Supporting Information

Reactivity of Monolayer Protected Silver Clusters Towards Excess Ligand: A Calorimetric Study

Ananya Baksi,[1] M. S. Bootharaju,[1] Pratap K. Chhotaray,[2] Papri Chakraborty,[1] Biswajit Mondal,[1] Shridevi Bhat,[1] Ramesh Gardas[2] and Thalappil Pradeep[1]*

[1]DST Unit of Nanoscience and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036, India.

[2]Department of Chemistry, Institute of Technology Madras, Chennai – 600036, India.

*Corresponding author, E-mail: pradeep@iitm.ac.in

Content:

Supporting Information 1:

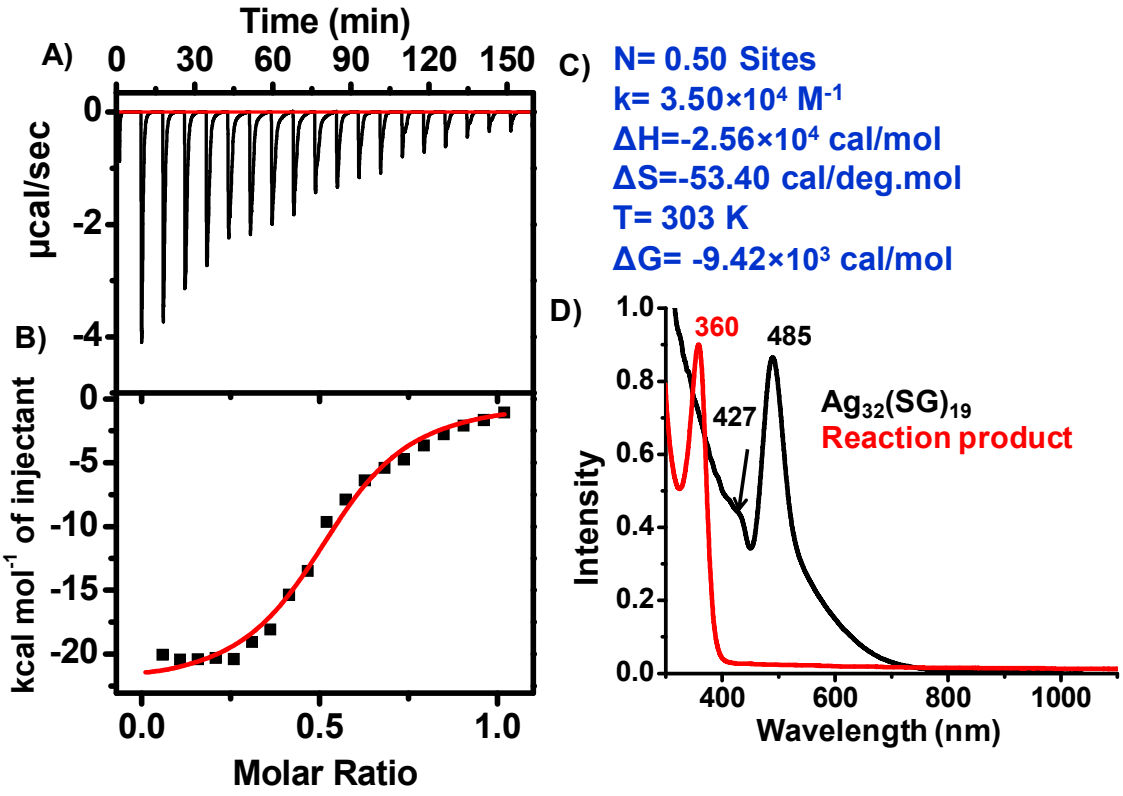

Figure S1. *A) Real time isothermal titration calorimetric data of $Ag_{32}(SG)_{19}$ (1 mM) vs. GSH (5 mM) (top) and B) respective heat change data (down) at 303 K. The thermodynamic parameters obtained are listed in C). Corresponding features were seen in UV-vis absorption as shown in D).*

Supporting Information 2:

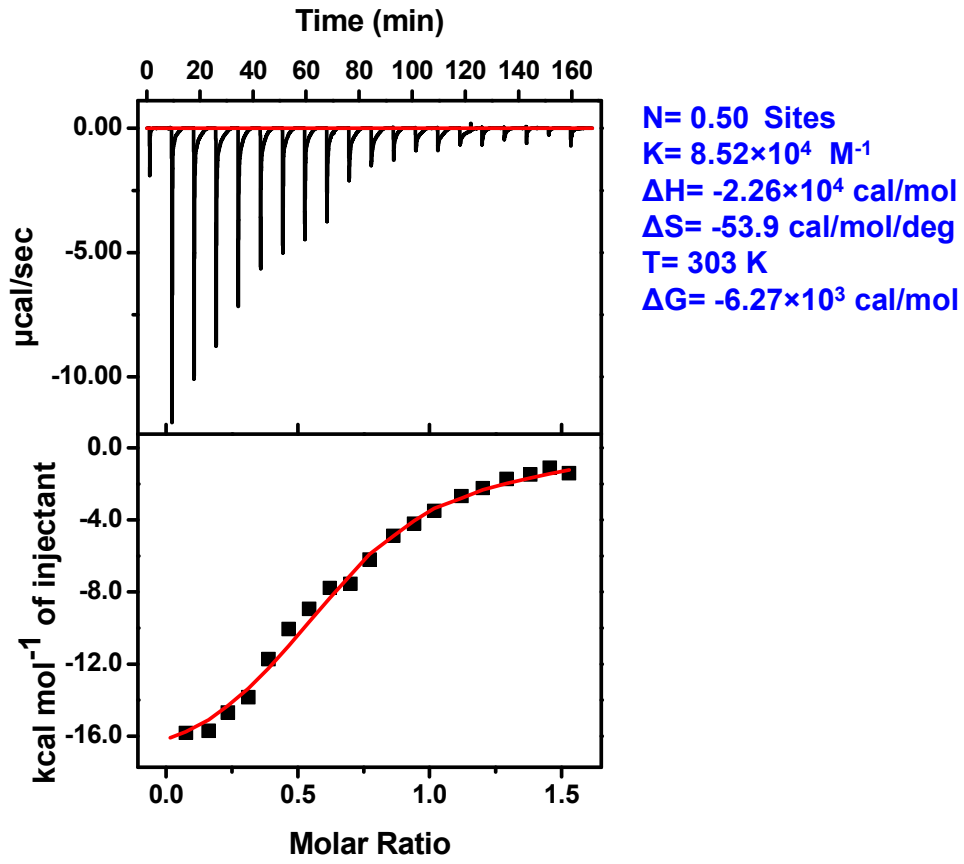

Figure S2. *A) Real time isothermal titration calorimetric data of* $Ag_{32}(SG)_{19}$*(1 mM) vs. GSH (7.5 mM) (top) and B) at 303 K respective heat change data (down). The thermodynamic parameters obtained are listed in C).*

