



Tetraphenylporphyrin on Cu(110)-(2×1)O

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S. Berkebile, R. Resel, M.G. Ramsey, F. P. Netzer

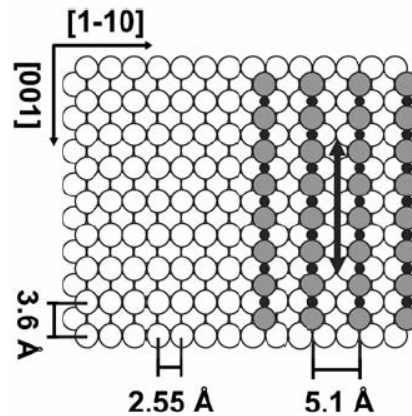
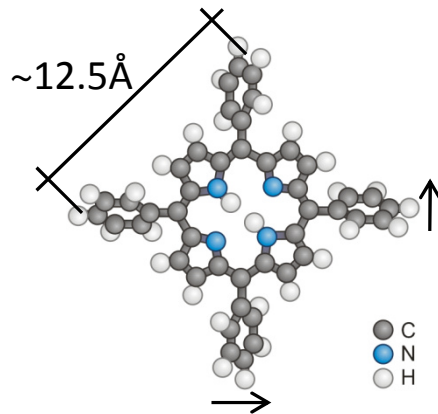
Karl-Franzens University Graz
Institute of Physics
Surface and Interface Physics
Solid-State Theory

ÖPG 2012

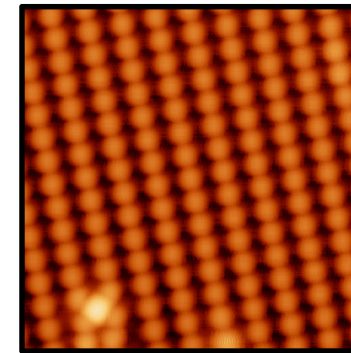
Outline & Substrate

Experiment

- Monolayer Tetraphenylporphyrin (H_2TPP) on $Cu(110)$ - $p(2 \times 1)O$ at $40^\circ C$
- LT-STM (5K)



