Electronic Supplementary Information (ESI) for:

Thiolate-protected Ag_{32} clusters: Mass spectral studies of composition and insights into the Ag-thiolate structure from NMR

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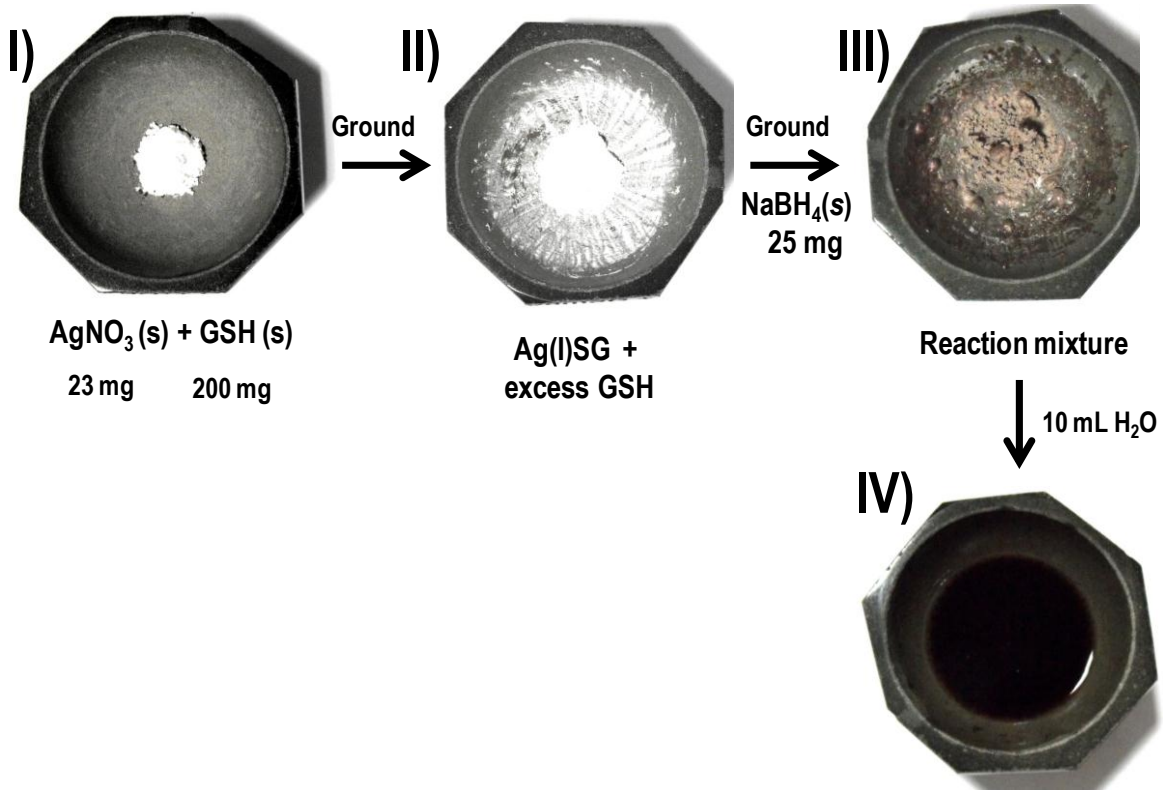

Scheme S1. Photographs representing the changes at various stages during the synthesis of $Ag_{32}SG_{19}$ clusters. Photograph I is the initial mixture of silver nitrate and glutathione (both are colorless solids). Grinding the above for 10 minutes leads to the formation of an Ag(I)SG thiolate (photograph II). This thiolate shows a featureless spectrum in its UV-vis profile (measured in water, data not shown). To this mixture, $NaBH_4$(s) was added and ground (photograph III). A 10 mL of distilled water was added to the above mixture (photograph IV). This solution contains mixture of clusters which shows distinct peaks as shown in Figure 1a.

Electronic Supplementary Information 2

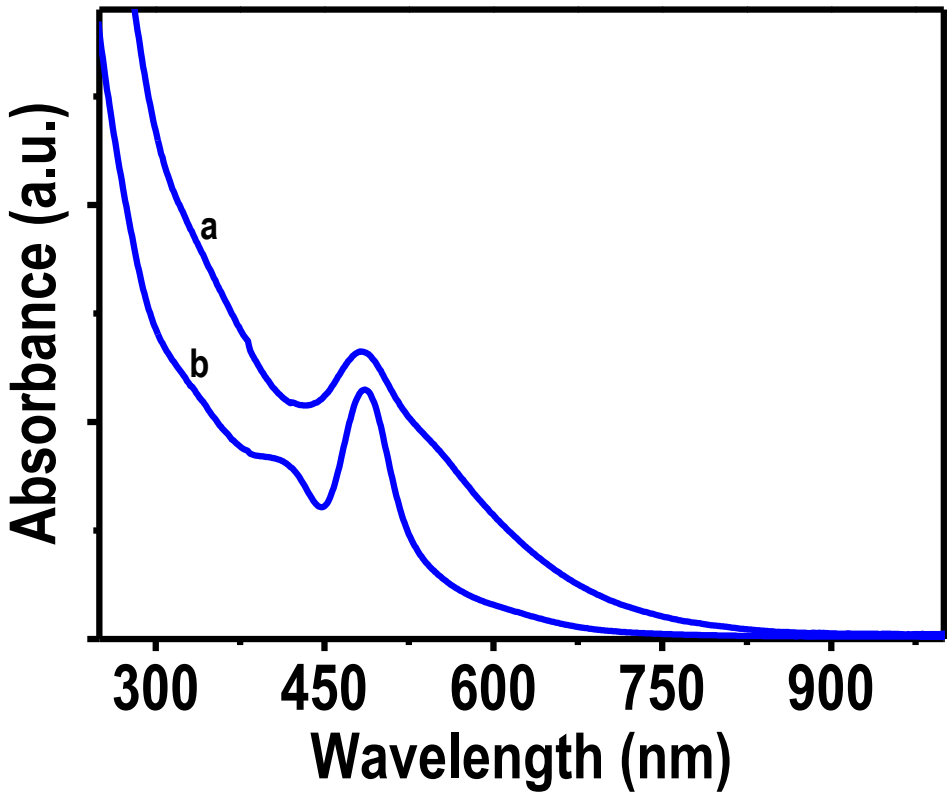

Figure S2. UV-vis absorption spectra of (a) the as-synthesized crude cluster, CC and (b) the solution obtained after keeping the crude cluster overnight at ambient conditions (giving aged crude, ACC). The spectrum of ACC is comparable to cluster 3 (trace 3, shown in Figure 1), except for the feature at 420 nm.

