Supporting information for

Reversible Size Control of Silver Nanoclusters *via* Ligand-exchange

Megalamane Siddaramappa Bootharaju,[†] Victor M. Burlakov,[‡] Tabot M. D. Besong,[†] Chakra P. Joshi,[†] Lina G. AbdulHalim,[†] David Black,[#] Robert Whetten,[#] Alain Goriely,[‡] and Osman M. Bakr*[†]

[†]Division of Physical Sciences and Engineering, Solar and Photovoltaics Engineering Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia, [‡]Mathematical Institute, University of Oxford, Woodstock Road, Oxford, OX2 6GG, UK, [#]Department of Physics and Astronomy, The University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249, United States

Characterization of $Ag_{35}(SG)_{18}$ nanoclusters

$Ag_{35}(SG)_{18}$ nanoclusters were synthesized according to the literature.[1] The purified cluster exhibited a characteristic UV-vis absorption band at 490 nm with an emission maximum at 650 nm when excited at 420 and 500 nm (Figure S1A, see below). Polyacrylamide gel electrophoresis (PAGE) analysis confirmed that the cluster formed is nearly monodisperse (inset of Figure S1A). The assignment of $[Ag_{35}(SG)_{18}\text{-}5H]^{5-}$ and its fragment, $[Ag_{34}(SG)_{18}\text{-}5H]^{5-}$ is confirmed by comparing experimental and simulated mass spectra (Figure 1 in manuscript and Figure S1B in SI). Matrix assisted laser desorption ionization mass spectrometry (MALDI MS) has a sharp single peak at m/z ~6.7kDa noticed at threshold laser power (40%) (Figure S1C). The discrepancy of 2.5kDa mass in the observed (~6.7kDa) and expected (9.28kDa) mass for $Ag_{35}(SG)_{18}$ is attributed to the fragmentation of HSG ligands under MALDI conditions which is not surprising.[2] The observed mass peak at ~6.7kDa can reasonably be assigned to ~$Ag_{35}(SG_F)_{18}$ (here SG_F: fragmented SG with a molecular weight of 177Da). Recently, Jin and coworkers[3] also observed a loss of ~1.2kDa in the fragmentation of $Au_{38}(SG)_{24}$. The magnitude of fragmentation is expected to be higher in the case of silver clusters compared to gold ones as the former are often fragile. At a high laser power of 90%, the parent peak at m/z ~6.7kDa is shifted to ~4.8kDa (inset of Figure S1C). This mass nearly matches with the molecular weight of ~$Ag_{35}S_{15}(SG_F)_3$. This indicates that the loss of HSG on cluster is not complete.[2] Analytical ultracentrifugation (AUC) was used to obtain the size distribution of particles. AUC data (Figure S1D) confirm the presence of nearly one component along with other minor components.

