Chaîne de mesure de spectroscopie de réflectance différentielle pour la mesure en temps réel du spectre d'absorption (UV-vis) de molécules organiques auto-assemblées dans le régime monocouche sur des substrats isolants et sous ultra-vide

Laurent Nony

laurent.nony@im2np.fr

Journée thématique « Couplage AFM et photonique », 11 Octobre 2016
Institut Pasteur, Lille

Aix-Marseille Université, Faculté des Sciences, site Etoile - Saint-Jérôme
IM2NP, UMR CNRS 7334

Outline

- Introduction to the group and to our equipment
- I- Examples of results in non-contact AFM
- II- Examples of DRS results (M2 thesis by Ph. Luangprasert)

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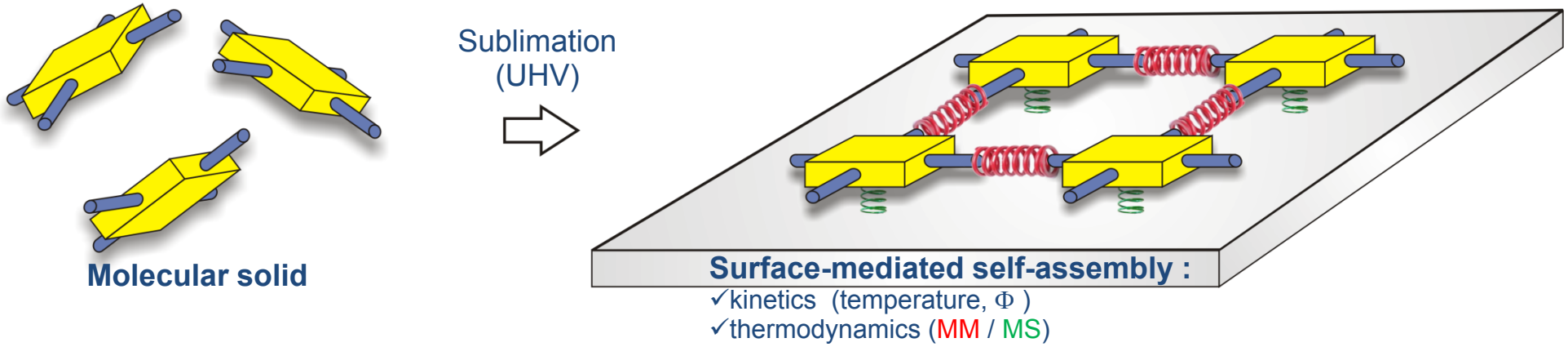
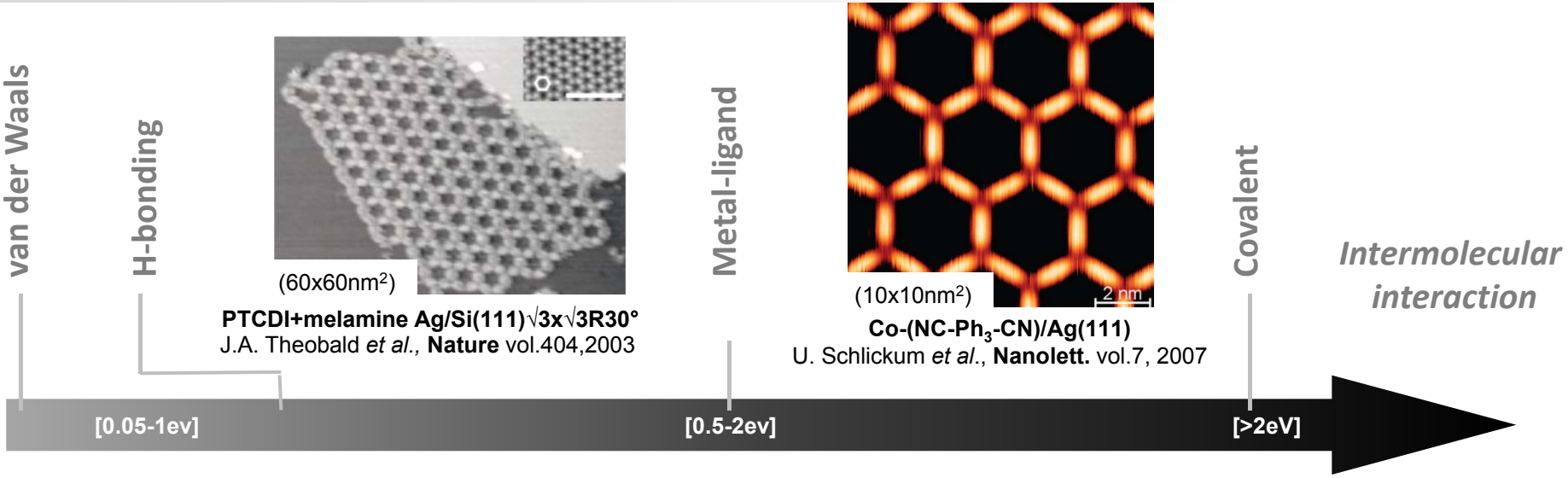
The « Nanostructuration » group at the IM2NP

❑ *Building molecular assemblies from supramolecular chemistry concepts*



❑ *Current trends…*



The « non-contact AFM » thematic within the group

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

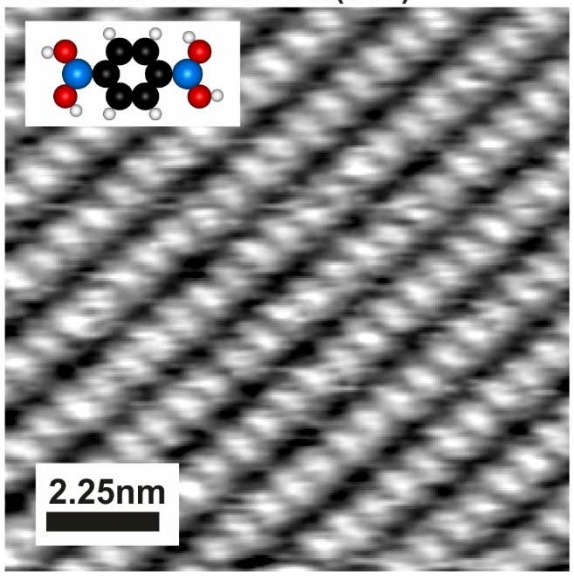
Optical & electronic properties in relation to structural properties

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

Growth fundamental processes (MM vs. MS interactions)

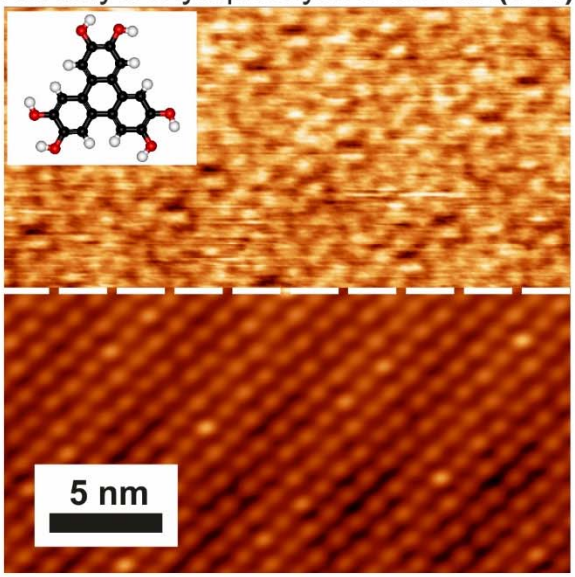
Insulating substrates:
- *mandatory for an efficient electronic decoupling (intrinsic properties)*
- *appropriate for transport properties*

Diboronic acid on **KCl(001)**



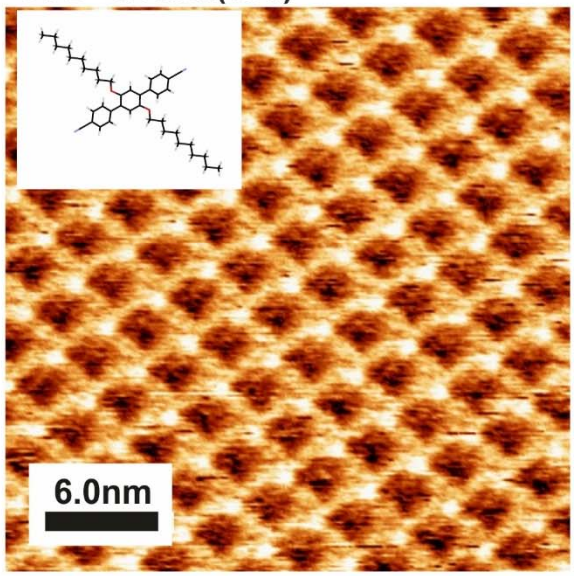
R.Pawlak et al., J.Phys.Chem.C (2010)

