Self-defined transition states in hybrid C70-Au clusters by the scanning tunnelling microscope tip
Kaya, Dogan; Wang, Yitao; Akyol, Mustafa; Karadag, Faruk; Ekicibil, Ahmet; Guo, Quanmin

DOI:
10.1021/acs.jpcc.9b08293

License:
Other (please specify with Rights Statement)

Document Version
Peer reviewed version

Citation for published version (Harvard):

Link to publication on Research at Birmingham portal

Publisher Rights Statement:
This document is the Accepted Manuscript version of a Published Work that appeared in final form in Journal of Physical Chemistry C, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see: https://doi.org/10.1021/acs.jpcc.9b08293

General rights
Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

• Users may freely distribute the URL that is used to identify this publication.
• Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
• Users may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
• Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Download date: 18. Apr. 2021
Abstract: Manipulation of C$_{70}$-Au hybrid nanoclusters was investigated using a scanning tunneling microscope (STM) tip. We demonstrate that removing a selected C$_{70}$ molecule from the cluster by STM-tip resulted in an intermediate transition state without thermal decomposition. The molecule rotates and diffuses around the cluster and leaves the cluster without taking an additional molecule and Au atoms due to the rather weak interaction between molecules and the surface atoms. After removing C$_{70}$ molecule, the van der Waals interaction among C$_{70}$ molecules squeeze the cluster components and move out the Au atoms in the island. This self-transition-state is due to a weak charge transfer between the molecules and the surface. The extraction of the molecules in a ring cluster resulted in polygonal Au island formation in a major surface direction of Au(111). This preferential state for Au atoms after manipulation is staying on the surface because of a strong charge transfer with the surface atoms and thermal energy of the surface rather than C$_{70}$ molecules.
Introduction

When the physical dimensions of materials are reduced to the nanometer scale, new electronic, optical, or chemical properties can emerge [1]. Controlling the structure and fine tuning the properties of nanoscale materials require precise techniques [2]. Scanning probe microscopes (SPM), such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM), are a family of versatile tools not only for atomic scale imaging, but also for material processing via atom manipulation [3-14]. Although these techniques are relatively slow and often needing cryogenic temperatures, recent scan speed improvement and multi-tip configurations significantly increase the speed of manipulation. The manipulations in the scanning tunneling microscope (STM) can be performed in many modes depending what is the fundamental force involved in manipulation as well as how atoms are transferred. Manipulation of atoms, molecules, clusters or nanoparticles by STM is always in direct competition with thermal processes and for this reason manipulation is usually performed at cryogenic temperatures. It is not straight forward to separate cleanly thermally excited processes from STM manipulation.

When atoms/molecules are deposited on solid surfaces, a number of events can occur including diffusion, nucleation, and island growth. These events depend on the surface temperature, structure, and adsorbate coverage. Under suitable conditions, magic number clusters can form [15, 16] via atomic close-packing, charge transfer, or van der Waals interactions [1, 17-20]. The investigation and manipulation of \((C_{70})_{m}Au_{n}\) magic number clusters on the Au(111) surface have been extensively studied in our lab [7, 8, 18]. For the \((C_{70})_{m}Au_{n}\) magic number cluster, only certain number of Au atoms \((n)\) and \(C_{60}\) molecules \((m)\) are allowed in the stable cluster. The cohesive energy of the \((C_{70})_{m}Au_{n}\) cluster derives mainly from the charge transfer from gold to the \(C_{70}\) molecule and the van der Waals interaction among the \(C_{70}\) molecules. There is also the contribution of metallic bonding between Au atoms. In previous investigations, we modified \((C_{60})_{m}Au_{n}\) clusters using the STM tip at both RT [8] and 110 K [7]. We were able to downsize the cluster using cascade manipulation in a controlled manner at RT. Here, we extend our study to the \((C_{70})_{m}Au_{n}\) clusters that have been successfully fabricated on Au(111) [21]. We manipulated the \((C_{70})_{m}Au_{n}\) cluster using the STM tip at RT and found metastable transition states for the cluster.

