

Driving Current through Single Organic Molecules

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We investigate electronic transport through two types of conjugated molecules. Mechanically controlled break junctions are used to couple thiol end groups of single molecules to two gold electrodes. Current-voltage characteristics (*IV*s) of the metal-molecule-metal system are observed. These *IV*s reproduce the spatial symmetry of the molecules with respect to the direction of current flow. We hereby unambiguously detect an intrinsic property of the molecule and are able to distinguish the influence of both the molecule and the contact to the metal electrodes on the transport properties of the compound system.

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Electronic transport through molecules was first described theoretically in the 1970s [1,2]. Since then, numerous experiments have been made where electrical current was driven through single-layer molecular films between two metallic electrodes [3–5]. Transport through single or at most a few molecules on a gold surface has been observed with scanning tunneling microscopes (STM), where the tip serves as a counterelectrode [6,7]. In the STM tunneling regime, the current-voltage characteristics (*IV*) reflects the electronic density of states in the molecule and the conductance depends very sensitively on the tip distance. Only a few experiments, however, have been realized which target current through a single molecule while the connection to both electrodes is symmetrically realized by a well defined chemical bond, which allows mechanical stability of the junction even at room temperature [8,9]. However, to identify the *IV*s observed in these experiments as arising from a current through indeed a single sample molecule, comparison with some theoretical assumptions is required concerning the conductance amplitude, the transport mechanisms, and the electrochemical potential of the sample. The experiment described in this Letter demonstrates clearly and without the necessity of any assumptions that we observe electronic transport through a single molecule (or at most very few) and not a large ensemble of molecules. This is achieved by comparing the *IV*s of spatially symmetric and asymmetric but otherwise similar molecules. Further, an analysis of the *IV* data gives new qualitative insight concerning the crucial role of the molecule-metal contact.

The two types of organic molecules were designed specifically for the present experiment (cf. Fig. 1). Both consist of a rigid rodlike central section with additional thiol functions on both ends to form stable covalent bonds to gold electrodes. Details of the synthesis will be published elsewhere. As the molecules are very similar, comparable electronic properties are expected. However, their main difference is their spatial symmetry. While the anthracene derivative (in the following referred to as “symmetric molecule”) has a symmetry plane perpendicular to the

molecule’s sulfur-to-sulfur axis, in the nitro acetamide derivative (“asymmetric molecule”), the mirror symmetry is absent. For the symmetric molecule the *IV*s may be expected to be symmetric with respect to voltage inversion; for the asymmetric molecule a current flowing in the positive direction or in the negative direction will not necessarily result in the same magnitude of the voltage drop along the molecule.

The length of both molecules is ≈ 2 nm. To obtain a contact to a single molecule from both electrodes, an electrode pair with a distance matching exactly this length is required. We have chosen a lithographically fabricated mechanically controlled break junction (MCBJ) to provide an electrode pair with tunable distance. The same technique was used in a previous experiment [9]. For more details on this technique, see Ref. [10]. A scanning electron microscope picture of a freshly prepared junction consisting essentially of a freestanding Au bridge is shown in Fig. 2. This setup is mounted in a three-point bending mechanism driven by a threaded rod. To prepare the experiment, we bend the substrate in order to elongate the bridge and finally it breaks. Then the two open ends form an electrode

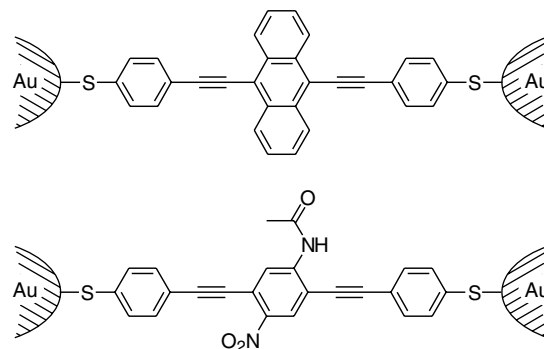


FIG. 1. Scheme of the experimental setup: a spatially symmetric [9,10-Bis((2'-*para*-mercaptophenyl)-ethynyl)-anthracene] and an asymmetric molecule [1,4-Bis((2'-*para*-mercaptophenyl)-ethynyl)-2-acetyl-amino-5-nitro-benzene] in between two gold electrodes.

