PAPER



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Unusual reactivity of dithiol protected clusters in comparison to monothiol protected clusters: studies using $Ag_{51}(BDT)_{19}(TPP)_3$ and $Ag_{29}(BDT)_{12}(TPP)_4$ [†]

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We report the synthesis and unique reactivity of a new green dithiol protected cluster (DTPC), Aq₅₁(BDT)₁₉(TPP)₃ (BDT and TPP are 1,3-benzenedithiol and triphenylphosphine, respectively). The cluster composition was confirmed by electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) mass spectrometric studies as well as by other supporting data. Surprisingly, the chemical reactivity between this DTPC and Au₂₅(SR)₁₈ involves only metal ion exchange in Au₂₅(SR)₁₈ without any ligand exchange, while reactions between monothiol protected clusters (MTPCs) show both metal and ligand exchange, an example being the reaction between Ag₂₅DMBT₁₈ and Au₂₅PET₁₈ (where DMBT and PET are 2,4-dimethylbenzenethiol and phenylethanethiol, respectively). The conclusions have been confirmed by the reaction of another DTPC, Ag₂₉(BDT)₁₂(TPP)₄ with Au₂₅BT₁₈ (where BT corresponds to butanethiol) in which only metal exchange happens in Au₂₅BT₁₈. We also show the conversion of $Ag_{51}(BDT)_{19}(TPP)_3$ to $Ag_{29}(BDT)_{12}(TPP)_4$ in the presence of a second monothiol, DMBT which does not get integrated into the product cluster. This is completely different from the previous understanding wherein the reaction between MTPCs and a second thiol leads to either mixed thiol protected clusters with the same core composition or a completely new cluster core protected with the second thiol. The present study exposes a new avenue of research for monolayer protected clusters, which in turn will give additional impetus to explore the chemistry of DTPCs.

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Introduction

The discipline of soluble atomically precise noble metal clusters protected with thiols is expanding rapidly.^{1–4} These materials are potential candidates for drug delivery, cancer therapy, catalysis, sensing, *etc.*^{4–14} Recently, they have been used for electrochemical and photocatalytic water splitting to produce hydrogen gas which is a promising fuel for the future.^{15–17} Synthesis, characterization and crystal structures of these materials have generated increasing interest in the last decade.^{4,18–31} Introduction of new thiols which inturn results in a new cluster system is considered as a promising synthetic

strategy for this new class of materials.^{7,29,32,33} The use of new thiols has resulted in several silver clusters, especially Ag₂₅DMBT₁₈,³⁴ Ag₄₄FTP₃₀,²³ Ag₄₄MBA₃₀,²² etc. (DMBT, FTP and MBA refer to 2,4-dimethylbenzenethiol, 4-fluorothiophenol and 4-mercaptobenzoic acid, respectively). The introduction of dithiols has lead to completely new cluster systems such as Ag₂₉(BDT)₁₂(TPP)₄ (BDT and TPP are 1,3-benzenedithiol and triphenylphosphine respectively);35 the chemistry of such systems is yet to be explored in detail. The metal thiol interface in such dithiol protected clusters (DTPCs) is distinctly different from the monothiol system and this difference must have profound influence on their chemistry and associated properties. In this paper, we have presented an unprecedented chemical reaction of a dithiol protected silver cluster in one of the most studied class of chemical reactions, namely metal atom substitution, using our newly reported DTPC, $[Ag_{51}(BDT)_{19}(TPP)_3]^{3-}$. This spontaneous reaction in solution at room temperature transforms only the metal core leaving the thiolate shell intact, in contrast to monothiol protected clusters (MTPCs), where simultaneous changes of both the core and the shell occur during such an event.36 This difference in the chemistry of monothiol and dithiol is compared in Scheme 1. Besides, we



