

Supporting Information

The Mystery of $\text{Ph}_3\text{P}=\text{S}$ Revealed in Magic-Size Ag–S Cluster Nucleation

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Experimental Section

Chemicals

Unless otherwise stated, all chemicals and solvents were purchased from Saen Chemical Technology Co., Ltd (Shanghai, China) and Jingchun Biochemical Technology Co., Ltd (Shanghai, China). Silver nitrate (AgNO_3 , $\geq 99.8\%$, metal basis), Triphenyl phosphorus sulfur ($\text{PPh}=\text{S}$, $\geq 99\%$), 3,3-Dimethyl-1-butyne ($\text{H}^t\text{BuC}\equiv\text{C}$, $\geq 96\%$), Silver hexafluoroantimonate (AgSbF_6 , $\geq 97\%$). Water-18O and Methanol (supreme anhydrous grade, 99.8% , $\text{H}_2\text{O} \leq 20$ ppm) were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Dichloromethane (CH_2Cl_2) was dried and distilled. All other chemicals and solvents for synthesis were of analytical grade and used without further purification. Polymeric $[\text{AgC}\equiv\text{C}^t\text{Bu}]_n$ were prepared according to the literature procedure.¹

Characterization

Intermediate reaction solutions were withdrawn using a dropper in the glass bottle. The samples were diluted with equal methanol before measuring its UV–vis absorption spectra. The ^{31}P NMR spectrum were measured under the same concentration and conditions. The reaction solutions were processed in the following way for ESI-MS measurements. Each reaction solution (100 μL) was cooled for 2 minutes first, mixed with methanol (2 mL) before ESI-MS measurement.

UV–vis spectra were measured on an Analytik Jena S600 UV–visible spectrophotometer. ^{31}P NMR spectra were measured by Bruker Advance nuclear magnetic resonance spectrometer at 160 MHz with H_3PO_4 as reference compound. Electrospray ionization mass spectrometry (ESI-MS) was done on a ESI-TOF-MS spectrometer Agilent 6224 (Agilent Technologies, USA) in the positive ion mode (sample injection rate $4 \text{ mL}\cdot\text{min}^{-1}$, capillary voltage 3500 kV, nebulizer 15 pisp, dry gas $12 \text{ L}\cdot\text{min}^{-1}$ at $325 \text{ }^\circ\text{C}$, and m/z 500–3000). The ESI-MS spectra presented in this study were obtained by monitoring at different times within 1 h. Powder XRD patterns were obtained using a Bruker D8 Advance X-ray diffractometer with (λ ($\text{CuK}\alpha$) = 1.5405 \AA) radiation.

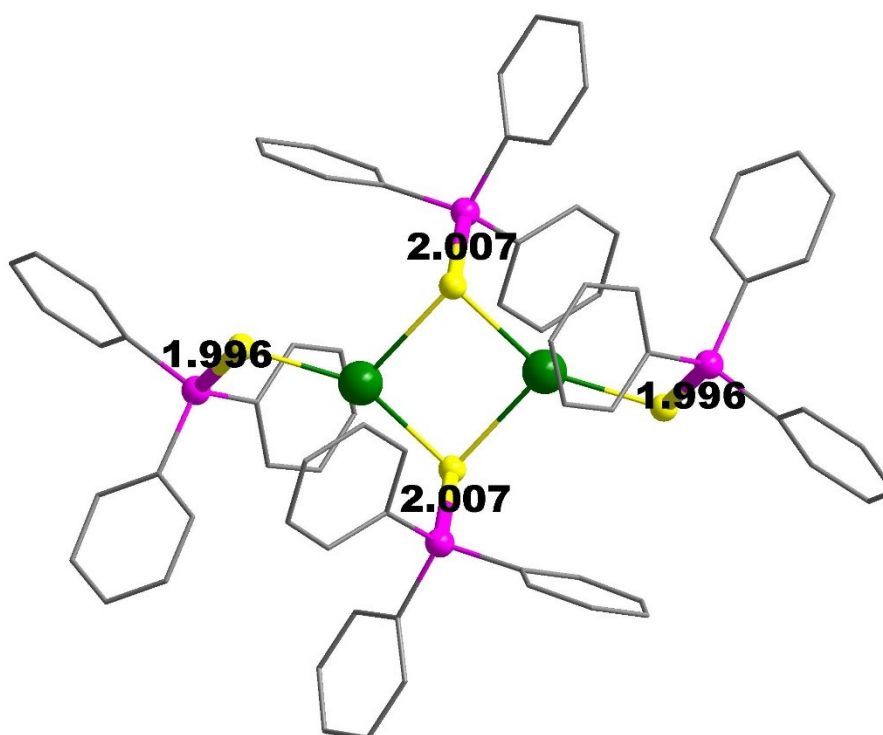
X-ray crystallography

The data collection for single crystal X-ray diffraction was carried out on a Bruker D8 VENTURE diffractometer under 293 K, using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$). With the aid of Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. Further details about of the crystal structure determinations may be obtained free of charge via the Internet at <https://www.ccdc.cam.ac.uk/> CCDC 2193753.

