Thermally induced polymerization of a perylene derivative on Cu(111)

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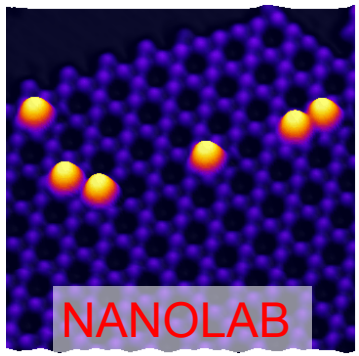
UNI BASEL



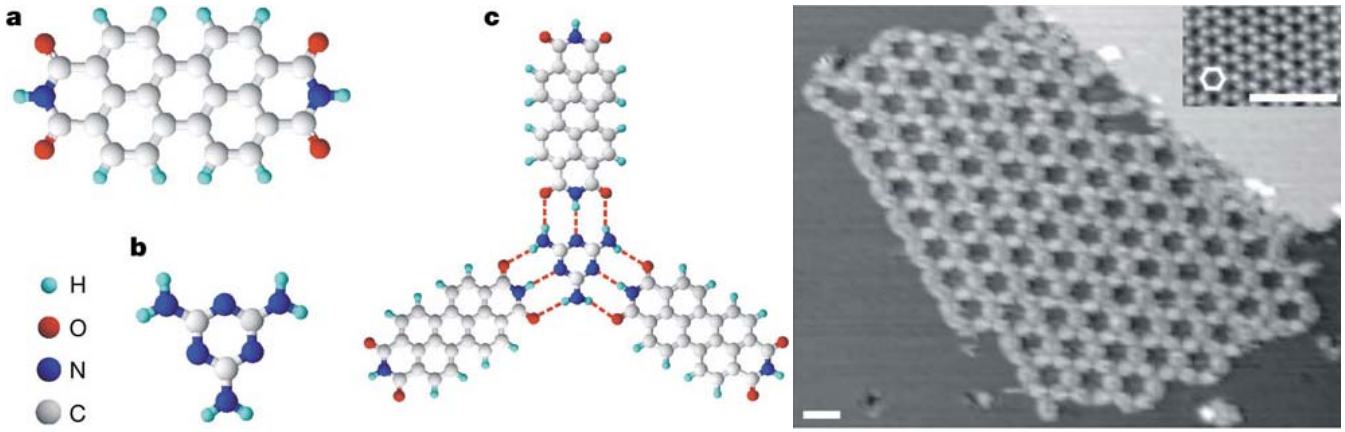
Introduction

Using organic molecules for tomorrow's electronic devices:

- Concept is based on electronic properties of individual molecules and their assembly.
- Research is needed to understand the relationship between molecular structure and potential assembly mechanisms, i. e. investigation of involved interactions to precisely tune desired structures.

International Technology Roadmap for Semiconductors 2005

Examples for 2D molecular assemblies: ***Hydrogen bond***



J.A. Theobald *et al.*, Nature **424** (2003) 1029

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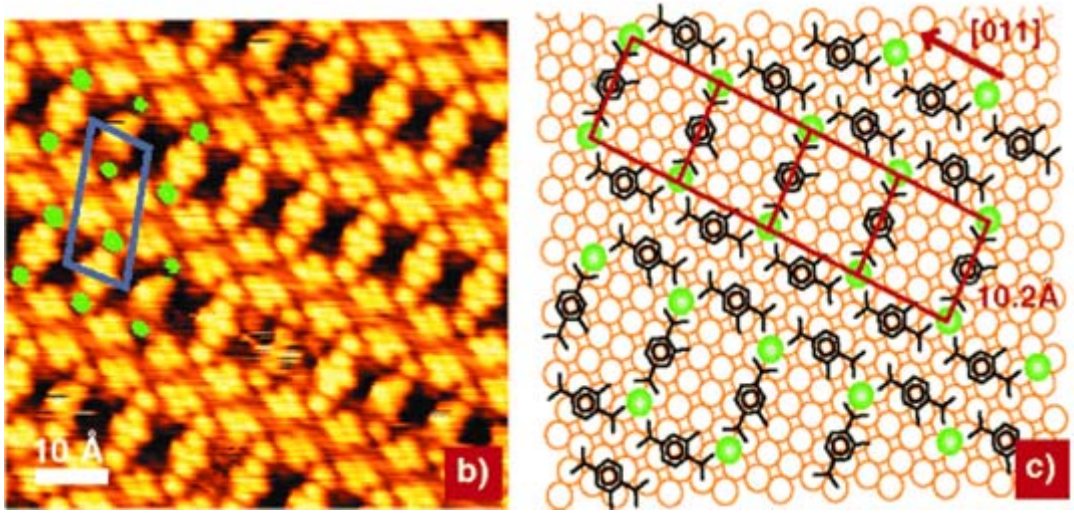
International Technology Roadmap for Semiconductors 2005

Examples for 2D molecular assemblies: ***Metal coordination***



Dmitriev *et al*., Angew. Chem. Int. Ed. **42** (2003) 2670

Introduction

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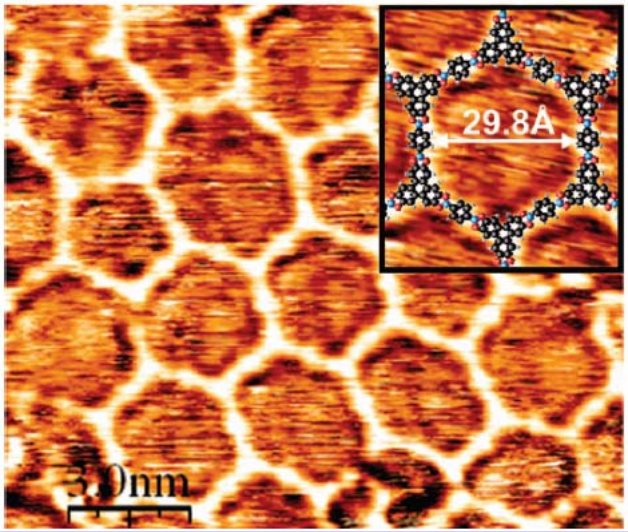
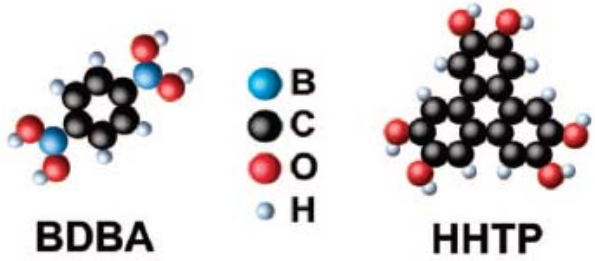
International Technology Roadmap for Semiconductors 2005

Examples for 2D molecular assemblies: ***Covalent bonding***

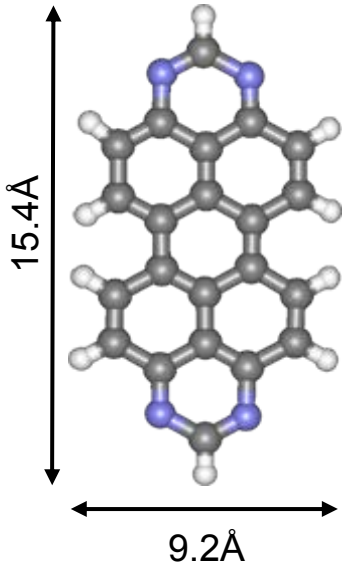




N.A.A. Zwaneveld, *et al.*, JACS **2008**, (2008) 6678.

