Light emitting quantum clusters of gold and silver

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Au_{25}, Au_8 and Ag_4

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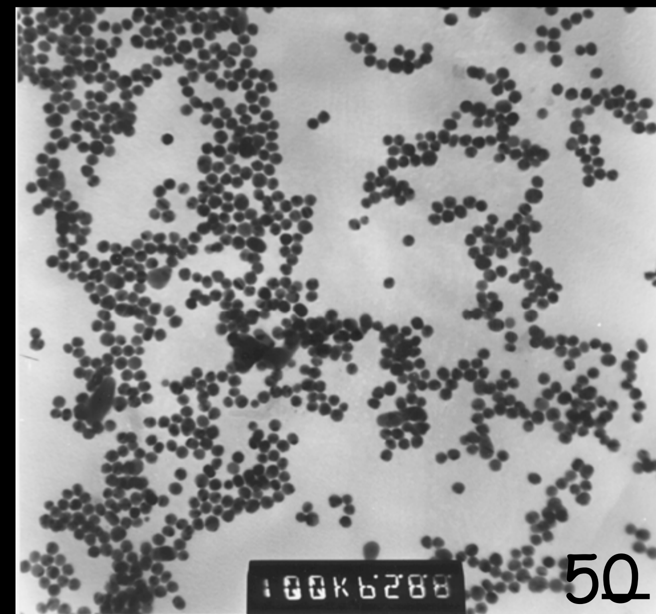
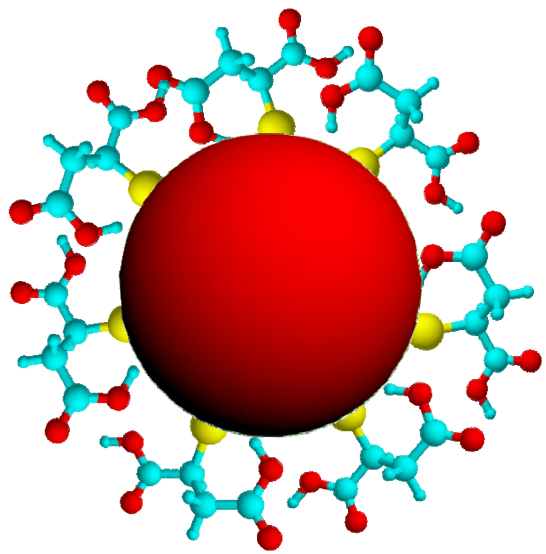


Faraday’s gold preserved in Royal Institution. From the site,
http://www.rigb.org/rimain/heritage/faradaypage.jsp

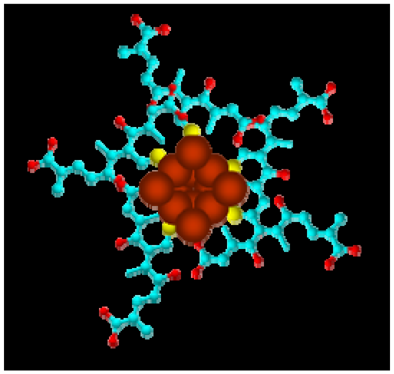
Monolayer Protected Metal Nanoparticles
Monolayer Protected Clusters (MPCs)

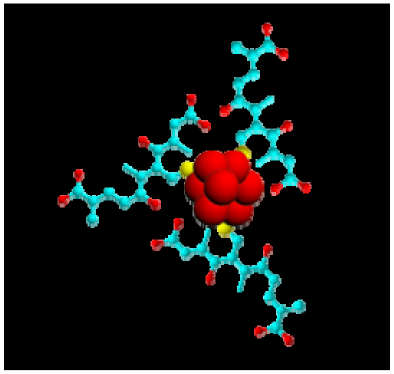


Synthesis of thiol-derivatised gold nanoparticles in a two-phase Liquid–Liquid system, Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *Chem. Commun.* **1994**, 801.

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

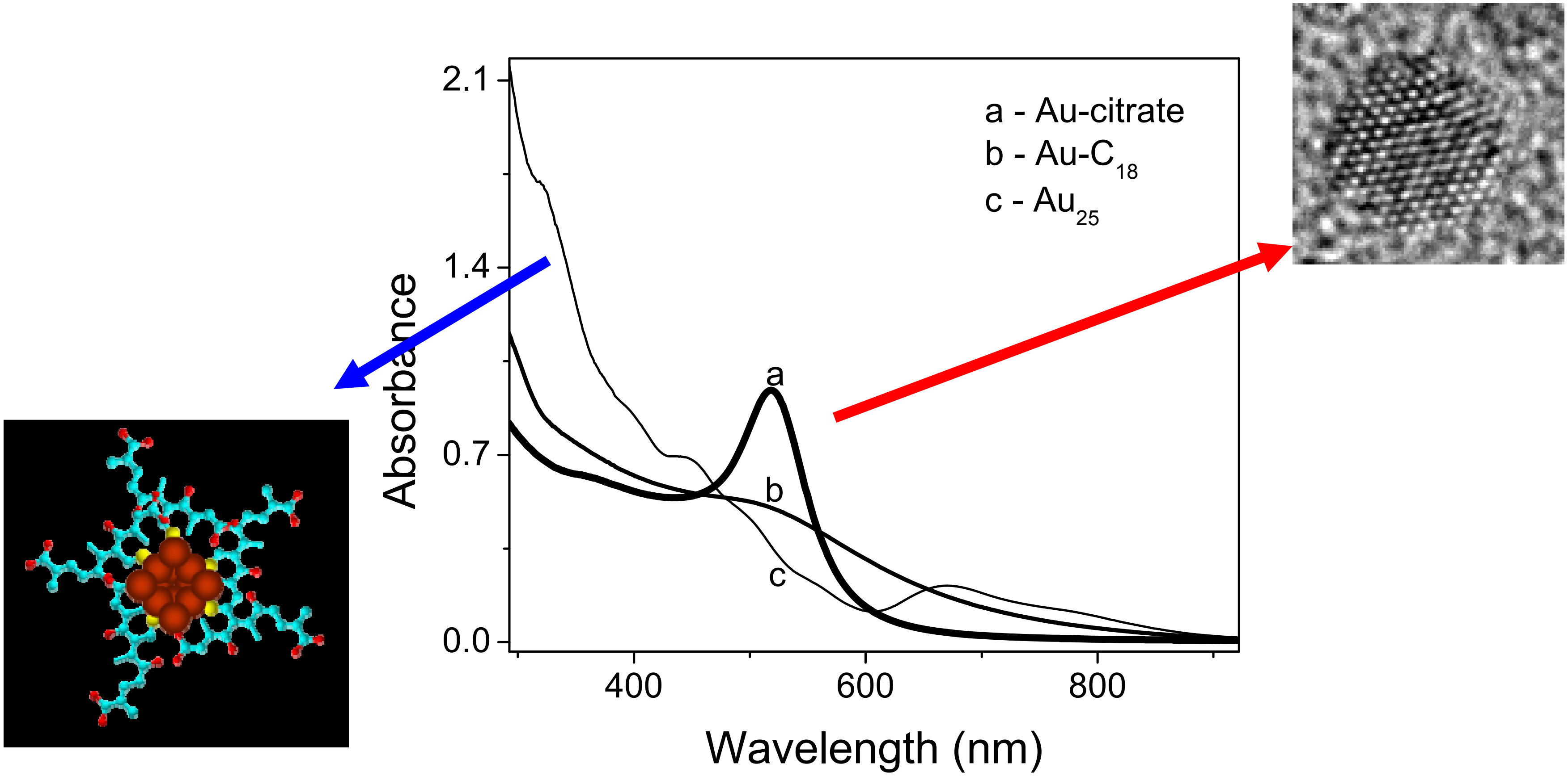
Molecular Clusters





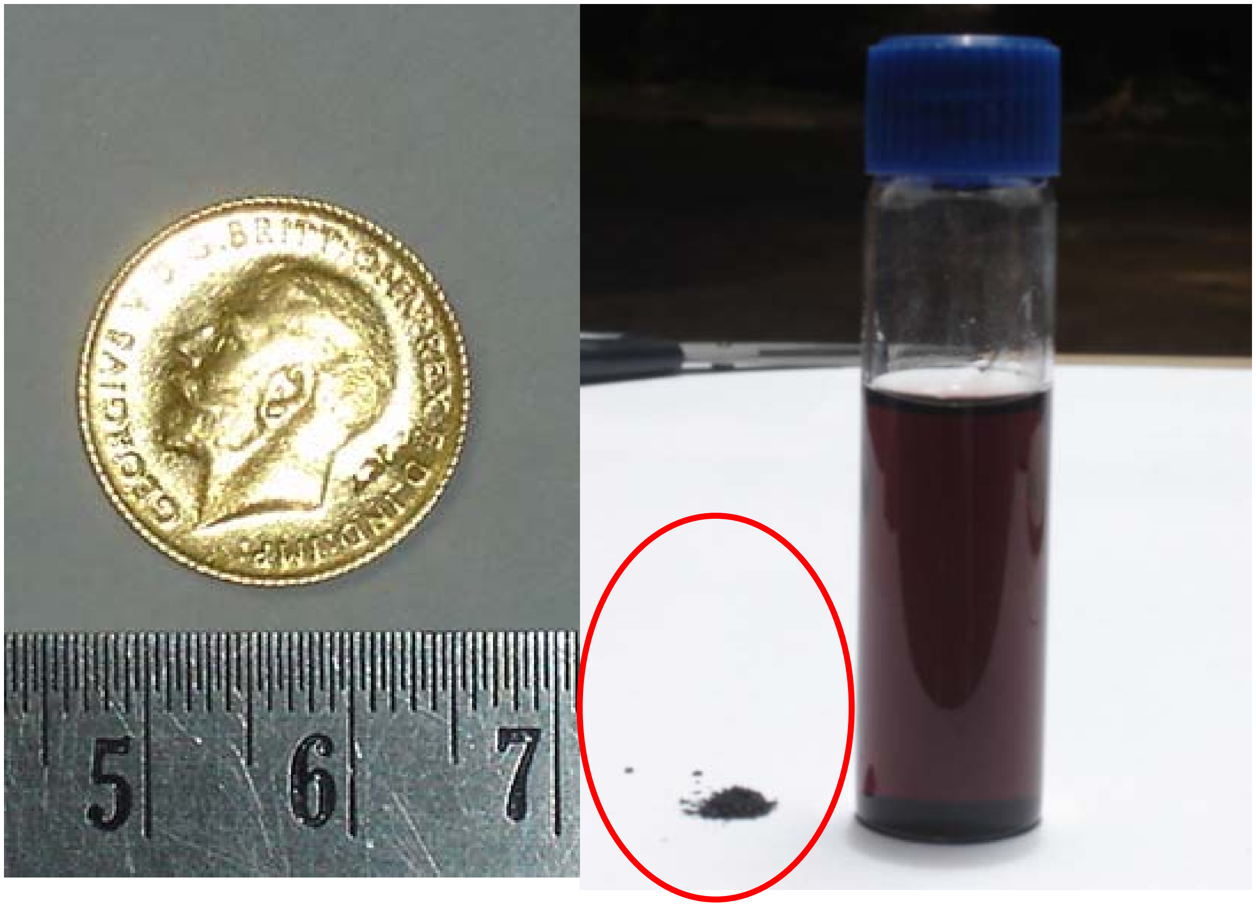
- **28 kDa Alkanethiolate-Protected Au Clusters Give Analogous Solution Electrochemistry and STM Coulomb Staircases,** Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. *J. Am. Chem. Soc.* **1997**, *119*, 9279.
- **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-BasedTransitions**, 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.

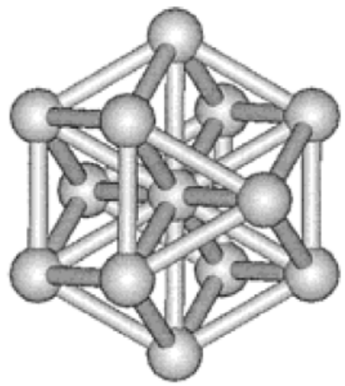


Optical absorption (extinction) spectrum of (a) 15 nm gold particles in aqueous solution (labeled Au@citrate). The spectrum of (b) 3 nm particles in toluene is also shown. See the broadening of the plasmon feature. The spectrum of (c) Au_{25} in water. In this, there is no plasmon excitation and all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

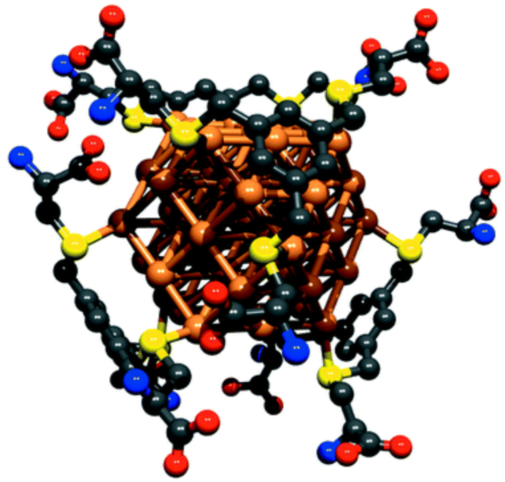
Das, Choi, Yu and Pradeep, *Nanofluids*, John Wiley, New York, 2008


5
6
7

Phosphine Capped Gold Clusters



Au_{13}



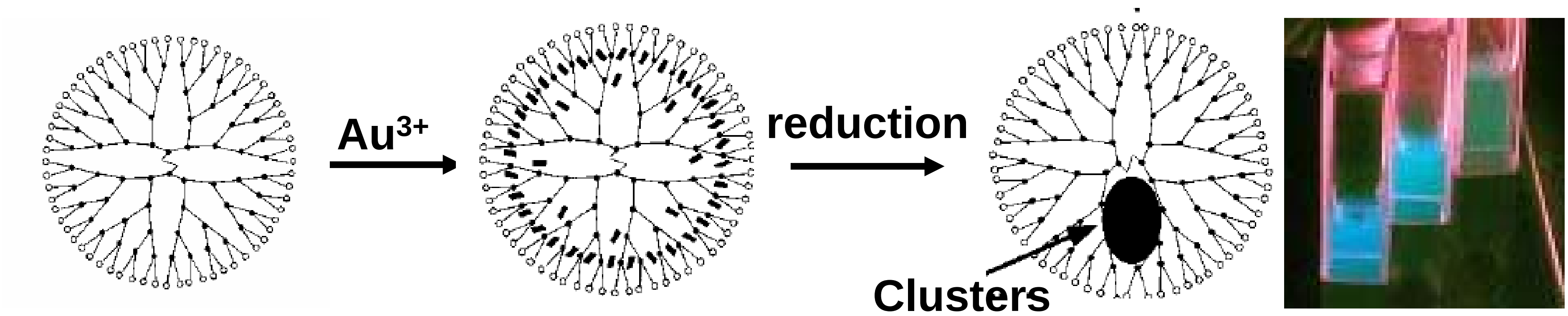
Au_{55}

▪ **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.

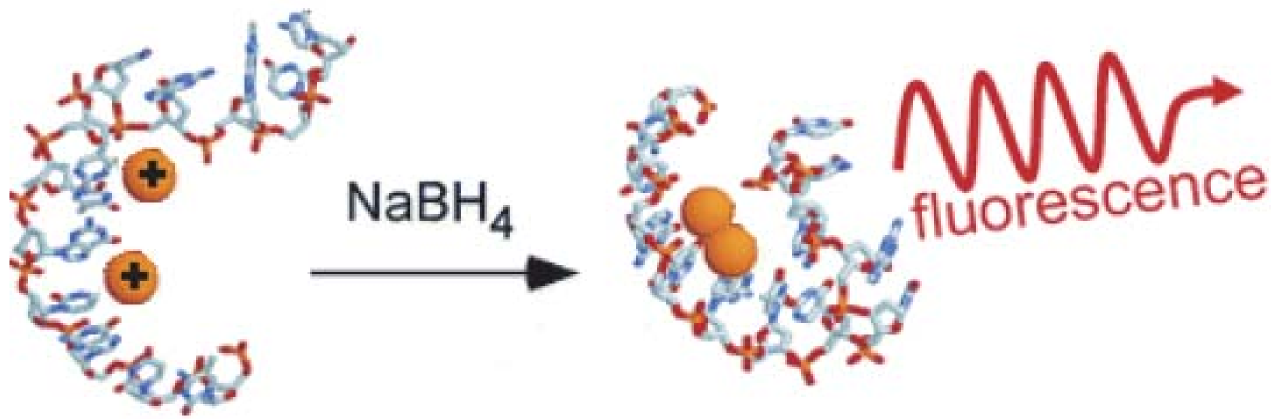
▪ **Synthesis of water-soluble undecagold cluster compounds of potential importance in electron microscopic and other studies in biological systems**, Bartlett, P. A.; Bauer, B.; Singer, S. *J. Am. Chem. Soc.* **1978**, *100*, 5085.

Dendrimer Encapsulated Clusters

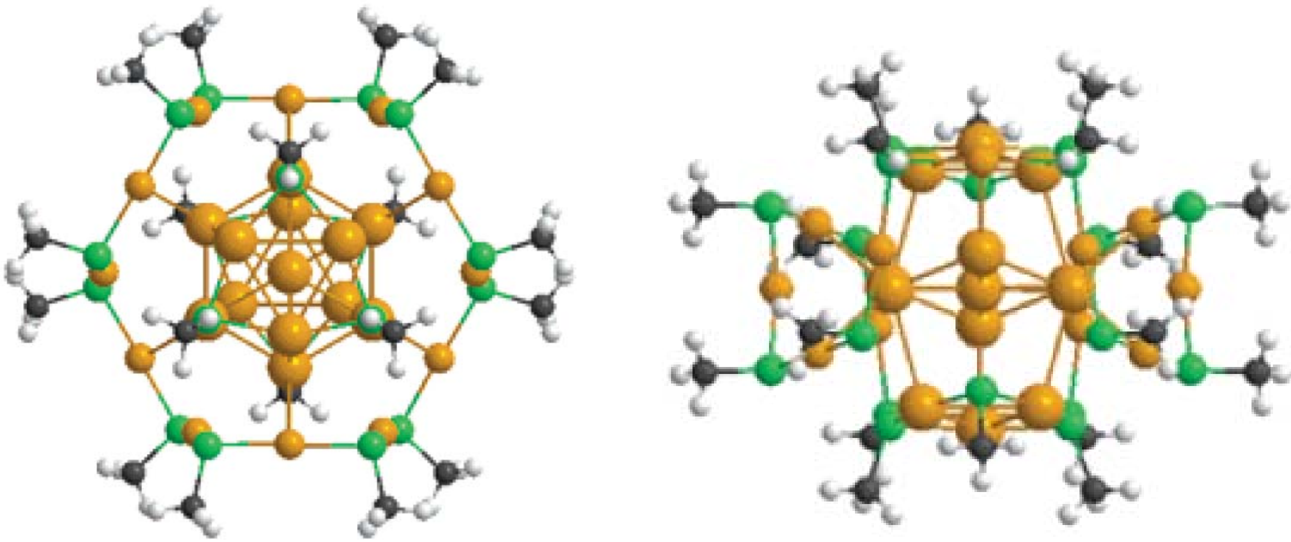


- **High quantum yield blue emission from water-soluble Au_8 nanodots**, Zheng, J.; Petty, J. T.; Dickson, R. M. *J. Am. Chem. Soc***. 2003**, *125*, 7780.
- **Highly fluorescent, water-soluble, size-tunable gold quantum dots,** Zheng, J.; Zhang, C. W.; Dickson, R. M. *Phys. Rev. Lett*. **2004**, *93*,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

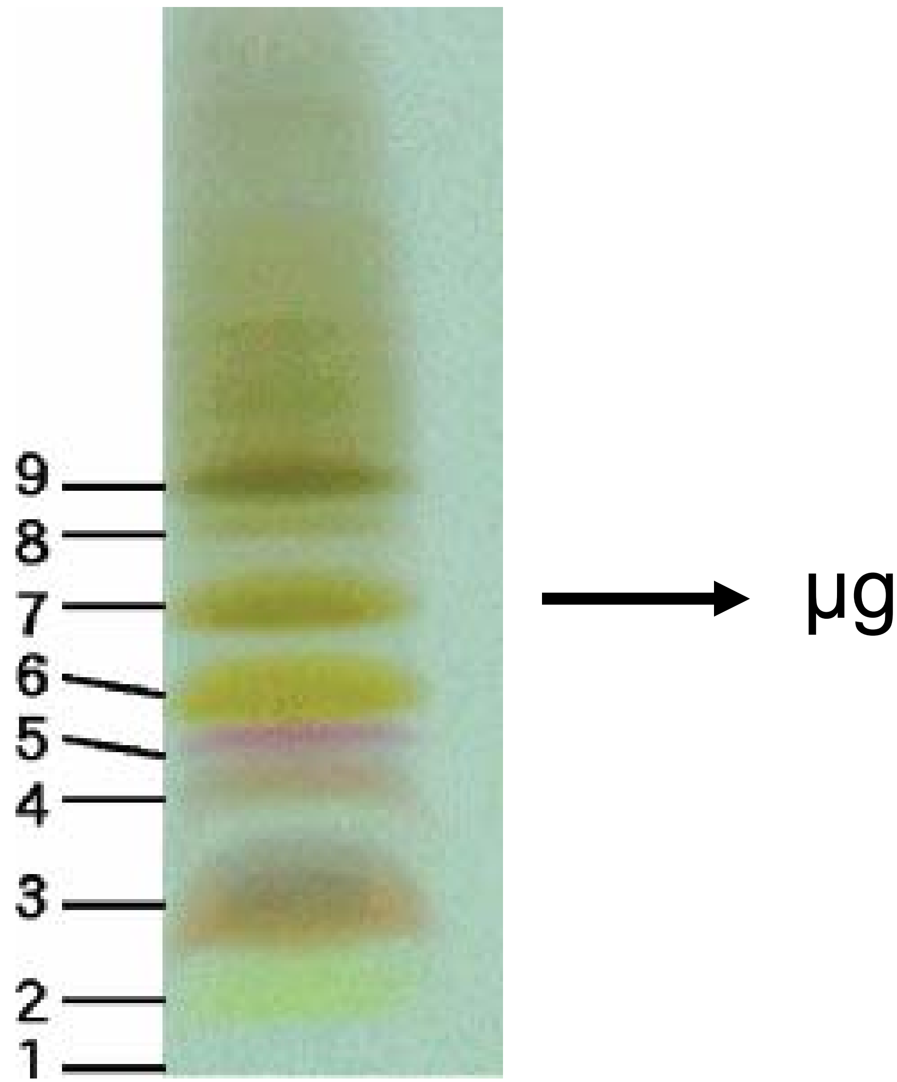


Top and side view of $[Au_{25}(SCH_3)_{18}]^+$

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.

