# Toward a Janus Cluster: Regiospecific Decarboxylation of Ag<sub>44</sub>(4-MBA)<sub>30</sub>@Ag Nanoparticles

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Supporting Information

**ABSTRACT:** The ligand shell structure of the aspicule  $Ag_{44}(4-MBA)_{30}$  (MBA: mercaptobenzoic acid, in the thiolate form) was modified in a precise, site-specific manner. Laser irradiation at 633 nm of a monolayer assembly of plasmonic Ag nanoparticles (NPs) covered with  $Ag_{44}(4-MBA)_{30}$  clusters leads to decarboxylation of 4-MBA ligands forming thiophenolate (TP) ligands. While the molecular identity and integrity of aspicules post laser irradiation were confirmed by ESI MS, time-dependent SERS spectra and computational studies suggest that the phenomenon of decarboxylation is limited to the 4-MBA ligands facing the NP surface. This creates modified  $Ag_{44}$  clusters, with 4-MBA ligands on one side



and TP ligands on the other, giving them a two-faced (Janus) ligand structure. The ligand distribution of such clusters gets equilibrated in solution. We show that such selective transformation can be used to create molecular patterns. Janus clusters may be important in chemistry at biphasic interfaces.

# INTRODUCTION

Noble metal nanoclusters having unique optical and physical properties have evolved into a distinct family of materials.<sup>1-3</sup> Gold clusters have been explored intensely<sup>4-6</sup> compared to their silver analogues because of the latter's reduced stability.<sup>7,8</sup> Several gold clusters with precise structures have been reported so far, $^{9-18}$  and many of them have been utilized in a variety of applications in many or train areas such as sensing, catalysis, biolabeling, imaging, etc.<sup>19,20</sup> Reports of silver clusters are limited mostly to mass spectrometry,<sup>21–28</sup> although crystal structures of a few clusters such as  $Ag_{14}(SR)_{12}(PR_3)_{8'}^{29}$   $Ag_{16}(SR)_{14}(DPR_3)_{4'}^{30} Ag_{25}(SR)_{18'}^{31} Ag_{29}(SR)_{12'}^{32}$   $Ag_{32}(SR)_{24}(DPR_3)_{5'}^{30}$  and  $Ag_{44}(SR)_{30}^{33,34}$  have been reported recently (SR, PR<sub>3</sub>, and DPR<sub>3</sub> refer to thiolate, phosphine, and diphosphine functional groups, respectively). Among these atomically precise silver clusters, Ag<sub>44</sub>SR<sub>30</sub> was the first example of a complete thiol protected cluster with known crystal structure. Bakr et al. in 2009 had developed the synthesis of this cluster which was named as intensely and broadly absorbing nanoparticles (IBANs).<sup>35</sup> Later, in 2012 Harkness et al. identified this highly stable silver cluster through highresolution electrospray ionization mass spectrometry (HRESI MS).<sup>36</sup> In 2013, the groups of Bigioni and Zheng solved its crystal structure independently.<sup>33,34</sup> The cluster consists of a Keplerate solid of concentric icosahedral and dodecahedral atom shells to form a hollow cage which is surrounded by six  $Ag_2(SR)_5$  staples in an octahedral fashion. A selenolate analogue of the Ag<sub>44</sub> cluster has also been reported which has

an identical optical spectrum with a shift.<sup>37</sup> This cluster has been synthesized with a wide variety of water-soluble (e.g., mercaptobenzoic acid) as well as organic soluble (e.g., fluorothiophenol) ligands. Ag<sub>44</sub>(SR)<sub>30</sub>, being the most stable silver cluster reported so far, has drawn tremendous interest of the cluster community to investigate its associated properties. Reversible transformation from thiolate to Ag<sub>44</sub>(SePh)<sub>30</sub><sup>38</sup> and reversible core change from Ag<sub>44</sub>(FTP)<sub>30</sub> to Ag<sub>35</sub>(SG)<sub>18</sub> by ligand exchange<sup>39</sup> have been reported recently.

