ISS 'NANOTECHNOLOGY: from fundamental research to innovations'

31st August, Bukovel, Ukraine

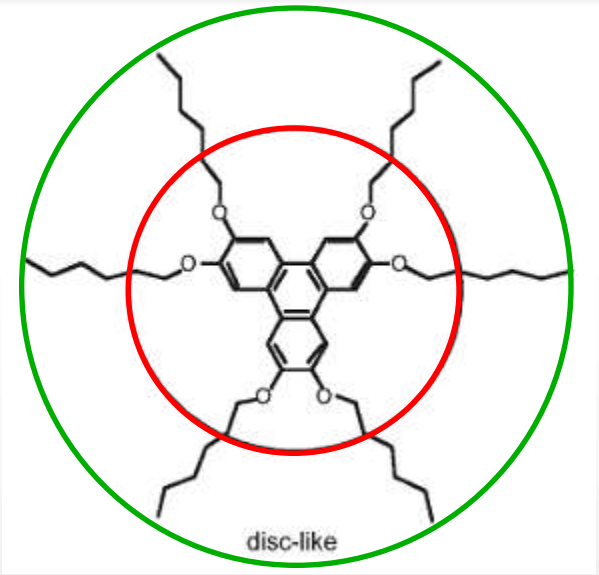
'Control of anchoring of discotic liquid crystals for understanding of organic electronic devices'

Piotr Ślęczkowski
Paris Institute of Nanosciences (INSP)
University of Pierre and Marie Curie (UPMC)

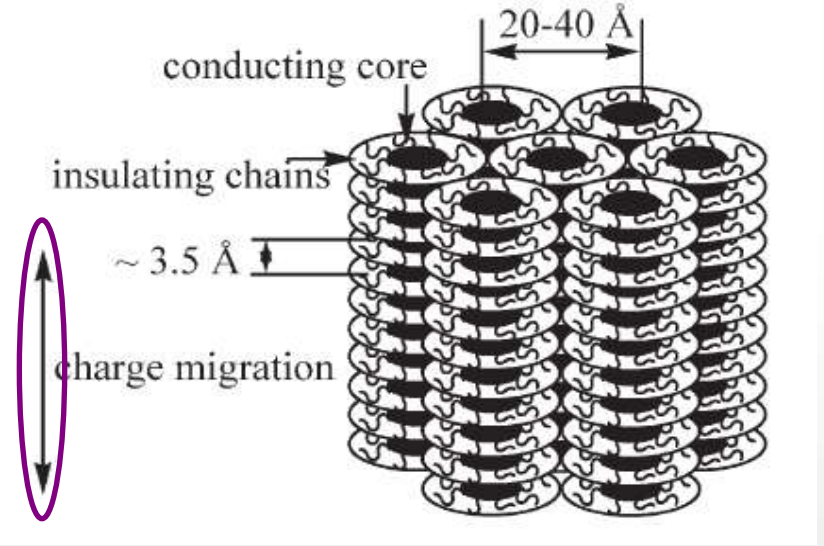
Outline

- Introduction to Discotic Liquid Crystals (DLCs)
- Goal & motivation
- Structure of substrates:
  - gold Au(111)
  - Highly Oriented Pyrolytic Graphite (HOPG)
- Control of DLCs monolayer self-assemblies by molecular engineering
- Summary & perspectives

Introduction to Discotic Liquid Crystals (DLCs)



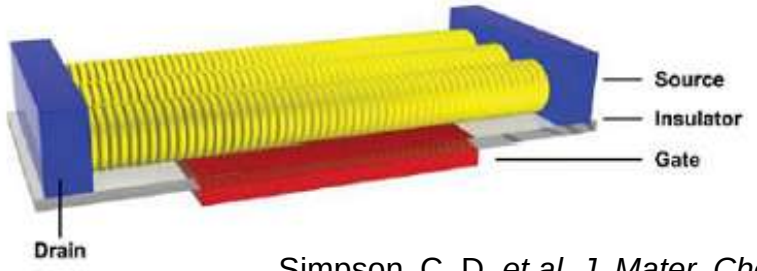
Shimizu, Y. *et al*. *J. Mater. Chem.*, **2007**, *17*, 4223



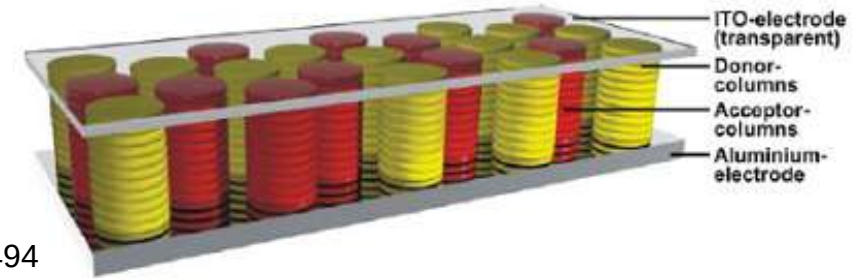
Kumar, S. *Chem. Soc. Rev.* **2006**, *35*, 83

2 types of building blocks:

polyaromatic central core + multiple peripheral alkyl or alkoxy tails



vs.

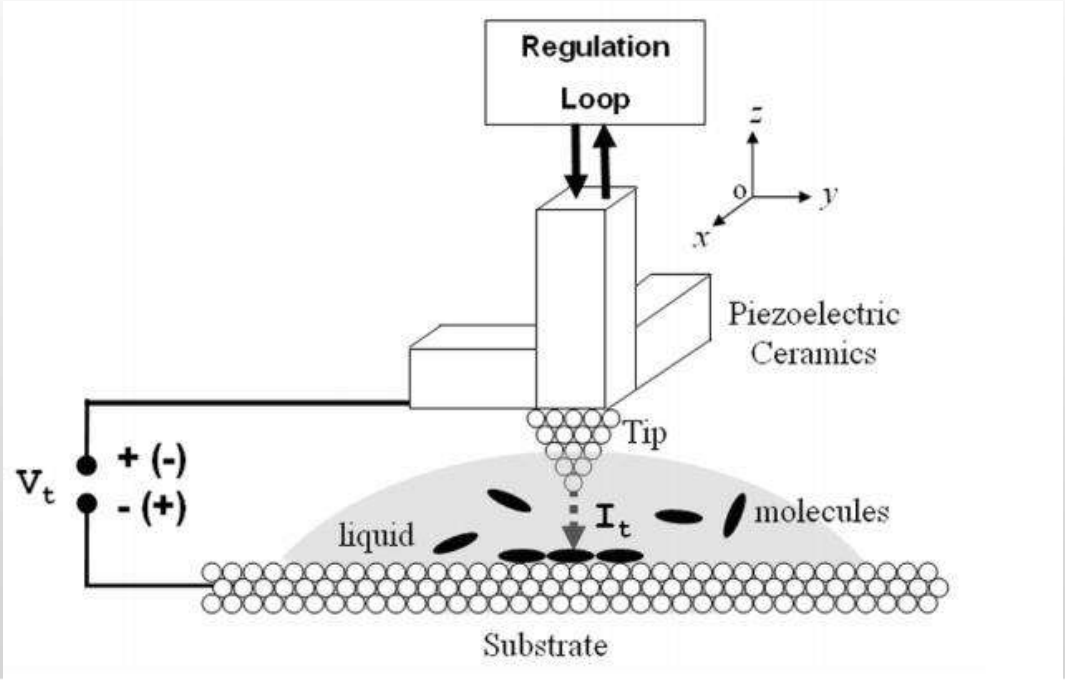


Simpson, C. D. *et al*. *J. Mater. Chem.*, **2004**, *14*, 494

Goal & motivation

- self-assembly of DLCs at crystalline substrates (YES/NO)?
- If YES → resolve structure & understand its origin
- how does the presence of order influence the bulk property (charge transport)?

