SUPRAMOLECULAR ARCHITECTURES ON BULK INSULATORS BY NON-CONTACT ATOMIC FORCE MICROSCOPY AT ROOM TEMPERATURE: INVESTIGATION DOWN TO THE SINGLE MOLECULE SCALE

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Journées thématique « Molécules organiques et UHV », 12-13th of October 2015

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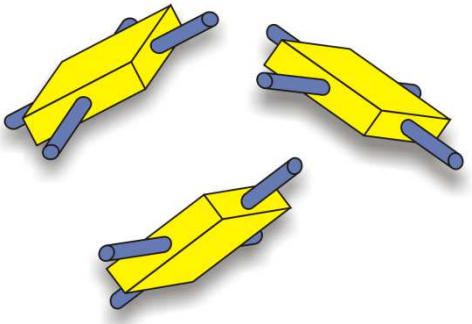
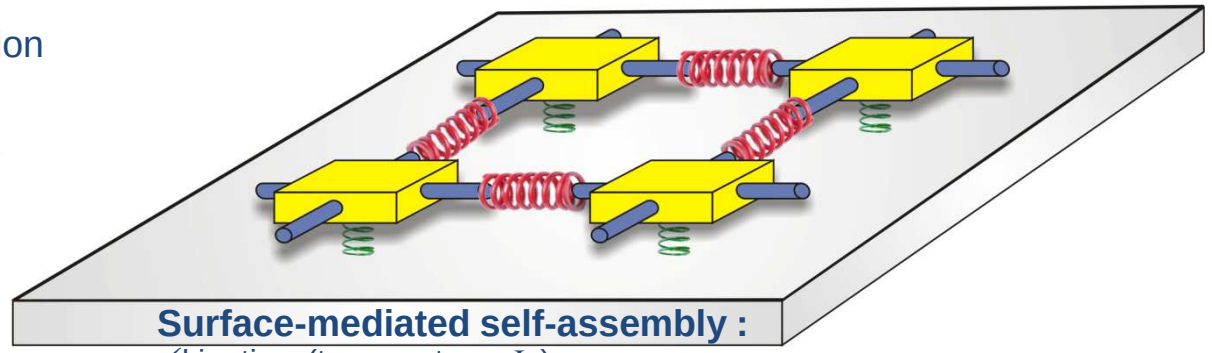
The « Nanostructuration » group at the IM2NP

❑ *Building molecular assemblies from supramolecular chemistry concepts*



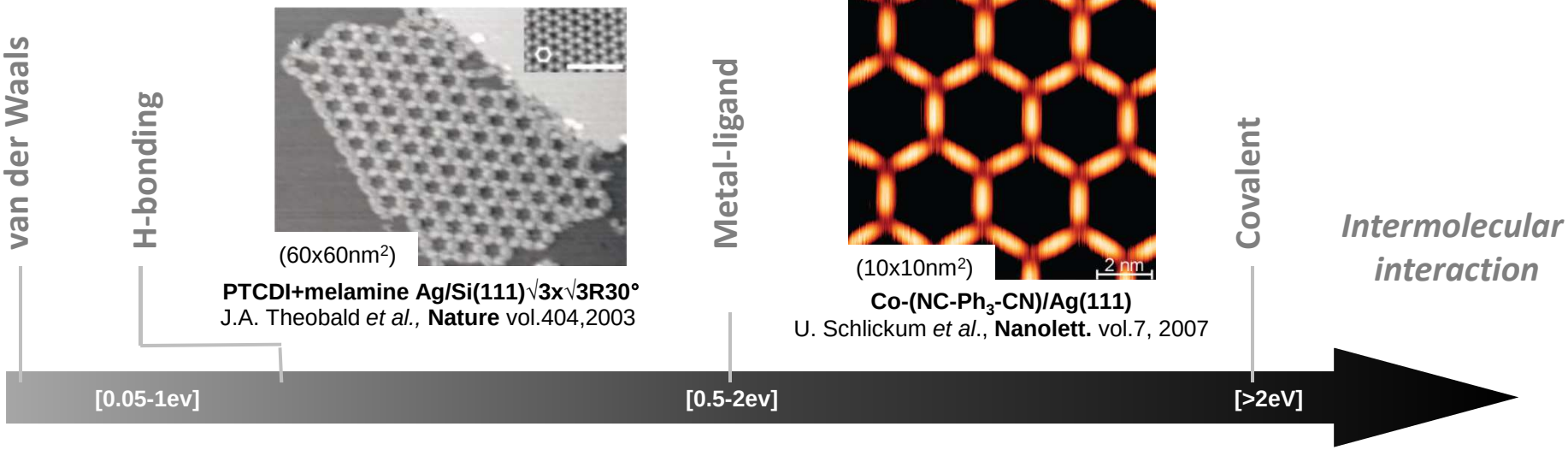
Molecular solid

Sublimation
(UHV)



Surface-mediated self-assembly :
✓kinetics (temperature, Φ)
✓thermodynamics (MM / MS)

❑ *Current trends…*



The « non-contact AFM » thematic within the group

Relevant heteroepitaxial systems:
- Influence of peripheral groups
- Symetry
- Epitaxy (?)

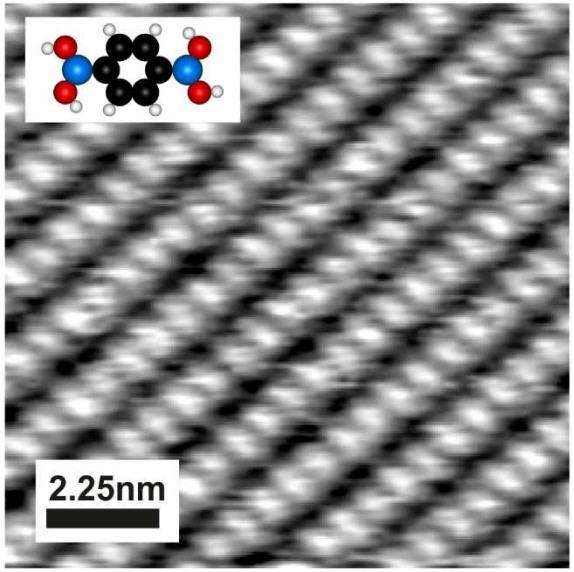
Optical & electronic properties in relation to structural properties

2D self-assembly of molecular films on insulating substrates (alkali halides ionic crystals)

Growth fundamental processes (MM vs. MS interactions)

