

Electronic Supplementary Information

Possible Isomers in Ligand Protected Ag₁₁ Cluster Ions Identified by Ion Mobility Mass Spectrometry and Fragmented by Surface Induced Dissociation

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Content:

S/N	Description	Page Number
FigureS1	ESI-IM-MS of Ag ₁₁ (SG) ₇	Page 4
FigureS2	ESI-IM-MS/MS of Ag ₁₁ (SG) ₇ ³⁻ at CID 10	Page 5
FigureS3	ESI-IM-MS/MS of Ag ₁₁ (SG) ₇ ³⁻ at CID 20	Page 6
FigureS4	ESI-IM-MS/MS of Ag ₁₁ (SG) ₇ ³⁻ at CID 30	Page 7
FigureS5	ESI-IM-MS/MS of Ag ₁₁ (SG) ₇ ³⁻ at CID 40	Page 8
FigureS6	ESI-IM-MS/MS of Ag ₁₁ (SG) ₇ ³⁻ in SID mode	Page 9
FigureS7	DFT optimized structures of Ag ₁₁ (SMe) ₇	Page 10

Materials and Methods:

Materials:

Silver nitrate, glutathione and sodium borohydride were purchased from Sigma Aldrich and used without any further purification. MilliQ water was used throughout the experiments.

Methods:

Synthesis of Ag₁₁(SG)₇:

Ag₁₁(SG)₇ was synthesized following recently reported procedure.¹ Briefly, 230 mg of GSH was added to 200 mL of ice cold MeOH and stirred for 15 min. 23 mg of AgNO₃ was dissolved in 0.5 mL of milliQ water and added drop wise to the GSH solution and the mixture was allowed to stir for about 30 min to form thiolate. The resulting thiolate was reduced by slowly adding 53 mg of NaBH₄ in 7 mL of ice cold milliQ water. The resulting mixture was allowed to stir for another half an hour. As-synthesized clusters are not soluble in MeOH; so once clusters start forming, they precipitate. At this moment, stirring was stopped and the solution was kept undisturbed for 30 min for complete precipitation of the clusters. The precipitate was washed repeatedly with MeOH to remove excess ligand and NaBH₄. These red luminescent ($\lambda_{em}=705$ nm) clusters showed three distinct absorption peaks at 487, 437 and 393 nm in the optical absorption spectrum. As-synthesized clusters are of high purity as confirmed from polyacrylamide gel separation. The sample was dried using a rotavapor and the powder was dissolved in 1:1 water:MeOH for further ESI MS analysis. ESI MS of these clusters showed 3- and 2- charged species with multiple Na attachments (see Figure S1). Detailed MS/MS analyses were carried out to study the fragmentation pattern.

Reference: Ag₁₁(SG)₇: A new cluster identified by mass spectrometry and optical spectroscopy, A. Baksi, M. S. Bootharaju, X. Chen, H. Hakkinen and T. Pradeep, *J. Phys. Chem. C*, **2014**, 118, 21722-21729.

Experimental Details:

All mass spectrometry experiments reported here were performed on a Waters Synapt G2S instrument that has been modified in-house to include a custom surface induced dissociation (SID) device inserted immediately after the first collision cell. Ionization was performed using electrospray ionization in negative mode using an ionization voltage of -1.6 to -1.8 kV and a source temperature of 40 °C. Following ionization and desolvation, the ions are transmitted through the T-wave region, including the ion mobility cell where ions are separated based on their size and shape, and finally into the TOF where the ions are detected. For dissociation studies ions are mass selected in the quadrupole which is situated before the T-wave region. In collision induced dissociation (CID) studies, CID was performed in the first T-wave region (trap) which has been truncated to accommodate the SID device, situated between the trap and ion mobility cell. In SID studies, the voltages applied to the DC electrodes is altered to direct the ions towards the surface for collision, further details of the instrument and its operation can be found elsewhere.² The collision energies given are relative numbers and have not been quantified accurately in the present studies.

