# One-step Route to Luminescent $Au_{18}SG_{14}$ in the Condensed Phase and its Closed Shell Molecular Ions in the Gas Phase

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### **Experimental Section**

**Chemicals:** All the chemicals are commercially available and used without further purification. HAuCl<sub>4</sub>.3H<sub>2</sub>O, methanol (GR grade) and GSH ( $\gamma$ -Glu-Cys-Gly, M.W. 307.13) were purchased from SRL Chemical Co. Ltd., India. NaBH<sub>3</sub>CN was purchased from Sigma Aldrich.

**Synthesis of Au<sub>18</sub>SG<sub>14</sub>:** To 1.2 mL methanolic solution, containing 150 mg of HAuCl<sub>4</sub>.3H<sub>2</sub>O, 1.8 mL water was added. 300 mg of glutathione was added to it. The solution was sonicated to dissolve glutathione. During sonication, the color of the solution changed from yellow to almost colorless. It was diluted to 96 mL by methanol. The solution was then stirred for 10 min. 4.5 mL aqueous solution of NaBH<sub>3</sub>CN (220 mM) was added to it. After 30 min of vigorous stirring, the precipitate was collected and washed repeatedly with methanol through centrifugal precipitation to remove the remaining precursors. The precipitate was dissolved in water and centrifuged to remove unreacted thiolate. Finally, the solution was freeze dried to obtain Au<sub>18</sub>SG<sub>14</sub> as a pale red powder.

**Polyacrylamide gel electrophoresis (PAGE):** PAGE separation of the clusters was performed as per the procedure given below.

A gel electrophoresis unit with 1 mm thick spacer (Bio-rad, Mini-protein Tetra cell) was used to process the PAGE. The total contents of the acrylamide monomers were 28% (bis(acrylamide:acrylamide) = 7:93) and 3% (bis(acrylamide:acrylamide) = 6:94) for the separation and condensation gels, respectively. The eluting buffer consisted of 192 mM glycine and 25 mM tris(hydroxymethylamine). The clusters, as a pale red powder, obtained in the reaction were dissolved in 5% (v/v) glycerol-water solution (0.5 mL) at a concentration of 20 mg/mL. The sample solution (1.0 mL) was loaded onto a 1 mm gel and eluted for 6 h at a constant voltage of 120 V to achieve separation shown in Figure 1.

We also performed high resolution electrophoresis using increased contents of acrylamide monomers of 35% and 3% for the separation and condensation gels, respectively. But, we did not observe any additional bands.

### Analytical procedures

### A. UV-vis spectrometer

UV/Vis spectra were measured with a Perkin Elmer Lambda 25 instrument in the range of 200- 1100 nm.

### B. Luminescence spectroscopy

Luminescence measurements were carried out using HORIBA JOBIN VYON Nano Log instrument. The band pass for excitation and emission was set as 3 nm.

### C. Transmission electron microscopy (TEM)

TEM images were collected using a JEOL 3010 microscope. A diluted solution was spotted on carbon coated copper grid and was dried in ambience. Images were collected at 200 keV, to reduce beam induced damage of the clusters. Our earlier studies had shown that small clusters are highly sensitive to electron beam and undergoes aggregation.

### D. Fourier-transform infrared (FT-IR) spectra

FT-IR spectra were measured with a Perkin Elmer Spectrum One instrument. For sample preparation KBr crystals were used as the matrix.

### E. SEM and EDX analyses

Scanning electron microscopic (SEM) and energy dispersive X-ray (EDX) analyses were done in a FEI QUANTA-200 SEM. For measurements, samples were drop-casted on an indium tin oxide coated conducting glass and dried in vacuum. After drying it is used for analysis.

### F. X-ray photoelectron spectroscopy

The photoelectron spectra of the samples were obtained using an ESCA probe/TPD of Omicron Nanotechnology. Sample in water was spotted on Mo plate and allowed to dry in vacuum. The size of the analyzed area was about 3 mm<sup>2</sup>. In view of the sensitivity of the sample, surface cleaning was not attempted. Al Kα radiation was used for excitation; a 180° hemispherical analyzer and a seven-channel detector were employed. The spectrometer was operated in the constant energy analyzer mode. Survey and high-resolution spectra were collected using pass energies of 50 and 20 eV, respectively. The pressure in the analyzer chamber was in the low 10<sup>-10</sup> mbar range during spectrum collection. Binding energies of the core levels were calibrated with C 1s B.E, set at 284.9 eV.

### G. Electrospray ionization (ESI) mass spectrometry

The ESI mass spectrometric measurements were done in the negative mode using LTQ XL, with a mass range of m/z 150-2000, in which the spray and the extraction are orthogonal to each other. The clusters, obtained after freeze drying were dispersed in 1:1 water-methanol solution and used for mass spectrometric measurements. The samples were electrosprayed at a flow rate of 10  $\mu$ L/min at a temperature of 150 $\Box$ C. The spectra were averaged for 75 scans.