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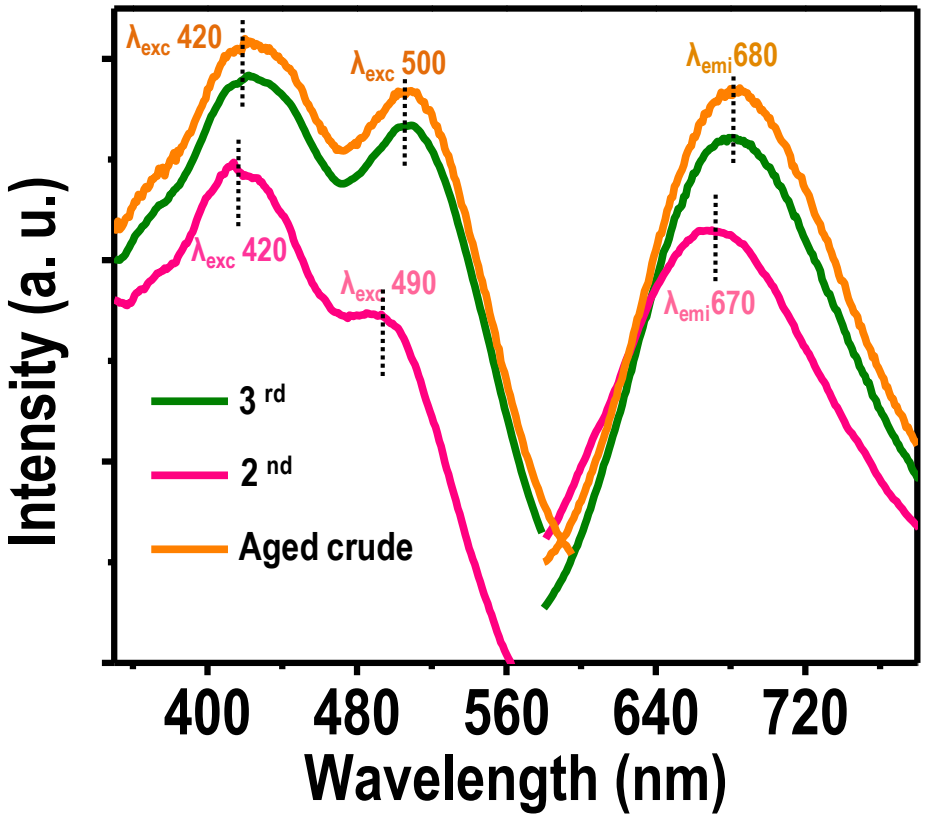

Figure S3. Photoluminescence spectra of clusters extracted from 2nd and 3rd bands of gel electrophoresis of CC. ACC also shows luminescence similar to cluster 3.

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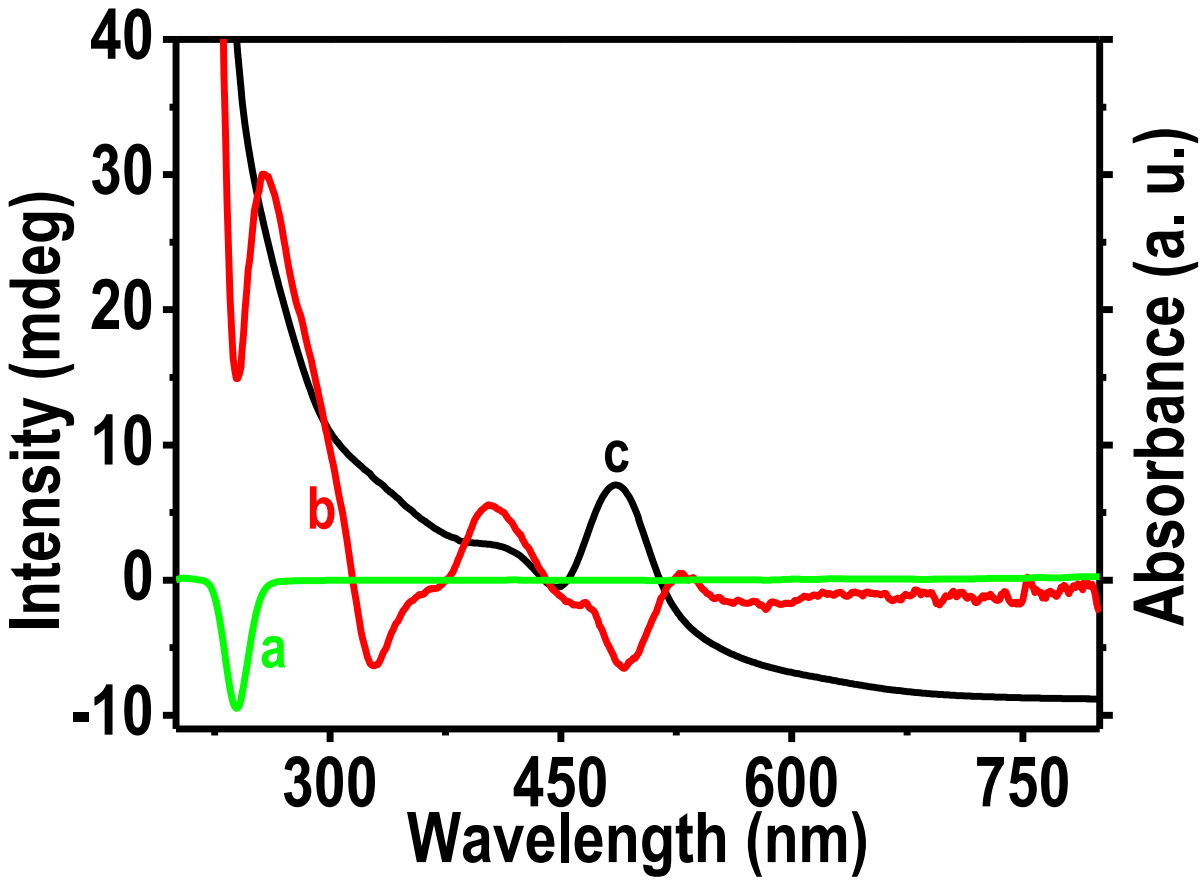

Figure S4. CD spectra of GSH (a) and $Ag_{32}SG_{19}$ (b) compared with the absorption of ACC solution (c).

