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Formation and manipulation of discrete supramolecular azobenzene assemblies

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Abstract Azobenzene derivatives were deposited onto a Au(111) surface and studied by scanning tunneling microscopy. The symmetry of the parent azobenzene was broken by introducing *tert*-butyl groups which are known to decouple the molecular core from the substrate, on the one end, and carboxylic acid groups which direct and stabilize the supramolecular assembly structure on the surface by intermolecular hydrogen bonding, on the other end. As a consequence of the interacting COOH groups, the molecules assemble on the surface either in extended, polymeric chains and/or in discrete, hexameric rosettes. The high stability of the rosette structure is proven experimentally by controlled lateral displacement on the surface without breaking the non-covalent interactions. Although switching attempts were not successful, the approach herein should facilitate the construction of well-defined multi-switch arrays.

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Organic molecules are known to interact on metal surfaces through strong covalent [1, 2] or weak non-covalent interactions, such as hydrogen bonding [3–6]. The interplay of various intermolecular forces in the presence of a sufficiently low diffusion barrier, resulting from subtle molecule–substrate interactions, lead to the formation of macro- or supramolecular nanostructures on surfaces. Importantly, the topology of the resulting structures reflects the chemical structure of its individual molecular building blocks and the relative spatial orientation of their interacting groups, leading to characteristic shapes [3, 5, 7–9]. Hence, by designing suitable molecular structures, supramolecular self-assembly can be controlled to construct nanostructures of well-defined size and dimensions [10, 11]. However, in order to utilize these sophisticated structures, their nanoscale order has to be translated into the precise arrangement of functional entities encoding a desired property, ideally by self-assembly of *functional* molecular building blocks.

Functional molecules are of great interest for future applications in ultimately miniaturized devices [12], where ideally single molecules perform specific mechanical or electronic operations. Molecular switches, i.e., molecules that can be reversibly switched between at least two stable states, are of great interest in this regard because their isomers exhibit markedly different properties [13]. Various molecular switches have been reported in the last few years [14–17], and it could be shown that it is possible to reversibly switch single molecules between their switching states on a surface. Azobenzene represents perhaps the most classical prototype of a molecular switch, existing as two stable yet interconvertable isomers, i.e., a planar *trans* and a three-dimensional *cis* configuration, with different optical and electronic properties [18], in particular having different conductances [19]. Azobenzene derivatives have been reported to form ordered structures on metal surfaces [20, 21]. Experiments have shown that azobenzene itself [22] and the azobenzene derivatives 3,3′5,5′-tetra-*tert*-butylazobenzene

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(TBA) [23–25, 27] and 4-amino-4′-nitroazobenzene (Disperse Orange 3) [26] can be isomerized on Au(111), while other metallic substrates turn out to be less suitable [27].

In the context of molecular switching, the mobility of such molecules on a surface and their interaction with neighbor molecules play a fundamental role. If the energy barrier for lateral translation on a surface is lower than the barrier for isomerization [23], it is not possible to switch *single* molecules in a controlled way. Instead, only molecules that are adsorbed in close-packed molecular islands could successfully be isomerized. However, the packing into a molecular island can impact the switching process by strong electronic and steric interactions between neighboring molecules. To avoid this complication and gain more insight into the fundamental switching mechanism, it is desirable to stabilize molecular switches on a surface in an alternative way that allows a precise isomerization study of single molecules in the absence of perturbing surrounding molecules.