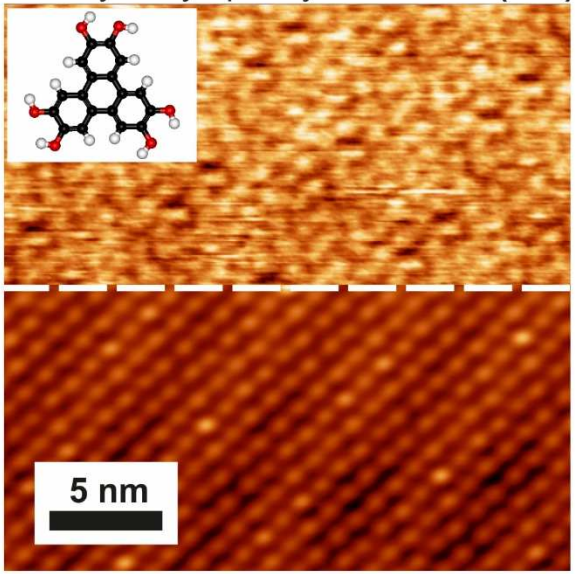
Insulating substrates:
- *mandatory for an efficient electronic decoupling (intrinsic properties)*
- *appropriate for transport properties*

Diboronic acid on **KCl(001)**



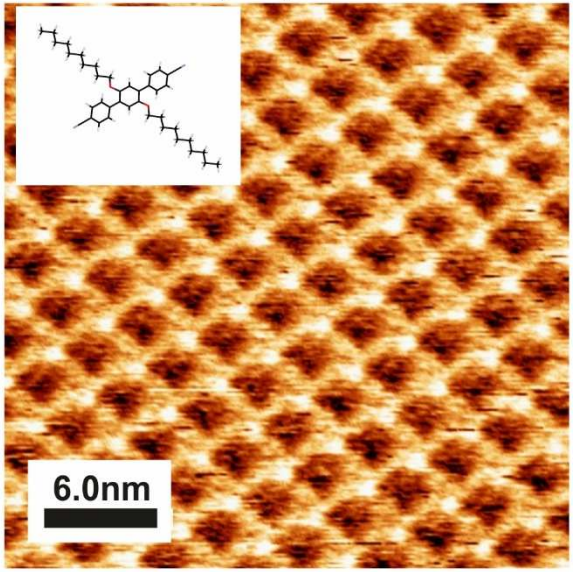
R.Pawlak et al., J.Phys.Chem.C (2010)

Hexahydroxytriphenylene on **KCl(001)**



F.Bocquet et al., Phys.Rev.Lett. (2012)

"CDB" on **KCl(001)**



A.Amrous et al., Adv.Mat.Interf. (2014)

The « non-contact AFM » thematic within the group

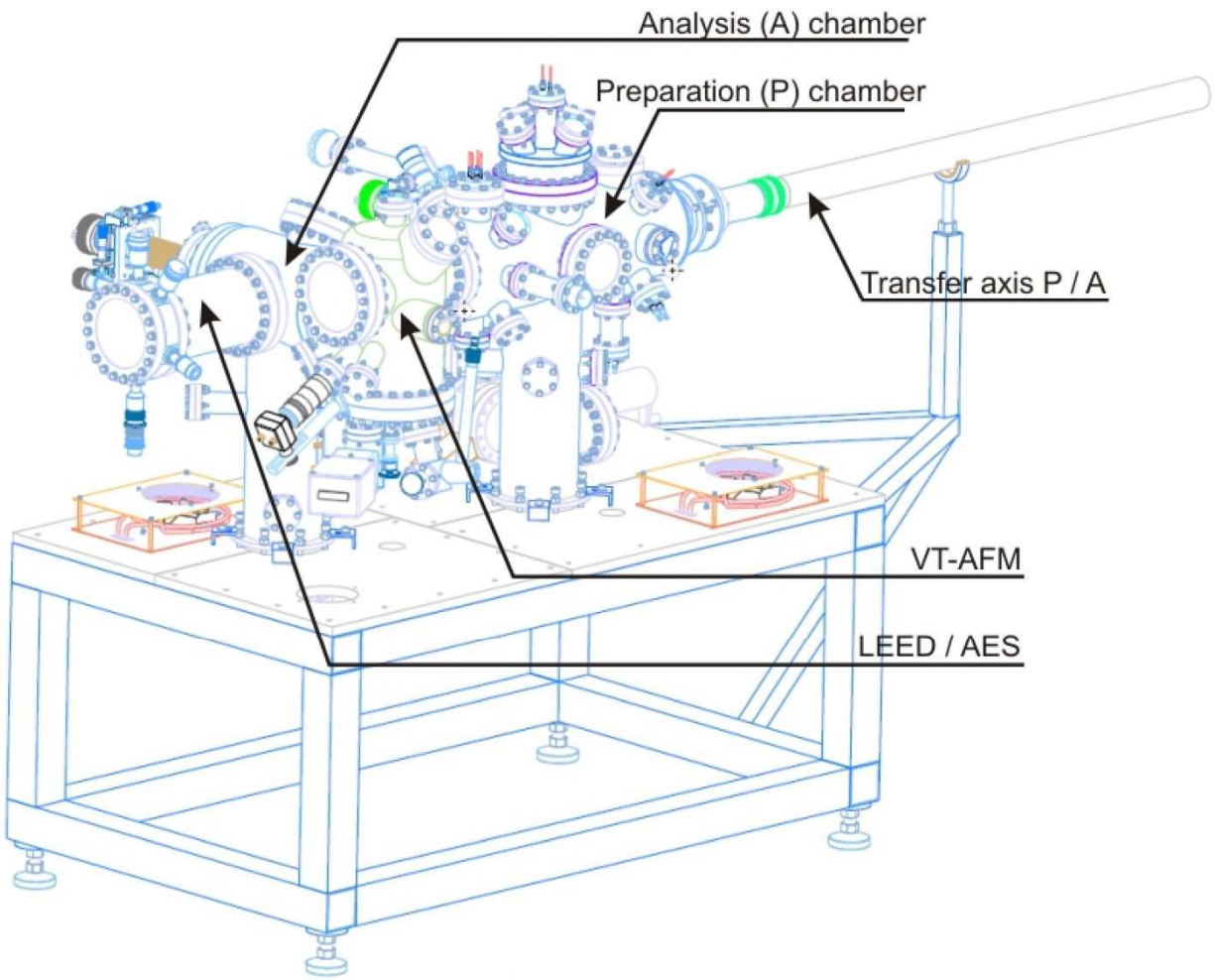
Ch. Loppacher (Pr.), F. Bocquet (MC), L.Nony (MC), F. Para (IE), A. Amrous (PhD)

