High-conductance surface-anchoring of a mechanically flexible platform-based porphyrin complex

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Abstract

The conductances of molecular model junctions comprising a triazatriangulenium platform with or without an ethynyl spacer and an upright Zn-porphyrin are probed with a low-temperature scanning probe microscope. The platform alone is found to be highly conductive. The ethynyl-linked Zn-porphyrin moiety reduces the conductance by three orders of magnitude and leads to an unexpected, non-monotonous variation of the force that was measured simultaneously at the tip of the microscope. Density functional theory calculations show that this variation results from an induced tilting of the porphyrin.

1. Introduction

Scanning tunneling microscopy (STM) is useful for probing the conductance of single molecules because it enables a detailed characterization of the junction via imaging of the molecule prior to and after the conductance measurement, in particular at low-temperature and under ultra-high vacuum conditions. Given the sensitivity of the conductance with respect to atomic distances, the forces between the electrodes and a molecule and their variation with the electrode separation are of great interest. Nevertheless, the number of studies combining conductance and force measurements on molecules using STM combined with non-contact atomic force microscopy (AFM) is limited. Planar molecules [1–3], fullerenes [4–6], and carbon monoxide [7] have been investigated. To implement advanced functions at the nanoscale, it is desirable to rationally design molecules that are more complex [8, 9]. Here we address a generic model (Por-TATA, figure 1(a)) comprising the molecular platform tri-octyl-triazatriangulenium (tri-octyl-TATA) [10], an intervening spacer (ethynyl), and a functional unit (Zn-porphyrin). The molecular complex was designed to attach functional molecules in an upright and free-standing position onto a surface as well as to ensure a high conductivity due to conjugated bonds within the platform, the spacer, and the Zn-porphyrin. STM and simultaneous AFM are used to characterize the conductance and the forces at the junction. To make these complex molecules accessible to measurements in a controlled ultra-high vacuum, low-temperature environment a home-built electrospray ionization source is used. The experiments are complemented by calculations of the electron transport and the forces.

The experimental data reveal that the platform itself exhibits a high conductance making it a suitable linker for conductive molecules. On the Por-TATA molecule, we observed unusual non-monotonous variation of the force which also leaves a footprint on the conductance. A comparison with the results of quantum chemical calculations show that a bending of the molecule occurs as the tip approaches the porphyrin moiety.

2. Experiment

Experiments were performed in a combined STM/AFM in UHV at 5 K with a base pressure of $5 \times 10^{-11}$ mbar. The AFM was operated in a non-contact frequency-modulation mode with a tuning fork probe [11]. The free
prong oscillated at a constant amplitude of $0.9(2) \text{ Å}$ at its resonance frequency of $\sim 23 \text{ kHz}$. A W-tip was attached to the free prong to simultaneously measure the conductance along with the frequency shift (see supplementary material, section 2 for more details). The differential conductance was measured with a lock-in amplifier and with the current feedback loop disabled. All STM images were acquired in constant-current mode with the bias voltage $V$ applied to the sample. The W-tip was prepared in situ by repeatedly indenting into the Au substrate until it was covered with surface material. Au(111) surfaces were cleaned by Ar$^+$ sputtering and annealing cycles. The synthesis of Por-TATA has been presented in [12]. Por-TATA was sprayed from a $\sim 0.1 \text{ mM}$ chloroform/methanol (1:1) solution in the positive ion mode using an in situ ultra-high vacuum electrospray ionization setup [13]. Before deposition, the molecular beam was analyzed by mass spectrometry. During deposition the Au(111) sample was kept in the preparation chamber at a pressure of $2 \times 10^{-9} \text{ mbar}$ over a period of $\sim 4 \text{ h}$. An ion impact energy of 8(4) eV was used.

