CONFORMATIONAL-CONTROLLED NETWORKING OF H-BONDED ASSEMBLIES ON SURFACES

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Directional intermolecular forces are considered promising candidates to study and prepare networks that could undergo phase transitions through a thermally-induced change of molecular conformation which in turn leads to a variation of intermolecular interactions. The intermolecular force that will be exploited is the H-bond due to their intermolecular interaction strength and geometry which can be controlled by the number and arrangement of available H-bonding donor and acceptor moieties.

The 2D self-organization of a conjugated molecule bearing terminal 2,6- di(acylamino)pyridine moieties [1], which are well known to form H-bonds, on a Ag(111) surface under ultrahigh vaccum has been studied by STM. For sample prepared at room temperature, the molecules arrange in a hexagonal network (Figure 1a-b).

Combining the information derived from STM and low-energy electron diffraction (LEED) measurements, a commensurate superstructure is found with the molecules arranged in a rhombic unit cell. In Figure 1e the structural model for this ad-layer is shown while the pores visible in the STM image in Figure 2b are denoted by back circles and the black arrow indicates a high symmetry direction of the Ag substrate.

The hexagonal porous network formed at room temperature deposition is transformed into a commensurate close packed rhombic pattern (Figure 1c-d) by a thermally induced trans-cis inversion of the terminal groups. This transformation can be explained by the fact that the system wants to minimize its energy: at the same time the free surface energy is minimized while the number of H-bonds per terminal group is doubled from two to four.

References:

[1] A. Llanes-Pallas et al., Angew. Chem. Int. Ed. 2008, 47, 7726
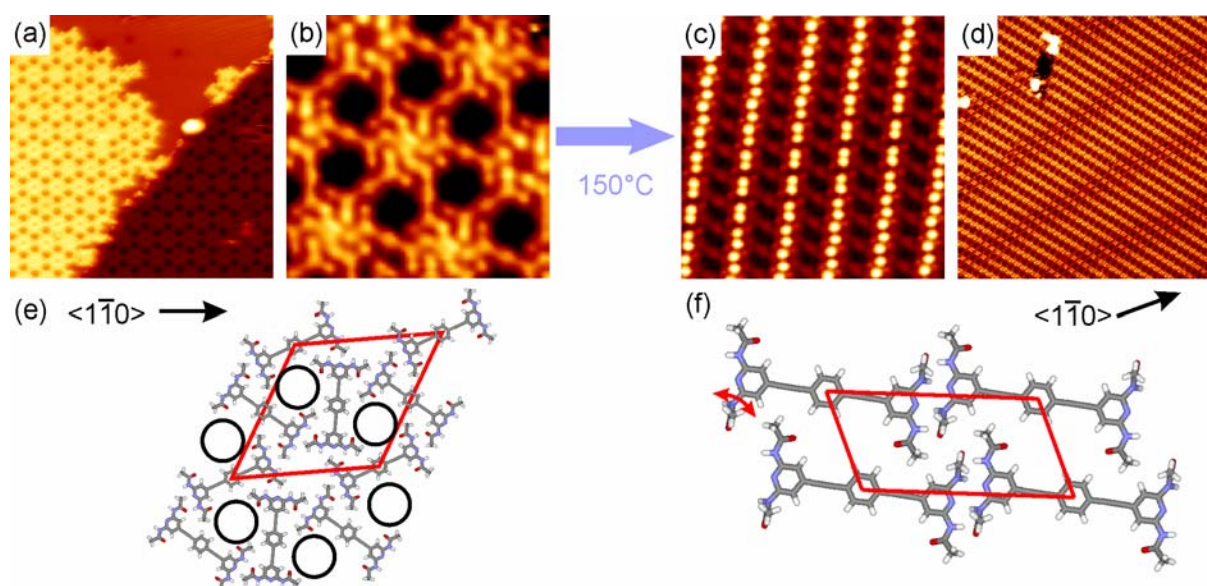
Figures:

Figure 1: a) STM image (34×34 nm², $V_{bias} = -1.7$ V, $I_t = 20$ pA, T = 77 K) of **1** on Ag(111). b) STM image (7×7 nm², $V_{bias} = -1.7$ V, $I_t = 20$ pA, T = 77 K) showing the porous network in detail. c), d) STM images (a: 10×10 nm², $V_{bias} = -2$ V, $I_t = 12$ pA, T = 77 K; b: 39×39 nm², $V_{bias} = -1.5$ V, $I_t = 12$ pA, T = 77 K) of **1** on Ag(111) after thermal annealing at 420 K. In d) a periodic modulation can be seen which is attributed to different conformations of the acetyl residues. e) Model for the porous network of **1** on Ag(111). The red rhombus indicates the unit cell while the black circles highlight the pores. f) Proposed model for the close-packed assembly.