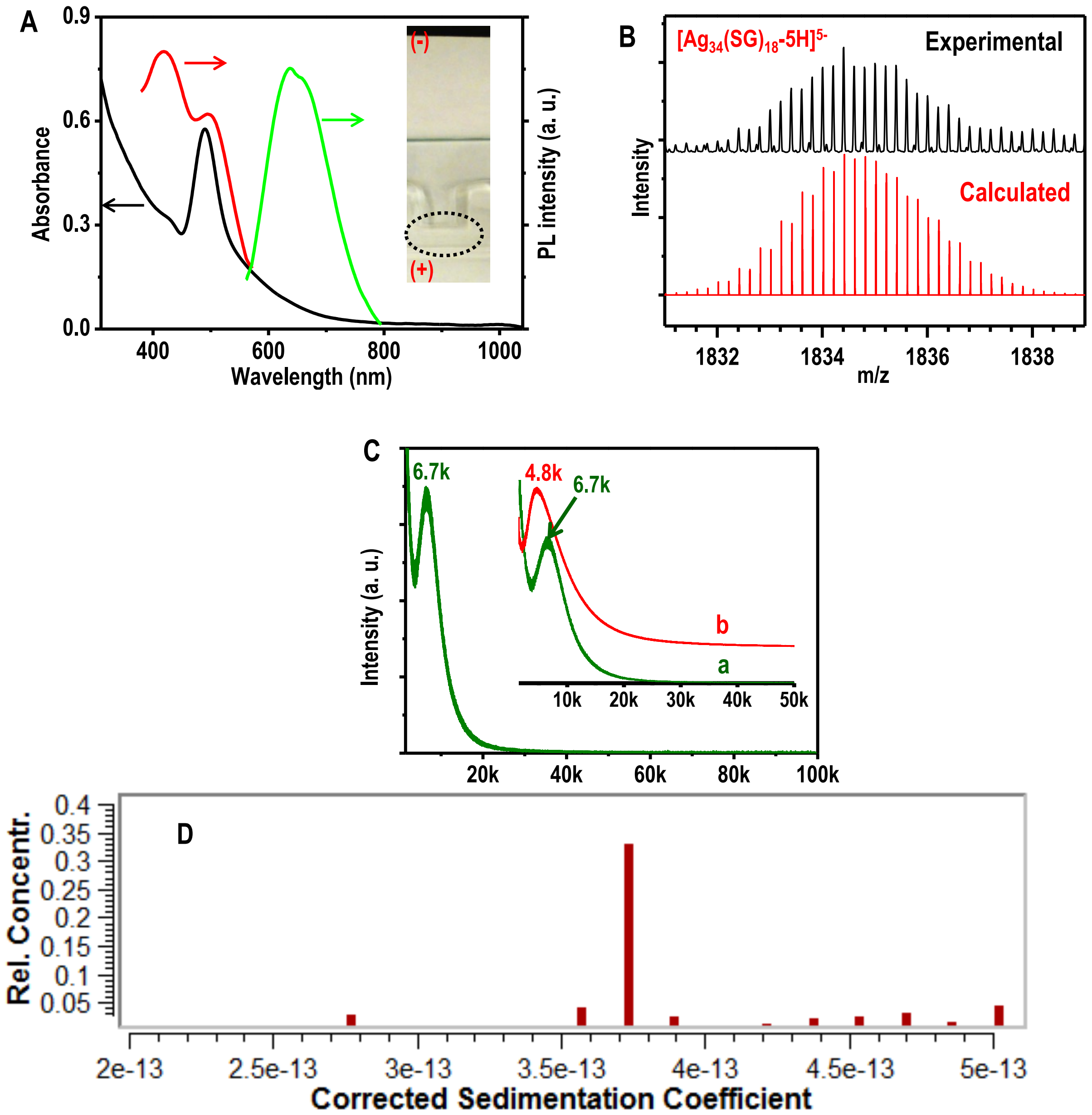


Figure S1. (A) UV-vis absorption and photoluminescence (PL) spectra of $Ag_{35}(SG)_{18}$ nanoclusters. Inset is a photograph of the PAGE of the same sample (marked band is for $Ag_{35}(SG)_{18}$). (B) Comparison of calculated and experimental mass spectra for $[Ag_{34}(SG)_{18}\text{-}5H]^{5-}$ shows that they match well. (C) MALDI MS of $Ag_{35}(SG)_{18}$ cluster in linear positive mode showing a single peak at ~6.7kDa. Inset is the comparison of laser intensity-dependent MALDI MS indicating a loss of m/z ~1.9kDa due to laser induced dissociation. Traces 'a' and 'b' correspond to low (40%) and high (90%) laser powers, respectively. (D) 2-Dimensional Spectrum Analysis (2DSA) AUC plot of $Ag_{35}(SG)_{18}$ showing a predominant component at ~3.7S.

