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FAST TRACK COMMUNICATION

Controlled transport through a single molecule

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Online at stacks.iop.org/JPhysCM/24/082201**Abstract**

We demonstrate how an electrode–molecule–electrode junction can be controllably opened and closed by careful tuning of the contacts' interspace and voltage. The molecule, an octanethiol, flips to bridge a ~ 1 nm interspace between substrate and scanning tunnelling microscope tip when an electric field exceeds a threshold (switch 'on'). Reducing the field below this threshold value leads to the reproducible detachment of the octanethiol (switch 'off'). Once contacted, a further reduction of the contacts' interspace leads to an increase of the conductance of the molecule.

(Some figures may appear in colour only in the online journal)

In the mid-1970s Aviram and Ratner [1] put forward the elegant idea to use single molecules as functional building blocks for electronic devices, such as transistors, diodes, memories and switches. In order to advance the field of 'molecular electronics' it is of utmost importance to be able to measure the electronic transport properties of single molecules [2]. The ability to understand, control, and exploit the transport properties of single molecules is not only of great interest from a technological point of view [3], but is also essential for further progress and expansion of science in general. For the measurement of electrical conduction through a single molecule one has to connect macroscopic electrodes to each end of the single molecule. This, at first glance, very elementary and simple task, turns out to be extremely difficult to implement [3–5]. Cross-wire junctions [6], mechanical break junctions [7, 8] and scanning tunnelling microscopy (break junctions) [4, 9–12] are the main techniques that have been used to probe the transport properties of molecules. In these studies the conduction often occurs through an ensemble of molecules and therefore the transport properties are averaged out. Moreover, there is also uncertainty about how the molecule(s) are trapped between the electrodes.

To overcome these uncertainties, a novel approach was devised where a pre-selected molecule has been lifted from

the substrate and analysed [13–17] by scanning tunnelling microscopy (STM). Using this approach Lafferentz *et al* [13] studied the transport properties of a single polyfluorene wire as a function of length, whereas Temirov *et al* [14] addressed the Kondo effect of perylene-tetracarboxylic-dianhydride molecules. More recently, similar methods were applied by Leary *et al* [15] to study the transport through bifluorene molecules that were capped with C₆₀ fullerenes and Toher *et al* studied the electrical transport of perylene-tetracarboxylic-dianhydride molecules [16]. In 2009, Kockmann *et al* [17] showed that a single octanethiol molecule can be trapped between a Pt nanowire and the apex of an STM tip. At a current setpoint of 1 nA and sample bias of +1.5 V the octanethiol molecule occasionally jumps into contact. This method allows the measurement of the conductance of a single, pre-selected octanethiol molecule. However, control over the attachment and detachment process of the octanethiol molecule was not obtained.

In this paper, we show controlled transport through a single octanethiol molecule trapped between an STM tip and Pt/Ge(001) substrate. Full control over the jump into and out of contact of the molecule has been obtained by carefully adjusting the distance between STM tip and substrate. This tip–molecule–substrate junction acts as a molecular switch that can be opened and closed by varying the voltage across the junction. A careful analysis reveals that the jump

¹ Both authors have contributed equally.

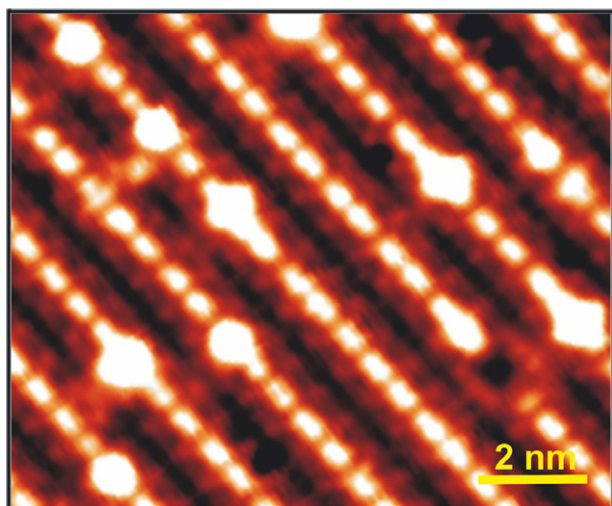


Figure 1. Filled state STM image recorded at 77 K of octanethiol molecules immobilized on a Pt/Ge(001) surface (setpoint: -0.9 V, 0.5 nA). The large, white features are octanethiol molecules adsorbed on the Pt nanowires (see [17]).

into and out of contact is governed by the electric field between both electrodes. The threshold electric field for attachment/detachment is $4\text{--}6 \times 10^9$ V m $^{-1}$. In addition, we show that further reduction of the contacts' interspace leads to an increase of the conductance of the molecule.