Supporting Information 3

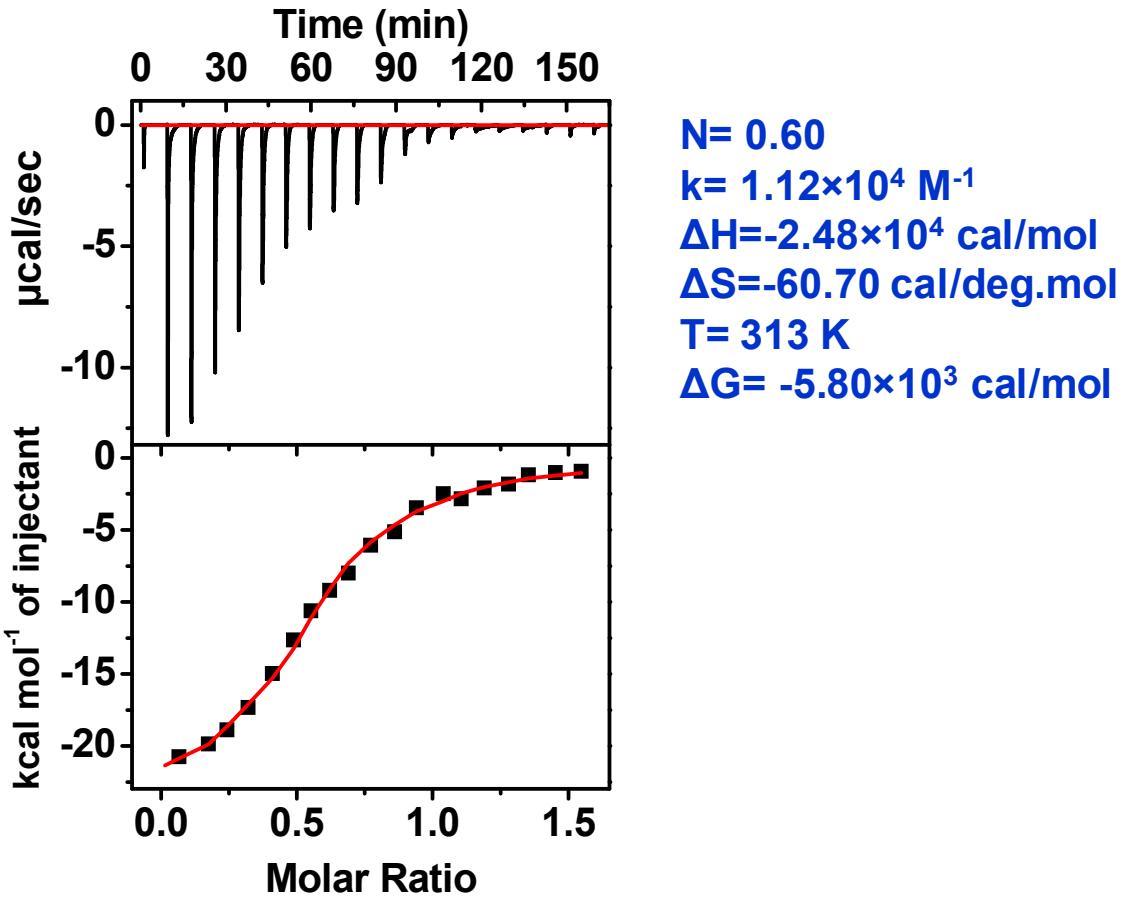

Figure S3. *A) Real time isothermal titration calorimetric data of $Ag_{32}(SG)_{19}$(1 mM) vs. GSH (7.5 mM) (top) and B) at 313 K respective heat change data (down). The thermodynamic parameters obtained are listed in C).*

Supporting Information 4:

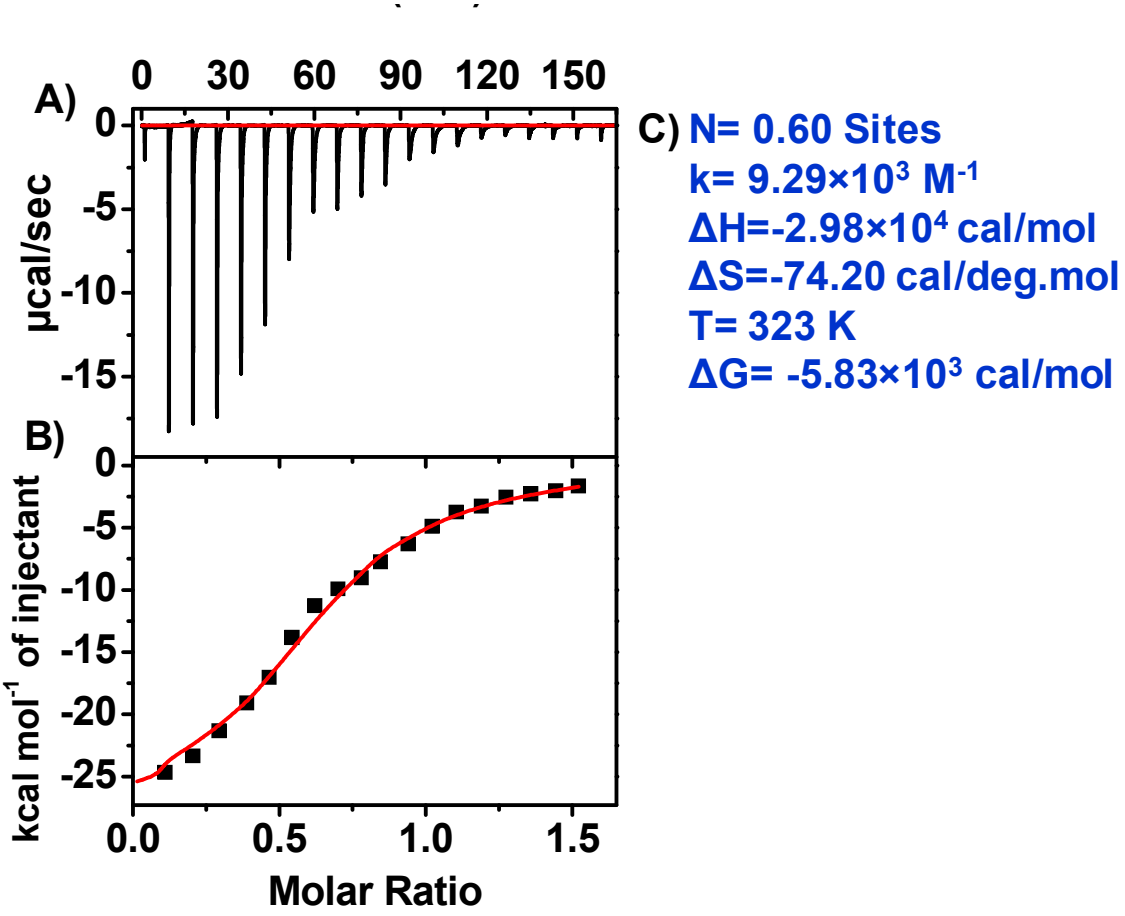

Figure S4. *A) Real time isothermal titration calorimetric data of* $Ag_{32}(SG)_{19}$*(1 mM) vs. GSH (7.5 mM) (top) and B) at 323 K respective heat change data (down). The thermodynamic parameters obtained are listed in C).*

