1
Max-Planck-Institut für Festkörperforschung, Stuttgart,
2
Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum,
3
Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne, Schweiz
4
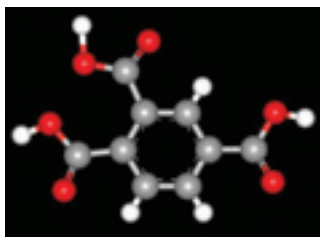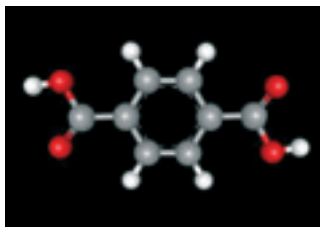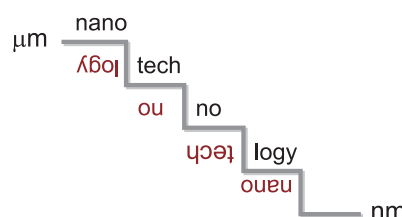*Advanced Materials and Process Engineering Laboratory, University of British Columbia, Vancouver, Canada*

Bottom-up nano-technology: molecular engineering at surfaces

S. Stepanow[1], M. Lingenfelder[1], A. Dmitriev[1], N. Lin[1], Th. Strunskus[2], Ch. Wöll[2], J.V. Barth[3,4], K. Kern[1,3]

Fig. 1:
Terephthalic acid - tpa (top) and Trimellitic acid - tmla (bottom) comprise two respectively three functional carboxyl groups.

References:
[1] Lehn, J.-M. Supramolecular Chemistry, Concepts and Perspectives (VCH, Weinheim, 1995).
[2] J. V. Barth et al., Appl. Phys. A 76, 645 (2003).
[3] O.M. Yaghi et al., Nature 423, 705 (2003).
[4] A. Dmitriev et al., J. Phys. Chem. B 106, 6907 (2002).
[5] A. Dmitriev et al., Angew. Chem. Int. Ed. 41, 2670 (2003).
[6] M. A. Lingenfelder et al., Chem. Eur. J., in print (2004).
[7] S. Stepanow et al., Nature Mat., in print (2004).
[8] M. Wühn et al., Langmuir 17, 7605 (2001).
[9] C. Mainka et al., Surf. Sci. 341, L1055 (1995).
[10] D. S. Martin et al., Phys. Rev. B 66, 155427 (2002).

A key issue in nanotechnology is the development of conceptually simple construction techniques for the mass fabrication of identical nanoscale structures. Conventional top down fabrication techniques are both top down fabrication techniques are both energy intensive and wasteful, because many production steps involve depositing unstructured layers and then patterning them by removing most of the deposited films. Furthermore, increasingly expensive fabrication facilities are required as the feature size decreases. The natural alternative to the top-down construction is the bottom-up approach, in which nanoscale structures are obtained from their atomic and molecular constituents by self-organised growth. Self-organised growth can be driven by thermodynamic forces or be the result of kinetic processes. The archetype of a thermodynamically driven structure formation at the mesoscopic scale is molecular self-assembly. This refers to the spontaneous association of molecules under conditions close to equilibrium into stable, well defined nanostructures joined by noncovalent bonds; it is one of the key building principles of all living matter [1]. To make full use of this approach in nanotechnology we have to understand the noncovalent intermolecular interactions and to develop methods to manipulate them in a controlled way [2].

We have performed combined scanning tunnelling microscopy (STM) and synchrotron investigations addressing the bonding, ordering and surface chemistry of the related molecules 1,4-benzenedicarboxylic acid (terephthalic acid - *tpa*) and 1,2,4-benzenetricarboxylic acid (trimellitic acid - *tmla*) on the Cu(100) surface. Molecules of this type are frequently employed in 3-D crystal engineering [3] and have proven to be useful for the fabrication of nanoporous supramolecular layers [4-7]. The molecules *tpa* and *tmla* with their respective twofold and threefold exodentate functionality are shown in Fig. 1. While the formation of organic layers and nano-structures can be nicely monitored by STM, X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) resolve conclusively the deprotonation of carboxylic acid group and molecular orientation.