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

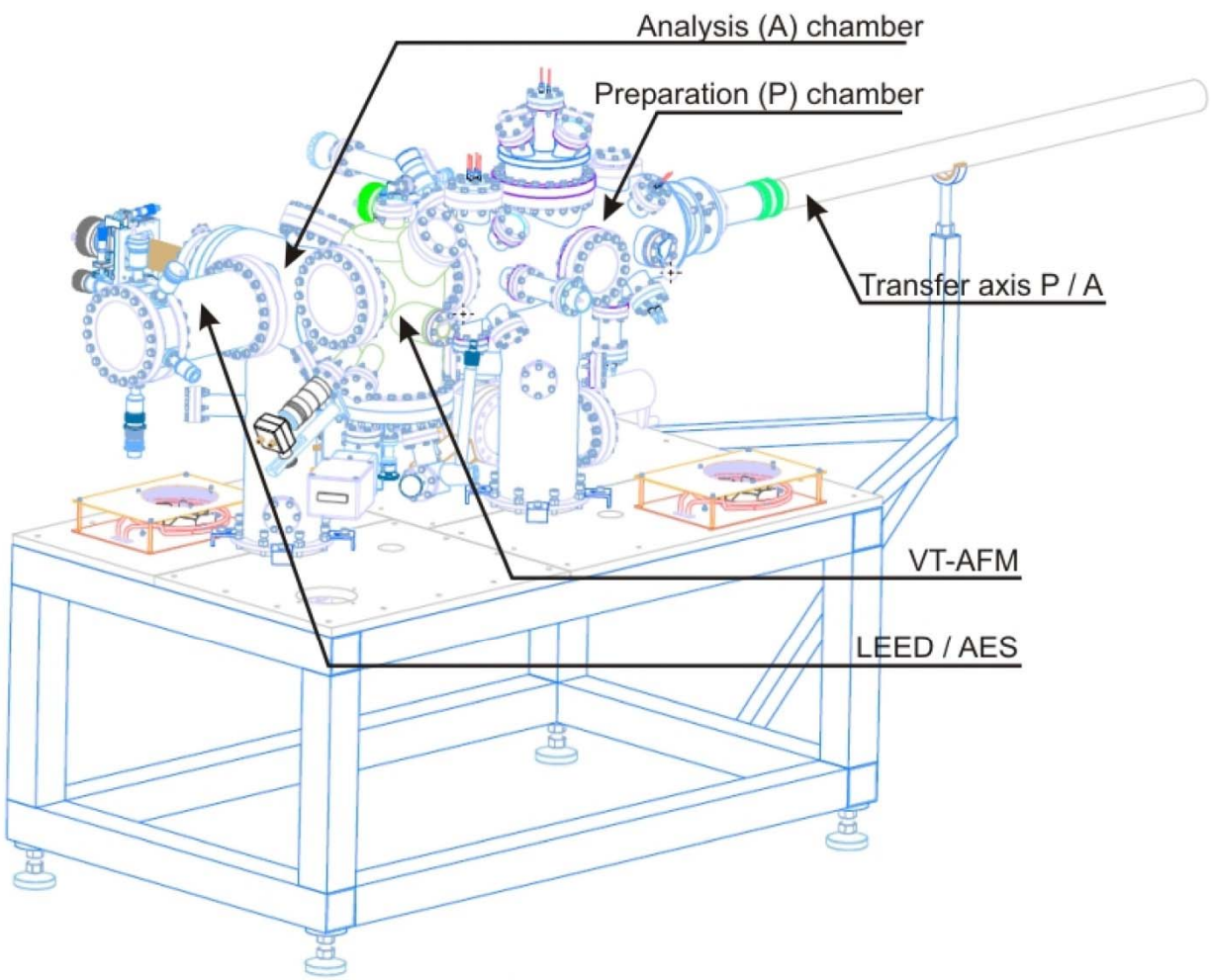
Ch. Loppacher (Pr.), F. Bocquet (MC), L.Nony (MC), F. Para (IE), A. Amrous (PhD)

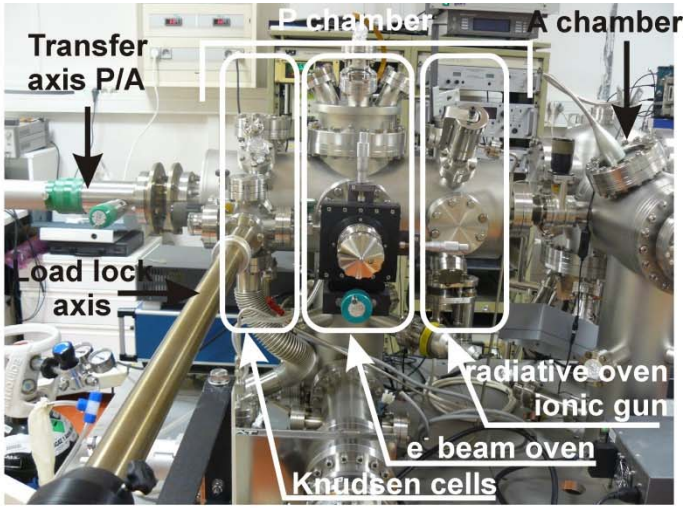
References:

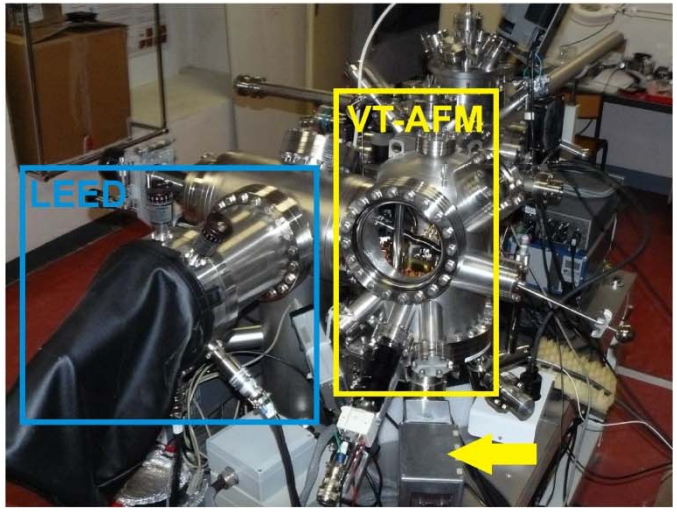
- P.Milde *et al.*, Nanotechnology **19**, 305501 (2008)
- F.Bocquet *et al.*, Phys. Rev. B **78**, 035410 (2008)
- L.Nony *et al.*, Nanotechnology **20**, 264014 (2009)
- L.Nony *et al.*, Phys. Rev. Lett. **103**, 036802 (2009)
- R.Pawlak *et al.*, J.Phys.Chem C **114**, 9290 (2010)
- F.Bocquet *et 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)

