

Single Molecular Wires Connecting Metallic and Insulating Surface Areas**

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Molecular wires are key components for future circuits in molecular electronics.^[1,2] Their utilization in a future electronic device requires the adsorption of the wire on a non-conducting substrate, which makes an electrical characterization on the molecular level challenging. Furthermore, such molecular electronics devices will require ultrathin insulators that electrically separate conducting components, and in particular wires, from each other. Ultrathin films of insulators, such as layers of metal oxides or alkaline halides that are a few atoms thick and grown on conducting substrates retain enough of their insulating properties to act as separators.^[3,4] At the same time, these films are thin enough to ensure for sufficient electron tunneling and thus for imaging of single atoms and molecules by scanning tunneling microscopy (STM). NaCl turns out to be a suitable insulating material; it already exhibits a large band gap as a bilayer,^[5,6] which grows on various metal surfaces^[7–17] in a flat and very homogeneous manner with a low number of defects. The study of single molecules on such films by STM allows to spatially image the orbitals of a single molecule by its reduced and oxidized tunneling resonances as a consequence of the decoupling by the intermediate NaCl film.^[6,18]

Single molecules have been studied either on metals or semiconductors or insulating films; that is, on substrates that provide very different environments. However, the adsorption of one and the same molecule on a surface with insulating and conducting areas has never been achieved. Such a planar configuration would provide unique insight into the intra-

molecular coupling and also access to the molecular wire during charge transport experiments. However, the creation of this particular configuration with large adsorption areas on both materials is an experimentally difficult task. First, it requires very long molecules, which are difficult to synthesize by conventional organic chemistry and can hardly be deposited intact under clean ultra-high vacuum conditions owing to their high molecular weight.^[19] To overcome this problem, it is necessary to covalently bind molecular building blocks directly on the surface, which we do by our thermally activated on-surface synthesis.^[20,21]

Second, it is even more challenging to make one and the same molecule adsorb simultaneously on different surfaces, as different surface areas exhibit vastly different diffusion properties for the same molecules. For example, molecules are much more mobile on NaCl films than on the metal surface,^[22] which requires low sample temperatures to enable adsorption on the NaCl areas upon molecular deposition.^[23] However, this condition is in contradiction with the presence of long molecular chains on the surface, because they can only be produced by on-surface synthesis, which requires at least temperatures that allow efficient precursor diffusion, and ideally involves heating of the sample to more than 500 K.^[20] The experimental challenge is therefore to connect the two processes, namely organic on-surface synthesis and inorganic crystal growth, which should neither suppress each other nor should they lower the quality of one of the in-situ generated components.

Herein, we present a method to adsorb one part of a long molecular wire on a NaCl island whilst the other part of the same wire is located in the metallic area of the surface. We demonstrate how the electronic properties of the wire depend on the local atomic-scale environment.

In principle, two preparation steps are required: 1) Covalently bound molecular chains are formed from dibromoterefluorene (DBTF) monomers consisting of three fluorene units carrying lateral methyl groups, and a bromine atom at each end. Very long molecular wires of more than 100 nm length are grown from these molecular precursors on Au(111) at 520 K (Scheme 1).^[21] 2) Thermal evaporation of NaCl on clean Au(111) at sample temperatures between 270 and 350 K leads to the formation of crystalline (001)-oriented NaCl islands with rectangular shape, owing to the preferential formation of non-polar step edges.^[16,17]

We investigated two methods that differ in the order of these two preparation steps and cause significantly different results; however, both methods yield intact molecules and crystalline NaCl islands (Figure 1). In method I, NaCl growth is initially obtained by evaporation of NaCl on Au(111) held

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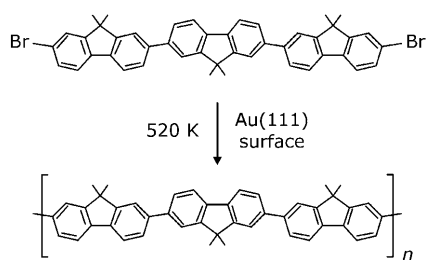
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Scheme 1. Thermal on-surface polymerization of dibromoterfluorene (DBTF) monomers to yield poly(9,9-dimethylfluorene).

