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Single-Molecule Manipulation

Chirality Change of Chloronitrobenzene on Au(111) Induced by Inelastic Electron Tunneling**

*Violeta Simic-Milosevic, Jörg Meyer, and Karina Morgenstern**

The uniform chirality (single-handedness) found for the essential molecules of life is one of the great mysteries in science. Natural sugars are almost exclusively right-handed, whereas natural amino acids are almost exclusively left-handed. Current life forms could not exist without the homochirality of these monomers. Ever since the famous experiment of Pasteur,[1] scientists have tried to generate excess left- or right-handed chiral molecules from achiral precursors without the intervention of preexisting molecular chirality. This problem, called absolute asymmetric synthesis, has turned out to be a major challenge.[2]

Scanning tunneling microscopy (STM) offers the fascinating possibility to image and manipulate single molecules. The first determination of the chirality of an individual molecule was performed using STM[3] and was soon followed by a repetition of Pasteur's experiment at the nanoscale.[4] In this experiment, clusters of prochiral molecules were sorted on a surface according to their chirality.

The orientation of molecules adsorbed on surfaces is determined by the detailed adsorption dynamics. The random orientation of prochiral molecules in the gas phase is converted into two possible enantiomers with equal probability on a surface.[5,6] Recently, it was shown for one particular case that this chirality might change thermally, despite the high energy usually needed to lift part of a molecule from the surface.[7]

Herein, we outline the possibility of changing the chirality of a randomly adsorbed prochiral molecule to give the desired enantiomer as well as the possibility of changing the rotational angle of the molecule, within limits. We investigate chloronitrobenzene ($C_6H_4ClNO_2$, abbreviated ClNB) on reconstructed Au(111), for which we determine threshold energies of approximately 260 and 380 meV for electron-induced chirality change and rotation, respectively.

The measurements were performed with a custom-built 5 K STM instrument housed in an ultra-high-vacuum chamber that is equipped with standard equipment for sample preparation.[8] We adsorbed *para*-ClNB molecules at 17 K on the clean Au(111) sample. Measurements were performed at 5 K.

Adsorption of *para*-ClNB on Au(111) leads to all three isomers, *ortho*-ClNB, *meta*-ClNB, and *para*-ClNB (Figure 1). This finding indicates that the molecule isomerizes on contact with the surface, even at 17 K. Images with submolecular resolution (Figure 1) are interpreted on the basis of previous adsorption experiments of nitrobenzene ($C_6H_5NO_2$) and ClNB on Cu(111) in connection with tight-binding calculations[9,10] and in agreement with semiempirical electrostatic potential (ESP) map calculations.[11] Both calculations suggest that the nitro group dominates the STM images of ClNB. The nitro group is imaged as an ellipsoidal protrusion of 110 to 120 pm in height on the face-centered cubic (fcc) domains of Au(111). The chlorine atom appears as a less prominent circular protrusion with an apparent height of 70 to 80 pm. In contrast to the situation on Cu(111), the aromatic ring is not visible on Au(111). Calculations suggest that the ring is not visible if the hydrogen atoms are in the plane of the carbon ring atoms.[9] As shown in Figure 1, the STM images of different isomers are discriminated through the relative position of the chlorine atom with respect to the nitro group. For the *meta* isomer, the angle between the long axis of the ellipsoid and the connection of the center of the ellipsoid with the circle (56°) is the same as on Cu(111).[9,10]

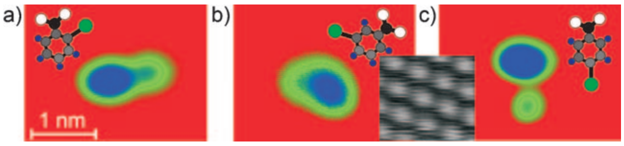

Figure 1. STM images of ClNB isomers on fcc domains of Au(111). The ball-and-stick depictions show the orientation of the molecules in the STM images. Cl green, O white, N black, C gray, H blue. a) *ortho*-ClNB, b) *meta*-ClNB, c) *para*-ClNB; red (lowest) to green to blue (highest) scale, in which the nitro group is blue and the chlorine atom green; inset: atomic resolution (to scale).

