



Light emitting gold

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Au_{25} , Au_{23} , Au_{22} , Au_8 and Ag_4

NIT, Warangal, June 24, 2009



Light emitting silver

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Light emitting metals

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Insulating gold

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Reactive gold

NIT, Warangal, June 24, 2009



Acknowledgements

M.A. Habeeb Muhammad

Mr. E.S. Shibu

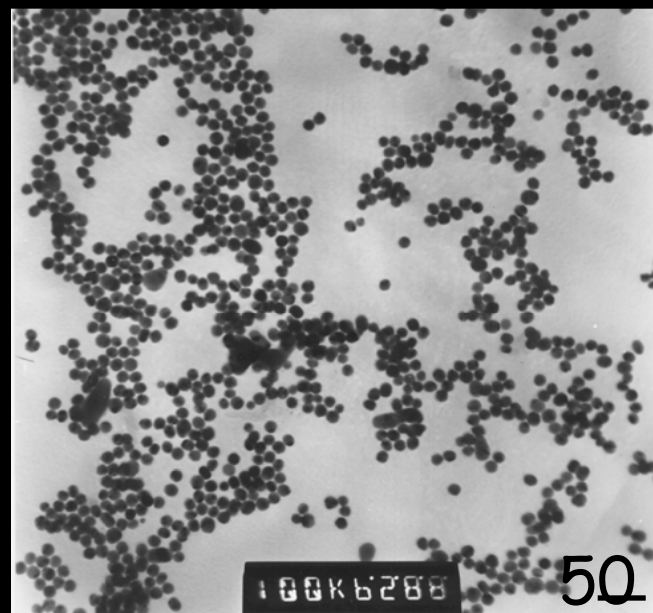
Mr. Udayabhaskar Rao Tummu

Ms. Mrudula

T. Tsukuda, IMS, Okazaki

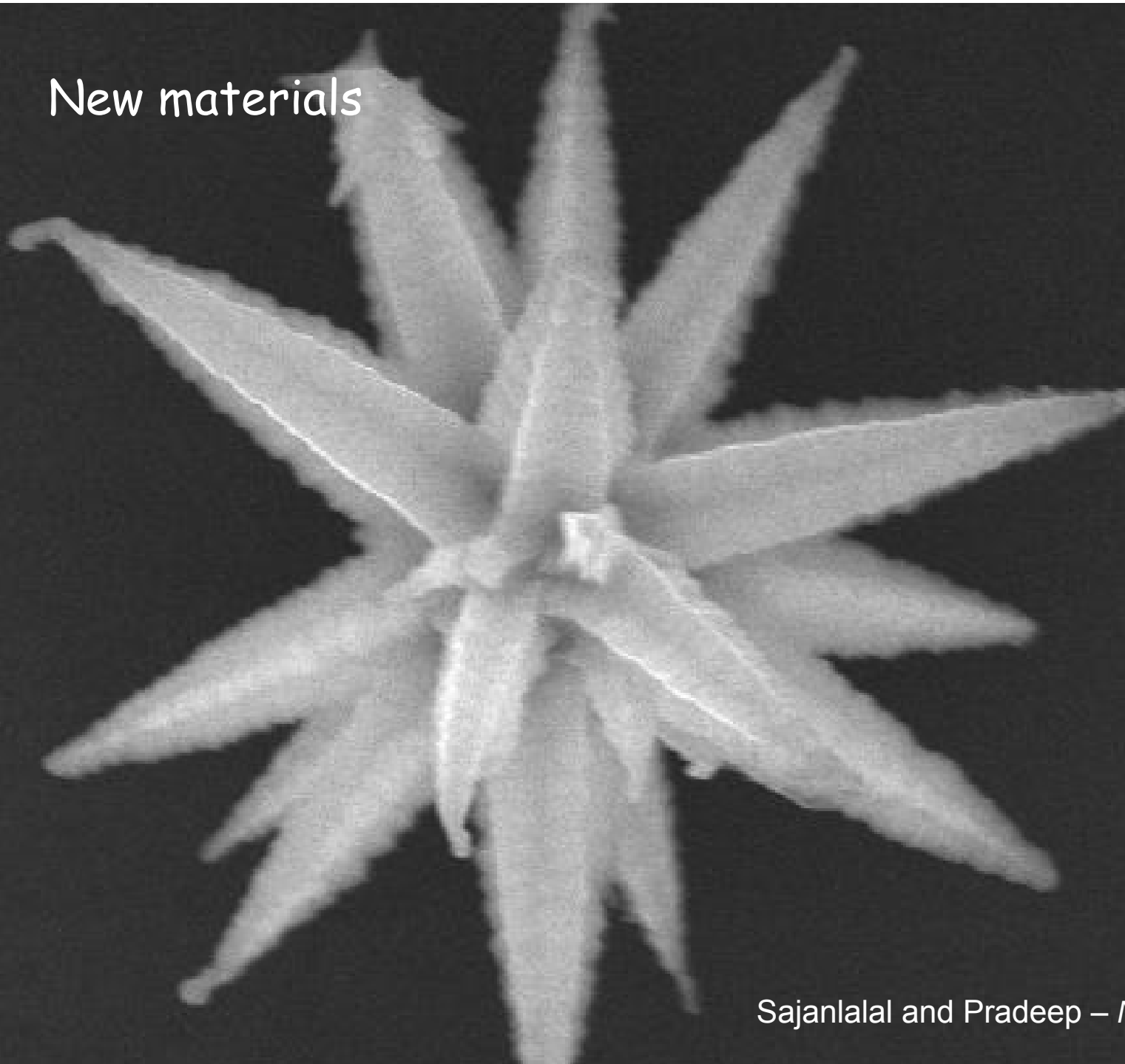
S. K. Pal, SNBS, Kolkata

G. U. Kulkarni, JNCASR, Bangalore

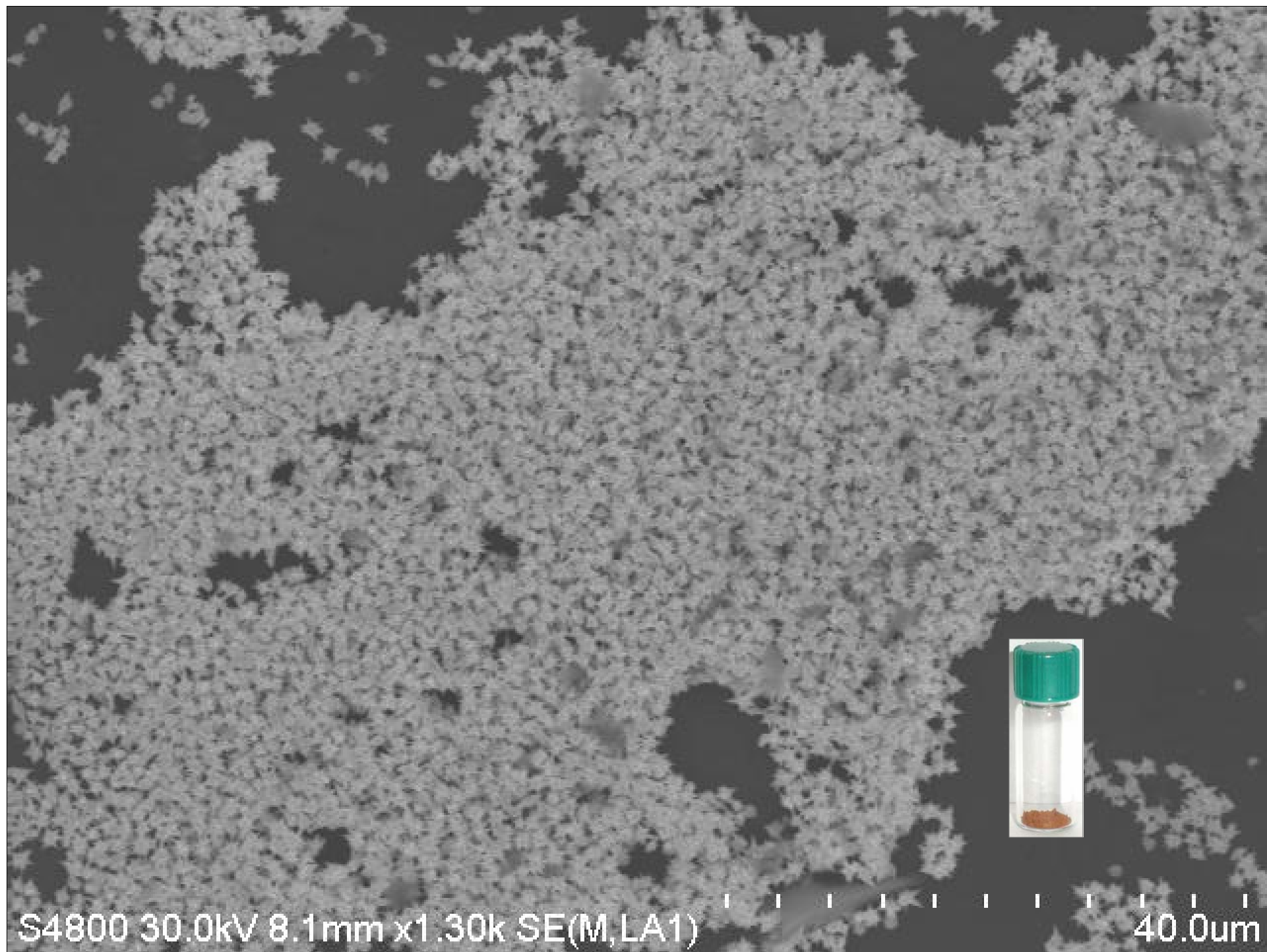


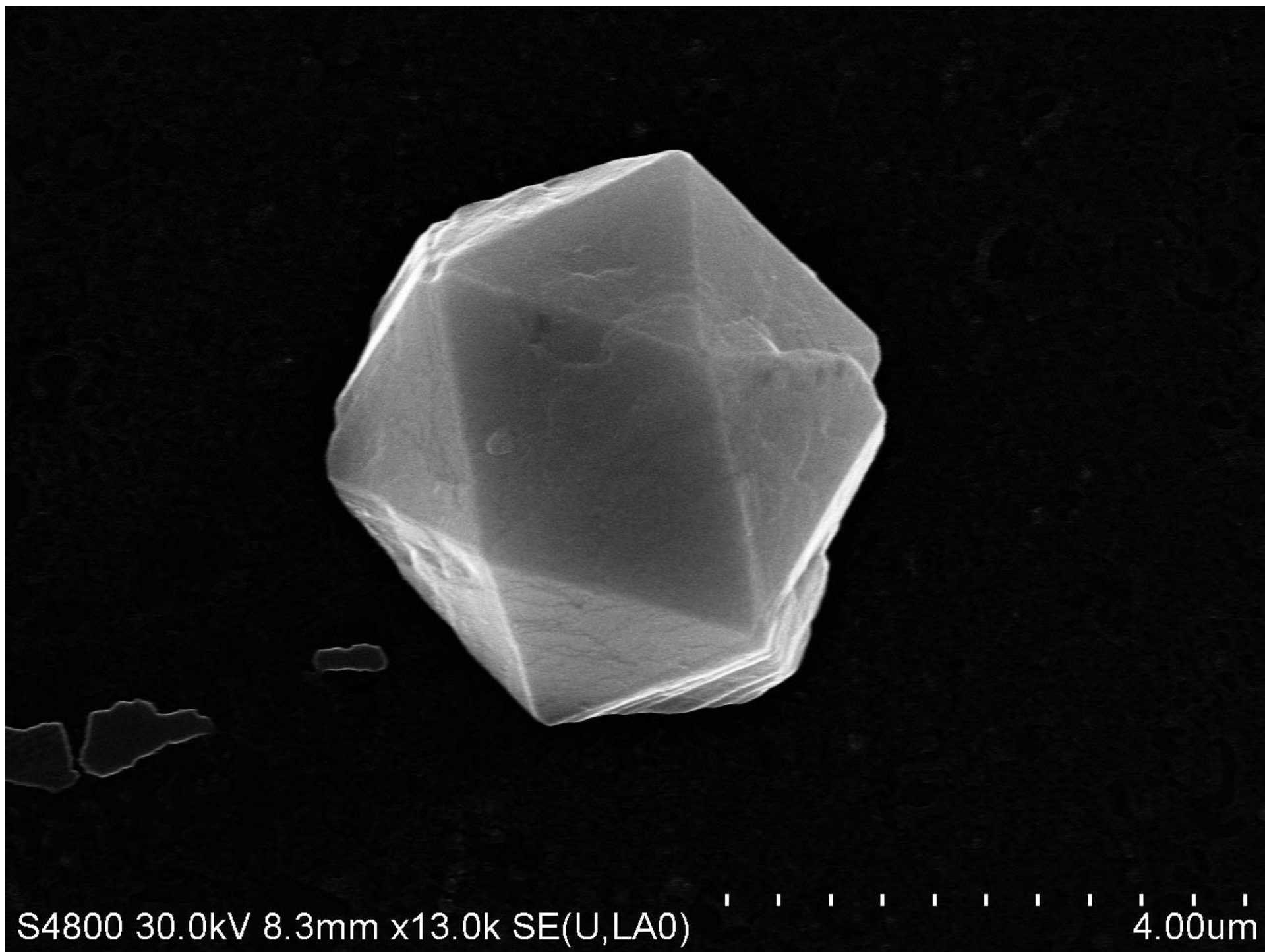
Faraday's gold preserved in Royal Institution. From the site,
<http://www.rigb.org/rimain/heritage/faradaypage.jsp>

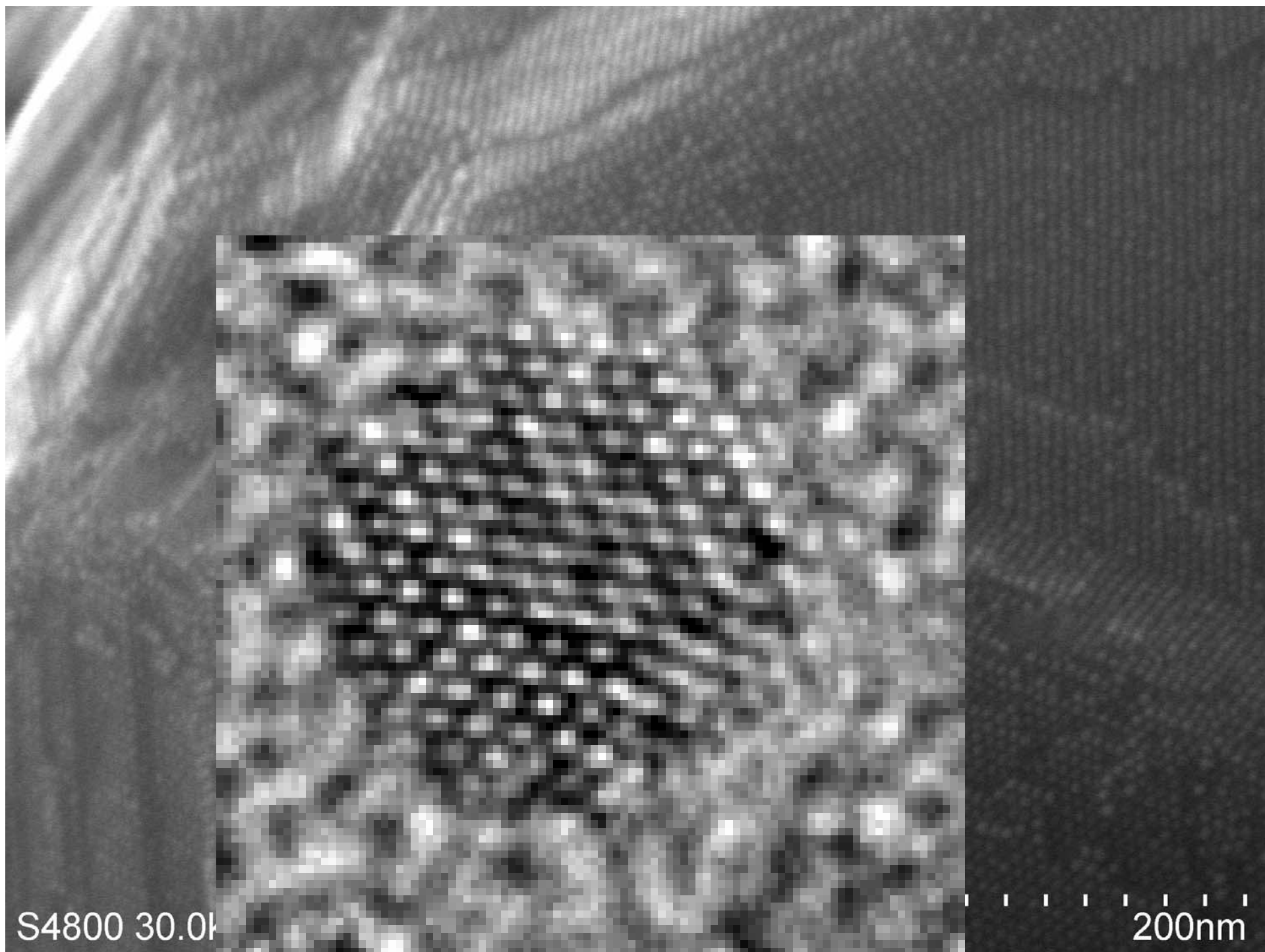
New materials

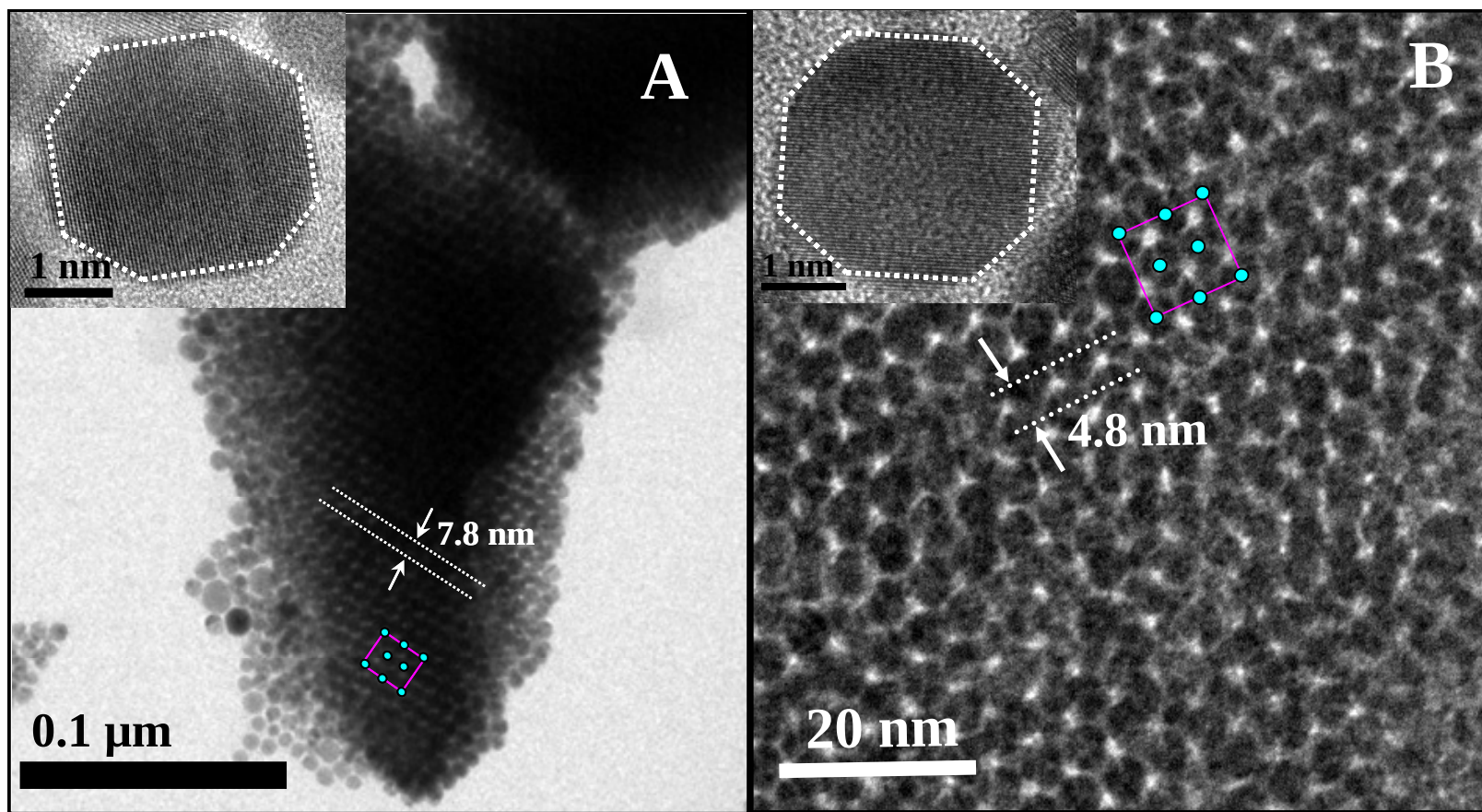


Sajanlalal and Pradeep – *Nano Res.* 2009

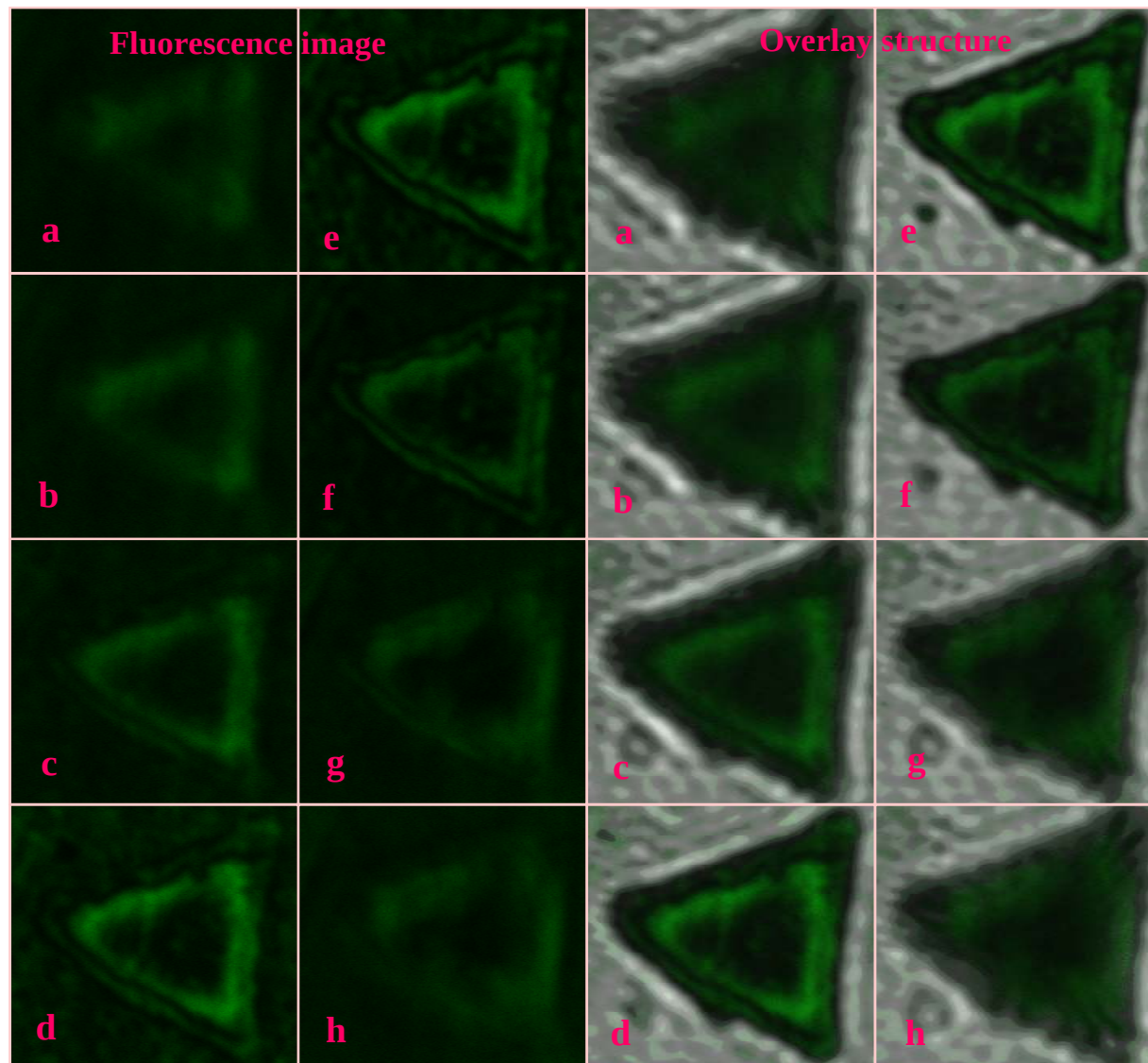




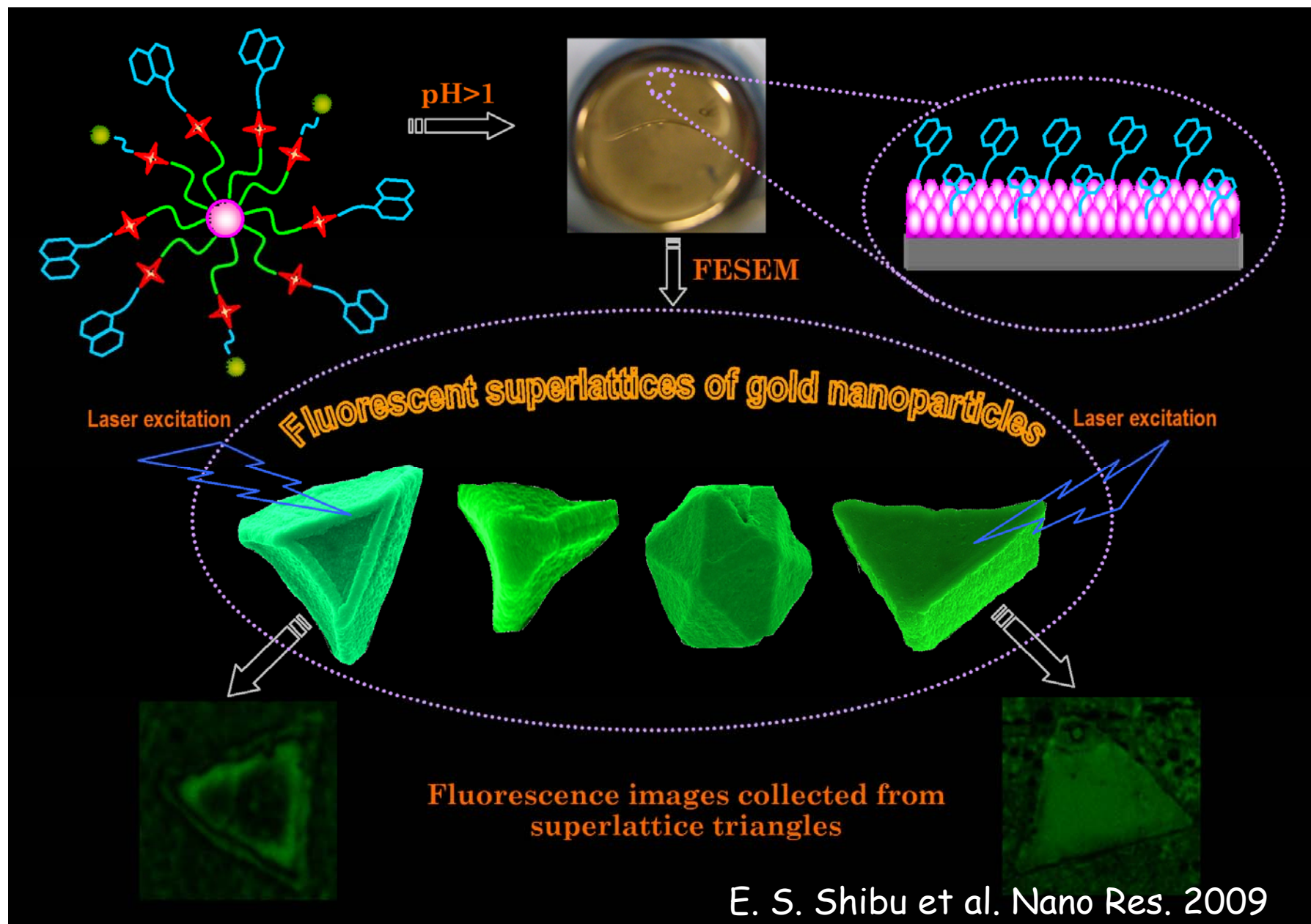




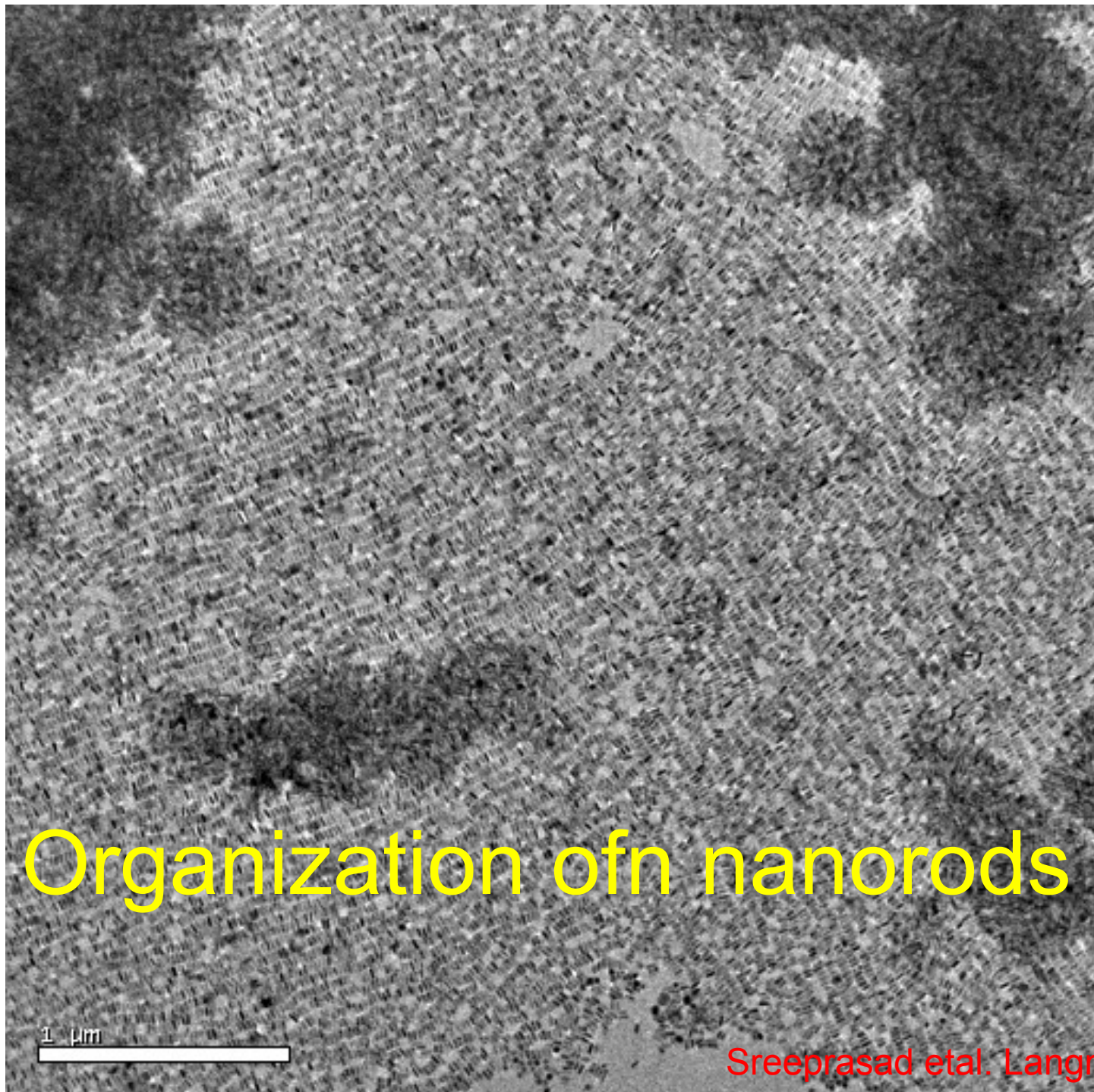
E. S. Shibu, et.al. *Adv. Mater.* 2008; *Nano Res.* 2009; *Chem. Mater.* 2009