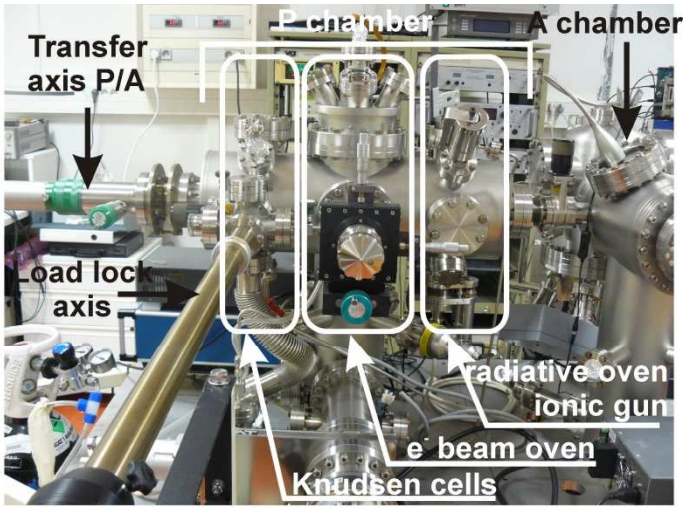
References:

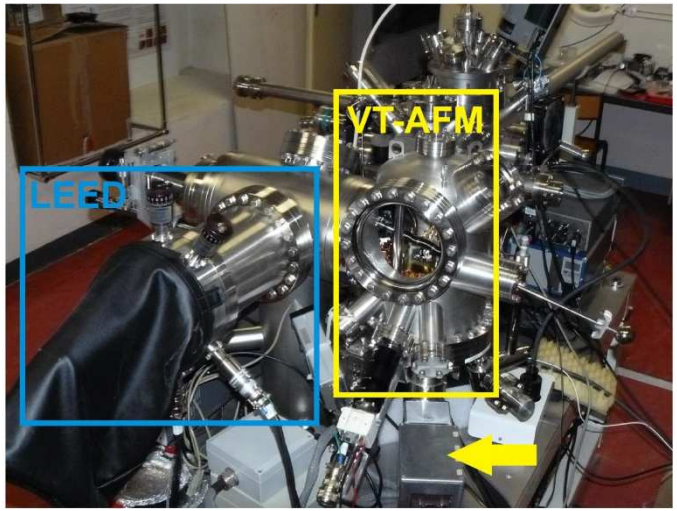
- P.Milde *et al.*, Nanotechnology **19**, 305501 (2008)
- F.Bocquet *et al.*, Phys. Rev. B **78**, 035410 (2008)
- L.Nony *et al.*, Nanotechnology **20**, 264014 (2009)
- L.Nony *et al.*, Phys. Rev. Lett. **103**, 036802 (2009)
- R.Pawlak *et al.*, J.Phys.Chem C **114**, 9290 (2010)
- F.Bocquet *et al.*, Phys. Rev. B **83**, 035401 (2011)
- F.Bocquet *et al.*, Phys.Rev.Lett. **108**, 206103 (2012)
- L.Nony *et al.*, Beilstein J. Nanotechnol. **3**, 301 (2012)
- A.Amrous *et al.*, Adv.Mat.Interf. **1**, 1400414 (2014)

- L.Nony, HDR (2013), downloadable from HAL CNS.

UHV setup (2008)

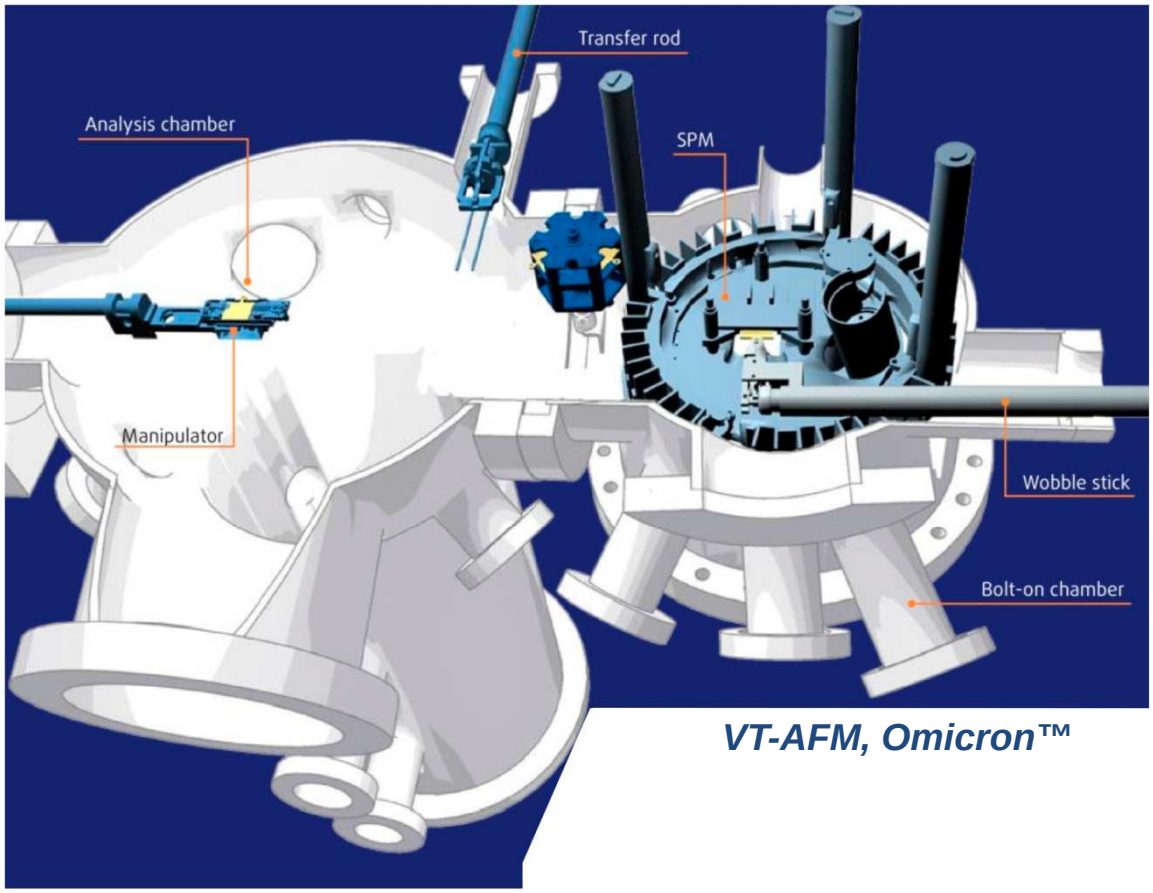






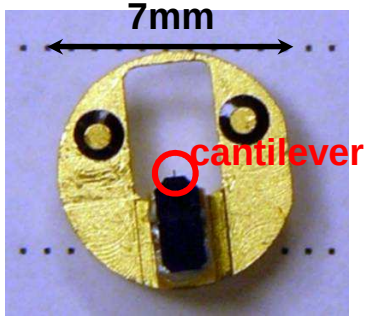
Base pressure (P/A): 2.10^{-10} mbar

Our AFM microscope



VT-AFM, Omicron™

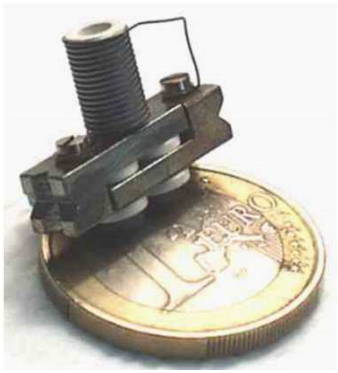
Cantilevers:
Nanosensors PPP-NCl: 120°C / 1h