Introduction

- Molecule: A perylene derivative with a pyrimidine end group (TAPP)
- Substrate: Cu(111).



TAPP
1,3,8,10-tetraazapero-
Pyrene.

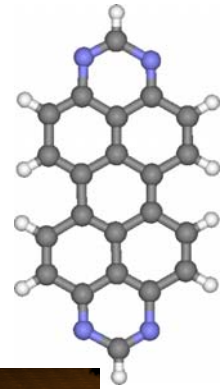
- Hydrogen
- Carbon
- Nitrogen

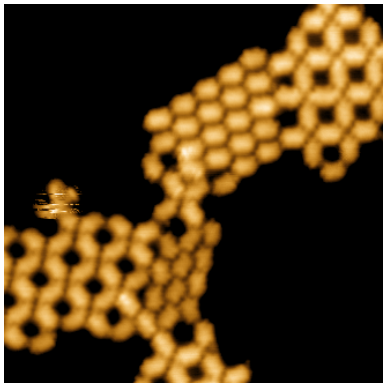
- Preparation and analysis under UHV conditions (base pressure: 10^{-10} mbar)
- Molecules were evaporated from a crucible and the rate was controlled by a quartz crystal microbalance.

- Experimental techniques: LT-STM at 77K, 5K and ESCA chamber.

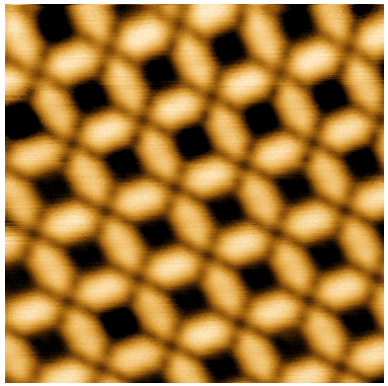
Different TAPP assemblies on Cu(111)

- Annealing to 150°C: Observation of exclusively porous network
- Below: Coexistence of closed-packed assemblies and porous network
- Above: Porous network replaced by chains

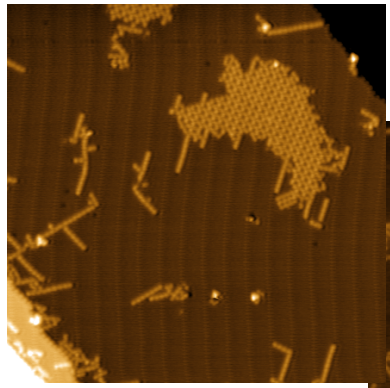




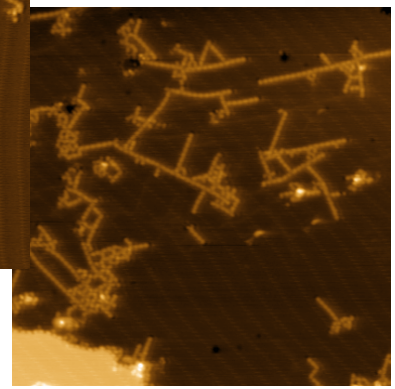
17x17 nm²



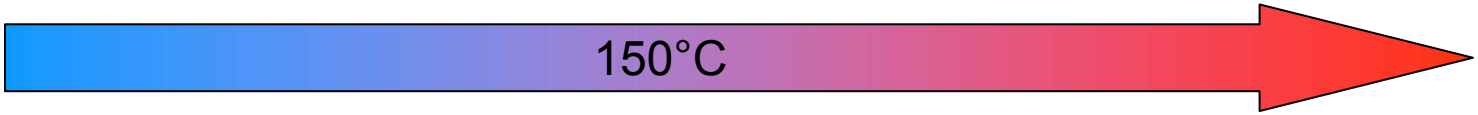
8x8 nm²



86x86 nm²



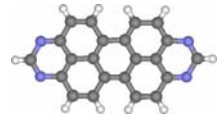
79x79 nm²



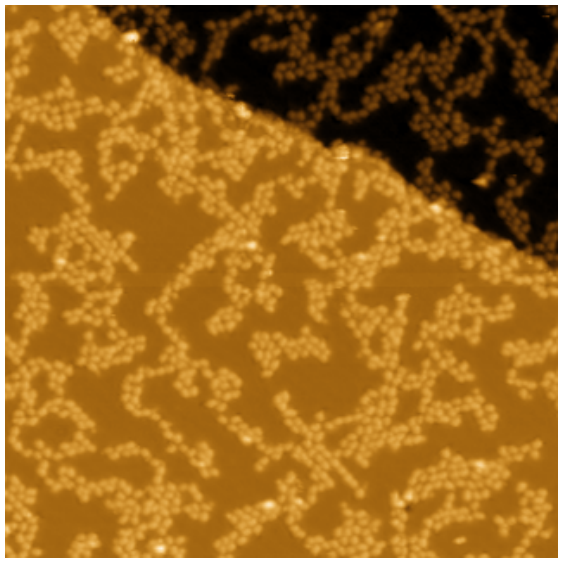
Deposition of TAPP with sample at -100°C and subsequent annealing to the different temperatures.

TAPP/Cu(111) - disordered

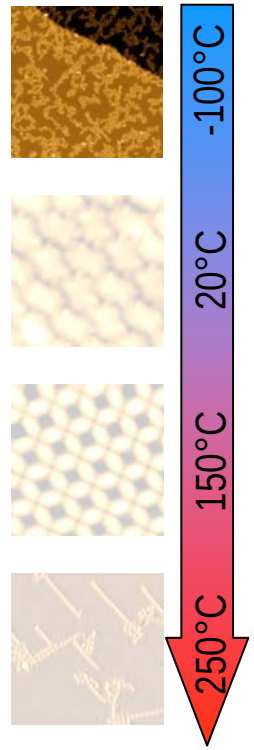
- Deposition of TAPP on Cu(111) with sample held at -100°C



