Design and synthesis of mono-molecular machines

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Abstract
A mono-molecular machine is a molecule designed to perform a function
providing energy, data and/or orders to the molecule. A 'monumentalization'
approach (the synthesis of very large molecules) is used to synthesize
technomimetic molecules, i.e. molecules able to transpose macroscopic objects
and their motions at the molecular level, and grants access to the study of
the mechanical properties of a single molecule. This paper focuses on the
mechanical molecular machines developed in our group which are controlled
one at a time by the tip of a scanning tunnelling microscope, like the molecular
wheelbarrow and the molecular gear, or in the future by an atomic force
microscope, as in the case of the molecular motor.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

There is no physical limitation to the miniaturization of a machine down to the scale of a
single molecule. Conversely, a molecule must certainly be very large to become a complete
machine. Starting from the atomic scale, this corresponds to a *monumentalization* procedure,
i.e. synthesizing 'monumental' molecules. A few simple prototypes of unimolecular machines
are already under test, such as the molecular wheelbarrow [1] or the molecular atom cleaner [2].
A few other molecules have been designed and used as experimental physical nanodevices,
like gear molecules [3] or the series of the Lander molecules [4] used to study the electronic
contact of a molecular wire to a metal at the atomic scale [5] or to interact with metal surface
standing waves [6]. Other molecules are in their early design and synthesis stages, like the
Morse molecule [7], the motor molecule [8] or the digital half adder molecule [9].

    In the following we are only concerned with single mechanical mono-molecular machines,
i.e. a single molecule (always the same) performing a mechanical task (e.g. a molecular
motor) or an ensemble of mechanical tasks embodied in the same molecule (the molecular
wheelbarrow). For mono-molecular machines in general, and more specifically for mechanical
mono-molecular machines, the major difficulties concern (1) the delivery of the required
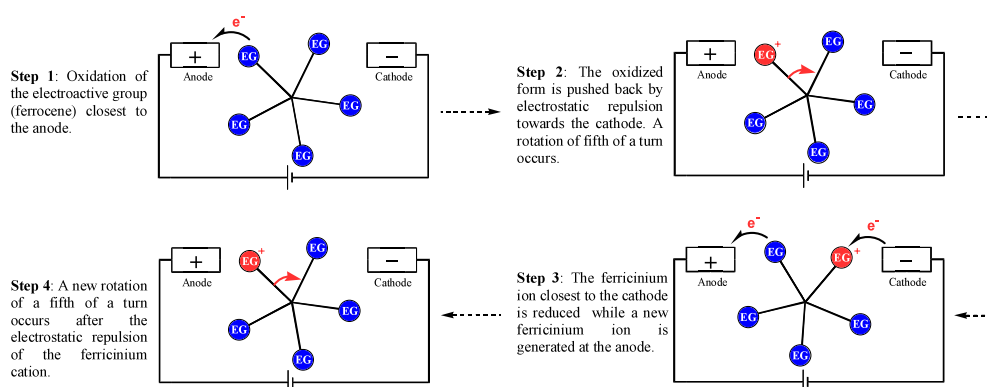
Figure 1. Schematic representation of a molecule placed between the two electrodes of a nanojunction (EG stands for electroactive group). The transfer of electrons from the cathode to the anode through successive oxidation and reduction processes is expected to result in the clockwise rotation of the entire upper part of the molecule. This figure represents a fifth of a turn corresponding to the movement induced by the transfer of one electron.

driving energy to a single and always the same molecule, (2) the design and synthesis of a molecule embodying the mechanical parts and the required auxiliary chemical groups for the molecule to perform on a surface, (3) the control of the directionality of the rotation [10] and (4) bringing to the observer experimental information about the exact motion, deformation or conformational change of the molecule during performance.

2. Design and synthesis

2.1. A single-molecular motor

A mono-molecular motor is a nanoscale machine which consumes energy to produce work via the unidirectional and controlled movement of one of its parts. Up to now, the molecules designed, synthesized and mounted on a surface for single molecule experiments have not undergone unidirectional rotation of their rotor part: their internal motion can be seen as random oscillations around a given axis [11, 12]. In our technomimetic [13] design for a molecular motor [8], the source of the energy is a tunnel current. Our target molecule is supposed to convert the electron transfer rate of the electrons tunnelling through the molecule into directionally controlled rotary motion. The molecular motor has been designed to be individually interconnected, after its deposition, to an N-electrode tunnel junction whose nanoelectrodes are separated by a few nanometres.

