Electronic Supplementary Information (ESI):

Formation of a new $Ag_{34}S_3SBB_{20}(CF_3COO)_6^{2+}$ cluster from a hydride protected silver cluster

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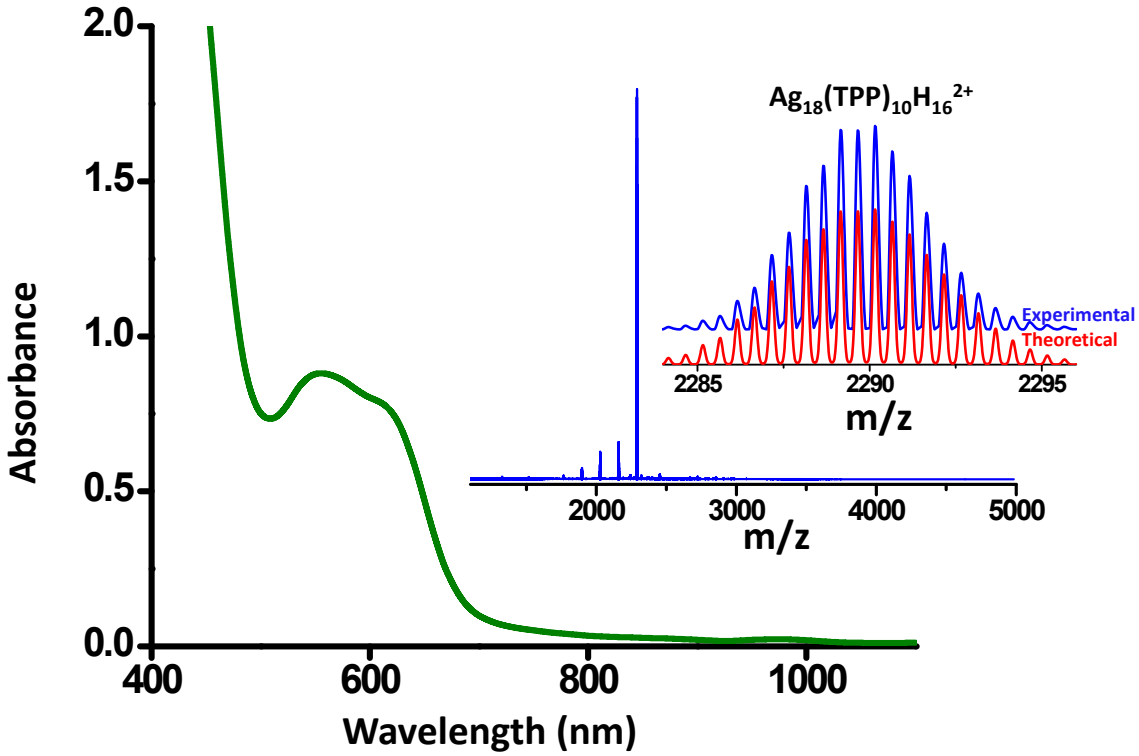


Fig. S1 UV-vis spectrum of Ag_{18} showed two main peaks at 545 and 614 nm. ESI MS spectrum is given inset. The peak at m/z 2290 is expanded and compared with the theoretical spectrum of $Ag_{18}(TPP)_{10}H_{16}^{2+}$.

