

Electronic Supplementary Information (ESI) for the paper:

[Ag₅₉(2,5-DCBT)₃₂]³⁻: A new cluster and a precursor for other clusters

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Synthesis of $[\text{Ag}_{44}(\text{4-FTP/4-CTP})_{30}]^{4+}$ (IIb, IIc)

About 20 mg of AgNO_3 was taken in an agate mortar and pestle and ground thoroughly for few min. Then, about 12 mg of PPh_4Br was added and mixed properly with AgNO_3 . Next $\sim 76 \mu\text{L}$ of 4-FTP was added in the mixture at a time. After proper grinding, about 45 mg of NaBH_4 was added and again ground until a brown color paste was formed. This mixture was extracted with 10 mL of DCM and kept at room temperature under dark condition for 24 h. After 24 h, the cluster formation was confirmed by checking the UV-vis absorption spectrum. Then the solvent was evaporated using a rotavapor. After complete evaporation of the solvent, the precipitate was washed with methanol repeatedly and the cluster was extracted by dissolving the residue in DCM (supernatant) followed by discarding the unreacted by-products (precipitate) by centrifugation. Synthesis of $[\text{Ag}_{44}(\text{4-CTP})_{30}]^{4+}$ was performed following the same synthetic procedure. About 38 mg of 4-CTP was used for the synthesis of this cluster.

Synthesis of $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$ (III)

About 38 mg of AgNO_3 (in 2 mL methanol) was taken in a synthesizer tube and 17 mL of DCM was added to this solution. Then, about 90 μL of 2,4-DMBT was added which resulted in the formation of yellow colored thick mixture. The mixture was kept under stirring for 20 min followed by the addition of about 6 mg of PPh_4Br (in 0.5 mL of methanol) in the reaction mixture. When the solution became colorless, the complex was reduced by the addition of 15 mg of NaBH_4 (in 0.5 mL of ice cold H_2O). The reaction was kept under stirring for 6-7 h at 0 °C. After the completion of reaction, the mixture was kept for 1 day at 4 °C. For purification, the cluster solution was transferred to a round bottomed flask and the solvent was evaporated until the total volume of the solution became 5 mL. After that methanol was added to the mixture to precipitate the cluster. The precipitate was collected through centrifugation and again washed with methanol. The residue was dissolved in DCM and cluster solution was collected after centrifugation discarding the precipitate of unreacted by-products.

Synthesis of $[\text{Ag}_{29}(\text{1,3-BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (IV)

About 20 mg of AgNO_3 was dissolved in a mixture of 5 mL of methanol and 9 mL of DCM. The solution was kept under stirring for 5 min. About 13.5 μL of BDT was added to this reaction mixture which turned the colorless solution to yellow. After 5 min, 200 mg of PPh_3 dissolved in 1 mL of DCM was added and the solution turned colorless, indicating the formation of Ag-S-P complexes. After 10 min, 11 mg of NaBH_4 (in 0.5 mL of ice cold H_2O) was added and immediately the color of the solution became dark-brown which gradually turned to orange. The reaction mixture was kept at room temperature under dark conditions for 3 h. After that the precipitate was collected after centrifuging the mixture, and the supernatant was discarded. The precipitate was then washed repeatedly with methanol to remove the unreacted by-products and orange colored cluster was extracted with DMF.

ESI MS measurements of the $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}] (\text{I})$

To get the mass spectrum of the $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ in ESI mode, the following instrumental parameters were used:

Sample concentration: $1\ \mu\text{g/mL}$

Solvent: DCM

Flow rate: $10\text{-}20\ \mu\text{L/min}$

Capillary voltage: $2\text{-}3\ \text{kV}$

Cone voltage: $20\ \text{V}$

Source offset: $30\ \text{V}$

Desolvation gas flow: $400\ \text{L/h}$

Source temperature: $40\ ^\circ\text{C}$

Desolvation temperature: $80\ ^\circ\text{C}$

Supplementary information 1

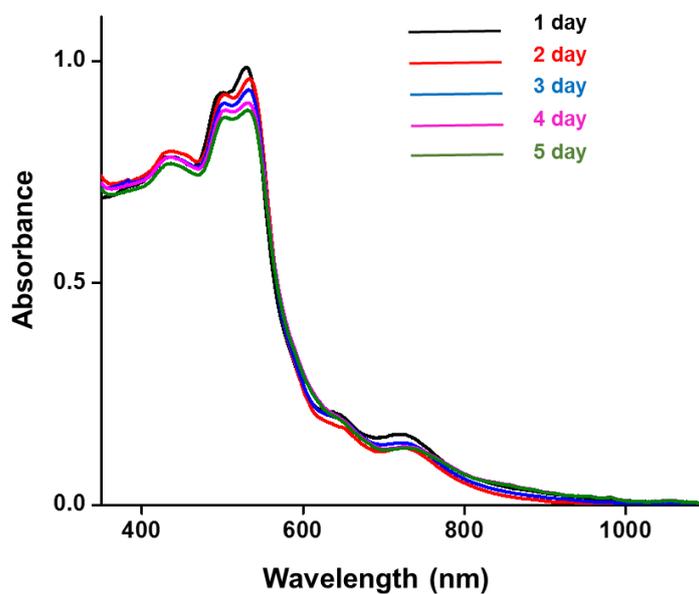


Fig. S1 UV-vis absorption spectra of the $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]$ as a function of time.