Ligand exchange reactions have been the key processes to functionalize nanoclusters which can introduce new properties to the system.<sup>40,41</sup> For a specific geometry, there are multiple possibilities for an incoming ligand to exchange with the existing ligand. Fernando and Aikens have theoretically investigated the kinetics and preferred exchange sites of the  $Au_{25}(SR)_{18}$  cluster.<sup>42</sup> They found that the terminal staples which are most accessible are favored for such exchange. Such preferential exchange can lead to the formation of geometric isomers due to the heterogeneity in the system. Niihoiri et al. were able to separate such isomers through reverse-phase high-performance liquid chromatography.<sup>43</sup>

Clusters, being three-dimensional (3D) entities, can be functionalized regiospecifically providing Janus-type particles, in the molecular size regime. These are similar to the

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corresponding nanoparticles, but with molecular features, enabling regiospecific conjugation to biological as well as chemical species. However, as these exchange reactions happen in solution, all the equivalent sites in a 3D geometry are equally available for exchange with the new ligands, making the formation of Janus-type clusters impossible through such solution phase ligand exchange. Traditionally, differently functionalized Janus NPs and quantum dots (QDs) are made at the liquid-liquid interfaces using differential solubility of the protecting groups or by selective masking-demasking on a solid substrate.<sup>44</sup> Formation of Janus particles through these processes can be confirmed from measurement of contact angle after depositing them onto hydrophobic and hydrophilic substrates.<sup>45</sup> This article reports the first example of regiospecific functionalization of Ag44SR30 cluster. Plasmon excitation induced decarboxylation of 4-MBA ligands of Ag<sub>44</sub>(4- $MBA)_{30}$  generates a mixed-ligand protected  $Ag_{44}(4-$ MBA)<sub>30-x</sub>(TP)<sub>x</sub> cluster (TP: thiophenol), which was identified through Raman spectroscopy and high resolution electrospray ionization mass spectrometry. Time-dependent Raman spectroscopy in conjunction with the computational results confirms that the process of decarboxylation is regioselective, producing Janus Ag<sub>44</sub>(4-MBA)<sub>30-x</sub>(TP)<sub>x</sub> clusters.

#### EXPERIMENTAL SECTION

**Chemicals Used.** All the chemicals were commercially available and were used without further purification. Silver nitrate (AgNO<sub>3</sub>, 99%), hydrogen tetrachloroaurate (HAuCl<sub>4</sub>·  $3H_2O$ , 49.0% Au basis), 4-mercaptobenzoic acid (4-MBA, 97%), trisodium citrate dihydrate (99%, Aldrich), and sodium borohydride (NaBH<sub>4</sub>, 99.99%) were purchased from Aldrich. Dimethylformamide (DMF, AR grade), dimethyl sulfoxide (DMSO, AR grade), toluene (AR grade), methanol (AR grade), ammonium acetate, citric acid, and sodium hydroxide (NaOH) pellets were procured from RANKEM, India.

Synthesis of Ag@PVP and Au@PVP Nanoparticles. PVP-protected Ag NPs were synthesized through reduction of AgNO<sub>3</sub> in a polyol process. 170 mg of AgNO<sub>3</sub> and 1 g of PVP (K25) were dissolved in 4 mL of ethylene glycol (EG) through magnetic stirring at room temperature to obtain a clear solution. The temperature of this solution was slowly increased to 120 °C. EG reduces Ag<sup>+</sup> at this elevated temperature, and nucleation of Ag NPs starts. The solution was maintained at this temperature for 30 min and then removed and cooled immediately to stop further reaction.

This EG dispersion of Ag NPs was then diluted 10 times with deionized water and finally separated through centrifugal precipitation.

Au@citate particles were synthesized through the reduction of HAuCl<sub>4</sub> (gold precursor) using sodium citrate.

