

Supporting information for the paper

Reversible Formation of Ag₄₄ from Selenolates

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Supporting Information

Materials and methods:

1. Chemicals

Silver trifluoroacetate (99%), sodium borohydride (NaBH_4 , 98%), benzeneselenol (97%), 4-fluorothiophenol (4-FTP, 98%), 3-fluorothiophenol (3-FTP), 2-phenylethanethiol (PETH, 98%) and thiophenol (98%) are from Aldrich and hydrogenperoxide (H_2O_2 , 30%), toluene, ethanol, and acetonitrile (AR grade) are from Rankem Chemicals, India. All the chemicals were commercially available and were used without further purification.

2. Synthesis of thiolated Ag_{44} cluster

The synthesis procedure is exactly same as selenolate protected Ag_{44} cluster. Here same concentrations of thiophenol, 4-FTP and 3-FTP have been used, instead of benzeneselenol.

3. Synthesis of Ag_{152} cluster

$\text{Ag}_{152}^{\text{I}}$ clusters have been synthesized using reported procedures.

4. Oxidation and reduction procedure

About 5 mL of the Ag_{44} cluster was taken in which 5 μL of 30% H_2O_2 was added and it was monitored with time with constant stirring. After the complete oxidation, 1.5 mg of NaBH_4 (s) was added and stirring was continued. After a few minutes a deep pink colored cluster was formed. Similar strategy has been followed for all the clusters.

5. Synthesis of thiolates and selenolates

For synthesizing *thiolate 2* and *selenolate 2*, same ratio of silver:ligand was taken as described for the cluster (solution A). Then the settled thiolate/selenolate was isolated from the solution which was used for characterization.

6. Instrumentation

UV-Vis spectra were measured with a Perkin Elmer Lambda 25 spectrometer in the range of 200-1100 nm. Matrix-assisted desorption ionization mass spectrometry (MALDI MS) studies were conducted using a Voyager-DE PRO Biospectrometry Workstation from Applied Biosystems. DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as 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 negative ion mode and were averaged for 200 shots. ESI MS measurements were done on LTQ XL mass spectrometer from Thermo Scientific, San Jose, CA. Methanol-acetonitrile mixture was used for selenolates and acetonitrile for Ag₄₄ cluster. Raman spectra and images were done with a WITec GmbH, Alpha-SNOM alpha 300 S confocal Raman microscope having a 532 nm laser as the excitation source.