We have used Pt/Ge(001) substrates [18, 19] to immobilize the octanethiol molecules and an ultra-high vacuum (UHV) system equipped with an Omicron low temperature scanning tunnelling microscope (LT-STM) for transport measurements. The flat, Pt/Ge(001) substrates (4×10 mm 2) were prepared and exposed to octanethiol molecules in a UHV chamber. Cleaning of Ge(001) substrate was done by cycles of ion bombardment using 500 eV argon ions followed by annealing at 1100 K. This process was repeated several times until atomically clean Ge(001) surfaces were obtained [20]. Subsequently, we deposited 0.5 monolayers of Pt onto the clean Ge(001) surface at room temperature followed by annealing at 1100 K. This leads to the formation of regions covered with atomic Pt chains. The majority of these chains exhibit a mutual spacing of 1.6 nm. More detailed information on the procedure, the formation and the properties of these self-organizing atomic Pt chains is given in [18, 19]. The Pt/Ge(001) substrate was subsequently exposed to octanethiol molecules (98.5% pure, purchased from Sigma-Aldrich) via a leak valve, with a precise control of exposure. We exposed the substrates to a pressure of 2.5×10^{-7} Torr for 40 s leading to an exposure of ~ 10 Langmuir (L). The substrate was then transferred to the STM chamber and cooled down to 77 K to carry out the measurements.

A filled state STM image of a Pt/Ge(001) substrate, exposed to 10 L of octanethiols ($\text{CH}_3(\text{CH}_2)_7\text{SH}$), recorded at 77 K is shown in figure 1. Open loop current–time measurements performed on top of an octanethiol molecule show that the gap between tip and substrate can be closed by the molecule making contact with the tip. During acquisition

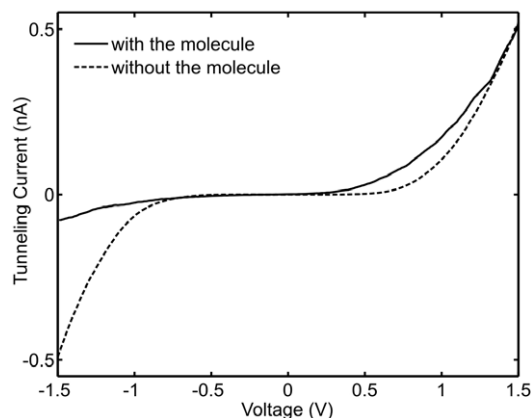


Figure 2. Tunnelling current–voltage (I – V) curves of the tunnel junctions recorded at 77 K before and after the STM tip has picked up an octanethiol molecule. For both traces we have used a setpoint value of 0.5 nA at 1.5 V.

of the current–time traces the tail (C–H end) of the molecule flips into contact with the tip, resulting in an increased current, jumping from its setpoint value (1 nA) to $11\text{--}15$ nA (see [17] for details). The tail typically remains in contact for a few tens of seconds before it detaches again. The length of the octanethiol molecule (~ 1 nm) nicely fits into the vacuum gap between the substrate and the STM tip and therefore the extracted resistance value of $100\text{--}140$ M Ω corresponds to a resistance of a single octanethiol molecule at $+1.5$ V, which is in good agreement with values reported in the literature [20–22]. It should be noted that the molecule jumps randomly in and out of contact and therefore it was not possible to obtain full control over the switching process.

In subsequent experiments we attached the head (S–H end) of a single octanethiol molecule to the tip by recording current–time traces at tip–surface distances smaller than 1 nm. When the sulfur atom of the octanethiol makes contact with the tungsten STM tip, it forms a strong bond and therefore the tail of the octanethiol is usually fully released from the surface upon retraction of the tip. I – V curves of the tunnel junctions recorded using a tip decorated with an octanethiol molecule are significantly different from I – V curves recorded using a tip without a molecule (see figure 2). Both I – V curves are recorded on the Pt nanowires at a setpoint of 0.5 nA and $+1.5$ V bias voltage. A molecule being attached to the tip leads to rectifying characteristics of the I – V traces of the junction. This behaviour can be attributed to the large band gap of alkanethiol molecules with the highest occupied molecular orbital (HOMO) being close to the Fermi level. In the case of alkanethiol molecules on Au, the HOMO lies 2 eV below the Fermi energy [23]. For a positive substrate bias, the electrons tunnel from the tip through the molecule to the surface giving rise to higher current compared to a negatively biased substrate.

