Celebrating 50 years

Sub-nanometer light emitting quantum clusters of gold and silver

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

G O L D 2 0 0 9 Heidelberg July 26-29, 2009

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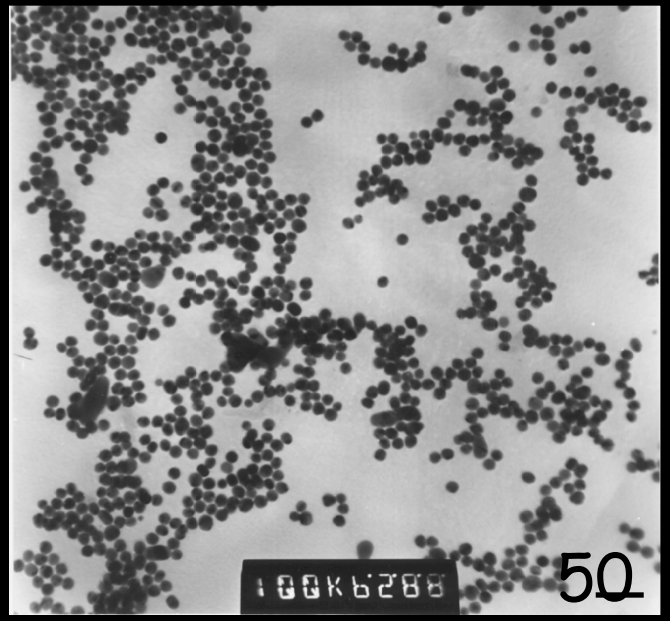
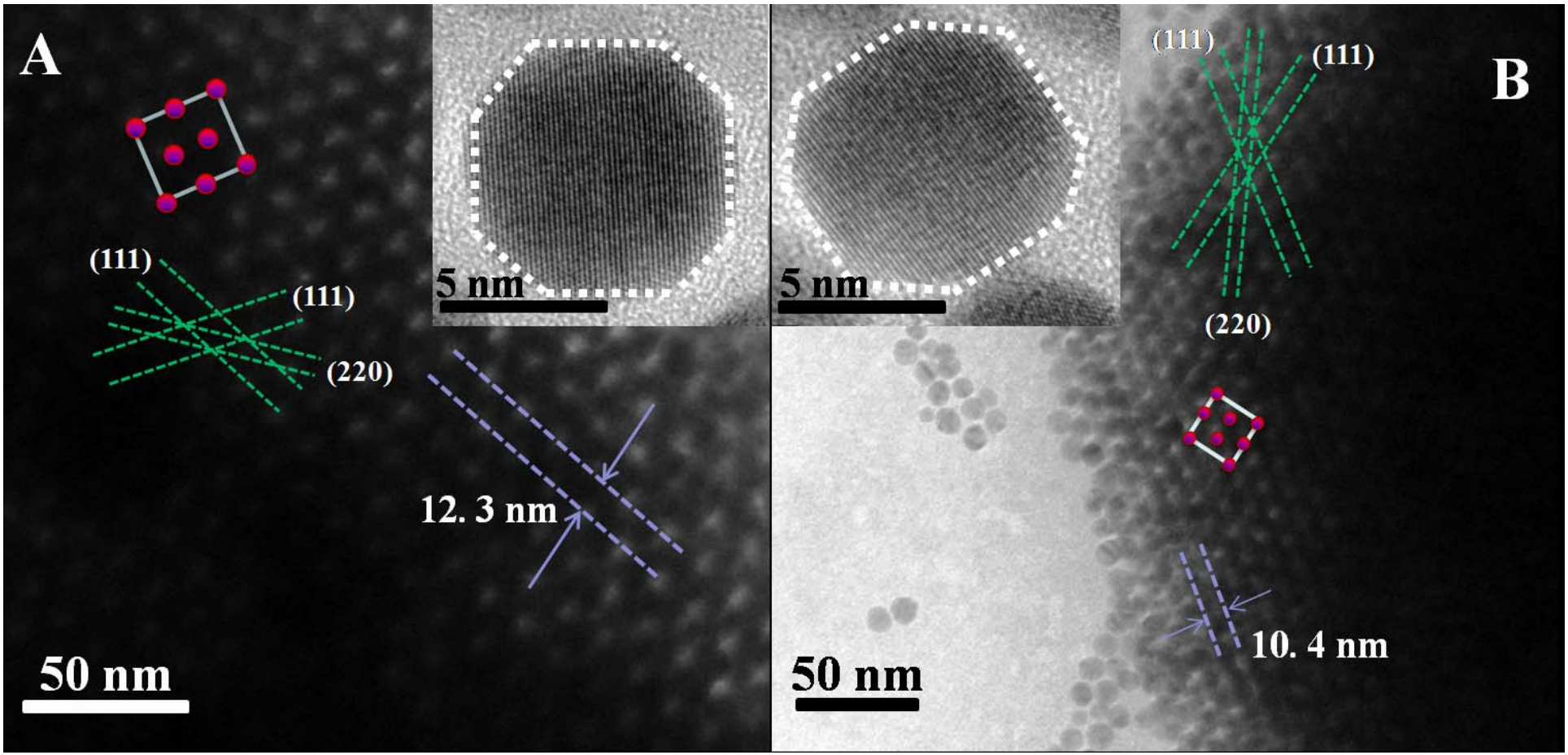
Nano Mission, Department of Science and Technology

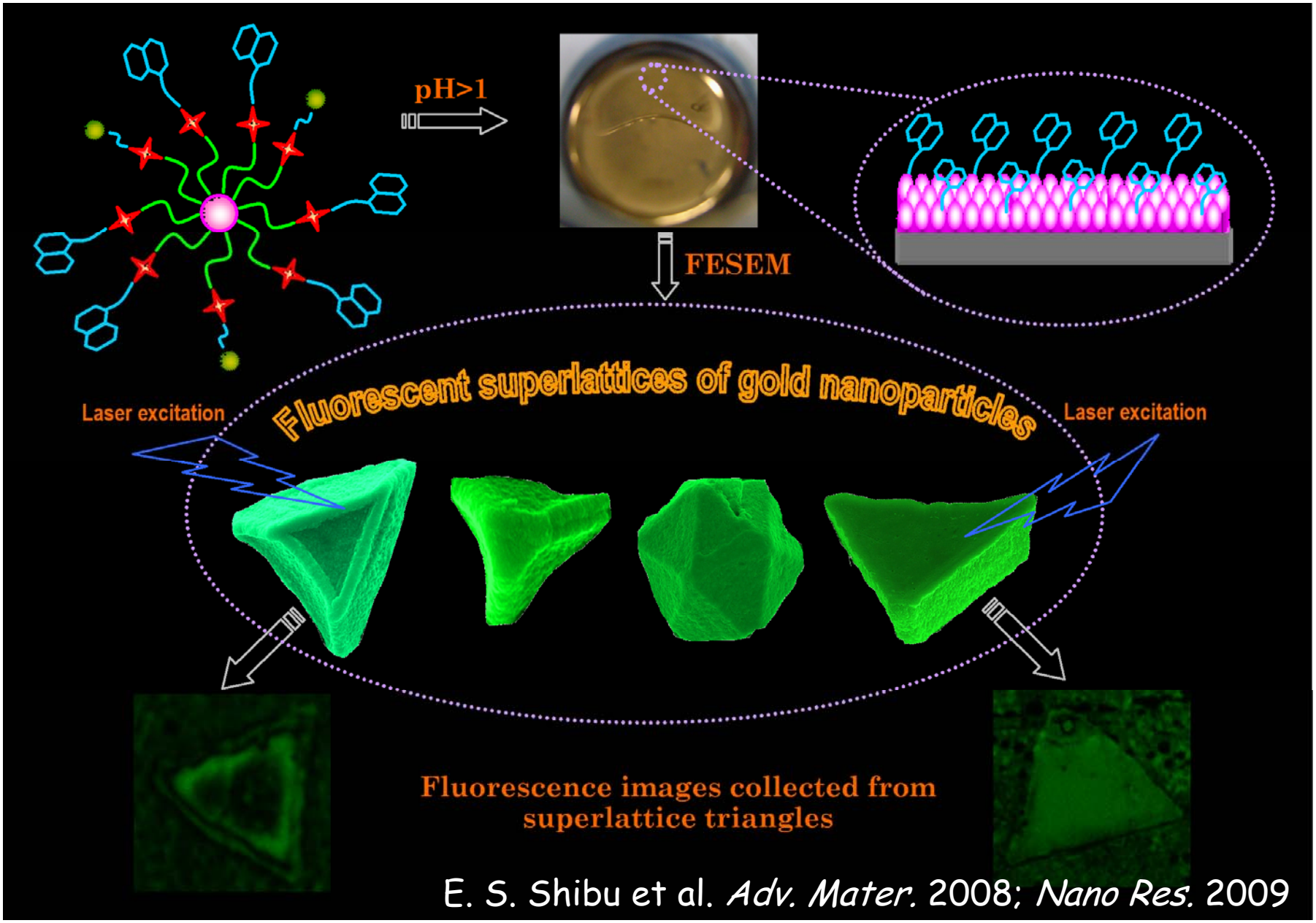


Faraday's gold preserved in Royal Institution. From the site, http://www.rigb.org/rimain/heritage/faradaypage.jsp



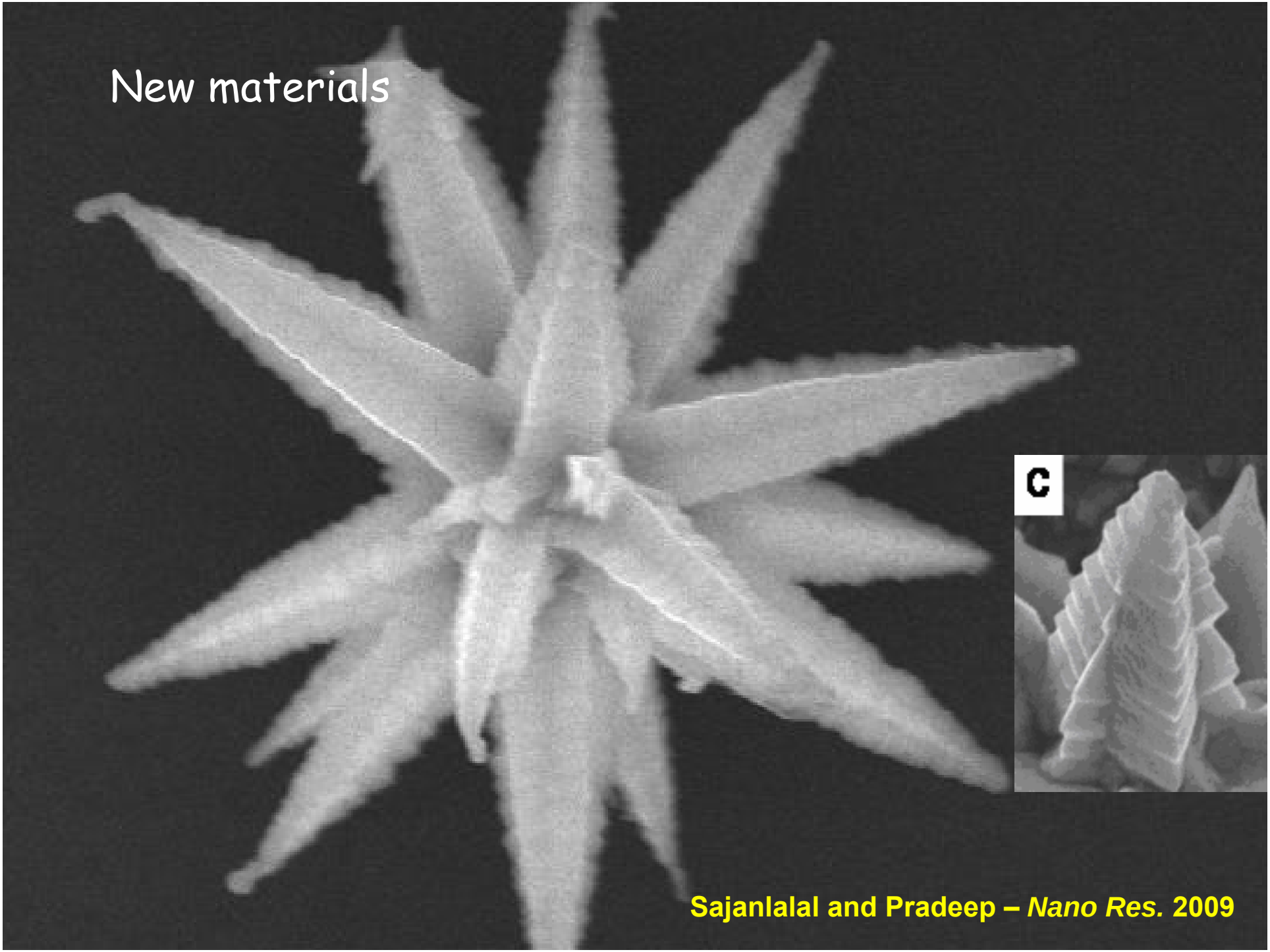
E. S. Shibu et al. Chem. Mater. 2009 (In Press)

Fluorescent superlattices

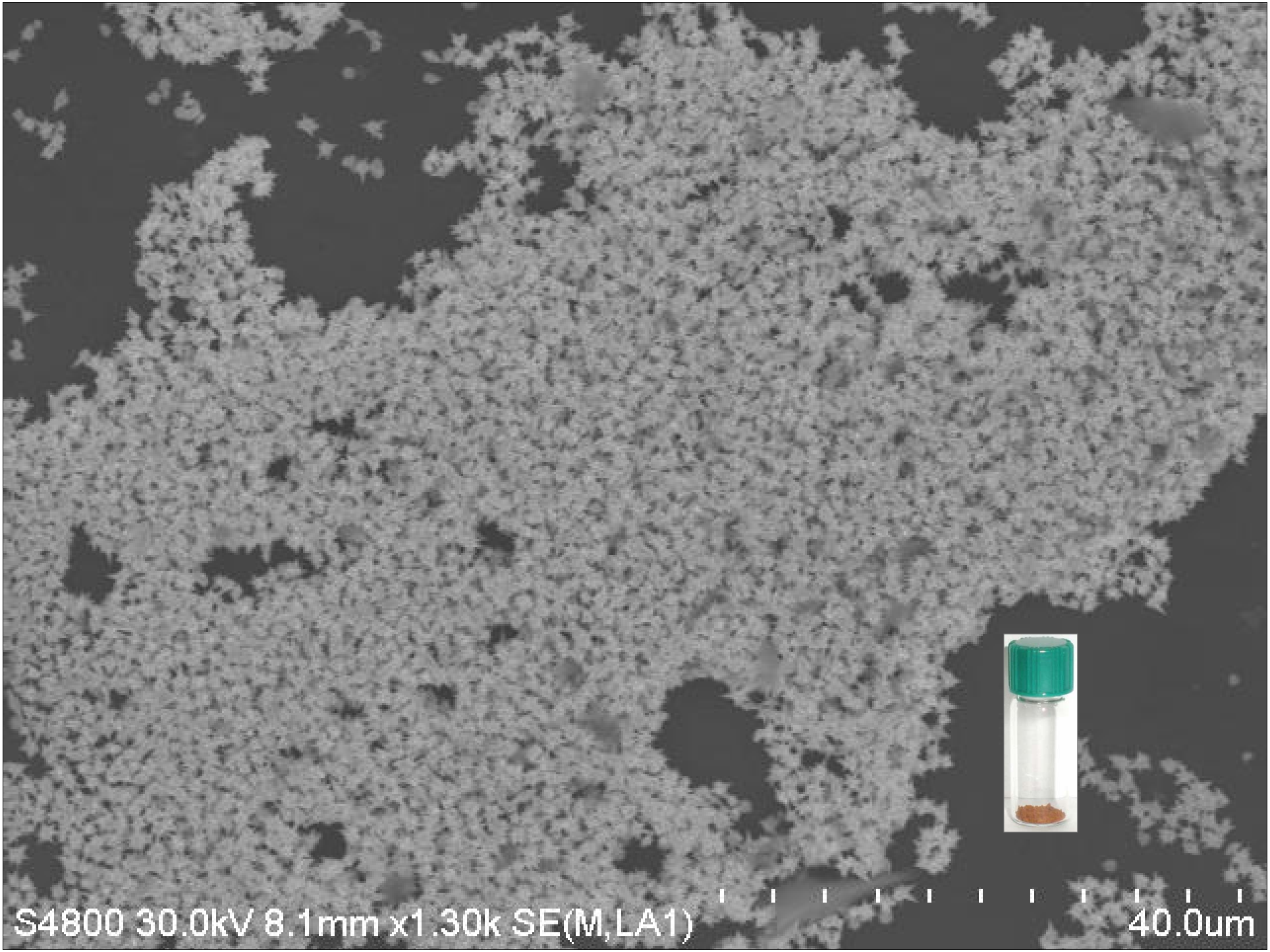


E. S. Shibu et al. *Adv. Mater.* 2008; *Nano Res.* 2009

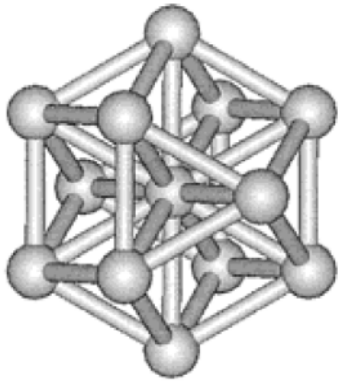
New materials



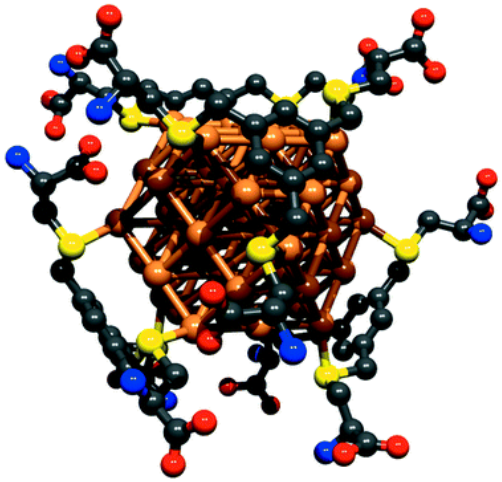
Sajanlalal and Pradeep – *Nano Res.* 2009


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

Gold clusters



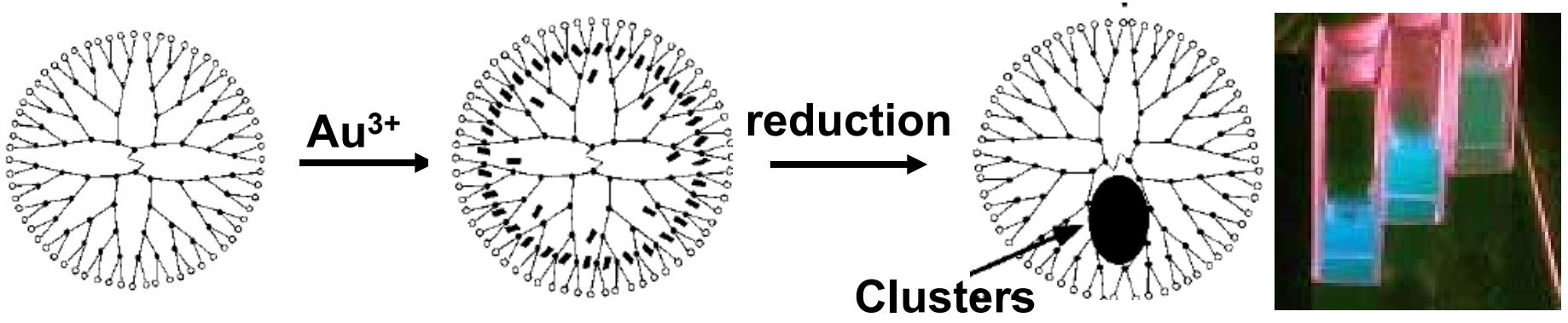
Au_{13}



Au_{55}

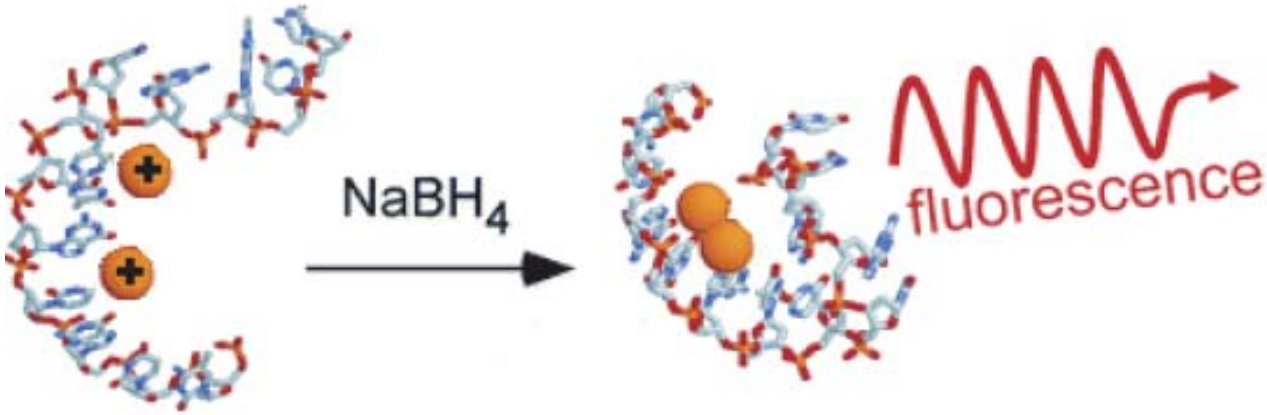
- **Au_{55} $[P(C_6H_5)_3]_{12}Cl_6$ - a gold cluster of unusual size,** Schmid, G.; Pfeil, R.; Boese, R.; Brandermann, F.; Meyer, S.; Calis, G. H. M.; Van der Velden.; Jan W. A. *Chemische Berichte* **1981**, *114*, 3634.
- **Synthesis and x-ray structural characterization of the centered icosahedral 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.

Dendrimer encapsulated clusters

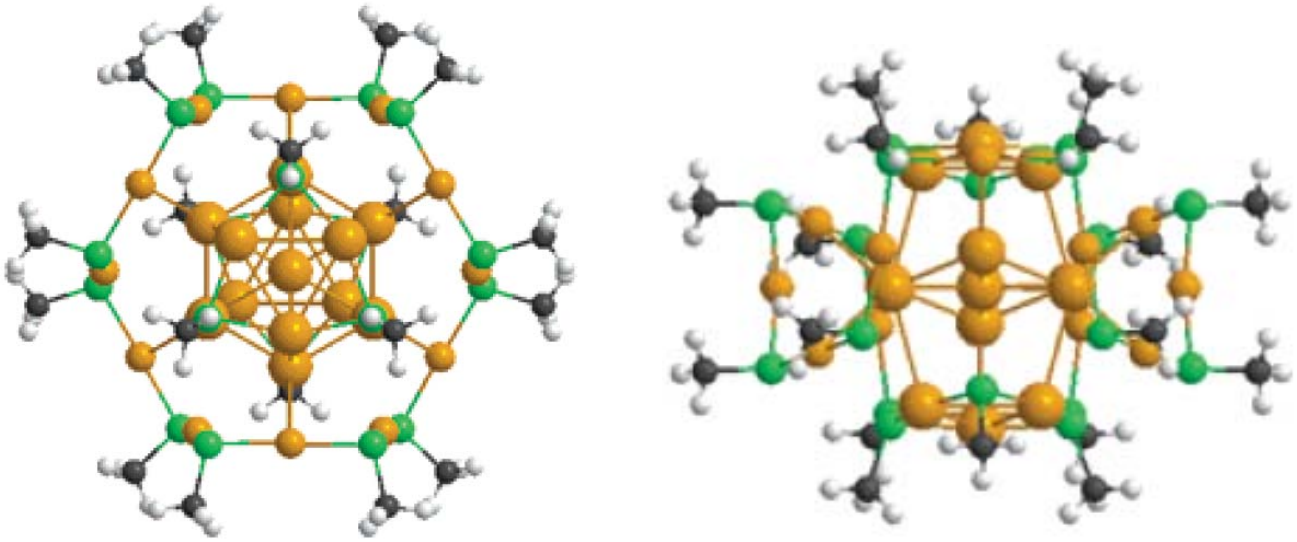


- **High quantum yield blue emission from water-soluble Au_8 nanodots**, Zheng, J.; Petty, J. T.; Dickson, R. M. *J. Am. Chem. Soc*. **2003**, *125*, 7780.
- **Highly fluorescent, water-soluble, size-tunable gold quantum dots,** Zheng, J.; Zhang, C. W.; Dickson, R. M. *Phys. Rev. Lett*. **2004**, *93*,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

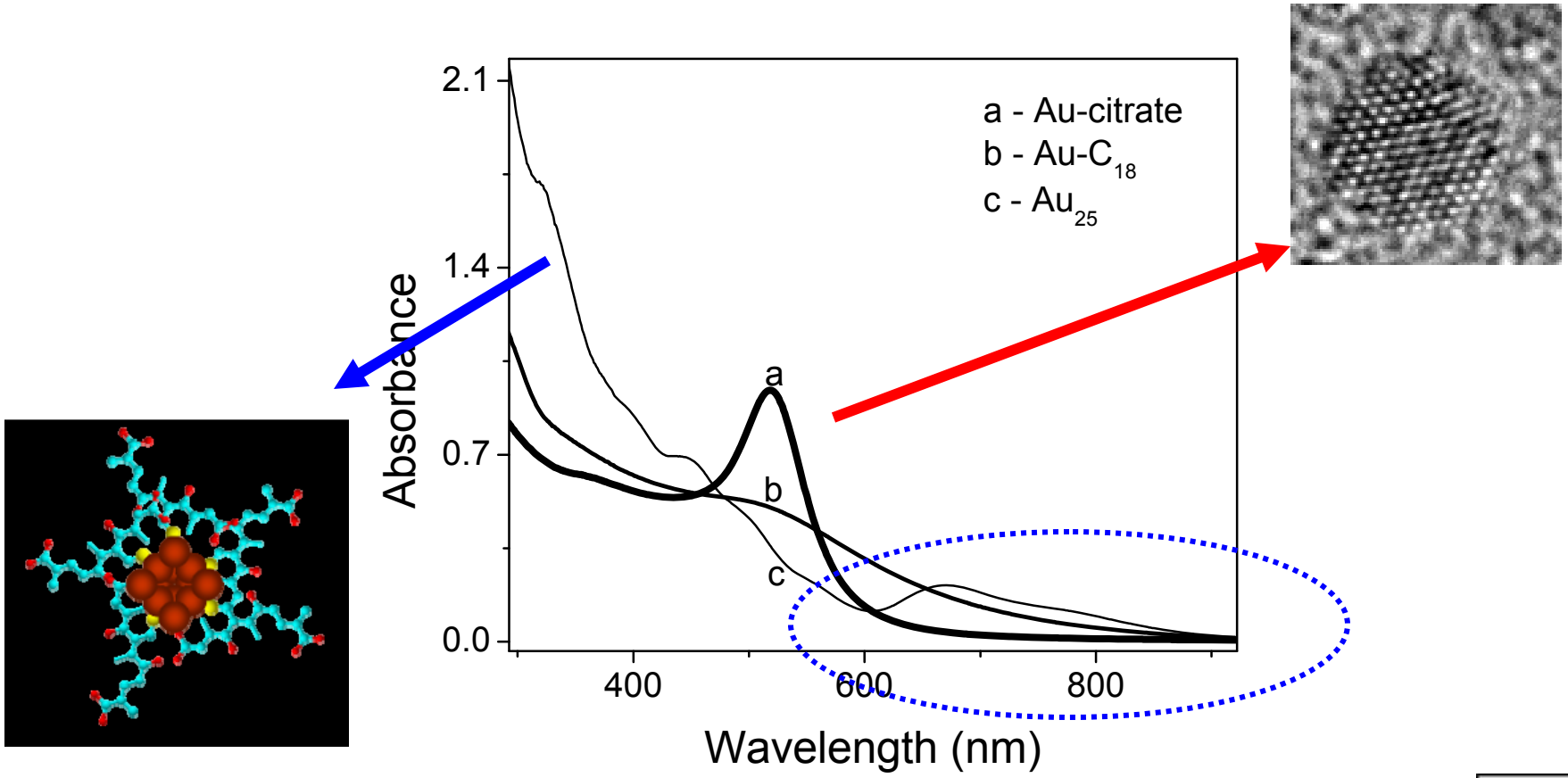


DNA-Templated Ag Nanocluster Formation, Petty, J. T.; Zheng, J.; Hud, N. V.; Dickson, R. M. *J. Am. Chem. Soc*. **2004**, *126*, 5207.