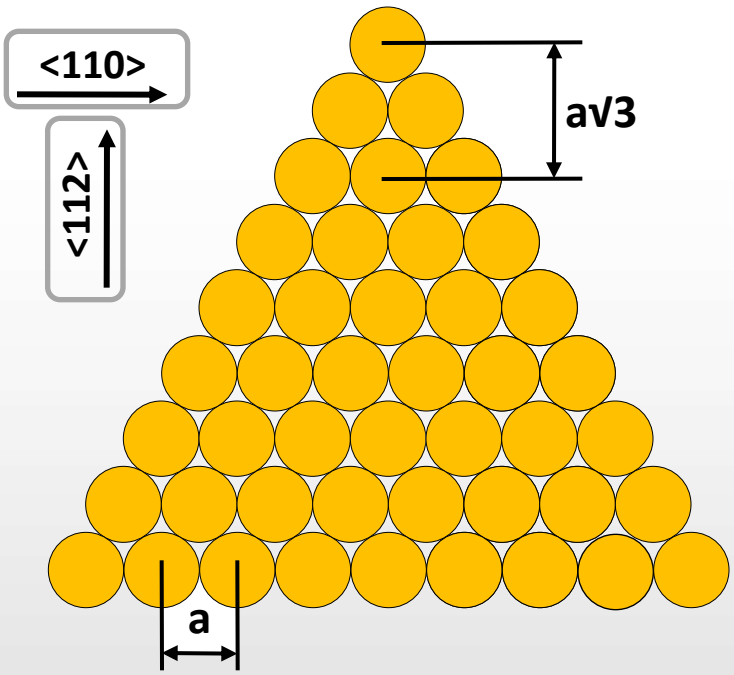
Tool:Scanning Tunneling Microscopy at a liquid/solid interface



Kudernac, T. *PhD Thesis;* **University of Groningen**, **2007**.

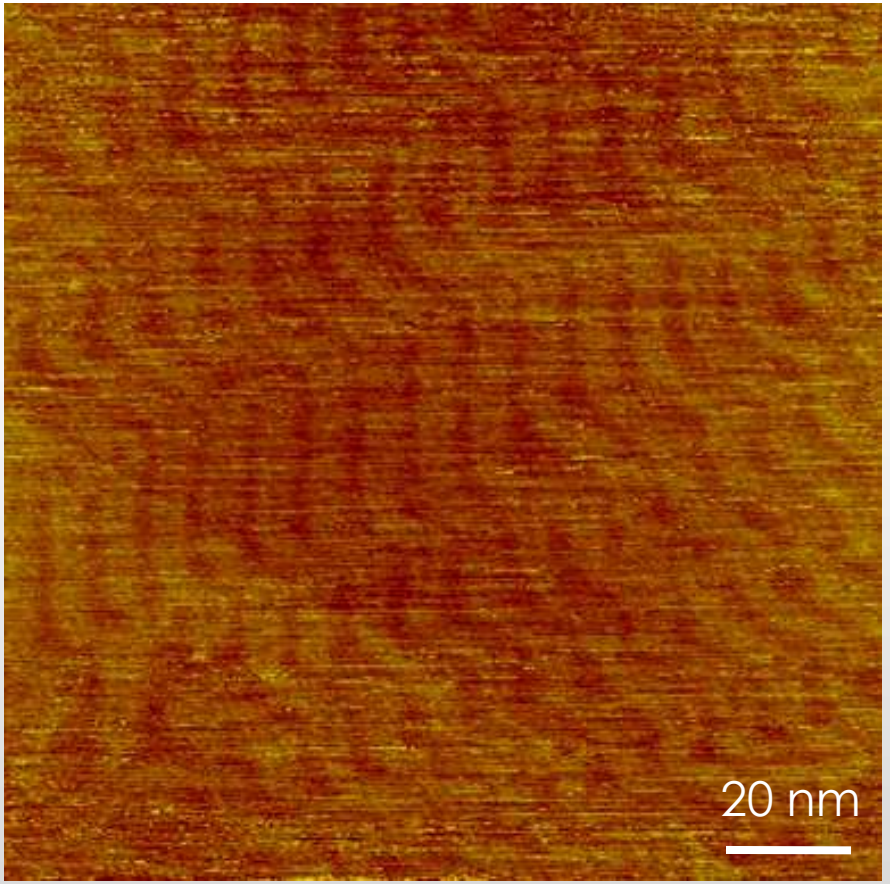
Structure of substrates used: Au(111)

a)



Parameter	Distance [nm]
a	0,288
a√3	0,499

b)



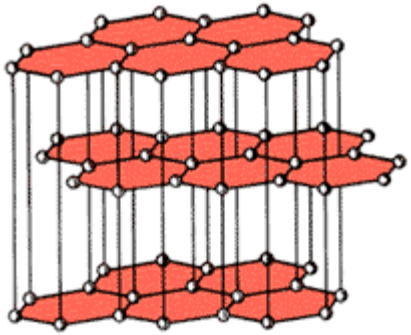
bias = -0.200 [V] set point = 1.2 [pA]

a) hard-sphere representation of non-reconstructed Au(111) surface;

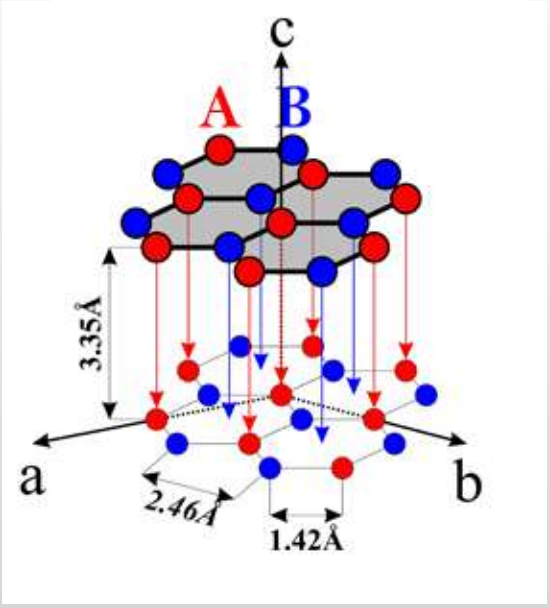
b) STM constant current image of Au(111) reconstructed surface.

