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Abstract

Reversible isomerization processes are rarely found when organic molecular switches are adsorbed on metal surfaces. One obstacle is the large energy difference of the isomeric forms, since usually the most planar conformer has the largest adsorption energy. In the example of an imine derivative, we show a strategy for also stabilizing the non-planar isomer by intermolecular bonding to its neighbors. Tunneling electrons from the tip of a scanning tunneling microscope can then be used to induce reversible switching between the *trans* and *cis*-like state. Supported by model force-field calculations, we illustrate that the most probable cause of the enhanced stability of the three-dimensional *cis* state at specific adsorption sites is the electrostatic interaction with N sites of the neighboring molecule.

S Online supplementary data available from stacks.iop.org/JPhysCM/24/394016/mmedia

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

1. Introduction

Molecular switches are organic compounds which can be reversibly transformed between isomeric states when exposed to external stimuli, like photons, electrons or elevated temperatures [1]. While photochromic molecules are mostly studied in solution, there is growing interest in attaching these molecular species to condensed thin films for exporting their natural isomerizability to solid materials as a method to control their optical, electronic, magnetic, etc, properties [2]. However, the switching behavior in these films is generally modified and reduced and, in many cases, even completely suppressed. There are several causes for this reduction of bi-stable dynamics: (i) Intermolecular interactions in condensed thin films only impose an enhanced stability on the conformation that fits into the crystalline structure of the layer [3]. (ii) The interaction with the supporting metal surface also improves the stability of the most planar form, which is the one that maximizes the adsorption energy [4]. The other isomers generally exhibit a reduced stability. (iii) The presence of the metal surface additionally inhibits the dynamics in the excited state, because its lifetime is notably reduced due to the relaxation of excited states into the continuous electronic bands of the substrate [5]. This leads to a significant decrease of the cross section for isomerization.

In spite of these drawbacks, isomerization of molecular switches on metal surfaces has been reported several times [6, 7, 3, 4, 8]. In all cases the switching yield is considerably reduced compared to the behavior in solution. Only in a few systems was the switching process found to be reversible [9–15]. Various strategies have been designed to compensate the causes of reduced switching cross section. To delay the quenching of stimuli-induced excitations, either organic decouplers [9, 13] or surfaces with a lower density of states (hence more passive) [14, 16–18] are used. To overcome the frustration of switching by intermolecular interactions requires strategies, where the molecular environment is controlled at the nanoscale [19], leaving space for conformational dynamics. One can envision using lateral forces with molecular neighbors to tune the stabilization of specific conformations that differ from the thermodynamically most stable isolated configuration on the surface.

Here, we show that the latter strategy can stabilize the less stable molecular isomers on a metal surface by means of non-covalent intermolecular interactions with specific atomic sites of the molecular environment. This leads to the coexistence of two isomeric conformations, allowing us to induce bi-stable motion between them using tunneling electrons. In this study, we use a substituted anil, the 4-carboxy benzylideneaniline (CBA) molecule, as a model *cis–trans* switch[3]. In CBA, the heterogeneous imine bridge mediates the photoisomerization between *cis–trans* conformers, in contrast to the more frequently studied compounds azobenzene and stilbene, which hold N=N and HC=CH bridges, respectively. The loss of intrinsic symmetry could help to stabilize non-planar molecular conformations, i.e. a *cis* isomer, on the surface if the nitrogen heteroatom forms a chemical bond with the metal surface [15]. The anil backbone incorporates a carboxy moiety prone to mediate molecular dimerization on the surface [20].

Scanning tunneling microscopy reveals the intended dimer formation, where the carboxy-phenyl sides interlock, while allowing the phenyl ring at the opposite side of the imine bridge to remain free to rotate. The initial dimer row structures consist of only *trans* isomers. At certain corner positions, tunneling electrons can initiate a reversible isomerization of the molecules into the *cis*-like form. Using model force-field calculations, we illustrate that electrostatic interactions with the N sites of the neighboring imine molecules account for the bi-stable structure.