In order to achieve such stabilization, two complementary approaches can be envisioned: While the commonly explored approach involves the covalent attachment of one part of the switch to the surface (usually giving rise to a more or less vertical adsorption geometry) [28], our alternative approach is based on the non-covalent bonding within a defined supramolecular aggregate (leading to a parallel adsorption geometry). The latter strategy of non-covalent stabilization of molecular switches involves the design and synthesis of a molecule, which carries groups for directional non-covalent bonding on one end of the azobenzene core for fixation, while the other end maintains its degrees of freedom (Fig. 1a). After the self-assembly of such building block into a defined aggregate structure, the molecular switch is strongly confined yet more or less isolated, i.e., not close-packed, and should allow for a detailed single molecule switching study. Thus far, only close-packed molecular islands of TBA and related derivatives have been intensely studied by us and others employing various methods [23–25, 27]. Here, we present our work towards the formation of defined supramolecular aggregates of a new azobenzene derivative, i.e., 3,5-di-*tert*-butyl-3′5′-dicarboxylazobenzene (DBDCA) (Fig. 1b). In DBDCA two carboxylic acid groups have been attached to one of the two phenyl rings, since such groups are well known to form reasonably strong hydrogen bonds upon intermolecular interaction in a well-defined linear carboxylic acid dimer structure on a surface [29]. Depending on the relative orientation of the two bridging linear carboxylic acid dimer moieties, in principle either a linear or a kinked structure (or mixtures thereof) are expected to form on surfaces (Fig. 1c) [3].

Experiments in this work were done with a home-built [30] low temperature scanning tunneling microscope (STM), working at 7 K, in an ultrahigh vacuum chamber with a base pressure of 10^{-10} mbar. The molecules were deposited onto the clean Au(111) sample, kept at room temperature, from a Knudsen cell at around 400 K. Images were taken in constant-current mode, applying the bias voltage to the sample. In contrary to other methods that integrate over larger surface areas, the STM is a very suitable tool to investigate functional molecules [31] or formation of supramolecular structures [29] on a surface because it allows to study single molecules in real space, even when present in spatially confined or rare structures. Working with an STM at liquid helium temperatures holds the additional advantage of molecular manipulation, which can be used to probe molecular stability [1] as well as conformational flexibility [32].

After deposition on the clean Au(111) surface, the DBDCA molecules were found to be mobile as they adsorb at step edges and form different types of clusters on terraces (Fig. 2a). All molecules adsorb in the *trans* state, having a planar shape with characteristic dimensions, i.e., distances between the protrusions. This observation is in agreement with the TBA study [23] since heating in the Knudsen cell favors thermal *cis* → *trans* relaxation. One of the two characteristic molecular assemblies, at the bottom of Fig. 2a, is presented enlarged in Fig. 2b. It consists of bright rows that undulate parallel to each other, which points to densely packed molecules. The bright lobes, with an apparent height of about 2.6 ± 0.2 Å, can be assigned to the *tert*-butyl groups, due to the good agreement with TBA molecules (2.7 ± 0.1 Å height [23]). Thus, it is unlikely that the molecules overlap each other, which would probably increase the apparent height of the *tert*-butyl groups. By comparing the dimensions of this structure with the computed molecular size in the gas phase, we find that these islands most likely consist of rows of DBDCA molecules (as indicated by the superimposed chemical structures). The orientation and intermolecular distances clearly point to the formation of supramolecular chains that are stabilized by hydrogen bonds as shown in Fig. 2c. The distance between the oxygen atoms, connected through a hydrogen bond, is estimated to be around 3.5 Å, which is in agreement with other studies (see below). According to their spatial matching, different chains can indent each other and thus stabilize themselves, probably by van der Waals contacts. Consequently, undulating rows are observed in the STM images reflecting mainly the *tert*-butyl groups.

The most common type of molecular adsorption geometry is the rosette structure (upper half of Fig. 2a). Interestingly, the rosettes are much more often found than chains, i.e., the ratio of molecules in rosette or chain structures was determined to be around 85 : 15. These rosettes have a hexagonal shape with six bright lobes forming a ring (Fig. 3a). Such rosette shapes, where the 120° angle between the carboxylic acid groups associated with the *meta*-linkage in the building blocks is transferred to the supramolecular assembly, are well known for clusters of organic mole-

