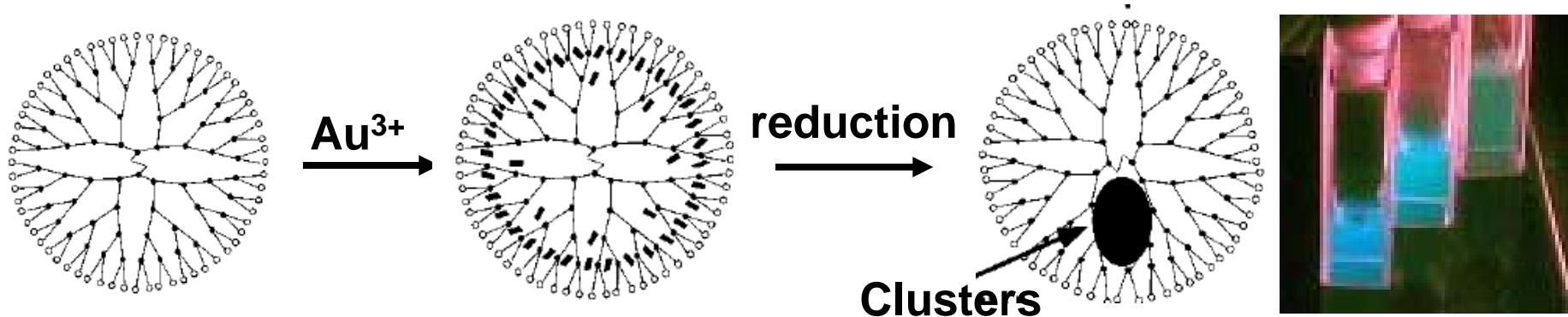
Au₁₀₂

Au₁₀₂(p-MBA)₄₄



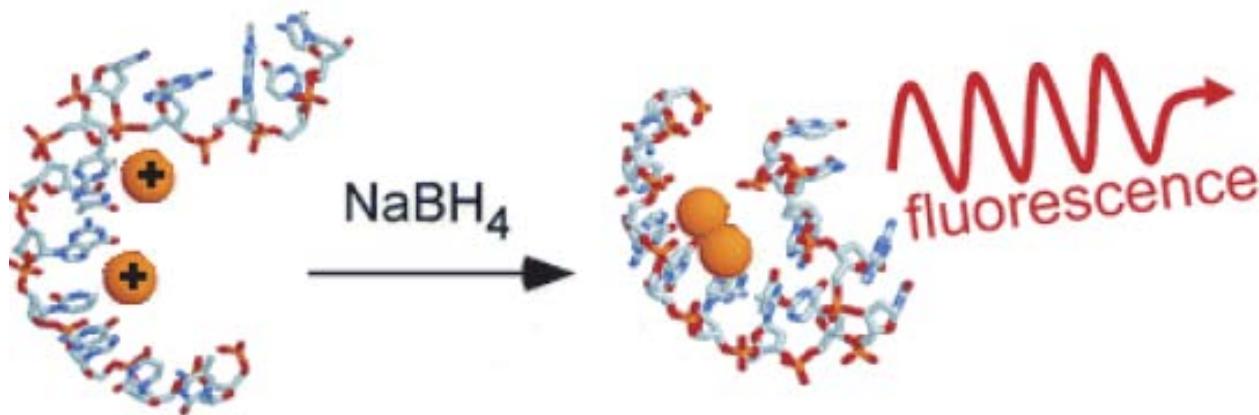
Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a Thiol Monolayer-Protected Gold Nanoparticle at 1.1 Å Resolution *Science* **2007**, *318*, 430.

Dendrimer Encapsulated Clusters

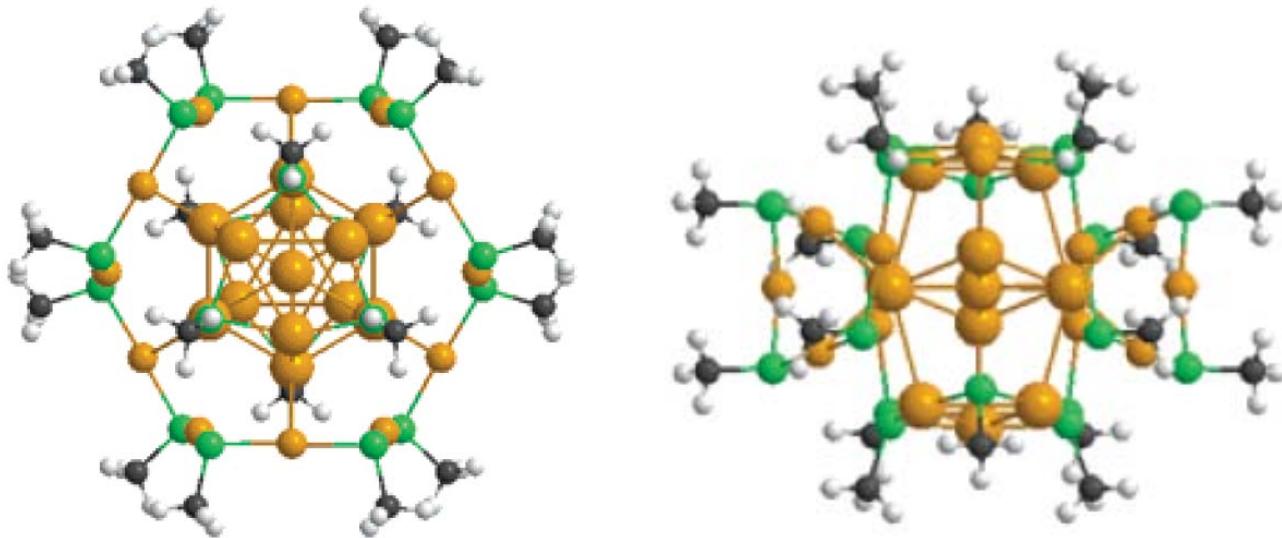


- **High quantum yield blue emission from water-soluble Au_8 nanodots**, Zheng, J.; Petty, J. T.; Dickson, R. M. *J. Am. Chem. Soc.* **2003**, 125, 7780.
- **Highly fluorescent, water-soluble, size-tunable gold quantum dots**, Zheng, J.; Zhang, C. W.; Dickson, R. M. *Phys. Rev. Lett.* **2004**, 93, 077402.
- **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.

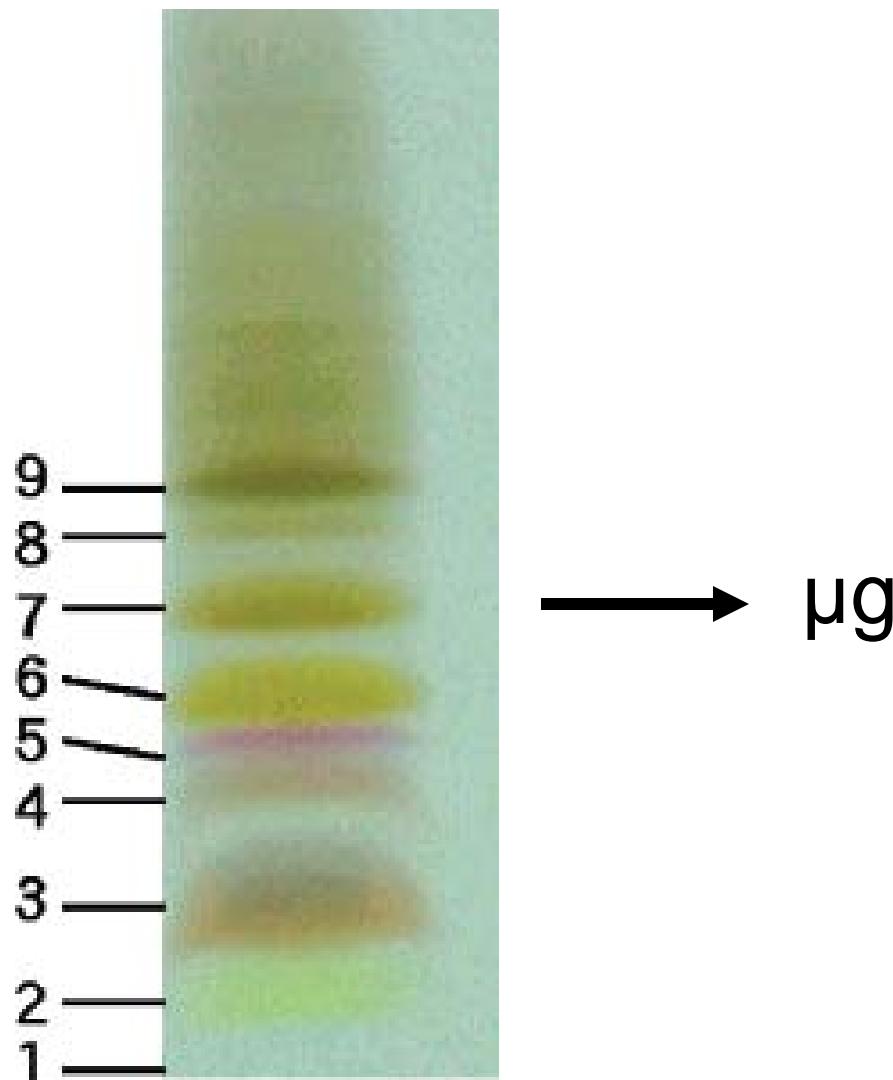


Top and side view of $[Au_{25}(SCH_3)_{18}]^+$

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.

How to make them?

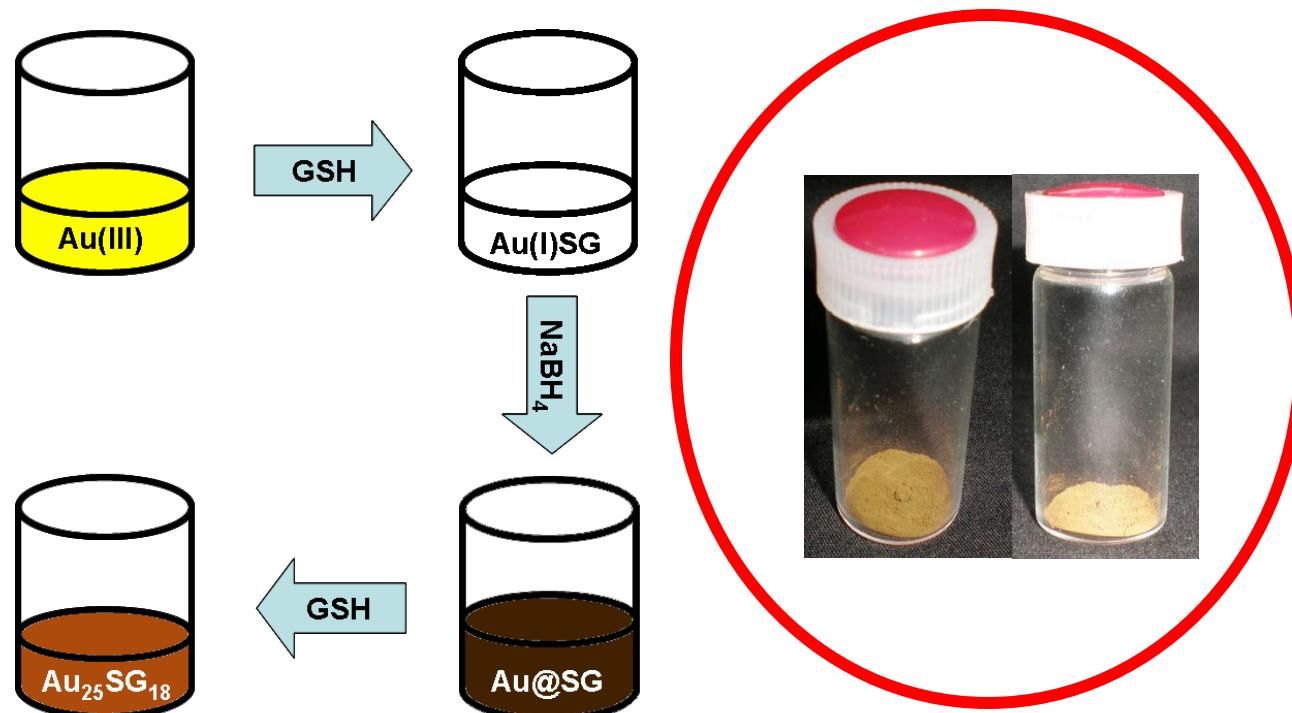
Polyacrylamide gel electrophoresis (PAGE)



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.

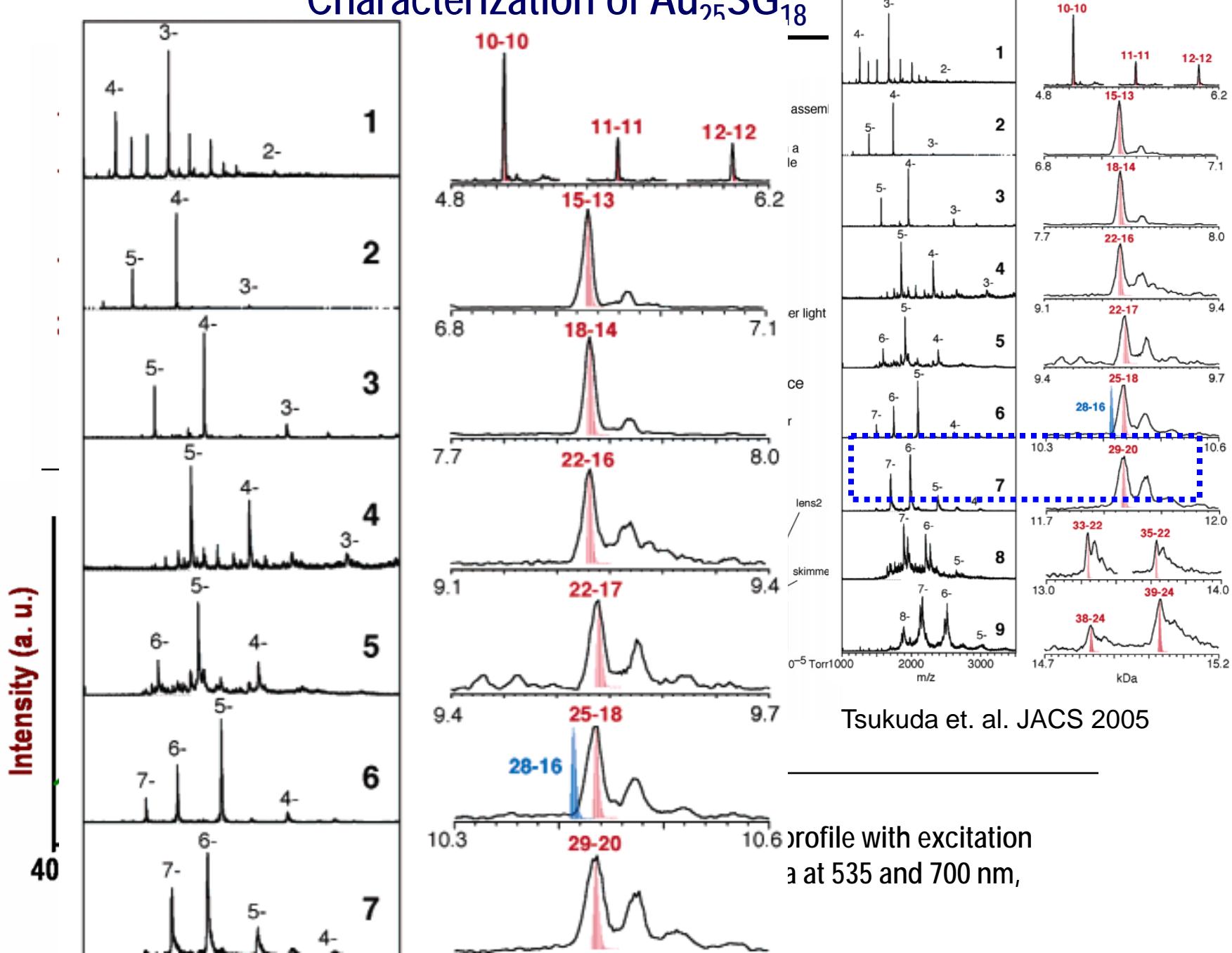
$\text{Au}_{25}\text{SG}_{18}$

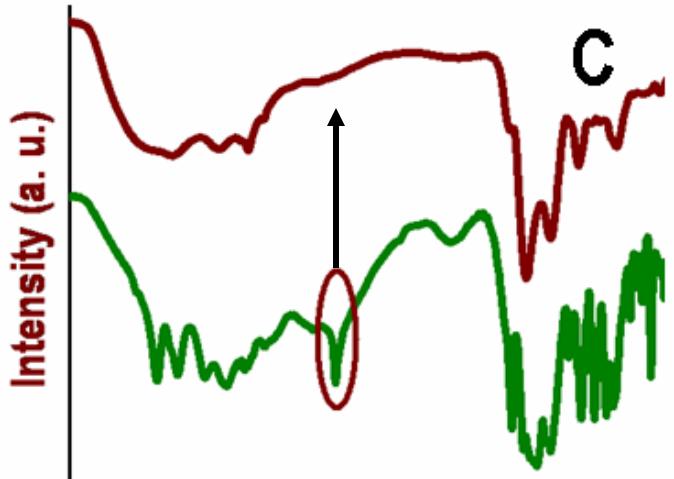
Synthesis: Au_{25} clusters can be preferentially populated by dissociative excitation of larger precursors



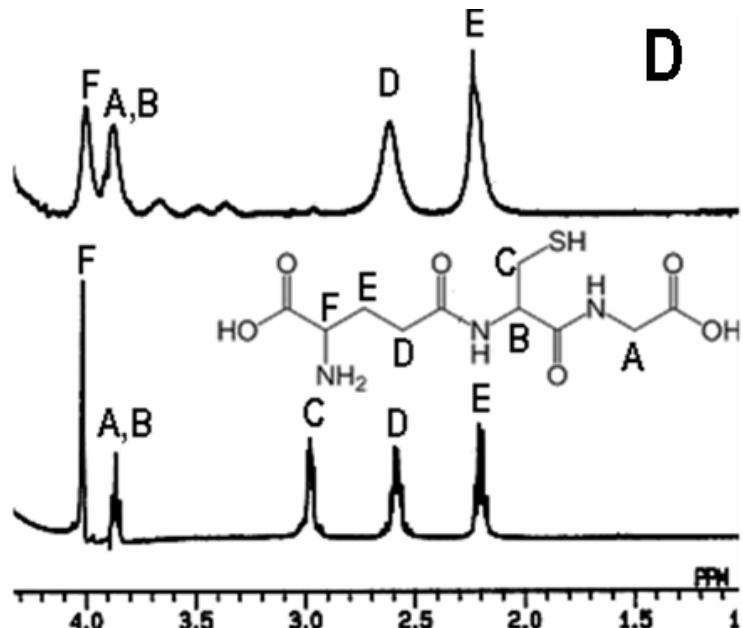
Scheme showing the synthesis of $\text{Au}_{25}\text{SG}_{18}$ clusters

Characterization of $\text{Au}_{25}\text{SG}_{18}$

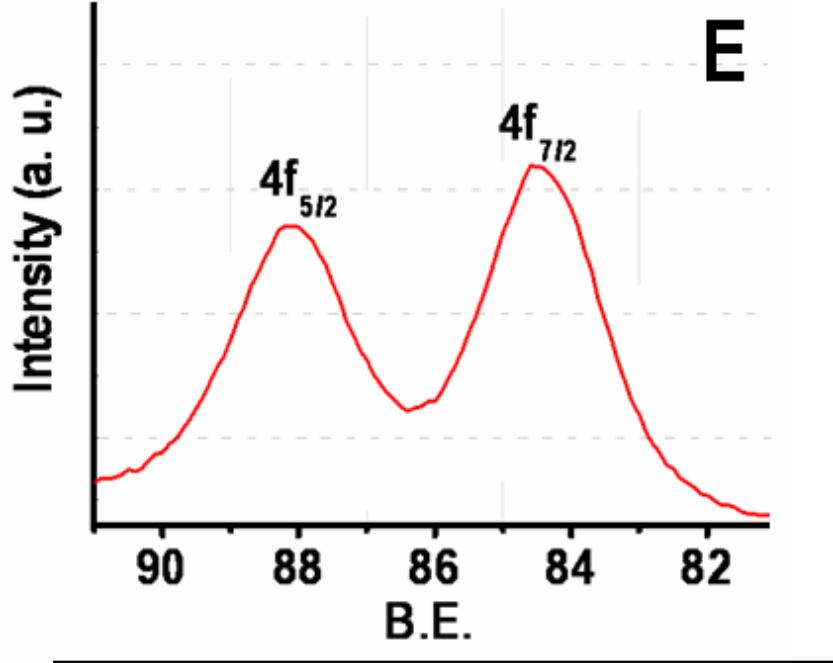




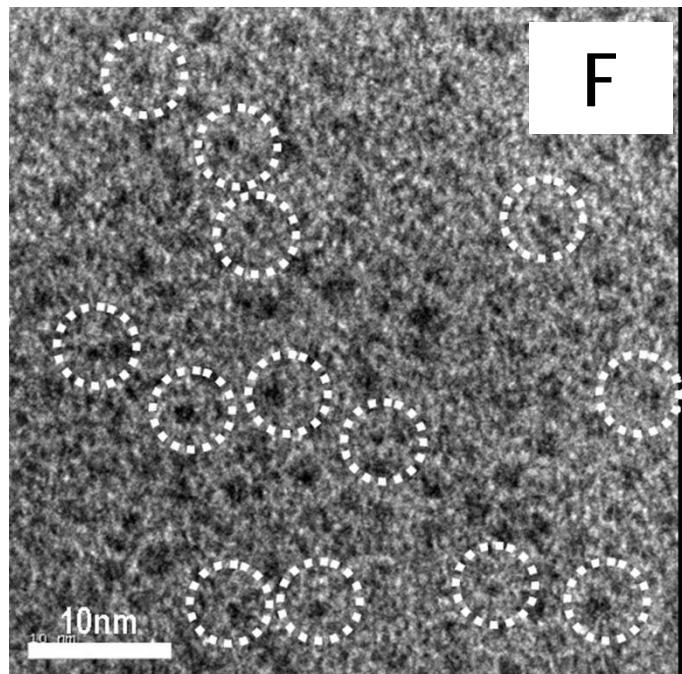
FTIR spectrum: The peak at 2526 cm^{-1} of glutathione due to $-\text{SH}$ stretching frequency is absent in IR spectrum of Au_{25} suggesting the ligand binding on cluster surface.



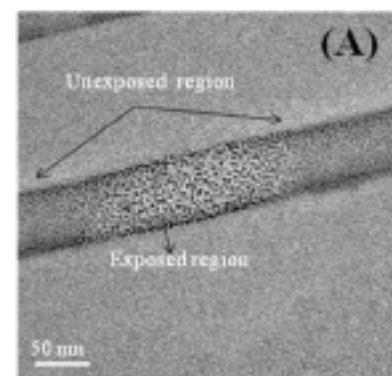
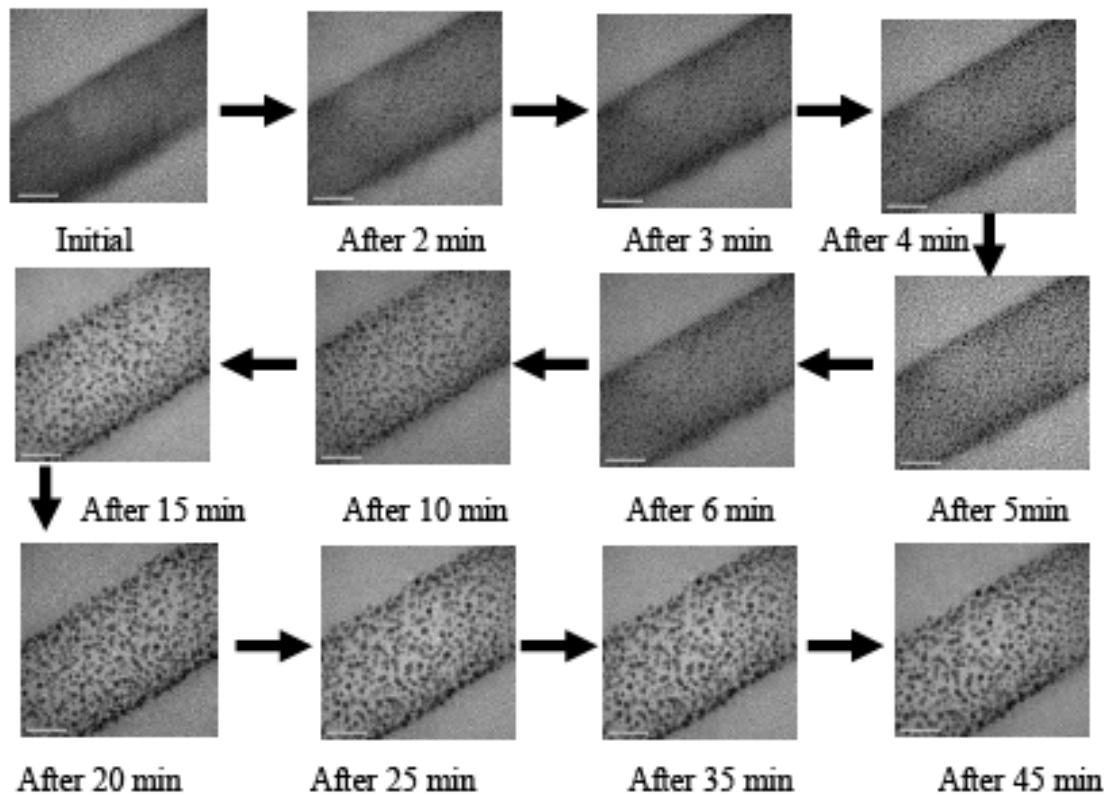
^1H NMR spectrum: There is one-to-one correspondence between the two spectra, except that the βCH_2 resonance (labeled as C) disappears completely in the cluster which is expected as it is close to the cluster surface. All the observed resonances have been broadened in view of their faster relaxation and non-uniform distribution of ligands.