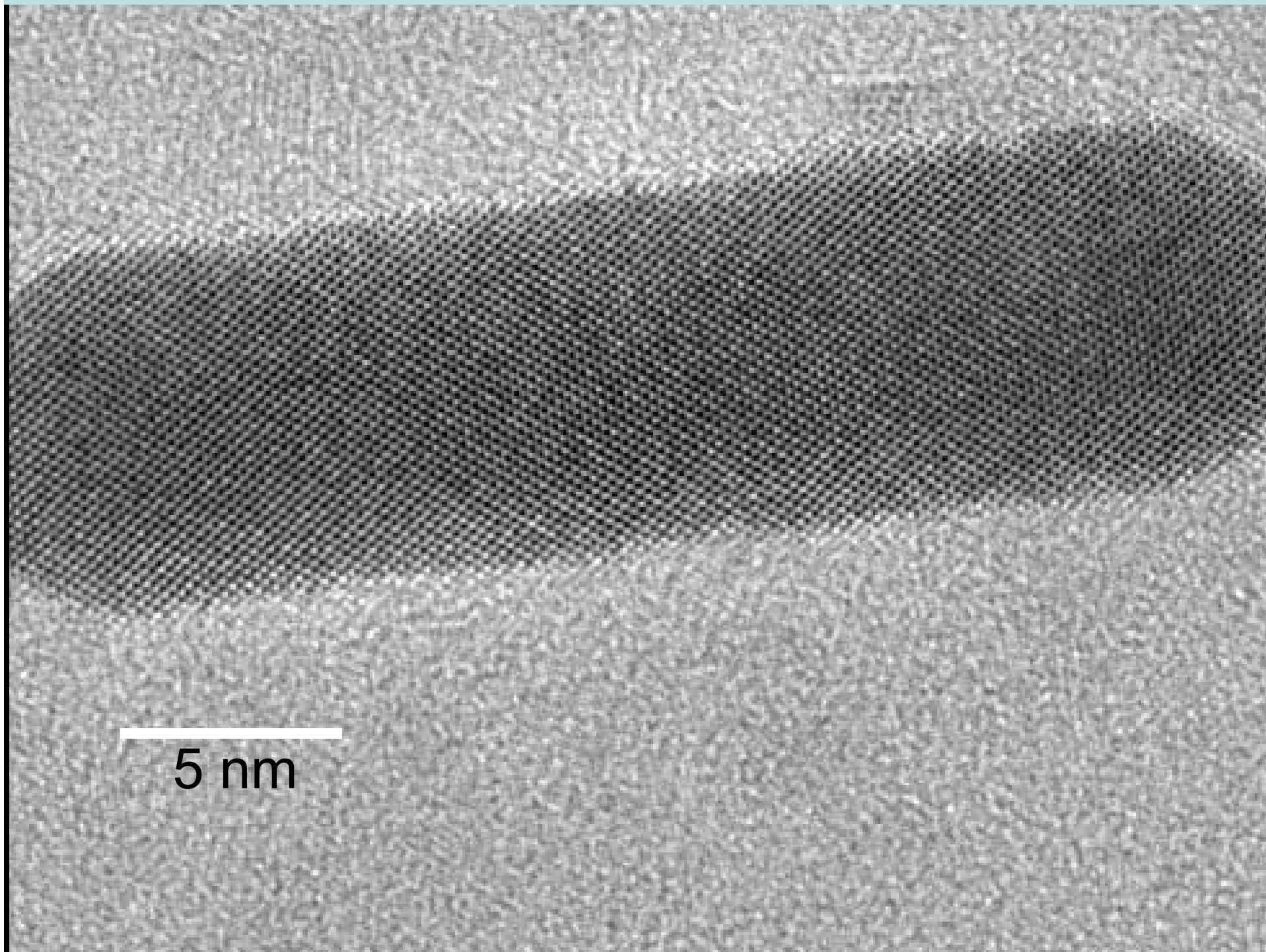
Fluorescent superlattices



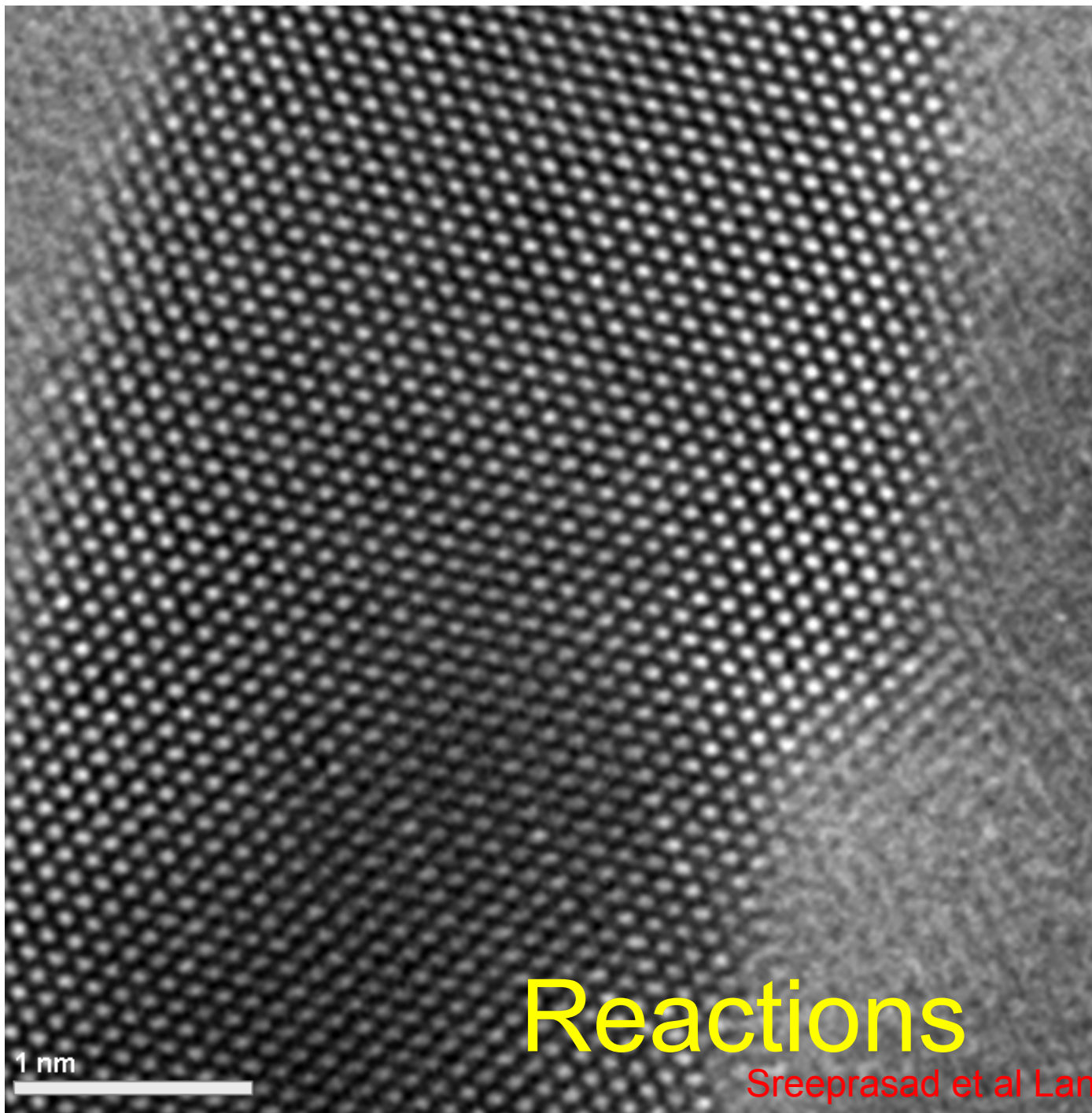
E. S. Shibu et al. Nano Res. 2009



Sreeprasad et al. Langmuir 2008



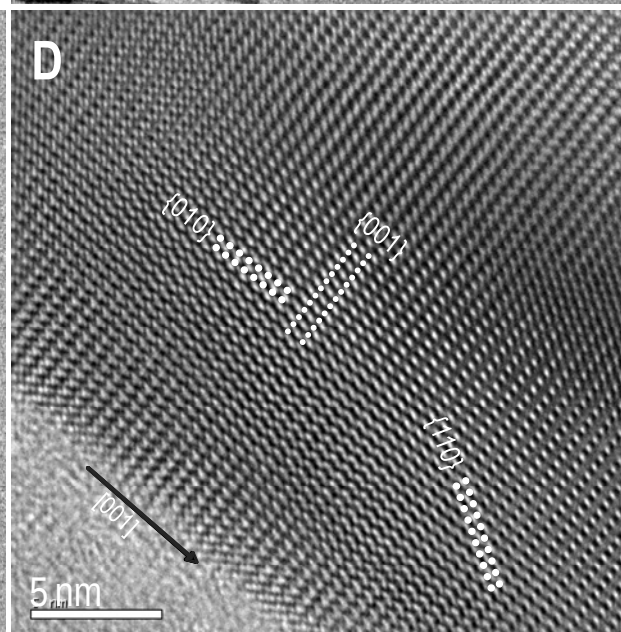
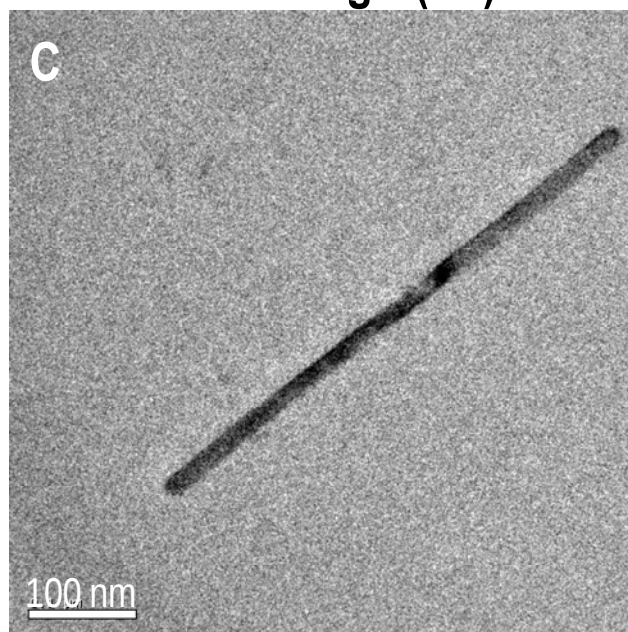
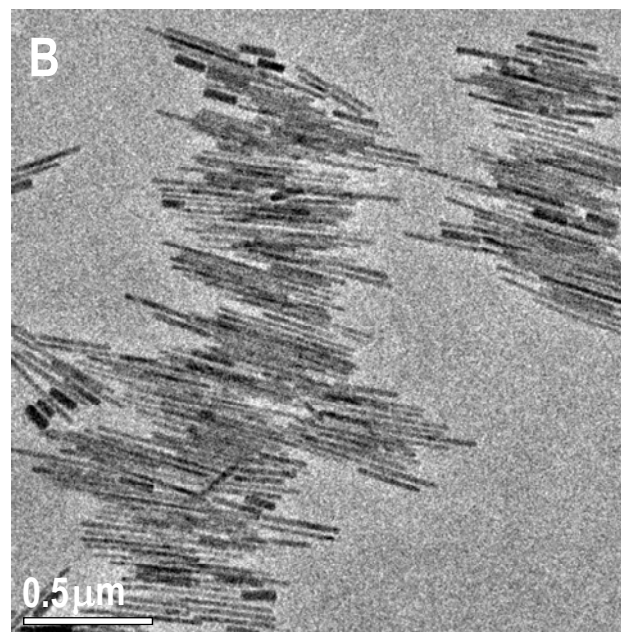
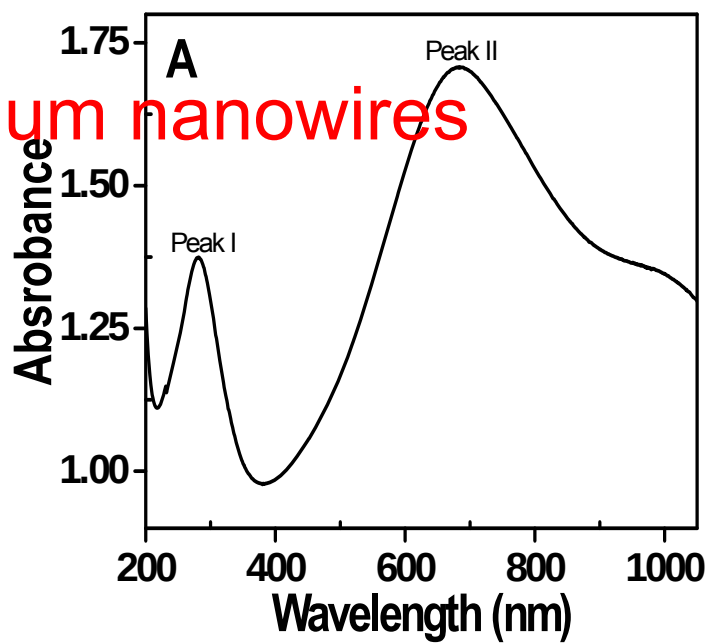
5 nm

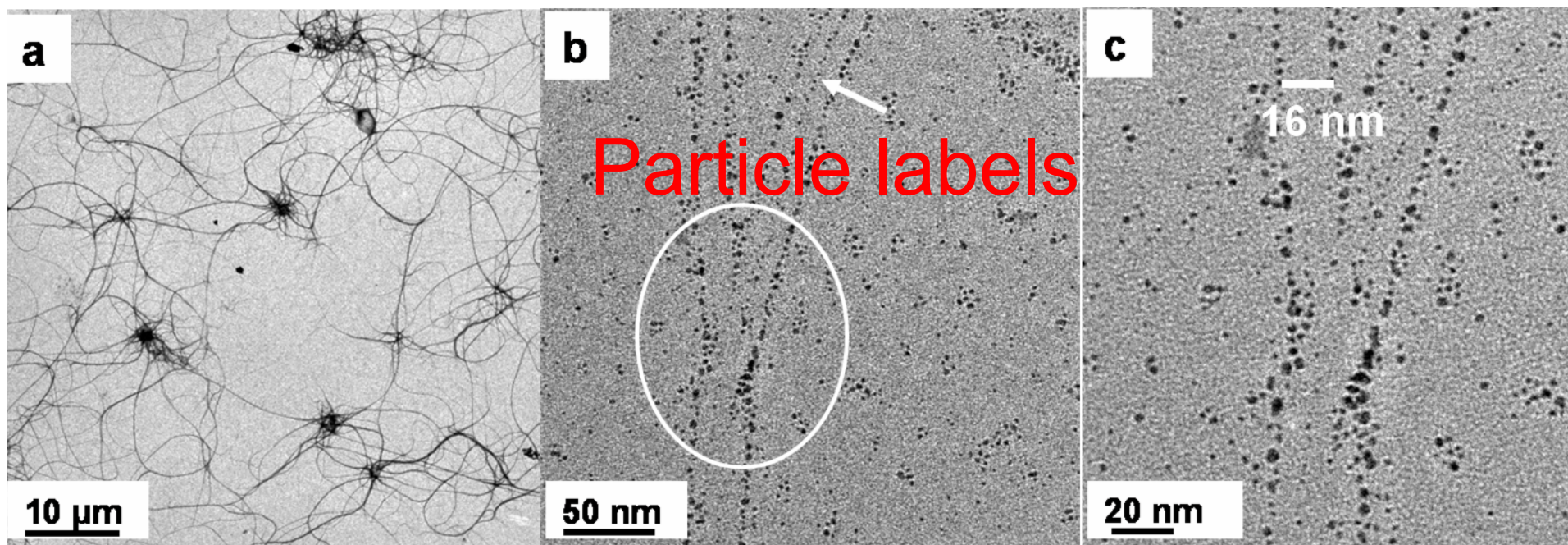
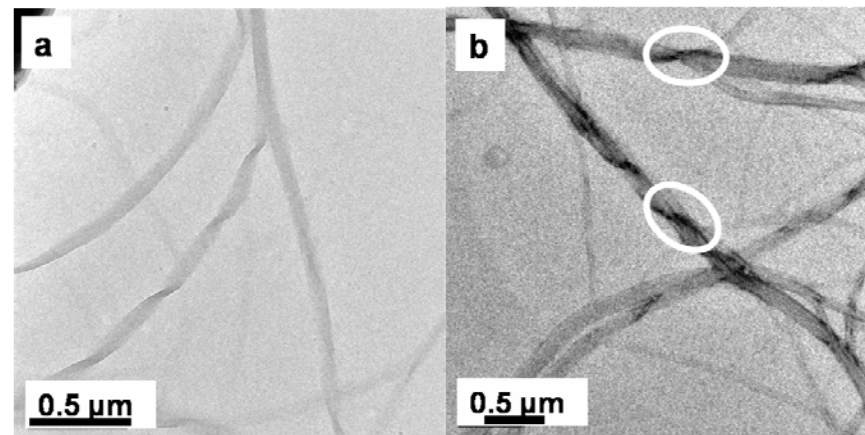
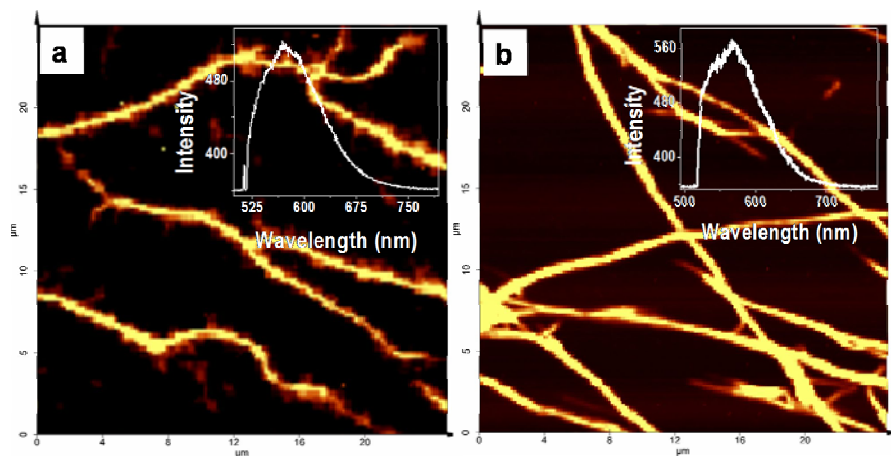


Reactions

Sreeprasad et al Langmuir 2007

Tellurium nanowires



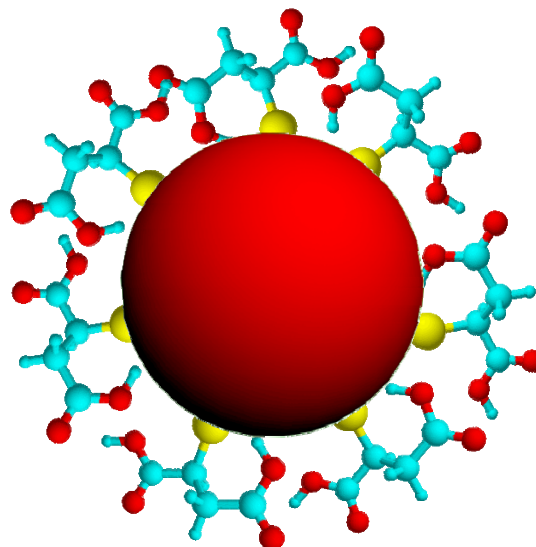


With A. Ajayaghosh

Rajeev Kumar et al. *Chemistry Asian J.* 2009

Monolayer Protected Metal Nanoparticles

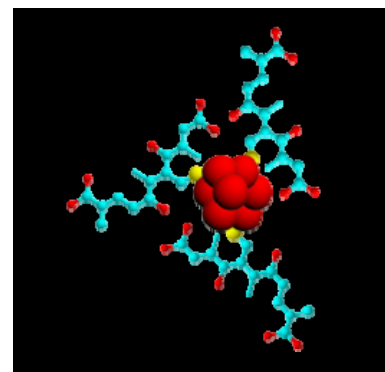
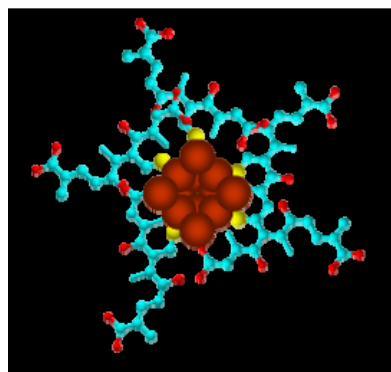
Monolayer Protected Clusters (MPCs)



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.

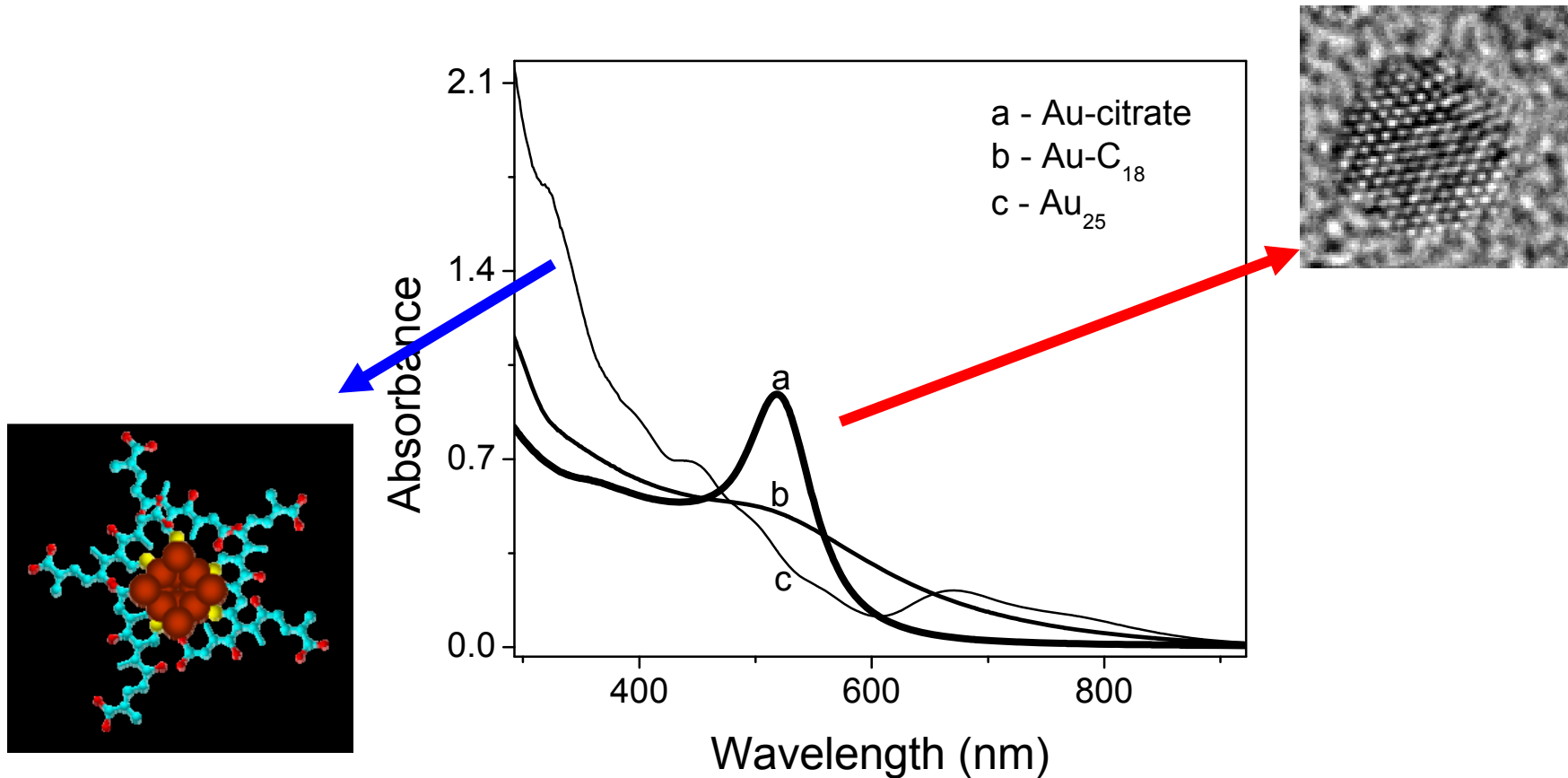
Monolayer-Protected Cluster Molecules, Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, 33, 27.

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.; Khoury, 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.; Shafigullin, M. N.; Khoury, 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.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M. N.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **1997**, *101*, 3706.

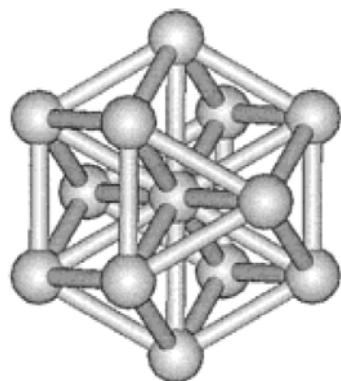
- **Isolation and Selected Properties of a 10.4 kDa Gold:Glutathione Cluster Compound**, Schaaff, T. G.; Knight, G.; Shafigullin, M. N.; Borkman, R. F.; Whetten, R. L. *J. Phys. Chem. B* **1998**, *102*, 10643.
- **Controlled Etching of Au:SR Cluster Compounds**, Schaaff, T. G.; Whetten, R. L. *J. Phys. 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.; Shafigullin, 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.



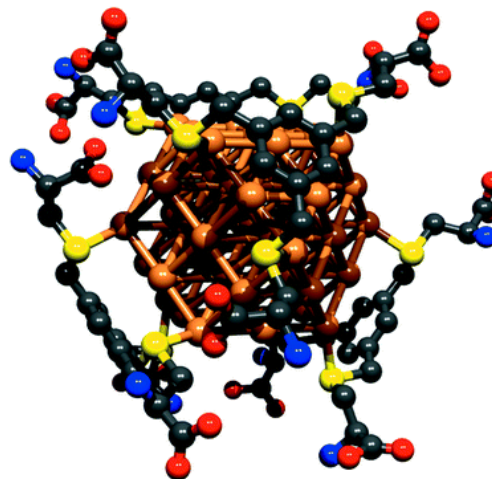
Optical absorption (extinction) spectrum of (a) 15 nm gold particles in aqueous solution (labeled Au@citrate). The spectrum of (b) 3 nm particles in toluene is also shown. See the broadening of the plasmon feature. The spectrum of (c) Au₂₅ in water. In this, there is no plasmon excitation and all the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



Phosphine Capped Gold Clusters



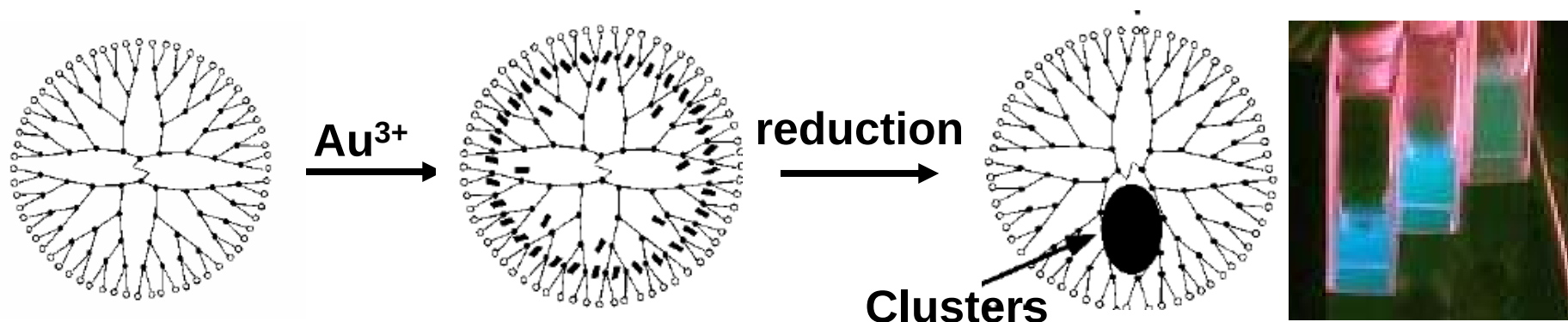
Au₁₃



Au₅₅

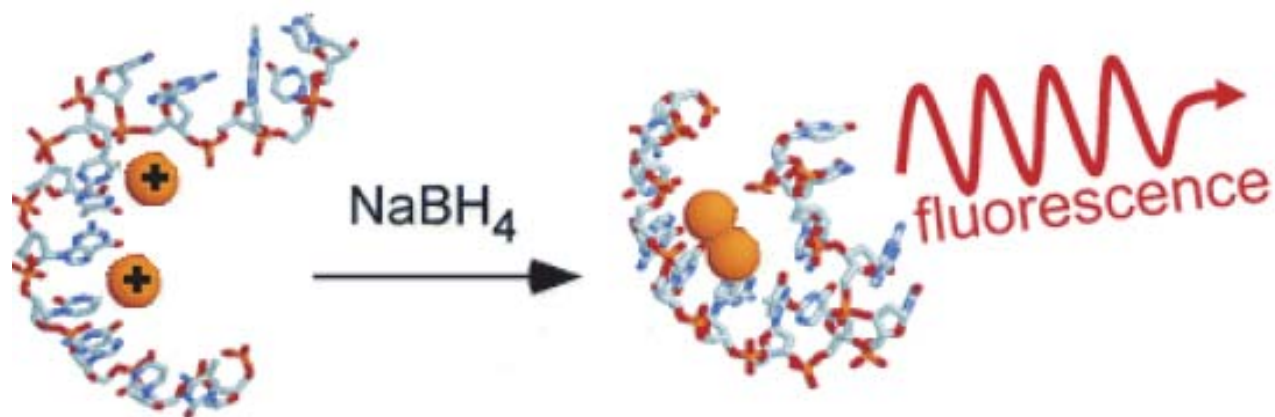
- **Au₅₅ [P(C₆H₅)₃]₁₂Cl₆** - a gold cluster of unusual size, Schmid, G.; Pfeil, R.; Boese, R.; Brandermann, F.; Meyer, S.; Calis, G. H. M.; Van der Velden.; Jan W. A. *Chemische Berichte* **1981**, 114, 3634.
- **Synthesis and x-ray structural characterization of the centered icosahedral gold cluster compound [Au₁₃ (PMe₂Ph)₁₀Cl₂](PF₆)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.

