Molecular Devices for Single Molecule STM Experiments

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Experiments on single molecules

UHV STM: ultraclean conditions,

imaging, manipulation, spectroscopy…

Design specific molecules for a given experiment

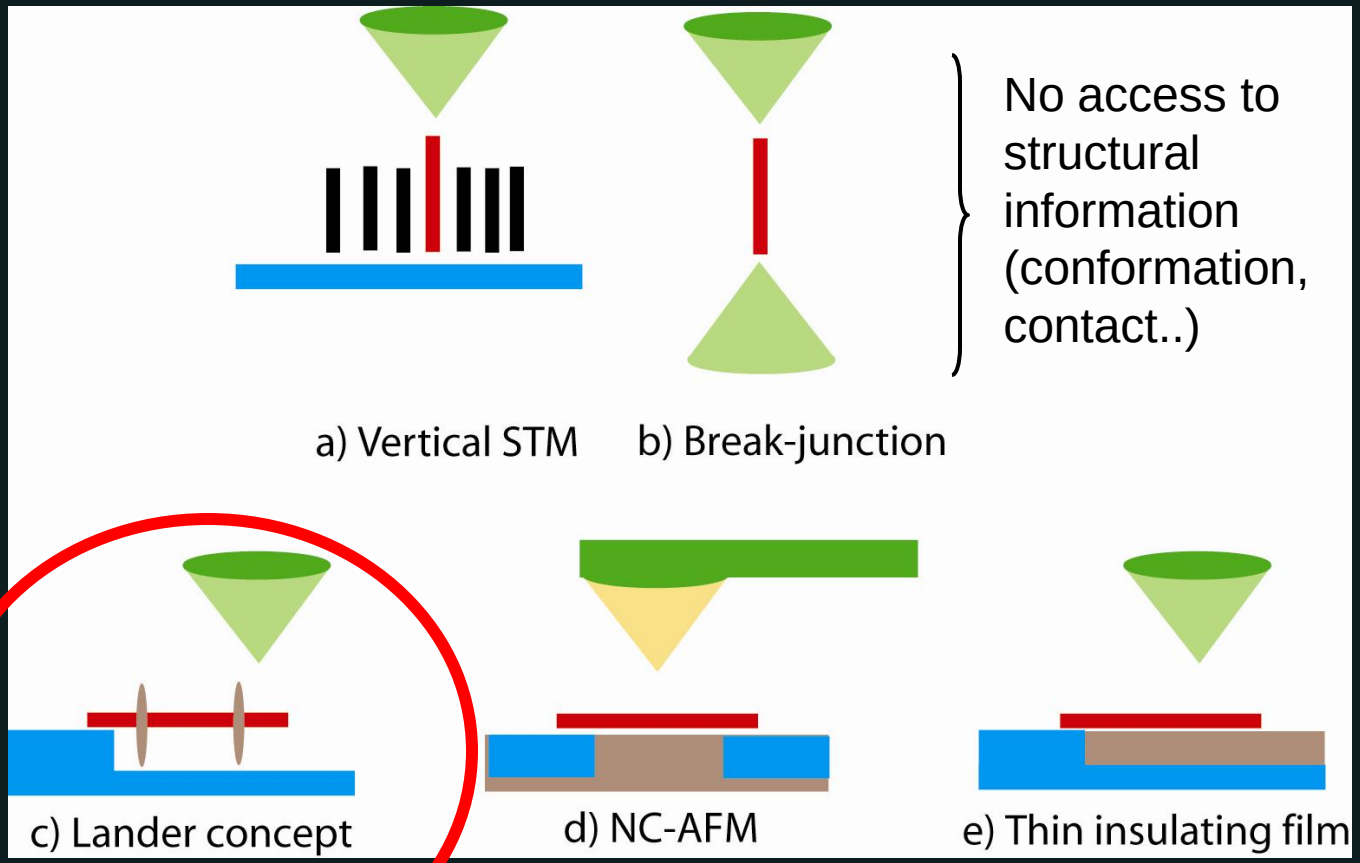
Outline:

-introduction to the lander-molecules

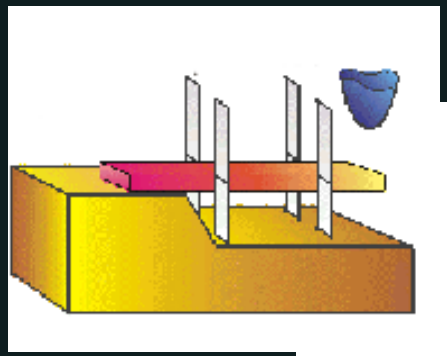
-molecular molding

-mechanics: a molecular rack and pinion

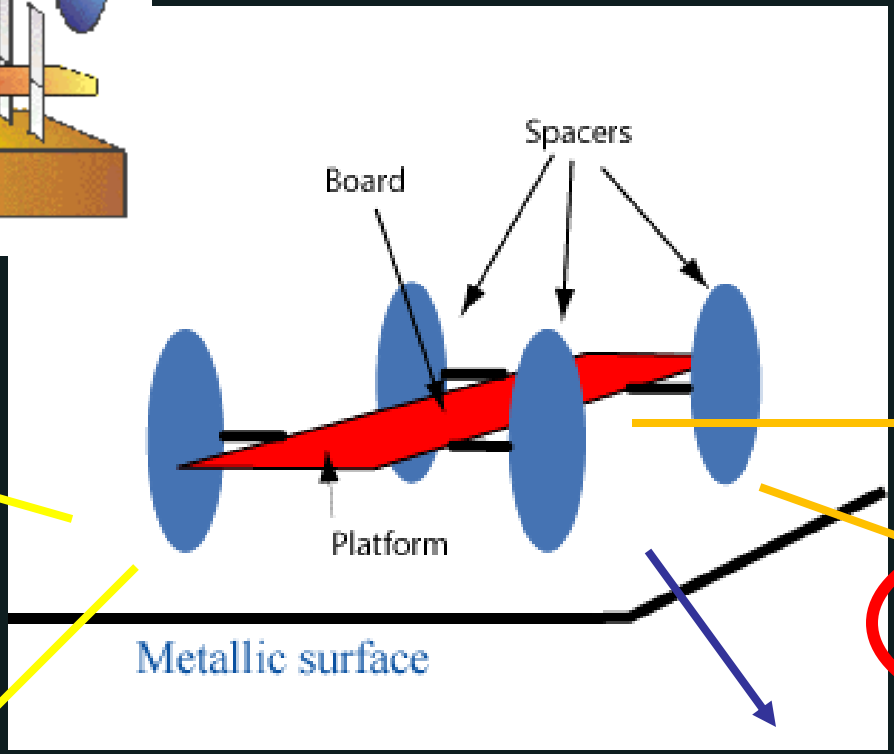
Initial objectives: electronic properties of single molecules:



Concept: Molecular Landers



The Mars lander « Sojourner » (NASA)



Optics

Surface molding

Mechanics

Switching

Conductance

The active part is decoupled from the surface by spacers

A. Gourdon, *Eur. J. Org. Chem.* (1999), 2797

Introduction to molecular « landers »

Top views

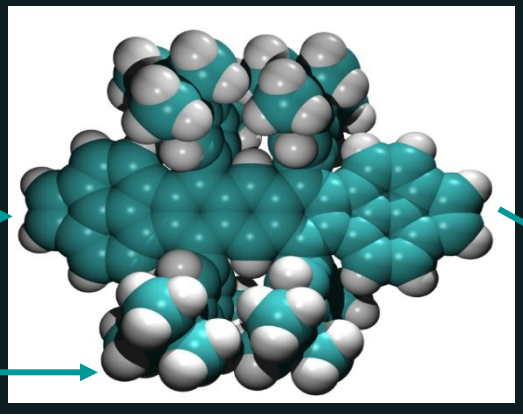
Board

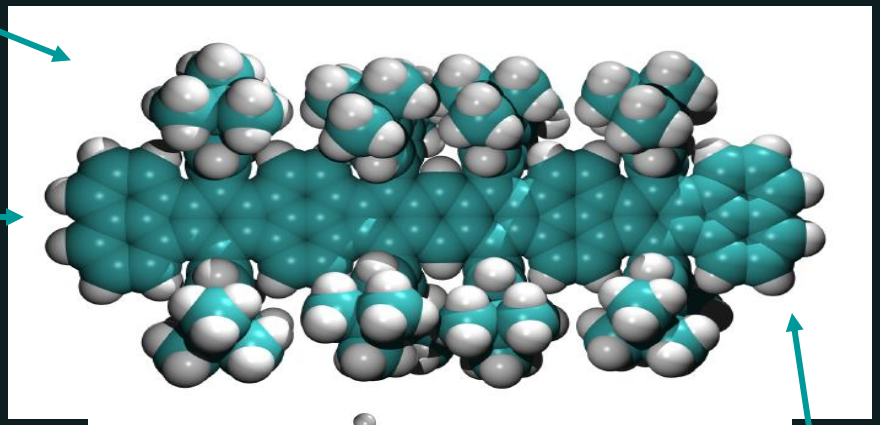
Spacers

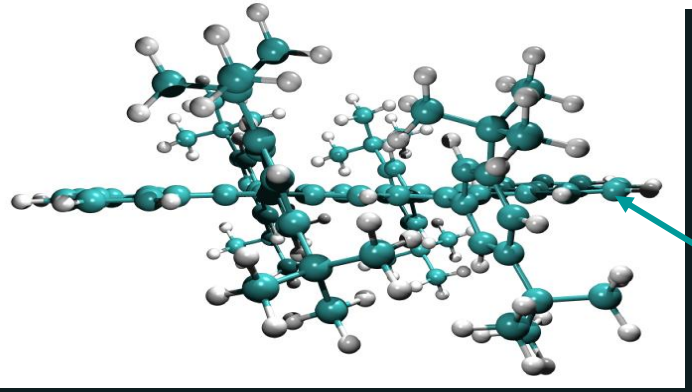
wire

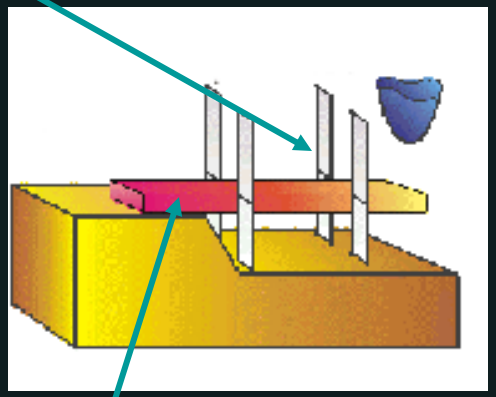
Side view

ca 6Å









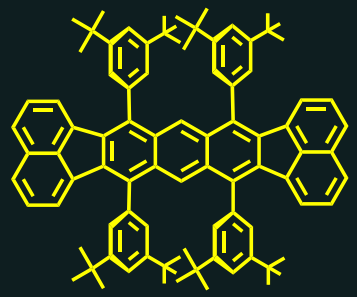
Platform for chemisorption

Wires

Wire: polyaromatic hydrocarbons; not reactive with the substrate

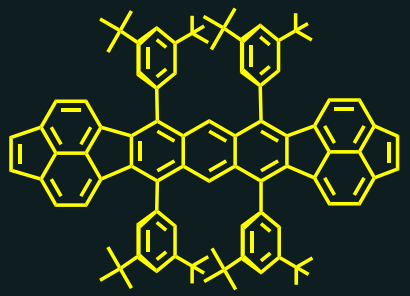
Spacers: di-tert-Butylphenyl

(decoupling + mobility)



