Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information for paper

Controlled Synthesis and Characterization of the Elusive Thiolated Ag_{55} Cluster

Indranath Chakraborty,[a] Shrabani Mahata,[b] Anuradha Mitra,[c] Goutam De[c] and Thalappil Pradeep[a*]

[a]DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India.

[b]National Institute of Science and Technology, Berhampur, Odisha, India.

[c]CSIR-Central Glass and Ceramics Research Institute, Kolkata, India.

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Supporting information 1

Materials and methods:

1. Chemicals

Silver nitrate ($AgNO_3$, 99% Aldrich), sodium borohydride ($NaBH_4$, 99.9%, Aldrich); 4-(tert-butyl) benzyl mercaptan (BBSH, 98%, Aldrich); Methanol (Changshu Yangyuan Chemical, China, AR grade) and toluene (Ranken) were used in this synthesis. All the chemicals were commercially available and were used without further purification.

2. Synthesis of $Ag_{55}(BBS)_{31}$

The synthesis of Ag_{55} cluster protected by BBSH (4-(tert-butyl) benzyl mercaptan) involves the following processes. Initially, at room temperature 23 mg of $AgNO_3$ and 97.65 μL of 4-(tert-butyl) benzyl mercaptan (BBSH) was ground and mixed well in a clean mortar using a pestle. The color of the mixture changes to pale orange showing the formation of silver thiolate. To this mixture, 25 mg of solid $NaBH_4$ was added and the content was ground well. Then 5 mL of toluene was added to extract the cluster and it was centrifuged for 4 minutes at 4000 rpm. Finally, the supernatant was collected, which was black in color. This contains the crude cluster which was further purified using MeOH. Methanol was added drop wise on the extracted cluster resulting in the precipitation of Ag_{55} cluster. The supernatant was removed and the precipitate was redispersed in toluene which contains the purified cluster. It is important to note here that selective extraction in toluene is required to observe the clusters. The solid state method was originally reported for Ag_9 clusters.[1] The cluster is stable for an week under ambient conditions in solution form; however, the powder form is stable for a month. It decomposed to greenish yellow colored thiolates.

3. HPLC separation

HPLC separation was tried with the purified cluster, here we could see a single peak but the cluster was found to be degrading and it lost some of its characteristic features under the HPLC condition. We have tried the separation with solvents such as THF and toluene but the features were getting lost within the column. This is probably due to the high pressure and the interaction with the stationary phase which leads to degradation of the cluster. We present the best chromatogram (A) and corresponding UV/Vis spectrum (B) using a normal phase column (A8-ST5SIL120-98). Broad hump-like baseline indicates that the broken cluster is sticking inside the column.

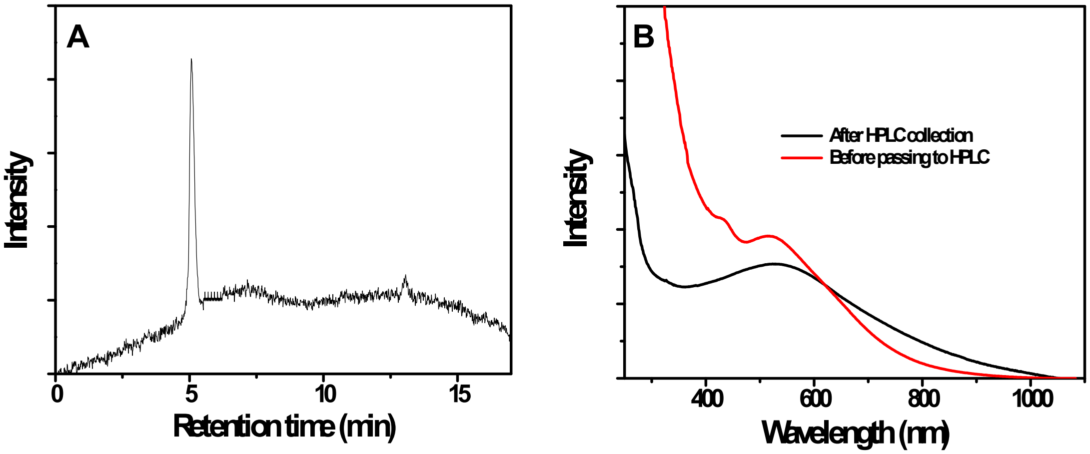

Fig. S1: (A) The chromatograph obtained using the purified cluster and (B) the optical absorption spectra (Jacobian corrected) due to the peak at 5 min retention time (black trace) and the cluster before passing through HPLC (red trace).