Dendrimer Encapsulated Clusters

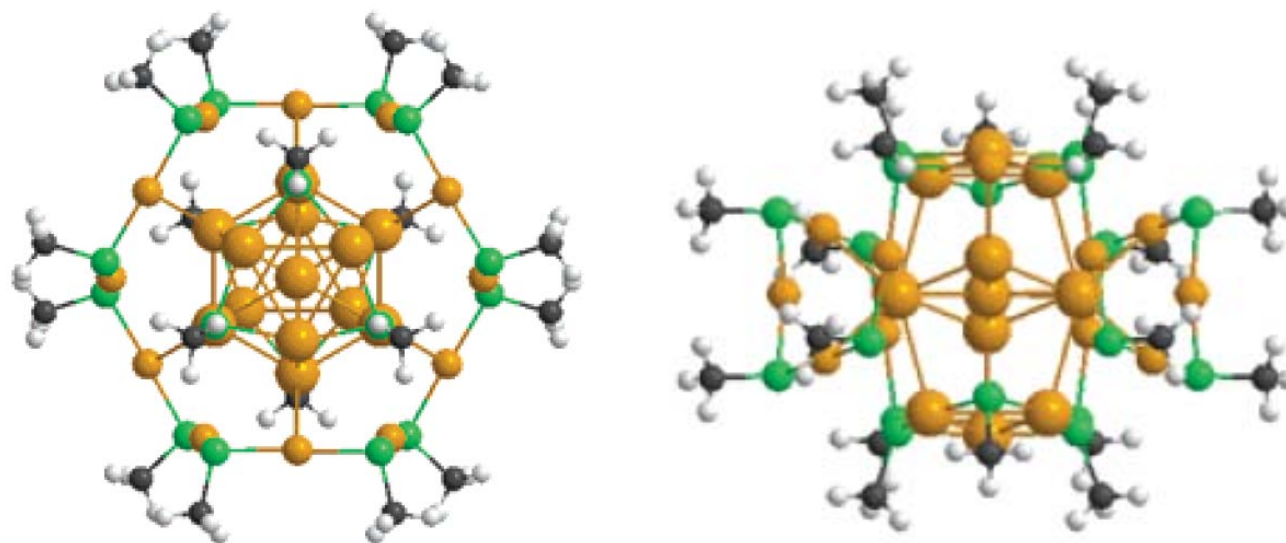


- **High quantum yield blue emission from water-soluble Au_8 nanodots**, Zheng, J.; Petty, J. T.; Dickson, R. M. *J. Am. Chem. Soc.* **2003**, 125, 7780.
- **Highly fluorescent, water-soluble, size-tunable gold quantum dots**, Zheng, J.; Zhang, C. W.; Dickson, R. M. *Phys. Rev. Lett.* **2004**, 93, 077402.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

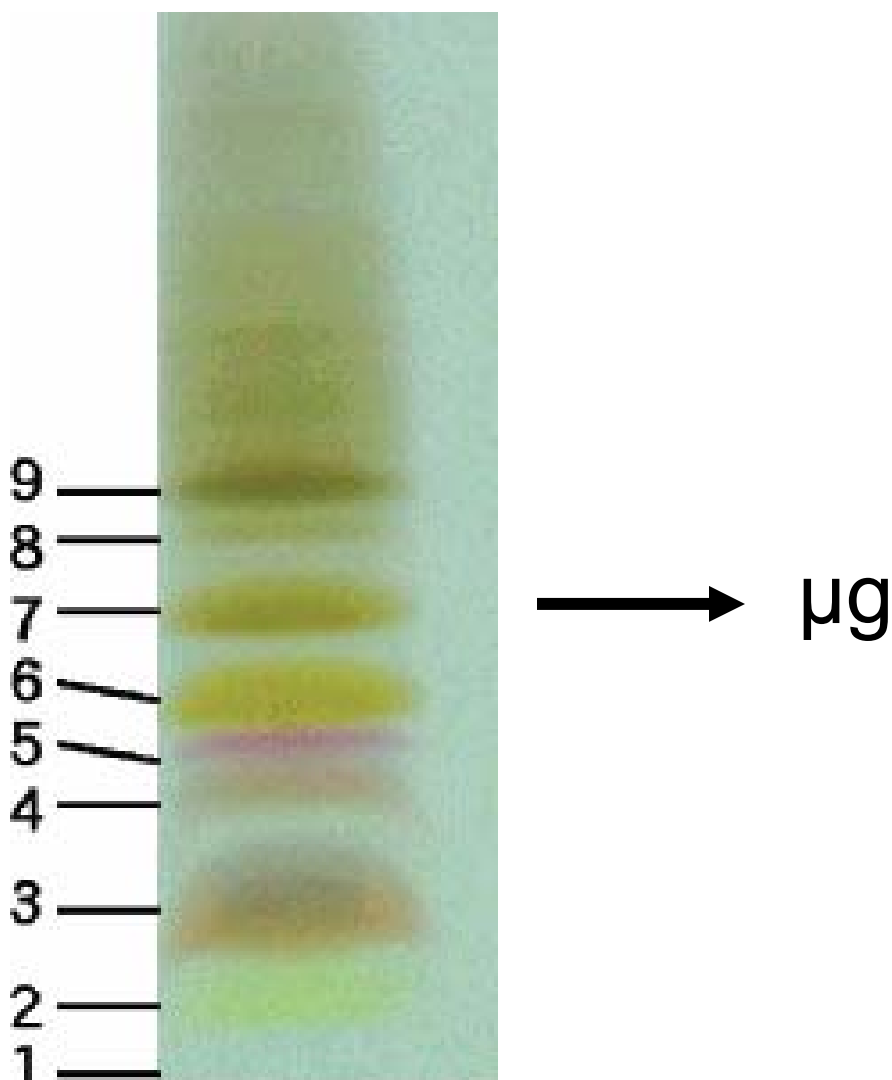


Top and side view of $[\text{Au}_{25}(\text{SCH}_3)_{18}]^+$

Theoretical Investigation of Optimized Structures of Thiolated Gold Cluster $[\text{Au}_{25}(\text{SCH}_3)_{18}]^+$, Iwasa, T.; Nobusada, K. *J. Phys. Chem. C* **2007**, *111*, 45.

How to make them?

Polyacrylamide gel electrophoresis (PAGE)

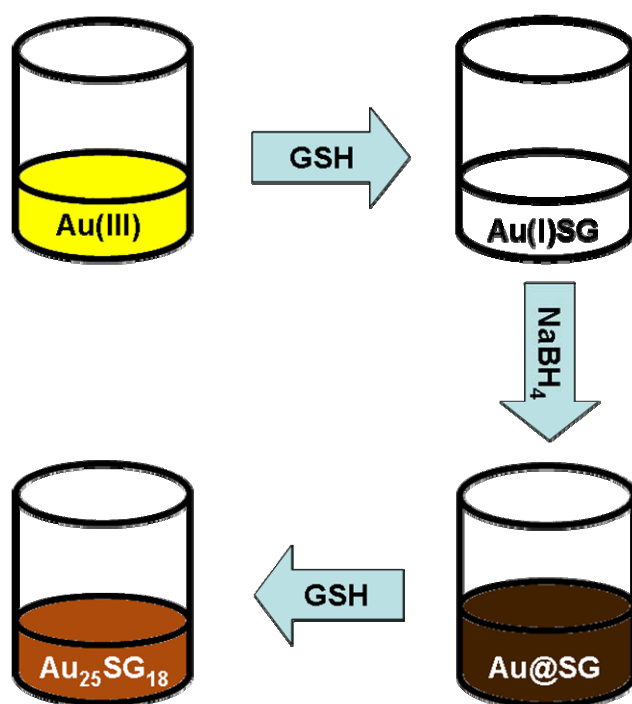


Negishi, Y.; Nobusada, K.; and Tsukuda, T. Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)-Thiolate Complexes and Thiolate-Protected Gold Nanocrystals. *J. Am. Chem. Soc.* **2005**, 127, 5261-70.

Gram scale synthesis

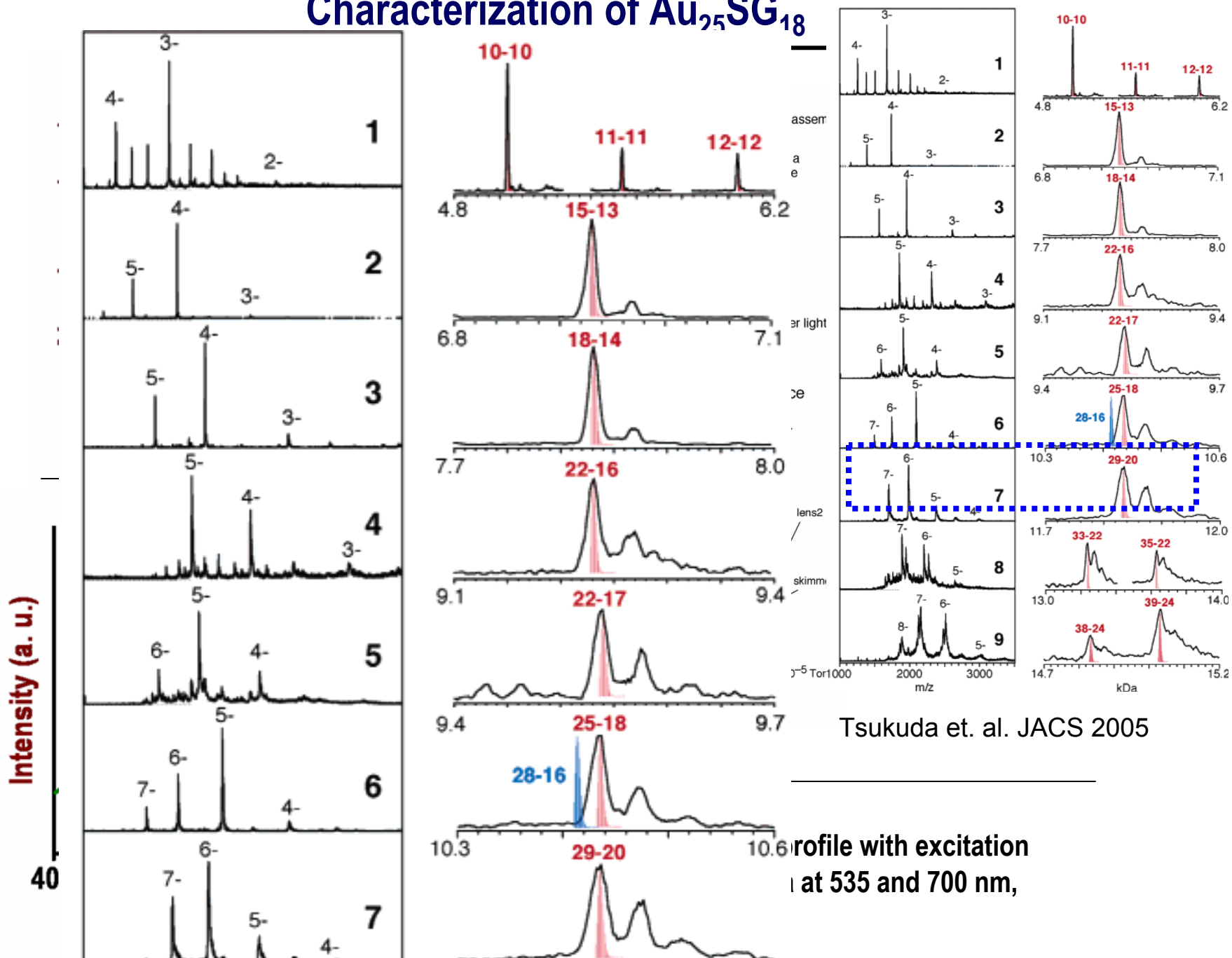
$\text{Au}_{25}\text{SG}_{18}$

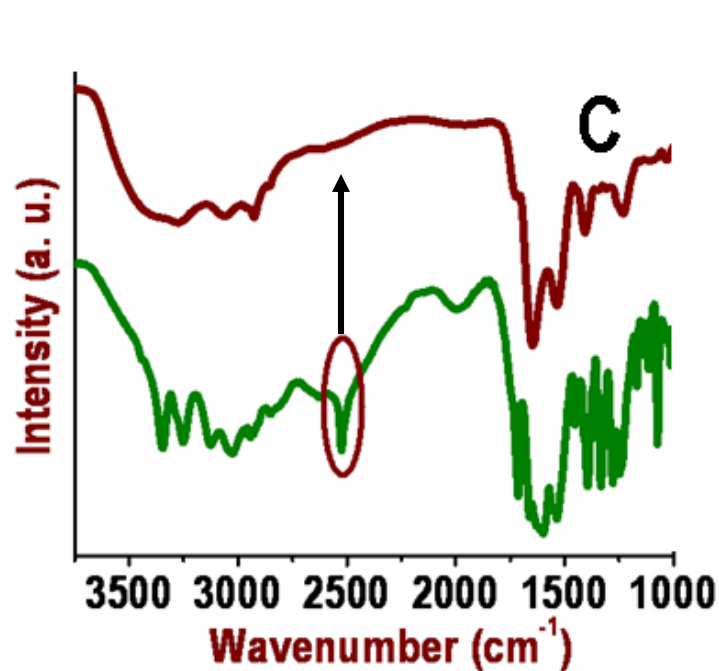
Synthesis: Au_{25} clusters can be preferentially populated by dissociative excitation of larger precursors



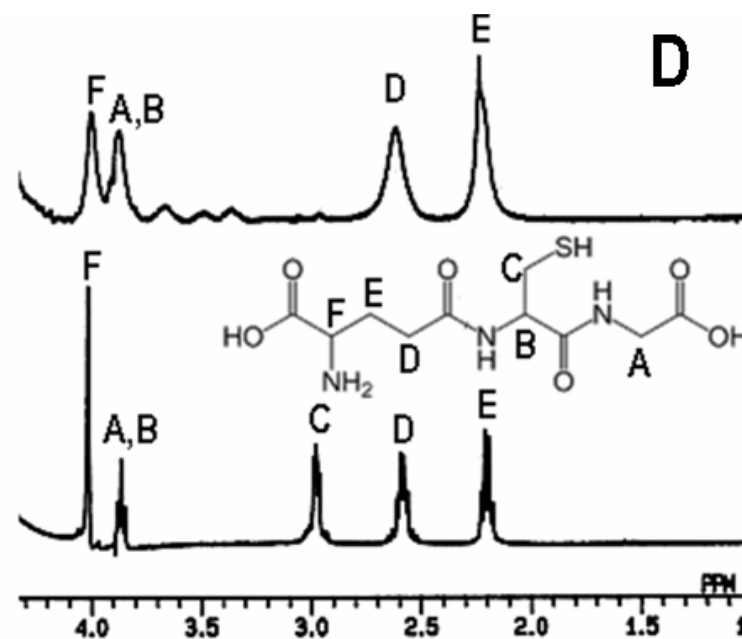
Scheme showing the synthesis of $\text{Au}_{25}\text{SG}_{18}$ clusters

Characterization of Au₂₅SG₁₈

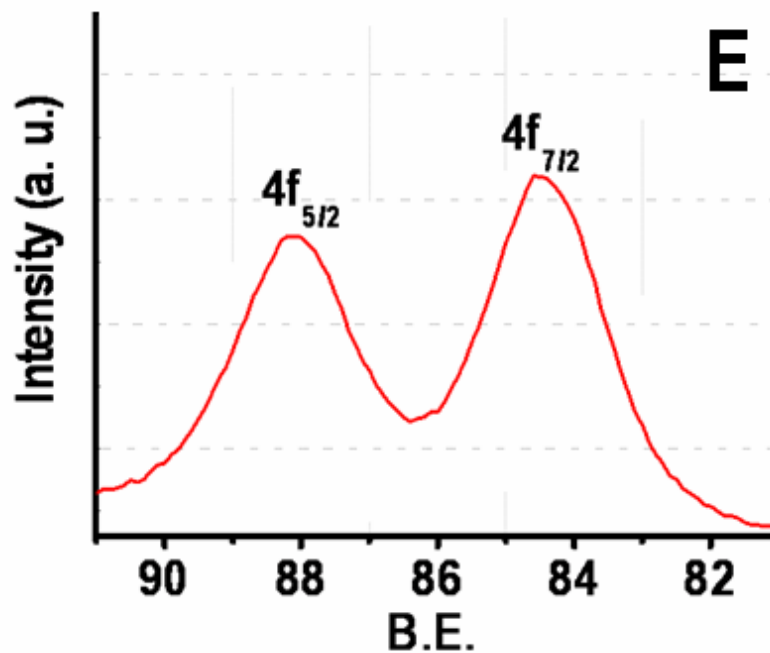




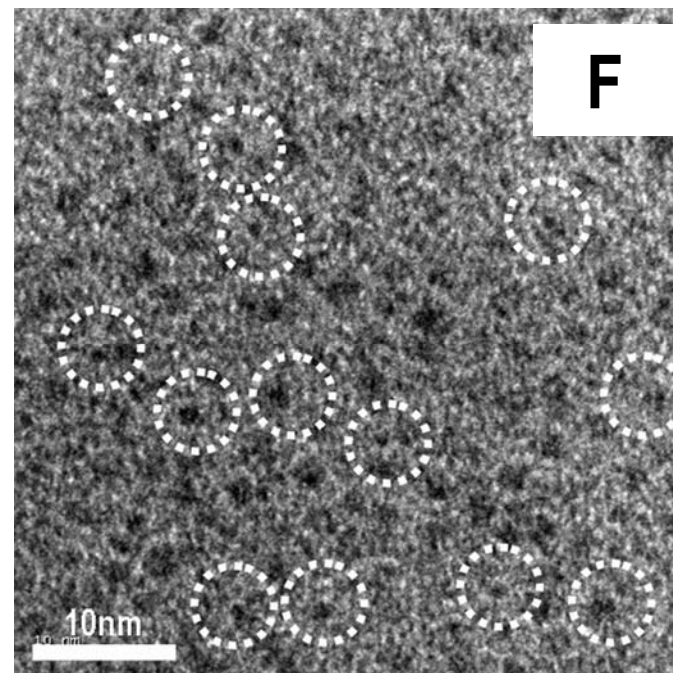
FTIR spectrum: The peak at 2526 cm^{-1} of glutathione due to $-\text{SH}$ stretching frequency is absent in IR spectrum of Au_{25} suggesting the ligand binding on cluster surface.



^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.

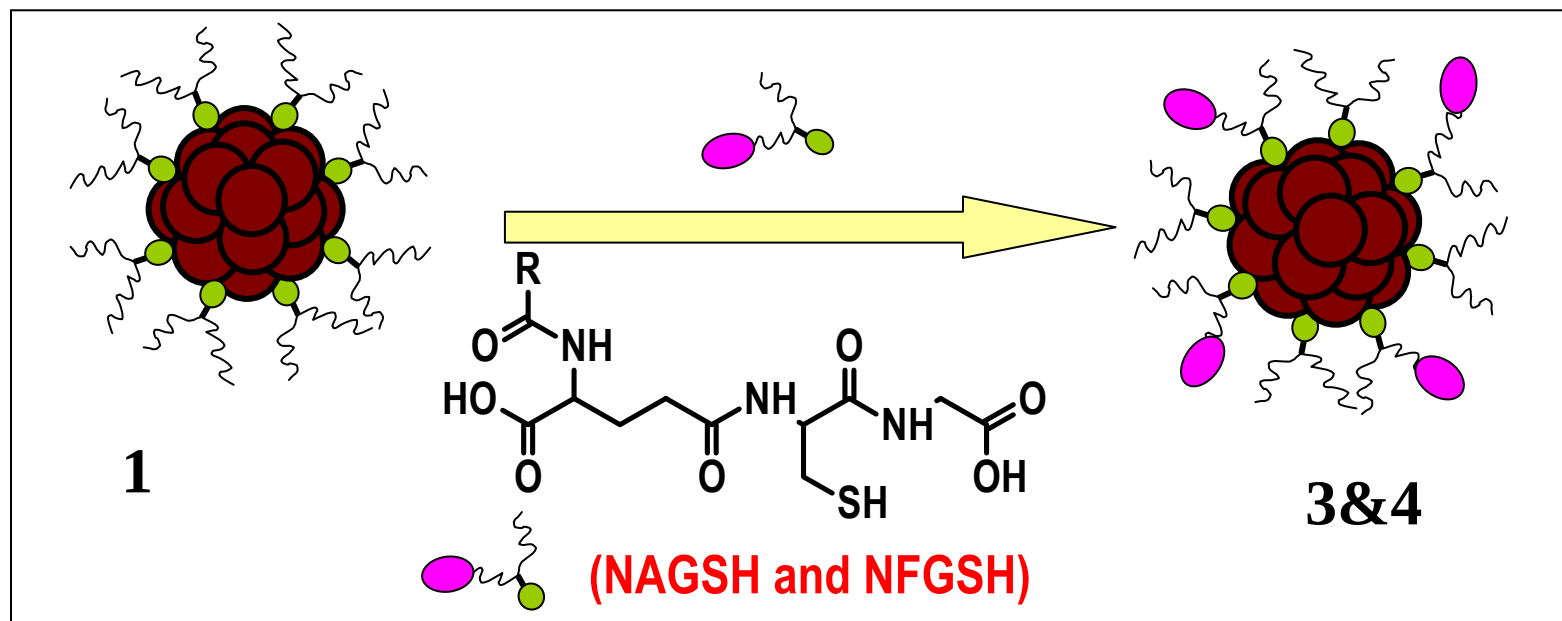
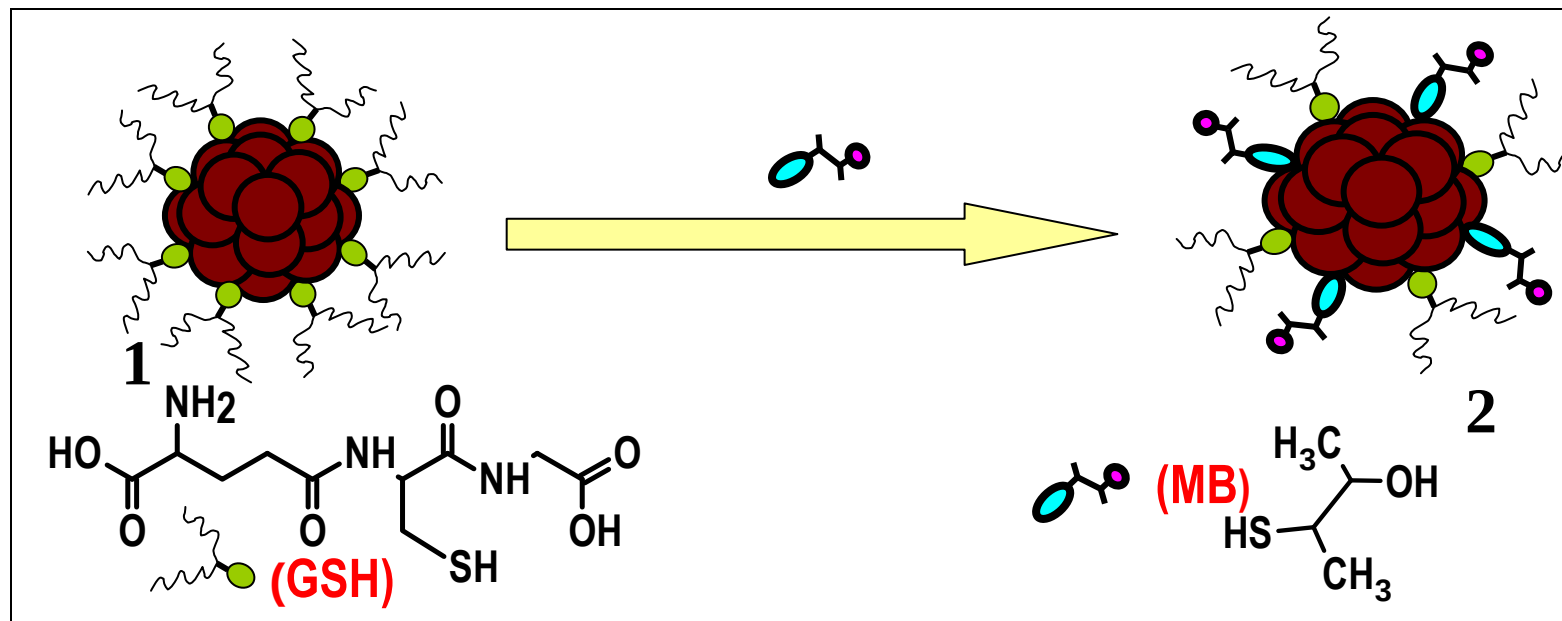