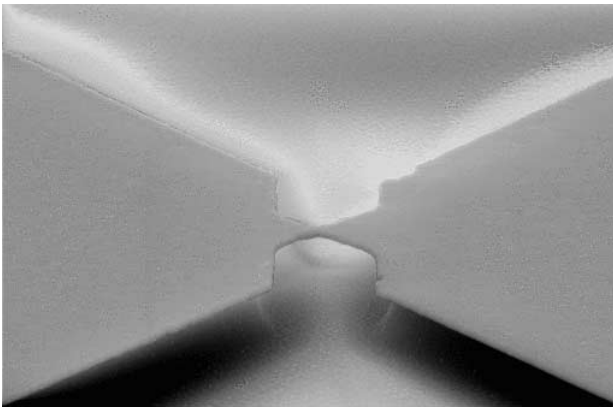


FIG. 2. Scanning electron microscope picture of the lithographically fabricated break junction. The setup consists of a metallic plate, covered by an insulating layer of polyimide. On top of this, a gold film with a small constriction (smallest diameter $50 \times 50 \text{ nm}^2$) is deposited, laterally structured by e -beam lithography. Two electrodes lead outside to connect the bridge electrically. The polyimide is partially etched away so that in the constriction region, the bridge is freely suspended over the polyimide substrate.

gap which can be adjusted mechanically with subangstrom precision.

The molecules with acetyl protection groups at the ends are dissolved in tetrahydrofuran. A droplet of this solution is put on top of the opened MCB (electrode distance 10 nm). The total exposure time is 10–30 sec. When the molecules approach the surface of any of the gold electrodes, one of the acetyl protection groups splits off and a stable chemical bond between the sulfur atom and the gold surface is established [11]. The opposite side of the molecule remains protected at this stage. The coverage of the molecules on the gold surface is expected to be far below a completed monolayer, which would be formed only after hours. This is in contrast to previous experiments [8,9]. Then the solvent is evaporated and the whole setup is mounted in an electromagnetically shielded box, which is pumped to a pressure of 10^{-7} – 10^{-6} mbar. When the electrodes are approaching each other from large distances, the resistance decreases exponentially with distance, as expected for tunneling. In this configuration, the conductance is highly unstable, in particular at higher bias voltage ($U > 0.2 \text{ V}$). At a certain distance, however, the system suddenly locks into a stable behavior, which allows one to record several IV s in the voltage range of $[-1 \text{ V}, 1 \text{ V}]$. This stable configuration is interpreted as a metal-molecule-metal junction: when the first molecule touches the opposite Au surface, the second acetyl end group is removed and a stable chemical bond is established from the single sample molecule to both electrodes.

Figure 3a shows nine IV s (dashed lines) obtained for a stable configuration with the asymmetric molecule. They are clearly nonlinear, displaying some rounded steplike features which appear presumably when transport through an additional molecular orbital is enabled by the bias voltage [12]. In addition, traces of Coulomb blockade should

