

Adsorption of carboxyphenyl-substituted porphyrin on titanium dioxide

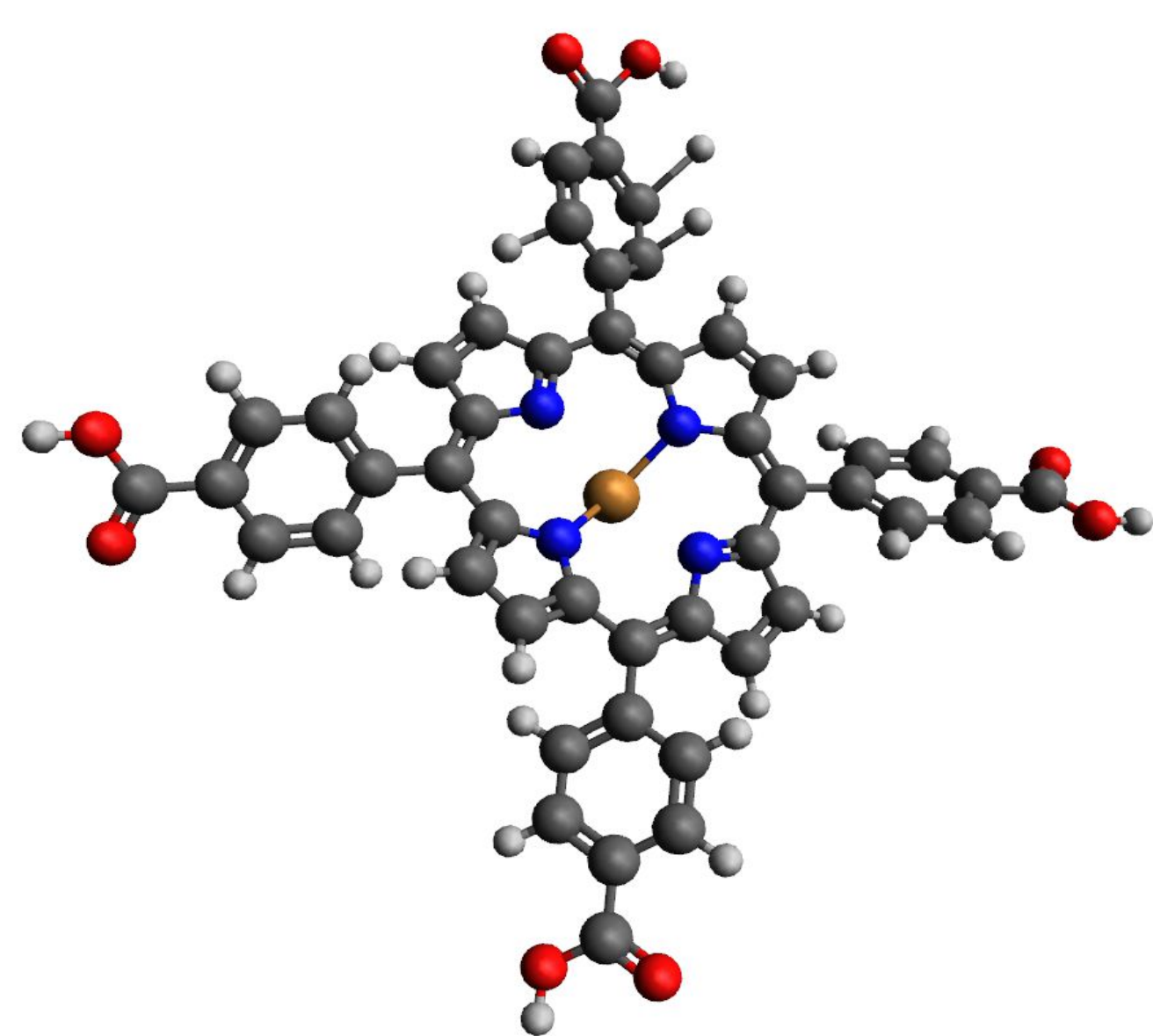
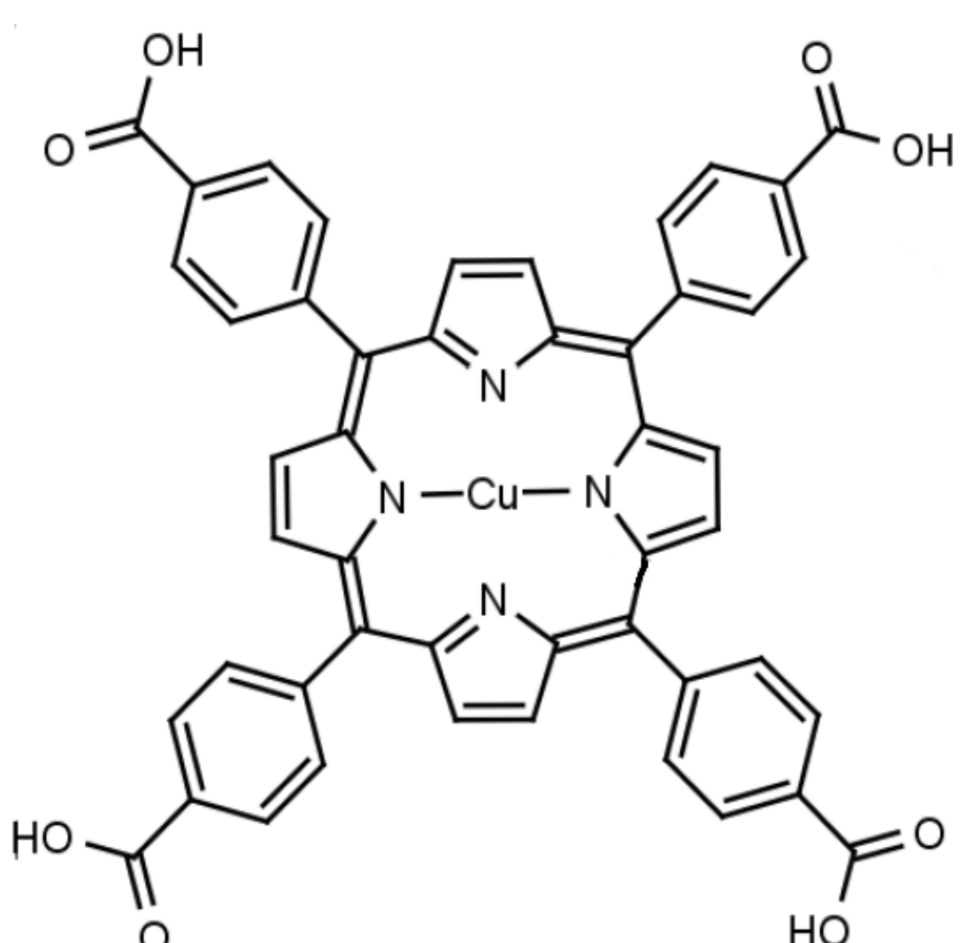
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 Swiss Contribution