2. Experimental methodology

Imaging and manipulation of individual CBA molecules was done under ultrahigh vacuum, in a custom-made scanning tunneling microscope operating at a base temperature of 4.8 K. A Au(111) single crystal was cleaned using repetitive cycles of Ne^+ sputtering and annealing. CBA molecules were vacuum-sublimated on the same experimental set-up using a Knudsen cell (K-cell temperature $\sim 170\,^\circ$C). The Au(111) sample was kept at room temperature during deposition to allow the self-organization in most stable structures. The precovered crystal was inserted in the low temperature STM for inspection. We used an electrochemically etched W tip which was prepared by controlled indentations into the clean Au(111) surface until it delivered stable STM imaging and spectroscopy.

3. Results and discussion

Figures 1(a) and (b) depict the self-assembled patterns formed by CBA on the Au(111) surface and reflect the competition between different types of interactions. All CBA molecules lie in the (planar) *trans* conformation. This is a common observation in planar aromatic molecules, even

when they exhibit conformational flexibility. The majority of the assemblies are composed by CBA dimers, which is consistent with the expected tendency of carboxylic terminations to mediate the formation of dimers [20]. The molecular dimers are oriented along specific directions of the surface, suggesting that CBA keeps some registry with the substrate atomic structure. At a weaker energy scale, lateral interactions between dimers favor their nucleation into extended rows following the folds of the Au(111) herringbone reconstruction.

The zoomed image in figure 1(b) shows that parallel dimer rows exhibit mirror-like structures (the prochiral CBA molecule can adopt two chiralities (λ and ρ) on the surface [21]). The image further emphasizes that several bonding sequences between dimers can occur in the rows, leading to straight or zig-zag-like row structures.

Although the free molecule has two minimum energy conformations (figure 2(a)), all the molecules lie on the Au(111) surface in the planar *trans* form, which maximizes the adsorption energy with the metal surface. The three-dimensional conformer, the *cis*-CBA, requires an additional stabilization mechanism to maintain the terminal phenyl lifted away from the surface.

To probe the electron-induced excitations of CBA molecules, we explore changes induced by the tunneling current during scanning, as the positive sample bias is gradually increased. For bias values below 1 eV, molecular structures are apparently unaffected by scanning. At higher values, discrete changes in the shape of some molecules indicate an electron-induced molecular transformation. As shown in figure 2(b), molecular changes are exclusively observed on molecules at the ends of the molecular rows and in small clusters lying in between. They mostly consist of the lateral motion of the plain phenyl terminations; the carboxylic sides remain unaffected, in agreement with the expected stabilization of this molecular end by stronger intermolecular bonds. Therefore, the effect of electrons probably corresponds to changes between λ-*trans* and ρ-*trans* isomers. A mere rotation of the phenyl ring, as that previously reported in [21], would lead here to indistinguishable effects in the molecular shape. However, a transient mediation of the three-dimensional *cis* isomer in the transformation cannot be concluded from these results.

Curiously, molecules sited at the 'wide-angle' corners of the chain ends (indicated as WA in figure 2(b)) exhibit a different behavior. Tunneling electrons injected in these molecules induce a transformation between original *trans* isomer and a three-dimensional form, in which the plain phenyl termination of CBA appears displaced and partly mounted on the neighboring molecule (figure 2(c)). The carboxylic part of CBA is unaffected. Comparison with the model structures of figure 2(a) suggests that this form is likely close to the shape of the three-dimensional *cis* isomer. We label it as *cis*-CBA, although its exact conformation may have some difference with the free *cis*-CBA conformation.

The transformation between both conformations (as shown in figure 2(c)) can be reproducibly induced by placing the STM tip on top of one of these active molecular sites