Supporting Information 5:

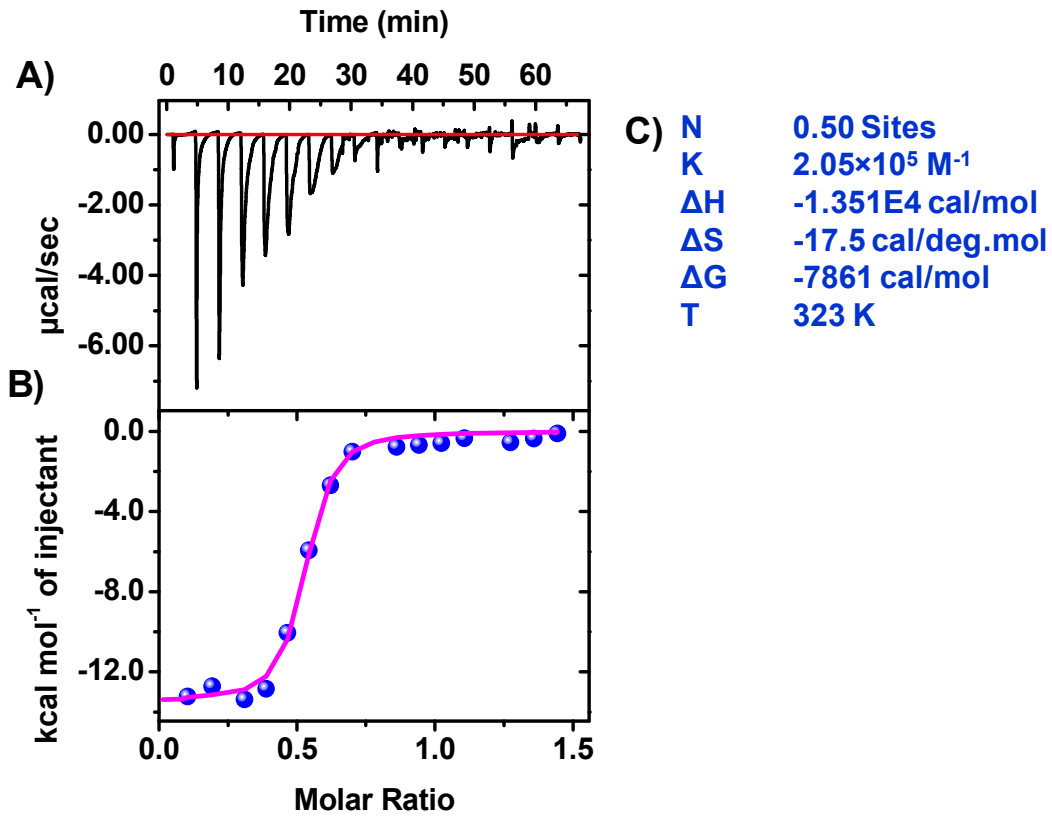

Figure S5. *A) Real time isothermal titration calorimetric data of $Ag_{11}(SG)_7$ (1 mM) vs. GSH (7.5 mM) (top) and B) at 323 K respective heat change data (down). The thermodynamic parameters obtained are listed in C).*

Supporting Information 6

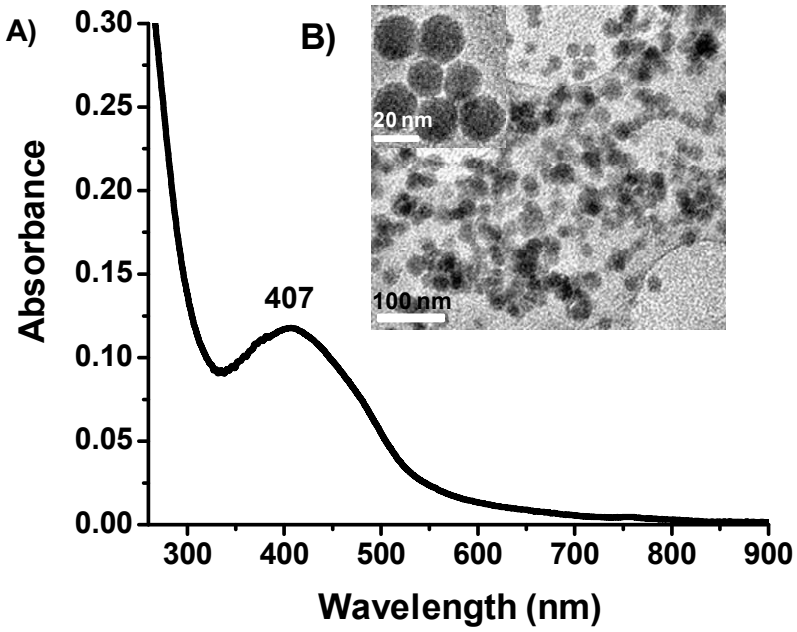

Figure S6. *A) UV-vis absorption spectrum of AgNP protected with GSH showing the plasmon band at 407 nm characteristic of silver nanoparticles. B) TEM image of AgNP@SG showing ~ 20 nm particles. A portion of the image is expanded.*