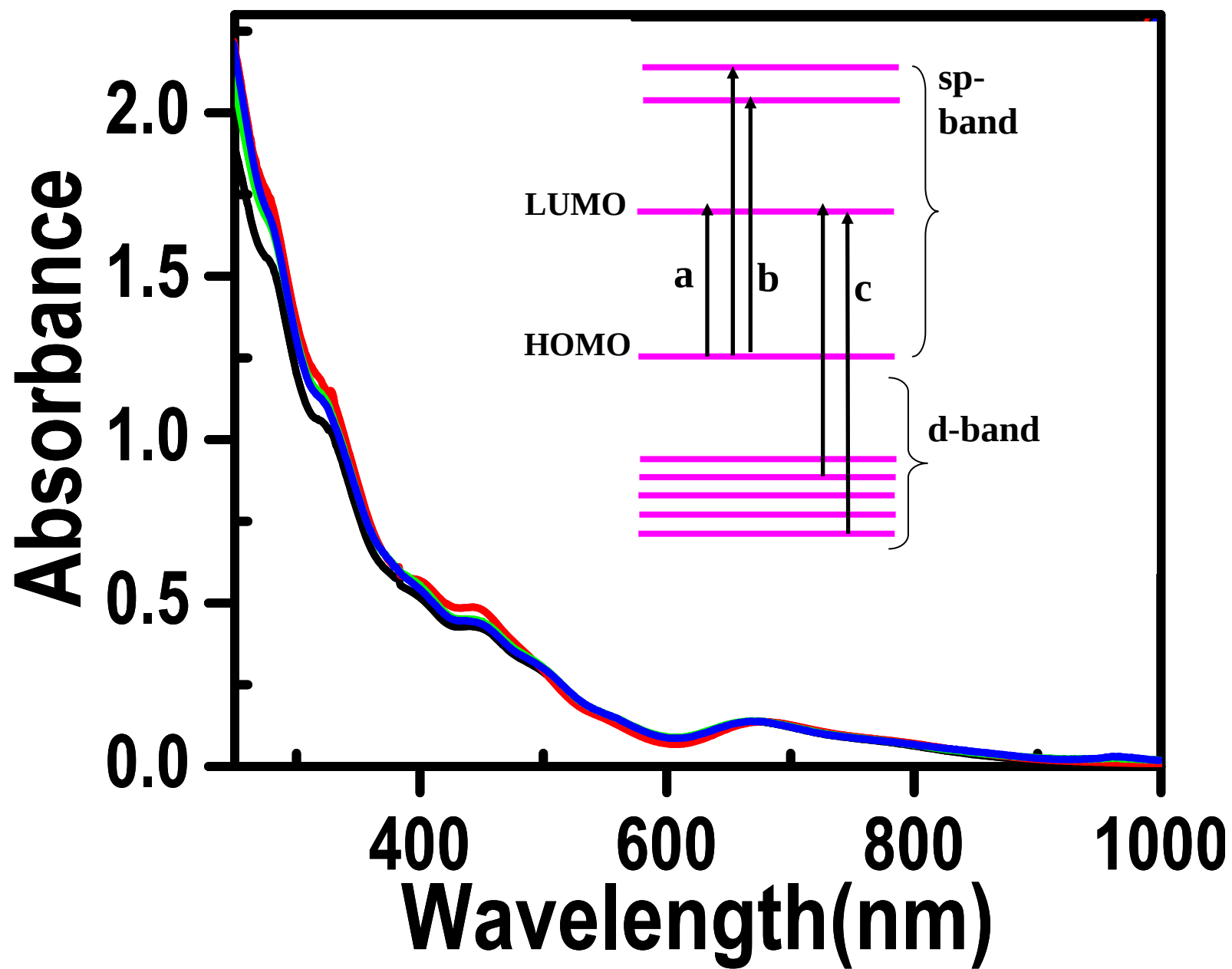
XPS spectrum

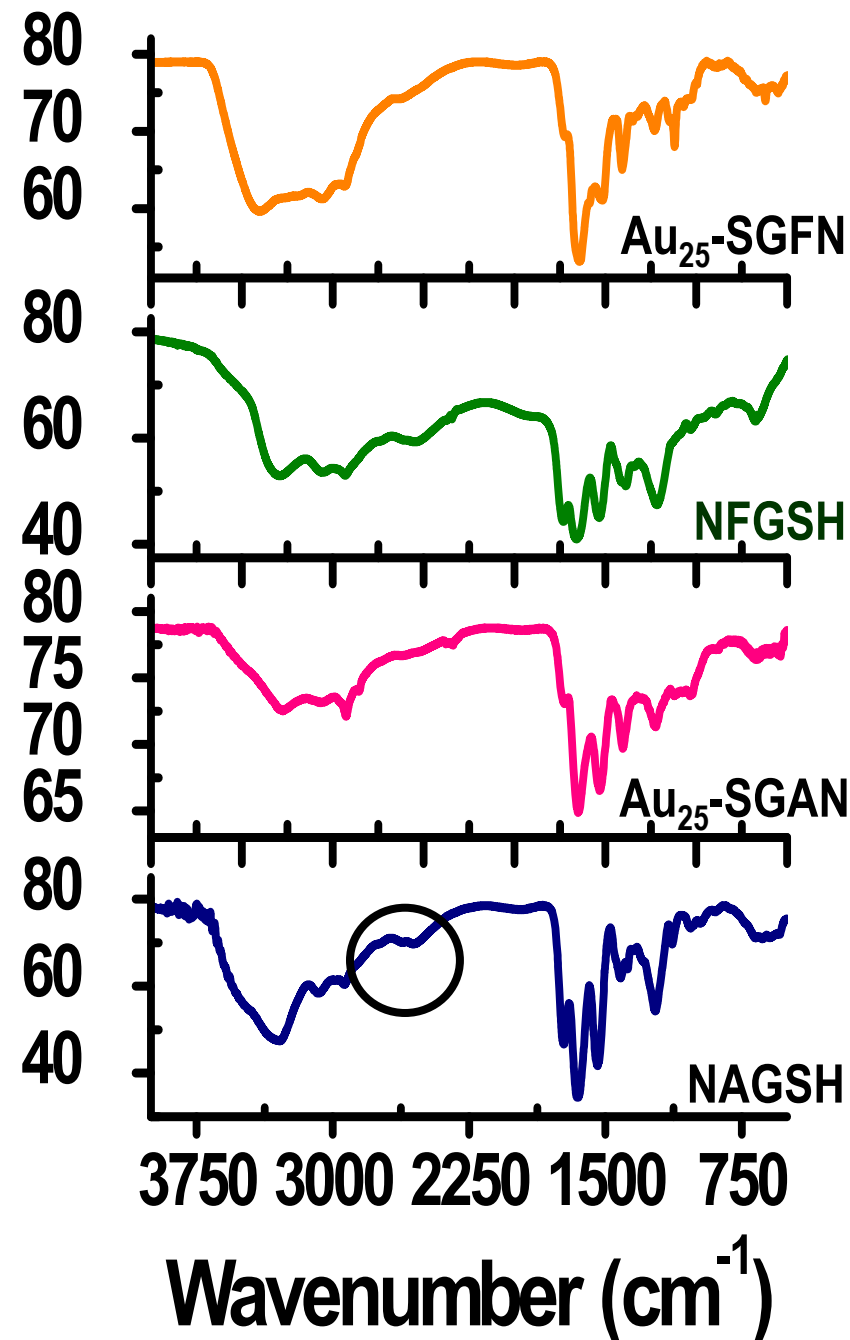
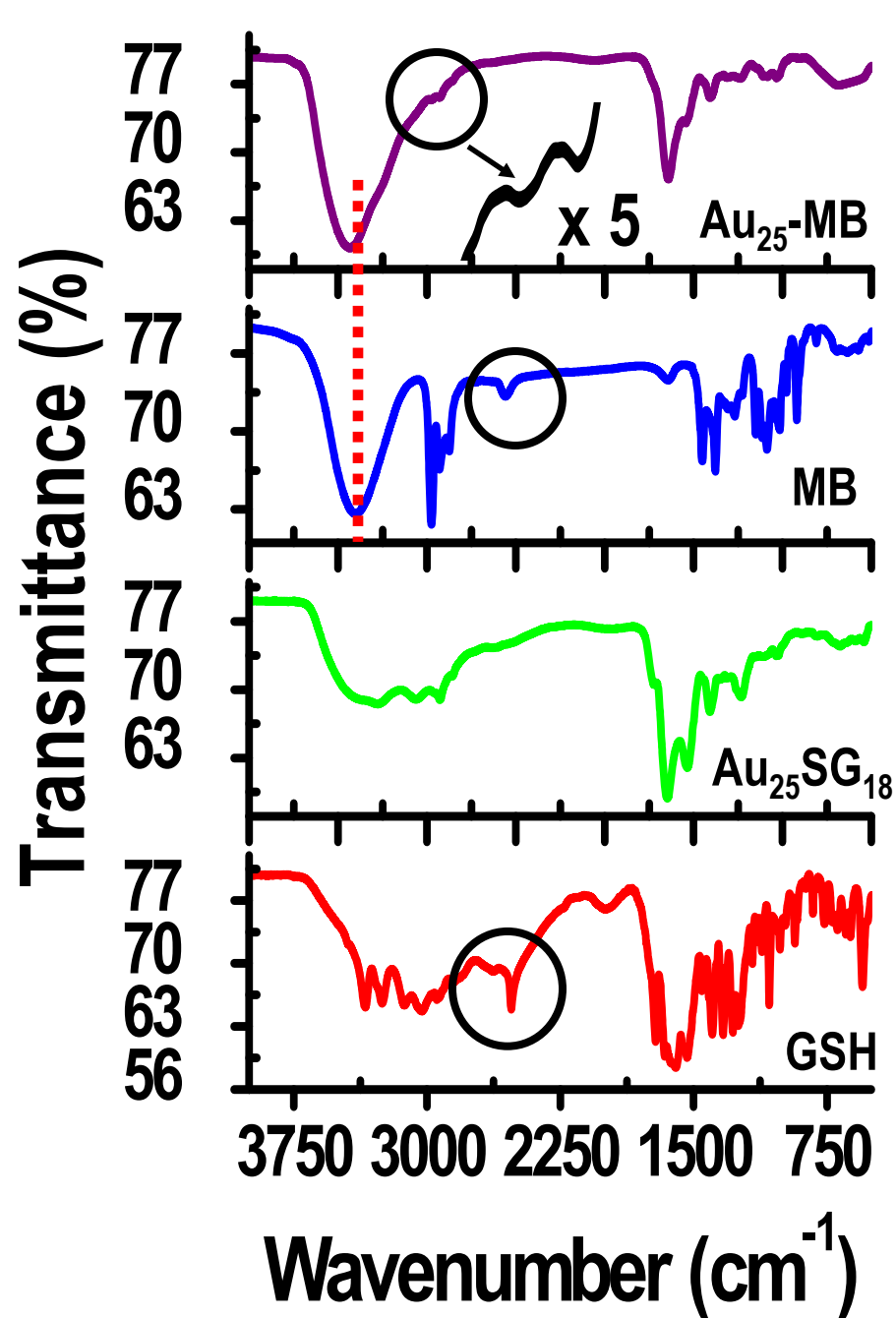


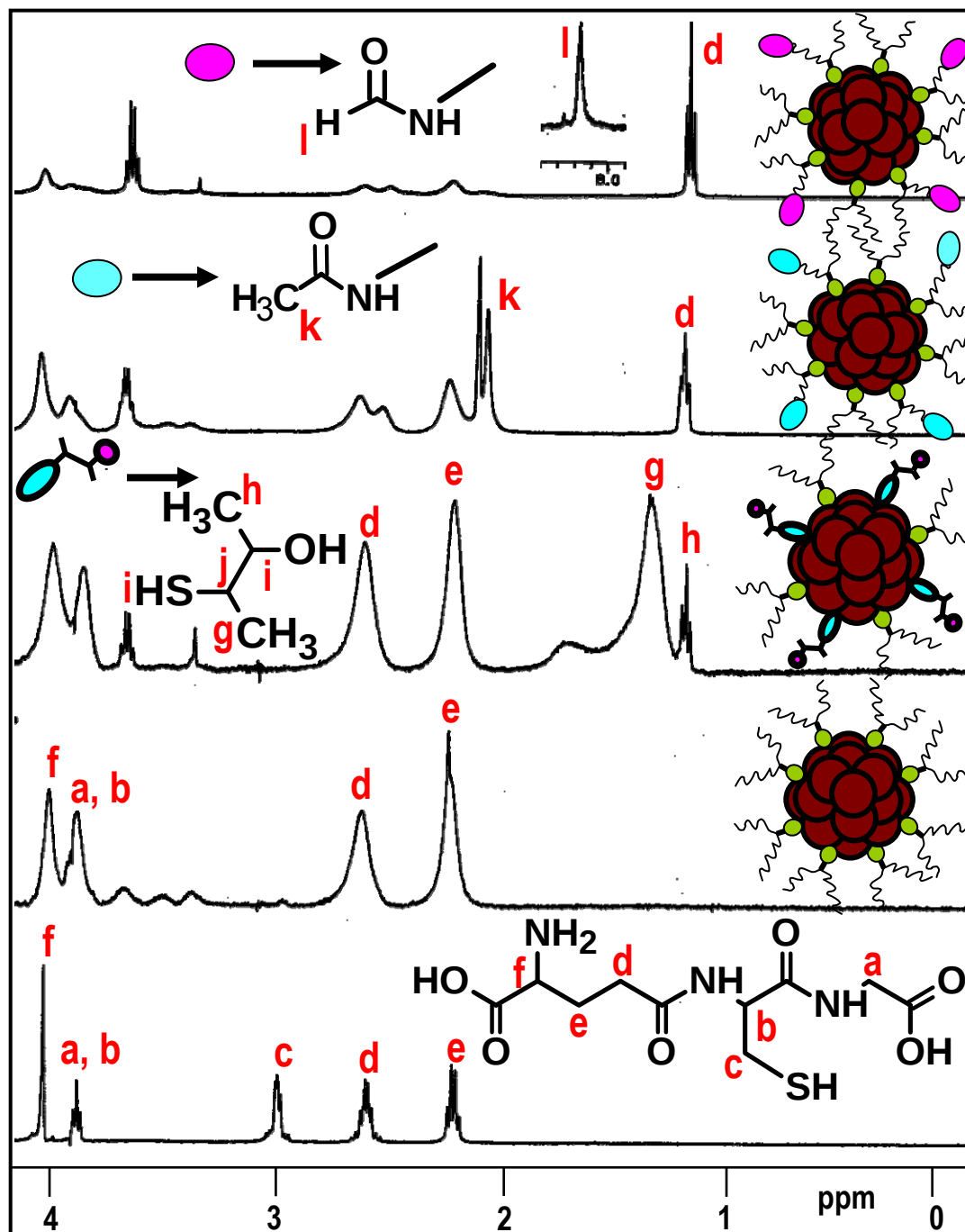
TEM image: The clusters are seen only faintly since the size is ~1 nm. Some of the individual clusters are shown by circles. There are also cluster aggregates which upon extended electron beam irradiation fuse to form bigger particles

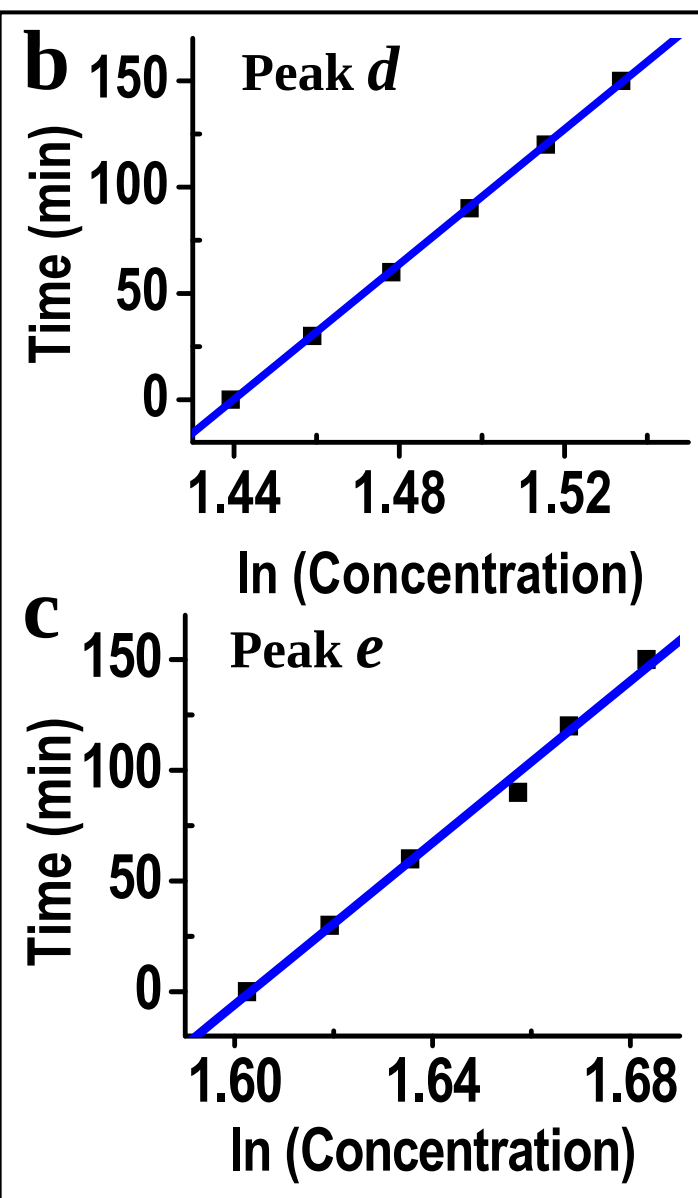
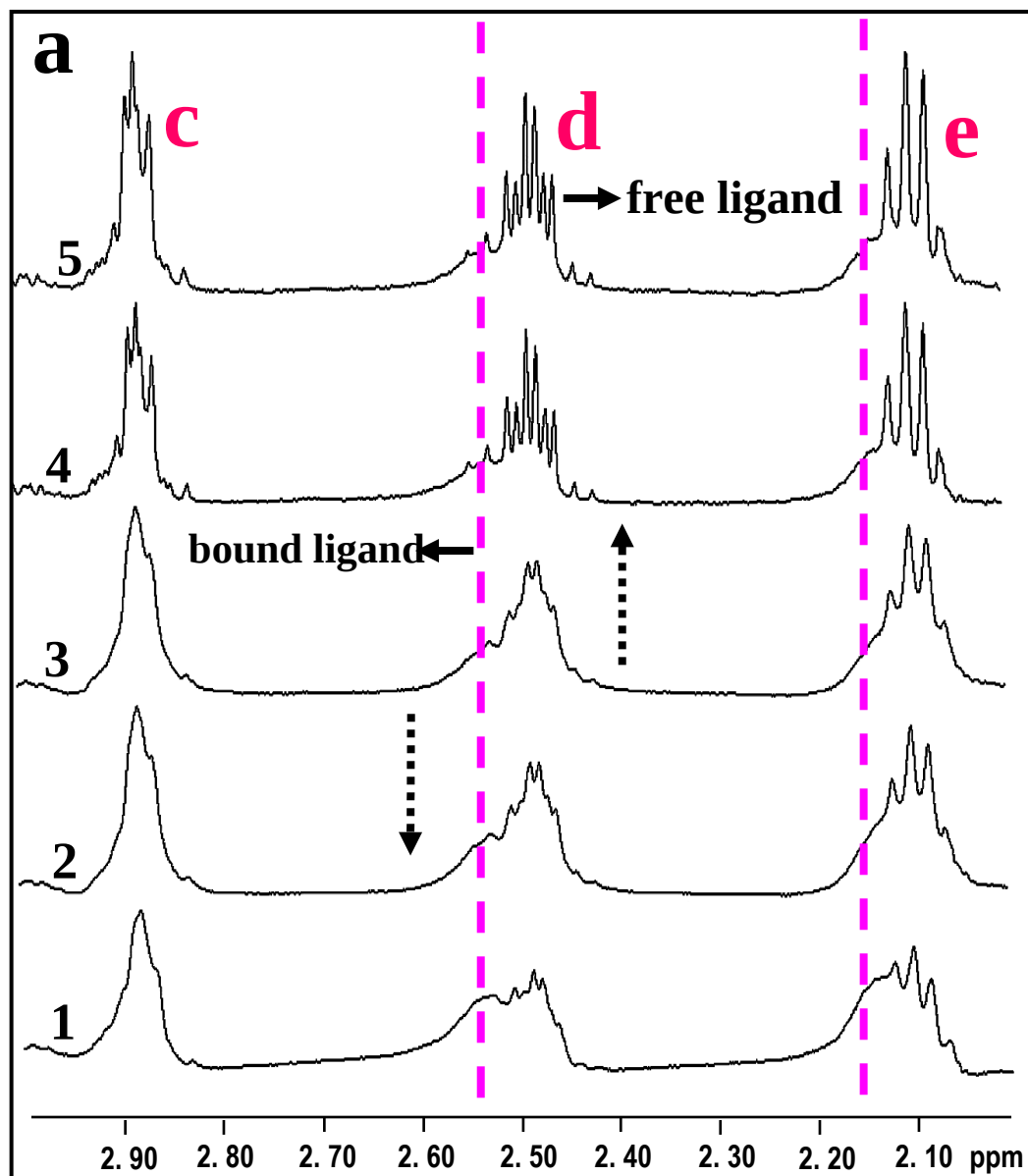
Ligand Exchange of Au₂₅

