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Two-dimensional self-assembly of magic supramolecular clusters

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Abstract. We report low-temperature scanning tunnelling microscope (STM) observations of magic two-dimensional supramolecular clusters formed after low-coverage deposition of 1-nitronaphthalene (NN) molecules on a reconstructed Au(111) substrate. The clusters that consist predominantly of ten NN molecules are chiral and form a racemic mixture on the surface. STM manipulation of the clusters shows that their internal structure does not depend on the atomistic details of the substrate. Manipulation of individual molecules within the clusters hints at utility for nanoscale devices. The enantiomers of these supramolecular clusters are discriminated and separated in a molecular-scale analogue to Pasteur's experiment.

1. Introduction

The current interest in nanostructures is motivated by their potential use in the mass fabrication of nanoscale devices. At present, modern integrated circuits contain structures with a lateral extension of $0.2\ \mu\text{m}$ that are only a few atoms thick. Building blocks as well as memory units for information get smaller and smaller. However, many of the nanoscale structures formed during nucleation and growth experiments are only metastable, and their stability is often a limiting factor on the scientists' ability to synthesize new structures. A promising way forward is to self-assemble thermodynamically stable nanostructures from appropriately functionalized molecules [1]. Molecules are particularly appealing because their interaction can be tailored and the additional degrees of freedom introduced by a non-spherical molecular shape result in rich ordering phenomena. Ideally, the size and the shape of molecular nanostructures are unequivocally determined by highly specific, directional intermolecular forces, while their lateral spacing is determined by the interaction with a suitable structured surface. We propose to utilize polar molecules for which electrostatic interactions are the dominant ones [2–4]. The thermodynamic stability of these nanostructures is only limited by entropic effects.

Submonolayer quantities of the aromatic molecule 1-nitronaphthalene (NN) adsorbed on the reconstructed Au(111) surface aggregate into pinwheel-shaped clusters of ten molecules on various inequivalent surface sites. These decamers exhibit two-dimensional chirality. While the interaction of the decamers with the substrate determines their nucleation sites, they are stabilized by intermolecular forces [3]. We demonstrate, using a digital switch built up of 11 NN molecules, that this system could also be used as building blocks for memory units [3].

Furthermore, the investigation of molecules with the STM opens up a wide area of nanochemistry for which we give an example. Separation of a racemic mixture of chiral molecules

into the enantiopure compounds is a fundamental and often challenging problem in chemistry which was first solved by Pasteur in 1848 [5]. In recent years, chiral aggregates [6] have been discriminated with molecular resolution and the manipulation capabilities of the STM have been demonstrated [7, 8]. We show how the decamer enantiomers can be discriminated and separated from a racemic mixture on the nanoscale [2].

2. Experimental procedure

The experiments were performed in an UHV system equipped with a home-built, low-temperature STM as well as standard facilities for sample preparation [9]. The Au(111) surface was cleaned by repeated cycles of Ar⁺ sputtering and annealing (≈ 700 K).

The Au(111) surface reconstructs (figure 1(a)) into a periodic sequence of uniaxial domains with alternating fcc and hcp stacking of the surface atoms with respect to the underlying bulk [10, 11]. Domain walls, where the surface atoms are displaced from the hcp or fcc sites, appear as bright stripes with a corrugation amplitude of 0.01–0.02 nm. The broad dark stripes correspond to domains with the energetically favourable fcc stacking of the surface atoms, and the narrow ones to hcp stacking. The periodicity in the $[\bar{1}10]$ direction is ≈ 6.3 nm, corresponding to a rectangular $\sqrt{3} \times 22$ surface unit cell. On a larger scale, two domain orientations rotated by 120° alternate and form a herringbone pattern. Two inequivalent types of turning point (elbows) of the herringbone pattern correspond to larger (y-elbows) or smaller (x-elbows) fcc domain widths [10]. The Au(111) surface thus offers inequivalent adsorption sites and the reconstruction is expected to influence the adsorption of atoms or molecules. Indeed, such effects have been reported in metal epitaxy [12–15]. Ni islands nucleate almost exclusively at the elbows of the Au(111) herringbone reconstruction [12]. It was proposed that dislocations at the elbows act as nucleation centres with an increased sticking probability for the

