Covalent self-assembly: steering highly directional nanostructures of porphyrins on Cu(110)

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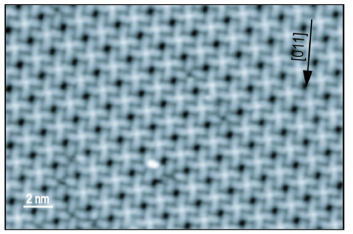
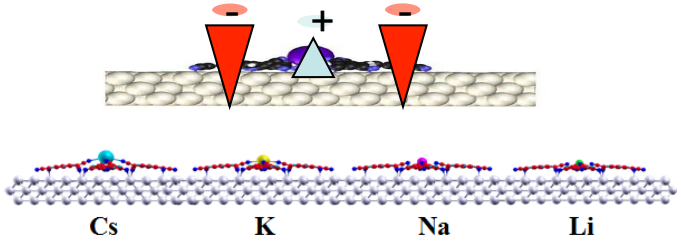
Functionalizing a surface by molecular self-assembly



- create chiral structures
- create particularly large domains on the surface
- create a networks with nanopores

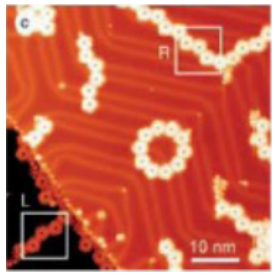
N. Abdurakhmanova, A. Floris *et al.,* Nature Comm. (2012)

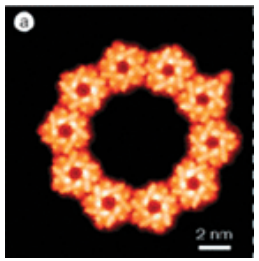
-
- change the surface work function



A. Floris, A. Comisso, A. De Vita, ACS Nano (2013)

- study the formation of highly selective structures





M.-C. Blüm *et al.*, Angew. Chem. (2005)

G. Tomba *et al*, ACS Nano (2010)

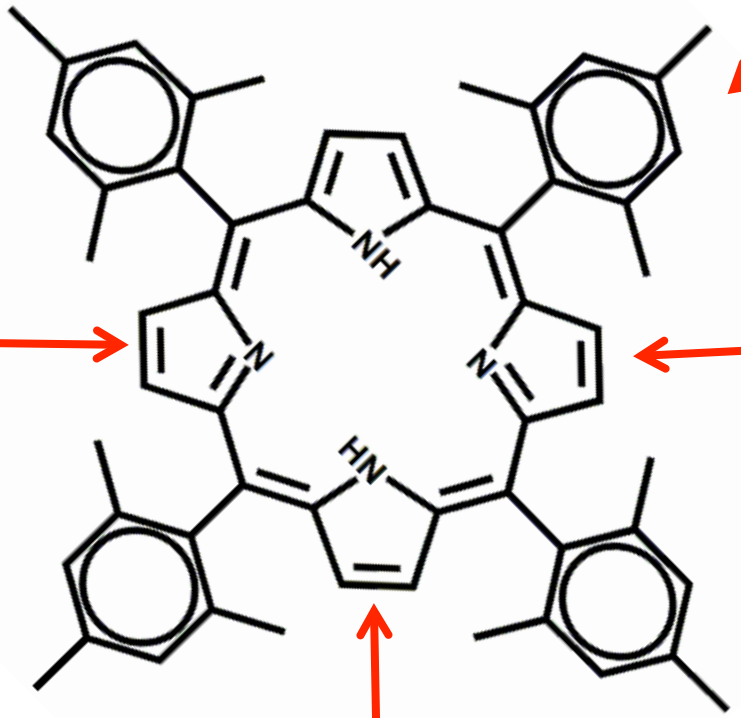
Covalent self-assembly

- Surface-molecule (SM) and molecule-molecule (MM) **interactions made of covalent bonds**
  (strong w.r.t. vdW, H-bond or electrostatic interactions)

- **Very robust structures**

Self-assembled functionalized porphyrins on Cu(110)

Molecule: Tri-Methyl-Tetra-Phenyl-Porphyrin (TMTPP)



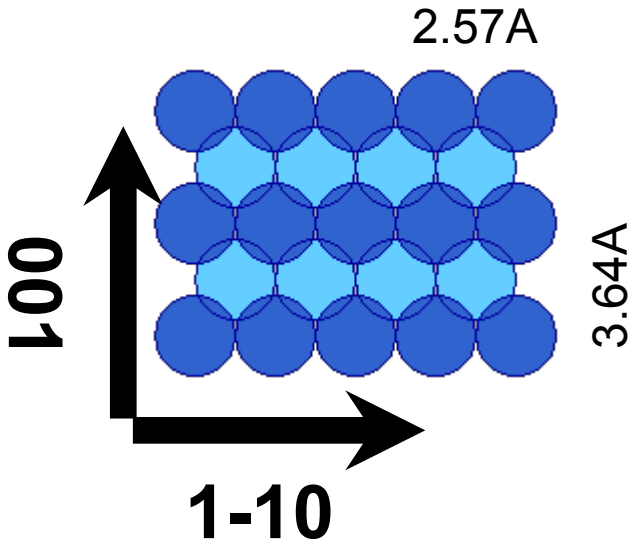
phenyls

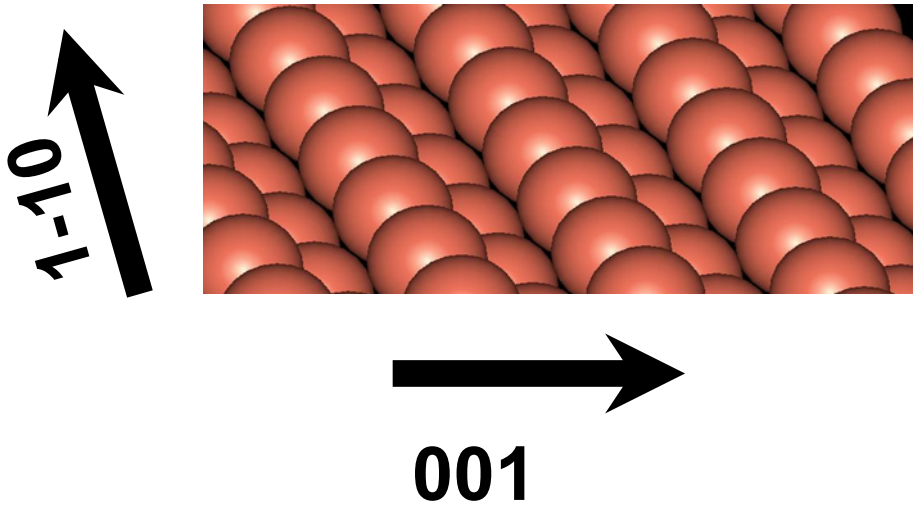
core

Pentagons with N:
Denoted **N**

Pentagons with –NH:
Pyrroles

Cu(110) surface: rows

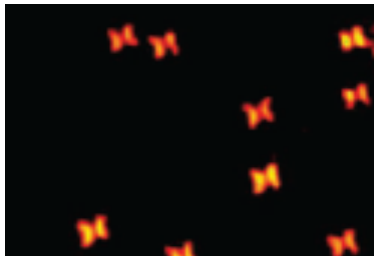




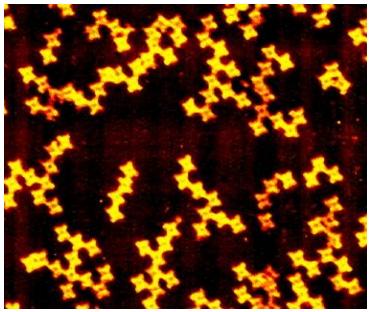
[1-10] : "easy" direction (=easy diffusion, along the rows)

[001] : "difficult" direction (=difficult diffusion,perpendicular to the rows)

Experimental facts



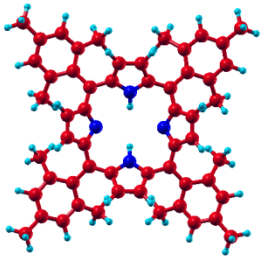
Before annealing (T=300K) :
isolated molecules, randomly distributed

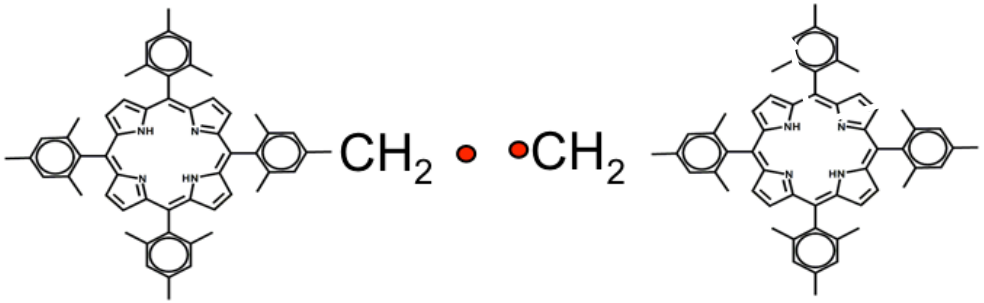


After annealing (at 550K) :
methyl groups connect: chains, zig-zag, 2D structures form

M. In't Veld, P. Iavicoli, S.Haq, D. B. Amabilino , R. Raval ,Chem. Comm (2008)

Hypothesis: dehydrogenation of peripherical methyls catalyzed by the substrate?