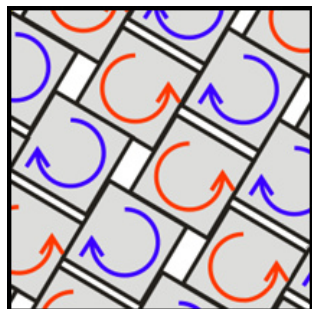
$Cu(110)$ - $p(2 \times 1)O$



50Å

Goals

- The monolayer structure, orientation of the molecules
- Adsorption site

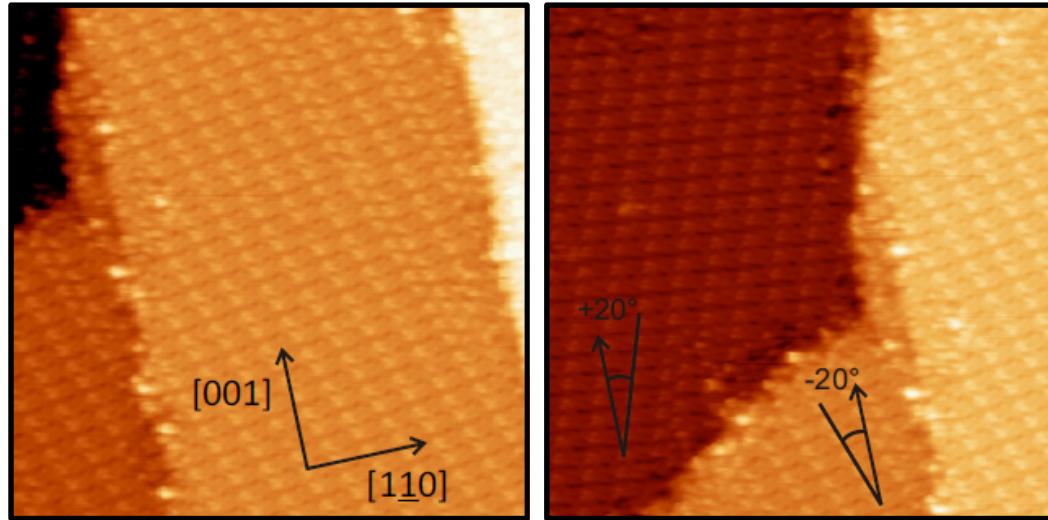


Proposal

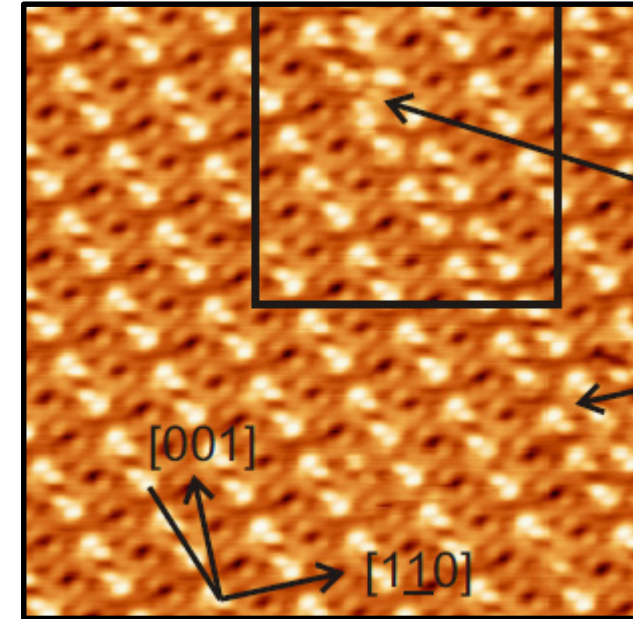
- ML is composed of molecules with alternating chirality!

The monolayer: mirror domains

2 mirror domains



1.3V, 0.1nA, (400×400)Å²

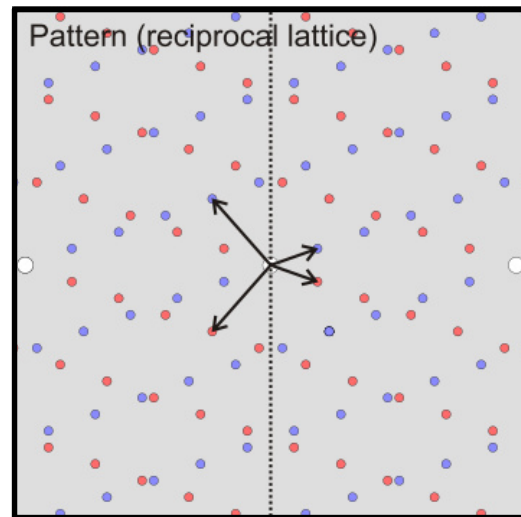


1.4V, 0.1nA, (200×200)Å²

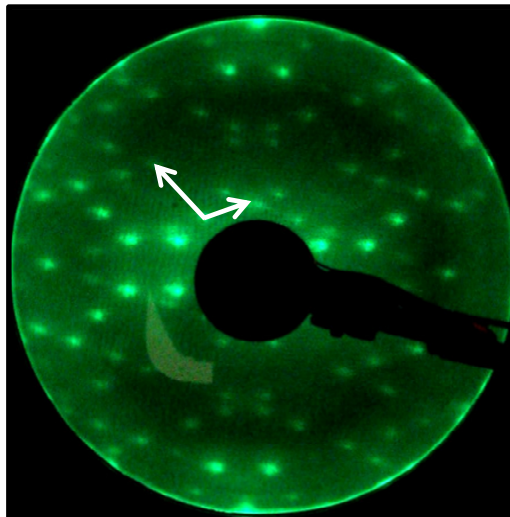
↑
size of a single
H₂TPP



Where are the molecules?