4. Synthesis of $Ag_{55}(SCH_2CH_2Ph)_{31}$

Similar to Ag_{152} synthesis,[2] the silver and thiol ratio was taken as 1:4. The cluster was washed with heptanes after ethanol wash followed by the extraction in toluene.

5. Instrumentation:

UV-Vis spectra were measured with a Perkin Elmer Lambda 25 instrument in the range of 200-1100 nm. The absorbance of raw spectral data are corrected [I(E)] using the following equation and plotted in terms of energy (1239.8/ Wavelength in nm = Energy (eV)).

$$I(E) = \frac{I(w)}{\partial E/\partial w} \propto I(w)w^2$$

HPLC separation was performed using a Shimadzu HPLC system equipped with a normal phase column (A8-ST5SIL120-98) and a UV/Vis detector. High resolution transmission electron microscopy of clusters was carried out with a JEOL 3010 instrument. The samples were drop casted on carbon-coated copper grids and allowed to dry under ambient conditions. Matrix-assisted desorption ionization mass spectrometry (MALDI MS) studies were conducted using a Voyager-DE PRO Biospectrometry Workstation from Applied Biosystems. DCTB was used as the matrix (at 1:100 ratio of sample to matrix). A pulsed nitrogen laser of 337 nm was used for the MALDI MS studies. Mass spectra were collected in positive ion mode and were averaged for 200 shots. Scanning electron microscopic (SEM) and energy dispersive X-ray (EDAX) analyses were performed with a FEI QUANTA-200 SEM. For measurements, samples were drop casted on an indium tin oxide (ITO)-coated glass and dried in vacuum. FT-IR spectra were measured with a Perkin Elmer Spectrum One instrument. TGA was measured using a TA instrument. A temperature range of 30^oC to 910^oC was used and the analysis was done in nitrogen atmosphere. 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 5 to 100 degrees in 2 theta using Cu Kα radiation. ESI MS measurements were done using a LTQ XL mass spectrometer from Thermo Scientific, San Jose, CA. Methanol-toluene mixture of solvent was used for this experiment. Small angle X-ray scattering (SAXS) experiments were performed on the sample solutions in transmission mode using Rigaku Smart Lab X-ray diffractometer operating at 9 kW (Cu- K_α radiation; λ=1.54059 Å). The sample solutions were placed in borosilicate capillary tubes (~1.5 mm internal diameter). NANO-Solver programme of Rigaku have been used to solve the SAXS profiles. The raw SAXS profiles obtained were corrected for background absorption and air scattering. Particle size distributions were obtained from simulated fittings of the corrected SAXS profiles using 'core-shell' model. The 'core-shell' model exhibited very good fittings and the results are in agreement with the size of the metal nanoclusters (NCs) from TEM studies. The capping agents have been considered as shells while the metal NCs as core. Densities of the capping agent (shell) and respective metal nanoclusters (core) are used to fit the SAXS profiles. The shell thickness and the size of the particles have been evaluated from the auto-fitted simulated profiles. The particles (i.e. metal NCs-capping agent) are highly monodisperse in nature.

