

Two-Dimensional Self-Assembly of Supramolecular Clusters and Chains

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Two-dimensional supramolecular clusters and chains are observed upon submonolayer deposition of 1-nitronaphthalene (NN) onto reconstructed Au(111). The molecules become pseudo-chiral upon adsorption. Their handedness is determined from high-resolution scanning tunneling microscope images and local-density calculations. Modeling shows that hydrogen bonds cause the observed self-assembly. Clusters and chains mutually interact via electrostatic repulsion.

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In molecular beams, atoms often aggregate into clusters with magic sizes due to electronic or geometric shell closing [1]. For organic molecules, due to their complex shapes and specific interactions [2], even richer ordering phenomena are expected. Molecules adsorbed on surfaces are particularly appealing because their arrangement is directly observable with the scanning tunneling microscope (STM), whereas, in most cases, the direct experimental determination of the structure of free clusters remains elusive [3]. The current interest in self-assembly is also motivated by its potential for future use in the mass fabrication of nanoscale devices [4]. Understanding supramolecular aggregation starting from the basic interactions of the constituent molecules is a prerequisite to eventually control the self-assembly process. The present work is a step in this direction which is achieved by combining STM observations and manipulations

with first-principles electronic structure calculations and molecular dynamics modeling.

The building block of our self-assembly system is the aromatic molecule 1-nitronaphthalene (NN) (Fig. 1a, inset), which we observe by STM after deposition onto a reconstructed Au(111) surface (Fig. 1) [5]. The molecules adsorb planar to Au(111) as indicated by their apparent height of ~ 0.15 nm in STM images, which is typical for planar molecules with a π system parallel to the surface [6,7]. We note that confinement of NN to two dimensions introduces a chirality not present in the gas phase. The molecule and its mirror image cannot be superimposed by translation and rotation within the surface plane.

Deposition of NN in the range of 0.3–0.75 monolayers (ML, 1 ML corresponds to a close packed molecular layer) at room temperature and slow cooling (>24 h) leads to the aggregation of well separated molecular

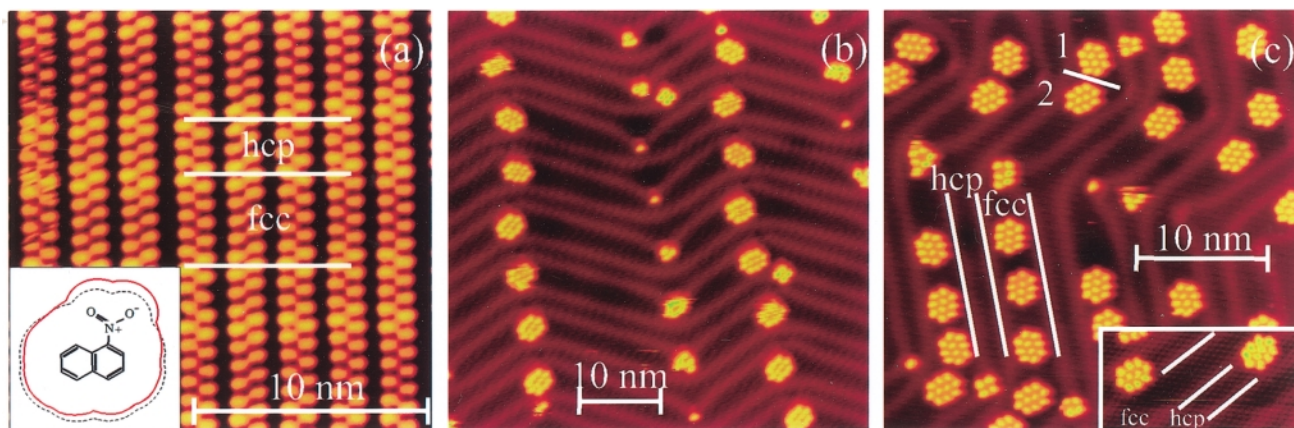


FIG. 1 (color). STM images at 50 K of a reconstructed Au(111) surface with adsorbed NN; (a) 0.7 ML NN. Inset: Structural formula of NN. The dashed line encloses the “exclusion” area resulting from steric repulsion. The distance of the red line from the dashed line indicates the strength of a negative electrostatic potential computed on the dashed line. (b) 0.1 ML NN at 65 K. (c) 0.2 ML NN at 50 K. Inset: 0.2 ML NN at 10 K.

