

**Electronic Supplementary Information (ESI) for the paper:**

**Unusual reactivity of dithiol protected clusters in comparison to monothiol  
protected clusters: Studies using Ag<sub>51</sub>BDT<sub>19</sub> and Ag<sub>29</sub>BDT<sub>12</sub>**

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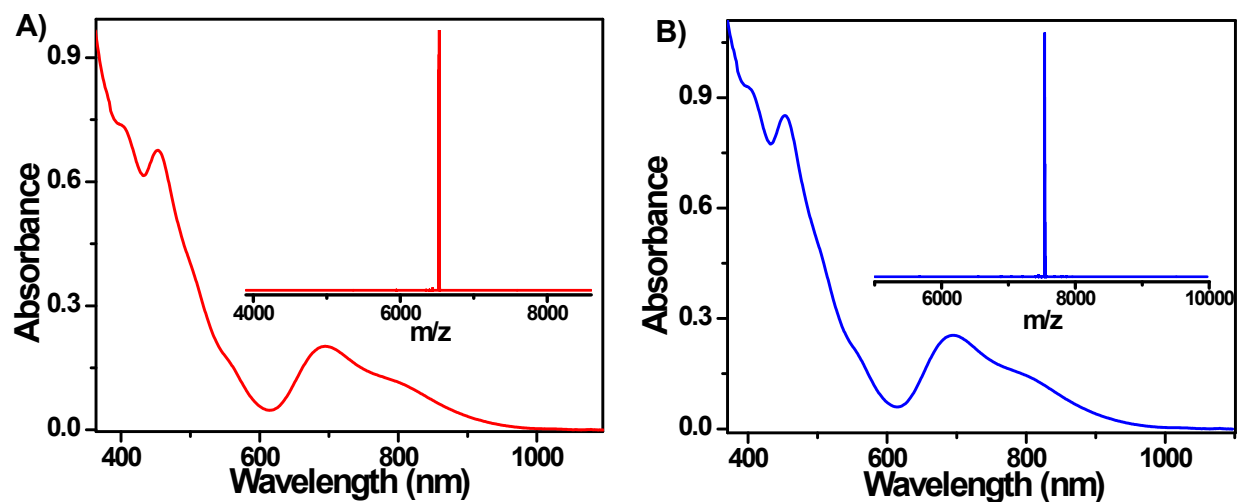
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## Supplementary Information 1

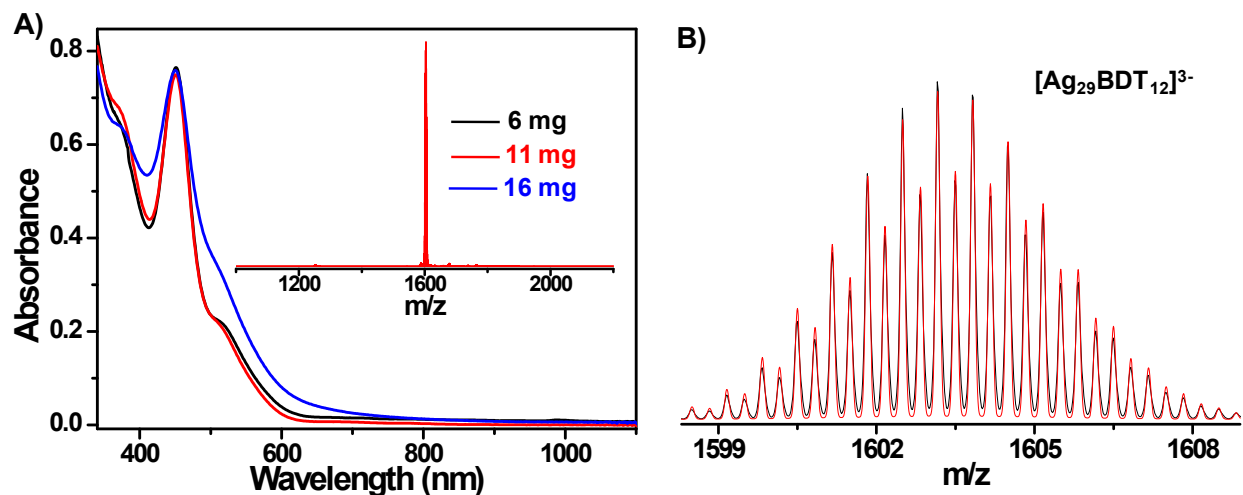
### Characterization of $\text{Au}_{25}\text{BT}_{18}$ and $\text{Au}_{25}\text{OT}_{18}$ clusters



**Fig. S1 A)** UV-vis spectrum of as synthesized  $\text{Au}_{25}\text{BT}_{18}$  cluster which matches with the published report.<sup>1</sup> Inset: ESI MS spectrum of the cluster solution. Presence of single peak at m/z 6530 confirms the composition and purity of the sample. **B)** UV-vis spectrum of  $\text{Au}_{25}\text{OT}_{18}$  cluster. Inset: ESI MS spectrum of the cluster solution. Composition and purity of the cluster is confirmed from the presence of single peak at m/z 7540.<sup>1</sup>

## Supplementary Information 2

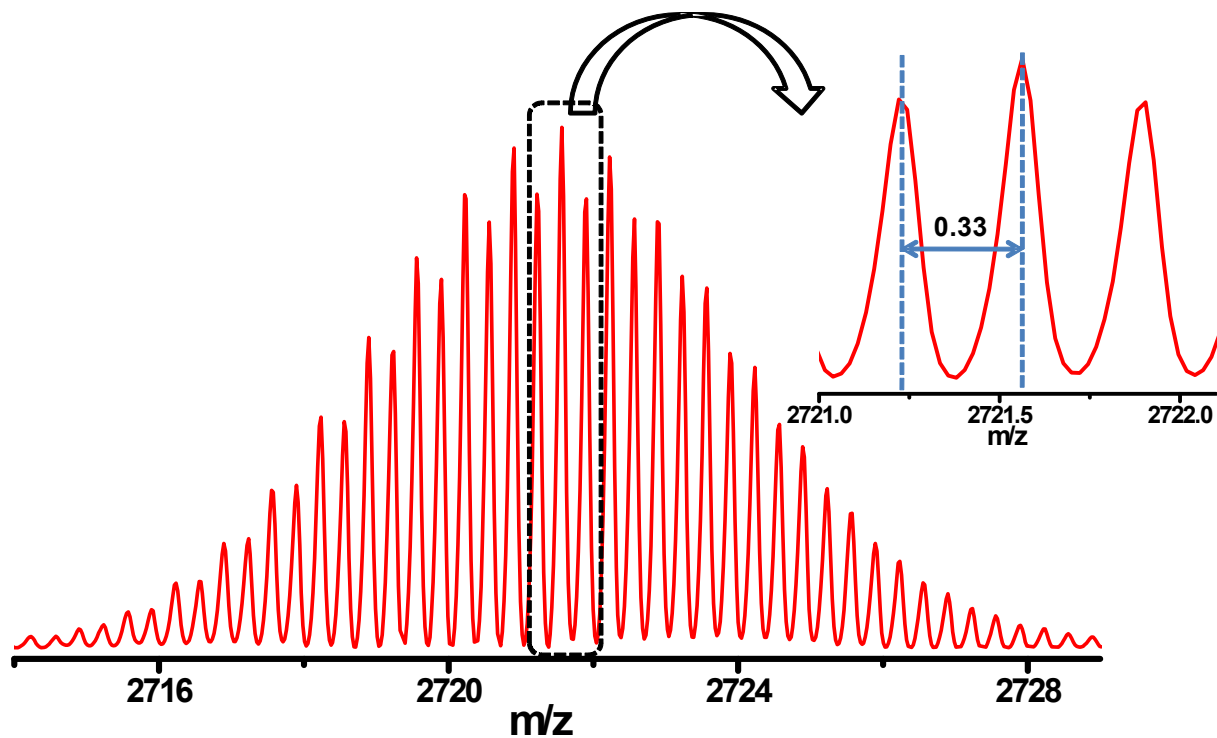
### UV-vis and ESI MS spectrum of cluster II



