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Stability of $(C_{60})_m-Au_n$ Magic Number Clusters

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Abstract

The interaction of magic number $(C_{60})_m-Au_n$ clusters with individual Au atoms and C_{60} molecules is investigated using scanning tunnelling microscopy. The $(C_{60})_m-Au_n$ cluster supported on Au(111) has a core-shell-like structure with Au_n forming the core and $(C_{60})_m$ the protective shell. When extra C_{60} molecules are deposited onto the Au(111) substrate, they become attached to the outside of the $(C_{60})_m$ shell without altering the structure of the existing $(C_{60})_m-Au_n$ cluster. When Au atoms are deposited onto the Au(111) substrate, they can move through the C_{60} "shell" to join the Au core leading to gross re-configuration of the cluster.

1. Introduction

Synthesis of novel organic/inorganic hybrid structures, in particular structures with nanometer dimensions, has been an active area of research for the past few decades. One of the promising techniques for mass production of nano structures is self-assembly which has been successfully employed to fabricate a wide range of structures¹⁻⁴. The building blocks in self-assembled structures can be connected through hydrogen bonding⁵⁻⁸ or metal-ligand coordination⁹⁻¹¹ allowing for both selectivity and directional bonding. Covalent bonding and dispersive interactions have also been employed. Recently, our group have successfully synthesized $(C_{60})_m-Au_n$ magic number clusters¹² and fullerene nano-rings¹³ on the Au(111) substrate. The molecules in these clusters are bonded by van der Waals (vdW) forces having no directional bonding properties. Nevertheless, the molecules and atoms within the magic number cluster are able to stay together with a well-defined topography as

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a result of a globally optimised interaction mechanism. The stability of the $(C_{60})_m-(Au)_n$ clusters have been probed using the tip of a scanning tunnelling microscope (STM) at both room temperature (RT)¹⁴ and at 110 K¹⁵. Here we report the transformation of these clusters when they are attacked by Au atoms and C₆₀ molecules.

2. Experimental methods

Experiments are performed in an ultra-high-vacuum system equipped with an Omicron variable temperature STM. The Au(111) sample is a thin Au film deposited onto a highly oriented pyrolytic graphite (HOPG) substrate using physical vapour deposition. Such deposited Au films have a preferential orientation with the (111) plane parallel to the HOPG surface. The sample is cleaned in UHV with cycles of Ar⁺ ion sputtering and annealing to 1000 K until STM shows large atomically flat Au(111) terraces with the characteristic herringbone reconstruction. Electrochemically polished tungsten tips are used for imaging under constant current mode. After cooling the clean Au(111) sample down to 110 K, Au atoms and C₆₀ molecules are deposited sequentially at 110 K and the sample is then warmed up gradually to RT to form the magic number clusters. Once the magic number clusters are formed on the surface, the sample is cooled again using liquid nitrogen to a specific temperature at which point either Au atoms or C₆₀ molecules are added to the substrate to investigate how the pre-formed clusters interact with diffusing atoms/molecules. Au is deposited using a commercial high temperature effusion cell from Createc. C₆₀ molecules are sublimed from a homemade sublimation source. With a continuous flow of liquid nitrogen, the sample can reach to 100 K. The temperature of the sample can be raised in a controlled way using a small integrated heater. The temperature of the sample is measured using a silicon diode. Giving a pre-set temperature, the power of the heater can be programmed to reach the pre-set temperature with certain heating rate. The temperature of the sample can be controlled with an accuracy much better than 1 K. The deposition fluxes of C₆₀ and Au have been calibrated by depositing for a fixed amount of time and then counting the number of molecules/atoms in a specified area from STM images. The amount of material deposited is measured with an accuracy better than 0.01 monolayer (ML).