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 $[\]dagger$ Electronic supplementary information (ESI) available: UV-vis and ESI MS spectra of BT and OT ligated Au₂₅ cluster; UV-vis and ESI MS spectra of cluster II; MALDI MS spectra for cluster I and cluster II; time dependent ESI MS spectra for inter-cluster reactions and ligand exchange reactions; concentration dependent ESI MS spectra for the inter-cluster reaction; ESI MS and UV-vis spectra comparison for ligand catalyzed inter-cluster conversion process. See DOI: 10.1039/c6nr07692k



Scheme 1 Reactions (1) and (2) are reproduced from the recent literature which show that the well known $Au_{25}BT_{18}$ cluster undergoes both metal and ligand exchange reactions upon exposure to monothiol protected Ag_{44} (FTP)₃₀ or Ag_{25} (DMBT)₁₈ clusters. Reaction (3) shows that unlike (1) and (2), the $Au_{25}BT_{18}$ cluster undergoes only metal exchange reaction upon exposure to the newly reported dithiol protected Ag_{51} (BDT)₁₉(TPP)₃ cluster.

show the conversion of one cluster to another, catalyzed by a different thiol which by itself does not get integrated into the reactant or the product. This observation is also completely different from the behavior of MTPCs, which has been known for a few years.^{1,18,19,37,38-43} The difference in chemistry involving the conversion of DTPCs is shown in Scheme 2.

Experimental

Chemicals and materials

Butanethiol (BT, 99%), octanethiol (OT, 99%), 1,3-benzenedithiol (BDT, \geq 99%), 2,4-dimethylbenzenethiol (DMBT, 99%), sodium borohydride (95%), tetraoctylammonium bromide (TOABr, 98%), and *trans*-2-[3-(4-*tert*butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, >98%) were purchased from Sigma-Aldrich. Gold(m) chloride trihydrate was synthesized in our laboratory. Silver nitrate (AgNO₃) was purchased from Rankem chemicals and PPh₃ was from Spectrochem. All the chemicals were used as received without further purification. All solvents (dichloromethane (DCM), *n*-hexane, tetrahydrofuran (THF), dimethylformamide (DMF), chloroform (CHCl₃) and methanol) were purchased from Rankem and were of analytical grade. The water used for the syntheses was of Milli-Q grade with a resistivity of 18.2 MΩ cm.

Synthesis of Ag₅₁(BDT)₁₉(TPP)₃

The material was synthesized by modifying the procedure used for $Ag_{29}(BDT)_{12}(TPP)_4$.³⁵ Initially 20 mg of AgNO₃ was dissolved

in 5 mL of methanol. To that, 9 mL of chloroform was added. After 1 min of stirring, 0.5 mL of chloroform solution containing 13.5 µL of BDT was added to the above mixture and it was covered with a black cloth. After 5 min, 0.5 mL of the chloroform solution containing 200 mg of PPh3 was added to the above mixture under stirring conditions. Ice cold aqueous solution (0.5 mL) of $NaBH_4$ (11 mg) was added to the above mixture after 5 minutes. Immediately the color of the solution changed from colorless to dark brown upon addition of NaBH₄. The reaction was continued for 3 h under dark conditions. After 3 h of stirring, the green colored supernatant was collected through centrifugation. Centrifugation was carried out for 10 min at a speed of 14 000 rpm. The volume of the supernatant was reduced to 5 mL by rotary evaporation. Then the supernatant was cleaned with millipore water 3-4 times to remove the water-soluble ingredients. During this process, the volume of the supernatant was reduced to 1.5 mL. Then the cluster was precipitated from the above solution by the addition of an equal volume of hexane. The precipitate was collected through centrifugation (3000 rpm, 3 min) and dissolved in DMF for further characterization. Hereafter we call it cluster I.

