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# [Au<sub>25</sub>(SR)<sub>18</sub>]<sub>2</sub><sup>2−</sup>: a noble metal cluster dimer in the gas phase†

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**We present the first example of dimer formation in the monolayer protected atomically precise cluster system, Au<sub>25</sub>(SR)<sub>18</sub>, using ion mobility mass spectrometry. These transient species are shown to be important in explaining chemical reactivity between clusters.**

Clusters of noble metals composed of a precise number of atoms and protected with ligands,<sup>1,2</sup> of which Au<sub>25</sub>(SR)<sub>18</sub> is a celebrated example, have become an expanding area of materials science.<sup>3–7</sup> Their structures, investigated using single crystal diffraction, reveal Au–SR or Ag–SR monomeric or dimeric staples, using which Borromean rings diagrams for these molecular species have been proposed. Clusters can interact through ligands as well as through aurophilic interactions (for Au clusters), leading to dimers and polymers, as shown from previous investigations.<sup>8</sup> Such interactions can be induced in the gas phase under controlled conditions leading to cluster aggregates<sup>9</sup> which may be separable by ion mobility mass spectrometry. Recent reports of ion mobility mass spectrometry (IMS) on different protected clusters confirm that it is indeed possible to identify many unknown species in the gas phase by integrating ion mobility (IM) separation with mass spectrometry (MS).<sup>10–14</sup> A recent report of inter-cluster reaction between two interacting clusters<sup>15</sup> suggests that inter-cluster aggregate formation could be a potential pathway for these reactions. In this article, we present the observation of distinct dimeric and trimeric species of the Au<sub>25</sub>(SR)<sub>18</sub> system in the gas phase and their complete absence in Ag<sub>25</sub>(SR)<sub>18</sub> emphasizing the importance of the nature of the metal and inter-cluster interaction in determining cluster chemistry.

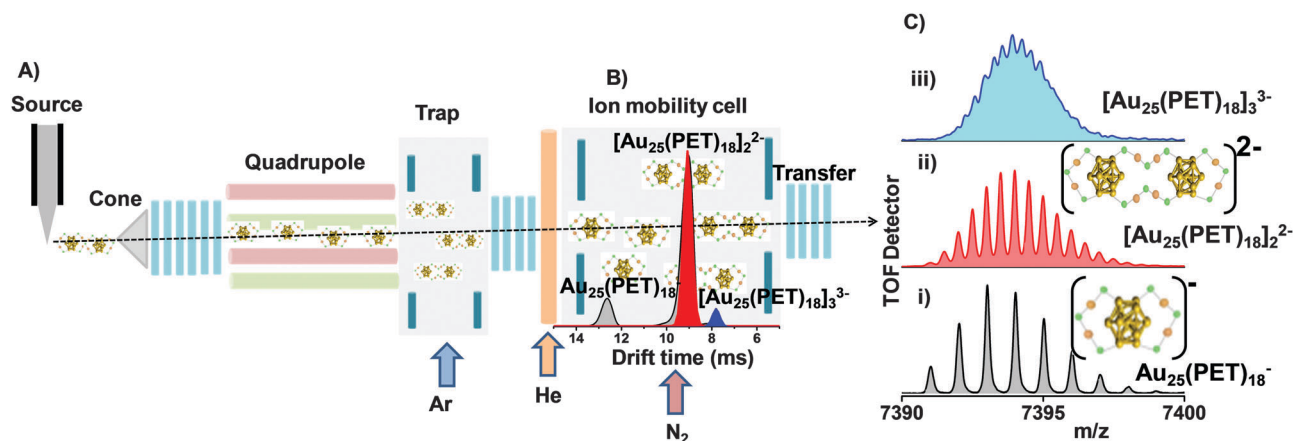
Au<sub>25</sub>(PET)<sub>18</sub> was prepared by an established route (see the ESI† for details) and characterized by electrospray ionization mass spectrometry (ESI MS) and UV-vis absorption spectroscopy (see Fig. S1, ESI†).<sup>15</sup> The mass selected ions were subjected to