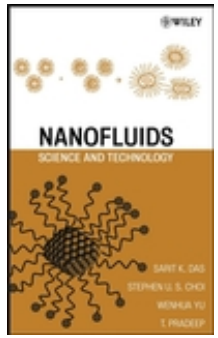


Top and side view of $[Au_{25}(SCH_3)_{18}]^+$

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.



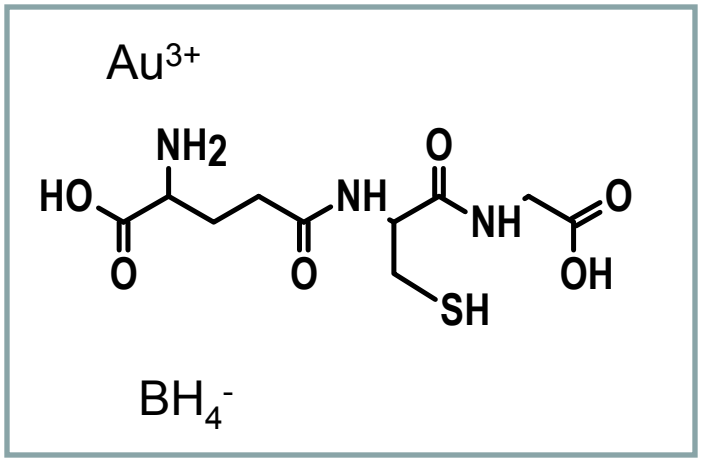
Optical absorption (extinction) spectrum of (a) 15 nm gold particles in aqueous solution (labeled Au@citrate). The spectrum of (b) 3 nm particles in toluene is also shown. See the broadening of the plasmon feature. The spectrum of (c) Au_{25} in water. In this, there is no plasmon excitation and all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

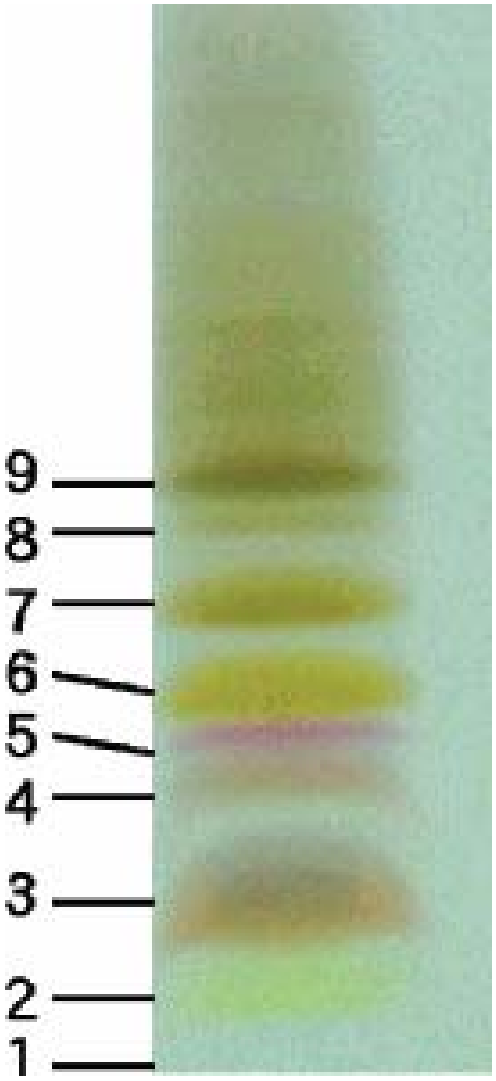


Das, Choi, Yu and Pradeep, *Nanofluids*, John Wiley, New York, 2008

Polyacrylamide gel electrophoresis (PAGE)

How to make them?



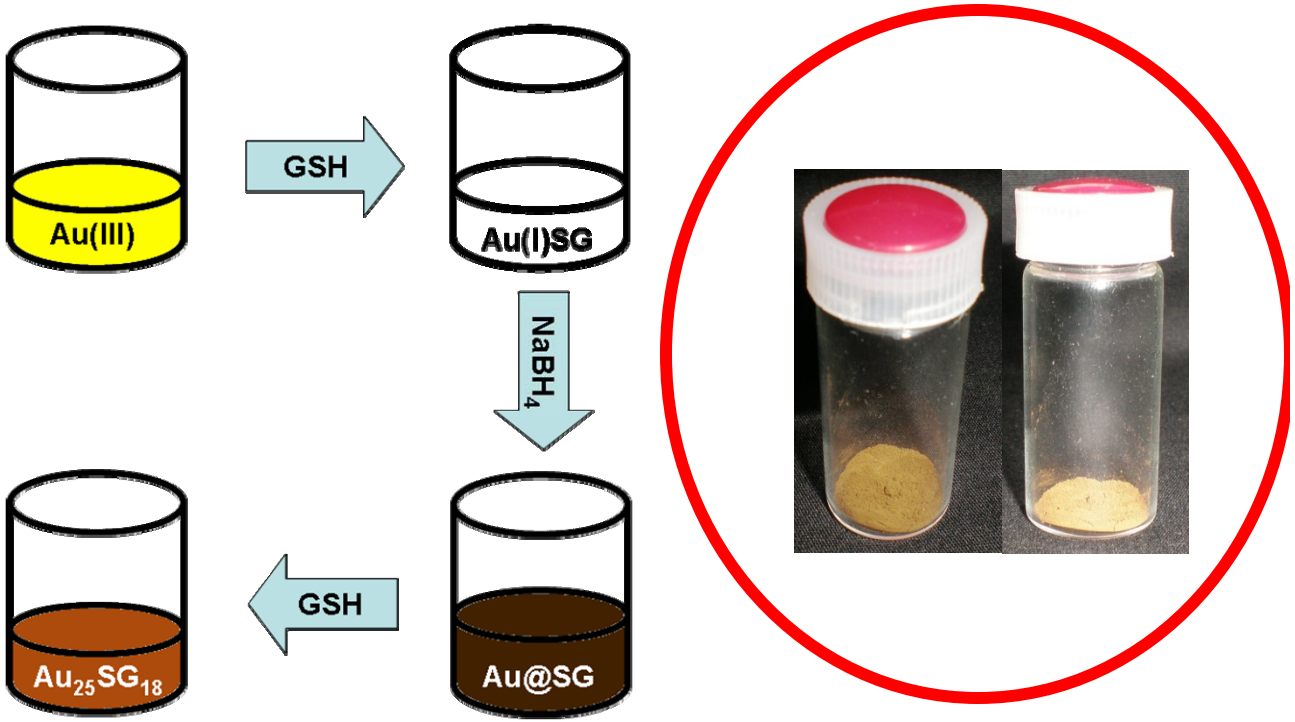


μg

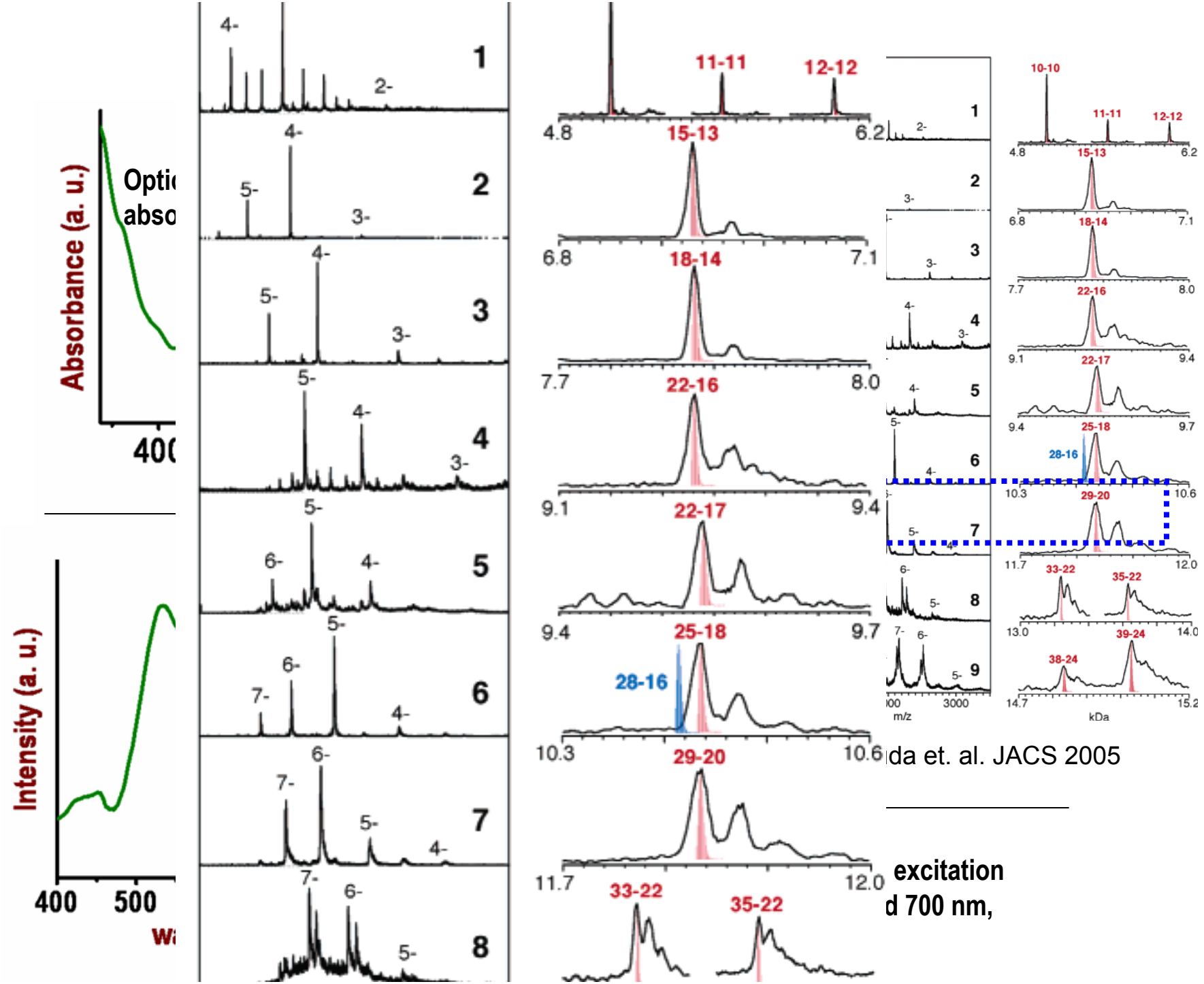
Negishi, Y.; Nobusada, K.; and Tsukuda, T. Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)-Thiolate Complexes and Thiolate-Protected Gold Nanocrystals. *J. Am. Chem. Soc*. **2005**, *127*, 5261-70.

$Au_{25}SG_{18}$

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

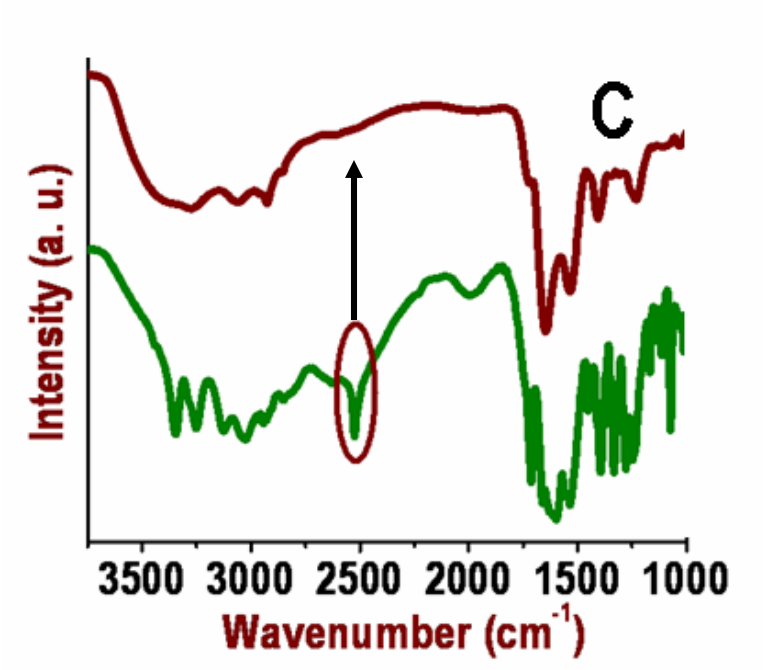


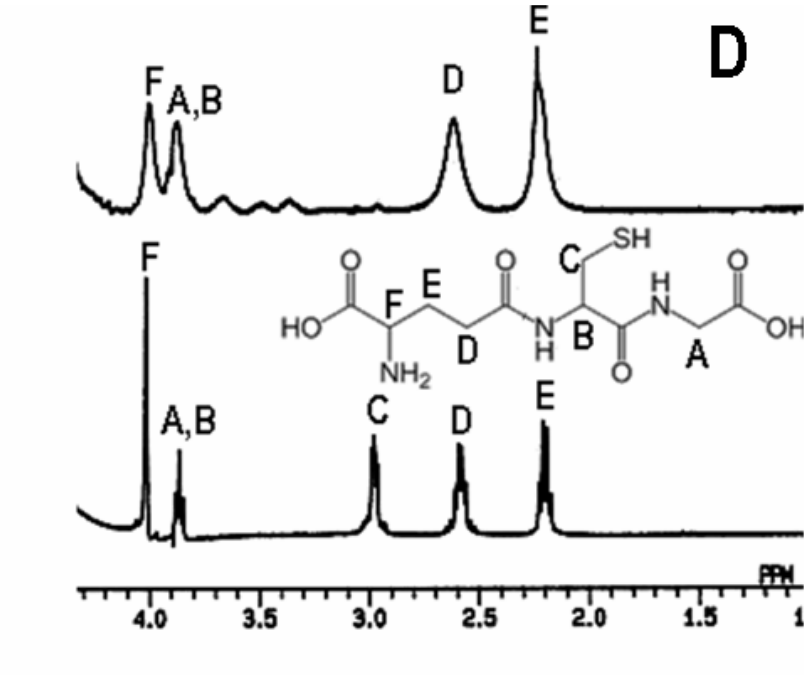
Scheme showing the synthesis of $Au_{25}SG_{18}$ clusters



da et. al. JACS 2005

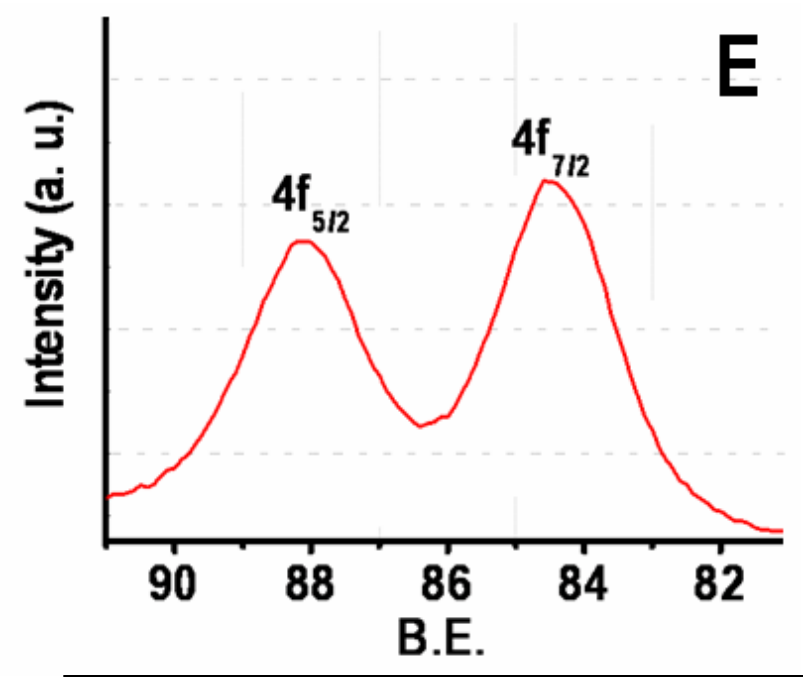
excitation
d 700 nm,



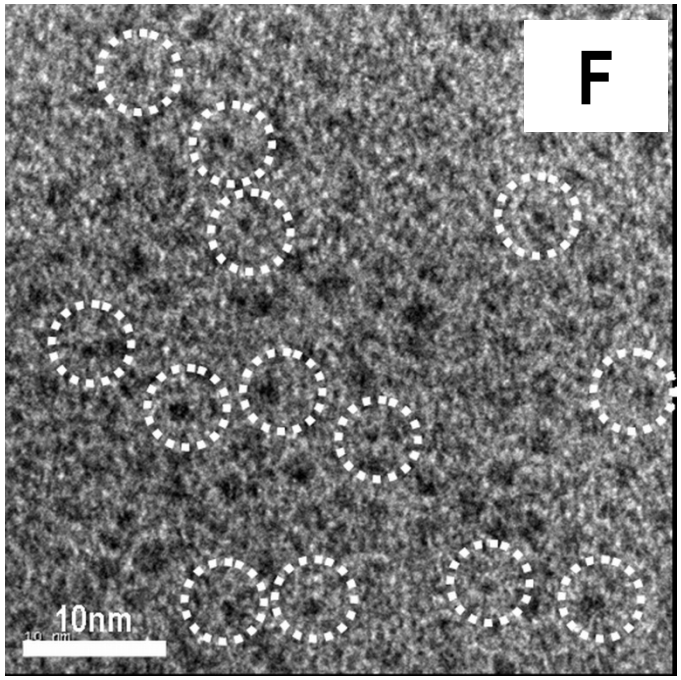


FTIR spectrum: The peak at 2526 cm^{-1} of glutathione due to –SH stretching frequency is absent in IR spectrum of Au_{25} suggesting the ligand binding on cluster surface.

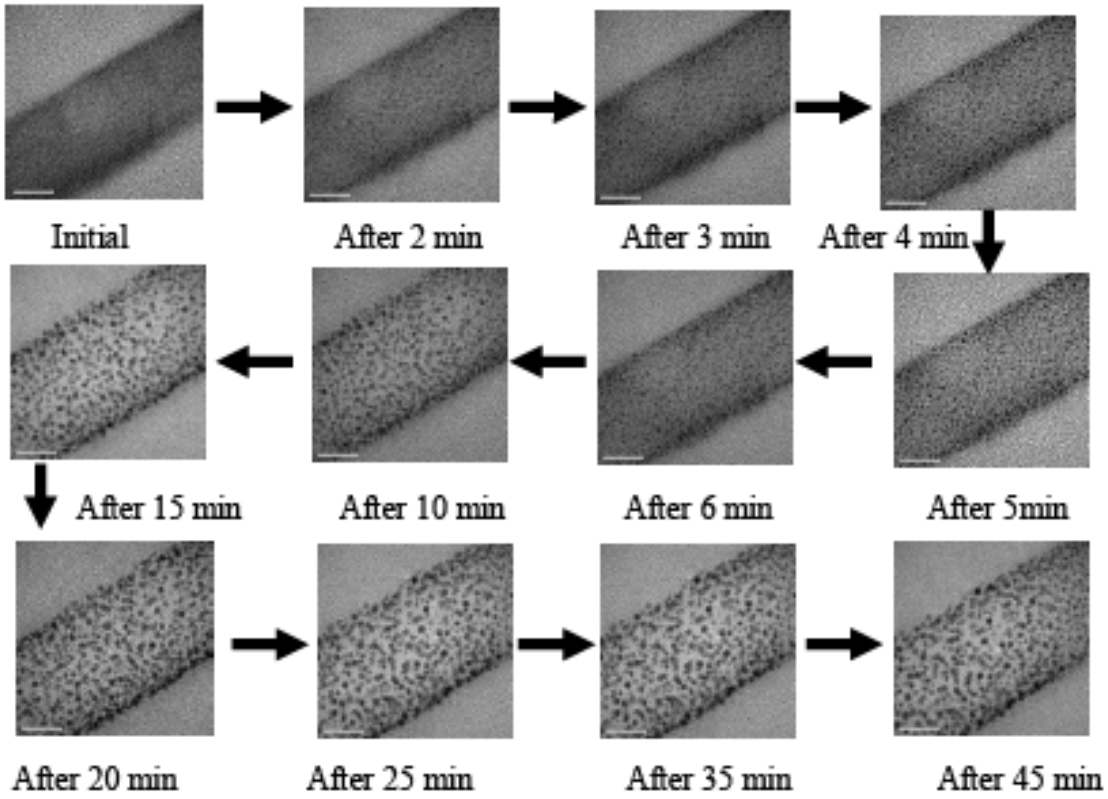
1H NMR spectrum: There is one-to-one correspondence between the two spectra, except that the βCH_2 resonance (labeled as C) disappears completely in the cluster which is expected as it is close to the cluster surface. All the observed resonances have been broadened in view of their faster relaxation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

