

**INTRAMOLECULAR DYNAMICS IN ADSORBED MOLECULAR LAYERS
STUDIED BY UHV-STM**

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To realize the goal of functional structures formed by molecular self-assembly, systematic studies of factors directing and affecting the assembly process are required, such as intermolecular interactions and molecular dynamics on surfaces.

Using scanning tunneling microscopy (STM) in ultra high vacuum (UHV) we have performed a comparative study of adsorption structures formed by a family of structurally different, but chemically similar, organic molecules adsorbed on the Au(111) surface. The molecules (see Fig. 1) consist of a central benzene ring with two (para-, meta-, or ortho-configuration) or three ethynylene spokes each terminating in a tert-butyl substituted salicylaldehyde moiety. This leads to highly conjugated pi-systems of linear, bent, v-shaped or three-spoke molecular geometry.

Upon adsorption at room temperature (and imaging at ~150K to reduce molecular mobility), a variety of close-packed phases is observed, most of which can be rationalized by a common motif of molecules adsorbed with their backbone parallel to the surface and with optimized intermolecular side-to-side interaction, most likely through van-der-Waals coupling (see Fig.2). Interesting exceptions to this picture are the linear molecules, which in addition form a more open nano-grid type structure thought to be dominated by intermolecular hydrogen bonding, and the v-shaped molecules where a reduced footprint indicates non-planar adsorption geometry.

The described results constitute a platform for ongoing experiments and analysis where (i) similar molecules with systematically altered functional moieties are used, e.g. disabling or further encouraging intermolecular hydrogen bond formation, (ii) structures formed through co-adsorption with transition metals (Ni, Fe) are investigated, and (iv) intermolecular covalent cross-linking is induced through co-adsorption with reactive diamines.

This contribution focuses in particular upon intramolecular dynamics for the adsorbed molecules. Our STM data reveals that the molecules are able to rearrange inside the close packed layers by rotating their end groups around the axis of the ethynylene spoke. Detailed analysis of this process will be presented.

Figures:

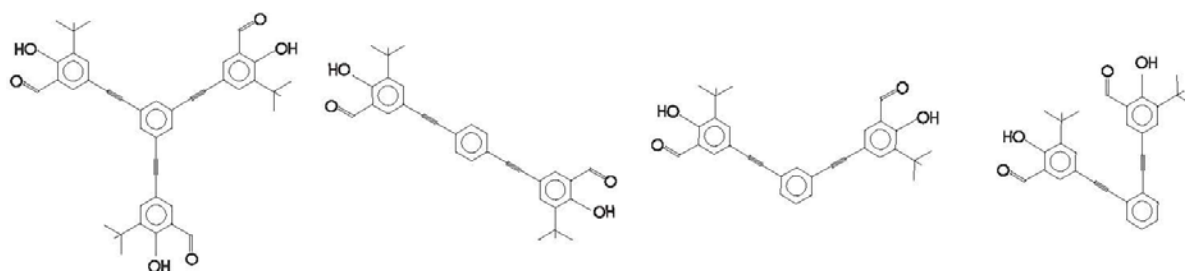


FIG. 1: The four investigated compounds with (from left to right) three-spoke-, para-, meta- and ortho-configuration.

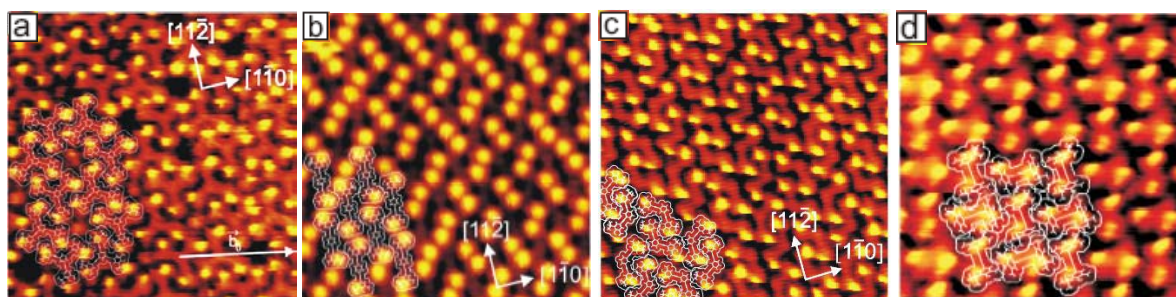


FIG. 2: Constant current STM images of packing patterns formed on the Au(111) surface for each of the four compounds shown in Fig. 1 (image sizes $120 \times 120 \text{ \AA}^2$). Other structures are also observed. The assumed adsorption geometry is indicated in the images. The three-spoke, para- and meta compound (image a, b, c) are adsorbed parallel to the surface while the ortho-compound (image d) has a non-planar adsorption resulting in an imaged projection of the molecules onto the surface in picture (d). For some tip states the entire molecule is clearly observed (a,c) while in other cases the image is dominated by the bright tert-butyl groups (b). In image (c) some molecules appear to have two tert-butyl groups. This artifact stems from a rotation of the end-group around the ethynylene spoke during the scan. Detailed analysis of such images enables this intramolecular dynamics to be investigated.