**Fig. S2** A) UV-vis spectra of DMF solutions of the clusters. Black, red and blue traces are for the solutions of 1A<sub>3</sub>, B<sub>3</sub> and C<sub>3</sub> of main manuscript, respectively. All the spectra match with those of  $[\text{Ag}_{29}\text{BDT}_{12}]^{3-}$  (cluster II).<sup>2</sup> Inset: ESI MS of the cluster solution. As all the solutions gave the same spectra, we have presented only one of them. Presence of a single peak at m/z 1603 confirms the formation of cluster II.<sup>2</sup> B) Comparison of experimental (black trace) and simulated isotopic pattern (red trace) which matches perfectly.

### Supplementary Information 3

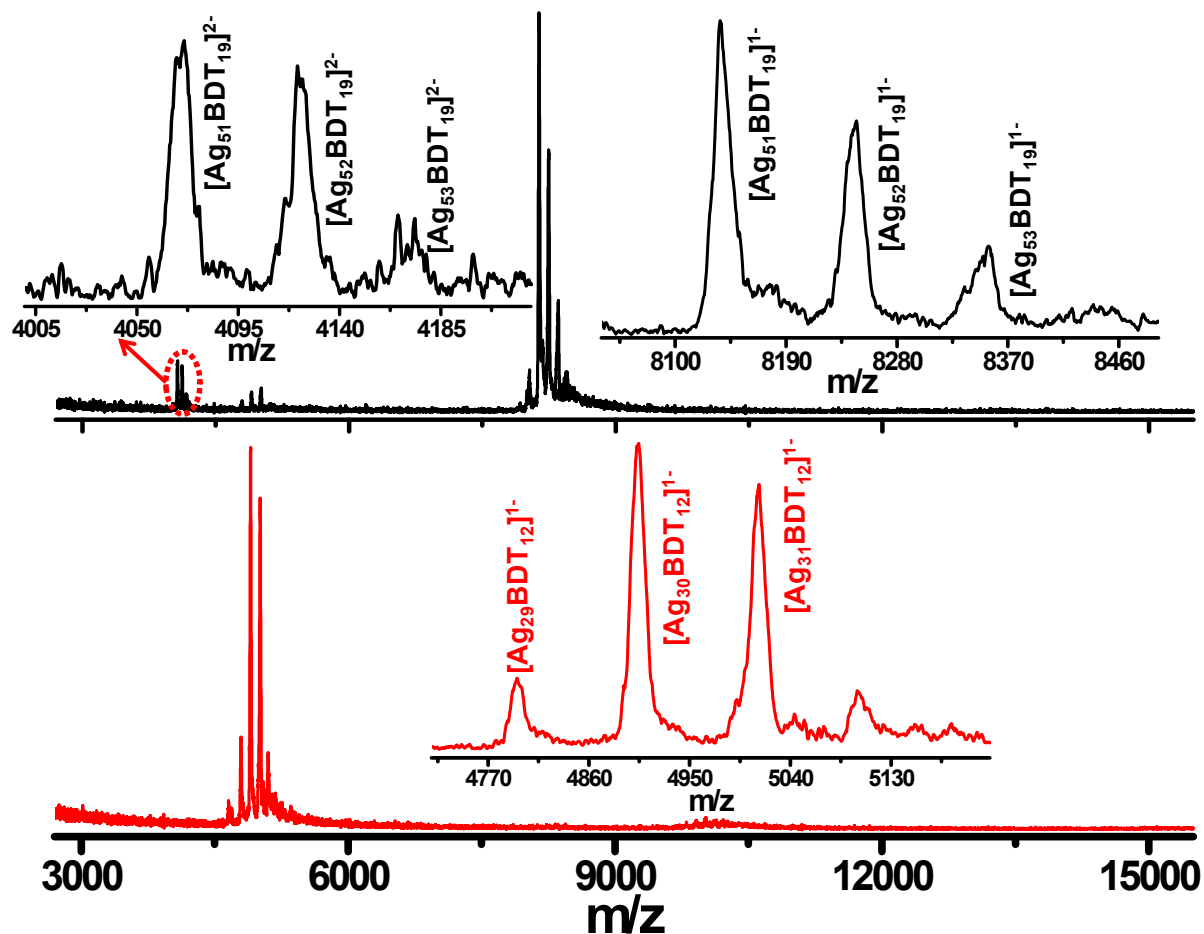
#### Expanded ESI MS region of cluster I



**Fig. S3** Peak at  $m/z$  2721.56 is expanded here. Separation between the two peaks is  $m/z$  0.33 which confirms that the cluster has 3- charge.

## Supplementary Information 4

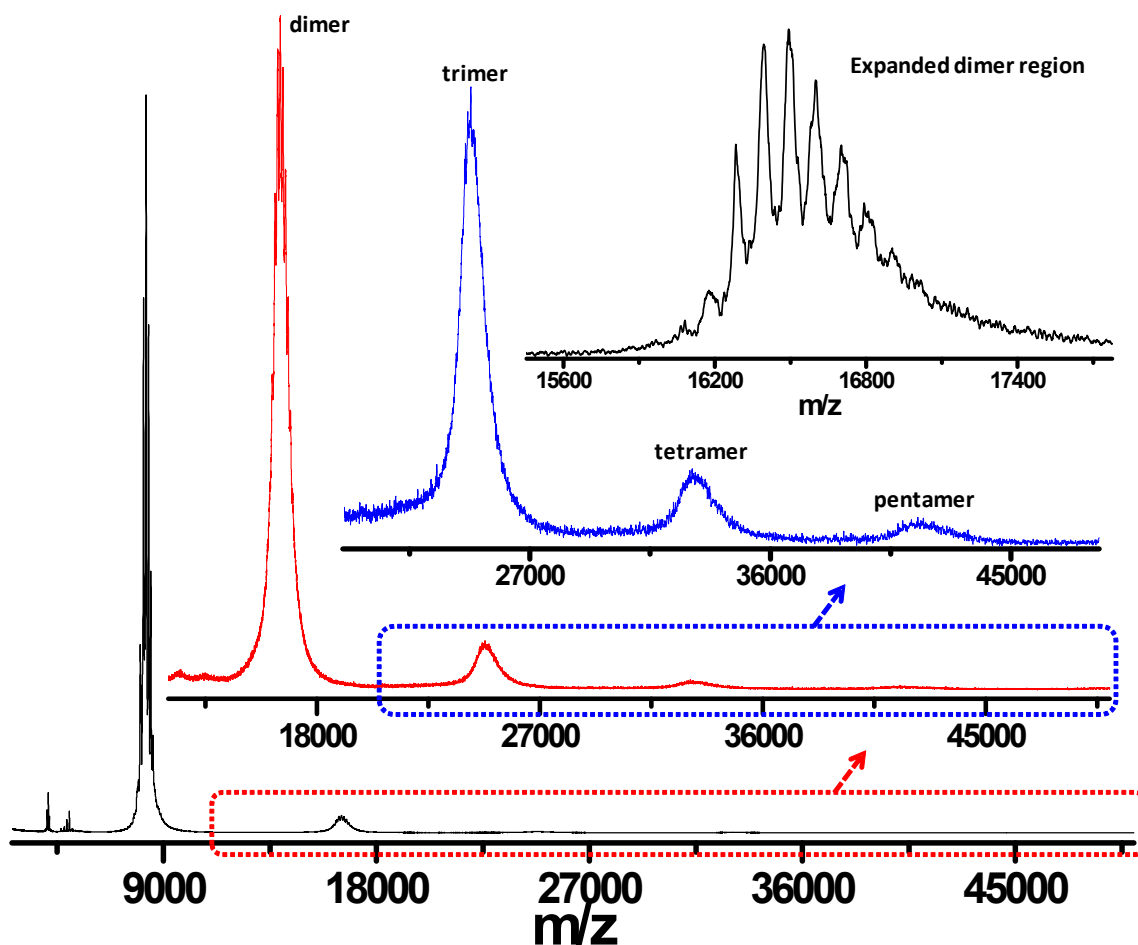
### MALDI MS data of cluster I and cluster II