3. Theoretical methods

Simulations of force and conductance curves of a platform-mounted Zn-porphyrin molecule were performed by combining constrained molecular structure optimizations using static Kohn–Sham density functional theory (KS-DFT) [14] and the Landauer–Imry–Büttiker approach [15, 16]. The optimization of molecular structures was carried out using the quantum chemical program package TURBOMOLE 6.0 [17] with the pure exchange-correlation functional BP86 [18, 19] and Ahlrichs’ split-valence triple-zeta basis set with polarization functions on all atoms (def-TZVP) [20, 21]. Dispersion interactions were taken into account via Grimme’s empirical correction scheme DFT-D2 [22]. In Turbomole 6.0 no C6 parameters for gold are available. The convergence criteria were $5 \times 10^{-4} \text{ kJ mol}^{-1} \text{ Å}^{-1}$ ($10^{-7}$ a.u.) for the energy in the self-consistent field algorithm and $0.5 \text{ kJ mol}^{-1} \text{ Å}^{-1}$ ($10^{-4}$ a.u.) for the gradient in molecular structure optimizations. The transmission functions, the conductance at zero-voltage, and central subsystem MOs were calculated using the post-processing tool ARTAIOS [23, 24]. In order to obtain the overlap and Fock matrices, single-point calculations using the Gaussian 09 quantum chemistry program package [25] with the hybrid functional B3LYP and the Los Alamos (LANL2DZ) effective core potentials [26] were employed. A small basis set was chosen to reduce ghost transmission [23].
B3LYP functional [27, 28] was chosen to bypass convergence problems with BP86. Further details on the calculation are provided in appendix A and in the supplementary material.

4. Characterization of Por-TATA

Molecular Por-TATA (figure 1(a)) ions sprayed from a chloroform/methanol solution were analyzed by mass spectrometry prior to deposition on the surface. The spectrum in figure 1(b) reveals singly charged, intact Por-TATA (1014 u/e) as well as tri-octyl-TATA [8, 9, 29] molecules (618 u/e). The partial fragmentation is most likely due to a protonation of the molecule during spraying, which destabilizes the bond between tri-octyl-TATA and Zn-porphyrin. The resulting tri-octyl-TATA cation as well as the 5-ethynyl-Zn-porphyrin are highly stable species. No peak corresponding to 5-ethynyl-Zn-porphyrin is observed, which indicates a low ionization cross-section.

The STM image in figure 1(c) is typical of the structures observed after deposition of Por-TATA on the Au surface. From an analysis of many surface areas we find that only ~2% of the adsorbed molecules are intact Por-TATA. We attribute the fragmentation during adsorption to the impact and adsorption energies [30]. In addition, excitation of molecular ions may occur during their passage through the mass spectrometer [31]. The STM image (figure 1(c)) shows a cluster of one Por-TATA and two tri-octyl-TATA molecules as well as a single Zn-porphyrin. The latter is readily identified owing to its four-fold symmetry [32]. The TATA platforms exhibit an expected threefold symmetry as reported in [10]. At the boundary of the cluster octyl groups (oct) oriented either clockwise or anti-clockwise are discernible [10]. Intact Por-TATA (figures 1(c) and (d)) is signaled by a protrusion at the center of the platform. This interpretation was tested by applying elevated voltages to a related molecule (Por-TATA with three phenyl groups attached to the meso positions of the porphyrin) to induce fragmentation (figure S1 in the supplementary material). After this procedure, tri-octyl-TATA and nearby Zn-porphyrin were observed. In addition, scanning tunneling spectra were recorded above the intact Por-TATA (figure 1(e)). While the relative intensity of the two molecular resonances may vary on different molecules, the data reveal an energy gap4 of 2.80 ± 0.05 eV as expected for Zn-porphyrin [33, 34]. This agreement between the energy gap of Por-TATA and Zn-porphyrins suggests that the molecular orbitals of the porphyrin are only weakly perturbed by orbitals of the platform and metal surface. The measured energy of the molecular resonance associated with the lowest unoccupied molecular orbitals (LUMO, at 1.6 V) is significantly different from those measured on the fragments Zn-porphyrin and tri-octyl-TATA (figure S3 of the supplementary material).

The gap calculated by DFT (B3LYP, 2.67 eV) between the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, figure 2(a)) of the Por-TATA on a Au monolayer agrees reasonably well with the experimental result. This value is only slightly larger than the calculated gap of isolated Por-TATA using the same exchange-correlation functional with dispersion correction (2.60 eV, section 7 in the supplementary material). Although quantitative differences occur using a pure functional (BP86-D), the MO energies are qualitatively in the same order. Furthermore, the HOMO–LUMO gaps of isolated Por-TATA fragments, e.g.