Goals

1. Find the stable structure on the substrate

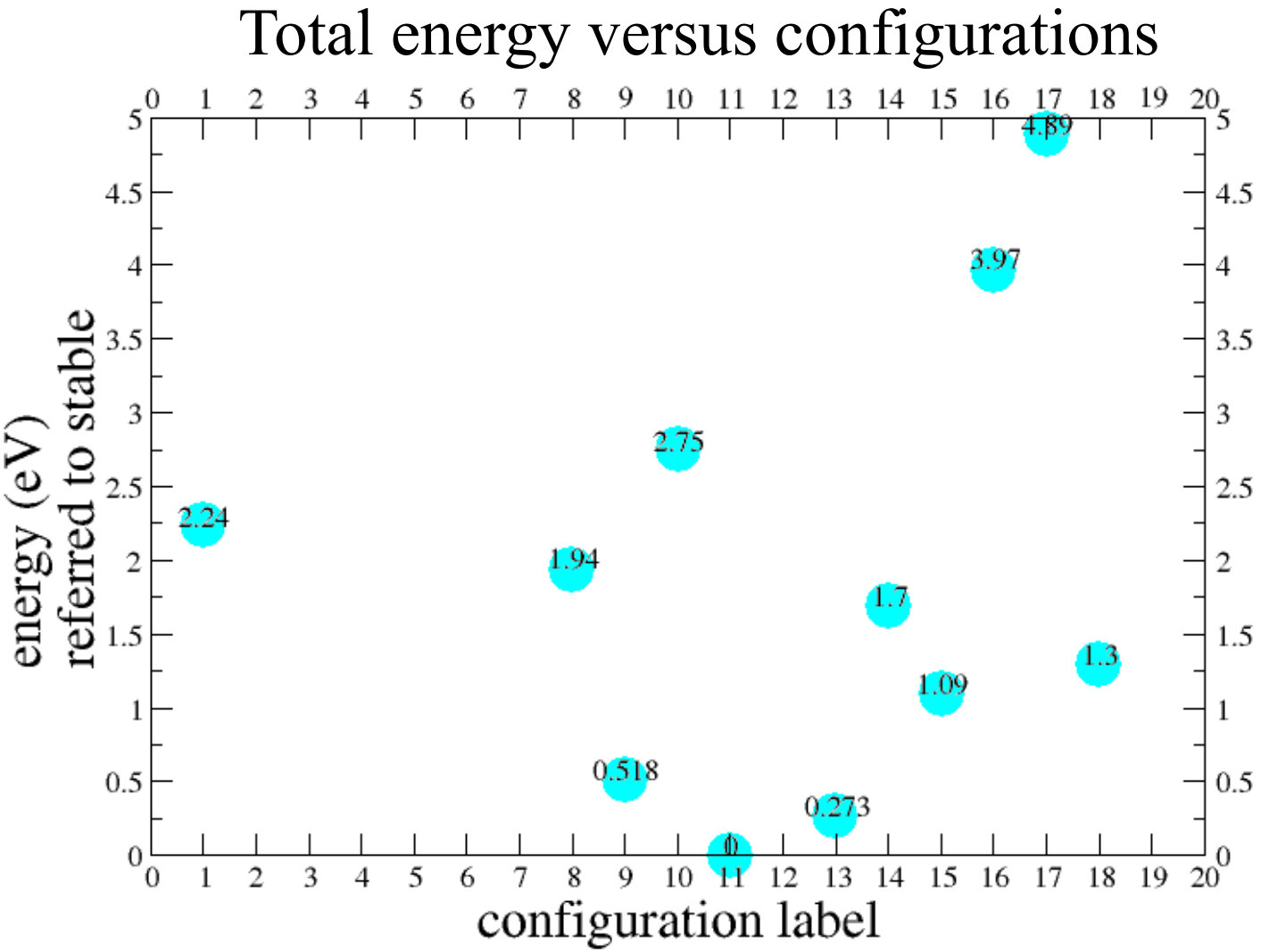
   - geometrical relaxations
   - simulations of STM images, compare with EXP

2. Understand the bonding mechanism

   - de-hydrogenation
   - diffusion
   - molecular bonding

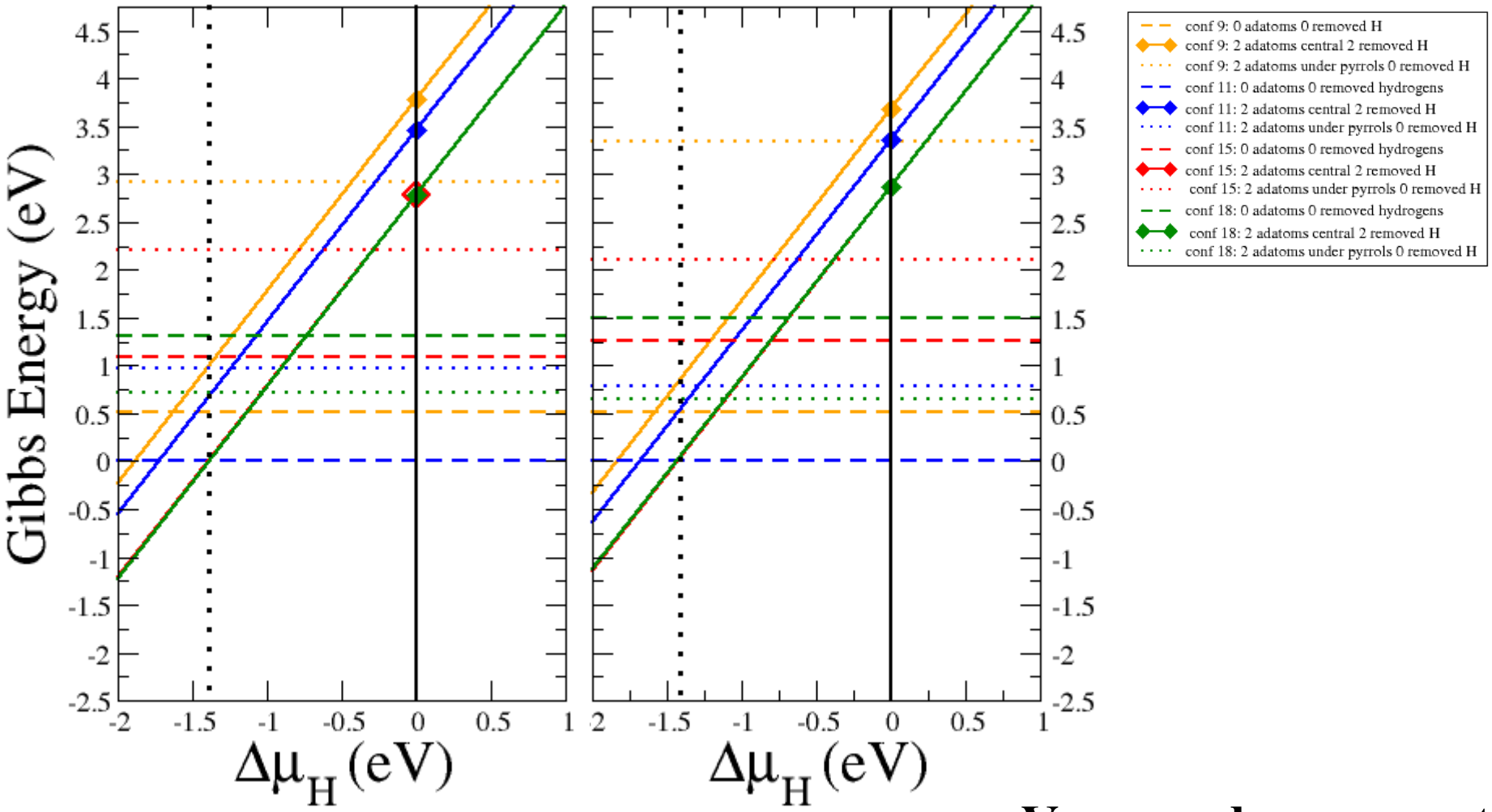
CP2K : RUN_TYPE= GEO_OPT, with D2-Grimme