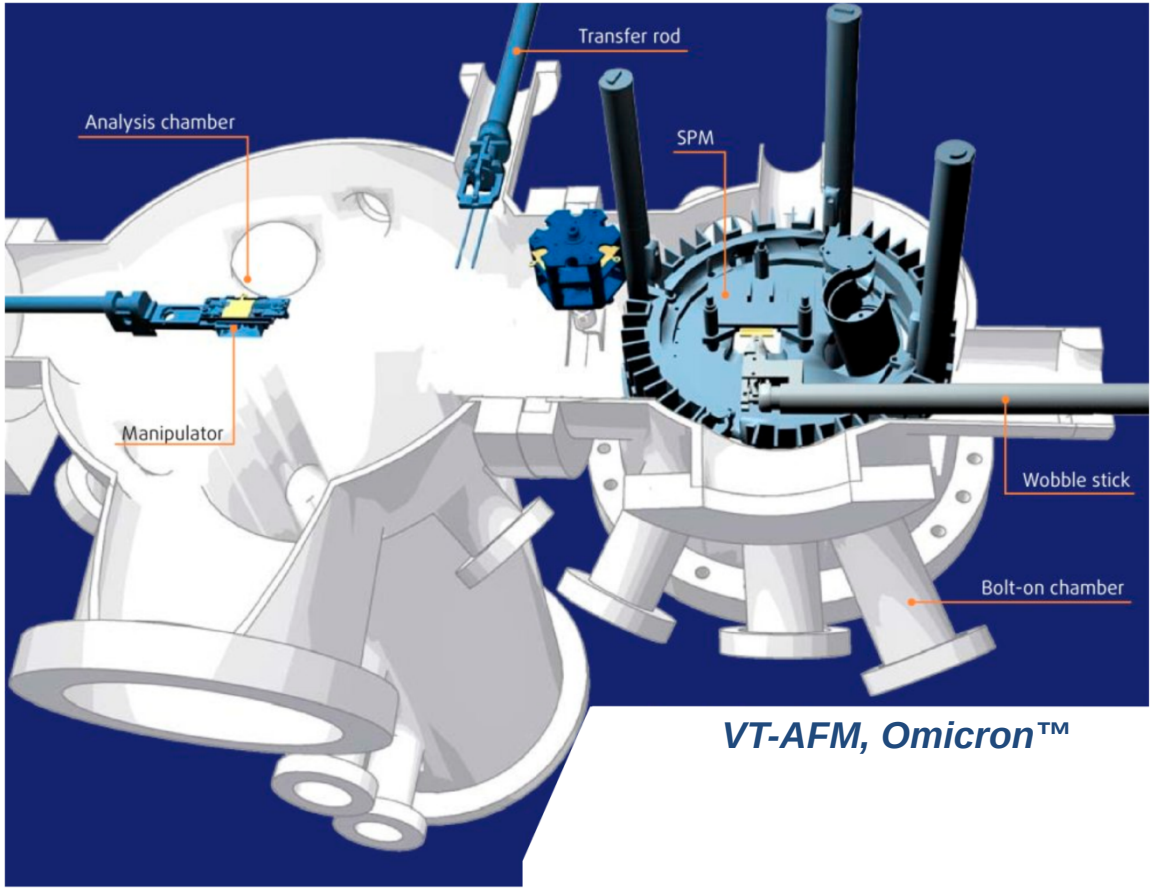






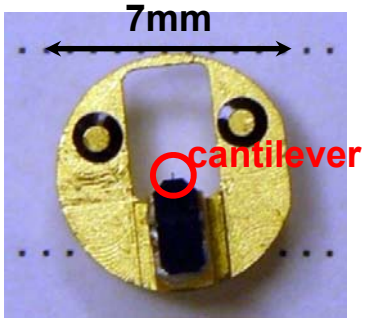
Base pressure (P/A): 2.10^{-10} mbar

Our AFM microscope



VT-AFM, Omicron™

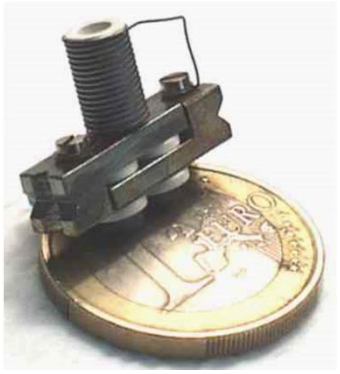
Cantilevers:
Nanosensors PPP-NCl: 120°C / 1h



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

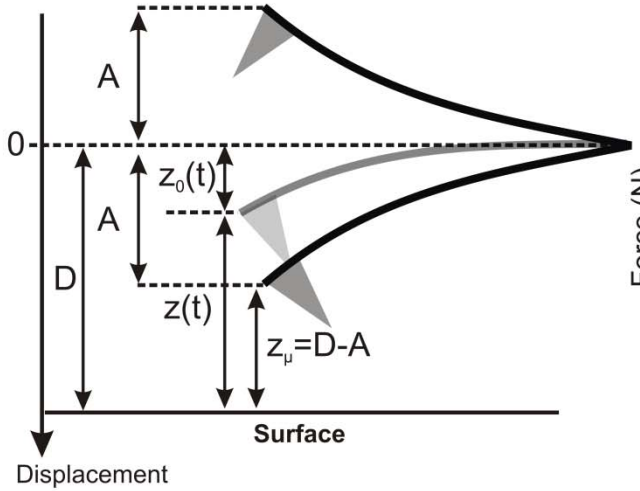
Molecules:
- 0.5-1 ML (rate ~ 1ML/min)
-substrate @ RT

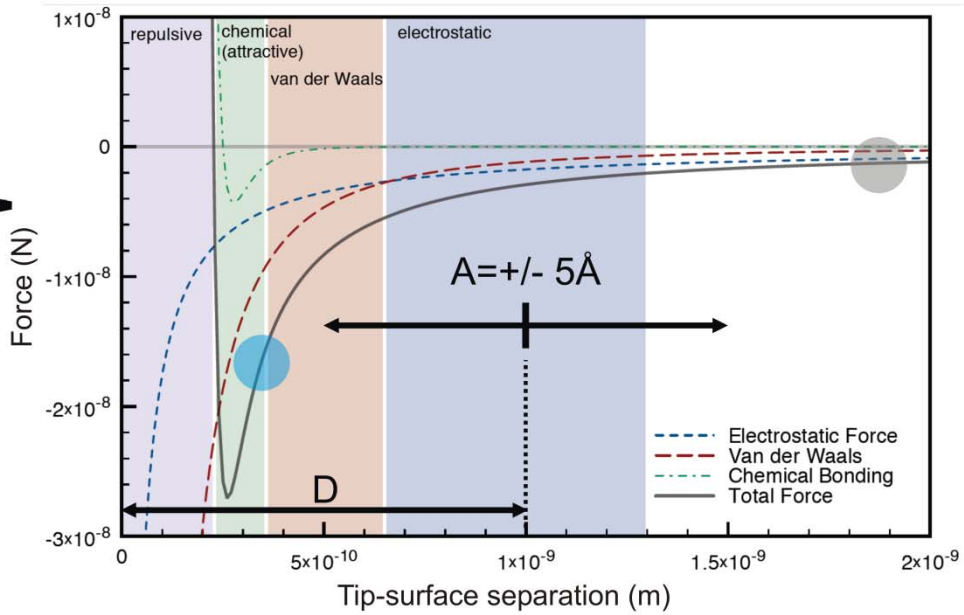
Samples:
- *Ex situ cleavage*
- Annealing 240°C/ 2h

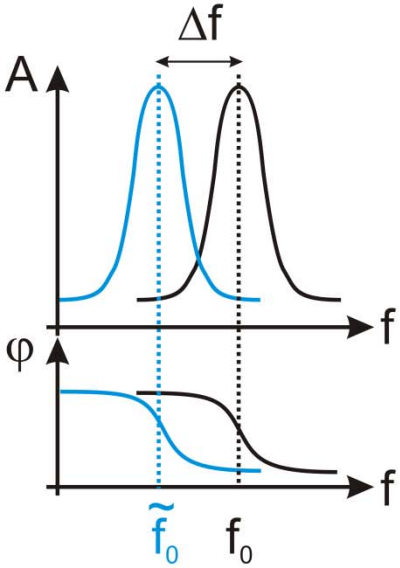


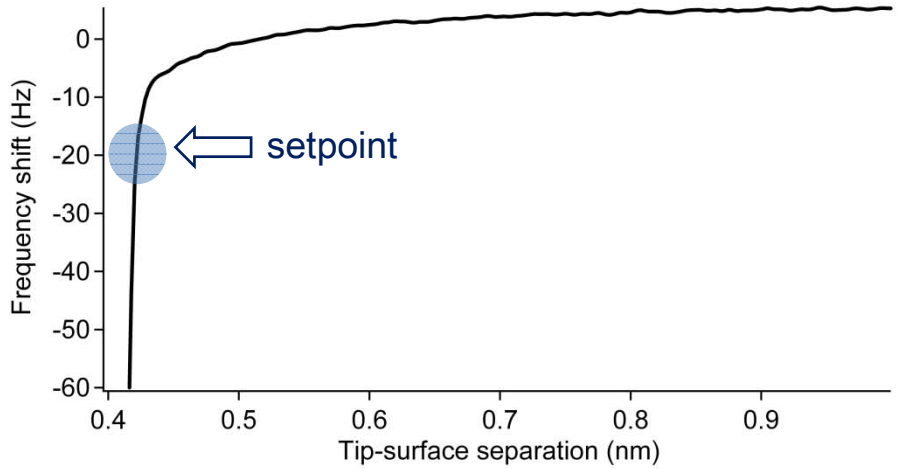
- ✓ ***Optimizations:***
  - *Wide-band (5 MHz) in situ preamp.*
  - *Temp. regulation to prevent drift*
- ✓ ***Experiments carried out at room temperature***