XPS spectrum



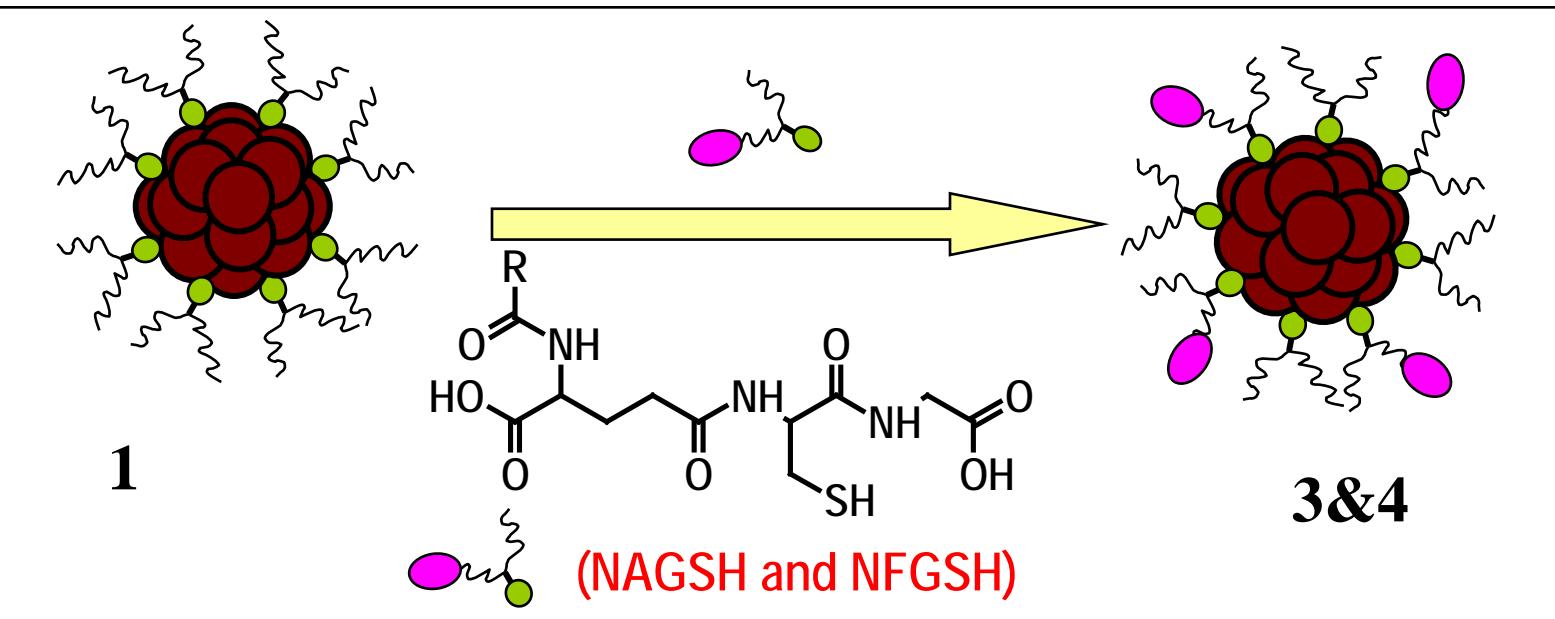
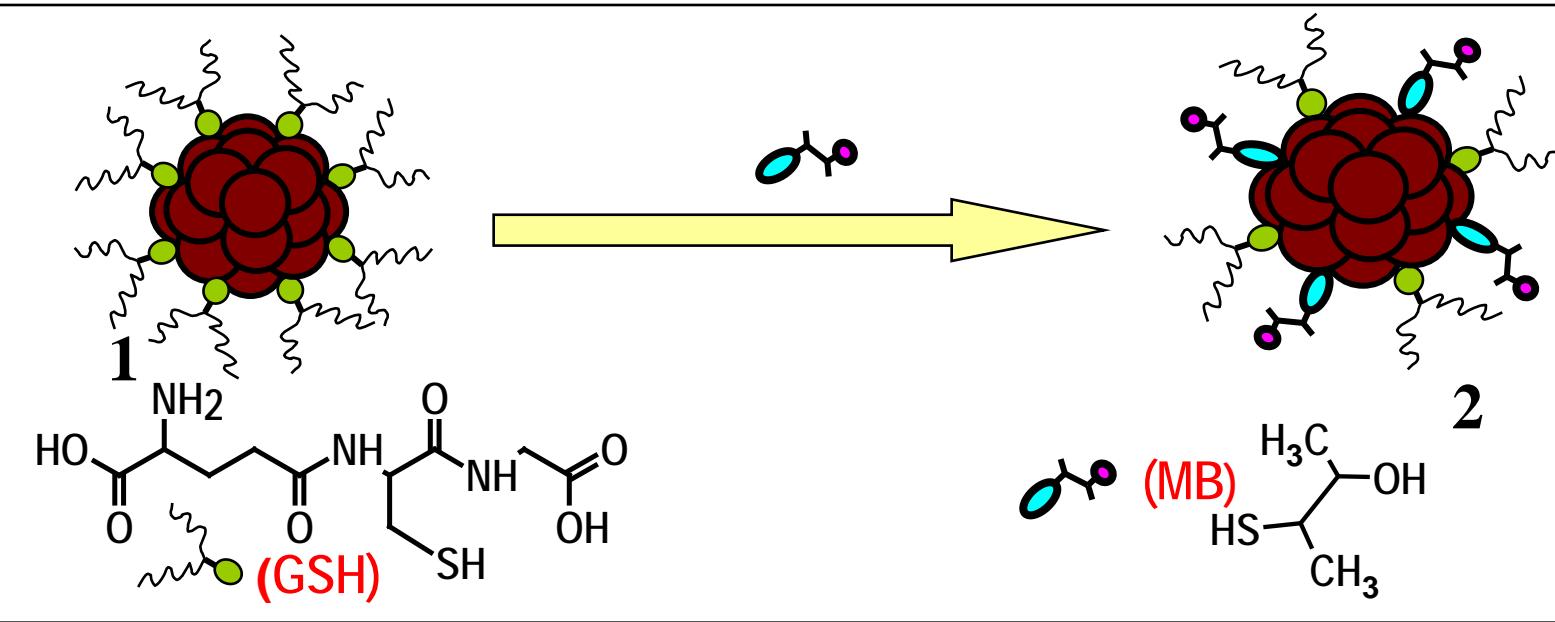
TEM image: The clusters are seen only faintly since the size is ~1 nm. Some of the individual clusters are shown by circles. There are also cluster aggregates which upon extended electron beam irradiation fuse to form bigger particles

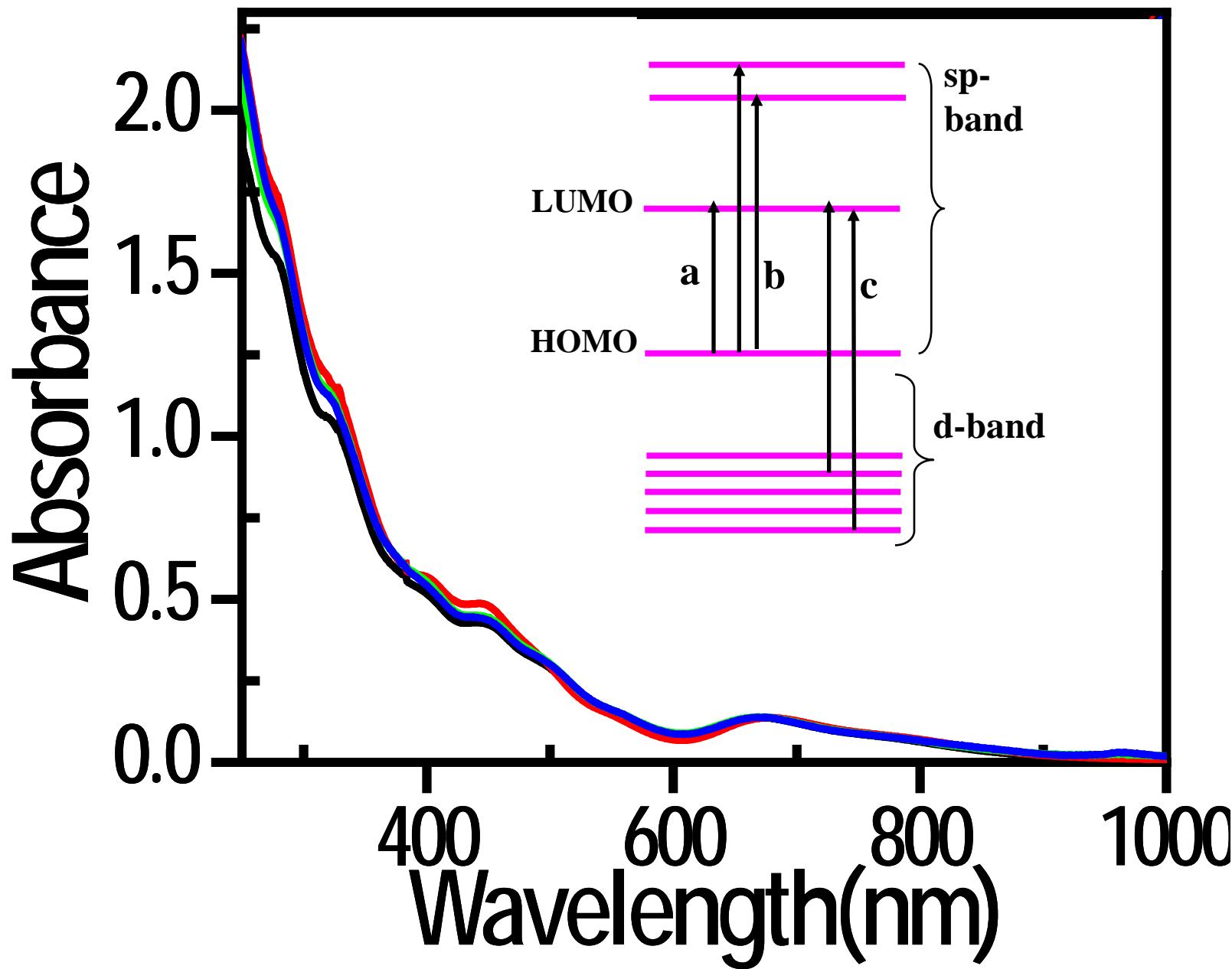


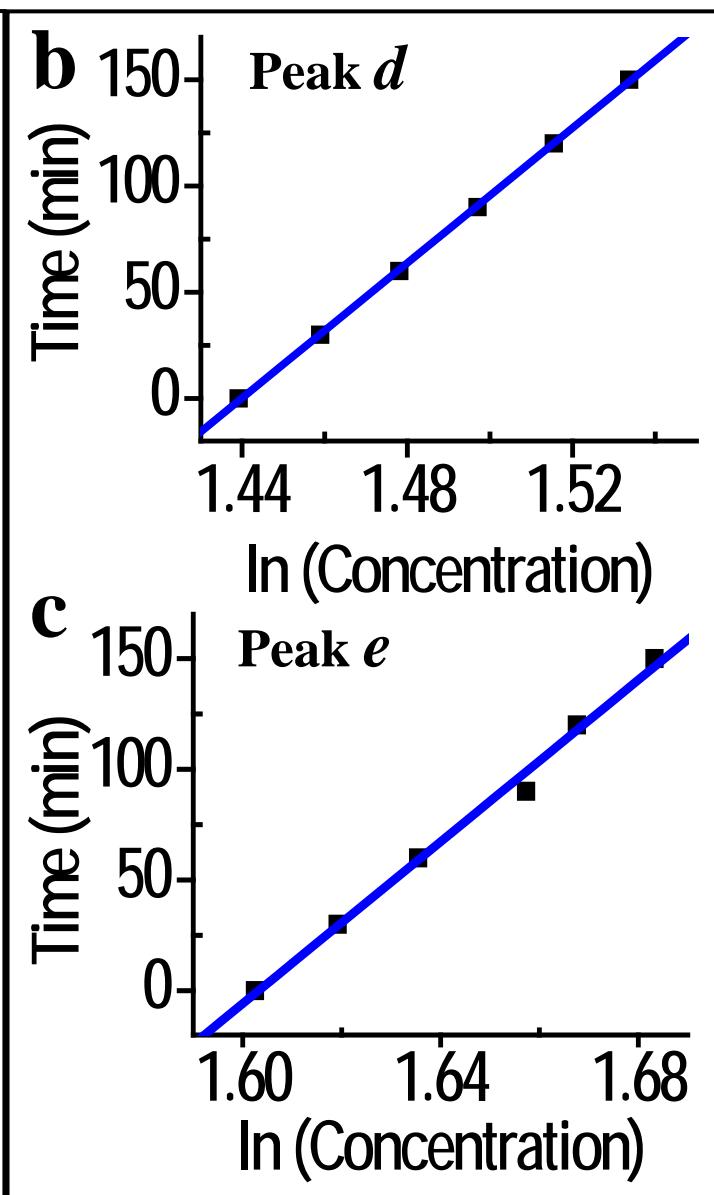
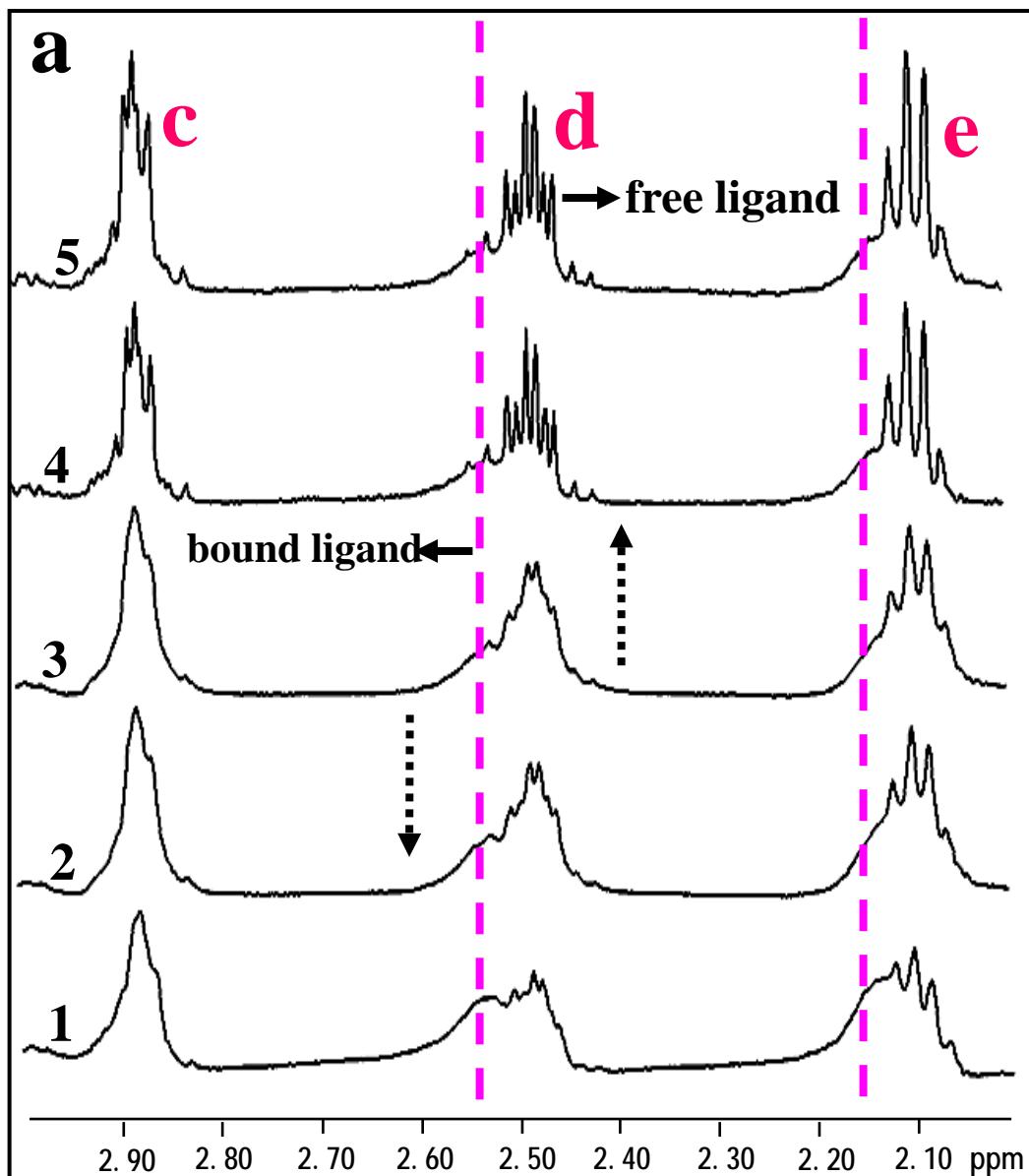
Perumal Ramasamy *et al.* *J. Mater. Chem.*, 2009, 19, 8456.

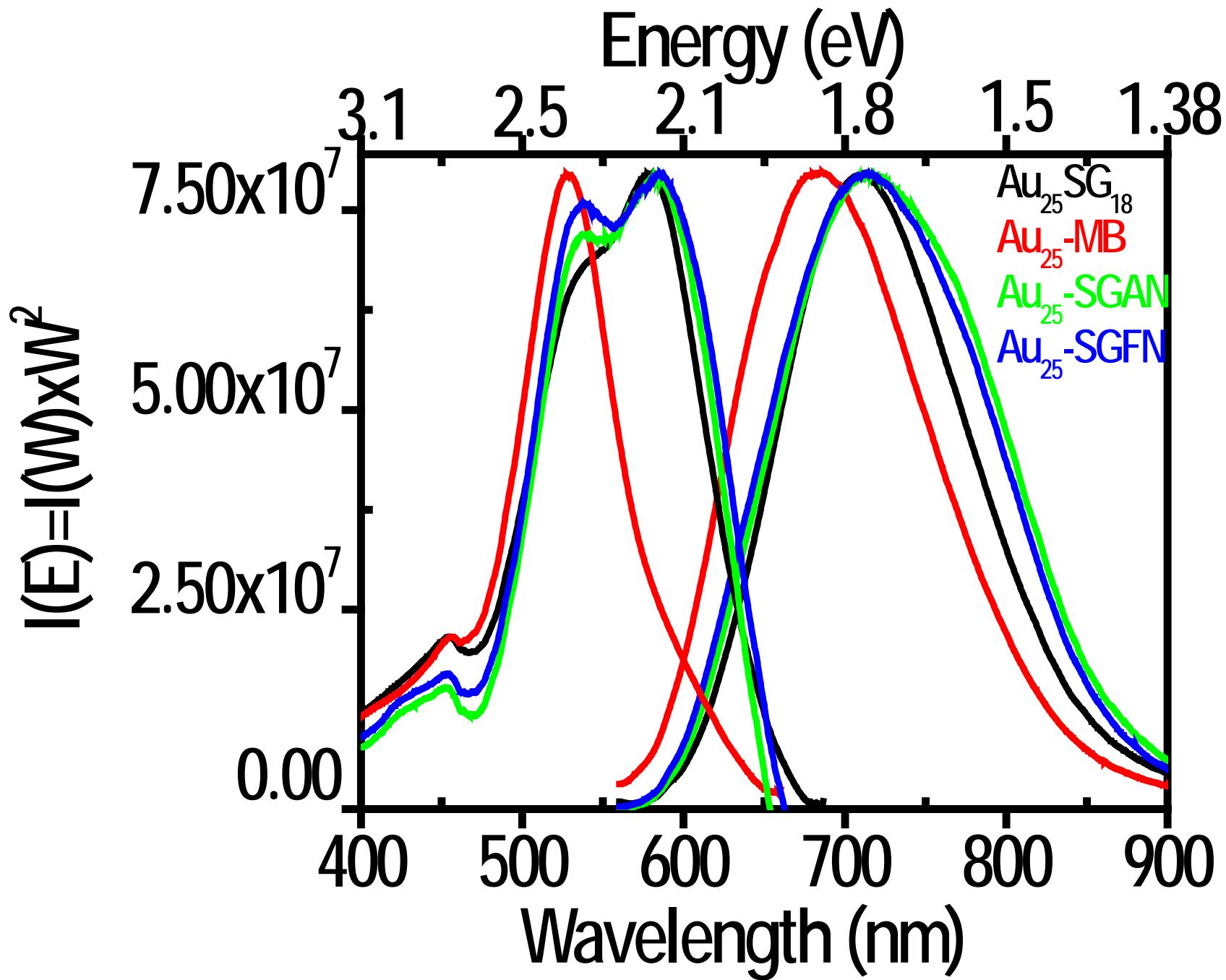
With Arindam Banerjee

Ligand Exchange of Au_{25}

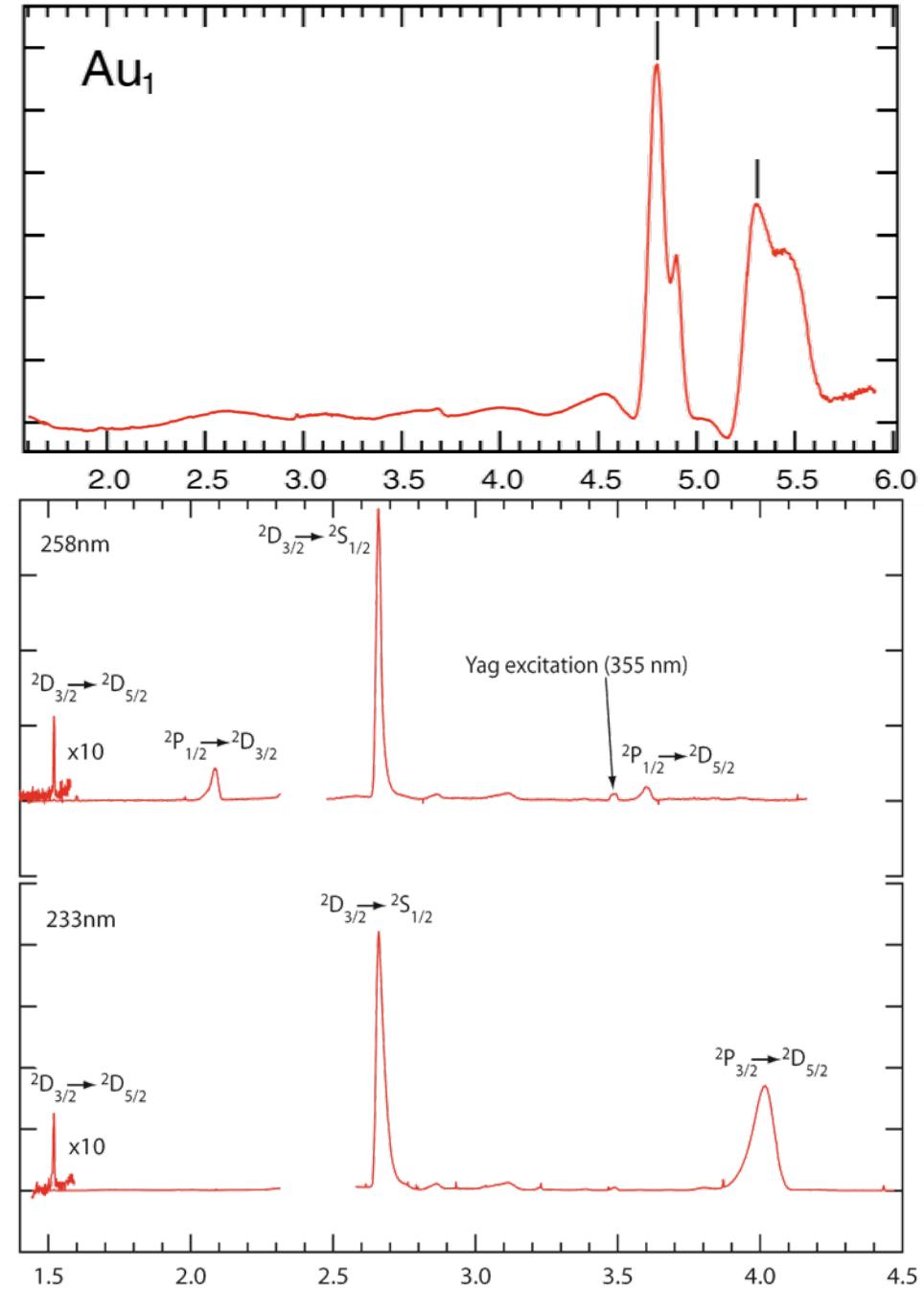
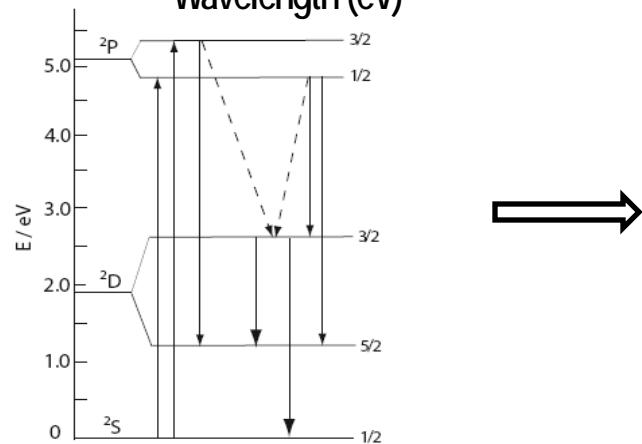
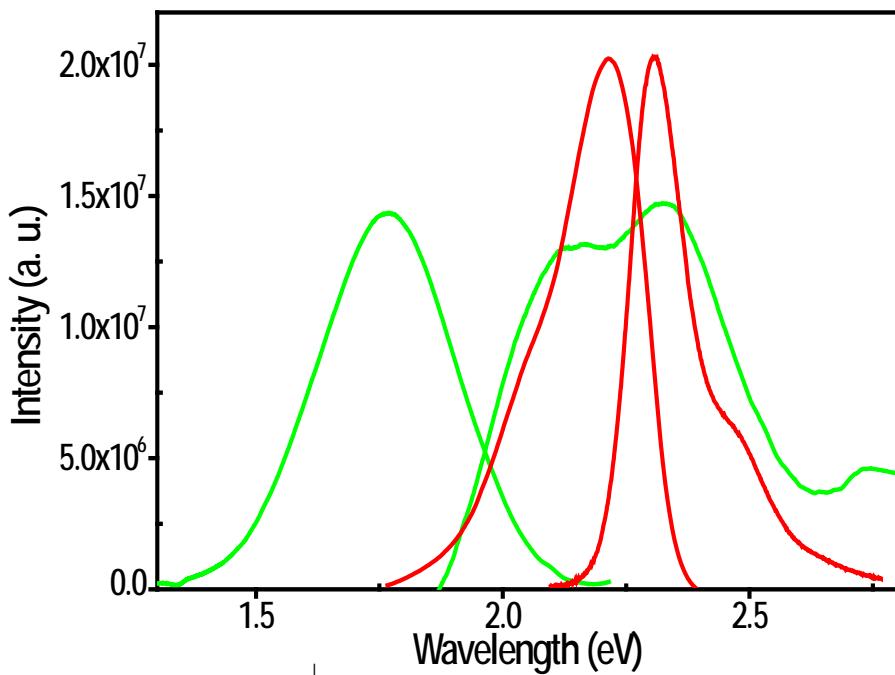








Fluorescence : A comprehensive study between organic dye, gold atoms and molecular clusters of gold



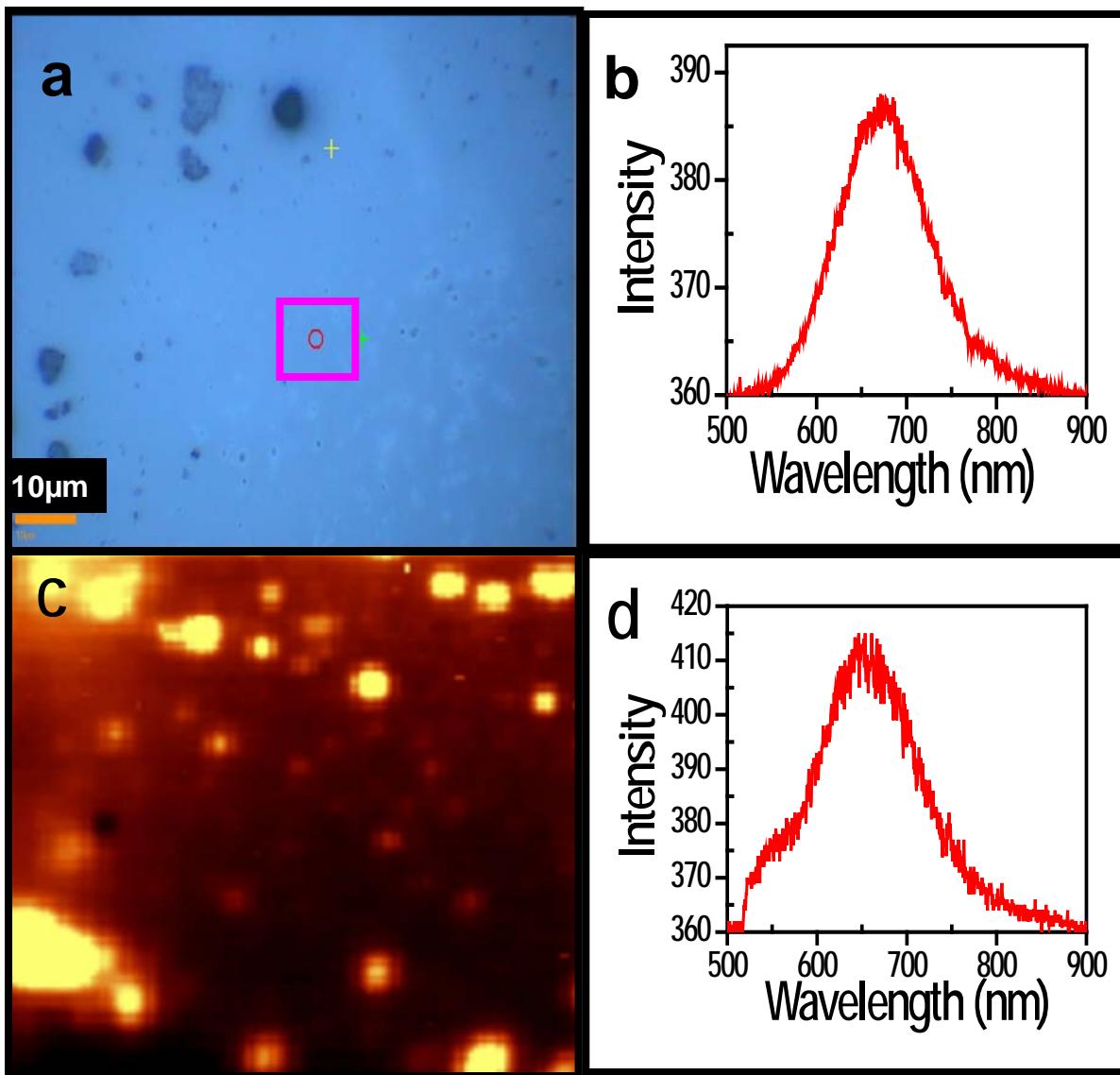
| Cluster | Q.Yield |
|--|----------------------|
| Au ₁₀ (SG) ₁₀ | 1*10 ⁻⁴ |
| Au ₁₁ (SG) ₁₁ | |
| Au ₁₁ (SG) ₁₁ | |
| Au ₁₅ (SG) ₁₃ | 2*10 ⁻⁴ |
| Au ₁₈ (SG) ₁₄ | 4*10 ⁻³ |
| Au ₂₂ (SG) ₁₆ | 4*10 ⁻³ |
| Au ₂₂ (SG) ₁₇ | 2*10 ⁻³ |
| Au ₂₅ (SG) ₁₈ | 1.9*10 ⁻³ |
| Au ₂₉ (SG) ₂₀ | 3*10 ⁻³ |
| Au ₃₃ (SG) ₂₂ | 2*10 ⁻³ |
| Au ₃₅ (SG) ₂₂ | |
| Au ₃₈ (SG) ₂₄ , Au ₃₉ (SG) ₂₄ | 2*10 ⁻³ |
| Gold nanoparticles | 1*10 ⁻¹⁰ |

