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Molecules with multiple switching units on a Au(111) surface: self-organization and single-molecule manipulation

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Abstract
Three different molecules, each containing two azobenzene switching units, were synthesized, successfully deposited onto a Au(111) surface by sublimation and studied by scanning tunneling microscopy at low temperatures. To investigate the influence of electronic coupling between the switching units as well as to the surface, the two azo moieties were connected either via π-conjugated para-phenylene or decoupling meta-phenylene bridges, and the number of *tert*-butyl groups was varied in the meta-phenylene-linked derivatives. Single molecules were found to be intact after deposition as identified by their characteristic appearance in STM images. Due to their mobility on the Au(111) surface at room temperature, the molecules spontaneously formed self-organized molecular arrangements that reflected their chemical structure. While lateral displacement of the molecules was accomplished by manipulation, *trans–cis* isomerization processes, typical for azobenzene switches, could not be induced.

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In the field of molecular electronics, molecular switches could play an important role, because they can possibly control the conductance in molecular circuits. Molecular switches have been studied intensively in solution and the gas phase [1–3], but this is of only limited relevance when constructing devices for molecular electronics as the devices have to be placed on a solid surface. Intense research has been done in the last few years on molecular switches on surfaces [4–7]. *Trans–cis* isomers, in particular azobenzene molecules and derivatives, turned out to be a promising class of molecular switches [8–14]. Many fewer studies exist on the similar imine [15, 16] and stilbene [17] switches. Azobenzene molecules exist in two stable isomers, a nearly planar *trans* and a non-planar *cis* configuration [18]. Different stimuli have been used to induce isomerization of such molecules: on the one hand, light to induce the conventional photoisomerization [11, 13, 19] as in solution. On the other hand, the tip of a scanning tunneling microscope (STM) can be used to manipulate single molecules in various ways [20] and azobenzene derivatives could be switched using the electric field [8] or the tunneling electrons [9, 10, 12] in the junction.

The incorporation of side groups has been investigated with the objective of decoupling the molecules from the surface and it was found that the use of *tert*-butyl groups, in particular in 3,3′,5,5′-tetra-*tert*-butylazobenzene (TBA), strongly changes the isomerization yield [11]. However, more recently it was found that, besides the structural argument, the electronic properties must also be taken into account [21]. Furthermore, other side groups can alter the switching properties, resulting in significantly different isomerization yields. This has been demonstrated by attaching one or two

methoxy groups in the 4- and 4′-positions of TBA molecules, giving rise to M-TBA and diM-TBA, respectively [22].

Most studies up to now have considered molecular switches as isolated units, independent of their isomerization properties from their environment. However, the adsorption of the same molecules onto different noble metal surfaces leads to very different switching properties [12]. By using M-TBA molecules, it could be shown that the precise adsorption site on the surface strongly influences the switching properties, leading to efficient isomerization in one case and no isomerization in the other case [22], which opens up the possibility of spatially addressing molecular functions via the substrate. Furthermore, the surrounding molecules play an important role as the same molecules switch or do not switch, depending on their arrangement relative to their neighboring molecules [22]. This result is particularly surprising as the coupling between the planarly adsorbed molecules is rather weak and involves no chemical bond. This finding opens the question of how more strongly coupled switching units do interact with each other and influence each other's isomerization behavior. In this paper, we report for the first time an investigation of covalently connected multiple switching systems.

Multiswitch systems can, in principle, be created in two ways: either by assembling molecular switches from the bottom up directly on a surface, which was achieved via hydrogen bonds between carboxyl side groups [23], but no switching could be induced in that case. The other possibility, which is addressed in this work, is to synthesize molecules that contain more than one switching unit *ex situ* and then deposit them under ultrahigh vacuum conditions onto a metal surface. This can become very challenging, because the incorporation of a function into the molecular skeleton is almost necessarily accompanied by a larger size and hence a higher molecular weight, which in turn leads to a rise in the required sublimation temperature. At high temperatures however, molecular fragmentation can occur during deposition [24, 25] and alternative techniques [26–30] need to be used. Hence, molecular deposition and subsequent analysis of the STM images must be done very carefully, considering the possibility of molecular dissociation. The aim of this work is to deposit molecules that contain multiple switching units onto a metal surface, to prove their intact structure and to study their adsorption configurations, self-organization and potential switching properties. Lateral manipulation is used to estimate their intermolecular interaction. If the deposition is successful, it is of interest to attempt switching of the molecules. Three different molecules are studied, all containing two identical azo switching units, in symmetrical yet different linking configurations and with varying numbers of *tert*-butyl groups.

