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STM Investigation of Flexible Supramolecules: Benzylic Amide [2] Catenanes

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Abstract

Benzylic amide [2] catenane (CAT1) deposited from a methanol solution onto highly oriented pyrolitic graphite (HOPG) has been investigated by ambient scanning tunneling microscopy (STM). Submolecular features are resolved which suggest that the adsorption of CAT1 is driven by the electrostatic attraction of carbonyl groups and HOPG. Our evidence shows that CAT1 is mobile at RT on HOPG surface. A statistical analysis of the observed features reveals a bimodal distribution of the lateral size which correlates with the expected diameter of a single macrocycle and the catenane respectively.

Keywords: catenanes, supramolecules, scanning tunneling microscopy, adsorption, solution processing.

1. Introduction

Benzylic amide [2] catenanes are novel supramolecular species which are versatile prototype for multifunctional materials. [1] A catenane (Fig. 1) consists of 2 interlocked amide macrocycles assembled by hydrogen bonds. The supramolecule in Fig. 1 is termed CAT1.

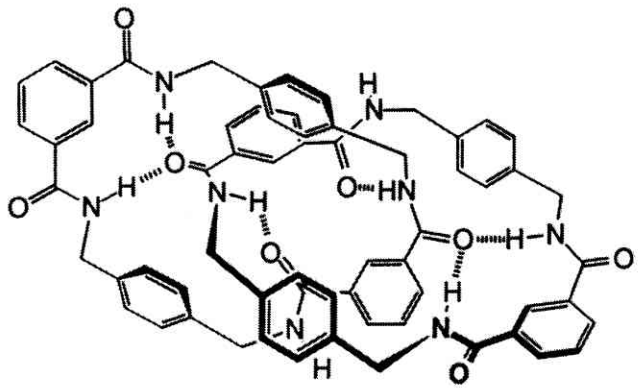

Fig. 1. Model of benzylic amide [2] catenane (CAT1).

The conformation of the macrocyclic rings and their rotation depend on the chemical substitution, the solvent, the oxidation state, and the excitated states. [2] Most of the existing studies concern solutions of CAT1 while little is known on their behaviour on surfaces, on the formation of aggregates in a condensed phase and thin films which might be relevant to potential applications.

Here we report a preliminary investigation of catenanes by means of scanning tunneling microscopy (STM). Our aim is to explore the behaviour of individual catenane molecules on surfaces.

2. Experimental

CAT1 has been deposited from a 20 µl drop of methanol solution (≈$1x10^{-4}$ M) onto freshly cleaved highly oriented pyrolitic graphite (HOPG). This amount corresponds roughly to 1 monolayer coverage on a 1 cm^2 surface. Ambient STM has been used to image the surface at high resolution after the solvent has dried out at RT. Etched tungsten tips have been used and typical imaging conditions were 0.3 nA setpoint current, 0.5 V sample bias, and 1 Hz scan rates. The solution was added only after steps on HOPG were resolved on the submicron scan range without exhibiting either decoration by impurities or extensive defects.

3. Results and Discussion

The protrusions which are visible on the STM images on HOPG (Fig. 2) magnify accordingly to the scan range. There is a clear correlation between the features in images acquired with opposite scan directions, while there is no correlation between features observed at successive frames. This suggests that the species which give rise to these features either move on the HOPG surface or they are swept away by the tip. Such protrusions do not appear for scans on bare HOPG, or upon addition of a pure methanol drop to the bare surface.

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Inset in Fig. 2 shows the comparison between a protrusion with a 4-lobe structure and a model of CAT1. According to the similarity, the catenane sits with several carbonyl groups in close proximity on the HOPG basal plane. This suggests that the electrostatic attraction between the partial charges on the carbonyl groups and their images inside the graphite might be the dominant contribution to adsorption. π-stacking interaction beween the phenyl groups and HOPG would require a flattening of the macrocycle which might be energetically and entropically unfavorable. [3]