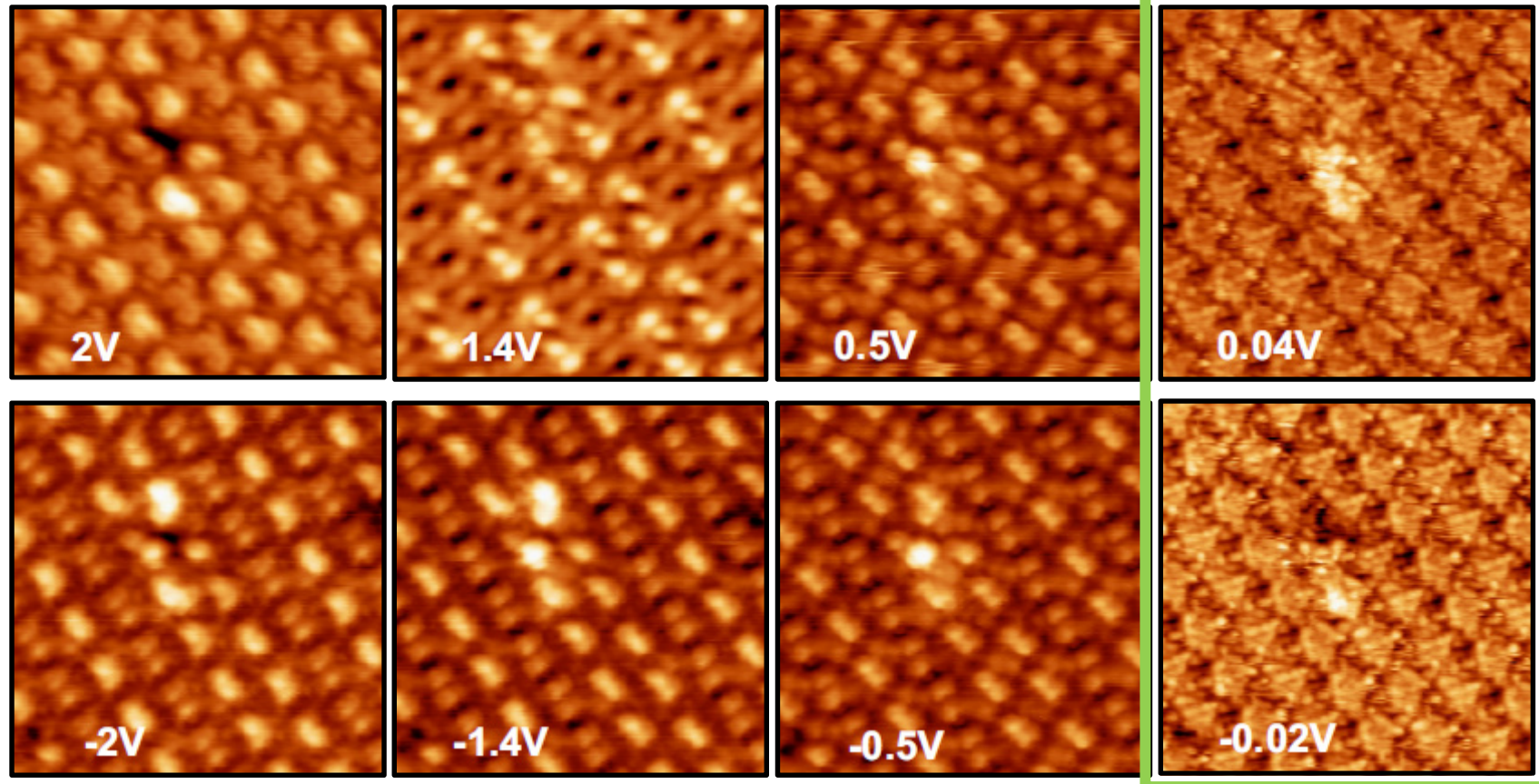
LEEDpat



LEED, 35eV

The monolayer: What do we see?