Non-contact Atomic Force Microscopy (nc-AFM)



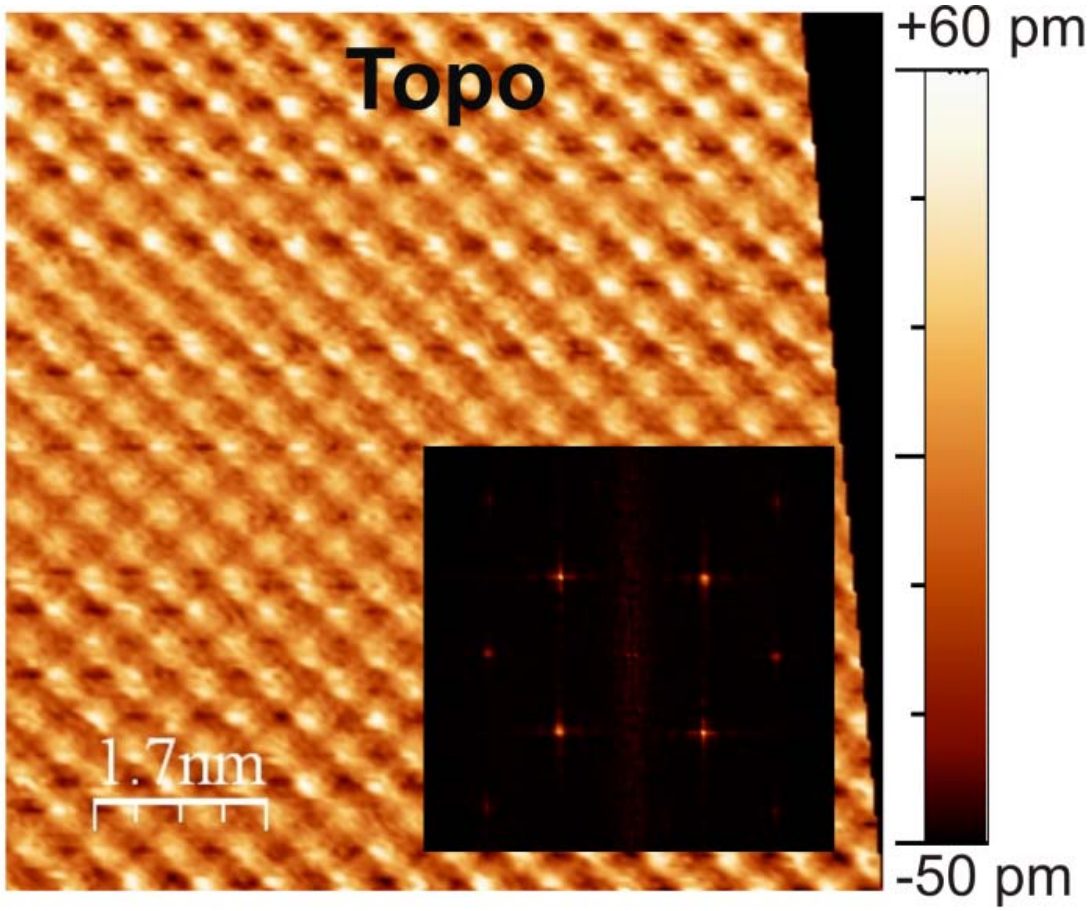






Illustration

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



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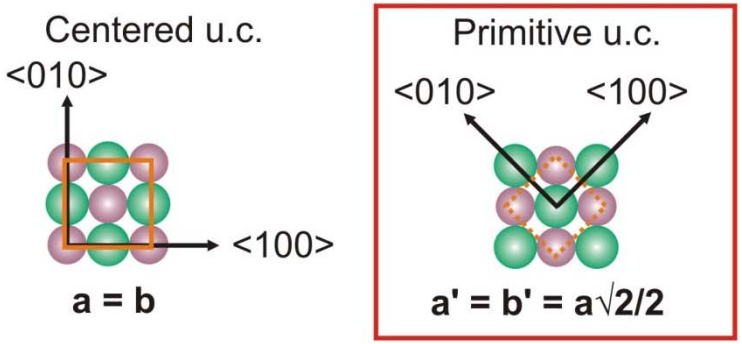
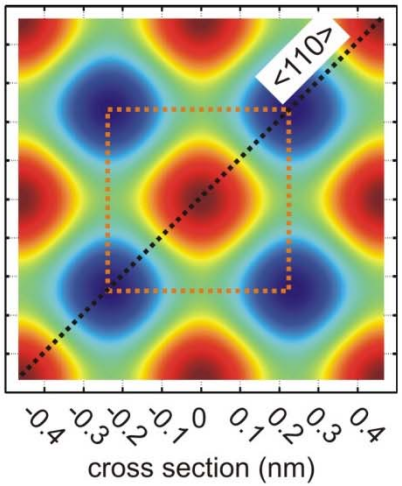
Alkali halides substrates

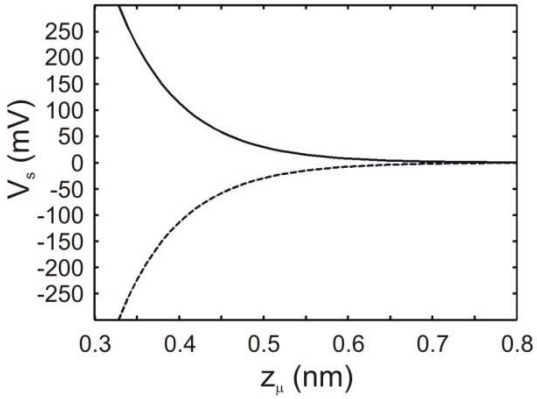
- Rock salt structure (fcc)
- Madelung surface potential[1]