We performed a series of current–distance measurements with an octanethiol molecule attached to the tip, at various locations on the sample surface. The sample bias was set to $+1.5$ V and the tunnelling current to 0.2 nA (see figure 3). After bringing the STM tip closer to the substrate by a distance

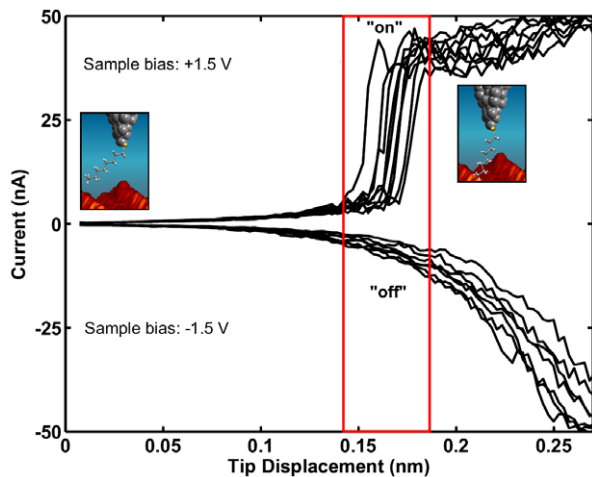


Figure 3. Current–tip–displacement traces recorded with an octanethiol molecule attached to the apex of the STM tip. Top: the sample bias is 1.5 V and the tunnelling current is set to 0.2 nA. As the STM tip approaches the substrate by ~ 0.15 nm the molecule makes contact and the current jumps to 35–40 nA (‘on’ state). Bottom: the sample bias is -1.5 V and the tunnelling current is set to 0.2 nA. The octanethiol molecule does not jump into contact (‘off’ state).

$\Delta Z = 0.15\text{--}0.18$ nm (ΔZ refers to the Z -displacement of the tip towards the surface with respect to the set point height), the octanethiol molecule makes contact with the substrate and the current jumps to a higher value of 35 ± 5 nA (see figure 3). The variation in the conductance may be attributed to the various contact geometries the molecule can have with the STM tip and the substrate. For a negative sample bias, however, the octanethiol never jumps into contact and the tunnelling current

shows an exponential dependence with distance. The position of the transition from ‘off’ to ‘on’ (see the box in figure 3) depends on the actual value of the applied bias voltage. The I – V and I – Z spectroscopy data provide strong evidence for a successful attachment of a single octanethiol molecule to the apex of the tip.

By using the current decay constants for electron transport through a vacuum gap (22.0 nm^{-1} [5]) and an alkanethiol molecule (8.1 nm^{-1} [5]), we can estimate the separation between the freely hanging end of the octanethiol molecule and the substrate using Simmons’s model [24]. The conductance, G_{contact} , corresponds to the case where the molecule makes contact with the substrate and the transport occurs through the molecule, while $G_{\text{non-contact}}$ refers to the case where the molecule is out of contact and the transport occurs through the molecule and vacuum gap. Since the bond between the tail of the octanethiol molecule and the substrate can easily be broken the contact resistance is substantial. Therefore G_{contact} should also include the contact conductance between molecule and substrate. However, the contact conductance is much larger than the conductance of a single octanethiol molecule and therefore it can safely be ignored. The conductance ratio, i.e. $G_{\text{contact}}/G_{\text{non-contact}}$ ($G_{\text{contact}}/G_{\text{non-contact}} \sim 23 \text{ nA}/0.16 \text{ nA} = 145$ at $+0.7$ V), can be extracted from figure 3. If L (~ 1 nm) is the length of the molecule, G_{contact} will be proportional to $e^{-8.1L}$ [5]. We can calculate $G_{\text{non-contact}}$ from the total resistance when the transport occurs through the molecule and the vacuum gap. The total conductance can in this case (coherent tunnelling) be factorized [5], i.e.