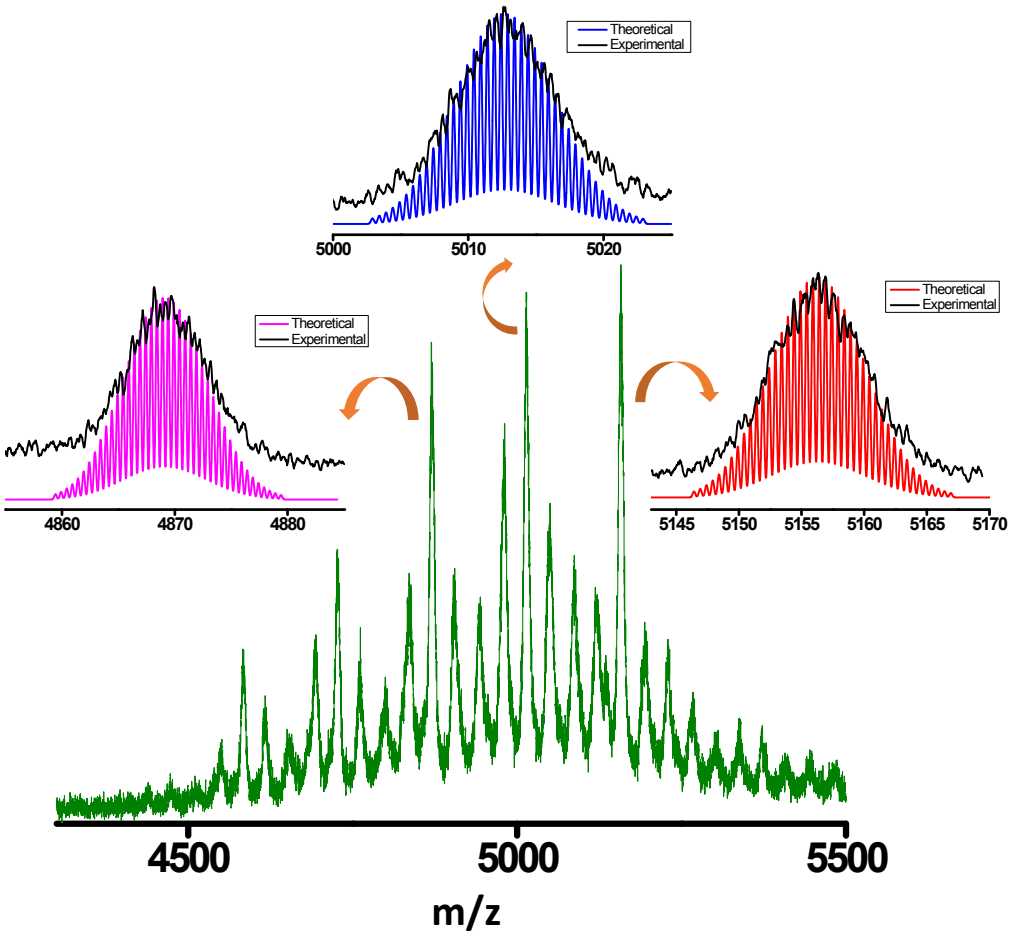


Fig. S2 ESI MS spectrum of 30 min reaction product. Three major peaks are seen at m/z 5156, 5013, and 4869 and are assigned as $Ag_{47}S_7SBB_{28}^{2+}$, $Ag_{46}S_7SBB_{27}^{2+}$, and $Ag_{45}S_7SBB_{26}^{2+}$ respectively.

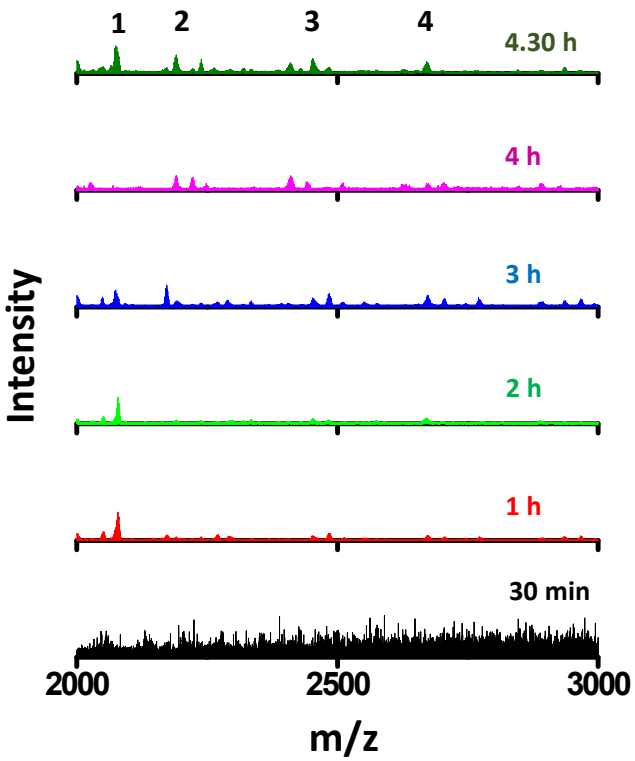


Fig. S3 Lower mass region of time-dependent cluster synthesis. Assignments for the species 1, 2, 3 and 4 are given in table S2.

