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$[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$: a new cluster and a precursor for three well-known clusters†

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We report the synthesis of a new silver cluster, $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**I**) (2,5-DCBT: 2,5-dichlorobenzenethiol), which acts as a precursor for the synthesis of three well-known silver clusters, $[\text{Ag}_{44}(\text{2,4-DCBT}/\text{4-FTP})_{30}]^{4-}$ (**II**) (4-FTP: 4-fluorothiophenol and 2,4-DCBT: 2,4-dichlorobenzenethiol), $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$ (**III**) (2,4-DMBT: 2,4-dimethylbenzenethiol) and $[\text{Ag}_{29}(\text{1,3-BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (**IV**) (1,3-BDT: 1,3-benzenedithiol and PPh_3 : triphenylphosphine). This newly synthesized silver cluster, **I**, is characterized using UV-vis absorption studies, high resolution electrospray ionization mass spectrometry (ESI MS) and other analytical tools. The optical absorption spectrum shows distinct features which are completely different from the previously reported silver clusters. We perform the rapid transformations of **I** to other well-known clusters **II**, **III** and **IV** by reaction with different thiols. The time-dependent UV-vis and ESI MS measurements reveal that **I** dissociates into distinct thiolate entities in the presence of thiols and the thiolates recombine to produce different clusters. The conversion mechanism is found to be quite different from the previous reports where it occurs through the initial formation of ligand exchanged products. Here, we also show the synthesis of a different cluster core, $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{4-}$ (**IIa**) using 2,4-DCBT, a structural isomer of 2,5-DCBT under the same synthetic conditions used for **I**. This observation demonstrates the effect of isomeric thiols on controlling the size of silver clusters. The conversion of one cluster to several other clusters under ambient conditions and the effect of ligand structure in silver cluster synthesis give new insights into the cluster chemistry.

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Introduction

The chemistry of atomically precise noble metal clusters has become increasingly rich in the recent past.^{1–4} The properties of clusters such as intense luminescence are the principal motivation to pursue the science of these materials, besides the interest in fundamental science at the nanoscale.^{5–18} Clusters are typically made in solution by reduction of the metal ion, in the presence of suitable protective ligands such as thiols.^{1,2,19–21} Clusters being metastable transform into fragments such as thiolates, which occur in the presence of excess thiol. Such a transformation can also lead to sulfides as in the case of $[\text{Ag}_{25}(\text{SG})_{18}]$, which produces Ag_2S nanoparticles.²² A cluster can make another cluster as in the case of $[\text{Ag}_{35}(\text{SG})_{18}]$.²³ Such transformations are known for several clusters such as $[\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}]$, $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$,

$[\text{Ag}_{44}(\text{4-FTP})_{30}]^{4-}$, etc.^{24–28} By manipulating the synthetic conditions, different types of clusters can be prepared for the same metal and ligand combination.^{21,27,29–33} Certain clusters are formed only with specific ligands as in the case of $[\text{Ag}_{29}(\text{1,3-BDT})_{12}(\text{PPh}_3)_4]^{3-}$, $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$, etc.^{34,35} The position of the functional groups in a ligand also affects the size and nuclearity of the cluster. Such an example is methylbenzenethiol (MBT), having three structural isomers, *ortho*-, *meta*- and *para*- which produce three different gold clusters, $[\text{Au}_{130}(\text{p-MBT})_{50}]$, $[\text{Au}_{104}(\text{m-MBT})_{41}]$ and $[\text{Au}_{40}(\text{o-MBT})_{24}]$, respectively.³⁶ Another emerging category of cluster chemistry is inter-cluster reactions where clusters of different types react with each other spontaneously producing new clusters.³⁷ Most often these are alloys of distinct compositions, difficult to synthesize directly. A new class of such reactions is one in which the number of core atoms is conserved but the composition undergoes continuous change.³⁸ As a result, $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$ can be systematically transformed to $[\text{Au}_{25}(\text{PET})_{18}]^{-}$. This rich chemistry suggests a cluster as a precursor for many others in systematic chemical reactions. Herein, we have synthesized a new cluster, $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**I**) by modifying a reported protocol.³⁵ Under the same reaction conditions and reactant compositions, a

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different cluster core, $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{4-}$ (**IIa**),²⁵ is formed using 2,4-DCBT, a structural isomer of 2,5-DCBT. This study also elucidates the effect of isomeric thiol on tailoring the size of silver clusters during synthesis. This prompted us to study a series of transformations starting from our newly synthesized cluster (**I**) which has formed three different clusters $[\text{Ag}_{44}(\text{2,4-DCBT}/\text{4-FTP}/\text{4-CTP})_{30}]^{4-}$ (**IIa**, **IIb** and **IIc**),^{25,39} $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$ (**III**)³⁵ and $[\text{Ag}_{29}(\text{1,3-BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (**IV**)³⁴ with three different ligands under the same conditions. These rapid and multicore transformations suggest the possibility of using cluster precursors for the synthesis of many other clusters. We have performed time-dependent UV-vis and ESI MS studies to understand the probable pathways of transformation. During such investigations, we have found the existence of distinct thiolate fragments in solution which recombine and produce new species, which are otherwise not formed directly from larger cluster fragments. This observation supports a mechanism of transformation where thiolates recombine systematically.⁴⁰

Experimental

Chemicals and materials

2,5-Dichlorobenzenethiol (2,5-DCBT, 99%), 2,4-dichlorobenzenethiol (2,4-DCBT, 99%), 4-fluorothiophenol (4-FTP, 99%), 4-chlorobenzenethiol (4-CTP, 99%), 2,4-dimethylbenzenethiol (2,4-DMBT, 99%), 1,3-benzenedithiol (1,3-BDT, ≥99%), sodium borohydride (NaBH_4 , 95%) and tetraphenylphosphonium bromide (PPh_4Br , 97%) were purchased from Sigma-Aldrich. Silver nitrate (AgNO_3) and triphenylphosphine (PPh_3 , 98%) were purchased from Rankem chemicals and Spectrochem, respectively. All the chemicals were used without further purification. All solvents (dichloromethane (DCM), *N,N*-dimethylformamide (DMF), *n*-hexane, chloroform (CHCl_3) and methanol) were purchased from Rankem and were of analytical grade.

