Interaction of metallo-carboxyphenyl porphyrins with rutile TiO_2 (110)

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Titania surfaces sensitized with metallo-porphyrins are of increasing interest for photocatalysis or photovoltaics. In these applications, the dye absorbs light and injects the exited electron into the conduction band of the titania. The binding configuration is thereby of great importance for the electron transfer process. To simultaneously investigate the binding configuration and its influence on the charge transfer process, nc-AFM and in particular KPFM are the methods of choice.
In our work we studied the adsorption configurations of single Cu-TCPP molecules, a sensitizer commonly used for photocatalysis, on rutile TiO_2 (110). Bimodal nc-AFM at room temperature and under UHV was applied to obtain high resolution on the molecules as well as on the substrate (Fig. 1a). FM-KPFM was used to investigate the electronic properties of the adsorbed Cu-TCPP. The experimental data revealed that the Cu-TCPP molecules align themselves with respect to the substrate structure resulting in two main orientations. In both cases the KPFM showed a lowered LCPD on the sensitizer (Fig. 1b,c), indicating that adsorption is accompanied by charge transfer from the sensitizer to the substrate. Results from DFT calculations using the deduced binding configurations as input were in good agreement with the experimental data. Our work was recently extended to the investigation of similar Zn-porphyrins including anatase TiO_2 (101) substrates as well. First results indicated similar behavior on rutile (110), but no binding to the terraces on anatase (101).

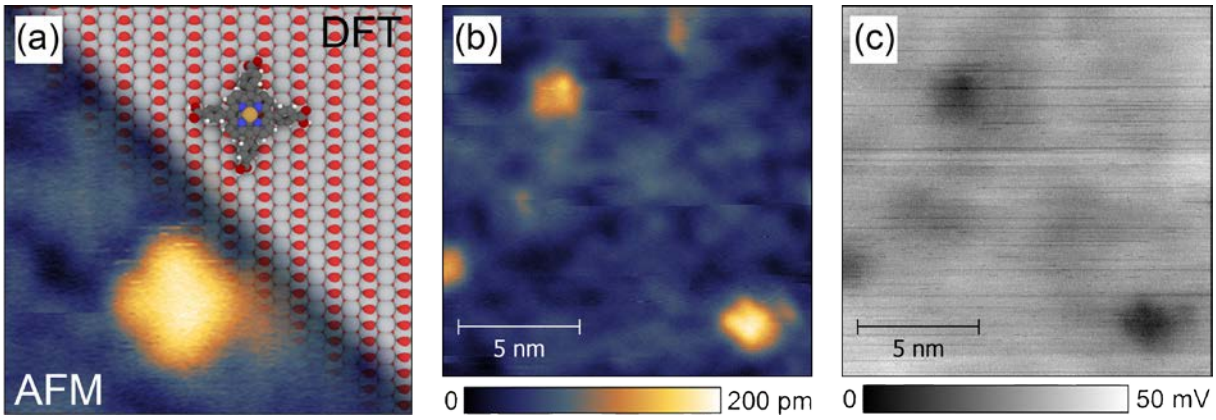

Fig 1: Cu-TCPP on TiO_2 rutile (110): (a) Comparison between high resolution FM-AFM image and adsorption geometry from DFT calculations, (b) FM-AFM topography image showing two adsorption orientations and (c) corresponding LCPD map.