empty states

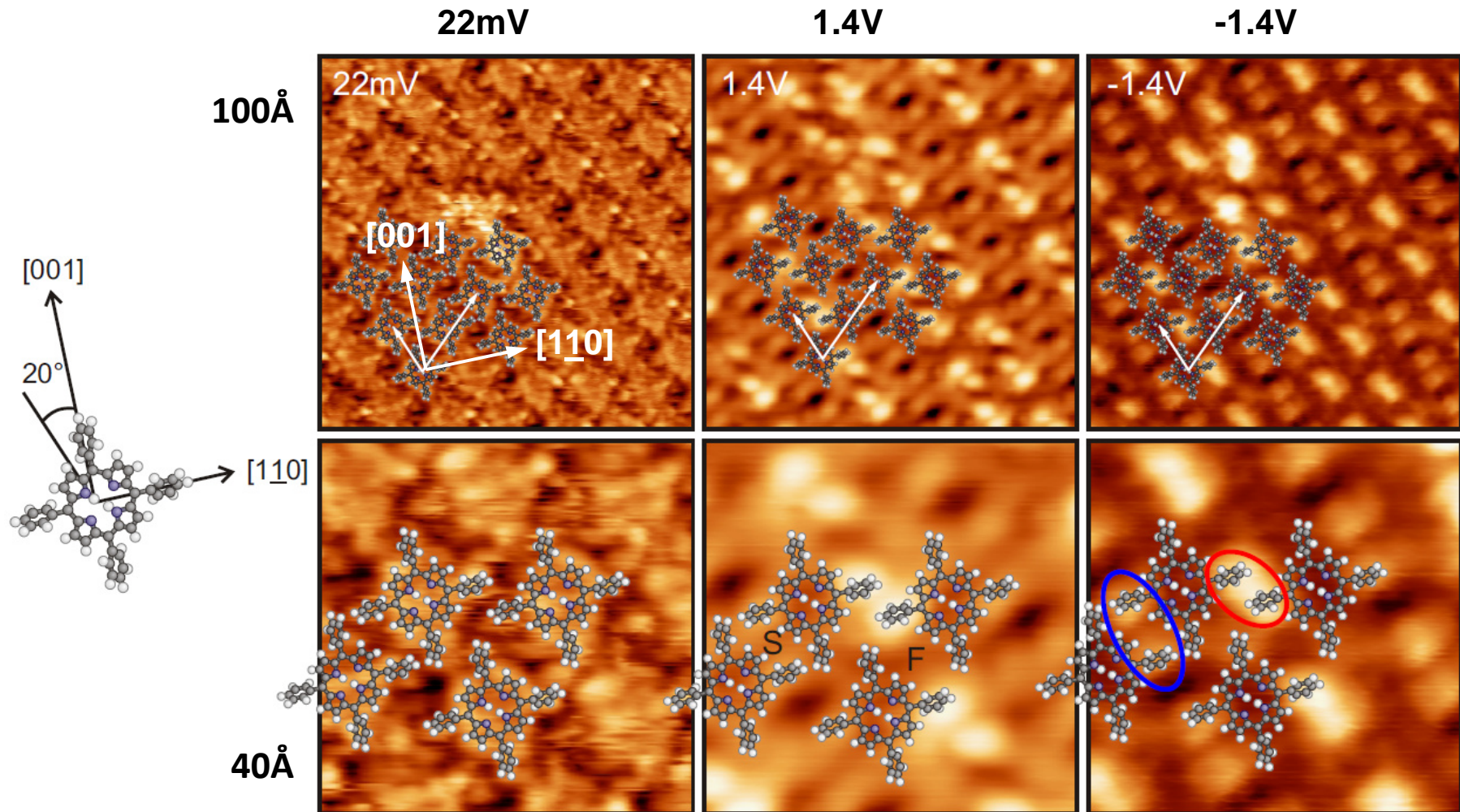


filled states

94pA, (100×100)Å²

- ❖ Molecular structure seen around E_F (all molecules are uniform!)

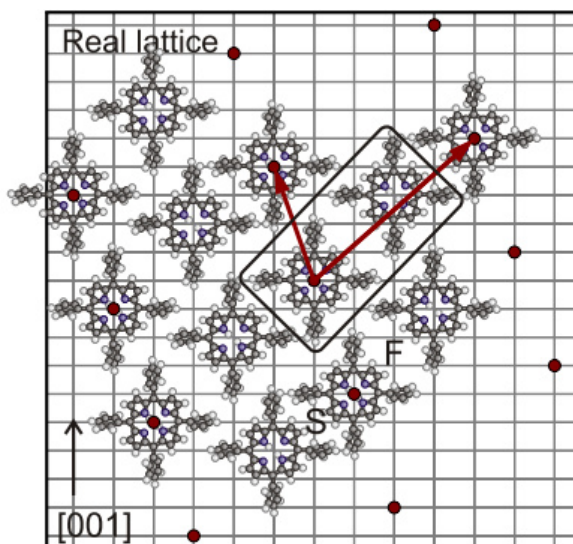
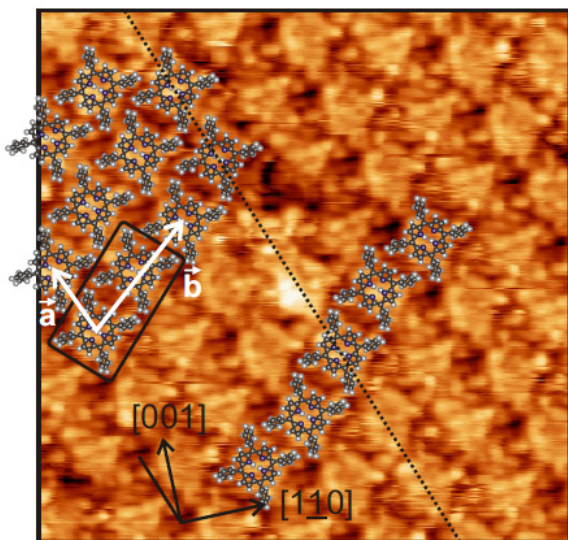
The monolayer



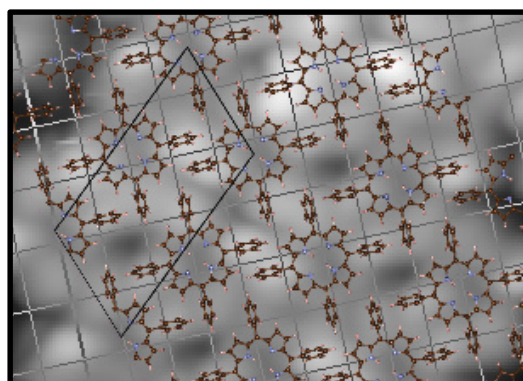
- ❖ Molecular structure seen around E_F (all molecules are uniform!)
- ❖ Some phenyl side groups seen at $>0.5V$

The monolayer structure

Monolayer



adsorption site



$$\begin{pmatrix} 4 & 5 \\ -1 & 4 \end{pmatrix} \begin{pmatrix} a_{[1\bar{1}0]} \\ a_{[001]} \end{pmatrix}$$

molecule #1: (0,0)

molecule #2: (2,3)

- ❖ Unit cell with 2 molecules
- ❖ Both have the same adsorption site
- ❖ Phenyl rings orient the molecules