Parameters:
f_0 = 150 kHz,
A_0 = 1-5 nm
Q = 40'000
k = 40 N/m

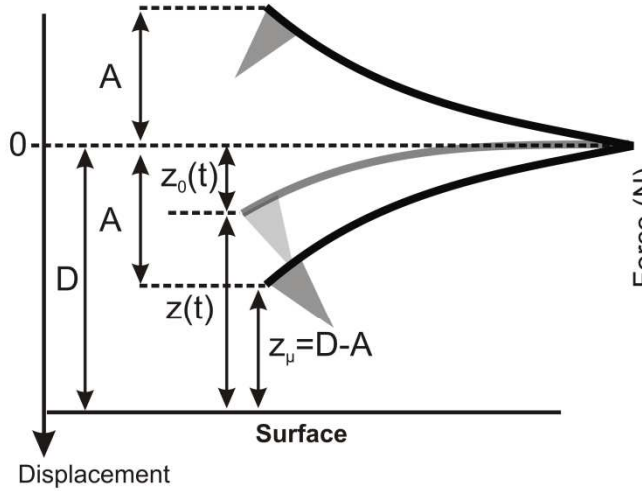
Molecules:
- 0.5-1 ML (taux ~ 1ML/min)
-substrate @ RT

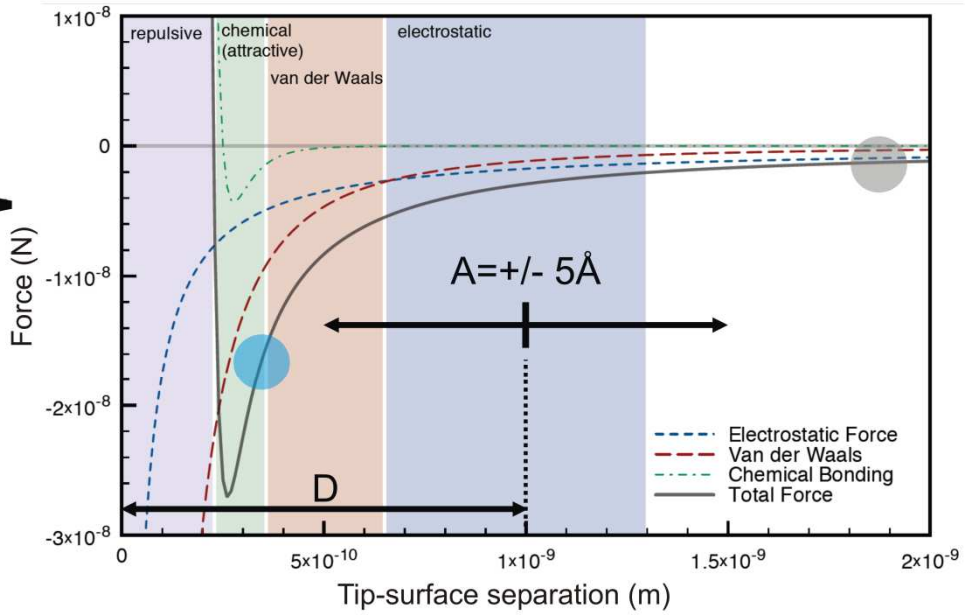
Samples:
- *Ex situ cleavage*
- Annealing 240°C/ 2h

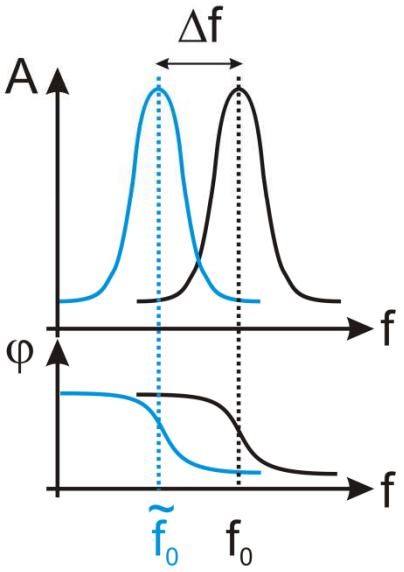


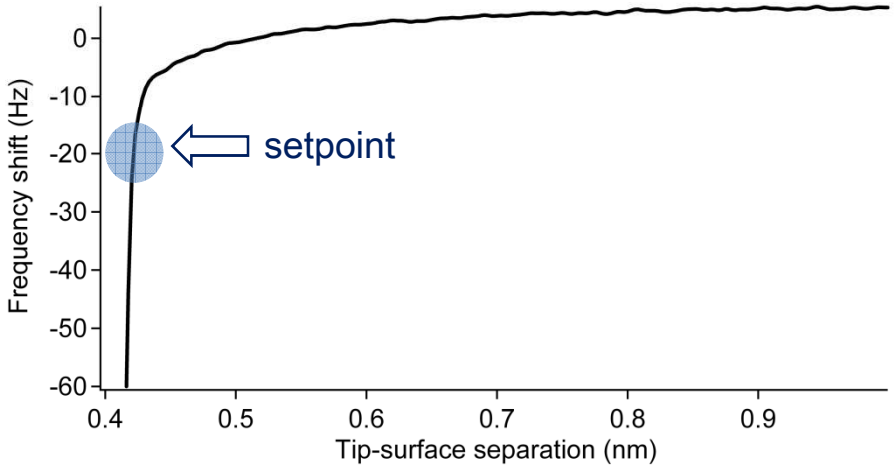
- ✓ ***Optimizations:***
  - *Wide-band (5 MHz) in situ preamp.*
  - *Temp. regulation to prevent drift*
- ✓ ***Experiments carried out at room temperature***

Non-contact Atomic Force Microscopy (nc-AFM)



