

# Supporting Information

## **Ag<sub>44</sub>(SeR)<sub>30</sub>: A Hollow Cage Silver Cluster with Selenolate Protection**

*Indranath Chakraborty,<sup>1</sup> Wataru Kurashige,<sup>2</sup> Keita Kanehira,<sup>2</sup> Lars Gell,<sup>3</sup> Hannu Häkkinen,<sup>3</sup> Yuichi Negishi,<sup>2\*</sup> and Thalappil Pradeep<sup>1\*</sup>*

1 DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India; Fax: 91-44-2257 0545;

2 Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan.

3 Departments of Chemistry and Physics, Nanoscience Center, University of Jyväskylä, Box 35, FI-40014 Jyväskylä, Finland.

<b>Number</b>	<b>Description</b>	<b>Page number</b>
	Materials and methods (experimental and theoretical)	2
S1	Photographs during synthesis	4
S2	Optical absorption spectra for clusters <b>1</b> and <b>2</b> and comparison of solid and solution state synthesized samples	5
S3	Time dependent UV/Vis for solid state and solution state synthesized samples	5
S4	Extended mass spectra for 3- and 4- regions	6
S5	SEM/EDAX of cluster <b>1</b>	7
S6	<sup>1</sup> HNMR of cluster <b>1</b>	8
S7	XPS survey spectrum of cluster <b>1</b>	9
S8	Table of comparative bond lengths	9
S9	PDOS of cluster <b>1</b>	10

## 1. Chemicals

Silver nitrate (AgNO<sub>3</sub>, 97%), silver trifluoroacetate (97%), sodium borohydride (NaBH<sub>4</sub>, 97%), bezeneselenol (95%), ethanol (AR grade), acetone (AR grade), tetrahydrofuran (AR grade) and acetonitrile (AR grade) are from Wako Pure Chemical Industries. All the chemicals were commercially available and were used without further purification.

## 2. Instrumentation

The UV/Vis measurements were carried out using a double-beam spectrometer (Jasco V-630). 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 in eV].

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

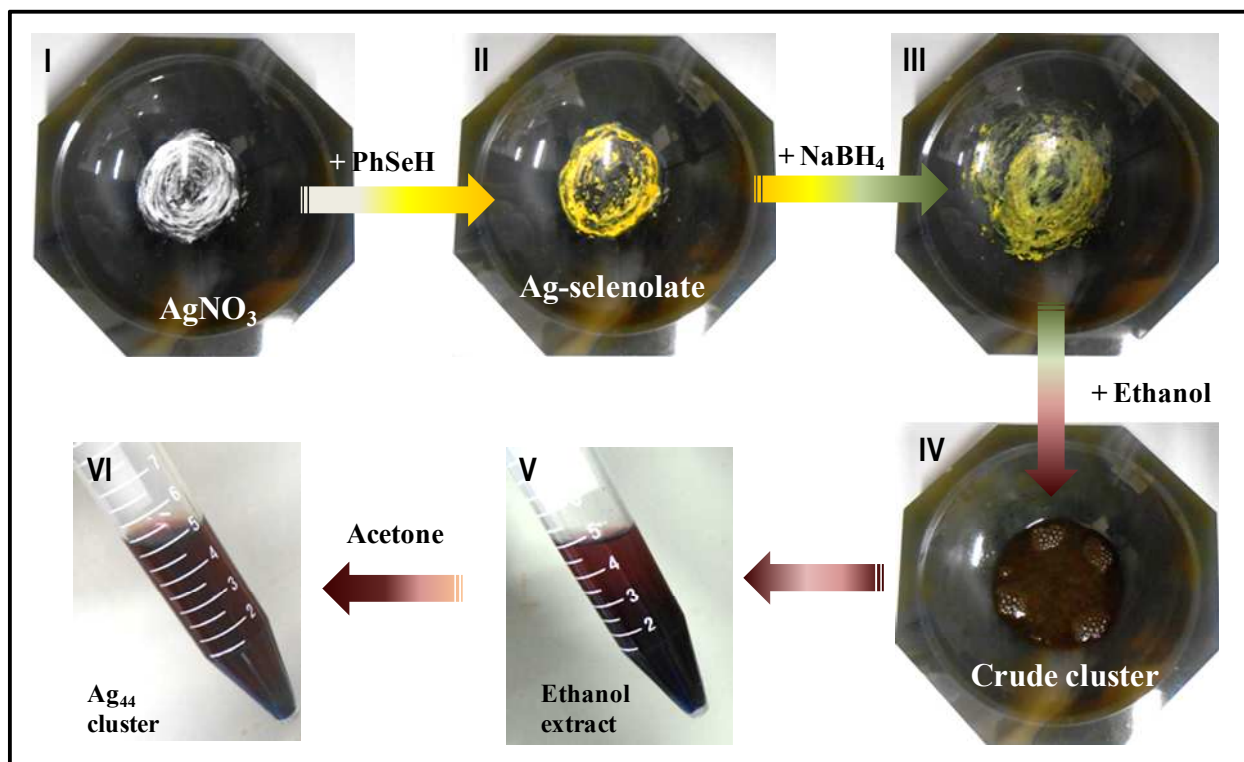
Electrospray ionization mass spectrometry (ESI MS) was performed using a Fourier-transform ion cyclotron resonance (ESI-FT-ICR) (Bruker, Solarix). 1 mg/mL solution of Ag<sub>44</sub> cluster (in acetone) was used for the measurements with a flow rate of 800 μL/h and the spectra were collected in negative mode. <sup>1</sup>HNMR spectra were measured using a 500 MHz Bruker Advance III spectrometer operating at 500.13 MHz and equipped with a 5 mm triple-resonance PFG probe. The sample was prepared in (CD<sub>3</sub>)<sub>2</sub>CO. Thermogravimetric analysis (TGA; Bruker, TGA2000SA) was performed using 4.7 mg of Ag<sub>44</sub> cluster at a heating rate of 10 °C/min in the temperature range of 25–500 °C. Transmission electron microscopy (TEM) images were recorded using an electron microscope (Hitachi, H-7650) operated at 100 kV, typically using a magnification of 100,000. The samples were drop casted on carbon-coated copper grids and allowed to dry under ambient conditions. 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. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an Omicron ESCA Probe spectrometer with polychromatic MgK $\alpha$  X-rays ( $h\nu=1253.6$  eV). The samples were spotted as drop-cast films on a sample stub. Constant analyzer energy of 20 eV was used for the measurements.