**Fig. S4** MALDI MS spectra of cluster **I** (black trace) and cluster **II** (red trace). The spectra were measured in the -ve mode at threshold laser fluence. Monoanionic and dianionic peaks of the cluster **I** are expanded which shows the presence of silver attached peaks along with the molecular ion ( $[Ag_{51}BDT_{19}]^{-}$ ) peak. MALDI MS spectrum of the purified cluster **II** (red trace) also shows the presence of silver attached peaks along with the molecular ion ( $[Ag_{29}BDT_{12}]^{-}$ ) peak. This silver attached peaks with the molecular ion peak may be a characteristic feature of dithiol protected clusters.

## Supplementary Information 5

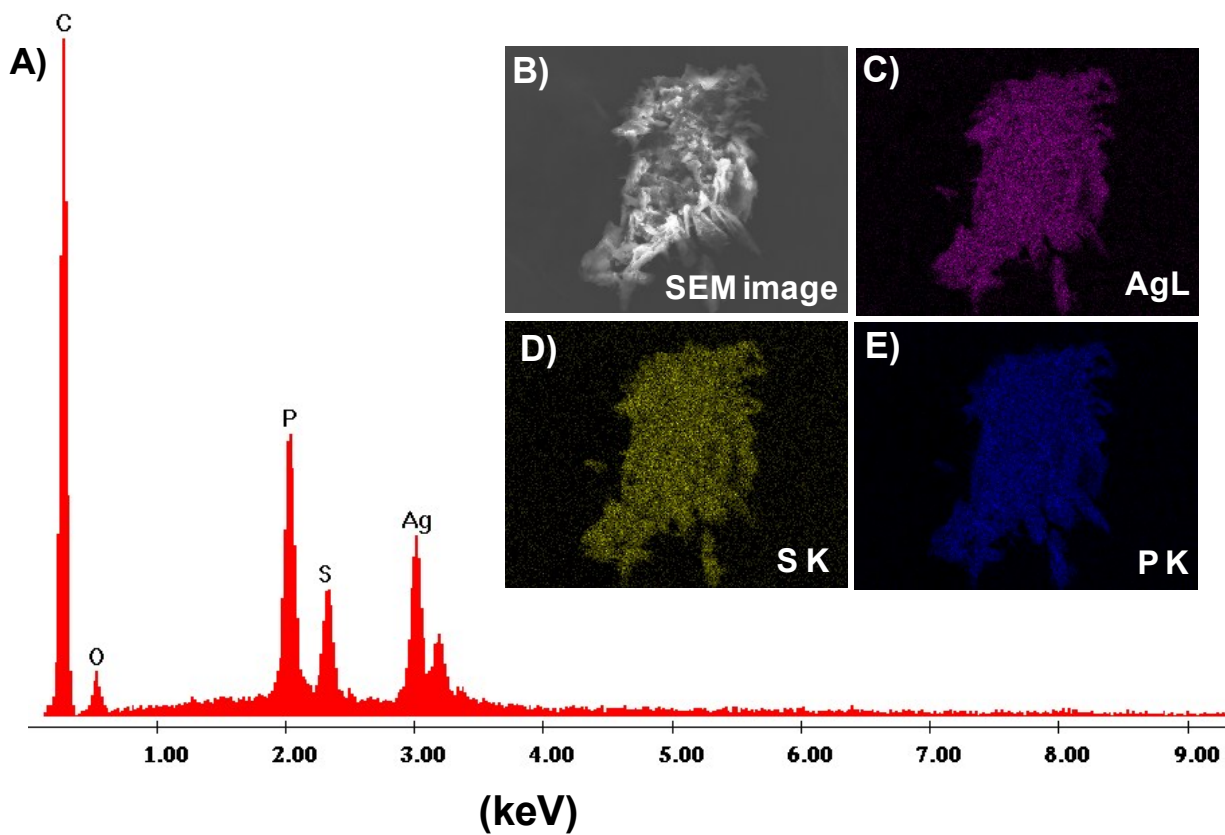
### Laser fluence dependent MALDI MS data of cluster I



**Fig. S5** MALDI MS data of cluster I measured at higher laser fluence. Expansion of higher mass region shows the presence of peaks at regular intervals of  $\sim m/z$  8100 along with the molecular ion peak. These higher mass peaks are due to the formation of dimer ( $\sim m/z$  16200), trimer ( $\sim m/z$  24300), tetramer ( $\sim m/z$  32400) and pentamer ( $\sim m/z$  40,500) of  $\text{Ag}_{51}\text{BDT}_{19}$  cluster which are marked. Inset: The peak corresponding to the dimer is expanded which also shows the silver attached peaks.

