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69451 Weinheim, Germany

Luminescent Ag7 and Ag8 Clusters by Interfacial Synthesis**

T. Udaya Bhaskara Rao and T. Pradeep*

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Supporting information for the paper:

Supporting information 1

Polyacrylamide gel electrophoresis (PAGE)

A gel electrophoresis unit with 1 mm thick spacer (Bio-rad, Mini-protein Tetra cell) was used to process the PAGE. The experimental conditions for PAGE are similar to those reported in ref. 1. The total contents of the acrylamide monomers were 30% (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 crude mixture of the Ag@(H₂MSA) clusters, as a orange color powder, obtained in the interfacial reaction was dissolved in 5% (v/v) glycerol-water solution (1.0 mL) at a concentration of 20 mg/mL. The sample solution (1.0 mL) was loaded onto a 1 mm gel and eluted for 4 h at a constant voltage of 100 V to achieve separation shown in Figure 1B. The gel fractions containing the clusters were cut out, ground, and dipped in ice cold distilled water (2 mL) overnight. Subsequently, the solutions were centrifuged at 20,000 rpm for 30 min at -10 °C, followed by filtering with filter paper having 0.22 μ m pores to remove the gel lumps suspended in the solution. The samples were freeze dried to get orange-red and yellow powders. Cluster 2 was highly hygroscopic which made it difficult to make an accurate elemental analysis.

Phase transfer: 10 mg of cluster 1 and cluster 2 samples, dissolved in 2 mL of water were transferred to toluene by the addition of 5 mg TOABr under stirring.

Analytical procedures

A. Fourier-transform infrared (FT-IR) spectra

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

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 5 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 coalesce to yield nanoparticles on the grid.^{3,4}

D. Electrospray ionization (ESI) mass spectrometry

The electrospray ionization (ESI) mass spectrometric measurements were done in the negative mode using an MDX Sciex 3200 QTRAP MS/MS instrument, with a mass range of m/z 50-1700, in which the spray and the extraction are orthogonal to each other. The clusters, obtained after interfacial etching reaction and after PAGE separation, were dispersed in 1:1 water-methanol solution and used for mass spectrometric measurements. The samples were electrosprayed at a flow rate of 10 μ L/min and ion spray voltage of 5 kV; the respective declustering potentials were - 65 V and -50 V. The spectra were averaged for 100 scans.

E. MALDI-TOF MS

The mass spectrometric studies were conducted using a Voyager DE PRO Biospectrometry Workstation (Applied Biosystems) MALDI–TOF MS instrument. A pulsed nitrogen laser of 337 nm was used (maximum firing rate: 20 Hz, maximum pulse energy: 300 mJ) for desorption ionization and TOF was operated in the delayed extraction mode.

For laser desorption ionization (LDI) MS study, silver clusters were dispersed in water and directly spotted on the target plate. The sample was left to dry in air and inserted into the spectrometer.

For MALDI MS study, DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldidene] malononitrile) matrix in 50% ethanol (5mg/ml) and 0.1% trifluoroacetic acid (TFA) was mixed with silver cluster in water (2mg/1mL) in 2:1 ratio and soincated for one hour 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 negative mode and were averaged for 100 shots. Most of the measurements were done in the reflectron mode. LDI studies were carried out to understand the gas phase clustering behavior.

The clusters were assigned by comparing their experimental and calculated isotope patterns. The spectra were simulated using the Data explorer version 4.0.0.0 software provided by Applied Biosystems Inc. which uses the isotope database of IUPAC.

F. SEM and EDAX analyses

Scanning electron microscopic (SEM) and energy dispersive X-ray (EDAX) 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.

G. 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 mm². In view of the sensitivity of the sample, surface cleaning was not attempted. Al K_{α} 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 10⁻¹⁰ mbar range during spectrum collection. Binding energies of the core levels were calibrated with C 1s BE, set at 284.7 eV.

H. Lifetime measurement

The TCSPC set up was from Edinburgh Instruments (LifeSpec-ps) with PicoQuant laser diode excitation (409 nm). The emission decay collected at 630 nm was fitted by the 'SOFTWARE' supplied with the instrument.

I. X-ray powder diffraction

Powder XRD patterns of the samples were recorded using PANalytical X'pertPro diffractometer. The powder samples of parent silver nanoparticles and clusters were taken on a glass plate and the X-ray diffractogram was collected from an angle of 5 to 100 degrees.

Supporting information 2 TEM of the cluster



Figure S1.TEM image of cluster 1 aggregates (I) which upon continuous electron beam irradiation (II) coalesce to form larger nanoparticles (indicated by circles). The same regions of the grid are shown in both the images. The image on the right is after an electron beam irradiation of 10 min. The contrast from the clusters is poor unlike in the case of nanoparticles. Cluster aggregates forming nanoparticles under electron beam exposure have been reported earlier.^{2,3}On one particle, the Ag(111) lattice is seen (shown by an arrow).

Temperature dependent luminescence



Figure S2. (A) Luminescence spectra of cluster 1 in water collected at various temperatures (276 K to 300 K). (B) Photograph of cluster 1 sample in water, in white light. Other photographs are under UV as a function of temperature from 276 K to 300 K. Observable emission disappears at 300 K. The sides of the sample warm up to different extent under ambient air, explaining the red color at certain parts of the 291 K image. (C) Luminescence spectrum of cluster 1 in the solid state collected at room temperature (RT). (D) Image of solid form of the sample at the bottom of an RB flask under UV light (273 K), as the RB is kept slanting.

Supporting information 4 Elemental analysis of cluster 1

Element	Wt%
С	18.6
Н	1.5
S	12.4
0	24.7
Total	57.2

This corresponds to Ag_{8.13} H_2MSA $_{7.90}$ or Ag and MSA in 1:1 ratio.

