Supporting Information

$Ag_{11}(SG)_7$: A new cluster identified by mass spectrometry and optical spectroscopy

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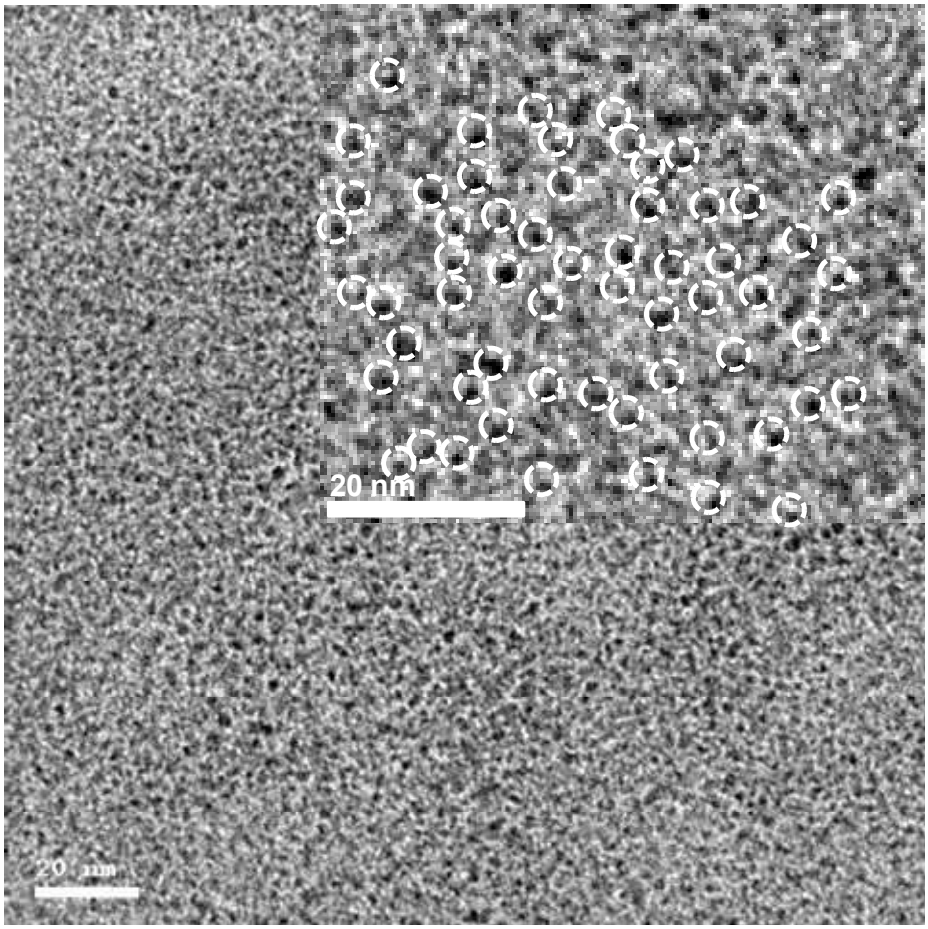

Figure S1: TEM image of the as-synthesized AgSG clusters. A few clusters are marked with circles in the inset (an expanded view).