3. Results and discussion

The clean Au(111) surface is reconstructed with its typical herringbone pattern and regularly spaced elbow sites¹⁶. The surface is divided into alternating fcc and hcp stacked domains by the discommensuration lines (DLs). The systematic bending of the DLs creates the bulged and pinched elbows as shown in Figure 1a. Figure 1b shows the formation of $(C_{60})_m-(Au)_n$ clusters at the elbow sites on the Au(111) substrate after deposition of 0.09 monolayer (ML) of Au and 0.2 ML of C_{60} at 115 K, followed by annealing to RT. The post deposition annealing to RT is a necessary procedure to allow surface diffusion of Au atoms and C_{60} molecules and hence the formation of magic number $(C_{60})_m-(Au)_n$ clusters¹². There are a number of large Au islands having their edges decorated by C_{60} molecules, but without any molecules sitting on top of the islands. These islands with step edges decorated by C_{60} molecules are called open clusters. The open clusters are not magic number clusters because the number of C_{60} molecules in each cluster does not have to be a specific value. Many clusters consist of close-packed C_{60} molecules and have regular shapes. These clusters are called compact clusters. The compact cluster consists of a core of “bright” C_{60} molecules and a “shell” of “dim” molecules. The “bright” molecules are taller than the “dim” molecule by ~ 0.23 nm and this is because they sit on a single-atomic-layer-high Au¹². Structural models of the $(C_{60})_m-(Au)_n$ clusters can be found in Ref. [12]. Although most of the elbow sites were initially populated by a Au/ C_{60} mixture at 115 K, the post annealing process leads to ripening. As a result, a significant number of empty elbows have been created due to the migration of some clusters to join other clusters at neighbouring elbow sites¹⁷. The sample with preformed $(C_{60})_m-(Au)_n$ clusters, Fig. 1b, is then cooled down to 125 K and a further deposition of 0.03 ML Au atoms was performed. Figure 1c shows an STM image acquired soon after at 125 K. In this image, we can easily identify features formed due to the newly deposited 0.03 ML of Au. The features highlighted with white circles represent Au islands formed at elbow sites that were free from either Au or C_{60} . The formation of Au clusters at the elbow sites is similar to what is found in the growth of metal islands on Au(111) in general¹⁸⁻²³. The Au islands are, however, much less stable than other metallic islands and disintegrate well before RT is reached if they are not protected by C_{60} .