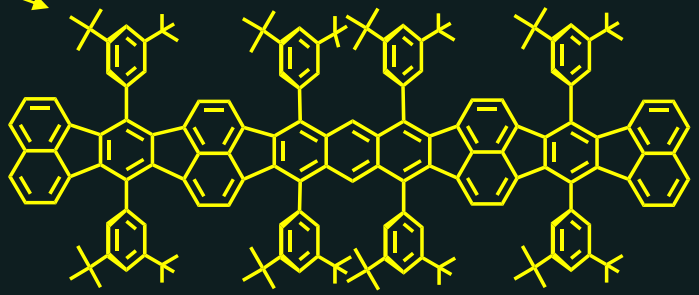
1

SL



2

RL

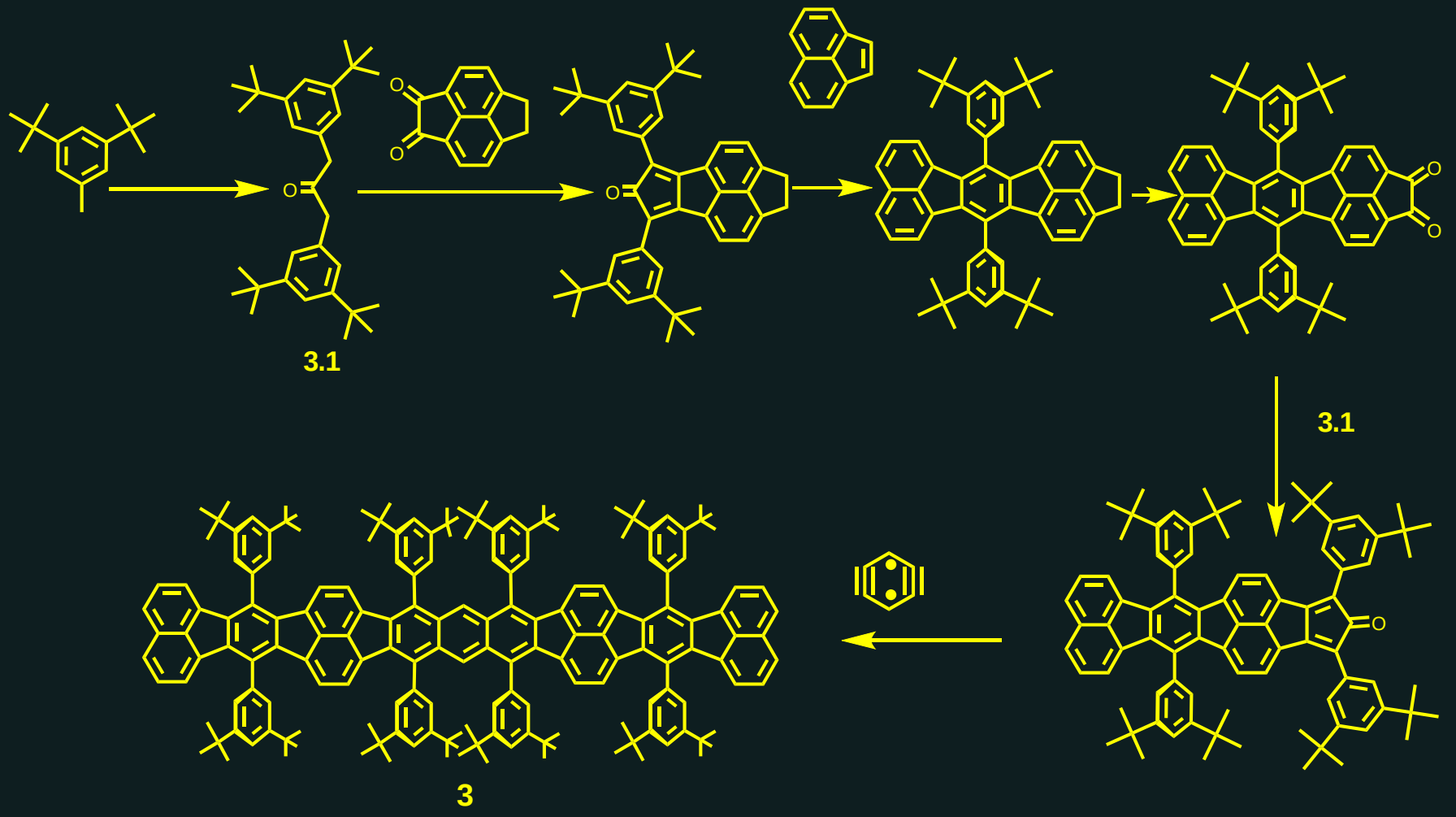


3

DL

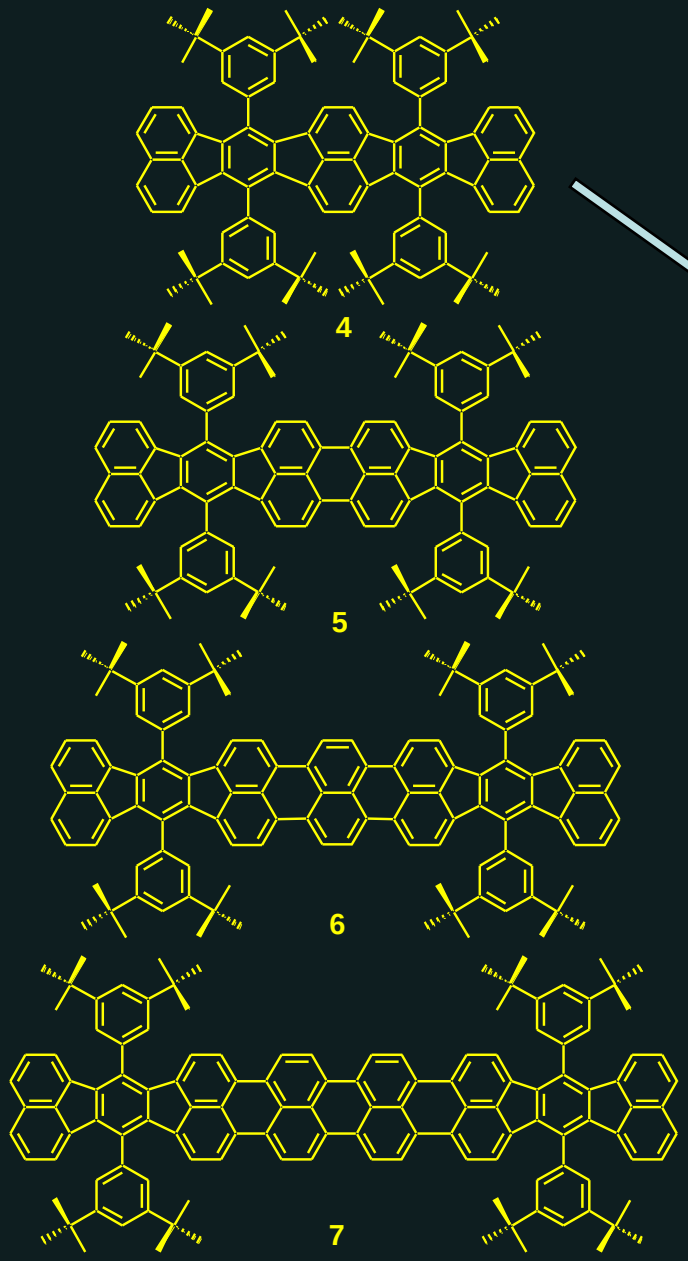
Large gap

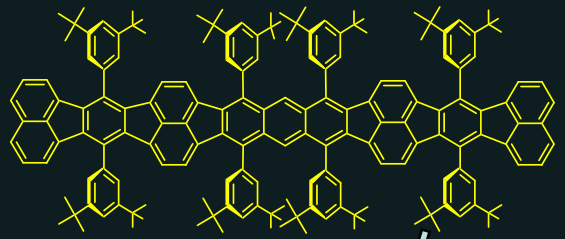
Representative synthesis

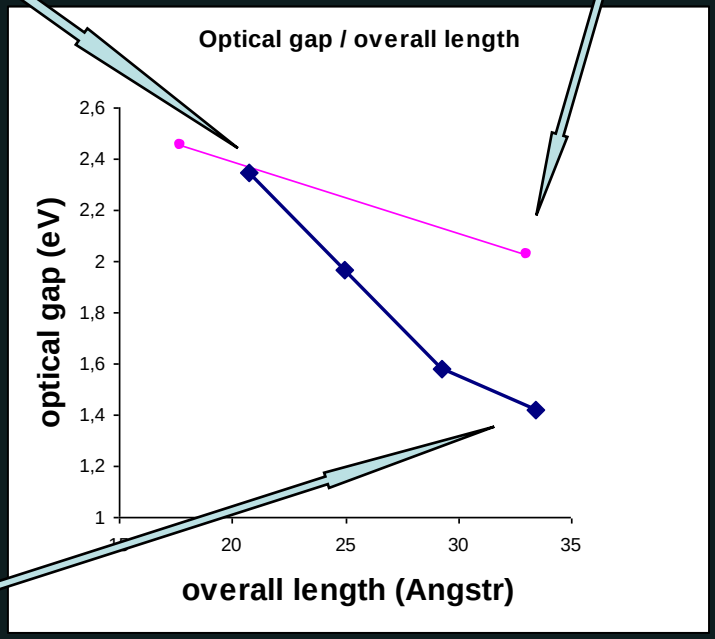


Optimization: small gap landers

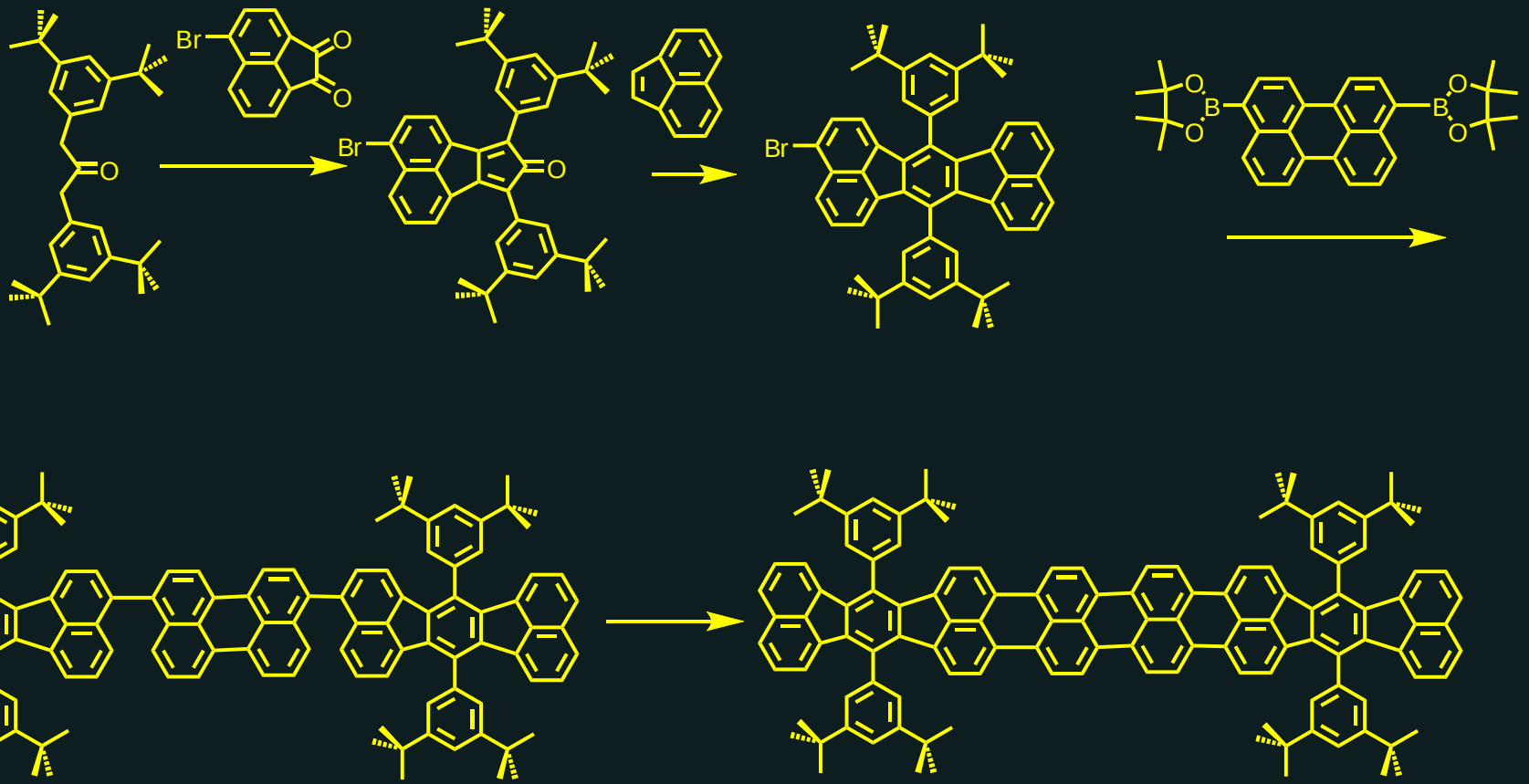
VL







Synthesis of 7



Properties

-electronics

-good electronic decoupling with the substrate

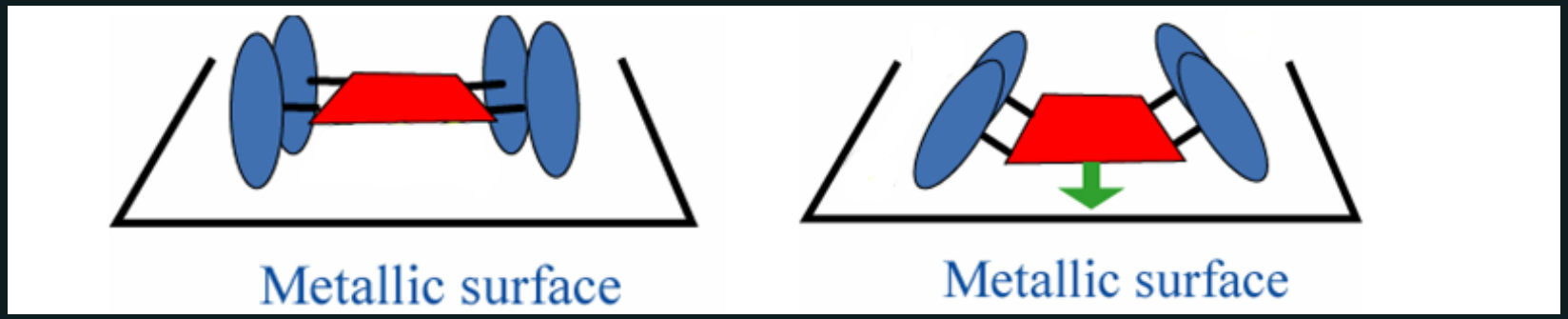
experiments on conductance, contact conductance

-mechanics

-can be reproducibly manipulated by STM at LT

-possibility of tip-induced conformational changes

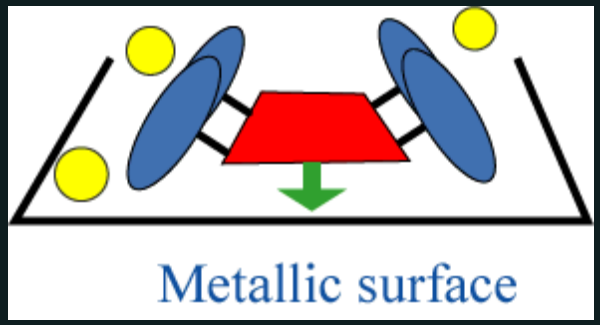
-high adsorption energy (up to 100 kcal/mol)

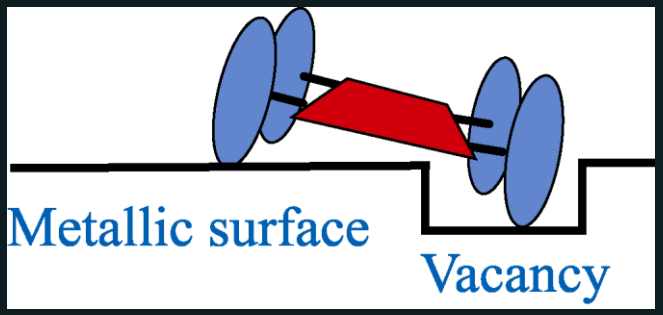


But also strong influence of the molecules on the substrate

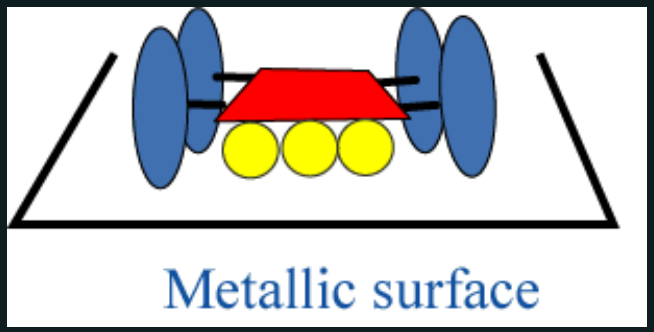
Influence of the molecule on the substrate

The molecules can modify the surface structure:



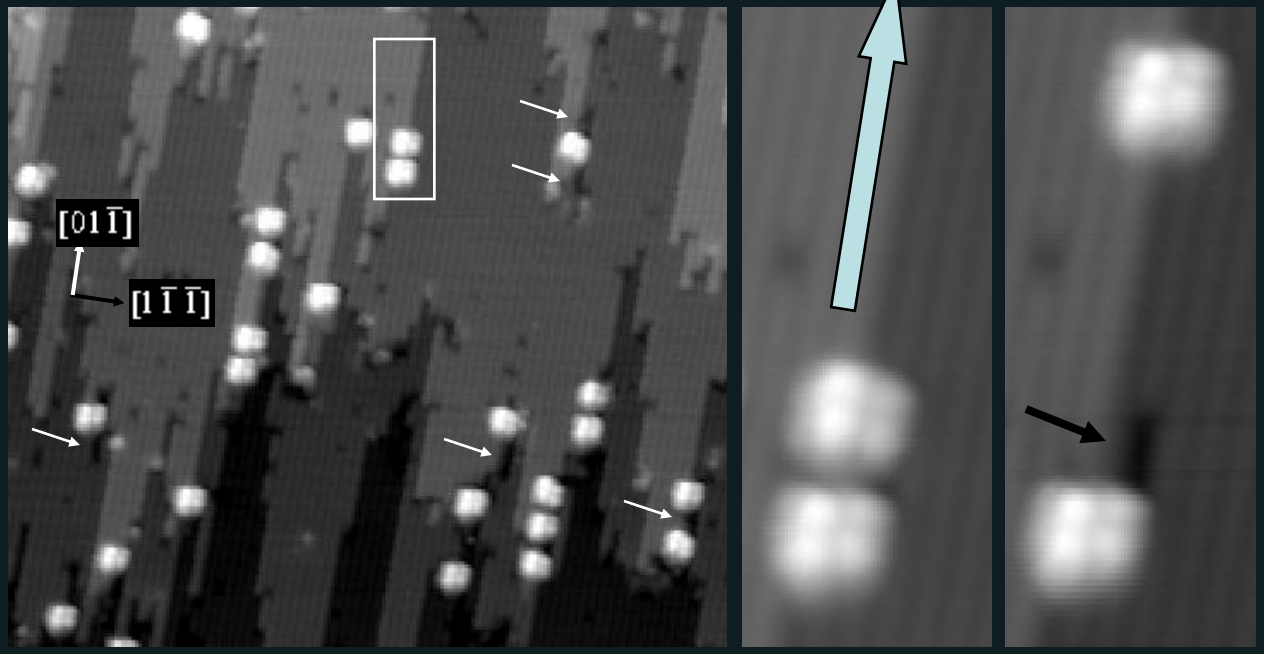


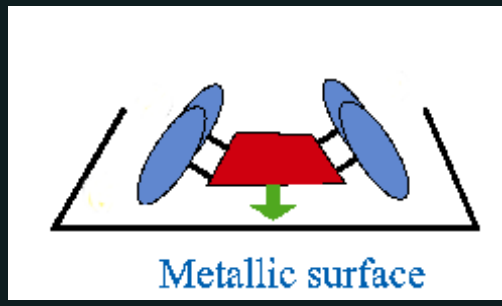
Creation/stabilization of vacancies

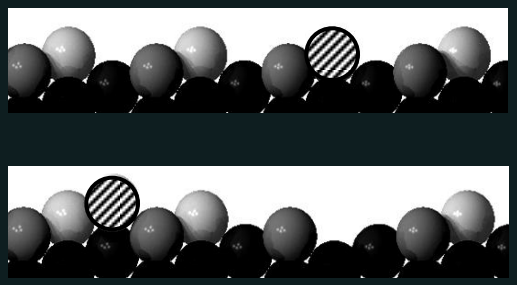


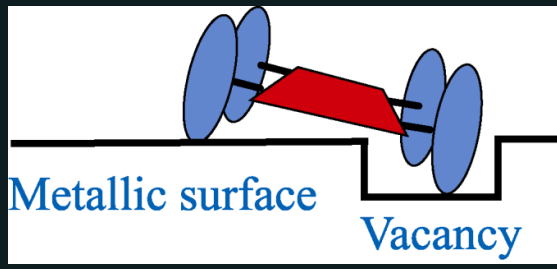
Templating/molding

Creation and/or stabilization of vacancies



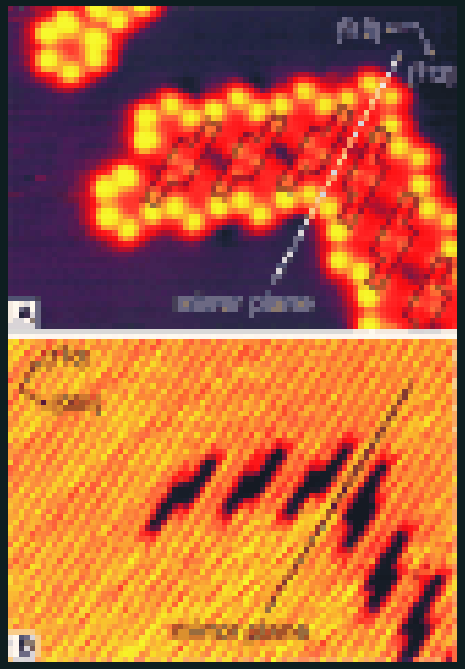


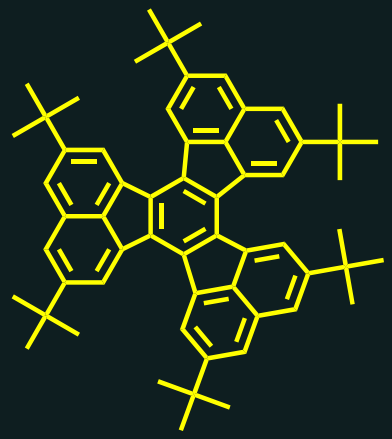




Many examples: here SL lander on Cu(211) *CPL* (2003), 371, 750

Other example





Seems rather general: physisorbed unsaturated hydrocarbons with spacers create and/or stabilize vacancies

Besenbacher, F. et al. Angew. Chem. Int. Ed. Engl. (2001), 40, 2623

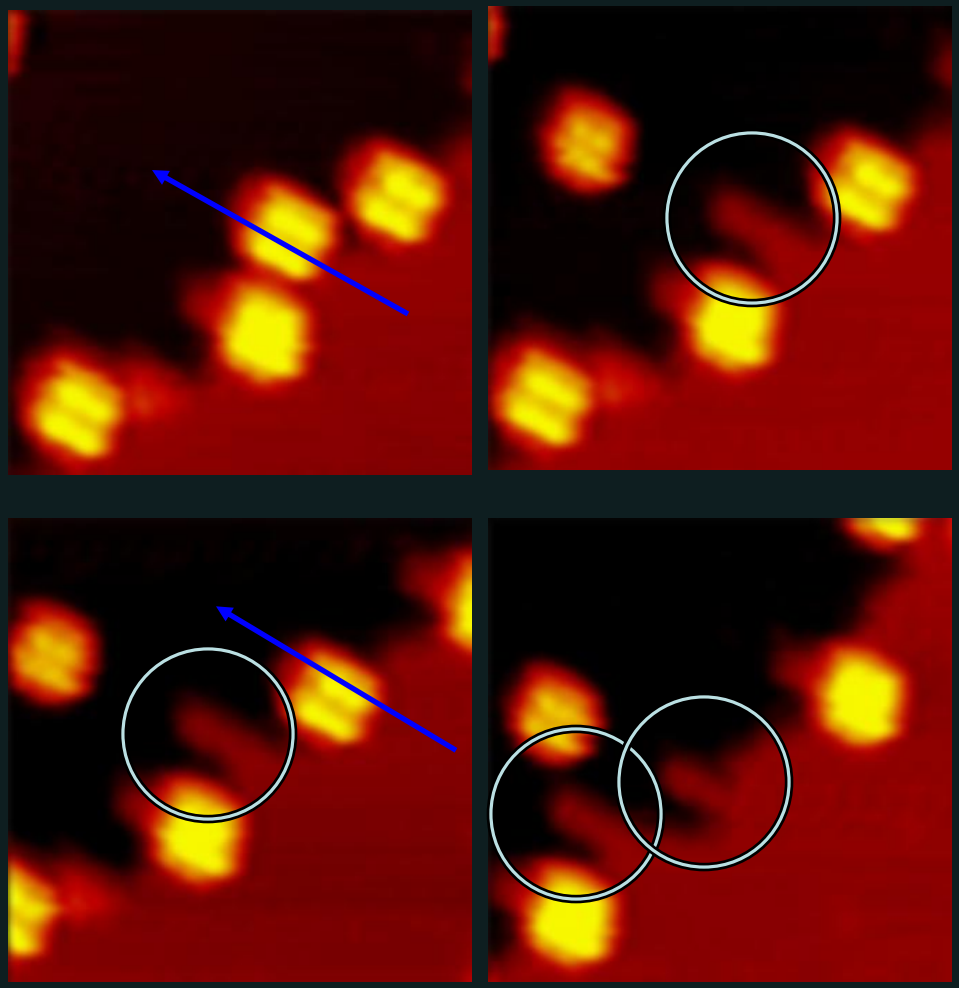
Templating/molding

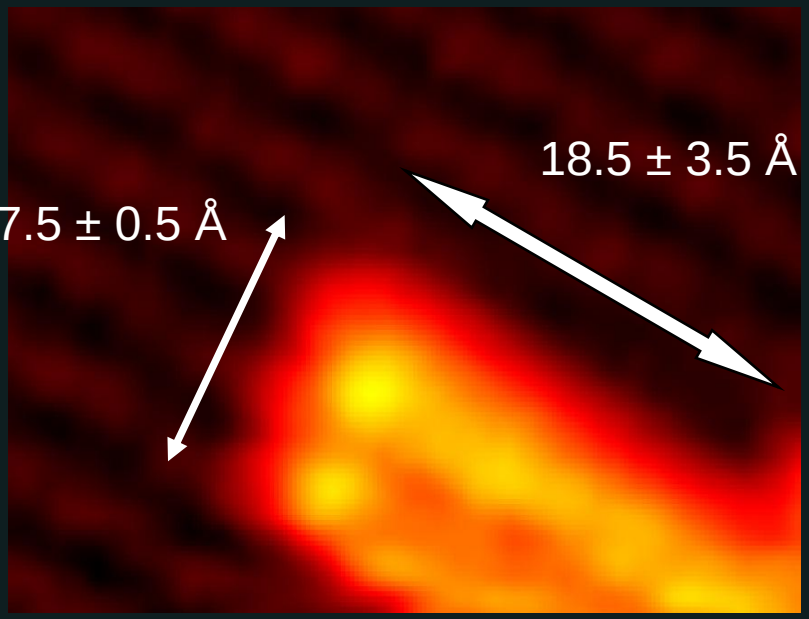
Static molding: fixed lander; mobile metal atoms

Dynamic molding: fixed metal atoms; mobile landers (LT)

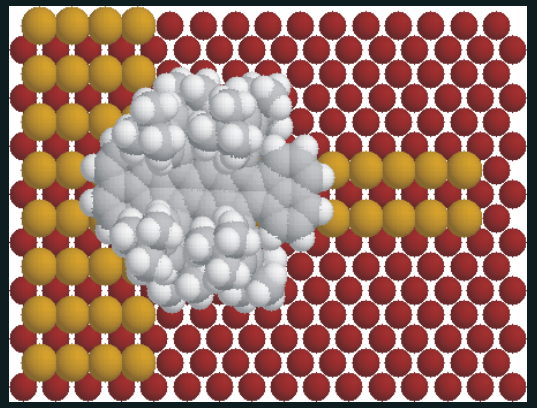
Static molding
lander on Cu(110): Restructuring the Step Edge

RT deposition; experiment at 100 K (Aarhus, F. Besenbacher)



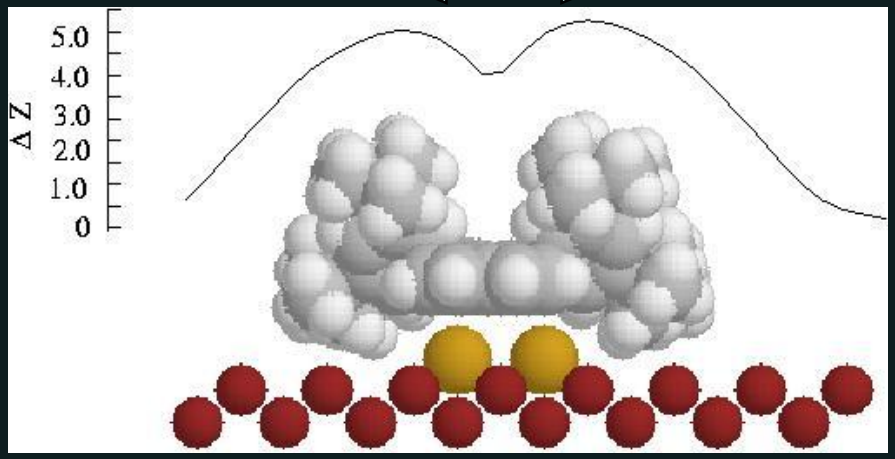


Landers: pinning center for step edge fluctuations

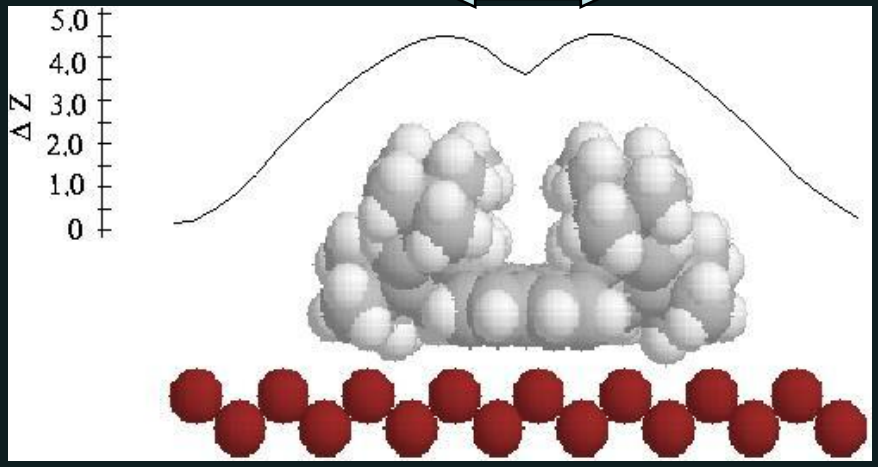


Mobile Cu atoms from the step-edge are stabilized and release the constraints by stacking underneath the board