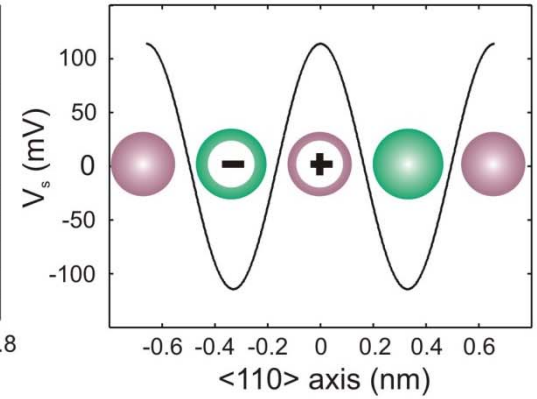


Sample	*NaCl(001)*	*KCl(001)*	*RbCl(001)*
a' (Å)	3.996	4.455	4.653

+11.5% +4.4%

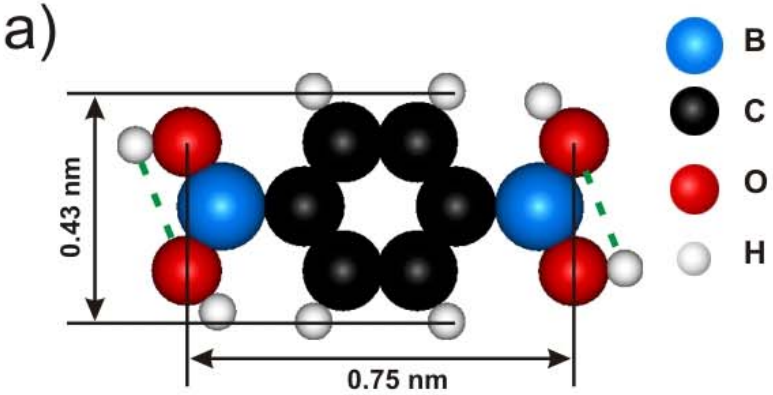




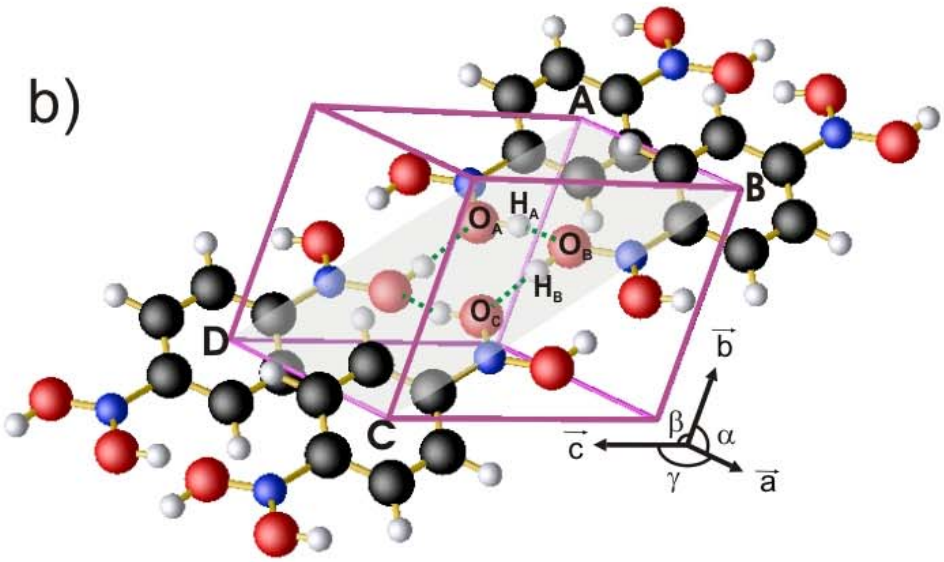


[1] R.E.Watson et al., Phys. Rev. B (1981); F.Bocquet et al., Phys. Rev. B (2008)

1,4-Benzene DiBoronic Acid (BDBA)



Most stable conformation (DFT)[1]

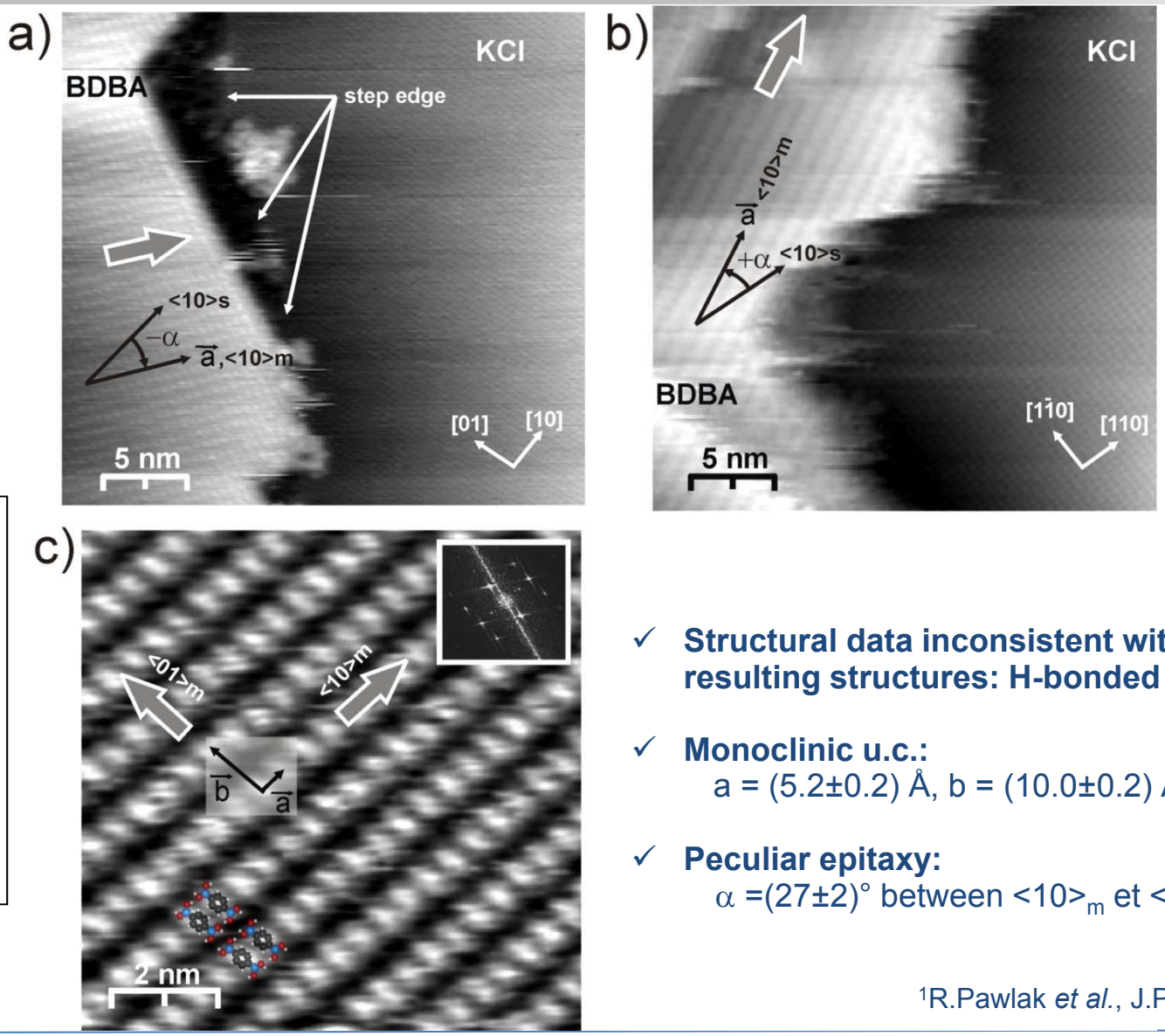


Bulk molecular crystal u.c.:
a=4.989 Å, b=5.305 Å, c=7.368 Å
α=93.797°, β=104.429°, γ=97.886°

- ✓ 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]



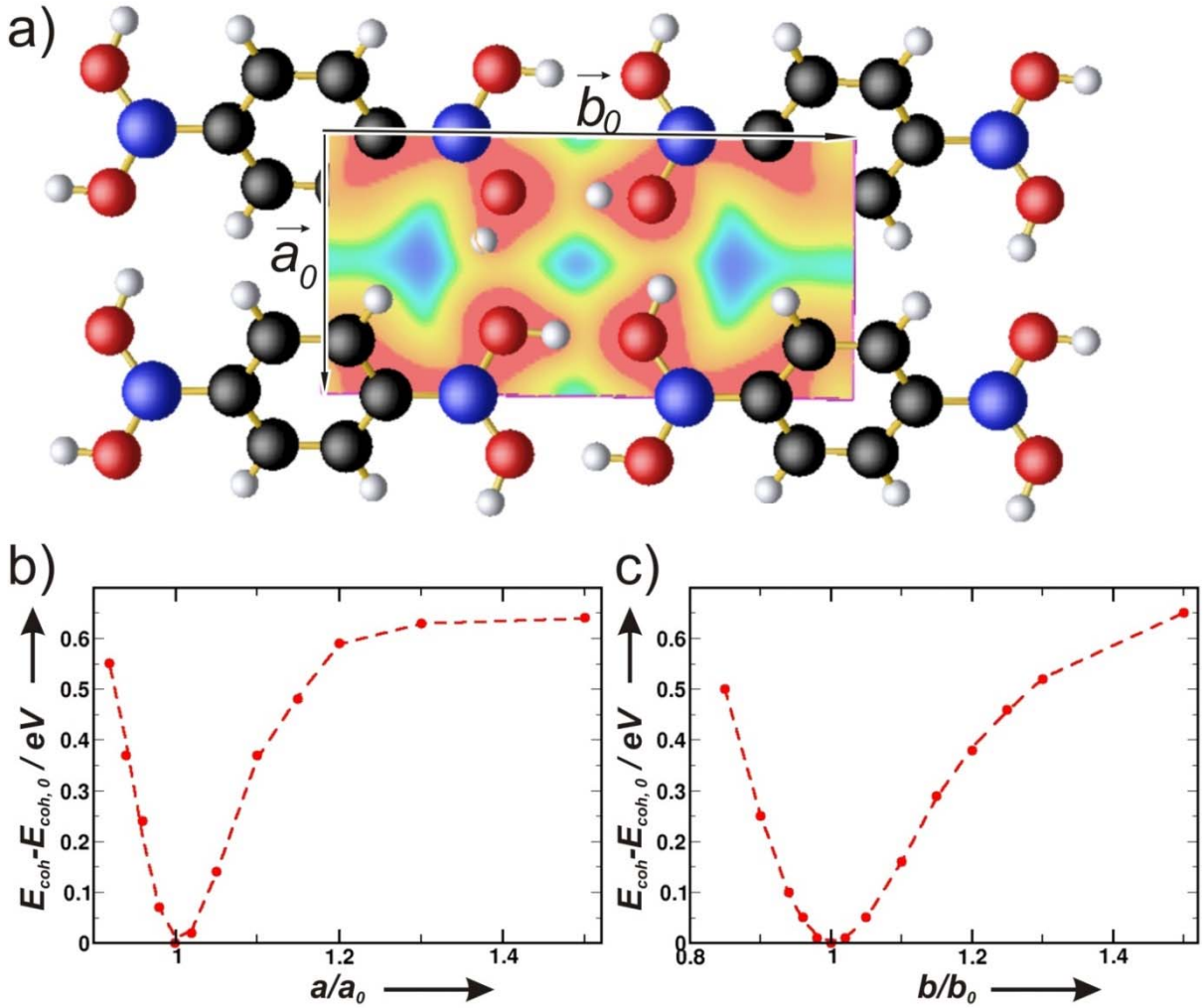
Exp. conditions:
a&b- (30x30)nm², γ =-0,085 nN.√nm
c- (9x9)nm², γ =-0,13 nN.√nm