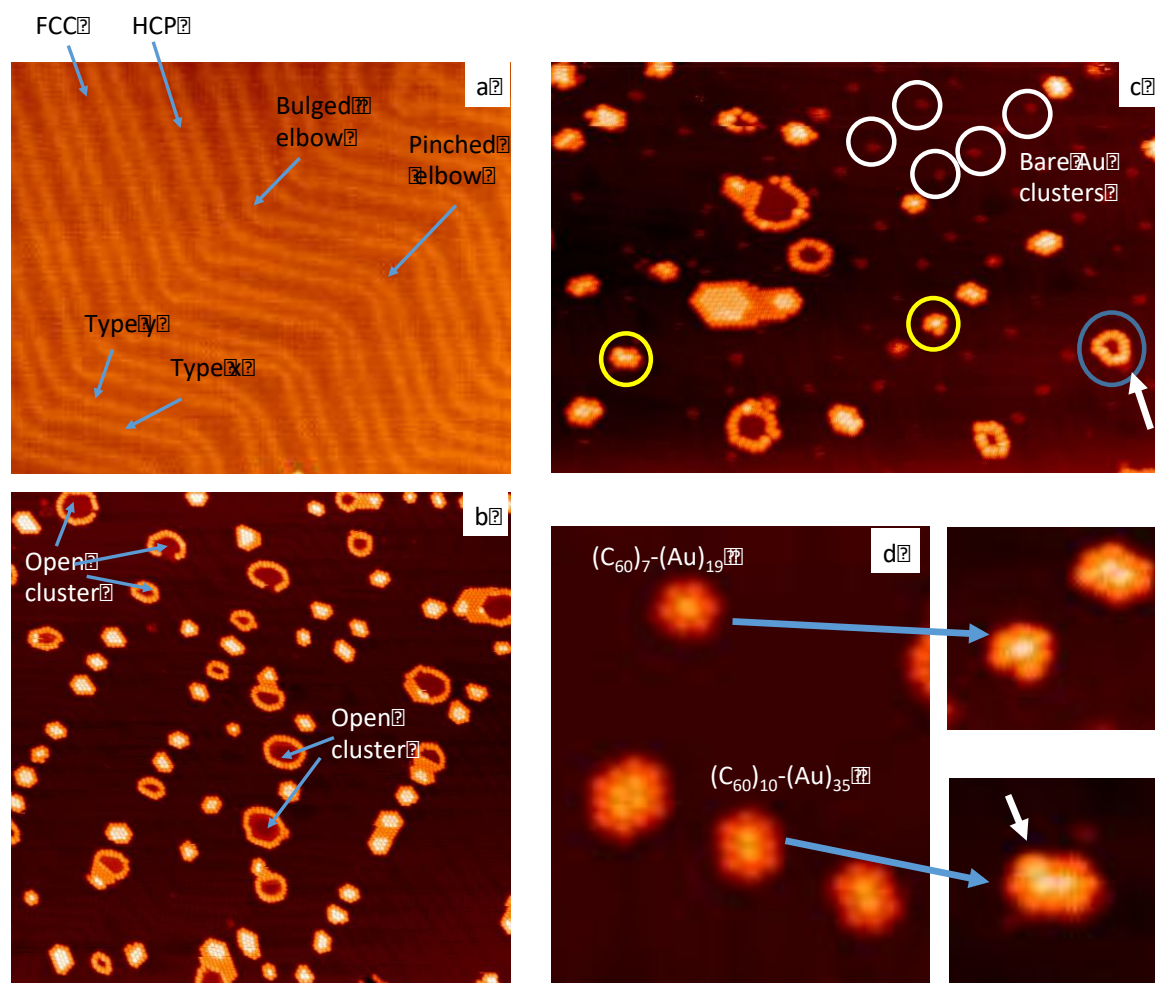


Figure 1. (a) The clean Au(111) substrate with its typical herringbone reconstruction. Type x and type y discommensuration lines divide the surface into alternating FCC and HCP stacked domains. (b) Two-dimensional C_{60}/Au clusters formed at the elbow sites following the deposition of 0.09 ML Au and 0.2 ML C_{60} at 115 K. The image, 122 nm x 122 nm, is acquired at RT with $V = -1.93$ V and $I = 0.05$ nA. (c) The Au(111) sample with preformed C_{60}/Au clusters as shown in (b) receives a further 0.03 ML Au at 125 K. The image, 100 nm x 61 nm is obtained using $V = -1.97$ V and $I = 0.05$ nA. A significant number of newly formed Au clusters are observed. Many of the pre-formed C_{60}/Au clusters have captured Au atoms and changed their appearances. (d) Examples showing how magic number C_{60}/Au clusters are transformed after capturing Au atoms.

A fraction of the 0.03 ML Au atoms is consumed to form the bare Au clusters. The rest is found to have joined the pre-formed C_{60}/Au clusters. For example, the open cluster marked with a blue circle has a small Au island attached to its side. A white arrow is there to help the reader to see this Au island. In this case, the Au island is formed and attached to the open cluster without grossly altering the structure of the open cluster. The STM image in Fig. 1c also demonstrates evidence of compact clusters changing their structure after capturing Au atoms. Two such clusters are marked with yellow circles. Figure 1d further

clarifies such structural changes. It can be seen that a $(C_{60})_7-(Au)_{19}$ compact cluster has opened up after capturing Au atoms. A $(C_{60})_{10}-(Au)_{35}$ cluster, initially with two bright molecules has changed into a cluster with three bright molecules as a direct consequence of the expansion of the Au core below the molecules. The white arrow in Fig. 1d points to the C_{60} molecule that has switched from dim to bright. The two examples of cluster change can be understood as a result of extra Au atoms being added to the Au core of the magic number cluster. For the $(C_{60})_{10}-(Au)_{35}$ cluster, the Au core has expanded sufficiently to support three molecules directly above. For the $(C_{60})_7-(Au)_{19}$ cluster, the expansion of the Au has created a visible gap between two neighbouring molecules. The Au_{19} core is almost the perfect size to accommodate 7 C_{60} molecules. By placing each molecule next to the edge of the Au_{19} hexagon, the distance between adjacent molecules is kept at ~ 1.0 nm which is the ideal nearest neighbour distance in C_{60} crystal. When Au atoms are added to the Au_{19} core, the core expands in lateral directions without changing its height and this pushes one or more C_{60} molecules sideways. This forces the C_{60} molecules to move away from the preferred close-packing arrangement. Therefore, the first sign that the Au_{19} core has captured Au atoms is the appearance of a gap between two neighboring C_{60} molecules.