The concept of our electron-fuelled molecular rotary motor is shown in figure 1. The electroactive group (EG) closest to the anode would be oxidized (oxidized form EG$^+$) and pushed back by electrostatic repulsion, as has been shown for a [60]-fullerene between two electrodes [14]. This motion corresponds to a fifth of a turn. As a result, the oxidized electroactive group would approach the cathode and subsequently be reduced.

At the same time, a second electroactive group would come close to the anode and a second cycle would occur. A complete 360° turn would be achieved after five cycles, corresponding to the shuttle of five electrons from the cathode to the anode. This would represent the conversion of an electron flow into a movement of rotation, i.e. a redox-triggered molecular rotary motor. In order for the rotation to be directional, the molecule should be placed in a dissymmetrical
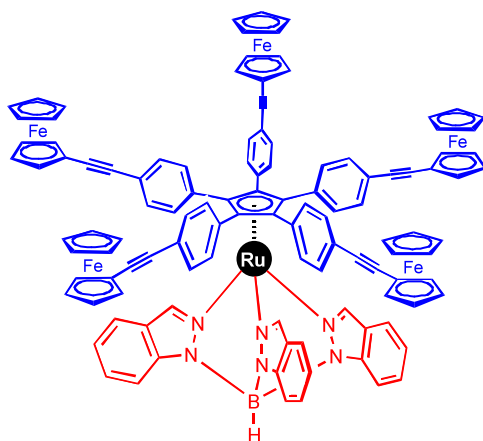
Figure 2. Structure of the active part of a single molecular motor. The lower ligand is the stator (in red) and the upper ligand is the rotor with five ferrocene-terminated arms (in blue). The ruthenium plays the role of the joint between the two ligands.

environment. This could be achieved either by its disposition at the nanojunction, or by a secondary electric field applied perpendicularly to the nanojunction.

The active part of our molecular motor is represented in figure 2. It comprises a stator, i.e. one part fixed between two electrodes, on which is connected a rotor which should transform a current of electrons into unidirectional rotational motion. The rotor is a rigid aromatic platform constructed around a cyclopentadienyl ligand (cp) with five rigid linear arms, each terminated by an electroactive group. Ferrocene was selected as the electroactive group because it exhibits reversible oxidation in various solvents [15]. The stator is a hydrotris(indazolyl)borate ligand of the family of scorpionates developed by Trofimenko [16], and has the shape of a piano stool. The joint between the rotor and the stator is a ruthenium(II) ion, to obtain a stable molecule bearing of zero net charge, both criteria being essential for surface deposition and hence allowing experiment on a single-molecule nanomotor. The upper part should be free to turn whilst the basis should stay still, anchored to the surface between the two electrodes of the addressing system.

The molecule was synthesized as shown in figure 3, starting from pentaphenyl cyclopentadiene **2** which was selectively brominated in the *para* positions and at the saturated carbon of the cyclopentadiene ring [17]. This new ligand was coordinated to ruthenium by reaction with $Ru_3(CO)_{12}$ and subsequently the tris(indazolyl)borate ligand was introduced before the last step, which consisted of quintuple coupling of the ethynyl ferrocene electroactive groups. We also developed the synthesis of a tris(indazolyl)borate ligand incorporating some anchoring groups [18], since it was to be deposited on the surface of an insulator for study at the molecular scale with a non-contact atomic force microscope (NC-AFM).