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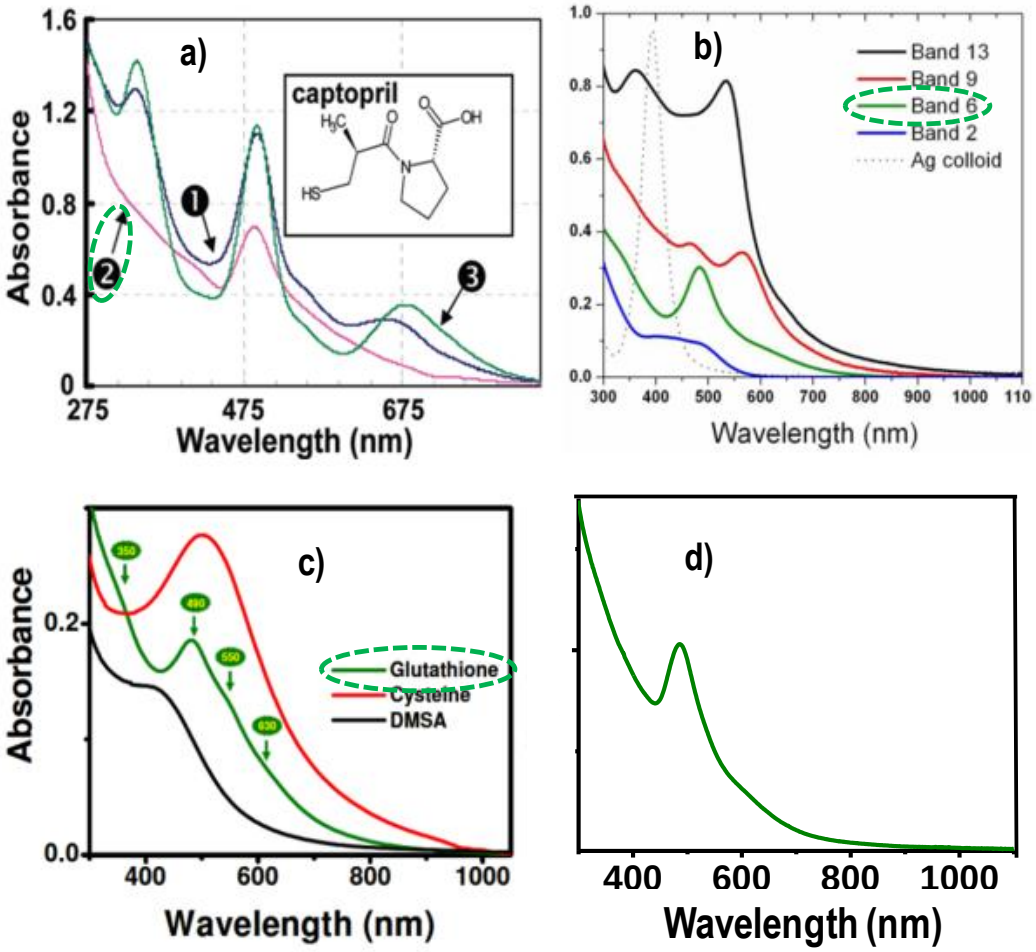

Figure S5. Absorption spectra of -SG protected Ag clusters (marked in green ellipse) from various groups, Kitaev *et al.*[1] (a), Bigoni *et al.*[2] (b) and Pradeep *et al.*[3] (c), compared with the present cluster (d). Spectra a, b and c are reprinted from references 1, 2 and 3, respectively.

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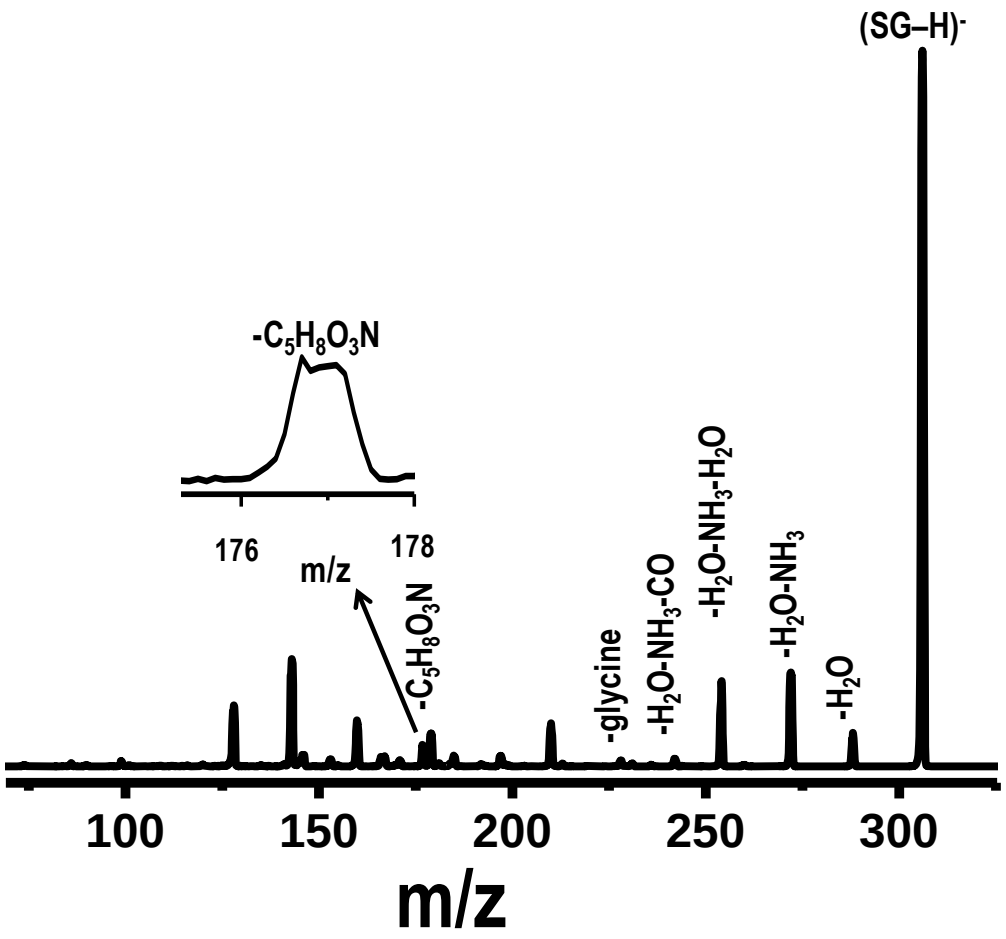