Synthesis of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**I**)

To synthesize $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**I**), a method reported for the synthesis of $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$ was followed with slight modifications,³⁵ although the cluster formed was completely different. About 20 mg of AgNO_3 was dissolved in 5 mL of methanol and then 9 mL of DCM was added. After stirring for 5 min, about 48 μL of 2,5-DCBT in 0.5 mL of DCM were added to this solution which produced yellow colored silver thiolate. After 5 min, 12 mg of PPh_4Br in 0.5 mL of DCM was added to the reaction mixture under stirring condition. During this process, the solution became colorless due to the formation of the silver-thiolate-phosphine complexes. After 20 min of stirring, about 23 mg of NaBH_4 (s) was dissolved in 2 mL of ice cold Milli-Q (18.2 $\text{M}\Omega\text{ cm}$) water and the solution was added dropwise to the reaction mixture. Immediately, the colorless solution changed to dark brown which implies the reduction of Ag^+ to Ag^0 . The reaction was kept under stirring condition overnight at ice-cold temperature. The precipitate was collected

by centrifugation and washed with hexane to remove excess thiol. The precipitate was collected and dissolved in DCM for further characterization.

Synthesis of $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{4-}$ (**IIa**)

The cluster was synthesized following exactly the same preparation method as that of **I**. Here, 2,4-DCBT, a structural isomer of 2,5-DCBT, was used as the protecting group. After the synthesis, the reddish brown colored cluster solution was transferred to a round-bottomed flask and the solvent was evaporated to dryness using a rotary vacuum evaporator. The precipitate was washed three times with methanol. Then the precipitate was collected and dissolved in DCM. The insoluble impurities were removed by centrifugation for 5 min. The supernatant was collected and dried by rotary evaporation.

Synthesis of $[\text{Ag}_{44}(\text{4-FTP}/\text{4-CTP})_{30}]^{4-}$ (**IIb**, **IIc**), $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$ (**III**) and $[\text{Ag}_{29}(\text{1,3-BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (**IV**)

These clusters were prepared following reported protocols with slight modifications,^{34,35,37} as explained in the ESI.†

Ligand-induced (**LI**) transformation of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**I**) to $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ (**II**) (SR: 2,4-DCBT, 4-FTP and 4-CTP)

The transformation of **I** to **IIa** was performed by the addition of 1 μL of 2,4-DCBT in 3 mL of DCM solution of **I** (~3 mg). The reaction mixtures were stirred slowly using a rice pellet and kept under ambient conditions. The UV-vis absorption spectra and ESI MS of the reaction mixtures were recorded at different time intervals to study the conversion in detail. Similarly, 4-FTP and 4-CTP were used for the LI transformation of **I** to **IIb** and **IIc**, respectively.

LI transformation of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**I**) to $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$ (**III**)

The transformation was carried out following the same procedure as mentioned above and 1 μL of 2,4-DMBT was used for the reaction.

LI transformation of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**I**) to $[\text{Ag}_{29}(\text{1,3-BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (**IV**)

The same process was repeated with 1 μL of 1,3-BDT and 5 mg of PPh_3 for the transformation of **I** to **IV**. PPh_3 was used for the stabilization of the product cluster.

Characterization

Optical absorption studies of the clusters were conducted using a PerkinElmer Lambda 25 UV-vis absorption spectrophotometer, typically in the range of 200–1100 nm. Samples were placed in a quartz cell of 1 cm path length. The emission spectra were measured using a JASCO FP-6300 spectrophotometer. Mass spectra of the cluster samples were analyzed using a Waters Synapt G2-Si mass spectrometer using electrospray ionization in the negative ion mode. It had a maximum resolution of 50 000 in the mass range of interest. Further

details are given in the ESI.† Thermogravimetric analysis (TGA) was conducted using a NETZSCH STA 449 F3 Jupiter instrument. The analysis was done under nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) measurement was conducted using an Omicron ESCA Probe spectrometer with polychromatic Al K α X-rays ($h\nu = 1486.6$ eV). The cluster solution (in DCM) was dropcasted on an XPS sample stub. During the experiment, X-ray power was maintained at 300 W and pass energy for survey scans was 50 eV and for specific regions, it was 20 eV. The spectrum was collected when the base pressure of the instrument was in the 10^{-10} mbar range. The binding energies of the core levels were calibrated with C 1s B.E. (set at 284.9 eV). High-resolution transmission electron microscopic (TEM) analysis of the cluster was conducted with a JEOL 3010 instrument. The samples were prepared by drop-casting cluster solution (DCM) on carbon-coated copper grids and allowed to dry under ambient conditions.

Results and discussion

The synthesis of the new silver cluster, $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**1**), was performed following a reported procedure with slight modifications, as described in the Experimental section. The DCM solution of the as-synthesized cluster is red in color (inset of Fig. 1A). Fig. 1A shows that the optical absorption spectrum of the cluster solution is completely different from previously reported silver clusters like, $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$,³⁵ $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$,³⁴ $[\text{Ag}_{35}(\text{SG})_{18}]$,²³ $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$,^{39,41} $[\text{Ag}_{35}(\text{H}_2\text{L})_2(\text{L})(\text{C}\equiv\text{CBu}^t)_{16}]^{3+}$,⁴² $[\text{Ag}_{51}(\text{BDT})_{19}(\text{PPh}_3)_3]^{3-}$,⁴³ $[\text{Ag}_{55}(\text{SR})_{31}]$,⁴⁴ $[\text{Ag}_{67}(\text{2,4-DMBT})_{32}(\text{PPh}_3)_8]^{3+}$,⁴⁵ $[\text{Ag}_{68}(\text{SBB})_{34}]$,²⁹ $[\text{Ag}_{50}(\text{DPPM})_6(\text{TBBM})_{30}]$,⁴⁶ $[\text{Ag}_{75}(\text{SG})_{40}]$,⁴⁷ $[\text{M}_3\text{Ag}_{17}(\text{TBBT})_{12}]$ ⁴⁸ and $[\text{Ag}_{152}(\text{PET})_{60}]$.⁴⁹ It consists of six distinct features around

