Luminescent quantum clusters of noble metals

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

University of Hyderabad, March 22, 2010
http://www.webexhibits.org/causesofcolor/9.html&usg=__eazWHmio6ubJtFEG_T6NScyGsc=&h=306&w=300&sz=9&hl=en&start=1&um=1&tbclid=g_xdRB5Fe6C6XM:&tbnh=117&tbnw=115&prev=/images%3Fq%3Dgold%2Bnanoparticles%2Bcolor%26hl%3Den%26sa%3DG%26um%3D1
Faraday’s gold preserved in Royal Institution. From the site, http://www.rigb.org/rimain/heritage/faradaypage.jsp
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Nano Mission, Department of Science and Technology
Monolayer Protected Metal Nanoparticles
Monolayer Protected Clusters (MPCs)

Fluorescent superlattices
New materials
Molecular Clusters

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.

Phosphine Capped Gold Clusters

- $\text{Au}_{55} \left[ \text{P} \left( \text{C}_6\text{H}_5 \right)_3 \right]_{12} \text{Cl}_6$ - a gold cluster of unusual size, Schmid, G.; Pfeil, R.; Boese, R.; Brandermann, F.; Meyer, S.; Calis, G. H. M.; Van der Velden.; Jan W. A. *Chemische Berichte* 1981, 114, 3634.

- Synthesis and x-ray structural characterization of the centered icosahedral gold cluster compound $[\text{Au}_{13} \text{(PMe}_2\text{Ph})_{10} \text{Cl}_2](\text{PF}_6)_3$; the realization of a theoretical prediction, Briant, C. E.; Theobald, B. R. C.; White, J. W.; Bell, L. K.; Mingos, D. M. P.; Welch, A. J. *Chem. Commun.* 1981, 5, 201.

Dendrimer Encapsulated Clusters

DNA Encapsulated Clusters

How to make them?
Polyacrylamide gel electrophoresis (PAGE)

Synthesis: $\text{Au}_{25}$ clusters can be preferentially populated by dissociative excitation of larger precursors

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

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

Optical absorption spectrum with an absorption maximum at 672 nm.

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

Tsukuda et. al. JACS 2005
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 $\beta$CH$_2$ resonance (labeled as C) disappears completely in the cluster which is expected as it is close to the cluster surface. All the observed resonances have been broadened in view of their faster relaxation and non-uniform distribution of ligands.
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 $\text{Au}_{25}$

1. $\text{NH}_2$\text{OH}OH\text{ONH}OH
2. $\text{SH}$\text{OH}\text{ONH}$\text{OH}$
3. $\text{HS}$\text{CH}_3$\text{OH}$\text{H}_3\text{C}$
4. $\text{NH}_2$\text{OH}OH\text{ONH}OH

1. (GSH)
2. (MB)
3. (NAGSH and NFGSH)
Absorbance vs Wavelength (nm)

HOMO

LUMO

sp-band

d-band

I(E) = A(W) x W

Energy (eV)

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

Au$_{25}$-MB

Au$_{25}$-SGAN

Au$_{25}$-SGFN

The figure shows a series of spectra (a) with different time points indicated by the peaks (d) and (e). The spectra are labeled with numbers 1 to 5, showing changes in concentration over time. The peaks are marked with arrows indicating the transition from bound to free ligand.

Graph (b) illustrates the relationship between time and the natural logarithm of concentration (In (Concentration)) with fitted lines for peaks d and e.

Graph (c) also plots the relationship between time and concentration, focusing on peak e.
$I(E) = I(W) \times W^2$

Energy (eV)

$\ Au_{25}^{SG_{18}}$
$\ Au_{25}^{\text{MB}}$
$\ Au_{25}^{\text{SGAN}}$
$\ Au_{25}^{\text{SGFN}}$
Fluorescence: A comprehensive study between organic dye, gold atoms and molecular clusters of gold