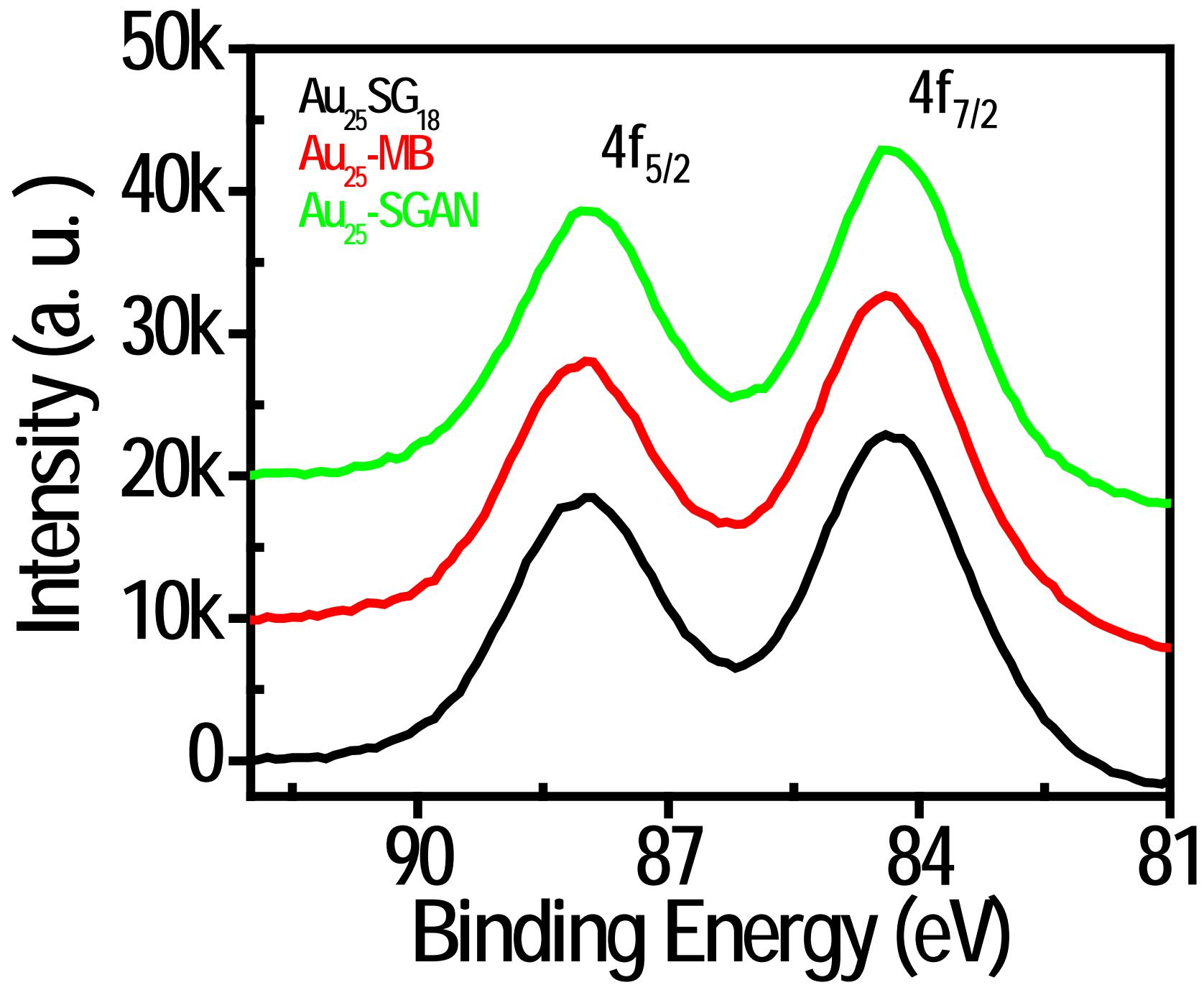
Recently developed clusters using Au₂₅ as precursor

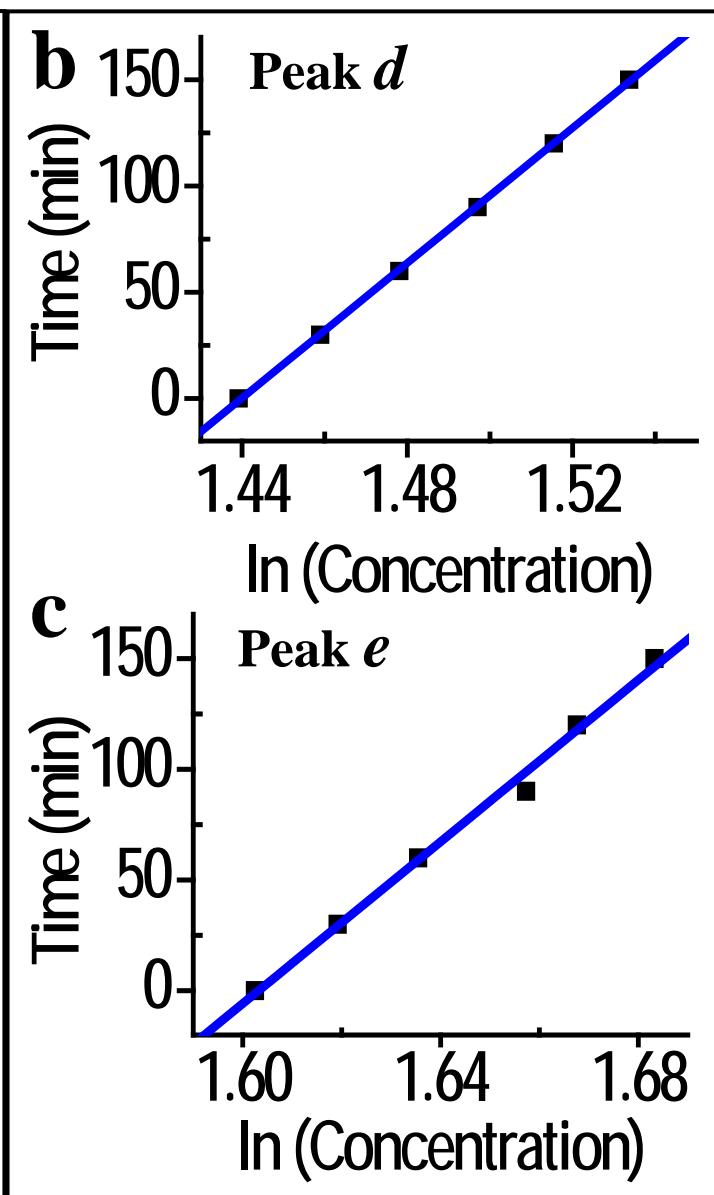
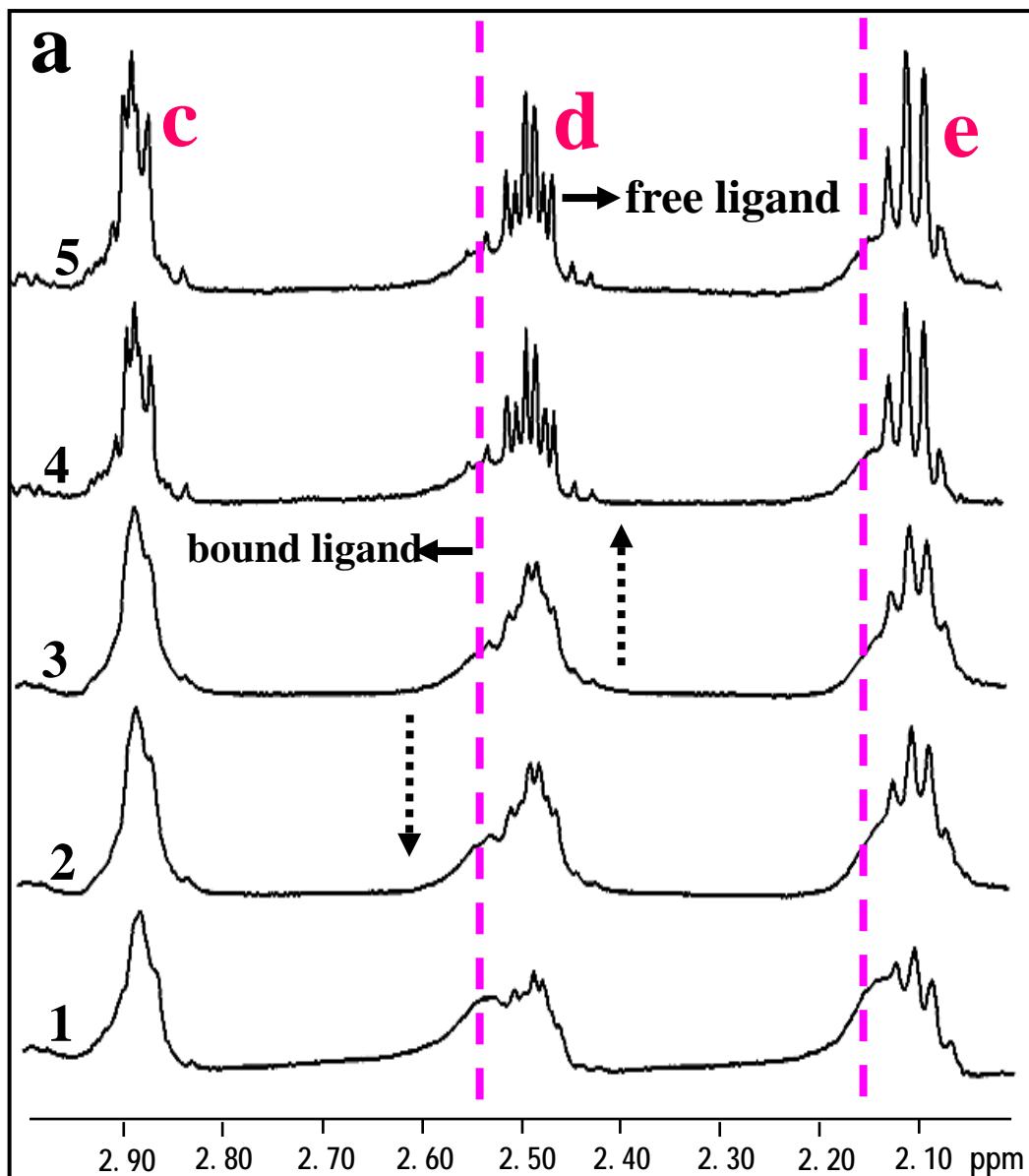
| Cluster | Q. Yield |
|-----------------------------------|----------------------|
| Au ₂₂ | 4.0*10 ⁻² |
| Au ₂₃ | 1.3*10 ⁻² |
| Au ₃₁ | 1.0*10 ⁻² |
| Au ₈ (SG) ₈ | 1.5*10 ⁻¹ |

Precursor
Using other ligands

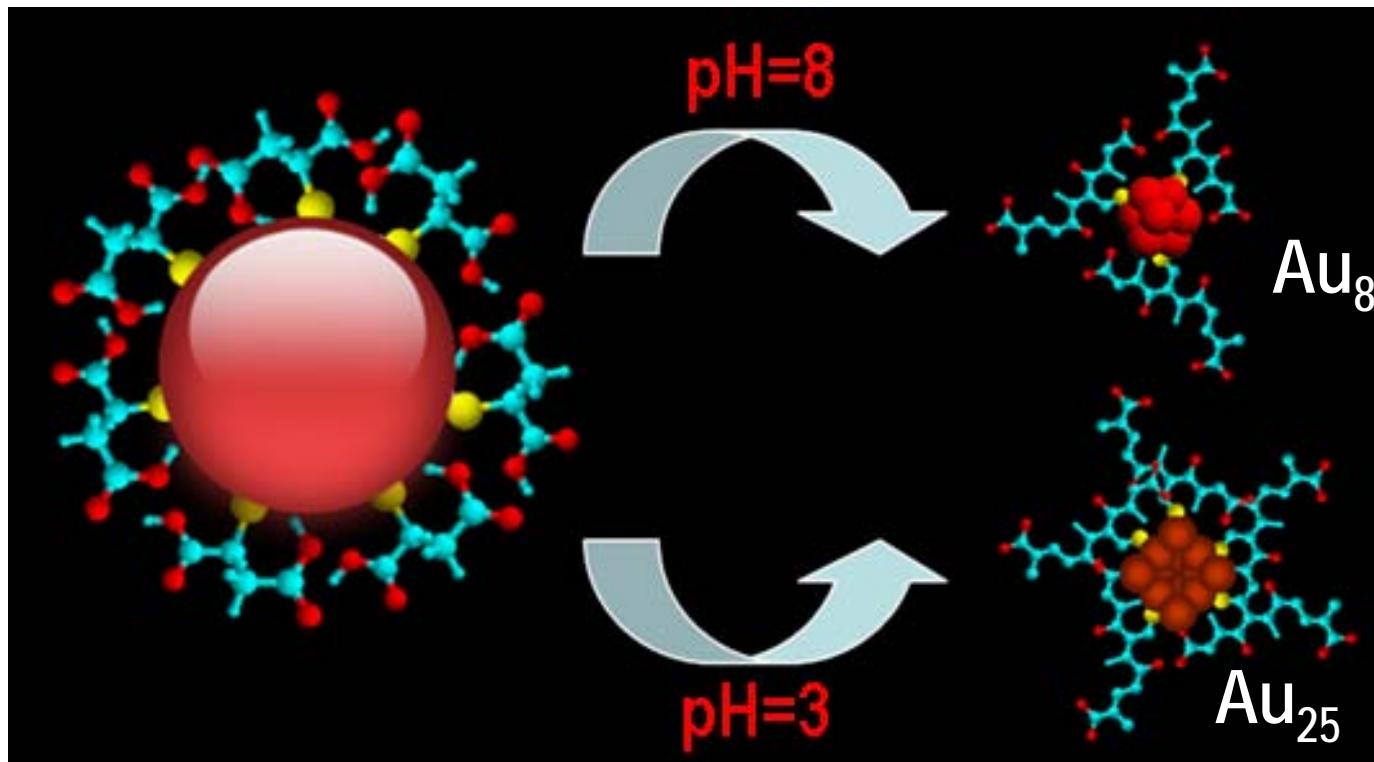
1. Nano Res., 1(2008) 333-340.
2. Chemistry A European Journal. (In Press).
3. ACS Applied Materials and Interfaces (in press)

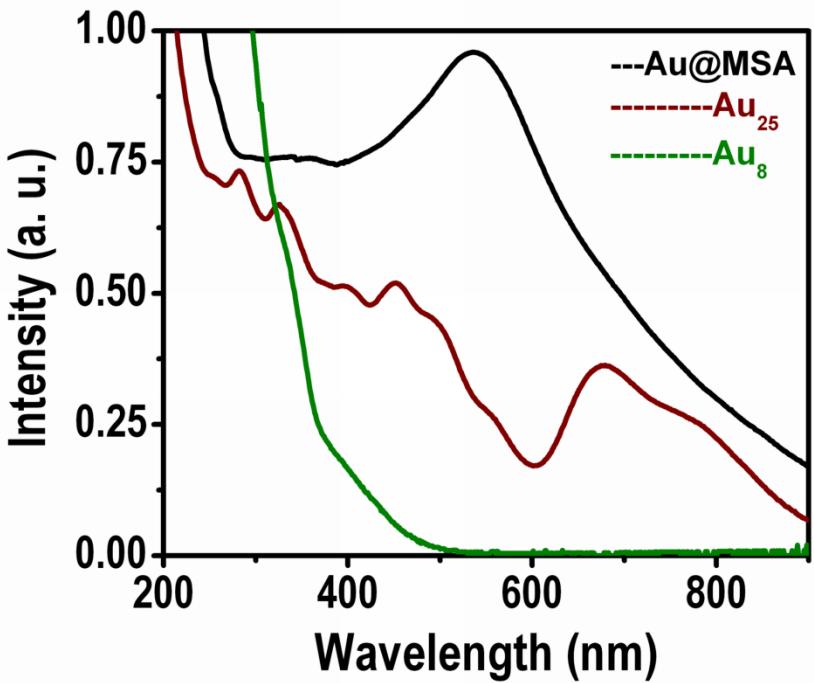




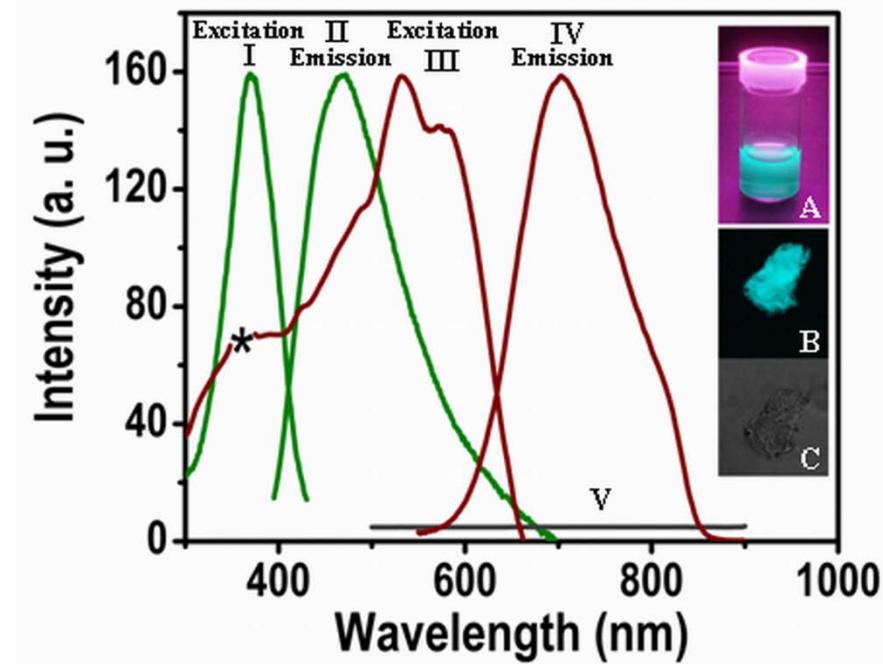


Au_8SG_8

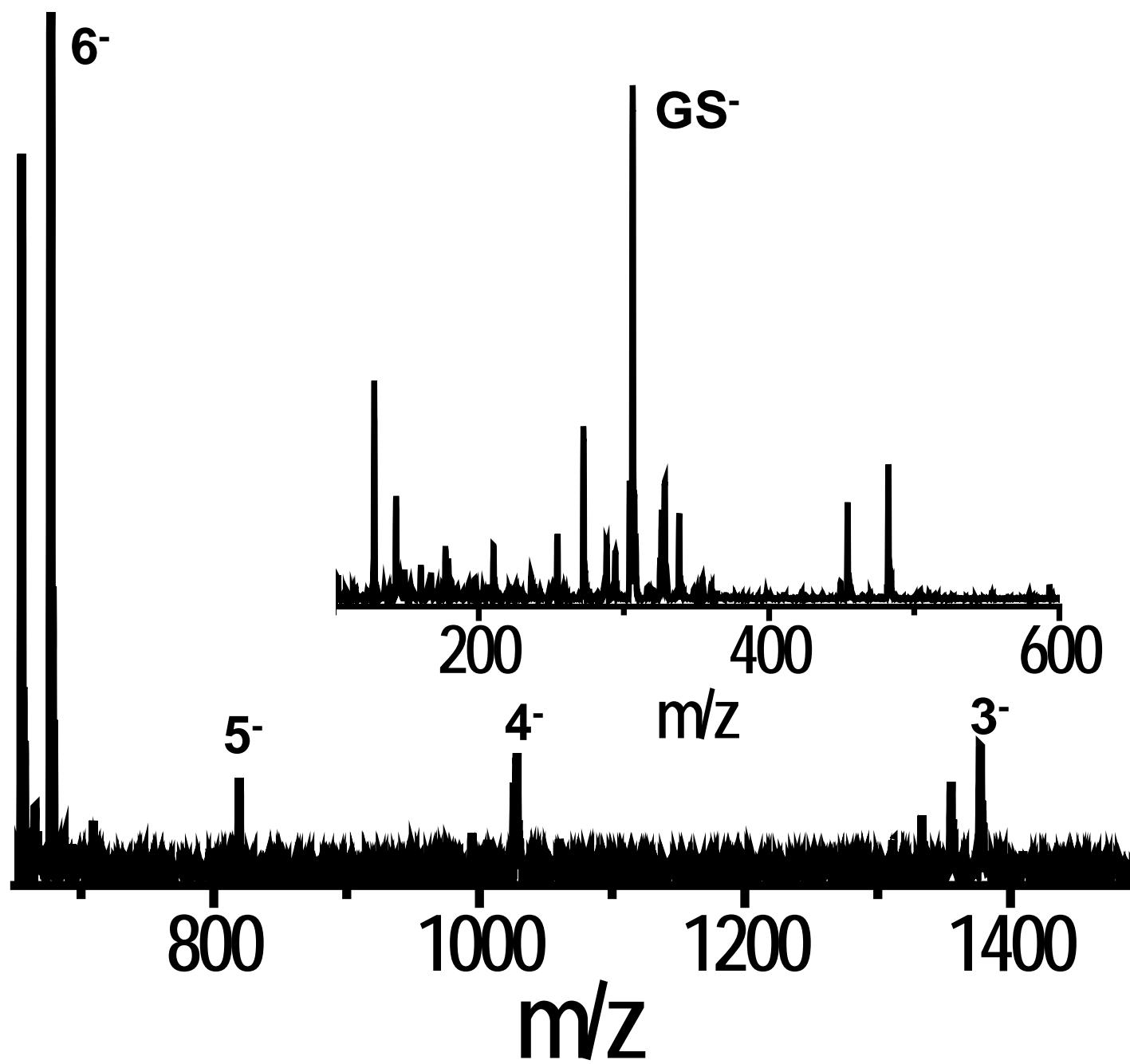


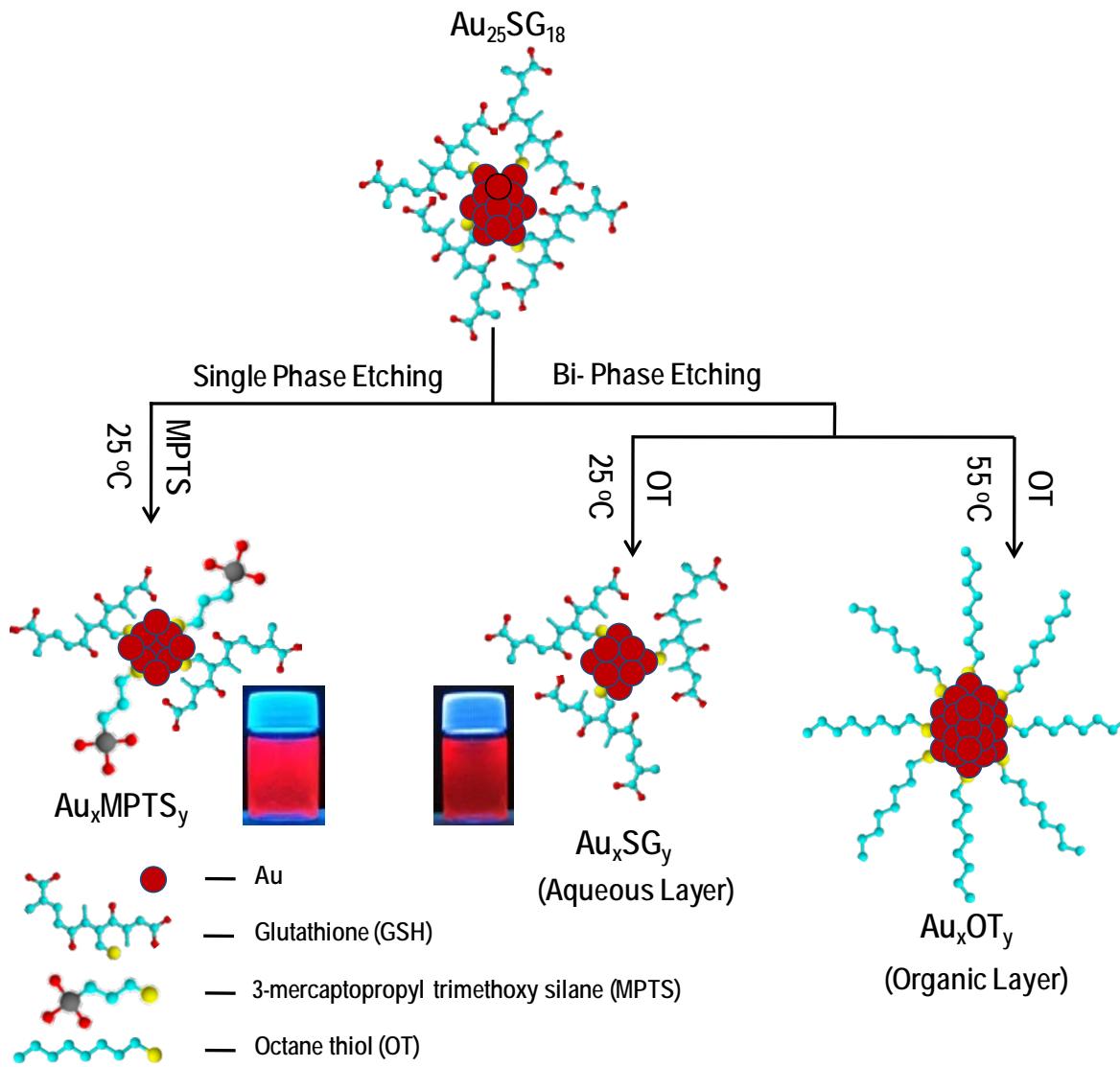


Comparison of the optical absorption profiles of Au@MSA, Au₂₅ and Au₈.