720, 645, 528, 495, 430 and 380 nm. Typically, the stability of silver clusters is an issue of concern which prompted us to test the stability of our newly synthesized cluster using UV-vis absorption spectroscopy. The absorption spectra presented in Fig. S1† show that the cluster solution is stable up to 5 days at 4 °C. The mass spectrum in negative mode is presented in Fig. 1B, in the mass range of m/z 1000–10 000. The instrumental conditions are given in the ESI.† In the ESI MS, an intense peak is obtained at m/z 4020. An expanded view of the spectrum is presented in Fig. S2A,† which shows that the separation between the two peaks is m/z 0.33. This observation and the prominence of the feature in the MS suggest that the cluster is likely to contain 3 $^-$ charge. The peak at m/z 4020 is assigned as $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$. The assignment was confirmed by comparing the theoretical (black trace) and experimental isotopic patterns (red trace), which match perfectly (inset of Fig. 1B). Along with the peak at m/z 4020 two less intense peaks are observed at m/z 1322 and 1608 (marked with green and blue asterisks, respectively in Fig. 1B). These peaks correspond to $[\text{Ag}_4(\text{2,5-DCBT})_5]^-$ and $[\text{Ag}_5(\text{2,5-DCBT})_6]^-$, respectively. These species might be thiolate byproducts formed during the synthesis and/or fragmented products of the cluster as mentioned in the previous report of $[\text{PdAg}_{24}(\text{2,4-DCBT})_5]^{2-}$.⁵⁰ No other peak was observed even after changing the instrumental conditions, which supports the purity and monodispersity of the cluster. Further characterization of the as-synthesized cluster was done by performing TGA measurement which shows good agreement between experimental (51.1%) and calculated (51.3%) mass loss values (see Fig. S2B†). To determine the oxidation state of the metal as well as ligand binding on the cluster surface, XPS was performed and the spectrum is presented in Fig. S3.† The XPS spectrum reveals the presence of Ag 3d_{5/2}, Cl 2p_{3/2}, and S 2p_{3/2}

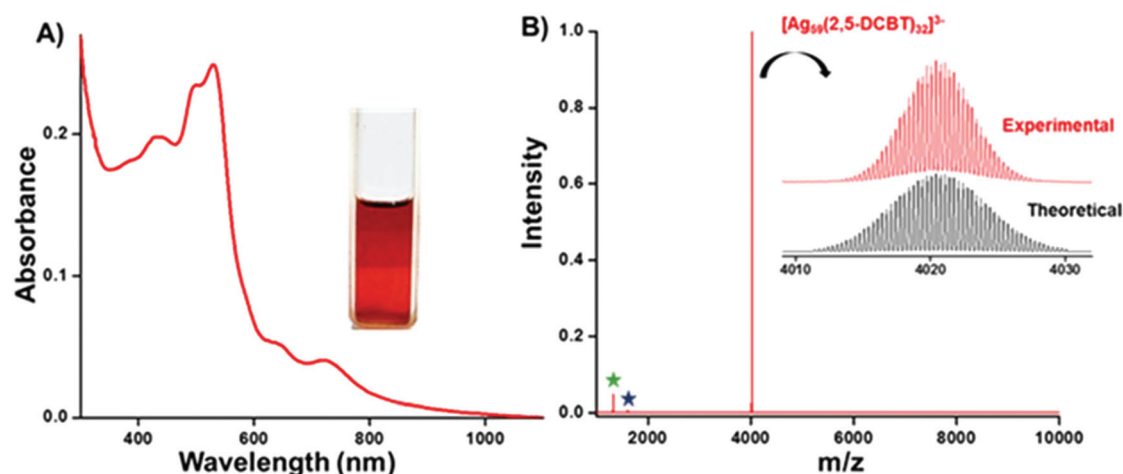


Fig. 1 (A) UV-vis absorption spectrum of the as-synthesized cluster which exhibits characteristic peaks around 430, 496, 529, 640 and 720 nm. Inset: Visible light photograph of the cluster solution in DCM. (B) Negative mode ESI MS of the as-synthesized cluster in the mass range of m/z 1000–10 000. An intense peak at m/z 4020 corresponds to $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$. Less intense peaks at m/z 1322 and 1608 marked with green and blue asterisks are due to the presence of $[\text{Ag}_4(\text{2,5-DCBT})_5]^-$ and $[\text{Ag}_5(\text{2,5-DCBT})_6]^-$, respectively. Inset: Comparison of the experimental and simulated mass spectra confirms the assigned composition. Note that the minor intensity variations predicted around the peak maximum are reproduced in the experiment (inset).

which occur at 367.7, 200.2 and 162.0 eV, respectively. The silver metal in the cluster is close to the zerovalent state; however, both Ag(I) and Ag(0) are likely to be present in the cluster which is clearly separable from this spectrum (Fig. S3A†). The Ag:Cl:S ratio obtained from the XPS measurement is 1.3:1:0.54, close to the calculated composition of the cluster (1.2:1:0.59). The clusters were also observed in TEM (Fig. S4†). The average size of the cluster is 2.0–2.5 nm as revealed from the particle size distribution graph (inset of Fig. S4†). The size of the cluster is larger than that expected as clusters are beam sensitive and aggregation occurs upon continuous electron beam irradiation (see Fig. S4,† clusters are marked with red circles in the higher magnification image while aggregated nanoparticles are encircled with yellow circles). Such nanoparticles show lattice structure, as expected. This behavior is similar to several other nanoclusters.^{44,51}

The synthesis of **I** also demonstrates an isomeric effect of thiol in silver cluster synthesis. The use of two isomeric thiols, 2,4-DCBT and 2,5-DCBT resulted in two different clusters, **I** and **IIa**, respectively under the same reaction conditions as mentioned in the Experimental section. The absorption spectrum and ESI MS of **IIa** are shown in Fig. S5.† This study led us to perform LI transformation of our newly synthesized cluster, **I**, using different thiols such as 2,4-DCBT, 4-FTP, 4-CTP, 2,4-DMBT and 1,3-BDT under ambient conditions.