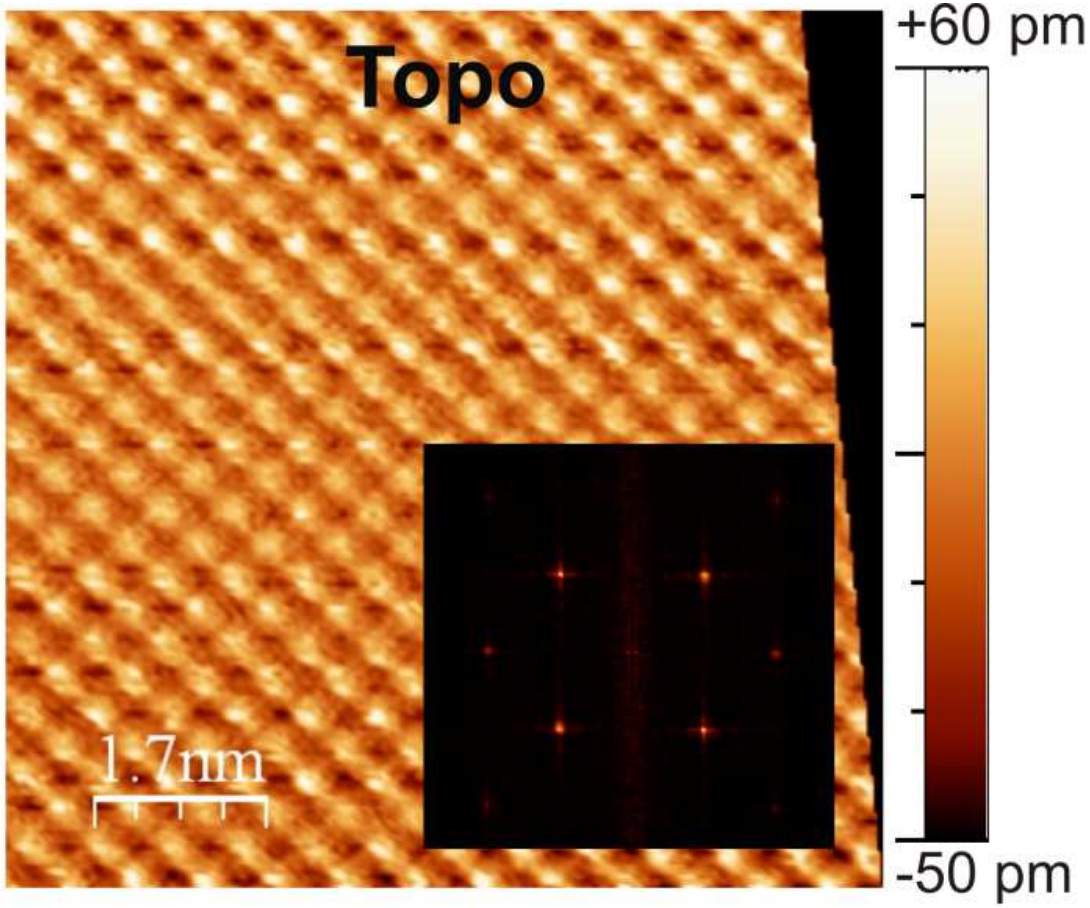






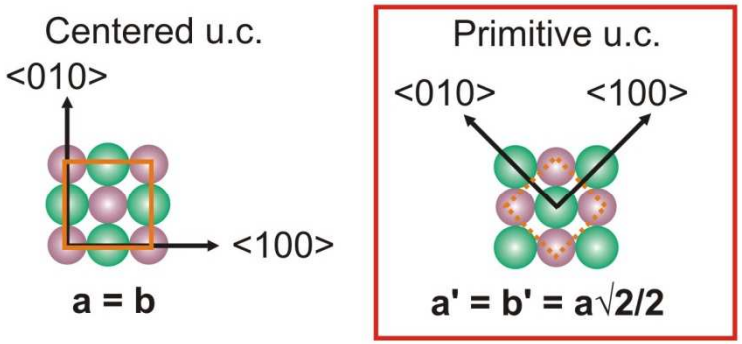
Illustration

✓ RbCl(001) (drift-corrected, raw data): A_0 = 5.6 nm, Δf = -21.5 Hz



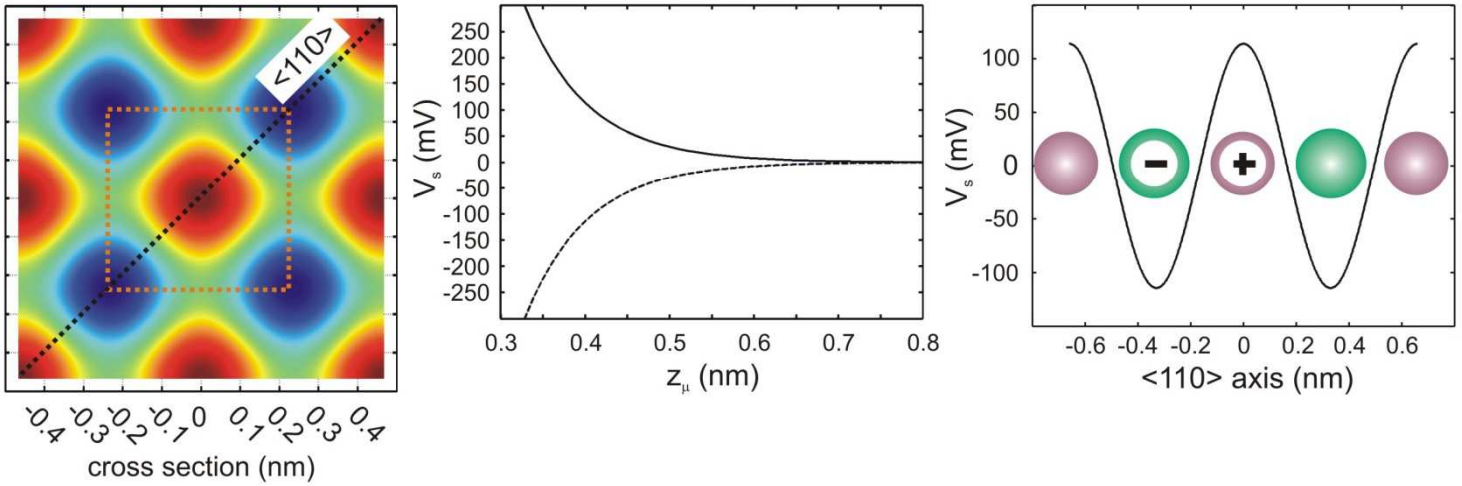
Alkali halides substrates

- Rock salt structure (fcc)
- Madelung surface potential[1]



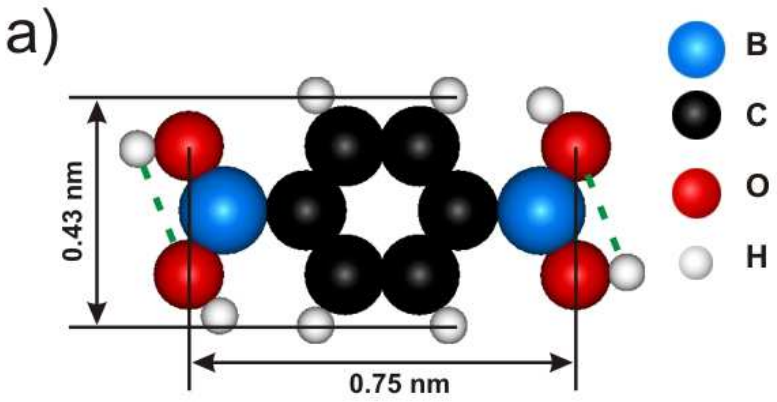
Sample	NaCl(001)	KCl(001)	RbCl(001)
a' (Å)	3.996	4.455	4.653