Supporting Information 7

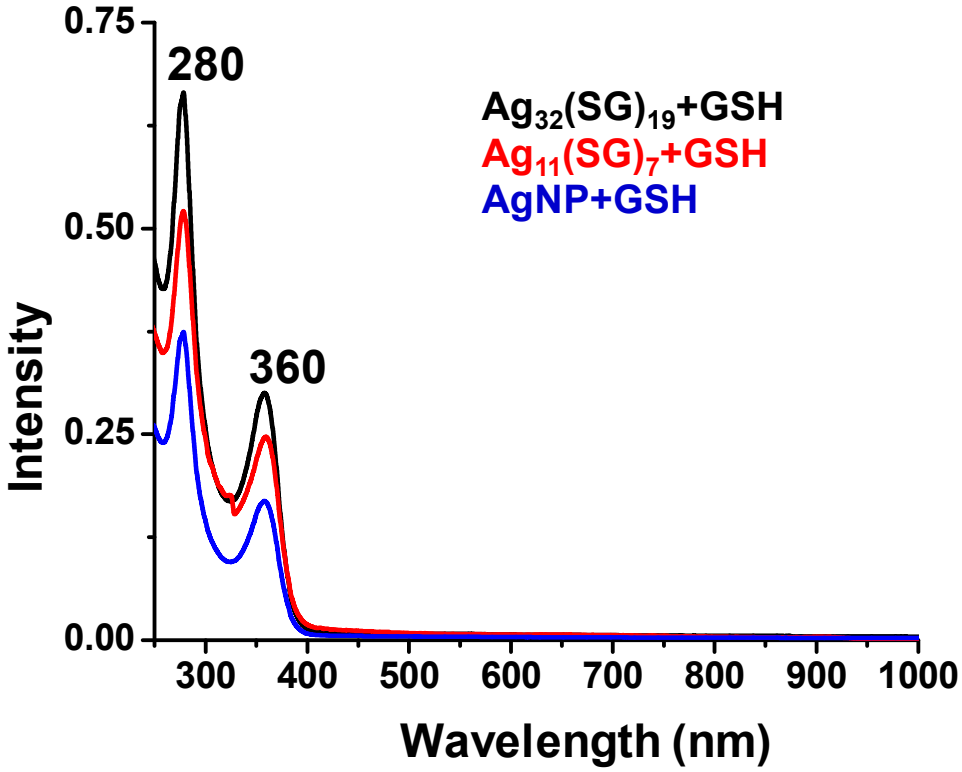

Figure S7. *UV-vis absorption spectra of reaction product from different reactions showing similar products.*

Supporting Information 8:

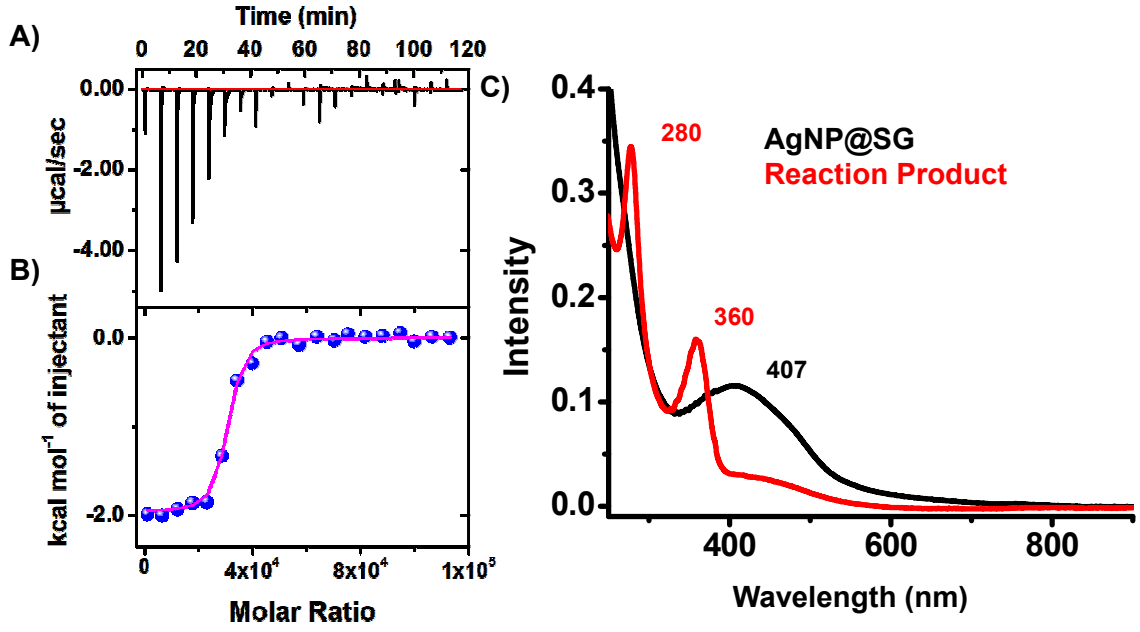

Figure S8. *A) Real time isothermal titration calorimetric data of AgNP@SG (3.6×10^{-8}mM) vs. GSH (7.5 mM) (top) and B) at 298 K respective heat change data (down). The thermodynamic parameters obtained are listed in C). Corresponding change in the UV-vis absorption is shown in D).*

Supporting Information 9:

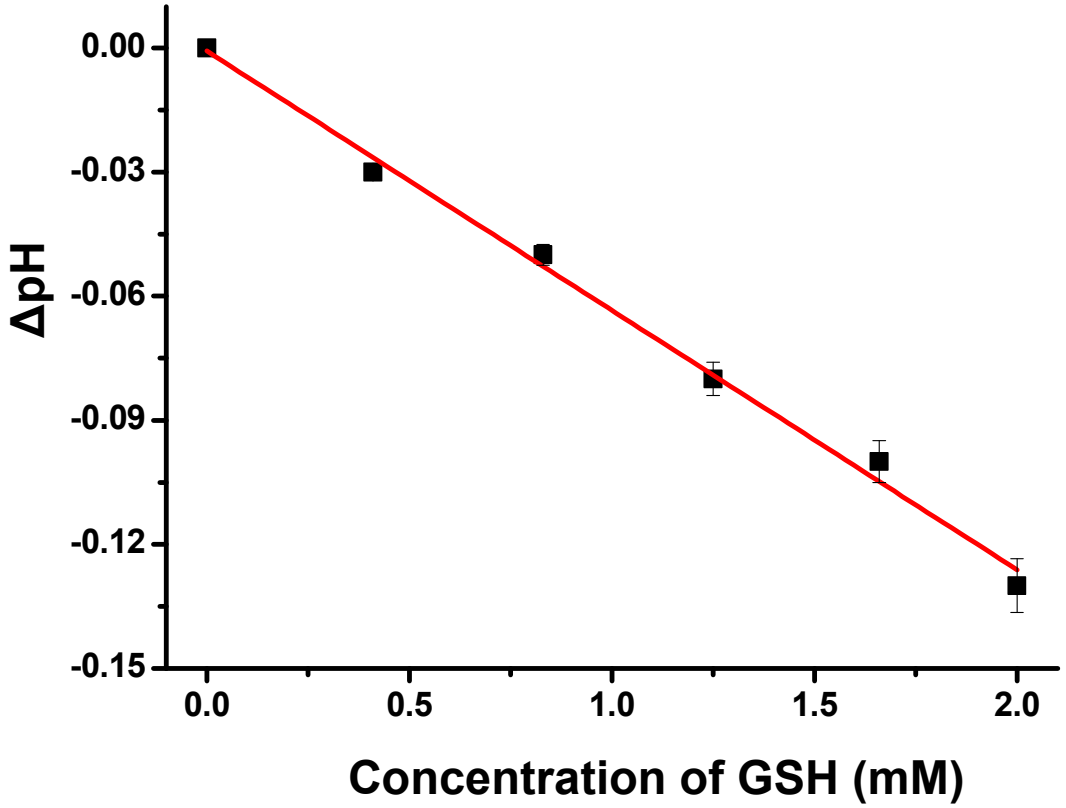

Figure S9: *Change in pH with reaction when 1 mM of* $Ag_{32}(SG)_{18}$ *cluster was reacted with 10 mM GSH solution. Equal volume of GSH was added at 10 minute interval. First data point is before the addition of GSH. Time was counted after adding GSH. We find that the solution becomes increasingly acidic in the course of the reaction. Free GSH contribution was ruled out by subtracting the contribution from GSH addition to pure water. The pH change observed in the reaction was measurable accurately. Experimental details are presented in the manuscript.*

Supporting Information 10:

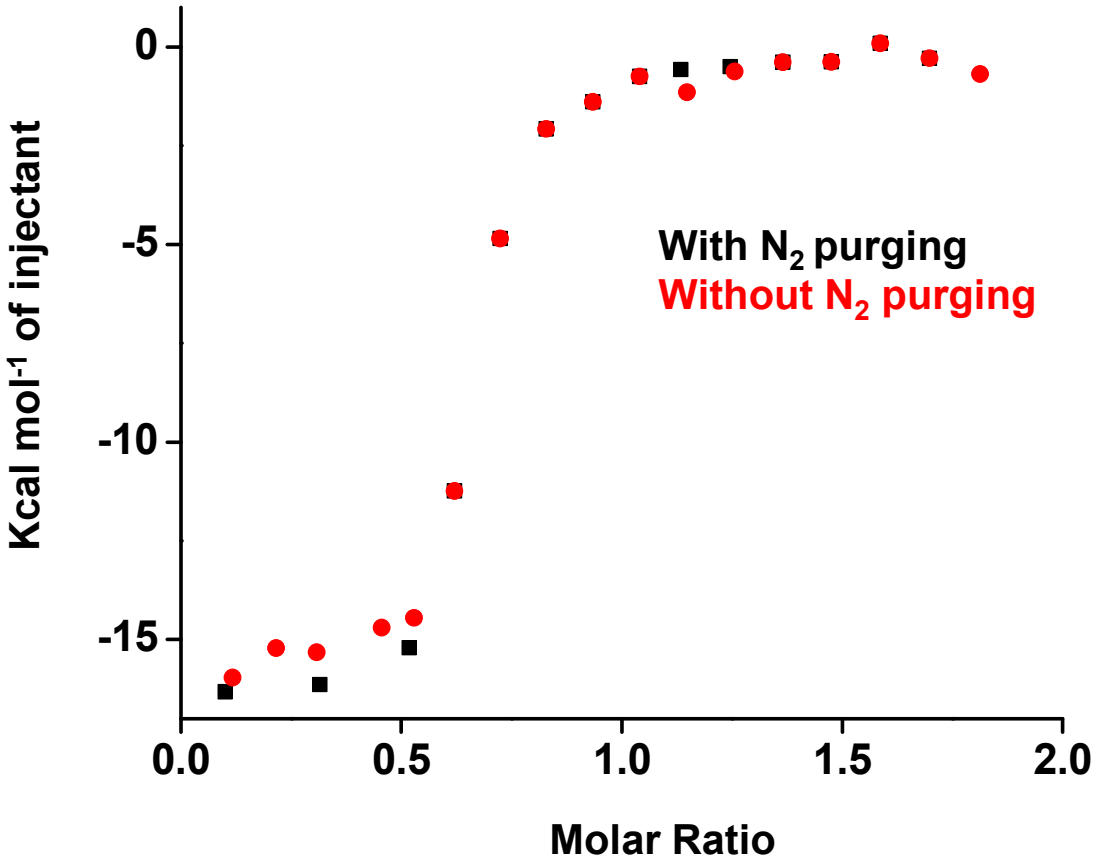

Figure S10. *Comparison of heat change for the reaction of $Ag_{32}(SG)_{19}$(1 mM) vs. GSH (10 mM) at 303 K with and without N_2 purging.*

Supporting Information 11:

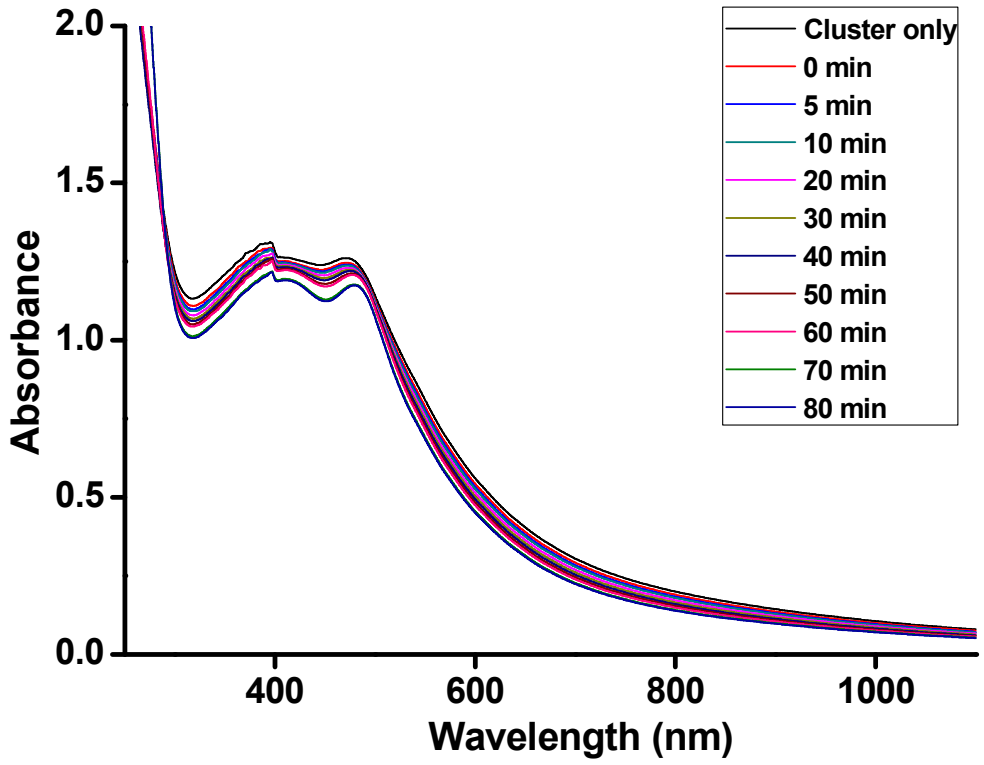

Figure S11: *Cluster solution (in water) was taken in cuvette and 10 µL of 1 mM ascorbic acid solution (in water) and time dependent UV-vis spectra were measured. As the cluster was stable after 40 min,10 µL ascorbic solution at each 10 min time interval was added and continued measurement up to 80 min.*