- ✓ **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:**

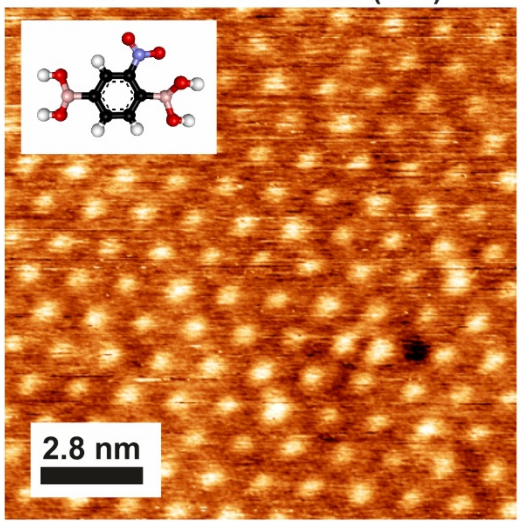


- ✓ Monoclinic u.c.:
  a_0=4.998 Å
  b_0=10.178 Å
- ✓ **Compliant with exp. data**
- ✓ H-bonds driven supramolecular phase
- ✓ Cohesion: 0.95 eV/mol.
- ✓ Conformationnal change required to reduce sterical hindrance
- ✓ 2D structure nearly similar to a sheet of the molecular crystal
- ✓ **But: susbtrate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

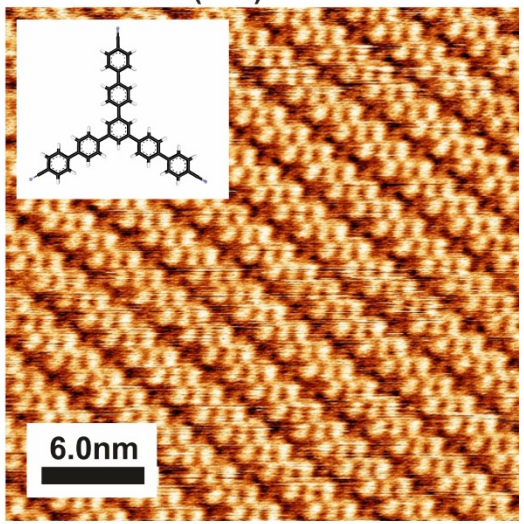
[1]R.Pawlak *et al.*, J.Phys.Chem.C **114,** 9290 (2010)