Even if we concentrate on only the *meta* isomer (Figure 1 b), a multitude of adsorption geometries are possible. Figure 2 a, b shows two out of six rotational orientations found after adsorption. The substituents point towards the ⟨110⟩ directions of the surface (cf. inset in Figure 1). Figure 2 c shows the other enantiomer in a different rotational orientation than in Figure 2 a, b. Thus, in total, the *meta* isomer might be found in one of 12 different adsorption geometries.

We employ inelastic electron tunneling (IET) manipulation[12] to alter the chirality of the molecule. IET is performed by first moving the tip above a specific part of the molecule.

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[*] Dr. V. Simic-Milosevic, J. Meyer, Prof. Dr. K. Morgenstern
Institut für Festkörperphysik, Abteilung Atomare und Molekulare Strukturen (ATMOS), Leibniz Universität Hannover
Appelstrasse 2, 30167 Hannover (Germany)
Fax: (+49) 511-762-4877
E-mail: morgenstern@fkp.uni-hannover.de

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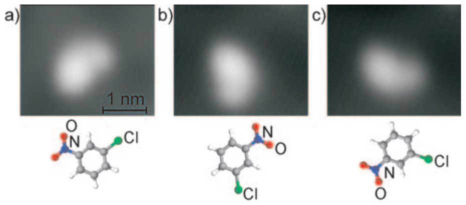

Figure 2. Different orientations and chiralities of *meta*-ClNB molecules with ball-and-stick models oriented as in the STM images (51 pA, 100 mV): a) *meta*-ClNB-r; b) different *meta*-ClNB-r orientation rotated by −120° with respect to (a). c) *meta*-ClNB-l; "r" and "l" denote that the chlorine is attached to right-hand and left-hand side, respectively, of the nitro group.

Then the feedback loop is switched off and the bias voltage is increased to a preset value. The tip–sample distance and voltage are kept fixed for several seconds while the tunneling current is recorded. Finally, the result of the manipulation is confirmed by imaging the same area again. IET has been used to manipulate individual molecules through bond breaking and formation[13–19] and isomerization,[20–24] but it has not been used for chirality changes to date.

Because of the statistical nature of IET, the exact outcome of the reaction is, however, often unpredictable. We outline how we can change an arbitrarily adsorbed molecule into a desired adsorption geometry by first changing its chirality and then its rotational orientation by IET manipulation. Figure 3a–c demonstrates that the chirality of a *meta*-ClNB molecule can be changed reversibly at 300 meV. This change could be explained either by a flip of the molecule, where the chlorophenyl group is transiently lifted from the surface, or by simultaneous isomerization and rotation. However, the nitro group stays stationary during this chirality change. The same result is observed in most other cases, whereas rotation (see below) can lead to many different final orientations. Moreover, the current–time (*I*–*t*) characteristics change between only two values. Therefore, we suggest that the chlorophenyl group is lifted from the surface and flipped while the oxygen atoms of the nitro group stay in close contact with it. This interpretation is further corroborated by the determination of the rotational barrier (see below).

For this flipping process, it is essential that the tip–sample distance exceeds the height of the molecule in an upright position. We estimate this distance by comparison to earlier measurements of water nanocrystallites, in which the tip was found to touch the crystallites (3.2 nm high) at tunneling parameters of 8 pA and 2 V.[25] On the basis of standard tunneling theory with the gold work function of 5.3 eV, we calculate that the distance is approximately 3 nm at the manipulation parameters of 40 pA and 300 mV used here. This distance is large enough for a molecule with a Cl−O separation of 0.62 nm to rotate below the tip without touching it.

During the first manipulation shown in Figure 3d, the current changes three times between 40 and 17 pA, indicating that the chirality changes three times. The same current values are observed for the reverse change. We extended our STM code to influence the outcome of the manipulation. The current value identified in the *I*–*t* plot is used as a threshold. As soon as this threshold is crossed during the manipulation, the voltage is automatically reduced to imaging conditions.