Supporting Information 12:

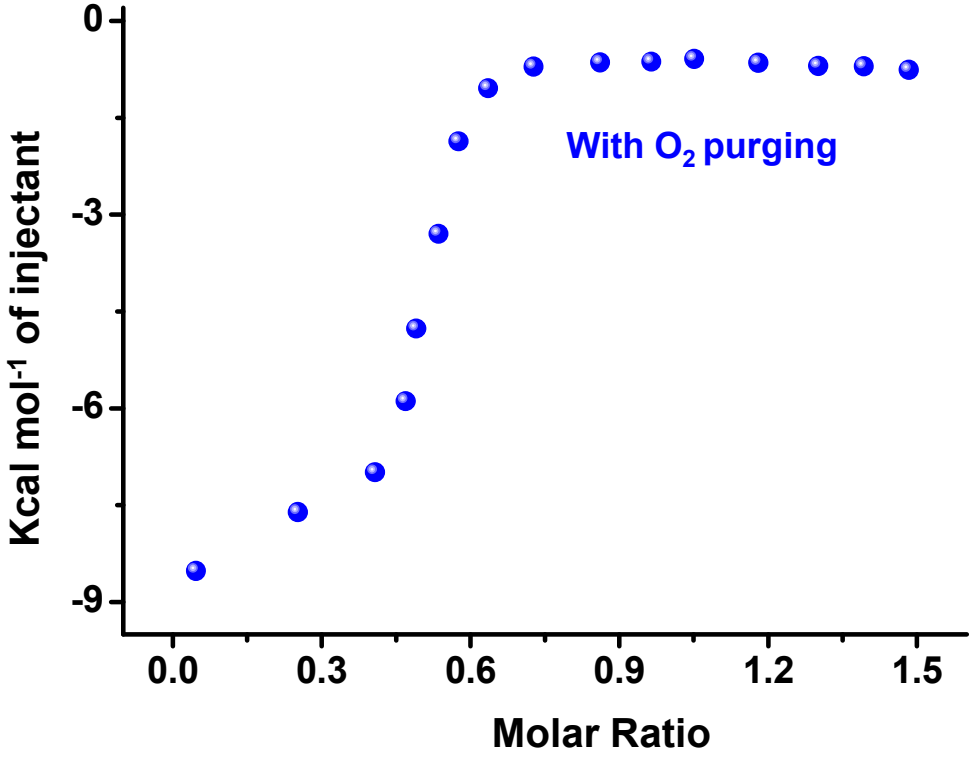

Figure S12. *Comparison of heat change for the reaction of $Ag_{11}(SG)_7$ (1 mM) vs. GSH (7.5 mM) at 303 K with O_2 purging.*

Supporting Information 13:

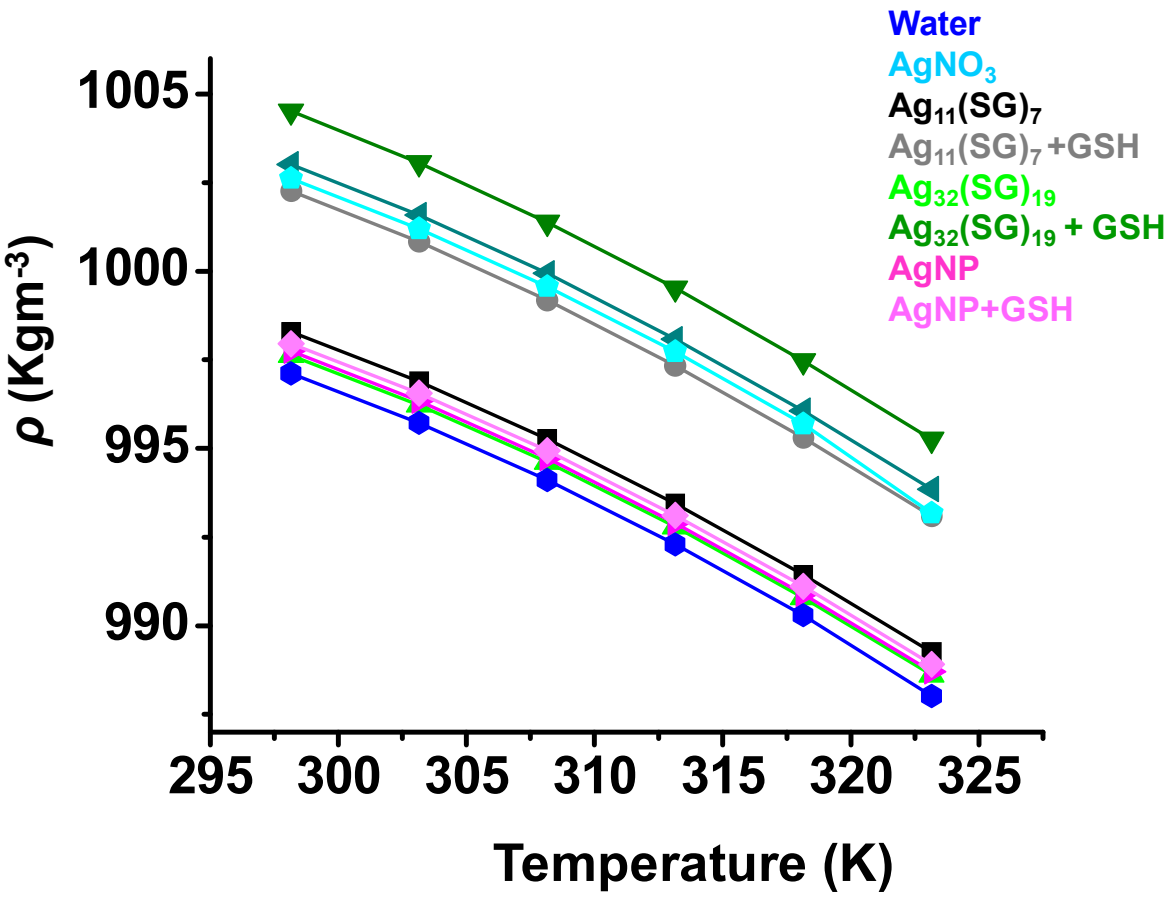

Figure S13. *Temperature dependent change in density of various samples is showing decrease in density with increasing temperature.*

