Scanning Tunneling Spectroscopy

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Broken Symmetry of an Adsorbed Molecular Switch Determined by Scanning Tunneling Spectroscopy**

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When functional molecules adsorb onto surfaces, their structure may be modified, and their properties can be affected. Scanning tunneling microscopy (STM) is often used to image such molecules, which tend to adsorb in complex patterns. Despite the exquisite resolution that STM can achieve, a quantitative interpretation of the images in terms of structural parameters is difficult. Although STM images may be predicted by the Tersoff–Hamann approach,[1] difficulties in precisely describing wavefunctions that are several Angstroms away from the surface, where STM tips are typically located, usually prevent quantitative image analyses.[2–4] Herein, we show that scanning tunneling spectroscopy (STS) can be particularly useful in determining molecular structure. The STM and STS data of tris[4-(phenylazo)phenyl)]amine (TPAPA) on a Au(111) surface are presented. Sharp spectral features in STS along with dispersion-corrected Density-Functional Theory (DFT) calculations, are used for the analysis. Although inelastic tunneling spectroscopy has been employed to discriminate between horizontal and vertical adsorption geometries of small molecules,[5,6] STS of complex molecules, which usually includes information about the substrate and the adsorbate,[7–14] has not been used to elucidate molecular structure thus far.

TPAPA is a three-fold symmetric molecule with three azobenzene (AB) units connected by an amino linker (Figure 1 a).[15,16] As far as its structure is concerned, steric repulsion between the hydrogen atoms of the inner phenyl rings (yellow in Figure 1 a) induces a propeller-like twist of the AB ligands by as much as ca. 40° out of the molecular plane.[16] On a surface, this three-dimensional shape of the molecule reduces the interaction of the AB units with the substrate.

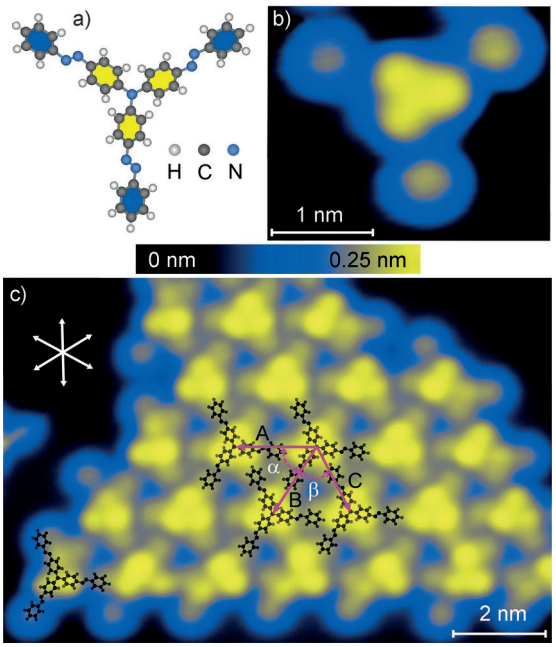

Figure 1. a) Optimized structure of (*EEE*)-TPAPA, as determined by DFT calculations. Yellow and blue highlight the inner and outer phenyl rings, respectively. b) STM topograph (1.7 V, 100 pA) of a single molecule next to the edge of an island. c) A densely packed island of TPAPA molecules on Au(111). Drawings of (*EEE*)-TPAPA are overlaid to indicate the positions and orientations of the molecules within the island. An improved model of the molecular structure and arrangement is shown in Section S4 of the Supporting Information. Double-headed arrows indicate the compact direction of Au(111). A, B, C are unit vectors of the overlayer, and the angles embedded between them are labeled α and β.

Previously, the *cis*/*trans* isomerism of AB and its derivatives has been shown to modify the electronic structure of the molecule in Langmuir–Blodgett films,[17] in solution,[18] in polymers,[19] and in adlayers on surfaces.[20–22]

Figure 1 a shows the optimized gas-phase structure of (*EEE*)-TPAPA. Below, we will address the phenyl groups connected to the amino nitrogen of TPAPA as inner phenyl groups (yellow in Figure 1 a), and the other ones as outer phenyl groups (blue in Figure 1 a). STM topographs of TPAPA on Au(111) prepared by molecular-beam epitaxy (from the previously degassed compound) in ultra-high vacuum are shown in Figure 1 b and c (for experimental details, see the Supporting Information, Section S1). The molecule in Figure 1 b shows a triangular maximum at the center, which consists of three protrusions of an apparent height of 0.25 nm. We attribute these features to the inner

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phenyl rings of the *EEE* isomer of TPAPA. The three lower protrusions (apparent height, 0.14 nm) next to the central part are attributed to the outer phenyl rings. The azo group (between the inner and outer phenyl groups) appears low, which is in agreement with previous STM reports of ABs.[20,21]