Table 1: SAXS parameters

Sample no.	**Avg. size (nm)**	**Vol (%)**	**Normalised dispersion (σ)**	**Shell diameter**	**Avg metal Nanocluster Core size***	**R-factor**
Ag_{55}	1.796	99.84 (rest are bigger particles[#])	0.032	0.6957	1.1003	1.45

Supporting information 2

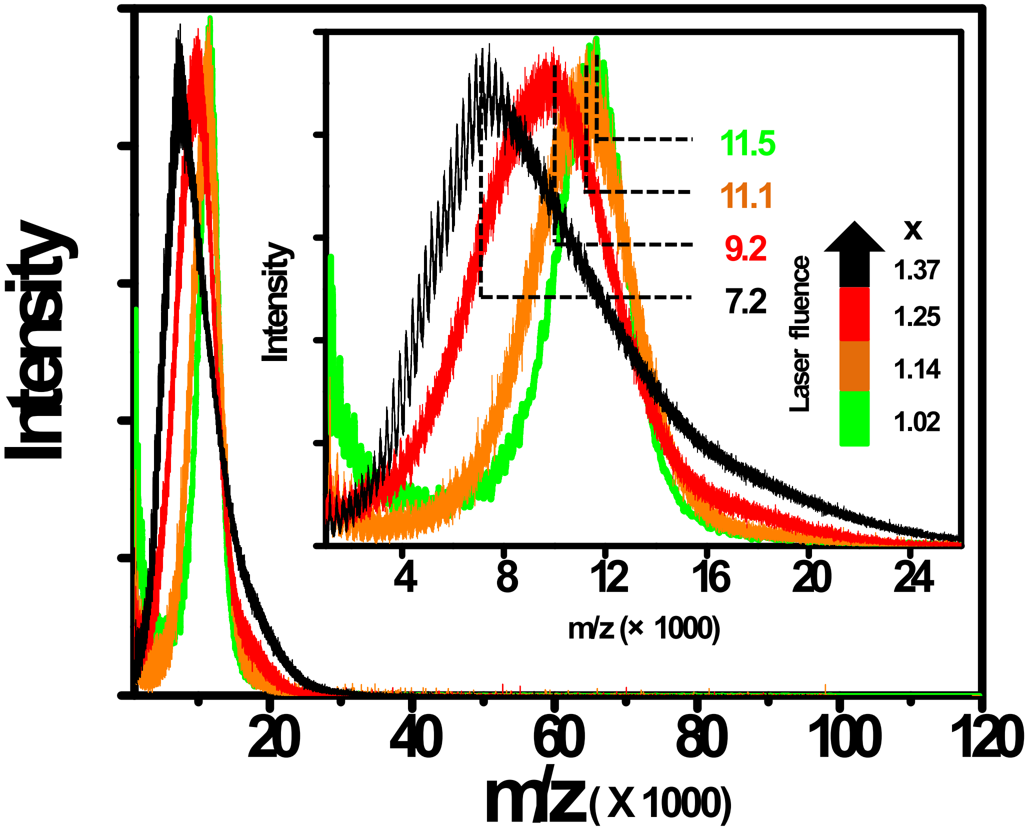

Fig. S2. *Laser fluence-dependent MALDI mass spectra of the purified* $Ag_{55}BBS_{31}$ *cluster. Inset is an expanded view. With increase in laser fluence (up to X = 1.37; X is defined as* f/f_{th} *where f is the laser fluence.), the peak position shifts to lower mass. Further increase in the laser fluence does not change the peak position.*

