**Supporting Information**

# $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$: Two New Hydride and Phosphine Co-Protected Clusters and Their Fragmentation Leading to Naked Clusters, $Ag_{13}^{+}$ and $Ag_{25}^{+}$

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## Supporting information 1

## Characterization of $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ cluster:

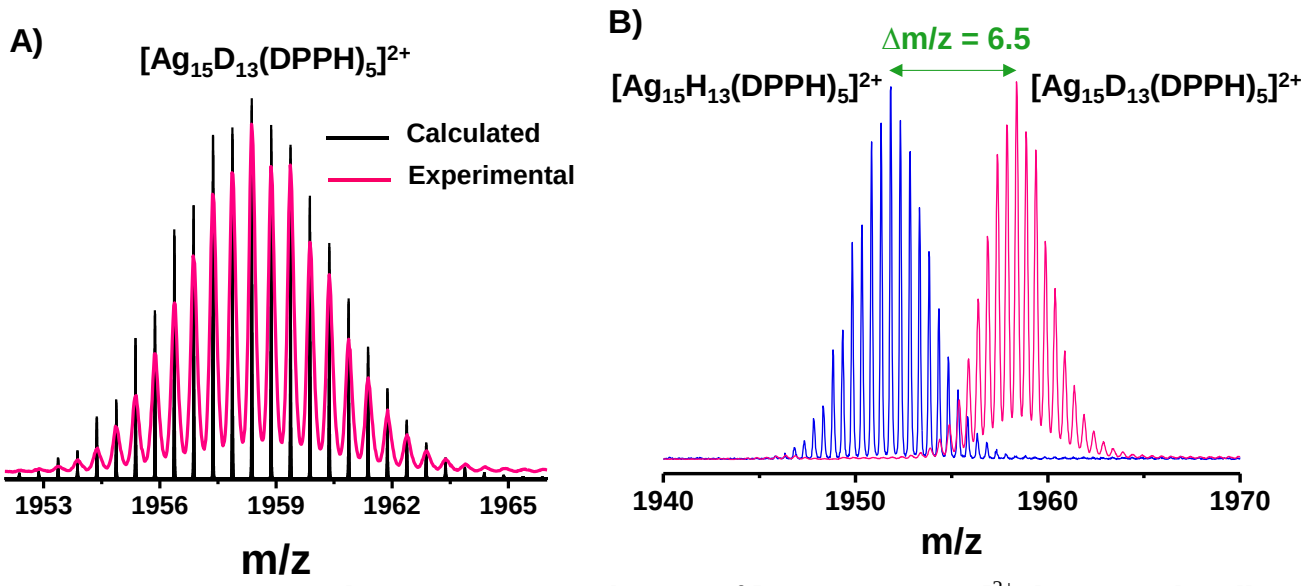



**Figure S1. (**A) Experimental mass spectrum (pink trace) of $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ cluster match well with its calculated (black trace) isotopic pattern. (B) The ESI MS of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ showing the mass shift due to the exchange of hydrogen atoms with deuterium atoms.

**Supporting information 2**

**Time dependent UV-vis spectra of sample I during synthesis:**

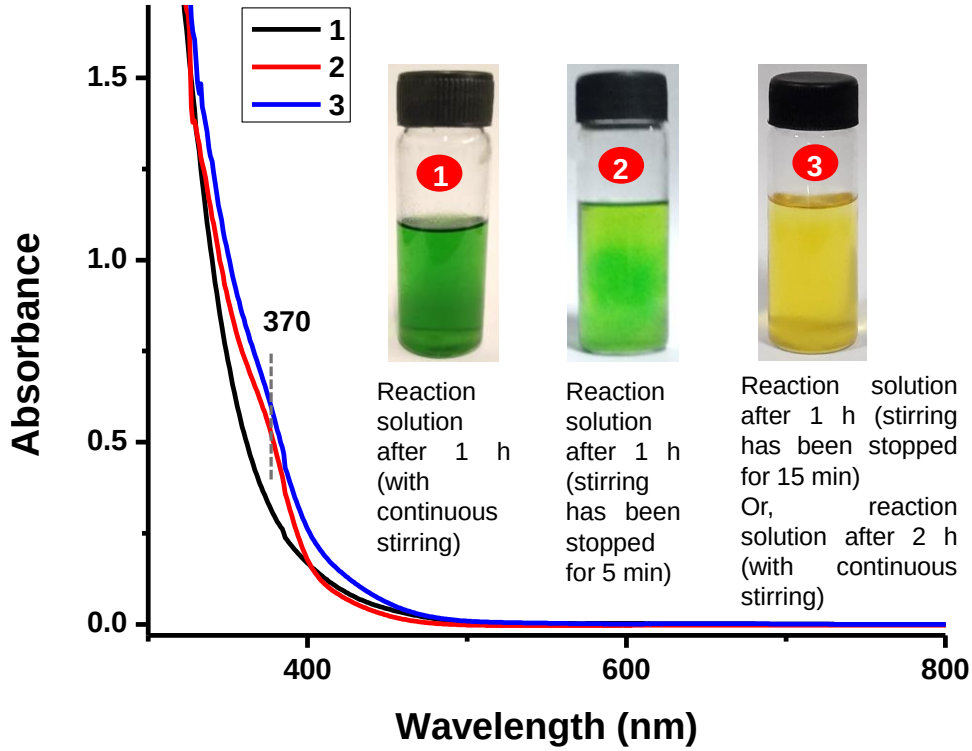



**Figure S2.** Time dependent UV-vis spectra during the synthesis of sample **I** with their corresponding photographs in inset. The photographs show that during 1 h of synthesis with continous stirring, the color oft he solution remains green (1). Whereas, by stopping the stirring after 1 h, the color changed immidiately from green to yellowish green within 5 min (2). After 15 min of stopping stirring, the color became fully dark yellow (3). The bottle labled 3 also represent the same solution when the reaction was continously stirred for 2 h.