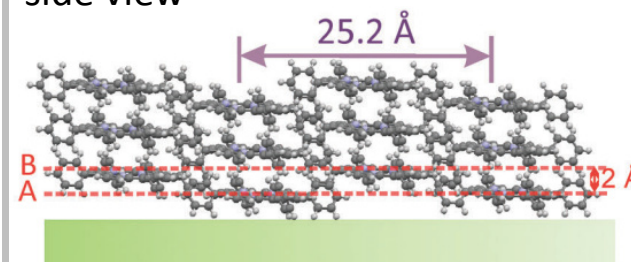


DFT calculations

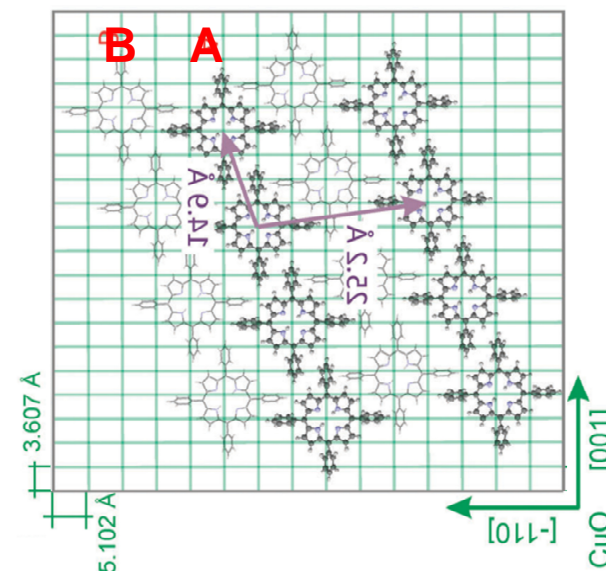
Thick film (37nm)

LEED + XRD: $H_2TPP(5 \underline{10} 3)$

side view



top view

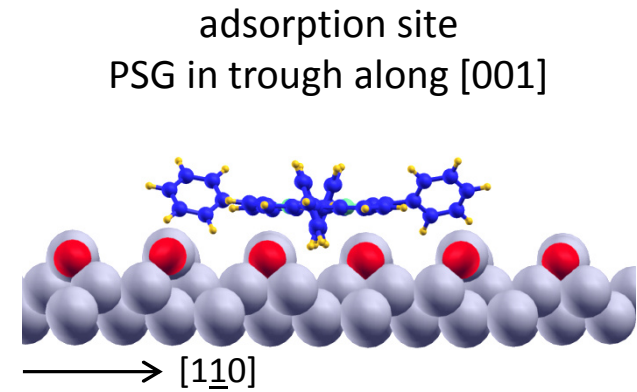
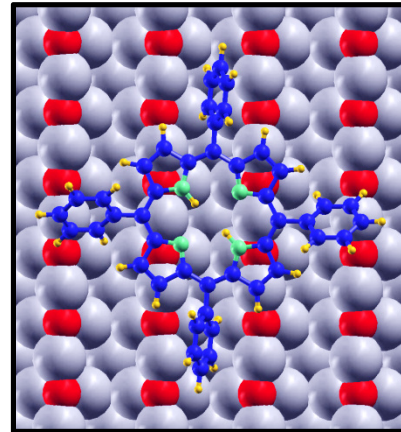


T. Djuric et al., Phys. Chem. Chem. Phys., 2012, 14, 262-272

DFT results for the monolayer

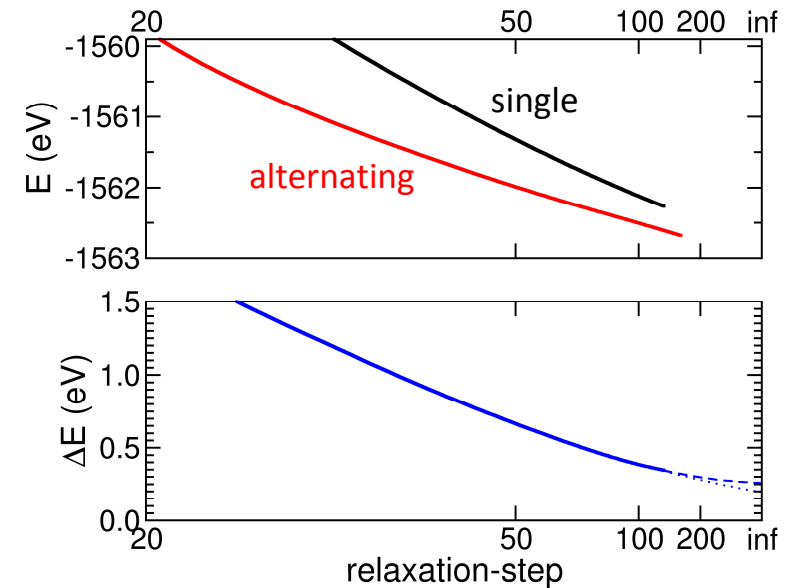
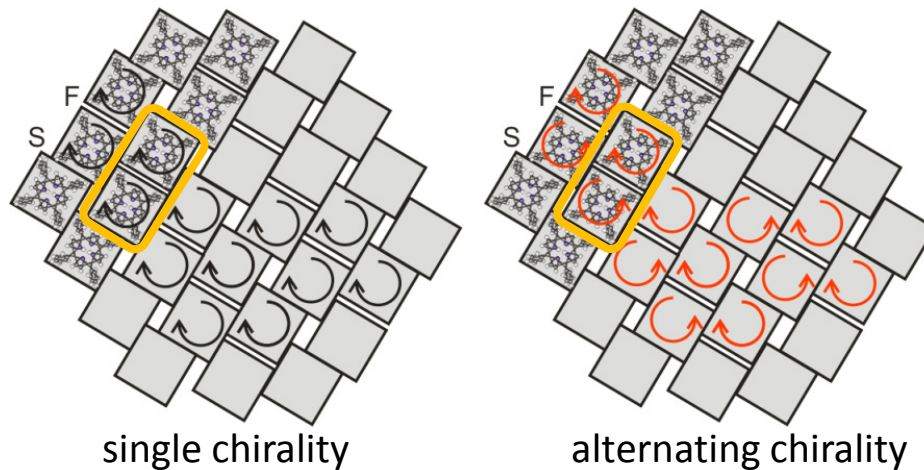
VASP with