Once the molecule **1** was synthesized, all the requirements for such a molecule to operate as a molecular motor were analysed: (i) The oxidation potential of the iron is lower that that of the ruthenium centre, which is compatible with our objective in the sense that the ruthenium centre will remain inert towards the redox cycles of the peripheral electroactive groups. (ii) Electrochemical processes are reversible, showing the robustness of the molecule towards oxidation. (iii) No intervalence band was observed, showing that the electronic communication between two iron centres is null or very weak. Electronic communication here is an unwanted phenomenon since it would allow charge transport by intramolecular
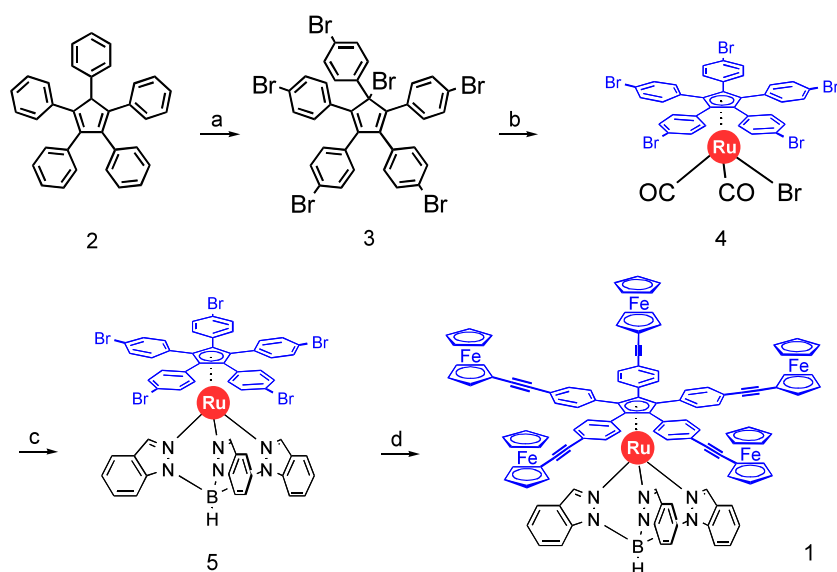
Figure 3. Synthetic scheme of the molecular motor—reagents and conditions: (a) Br_2, 2 h, Ar, 20 °C, 98%; (b) $Ru_3(CO)_{12}$, toluene, 2 h, Ar, reflux, 78%; (c) KTIB, THF, 24 h, Ar, reflux, 30%; (d) ferrocenylethynylzinc chloride, $Pd(PPh_3)_4$ 10 mol%, THF, 48 h, Ar, reflux, 32%.

electron hopping between different ferrocene centres, without real motion of the rotor. (iv) The rotation barrier of the rotor is very low, as shown by nuclear magnetic resonance (NMR) and by theoretical calculations.

2.2. Rotating unidirectionally?

Looking in more detail at the requirements for true unidirectional rotation, several difficulties can be identified. First, the molecule must be made of two essentially rigid parts. This requirement is frequently absent in many proposals for molecular motors, which neglect the extreme flexibility of most molecules. For molecule **1**, there is indeed essentially one degree of freedom: the rotation of the upper part with respect to the lower one. The lower part has a locked conformation. As far as the upper part is concerned, rotation about the single and triple bonds of the arms is of course possible but it does not alter significantly the geometry of the molecule.

Solution studies such as NMR show the possibility of 'rotation', because several nuclei are found to be magnetically equivalent. This is a random process in which the rotor part of the molecule rapidly explores many conformations, with irregular back and forth motions. This is very different from the rotation occurring in a macroscopic mechanical motor. At the molecular scale, the inertial forces play a negligible role and cannot sustain the directionality of the motion [1, 10].

To achieve directionality in the rotation, one could think of introducing chirality either on the lower or the upper part. This is useful, but not sufficient: using the sole chirality for a movement driven only by thermal energy is not enough. If so, the second principle of thermodynamics would be overlooked [11, 19]. In addition, a source of energy is required. In our proposition, the energy source is electrical, and comes from the irreversible transport of electrons from the negative to the positive electrode through a tunnel junction. The

directionality is obtained because the two senses of rotation are not equivalent: this is clear in figure 2, as a result of the asymmetric disposition of the molecule with respect to the electrodes, this disposition of course being obtained by chance.

Finally, let us consider the problem of the behaviour of the molecule once it is inserted between two electrodes. For a molecule such as **1**, oxidation is much easier than reduction due to the presence of ferrocene groups. Thus, when the junction is biased at a bias voltage close to the electronic resonances, there is a tendency to generate the cation-radical $1^{\circ+}$ (see recent work with atoms or molecules inside a junction [20, 21]). The detailed behaviour depends on several factors: the position of the molecular levels with respect to the Fermi levels of the electrodes, the degree of metal–electrode electronic coupling and finally electrostatic repulsion effects.