Experimental Methods
We use a (111) oriented gold film as the sample which is prepared in a BOC Edward 306 evaporator with a base pressure of $10^{-7}$ mbar via depositing Au onto preheated highly oriented pyrolytic graphite (HOPG) substrate at 493 K. The thickness of the Au film is estimated to be ~300 nm using a quartz-crystal thicknesses monitor close to the sample holder. The Au film is then transferred into an ultra-high vacuum (UHV) Omicron VT-STM chamber and Ar+ ion bombardment and thermal annealing, up to 1000 K, cycles are performed to provide a large flat herringbone reconstructed Au(111) surface. An electrochemically etched W tip is used for imaging and manipulation of $(C_{70})_{n_m}-(Au)_n$ clusters after annealing in-situ up to 550 K. Hybrid $(C_{70})_{m_n}-(Au)_n$ clusters are produced via simultaneous deposition of 0.04 monolayer (ML) of $C_{70}$ molecules and ~0.04 ML of Au atoms onto the Au(111) surface which is kept at 110 K. At this temperature, both the $C_{70}$ molecules and the Au atoms diffuse on the surface and terminate either at the step edges or form irregular $C_{70}$-Au mixture at the elbow sites on the herringbone reconstructed Au(111) surface. Upon annealing to room temperature, the irregular $C_{70}$-Au mixture transforms into the hybrid $(C_{70})_{m_n}$-Au$_n$ clusters at the elbow site. Manipulation is conducted at RT.

Results and Discussion

All manipulation experiments were performed as follows [7, 8]. First, a selected area with cluster or island is scanned with -1.8 V sample bias voltage and 50 pA tunneling current. These tunnelling parameters are used for passive scanning because they do not cause any changes to the sample [22]. Then the STM tip is located above a preselected $C_{70}$ molecule and driven towards the molecule for 1.25 nm over 12.8 ms which results in a mechanical interaction between the tip and the target molecule. The tip is then withdrawn to its initial height. During manipulation, the tunneling current is recorded as a function of the tip-surface distance for each experiment. After the manipulation event, we scan the area in order to find if the manipulation is successful or not. Figure 1 shows the extraction of a single $C_{70}$ molecule from a compact $C_{70}$ island. The successful manipulation accomplished at the tip-sample distance of 1.25 nm which is quite similar to the manipulation of the $C_{60}$ molecule in a $C_{60}$-Au cluster [7, 8]. Figure 1 (A) is an STM image acquired just before the manipulation events and a single molecular vacancy can be seen in the middle of the molecular patch. In Figure 1 (B), the green dots indicate the locations where manipulation is performed. Two separate manipulation events, M1 and M2, take place. After each manipulation, the tip resumes to its normal scanning mode. Two new vacancies are created. The
one created by M1 stays in the location where it is created. The one created by M2 quickly diffuses away to the left edge of the C\textsubscript{70} island. The pre-existing vacancy has also moved, Figure 1 (C).

There are two possible orientations of the C\textsubscript{70} molecule on the Au(111) surface due to its unique rugby ball shape: the molecule can have its long or short molecular axis perpendicular to the substrate. At RT, the C\textsubscript{70} molecules are able to rotate around both the long and short axis in the close-packed C\textsubscript{70} layer at [23]. Therefore, the molecule does not take a fixed orientation at RT. The C\textsubscript{70} island has well-defined edges parallel to the principal crystallographic directions of the Au(111) surface, such as [11\bar{2}], [0\bar{1}1], and [\bar{1}1\bar{0}] directions [24].

Figure 1: Manipulation of individual C\textsubscript{70} molecules in a C\textsubscript{70} island. A. Before manipulation. B. During manipulation images on selected points (green dots). C. After manipulation image shows the created and recovered C\textsubscript{70} vacancy on the island.