**Synthesis of Ag<sub>44</sub>(4-MBA)<sub>30</sub> Cluster.** The Ag<sub>44</sub> cluster was synthesized using a reported procedure.<sup>34</sup> Initially 128 mg of AgNO<sub>3</sub> was taken in a beaker containing DMSO and water (4:7 volume ratio) mixture under constant stirring. 173 mg of 4-MBA was added to the mixture, and stirring was continued. 50% CsOH was added dropwise until the cloudy nature of thiolates became clear and a greenish-yellow color appeared. Then 283 mg of NaBH<sub>4</sub> in 9 mL of water was added dropwise to obtain a brown solution. The color of this solution changed to deep red after 1 h, which confirmed the cluster formation. This crude cluster was purified using DMF, which precipitated the cluster, and the solution was centrifuged. After removing the centrifugate, the cluster was extracted in citric acid-

containing DMF solution. This was to acidify all the protons of carboxylic acid, which makes the cluster soluble in DMF. The extracted cluster was again precipitated using toluene, and the solution was centrifuged. The acidification step was repeated one more time. After this, the precipitate was redissolved in 25 mL of DMF to get the purified cluster. It is important to mention here that when all carboxylates are protonated, there is no need of citric acid, and DMF can extract the cluster directly. Protonation is the key step for this purification.

**Synthesis of Ag<sub>44</sub>(TP)<sub>30</sub> Cluster.** The Ag<sub>44</sub>(TP)<sub>30</sub> cluster was synthesized using a two-step solution phase route.<sup>37,38</sup> First, silver trifluoroacetate (12.5 mg) was dissolved in 7.2 mL of acetonitrile and stirred for 5 min. Thiophenol (10  $\mu$ L) was added to that solution and was left to stir for another 15 min (solution A). In another conical flask, 28.6 mL of acetonitrile solution of NaBH<sub>4</sub> (10.8 mg) was kept for stirring for 30 min (solution B). Then, solution B was added to solution A, and the reaction mixture was left to stir for 3 h at room temperature. The deep pink cluster was formed after 2 h which was then centrifuged, and the centrifugate was stored at 4 °C in fridge for the experiment.

**Preparation of Ag NP Monolayer.** Prepared Ag NPs were subjected toward consecutive centrifugation—redispersion cycles in water and ethanol to remove possible unreacted AgNO<sub>3</sub> and excess PVP. Those were finally redispersed in 2 mL of 1-butanol by gentle sonication.

This dispersion of Ag NPs in butanol was slowly drop cast on the surface of water taken in a beaker. As butanol spreads on water, it drags the NPs along and gets aligned at the interphase. Finally, the NPs floats in the form of a monolayer on water which was then transferred onto microscope coverslips which were used as substrates for the decarboxylation experiment.

**Decarboxylation Experiment.** A dilute solution of  $Ag_{44}(4-MBA)_{30}$  in DMF was drop cast on Ag NPs monolayer, and it was dried under ambient conditions. This sample was then placed under a Raman microscope, and Raman spectra from a chosen spot were collected in a time-dependent fashion. The time-dependent spectra showed emergence of new peaks and increase in their intensity, indicating *in situ* changes in the analyte (cluster, in this case) under laser irradiation.

**Instrumentation.** Raman spectroscopy and imaging were done on a WITec GmbH, AlphaSNOM alpha 300 S confocal Raman microscope having a 633 nm laser as the excitation source. A Zeiss 20× objective (NA 0.4) was used for spectral acquisition. Spectral data were analyzed on Witec Project Plus software. The UV/vis spectra were recorded using a PerkinElmer Lambda 25 UV/vis spectrometer. A Waters Synapt G2-Si high definition mass spectrometer equipped with electrospray ionization was used in the negative mode. The concentration used was about 1 ppm for both the samples. The instrument was calibrated using NaI as the calibrant. The optimized conditions were as follows: sample concentration: 1 ppm; flow rate:  $5-10 \ \mu L/min$ ; source voltage:  $2.5-3 \ kV$ ; cone voltage:  $120-140 \ V$ ; source temperature:  $80-100 \ ^\circ$ C; and desolvation temperature:  $150-200 \ ^\circ$ C.

