ESRP: Exploring Fundamental Chiral Molecular Self-assembly: Proline on Cu(111) Surfaces

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Abstract
In this study we performed the first atomic-scale exploration of molecular self-assembly of the chiral amino acid proline on Cu(111). The goal of this research was to further the knowledge and understanding about how D- and L-proline self-assemble, noting how the chirality affects their interactions. To accomplish this, homochiral samples of proline on a Cu(111) surface were individually explored. 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 both L- and D-proline form molecular trimers as base units that assemble into larger hexagonal tilings. However, the orientation of these hexagonal tilings is different between the L- and D-proline, which is due to the chirality of the amino acids.

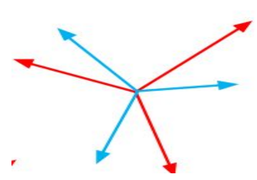
Motivation

Molecular self-assembly is present everywhere in nature and plays a vital role in biological systems. By understanding the ways amino acids bond with themselves, one can further understand how proteins form and function. This research helps establish an understanding of how chirality affects self-assembly; which leads to a variety of useful applications, including the potential of building new proteins, drug development, and even unlocking secrets to the origins of life on Earth.

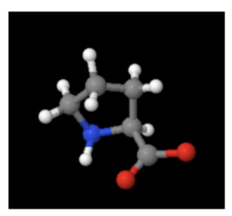
Results

After analyzing the processed images from Gwyddion, it is clear both L- and D-proline form molecular trimers as base units that then assemble into larger hexagonal tilings at higher concentrations. However, due to the chirality of each acid, the orientation of these tilings have a significantly different angle. The angle from the center to the three of the vertices were measured, and the difference between the L- and D-proline was taken. L- and D-proline have an approximate difference of 30 degrees between the hexagonal shapes after analysis, with a variation of around 10 degrees, most likely to human error. In addition, the base molecular trimers in D-proline are oriented at an approximate 180 degrees rotation compared to L-proline, due to chiral differences that affect intermolecular bonding. The length of each hexagonal figure was also measured from the outermost edge of two trimers opposite from each other. Nine different hexagons were measured, and the mean of the distance was taken to find the average diameter.

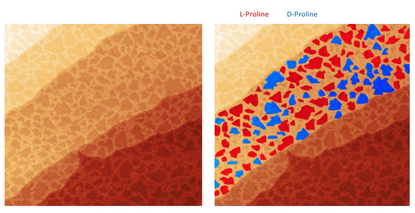
Procedure
All experiments were carried out at the Argonne CNM Laboratory. Both L-proline and the D-proline were separately deposited and imaged over a Cu(111) surface using a scanning tunneling microscope. The data collected from the microscope was distributed and analyzed throughout the group. All data was filtered and analyzed using a program named Gwyddion. This program allows the filtering of tip sound, cutting, and the modifying of sample images. However, the images were carefully modified in order for the gathered data to be more clear for interpretation. It was in no way used to modify or alter the actual data gathered.

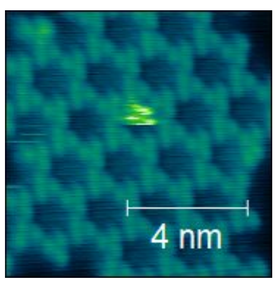


Blue represents the angles of the L-proline and red represents the angles of the D-proline

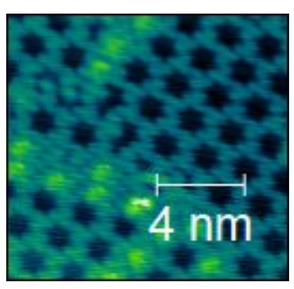


3D model of a L-Proline molecule

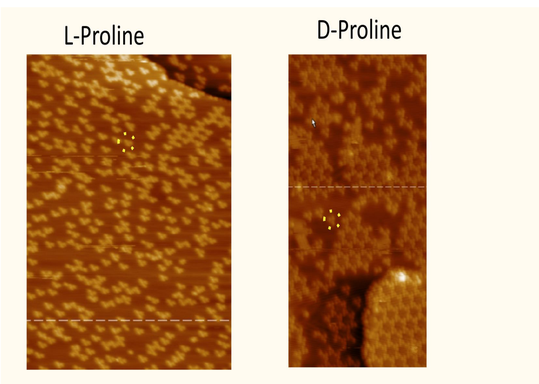


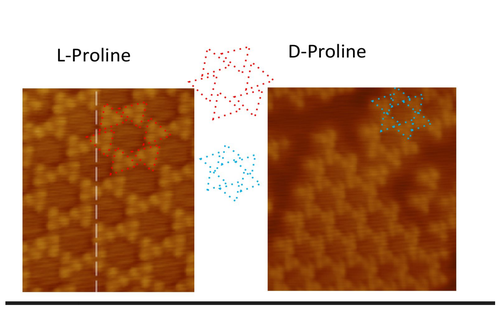


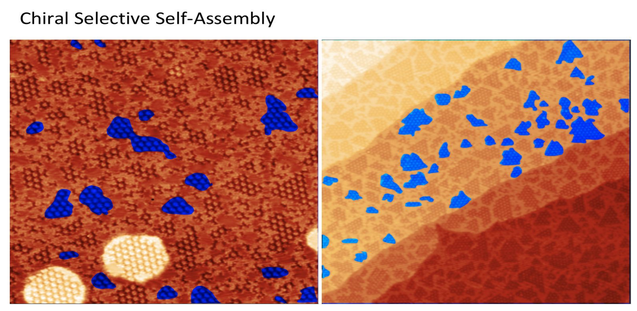
D-proline on a Cu(111) surface. Used to determine rotation and size.



L-proline on a Cu(111) surface. Used to determine rotation and size.







Each L-proline hexagonal group of molecules has an approximate average diameter of 3.2095 nanometers, with an approximate deviation of 0.126. Each D-proline hexagonal group of molecules has an approximate average diameter of 3.05, with an approximate deviation of 0.4. Due to the similarity, it is likely that the type of proline plays no role in determining the size of each hexagonal figure, but rather that the size of each figure simply varies at random.

Conclusion
Through the analysis of the self-assembly of homochiral proline, in both L- and D- varieties, on a Cu(111) surface with the use of a scanning tunneling microscope, it was discovered that the patterns in assembly have not been observed prior to this experiment. Through these patterns one was able to distinguish the exact angle between molecules of proline and also see what shape each chiral variations of proline assembles in. To further this research other amino acids and biomolecules will be analyzed in the same fashion. By looking at racemic mixtures and the difference in assembly on variation of metallic surfaces one will get a deeper understanding of each molecule.

Next Steps
Going forward, the self assembly of chiral amino acids on different surfaces needs to be further tested and improved. The uses of different amino acids based on their chirality and properties would be beneficial for the development of medical drugs and the improvement of treatments for various illnesses.

- Since it was proven that L-Proline and D-Proline change orientations based on the differences in their chirality on a Cu(111) surface, using a polar chiral amino acid may completely alter the protein's position.
- Additionally, since using a transitional metallic surface resulted in L-Proline and D-Proline to form a hexagonal structure, using an alkali metal surface may change the organization of the trimers.

Acknowledgements
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References

C. J. Chen, Introduction to scanning tunneling microscopy, Oxford University Press (1993).
D. G. Blackmond, The origin of biological homochirality, Cold Spring Harb Perspect Biol. 2 (5): a002147 (2010).
Jeong, Yongchan, et al. "Breakdown of Chiral Recognition of Amino Acids in Reduced Dimensions." *Scientific Reports*, vol. 10, no. 1, 2020, doi:10.1038/s41598-020-73300-z.