## Supporting information 3

## Time dependent ESI MS of sample I during synthesis:

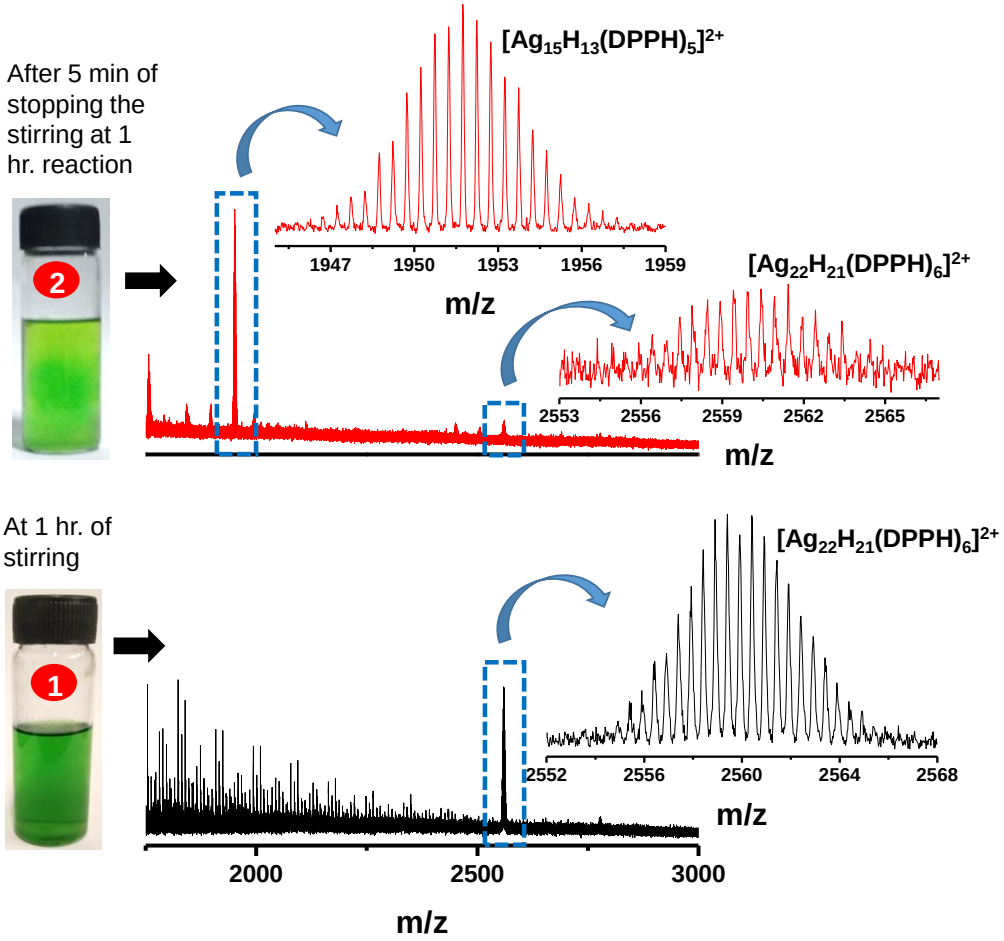



**Figure S3.** Time dependent ESI MS during the synthesis of sample **I** with their corresponding photographs (on the left). The ESI MS of green solution (1) shows the presence of $[Ag_{22}H_{21}(DPPH)_6]^{2+}$ cluster during 1 h stirring. Whereas, after 5 min of stopping the stirring the green color was converted to yellowish green (2) and the intensity of $[Ag_{22}H_{21}(DPPH)_6]^{2+}$ decreased significantly in the ESI MS along with increased intensity of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (sample **I).**

## Supporting information 4

## $^1$H NMR spectra of DPPH and $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster:

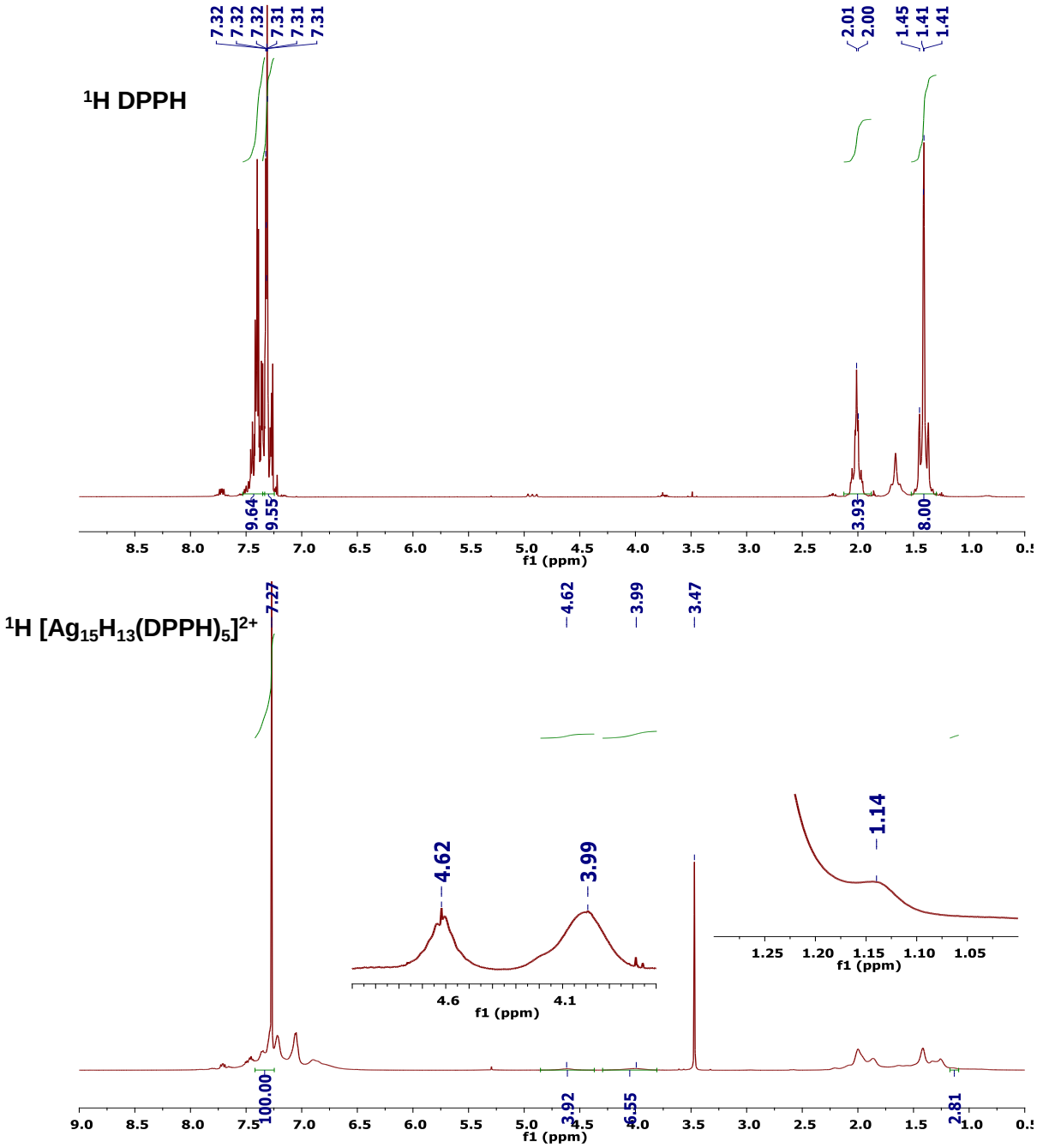



**Figure S4.** $^1$H NMR spectra of DPPH and $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ clusters. Broad peaks of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ at 1.14, 3.99 and 4.62 ppm confirm the presence of hydride protected clusters.