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Q. Yield</th>
</tr>
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<tbody>
<tr>
<td>Au\textsubscript{10}(SG)\textsubscript{10}</td>
<td>1*10\textsuperscript{4}</td>
</tr>
<tr>
<td>Au\textsubscript{11}(SG)\textsubscript{11}</td>
<td>1*10\textsuperscript{4}</td>
</tr>
<tr>
<td>Au\textsubscript{11}(SG)\textsubscript{11}</td>
<td>1*10\textsuperscript{4}</td>
</tr>
<tr>
<td>Au\textsubscript{15}(SG)\textsubscript{13}</td>
<td>2*10\textsuperscript{4}</td>
</tr>
<tr>
<td>Au\textsubscript{18}(SG)\textsubscript{14}</td>
<td>4*10\textsuperscript{3}</td>
</tr>
<tr>
<td>Au\textsubscript{22}(SG)\textsubscript{16}</td>
<td>4*10\textsuperscript{3}</td>
</tr>
<tr>
<td>Au\textsubscript{22}(SG)\textsubscript{17}</td>
<td>2*10\textsuperscript{3}</td>
</tr>
<tr>
<td>Au\textsubscript{25}(SG)\textsubscript{18}</td>
<td>1.9*10\textsuperscript{3}</td>
</tr>
<tr>
<td>Au\textsubscript{29}(SG)\textsubscript{20}</td>
<td>3*10\textsuperscript{3}</td>
</tr>
<tr>
<td>Au\textsubscript{33}(SG)\textsubscript{22}</td>
<td>2*10\textsuperscript{3}</td>
</tr>
<tr>
<td>Au\textsubscript{35}(SG)\textsubscript{22}</td>
<td>2*10\textsuperscript{3}</td>
</tr>
<tr>
<td>Au\textsubscript{38}(SG)\textsubscript{24}, Au\textsubscript{39}(SG)\textsubscript{24}</td>
<td>2*10\textsuperscript{3}</td>
</tr>
<tr>
<td>Gold nanoparticles</td>
<td>1*10\textsuperscript{-10}</td>
</tr>
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</table>

Recently developed clusters using Au\textsubscript{25} as precursor:

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Q. Yield</th>
</tr>
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<tbody>
<tr>
<td>Au\textsubscript{22}</td>
<td>4.0*10\textsuperscript{-2}</td>
</tr>
<tr>
<td>Au\textsubscript{23}</td>
<td>1.3*10\textsuperscript{-2}</td>
</tr>
<tr>
<td>Au\textsubscript{31}</td>
<td>1.0*10\textsuperscript{-2}</td>
</tr>
<tr>
<td>Au\textsubscript{8}(SG)\textsubscript{8}</td>
<td>1.5*10\textsuperscript{-1}</td>
</tr>
</tbody>
</table>

3. ACS Applied Materials and Interfaces (2009)

$\text{Au}_8\text{SG}_8$
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. Unpublished
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.

Comparison of the optical absorption features of \( \text{Au}_x\text{SG}_{18} \) (green trace) with \( \text{Au}_{x\frac{25}{18}}\text{OT}_y \) (grey trace), \( \text{Au}_x\text{SG}_{y} \) (pink trace) and \( \text{Au}_x\text{MPTS}_y \) (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 °C (interfacial etching) for 1 h.
Figure 2. A) MALDI-MS of Au\textsubscript{x} SG\textsuperscript{y} which shows bunch of peaks due to Au\textsuperscript{m} S\textsuperscript{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\textsubscript{23} S\textsubscript{18-23}.
Comparison of the Au(4f) XPS spectra of Au$_{22}$, Au$_{23}$ and Au$_{33}$ along with parent Au$_{25}$. 
Comparison of the photoluminescence profiles of Au$_{22}$, Au$_{23}$ and Au$_{33}$ along with parent Au$_{25}$. Photographs of the aqueous solutions of Au$_{22}$ and Au$_{23}$ under white light (A and C, respectively) and UV light (B and D, respectively) are also given.
Fluorescence decay pattern of $\text{Au}_{25}$, $\text{Au}_{33}$, $\text{Au}_{23}$, and $\text{Au}_{22}$ 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 represent 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.
Photoluminescence profile of Au$_{23}$ cluster before (pink trace) and after (orange trace) phase transfer. Emission of the cluster enhances considerably after the phase transfer. Photographs of the aqueous-toluene mixture containing the cluster before and after phase transfer under white light (A and B, respectively) and UV light (C and D, respectively). In C, only the interface is illuminated as the UV is attenuated as the sample was irradiated from the top.
A) Solvent dependent fluorescence of 50 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.
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.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_1$ (ps)</th>
<th>%</th>
<th>$\tau_2$ (ns)</th>
<th>%</th>
<th>$\tau_3$ (ns)</th>
<th>%</th>
</tr>
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<tbody>
<tr>
<td>Ethylene Glycol</td>
<td>47</td>
<td>86.5</td>
<td>2.67</td>
<td>5.5</td>
<td>70.06</td>
<td>7.9</td>
</tr>
<tr>
<td>Methanol</td>
<td>36</td>
<td>87.6</td>
<td>3.27</td>
<td>5.8</td>
<td>62.91</td>
<td>6.6</td>
</tr>
<tr>
<td>Water</td>
<td>39</td>
<td>92.4</td>
<td>2.41</td>
<td>3.6</td>
<td>68.55</td>
<td>3.9</td>
</tr>
<tr>
<td>Dioxane</td>
<td>16</td>
<td>98.0</td>
<td>5.07</td>
<td>1.1</td>
<td>31.63</td>
<td>0.9</td>
</tr>
</tbody>
</table>
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$_{23}$. 
Fluorescence (A), bright field (B) and overlay of fluorescent and bright field images (C) of human hepatoma (HepG2) cells stained with streptavidin conjugated Au$_{23}$. 