LI conversion of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**I**) to $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ (**II**) (SR: 2,4-DCBT, 4-FTP and 4-CTP)

LI conversions of **I** to **IIa**, **IIb** and **IIc** were performed as described in the Experimental section using 2,4-DCBT, 4-FTP, and 4-CTP ligands, respectively. Immediately after the addition of the thiols, the color of the cluster solution darkened to reddish black and slowly it transformed into pink. The optical absorption spectra of **I** (black trace), LI product using 2,4-DCBT (red trace) and pure **IIa** (blue trace) are displayed in Fig. 2A. The absorption features of the LI product match exactly with those of **IIa**, synthesized separately (red and blue spectra). The spectrum of the LI product has some thiolate impurities which contribute to an exponential background. The negative mode ESI MS of the initial and final products are shown in Fig. 2B. The red trace describes the mass spectrum of the final product. It exhibits a peak at m/z 2521 corresponding to $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{4-}$ whose theoretical and experimental isotopic patterns fit exactly (inset of Fig. 2B). Along with the 4^- charged species, there are peaks corresponding to $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{3-}$, $[\text{Ag}_{43}(\text{2,4-DCBT})_{28}]^{3-}$ and $[\text{Ag}_{42}(\text{2,4-DCBT})_{27}]^{3-}$ (the region is marked with a red asterisk as shown in Fig. 2B) which are in accordance with previous reports.^{37,41}

To investigate the detailed mechanism of this conversion, time-dependent optical absorption spectroscopy and ESI MS measurements were performed (Fig. 3). The absorption spectra

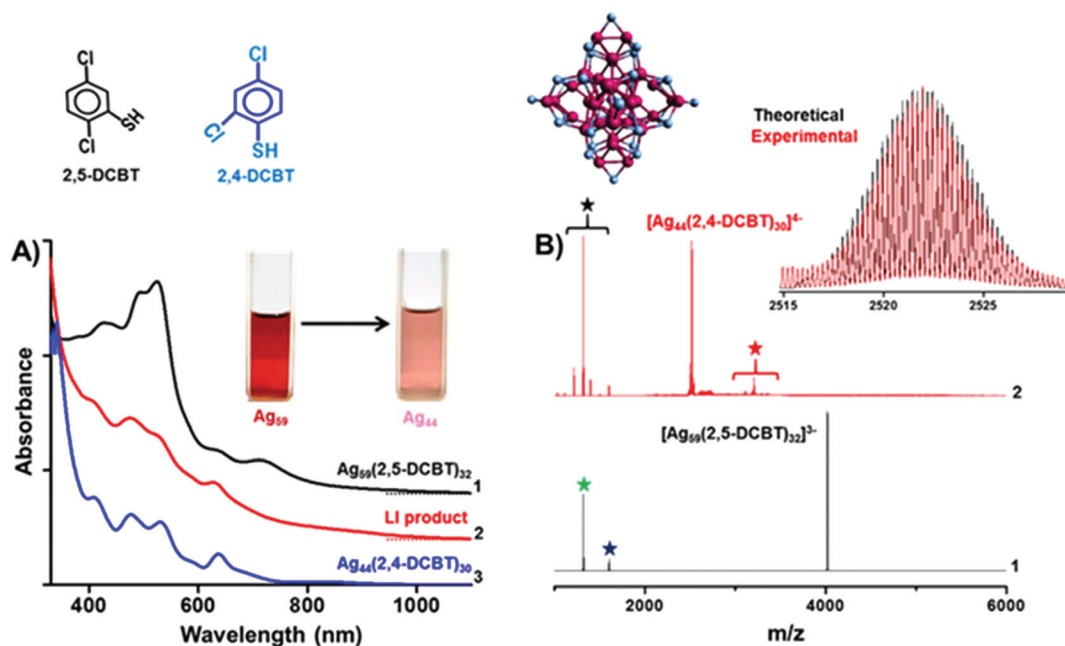


Fig. 2 (A) Comparison of the absorption spectra of **I** (black trace), 2,4-DCBT induced product (red trace) and pure **IIa** (blue trace). The spectrum of the LI product has some thiolate impurities resulting in the exponential background. Spectra 1 and 2 are vertically shifted for clarity. Inset: The photographs of cluster solution before and after LI transformation. (B) ESI MS of **I** (black) and 2,4-DCBT induced product (red). Red asterisk represents $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{3-}$ and its fragments. The black asterisk denotes the smaller thiolates produced along with **IIa** during the transformation. The fragments of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ are labelled with asterisks as in Fig. 1B. Inset: The experimental isotopic pattern of the 2,4-DCBT induced product which matches exactly with the theoretical isotopic pattern of $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{4-}$. The structures of 2,4-DCBT and 2,5-DCBT are shown above (A). Ball and stick model of **II** is shown above (B). The R group is not shown.