## Supporting information 5

## $^{31}$P NMR spectra of DPPH and $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster:

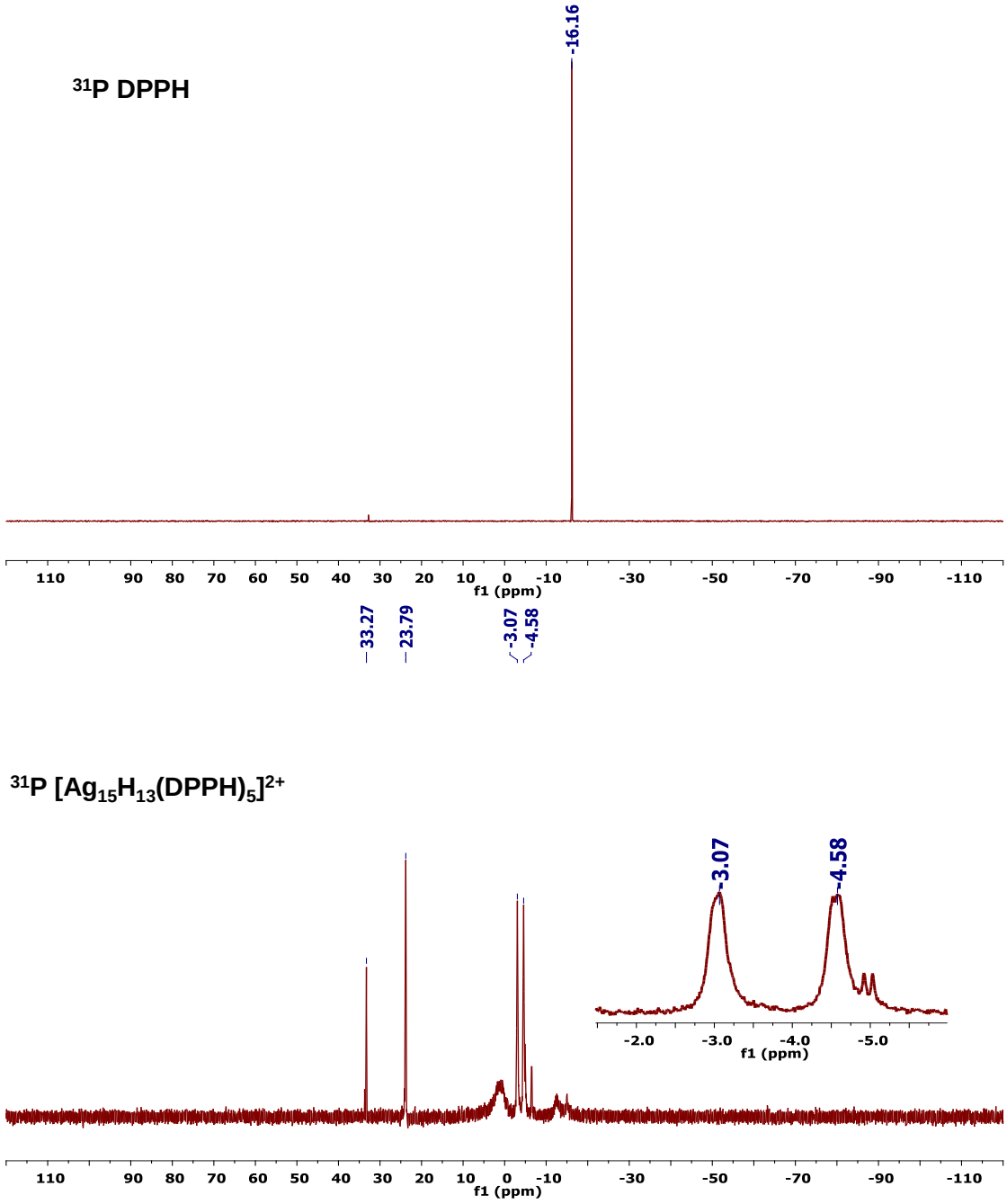



**Figure S5.** $^{31}$P NMR spectra of DPPH and $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ clusters. The $^{31}$P signal at -16.16 ppm for DPPH ligand disappears in the $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster due to the binding of liagnds with metal core, which is also confirmed by the appearence of new broad peaks at -4.58 and -3.07 ppm in the nanoclusters. Peaks at 23.79 and 33.27 ppm are due to phosphine oxides.

## Supporting information 6

## XPS spectra of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster:

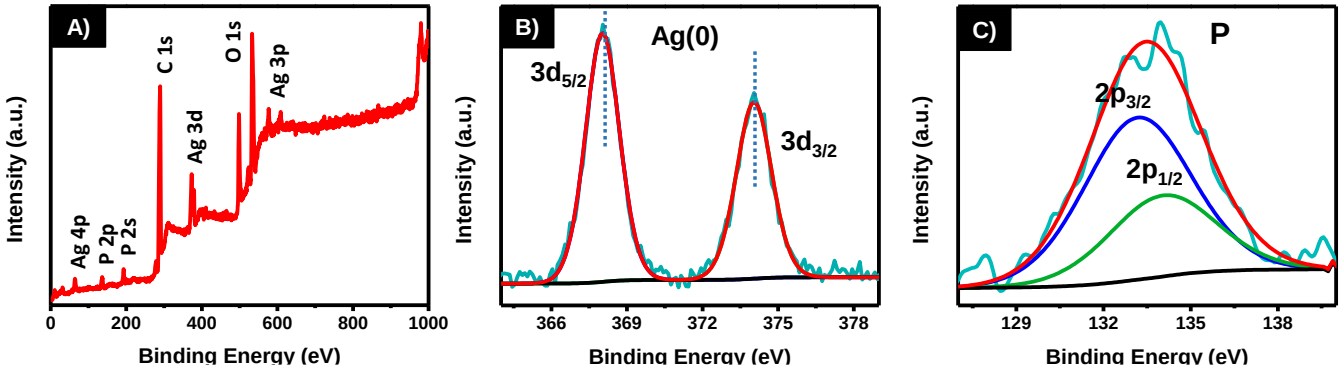
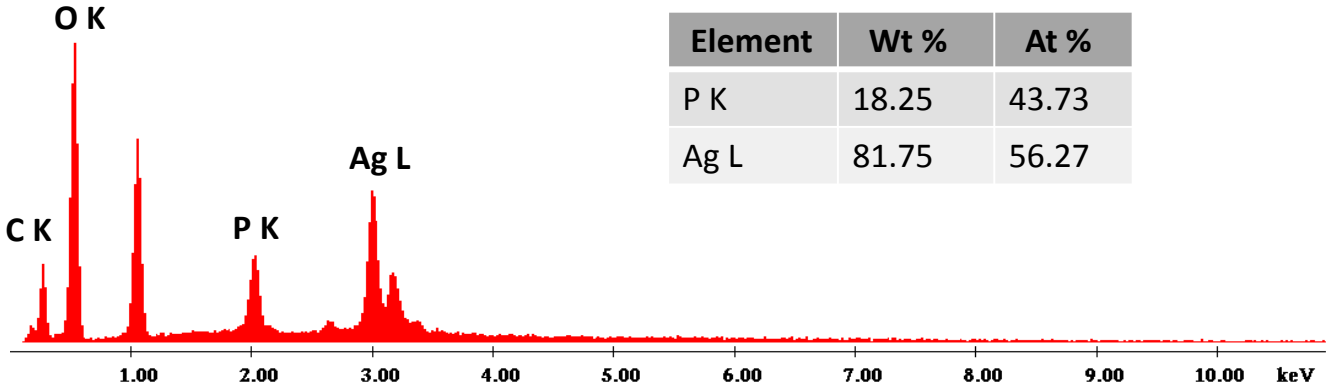



**Figure S6. (**A) XPS survey spectrum of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ showing all the expected elements (Ag, P and C). (B) The Ag 3d region. Ag $3d_{5/2}$ at 368.04 eV indicates the presence of Ag(0) state. (C) P 2p region of the nanocluster. P $2p_{3/2}$ appears at 133.24 eV.

