# Controlled Manipulation of Magic Number Gold-Fullerene Clusters Using Scanning Tunnelling Microscopy

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## Abstract

We report controlled manipulation of magic number gold-fullerene clusters, $(C_{60})_m$–$(Au)_n$, on a Au(111) substrate at 110 K using the scanning tunnelling microscope (STM). Each cluster consists of a two-dimensional gold island of *n* Au atoms confined by a frame of *m* $C_{60}$ molecules. Using the STM, $C_{60}$ molecules are extracted from the molecular frame one at a time. The extraction is conducted by driving the STM tip into the cluster leading to one of the molecules being squeezed out of the frame. Unlike at room temperature, the extracted molecules do not move away from the cluster due to the lack of thermal energy at 110 K, they are found to be attached to the outside of the frame. Reversible manipulation is also possible by pushing an extracted molecule back into the frame. This reversible manipulation is possible only for molecules from the edge of the cluster.

**Keywords:** Two-dimensional clusters; metal-organic coordination; atom manipulation; Au(111); Scanning tunnelling microscopy; Fullerenes; $C_{60}$; nucleation and growth.

## Introduction

A great challenge in the synthesis of small atomic/molecular clusters or nanoparticles is the control over the cluster size and shape [1, 2]. The demand for accurate size and shape control arises from the size- and shape-dependent properties of nanometer-sized particles and the potential applications of these particles in, e.g., solar cells, organic electronics, or single molecule devices [3-5]. While the size and shape of clusters can be controlled to some extent during synthesis, post-synthesis manipulation is also an effective way for tailoring clusters. In particular, for clusters deposited onto a solid support, atom-by-atom manipulation can be performed using the scanning tunnelling microscope (STM) or the atomic force microscope (AFM) [6-13]. In order to conduct controlled manipulation using the STM or AFM, samples are usually kept at cryogenic temperatures so that thermal effect does not interfere with the manipulation process [14, 15].

Magic number $(C_{60})_m$–$(Au)_n$ clusters [16] and fullerene-gold nanorings [17] have been self-assembled recently on the Au(111) surface by depositing $C_{60}$ molecules and Au atoms onto the surface at 110 K followed by annealing to room temperature (RT). The combination of the Van der Waals interaction among $C_{60}$ molecules and the charge transfer from Au atoms to $C_{60}$ molecules keeps the $(C_{60})_m$–$(Au)_n$ clusters stable well above room temperature (~400 K [16]). In our earlier work, we demonstrated "tip-triggered thermal cascade manipulation" of the magic number clusters at RT [18]. In that case, we disturbed the cluster by driving the STM tip into the cluster, followed by withdrawal. Under well-controlled experimental conditions, the STM tip is able to eject a single $C_{60}$ molecule mechanically from the cluster. The disturbed cluster is able to

re-organise at RT by downsizing to a smaller magic number cluster, under the influence of thermal energy.

In this paper, we report controlled manipulation of the magic number clusters at 110 K. At this low temperature, the lack of thermal energy prevents the disturbed clusters from reaching thermal equilibrium. Hence we observe a number of meta-stable structures. The observations at 110 K help to further understand the cascade manipulation performed at RT [18].

**Experimental**

The Au(111) substrate was in the form of a thin gold film grown on a 4 mm x 8 mm HOPG (highly oriented pyrolytic graphite) substrate. The film was formed by thermally evaporating Au inside a BOC Edward 306 deposition chamber under a base pressure of 2 x $10^{-7}$ mbar. The HOPG substrate was heated to 493 K during deposition. The thickness of the Au film was estimated to be ~300 nm by using a quartz crystal thickness monitor. The sample was transferred via the air into the UHV chamber which housed the STM, and cleaned with cycles of Ar ion sputtering and 90 minutes of thermal annealing at 1000 K. The energy of the Ar ions was 1 keV and the ion current density ~10 $\mu A/cm^2$. Magic number cluster preparation and manipulation experiments were conducted in an ultra-high vacuum chamber with base pressure below 9 x $10^{-10}$ mbar. For STM imaging, an electrochemically etched W tip was used. The tip was heated to 473 K to desorb organic contaminants before use.