## RESULTS AND DISCUSSION

In this experiment, first polyvinylpyrrolidone (PVP)-protected silver (Ag NPs) nanoparticles were synthesized through a polyol method. A monolayer film of these Ag NPs was then prepared through a solvent drying process at the air-water interface, and it was then transferred onto microscope coverslips. The TEM images of the assembly and a photograph Scheme 1. Schematic View of the Decarboxylation of Ag<sub>44</sub> Which Results in Janus-Type Clusters



**Figure 1.** (A) Raman spectra of the clusters;  $Ag_{44}(4-MBA)_{30}$  on a microscope coverslip (a) and that of  $Ag_{44}(4-MBA)_{(30-x)}TP_x$  (b) and  $Ag_{44}TP_{30}$  (c) on a Ag NP monolayer film, respectively (for a clear comparison, trace a has been multiplied by 100, since it is a Raman spectrum while the other two are SERS). Insets I and II are expanded views of the regions marked. Prominent features of TP appear in the spectrum (red trace) upon laser irradiation of  $Ag_{44}(4-MBA)_{30}$ , confirming the decarboxylation of 4-MBA ligands. Features of both 4-MBA and TP are present in the resultant cluster spectrum (red trace), confirming the formation of  $Ag_{44}$  with mixed ligand protection. For clarity, the spectrum was fitted (in II) with two individual components (pink and green traces, respectively). (B) The corresponding structures of the three clusters  $Ag_{44}(4-MBA)_{30}$  (a),  $Ag_{44}(4-MBA)_{20}(TP)_{10}$  (b), and  $Ag_{44}(TP)_{30}$  (c), respectively. The characteristic features are labeled ( $\beta$  and  $\nu$  indicate the in-plane bending and the stretching modes, respectively). There are certain minor features indicated with an asterisk, which are likely to be due to conformational changes of the ligands and have not been assigned accurately.

of the corresponding nanoparticle film are given in the Supporting Information (Figure S1). The  $Ag_{44}(4-MBA)_{30}$ cluster was synthesized using a reported procedure.<sup>34</sup> Briefly, a basic Ag-thiolate (4-MBA) solution was slowly reduced by dropwise addition of aqueous sodium borohydride (NaBH<sub>4</sub>) to obtain the crude cluster. It was purified 2-3 times and was finally extracted in dimethylformamide (DMF) to get the pure cluster (see Experimental Section). The unique "molecule-like" features in the UV/vis spectrum confirm the formation of Ag<sub>44</sub> cluster (Figure S2). Synthesis was also confirmed by electrospray ionization mass spectrometry (ESI MS, Figure S2). The cluster was stable for months under ambient conditions in solution as well as in the solid state. Essential details of characterization of the cluster are given in the Supporting Information. Next, the DMF solution of  $Ag_{44}(4-MBA)_{30}$  cluster was drop-casted on the Ag NP film and dried in air. These films were used for Raman spectroscopic experiments using 633 nm laser excitation (details are in the Supporting Information). Exposure to 532 nm laser excitation was seen to make darker spots indicating degradation of clusters, and so we did not pursue experiments with this laser source. Scheme 1 describes

the experiment pictorially. In order to confirm decarboxylation,  $Ag_{44}(TP)_{30}$  was prepared separately, which was also characterized by UV/vis (Figure S2). Exact match of the UV/vis features confirms the formation of the cluster. The Raman spectrum of the  $Ag_{44}(4-MBA)_{30}$  clusters, drop cast onto glass coverslips, is displayed in trace a of Figure 1A. The intensity has been multiplied by 100 as the other spectra (to be discussed later) are more intense resulting from the surface enhancement of the supporting nanoparticles. Because of the Raman-active mercaptobenzoic acid ligand (Figure S3), the  $Ag_{44}(4-MBA)_{30}$ cluster shows Raman features between 200 and 1600 cm<sup>-1.4</sup> Strong bands are exhibited at 1076 and 1587  $\mbox{cm}^{-1}$ corresponding to  $\nu_{12}$  and  $\nu_{8a}$  aromatic ring vibrations, respectively.<sup>35</sup> Ag<sub>44</sub> clusters were then drop cast on a selfassembled silver nanoparticle film (Ag44@Ag NPs) to obtain a better resolved spectrum. Monolayer assembly of Ag NPs generates "hot spots" at the junctions of adjacent particles. Coupling of localized surface plasmon (LSP) of two adjacent particles creates a strong electric field, which increases the Raman signal significantly for the molecules located near the hot spots.<sup>47</sup> Exposure of the 633 nm laser onto Ag<sub>44</sub>@Ag NPs,