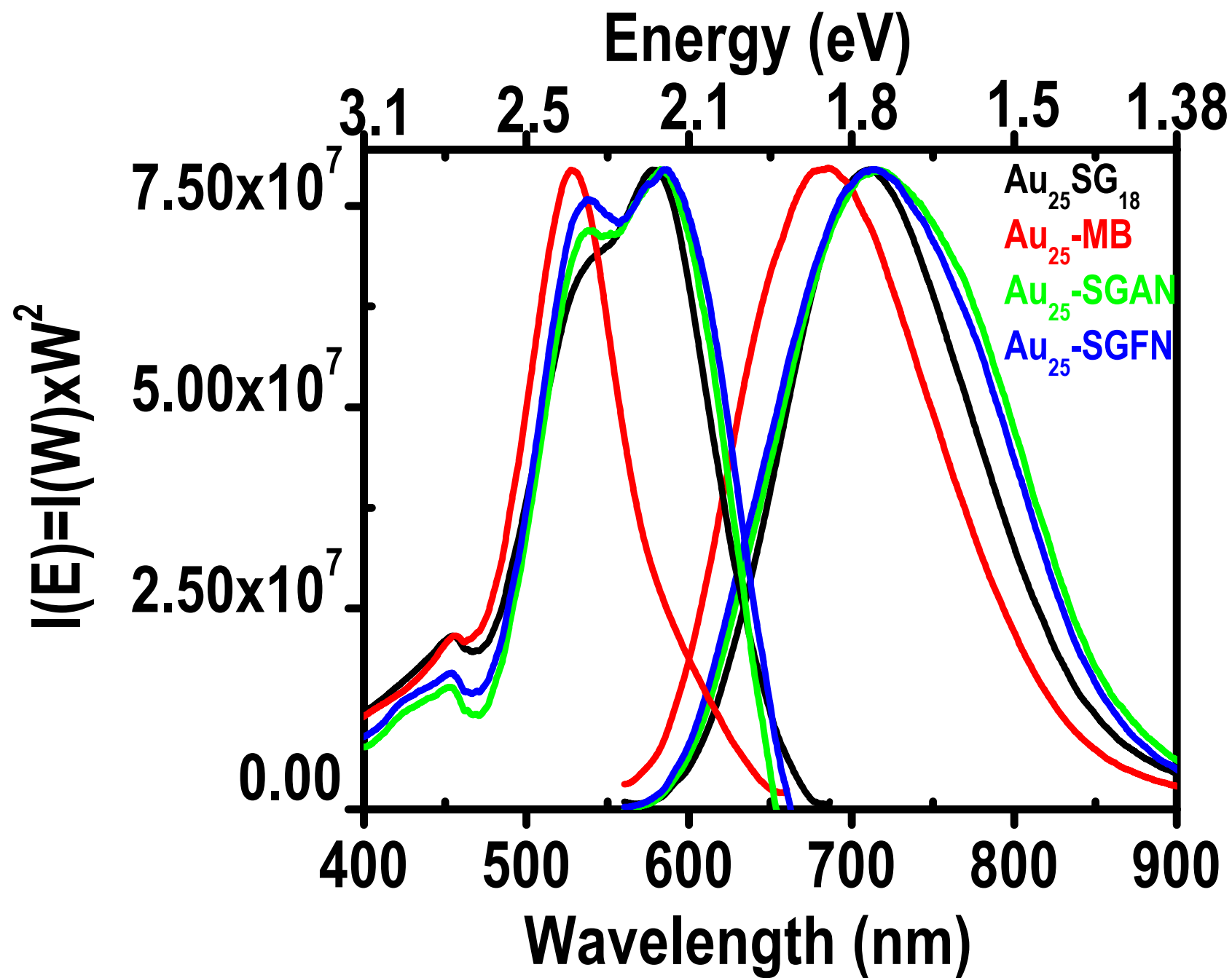


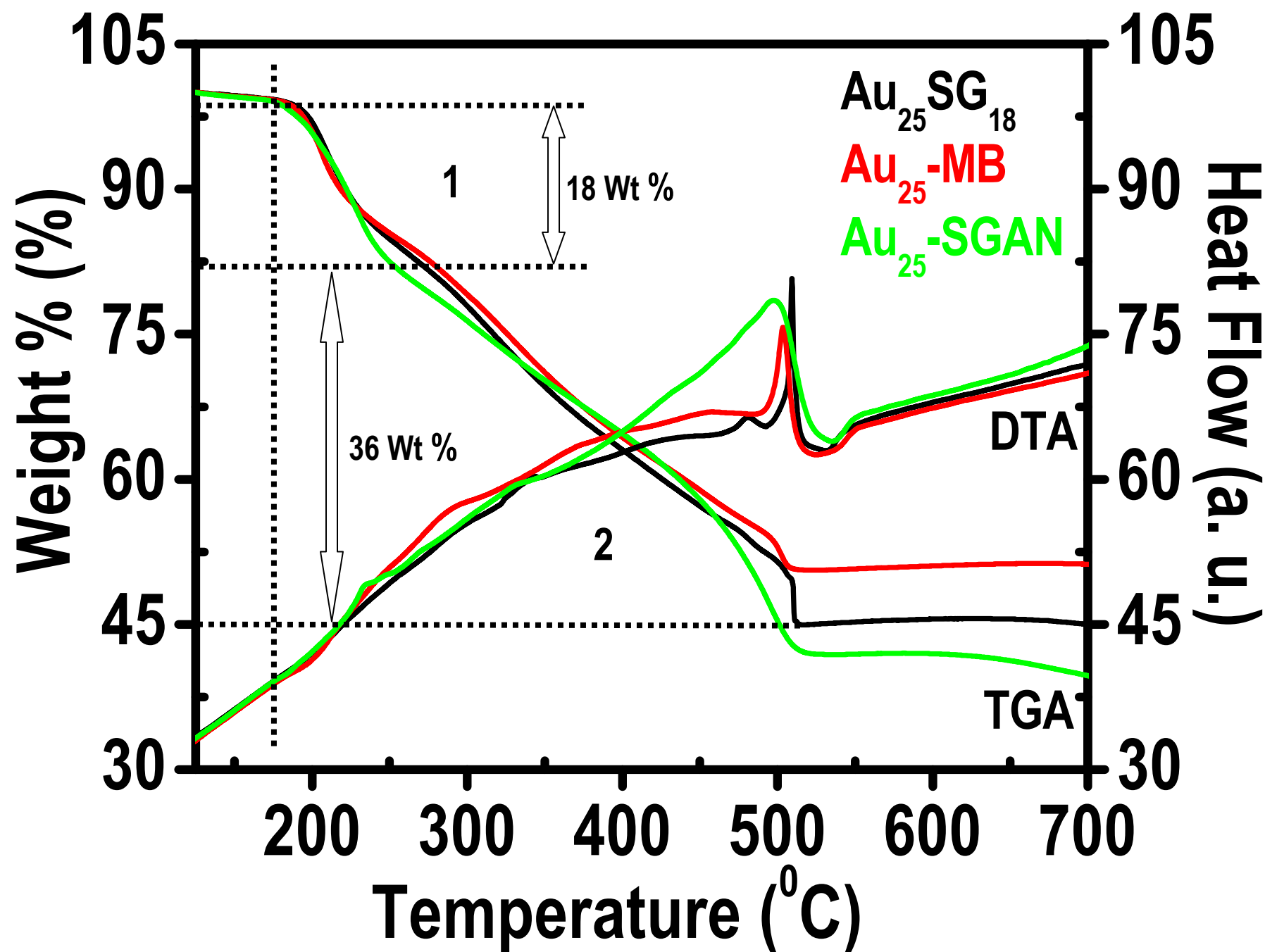


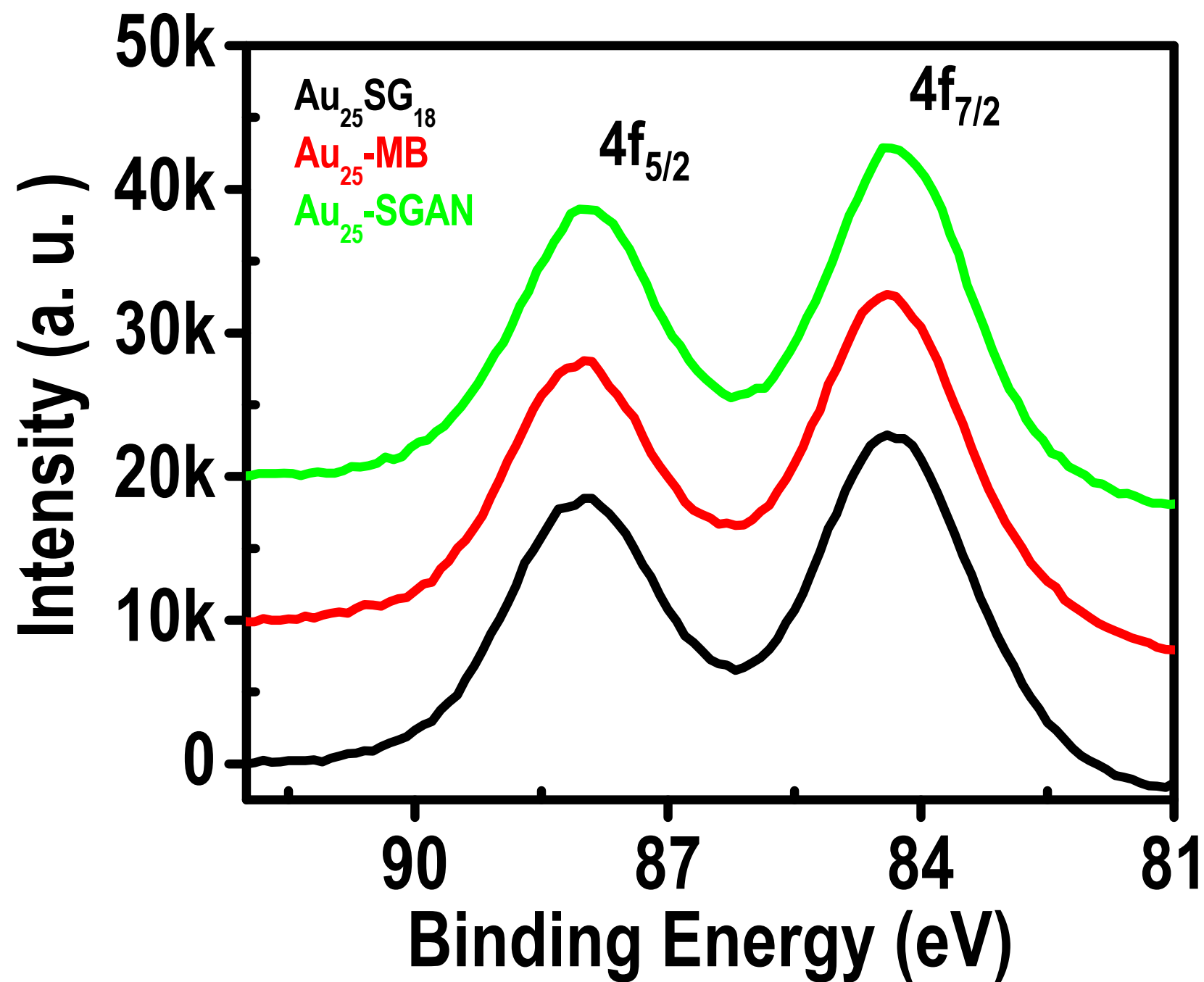


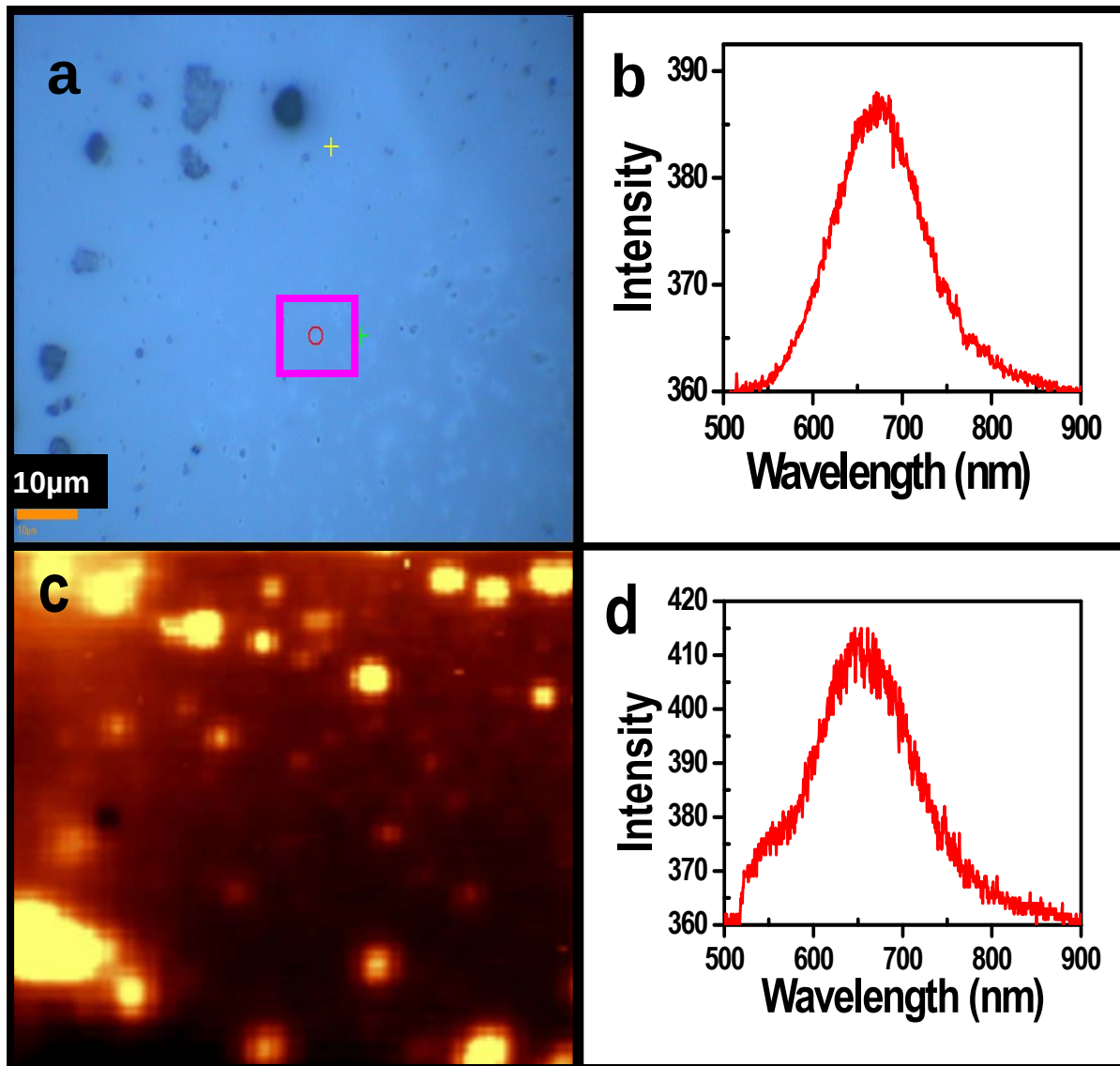


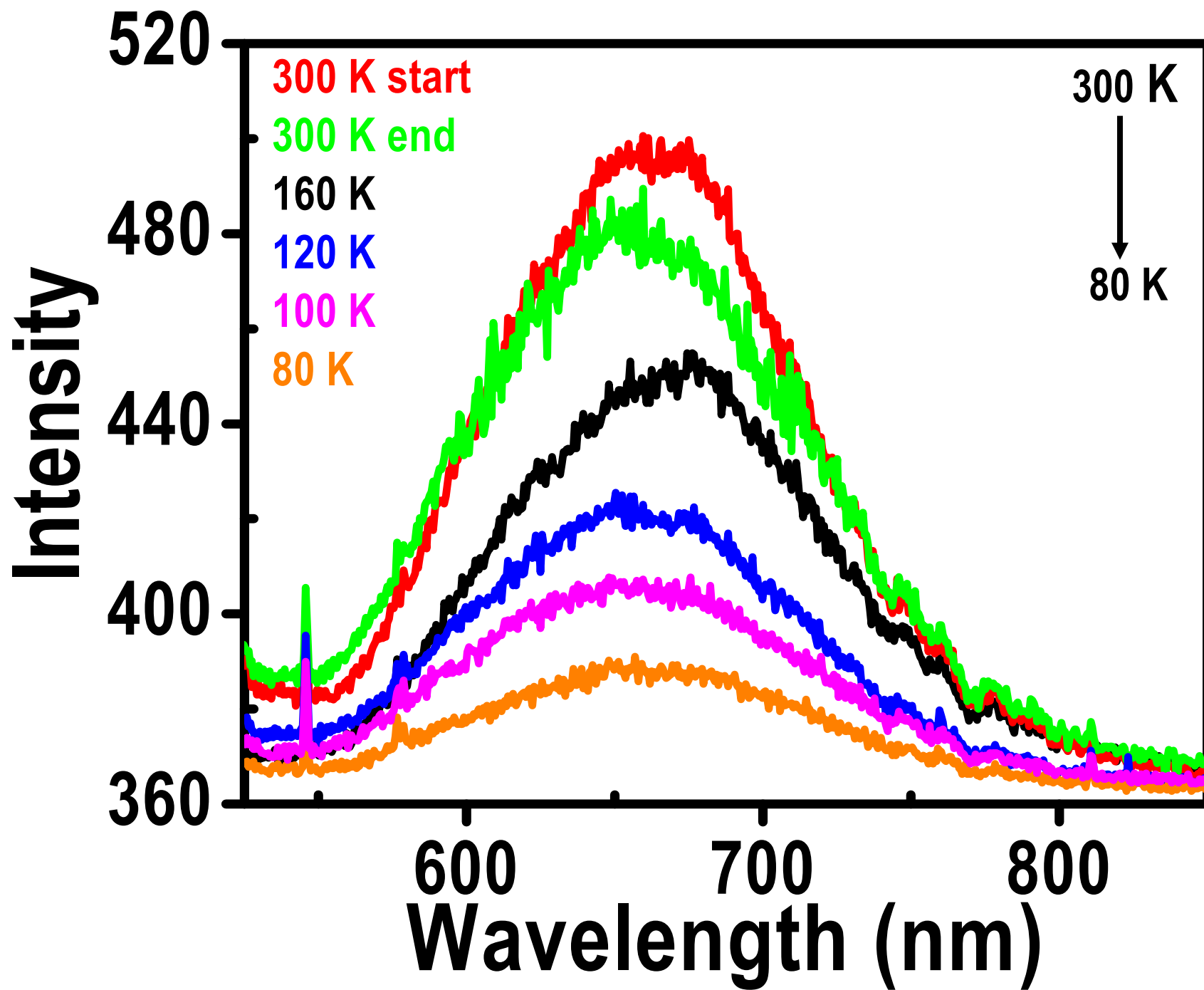


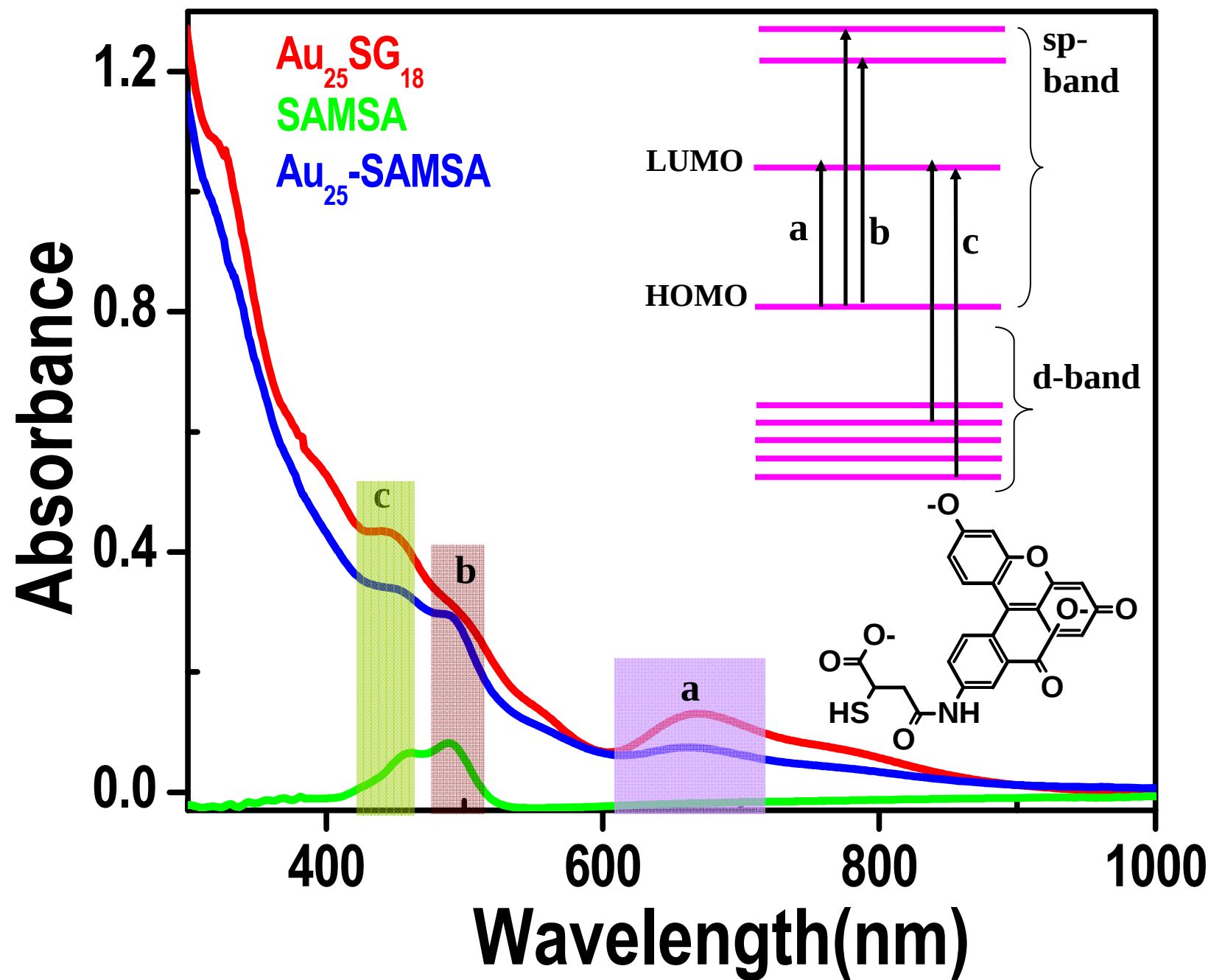


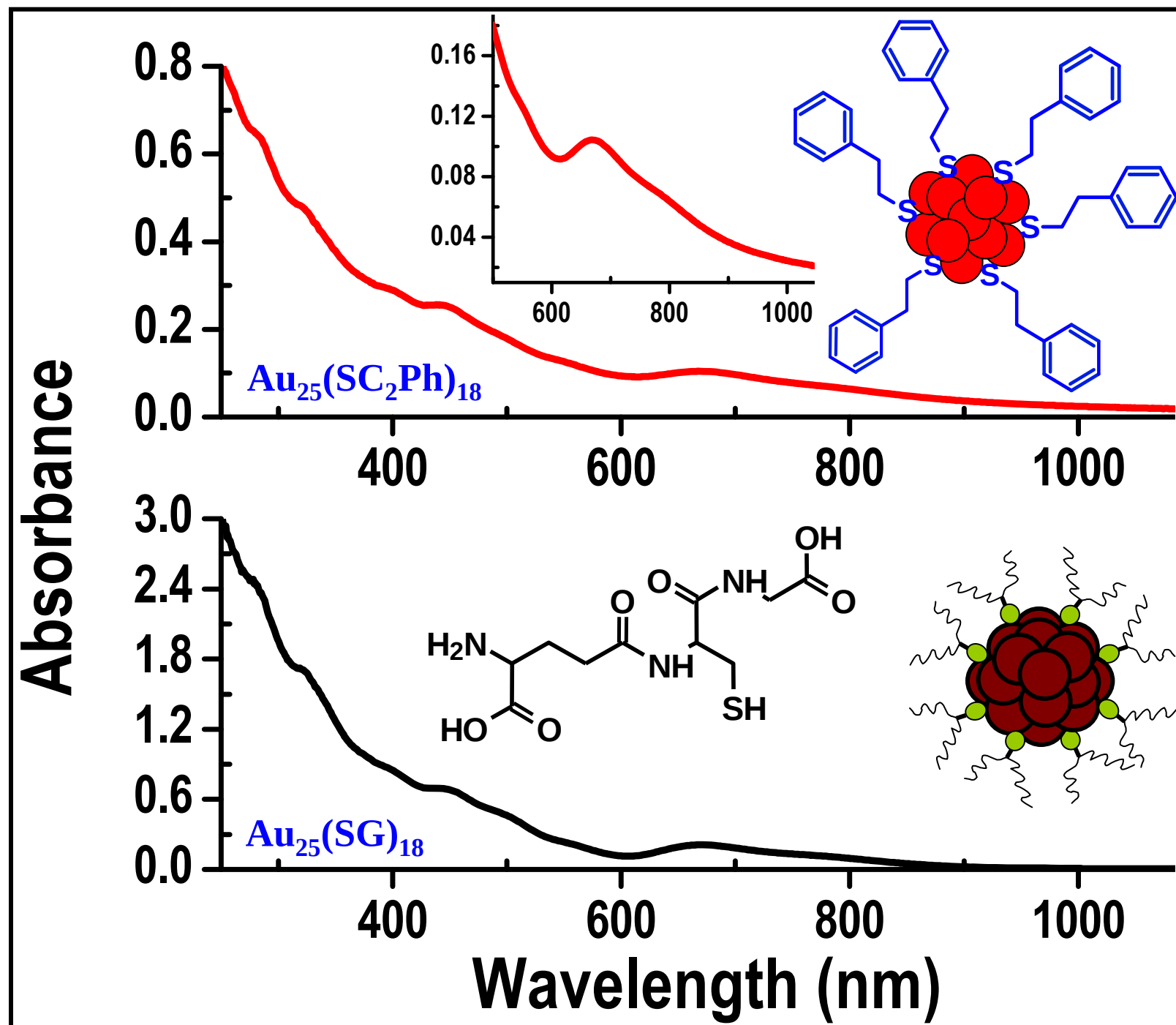


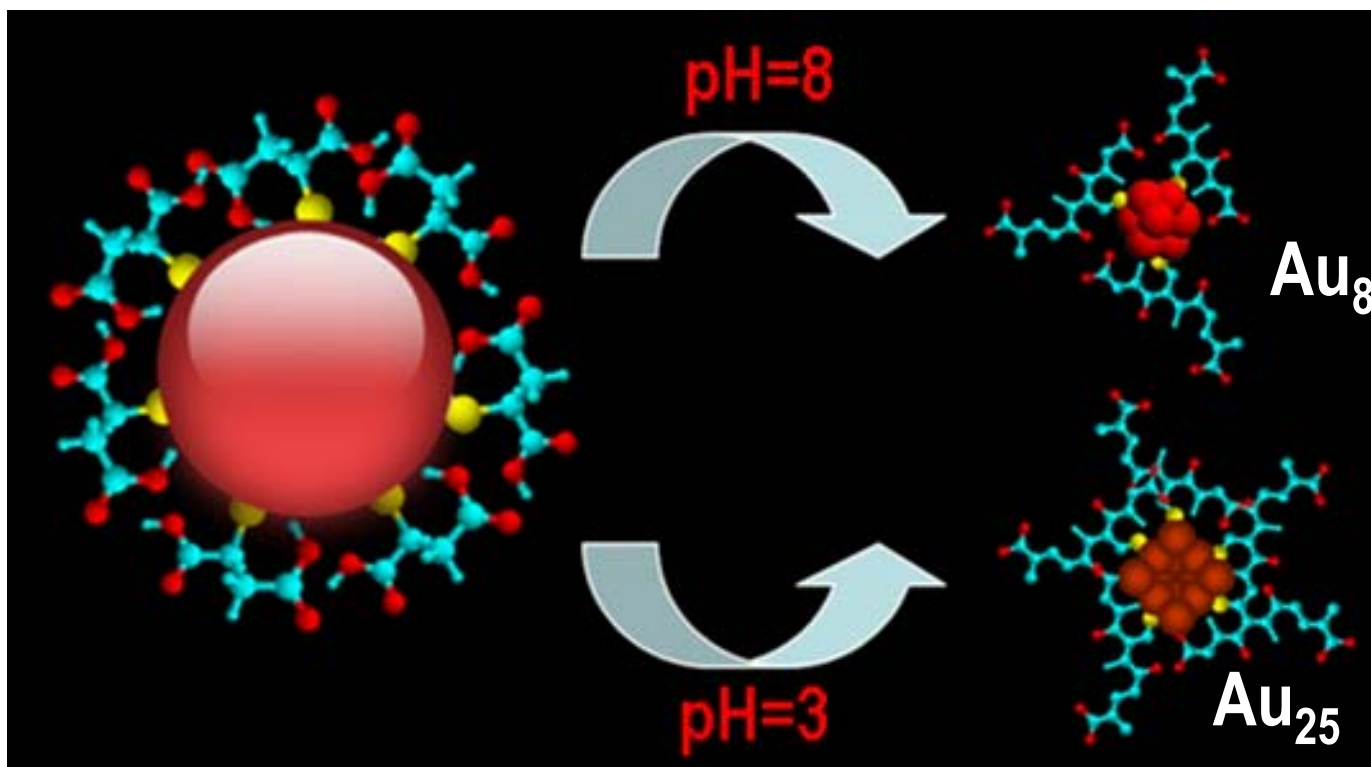


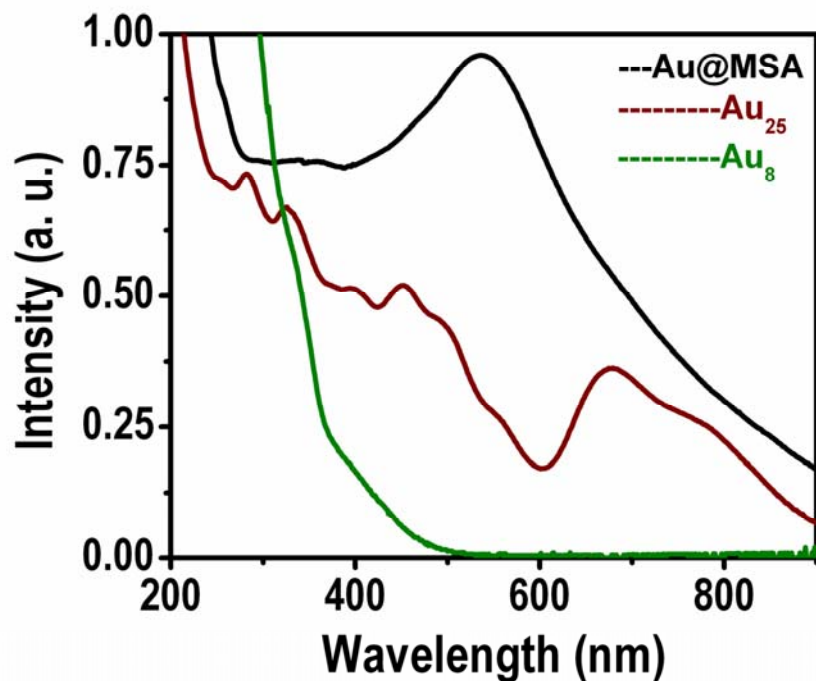




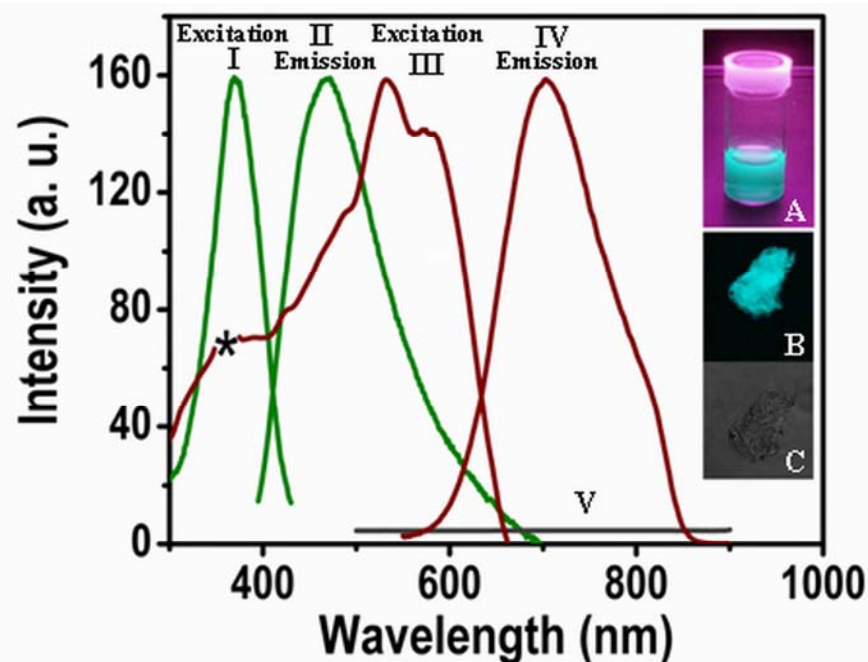




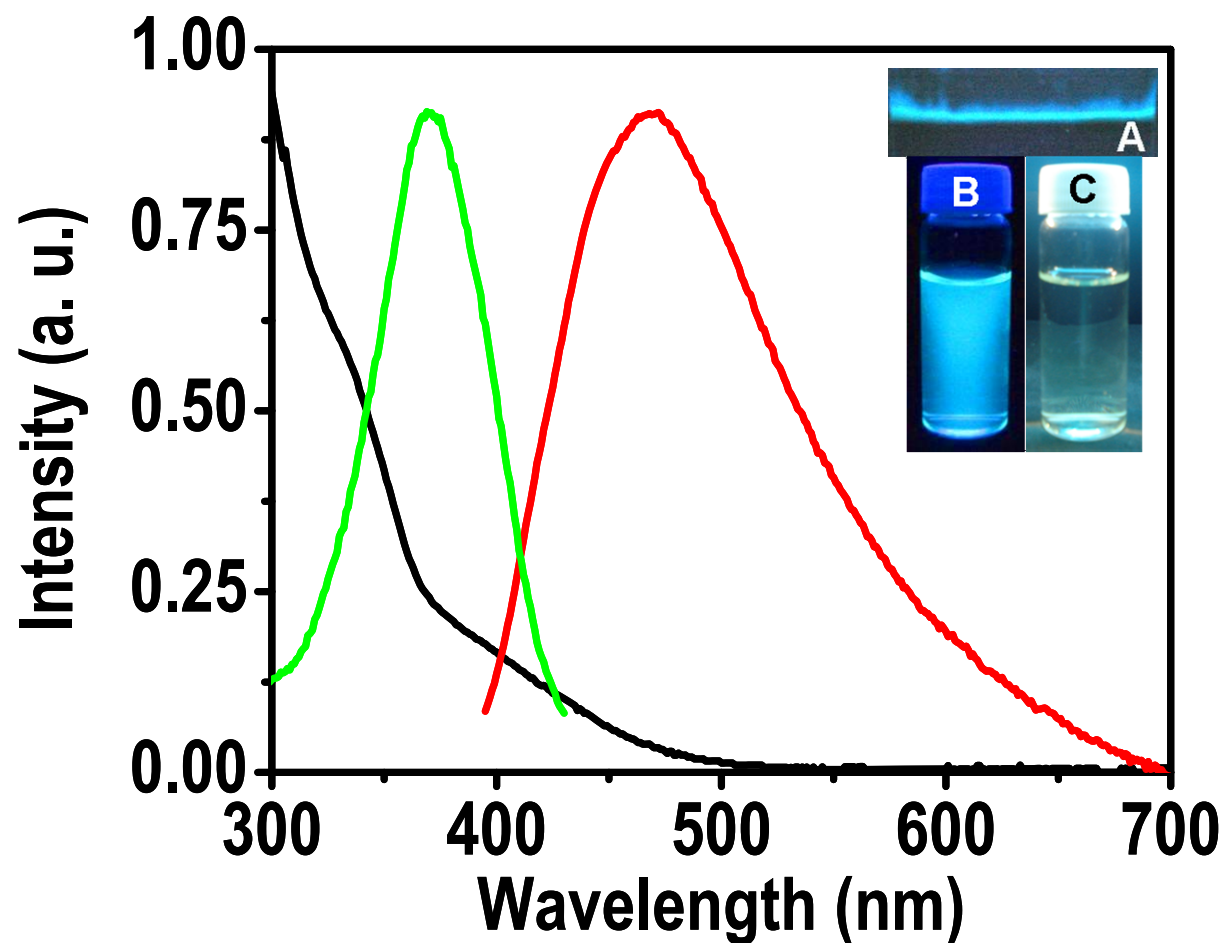




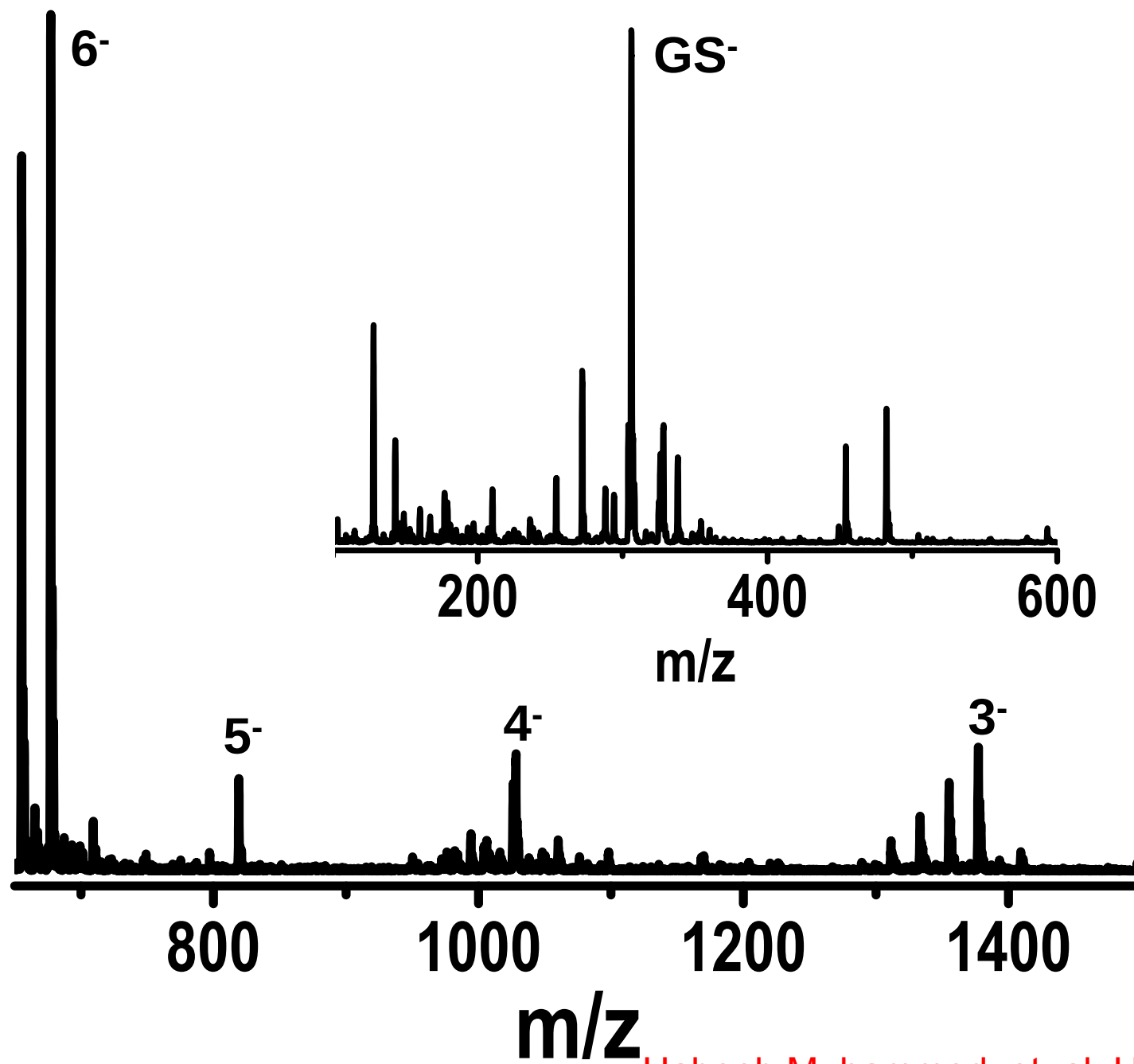
Comparison of the optical absorption profiles of Au@MSA, Au₂₅ and Au₈.



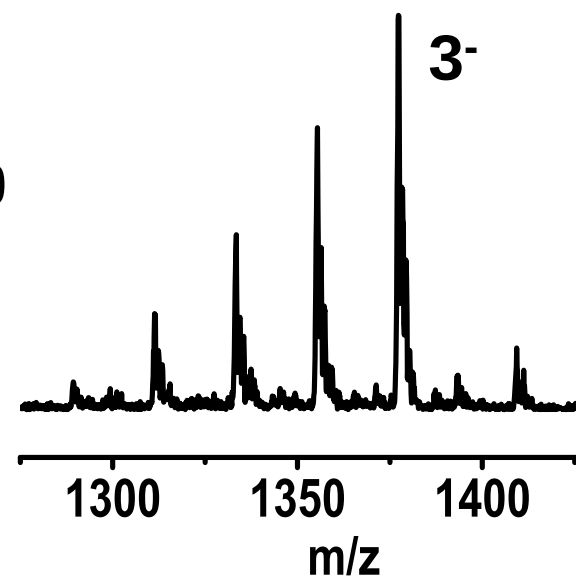
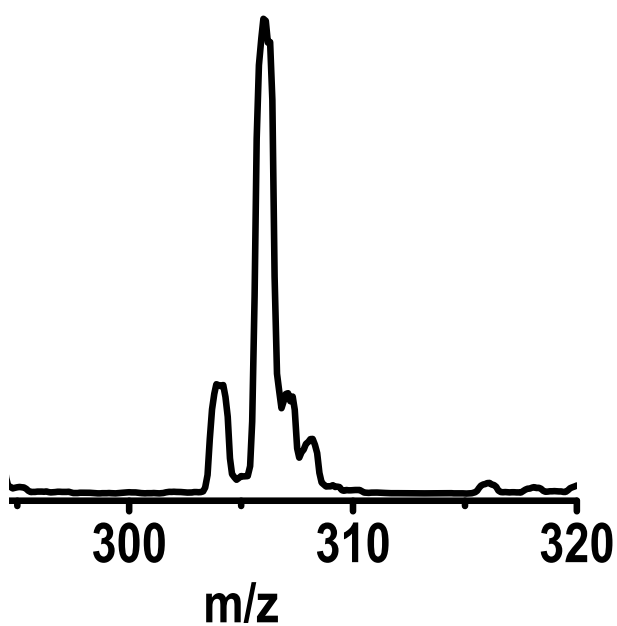
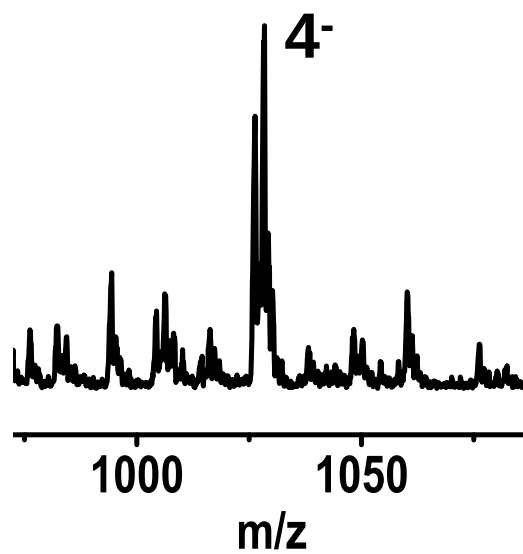
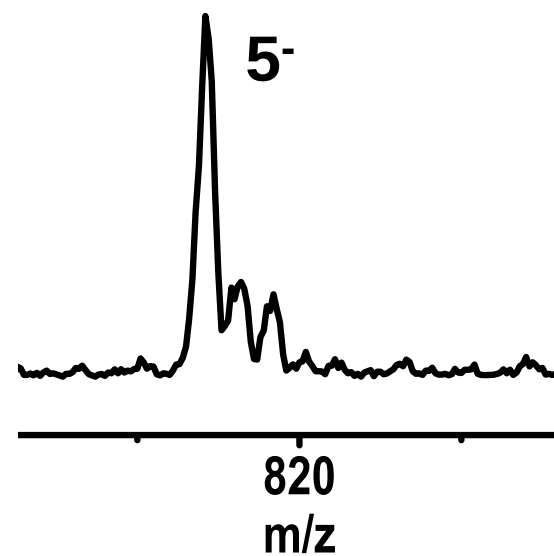
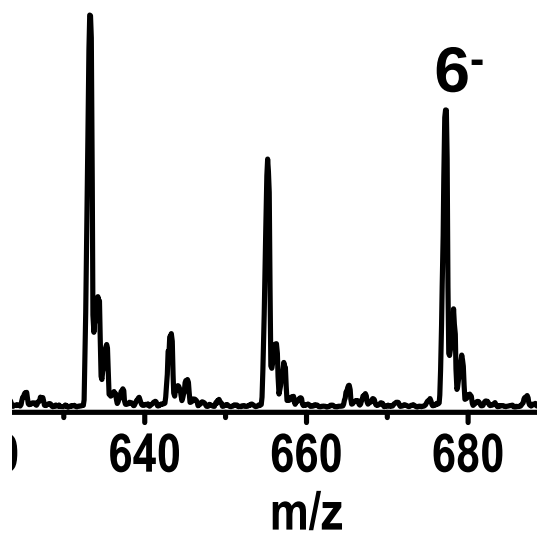
Comparison of the photoluminescence profiles of the clusters with Au@MSA. Traces I and II are the excitation and emission spectra of Au₈, respectively. Traces III and IV are the excitation and emission spectra of Au₂₅, respectively and trace V is the emission spectrum of Au@MSA.