Structure of substrates used: graphite

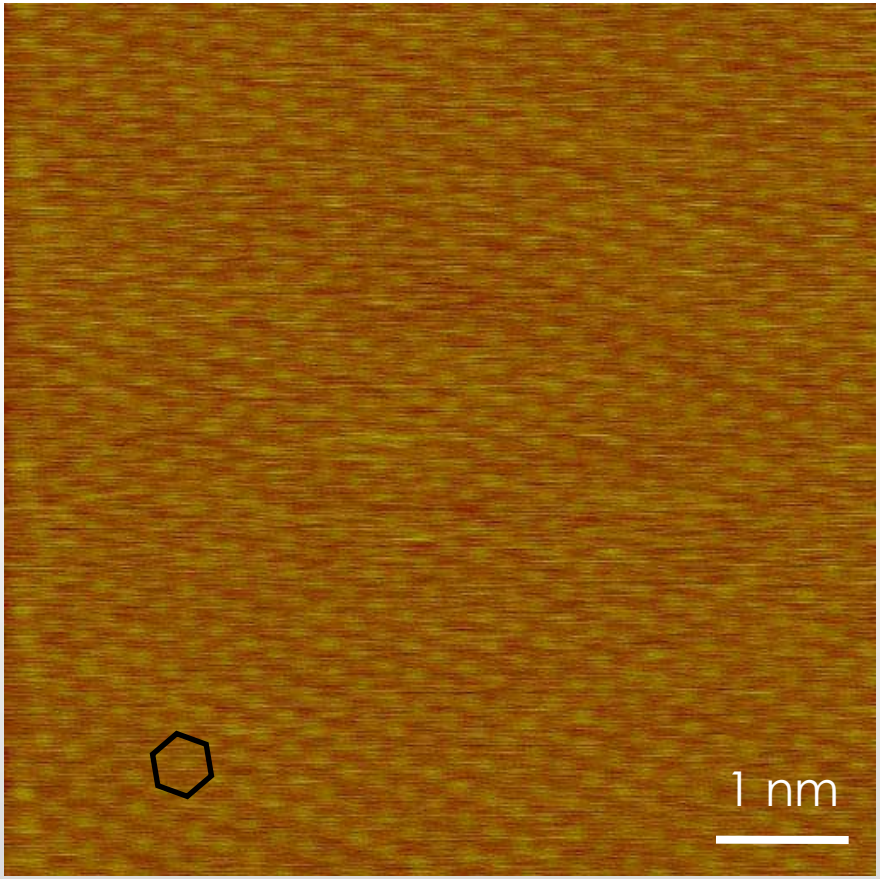
a)



b)



c)



bias = -0.200 [V] set point = 1.2 [pA]

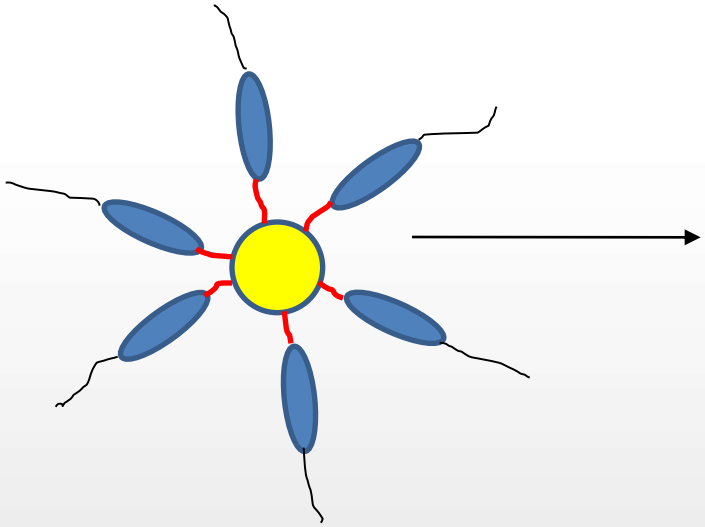
a) molecular structure of graphite; b) scheme indicating shift between two subsequent layers

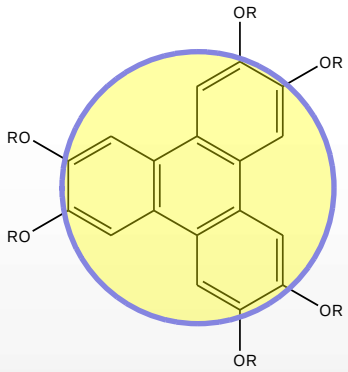
c) STM constant current image of HOPG

STM of novel photoswichable mesogenic systems

Synthesis: prof. Kingo Uchida (Ryukoku University, Japan)

Y. Shimizu, Y.; Kurobe, A.; Monobe, H.; Terasawa, N.; Kiyohara, K.; Uchida, K.; *Chem. Commun.*, **2003**, *14*, 1676

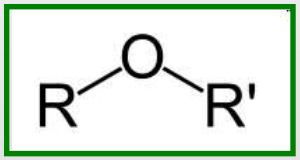




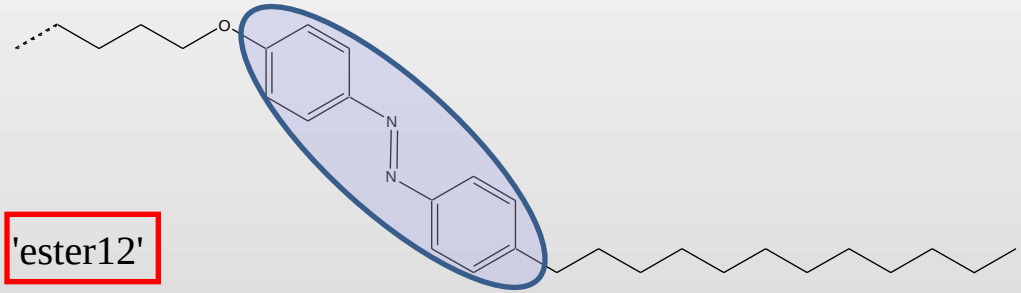
...

'ether12'

A) ether

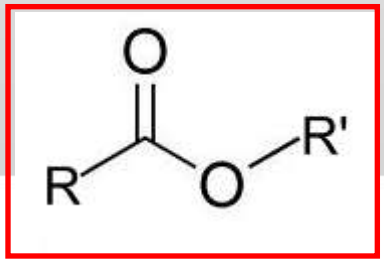


R =

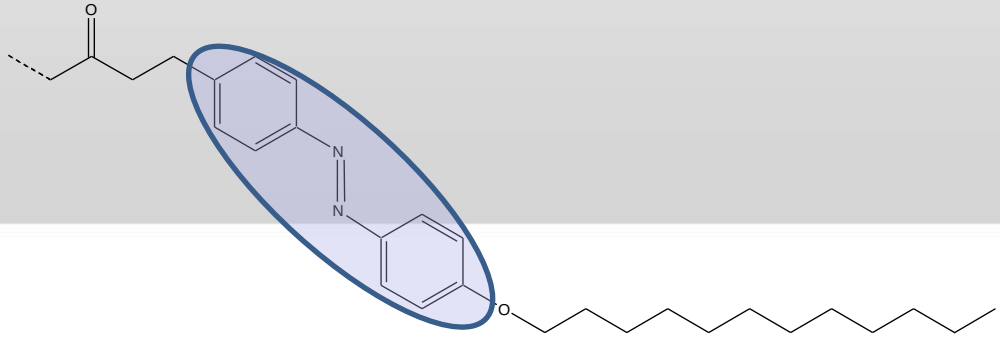


'ester12'