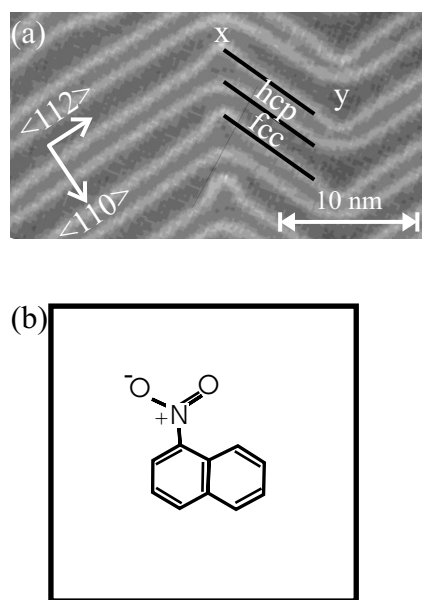


Figure 1. (a) An STM image of the reconstructed Au(111) surface; $U = -0.82$ V, $I = 10$ pA. (b) The structural formula of 1-nitronaphthalene (l enantiomer).

diffusing Ni adatoms. Similar phenomena were observed for Fe [13] and Co [14]. Recently, Ni nucleation on Au(111) was re-examined [15]. An alternative two-step scenario was proposed involving exchange of Ni atoms with substrate atoms at the elbows and subsequent nucleation at the substitutional Ni atoms.

NN (see figure 1(b)) is purified by vacuum sublimation prior to use and admitted to the preparation chamber via a leak valve from a gas-handling line kept at ~ 350 K; the sample is at room temperature. Attempts to image NN on Au(111) at room temperature failed even after saturation of the surface with molecules due to the high mobility of NN. Therefore, the sample is cooled to 50 K within 30 h. The fast molecular diffusion at ambient temperature and the low cooling rate ensures that all molecular arrangements observed at low temperature represent thermodynamically stable structures.

The NN coverage is estimated from STM images after cooling. We define one monolayer (ML) as the coverage corresponding to a close-packed molecular layer at saturation coverage [4], where 1 ML corresponds to one NN molecule per $\approx 62.2 \text{ \AA}^2$ surface area (nine surface atoms).

Due to the weak interaction between the molecule and substrate, the molecular structures are easily disturbed by the imaging process as observed previously for other organic molecules [16]. In order to minimize tip-induced motion of the molecules, imaging is performed at small tunnelling currents $I \sim 10$ pA.

3. Results

The interaction among the NN molecules is related to the asymmetry of the molecular charge distribution induced by the NO_2 group acting as a π -electron acceptor resulting in an approximately dipolar electrostatic charge distribution. Usually, dipole moments tend to arrange perpendicularly to a metal surface due to the image charge [17]. On the other hand, π -systems have the tendency to orient parallel to metal surfaces [18]. Near-edge x-ray absorption fine-structure (NEXAFS) measurements show that NN is weakly adsorbed with the naphthalene (π -) system oriented parallel to the Au(111) surface within $\pm 5^\circ$ [4], i.e., with its polar momentum arranging *parallel* to the surface. The confinement of the NN molecules to two dimensions in a planar adsorption geometry induces a chirality not present in the gas phase [3]. The molecule and its mirror image cannot be superimposed by translation and rotation within the surface plane. Equal amounts of enantiomeric monomers are expected to be present on the surface.

Upon deposition of NN in a coverage range between 0.05 and 0.20 ML, well separated self-assembled supramolecular clusters of distinct size and structure aggregate (figure 2). The planar adsorption geometry of the molecules manifests itself in their apparent height of ~ 0.15 nm in STM images, which is typical for planar molecules with a π -system parallel to the surface [18].

Depending on coverage and temperature, $\sim 85\%$ of these clusters are composed of ten molecules (decamers), 5% of four molecules (tetramers), and 4% of eleven molecules (undecamers) (figure 2(a)). The most common species, i.e., the decamers, form first at ~ 65 K within the wide fcc regions of the γ -type elbows of the herringbone reconstruction [3]. Upon further cooling and increase of the coverage, more decamers nucleate within the narrower regions of the fcc domains and within hcp domains, and on domain walls [3]. The Au(111) reconstruction therefore influences the lateral distribution of the decamers.