Figure S6. MS/MS spectrum of m/z 306 peak (anoin of glutathione) in the negative mode. Apart from the common H_2O and NH_3 losses, one prominent loss is due to $C_5H_8O_3N$.

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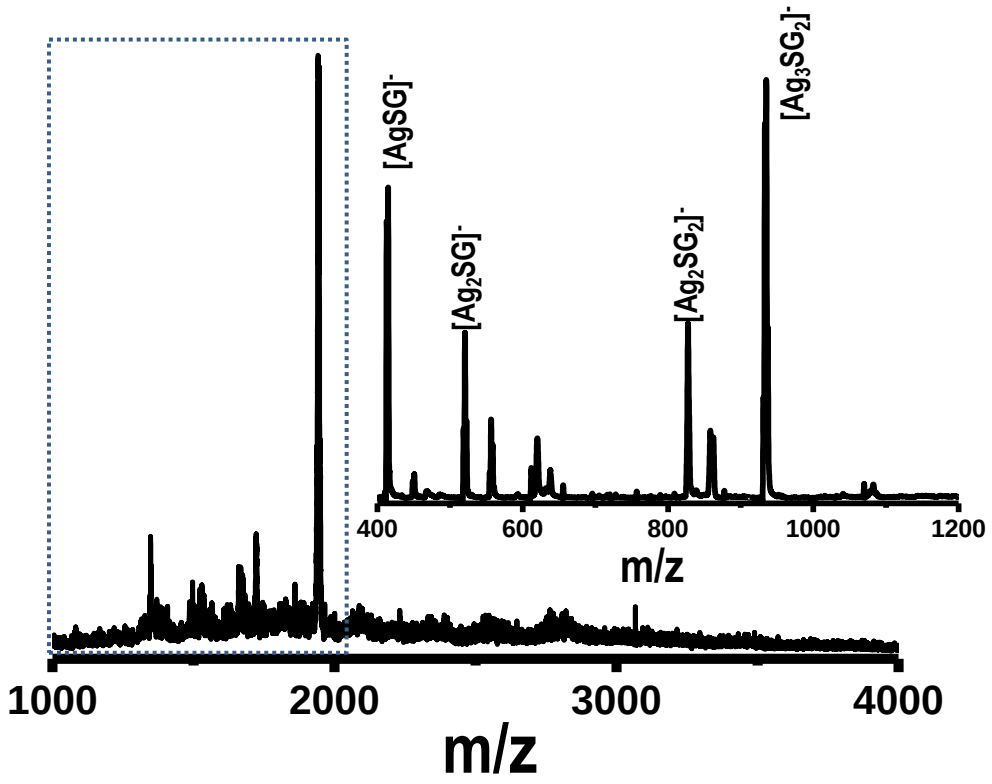

Figure S7. ESI MS of $Ag_{32}SG_{19}$ measured in the negative mode in the range of m/z 500-4000. The peaks of interest given in main text are in the marked region. Inset shows the ESI MS at the low mass region (m/z 400-1200). Peaks at m/z 936, 828, 522 and 414 are assigned to $[Ag_3SG_2\text{-}H]^-$, $[Ag_2SG_2\text{-}H]^-$, $[Ag_2SG\text{-}H]^-$ and $[AgSG\text{-}H]^-$, respectively.

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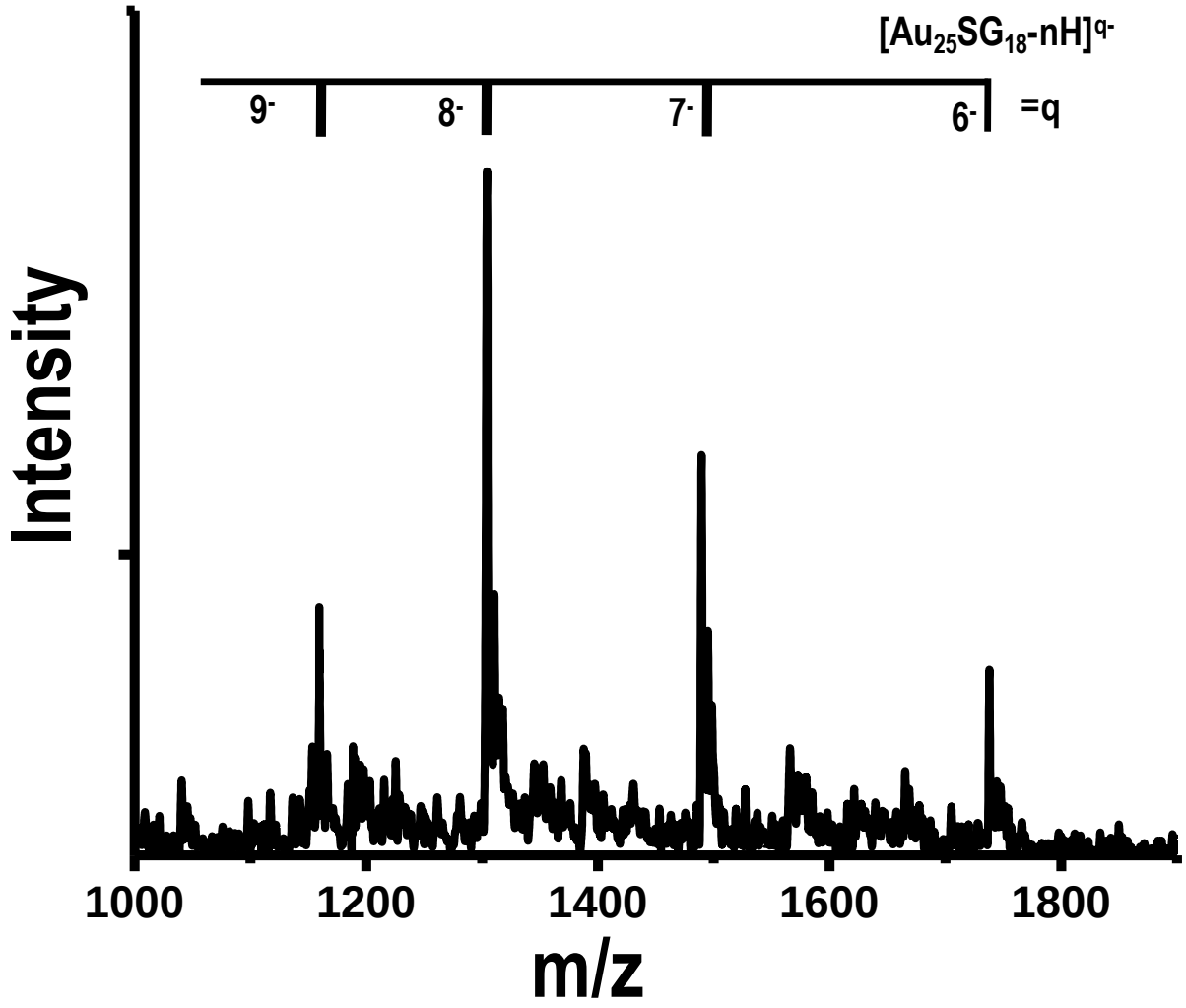