No	Assignment	m/z
1	$Ag_6SSBB_7CF_3COO^+$	2045
2	$Ag_6S_2SBB_7CF_3COO^+$	2077
3	$Ag_6S_2SBB_7(CF_3COO)_2^+$	2189
4	$Ag_8SBB_7(CF_3COO)_5^+$	2677

Table. S1 Thiolates species present in the lower mass region of time-dependent ESI MS.

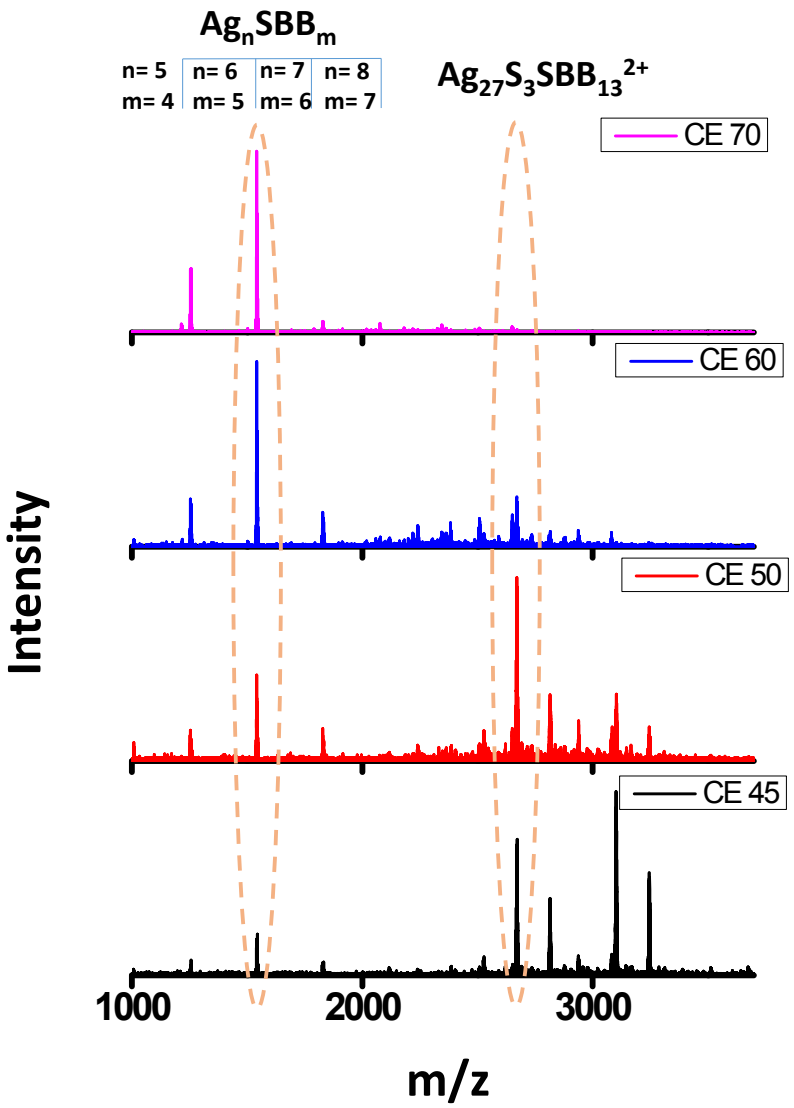
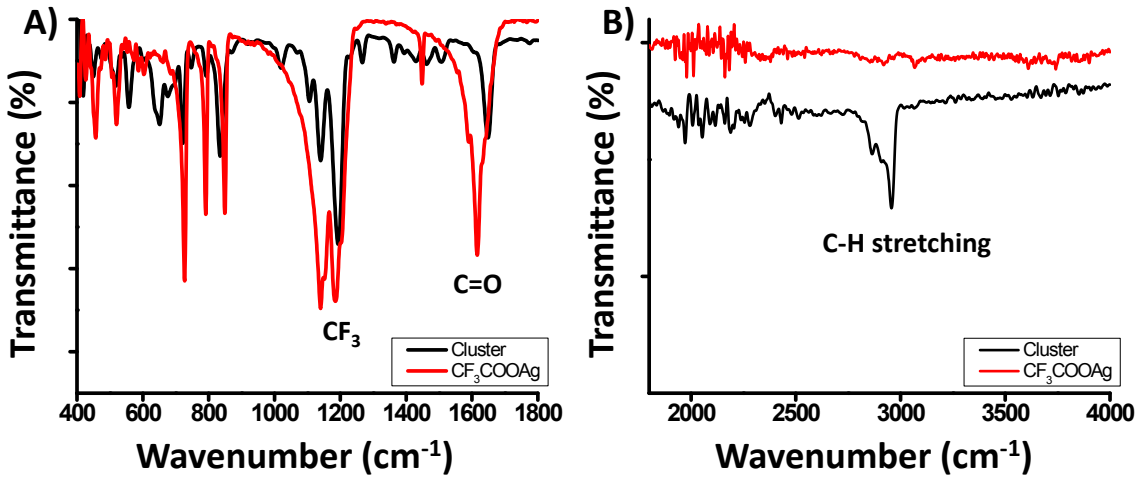