To prepare the magic number clusters, we deposited 0.04 monolayers (ML) of $C_{60}$ molecules and then added 0.04 ML of Au atoms onto the Au(111) surface at 110 K. The $C_{60}$ molecules and

the Au atoms were able to diffuse on the surface and aggregate at the elbow sites of the herringbone-reconstructed Au(111) surface. The sample was then warmed up to RT at which point a large number of magic number $(C_{60})_m$–$Au_n$ clusters were observed before cooling back down to 110 K for manipulation with the STM tip.

**Results and Discussion**

Cluster manipulation is conducted by driving the STM tip towards a selected $C_{60}$ molecule within a magic number cluster, followed by withdrawing the tip. The round trip takes 12.8 ms. The initial vertical position of the STM tip is controlled by fixed tunneling parameters of 47 pA and -1.74 V. The actual distance between the tip and molecule is not known. However, from an earlier study, we found that the STM tip makes mechanical contact with the molecule when it is displaced by 0.5 nm towards the surface. A displacement of 1.2 nm leads to direct contact between the tip and the Au(111) substrate [18]. Optimal tip displacement for manipulation is found experimentally by repeating the manipulation process with different tip-displacements in the range between 1.2 and 1.8 nm (see Ref. [18]).

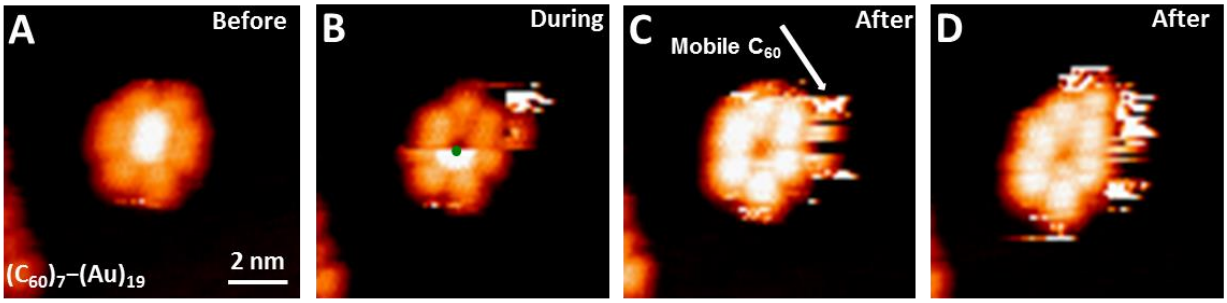


Figure 1: Manipulation of a $(C_{60})_7$-$(Au)_{19}$ cluster at 110 K. The molecule in the centre of the cluster is targeted. (A) STM image (10 x 10 $nm^2$) showing the cluster before manipulation. (B) Image obtained during manipulation. The tip rasters up from the bottom of the image and stops

at the location highlighted by the green dot, where the tip makes its vertical round trip. Normal scanning is resumed once the tip returns to its initial height. (C) and (D) Images showing the vacancy created in the middle of the cluster and the diffusion of the displaced $C_{60}$ mobile molecule around the edge.

The STM images of Figure 1 show a manipulation event for a $(C_{60})_7$-$(Au)_{19}$ cluster, which contains seven $C_{60}$ molecules and 19 gold atoms [18]. The 19 Au atoms form a single atomic layer hexagonal island; six of the seven $C_{60}$ molecules are attached to the six step edges of the Au island, while the seventh molecule sits directly above the island [18]. First, the cluster is imaged before manipulation (Figure 1A). During the next scan, Figure 1B, the tip rasters the surface from bottom to top. The tip stops at the chosen location, approximately directly above the central molecule, marked with the green dot. At this point, the tip is moved towards the substrate by 1.3 nm and then retracts to its original position. Afterwards, normal scanning is resumed to complete the frame. The top half of the central molecule is missing in Figure 1B, suggesting that it has been removed by the manipulation process. This is confirmed by images taken afterwards, Figure 1C and D, showing a vacancy in the middle of the cluster. The displaced central molecule is found to be relocated just outside the ring of the remaining six molecules. This displaced, stray, molecule is mobile and observed to diffuse around the cluster. The streaks in Figure 1C and D are typical features of molecular displacement. The movement of this molecule is possibly influenced by the STM tip, although thermally activated diffusion of single $C_{60}$ molecules is quite likely at this temperature; complete freezing of the molecular motion of $C_{60}$ molecules requires a very low temperature of 10 K [20, 21]. It is not clear if any Au atoms are removed from the 19-atom island during the manipulation event. However, the lateral size of the vacancy,

Figure 1C and D, suggests that the Au-island is largely unaffected. The presence of the Au island within this vacancy prevents the molecules from collapsing into a close-packed structure. In principle, it would be possible to perform manipulation in a low temperature STM operating at 5 K or lower. By stripping all $C_{60}$ molecules from the cluster using the STM tip, one can then count the number of Au atoms in the 2D Au island.

