AIP The Journal of Chemical Physics

Chirality at two-dimensional surfaces: A perspective from small molecule alcohol assembly on Au(111)

Melissa L. Liriano,[1] Amanda M. Larson,[1] Chiara Gattinoni,[2] Javier Carrasco,[3] Ashleigh E. Baber,[1] Emily A. Lewis,[1] Colin J. Murphy,[1] Timothy J. Lawton,[1] Matthew D. Marcinkowski,[1] Andrew J. Therrien,[1] Angelos Michaelides,[2] and E. Charles H. Sykes[1,a)]

[1]*Department of Chemistry, Tufts University, Medford, Massachusetts 02155, USA*
[2]*Thomas Young Centre, London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom*
[3]*CIC Energigune, Albert Einstein 48, 01510 Miñano, Álava, Spain*

(Received 16 April 2018; accepted 21 June 2018; published online 18 July 2018)

The delicate balance between hydrogen bonding and van der Waals interactions determines the stability, structure, and chirality of many molecular and supramolecular aggregates weakly adsorbed on solid surfaces. Yet the inherent complexity of these systems makes their experimental study at the molecular level very challenging. In this quest, small alcohols adsorbed on metal surfaces have become a useful model system to gain fundamental insight into the interplay of such molecule-surface and molecule-molecule interactions. Here, through a combination of scanning tunneling microscopy and density functional theory, we compare and contrast the adsorption and self-assembly of a range of small alcohols from methanol to butanol on Au(111). We find that longer chained alcohols prefer to form zigzag chains held together by extended hydrogen bonded networks between adjacent molecules. When alcohols bind to a metal surface datively via one of the two lone electron pairs of the oxygen atom, they become chiral. Therefore, the chain structures are formed by a hydrogen-bonded network between adjacent molecules with alternating adsorbed chirality. These chain structures accommodate longer alkyl tails through larger unit cells, while the position of the hydroxyl group within the alcohol molecule can produce denser unit cells that maximize intermolecular interactions. Interestingly, when intrinsic chirality is introduced into the molecule as in the case of 2-butanol, the assembly changes completely and square packing structures with chiral pockets are observed. This is rationalized by the fact that the intrinsic chirality of the molecule directs the chirality of the adsorbed hydroxyl group meaning that heterochiral chain structures cannot form. Overall this study provides a general framework for understanding the effect of simple alcohol molecular adstructures on hydrogen bonded aggregates and paves the way for rationalizing 2D chiral supramolecular assembly. *Published by AIP Publishing.* https://doi.org/10.1063/1.5035500