Imine Derivatives on Au(111): Evidence for “Inverted” Thermal Isomerization

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ABSTRACT Molecules that undergo reversible isomerization between *trans* and *cis* states, typically upon illumination with light at appropriate wavelengths, represent an important class of molecular switches. In this combined scanning tunneling microscopy (STM) and high-resolution electron energy loss spectroscopy (HREELS) study, we report on self-assembled arrays of imine derivatives on a Au(111) surface. Most of the molecules are found in the *trans* state after deposition at room temperature, but many of them change their conformation upon heating, which we assign to switching to the *cis* state. As for many molecular switches, the *trans* isomer is the energetically more stable compound in solution, resulting in thermal *cis* to *trans* relaxation upon sufficient heating. On the surface, however, the number of *cis* isomers increases with temperature, pointing toward an “inverted” thermal isomerization behavior. The reason for this surface-mediated effect could be a stronger coupling, as compared to the *trans* state, of the central imine part of the molecule to the gold surface, which is sterically only possible in the *cis* state.

KEYWORDS: molecular switch · isomerization · scanning tunneling microscopy (STM) · electron energy loss spectroscopy (EELS) · metal surface · single-molecule manipulation

The miniaturization of electronic devices down to the atomic scale represents the central challenge in the field of molecular electronics where single molecules with a specific function are connected to nanocircuits.[1] Such an ultimate miniaturization would revolutionize electronic devices with regard to size, operation speed, and energy consumption.[2] Molecular switches represent a particularly interesting class of molecules in this context because they could control the conductance of wires.[3,4] Such molecules exhibit at least two stable states with characteristic physical and chemical properties that can be obtained reversibly and in a controlled way by external stimuli as light. They are therefore also discussed as candidates for molecular machines that convert light energy into oriented molecular mechanical motion.[5] While molecular switches have been studied for many years in the gas phase[6] and in solution,[7] their adsorption on a surface is of much higher interest in view of potential applications.

Various molecular switches adsorbed on surfaces have been studied in the last years,[8,9] in particular, azobenzene derivatives.[10−22] These molecules exist in two isomers, a nearly planar *trans* and a nonplanar *cis* form, which undergo reversible isomerization of a N=N bond upon illumination with light at appropriate wavelengths.[23] Different isomers can be identified at the single-molecule level by scanning tunneling microscopy (STM), which is also capable of manipulating individual molecules[24] or nanocrystallites[25] in a precise way. By using this technique, switching of the molecules on surfaces has been achieved by tunneling electrons[11,12,17] and the electric field[10] in an STM junction in addition to photoisomerization.[14] On the other hand, the conformational changes of molecular switches at surfaces can be investigated by high-resolution electron energy loss spectroscopy (HREELS).[26,27]

The use of molecular side groups is advantageous in terms of electronic decoupling from the surface,[14] whereas azobenzene with four *tert*-butyl side groups (*i.e.*, 3,3′,5,5′-tetra-*tert*-butylazobenzene (TBA))[10,28] turns out to be a particularly efficient switch. The role of the side groups goes even beyond their decoupling ability as the attachment of methoxy groups to the TBA molecules reveals a strong dependence of the isomerization efficiency on the atomic-scale environment, that is, the surrounding molecules and surface lattice underneath.[16] This phenomenon results in periodic switching patterns on the surface, due to the commensurability with the substrate.

The characteristic potential landscape of a *trans*−*cis* isomer consists of a double potential well, representing the two isomers as sketched in Figure 1a. The total energy of the *cis* isomer is typically higher than that of

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Received for review December 2, 2010 and accepted February 8, 2011.