Supplementary information 2

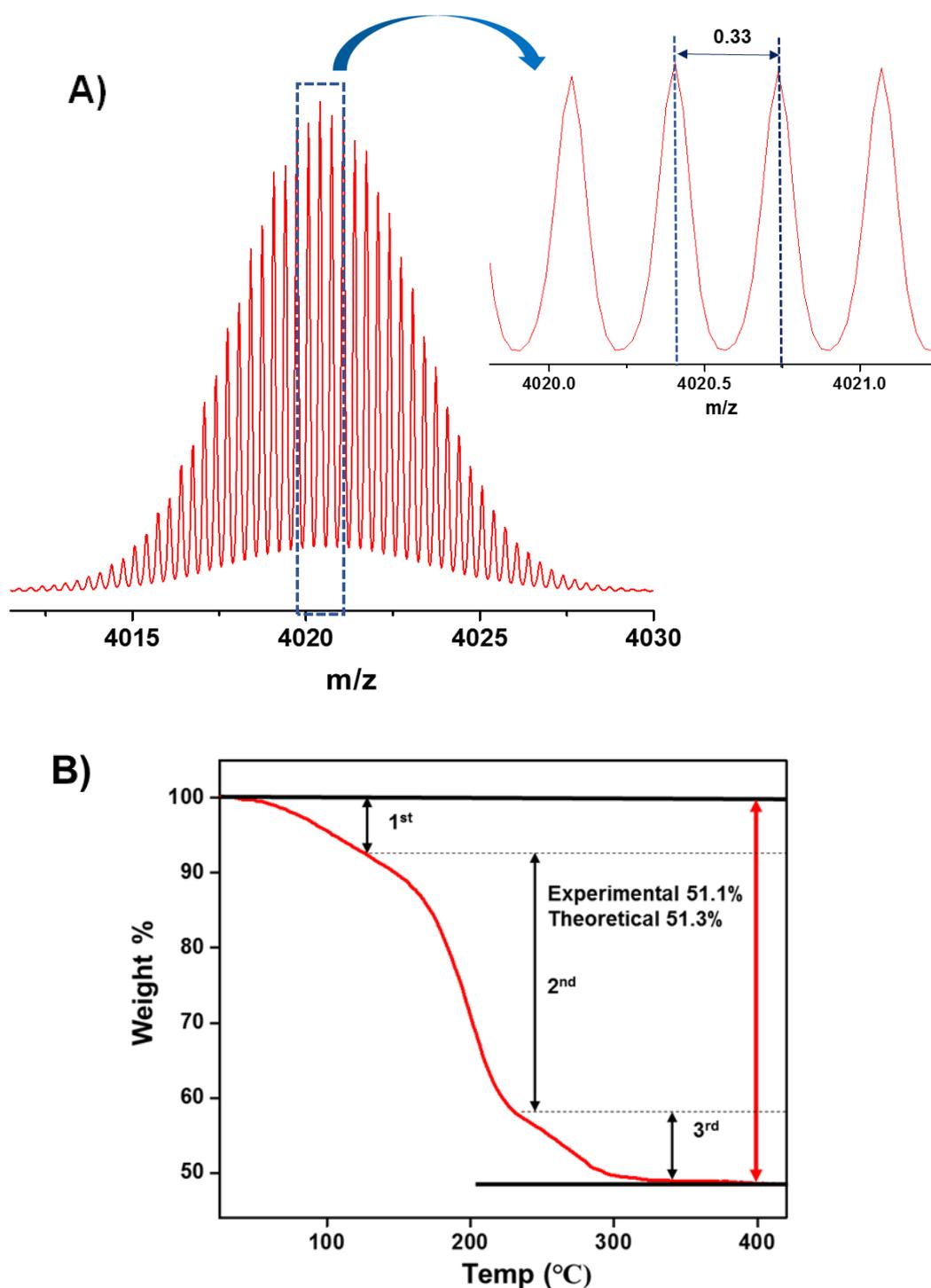


Fig. S2 (A) ESI MS of the $[Ag_{59}(2,5-DCBT)_{32}]$. The expanded region shows that the separation between two subsequent peaks comes at 0.33, which confirms the charge state of the cluster ion. (B) Thermogravimetric analysis (TGA) of the as-synthesized cluster under nitrogen atmosphere. It shows three types of weight losses among which the first one is due to loss of three PPh_4 which stabilize the cluster ion. The second loss is due to carbon-hydrogen content of ligand and the third one is due to loss of sulfur which sits on the metal surface. The total organic content in the cluster is 51.1% which is nearly matching with calculated formula (51.3%).