EDAX of cluster 1 and cluster 2



Figure S3. (A) (a) EDAX spectrum of cluster 1 and (b) SEM image of the cluster 1 aggregate from which the EDAX spectrum was taken. EDAX maps using (c) Ag L_{α} , (d) Ag M_{α} , (e) S K_{α} , (f) O K_{α} and (g) C K_{α} are shown. Sn L_{α} In L_{α} and Si K_{α} are due to the indium tin oxide substrate used. Ag:S atomic ratio measured is 1:1, as expected. (B) (a) EDAX spectrum of cluster 2 and (b) SEM image of the cluster 2 aggregate from which the EDAX spectrum was taken. EDAX maps using (c) Ag L_{α} , (d) Ag M_{α} , (e) S K_{α} , (f) O K_{α} and (g) C K_{α} are shown. Sn L_{α} , In L_{α} and Si K_{α} are due to the indium tin oxide substrate used. Ag:S atomic ratio measured is 1:1, as expected.



Figure S4. A) Expanded view of ESI-MS (negative mode) in the m/z 1020-1170 region of the crude cluster mixture obtained after interfacial etching in 1:1 water-methanol mixture. The peaks are assigned. Sodium addition is shown. Sodium arises from NaBH₄ used in the synthesis of Ag@(H₂MSA). As H₂MSA is a dicarboxylic acid, it can ionize to give HMSA⁻ and MSA²⁻. Each carboxylate ion can pick-up sodium. All the ions observed are assigned. Note that mercaptosuccinic acid on the cluster is in the thiolate form. The cluster of peaks around m/z 1138 has contributions from Ag₅(H₂MSA)₄⁻ also. B) Specific regions of the mass spectrum of iii. The fragments, e, f and g are not seen in spectrum of cluster 1. Theoretical spectrum for each species, depicted with lines matches completely with the experiment. The prominent cluster peaks are marked.





Figure S5. (a) XPS survey spectrum of the nanoparticle (i), crude cluster (ii), $Ag_8(H_2MSA)_8$ (iii) and $Ag_7(H_2MSA)_7$ (iv). The spectra b, c, and d are the high-resolution XPS of, S 2p , O 1s, C 1s and core levels, respectively. The Ag:S atomic ratio is 1:1 in accordance with the expectation. The C:O ratio is not reliable in view of the surface contamination. The two O1s peaks are expected to be of the same intensity, in view of the structure of H_2MSA but the high binding energy peak is larger in intensity due to water contamination. C1s shows three features, as expected for H_2MSA and at the expected positions (C=O at 290.3, CH connected to S at 286.0 and CH₂ at 284.7 eV) but the intensities are distorted due to surface contamination. In view of the sensitive nature of the sample, surface cleaning was not attempted. The S2p of the two clusters are quite similar and exhibits a thiolate position of 161.7 eV.

Supporting information 8 IR spectra



Figure S6. FT-IR spectra of pure (a) H_2MSA , (b) as-prepared Ag@(H_2MSA), (c) Ag₈(H_2MSA)₈, (d) Ag₇(H_2MSA)₇ obtained after PAGE. The -SH stretching feature at 2572 cm⁻¹ in H_2MSA is marked by the dotted-circle in (a) which is absent in other spectra, in agreement with the XPS and mass spectra. H_2MSA features in the region of 2000-500 cm⁻¹ confirm the presence of H_2MSA in cluster 1 and cluster 2.

X-ray diffraction pattern



Figure S7. X-ray diffraction pattern of the silver parent nanoparticles of size 5-10 nm and crude clusters after interfacial etching.



Figure S8. Luminescence spectra of the crude cluster solution in water (supernatant) collected after adding different amounts of Al_2O_3 . Luminescence spectra are of the supernatant solutions corresponding to a, b, c, d, and e in Figure 3D. The data are at 273 K. As can be seen, luminescence of e resembles that of $Ag_7(H_2MSA)_7$ suggesting that $Ag_8(H_2MSA)_8$ has been completely adsorbed on Al_2O_3 .

Luminescence decay profiles of Ag₈(H₂MSA)₈ and Ag₇(H₂MSA)₈



Figure S9. Luminescence decay profile of $Ag_8(H_2MSA)_8$ and $Ag_7(H_2MSA)_7$. For $Ag_8(H_2MSA)_8$ the data were collected for a film which was spotted on a glass plate. A film was used due to low luminescence yield at room temperature. Luminescence decay profile of $Ag_7(H_2MSA)_7$ was collected in water. IRF refers to the instrument response function.



Figure S10. Luminescence spectra of $Ag_8(H_2MSA)_8$ in water and in toluene after phase transfer. Phase transfer increases Luminescence yield. Photographs of a solution of $Ag_8(H_2MSA)_8$ before (left) and after (right) phase transfer are shown in the inset.

Luminescence spectra of Ag₈(H₂MSA)₈ in water: methanol mixture



Figure S11. Luminescence spectra of cluster 1 collected in water and water:methanol mixture. Data are at the same concentration. Inset a) photograph of $Ag_8(H_2MSA)_8$ in water (left) and in water:methanol mixture (right). b) Corresponding photographs in UV light. The $Ag_8(H_2MSA)_8$ emits observable luminescence at room temperature. The data are at room temperature.

Luminescence of Ag₈(H₂MSA)₈ in different solvents



Figure S12. (A) Photographs of the $Ag_8(H_2MSA)_8$ in the solid state. Image a) is the dried powder of the gel with the cluster in white light; b) the same under UV light, c,d) images after the addition of acetone and methanol, respectively; e) after sprinkling water on the sample except on the portion marked by the circle and f) after the whole sample has been wetted with water.

References

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