Manipulation experiments conducted on the close-packed C\textsubscript{70} layers allow us to find the optimal operating conditions. For example, the probability of successfully extracting a C\textsubscript{70} molecule depends strongly on the distance the tip travels towards the molecule. Once we have identified the optimal operating conditions, we begin to manipulate (C\textsubscript{70})\textsubscript{m}-\textsubscript{(Au)}\textsubscript{n} clusters. Similar to the formation of (C\textsubscript{60})\textsubscript{m}-\textsubscript{(Au)}\textsubscript{n} clusters [18], we find the following magic number clusters with C\textsubscript{70}: (C\textsubscript{70})\textsubscript{7}-\textsubscript{(Au)}\textsubscript{19}, (C\textsubscript{70})\textsubscript{10}-\textsubscript{(Au)}\textsubscript{35}, (C\textsubscript{70})\textsubscript{12}-\textsubscript{(Au)}\textsubscript{49}, (C\textsubscript{70})\textsubscript{13}-\textsubscript{(Au)}\textsubscript{51}, (C\textsubscript{70})\textsubscript{14}-\textsubscript{(Au)}\textsubscript{63}. Figure 2 shows the manipulation of a (C\textsubscript{70})\textsubscript{7}-\textsubscript{(Au)}\textsubscript{19} cluster. The C\textsubscript{70} molecule in the middle of the cluster sits on a 2D hexagonal Au\textsubscript{19} island. Therefore, orange and bright orange colors in the images represent lower and higher positions of C\textsubscript{70} molecules. The three STM images are acquired before (A), during (B), and after (C) the manipulation which is performed at the location marked by a green dot in Figure 2 (B). The manipulation has
extracted a single C\textsubscript{70} molecule from the cluster. The remaining six molecules stay together. We do not know if Au atoms have left the cluster or how many have left. Since there is still a raised C\textsubscript{70} molecule, we came to the conclusion that most of Au atoms remain part of the cluster. In Figure 2 (C), we use the notation \((\text{C}\textsubscript{70})\text{c}-(\text{Au})\text{19}\) to show that there are six molecules left, although the number of Au atoms may be rather different from 19. The illustration of the cluster schematics are presented with before, during and after model in Figure 2 (D, E, and F), respectively. The schematic images show the cluster configuration with a ball model where the yellow balls show the Au island which is surrounded 6 C\textsubscript{70} molecules and one on top of it and blue balls are the surface adatoms.

![Figure 2](image_url)

Figure 2: STM images demonstrate a single C\textsubscript{70} manipulation by the driving STM tip in the hybrid \((\text{C}\textsubscript{70})\text{c}-(\text{Au})\text{19}\) cluster at room temperature. A, B and C are before, during, and after manipulation images, respectively. B. The manipulation performed on a selected C\textsubscript{70} molecule indicated with a green dot. C. \((\text{C}\textsubscript{70})\text{c}-(\text{Au})\text{19}\) cluster obtained after manipulation. D, E, and F are the schematics diagram of the cluster and the manipulation processes with before, during and after manipulation, respectively. Yellow and blue balls represent Au island and the surface adatoms, respectively.
Figure 3 shows a series of STM images before and after the manipulation on a \((C_{70})_{13}-(Au)_{51}\) cluster. The \((C_{70})_{13}-(Au)_{51}\) cluster shown in Figure 3(C) has three raised (bright) \(C_{70}\) molecules. Each of the raised molecule sits on a hexagonal Au island. There are three edge-sharing Au islands in a row with a total number of 51 Au atoms. The manipulation performed by positioning the tip above the center molecule (indicated with green dot) and then the tip lowered to the molecule for mechanical interaction. As can be seen in Figure 3(C), the cluster has transformed into a new shape without loosing \(C_{70}\) molecules. The arrangement of the cluster changes without changing total number of \(C_{70}\) molecules and Au atoms. It seems that the linear row of the three Au hexagonal islands has changed into a V-shaped row. A second manipulation event, Figure 3(E), has caused further changes to the cluster. The three raised \(C_{70}\) molecules have become close-packed, Figure 3(F). This suggests that the three hexagonal Au islands have fused together so that each hexagon shares two edges with other two hexagons. This is similar to the \((C_{60})_{12}-(Au)_{49}\) cluster. Since only 49 gold atoms to require for such a three-hexagon configuration, there are thus two redundant gold atoms. The redundant Au atoms can escape the cluster altogether. However, based on the STM image in Figure 3(F), the two redundant Au atoms seem to be attached to one edge of a hexagon. The number of molecules has dropped to 12. A third manipulation, Figure 3(H), has caused the cluster to loose another molecule. Since all the molecules in the cluster have become close-packed with no gaps, the gold core now has 49 atoms. The further manipulation achieved to the \((C_{70})_{7}-(Au)_{19}\) cluster (see supplementary information SupFig.1).
Figure 3: Manipulation of selected C70 molecules by one by in the (C70)_{13}-(Au)_{51} hybrid cluster by the STM tip at room temperature. A, B and C show removing a single C70 molecule (indicated with a green dot) result in a metastable form similar to (C70)_{14}-1-(Au)_{63} cluster with a missing C70 molecule. D, E, and F. Continues manipulation led to form (C70)_{12}-(Au)_{69} cluster. H, I and J. Manipulation (C70)_{12}-1-(Au)_{69} cluster to (C70)_{12}-1-(Au)_{69} cluster. Following the cluster further, scale down to (C70)_{7}-(Au)_{19} hybrid cluster (see supplementary information SupFig.1). Inset images show the atomic configuration of the cluster before (A) and after (D, G, I) manipulation.
Figure 4: Tip-triggered manipulation of \((C_{70})_{14}-(Au)_{63}\) cluster further down to \((C_{70})_{10-1}-(Au)_{35-49}\) cluster. A. STM image before manipulation and B-F. After manipulation images (see all images in supplementary information SupFig.2.)