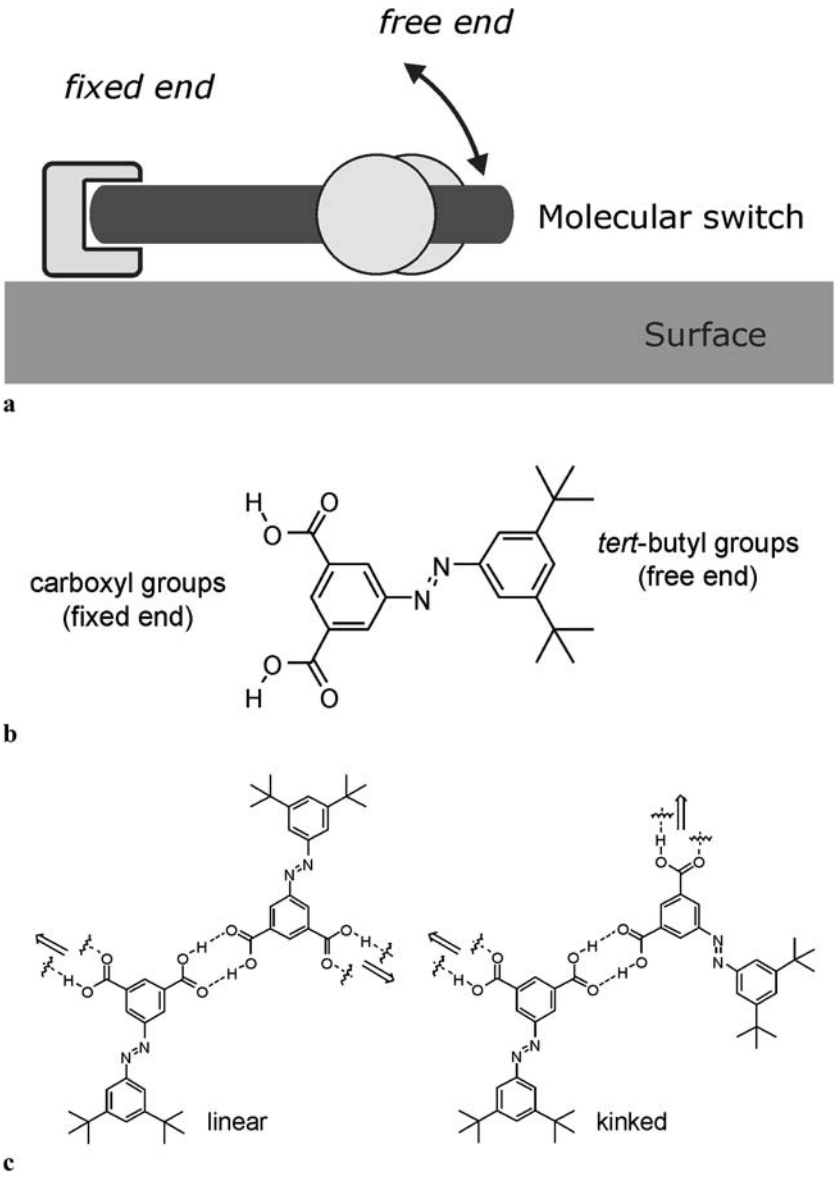

Fig. 1 (**a**) Scheme of the controlled stabilization of switching molecules on a surface. By fixing one end, the switching process is still feasible through the other (free) end of the molecule. (**b**) Chemical structure of the investigated 3,5-di-*tert*-butyl-3′,5′-dicarboxyl-azobenzene (DBDCA) molecules, consisting of an azobenzene core, equipped with carboxyl groups that should fix one end by intermolecular interaction and *tert*-butyl groups which do not hinder the isomerization process and serve as STM-label. (**c**) Two principle bridging modes by which two DBDCA molecules can be connected through hydrogen bonds in either linear or kinked structures

cules [33]. In analogy to the chains, the bright lobes, having the same apparent height, can be assigned to the *tert*-butyl groups. They can be resolved as two intensity maxima at a distance of 5.4 ± 0.3 Å (Fig. 3b), which is in good agreement with the 5.1 Å distance between the central carbon atoms of the *tert*-butyl groups in the gas phase. According to this assignment and the molecular dimensions, the inner (weaker) lobes reflect the carboxylic acid groups. The rosettes are therefore stabilized by hydrogen bonds between the carboxylic acid groups as shown schematically in Fig. 3c. In the circular array each molecule is connected to both of its neighbors, thus maximizing the resulting binding energy per molecule by forming the maximum number of non-distorted carboxylic acid dimer motifs.

