STM Observation and Manipulation of Dimethyl Indolino Benzo-Nitrile (IBN) Molecules on Au <111> Surfaces

Paola Perez, 2018 CNF iREU Intern

Electrical and Computer Engineering Department, University of Texas at El Paso

REU Program: 2018 Cornell NanoScale Facility International Research Experience for Undergraduates (CNF iREU) Program at the National Institute of Material Science (NIMS), Tsukuba, Ibaraki, Japan

CNF iREU Principal Investigator & Mentor: Dr. Keisuke Sagisaka, Nanomechanics Group, Research Center for Advanced Measurement and Characterization, NIMS

Primary Source of CNF iREU Funding: National Science Foundation under Grant No. OISE-1559368

Contact: paperez5@miners.utep.edu, sagisaka.keisuke@nims.go.jp

Website: http://www.cnf.cornell.edu/cnf_2018reu.html

Abstract:

Controlling and understanding the structure and conformation change of a dimethyl indolino benzo nitrile (IBN) single molecule is key to fabricating molecular machines for future applications. A scanning tunneling microscope is used to conduct an atomic study of IBN molecules on an Au<111> surface. In this study, a scanning tunneling microscopy (STM) machine is used to image molecules in real space, give 3D profile of the surface, manipulate molecules to obtain spectroscopic data, and characterize molecular arrangements on the surface. Different alignments were observed depending on molecular coverage. Single molecules were able to be controllably moved and rotated after high-bias application. Additionally, excitation voltages of a single molecule were found at 10, 20, 40, and 80 pA currents.

Introduction:

Molecular manipulation with STM has gained greater attention since the Nobel Prize in Chemistry 2016 awarded to Jean-Pierre Sauvage, Sir J. Fraser Stoddart, and Bernard L. Feringa "for the design and synthesis of molecular machines" [1]. Molecular machines have potential applications in drug delivery, electrical sensors, actuators, energy storing devices, among others. Molecular manipulation is usually achieved by stimulants such as light, current, force, and magnetic field in solutions. We make use of tunneling current injected from an STM tip to analyze the IBN molecule that has particularly been synthesized for the study of molecular conformation manipulation on a solid surface.

Materials and Methods:

A low temperature, ultra-high vacuum STM was used to control single IBN molecules, analyze its properties in the atomic scale, and characterize molecular arrangements on a gold surface. The Au<111> surface used was cleaned through sputtering and annealing at 550°C. Then, IBN molecule was evaporated from a crucible at ~ 58°C on a room temperature substrate. STM imaging was done with a platinum-iridium alloy tip at low temperatures to reduce noise, suppress molecule diffusion, and minimize image drift. Deposition rate was controlled by temperature of the crucible and pressure in the deposition chamber. Molecular coverage was controlled by deposition time. Changing the parameters allows for different molecular motion and electronic properties.

Results and Discussion:

Figure 1 shows three STM images captured in constant-current mode. Different alignments were observed depending on molecular coverage (affected by pressure, temperature, and deposition time parameters). Figure 1(a) shows an STM image of one monolayer of IBN molecule covering the whole surface. The herringbone patterns of the gold surface are slightly visible through the molecular layer. This indicates that IBN molecules are weakly bonded to the surface. Figure 1(b) shows an STM image of 0.338 monolayers of IBN after decreasing the temperature and deposition time. The molecule showed organized line alignments and started forming clusters on the surface. Figure 1(c) shows 0.036 monolayers of IBN after decreasing the parameters even further. For this coverage, the molecule only formed clusters, mainly made of three or four single molecules. In order to understand the conformation change property of the single IBN molecule, further analysis was mainly done with low coverage deposition.

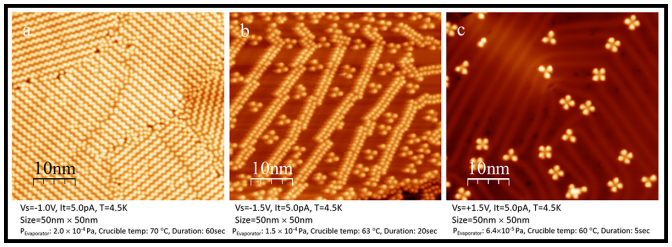

Figure 1: IBN coverages and alignments: (a) 1 monolayer, (b) 0.338 monolayer, and (c) 0.036 monolayer.

Prior to molecule manipulation, the molecule clusters were broken to separate a single IBN through the application of high bias voltages (Figure 2). After breaking the molecule clusters, a single IBN molecule was controllably isolated using tip-molecule interaction with high current for further analysis. The breaking of the clusters also helps identify molecular orientation. High bias voltage (typically 2.2 ~ 2.4 V at 5pA) was applied to the single molecule to observe that the tip height over the molecule switched between two slightly different states. We believe that this corresponds to molecular conformation changes, but the excited state (lower height state) was not successfully imaged by the STM due to instability of this state. In contrast, higher bias voltage (typically > 2.4 V at 5 pA) was able to rotate and move the single molecule across the surface as shown in Figure 3(a). Excitation voltages were found for the single molecule at different currents. This was done at 10, 20, 40, and 80 pA currents. Fig.3(b) shows that excitation voltage decreased as current increased.