Distinct hydrogen-bonded assemblies were obtained at low temperature (up to 275 K) with *tpa*. The STM image in Fig. 2 reveals that molecular ribbons evolve on the square substrate. The corresponding C 1s and O 1s XPS data confirm that the *tpa* carboxyl groups remain largely complete, i.e., the well-known splitting of the C 1s peak is observed reflecting the contribution from the atoms in carboxyl and phenyl moieties at an

Fig. 2:
Low-temperature supramolecular ordering of tpa on Cu(100): H-bonded molecular ribbons clearly resolved by STM are stable up to 275 K. In the corresponding O 1s XPS data a broadened peak appears due to overlapping hydroxyl and carbonyl intensities, i.e., tpa carboxylic groups remain complete. In conjunction with the NEXAFS analysis demonstrating flat adsorption, the modeling indicates a 2-D H-bond coupling scheme.
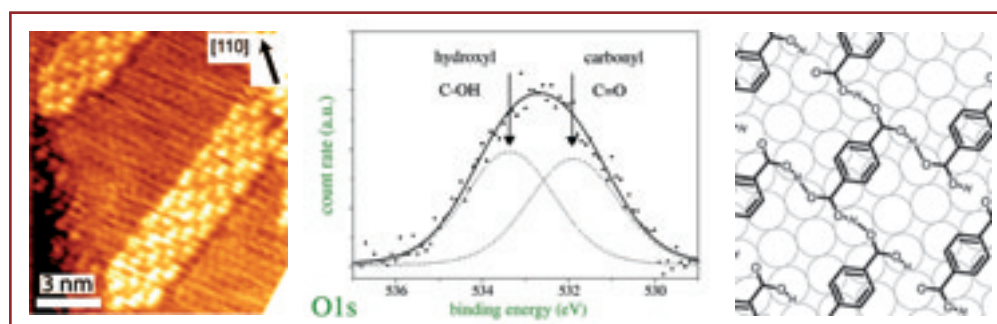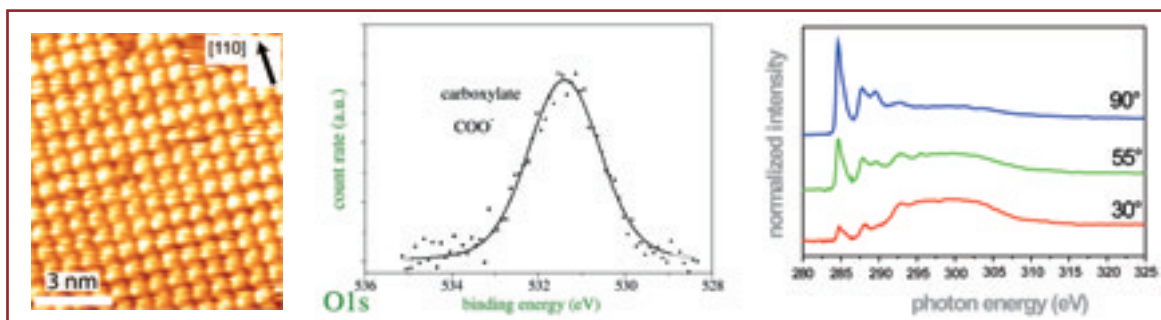
energy of 285.2 and 289.8 eV, respectively [8]. Accordingly, the O 1s peak appears broadened due to overlapping carbonyl and hydroxyl intensities (531.9 and 533.4 eV, Fig. 2). The NEXAFS analysis of this phase indicates that adsorption with the aromatic ring parallel to the substrate prevails. Interestingly, the modelling reveals that the H-bonds formed between the adsorbed molecules do not obey the R-COOH pairing motif typically observed for pure *tpa* or other carboxylic acids, rather the interplay between substrate corrugation and functional group interactions makes a lateral 2-D coupling scheme preferable. For the related case of low-temperature *tmla* adsorption (T < 200 K) synchrotron data similarly reveal flat adsorption of integral molecules. However, no supramolecular ordering could be observed by STM, which is associated with the reduced symmetry and mobility of the molecule.