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4 The conductance gap may appear larger than the HOMO–LUMO gap if the applied voltage does not entirely drop over the vacuum gap. In the present case, however, this effect appears to be negligible. The resistance of the molecule–substrate junction is much smaller than the impedance of the vacuum gap due to a sufficient electron density of states at the ethynyl spacer (figure 2(b)).
ethynyl-TATA and ethynyl-Zn-porphyrin, are significantly larger than for the intact Por-TATA, which supports the interpretation of intact Por-TATA molecules (figure S7). The roundish shape of Por-TATA (figure 2(d)) suggests that the porphyrin may rotate around the ethynyl linker. This is consistent with the calculated rotation barrier of Zn-porphyrin on tri-octyl-TATA of 1.3 kJ mol$^{-1}$ (figure S4). If Zn-porphyrin was rotationally restricted, an elongated shape would be expected similar to upright coronene [35].

Closer inspection of images of single Por-TATA molecules (figure 1(d)) shows that the Zn-porphyrin is not centered on the tri-octyl-TATA platform. This is likely due to a deformation of the molecule in the presence of the STM tip. From an interpolation between a straight and a bent structure (obtained from constrained molecular structure optimizations, appendix A) for a given tip–molecule distance we find a fairly flat potential energy surface (figure 2(b)) with two almost degenerate minima. They correspond to straight and bent structures of the porphyrin and are separated by a barrier (0.1 kJ mol$^{-1}$) well below the expected accuracy of KS-DFT. This is consistent with the low lateral stiffness of the molecule (less than 1 N m$^{-1}$, section 6 in the supplementary material). Hence, a tip-induced bending of the porphyrin is likely and consistent with the off-centered position of Por-TATA in the STM images (figures 1(c) and (d)).

5. Contact formation to Por-TATA

To investigate the contact formation between a single Por-TATA molecule and the STM tip the short-range force$^5$ $F_s$ and conductance $G$ are measured simultaneously with respect to the tip-molecule distance (figure 3(a), circles and squares). The tip was initially retracted by 1.5 nm from the molecule to prevent a tilt due to the influence of the tip. As the tip is brought closer again, a shallow minimum of the short-range force $F_s$ (arrow 1 in figure 3(a)) occurs with a maximal attractive force $F_{\text{max}} = (0.2 \pm 0.1)$ nN. According to our DFT calculations

$^5$ More precisely, the force $F$ was calculated from the measured shift of the quartz sensor resonance (supplementary material, section 2, available at stacks.iop.org/njp/17/013012/mmedia).
(vide infra), this corresponds to the tip contacting one of the topmost hydrogen atoms or, as the molecule may be slightly tilted, the upper carbon atoms of the Zn-porphyrin macrocycle. As the tip further approaches the molecule, the force initially becomes less attractive as expected. However, subsequently the attraction increases again to large values. Further reduction of the tip–molecule distance beyond the range shown in figure 3(a) lead to damage of the molecule or the tip.

The simultaneously measured conductance $G(z)$ increases monotonously. At the point of maximal attraction, we determine a contact conductance $G_C = (2 \pm 1) \times 10^{-4} G_0$ (with $G_0 = 2 e^2/h$ the conductance quantum, $e$ elementary charge, and $h$: Planck’s constant). The contact conductance is within the range $(10^{-3} \ldots 10^{-5} G_0)$ measured for a similar junction (Zn-porphyrin with two thiophenyl linkers) using mechanical break-junction techniques [36–38].

We first discuss the surprising observation of two attractive wells. It might be linked to plastic deformations of the junction. However, no corresponding increase of the dissipation of the tuning fork was observed. Furthermore, data recorded during approach and retraction of the tip show no hysteresis, which indicates an elastic deformation. An alternative explanation for force variation is a slight bending or tilting of the Zn-porphyrin that occurs when the interaction with the tip apex atom becomes repulsive at $z = 3.7$ Å. This idea is further developed using DFT calculations to simulate force and conductance measurements of a platform-mounted Zn-porphyrin molecule. The tip was placed above the middle H-atom of the Zn-porphyrin of a straight Por–TATA molecule (figure 3(b), structure S). Next, the tip–molecule distance $d$ was decreased in a stepwise fashion and the structures were optimized while holding selected atoms of the tip and the TATA platform fixed (see figure A1(a)). When $d$ is reduced the structure $S_1$ undergoes an abrupt change to a more bent shape $S_2$. This change corresponds to the transition from the left to the right minimum in figure 2(b), which is presumably less abrupt in the experiment due to fluctuations of the molecule. For smaller $d$ the energy of the right minimum is expected to shift to lower energies than the left minimum due to strong repulsive tip–molecule interactions. Figure 3(c) shows the calculated forces and conductances. The dashed line indicates the positions where abrupt bending occurred ($d = 0.9$ Å). The force exhibits two minima (arrows 1 and 2) that correspond to maximal attraction. The first, shallow maximum occurs when the tip contacts the middle H-atom of the porphyrin ring while the second one reflects the interaction of the Au tip with carbon atoms from the porphyrin macrocycle (figure A1(b)). As the barrier between a straight and a bent Por–TATA is below the estimated error margin of the DFT calculations (0.1 kJ mol$^{-1}$, figure 2(b)), the calculations were also performed for a bent Por–TATA as starting structure, which virtually leads to the same results (appendix A.3).