The distance between the oxygen atoms (involved in one intermolecular hydrogen bond) can be estimated by measuring the distance between neighboring lobes in the STM images (as shown by an arrow in Fig. 3b), assigned to the dicarboxyl phenyl parts of the molecules. Calculating the interatomic distances in the molecules (in the gas phase) via geometry optimization, allows determining the O···O distance. We obtain a distance between the oxygen atoms in hydrogen bonds of 3.6 ± 0.7 Å, which is in agreement with previous studies of supramolecular networks on surfaces, stabilized via carboxylic acid groups, that reveal distances of, for instance, 3.4 ± 0.5 Å [34]. Note that this O···O distance cannot be determined in STM images of the DBDCA chains (Fig. 2b), due to the vicinity of the adjacent chain.

As apparent in Figs. 2a and 3a, rosettes are often found in clusters together with other rosettes, suggesting a certain mobility of entire clusters at room temperature. Figure 3d–e shows a series of lateral manipulations during which two

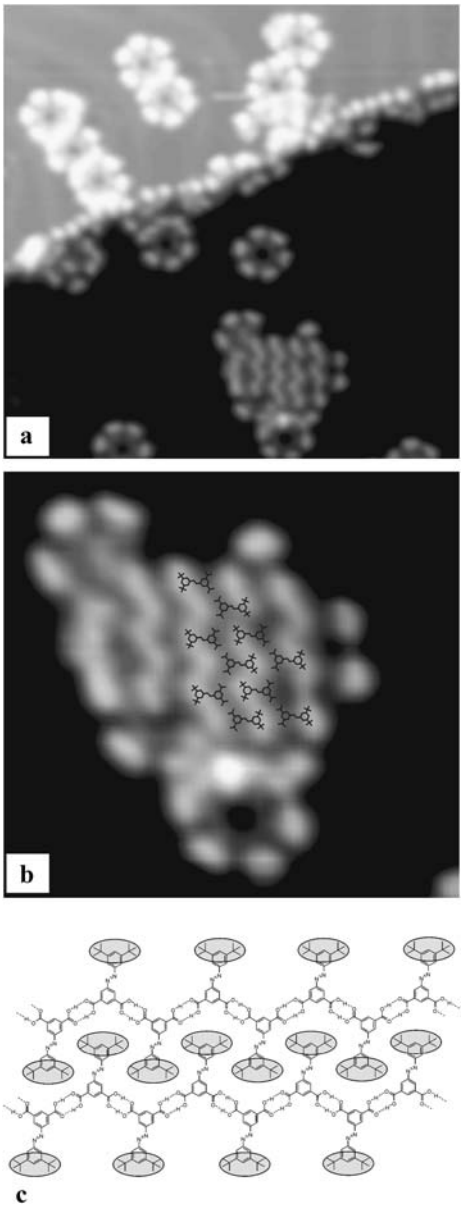

Fig. 2 (**a**) STM overview image (43×43 nm^2; $I = 0.11$ nA; $U = 1$ V) of DBDCA molecules adsorbed on a Au(111) surface. (**b**) STM image (15.5×14.6 nm^2; $I = 0.11$ nA; $U = 1$ V) of a densely packed island (see text). The chemical structure of the molecules is superimposed on the image (with the same length scaling). (**c**) Scheme of the molecular surface structure, where parallel chains, stabilized by hydrogen bonds, are indenting each other (double bonds are not drawn for the sake of clarity). The bulky *tert*-butyl groups, mainly contributing to the STM intensity due to their bulky structure, are indicated by *gray shades*