+11.5% +4.4%

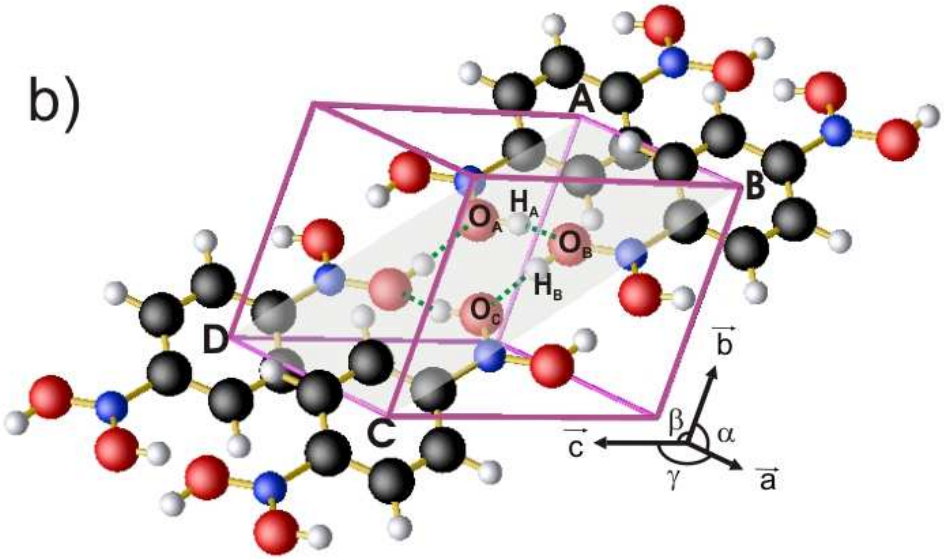


[1] R.E.Watson et al., Phys. Rev. B (1981); F.Bocquet et al., Phys. Rev. B (2008)

1,4-Benzene DiBoronic Acid (BDBA)



Most stable conformation (DFT)[1]

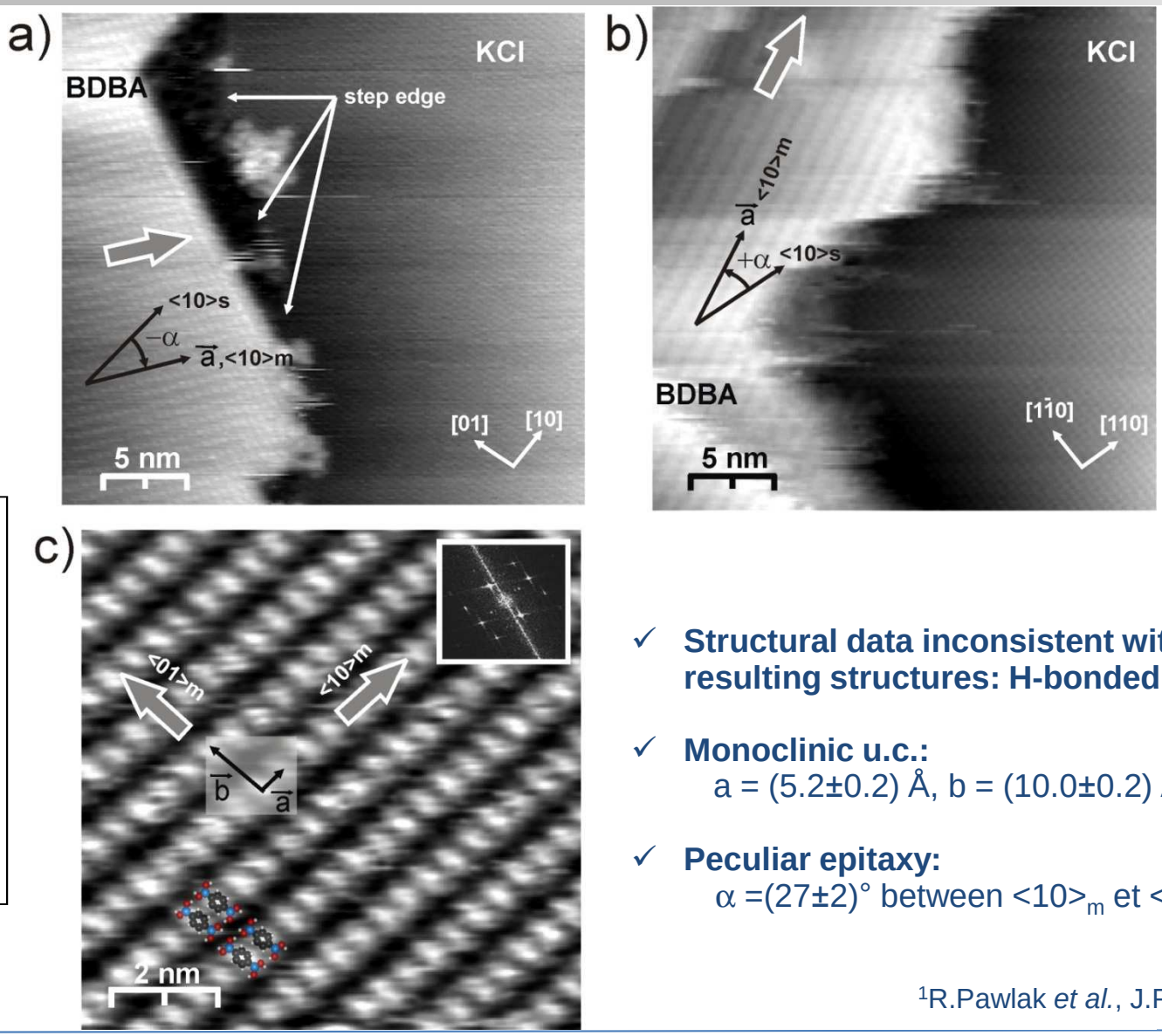


Bulk molecular crystal u.c.:
a=4.989 Å, b=5.305 Å, c=7.368 Å
α=93.797°, β=104.429°, γ=97.886°

- ✓ Molecular crystal = stack of 2D sheets (vdW interactions, similar to graphite)
- ✓ On metallic substrates, the molecule promotes the formation of covalent organic frameworks (COF)

[1]R.Pawlak *et al.*, J.Phys.Chem.C **114,** 9290 (2010)

BDBA on KCl(001)[1]