Experiments were done in an ultrahigh vacuum chamber with a base pressure of 10^{-10} mbar. Scanning tunneling microscopy (STM) measurements were done with a homebuilt [31] and a modified Createc instrument at low temperatures of about 10 K. After cleaning the Au(111) substrate by conventional sputtering and annealing cycles, molecules were deposited onto the surface by sublimation from a Knudsen cell. While the sample is kept at around room temperature during deposition, it is then cooled when transferring it to the STM. Bias voltages are applied to the sample, while the tip is grounded.

In para-phenylene-bridged bis(tetra-*tert*-butylazobenzene) (para-P-BTBA) molecules, two azo groups are connecting three phenyl rings (figure 1(a)). The azo groups are attached to the central phenyl ring in a para-relationship and each of the outer phenyl rings carries two *tert*-butyl groups, mimicking the TBA structure, which was observed to switch on a Au(111) surface [8, 11, 14]. After deposition of these molecules onto Au(111), the molecules appear to be mobile and diffuse on the surface at room temperature as they form large and highly ordered islands (figure 1(b)). The herringbone reconstruction of the gold surface is still visible and the molecular layers follow this small corrugation, thus pointing to a rather weak molecule–surface interaction.

When recording STM images of smaller areas (figures 1(c) and (d)), the precise molecular arrangement can be determined from two properties: first, it is well known that the bulky *tert*-butyl groups exhibit the largest apparent height within such molecules, thus being clearly visible as intense protrusions as in the case of TBA [8]. Second, the molecular dimensions are known from gas phase calculations (using HyperChem and the AMBER force field) and we find that the four *tert*-butyl groups of the molecule form a planar rhombus with side lengths of 5.09 and 15.76 Å. In the STM image (figure 1(d)) we find intense lobes at an average distance of 4.9 ± 0.2 Å and 15.2 ± 0.7 Å, respectively, which is in very good agreement with the gas phase values. Furthermore, a weaker lobe is present at the center of each molecule, reflecting its central benzene ring. Based on this assignment, we can precisely determine the supramolecular architecture on the surface (see the superimposed structure in figure 1(d)) and find that the molecules, which probably interact by weak van der Waals forces with each other, form a close-packed structure to maximize the intermolecular interaction.

On the Au(111) surface, no isomerization, i.e. switching, processes can be induced for the para-P-BTBA molecule. Even in solution illumination with UV light (368 nm) leads to generation of only 25% of the *trans, cis*-isomer and 3% of the *cis, cis*-isomer [32]. While the first photoisomerization step is already less efficient as compared to the parent azobenzene due to the electron-accepting character of the para-azo substituent, the second switching event is even less efficient, presumably because of the increased accepting character of the *cis*-configured azo group. On the surface, voltage pulses of up to 3.5 V (and currents up to 30 nA) from the STM tip did not lead to any isomerization events. At high voltages, fragmentation of the molecules can occur instead. Based on these results, both in solution and on the surface, we have studied meta-phenylene-bridged bis(tetra-*tert*-butylazobenzene) (meta-P-BTBA, see figure 2(a)). In meta-P-BTBA the switching moieties are decoupled due to the cross-conjugated nature of the meta-phenylene linkage and thus in solution isomerization occurs both more efficiently, giving rise to formation of 21% of the *trans, cis*-isomer and 67% of the *cis, cis*-isomer, and both switching events are