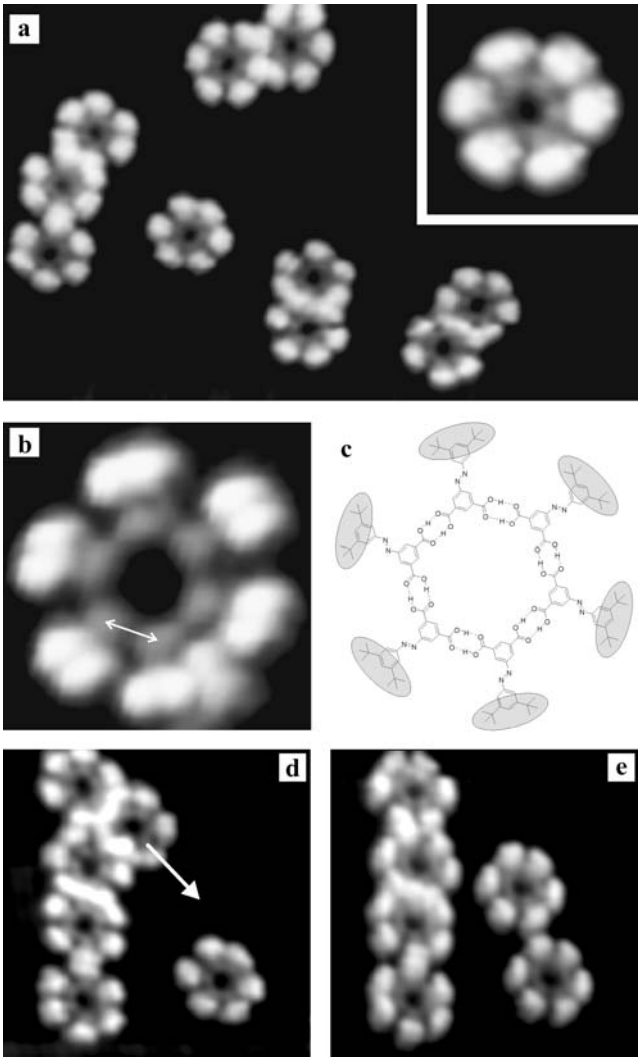

Fig. 3 (**a**) STM overview image (37×23.2 nm^2; $I = 0.11$ nA; $U = 1$ V) of DBDCA molecules arranged in a rosette structure. The *inset* shows an image (6.2×6.2 nm^2) of a single rosette with the characteristic hexagonal shape. (**b**) STM image (5.2×5.2 nm^2; $I = 0.11$ nA; $U = 1$ V) of a single rosette structure (a surface defect is visible in the lower right corner) with the corresponding scheme in (**c**). The *arrow* in (**b**) indicates the distance between two adjacent lobes, assigned to the dicarboxyl phenyl groups. Lateral manipulation with the STM tip can be used to separate rosettes from each other, as shown in (**d**–**e**) (each 17×17 nm^2; $I = 0.11$ nA; $U = 1$ V). The *arrow* indicates the pathway of the tip during manipulation

rosettes are separated by using the STM tip at a suitable tunneling resistance. It can be seen that both rosettes remain intact since their individual appearance cannot be distinguished from the initial image, where they are very close or even overlap. It turns out that indenting clusters, constituting a characteristic feature on the surface, mostly consist of intact rosette rings, each composed of six molecules.

This observation not only proves the structural integrity of the rosettes when clustering together, but also shows that entire rosettes can be displaced on the surface. After the successful manipulation of single atoms and molecules, it has been shown that it is possible to induce a concerted motion of small CO molecules due to the presence of a unidirectional repulsive neighboring interaction [35] or to displace covalently connected macromolecules by using the STM tip [1]. However, no lateral manipulation of supramolecular assemblies stabilized by weak non-covalent intermole-