The existence of the decamers at different adsorption sites shows that, in contrast to the case for magic islands observed on semiconductor surfaces [20], their internal structure and their size are predominantly determined by intermolecular interactions. Manipulation experiments at decreased tunnelling resistance corroborate the dominance of intermolecular

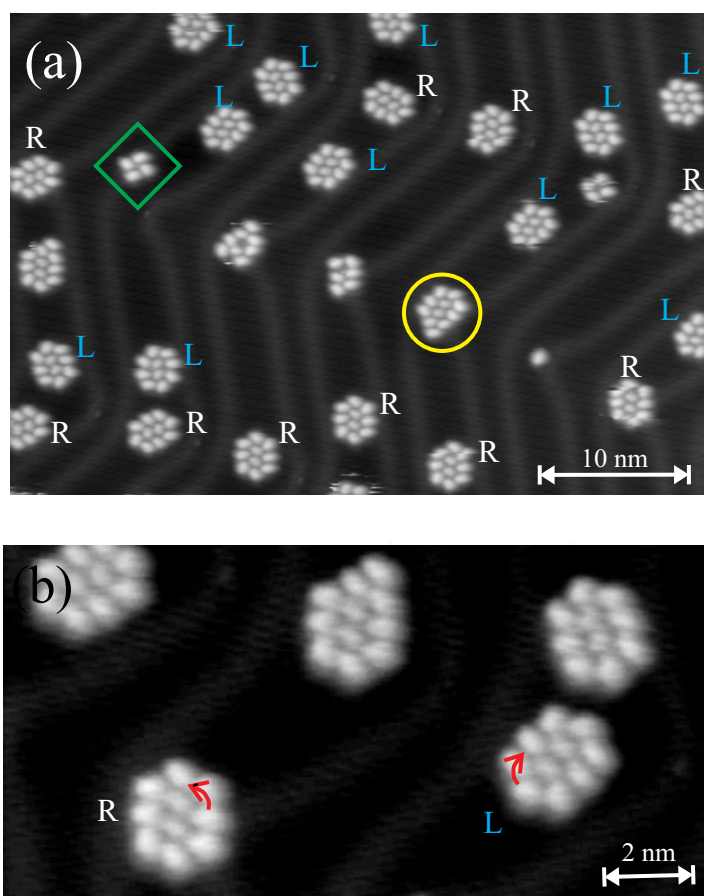


Figure 2. STM images of NN decamers on Au(111): (a) 0.10 ML; in addition to equal amounts of L and R decamers forming a racemic mixture, tetramers (grey diamond) and undecamers (white circle) were formed; $U = -0.33$ V, $I = 10$ pA. (b) The pinwheel-shaped decamer exists in two enantiomeric forms; $U = -0.2$ V, $I = 20$ pA.

(This figure can be viewed in colour in the electronic version of the article; see www.iop.org)

over substrate–molecule interactions. Decamers can be displaced laterally. Figure 3 shows an experiment where a decamer is shifted from a fcc to an adjacent hcp domain by decreasing the tunnelling resistance and changing the mode of operation from imaging to manipulation [7]. After figure 3(a) was recorded at high tunnelling resistance ($R = 6 \times 10^{10} \Omega$), the tip was positioned above the decamer and the tunnelling resistance decreased by more than three orders of magnitude ($2.5 \times 10^7 \Omega$) and the tip was moved slowly (within seconds) to the centre of the adjacent hcp domain. There, high-resistance imaging conditions were restored and the same area imaged again to inspect the result of the manipulation (figure 3(b)). We find the complete decamer moved to the hcp domain. This motion is reversible, i.e., the decamer can be pushed back into the fcc domain. With appropriate tunnelling parameters these manipulations can be performed without changes in the internal structure of the decamers.

