Light emitting quantum clusters of gold and silver

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$\text{Au}_{25}, \text{Au}_{23}, \text{Au}_{22}, \text{Au}_{8}$ and $\text{Ag}_{8}$

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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
Monolayer Protected Metal Nanoparticles
Monolayer Protected Clusters (MPCs)

Fluorescent superlattices

Fluorescent superlattices of gold nanoparticles

Fluorescence images collected from superlattice triangles

New materials


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


- **Synthesis and x-ray structural characterization of the centered icosahedral gold cluster compound** [ Au$_{13}$ (PMe$_2$Ph)$_{10}$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.

Dendrimer Encapsulated Clusters

DNA Encapsulated Clusters

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

How to make them?
Polyacrylamide gel electrophoresis (PAGE)

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

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 \(-\text{SH}\) 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 \(\beta\text{CH}_2\) 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.
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 \( \text{Au}_{25} \)

1. \( \text{NH}_2 \)
   \[ \text{HO-C-CONH-COOH} \]
   (GSH)

2. \( \text{OH} \)
   \[ \text{HO-CH}_3 \]
   (MB)

3. \( \text{NH} \)
   \[ \text{HO-C-CONH-COOH} \]
   (NAGSH and NFGSH)

4. \( \text{OH} \)
1. The graph shows the concentration of a ligand over time (min) for different samples.

2. The concentration is plotted on the Y-axis, and the time on the X-axis.

3. The ligand concentrations are given as ppm (parts per million).

4. Peak d and peak e are highlighted on the graph.

5. The free ligand is shown by the arrows and labeled.

6. The bound ligand is also shown by arrows and labeled.

7. The graph shows a linear relationship between ln (Concentration) and Time (min) for both peaks d and e.

8. The concentration values for ppm are: 2.90, 2.80, 2.70, 2.60, 2.50, 2.40, 2.30, 2.20, 2.10.

9. The concentration values for ln (Concentration) are: 1.60, 1.64, 1.68.
Energy (eV)

Wavelength (nm)

\[I(E) = I(W) \times W^2\]

\[
\begin{align*}
\text{Wavelength (nm)} &\quad \text{Energy (eV)} \\
400 &\quad 1.38 \\
500 &\quad 1.51 \\
600 &\quad 1.82 \\
700 &\quad 2.1 \\
800 &\quad 2.5 \\
900 &\quad 3.1 \\
\end{align*}
\]
Fluorescence: A comprehensive study between organic dye, gold atoms and molecular clusters of gold

### Cluster Q. Yield

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

### Recently developed clusters using $\text{Au}_{25}$ as precursor

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

3. ACS Applied Materials and Interfaces (Under Revision)

The graph shows the binding energy (eV) on the x-axis and intensity (a. u.) on the y-axis for different samples: $\text{Au}_{25}\text{SG}_{18}$, $\text{Au}_{25}\text{-MB}$, and $\text{Au}_{25}\text{-SGAN}$. The peaks at 4f\textsubscript{5/2} and 4f\textsubscript{7/2} are highlighted, indicating the energy levels of the 4f states for gold.
$\text{Au}_8\text{SG}_8$

![Diagram showing the conversion of $\text{Au}_8$ to $\text{Au}_{25}$ at pH=8 and pH=3](image)
Comparison of the optical absorption profiles of Au@MSA, Au\textsubscript{25} and Au\textsubscript{8}.

Comparison of the photoluminescence profiles of the clusters with Au@MSA. Traces I and II are the excitation and emission spectra of Au\textsubscript{8}, respectively. Traces III and IV are the excitation and emission spectra of Au\textsubscript{25}, respectively and trace V is the emission spectrum of Au@MSA.

Habeeb Muhammed et al. *Nano Res.* 2008
Habeeb Muhammed, et. al. Unpublished
Two Different Fluorescent Quantum Clusters of Gold in Gram Quantities from Metallic Nanoparticle

Nano Research October 2008 Back Cover Art
Reversible phase transfer of \( \text{Au}_{25} \) from aqueous to toluene

Comparison of the optical absorption profiles of Au$_{25}$ in 1) aq. Phase, 2) toluene phase after phase transfer 3) aq. phase after reversible phase transfer.
Comparison of the photoluminescence profiles of Au$_{25}$ 1) aq. phase, 2) toluene phase after phase transfer 3) aq. phase after reversible phase transfer.
Clusters from clusters: \( \text{Au}_{25} \) to make other clusters