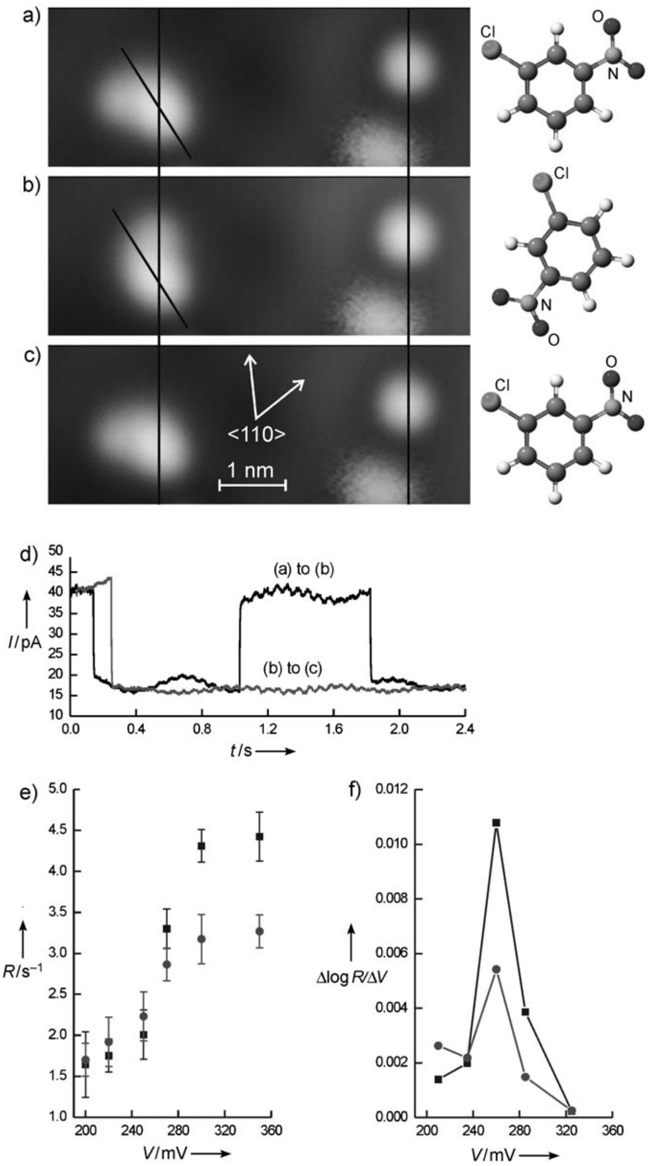

Figure 3. Change of *meta*-ClNB on an fcc domain of Au(111). a)–c) Excerpts of a series of more than 100 reversible chirality changes by IET manipulation with 300 meV and 40 pA for 2.4 s. Lines serve to guide the eye: right line: no measurable drift during manipulation series; left line: nitro group is stationary during manipulation; tilted lines: mirror planes; 11 pA, 100 mV; ball-and-stick models indicate the orientation of the molecule. d) Current during manipulation. e) Reaction rate as a function of voltage for injecting electrons into the center of the chlorine atom (■) and at a distance of 0.4 nm from it (●). f) Change in slope of log *R* from (e).

To elucidate the excitation mechanism, we repeated the chirality change for six different manipulation voltages between 200 and 350 meV, three different currents (45, 120, and 280 pA), and two injection points: for the first injection point, we position the tip directly above the chlorine atom; for the second one, we move it by 0.4 nm towards the nitro group. From the *I*–*t* characteristics we determine the time between the current changes (Figure 3d) and thus the reaction rate.

The dependence of the rate on current is linear for both injection points. The distribution of residence times in the low- and high-current states is exponential. These observations are consistent with a statistically independent, one-electron process for the chirality change.

Figure 3e shows the reaction rate as a function of voltage for both injection points. Both rates show an increase at a similar value. However, the overall rate is higher for electrons injected directly into the chlorine atom than for electrons injected at a distance of 0.4 nm. Thus, the probability of excitation drops with increasing manipulation distance from the center of the chlorine atom. This conclusion is substantiated by qualitative observations at points that are different distances from the chlorine atom. The threshold voltages are determined by plotting the slope of log R (Figure 3f). They are (260 ± 7) meV for both injection points.

