The Self-Assembly and Chirality of Histidine on a Copper(111) Substrate

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ABSTRACT

The exploration of molecular self-assembly of biological molecules can provide insight into an array of biological processes that occur throughout nature. Amino acids are chiral molecules, which, in nature, are only present in the left-handed orientation (L enantiomer). It is hoped that increasing the understanding of amino acid molecular self assembly under various proportions of L-D enantiomers can lead to advancements in pharmaceuticals, medical nanoscale diagnostics, and even the understanding of the origins of life on Earth. This is the first study investigating the molecular self assembly of the amino acid histidine on Cu(111). Previous studies on amino acids such as alanine and tryptophan have discovered unique molecular superstructures that form chiral homogeneous networks with specific geometry. Using Scanning Tunneling Microscopy (STM), necessary for its capability to image with atomic resolution, we sought to determine if there were similarities between previously characterized amino acid superstructure assemblies to that of histidine on Cu(111). We found that, like many other amino acids, histidine formed chiral superstructures. The superstructure assemblies included trimers, chains, and “dog bone” formations. Chiral angles were measured at about 15 degrees.

INTRODUCTION

Invented by Gerd Binnig and Heinrich Rohrer, earning them the 1986 Nobel Prize in Physics, the Scanning Tunneling Microscope (STM) is a device used to image atoms and molecules and the nanoscale level (Baird et Shew, 2004). In recent years, the STM has been used to observe various amino acid superstructures. Amino acids (other than Alanine) are chiral, and in previous research, many of the superstructures formed by amino acids have been chiral as well (Xu et al., 2011; Yt tamben et al., 2013). In this research, we utilized Scanning Tunneling Microscopy (STM) to study the self-assembly of the L and D enantiomers of histidine to observe the superstructures that the histidine molecules form. In addition to studying the shapes of the superstructures, we sought to determine whether these superstructures were chiral.

METHODS

Histidine samples were prepared in an Ultra-High Vacuum (UHV) chamber through a process called annealing, explained as follows:

- Histidine samples are loaded into a chamber of the UHV
- Doser is connected to the STM (Figure 2)
- Sample molecules were heated to a temperature of 423 K for 15 minutes
- In addition to being purified, Histidine sublimes onto the Copper(111) substrate
- Sample is then transferred directly to the imaging chamber, never leaving the UHV environment

RESULTS

In both low and high concentrations, histidine enantiomers formed trimers that grouped into chains and dog-bone superstructures. It is believed that the functional groups of the amino acid, the carboxylic acid group and the amine group, form tridentate bonds with the copper crystal hexagonal network. The variable R-group of the amino acid, which for histidine is an aromatic ring, is believed to then determine the overall superstructures (chains and dog-bones) as they interact above the copper surface. When the histidine is highly-concentrated it self-assembles into far longer chains than when it is less concentrated. Additionally, the higher the concentration, the more frequently the dog-bone structures appear. Amino acid “clustering” (figures 11 and 14) occurred because of errors in the annealing process on the Cu(111) substrate. Similarity in superstructure chain formation has been found in multiple amino acid analyses. This may be due to the tridentate bond formed when the common amino acid functional groups bond on the substrate. Our measured chiral angle of 15 degrees is also similar to other amino acid analyses. Further research is needed to determine superstructure differences in racemic mixtures. We suspect that L and D formations will remain separated on the substrate.

REFERENCES