Figure 2. Calculated Raman spectra of model species  $Ag_1(TP)_1(4-MBA)_1$ ,  $Ag_1(4-MBA)_2$ , and  $Ag_1(TP)_2$  in regions (A) 900-1200 cm<sup>-1</sup> and (B) 1500-1650 cm<sup>-1</sup>.

however, led to the appearance of two new peaks at 1003 cm<sup>-1</sup> ( $\beta_{\rm CCC}$ ) and 1026 cm<sup>-1</sup> ( $\beta_{\rm CH}$ ) along with a shoulder peak near 1575 cm<sup>-1</sup> ( $\nu_{\rm CC}$ ), indicating the formation of new species (trace b, Figure 1A).<sup>48</sup> Note that the standard features of 4-MBA are also present. The spectral intensity is enhanced due to the supporting plasmonic particles. As this is not the subject of our discussion, we will not dwell upon the enhancement aspect further.

4-MBA has been used as a SERS probe for several decades because of its strong interaction with noble metals through the S-metal bond. It is known to undergo decarboxylation on metal surfaces upon laser illumination.<sup>49,50</sup> The new peaks observed in the spectrum (1003, 1026, and 1575 cm<sup>-1</sup>) match with the prominent peaks of TP, the decarboxylation product of 4-MBA. For clarity, the expanded spectra for these two specific regions are presented in the inset of Figure 1A. The Raman spectrum of the corresponding TP-protected Ag<sub>44</sub> cluster (trace c, Figure 1A) drop cast on Ag NP film shows similar bands at appropriate positions, confirming the catalytic transformation of Ag<sub>44</sub> bound 4-MBA to TP.

Raman spectra of small model compounds  $Ag_1(TP)_1(4-$ MBA)<sub>1</sub>, Ag<sub>1</sub>(4-MBA)<sub>2</sub>, and Ag<sub>1</sub>(TP)<sub>2</sub> were calculated to confirm the aforementioned Raman spectral assignments using the density functional theory (DFT) method as available with Gaussian 09 software.<sup>51</sup> Details of the calculations are provided in the Supporting Information. The spectra corresponding to regions 900-1200 cm<sup>-1</sup> and 1500-1650 cm<sup>-1</sup> are presented in Figure 2. The characteristic peaks of  $Ag_1(TP)_2$  at ~980 and 1020 cm<sup>-1</sup> which are absent for  $Ag_1(4 MBA)_2$  are clearly observable in the spectrum of  $Ag_1(TP)_1(4-$ MBA)<sub>1</sub>. Furthermore, the peak at ~1565 cm<sup>-1</sup> for Ag<sub>1</sub>(TP)<sub>2</sub> is shifted to a higher frequency (~1575  $\text{cm}^{-1}$ ) in the spectrum of  $Ag_1(TP)_1(4-MBA)_1$ , similar to that of  $Ag_1(4-MBA)_2$ . These above-mentioned features, similar to that of  $Ag_1(TP)_1(4-$ MBA)<sub>1</sub>, were exhibited in the experimental Raman spectra of cluster@Ag NPs, excited by a 633 nm laser (trace b, Figure 1A, traces b, c). This supports our experimental analysis that decarboxylation has occurred, resulting in a cluster which has both 4-MBA and TP as protecting ligands.

High-resolution electrospray ionization mass spectrometry was carried out to identify the final product (Figure 3). For this, the cluster was drop-casted on a specific area of the film of nanoparticles (marked originally) and was exposed to the laser



**Figure 3.** (A) HR ESI mass spectrum (negative mode) of the parent  $Ag_{44}(4-MBA)_{30}$  cluster in the 4<sup>-</sup> region, (a) and the decarboxylated product in DMF-acetonitrile mixture after laser exposure for 90 min. The spectra are collected (b) immediately, (c) after 10 min, (d) after 15 min, and (e) after 30 min, after extraction into solution (see text for details). The  $Ag_{44}(4-MBA)_{30}$  peak at m/z 2335 is expanded in (B), and the corresponding calculated pattern is given as a red trace. The decarboxylated product, taken in solution, shows a series of peaks for  $Ag_{44}(4-MBA)_{30-x}$ (TP)<sub>x</sub> cluster where x varies from 3 to 20. The highest intensity was seen near x = 10, which is expanded in (C). It shows an exact match with the corresponding calculated pattern (blue trace). Time-dependent data suggest the intercluster ligand exchange in solution. Higher intensity of the experimental spectrum on either side of the main feature is due to the overlapping peaks on either side.

