Heterogeneous Mixture of Amino Acids and Self-assembly on Metal Surfaces

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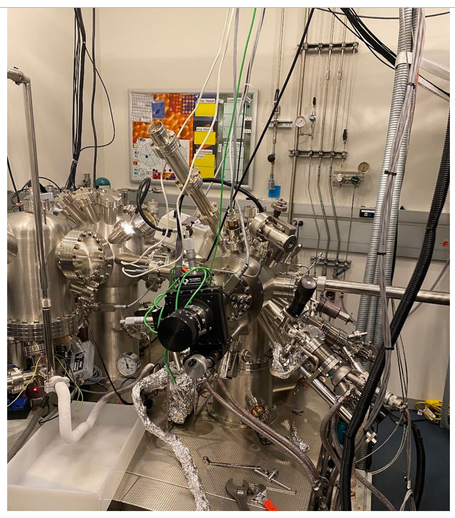
ABSTRACT

In this study, novel atomic-scale exploration of molecular self-assembly of the chiral amino acid proline and tryptophan on Cu(111) was demonstrated. This research aimed to further the knowledge and understanding about how L-proline and L-tryptophan self-assemble, noting how chirality affects their interactions. Homochiral samples of both L-tryptophan and L-proline on a Cu(111) surface were individually explored, as well as a racemic (50-50) mixture. A scanning tunneling microscope was used to map the self-assembly at a clear molecular resolution. This experiment was performed in an ultrahigh vacuum to avoid interference from outside particles. By analyzing the results, it was found that L-proline forms molecular trimers as base units that assemble into larger hexagonal tilings. Similarly, L-tryptophan forms molecular trimers on base units that assemble into long chains. There was also findings of individual molecules within the hexagonal tiling of proline. The findings for the L-tryptophan and L-proline racemic mixture were found inconclusive.

MOTIVATION

Molecular self assembly is an essential part of nature and is vital in all biological organisms. Having insight into how chirality works with L-proline and L-tryptophan will lead to a variety of useful applications including the fabrication of proteins, drug development and innovation, and discovering more about how life works. This research may even lead to further understanding on why all life is based on the L-enantiomer of amino acids.



Scanning Tunneling Microscope used for this experiment

METHODS

Experiments were performed at Argonne's CNM Laboratory. L-tryptophan and L-proline were deposited onto a copper surface both separately and in a 50-50 mixture. Scanning Tunneling Microscopy (STM) was used to capture the images. Gwyddion program was used to enhance the images for better analysis.

RESULTS

Proline molecules on a Copper(111) surface self-assemble into a hexagonal tiling (Figure 1). Due to chirality, however, there is an approximate 30° difference in orientation. Each hexagon is made up of 6 trimers, which is a group of 3 molecules. A new discovery is that it is possible for a stray molecule to be trapped inside of the hexagonal structure. The stray molecule trapped inside moves to one of the six corners of the hexagon it is within (Figures 2 and 3). It is unclear whether these molecules are proline molecules or dust molecules due to an imperfect vacuum.