Fig. S4 ESI MS/MS spectrum of the cluster at higher collotion energy (CE, in instrumental unit). Intensity of $Ag_{27}S_3SBB_{13}^{2+}$ peak increased as the CE increased. At higher CE, $Ag_8SBB_7^+$, $Ag_7SBB_6^+$, $Ag_6SBB_5^+$ and $Ag_5SBB_4^+$ were also observed in the lower mass region.



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S5 Comparison of the IR spectrum of cluster and CF_3COOAg (A and B). Cluster showed peaks corresponding to CF_3 and C=O groups.

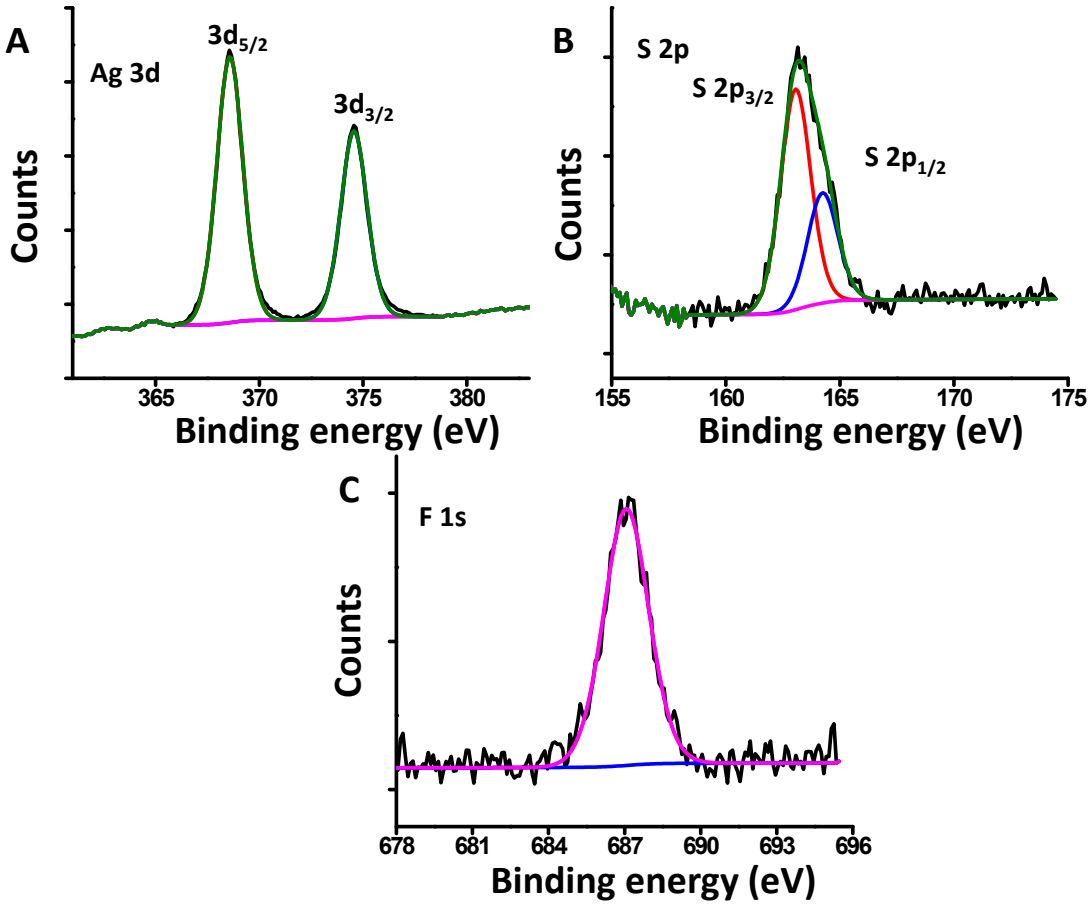

Fig. S6 XPS spectrum of cluster showed the presence of Ag, S and F. Expanded region for (A) Ag 3d, (B) S 2p, and (C) F 1s.

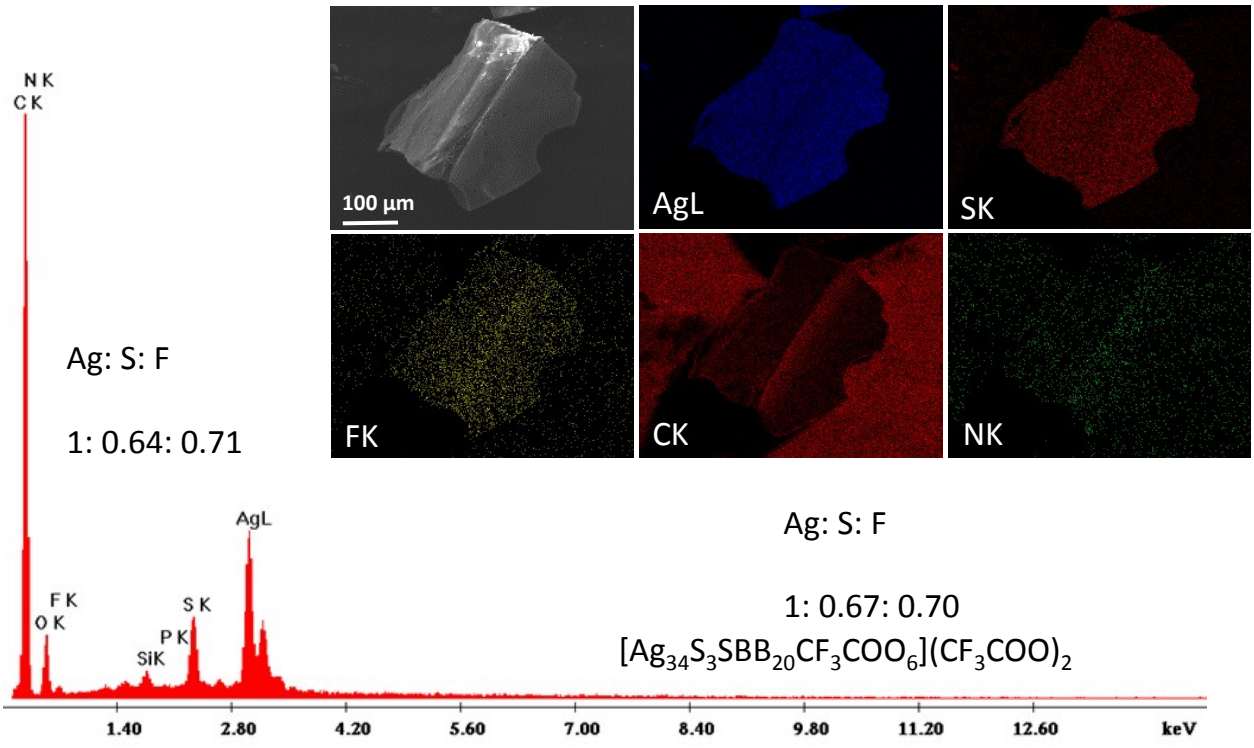

Fig. S7 SEM EDS spectrum and elemental mapping of the cluster.