double chains in two orientations: either perpendicular (Fig. 1a) or parallel to the reconstruction domains. A striking observation is made in a wide range of low coverages (0.05–0.2 ML). We find that self-assembled supramolecular clusters of distinct size and structure first appear at ~ 65 K at the fcc elbows of the reconstruction, thus, building regular arrays (Fig. 1b) [8]. Upon further cooling these clusters do not grow in size. Rather, identical clusters are observed within fcc domains at 50 K (Fig. 1c) and, sporadically, within hcp domains and on domain walls at 10 K (Fig. 1c, inset). We find $\sim 85\%$ decamers, $\sim 5\%$ tetramers, and $\sim 5\%$ undecamers. Owing to the fast molecular diffusion observed at room temperature and the low cooling rate, these clusters represent equilibrium structures. In analogy to gas phase clusters [1], they may be referred to as magic clusters.

All decamers appear identical in STM images, except for a mirror symmetry (clusters 1 and 2 in Fig. 1c). They consist of a eight-molecule ring surrounding a two-molecule core [9]. Manipulation experiments at decreased tunneling resistances show that the decamers are robust supermolecules: they can be rotated around the surface normal or displaced laterally, e.g., from a fcc to an adjacent hcp domain, without structural changes [10]. When two decamers are pushed towards each other they separate spontaneously to a distance of 0.9 nm. We conclude that the

internal structure, the size, and the mutual repulsion of the decamers are predominantly determined by intermolecular interactions [11].

The interaction among NN molecules on Au(111) is related to the asymmetry of the molecular charge distribution induced by the NO_2 group. STM images with submolecular resolution observed at increased negative tunneling voltages closely reflect this asymmetry. The NN molecules appear as four lobes of different intensity, both in the double chain (Fig. 2b) and in the decamer (Fig. 2g). In the double chain (Fig. 2b), two lobes of equal intensity are located at the outside of a chain; a third weaker lobe points inwards. The fourth, very weak lobe also points inwards and is visible in most molecules as a lateral protrusion of the third lobe (Fig. 2b). By comparing these images with density functional theory (DFT) calculations [12] we determine the position of the NO_2 group and distinguish the two enantiomeric NN species. Figure 2c (upper) displays the calculated charge density of the highest occupied molecular orbital (HOMO) of an isolated NN molecule in a plane 0.5 nm above a molecule with the nitro group attached to the right (“R”) ring of the naphthalene system [Fig. 1, inset, and Fig. 2c (lower)]. The opposite chirality is denoted by “L” (left ring). For the weakly adsorbed NN, the molecular states are expected to be only slightly disturbed