The most probable reason for the chirality change at low energies is the excitation of molecular vibrations. We used the same calculations as discussed in reference [23] for the determination of the vibrations involved. Vibrational modes (Table 1) were calculated for gas-phase ClNB within density functional theory (DFT-GGA PW91) as implemented in the quantum chemistry package Gaussian03[27] using a basis set consisting of 6-31G (d,p) for H and 6-311G (d,p) for C, N, O, and Cl. For chlorobenzene (C_6H_5Cl) and nitrobenzene ($C_6H_5NO_2$), these parameters led to an agreement with the experimental data (even for adsorbed molecules) within 2 meV for modes below 200 meV and 5 meV for the remaining modes.

Table 1: Calculated vibrational modes of ClNB molecule in the gas phase.[26]

Ring	*E* [meV]	Chlorine atom	*E* [meV]	Nitro group	*E* [meV]
C–H stretch	394/393/391/389			NO_2 stretch	192/163
C–C stretch	199/196/180/176/168			C–NO_2 stretch	136
C–H in-plane bend	155/143/133/130			NO_2 bend	107
breathing	122			NO_2 out-of-plane bend	88
C–H out-of-plane bend	118/112/108/97	C–Cl stretch	137/92/50	NO_2 in-plane bend	66
out-of-plane deformation	81/52	C–Cl in-plane bend	40	C-NO_2 in-plane bend	21
in-plane deformation	81/46	C–Cl out-of-plane bend	61/24	C-NO_2 out-of-plane bend	18

As no single vibrational mode lies at the experimentally determined threshold, we propose that the chirality change is induced by the simultaneous excitation of two vibrational modes.[23] There is a multitude of possible combinations that sum up to the threshold (within experimental error). However, the efficiency decrease for injection at points away from the chlorine atom suggests that a chlorine-related mode is involved in the excitation, while a NO_2-related mode is not likely to be involved. This restriction leaves five possible combinations (Table 2). To initiate the lifting off the surface, only the C–Cl out-of-plane bending mode gives the correct atomic displacements. We propose that excitation of this mode and the C–C stretch vibration at 196 or 199 meV initiates the chirality change. The latter mode is also involved in isomerization of ClNB on Cu(111), where the total threshold energy is considerably smaller (227 mV).[23]

Table 2: Combination of vibrational modes that sum up to the experimentally found threshold considering a possible adsorption-induced shift of ±2 meV; most likely combination in bold face.

Cl mode: ν [meV]	Ring mode: ν [meV]	Sum
C–Cl stretch: 137	C–H in-plane bend: 130	267
C–Cl stretch: 92	C–C stretch: 168/176	260/268
C–Cl out-of-plane bend: 61	**C–C stretch: 196/199**	**257/260**

Up to energies of 300 mV the tunneling electrons preferentially excite the chirality change by flipping the molecule over the nitro group. During injection of tunneling electrons with energies above 350 meV, rotation of the molecule dominates. Only in the energy range between 300 and 350 meV do we observe simultaneous excitation of the chirality change with either rotation (Figure 4a) or diffusion (Figure 4b). Thus, by tuning the excitation energy to either under 300 meV or above 350 meV, we can select either the chirality change or the rotation of the molecule.

Two examples of IET-induced rotation are shown in Figure 5. The rotation into different orientations is evident in the current counts for extended manipulation periods, which display maxima at certain current values. The rotation takes place mostly around a point close to the chlorine-related protrusion. The actual distance of this point to the maximum of the protrusion varies between 0.1 and 0.3 nm in an arbitrary direction. Rotations by multiples of 120° may lead to symmetry-equivalent adsorption geometries, in contrast to rotations by other angles (Figure 5c). We thus suggest that the apparent rotation center includes a slight diffusion of the molecule into the next adsorption minimum of the chlorophenyl ring.

