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Thesis Report

The thesis entitled *„Molecular Self-Assembly on Surfaces: The Role of Coverage, Surface Orientation and Kinetics"* submitted by **Anton Olegovich Makoveev** represents an in depth study of environmental parameters affecting the formation of supramolecular structures on metal surfaces and non-thermal activation of chemical changes that trigger structural transitions. The ditopic compound 4,4'-biphenyldicarboxylic acid (BDA) was studied on crystalline Ag surfaces by a set of complementary analytical techniques, namely Scanning Tunneling Micros-copy (STM), Low Energy Electron Microscopy (LEEM) and X-ray Photoelectron Spectroscopy (XPS).
Thermal annealing of BDA adsorbed on moderately reactive Ag surfaces initiates its progressive deprotonation, resulting in an extremely rich self-assembly behavior with many distinct and related phases observed. Alternatively, deprotonation has been initiated non-thermally by low energy electron beam irradiation.
Understanding the molecular processes that govern the self-assembly process is extremely important in the field, as it will eventually allow to advance the fundamental understanding and control of structure formation. In this respect, the present work is valuable to the field for three reasons: **(1)** it is very focused on a single, appropriately chosen model compound, thus allowing the direct comparison of different aspects that are important for self-assembly but not routinely considered. Accordingly, this study aims at, and ultimately provides, a consistent and more holistic picture; **(2)** a highly appropriate combination of analytical techniques is used that allows to capture all physicochemical aspects relevant to structure formation. STM, as a high-resolution real-space technique, allows direct assessment of the arrangement of molecules; LEEM provides accurate lattice parameters and, more importantly, also captures the dynamics of structural changes at the domain level; last but not least, it was extremely important for this work to assess the degree of deprotonation by XPS as a chemically sensitive method. **(3)** The use of an electron beam to induce chemical changes in the molecule as a non-thermal means of activation represents a barely studied but promising alternative. **In summary, with the scientific goals set, the combined experimental approach chosen, the aspects studied and the results obtained, the thesis is highly topical.**

The dissertation is divided into five chapters and is written in accessible, mostly correct and easy to read English. The thesis is almost free of typos and errors, with the most serious error occurring in the abstract, where the Ag(111) surface is not correctly mentioned. I could not find any obvious scientific errors. After a general introduction, the main topic of the thesis and its relevance to nano-science and -technology are clearly defined. The first chapter provides a comprehensive overview of molecular self-assembly, acknowledging the

importance of kinetic versus thermodynamic influences. Here I find the illustrations particularly useful and didactically valuable. Although quite detailed, the relevance of this elaborate fundamental chapter for understanding and interpreting the reported experimental results is not always clear. For example, various nucleation models are explained in great detail, but later on they seem to play no role. The detailed description of electron-molecule interactions is particularly important and useful, as this is not necessarily common knowledge in the self-assembly community. The second chapter briefly describes the experimental equipment and analytical techniques used in this thesis. While most of the relevant aspects are well covered, I am missing a description of the chemical shifts in XPS, which are quite relevant in the context of this work.

The following three chapters deal with the three experimental studies, each of which resulted in a peer-reviewed publication, with the candidate being first author on two of the publications. The candidate has clearly stated his own contribution according to the scientific standards for cumulative dissertations. Each publication is preceded by a paragraph, most of which is a more detailed version of the introduction of the following publication.

The study in Chapter 3 addresses the interesting question of how thermally activated phase transitions are affected by surface coverage by comparing results obtained for full monolayer and submonolayer coverages on Ag(100). Interestingly, the evolution of different phases strongly depends on the coverage, and even a previously unobserved phase appeared when heating fully covered samples. This is an interesting study of how spatial constraints affect structure formation. Everyone in the field knows the importance of coverage, but I see it is rarely studied so systematically. In addition, I would have been very interested in a more detailed discussion and modeling of the superstructures formed by fully deprotonated BDA that resulted in uneven molecular spacing.