### **3. Computational methods**

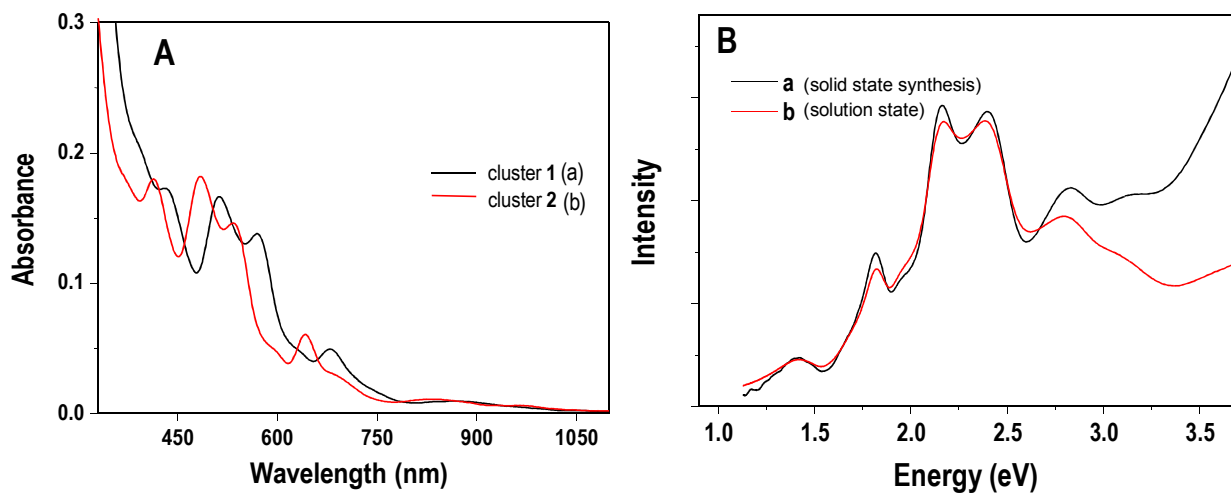
We used density functional theory (DFT) as implemented in the real-space code-package GPAW (Grid-based projector-augmented wave method).<sup>2</sup> Structure optimization was performed using full ligands as used in the experiment, the Perdew-Burke-Ernzerhof (PBE) functional,<sup>3</sup> 0.2 Å grid spacing and 0.05 eV/Å convergence criterion for the maximum forces acting on atoms in clusters. The GPAW set-ups for Ag include scalar-relativistic corrections. Superatom electron state symmetries were analyzed by projecting the wave functions to spherical harmonics with respect to the center of mass of the cluster as described in Ref. 4. Optical absorption spectra were calculated for the PBE relaxed structures using linear response time-dependent DFT and Casida method.<sup>5</sup>