10.1021/nn103297e

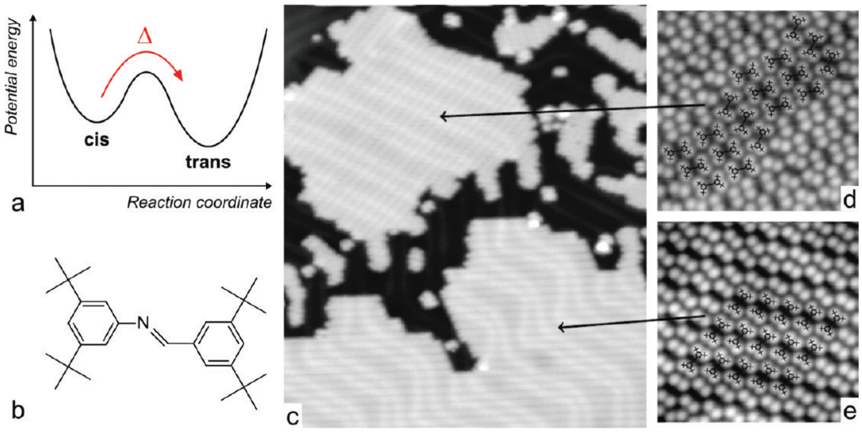

Figure 1. (a) Scheme of the double potential well for a *cis*/*trans* isomer of TBI in the gas phase. The arrow marks the thermal relaxation from the *cis* state to the energetically lower *trans* state. (b) Chemical structure of the (*E*)-3,5-di-*tert*-butyl-*N*-(3,5-di-*tert*-butylbenzylidene)benzenamine molecules (TBI). (c) STM image (64 × 75 nm^2) of TBI molecules on Au(111). Enlarged areas of two kinds of molecular structures are shown in (d) (image size 8.7 × 8.7 nm^2) and (e) (8.3 × 8.3 nm^2).

the *trans* isomer,[29] which causes a *cis* to *trans* relaxation of the molecules upon heating (marked by an arrow in Figure 1a). Azobenzene molecules, for instance, usually adsorb in the *trans* state on a metal surface because they require heating to around 370 K for sublimation from a Knudsen cell and self-assemble in large, highly ordered islands in a close-packed fashion as long as the interaction with the substrate is weak.[17] It has been shown for TBA molecules that heating of the sample to 320 K already induces efficient *cis* to *trans* isomerization.[13,30]

Another class of molecular switches, closely related to azobenzene, are imine molecules. Such compounds, containing a carbon−nitrogen double bond, undergo a reversible photoinduced *trans*/*cis* isomerization in solution, resulting in an alteration of the molecular conformation. The first spectroscopic observation of the *trans*/*cis* photoisomerization of imines was reported by Fischer and Frei in 1957.[31] It was found that the UV spectra of some diarylamines in solution significantly changed upon illumination at −100 °C and the spectra of the original isomer afterward restored while raising the temperature. Afterward, substituent effects and solvent effects for *trans*/*cis* isomerization of imine compounds were also studied experimentally and by theoretical calculations.[32−34]

In contrast to azobenzene derivatives, imine-based switches have been scarsely investigated on surfaces, and only two very recent studies exist. First, it was found that carboxybenzylideneaniline on Au(111) adopts a planar adsorption geometry in the first monolayer and that they lose their ability to change the conformation by optical excitation.[35] Second, the same molecules as in the present study have been studied very recently but focused on the electronic structure at the molecule−metal interface and not the isomerization behavior.[36]

In this work, we have studied (*E*)-3,5-di-*tert*-butyl-*N*-(3,5-di-*tert*-butylbenzylidene)aniline (TBI) on a Au(111) surface. It was synthesized by condensed reaction and exhibits the reversible *trans*/*cis* isomerization behavior in solution as observed in ^1H NMR measurements. This molecule, sketched in Figure 1b, is similar to the previously studied TBA molecule,[10] but the central switching unit has been changed from a diazo (−N=N−) to an imine (−CH=N−) group. The main difference of the two molecules is a much faster thermal relaxation from *cis* to *trans* in the case of imines than in the analogue azobenzene or stilbene molecules. The activation energy in this thermal relaxation process is about 16−17 kcal mol^{-1} (≈0.69 eV), which is appreciably lower than for azobenzene (23 kcal mol^{-1}) and stilbene (42 kcal mol^{-1}), and results in a far shorter half-life of the *cis* isomer of only about 1 s at 25 °C.[37] Accordingly, the first observation of the *cis* state of an imine molecule was achieved by cooling a solution with the molecules to 130 K and thereby lowering the speed of the thermal back reaction.[31] In this work, we study TBI on Au(111) in view of their isomerization behavior and in comparison to the previously studied TBA molecules.