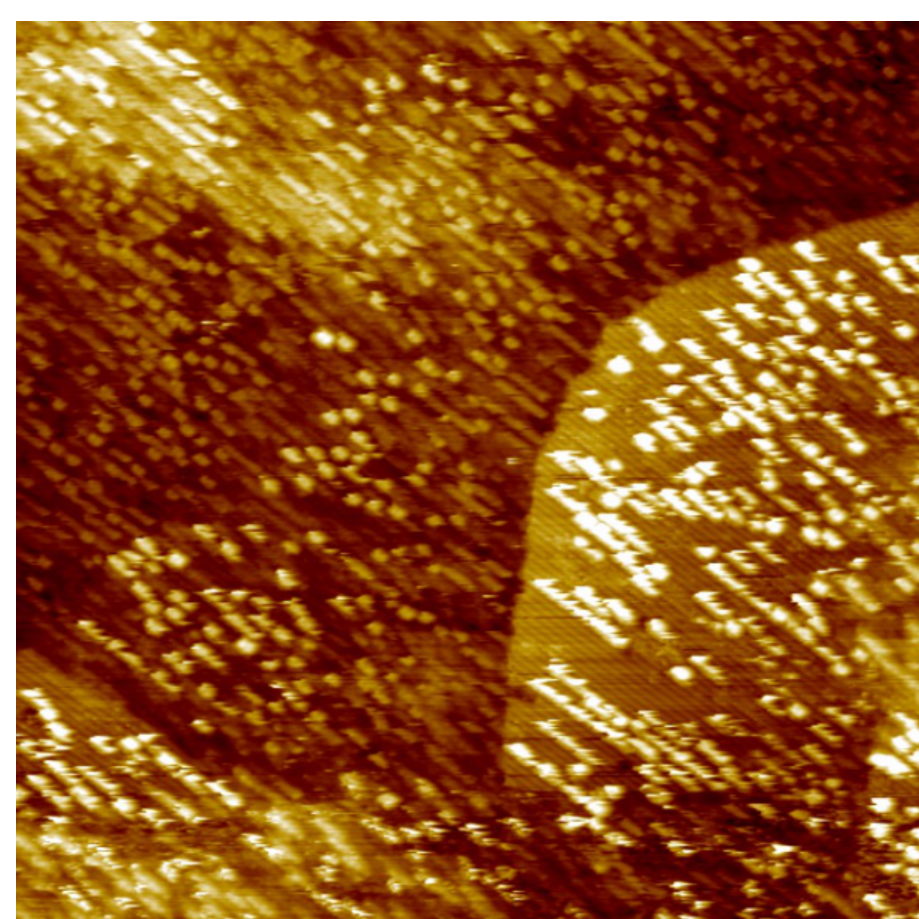
 Polish-Swiss Research Programme

Abstract

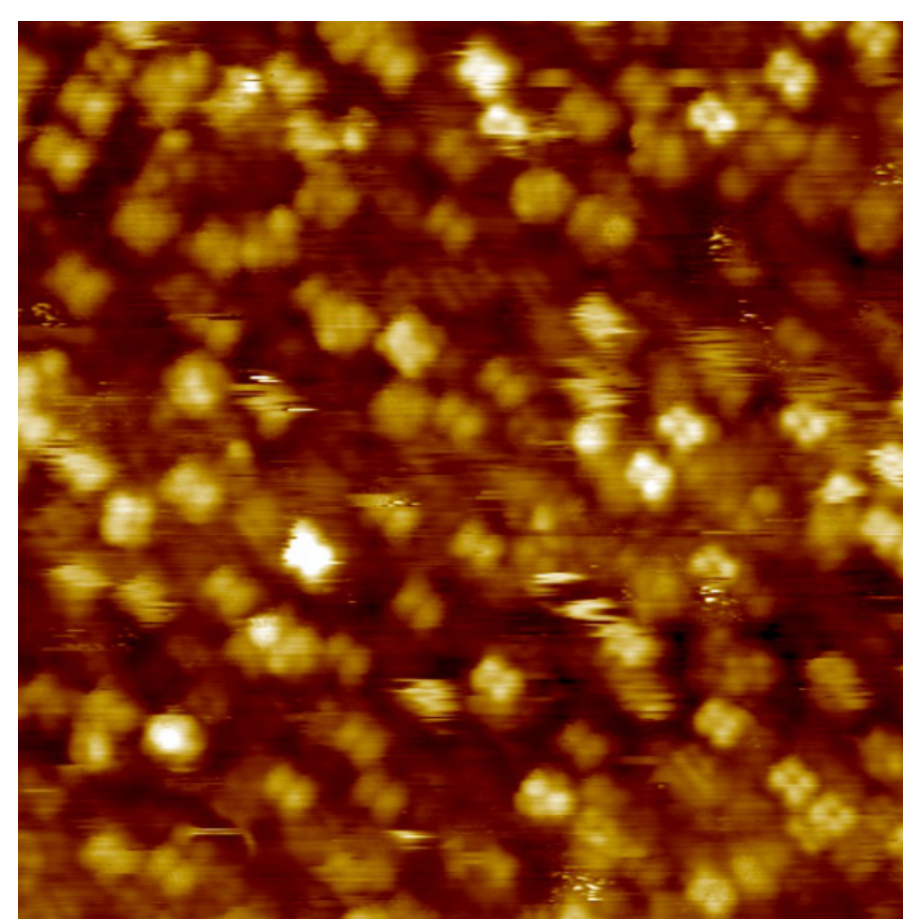
Understanding and engineering the molecule-substrate interaction is crucial for technologies relevant for dye-sensitized solar cells (DSSC). In the presentation we present results of the studies into the influence of substrate orientation on the molecular structure of the thin porphyrin layer. Porphyrins were one of the first sensitizers used in dye-sensitized light harvesting applications[1]. We have used carboxyphenyl-substituted porphyrin, tetrakis(4-carboxyl-phenyl)porphyrin cooper(II) (CuTCPP). The presence of anchoring carboxylic group plays major role in the adsorption as well as the electron transfer processes[2]. With use of scanning tunnelling microscopy (VT-STM) and analyze CuTCPP /TiO₂(110) and CuTCPP/TiO₂(011) systems. The measurements were carried out at low temperatures in order to immobilize molecules and allow for high-resolution structural characterizations.