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[3] The same amounts of aldehyde and aniline were dissolved in p.a. methanol and p.a. dichloromethane; the mixture was stirred at room temperature. After the complete conversion of the starting materials, the solution was concentrated. Afterwards, recrystallization was performed with p.a. toluene to obtain pure crystalline solids.
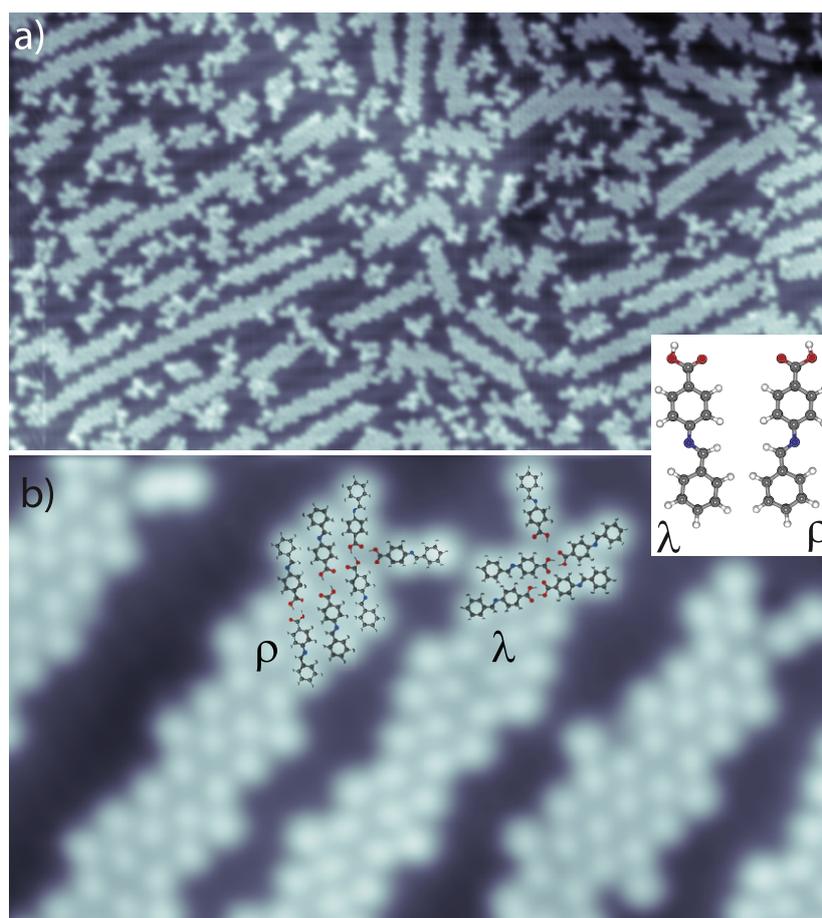
Figure 1. (a), (b) STM images of the CBA precovered Au(111) surface. CBA is deposited on the gold surface at room temperature ($V_s = 66$ mV; $I_t = 55$ pA). The inset shows the two structures of the two enantiomeric forms of *trans*-CBA when confined into a plane. Data analysis was done with the free software WSxM [29].

and raising the bias voltage until a bi-stable behavior is observed. Figure 3(a) shows this behavior as discrete changes in the vertical position of the tip, kept under closed feedback loop (constant current) conditions. In this experiment, the tip is located on top of the plain phenyl side of a CBA *trans* isomer, at a 'wide-angle' corner site, and the bias pulsed to ∼2.0 V. The excitation of molecular transformations between the *trans* and *cis* states leads to a higher or lower position of the STM tip, in response to the presence or removal of the phenylene group from the tunnel junction, respectively. A further proof of the correspondence between the bi-stable behavior and the isomerization can be obtained after subsequent imaging of the manipulated CBA molecule. It can then be verified that the last state (high or low tip position) in the time spectrum in figure 3(b) is correlated with the *trans* or *cis* molecular shape. This also proves that the isomerization state of these molecules can be controlled simply by stopping the electron injection when the tip position reveals the desired conformation.

Usually, three-dimensional isomers show a lower stability on surfaces because they do not maximize the interaction with the substrate as much as the corresponding planar form. However, the electron-induced *cis*-CBA conformer is stable at the low temperature of our experiment and in a timescale of

days. This can be verified by the results shown in figure 3(b). An individual 'wide-angle' CBA molecule was excited to its *cis* form, which stayed in this configuration for the next 67 h until it was deliberately returned to the original *trans* form. To avoid any effect of the STM tip, no imaging was done during the waiting period[4]. The stability of the three-dimensional isomer is remarkable; a probable origin will be proposed later, based on model force-field simulations of the molecular rows.