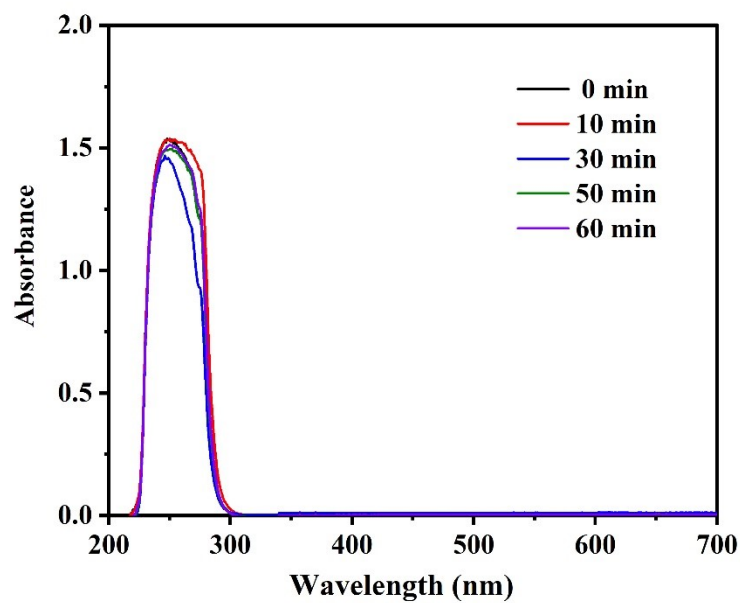
Synthesis and Crystal Data for $[\text{Ag}_2(\text{Ph}_3\text{P}=\text{S})_4](\text{SbF}_6)_2(\text{CH}_2\text{Cl}_2)_2$: AgSbF_6 and Ph_3PS were dissolved in a mixed solvent of methanol and dichloromethane at a molar ratio of

1:2, then the mixture was put in a 60°C oven for 1 h, colorless crystals with a yield of 95% were isolated by evaporating the solvent. $C_{74}H_{64}Ag_2Cl_4F_{12}P_4S_4Sb_2$ ($M = 2054.25$ g/mol): monoclinic, space group $P2_1/c$, $a = 11.425(2)$ Å, $b = 16.178(4)$ Å, $c = 22.012(5)$ Å, $\alpha = 90^\circ$, $\beta = 96.707(8)^\circ$, $\gamma = 90^\circ$, $V = 4040.4(2)$ Å³, $Z = 2$, $T = 298$ K, $\mu = 1.556$ mm⁻¹, $D_{calc} = 1.689$ g/cm³, 24003 reflections, 2 θ range for data collection/° 5.468 to 50.156, 7075 unique ($R_{int} = 0.0401$, $R_{sigma} = 0.0375$) which were used in all calculations. The final R_1 was 0.0542 ($I > 2\sigma(I)$) and wR_2 was 0.1496. Largest diff. peak/hole / e Å⁻³ 1.09/-0.80.

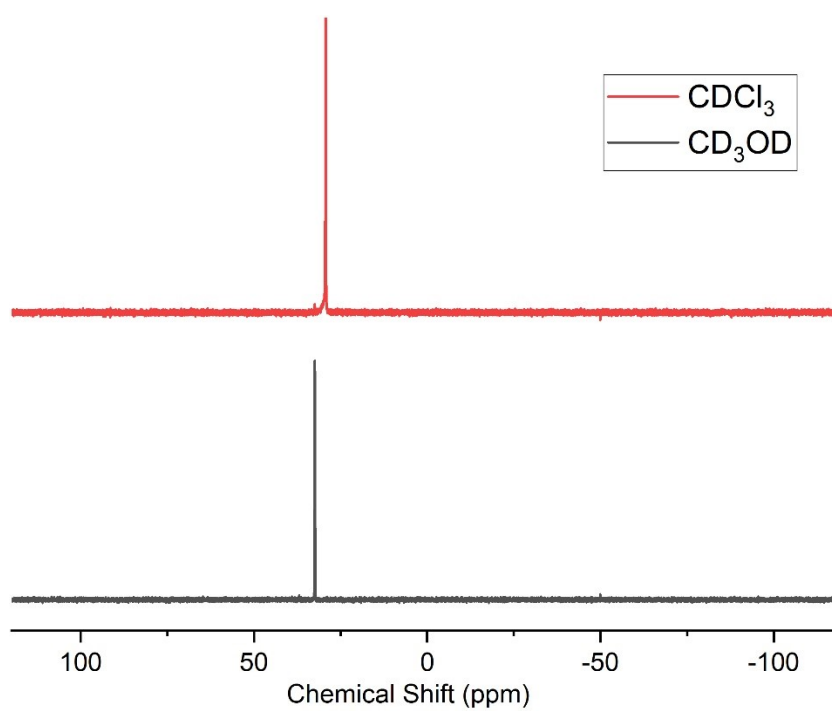
Additional Figures:



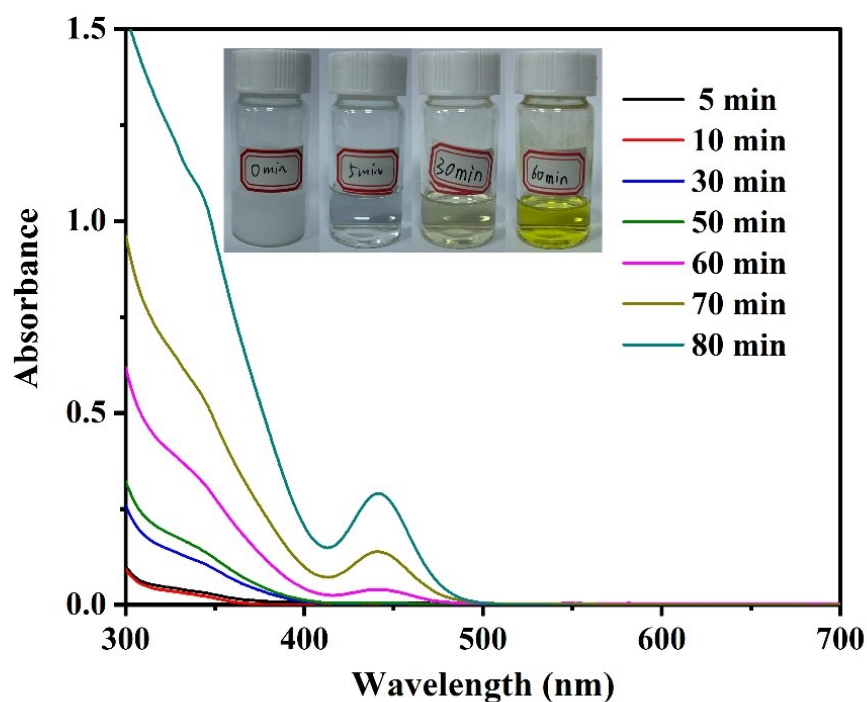
Supplementary Figure 1. Crystal structure of $[Ag_2(Ph_3PS)_4]^{2+}$ (**1**). Color: Ag, green; S, yellow; C, gray; P, purple. The H atom has been omitted for clarity. Bond lengths of P=S are marked in black (Å).



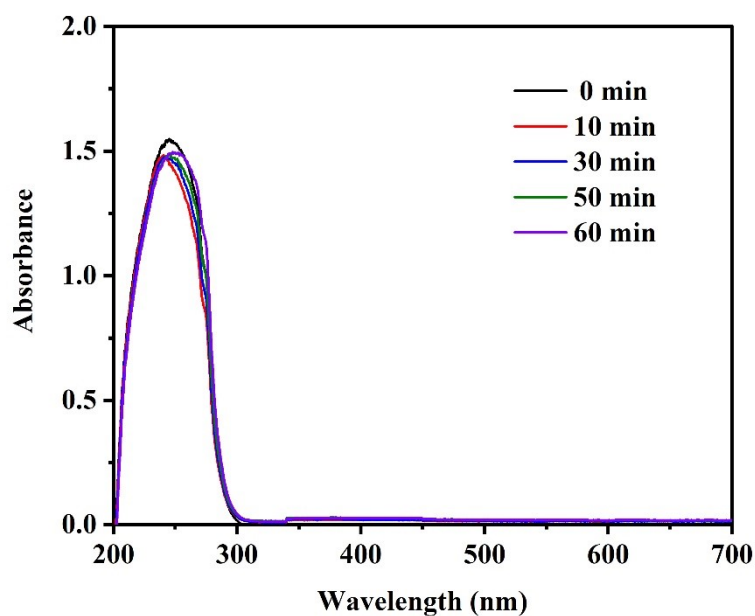
Supplementary Figure 2. Time-dependent UV-vis spectrums of **1** were monitored at 80 °C.



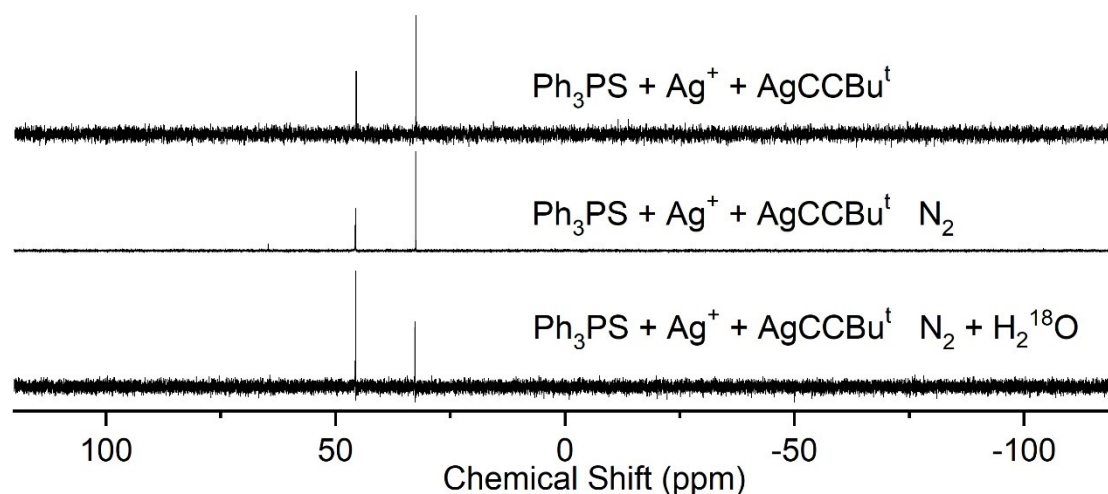
Supplementary Figure 3. ³¹P NMR spectra of Ph₃P=O in CDCl₃ and CD₃OD.