mobility separation in the drift tube and were mass analyzed subsequently (Fig. 1). Under conditions optimized for collecting the mass spectrum, the peak of Au<sub>25</sub>(PET)<sub>18</sub> was observed at *m/z* 7393 (average mass) (see Fig. S1, ESI†). From the isotope distribution, each peak is found to be separated by one mass unit confirming singly charged species (Fig. 1C(i)). The minimum concentration of the 1 µg mL<sup>−1</sup> sample was infused at a flow rate of 20 µL min<sup>−1</sup> at a capillary voltage of 2 kV to obtain a well resolved mass spectrum. To collect the spectrum, cone voltage and source offset were fixed at 120 and 100 V, respectively (see the ESI† for details). Trap gas flow (Ar) was 2 mL min<sup>−1</sup> and desolvation gas (N<sub>2</sub>) flow was 400 L h<sup>−1</sup>. At slightly higher trap pressure and lower cone voltage (8 mL min<sup>−1</sup> and 20 V, respectively), the isotope distribution changed drastically where the peaks were separated by *m/z* 0.4998 confirming the presence of a doubly charged dimer of Au<sub>25</sub>(PET)<sub>18</sub> (Fig. 1C(ii)). Several control experiments were performed to understand the best possible conditions where only dimer and higher aggregates were formed (Fig. S2 and S3, ESI†). As mentioned earlier, increased gas flow allows the formation of cluster aggregates which prompted us to increase it at different parts of the instrument. Optimized conditions for Au<sub>25</sub>(PET)<sub>18</sub> in the ion mobility mode were; trap gas flow rate: 5 mL min<sup>−1</sup>, He flow: 100 mL min<sup>−1</sup> and that within the mobility cell: 50 mL min<sup>−1</sup>. When He flow was increased to 120 mL min<sup>−1</sup>, [Au<sub>25</sub>(PET)<sub>18</sub>]<sub>2</sub><sup>2−</sup> started appearing which was evident from two peaks located at 12.7 and 10.8 ms in the ion mobility drift time plot (Fig. 1B and Fig. S2, ESI†). The peak at 12.7 ms corresponds to Au<sub>25</sub>(PET)<sub>18</sub><sup>−</sup> while the other peak at 10.8 ms corresponds to [Au<sub>25</sub>(PET)<sub>18</sub>]<sub>2</sub><sup>2−</sup>. At a higher He flow rate (150 mL min<sup>−1</sup>), another peak started appearing at 8.3 ms which corresponds to [Au<sub>25</sub>(PET)<sub>18</sub>]<sub>3</sub><sup>3−</sup> (with a separation of *m/z* 0.3330, Fig. 1C(iii)). By increasing the trap as well as the He flow rate it was possible to create only the dimer and the trimer of Au<sub>25</sub>(PET)<sub>18</sub><sup>−</sup>. At a slightly lower DC bias voltage of 35 V, a complete conversion of Au<sub>25</sub>(PET)<sub>18</sub><sup>−</sup> to its dimer and trimer was observed. Fig. 1 represents the schematic of the experiment under optimized conditions to create such cluster polymers. Various optimization experiments

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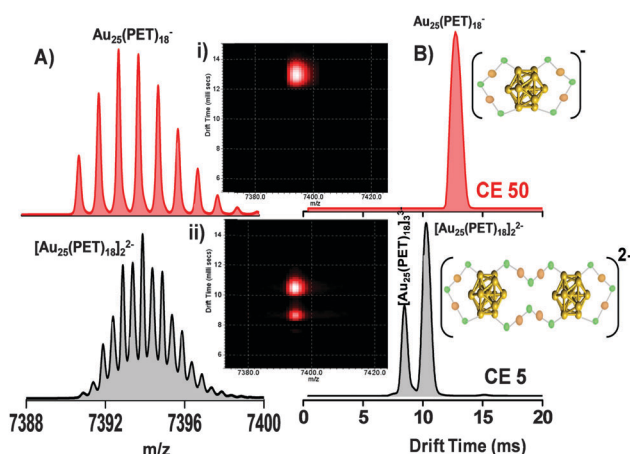