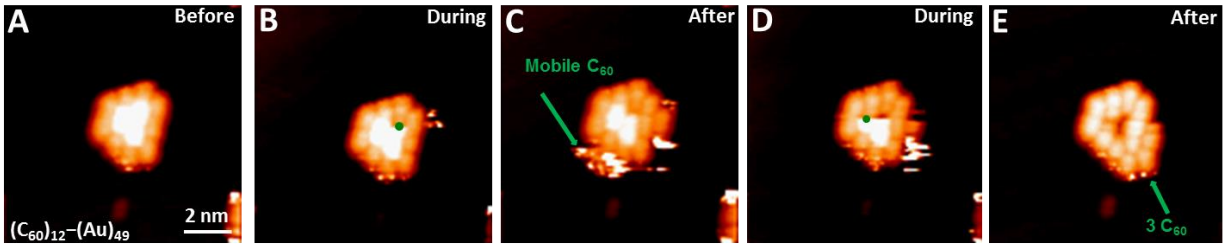


Figure 2: Manipulation of a $(C_{60})_{12}$-$(Au)_{49}$ cluster at 110 K. (15 x 15 $nm^2$). (A) STM image of a $(C_{60})_{12}$-$(Au)_{49}$ cluster. (B) STM tip stopped at the location marked by the green dot during scanning and moved towards the surface by 1.3 nm. This leads to the displacement of a molecule. (C) The displaced $C_{60}$ molecule is observed moving around the cluster (green arrow). (D) Displacing another $C_{60}$ molecule marked with a green dot. (E) Successive manipulations lead to the removal of all three $C_{60}$ molecules from top of the $Au_{49}$ island. All images are 15 x 15 $nm^2$.

The set of STM images shown in Figure 2 record the manipulation of a $(C_{60})_{12}$-$(Au)_{49}$ cluster which has 3 $C_{60}$ molecules sitting on an $Au_{49}$ island. The remaining 9 molecules are attached around the step edges of the Au island. We have succeeded in moving all three molecules from the top of the $Au_{49}$ island, one at a time. Similar to what is observed for the $(C_{60})_7$-$(Au)_{19}$ cluster, the displaced molecules do not move away from the cluster. There is a strong enough interaction to keep the displaced molecules part of the new cluster. As can be seen in Figure 2E,

the three relocated molecules form a local close-packed structure with other molecules in the cluster. By doing so, they have lost their mobility.

The displacement of $C_{60}$ molecules from the $(C_{60})_m{-}Au_n$ cluster is a result of repulsive interaction when the STM tip is pushed into a location occupied by a molecule [18]. For relatively large $(C_{60})_m{-}Au_n$ clusters, the area of the $Au_n$ island is large enough to support quite a few molecules. As we extract more and more of these molecules sitting on the $Au_n$ island, the vacancy become larger. Thus, for large $(C_{60})_m{-}Au_n$ clusters, it becomes harder to extract the last few molecules from top of the $Au_n$ island, because an alternative channel (lateral displacement) opens up. This is demonstrated with the manipulation of a $(C_{60})_{16}$-$(Au)_{77}$ cluster as shown in Figure 3. In this case, there are five molecules sitting on a $(Au)_{77}$ island and eleven molecules attached to the step edges. After successfully extracting three molecules, Figure 3B-G, an attempt is made to remove a fourth one. In Figure 3H-I, it can be seen that a standard manipulation causes the molecule to slide sideways into a vacant site. Therefore, once a large enough vacancy is created, $C_{60}$ molecules tend to translate on the surface of the Au island rather than being pushed off the island.