The calculated forces reproduce the essential features of the experimental force data. They exhibit a similar shallow attractive well and are also consistent with the growing attraction at shorter distances. The transport calculations showed an artificially high transmission in the energy range of the expected Fermi energy caused by the so-called ‘ghost transmission’ ([23] and supplementary material, section 9). After subtracting the ghost transmission the calculated conductances are similar to the experimental results. We verified that the calculated conductances are independent of the choice of the Fermi energy $E_F$ over the range from $-4.0$ to $-4.5$ eV. Moreover, no transmission peaks are present near the Fermi energy for all examined tip–molecule distances (figure S8), which suggests that the Landauer formalism is a good description of electron transport through the junction [39]. We note that the quantitative agreement of the conductances observed at the position of the first attractive force maximum may be due to a favorable cancellation of errors.

To estimate the contribution of the TATA platform to the resistance of the Por–TATA molecule we repeated the experiments on the platform alone. Figure 3(d) shows force (circles) and conductance (squares) data recorded above the center of a TATA molecule. Compared to Por–TATA the maximal attractive force is larger by an order of magnitude. This is expected because the tip gets closer to the platform, which increases the dispersion force. At the force minimum (dashed line in figure 3(d)) the conductance is $\approx 10^{-3} G_0$. DFT calculations (figure S10) predict a conductance of $4.4 \times 10^{-1} G_0$ in reasonable agreement with the measured value. This high value comes close to that of $G_{th}$ [40]. In other words, the TATA platform is a highly conductive linker to metal surfaces.

In the Landauer model of coherent transport the total transmission is the product of the transmissions of the subunits [41]. This implies that the contact conductance of Por–TATA ($2 \times 10^{-4} G_0$) may be attributed to the combined effects of the platform ($10^{-1} G_0$) and the Zn-porphyrin together with an ethynyl spacer ($\approx 10^{-3} G_0$) as estimated from a calculation on an ethynyl thiolate spacer (figure S10).

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6 Figures 1(c) and (d) suggest that Zn-porphyrin may start to rotate around the ethynyl spacer induced by the tunneling electrons. This rotation may influence the orbitals localized at the ethynyl spacer and thus the conductance. Owing to the time resolution in the measurements (100 ms per point) no conductance variations are observed.
6. Conclusion

In conclusion, single-molecule junctions of Zn-porphyrin functionalized tri-octyl-triazatriangulenium were prepared in a low-temperature STM/AFM. The molecular platform leads to an almost upright orientation of the Zn-porphyrin moiety. The ethynyl spacer reduces the electronic coupling between the Zn-porphyrin and the surface as shown by tunneling spectroscopy. Measurements and DFT calculations show that the presence of the tip induces a tilting of the porphyrin. Force and conductance curves on the platform alone show that it is a highly conductive molecular linker to metal surfaces.

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Appendix A. Theoretical details

In general, either static DFT calculations or molecular dynamic (MD) simulations [42] are performed to simulate STM and AFM processes. MD simulations provide richer information but are typically much more computationally demanding (for a given method of calculating energies and forces). In order to address the unexpected flexibility of the molecule, MD simulations may achieve a comprehensive understanding. However, since the experiments have been performed at time scales up to one minute, MD simulations will not correctly reproduce the behavior of the system due to a sliding speed that has to be larger by several orders of magnitude due to practical limitations on simulation time. Therefore, we performed constrained optimizations using static DFT.

A.1. Structure optimization

The tip was modeled by a pyramid consisting of 20 gold atoms. The octyl chains attached to the nitrogen atoms were replaced with methyl groups (unless otherwise mentioned) to reduce computation times. This substitution does not modify the electronic structure of TATA (section 8 in the supplementary material).

