

DELIVERABLE D1.1

REPORT ON THE IMPLEMENTATION OF DIFFERENT AXLE STRATEGIES

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1. INTRODUCTION

The main goal of the MEMO work package WP1 is to study the step-by-step rotation of a molecule-gear relatively to the structure of the teeth, the rotational axle, the chemical composition, and the preparation of the supporting surface. Particularly important is the construction of atomic scale axles. It was planned in MEMO to first use atomic scale defects natively present at the elbows of the Au(111) surface reconstruction [1] and to study those defects as a function of the preparation conditions, with the aim of tuning their average distance to support a train of molecule-gears. Further atomic scale axles were identified by atom by atom construction on a metal surface, producing single metal atoms by dipping the STM tip into the surface and use STM manipulation to build up a nanoscale cluster terminated by a single atom for the molecule-gear vertical axle. As a third possibility, we proposed to use the molecular support of a transition metal atom. Organometallic chemistry can provide in fact an organic support to a transition metal atom maintained a few Å above a metal surface. As first demonstrated in [2] by a collaboration including partner P2.1-Toulouse, the d_{z2} orbital of the transition metal provides both a coordination bonding for the top gear and a vertical rotation axle. In reference [2] a molecular motor composed of a tripodal stator for vertical positioning, a five-arm rotor for controlled rotations, and a ruthenium atomic ball working as axle was reported. Such kind of anchoring possibility surely represents a successful strategy for the MEMO purposes and will be further used in WP2 and WP3 for studying both the motive power of a molecule motor and the transmission of motion from gear to gear. However, being already demonstrated, it will not be further discussed in this report. A last anchoring strategy was identified after starting the MEMO project and consists on the chemical bonding of a molecule-gear to a metallic surface, induced either by inelastic tunneling electrons coming from the STM tip or by thermal annealing.

The aim of the MEMO deliverable D1.1 is to report about the development of strategies to anchor a molecule on a metallic surface controlling its rotation and making therefore possible to utilise it as a gear. Scanning Tunnelling Microscope (STM) at low temperature (5K) in ultra-high vacuum (UHV) conditions is used for this purpose, since this technique not only allows the visualisation of molecules with atomic resolution but also their manipulation by tip-sample interactions. Low-Temperature STM has already been used in collaboration works of partner P1-Dresden to emulate a rack-and-pinion [3] and a rotor-translator [4] device at the nanoscale. In the rack-and-pinion study, the STM tip was used to displace HB-NBP, a molecule with six outer t-butyl groups that were engaged to those of neighbouring molecules, so its motion was a synchronised translation and rotation. In the rotor-translator study, a supramolecular structure that was observed to rotate upon application of voltage pulses was used to displace single gold atoms, confirming that molecular rotors can also perform mechanical work. Another molecular rotor, based on four external t-butyl groups and one central phthalocyanine, was investigated by the group of H. Fuchs [5]. This molecule, which was pinned on a defect of the Au(111) surface, hopped spontaneously between two equivalent adsorption states upon an increase in the temperature, and it was found that its switching behaviour could be controlled with the tip-sample distance and the applied bias. The first report of a molecular gear was presented by the group of Partner P2.1-Toulouse [1], which mounted HB-NBP on an atomic-sized defect of the Au(111) surface and demonstrated its controlled step-by-step rotation by lateral manipulation with the STM tip. These findings opened the door for exploring further options of molecules that could exhibit a similar behaviour. In particular, it would be advantageous if the pinning centre, instead of a natural defect, could be a purposely chosen point of the surface.

Several strategies to anchor molecule-gears on a surface providing an atomic-scale axle have been followed in the first year of the MEMO project and will be presented in this report. We first investigated (section 2) the



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possibility to anchor molecules at the elbows of the Au(111) reconstruction, as was successfully reported in [1]. Then partner P1-Dresden concentrated his effort on the chemical anchoring of molecules after on-surface synthesis with the STM tip (section 3). Finally, the successful strategy of partner P2.1-Toulouse to use a single atom axle is described in section 4, followed by a conclusion and an outlook in section 5.