8.5 Å

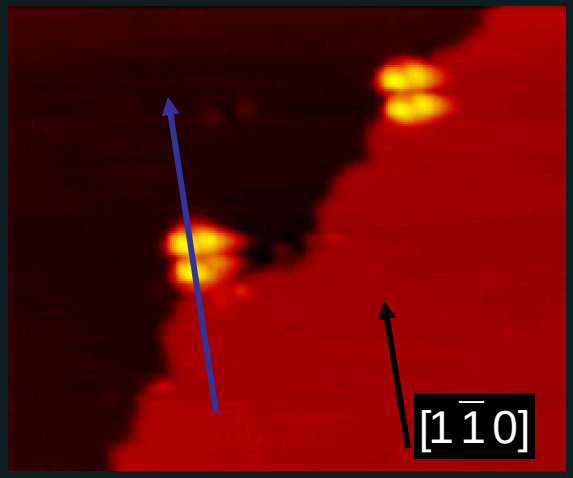


6 Å

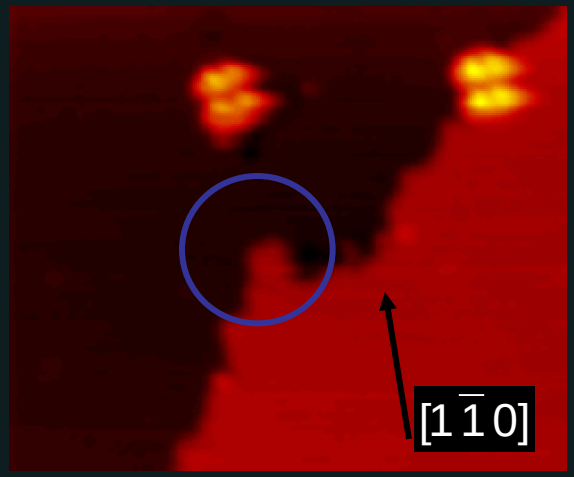


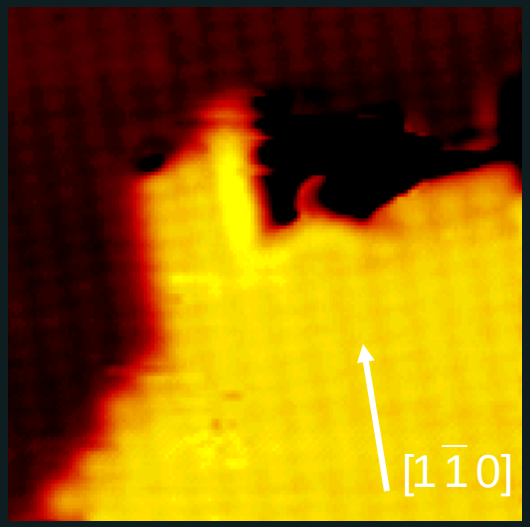
M. Schunack *et al.* Science (2002), 296:5566, 328.

The shape of the nanoelectrode is function of the molecular mould:
step edge restructuring with VL lander



235 × 195 Å^2, -0.13 nA,
-1.25 V





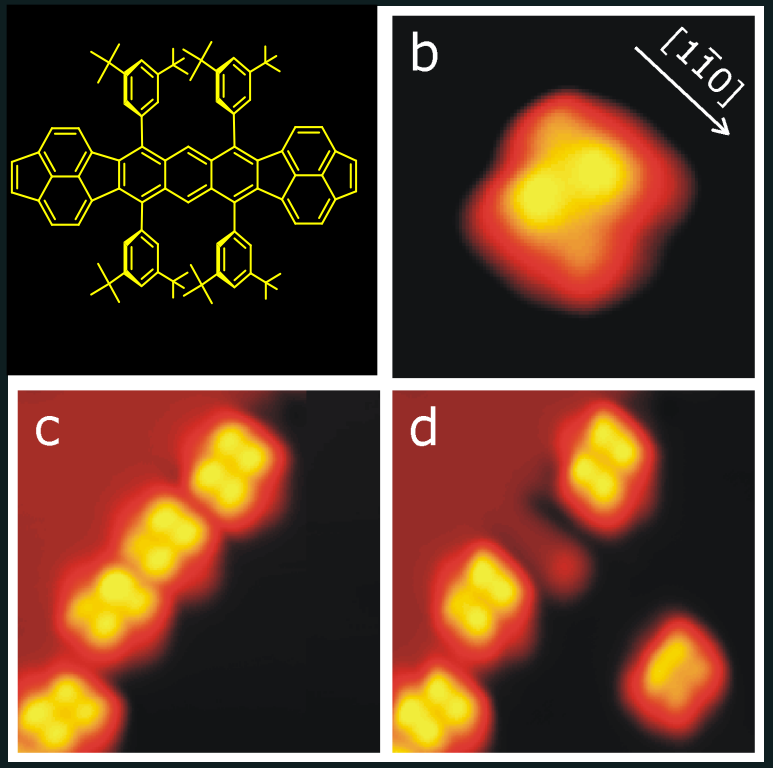
50 × 50 Å^2, -0.81 nA,
-0.44 V

The nanotooth is now 2 or 3 atomic rows wide

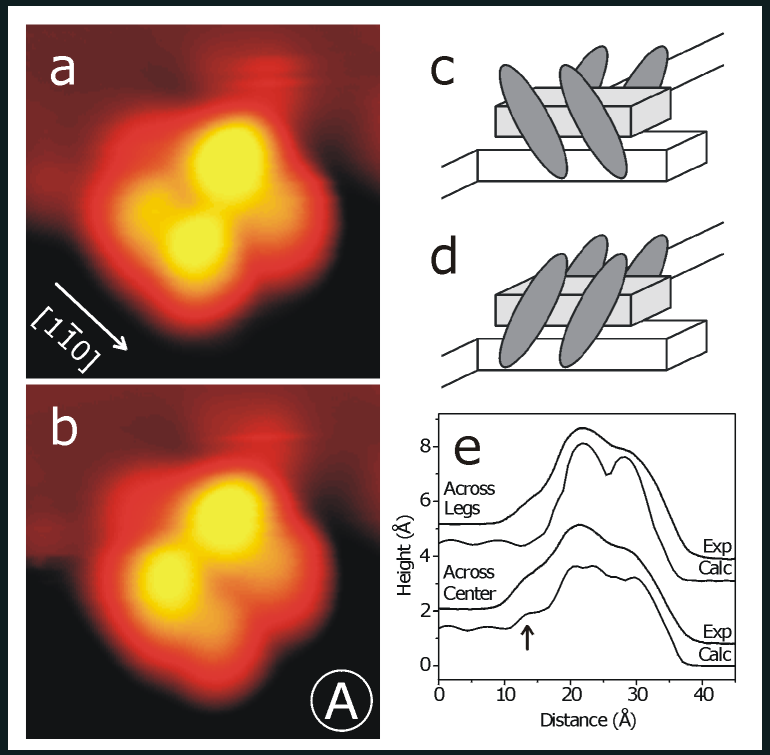
R. Otero, *et al* Nanoletters (2004), 4:1, 75-78.

Application: study of the electronic properties of a single molecule using its self-fabricated nanoelectrode

molecular moulding + manipulation



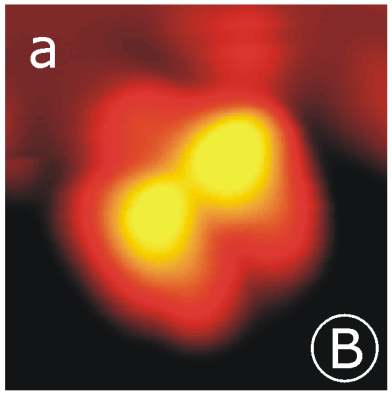
Cu(110) 80 x 80 Å

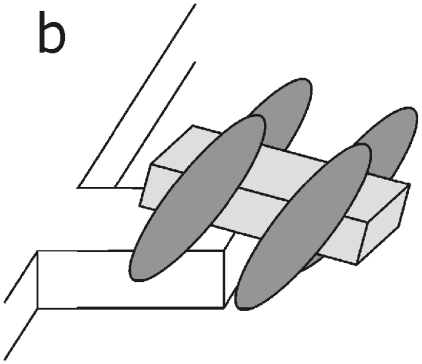


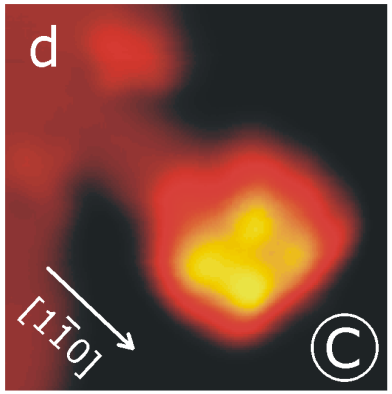
35 x 35 Å

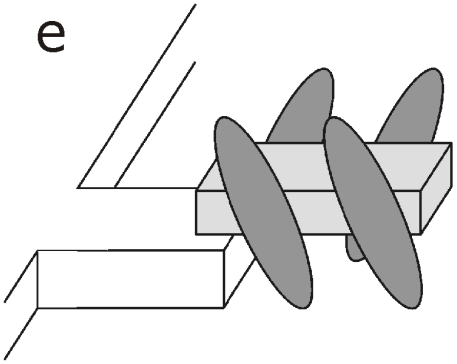
Coll. FU Berlin

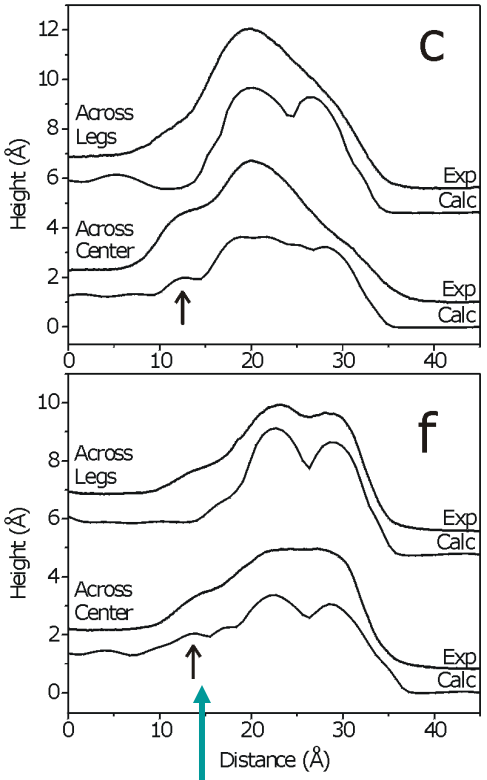
A two electrodes experiment: tip-molecule-nanoelectrode











Nanoletters (2005) 5:5, 859

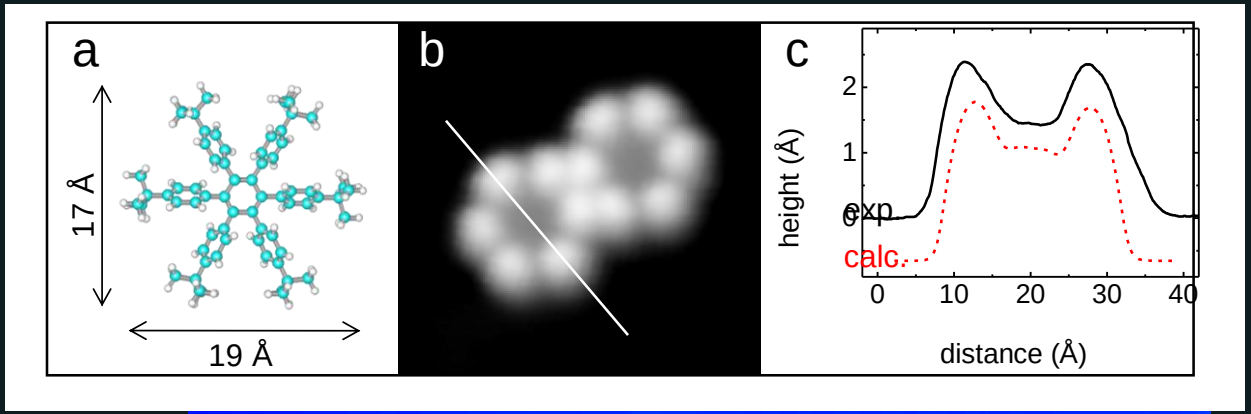
Contact bump

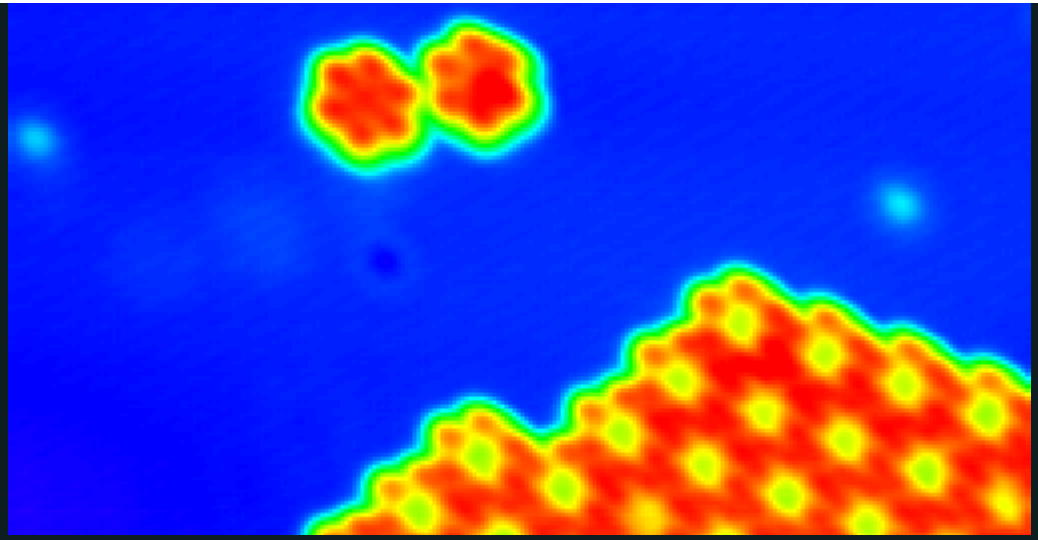
Templating/molding

Static molding: fixed lander; mobile metal atoms

Dynamic molding: fixed metal atoms; mobile landers (LT)

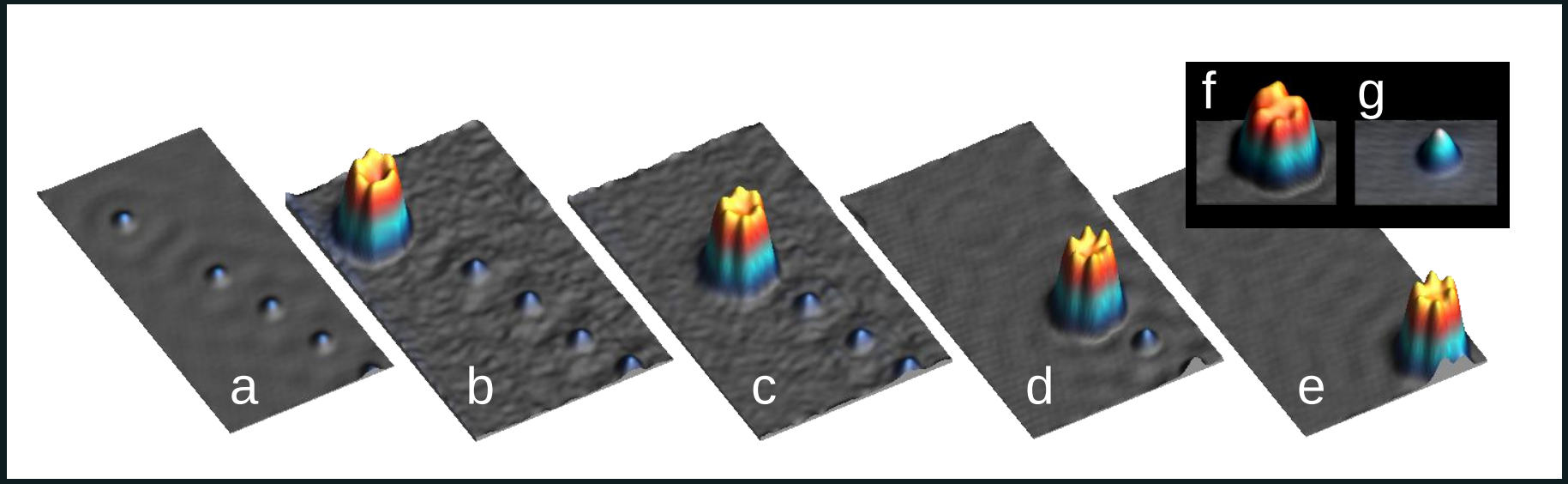
Dynamic molding: a molecular Hoover





HtB-HPB: accumulating metal adatoms

Along a line of Cu adatoms on Cu(111)

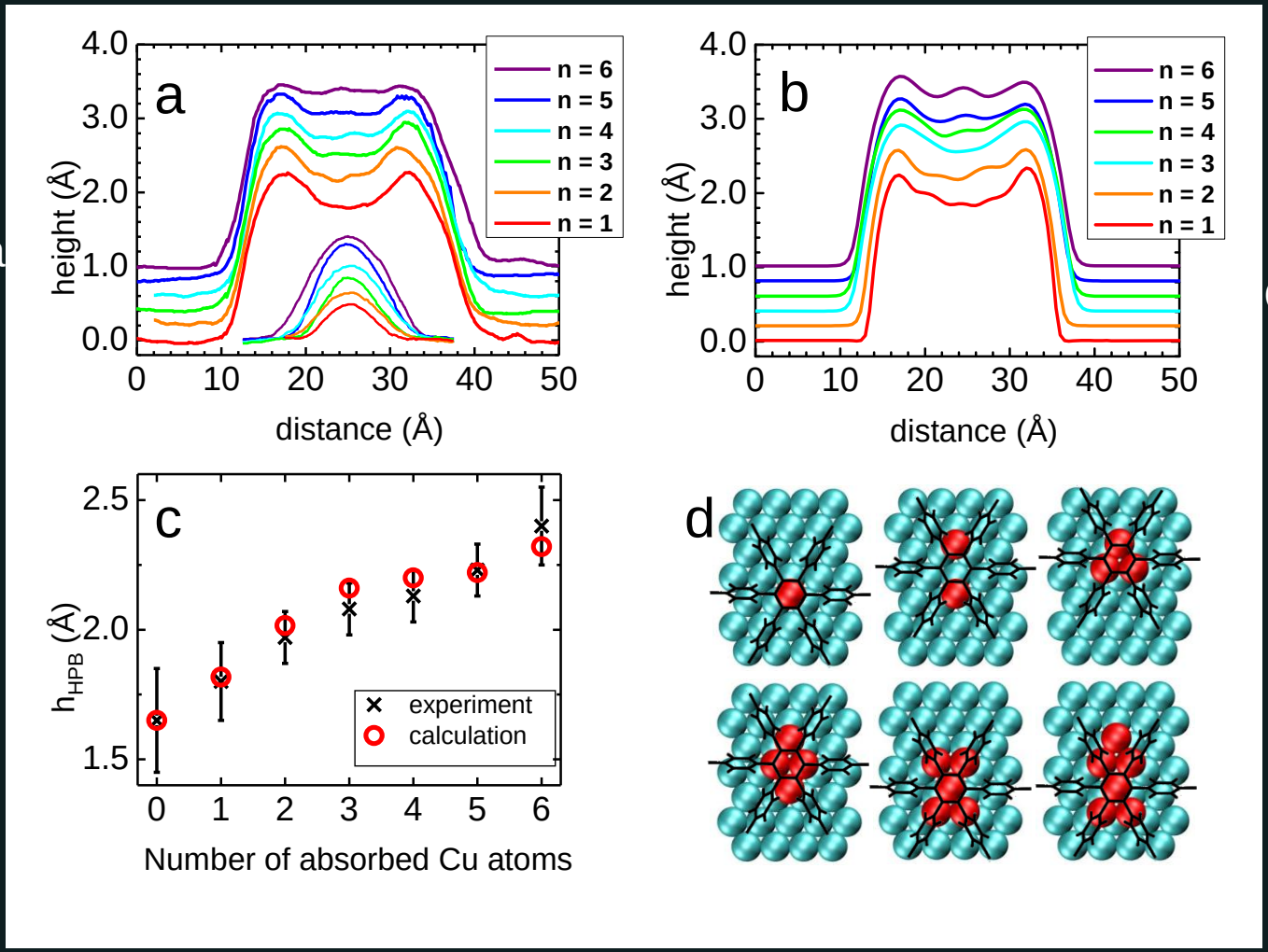


Up to 6 Cu atoms with decreasing mobility

Apparent height across the molecule:

Experimenta

U: 100mV



Calculated

Nature Materials, (2005) 4(12) 892-895

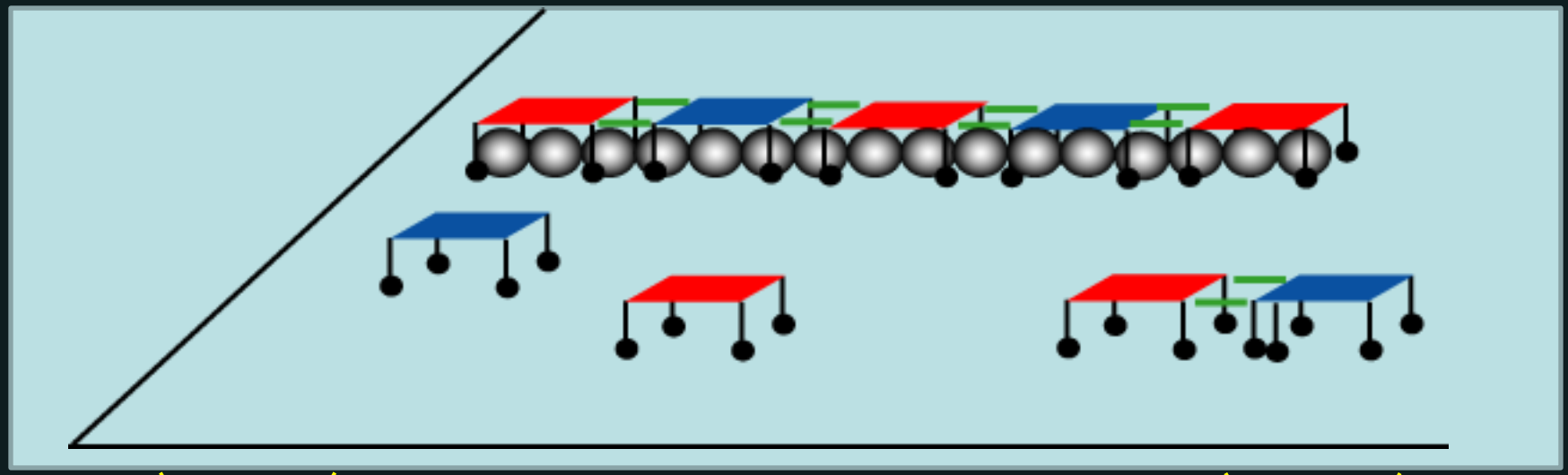
Work in progress

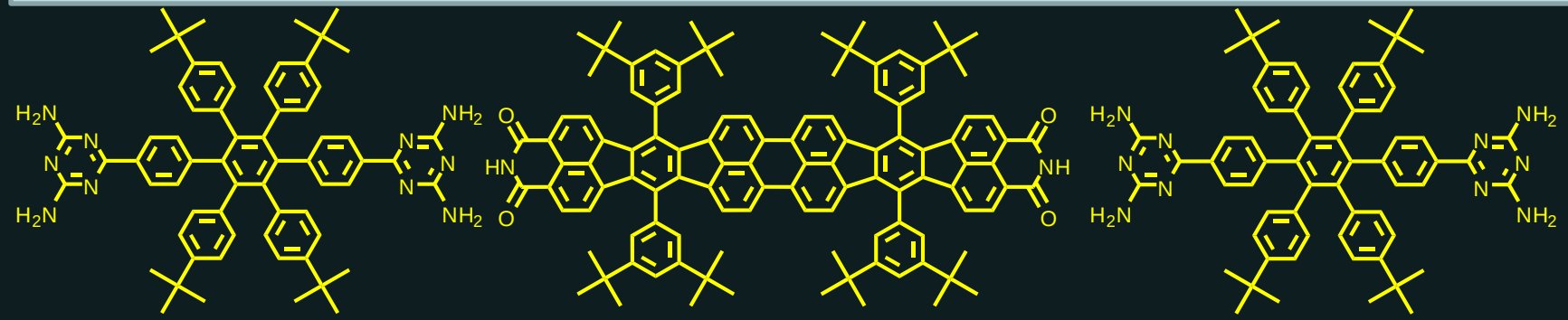
Supramolecular assemblies of molecular moulds for templating electrical circuitry:

1-coevaporation of “complementary” lander molecules that self-assemble on a substrate

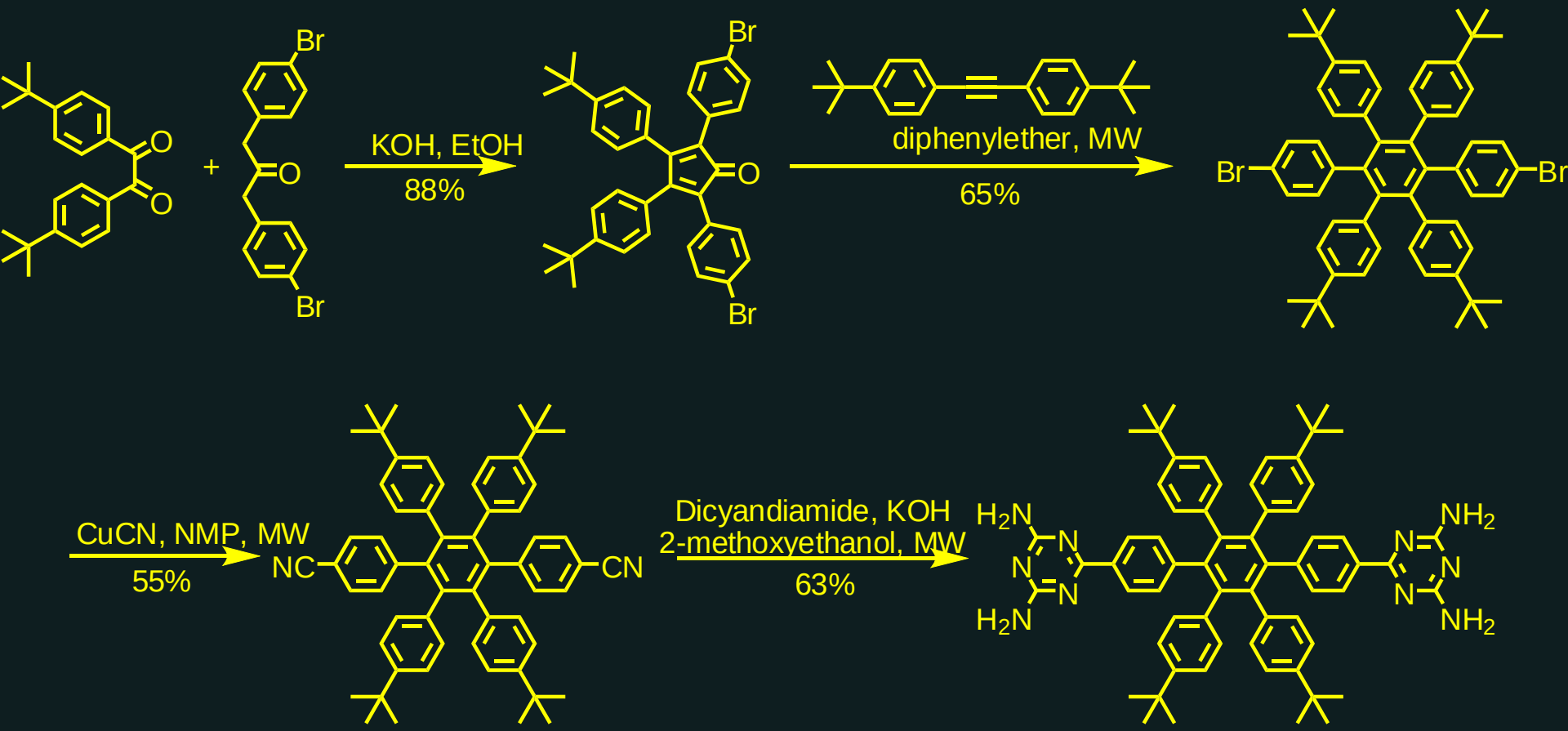
2-then diffusion of metal atoms

3-trapping of these atoms to create “molded nanostructures”

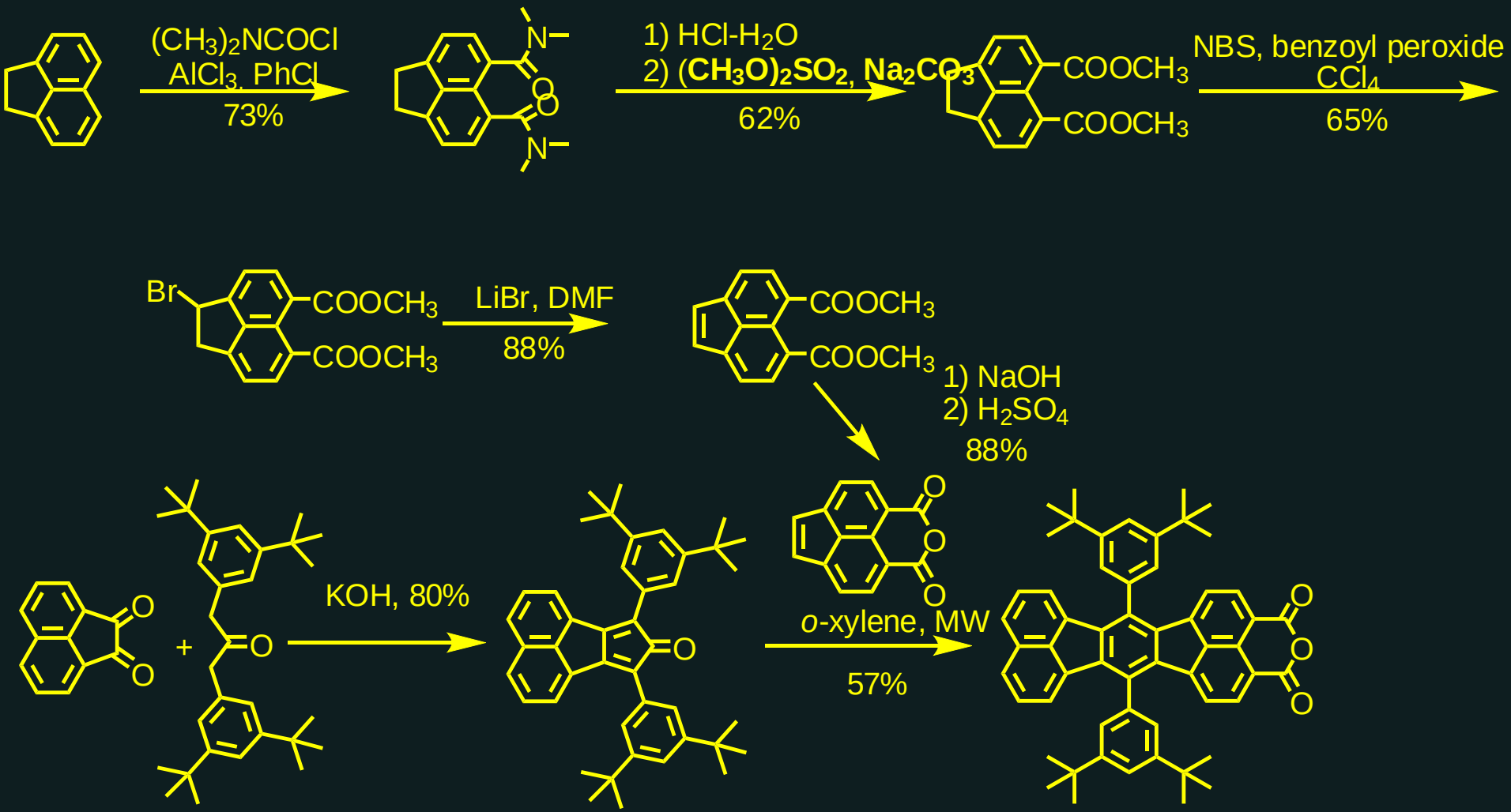




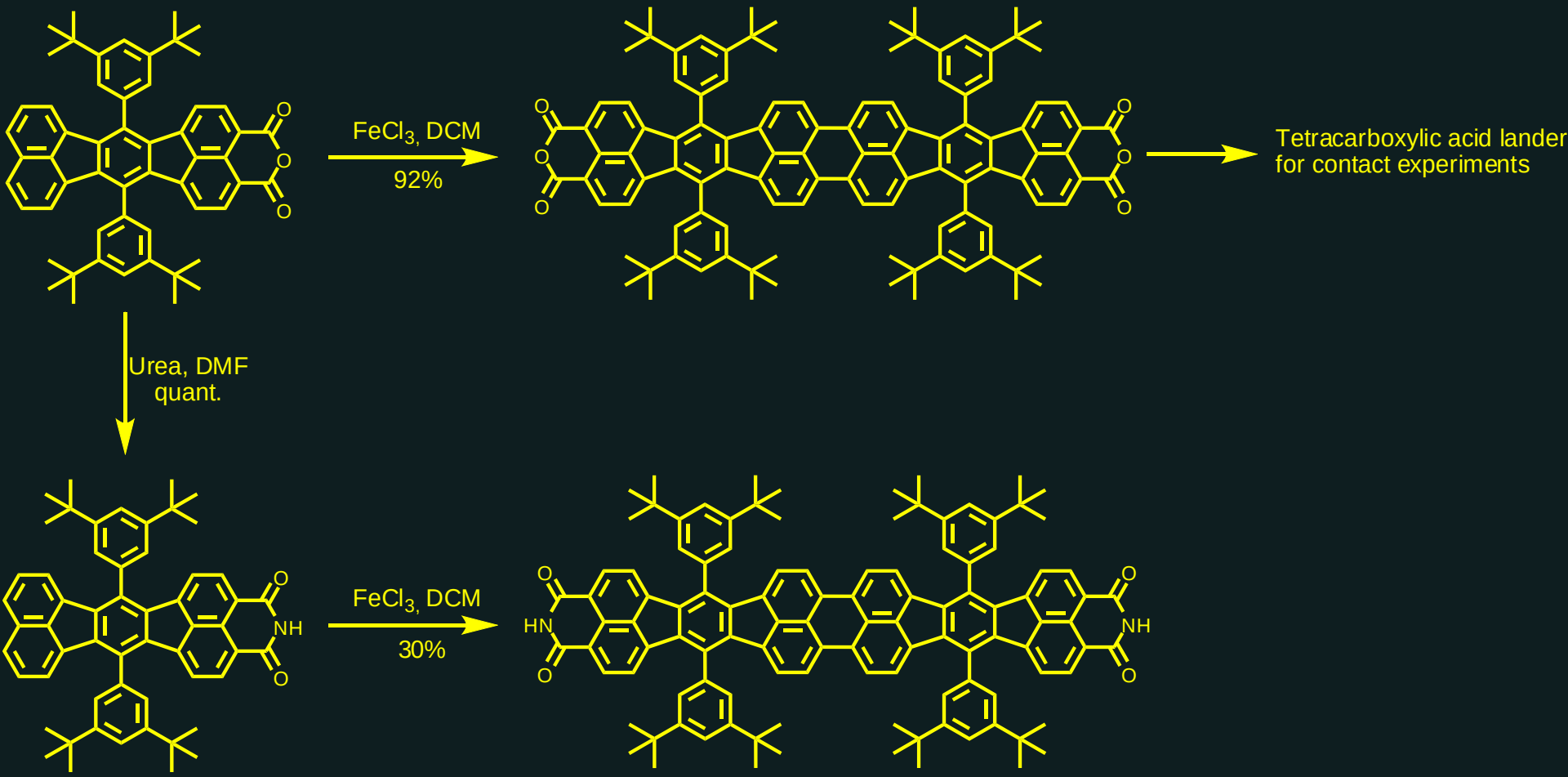
First molecule



Second molecule (B): first steps



- Homo-coupling



Outline:

-introduction to the lander-molecules

-molecular molding

-mechanics: a molecular rack and pinion

Outline:

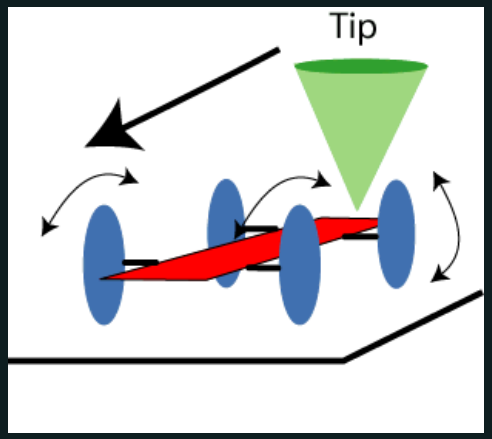
-introduction to the lander-molecules

-molecular molding

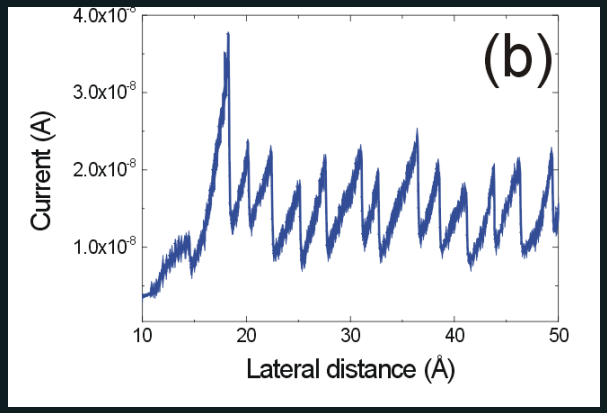
-mechanics: a molecular rack and pinion

Single molecule mechanics

The lander geometry allows very controlled tip-induced manipulations

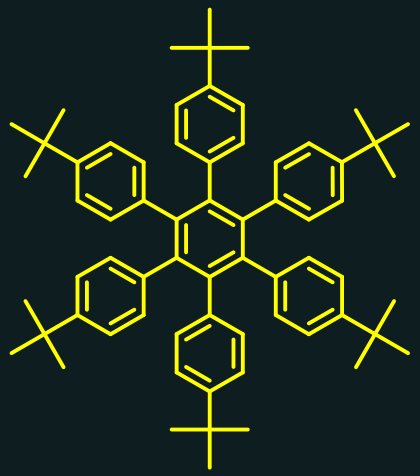


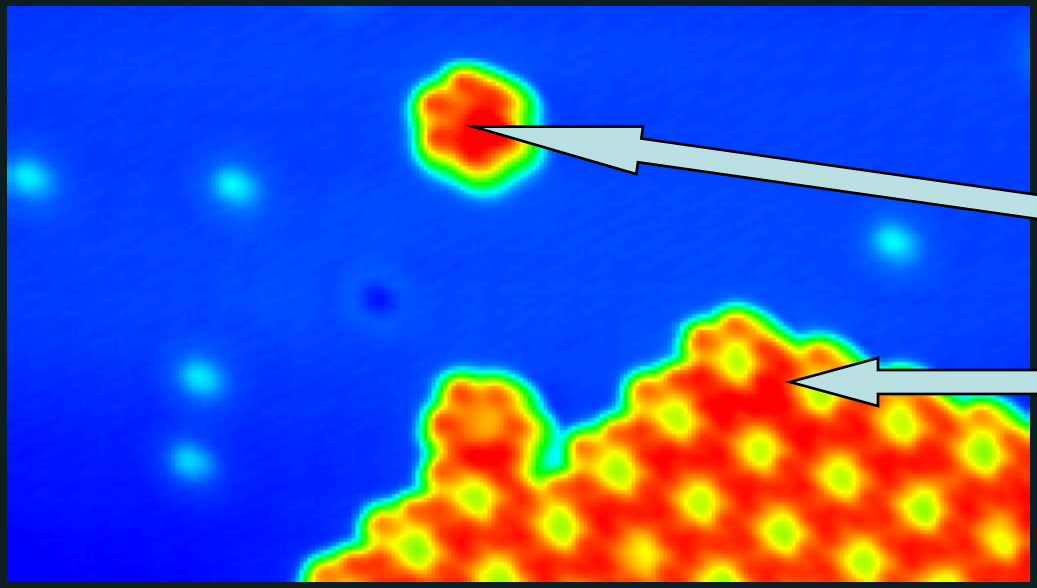
At constant tip-height, monitoring of the tunnel current gives detailed information on the single molecule mechanics

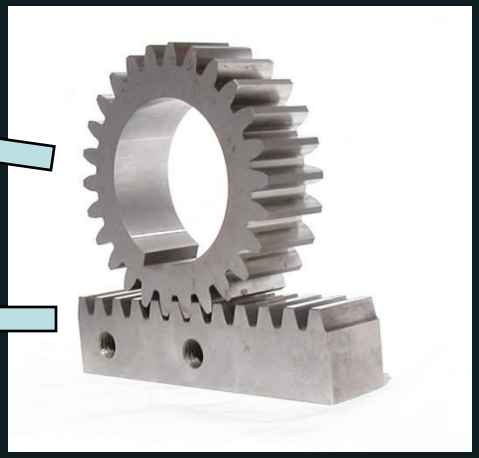


Objective: controlled rotation of a single molecule

A rack and pinion mechanism ???

