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“Development of a toolbox of organic synthetic reactions that can be induced on individual molecules by STM”

Abstract

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The key scientific objective of this project is the development of a set of reliable techniques for the addressal of specific bonds of individual molecules in order to assemble functional molecules on a metal surface at single-atom precision. Success in this direction will open up a conceptually novel route to single molecule chemistry, which can provide its products at *any desired surface location* without involving any lithographic steps at all. In the course of this project a number of halo-substituted aryls and alkyls were investigated with special concern to two properties: clean deposition of the reactants from the gas phase on metallic surfaces and STM-based addressability of individual substituents of them. In order to prevent contamination of the sample by deposition of solvent residue, a special depositions source was developed that uses a skimmed molecular beam. Exemplary substances studied were 1,3-iodobromobenzene (IBB), 3-bromopropionitrile (BPN) and 4,4'-dibromobiphenyl (DBB). In STM-induced reactions, IBB shows concerted activation of both halogens, which does not allow the individual addressal of one bond at a time. The concept of individual addressabilities of bonds in bi-substituted

molecule was confirmed by use of BPN. This reactant is, however, strongly bound to the substrate and, hence, not very suitable for the assembly of larger aggregates, even if the nitrile group could be activated. We found individual activation of one of the bromines of DBB. This molecule lies flat on the surface and it is a promising candidate for the assembly of larger molecular aggregates, if ever future research will address STM-based molecular assembly.

In order for STM-based assembly of molecular structures ever to become useful, the rigid attachment of the resultant product molecules to the substrate is a requirement. Unsubstituted aryls are mobile on Cu surfaces even at liquid nitrogen temperatures. In many molecular schemes aromatic thiols have shown good substrate attachment at sufficient electrical conductivity even at ambient temperatures. We investigated the possibility of depositing aromatic thiols on Cu(111) at low enough temperature, so that the thiolates is not formed spontaneously. Subsequently, we could form the thiol substrate bonds at will on molecules that were located at desired surface location. We also identified effects of surface induced chirality on the adsorption behavior of such molecules.

In summary, during this two-years project a molecule suitable for controlled intermolecular attachment was identified. The deposition of the molecules was optimized and a route to proven substrate attachment was established.

Equipment and Facilities

This project was addressed using a low-temperature scanning tunneling microscopy setup completed in the summer of 2001, which was originally funded by a DURIP Equipment Development Grant of the Air Force.

The equipment consists of an ultra-high vacuum chamber complete with pumping system, mass spectrometer, sample heater, sputter gun, etc. In the project duration a deposition system for the desired reactants was developed. This involved a heatable reactant container, a thermally controlled transfer tube and a series of shutters and valves.

Personnel

Following a broad search, a postdoctoral researcher was hired to support this project. Unfortunately, Dr. Liu, who was originally anticipated to perform the majority of the measurements and experiments anticipated here, has not been available, as by the time the project was approved he had already committed himself to work on the set up of an STM facility at UCR, a project funded by the NSF. In fall of 2001 Dr. Rao Bomisetty was be hired, who has extensive scanning probe experience from his previous work on semiconductor nanoscience in Tokyo, Japan.

Considerable amount of training in vacuum preparation, maintenance and integrity were necessary, in which a number of first- and second-year graduate students (Ki-Yong Kwon, Qibin Zhang, Robert Perry, Erick Ulin, Jintao Zhang, Xing Lin) and three undergraduate student (Gregory Pavin, Casey Dugger, Luke Nysen) were included. These students received support from this DOE grant during the summer months (with one exception). A broad range of issues had to be addressed in order to allow safe operation of the system and to prevent errors from occurring or having an overly adverse effects on the project. As the graduate students all started their graduate studies in the course of this project, their work in the lab had predominantly educational value.

Experimental Procedure

The PI joined the University of California in the summer of 2000. During the last 3 years he set up his lab and designed and built a new low-temperature STM system including the scanner, the cryogenic-unit and the remaining vacuum chamber and he realized his own control-electronics and –software. The investigation funded here focused on both experimental improvement and the excitation of molecular reactions in five different systems: 4,4'-di-bromo-biphenyl (DBB), 1,3-iodo-bromo-benzene (IBB), 3-bromopropionitrile (BPN) and 2,5-di-chloro-thio-phenol (DCTP) as well as 4-bromo-thio-phenol (BTP).