No ordered structure

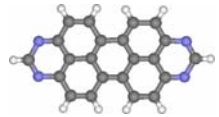


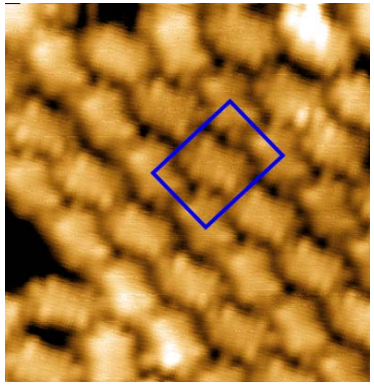
66x66 nm²



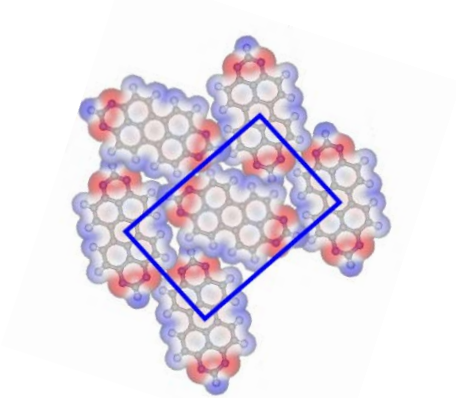
TAPP/Cu(111) – vdW-interaction

- At room temperature: formation of closed packed assemblies
- Formation of small islands with defects
- Tentative model: interaction via vdW-forces

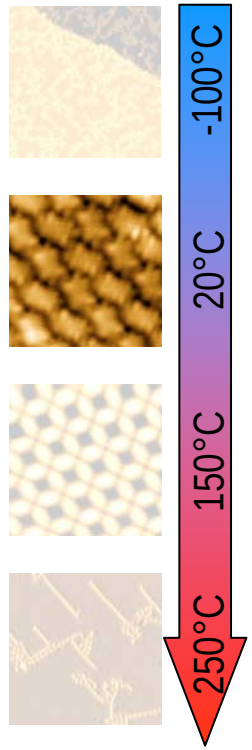


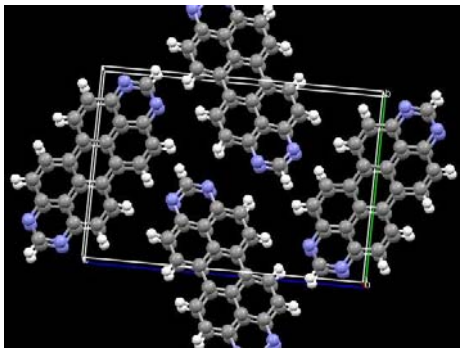


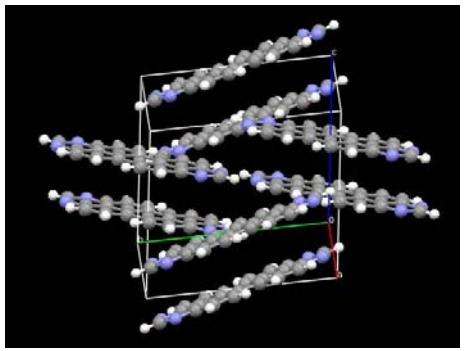
6.3x6.3 nm²



Tentative model



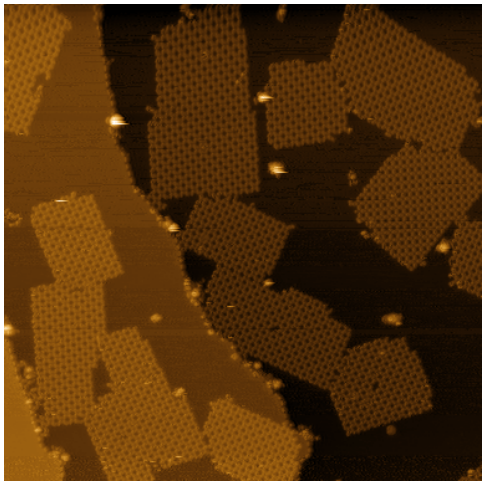




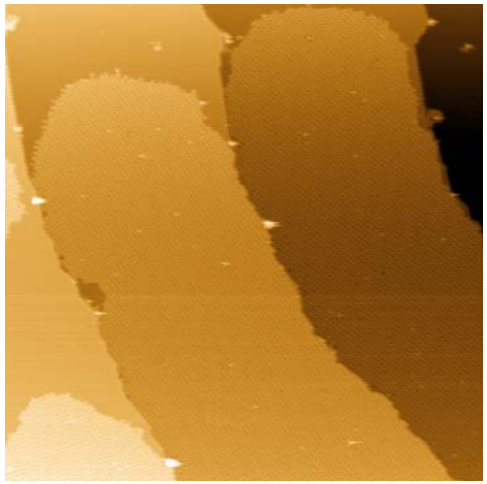
Surface assembly resembles the crystal structure of TAPP

