

## Melting Point Enhancement of a Self-Assembled Monolayer Induced by a Van-Der-Waals-Bound Capping Layer

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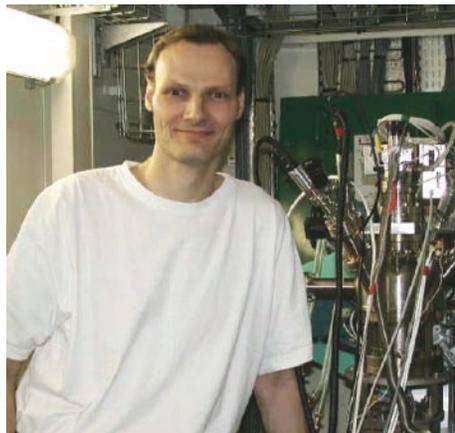
*Using in-situ surface x-ray diffraction, the temperature dependence and thermal stability of a self-assembled monolayer (SAM) of decanethiol, sandwiched between the Au(111) substrate and a van-der-Waals-bound capping layer of PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride), are measured. While the bare SAM on Au(111) undergoes a melting transition at 100°C, this transition temperature is raised to 115°C if the SAM is capped by PTCDA. Possible mechanisms and implications of this capping-layer-mediated melting point enhancement are discussed.*

Phase transitions in reduced geometry are a very fundamental issue in condensed matter science, and even the seemingly simple case of hard discs in two dimensions continues to be a matter of discussion. A particularly interesting situation arises if a thin film is subject to interactions on both the bottom and top interfaces.

For phase transitions in complex low-dimensional organic materials, the internal degrees of freedom of the molecules, which are an important characteristic of organics, have to be considered and a very rich phase behavior, as seen, for example, in Langmuir films (on liquid surfaces), can be found. Among the well-defined, crystalline two-dimensional organic thin films chemisorbed on a solid substrate, self-assembled monolayers (SAMs) are probably the best characterized systems, and the phase behavior of the archetypal SAM system (alkanethiols on Au(111)) as a function of coverage and temperature has been thoroughly studied.

Here we present the case of rather soft boundary conditions for an organic monolayer, namely a SAM of decanethiol on Au(111) capped by a van-der-Waals-bound crystalline multilayer of PTCDA, a model compound for organic molecular beam deposition (**Figure 1**).

The SAM melting curve is obtained from the area under a Bragg reflection as a function of temperature,  $T$ . Compared to the uncapped SAM, we found that the melting temperature of the PTCDA-capped SAM is enhanced by about 15°C, while the character of the transition appears unaltered (**Figure 2**). Note that PTCDA remains solid to well above 200°C – i.e., at the SAM melting  $T$  it is still a solid capping layer.



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Since the PTCDA layer is only coupled to the SAM itself, it cannot directly exert a significant pressure on the SAM. Therefore, we believe that the mechanism for the melting point enhancement observed here is different from a pressure-induced scenario. We note that the system studied here does not correspond to a confined-melting phenomenon in

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the conventional sense of a hard confinement, since the capping layer is connected only to the SAM and thus is not at a fixed height above the substrate. In fact, one way for the SAM to gain space and thus reduce its density during the phase transition is to reduce the tilt angle of the chains, and thereby increase the effective chain-to-chain distance in the plane. The exact need for this extra volume is not known, but it is clear that the capping layer would not impose serious restrictions on this change of the SAM's effective height, due to the weak interaction of the capping layer with the substrate over this distance. Nevertheless, one should expect that the PTCDA layer at least tends to reduce the fluctuations along the surface normal, which may have an impact on the phase transition.

In addition, the capping layer can have an effect on the lateral interactions within the SAM, in that it tends to “clamp” the chain termina to certain positions in the corrugated potential of the flat-lying PTCDA molecules and, thereby, effectively stabilizes a certain chain-to-chain distance. In this context, it is important to note that PTCDA grows with a well-defined epitaxial relationship, implying that the lateral variation of the PTCDA-SAM interaction potential does not average out. While it is difficult to quantify these interactions, the impact of the capping layer on the fluctuations both along the normal and on the (indirect) in-plane interaction appear to be plausible mechanisms for the melting point enhancement.

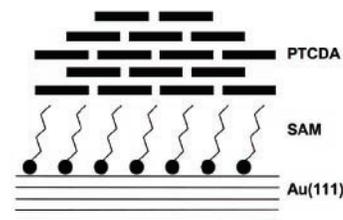


Figure 1. Schematic of the layered structure of the sample (Au(111) substrate / SAM / PTCDA).

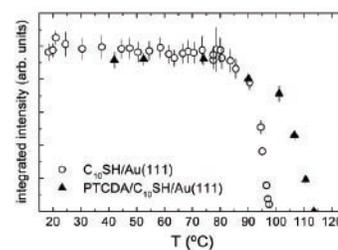


Figure 2. Melting curve as determined from the temperature dependence of the Bragg intensity (integral of the hexagonal in-plane reflection) of the SAM with and without the PTCDA capping layer. For the capped SAM, the melting temperature is enhanced by ~ 15 K.