## Supplementary Information 6

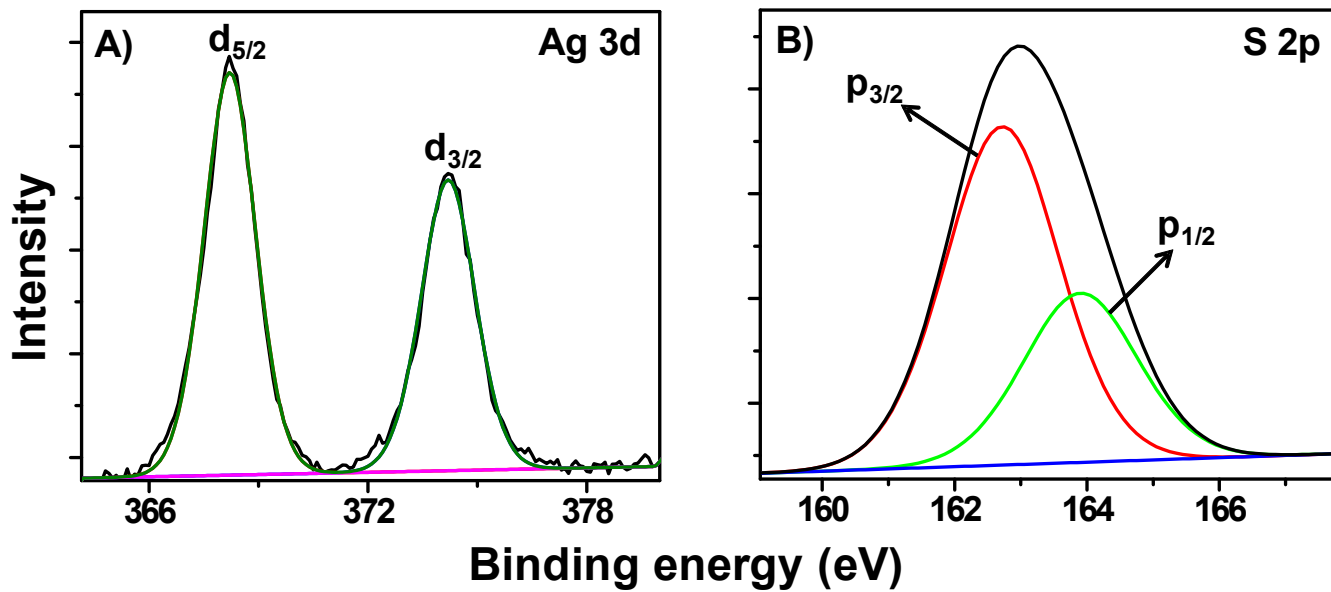
### SEM/EDAX



**Fig. S6** (A) EDAX spectrum of  $\text{Ag}_{51}\text{BDT}_{19}$  and (B) SEM image of  $\text{Ag}_{51}\text{BDT}_{19}$  aggregate from which the EDAX spectrum was taken. Ag:S atomic ratio measured is 1:0.76, as expected (actual is 1:0.74).

## Supplementary Information 7

XPS

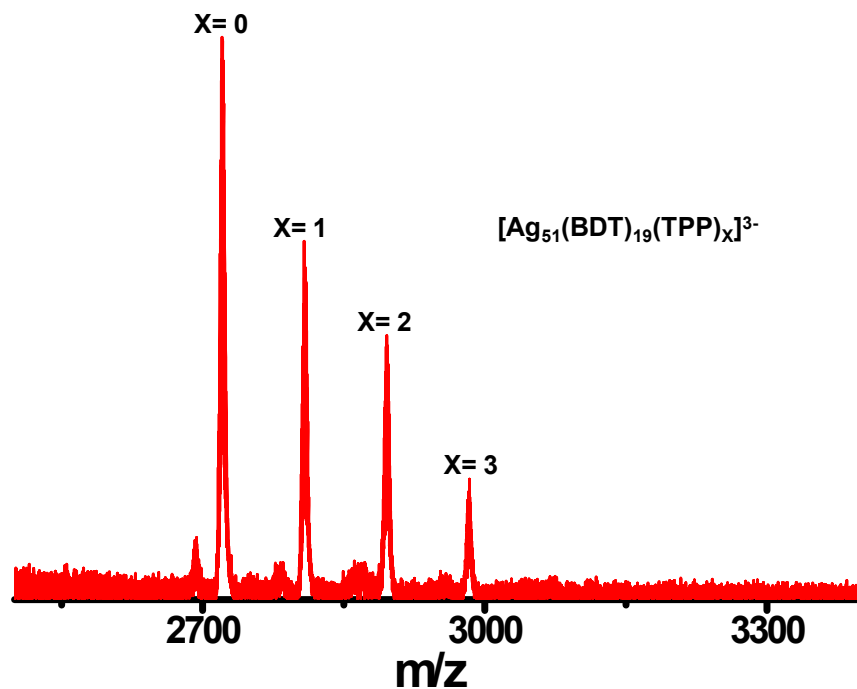


**Fig. S7** (A) and (B) represent the XPS spectra for Ag 3d and S 2p, respectively with multiple component fitting. It shows that Ag is almost in the zero oxidation state.



## Supplementary Information 8

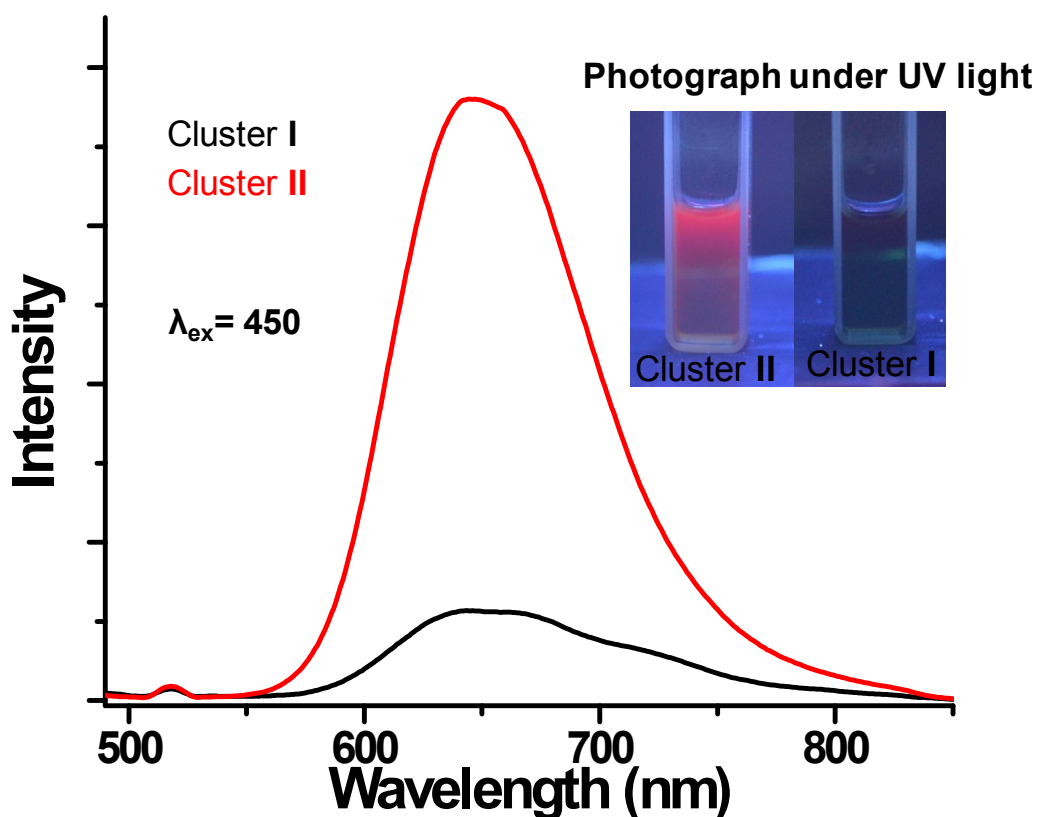
### ESI MS spectrum of cluster I



**Fig S8** ESI MS spectrum of the purified cluster in the negative mode. The peaks are separated by  $m/z = 87.5$ . As the cluster has 3- charge, the peak separation of 87.5 is assigned to the loss of one phosphine (molecular mass 262.3) from the parent ion. It shows the sequential dissociation of three phosphines from the parent peak. The peak at  $m/z$  2721.56 (where  $X=0$ ) corresponds to  $[Ag_{51}(BDT)_{19}]^{3-}$ . Therefore the assigned composition of the parent material is  $[Ag_{51}(BDT)_{19}(TPP)_3]^{3-}$ .