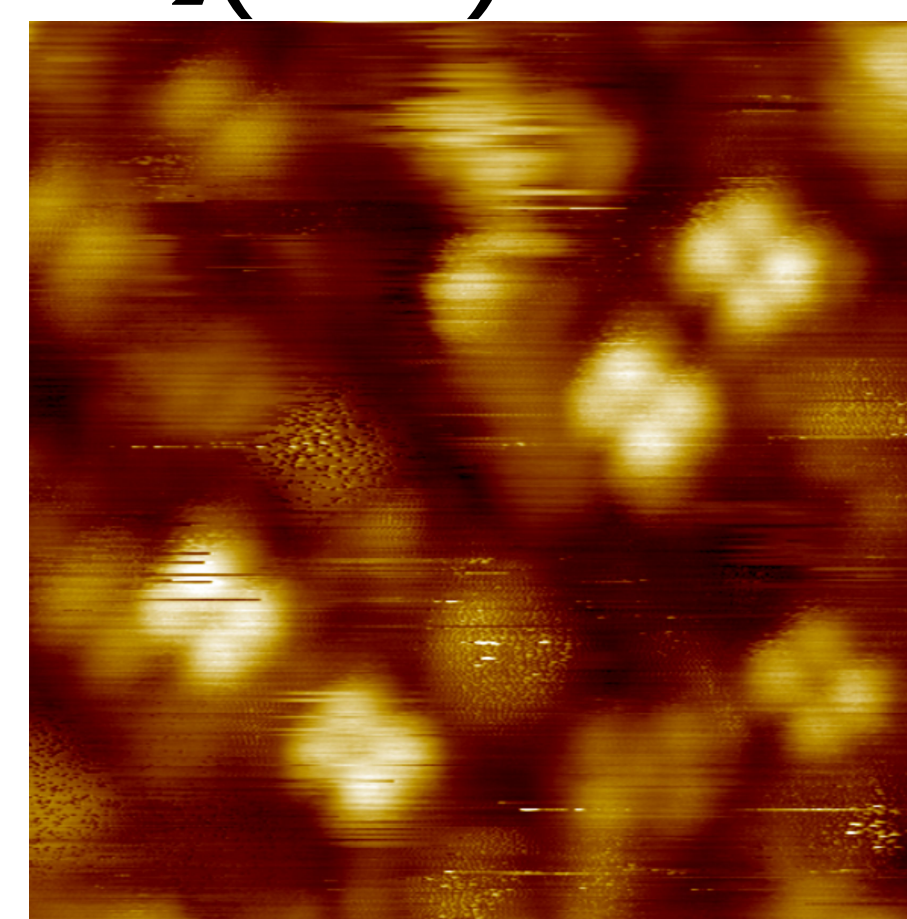
CuTCPP/TiO₂(011)



