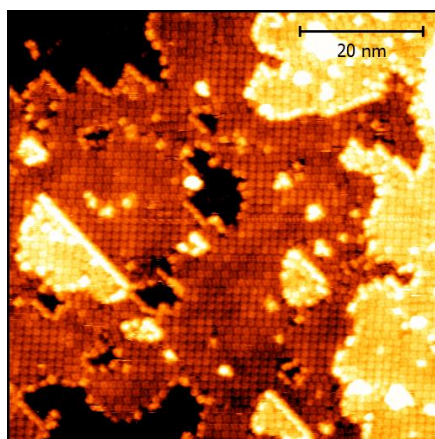


# Layer formation of molecular dyes on titania surfaces

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Anchoring of the molecular dyes on titania surfaces are studied due to their wide applications in light-harvesting solutions. In the presentation we will report on the results of the UHV-based scanning probe microscopy (SPM) studies of the adsorption and layer formation of the dyes on the most stable titania surfaces: rutile (110) [1] and (011) [2] and anatase (101) [3]. The meso-tetraphenyl porphyrin-Zn(II) molecule (ZnTPP) adsorbs in a flat configuration on all the three investigated surfaces, however at room temperature isolated molecules can only be immobilized on surface defects and terrace edges. For anatase, due to steric considerations there is a clear preference for adsorption only on one type of steps. The ZnTPP molecules are immobilized at coverages close to a monolayer forming structures in which the proximity of phenyl groups of neighbouring molecules allows for  $\pi$ - $\pi$  intermolecular interactions to stabilize the structure (see the Fig. 1 for an 60x60 nm<sup>2</sup> STM image of a ZnTPP monolayer on anatase (101)). Braking the symmetry of a molecule by adding a carboxyl group to one of a methyl groups does not result in adsorption in upright geometry. The lifting of a molecular board of COOH-ZnTPP molecules was observed only for (011) surface of rutile. The importance of intermolecular forces stemming from the interaction of phenyl groups in organization of dye molecules in the layer can be shown by comparison to the behaviour of tin phthalocyanine (SnPc) molecules which do not possess such groups. SnPc molecules interact quite strongly with the substrate due to their exposed Sn atom, however there is no organization in the layer if they stay flat on the surface. It is for coverages exceeding a monolayer that the molecular boards are lifted from the surface and they can interact with each other enough to form an organized structure.



## References:

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- [2] P. Olszowski, et al. Journal of Physical Chemistry C. 2015;119(37):21561–21566
- [3] L. Zając, et al. Applied Surface Science, accepted