## Supporting information 7

## SEM EDS of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster:




| Element | Wt % | At % |
|---|---|---|
| P K | 18.25 | 43.73 |
| Ag L | 81.75 | 56.27 |

**Figure S7.** SEM EDS of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster with quantification of elements. Ag:P atomic ratio matches well with the Ag:P ratio obtained from the molecular formula of the cluster.

## Supporting information 8

## TEM analysis of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster:

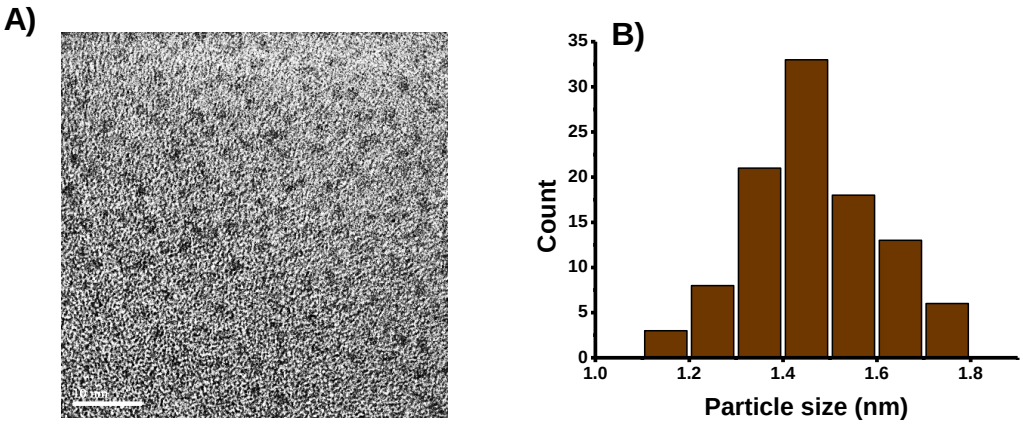



**Figure S8.** (A) TEM image of the $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster. Scale bar is 10 nm. (B) Particle distribution shows an average size of 1.46 ± 0.13 nm for this nanocluster.

**Supporting information 9**

**Comparision of the fragmentation pathway of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{15}D_{13}(DPPH)_5]^{2+}$clusters:**

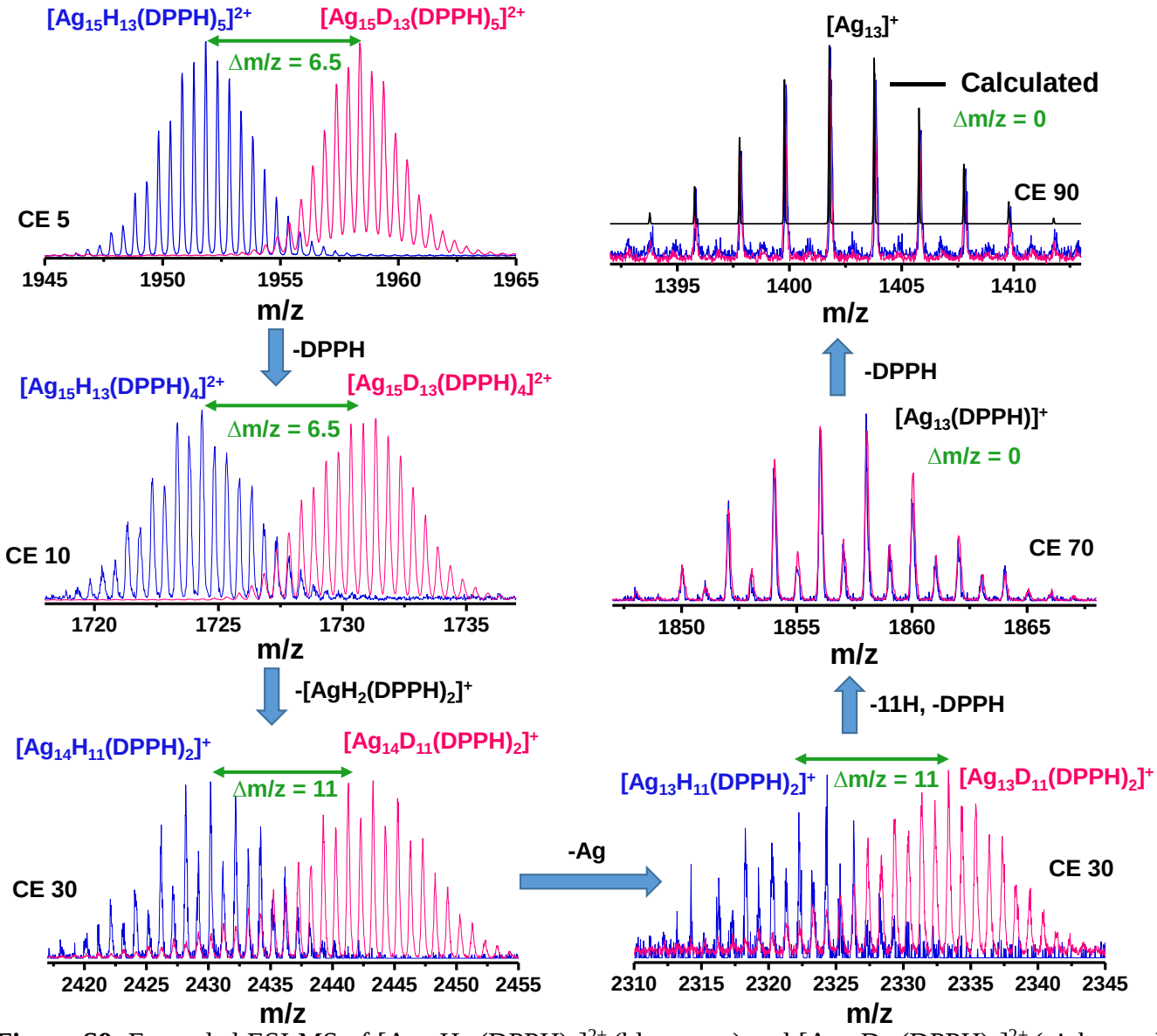



**Figure S9.** Expanded ESI MS of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (blue trace) and $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ (pink trace) at different collision energies during the formation of naked cluster, $Ag_{13}^{+}$ by another possible pathway. The mass shift (Δm/z) in between the blue and pink traces confirms the presence of hydrogen in the particular fragmented ions. The isotopic distribution of $Ag_{13}^{+}$ confirms the absence of hydrogen atoms, which also matches with the calculated pattern (black trace).