Schematic representation of the conjugation of streptavidin on Au$_{23}$ by EDC coupling.
A B

Bright field (A) and fluorescence (B) images of HepG2 cells stained with unconjugated Au$_{23}$ clusters. No fluorescence was observed from the cells after washing.
Fluorescent microscopic images showing interaction of Au-BSA-FA NCs with different types of cell lines: a1-a2) FR-ve lung carcinoma A549 after 2 hours of incubation, b1-b2) FR-ve lung carcinoma A549 after 24 hours of incubation, c1-c2) FR+ve KB cells with unconjugated Au clusters, d1-d2) FR+ve KB cells with FA conjugated Au clusters at 2 hrs, e1-e2) 4 hrs and f1-f2) 24 hrs of incubation [Archana R, Sonali S, Deepthy M et al. Molecular Receptor Specific, Non-toxic, Near-infrared Emitting Au Cluster-Protein Nanoconjugates for Targeted Cancer Imaging. Nanotechnology (2010)]
Clusters for metal ion detection

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

FRET between Au$_{25}$ and Dansyl Chromophore

Approaches Used for the Functionalization of Dansyl Chromophore on the Au$_{25}$ Cluster.

Cluster based patterns

\[(H_2TPPOASH)_{Toluene} \rightarrow \text{Core reduction/ligand exchange} \rightarrow [Au_{25}SG_{18}]_{aq} \rightarrow [Au_{22}(SG)_{15}(H_2TPPOAS)_2]_{aq}\]

\(\text{Au}_{25}\) \(\rightarrow\) \(\text{H}_2\text{TPPOASH}\) \(\rightarrow\) \(\text{Au}_{22}\)

\((\text{GSH})\)

\[\text{1,8-dibromooctane }\]
\[\text{K}_2\text{CO}_3/\text{DMF}\]

\[\text{(Me}_3\text{Si)}_2\text{S/ TBAF/THF}\]

\[\text{III}\]

\[\text{II}\]

\[\text{I}\]

\[\text{A}\] \(\rightarrow\) \(\text{B}\) \(\rightarrow\) \(\text{C}\) \(\rightarrow\) \(\text{D}\)

\[\text{RT} \quad 5^\circ\text{C}\]
Au$$^{22S_{17}}$$ + Au$$^{20S_{15}}$$ + Au$$^{18S_{13}}$$ + Au$$^{16S_{11}}$$ + Au$$^{14S_{9}}$$ + Au$$^{12S_{7}}$$

$$^{(A_{n}S_{m})^+}$$

775

4878

821

A

m/z

2000 4000 6000 600 750 900

8.0 K

20.0 K

0.0 K

Intensity

x 9

550 600 650 700 750 800 850

0

1x10$$^{-6}$$

2x10$$^{-6}$$

3x10$$^{-6}$$

4x10$$^{-6}$$

5x10$$^{-6}$$

6x10$$^{-6}$$

Addition of Cu$$^{+2}$$ (mM)

d (300 µL)

c (100 µL)

b (50 µL)

a (0 µL)

Wavelength (nm)

Intensity (cps)

1 2 3 4

550 600 650 700 750 800 850

0

1x10$$^{-6}$$

2x10$$^{-6}$$

3x10$$^{-6}$$

4x10$$^{-6}$$

5x10$$^{-6}$$

Addition of Zn$$^{+2}$$ (mM)

d (300 µL)

c (150 µL)

b (20 µL)

a (0 µL)