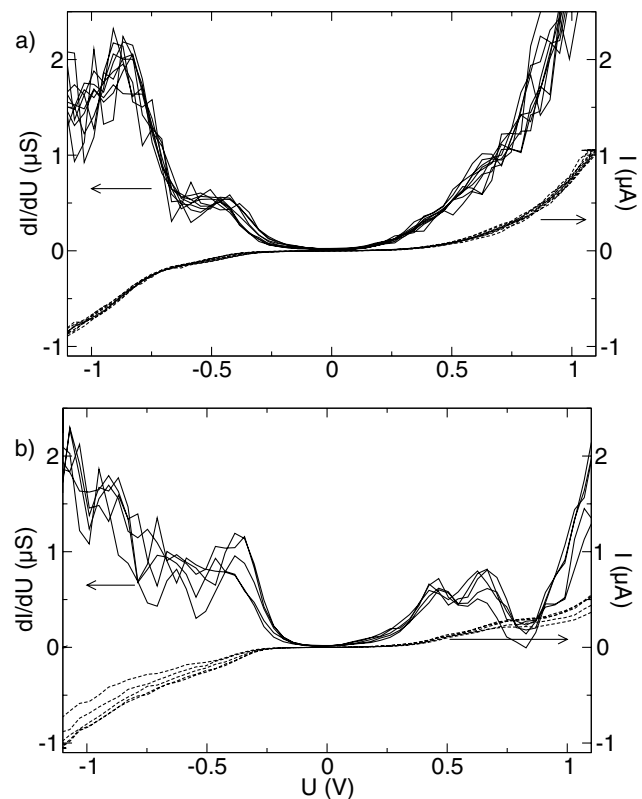


FIG. 3. Transport data of the asymmetric molecule. (a) Current-voltage (IV) raw data (dashed lines, nine subsequent voltage sweeps) on a stable junction and the numerically differentiated data dI/dU (solid lines) from the above IV . (b) Data from a subsequent junction.

be present in the system (its conductance is 2 orders of magnitude smaller than e^2/h) [13]. Both effects were experimentally identified for example in tunneling through single semiconductor clusters [14]. Our data are highly reproducible as long as the junction remains stable. The current amplitude is about $0.7 \mu\text{A}$ at 1 V. All observed stable junctions show currents in the range of 0.2 – $1 \mu\text{A}$ at 1 V. Beyond $U \approx 1.2 \text{ V}$, the current rises strongly and if higher voltages are applied, the junction becomes unstable. Figure 3a also displays the differential conductance dI/dU (solid lines, numerical derivative). Here, the step-like features in the IV appear as peaks. The data are clearly asymmetric with respect to voltage inversion. Such IV s are stable within a time interval ranging from 1 to 100 min. Thereafter, the system enters suddenly into a state of either considerably higher or lower conductance. Upon slight change of the electrode gap, often another stable configuration can be established. Figure 3b displays a data set obtained with the same MCB (and obviously an identical molecule) after the junction in Fig. 3a had become unstable. Compared to Fig. 3a, it shows similarities, but also differences. The first similarity is the amplitude of the current. This current is barely sensitive to variations of the electrode distance, which indicates that indeed the current through a molecule is observed, with only a minor current contribution, if any, from direct metal-to-metal tunneling.

On the other hand, considerable differences can be seen: For example, two peaks at positive voltage appear in Fig. 3a, which are not visible in Fig. 3b. There are at least three reasons why differences may appear: First, different amounts of strain may have been applied to the molecule while establishing the contact. However, we do not believe that strain plays a dominant role in our experiments, because for stable contacts we can occasionally change the electrode distance by a few angstroms without altering the shape of the IV . Apparently, the strain is relaxed by the soft and mobile gold surface. Second, the proximity of neighboring molecules/adsorbates or inhomogeneities of the electric fields may affect transport through the molecule. Inhomogeneous fields may influence spectroscopic properties of molecules only on energy scales in the mV range [15], yet only little is known about its influence on transport properties. Third, the atomistic structure of the contact region between molecule and electrode, which is different from junction to junction, may strongly influence the IV s. This is probably the dominant mechanism in our samples. An important indication is given by analyzing the first peak at negative voltage, which appears at ≈ 450 mV in Fig. 3a and ≈ 360 mV in Fig. 3b. This peak shift can be explained by different contact realizations in the following way: The gold-sulfur bond is a covalent, but strongly polarized bond. When the bond is established, a fraction of an electron charge is transferred onto the molecule due to the electronegativity of the S atom. Depending on the microscopic realization of the bond (e.g., if the sulfur atom bonds to gold atoms at corners or kinks of the irregular surface, etc.), this charge transfer may vary and the molecule will be charged differently, which leads to an energy shift of the molecular orbitals. Hence, the peak belonging to the same molecular orbital will appear at different bias voltages, depending on the microscopic realization of the contact. At first sight, one would expect by the same token that the conductance is very sensitive to contact variations, too, as this is where the potential drops presumably. Theoretical predictions for molecules of a similar type yielded even stronger variations for different bonding realizations [16,17]. Yet, the observed overall conductance seems not to be highly sensitive to these variations. Our experimental conditions, however, might select certain bond types and therefore limit the span of observed conductances.