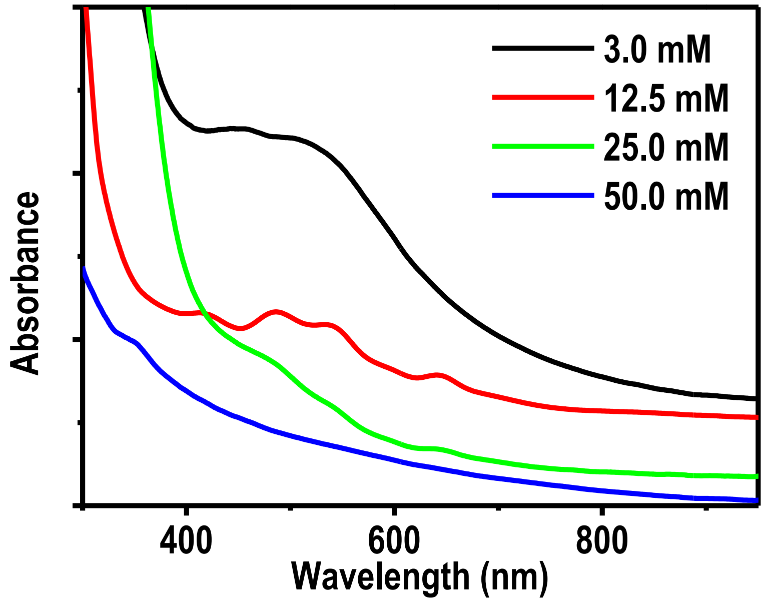
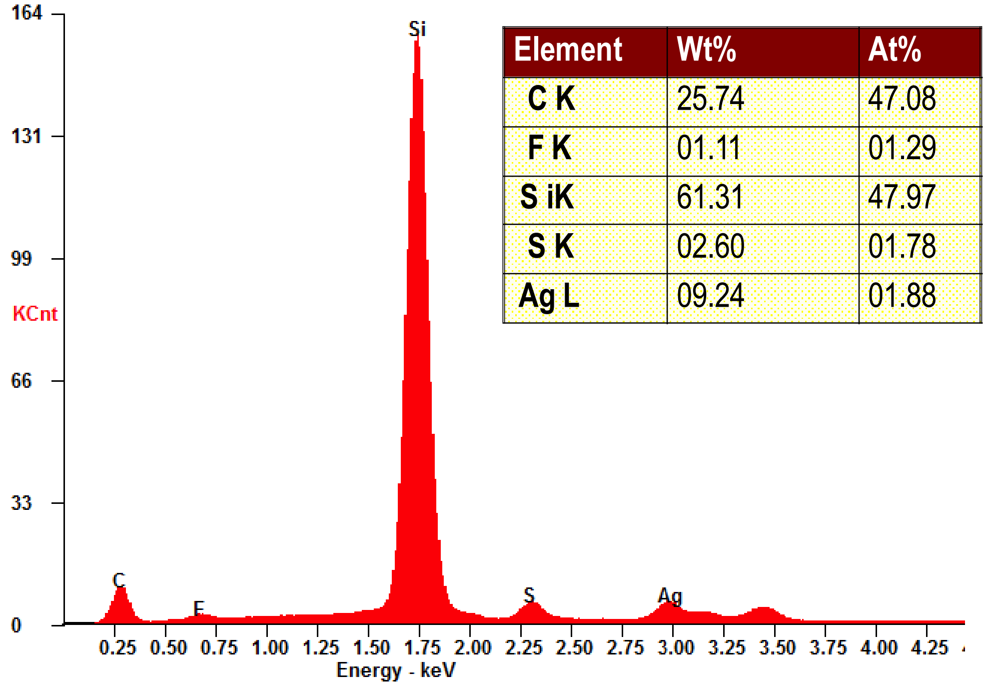


Figure S2. UV-vis absorption spectra of 4-FTP-exchanged products of $Ag_{35}(SG)_{18}$ obtained using different 4-FTP concentrations. The products were stable when 12.5 mM 4-FTP was used whereas unstable at low and high thiol concentrations.



Element	Wt%	At%
C K	25.74	47.08
F K	01.11	01.29
S iK	61.31	47.97
S K	02.60	01.78
Ag L	09.24	01.88

Figure S3. SEM EDAX spectrum of the 4-FTP-exchanged product of $Ag_{35}(SG)_{18}$. Inset is the table of elements in their weight and atomic percentages. Spectrum confirms the presence of Ag, S and F; and the absence of elements, N and O from HSG confirms the complete ligand-exchange. Spectrum was collected after spotting the sample on Si wafer.

Table 1. Elemental analysis of $Ag_{35}(SG)_{18}$ and its 4-FTP-exchanged product. N from HSG is almost absent after exchange with 4-FTP which confirms the complete protection of cluster by 4-FTP.

