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Extended Abstract

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Manipulation of single molecules at surfaces: switches, wires and motors

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Molecular nanotechnology aims to use functional molecules as individual machines or electronic devices. Hence, their self-assembly into pre-defined architectures and the full control over each individual molecule are key objectives. Various examples of functional molecules, ranging from molecular wires to molecular switches and machines that are studied and manipulated at the single-molecule level by scanning tunneling microscopy (STM) under ultrahigh vacuum conditions, will be discussed in this presentation. Molecular wires or molecular nodes with different conjugation pathways can be fabricated from specifically designed molecular building blocks that are connected to two-dimensional networks or one-dimensional chains.

In the case of molecular switches, the switching rate can be tuned up and down by only one single atom in the vicinity of the molecule. The same effect is then extended to molecular assemblies where cooperative effects in single molecules are directly observed. The switching process can also be used to trigger a molecular motor where the lateral translation of molecular machines on a surface can be enhanced by light of specific wavelengths that match the absorption properties of the molecule. By comparing molecules with and without a motor unit, the enhanced motion can be directly assigned to the motor that is incorporated in the molecules. STM manipulation gives detailed insight into the physical and chemical processes at the single-molecule level by varying the relevant parameters as tip height over the surface, bias voltage or tunneling current. While the speed is typically of minor importance in these experiments, it becomes crucial when studying so-called nanocars. By implementing a dipole moment into the molecular structure, we could show that very efficient and therefore fast manipulation can be realized. The key property is that no continuous imaging is required, rendering the manipulation fast enough to win the first nanocars race.

The use of functional molecules as electronic devices and their self-assembly into pre-defined architectures are key objectives of molecular nanotechnology. In this presentation, various types of functional molecules, adsorbed at surfaces and studied by scanning tunneling microscopy (STM), will be discussed. STM is not only capable of high-resolution imaging, but also the manipulation of single molecules. Typically, this is used to get insight into the molecular function, but molecules can also be studied in view of fast lateral motion that could be achieved by specific molecular side groups and an improved manipulation protocol.

To construct molecular wires from the bottom-up in a highly controlled fashion, specifically designed molecular building blocks are connected by "on-surface polymerization". When pulling with the STM tip, not only the electric current through a single molecular wire can be measured but also various charge transport channels – with different chemical conjugations – can be identified in non-symmetrical molecular nodes. An important issue for any molecular function is the role of the direct environment. It will be shown for different types of molecular switches (based on isomerization or tautomerization) how their atomic scale surroundings determine their function, leading to periodic switching patterns for azobenzene derivatives and control over the switching by only one atom in the vicinity of a porphycene molecule. By using isomerization-based molecular motors, photo-induced translation of molecular machines is observed on a metal surface. The effect vanishes if an incompatible photon energy is used or if the motor unit is removed from the molecule, revealing that the enhanced motion is due to the presence of the wavelength-sensitive motor in each molecule. Molecular switches and motors respond structurally, electronically, optically, and/or mechanically to external stimuli, testing and potentially enabling extreme miniaturization of optoelectronic devices, nanoelectromechanical systems, and medical devices. Assembling motors and switches on surfaces makes it possible both to measure the properties of individual molecules as they relate to their environment, and to couple function between assembled molecules. In this review, we discuss recent progress in assembling molecular switches and motors on surfaces, measuring static and dynamic structures, understanding switching mechanisms, and constructing functional molecular materials and devices. As demonstrative examples, we choose a representative molecule from three commonly studied classes including molecular switches, photochromic molecules, and mechanically interlocked molecules. We conclude by offering perspectives on the future of molecular switches and motors on surfaces. Molecular landers are molecules comprising of a central rigid molecular wire maintained above a metallic surface by organic spacers, which allows specific ultrahigh vacuum-scanning tunneling microscopy experiments to be performed at the single-molecule level. The understanding of the molecule–surface interactions, intramolecular mechanics, and the possibility to perform extremely precise tip-induced manipulation permit these molecules to be brought in contact with a nanoelectrode and the resulting electronic interaction to be analyzed in well controlled conditions.

Bottom Note: *This work is partly presented at 5th International Conference on Physical and Theoretical Chemistry October 11-13, 2018, Edinburgh, Scotland*