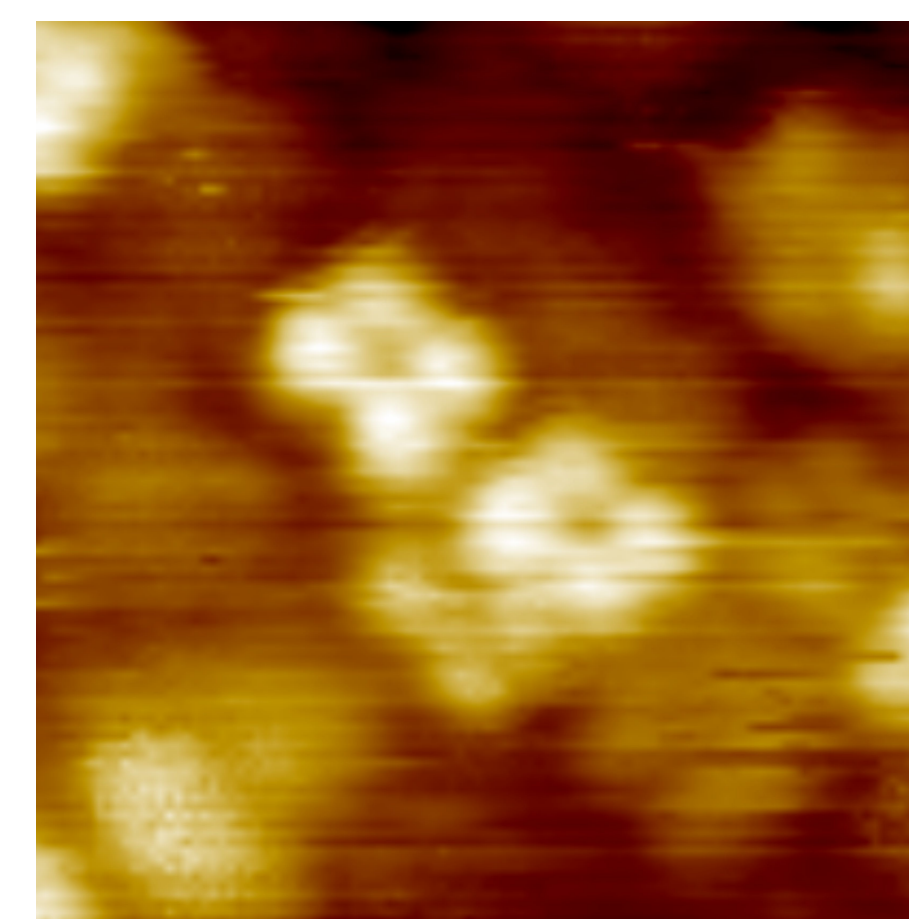
100x100nm, 3pA, 0.8V



40x40 nm, 5pA, -3V

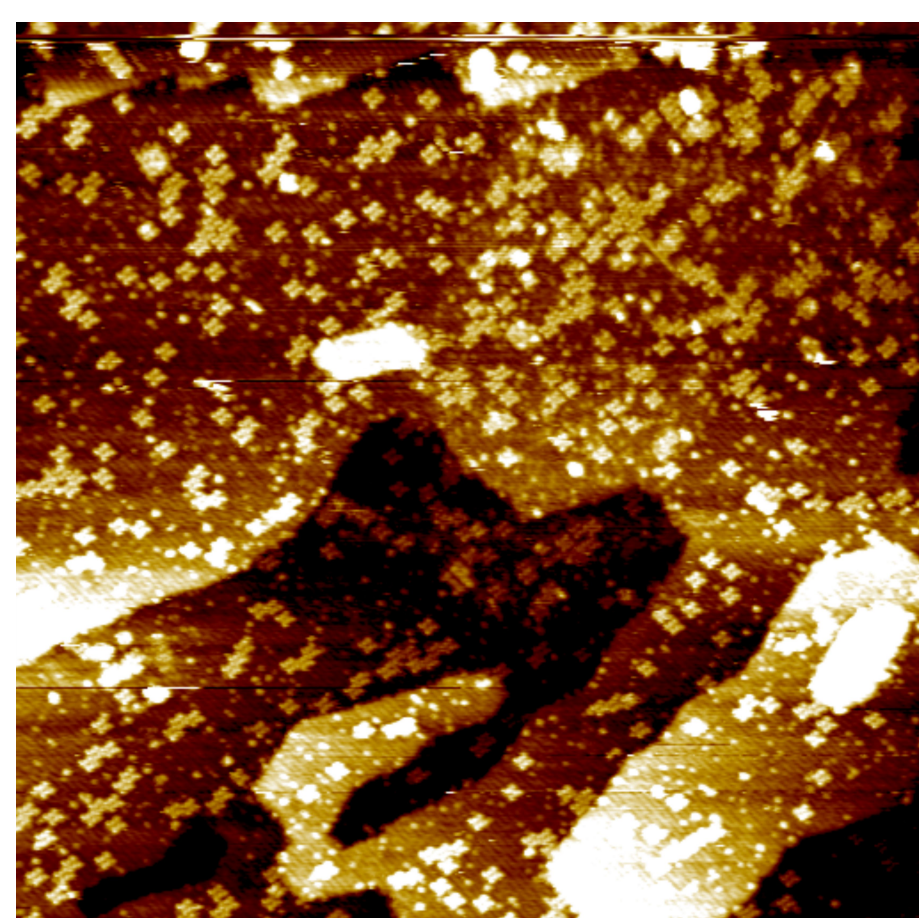


10x10 nm, 5pA, -3V

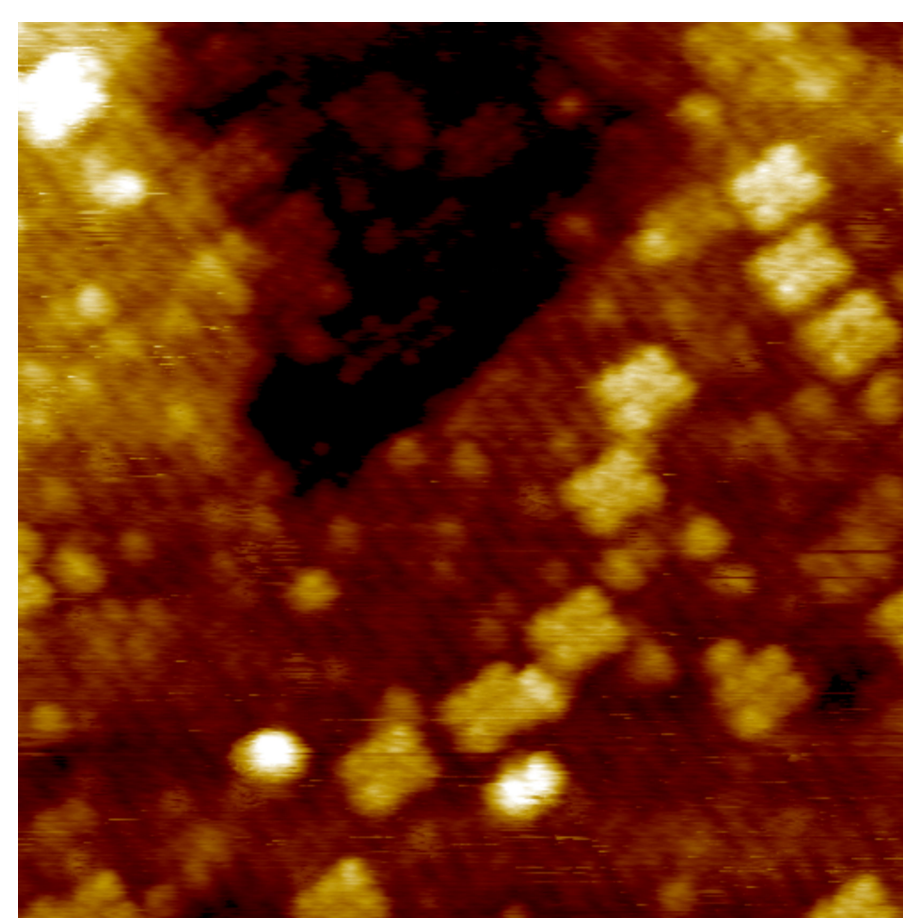


6x6nm, 5pA, -3V

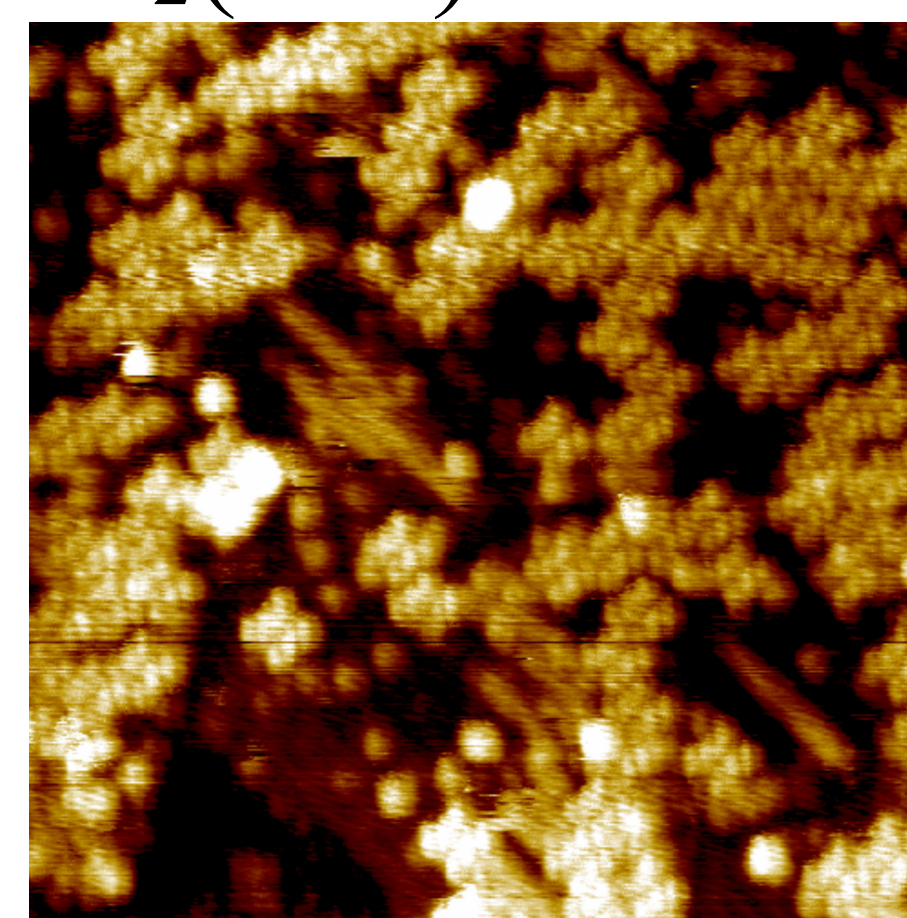
CuTCPP/TiO₂(110)