For all experiments reported here, the wave velocity and wave height in the trap cell were as follows: 300 m/s and 10 V, respectively. A wave velocity of 900 m/s and height of 20 V were used in the ion mobility cell and a wave velocity of 140 m/s and height of 7 V was implemented in the transfer cell. The helium and nitrogen gas flows for the helium and ion mobility cells were set to 120 and 30 mL/min, respectively.

Typical instrument resolution ($m/\Delta m$) is in the range of 27000 for the mass range and charge state studied which allows precise assignment of the masses and charge state.

Reference: Surface-Induced Dissociation of Ion Mobility-Separated Noncovalent Complexes in a Quadrupole/Time-of-Flight Mass Spectrometer, M. Zhou, C. Huang, V. H. Wysocki, *Anal. Chem.* **2012**, 84, 6016-6023

Electronic Supplementary Information 1

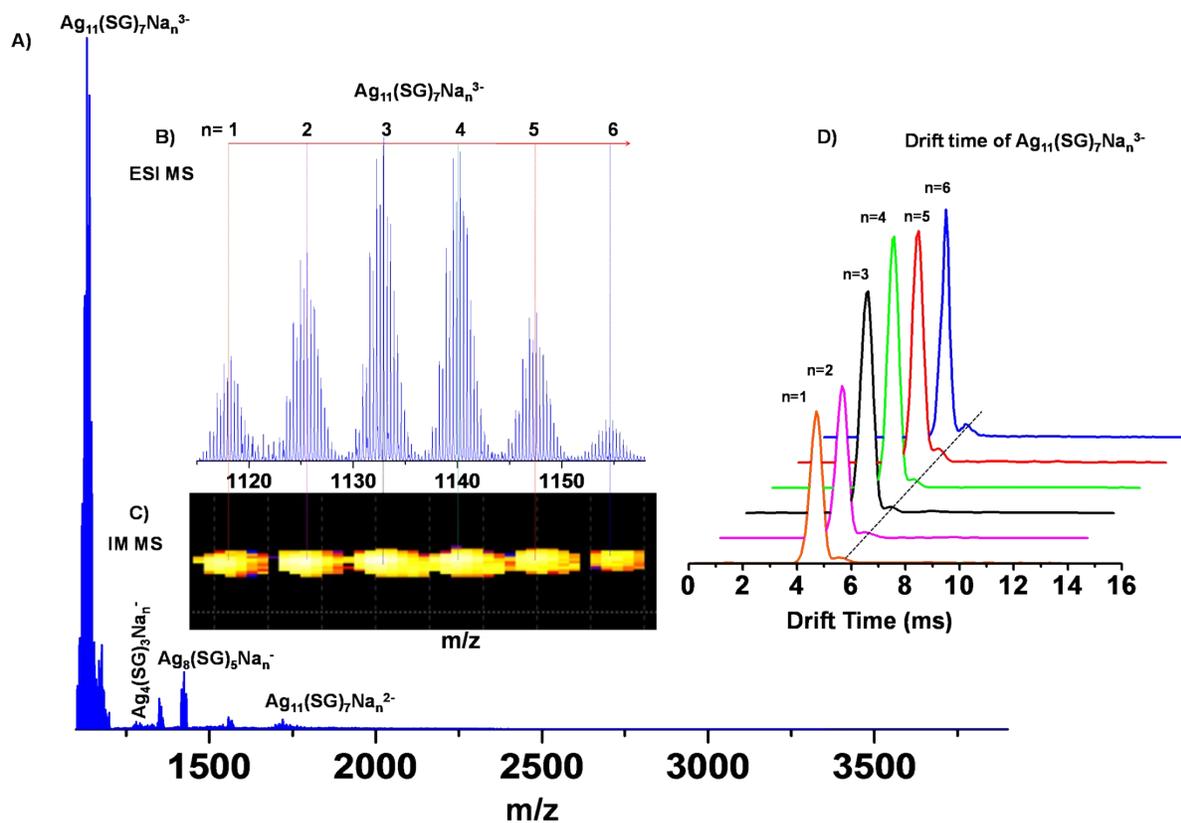


Figure S1: A) ESI MS of $\text{Ag}_{11}(\text{SG})_7$ showing triply and doubly charged ion with multiple Na attachments to the carboxylic groups of the ligand glutathione. B) Triply charged ion is expanded. The corresponding IM-MS is shown in C) and the peak positions are compared. D) Selected ion drift time of these species where two peaks imply presence of two isomers.