On the experimental side, the setup of a molecular beam type evaporation system was realized, which is specifically suitable for the deposition of low vapor-pressure organic compounds (Fig. 2). The deposition of halo-substituted aromatic molecules is somewhat more difficult than the adsorption of CO or similarly small molecules onto metal surfaces: generally, halo-substituted aromatic molecules have melting points exceeding room temperatures but decompose or evaporate completely at temperatures typical for vacuum chamber bake-out. The relatively high melting point makes it hard to introduce them into UHV through a leak valve and the low temperature of complete evaporation prevents introduction into a Knudsen-type evaporator inside the UHV chamber before bake-out. The task is further complicated by the fact that better purity than 99% is often hard to obtain, even if various types of chromatography are used for the purification of commercial

compounds. As a consequence, if these reactants are heated to produce sufficient vapor pressures for UHV experiments, the resulting pressure is often composed predominantly of solvent residue and decay products. In order to achieve clean adsorbate populations we

set up a differentially pumped evaporator source consisting of a glass capillary, which can be heated from the outside and which is evacuated by an oil-free scroll pump to better than 10^{-3} torr. From here the molecules can be passed in line of sight through a tiny orifice into a small chamber (composed of a 2 3/4" T-piece), which is pumped by a turbo pump. A second, aligned orifice allows the molecules into a 2 3/4" X piece with a shutter at its entrance. Here, a mass spectrometer can be used to ascertain the purity of the arriving molecules. When satisfactory molecular flux is reached, a gate valve is opened, which passes the molecular beam into the main vacuum chamber and directly onto the sample. This system became fully operational towards the end of the funding period; the majority of the experiments described below were specifically designed to use molecules with relatively high vapor pressure, which do not require this setup.

Results

We investigated the deposition and excitation of 1,3-Iodobromobenzene (IBB) on a Cu(111) surface. The figure on the right shows the mass-spectrum of IBB in our chamber prior to deposition along with the NIST reference data. The agreement is satisfactory and allows for the preparation of clean coverages of 1/1000 of a monolayers on the surface. We find that IBB molecules diffuse to the step edges at 15 K. Here, they appear as elongated protrusions that are aligned with the step edge and topped at one side by a tip. The model shows two IBB molecules attached to a step edge. The horizontally bound halogens point towards each other. The STM image on the bottom left shows two molecules in the same position.

Attachment of electrons from the tunneling current to one of the molecules can cause abstraction of both its halogens. The minimum electron energy to induce abstraction is 1400 meV. The STM image on the bottom right shows the molecules after halogen abstraction. Clearly the excitation process is local enough not to affect neighboring molecules. There are two fragments visible on the higher terrace. Additionally, a barely visible protrusion at the lower step edge shows the new adsite of one of the halogens. Similar experiments

performed on isolated molecules on a flat terrace confirm that both halogens are split off simultaneously albeit the difference in their binding energy.

The concerted abstraction of both halogens, however, prevents the use of IBB for the assembly of larger organic structures, as the product is immobile on the surface.

In order to understand the generality of the problem, we used 3-bromo-propionitrile (BPN) to investigate, whether individual abstraction of one substituent becomes possible, if sufficiently disparate substituents are incorporated into a molecule. The figure on the right shows a BPN molecule before addressal by the tip. The molecule adsorbs next to a step edge and is shown as pointed protrusion followed by a broader but less high one. We assume the prominent feature to be the alkane group, which has to protrude from the surface due to steric repulsion between its hydrogens and the substrate. The second image shows the same molecule after excitation. Electron attachment split it into two parts, one of which is attached to the step edge, the other is located at some spacing from it.

We performed experiments on 4,4'-dibromobiphenyl (DBB) to investigate electron attachment to further separated halogen atoms. The graph on the right shows the mass spectrum of DBB obtained in our chamber before dosing.