## Supporting information 1.



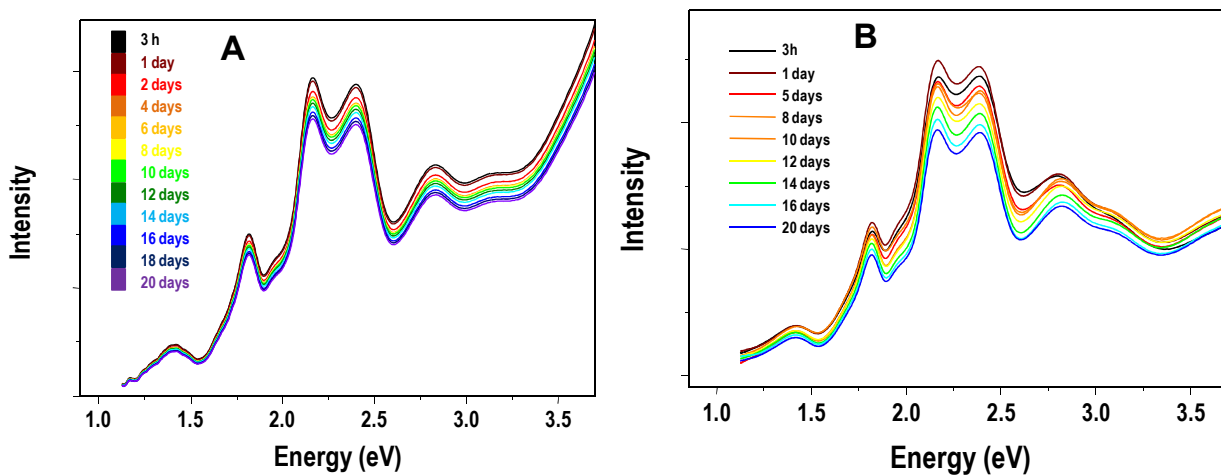
**Figure S1.** Photographs of various steps during the synthesis. I) ground silver nitrate in a mortar, II) addition of benzeneselenol (PhSeH) to I, III) addition of NaBH<sub>4</sub> to II, IV) ethanol addition to III, V) reaction mixture in a centrifuge tube for centrifugation, VI) residue after centrifugation, extracted in acetone. The solution, being concentrated, does not show the pink color clearly. The reduction started when NaBH<sub>4</sub> was added and the limited supply of humidity from laboratory atmosphere and moisture from ethanol controlled the growth. Up to step 3, reaction occurs in the solid state. Extraction and washing can also contribute to reduction but the process has started in step 3 itself which gets completed in step 4, after the addition of ethanol. However, upon keeping the system in humid air, reaction can be completed, but will take longer time. The product is also different.