- PAW, plane wave cut-off at 500eV
- GGA XC functional
- empirical VdW correction
- corrections according to Grimme
- 3 layers of substrate
- STM: Tersoff-Hamann approach



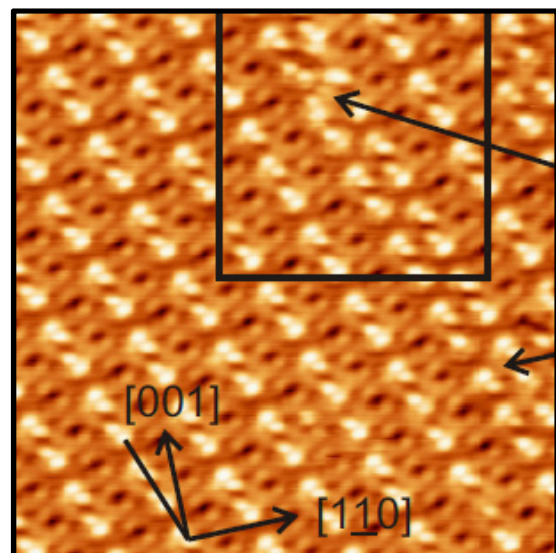
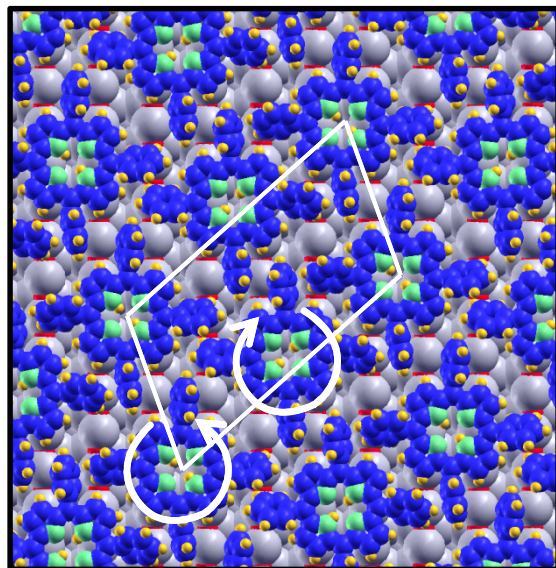
Chirality

- ❖ Comparison of single and alternating chirality
- ❖ Total energy: $\Delta E = 350\text{meV}$