Figure S8. ESI MS of $Au_{25}SG_{18}$, measured under the same conditions as in the case of $Ag_{32}SG_{19}$. Spectrum shows the multiply charged species of $[Au_{25}SG_{18}\text{-}nH]^{q-}$ (where q= 6, 7, 8 and 9), which are labeled. The optimized conditions for this measurement are reported in the instrumentation section.

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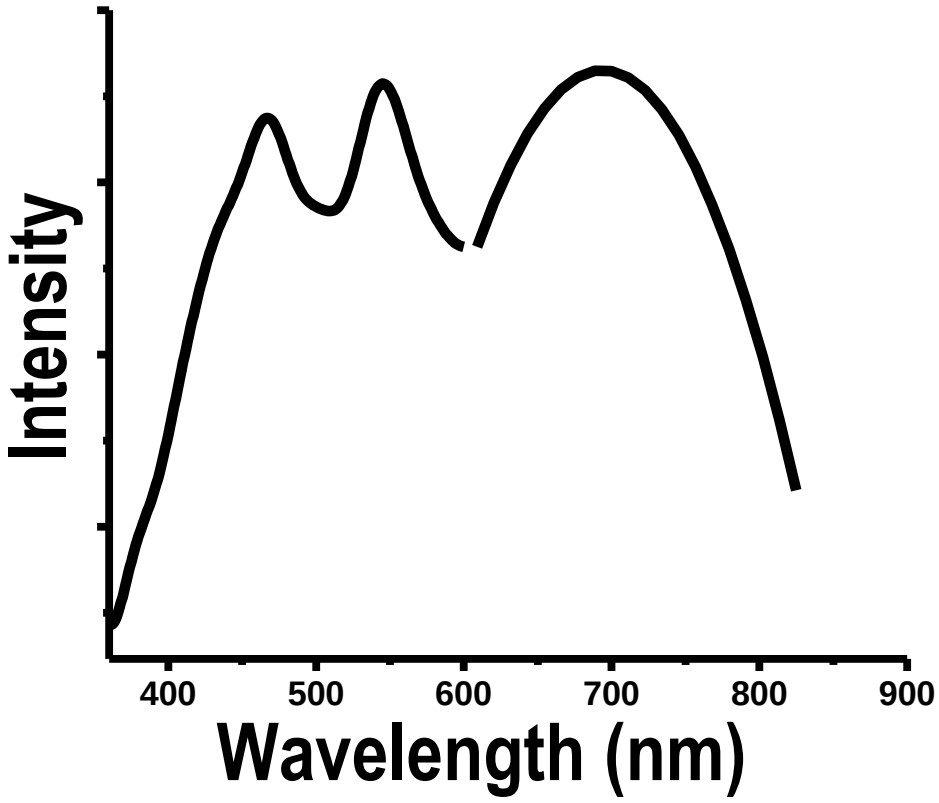

Figure S9. Photoluminescence spectra of Ag@MPG clusters in water at room temperature.