Electronic Supplementary Information 2

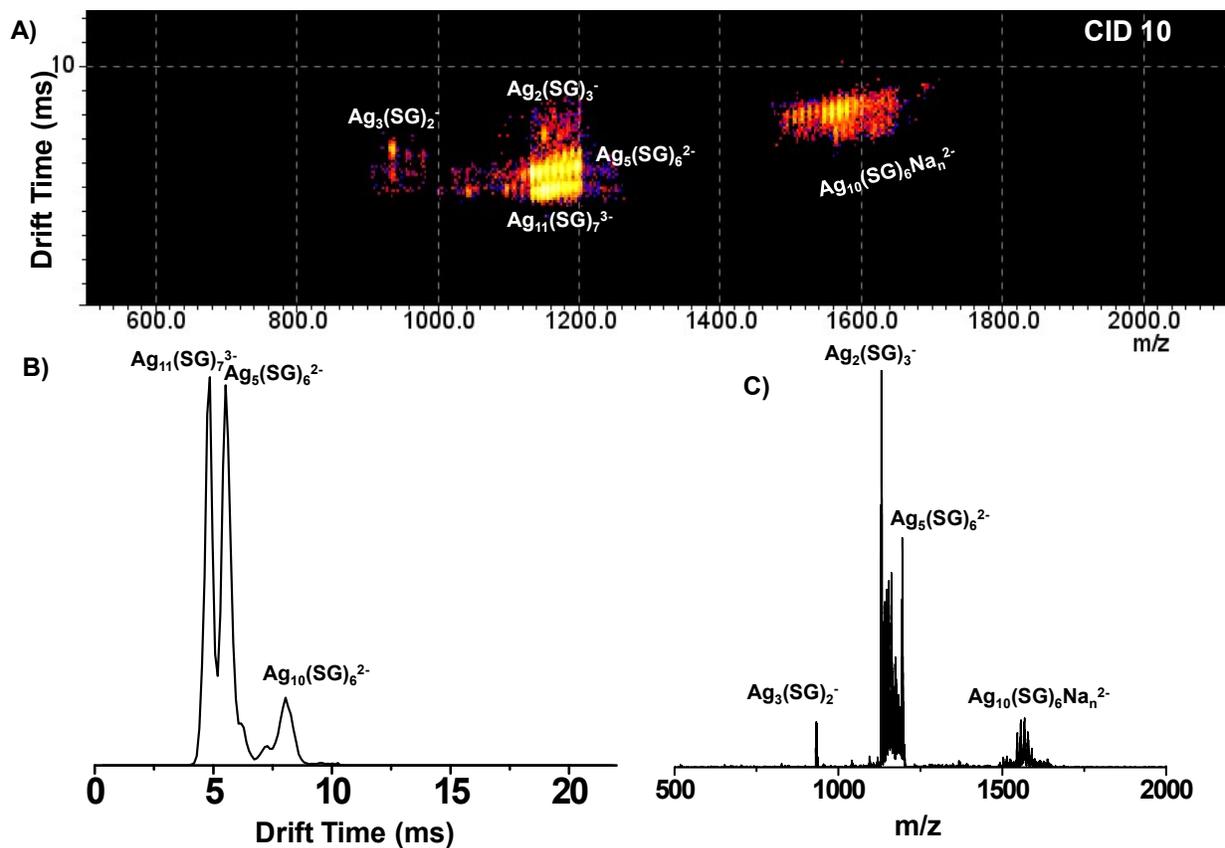


Figure S2: A) ESI-IM-MS of $\text{Ag}_{11}(\text{SG})_7^{3-}$ at CID 10 showing multiple fragmentation in the plot of ion mobility drift time versus m/z . Corresponding drift time profile and mass spectra are shown in B) and C), respectively.