From the STM images in Fig. 1, we can conclude that Au atoms deposited onto Au(111) at 125 K are able to join the Au core of an existing cluster. This is either due to Au atoms directly moving through the gaps between C_{60} molecules, or the formation of small Au clusters next to the $(C_{60})_m-(Au)_n$ cluster followed by out diffusion of C_{60} molecules. In the following, we describe further changes to the compact clusters as the temperature is raised. The STM images in Fig. 2 are taken from a small area containing three C_{60}/Au clusters. Cluster 1 and 2 has seven C_{60} molecules each. They are derived from the $(C_{60})_7-(Au)_{19}$ magic number cluster. Cluster 3 has ten molecules, hence it came from a $(C_{60})_{10}-(Au)_{35}$ cluster. All three clusters have captured Au atoms resulting in an enlarged Au core. The enlargement of the Au core has a strong effect on the bright molecules by reducing their coordination number. As a result, the bright molecules become mobile and eventually jump down the Au core. For cluster 1 or 2, the single bright molecule jumps down when temperature reaches ~ 195 K. For cluster 3, the two bright molecules eventually jump down the Au core at 257 K. At 257 K, all three clusters have taken a similar configuration with a Au core and C_{60} molecules decorating the step edges of the core. No C_{60} molecule leaves the cluster at this stage.