**Fig. 1** (A) Schematic representation of the instrumental setup where  $\text{Au}_{25}(\text{SR})_{18}$  cluster aggregates are created and (B) subsequently separated by ion mobility mass spectrometry. (C) Each of the peaks obtained from ion mobility is expanded. Peaks at 12.7, 10.8 and 7.8 ms in B correspond to  $\text{Au}_{25}(\text{PET})_{18}^-$ ,  $[\text{Au}_{25}(\text{PET})_{18}]_2^{2-}$ ,  $[\text{Au}_{25}(\text{PET})_{18}]_3^{3-}$ , respectively, as shown in (i–iii). Representative structures are shown in the insets.

are presented in the ESI,<sup>†</sup> Fig. S2–S4. It was also evident that the formation of these cluster aggregates is highly dependent on the cone voltage used which actually is the extraction voltage. At a sufficiently higher cone voltage ( $> 80$  V), only  $\text{Au}_{25}(\text{PET})_{18}^-$  was detected even at a high trap gas flow ( $8 \text{ mL min}^{-1}$ ). By lowering the cone voltage to 10 V, it is possible to create dimers even at a trap flow rate of  $5 \text{ mL min}^{-1}$ . The data are presented in Fig. S2 (ESI<sup>†</sup>). Therefore, such loosely bound cluster polymers may be forming in the ionization chamber too after spraying which can be broken apart by applying a higher extraction voltage at the cone. It is clear that the monomer aggregates to form dimers and polymers in the drift tube under favourable conditions.

To confirm dimerization, we have created the dimer and trimer of  $\text{Au}_{25}(\text{PET})_{18}^-$  following the above stated instrument conditions, without any monomer contribution. Collision induced dissociation (CID) was performed at  $m/z$  7393 which consisted of 75% dimer  $[\text{Au}_{25}(\text{PET})_{18}]_2^{2-}$  and 25% trimer  $[\text{Au}_{25}(\text{PET})_{18}]_3^{3-}$ , as calculated from the area under the curve in the drift time profile (see Fig. 2). Upon increasing laboratory collision energy (CE)§ from 5 to 50 V, dimers and trimers started separating out to form  $\text{Au}_{25}(\text{PET})_{18}^-$ . Regular fragmentation from  $\text{Au}_{25}(\text{PET})_{18}^-$  was observed at CE more than 85 V which (Fig. S4, ESI<sup>†</sup>) matches well with the previously reported fragmentation pattern of  $\text{Au}_{25}(\text{PET})_{18}^-$ .<sup>10</sup>

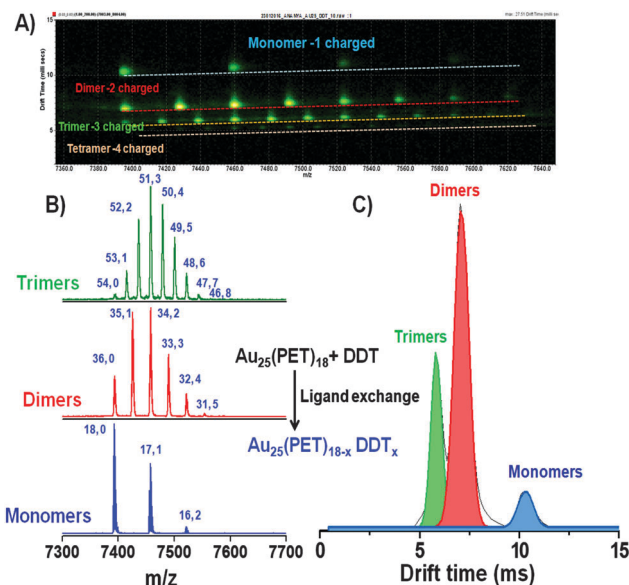
This polymerization is ligand independent as confirmed from a study performed with  $\text{Au}_{25}(\text{DDT})_{18}^-$  (Fig. S5, ESI<sup>†</sup>). A collision energy dependent study reveals a similar type of dissociation of the dimer to the monomer at higher collision energy as shown in Fig. S5 (ESI<sup>†</sup>). As all the polymers appear at the same  $m/z$ , albeit at reduced peak separation, it is difficult to identify the polymers by a normal ESI MS measurement. To overcome this issue, a few PET ligands have been exchanged with dodecanethiol (DDT). By controlling the free ligand concentration, a maximum of 3 ligand exchange products were seen in ESI MS. These specific ligand exchanged clusters (0–3 DDT exchanged) were used for polymerization. Under optimized conditions, all these ligand exchanged products react together