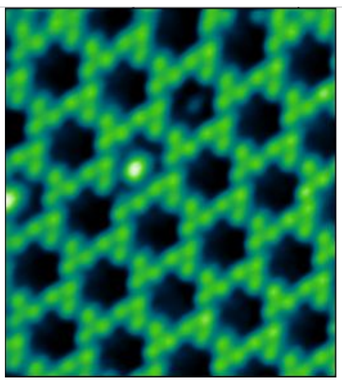


Figure 1
L-Proline on a Cu(111) surface

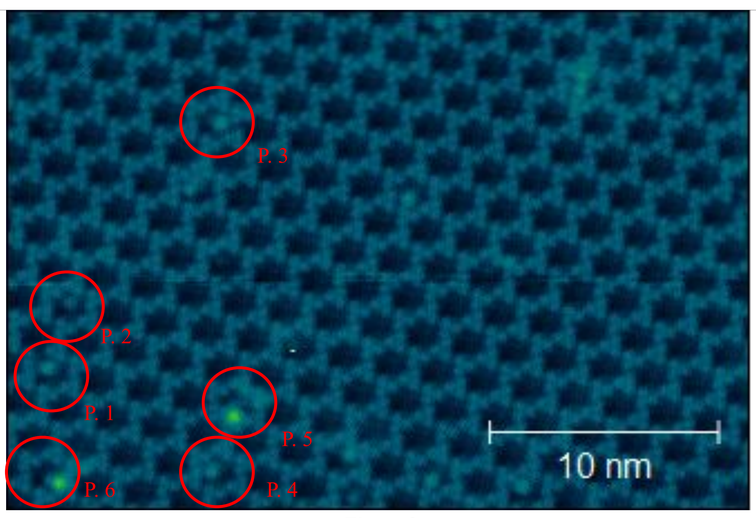


Figure 2
Possible molecule positions over a surface

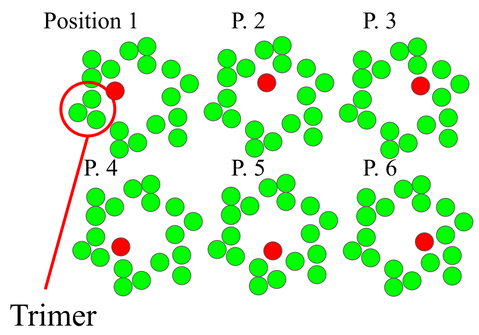


Figure 3
Molecule positions

L-tryptophan assembles in long chain structures, in which subsequent molecules generally have the same orientation (Figure 4). There are three orientations that these chains generally map to, each that is approximately 120 degrees from each other with small deviation (Figure 5). Additionally, these chains sometimes change direction, forming a curved segment as it transitions. Two segments can also be observed to sometimes cross into one continuous segment, allowing for more complicated structures to be formed. Each tryptophan molecule has a length of approximately 1.709 nm, with a standard deviation of 0.074 nm, and a width of 0.556 nm, with a deviation of 0.074 nm. These measurements were averaged from 15 individual tryptophan molecules.

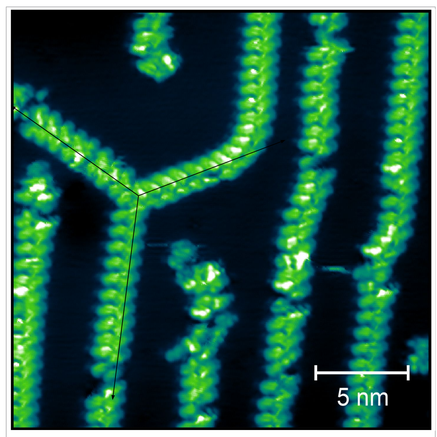


Figure 4
L-Tryptophan on a Cu(111) surface

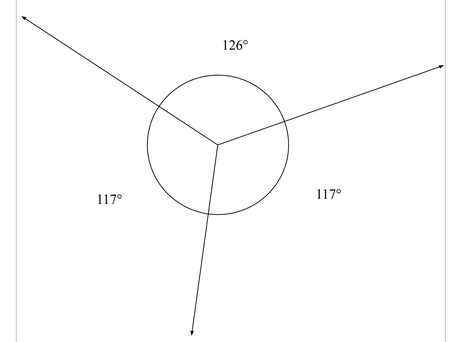


Figure 5
Angles between the axes of L-tryptophan

When L-tryptophan and L-proline were mixed in a 50-50 solution on a copper surface, they formed two distinct regions. One region consisted of a regular proline structure, in which it assembled into a large hexagonal complex. The other region is composed of random arrangements of tryptophan molecules, (and possibly proline) with no generalized pattern (Figure 6). While this could be due to some other factor, it was most likely degradation of the source tryptophan material. The original isolated tryptophan data was collected from a control sample different from the tryptophan used in the 50-50 mixture, and when the new tryptophan was analyzed in an isolated assembly, it could not replicate the initial control. No conclusions can be made at this time based upon the mixture until a proper sample set is obtained.

CONCLUSIONS AND NEXT STEPS

After the analysis of the self-assembly of L-proline and L-tryptophan, on a Cu(111) with the use of a scanning electron microscope, two separate patterns were identified in assembly. The self-assembled amino acids repeated their pattern enough times to create honeycomb structures in the L-proline mixture, and chains in the L-tryptophan mixture. Within these honeycombs some amino acid molecules that did not assemble into the honeycomb structure got encased within the structure.To be able to further research in this field, the same form analysis for each type of amino acid would be required. Rerunning the Tryptophan and Proline mixture in order to verify findings would be a small step forward. The data gathered from potential self-assembly patterns on different metal surfaces as well as racemic mixtures of different amino acids would be another next step.

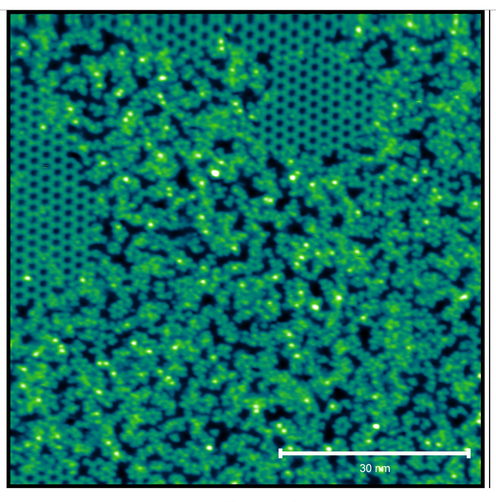


Figure 6
50/50 mixture

ACKNOWLEDGEMENTS

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