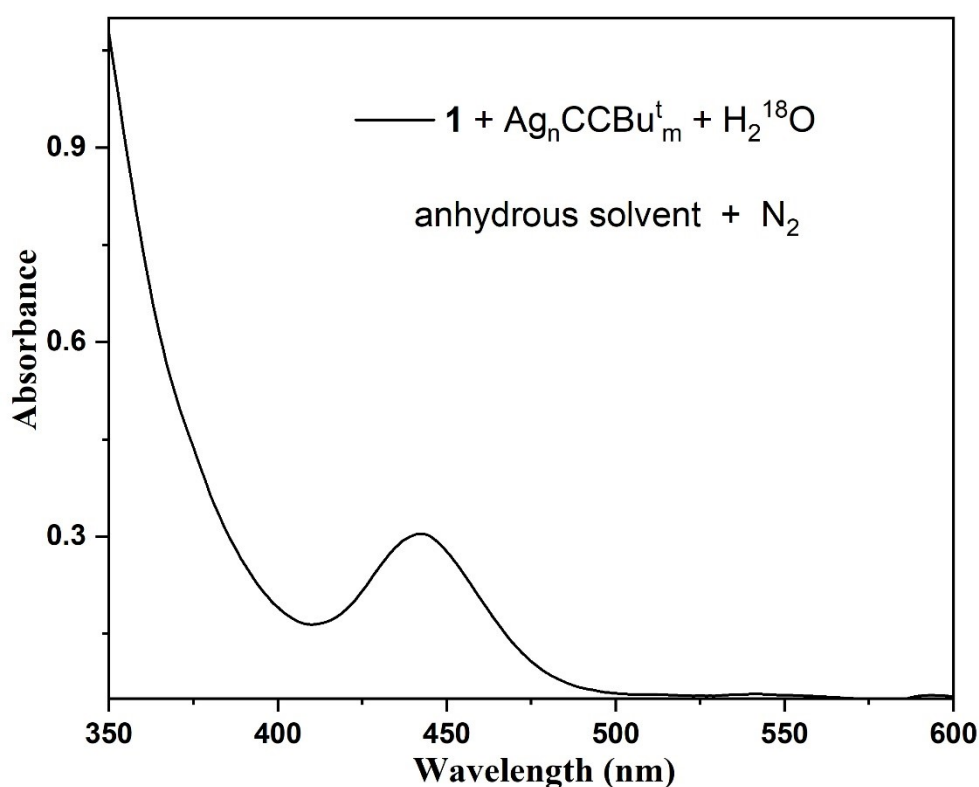
Supplementary Figure 4. Time-dependent UV-vis spectra of **1** and $\text{AgC}\equiv\text{CBu}^\dagger$ at 60°C . The reaction solution was a suspension before heating, and it became colorless and clear after heating for 5 minutes, from which point the reaction solution was monitored by time-dependent UV-Vis spectrums. Insert: digital photos of the reaction solution at different times.



Supplementary Figure 5. Time-dependent UV-vis spectra of **1** and $\text{HC}\equiv\text{CBu}^\dagger$ were monitored at 60°C .

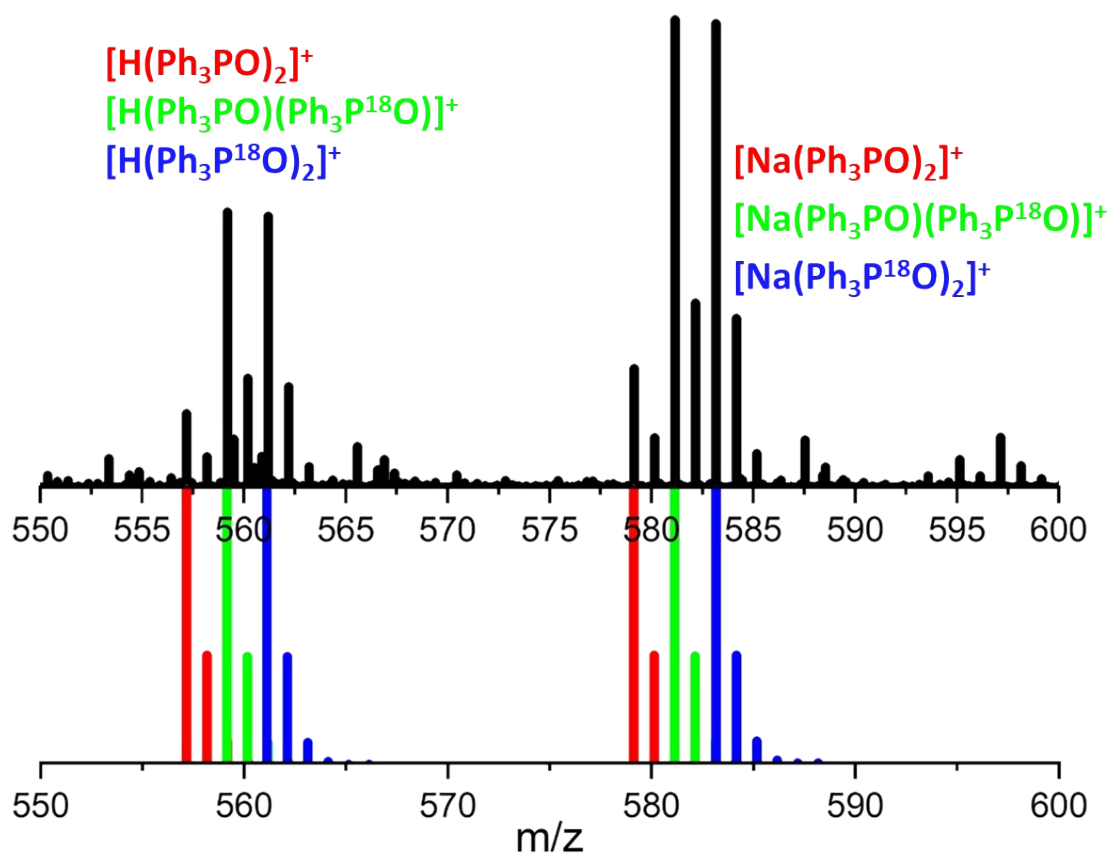


Supplementary Figure 6. The ^{31}P NMR spectra of the reaction solution in atmosphere, N_2 (hydrous solvent) and (anhydrous solvent with H_2^{18}O).