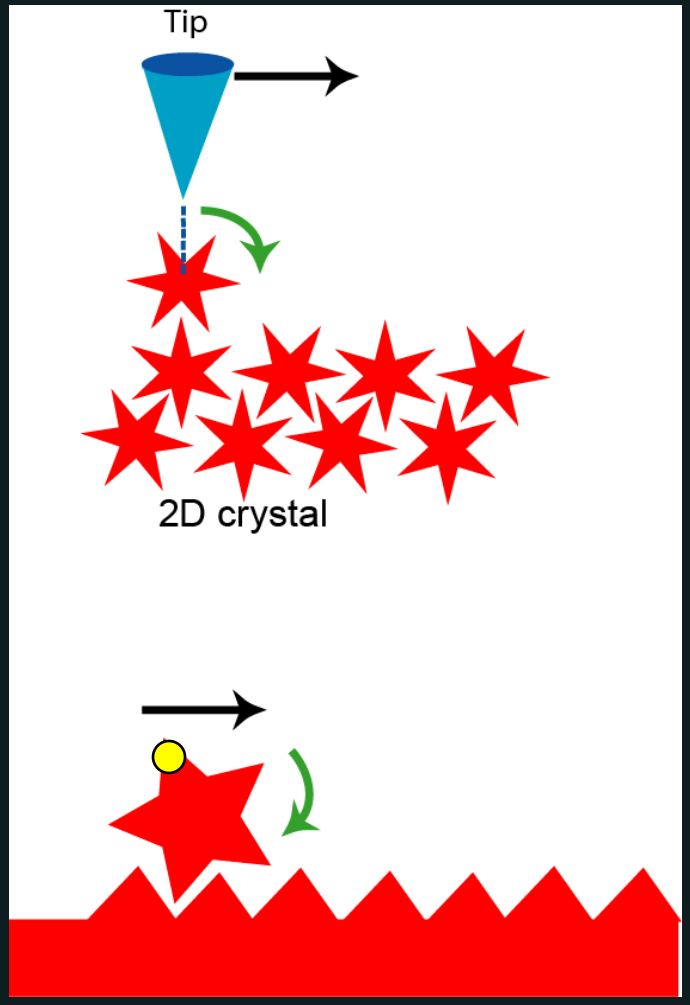


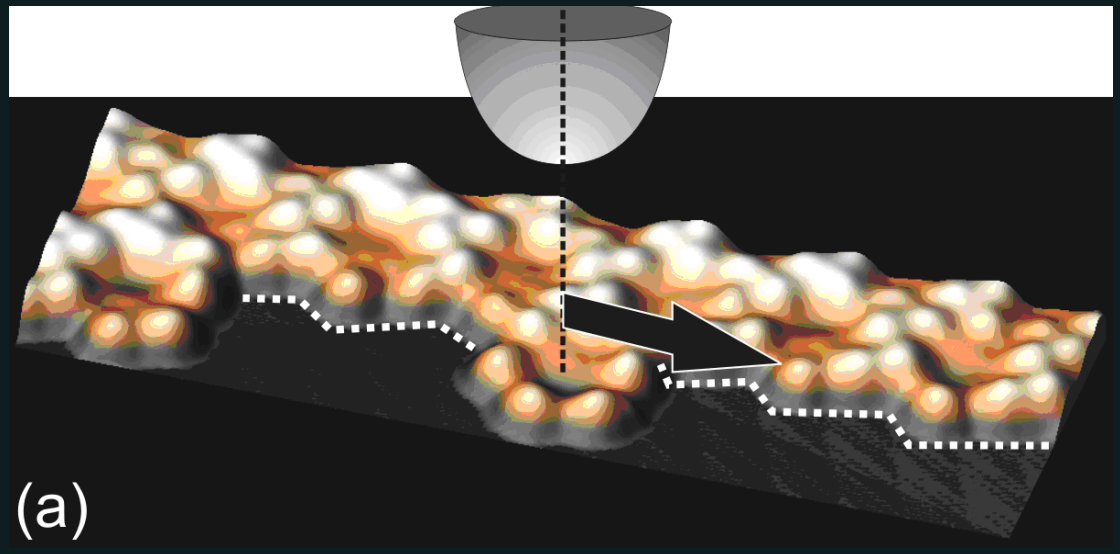




S.K. Sadhukhan *et al.* Synthesis (2003) *10*, 1521.

Objective: tip translation ➡ rotation of the molecule



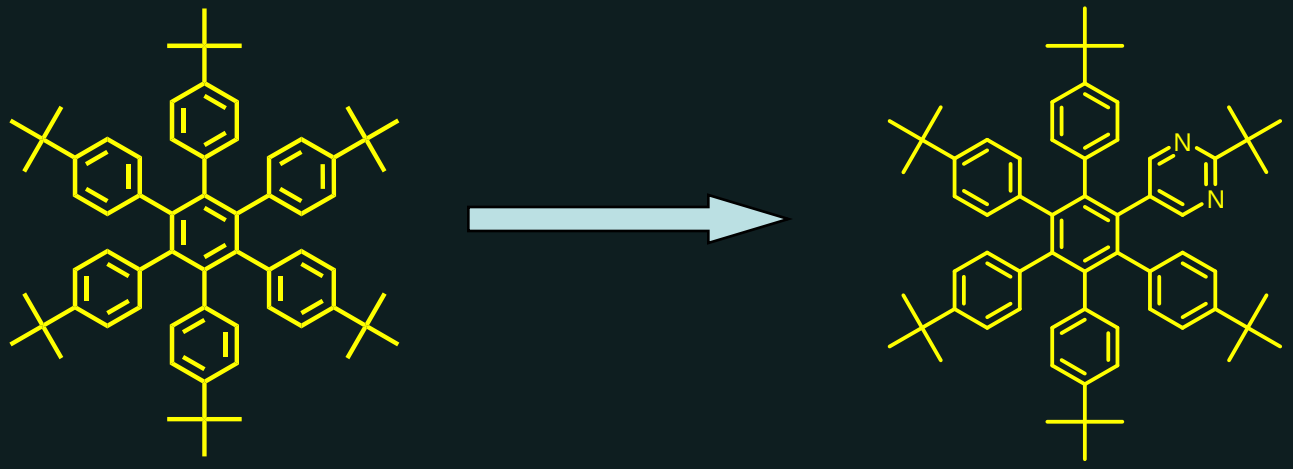


Proof of a rotation???

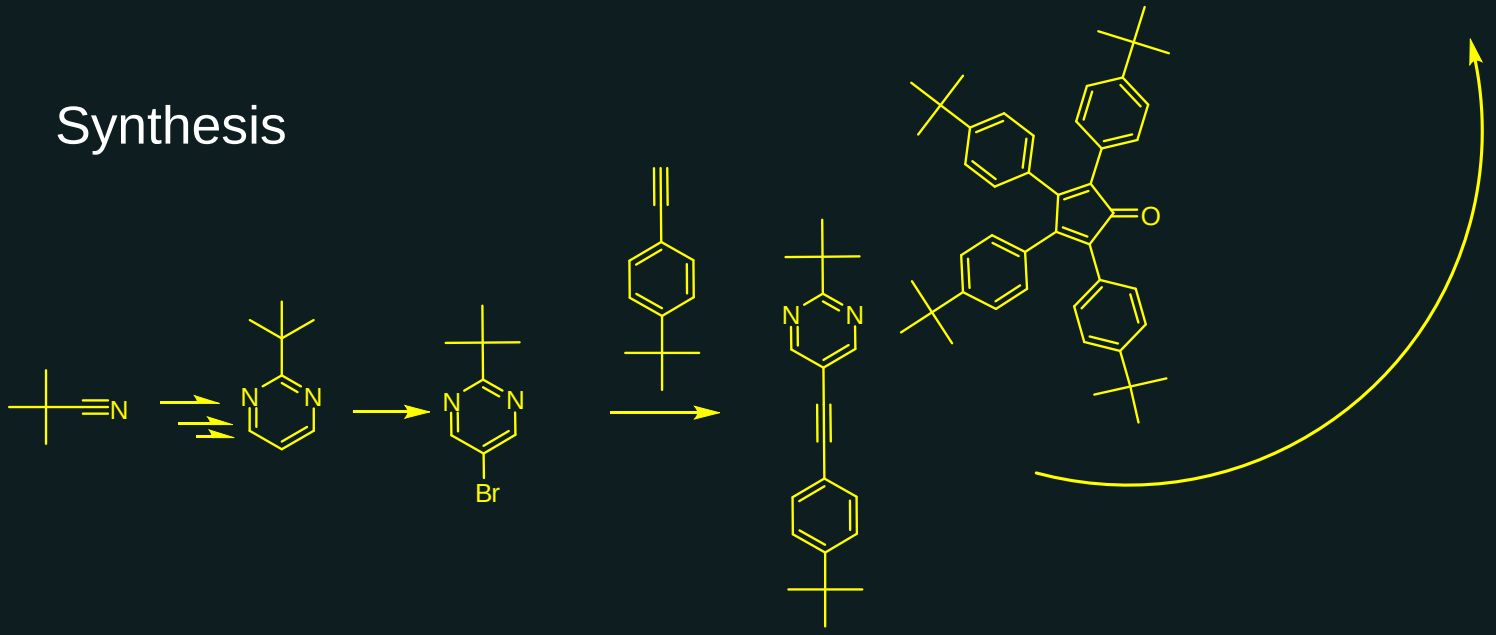
We need a tag ! ●

The tag

Open a new tunnel channel

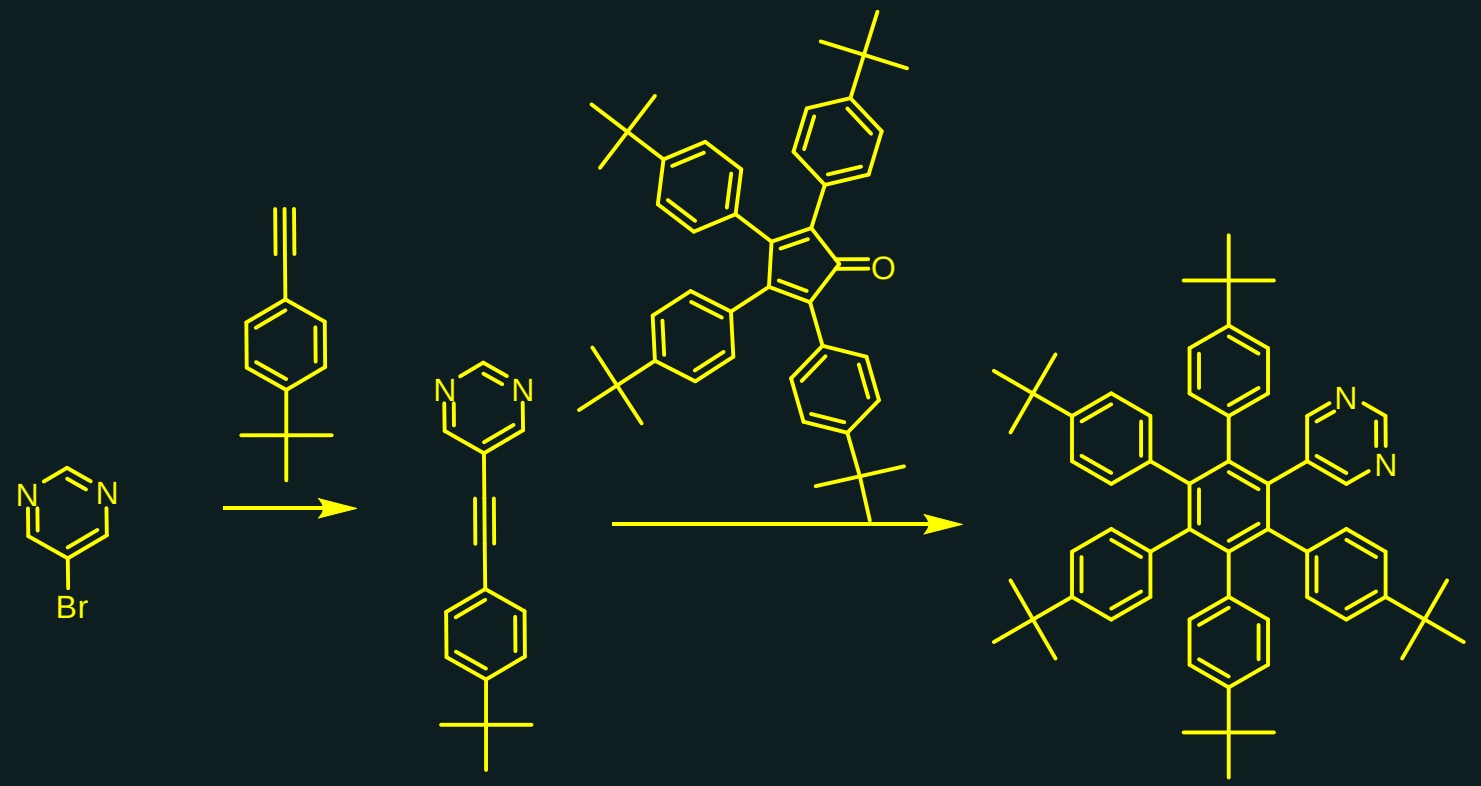


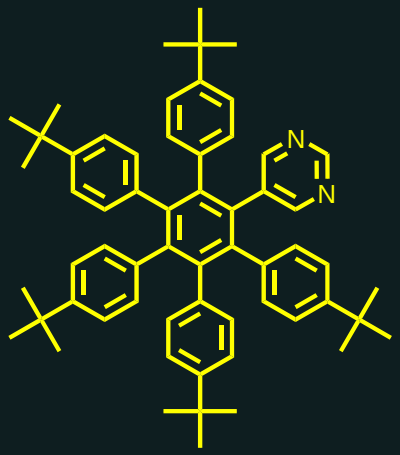
Synthesis

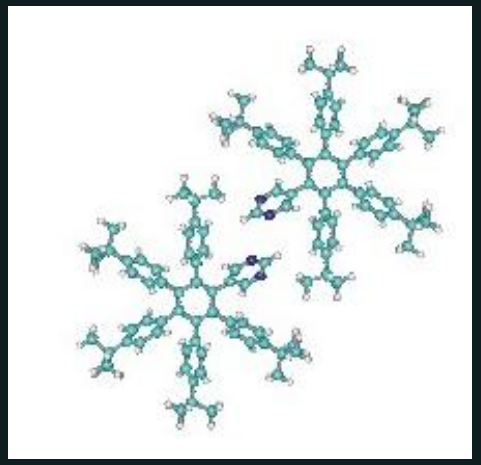


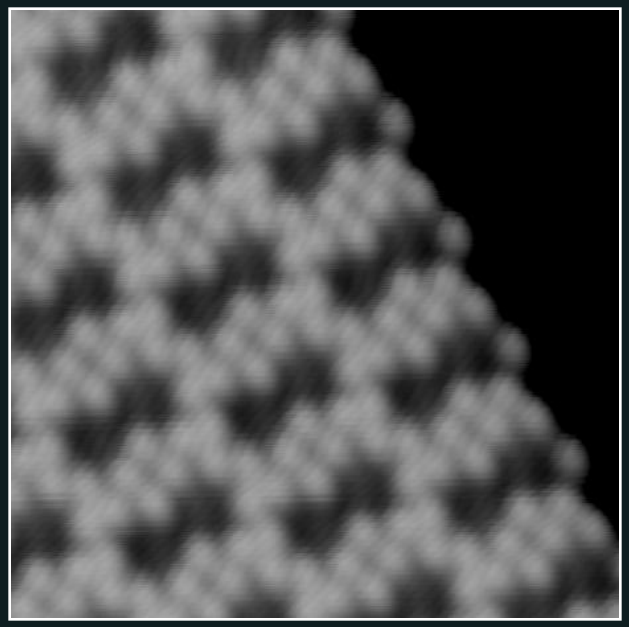
Preliminary work: test the tag

with a similar molecule



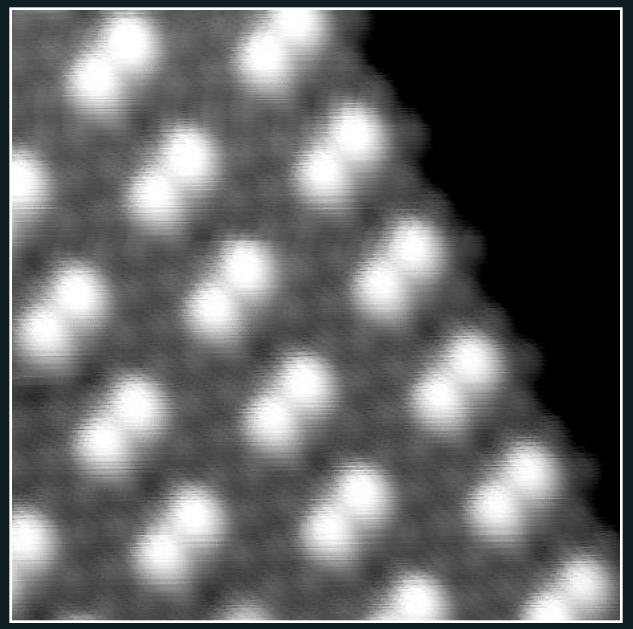






040317.1240
0.24nA
80 x 80 Å²

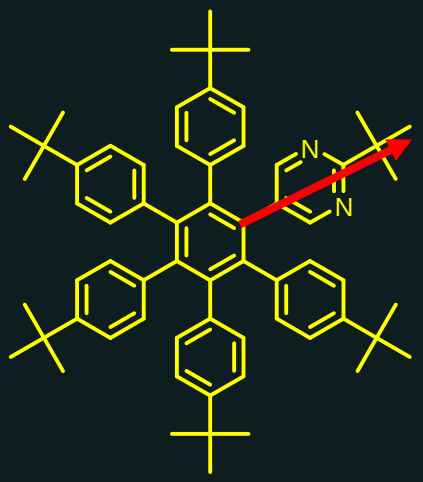
0.5 V

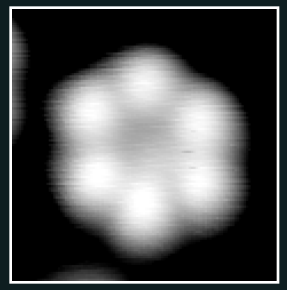


040317.1439
0.24nA
80 x 80 Å²

2.7 V

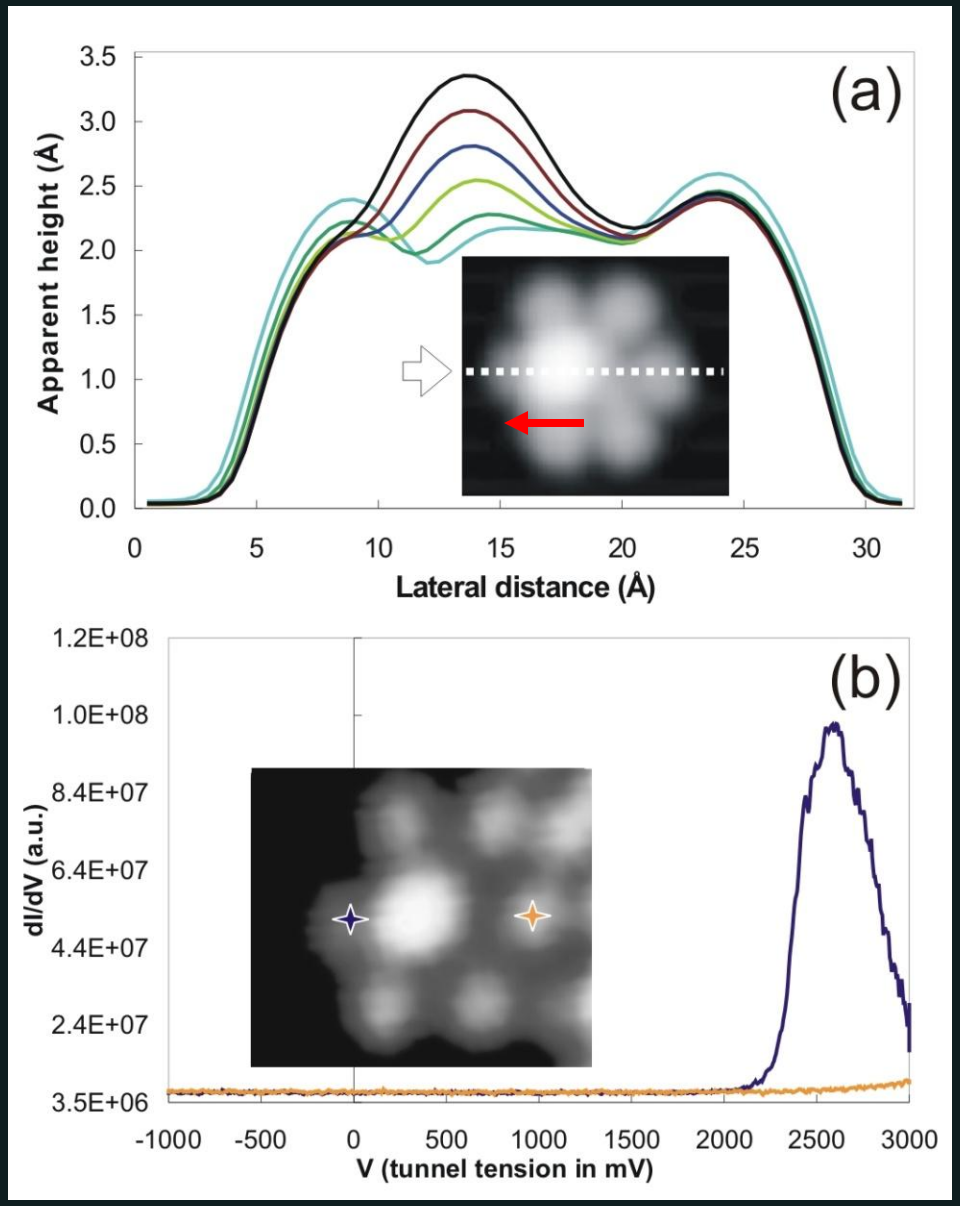
The pinion: testing the tag..