Synthesis of Au₂₅BT₁₈ and Au₂₅OT₁₈

An $Au_{25}BT_{18}$ cluster was synthesized by using a reported method.⁴⁴ Briefly, HAuCl₄·3H₂O (40 mg) was dissolved in 7.5 mL of THF and 65 mg of TOABr was added to this under stirring conditions. Stirring was continued for 15 min. During



Scheme 2 Reactions (4)–(6) are reproduced from previous reports which show that monothiol protected Au_{25} , Au_{38} and Ag_{44} clusters react with a second thiol leading to either mixed thiol protected clusters with the same core composition or a new cluster core protected with the second thiol. Unlike the above reactions, in a DTPC (shown as reaction (7)), the second thiol does not get integrated into the product. The second thiol acts as a catalyst for the conversion of $Ag_{51}BDT_{19}$ to $Ag_{29}BDT_{12}$.

this period, the color of the solution changed from yellow to orange-red. To this solution, 55 μ L of butanethiol (BT) was rapidly added under vigorous stirring (1200 rpm). The mixture was stirred for 2 h during which it turned colorless. After that, 39 mg of NaBH₄ dissolved in 2.5 mL of ice-cold water was

added rapidly to the reaction mixture, again under vigorous stirring. Stirring was continued for 6 h. The solvent was removed from the reaction mixture by rotary vacuum evaporation. Methanol was added for the removal of thiol and other impurities. The insoluble cluster was collected as a precipitate

through centrifugation. The process was repeated 4 times and subsequently 4 mL acetone was added to dissolve the cluster. Other impurities such as insoluble thiolate and the Au₁₄₄ cluster were removed by centrifugation. The supernatant was collected and dried by rotary evaporation. Au₂₅OT₁₈ was synthesized following the same procedure and 89 μ L thiol was used for the synthesis.

Reaction of Ag_{51}(BDT)_{19}(TPP)_3 (cluster I) with Au_{25}BT_{18} or Au_{25}OT_{18}

A required amount of the $Ag_{51}BDT_{19}TPP_3$ cluster (cluster I) was dissolved in 3 mL of DMF in such a way that the absorbance at 420 nm was 1. To this solution, different quantities of the $Au_{25}BT_{18}$ cluster were added and UV-vis spectra of the mixture were taken at different time intervals. Each time 200 µL of the sample mixture was taken from the mixture and diluted three times for ESI MS measurements. The same was repeated with the $Au_{25}OT_{18}$ cluster.

Reaction of $Ag_{51}(BDT)_{19}(TPP)_3$ (cluster I) with DMBT thiol

 $Ag_{51}BDT_{19}TPP_3$ cluster (cluster I) was dissolved in 3 mL of DMF in such a way that the final absorbance at 420 nm was 0.8. To that, different volumes of DMBT were added. The UV-vis spectra of the mixture were taken at different time intervals. It was observed that during this process, the color of the mixture changed from green to red. Each time, a 200 µL sample mixture was taken from the mixture and was diluted twice for ESI MS measurements and diluted four times for fluorescence measurements.

Characterization

UV-vis measurements

Absorption spectra of the cluster solution were measured with a Perkin Elmer Lambda 25 UV-vis absorption spectrophotometer. Spectra were typically measured in the range of 190–1100 nm. The clusters were dissolved in the respective solvents and spectra were recorded in quartz cells with a 10 mm path length.

Luminescence measurements

Luminescence measurements were carried out using the HORIBA JOBIN VYON Nano Log instrument. The band pass for excitation and emission was set at 3 nm. Diluted cluster solutions were used for these measurements.

MALDI MS measurements

Matrix-assisted laser desorption ionization (MALDI) mass spectra of the clusters were measured using a Voyager DE PRO Bio spectrometry Workstation (Applied Biosystems) MALDI TOF MS instrument. A pulsed nitrogen laser of 337 nm was used for desorption ionization and TOF was operated in the delayed extraction mode. Typical delay times employed were of the order of 75–150 ns. DCTB in DMF (12.5 mg mL⁻¹) was used as the matrix. The measurements were performed in were acquired.