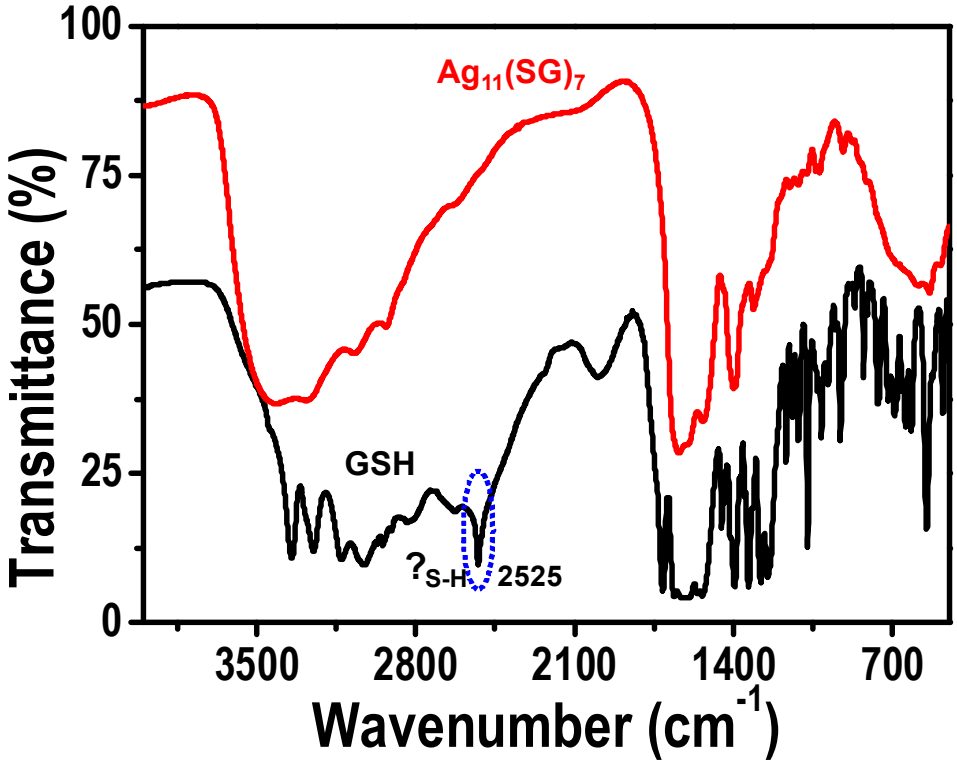

Figure S2: FTIR spectra of GSH and AgSG cluster showing absence of S-H stretching (at 2525 cm^{-1}) for clusters which confirms successful binding of the ligand with Ag.