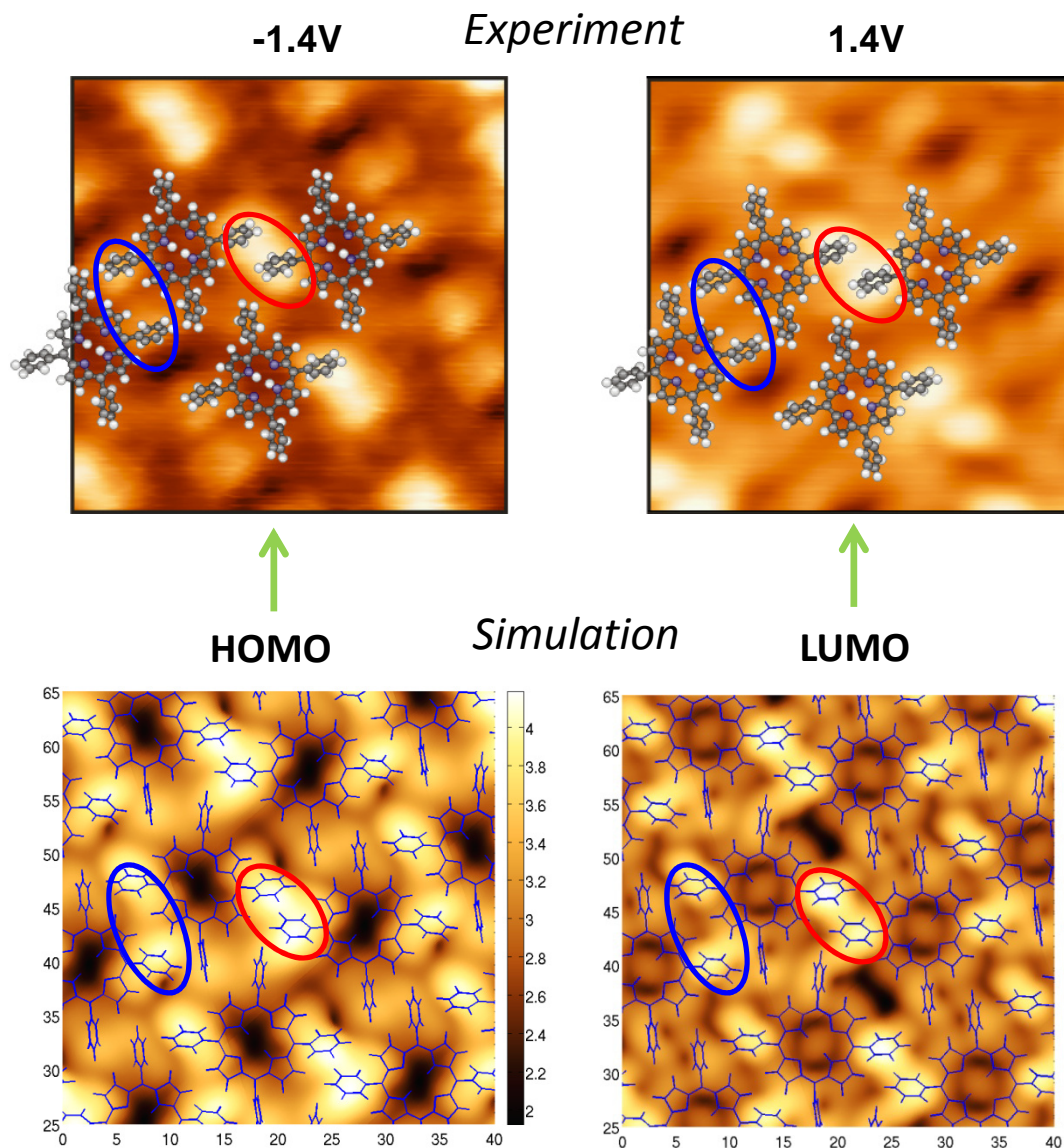


DFT results for the monolayer

Relaxed structure, alternating chirality

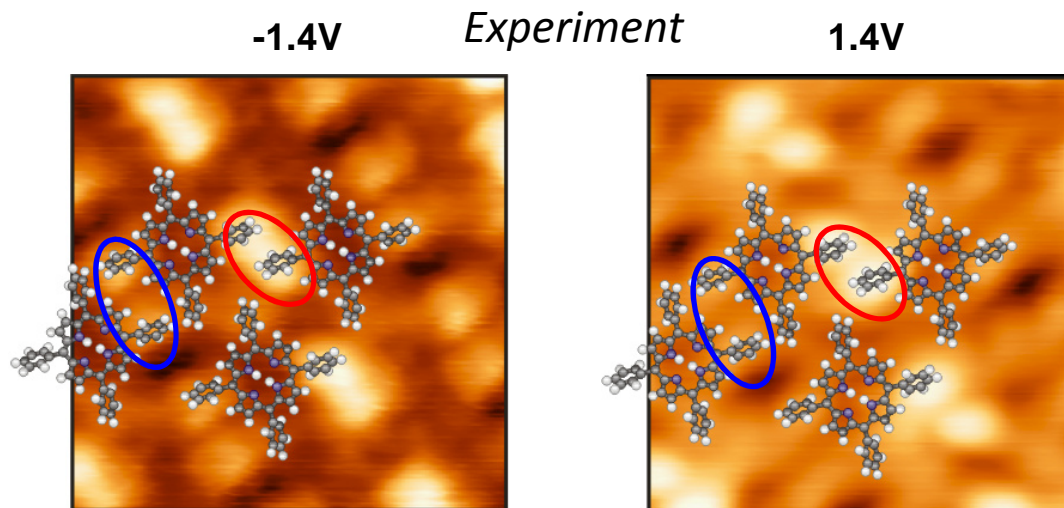
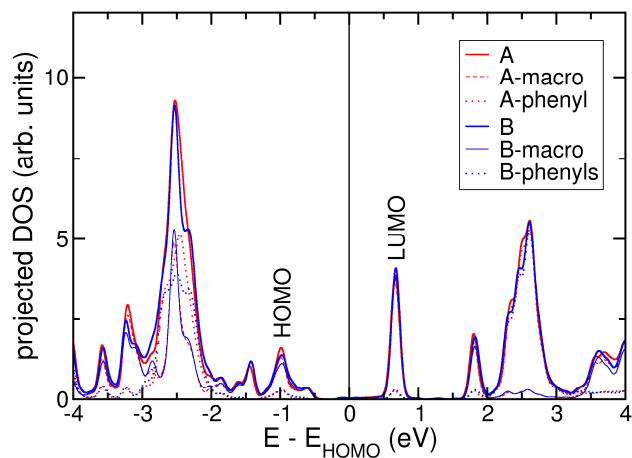
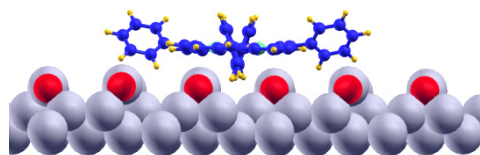
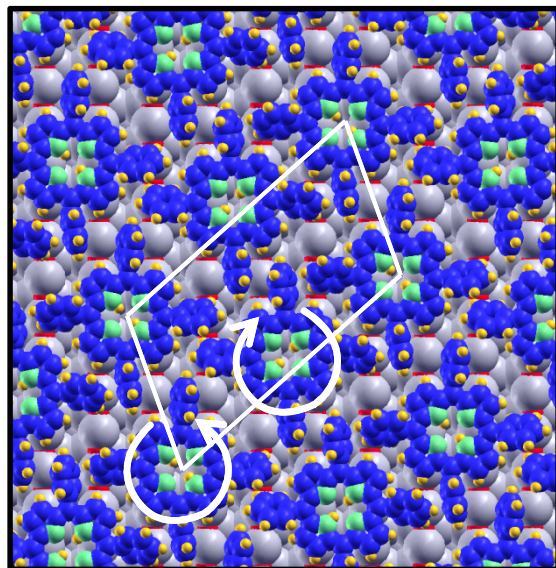