How to make them?

Polyacrylamide gel electrophoresis (PAGE)

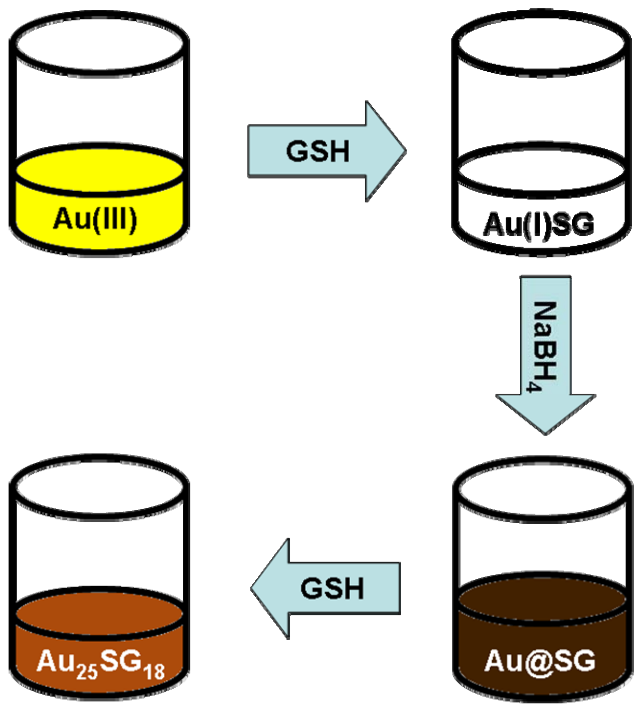


Negishi, Y.; Nobusada, K.; and Tsukuda, T. Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)-Thiolate Complexes and Thiolate-Protected Gold Nanocrystals. *J. Am. Chem. Soc*. **2005**, *127*, 5261-70.

Gram scale synthesis

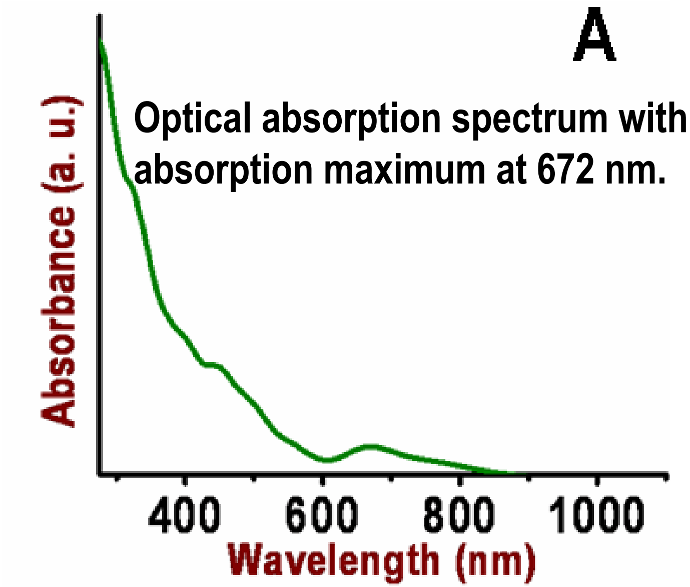
$Au_{25}SG_{18}$

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

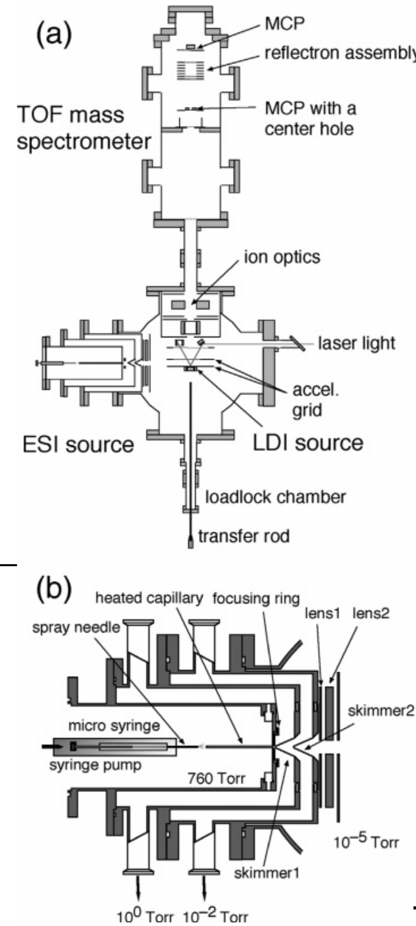


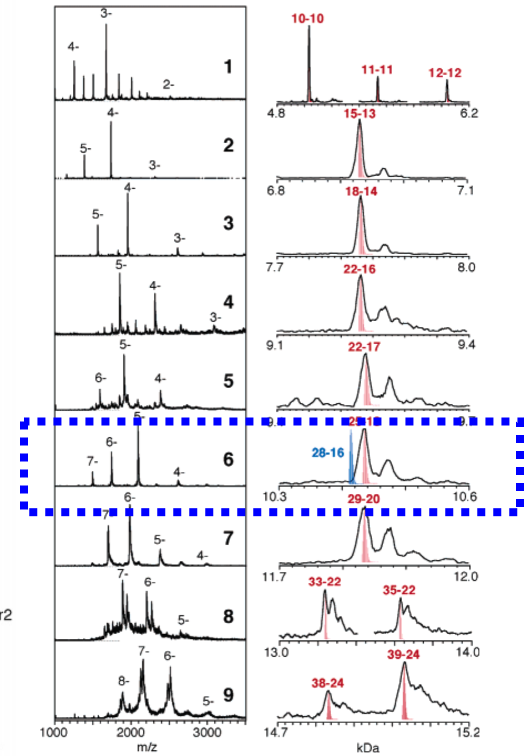
Scheme showing the synthesis of $Au_{25}SG_{18}$ clusters

Characterization of $Au_{25}SG_{18}$

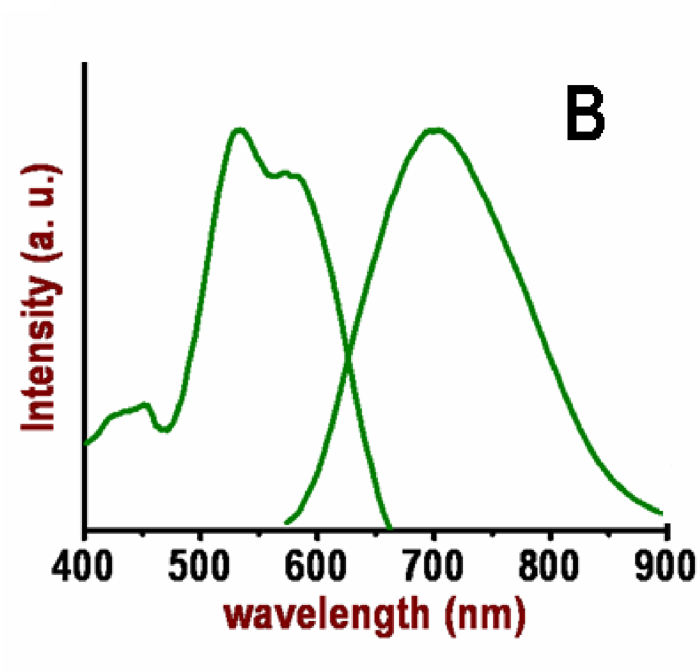


Optical absorption spectrum with an absorption maximum at 672 nm.

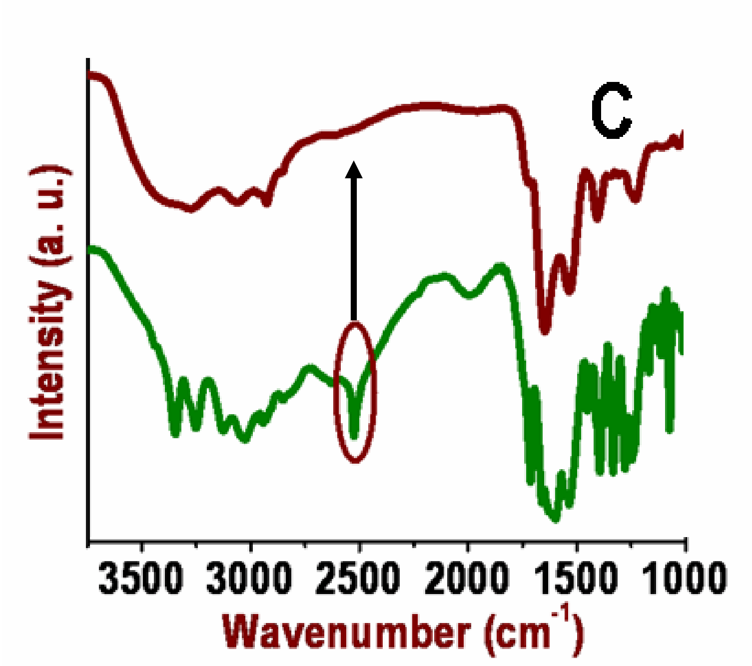


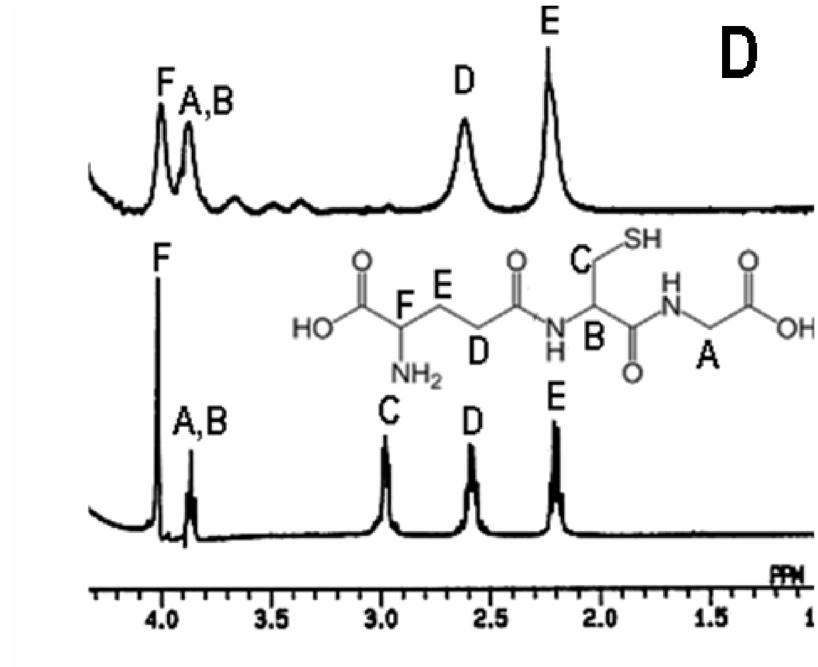


Tsukuda et. al. JACS 2005



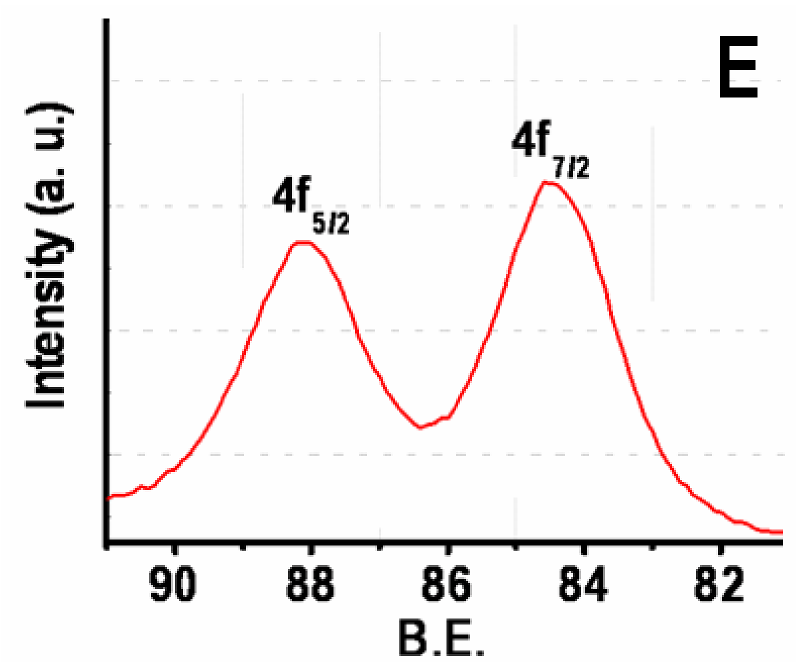
Photoluminescence profile with excitation and emission maxima at 535 and 700 nm, respectively.



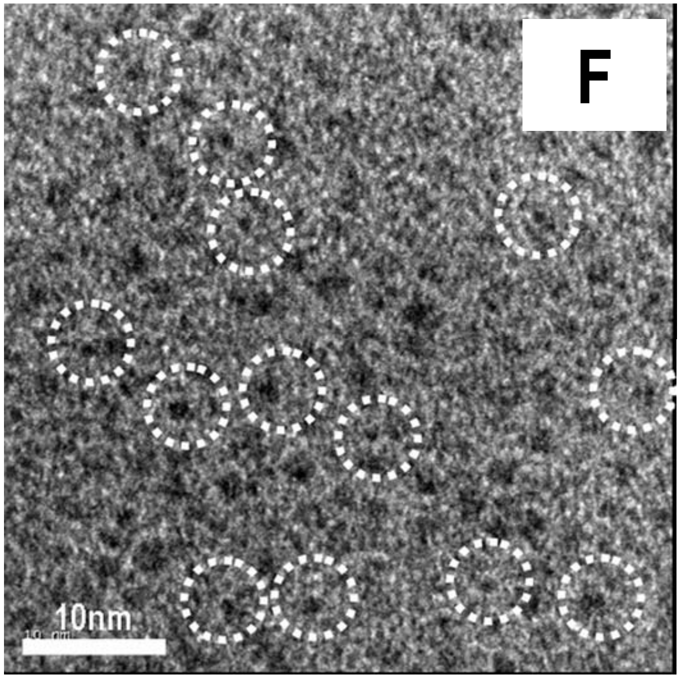


FTIR spectrum: The peak at 2526 cm^{-1} of glutathione due to –SH stretching frequency is absent in IR spectrum of Au_{25} suggesting the ligand binding on cluster surface.

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.