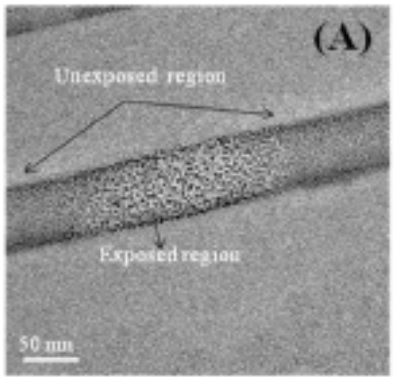


XPS spectrum



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

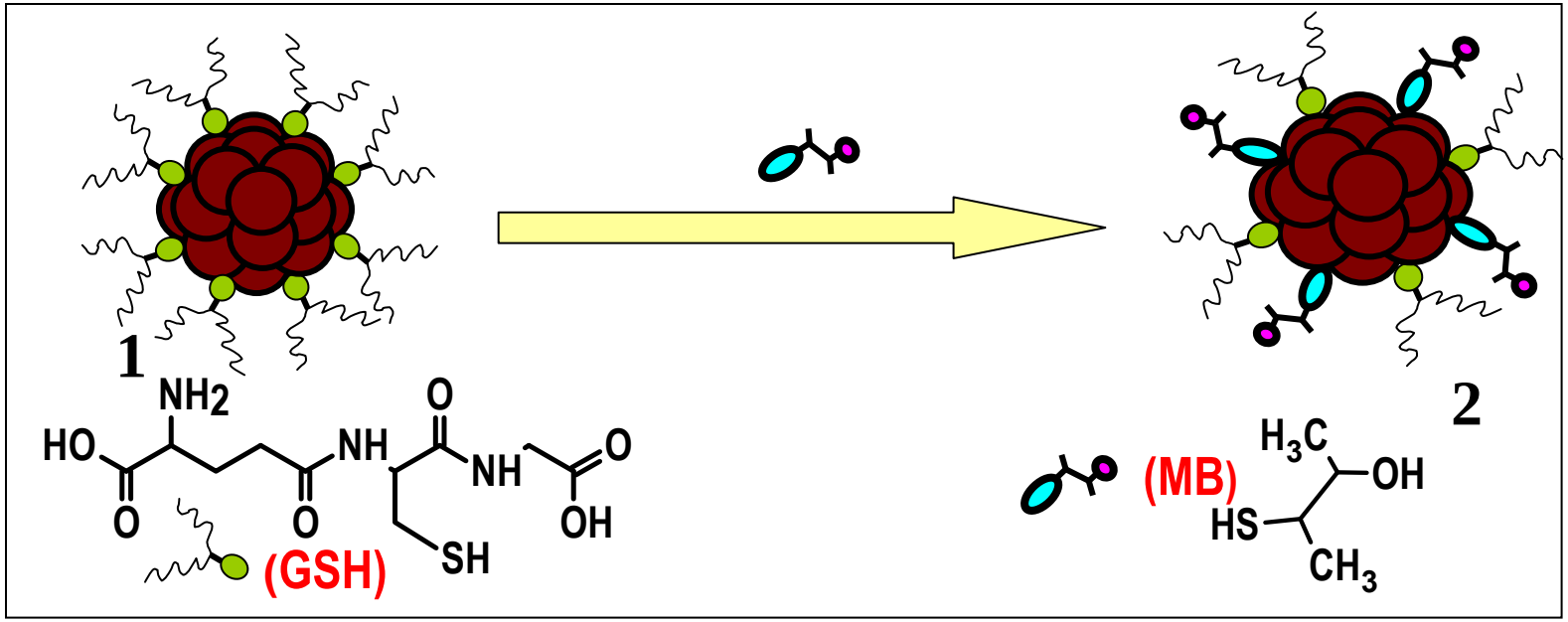


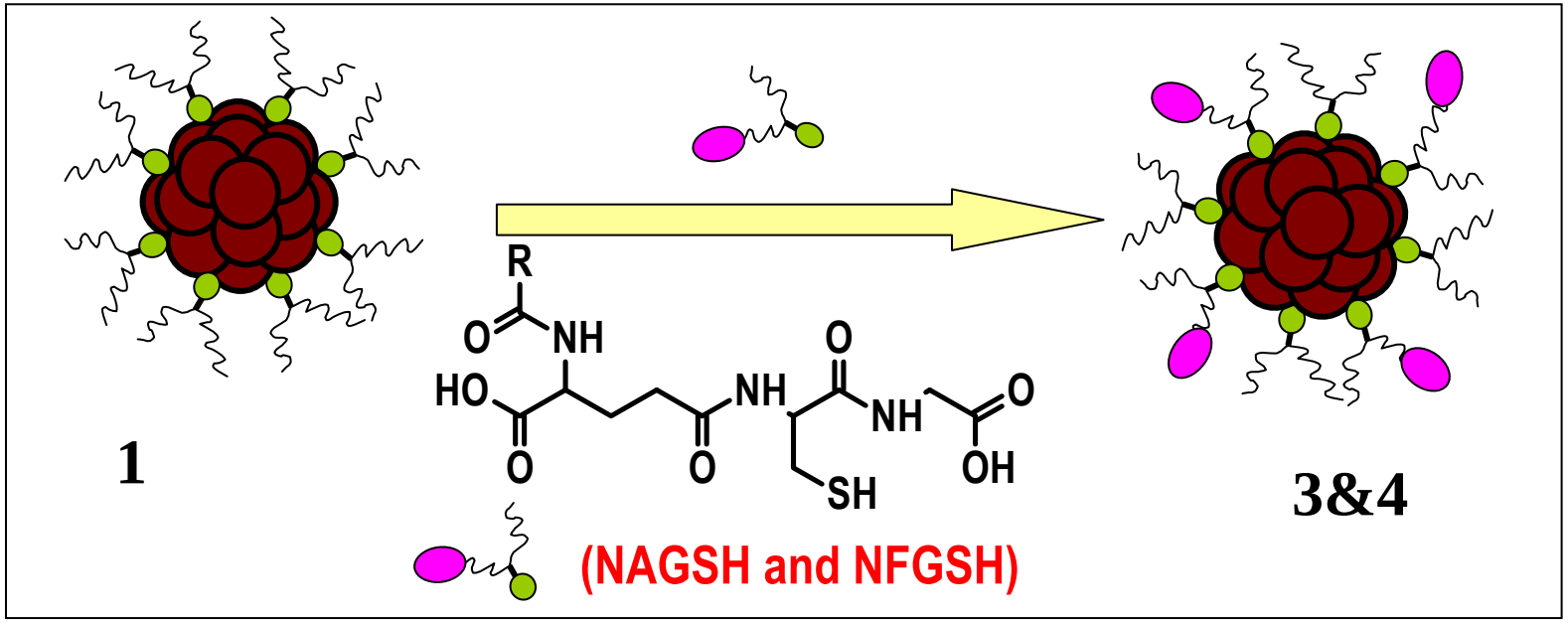


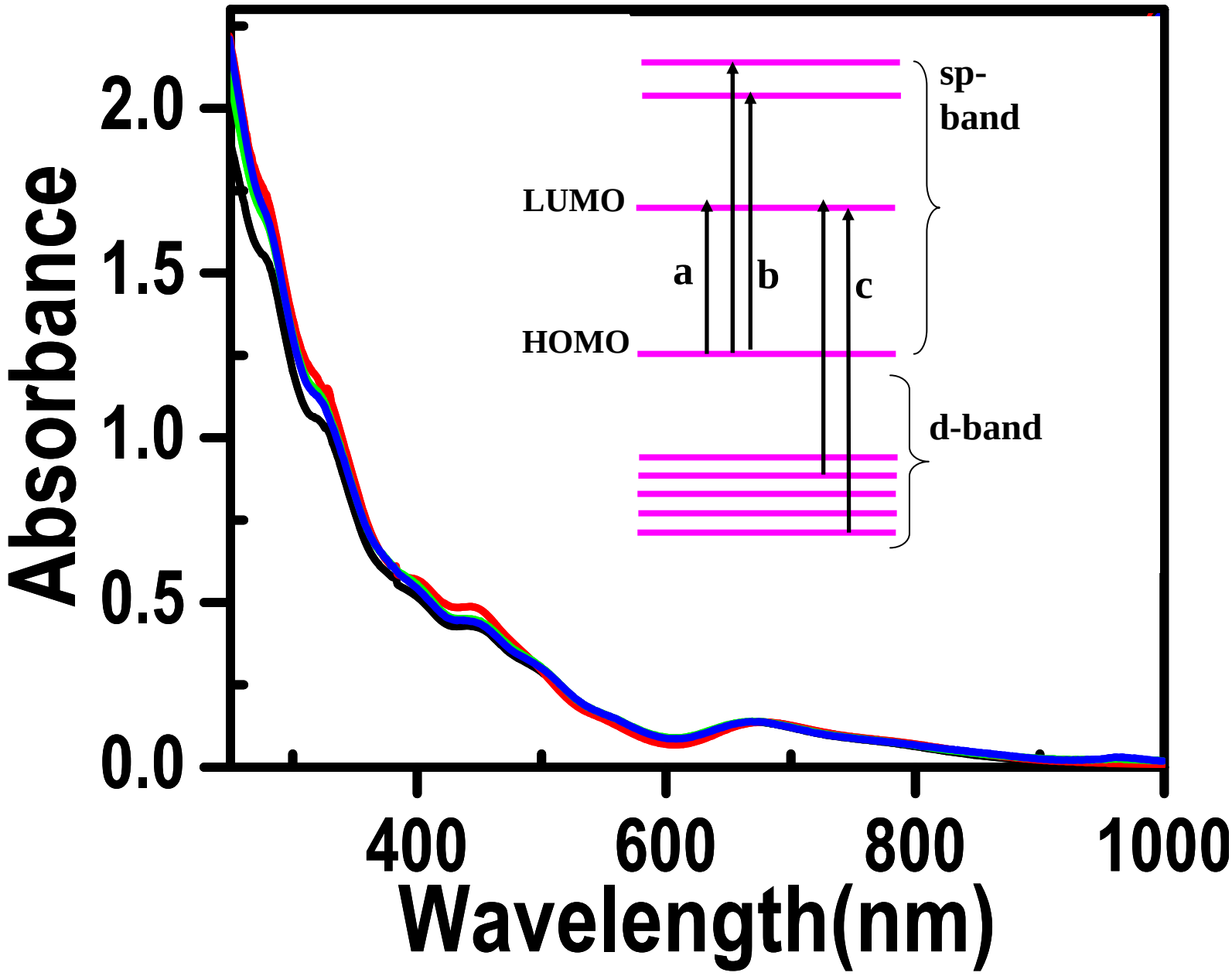
With Arindam Banerjee

Perumal et al. Submitted

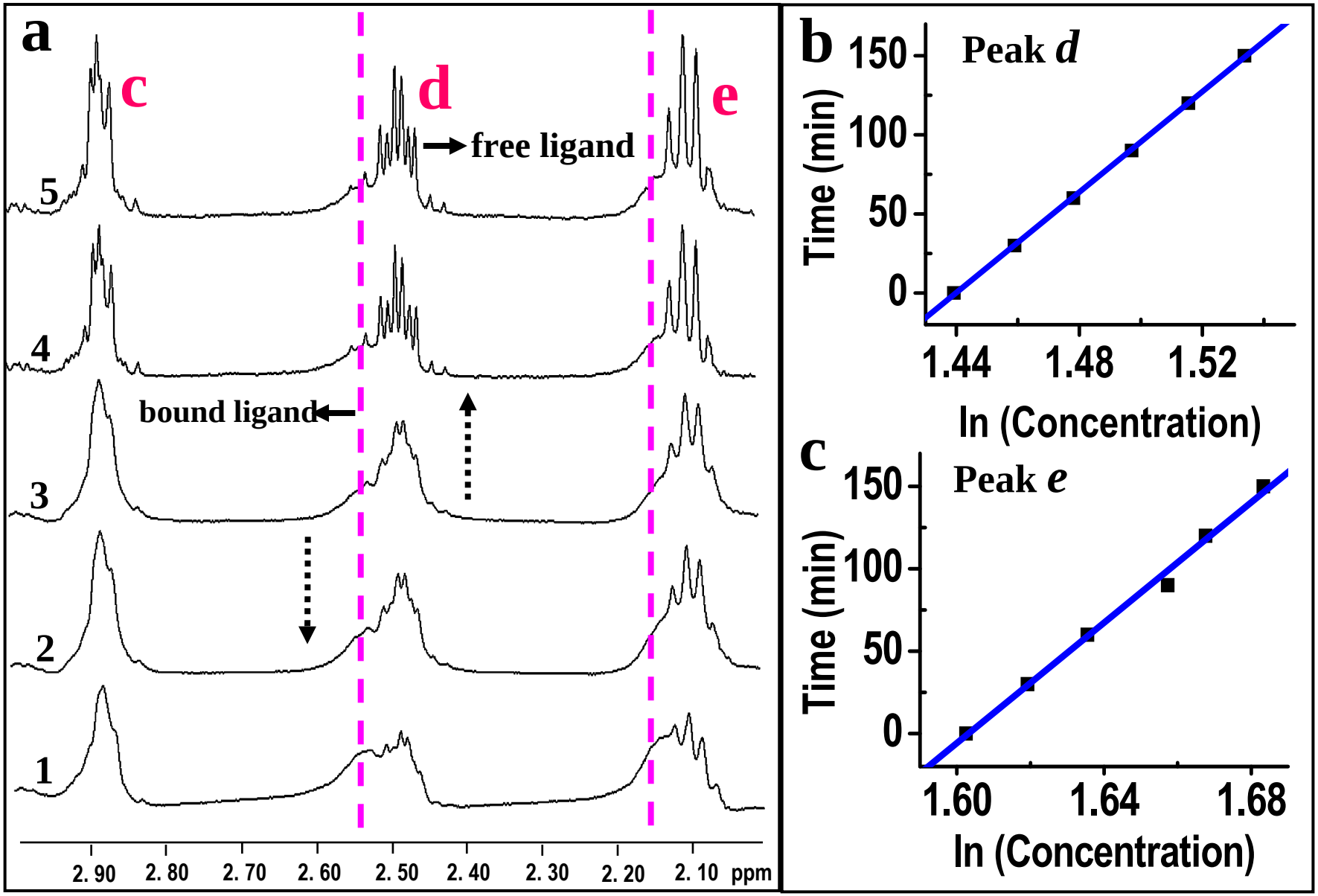
Ligand exchange of Au_{25}

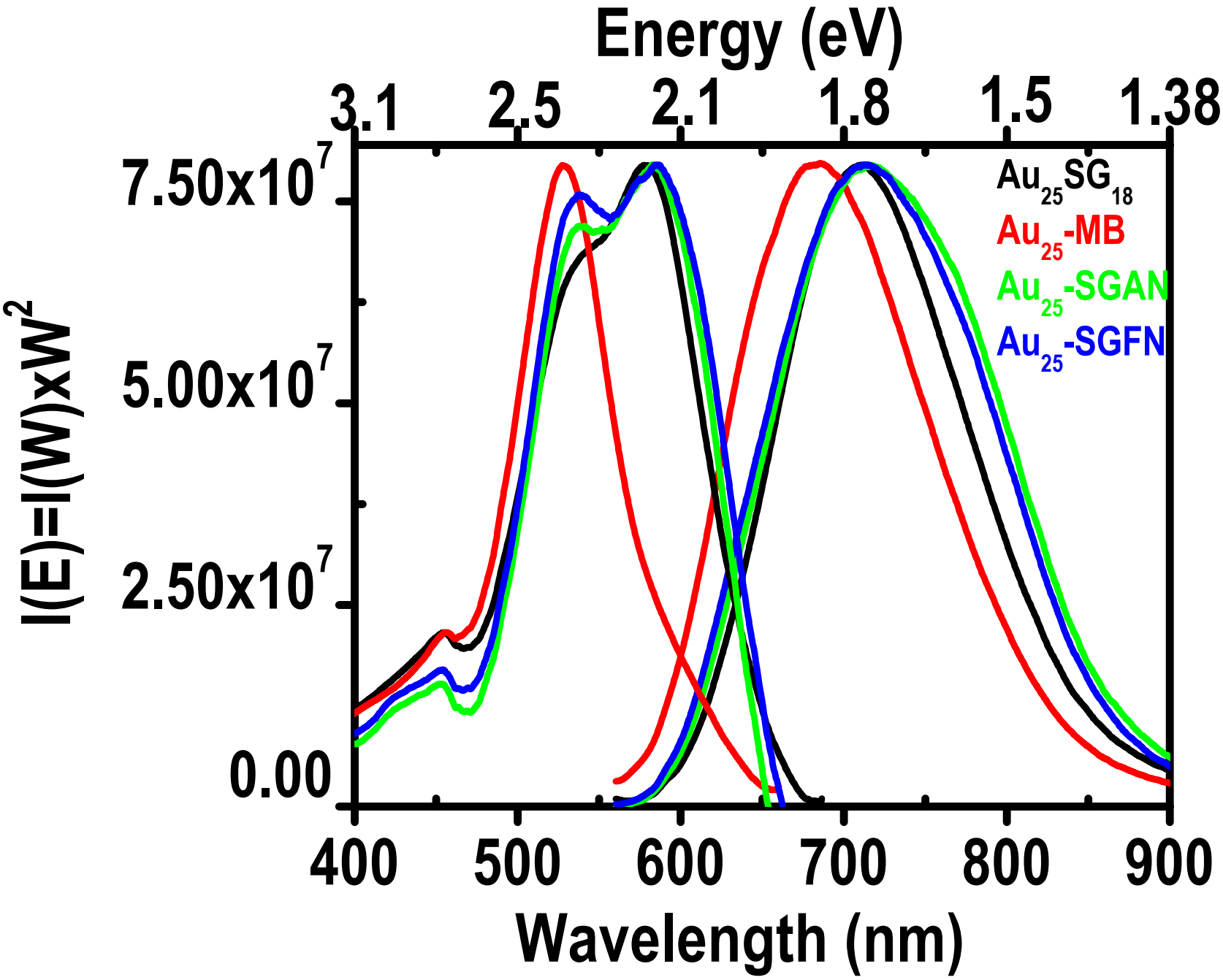




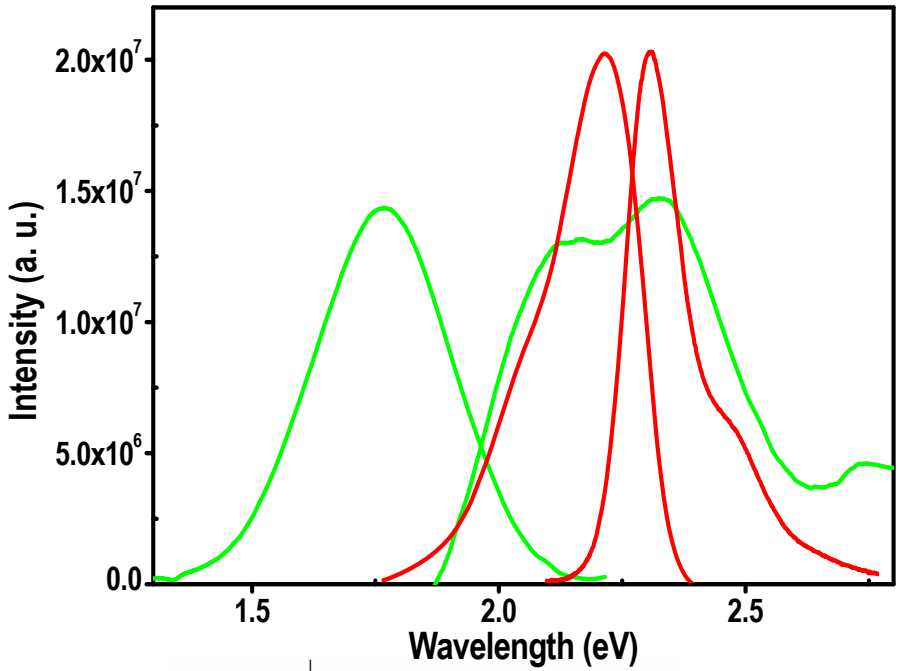


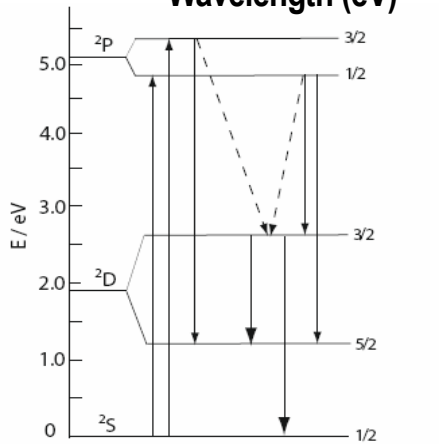
Shibu *et al. J. Phys. Chem. C* 2008

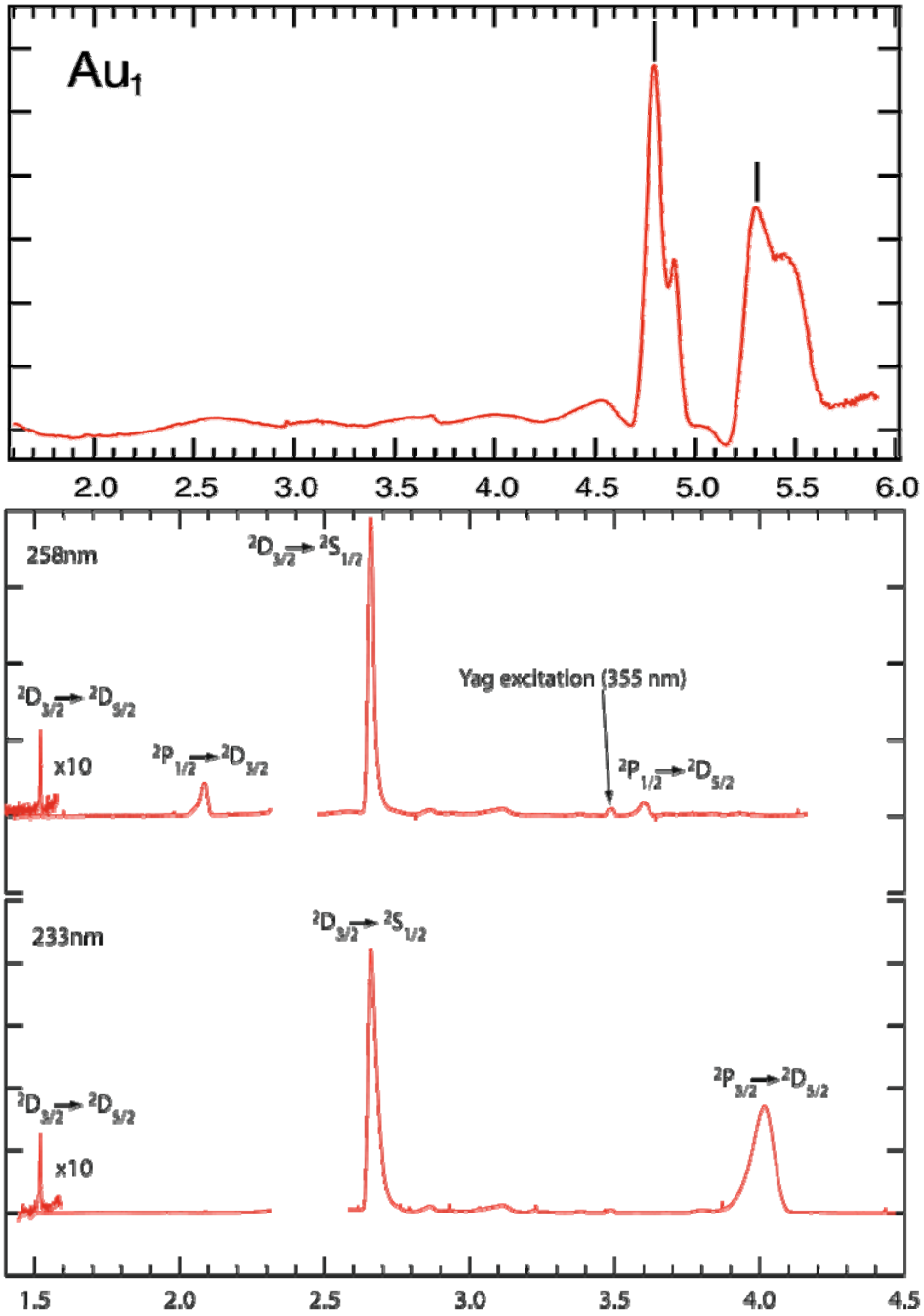

a
c
d
e
free ligand
bound ligand
5
4
3
2
1
2. 90
2. 80
2. 70
2. 60
2. 50
2. 40
2. 30
2. 20
2. 10
ppm
b
Peak d
Time (min)
150
100
50
0
1.44
1.48
1.52
ln (Concentration)
c
Peak e
Time (min)
150
100
50
0
1.60
1.64
1.68
ln (Concentration)


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
400
500
600
700
800
900
Wavelength (nm)
Au25SG18
Au25-MB
Au25-SGAN
Au25-SGFN