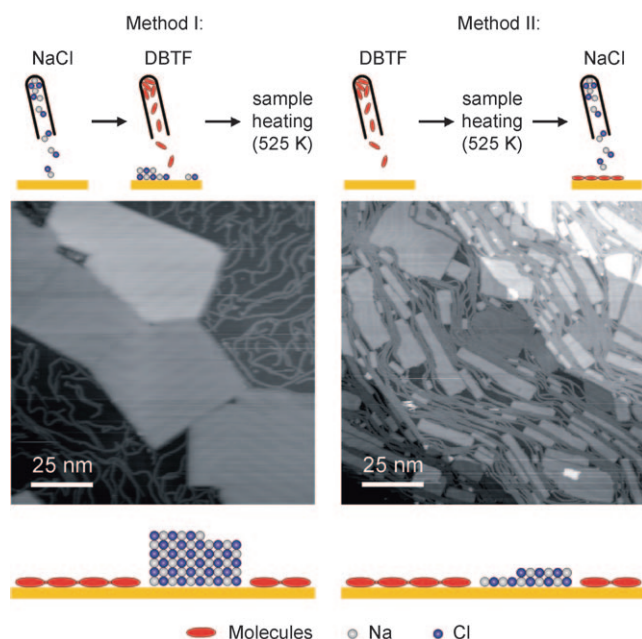


Figure 1. Methods I and II used for the preparation of co-existing molecular wires and crystalline NaCl films. Top: the order of the preparation steps; center: STM images ($I_t = 79$ pA (left) and 10 pA (right); $V_t = -1.0$ V); bottom: corresponding illustrations of the resulting surface structures. Different terraces of the Au(111) substrate, separated by step edges, appear at different heights (i.e., brightness). The apparent height of the presented NaCl islands for method I is 6.3 ± 0.1 Å, which is larger than the geometrical height of a NaCl bilayer, thus at least three layers of NaCl are present.

at room temperature. Then, DBTF molecules are deposited on the Au(111) substrate, which is partly covered with NaCl islands, followed by sample annealing to 525 K (required to activate and connect DBTF monomers). The undisturbed formation of covalently bound molecular chains from mobile activated TF monomers in the presence of mobile NaCl is remarkable. Highly crystalline NaCl islands separate flat Au(111) terraces, which are covered with homogeneous, long chains (STM image in Figure 1, left). However, these islands are rather high (thicknesses of at least 3–5 ionic layers) and therefore the final annealing step in this preparation causes a multilayer NaCl island ripening, whereas the polymers are found in the gaps between these nano-crystallites and are never adsorbing on the islands, even at very high molecular coverages.

In method II (Figure 1, right), the polyfluorene chains are synthesized first, and NaCl is subsequently deposited on the slightly cooled (270 K) Au(111) surface. The lower substrate temperature limits the mobility of NaCl during island growth and NaCl islands that are predominantly one or two ionic layers in height are formed between the polymers. The NaCl islands are rather small and elongated owing to the presence of the chains, which is in contrast to the NaCl growth on clean Au(111).^[16,17] Nevertheless, NaCl islands are highly crystalline and form straight non-polar step edges. It is important to note that the flexible polymers only weakly interact with the gold substrate^[21] and can thus adapt their shape and adsorption site to the growing inorganic crystallites. In contrast to method I, the island height is limited. However, the co-adsorption of the wires on the metal and the NaCl still remained an open question.

Starting from method II, we found that the lateral size of the NaCl islands can be increased and their crystalline structure maintained^[24] until molecular wires are forced to adsorb on the insulating film. Figure 2 a–c demonstrates the structural evolution of a sample upon increasing the NaCl coverage. NaCl islands grow upon deposition from mainly 1–2 atomic layers to mainly 2–3 atomic layers, as indicated in the STM images. As intended, the growing NaCl islands laterally repel the polymer chains; this process is enabled by the mobility and flexibility of the molecular wires. The area of