At an average coverage of ca. 0.3 monolayers[23] TPAPA arranges into a honeycomb pattern (Section S2) and hexagonal compact islands (Figure 1c). Below, we focus on the dense hexagonal structure. The orientation of single molecules within islands may be understood using the *EEE* isomer, which is the ground-state structure of free TPAPA. Models of this isomer are superimposed on the STM image. By observing many islands we found that the STM images of a vast majority of molecules are consistent with this structure. The center-to-center distances between the molecules in the densely packed hexagonal overlayer are not equal along the compact directions ($A = 1.76 \pm 0.05$ nm, $B = 1.67 \pm 0.05$ nm, $C = 1.58 \pm 0.05$ nm). Second, the angles α and β are slightly different ($\alpha = 66 \pm 1°$ and $\beta = 60 \pm 1°$) (Figure 1c). These distances do not correspond to any overlayer that would be commensurate to the substrate distances in the hcp or fcc domains of the herringbone-reconstructed Au(111) surface.

Figure 2b displays a dI/dV spectrum of the frontier orbitals measured at the center of a molecule (above the magenta dot in Figure 2a) in a closely packed arrangement. A positive ($V \approx -1.2$ V), and a negative ($V \approx 1.85$ V) ion resonance, along with additional smaller features ($V \approx -1.35$, -1.60, -1.78 V), are resolved. More detailed spectra at negative sample bias are shown in Figure 2c. The data were recorded at the center of the molecule (magenta) and at each of the three inner phenyl rings (gray). Although these data display some variations in peak energies and intensities, they are generally comparable.

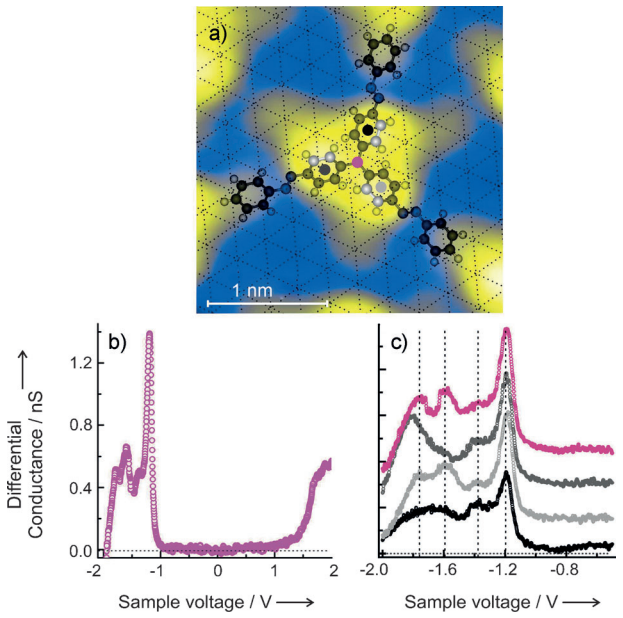

Figure 2. a) STM topograph and the structure of a single (*EEE*)-TPAPA molecule within a compact island. The dashed grid indicates the Au(111) lattice. The inner phenyl rings are fitted to the STM image in such a way that the higher carbon atoms (highlighted with light gray dots) match the maxima. b) Differential conductance (d*I*/d*V*) spectrum acquired above the center of the TPAPA molecule. c) d*I*/d*V* spectrum acquired at the positions indicated by the colored dots in (a). Vertical lines indicate peak positions extracted by fitting four Gaussians to the spectrum from the center (magenta).

To analyze the dI/dV spectra, we performed dispersion-corrected DFT calculations of a TPAPA molecule in a densely packed surface unit cell on an unreconstructed Au(111) surface (for details, see Section S3). In short, employing the pseudopotential plane-wave code CASTEP[24] we have optimized molecular overlayers in different coverages on four-layer frozen Au(111) slabs. Although exchange and correlation have been treated on a semi-local GGA-PBE level,[25] the dispersion interaction thereby neglected was modeled using a very recent correction scheme that also accounts for the many-body screening of dispersive forces within the substrate.[26,27] The calculations closely follow the approaches used in recent studies.[26,28]

The best agreement with the experimentally found incommensurate unit-cell parameters (Figure 1c) was achieved with commensurate symmetric (6×6) ($A = B = C = 1.78$ nm) and commensurate asymmetric (6×5) unit cells ($A = 1.78$ nm, $B = 1.65$ nm, $C = 1.48$ nm) of TPAPA on Au (111). The simulated commensurate asymmetric (6×5) structure of TPAPA is shown in Figure S4a. In both cases, the adsorbed molecular geometry shows subtle differences compared to the free TPAPA molecule. The outer phenyl rings maximize dispersion interactions by adsorbing onto the substrate in a flat manner, whereas the inner phenyl rings are tilted because of steric hindrance. These findings nicely agree with the experimentally observed apparent height difference of the inner and outer protrusions in the STM. Whereas, in the symmetric (6×6) unit cell, all geometric parameters still show the three-fold symmetry of the gas-phase TPAPA molecule, the TPAPA molecule is distorted in the asymmetric (6×5) overlayer owing to different intermolecular distances in the three compact directions (Table SII). The adsorption is almost isoenergetic at different adsorption sites within the unit cell (Table SI), which rationalizes the incommensurability of the TPAPA overlayer.