B) ester

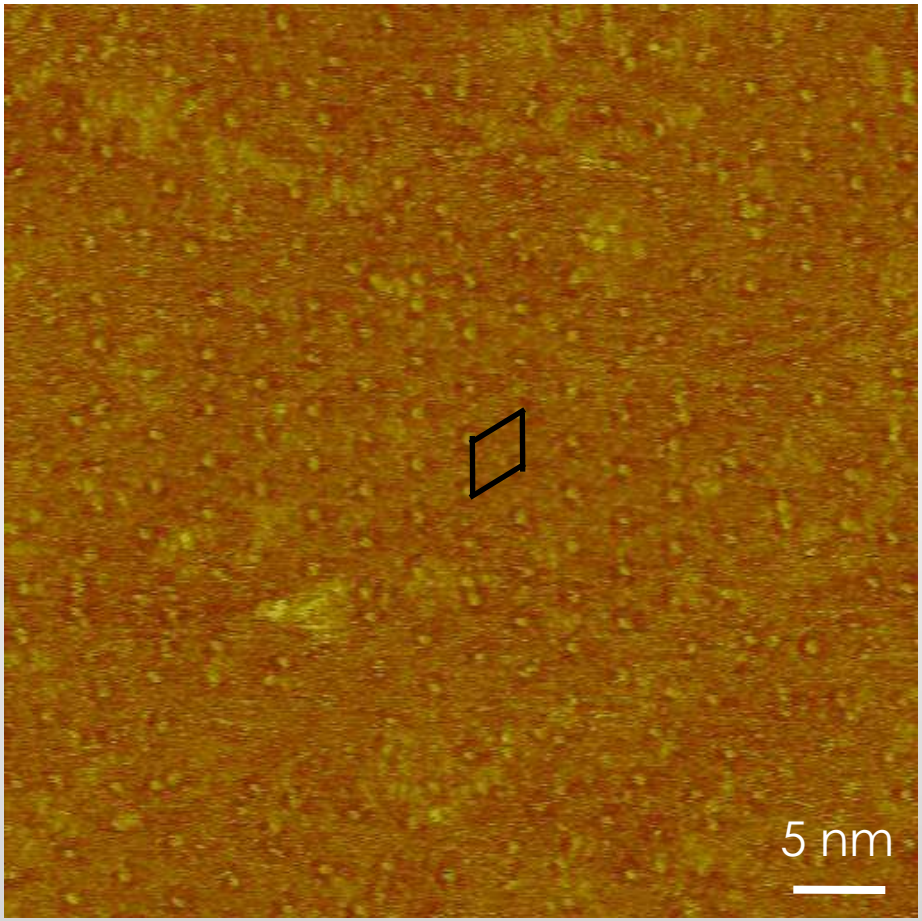


R =

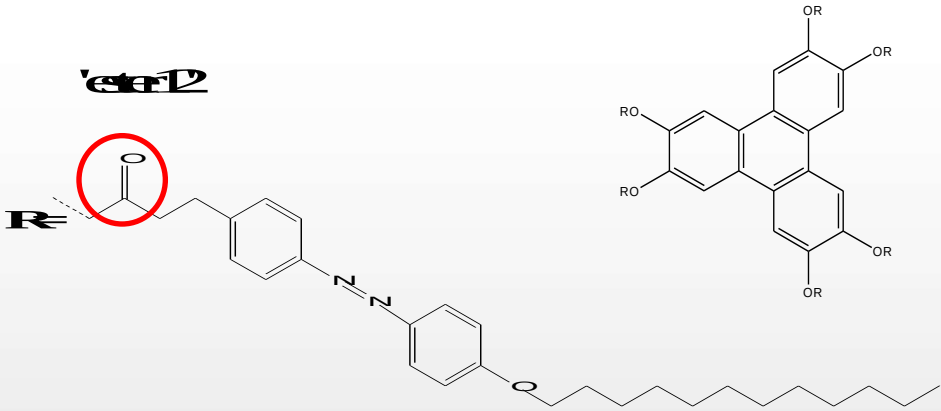


STM of '**ester12**' at a 1,2,4-trichlorobenzene /Au(111) interface

Hexagonal symmetry of domains



bias = +0.15 [V] set point = 5 [pA]



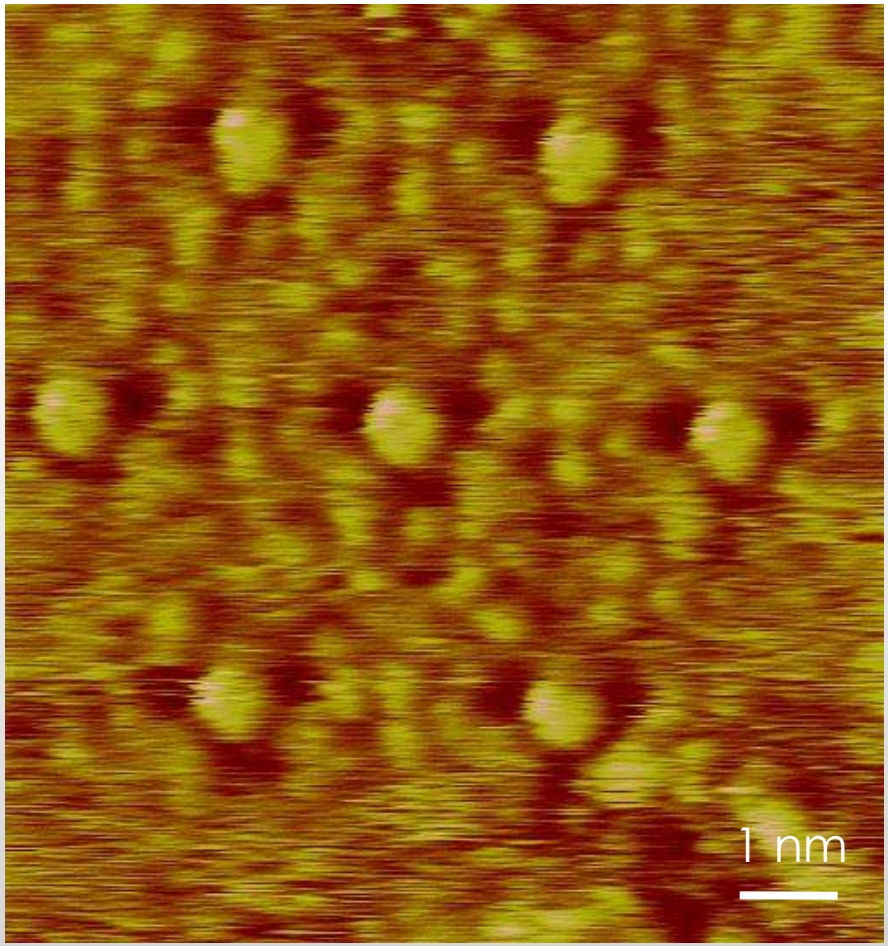
- large areas of coverage
- lattice parameter: **3,5 nm**

