

Expanding the Scope of Molecular Self-organization Studies through Temperature Control at the Solution/Solid Interface

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Manuscript received: 19 April 2011.

Manuscript accepted: 8 June 2011.

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Studying the self-assembly of molecules at the solution/solid interface (SSI) provides unique insight into bottom-up molecular architectures, which have applications varying from solar conversion^[1–3] and electronic devices^[4–7] to providing insight into fundamental biological mechanisms.^[8,9] The investigation of molecular organization at the SSI is largely conducted via scanning tunnelling microscopy (STM), which can be used to directly visualize molecular kinetics and geometries *in situ*.^[10–14] The development of this technique has provided unprecedented access to the details of surface molecular self-assembly.^[15,16]

The Gibbs free energy for molecular systems at the SSI comprises an enthalpic contribution dominated by the interaction energies of the adsorbed species (intermolecular and molecule-substrate) and an entropic component primarily associated with the molecules in solution. The details of the energy balance are quite subtle, and the level of *ab initio* predictive power necessary for the ground-up design of molecular networks remains elusive. However, empirical heuristics describing the interplay of physisorption, molecule-molecule interaction, solvent and concentration effects are emerging from carefully-controlled experiments.^[17–20] Until recently, temperature was the only variable in the Gibbs free energy expression that had not been systematically varied, even though it has implications for both thermodynamics and kinetics, as well as for critical parameters like solubility and viscosity. We highlight here the first few reports of temperature control in SSI-STM experiments.

The infrastructure required to modify an existing STM for temperature control is modest, and designs can be easily adapted from add-on stages originally intended for commercial atomic force microscopy.^[21–23] In general, temperatures above room temperature are achieved by inserting either a small heater^[24,25] or a thermoelectric (Peltier) device^[26] under the sample. The latter is the more versatile solution, since driving current in the opposite direction through the Peltier device results in cooling. In either case, the temperature at the sample must be monitored with a thermocouple or similar, and the heater should ideally be controlled via a proportional-integral-derivative (PID) algorithm.

The first temperature-controlled SSI-STM study was reported by English and Hipps, who imaged coronene at the heptanoic acid/Au(111) interface at temperatures up to 55°C.^[24] This early work established a proof-of-principle, and has since been followed by examples of temperature control in SSI-STM designed to systematically elucidate the energetics of SSI self-assembly.

In an elegant illustration of the principle of closest packing,^[27,28] Marie et al. showed that in increasing from room temperature to 50°C, hexakis(*n*-dodecyl)-*peri*-hexabenzocoronene (HBC-C₁₂) at the *n*-tetradecane/Au(111) interface undergoes successive, irreversible phase transitions that increase its density of packing (Fig. 1).^[26]

Gutzler et al. used temperature-controlled SSI-STM to reveal a rich interplay of energetics in the physisorption of 1,3,5-tris(4-carboxyphenyl)benzene (BTB) at the solution/highly oriented pyrolytic graphite interface.^[25] The molecular packing reversibly changes from an open-pored chicken wire structure at lower temperatures to a higher-density row structure at higher temperatures, with the exact transition temperature depending on the solvent: ~43°C (55°C) for octanoic (nonanoic) acid (Fig. 2). The authors' thermodynamic analysis suggests that the enthalpic/entropic balance of the phase transition can only be explained if the porous structure is stabilized by solvent coadsorption.

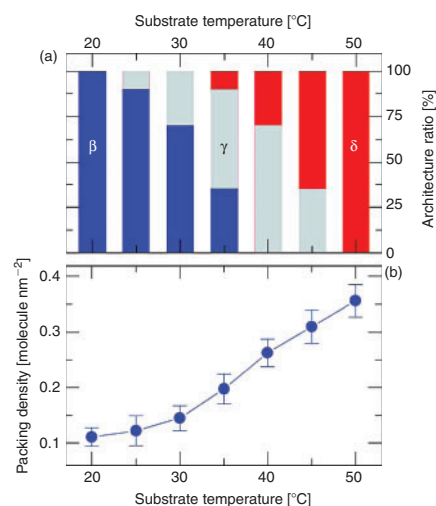


Fig. 1. Temperature-induced phase transitions in HBC-C₁₂ at the *n*-tetradecane/Au(111) interface, showing a trend towards increased density with higher temperature. Molecular structure and structural diagrams for the different phases are provided in the original reference. Reprinted with permission from C. Marie, F. Silly, L. Torteck, K. Mullen, D. Fichou, *ACS Nano* 2010, 4, 1288. Copyright 2010 American Chemical Society.

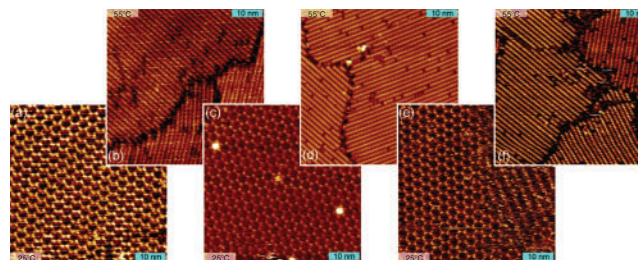


Fig. 2. Repeated cycles of heating and cooling a 1,3,5-tris(4-carboxyphenyl)benzene (BTB) molecular assembly at the nonanoic acid/highly oriented pyrolytic graphite interface. The structure switches between chicken wire (a, c, e) at 25°C and a row structure (b, d, f) at 55°C. Molecular structure and structural diagrams for the different phases are provided in the original reference. Reprinted with permission from R. Gutzler, T. Sirtl, J. F. Dienstmaier, K. Mahata, W. M. Heckl, M. Schmittl, M. Lackinger, *J. Am. Chem. Soc.* 2010, 132, 5084. Copyright 2010 American Chemical Society.

Temperature-controlled SSI-STM is an experimental area poised for growth. Although ex situ annealing experiments have also produced striking results,^[29,30] the ability to visualize dynamic processes and observe metastable states is invaluable to creating a full picture of the energetics. We anticipate that the temperature control of SSI-STM experiments, including the extension to temperatures below room temperature, will soon expand the scope of fundamental investigations of molecular assembly. Even with pragmatic temperature limitations imposed by factors like solvent volatility

and STM drift, SSI-STM experiments will have access to a range of temperatures salient to both technological and biological processes. This will allow for the exploration of questions such as how elevated operational temperatures may affect molecular architectures in devices, whether the self-assembly of DNA base pairs proceeds differently at body temperature, and for the pursuit of novel approaches to materials synthesis, like surface-confined polymerization,^[31] which has been demonstrated^[32,33] but remains a nascent field at the SSI.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) in the form of a postdoctoral fellowship (J.M.M.) and a Discovery Grant (F.R.). F.R. also acknowledges the Canada Research Chairs program for partial salary support.

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