A Waters Synapt G2-Si High Definition mass spectrometer equipped with Electrospray ionization, Matrix-assisted laser desorption ionization and ion mobility separation was used. All the samples were analyzed in the negative mode of electrospray ionization. The instrumental parameters were first optimized for $Ag_{51}(BDT)_{19}$ and other samples were analyzed using similar settings with slight modifications depending on the sample. The instrument was calibrated using CsI as the calibrant.

negative ion mode. For each measurement, typically 500 scans

XPS

X-ray photoelectron spectroscopy (XPS) measurements were performed using an Omicron ESCA Probe spectrometer with polychromatic Mg Ka X-rays ($h\nu$ = 1253.6 eV). The powder sample was taken on a Mo plate using double sided adhesive conductive carbon tape. Experiments were carried out at an X-ray power of 300 W and pass energies of 50 eV for survey scans and 20 eV for specific regions. The base pressure of the instrument was in the 10⁻¹⁰ mbar range during spectrum collection. Binding energies of the core levels were calibrated with C 1s B.E, set at 284.9 eV.

SEM and EDAX analyses

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) analyses were performed in a FEI QUANTA-200 SEM. For measurements, the powder sample was used.

Characterization of Au₂₅BT₁₈ and Au₂₅OT₁₈

Characterization of Au_{25} was reported earlier in great detail by various studies. In view of this, we have presented only essential details of characterization here (Fig. S1[†]). The UV-vis and ESI MS spectra of the as synthesized $Au_{25}BT_{18}$ cluster are comparable with the published data (S1A[†]). Similarly, UV-vis and ESI MS spectra presented in Fig. S1B[†] confirm the formation of the $Au_{25}OT_{18}$ cluster.

Results and discussion

Most of the results of chemical reactivity are presented with our newly synthesized cluster **I**. The synthesis of cluster **I** involves the known synthetic protocol of $Ag_{29}(BDT)_{12}(TPP)_4$ (hereafter we call it as cluster **II**) with slight modification.³⁵ We note that the formation of cluster **I** is strongly affected by the concentration of NaBH₄ used in the synthesis. We varied this for a fixed concentration of Ag^+ and thiol. At a lower concentration of NaBH₄, only cluster **II** was formed, whereas at a higher concentration, we observed a completely new cluster with associated properties. This drastic change in the product composition is depicted in Fig. 1 where the synthesis was performed at three concentrations of NaBH₄ (Fig. 1A₁, B₁ and C₁) keeping the concentration of other reactants and conditions the same. While cluster **II** formed at every concentration of



Fig. 1 Photographs of synthesis. A_1 , B_1 and C_1 show the synthesis performed using 6, 11 and 16 mg of NaBH₄, respectively. This corresponds to 10, 19 and 28 mM of NaBH₄ in the reaction mixture. A_2 , B_2 and C_2 are the results of centrifugation of A_1 , B_1 and C_1 , respectively. Image B_2 shows that the green supernatant is formed only from 11 mg of NaBH₄. The precipitates in A_2 , B_2 and C_2 were dissolved in DMF and the photographs of the corresponding DMF solutions are presented in A_3 , B_3 and C_3 , respectively.

NaBH₄ (precipitate shown in Fig. 1A₂, B₂ and C₂), cluster I formed only for 11 mg of NaBH₄ (green supernatant, Fig. 1B₂). Using the polarity difference of solvents, two clusters were separated. In all the cases, the precipitate was dissolved in DMF. Photographs of the DMF solutions of the clusters are shown in Fig. 1A₃, B₃ and C₃. Measured optical and mass spectral data of all the above cluster solutions matched with those reported for Ag₂₉BDT₁₂ (Fig. S2[†]).³⁵ While this is identified as Ag₂₉BDT₁₂, the other cluster (cluster I, green supernatant, Fig. $1B_2$) shows a completely different optical spectrum presented in Fig. 2A. The spectrum shows 5 features at 775, 698, 665, 605 and 415 nm. Under the synthesis conditions, only cluster formation is possible and no complex or silver sulfide colloids are likely. Comparison of the spectrum with all the silver clusters known so far has also suggested the same. A photograph of cluster I in visible light, presented in the inset of Fig. 2A, shows that the material is green in color which is also different from the color of cluster II.