vs

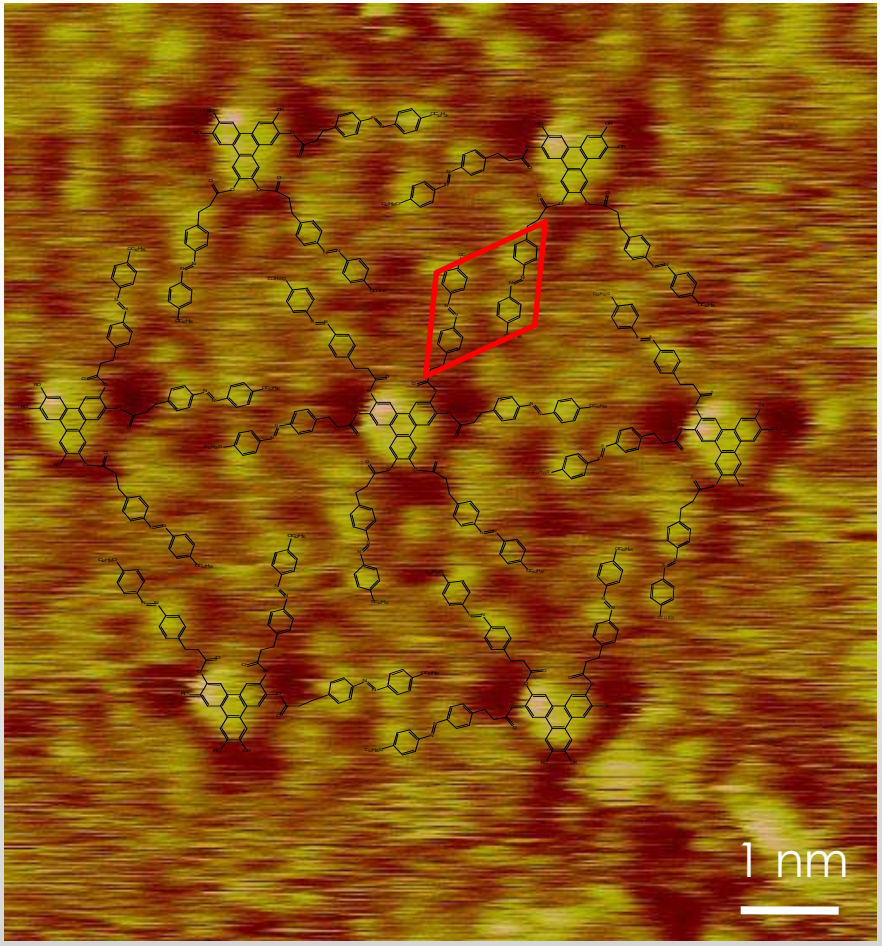
5,66 nm (XRD, Shimizu *et al.*)

STM of '**ester12**' at a 1,2,4-trichlorobenzene /Au(111) interface

Intramolecular resolution of hexagonal-type domain:



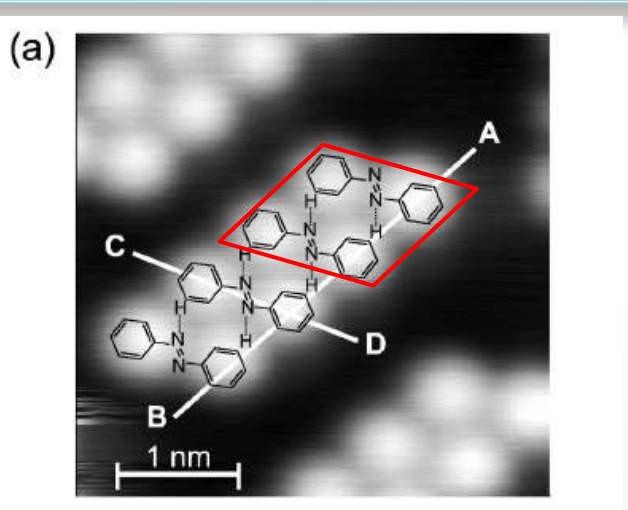
bias = +0.315 [V] set point = 3,93 [pA]



bias = +0.315 [V] set point = 3,93 [pA]

equal interactions with all 6 neighboring molecules, azobenzene-group pairing

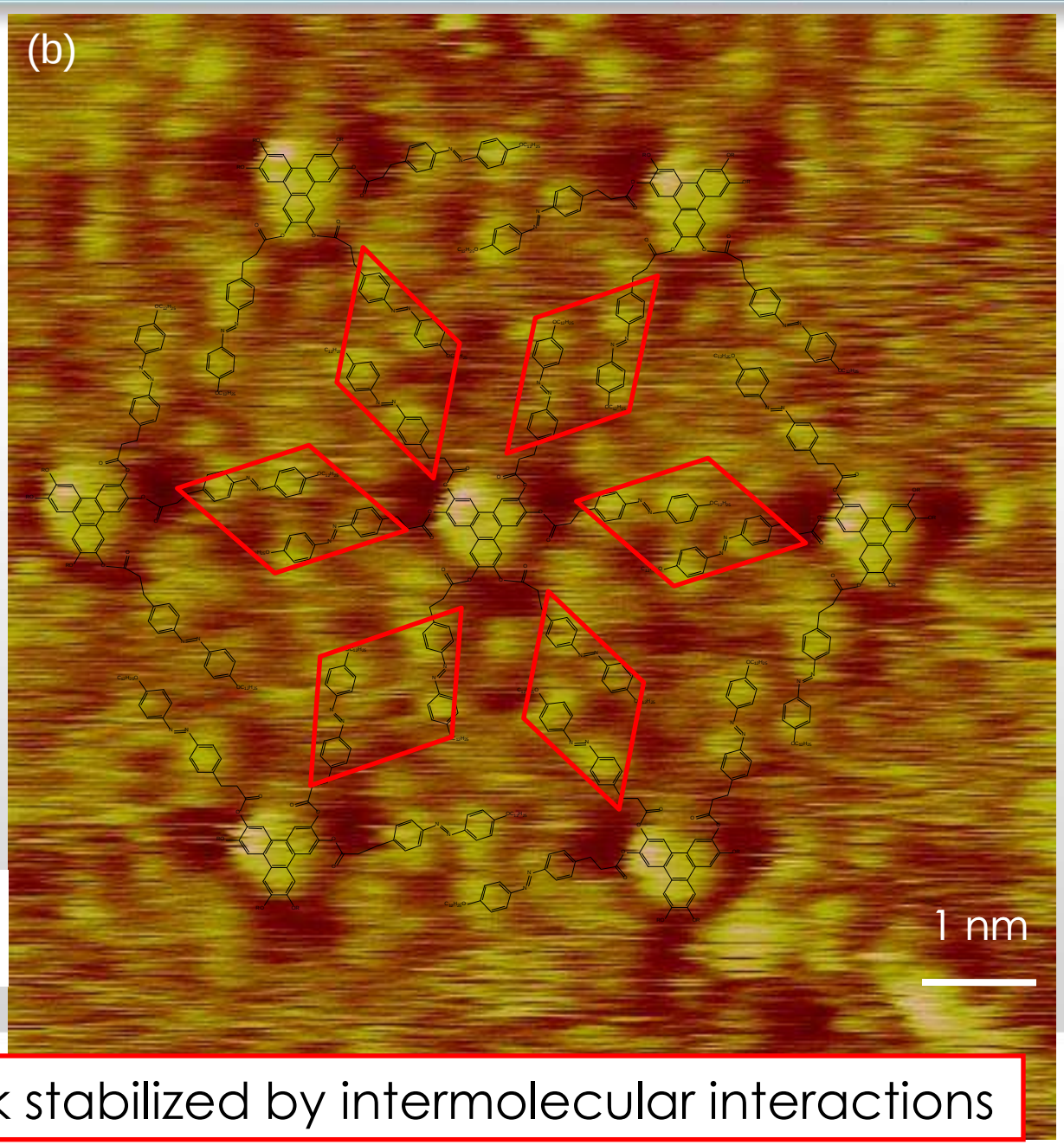
Azobenzene interactions on Au(111)