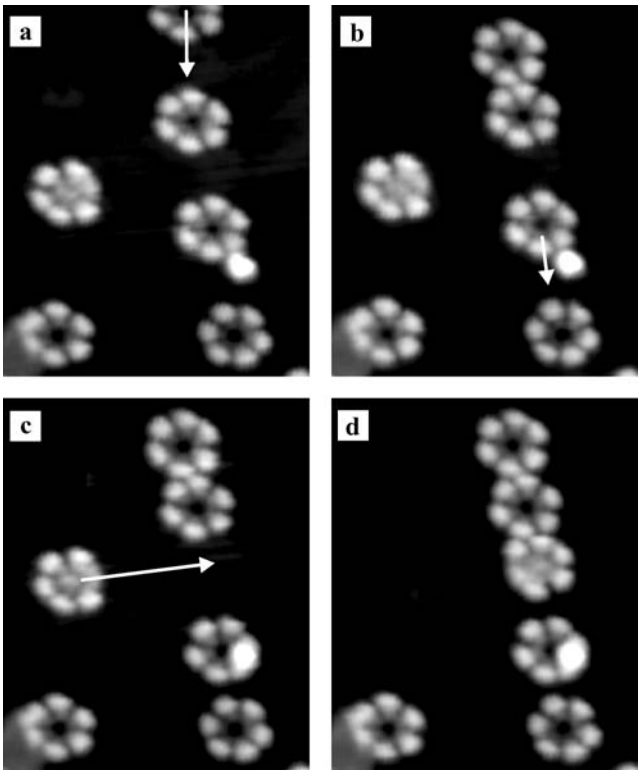

Fig. 4 Construction of a row of rosette clusters by lateral manipulation with the STM tip. (**a**–**d**) STM images (all 21.4 × 26 nm^2 in size; Imaging parameters: 0.11 nA and 1 V) during the manipulation series. The *arrows* mark the tip pathways during lateral manipulation. The defect in bottom right area remains at the same position after the manipulation, showing that it is not displaced by the rosette, which seems to be moved onto it

cular forces has been reported, to our knowledge, thus far. Here, a series of lateral manipulation experiments was used for the rational arrangement of several rosettes into a linear array (Fig. 4). It can be clearly seen that in each manipulation step the displaced rosette maintains its structure and precisely reaches the pre-defined position. Consequently, a row of rosettes is created in Fig. 4d. It is important to note that the starting points of the manipulation pathways (indicated by arrows in the images) are always located at the center or towards the end of the rosette (in the direction of manipulation). The STM tip is thus rather pulling and not pushing the entire rosettes, which could be the case if the pathway would start in front of the rosette.

As a result of the structural design, chains and rosettes usually do not mix and consist exclusively of one type of the two structural motifs (Fig. 1c). However, at the border of the island (Fig. 2b) other topologies are present, which are eventually connected through hydrogen bonds to the chain ends. This rather rare case possibly represents a mixing of the two basic motifs, probably caused by maximizing by intermolecular hydrogen bonding interactions.

Similarly to our previous study of TBA molecules [23] we then applied voltage pulses to the rosettes in order to induce *trans* → *cis* isomerization. However, although the relevant parameters have been varied over a wide range (voltages up to 2.7 V and pulse lengths from a few seconds to several minutes), no switching event could be observed. Instead, separation of single molecules, structural modifications and eventually dissociation of the molecules were induced at high voltages (above about 2 V). The absence of isomerization is surprising since irradiation of the molecules in solution induced the switching behavior typical for azobenzene derivatives [36]. The reason for the suppressed isomerization on the surface is not completely clear, but it is most likely associated with the lack of the *tert*-butyl groups on the inner hydrogen-bonding phenyl fragment leading to an increased coupling to surface, and therefore shut down the isomerization process. The necessity of introducing sufficient steric bulk, i.e., attaching a minimum number of two *tert*-butyl groups per phenyl fragment, to decouple the azobenzene core from the metallic substrate has been noted recently [25].

In conclusion, we could show that molecular clusters of discrete size and shape can be produced from functional molecules by the appropriate choice of molecular side groups. Two types of surface structures, i.e., chains and rosettes, are stabilized on the surface by hydrogen bonds via their carboxylic acid groups. The highly abundant rosettes are discrete supramolecular objects of uniform size and shape composed of six hexagonally arranged DBDCA molecules. Our results prove that the rosettes are sufficiently stable to be precisely manipulated to a pre-defined position on a metal surface without changing their structure or conformation. Current molecular design efforts aim at the structural integration of the molecular switch into similar discrete supramolecular assemblies, while maintaining the switching function.

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