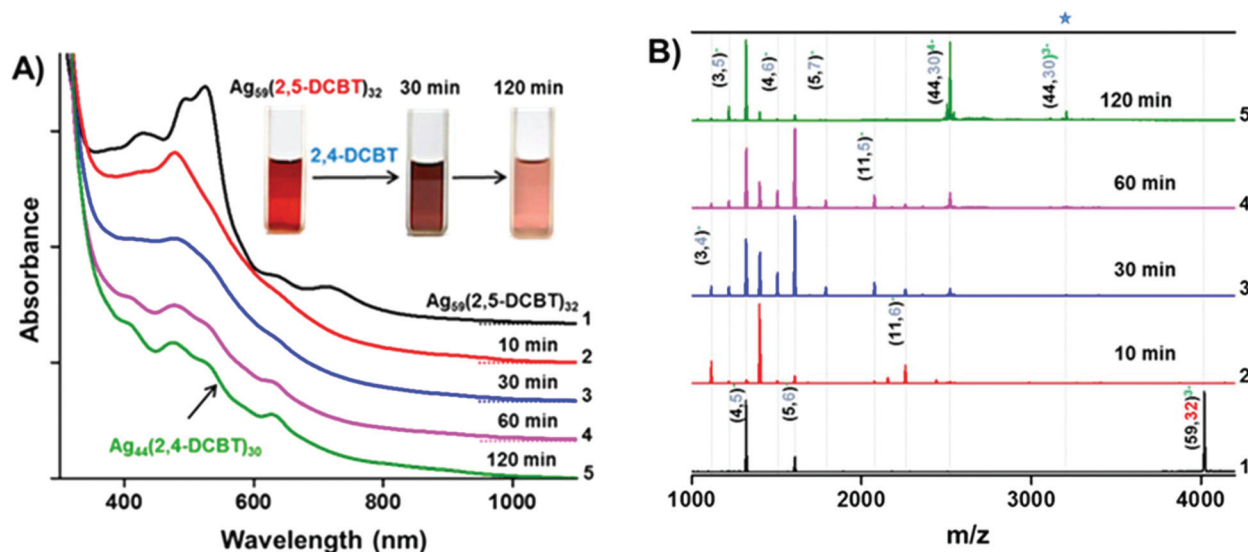


Fig. 3 (A) Time-dependent absorption spectra of **I** during LI transformation in the presence of 2,4-DCBT. Spectra are shifted vertically for clarity. Complete conversion of **I** to **IIa** occurs within 120 min. Inset: Photographs of **I** and LI product as a function of time. (B) Time-dependent ESI MS of **I** during LI transformation with 2,4-DCBT. The numbers in black, red and blue correspond to the number of Ag atoms, 2,5-DCBT, and 2,4-DCBT ligands, respectively. The numbers in green represent the charge of the clusters. Asterisks represent $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{3-}$ and its fragments.

at different reaction times are presented in Fig. 3A. After 10 min of 2,4-DCBT addition, the absorption spectrum (red) shows a peak at ~ 485 nm along with three small peaks around 430, 536 and 645 nm. The Ag_{11} cluster shows a characteristic feature at ~ 485 nm.⁵ The peaks at ~ 430 and 536 nm are the characteristic features of **I** and **IIa**, respectively. The peak at ~ 645 nm is characteristic of both **I** and **IIa**. This observation suggests the presence of **I**, **IIa** and Ag_{11} after 10 min of the conversion. With time, more and more **IIa** is formed and hence its absorption features become pronounced. Fig. 3A reveals the complete transformation of **I** into the LI product within 120 min. No further change in the absorption features occurs beyond this timescale, suggesting the stability of the final product (Fig. S6†).

The intermediates of this conversion are corroborated by ESI MS performed at different intervals (Fig. 3B). The black spectrum is consistent with the parent cluster, **I**. After 10 min of 2,4-DCBT addition, the mass spectrum (red color) shows the presence of peaks at m/z 1037, 1215, 1323, 1608, 2257 and 2079. Among these peaks, the first four are assigned as $[\text{Ag}_3(\text{SR})_4]^-$, $[\text{Ag}_3(\text{SR})_5]^-$, $[\text{Ag}_4(\text{SR})_5]^-$ and $[\text{Ag}_5(\text{SR})_6]^-$, respectively while the other two peaks correspond to $[\text{Ag}_{11}(\text{SR})_6]^-$ and its single ligand loss species, $[\text{Ag}_{11}(\text{SR})_5]^-$ (SR: 2,4-DCBT and/or 2,5-DCBT). The compositions of $[\text{Ag}_{11}(\text{SR})_6]^-$ and $[\text{Ag}_{11}(\text{SR})_5]^-$ were confirmed by matching isotopic distributions (Fig. S7†). In addition, there is a weak peak at m/z 2521 due to $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ (isotopic distribution is presented in the inset of Fig. 2B). After 30 min, along with these peaks, two other peaks arise at m/z 1500 and 1787 corresponding to $[\text{Ag}_4(\text{SR})_6]^-$ and $[\text{Ag}_5(\text{SR})_7]^-$, respectively which are not seen in the spectrum recorded after 120 min. With the progress of the reaction, the peak intensity of $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ gradually increases (Fig. 3B). After 120 min, the spectrum comprises of peaks corresponding

to $[\text{Ag}_3(\text{SR})_4]^-$, $[\text{Ag}_3(\text{SR})_5]^-$, $[\text{Ag}_4(\text{SR})_5]^-$, and $[\text{Ag}_5(\text{SR})_6]^-$ species as well as the $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ cluster. The peaks belonging to $[\text{Ag}_{11}(\text{SR})_6]^-$ and $[\text{Ag}_{11}(\text{SR})_5]^-$ are absent after 60 min. This observation implies the conversion of unstable $[\text{Ag}_{11}(\text{SR})_6]^-$ to stable $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$. The exact numbers of both the ligands present in these species are difficult to determine due to their isomeric nature and hence in our assignment, ligands are represented by 'SR'. The distinct mass separations in ESI MS are largely due to the number of silver atoms and not the ligands. To ensure the number of ligands present in the LI product, similar experiments were repeated with 4-FTP and the reaction was monitored by the same techniques. The time-dependent absorption spectra and ESI MS are shown in Fig. S8†. The ESI MS comprise of peaks at m/z 1068, 1119, 1169, 1303, 1354 and 1405 of which the first three correspond to $[\text{Ag}_4(\text{FTP})_{5-n}(\text{2,5-DCBT})_n]^-$ whereas the last three correspond to $[\text{Ag}_5(\text{FTP})_{6-n}(\text{2,5-DCBT})_n]^-$ (n : 0–2) (Fig. S8B†). Along with these peaks, a series of peaks in the range of m/z 2140–2205 are observed corresponding to $[\text{Ag}_{44}(\text{FTP})_{30-n}(\text{2,5-DCBT})_n]^{4-}$ (n : 0–5) whose fitted experimental and theoretical isotopic patterns are shown in Fig. S9†. The 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) (see Fig. S10†). Further repetition of these conversion reactions was conducted using 4-CTP, as described in the ESI (Fig. S11†). Apart from these thiolate species, no other intermediates were detected during LI transformations in the presence of 4-FTP and 4-CTP.