Electronic Supplementary Information 3

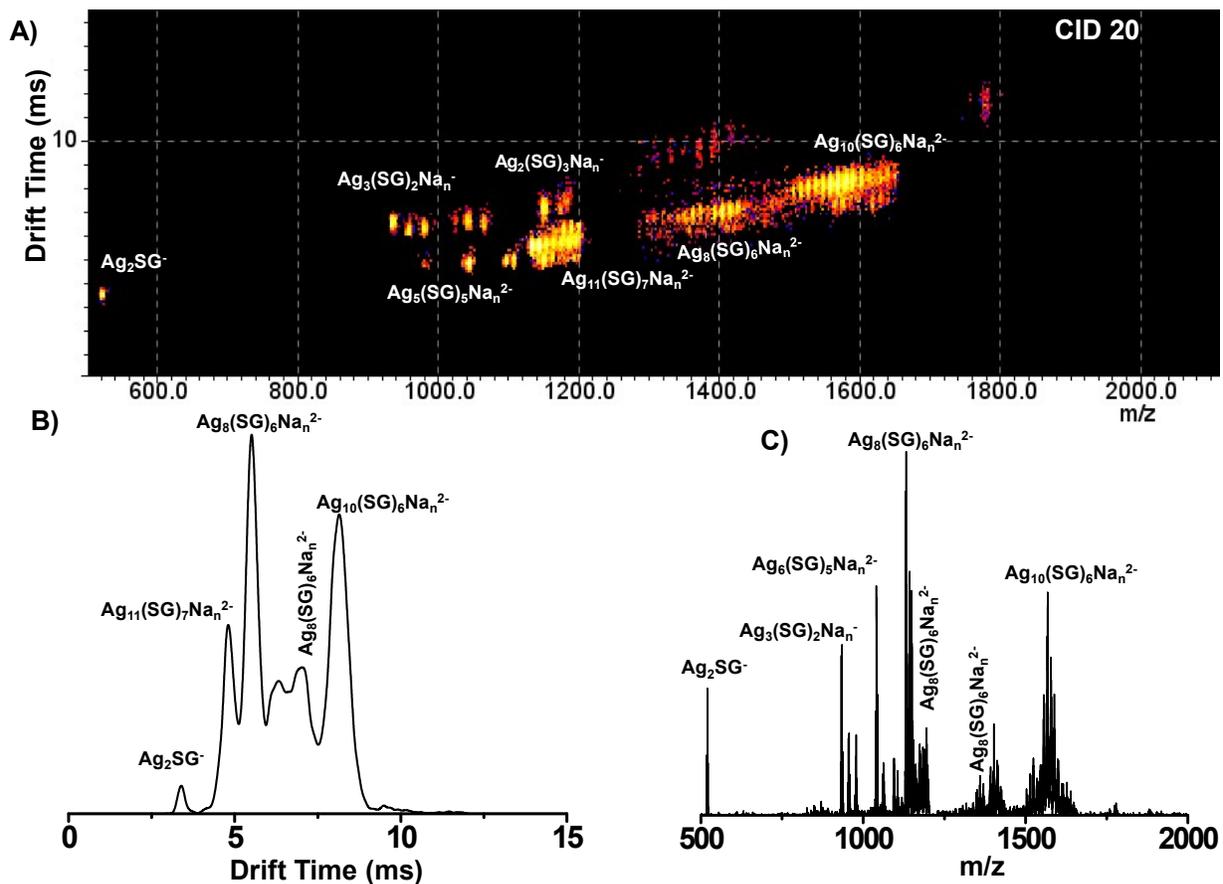


Figure S3: A) ESI-IM-MS of $\text{Ag}_{11}(\text{SG})_7^{3-}$ at CID 20 showing multiple fragmentation in the plot of ion mobility drift time versus m/z . Corresponding drift time profile and mass spectra are shown in B) and C), respectively.