2. AXLE AT THE ELBOW OF THE AU(111) SURFACE RECONSTRUCTION

The possibility to use atomic scale defects natively present at the elbows of the Au(111) surface reconstruction to anchor a molecule-gear was first demonstrated by some of the P2.1-Toulouse partners in ref. [1] by showing the step-by-step rotation of a HB-NBP molecule-gear mounted on a defect present at the elbows of the Au(111) surface reconstruction. The Au(111) surface was chosen because of its well-known herringbone surface reconstruction, where protruding rows of Au atoms separate alternating hexagonal close-packed (hcp) and face-centred-cubic (fcc) domains creating native rails of different inter-row distances [6]. Single non-identified atomic-scale impurities are very often adsorbed at the elbows of a herringbone reconstruction. These impurities define a stable pinning centre ideal for mounting single molecules and constructing a molecule-gear. In preliminary experiments, HB-NBP molecules were mounted on three different types of atomic-scale pinning centres: a clean elbow formed by the herringbone reconstruction, a single Au atom produced by soft indenting the STM tip on the Au(111) surface, and the single atomic-sized impurity natively bound to a herringbone elbow already discussed. To test the quality of the anchoring, the molecule was manipulated by the STM tip by pushing on one of its legs. Neither the elbow nor the Au atom is suitable for a centred step-by-step rotation. Although it is possible to rotate HB-NBP when mounted on a herringbone elbow, small lateral displacements are observed during its rotation. When HB-NBP is mounted on top of a single Au atom, it does not rotate but is laterally moved by the tip, as demonstrated with a structurally similar molecule by an older collaboration of P1-Dresden and P2.1-Toulouse partners [7]. In conclusion, the atomic defect bound to the elbow represents a successful anchoring of the molecule-gear, allowing the controlled rotation of the molecule around its axis. In Fig. 1 different cases of Au(111) surface reconstructions are shown. Fig. 1a is an example of pyrene-derivative molecules adsorbed at the elbows, while Fig.1c presents an overview STM images of a clean surface, where defects at the elbows are visible.

However, to reach the goals of the MEMO project, molecule-gears should not only have an axle and be able to rotate, but also should have the possibility to form a train of several gears, being the molecule anchored at a distance comparable with the lateral dimension of the used gear. As one can see in Fig. 1c, the average distance between two elbows is about 6 nm, much larger than the lateral dimension of a molecule-gear, which is of the order of 1 nm. We have therefore studied in MEMO possible strategies to modify the Au(111) surface reconstruction reducing the elbow-to-elbow distance. As one can see in Fig. 1b, a controlled tip crashing can modify the surface reconstruction in the neighbouring area in a clear visible way. The strong modified part is highlighted with the yellow rectangle in Fig. 1b. The distance between the elbows is reduced, with minimum values of about 2 nm.







Figure 1. The herringbone reconstruction. (a) STM image of pyrene-derivatives adsorbing at the elbow-sites. (image size: $30 \text{ nm} \times 6.8 \text{ nm}$; V = 0.5 V; I = 100 pA) (b) STM image of the changed reconstruction after a tip crash nearby. The strongly modified part is highlighted with the yellow rectangle. Distances between the elbow sites are in the range of 2 - 4 nm in this area (image size: $25 \text{ nm} \times 27.5 \text{ nm}$; V = 0.2 V; I = 100 pA) (c) Overview STM images of a Au(111) clean surface free of any adsorbates and (d) after reconstruction change induced by adatoms. (V = 0.5 V, I = 30 pA, image size: $80 \text{ nm} \times 40 \text{ nm}$). The black arrows show the distance between the soliton lines, which was used as a measure of reconstruction distortion.

A second possible strategy to engineer the Au(111) surface reconstruction is presented in Fig. 1d. By depositing on the surface DPP molecules equipped with Br atoms [8] it is possible to observe a distortion of the Au(111) herring-bone reconstruction caused by the deposition of the molecules and subsequent annealing leading to debromination of the molecules. The observed soliton line distance changes from 6.1 ± 0.3 nm of a clean Au(111) substrate to 7.8 ±0.6 nm after the distortion.