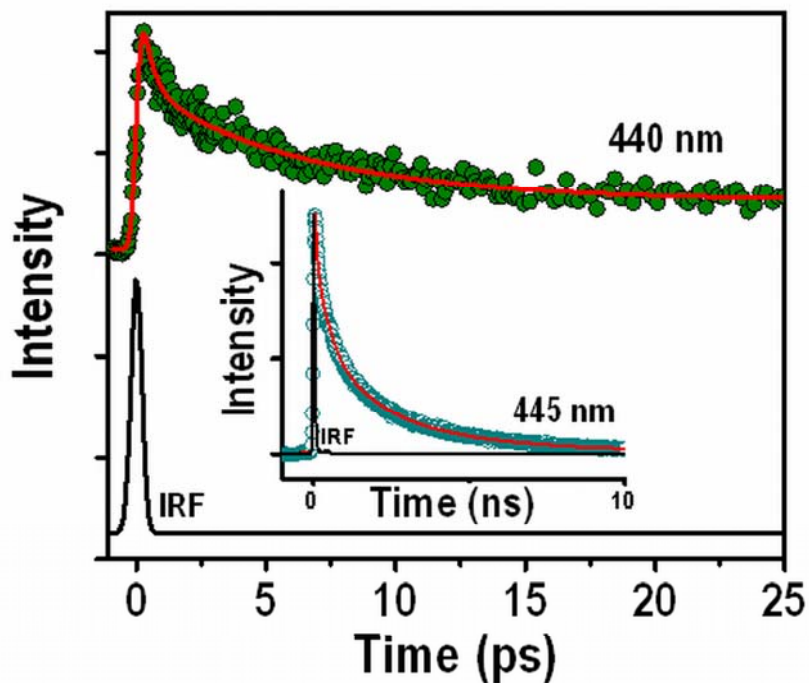


Optical absorption (black trace), Fluorescence excitation (green trace) and emission (red line) of the Au_8 cluster. Inset: photographs of PAGE band (A), Au_8 solution in water under normal light irradiation (B) and under uv light irradiation (C).



Habeeb Muhammed, et. al. Unpublished



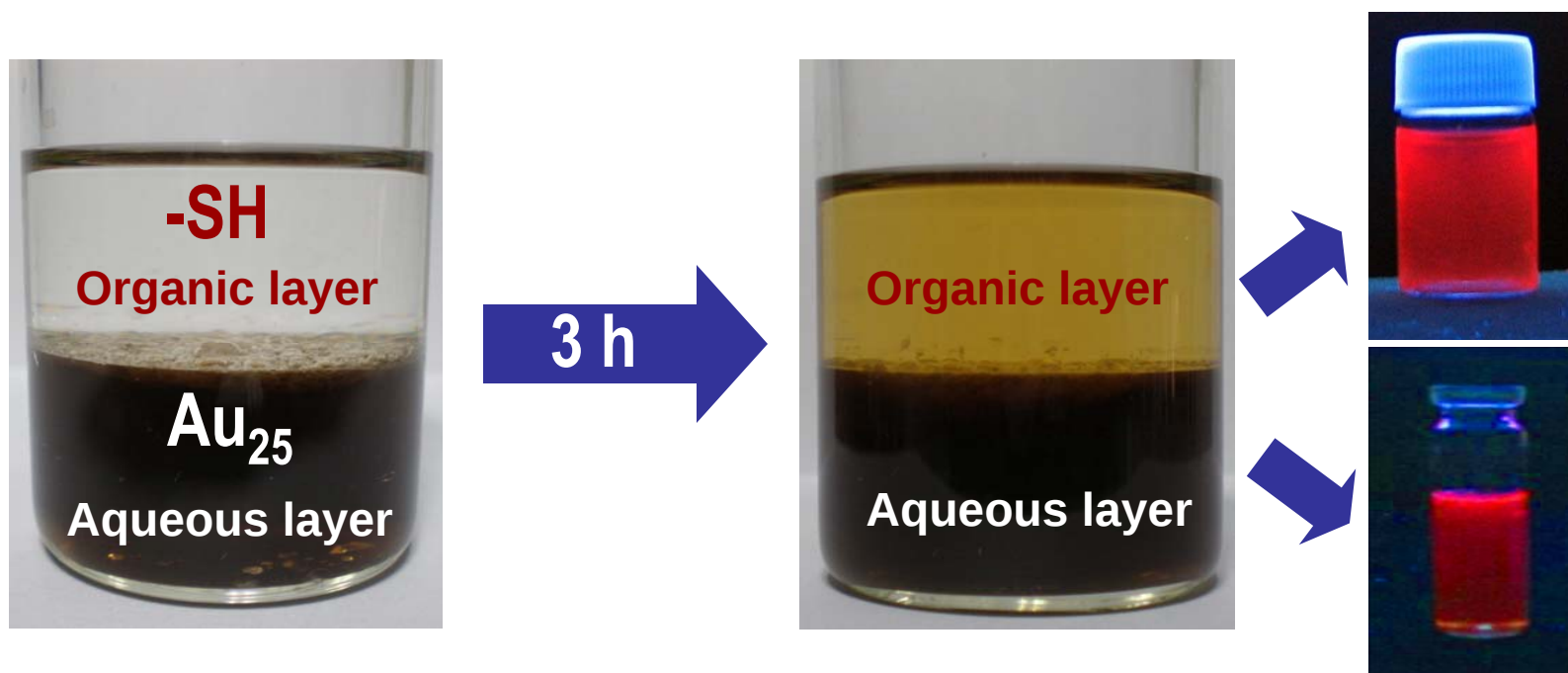


Fluorescence decay profile of Au_8 in water at 440 nm (excitation 364 nm) by fluorescence upconversion technique (IRF = 165 fs). Inset shows the fluorescence transient of the sample at 445 nm (excitation = 375 nm) in a longer time window of TCSPC (IRF = 70 ps) set-up.

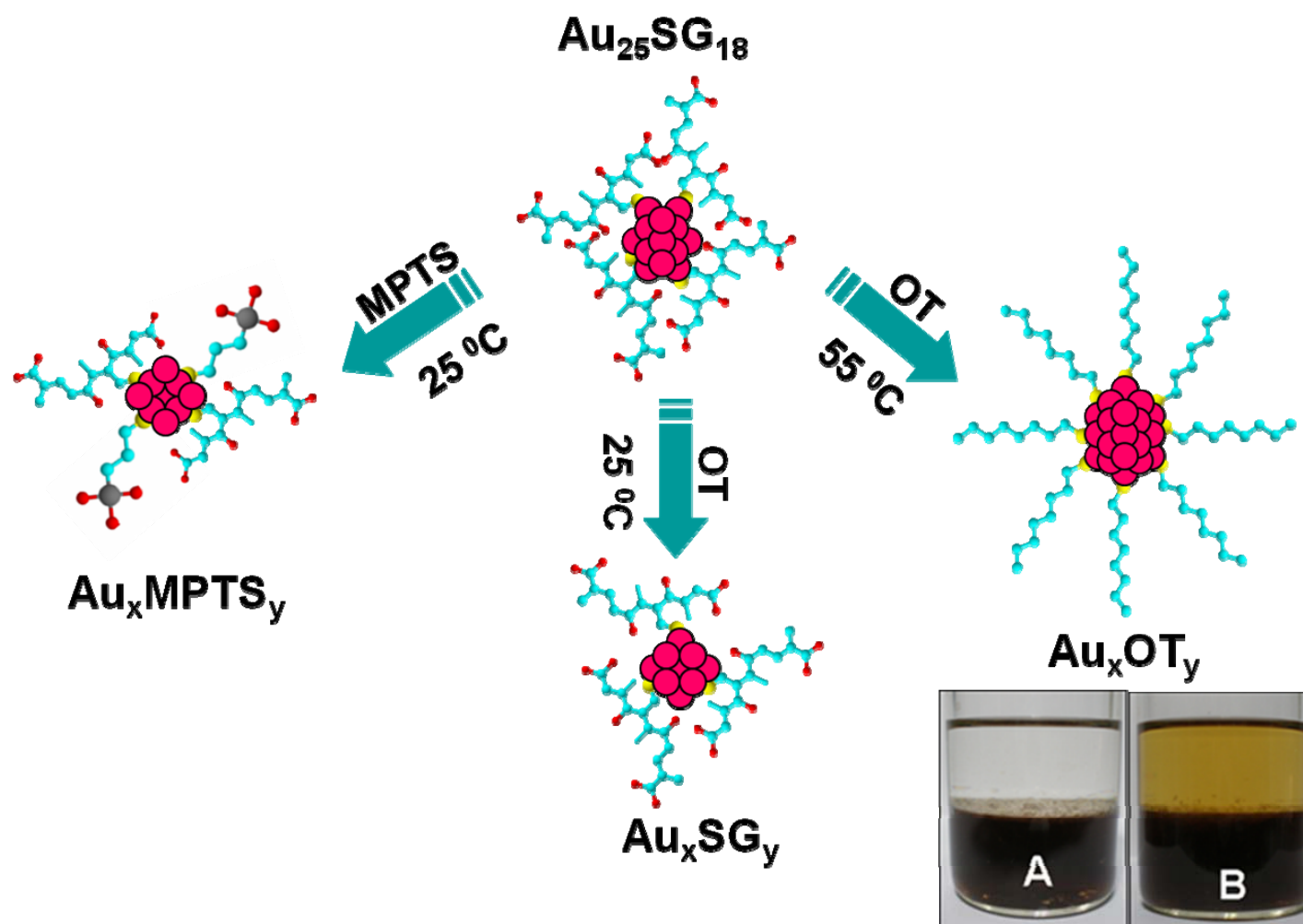
Quantum Yield	
Au_{25}	Au_8
1.9×10^{-3}	0.15

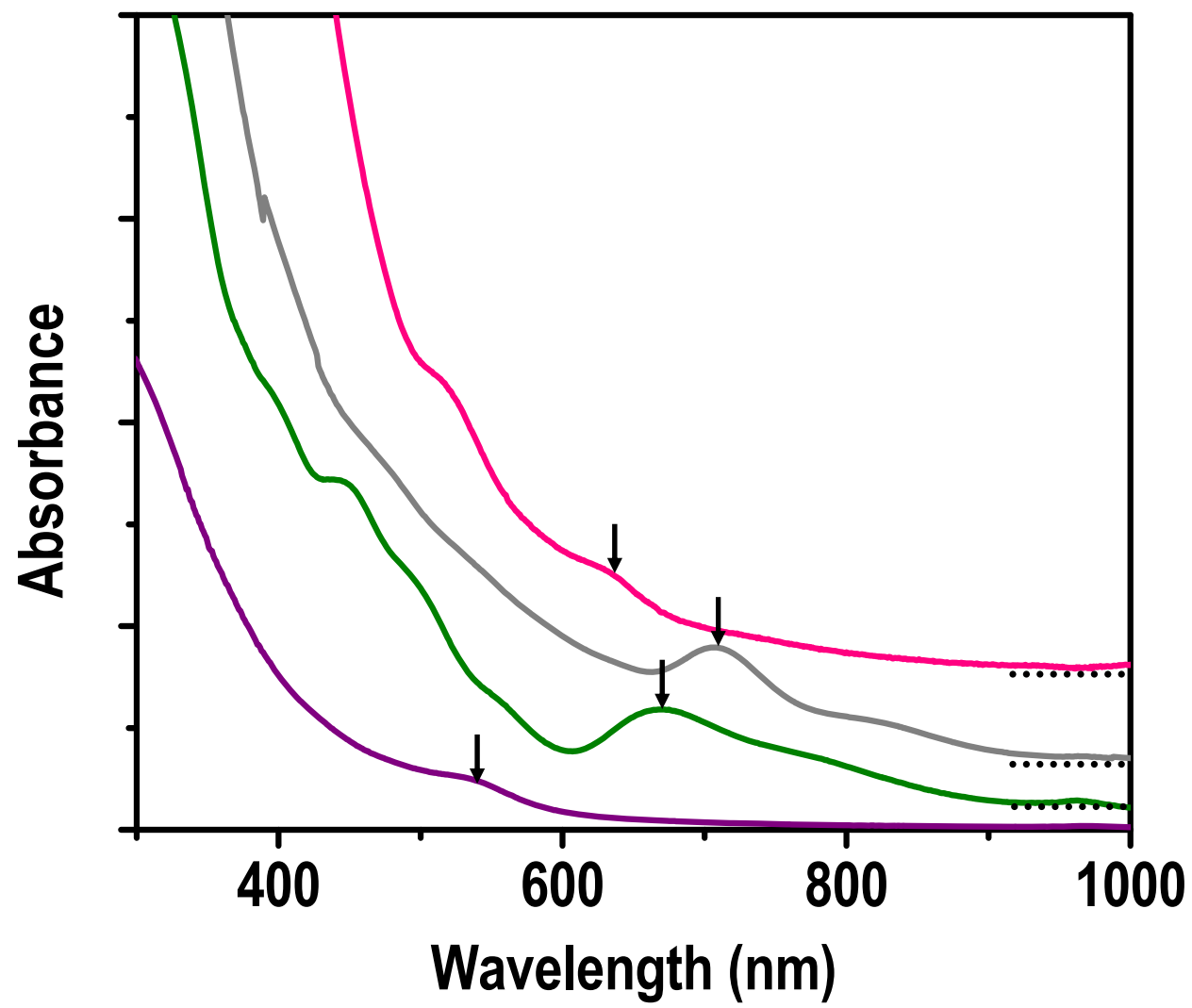
Life Time Measurements
30 ps (0.4 ps & 6.3 ps) (53%), 310 ps (22%), 1.6 ns (18%) , 5.3 ns (7%)

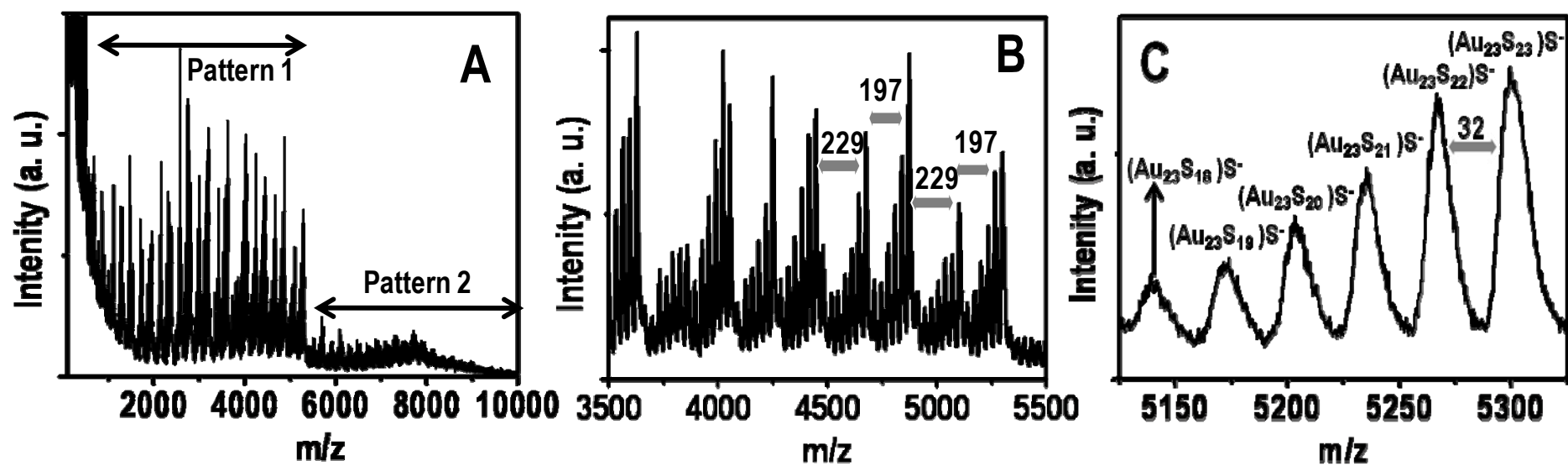
Au_{25} to make other clusters



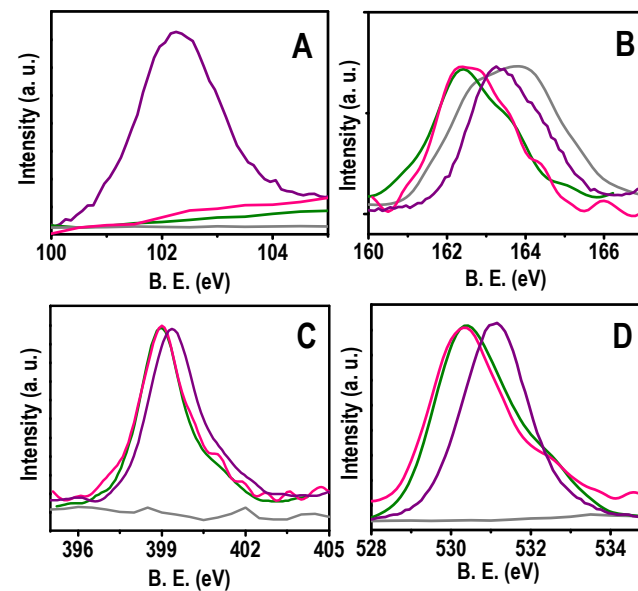
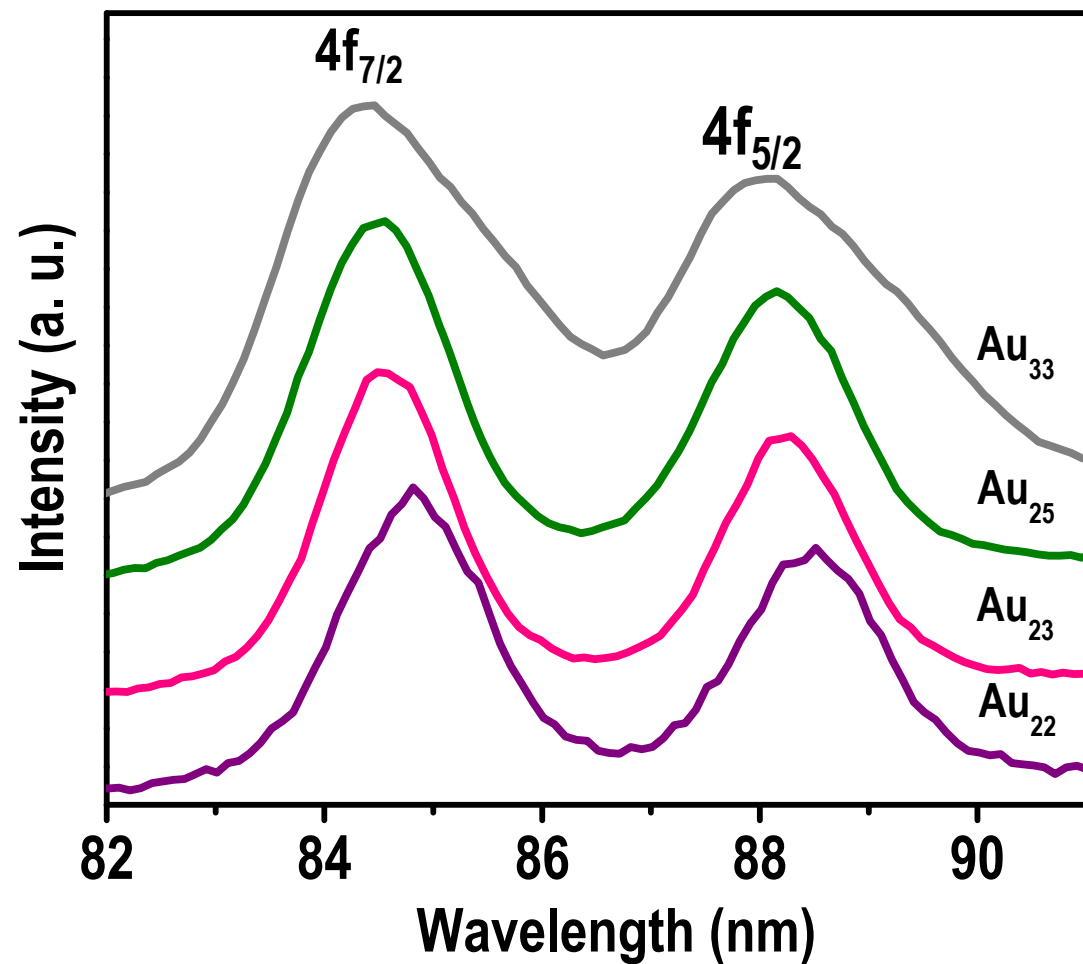
Schematic of the interfacial synthesis of red emitting clusters from $\text{Au}_{25}\text{SG}_{18}$.



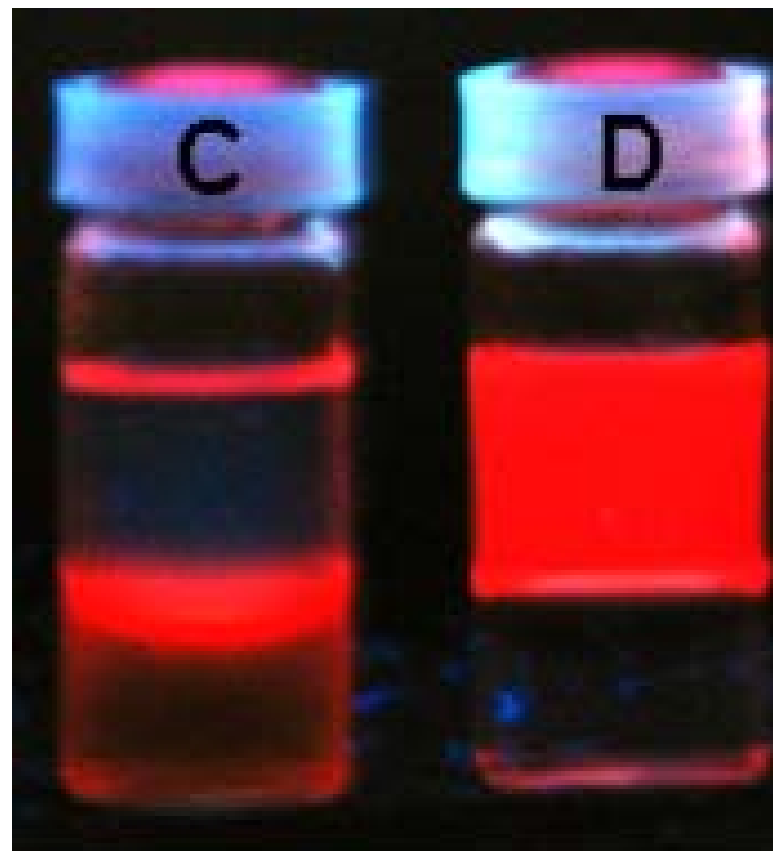
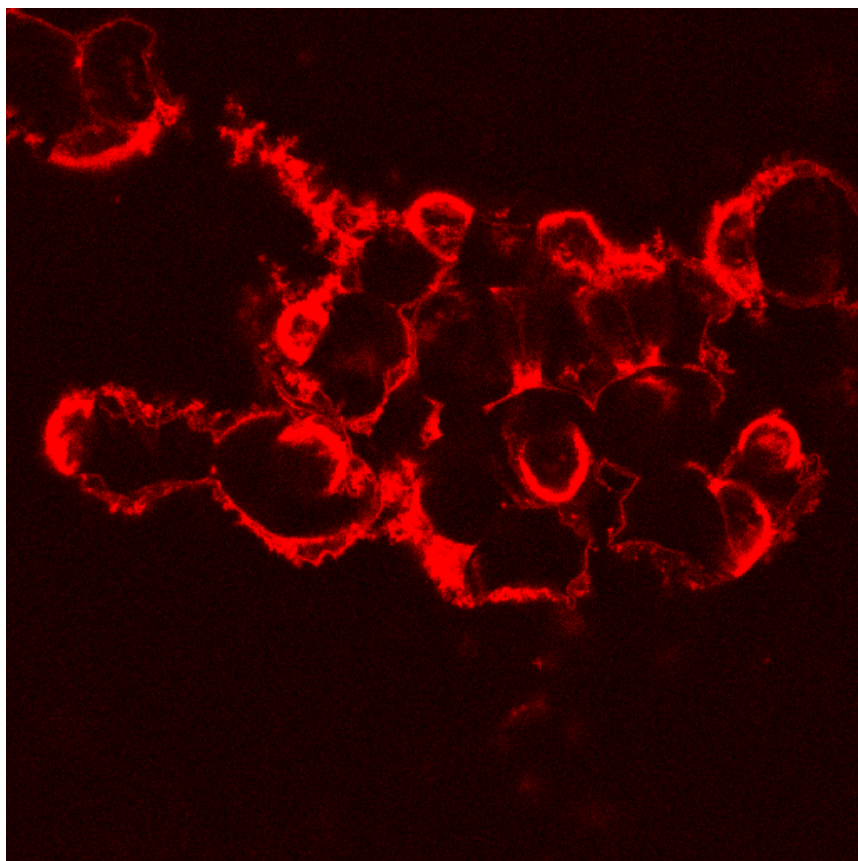




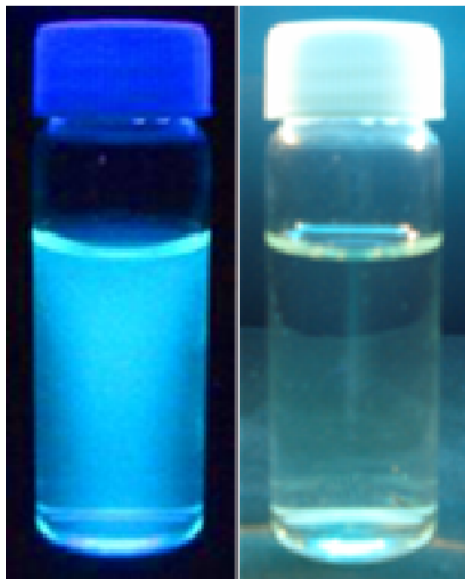
Habeeb Muhammed et al. Chem. Euro. J. (In Press)



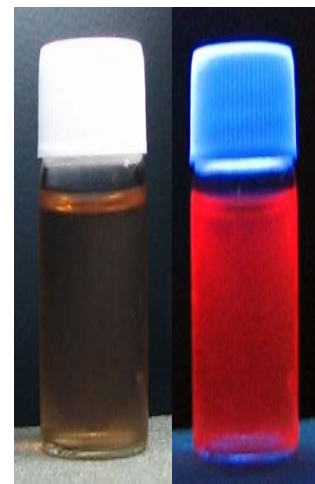
Comparison of the optical absorption spectra of $Au_{25}SG_{18}$ (black trace), red emitting cluster in aqueous (green trace) and organic layers (red trace).



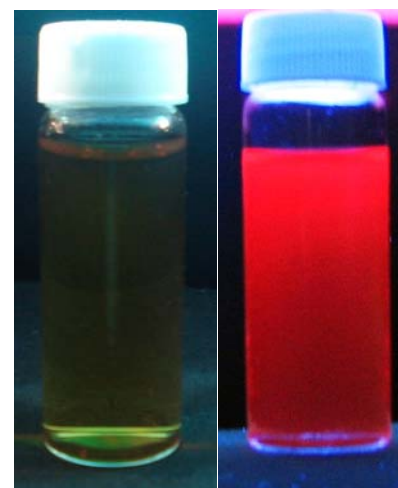
Au_8SG_8



Organic soluble red emitting clusters

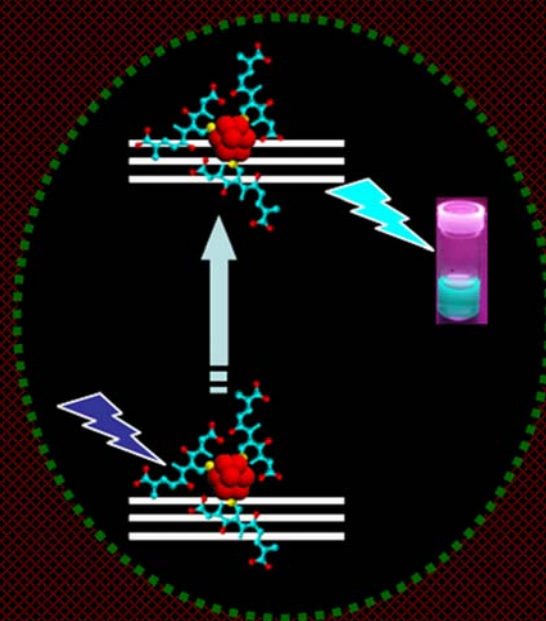


Water soluble red emitting clusters

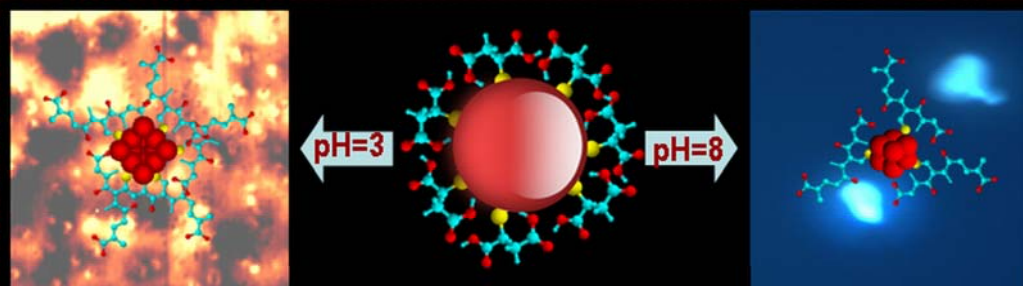


PAGE image of Au_8SG_8 cluster

Two Different Fluorescent Quantum Clusters of Gold in Gram
Quantities from Metallic Nanoparticle

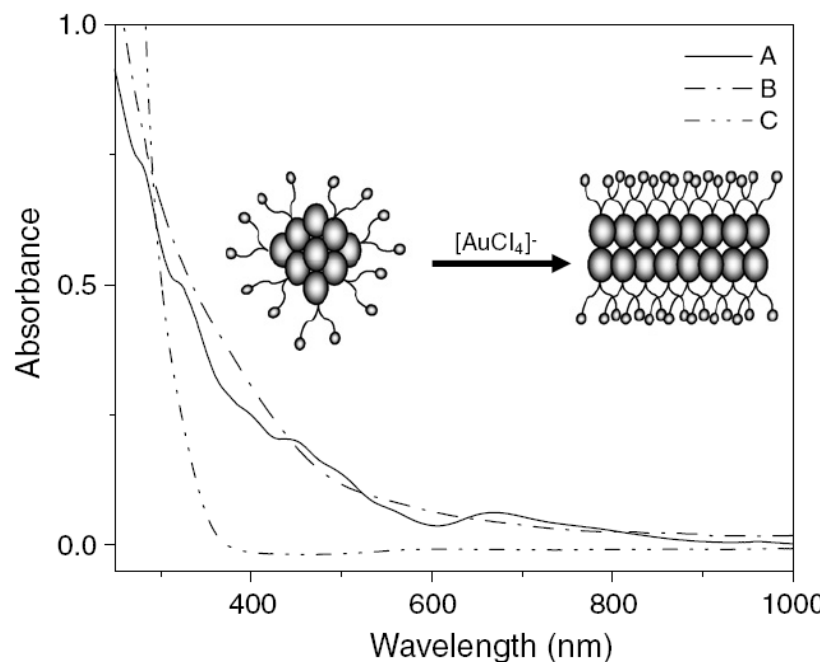


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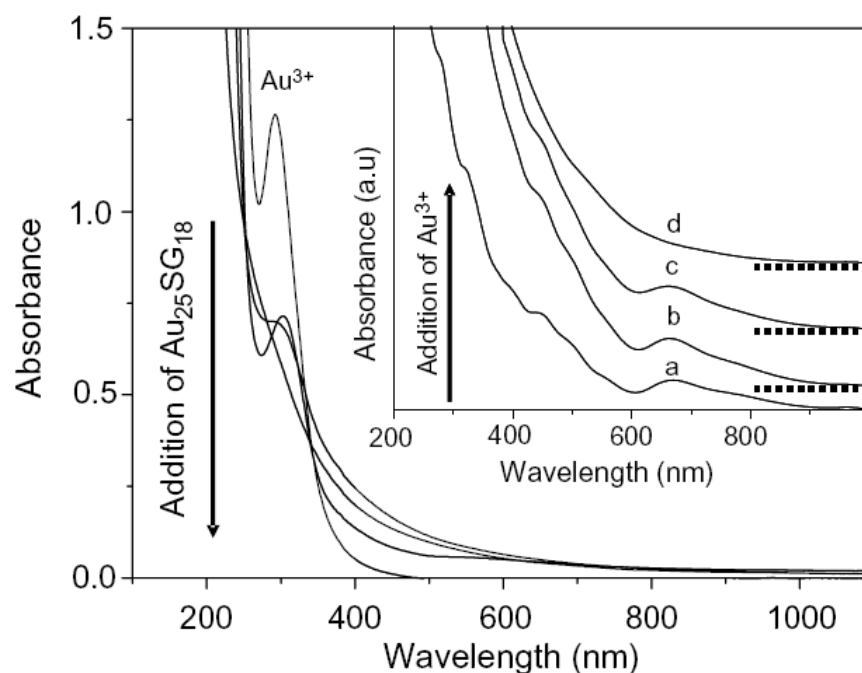


Reactivity and Applications of Molecular Clusters

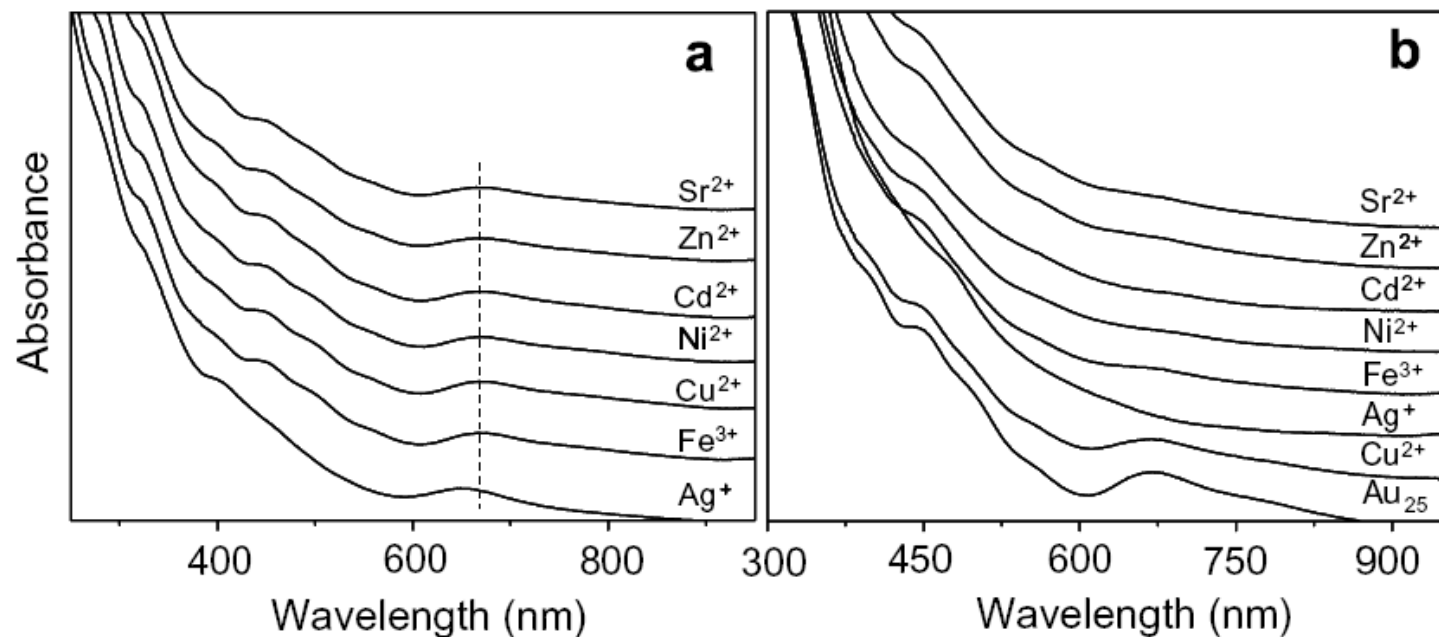
Reactivity of Au₂₅



Optical absorption spectra of (A) Au₂₅SG₁₈ cluster, (B) after adding 50 μM AuCl₄⁻ ions to the cluster and (C) the synthesized Au(I)SG polymer. The scheme (inset) represents the dissociation of the Au₂₅SG₁₈ cluster.