Supporting information 3

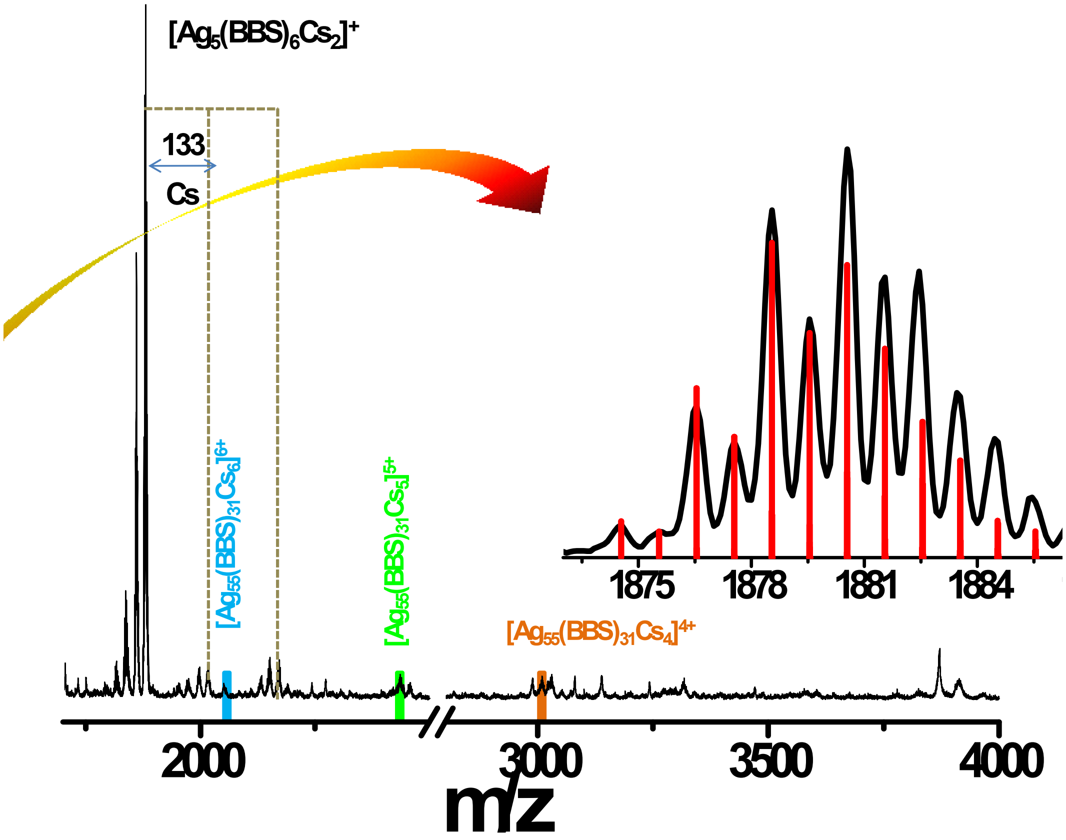

Fig. S3. *ESI mass spectrum of the purified* Ag_{55} *cluster [in toluene-methanol (1:1) mixture] in the positive ion mode. Insets; is the isotope distribution of a well-defined fragment [* $Ag_5(BBS)_6Cs_2$*]*$^+$.