From a geometrical point of view what will happen once the molecule is oxidized? The coupling of electron transport through a molecule with molecular motions (inelastic effects) has been addressed only recently. There are, however, two phenomena to consider: (i) the motions induced by a tunnelling process, leading for instance to tunnel heating [22]; in this case only a tiny amount of energy is lost by the electrons when transferred through the junction, still enough to excite some vibrational degree of freedom; (ii) the motion is induced by a 'redox' process, in which some orbitals of the molecule inside the junction are either fully populated or depopulated. In this last case, an additional electron (or hole) resides on the molecule for a sufficient time so that the molecular framework has time to adapt to the new charge state. Molecule **1** has been devised for mechanism (ii), meaning that the oxidation of the molecule is supposed to give access to a conformational change corresponding to motion of the rotor from one station to the other. On the multi-dimensional potential energy surfaces of molecule **1**, this supposes that the oxidized state will cross a new state with a different energy minimum corresponding to a new station of the rotor. The crossing will certainly be facilitated by mechanism (i). This semi-classical intramolecular process is currently under investigation.

2.3. An organometallic molecular turnstile with a correlated gear effect

During the synthesis of the active part of our molecular motor, we became particularly interested in the intermediate **5** represented in figure 3. This key molecule in our synthetic pathway was an interesting candidate for studying the random rotation of the upper part of the molecule, for which an interesting behaviour was discovered [17]. The x-ray structure showed the two ligands to be interpenetrating, and thus there is a steric hindrance imposed by the three parts of the lower tripodal ligand. Despite that, the ^{1}H-NMR showed the five *p*-bromophenyl rings to be equivalent, and furthermore that the *p*-bromophenyl groups could rotate around the bond connecting them to the cyclopentadienyl ligand. Molecular modelling and theory show that this is possible only if the rotation of the upper cyclopentadienyl ligand (random rotation induced by the thermal bath surrounding them) results in the correlated rotation of the *p*-bromophenyl paddles. These groups must tip over to settle in the vacant spaces of the tripodal ligand like a Fosbury flop[1]. Figure 4 represents the secondary rotation of the *p*-bromophenyl rings (action 2) induced by the rotation of the upper cp ligand (action 1). These two rotations are correlated and this molecule behaves like a molecular turnstile with a correlated gear effect.

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[1] From the name of Dick Fosbury who revolutionized high jump in 1968, by introducing the technique of leaping backward over the bar, and rolling around it.
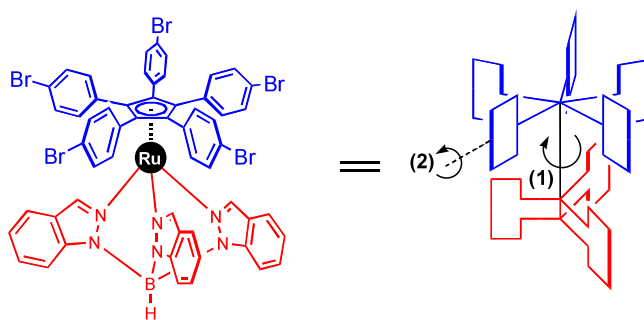
Figure 4. Rotation of the upper cp ligand (action 1) results in the paddles tipping over (action 2).