(a) [Kirakosian, A. *et al. Phys. Rev. B*, **2005**, *71*, 113409]

- dipole-dipole interactions
- hydrogenlike bonds

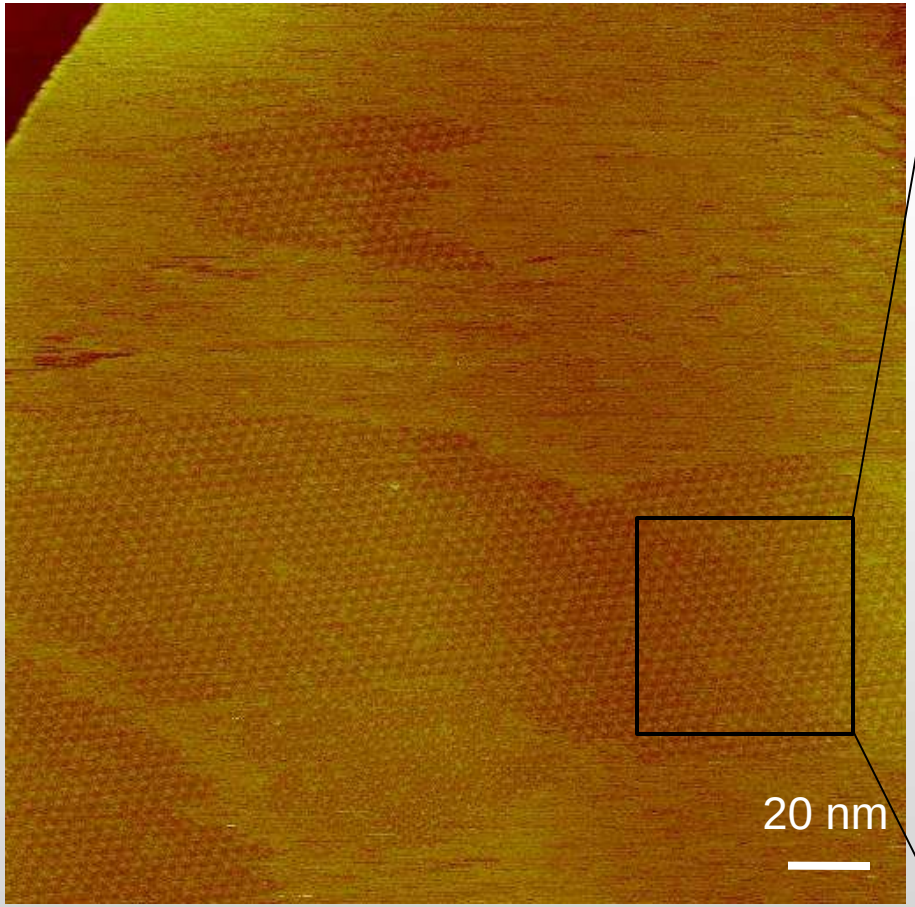
no space for physisorption of alkyl tails!



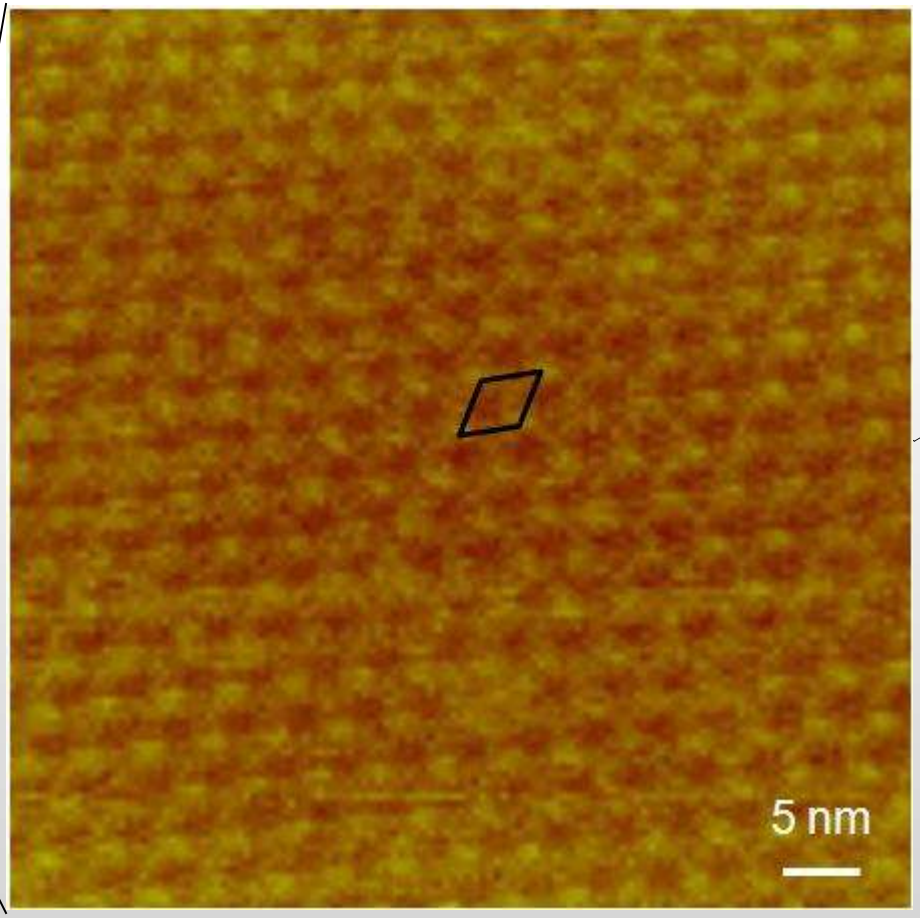
hexagonal network stabilized by intermolecular interactions

STM of '**ester12**' at a 1,2,4-trichlorobenzene /HOPG interface

Hexagonal packing – preserved



bias = +0.35 [V] set point = 10 [pA]