**Supporting information 10**

## MS/MS of $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ cluster:

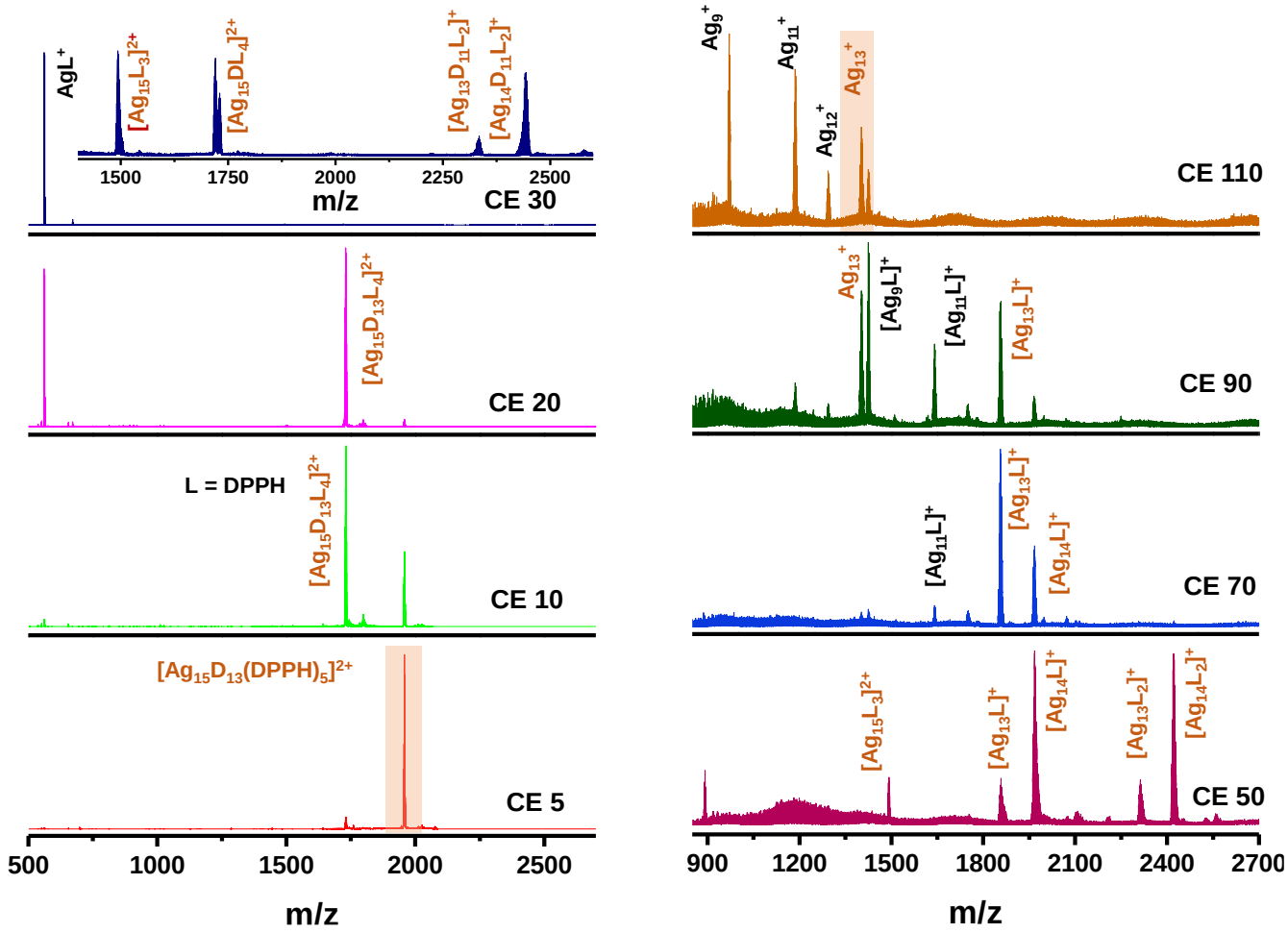



**Figure S10.** Collision energy dependent MS/MS spectra of the $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ cluster. Increase in collision energy from 5 to 110 (in instrumental units) results in the detachment of deuterium, DPPH and $[AgDPPH]^+$ from $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ resulting in $Ag_{13}^+$. Fragments labeled in brown lead to the formation of naked cluster, $Ag_{13}^+$.

## Supporting information 11

## Fragmentation pathway of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster:

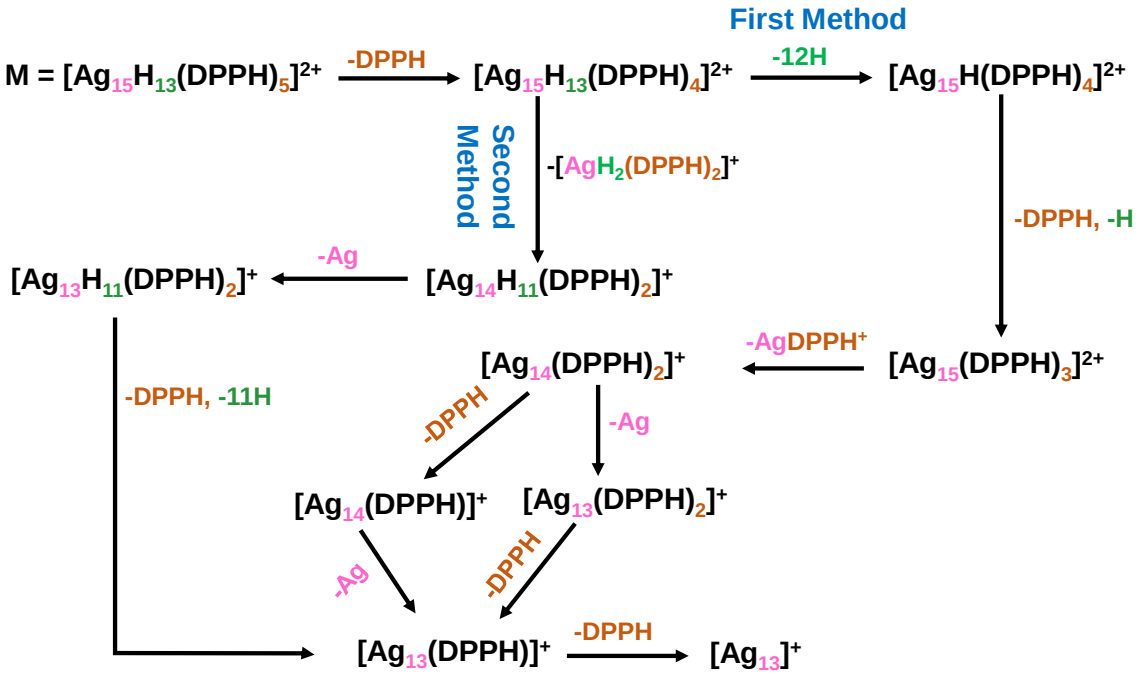



**Figure S11.** Collision energy dependent fragmentation pathway of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster towards the formation of naked cluster, $Ag_{13}^{+}$. Hydrogen and DPPH loss do not involve any alternation of charge state of the resulting cluster. Whereas, $[AgDPPH]^{+}$ loss results in the reduction of charge state from +2 to +1.