The release of Au atoms off the surface can be induced by several factors and might lead to the mediation of the molecular systems. Such effect has been previously observed for deposition of thiolates [9-12], pyridine-functionalized porphyrins [13] and other molecules containing electronegative atoms [14-18]. Interestingly, most of these molecular systems contain sulphur or oxygen groups, which have a high affinity to gold. In the studied DPP molecule, both sulphur and oxygen atoms are present in the donor thiophene and acceptor diketopyrrolopyrrole, respectively. Quantitatively, the effect of reconstruction lifting can be measured by the distance between the soliton lines.

In conclusion, the defects natively present at the elbows of the Au(111) herringbone reconstruction have demonstrated to successfully anchor molecule-gears acting as axles for rotation. The distance between two elbows is however too large to build chain of gears or even to study the transmission of motion between two molecule-gears. By tip indentation or by depositing Br atoms it is possible to influence the reconstruction,



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reducing or increasing the distance between the soliton lines. The minimum observed distance between two elbows is about 2 nm and can eventually be used to place two molecule-gears and study their relative rotation. The reconstruction is however not regular and no periodic distribution of elbows at shorter distance could be observed or produced. Further strategies should be therefore followed to obtain a train of gears anchored on axles regularly positioned at a distance of the order of 1 nm. Two further strategies to obtain axles at distances comparable with the dimension of a rotating molecule-gear have been studied in the first year of MEMO and are described in the next sections.

3. CHEMICAL ANCHORING OF MOLECULE-GEARS

In this section we will discuss three different experiments performed in the first year of the MEMO project by partner P1-Dresden, where the anchoring of a single molecule on the Au(111) surface is obtained by inducing a chemical reaction. Depending on the cases, such reaction can spontaneously happen upon molecular deposition or be induced by annealing or by inelastic electrons, locally applying a voltage pulse with the STM tip.

In the first example, a molecular precursor was chemically anchored to the Au(111) surface upon deposition (Fig. 2) and studied by LT-STM in UHV conditions by partner P1-Dresden. We deposited the *o*-MeO-DMBI-I (2-(2-MethoxyphenyI)-1,3-dimethyl-1*H*-benzoimidazol-3-ium iodide) molecular precursors at submonolayer coverage on a clean Au(111) surface kept at room temperature. During evaporation at 490 K, the precursors are reduced by cleaving iodine and resulting in *o*-MeO-DMBI (Fig. 2a). Due to this reduction, that has been verified by X-ray photoelectron spectroscopy elsewhere [19], the sublimated molecules work as n-dopant in organic electronic devices and were widely investigated for applications in organic electronics [20,21]. The iodine atoms adsorb on the Au(111) surface restructures and the distances between the next-nearest neighbor soliton walls increases by about 1.5 nm as compared to the unaltered herringbone reconstruction, as known in the literature [22,23].

The presence of a methoxy-group and of a possible radical form (Fig. 2a) suggests a strong molecule-surface interaction that can be tested by pushing the single molecules by lateral manipulation with the STM tip. As one can see in Fig. 2b, the molecules do not translate, but change the orientation, rotating around a fixed anchoring point. Manipulation trials with reduced tip height and consequently stronger tip-molecule interaction never lead to a translation of the molecule. The lateral manipulation experiments demonstrate that the molecules are not physisorbed, but are chemically anchored to the Au(111) surface, as expected considering the similar case of thioether-molecules, which are known to strongly bind to surface atoms on coinage metals [24]. We therefore conclude that the o-MeO-DMBI molecule is anchored to a gold atom through one of the two lone pairs of electrons of the oxygen (Fig. 2a). Upon application of a sustained voltage pulse with the STM tip, o-MeO-DMBI rotated step by step between six stable positions, always in a clockwise or counter-clockwise fashion depending on the molecule's chirality, as reported in [25] and observed in further experiments described in WP2 task 2.1.