Crystal structure of TAPP: S. Martens, T. Riehm, L. H. Gade

TAPP/Cu(111) – porous network

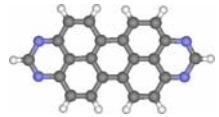


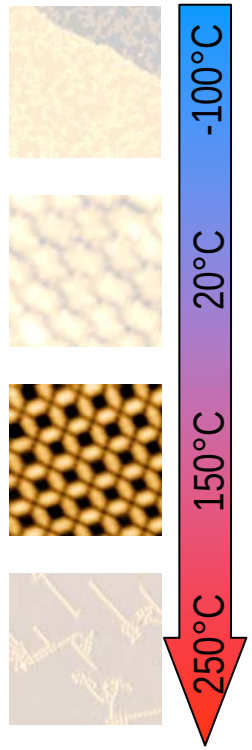
100x100 nm²



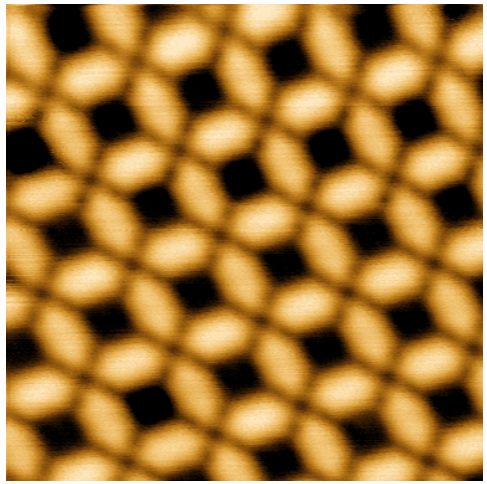
165x165 nm²

Coverage





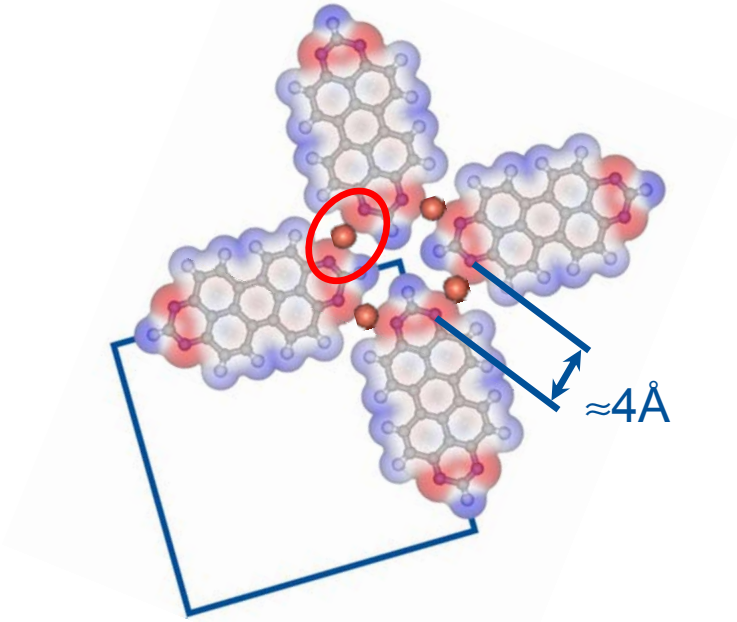
8x8 nm²

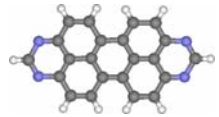


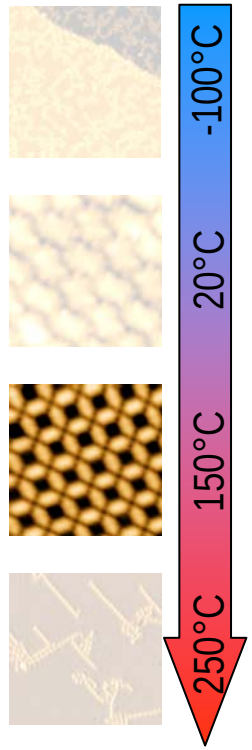
- Annealing at 150°C: Formation of an open rectangular network
- Increasing the coverage and subsequent annealing leads to large islands

The porous network in detail

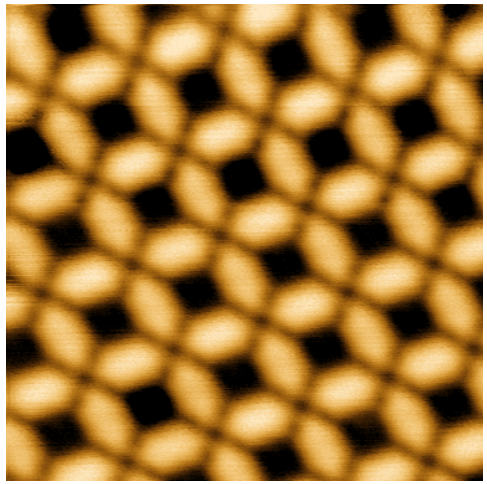
- LEED to determine the size of the unit cell: 1.79 x 1.68 nm², angle: 89.4°
- Commensurate structure of TAPP on Cu(111) surface







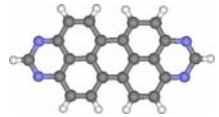
8x8 nm²



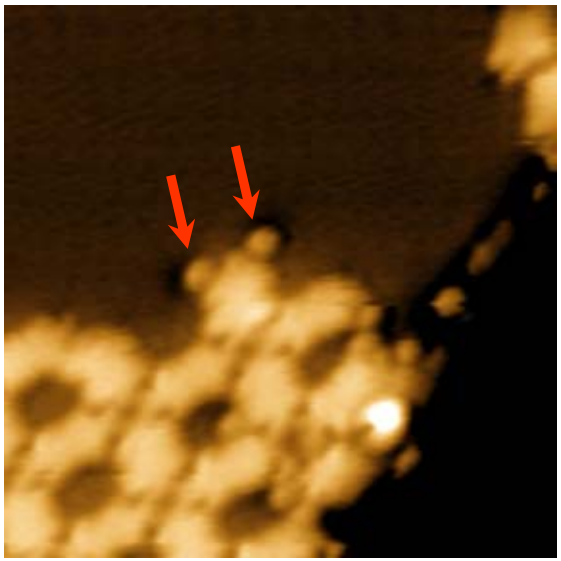
- Coulomb repulsion between nitrogen atoms of neighbouring molecules

- Explanation: Coordination bonds via Cu-atoms

TAPP/Cu(111) – metal coordination bonds



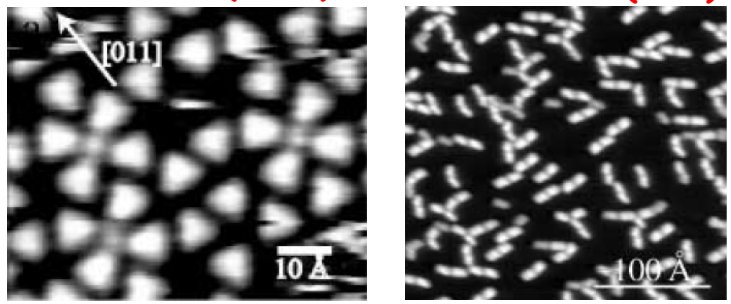
- Cu atoms could not be observed inside the rectangular TAPP network, but sometimes at its edges.



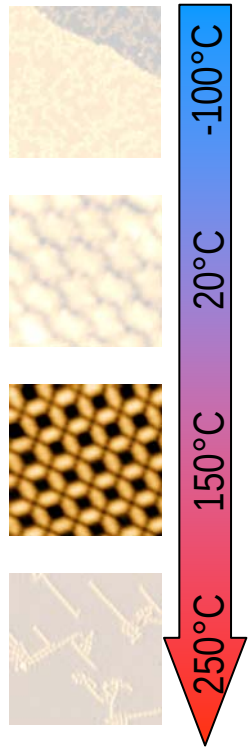
7.5x7.5 nm²

STM-image recorded after sample annealing to 40°C

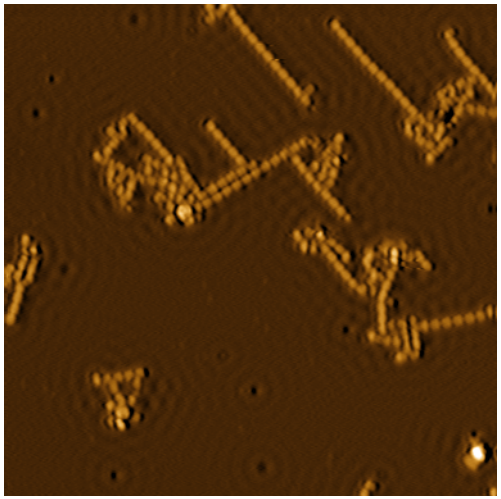
TMA/Cu(100) PVBA/Cu(111)



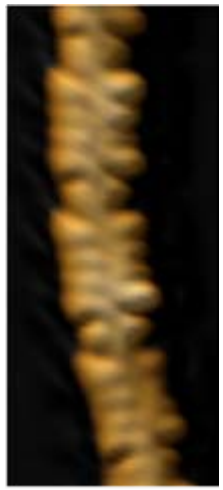
Barth *et al.*, Appl. Phys. A, **2003**, 76, 645