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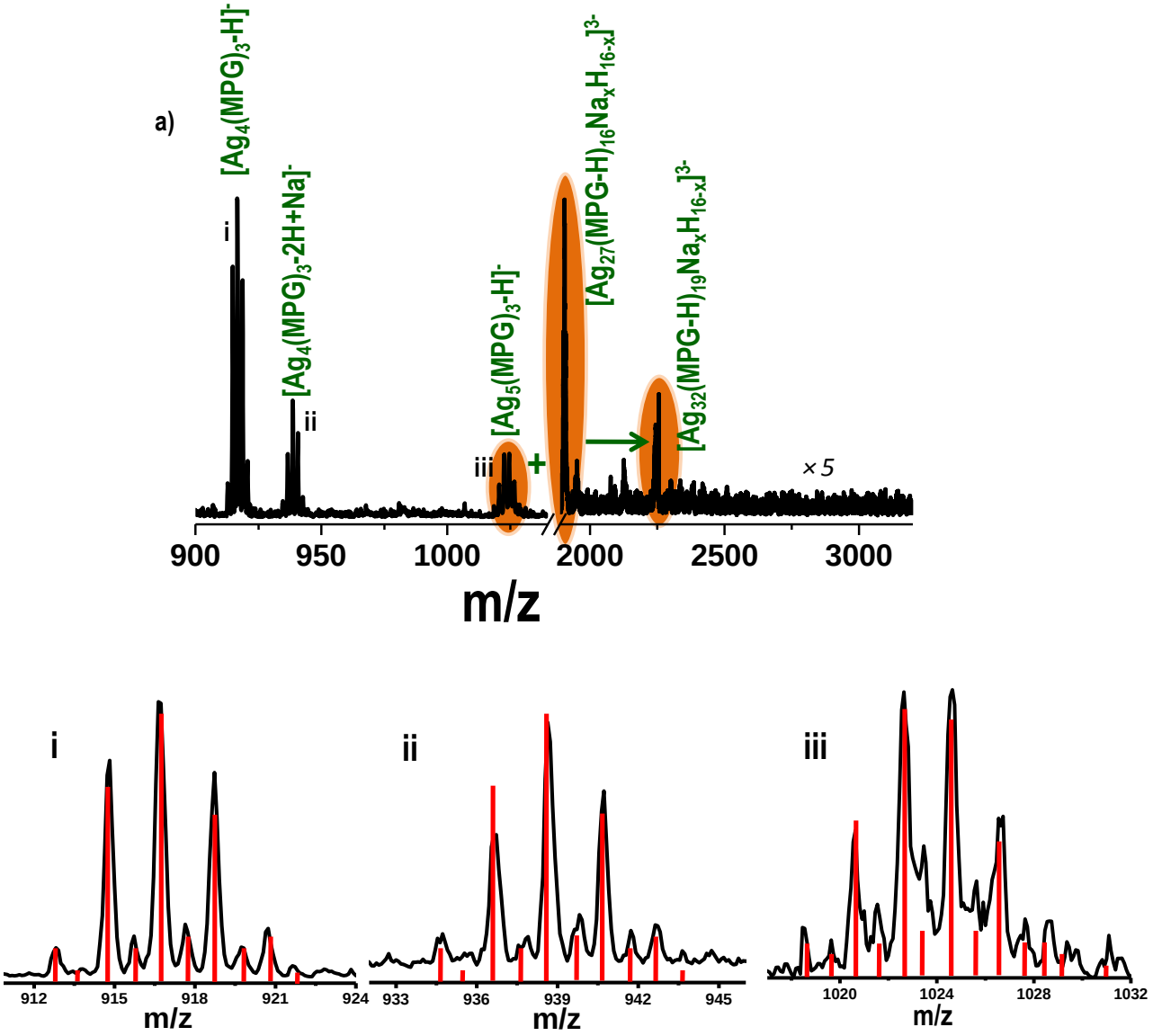

Figure S10. a) ESI MS of $Au_{32}MPG_{19}$, measured in the negative mode in the range of m/z 900-3200. All the peaks are marked with their respective ions. Sodium adduct of $Ag_{27}MPG_{16}$ is obtained due to the loss of Ag_5MPG_3 species (iii) from $[Ag_{32}(MPG\text{-}H)_{19}Na_xH_{16-x}]^{3-}$. Mass spectrum in the range m/z 1000-3200 is enhanced for 5 times in the vertical axis. Labels i, ii and iii are $[Ag_4MPG_3\text{-}H]^-$, $[Ag_4MPG_3\text{-}H+Na]^-$ and $[Ag_5MPG_3\text{-}H]^-$, respectively. Simulated spectra for i, ii and iii, depicted with lines match well with the experiment.

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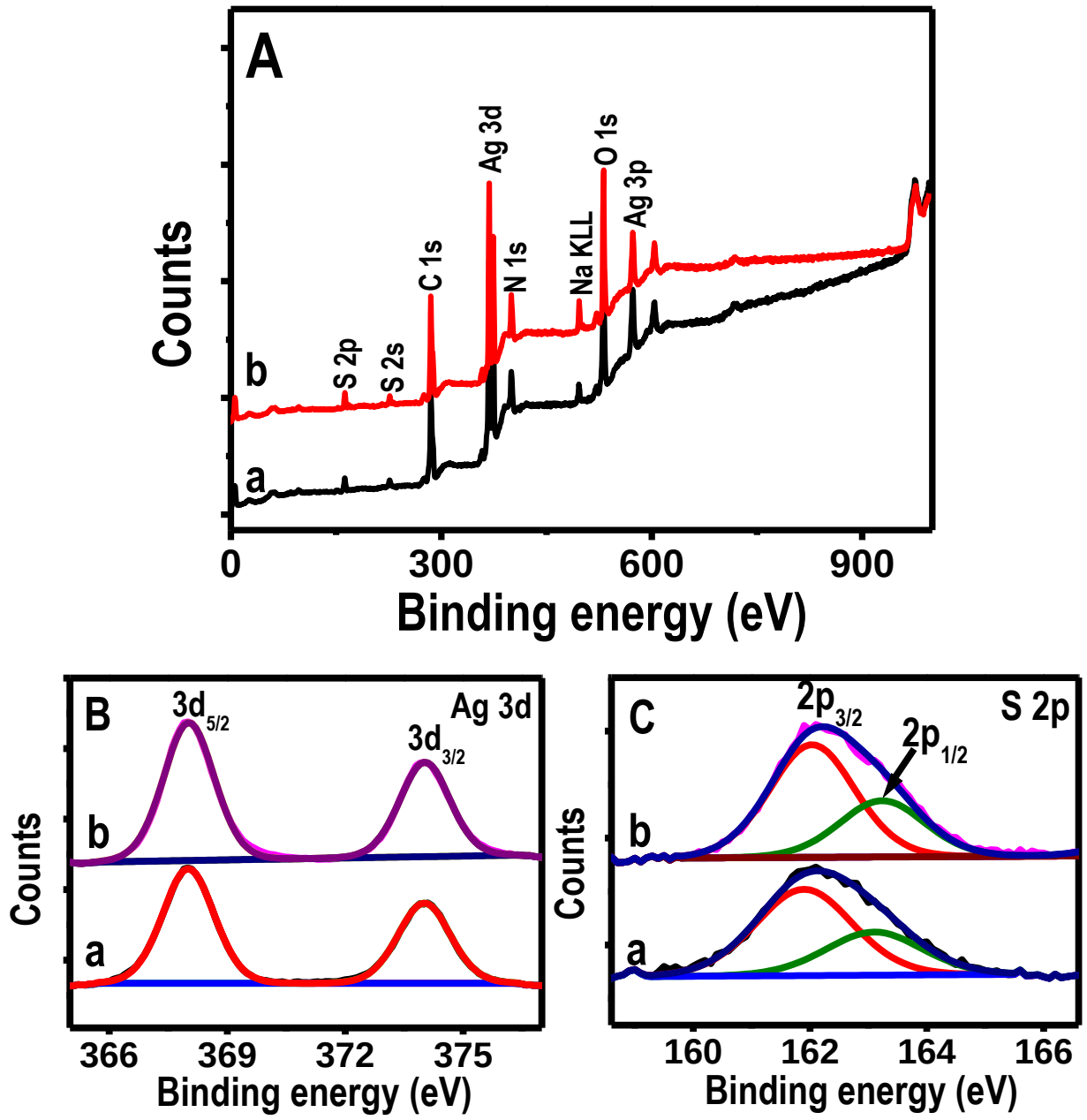