$$\frac{G_{\text{contact}}}{G_{\text{non-contact}}} = \frac{e^{-8.1L}}{e^{-8.1L}e^{-22d}} = e^{22d} \approx 145 \quad (1)$$

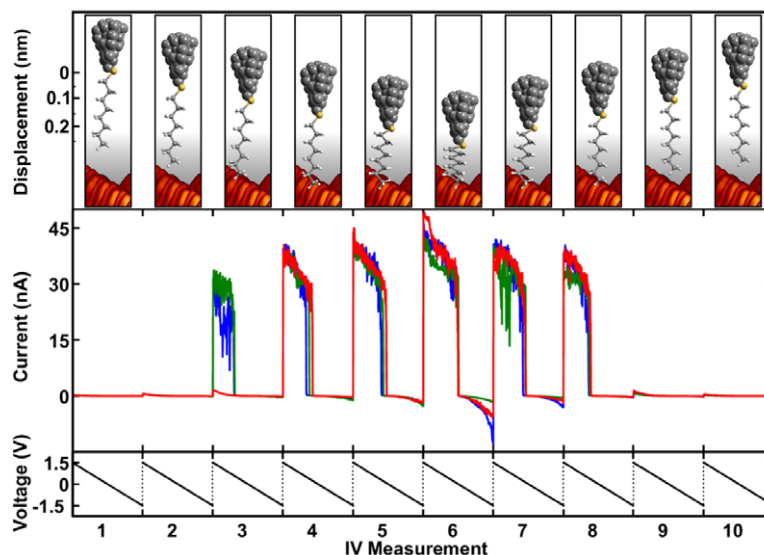


Figure 4. A set of three I – V curves (middle section; red, blue and green curves) recorded in series, with varying tip–substrate distance and the feedback loop disabled. The top section shows a simplified diagram of the molecule attached to the apex of the tip and its relative position with respect to the substrate. The bottom section shows a series of voltage ramps from $+1.5$ to -1.5 V as the tip has moved, in steps of 0.05 nm. Traces 1–6 correspond to the tip’s relative position from the setpoint height (i.e. 0.2 nm and 1.5 V) to 0.25 nm, while traces 7–10 correspond to the relative position from 0.1 to 0.05 nm. After approaching the substrate by 0.1–0.15 nm (traces 3–4) the octanethiol molecule jumps into contact and for I – V curve no. 8 the molecule jumps out of contact.

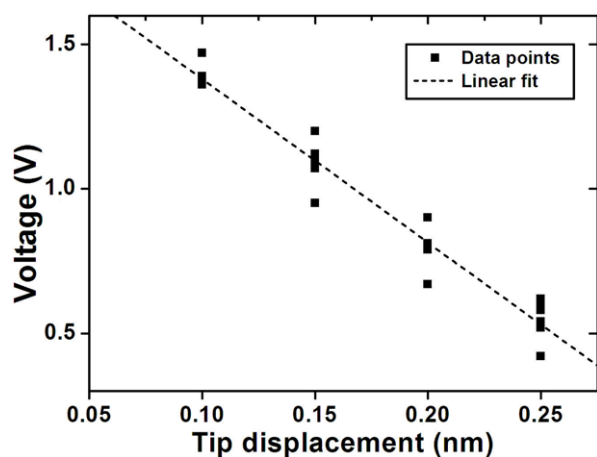


Figure 5. Threshold voltage is plotted against tip displacements while the tip moves towards the surface. We extract a threshold electric field value from the slope of the linear fit to be $4\text{--}6 \times 10^9 \text{ V m}^{-1}$.

where d is the vacuum gap between the freely hanging end of the molecule and the substrate when the tip is positioned at its setpoint height. From equation (1) we find that d is about 0.23 nm. Near zero bias the required tip displacement for jumping into contact is 0.36 nm as extracted from the fit in figure 5.