The optical features of purified cluster I are completely different from the well known reported silver clusters, $Ag_{25}DMBT_{18}$, ³⁴ $Ag_{29}BDT_{12}$, ³⁵ $Ag_{44}(SR)_{30}$, ^{22,23} $Ag_{152}(PET)_{60}$, ⁴⁵ $Ag_{68}(SBB)_{34}$, ⁴⁶ $Ag_7(DMSA)_4$ ⁴⁷ and $Ag_9(H_2MSA)_7$. ⁴⁸ This prompted us to measure the mass spectrum of cluster I to

determine the exact molecular mass and formula of the $Ag_m(BDT)_n$ cluster. The ESI MS was measured in -ve mode. Details of the sample preparation and instrumental conditions are given in the Experimental section. The mass spectrum is presented in Fig. 2B with a mass range of m/z 1000–10000. There is a peak at m/z 2721.56. The expanded spectrum presented in Fig. S3^{\dagger} shows that the peaks are separated by m/z0.33 which implies that the cluster core contains 3- charge. The corresponding composition is $[Ag_{51}(BDT)_{19}]^{3-}$. The presence of a small quantity of $[Ag_{29}(BDT)_{12}]^{3-}$ as a side product is marked with a blue asterisk. ESI MS data (Fig. 2B) shows that the cluster is highly pure as no peaks other than those of interest were found in the mass range of m/z 1000–10 000. The isotopic structures of silver are important to assign accurate composition. In view of the difference in the abundances of ¹⁰⁷Ag and ¹⁰⁹Ag isotopes, the isotopic pattern is likely to reflect characteristic features for this cluster. In Fig. 2C we presented a comparison of the experimental isotopic pattern (black trace) with simulation (red trace) which matches perfectly. Minor variations in the intensities of adjacent peaks are matched perfectly besides a complete match of the mass spectral peak positions. The composition $[Ag_{51}(BDT)_{19}]^{3-}$ may be confirmed from this spectra. We note here that such an accurate match of isotopic patterns is rarely seen in cluster mass spectrometry of clusters. Confirmation of the assignment was also made with the help of a MALDI MS study. MALDI MS of the sample was taken using the matrix, trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene] malononitrile, popularly known as DCTB. At threshold fluence, the mass spectrum (black trace, Fig. S4[†]) shows a monoanionic peak at m/z 8162 which is assigned to $[Ag_{51}BDT_{19}]^{-}$ and a dianionic peak at m/z 4081. The MALDI MS spectrum shows silver attached peaks along with the molecular ion peak which was also seen for cluster II (red trace, Fig. S4[†]). Both the dithiol protected clusters show the same behavior which is quite different from the MALDI MS of monothiol protected clusters reported so far. This is the first report on MALDI MS of dithiol protected atomically precise silver clusters. At present, we do not have any definite explanation for the above observation. It could be that in dithiol protected clusters, there may be hanging ligands with one thiol attached to the cluster core, the other end being free may bind with the silver ion. Or the sulphur bound to the cluster core readily accepts free silver. MALDI MS analyses also show that the cluster is highly pure as no peaks other than those of interest were found in the mass range of m/z 3000–50000 (Fig. S5[†]). With increasing laser fluence, additional peaks were observed in the mass spectrum. The peaks appeared at regular intervals of $\sim m/z$ 8100. These peaks are due to the dimer ($\sim m/z$ 16 200), trimer ($\sim m/z$ 24 300), tetramer ($\sim m/z$ 32 400) and pentamer $(\sim m/z \ 40 \ 500)$ of the Ag₅₁BDT₁₉ cluster. Such association reactions are expected in the gas phase upon desorption.⁴⁹ The corresponding peaks are marked in Fig. S5.† This is the first report where monolayer protected silver clusters are seen to form aggregates upon exposure to higher laser fluence. The appearance of dimers, trimers and oligomers of cluster I suggests the feasibility of the interaction between the clusters.