Supporting Information 1

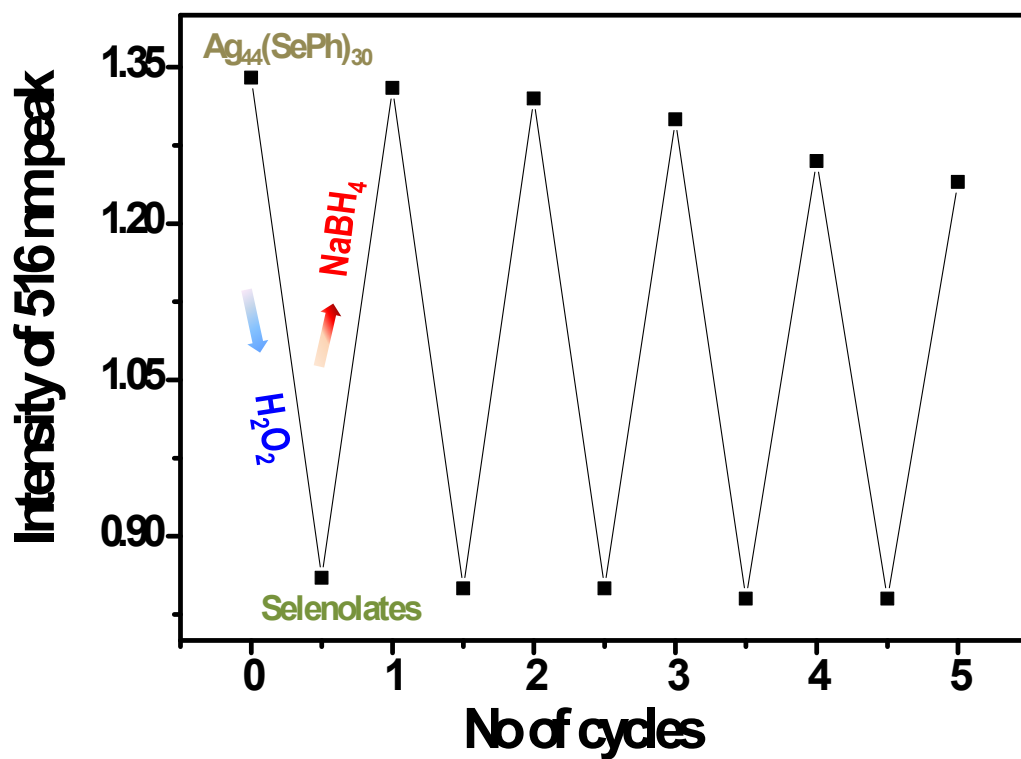


Fig. S1. Reversible cycles during the oxidation and reduction of $\text{Ag}_{44}(\text{SePh})_{30}$ cluster considering the 516 nm peak intensity of the cluster.

Supporting Information 2

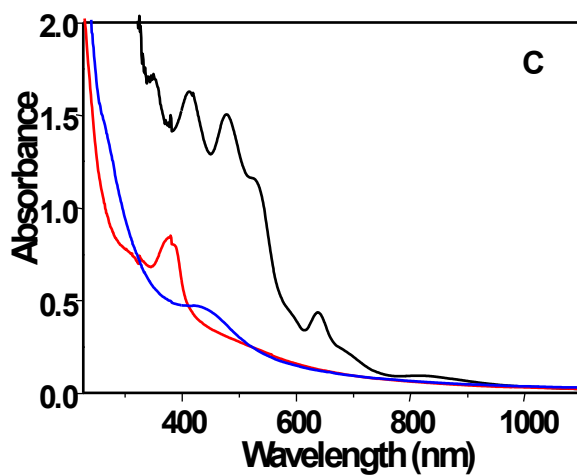
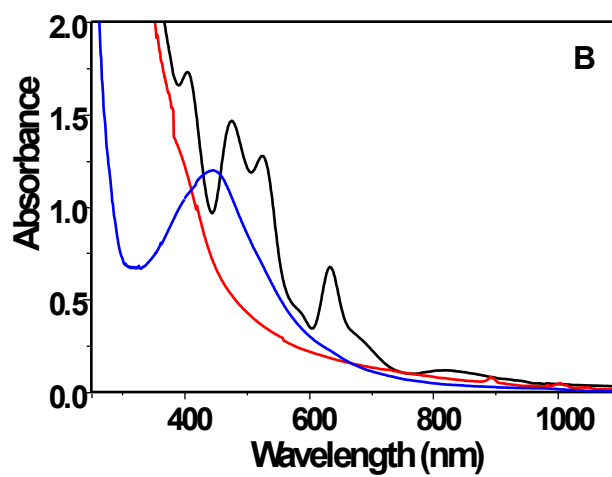
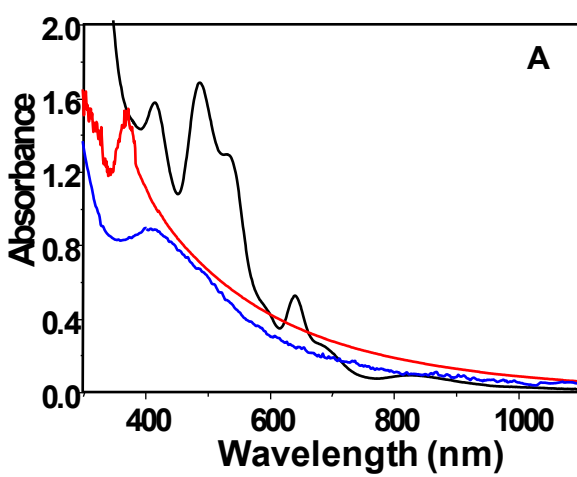


Fig. S2. Comparative UV/Vis spectra (black traces) of $\text{Ag}_{44}(\text{SPh})_{30}$ (A), $\text{Ag}_{44}(\text{4-FTP})_{30}$ (B) and $\text{Ag}_{44}(\text{3-FTP})_{30}$ (C). Red and blue traces show (in A, B and C) the UV/Vis spectra for H_2O_2 oxidation and NaBH_4 reduction of cluster and thiolates, respectively.