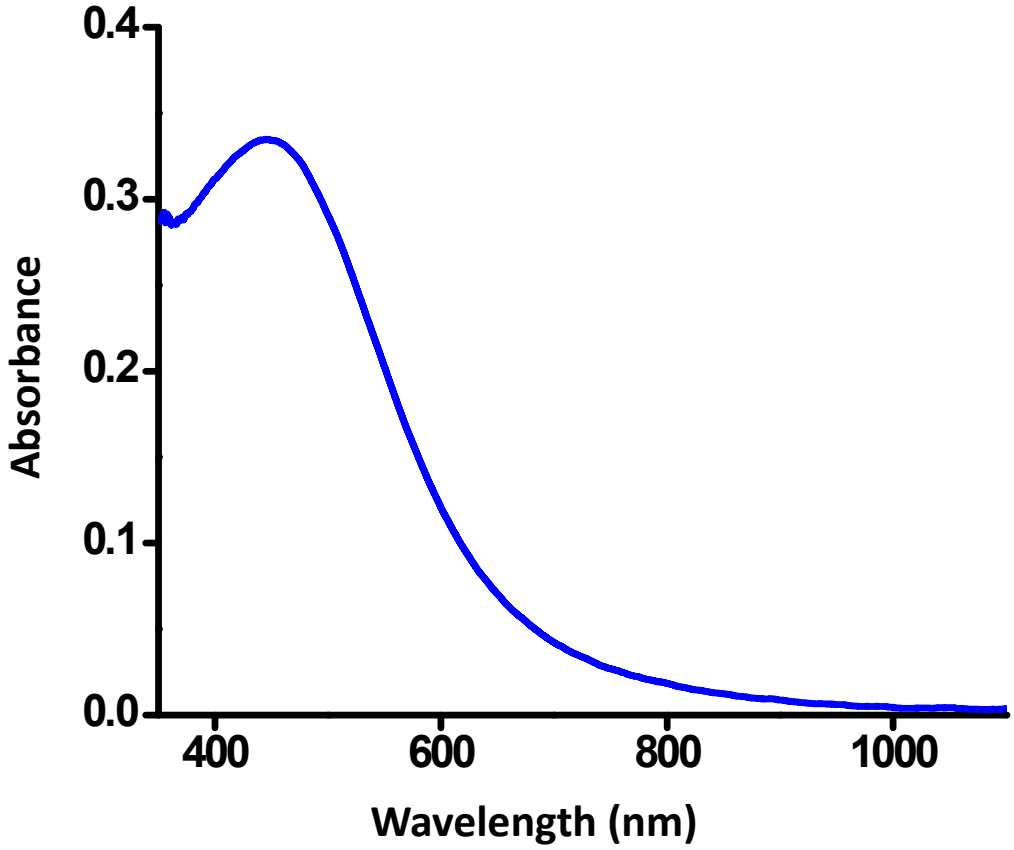

Fig. S8 UV-vis spectrum of the control experiment without the addition of CF_3COOAg. A hexane solution of this showed a peak at 440 nm.

