The chemical reaction between \([\text{Au}^{11}(\text{PPh}_3)^{8}\text{Cl}_2]^+\) and \(n\)-alkanethiol \(\text{CnH}_{2n+1}\text{SH}\) (\(n=2, 8, 10, 12, 14, 16, \text{and} 18\)) serendipitously yielded stable \(\text{Au}^{25}\) cluster compounds with the formula, \([\text{Au}^{25}(\text{PPh}_3)^{10}(\text{SCnH}_{2n+1})^5\text{Cl}_2]^2+\).

**INTRODUCTION**

Fluorescence in biology and other fields

QDs, lanthanide NPs, carbon nanodots

Metal clusters: low toxicity, stability
LOWER QY

Surface engineering, doping, etc to improve QY


Tatsuya Tsukuda et al., *J. Phys. Chem. C* 2007, 111, 7845
Synthesis routes for biicosahedral Au25 clusters

\[
[Au11(PPh_3)8Cl_2]^+ \xrightarrow{n\text{-alkanethiols}} [Au25(PPh_3)10(SCnH2n+1)5Cl_2]^{2+}
\]

Tert-butylamine-Borane complex

\[
\text{AuPPh}_3\text{Cl} + \text{n-hexanethiol} \xrightarrow{3\text{h, stir, 25 oC}} [Au25(PPh_3)10(SC_6H_{13})5Cl_2]^{2+}
\]

Methanol purification

(D. Lee et al. Langmuir 2012, 28, 7049)

Synthesis routes for biicosahedral AgxAu25-x clusters

Au nanoparticles (PPh3-protected)

\[
[Au11(PPh_3)8Cl_2]^+
\]

Ag-thiolates

\[
[AgxAu25-x (PPh_3)10-(SC_2H_4Ph)5Cl_2]^{2+}
\]
UV-vis spectra and TEM images of raw materials
ESI mass spectra

Product I: nanoparticle route

Product II: Au11 route

General formula of I and II is \([\text{Ag}_x\text{Au}_{25-x}(\text{PPh}_3)_{10-(\text{SC}_2\text{H}_4\text{Ph})_5\text{Cl}_2}]^2+\)
ESI-TOF Mass Spectrum of Au$_{25}$
ESI-TOF Mass Spectrum of Product I

\[
\text{Ag}_{12}\text{Au}_{13}(\text{PhC}_2\text{H}_4\text{S})_5(\text{PPh}_3)_{10}\text{Cl}_2^{2+}
\]
ESI-TOF Mass Spectrum of Product II

\[ \text{Ag}_{13}\text{Au}_{12}(\text{PhC}_2\text{H}_4\text{S})_5(\text{PPh}_3)_{10}\text{Cl}_2^{2+} \]
UV/Vis and photoluminescence spectra of Au25, I, and II

λ_em of Au25: 827 nm; QY: 0.1%

λ_em of II: 680 nm; QY: 40.1%
X-ray structures of: a) \([\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_2\text{H}_4\text{Ph})_5\text{Cl}_2]^{2+}\), b) \(\text{I}\), and c) \(\text{II}\). \(\text{M}=\text{metal atom}\)

Products I and II were crystallized

Also proved by the 1H-NMR, 31P-NMR and 1H-1H COSY NMR
DPV and SWV of product II

HOMO-LUMO gap of Au25: 1.54 eV

HOMO-LUMO gap of II: 1.79 eV

This shows that emission of Au25 clusters and the product II is due to the HOMO-LUMO transitions
### Electronic structure of Au25 rod clusters

![Diagram showing electronic structure of Au25 rod clusters]

### Comparison of bond lengths in the nanocluster structures

<table>
<thead>
<tr>
<th>“waist” region</th>
<th>Au$_{25}$ (weakly fluorescent)</th>
<th>Product I (weakly fluorescent)</th>
<th>Product II (strongly fluorescent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-S</td>
<td>$2.33 \pm 0.09 \text{ Å}$</td>
<td>$2.42 \pm 0.01 \text{ Å}$</td>
<td>$2.41 \pm 0.04 \text{ Å}$</td>
</tr>
<tr>
<td>M-M (between two pentagons)</td>
<td>$3.05 \pm 0.03 \text{ Å}$</td>
<td>$3.03 \pm 0.01 \text{ Å}$</td>
<td>$3.03 \pm 0.02 \text{ Å}$</td>
</tr>
<tr>
<td>Radial M-M</td>
<td>$2.90 \pm 0.03 \text{ Å}$</td>
<td>$2.87 \pm 0.004 \text{ Å}$</td>
<td>$2.89 \pm 0.01 \text{ Å}$</td>
</tr>
</tbody>
</table>
Fluorescence confocal images

$[\text{Ag}_x\text{Au}_{25-x}(\text{PPh}_3)_{10}($SC$_2$H$_4$OH)$_5\text{Cl}_2)]^{2+}$

Excitation: 405 or 633 nm laser

human cancer cell 7402

![Cell Viability Graph](chart.png)
Summary and conclusions

- Identified a highly fluorescent Ag\(_{13}\)Au\(_{12}\) nanocluster by comparing two series of Ag-doped Ag\(_x\)Au\(_{25-x}\) nanoclusters prepared by two different routes.

- Au nanoparticles with AgI thiolate gives rise to Ag\(_x\)Au\(_{25-x}\) with \(x=12\), with all of these species only weakly fluorescent (QY:0.2%).

- Au\(_{11}\) clusters with AgI-thiolate gives rise to Ag\(_x\)Au\(_{25-x}\) with \(x=13\), and the unique Ag\(_{13}\)Au\(_{12}\) species in the distribution is highly luminescent (QY:40.1%).

- The atomic-level structural and electronic insight provides a promising design principle for highly fluorescent metal nanoclusters, and may stimulate future work on the deep understanding of the atomic-level origin of fluorescence from metal nanoclusters, as well as on the development of applications in biolabeling, sensing, and other fields.