Do we really observe individual molecules? Experimentally, the “lock-in” behavior described above with a stable conductance not sensitive to the electrode distance (within ± 1 Å) is a strong indication for a small discrete number of contributing molecules. The overall conductance does not vary by large amounts; therefore we deal always with approximately the same number of molecules. Indeed, when approaching the electrodes in a stable configuration further, we sometimes observe a discrete stable configuration where the conductance has roughly doubled, suggesting that we started out with a single molecule. Upon variation from one stable configuration to another, peak positions of

the differential conductance may shift as described above and their width may change; peaks may even appear or disappear altogether. In particular, we observe in a number of cases that the distinct asymmetry appears to be “mirrored” with respect to the bias voltage. This latter observation indicates clearly that we are not dealing with a large ensemble of molecules in parallel, where sample-to-sample fluctuations are averaged out, but rather with individual realizations of metal-molecule-metal junctions, which differ most probably in the microscopic arrangement of the contact. Our results, by exploring a number of different contact configurations, reflect the important effect of the environment on the transport properties of a single molecule. Note that sample-to-sample fluctuations are very familiar in single molecule spectroscopy in random media [18]. To conclude, the data reported thus far yield no definite proof, but there are strong indications that we observe electron transport through single molecules.

This is further confirmed by the data on symmetric molecules shown in Figs. 4a and 4b. The experimental procedure was the same as described above for the asymmetric molecule. The overall amplitude of the current $I \approx 0.6$ μ A at $U = 1$ V is similar to the values observed with the asymmetric molecule. At $U \approx 0.35$ V, a peak occurs in dI/dU (Fig. 4b). A similar peak in Fig. 4a is less pronounced and less symmetric. Apart from this slight asymmetry, the dI/dU data look rather symmetric, in particular,

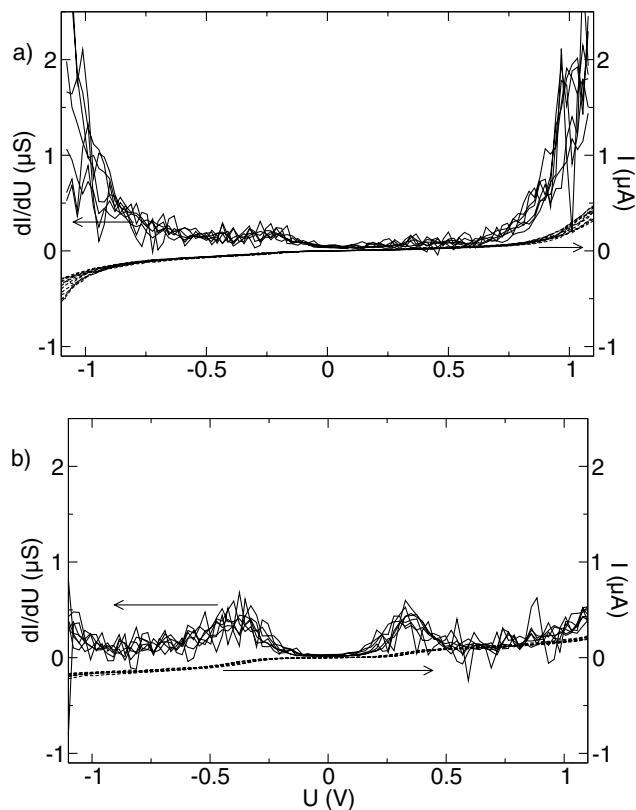


FIG. 4. Current I (dashed lines) and dI/dU (solid lines) as a function of the bias voltage U from two subsequent junctions with the symmetric molecule.