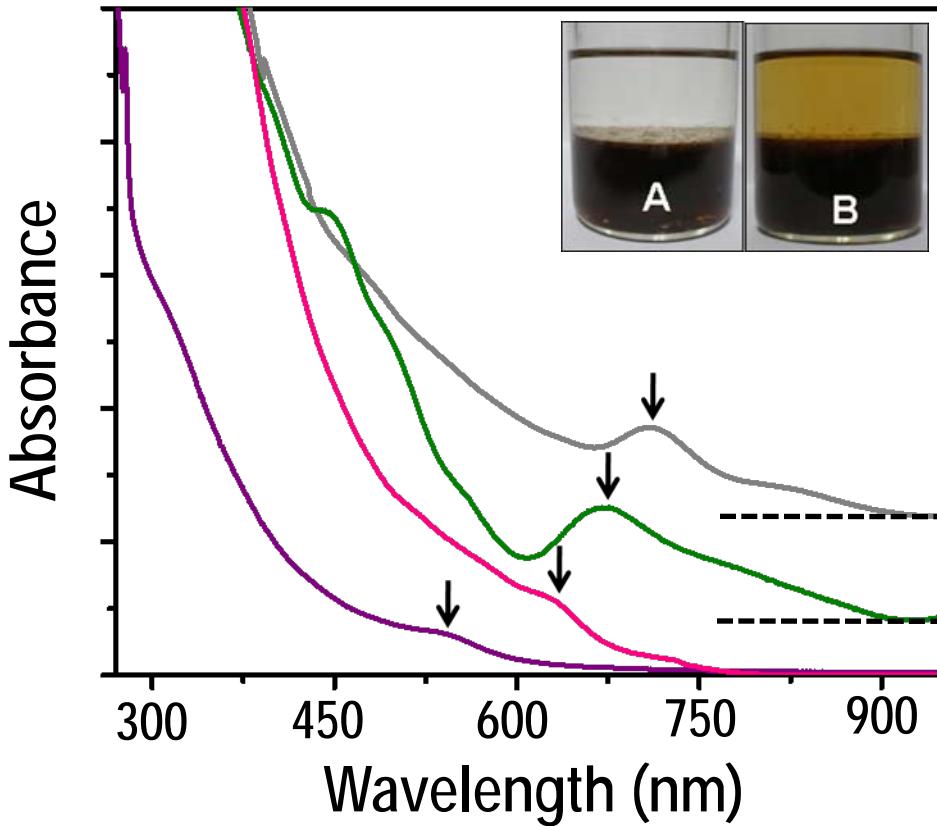


Comparison of the photoluminescence profiles of the clusters with Au@MSA. Traces I and II are the excitation and emission spectra of Au₈, respectively. Traces III and IV are the excitation and emission spectra of Au₂₅, respectively and trace V is the emission spectrum of Au@MSA.





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



Comparison of the optical absorption features of $\text{Au}_{25-18}^{\text{x-y}}$ SG (green trace) with $\text{Au}_{x-y}^{\text{x-y}}$ OT (grey trace), $\text{Au}_{x-y}^{\text{x-y}}$ SG (pink trace) and $\text{Au}_{x-y}^{\text{x-y}}$ MPTS (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 °C (interfacial etching) for 1 h.

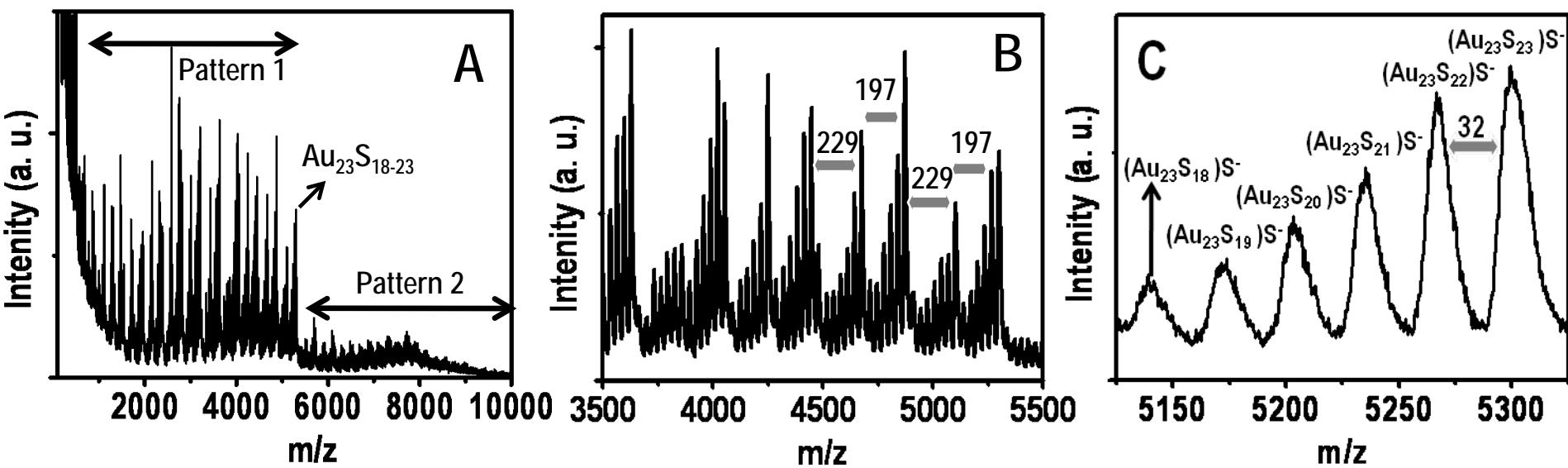
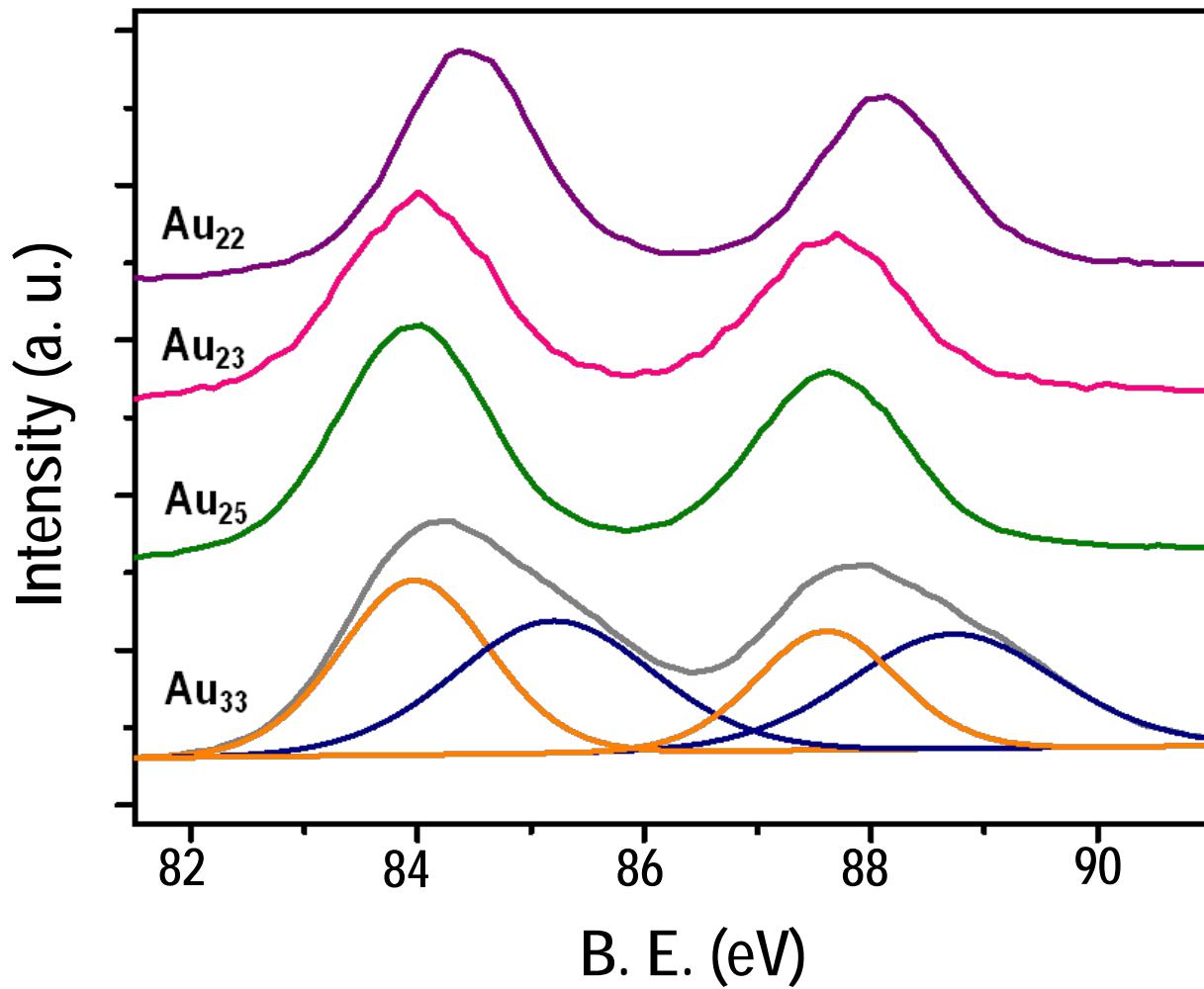
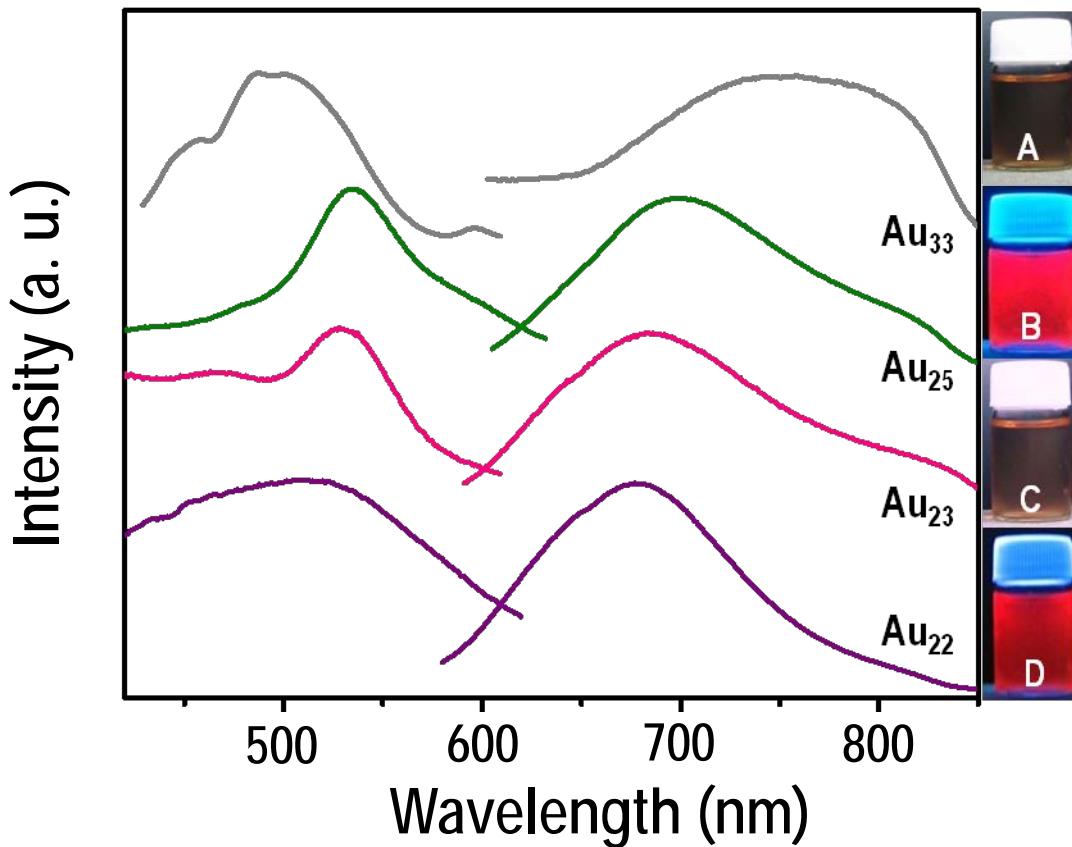


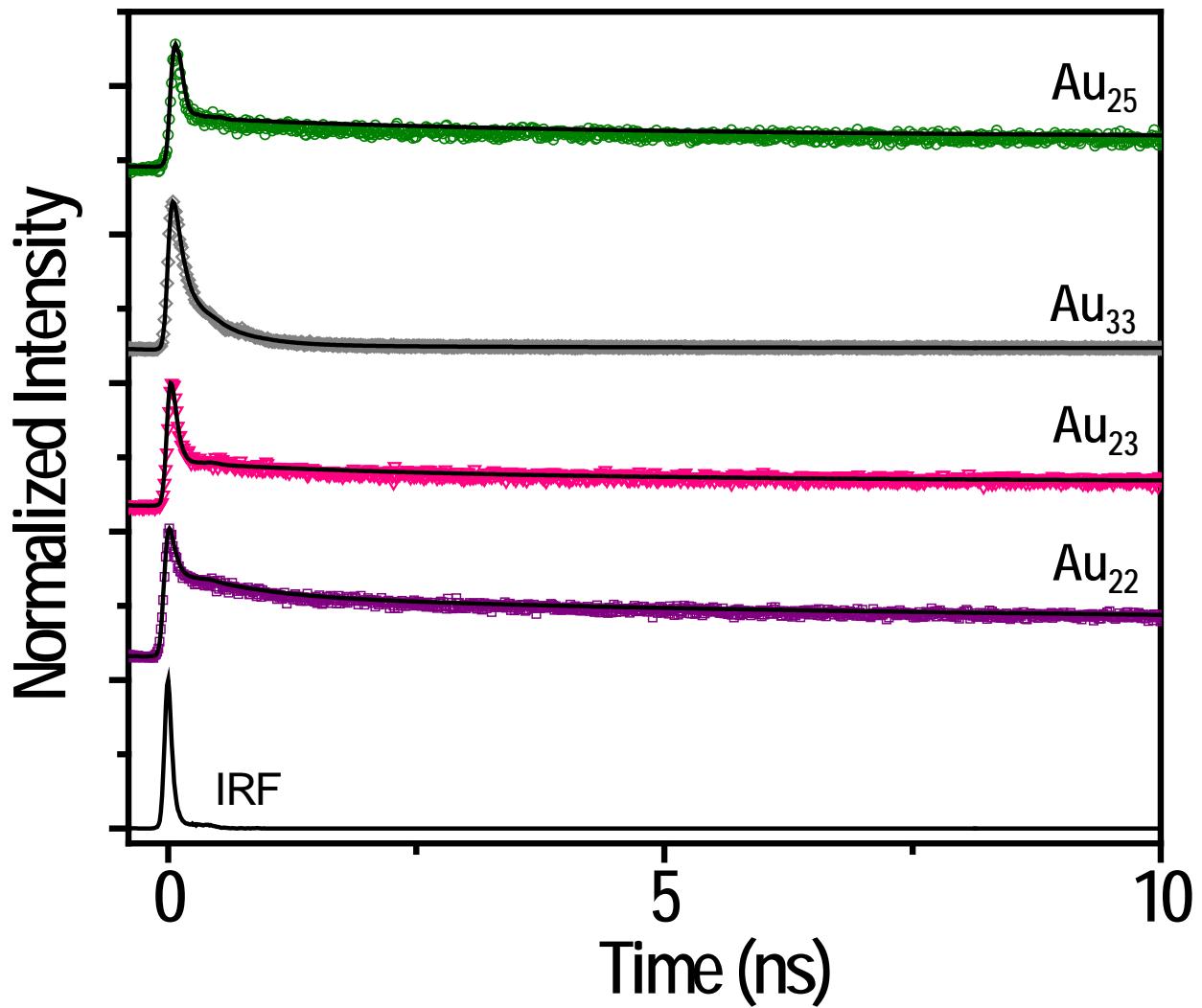
Figure 2. A) MALDI-MS of $\text{Au}_{\text{x}}\text{SG}_{\text{y}}$ which shows bunch of peaks due to $\text{Au}_{\text{x}}\text{S}_{\text{y}}$ clusters. B) A group of peaks with m/z spacing of 197 or 229 between the major peaks of the adjacent group of peaks. C) Expanded view of peaks due to $\text{Au}_{\text{23}}\text{S}_{\text{18-23}}$.



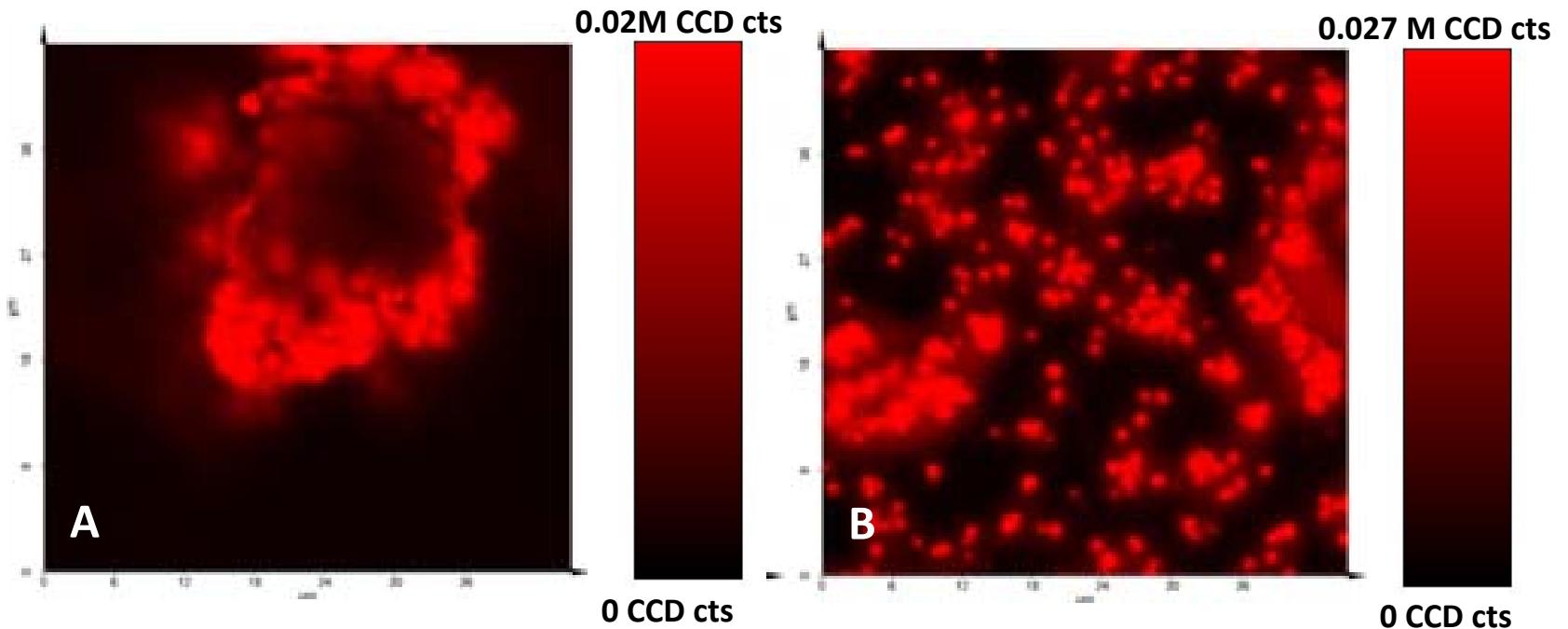
Comparison of the $\text{Au}(4\text{f})$ XPS spectra of Au_{22} , Au_{23} and Au_{33} along with parent Au_{25} .



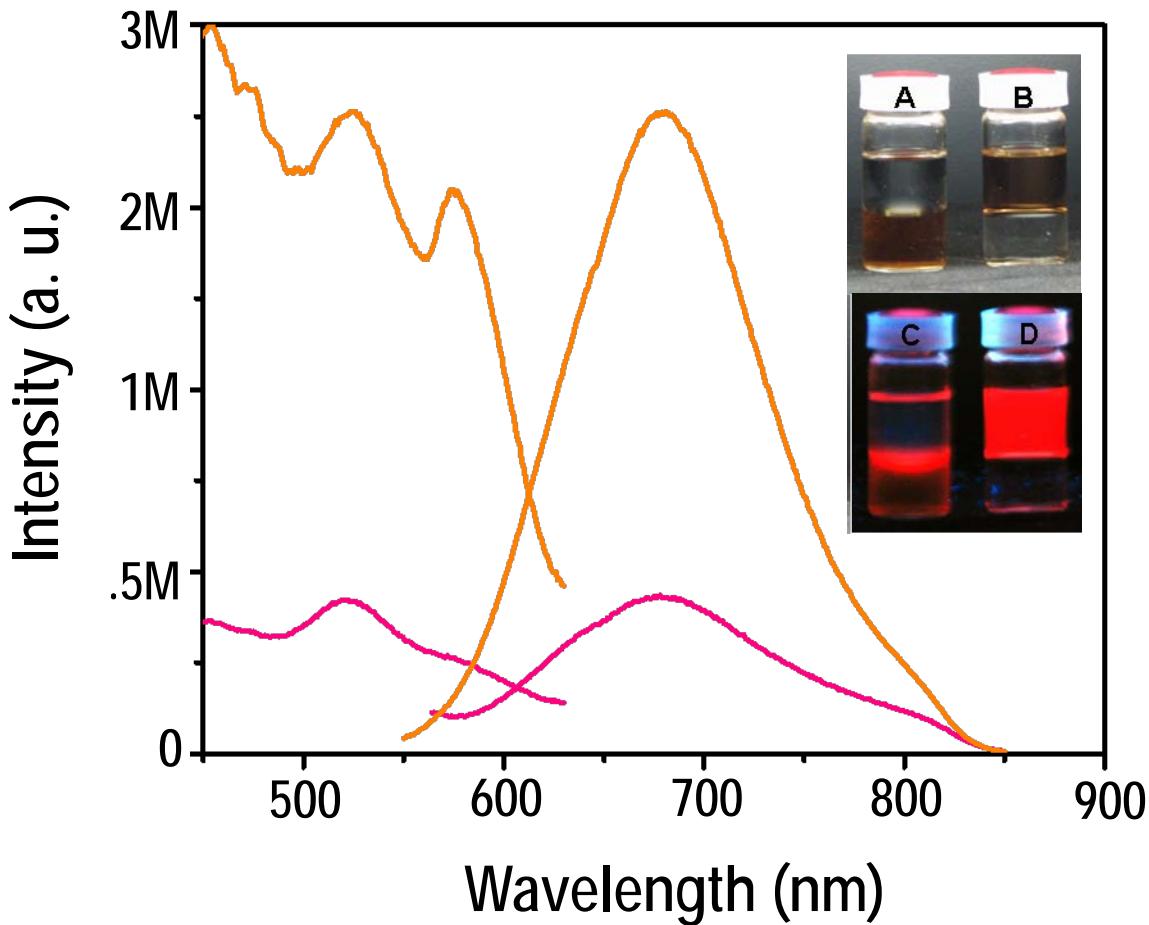
Comparison of the photoluminescence profiles of Au_{22} , Au_{23} and Au_{33} along with parent Au_{25} . Photographs of the aqueous solutions of Au_{22} and Au_{23} under white light (A and C, respectively) and UV light (B and D, respectively) are also given.



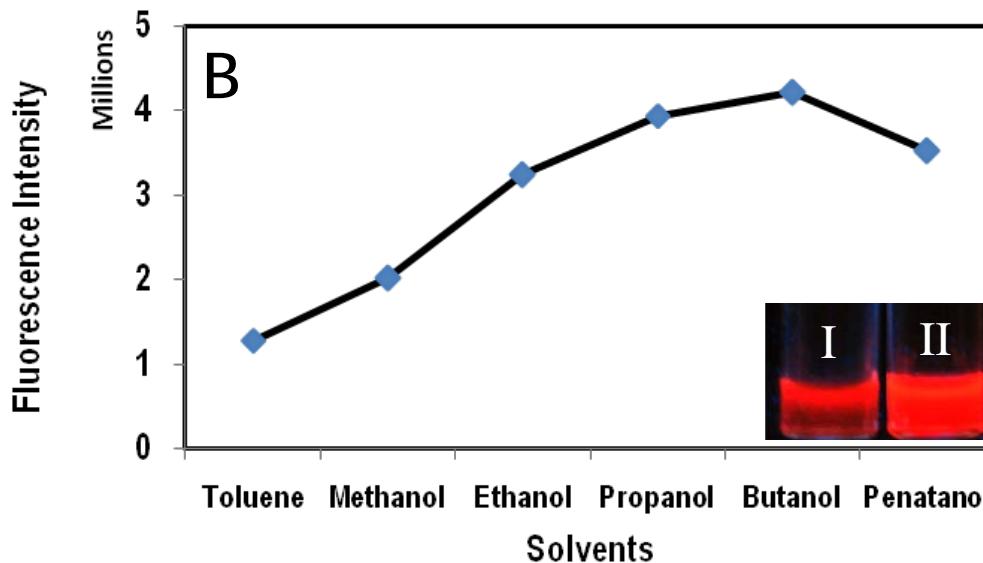
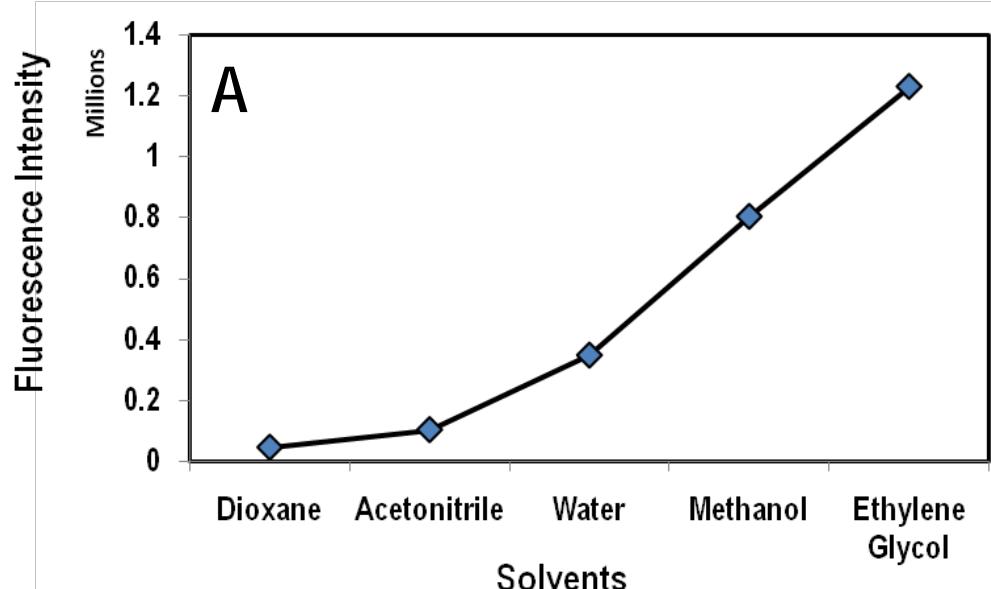
Fluorescence decay pattern of Au_{25} , Au_{33} , Au_{23} , and Au_{22} collected at 630 nm.