To ensure the generation of $[\text{Ag}_3(\text{SR})_4]^-$, $[\text{Ag}_4(\text{SR})_5]^-$ and $[\text{Ag}_5(\text{SR})_6]^-$ from the parent cluster, the ESI MS of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ was monitored by varying the cone voltage of the mass spectrometer (Fig. 4). According to previous reports, it is known that fragmentation of silver clusters can occur by the

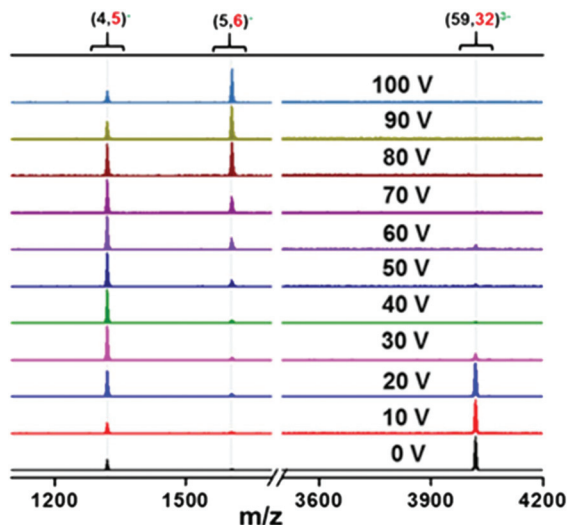
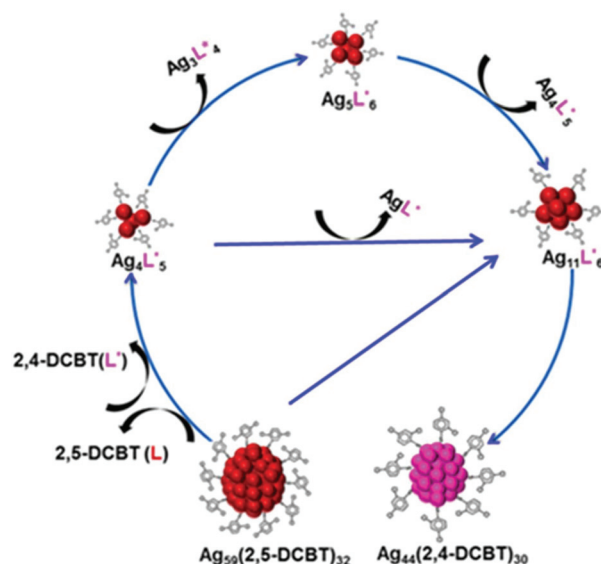


Fig. 4 ESI MS of **I** by varying the cone voltage of the mass spectrometer. The numbers in black, red and green correspond to Ag atoms, 2,5-DCBT and charge of the cluster, respectively.

systematic loss of species like $[\text{Ag}_5\text{L}_6]^-$, $[\text{AgL}_2]^-$, $[\text{Ag}_2\text{L}_3]^-$ or $[\text{Ag}_3\text{L}_3]^-$.^{5,52} In our study, thiolates like $[\text{Ag}_4(2,5\text{-DCBT})_5]^-$ and $[\text{Ag}_5(2,5\text{-DCBT})_6]^-$ were observed upon fragmentation. The mass spectrum at zero cone voltage shows a strong peak corresponding to $[\text{Ag}_{59}(2,5\text{-DCBT})_{32}]^{3-}$ along with two weak peaks corresponding to $[\text{Ag}_4(2,5\text{-DCBT})_5]^-$ and $[\text{Ag}_5(2,5\text{-DCBT})_6]^-$ species (Fig. 4). As mentioned previously, these small peaks might occur due to the presence of some thiolate species formed during the reaction and/or may be due to the specific cluster fragments under ESI MS conditions. Subsequently, the cone voltage of the mass spectrometer was increased to study the fragmentation of the as-synthesized cluster. With the increase of the cone voltage, the cluster peak intensity gradually decreased while the intensities of the thiolate peaks increased. The absence of other new peaks suggest that the cluster fragments and converts into these thiolate species. Along with these two thiolate species, some $[\text{Ag}_3(2,5\text{-DCBT})_4]^-$ was also formed by fragmentation (Fig. S12†). Above 60 V cone voltage, the cluster peak vanishes completely and only thiolate peaks were found to exist. When the cone voltage was further increased, the peak intensity of $[\text{Ag}_5(2,5\text{-DCBT})_6]^-$ increased along with the decrease of $[\text{Ag}_4(2,5\text{-DCBT})_5]^-$ which could be due to greater stability of the former fragment than the later. The mass spectrum at the maximum cone voltage (100 V) contains peaks corresponding to $[\text{Ag}_4(2,5\text{-DCBT})_5]^-$ and $[\text{Ag}_5(2,5\text{-DCBT})_6]^-$ species alone. After a detailed fragmentation study, we correlated the gas phase fragmentation of the as-synthesized cluster with that of the solution phase. From the above experiments, it was discovered that the cluster produced similar types of fragments both with the change in the cone voltage as well as in the presence of different thiols. Therefore, for the transformation of **I** to **IIa**, we proposed a reaction mechanism depicted in Scheme 1. According to this scheme, at first, the parent cluster was dissociated into some small



Scheme 1 Ligand-induced conversion pathway of **I** to **IIa**. L in red color denotes 2,5-DCBT and L* in pink color denotes 2,4-DCBT.