Supplementary information 3

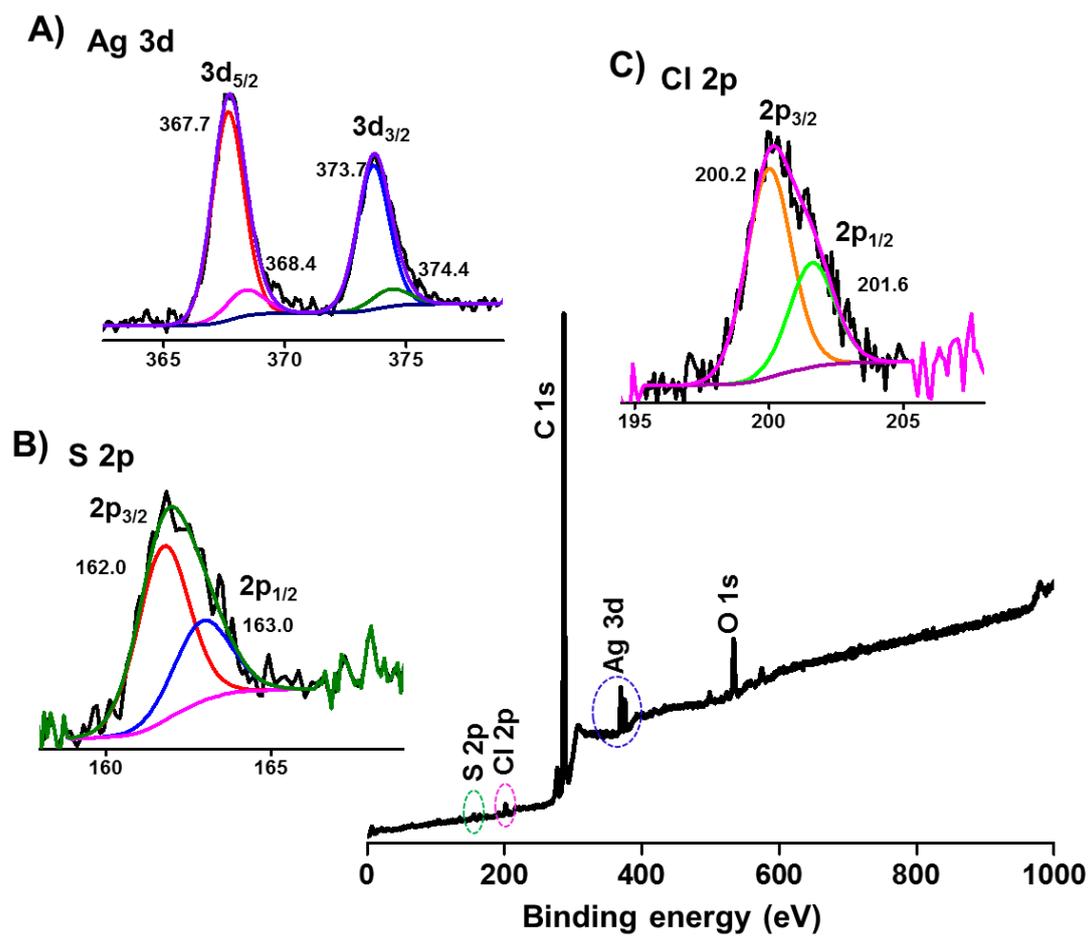


Fig. S3 Full range XPS spectrum of the $[Ag_{59}(2,5-DCBT)_{32}]$. Insets: (A), (B) and (C) are expanded XPS spectrum in the Ag 3d, S 2p and Cl 2p regions, respectively.

Supplementary information 4

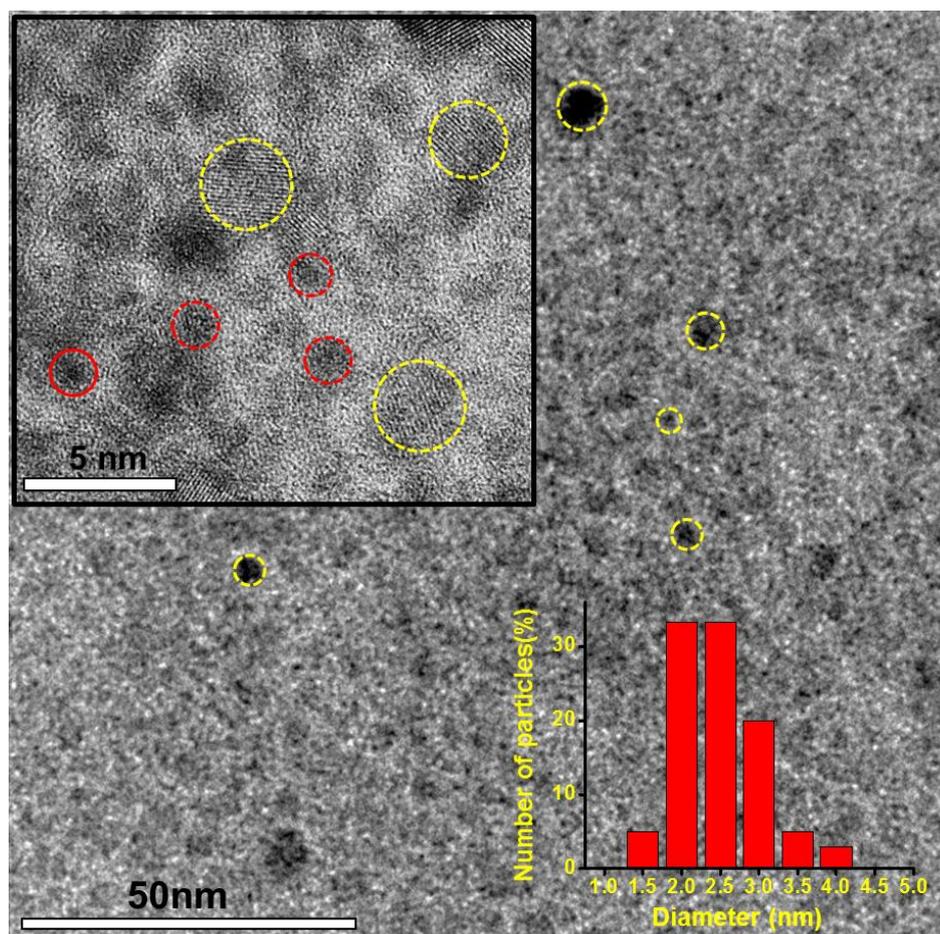


Fig. S4 TEM images of the [Ag₅₉(2,5-DCBT)₃₂] obtained by drop casting DCM solution of cluster on a carbon-coated copper grid. Several individual clusters are marked. Many of particles aggregate upon continuous irradiation. In the higher magnification image some clusters are encircled in red and cluster aggregated nanoparticles are encircled in yellow. Inset shows the particle size distribution. Average size of clusters is 2-2.5 nm. Aggregation makes size determination uncertain.