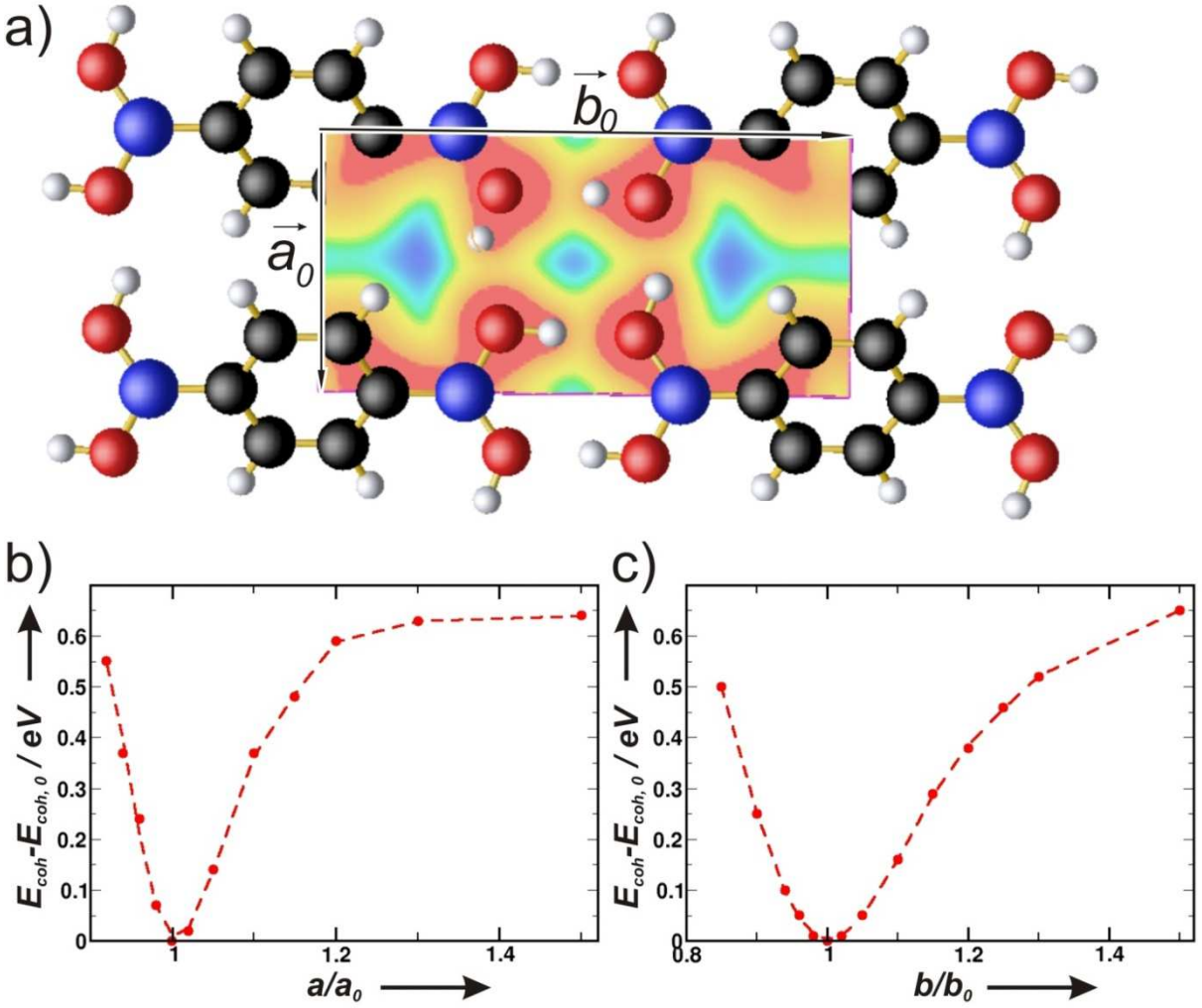
Exp. conditions:
a&b- (30x30)nm², γ=-0,085 nN.√nm
c- (9x9)nm², γ=-0,13 nN.√nm

- ✓ **Structural data inconsistent with polymerized resulting structures: H-bonded supramolecular phase**
- ✓ **Monoclinic u.c.:**
  a = (5.2±0.2) Å, b = (10.0±0.2) Å
- ✓ **Peculiar epitaxy:**
  α =(27±2)° between $<10>_m$ et $<10>_s$

[1]R.Pawlak *et al.*, J.Phys.Chem.C **114,** 9290 (2010)

BDBA on KCl(001)[1]: DFT approach

✓ **DFT-calculated free standing film:**

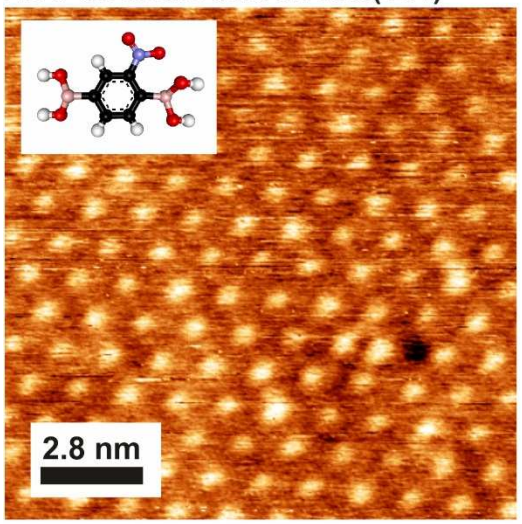


- ✓ Monoclinic u.c.:
  a_0=4.998 Å
  b_0=10.178 Å
- ✓ **Compliant with the exp. data**
- ✓ H-bonds driven supramolecular phase
- ✓ Cohesion: 0.95 eV/mol.
- ✓ Conformationnal change required to reduce sterical hindrance
- ✓ 2D structure nearly similar to a sheet of the molecular crystal
- ✓ **But: susbtrate influence (27° angle): trace of a line on line epitaxy which is electrostatically driven**

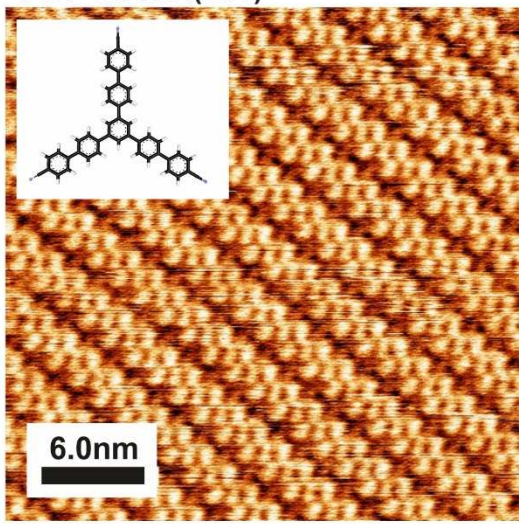
[1]R.Pawlak *et al.*, J.Phys.Chem.C **114,** 9290 (2010)