When depositing TBI molecules onto a Au(111) surface, which is kept at room temperature during deposition, it turns out that they are mobile at this temperature, forming islands of different structures by self-assembly (Figure 1c). By varying the surface temperature during deposition, we found that molecular diffusion is already present at a sample temperature of 128 K, where disordered islands are formed. However, the diffusion barrier for the formation of ordered islands turns out to be higher, as they were not observed at this stage but after annealing the sample to about 230 K. In addition to small disordered islands, the TBI molecules adsorb in two different types of ordered islands, either in a zigzag pattern (Figure 1d) or in ordered rows (Figure 1e), similar to the dominating structure of TBA molecules on Au(111).[10,17,38] In comparison, the TBA molecules with a single methoxy group assemble in four geometries

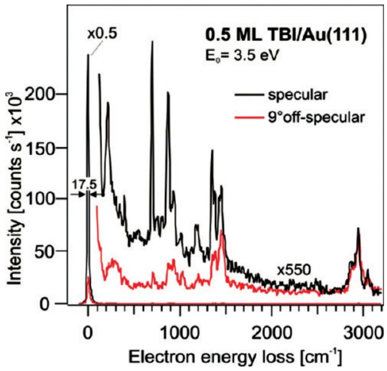

Figure 2. HREEL spectra of 0.5 ML TBI adsorbed on Au(111) recorded in specular and 9° off-specular scattering geometry, respectively, with a primary electron energy of 3.5 eV. The energy resolution is 17.5 cm^{-1} (≈2.2 meV).

with comparable relative abundances, probably as a result of the present dipole moment, while those with two methoxy groups appear in only one structure.[16] The herringbone reconstruction of the underlying Au(111) substrate can also be seen on top of the molecular islands, which means that the molecules do not alter the surface structure and indicates that they are only weakly bound to the surface. Such a weak interaction can be explained by the presence of the *tert*-butyl groups, which lift molecules from the surface.

Single molecules (some are indicated in Figure 1d,e) appear in STM images as four lobes at distances of 9.0 ± 0.4 Å on the long side and 4.5 ± 0.4 Å on the short side of the molecule. By comparison with the calculated dimensions in the gas phase, these protrusions can be assigned to the *tert*-butyl groups of TBI. The four lobes appear at equal heights in the images, pointing to a planar adsorption of the phenyl rings on the surface. Hence, there is no indication for a rotation of the phenyl rings out of the plane, in contrast to molecules in solution,[39] the crystalline,[40] and the gas phase.[41] For instance, a torsion of the *N*-phenyl group by around 50° out of the C−N═C−C plane has been reported.[42] Due to this planar adsorption geometry and their resemblance with the TBA molecules in the *trans* configuration,[10] this appearance is assigned to the *trans* state.

Due to the imine group in the center, the TBI molecule is asymmetric in the gas phase. Its contour resembles more a trapezoid than a rectangle as the long side distance between two *tert*-butyl groups at opposite phenyl rings is about 9.1 Å on one side and 9.9 Å on the other side (with the average value of 9.5 Å given above). This asymmetry seems to be lost when the molecules self-assemble in islands on the surface and appear as symmetric rectangles, indicating that it is energetically more favorable for the molecules to form highly ordered islands than to keep their asymmetry. Accordingly, some molecules at the border of large islands are found to be asymmetric.

In order to gain further information on the adsorption geometry of TBI in the submonolayer regime, we carried out angular-dependent HREELS measurements in specular and 9° off-specular geometries (Figure 2). Most striking are the pronounced intensity drops of the out-of-plane torsion modes of the phenyl rings (τ(C−C)), at 217, 703, and 875 cm^{-1},[26,43] in the off-specular spectrum, indicating that their intensities in the specular spectrum mainly originate from dipole scattering. The strong dipole activity of the phenyl ring torsion modes clearly points toward a planar (*trans*) adsorption geometry since, in this orientation, these modes have a strong dipole moment change upon vibration perpendicular to the surface. Note that a similar adsorption behavior has been observed for TBA and the stilbene analogue on Au(111).[26,44] Thus, the HREEL data confirm the STM results, indicating a planar geometry of the molecules.