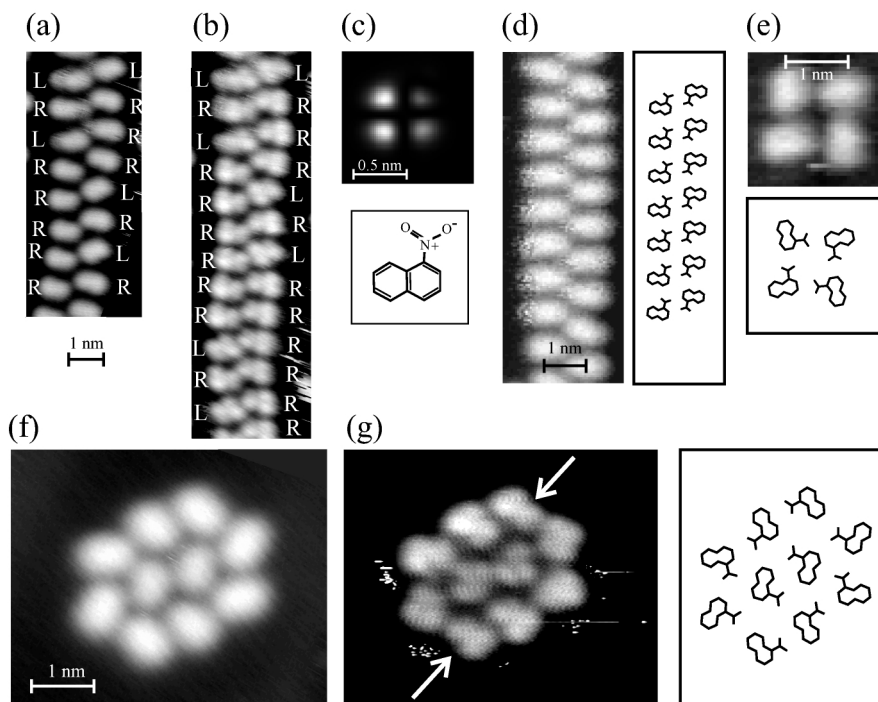


FIG. 2. STM images and theoretical structures: (a) STM image of a double chain. (b) Same at high resolution. *L*, *R*, denote the chirality of individual NN molecules. (c) Theoretical local density of the HOMO level of NN. The NO_2 group is top right (*R*-enantiomer) as indicated (lower). (d) STM image of a double chain structure and (right) structure of the double chain obtained by theoretical modeling. The calculated cohesive energy in the infinite double chain is (E_c) = 0.1394 eV/molecule. (e) STM image and (lower) theoretically predicted structures for the tetramer; $E_c = 0.0969$ eV/molecule. (f) STM image of a decamer and (g) at high resolution ($I = 100$ pA, $V = -2.3$ V). Arrows: see Ref. [17]. (g, right) Theoretical local minimum structure for the observed decamer obtained from the force model. $E_c = 0.1277$ eV/molecule.

by the interaction with the Au substrate [13]. From the agreement between Figs. 2b and 2c, we conclude that, for tunneling voltages near -2.3 V, the submolecular contrast is determined by the NN HOMO. Comparing to the HOMO of naphthalene [14], we find a decreased charge density at the carbon ring carrying the NO_2 group, in particular at the carbon atom to which the substituent is attached, as expected from the charge pulling effect of the nitro group. These observations enable an assignment of the chiral monomers R and L to the molecules resolved in STM (Figs. 2a and 2b). Moreover, by comparing the low-resolution images with the corresponding images showing submolecular structure (Figs. 2a and 2b and Figs. 2f and 2g), we identify the long axis of the STM ellipsoidal spots with the long axis of the naphthalene core.

To interpret the striking stability of double chains and decamers we model the intermolecular interaction with a classical force field and use molecular dynamics to find the stable structures. From the electrostatic potential of an isolated NN molecule in vacuum as calculated by DFT, we determine point charges located on the C, N, O, and H atoms which best fit this potential outside the van der Waals exclusion area [15]. The resulting intermolecular force field includes the electrostatic interaction and a repulsive short range potential as given by hard spheres centered on the C, N, and O atoms with van der Waals radii of 0.20, 0.14, and 0.13 nm, respectively. Similar force fields have been successfully applied to a variety of hydrogen bonded systems [16]. The NN molecules are free to move parallel to the Au(111) surface at a typical physisorption distance of 0.35 nm. Electrostatic screening of the metallic substrate is accounted for via image charges. We find that the electric charge distribution along the perimeter of the molecule changes polarity (Fig. 1a, inset). Therefore, the formation of elongated chainlike structures is favored in which O atoms of one molecule link to CH groups of a neighboring molecule. On the basis of their directional character and typical lengths, these bonds can be referred to as hydrogen bonds.

The lowest energy chain structure found [Fig. 2d (right)] compares well with the STM images at high coverage (Figs. 2a and 2d). The double chain consists of two antiparallel chains composed of molecules with equal chirality. Single chains aggregate into double chains, because of the alternating positive-negative polarity of their sides including the NO_2 groups. The double chains are positively charged outside and therefore mutually repel as observed experimentally. When molecules of opposite chirality are introduced into these chains, the force-field model predicts stable structures, which compare well with the observed, slightly disordered patterns. The oxygen atoms continue to take part in hydrogen bonding (Figs. 2a and 2b).