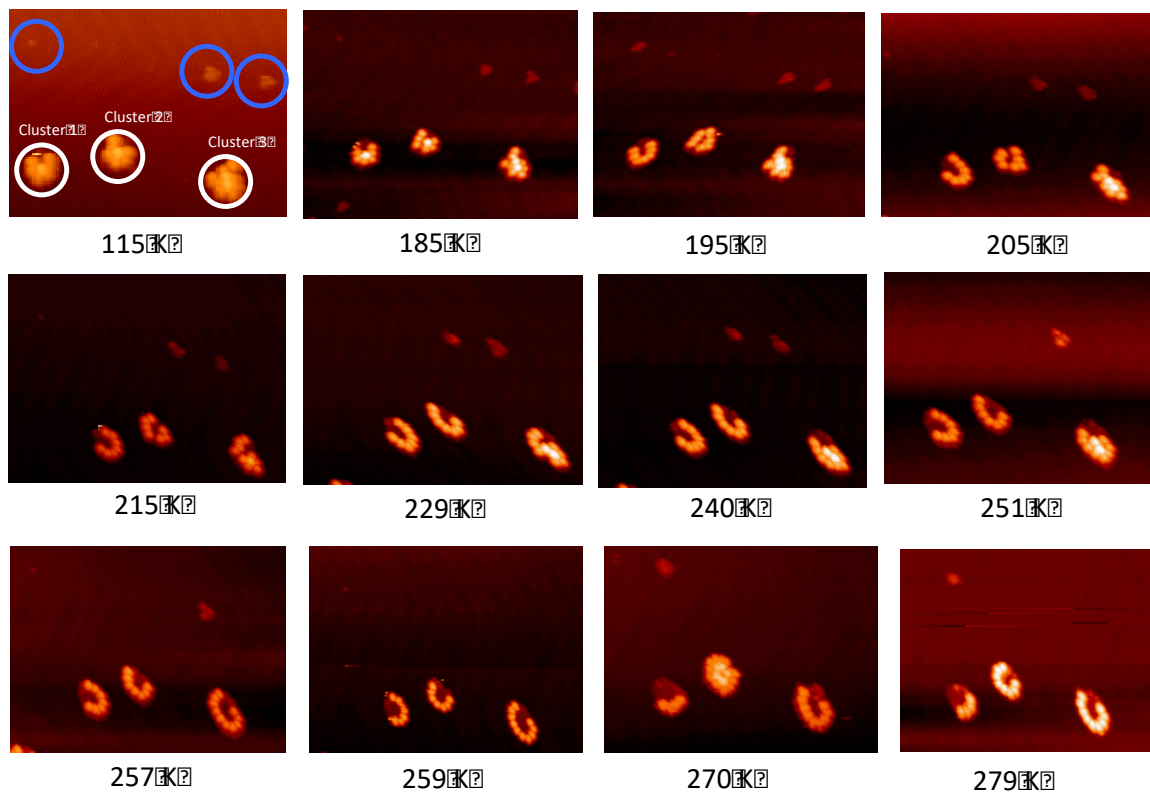


Figure 2. Structural changes of C_{60}/Au clusters as temperature increase from 115 K to 279 K. In the top-left image, the three features marked with blue circles are bare Au clusters with no C_{60} molecule attached. The three features marked by white circles are C_{60}/Au clusters. Cluster 1 and 2 has seven C_{60} molecules each. Cluster 3 has 10 C_{60} molecules. All these three clusters are derived from magic number clusters.

When the temperature is increased to 259 K, the three bare Au clusters, inside the blue circles in the top left image of Fig. 2, have all disappeared. This is consistent with earlier studies that bare Au clusters are not thermally stable beyond ~ 250 K¹². The feature near the top left corner in images at 270 K and 279 K is a transient feature that comes and goes randomly due to diffusing molecules/atoms. Figure 3 shows how the area of the Au core increases based on the measurements taken from clusters 1 and 2. The size of the Au core of both clusters is initially the same. This is understandable since they both start as $(C_{60})_7-(Au)_{19}$. Ideally, we would plot the number of Au atoms as a function of temperature. However, counting the atoms is not possible here. In order to minimise the influence from the STM tip and make sure what we observe is mainly a thermal process, we needed to use very low tunnel current (< 50 pA) and relatively high bias voltage (~ 2 V). These tunnelling parameters allow the C_{60} molecules to be sufficiently resolved, but are not the parameters that one would use to resolve the Au atoms. The area of the Au island is digitally calculated

using the C_{60} - C_{60} separation as a distance standard. Since the Au island is far from circular in shape, we cannot just measure its radius. Instead, we use the number of pixels to evaluate the area. This method is reasonable accurate but has uncertainties. For example, clusters 1 and 2 are the same size to start with, but the measured areas for the two Au cores are different as shown in Fig. 3. What is significant of the plot in Fig. 3 is the general trend of increasing area of the Au core when temperature increases from 190 K to ~ 270 K, and there is no further increase beyond 270 K.