## Supporting information 2.



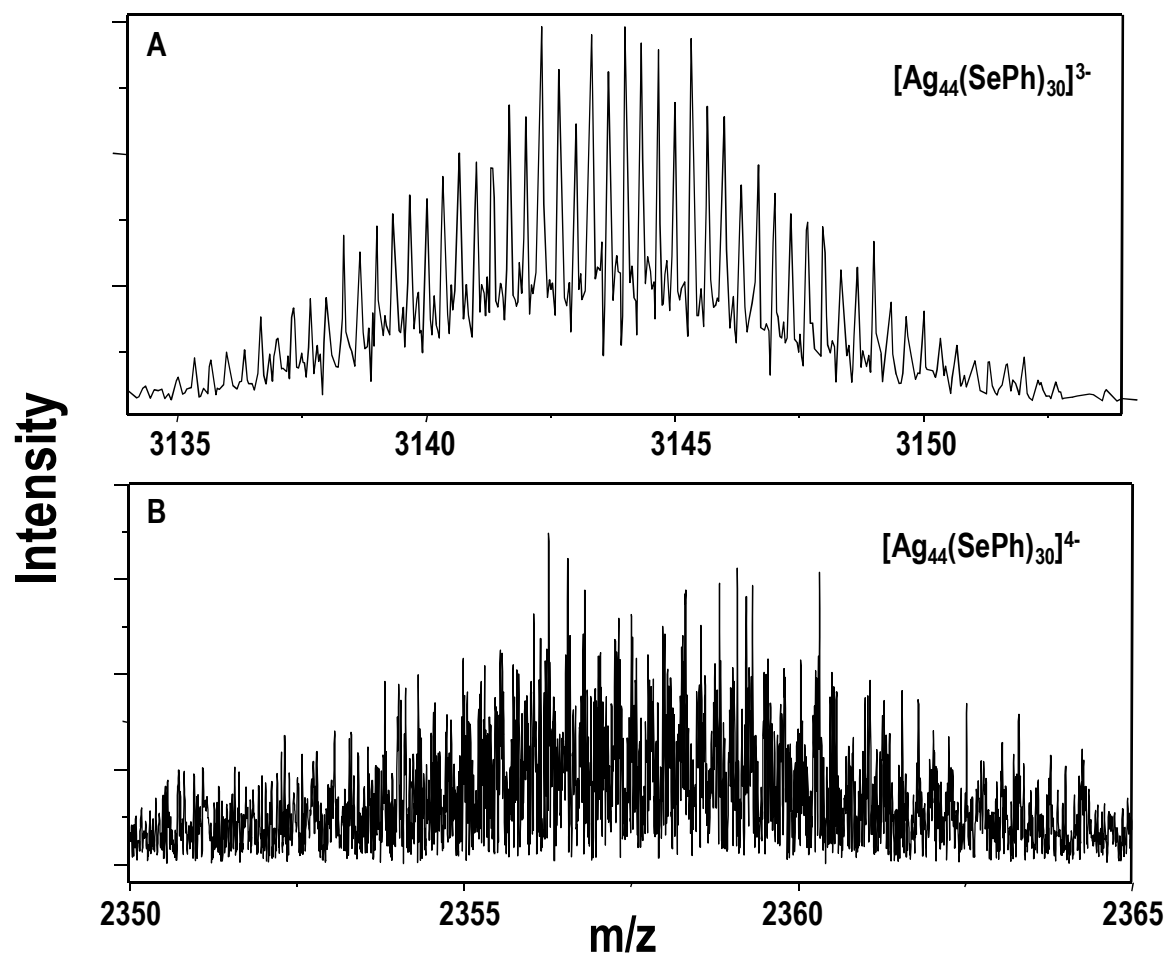
**Figure S2.** A: The optical absorption spectra for clusters 1 and 2 in acetone and THF, respectively. ‘B’ shows Comparative UV/Vis spectra of cluster 1 synthesized through solid (a) and solution state (b) routes. Difference, especially in the high energy region is due to the solvents used for measurements (solution phase – acetonitrile and solid state - acetone).