Directly after adsorption at room temperature, some of the molecules appear as bright spots (Figure 3a) with an apparent height of 3.9 ± 0.3 Å above the surface, while the protrusions of the *trans* isomers appear at 2.4 ± 0.2 Å. A characteristic height profile across such a feature is presented in Figure 3b. These bright spots are typically found either in small, disordered islands or at the border of large islands, but only in very rare cases inside the ordered islands. It is important to note that these spots have a very similar appearance as TBA *cis* molecules.[17] First, they exhibit almost the same apparent height of 4.1 ± 0.3 Å, and second, three small protrusions are imaged in a characteristic arrangement close to the bright lobe (inset in Figure 3a) as for TBA molecules, where they could be assigned to *tert*-butyl legs of the molecule by calculations.[17] These bright spots can hardly be assigned to fragments or contamination because the entire molecule can be removed by STM manipulation (Figure 3c,d).

When applying a voltage pulse above an individual molecule (at the marked cross in Figure 3c), we sometimes observe that the entire protrusion has vanished from this area (see subsequent STM image in Figure 3d). In its place, a hole is found in the molecular island instead, which exhibits a contour that precisely resembles the rectangular shape of a single *trans* isomer. First, it shows that the spots are a phenomenon of a single molecule, which has been transferred to the STM tip. Due to this tip modification, the resolution is clearly improved in the STM image after the voltage pulse (Figure 3 panel d compared to panel c). Second, this strongly points to the interpretation that the bright protrusion represents a single TBI molecule, which has been in the *trans* state during island formation and later changed its configuration. Together with their typical appearance in STM images, we therefore assign these bright lobes to individual *cis* isomers of the TBI molecules. Note that this appearance is in agreement with density functional theory calculations of *cis* TBI isomers on a Au(111) surface that predict an upright standing phenyl ring,[45] similar to the TBA case.[17]

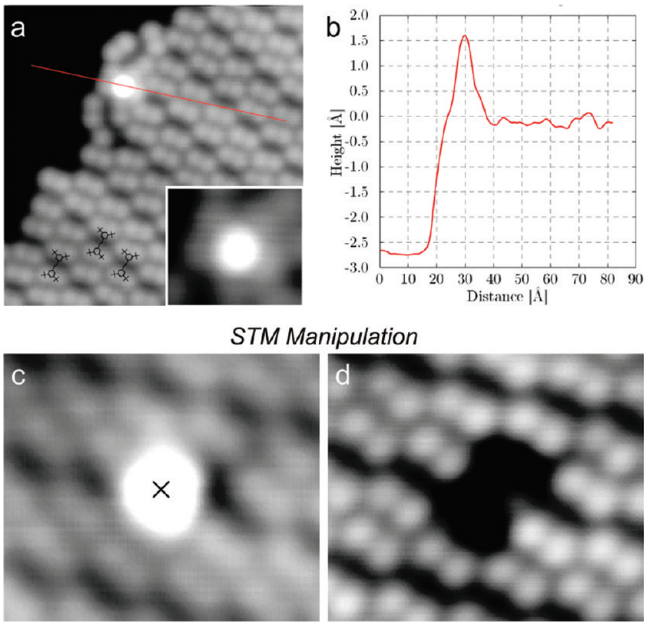

Figure 3. (a) STM image (9.4 × 9.4 nm^2) of an island with close-packed TBI molecules, one of them appearing as a bright protrusion. The inset (1.9 × 1.7 nm^2) shows the area of the bright protrusion, revealing the typical appearance with two weaker protrusions at the left side and one at the right side of the bright spot. (b) Height profile along the line in (a): the average spot height above the gold surface is 3.9 ± 0.3 Å. (c,d) STM images (both 4.7 × 4.0 nm^2) of the same surface area before (c) and after (d) applying a voltage pulse with the STM tip above the bright protrusion (marked by a cross in (c)). During the pulse, the voltage is increased linearly during 1 min from 1 to 2.5 V (with a tunneling current up to 7 nA).