Other examples of extended networks

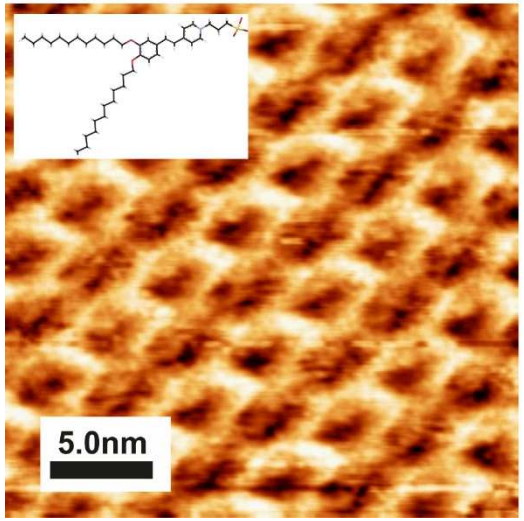
Nitro-diboronic acid on **KCl(001)**



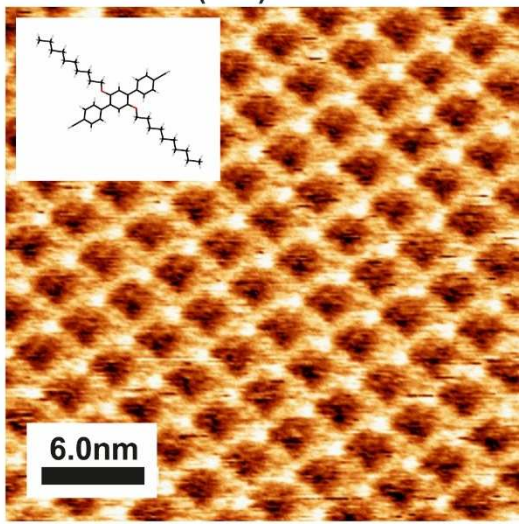
"TCB" on **KCl(001)**



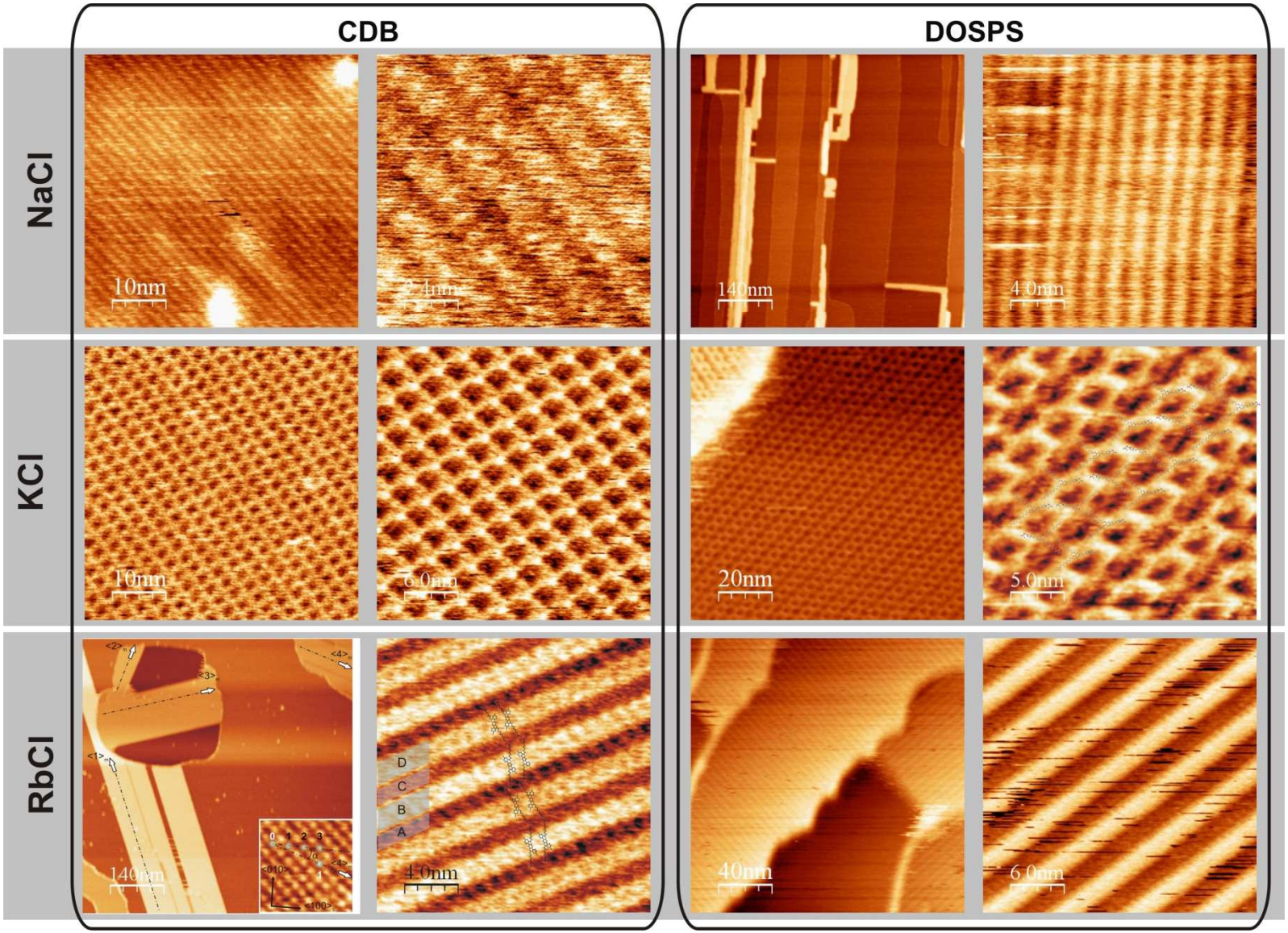
"DOSPS" on **KCl(001)**



"CDB" on **KCl(001)**



Other alkali halides substrates



Conclusions / Outlook

- ✓ **Nc-AFM in UHV: sensitive and non-destructive method for the investigation of organic phases on bulk insulators**

- ✓ **Supramolecular networks on alkali halides:**
  - ❑ *Complex, but original systems:*
    - Polymerization process ≠ metals
    - H-bonds driven supramolecular phases
    - Conformationnal adaptation
    - Peculiar epitaxies
  - ❑ *Fine energy MM vs. MS balance (~350 vs. ~250 meV/mol.)*

- ✓ **Connexion between experiments and calculations (DFT, PG)**

- ✓ **Several substrates for a single molecular synthon: site specific interaction**

- ✓ **<u>Outlook</u>:**
  → ***Optical properties***: Differential Reflectance Spectroscopy (absorption)
  → ***Entropic contribution*** (DFT vs. MD)