Supplementary information 5

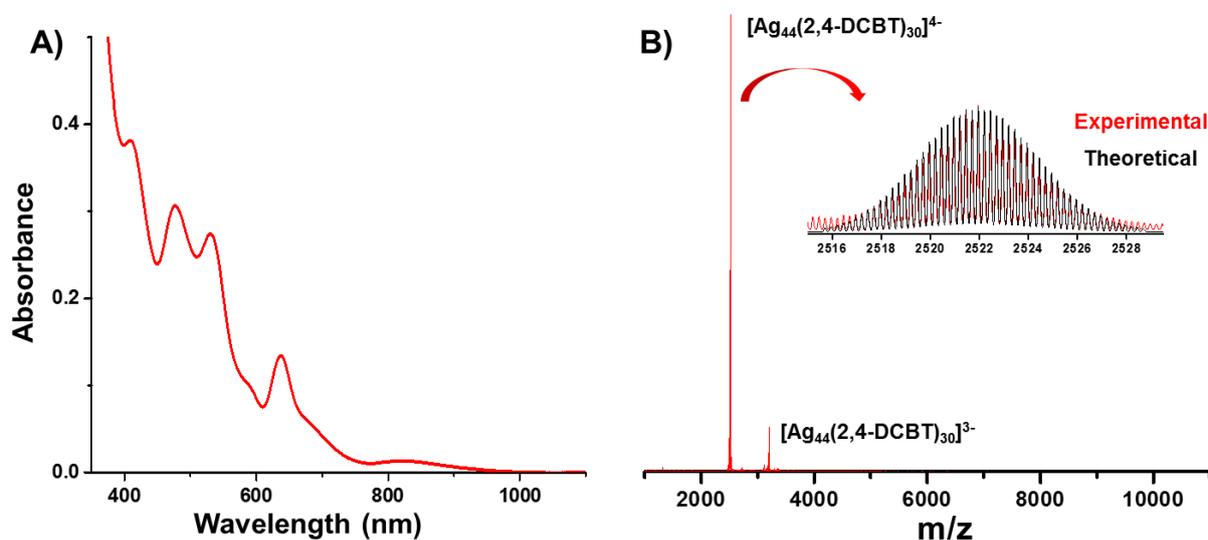


Fig. S5 (A) The optical absorption spectrum of the $[Ag_{44}(2,4-DCBT)_{30}]^{4-}$. (B) The ESI MS of the $[Ag_{44}(2,4-DCBT)_{30}]^{4-}$. Inset: The experimental and theoretical isotopic patterns which show an exact fit.

Supplementary information 6

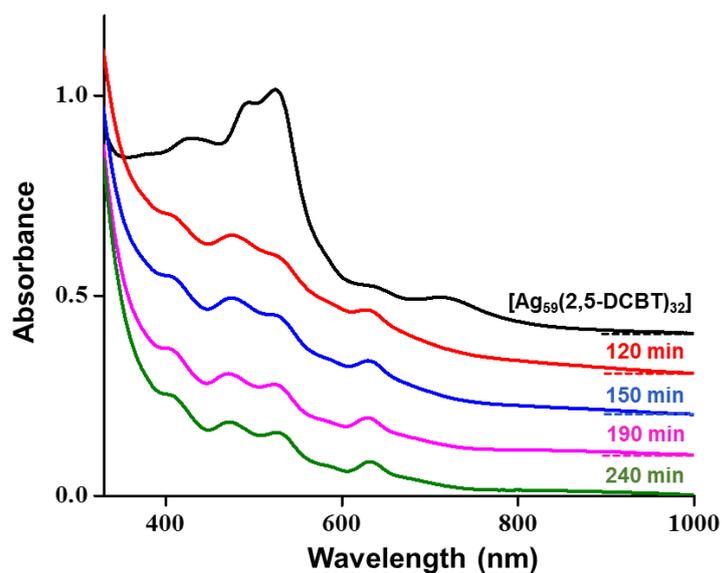


Fig. S6 Absorption spectra of the $[Ag_{59}(2,5-DCBT)_{32}]$ upon exposure to 2,4-DCBT. The black spectrum corresponds to the parent cluster. Others correspond to the LI product at different time scales. The spectra shows the stability of the product cluster. Spectra are shifted vertically for clarity.

Supplementary information 7

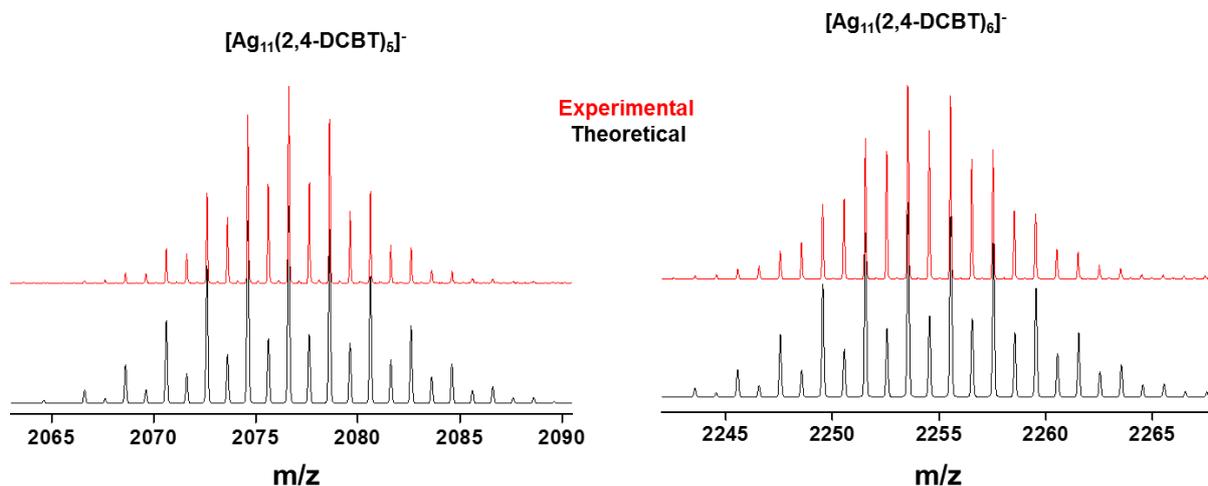


Fig S7: Theoretical and experimental isotopic patterns of the $[\text{Ag}_{11}(\text{2,4-DCBT})_5]^-$ and $[\text{Ag}_{11}(\text{2,4-DCBT})_6]^-$ species.