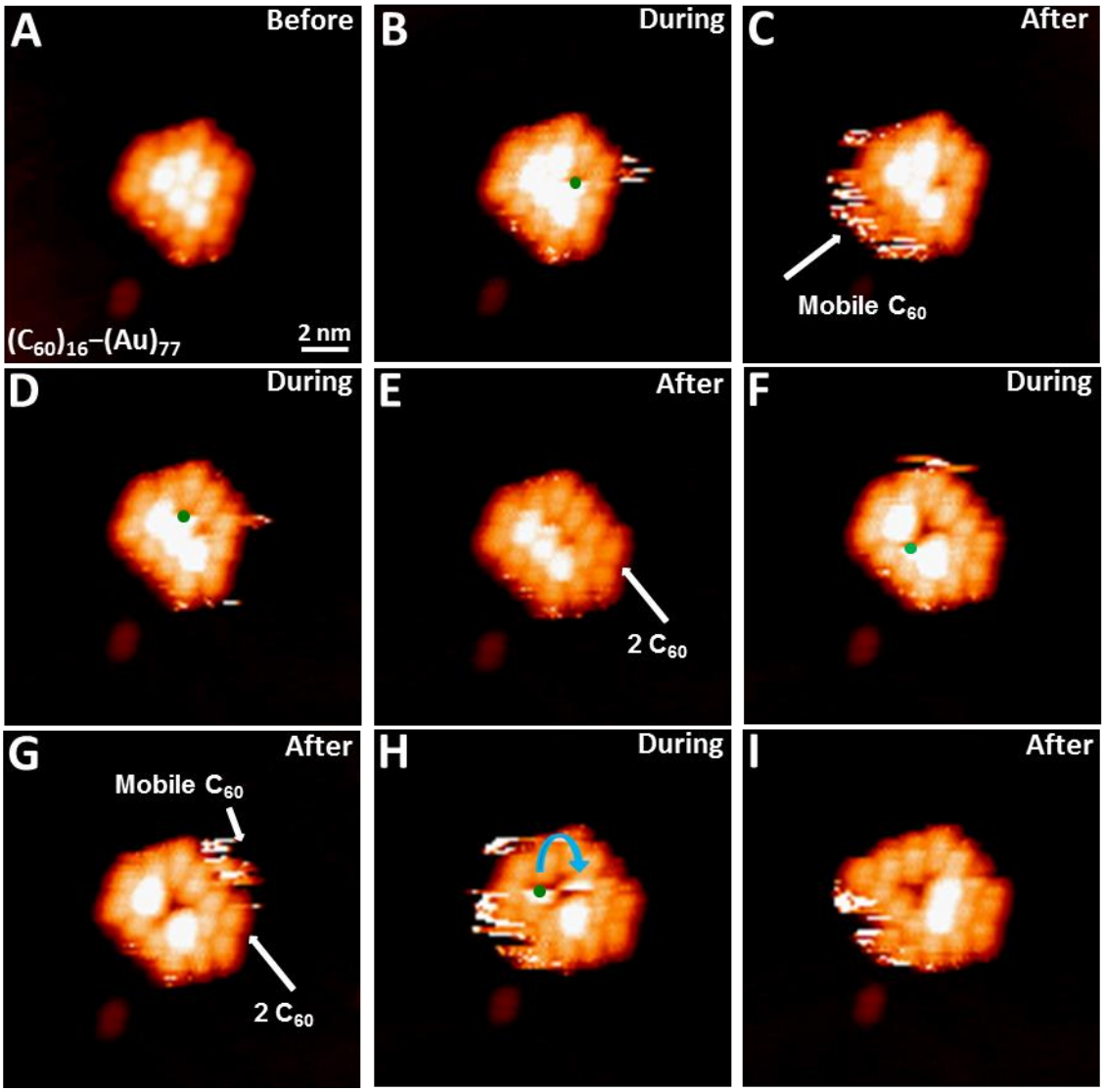


Figure 3: Manipulation on a $(C_{60})_{16}$-$(Au)_{77}$ cluster at 110 K (15 x 15 $nm^2$). (A-C) show the extraction of the first $C_{60}$ molecule. (D-E) show the extraction of the second $C_{60}$ molecule. (F-G) demonstrate the successful extraction of the third molecule. (H-I) Further manipulation of the remaining atop molecules causes lateral motion.