## Supporting information 12

## Characterization of $[Ag_{27}D_{22}(DPPB)_7]^{3+}$ cluster:

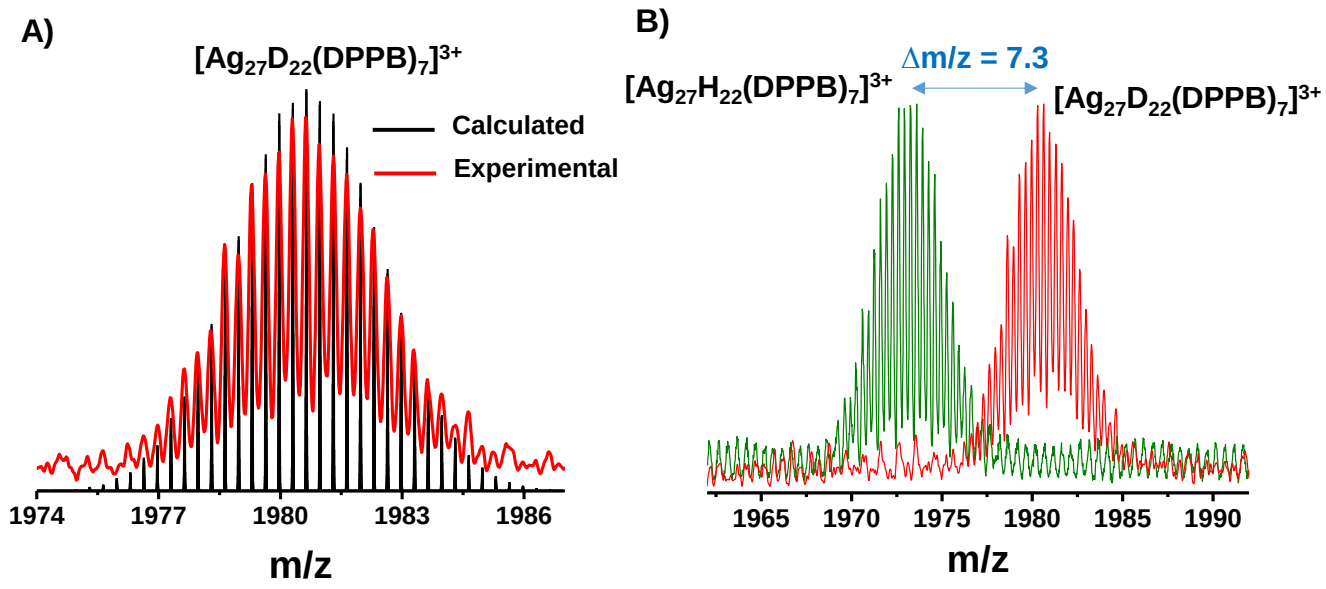



**Figure S12. (**A) Experimental mass spectrum (red trace) of $[Ag_{27}D_{22}(DPPB)_7]^{3+}$ cluster and it matches well with its calculated (black trace) isotopic pattern. (B) The ESI MS of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ and $[Ag_{27}D_{22}(DPPB)_7]^{3+}$ showing a mass shift due to the exchange of hydrogen atoms with deuterium atoms.

## Supporting information 13

## $^1$H NMR spectra of DPPB and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster:

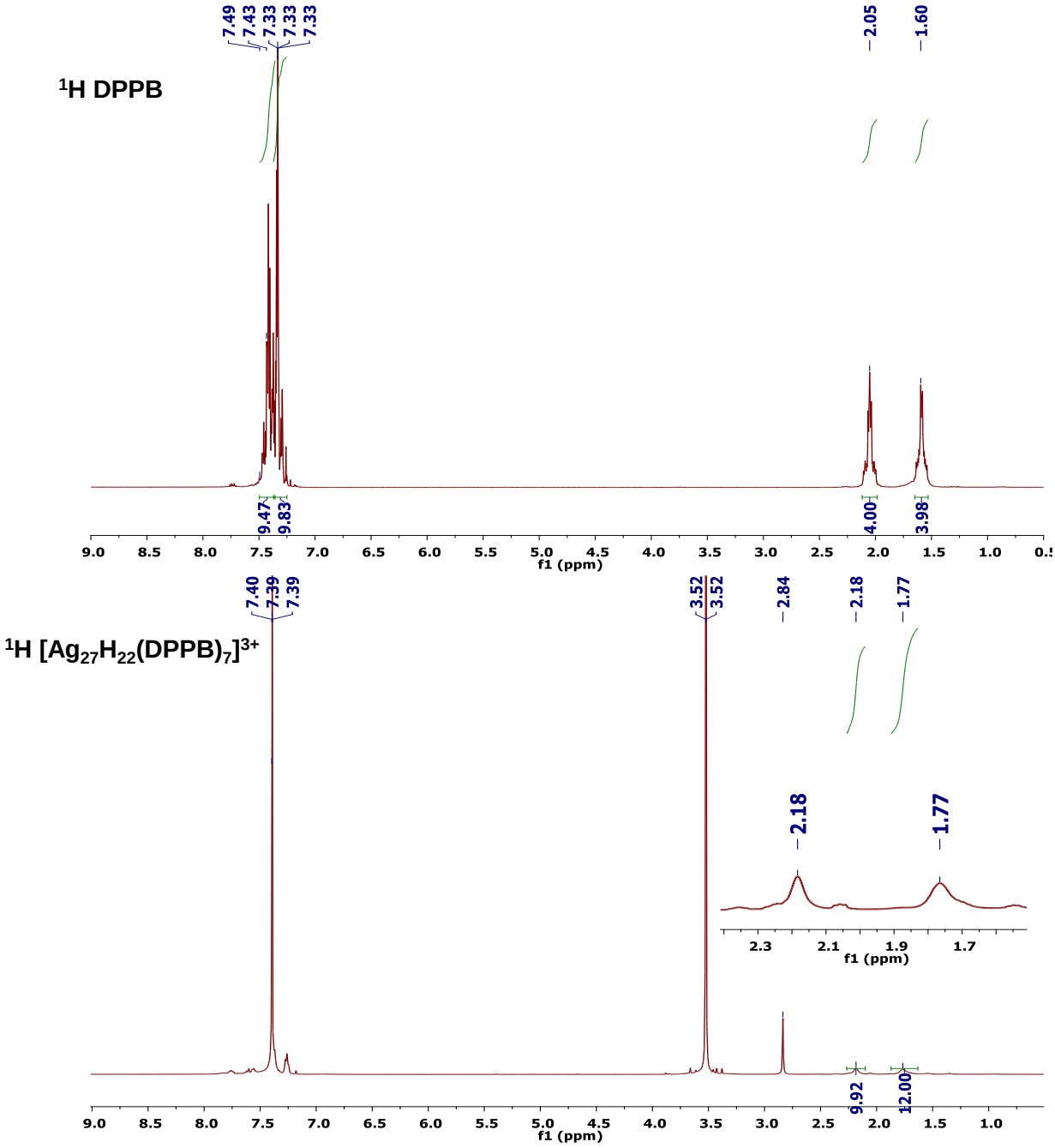



**Figure S13.** $^1$H NMR spectra of DPPB and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ clusters. Broad peaks of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ at 1.77 and 2.18 ppm confirm the presence of hydride protected nanoclusters.