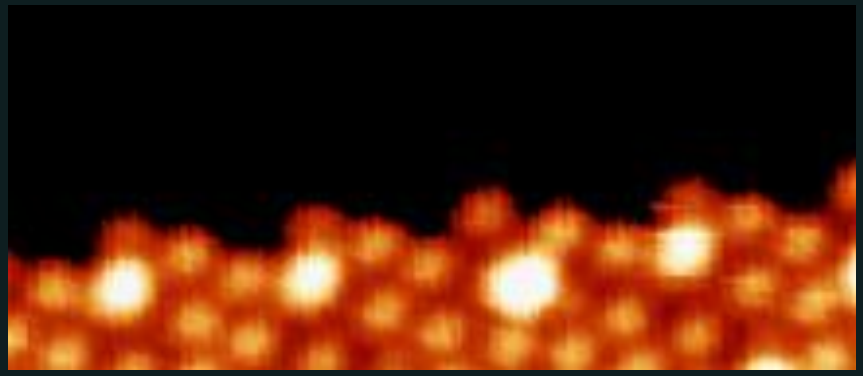
1.0 V

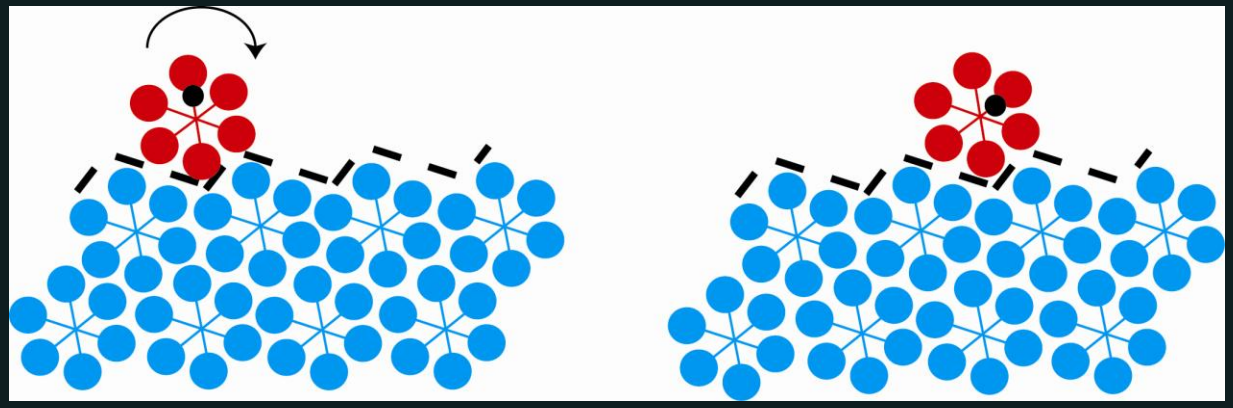
Now possible to describe the orientation by the vector: center to tag



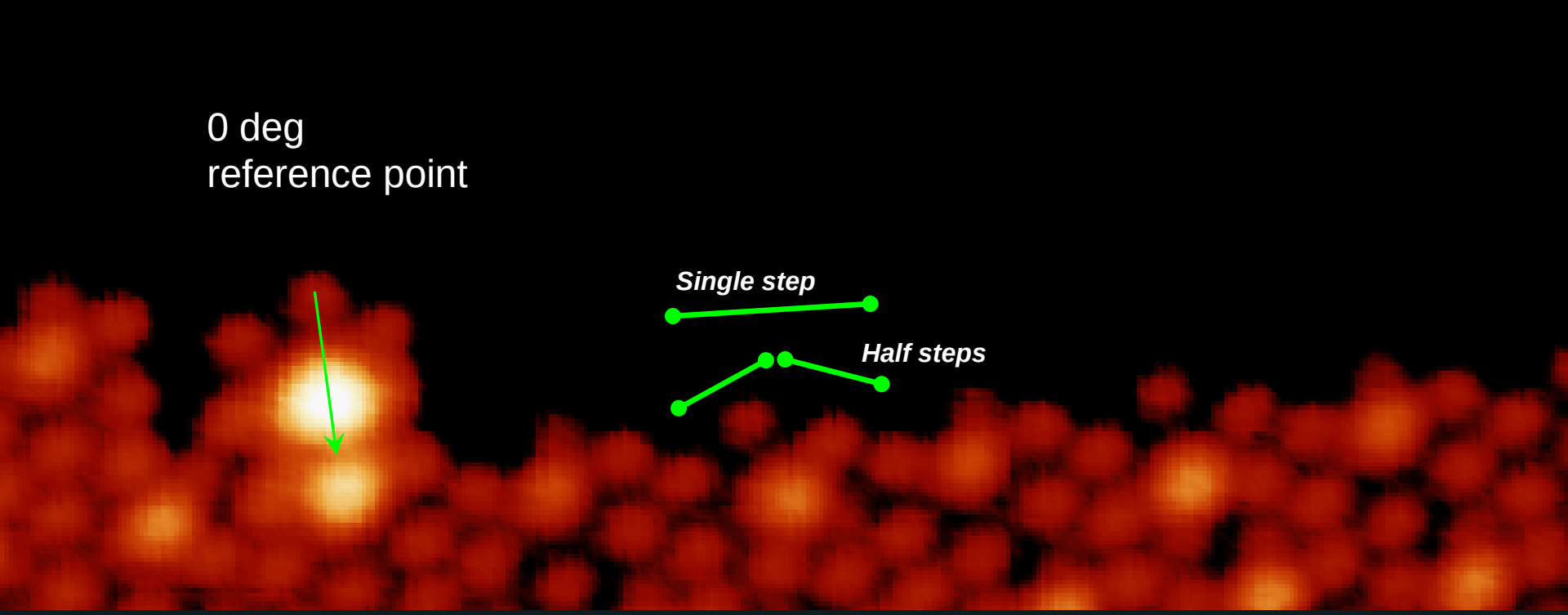
The rack :islands step-edges

Asymmetric steps:

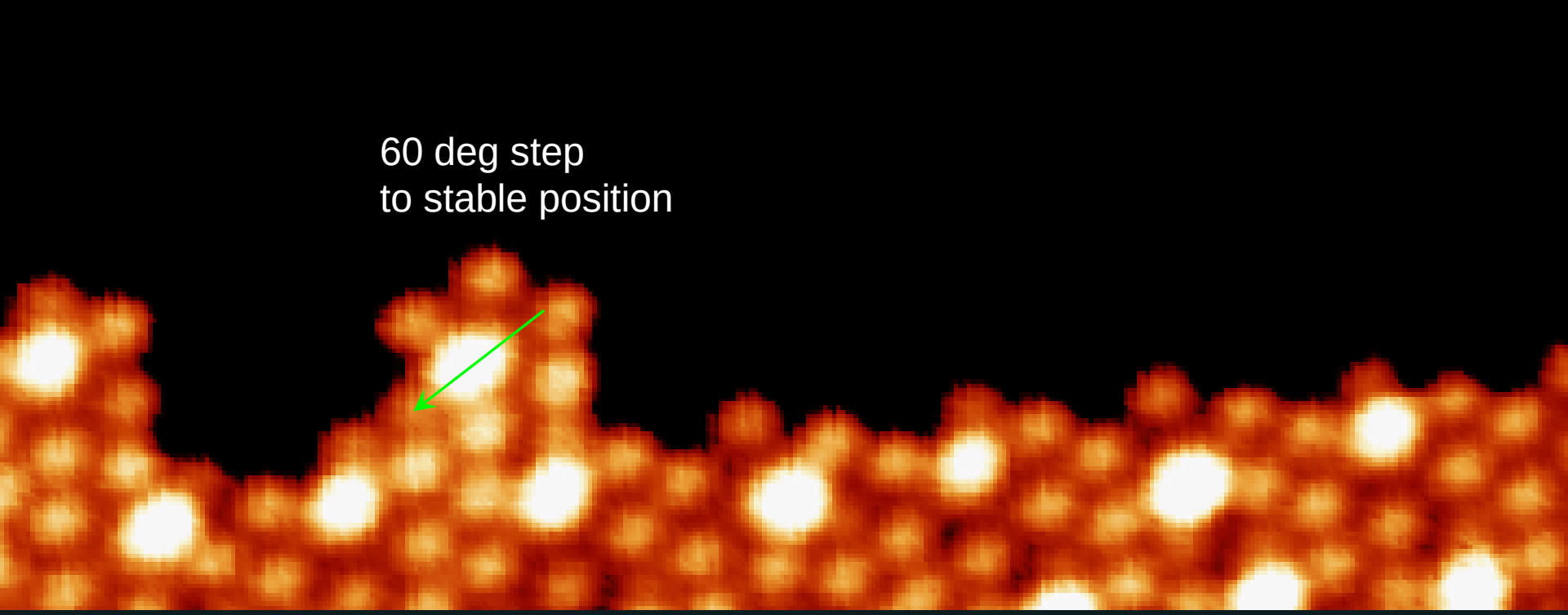


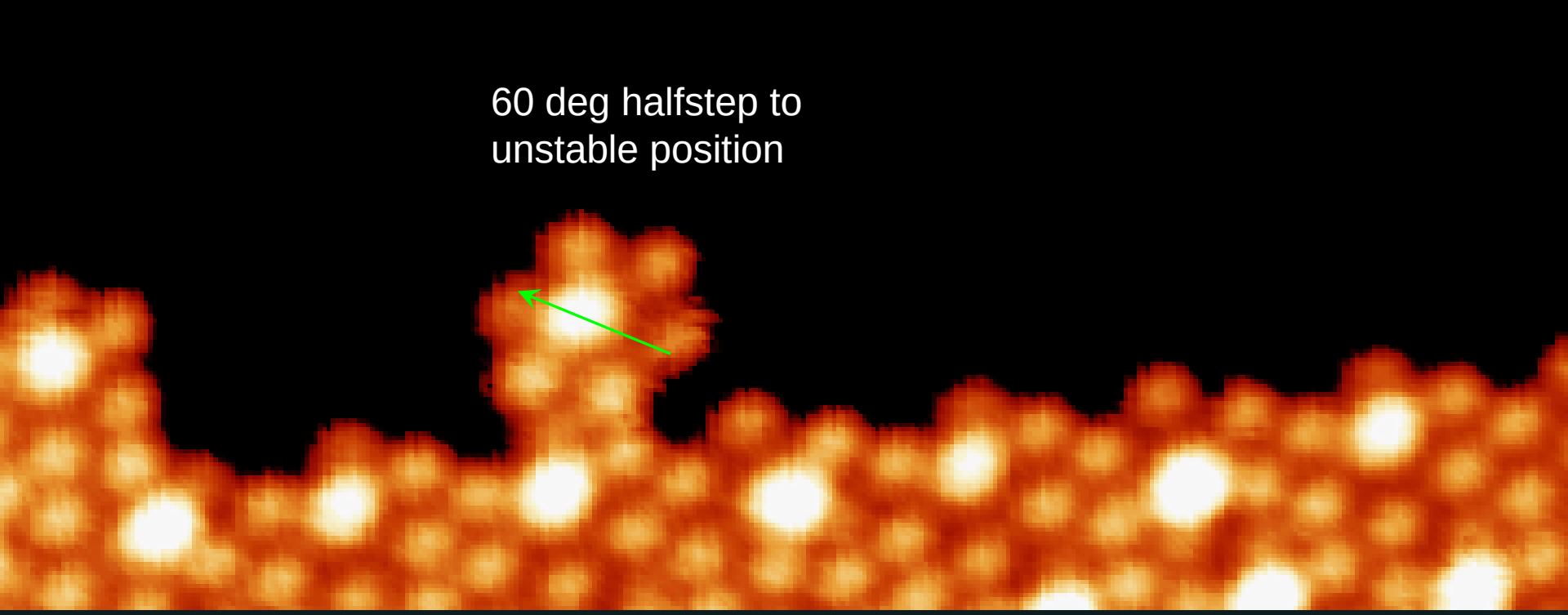


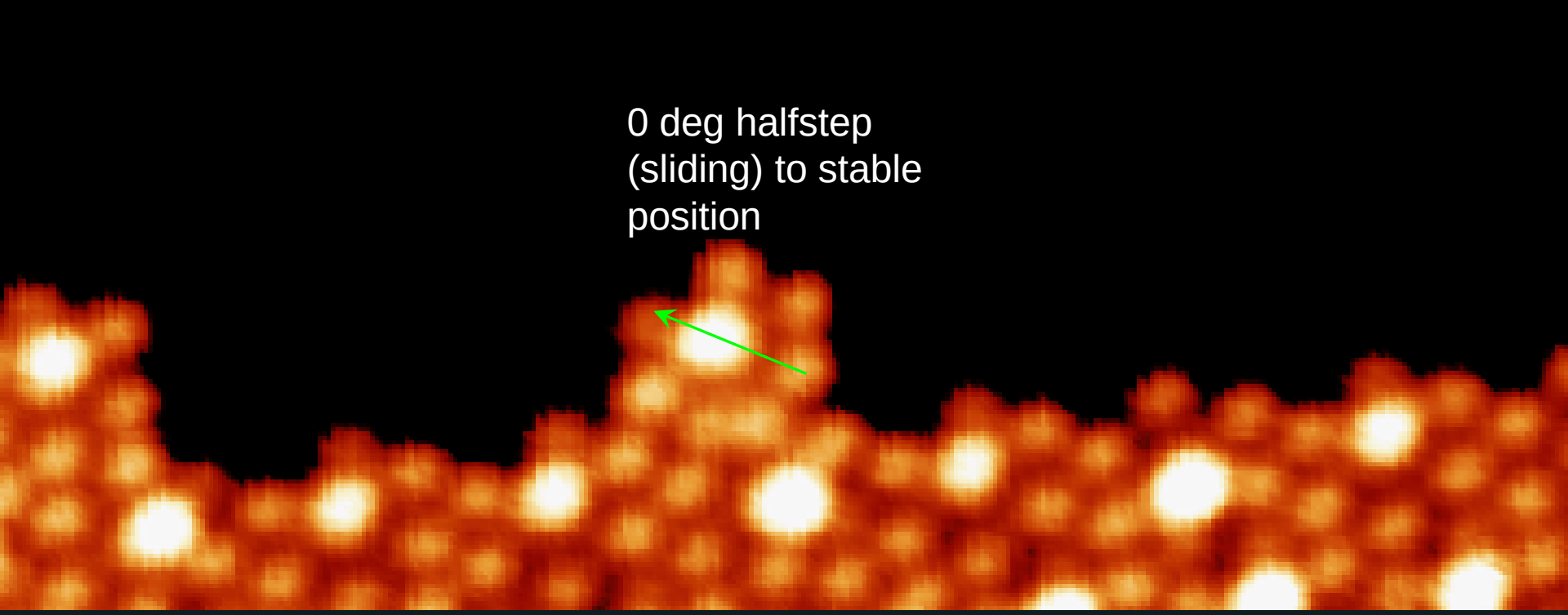
Asymmetry in the movement ???

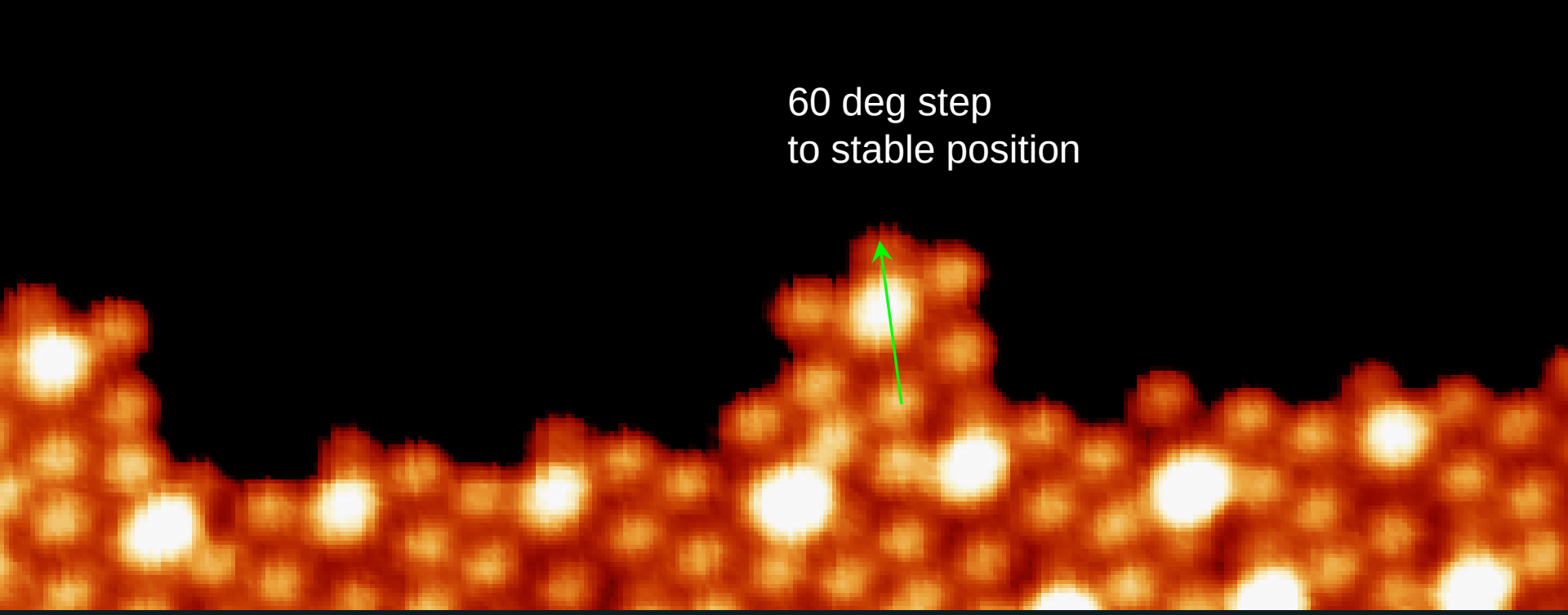


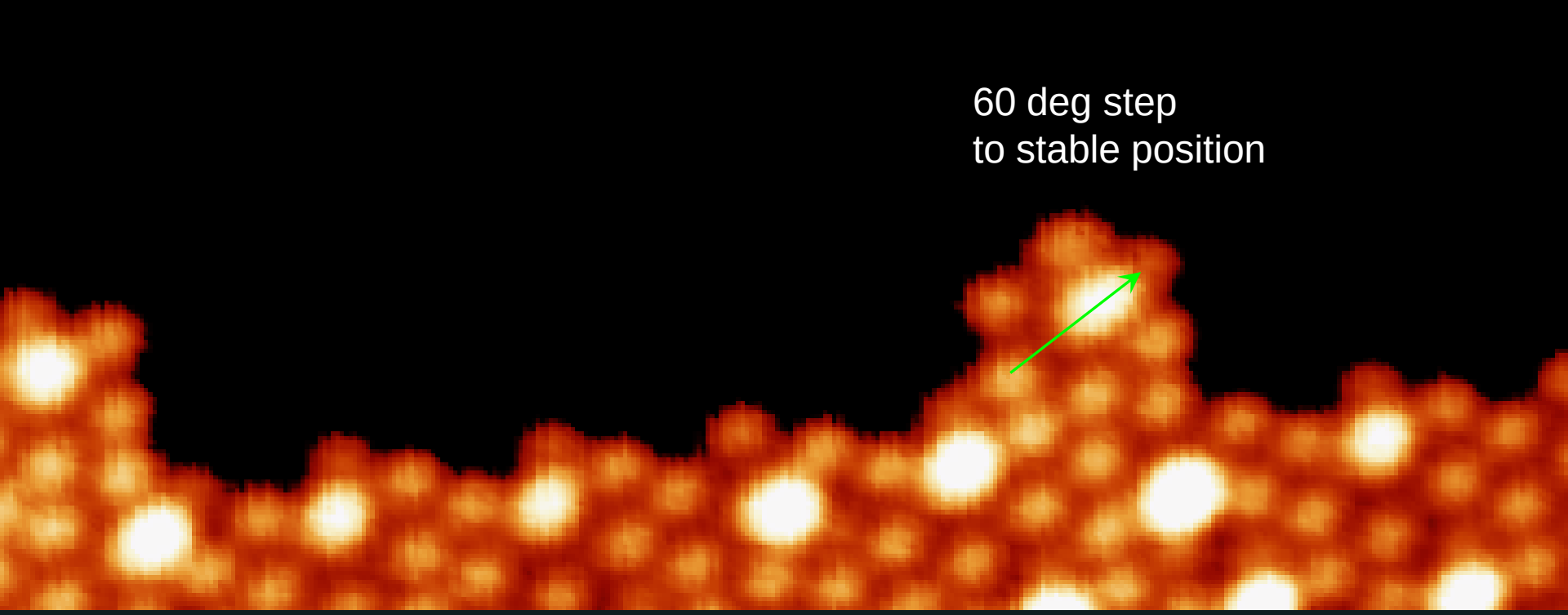
Manipulations are performed always starting from the center of the molecule moving parallel to the island border, with a length equal to a molecular radius.