## Supplementary Information 9

### Comparison of luminescence property of cluster I and cluster II



**Fig S9** Comparison of luminescence property of  $\text{Ag}_{51}$  (cluster I) and  $\text{Ag}_{29}$  (cluster II) clusters. Both, the luminescent spectra and the photograph under UV light (inset) show that the cluster I is weakly luminescent in comparison to cluster II.

## Supplementary Information 10

Time dependent UV-vis spectra of the reaction between cluster I and  $\text{Au}_{25}\text{BT}_{18}$

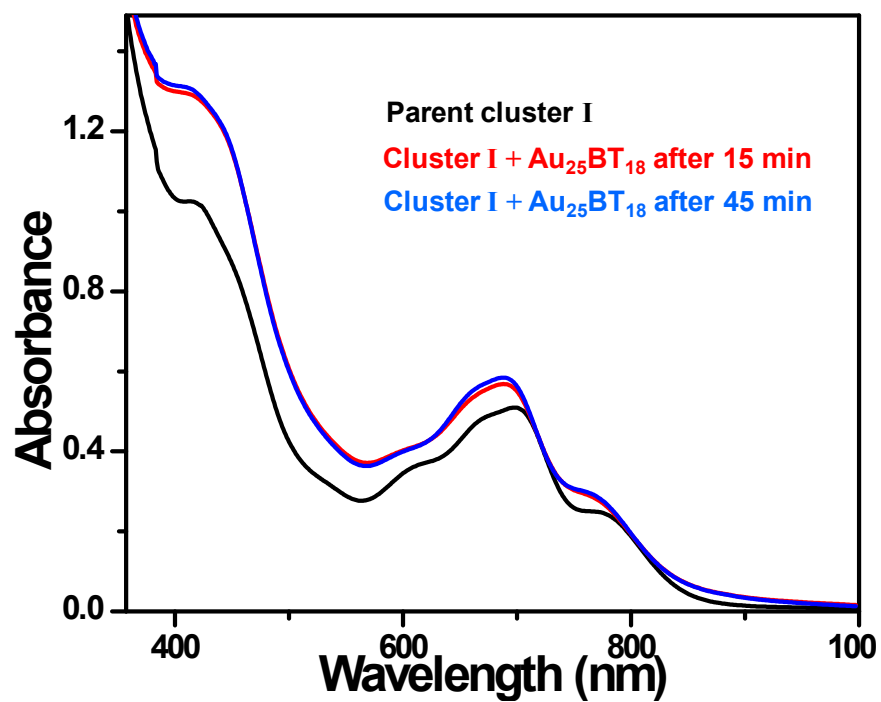
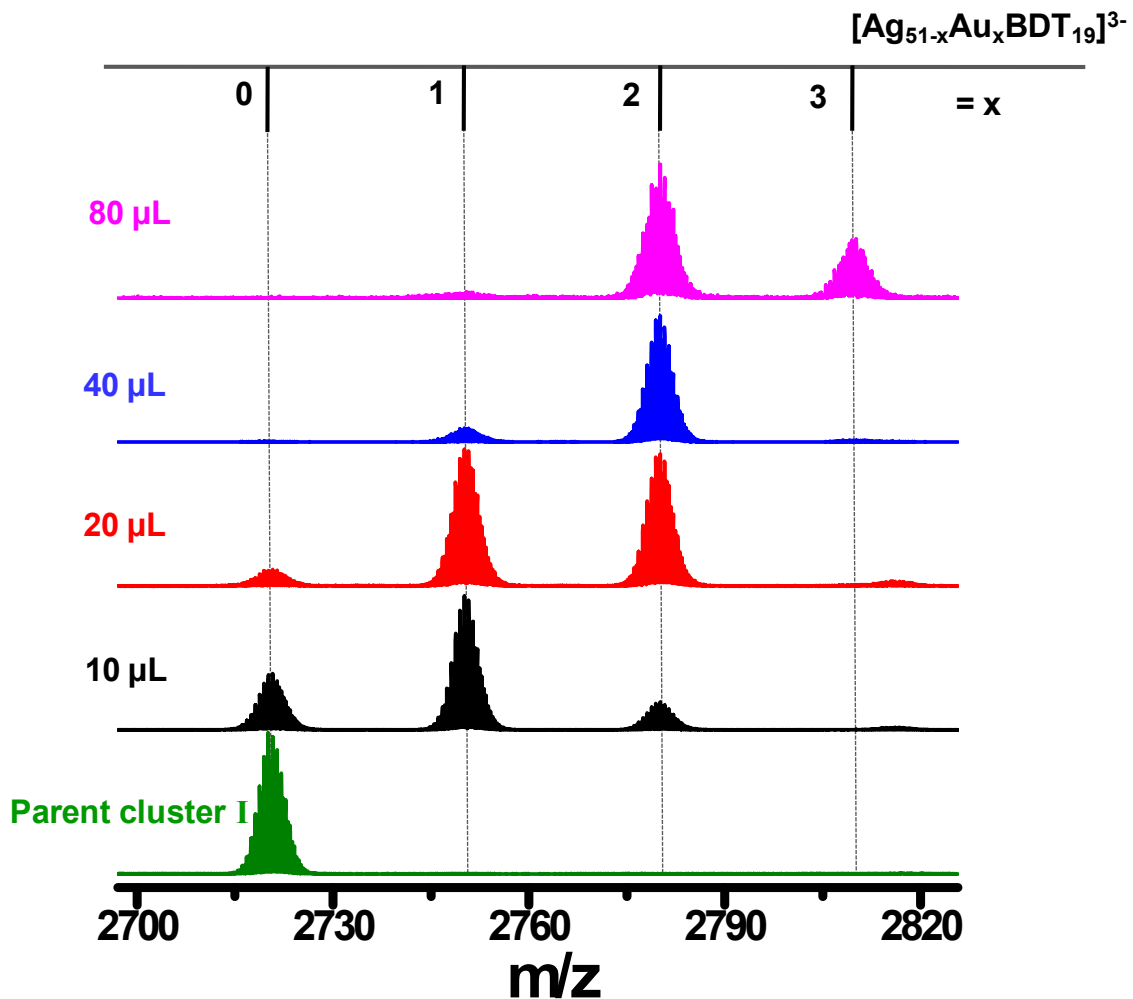


Fig. S10 Time dependent UV-vis spectra of inter-cluster reaction.