## Supporting information 14

## $^{31}$P NMR spectra of DPPB and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster:

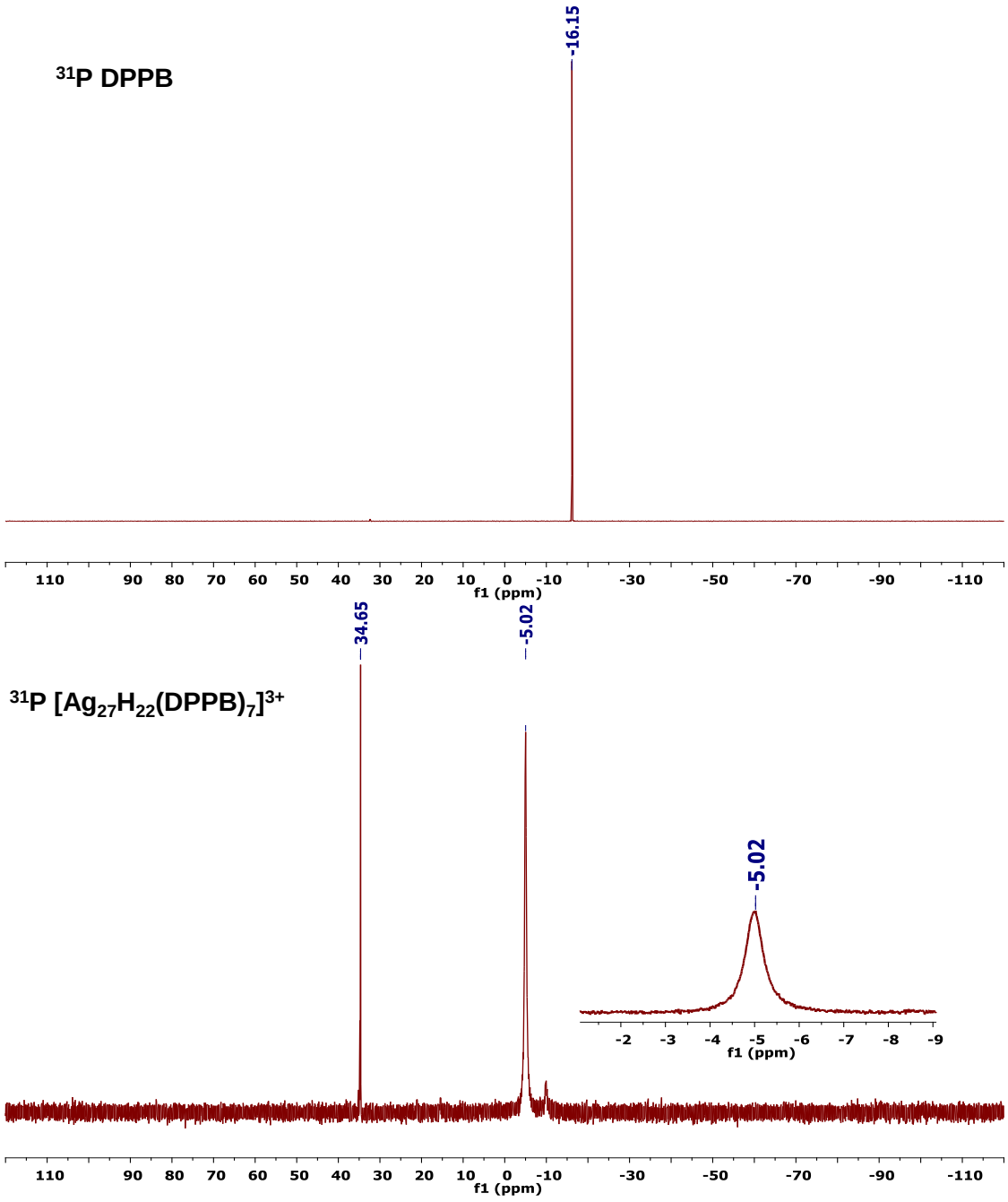



**Figure S14.** $^{31}$P NMR spectra of DPPB and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ clusters. The $^{31}$P signal at -16.15 ppm for DPPB ligand disappears in the $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster due to the binding of liagnds with the metal core, which is also confirmed by the appearence of new broad peaks at -5.02 ppm in the nanoclusters. Peak at 34.65 ppm is due to phosphine oxides.

## Supporting information 15

## XPS spectra of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster:

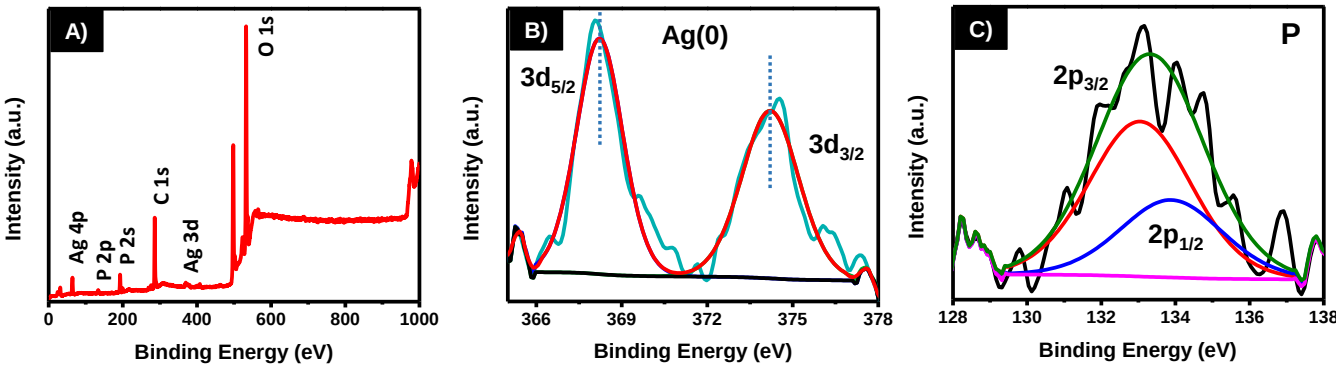
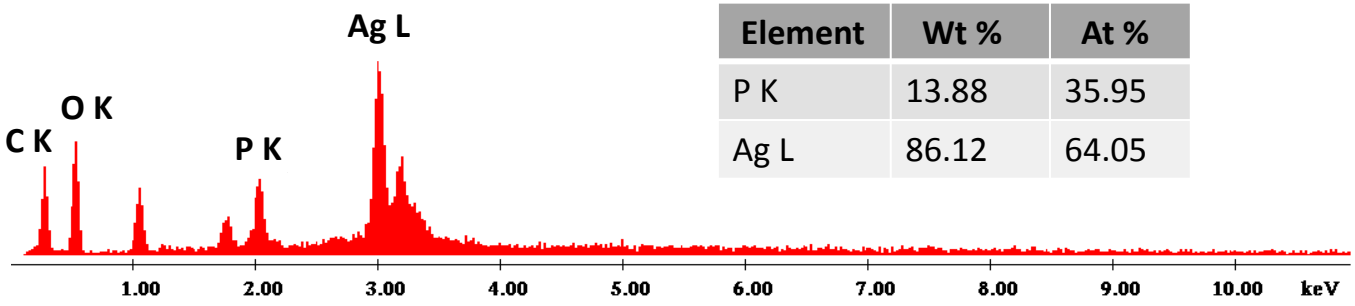



**Figure S15.** (A) XPS survey spectrum of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ showing all the expected elements (Ag, P and C). (B) Ag 3d spectrum of the nanocluster. Ag $3d_{5/2}$ appears at 368.22 eV indicating the presence of Ag(0) state. (C) P 2p spectrum of the nanocluster. P $2p_{3/2}$ appears at 133.03 eV.