All decamers show a modified pinwheel structure with an eight-molecule ring surrounding a two-molecule core (figure 2(b)) [3]. This is reminiscent of pinwheel structures deduced

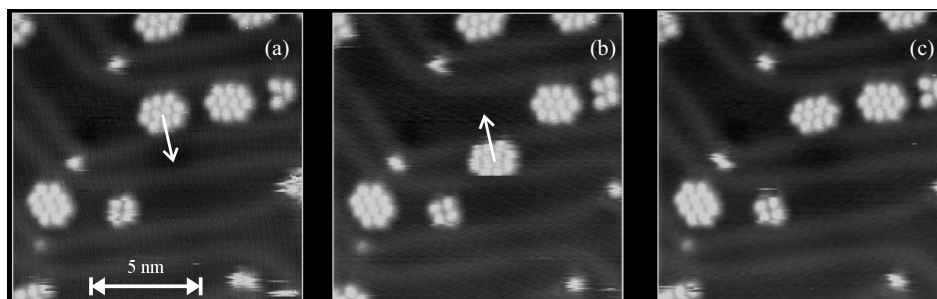


Figure 3. STM manipulation with $U = -0.005$ V, $I = 0.2$ nA: the decamer is moved with the STM tip along the arrow from a fcc domain (a) to the adjacent hcp domain. (b), (c) During imaging, the weakly adsorbed decamer moves back to the fcc domain (imaging at $U = -0.6$ V, $I = 0.01$ nA).

for densely packed monolayers of diatomic molecules where a central upright molecule is surrounded by six flat-lying molecules; see, e.g., [19]. Two related kinds of decamer (L, R) exist, corresponding to a right-turning and a left-turning pinwheel (figure 2(b)), which behave like an object and its mirror image and cannot be transformed into one another by rotation and translation within the surface plane. From a chemical point of view, these two types may be considered as two-dimensional enantiomers. Equal amounts of the two enantiomers exist on the surface (figure 2(a)).

Therefore, the decamers can be viewed as supermolecules, whose stability, structure, and chirality are determined by strong intermolecular interactions and which attach to the most favourable adsorption sites as stable entities [3].

3.1. The molecular switch

About 4% of the clusters observed are undecamers (figure 2(a)) which can be imaged repeatedly at low tunnelling currents (typically 10 pA) without structural changes (figure 4(a)). These stable undecamers consist of a ten-molecule core with an extra molecule attached to its periphery near the molecule marked with the ellipse. This core molecule is rotated within the surface plane by $\sim 50^\circ$ anticlockwise with respect to the same molecule in decamers (figure 2(b)). By increasing the tunnelling current from 10 pA to 42 pA, the additional

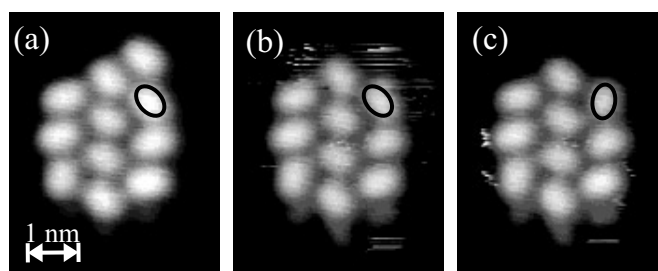


Figure 4. STM images with the fast-scanning direction horizontal and scanning from bottom to top: (a) a stable undecamer; $U = 79$ mV, $I = 10$ pA; (b) removal of the eleventh molecule by scanning at $I = 42$ pA; (c) the resulting decamer.

molecule can be selectively removed with the STM tip (figure 4(b)). This manipulation leads to a switching of the marked core molecule clockwise (figure 4(c)). The molecule is not yet rotated in figure 4(b) owing to sequential data acquisition from bottom to top.

Molecular switches could be utilized in read-only memory devices with the advantage of a thermodynamical stability of both entities, the decamer (0) and the undecamer (1).

3.2. Pasteur's experiment on the nanoscale

An instrument to distinguish chirality (a light microscope) and one to manipulate the chiral entities (a pair of tweezers) were the prerequisites for Pasteur in 1848 to discriminate and to separate small enantiomorphous crystals obtained from a solution of racemic sodium ammonium tartrate into enantiomerically pure components. With the STM we possess both of these instruments, operable at the nanometre scale, in one tool, and we therefore have the capability to repeat Pasteur's experiment on the nanoscale [2].

