Spectroscopic Scanning Tunneling Microscopy Studies of Single Surface-Supported Free-Base Corroles

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ABSTRACT: Corroles are versatile chemically active agents in solution. Expanding their applications toward surface-supported systems requires a fundamental knowledge of corrole−surface interactions. We employed the tip of a low-temperature scanning tunneling microscope as local probe to investigate at the single-molecule level the electronic and geometric properties of surface-supported free-base corrole molecules. To provide a suitable reference for other corrole-based systems on surfaces, we chose the archetypal 5,10,15-tris(pentafluorophenyl)-corrole [H3(TpFPC)] as model system, weakly adsorbed on two surfaces with different interaction strengths. We demonstrate the nondissociative adsorption of H3(TpFPC) on pristine Au(111) and on an intermediate organic layer that provides sufficient electronic decoupling to investigate geometric and frontier orbital electronic properties of almost undisturbed H3(TpFPC) molecules at the submolecular level. We identify a deviating adsorption behavior of H3(TpFPC) compared to structurally similar porphyrins, characterized by a chiral pair of molecule−substrate configurations.

Since the first published one-pot synthesis of corroles by Gross and Paolesse in 1999,1 corrole research has strongly increased as well as the scope of corrole applications in catalysis, photochemical sensing, molecular electronics, and biomedicine.2 Unlike porphyrins, corroles contain a direct pyrrole−pyrrole link and three pyrrole-type hydrogens (Figure 1a) beneficial for stabilizing high-valent transition metal ions and prefer +III, +IV, and +V coordinate complexes well-suited for a number of catalytic reactions (hydroxylation of alkanes, epoxidation, sulfoxidation).3 Corroles tend to break to open-chain structures in aerobic solution under ambient light.4 Free-base corroles are unstable against light and air due to the reduced aromaticity and nonplanarity of the macrocycle. The stability depends on the substitution pattern of the tetrapyrrolic macrocycle and is improved by electronegative substituents. Nevertheless, certain corroles with electronegative substituents are known to degrade even at room temperature under ambient light.5 The archetypal 5,10,15-tris(pentafluorophenyl)-corrole [H3(TpFPC)], reportedly one of the most stable free-base corroles,4a has been intensively studied in the liquid phase (Figure 1a). H3(TpFPC) derivatives are promising tumor inhibitors2 and photosensitizers for solar cells.3a

Figure 1. (a) Chemical structure of H3(TpFPC). (b) Topographic STM overview of 1.1 monolayers H3(TpFPC) on Au(111) (+1 V, 50 pA). The first H3(TpFPC) monolayer is completely filled and regularly ordered (blue). Individual H3(TpFPC) molecules of the second layer are colored orange. Circles mark single H3(TpFPC) molecules of configurations I and II (see text). Inset: 2×2 nm2 STM topograph of a single type-I admolecule. (c) Topographic STM image of type-I and type-II molecules of the second layer (4.4×3.8 nm2, 1.25 V, 50 pA). (d) Adsorption model of type-I and type-II H3(TpFPC) configurations. The nonprotonated pyrrole N is colored red for better visibility.

Here, we employ the tip of a low-temperature scanning tunneling microscope (LT-STM) as local probe to investigate at the single-molecule level the electronic and geometric properties of surface-supported H3(TpFPC) molecules for two different weak-bonding situations: adsorbed on Au(111) or electronically decoupled by an intermediate organic layer. On both surfaces we demonstrate the nondissociative adsorption of H3(TpFPC) and identify two different molecule−substrate configurations that are distinguishable by both the handedness of the STM topographic appearance and the energies of the unoccupied frontier molecular orbitals (MOs) observed by...
scanning tunneling spectroscopy (STS). In ordered H$_3$(TpFPC) monolayer films both chiral configurations coexist, forming an alternating sequence of homochiral rows of molecules. The observed tilted adsorption of H$_3$(TpFPC) is distinctly different from that of porphyrins on weakly interacting surfaces.

The Au(111) surface was prepared by repeated cycles of 0.5 keV Ar$^+$ bombardment and annealing at 820 K. H$_3$(TpFPC) (C$_{16}$H$_{18}$F$_{14}$N$_8$) was thermally evaporated from a thoroughly degassed quartz crucible at a source temperature of 403 K and a base pressure of $<1 \times 10^{-9}$ mbar onto Au(111) held at 300 K. STM experiments were performed at 7 K and a base pressure below 5 $\times 10^{-11}$ mbar. W tips were electrochemically etched, vacuum-annealed above 1100 K, and subsequently Au-coated by controlled indentation into the pristine gold surface.