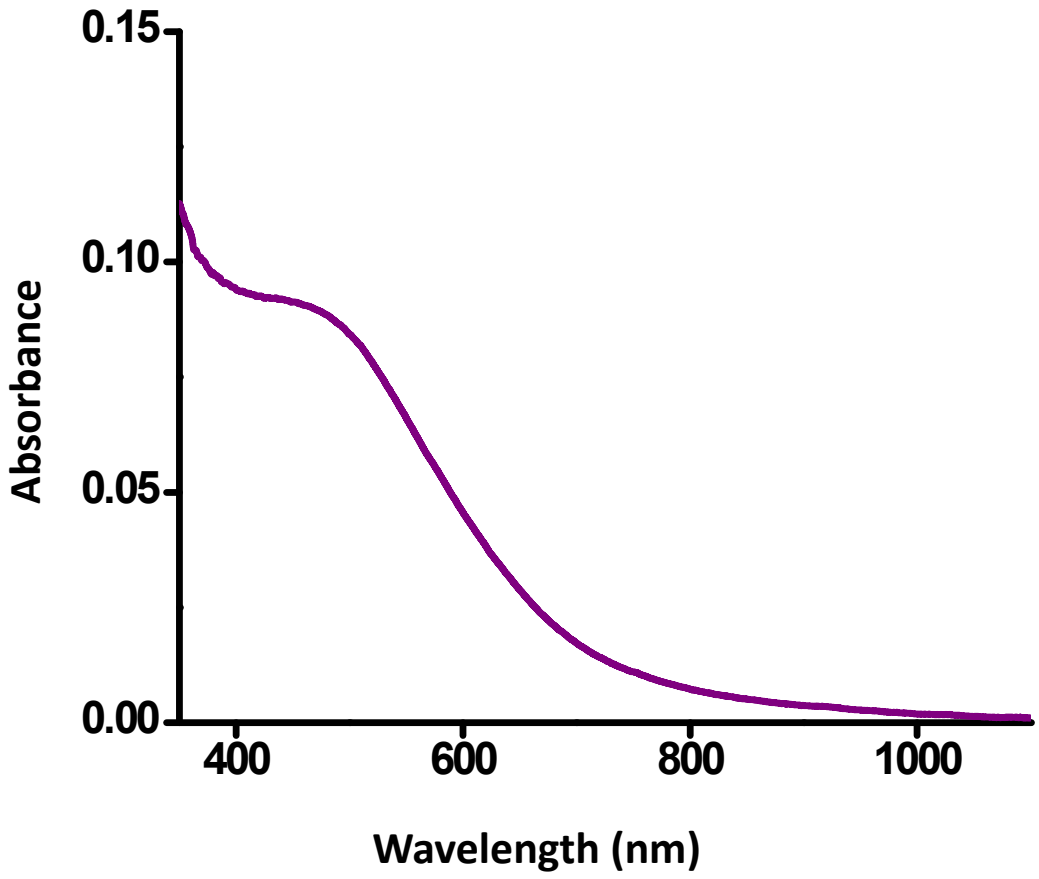

Fig. S9 UV-vis spectrum of the control experiment with Ag_{18} synthesized using CF_3COOAg as a precursor. This sample in hexane showed a broad peak at 465 nm.