**Fig. 2** (A) Collision induced dissociation of  $[\text{Au}_{25}(\text{PET})_{18}]_2^{2-}$ ,  $[\text{Au}_{25}(\text{PET})_{18}]_3^{3-}$  mixture gave  $\text{Au}_{25}(\text{PET})_{18}^-$ . Corresponding drift time profiles are shown in (B). Ion mobility drift time vs.  $m/z$  plots are shown in insets (i) and (ii) for laboratory CE 5 and 50 V, respectively. <sup>a</sup> Representative structures are also shown.

to give various possible dimers, trimers and some amounts of tetramers (see Fig. 3A). Fig. 3A represents the ion mobility drift time vs.  $m/z$  plot showing different ligand exchanged  $\text{Au}_{25}$  monomers, dimers, trimers and tetramers. Inter-cluster polymerization will result in a more number of mixed ligand protected dimers, trimers, etc. For example, from 0 to 3 ligand exchanged products, 6 possible dimers and 9 possible trimers can form during polymerization (Fig. S8, ESI<sup>†</sup>). The data are shown in Fig. 3B. The number increases with the number of ligand exchanged products existing in the solution. The corresponding drift time profile is shown in Fig. 3C. The peaks are labelled as monomers, dimers and trimers. Interdigitation among the DDT ligands might help in a higher degree of polymerization (Fig. S6 and S7, ESI<sup>†</sup>).

The possible cause of this kind of aggregate formation could be van der Waals forces, dipole–dipole interactions, electron transfer between neighbouring clusters, aurophilic interaction among neighbouring clusters which may allow two negatively



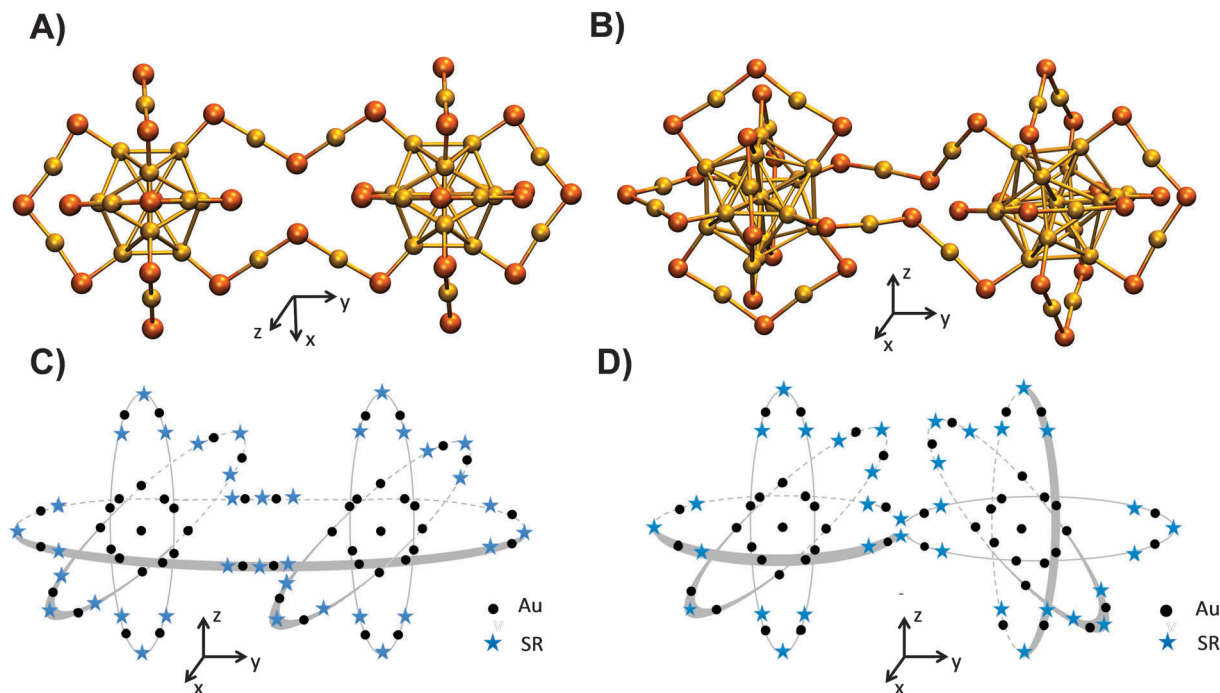
**Fig. 3** (A) Plot of ion mobility drift time vs.  $m/z$  of reaction products of  $\text{Au}_{25}(\text{PET})_{18}$  and dodecanethiol, showing the formation of cluster polymers. Multiple ligand exchanged cluster monomers, dimers and trimers are shown in (B). Corresponding drift time profile is shown in (C). Peaks assigned are with two labels, the first number corresponds to the total PET and the second number corresponds to the total DDT.