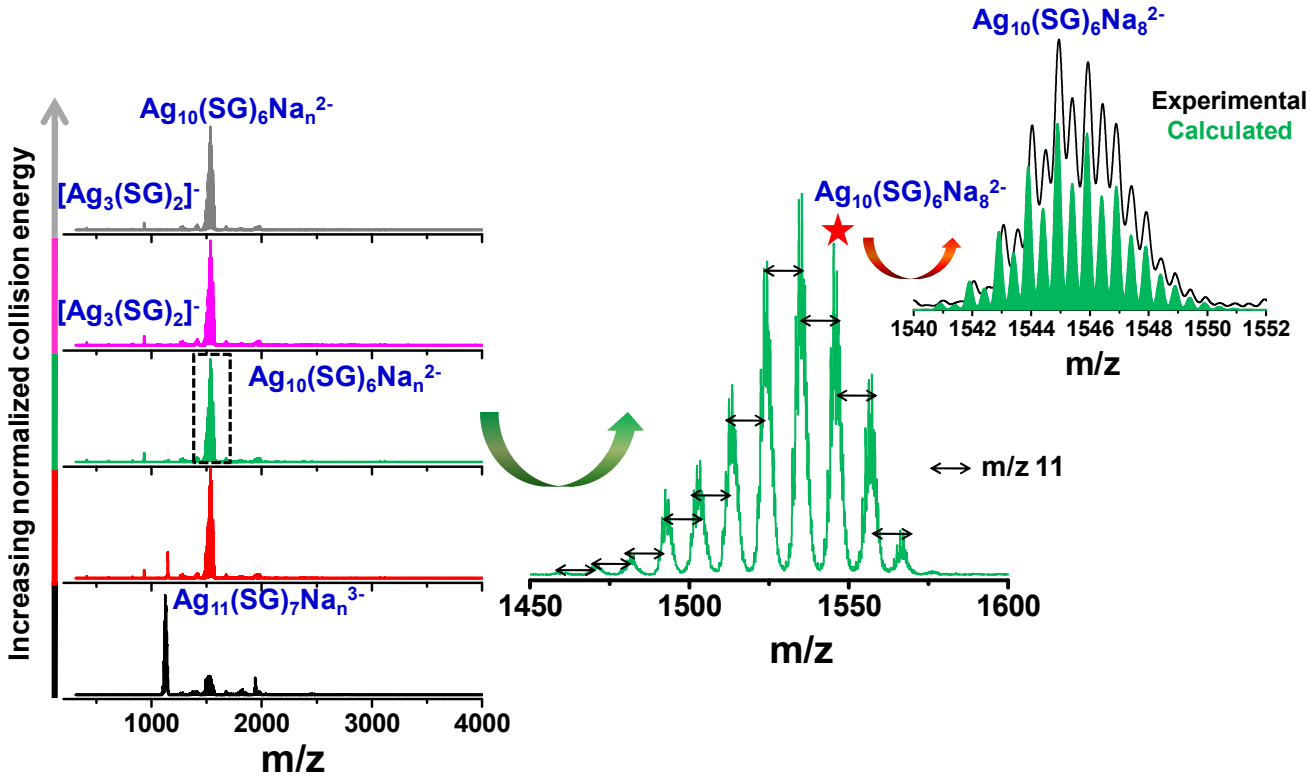

Figure S3: Collision energy dependent ESI MS/MS of $Ag_{11}(SG)_7Na_n^{3-}$ showing one AgSG loss to give $Ag_{10}(SG)_6Na_n^{2-}$. As we keep on increasing the collision energy selectively, $Ag_{10}(SG)_6Na_n^{2-}$ species forms. The Na attachment series is expanded in the inset. The separation in m/z corresponds to Na attachment for a -2 charged species. The experimentally observed isotope pattern matches well with the theoretically calculated one as shown for $Ag_{10}(SG)_6Na_8^{2-}$.