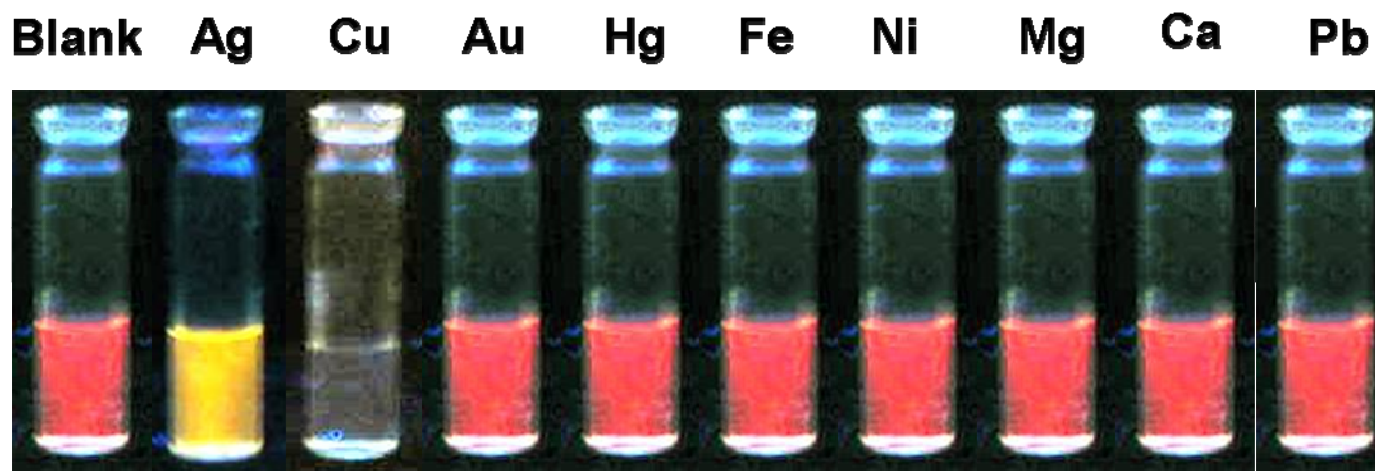


Optical absorption spectra showing the decrease in the intensity of AuCl₄⁻ peak proving that gold ions added are used up and the small cluster is converting to (Au-SG)_m polymer. Inset shows the progress of the reaction when Au³⁺ is added.



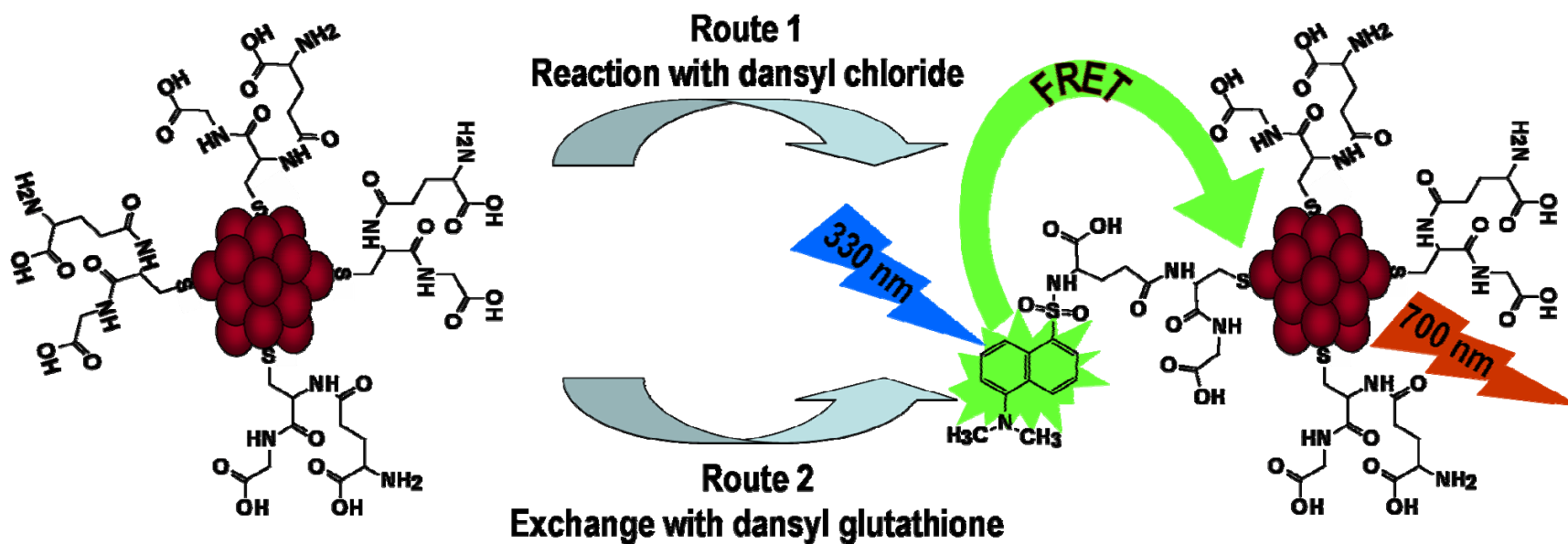
Optical spectra showing the reactivity of the cluster in the presence of various metal ions. (A) Immediately after adding metal ions and (B) after two days of incubation. Note that, the cluster is most stable in the presence of Cu²⁺.

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.

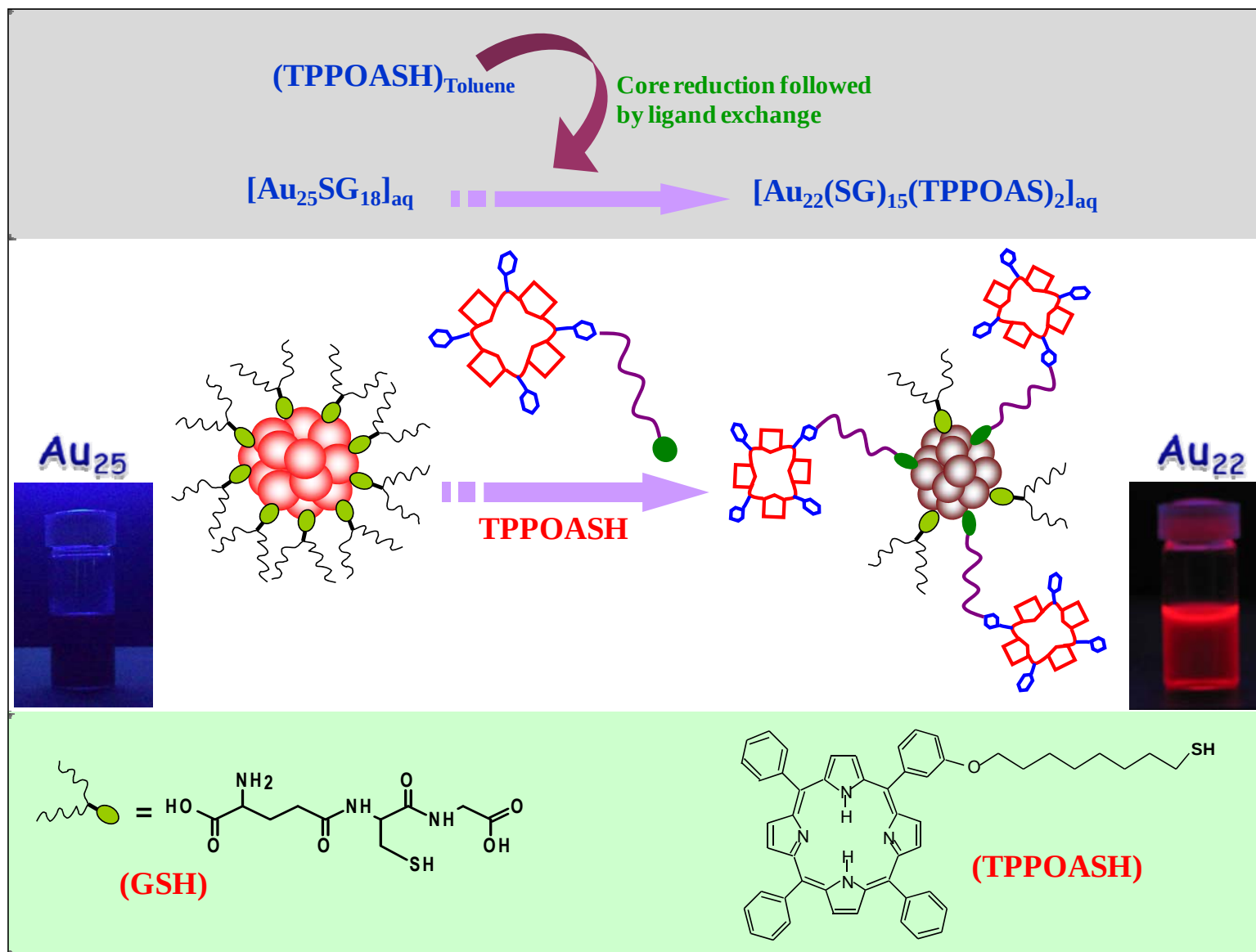
FRET between Au₂₅ and Dansyl Chromophore

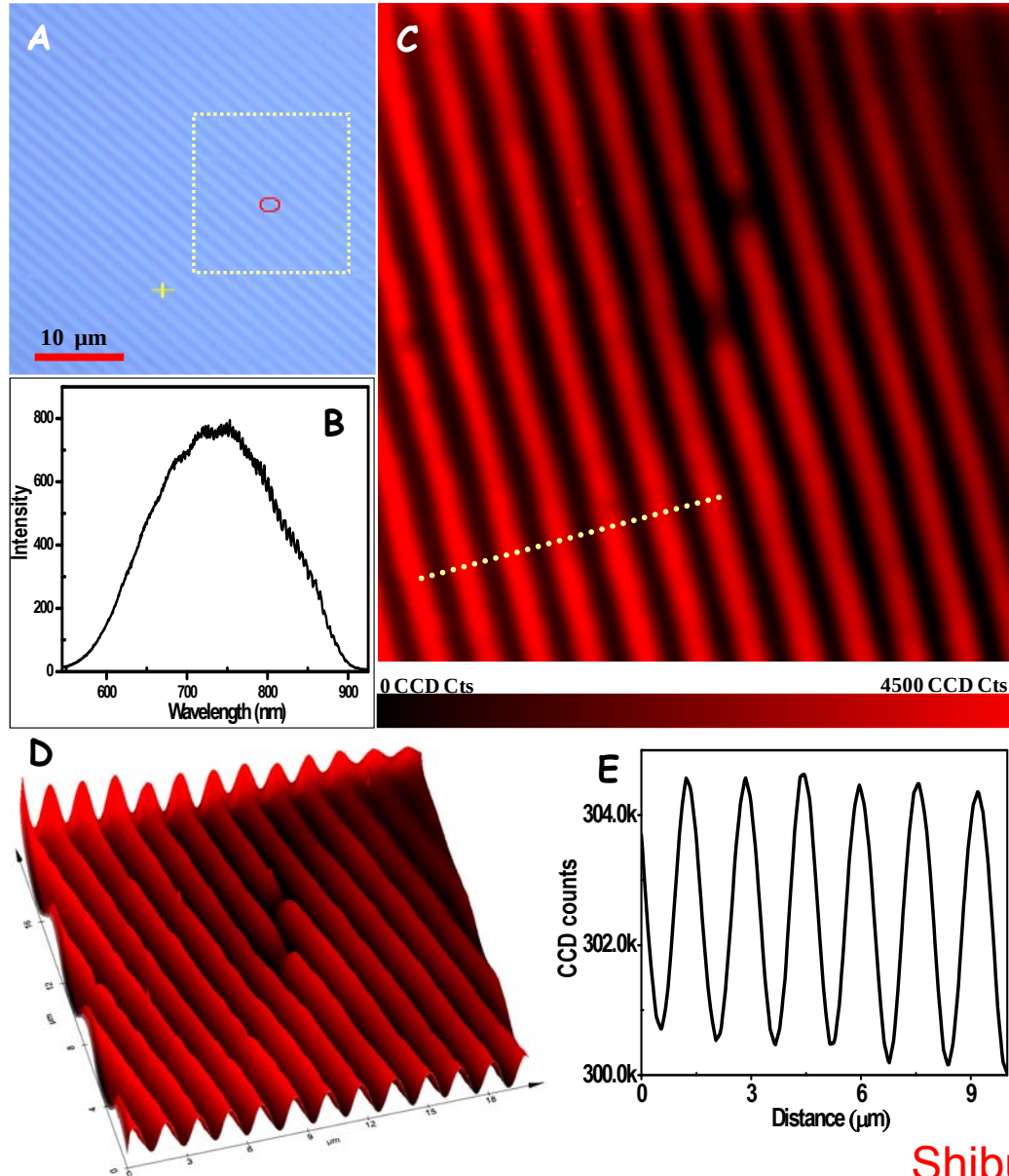


Approaches Used for the Functionalization of Dansyl Chromophore on the Au₂₅ Cluster.

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

Functionlized clusters





Shibu et al. Submitted

Silver clusters

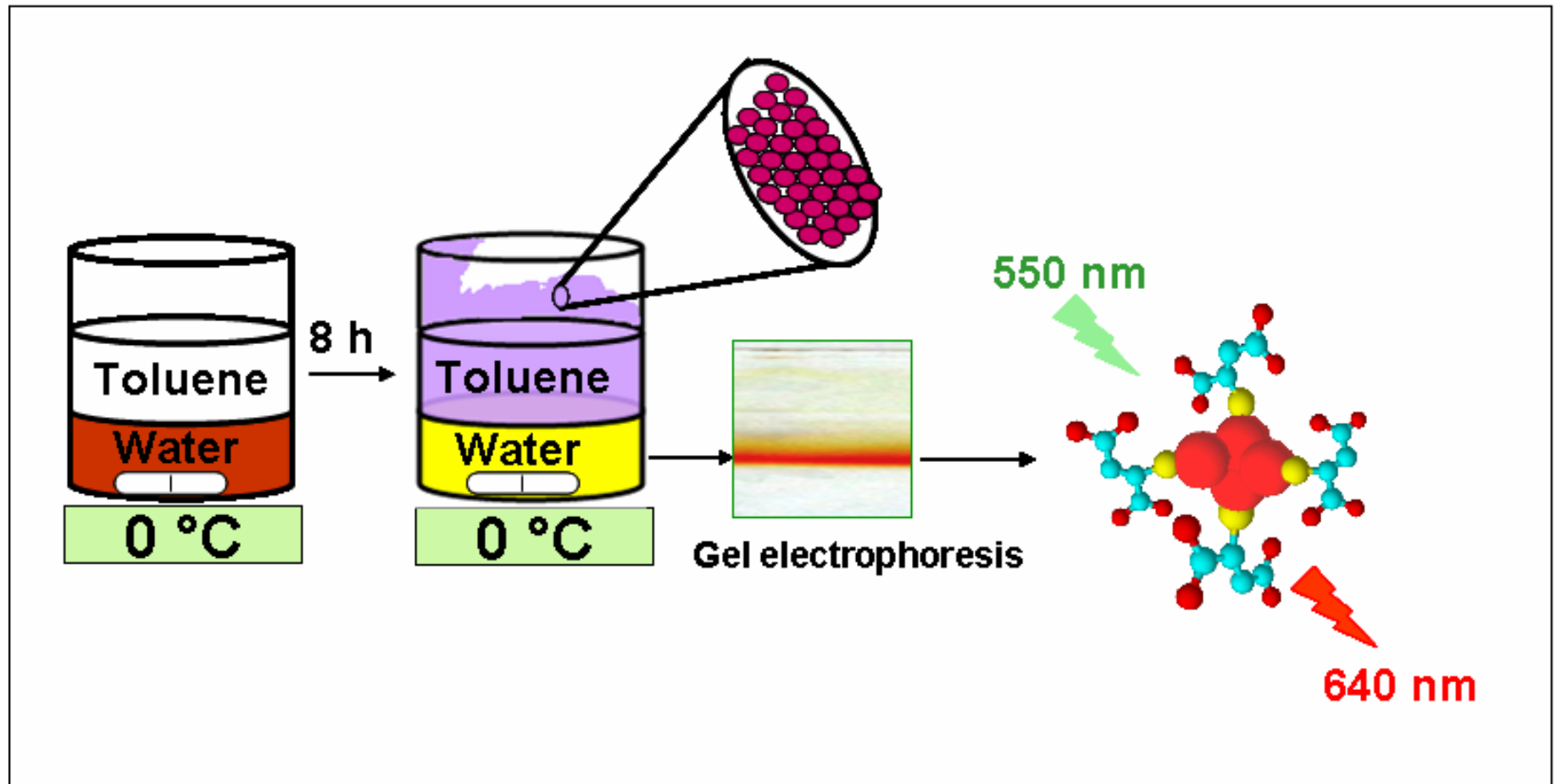
Size selected metal clusters

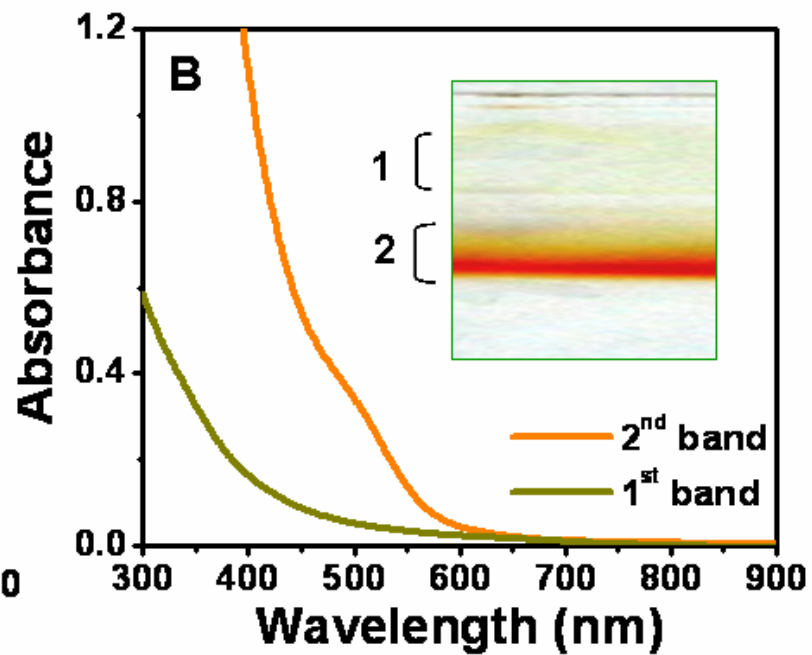
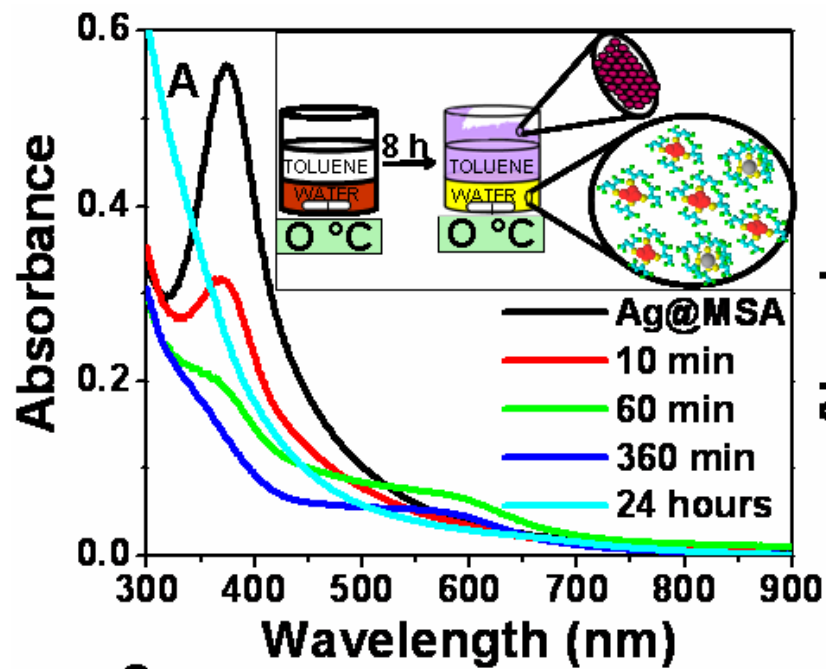
- The Optical Absorption Spectra of Small **Silver Clusters** (5-11) Embedded in Argon Matrices. Harbich, W.; Fedrigo, S.; Buttet, J. *Chem. Phys. Lett.* **1992**, 195, 613
- Soft Landing and Fragmentation of Small Clusters Deposited in Noble-Gas Films. Harbich, W.; Fedrigo, S.; Buttet, J. *Phys. Rev. B* **1998**, 58, 7428
- CO combustion on supported gold clusters. Arenz M, Landman U, Heiz U. *Chemphyschem* **2006**, 7, 1871
- Charging effects on bonding and catalyzed oxidation of CO on Au-8 clusters on MgO. Yoon, B.; Hakkinen, H, Landman, U.; Worz, A.S.; Antonietti, J. M.; Abbet, S, Heiz, U
- 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

Recent studies

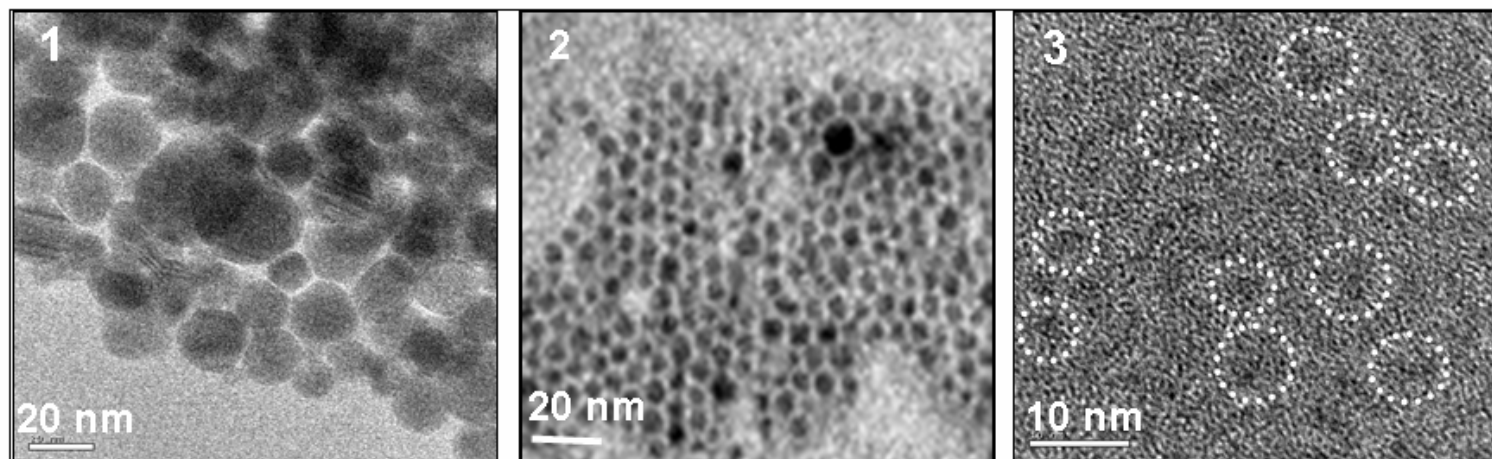
- **Structural and Functional Characterization of Luminescent Silver-Protein Nanobioconjugates.** Narayanan, S. S.; Pal, S. K. *J. Phys. Chem. C* **2008**, *112*, 4874
- **Sensitized emission from a chemotherapeutic drug conjugated to CdSe/ZnS QDs.** Narayanan, S. S.; Pal, S. K. *J. Phys. Chem. C* **2008**, *112*, 12716
- **In search of a structural model for a thiolate-protected Au-38 cluster.** Jiang, D. E, Luo, W, Tiago, M. L, Dai, S. *J. Phys. Chem. C* **2008**, *112*, 13905
- **Preparation and characterization of dendrimer-templated Ag-Cu bimetallic nanoclusters** Li, G. P.; Luo. *Inorg. Chem.* **2008**, *47*, 360
- **Stability and dissociation pathways of doped Au_nX^+ clusters ($X = Y, Er, Nb$).** Veldeman. N.; Janssens, E.; Hansen K. *Faraday Discussions* **2008**, *138* 147
- **From discrete electronic states to plasmons: TDDFT optical absorption properties of $Ag-n$ ($n = 10, 20, 35, 56, 84, 120$) tetrahedral clusters.** Aikens, C. M.; Li, S. Z; Schatz, G. C. *J. Phys. Chem. C* **2008** *112*, 11272