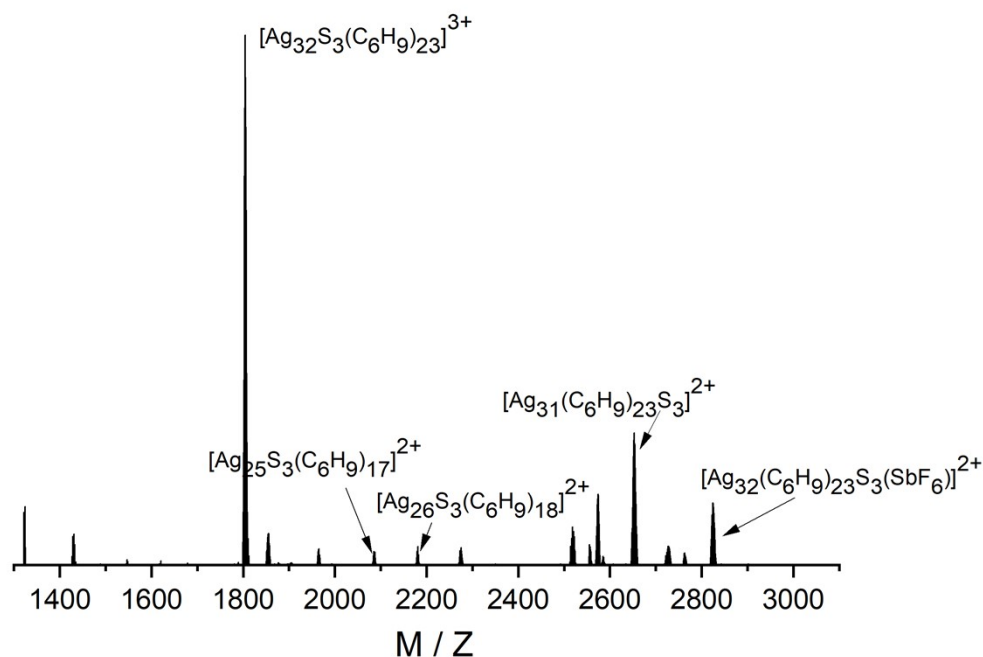


Supplementary Figure 7. The UV spectra of the mixture of $\text{Ag}_n(\text{C}\equiv\text{CBu}^t)_m$ and **1** (0.2 mmol and 0.1 mmol) in anhydrous solvent and N_2 at $60\text{ }^\circ\text{C}$ for 30 min, obtained by adding additional $200\text{ }\mu\text{l}$ H_2^{18}O .

The reactions were carried out under dry nitrogen atmosphere using Schlenk techniques. Methanol (supreme anhydrous grade, 99.8%, $\text{H}_2\text{O} \leq 20\text{ ppm}$) were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Dichloromethane (CH_2Cl_2) was dried and distilled.



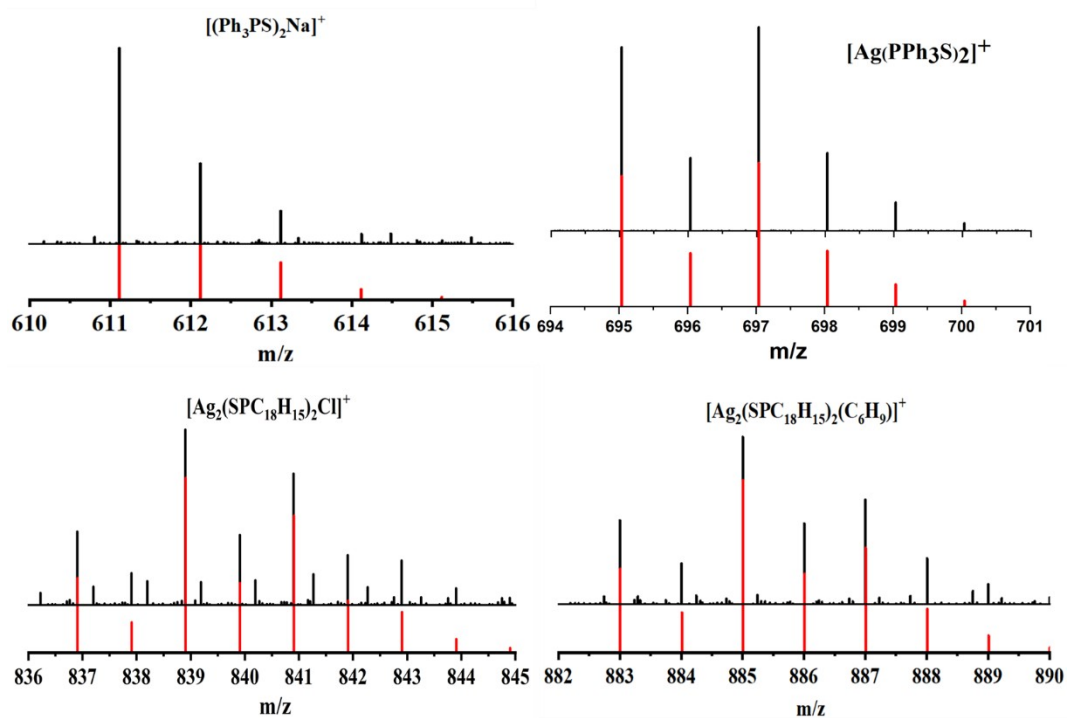
Supplementary Figure 8. Comparison diagram of experimental peak (black line) and simulated isotope distribution peak (colorful line) within 550-600 m/z.