On the basis of the known isomerization of molecules by STM manipulation,[10−12,16,17] we attempted to switch the TBI molecules by applying voltage pulses. Two strategies were used, either increasing the voltage up to ±2.5 V (with currents in the range of about 10 nA) or rather small voltages of around ±200 mV with the tip approached very closely to the sample to obtain a high current (up to 100 nA) and thus excite processes with very small yields. However, it turned out that no isomerization process can be induced by such manipulation attempts. The parameters (voltage and current) were increased step-by-step in these experiments until the molecule is irreversibly modified, probably dissociated, or removed from the surface to the tip (as in Figure 3d). As the TBA molecules, which form similar islands as the TBI, can be isomerized on Au(111) by STM manipulation, steric hindrance is unlikely to hinder the switching in the present case, and the switching is probably quenched by electronic interaction with the substrate.

Another way to induce molecular isomerization and overcome the potential barrier (Figure 1a) is to heat the sample and thus supply sufficient thermal energy. The thermodynamically stable form of the TBI molecules in solution is the *trans* conformation (Figure 1a) as imine molecules in the *cis* state thermally isomerize back to the *trans* state very quickly.[46] It has been, for instance, observed for the azobenzene derivatives TBA on a metal surface that *cis* isomers switch to the *trans* state when the temperature in increased.[13,30] In order to investigate whether this behavior can also be found for TBI, the molecules were deposited onto a cold sample, kept at 128 K during deposition, and then heated at different temperatures, while imaging is always done at low temperatures of about 9 K (Figure 4). No ordered islands (*i.e.*, "large islands" in Figure 4b) are present directly after deposition, but they are formed upon heating at 230 K. Upon further heating, the molecules start to desorb at around 330 K, and the coverage consequently decreases. At the same time, the number of spots rises strongly, which concerns both the relative values (plotted in Figure 4) and the absolute values. For instance, 1% of the molecules is found as bright spots before the heating sequence (at a total coverage of 0.44 ML), but this value rises to 10% after heating at 430 K (and a reduction of the total coverage to 0.27 ML). The characteristic situation after heating at 430 K, visible in the STM image in Figure 4a, consists of a reduced molecular coverage with rather small islands, only very few of them ordered, and a quite large number of bright spots. Upon further heating to 486 K, the coverage drops drastically, which is also seen in TDS measurements, while the total number of spots continues to increase and no ordered islands are found on the surface any more. Note that the spots that were observed directly after deposition and those obtained by heating steps appear equivalently in the STM images and thus seem to be chemically identical.

The most remarkable observation is that the number of spots rises significantly upon heating, and the spots must therefore be related to the TBI molecules and not contamination. However, if the assignment to *cis* isomers discussed above is correct, their behavior is totally