Figure S11. XPS survey spectra, Ag 3d and S 2p regions (A, B and C, respectively) of the crude and $Ag_{32}SG_{19}$ clusters (traces a and b, respectively). The Ag:S atomic ratio is 1:0.57±0.03 for $Ag_{32}SG_{19}$ which matches with the expected value 1:0.59.

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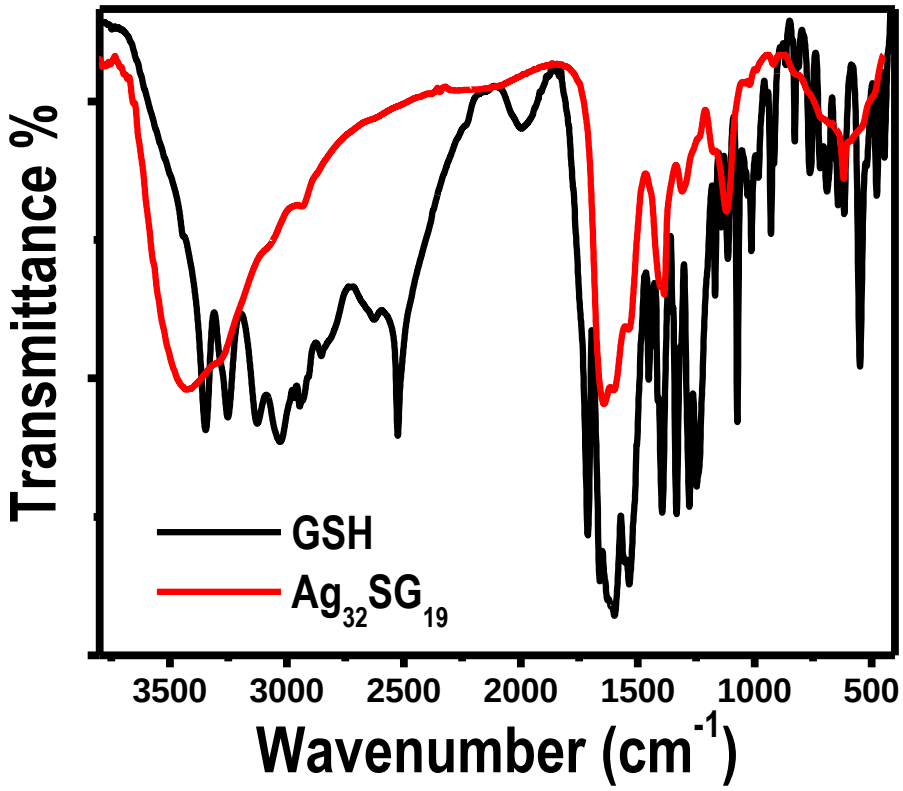

Figure S12. FTIR spectra of GSH and $Ag_{32}SG_{19}$. The S−H stretching feature at 2572 cm^{-1} in GSH is absent in cluster which is in agreement with the XPS data. GSH features in the region 2000-500 cm^{-1} confirm the presence of SG protection of the cluster.

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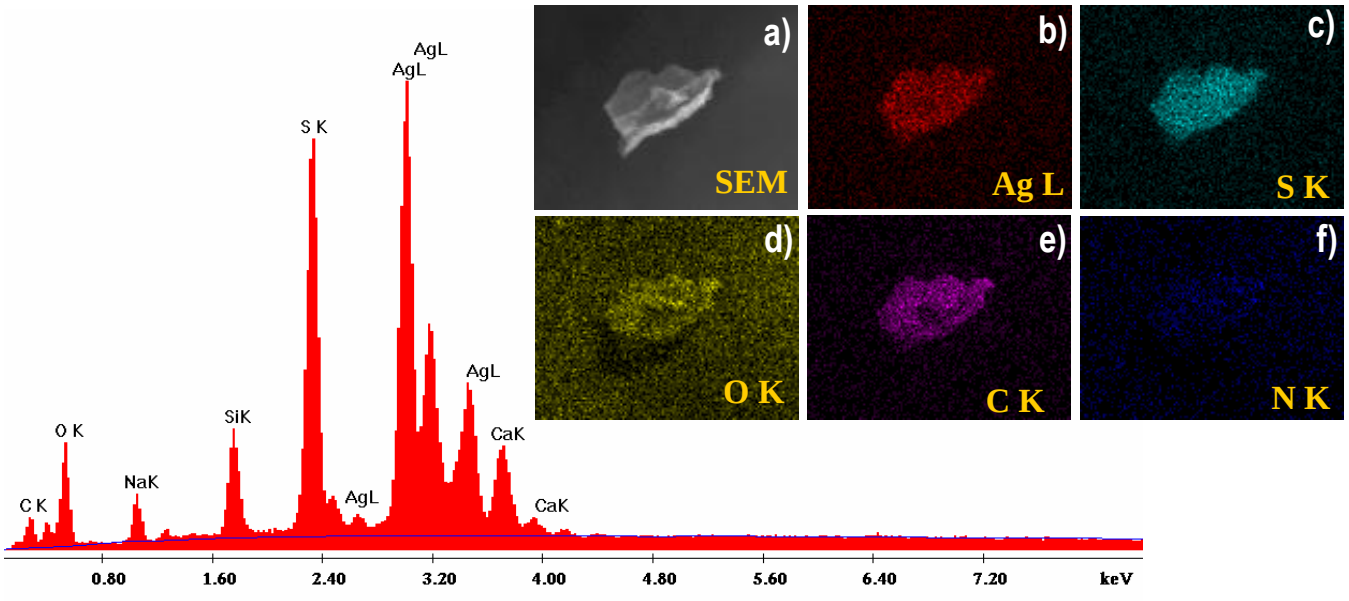

Figure S13. SEM-EDAX spectrum of $Ag_{32}SG_{19}$. (a) SEM image of the $Ag_{32}SG_{19}$ cluster aggregate from which the EDAX spectrum is taken. Elemental maps of (b) Ag L_α, (c) S K_α, (d) O K_α, (e) C K_α and (f) N K_α are shown. Si K_α is due to the substrate used. Ag:S atomic ratio measured is 1:0.56±0.03 which matches with the expected value of 1:0.59 for $Ag_{32}SG_{19}$.