Figure 4 demonstrates that another type of transition states occurs via the manipulation of \((C_{70})_{14}-(Au)_{63}\) cluster (see supplementary information SupFig.2 with before, during and after images). We were able to delicately trim \((C_{70})_{14}-(Au)_{63}\) cluster into a smaller cluster, the outcome was the \((C_{70})_{10-1}-(Au)_{35-49}\) cluster in this experiment. It can be seen from after images there is no cascade downsizing from one stable cluster to another. There is a high probability that the multiple phases of the hybrid cluster can be seen between two stable clusters, such as reshape, transition or interstate. The molecule on the top of the cluster also may diffuse on Au island and move to the cluster edge and fill the empty position of the frame without affecting the Au island shape. This is quite similar to tip-triggered \(C_{60}\) manipulation in \((C_{60})_{n}-(Au)_{n}\) at room temperature [8].

It is well known that individual/2D Au islands are not stable on the Au(111) terraces and they move to step edges via atomic diffusion above 240 K [25]. The stability of the 2D Au islands can be dramatically increased if the edges of the Au islands are decorated by \(C_{60}\) or \(C_{70}\) molecules. In the following, we describe the changes to 2D
Au islands when we remove C\textsubscript{70} molecules from the step edges with the STM tip in Figure 5. In Figure 5 (A), there is Au island with its edges partially covered by 13 C\textsubscript{70} molecules. The sequence of STM images of the ring cluster downsized by removing C\textsubscript{70} molecules one at a time until there are just 5 molecules left. During manipulation, the island shape is disturbed each time and the island eventually formed a polygonal shape (A, B and C) with a direction of [1\overline{1}0], [11\overline{2}], and [011], respectively. If all the molecules are removed from the cluster, the 2D Au island would not be stable. The Au island becomes stable when there are C\textsubscript{70} molecules attached to the edges. It is not necessary to cover all the edges with the molecule. The island size can be defined with the number of C\textsubscript{70} molecules. When we remove a molecule Au atoms in the islands do not leave the cluster. The fixed number of Au atoms in the cluster can have different geometry with similar energy value to increase the cluster components interaction [21]. The sudden change of C\textsubscript{70} molecules orientation can be led to a new geometry without losing Au atoms.
Figure 5: Manipulation of individual C\textsubscript{70} molecules around an open ring cluster. Removing a C\textsubscript{70} molecules from (C\textsubscript{70})\textsubscript{13}-(Au) cluster individually to (C\textsubscript{70})\textsubscript{5}-(Au) cluster led to polygonal Au island appear with A, B, C directions refer [\textsubscript{110}], [\textsubscript{112}], and [\textsubscript{011}], respectively (see all images in supplementary information SupFig3).

A successful tip-induced manipulation event can be revealed via imaging half of the molecule and immediate change in the cluster. Although C\textsubscript{70} displacement hard to determine, it usually undergoes rotation and removal from the cluster by the thermal energy of the surface [16]. We observed that once the cluster frame is broken via
the tip displacement on a selected molecule, it diffuses on the surface and attach a cluster, the step edges or stay around the cluster. The interaction among C\(_{70}\) molecules is the van der Waals interaction which is also responsible for the molecular displacement. Therefore, the right after manipulation the cluster can reshape or transform another cluster with an exact number of C\(_{70}\) molecules and Au atoms. Further removing C\(_{70}\) molecules result in inevitable Au atoms leave due to squeezing cluster components due to van der Waals force [19] so transformation or intermediate transition state may occur. This is an irreversible change and the new geometry of the cluster can be defined by the thermal energy of the surface or C\(_{70}\) orientations.

