

A MOLECULAR SCALE NON-CONTACT AFM STUDY OF FUNCTIONAL ROTAXANE MOLECULES ON GRAPHITE.

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Molecular analogues of simple mechanical components of the macroscopic world are currently under investigation for use as devices that might function via motion at the sub molecular level.[1,2] Such devices present possibilities for the development of functional surfaces that change their properties as a result of some external stimulus and solid-state devices such as switches, memory storage devices and sensor devices. Rotaxanes, interlocked molecules, consisting of macrocycles trapped onto a linear unit (the 'thread') by two bulky substituents ('stoppers'), are interesting because their components are connected by a mechanical rather than a chemical bond. As such the relative motion of the sub-molecular components, in terms of either their rotational or translational degrees of freedom, can be controlled through local environmental or external stimuli. The macrocycle populates thermodynamically favourable sites on the thread. An external stimulus can be applied to destabilize this preferred site and/or increase the binding strength of some other site on the thread. Background thermal energy results in a net change of the position of the macrocycle through Brownian motion, this process is known as 'shuttling'. In a symmetrical rotaxane shuttle the molecule is in continuous motion between sites and destabilization of the sites results in an increase of the rate of motion. The molecules have been extensively studied in solution, however in the solid state such molecules are easily immobilised due to interactions with neighbouring molecules. Stimulated sub-molecular motion has not yet been directly observed on a surface – this would be an important step towards the use of such molecules in nanoscale devices and sensors.

We present a molecular scale NC-AFM (Non-Contact Atomic Force Microscopy) study of thin films of a series of hydrogen-bond assembled rotaxane molecules on graphite at the molecular scale. Film structure differences depending on the molecular type are discussed. As is shown in figure 1 almost identical molecules can show great differences in film structure. Furthermore, the activation of these molecules by the appropriate stimulus - UV light - was locally investigated through measurement of energy dissipation contrasts before and after application of the stimulus. The contrast in energy dissipation images in NC-AFM provides local information about the energy loss of the vibrating cantilever as a result of the tip-sample interaction. Although the mechanism of contrast formation is not yet completely understood some experimental results suggest that it is closely related to the stability of the film against the tip-sample interaction and that it is dependent on the mobility of the molecules in the film.[3] A further purpose of this study was to investigate the fundamental contrast mechanism of energy dissipation at the molecular level.

References:

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- [3] Fukuma, T.; Ichii, T.; Kobayashi, K.; Yamada, H.; Matsushige, K. *J. Appl. Phys.*, **2004**, 95, 1222-1226.

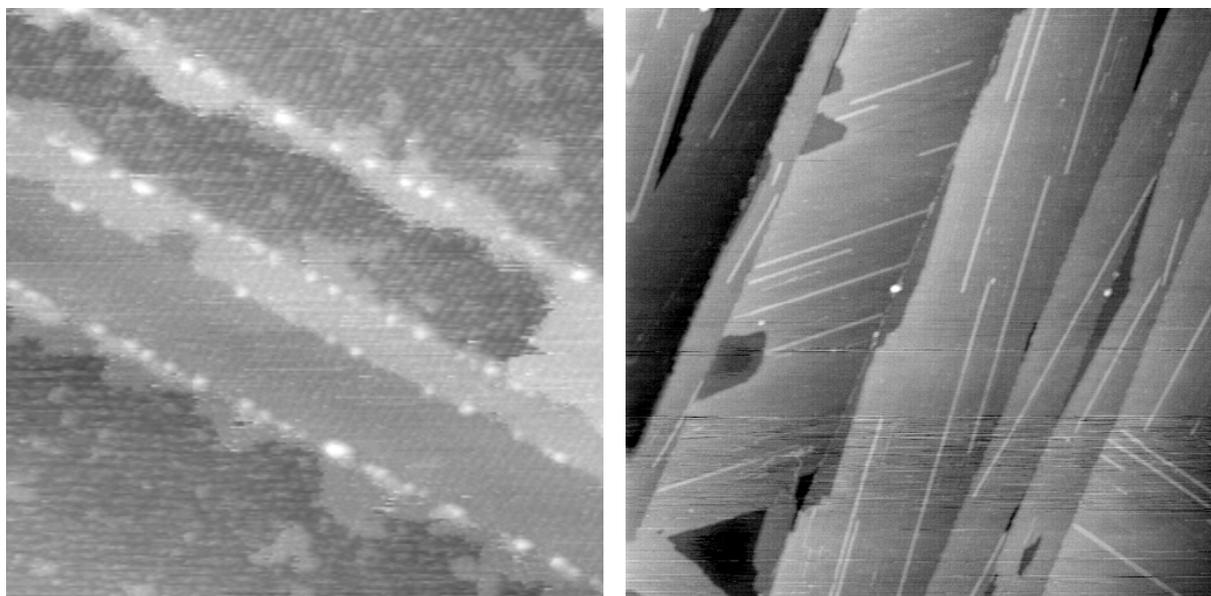
Figures:

Figure 1: Topographic NC-AFM images of the film structure of two types of almost identical rotaxane molecules. Both scans are 500 nm x 500 nm.