The three-dimensional shape of the *cis* isomer is also expected to lead to small changes in the electronic structure. We probe it by means of tunneling spectroscopy. Figure 4(b) compares the differential conductance (dI/dV) spectra obtained on top of a 'wide-angle' CBA before and after its electron-induced isomerization. To reduce the probability that tunneling electrons induce changes during the spectroscopy, the measurements were performed as well in constant current mode [22], using very low current set points and short acquisition times. Both species show a peaked increase of the dI/dV-signal in the positive bias

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[4] No STM imaging is done during the waiting period; however, spontaneous *cis–trans–cis* events can be discarded: CBA molecules in a *trans* state never showed any activity even under continuous imaging unless they are deliberately scanned using higher sample bias values.
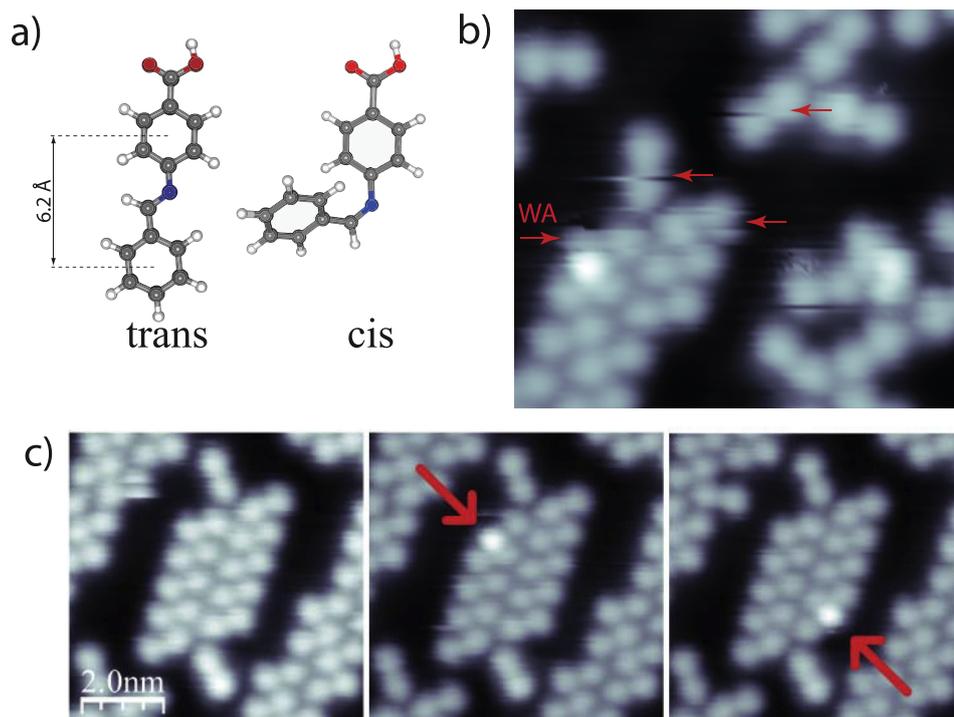
Figure 2. (a) Two minimum energy configurations of free CBA molecules labeled as the planar *trans* and the three-dimensional *cis* isomers. The structures are obtained using MM3 force-field simulations. (b) STM image of a CBA precovered Au(111) region, measured with sample bias $V_s = 1.8$ V. At such bias values, molecules at 'wide-angle' (WA) corners exhibit mobility during the imaging (indicated by arrows). This is attributed to electron-induced processes. 'WA' indicates a specific site at the termination of a dimer chain, where a three-dimensional form is stabilized. (c) Series of three STM images showing molecules at the 'WA' angle sites lying stable in their two possible conformations. The higher one is associated with the *cis* isomer of CBA. The manipulation follows the description in the text and in figure 3; ($V_s = 1.8$ V, $I_t = 0.1$ nA).

region, associated with resonant tunneling through the lowest unoccupied molecular orbital (LUMO). These peaks are thus an indication of the alignment of the LUMO-derived state with respect to the Fermi level of the sample. The position of the resonance turns out to depend on the isomer, lying for *cis*-CBA approximately 300 meV higher in energy than in the *trans* form. Variations of the screening of electron excitations by image charges of the substrate, caused for example from the different molecular geometry, can also lead to changes of resonance alignment in the spectra [23]. These, however, cannot solely explain the differences in resonant alignment because they produce generally smaller shifts when molecules lie on a metal surface. Hence, we attribute the different spectral resonances to intrinsic differences in the electronic structure of the CBA isomers.