2.4. A molecular wheelbarrow

In the field of single-molecule manipulation, it is a challenge to manipulate a molecule which would at the same time undergo translational and rotational motion [23, 24]. On a surface, the mechanical motions of a single molecule are essentially classical due to the reservoir role of the surface inducing decoherence and relaxation processes [10]. Any coherent or classical motions of a given group of atoms in a single molecule will require specific preparation of this molecule [10]. Pushing a molecule with the tip apex of an STM is a convenient way to drive a motion or a movement, adapted to the classical motion we are trying to reproduce [25]. For a macroscopic wheelbarrow, pushing the wheelbarrow results in the rotation of the front wheel. At the scale of a single molecule, the interesting question is: how can we master the increase in molecule potential energy induced by the tip apex pushing on the rear part of a mono-molecular wheelbarrow so that a large part of this energy is converted into a rotation of its front wheel [26]?
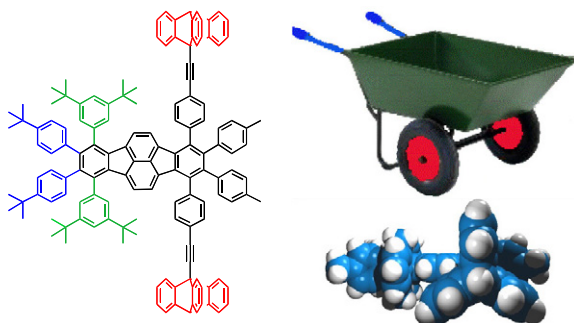

Figure 5. Chemical structure of a molecular wheelbarrow (left), side view of the CPK model showing the minimum energy conformation of the molecular analogue (bottom right) and its macroscopic analogue (top right).

Figure 5 shows a molecular analogue of a wheelbarrow. Its skeleton is made of polycyclic aromatic hydrocarbons (PAHs) which, due to their rigidity, are easily manipulated by the STM tip. The wheelbarrow has two legs (3,5-di-*tert*-butyl phenyl groups, in green) and two wheels (ethynyl triptycene groups, in red) connected to a polycyclic aromatic hydrocarbon platform. It belongs to the family of asymmetric Lander molecules developed specifically for their study on various metallic surfaces [27, 32].
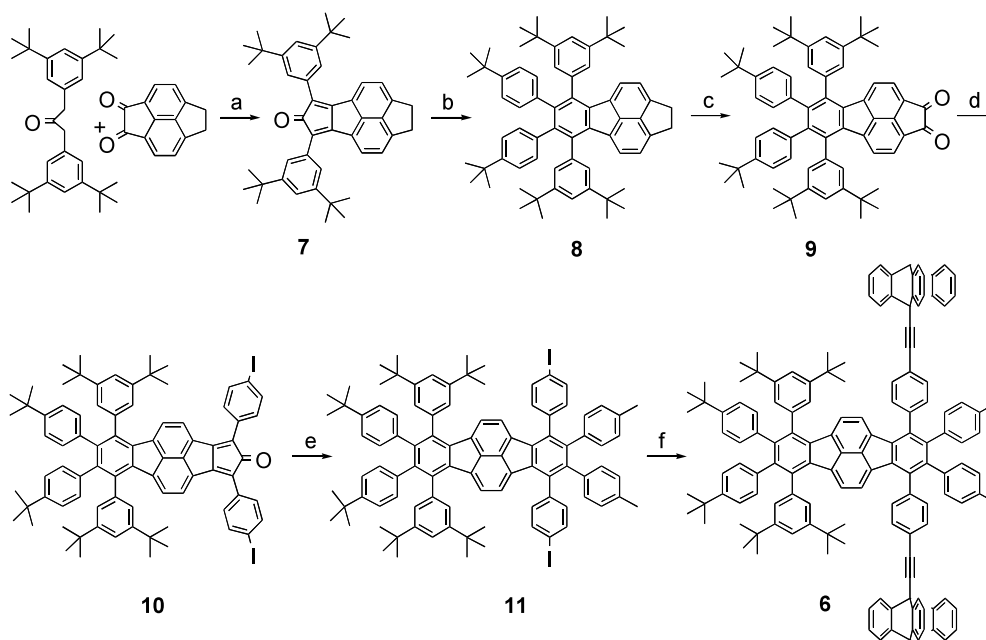
Figure 6. Synthetic scheme for the molecular wheelbarrow—reagents and conditions: (a) ethanol (EtOH), 20 h, Ar, 20 °C, 90%; (b) di(4-*tert*-butylphenyl)acetylene, diphenylether, 16 h, Ar, reflux, 97%; (c) ($C_6H_5SeO)_2O$, chlorobenzene, 62 h, Ar, reflux, 60%; (d) 1,3-bis(4-iodophenyl)propan-2-one, KOH, EtOH, Ar, reflux, 100%; (e) di(4-tolyl)acetylene, diphenylether, 16 h, Ar, reflux, 30%; (f) 9-ethynyltriptycene, Pd($PPh_3)_4$ 10 mol%, CuI 20 mol%, piperidine-THF (1:1), 24 h, Ar, 20 °C, 46%.