Other examples of extended networks*

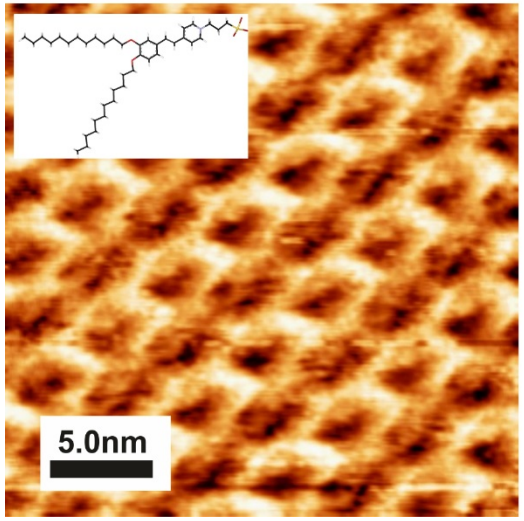
Nitro-diboronic acid on **KCl(001)**



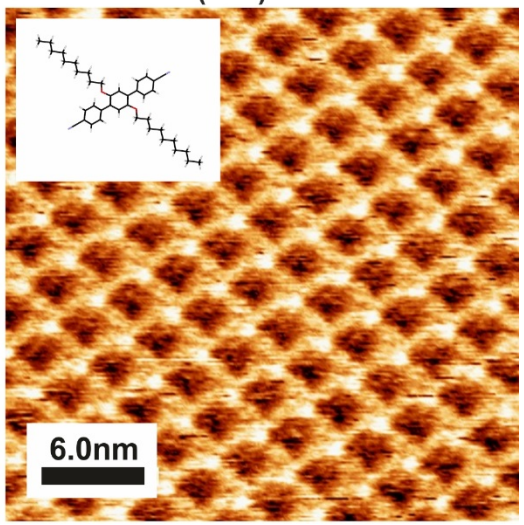
"TCB" on **KCl(001)**



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

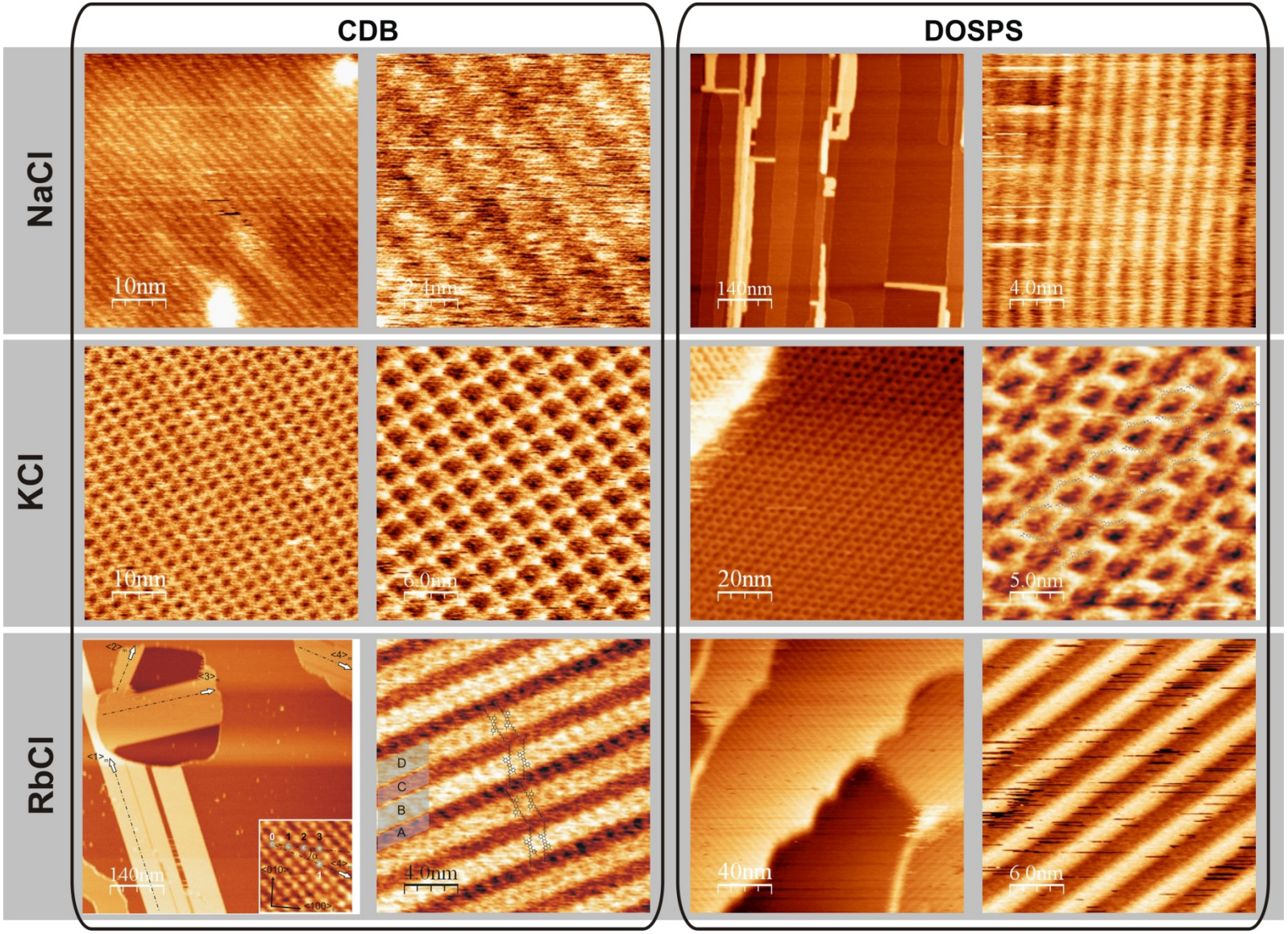


"CDB" on **KCl(001)**



* Molecules by F. Chérioux, Femto-ST Besançon

Other alkali halides substrates



Part I: conclusions and 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)

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Differential Reflectance Spectroscopy (DRS) of self-assembled molecular structures on insulating substrates

Philipda Luangprasert

Supervisors:
Christian Loppacher
Laurent Nony
Franck Bocquet
Ulrich Lemmer

Overview

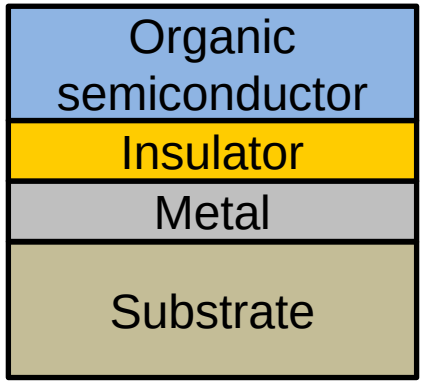
- Introduction
- Theory and setup of DRS
- Results and discussions
  - Test measurement
    - Software, Stability, Back surface reflection
  - Measurement of deposited molecules
    - Pyrene: pyr8
    - Porphyrin: CKRS16
- Conclusion & future work

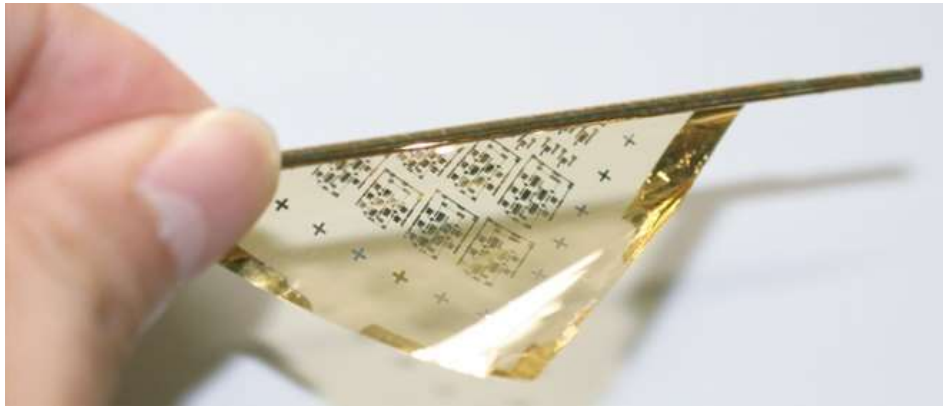
Introduction – organic electronics

Advantages

- light weight
- flexible
- large area
- low cost

Basic structure

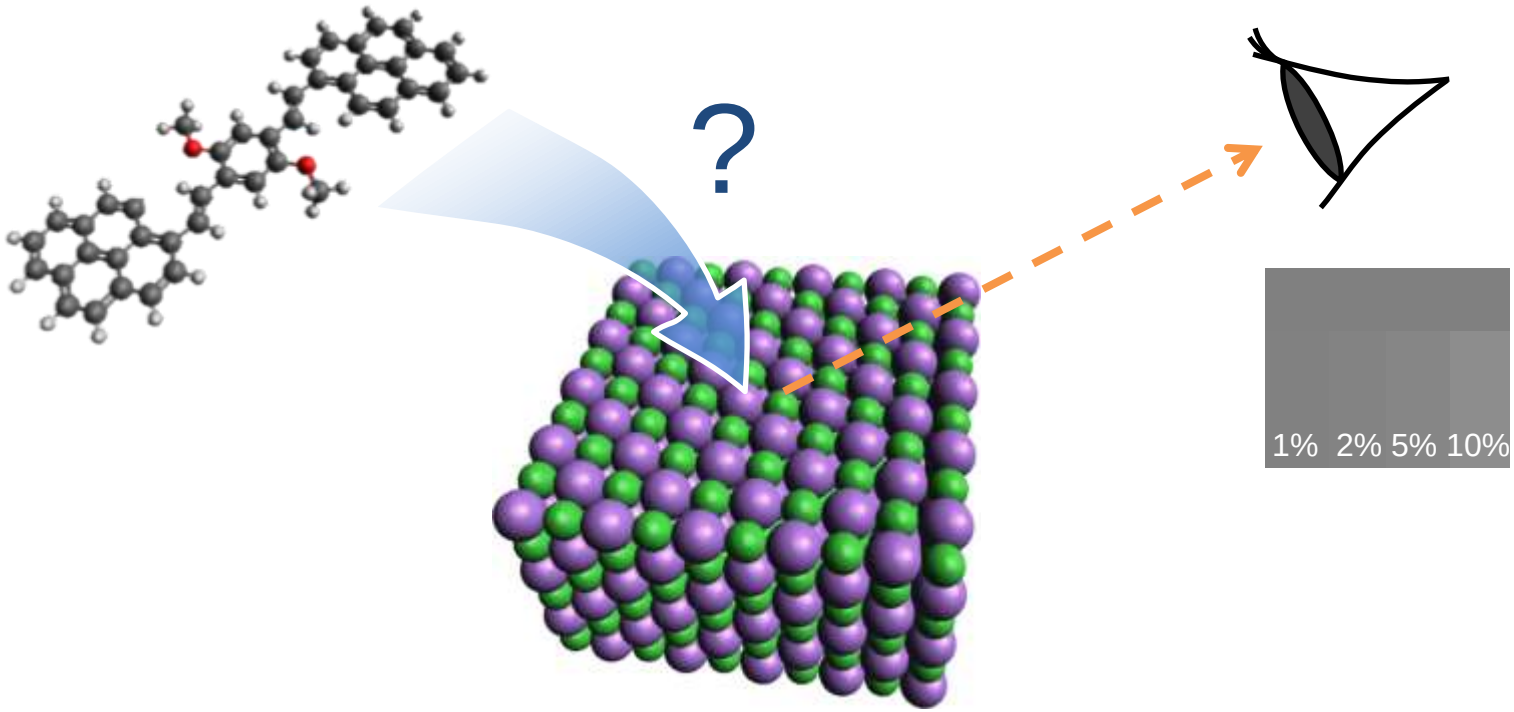




[1] T. Sekitani et al., *Nature Mater.* **9**, 1015 (2010).
[2] LG Display, Press Center CES 2016. http://www.lgdisplay.com/eng/prcenter/newsView?articleMgtNo=4962