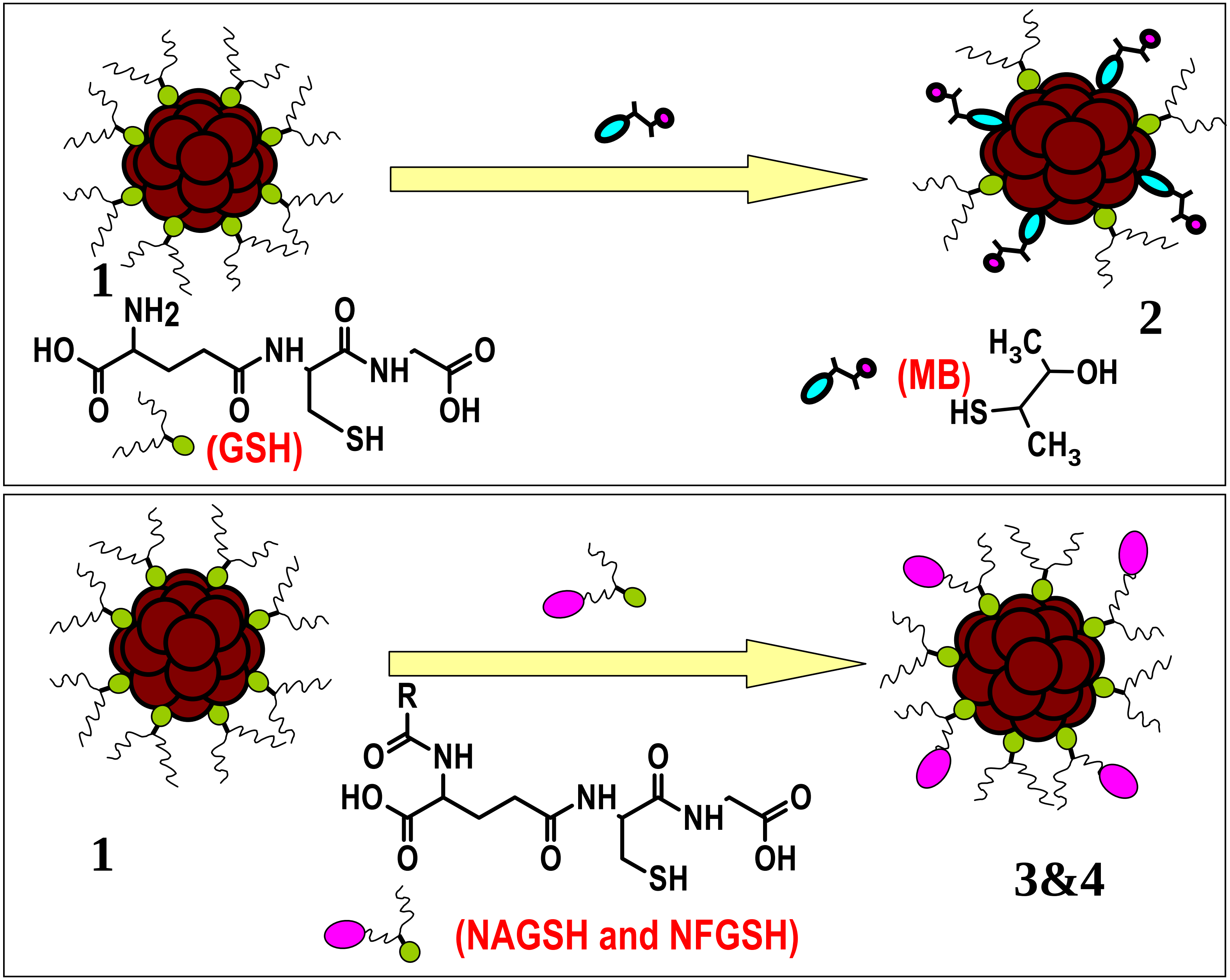


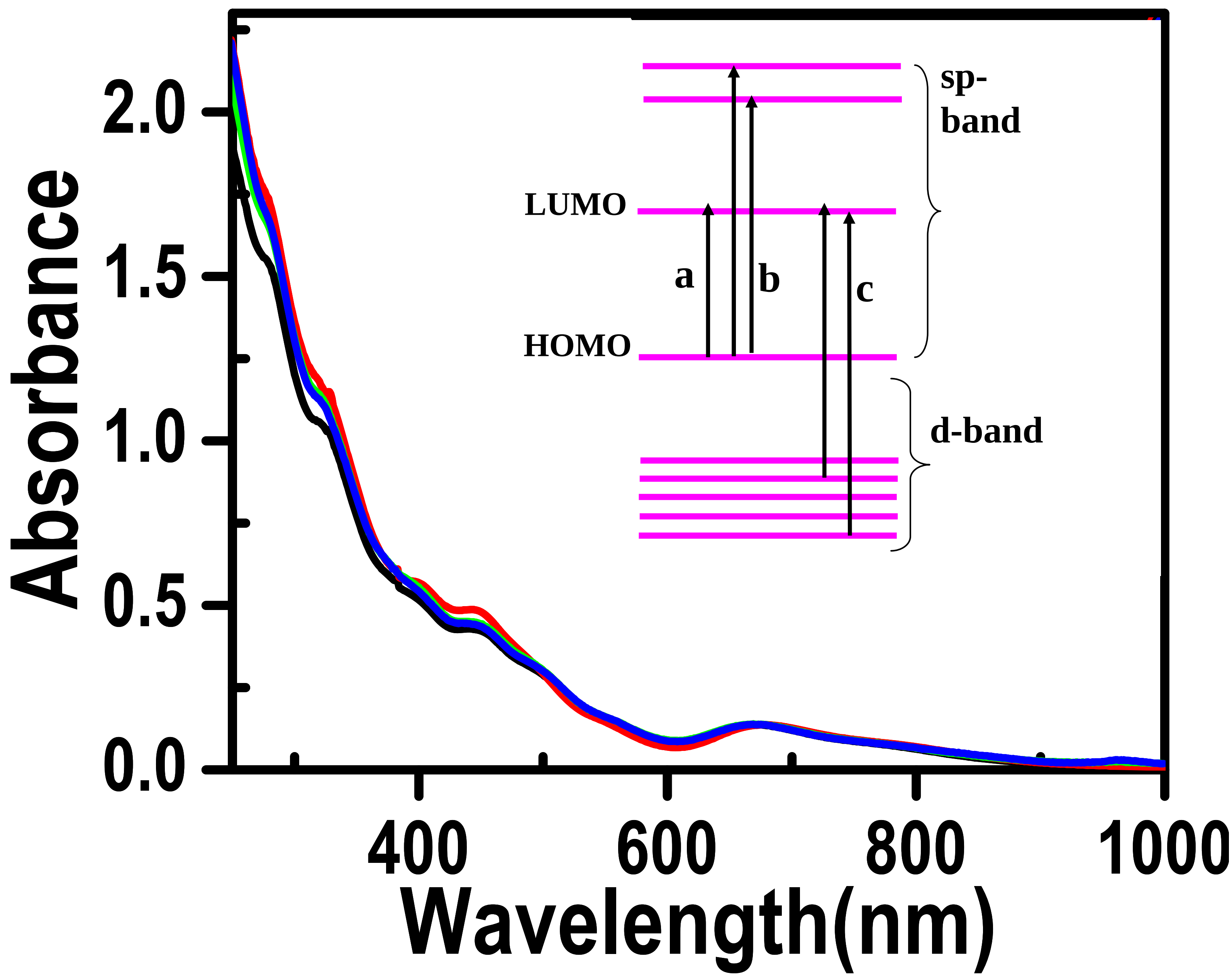
XPS spectrum



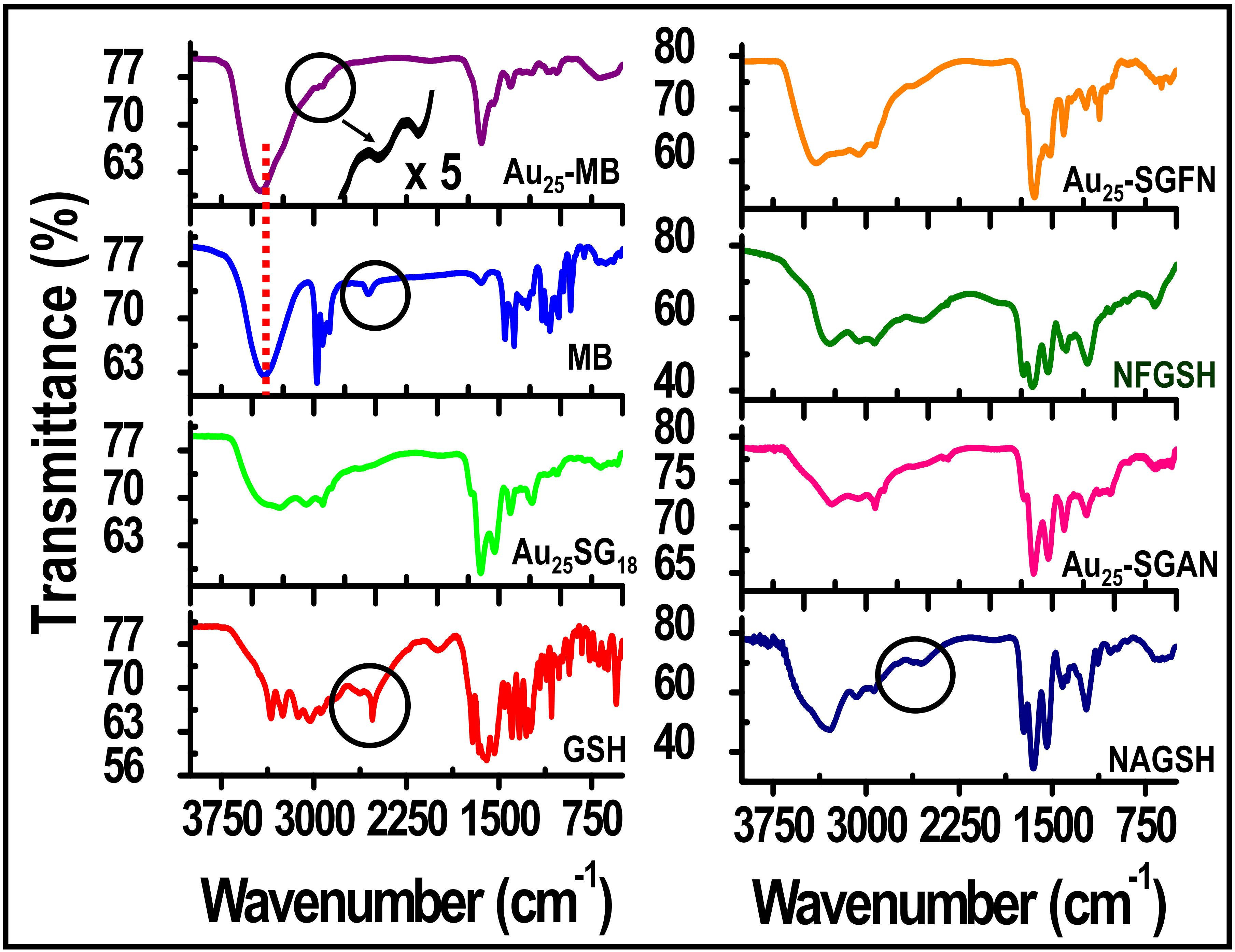
TEM image: The clusters are seen only faintly since the size is ~1 nm. Some of the individual clusters are shown by circles. There are also cluster aggregates which upon extended electron beam irradiation fuse to form bigger particles

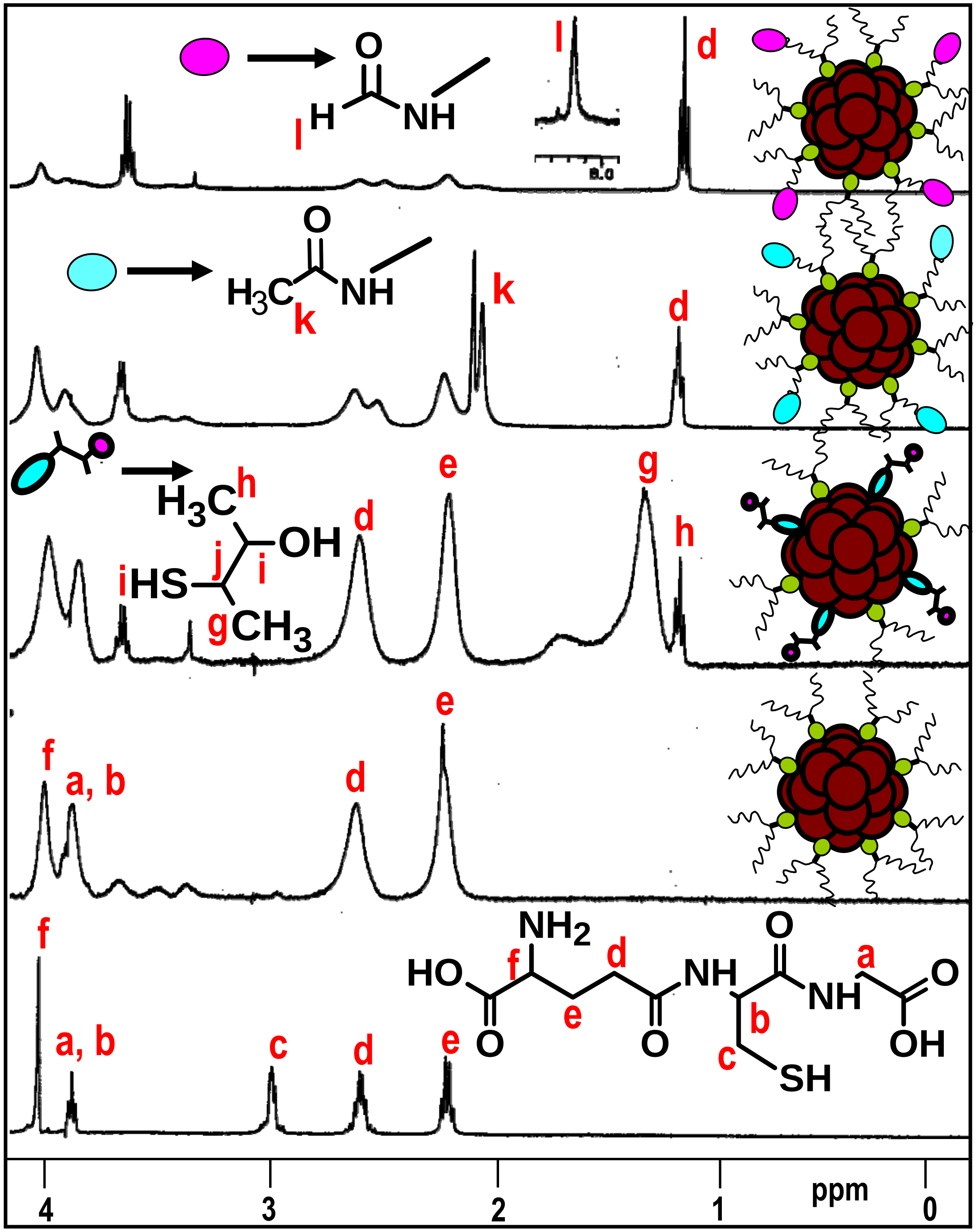
Ligand Exchange of Au_{25}



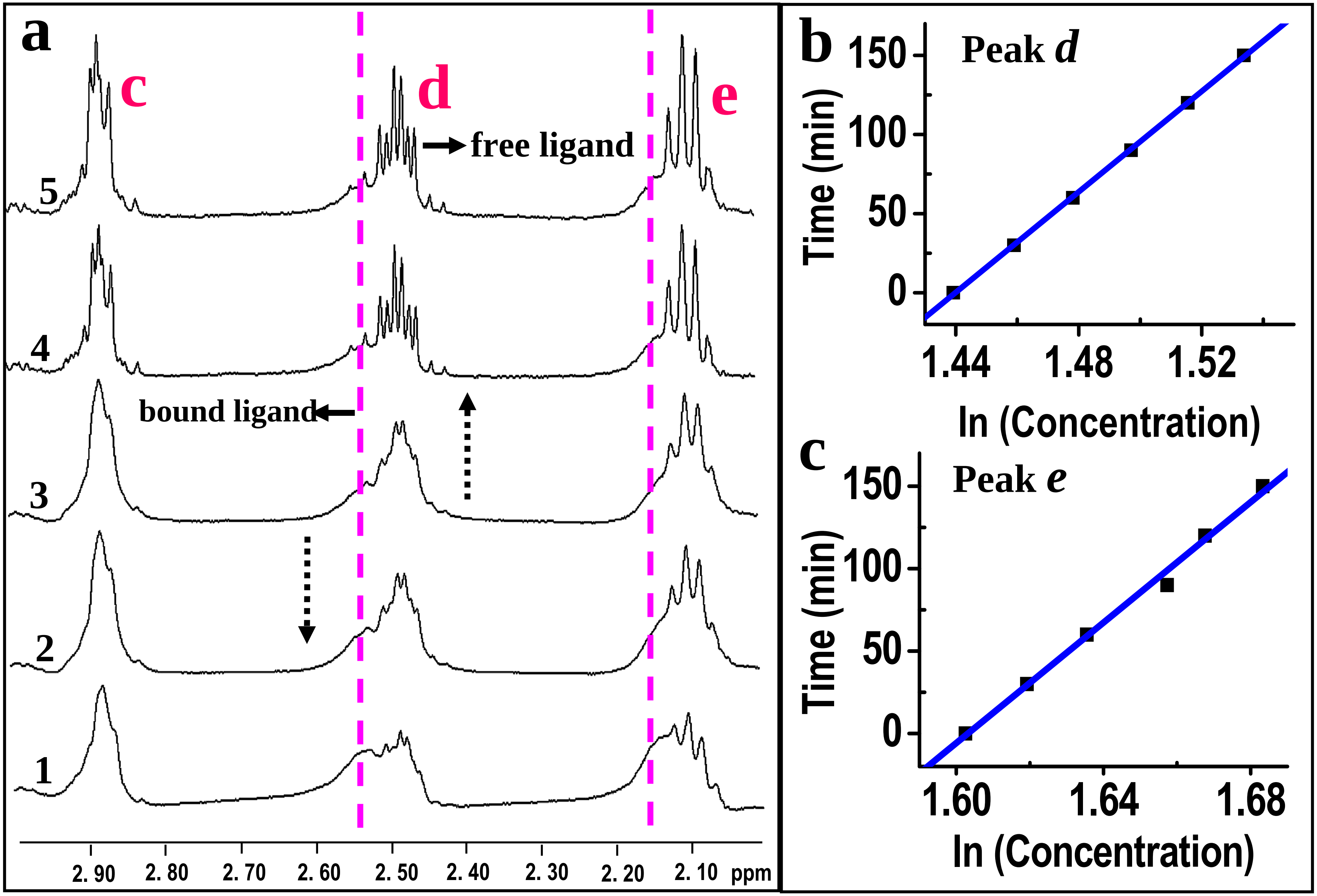


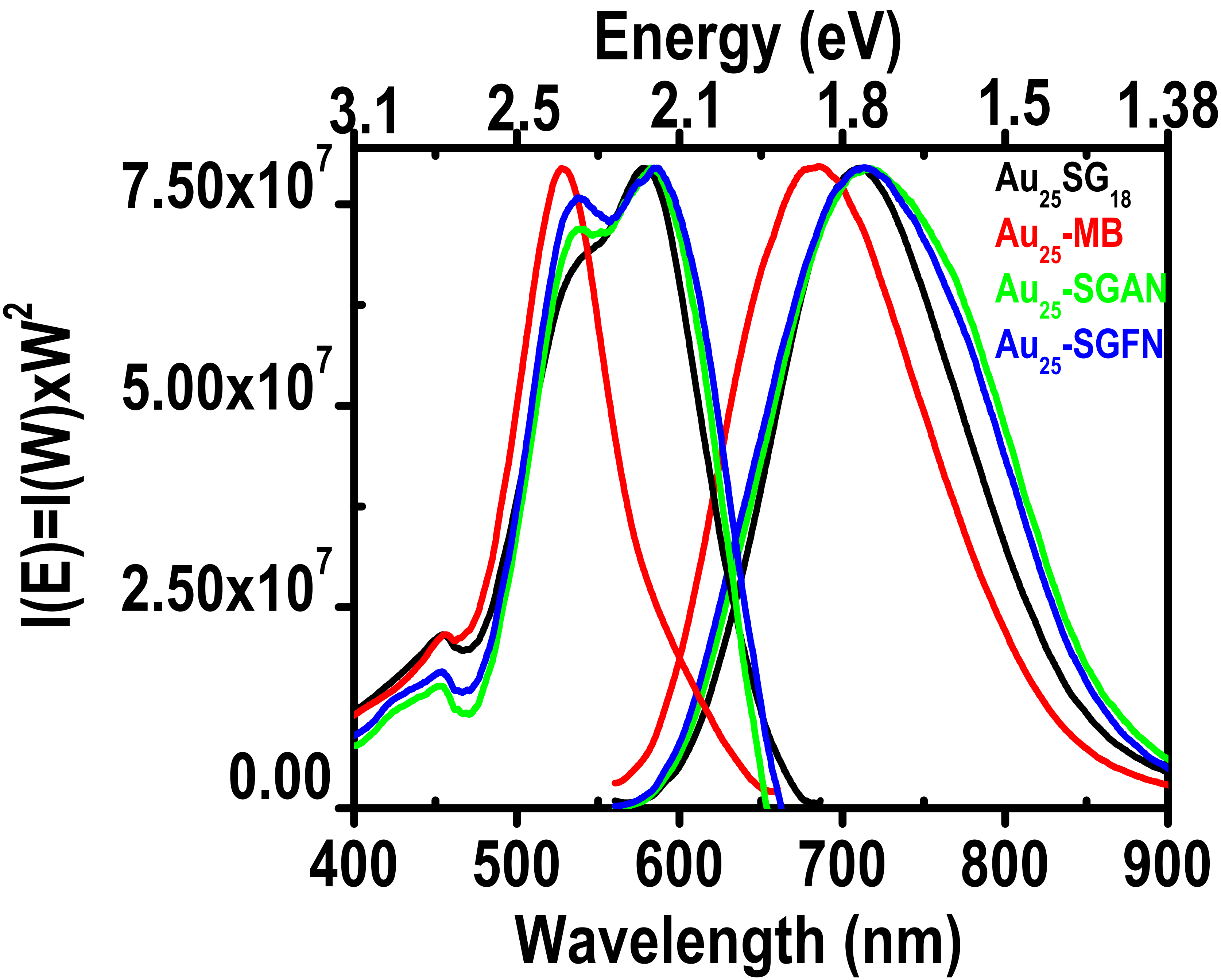
sp-
band
LUMO
HOMO
a
b
c
d-band
Absorbance
2.0
1.5
1.0
0.5
0.0
400
600
800
1000
Wavelength(nm)