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







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	$1*10^{-10}$

Precursor

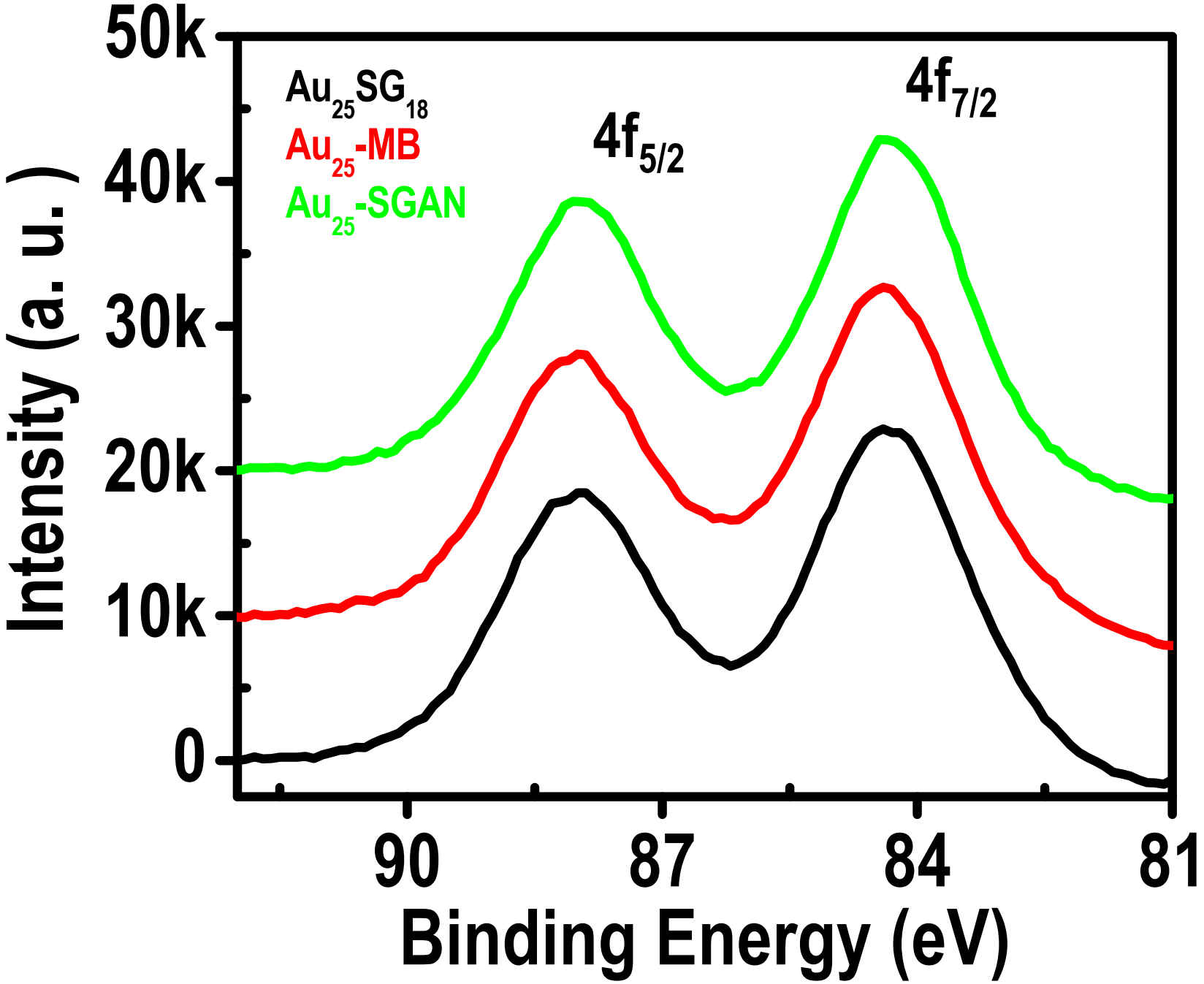
Using other ligands

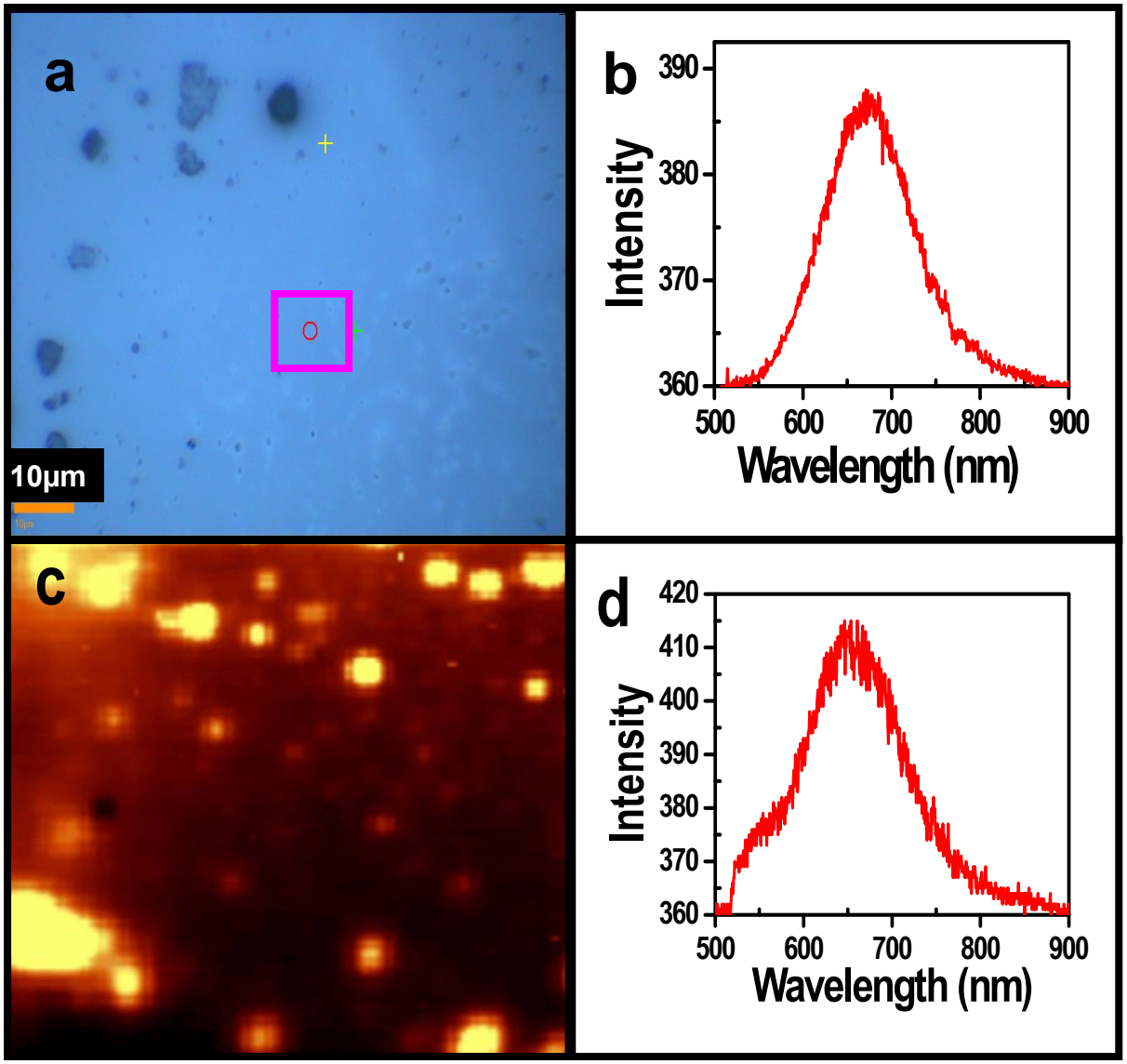
Recently developed clusters using Au_{25} as precursor

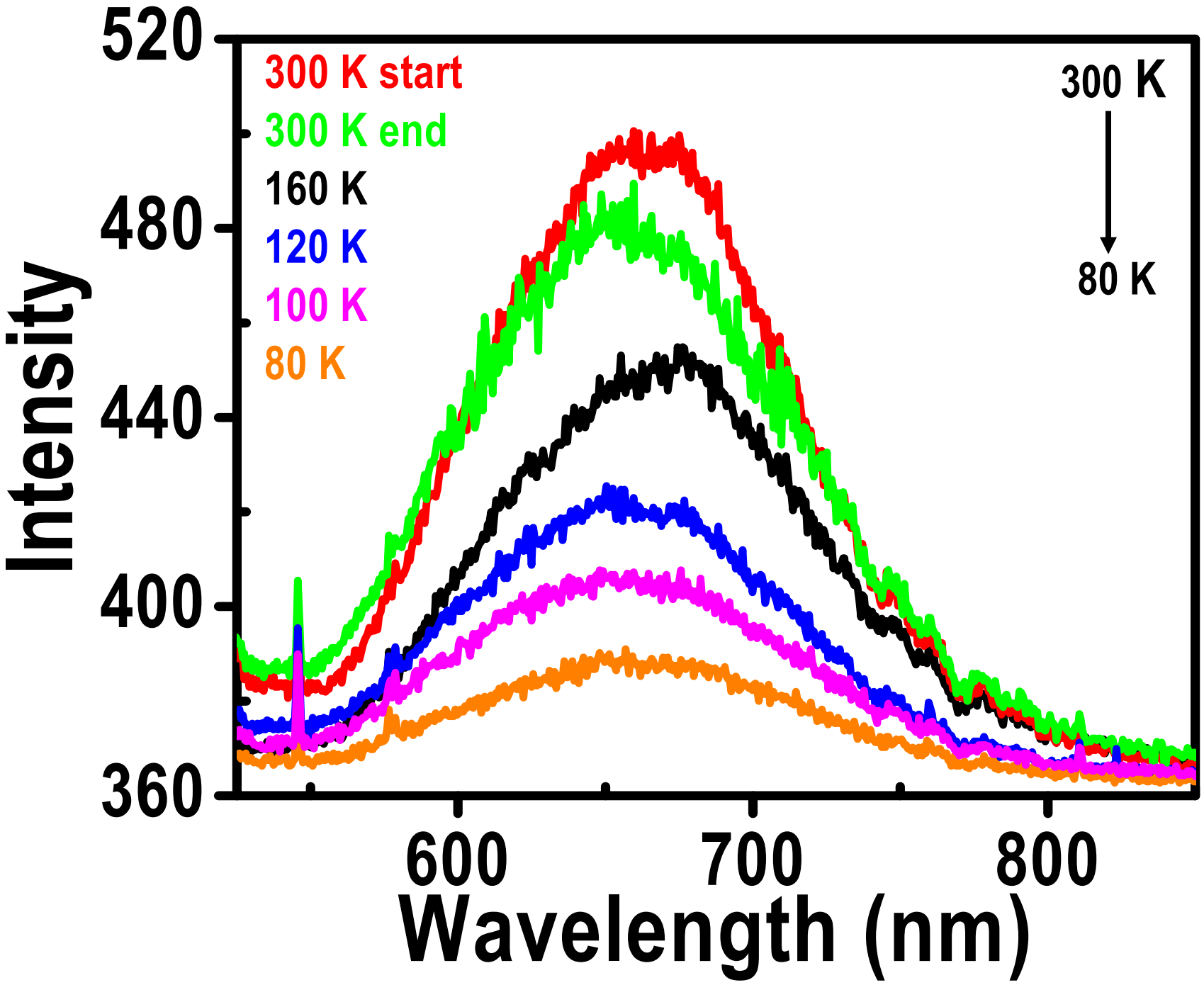
Cluster	Q. Yield
Au_{22}	$4.0*10^{-2}$
Au_{23}	$1.3*10^{-2}$
Au_{31}	$1.0*10^{-2}$
$Au_8(SG)_8$	$1.5*10^{-1}$

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

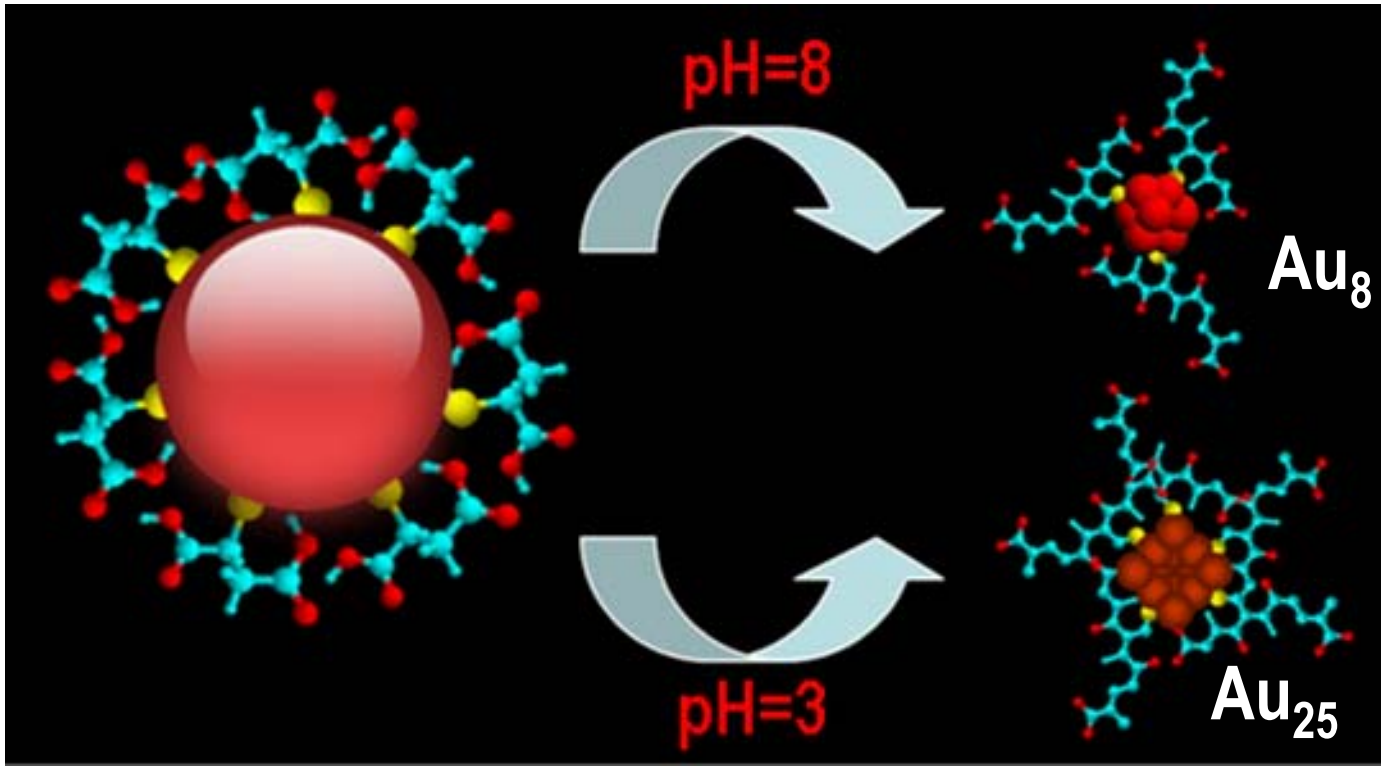
Negishi, Y.; Nobusada, K.; Tsukuda, T. J. Am. Chem. Soc. 2005, 127, 5261.

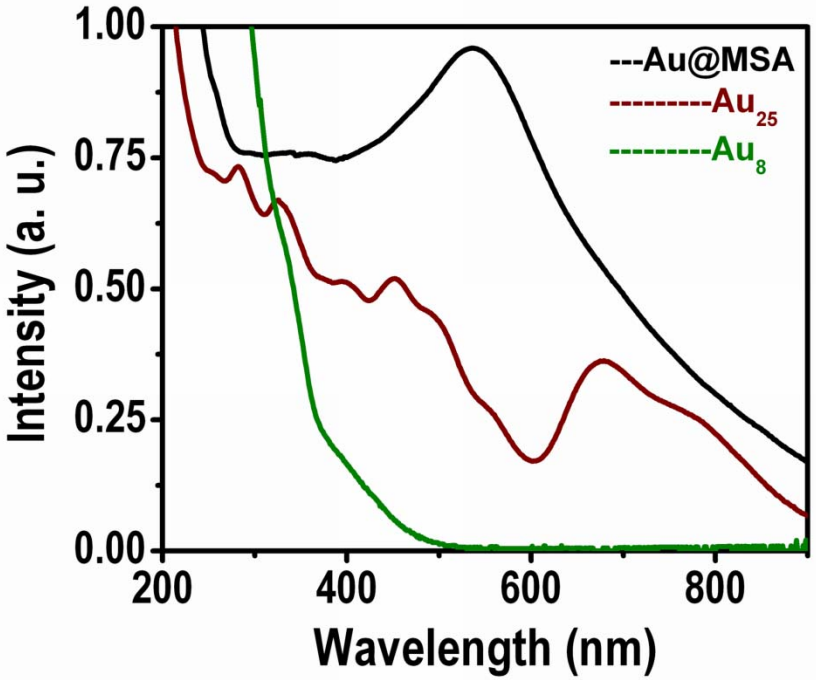

50k
40k
30k
20k
10k
0
Intensity (a. u.)
Au25SG18
Au25-MB
Au25-SGAN
4f5/2
4f7/2
90
87
84
81
Binding Energy (eV)


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)

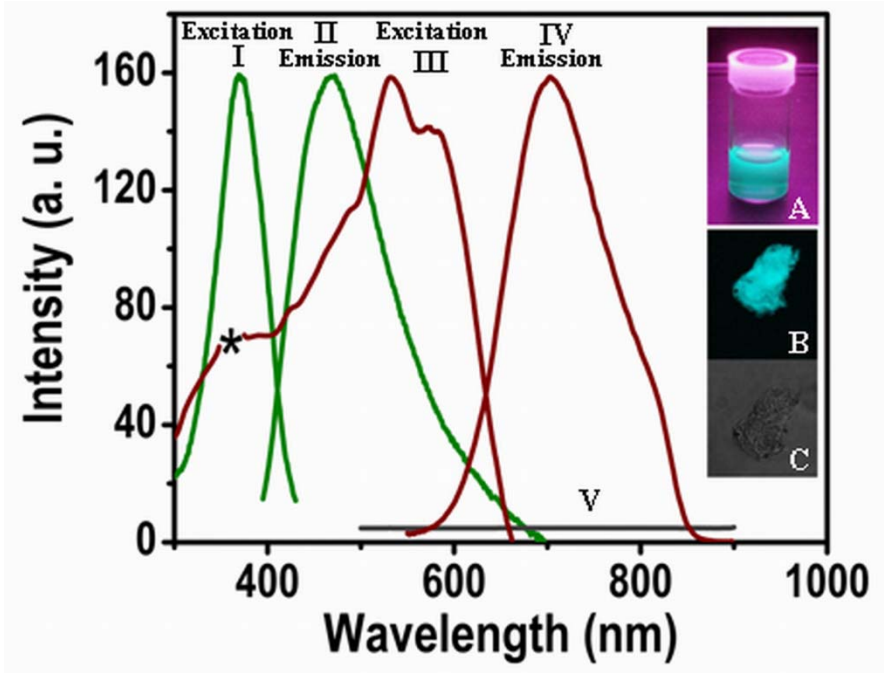

520
480
440
400
360
Intensity
300 K start
300 K end
160 K
120 K
100 K
80 K
300 K
80 K
600
700
800
Wavelength (nm)

Au_8SG_8



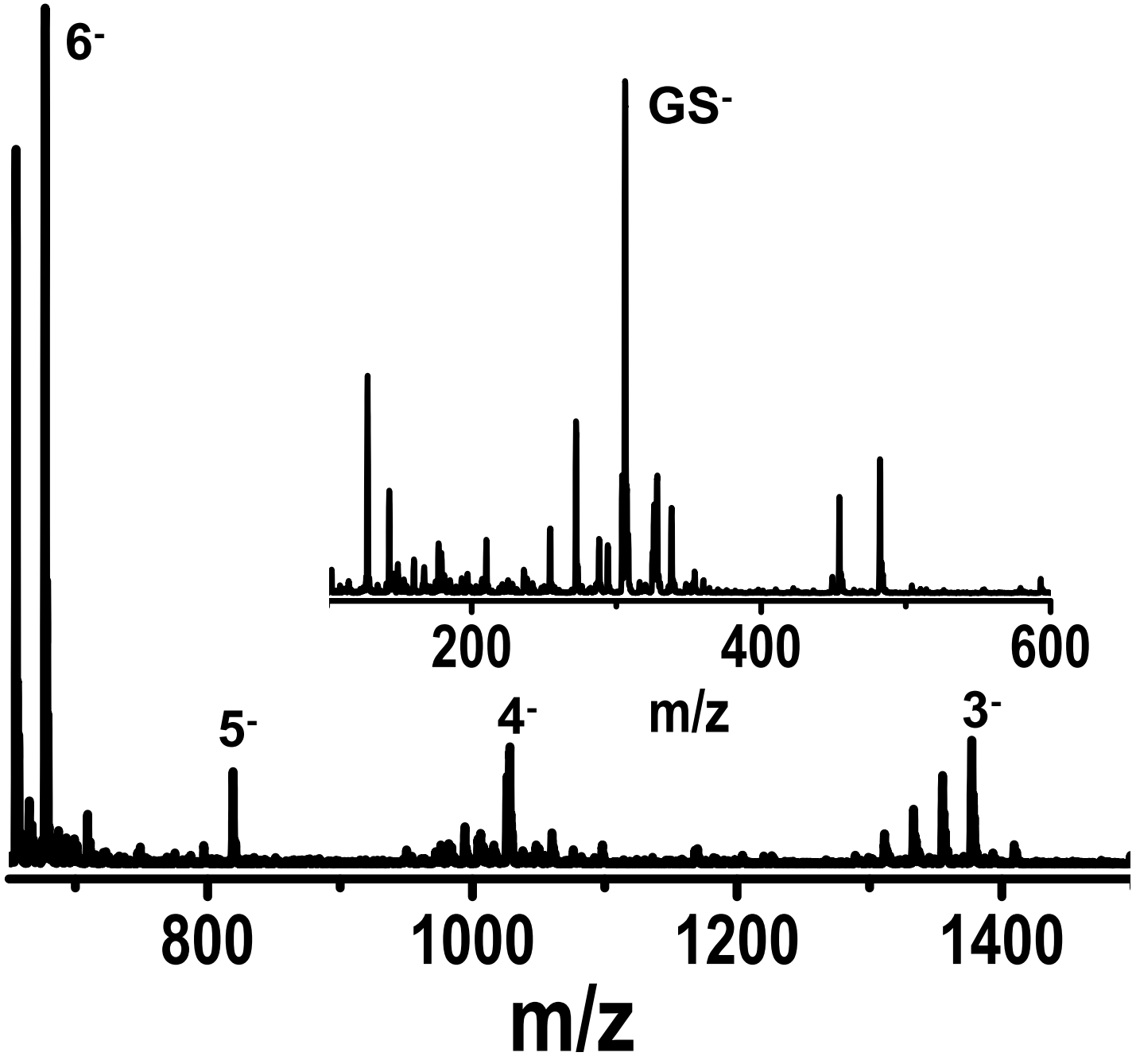


Comparison of the optical absorption profiles of Au@MSA, Au_{25} and Au_8.



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.

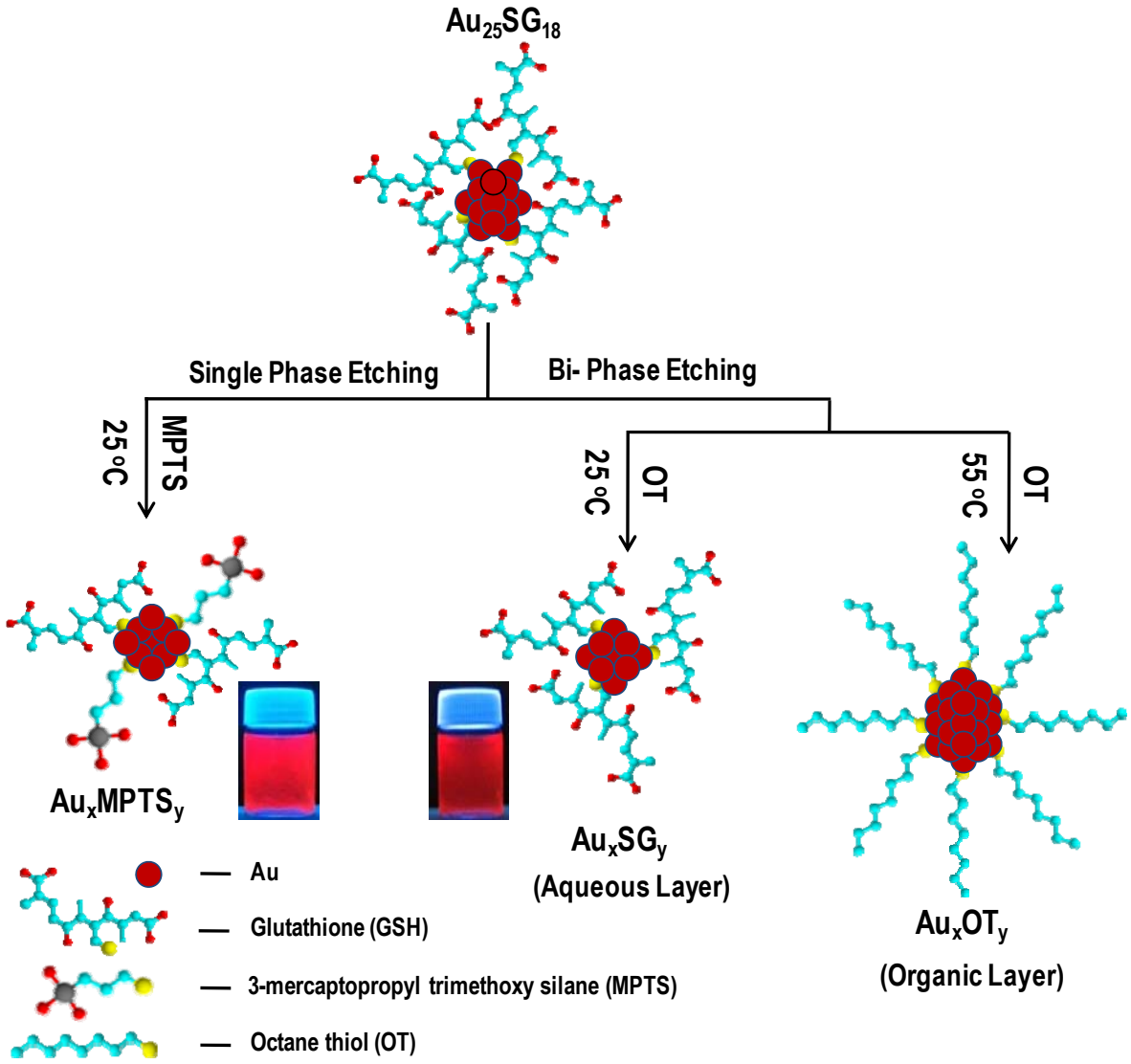
Habeeb Muhammed et al. *Nano Res.* 2008



Habeeb Muhammed, et. al. Unpublished

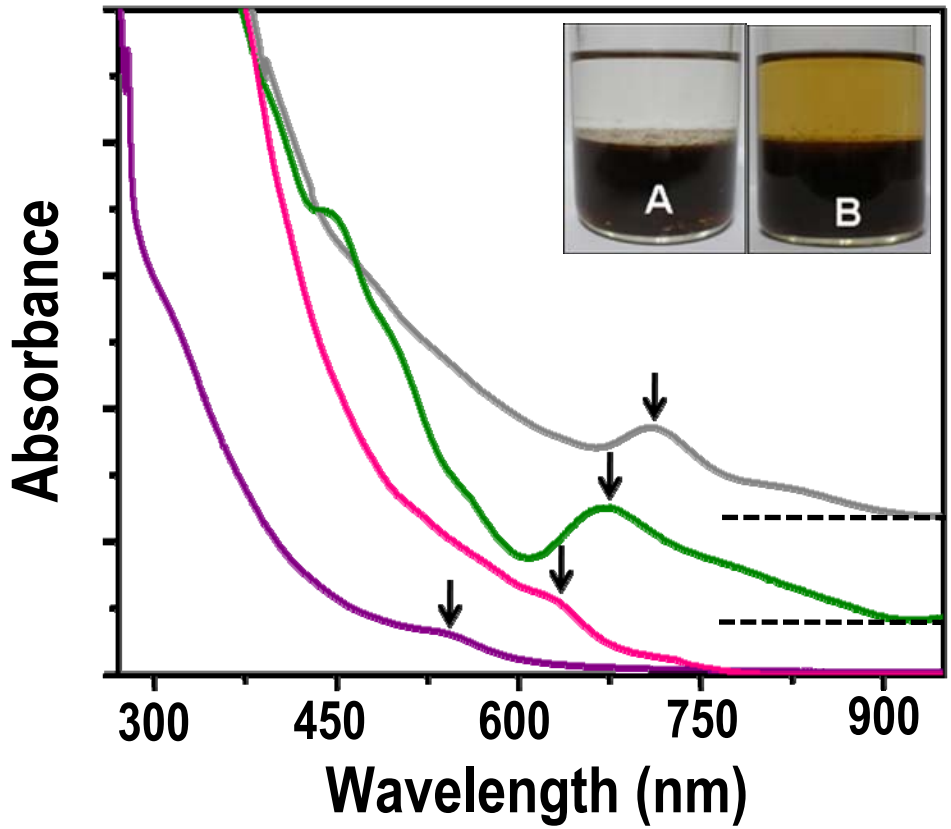
Clusters from clusters: Au_{25} to make other clusters

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.