Geometry on the substrate



Energetics: CP2K versus Quantum-ESRPESSO

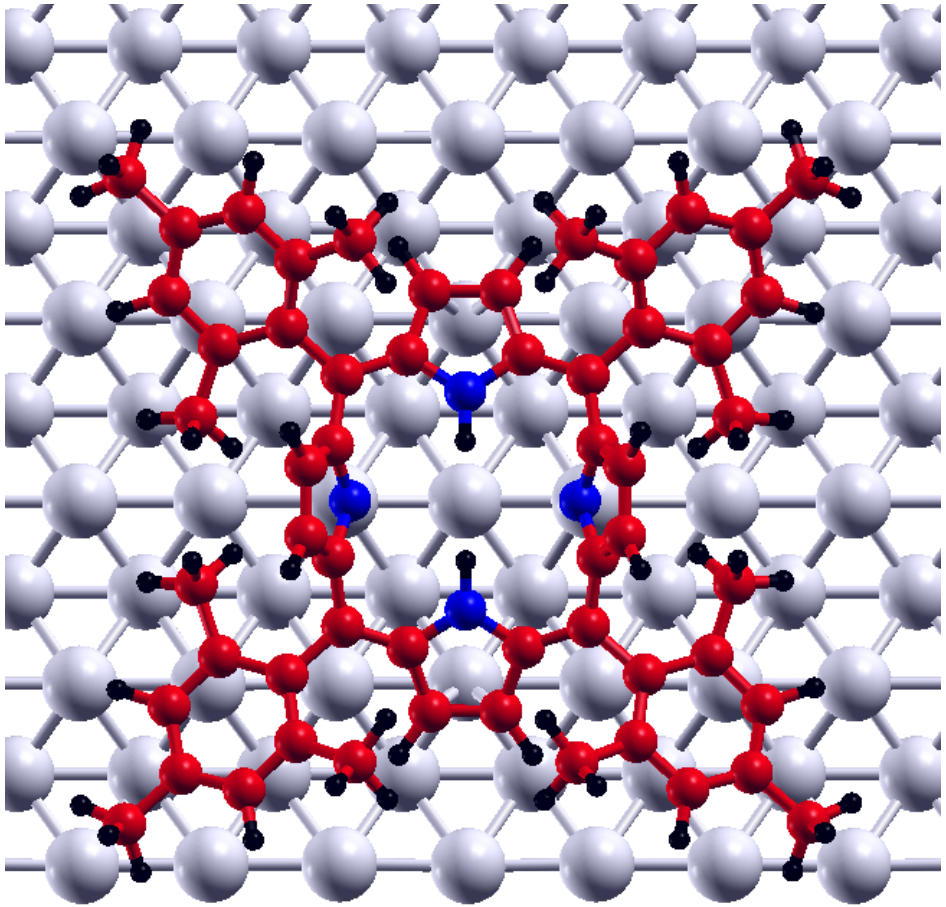
CP2K **Quantum-ESPRESSO**

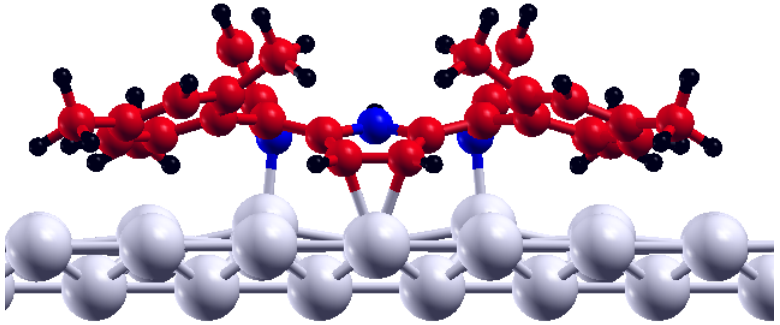


Very good agreement

Geometries on the substrate

Two most stable configurations

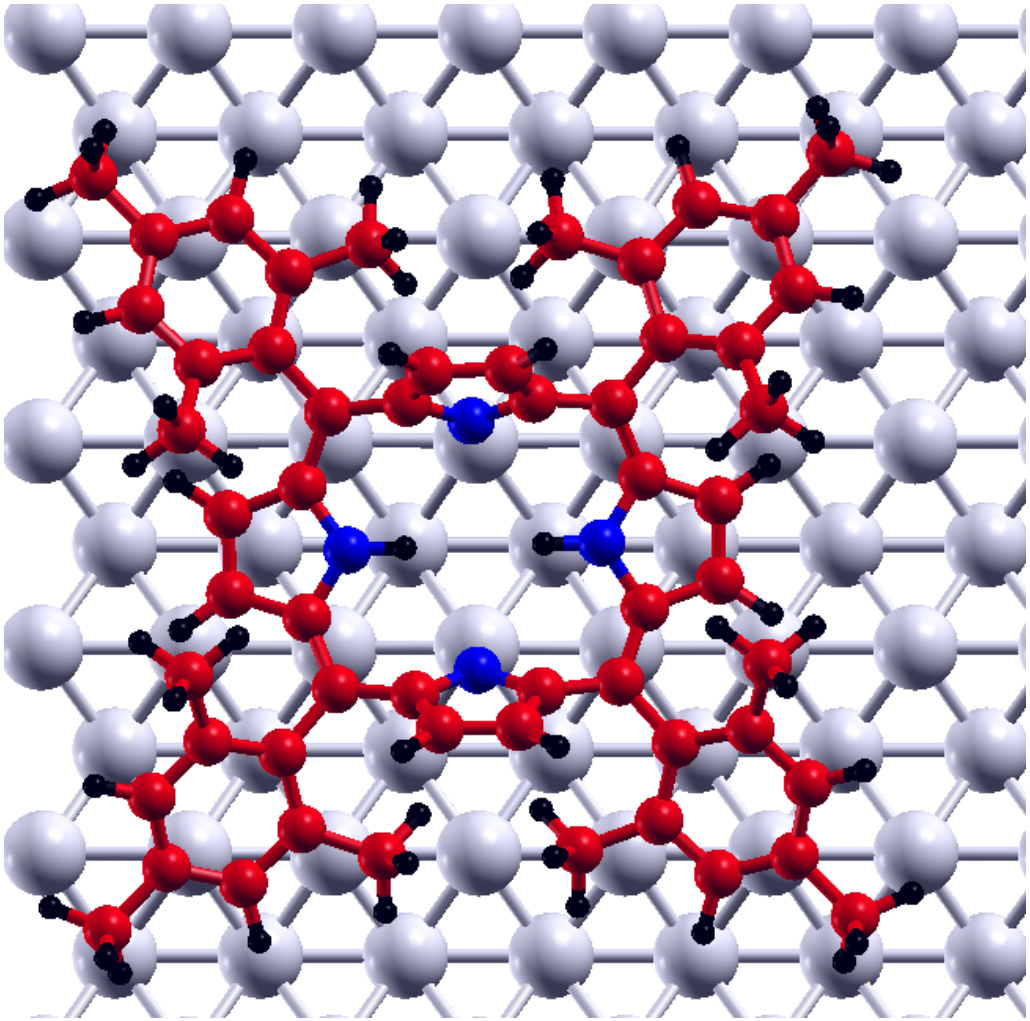


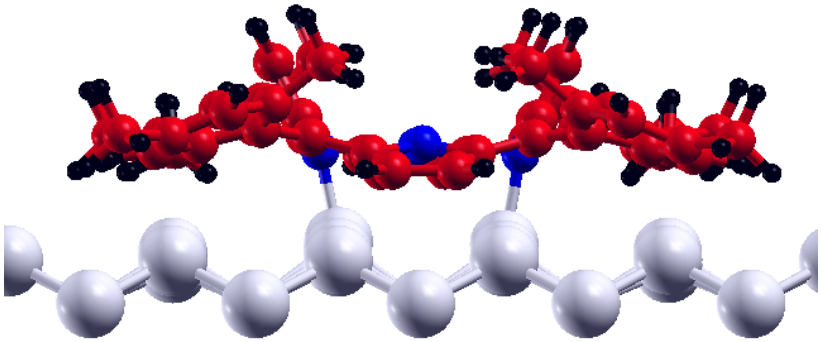


Conf 11: Most stable (0 eV):

- Horizontal pyrroles
- vertical N
- slightly rotated phenyls
- 2 N-Cu bond
- 4 C-Cu bonds
- Horizontal phenyls exposed to the substrate (vdW)
- 6 bonds