The molecular resonances play an active role in the isomerization process of CBA at these sites. Figure 4(a) shows a similar constant current dI/dV spectrum as in figure 4(b) but measured using a larger tunneling current set point. Both the tip height and the dI/dV are stable until biases of the order of 1.7 V are reached. Above this point, the STM tip height (the measurement is also performed in constant current mode) shows a bi-stability in response to the fluctuations of the probed molecule between two states. Simultaneously, the dI/dV signal fluctuates between the two types of conductance spectra, those corresponding to *trans* and *cis* isomers. We therefore confirm that the bi-stable changes in tip height are

caused by the CBA molecule switching between these two conformations.

The results in figure 4(a) further prove that the isomerization is mediated by electron tunneling into the molecular LUMO resonance, thus involving the transient formation of an anionic state [21]. In this transition state the molecular system can be driven, with some (low) probability, into the other minimum, with the ring stabilized in the three-dimensional form. The relatively low (but finite) yield of this process can be estimated by analyzing the time behavior of current-induced bi-stabilities, as in figure 3(a), for several values of the set-point currents. Figure 4(c) shows that the switching rate depends linearly with I_t, with a slope close to one. This is a fingerprint of single-electron processes [24], which here provides sufficient energy to initiate a transformation. The rate values of the switching correspond to a quantum yield of the order of $\sim 10^{-10}$ e^{-1} at a sample bias of 1.85 V. This is a small value, but comparable to generally observed values for electron-induced reactions of molecular adsorbates on metal surfaces [21, 5].

As shown in figure 2, tunnel electrons only induce molecular changes in low coordinated molecules, those at the edges of the domains or forming small clusters. The absence of one of the two molecular neighbors is then crucial to allow motion of the plain phenyl ring. Beyond this, the stability of *cis*-CBA isomers only at the 'wide-angle' sites suggests that the specific molecular neighborhood is crucial to freeze this three-dimensional conformation.
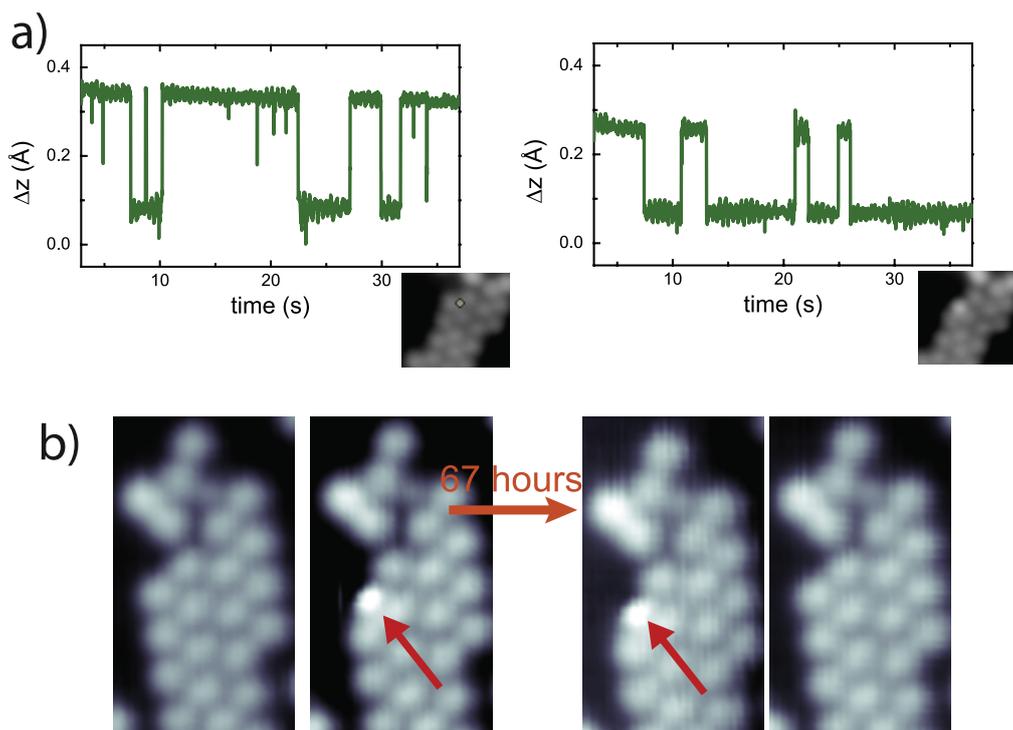
Figure 3. Electron-induced bi-stability of a CBA molecule at the 'wide-angle' sites. (a) Time evolution of the vertical position of the STM tip (with respect to the position on the imine bridge at the same tunneling conditions) when it is placed on the plain phenyl termination of a CBA molecule at one of these sites and the bias pulsed to 2.05 V for 35 s. The measurements are performed keeping a constant current of 0.1 nA. In both cases, the initial state was a *trans*-CBA molecule. The final state of the molecule (shown in the inset) is correlated with the tip height when the pulse ends. The bi-stability of the tip position reflects the presence (high) or absence (low) of that molecular end from the junction, due to its isomerization. (b) STM image series, where the molecule was switched from the *trans* to the *cis* state (images 1–2) and back from *cis* to *trans* (images 3–4) 67 h later. In between images 2 and 3 no images were acquired to avoid any influences of the STM tip.