### H. MALDI TOF MS

The mass spectrometric studies were done using a Voyager Biospectrometry Workstation (Applied Biosystems) MALDI TOF MS instrument. A pulsed nitrogen laser of 337 nm was used for desorption ionization and TOF was operated in the delayed extraction mode. For MALDI MS study, α-cyano-4-hydroxycinnamic acid (CHCA) matrix in 0.1% trifluoroacetic acid (TFA) was mixed with cluster in water (2mg/1mL) in 2:1 ratio and soincated for 15 minute and directly spotted on the target plate. Typical delay times employed were of the order of 75–150 ns. The mass spectra were collected in positive mode and were averaged for 200 shots. Most of the measurements were done in the reflectron mode.

XPS



**Figure S1.** (A) XPS survey spectrum of the as synthesized  $Au_{18}(SG)_{14}$ . B, C, are the expanded C 1s and O 1s core level regions, respectively. The multiple components are fitted. The peaks are assigned. The components in the C 1s and O 1s regions can be understood from the structure of the ligand.

# TEM, effect of electron beam irradiation



**Figure S2.** (A) TEM image of Au<sub>18</sub>SG<sub>14</sub>; particles were observable only faintly. (B-D) The systematic conversion of the clusters into bigger nanoparticles upon the irradation with the electron beam. TEM images were taken from same area after 5, 10 and 15 minutes of irradiation in B, C and D, respectively.

# ESI MS



**Figure S3.** (A) A<sub>1</sub>, A<sub>2</sub> and A<sub>3</sub> showed expanded views of 4<sup>-</sup>, 5<sup>-</sup> and 7<sup>-</sup> charges (black line) with simulated values (red line) and (B) the deconvoluted mass spectrum based on all the multiply charged species observed.

### MALDI MS



**Figure S4.** (A) MALDI MS in positive mode of the crude product using the matrix  $\alpha$ -cyano-4- hydroxycinnamic acid (CHCA). (B) Expanded view giving the most intense peak at m/z 3962, well matched with Au<sub>18</sub>S<sub>13</sub><sup>+</sup> showing the likely presence of the Au<sub>18</sub> core and (C) expanded view of the intense peak (Au<sub>18</sub>S<sub>13</sub><sup>+</sup>) showing a separation of m/z 32 due to sulfur. Laser induced fragmentation and reaction in the plasma complicate the spectrum.

### SEM/EDAX



**Figure S5.** (A) EDAX spectrum of Au<sub>18</sub>SG<sub>14</sub> and (B) SEM image of Au<sub>18</sub>SG<sub>14</sub> aggregate from which the EDX spectrum was taken. Au:S atomic ratio measured is 1:0.76, as expected (actual is 1:0.78).

# 7. Supporting information 7 FT-IR



**Figure S6**. Expanded FT-IR of GSH and Au<sub>18</sub>SG<sub>14</sub>; the disappearance of the peak at 2526 cm<sup>-1</sup> for Au<sub>18</sub>SG<sub>14</sub> indicated that the S-H bond was absent in it. This proved that sulphur is connected to the metal in Au<sub>18</sub>SG<sub>14</sub> in the thiolate form.





**Figure S7.** <sup>1</sup>H NMR spectra of GSH (red) and Au<sub>18</sub>SG<sub>14</sub> (black). Structure of glutathione linked to Au core is shown wherein the assignment is indicated.

# MS/MS of [Au<sub>18</sub>SG<sub>14</sub>]<sup>4-</sup>



**Figure S8.** MS/MS spectra of the  $[Au_{18}SG_{14}]^{4-}$  with increasing collision energy. Schematic diagram on the top of the figure showing the cleavage of bond and loss of water molecule in glutathione ligand. The red boxes show the peak corresponding to  $[Au_{17}SG_{12}SG_F]^{4-}$  formed due to loss of AuSG from  $[Au_{18}SG_{13}SG_F]^{4-}$ . The green boxes show the peak corresponding to  $[Au_{16}SG_{11}SG_F]^{4-}$  formed due to the loss of  $Au_2SG_2$  from  $[Au_{18}SG_{13}SG_F]^{4-}$  and the black boxes present the peak corresponding to  $Au_2SG_2$ .

### 10. Supporting information 10 MS/MS of [Au<sub>18</sub>SG<sub>14</sub>]<sup>5-</sup>



**Figure S9.** MS/MS spectra of the  $[Au_{18}SG_{14}]^{5-}$  with increasing collision energy. At lower collision energy, peak corresponding to  $[Au_{18}SG_{14}]^{5-}$  alone is present (bottom-most trace). With increasing collision energy, fragmentation of  $[Au_{18}SG_{14}]^{5-}$  happened which gave ions containing 4<sup>-</sup> charge at higher m/z. Corresponding peaks are marked on the figure.