Supplementary information 8

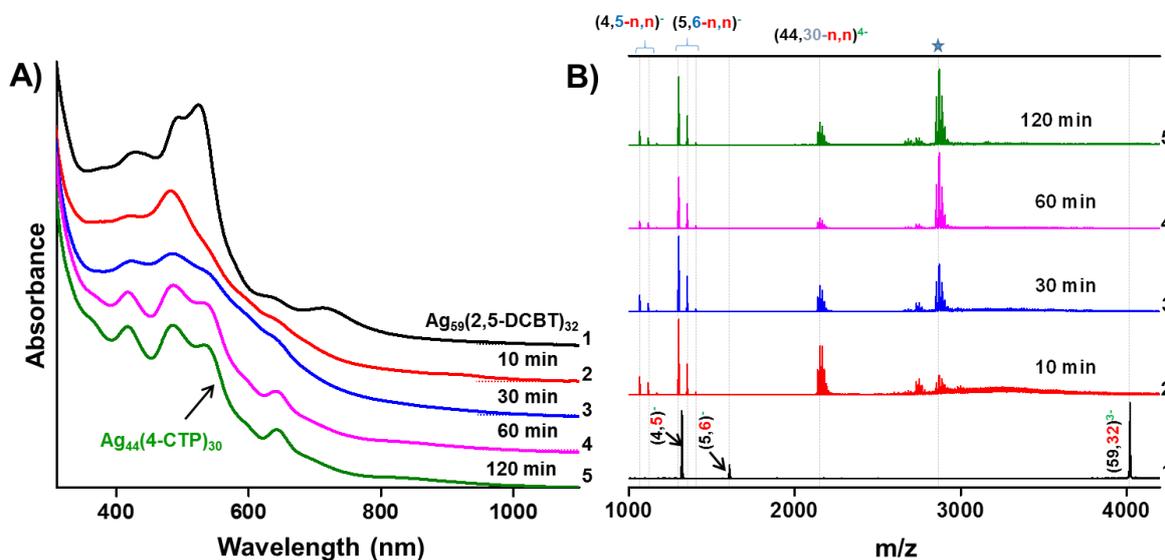


Fig. S8 (A) Time-dependent absorption study of the $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]$ upon exposure to 4-FTP. Spectra are shifted vertically for clarity. (B) Time-dependent ESI MS of the as-synthesized cluster of the same reaction. The numbers in black, red, and blue correspond to the number of Ag atoms, 2,5-DCBT and 4-FTP ligands, respectively. Numbers in green represent the charge of the clusters. Asterisks represent $[\text{Ag}_{44}(\text{4-FTP})_{30}]^{3-}$ and its fragments.

Supplementary information 9

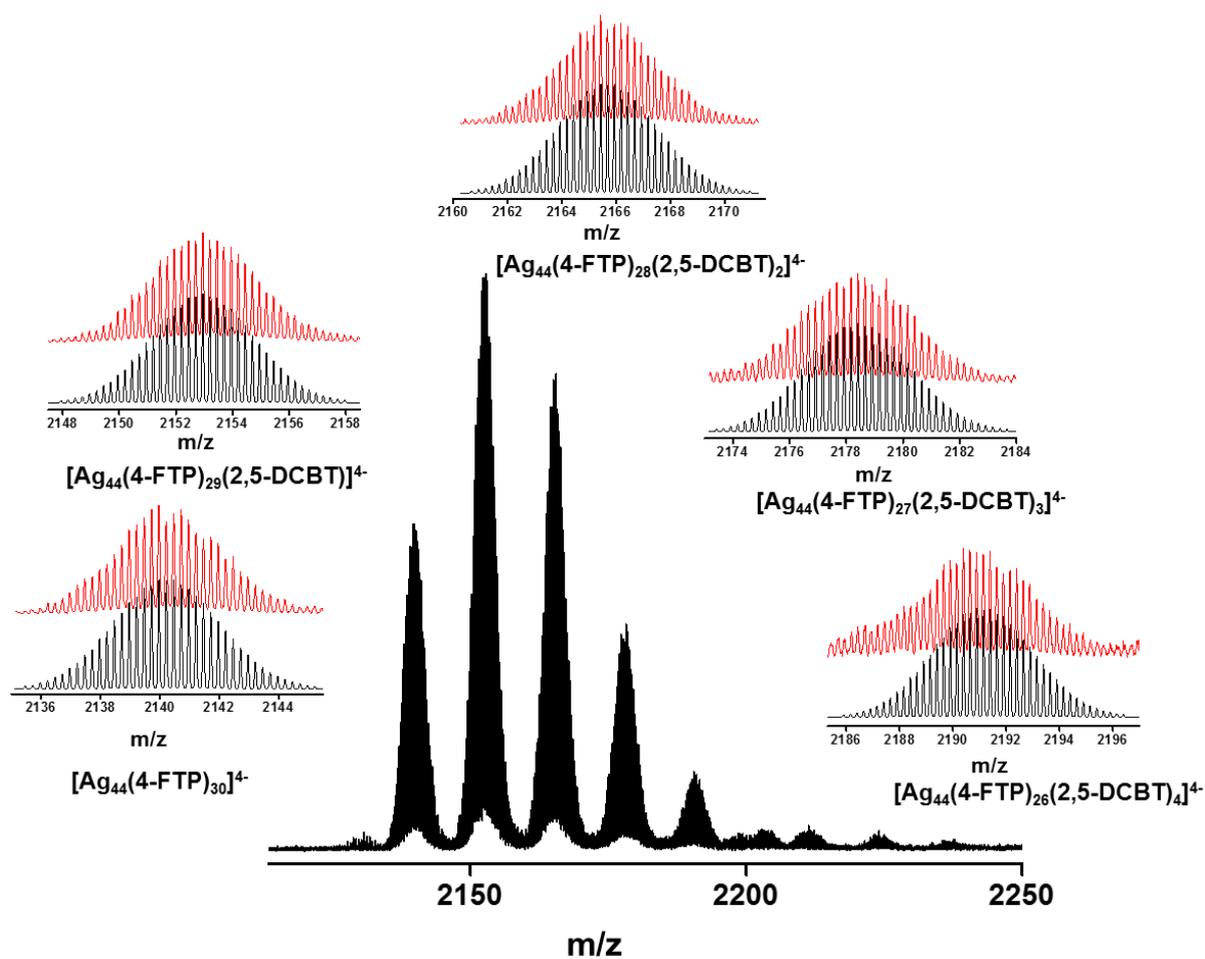


Fig. S9 The ESI MS of the $[\text{Ag}_{44}(\text{FTP})_{30-n}(\text{2,5-DCBT})_n]^{4-}$ ($n: 0-5$). Insets: The experimental and theoretical isotopic patterns of each species are shown.