Nanocluster	$Ag_{35}(SG)_{18}$	$Ag_{44}(4\text{-FTP})_{30}$
N (wt%)	7.567	0.082
C (wt%)	22.818	56.181
H (wt%)	3.313	4.278

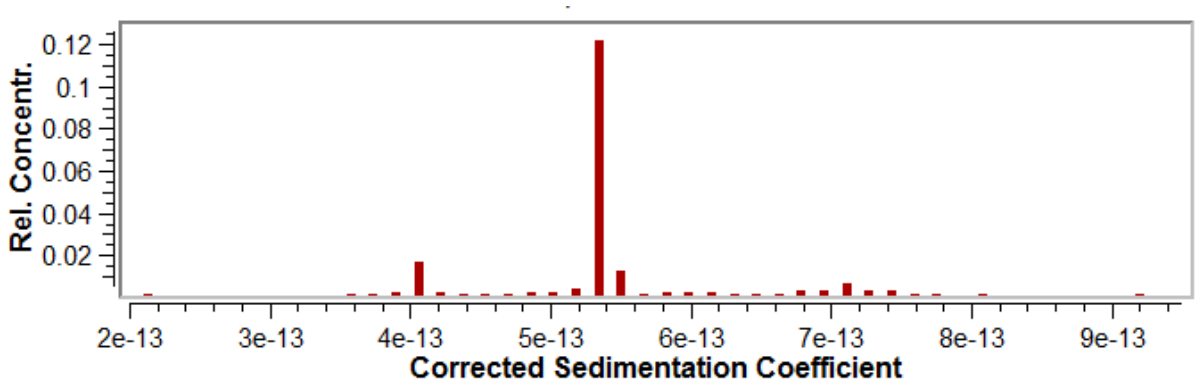


Figure S4. 2-Dimensional Spectrum Analysis (2DSA) AUC plot of 4-FTP-exchanged $Ag_{35}(SG)_{18}$ showing a narrow size distribution with a principal component at ~5.4S.

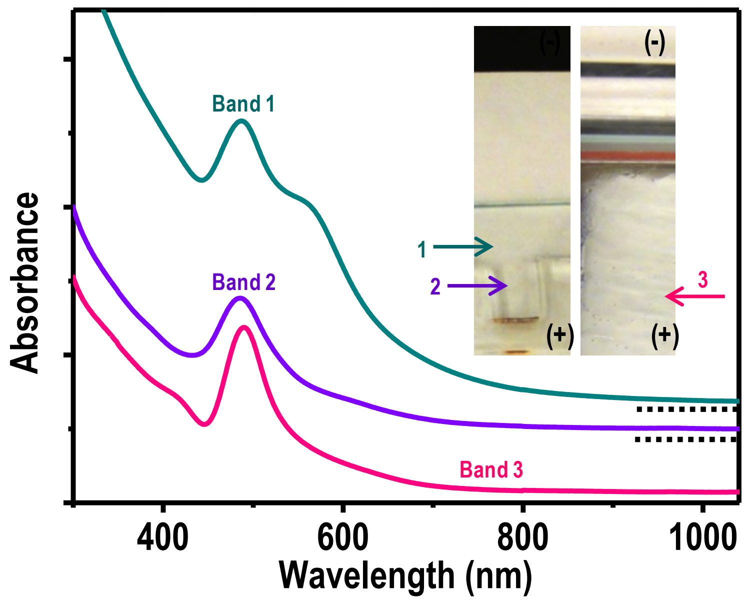


Figure S5. Absorption spectra of PAGE-separated products (bands 1 and 2) of 5 h-exchanged and reversed $Ag_{35}(SG)_{18}$ clusters (band 3) of $Ag_{44}(4\text{-FTP})_{30}$ with HSG. Insets are the PAGE photographs of 5 h-exchanged product of $Ag_{44}(4\text{-FTP})_{30}$ with HSG (left) and its reversed $Ag_{35}(SG)_{18}$ product (right). Some of the spectra are shifted vertically for clarity.