Figure 1b shows an STM topographic image of the sample surface after deposition of $\sim 1.1$ monolayers of H$_3$(TpFPC) on Au(111) at room temperature. A continuous layer of regularly packed H$_3$(TpFPC) molecules is clearly discernible (blue) and evidences layer growth for the first monolayer. The characteristic double lines of the Au(111) herringbone reconstruction along the (112) direction are still visible and “shine through” the H$_3$(TpFPC) monolayer (green arrows in Figure 1b). The Au(111) reconstruction is not lifted upon adsorption, indicating, as expected, a weak molecule–substrate interaction. The regular H$_3$(TpFPC) monolayer is aligned parallel to these lines, and domains of up to 90 nm diameter are azimuthally rotated by $120^\circ$ and separated by domain boundaries along the (112) direction (see Supporting Information). On top of the completed first H$_3$(TpFPC) layer, individual H$_3$(TpFPC) molecules and small two-dimensional clusters of H$_3$(TpFPC) molecules are observed (orange). Circles in Figure 1b show single H$_3$(TpFPC) molecules in the second layer. We employ this particular sample configuration to study single H$_3$(TpFPC) molecules weakly bound with different interaction strengths: those in direct contact with the metal that modifies and rearranges the frontier orbital electronic structure, and those decoupled by the underlying organic (first) monolayer, allowing us to obtain topographic and electronic information about almost undisturbed single H$_3$(TpFPC) molecules, similar to the gas phase.

First, we focus on single H$_3$(TpFPC) molecules of the second layer. At positive bias voltages from about $+1$ to $+1.5$ V, STM topographs reveal a characteristic three-lobe shape of single H$_3$(TpFPC) molecules, each lobe having a different apparent height (Figure 1b inset). By comparing the measured lobe–lobe separations with those of the molecular structure, we attribute the three lobes to the fluorophenyl meso-substituents (further corroborated by our STS data, below). A flat-on adsorption configuration of H$_3$(TpFPC) with the tetrapyrrolic macrocycle parallel to the substrate plane would imply an STM contour with C$_{2v}$ symmetry (Figure 1a). The observed C$_1$ symmetry of the STM contours of Figure 1b indicates that the H$_3$(TpFPC) molecules are tilted with respect to the substrate. Each molecule lies edge-on with two fluorophenyls closer to the interface and the third one above, which appears as the most intense lobe in STM topographs (Figure 1b inset). From the side-to-side ratio of the STM contour a tilt angle of $\sim 50^\circ$ is estimated.

Intriguingly, two chiral molecule–substrate configurations are observed by STM, manifested by two L-shaped contours that are both mirrored and rotated with respect to each other. This is best seen in Figure 1c, displaying a surface area with two adjacent second-layer molecules marked by red and yellow L lines as guides to the eye. The model in Figure 1d explains the existence of these two configurations: a side-tilt about the lower edge of the molecule to either the right or left side, labeled I and II, respectively. Two additional chiral configurations (not shown) are obtained when the 10,15 fluorophenyls are closest to the substrate instead of the 5,10 displayed in Figure 1c. We remark, however, that from our experimental results we cannot distinguish whether the two chiral configurations observed by STM are two different enantiomers (or atropisomers) or just two molecules oriented differently with respect to the substrate plane, or mixtures of both.

The STS results in Figure 2 unveil the frontier orbital electronic properties of electronically decoupled H$_3$(TpFPC) molecules in the second layer. The local differential tunneling conductance, $dI/dV$, was recorded in constant-current mode (active feedback loop). The $df/dV$ signal was obtained with lock-in technique and a sinusoidal modulation peak-to-peak voltage of $V_{pp} = 20$ mV and 700 Hz added to $V$, averaging 10 consecutively recorded spectra. Reliable judgment of the cleanliness and condition of our STM tips was based on routinely monitoring the $df/dV$ signature of the Au(111) surface state obtained over pure substrate regions and comparing its position and shape with literature values.