Supplementary information 10

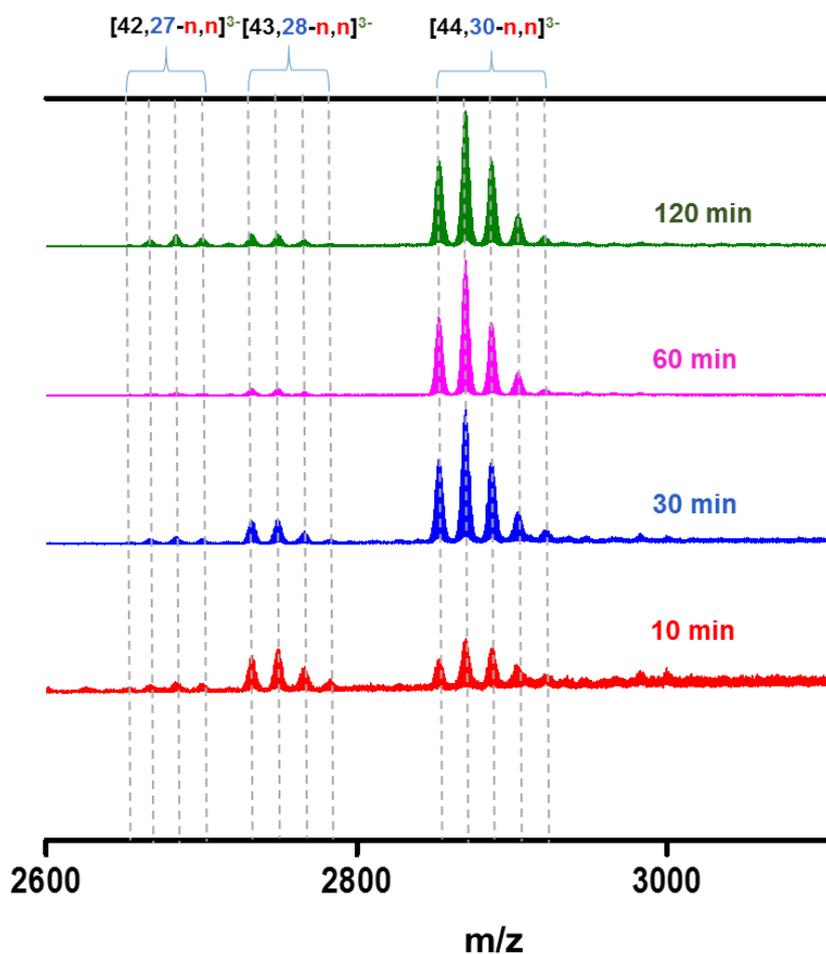


Fig. S10 Expanded region of ESI MS of the $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]$ during LI reaction in presence of 4-FTP at different times. The numbers in black, red, and blue correspond to the number of Ag atoms, 2,5-DCBT and 4-FTP ligands, respectively. Numbers in green represent the charge of the clusters. Peaks at m/z 2600-2900 are due to $[\text{Ag}_{44}(\text{FTP})_{30-n}(\text{2,5-DCBT})_n]^{3-}$ (n : 0-4) along with $[\text{Ag}_{43}(\text{FTP})_{28-n}(\text{2,5-DCBT})_n]^{3-}$ (n : 0-3) and $[\text{Ag}_{42}(\text{FTP})_{27-n}(\text{2,5-DCBT})_n]^{3-}$ (n : 0-3).

Supplementary information 11

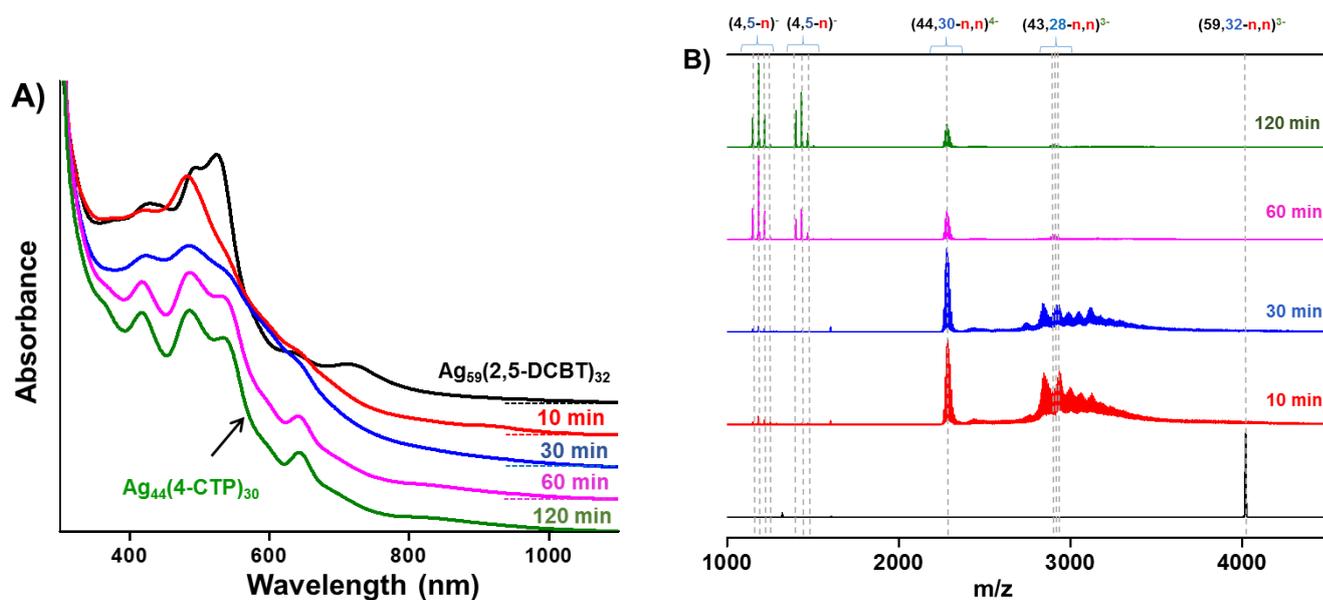


Fig. S11 (A) Time-dependent absorption study of the $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]$ upon exposure to 4-CTP. Spectra are shifted vertically for clarity. (B) Time-dependent ESI MS of the parent cluster during this LI conversion. The numbers in black, red, and blue correspond to the number of Ag atoms, 2,5-DCBT and 4-CTP ligands, respectively. Numbers in green represent the charge of the clusters.