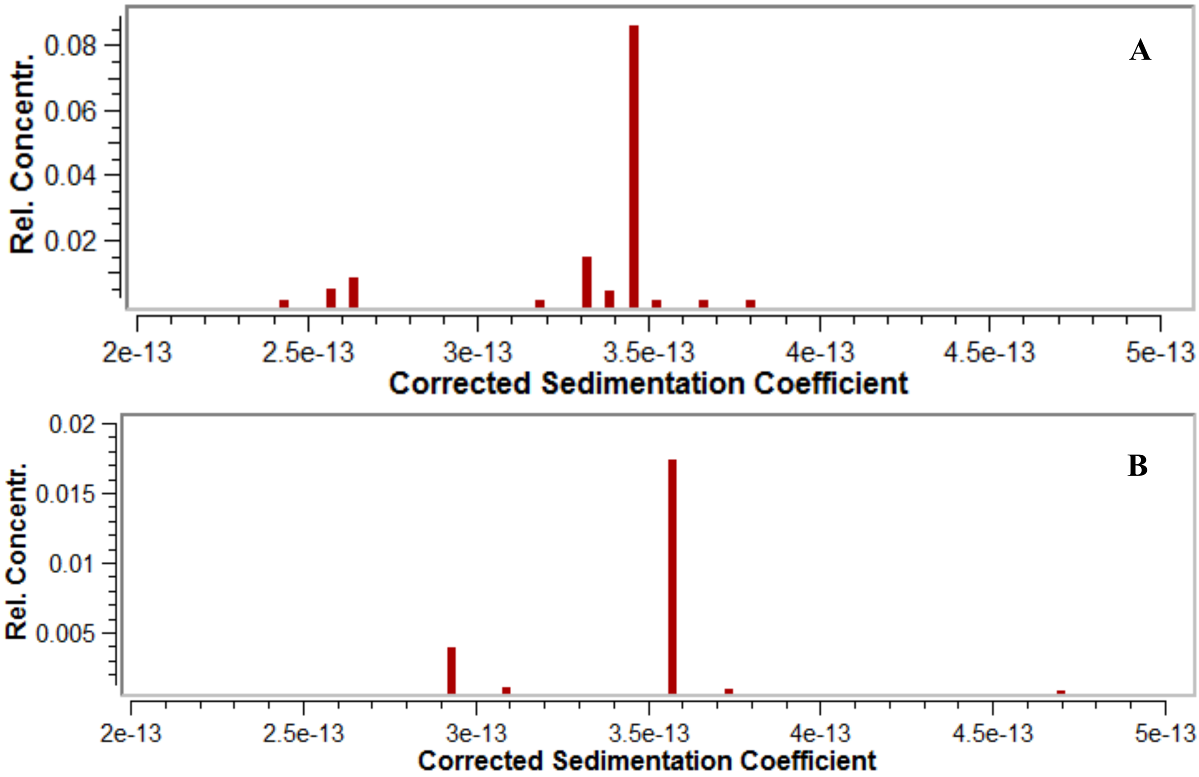


Figure S6. 2-Dimensional Spectrum Analysis (2DSA) AUC plots of HSG-exchanged $Ag_{44}(4\text{-}FTP)_{30}$. (A) 5 h-exchanged clusters showing a distribution of solution components and (B) reversed $Ag_{35}(SG)_{18}$ clusters indicating the presence of nearly a single component at ~3.6S.

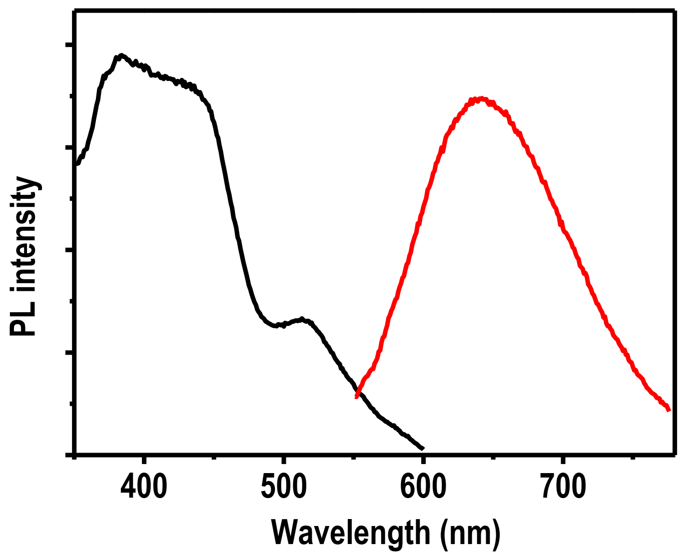


Figure S7. PL excitation (black trace) and emission (red trace) spectra of reversed $Ag_{35}(SG)_{18}$ cluster starting from $Ag_{44}(4\text{-}FTP)_{30}$.