Supporting Information 14:

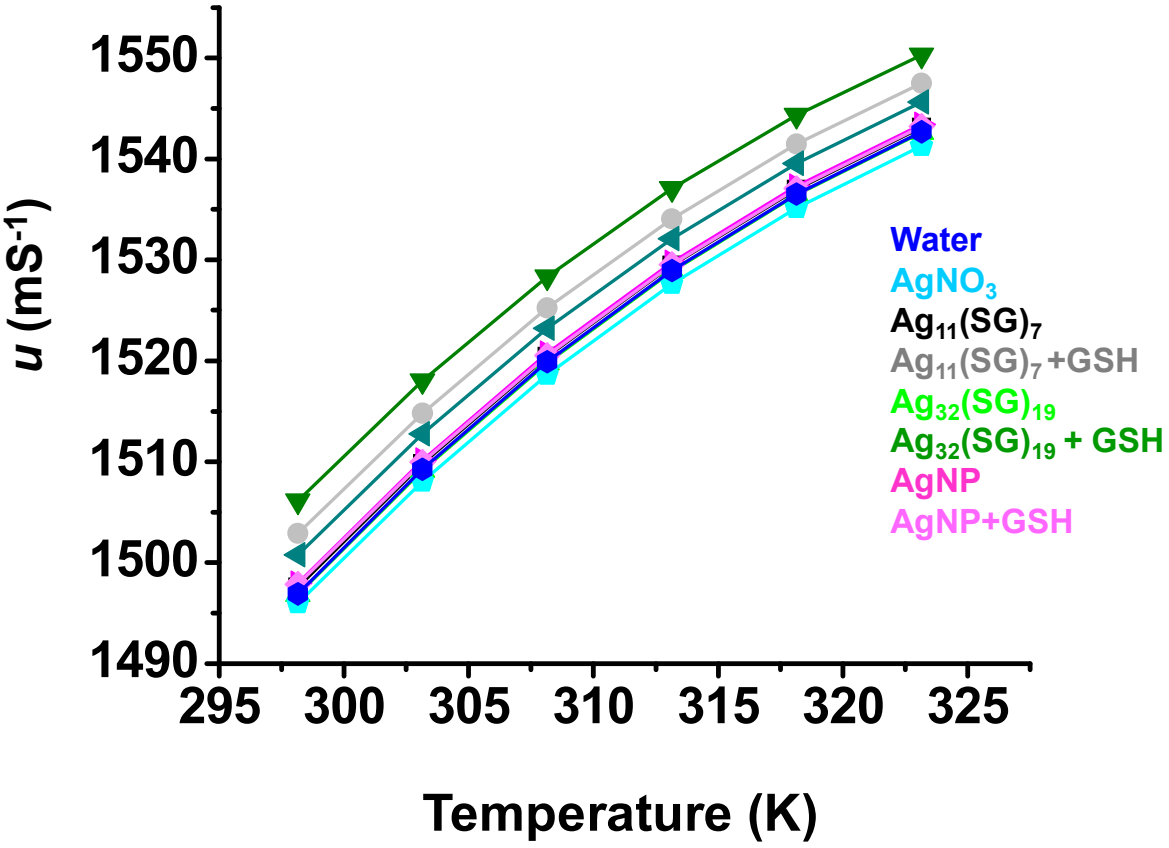

Figure S14. *Temperature dependent change in sound velocity of various samples is showing increase in speed of sound with increasing temperature.*

Supporting Information 15:

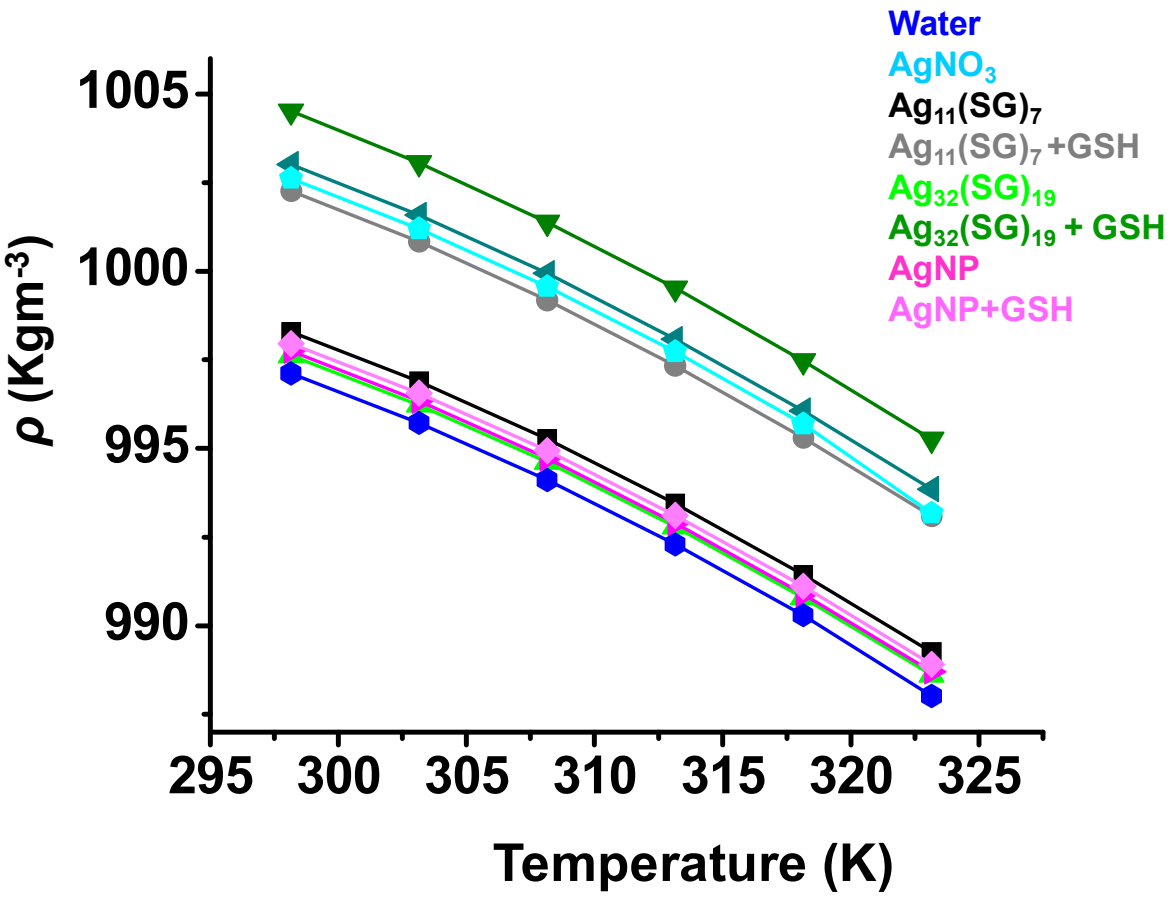

Figure S15. *Temperature dependent change isentropic compressibility of various samples is showing thiolates are more compressible than clusters or nanoparticles.*