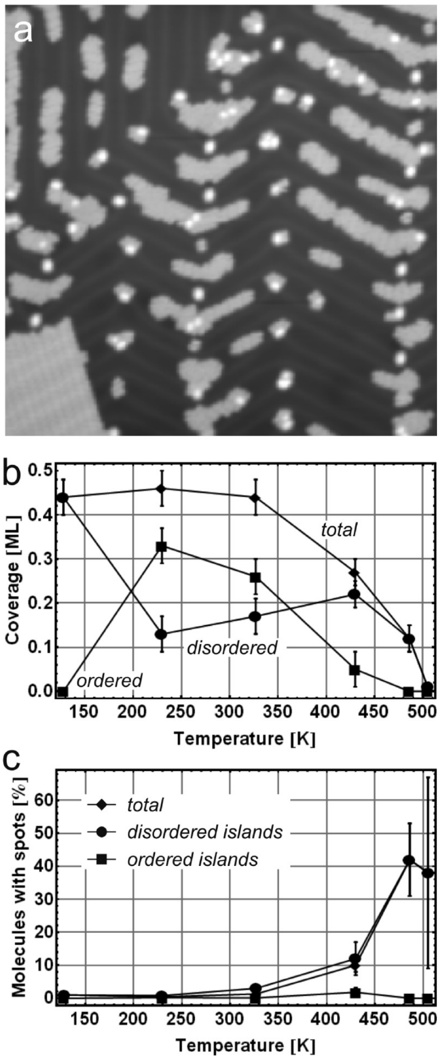

Figure 4. (a) STM image (75 × 75 nm^2, 9 K sample temperature) of TBI molecules on Au(111) after deposition onto the cooled sample, kept at 128 K, and subsequent annealing to 430 K. (b) Molecular coverage and (c) relative number of bright molecules as a function of the annealing temperature (diamonds, total coverage/number of molecules; circles, disordered, small islands; squares, ordered, large islands). Annealing at the given temperatures was done for 10 min.

different than expected because the *cis* to *trans* relaxation should increase with rising temperature as observed for *cis* TBA,[13] but the opposite is the case. Hence, molecules that were in the *trans* state after deposition (because they adsorb from the gas phase where this is the more stable state) seem to be switched to the *cis* state by sample heating, but the thermal back-switching is suppressed on the surface as compared to the molecules in the gas phase or in solution. We furthermore observe that the spots are preferentially located in disordered islands. However, it is unlikely that they are more easily formed in disordered islands because, at the elevated temperature of their formation, the molecules probably diffuse on the surface and steric hindrance of other molecules does not play an important role (at submonolayer coverages). It seems more likely instead that disordered islands are formed around the spots by thermal diffusion, and the disorder is caused by the contour of the spot molecule, which differs from that of a *trans* molecule (whereas the assembly of only *trans* molecules leads to highly ordered arrays if the thermal energy is sufficient). This interpretation also explains the correlation between the increasing number of spots with the heating temperature and the abundance of disordered islands (see Figure 4). We believe that this is the dominating process, which does of course not exclude the rare cases of spots in ordered islands (Figure 3c), most likely due to molecular switching when the ordered island has already been formed as discussed above.

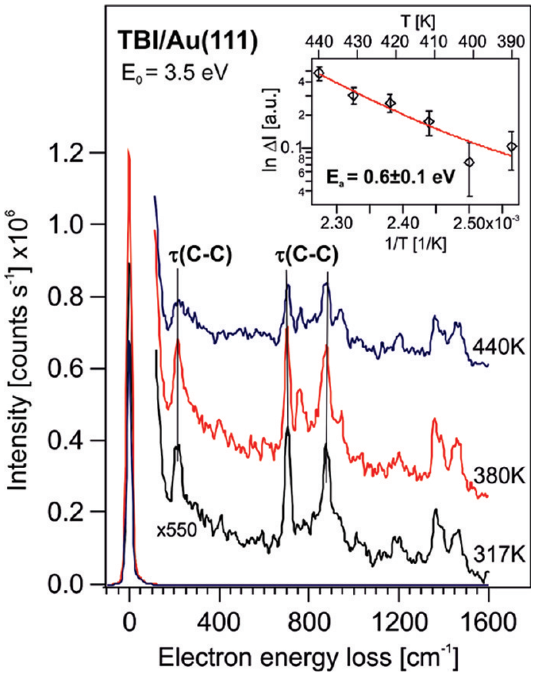

Figure 5. HREEL spectra of 0.5 ML TBI on Au(111) deposited at a substrate temperature of 100 K and after annealing at different temperatures, recorded in specular scattering geometry with a primary electron energy of 3.5 eV. The sample was heated for 2 min at the given temperatures, using a heating rate of 1 K/s, and subsequently cooled down to 100 K. Inset: Intensity change of the phenyl ring torsion mode at 705 cm^{-1} as a function of the substrate temperature. The activation energy (E_a) for the thermally induced *trans* to *cis* isomerization of TBI on Au(111) was obtained by using the Arrhenius expression to fit the data (see text). Note that these temperature series were done on freshly prepared films using the same annealing time (2 min) at each particular temperature.