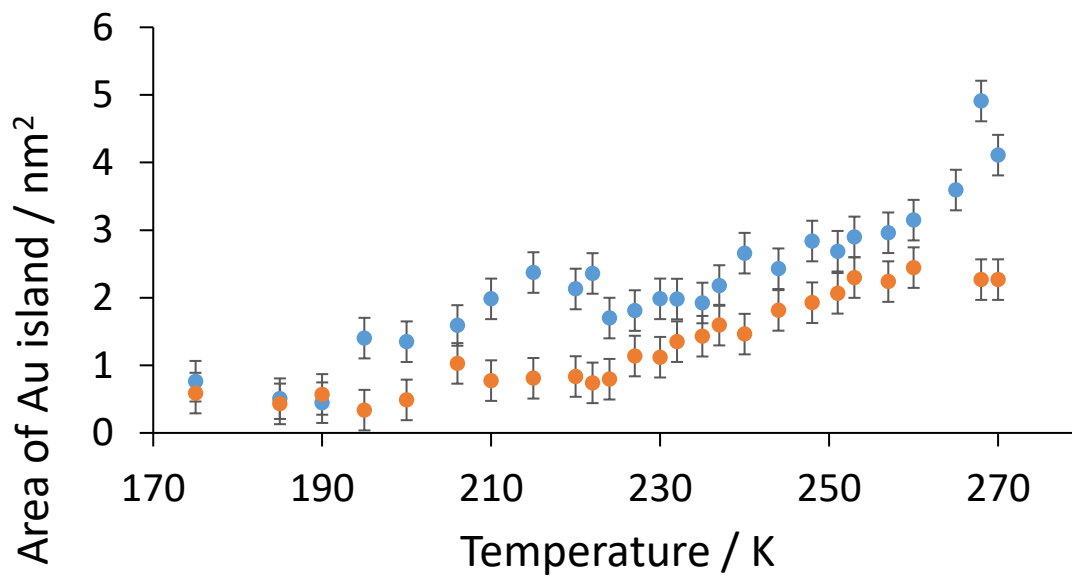


Figure 3. The area of the Au core as a function of temperature. Data shown are based on measurement of two clusters starting with the same core size of 19 Au atoms.

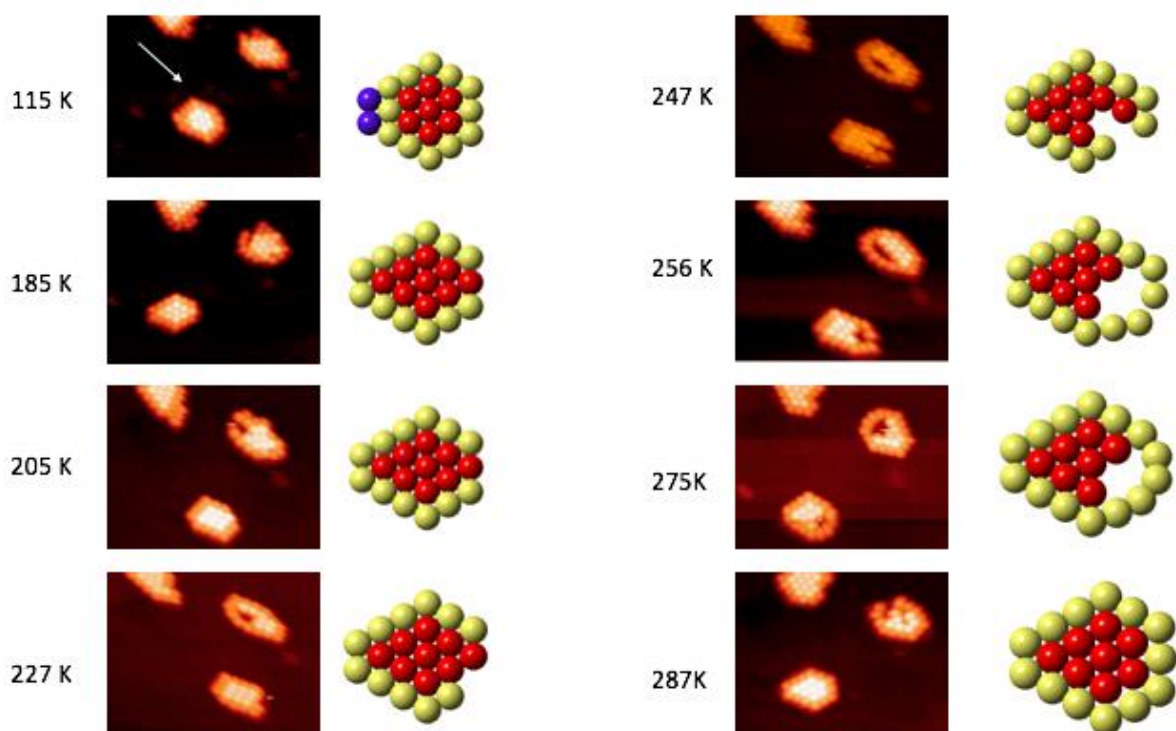


Figure 4. Transformation from one compact cluster to another by capturing Au atoms. The cluster, pointed at by a white arrow, has 21 C_{60} molecules at 115 K. The Au core at 115 K is big enough to support 7 C_{60} molecules. As temperature increases, the Au core increases in size. At 287 K, a typical magic number cluster is formed with 8 C_{60} molecules sitting on top of the Au core and 13 molecules decorating the step edges. Ball model for the cluster at each temperature is shown on right hand side of the corresponding STM image. The yellow spheres correspond to molecules decorating the step edges, red spheres are molecules sitting above the Au core.