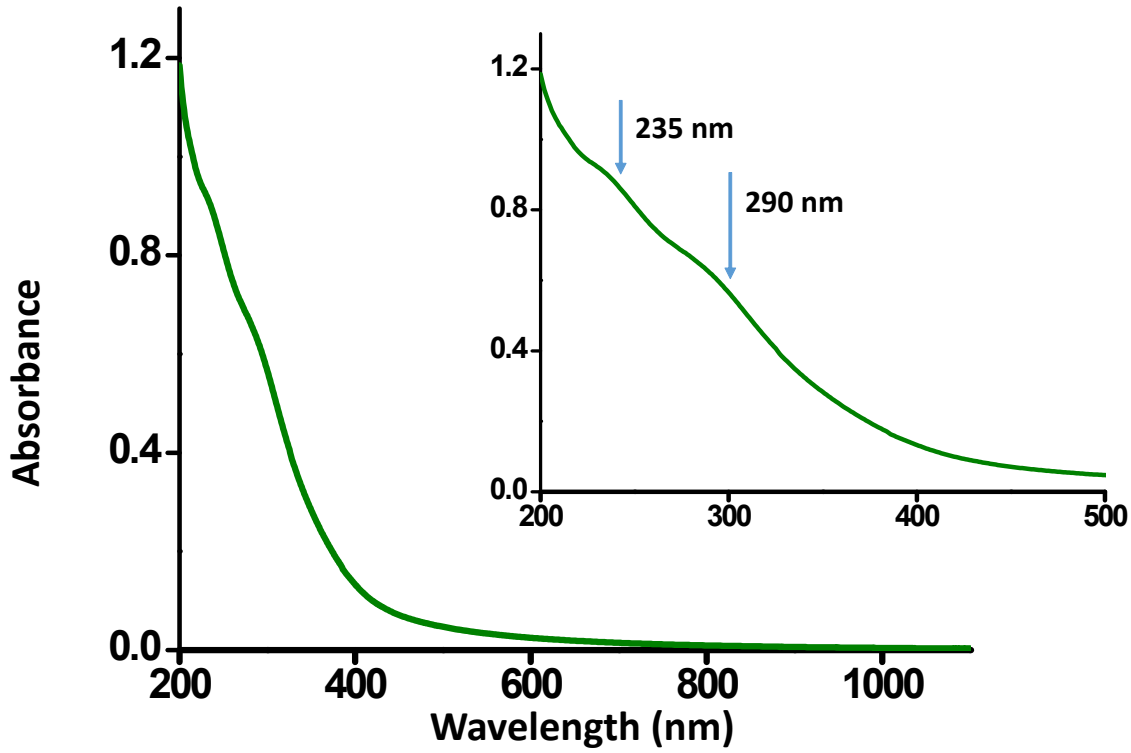

Fig. S10 UV-vis spectrum of the reaction between Ag-SBB and CF_3COOAg. The 200-500 nm region is expanded in the inset. Two humps were observed at 235 nm and 290 nm.

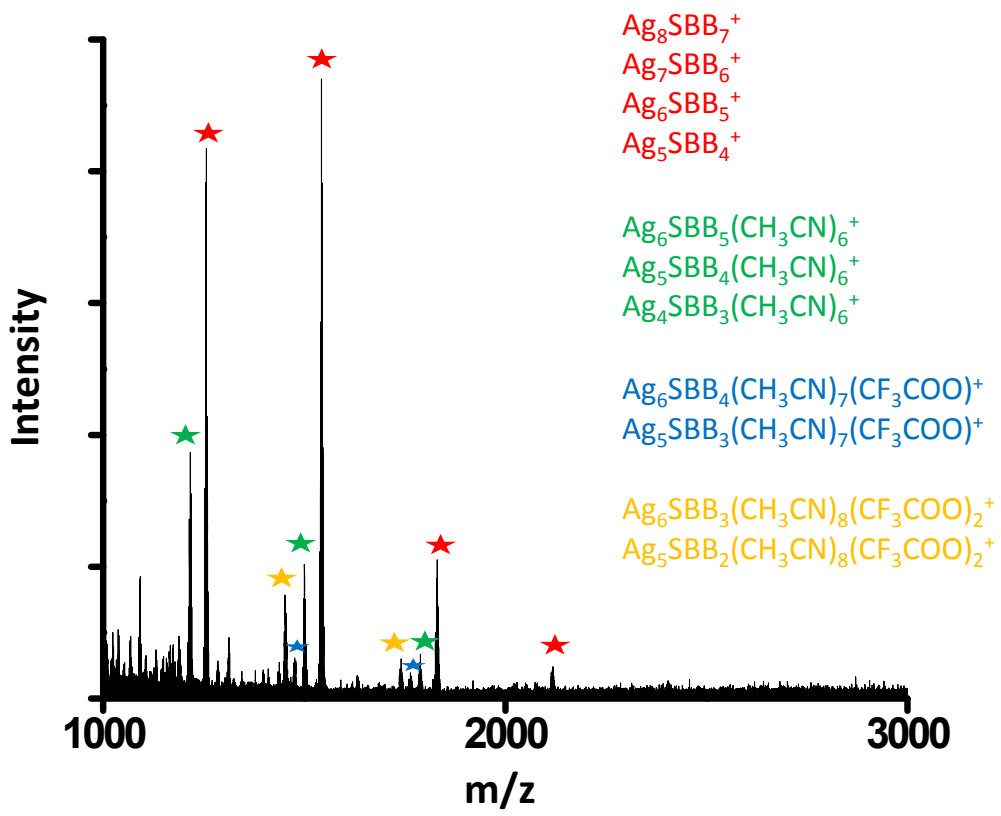

Fig. S11 ESI MS spectrum of the reaction between Ag-SBB and CF_3COOAg. Formation of smaller silver-chalcogenolate clusters were observed.