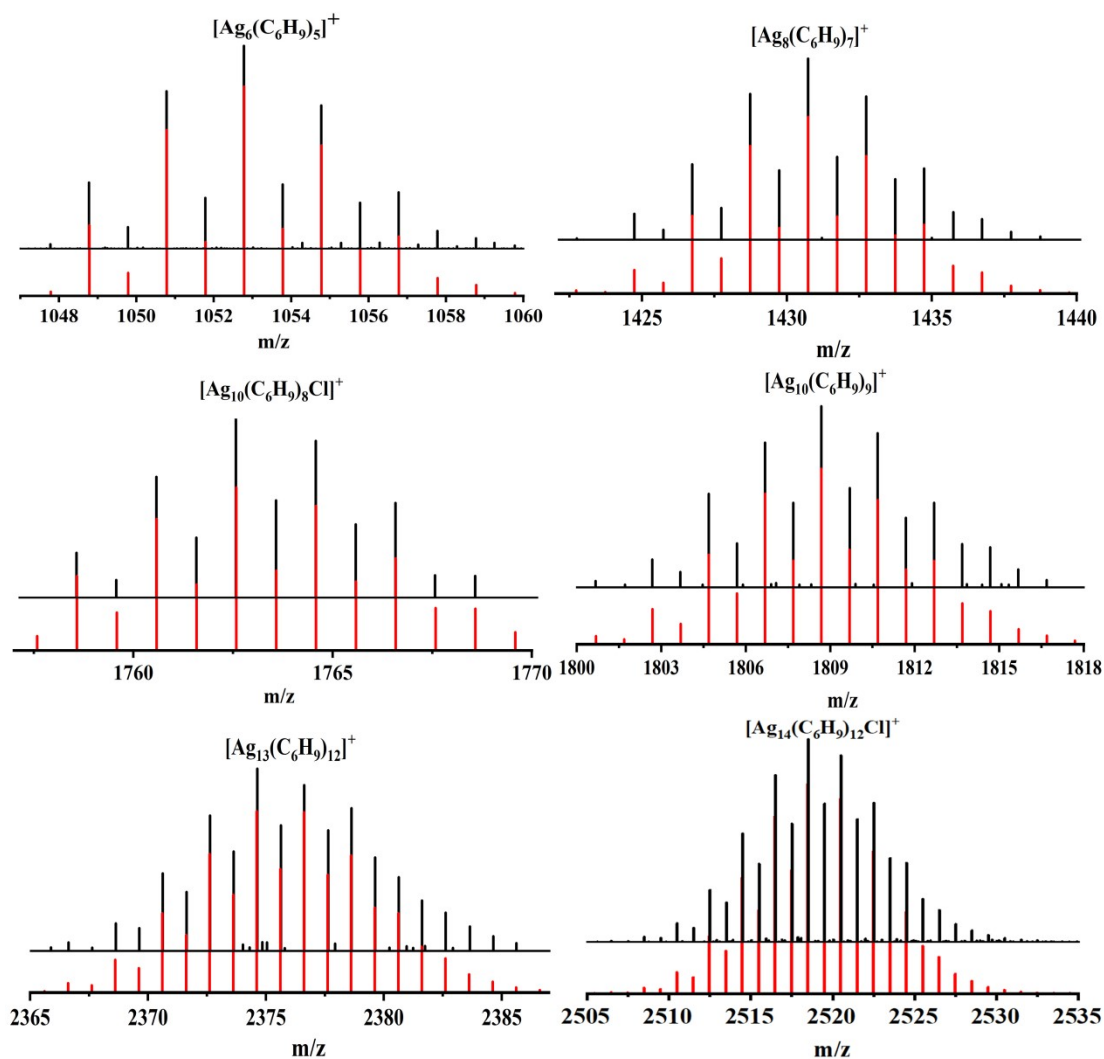
Supplementary Figure 9. ESI-MS of $\{Ag_{32}S_3\}$ of crystal samples.

The ESI-MS experiment by using crystals of $\{Ag_{32}S_3\}$ cluster had been performed, it can be observed that the $[Ag_{25}S_3(C\equiv CBut)_{17}]^{2+}$, $[Ag_{26}S_3(C\equiv CBut)_{18}]^{2+}$ and $[Ag_{31}S_3(C\equiv CBut)_{23}]^{2+}$ species with obviously weak peak intensity coexist with the main peak of $[Ag_{32}S_3(C\equiv CBut)_{23}]^{3+}$. The result indicates the $[Ag_{25}S_3(C\equiv CBut)_{17}]^{2+}$, $[Ag_{26}S_3(C\equiv CBut)_{18}]^{2+}$ and $[Ag_{31}S_3(C\equiv CBut)_{23}]^{2+}$ species detected in the time-course ESI-MS of Figure 4 are identified as the fragments of the $[Ag_{32}S_3(C\equiv CBut)_{23}]^{3+}$.

