TEMPERATURE INDUCED CONFORMATIONAL CHANGE OF TETRAPYRIDYLPORPHYRIN ON Cu(111)

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Recently there has been much interest in the self-assembly of functional organic molecules on various metal substrates, preparing the ground for the control and synthesis of low-dimensional supramolecular nanosystems, which are potentially useful for a variety of applications (e.g., molecular electronics, sensing, nano-optics or molecular magnetic devices).

Here we present Low-Temperature Scanning Tunneling Microscopy (LT-STM) and Scanning Tunneling Spectroscopy (STS) results of tetrapyridylporphyrin molecules ($C_{40}H_{26}N_8$, TPyP) adsorbed on a Cu(111) surface. In particular, we discuss the molecular ordering at various substrate temperatures and address a temperature induced conformational change. Figure 1 shows STM images of TPyP molecules deposited on Cu(111) at 270K, 390K and 510K. All STM data were recorded after cooling the sample below 15K.
Evaporated at room temperature, the TPyP molecules adsorb individually along the 6-fold symmetry of the substrate surface. In STM images the molecules exhibit a two-fold symmetry showing no change in appearance over a wide bias voltage range from -2 eV to +2 eV. Above room temperature the TPyPs form one-dimensional chain segments and hexagonal structures. In contrast, on Ag(111) densely packed molecular islands readily evolve already at low coverage, indicating appreciable molecular surface mobility and moderate substrate coupling [1,2].
To determine the adsorption sites of TPyP on the Cu(111) surface, CO molecules were deposited in-situ. In the low coverage regime they exclusively decorate the on-top adsorbtion sites on Cu(111) and can consequently be used as markers for the substrate lattice, (compare figure 2).
Once the sample is annealed over 470K, the molecular contrast changes considerably: the TPyP molecules appear as four lobes, supposing a conformational change of the TPyP on the substrate. In this new state, we can further distinguish two types of molecules by considering subtle contrast variations: One appearing hollow in the center and the other one showing contrast in the center (compare figure 3).
This conformational change is also underlined by differences in the tunneling spectroscopy over the admolecules. Tunneling spectra on single TPyPs adsorbed at room temperature do not show any contribution from additional molecular electronic states and strongly resemble the data taken on the pure Cu(111) substrate. In the new state after annealing, the spectra taken on the hollow appearing TPyPs, show an electronic state at 2 eV, which is 300 meV wide.
Furthermore, the conformational change of the molecules is accompanied by a change in the nearest neighbor distance between the molecules in the one-dimensional chain segments.

The formation of one dimensional chains on Cu(111) above room temperature along the substrate surface symmetry we account to interactions of Cu adatoms with TPyP. This assumption is supported by experiments, exploiting coordination interactions between the pyridil functional moiety and co-deposited metal atoms. This work is part of a strategy to fabricate metallosupramolecular networks with specific topologies and a high structural stability.

References:

[1] Self-assembly and conformation of Tetrapyridil-porphyrin molecules on Ag(111**)** W.Auwärter, A. Weber-Bargioni, A. Riemann, A. Schiffrin, O. Gröning, R.Fasel and J.V. Barth, **J. Chem. Phys.** 124(2006), 194708

[2] The make of metallo-porphyrins in two dimensions W. Auwärter, A. Weber-Bargioni, S. Brink, A. Riemann, A. Schiffrin, M. Ruben and J.V. Barth, to be publishedP

Figures:

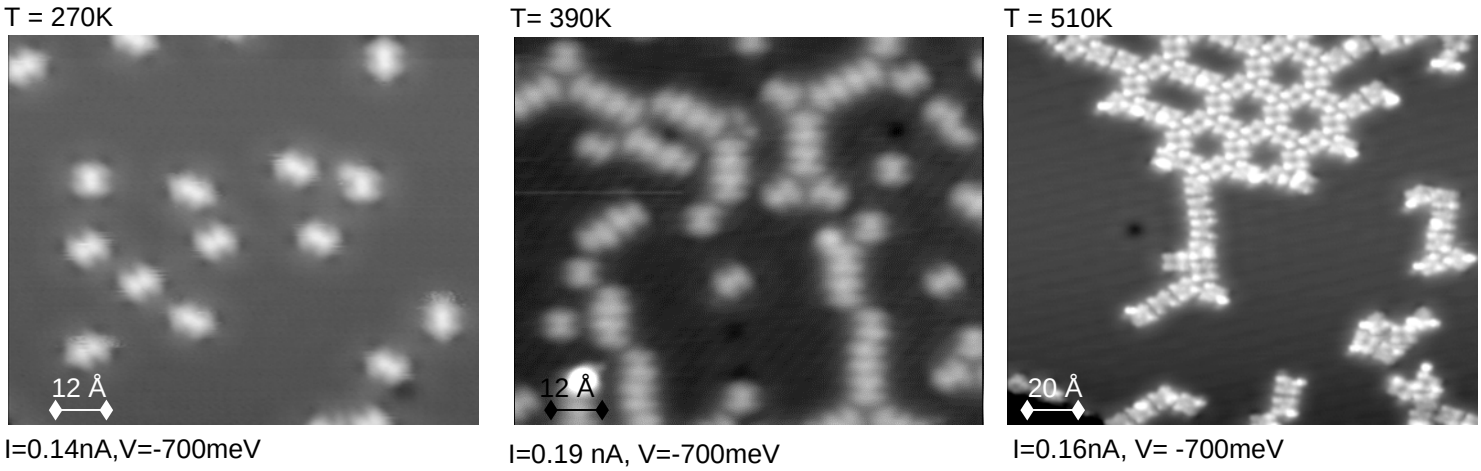

Figure 1: TPyP deposited at 270K, 390K and 510K on Cu111. The admolecules assemble to complex structures at higher temperatures and show a conformational change above 450K

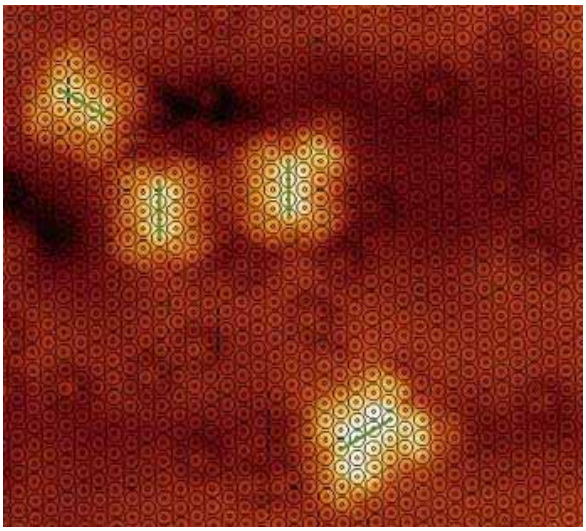

Figure 3: after annealing at 470K two different contrasts are observable in the center. The hollow appearing admolecules show information in STS

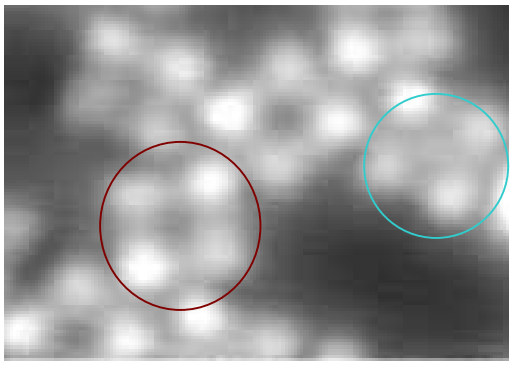

Figure 2: determination of adsorption site on the Cu111 via C-O admolecules as markers.