At increased temperatures (T=300 - ~500 K) regular organic layers can be obtained with both molecules, already imaged by STM (Figs. 3,4). The photoemission data show that a (partial) deprotonation of the carboxylic acid groups occurs because of the catalytic activity of the Cu substrate. With tpa the formation of a biterephthalate is encountered, as deduced from the reduced separation of the splitted C 1s contributions (now at 285.1 and 288.2 eV, respectively) and the existence of a narrowed O1s peak centred at 531.4 eV (Fig. 3). Again the NEXAFS analysis reveals that the *tpa* phenyl ring is oriented parallel to the substrate lattice - the pronounced C 1s -> π^* resonance exhibits a marked intensity variation with the angle of incidence. The fact that the intensity of the resonance does not vanish completely at an incidence angle of 90° as expected for a perfectly flat lying *tpa* molecule is attributed to adsorption induced intramolecular distortions, involving a bent of the CH-bonds out of the ring plane. Such distortions of aromatic compounds interacting with metal surfaces are observed frequently [9]. Surprisingly, the STM data show that the packing density with the negatively charged biterephthalate species is increased as compared to the integral

molecule, which is associated with a lateral coupling scheme where the anionic *tpa* carboxylate groups are engaged in O···HC hydrogen bridges with phenyl rings of adjacent molecules. For comparison, on Cu(110) under similar conditions an upright standing monoterephthalate layer is formed [10]. This demonstrates that the geometry and symmetry of the substrate can be used to tune the orientation of functional organic layers. A somewhat different scenario is encountered with *tmla* layers evolving with the substrate held at elevated temperature (450 K), whose topography is shown in Fig. 4. Now the XPS data indicate merely a partial deprotonation of the carboxyl groups, which signals the formation of a monocarboxylate species. Moreover, the NEXAFS analysis of this phase clearly reveals a striking change in the bonding geometry (Fig. 4). The phenyl ring plane of the mono-trimellate is, on average, oriented at an angle of approximately 65°±5° relative to the Cu(100) surface. This observation is consistent with the only partial deprotonation of the tmla molecule, where the carboxylate anchoring is dominated by just one of the three functional groups.

Fig. 3:
A molecular monolayer with a biterephthalate species is obtained upon room temperature deposition. STM data reveal an increased packing density of the overlayer lattice oriented along [110]. While the O 1s XPS data indicate a deprotonation of both tpa carboxyl groups, the NEXAFS analysis shows that the phenyl ring is oriented parallel to the substrate lattice.
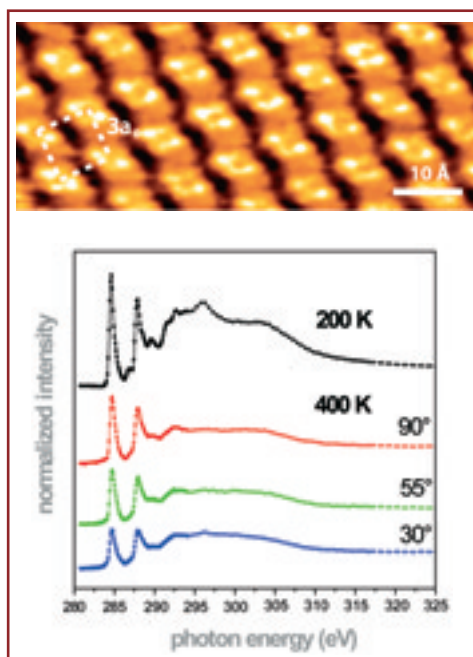
Fig. 4:
Regular organic layer upon deposition of tmla at 450 K, with a characteristic three-lobe inner structure of individual molecules in STM imaging. Corresponding NEXAFS data indicate a reorientation of the phenyl ring oriented approximately 65°±5° relative to the Cu(100) surface.

Contact
Johannes Barth
johannes.barth@epfl.ch

Thomas Strunskus
strunsku@pc.ruhr-uni-bochum.de