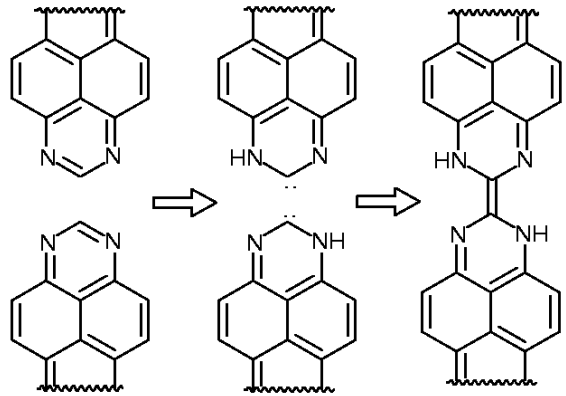
TAPP/Cu(111) – Formation of chains

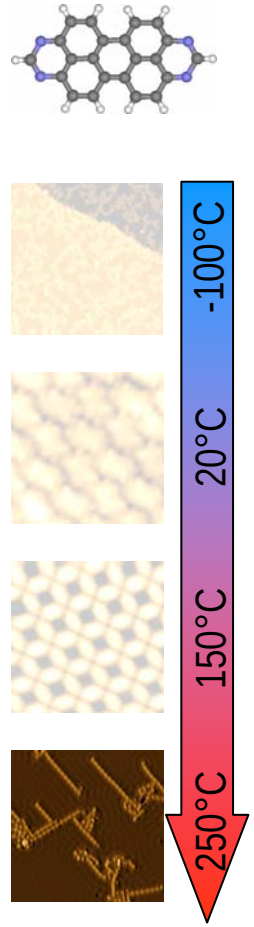


50x50 nm²



1.8x4 nm²

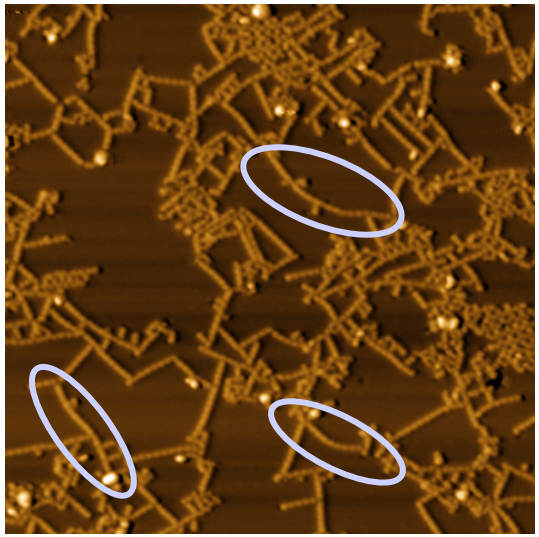




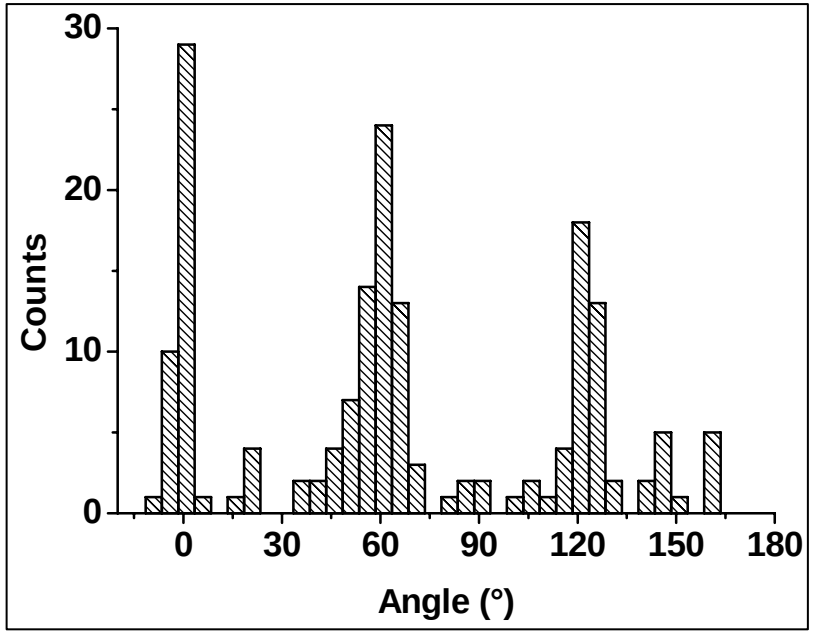
- Annealing at 250°C: Polymerisation of TAPP
- Thermally induced tautomerisation of pyrimidine end group forms a carbene
- Covalent linkage of these radicals leads to the formation of chains
- Confirmed by gas-phase calculations: T. Riehm, L. H. Gade

M. Matena *et al.*, Angewandte Chemie Int. Ed., **2008**, 47, 2414

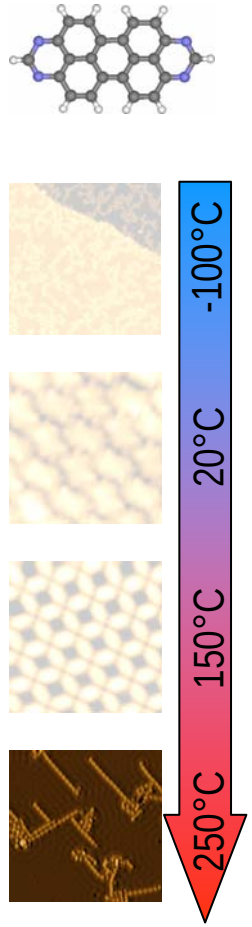
TAPP/Cu(111) – Formation of chains



80x80 nm²



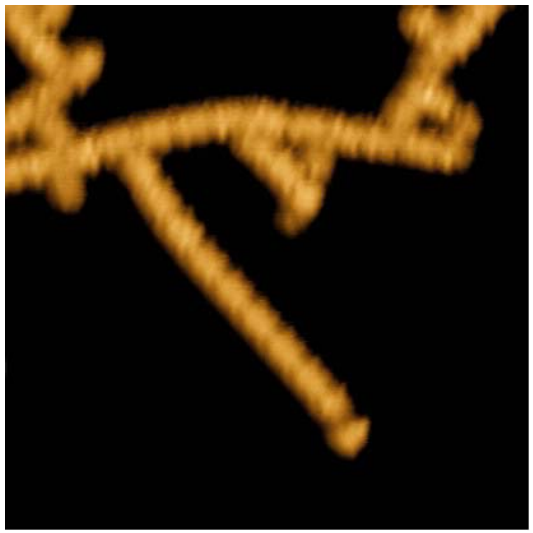
Histogram showing the directions of alignment of 178 chains at low coverage.



