Chemical Imaging and Dynamical Studies of Complex Interfacial Systems

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This presentation will begin with a discussion of emergent chirality in molecularly adsorbed films. Ever since Pasteur first uncovered the direct correlation between the structure of a crystal and the handedness of its component molecules, researchers have been intrigued by the mechanisms of chiral separation. Scanning tunneling microscopy (STM) provides the ultimate technique for determination of the exact structure and chirality of adlayers on a substrate. The structure of an adlayer is the result of a delicate balance of lateral molecule-molecule interactions and adsorbate-substrate forces. The strength of the adsorbate-substrate interaction must be balanced such that adsorbed molecules are mobile enough to self-assemble into an organized array but greater than the adsorbate-adsorbate energy to allow two-dimensional crystallization. Our initial work involves metalloporphyrin adlayers on Au(111) as such systems meet these criteria perfectly. These porphyrin arrays are especially interesting because they self-assemble at room temperature without the need for annealing, making them a likely candidate for technological applications. We will focus initially on NiTPP (nickel 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine) and NiOEP (nickel 5,10,15,20-tetraphenyl-21H,23H-porphine) on Au(111), as well as C_{60} decoration of these systems [1]. These molecules are achiral when isolated in the gas phase but we find that symmetry is broken when the molecules adsorb onto a surface in small clusters, where they form local chiral ensembles, Figure 1. We hope to elucidate not only general rules for the formation of racemic mixtures, but also methods of forcing (guiding) the system to form only one of the two mirror image structures. This might be achieved, for example, by the introduction of a "seed" chiral entity or the use of a high index crystal face. Coadsorption of C_{60} with these porphyrins produces a wealth of complex structures including quite evident effects due to the long-range herringbone reconstruction of the 23 x √3 Au(111) substrate. If time permits, a discussion of polymer dynamics in confined thin film geometries will also be included. Here, we will report on scattering studies at polymeric interfaces as a function of composition (PMMA, PS, PB), molecular weight, thickness (nanoconfinement), temperature, and annealing [2-4], with recent extension to include the surface dynamical properties of PET polymer thin films in their glassy vs. crystalline phases [5].

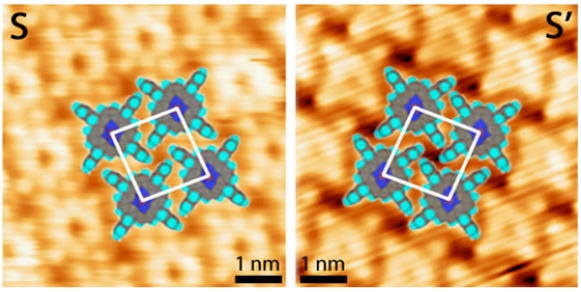

Figure 1. STM images of NiTPP/Au(111) showing two chirally distinct domain conformations with an overlaid structural model. STM tunneling setting: 1.0 nA at 1.0 V.

[1] L. Teugels, G. Avila-Bront, and S. J. Sibener, submitted (2010).
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[3] M. A. Freedman, J. S. Becker, A. W. Rosenbaum, and S. J. Sibener, *J. Chem. Phys*. **129**, 044906 (2008).
[4] M. A. Freedman, J. S. Becker, and S. J. Sibener, *J. Phys. Chem. B* **112**, 16090 (2008).
[5] J. S. Becker, R. D. Brown, D. R. Killelea, H. Yuan, and S. J. Sibener, PNAS, DOI 1008268107.