## Supplementary Information 11

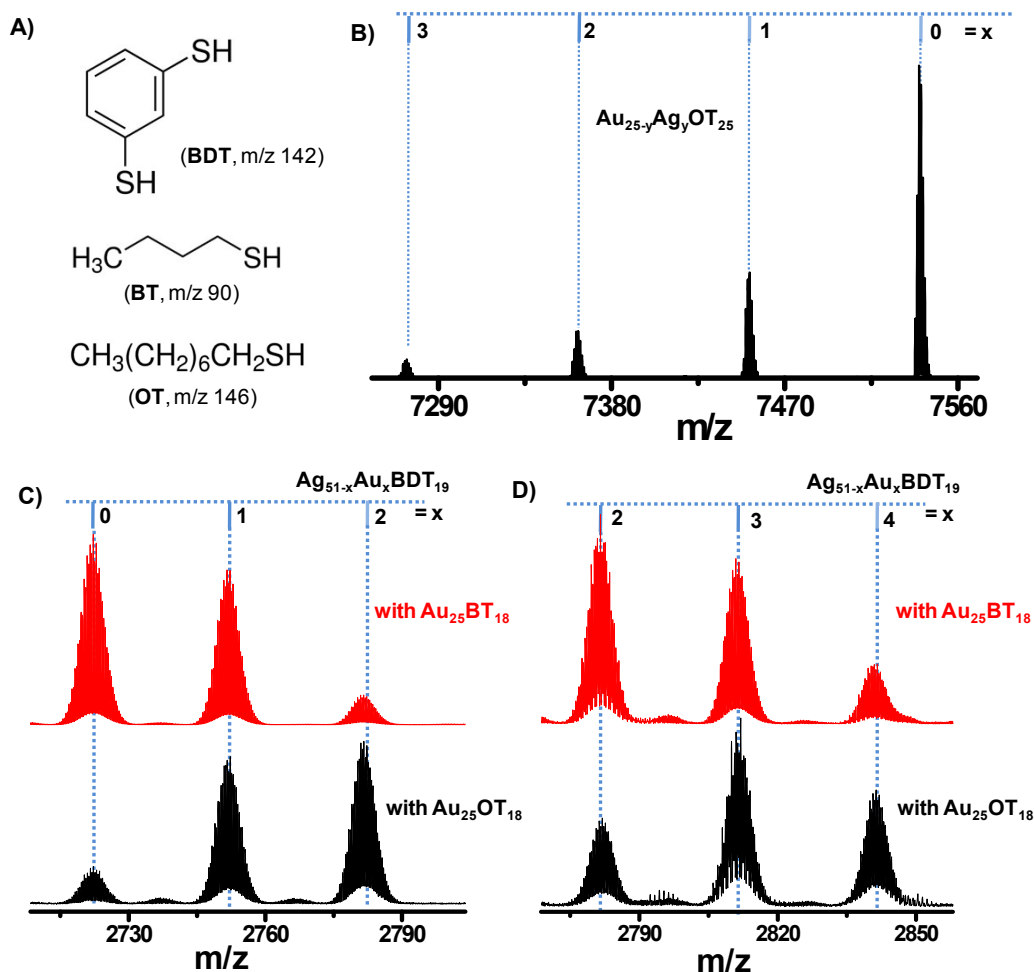
Concentration dependent ESI MS spectra of the reaction between cluster I and Au<sub>25</sub>BT<sub>18</sub>



**Fig. S11** Reaction of cluster I (fixed concentration) with increasing concentrations of Au<sub>25</sub>BT<sub>18</sub> clusters. As the amount of Au<sub>25</sub>BT<sub>18</sub> cluster increases in the reaction medium, more and more silver of cluster I get substituted by gold of Au<sub>25</sub>BT<sub>18</sub> cluster leading to the formation of [Ag<sub>51-x</sub>Au<sub>x</sub>BDT<sub>19</sub>]<sup>3-</sup> alloy.

## Supplementary Information 12

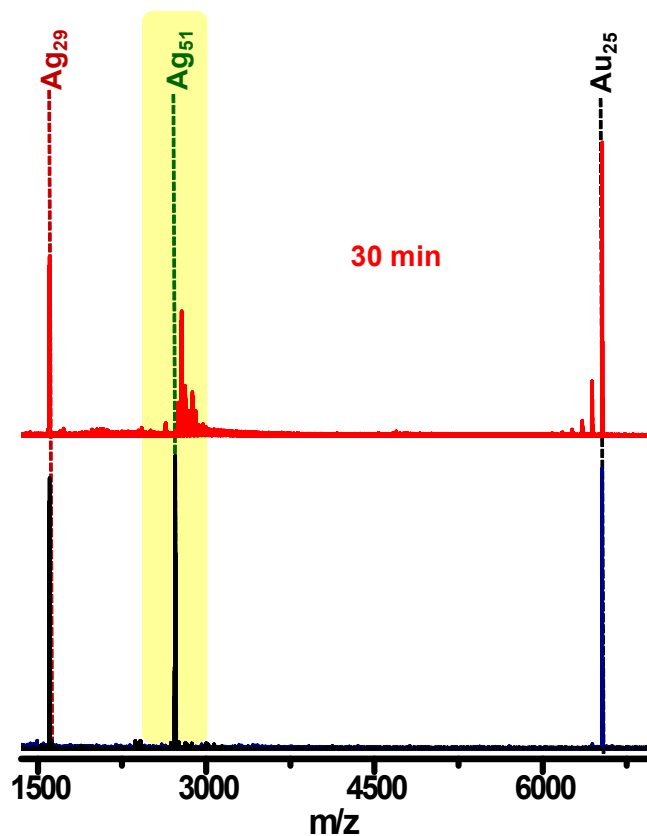
### Reactions of cluster I with BT and OT ligated Au<sub>25</sub> clusters



**Fig. S12** **A)** Compositions and masses of protecting ligands, BDT, OT and BT thiols. **B)** The Au<sub>25</sub>OT<sub>18</sub> region during reaction with cluster I. The peaks are due to the formation of [Au<sub>25-y</sub>Ag<sub>y</sub>BT<sub>18</sub>]<sup>-</sup> alloy cluster. No peaks other than those of metal exchange were found. **C)** and **D)** compares the [Ag<sub>51-x</sub>Au<sub>x</sub>BDT<sub>19</sub>]<sup>3-</sup> region while cluster I reacting with BT and OT ligated Au<sub>25</sub> clusters. No new peaks were observed here. Absence of new peaks upon using the differently ligated Au<sub>25</sub> clusters confirms that the ligand shell is not involving for this type of reaction.