Manipulation has also been performed on $C_{60}$ molecules attached to the step edges of the Au island. We have explored the possibility of moving a $C_{60}$ molecule in a specified lateral direction by fine-tuning the contact point between the tip and the molecule. A schematic diagram for such a directional manipulation on a $C_{60}$ molecule is illustrated in Figure 4 A-B. The green line in Figure 4A and B indicates the imaginary center line of the molecule. By contacting the molecule at a point shown by the cross, off the center line, we expect to generate a horizontal force component to push the molecule in a specific direction. Yellow arrows in Figure 4A and B indicate the proposed directions of motion. In a typical directional manipulation process, we raster the STM tip under normal imaging conditions. Once the tip has passed a target molecule or just a fraction of the target molecule, we stop the tip and move it to a position above the target molecule. The exact location of the tip relative to the position of the target molecule can be controlled to a limited level of accuracy. Thus, we can place the tip either below or above the central line before driving it into the molecule. We know which half the molecule is contacted by the tip, but we have not yet achieved the level of accuracy to study how the manipulation process depends on the distance of the tip from the center of the molecule. We performed an experiment with a $(C_{60})_{16}$-$(Au)_{77}$ cluster shown in Figure 4C. Controlled displacement of one of the edge molecules along a specified direction is demonstrated in Figure 4D and E. In Fig. 4D, the tip performs left-right scans and gradually moves upwards. During the collection of the image, the tip is stopped at the position indicated by the green dot. At that point, the tip drives into the molecule and then withdraws. It then resumes normal scanning from that point upwards to complete the image. The green dot is chosen at a location just above the center line of a $C_{60}$ molecule. This produces a downwards force component which pushes the molecule down. Fig.

4E shows that the manipulated $C_{60}$ molecule has indeed displaced downwards from its initial position. A second manipulation step, Fig. 4F, has succeeded in bringing this displaced molecule back into its initial position.

Figure  shows another example of directional manipulation. Here, a single $C_{60}$ molecule is caused to move around the cluster in the clockwise direction. This edge diffusion of single molecule is significantly influenced by thermal energy at 110 K. However, the thermal mobility is low enough that tip-induced movement does not get buried under the thermal noise. Note that 110 K is the lowest temperature that can be achieved using liquid nitrogen cooling in our system. Future experiments at lower temperatures would of course be interesting. The success rate in directional manipulation is quite high. The only factor that prevents a 100% success rate seems to be thermal excitation. At the lowest achievable temperature of 110 K using liquid nitrogen cooling in our system, a single $C_{60}$ molecule such as the one shown in Fig. 5 is able to move via thermal diffusion. However, thermal diffusion is slow enough to allow directional manipulation achievable.  We have shown earlier that when a single molecule is displaced from a magic number cluster, Figs. 1-3, this displaced molecule moves around so quickly that the STM tip is unable to follow it and hence all the streaks in the images. We suspect that this high mobility of the displaced molecule is partly associated with the reduced stability of the remnant of the cluster. In Figs. 4 and 5, the extra molecule in each case is attached to an undamaged stable cluster.

