

**ORGANIC REACTION BETWEEN ADSORBED MOLECULAR BUILDING
BLOCKS AS DESIGN PARADIGM FOR FORMATION OF SURFACE
NANOSTRUCTURES.**

*Sigrid Weigelt¹, Carsten Busse^{1,2}, Christian Bombis¹, Martin M. Knudsen³, Kurt V. Gothelf³,
Thomas Strunskus³, Christof Wöll³, Mats Dahlbom¹, Bjørk Hammer¹, Flemming
Besenbacher¹ and Trolle R. Linderoth¹*

¹ Department of Physics and Astronomy, and iNANO, University of Aarhus, DK-8000 Aarhus C, Denmark

² Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum,
D-44780 Bochum, Germany

³ Department of Chemistry, and iNANO, University of Aarhus,
DK-8000 Aarhus C, Denmark

sigrid@phys.au.dk

Molecular self-organization on solid surfaces is a promising tool for the controlled formation of nanostructures. Extensive studies into molecular self-assembly based on reversible interactions such as Van der Waals forces, hydrogen bonding, or metal complexation have by now been performed. However, the resulting structures often express poor thermal stability due to comparatively weak intermolecular interactions. Chemical reaction between molecules adsorbed on surfaces, leading to covalent bonding between the building blocks, is expected to result in more stable structures, but has received much less attention. Here we present the first study on self-organization by spontaneous chemical reactions between co-adsorbed organic molecules under Ultra-High Vacuum (UHV) conditions. Fundamentally, the key differences compared to bulk chemistry is the confinement of the molecules in two dimensions with associated steric constraints and the absence of a solution phase which often directly or indirectly participates in the reaction

In our experiments, we have studied the reversible imine formation reaction, in which an aldehyde is linked to an amine via the formation of a covalent imine-bond. As the aldehyde containing educt we focused on a family of highly conjugated rigid molecules with varying geometry (both di- and tri-aldehydes) and as reactant partner we used aliphatic mono- and diamines. The molecules were co-deposited onto the inert gold(111) substrate under UHV conditions in the sub-saturation coverage regime and chemical reaction occurred upon thermal activation. In the case of the mono-amines we found well-ordered molecular islands formed by the reaction products as visualized with STM. To explore stereo- and topochemical effects, the surface reaction product was compared with the structure formed by the same educts reacted ex-situ and deposited directly onto the substrate. The reaction with the diamines led to two-dimensional polymeric networks in which the individual building blocks and the local bonding pattern could clearly be resolved. Formation of covalent bonds is evidenced from the geometry of the reaction products, as determined by STM, and is also supported by XPS and NEXAFS measurements. Theoretical modeling elucidating details of the reaction mechanism is currently being performed.

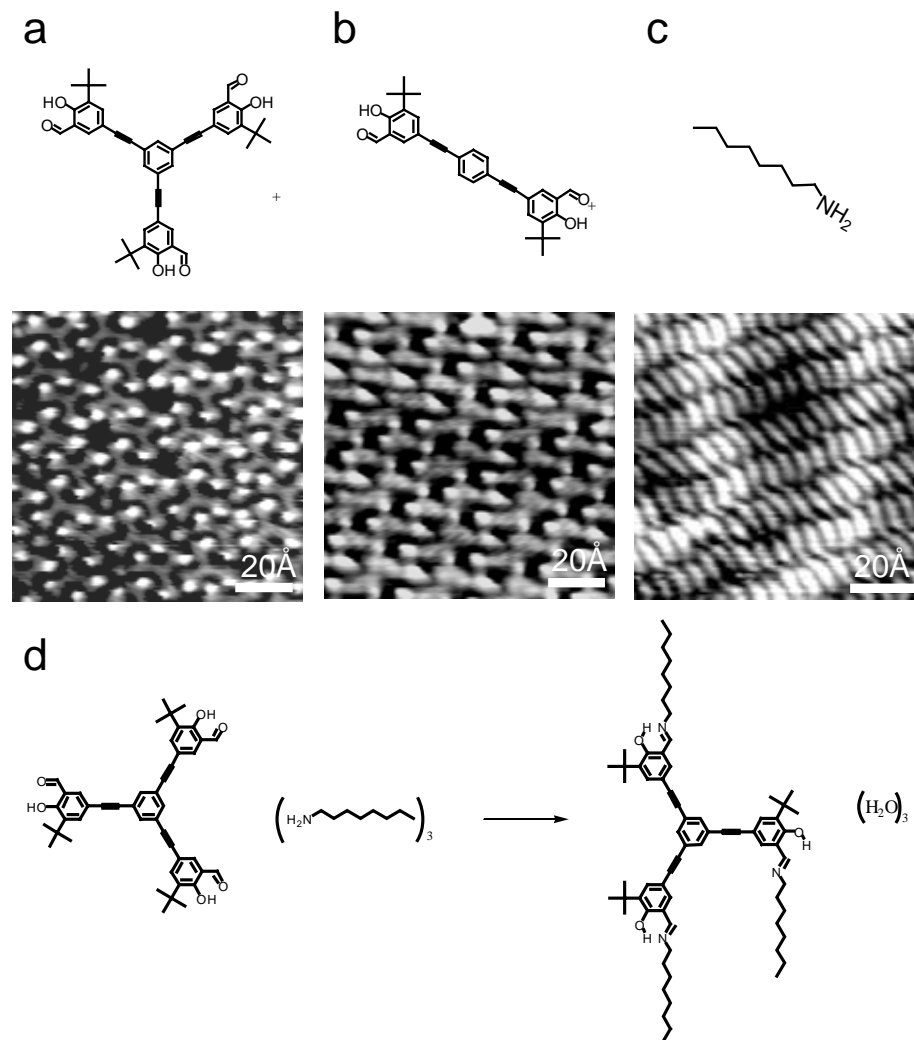
References:

[1] Y. Okawa and M. Aono: Nature, **409** (2001), 683.

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Figures:



Some educts with STM images: Tri-aldehyde (a), Di-aldehyde (b), Octylamine (c) and a reaction model (d).