In order to explore the origin of the enhanced stability of these sites, we have analyzed the packing arrangements of two CBA dimers using molecular dynamics simulations based on the *MM*3 force field, as implemented in the Tinker package [25, 26]. The planar structure of the molecular arrangements has been imposed in the simulations by confining into a plane the motion of six carbon atoms, those at the carboxylic phenyl rings, similar to the previously described work in [4]. The other atoms were left free to move in three dimensions. The energetically most stable structures formed by four molecules were obtained by repetitive application of a simulated annealing algorithm (including exponential cooling from 600 K to 0 K) and a subsequent structure minimization until a global minimum energy configuration was found. The four most stable structures[5] were all found to consist of parallel neighboring dimers of the same chirality. In spite of not including a surface specifically in our simulations, all these four possible dimer configurations can be readily identified in STM images like figure 1(b). However, the atomic structure of the surface probably causes that two of them (labeled as β (-0.962 eV) and δ (-0.937 eV) in figure 5(b)) are most frequently found ($>80\%$ of the chains). They usually appear alternating along regular chains like the ones shown in figure 5(a)[6], resulting in an overall zig-zag chain shape. This configuration allows the CBA chains to follow the troughs of the Au(111) reconstruction while maintaining some commensuration with the Au(111) lattice underneath, for example, as in figure 5(a).

An interesting result from the simulation is the fact that the simulated arrangements maintain all monomers in the same in-plane chiral form (all are of λ type in figure 5(b)). This suggests that chiral selectivity is active in the chain formation [27, 28], most probably because of a 'hot' molecular transient state at room temperature that dynamically varies the orientation of the imine bridge to conformationally adapt the CBA shape to a specific chain site. The mirror-symmetric structure, also observed in our STM images (see, e.g., figure 1), involves CBA molecules of the opposite chiral form (ρ type).

The minimum energy structures from the simulations can be rationalized in terms of electrostatic interactions (weak hydrogen bonds) between dimers, involving N and O as acceptor sites and H atoms as donors. In particular, the stability of the structures in figure 5(b) seems to be sustained by electrostatic bonds connecting plain phenyl sides of CBA with N sites in neighboring molecules. Interestingly, the

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[5] The four structures with the minimum energy configuration found are shown as supplementary material (available at stacks.iop.org/JPhysCM/24/394016/mmedia).