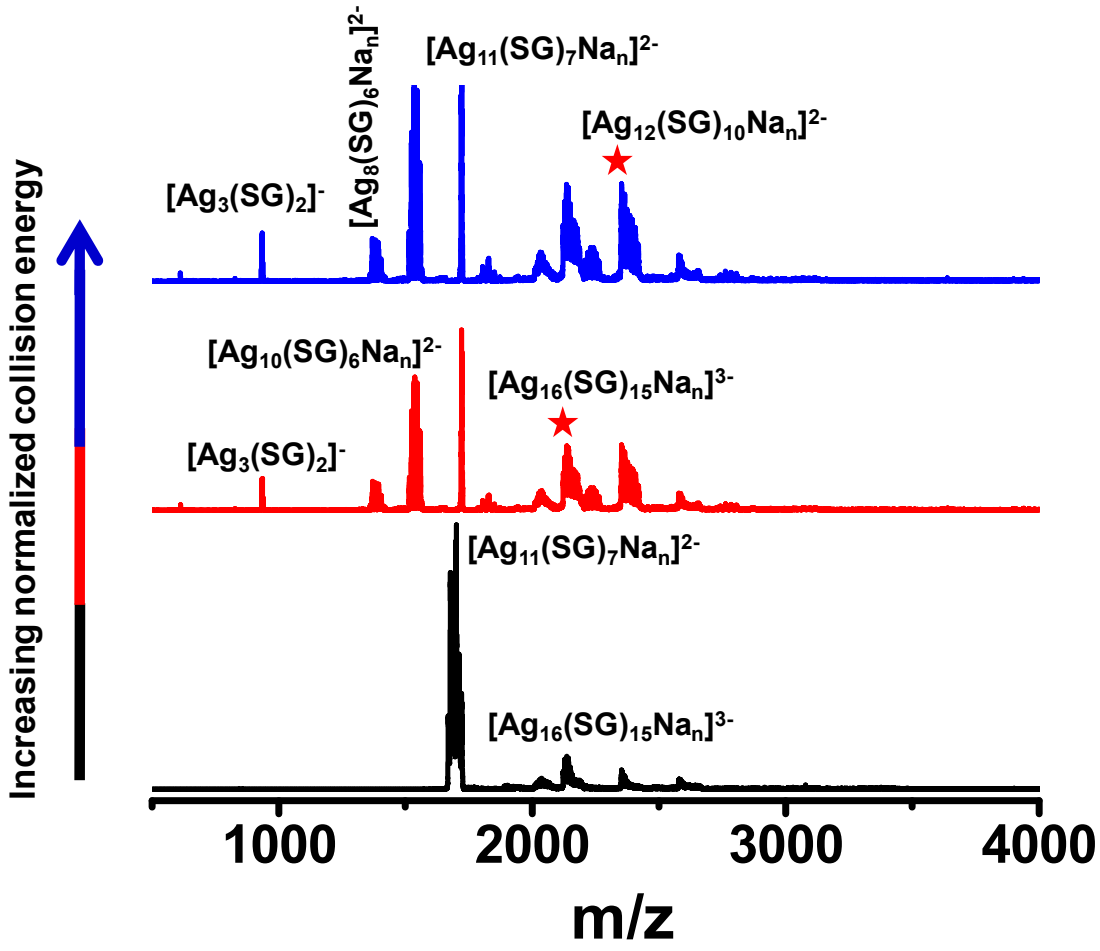

Figure S4: Collision energy dependent ESI MS/MS of $[Ag_{11}(SG)_7Na_n]^{2-}$ showing AgSG loss to give $[Ag_{10}(SG)_6Na_n]^{2-}$. Some higher mass species are also formed. These can be attributed to gas phase association of the fragments in the ion trap.

Computational Methods

The DFT calculations were performed with the GPAW code (1), which implements projector-augmented wave method in a real-space grid. The grid spacing is 0.2Å. Ag($4d^{10}5s^{1}$) , S($3s^{2}3p^{4}$), C($2s^{2}2p^{2}$) and H($1s^{1}$) electrons were regarded as the valence. The PAW setups for Ag included scalar-relativistic corrections. Total energies were evaluated at the GGA-PBE (gradient-corrected functional of Predew, Burke, and Ernzerhof) level (2). All the atoms were relaxed during the geometry optimization until the maximum force acting on atoms was below 0.5eV/Å. Optical absorption spectrum was calculated at the GGA-PBE level using linear-response (LR) time-dependent DFT (LR-TDDFT) formalism in GPAW (3).

(1) Enkovaara, J.; et al. *J. Phys.: Condens. Matter* **2010**, 22, 253202.

(2) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3.

(3) Walter, M.; Häkkinen, H.; Lehtovaara, L.; Puska, M.; Enkovaara, J.; Rostgaard, C.; Mortensen, J. J. *J. Chem. Phys.* **2008**, *128*, 244101.