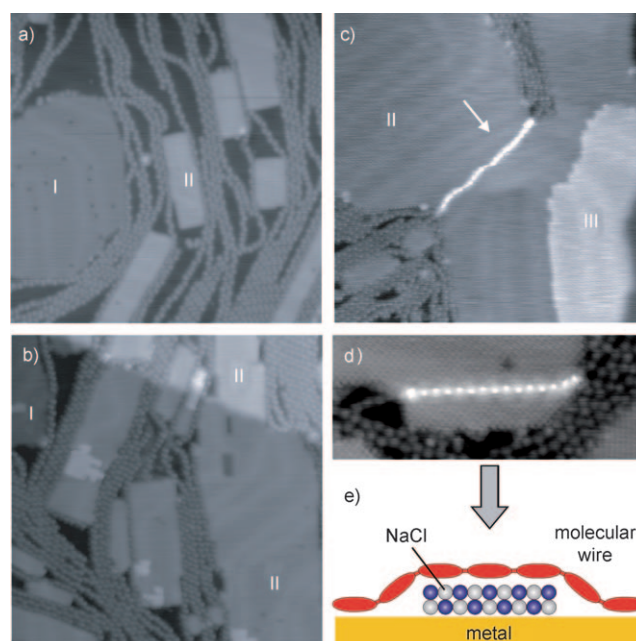


Figure 2. a–c) STM image series ($I_t = 10$ pA; $V_t = -1.0$ V, all 31×31 nm²) for a successive increase in the coverage of NaCl from 0.4 ML (a) to 0.8 ML (b) and 1.2 ML (c) of NaCl (1 ML NaCl refers to a surface that is completely covered with a single NaCl layer, or half of it with a bilayer). Different thicknesses of NaCl are indicated by I (single layer), II (bilayer), and III (three layers). In (c), a single molecular chain is adsorbed partly on the metal and partly on top of a NaCl bilayer (marked by an arrow). (d) STM image ($I_t = 10$ pA; $V_t = -1.0$ V, 15.4×6.1 nm²) of a smaller region with this particular co-adsorption configuration (on an atomically resolved NaCl bilayer) with the corresponding model in (e).

clean Au(111) is thus continuously decreased during NaCl deposition. Note that even for small NaCl coverages, and although the surface is densely covered with molecular wires, the islands show crystalline order and form preferentially straight edges in the case of bilayers (Figure 2a).

Molecular growth by method II not only leads to clean NaCl areas and polymer/Au(111) areas, but also to a very particular configuration: the co-adsorption of molecular wires on both materials. Above a critical NaCl coverage, some chains rise to the top of the growing NaCl film and are thus lifted from the Au(111) surface, which is due to the lateral growth of the islands and thus the continuous reduction of space in the gaps between them. In Figure 2c,d, such a long polymer chain with both ends adsorbed on clean Au(111) (illustrated in Figure 2e) is visible. Thus, by following the preparation order of method II, and by adjusting the coverage of NaCl, single molecular chains routinely adsorb with one part on an insulating film^[25] and with another part of the same chain on a metallic portion of the substrate. The NaCl islands are also found to be crystalline directly underneath the molecular chain. We also investigated partial adsorption of a single molecular chain on a single layer of NaCl by lifting single chains from the Au(111) surface onto the NaCl film with the STM tip.^[24] However, the success rate of this manipulation and the length of the molecular wire portion adsorbed on NaCl with this method are limited.

Owing to the particular hybrid adsorption configuration (Figure 2c–e), the molecular wire units adsorbed on the NaCl surface are expected to be electronically decoupled from the metal surface underneath, in contrast to the units directly physisorbed on the Au(111) surface. To investigate how the different environments affect the molecular wire, STM images were recorded on both portions, that is, on NaCl and Au(111), for different bias voltages, thus probing the electronic structure of the molecular wire. The experimentally determined apparent height (in constant-current scanning) is given by the conductance of the tip–vacuum–molecule–surface tunneling junction at the chosen bias voltage, which is directly related to the electron transmission through the molecule and thus to its electronic structure.^[28,29]

Figure 3b–d demonstrates how the apparent height of one and the same chain, partially adsorbed on a NaCl bilayer, varies in such a series. The height clearly increases at more negative bias voltages, which points to an electronic (and not topographic) effect, thus indicating a resonant tunneling process through the molecular wire at these electron energies. This intensity difference is only observed for the part on top of the NaCl film; the appearance of the other part of the same chain adsorbed on Au(111) does not change (owing to the lack of electronic decoupling) and shows the characteristic appearance of molecular chains that are entirely adsorbed on Au(111) (see Figure 3a for comparison).^[21]

To characterize bias-dependent imaging quantitatively, we have determined the apparent heights (Δz) of chains on Au(111) as well as on monolayer and bilayer NaCl films at different bias voltages (Figure 3e). The apparent height of the chain portion adsorbed on Au(111) remains constant ($2.03 \pm 0.10 \text{ \AA}$) over the entire bias range and is identical to that observed on the portion on ultrathin NaCl films (monolayer