Supporting Information 16:

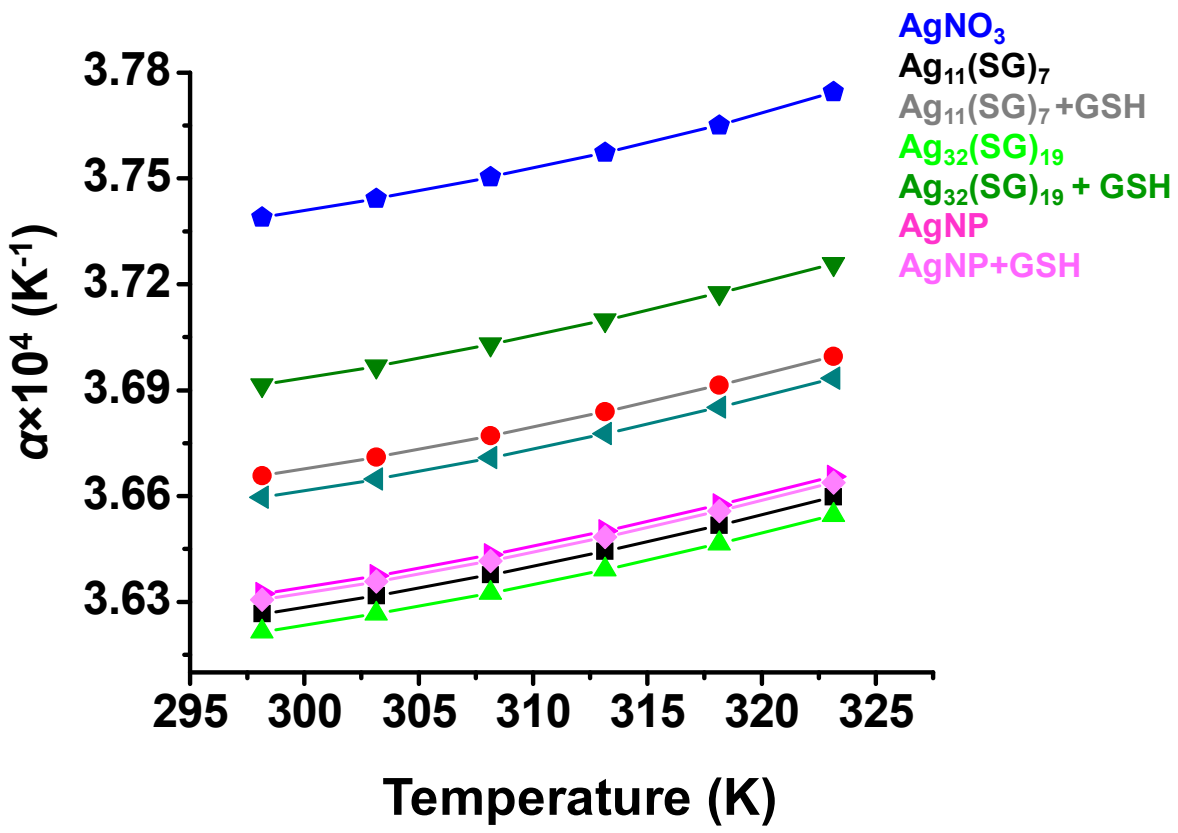

Figure S16. *Temperature dependent change in coefficient of thermal expansion of various samples is showing thiolates are more expandable than clusters or nanoparticles.*

Supporting Information 17:

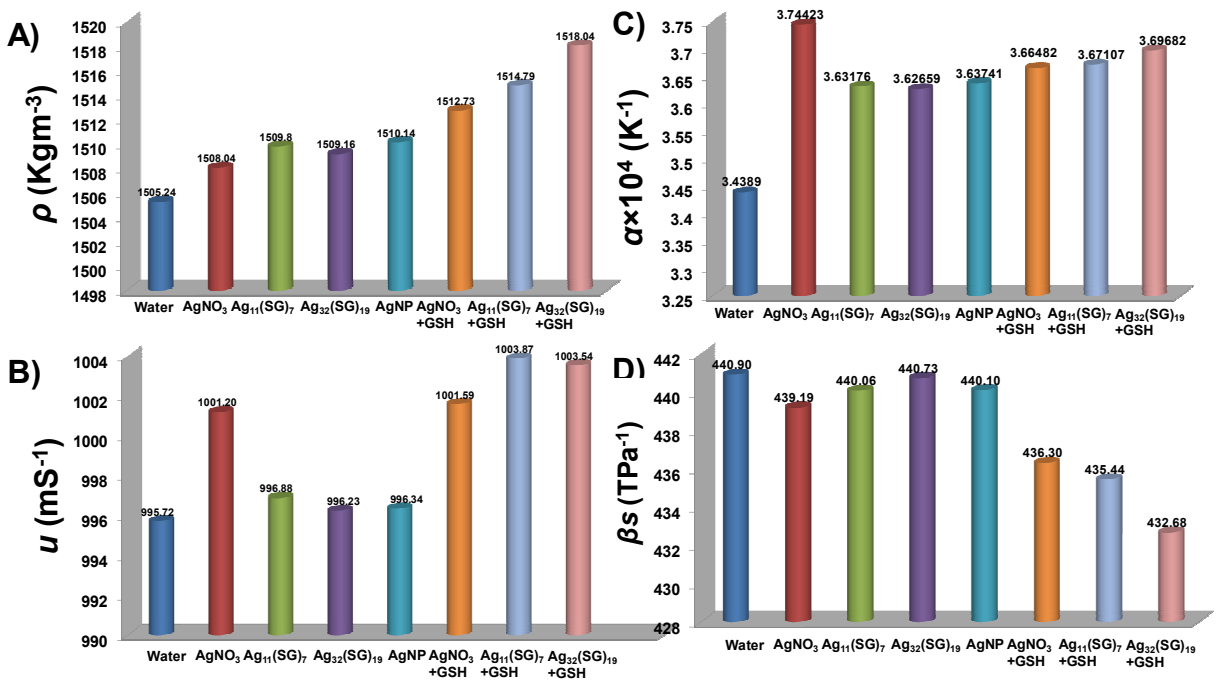

Figure S17. *Comparative A) speed of sound, B) sound velocity, C) isothermal expansion and D) isentropic compressibility of different materials at 303K.*