## Supporting information 3.



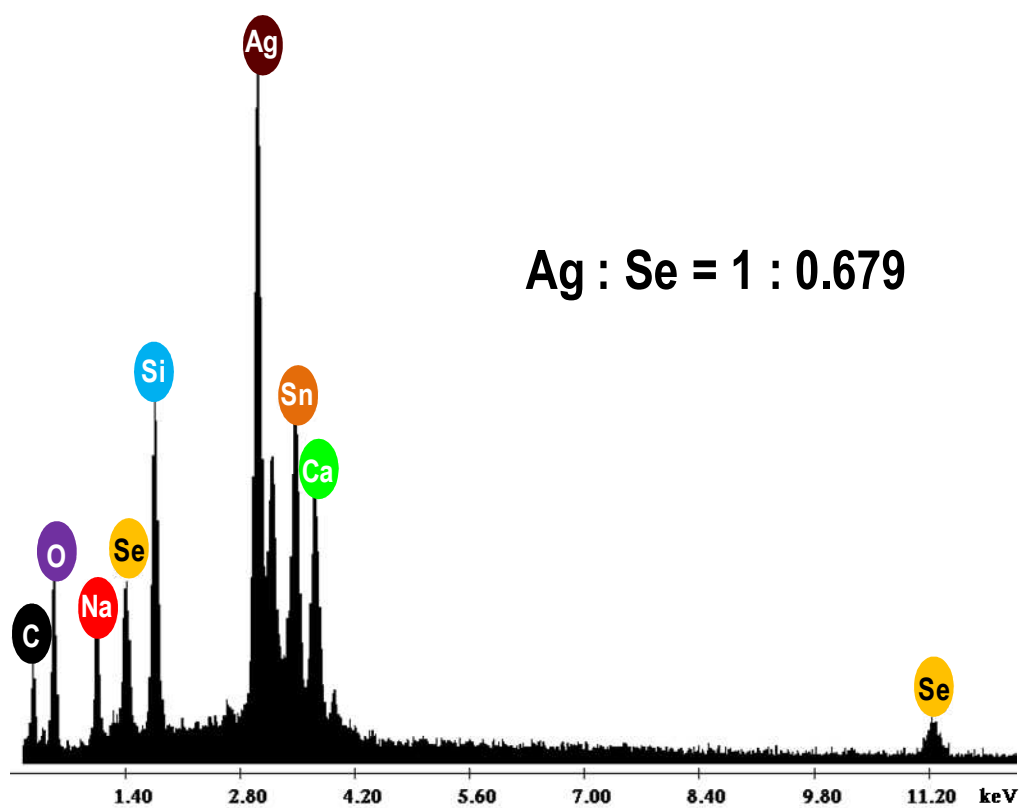
**Figure S3.** Time dependent UV/Vis spectra of cluster 1 synthesized through the solid and solution state routes (A and B, respectively).

Supporting information 4.



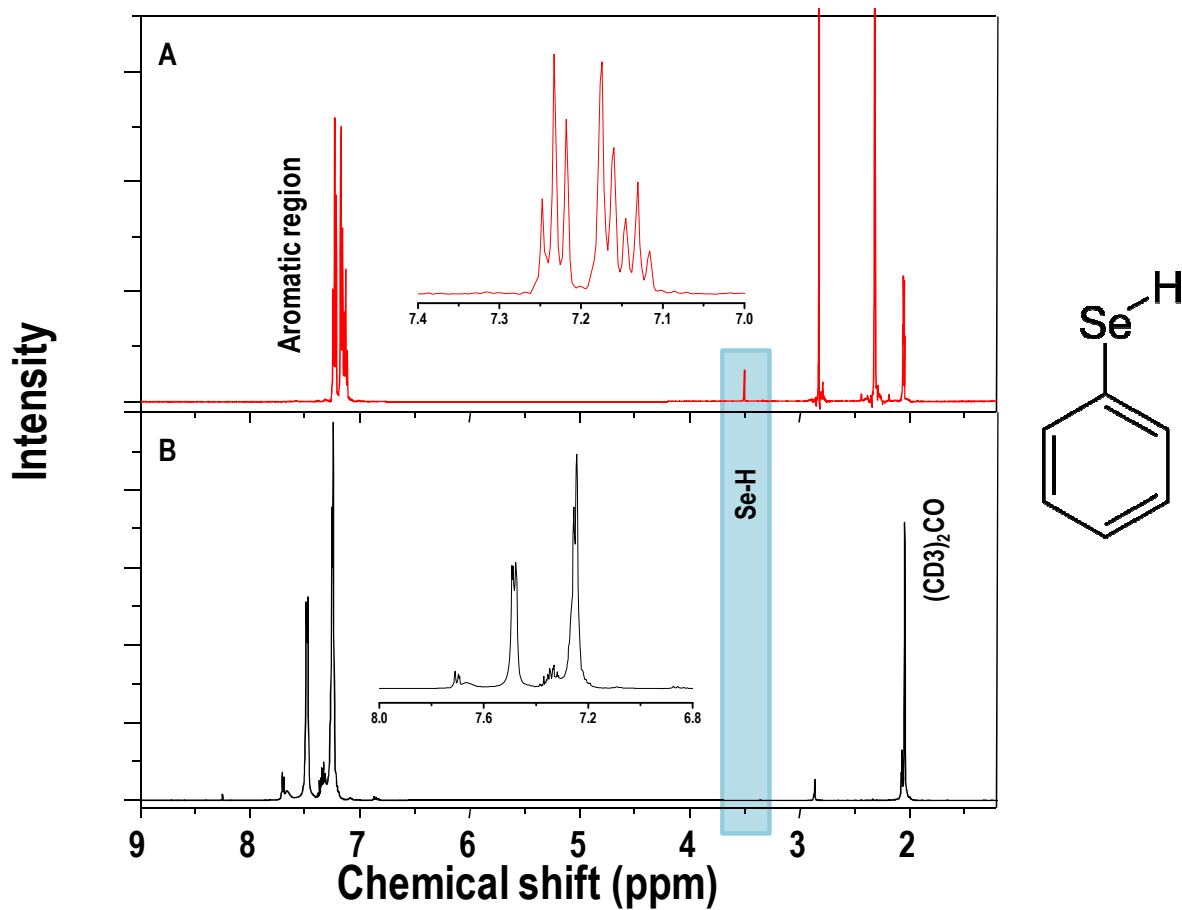
*Figure S4.* Expanded mass spectra in the 3- and 4- regions of cluster 1.