[6] No surface structure was introduced in the simulations. It is reasonable to assume that the apparent tendency of dimer chains to follow the troughs of the Au(111) reconstructions imposes an additional stability to these two particular dimer arrangements.
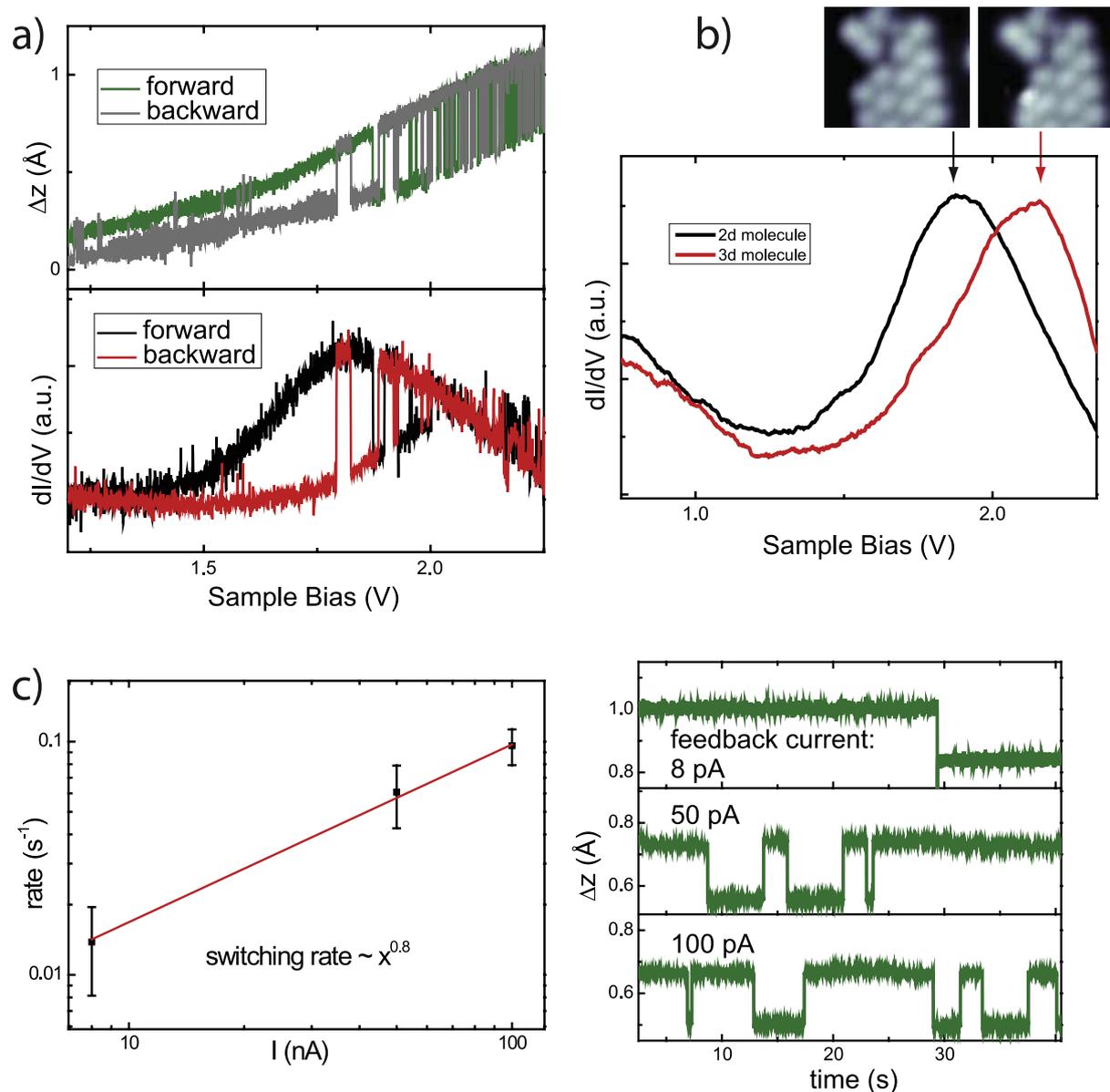
Figure 4. (a) Tip vertical position (top) and dI/dV (bottom) during the acquisition of a bias spectrum with larger set point current ($I_t = 0.2$ nA). The molecule switches between the two conformations as soon as the tunneling electron energy is in the energy range of the LUMO resonance. Above 2 V, the switching rate is so high (see top) that the dI/dV plot shows an average of both *cis* and *trans* spectra. (b) Constant current dI/dV spectrum measured on a CBA molecule in its *trans* and *cis* isomeric forms, showing the displacement of a resonance associated with the LUMO. A low tunneling current ($I_t = 50$ pA) and short recording times were used in order to reduce the probability of isomerization during acquisition of the spectrum. (c) Dependence of the switching rate (*trans*-to-*cis*) with the tunneling current (left), as obtained by averaging the time spent in the higher z position (hence, *trans*) in plots like the one shown at the right. The linear increase of the rate with the current is characteristic of switching by single-electron excitations. ($V_s = 1.85$ V.)