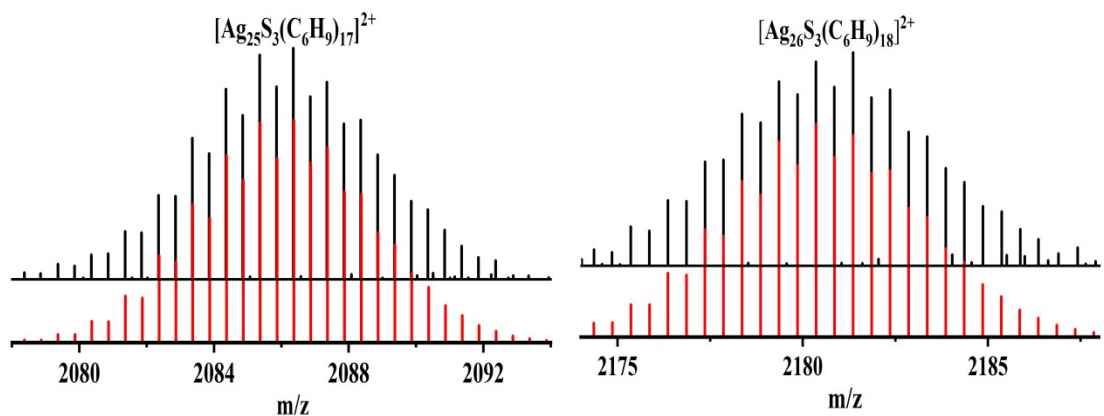
ESI-MS Spectra for the Assignment of Molecular Formulas



Supplementary Figure 10. Comparison diagram of experimental peak (black line) and simulated isotope distribution peak (red line) within 500-900 m/z.

