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
- change the surface work function
- 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)
[1-10] : “easy” direction (=easy diffusion, along the rows)
[001] : “difficult” direction (=difficult diffusion, perpendicular to the rows)
After annealing (at 550K):
- methyl groups connect to form chains, zig-zag, 2D structures.

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

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

Total energy versus configurations

energy (eV) referred to stable

configuration label
Energetics: CP2K versus Quantum-ESRPESSO

Very good agreement
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
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 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:
• 1\textsuperscript{st} dehydrogenation
• 2\textsuperscript{nd} dehydrogenation
• diffusion-bonding

CP2K RUN\_TYPE=BAND
STM: theory versus experiment

V = -0.284  I = 0.26 nA

CONF11 (stable)
V = -0.5  I = 1.0E-07

CONF9 (+0.518 eV)
V = -0.284  I = 1.0E-06

CONF15 (+1.09 eV)
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

- Steering different directions via different functional groups
Walker molecule

Ph.D students:
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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

(0.0)(2.0)
“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