Supporting Information 3

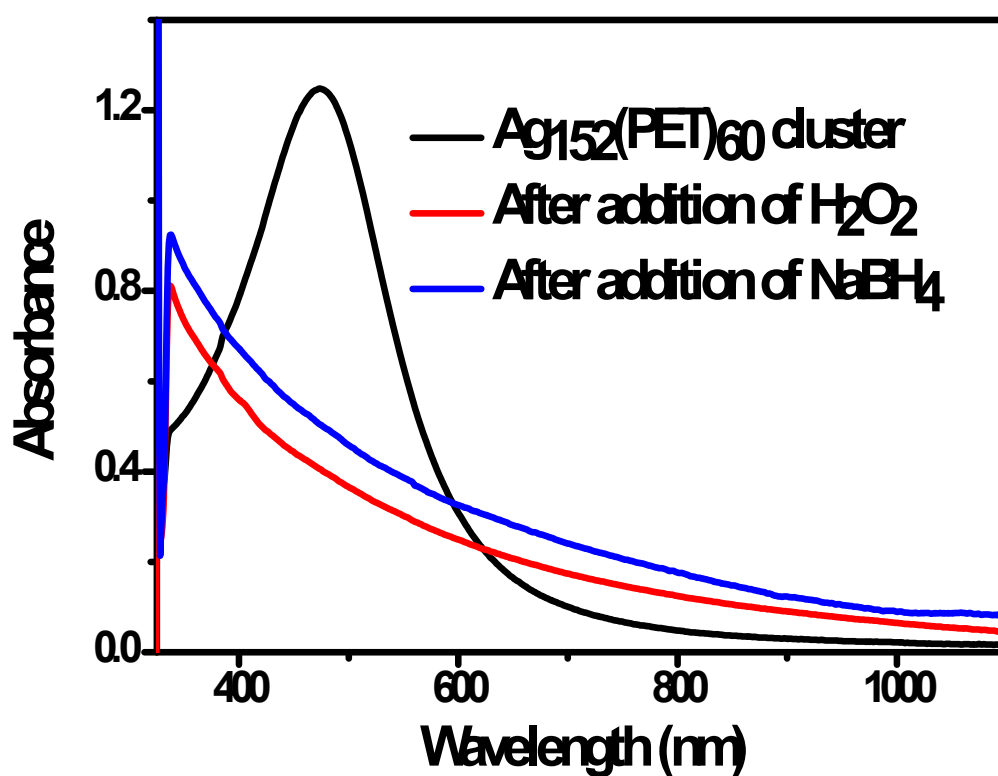


Fig. S3. UV/Vis spectra (black trace) of $\text{Ag}_{152}(\text{PET})_{60}$. Red and blue traces show the UV/Vis spectra for H_2O_2 oxidation and NaBH_4 reduction of cluster and thiolates, respectively.

