

# Dynamical aspects of molecular self-assembly at solid surfaces

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## Abstract

Most of the studies on molecular self-assembly on solid surfaces focus on the thermodynamic driving forces (intermolecular interactions, molecule-molecule interactions, etc) that control the ordering of the molecular species. This is related to the fact that in most cases the energy barriers that control the kinetic processes involved in the assembly (diffusion barrier, rotational barriers, conformational barriers) are much lower than the relevant thermal energy, while the energy gain associated with the nucleation and growth of ordered structures is larger than the thermal energy (at least for a sufficiently large nucleus size). Under such conditions the structure is almost completely determined by thermodynamic reasons and little space is left for kinetic effects.

However, there exist relevant situations in which dynamical effects cannot be disregarded as unimportant. In this presentation we will investigate two of such situations:

- Thermodynamics by itself cannot explain completely the existence of defects. Defects such as vacancies, are however key in controlling mass transport in solids, with implications for mechanical properties and thermal stability. In our first example we will investigate the diffusion of individual vacancies in a self-assembled monolayer of a tetrathiofulvalene derivative (exTTF) on a Au(111) surface. Our experiments allow for a direct identification of the individual vacancies and their thermally induced displacements (see Figure 1), in contrast with other methods that follow tracer atoms that occupy the vacancy sites. A complete analysis of the displacement distribution function shows that correlated jumps of vacancies are actually very frequent, and the rates for long-jump events is inversely proportional to the jump length. We propose that this inverse proportionality is related with the dispersion of the longitudinal phonon bands along the direction of the chains.
- Molecules with different isomeric forms might assemble into different structures corresponding to the different isomers. The growth and self-assembly of such molecules will thus be controlled by the kinetic rate at which the isomerization will take place. We will show that the self-assembly structure of dicyanoquinodiimide (DCNQI) molecules depends on the deposition temperature, being controlled by an isomerization reaction (see Figure 2) which is facilitated by the uptake of one electron from the surface.

## Figures

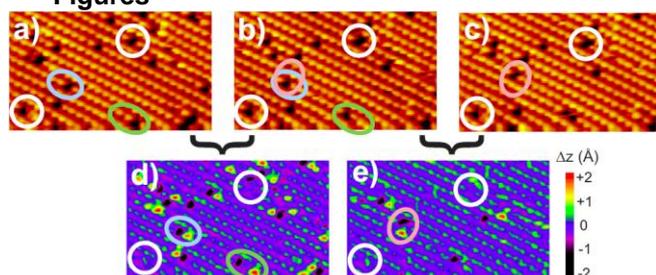


Figure 1. a), b) and c) Consecutive STM images of the same area of ( $15 \times 9 \text{ nm}^2$ ,  $V_{\text{Bias}} = 1.2 \text{ V}$ ,  $I_t = 1 \text{ nA}$ ) of a self-assembled monolayer of exTTF deposited on Au(111). Two vacancies (white circles) remain in the same position that they occupied in the first frame. Some examples of vacancy diffusion events are marked by blue ovals (single displacement along the **a** direction), pink ovals (single displacement along **b**) or green ovals (double displacement along **a**). d) and e) show the difference between consecutive images, in which the diffusion events can be easily identified. The time interval between the two images is 16 seconds.

Figure 2. a) STM image ( $8 \times 8 \text{ nm}^2$ ) of the self-assembled structure obtained by depositing DCNQI molecules with the substrate held at 120 K. The structure and the appearance of the molecules are consistent with DCNQI molecules being in the anti-isomeric state. b) STM image ( $6 \times 5 \text{ nm}^2$ ) of the structure obtained after RT deposition, which can only be explained by assuming that the molecules are now all of them in the syn-isomeric state.