charged entities to come closer to form dimers and higher polymers.<sup>15</sup> Although the clusters are negatively charged, the overall charge is not localized and distributed all over the cluster. Thiolate protected  $\text{Au}_{25}(\text{SR})_{18}$  has been studied theoretically as a building block for the formation of dimers and polymers.<sup>16</sup> Two  $\text{Au}_{25}(\text{SMe})_3^-$  were connected by one di-thiol ligand replacing two  $-\text{SMe}$ . The calculated structure was energetically favourable. In another report,  $\text{Au}_{25}(\text{BT})_{18}$  (BT is butanethiol) was suggested to form a one-dimensional polymer on the  $\text{Au}(111)$ .<sup>17</sup> The crystal structure revealed the Au–Au linkage between two neighbouring clusters. Due to Au–Au bond formation, S–Au–S bond angle becomes almost linear ( $177^\circ$ ) suggesting significant structural modification. Different ligand protected  $\text{Au}_{25}$  clusters were used and ligand effects were checked. Too small or too long ligands were found to be ineffective in polymerization. Interdigitation of the ligand plays a significant role in determining polymerization, which explains the formation of more polymers when a few PET ligands were exchanged with DDT in the current study. All these previous studies point towards the dimer or polymerization efficiency of monolayer protected  $\text{Au}_{25}(\text{SR})_{18}$  clusters. An early example of dimerization was observed by Wataru *et al.*<sup>18</sup> during the exchange of tellurolates with thiolates of  $\text{Au}_{25}(\text{SC}_8\text{H}_{17})_{18}$ . We find that the  $\text{Ag}_{25}(\text{SR})_{18}$  cluster did not show any dimers (Fig. S9, ESI†) under the experimental conditions used for  $\text{Au}_{25}(\text{SR})_{18}$ . Gold thiolates are known to form such a type of aggregate due to aurophilic interaction. Gold thiolates are also known to form longer chains which are very limited for silver thiolates which might be responsible for no dimer formation for  $\text{Ag}_{25}(\text{SR})_{18}$ .