STM images of 3-bromo-propionitrile adsorbed at the step edge of Cu(111) at 15K (14 Åx14 Å, bias -400 mV, I=114 pA).

Mass spectrum of 4,4'-di-bromo-biphenyl (DBB) (red) and NIST reference data (blue).

(top) STM-image mage of a DBB molecule adsorbed at a step edge of a Cu(111) substrate at 15K (26Åx16Å, bias=200 mV, I=140 pA. The molecular axis is aligned with the step edge. Prior to imaging, DBB was excited and one bromine atom was removed from the left side. (middle). A linescan across the molecule along the red line confirms this. (bottom) Schematic representation of the IBB adsorption geometry

Around 100 amu some weight is found, that is not part of the NIST spectrum and most likely stems from solutions residue in the commercial compound. This experiment was performed before the new dosing system became available. The contamination becomes apparent as streaks in the STM image on the right.

The image on the previous page shows a DBB molecule after electron attachment to one of its sides. An asymmetric shape of the molecule results. The asymmetric nature of the excitation products makes it clear, that separated addressal of the individual species is possible. Consequently, DBB is a promising candidate for future experiments in STM-based molecular synthesis.

A key problem with the assembly of functional molecules by STM is that a reliable scheme for their attachment to the substrate is required. Unsubstituted aryls diffuse rapidly on Cu(111) even before nitrogen temperatures are reached. Typical molectronic schemes utilize thiols to attach functional molecules to metallic surfaces. Hence, we addressed the anchoring of thiols to predetermined surface sites by STM.

We deposited ultra-low coverages of DCTP and BTP on a Cu(111) surface at 15K

and observe ‘flower-like’ features. Using atomic corrugation for reference, they appear to be significantly larger than the molecular diameter (figure on previous page). Careful investigation of these features shows, that they originate from the rotation of a single molecule around a sulfur substrate-anchor through 6 (DCTP)/ 12 (BTP) ‘identical’ adsites, in each of which the halogens are located in hollow sites of the substrate. STM-based vibrational spectroscopy (d^2I/dV^2 spectroscopy) shows a pronounced peak on these molecules between 300 and 350 mV, which is similar to the gas-phase S-H stretch mode. Intramolecularly two-fold coordinate sulfur, as e.g. in thiophene, is known to absorb at on-top positions, which matches well with the on-top position of the center of these features.

Due to the asymmetric Cl-substitution of DCTP, once the molecule is adsorbed on the surface, there are two chiral DCTP-substrate complexes. In one of them the molecule appears to rotate to the left, in the other to the right. However, this appearance rather reflects the handedness of the adsorbate substrate complex than the true rotation direction, which is unknown. The higher symmetry of BTP allows for 12 identical adsites, which come in six pairs of closely adjacent ones.

Injection of electrons in excess of 300 mV (DCTP)/ 500 mV (BTP) can transfer the

‘flower’-shaped species into a single protrusion which comes to rest between the petals of the original flower at $\frac{1}{2}$ adsite offset. d^2I/dV^2 spectra of the resultant molecule do not show the S-H mode. Hence, we assume that we succeeded in the controlled abstraction of hydrogen from the molecule. The product molecule is bound with the sulfur in a hollow site. This leads to a tighter substrate bond, which prevents the molecule from rotating. This result underlines the applicability of thiol-coupling for secure anchoring of molecules even on the individual molecule scale.

We investigated the hydrogen abstraction from DCTP in detail and find that at 500 mV energy the abstraction rate depends linearly on the applied current indicating a one-electron process. 500meV is insufficient for a twofold excitation of the S-H stretch mode which, hence, cannot correspond to the coordinate relevant for the abstraction process. We developed a model for hydrogen abstraction based on excitation of the Cu-S-H bending mode through transient charging of the molecule. This mode is lower in energy and can be excited to a high overtone by the available energy.

