PTCDA on calcite(104) – unveiling strong anchoring by sub-molecular imaging and single electron charging experiments

P. Laubrock[1#], J. Huang[2], A. S. Foster[2], P. Rahe[1]

[1] *Institut für Physik, Universität Osnabrück, Germany*
[2] *Department of Applied Physics, Aalto University, Finland*

Presenting author's e-mail: plaubrock@uni-osnabrueck.de

The future development of information technology and (opto-)electronical systems with molecular materials hinges on innovative approaches to steer molecular assembly, to electronically isolate molecular structures, to establish defined electrical contacts to single molecular end points, and to apply novel tools for atomic-scale characterization. Along these lines, molecular self-assembly on dielectric surfaces emerged as a most promising approach, given the intrinsic electronic isolation from the supporting material together with a variety of proven concepts for molecular structure formation. While early studies reported molecular dewetting [1], it is now understood that molecular anchoring [2] is essential for the realization of molecular structures on dielectrics.

Here, we study the adsorption structure and functional aptitude of single perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) molecules on the dielectric calcite(104) surface. Non-contact atomic force microscopy (NC-AFM) performed with CO-functionalized tips achieves sub-molecular contrast on the bulk dielectric surface (see Fig. 1(a)), with a resolution power comparable to metal-supported systems [3]. In combination with density functional theory (DFT) calculations, the high-resolution data evidences a strong molecular deformation upon adsorption as a consequence of strong molecule-surface interactions. The strong bonding between the PTCDA carboxylic oxygen atoms and the calcium surface ions leads to a preferred adsorption position within the reconstructed [4] calcite(104)-(2×1) surface lattice (see Fig. 1(b)). Furthermore, we investigate the charging behavior of isolated molecules and PTCDA molecule pairs by tunneling single electrons from the tip contact [5] (see Fig. 1(c)). Minor molecular reorganization is revealed and the influence of residual charges typical for bulk dielectrics after cleaving in ultrahigh vacuum [6] found to be negligible for the charging process parameters.

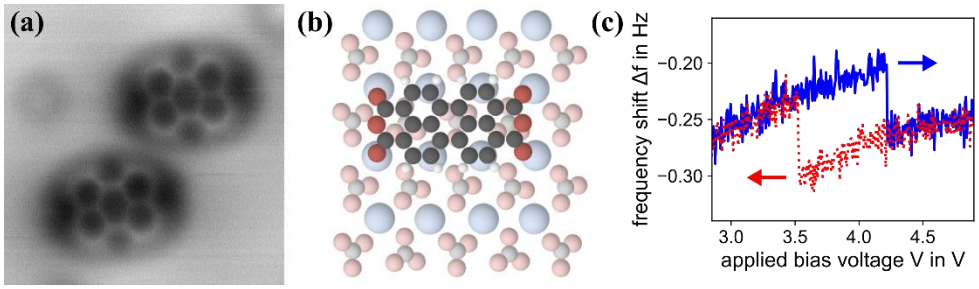

Figure (1). (a) High-resolution image of PTCDA on calcite(104) obtained with a CO-functionalized tip. (b) Adsorption geometry as obtained from DFT calculations. (c) Fingerprint of a single charging event.

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