Supporting Information 4

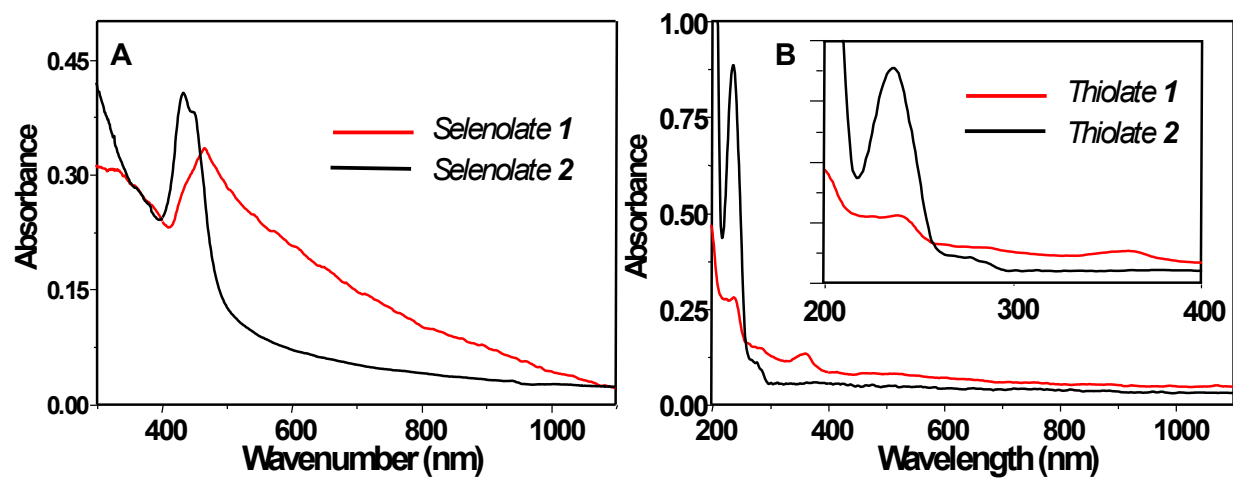


Fig. S4. Comparative UV/Vis spectra of degraded and as-synthesized selenolates (A) and thiolates (B). Inset shows an expanded view in the lower wavelength regions.

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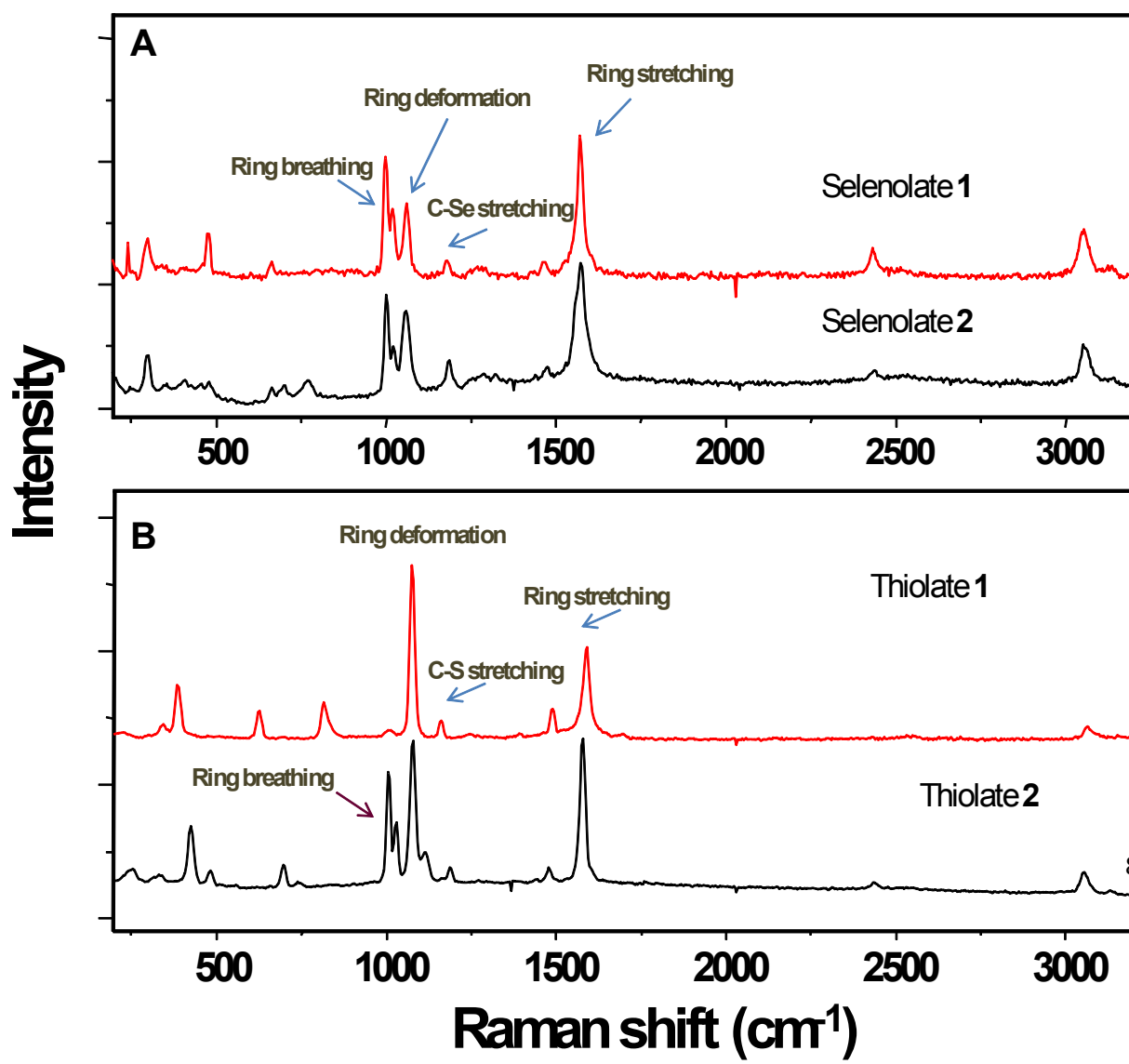


Fig. S5. Raman spectra of selenolates (A) and thiolates (B).