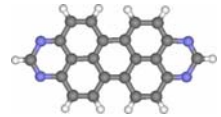
- Chains arrange in curves ⇒ first indication for a dominating molecular interaction

TAPP/Cu(111) – Formation of chains

- Tip is used to bend a chain which stays intact during this process



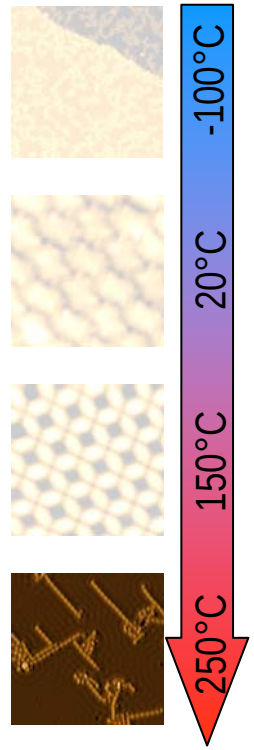
16x16 nm²



- Monomer distance (STM): 12.3 Å
- Monomer distance (gas-phase calculation): 12.7 Å
- Substrate commensurate? 5 x 2.55 Å = 12.8 Å

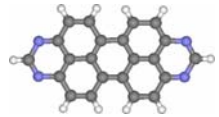
Substrate plays a role in chain formation.

Chains not observed in Ag(111).

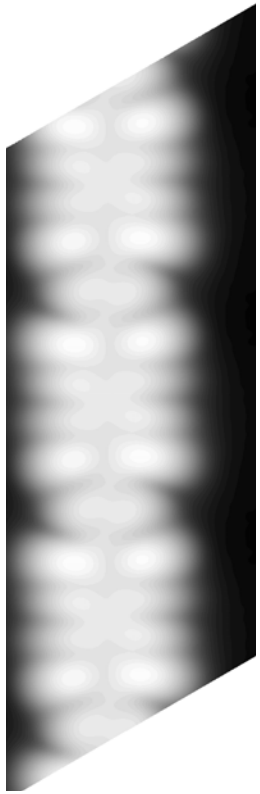


Chains/Cu(111) – Calculations

DFT calculations: J. Bjork, M. Persson



1.8 x 4 nm², V_s = -0.6 V



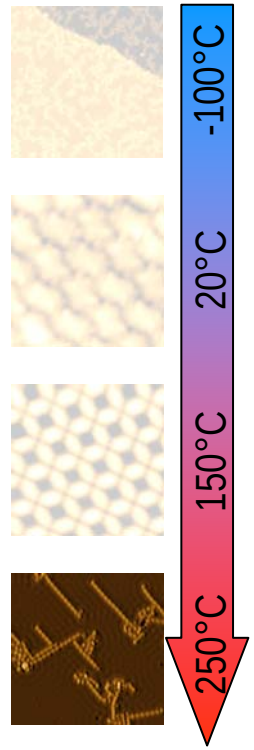
Simulated STM-image for small biases

- Monomers are more strongly bound to each other than to substrate

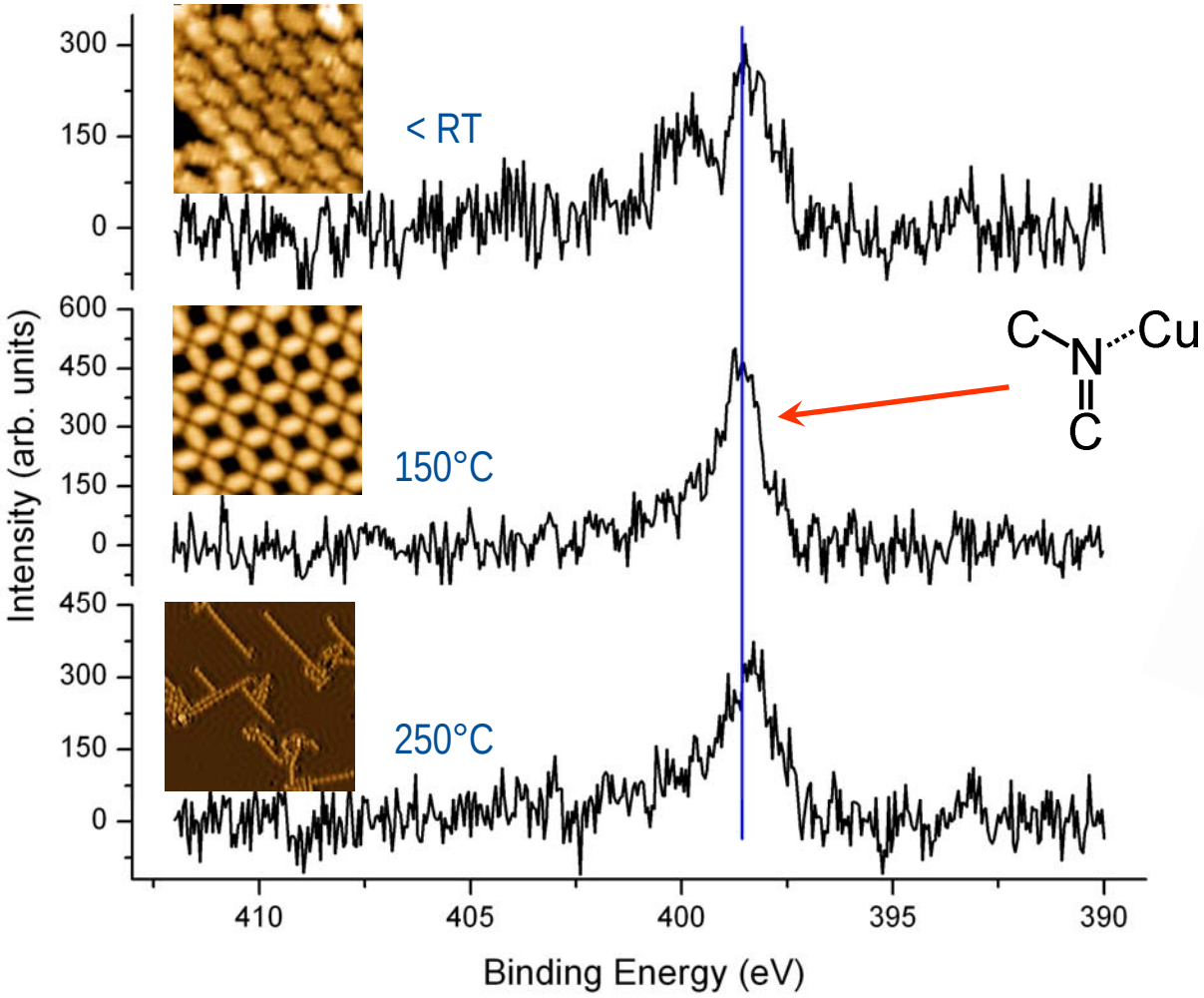
Formation of the chains:

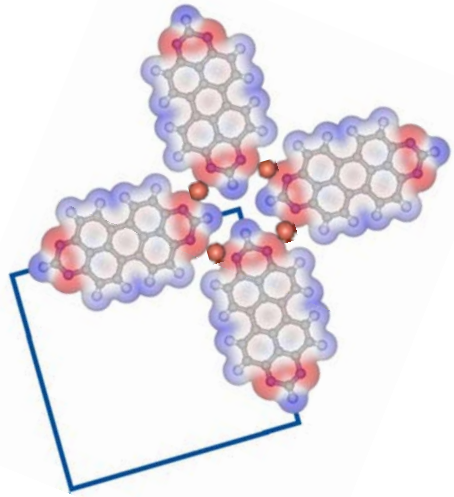
1) "Commensurate Formation": Alignment along the high symmetry directions

2) After the formation: Rearrangement of the chains (e.g. curves) due to mutual interactions



XPS: The N1s peak





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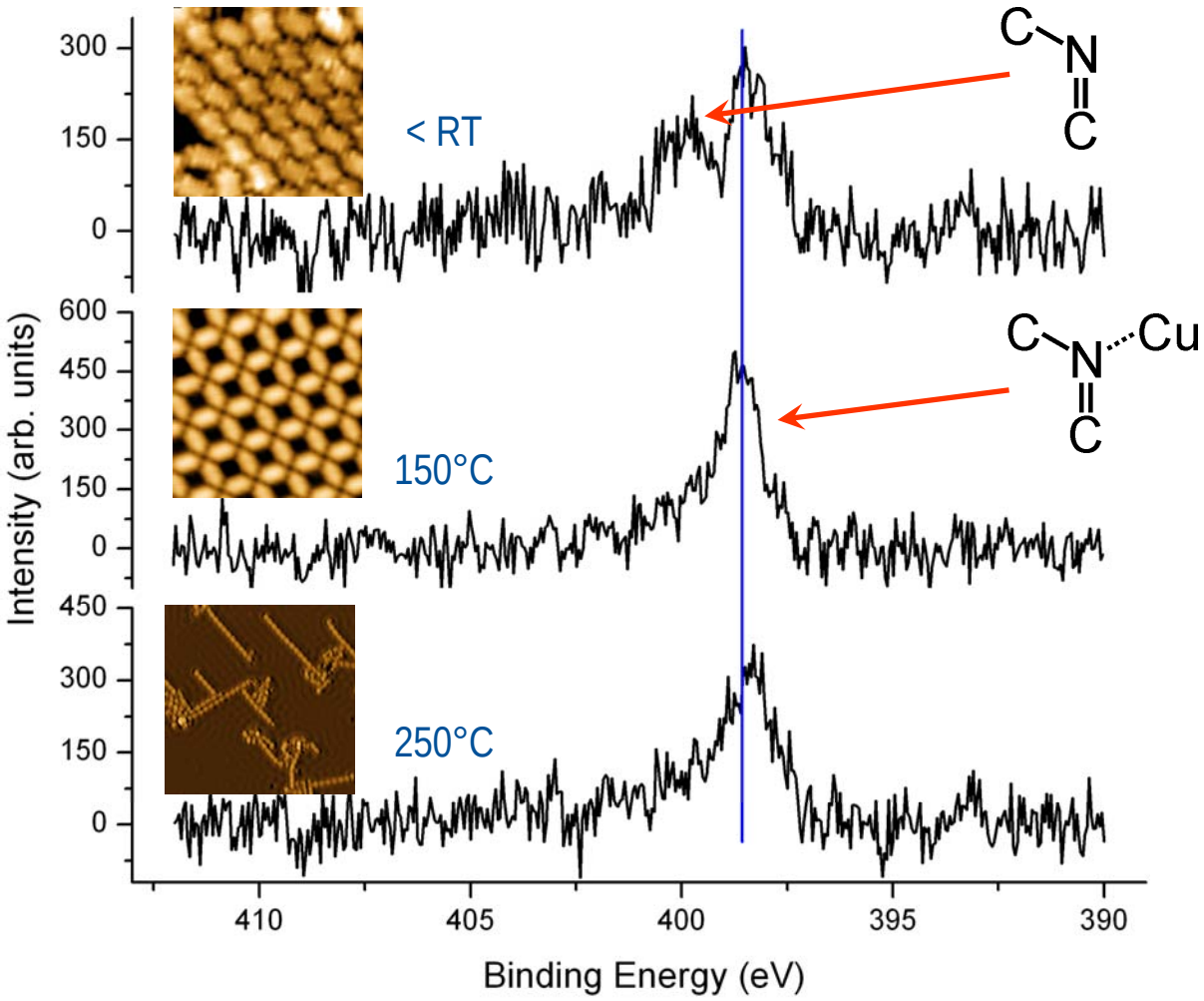