Supplementary information 12

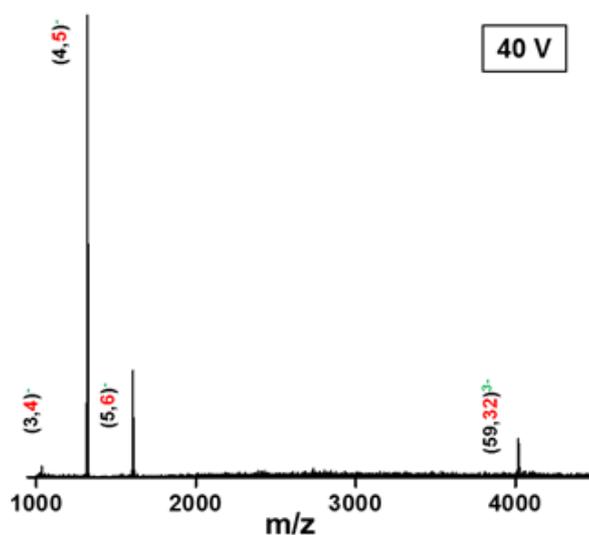


Fig. 5 An expanded view of the ESI MS at 40 V cone voltage. It shows that the $[\text{Ag}_3(\text{2,5-DCBT})_4]^-$ species is also forming along with other two fragments, $[\text{Ag}_4(\text{2,5-DCBT})_5]^-$ and $[\text{Ag}_5(\text{2,5-DCBT})_6]^-$, during the fragmentation of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{2-}$. The numbers in black, red and green correspond to Ag atom, 2,5-DCBT, and charge of the cluster, respectively.

Supplementary information 13

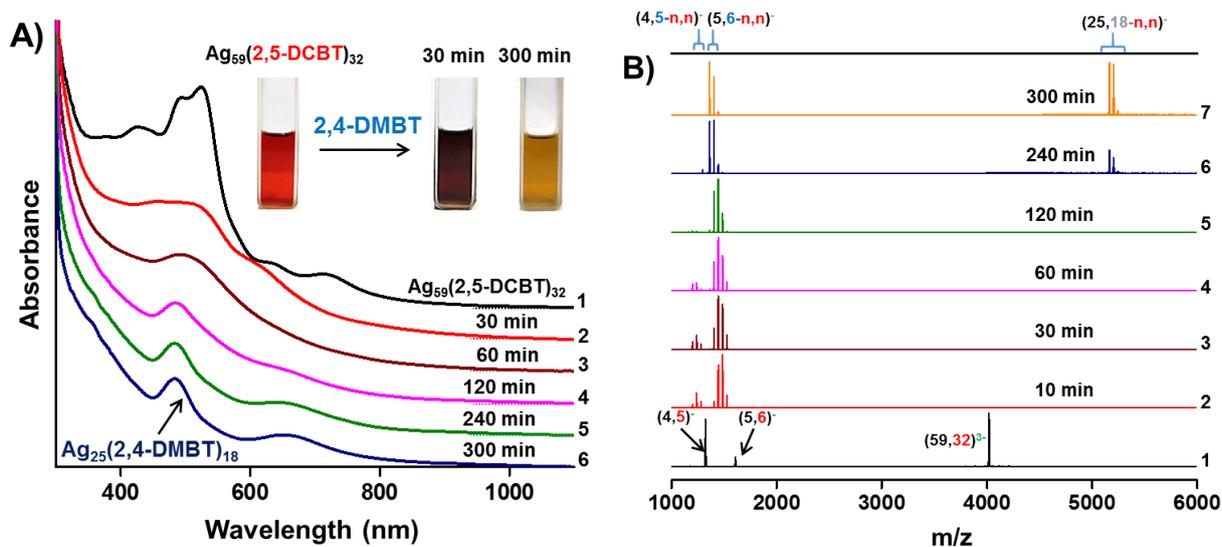


Fig. S13 (A) Time-dependent absorption study of the $[Ag_{59}(2,5-DCBT)_{32}]$ during LI reaction in presence of 2,4-DMBT. Spectra are vertically shifted for clarity. (B) Time-dependent ESI MS of the $[Ag_{59}(2,5-DCBT)_{32}]$ during the conversion. The numbers in black, red, and blue color correspond to the number of Ag atoms, 2,5-DCBT, and 2,4-DMBT ligands, respectively. The numbers in green represent the charge of the clusters. Inset: photographs of the $[Ag_{59}(2,5-DCBT)_{32}]$ during LI reaction at various times.