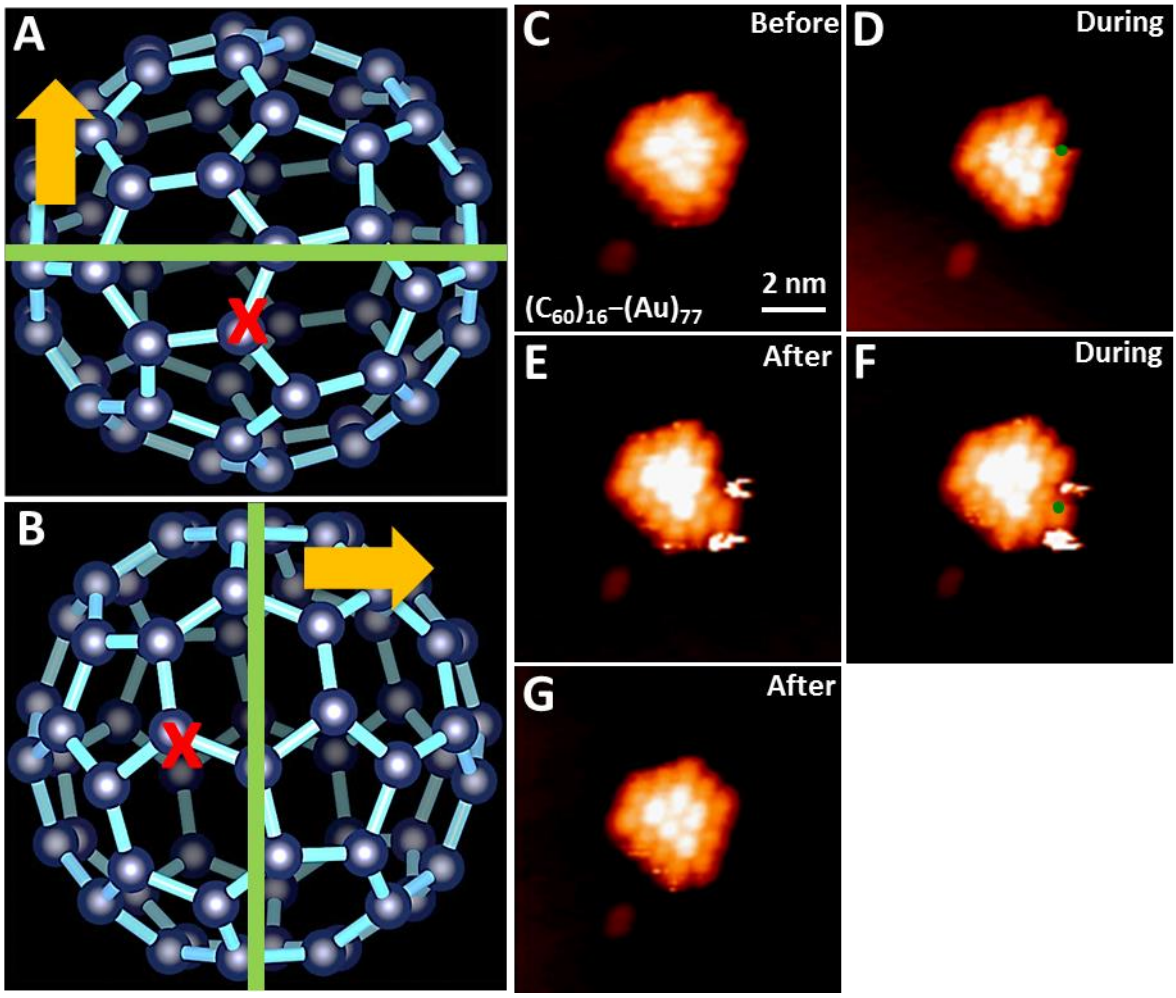


Figure 4: Directional manipulation of a selected $C_{60}$ molecule within a $(C_{60})_{16}$-$(Au)_{77}$ cluster. (A-B) Schematic diagram showing manipulation by contacting the molecule at a chosen point marked with a red cross. The yellow arrow indicates the desired direction of molecular motion. The tip moves in the vertical direction only. (C-E) Successful displacement of a single $C_{60}$ molecule at the edge of $(C_{60})_{16}$-$(Au)_{77}$ cluster. (F-G) The displaced molecule is brought back to its starting position by a second manipulation event.