Electronic Supplementary Information 4

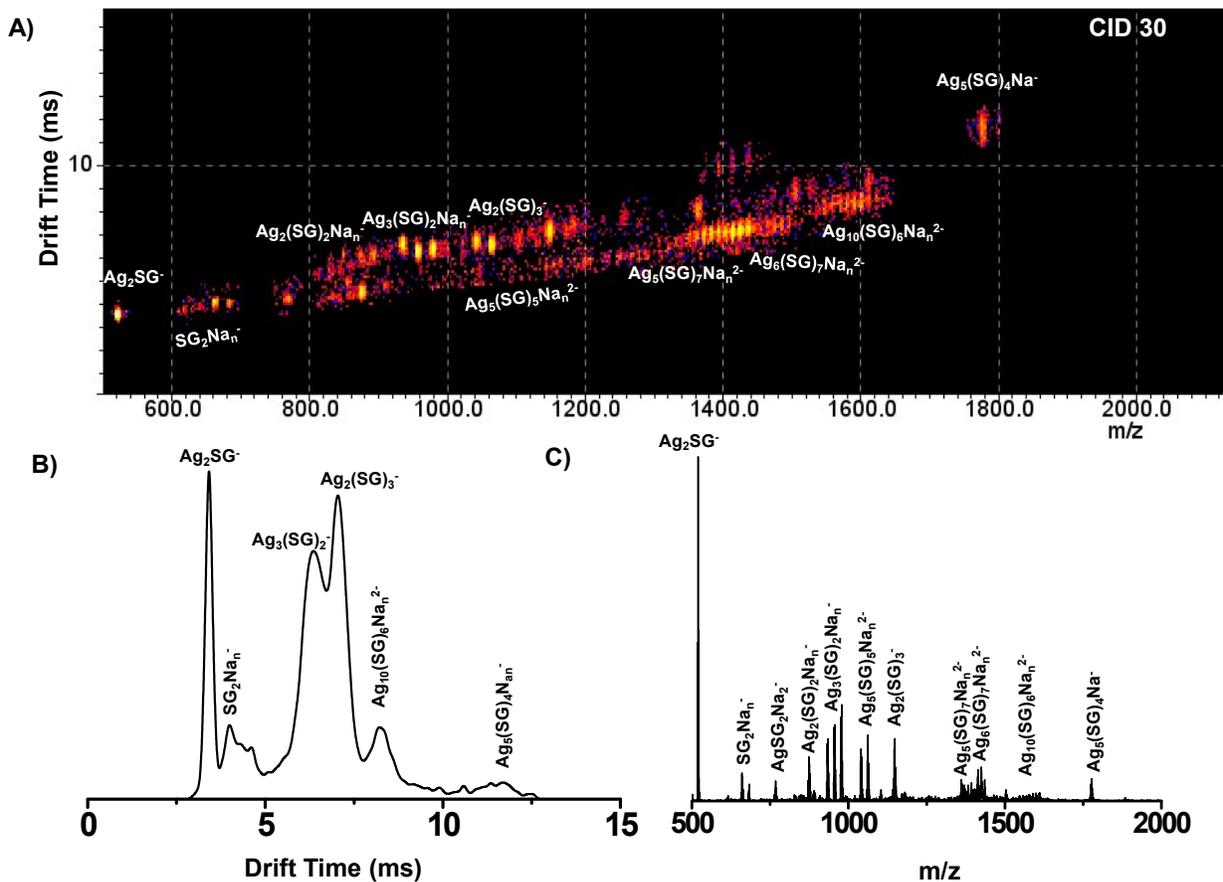


Figure S4: A) ESI-IM-MS of $\text{Ag}_{11}(\text{SG})_7^{3-}$ at CID 30 showing multiple fragmentation in the plot of ion mobility drift time versus m/z . Corresponding drift time profile and mass spectra are shown in B) and C), respectively.