Supporting information 5.



*Figure S5.* SEM/EDAX spectrum of cluster **1** showing the expected elements. Ca, Sn, and Si are coming from the indium tin oxide plate used as the substrate for drop casting the sample.

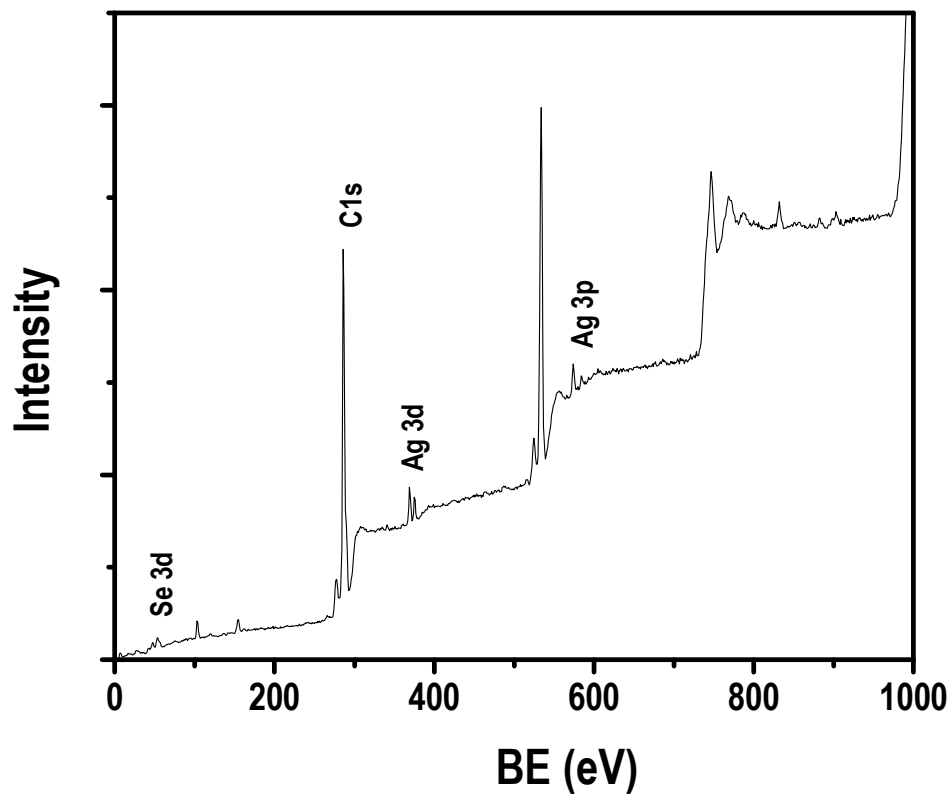
Supporting information 6.



**Figure S6.** <sup>1</sup>H NMR spectra of benzeneselenol (A) and cluster 1 (B). The sample was taken in (CD<sub>3</sub>)<sub>2</sub>CO.