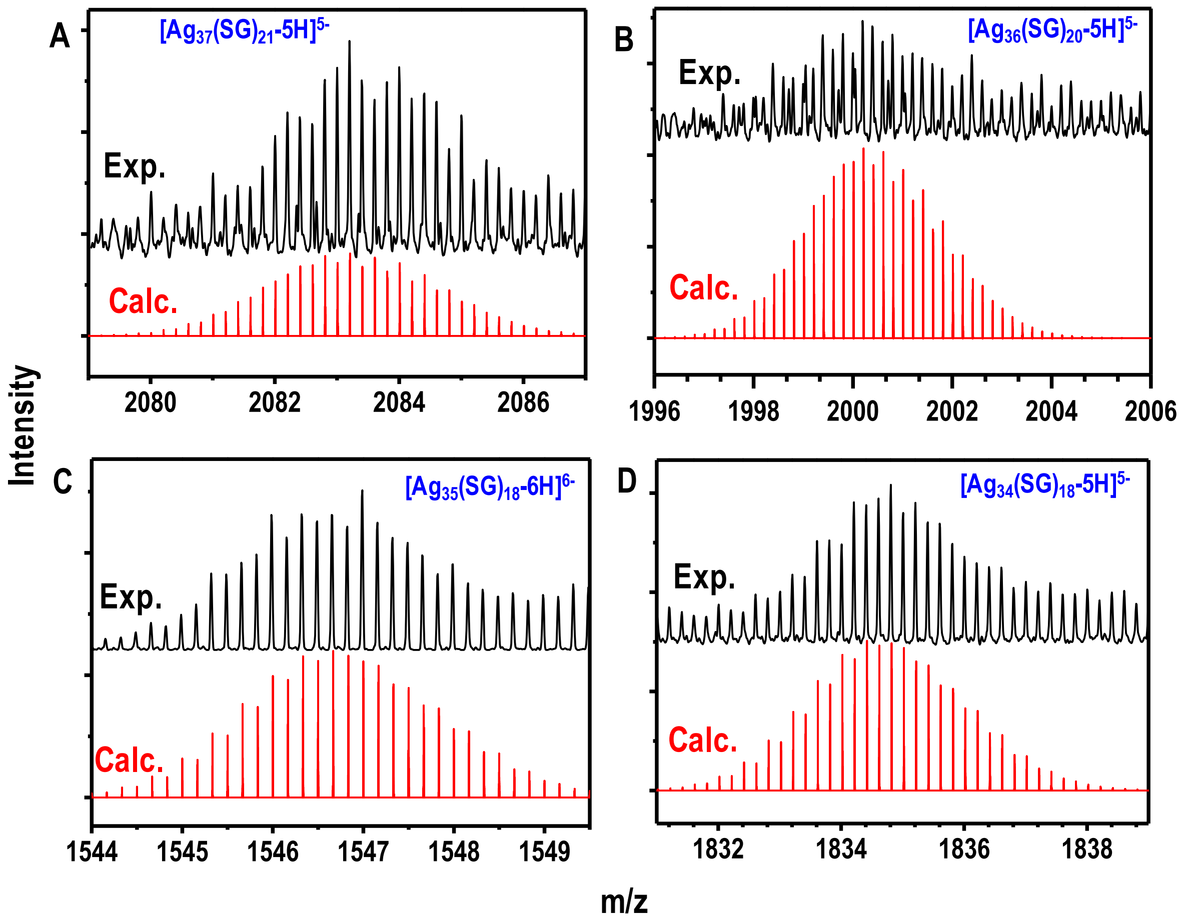


Figure S8. Negative mode ESI MS of 5 h-HSG-exchanged product [intermediates, $Ag_{37}(SG)_{21}$ and $Ag_{36}(SG)_{20}$] of Ag_{44}(4-FTP)$_{30}$ (A and B) and its completely reversed $Ag_{35}(SG)_{18}$ along with its fragmented species, $Ag_{34}(SG)_{18}$ (C and D). Simulated and experimental mass spectra for these compositions match well.