Electronic Supplementary Information 5

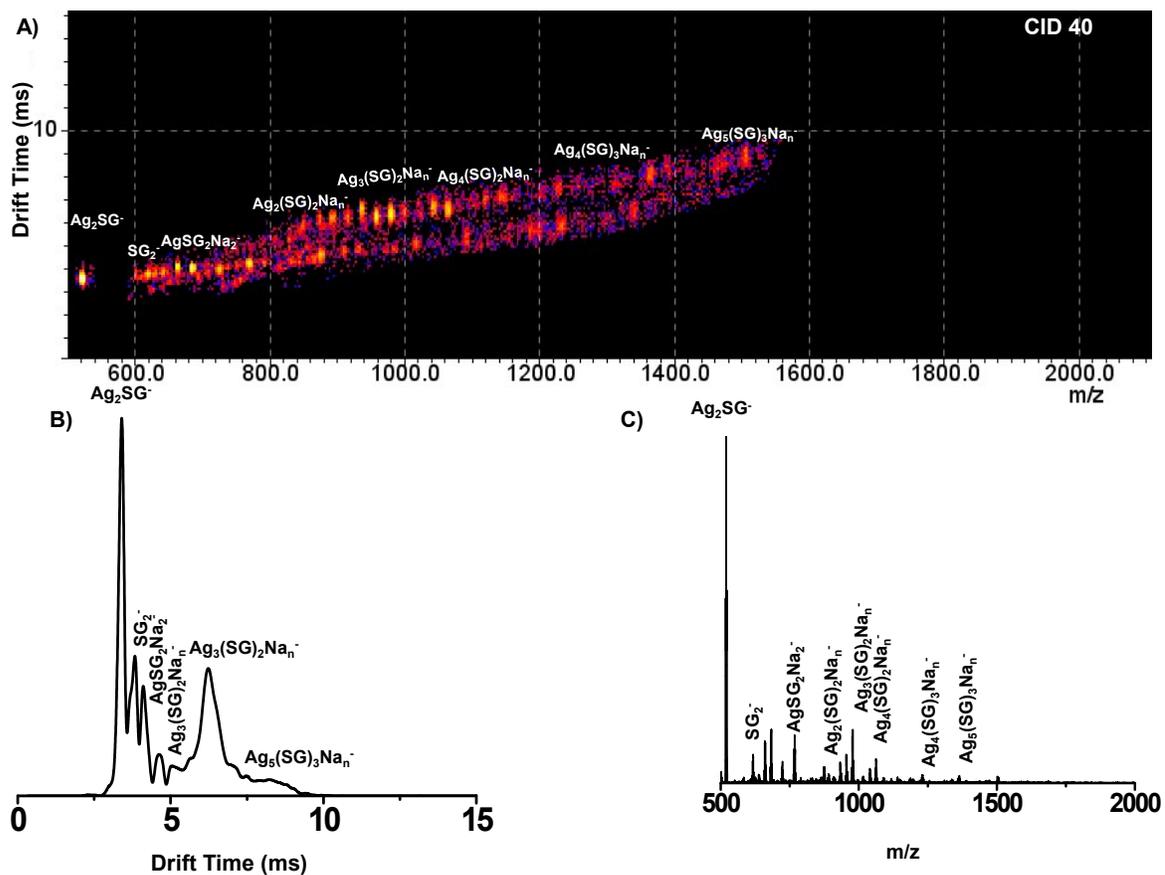


Figure S5: A) ESI-IM-MS of $\text{Ag}_{11}(\text{SG})_7^{3-}$ at CID 30 showing multiple fragmentation in the plot of ion mobility drift time versus m/z . Corresponding drift time profile and mass spectra are shown in B) and C), respectively.