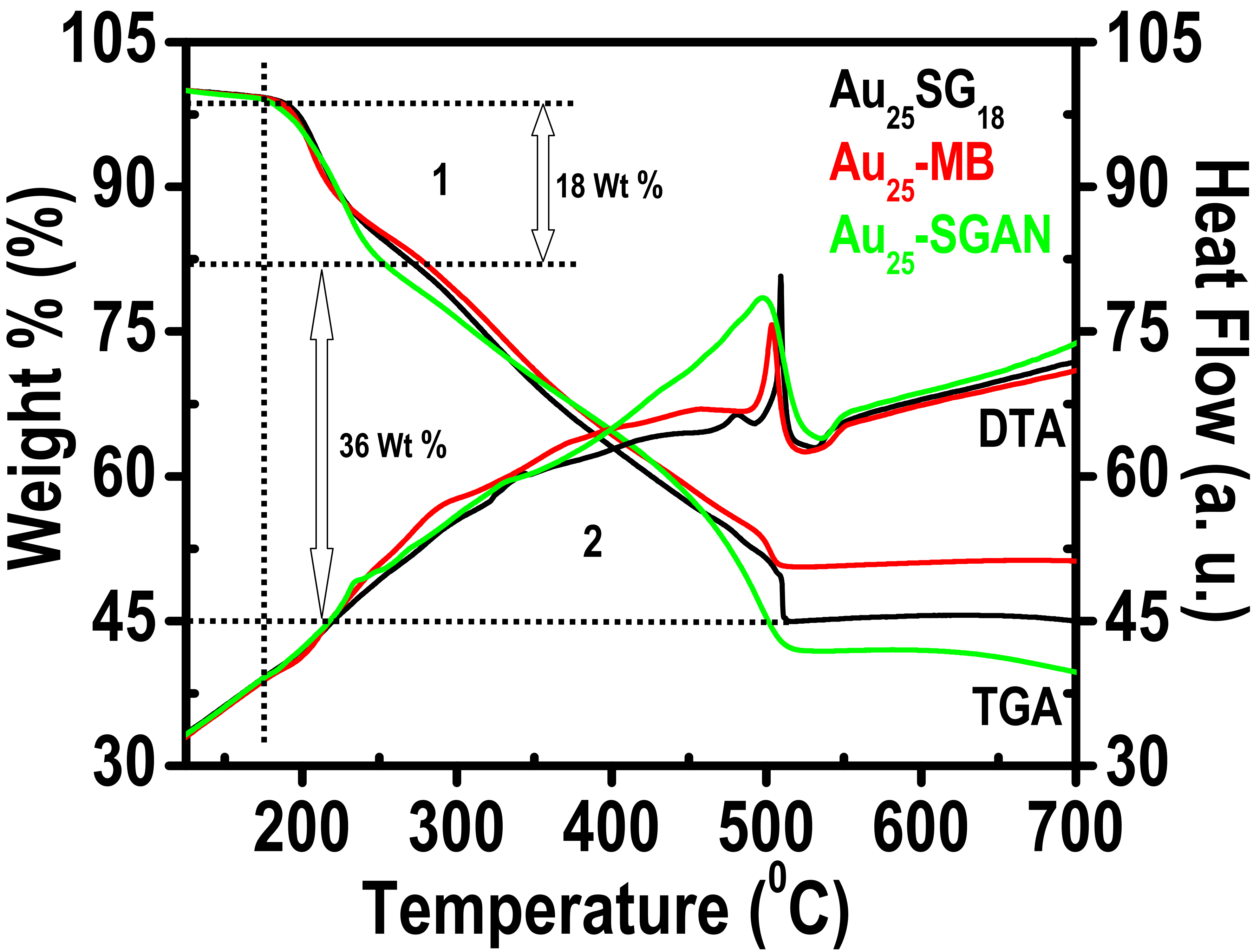

Transmittance (%)
Wavenumber (cm-1)
Au25-MB
x 5
MB
Au25SG18
GSH
Au25-SGFN
NFGSH
Au25-SGAN
NAGSH
77
70
63
56
80
75
65
60
40
3750
3000
2250
1500
750



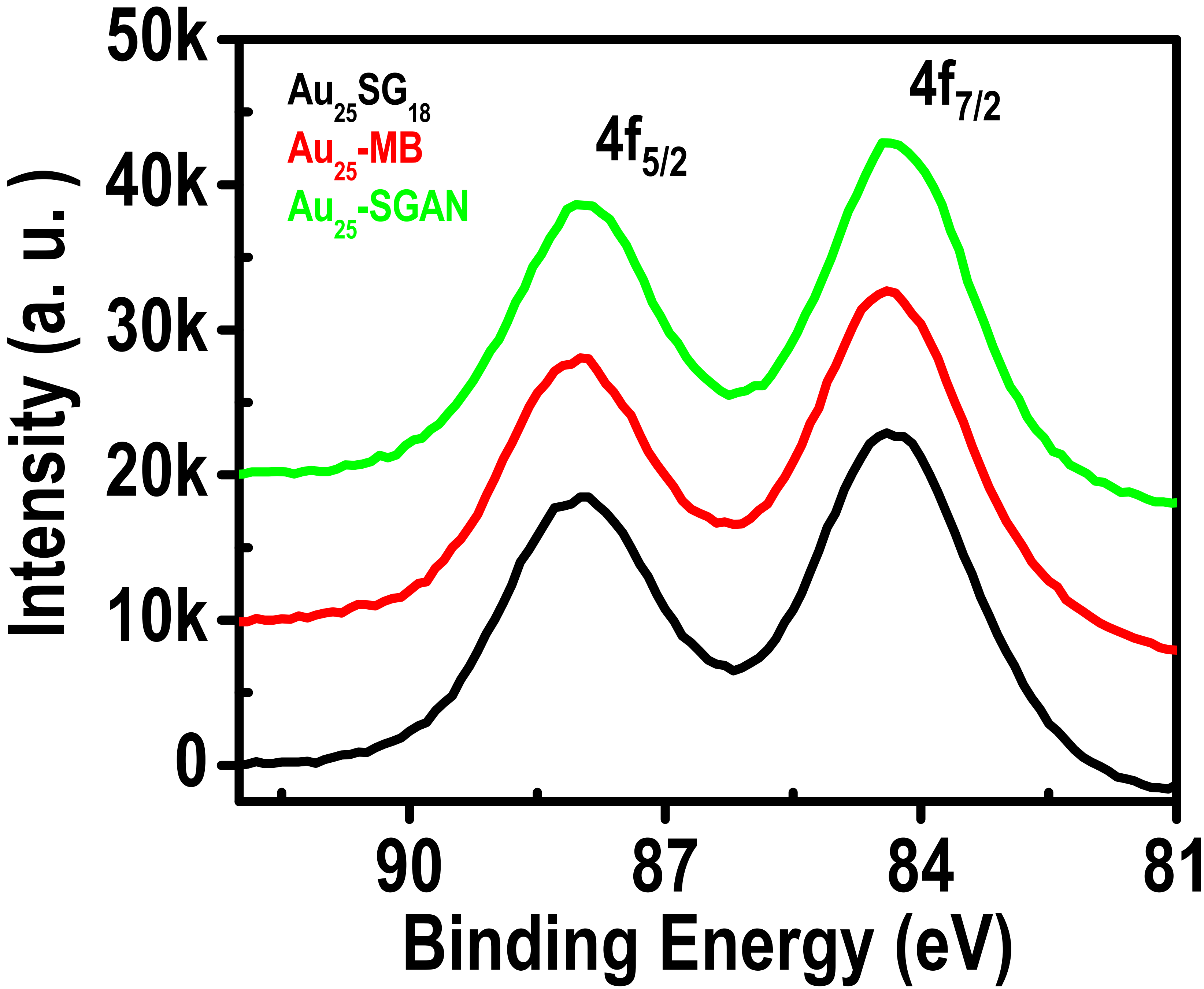
O
H
NH
l
d
O
H3C
NH
k
d
H3C h
OH
i
j
iHS
g CH3
d
e
g
h
f
a, b
d
e
f
a, b
c
d
e
NH2
HO
O
NH
NH
O
OH
SH
ppm
4
3
2
1
0

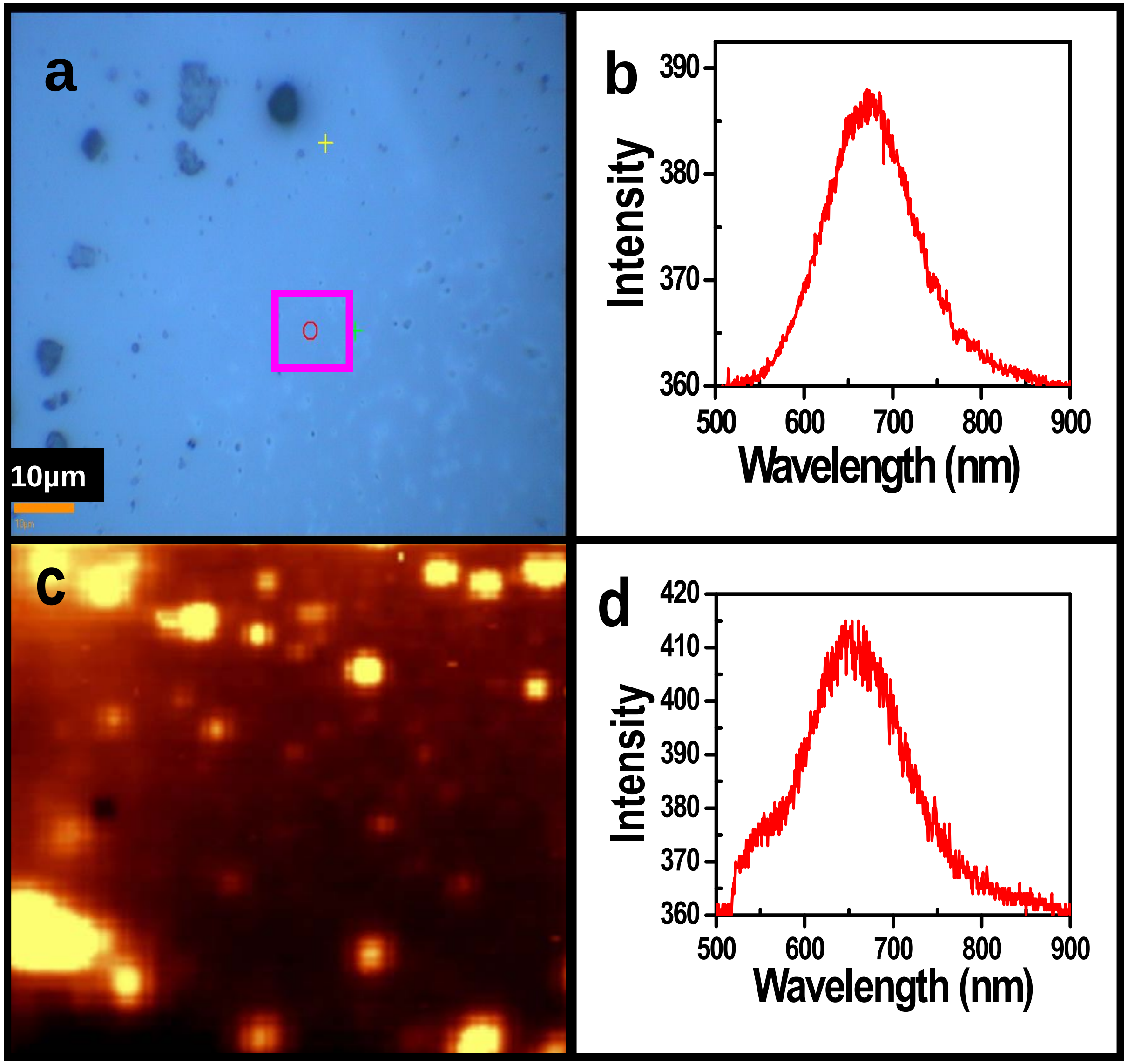

a
c
d
e
free ligand
bound ligand
5
4
3
2
1
2.90
2.80
2.70
2.60
2.50
2.40
2.30
2.20
2.10
ppm
b
Peak d
Time (min)
150
100
50
0
1.44
1.48
1.52
ln (Concentration)
c
Peak e
Time (min)
150
100
50
0
1.60
1.64
1.68
ln (Concentration)

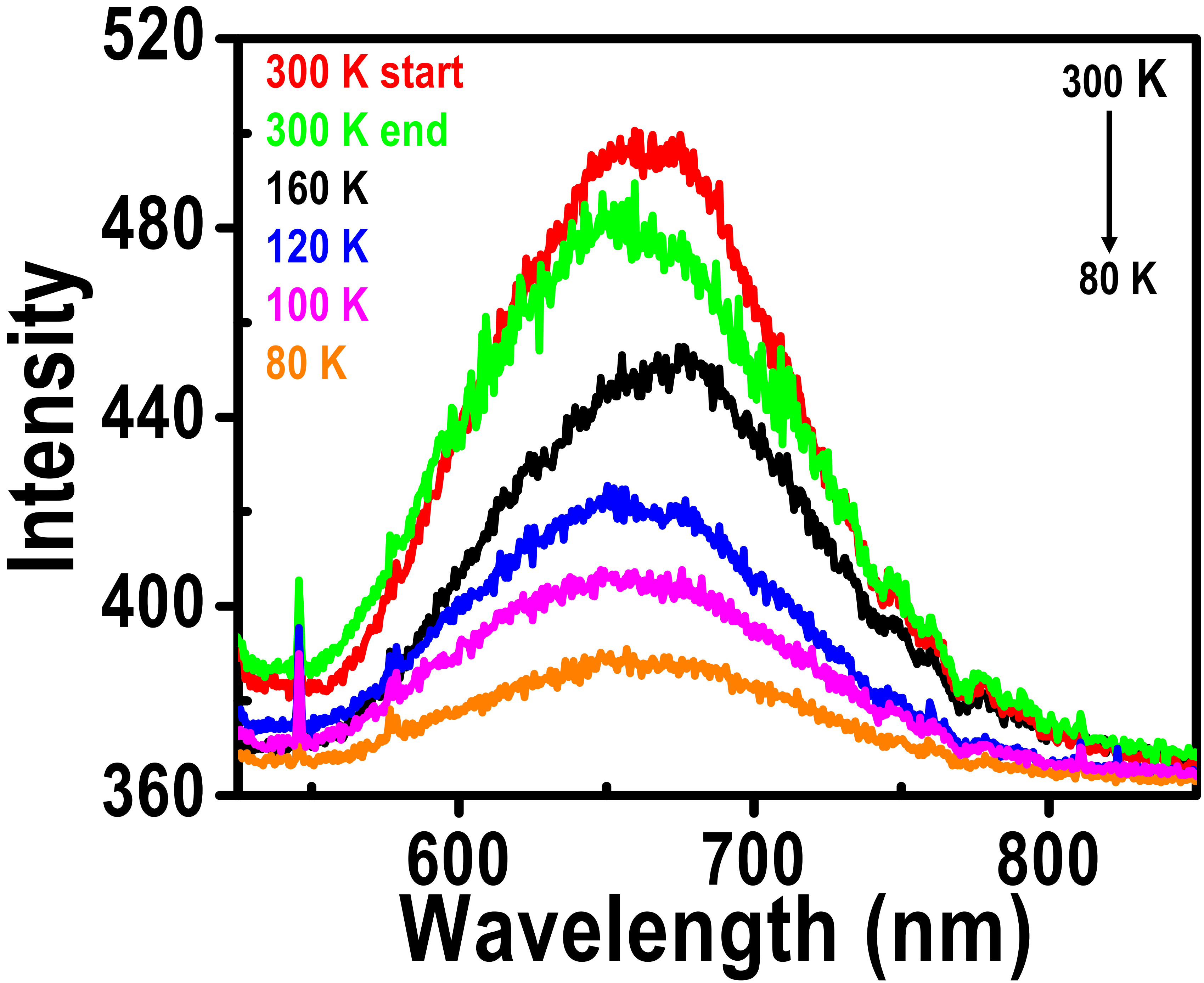

Energy (eV)
3.1
2.5
2.1
1.8
1.5
1.38
7.50x10^7
5.00x10^7
2.50x10^7
0.00
I(E)=I(W)xW^2
Au25SG18
Au25-MB
Au25-SGAN
Au25-SGFN
400
500
600
700
800
900
Wavelength (nm)



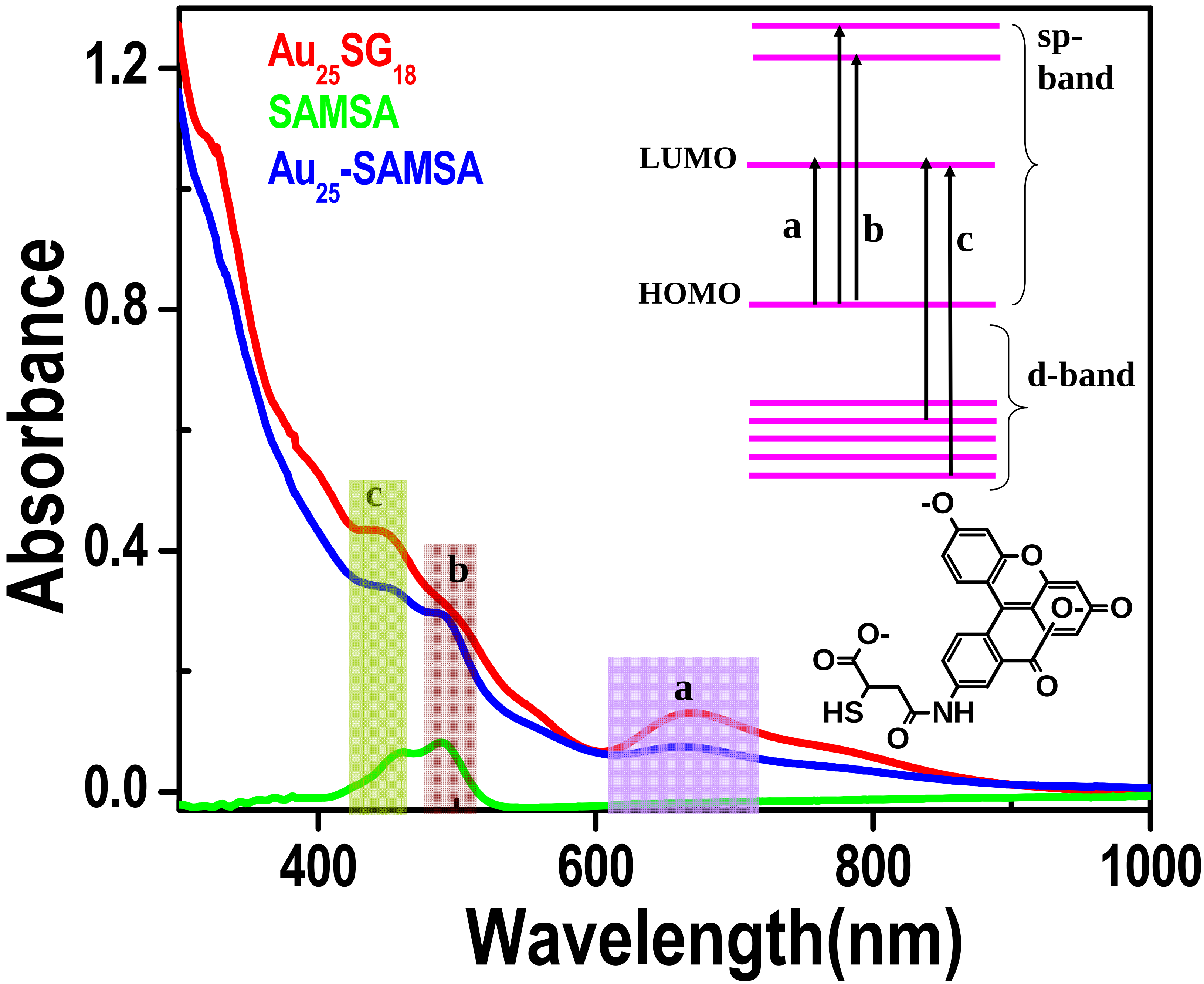
105
90
75
60
45
30
Weight % (%)
Heat Flow (a. u.)
200
300
400
500
600
700
Temperature (0C)
Au25SG18
Au25-MB
Au25-SGAN
1
2
18 Wt %
36 Wt %
DTA
TGA