Figure 2. The molecule o-MeO-DMBI on Au(111). (a) Scheme of the adsorption of o-MeO-DMBI on Au(111). (b) STM images of an o-MeO-DMBI molecule on Au(111) before and after lateral manipulation is performed along the black arrow (parameters: I = 4.0 nA; V = 10 mV) (image sizes: $6 \text{ nm} \times 5 \text{ nm}$; V = 0.2 V; I = 30 pA). (c) STM image of an o-MeO-DMBI molecule before and after the lateral manipulation along the black arrow (I = 20 nA; V = 10 mV). Afterwards the molecule has been picked up together with the underlying gold-atom (image sizes: $10 \text{ nm} \times 4.4 \text{ nm}$; V = 0.5 V; I = 38 pA).

Further chemical-anchoring experiments were performed by partner P1-Dresden on molecules where the anchoring can be induced by an on-surface reaction. Such reaction can be produced by annealing and/or by voltage pulses with the STM tip. Based on its experience in the on-surface synthesis of acenes [26] partner P1-Dresden used a tetracene-precursor with two methylamine groups within the molecular backbone (Fig. 3a). As one can see, the STM image of these isolated precursor molecules shows a dumbbell-shaped topography. The protruding parts can be assigned to the methylamine groups of the molecule. After annealing the Au(111) surface to 170 °C for five minutes, we observed different planar molecular species on the surface (Fig. 3b-e, upper row). To understand the different reacted molecular species, we functionalized the tip with a single CO molecule, and enhanced the resolution of the STM images by measuring over the molecules in a constant height mode (Fig. 3b-e, middle row). From these images the benzene rings of the tetracene unit can be nicely resolved and the molecules of Fig. 3b-e have a side-group at the outer benzene rings. It seems that within the planar molecules the methylamine group can be either cleaved from one carbon atom leading to the formation of a benzene ring with a methylamine group at the side, or can be detached completely from the molecule leading to the formation of an acene. The molecular structures of the reacted molecules are presented in the bottom row of Fig. 3b-e. Interestingly, it was also possible to trigger this reaction by voltage pulses with voltages above 3.0 V.



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Figure 3. The molecule $Tn(NCH_3)_2$. (a) Chemical structure of the precursor molecule and overview STM image of a submonolayer of precursor molecules on Au(111). (image size: 6.25 nm x 12.5 nm; V = -0.56 V; I = 73 pA) (b)-(e) Top row: Constant-current STM images of the different species found after annealing to 170 °C. (V = 0.5 V; I = 100 pA; image sizes: 2.5 nm x 2.5 nm); Middle row: Constant-height STM images of the same molecules achieved with a CO-functionalized tip. (image sizes: 2.5 nm x 2.5 nm; V = 10 mV); Bottom row: Proposed chemical structures of resulting molecules.

To prove the possible anchoring at the nitrogen position of the new formed molecules, we used the lateral manipulation mode of the STM. While it was not possible to move species of Fig. 3b,c, which suggests a strong anchoring at two positions, we were able as expected to rotate the species of Fig. 3d. A series of this rotation can be seen in Fig. 4. The molecule can be rotated step-wise into six stable positions by lateral manipulation, indicating a strong molecule-surface interaction due to the nitrogen of the side-group. On the contrary the acene molecule (Fig. 3e) can be easily moved on the surface with these manipulation parameters ($R = 5 M\Omega$). Hence, we could show that we are able to achieve an anchoring of a molecule after a chemical reaction within the molecule.

The molecular rotors previously described, although strongly pinned and highly controllable, do not have a shape that resembles that of a gear, which pentaphenylcyclopentadiene (C_5Ph_5H) does have (Fig. 5). Its five outer phenyl rings can be thought of as the gear's teeth, whereas the carbon atom carrying the the hydrogen in the middle could, in principle, be used as an anchoring point. In the field of molecular machines, a penta(aryl)cyclopentadiene was used as part of an `organometallic molecular turnstile' whose axis was a Ruthenium atom on top of which the cyclopentadiene was mounted, in collaboration with members of the P2.1-Toulouse group [27]. Later on, a stand-alone molecular motor was synthesised using the penta(aryl)cyclopentadiene-Ru complex as the rotor element, and it was proven that its motion could be triggered by selective inelastic electron tunnelling [2]. P1-Dresden investigated the anchoring of C_5Ph_5H provided by partner P2.1-Toulouse on Au(111) by inducing its dehydrogenation and studied it as molecule-gear with chemical bonded axle.