### Supporting information 7.



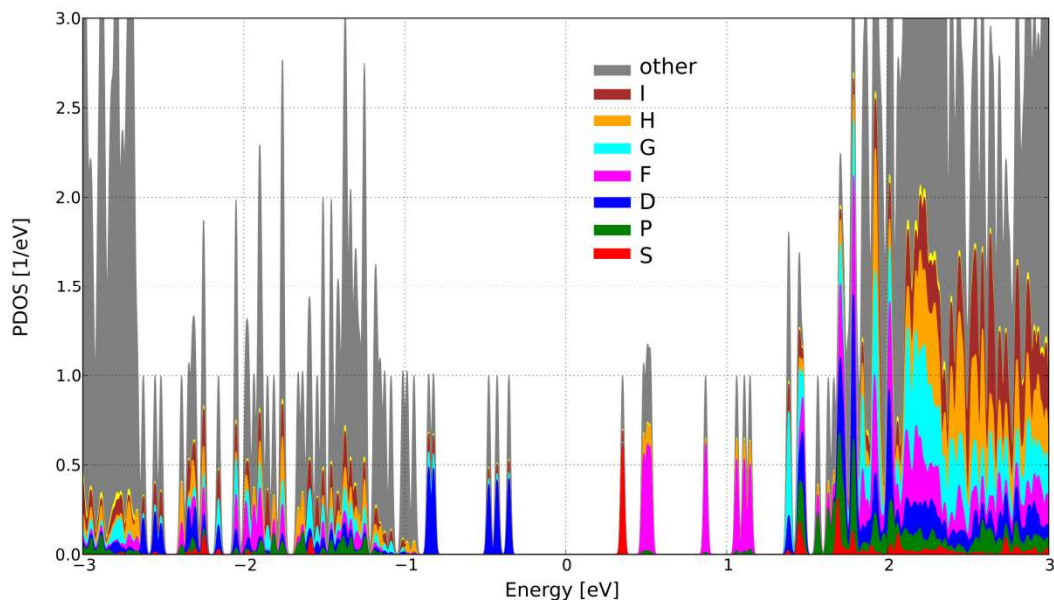
*Figure S7.* XPS survey spectrum of cluster 1.

### Supporting information 8.

	Ag <sub>12</sub>	Ag <sub>12</sub> → Ag <sub>20</sub>	Ag <sub>20</sub>	Ag - X (X = Se, S)
<sup>a</sup> Ag <sub>44</sub> (SePh) <sub>30</sub> <sup>4-</sup>	2.908	2.906	3.262	2.713
<sup>b</sup> Ag <sub>44</sub> (SPhF <sub>2</sub> ) <sub>30</sub> <sup>4-</sup>	2.881	2.879	3.231	2.595

**Table 1.** Selected bond lengths in the clusters (in Å).  $Ag_{12}$  denotes bond lengths in the first icosahedral shell,  $Ag_{12} \rightarrow Ag_{20}$  between the first and the second (dodecahedral) shell, and  $Ag_{20}$  within the second shell. <sup>a</sup> This work, <sup>b</sup> from ref. 38 in the main text.

### Supporting information 9.



**Figure S9.** Analysis of the electronic structure of  $[Ag_{44}(SePh)_{30}]^{4-}$  as shown by a projected density of electron states (PDOS) vs. state energy in eV. The colors denote weights of projections of individual Kohn-Sham electronic states onto various spherical harmonics centered at the center-of-mass of the cluster. The projection is done up to the angular momentum of  $L = 6$  (I symmetry) as described in detail in ref. 38. (C). The gray area in the peaks shows the weights of angular momenta  $L > 6$ . The HOMO-LUMO gap is centered around zero energy. The states around the HOMO- LUMO gap, in the region -1 eV to +1.5 eV, can be described by a single dominant angular momentum character that changes from D-symmetry (blue) to S-symmetry (red) over the HOMO-LUMO gap. Immediately after the S-state, there is a sequence of 7 F – symmetric states. Thus in this energy region, the superatom state sequence  $1D^{10} 2S^2 2F^{14}$  is seen. The occupied states in the region -2.6 eV to -1 eV are dominantly ligand states, and the silver 4d states span energies  $< -2.6$  eV.

## References

- (1) Bakr, O. M. et al., *Angew. Chem.* **2009**, *121*, 6035.
- (2) Enkovaara, J. et al., *J. Phys. Condens. Matter* **2010**, *22*, 253202.
- (3) Perdew, J.P.; Burke. K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (4) Walter, M. et al., *PNAS* **2008**, *105*, 9157.
- (5) Walter, M. et al., *J. Chem. Phys.* **2008**, *128*, 244101.