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Fig. 2 (A) UV-vis spectrum of the purified cluster in DMF. The spectrum has distinct features which are characteristic of small clusters. Inset: Visible light photograph of the cluster solution. (B) ESI MS spectrum of the purified cluster in negative mode, in the region of $m/z \ 1000-10 \ 000$. The main peak at $m/z \ 2721.56$ corresponds to $[Ag_{51}(BDT)_{19}]^{3-}$. The peak at $m/z \ 1603$ is marked with a blue asterisk which is due to the presence of a small quantity of the $[Ag_{29}(BDT)_{12}]^{3-}$ cluster as a side product. (C) Comparison of the experimental (black trace) and simulated (red trace) isotopic patterns which match perfectly. Minor variations in intensity between successive peaks match perfectly besides a complete match of the mass spectral positions. It confirms the assigned composition, $[Ag_{51}(BDT)_{19}]^{3-}$.

The composition was further proven by elemental analysis. An Ag:S ratio of 1:0.76 was seen in energy dispersive spectroscopic (EDS) analysis, in agreement with the formula (Fig. S6[†]). X-ray photoelectron spectroscopy (XPS) shows an Ag 3d_{5/2} peak at 368.0 eV and S 2p_{3/2} at 163.0 eV (Fig. S7†). Although it is likely that both Ag(I) and Ag(0) are present in the cluster, no clear separation between them was seen in XPS (Fig. S7A[†]). These observations are in agreement with the expected values of such clusters. The Ag:S ratio value was 1:0.74, in agreement with the expected composition. The number of phosphines in cluster I was confirmed by detailed ESI MS studies (Fig. S8[†]). The spectrum shows sequential loss of three phosphines, from the parent peak. The peak at m/z2721.56 corresponds to $[Ag_{51}(BDT)_{19}]^{3-}$. So the actual formula of the parent material is $[Ag_{51}(BDT)_{19}(TPP)_3]^{3-}$. The yield of cluster I is only 30-35% as both the clusters (I (supernatant) and **II** (precipitate)) are formed together in a single synthesis

(Fig. 1B₂). The purified material is stable for 3–4 days in the solution phase at 30 °C and for a month at 4 °C. Cluster I is weekly luminescent. A comparison of the luminescence properties of cluster I and cluster II is shown in Fig. S9.†

An aspect of cluster science studied intensely today is chemical reactivity.^{36,50–52} We investigated the reaction between cluster I and the well known $Au_{25}BT_{18}$ cluster. In general, reactions between clusters exchange both the metal and the ligand between the reacting clusters.³⁶ It was surprising to see that cluster I underwent reactions with $Au_{25}BT_{18}$ by metal atom exchange alone without affecting the ligand shell. The results of the investigation are presented in Fig. 3 where, as a function of time of reaction, more and more silver of the cluster I get substituted by gold of $Au_{25}BT_{18}$ leading to $[Ag_{51-x}Au_xBDT_{19}]^{3-}$ alloy clusters. In 45 minutes, the reaction mixture loses all of cluster I indicating high chemical reactivity of the system. Corresponding transfer is also seen in $Au_{25}BT_{18}$



Fig. 3 Time dependent ESI MS spectra of the cluster I region during the reaction with the $Au_{25}BT_{18}$ cluster. As the time of reaction increases, more and more silver gets substituted by gold derived from $Au_{25}BT_{18}$, leading to the formation of $[Ag_{51-x}Au_xBDT_{19}]^{3-}$ alloy clusters. Within 45 min of reaction, the parent peak vanishes completely. Although metals exchange between the two reacting clusters, there is no change in the ligand shell of the cluster. All clusters could be defined.