In analogy to chemical reactions, the formation of stable molecular NN decamers on the Au(111) surface may be viewed as the synthesis of two-dimensional chiral supermolecules from an achiral precursor, namely the gas-phase NN. The inversion symmetry of the decamers implies that they are comprised of even numbers of *l* and *r* molecules. Molecular dynamic simulations predict a 8:2 ratio (or 2:8 ratio for the opposite chirality) [3]. The equal numbers of enantiomorphous decamers on the surface (figure 2(a)) can be explained by the equal numbers of *r* and *l* adsorbed molecules.

Figure 5 displays an experiment where the imaging and manipulation capabilities of the STM are used to line up decamers within one fcc domain, so that right-handed supermolecules are found in the upper part and left-handed ones in the lower part of the domain. First, figure 5(a) is recorded at imaging conditions. Then the chosen decamers are moved via an increased interaction with the tip along the paths indicated by the arrows. The result of the

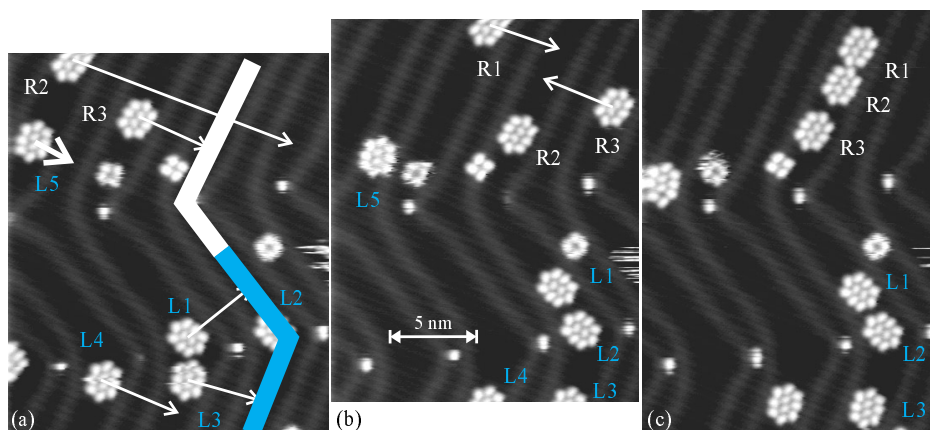


Figure 5. Pasteur's experiment in two dimensions on the nanoscale: decamers are moved by the STM tip along the paths indicated by the arrows at manipulation conditions ($U = -5$ mV, $I = 200$ pA). (a) The image of decamers prior to manipulation (imaging at $U = -0.6$ V, $I = 10$ pA). (b) The intermediate result of the manipulations: decamer L5 has been moved into the neighbouring hcp domain; being disturbed there by the imaging process, it is disregarded for the rest of the manipulation experiment. (c) The final arrangement: L decamers are located in the lower part and R decamers in the upper part of a fcc domain.

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manipulation is inspected at imaging conditions as shown in figure 5(c). The decamers were lined up along one fcc domain, thereby separating the racemic mixture into the pure compounds. L clusters are assembled in the lower part of the domain while R decamers are located above. The decamers have been moved without changing their internal structure. In particular, the chirality of the decamers remains unaltered. We note that an enantiomerization of an L to an R decamer requires a change from an 8:2 to a 2:8 ratio of l and r NN molecules.

The two fractions of chiral supermolecules are enantiomerically pure. In terms of the two-dimensional chiral NN molecules, this is equivalent to an enantiomer excess of 20%.

4. Conclusions

In conclusion, we have shown the self-assembly of thermodynamically stable decamers from the polar molecule 1-nitronaphthalene on Au(111) due to electrostatic interaction. We propose to make use of even more strongly interacting molecules to produce structures that are also stable at higher temperatures. Furthermore, we have shown that appropriately chosen molecules can be arranged to act as a molecular switch. Finally, the molecular-scale analogue to Pasteur's experiment adds the important capability of enantiomer separation to the emerging arsenal of scanning-probe-based techniques for nanochemistry.

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