The appearance of *cis* TBI molecules upon thermal activation is supported by HREELS measurements, where the spectra are dominated by the intense dipole-active torsion modes of the phenyl rings (217, 703, and 875 cm^{-1}) up to heating temperatures of 380 K, due to the planar (*trans*) adsorption geometry (Figure 5). However, at 440 K, a very strong intensity decrease of these vibrational modes is observed, which we assign to a conformational change to *cis* isomers with one phenyl ring pointing upward, in analogy to *cis*

TBA on Au(111).[26] Note that the spectral changes are not caused by a reduced TBI coverage since thermal desorption spectroscopy shows a molecular desorption of only 5% of the coverage under these conditions.

In order to gain a quantitative insight into the activation barrier governing the thermally induced *trans* to *cis* isomerization, we studied the changes in the vibrational loss intensities during the *trans* to *cis* transition. Specifically, intensity changes of the phenyl ring torsion modes at 703 and 875 cm^{-1}, respectively, were used as a quantitative measure for the reaction. The activation energy (E_a) is determined from the relative change ΔI in peak intensity ($\Delta I = (I_0 - I_i)/I_0$) between the *trans* TBI covered surface at 317 K and the same surface annealed at a particular temperature, using the Arrhenius-like expression $\Delta I = I_p \exp(-E_a/k_B T)$ (with I_p an intensity factor and k_B the Boltzmann constant[26]). From these measurements, we derive a value of 0.6 ± 0.1 eV for the activation energy (see inset of Figure 5). In comparison, the calculated barrier between the stable *trans* and the metastable *cis* form for free imine derivatives in solution is around 1 eV.[47] Thus, we find a barrier reduction of about 0.4 eV for the surface-bound TBI, indicating that the potential energy landscape is significantly different from that in the free molecule.

While the *trans* TBI molecules interact rather weakly with the Au(111) surface, due to the *tert*-butyl legs and in similarity with the TBA molecules,[14] this might be different when they are in the *cis* state because the lone pair electrons of the N atom can eventually reach the metal surface. A possible chemical interaction could be a σ-bond of the lone pair electrons with the metal substrate, similar to the complexation of metal atoms with imine compounds.[48] The observed inverted thermal isomerization behavior could be due to such an increased coupling to the surface as well as to a modified potential landscape and thus (de)stabilization of certain configurations with respect to the gas phase. The fact that the *cis* isomers are almost exclusively found in disordered islands after heating (see Figure 4) could be an indication that their coupling to the surface results in a higher diffusion barrier than the *trans* isomers, which assemble around the "anchored" *cis* isomers during sample cooling at the end of the heating sequence.

To explore the reversibility of the thermally activated *trans* to *cis* reaction process, illumination experiments were performed in order to drive a photoinduced *cis* to *trans* isomerization. We illuminated the sample with a continuous wave laser diode at wavelengths of 405 and 445 nm (output power of 125 $\mathrm{mW/cm^2}$ and a photon dose of around 10^{21} $\mathrm{photons/cm^2}$) in both experimental chambers independently. However, no reduction of the *cis* species and thus an evidence for a back-switching of the *cis* TBI molecules was found in STM imaging and HREEL spectroscopy. This could be a result of the above-mentioned chemical interaction with the surface or due to steric effects: The *cis* isomers occupy less surface area than the *trans* molecules (see Figure 3c,d) and can therefore not return to the *trans* state, which does not fit into the densely packed (disordered) molecular array.