Supporting information 4

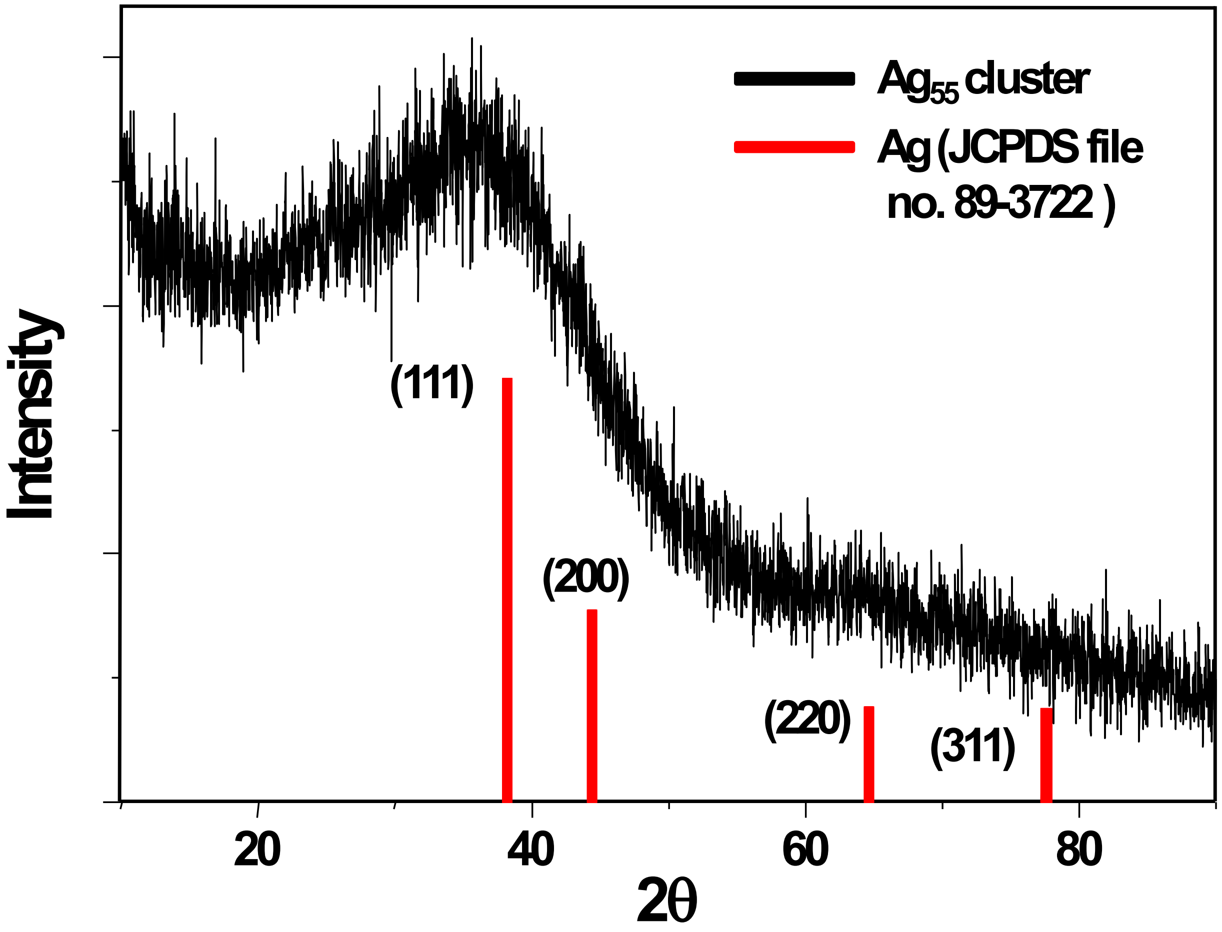

Fig. S4. *X-ray diffraction pattern of the as-synthesized Ag_{55} cluster. It shows a broad feature at 2θ~37^o and 44^o as expected.*