The two 3,5-di-*tert*-butyl phenyl legs (in green) which equip the left side of our molecule were shown to be held in a conformation in which the phenyl groups are nearly perpendicular to the main aromatic board. Moreover, *tert*-butyl groups connected to PAHs are also used to increase organic solubility and are easily observed using STM techniques, inducing a good contrast in the image. The two 4-*tert*-butyl phenyl groups (in blue) play the role of handles for subsequent manipulation with the tip of the microscope. The right side corresponds to the axle with two 9-triptycenyl groups of C_3 symmetry acting as wheels (in red). We opted for two wheels instead of one for obvious synthetic reasons. Figure 5 (CPK model) shows one of the possible conformations of this molecule obtained by molecular mechanics calculations. The two three-cogged wheels can freely rotate around the axle due to the acetylenic spacers.

The synthesis of a polyaromatic hydrocarbon designed by analogy with a wheelbarrow has been achieved in 12 steps and with an overall yield of 2% [28]. As shown in figure 6, our strategy is based on the repetition of a double Knoevenagel–Diels–Alder reaction sequence on an α-diketo fragment. The first sequence allows the connection of the two 3,5-di-*tert*-butyl phenyl legs, while the second sequence provides the precursor for connection of the wheels. Finally, a double Sonogashira coupling yields the molecular wheelbarrow. The starting cyclopentadienone **7** was obtained via a first double Knoevenagel reaction of 1,3-bis(3,5-di-*tert*-butyl phenyl) propan-2-one with diketopyracene (step a) following a described procedure. The Diels–Alder reaction of **7** with di-(4-*tert*-butyl phenyl)acetylene (step b) provided, after CO extrusion and aromatization, ethane-bridged **8** with a 97% yield. The ^{1}H-NMR spectrum of **8** clearly showed the 2:1 ratio between the different types of *tert*-butyl groups. Oxidation of the ethane bridge of the pyracene in **8** with benzeneseleninic anhydride (step c) yielded the
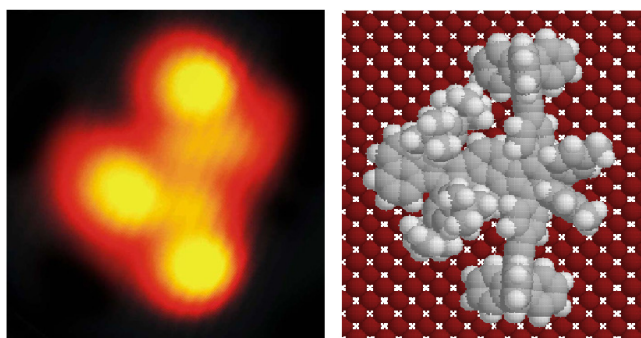
Figure 7. Experimental STM image of the molecular wheelbarrow on Cu(100) (left) and the molecular conformation corresponding to the calculated image (right).

diketo fragment **9** necessary for the connection of the second axle. This is the key step of our strategy. Halogens are introduced at this stage for subsequent coupling in order to connect the triptycene wheels. The double Knoevenagel condensation of **9** with 1,3-di(4-iodophenyl)-propan-2-one (step d) gave the diiodide derivative of cyclopentadienone **10** with a quantitative yield, due to the strong acidic character of the protons involved in the reaction. The Diels–Alder reaction of **10** with di-(4-tolyl)acetylene provided, after CO extrusion and aromatization, the precursor **11** with 30% yield (step e). This low yield may be due to steric hindrance between the overcrowded alkyne and the *tert*-butyl groups of the substrate, but the methyl groups are necessary to improve the solubility of this family of molecules in organic solvents. The two wheels were then simultaneously covalently attached to the axle by a double coupling of 9-ethynyltriptycene with **11** under classical Sonogashira conditions (step f). The double coupling afforded the molecular wheelbarrow **6** with 46% yield. ^{1}H-NMR clearly showed the free rotation of the wheels down to $-90\,^\circ$C, allowed by the presence of the alkyne connectors.