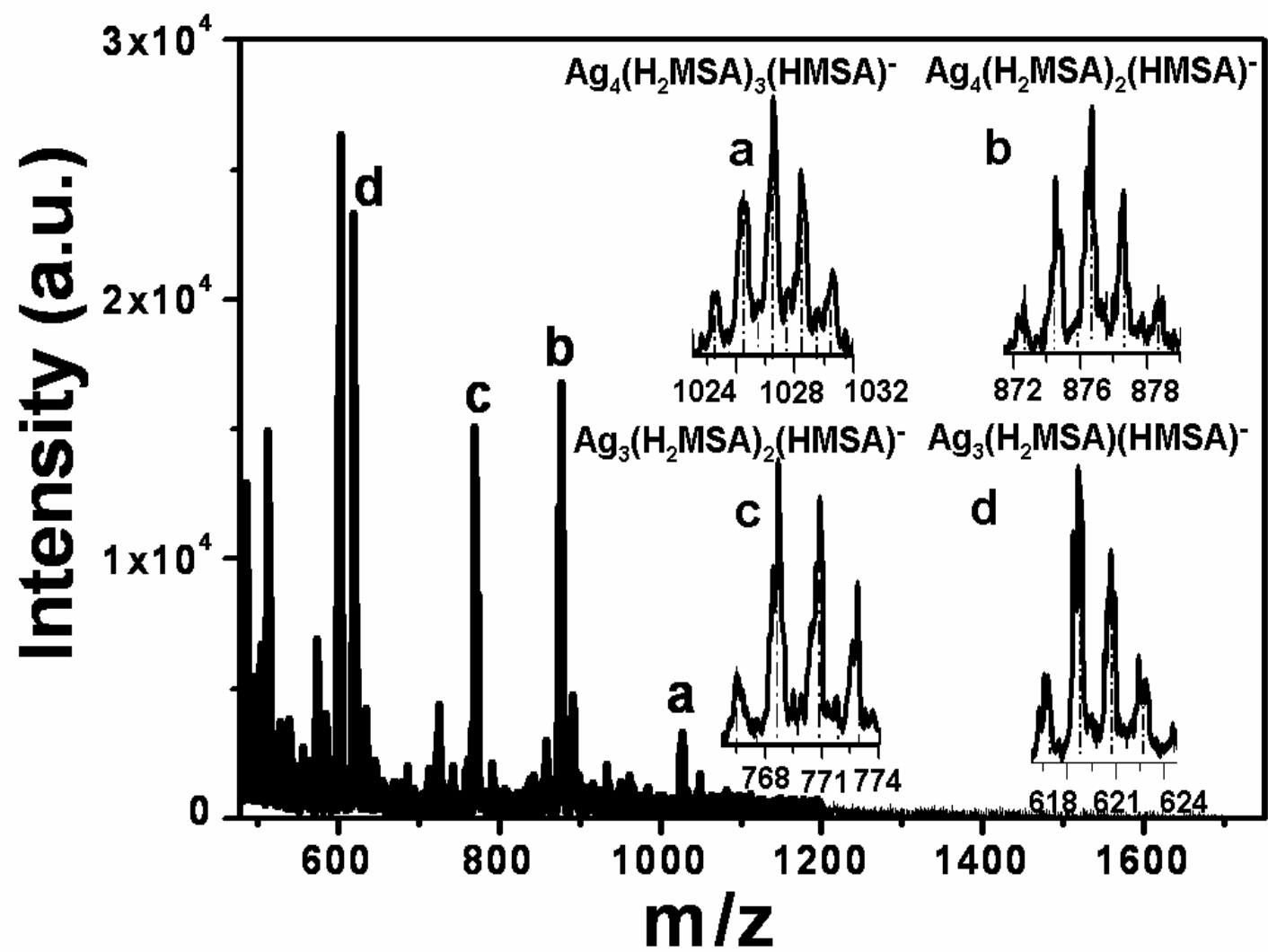
Interfacial etching

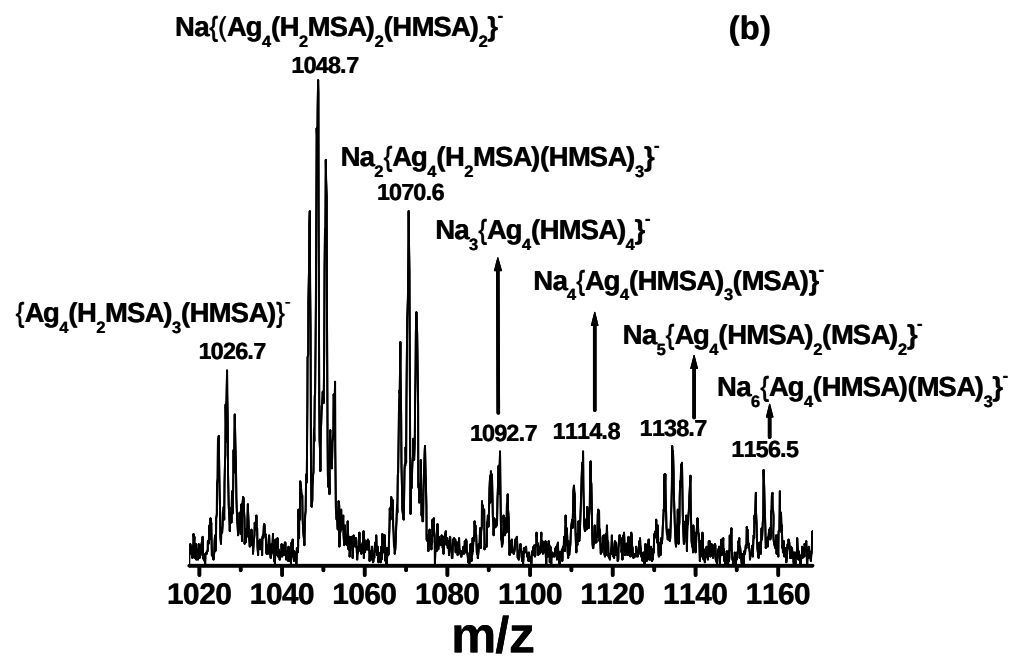
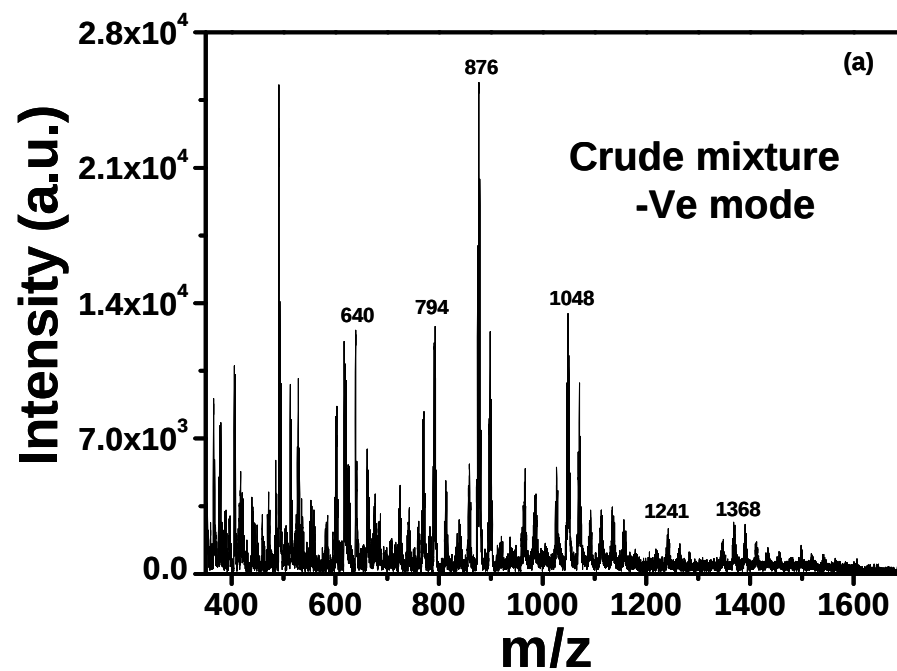


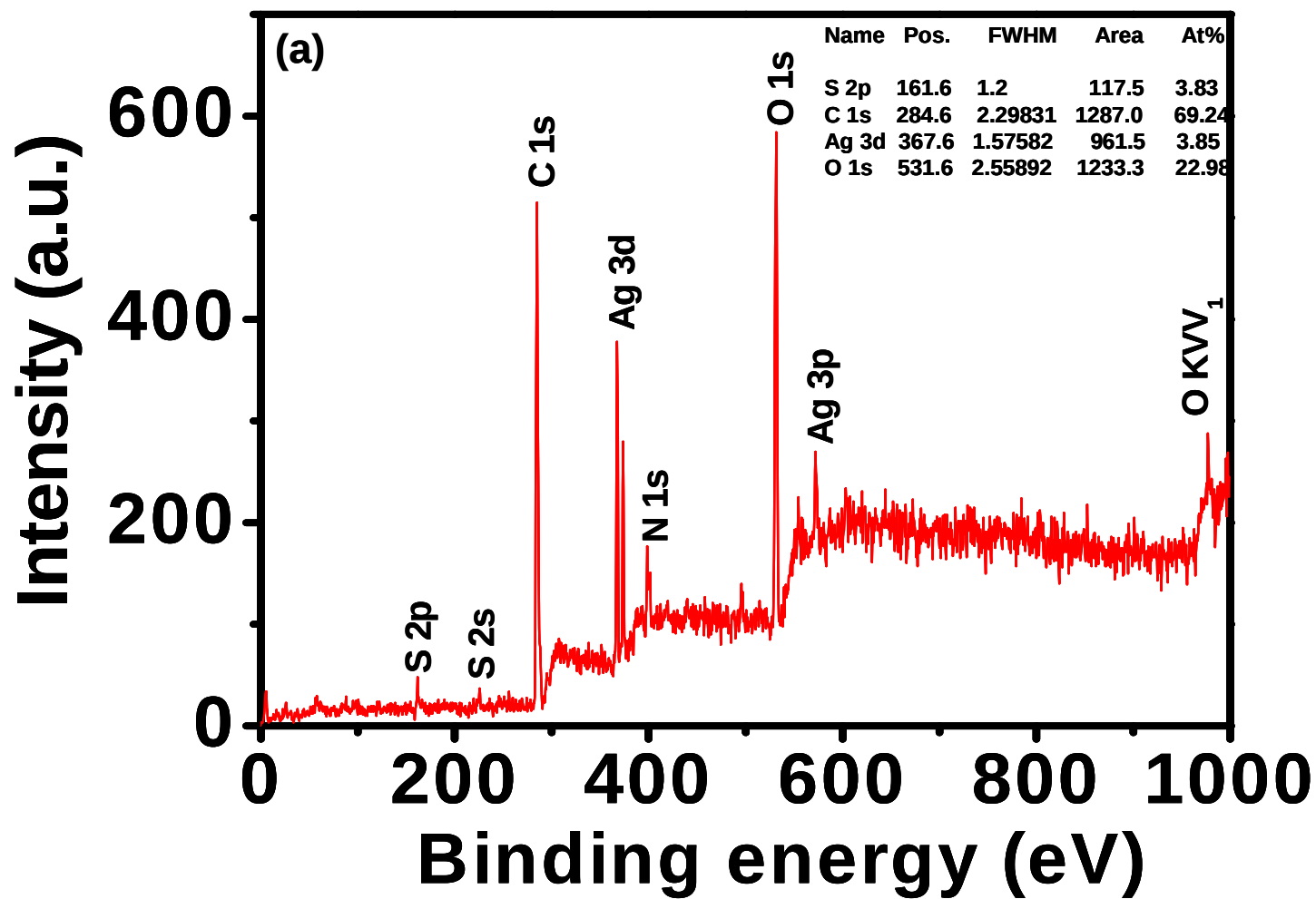


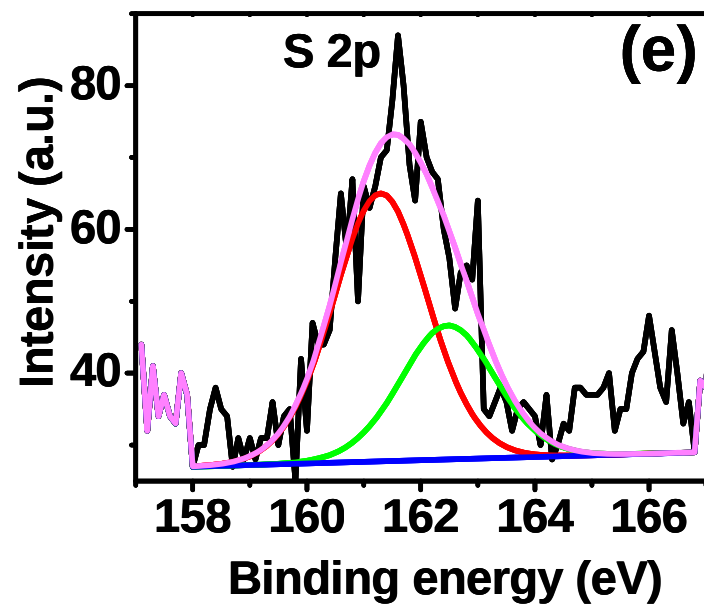
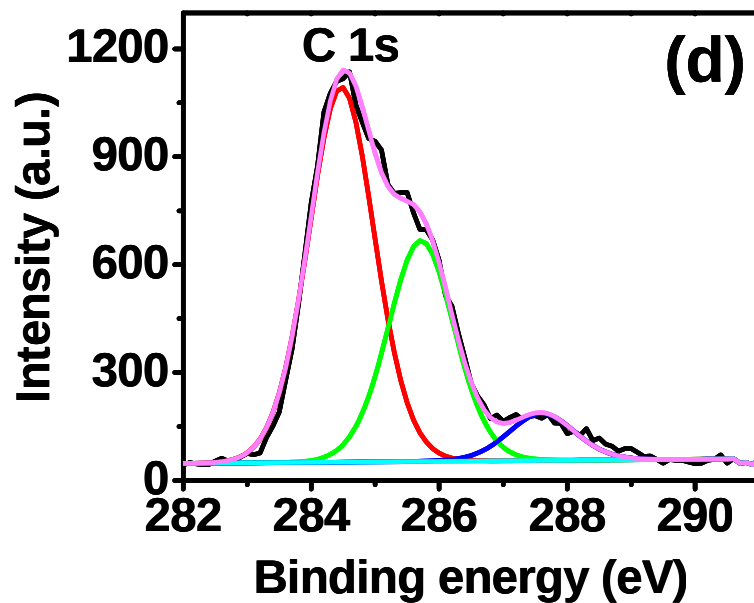
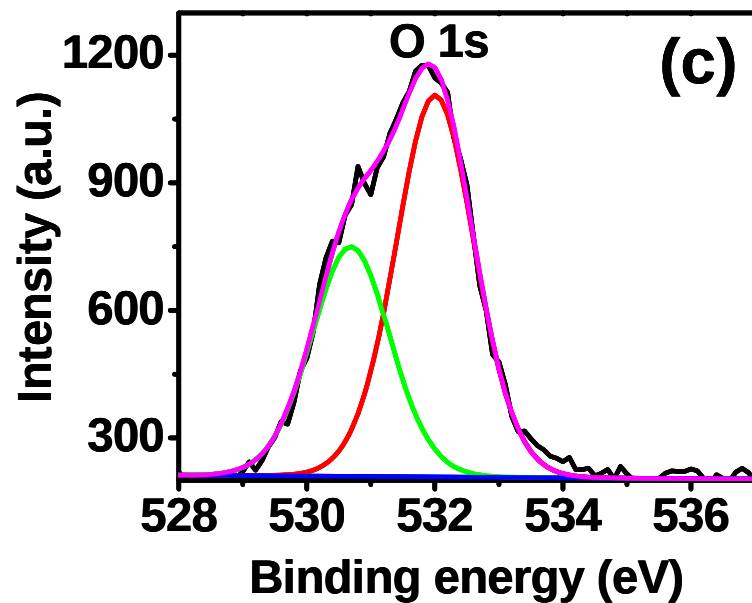
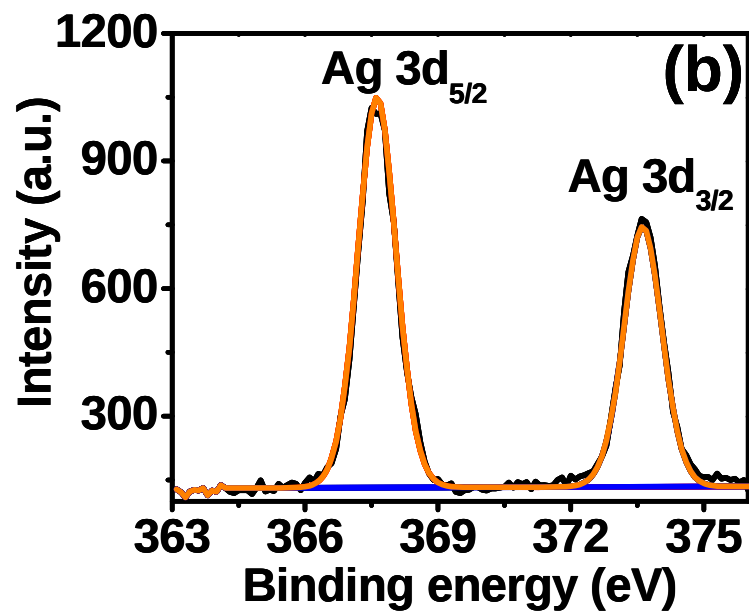
C

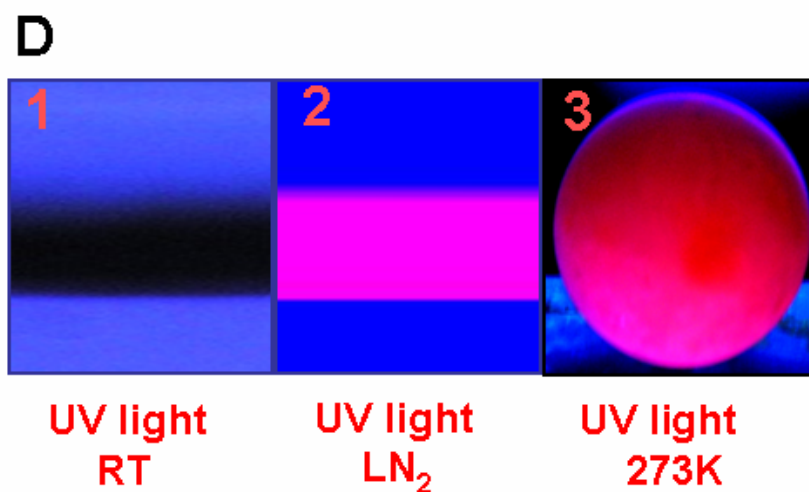
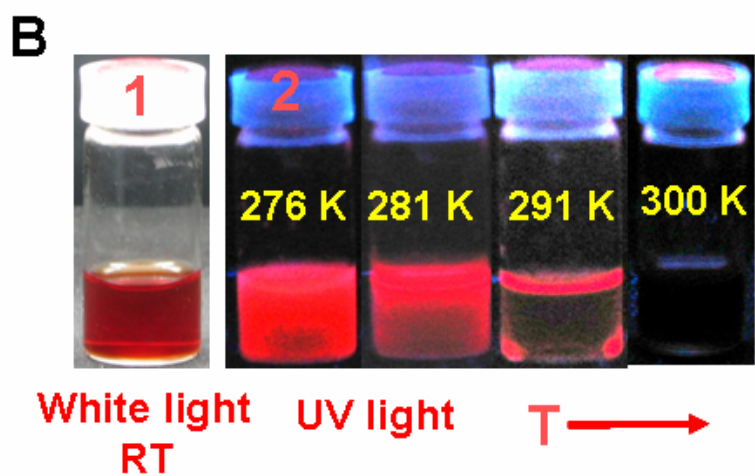
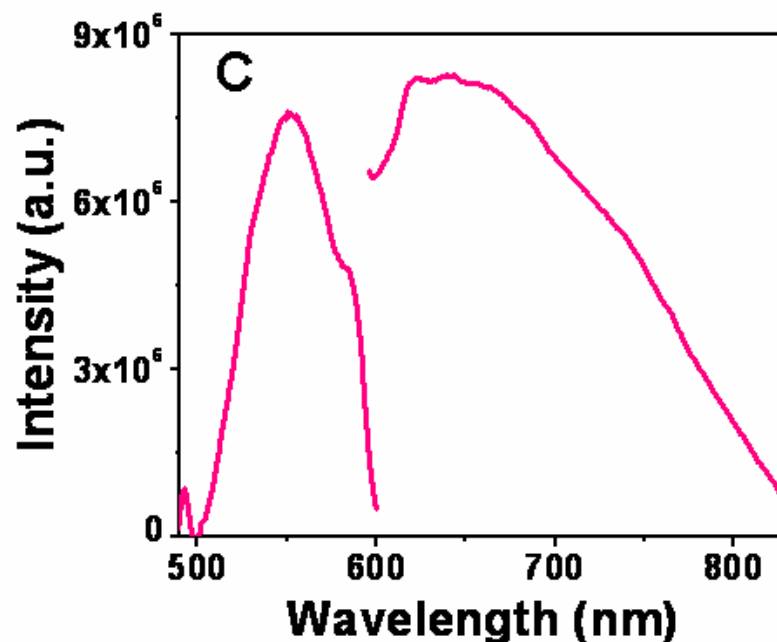
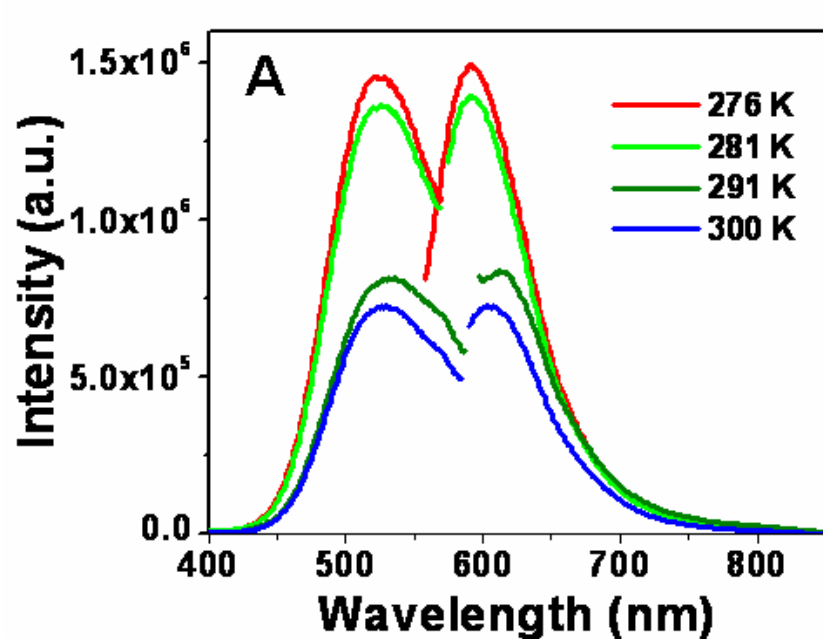


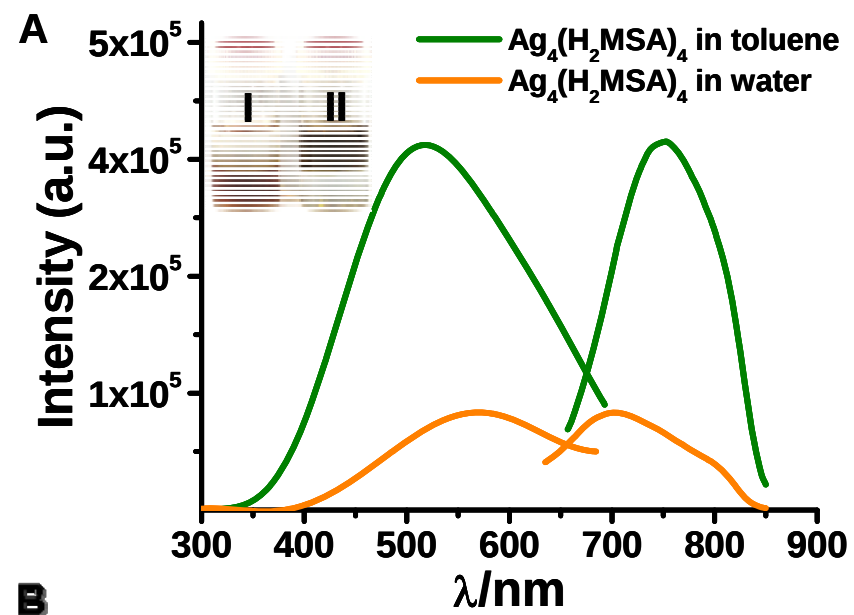




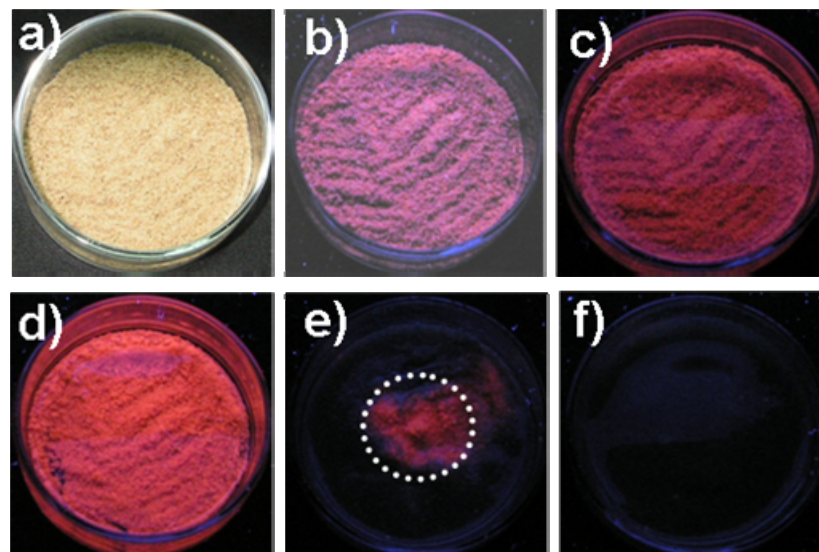


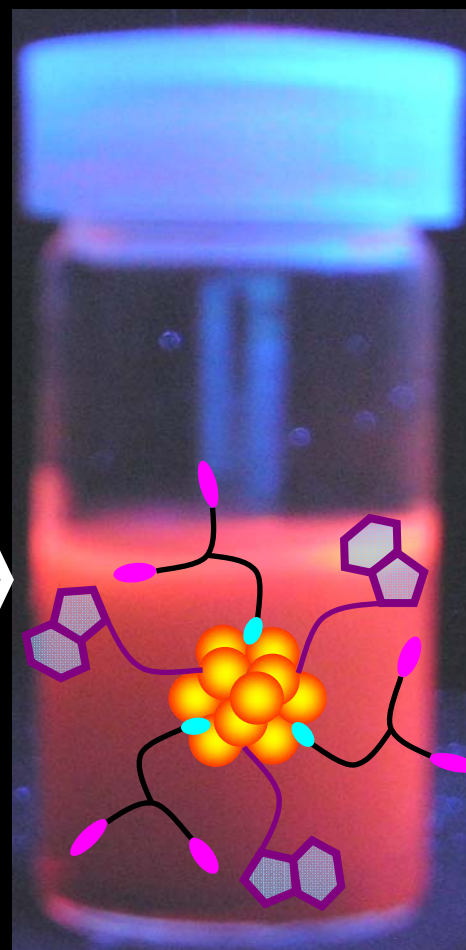
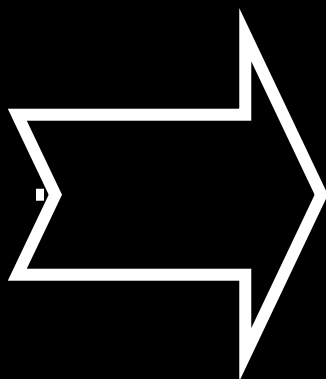
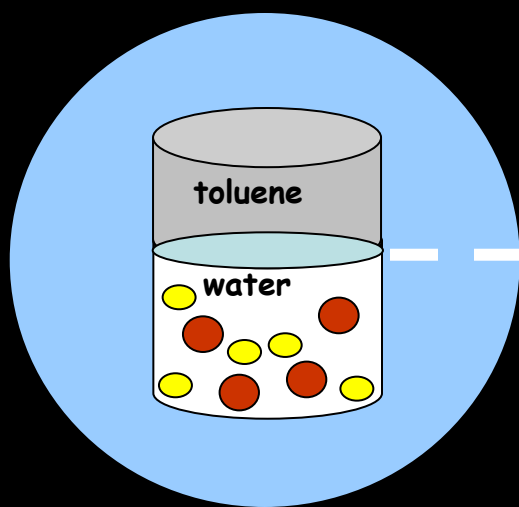


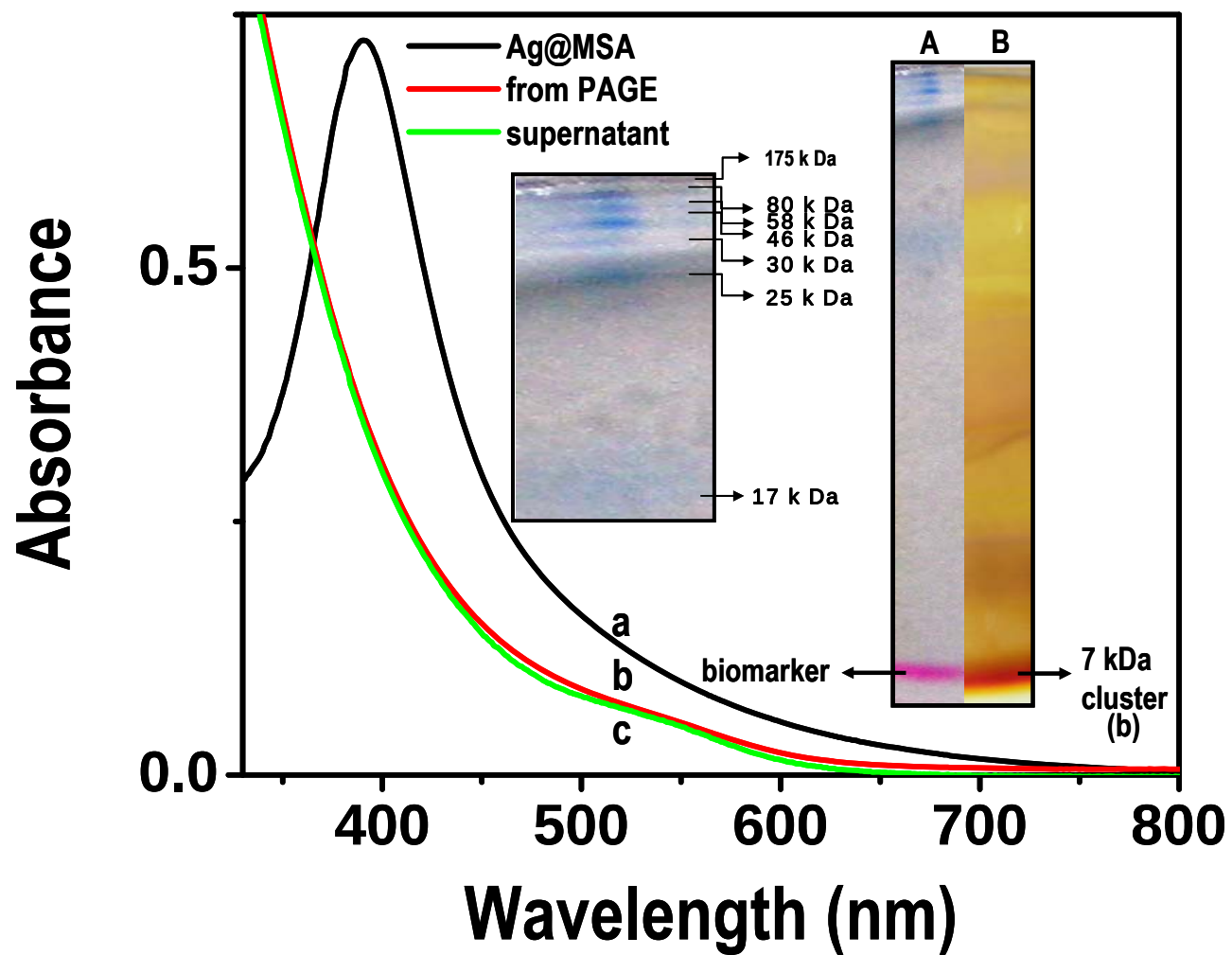




B







Ongoing....

Quantum clusters and white light

Applications in cell imaging

Metal and molecular detection

Crystallisation.....

To summarise....

Quantum clusters are made in gram quantities.

The optical properties in the visible region are largely due to the metal core.

New clusters, Au_8SG_8 , Ag_4MSA_4 , Au_{22} , $\text{Au}_{23}\text{SG}_{17}$, etc. are synthesised.

They show temperature dependent emission, metal ion sensing, FRET, etc.

Interfacial synthesis offers new possibilities for quantum clusters.

A variety of new properties are being explored.



Nano Mission, Department of Science and Technology



IIT Madras



Thank you all