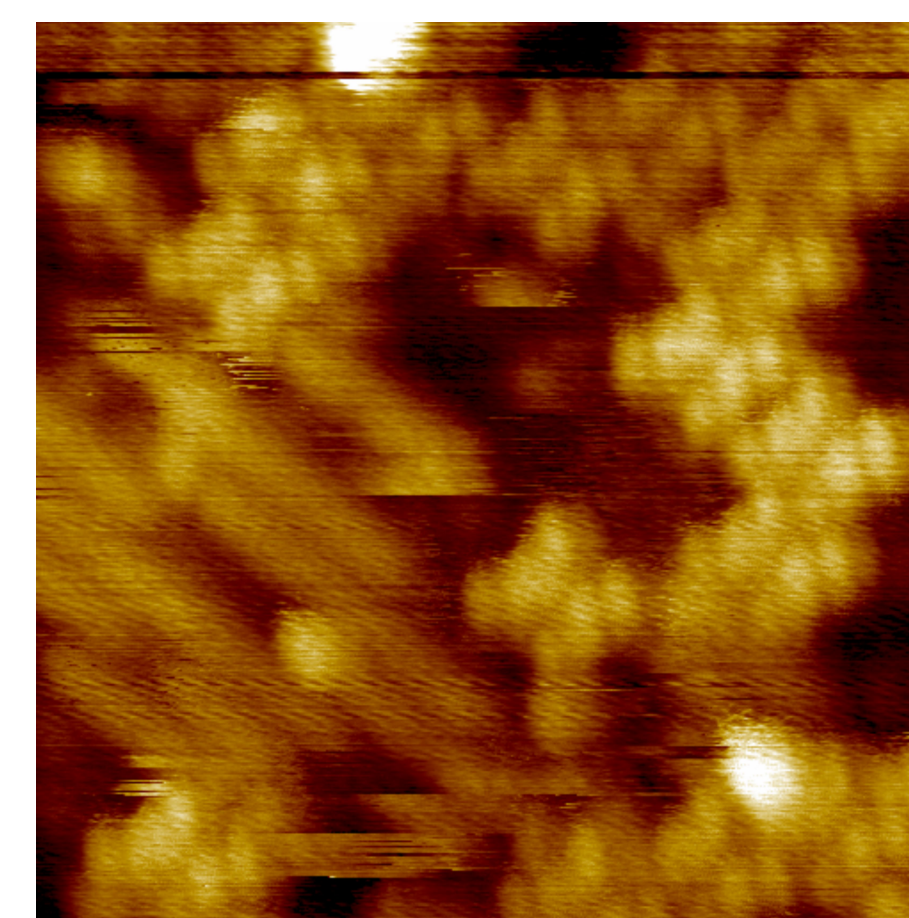
100x100nm, 10pA, 1.5V



25x25nm, 5pA, 1.3V



25x25nm, 5pA, 1.3V



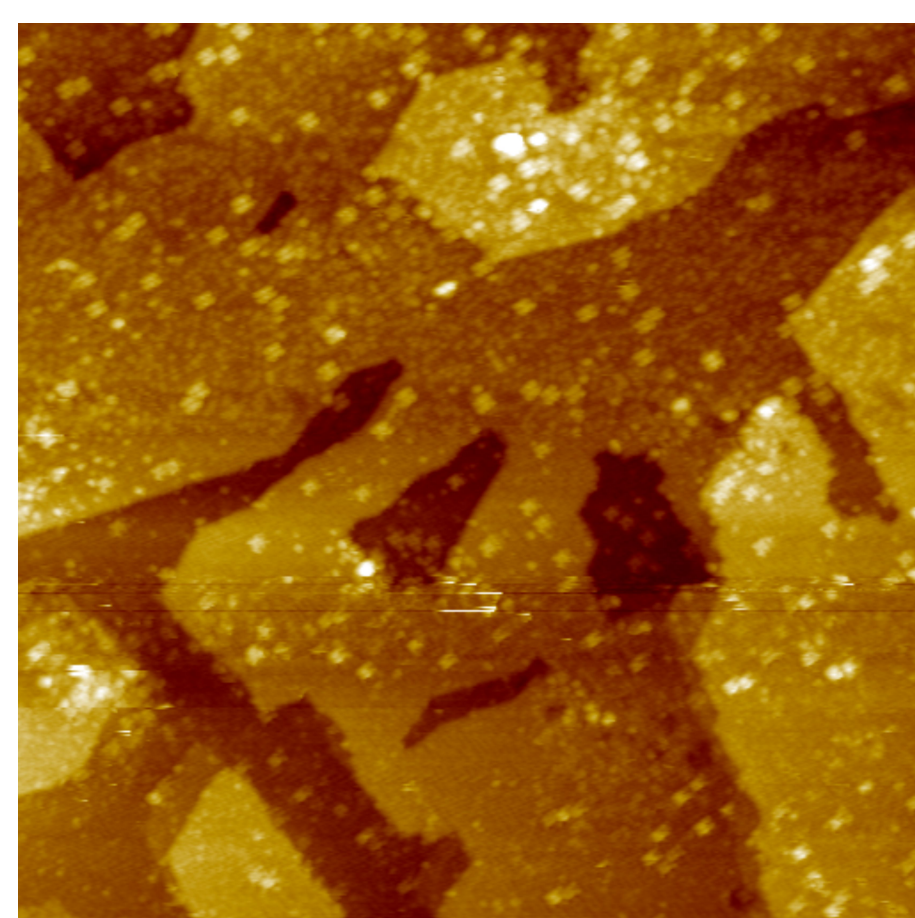
10x10nm, 5pA, 1.3V

Structure dependence on the coverage

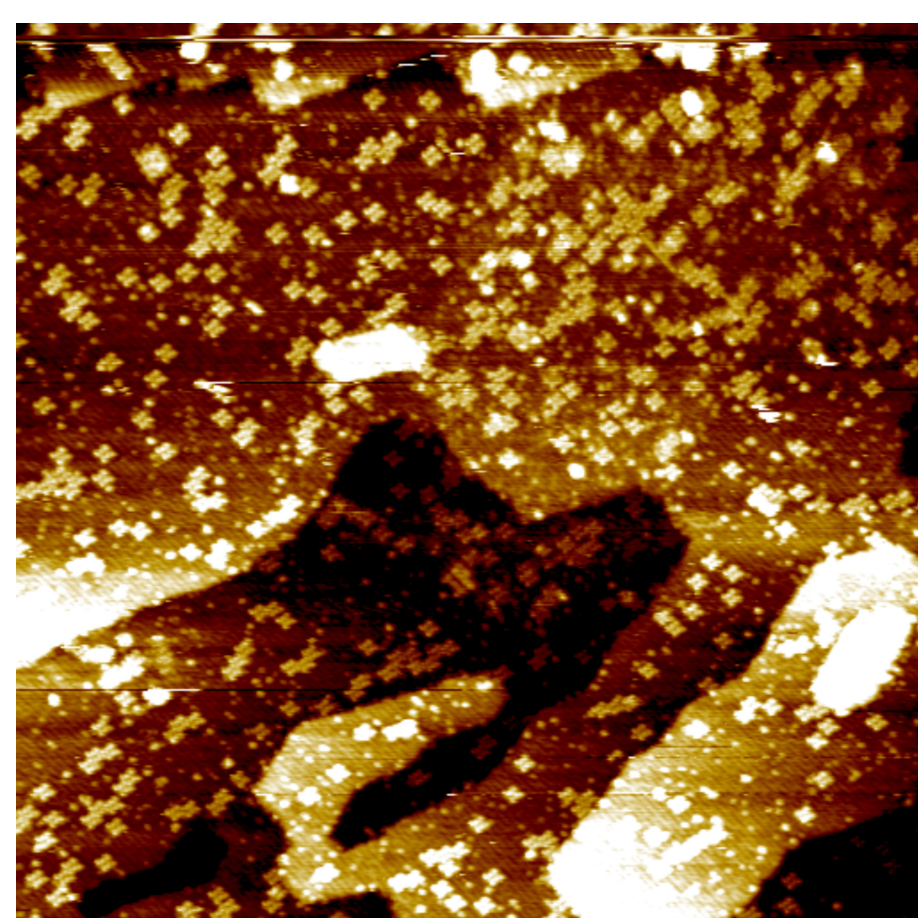
10 min

60 min

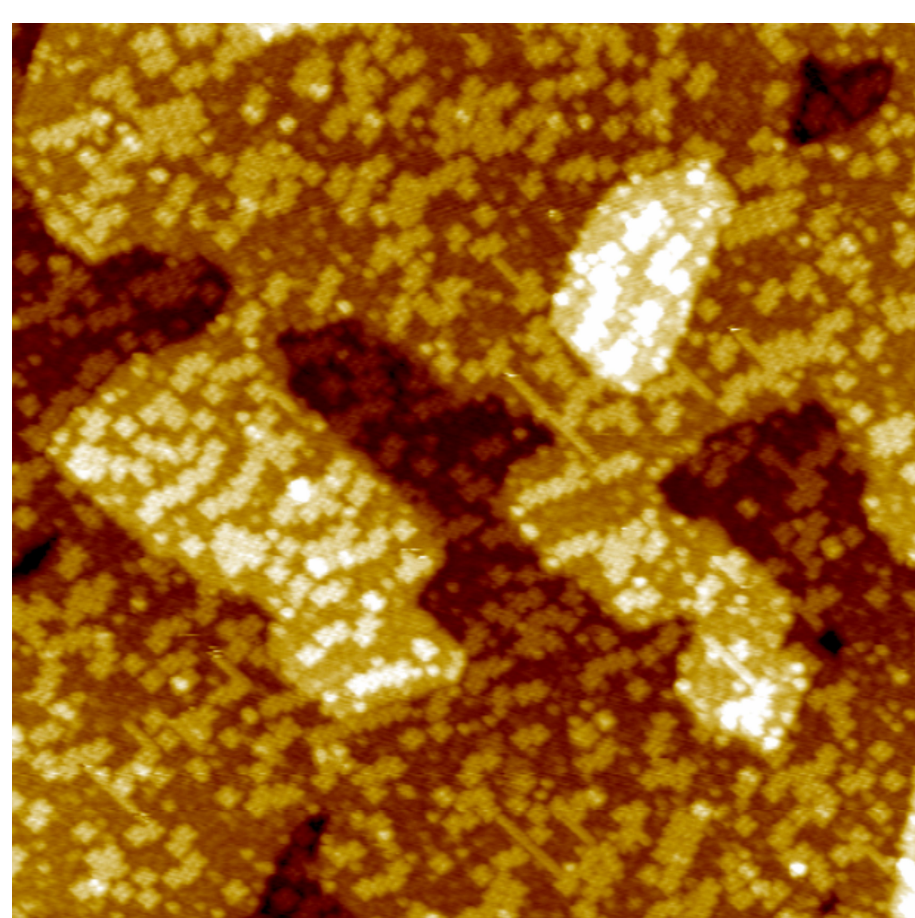
90 min



100x100 nm, 10pA, 2 V



100x100 nm, 10pA, 1.5 V

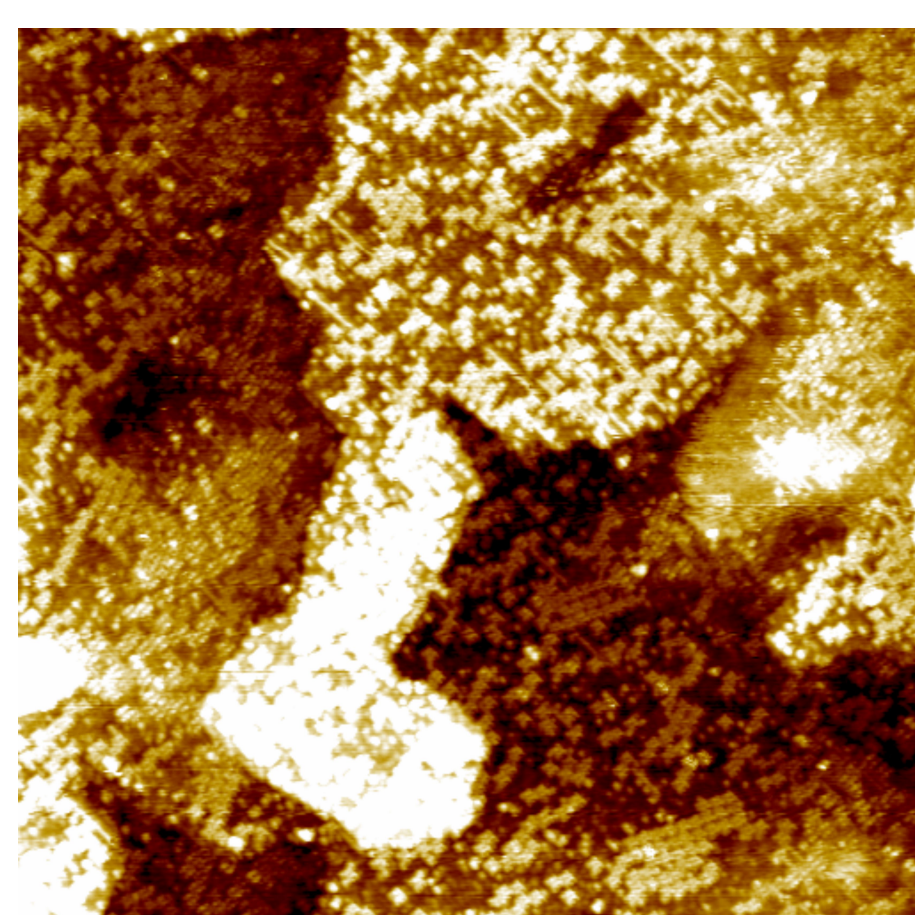


100x100 nm, 10pA, 2 V