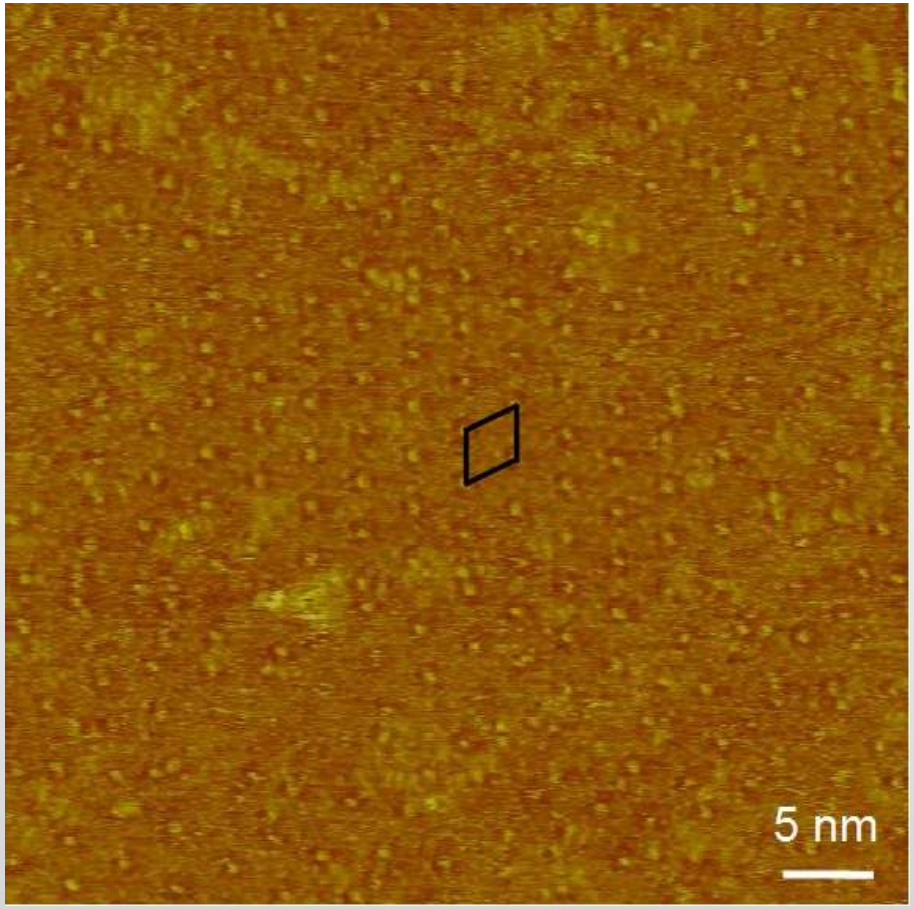
- lattice parameter: **4,3 nm**

increased lattice parameter → azobenze[illegible]up pairing

STM of '**ester12**': Au(111) vs HOPG comparison

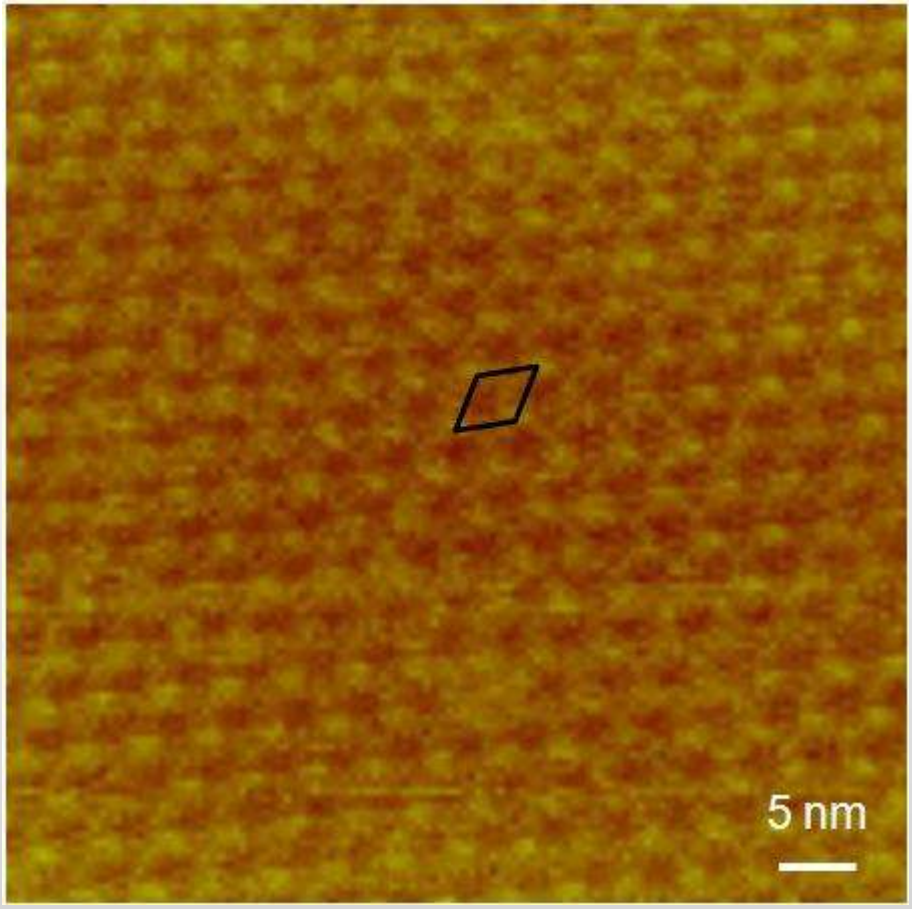
Hexagonal packing – preserved, nearest neighbor distance - CHANGED

Au(111)