Fig. 2 demonstrates the transformation from compact clusters to open clusters due to the addition of extra gold atoms to the Au core. This type of transformation is rather common for small C_{60}/Au clusters. For larger sized C_{60}/Au clusters, there are several bright molecules sitting on top of the Au core. The interaction of these bright molecules presents a higher energy barrier preventing them from jumping down the Au core. As a result, such a large C_{60}/Au cluster can transform from one compact cluster to another as shown in Figure 4. In Fig. 4, we follow a specific cluster, pointed by a white arrow in the image at 115 K. Initially, this cluster has seven bright molecules sitting on a Au core and twelve molecules decorating the edges of the Au core. There are extra two molecules, represented by the two blue spheres in the structural model, attached to the shell of the twelve molecules. As temperature increases gradually to 287 K, we observe a series of changes due to the addition of Au atoms to this cluster. The final product at 287 K is a compact cluster with eight bright molecules and thirteen molecules decorating the step edges of the Au core. From beginning to end, the total number of C_{60} molecules remains the same. However, the

Au core has gone through a process of capturing and releasing Au atoms. The cluster seen at 287 K has the typical structure of a stable compact cluster: All C_{60} molecules in a close-packed form with a single row of C_{60} molecules lining the step edges of the Au core and no molecules attached to the C_{60} shell from the outside.

We have shown above that when Au atoms are added to Au(111) in the presence of magic number $(C_{60})_m-(Au)_n$ clusters, the clusters go through structural transformations due to the incorporation of Au atoms. In the following, we describe how C_{60} molecules interact with magic number $(C_{60})_m-(Au)_n$ clusters on Au(111). We start with a sample which has already $(C_{60})_m-(Au)_n$ clusters formed, see Fig. 1b. We then deposit 0.07 ML of C_{60} molecules onto the sample at 115 K. Figure 5a is an STM image taken after the C_{60} deposition. It can be seen that nearly all pre-formed clusters, no matter they are compact or open, have captured extra C_{60} molecules. An open (ring) cluster shown in Fig. 5b has captured an extra of 7 molecules. Five of them are attached to the ring from outside and the remaining two sit above the Au core. Fig. 5c shows an $(C_{60})_{10}-(Au)_{35}$ cluster after it has captured three molecules. For this cluster, the Au core was already covered by two C_{60} molecules, so the extra molecules can only be attached to the pre-existing cluster from the outside. There are also a number of isolated C_{60} molecules as highlighted in Fig. 5d. When the sample is warmed up towards RT, the “captured” molecules tend to be evaporated off the cluster because these molecules are less strongly bound to the rest of the cluster. Most clusters lose their extra molecules before temperature reaches 270 K. Therefore, clusters will resume their initial configuration once the extra molecules are evaporated off at RT. This is in contrast to the role of Au atoms, described earlier, that can change the clusters irreversibly.