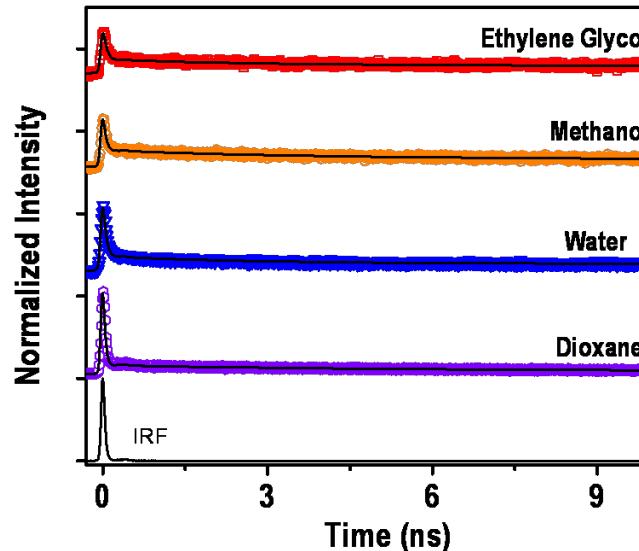
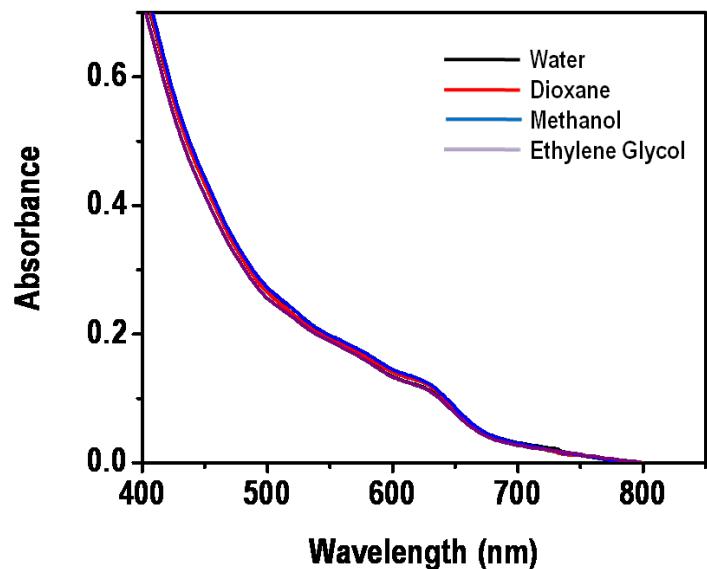
Inherent fluorescence image of Au_{22} (A) and Au_{23} (B) collected by the spectroscopic mapping at an excitation wavelength of 532 nm. Regions coded red represents the pixels where the signal (used for mapping) is a maximum, the minima being represented with black colors. The scan area was $40 \mu\text{M}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



Photoluminescence 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

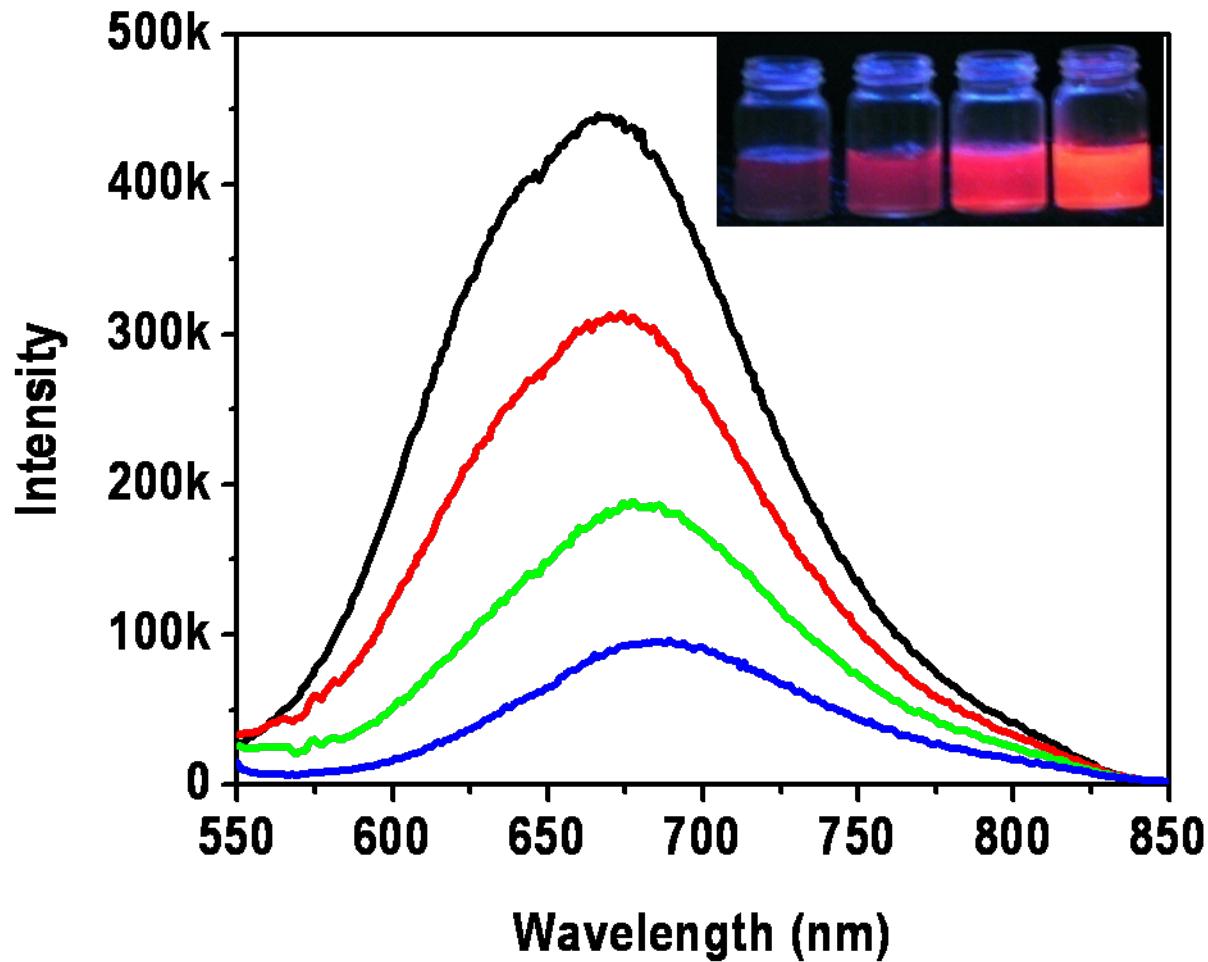


A) Solvent dependent fluorescence of $50 \mu\text{M}$ Au_{23} in ethylene glycol, methanol, water, acetonitrile and dioxane before phase transfer. **B)** Solvent dependent fluorescence of Au_{23} in methanol, ethanol, propanol, butanol and pentanol after phase transfer. Inset of B shows the photograph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

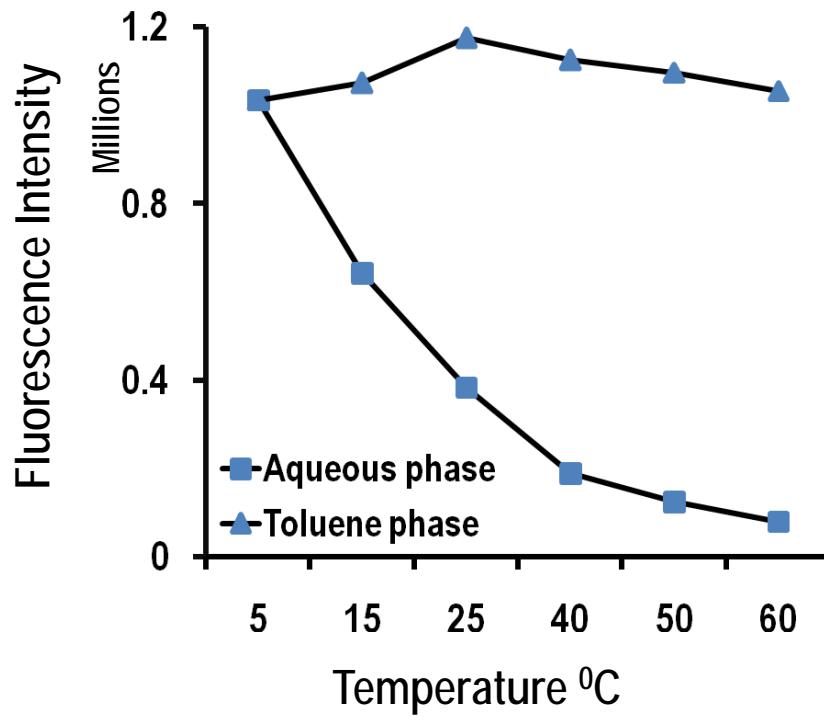


| Solvent | τ_1 (ps) | % | τ_2 (ns) | % | τ_3 (ns) | % |
|-----------------|---------------|------|---------------|-----|---------------|-----|
| Ethylene Glycol | 47 | 86.5 | 2.67 | 5.5 | 70.06 | 7.9 |
| Methanol | 36 | 87.6 | 3.27 | 5.8 | 62.91 | 6.6 |
| Water | 39 | 92.4 | 2.41 | 3.6 | 68.55 | 3.9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

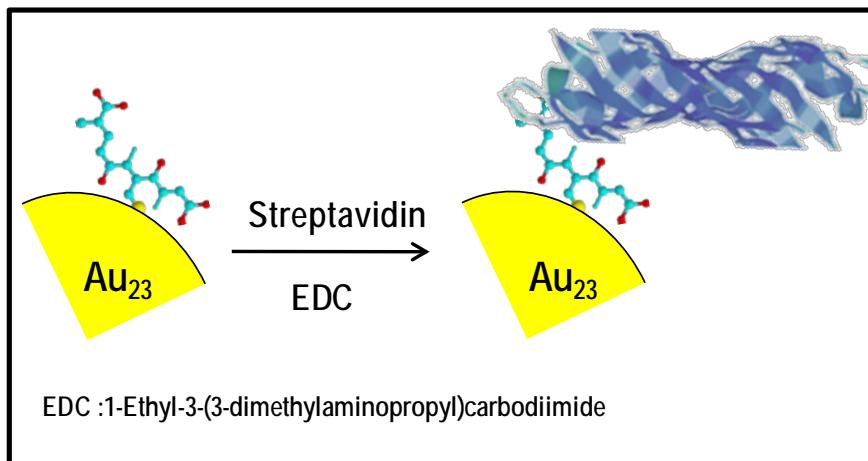
A) Optical absorption spectra of Au_{23} in dioxane, water, methanol and ethylene glycol. B) Fluorescence decay of Au collected at 630 nm in various solvents. Table tabulates the life time of the cluster in various solvents.



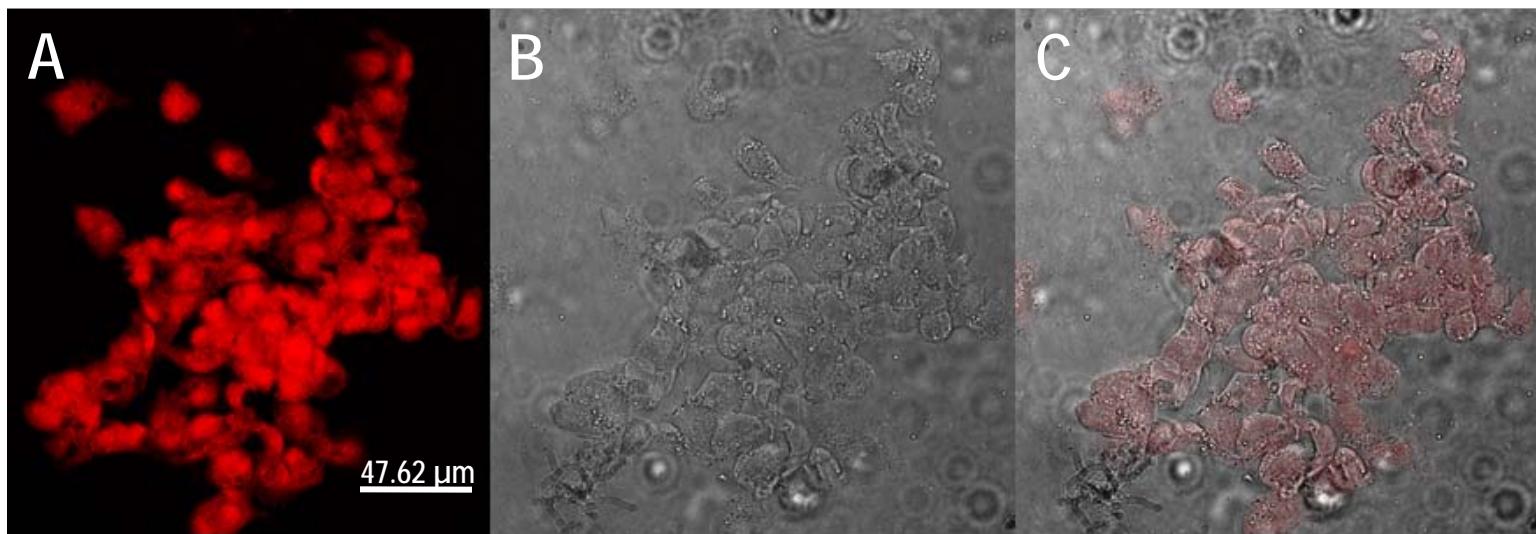
Plot of fluorescence intensity of Au_{23} cluster in water-DMSO mixture starting from pure water (blue line) to 1:1 (green line), 1:2 (red line) and 1:3 (black trace) water-DMSO mixtures. Inset shows the photographs of the corresponding solutions under UV light irradiation



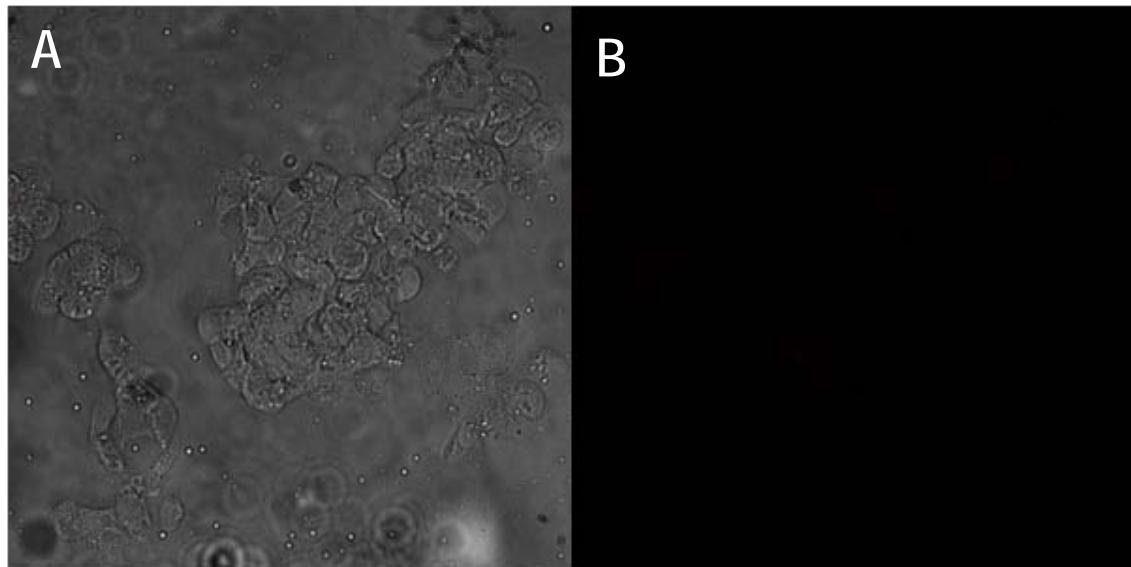
Plot of temperature vs fluorescence intensity of the cluster in the aqueous and toluene layers. While the intensity of emission of aqueous solution of Au_{23} decreases with increase in temperature, the emission intensity remains unaltered for phase transferred Au_{23} .



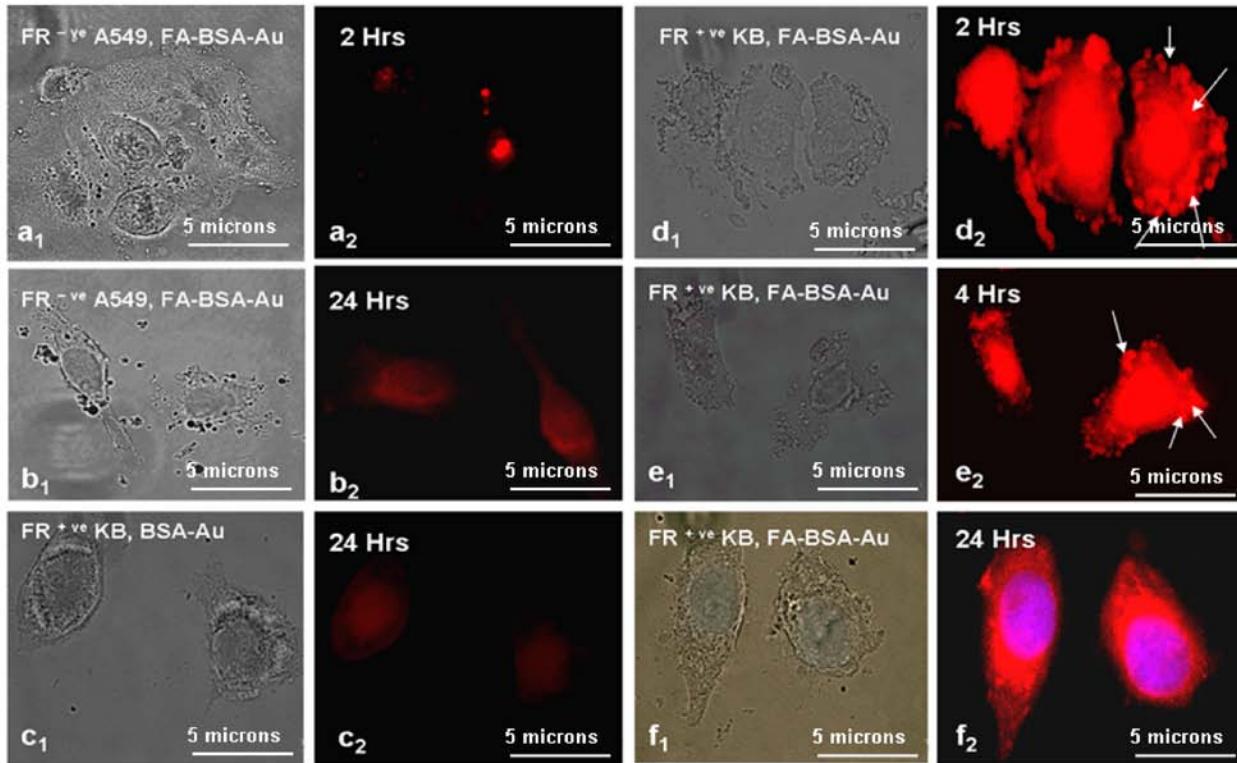
Schematic representation of the conjugation of streptavidin on $\text{Au}_{23} \text{ SG}_{18}$ by EDC coupling.



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} .

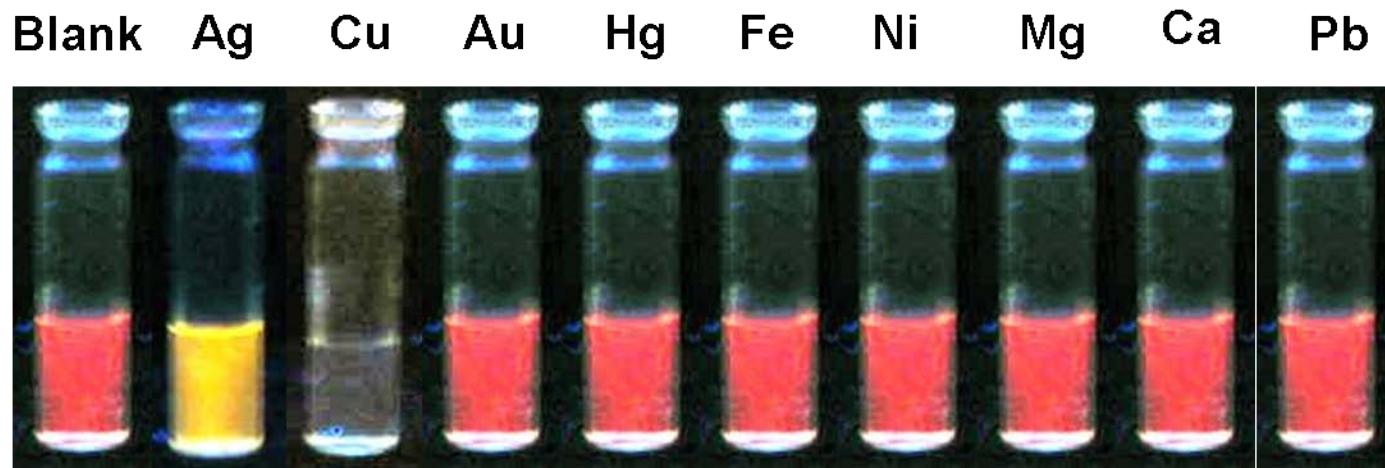


Bright field (A) and fluorescence (B) images of HepG2 cells stained with unconjugated Au_{23} clusters. No fluorescence was observed from the cells after washing



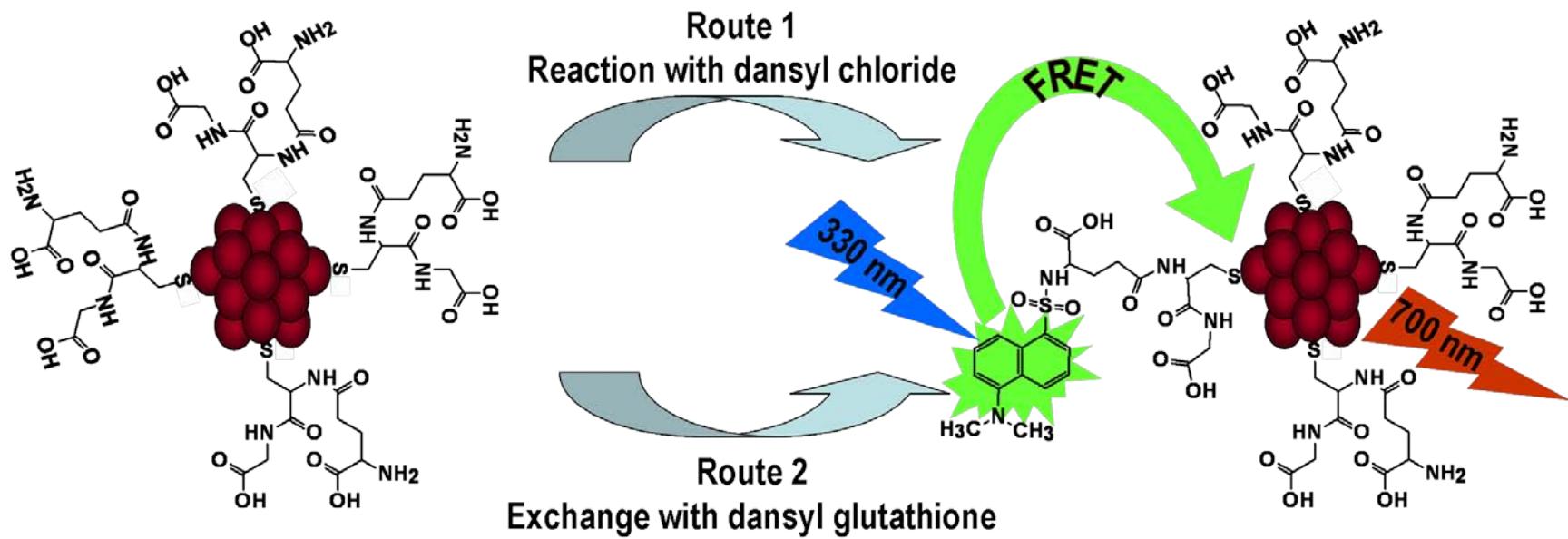
Fluorescent microscopic images showing interaction of Au-BSA-FA NCs with different types of cell lines: a1-a2) FR-ve lung carcinoma A549 after 2 hours of incubation, b1-b2) FR-ve lung carcinoma A549 after 24 hours of incubation, c1-c2) FR+ve KB cells with unconjugated Au clusters, d1-d2) FR+ve KB cells with FA conjugated Au clusters at 2 hrs, e1-e2) 4 hrs and f1-f 2) 24 hrs of incubation [Archana R, Sonali S, Deepthy M et al (2009) Molecular Receptor Specific, Non-toxic, Near-infrared Emitting Au Cluster-Protein Nanoconjugates for Targeted Cancer Imaging. Nanotechnology (in press)]

Clusters for metal ion detection



Water soluble red emitting clusters were 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 altered in case of other ions.

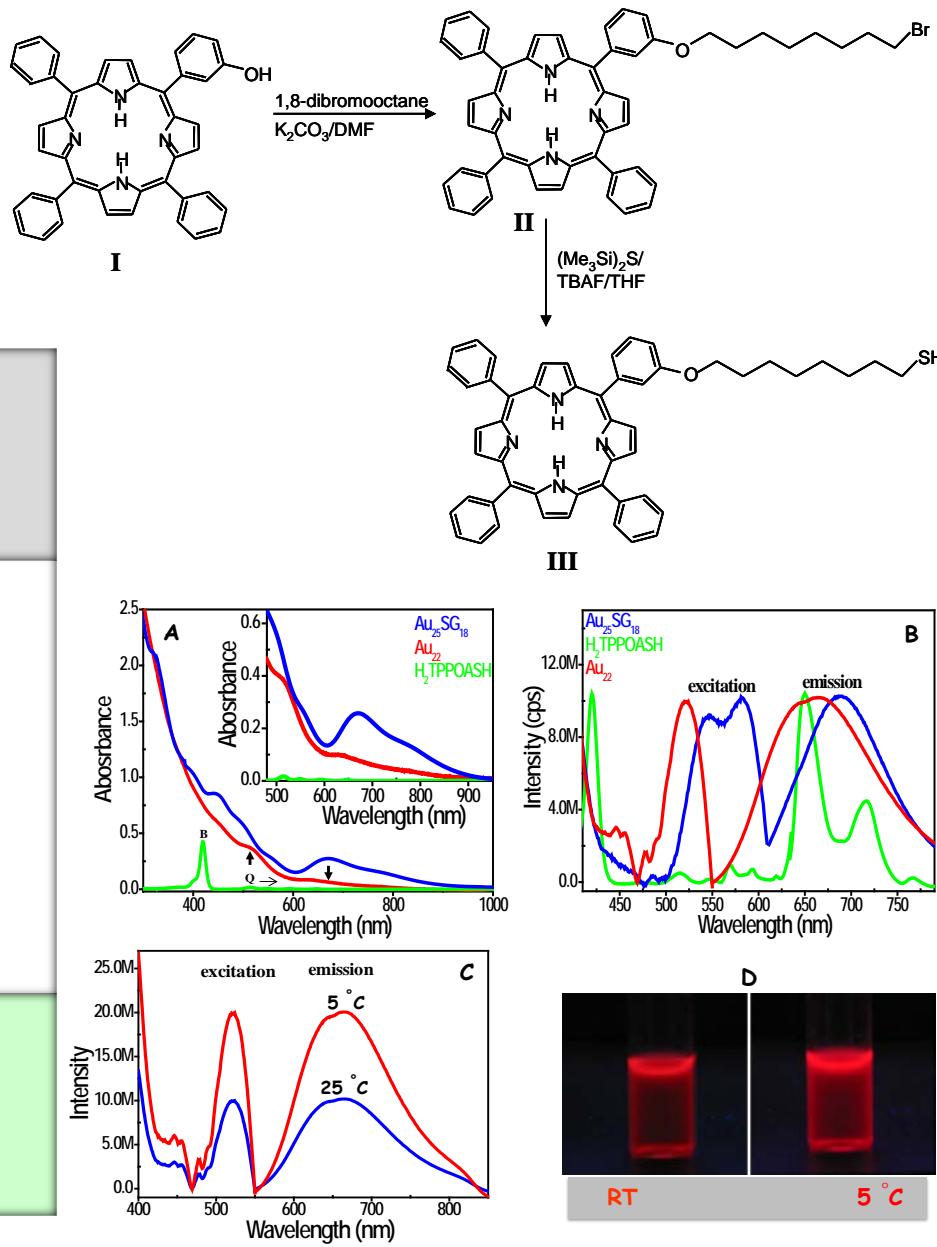
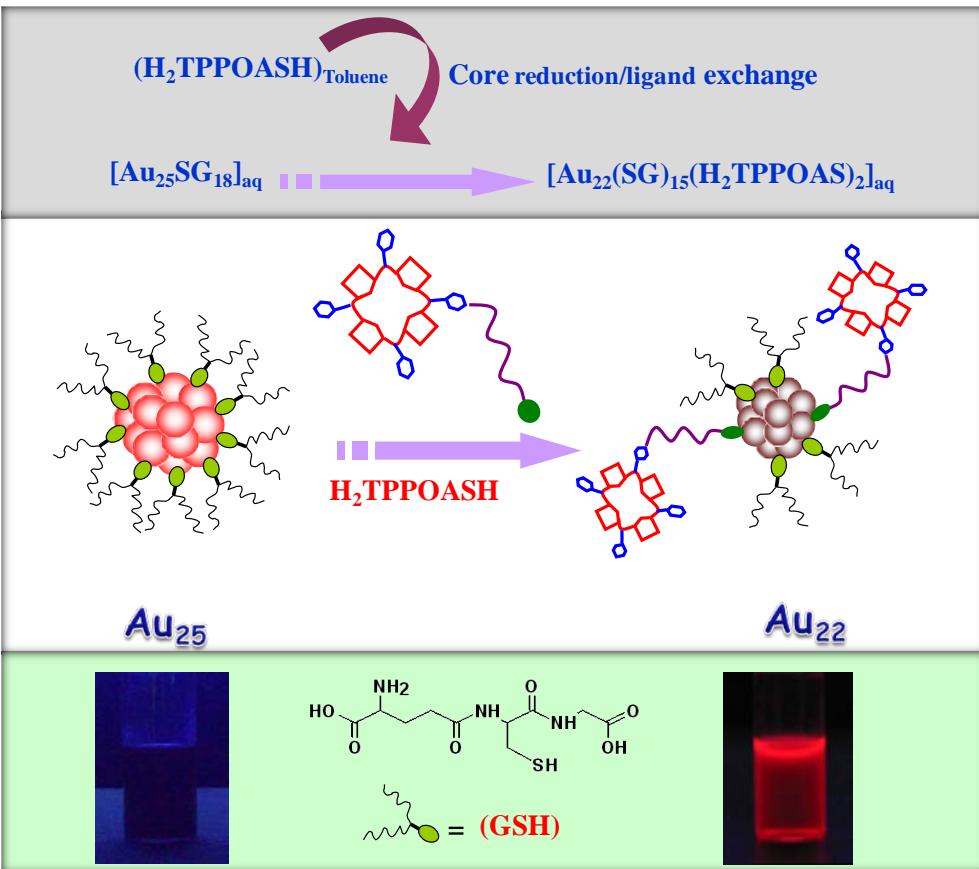
FRET between Au_{25} and Dansyl Chromophore