Supporting information 5

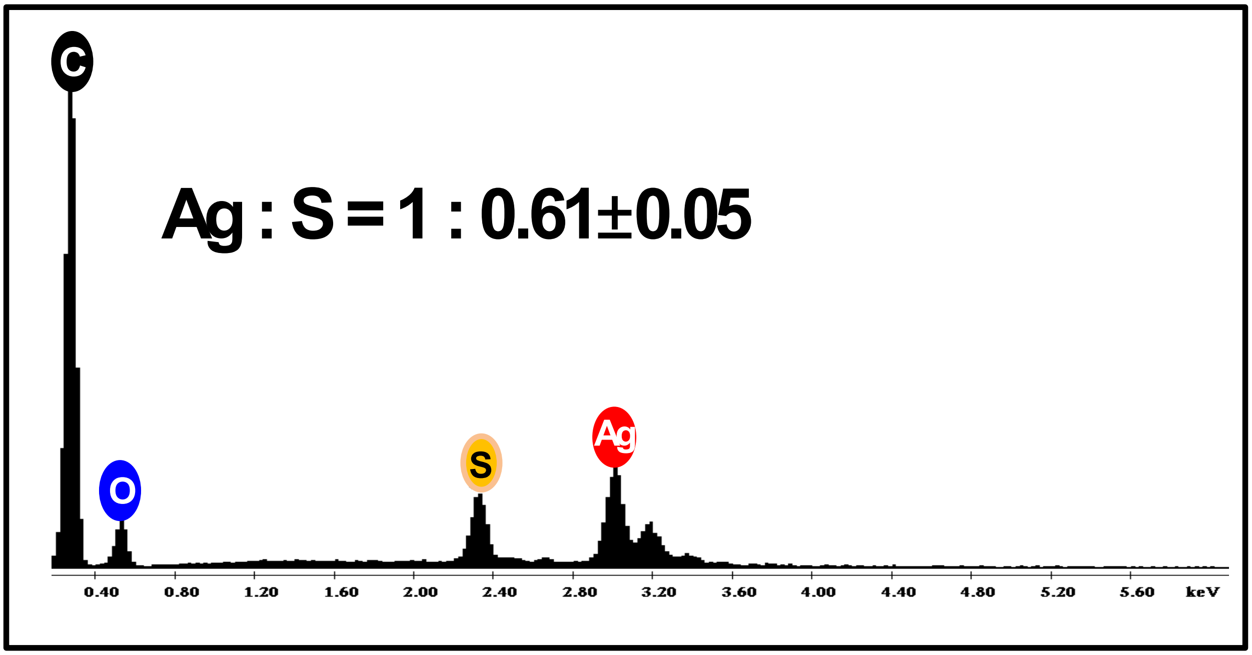

Fig. S5. *EDAX spectrum of the purified* Ag_{55} *cluster.*

Supporting information 6

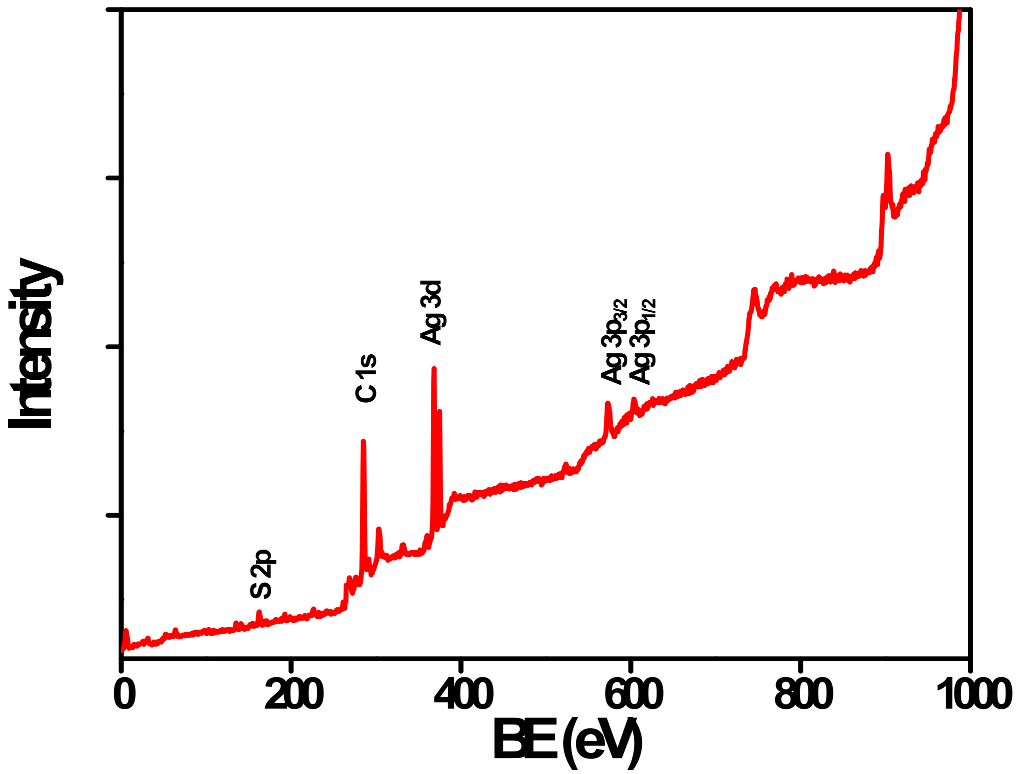

Fig. S6. *XPS survey spectrum of the* Ag_{55} *cluster. Peaks are labeled.*

1. Rao, T. U. B.; Nataraju, B.; Pradeep, T. *Journal of the American Chemical Society* **2010**, *132*, 16304.
2. I. Chakraborty, A. Govindarajan, J. Erusappan, A. Ghosh, T. Pradeep, B. Yoon, R. L. Whetten and U. Landman, *Nano Letters*, 2012, **12**, 5861-5866.