Geometries on the substrate

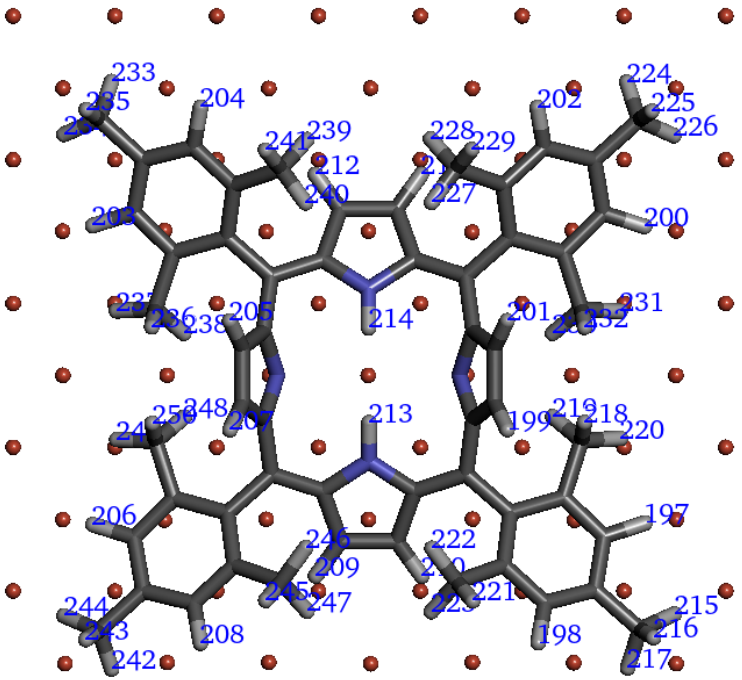


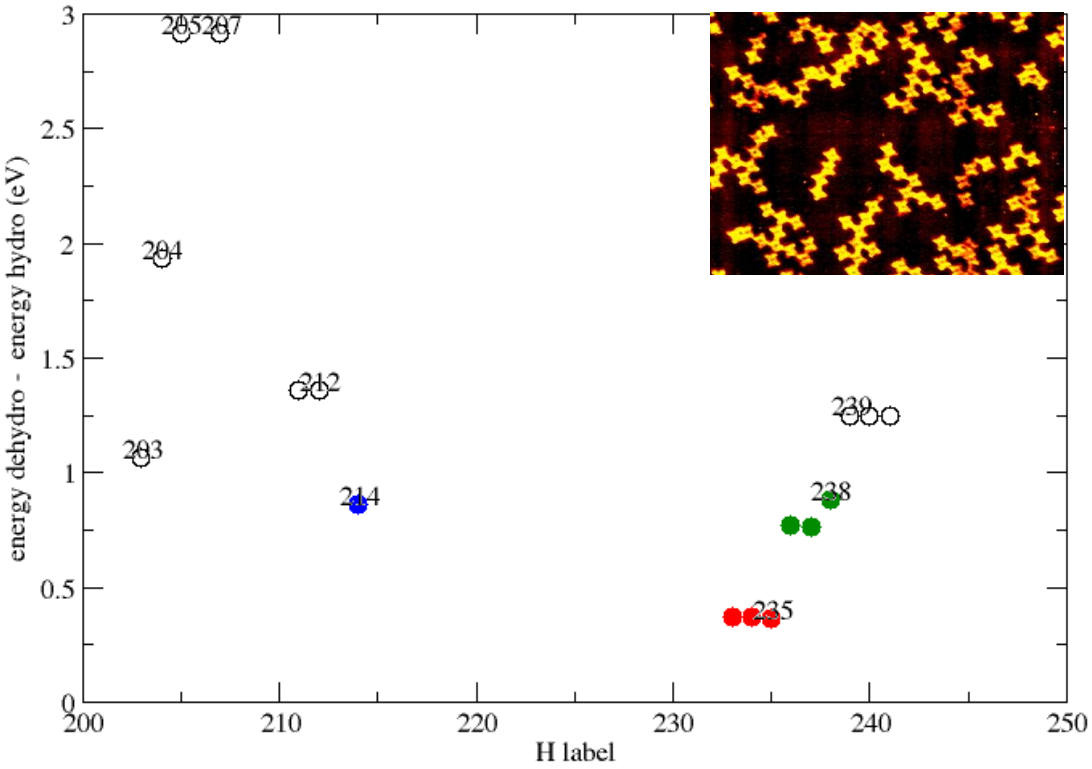


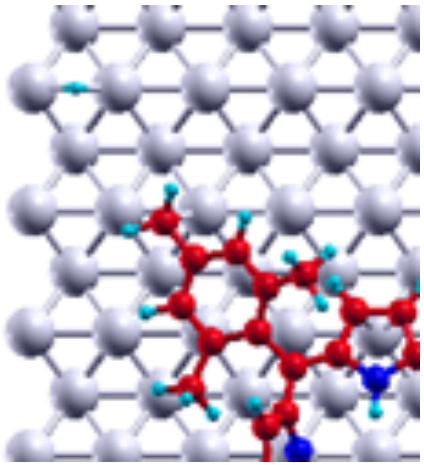
Conf 9, rotated 90 deg (+0.518 eV):

- Similar to conf11
- **NO C-Cu bonds**

De-hydrogenation: H removal at T=0K

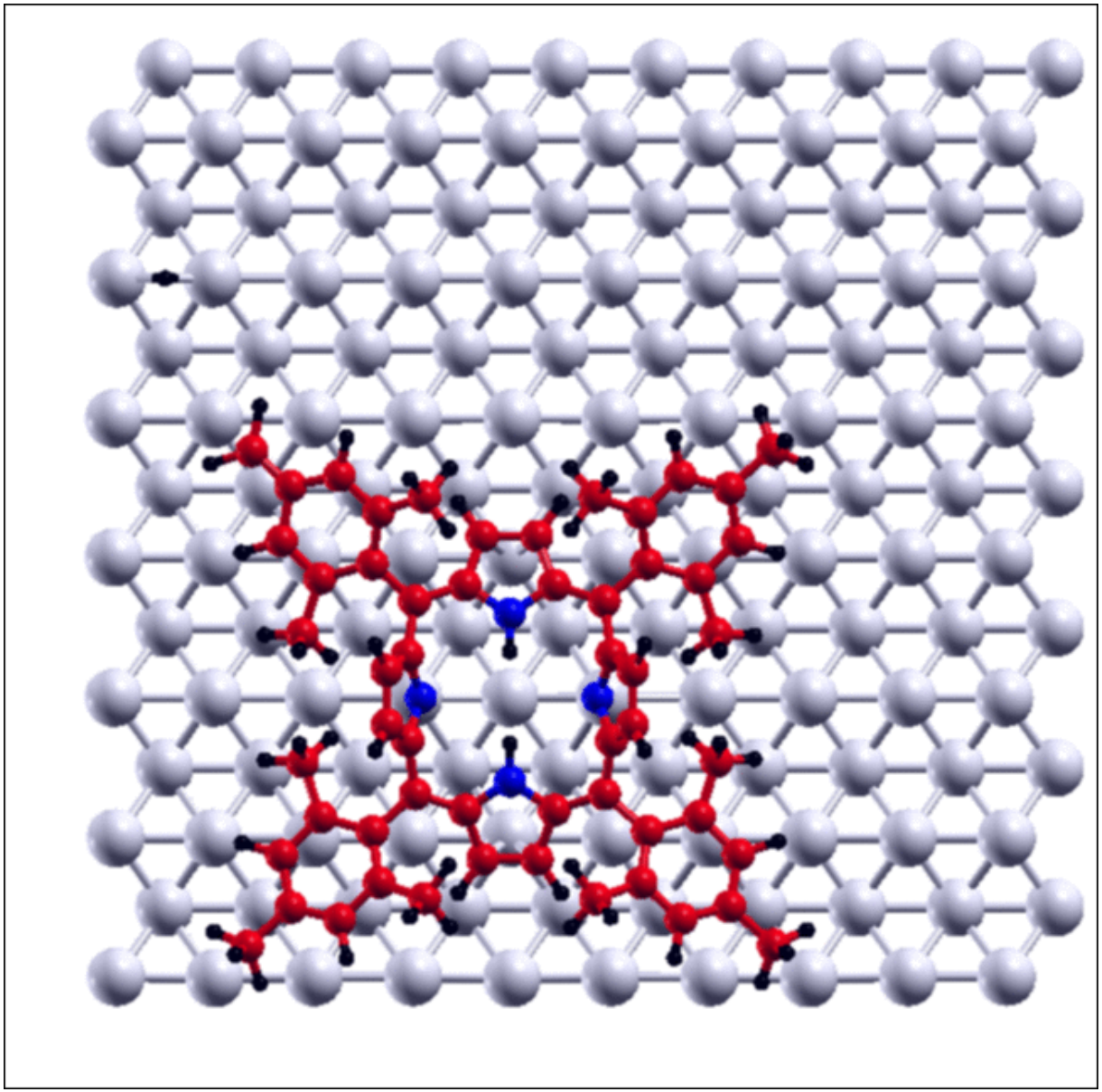






- Removing a H at T=0K H **costs energy**
- **Peripherical H: the easiest to remove** (~0.35eV)
- Core central H also “easy”