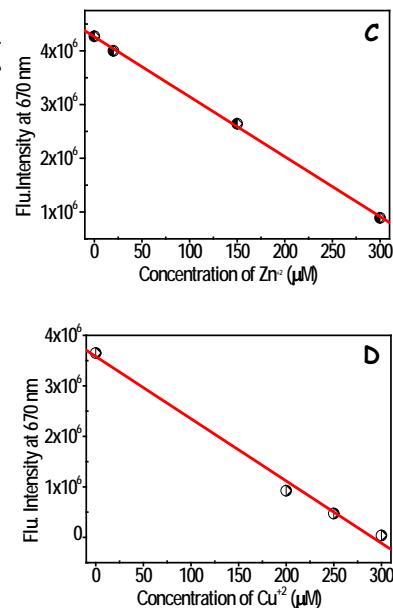
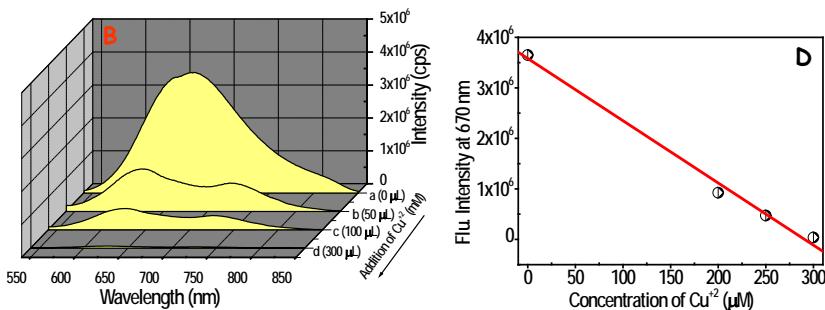
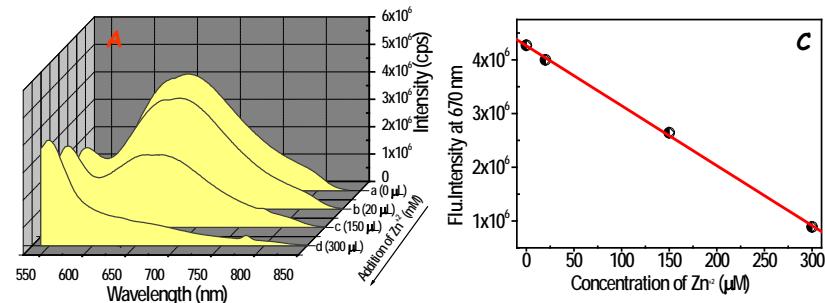
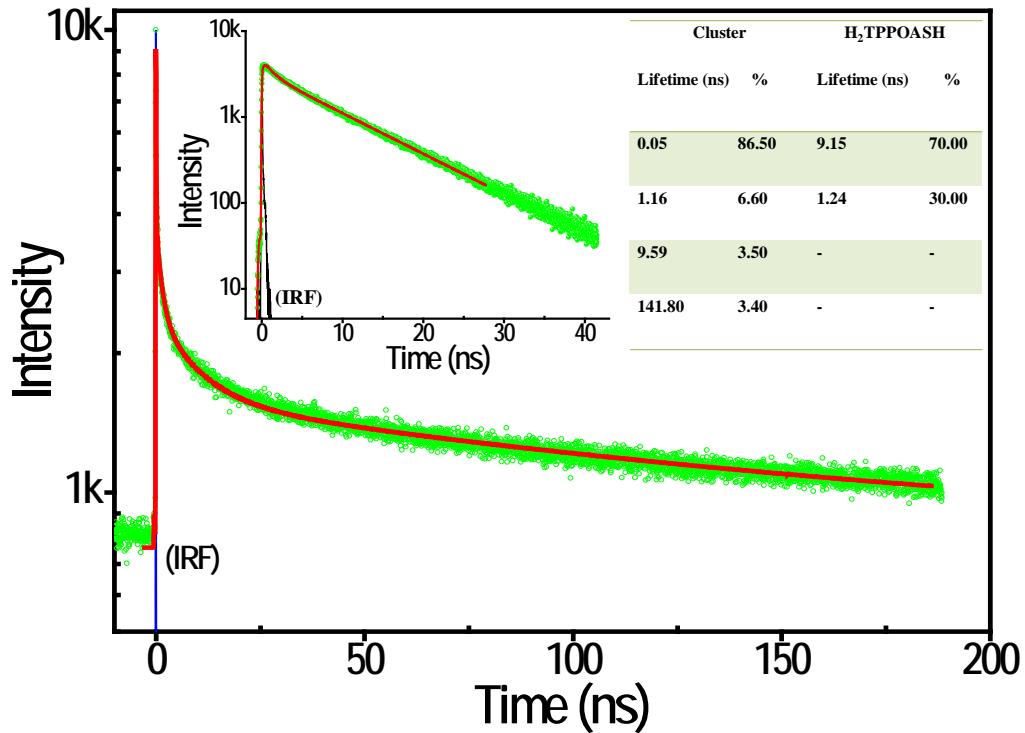
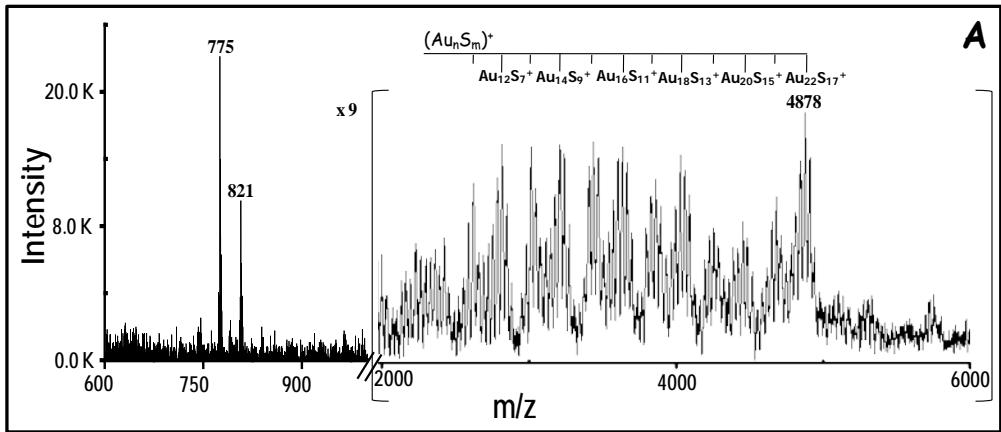


Approaches Used for the Functionalization of Dansyl Chromophore on the Au_{25} Cluster.

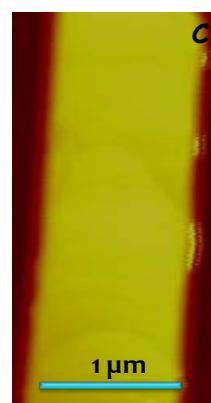
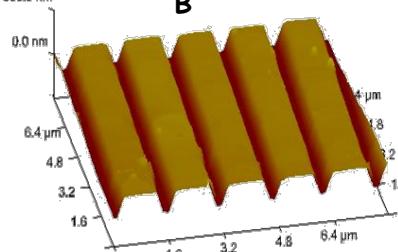
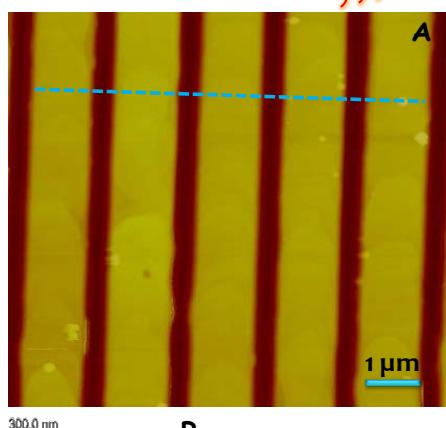
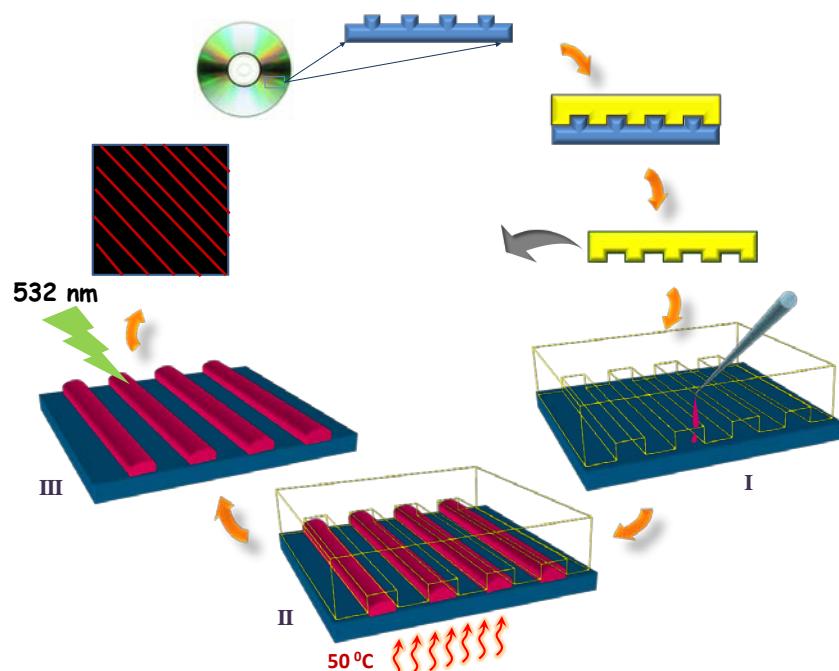
Habeeb Muhammed *et al.* *J. Phys. Chem. C* 2008, 112, 14324.

Cluster based patterns

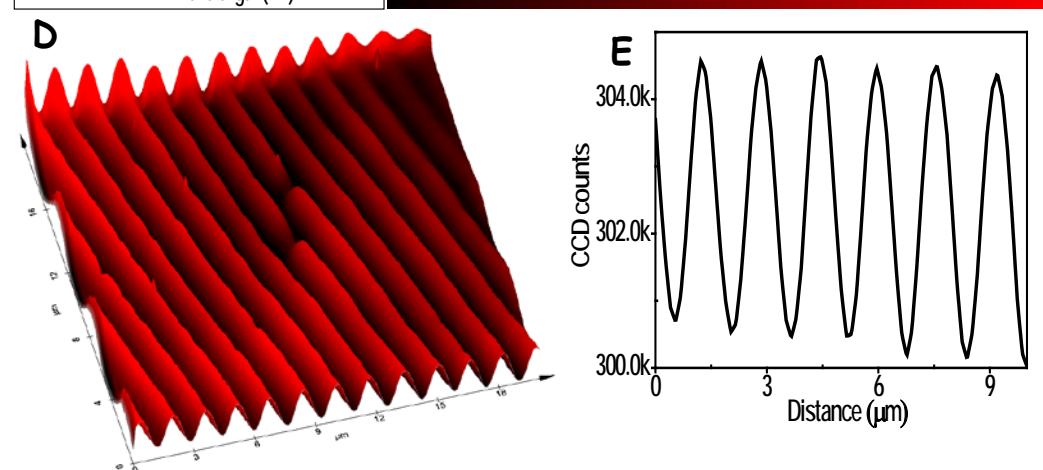
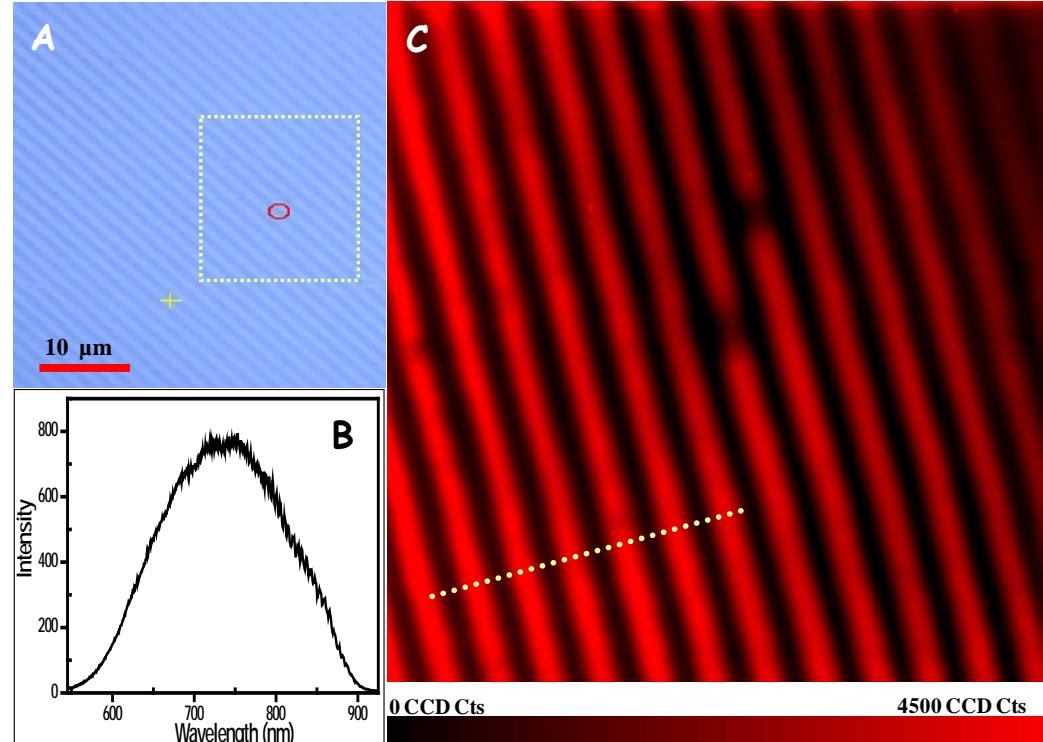
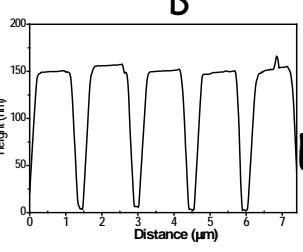




With G. U. Kulkarni

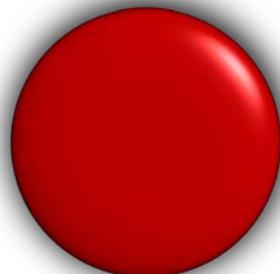


D



E. S. Shibu *et al.* ACS Appl. Mater. 2009, 1, 2199.

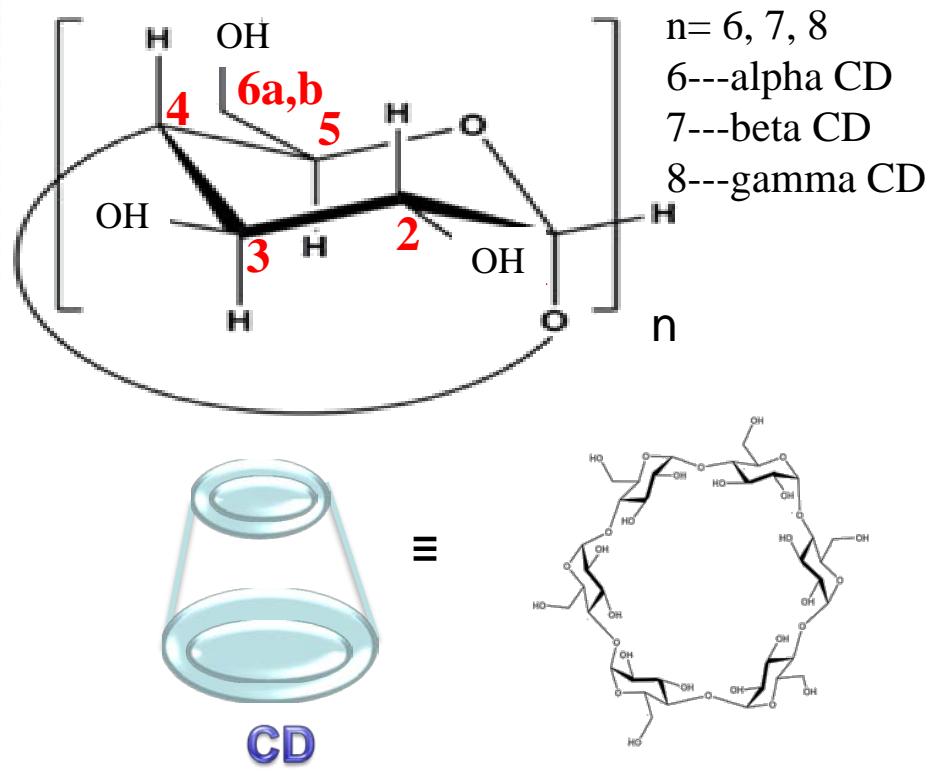
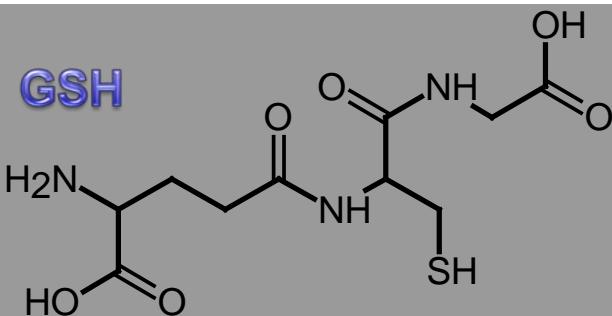
Au@SG – glutathione (GSH) protected gold nanoparticle



GSH
CD

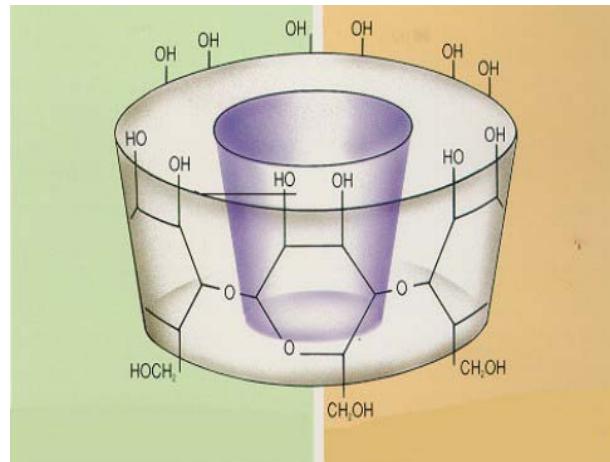


Au@SG



$n = 6, 7, 8$
6---alpha CD
7---beta CD
8---gamma CD

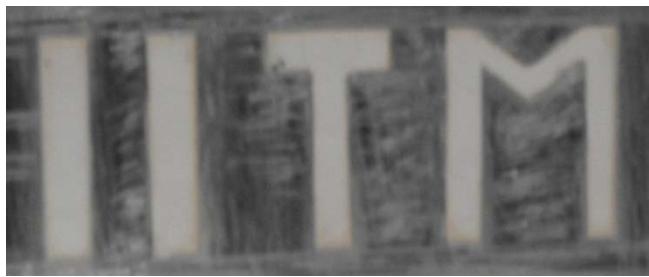
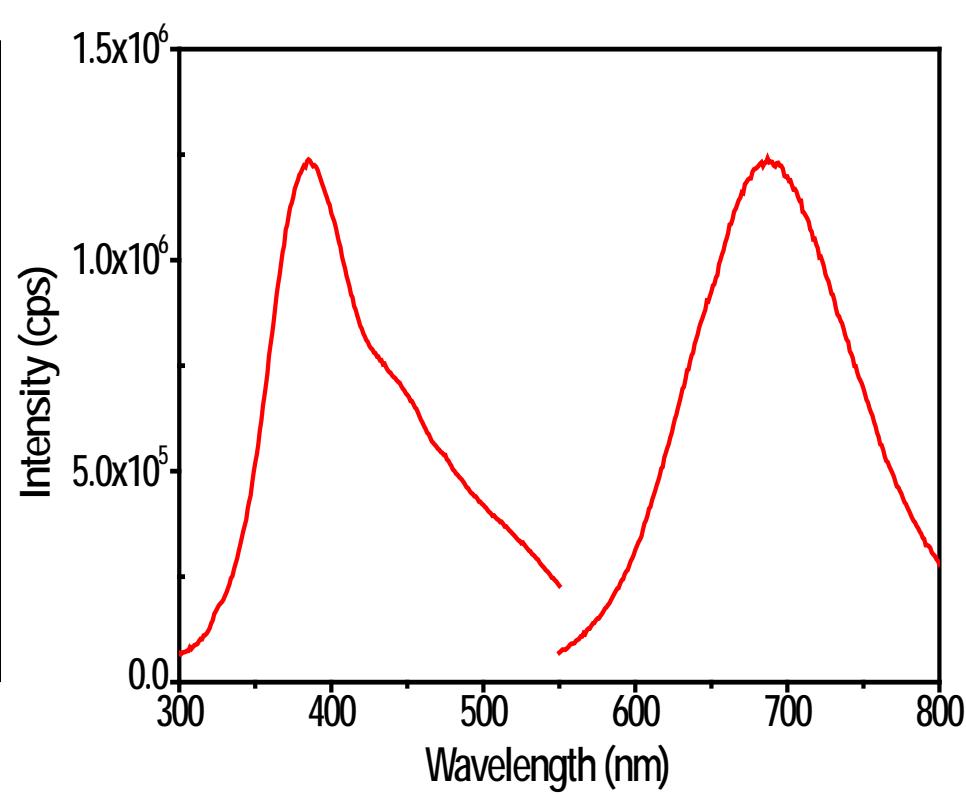
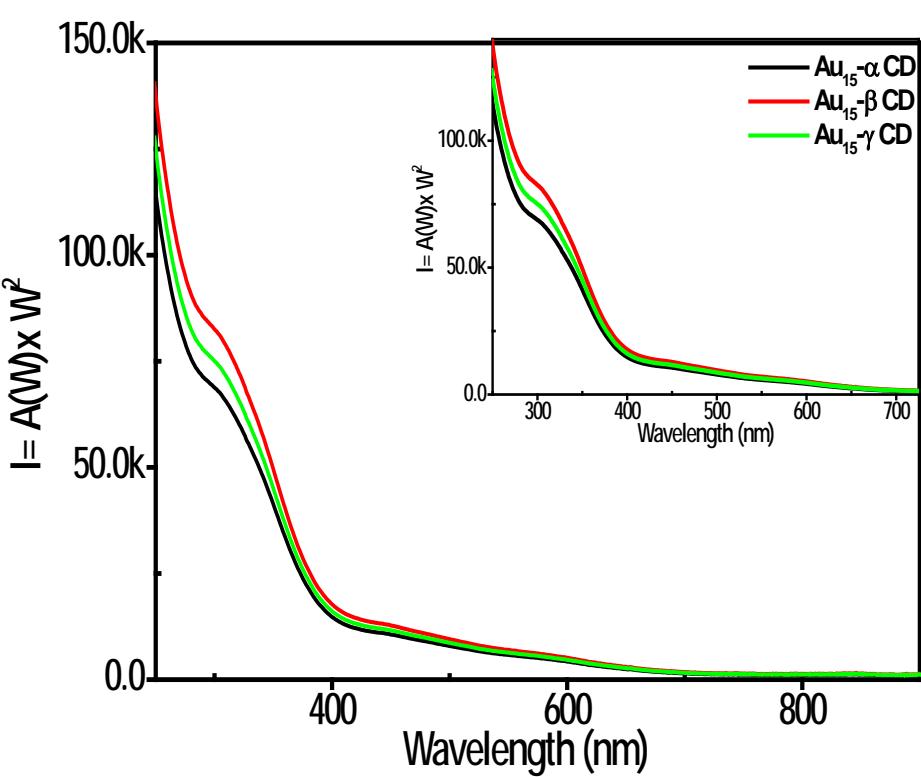
Basic unit of CD is 6 membered glucose



3D image of CD showing the nanometer cavity

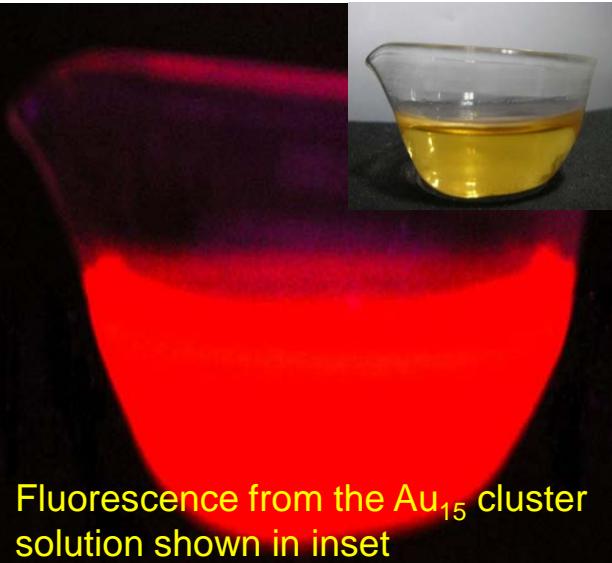
Scheme: Au_{15} was synthesized inside the cyclodextrin (CD) cavity (*in situ*). Note: CD and GSH are the abbreviations of cyclodextrin and glutathione, respectively. For our synthesis we have used all 3 CDs (alpha, beta and gamma)

E. S. Shibu and T. Pradeep. Unpublished

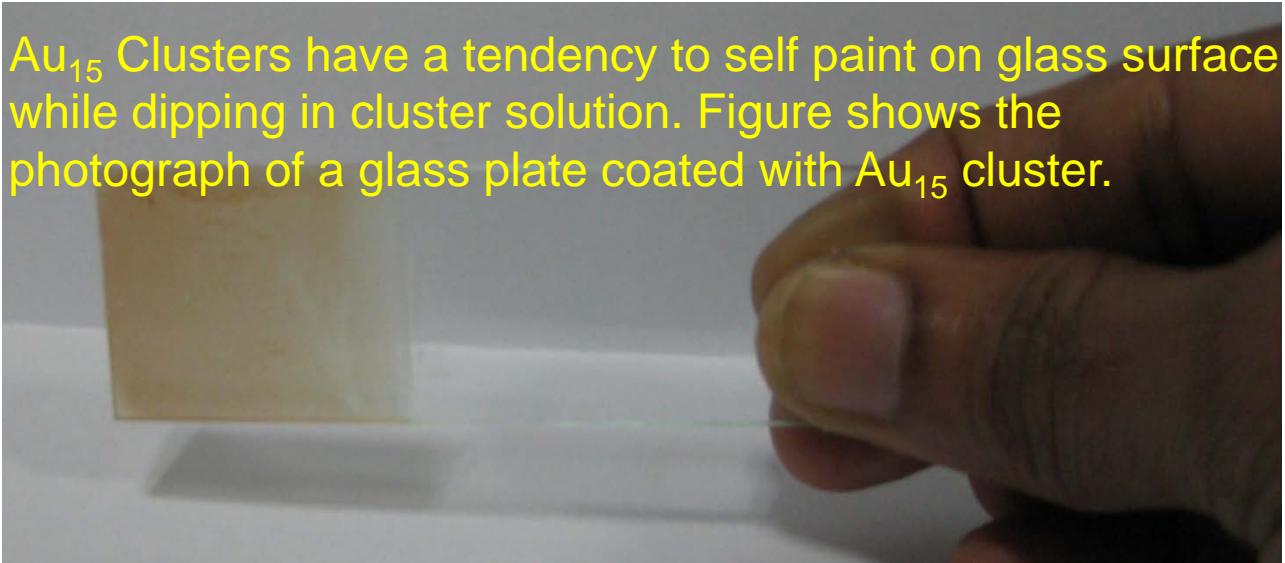


E. S. Shibu and T.
Pradeep. Unpublished

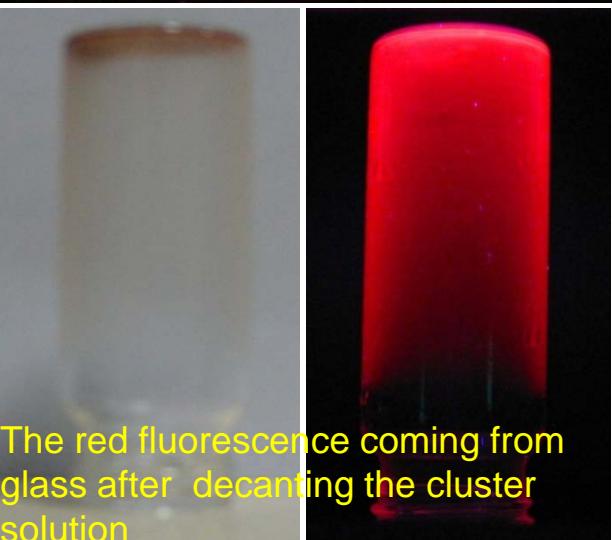
Glass coating and fluorescence



Fluorescence from the Au_{15} cluster solution shown in inset



Au_{15} Clusters have a tendency to self paint on glass surface while dipping in cluster solution. Figure shows the photograph of a glass plate coated with Au_{15} cluster.