Supplementary information 14

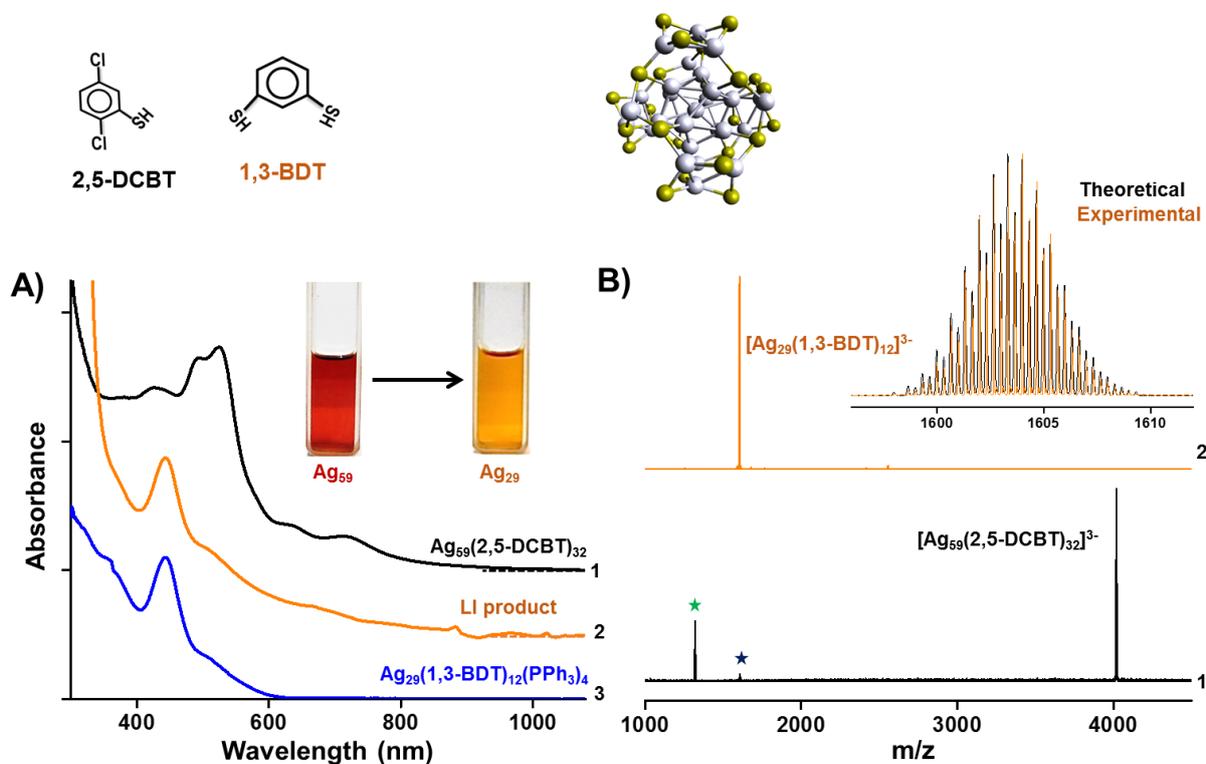


Fig. S14 (A) Comparison of absorption spectra of the $[Ag_{59}(2,5-DCBT)_{32}]^{3-}$ (black line), 1,3-BDT induced product (orange line) and pure $[Ag_{29}(1,3-BDT)_{12}(PPh_3)_4]^{3-}$ (blue line). Inset: The photographs of the cluster solution before and after LI transformation. Spectra 1 and 2 are shifted vertically for clarity. (B) ESI MS of the $[Ag_{59}(2,5-DCBT)_{32}]^{3-}$ (black) and 1,3-BDT induced product (orange). The fragments of $[Ag_{59}(2,5-DCBT)_{32}]^{3-}$ are labelled as in Fig. 1B. Inset: The experimental isotopic pattern of 1,3-BDT induced product which matches exactly with the theoretical isotopic patterns of the $[Ag_{29}(1,3-BDT)_{12}]^{3-}$. The structures of 1,3-BDT and 2,5-DCBT are shown above (A). Ball and stick model of IV is shown above (B). The R group is not shown.

Supplementary information 15

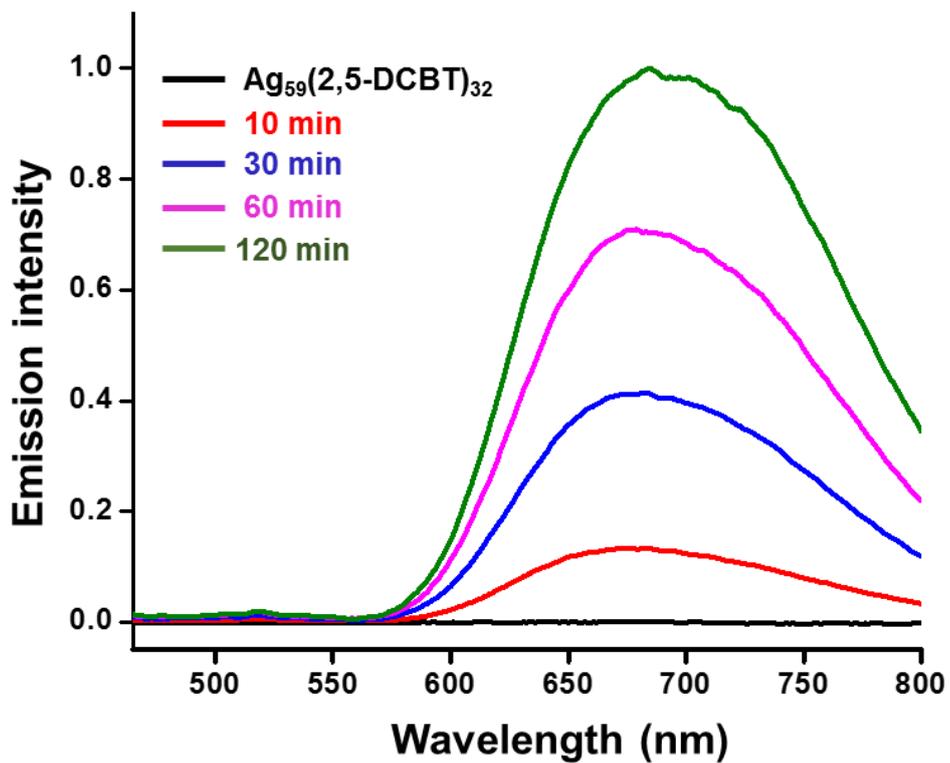


Fig. S15 Time-dependent emission spectra of the $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]$ LI with 1,3-BDT thiol at 450 nm excitation. $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]$ does not exhibit emission at 450 nm excitation. After addition of 1,3-BDT, the cluster shows emission at 670 nm and the intensity increases with time which suggests the formation of cluster **IV**.