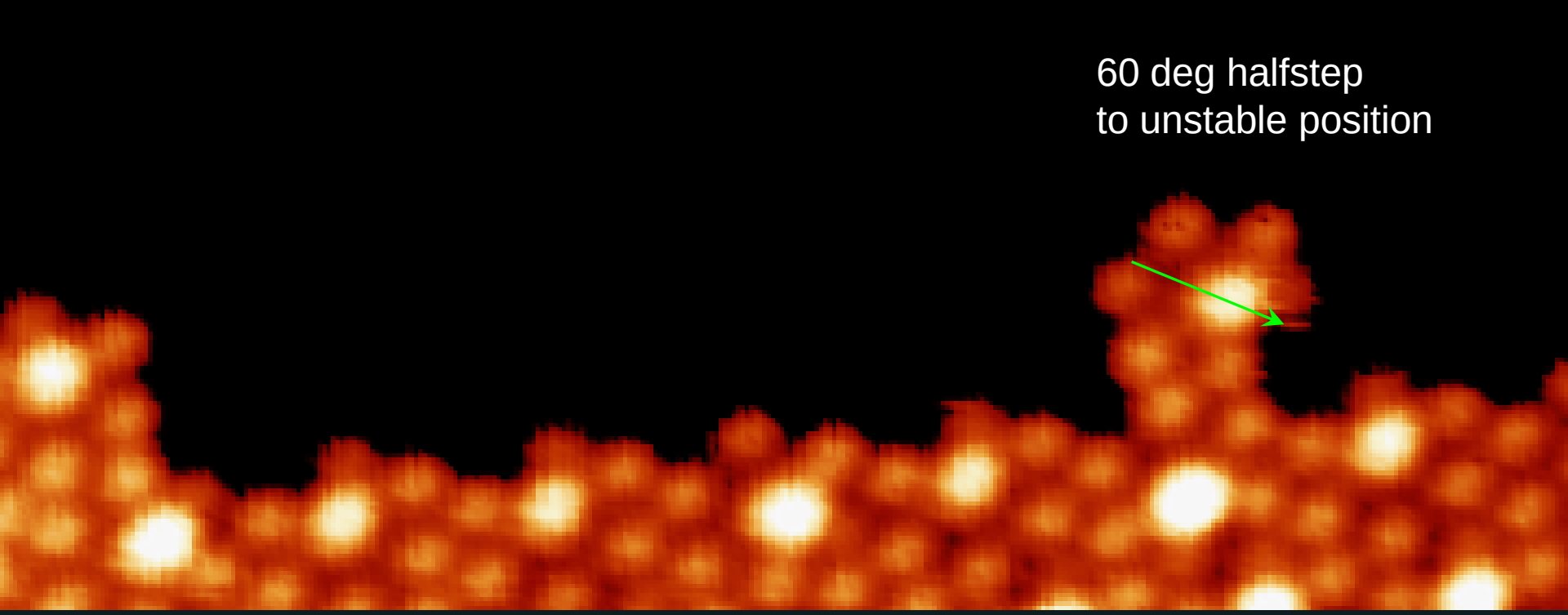

60 deg step
to stable position

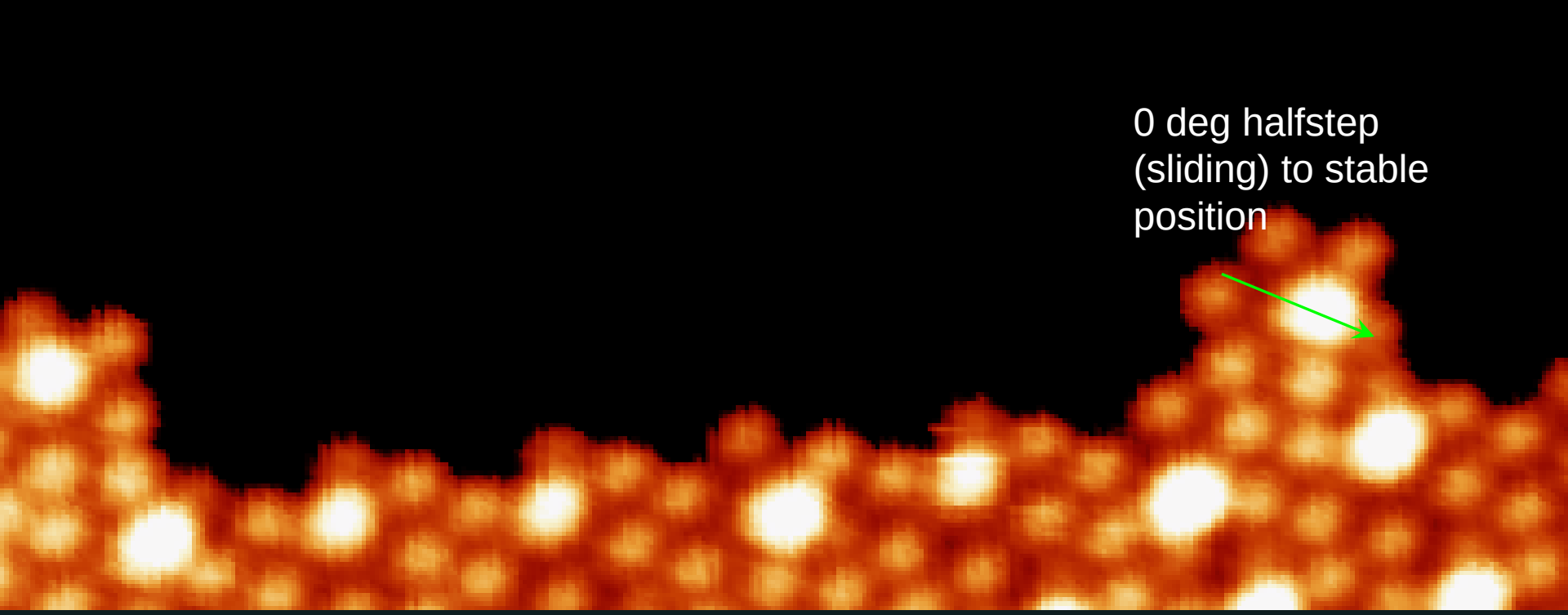

60 deg halfstep to
unstable position

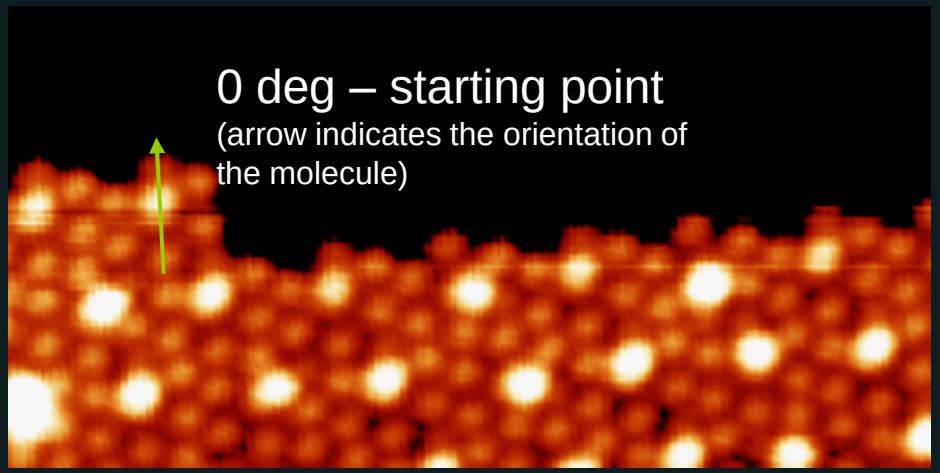

0 deg halfstep
(sliding) to stable
position

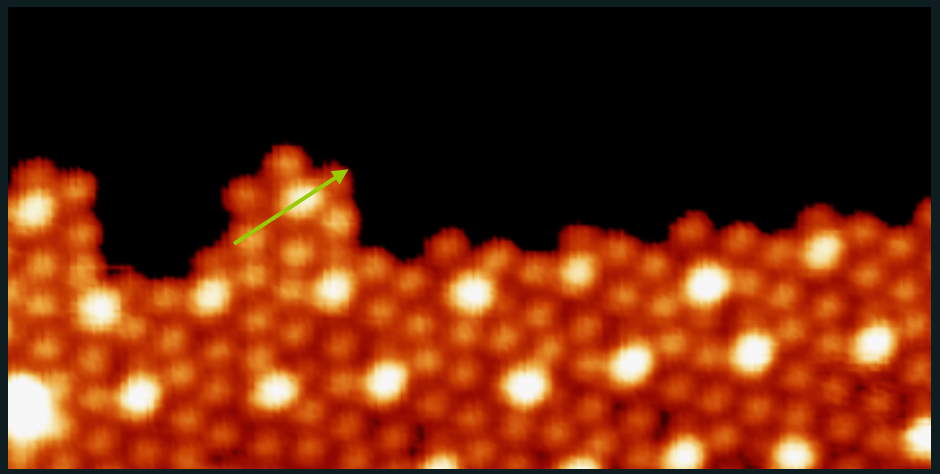

60 deg step
to stable position

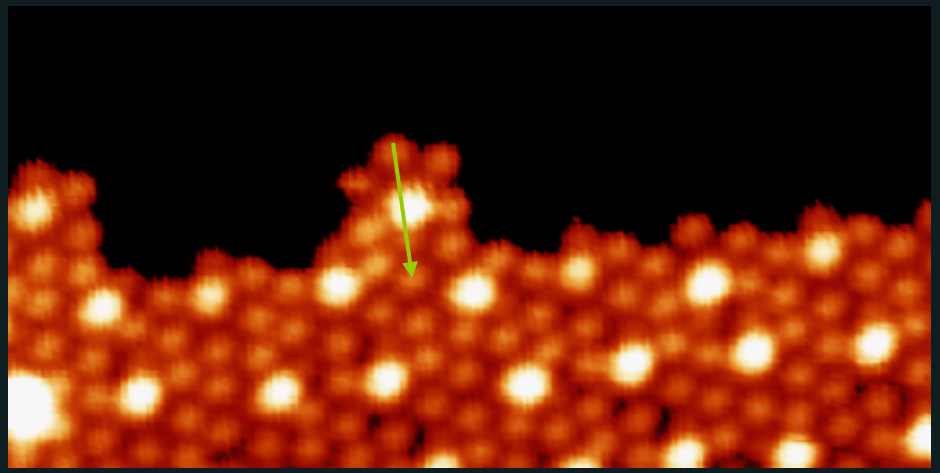

60 deg step
to stable position

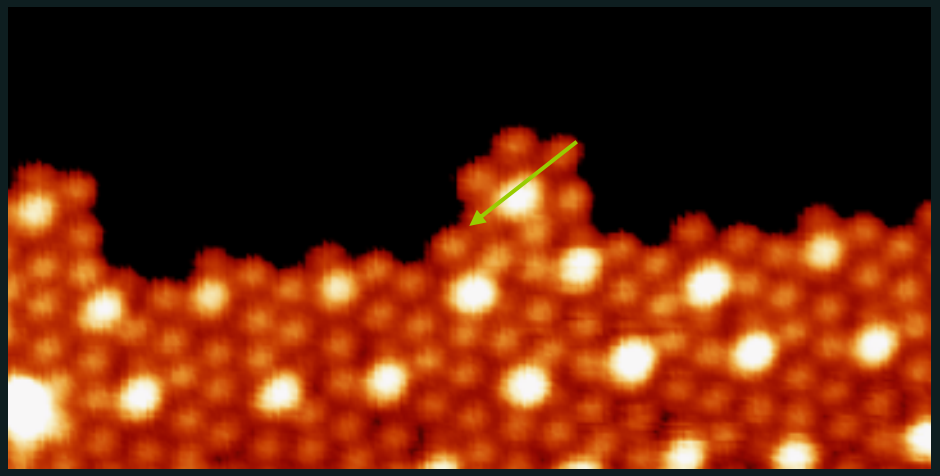

60 deg halfstep
to unstable position

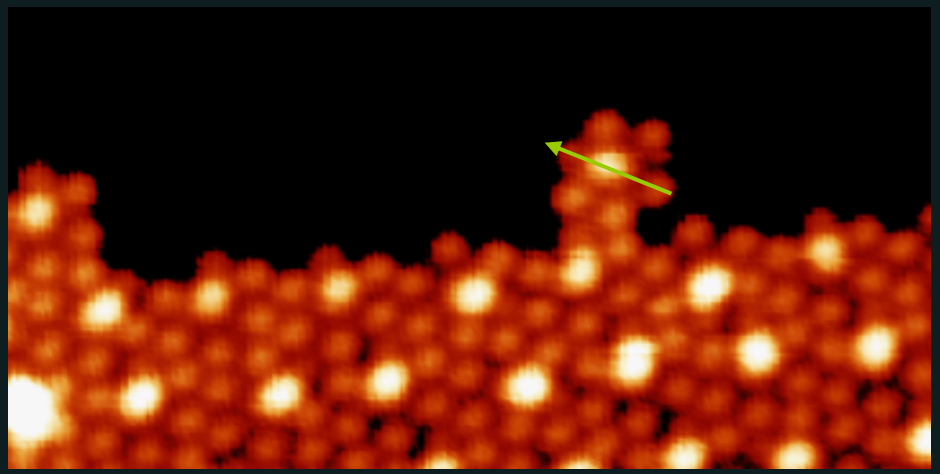

0 deg halfstep
(sliding) to stable
position

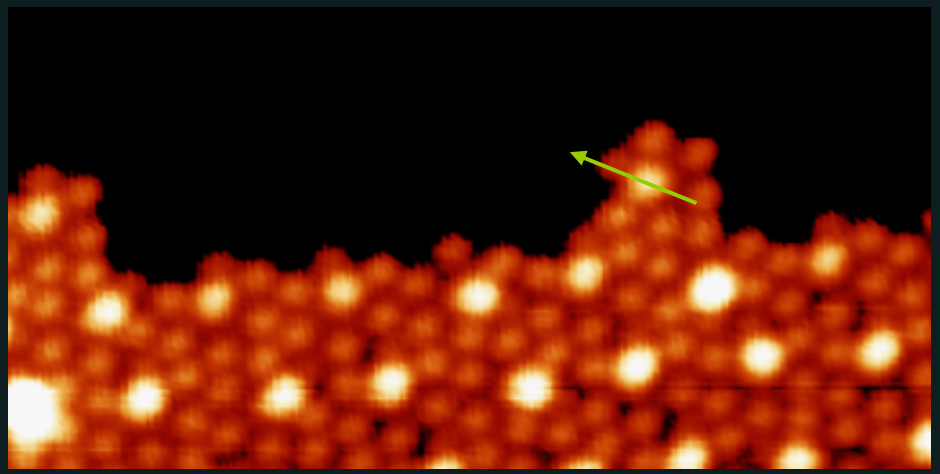

0 deg – starting point
(arrow indicates the orientation of
the molecule)