Supporting Information 6

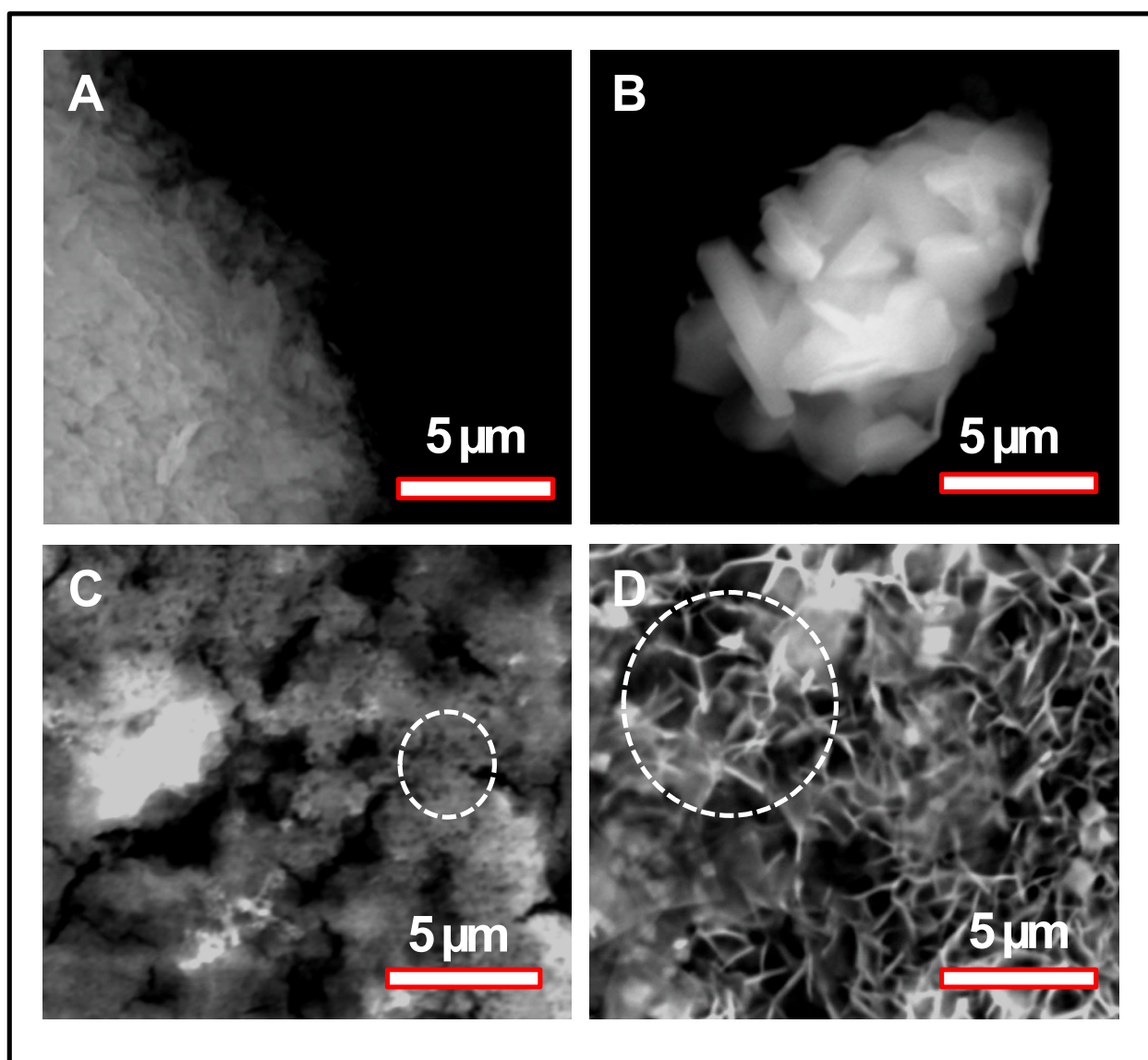


Fig. S6. SEM images of thiolates (as-synthesized (A) and degraded (B)) and selenolates (as-synthesized (C) and degraded (D)). Looking at the circled regions, some similarity can be noticed.