Relax upon peripherical H removal

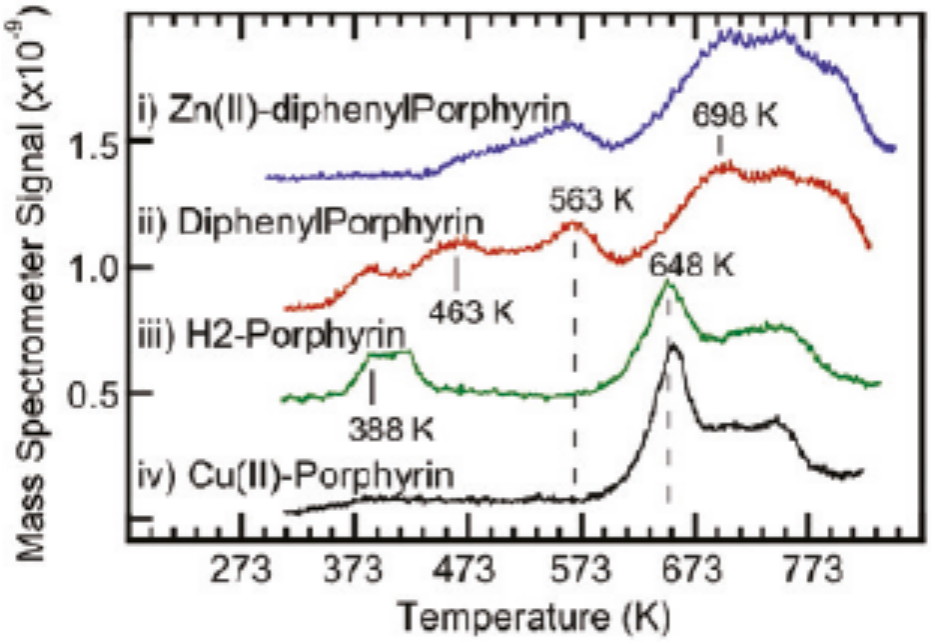


H de-adsorption: role of T crucial

Experimentally at T=300K:

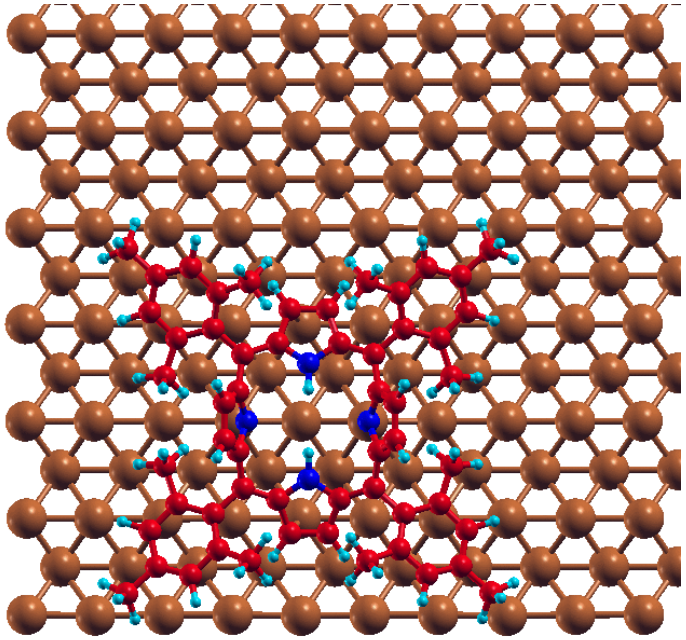
- No bonding is observed

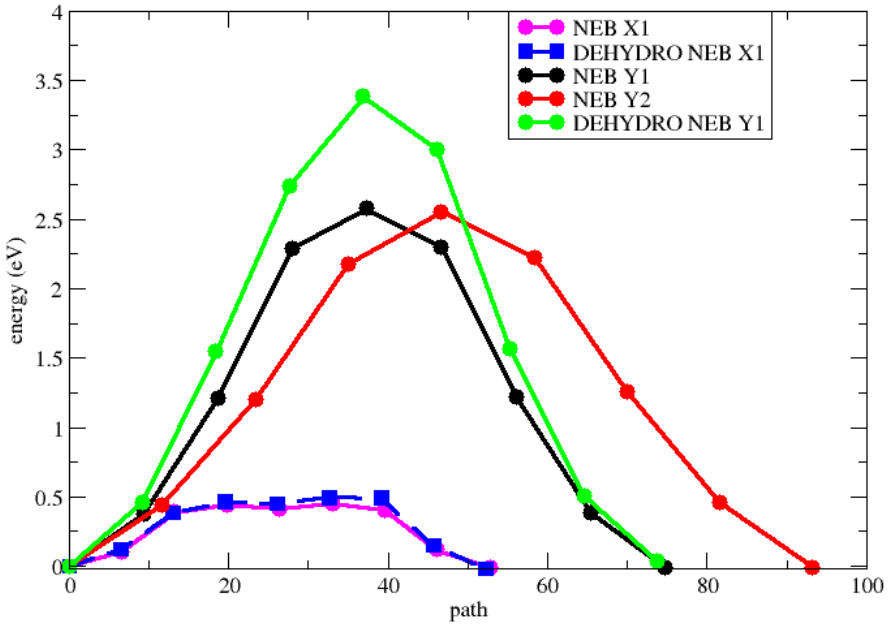
- No H de-adsorption is observed

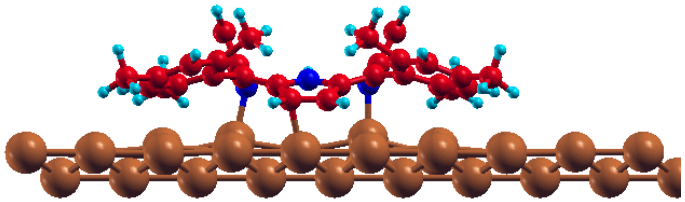


H de-adsorption starts at 500K

Molecular diffusion: Nudge Elastic Bands (NEB)





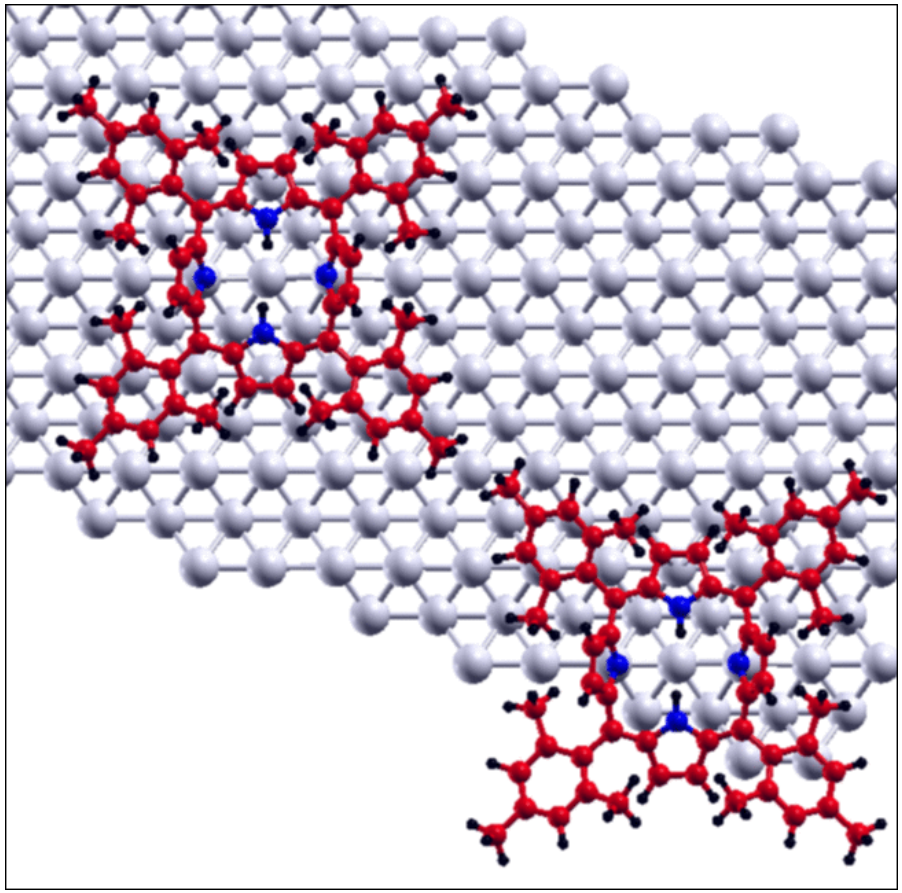


- Diffusion is **much more favourable along the rows**
- DH does not affect diffusion along rows, while it does across