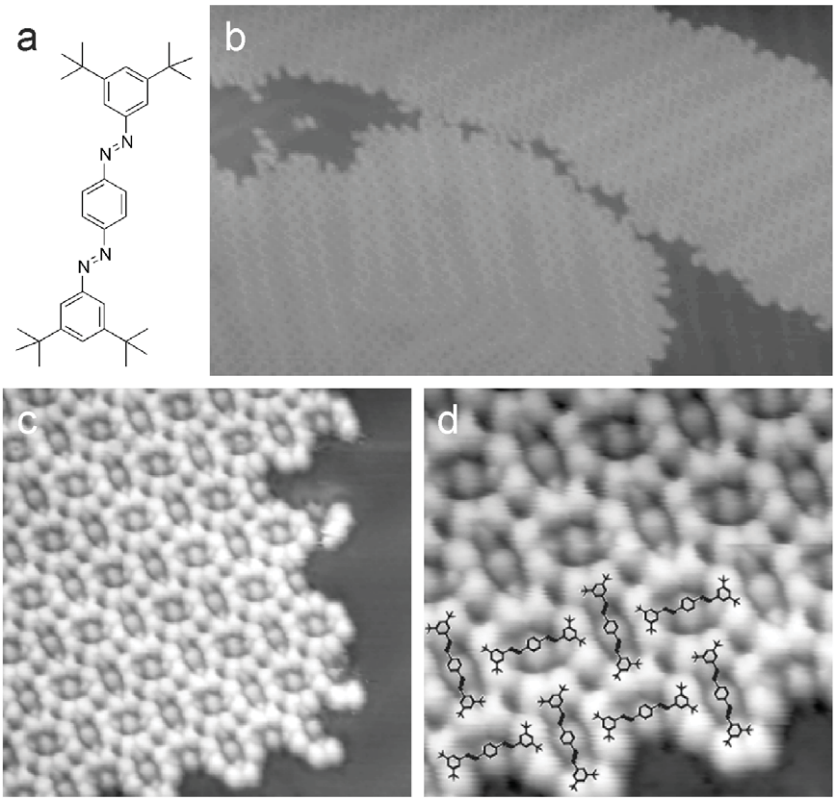

Figure 1. Para-P-BTBA on Au(111). (a) Chemical structure of the molecule. (b) Overview STM image ($U_{bias} = -0.3$ V, $I_T = 0.13$ nA, 120×200 nm^2). STM images of smaller areas are shown in (c) ($U_{bias} = -0.3$ V, $I_T = 0.12$ nA, 12×12 nm^2) and (d) ($U_{bias} = -0.3$ V, $I_T = 0.12$ nA, 6.8×6.8 nm^2). The molecular structures are superimposed onto the latter one.

independent of each other (see supplementary data available at stacks.iop.org/JPhysCM/24/394013/mmedia) [33].

After deposition of meta-P-BTBA onto the Au(111) surface, single molecules consist of four intense and one weaker lobe (figure 2(b)). When comparing the distances between the intensity maxima of the lobes with those from gas phase calculations, it becomes clear that also here the intense lobes correspond to the *tert*-butyl groups and the smaller lobe to the central phenyl ring. When determining the apparent heights of the different lobes in a bias voltage range between -2 and $+2$ V, we find that the *tert*-butyl legs appear always at 2.7 ± 0.1 Å, while the central benzene ring changes its height from 1.2 ± 0.1 Å at negative bias voltages to increasing values at positive values up to 1.7 ± 0.1 Å at $+2$ V. Such a voltage-dependent appearance has neither been observed for the TBA [8] nor for the M-TBA [22] molecules, probably because these molecules are smaller and the *tert*-butyl groups therefore dominate the STM image and hide the phenyl ring.

As can be seen in figure 2(c), the molecules adsorb as single molecules as well as in disordered and ordered islands. Their growth is guided by the well-known herringbone reconstruction of the Au(111) surface [34]. Small islands, consisting of up to about 30 molecules, are found in the elbows and grow along the reconstruction lines. The molecules therefore exhibit sufficient mobility on the surface at room temperature to form supramolecular arrangements. Two kinds of architectures are present on the surface, presented in figures 2(d) (type I) and (e) (type II). Note that, when increasing the coverage, only islands of type I increase in size while islands of type II were found exclusively as small chains, which form along the herringbone reconstruction and typically consist of not more than ten molecules. This indicates that type I, if extended in two dimensions, is the energetically preferred one, while at low coverage the growth of narrow islands prevails and thus islands of type I and II appear at similar abundances.