thiolates like, $[\text{Ag}_3(\text{SR})_4]^-$, $[\text{Ag}_4(\text{SR})_5]^-$, $[\text{Ag}_5(\text{SR})_6]^-$, etc. After that, small thiolate species recombined and rearranged in the reaction to form $[\text{Ag}_{11}(\text{SR})_6]^-$ and $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$. The $[\text{Ag}_{11}(\text{SR})_6]^-$ species can be formed directly from $[\text{Ag}_{59}(2,5\text{-DCBT})_{32}]^{3-}$ in the presence of external thiols. $[\text{Ag}_{11}(\text{SR})_6]^-$ being unstable, got converted to $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ gradually. All these successive processes occurred so rapidly that it could be described as one step conversion where immediately after the addition of 2,4-DCBT, the parent cluster got converted to $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ along with the formation of some thiolates. Initially, a smaller amount of the $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ cluster was formed. Then, continuously thiolate entities recombined and rearranged to produce more and more $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ clusters. The unstable $[\text{Ag}_{11}(\text{SR})_6]^-$ cluster was also formed by the recombination of thiolates and then converted to stable $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$. Due to the faster reaction in the presence of 4-FTP and 4-CTP, reaction intermediates were not detected even upon conducting the reaction under ice-cold conditions.

LI conversion of $[\text{Ag}_{59}(2,5\text{-DCBT})_{32}]^{3-}$ (**I**) to $[\text{Ag}_{25}(2,4\text{-DMBT})_{18}]^-$ (**III**)

The LI conversion of **I** to **III**, using 2,4-DMBT was performed by using a similar procedure (details are mentioned in the Experimental section). The absorption features of the conversion are clearly shown in Fig. 5A where the optical spectrum of the final product (brown) matches with that of pure **III** (blue). The ESI MS of the final product exhibits peaks at m/z 5165 corresponding to $[\text{Ag}_{25}(2,4\text{-DMBT})_{18}]^-$ which was also confirmed by exact matching of the theoretical and experimental isotopic patterns (inset of Fig. 5B). The peaks marked with orange asterisk belong to $[\text{Ag}_{25}(2,4\text{-DMBT})_{18-n}(2,5\text{-DCBT})_n]^-$ (n : 1–3). As in the previous case, a detailed study of this transformation was performed and the data are presented in

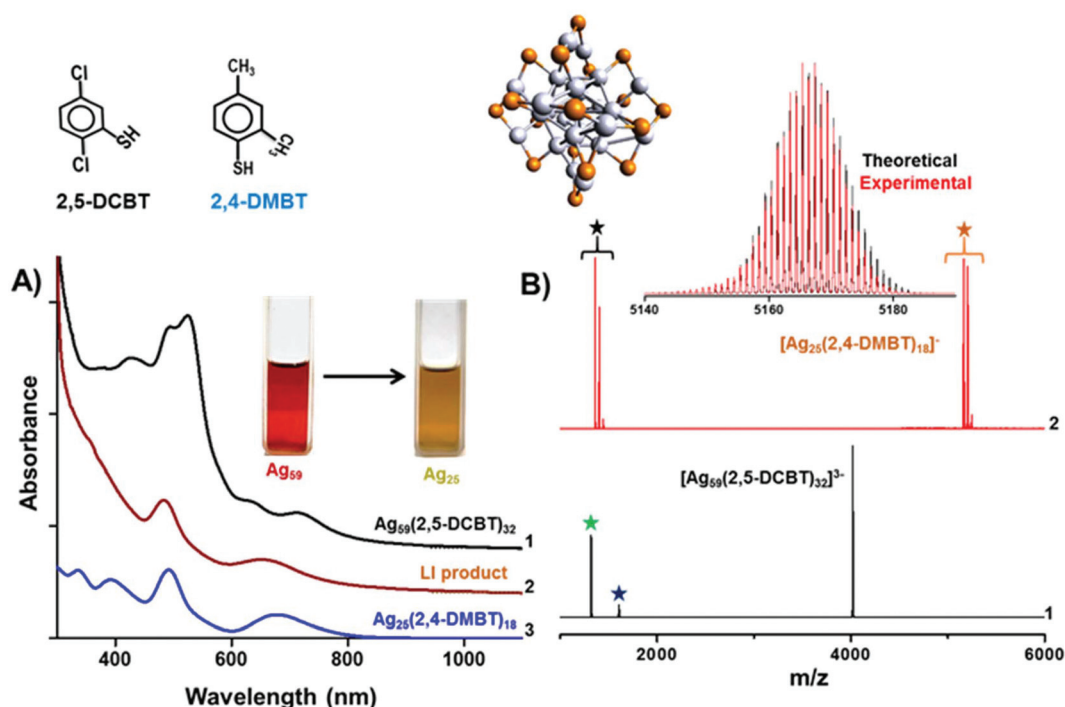


Fig. 5 (A) UV-vis absorption spectra of I (black trace), 2,4-DMBT induced product (brown trace) and pure III (blue trace). Inset: Photographs of I and LI product. (B) ESI MS of I (black trace) and its 2,4-DMBT induced product (red trace). The orange asterisk represents $[\text{Ag}_{25}(\text{2,4-DMBT})_{18-n}(\text{2,5-DCBT})_n]^{3-}$ (where n : 1, 2 and 3). The black asterisk denotes the smaller thiolates produced along with III during the transformation. The fragments of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ are labeled with asterisks as in Fig. 1B. Inset: The theoretical isotopic pattern of $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{3-}$ which exactly matches with the experimental isotopic pattern of the 2,4-DMBT induced product. The structures of 2,4-DCBT and 2,5-DCBT are shown above (A). Ball and stick model of III is shown above (B). The R group is omitted.