50k
40k
30k
20k
10k
0
Intensity (a. u.)
$Au_{25}SG_{18}$
Au_{25}-MB
Au_{25}-SGAN
$4f_{5/2}$
$4f_{7/2}$
90
87
84
81
Binding Energy (eV)

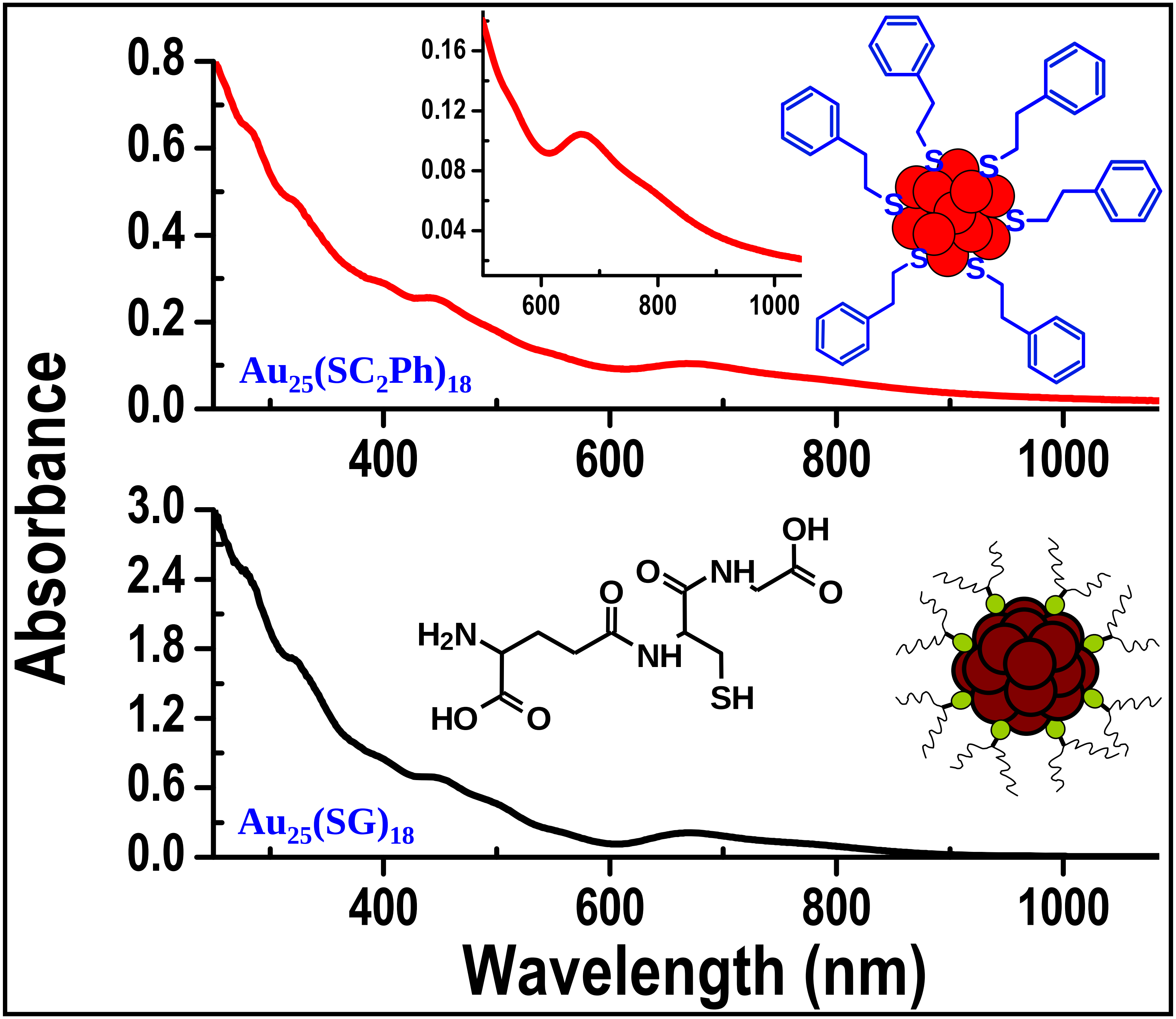

a
10µm
b
Intensity
390
380
370
360
500
600
700
800
900
Wavelength (nm)
c
d
Intensity
420
410
400
390
380
370
360
500
600
700
800
900
Wavelength (nm)



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

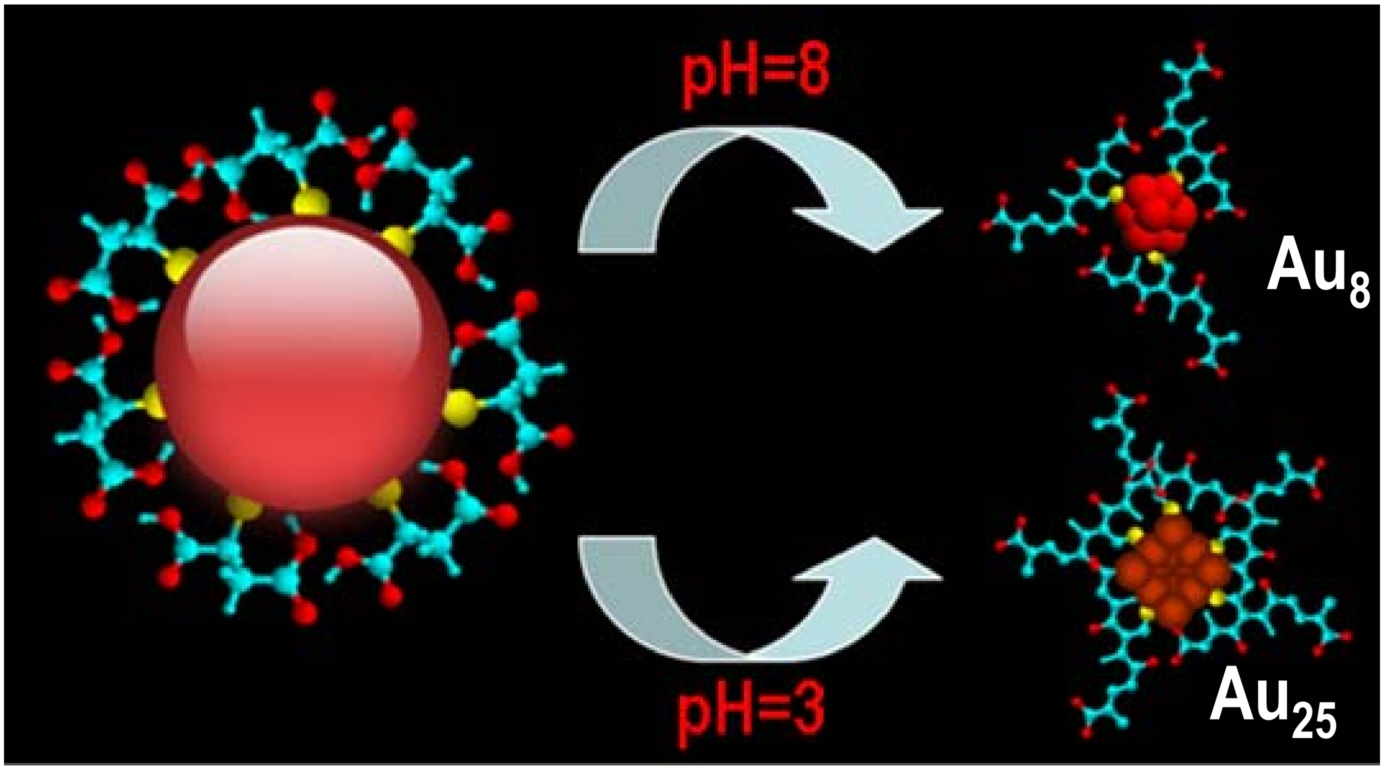


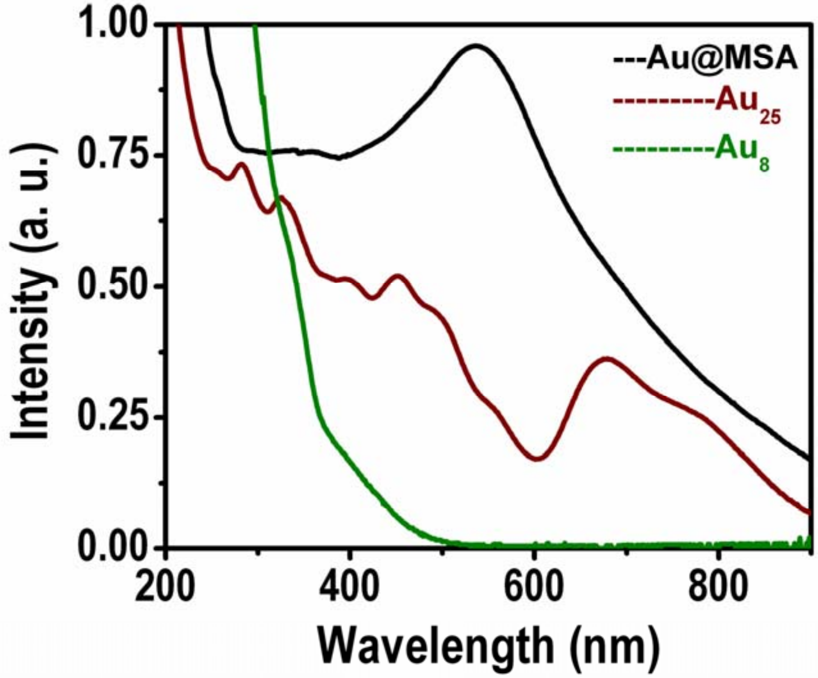
Au25SG18
SAMSA
Au25-SAMSA
LUMO
HOMO
sp-band
d-band
a
b
c
-O
O
O-
O
O-
O
HS
NH
O
O
Absorbance
1.2
0.8
0.4
0.0
400
600
800
1000
Wavelength(nm)



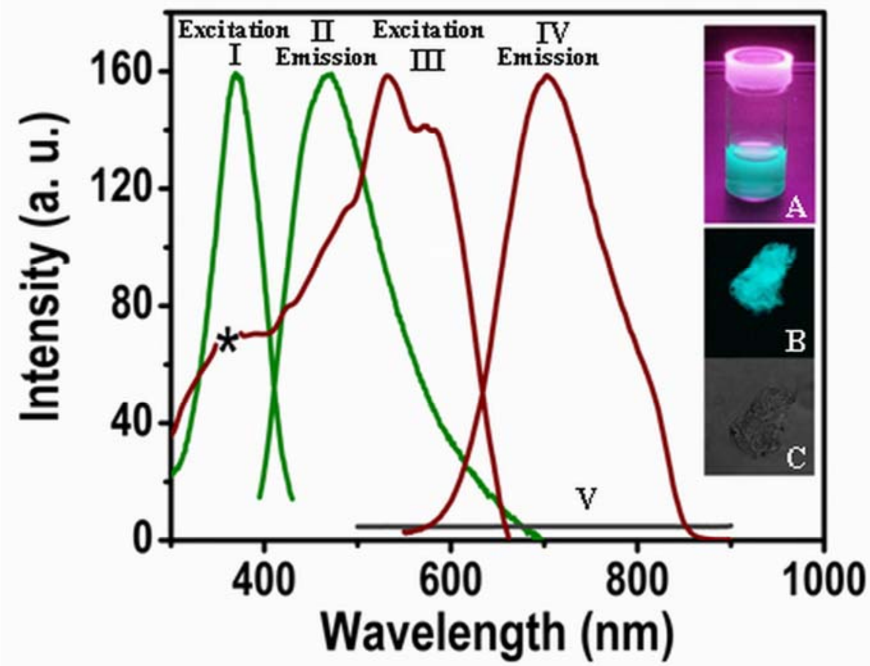
Absorbance
Wavelength (nm)
$Au_{25}(SC_2Ph)_{18}$
$Au_{25}(SG)_{18}$
0.8
0.6
0.4
0.2
0.0
400
600
800
1000
0.16
0.12
0.08
0.04
3.0
2.4
1.8
1.2
0.6
S
H2N
HO
O
NH
OH
SH

Au_8SG_8

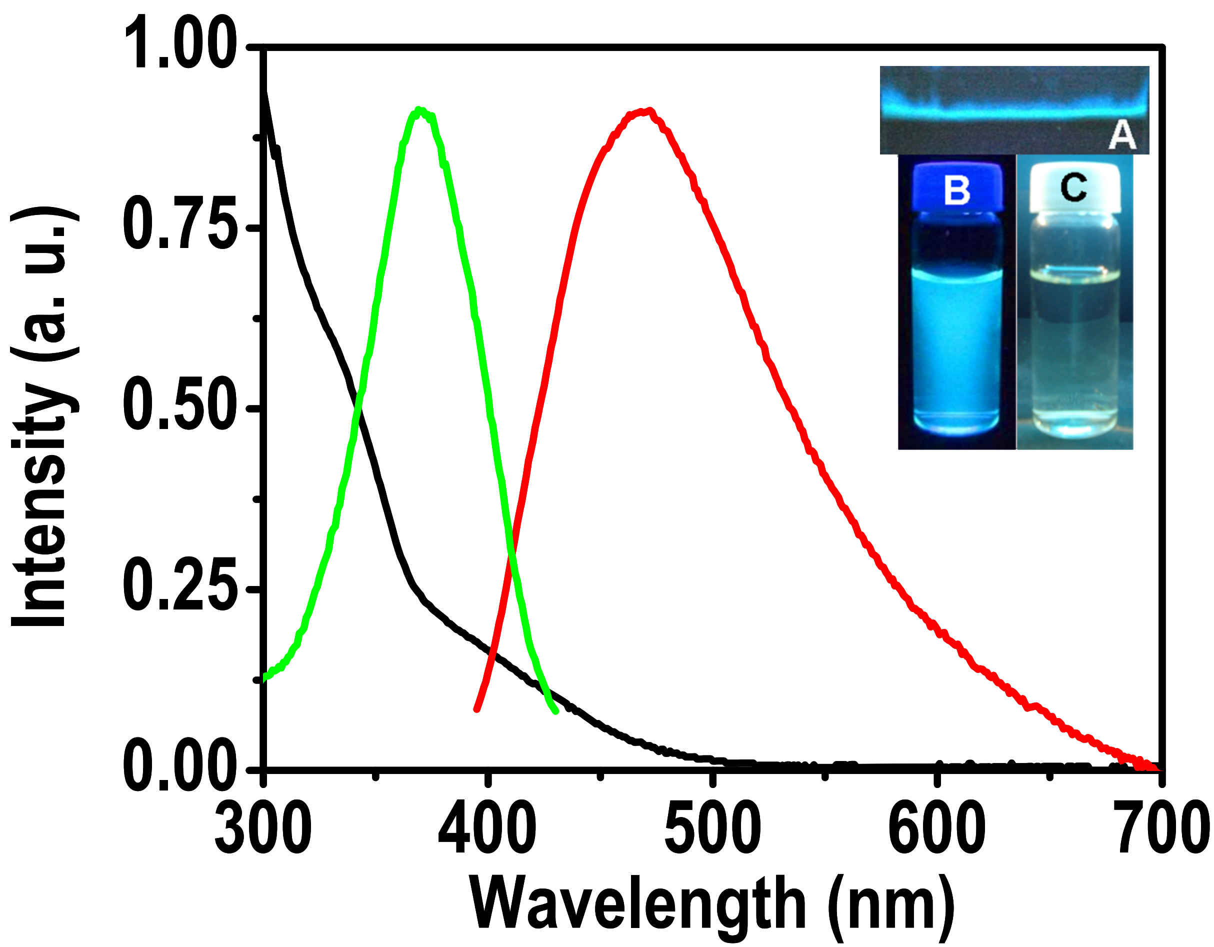




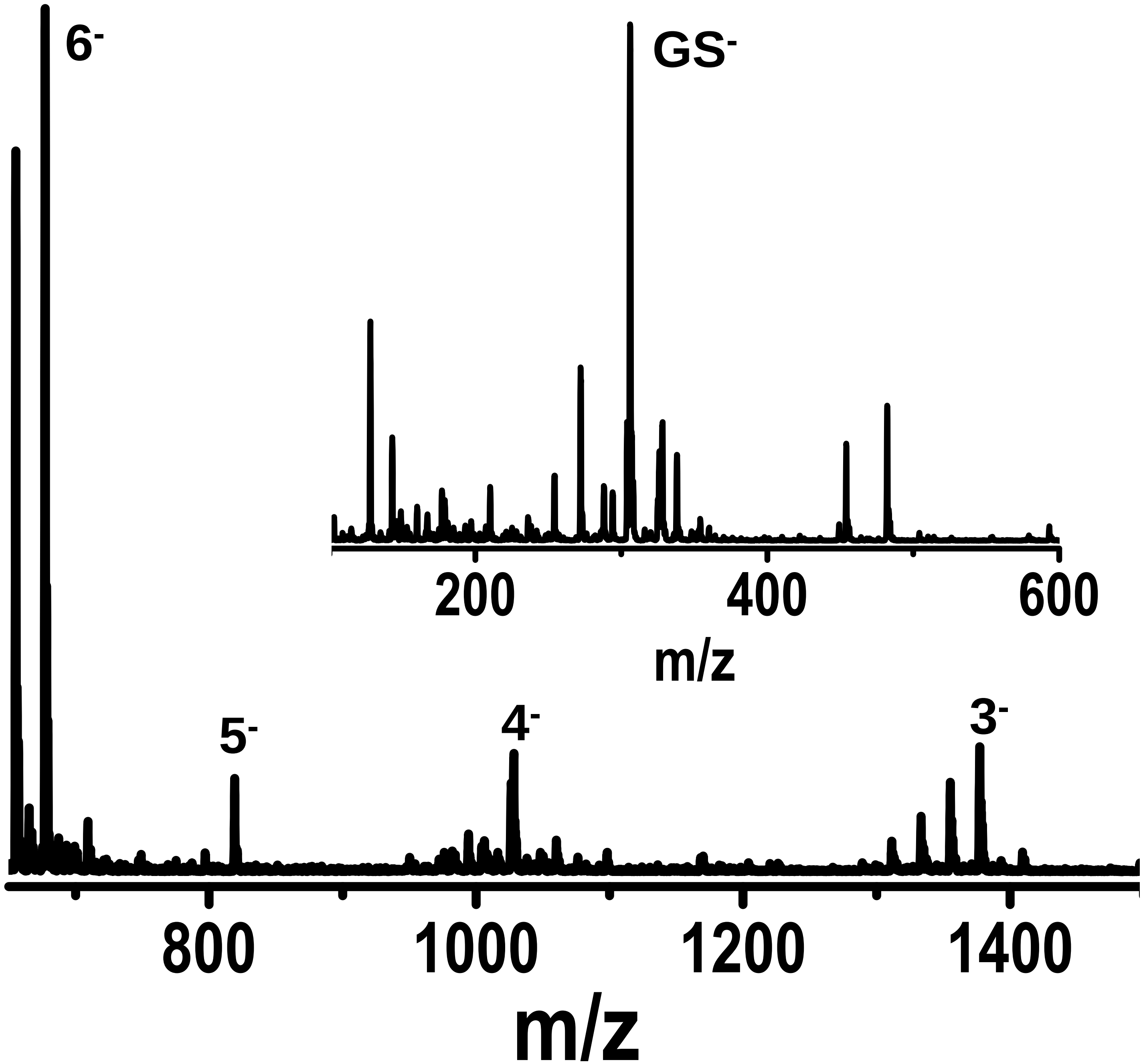
Comparison of the optical absorption profiles of Au@MSA, Au_{25} and Au_8.