A series of structures consisting of the Por-TATA and the 20 atom gold tip were optimized first with no constraint and subsequently with the constraint that the coordinates of three hydrogen atoms of the TATA platform and the topmost slab of the tip are held fixed (figure A1(a), marked in red). The structure obtained from an unconstrained optimization has an internuclear Au–H distance of \( d_{\text{Au–H}} = 1.30 \) Å. Note that the distance between the Au and H nuclei \( d_{\text{Au–H}} \) is not the same as the tip–molecule distance \( d \) (figure A1(b)). For the constrained optimizations and subsequent force calculations the gold surface was neglected (contrary to the electron transport calculations).

A.2. Transmission and molecular orbitals

For the calculation of the transmission the methyl-TATA platform of the isolated, optimized Por-TATA was replaced by a platform (tri-octyl-TATA) that was previously optimized on four layers of Au (DFT(PBE-D)/SVP) [10]. Additionally, the Por-TATA was hosted on a single Au layer consisting of 20 atoms with N–Au distances of 3.2 Å as optimized in [10]. Details on the electron transport calculations as well as Cartesian coordinates are given in sections 5 and 11 of the supplementary material.

The resulting finite-cluster system was divided into tip (left), surface (right), and Por-TATA molecule (central) subsystem (supplementary material, figure S5). All gold atoms were assigned to the electrodes. Thus, the definition of the central subsystem comprises only the Por-TATA molecule.

The central subsystem MOs of the Por-TATA were calculated by solving the central subsystem’s secular equations and determined by comparing its shape with the MOs of the isolated Por-TATA. Increasing the basis set to triple-zeta quality (def-TZVP) for the isolated Por-TATA did not result in significant changes in the energy gaps (supplementary material, section 7). The MOs were visualized with MOLDEN [43] and a local postprocessing tool.

A.3. Calculated contact curves

The force was approximated as the negative of the numerical derivative of the energy values with respect to the tip–molecule distance \( d \), which represents the displacement along the tip–TATA platform direction. \( d \) is defined as the height of the whole tip–Por-TATA system (distance between the highest coordinate of the tip and the
lowest coordinate of the Por-TATA) minus the height of the fully optimized structure that corresponds to
\(d = 0.00\ \text{Å}\), figure A1(b).

The constrained optimizations using DFT(BP86-D)/def-TZVP were started from structure \(S_i\) (straight, figure 3(b)). The tip–molecule distance \(d\) was elongated and reduced by steps of 0.20 \(\text{Å}\) over a range of 5.00 \(\text{Å}\), starting with an elongation of 3.00 \(\text{Å}\). For distances \(d > 0.00\ \text{Å}\) (see abscissa in figures 3(c) and A1(d)) the porphyrin position remains qualitatively unchanged after the relaxation. For smaller distances the Por-TATA tilts and the lowest energy structure changes to the bent structure \(S_f\) (figure 3(b), \(\alpha = 6.7°\)) at a tip–molecule distance \(d = 0.7\ \text{Å}\). The tip–molecule distance \(d = 0.00\ \text{Å}\) corresponds to the equilibrium structure, see straight Por-TATA structure in (b).

However, using the bent structure (\(\alpha = 6.7°\)) as starting structure for the constrained optimizations leads to energetically more favorable converged structures for distances \(d < 0.80\ \text{Å}\) (figure 3(c)) compared with the straight structure. Therefore, structures of the type \(S_i\) (straight) are used for distances \(d > 0.80\ \text{Å}\) and structures of the type \(S_f\) (bent by \(6.7°\)) at a tip–molecule distance \(d = 0.7\ \text{Å}\) for larger tip–molecule distances, which can be observed in calculations without the Au tip as well (see figure 2(b) and figure S6, respectively).

The same procedure has been applied for the structures \(B_i\) (\(\alpha = 6.7°\)) and \(B_f\) (\(\alpha = 13.2°\), figure A2(b)), which virtually results in the same shape of the force and conductance curves than the calculations shown in figure 3(c).

Figure A1(d) illustrates the sudden increase of the distance between the tip atom and the middle H-atom of the porphyrin ring as the molecule slips past the tip. This sudden increase of \(d\) causes the sharp kink in the conductance curve at \(d = 0.80\ \text{Å}\) (figure 3(c)) and \(d = 0.50\ \text{Å}\) (figure A2(b)).
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