# 11. Supporting information 11 MS/MS of [Au<sub>18</sub>SG<sub>14</sub>]<sup>6-</sup>



**Figure S10.** A) MS/MS spectra of  $[Au_{18}SG_{14}]^{6-}$  (m/z 1304.3) with increasing collision energies. Corresponding peaks are marked on the above figure. Fragmentation of  $[Au_{18}SG_{14}]^{6-}$  gave ions containing 4<sup>-</sup> charge. The ion,  $[Au_{16}SG_{12}]^{4-}$ , formed due to fragmentation, undergoes  $Au_2SG_2$  loss to form  $[Au_{14}SG_{10}]^{4-}$ . The parent ion region is expanded.

12. Supporting information 12 MS/MS of [Au<sub>18</sub>SG<sub>14</sub>]<sup>7-</sup>



**Figure S11.** A) MS/MS spectrum of [Au<sub>18</sub>SG<sub>14</sub>]<sup>7</sup>. At higher collision energy [Au<sub>18</sub>SG<sub>14</sub>]<sup>7</sup> undergoes fragmentation and produced ions containing 4<sup>-</sup> charge. All the ions formed in the above figure exhibited the 8e<sup>-</sup> rule. The parent ion is expanded.

Table 1. Calculated and experimental masses of the ions observed

Cluster formula	Calculated mass	Experimental mass
[Au <sub>18</sub> SG <sub>14</sub> ] <sup>4-</sup>	1956.5	1956.2
[Au <sub>18</sub> SG <sub>14</sub> ]⁵-	1565.0	1565.2
[Au <sub>18</sub> SG <sub>14</sub> ] <sup>6-</sup>	1304.0	1304.3
[Au <sub>18</sub> SG <sub>14</sub> ] <sup>7-</sup>	1117.5	1117.4
[Au <sub>18</sub> SG <sub>13</sub> (SG <sub>F</sub> )] <sup>4-</sup>	1924.6	1924.3
[Au <sub>18</sub> SG <sub>13</sub> (SG <sub>F</sub> )-H <sub>2</sub> O] <sup>4-</sup>	1920.0	1920.3
[Au <sub>18</sub> SG <sub>12</sub> (SG <sub>F</sub> ) <sub>2</sub> ] <sup>4-</sup>	1892.5	1891.9
[Au <sub>18</sub> SG <sub>12</sub> (SG <sub>F</sub> ) <sub>2</sub> -H <sub>2</sub> O] <sup>4-</sup>	1888.0	1887.6
[Au <sub>18</sub> SG <sub>11</sub> (SG <sub>F</sub> ) <sub>3</sub> ] <sup>4-</sup>	1860.5	1860.1
[Au <sub>18</sub> SG <sub>11</sub> (SG <sub>F</sub> ) <sub>3</sub> -H <sub>2</sub> O] <sup>4-</sup>	1856.0	1855.7
[Au <sub>18</sub> SG <sub>10</sub> (SG <sub>F</sub> ) <sub>4</sub> ] <sup>4-</sup>	1828.5	1828.3
[Au <sub>18</sub> SG <sub>10</sub> (SG <sub>F</sub> ) <sub>4</sub> -H <sub>2</sub> O] <sup>4-</sup>	1824.0	1824.1
[Au <sub>17</sub> SG <sub>12</sub> (SG <sub>F</sub> ) <sub>1</sub> ] <sup>4-</sup>	1799.3	1799.0
[Au <sub>16</sub> SG <sub>11</sub> (SG <sub>F</sub> ) <sub>1</sub> ] <sup>4-</sup>	1673.6	1674.1
[Au <sub>16</sub> SG <sub>12</sub> ] <sup>4-</sup>	1705.0	1704.9
[Au <sub>14</sub> SG <sub>10</sub> ] <sup>4-</sup>	1453.5	1453.6

 Table 2. Mass of the cluster calculated from ion masses

Formula of ions	Mass of ions	Mass of cluster
[Au <sub>18</sub> (SG) <sub>14</sub> -4H] <sup>4-</sup>	1956.2	(1956.2*4+4) = 7828.8
[Au <sub>18</sub> (SG) <sub>14</sub> -5H] <sup>5-</sup>	1565.2	(1565.2*5+5) = 7831.0
[Au <sub>18</sub> (SG) <sub>14</sub> -6H] <sup>6-</sup>	1304.3	(1304.3*6+6) = 7831.8
[Au <sub>18</sub> (SG) <sub>14</sub> -7H] <sup>7-</sup>	1117.4	(1117.4*7+7) = 7828.8





**Figure S12**. UV feature of different clusters synthesized by changing the ratio of glutathione and the reducing agent. The red line is almost matching with the previously reported Au<sub>25</sub> cluster. This suggests that optimization of synthetic conditions can get other specific clusters.