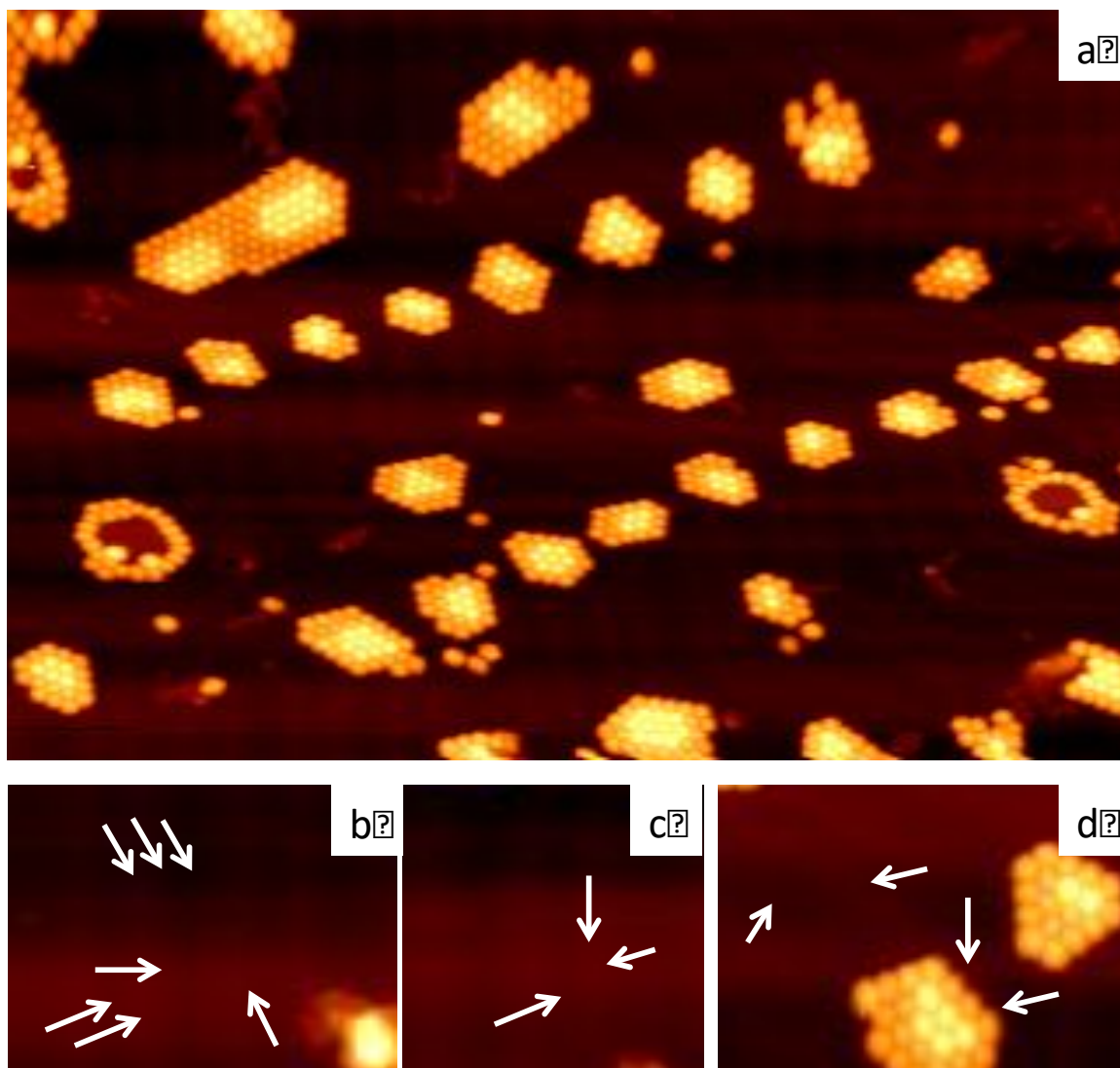


Figure 5. Interaction of C_{60} molecules with pre-formed C_{60}/Au clusters on $Au(111)$. (a) STM image acquired after 0.07 ML of C_{60} is added at 115 K. (b) Arrows point to the captured molecules by an open cluster. (c) A magic number, $(C_{60})_{10}-(Au)_{35}$, cluster with three extra molecules attached. (d) Isolated C_{60} molecules not attached to any pre-formed cluster.

Conclusion

We have investigated the stability of the Au/C_{60} clusters supported on $Au(111)$ when Au atoms or C_{60} molecules are added. Au atoms are able to merge with the Au core of the cluster and irreversibly change the cluster configuration. The change is a direct result of the enlargement of the Au core and it causes compact clusters to open up. C_{60} molecules are able to attach to existing clusters by interacting with C_{60} molecules within the shell of the

cluster. This attachment is reversible. The captured molecules become detached from the cluster once temperature reaches around 270 K. The findings from this study provide useful information for refining the Au/C₆₀ hybrid clusters with a view to more accurate size and shape selection. The Au/C₆₀ hybrid clusters represent a system which is assembled completely via non-specific interactions. The lack of specific bonding such as hydrogen bonding or metal-organic coordination makes such clusters flexible to changes.

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