Figure 2a displays tunneling spectra recorded at well-selected tip positions labeled $\alpha$–$\varepsilon$ over different submolecular units of second-layer type-I H$_3$(TpFPC). Enhanced conductance is observed at certain energies independent of the tip position. We start with the spectrum at position $\gamma$. Comparison with the spectrum of pristine Au(111) (dashed line in Figure 2a) enables us to distinguish substrate-related features from resonant tunneling through distinct frontier MOs of H$_3$(TpFPC). In the energy range from about $-0.8$ to $+0.6$ eV, the spectrum resembles that of pristine Au(111). The shoulder around $-0.5$ eV corresponds to the onset of the Au(111) surface-state band and indicates direct tunneling between tip and metal substrate. Note that constant-current spectroscopy leads to point contact when the bias voltage approaches zero, causing the sharp increase of the signal observed in the respective energy range. The distinctly discernible resonances at higher/lower energies are attributed to resonant tunneling through distinct MOs of H$_3$(TpFPC). The respective peak energies are listed in Table 1. The peaks at $-1.15$ and $+0.79$ eV are attributed to HOMO and LUMO, respectively.
Table 1. STS Peak Energies (in eV) of H₃(TpFPC) Molecules in the First and Second Layers

|          | second layer | first layer |          |          |
|----------|--------------|-------------|----------|----------|
|          | II           | I           | II       | I         |
| HOMO−1   | −1.25        | −1.25       | (−1.1)   | (−1.1)   |
| HOMO     | −1.15        | −1.15       | −0.85    | −0.85    |
| LUMO     | +0.79        | +0.72       | +1.29    | +1.20    |
| LUMO+1   | +1.00 (+0.9) | +1.41       | +1.44    |          |
| LUMO+2   | +1.25        | +1.15       | +1.80    | +1.72    |

“The estimated experimental error is ±0.05 eV.”

yielding a respective energy gap of 1.9(4) eV, in very good agreement with the HOMO/LUMO gap of 1.91 eV measured by UV/vis spectroscopy in solution.9

At other tip positions the HOMO/LUMO intensity is lowered, indicating weaker overlap of specific MOs with the STM tip in constant-current mode. Spectrum α clearly differs from the others by the very weak LUMO and LUMO+1 signals, indicating that the STM tip over the “high” fluoro phenyl (farthest away from the surface) no longer overlaps with the LUMO and LUMO+1, in accordance with the localization of LUMO (and HOMO) over the macrocycle known from free-base corroles10 and metallocorroles.11 To rationalize our experimental results we performed DFT single-point energy calculations of a single H₃(TpFPC) molecule with the Gaussian 03 package12 using Becke three-parameter hybrid functional (B3LYP),13 Pople’s 6-311+G(dp) compound basis set,14 and a fixed conformation of the H₃(TpFPC) obtained from bulk-phase data.1c

Although the predictive quality of DFT-calculated MO energies is generally poor,7 the symmetry and spatial extent of MOs typically are reliable and hence useful for interpreting our experimental data. Figure 3 displays our DFT results for selected MOs. LUMO and LUMO+1 are mainly localized over the corrole macrocycle, while the almost degenerate LUMO+2, +3, and +4 are restricted to the fluoro phenyl substituents. This corroborates the above interpretation of spectrum α, where electrons tunnel mainly into the almost degenerate LUMO+2, +3, and +4, in agreement with the tilted adsorption configuration derived from our STM images.

Figure 2b compares spectra of type-I (solid) and type-II (dashed) molecules recorded over equal positions α−ε. Intriguingly, the unoccupied frontier MOs of type-II molecules are significantly shifted by ~70−100 meV toward lower energies (see Table 1), whereas the occupied MOs are almost unaffected (not shown). These energy shifts are characteristic of type-II configuration and allow us to unambiguously distinguish type-I and type-II configurations by STS. The observed shifts may be due to the nonequivalent adsorption positions of fluoro phenyls and pyrroles relative to the underlying surface, with opposite sides of the nonplanar macrocycle (due to the H arrangement) facing the surface (Figure 1d), which may modify the molecular buckling. In a recent study we found that in buckled porphyrins on Au(111) slight geometric variations of the macrocycle can give rise to energy shifts of up to 200 meV.15