Figure 3 shows the frontier molecular orbitals projected from the Density-of-State (MO pDOS) for the two calculated overlayer structures. We found that the broken symmetry of the molecular geometry in the (6×5) cell induces a splitting of the previously three-fold degenerate HOMO-1 orbitals, which are non-bonding in nature. The corresponding calculated splitting is smaller (0.05 eV) than experimentally observed (0.20 eV). Considering the energetic difference between the HOMO (π), the previously degenerate HOMO-1, and HOMO-2 (see Table SIII), we can nevertheless clearly identify the experimentally observed resonances as the HOMO and three inequivalent HOMO-1 orbitals. Whereas the HOMO (π) is centrally localized at the amine center, the three non-bonding orbitals are centered at the three azo-bridges of the azobenzene groups. In an asymmetric overlayer these orbitals are no longer equivalent, owing to the collective change of dihedral angles around the three azo-bridges (Table SII).

This qualitative agreement directly shows how the use of STS in conjunction with DFT allows intramolecular degrees

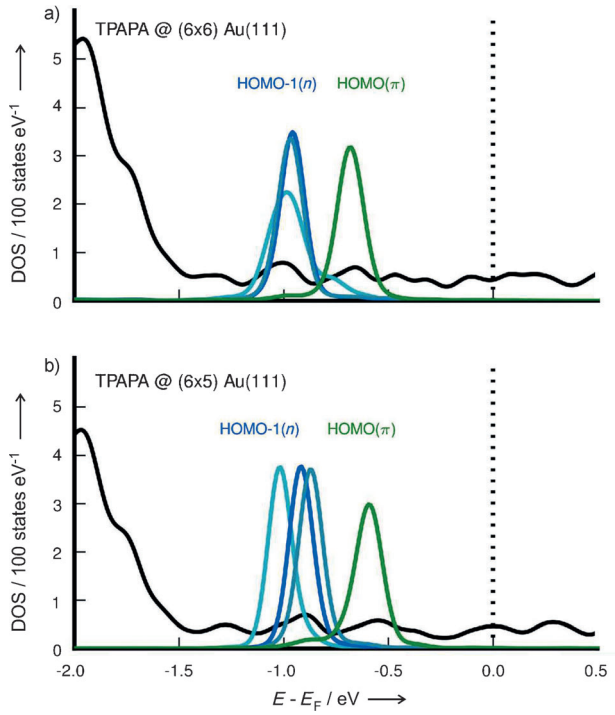

Figure 3. Density-of-State (DOS) and molecular-orbital-projected DOS plots for the frontier orbitals of the TPAPA molecule in a symmetric (a) and an asymmetric (b) overlayer structure on Au(111). The HOMO and the HOMO-1 orbitals are shown in green and in different shades of blue, respectively. The MO pDOS peaks are scaled up by a factor of 30 to make them visible.

of freedom to be related to directly observable features in tunneling experiments. The incommensurability of the molecular dimension with the underlying metal substrate, together with the preference for dense and interlaced packing, and the small site preference of the extended molecule creates a complex overlayer network, in which the threefold symmetry of both molecule and surface is broken. This asymmetry in the overlayer induces an asymmetric molecular adsorption geometry, which breaks the degeneracy of the electronic states, as clearly seen in the tunneling spectra. Thus, the quantitative difference in calculated and measured splittings can primarily be attributed to the impossibility of modeling the incommensurate overlayer in feasible periodic-boundary-condition supercells, as well as to shortcomings in representing the molecular resonances by ground-state Kohn–Sham orbitals, which result from approximate semi-local DFT functionals. This does not affect the identified relation between the state degeneracy and the overlayer symmetry as validated by detailed higher-level calculations for isolated molecules (Section S5).

As a final test of the proposed model, we analyzed the spectra of molecules from patterns other than densely packed islands (Section S6). In particular, we recorded data from isolated molecules without any neighbors. Their HOMO-1 does not exhibit any clear splitting. Moreover, spectra of linear chains, where each molecule has two neighbors, exhibit splitting of the HOMO-1 into two levels. Although the number of nearest neighbors has a strong influence on the splitting, it is not the only relevant factor. As shown in Section S7 of the Supporting Information, the molecules in large dense islands are not perfectly identical. Most likely this is due to small variations in the positions of the azobenzene units with respect to the atoms of the reconstructed Au(111) substrate. A detailed analysis and modeling of such effects would require the inclusion of the reconstruction of Au(111), which is unfeasible with current computational resources.

In summary, the multifunctional molecule TPAPA on Au(111) was studied using low-temperature STM and dispersion-corrected DFT calculations. It has been demonstrated that scanning tunneling spectroscopy data may be used to obtain details of the molecular structure that are difficult to address by STM imaging alone. The analysis relies on the presence of fairly sharp spectral features originating from a degenerate marker state, and may therefore be particularly suitable for molecules that are partially decoupled from the substrate, for example by their three-dimensional shape or by spacers.

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