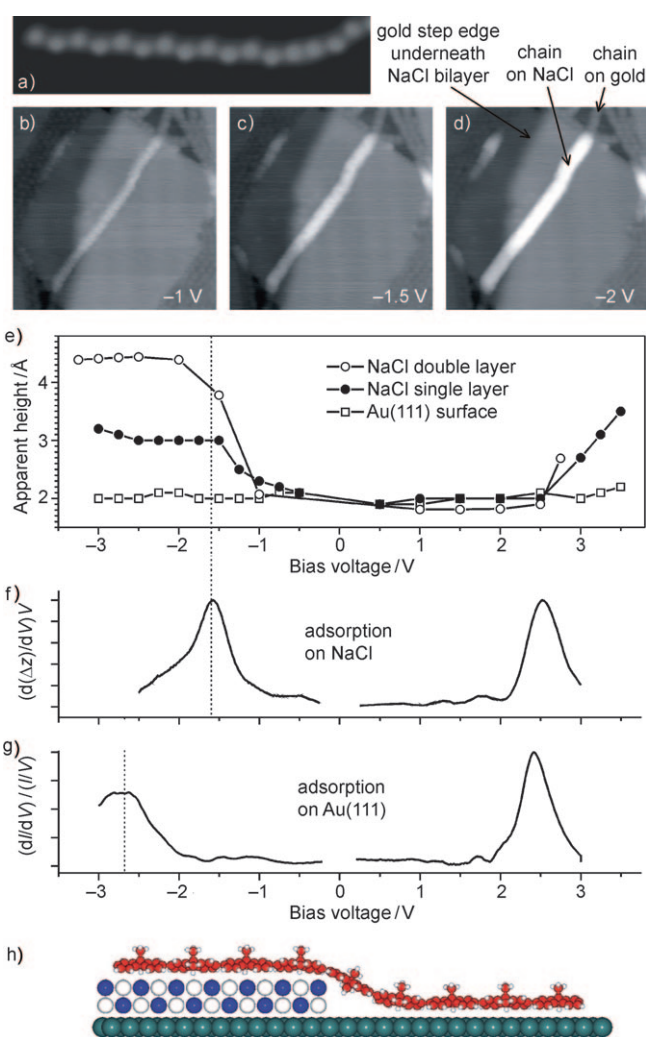


Figure 3. a) STM image ($I_t = 0.1 \text{ nA}$; $V_t = 1 \text{ V}$; $14.4 \times 3.2 \text{ nm}^2$) of a polyfluorene chain on Au(111) (preparation without NaCl). b–d) Bias-dependent imaging of a molecular polyfluorene chain on a NaCl bilayer on Au(111) ($I_t = 10 \text{ pA}$, image size = $15.4 \times 15.4 \text{ nm}^2$). e) Apparent height (above the respective surface area indicated in the legend) of chains co-adsorbed on NaCl and Au(111) at different bias voltages. f) $d(\Delta z)/dV$ spectra of the polymer adsorbed on a NaCl bilayer. No dI/dV spectrum could be obtained for the entire range of interest because of the low diffusion barrier of the polymer chains on NaCl. $d(\Delta z)/dV$ spectroscopy enables to access higher voltages, whilst keeping the tunneling current constant at values ranging from 0.01 to 0.1 nA.^[26,27] g) $d(I)/dV/(I/V)$ spectrum of a polyfluorene chain on Au(111). h) Calculated configuration of a single molecular chain adsorbed simultaneously on the NaCl layer (left) and on the Au(111) surface (right). All observed features are located within the NaCl band gap.

and bilayer) from -1.5 V to $+2.5 \text{ V}$. However, larger apparent heights emerge for the chain portion on NaCl at voltages beyond: Increasing apparent heights are obtained above $+2.5 \text{ V}$ (stable imaging of the chains was impossible at higher bias voltages), whilst at negative bias voltages below -1.5 V saturation is observed. The appearance of the molecular chains on the NaCl layer at higher voltages is typically very homogeneous, lacking intramolecular structure. This could be due to local motion of the monomer segments

of the polymer chain caused by resonant tunneling through the molecule^[30] or attractive forces from the STM tip. As molecular motion is much faster than the scanning speed, it can not be resolved in the STM images.