From azobenzene molecules with only one switching unit and different side groups, it is known that the isomerization can be suppressed by the molecular interaction with the substrate [11] and the attachment of *tert*-butyl groups therefore turned out to be successful [8]. Thus, in addition we have investigated a related molecule with two switching units, meta-*tert*-butyl-phenylene-bridged bis(tetra-*tert*-butylazobenzene) (meta-TBP-BTBA); figure 3(a), which has an additional *tert*-butyl group attached on the central phenyl ring that was introduced to reduce the coupling between the switching units and the substrate. An STM image of a single meta-TBP-BTBA molecule consists of five lobes (figure 3(b)). A comparison of the measured distances between the protrusions with the intramolecular distances from gas phase calculations again reveals that these are single intact molecules with *tert*-butyl groups as the most prominent features in STM images. Unlike for the meta-P-BTBA molecule, no voltage dependence of the topography could be observed, which might be due to the *tert*-butyl group attached to the central phenyl ring that dominates the appearance at

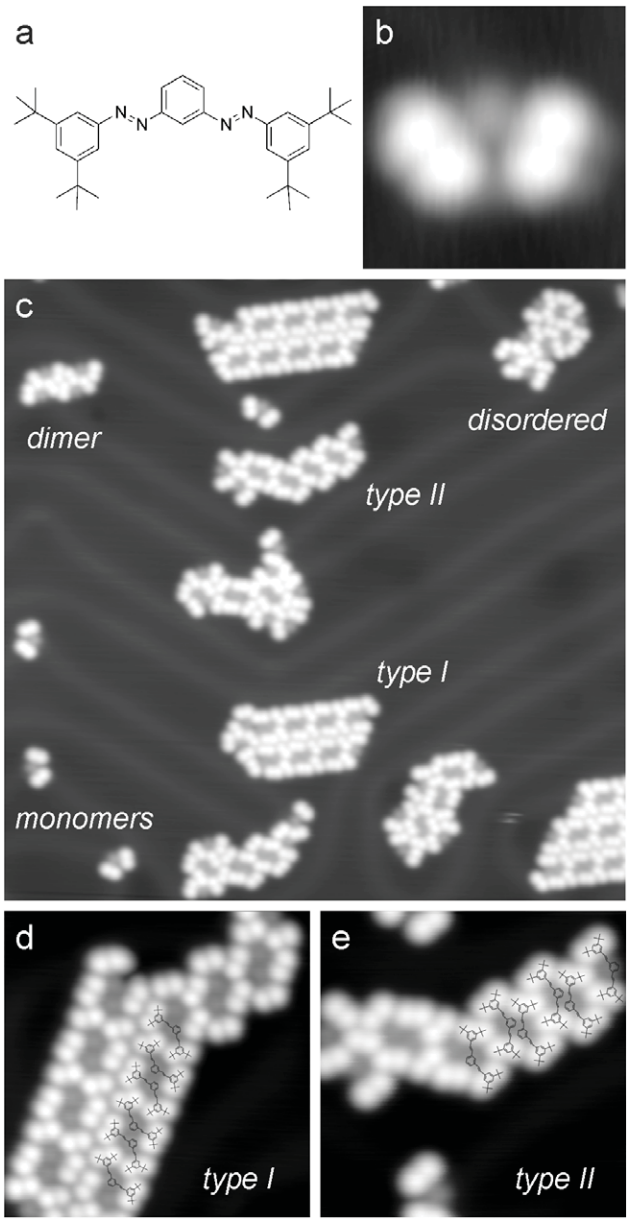

Figure 2. Meta-P-BTBA on Au(111). (a) Chemical structure of the molecule. (b) Single molecule on Au(111) ($U_{bias} = 1$ V, $I_T = 0.1$ nA, 3×3 nm^2): the bright lobes reflect the *tert*-butyl groups (same orientation as in (a)). (c)–(e) Overview and images of the two possible types of ordered structures partially with superimposed molecular structures ($U_{bias} = 1$ V, $I_T = 0.1$ nA, 37.5×37.5 nm^2 (c) and 9.4×9.4 nm^2 (d) and (e)).