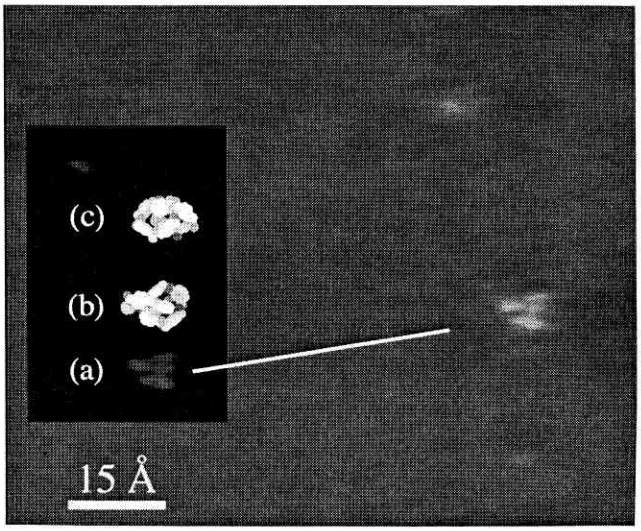

Fig. 2. STM image after addition of CAT1 solution. Sample bias is 0.5 V, tunneling current 0.3 nA, height range is 2 nm. In the inset are shown (a) contrast-enhanced 4-lobe feature corresponding to the protrusion to the right. (b) top-view and (c) sideview of a space filling model with respect to the basal plane of HOPG. The model is scaled with respect to the scan size. Atoms are C (grey and white), O (red) and N (blue).

We performed a statistical analysis of the size of the protrusions, by thresholding the features at full-width-half-maximumabove the mean image height. A set of 71 particles was taken from 10 different 20 nm x 20 nm images. The analysis was carried out both on the full set and on a subset of 54 particles whose mean height (3 nm) corresponds to the mode in the height distribution. The area distribution is bimodal, as it is shown in Fig. 3. The fit of the histogram to a double gaussian distribution yields mean±r.m.s. effective diameter equal to 6.0±0.2 and 9.5±0.3 Å for the two respective peaks. These values correlate with the expected internal size of the single macrocycle and the catenane respectively. This might indicate 2 different orientations of CAT1 on HOPG, which is in agreement with molecular mechanics simulations. [3] Alternatively, a fraction of deposited catenane population might be disrupted into 2 macrocycles. Although HOPG is an apparently inert surface, disruption might result because of increased entropy on one hand, and the balance between weak hydrogen bonding (few tens of eV) and a considerable adsorption energy (up to few eV for the macrocycle and CAT1 [3]).

The scarce observations of submolecular features together with the shifting protrusions indicate that CAT1 diffuse easily on HOPG at room temperature and upon STM imaging conditions. The smoothness of the HOPG surface potential is due to the large catenane size with respect to graphite unit cell (1 vs 0.25 nm respectively), the absence of registry and the abundance of internal conformations of the supramolecule.

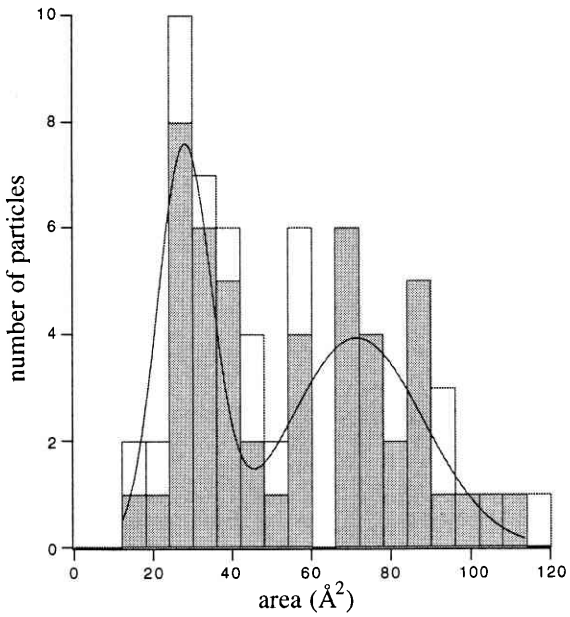

Fig. 3. Distribution of the lateral size of the protrusions observed with STM for sets of 71 particles (blank) and 54 particles (shadowed bins). Continuous line is the fit to the latter with a linear combination of gaussian distributions.

It would be necessary for reliable STM imaging either to lower the substrate temperature, or to use an atomically flat surface with larger potential corrugation. Thus, we performed a second series of STM experiments where CAT1 was dosed on the Si(111) 7x7 reconstructed surface by sublimation in ultra-high vacuum. This surface, which is well-characterized by STM, has a large electron corrugation because of the larger lattice parameter (7.7 Å interatomic distance between surface adatoms) and the presence of dangling bonds in correspondence of the adatoms. Our results, which will be reported elsewhere, [4] show the possibility to anchor steadily CAT1 on this surface while retaining at the same time the 2-ring structure.

4. Acknowledgements

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5. References

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