as well where systematic silver addition occurs. Fig. 4 shows the formation of the $[Au_{25-\nu}Ag_{\nu}BT_{18}]^{-}$ alloy cluster. The absence of change in the ligand structure is uncommon in the reaction of Au₂₅.³⁶ We noted that no free BT or BDT enters into the solution. This chemical reactivity was also probed by optical absorption spectroscopy presented in Fig. S10.[†] The reaction was studied at various concentrations of clusters. The results are presented in Fig. S11.† In order to confirm the absence of a ligand exchanged product, we repeated the reaction of cluster I with the Au₂₅OT₁₈ cluster. The results of this reaction are presented in Fig. S12.[†] As the masses of the protecting ligands, BT (m/z 90) and OT (m/z 146) are quite different (Fig. S12A[†]), it is expected that new peaks will appear in the mass spectrum if ligands are changed in the reaction. In the Au₂₅OT₁₈ region we did not see any new peaks other than the metal exchanged product $[Au_{25-\nu}Ag_{\nu}OT_{18}]^{-1}$ (Fig. S12B[†]). Fig. S12C and D[†] show the comparison of the $[Ag_{51-x}Au_{x}BDT_{19}]^{3-}$ region upon reaction of cluster I and $Au_{25}BT_{18}$ (and $Au_{25}OT_{18}$). All the peaks are the same for these two cases ($Au_{25}BT_{18}$ and $Au_{25}OT_{18}$). The absence of new peaks with differently ligated Au₂₅ clusters confirms that the ligand shell is not involved in this type of reactions. We hope that the above observation will be helpful for the synthesis of new alloy clusters keeping the ligand shell unaffected.

We were also curious to study the difference between the reactivity of clusters I and II in the metal atom exchange reaction. For this, an equimolar mixture of clusters I and II was reacted with Au₂₅BT₁₈. While a rapid disappearance of cluster I was observed, cluster II underwent a much slower reaction. Mass spectral data at two different times are presented in Fig. S13.† Cluster II also underwent only the metal exchange reaction when it was reacted with Au25BT18 separately (Fig. S14[†]). These experiments show that while dithiol on the cluster surfaces cannot be exchanged with monothiols, metal atom exchange is feasible. Independent studies have also shown that dithiols in solution can exchange monothiols on Au₂₅ surfaces (Fig. S15[†]). These observations together would imply that metal atom alone exchanges are more likely than metal thiolate exchanges in these clusters. In contrast, metal thiolate ligand and metal thiolate exchanges are manifested in Au₂₅SR₁₈.³⁶ However, both cluster I and cluster II undergo only metal exchanges. It is likely that thermodynamics of these processes are critical in such events. Further insight into the process requires understanding of the initial metal atom transfer without disrupting the dithiol binding. The nature of the intermediate as well as inter-cluster approach facilitating atom transfer are important aspects to study further. We have very little understanding of the events involved in the inter-cluster



Fig. 4 Time dependent ESI MS spectra of the $Au_{25}BT_{18}$ cluster region during the reaction with cluster I. New peaks appear at the lower mass region with a separation of m/z 89. This is due to the substitution of gold (m/z 197) of the $Au_{25}BT_{18}$ cluster with Ag (m/z 108) of cluster I. The peaks are marked as $[Au_{25-y}Ag_vBT_{18}]^-$. No peaks other than those due to metal exchange were found.