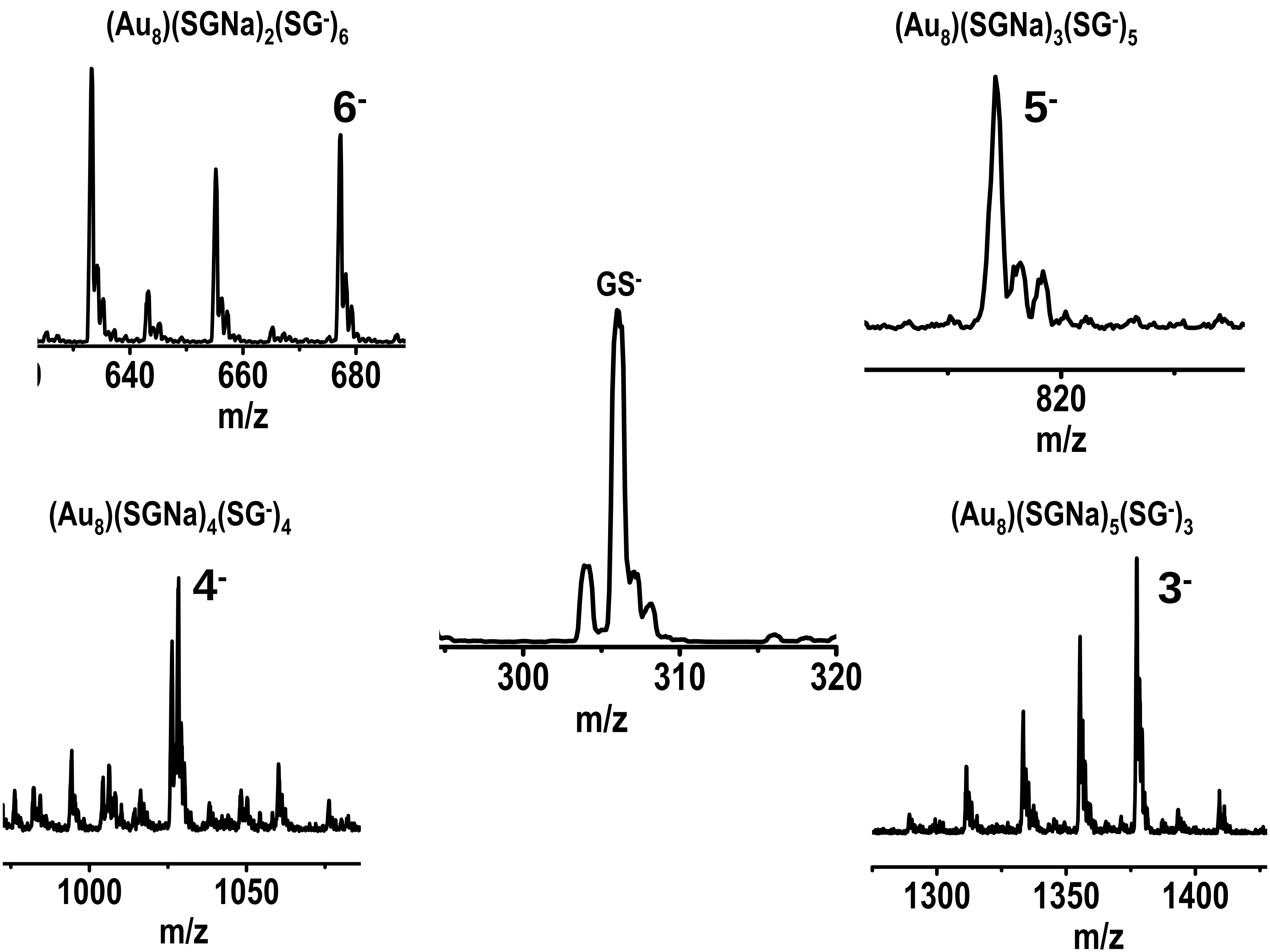
Comparison of the photoluminescence profiles of the clusters with Au@MSA. Traces I and II are the excitation and emission spectra of Au_8, respectively. Traces III and IV are the excitation and emission spectra of Au_{25}, respectively and trace V is the emission spectrum of Au@MSA.



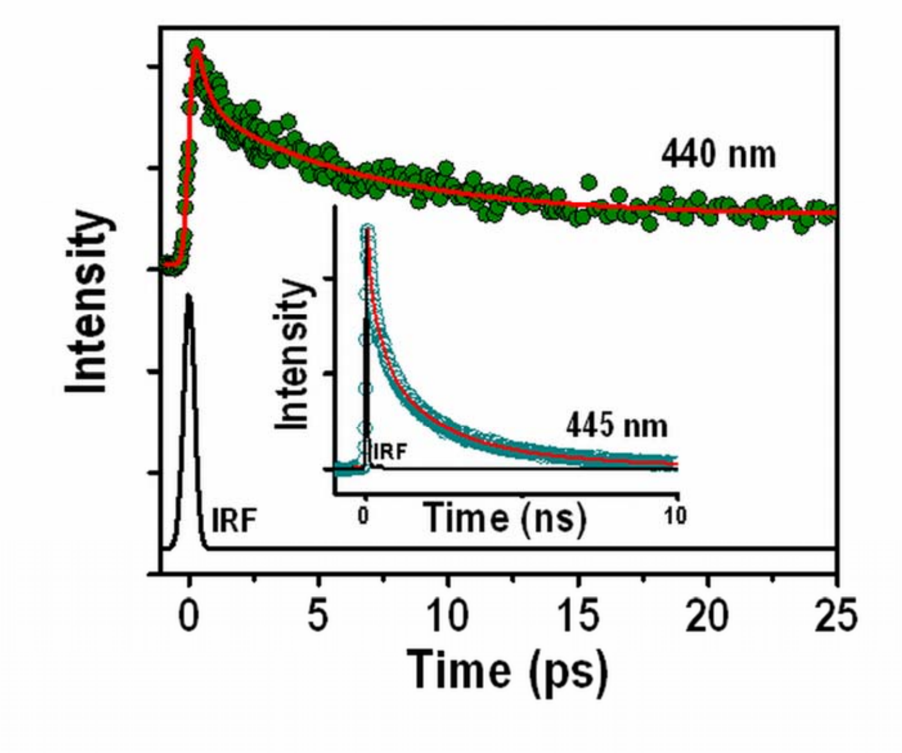
Optical absorption (black trace), Fluorescence excitation (green trace) and emission (red line) of the Au_8 cluster. Inset: photographs of PAGE band (A), Au_8 solution in water under normal light irradiation (B) and under uv light irradiation (C).



6-
5-
4-
3-
800
1000
1200
1400
m/z
GS-
200
400
600
m/z



(Au8)(SGNa)2(SG-)6
6-
640
660
680
m/z
(Au8)(SGNa)3(SG-)5
5-
820
m/z
GS-
300
310
320
m/z
(Au8)(SGNa)4(SG-)4
4-
1000
1050
m/z
(Au8)(SGNa)5(SG-)3
3-
1300
1350
1400
m/z



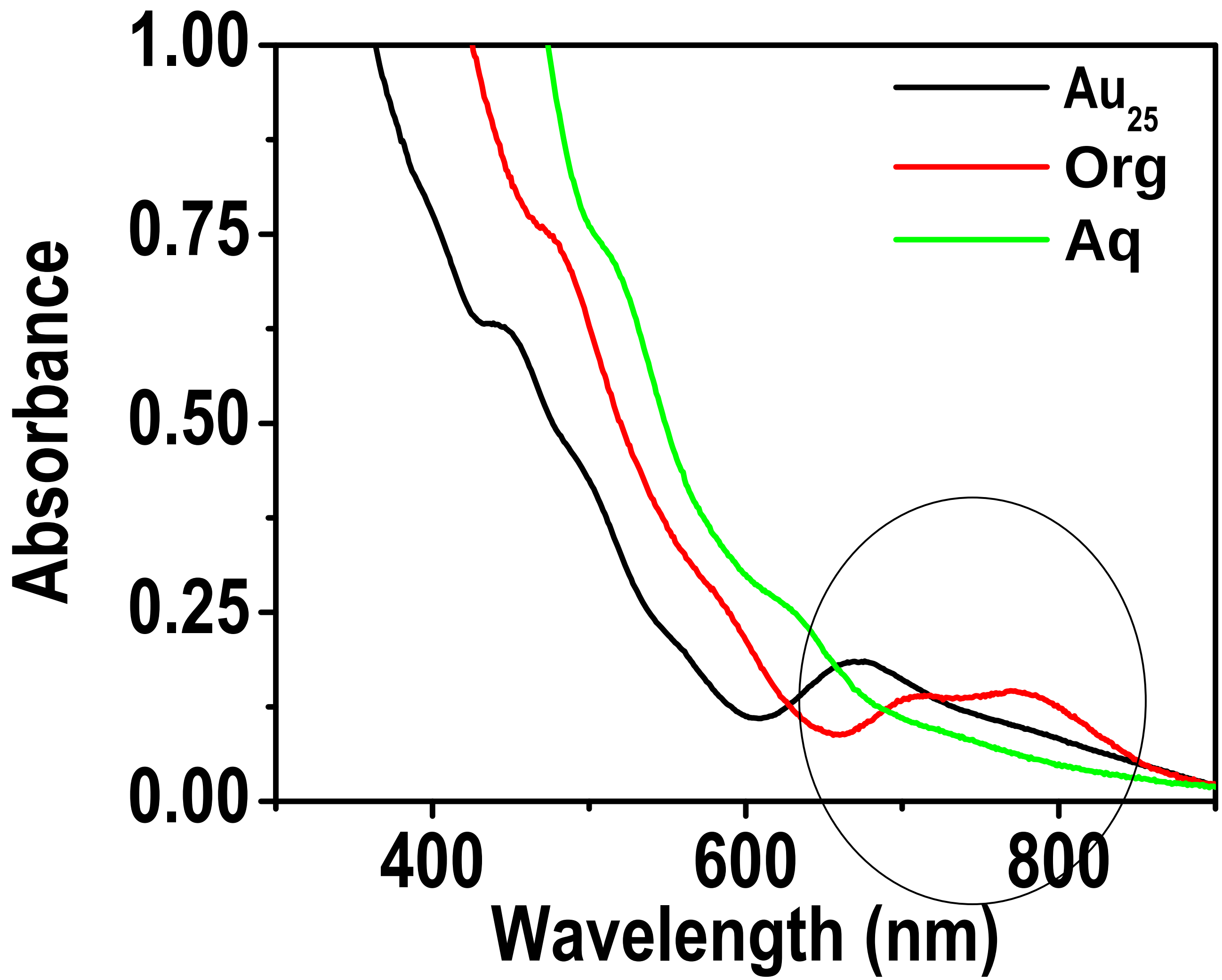
Fluorescence decay profile of Au_8 in water at 440 nm (excitation 364 nm) by fluorescence upconversion technique (IRF = 165 fs). Inset shows the fluorescence transient of the sample at 445 nm (excitation = 375 nm) in a longer time window of TCSPC (IRF = 70 ps) set-up.

Quantum Yield	
Au_{25}	Au_8
$1.9x10^{-3}$	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%)

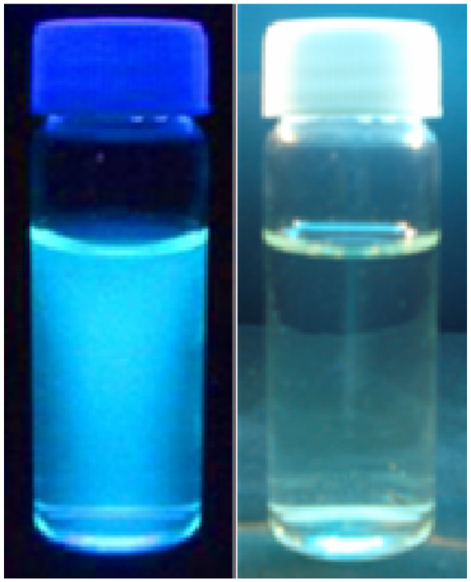
Interfacial Etching

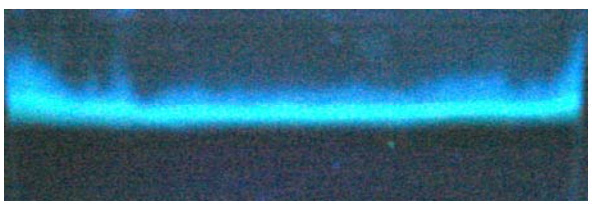
Schematic of the interfacial synthesis of red emitting clusters from $Au_{25}SG_{18}$.



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).

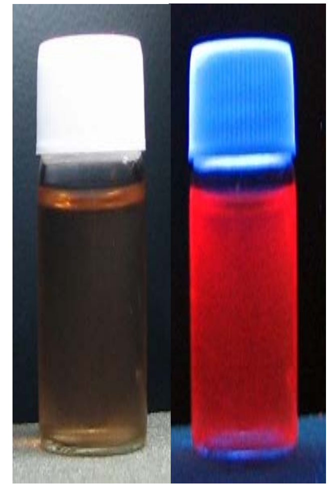
Au_8SG_8



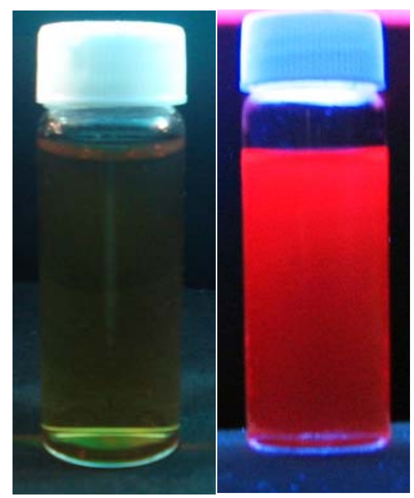


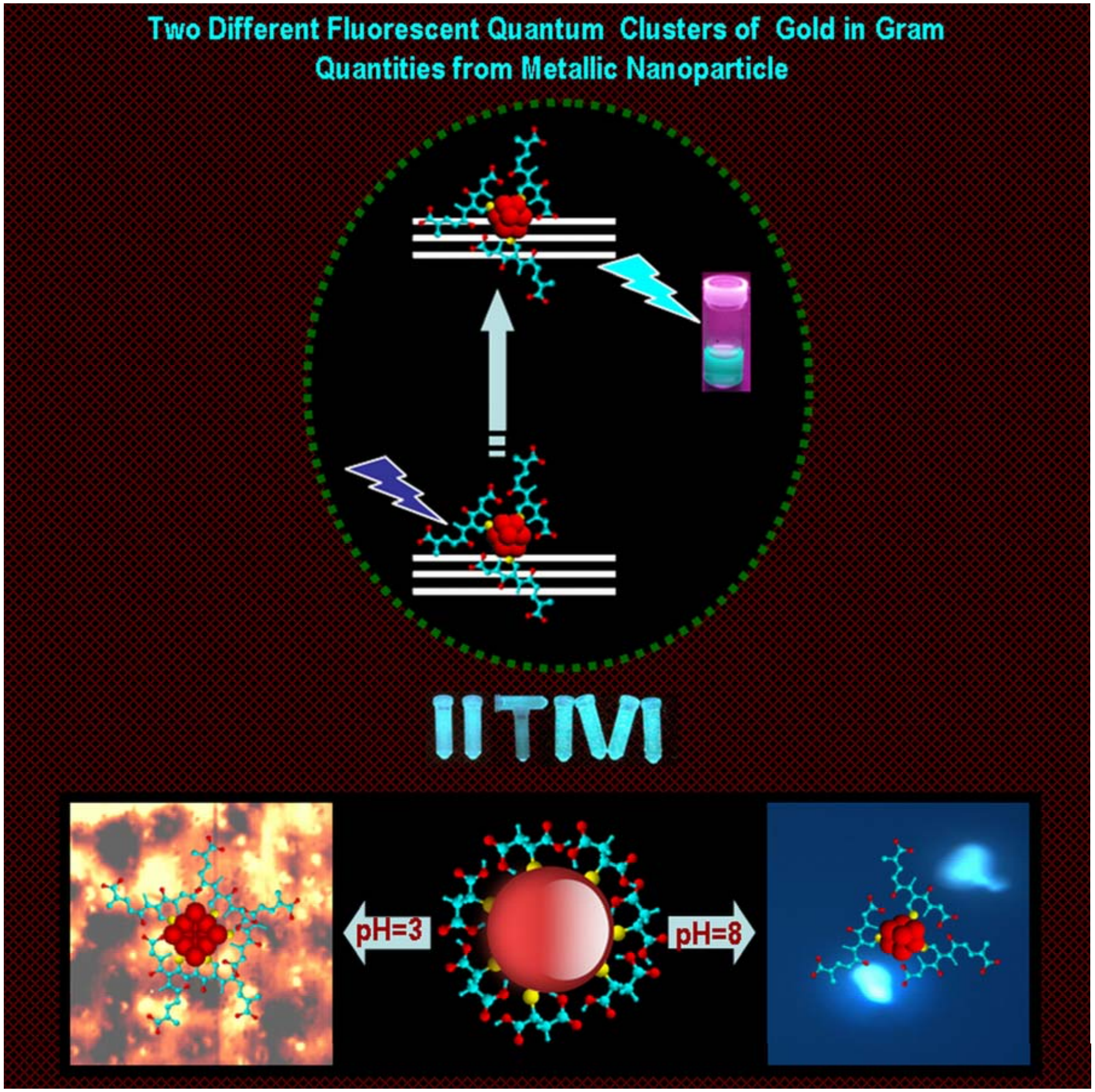
PAGE image of Au_8SG_8 cluster

Organic soluble red emitting clusters



Water soluble red emitting clusters





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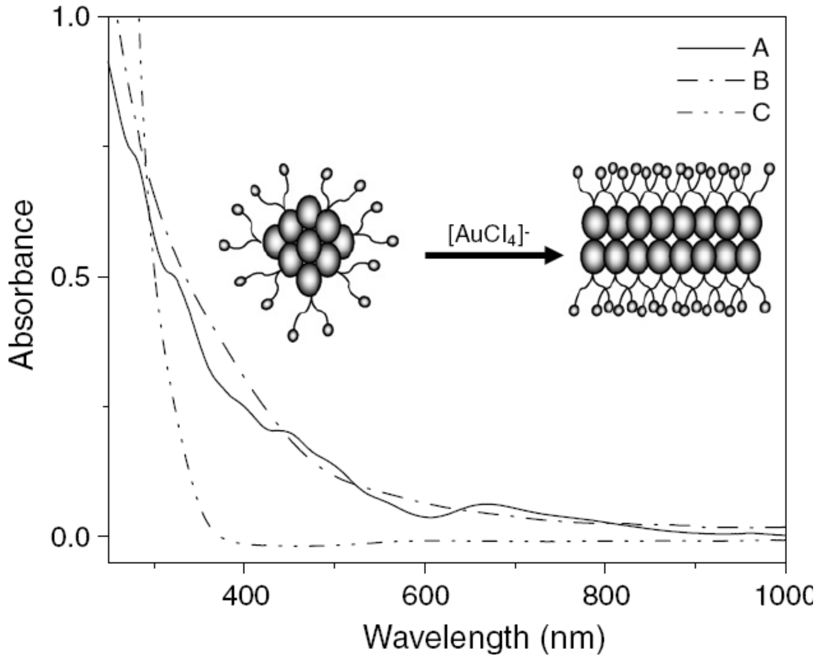
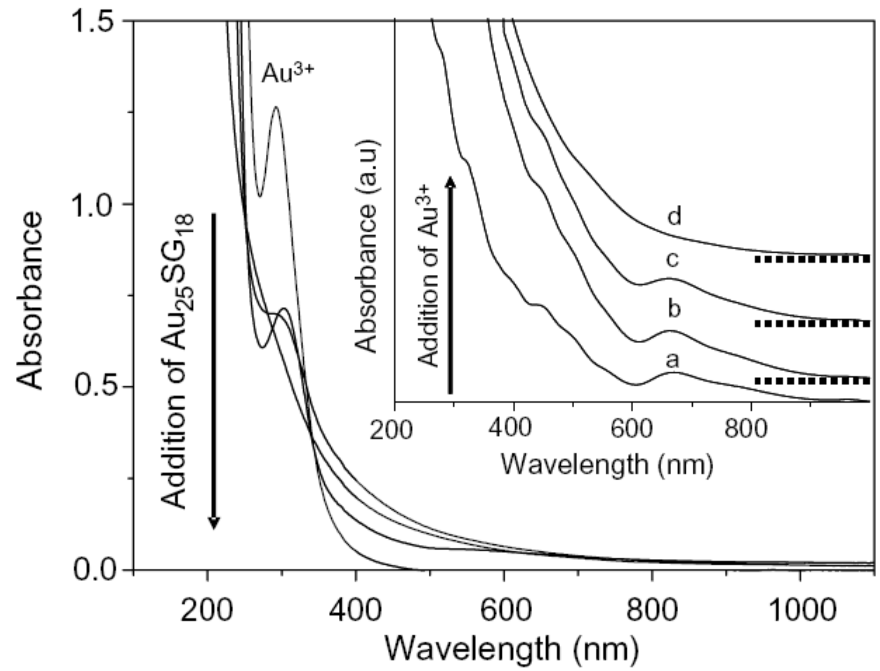
Reactivity and Applications of Molecular Clusters