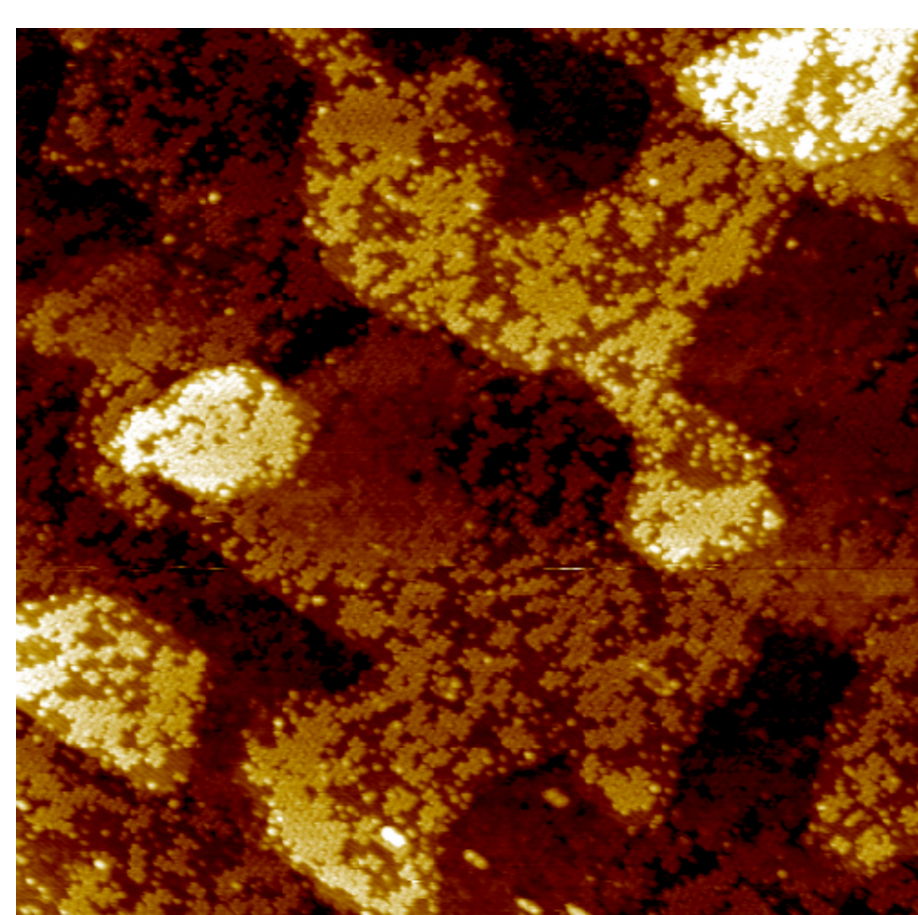
120 min

180 min

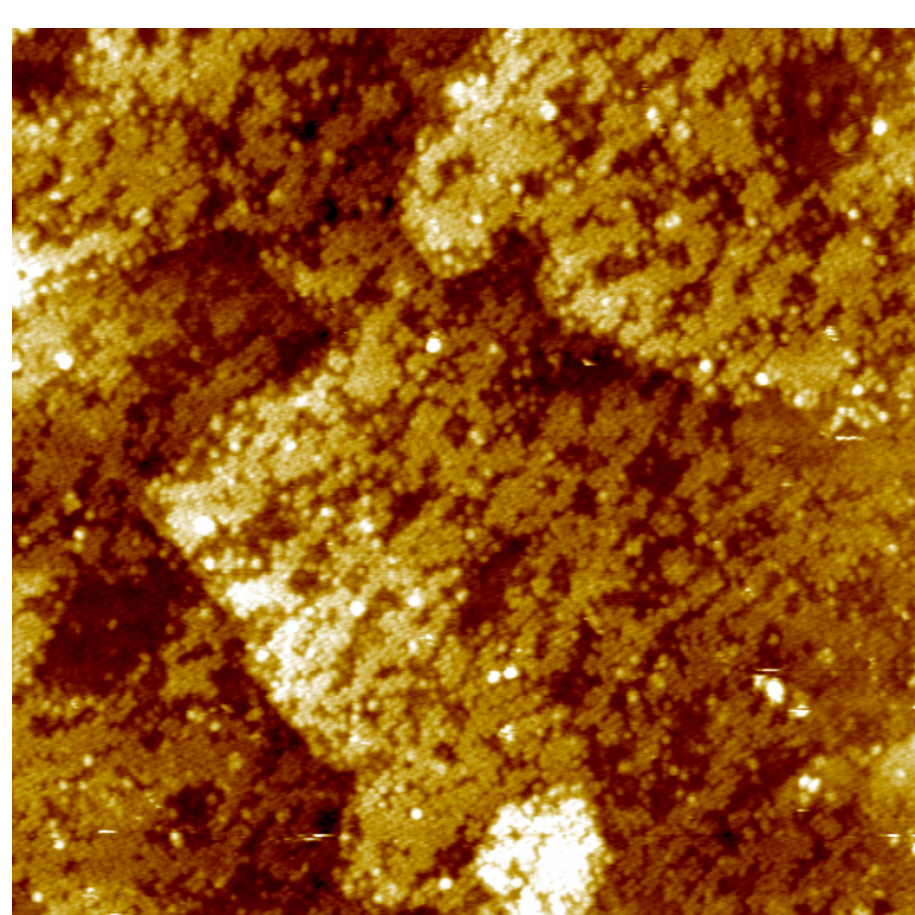
270 min



100x100 nm, 10pA, 2 V

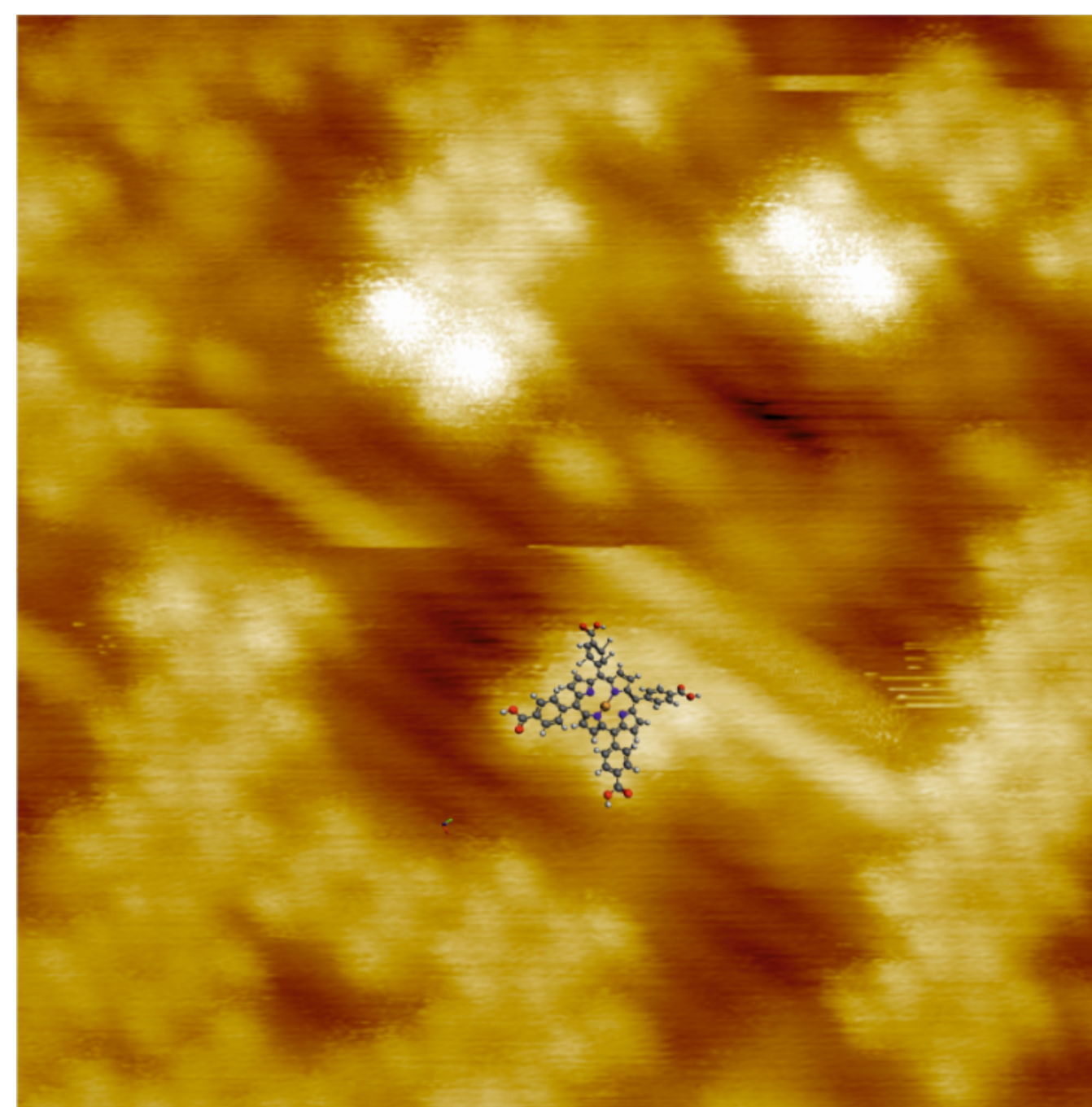


100x100 nm, 5pA, 1.3 V

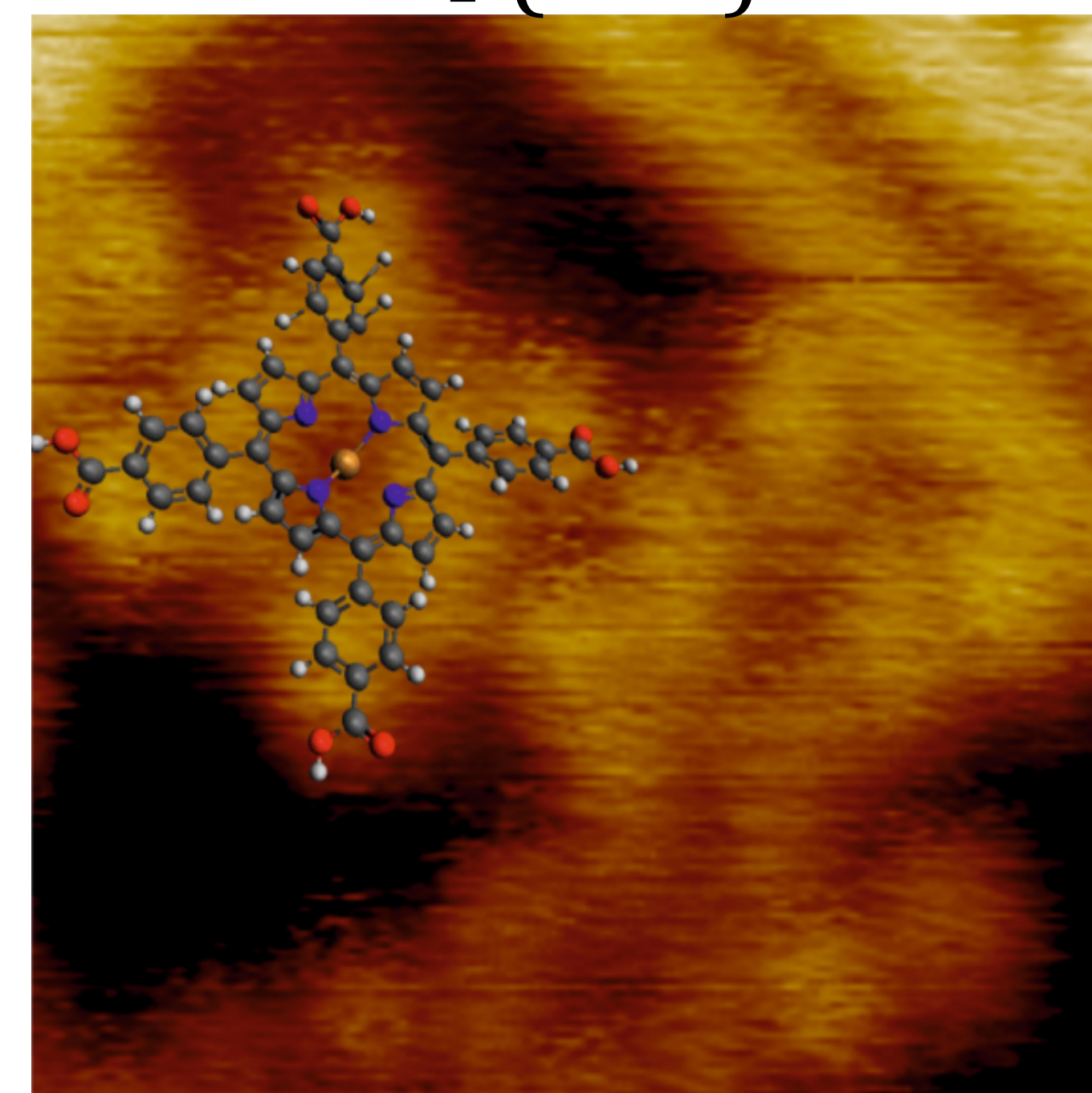


100x100 nm, 5pA, 1.3 V

Molecular structure on TiO₂ (110)



12x12 nm, 70pA, 1.4 V



5x5 nm, 70pA, 1.4 V

Conclusions

CuTCPP/TiO₂(011)

- No regular pattern observed

CuTCPP/TiO₂(110)

- Molecules are bound strongly to the surface
- Ordered in chain
- The carboxylic groups are bound with oxide rows
- Molecules are still bound to the surface after post-deposition annealing above evaporation temperature
- We have observed a saturation of surface coverage

Outlook

The further investigation CuTCPP /TiO₂(110) and CuTCPP/TiO₂(011) systems with using carboxyphenyl-substituted porphyrin with one and two carboxylic groups.

Acknowledgement

This work was supported by a grant from Switzerland through the Swiss Contribution to the enlarged European Union (Joint Polish-Swiss Research Programme) no PSPB-085/2010 “Molecular assemblies on semiconductors and insulating surfaces”. www.molsurf.eu

References:

- [1] A. Hagfeldt, G.Boschloo, L. Sun et al., Chem. Rev. 110,6595-6663, (2010).
[2] A. Karhiravan, R. Renganathan, Journal of Colloid and Interface Science 331, 401-407, (2009)