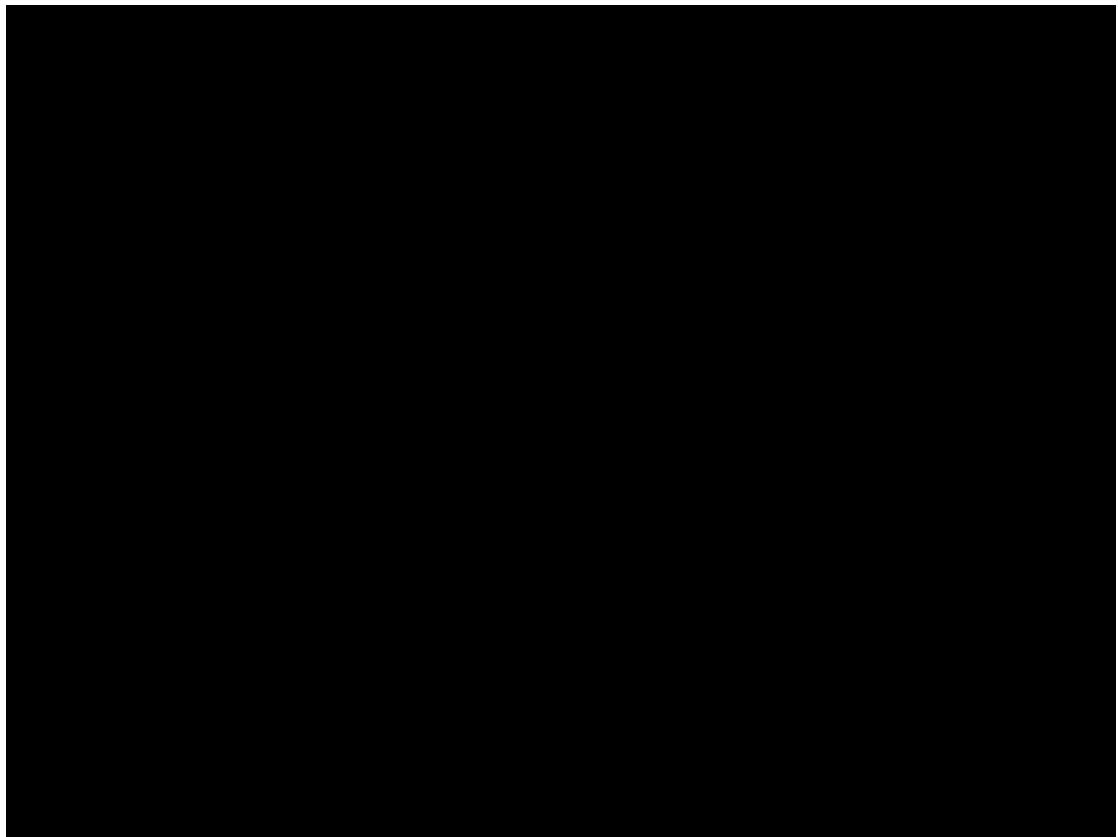
The red fluorescence coming from glass after decanting the cluster solution



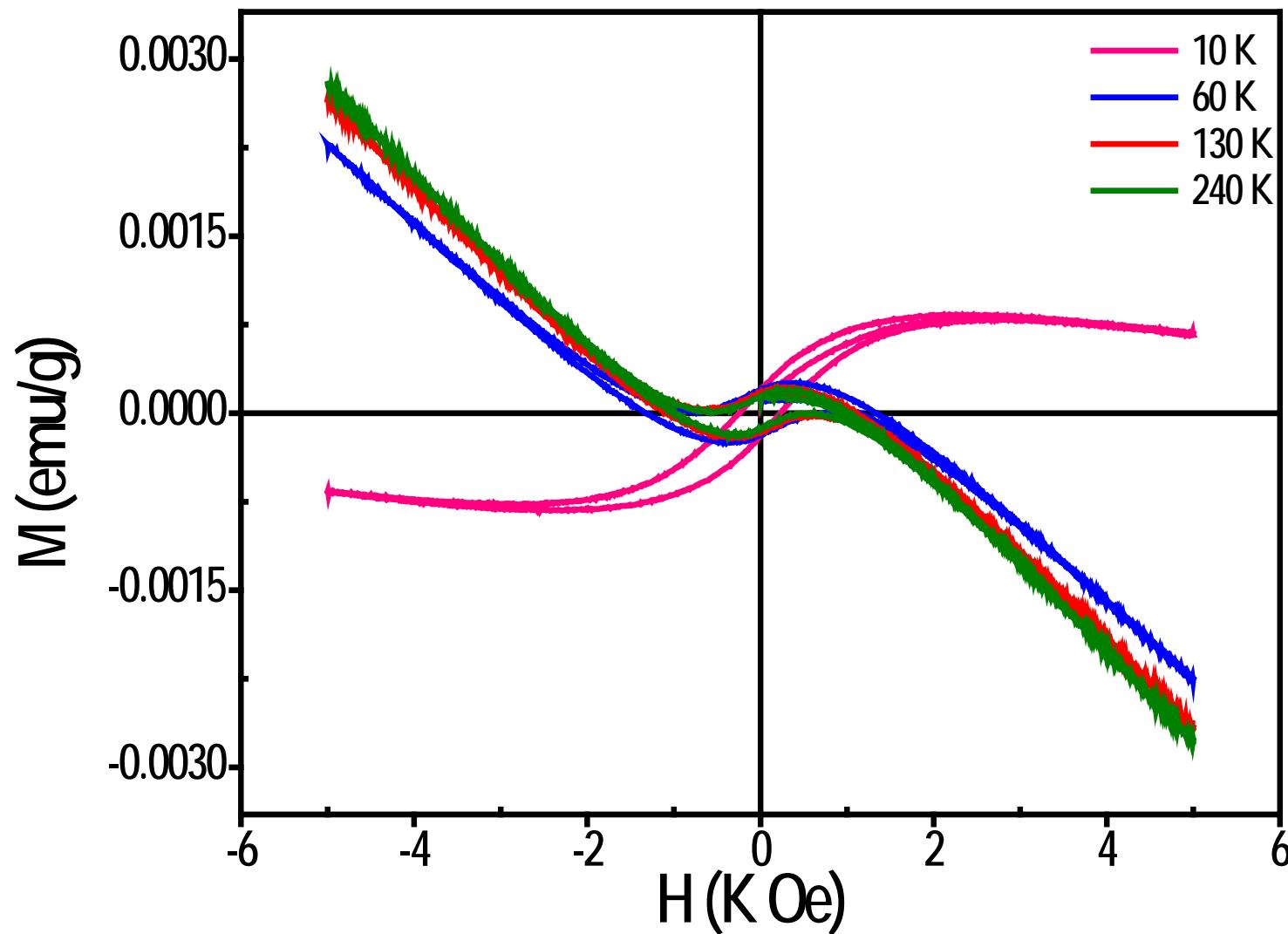
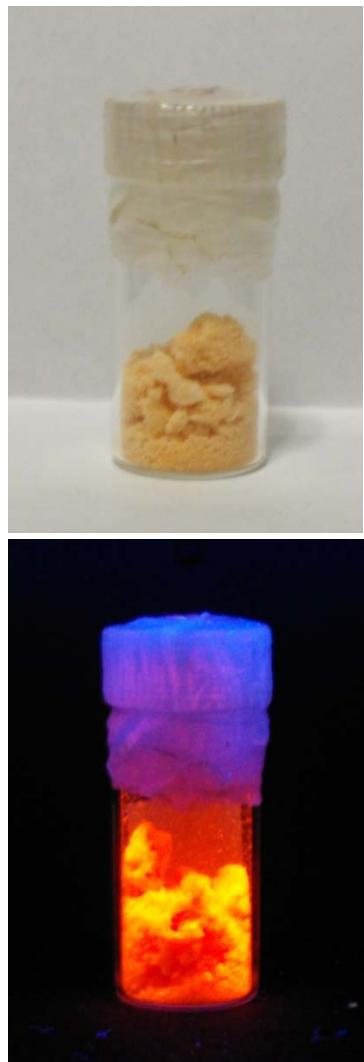
Photograph shows the red fluorescence coming from glass plate after the self painting of Au_{15} cluster.



E. S. Shibu and T. Pradeep. Unpublished



Magnetism in Au_{15} cluster



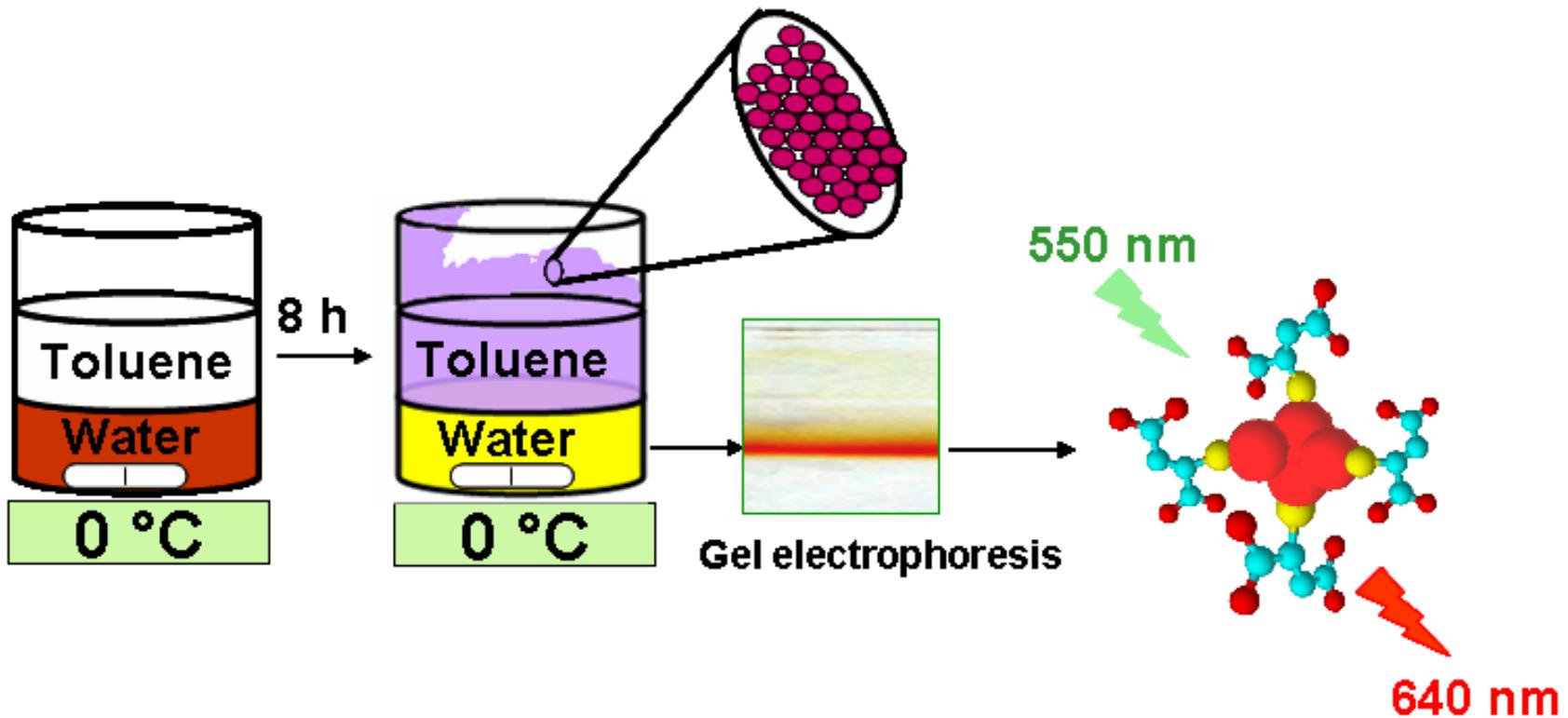
E. S. Shibu and T. Pradeep. Unpublished

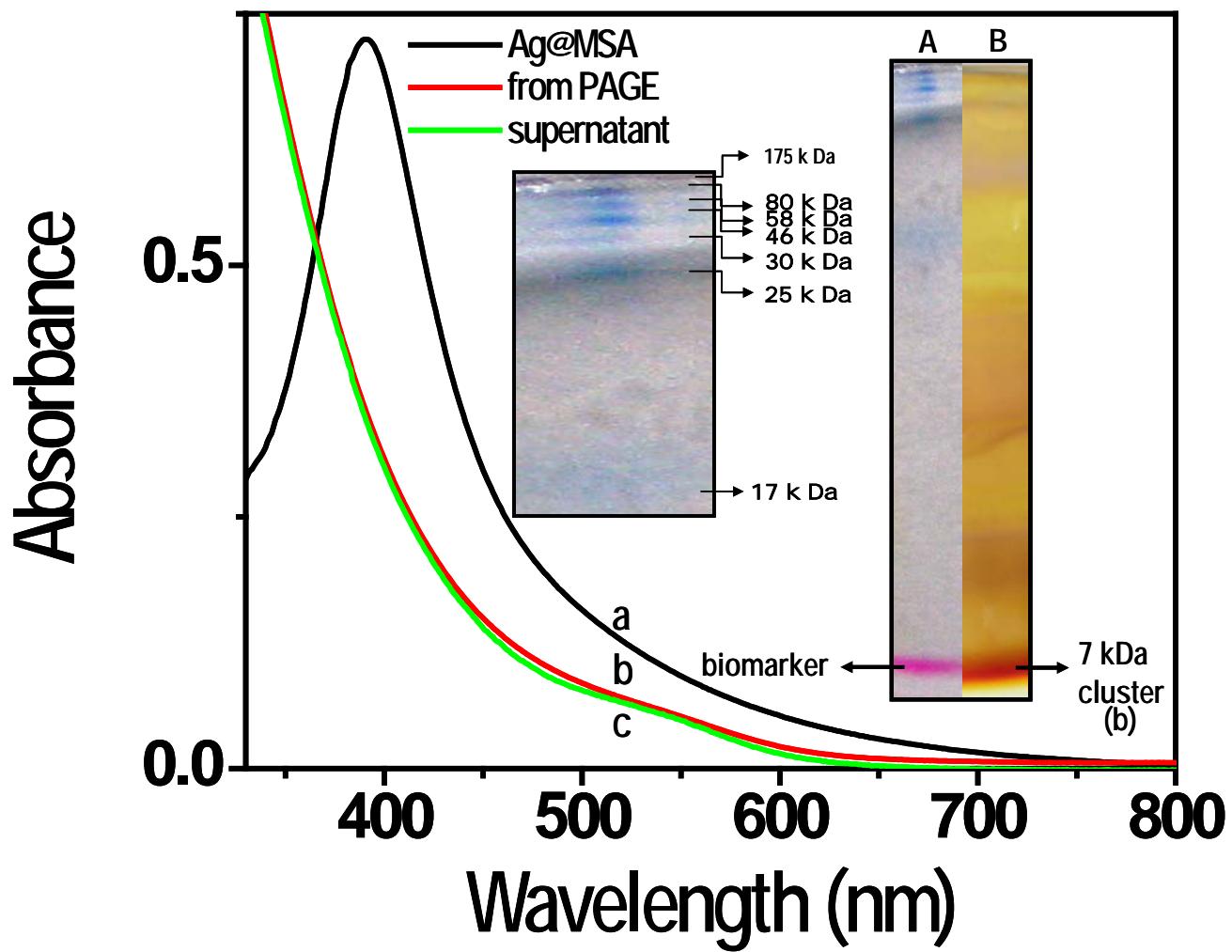
Size selected metal clusters

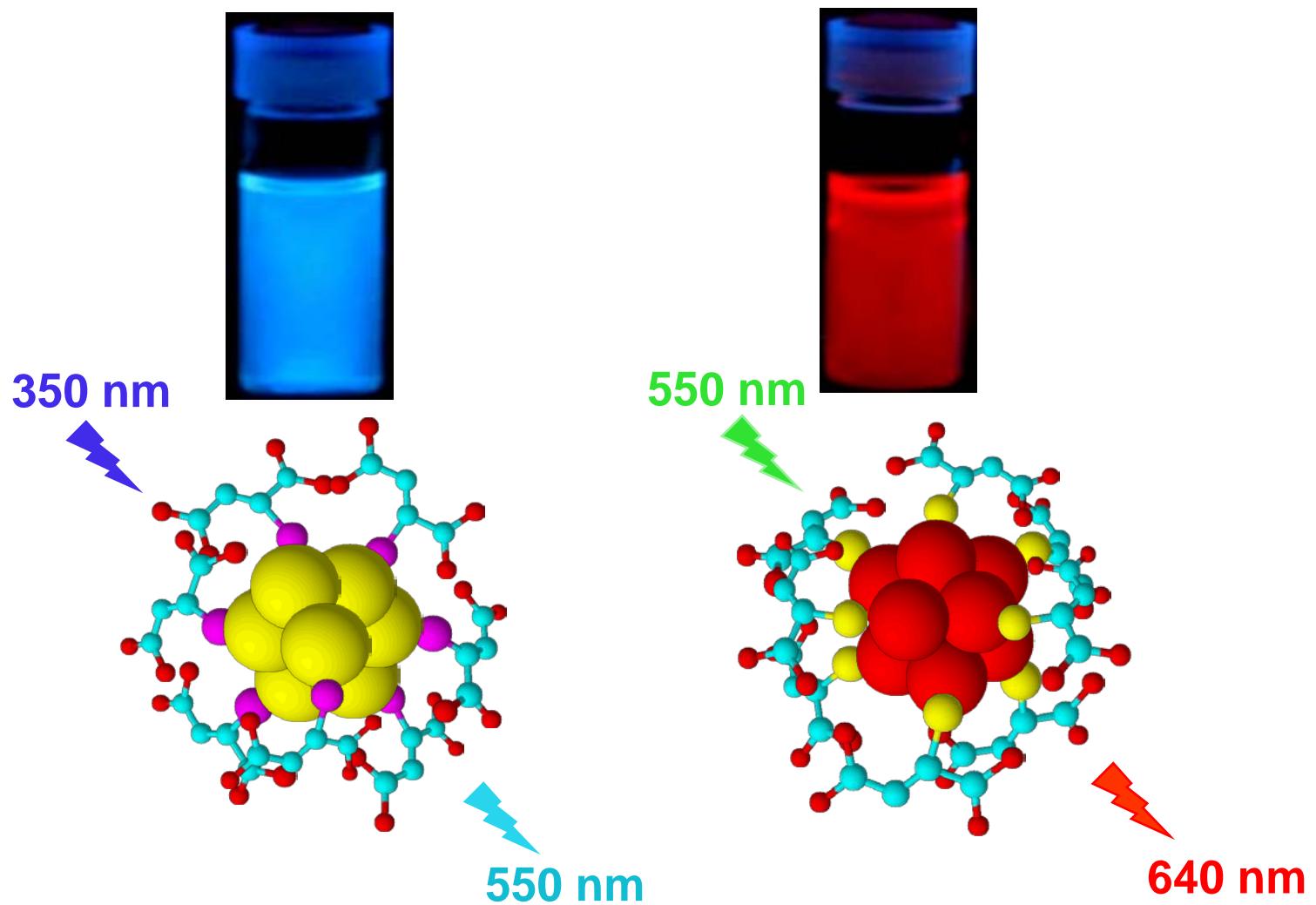
- The Optical Absorption Spectra of Small Silver Clusters (5-11) Embedded in Argon Matrices. Harbich, W.; Fedrigo, S.; Buttet, J. *Chem. Phys. Lett.* **1992**, *195*, 613
- Soft Landing and Fragmentation of Small Clusters Deposited in Noble-Gas Films. Harbich, W.; Fedrigo, S.; Buttet, J. *Phys. Rev. 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.

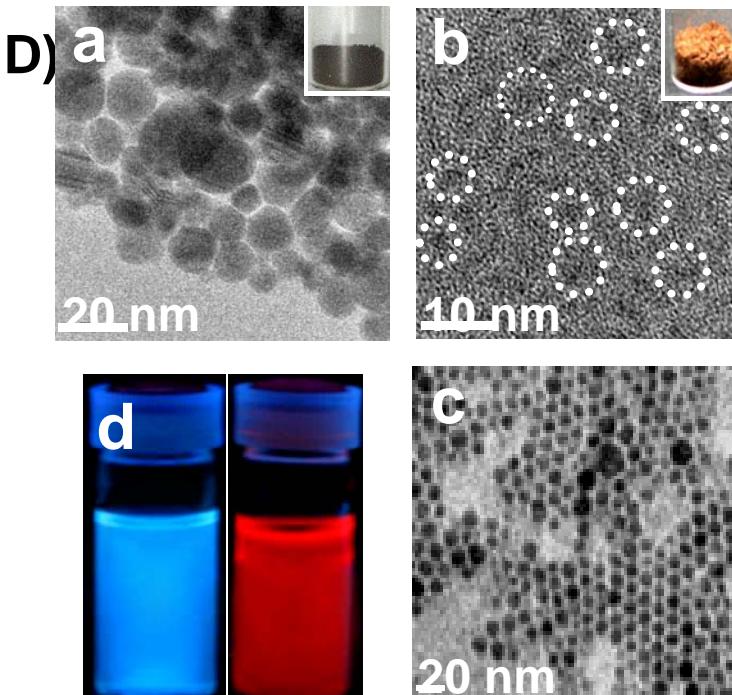
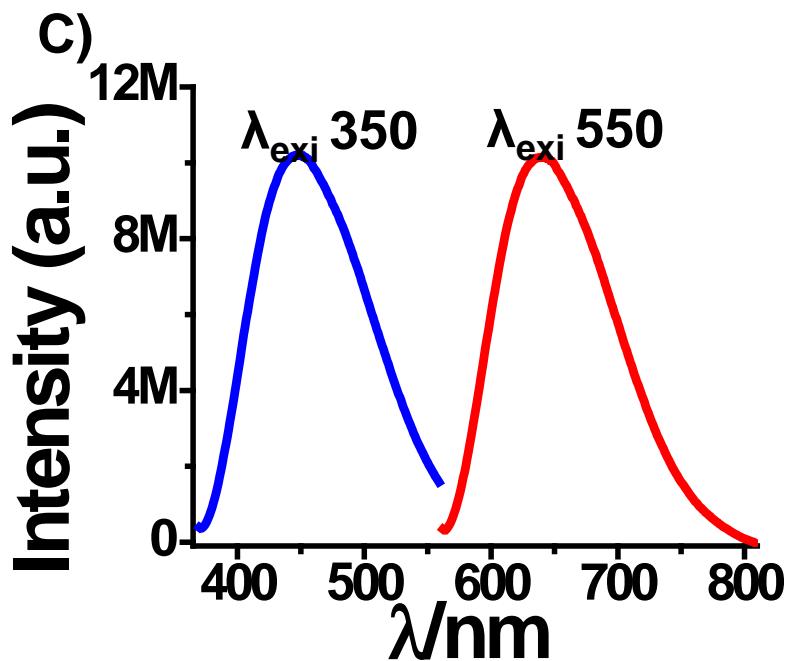
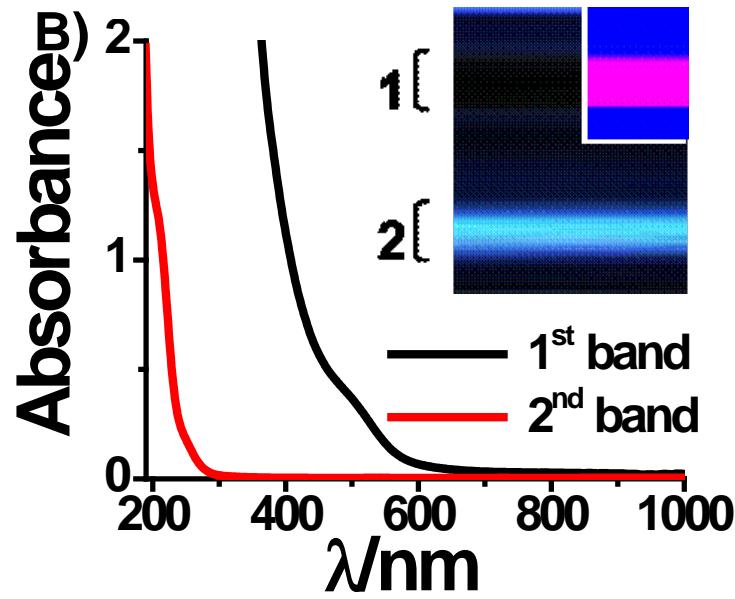
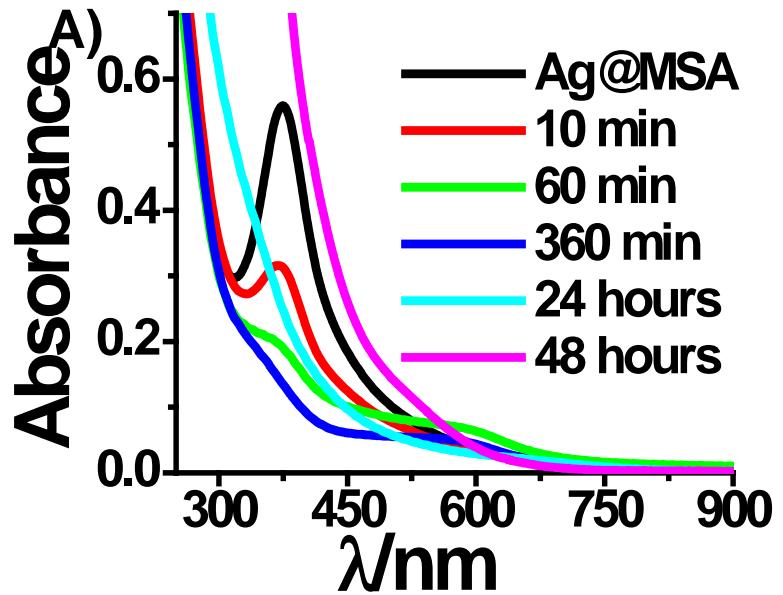
Silver clusters