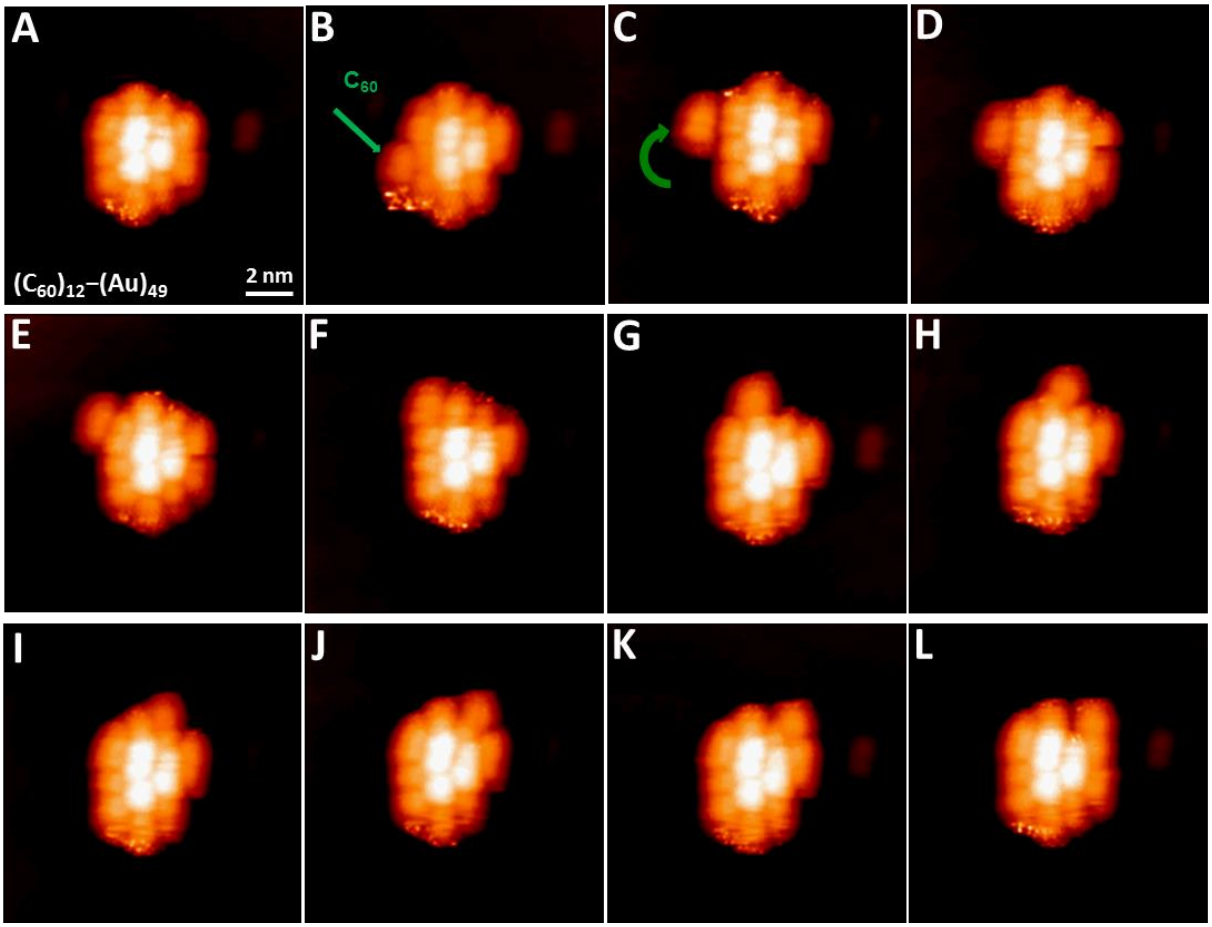


Figure 5: Using the scheme depicted in Figure 4, a $C_{60}$ molecule is moved around the cluster in the clockwise direction. From I to K, the molecule appears to have stuck due to another molecule sitting directly in front of its path.

We presented cascade manipulation of magic number clusters at RT triggered by the STM tip in our earlier work [18]. The manipulation reported here at low temperature 110 K is consistent with the earlier proposal that the modification to a $(C_{60})_m$-$(Au)_n$ cluster begins with the displacement of a single $C_{60}$ molecule. The displacement of the molecule is achieved by a repulsive interaction when the STM tip is forced into molecular array. Under suitable experimental conditions, we are able to displace just a single molecule. The displaced molecule

stays on the surface rather than being picked up by the STM tip. The low temperature manipulation experiment provides the opportunity to identify the location of the displaced molecule after manipulation as well as confirming that just a single molecule is displaced. This helps to understand the mechanism of the cascade manipulation reported earlier [18]. The cascade manipulation performed at RT starts with the displacement of a single molecule. The remaining molecules and Au atoms are able to self-organise under the influence of the thermal energy. As a consequence, self-organisation always leads to the formation of a new magic number $(C_{60})_m$-$(Au)_n$ cluster after the initial disturbance by the STM tip. At 110 K, the lack of thermal energy allows the disturbed cluster to exist in meta-stable configurations.

In conclusion, we have demonstrated the extraction of individual $C_{60}$ molecules from a $(C_{60})_m$-$(Au)_n$ cluster on the Au(111) surface. The manipulation is achieved by mechanically repelling a molecule out of a preformed stable cluster. Once a single molecule is removed from the molecular frame, it remains part of the cluster by weakly attaching to the outside of the frame. This weakly attached molecule would detach from the cluster at RT. More than one molecule can be displaced in such a manner by repeated manipulation. However, it gets harder to remove a molecule once the vacancy in the frame become too large because the molecule keeps "skipping" sideways inside the vacancy.

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