## Supplementary Information 13

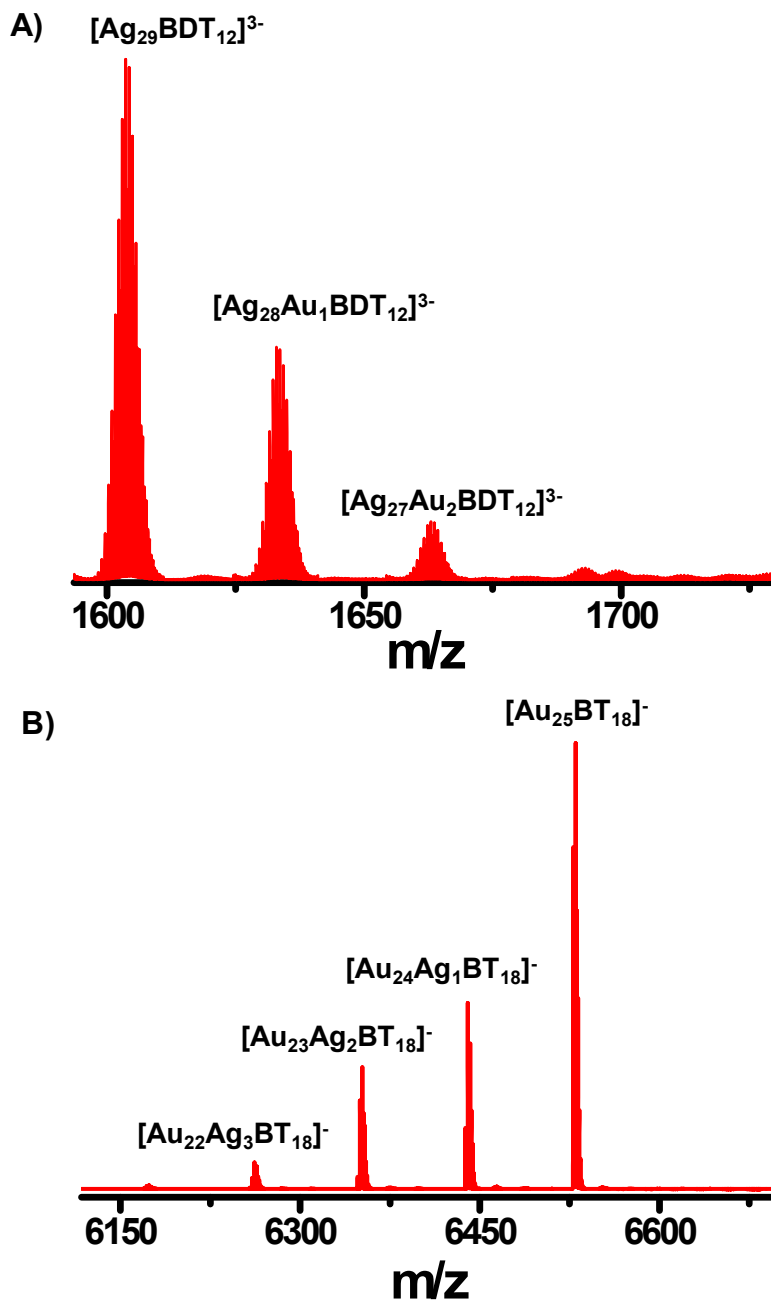
Comparison of reactivity of cluster I and cluster II with  $\text{Au}_{25}\text{BT}_{18}$



**Fig. S13** Reactions of equimolar mixture of cluster I and II with  $\text{Au}_{25}\text{BT}_{18}$  cluster. After 30 min of reaction cluster I disappeared (highlighted portion) whereas cluster II underwent slow reaction.

## Supplementary Information 14

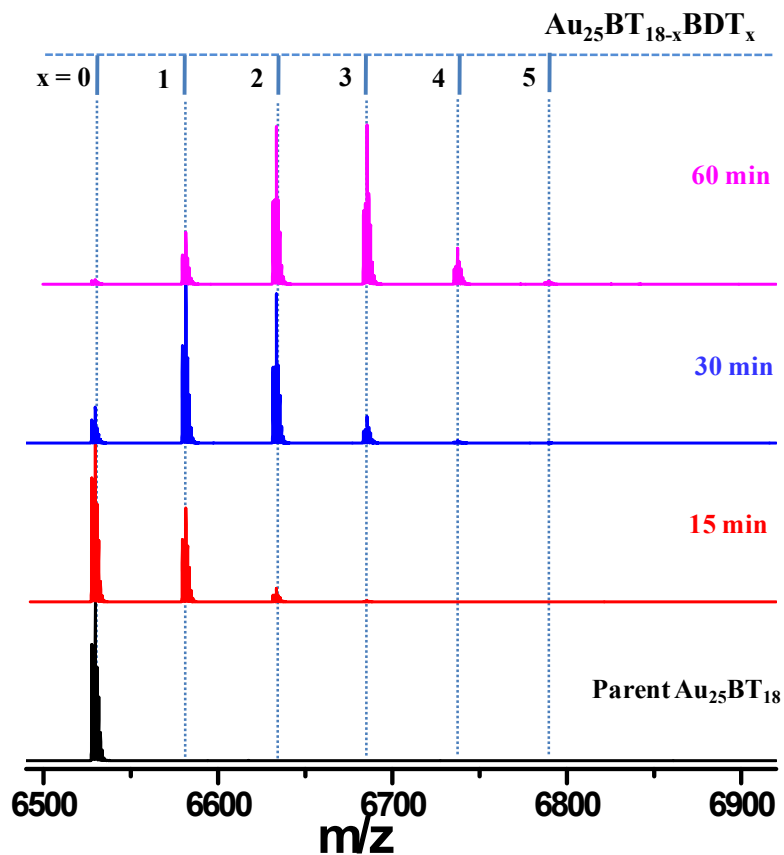
Reaction of cluster II with  $\text{Au}_{25}\text{BT}_{18}$



**Fig. S14** ESI MS spectra of reaction of cluster II with  $\text{Au}_{25}\text{BT}_{18}$  cluster. **A)** Cluster II undergoes only metal exchange reaction leading to the formation of  $[\text{Ag}_{29-x}\text{Au}_x\text{BDT}_{12}]^{3-}$  alloy cluster. **B)** On the other side,  $\text{Au}_{25}\text{BT}_{18}$  also under goes metal exchange reaction leading to the formation of  $[\text{Au}_{25-x}\text{Ag}_x\text{BT}_{18}]^{-}$  alloy cluster.