Figure 4. Rotation of a reacted $Tn(NCH_3)_2$ presented in Figure 3d on Au(111). (a)-(f) Step-wise rotation of a tetracene-molecule with one methylamine group by lateral manipulation. Manipulation is performed along the black arrows. (image sizes: 10 nm x 10 nm; V = 0.5 V; I = 100 pA; manipulation parameter: I = 2.0 nA; V = 10 mV)



Figure 5. The molecule C_5Ph_5H on Au(111). (a) Chemical structure of the precursor and proposed structure after dehydrogenation induced via voltage pulses. (b) STM image of two C_5Ph_5H molecules, the upper left dehydrogenated by a 3.1 V voltage pulse, the lower right one being initial. (b)-(f) Sequence of STM images. The black arrows indicate lateral tip manipulation events while laterally manipulating the molecule at V = 10 mV, I = 300 pA (image sizes: 10 nm × 6.5 nm; V = 0.5 V; I = 20 pA).

After evaporating C_5Ph_5H at 175°C for 30s, the Au(111) surface was covered with a sub-monolayer film of this molecule. Interestingly, C_5Ph_5H molecules were found to either cluster along the step edges or to form supra-molecular assemblies on the surface, especially of three and four molecules. C_5Ph_5H appears therefore to have a rather weak interaction with the Au(111) surface, at least much weaker than the interaction with other C_5Ph_5H



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molecules. A conspicuous feature of this molecule is the bulge near its centre. If the five lobes that delineate the contour of the molecule are the five phenyl rings, then this bulge must correspond to the hydrogen atom. The application of a sustained voltage pulse with the STM tip can remove single atoms, then it should be possible to dehydrogenate this molecule. Indeed, the application of a pulse of 3.1 V right above the bulge alters the shape of the molecule. In some occasions the change is almost imperceptible, but the repeated application of such a pulse leads to the `removal' of this bulge. Fig. 5a shows the principle of the dehydrogenation and Fig. 5b the STM image of two C_5Ph_5H molecules where the upper one was flattened. The flattening of the molecule, *i.e.* the removal of the central bulge, is a strong support for a dehydrogenation of the molecule. We observe however different conformation of the dehydrogenated molecule, due to the fact that the phenyl rings are connected by single bonds and can rotate around the bond assuming different conformations.

If C_5Ph_5H can be dehydrogenated, then possibly the remaining dangling bond would act as a pinning centre around which the molecule could rotate. Following this logic, a series of lateral manipulation experiments were done. As the sequence of events in Fig. 5b-g shows, it is possible to rotate the molecule step by step by a very gentle lateral manipulation (STM tunnel junction resistance R = 30 M Ω) achieving a full counter-clockwise rotation in six steps. The rotational centre corresponds to the position of the bulge, but the anchoring is very weak and a tiny displacement of the molecule in many cases accompanies the rotation. Further attempts to fix the molecule on a Au adatom were not successfully, being the molecule very weakly bonded to the surface and to the adatom. The same result was observed by using a cluster of two gold atoms. The chemical anchoring of pentaphenylcyclopentadiene-like molecules seems however a very promising strategy to provide a rotational axle to a molecule-gear. In collaboration with project partner P2.1-Toulouse, the anchoring group of C₅Ph₅H will be modified to achieve a stronger anchoring to the surface, and further investigated in the next MEMO reporting period.