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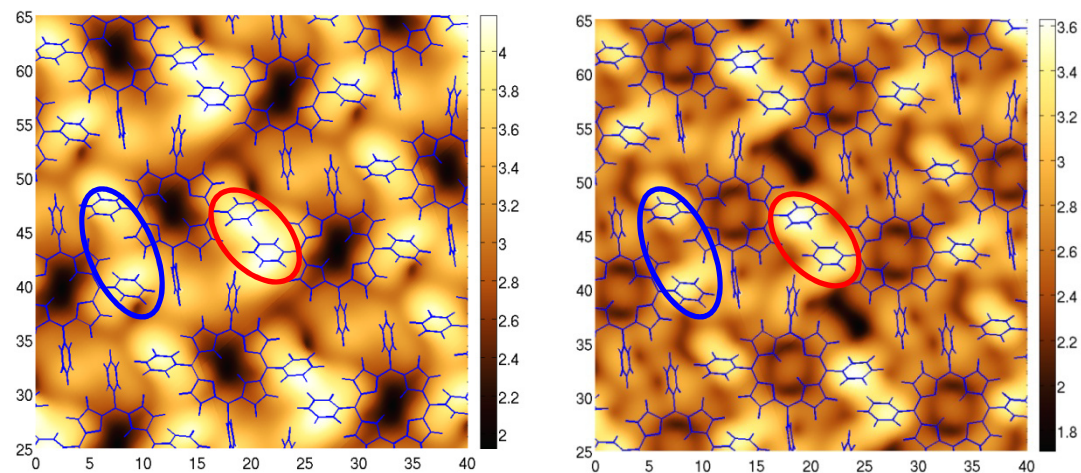


DFT results for the monolayer

Relaxed structure, alternating chirality



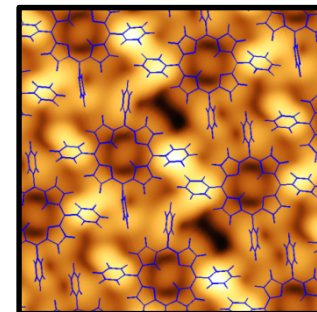
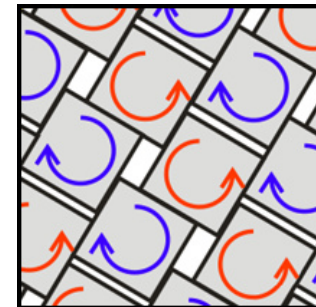
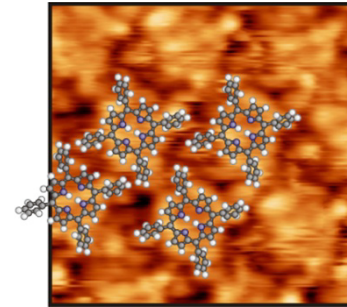
HOMO LUMO



Summary

The monolayer $\text{H}_2\text{TPP}/\text{Cu}(110)$ -(2×1)O

- ❖ ML + STM images are understood!
- ❖ ML is commensurate to substrate and bulk planes that grow on top!
- ❖ ML is a layer of alternating chirality!



Acknowledgements



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Thank you for your attention!

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