Below a critical number of molecules, open linear chains with unsaturated bonds at their ends energetically prefer to close into rings as observed for the decamers. The C_2 symmetry of the decamers in the experimental images requires the number of molecules of each type of chirality, n_1 and n_2 , in the cluster to be even. Thus, the decamers have a well defined *overall* chirality and each cluster has a mirror-symmetric isomer with the same energy in which n_1 and n_2 are interchanged (clusters 1 and 2 in Fig. 1c). The lowest energy structure has n_1 equal to 6 and is stabler than the corresponding linear double chain fragment by 3 meV/molecule. Its structure allows the H bonding of all O atoms in the cluster [Figs. 2f and 2g (right)] [17]. The perimeter of the decamer is positively charged giving rise to repulsion between clusters. The stable ring structure for the tetramer is also in good agreement with experiment (Fig. 2e).

Finally, we report on single molecular switching at specific aggregates. About 5% of the clusters observed at 50 K are undecamers (Fig. 3a) which can be imaged repeatedly at low tunneling currents (typically 10 pA) without structural changes. These stable undecamers consist of a 10 molecule core with an extra molecule 1 attached exclusively to its periphery near molecule 2. Interestingly, molecule 2 of the core is rotated $\sim 50^\circ$ anticlockwise with respect to molecule 2 in the decamers (Fig. 2f). By

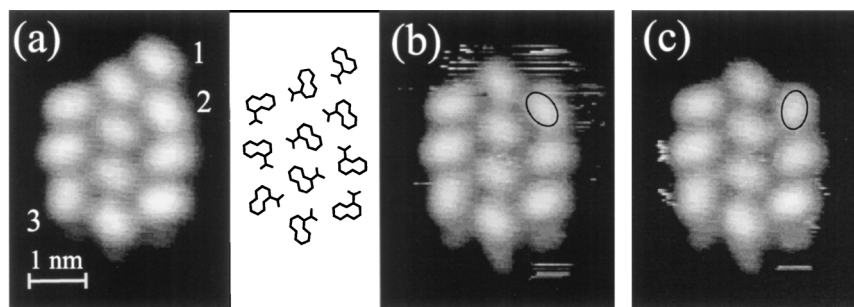


FIG. 3. (a) Undecamer stable at 50 K and theoretical structure; 50 K, $I = 10$ pA, $V = 79$ mV. (b) Removal of molecule 1 in (a) by scanning at $I = 42$ pA. The images are displayed such that the fast scan direction is horizontal and scanning proceeds from the bottom to the top. (c) Resulting decamer with molecule 2 rotated by $\sim 50^\circ$ clockwise. Molecule 2 is not rotated in Fig. 2b owing to sequential data acquisition from bottom to top.

increasing the tunneling current, the additional molecule 1 can be selectively removed with the STM tip (Fig. 3b). This manipulation leads to an intriguing switching behavior; molecule 2 turns clockwise (Fig. 3c). We also observe unstable and short lived undecamers in which, at 50 K for less than a second or at 10 K for up to some minutes, individual molecules bind transiently to decamers without any site specificity. No reorientation of core molecules upon attachment/detachment of an 11th molecule is observed in these cases. We conclude that the cores of the stable undecamers (Fig. 3c) are different from those of the stable decamers (Fig. 2).

Within our force-field model, switching occurs only if we assume that the decamer core of the undecamer contains a molecule of opposite chirality at position 2. Such a molecule has a bistable potential energy surface with two local minima of very similar energy. The two corresponding molecular orientations agree well with those observed experimentally (Figs. 3a–3c).

In conclusion, we have combined STM observations and manipulations with theoretical modeling based on first-principles calculations and an intermolecular force field to achieve a detailed understanding of the stability and the internal arrangement of self-assembled supramolecular clusters of NN. Many other self-assembling supramolecular structures are stabilized by hydrogen bonding as seen for the system studied here. These include synthetic systems [18], as well as the tertiary structures of proteins and DNA.

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