when compared with the strong asymmetry in dI/dU of the asymmetric molecule (Fig. 3), with a very similar molecular structure along the sulfur-to-sulfur axis. More than 50% of the stable IV s of the symmetric molecule were highly symmetric, while all of the IV s we observed with the asymmetric molecule were clearly asymmetric. This may not be very surprising, but it allows a very important conclusion: what we measure is indeed the sample molecule and not an artifact caused by adsorbates or anything else. The IV s we observe reflect unambiguously an intrinsic property of the sample molecule: its spatial symmetry.

Some of the IV s observed with the symmetric molecule, however, were asymmetric. An asymmetric IV with a symmetric molecule was previously observed in Ref. [9]. For small asymmetries, there are several possible reasons: the symmetry can be broken by additional molecules, different electrode surfaces, etc. To elucidate the question of more pronounced asymmetries, we intentionally manipulated a junction by slightly adjusting the electrode distance several times. This led to a sequence of stable IV s shown in Figs. 5a–5c. Starting from a symmetric IV (not shown), we increased the electrode distance and observed several IV s with a shallow slope at negative bias and a steep increase at positive bias (Fig. 5a). Obviously, one of the two molecule-metal contacts was altered. After further manipulations, we briefly recovered a symmetric case (Fig. 5b), followed by a few asymmetric IV s (Fig. 5c) which are a mirror image of (Fig. 5a), indicating a spatial inversion of the above contact configuration. Note that the molecule was not “lost” during this protocol, as no disruption of the IV measurement occurred. Hence, we apparently manipu-

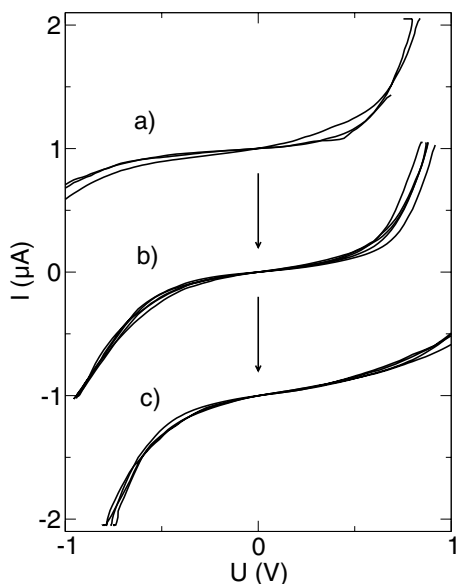


FIG. 5. Three subsequent stable IV s with the symmetric molecule, observed during skillful manipulation of the electrodes. (a) An asymmetry was mechanically induced. After an intermediate symmetric regime (b), the IV appears inverted with respect to bias voltage (c). Note that the junction was not lost during this procedure. Data (a) and (c) are offset for visibility by $+1 \mu\text{A}$ and $-1 \mu\text{A}$, respectively.

lated the contacts of only one molecule. In particular, the fact that asymmetric contact realizations can cause strong asymmetries in the IV s demonstrates the crucial importance of microscopic details within the contact region: although all contacts were chemically stable, different types of IV s could be observed with the same molecule.

In conclusion, we have performed conductance measurements through a self-assembled metal-molecule-metal junction. By comparison of spatially symmetric and asymmetric but otherwise similar organic molecules, we unambiguously identify an intrinsic property of the molecule: its symmetry. The body of data strongly suggest that individual molecules are observed, in particular, a lock-in in stable configurations can be observed. This is further corroborated by the observation of sample-to-sample fluctuations which demonstrate the crucial importance of the coupling to the “environment,” i.e., the electrodes.

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