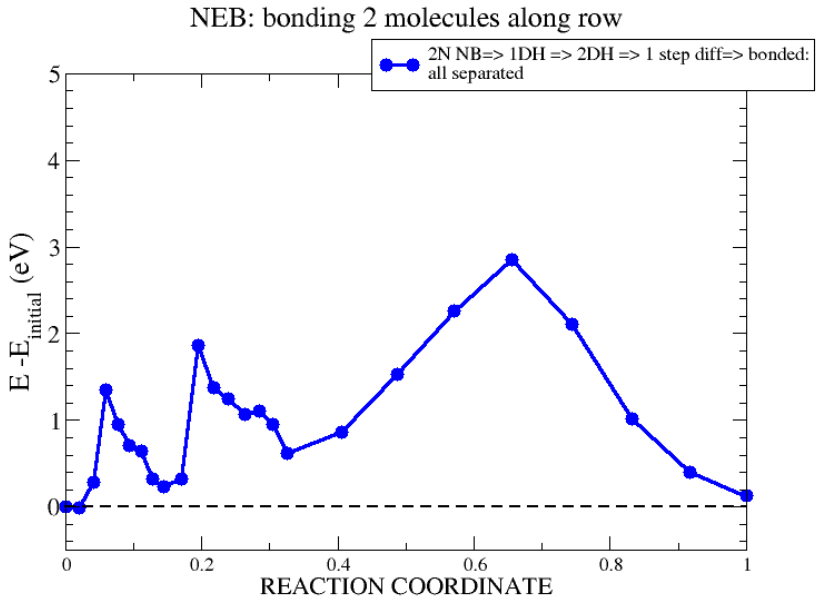
Molecular bonding: energy barriers

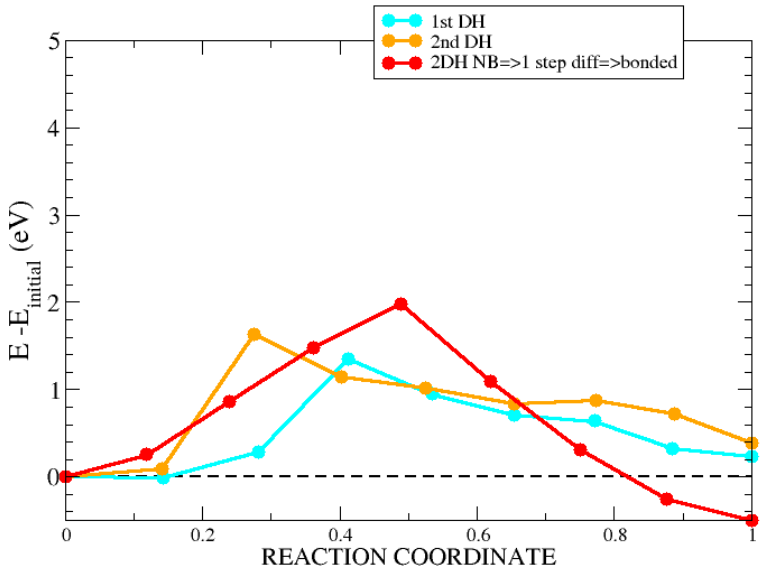
3 consecutive processes:

- 1st dehydrogenation
- 2nd dehydrogenation
- diffusion-bonding

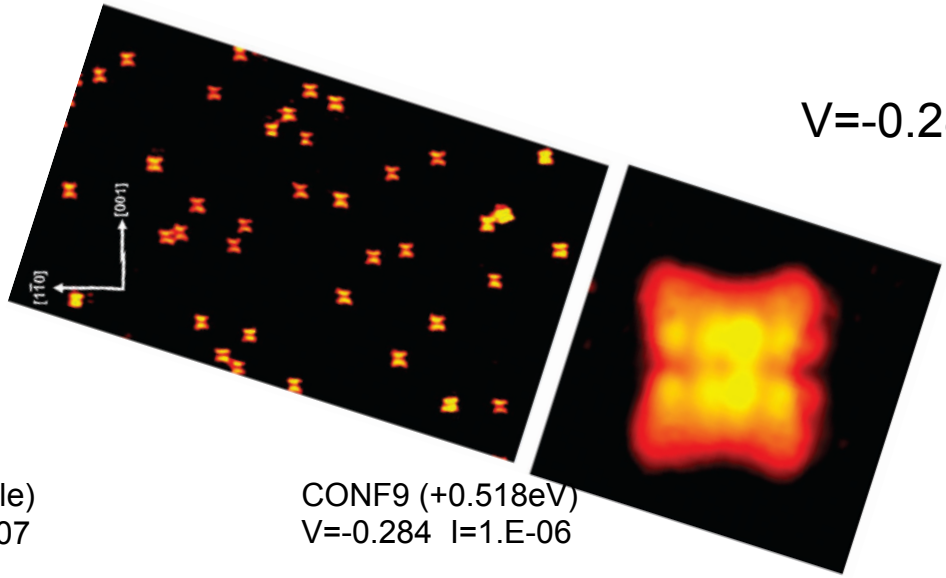


CP2K RUN_TYPE=BAND





STM: theory versus experiment

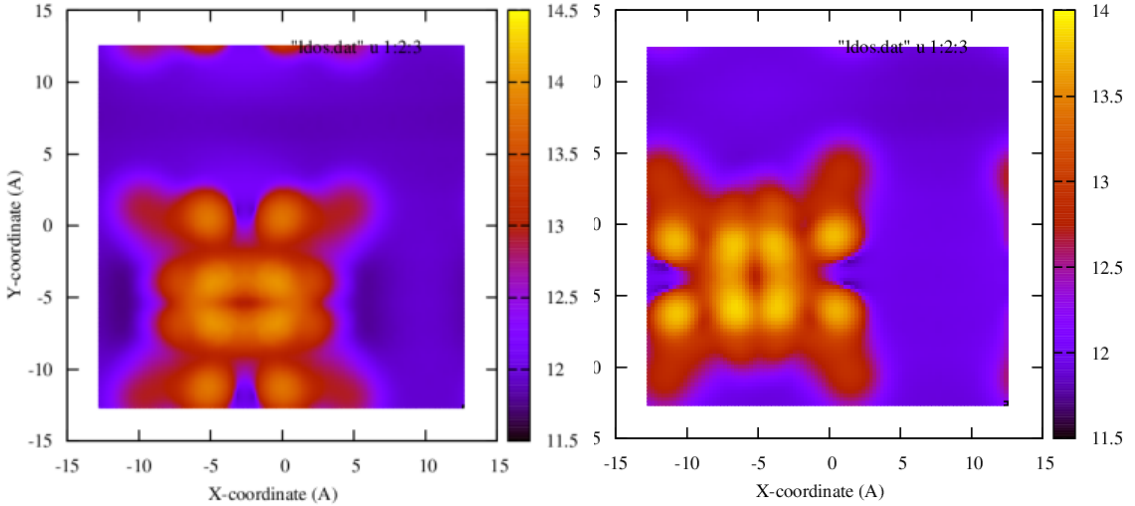


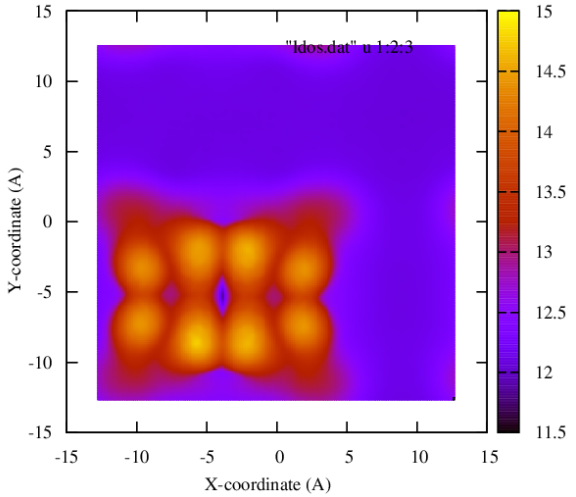
V=-0.284 I=0.26nA

CONF11 (stable)
V=-0.5 I=1.E-07

CONF9 (+0.518eV)
V=-0.284 I=1.E-06

CONF15 (+1.09eV)
V=-0.5 I=0.6E-07



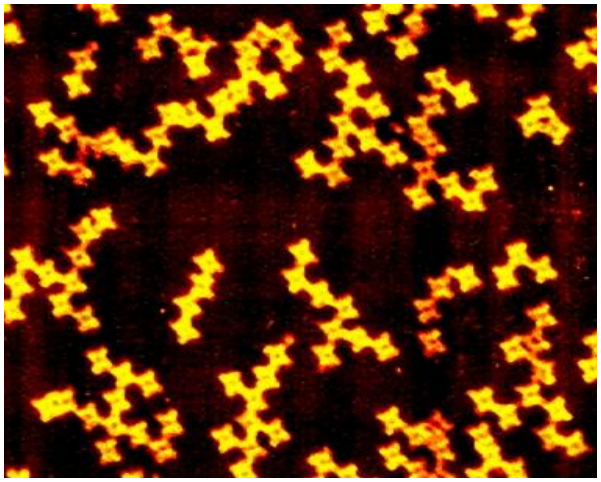


- **Quantum-ESPRESSO (ILDOS)**
- **LEV00 (simulation of STM at constant current)**