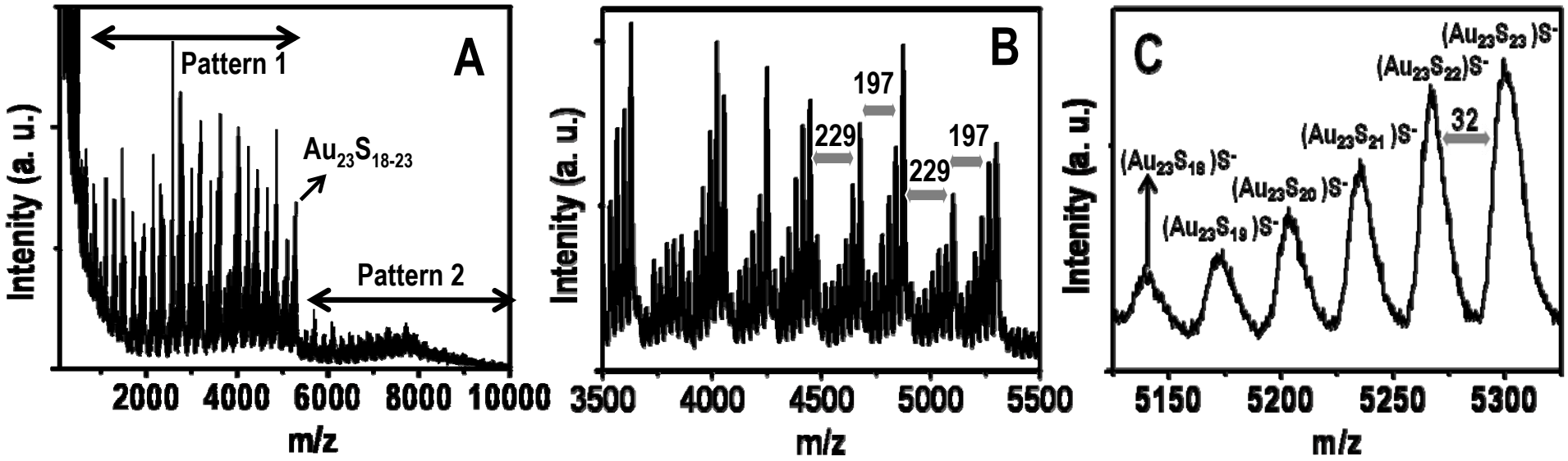
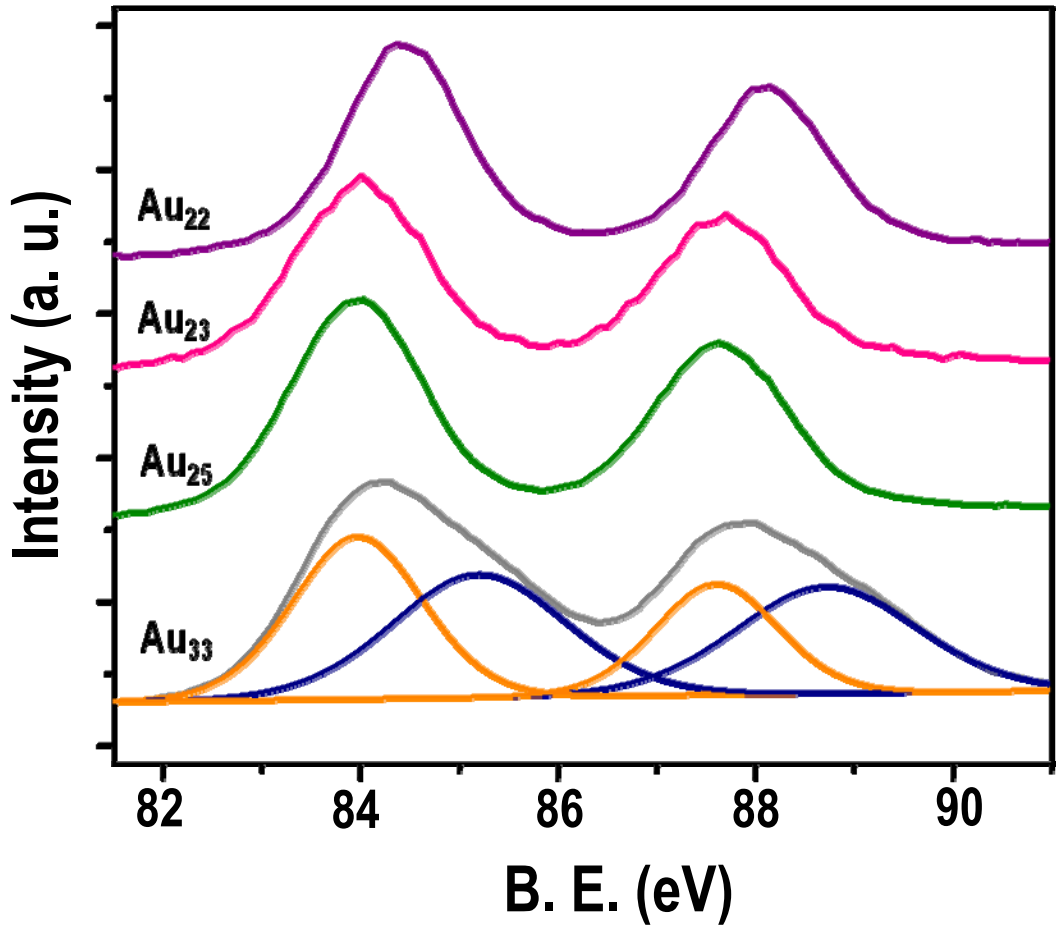


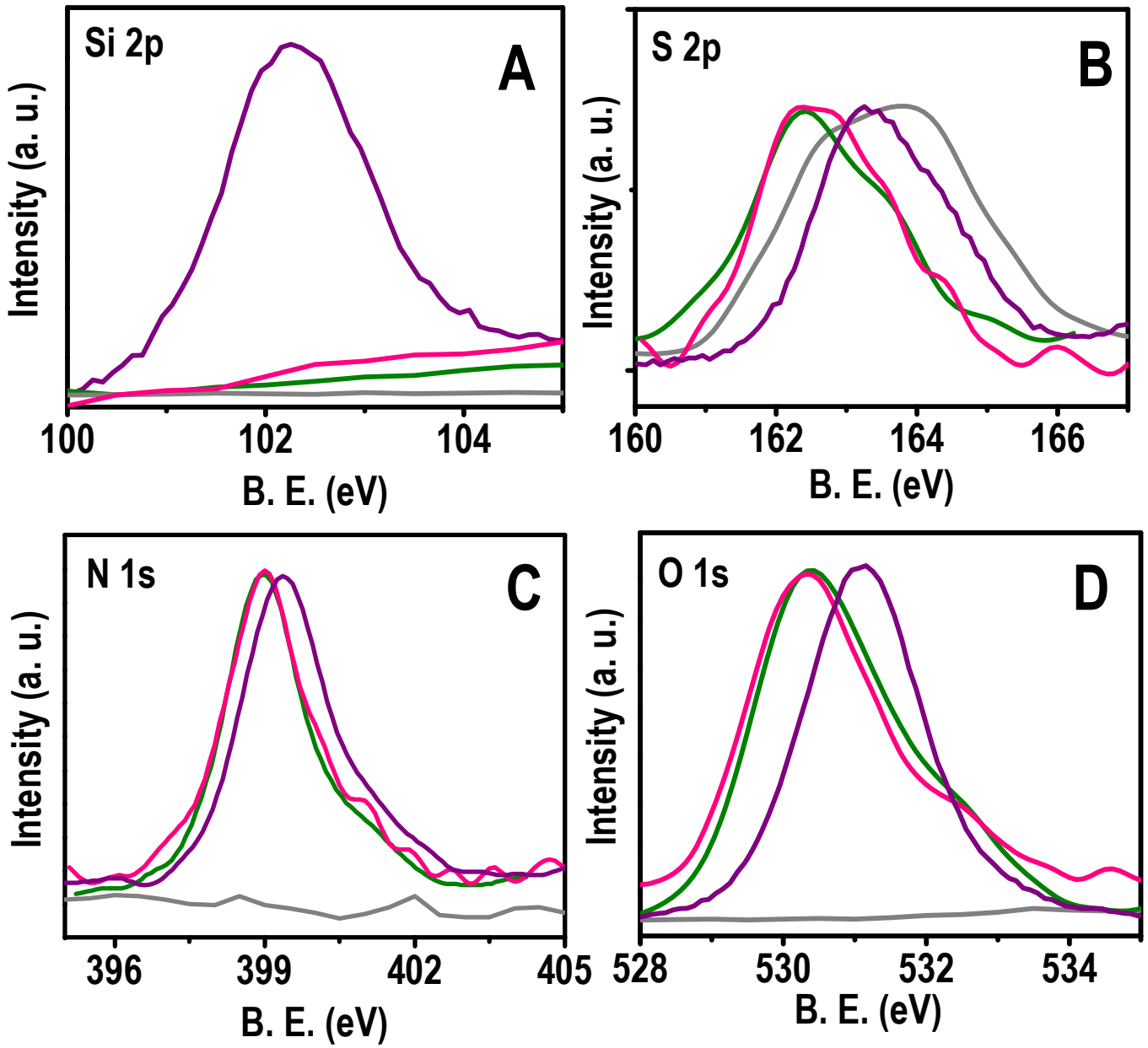
Figure 2. A) MALDI-MS of $Au_x SG_y$ which shows bunch of peaks due to $Au_m S_n$ clusters. B) A group of peaks with m/z spacing of 197 or 229 between the major peaks of the adjacent group of peaks. C) Expanded view of peaks due to $Au_{23} S_{18-23}$.

Sample	Element	% of element (Experimental)	% of element (Calculated)	Molecular formula
Au_xMPTS_y	N	03.85	03.68	$Au_{22}(MPTS)_{10}(SG)_7$
	C	15.29	15.03	
	H	02.71	02.62	
	S	06.31	06.81	
Au_xSG_x	N	07.75	07.53	$Au_{23}SG_{18}$
	C	20.68	21.52	
	H	03.45	02.87	
	S	05.48	05.74	
Au_xOT_y	N	00.00	00.00	$Au_{33}OT_{22}$
	C	22.01	21.78	
	H	04.15	03.86	
	S	07.18	07.26	

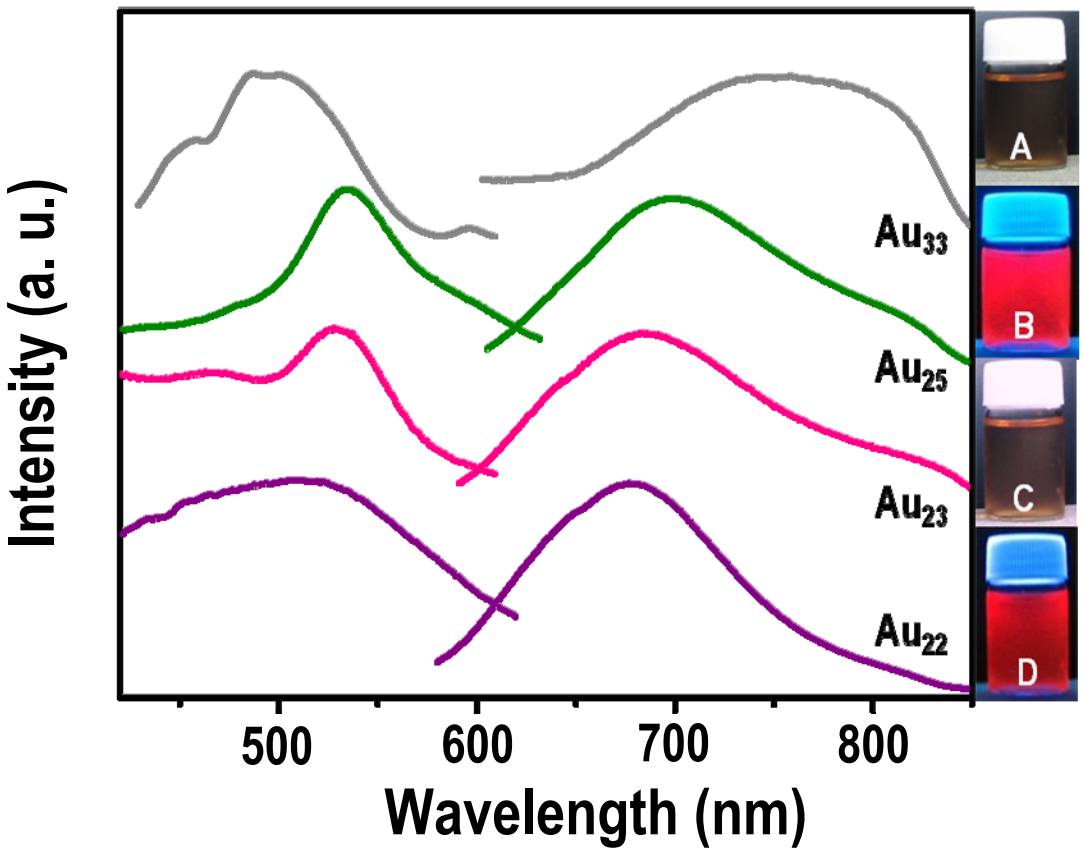
Table shows CHNS elemental analysis data of the three clusters.



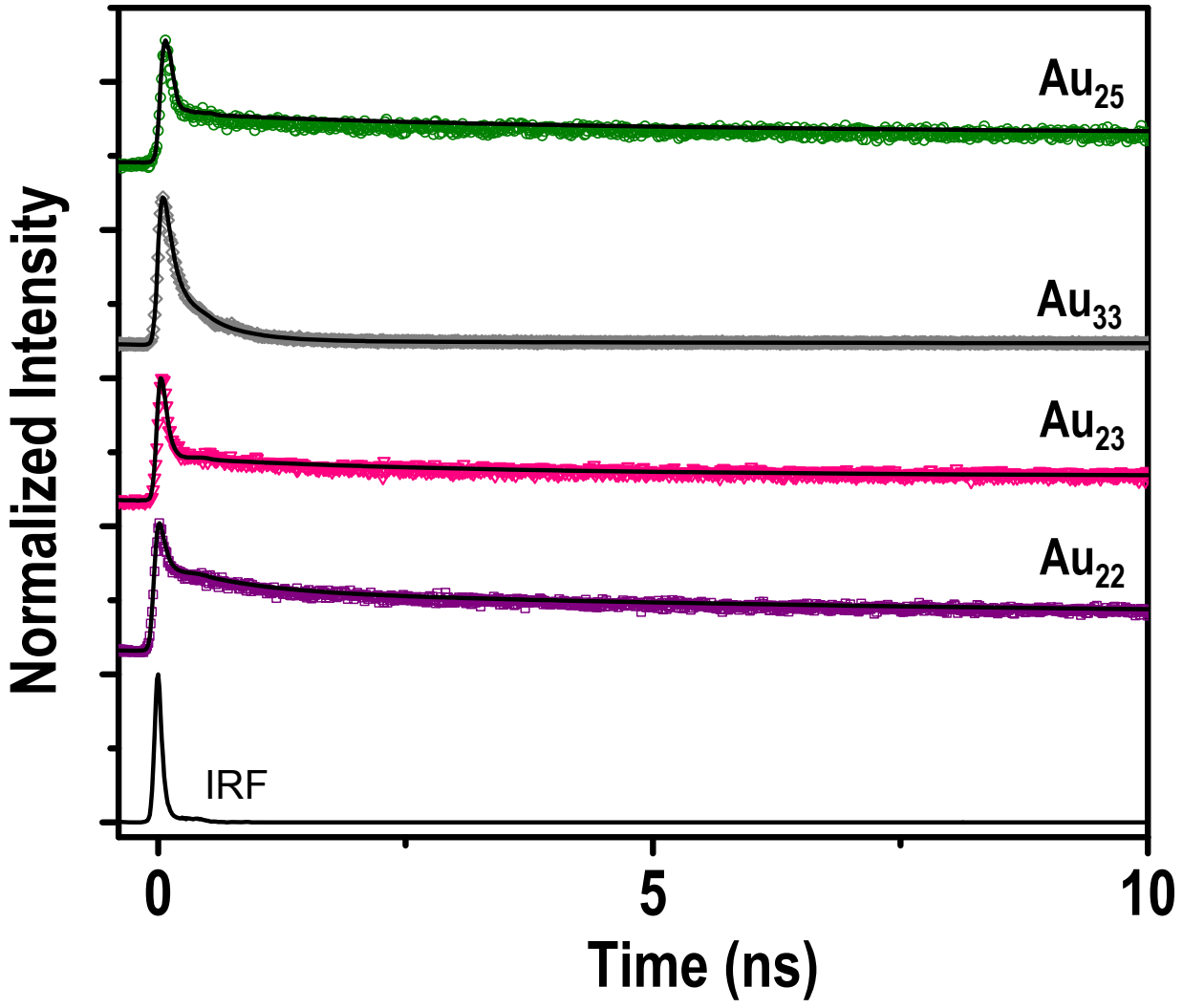
Comparison of the Au(4f) XPS spectra of Au_{22}, Au_{23} and Au_{33} along with parent Au_{25}.



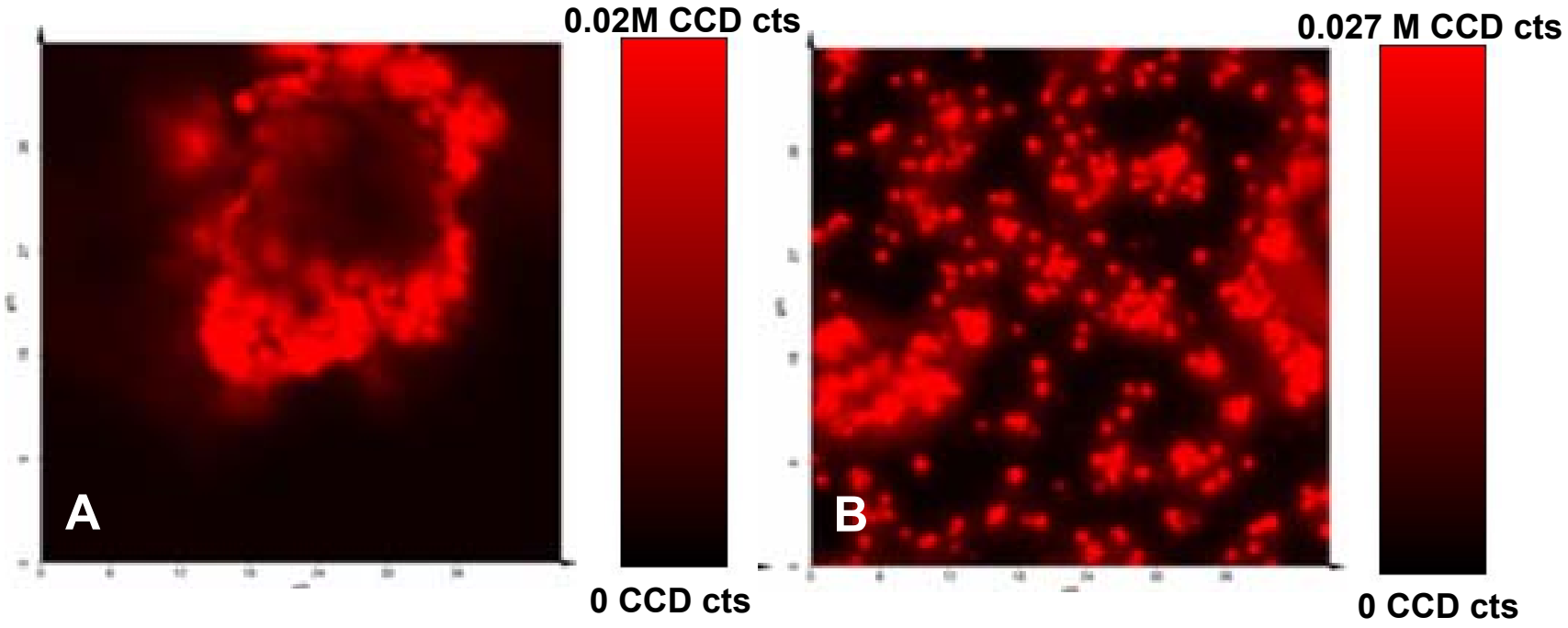
Comparison of XPS spectra due to the core level photoemission from Si2p, S2p , N1s and O_1s of Au_{33} (grey trace), Au_{25} (green trace), Au_{23} (pink trace) and Au_{22} (purple trace).



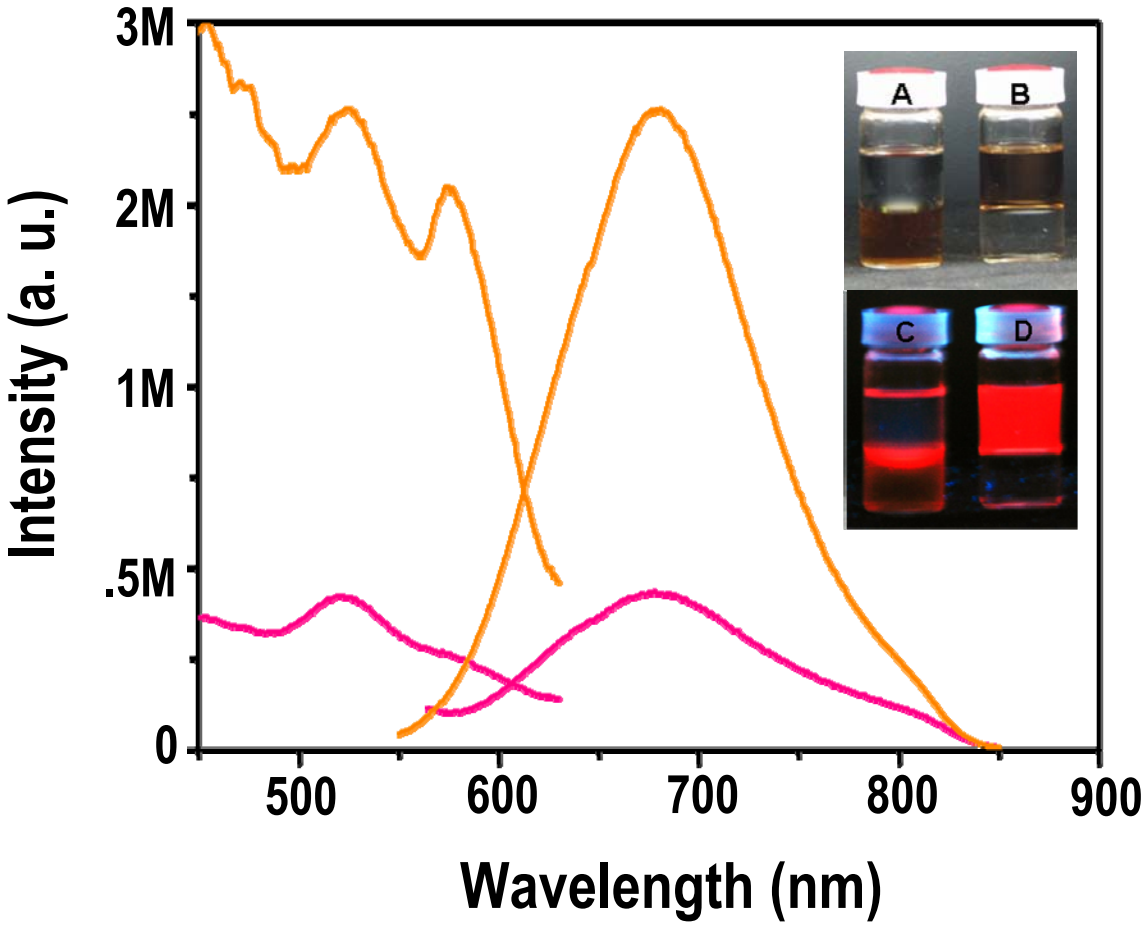
Comparison of the photoluminescence profiles of Au_{22}, Au_{23} and Au_{33} along with parent Au_{25}. Photographs of the aqueous solutions of Au_{22} and Au_{23} under white light (A and C, respectively) and UV light (B and D, respectively) are also given.



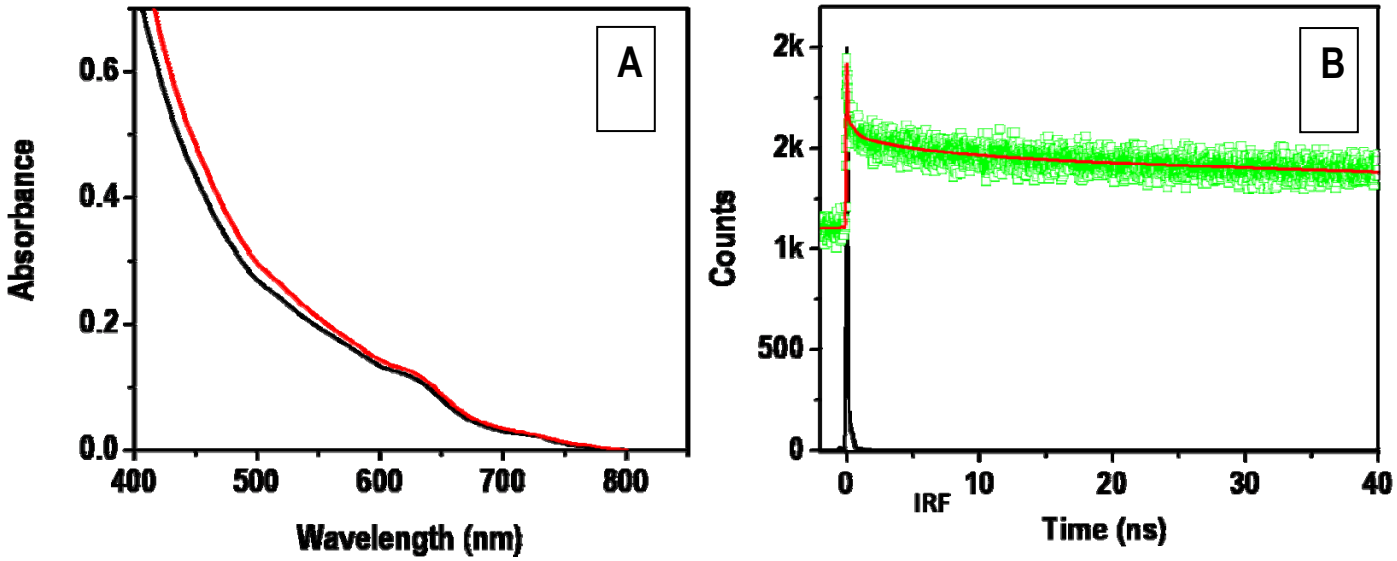
Fluorescence decay pattern of Au_{25}, Au_{33}, Au_{23}, and Au_{22} collected at 630 nm.