3. Surface deposition

One major issue in the study of mono-molecular machines at the single-molecular level is the deposition of the molecule on the surface. Such molecular-scale machineries are inevitably complex due to the embodiment of several functions on the same molecule. This complexity leads to relatively large molecular weights, e.g. 1802 g mol^{-1} for the wheelbarrow. This is a problem for the surface deposition due to the possibility of thermal fragmentation. Standard sublimation techniques are in use for many low temperature ultra-high vacuum (LT-UHV) STM experiments up to the size of the Lander molecules, for example. But even for the double Lander molecules it was necessary to abandon the sublimation technique for a specific 'rapid heating' procedure, dipping a metallic wire in the solution of the molecules and pulsing a very large current intensity through the wire [29, 30].

In the wheelbarrow case, the required linear wheel axle includes two thermally sensitive triple bonds. Following this 'rapid heating' procedure [31], we successfully imaged intact molecular wheelbarrows on a Cu(100) surface, as shown in figure 7. The identification of the molecule and the determination of the surface conformation of each imaged molecule was obtained by a comparison between experimental and calculated images [1]. As expected for such a complex chemical structure, it leads to a rather complicated STM image, dominated by three intense maxima separated by various weaker structures. Those weaker bumps were attributed to the molecular legs equipping the wheelbarrow, legs which can adopt different

conformations on the surface. Given the similarities between different wheelbarrow molecules in the experimental STM images and calculated images using the electron scattering quantum calculation (ESQC) technique, it is very likely that intact molecular wheelbarrows have indeed been imaged.

So far, we have not reproduced the mechanical behaviour of a wheelbarrow at the molecular level, i.e. converting the translational movement of the tip into rotation of the wheels. Lateral motion of the wheelbarrow appeared to be impossible, due to the very strong interaction of the front wheels with the Cu(100) surface. This could be overcome by, for instance, using a less regular surface such as Cu(111) or by exploring such a manipulation on the surface of an ultra-thin insulating layer deposited on a metal surface, where the interaction is presumably weaker. Nevertheless, the manipulation resulted in a change of conformation of the molecule which confirmed the molecular nature of the object observed; the spots observed in the STM images do not correspond to an assembly of molecular fragments.

4. Recording intramolecular mechanical motion of a single molecule

In the absence of direct time-resolved microscopy to provide an image of the real intramolecular motion or movement of a mono-molecular machine, one has to record those changes via a variation in the tunnelling current [32] or a change in forces using a non-contact atomic force microscope [33]. In both cases, this puts another constraint on molecular design: to simplify or amplify this recording and the way it is reported to the macroscopic scale.

For the molecular wheelbarrow, the design is such that the central board must move up and down when the wheels are turning [26]. This movement will change the tunnelling current passing through the molecular board of the wheelbarrow from the front to the rear part where the tip apex is supposed to push. The explanation of this change is that any variation in height relative to the surface of a part of the molecule decreases the electronic coupling between this part and the surface. This modifies drastically the contribution of the tunnel channel to the overall tunnelling current intensity measured via the current–voltage converter of the STM.

This concept was recently tested experimentally on a Lander molecule, showing that the motion of the board can be detected in the tunnelling current better than the motion of the legs, even if the tip apex is pushing on a leg [34]. This experiment required a specific Cu(211) surface. This surface presents characteristic atomic rows forming rails along which the Lander molecules can be manipulated, the atomic rows pointing in the direction of the Lander central board. A small change in the altitude of the board relative to these rows induces a large change in the tunnelling current (figure 8). While it is being manipulated by being pushed on the lateral legs, the intramolecular mechanics of a Lander molecule is such that pushing on a leg creates a change in the height of the central board relative to the surface.

For force detection, we have recently demonstrated how a non-contact force microscope equipped with a metallic tip can give access to the energetics of the conformation change of a mono-molecular electronic switch [33]. In this case, the tip is positioned at the location of the moving part of the switch. While pushing with the tip apex to pass from the meta-stable 'ON' state to the stable 'OFF' state, the deflection of the cantilever holding the metallic tip is recorded at the same time as the change in the tunnelling current intensity. Knowing the characteristics of the cantilever, one can know the force involved and then the energetics of the switching. This technique will be of interest for following the work produced by the motor molecule we have described here.