- lattice parameter: **3,5 nm**

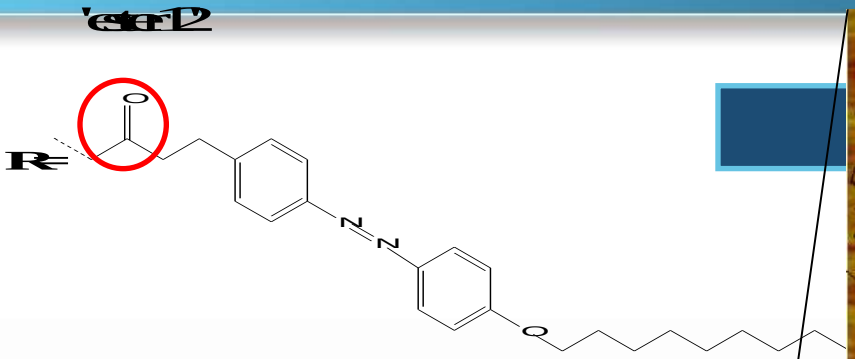
HOPG

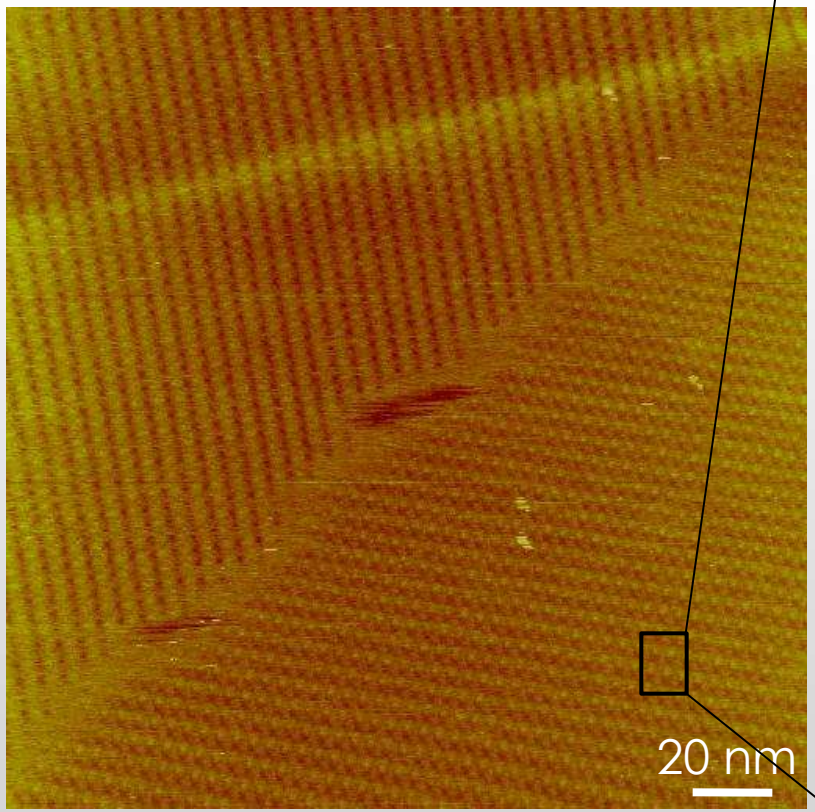


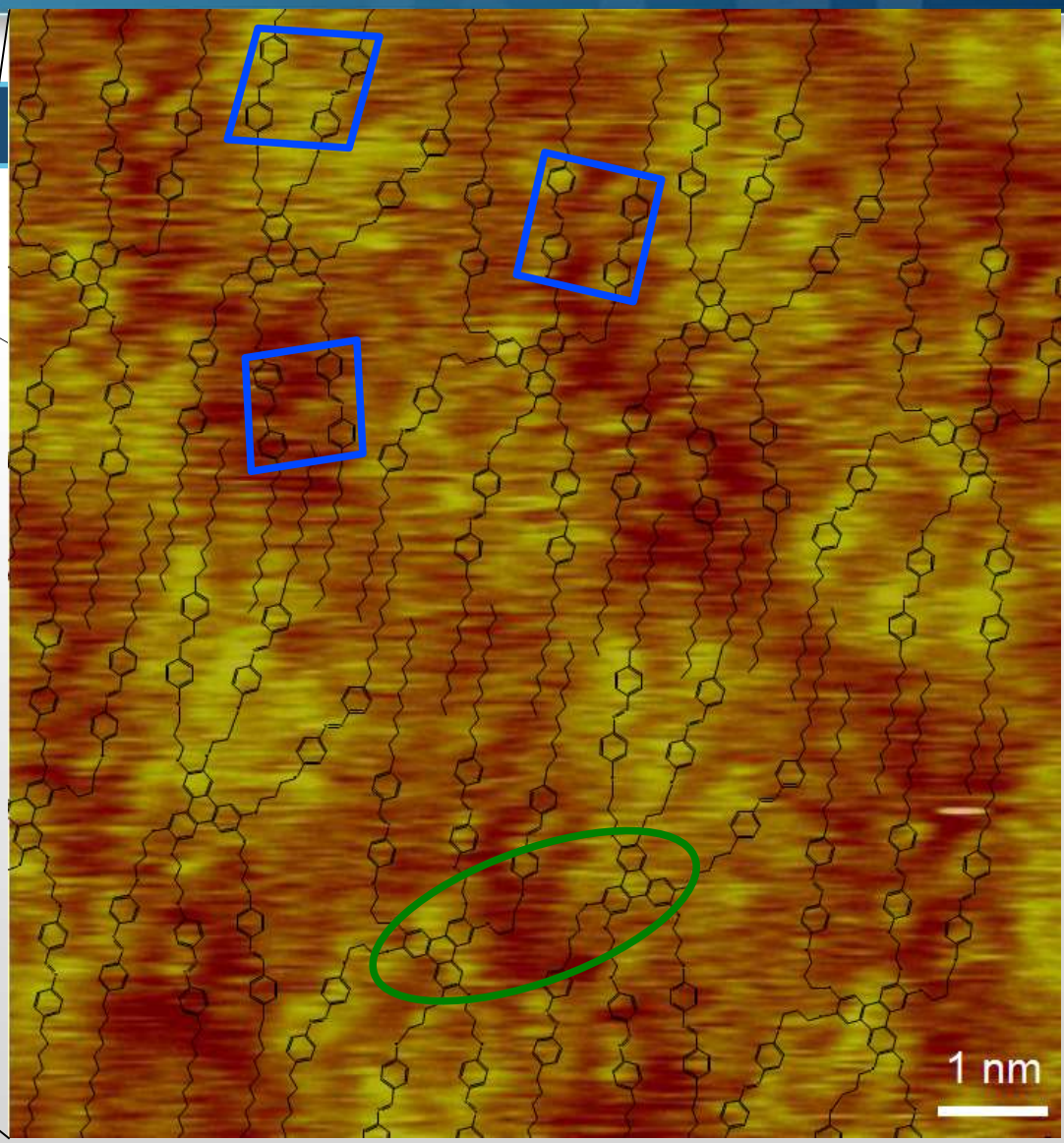
- lattice parameter: **4,3 nm**

Au(111):Y, substrate mediated azobenzene-pairing; HOPG: X

STM of '**ether12**' at a 1,2,4-trichlorobenzene /HOPG interface







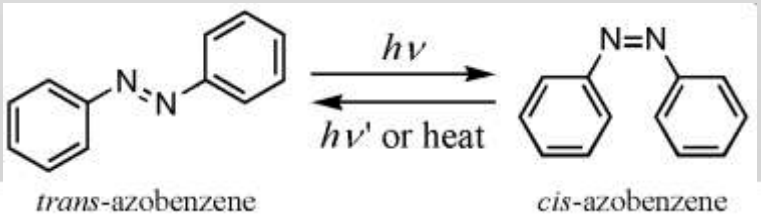
bias = +0.35 [V] set point = 10 [pA]

HOPG: ester to ether → breaking of hexagonal symmetry

Summary & perspectives

- self-assembly of a novel hybrid system at a solid/liquid interface
- **ester**-linked molecule → hexagonal packing (regardless on the substrate type)
  - substrate mediated pairing effect of azobenzene units, on **Au(111)** (stabilizing the monolayer)
- **ester** to **ether** linkage change results in the hexagonal symmetry breaking on HOPG (row-like structure → dimers)
  - **Au(111)**: probably as a result of unfavorable conformational changes of molecule in the solution.

- exploring the switching properties of physisorbed **ester** & **ether** analogues



Acknowledgments

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- Dr Alexandr Marchenko (Institute of Physics, NAS of Ukraine)
- Dr Sergey Snegir (Chuiko Institute of Surface Chemistry, NAS of Ukraine)

Thank you for your attention