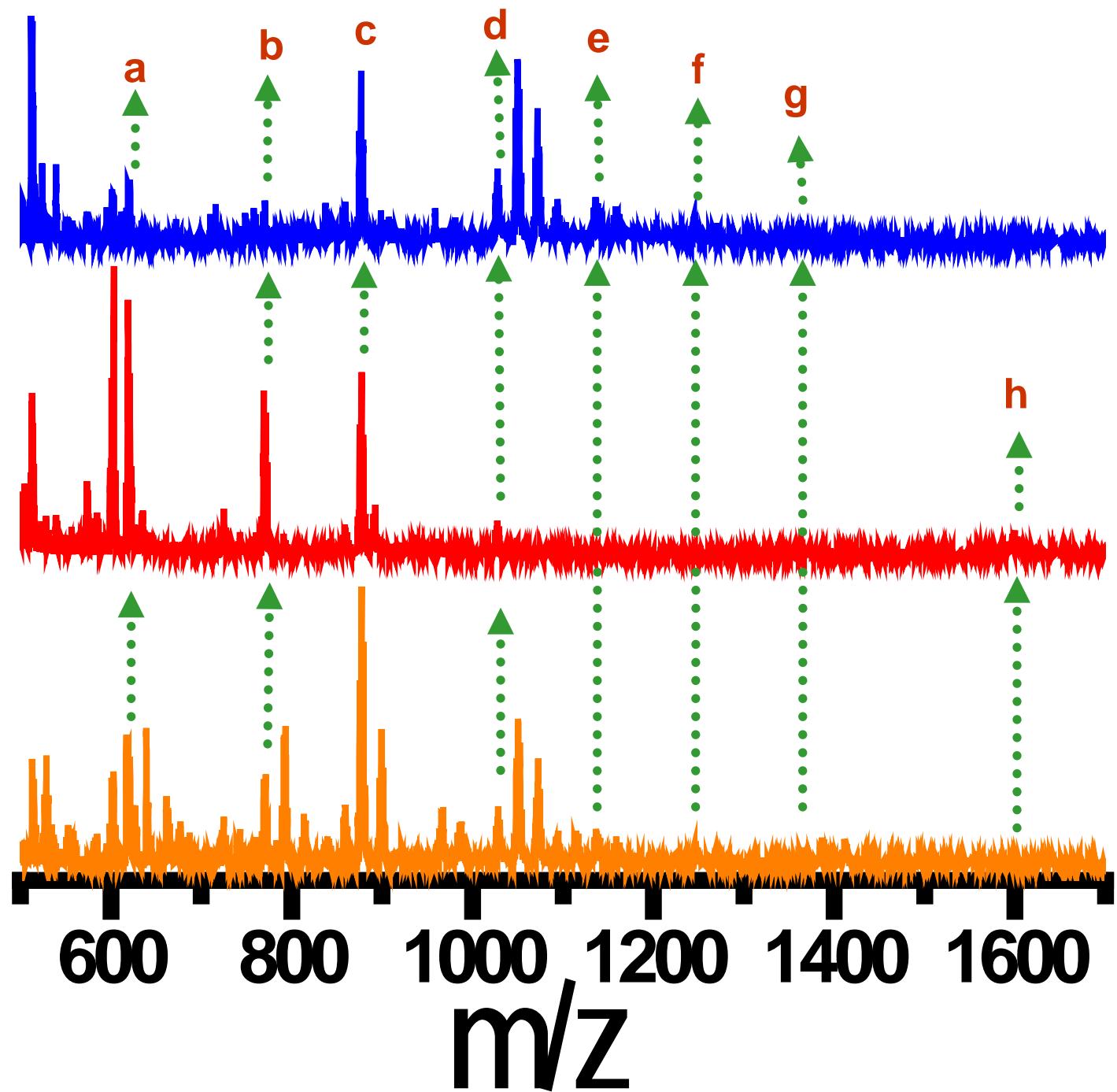
Interfacial etching

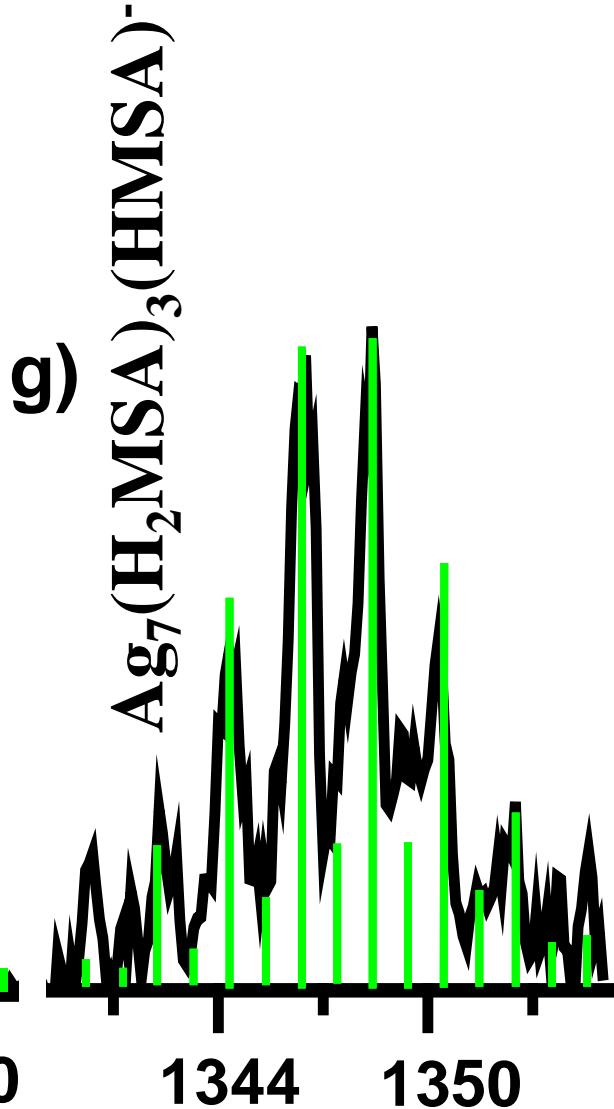
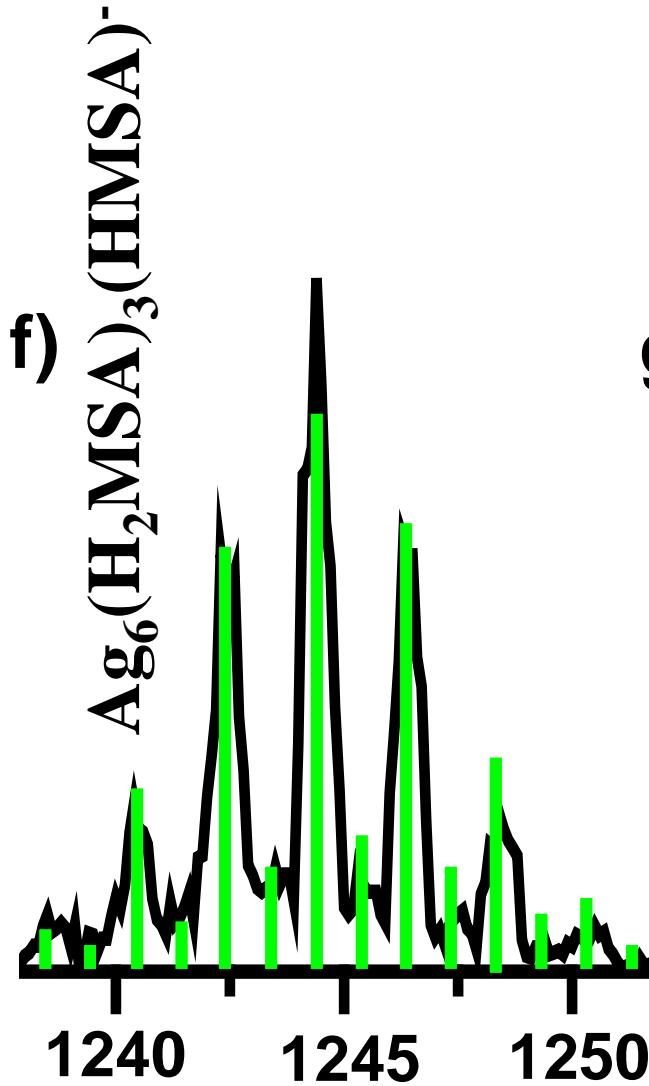
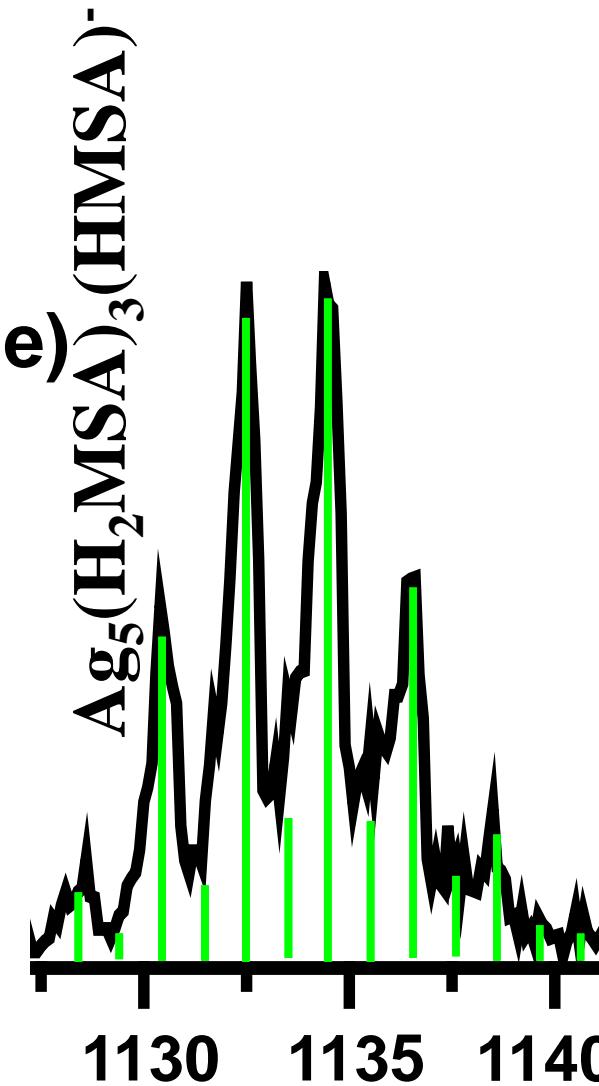


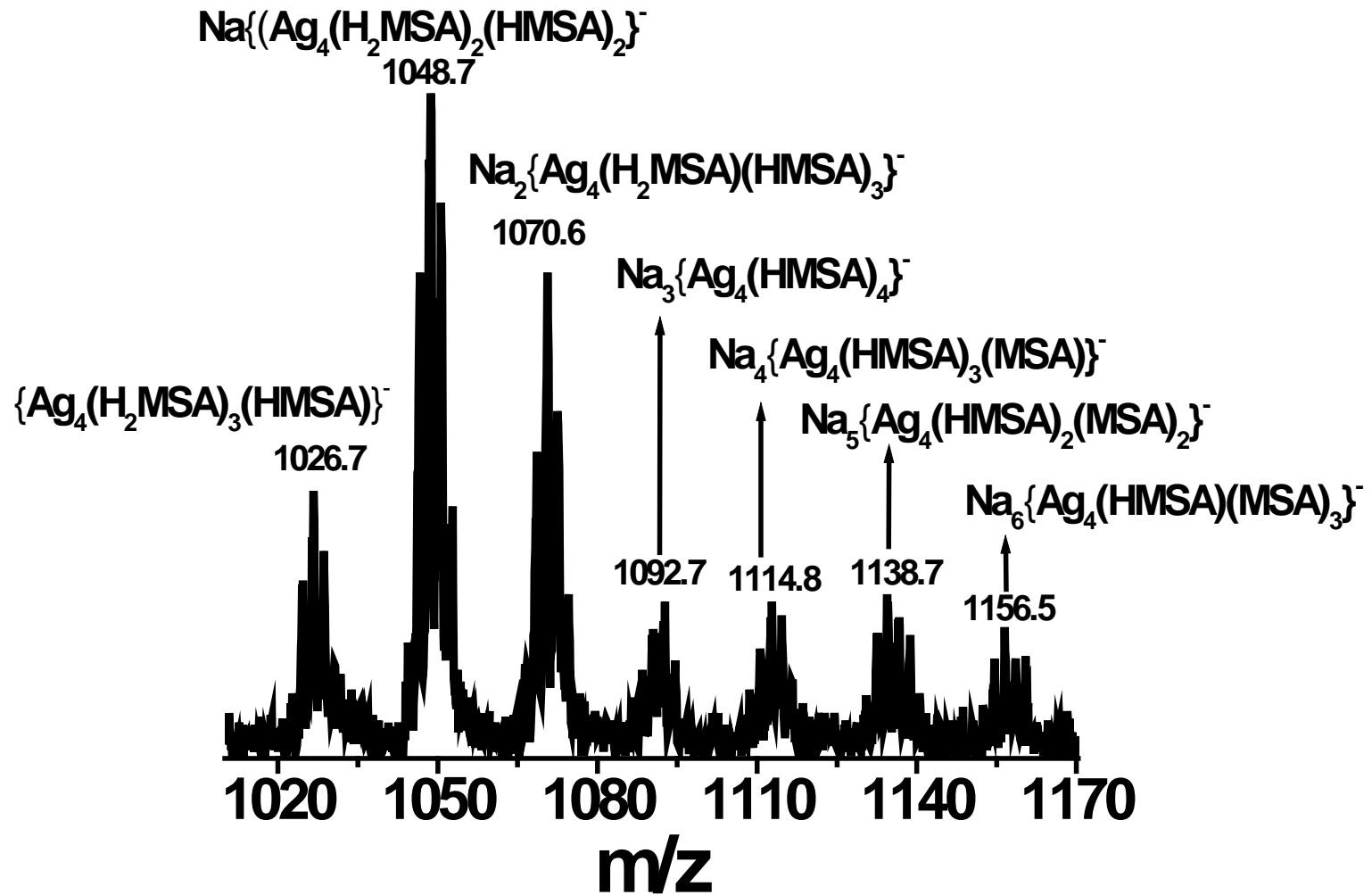


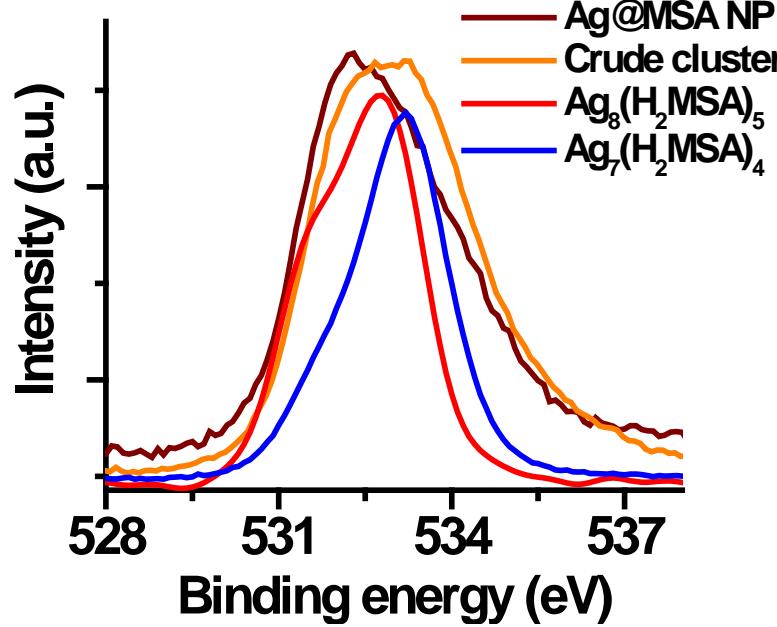
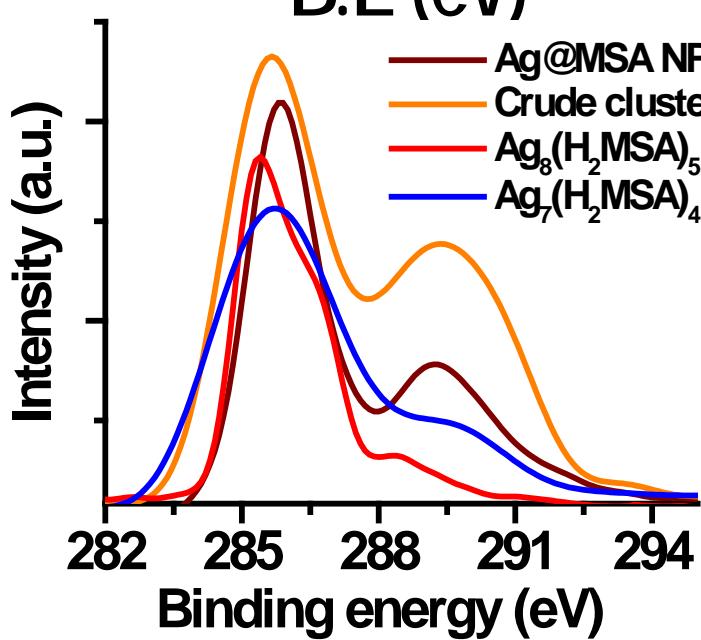
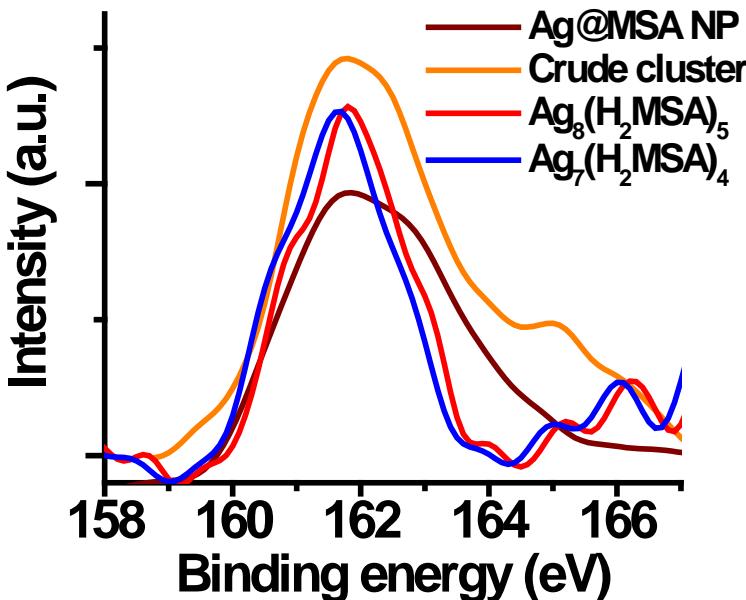
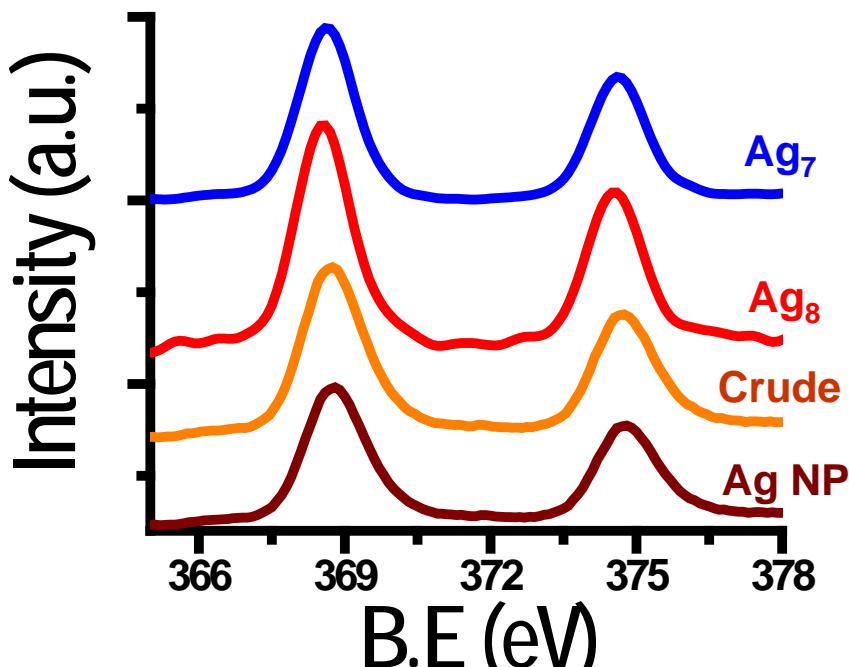


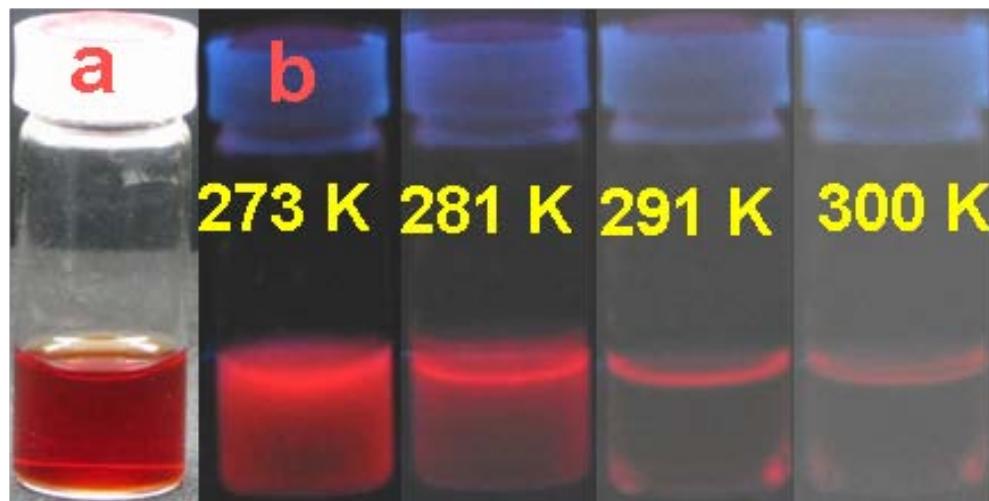




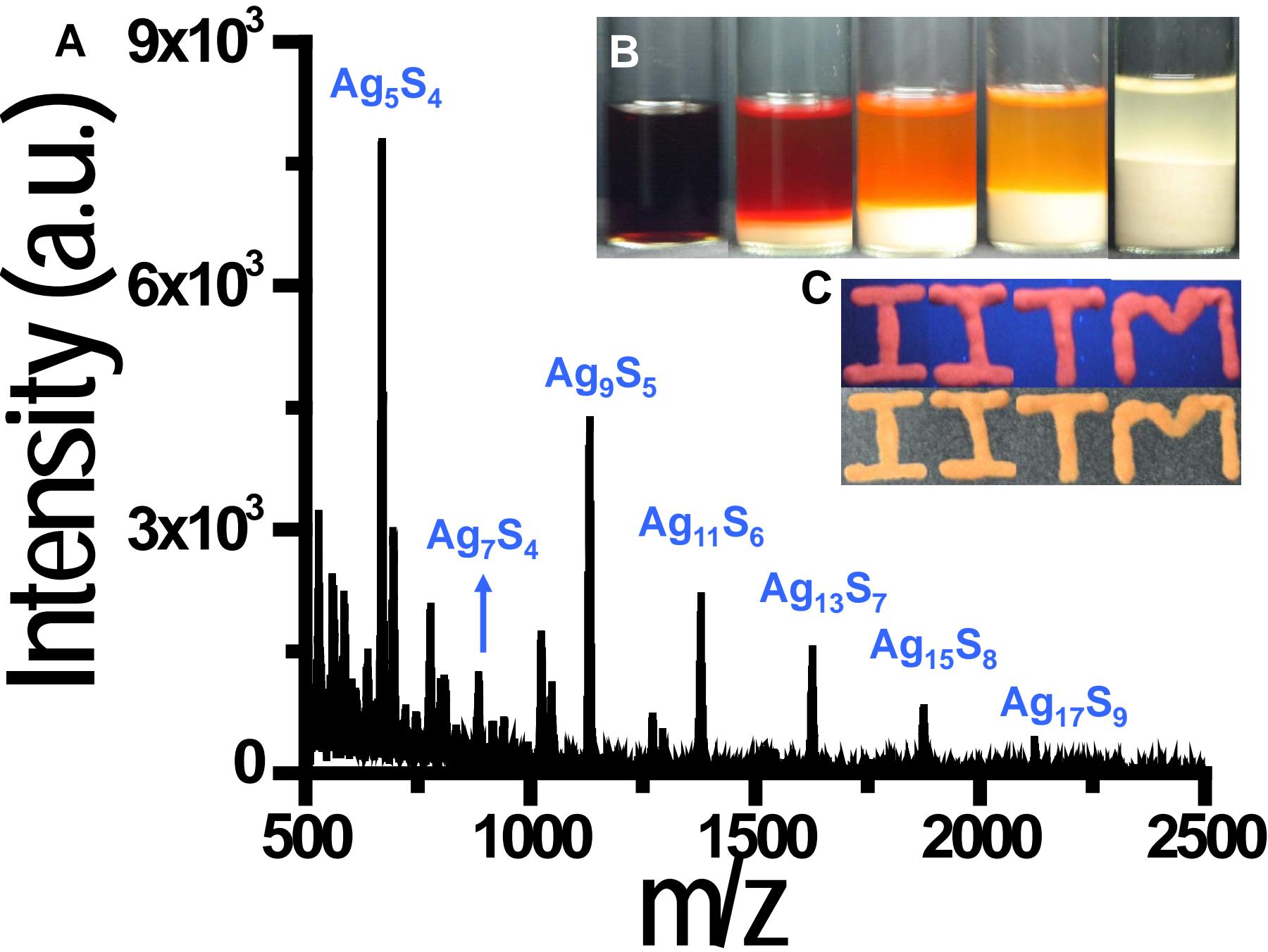


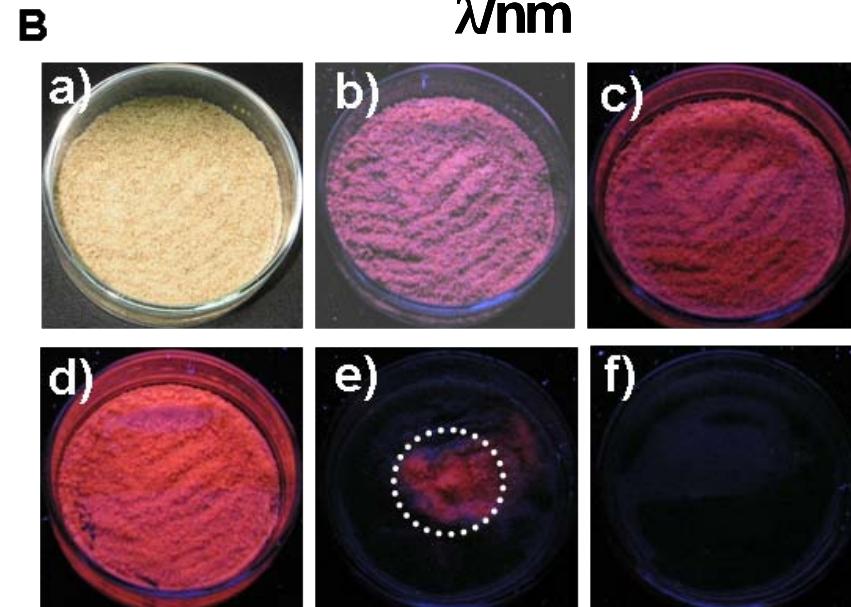
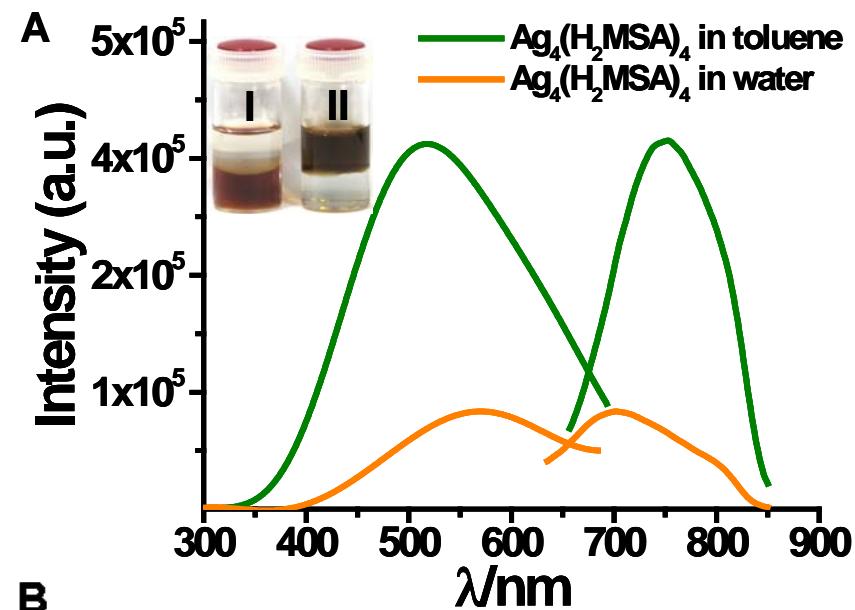






White light UV light T →
RT

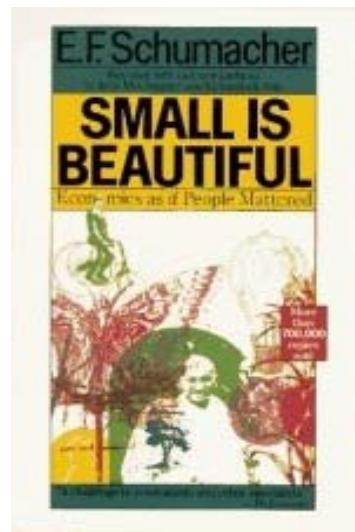




Clusters in proteins



Lourdu Xavier, Kamalesh Choudhari





Nano Mission, Department of Science and Technology



IIT Madras
Thanks!