for 90 min. The exposed area was then scratched, extracted in a DMF–acetonitrile mixture, and centrifuged to precipitate the Ag NPs, and the solution was subjected to ESI MS instruments. These processes of extracting the laser-irradiated cluster into solution took about 5 min, and this time was taken as time zero (immediate after irradiation) for mass spectral measurements. The UV/vis spectrum of the extracted solution (Figure S4) confirmed the integrity of the cluster on Ag NP monolayer film post laser irradiation. From previous studies we had established that slight changes in the ligands do not affect the optical absorption spectrum of clusters.<sup>40</sup> The mass spectrum, taken immediately after extraction (trace b, Figure 3A), showed a series of peaks, occurring at a lower m/z than the parent peak for Ag<sub>44</sub>(4-MBA)<sub>30</sub><sup>4-</sup>. The mass spectrum of the ion due to



**Figure 4.** Time-dependent evolution of TP features in the Raman spectrum of  $Ag_{44}(4-MBA)_{30}$  upon laser irradiation: (A)  $\beta_{CCC}$  and  $\beta_{CH}$  regions and (B)  $\nu_{CC}$  region.  $\beta$  and  $\nu$  indicate the in-plane bending and the stretching modes, respectively.

 $Ag_{44}(4-MBA)_{30}^{4-}$  (trace a, Figure 3A; an expanded view is shown in Figure 3B) showed a peak centered around m/z 2335. In the spectrum immediately after exposure of laser showed the complete absence of the peak at m/z 2335, and a series of peaks at lower masses appeared (Figure 3A, trace b). A mass difference of m/z 11.1 between the successive peaks is seen, suggesting the formation of mixed-ligand-protected Ag44(4-MBA)<sub>30-x</sub> $TP_x$  cluster (mass difference of 4-MBA and TP is 44.4 and the charge is 4-, giving a separation of 11.1). The cluster underwent solution-phase intercluster ligand exchange with time, which contributed to the increase in the number of ligand exchange products with time which can be seen from the time-dependent mass spectra (traces b-e, Figure 3A). Intercluster ligand exchange in solution makes it impossible to capture the specific  $Ag_{44}(4-MBA)_{30-x}TP_x$  cluster produced onto the Ag NP surface in their native form through solvent extraction. This prohibited us in further analysis into the ligand geometry of the transformed  $Ag_{44}(4-MBA)_{30-x}TP_x$  through mass spectrometry. The value of x for  $Ag_{44}(4-MBA)_{30-x}TP_x$  for solution extracted clusters was 3-20, with maximum intensity for x = 10 after 30 min of extraction (trace e, Figure 3A). The system equilibrates after this point, and no further ligand exchange was observed. An expanded view of Ag<sub>44</sub>(4- $MBA)_{20}TP_{10}$  region is shown in Figure 3C. The apparent broadness of the experimental peak is due overlapping features from neighboring  $Ag_{44}(4-MBA)_{30-x}TP_x$  features.

Monitoring of time-dependent evolution of TP features in the Raman spectra (Figure 4) suggests that number of 4-MBA ligands transforming to TP increases with exposure time up to a certain point and saturates beyond. This was confirmed by plotting the relative intensities of the peaks at 1003, 1026, 1576, and 1587 cm<sup>-1</sup> with time. The plots displayed an increase in intensity of the first three peaks (Figure S5) and a decrease in intensity for the last peak up to a certain exposure time (100 s), following which the intensity remained constant. The Raman spectrum of the final product after an exposure time of 140 s (trace b, Figure 1A) suggested that it has a combination of thiophenol and 4-MBA as protecting ligands, and the percentage of 4-MBA to TP can be calculated by comparing the relative intensities of the TP only peaks at 998 and 1022 cm<sup>-1</sup> with that of Ag<sub>44</sub>TP<sub>30</sub> (trace c, Figure 1A). This also suggests decarboxylation of approximately 10 ligands and corroborates with the conclusion drawn from ESI MS data.