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.

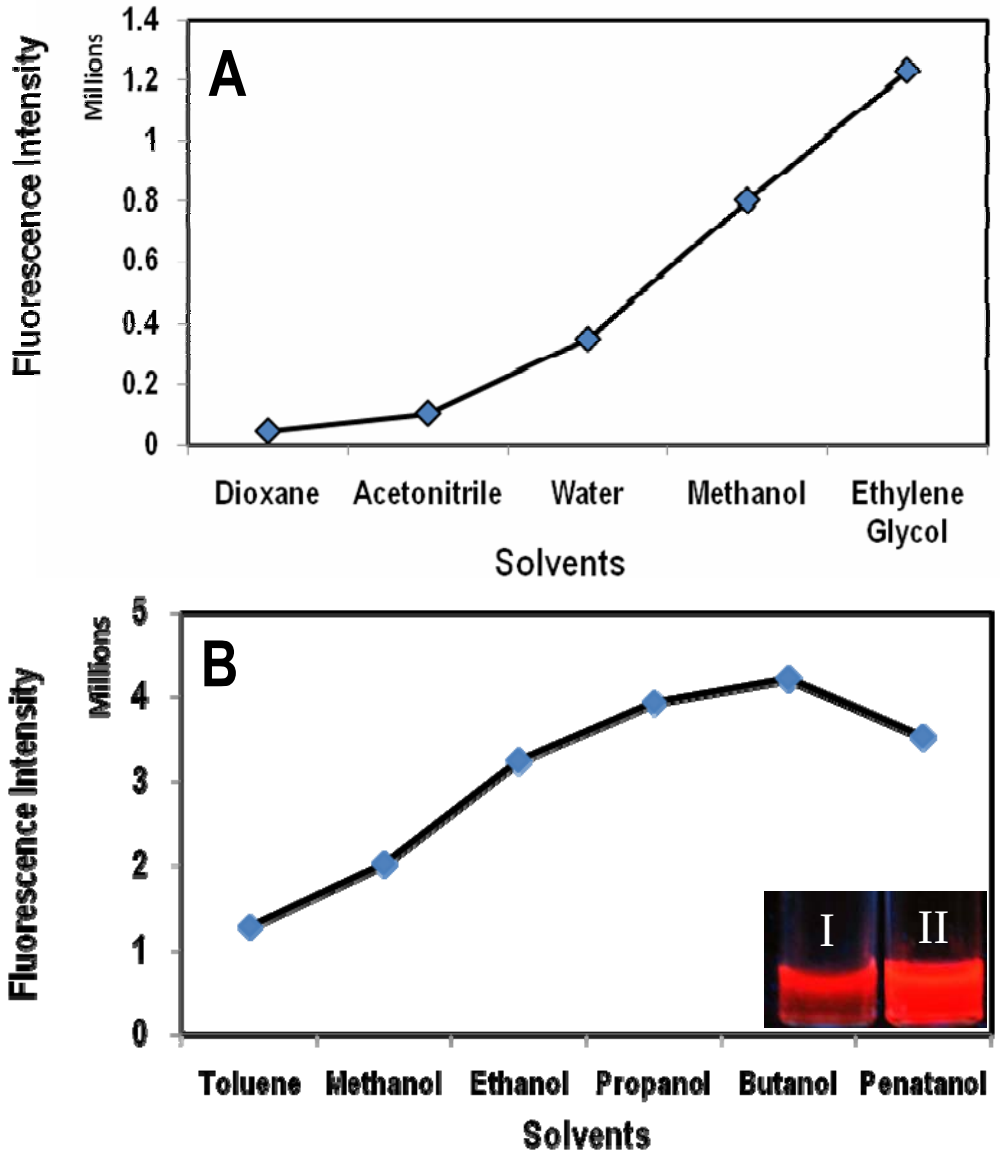


Photoluminescene profile of Au_{23} cluster before (pink trace) and after (orange trace) phase transfer. Emission of the cluster enhances considerably after the phase transfer. Photographs of the aqueous-toluene mixture containing the cluster before and after phase transfer under white light (A and B, 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

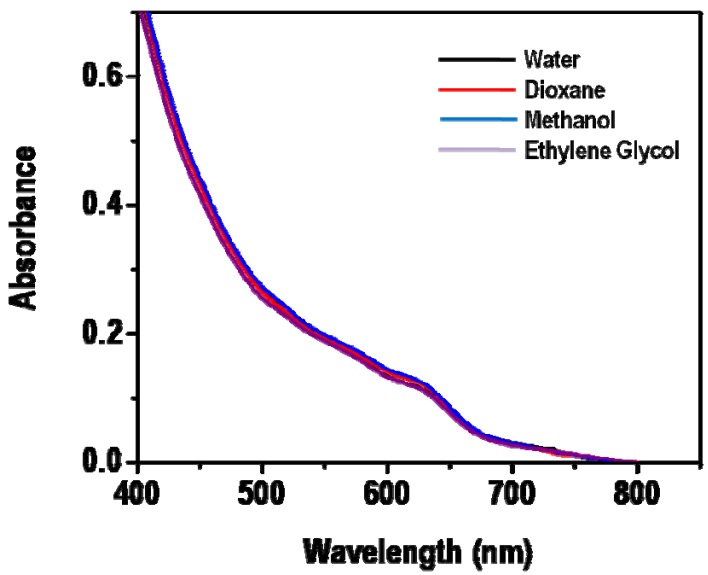


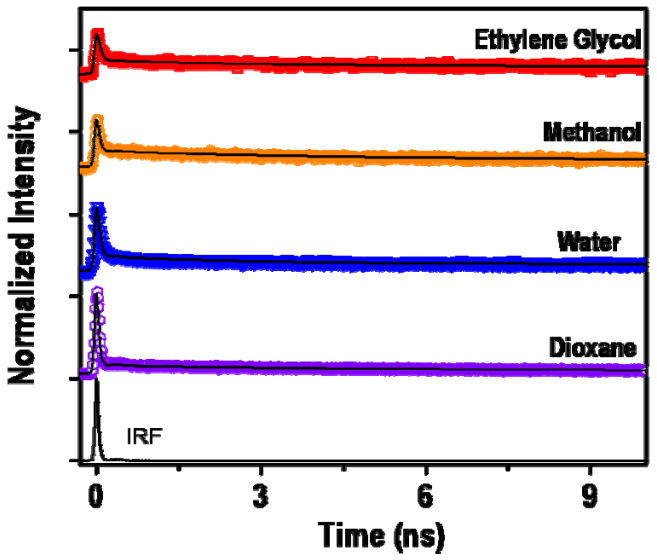
Solvent	τ_1(ps)	%	τ_2 (ns)	%	τ_3 (ns)	%
Toluene	34	82.8	4.11	4.3	80.35	12.9
Water	39	92.4	2.41	3.6	68.55	3.9

A) Optical absorption spectra of Au_{23} before (red trace) and after (black trace) phase transfer. B) Fluorescence decay of Au_{23} after phase transfer. Table tabulates the life time values of the cluster before and after phase transfer.



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



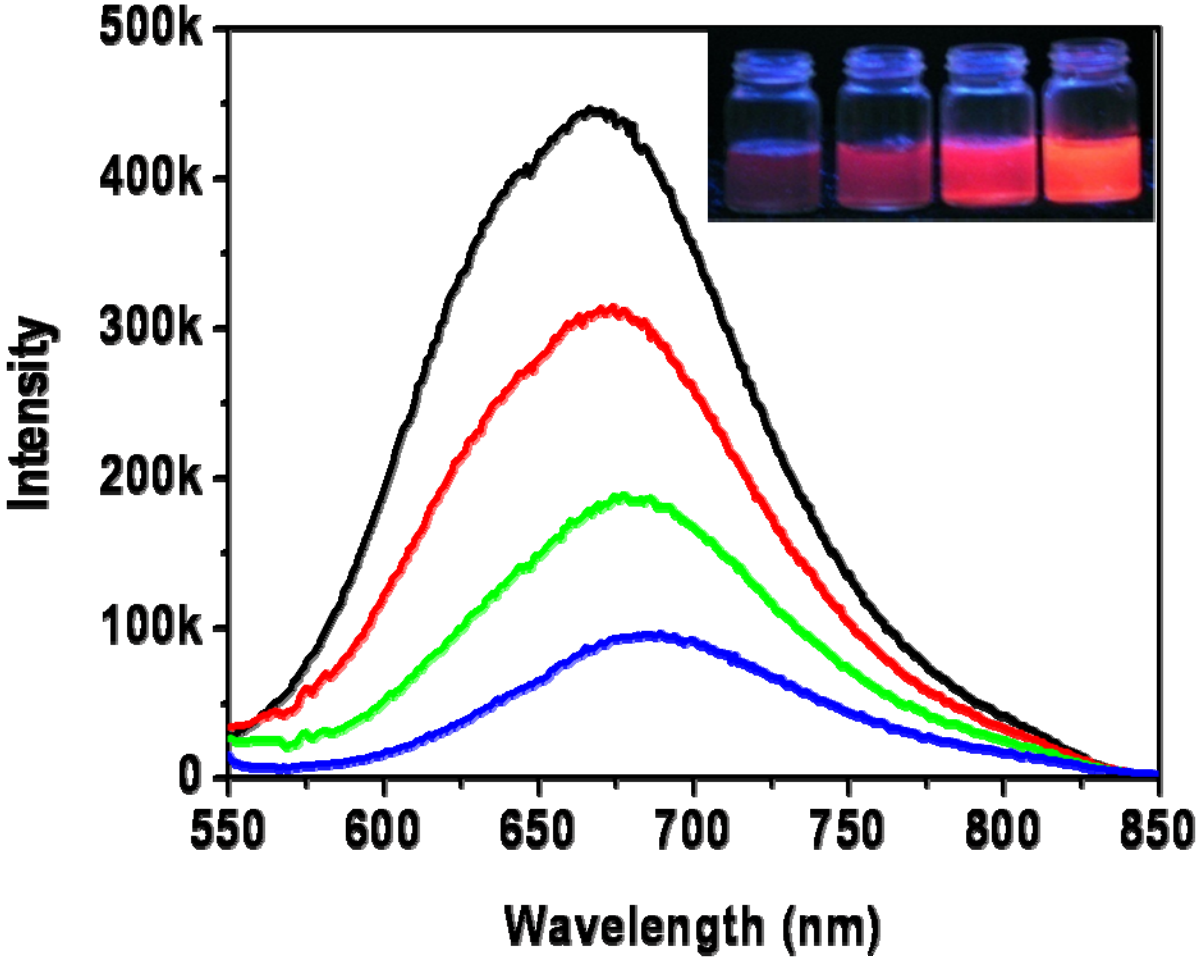


Solvent	τ_1(ps)	%	τ_2(ns)	%	τ_3 (ns)	%
Ethylene Glycol	47	86.5	2.67	5.5	70.06	7.9
Methanol	36	87.6	3.27	5.8	62.91	6.6
Water	39	92.4	2.41	3.6	68.55	3.9
Dioxane	16	98.0	5.07	1.1	31.63	0.9

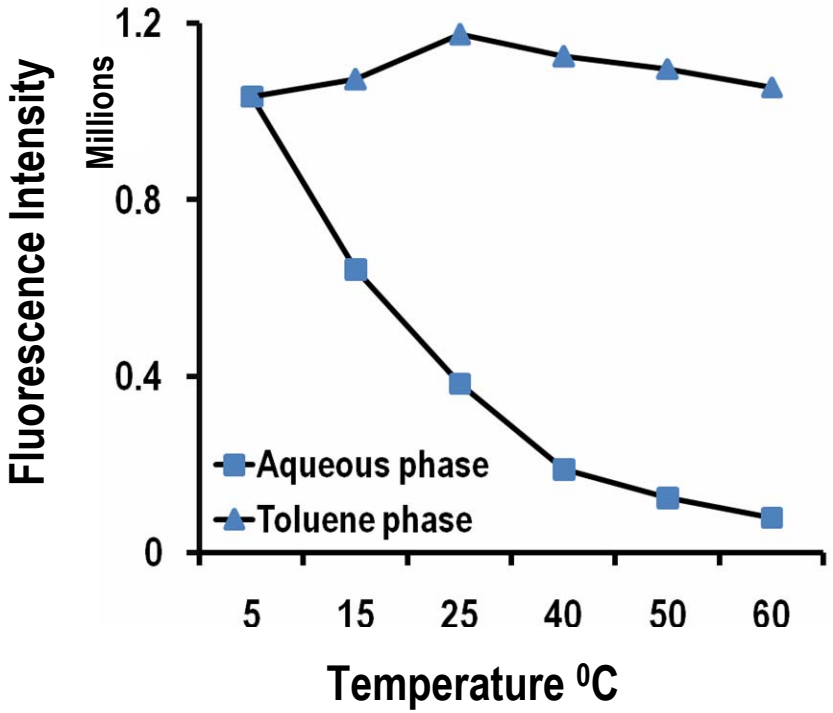
A) Optical absorption spectra of Au_{23} in dioxane, water, methanol and ethylene glycol. B) Fluorescence decay of Au collected at 630 nm in various solvents. Table tabulates the life time of the cluster in various solvents.

Solvents	Quantum yield ,Φ	Fluorescence lifetime, τ(ns)	Radiative rate constant, $k_r(10^7\ s^{-1})$	Nonradiative rate constant, $k_{nr}(10^7\ s^{-1})$
Water	0.013	0.4	3.250	246.75
Toluene (phase transferred)	0.050	2.6	1.900	36.10
Dioxnae	0.001	6.5	0.015	15.38
Ethylene Glycol	0.045	10.6	0.420	8.91

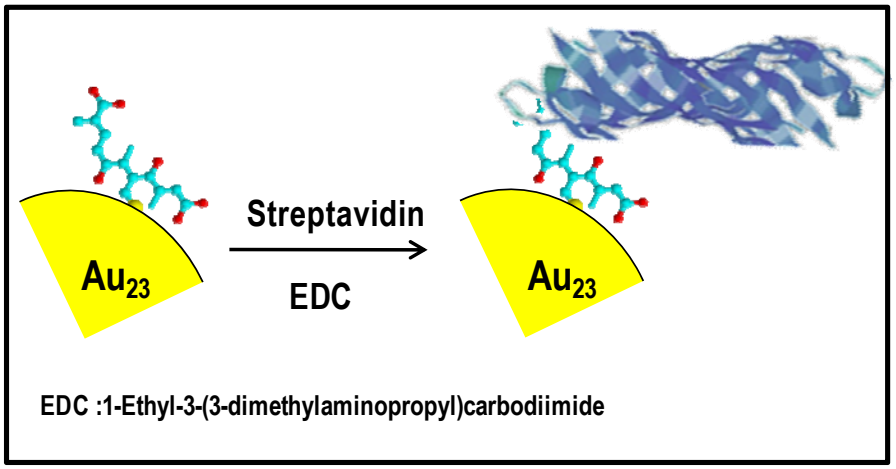
Tabulation of radiative and non-radiative decay rates of Au_{23} in water, toluene, dioxane and ethylene glycol. The first two datasets compare the values before and after phase transfer, respectively.



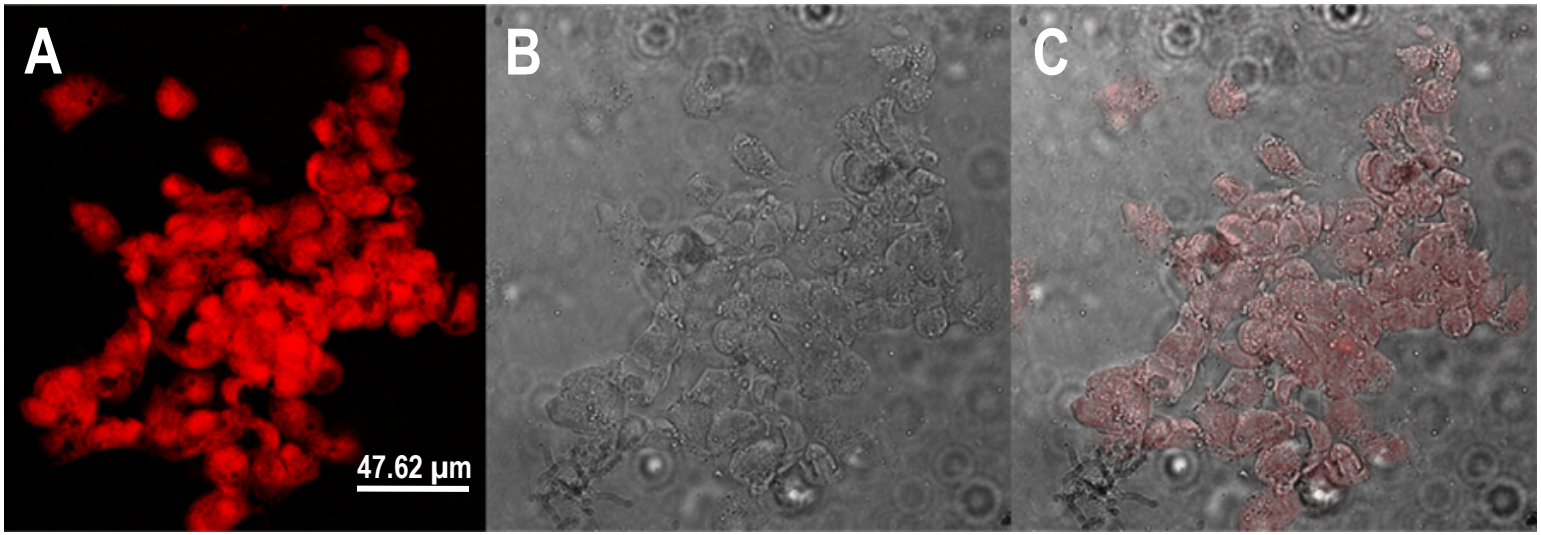
Plot of fluorescence intensity of Au_{23} cluster in water-DMSO mixture starting from pure water (blue line) to 1:1 (green line), 1:2 (red line) and 1:3 (black trace) water-DMSO mixtures. Inset shows the photographs of the corresponding solutions under UV light irradiation



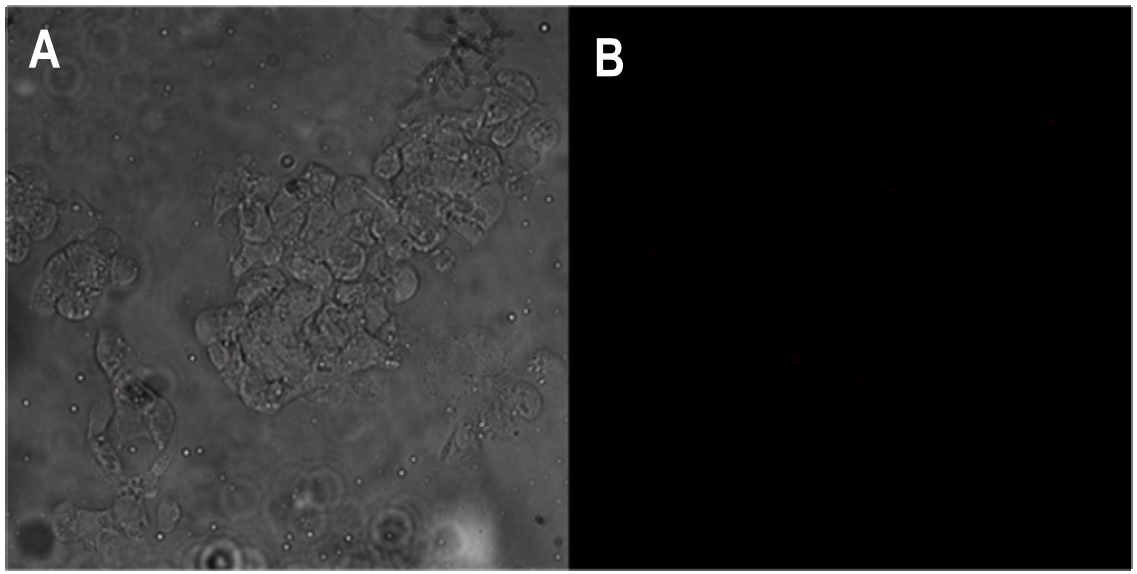
Plot of temperature *vs* fluorescence intensity of the cluster in the aqueous and toluene layers. While the intensity of emission of aqueous solution of Au_{23} decreases with increase in temperature, the emission intensity remains unaltered for phase transferred Au_{23}.



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

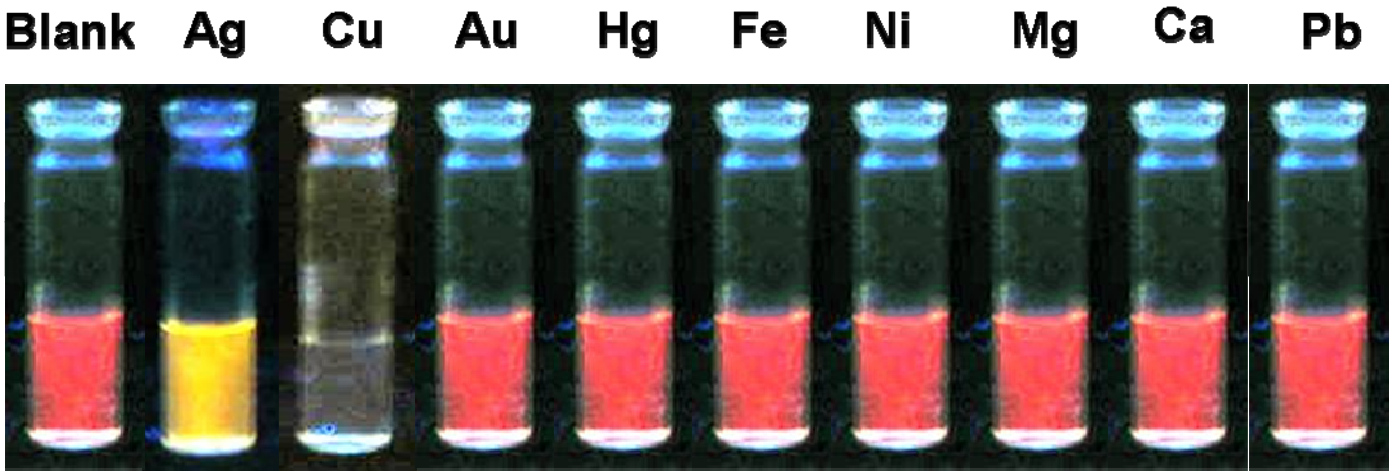


Fluorescence (A), bright field (B) and overlay of fluorescent and bright field images (C) of human hepatoma (HepG2) cells stained with streptavidin conjugated Au_{23}.