Fig. 5 Thiol (DMBT) catalyzed inter-conversion of cluster I to cluster II. (A) Comparison of ESI MS spectra of parent cluster I with reaction mixtures containing different volumes of DMBT with a fixed amount of cluster I after 24 h of reaction. The ESI MS spectrum of the parent cluster I is presented with a black trace. Red, blue and pink traces are the ESI MS spectra of 2.5, 5 and 10 μ L DMBT added solutions of cluster I. Complete conversion of cluster I to cluster I to cluster II occurred for 10 μ L of DMBT whereas for 2.5 and 5 μ L of DMBT, more cluster I remained without conversion. (B) Emission spectra of the corresponding solutions. Intensity of emission enhances with increasing the volume of DMBT in solution. As cluster II is more luminescent than cluster I, enhancement of emission intensity confirms the formation of more and more cluster II in solution upon increasing the volume of DMBT. The sample was excited at 450 nm.

reaction. In our recent paper we have discussed the possible mechanism of the inter-cluster reaction between two mono thiol protected clusters.^{36b} Here the situation is more complicated due to the presence of dithiol.

The co-existence of clusters I and II and the preferential formation of either of them as a function of NaBH₄ prompted us to study their inter-conversion. To our surprise, we noted that upon addition of DMBT (2,4-dimethylbenzenethiol) to cluster I, mass spectra showed the appearance of cluster II with an increase of time. This is shown in Fig. S16.[†] The peak at m/z1603 due to cluster **II** increases gradually while the peak at m/z2721 due to cluster I disappears. We noted that this transformation occurs with rapid loss of one silver atom leading to the formation of $[Ag_{50}BDT_{19}]^{3-}$ marked in Fig. S16[†] and 5A. The cluster $[Ag_{50}BDT_{19}]^{3-}$ may be viewed as the dimer of $Ag_{25}(BDT)_9$ linked with BDT as BDT is a dithiol. $Ag_{25}(BDT)_9$ is equivalent to Au₂₅(SR)₁₈ and the dimer of the same has been detected recently.⁵³ At the end of the reaction, the solution consists of only cluster II as seen in the optical absorption spectra, and the spectra of clusters I and II are compared with the reaction product in Fig. S17.† The mass spectra shown in Fig. S16[†] show that there is no incorporation of DMBT in the cluster formed, which implies that it acts as a catalyst in the reaction. Experimental and simulated isotope distributions of the final product are shown in Fig. S16B and C[†] which confirm the formation of cluster II. We have also seen that the inter-cluster conversion is highly dependent on the concentration of DMBT. Fig. 5A shows that after 24 h of reaction, while complete conversion occurs for 10 µL of DMBT (pink trace), for 2.5 and 5 µL of DMBT more clusters remain without conversion (red and blue traces). Emission spectra of the corresponding samples are shown in Fig. 5B. As cluster II is more luminescent than cluster I, the intensity of the emission spectra increases with an increase in the amount of cluster II in solution. This reflects in the emission spectra of different volumes of DMBT-added cluster I solutions. In the case of the 10 µL DMBT-added cluster solution, the intensity is maximum as the amount of cluster II is maximum (Fig. 5B). Such catalytic inter-cluster transformation by thiols has not been reported earlier. The transformation is not a reversible process. It is not specific to DMBT also. The transformation can be carried out in the presence of other thiols (Fig. S18[†]).

Conclusions

In conclusion, we show the extreme dependency of the reducing agent concentration in cluster synthesis which resulted in the formation of a new cluster, $Ag_{51}(BDT)_{19}(TPP)_3$. The cluster undergoes metal atom exchange without ligand exchange, upon reaction with $Au_{25}(SR)_{18}$. The complete absence of ligand exchange products has been proven by carrying out reactions with two differently ligated Au_{25} clusters. The experiment showed an increased reactivity of $Ag_{51}(BDT)_{19}(TPP)_3$. An unusual inter-cluster transformation catalyzed by thiol is demonstrated. We hope that these unusual properties will generate increasing interest in dithiol protected clusters and exploration of their properties. While the inter-cluster reaction and exchange of metal atoms without ligand exchange poses new questions about the intermediate and mode of atom transfer, these questions require computational inputs with high sophistication. Cluster dimers mediated through thiols⁵³ and the possibility of metal transfer upon interaction of clusters³⁶ would suggest that the current observations are indeed feasible.

Conflicts of interest

The authors declare no competing financial interests.

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