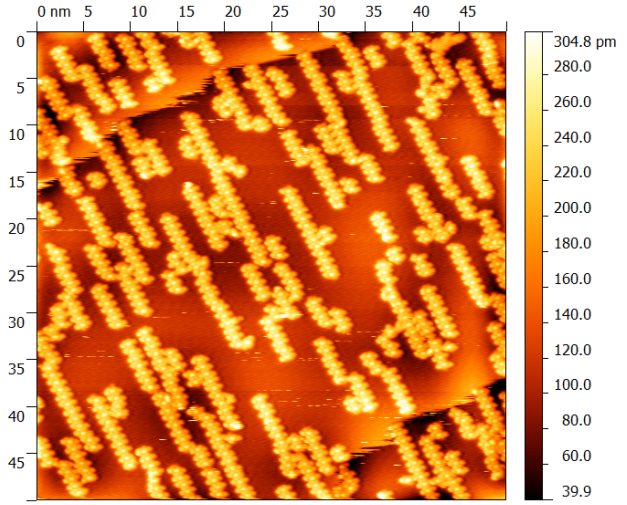
http://

www.cmmp.ucl.ac.uk/~lev/codes/lev00/

1D structures

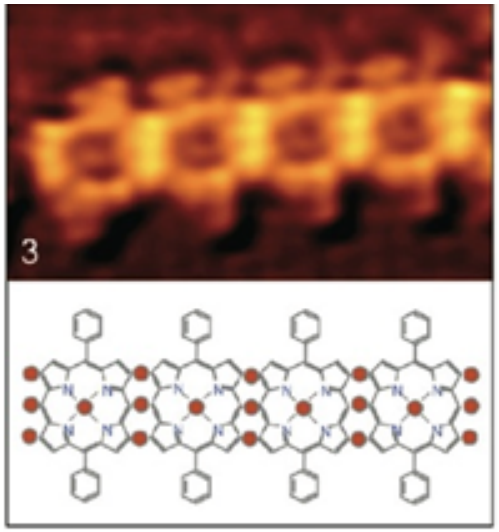


TMTPP chains



CoDPP chains

- Steering different directions via different functional groups

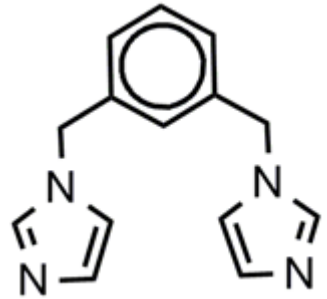


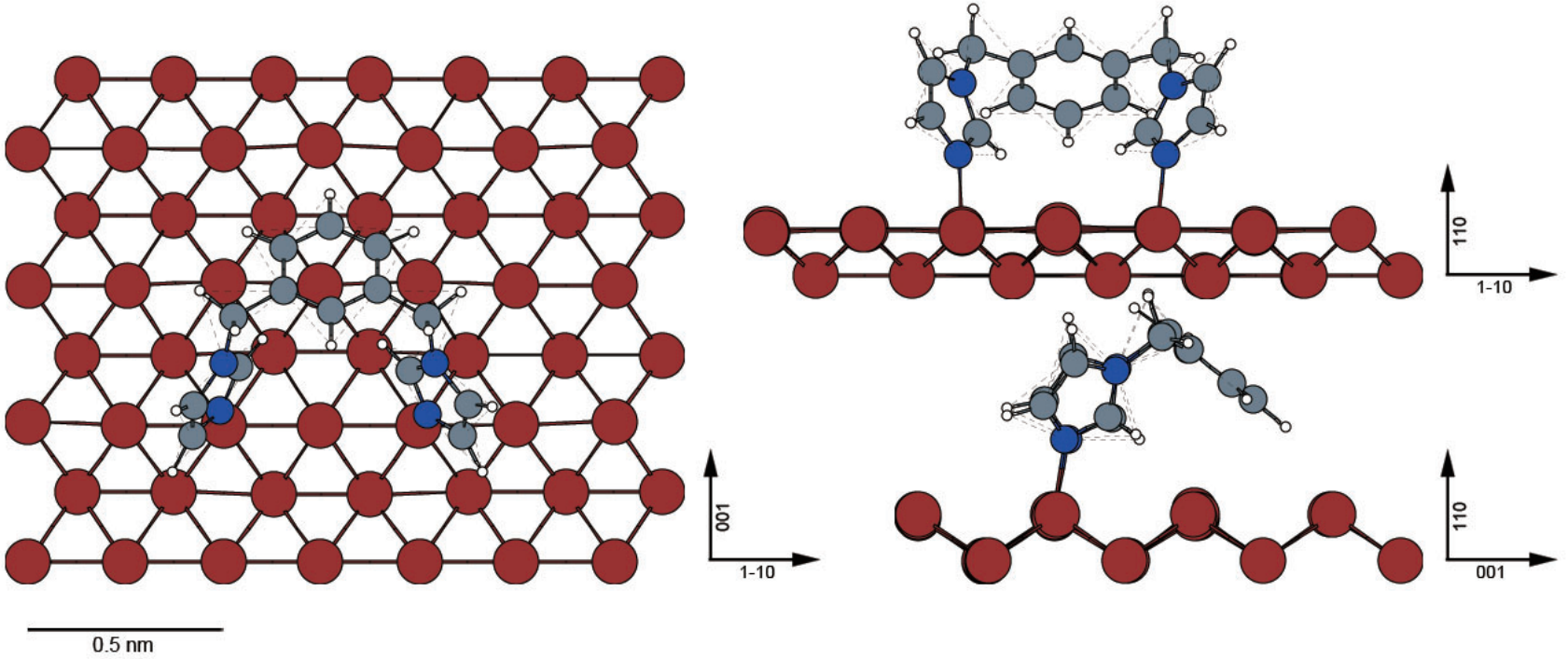
Walker molecule

Ph.D students:

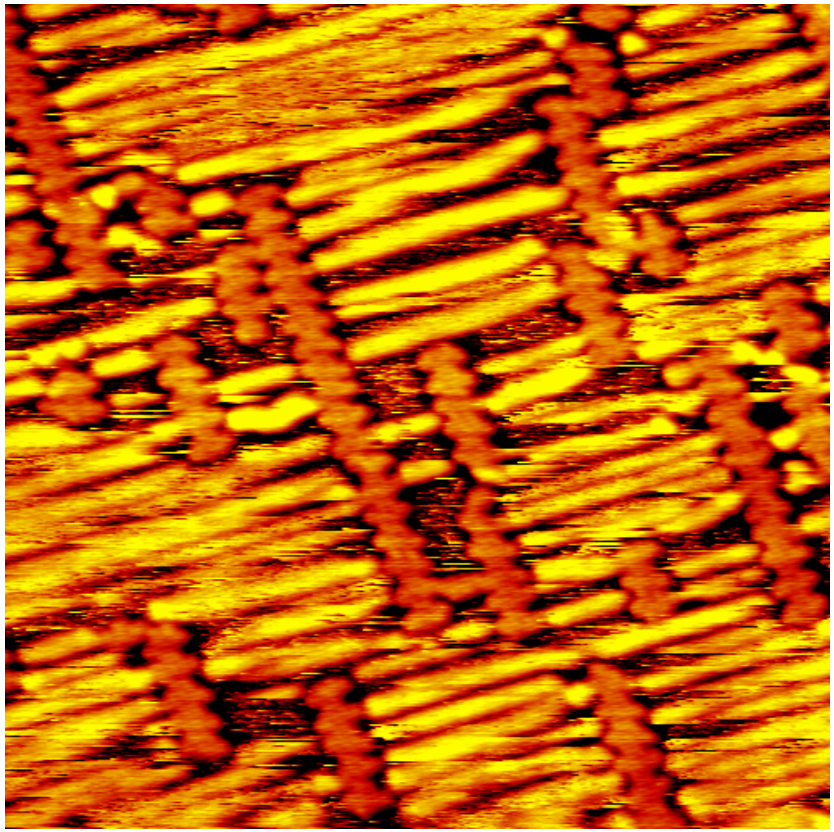
Bart Wit

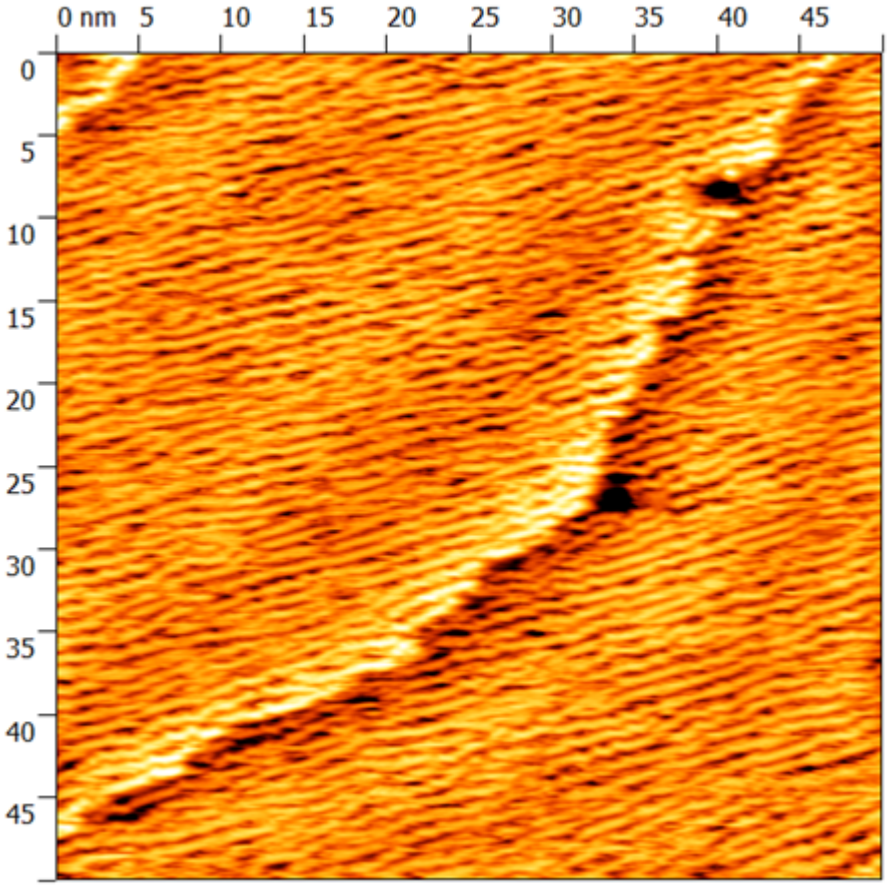
Sang Hongqian





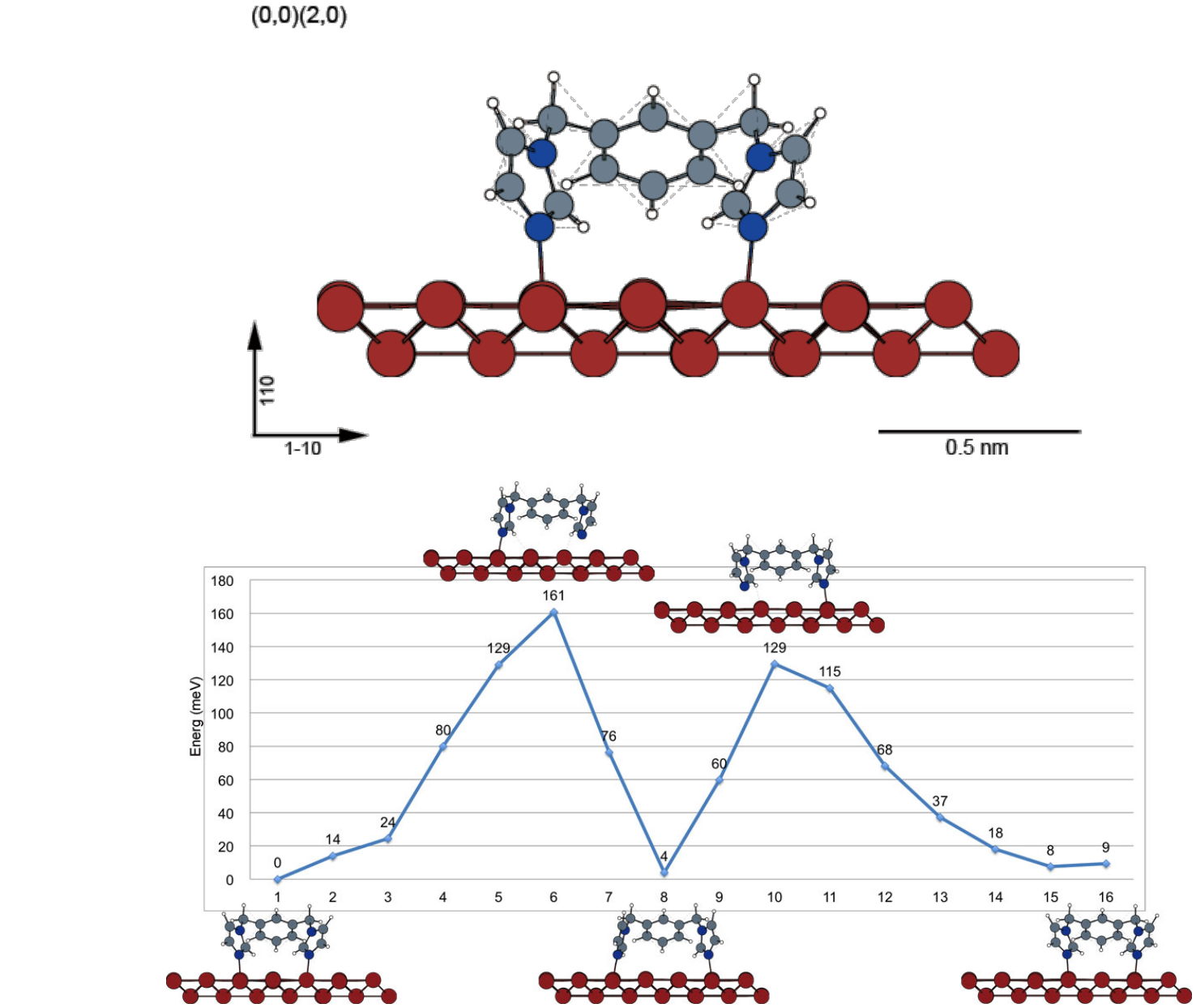
Diffusion lines observed by STM



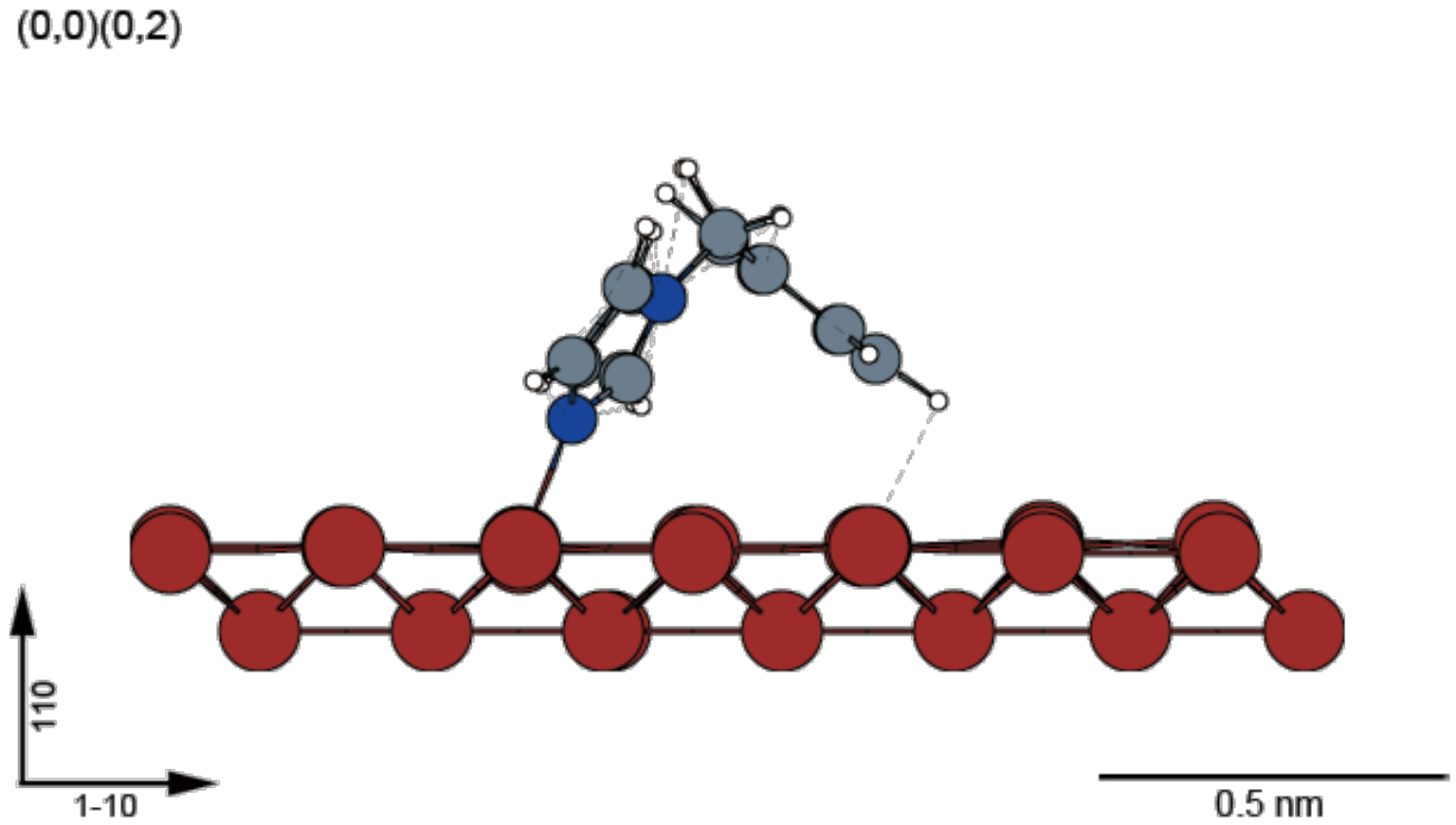


B. Wit, S. Hongqian, S. Haq, A. Floris, L. Kantorovich, D. Amabilino, R. Raval,
to be published

“Walking” mechanism along the rows



“Walking” mechanism along the rows



B. Wit, S. Hongqian, S. Haq, A. Floris, L. Kantorovich, D. Amabilino, R. Raval,
to be published

Summary

1) Surface functionalization via **self-assembled molecules**

2) Functionalized porphyrins realize **robust, covalent** structures **by heating**

3) Bonding mechanism: **dehydrogenation, diffusion, bonding**

4) **1D fences and walking molecules:** huge playground for creating specific patterns on substrates

5) **CP2K:**

- Very good agreement with PW codes.
- Efficient RUN_TYPE= GEO_OPT and BAND