THERMODYNAMIC BALANCE OF PERYLENE SELF-ASSEMBLY ON Ag(110)

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We present a room temperature STM study of perylene adsorption on Ag(110) at the monolayer coverage regime. We found that structure and symmetry of the flat perylene monolayer is determined by thermodynamic balance of the three factors: (i) the site recognition effect, (ii) the intermolecular interaction and (iii) the thermal motion of the perylene molecules. The moderate strength of the site recognition and intermolecular interactions, of the same order of magnitude as *kT* ~25 meV, represented a key feature of the thermodynamic balance.

The thermodynamic balance bestowed to this system the unique quality to form a flexible monolayer of epitaxial as well as self-assembling character. The increasing perylene coverage induced gradual crystallization of the initially fluid monolayer (<0.1 ML) into the crystalline (2 5 3 -2)/(2 -5 3 2) monolayer (0.1053 ML). The crystalline monolayer further incorporated extra molecules modifying its structure and symmetry albeit maintaining its true commensurate character. The recognition effect of moderate strength was able to lock some of the perylene molecules into favorable adsorption sites of the (110) lattice providing a skeleton of the crystalline phases. We have found that the crystalline monolayer did not quench thermal motion of the included molecules but rather accommodated it modifying its skeleton by reselecting a new set of available adsorption sites favorable in terms of intermolecular interaction.

The ability of the perylene crystalline structure to accommodate its thermal motion made possible formation of the epitaxial and self-assembled perylene monolayer free of domain boundaries in the whole coverage range.

Key words: perylene, Ag(110), organic monolayer, self-assembly, epitaxy, surface mobility, thermodynamics, fluid phase, STM