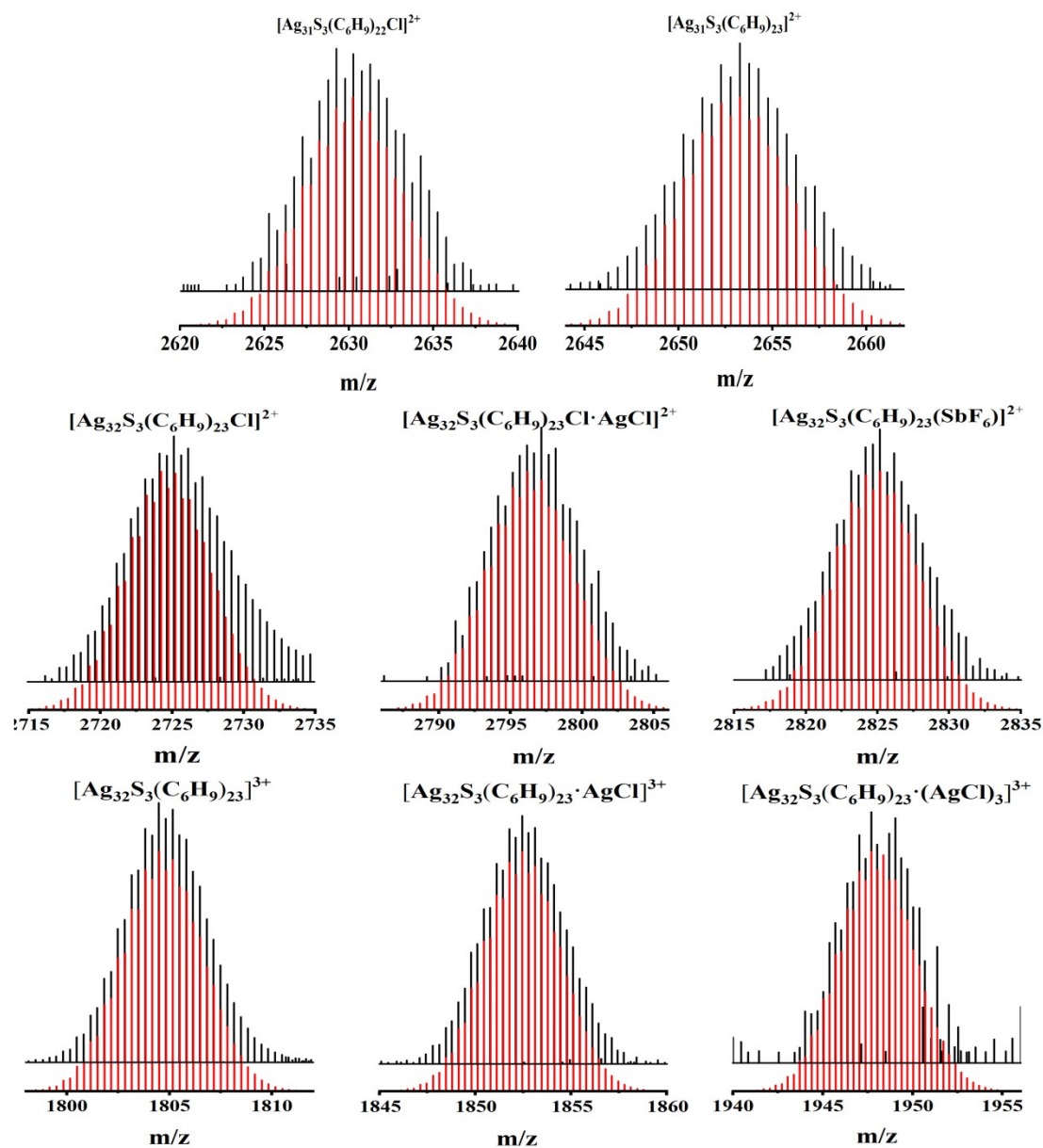


Supplementary Figure 11. Comparison diagram of experimental peak (black line) and simulated isotope distribution peak (red line) within 1000-2600 m/z. Some peaks in figure can be assigned to Ag-acetylene clusters with a +1 charge.



Supplementary Figure 12. Comparison diagram of experimental peak (black line) and simulated isotope distribution peak (red line) within 2080-2185 m/z.

simulated isotope distribution peak (red line) of $[\text{Ag}_{25}\text{S}_3(\text{C}_6\text{H}_9)_{17}]^{2+}$ and $[\text{Ag}_{26}\text{S}_3(\text{C}_6\text{H}_9)_{18}]^{2+}$.



Supplementary Figure 13. Comparison diagram of experimental peak (black line) and simulated isotope distribution peak (red line) within 1800-2900 m/z. The peaks in figure can be assigned to a series of species associated with Ag-S species.

Supplementary Table 1 | ESI-MS peak positions for selected precursors or Ag-thiolate/ acetylene clusters of $[\text{Ag}_{32}\text{S}_3(\text{C}_6\text{H}_9)_{23}]^{3+}$ and their assignments.

Peak (m/z)	Assigned Formula	Theoretical Value (m/z)	Error
579.17	$[(\text{Ph}_3\text{PO})_2\text{Na}]^+$	579.16	0.01
611.15	$[(\text{Ph}_3\text{PS})_2\text{Na}]^+$	611.11	0.04
696.04	$[(\text{Ph}_3\text{PS})_2\text{Ag}]^+$	696.03	0.01
838.88	$[(\text{Ph}_3\text{PSAg})_2\text{Cl}]^+$	838.90	0
884.83	$[(\text{Ph}_3\text{PSAg})_2(\text{C}_6\text{H}_9)]^+$	885.01	0.18
1052.76	$[\text{Ag}_6(\text{C}_6\text{H}_9)_5]^+$	1052.78	0.02
1431.09	$[\text{Ag}_8(\text{C}_6\text{H}_9)_7]^+$	1430.73	0.36
1762.61	$[\text{Ag}_{10}(\text{C}_6\text{H}_9)_8\text{Cl}]^+$	1762.58	0.03
1808.65	$[\text{Ag}_{10}(\text{C}_6\text{H}_9)_9]^+$	1808.68	0.03
2734.68	$[\text{Ag}_{13}(\text{C}_6\text{H}_9)_{12}]^+$	2374.61	0.07
2518.66	$[\text{Ag}_{14}(\text{C}_6\text{H}_9)_{12}\text{Cl}]^+$	2518.48	0.18
1241.76	$[\text{Ag}_{14}(\text{C}_6\text{H}_9)_{12}]^{2+}$	1241.75	0.01
1964.57	$[\text{Ag}_{22}\text{S}(\text{C}_6\text{H}_9)_{15}\text{Cl}_2(\text{SbF}_6)]^{2+}$	1964.38	0.19
2086.03	$[\text{Ag}_{25}\text{S}_3(\text{C}_6\text{H}_9)_{17}]^{2+}$	2086.37	0.34
2180.24	$[\text{Ag}_{26}\text{S}_3(\text{C}_6\text{H}_9)_{18}]^{2+}$	2180.35	0.11
2630.26	$[\text{Ag}_{31}\text{S}_3(\text{C}_6\text{H}_9)_{22}\text{Cl}]^{2+}$	2630.24	0.02
2653.27	$[\text{Ag}_{31}\text{S}_3(\text{C}_6\text{H}_9)_{23}]^{2+}$	2653.29	0.02
2725.20	$[\text{Ag}_{32}\text{S}_3(\text{C}_6\text{H}_9)_{23}\text{Cl}]^{2+}$	2724.23	0.97
2796.14	$[\text{Ag}_{32}\text{S}_3(\text{C}_6\text{H}_9)_{23}\text{Cl}\cdot\text{AgCl}]^{2+}$	2796.16	0.02
2825.19	$[\text{Ag}_{32}\text{S}_3(\text{C}_6\text{H}_9)_{23}(\text{SbF}_6)]^{2+}$	2825.19	0
1808.51	$[\text{Ag}_{32}\text{S}_3(\text{C}_6\text{H}_9)_{23}]^{3+}$	1808.49	0.02
1852.47	$[\text{Ag}_{32}\text{S}_3(\text{C}_6\text{H}_9)_{23}\cdot\text{AgCl}]^{3+}$	1852.45	0.02
1947.69	$[\text{Ag}_{32}\text{S}_3(\text{C}_6\text{H}_9)_{23}\cdot(\text{AgCl})_3]^{3+}$	1947.70	0.01

Reference:

1. Blake, D.; Calvin, G.; Coates, G. E., Proc. Chem. Soc. 1959, 396.