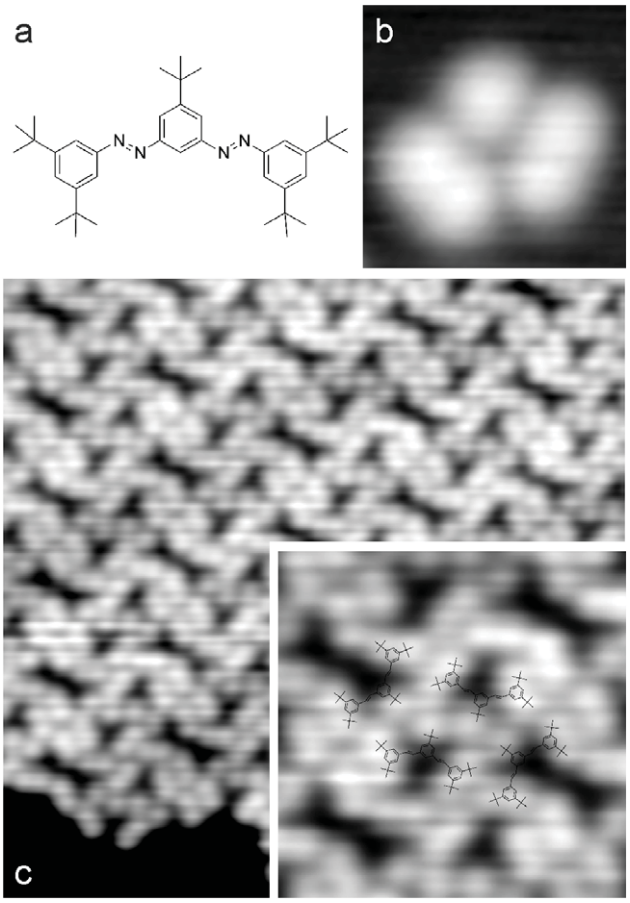

Figure 3. Meta-TBP-BTBA on Au(111). (a) Chemical structure of the molecule. (b) Single molecule on Au(111) ($U_{bias} = -1$ V, $I_T = 0.1$ nA, 3×3 nm^2). The additional *tert*-butyl group (as compared to meta-P-BTBA) can be clearly seen as an intense protrusion in the center. (c) Overview image of an ordered molecular island partially with superimposed molecular structures ($U_{bias} = -1$ V, $I_T = 0.1$ nA, 18.8×18.8 nm^2, inset 5.9×5.9 nm^2).

the center of the molecules. Also here, the mobility at room temperature leads to close-packed arrangements (figure 3(c)), but due to the additional *tert*-butyl group in the center of the molecule, the self-organized architectures look very different as compared to meta-P-BTBA. While some molecules form disordered chains, following the herringbone reconstruction, most molecules assemble in quartets of almost rectangular shape with the additional *tert*-butyl group pointing inwards (see the inset in figure 3(c)).

In order to test the stability of the molecules and to estimate the strength of the intermolecular interaction, lateral manipulation with the STM tip was done, revealing that single molecules can be displaced on the surface without fragmentation. The case of meta-P-BTBA molecules is presented in figures 4(a) and (b), but the meta-TBP-BTBA molecules behave similarly. The important parameter for lateral manipulation is the threshold resistance, which reflects the largest tunneling junction resistance at which molecules can be removed from an island (no displacement occurs at higher values). The resulting value is 20 MΩ for meta-P-BTBA and 8 MΩ for meta-TBP-BTBA, which is more than an order of magnitude larger than for para-P-TBA (400 kΩ), meaning that in the latter case the tip needs to be closer to the surface. Hence, larger forces are required and the molecules apparently have a higher potential barrier to overcome, which is probably due to the stronger interlocking (see figure 1(d)) than for meta-P-BTBA and meta-TBP-BTBA.