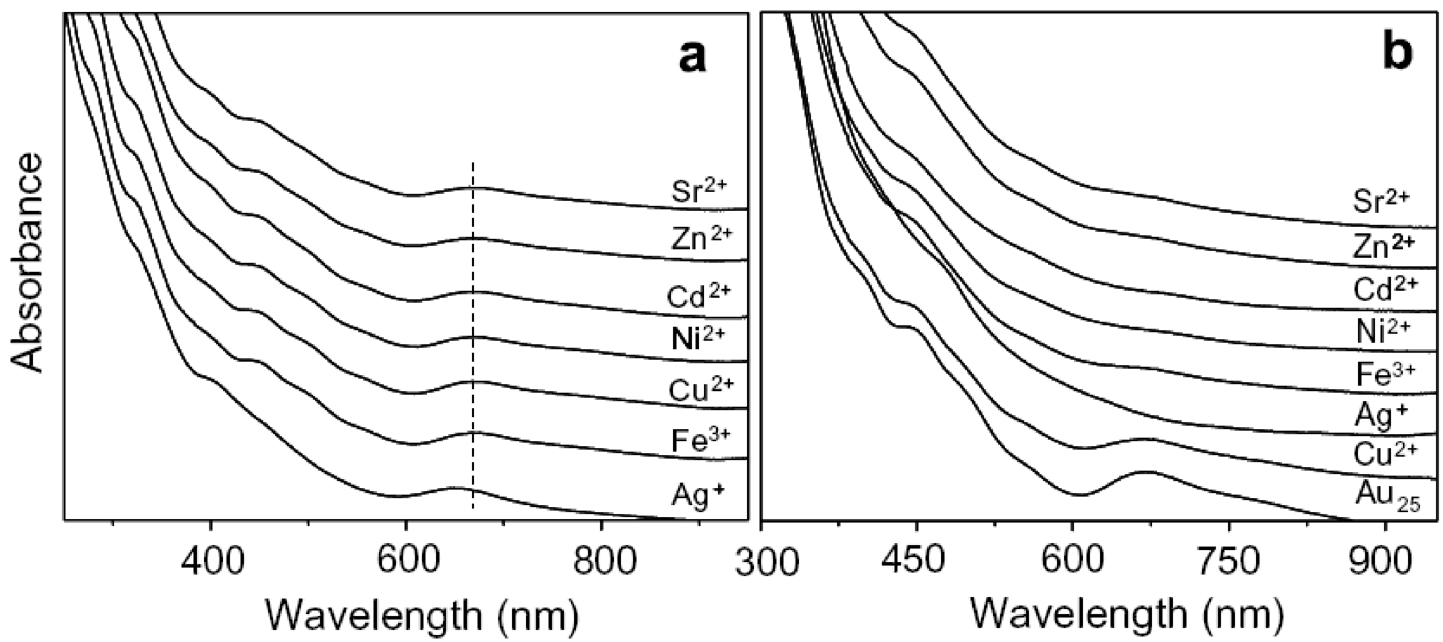
Reactivity of Au_{25}



Optical absorption spectra of (A) $Au_{25}SG_{18}$ cluster, (B) after adding 50 μM $AuCl_4^-$ ions to the cluster and (C) the synthesized Au(I)SG polymer. The scheme (inset) represents the dissociation of the $Au_{25}SG_{18}$ cluster.

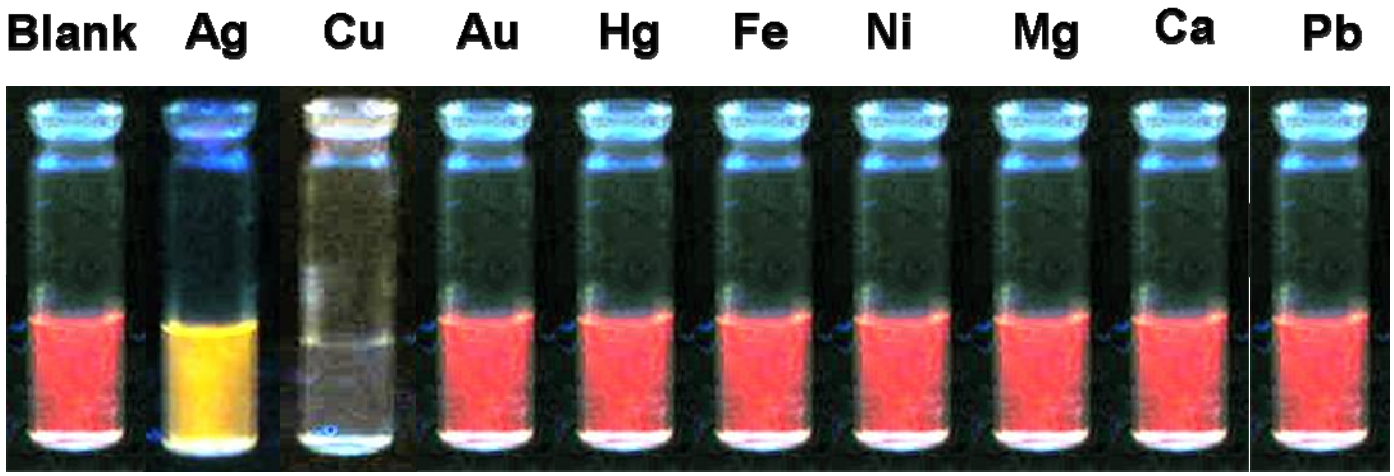


Optical absorption spectra showing the decrease in the intensity of $AuCl_4^-$ peak proving that gold ions added are used up and the small cluster is converting to $(Au–SG)_m$ polymer. Inset shows the progress of the reaction when Au^{3+} is added.



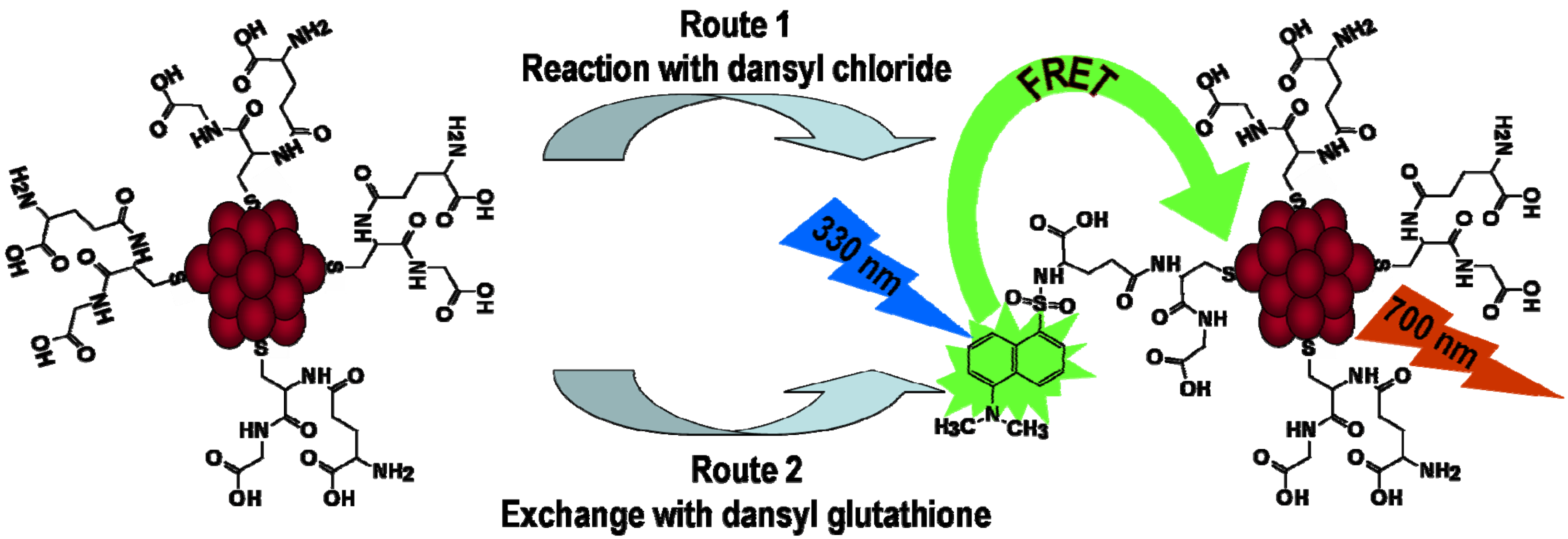
Optical spectra showing the reactivity of the cluster in the presence of various metal ions. (A) Immediately after adding metal ions and (B) after two days of incubation. Note that, the cluster is most stable in the presence of Cu^{2+}.

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.

FRET between Au_{25} and Dansyl Chromophore



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

Silver clusters

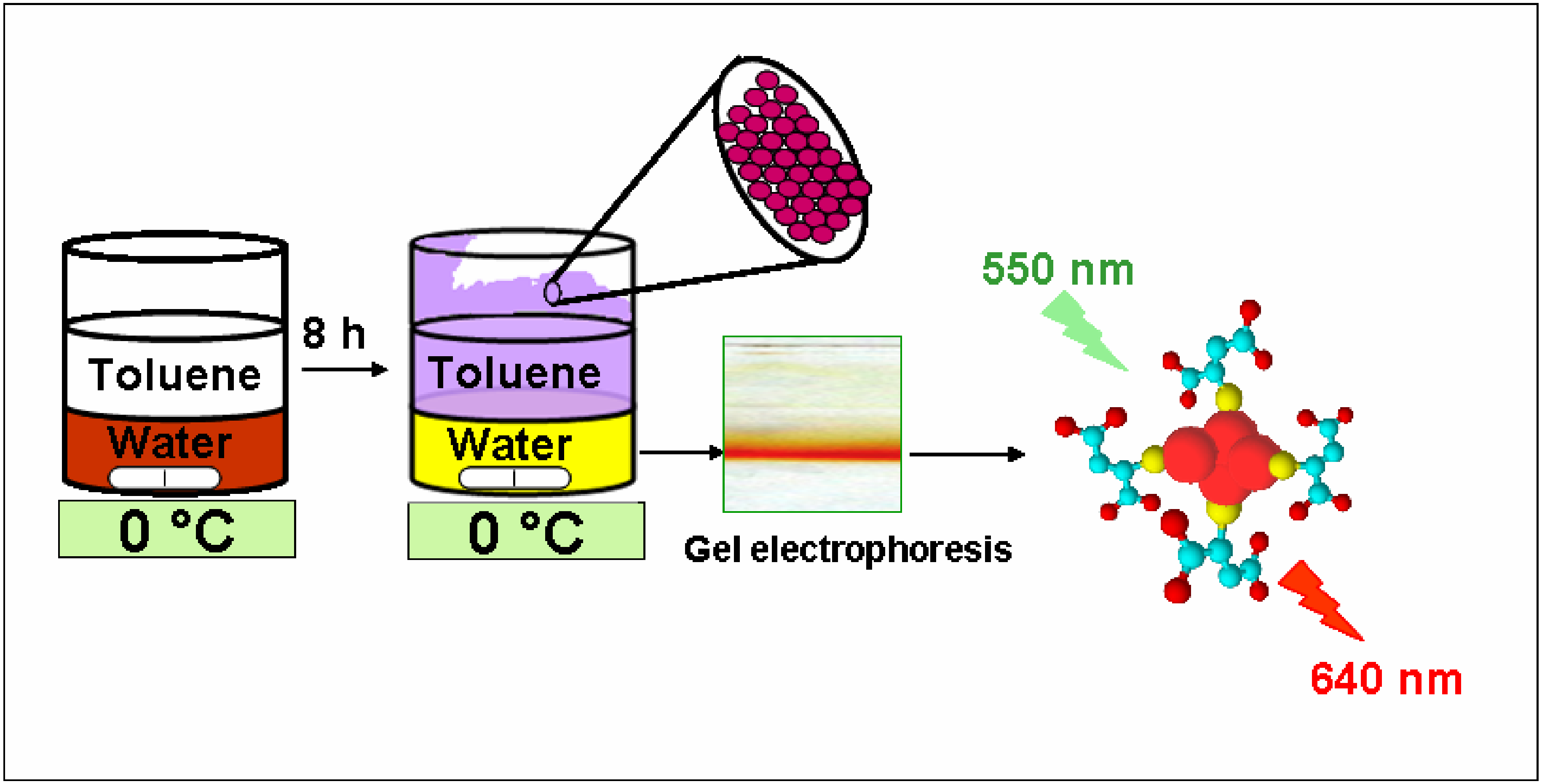
Size selected metal clusters

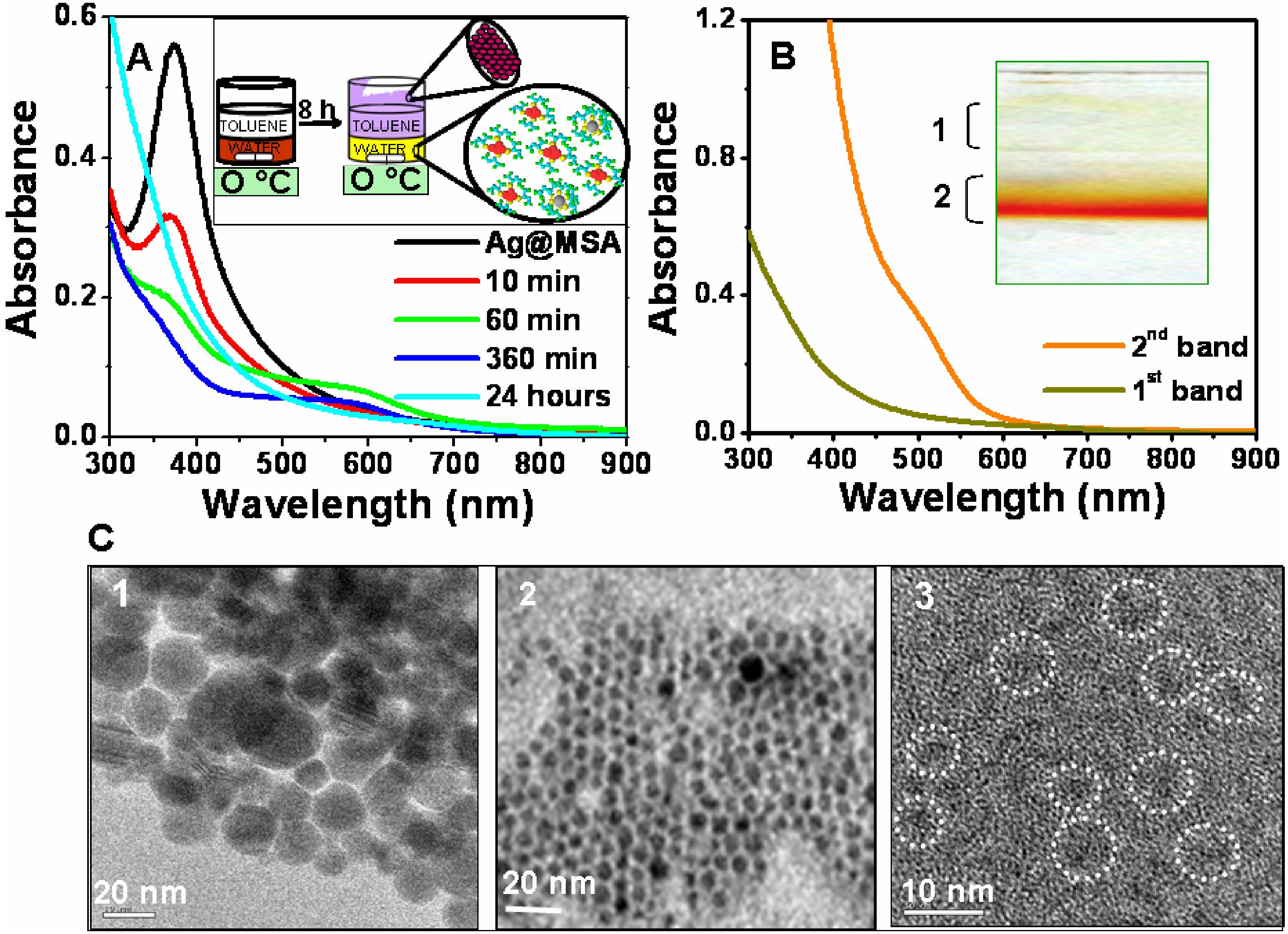
- The Optical Absorption Spectra of Small Silver Clusters (5-11) Embedded in Argon Matrices. Harbich, W.; Fedrigo, S.; Buttet, J**.** *Chem. Phys. Lett.* **1992,** *195,* 613
- Soft Landing and Fragmentation of Small Clusters Deposited in Noble-Gas Films. Harbich, W.; Fedrigo, S.; Buttet, J**.** *Phys.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

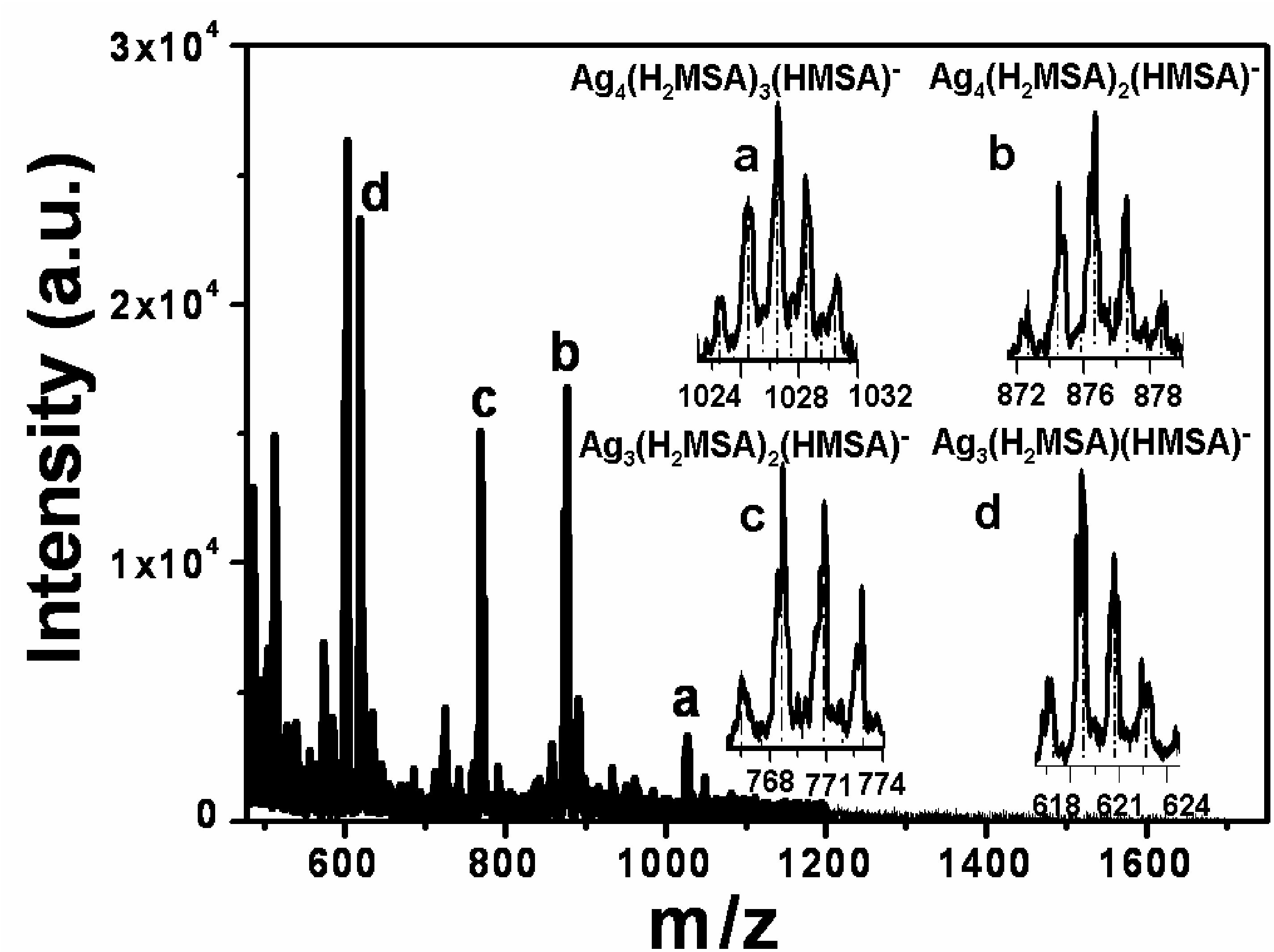
Recent studies

- **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 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