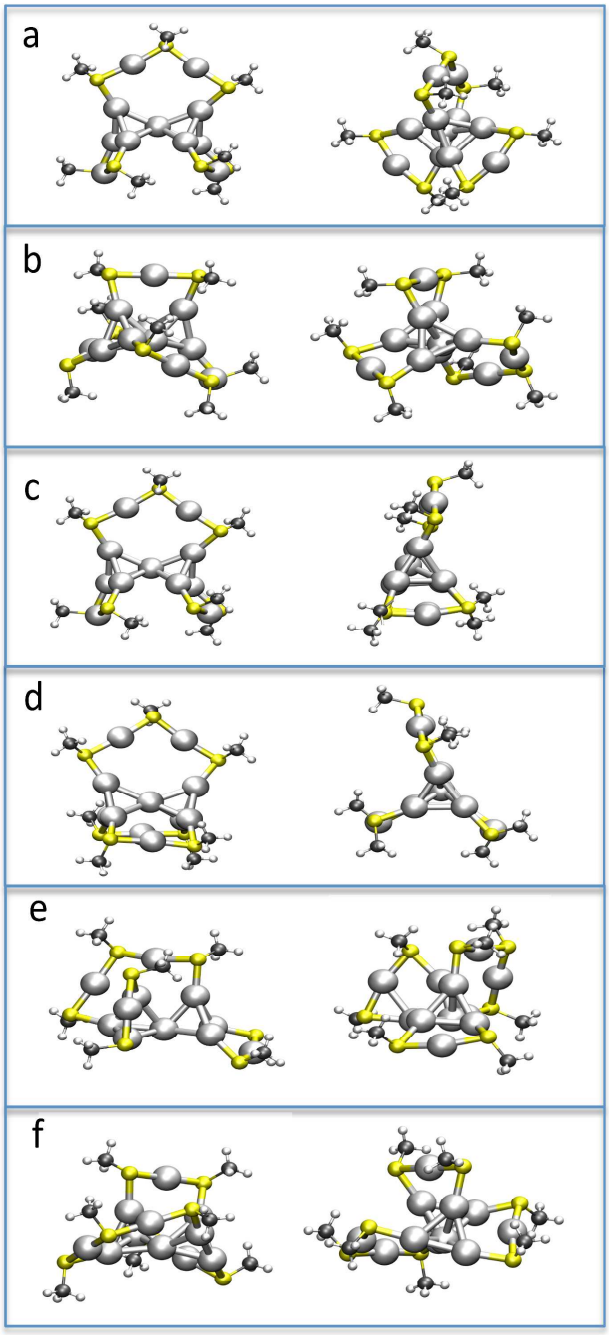

Figure S5: Two views of each of the six low-energy isomers of $Ag_{11}(SCH_3)_7$. Ag: grey, S: yellow, C: dark grey, H: white.

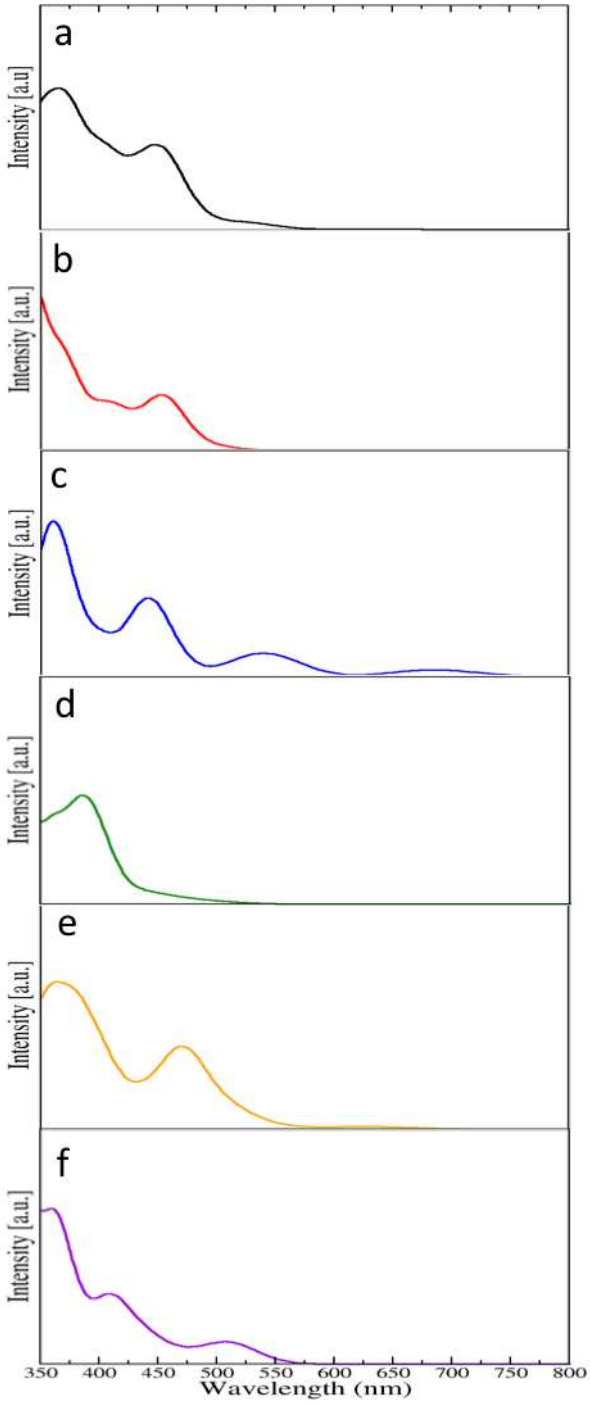

Figure S6: Computed optical spectra of cluster isomers **a** to **f** shown in Figure S10. The individual optical transitions have been folded into a smooth curve by using a Gaussian width of 0.05 eV.

Table S1: Calculated relative total energies and HOMO-LUMO (HL) gaps of isomers **a** to **f** of $Ag_{11}(SCH_3)_7$.

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