Fig. S13.† The absorption spectra, shown in Fig. S13A,† reveal a systematic evolution of III from I. With the addition of the thiol, the color of the solution changed from red to reddish black and to yellow (inset of Fig. S13A†). ESI MS at different time intervals are presented in Fig. S13B.† After 10 min of thiol addition, it exhibits peaks at m/z 1158, 1197, 1240, 1281 and 1322 corresponding to $[\text{Ag}_4(\text{2,4-DMBT})_{5-n}(\text{2,5-DCBT})_n]^{3-}$ (n : 1–5) along with peaks at m/z 1404, 1444, 1485, 1527 and 1567 corresponding to $[\text{Ag}_5(\text{2,4-DMBT})_{6-n}(\text{2,5-DCBT})_n]^{3-}$ (n : 1–5). Initially, there was no peak at m/z 1362 which belongs to the $[\text{Ag}_5(\text{2,4-DMBT})_6]^{3-}$ species. After 60 min, this peak appears and increases with time. After 120 min, $[\text{Ag}_4(\text{2,4-DMBT})_{5-n}(\text{2,5-DCBT})_n]^{3-}$ started disappearing along with the appearance of $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{3-}$. The conversion is quite slow unlike that of I to II.

LI conversion of $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (I) to $[\text{Ag}_{29}(\text{1,3-BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (IV)

Similar to II and III, another well-known cluster is IV, obtained using 1,3-BDT. In the case of previous transformations, one monothiol protected cluster was converted under the influence of another monothiol. To investigate the conversion pathway in the presence of dithiol, 1,3-BDT was used. The procedure of conversion is mentioned in the Experimental section. The UV-vis spectra of the parent cluster (black trace) and the LI product (orange trace) are shown in Fig. S14A.† All absorption

features of the LI product match with that of pure IV (blue trace). Fig. S14B† presents the ESI MS of the parent and product cluster. The assignment of the LI cluster was confirmed by the exact fitting of the theoretical and experimental isotopic distributions (inset of Fig. S14B†). The systematic evolution of IV is depicted in Fig. 6. The optical absorption spectra (Fig. 6A) and ESI MS (Fig. 6B) clearly suggest the direct transformation of I to IV in the presence of BDT. In Fig. 6B the black spectrum corresponds to the parent cluster. In the other spectra, the peak around m/z 1604 is assigned as $[\text{Ag}_{29}(\text{1,3-BDT})_{12}]^{3-}$. The absorption spectrum of IV shows a peak at 520 nm which suggests the presence of a PPh_3 ligand. But, the PPh_3 ligand is weakly bound to the cluster and it is lost easily during ionization.³⁴ Hence, most often, the peak at m/z 1604 appears as the main peak in ESI MS.^{9,43,52} The formation of IV was further studied using time-dependent emission spectra. The time-dependent emission spectra of I LI with 1,3-BDT at 450 nm excitation wavelength are presented in Fig. S15.† I does not exhibit emission at 450 nm excitation while IV shows an emission maximum around 670 nm. Thus, initially there was no emission and after addition of 1,3-BDT, the cluster shows an emission maximum around 670 nm. The intensity of the emission spectrum increases with time which suggests the formation of IV. Due to the faster rate of the reaction of dithiol, the intermediates of this conversion are difficult to trace.

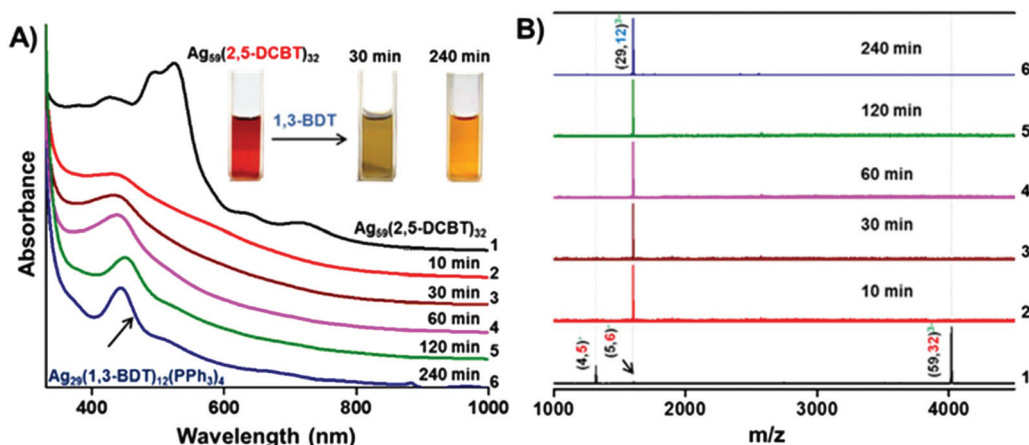


Fig. 6 (A) Time-dependent absorption study of **I** in the presence of 1,3-BDT. Spectra are vertically shifted for clarity. (B) Time-dependent ESI MS of **I** during the LI transformation. The numbers in black, red, and blue color correspond to the numbers of Ag atoms, 2,5-DCBT and 1,3-BDT ligands, respectively. The numbers in green represent the charge of the clusters. Inset: Photographs of **I** and the LI product, **IV** as a function of time.

While the structure of **I** is unknown, the rapid LI transformation of the cluster to other well-known clusters suggests a structural similarity between all of these clusters. The Ag_{59} metal core without ligand has been the subject of a computational investigation.⁵³ The structure is a distorted Ag_{55} icosahedron composed of three additional atoms integrated into the outer layer forming a rosette-like structure and one atom on the outer layer. The rapid chemical transformation of **I** to **II** suggests that the ligated Ag_{59} may be structurally related to ligand-protected Ag_{44} .

Conclusions

In conclusion, we present the synthesis of a new silver cluster, **I** using 2,5-DCBT. The use of 2,4-DCBT, a structural isomer of 2,5-DCBT, creates a cluster with a different core, **IIa** under exactly the same conditions. This result suggests the effect of ligand isomers in silver cluster synthesis. The as-synthesized cluster is used as a precursor for the synthesis of some well-known clusters, **II**, **III** and **IV** via ligand-induced transformation. The mechanistic path of these conversions was examined in detail from which we understand that the transformations occur rapidly through the formation of distinct thiolate fragments in solution. This study demonstrates that precursor clusters can be used for the synthesis of new silver clusters under ambient conditions with several other ligands which would help to expand silver cluster chemistry.

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