Experimentally calculated CCS values for  $\text{Au}_{25}(\text{SR})_{18}^-$ ,  $[\text{Au}_{25}(\text{SR})_{18}]_2^{2-}$  and  $[\text{Au}_{25}(\text{SR})_{18}]_3^{3-}$  are 297.8, 453.4 and  $668.3 \text{ \AA}^2$ , respectively (see Tables S1 and S2, ESI† for details). From the ion mobility drift time data, it is evident that the dimer size is slightly lesser than twice the monomer. This is also the case when trimer is considered. This prompted us to think that there might be bonding between two adjacent  $\text{Au}_{25}(\text{SR})_{18}^-$  units which can share their equivalent  $\text{Au}_2(\text{SR})_3$  staples to form a dimer. For this to occur, one Au–SR bond has to break and a new Au–SR bond has to form with the next cluster. Recently monolayer protected clusters are termed as “aspicule” which means shielded molecule.<sup>19</sup> Possible structures are understood considering the aspicule<sup>19</sup> model of the  $\text{Au}_{25}(\text{SR})_{18}^-$  cluster system. Isomer structures of the dimer were constructed based on utilizing common staples as a linkage between the clusters. The structures of the three isomers, A, B and C, were geometry optimized, and their binding energies with respect to two isolated  $\text{Au}_{25}(\text{SH})_{18}$  clusters were calculated. Two DFT optimized structures of isomers A and B are shown in Fig. 4A and B and their linkages can be visualized schematically using the Borromean rings diagrams shown below them in Fig. 4A and C, respectively (computational details are given in the ESI†). Isomer A is the most symmetric with both halves of the cluster being in the same orientation with the common staples parallel to each other, while in isomer B the half of the cluster on the right is rotated  $90^\circ$  with respect to the other half on the left, with the opposite ends of the common staples lying in perpendicular planes in a twisted configuration. A third possibility, isomer C, is shown in Fig. S10 (ESI†) where linking takes place at staple edges which are aligned parallel to each other, and the relative orientations of the two halves of the cluster are also different from isomers A and B in this configuration.

Table S3 (ESI†) shows the energies and binding energies of each of the isomers. The binding energies of the common staple dimer isomers A, B, and C, were 1.18 eV, 1.49 eV, and 2.36 eV, respectively. We found that A is the most stable and lowest in energy, closely followed by isomer B, whose binding energy was greater than that of isomer A by 0.31 eV, while isomer C was higher in binding energy than isomer A by 1.18 eV. We found these endothermic binding energies, calculated as  $E(\text{dimer}) - 2E(\text{monomer})$ , indicate that transfer of kinetic energy from cluster–gas molecule collisions and inter-cluster collisions would be required for the staple bond breakage and rearrangement which results in the formation of common-staple dimers, which is in agreement with the ion-mobility measurements presented here.

The results presented above suggest the existence of gas phase dimeric species of  $\text{Au}_{25}$  and its controlled fragmentation with or without ligand exchange leading to the parent or new clusters. Similar phenomena between reacting clusters can lead to transient cluster aggregates and their subsequent products. While the structures of dimers and their properties are areas for further investigation, chemical reactivity through such an interacting state is clearly established by this study. Although results of two prominent cluster systems, namely  $\text{Au}_{25}(\text{SR})_{18}$  and  $\text{Ag}_{25}(\text{SR})_{18}$ , are presented here, many of the noble metal



**Fig. 4** (A and B) Possible structural isomers of the  $[\text{Au}_{50}(\text{SR})_{36}]^{2-}$  dimer considering inter-cluster bonding via common  $\text{Au}_2\text{S}_3$  staples. The structures shown in (A and B) are DFT-optimized and correspond to isomers (A and B), respectively. The ligand R-groups have been removed for clarity and gold atoms are shown in gold and sulphur atoms in orange, in the ball and stick representation. In (A), there is bonding between the two clusters by two parallel  $\text{Au}_2\text{S}_3$  chains. The view shown is along the negative z-direction (top view). In (B), a twisted linkage between the  $\text{Au}_2\text{S}_3$  staples of two clusters is shown with the cluster on the right being rotated by  $90^\circ$  anticlockwise about the x-axis coming out of the paper, according to the Cartesian axes shown. (C and D) are representations of (A and B), respectively, utilizing the Borromean-rings diagram of ref. 19. In the twisted-linked dimer shown in (D), the orientation of the diagram of the cluster on the right side is obtained by rotating the diagram of the cluster on the left side by  $90^\circ$  anticlockwise about the x-axis.

clusters are expected to show such properties and we are currently investigating this transient phenomenon and its implications.

## Notes and references

§ Nominal collision energy, not calibrated.

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