The experimental study and theoretical calculation showed that removing a selected C\(_{60}\) molecule from (C\(_{60}\))\(_m\)-(Au)\(_n\) clusters resulted in a transformation which formed a down-sized the magic number clusters. Creating a vacancy in the cluster by STM-tip impact accumulate strain energy of the cluster and cause a release and diffusion of the C\(_{60}\) along with Au atoms in the cluster [7, 8]. This was due to the surface thermal energy and the minimum energy required holding the cluster components. The van der Waals interactions between C\(_{60}\) molecules relatively strong which led to bringing molecules closer so squeeze the island and transformed the cluster to one size smaller stable magic number cluster. Addressing the possible mechanisms underlying stability of the C\(_{70}\)-Au cluster is similar to C\(_{60}\)-Au clusters [7, 8, 18]. They are the molecule-molecule close-packing, the molecule-surface adatom, and molecule-2D Au island interactions. Although similar formations between C\(_{70}\)-Au and C\(_{60}\)-Au, the intermolecular differences play an important role in the cluster stability due to the rather weak interaction of Au(111) surface to C\(_{70}\) [23]. To obtain a close-packed arrangement with C\(_{70}\) molecules, the van der Waals force plays a significant role in the cluster stability [19]. Besides, the molecule on the top of the Au island contributes extra stability by interacting with all surrounding molecules as well as 2D-Au island in the cluster. Additional interaction between molecule and Au atoms enhance the cluster stability by transferring charge from the surface and 2D island Au atoms. For example, C\(_{70}\) charge transfer is 1.1 ± 0.1 electron/molecule [26] and for C\(_{60}\) 1.6 electron/molecule on the Cu(111) surface [27]. While the charge transfer from Au(111) to C\(_{60}\) is 0.8 electron/molecule [28], it is less for C\(_{70}\) which is observed experimentally [23].

Differently, for (C\(_{70}\))\(_m\)-(Au)\(_n\) clusters the interaction between C\(_{70}\) molecules and Au-C\(_{70}\) relatively weak and removing a single C\(_{70}\) does not trigger cluster size to another small stable cluster. After the tip approach and
retract the pre-selected C\textsubscript{70} molecule disappears and the number of Au atoms in the cluster usually remains constant until removal of another C\textsubscript{70} molecule from the cluster. Therefore, the cluster is either reshape or transform to the intermediate transition state until another C\textsubscript{70} removed from the cluster. Au atoms forced to leave the cluster when there is no place in the C\textsubscript{70} cluster frame here molecule/molecule interaction become dominant thus the van der Waals force. The intermediate state of the cluster is energetically more favourite for molecules due to missing C\textsubscript{70} molecule.

Our observation indicates that a simple repulsive interaction is responsible for the displacement of the C\textsubscript{70} molecule without affecting other molecules and Au atoms. The created vacancy disturbs the interaction among the molecules which preferably stay in the cluster but the cluster obtains a new form. Further C\textsubscript{70} extraction and migration away from the cluster result in losing Au atoms in the cluster so that the cluster can transform another stable cluster. When the tip does not accumulate sufficient energy on a selected molecule, the molecule may displace to a position, where less energy requires, and the cluster preserve the number of atoms/molecules but it is reshaped. The extracted molecule and atoms can be freely migrated on the surface until they are trapped by another cluster or the step edges of the (111) surface.

Conclusion

In conclusion, we used the high-resolution STM imaging/lateral manipulation method and achieved the tip-induced manipulation of a pre-selected C\textsubscript{70} molecule without affecting other molecules/atoms in the (C\textsubscript{70})\textsubscript{m}-(Au)\textsubscript{n} clusters. The results of manipulation, which is a purely mechanical origin, showed that either an intermediate transition-states between the stable hybrid clusters or a transformation of the cluster occurred at room temperature. These states have preferably occurred either a weak interaction between C\textsubscript{70} molecules and C\textsubscript{70}-Au bonding or Au atoms in the 2D island but required sufficient energy to transform the cluster. Therefore, after tip approach/retract and induce stress on a selected molecule, the molecule can be removed and the components of the cluster stay in the frame until another C\textsubscript{70} molecule moved away. We suggest that the van der Waals interaction among C\textsubscript{70} molecules squeeze the cluster components and knockout the Au atoms from the island. These intermediate transition-states are due to van der Waals interaction and charge transfer between the
molecules and the surface. So achieving tip-induced manipulation, we can directly perturb a single molecule of a cluster to modulate its geometry, thus the electronic properties of the 2D molecule/atom clusters.

Author Contributions

D. K. and Y. W. performed all the experiments. All authors contributed to data analysis and writing of the manuscript. This work was supported by Cukurova University Scientific Research Funding Grand No: FBA-2018-10813.

Notes

The authors declare no competing financial interest.

REFERENCES