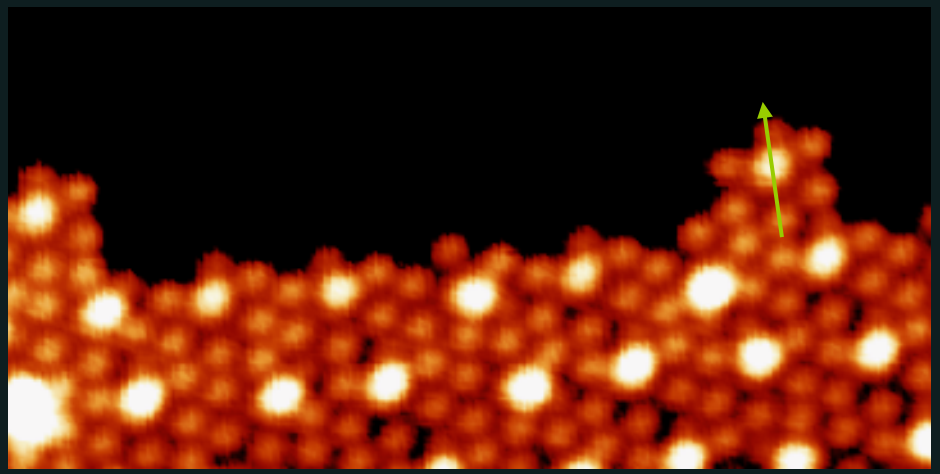


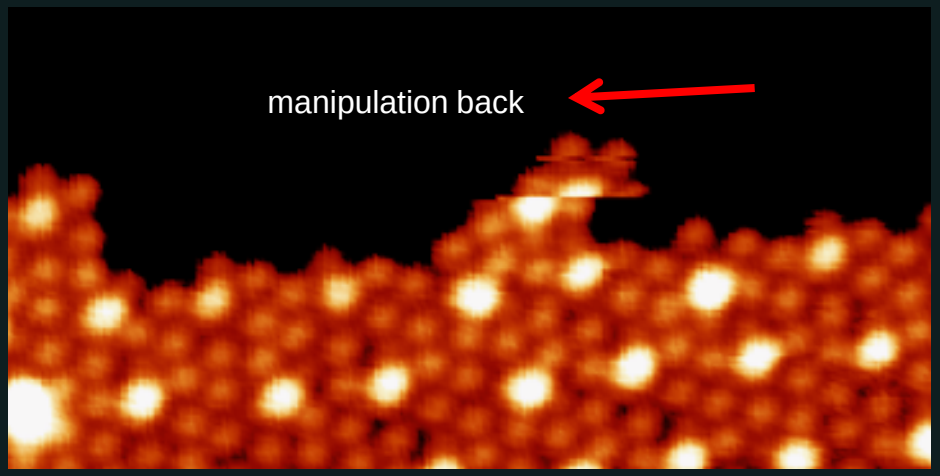


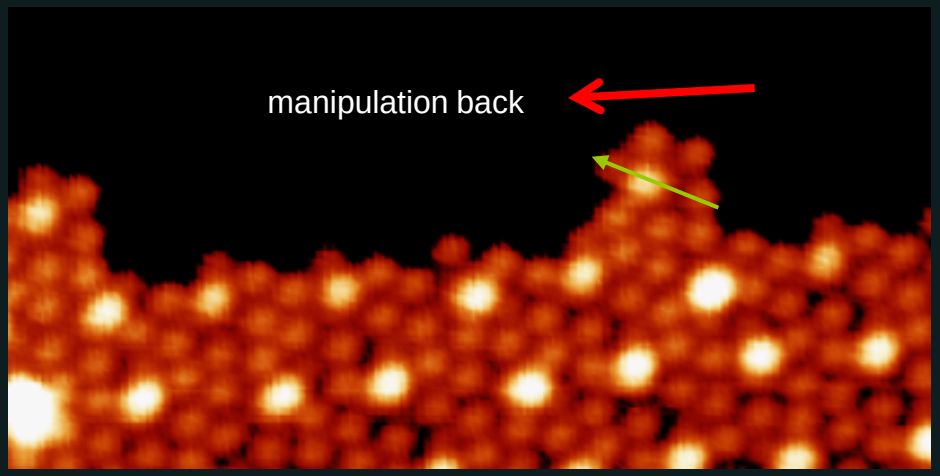


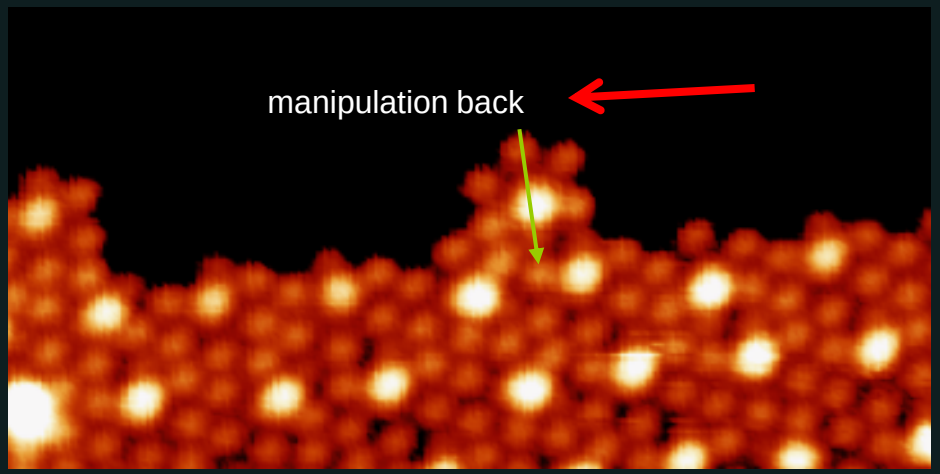


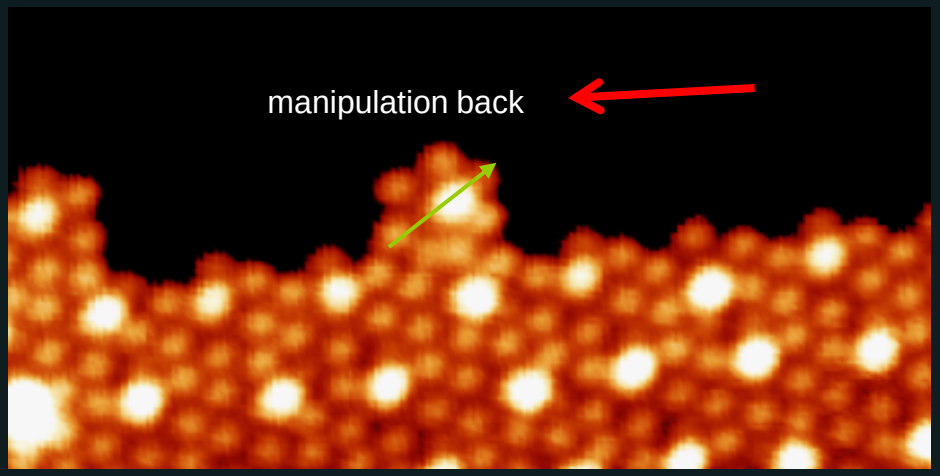


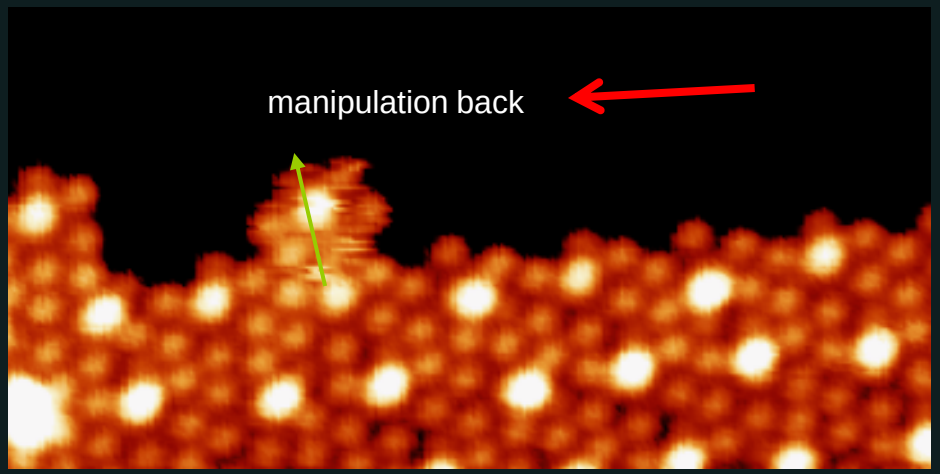


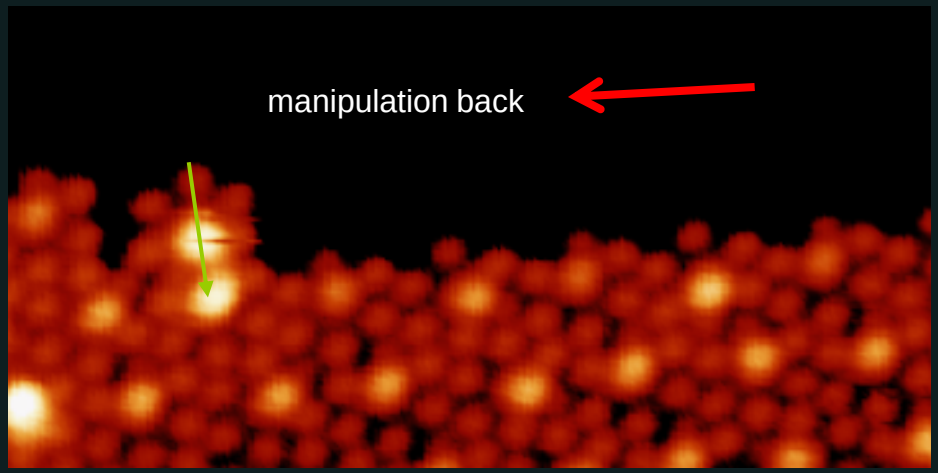

manipulation back

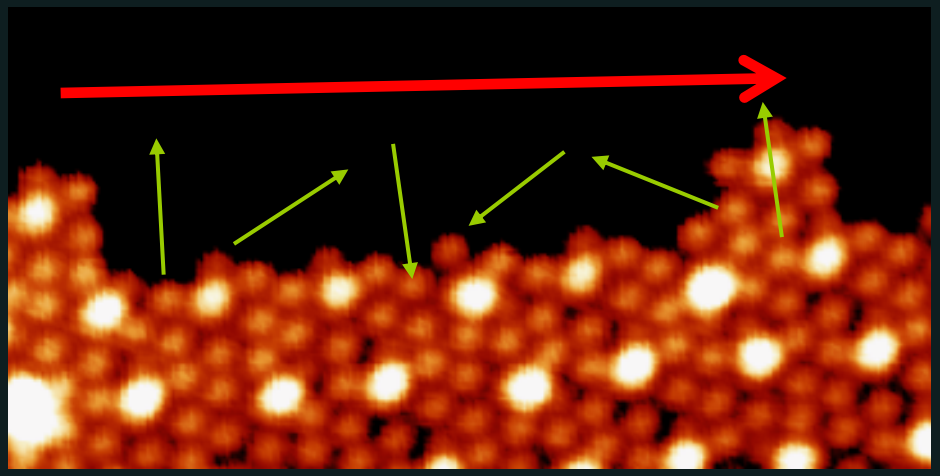

manipulation back


manipulation back


manipulation back

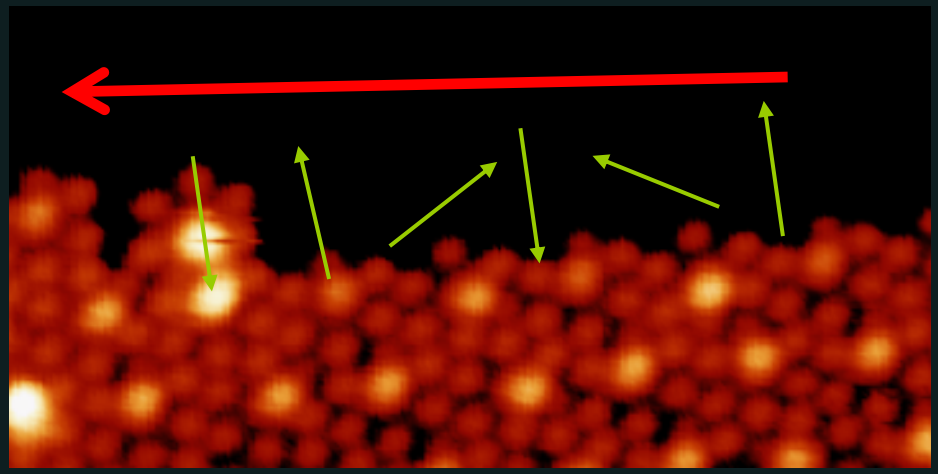

manipulation back


manipulation back

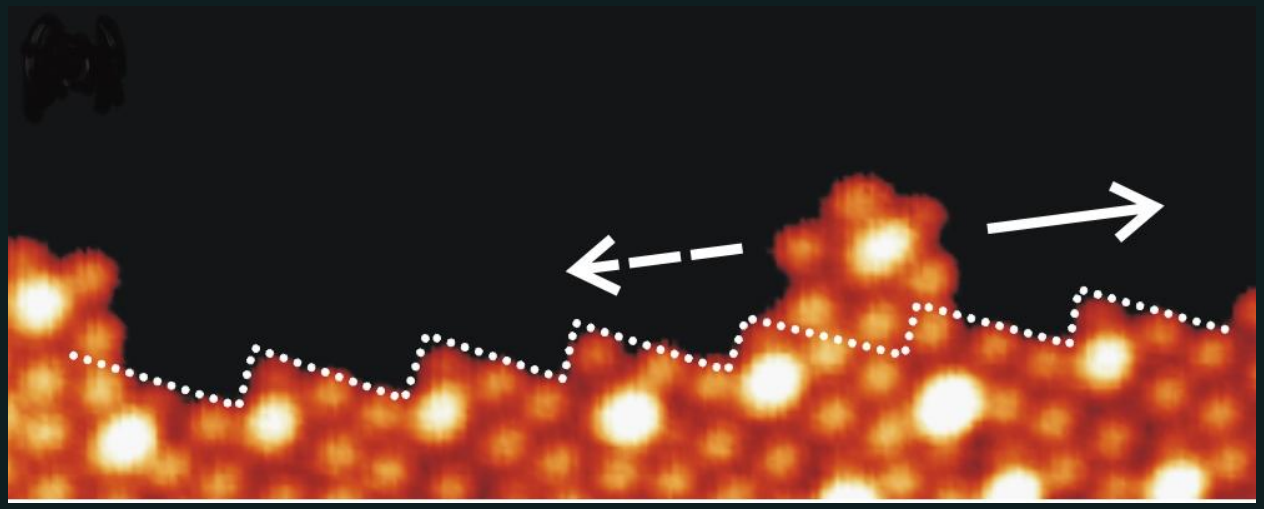


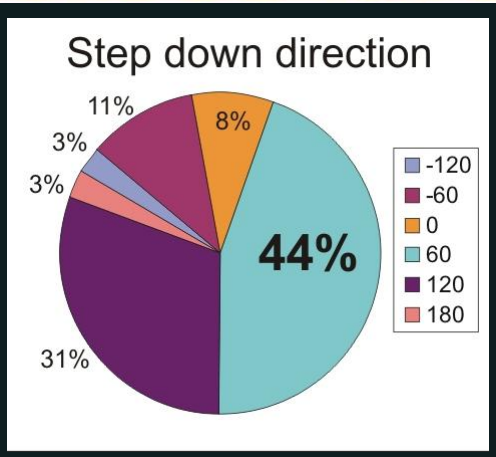
In this direction the molecule rotates always by 60° in the expected direction, always reaching stable positions (except for the fifth step, which consists in a 60° rotation to an unstable position followed by a simple sliding of the molecule).

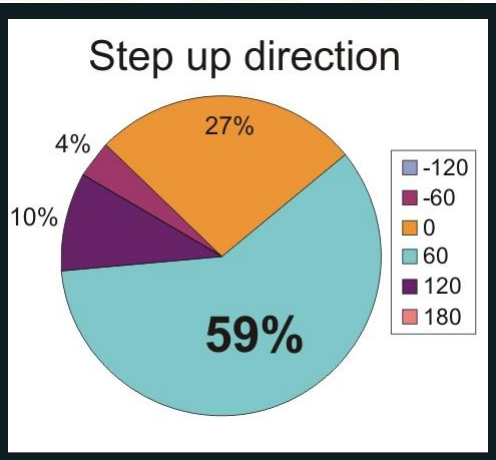
In this direction the molecule rotated not definitely, not always reaching stable positions.



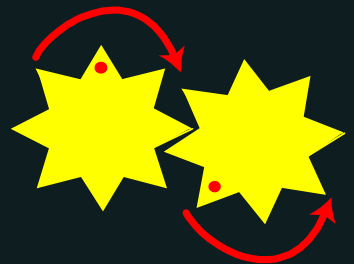
Statistics







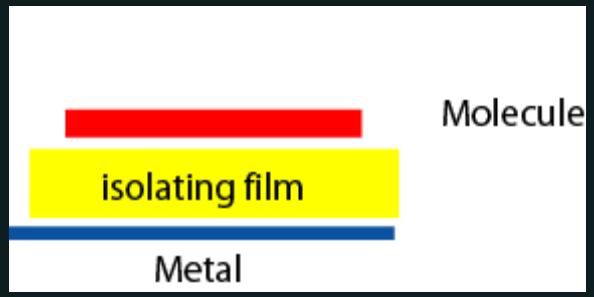
Work in progress: a gear with 2 pinions…



One of the perspectives

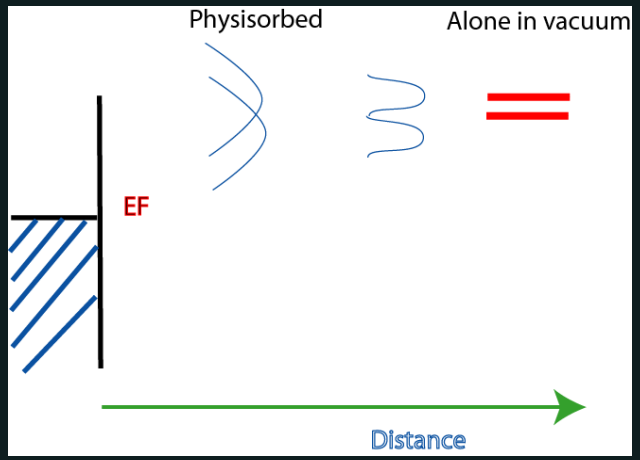
Electronic decoupling

Get rid of the spacers !!!

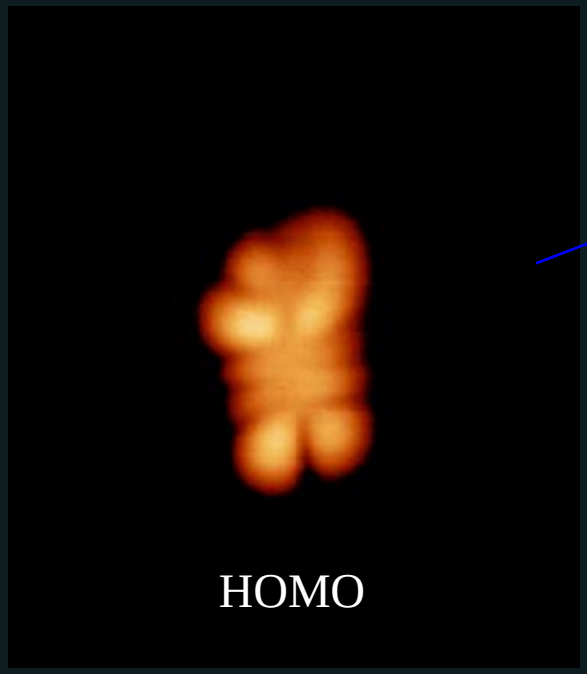


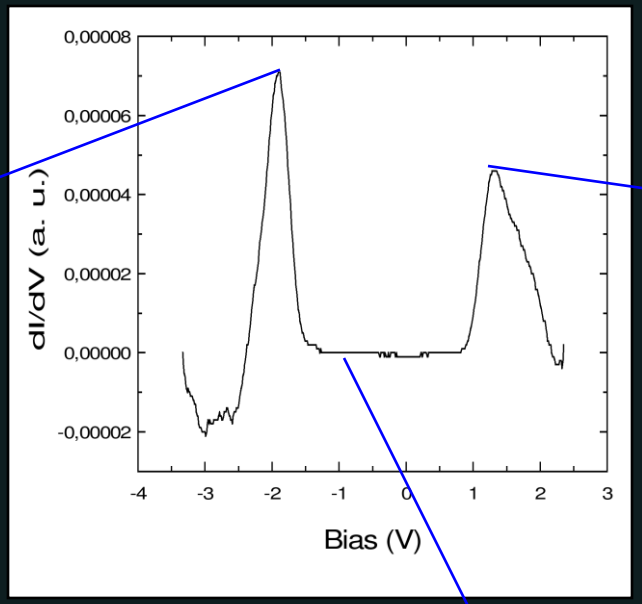
From landers to molecules/thin insulating films/metal (STM<1pA)

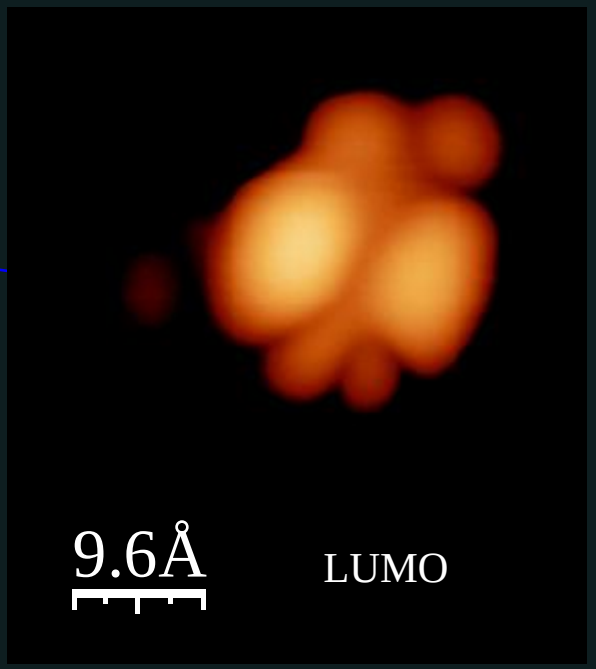
less perturbed molecular orbitals. Experiments on molecules “as in vacuum”
Larger molecule-substrate distance: less level broadening.

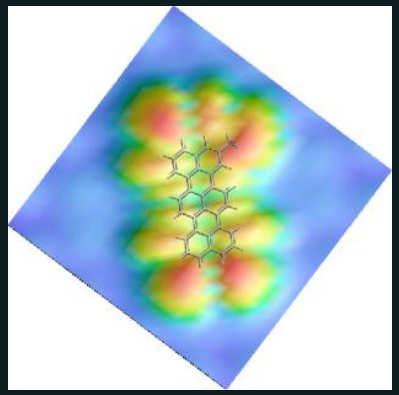


Seeing the orbitals ! Methylterrylene /2ML NaCl/Cu

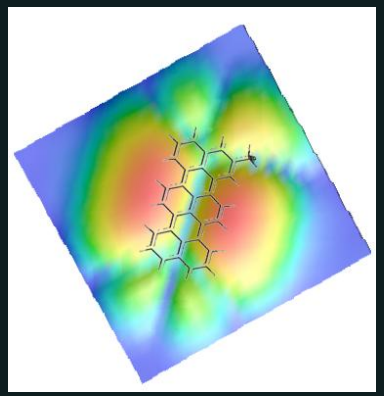




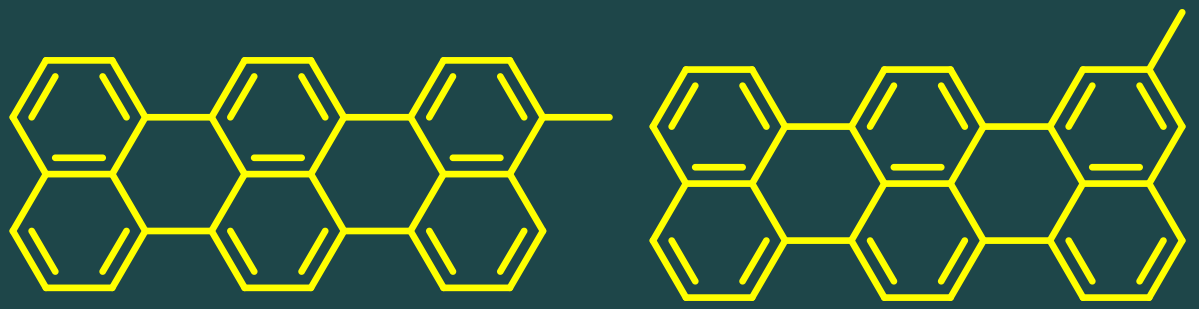




5nm x 6nm

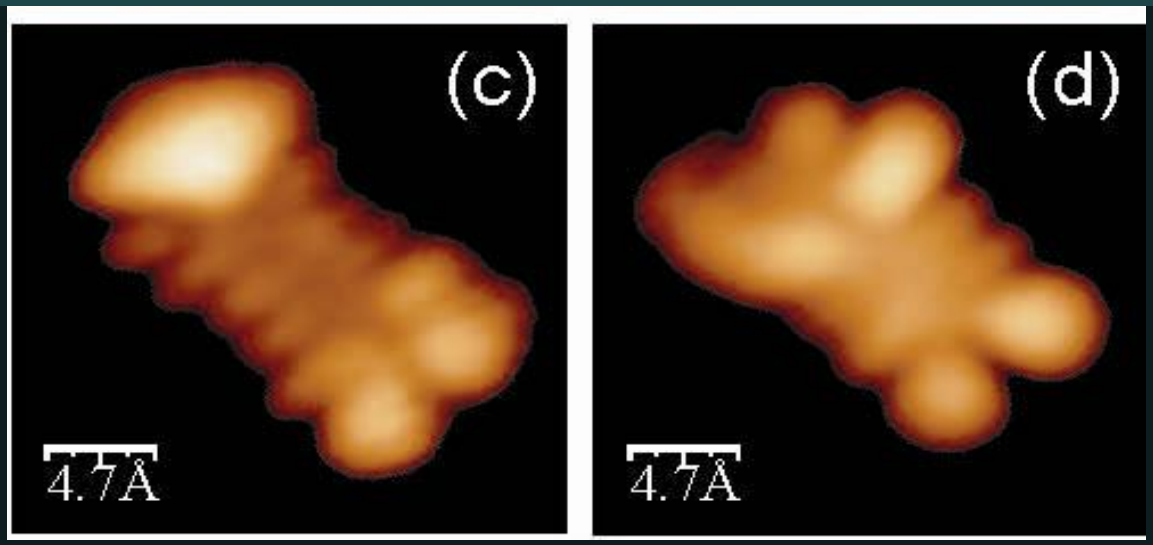


See also: Pentacene/NaCl/Cu Coll IBM:PRL (2005), 94, 026803 1-4



MeT-iso1

MeT-iso2



V_t = -2.5 V

We see the hyperconjugation between the P-system end the methyl

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CHIC, Pico-Inside

Single Molecule Synthesis

(Coll. K.H Dieter & F. Moresco)