Electronic Supplementary Information 6

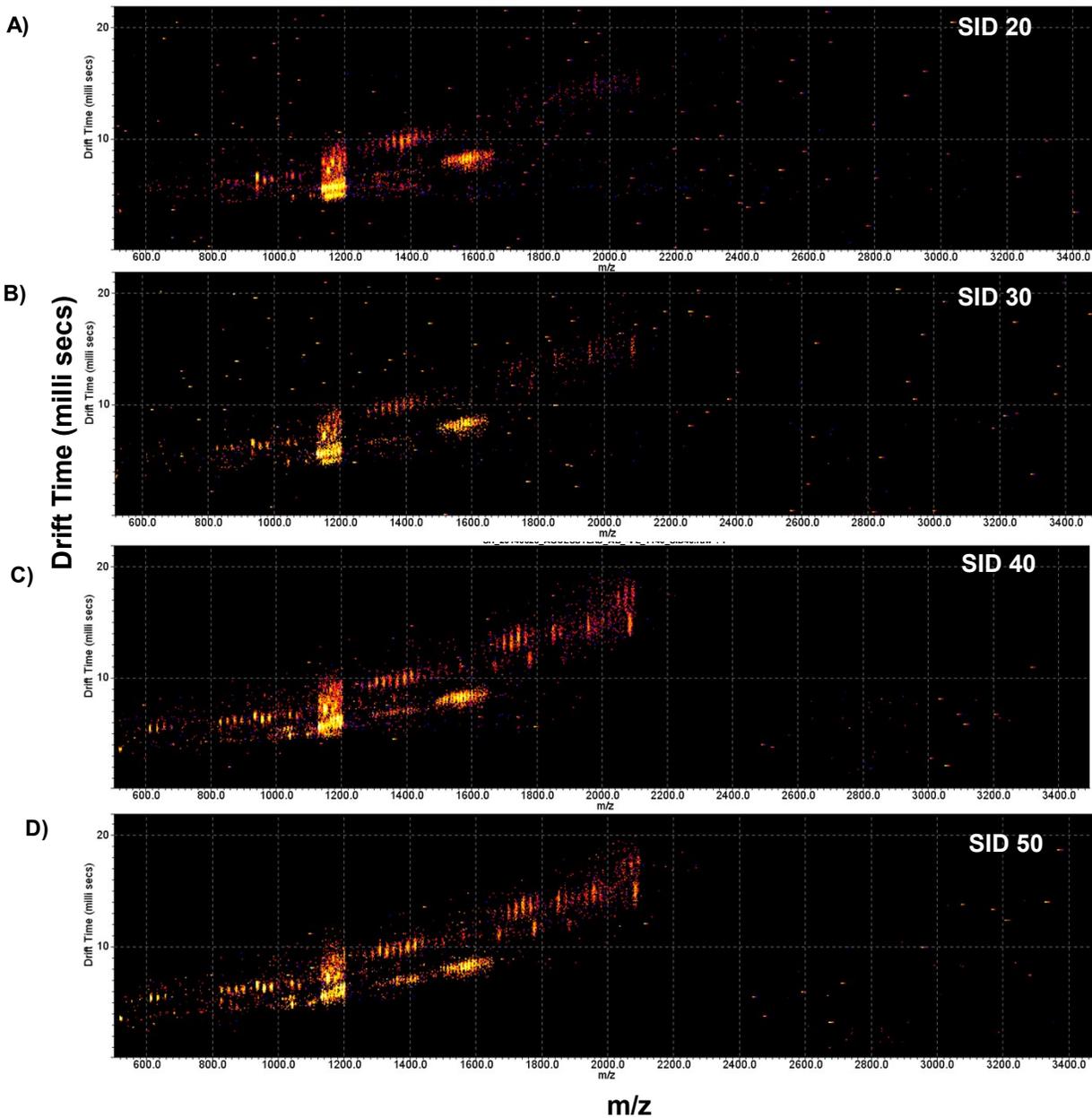
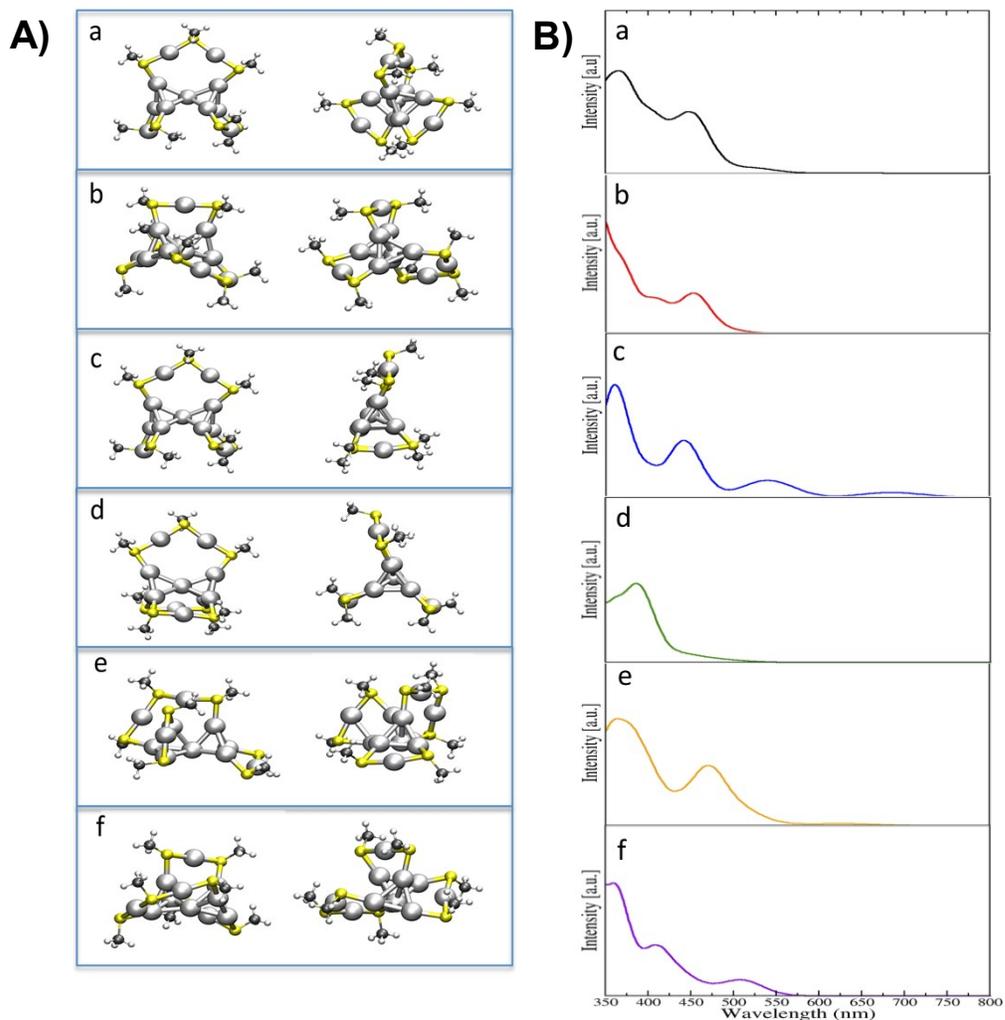