In the following we discuss the structural properties of the regular first H₃(TpFPC) monolayer on Au(111), shown in Figure 4a at different bias voltages. Note the almost identical STM topography of single H₃(TpFPC) molecules observed in the first monolayer at the LUMO−2 energy of +1.8 V (Figure 4a, top left) and at +1.25 V in the second layer (Figure 1c), indicating similar side-tilted orientations of the respective H₃(TpFPC) molecules. Compared to the second layer, the bias dependence of the STM topographs in Figure 4a reflects the different bonding situation (interaction strength) at the molecule−Au(111) interface of the first layer, where the energies of specific MOs (probed by the tunneling electrons) are shifted (Table 1). No significant effect on the STM topographs or the STS data was observed due to the Au(111) herringbone reconstruction (periodic modulation of the substrate lattice between fcc- and hcp-type packing). Near the energy of LUMO+2, the three fluoro phenyl substituents of each H₃(TpFPC) molecule can be discerned (images at +1.8 and +1.5 V). The same molecular units also dominate the topographic contrast near the HOMO energy, where the relative intensities have changed (image at −0.9 V). Finally, the corrole macrocycle becomes visible at energies slightly below the HOMO, causing a distinct change of the topography (image at −1.1 V).

As in the second layer, we observed that H₃(TpFPC) molecules in the first monolayer exhibit either type-I or type-II configuration (Figure 4a, red and yellow L lines). Figure 4b juxtaposes the tunneling spectra of type-I (solid) and type-II (dashed) molecules recorded over intramolecular positions α−ε, taken analogously to Figure 2a. The respective spectra are qualitatively similar to those of the decoupled second layer (compare with Figure 2), but the MO resonances are shifted toward higher energies by ~0.3−0.4 eV and the HOMO/
LUMO gap is increased by 0.11 eV (see Table 1). Most likely, this is caused by the different work functions of the respective surfaces, affecting the surface dipole layer at the interface. The weak LUMO + 2 resonance at positions δ and γ (also observed in the second layer, see Figure 2) indicates that the respective fluorophenyls are closer to the substrate, in accordance with a tilted adsorption of H₃(TpFPC) (Figure 1d).

The first monolayer exhibits a stripe pattern aligned along the [11̄2] direction of Au(111) (Figure 1b) that originates from a lateral sequence of ordered rows of H₃(TpFPC) molecules with alternating type-I or type-II configuration. This regular pattern can be recognized in the STM images of Figure 4a, from which we have determined the parameters of the corresponding surface unit cell: \( \ell_{b1} = 1.5(1) \text{ nm}, \ell_{b2} = 2.4(0) \text{ nm}, \) and \( \beta = 90° \pm 2°. \) The epitaxy matrix of the H₃(TpFPC) monolayer relative to the rectangular unit cell of the reconstructed Au(111) lattice reads \( C \approx (0.53, 0.24) \). The rational numbers indicate a coincident \(^{16}\) registry of the H₃(TpFPC) monolayer with respect to the reconstructed Au(111) lattice. Although in the first monolayer it seems possible to accommodate two flat-lying molecules per unit cell without mutual steric hindrance, the observed side-tilt indicates a less dense packing. This can be explained by mutual repulsion between neighboring H₃(TpFPC) molecules, similar to that observed for comparable hydrocarbon molecules on weakly interacting surfaces.\(^{17}\) The H₃(TpFPC) molecules seem to lower their mutual repulsion by tilting away from the surface plane, similar to the molecules of the second layer (discussed above) and similar to the bulk structure exhibiting parallel rows of regularly \( \pi \)-stacked H₃(TpFPC) molecules in the [010] direction.\(^{16}\) We remark that the observed layer-like growth of regularly \( - \)stacked H₃(TpFPC) molecules in the \( [010] \) direction of Au(111) (Figure 1b) that originates from \( \langle 011 \rangle \) Au(111) surfaces on the submolecular scale by LT-STM and STS, affecting the surface dipole layer at the interface. The this is caused by the different work functions of the respective surfaces, influencing the surface dipole layer at the interface. The LUMO gap is increased by 0.11 eV (see Table 1). Most likely, this is caused by the different work functions of the respective surfaces, affecting the surface dipole layer at the interface. The weak LUMO + 2 resonance at positions δ and γ (also observed in the second layer, see Figure 2) indicates that the respective fluorophenyls are closer to the substrate, in accordance with a tilted adsorption of H₃(TpFPC) (Figure 1d).

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