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

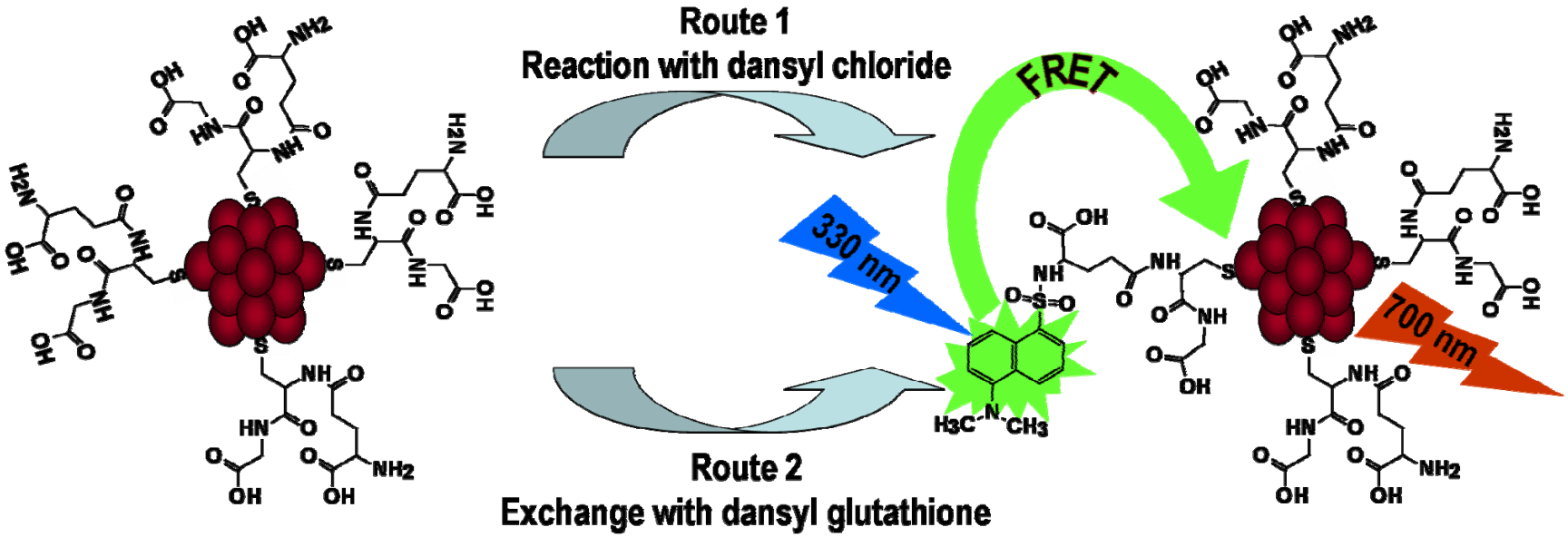
Clusters for metal ion detection



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)

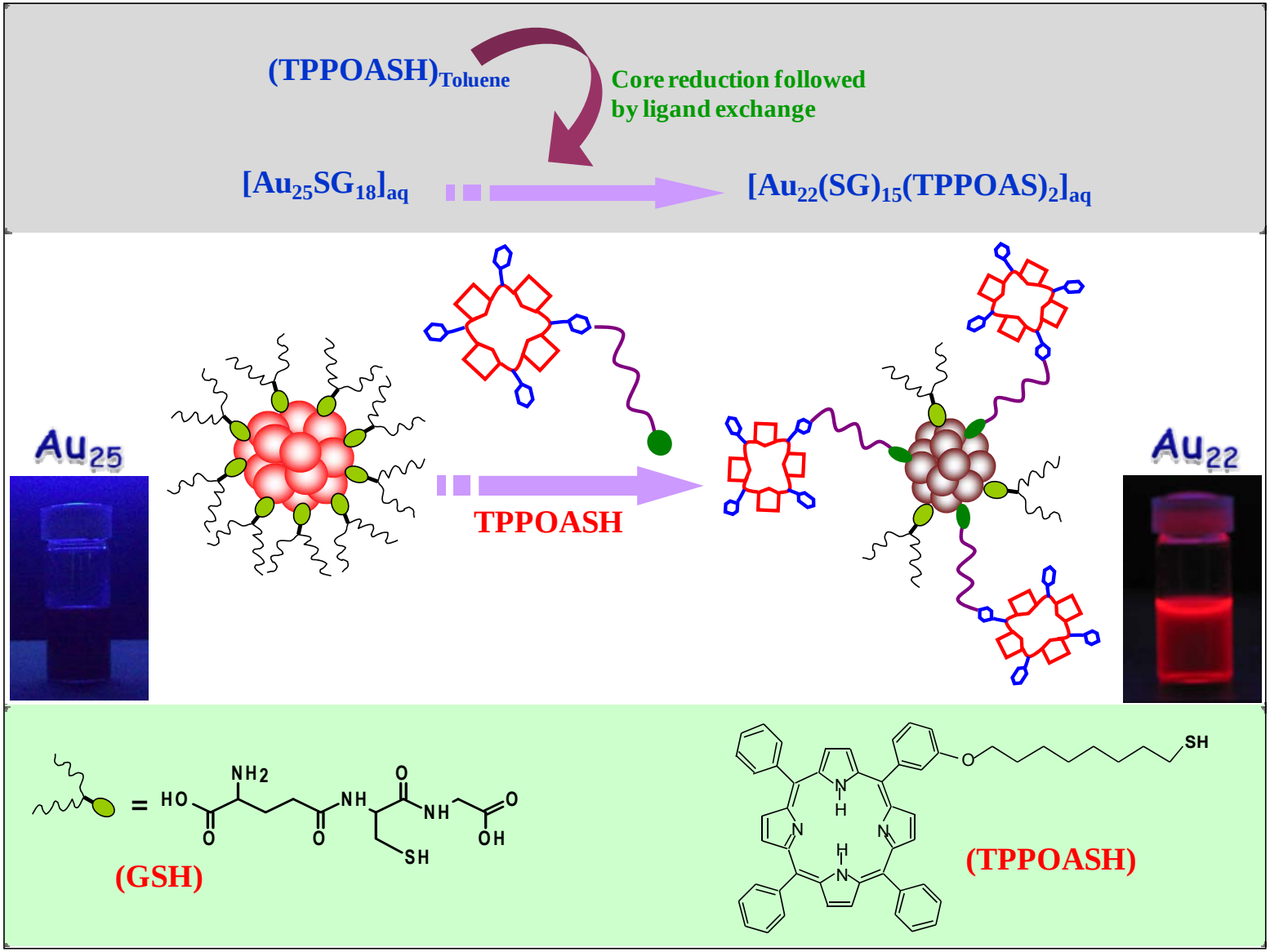
FRET between Au_{25} and Dansyl Chromophore

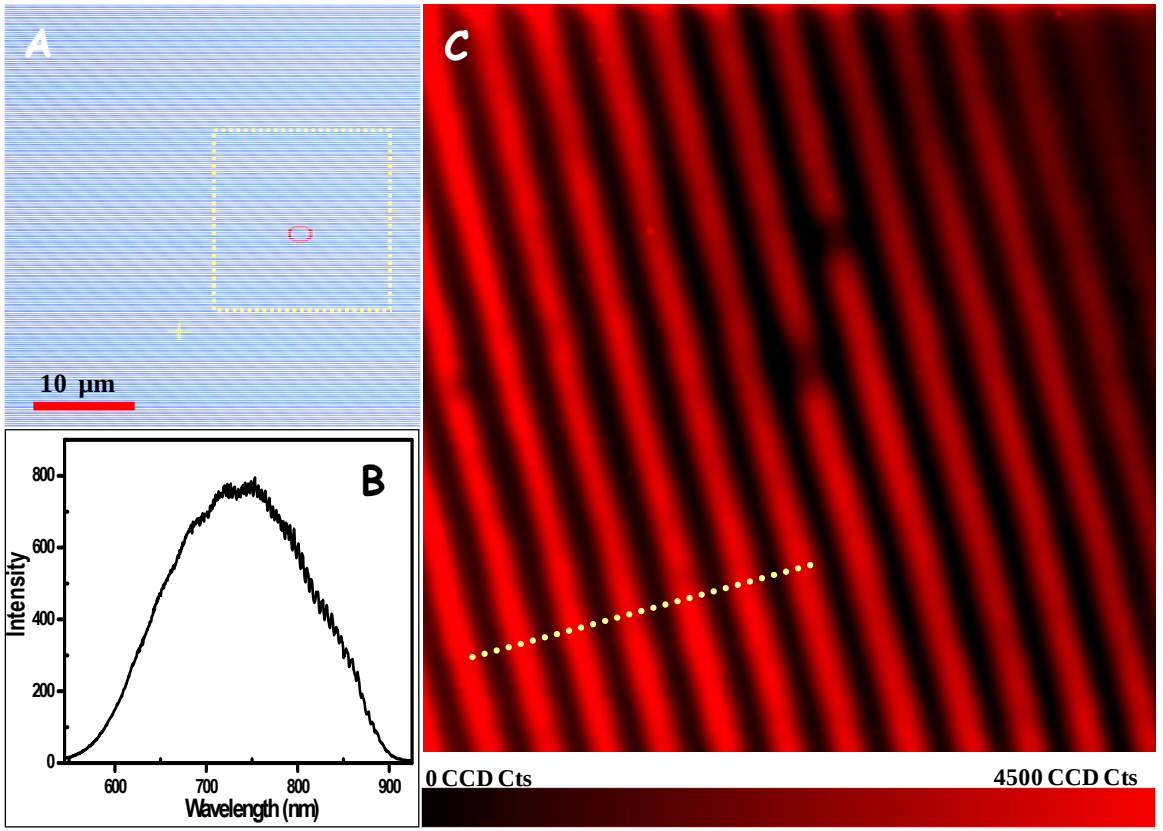


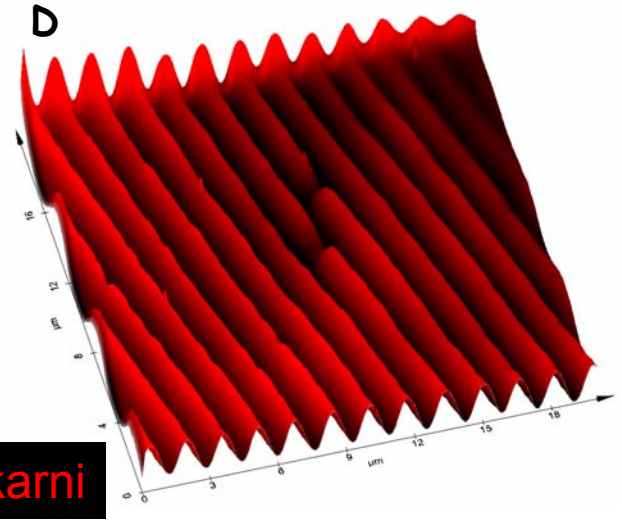
Approaches Used for the Functionalization of Dansyl Chromophore on the Au_{25} Cluster.

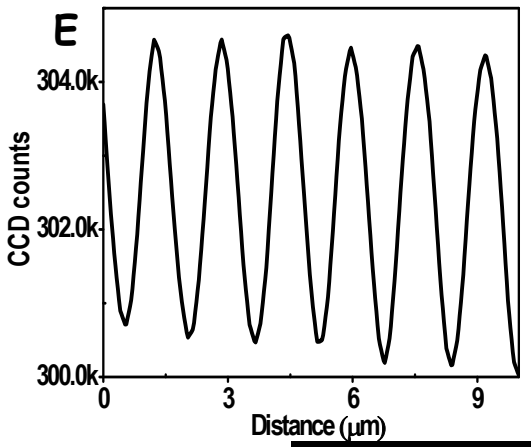
Habeeb Muhammed et al. *J. Phys. Chem. C* 2008

Cluster based patterns









With G. U. Kulkarni

Shibu et al. 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
- 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

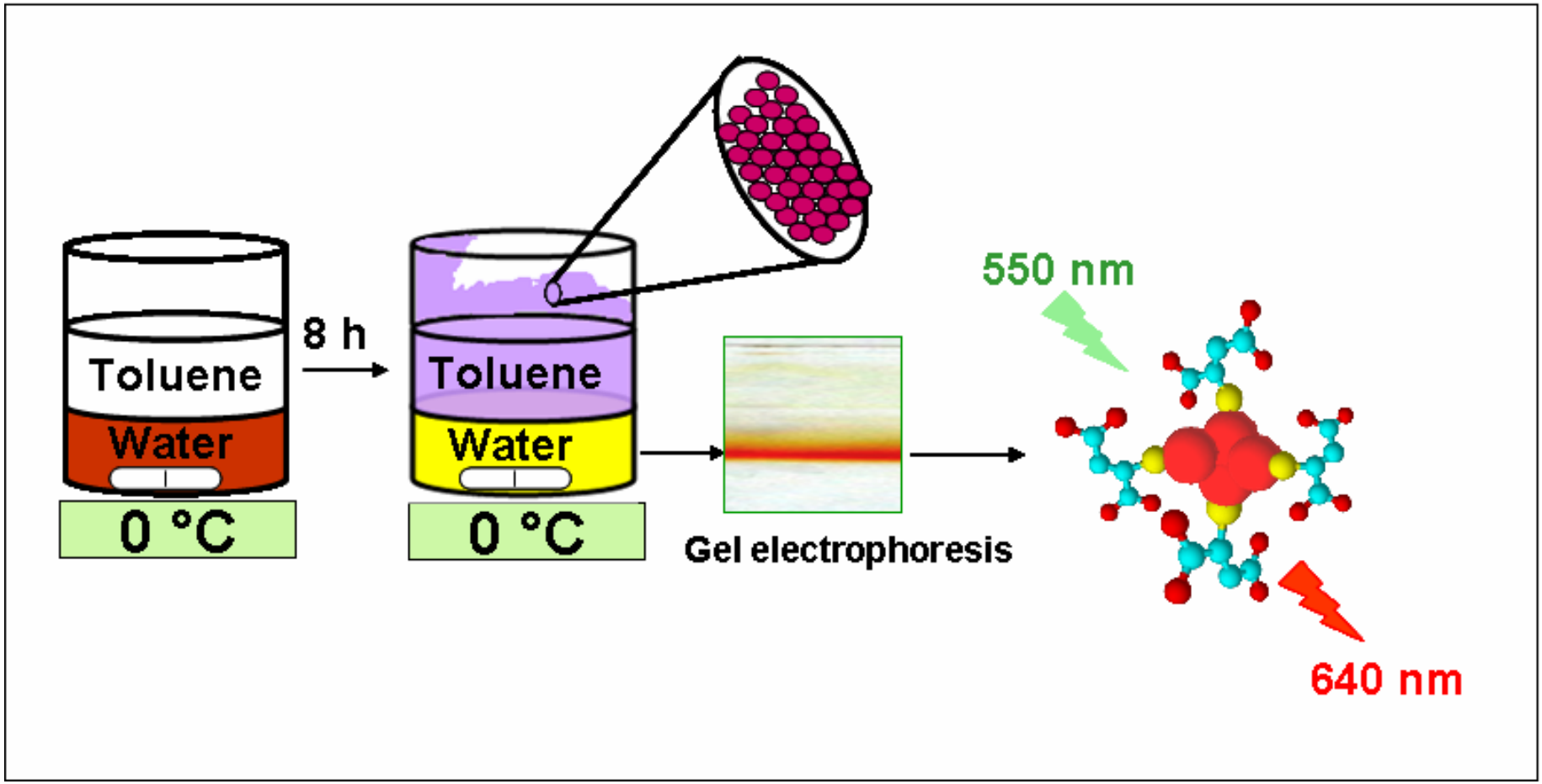
•**In search of a structural model for a thiolate-protected Au-38 cluster.** Jiang, D. E**,** Luo, W, Tiago, M. L, Dai, S**.** *J. Phys. Chem. C* **2008,** *112*, 13905

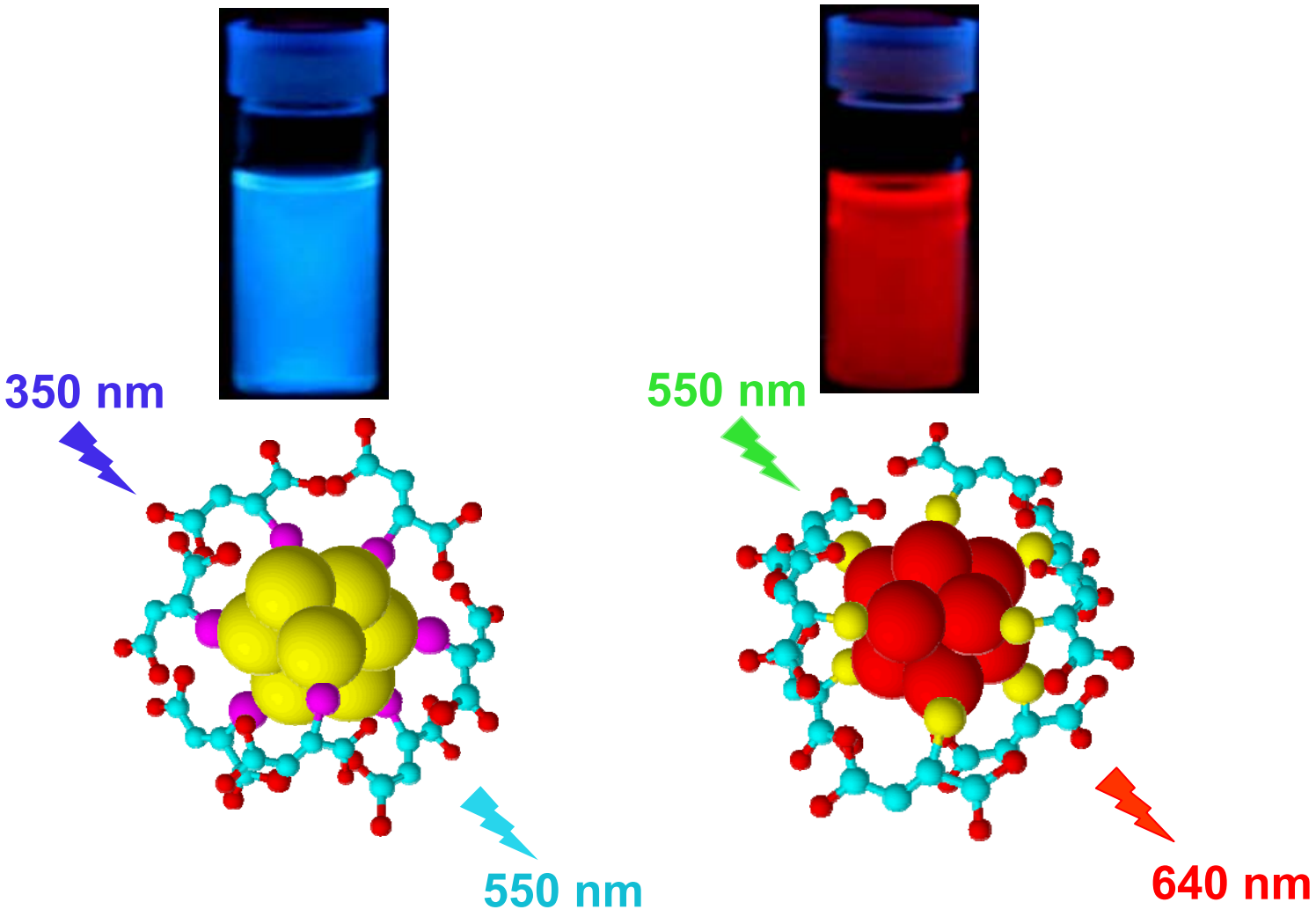
•**Preparation and characterization of dendrimer-templated Ag-Cu bimetallic nanoclusters** Li, G. P.; Luo. *Inorg. Chem.* **2008,** *47,* 360

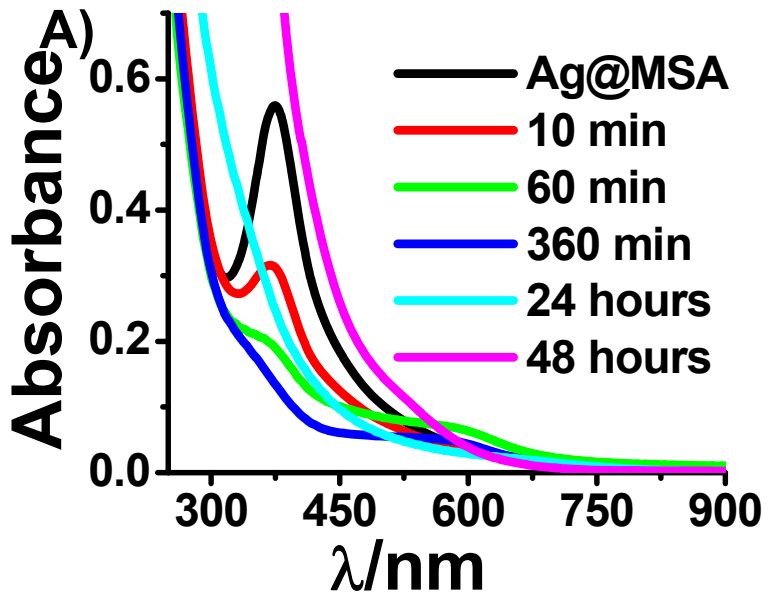
•**Stability and dissociation pathways of doped AunX+ clusters (X = Y, Er, Nb).** Veldeman. N.; Janssens, E.; Hansen K. *Faraday Discussions* 2008,*138* 147

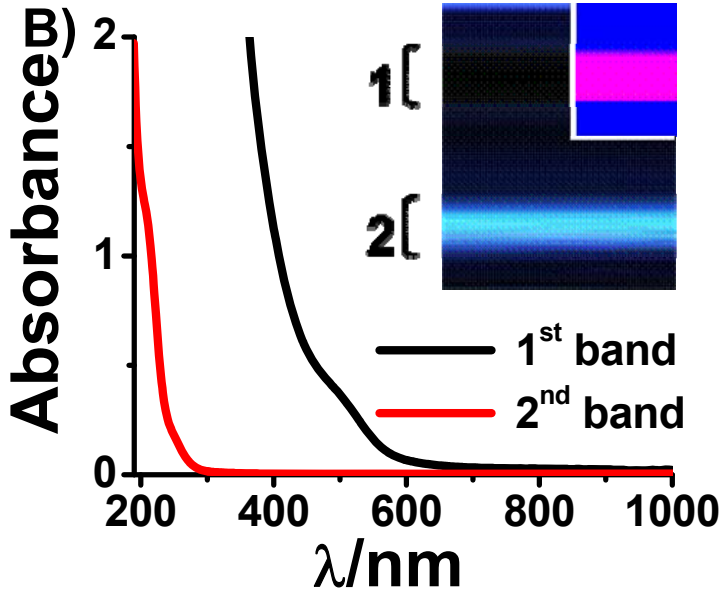
•***From discrete electronic states to plasmons: TDDFT optical absorption properties of Ag-n (n = 10, 20, 35, 56, 84, 120) tetrahedral clusters.*** Aikens, C. M.; Li, S. Z; Schatz**,** G. C**.** *J. Phys. Chem. C* **2008** *112,* 11272