We investigated the controlled lateral translation of individual deprotonated BTP

molecules. Lateral manipulation of the reactants is a crucial step of the assembly of functional objects on surfaces. The bromophenylthiolate appears as an elongated protrusion, which is associated with an apparent indentation of the substrate on the side where the sulfur is attached. In the figure a large number of lateral manipulation events can be seen. The tip movement direction is indicated by the yellow arrows and shown at an offset for clarity. Each of the manipulations proceeded using 100mV tunneling current and a setpoint current of 6 nA. From the images it is apparent, that the lateral manipulation is successful, if the molecule is pulled by its bromine side. The sulfur side functions as an anchor on the surface and always drags behind. This leads to the rotation of the molecule during lateral manipulation: after manipulation is finished, always the side with the bromine points in the manipulation direction and the sulfur side points towards the initial side.

We acquired tip height traces before, during and after lateral manipulation. In the traces before and after manipulation the initial and final positions of the molecule can be made out. The trace during manipulation bears witness of the tip approaching the initial site of the molecule. A pronounced step shows how attractive interaction between the tip and

the molecule turns the latter towards the tip, which causes a step-like retraction of the tip. Then the bromine side of the molecule is smoothly rotated around the sulfur anchor thereby following the tip movement along the manipulation path. Once rotation is not sufficient anymore to keep the bromine side in close proximity to the tip, the molecule starts to perform single adsite hops trailing the tip motion.

Such high-precision modifications of the position and orientation of a single molecule may be useful for both assembly of molecular structures and information storage.

We investigated higher coverages of DCTP and BTP in order to ascertain that these molecules behave similar to molecules used in molelectronics. With increasing coverage of DCTP on Cu(111) at 85K we find a succession of step-edge decoration, islands formation, aggregation of the molecules in extended patches of local order, the formation of ordered films of flat lying molecules and, finally, a quasi-disordered film with molecules standing upright.

Notably, we find that there are only three orientation of the Cl-Cl-axis of the molecule on the surface, independent both of the nature of the hollow site (hcp or fcc) and

the chirality the molecule is adsorbed in. Thus, we find exclusively three orientations of the elliptical feature that represents the molecule on the surface (part a of figure on the bottom).

Disordered coverages show a clear shell pattern in neighbor separations. For molecules at closest proximity, a smaller separation is found, if they are lying side-by-side rather than head-to-tail (figure on the right).

The ordered film at intermediate coverage shows rows of pairs of molecules. Some of these rows run parallel to the step edges and represent a 7×2 superstructure. The remainder of the rows is angled by 18° towards them. Its unit cell is sheared by one Cu-Cu-spacing with respect to the 7×2 cell. Both unit cells have the same area and careful analysis of a large number of images shows, that they are each filled with a pair of molecules of identical chirality. Consequently, continuous films of such structures require dislocations, at which they can switch between molecular handedness in order to accommodate a racemic mixture on the surface. These are shown in the bottom of this page. We conclude that chiral recognition is an important aspect of pattern formation even in the presence of otherwise very strongly interacting thiol- and halo-groups.

While at intermediate coverage the molecules lie horizontally on the surface, at increases coverage the competition between sulfur groups and aryl rings for substrate sites forces the latter in an upright position. Initially, upright molecules are found at the dislocation lines between patterns of opposite helicity. The formation of upright molecules rather than a compressed film suggests that the ortho-halosubstitution renders the upright orientation of the molecule more stable than it is the case for unsubstituted molecules. The bottom figure of the previous page shows, that we can turn a molecule into the upright position by use of the STM tip.

A number of publications are presently in various stages of completion. Most advanced is an article on the deprotonation of DCTP, which is slated to appear in one of the November issue of the Journal of Chemical Physics. Other articles are in the review process.

This work was presented on the following occasions:

University of California at San Diego, Physical Chemistry Seminar, Oct. 2002

University of Southern California, Physics Seminar, Nov. 2002

AVS National Meeting, Denver, Nov. 2002

GRC on Chemical Reactions at Surfaces, Ventura, Feb. 2003

International STM Conference, Eindhoven, July 2003

Freie Universitaet, Fachbereich Physik, Berlin, July 2003

GRC on Dynamics at Surfaces, Andover, Aug. 2003