Using the variation of a tunnelling current or a force can be considered as the wiring of a mono-molecular machine. It is experimentally convenient to be able to capture information
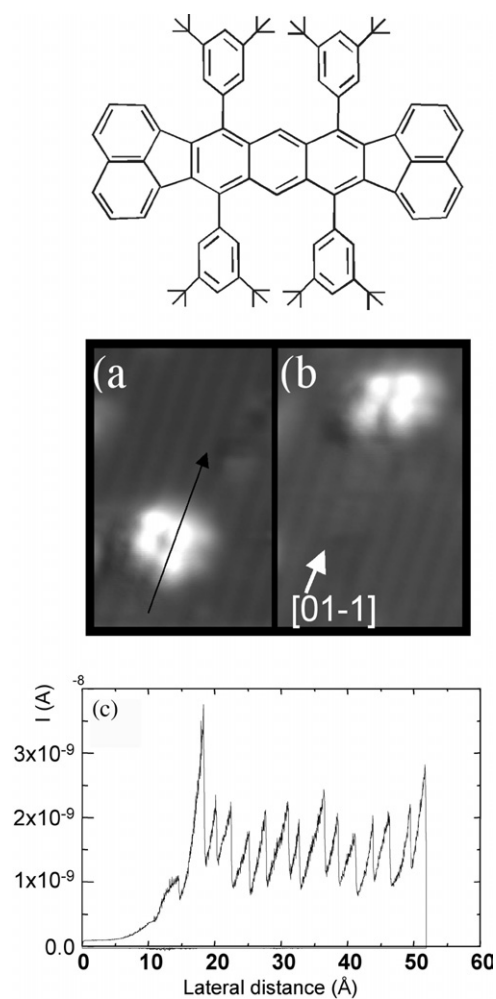
Figure 8. Experimental STM manipulation signal recorded by Moresco and co-workers on a single Lander molecule adsorbed on a Cu(211) surface. Top: chemical structure of the Lander molecule, STM image of the molecule before (a) and after (b) the manipulation and (c) the recorded manipulation signal (from [34]).

such as change in intramolecular conformation, variation in board height or rotation of specific molecular groups. But in the actual experiments the tip apex of the STM is playing two roles: driving the mechanical changes and detecting them. In the future, and with the progress of atomic scale technology, wiring the mono-molecular machine directly from the surface will free the tip apex for motion detection. The problem is the bandwidth of the motion detection as compared to $1/f$ noise. For example, in the tunnelling current noise it has been attempted to detect a characteristic signature of the rotation of a decacyclene molecule by positioning the STM tip apex on its rotor part [11]. But the STM bandwidth was too small to have access to a clear signature of a non-random fluctuation in the recorded signal.

The interpretation of the recorded signal is very delicate. It requires the simulation of the full experiment: the surface, the molecule adsorption, the influence of the tip apex on the molecule and the calculation of the corresponding tunnelling current [32] or force [33].

Since mono-molecular machines have a large weight, only semi-empirical calculations for the mechanics, the tunnelling current and the force are in use. Improvements in this direction have started to emerge with some very recent work on the interpretation of the manipulation of C_{60} on Si(100) [35].

5. Perspectives

The achievement of functional mono-molecular machines is a tremendous long-term task. Here we have given some pointers. Chemical synthesis can yield molecules of a high complexity, which now can be positioned in a very accurate way on metal surfaces. One issue was to have sufficiently rigid systems in order to have exploitable movements inducing mechanical work. This begins to be the case with the molecules presented here, because we have limited their possible degrees of freedom as much as possible, although the molecules always turn out to be 'softer' than assumed. In addition, we now have experimental and theoretical tools allowing us to monitor and understand the behaviour of these tiny machines on surfaces.

But many difficulties remain. Taking the risk of disappointing science-fiction lovers, our machines are still very crude objects, far from being autonomous. They rely totally on the supply of energy, information and orders brought by the STM tip, itself manipulated from the macroscopic world. The next challenges will be to make them more active, by providing them with energy at the right place and at the right time without the detailed intervention of a human operator, and by organizing their environment to make their actions useful.

Acknowledgments

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