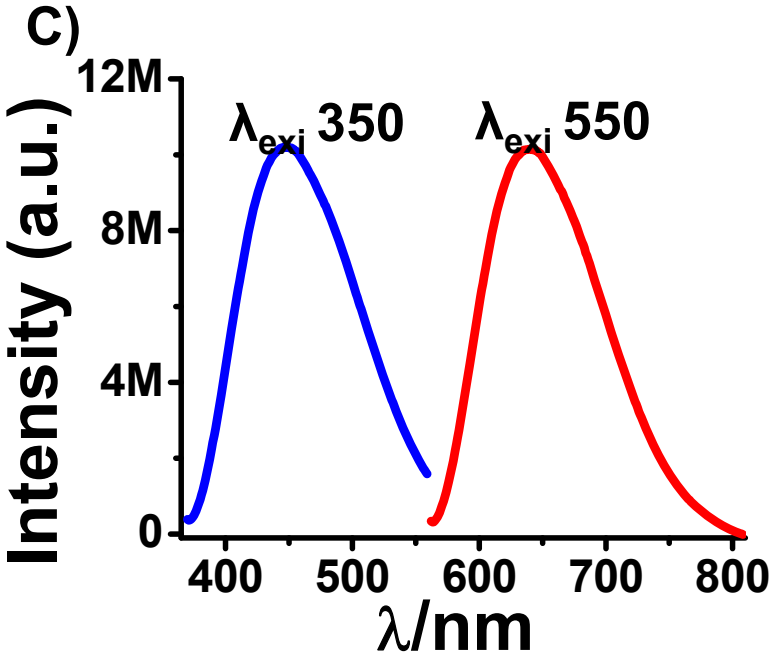
Interfacial etching

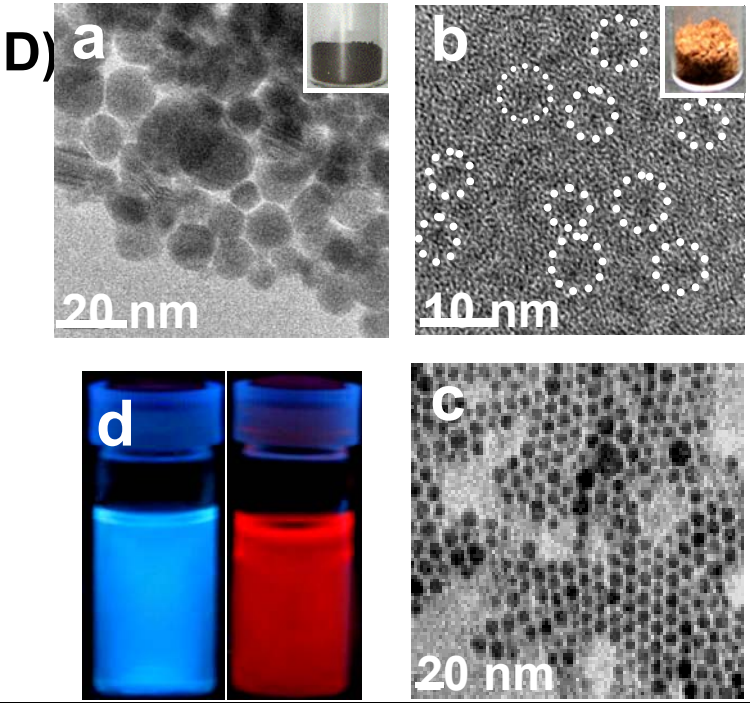



350 nm
550 nm
550 nm
640 nm

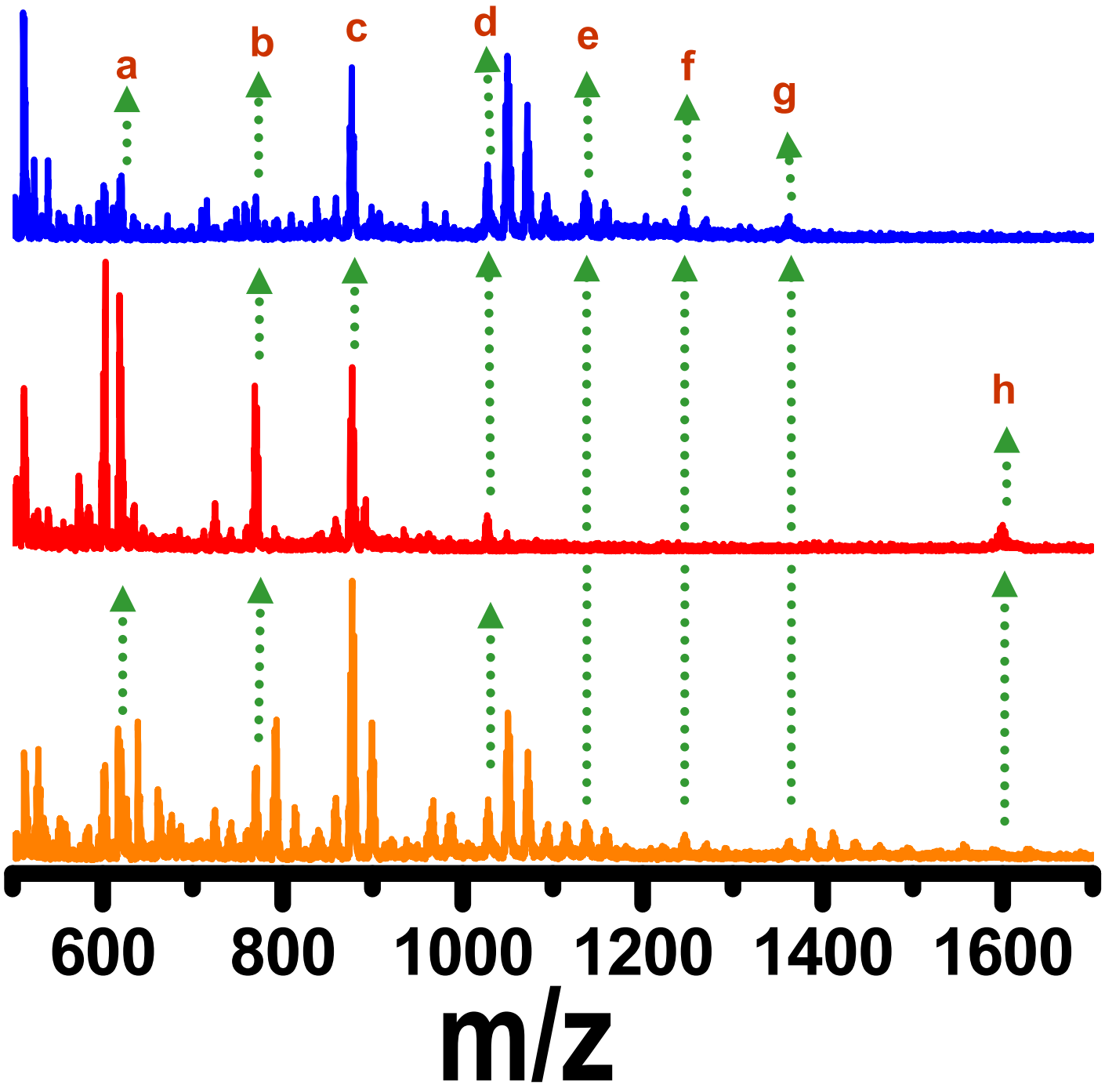


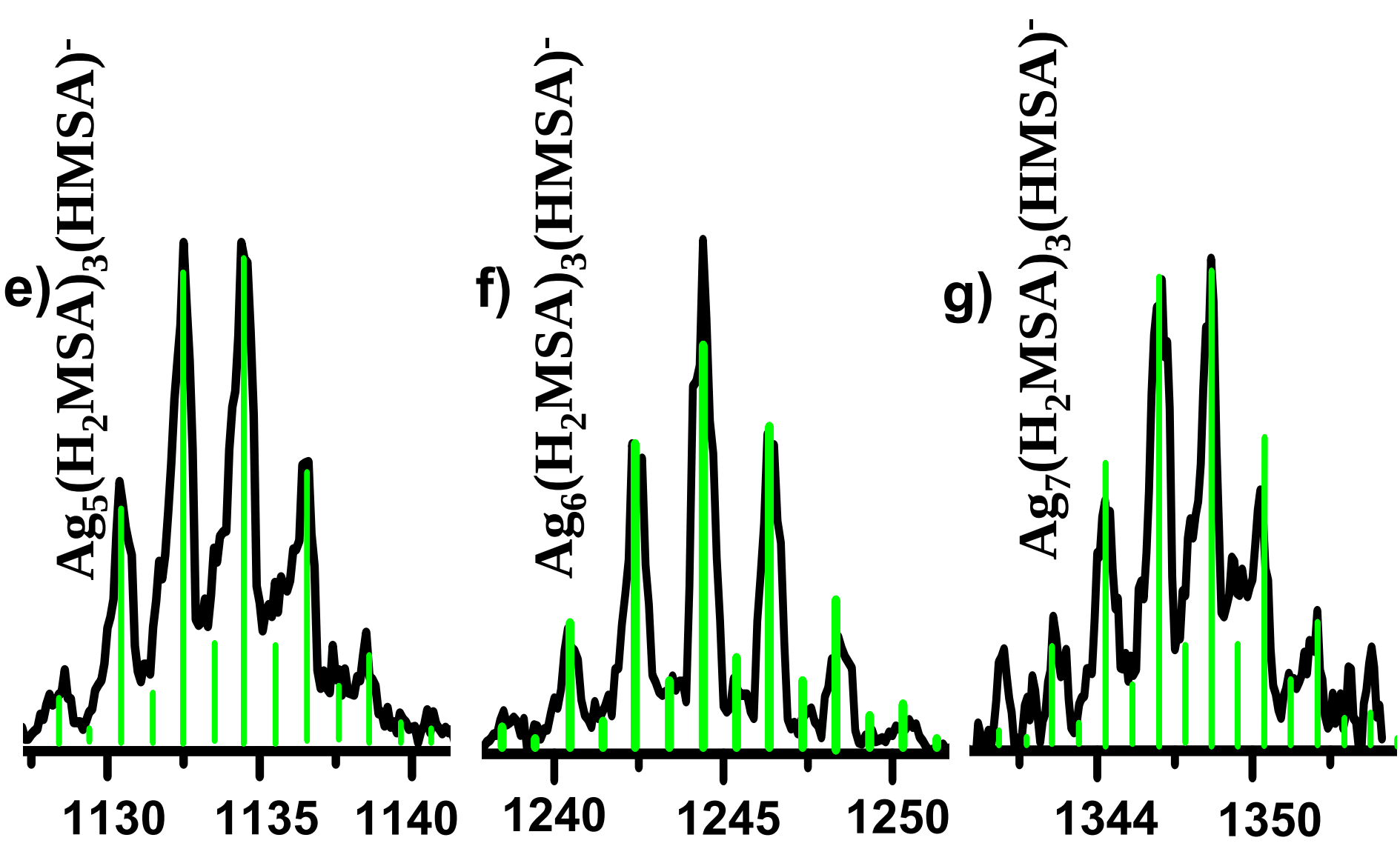


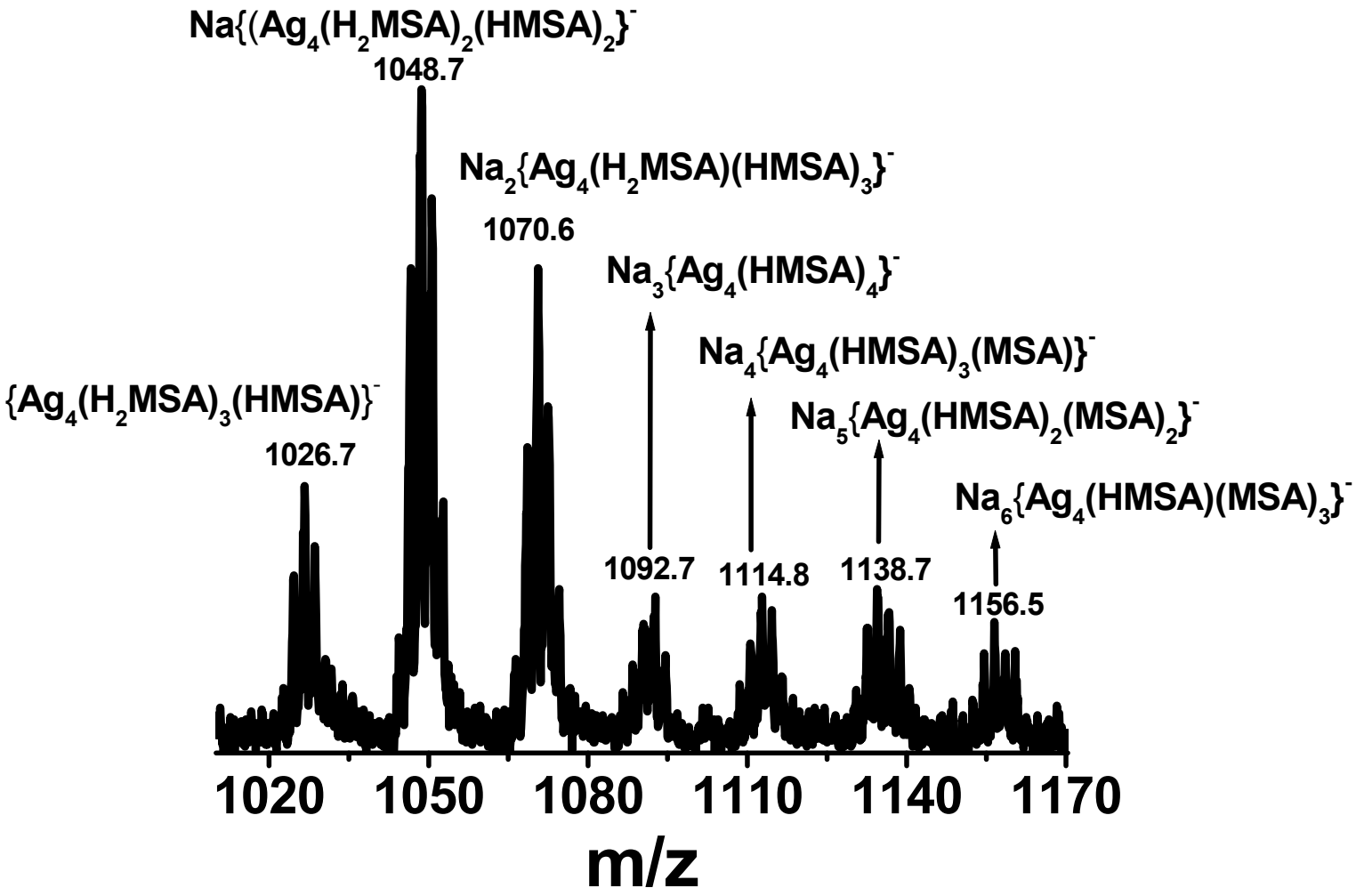


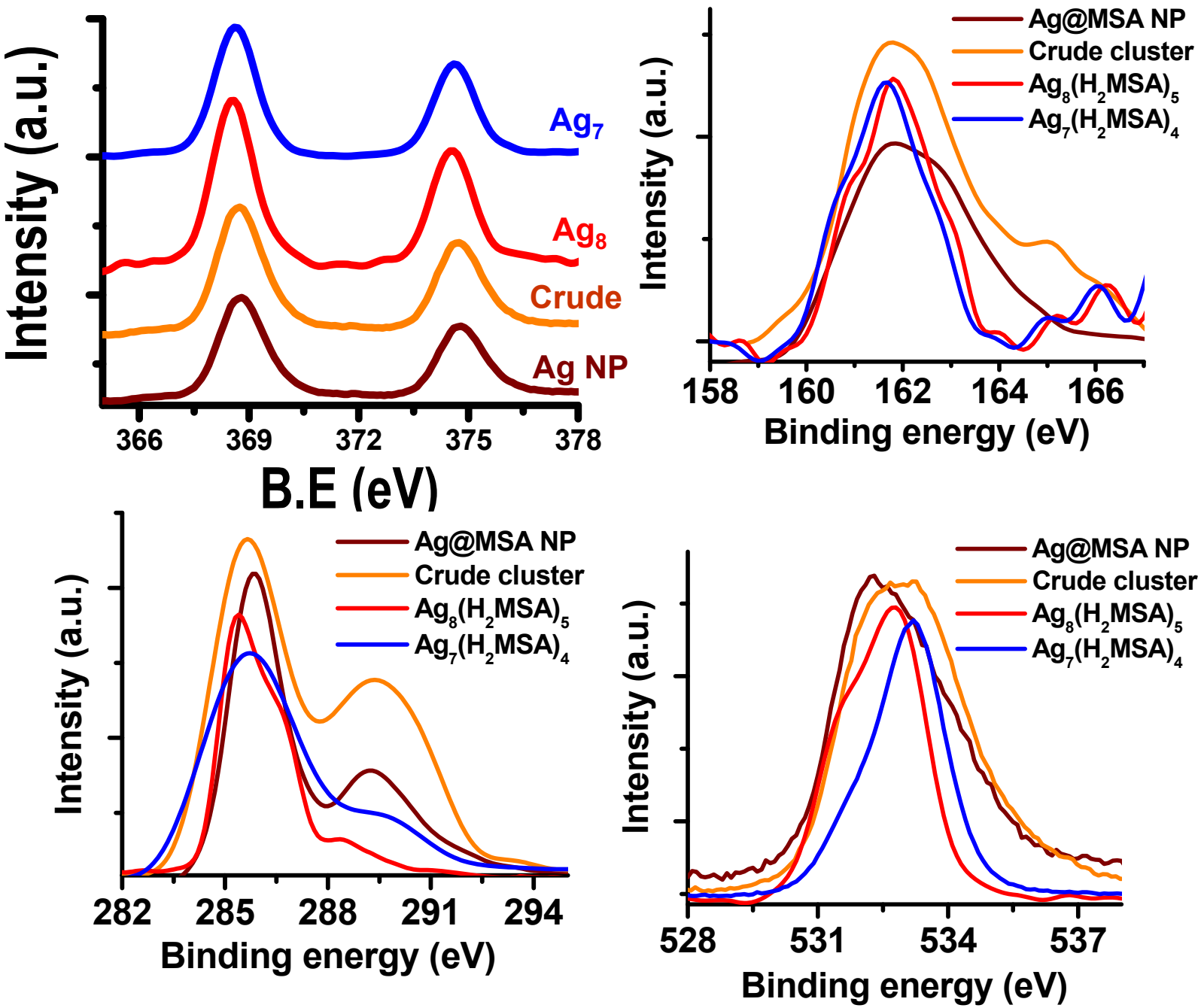


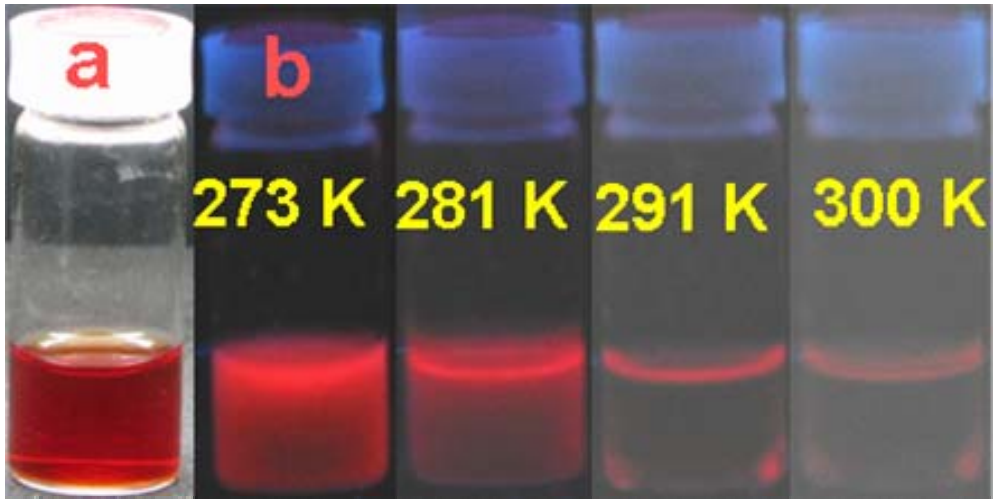
Udaybhaskar Rao and Pradeep, Submitted

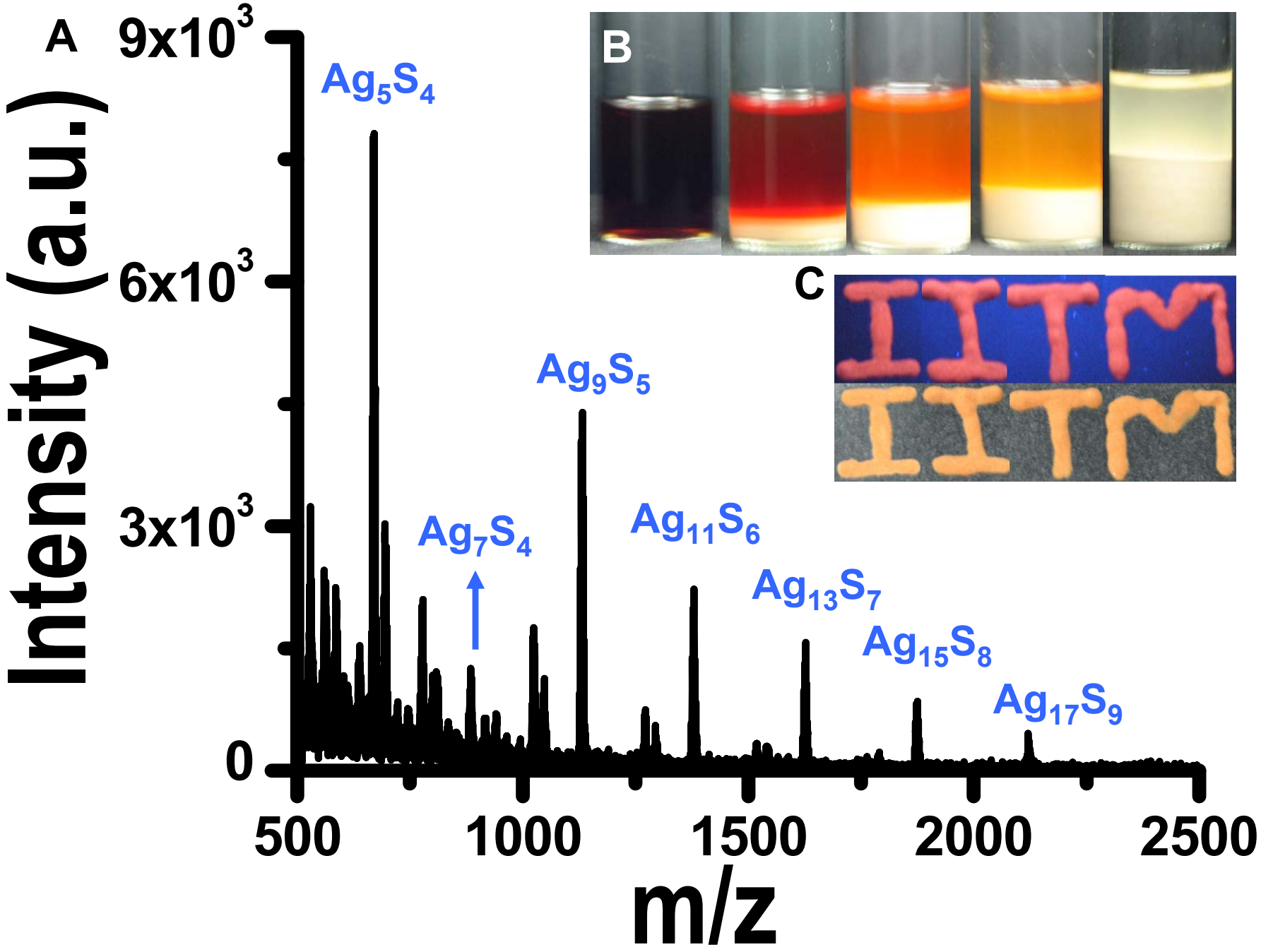

a
b
c
d
e
f
g
h
600
800
1000
1200
1400
1600
m/z

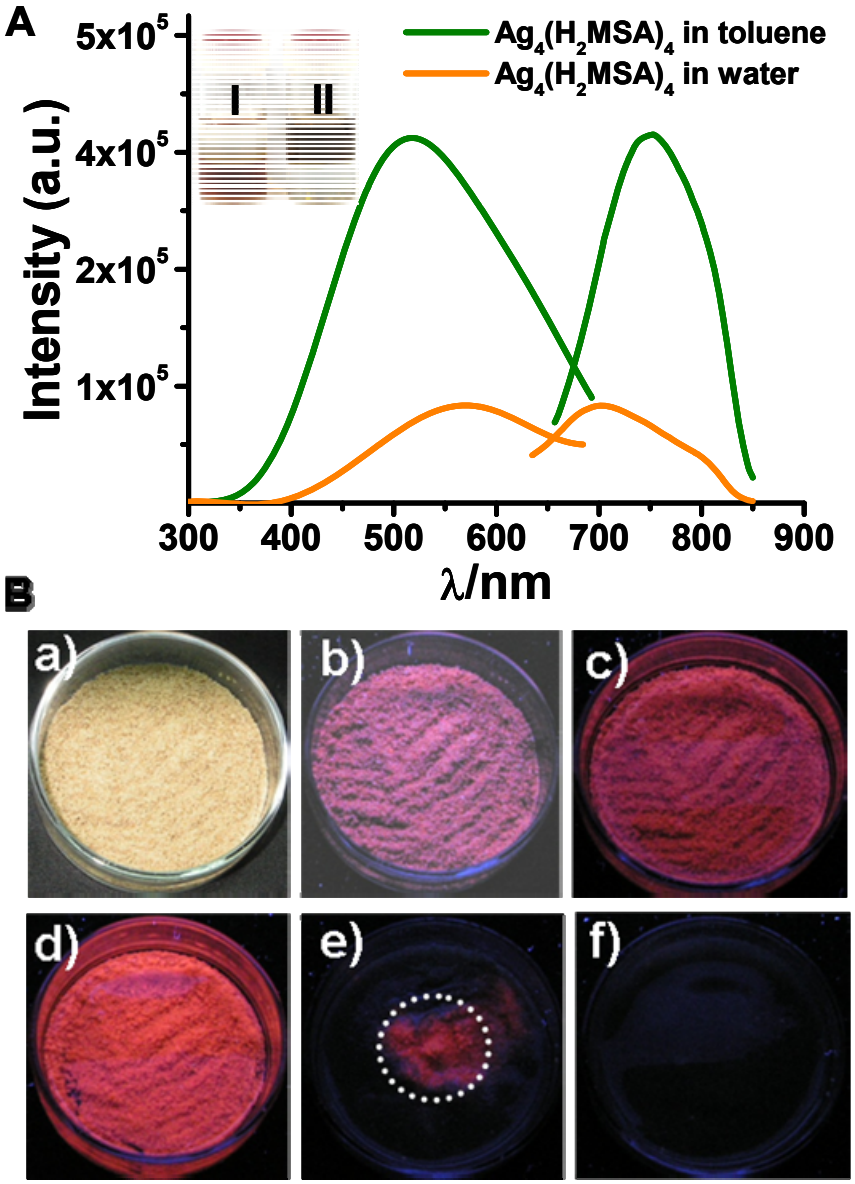

e)
$Ag_5(H_2MSA)_3(HMSA)^-$
1130
1135
1140
f)
$Ag_6(H_2MSA)_3(HMSA)^-$
1240
1245
1250
g)
$Ag_7(H_2MSA)_3(HMSA)^-$
1344
1350

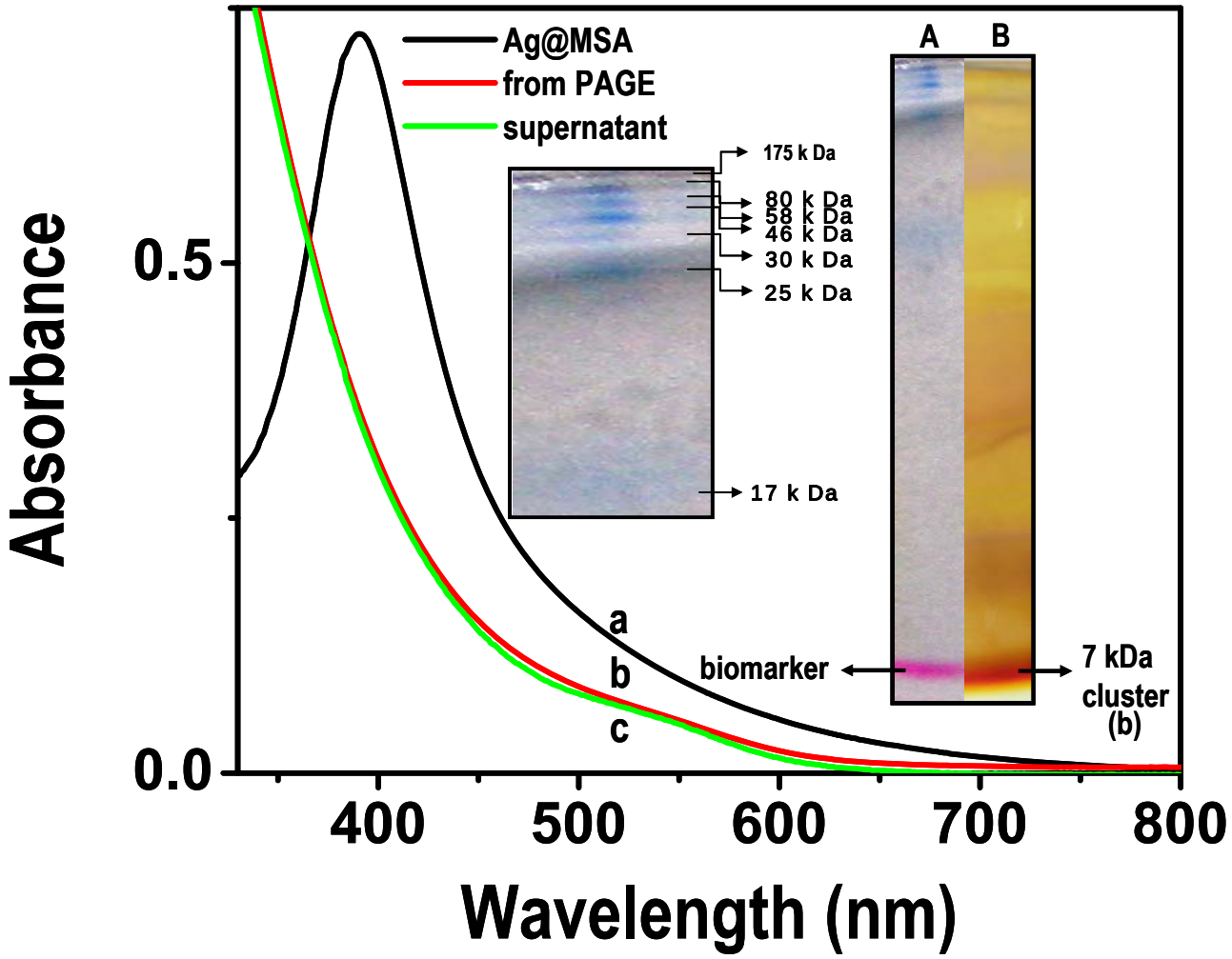

Na{(Ag4(H2MSA)2(HMSA)2}-
1048.7
Na2{Ag4(H2MSA)(HMSA)3}-
1070.6
Na3{Ag4(HMSA)4}-
Na4{Ag4(HMSA)3(MSA)}-
Na5{Ag4(HMSA)2(MSA)2}-
Na6{Ag4(HMSA)(MSA)3}-
{Ag4(H2MSA)3(HMSA)}-
1026.7
1092.7
1114.8
1138.7
1156.5
1020
1050
1080
1110
1140
1170
m/z


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)


a
b
273 K
281 K
291 K
300 K
White light
RT
UV light
T


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


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)



K.V. Mrulula et al. *J. Mater. Chem. 2009 CNR Rao Special Issue*

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, $Au_8(SG)_8$, Ag_8MSA_8, Au_{22}, $Au_{23}SG_{17}$, etc. are synthesized.
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

Thanks!