It is important to note that this separation is significantly larger than the tip displacement required for the molecule to make contact. Therefore it is very likely that the flexible tail of the molecule jumps into contact beyond a certain threshold value of the electric field. Before jumping into contact the tail of the molecule is at an angle with respect to the shortest tip/substrate trajectory, as shown in figure 3. This angle tends to decrease upon changes in the electric field between tip and substrate as the tip approaches the surface. It is also evident from these traces that only one molecule is attached to the tip. For the attachment of more than one molecule, one would see multiple jumps in the current. The current in contact is about ~ 2.5 times larger than reported for the case where the sulfur atom of the octanethiol is attached to the Pt nanowire [17]. There can be several reasons for that. One viable explanation for this difference is that the number of C atoms trapped in the junction is now seven rather than eight [17]. The conductance G of an alkanethiol molecule decreases exponentially with the length of the molecule, i.e. $G \propto e^{-\beta L}$. The value of the decay constant β is 8.1 nm^{-1} . If one carbon atom less is involved in the transport, the effective length of the molecule is reduced and the conductance will increase by a factor 2.5.² This is in very good agreement with our observations. Other possibilities may include a different adsorption geometry of the molecule at the apex of the tip as compared to the situation in figure 1 [17], e.g. sliding of the molecule along the electrode, a different electrode material (Pt or W) or a deformation of the electrode. At this stage, it is difficult to determine the exact adsorption geometry of the molecule at

the apex of the STM tip or the exact morphology of the electrodes.

In figure 4, a set of three consecutively recorded current–voltage traces are shown. For each measurement the voltage is repeatedly ramped (ten times) from +1.5 V to -1.5 V as shown in the bottom section. During the whole measurement the feedback loop of the scanning tunnelling microscope is disabled [25]. In addition, after each I – V trace, the STM tip is moved 0.05 nm closer or away from the substrate as shown in the top section. The I – V traces are shown in the middle section. For I – V traces numbered 1–6, the tip was moved closer to the surface and similarly for I – V traces numbered 7–10 the tip was moved away from the surface in steps of 0.05 nm before the measurement. After approaching the substrate by 0.1–0.15 nm at +1.5 V the octanethiol molecule immediately jumps into contact (‘on’ state). However, at negative sample bias the molecule remains always in its ‘off’ state. The contact at positive bias breaks again as soon as the voltage is below a threshold value of about 0.4 V. This threshold voltage changes with changing gap spacing indicating that the attachment/detachment is governed by the electrical field, rather than the voltage, as shown in figure 5. The molecule jumps into (out of) contact for an electric field threshold higher (lower) than $\sim 4\text{--}6 \times 10^9 \text{ V m}^{-1}$. This is also consistent with the I – Z measurements recorded at various substrate bias values. We found that for smaller sample biases attachment occurs at slightly larger ΔZ . However, it should be noted that this controlled switching only occurs if the STM tip is sufficiently close to the surface (i.e. 0.7–0.8 nm). Traces 3 and 8 are borderline cases ($\Delta Z = 0.1$ nm) since the jump into and out of contact is not fully under control yet (see I – V measurement 3). We believe that the latter is related to the length of the octanethiol molecule. The octanethiol molecule has a length of about 1 nm and thus nicely fits in the tunnel junction for a tunnelling current of 0.2–1.0 nA, however in this case the bonding is rather weak since only one C atom can interact with the electrode. For a substrate–tip separation of less than 1 nm (after a tip displacement of 0.15 nm with respect to the setpoint height) the bonding becomes significantly stronger due to the possibility of more C atoms interacting with the electrode (see diagram of figure 4). This interpretation is strongly supported by the observation that the conductance of the trapped octanethiol molecule is larger by a factor of 2.5 as compared to the case where the tip–substrate separation is at its initial distance, i.e. $\Delta Z = 0$ nm.

Upon a further reduction of the contacts’ interspace the conductance of the octanethiol molecule gradually increases. From figures 2 and 4 we extract that the conductance increases roughly by 20% per 0.1 nm of compression. This value is substantially smaller than the increase of about 200% as predicted by the exponential dependence of the conductance, G , on the length of the molecule (see footnote 2). The C–C bonds are arranged in a zigzag structure, with a bond length of 0.154 nm and a C–C–C bond angle of 109° . It is likely that the bond angles become slightly smaller upon compression with the C–C bond length remaining unaltered. In order to explain our experimental data we have to assume that either

² The projected C–C bond length along the long axis of the octanethiol molecule is 0.125 nm.

the change in C–C–C bond angle significantly reduces the decay constant or that the molecule is bent within the tunnel junction or it is sliding along the contact.

In summary, we have shown controlled electronic transport through a single octanethiol molecule trapped between a Pt/Ge(001) substrate and an STM tip. The molecule can be controllably attached and detached to the substrate by adjusting the electric field between tip and substrate. Once contacted, a further reduction of the contacts' interspace leads to an increase of the conductance of the molecule.

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