In the next Chapter 4, more light is shed on the role of crystallographic orientation of the surface by comparing Ag(111) and Ag(100) surfaces, which is a more common approach. While the initial fully protonated and the final fully deprotonated BDA phases are essentially similar on both surfaces, differences were observed for the partially deprotonated phases, the reason for which remains unclear. In addition, a particularly interesting nucleation mechanism is described that has not been previously reported in the context of surface self-assembly. This work represents a fully consistent study and nicely demonstrates the richness of the physicochemical processes encountered with chemically diverse tectons on surfaces.

Chapter 5 deals with the non-thermal deprotonation of the carboxyl groups by an electron beam. As the candidate rightly points out, such studies are particularly interesting because they introduce a new level of possible control that cannot be achieved by mere thermal activation. For a given system, upon heating, the activation energies of the respective elementary processes determine their sequence. Remarkably, the candidate demonstrates a degree of control by showing that the phase sequence depends on the electron energy. In addition, a new phase has been observed that cannot be achieved by thermochemistry. A major asset of the present study is the very systematic approach taken, where important parameters such as electron energy have been studied in great detail. The candidate has also performed an important control experiment, namely the study of a possible influence of X-ray induced deprotonation, i.e. beam damage.

The thesis concludes with a concise summary of all three publications and a brief, perhaps too brief, outline of future research questions worth addressing. While the dissertation contains a large number of high quality experiments, the discussion is mostly descriptive. The main concept used to explain the phase transition is that deprotonation of one carboxyl group in a pair of two opposing carboxyl groups still allows H-bond formation, while deprotonation of both carboxyl groups precludes it. Nevertheless, a more detailed discussion of why these chemical changes lead to the observed structures, i.e., what determines the actual observed arrangement of molecules within the unit cell, would have added considerable value to the thesis.

In summary, Anton Olegovich Makoveev presents a series of very systematic and thorough experimental stud-ies focused on a particular model system. The chosen analytical techniques are complementary and allow for a fairly holistic understanding. Such a complete picture of a model system, i.e. a given molecule on different surface facets of a given metal, in this case Ag, is rarely obtained by carefully designed systematic studies. Although the level of theoretical understanding could still be improved, the candidate has clearly demonstrated a high level of experimental skill, his ability to analyze and interpret data obtained from different analytical techniques, and his competency to summarize the experimental results in consistent high-level publications that are interesting and enjoyable to read. The objectives defined in the introduction are fully achieved. I am convinced that the related publications will have a great impact on our research field.

In my opinion, the reviewed thesis fulfills all requirements posed on theses aimed for obtaining PhD degree. This thesis is ready to be defended orally, in front of respective committee.

Questions to the candidate:

(1) What are the possible reasons for the formation of aperiodic molecular structures on surfaces? Are aperiodic structures necessarily out of thermodynamic equilibrium?

(2) (Partial) deprotonation of carboxyl groups is clearly detected by XPS, but not by STM. Is it in principle possible to resolve deprotonation in Scanning Probe Microscopy either by imaging or spectroscopy? What signatures of deprotonation could be expected in either images or spectra?

(3) The thesis repeatedly claims that the molecule-surface interactions on Ag surfaces are only of van der Waals type. How can van der Waals interactions be identified experimentally, i.e. from accurate structural data in general? What is the rationale in the present cases for the molecules interacting with Ag surfaces only by van der Waals bonding?

(4) How does the strength (binding energy) of a cyclic double H-bond in the carboxyl dimer compare to the strength of a corresponding single H-bond? What is the reason for this cooperative effect and what are the implications for the present study?

(5) Regarding electron beam induced deprotonation: Does the lack of a clear resonance in the energy depend-ence allow an electron attachment mechanism to be completely ruled out? What is the most likely mechanism, and can this assignment be supported by means other than exclusion?

(6) Is the spatial extent of photochemical activation by light irradiation necessarily diffraction limited? How can highly localized photochemical activation be achieved?

Sincerely Yours,

Prof. Dr. Markus Lackinger