When attempting molecular isomerization, voltage pulses up to ±3 V were applied from the STM tip to single meta-P-BTBA and meta-TBP-BTBA molecules. It was tried to apply the pulses either to the *tert*-butyl legs or to the

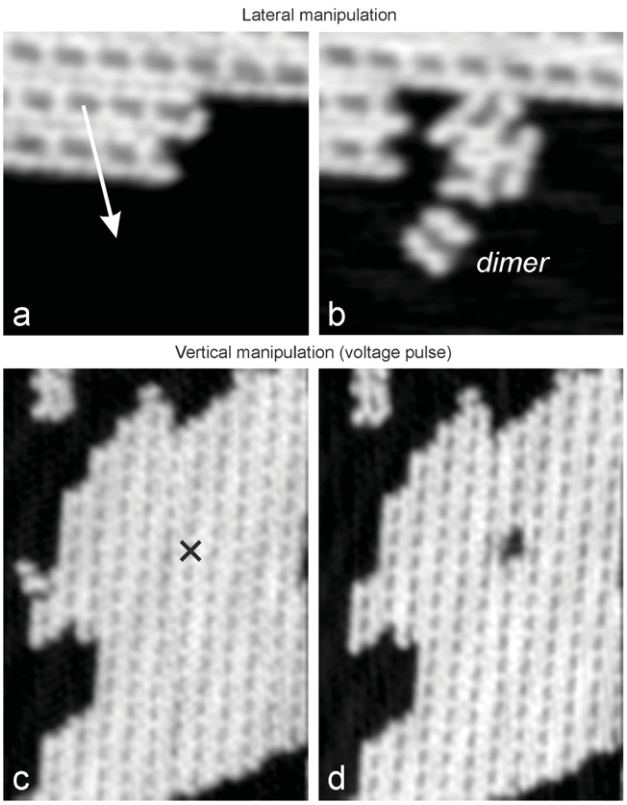

Figure 4. Manipulation of meta-P-BTBA molecules. (a) and (b) STM image ($U_{bias} = -1$ V, $I_T = 0.13$ nA, 13.3×13.3 nm^2) before and after a lateral manipulation (the tip pathway is indicated by an arrow) in the constant-current mode ($U_{bias} = -0.4$ V, $I_T = 100$ nA, $v = 1$ nm s^{-1}). (c) and (d) STM images ($U_{bias} = -1$ V, $I_T = 0.13$ nA, 37.5×26.4 nm^2) before and after a vertical manipulation (the position of tip approach is indicated by a cross). During the pulse the voltage is linearly increased from -1 to -3 V and a chemically modified (probably dissociated) molecule is found afterwards.

central phenyl ring and on single molecules and all observed island types, but switching was never observed, in contrast to the molecules in solution (see above). When a pulse did not change anything in the appearance of the molecules on the surface, a similar pulse, either with a higher voltage or at a smaller tip height, was applied. In this way the voltage and current were increased until the molecule under the tip was dissociated (figures 4(c) and (d)). Even the additional decoupling of the central benzene ring from the surface in the case of meta-TBP-BTBA was not sufficient to enable an isomerization process on the surface.

In conclusion, we prepared various covalently connected bisazobenzenes that contain the switching units in coupled as well as decoupled relationship and with varying degrees of coupling to the surface. We could show that it is possible to deposit these complex molecules onto a surface under clean ultrahigh vacuum conditions, their weight and stability is thus still suitable for thermal sublimation. The molecules, which can be clearly identified from their characteristic appearance in STM images, are found to self-organize in large ordered islands of different arrangements, depending on their chemical structure. While lateral manipulation can be achieved, no switching processes could be induced by voltage pulses over different parts of the molecules and in different environments, although very high parameters up to molecular dissociation were used. There are two main reasons why molecular isomerization on the surface is blocked: (1) the motion of the molecule can be sterically constrained either by the surface or by the neighboring molecules. (2) The electronic coupling with the surface may reduce the lifetime of excited states in the molecule. When the lifetime becomes shorter than the time the molecule needs for the change of its configuration, the isomerization is quenched. For the three bisazo switches studied here, steric hindrance by the surrounding molecules is unlikely as switching was attempted in large islands as well as with isolated molecules. The origin of the suppressed switching could indeed be found in the steric hindrance from the surface, e.g. sufficiently strong binding of specific groups, or by electronic effects due to the coupling with the metal substrate.

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