論文審査の結果の要旨

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The present thesis presents the self-assembly and electronic structure of aromatic molecules on metal surfaces. In order to gain insight into the effect of lateral interactions and molecular orientation on the self-assembly and electronic structure of adsorbates, the study was performed by combining complementary techniques: scanning tunneling microscopy (STM) and spectroscopy (STS) at 4.7 K, near edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS). The thesis consists of 6 chapters. Chapter 1 presents the background and purpose of the present research. Chapter 2 describes the experimental techniques. Chapter 3 focuses on the self-assembly of functionalized aromatic molecules, while Chapter 4 present the electronic structure of these molecules. Chapter 5 presents the tunneling electron induced chemical reactions of 4-aminobenzenetiolate ($4\text{-}NH_2\text{-}C_6H_4S^-$) on Cu(110).

Chapter 1 introduces the background and purpose of the present research. Lateral interactions and molecular orientation of adsorbates on metal electrodes critically impacts their self-assembly and electronic structure and could have important applications for functional materials and organic molecular devices.

Chapter 3 describes the self-assembly of functionalized aromatic molecules on metal surfaces: benzoic acid (C_6H_5COOH) on Au(111), benzoate ($C_6H_5COO^-$) on Cu(110) and meta-aminobenzoate ($3\text{-}H_2NC_6H_5COO^-$) on Cu(110). Benzoic acid molecules physisorb on Au(111) and form dimers via hydrogen bonding while they chemisorb after deprotonation in the form of benzoate molecule on Cu(110) due to the higher reactivity of the substrate. Molecular models were proposed for the self-assembly of benzoate on Cu(110) to explain the complex coverage-dependence of the self-assembly. The self-assembly of meta-aminobenzoate was characterized with STM and revealed a variety of superstructures and molecule-surface angles.

Chapter 4 presents the effect of lateral interactions and molecular orientation on the electronic structure of benzoate, para-aminobenzoate ($4\text{-}H_2NC_6H_5COO^-$) and meta-aminobenzoate on Cu(110). The study reveals a molecular orientation-dependant electronic structure, which consists of an upward energy shift of the LUMO level accompanied with downward energy shifts of the O1s and C1s core-levels and an upward energy shift of the N1s core-level of up-right molecules as compared to flat-lying molecules. The origin of the energy shifts turned out to be orientation-dependant charge transfers between the molecules and the metal electrode.

Chapter 5 shows that it is possible to induce a change of molecular orientation of selectively dissociate a chemical group from 4-aminobenzenethiolate molecules on Cu(110) by tuning the energy of tunnel electrons injected from an STM tip into the molecules.

Chapter 3 contains contributions from Prof. Maki Kawai, Dr. Yousoo Kim and Dr. Sylvain Clair. Additionally, Chapter 3 includes courtesy images from Mr. Masafumi Hori and Dr. Satoshi Katano. Chapter 4 contains contributions from Prof. Maki Kawai, Dr. Yousoo Kim, Dr. Yasutaka Takata, Dr, Jun Miyawaki, Prof. Shik Shin and Mr. Shinji Doi. Chapter 5 contains contributions from Prof. Maki Kawai, Dr. Yousoo Kim and Dr. Lee Hyun-Sook. The main contribution of the full thesis is the work of Caroline Rabot.