The dependence of the reaction yield on current (Figure 6) shows a threshold at (380 ± 25) meV. This value clearly relates to the C–H stretch modes (Table 1). In

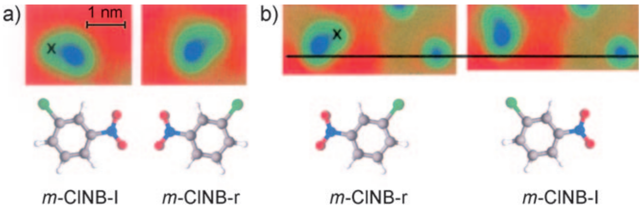

Figure 4. Chirality change of ClNB on Au(111) by IET at 300 meV with simultaneous a) rotation and b) diffusion; the line serves to guide the eye to detect the diffusion; left and right STM images show molecule before and after manipulation, respectively; the cross indicates injection point.

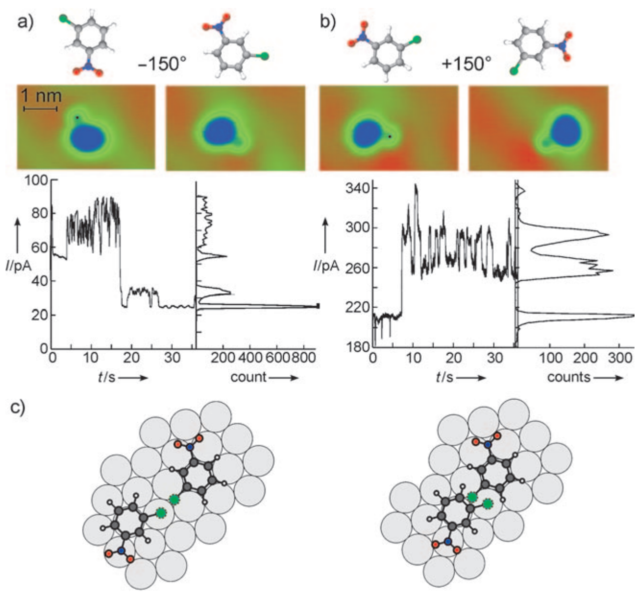

Figure 5. IET-induced rotation at 500 meV at positions indicated by dots in left STM images for molecules adsorbed a) on a hexagonal close-packed domain and b) on a domain boundary; left and right STM images show molecule before and after manipulation, respectively; *I–t* characteristics recorded during manipulation and frequency counts of current values are also shown. c) Schematic depictions illustrating rotation by 150° around the chlorine atom.

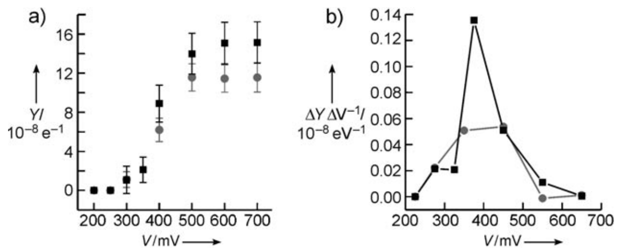

Figure 6. Rotation: a) Dependence of reaction yield *Y* on tunneling voltage for injecting tunneling electrons into the chlorine atom (●) or 0.4 nm displaced from the chlorine atom towards the nitro group (■). b) Slope of (a).

agreement with this assignment, the reaction yield depends much less on the position of injection than the chirality change does. The C–H stretch modes that are asymmetric with respect to the ring[26] can directly lead to rotational motion. The high thresholds and the more complicated *I–t* characteristics during rotation corroborate our conclusion that the chirality change is not an isomerization with subsequent rotation of the molecule.

In conclusion, we demonstrate hitherto unachieved chirality control of a single molecule, which we analyzed quantitatively for ClNB molecules adsorbed on the Au(111) surface. We show that by tuning the excitation energy under 300 meV and above 350 meV, chirality changes or rotations can be preferentially induced. Both reactions are induced by resonant inelastic electron tunneling. By analyzing the current characteristics during manipulation and stopping the manipulation at a preset current value, we are able to change the arbitrarily adsorbed molecule in a desired stereochemical form and alter the rotational angle. This manipulation constitutes an important step towards the controlled conversion of molecular properties at the ultimate spatial limit.

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