bonding configuration of the β dimer corresponds to that of 'wide-angle' corners in our experiment. Hence, we have minimized the structure resulting by inserting a *cis*-CBA isomer into one of these 'wide-angle' sites and found that there is indeed a stable energy minimum configuration keeping this three-dimensional shape (figure 5(c)). Although the validity of the model is restricted due to the absence of a realistic metal surface in the simulations, it provides a hint about the origin of the stabilization of a three-dimensional form on a metal surface. The model of figure 5(c) shows that an up-standing phenyl ring of the *cis*-CBA molecule lies closer to the neighboring N site of the neighboring

molecule. Its stabilization can hence be pictured as due to electrostatic intermolecular forces primarily attracting the positive hydrogen atoms to the negative N site. This interaction probably competes with van der Waals interactions forcing molecules to adopt a planar configuration on the metal surface. The result is a potential energy landscape with two local minima corresponding to each isomer.

4. Summary

In summary, we report here the controlled and reversible *cis–trans* isomerization of the molecular switch CBA on a
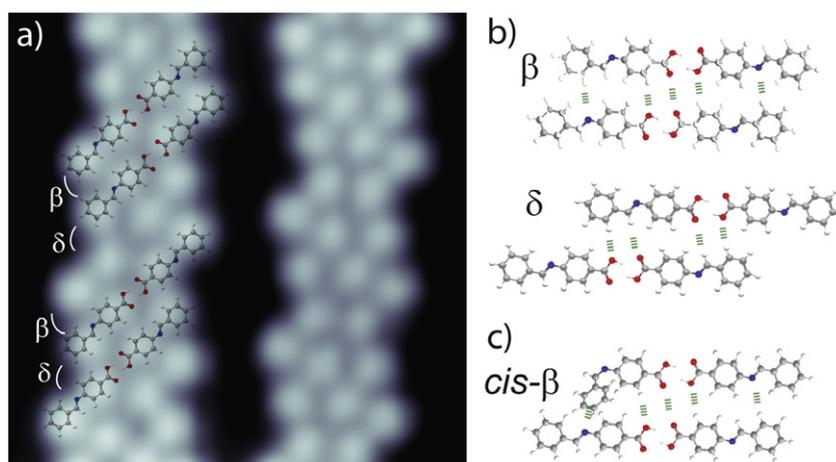
Figure 5. (a) STM image of two CBA rows with similar chiral arrangement. (b) Lowest energy configurations of two CBA dimers, as obtained by simulated annealing in molecular dynamics simulations. The expected hydrogen bonds stabilizing both structures are indicated by green dashed lines. The two structures alternate in the regular shape of CBA dimer chains (as shown superimposed to the data in (a)). (c) Stabilization of one *cis* isomer in the *β*-type structure, as obtained by an energy minimization in molecular dynamics after changing one of the four molecules from the *β* structure into a gas phase like *cis* form.

Au(111) surface. Although the planar *trans* isomer is more stable on the surface, electrons can induce switching into a *cis* conformer in a particular adsorption environment. In these sites, intermolecular interactions to neighboring molecules compete with the preferred flat adsorption configuration. The switching process is mediated by the transient excitation of a negative ion resonance. The corresponding quantum yield is small (of the order of 10^{-10} e^{-1} at 1.85 V), which allows us to connect the fast tunneling rate (typically in the GHz range) with the rate accessible by our STM investigations (Hz regime).

Acknowledgments

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