The fact that decarboxylation remained limited to a certain number of 4-MBA ligands and did not extend beyond, even after an extended period of irradiation, hints that laser irradiation can excite only a fixed number of 4-MBA ligands out of total 30 available per cluster. Laser irradiation of dropcast films of  $Ag_{44}(4-MBA)_{30}$  onto coverslips as well as onto TLC plates (composed of silica particles) did not show any signatures of TP. It is clear that self-assembled Ag NPs (Figure S6A) helped in decarboxylation. These experiments confirm that nature of the underlying surface plays an important role in absorbing and channeling the laser energy to bring about decarboxylation.

Transmission spectroscopic measurements of the Ag NP film showed plasmon excitation at 470 nm, in contrast to the excitation maximum of 412 nm in solution (Figure S6B). This confirms the involvement of coupled plasmon excitation in the decarboxylation process. The clusters attach themselves onto the Ag NP surfaces through carboxylate ends of some of the 4-MBA ligands, and these 4-MBA ligands (attached to NP surface) can be influenced easily by the plasmon excitation. A similar laser irradiation experiment, carried out on Ag<sub>44</sub>(4-MBA)<sub>30</sub> over a monolayer film of Au NPs (Figure S7), resulted in the decarboxylation of 10 4-MBA ligands, albeit the rate was slower than on Ag NPs. This again hints at the role of coupled plasmon excitation of metal NPs in energizing the 4-MBA ligands leading to their decarboxylation. These experiments hint toward a site-specific decarboxylation of the parent Ag<sub>44</sub>(4-MBA)<sub>30</sub> NCs, forming Janus Ag<sub>44</sub>(4-MBA)<sub>30</sub> clusters protected with TP ligands on one side (close to NPs) and with 4-MBA ligands on the other (away from NPs). The approximate value of 10 can be rationalized from the involvement of two  $Ag_2(SR)_5$ staple motifs present near the silver nanoparticles.

As decarboxylation is presumably governed by the proximity of carboxylate ligands with the "hot spots", the binding or interaction of the ligand with the silver nanoparticle surface is an important factor in this transformation. To develop an understanding of the adsorption and decarboxylation processes, we performed periodic DFT calculations using the Pythonbased GPAW code<sup>52</sup> within the atomic simulation environment (ASE).<sup>53</sup> A van der Waals density function<sup>54</sup> was employed to calculate adsorption and decarboxylation energies for geometries optimized using the revised Perdew-Burker-Ernzerhof (RPBE) function.<sup>55</sup> For more details of the computations please refer to the Supporting Information. We considered binding of 4-MBA radical (4-MBA\*), TP radical (TP\*), benzoic acid, and benzene at different adsorption sites over the Ag(111) surface, chosen as a representative surface on the Ag NPs. Each adsorbate/Ag(111) models adsorption of a ligand (protecting the Ag<sub>44</sub> core) on the Ag NP surface. Only ligand interaction with this Ag (111) was explored as adsorption of the whole  $Ag_{44}(4-MBA)_{30}$  cluster on Ag(111) would have been computationally much more expensive. We chose this also because only the ligands are going to interact with the Ag NP Table 1. Theoretically Calculated Adsorption Energies and Decarboxylation Energies Including van der Waals Correction of Ligands Adsorbed on Ag(111) Surface<sup>a</sup>

System	Optimized structure	Adsorption energy (ev)	Decarboxylation energy (ev)
Benzene	₩ ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° °	-0.293 [fcc] -0.267 [bridge]	
Benzoic acid (parallel orientation)	***	-0.544 [fcc]	-0.115
Benzoic acid (vertical orientation)		-0.292 [bridge]	-0.367
TP*	₩, °	-1.654 [bridge]	
4-MBA*	·•***	-1.836 [bridge]	-0.220

<sup>a</sup>Decarboxylation energies are with reference to CO<sub>2</sub> gas. The adsorption site for each species is given in the square brackets.