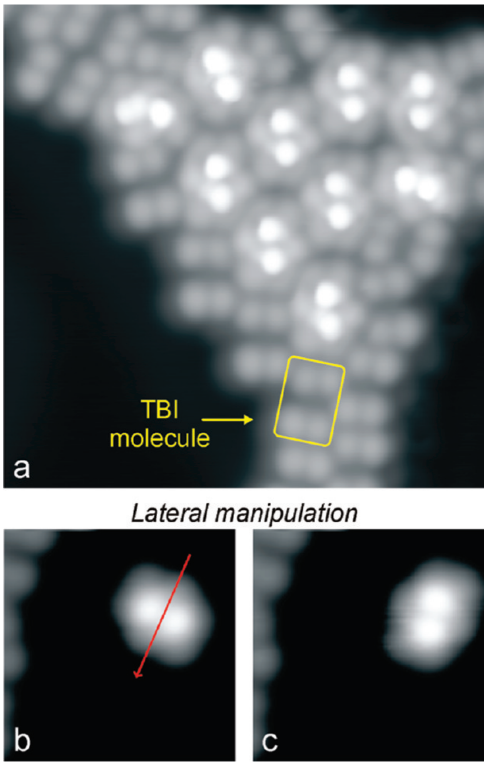

Figure 6. (a) STM image (9.4 × 9.4 nm^2) of a molecular island with double lobe structures after annealing the sample to 430 K. (b,c) STM images of a double spot before and after, respectively, a lateral manipulation. The STM tip is moved in the constant-current mode (−0.4 V, 40 nA) along the indicated pathway with a speed of 10 Å/s. It can be seen that the double spot moves as a whole and does not separate during manipulation.

When the sample is heated at temperatures above 390 K, the spots appear not only in larger numbers but also many of them in pairs with increasing abundance for higher temperatures (almost all spots appear in such pairs after heating at 430 K). These double spots (Figure 6a) have a distance of 5.7 ± 0.5 Å between the two protrusions and occupy (together with the surrounding weaker ring) an area of about 1.8 nm^2, which is roughly twice that of *cis* isomers, while their height is the same as for single spots. Their chemical identity cannot be determined from the STM images, and theoretical simulations would be helpful, but their characteristic size and height point to pairs of interacting TBI molecules, each of them being identical or at least very similar to the single spots that were assigned to the *cis* state. When laterally manipulating these double spots by moving the STM tip across them, they appear very stable. They are moved as entire objects (and do not decompose) and change their location on the surface and their orientation (Figure 6b,c), which indicates a rather strong chemical interaction.[24] Separation of the double spots during such lateral manipulation attempts could never be achieved.

In conclusion, we have adsorbed TBI molecules on Au(111), which form two types of ordered islands with all molecules in the *trans* state. Some of the molecules show bright protrusions and are assigned to the *cis* state, due to their very characteristic appearance in STM and indication of one upward pointing phenyl ring, in analogy to *cis* azobenzene molecules. When sufficiently heated, the abundance of *cis* isomers increases significantly, indicating an "inverted" thermal isomerization behavior, where the *cis* molecules are energetically more stable than the *trans* isomers. This phenomenon might be mediated by the substrate, which stabilizes the *cis* state by an additional bond to the surface, lowering the corresponding potential well. Further heating results in double spots in STM images, which seem to reflect pairs of *cis* isomers that interact with each other in a rather strong manner. Accordingly, they can be moved intact by lateral STM manipulation.

METHODS

Experiments were performed in ultrahigh vacuum chambers with a base pressure of 10^{-10} mbar, using two different setups for STM and HREELS. Less than one monolayer of TBI molecules was deposited onto the Au(111) surface, which has been cleaned before by Ar ion sputtering and subsequent annealing. During deposition at a molecular flux between 0.2 and 0.3 monolayers (ML) per minute, the sample was kept at room temperature, if not stated differently. The temperature of the molecule evaporator, a Knudsen cell, was 355 K as controlled by a thermocouple, and the coverages were determined from the STM images and by thermal desorption spectroscopy (TDS). All STM images were taken in the constant-current mode at temperatures of about 9 K by a modified commercial low-temperature STM (Createc), using a bias voltage of -1 V (applied to the sample) and a tunneling current of 0.1 nA unless stated differently. The HREELS experiments were performed at a sample temperature of 100 K in both specular and off-specular scattering geometry. The energy of the primary electrons was set to 3.5 eV with an overall resolution of ≤ 2.5 meV measured as the full width at half-maximum (fwhm) of the elastic peak.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support through the Sonderforschungsbereich 658.

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