Figure S6: $\text{Ag}_{11}(\text{SG})_7^{3-}$ was fragmented by surface induced dissociation (SID) at different collision energies. Corresponding plots of ion mobility drift time versus m/z are shown in A to D.

Electronic Supplementary Information 7



C)

Isomer	Rel. energy (eV)	HL gap (eV)
a	0.854	1.79
b	0.020	2.08
c	0.647	1.65
d	0	2.29
e	0.535	1.78
f	0.196	2.03

Figure S7: A) Six low energy isomeric structures proposed from density functional theory (two views of each of the structures are shown). Corresponding calculated UV-vis absorption spectra are shown in B. Among which 'f' is matching well with the experimentally observed one. C) HOMO-LUMO gap of the structural isomers are listed. The figures are taken from *J. Phys. Chem. C* **2014**, *118*, 21722–21729.

In our previous work, we have shown six low-energy structures which share an Ag_7 core protected with two $\text{Ag}(\text{SR})_2$ and one $\text{Ag}_2(\text{SR})_3$ motifs (R is taken as CH_3). Figure S7 A shows six structural candidates that are all located within a HOMO-LUMO (HL) gap of 0.85 eV (gaps are given in Figure S7 C) suggesting remarkable electronic stability for them. The computed optical spectra show two to three absorption features (Figure S7 B, a-f), among which structure 'f' is in best agreement. This structural isomer is within 0.2 eV from the lowest-energy structure. Structure 'b' also possesses similar HL gap suggesting a potential isomeric candidate seen experimentally in the gas phase. However, considering the actual ligand GSH, the overall structure may vary slightly as different type of ligand interaction is possible. Moreover, H-bonding among the adjacent ligands may alter the structures significantly (thiolate staple structure). Degree of H-bonding in the case of different isomeric structures may alter the overall size and shape of the cluster ion in the gas phase. Use of glutathione as a ligand would increase the computational effort significantly.