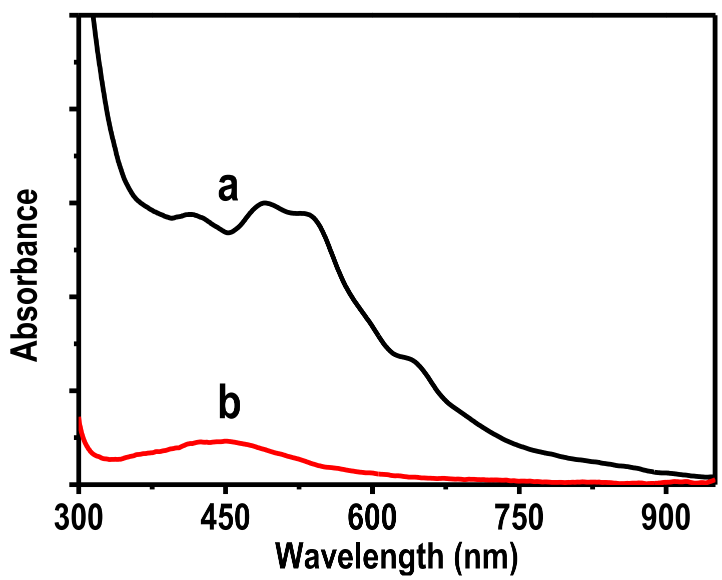


Figure S9. UV-vis absorption spectra of 4-TFMTP- and p-MBA-induced products of $Ag_{35}(SG)_{18}$ clusters (traces a and b, respectively).

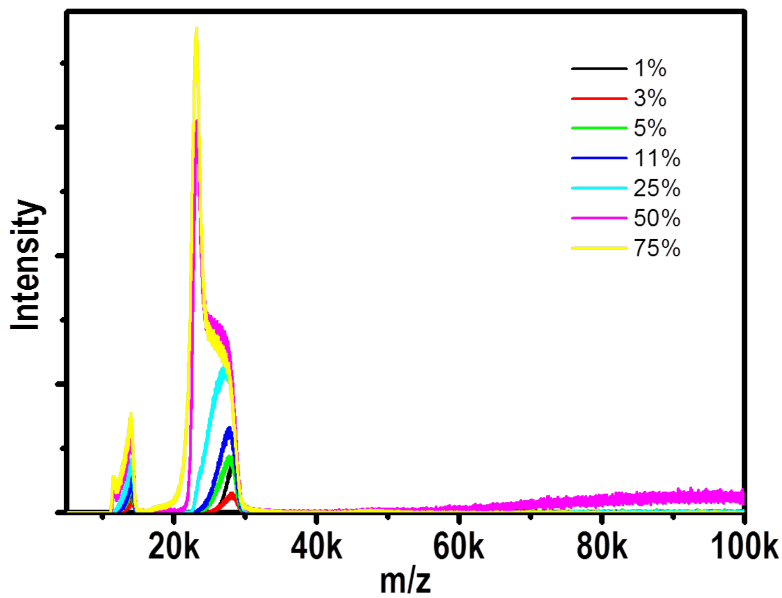


Figure S10. Laser intensity-dependent MALDI MS of CHT-exchange-induced product of $Ag_{35}(SG)_{18}$ clusters.

References

1. Udayabhaskararao, T.; Bootharaju, M. S.; Pradeep, T. *Nanoscale* **2013,** *5*, 9404-9411.

2. Farrag, M.; Thämer, M.; Tschurl, M.; Bürgi, T.; Heiz, U. *J. Phys. Chem. C* **2012,** *116*, 8034-8043.

3. Li, G.; Jiang, D. E.; Kumar, S.; Chen, Y.; Jin, R. *ACS Catal.* **2014,** *4*, 2463-2469.