Wavelength (nm)

Intensity (cps)

0 50 100 150 200 250 300

0

1x10$$^{-6}$$

2x10$$^{-6}$$

3x10$$^{-6}$$

4x10$$^{-6}$$

5x10$$^{-6}$$

Flu. Intensity at 670 nm

Concentration of Zn$$^{+2}$$ (µM)

0 50 100 150 200 250 300

0

1x10$$^{-6}$$

2x10$$^{-6}$$

3x10$$^{-6}$$

4x10$$^{-6}$$

5x10$$^{-6}$$

Flu. Intensity at 670 nm

Concentration of Cu$$^{+2}$$ (µM)

0 50 100 150 200

1k

10k

100

10

0

Time (ns)

(IRF)

0 10 20 30 40

50 100 150 200

10k

1k

100

10

0

Time (ns)

(IRF)

Clustering Efficiency of H$_2$TPPOASH

<table>
<thead>
<tr>
<th>Cluster</th>
<th>H$_2$TPPOASH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Life (ns)</td>
<td>%</td>
</tr>
<tr>
<td>0.05</td>
<td>86.50</td>
</tr>
<tr>
<td>1.16</td>
<td>6.60</td>
</tr>
<tr>
<td>9.59</td>
<td>3.50</td>
</tr>
<tr>
<td>141.80</td>
<td>3.40</td>
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</table>

0 10 20 30 40

Wavelength (nm)

Flu. Intensity at 670 nm

Concentration of Cu$$^{+2}$$ (µM)

0 50 100 150 200 250 300

0

1x10$$^{-6}$$

2x10$$^{-6}$$

3x10$$^{-6}$$

4x10$$^{-6}$$

5x10$$^{-6}$$

Flu. Intensity at 670 nm

Concentration of Zn$$^{+2}$$ (µM)

0 50 100 150 200 250 300

0

1x10$$^{-6}$$

2x10$$^{-6}$$

3x10$$^{-6}$$

4x10$$^{-6}$$

5x10$$^{-6}$$

Flu. Intensity at 670 nm

Concentration of Cu$$^{+2}$$ (µM)
With G. U. Kulkarni

E. S. Shibu et al. ACS Appl. Mater. 2009, 1, 2199.
Scheme: Au$_{15}$ was synthesized inside the cyclodextrin (CD) cavity \textit{(in situ)}. Note: CD and GSH are the abbreviations of cyclodextrin and glutathione, respectively. For our synthesis we have used all 3 CDs (alpha, beta and gamma) and GSH – glutathione (GSH) protected gold nanoparticle.

Basic unit of CD is 6 membered glucose.

E. S. Shibu and T. Pradeep. Unpublished
E. S. Shibu and T. Pradeep. Unpublished
Au$_{15}$ Clusters have a tendency to self paint on glass surface while dipping in cluster solution. Figure shows the photograph of a glass plate coated with Au$_{15}$ cluster.
Size selected metal clusters


Silver clusters
Interfacial etching

8 h

Toluene → Toluene

0 °C → 0 °C

Gel electrophoresis

550 nm

640 nm
A) Cluster 2 $[\text{Ag}_7(\text{HMSA})_7]^- - n\text{H} + n\text{Na}$

$n = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6$

ii) $\times 3$

Cluster 1 $\text{Ag}_8(\text{HMSA})_8 - n\text{H} + n\text{Na}$

$n = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6$

ii) $\times 3$
$\text{Na}_6\{\text{Ag}_4\text{(HMSA)}_3\text{(MSA)}\}$

$\text{Na}_5\{\text{Ag}_4\text{(HMSA)}_2\text{(MSA)}_2\}$

$\text{Na}_4\{\text{Ag}_4\text{(HMSA)}_3\text{(MSA)}\}$

$\text{Na}_3\{\text{Ag}_4\text{(HMSA)}_4\}$

$\text{Na}_2\{\text{Ag}_4\text{(H}_{2}\text{MSA})(\text{HMSA})_2\}$

$\text{Na}\{\text{Ag}_4\text{(H}_{2}\text{MSA})_3\text{(HMSA)}\}$

$m/z$
Nano Mission, Department of Science and Technology

IIT Madras

Thanks!