## Supporting information 16

## SEM EDS of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster:




| Element | Wt % | At % |
|---|---|---|
| P K | 13.88 | 35.95 |
| Ag L | 86.12 | 64.05 |

**Figure S16.** SEM EDS of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster with quantification of elements. Ag:P atomic ratio matches well with the Ag:P ratio obtained from the molecular formula of the cluster.

## Supporting information 17

## TEM analysis of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster:

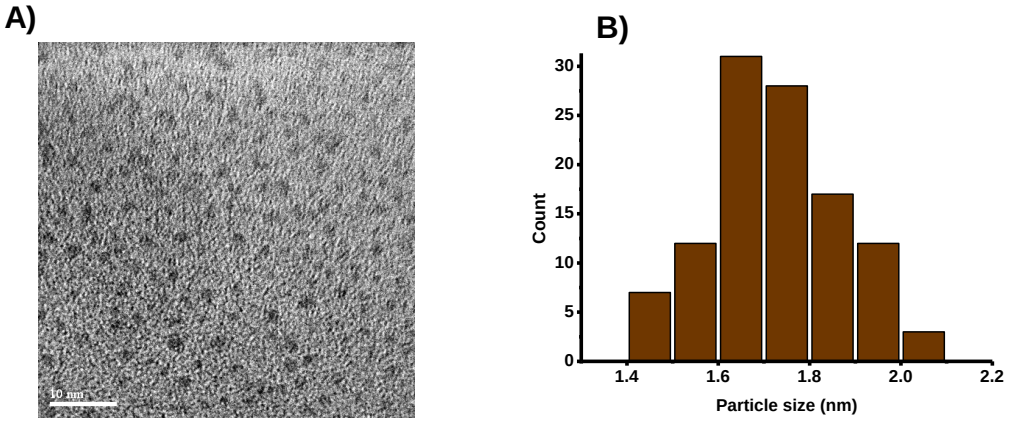



**Figure S17.** (A) TEM image of the $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster. Scale bar is 10 nm. (B) Particle distribution shows an average size of 1.72 ± 0.14 nm for this nanocluster.

## Supporting information 18

## Comparison between the experimental and the calculated spectra of $Ag_{25}^{+}$:

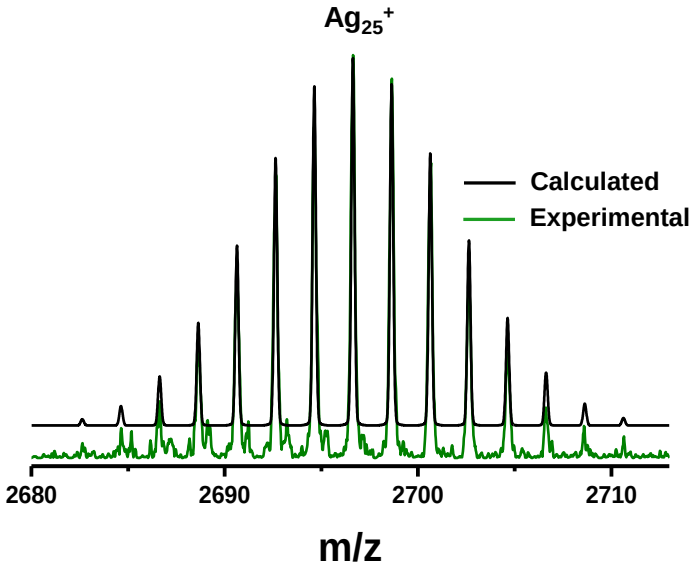



**Figure S18.** Experimental mass spectrum (green trace) of $Ag_{25}^{+}$ matches well with the calculated (black trace) isotopic pattern.

**Supporting information 19**

## Fragmentation pathway of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster:

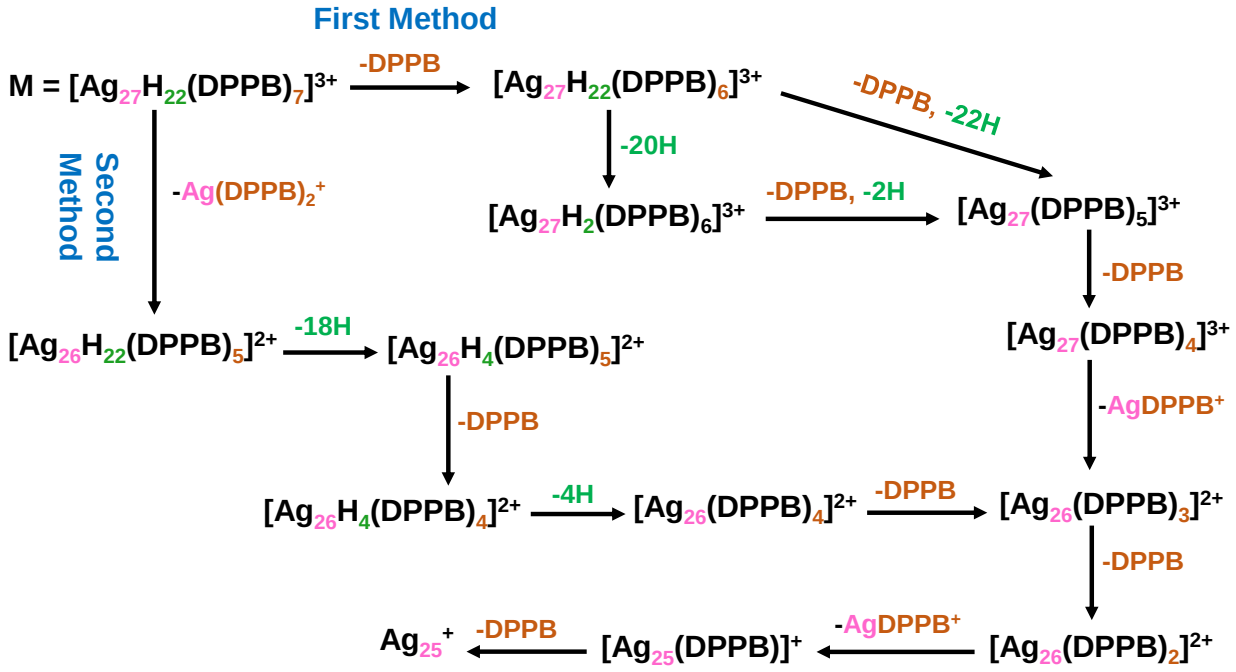



**Figure S19.** Collision energy dependent fragmentation pathway of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster towards the formation of naked cluster, $Ag_{25}^{+}$. Hydrogen and DPPB loss do not involve any alternation of charge state of the resulting cluster. Whereas, $[AgDPPB]^{+}$ loss results in the reduction of charge state from +3 to +2 and from +2 to +1.