## Supplementary Information 15

### Reaction of $\text{Au}_{25}\text{BT}_{18}$ cluster with BDT thiol

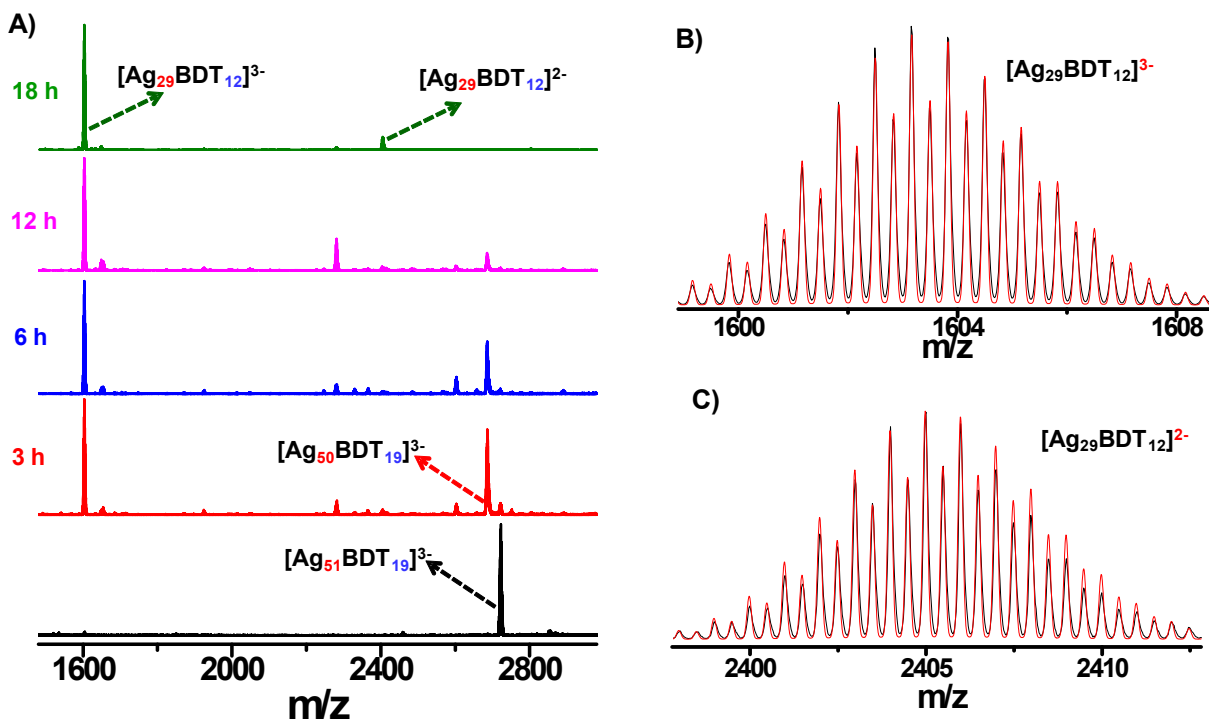


**Fig. S15** Time dependent ESI MS spectra for the reaction of  $\text{Au}_{25}\text{BT}_{18}$  with BDT thiol. As time increases more and more BT ligands of  $\text{Au}_{25}\text{BT}_{18}$  get exchanged by BDT thiol.



## Supplementary Information 16

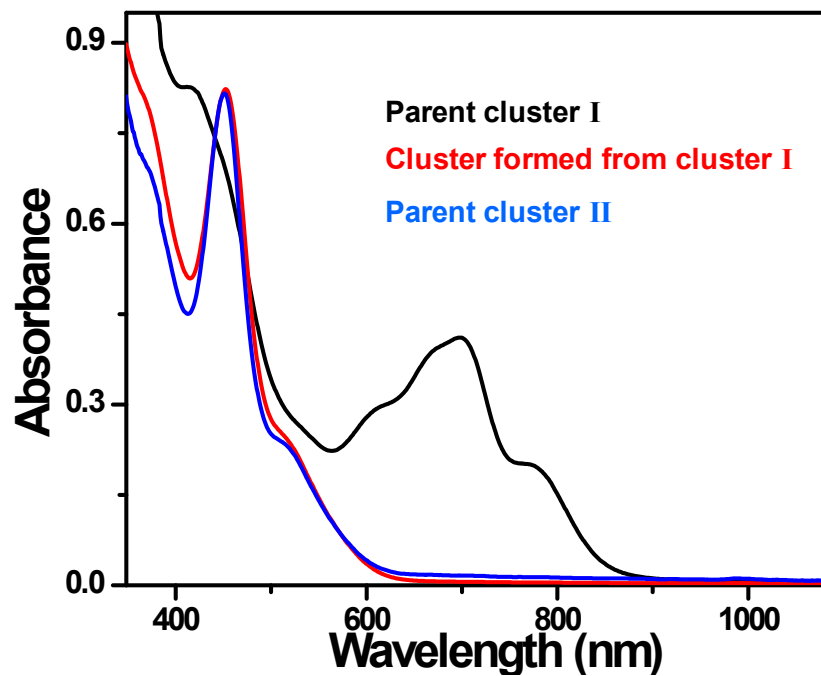
### Time dependent ESI MS spectra for inter-cluster conversion process



**Fig. S16 A)** Time dependent ESI MS spectra for the reaction of cluster **I** with DMBT (15  $\mu$ L). As time progresses, peak at m/z 2721 = due to the parent cluster **I** disappears slowly. At the same time, peak at m/z 1603 which is due to the cluster **II** increases gradually. After 18 h of reaction, cluster **I** was completely converted to cluster **II**. Upon addition of DMBT, cluster **I** immediately loses one Ag ion and forms  $[Ag_{50}BDT_{19}]^{3-}$  which is marked in the figure. **B)** and **C)** Compare the experimental (black trace) and simulated (res trace) isotopic distribution for 2- and 3- charge states of cluster **II**.

## Supplementary Information 17

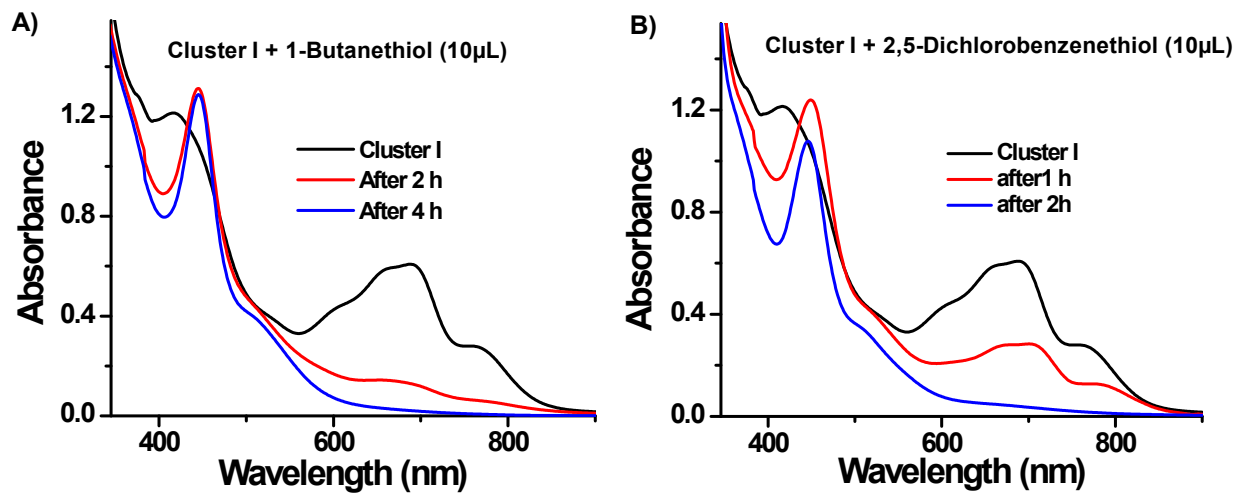
A UV-vis study of the inter-cluster conversion process



**Fig. S17** Optical absorbance spectra where spectra of cluster **I** (black trace) and **II** (blue trace) are compared with the reaction product (red trace). It confirms the formation of cluster **I**.

## Supplementary Information 18

### Transformation of Cluster I to cluster II



**Fig. S18** A) Time dependent UV-vis spectra for the transformation of Ag<sub>51</sub> to Ag<sub>29</sub> in presence of 1-butanethiol. B) Time dependent UV-vis spectra for the transformation of Ag<sub>51</sub> to Ag<sub>29</sub> in presence of 2,5-dichlorobenzenethiol.

- 1 A. Ghosh, J. Hassinen, P. Pulkkinen, H. Tenhu, R. H. A. Ras and T. Pradeep, *Anal. Chem.*, 2014, **86**, 12185-12190.
- 2 L. G. AbdulHalim, M. S. Bootharaju, Q. Tang, S. Del Gobbo, R. G. AbdulHalim, M. Eddaoudi, D.-e. Jiang and O. M. Bakr, *J. Am. Chem. Soc.*, 2015, **137**, 11970-11975.