Figure 4 shows the molecule's structure model and electrostatic potential map. Electrostatic calculations showed that the IBN molecule has a total neutral charge. However, it also has slight internal polarity. The slightly positive side (blue) and a slightly negative side (yellow) makes IBN a dipole. For the full coverage deposition, the molecule aligns in a conventional + - way. On the other hand, for low coverage deposition, the clusters show different, very interesting phenomena. The clusters don't follow the + - convention, but instead, have all the negative sides connected in the middle. Therefore, we hypothesize that there must be something in the middle holding the clusters together. The hypothesis is that a gold atom acts as a mediator to allow molecule clustering. This is because deposition is done in a room temperature substrate at which the IBN molecules easily diffuse over the gold surface to pick up gold atoms, possibly from step edges, and the CN functional group in the molecule tends to form strong bonds with gold. However, further testing is needed for confirmation.

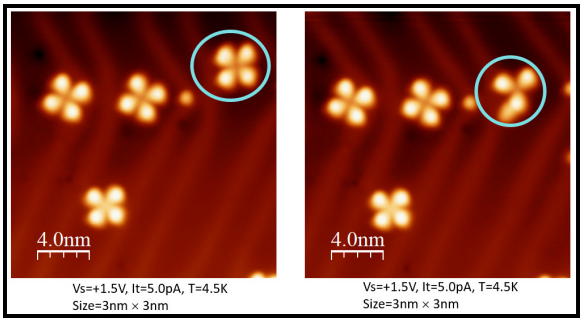

Figure 2: Effect of application of high bias voltages of molecule clusters.

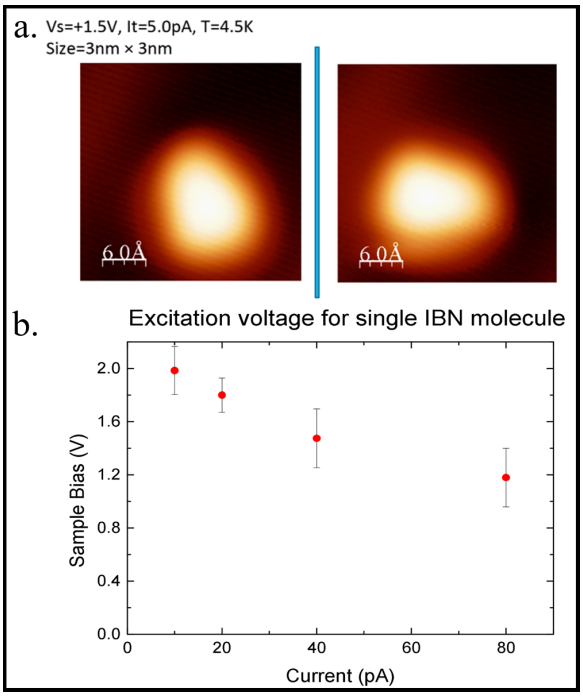

Figure 3: (a) Excitation and manipulation of single IBN molecule with high bias. (b) Excitation voltages for single IBN molecule.

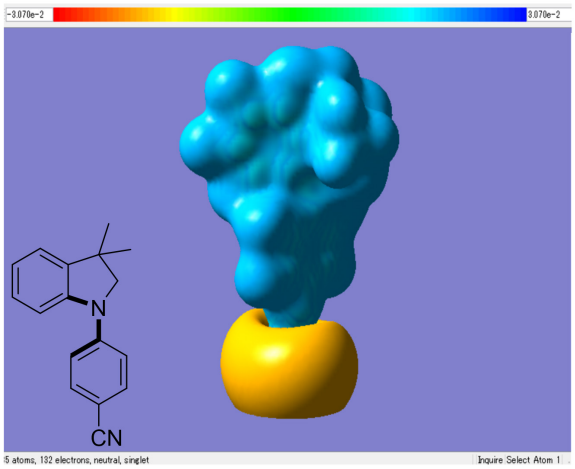

Figure 4: Electrostatic potential map.

Conclusions and Future Work:

In conclusion, the IBN molecule has different alignments depending on coverage, rotation and movement of single molecule is possible, and excitation parameters of a single molecule were found. Future studies consist of testing different molecular coverages, doing atomic force microscopy imaging with a CO tip for identification of the molecule's internal structure, and changing the surface to a different material such as silver or copper for testing with different molecule-surface interactions.

Acknowledgements:

This work was supported by the CNF iREU Program and National Science Foundation grant OISE-1559368. Special thanks to Keisuke Sagisaka, Oscar Custance, Waka Nakanishi, and Lynn Rathbun for all their assistance and guidance.

References:

[1] The Nobel Prize in Chemistry 2016, https://www.nobelprize.org/prizes/chemistry/2016/summary/