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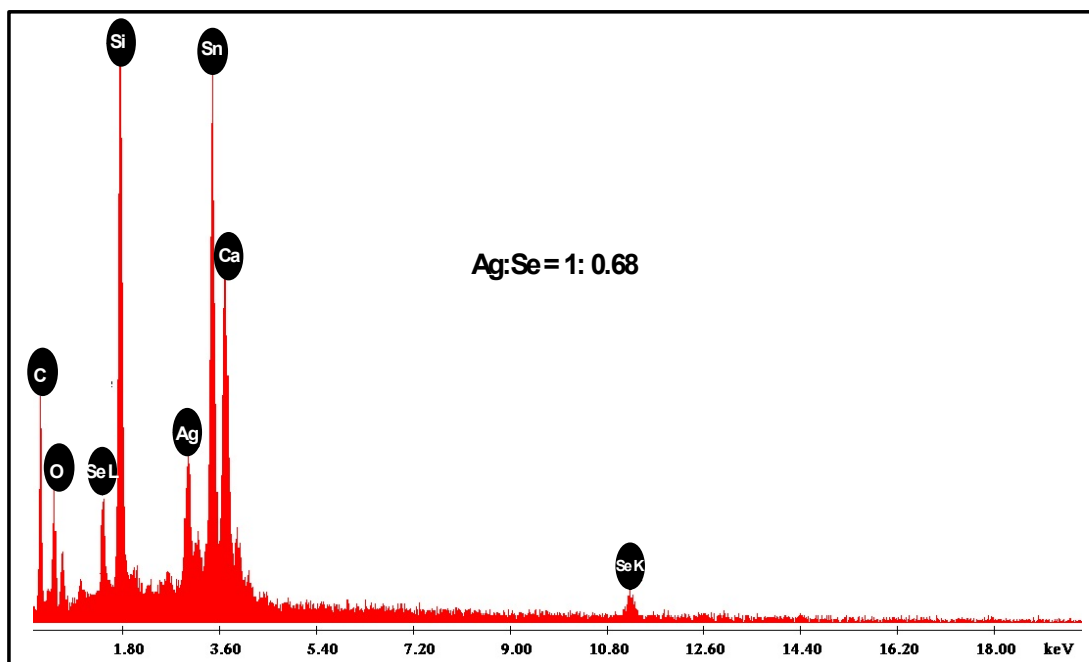


Fig. S7. SEM/EDAX spectrum of degraded selenolates.