4. CONSTRUCTION OF AN ATOMIC AXLE

During MEMO year 1, partner P2.1-Toulouse has explored how to produce axles for mounting and rotating molecule-gears, which are formed by single atoms on a metallic surface. One of the most important parameter to anchor a molecule-gear on an atomic scale axle is its surface height. Previously reported atomic scale axles for molecule-gear were atomic-sized unknown native defects found at the herringbone elbows of the reconstructed Au(111) surface with an apparent height of 60 pm [1]. It was decided in MEMO to study the deposition of different single metallic atoms at low coverage on different metallic surfaces. Table 1 presents a series of adatoms heights on selected metal surfaces obtained using DFT calculations performed during MEMO Year 1 by partner P3-San Sebastian to support the P2.1-Toulouse experiments. The measurement of the physical height of the single adatoms using STM apparent height observed is experimentally difficult. However, according to this table, Cu and Co on Pb(111) are interesting to test a couple of short distance combinations and to certify the mounting of a single molecule-gear per adatom. Lead being a superconductor with Tc = 7.3 K, the surface electronic friction is expected to be minimized for molecular adsorbates on Pb(111) at 4.3 K. Partner P2.1-Toulouse used its LT-UHV 4-STM to perform the experiments in preparation of the construction of a long train of molecule-gears requiring more than one STM tip to measure the gear rotation propagation along the train.





	Co dist [Å] fcc-hollow	Co dist [Å] hcp-hollow	Cu dist [Å] fcc-hollow	Cu dist [Å] hcp-hollow	Ag dist [Å] fcc-hollow	Ag dist [Å] hcp-hollow	Ge dist [Å] fcc-hollow	Ge dist [Å] hcp-hollow
Cu(111)	1.72	1.73	1.85	1.86		2.11	1.88	1.89
Ag(111)	1.80	1.81	1.91	1.92	2.18	2.18	1.91	1.92
Au(111)	1.58	1.55	1.77	1.79	2.09	2.09	1.73	1.78
Pb(111)	1.23 -1.15(in)	1.19 -0.79(in)	1.64	1.71	2.08	2.18	2.01	1.70

Table 1. DFT calculations by partner P3-San Sebastian of the surface physical height of Co, Cu, Ag and Ge single and isolated ad-atoms on the Cu(111), Ag(111), Au(111) and Pb(111) surfaces. The Pb(111) surface was experimentally tested by partner P2.1-Toulouse during MEMO year 1.

The investigated molecule-gear was the HB-NBP ($C_{64}H_{76}N_2$) molecule, with a central planar benzene core surrounded by six sterically similar teeth : five *tert*-butylphenyl groups and one *tert*-butylpyrimidine group as a chemically-tagged tooth (see Fig. 6). It was re-synthesized by partner P2.1-Toulouse.



Figure 6. Molecular structure, ball model and LT-UHV STM image of the HB-NBP molecule-gear used in the single atom axle mounting experiments performed by partner P2.1-Toulouse during MEMO year 1. LT-UHV STM image: 140 pA, 1.0 V on Cu(111). Image size: 3 nm x 3 nm, corrugation: 0.25 nm The nitrogen chemical tag is apparent on Cu(111) but not on Pb(111). Lateral van der Waal molecule-gear diameter: 1.6 nm.

Those molecule-gears were deposited at a sub-monolayer coverage on a clean Pb(111) surface kept at room temperature, the sample transferred to the P2.1-Toulouse LT-UHV 4-STM and thermalized at 4.3 K. Then, Cu and Co atoms were evaporated through a small hole present in the cryostat, while the sample was maintained at cryogenic temperature. Molecules form small 2D islands on the terraces and also adsorb a few together around impurities. Isolated molecules are not stable on the terraces neither at step edges, probably due to the small electronic friction on the Pb(111) surface below its Tc. The superconducting state of the STM junction was tested by recording the dI/dV superconducting gap.



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As presented in Fig.7, the apparent height of a Cu ad-atom on the Pb(111) surface is 60 pm, exactly the same as the atomic defects on the herringbone elbows of the reconstructed Au(111) surface. In contrast, the apparent height of a Co adatom is slightly lower, about 50 pm. This corresponds well with the physical height calculated by DFT and shown in Table 1.



