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Constructing low-dimensional molecular networks on metal surfaces

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Summary

The continuous progress in nanoscience has an impact in material science and thus, has opened new pathways for developing novel functional materials. Among them, the creation of low-dimensional molecular structures confined to surfaces has been quickly identified as a promising alternative to the conventional top-down techniques for the design and fabrication of future electronic devices. In this thesis, various low-dimensional molecular networks were successfully constructed on different metal surfaces and their structural formation was investigated in detail by a combination of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) together with density functional theory (DFT) calculations. The thesis contains two main research subjects. The first subject focuses on the construction of self-assembled structures of organic molecules on metal surfaces by employing various types of non-covalent interactions, including van der Waals interactions, halogen bonding and coordination bonding (chapters 4, 5 and 6, respectively). The second subject deals with the fabrication of covalently linked molecular networks on metal surfaces using two different chemical routes: Ullmann coupling and protecting group chemistry (chapters 7 and 8, respectively). The following gives a comprehensive summary of the findings obtained during the course of this thesis.

It is known that the formation of 2D supramolecular networks on metal surfaces strongly depends on both the chosen molecular building block and the underlying substrate. In **chapter 4**, the influence of a delicate interplay of molecule–molecule and molecule–substrate interactions on the structural formation of the 2D patterns of metal-free naphthalocyanine (H_2Nc) on Au(111) was examined in detail. Upon deposition of H_2Nc on Au(111) held at room temperature, a close-packed 2D supramolecular network was observed by STM. We found that the highly-ordered 2D network is stabilized by van der Waals interactions through interdigitation of the naphthalene units of the H_2Nc molecules. Based on the combination of the information obtained from STM, LEED and XPS measurements, we could demonstrate that the Au

substrate has a weak but not negligible influence on the molecular self-assembly process. A dominating intermolecular interaction was found to be responsible for the network formation while the underlying substrate determines the molecular orientations.

Halogen bonding (X-bonding) has recently attracted a great deal of attention as a valuable tool for tailoring molecular self-assembly on metal surfaces due to the directionality and tunability compared to other non-covalent interactions. However, in order to effectively employ X-bonding for the design and construction of supramolecular networks on metal surfaces, a detailed understanding of the role of the halogen substituents with respect to the structural formation of such molecular networks is highly required. With this in mind, we investigated the self-assembly of two different brominated pyrene derivatives on Au(111) (see **chapter 5**). Namely, we choose 1,3,6,8-tetrabromopyrene (Br_4Py) and 2,7-dibromopyrene (Br_2Py), which possess four and two functional bromine groups, respectively, at different substituent positions. On the basis of the information obtained from STM and LEED measurements, supported by DFT calculations, we concluded that the 2D self-assembled patterns of Br_4Py are stabilized by both X-bonds and Br-H hydrogen bonds, while the 2D pattern of Br_2Py is exclusively driven by Br-H hydrogen bonds. Thus, by varying the number and positions of the bromine substituents, the possibility to steer the resulting intermolecular interactions, which are responsible for the network formation of the pyrene derivatives on Au(111), is opened up. Additionally, we discovered an up to now not reported fourfold halogen interaction motif on Au(111), which is dependent on the choice of pyrene derivatives (Br_4Py). Our results are expected to deliver significant information for using X-bonding to controllably construct on-surface supramolecular assemblies.

Metal-ligand coordination bonding is currently regarded as an important tool for the construction of low-dimensional molecular networks on metal surfaces due to the possibility to steer both the size and geometry of the molecular networks by the choice of organic ligands and transition metal centres as well as the underlying substrates. Moreover, the strength of coordination bonds is higher than that of hydrogen bonds, which offers the possibility to build-up robust molecular networks on

metal surfaces. In this context, although various molecular coordination networks were reported till date, the formation of such molecular networks on Au surfaces with native Au atoms (without the addition of transition metal atoms) is very rare and not well understood. In **chapter 6**, we show that 1D coordination polymers of cyano-substituted porphyrin derivatives can be obtained on Au(111) upon thermal annealing. The polymer is stabilized by an unusual threefold coordination motif formed between a native Au adatom and the nitrogen atoms of three cyano groups of the porphyrin derivatives. This conclusion is strongly supported by the formation of similar 1D coordination polymers with the same binding motif upon Co deposition onto the porphyrin-covered Au(111) surface. Interestingly, the Au step edges were found to induce a fourfold coordination motif, which might be exploited to build up straight 1D polymers when using vicinal Au surfaces. Moreover, the possibility to tune the dimensionality of the molecular networks from 1D to 2D is given by varying the position of the cyano functional endgroups, i. e. via the choice of a *cis*- or *trans*-isomer of the porphyrin derivative.

Over the recent years, on-surface polymerization based on Ullmann coupling has been proven as the most versatile protocol for the fabrication of 1D/2D covalently-linked molecular networks on metal surfaces. However, the impact of the underlying substrate on the on-surface polymerization process still is not fully understood. In **chapter 7**, we investigated the role of different underlying substrates (Cu(111) and Au(111)) in the on-surface polymerization of 1,3,6,8-tetrabromopyrene (Br_4Py) by a combination of STM and XPS measurements and DFT calculations. We found that the chosen substrate does not only play an important role as catalyst for the debromination reaction, but also determines the polymer network morphology. Our results are expected to add significant information for a more detailed understanding of the on-surface polymerization based on Ullmann coupling, also in view to gain more control over the outcome of the polymerization process.

Although the on-surface polymerization based on Ullmann coupling has many advantages, the presence of halogen atoms on the surface after the Ullmann reaction represents a main drawback because they may prevent the formation of long-range ordered polymer networks. These halogen atoms cannot always be desorbed from the

surface by thermal annealing without destroying the newly formed polymer. Therefore, a “clean” on-surface polymerization process in which no halogen atoms are released during the coupling reaction is highly desirable. With this in mind, we developed a new approach for the on-surface polymerization using the concept of protecting group chemistry (see **chapter 8**). The main advantage of this approach in comparison to the on-surface Ullmann coupling is that the cleaved protecting groups can be easily desorbed from the surface upon annealing. Thus, no by-products can influence on the formation of desired polymer network on the surface. In this work, the stepwise growth of covalently-linked polymer networks of a biphenyl derivative on Ag(111) was observed by a combination of STM and XPS measurements and further investigated by DFT calculations. By varying annealing temperature and time, the monomers can be linked up to dimers, trimers or one-dimensional (1D) polymer chains. Moreover and unexpectedly, the co-existence of different covalent bonding motifs within the formed polymer networks was observed. Thus, the obtained results in this chapter are expected to represent a new paradigm for the tailored construction and design of polymer networks on metal surfaces with a high degree of order.