Supporting Information 8

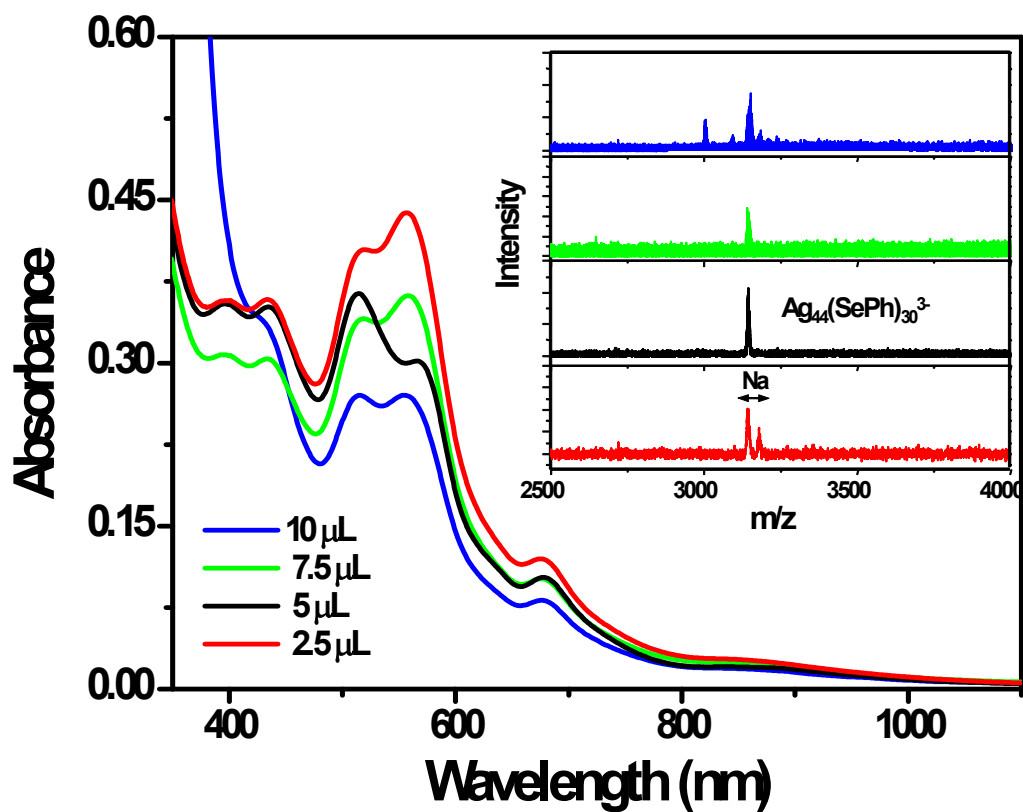


Fig. S8. UV/Vis spectra of $\text{Ag}_{44}(\text{SePh})_{30}$ cluster synthesized using different concentrations of benzeneselenol. The corresponding amounts of benzeneselenol are mentioned. Inset shows the corresponding ESI mass spectra.

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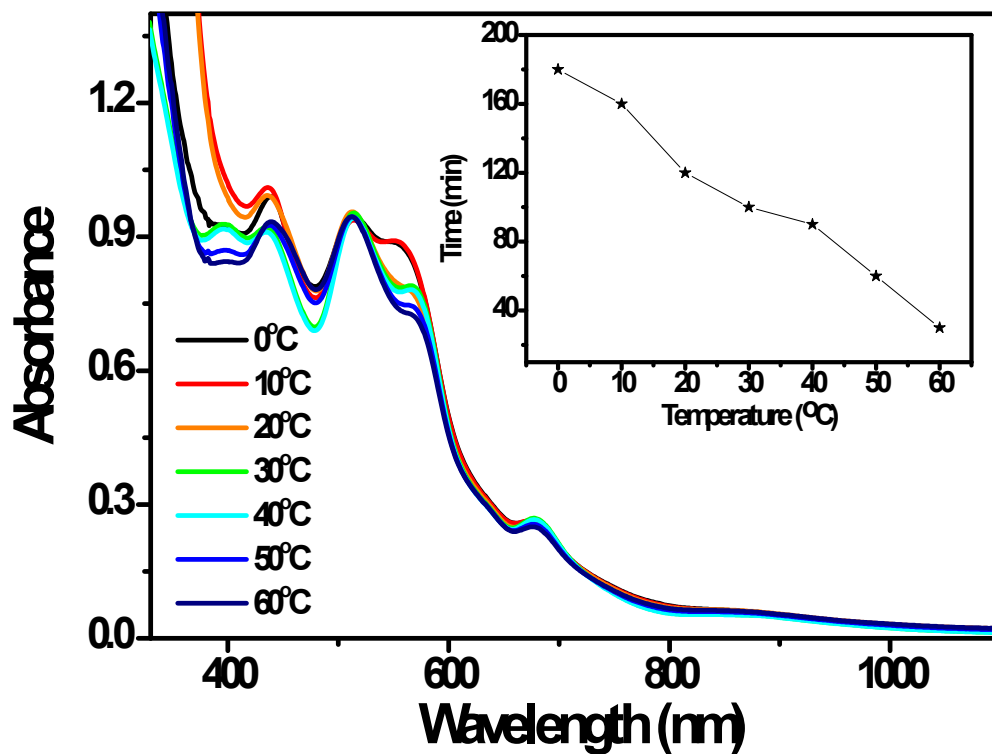


Fig S9. UV/Vis spectra of $\text{Ag}_{44}(\text{SePh})_{30}$ cluster synthesized at different temperatures. The spectra have been normalized. Inset shows the formation time for each case.

1. I. Chakraborty, A. Govindarajan, J. Erusappan, A. Ghosh, T. Pradeep, B. Yoon, R. L. Whetten and U. Landman, *Nano Lett.*, 2012, 12, 5861-5866.