Local spectroscopic measurements on different positions of the molecular chain, adsorbed on Au(111) or on the NaCl film, confirm these results. The molecular orbitals of the chain on the Au(111) surface (Figure 3 g) are located at -2.71 ± 0.10 V (occupied orbital) and at $+2.58 \pm 0.10$ V (unoccupied orbital). In strong contrast, molecular chains on bilayer NaCl films show a tunneling resonance at -1.60 ± 0.10 V in $d(\Delta z)/dV$ spectra (Figure 3 f) and in dI/dV spectra.^[24] For the other polarity, a resonance is observed at $+2.41 \pm 0.10$ V and thus at about the same energy as for chains on clean Au(111). Note that the spectroscopic results of a molecular chain on clean Au(111) are equivalent for the case of co-adsorption (that is, another portion of the chain is adsorbed on NaCl) and for a chain that is entirely adsorbed on Au(111).

These observations are due to the local adsorption area of the molecule, thus demonstrating the possibility to partially decouple a molecular chain from a metal and thus to visualize the electronic structure of one and the same molecule in dependence of its local atomic scale environment (Figure 3 h). Therefore, the resonance at -1.6 V is suppressed for molecular adsorption on the metal, but is visible on NaCl owing to the electronic decoupling. This resonance is also visible on polyfluorene chains that are adsorbed in the second layer and is thus clearly related to the wire (and not to the NaCl layer).^[24] Furthermore, the onset remains at about the same position for a single and a double layer of NaCl (Figure 3 e) and it therefore seems to reflect the tunneling resonance through the highest occupied molecular orbital (HOMO) of the polyfluorene chain, which is suppressed on the pure Au(111) surface. The position of this resonance in the spectra is in agreement with spectroscopy measurements of poly(9,9'-dioctylfluorene) films, which shows a peak in the same region.^[31] The larger HOMO–LUMO gap in our spectra (4 eV compared to 3 eV) is most likely due to the deviation from planarity upon adsorption.^[24]

When the STM tip is positioned above the portion of the wire adsorbed on NaCl, in principle, two tunneling paths exist from the tip to the gold substrate: Either *laterally* along the molecular chain towards the Au(111) surface, or *vertically* through the molecule and the NaCl layers (see the Supporting Information, Figure S6).^[24] The competition between the two is determined by two sets of parameters: the inverse decay factors of electron tunneling, and the lengths of the two current paths. The inverse decay length through the molecular wire is only 0.3 \AA^{-1} ,^[21] whilst that through a few NaCl layers is 1.2 \AA^{-1} .^[24] But a molecular unit has a length of 9 \AA , whereas a NaCl layer is only 2.82 \AA thick.

In a first approximation, we can estimate from a simple comparison of the two current channels that the leakage current through the NaCl bilayer is too large with respect to the tunneling decay along the molecular wire. The exponential factor of the conductance is given by the product of the inverse decay length and the corresponding geometrical distance. As about four fluorene units (9 \AA length each) are required between the contact to the metal surface and the

planar adsorption on the NaCl layer, this factor is in a first approximation at least $(4 \times 9 \text{ \AA}) \times 0.3 \text{ \AA}^{-1} = 10.8$ for the molecular wire. Almost the same value is obtained for the NaCl tunneling channel if three NaCl layers are used: $(3 \times 2.82 \text{ \AA}) \times 1.2 \text{ \AA}^{-1} = 10.15$. Therefore, three to four NaCl layers are needed to achieve a tunneling current *along* the molecular wire to the Au(111) surface that is comparable with the vertical leakage current through NaCl (not considering contact effects), which is in agreement with calculations.^[24] Thus, vertical tunneling through the NaCl film is dominating at the investigated NaCl thicknesses, and the major part of the tunneling current does not flow along the molecular wire as it may be intuitively inferred from this particular arrangement. If charge transfer along the molecular wire would dominate, smearing of the molecular appearance in the step edge area would occur,^[24] whereas a sharp transition (in molecular brightness and contrast in the STM image) between the two areas at the NaCl step edge is observed in the experiments, which is in agreement with the considerations above.

In future experiments, it would be of interest to study charge transport through the molecular chains in this particular horizontal interconnection configuration as it allows for simultaneous imaging, in contrast to our previous vertical measurements.^[21] Thicker layers would decouple the molecular chain more efficiently and reconfigure the tunneling paths in favor of the molecular wire. This tendency is apparent in Figure 3 e, where a polyfluorene chain appears $3.04 \pm 0.03 \text{ \AA}$ high on a NaCl monolayer, whilst it appears clearly higher on a bilayer ($4.39 \pm 0.07 \text{ \AA}$). This enhanced apparent height proves the increased decoupling strengths of a NaCl bilayer as compared to a monolayer. Furthermore, a polymer strand with a significantly higher intrinsic conductance would be desired to provide more efficient charge transport also on a NaCl bilayer.

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