**Figure 5.** Patterned modification of  $Ag_{44}(4-MBA)_{30}$  into  $Ag_{44}(4-MBA)_{30-x}TP_x$  through the decarboxylation process. (A) Schematic of the experiment. A 200 mesh TEM grid was used as mask, and the area coated with  $Ag_{44}(4-MBA)_{30}$  was irradiated with a 633 nm laser. Inset shows the selected spectral region which was being used for the Raman image. (B) Raman image of the irradiated area after removal of the TEM grid.  $Ag_{44}(4-MBA)_{30}$  remains intact in the areas covered with the grid while in the areas exposed to the laser transforms into  $Ag_{44}(4-MBA)_{30-x}TP_x$ . The increased intensity of the exposed regions indicates the transformation. Intensity scale is marked on the right.

surface. Benzoic acid and benzene were chosen as ligands because, being already attached to the cluster core through S, 4-MBA and TP are not likely to interact with the Ag NP particle surface through S, instead via the – COOH or the aromatic ring. The calculated van der Waals corrected adsorption and decarboxylation energies are listed in Table 1. It can be seen from the table that decarboxylation is thermodynamically favorable for benzoic acid and 4-MBA\* which represent the

ligands around the  $Ag_{44}$  cluster in different orientations. Second, the adsorption energies of benzoic acid in vertical orientation and benzene in parallel orientation are quite similar; so is the case of 4-MBA\* and TP\*. Furthermore, the preferred adsorption sites of the decarboxylated species, i.e., benzene and TP\*, are the same as those of benzoic acid and 4-MBA\*, respectively. These points suggest that following decarboxylation of the 4-MBA ligands (conversion to TP) in proximity

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to the Ag NP surface, the decarboxylated  $Ag_{44}$  cluster is likely to remain at the same position and will not roll off on to Ag NP surface as the interaction energies through –COOH and aromatic ring are similar. This prevents the other 4-MBA ligands (away from the Ag NPs) from interacting with the NP surface, and those remain intact. These computational findings in conjunction with the time-dependent Raman spectroscopy explains regiospecific decarboxylation of the parent clusters and the fact that it stops after a certain number of 4-MBA ligands are decarboxylated.

Using decarboxylation induced spectral changes of the clusters, specific patterns can be drawn onto cluster coated nanoparticle films, which are otherwise invisible, and can be read out through Raman spectral imaging. To demonstrate this, specific areas of a cluster coated Ag NP film was exposed to the 633 nm laser beam using a center-marked (used as the marker for position) uncoated TEM grid as mask (Figure 5A). Raman spectral imaging was performed from an exposed 600  $\mu$ m × 600  $\mu$ m area on stepper motor driven XY stage after removing the mask (TEM grid). A total of  $150 \times 150$  Raman spectra were collected from the area for constructing the Raman image, giving a spatial resolution of 4  $\mu$ m. It is to be noted that much better spatial resolution is obtainable (~1  $\mu$ m), but it was avoided to minimize the imaging time and laser-induced damage. The Raman image constructed by taking the prominent feature of  $Ag_{44}(4-MBA)_{30-r}TP_r$  (marked in the inset of Figure 5A) is shown in Figure 5B, which shows different contrast for exposed and unexposed areas. Decarboxylation happens where the area was exposed to the laser, and that creates the specific pattern.

## CONCLUSION

In summary, a Janus type of atomically precise cluster has been formed in situ through plasmon excitation induced decarboxylation of Ag44(4-MBA)30. A cluster film was made on a selfassembled silver nanoparticle surface which helps in propagating the plasmon to generate local heat at the cluster surface attached to the particles, upon 633 nm laser irradiation. The decarboxylation was monitored by Raman spectroscopy where new peaks due to the decaroxylated product TP, started appearing. The transformation saturates after a certain time, and from intensity ratios of the peaks involved, we estimate that approximately ten ligands per cluster have been transformed to TP. HR ESI mass spectral data further support this precise transformation. Considering a simple model of thiolates, DFT calculations were done to understand the decarboxylation and adsorption processes. Specific Raman patterning due to the decarboxylation can be implemented in generating hidden molecular signatures using appropriate masks.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b04769.

Details of computation, characterization of nanoparticles, UV/vis of  $Ag_{44}$  cluster, comparative Raman spectra, intensity vs exposure time plot, and Raman spectral data of control experiments with Ag@PVP and Au@citrate nanoparticles (PDF)

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#### Notes

The authors declare no competing financial interest.

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