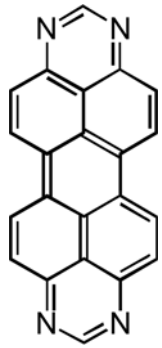

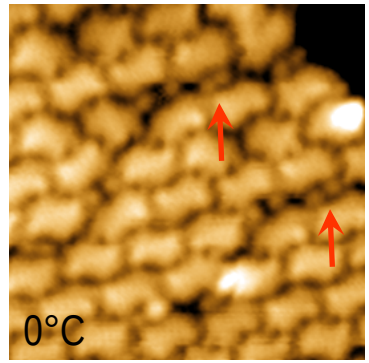

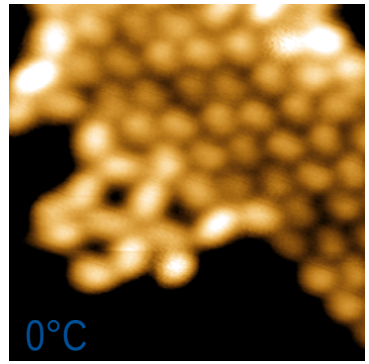

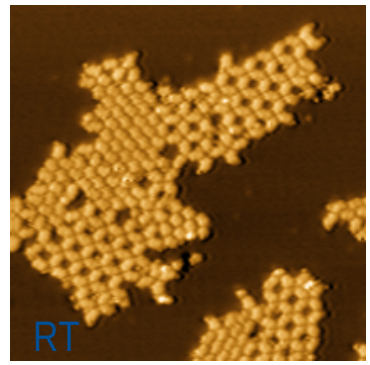

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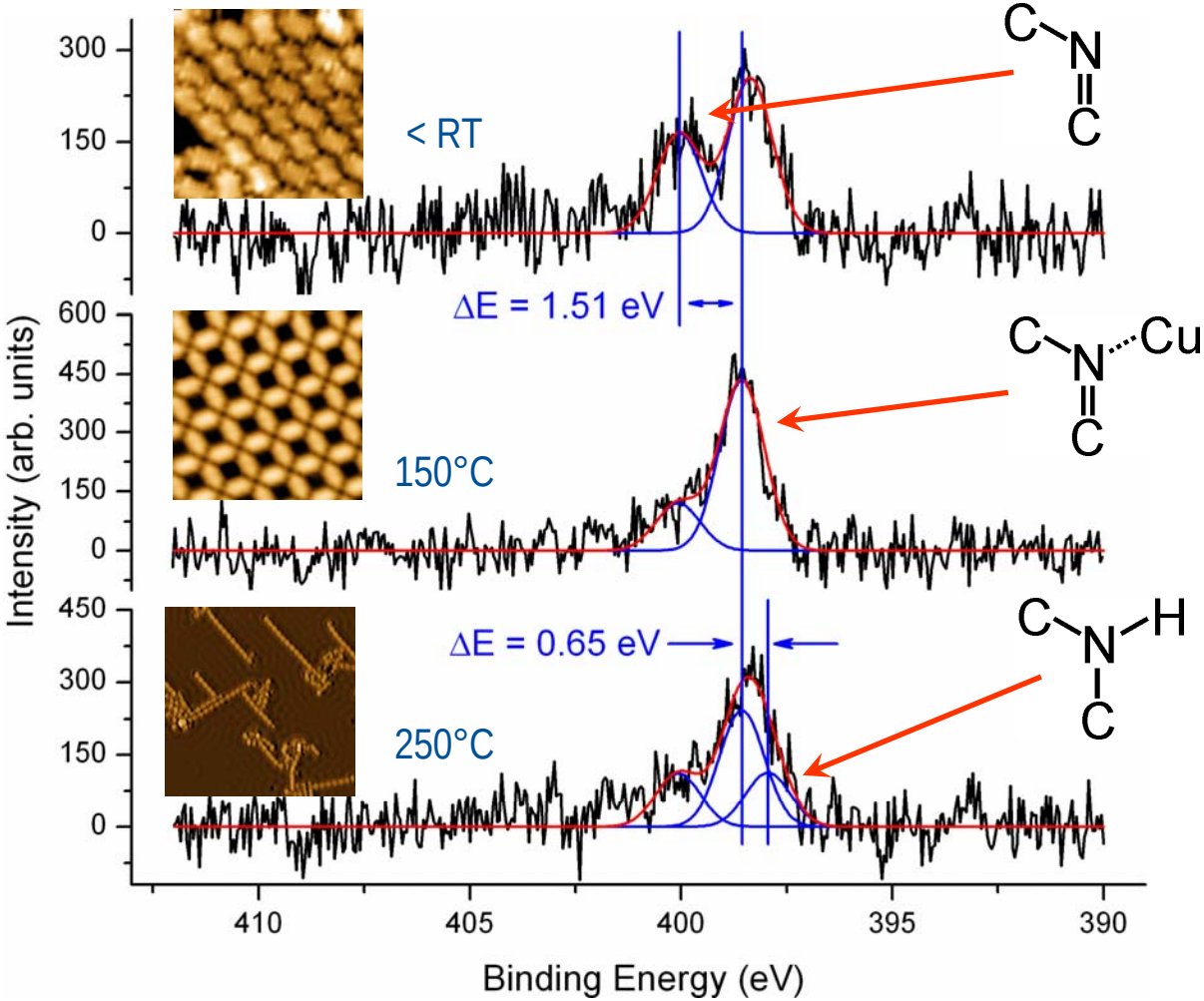
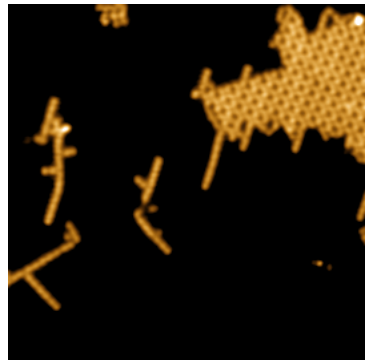
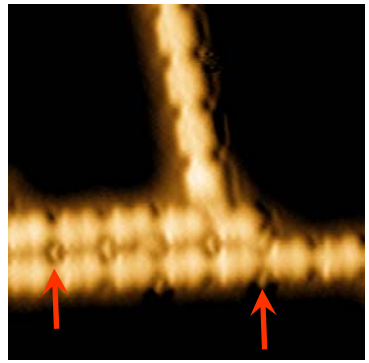


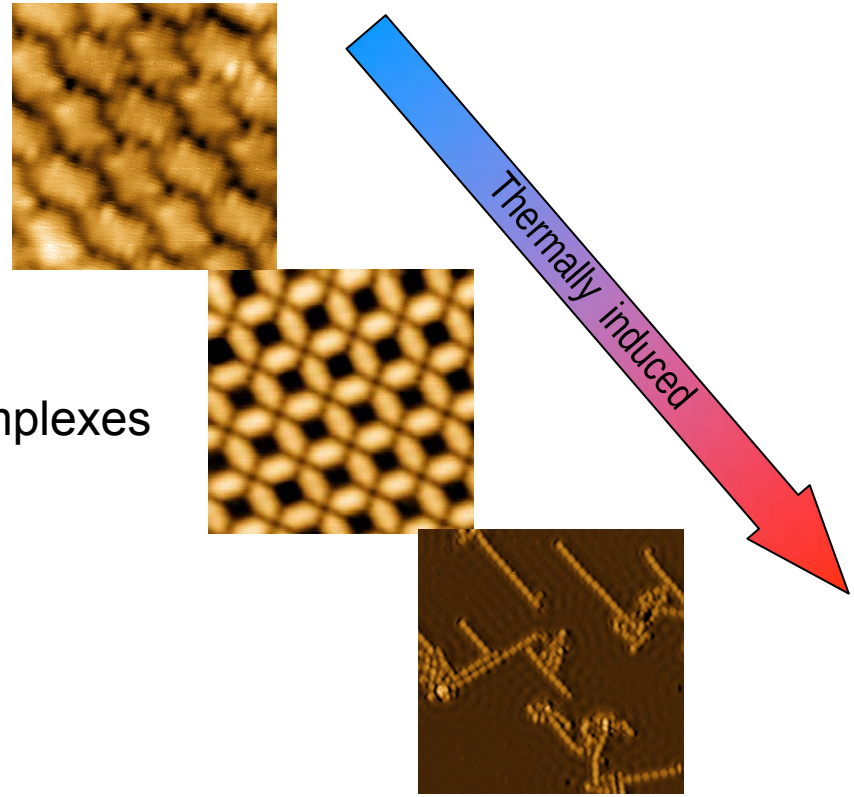




Conclusions

Influencing the molecular interactions of TAPP on Cu(111):

- vdW-interactions
- Formation of metal organic complexes
- Chain polymerisation



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Thank you for your attention!