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

Figure 1. Comparison of the optical absorption features of Au$_{25}$SG$_{18}$ (green trace) with Au$_{x}$OT$_{y}$ (grey trace), Au$_{x}$SG$_{y}$ (pink trace) and Au$_{x}$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 ºC (interfacial etching) for 1 h.
Figure 2. A) MALDI-MS of Au$_x$S$_{18-23}$ 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$_{23}S_{18-23}$.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>% of element (Experimental)</th>
<th>% of element (Calculated)</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au₂₃(MPTS)₁₀(SG)₇</td>
<td>N</td>
<td>03.85</td>
<td>03.68</td>
<td>Au₂₃(SG)₁₈</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>15.29</td>
<td>15.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>02.71</td>
<td>02.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>06.31</td>
<td>06.81</td>
<td></td>
</tr>
<tr>
<td>Au₃₃OT₂₂</td>
<td>N</td>
<td>00.00</td>
<td>00.00</td>
<td>Au₃₃OT₂₂</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>22.01</td>
<td>21.78</td>
<td></td>
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<tr>
<td></td>
<td>H</td>
<td>04.15</td>
<td>03.86</td>
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<tr>
<td></td>
<td>S</td>
<td>07.18</td>
<td>07.26</td>
<td></td>
</tr>
</tbody>
</table>

Table shows CHNS elemental analysis data of the three clusters.
Comparison of the Au(4f) XPS spectra of $\text{Au}_{22}$, $\text{Au}_{23}$ and $\text{Au}_{33}$ along with parent $\text{Au}_{25}$. 
Comparison of XPS spectra due to the core level photoemission from Si2p, S2p, N1s and O1s of Au$_{33}$ (grey trace), Au$_{25}$ (green trace), Au$_{23}$ (pink trace) and Au$_{22}$ (purple trace).
Comparison of the photoluminescence profiles of \( \text{Au}_{22} \), \( \text{Au}_{23} \) and \( \text{Au}_{33} \) along with parent \( \text{Au}_{25} \). Photographs of the aqueous solutions of \( \text{Au}_{22} \) and \( \text{Au}_{23} \) 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 $\text{Au}^{22}$ (A) and $\text{Au}^{23}$ (B) collected by the spectroscopic mapping at an excitation wavelength of 532 nm. Regions coded red represents the pixels where the signal (used for mapping) is a maximum, the minima being represented with black colors. The scan area was 40 $\mu\text{M} \times 40$ $\mu\text{M}$.
Photoluminescence profile of Au$_{23}$ cluster before (pink trace) and after (orange trace) phase transfer. Emission of the cluster enhances considerably after the phase transfer. Photographs of the aqueous-toluene mixture containing the cluster before and after phase transfer under white light (A and B, respectively) and UV light (C and D, respectively). In C, only the interface is illuminated as the UV is attenuated as the sample was irradiated from the top.
A) 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.

<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>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>34</td>
<td>82.8</td>
<td>4.11</td>
<td>4.3</td>
<td>80.35</td>
<td>12.9</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>
</tbody>
</table>
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>
</thead>
<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>
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.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Quantum yield, $\Phi$</th>
<th>Fluorescence lifetime, $\tau$ (ns)</th>
<th>Radiative rate constant, $k_r$ (10$^7$ s$^{-1}$)</th>
<th>Nonradiative rate constant, $k_{nr}$ (10$^7$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.013</td>
<td>0.4</td>
<td>3.250</td>
<td>246.75</td>
</tr>
<tr>
<td>Toluene (phase transferred)</td>
<td>0.050</td>
<td>2.6</td>
<td>1.900</td>
<td>36.10</td>
</tr>
<tr>
<td>Dioxane</td>
<td>0.001</td>
<td>6.5</td>
<td>0.015</td>
<td>15.38</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>0.045</td>
<td>10.6</td>
<td>0.420</td>
<td>8.91</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$_{23}$. 
Schematic representation of the conjugation of streptavidin on Au$_{23}^\text{SG}_{18}$ by EDC coupling.

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

EDC : 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
Bright field (A) and fluorescence (B) images of HepG2 cells stained with unconjugated \( \text{Au}_{23} \) clusters. No fluorescence was observed from the cells after washing.
Au$_8$SG$_8$

Organic soluble red emitting clusters

Water soluble red emitting clusters

PAGE image of Au$_8$SG$_8$ cluster
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 $\text{Au}_{25}$ and Dansyl Chromophore

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

Cluster based patterns

\[ (\text{TPPOASH})_{\text{Toluene}} \]

Core reduction followed by ligand exchange

\[ [\text{Au}_{25}\text{SG}_{18}]_{\text{aq}} \rightarrow [\text{Au}_{22}(\text{SG})_{15}(\text{TPPOAS})_{2}]_{\text{aq}} \]

Cluster based patterns

\[ \text{(GSH)} \]

\[ \text{(TPPOASH)} \]
Silver clusters
Size selected metal clusters


Recent studies


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


• **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

Toluene → 8 h → Toluene

Water

0 °C

0 °C

Gel electrophoresis

550 nm

640 nm
Udaybhaskar Rao and Pradeep, Submitted
$\text{Ag}_3(\text{H}_2\text{MSA})(\text{HMSA})^-$

$\text{Ag}_3(\text{H}_2\text{MSA})_2(\text{HMSA})^-$

$\text{Ag}_4(\text{H}_2\text{MSA})_3(\text{HMSA})^-$

$\text{Ag}_4(\text{H}_2\text{MSA})_3(\text{HMSA})^-$
e) $\text{Ag}_5(\text{H}_2\text{MSA})_3(\text{HMSA})^-$

f) $\text{Ag}_6(\text{H}_2\text{MSA})_3(\text{HMSA})^-$

g) $\text{Ag}_7(\text{H}_2\text{MSA})_3(\text{HMSA})^-$
Intensity (a.u.)