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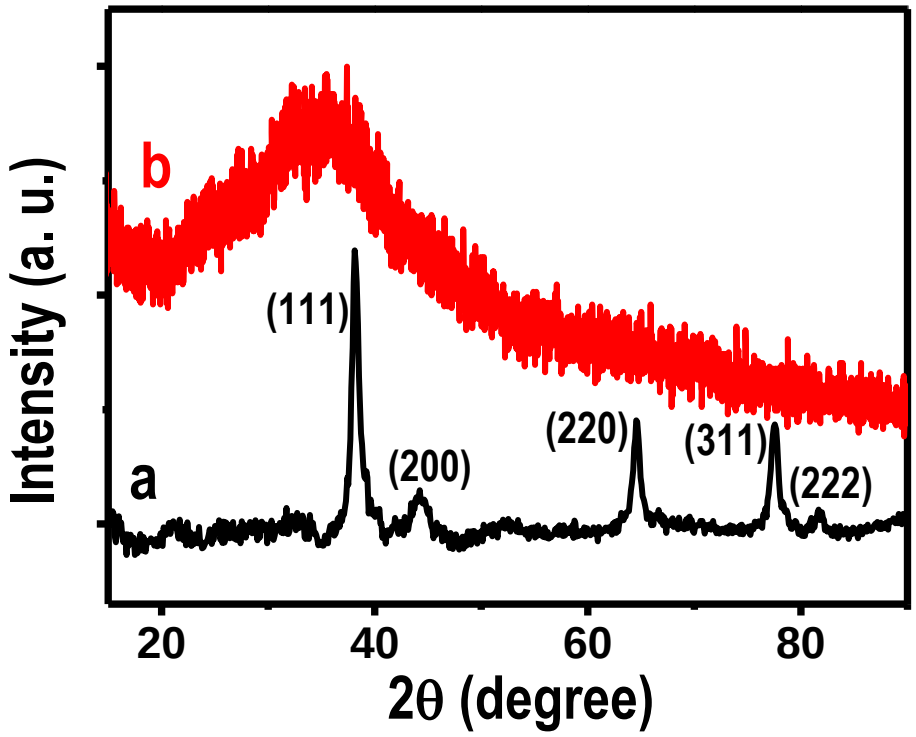

Figure S14. Comparison of the X-ray diffraction patterns of glutathione protected silver nanoparticles (Ag@SG NPs) and $Ag_{32}SG_{19}$ clusters (traces a and b, respectively). Nanoparticles show peaks corresponding to Ag planes (111), (200) (220), (311) and (222) whereas $Ag_{32}SG_{19}$ shows a broad peak around $2\theta \approx 38^{o}$.

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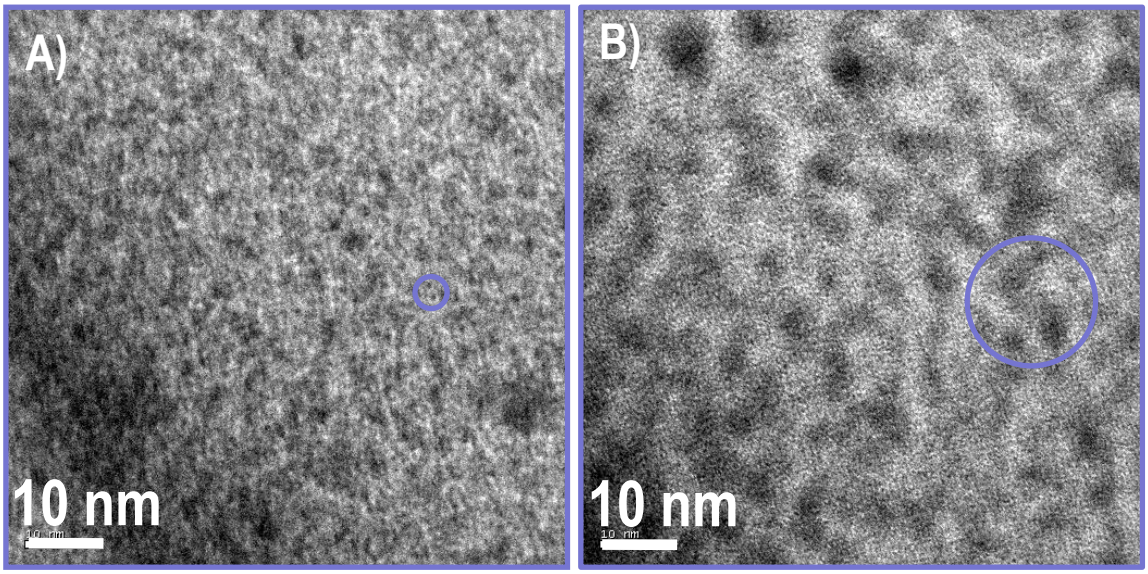

Figure S15. TEM images of the $Ag_{32}SG_{19}$ before (A) and after electron beam irradiation for 5 min (B). Both are from the same regions of the grid. QCs are strongly sensitive to electron beam exposure and they convert gradually to larger aggregates or nanoparticles during TEM examination.

References

(1) N. Cathcart and V. Kitaev, *J. Phys. Chem. C* 2010, **114**, 16010.
(2) S. Kumar, M. D. Bolan and T. P. Bigioni, *J. Am. Chem. Soc.* 2010, **132**, 13141.
(3) T. Udayabhaskararao, B. Nataraju and T. Pradeep, *J. Am. Chem. Soc.* 2010, **132**, 16304.