Figure 7. Apparent heights of atomic-sized physical axles. **LEFT** natively formed defect on the herringbone reconstructed Au(111) surface and **RIGHT** Cu adatoms deposited on Pb(111) surface have the same height of about 60 pm as can be seen on the LT-UHV STM scans presented below the STM images. All images and scans recorded on the P2.1-Toulouse LT-UHV 4-STM. On the **RIGHT** LT-UHV STM image, 6 molecule-gears are imaged.

For anchoring a molecule-gear on a single adatom axle, LT-STM lateral manipulation was applied. The STM tip apex was first positioned in the centre of a molecule-gear adsorbed around an impurity. Then, the STM tunnel junction resistance was reduced to 5 M Ω to perform single molecule manipulation to the top of the targeted adatom. After a successful manipulation event, where the molecule-gear is anchored and centred on-top the axle, a protrusion is clearly imaged at the molecule-gear centre as presented in Fig. 8. Molecule-gears were mounted and centred on-top of both Cu and Co adatom axles. However, the molecule-gear was anchored loosely to the Co adatom and not centred. Performed by partner P2.1-Toulouse, single molecule-gear rotation experiments requiring a definitive torque are presented in WP3.







Figure 8: Two LT-UHV STM mechanical manipulations of a molecule-gear to mount it on-top a single Cu ad-atom axle. LT-STM images **(a)** before manipulation with tip trajectories of those manipulations indicated and **(b)** after manipulation where the molecule-gear is mounted on its Cu axle. **(c)** Tip height signal recorded in real time during those manipulations showing a clear jump up due to molecule anchoring. When the molecule is over manipulated and dismounted from the axle, tip is jumped down. **(d)** LT-STM image of the molecule-gear anchored and exactly centred on its Cu ad-atom showing the central Cu protrusion.

5. CONCLUSIONS

Several strategies to anchor molecule-gears on a surface providing an atomic-scale axle have been followed in the first year of the MEMO project and presented in this report. We first investigated the possibility to anchor molecules on defects at the elbows of the Au(111) reconstruction. We concluded that the defects natively present at the elbows of the Au(111) herringbone reconstruction can successfully anchor molecule-gears acting as axles for rotation. However, the distance between two elbows is too large to build chain of gears or even to



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study the transmission of motion between two molecule-gears. By tip indentation or by depositing Br atoms it is possible to influence the reconstruction, reducing or increasing the distance between the soliton lines. The minimum distance observed between two elbows is about 2 nm and can eventually be used to place two molecule-gears and study their relative rotation. The reconstruction is however not regular and no periodic distribution of elbows at shorter distance could be observed or produced. Further strategies should be therefore followed to obtain a train of gears anchored on axles regularly positioned at a distance of the order of 1 nm.

Partner P1-Dresden concentrated his effort on the chemical anchoring of molecules after on-surface synthesis with the STM tip. Three different experiments were performed, where the anchoring of a single molecule on the Au(111) surface is obtained by inducing a chemical reaction. Depending on the cases, such reaction can spontaneously happen upon molecular deposition or be induced by annealing or by inelastic electrons, locally applying a voltage pulse with the STM tip. In all three cases, chemical reactions demonstrated to be a useful strategy to build atomic scale axles for molecule-gears. In the specific case of pentaphenylcyclopentadiene (C_5Ph_5H), the molecule also after dehydrogenation is weakly anchored to the surface and can rotate and translate by weak lateral manipulation parameters. The chemical anchoring of pentaphenylcyclopentadiene-like molecules is however a very promising strategy to provide a rotational axle to a molecule-gear. In collaboration with project partner P2.1-Toulouse, the anchoring group of C_5Ph_5H will be modified to achieve a stronger anchoring to the surface, and further investigated in the next MEMO reporting period.

Finally, Partner P2.1-Toulouse developed a strategy to use a single atom axle, mounting a molecule-gear centred on-top of both Cu and Co adatom axles on the Pb(111) surface. While Cu adatoms are forming a useful axle for the molecule, the molecule-gear was anchored loosely to the Co adatom and not centred.

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