B.E (eV)

366 369 372 375 378

Intensity (a.u.)

Binding energy (eV)

158 160 162 164 166

Intensity (a.u.)

Binding energy (eV)

282 285 288 291 294

Intensity (a.u.)

Binding energy (eV)

528 531 534 537

Intensity (a.u.)

Binding energy (eV)

Ag@MSA NP
Crude cluster
Ag$_8$(H$_2$MSA)$_5$
Ag$_7$(H$_2$MSA)$_4$

Ag NP

Ag$_7$
Ag$_8$
Crude
A 9x10^3
6x10^3
3x10^3

Intensity (a.u.)

500 1000 1500 2000 2500

m/z

Ag_{5}S_{4}  Ag_{9}S_{5}  Ag_{11}S_{6}  Ag_{13}S_{7}  Ag_{15}S_{8}  Ag_{17}S_{9}

B

C

IITM

IITM
A) The graph shows the intensity (a.u.) of the emission spectra for \( \text{Ag}_4(\text{H}_2\text{MSA})_4 \) in toluene (green line) and water (orange line) as a function of wavelength (\( \lambda \) in nm). The intensities are indicated by the peaks at different wavelengths.

B) Images (a) to (f) illustrate the visual appearance of the samples in different conditions. (a) shows a sample in toluene, (b) and (c) are in water, while (d) to (f) represent different states or conditions of the sample.
Ongoing…..

Quantum clusters and unusual properties
Applications in cell imaging
Metal and molecular detection
Crystallisation
Catalysis

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$_8$MSA$_8$, Au$_{22}$, Au$_{23}$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.
IIT Madras

Thank you all
Emission is the process by which the energy of a photon is released by another entity, for example, by an atom whose electrons make a transition between two electronic energy levels. The emitted energy is in the form of a photon.


Fluorescence is a luminescence that is mostly found as an optical phenomenon in cold bodies, in which the molecular absorption of a photon triggers the emission of a photon with a longer (less energetic) wavelength. The energy difference between the absorbed and emitted photons ends up as molecular rotations, vibrations or heat. Sometimes the absorbed photon is in the ultraviolet range, and the emitted light is in the visible range, but this depends on the absorbance curve and Stokes shift of the particular fluorophore. The term 'fluorescence' was coined by George Gabriel Stokes in his 1852 paper[1]; the name was given as a description of the essence of the mineral fluorite, composed of calcium fluoride, which gave a visible emission when illuminated with "invisible radiation" (UV radiation).

[1] Fluorescence Applications & Instruments Slideshows | HORIBA Jobin Yvon

http://en.wikipedia.org/wiki/Fluorescence
**Luminescence** is light that usually occurs at low temperatures, and is thus a form of cold body radiation. It can be caused by chemical reactions, electrical energy, subatomic motions, or stress on a crystal. This distinguishes luminescence from incandescence, which is light generated by high temperatures. Historically, radioactivity was thought of as a form of "radiloluminescence", although it is today considered to be separate since it involves more than electromagnetic radiation.

The following are types of luminescence
1. Bioluminescence, by a living organism
2. Chemoluminescence, resulting of a chemical reaction
3. Electrochemiluminescence, by an electrochemical reaction
4. Crystalloluminescence, produced during crystallization
5. Electroluminescence, in response to an electric current passed through it
6. Cathodoluminescence, where beam of electrons impacts on a luminescent material such as a phosphor
7. Mechanoluminescence, resulting from any mechanical action on a solid
8. Triboluminescence, generated when bonds in a material are broken when that material is scratched, crushed, or rubbed
9. Fractoluminescence, generated when bonds in certain crystals are broken by fractures
10. Piezoluminescence, produced by the action of pressure on certain solids
11. Photoluminescence, absorption of photons causing re-radiation of photons
12. Phosphorescence, delayed re-radiation
13. Fluorescence, where the emitted photons are of lower energy than those absorbed
14. Radioluminescence, produced in a material by the bombardment of ionizing radiation
15. Sonoluminescence, from imploding bubbles in a liquid when excited by sound
16. Thermoluminescence, when absorbed light is re-emitted on heating.

http://en.wikipedia.org/wiki/Luminescence
Luminescence

Luminescence is the emission of light from any substance and occur from electronically excited states. It has two categories, depends on the nature of the excited state.
1. Fluorescence
2. Phosphorescence

**Fluorescence:** The non radiative emission between two electronic states having same multiplicity. The emission rate of fluorescence is typically $10^8$ S$^{-1}$, so that a typical fluorescence life time is near 10 ns.

**Phosphorescence:** The non radiative emission between two electronic states having different multiplicity (from triplet excited state to singlet ground state. This transition is forbidden hence the emission rate is slow ($10^3$-$10^0$ S$^{-1}$), So the phosphorescence is called delayed fluorescence. Life time will be of the order of milliseconds.