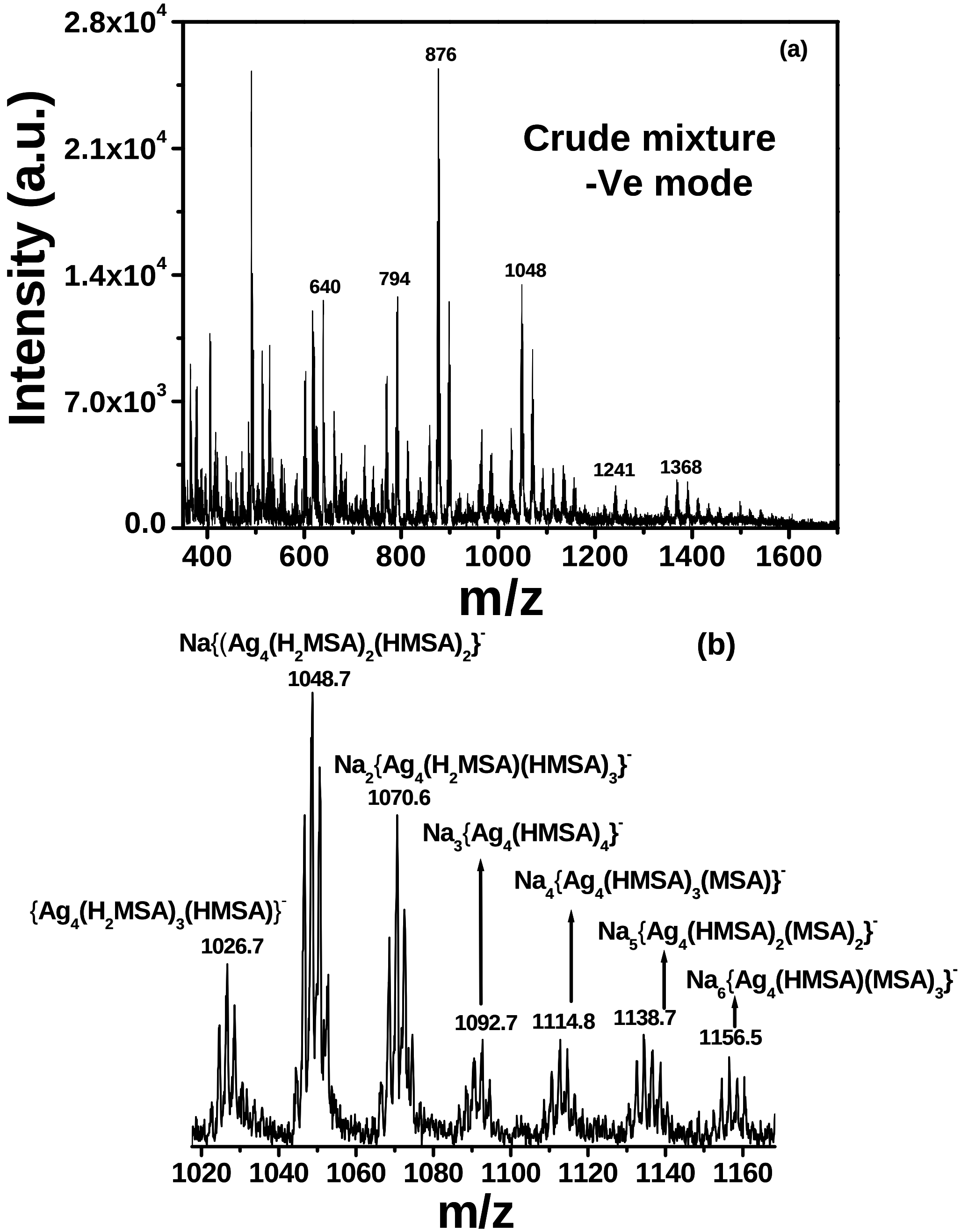
Interfacial etching



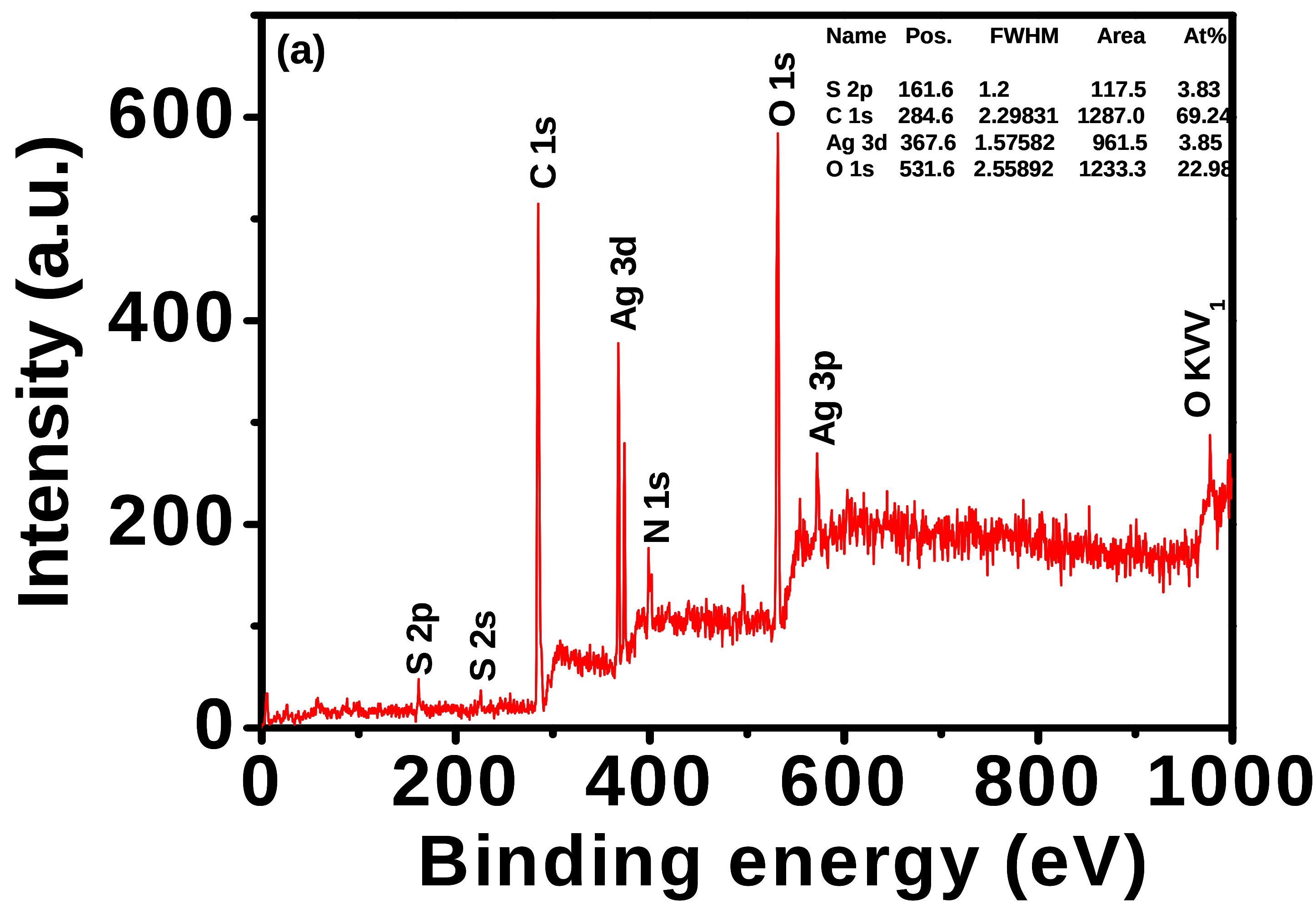

A
TOLUENE
WATER
8 h
TOLUENE
WATER
O °C
O °C
Ag@MSA
10 min
60 min
360 min
24 hours
Absorbance
Wavelength (nm)
B
1
2
2nd band
1st band
Absorbance
Wavelength (nm)
C
1
20 nm
2
20 nm
3
10 nm

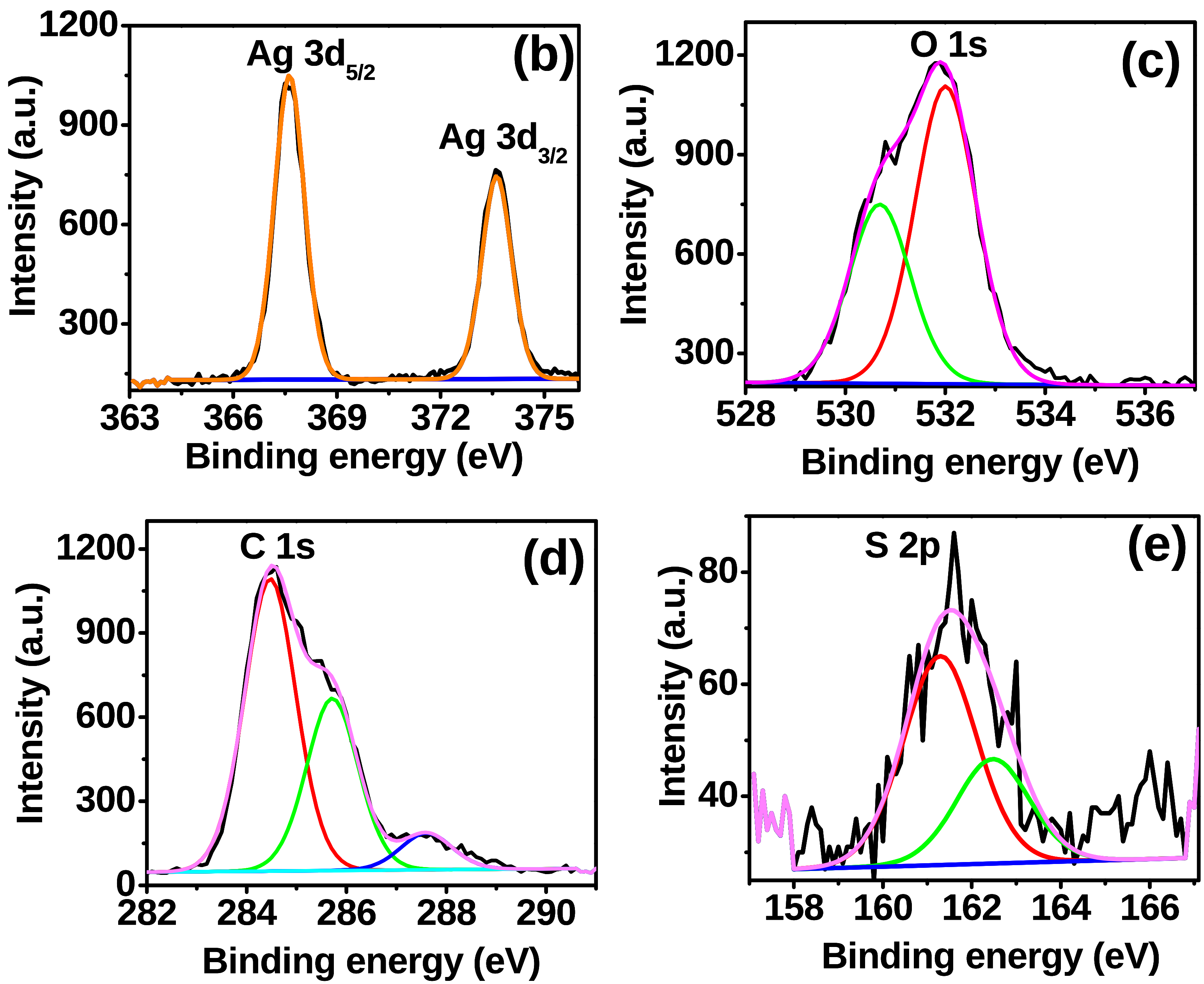


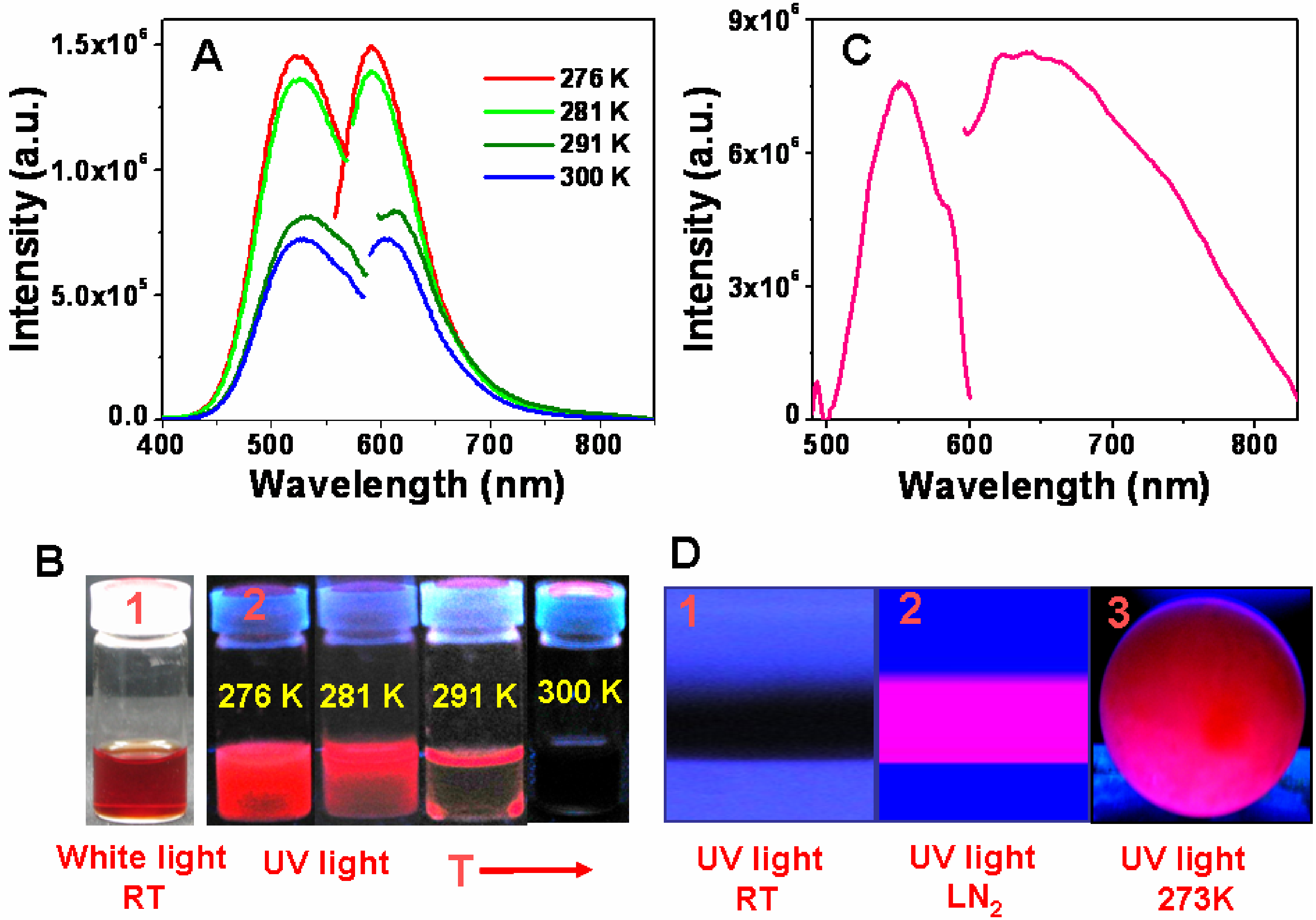
Intensity (a.u.)
m/z
3x10^4
2x10^4
1x10^4
0
600
800
1000
1200
1400
1600
a
b
c
d
Ag4(H2MSA)3(HMSA)-
Ag4(H2MSA)2(HMSA)-
Ag3(H2MSA)2(HMSA)-
Ag3(H2MSA)(HMSA)-
1024
1028
1032
872
876
878
768
771
774
618
621
624



(a)
Crude mixture
-Ve mode
876
640
794
1048
1241
1368
Intensity (a.u.)
2.8x10^4
2.1x10^4
1.4x10^4
7.0x10^3
0.0
400
600
800
1000
1200
1400
1600
m/z
(b)
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
1040
1060
1080
1100
1120
1140
1160
m/z


(a)
Name Pos. FWHM Area At%
S 2p 161.6 1.2 117.5 3.83
C 1s 284.6 2.29831 1287.0 69.24
Ag 3d 367.6 1.57582 961.5 3.85
O 1s 531.6 2.55892 1233.3 22.98
S 2p
S 2s
C 1s
Ag 3d
N 1s
O 1s
Ag 3p
O KVV1
Intensity (a.u.)
Binding energy (eV)
0
200
400
600
800
1000

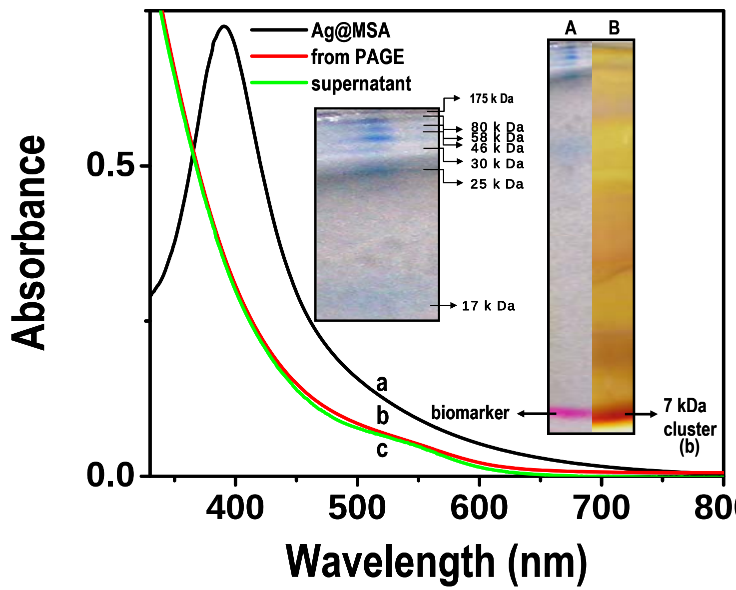

(b)
Ag 3d5/2
Ag 3d3/2
Intensity (a.u.)
Binding energy (eV)
1200
900
600
300
363
366
369
372
375
(c)
O 1s
Intensity (a.u.)
Binding energy (eV)
1200
900
600
300
528
530
532
534
536
(d)
C 1s
Intensity (a.u.)
Binding energy (eV)
1200
900
600
300
0
282
284
286
288
290
(e)
S 2p
Intensity (a.u.)
Binding energy (eV)
80
60
40
158
160
162
164
166



A
1.5x10^6
1.0x10^6
5.0x10^5
0.0
Intensity (a.u.)
400
500
600
700
800
Wavelength (nm)
276 K
281 K
291 K
300 K
C
9x10^6
6x10^6
3x10^6
0
Intensity (a.u.)
500
600
700
800
Wavelength (nm)
B
1
2
276 K
281 K
291 K
300 K
White light
RT
UV light
T
D
1
2
3
UV light
RT
UV light
LN2
UV light
273K

Ongoing….

Quantum clusters in FRET
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, 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

All my friends in DST