Introduction – objective

Toward understanding of
molecular structures on surface



Using simple optical spectroscopy in situ
with sensitivity better than 1/1000

Theory of DRS

- Differential reflectance spectroscopy (DRS)

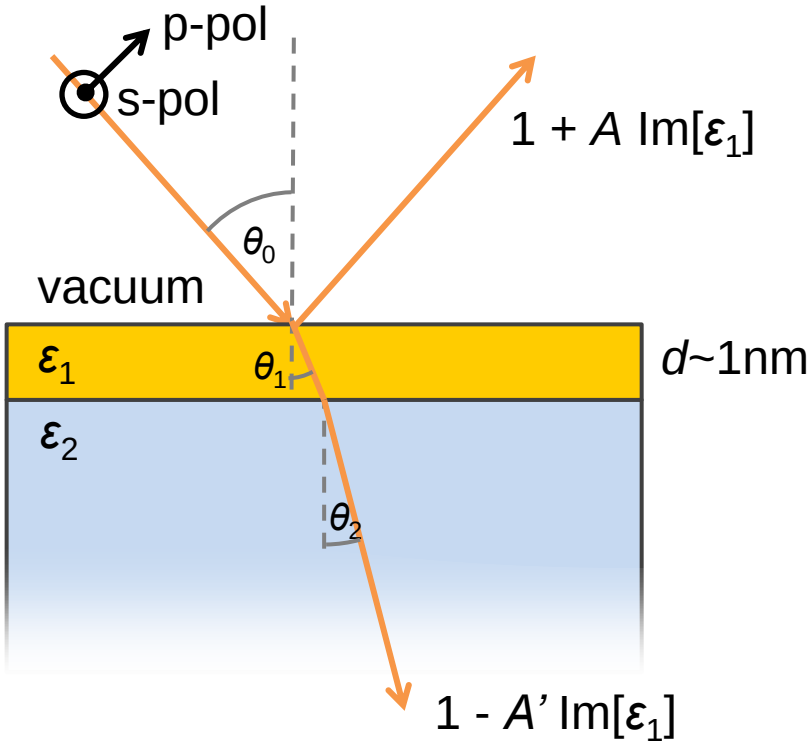
$$DRS := \frac{R(d) - R(0)}{R(0)} = \frac{R(d)}{R(0)} - 1$$

- Interference from a thin layer $R(d)$

- Linearized [1] for thin layer $d \ll \lambda$

$$DRS_s = -\frac{8\pi d \cos\theta_0}{\lambda} \mathrm{Im}\left[\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 - 1}\right] = \frac{8\pi d \cos\theta_0}{\lambda(\epsilon_2 - 1)} \mathrm{Im}[\epsilon_1]$$

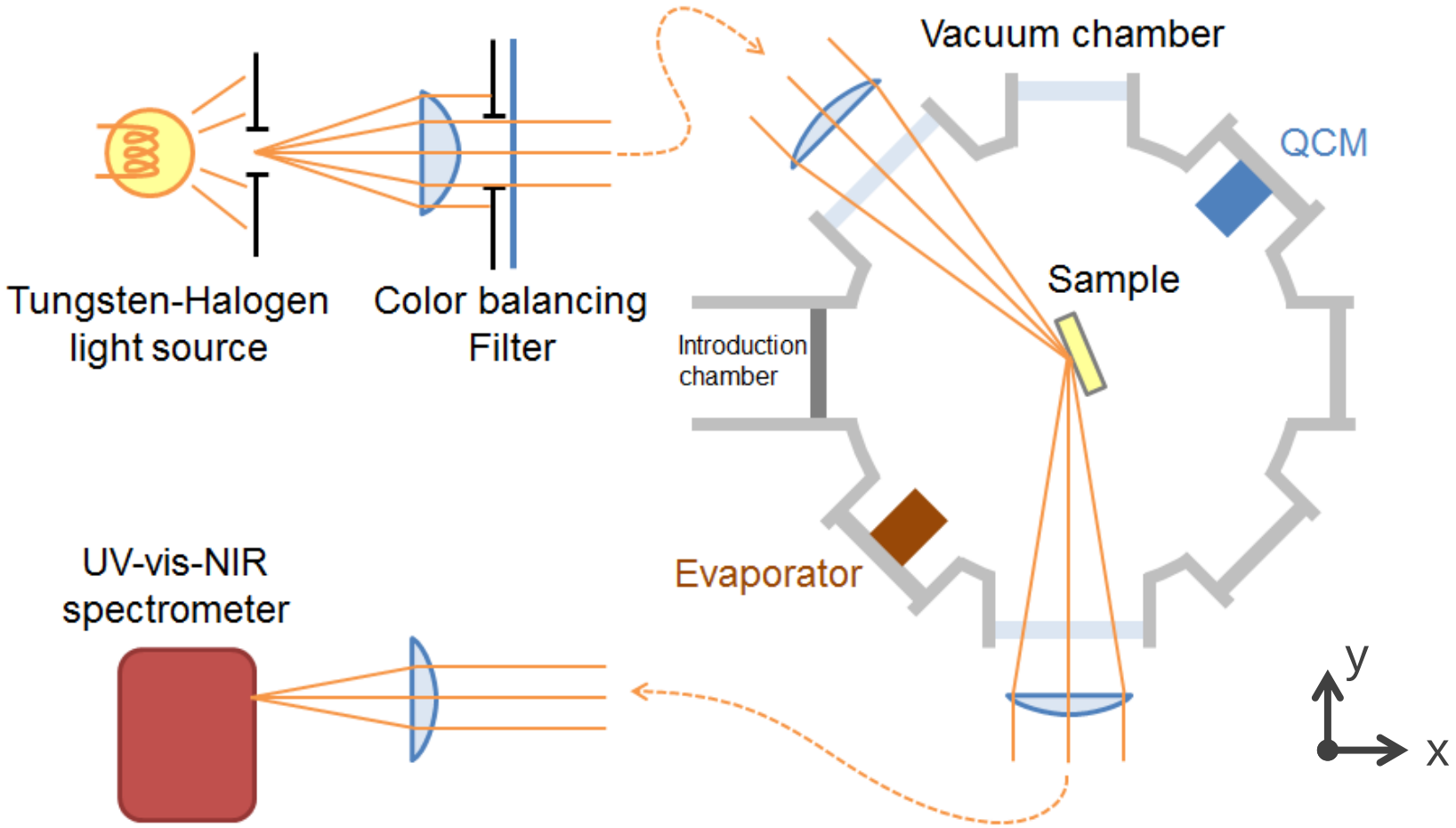
$$DRS_p = -\frac{8\pi d \cos\theta_0}{\lambda} \mathrm{Im}\left[\frac{\epsilon_2 - \epsilon_1 - (\epsilon_2 - \epsilon_1^2/\epsilon_2)\sin^2\theta_1}{\epsilon_2 - 1 - (\epsilon_2 - 1/\epsilon_2)\epsilon_1 \sin^2\theta_1}\right]$$



- Positive DRS for an absorbing adsorbed layer on a transparent substrate

[1] J. D. E. McIntyre and D. E. Aspnes, *Surf. Sci.* **24**, 417 (1971).

Experimental setup

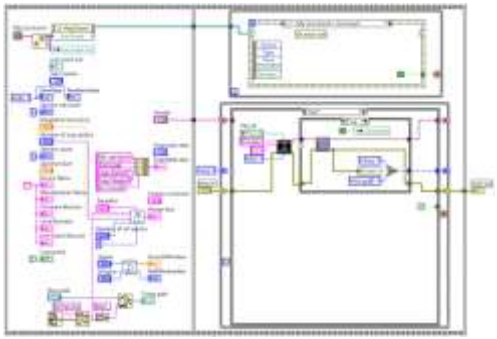


Results and Discussions

- Test measurement
  1. Software development
  2. Stability test
  3. Back surface reflection
- Real measurement
  1. Pyrene: pyr8
  2. Porphyrin: CKRS16

1. Software development

light → Spectrometer ThorLabs CCS200 ↔ 3684 floating points → Computer with LabVIEW



shutter
min. 10 µs

↓ 10^{-3} accuracy

integration time
10 ms

communication
min. 5 ms

↓

instrument limit
15 ms/scan

hard coded delay +
slow graphic access +
redundancy +

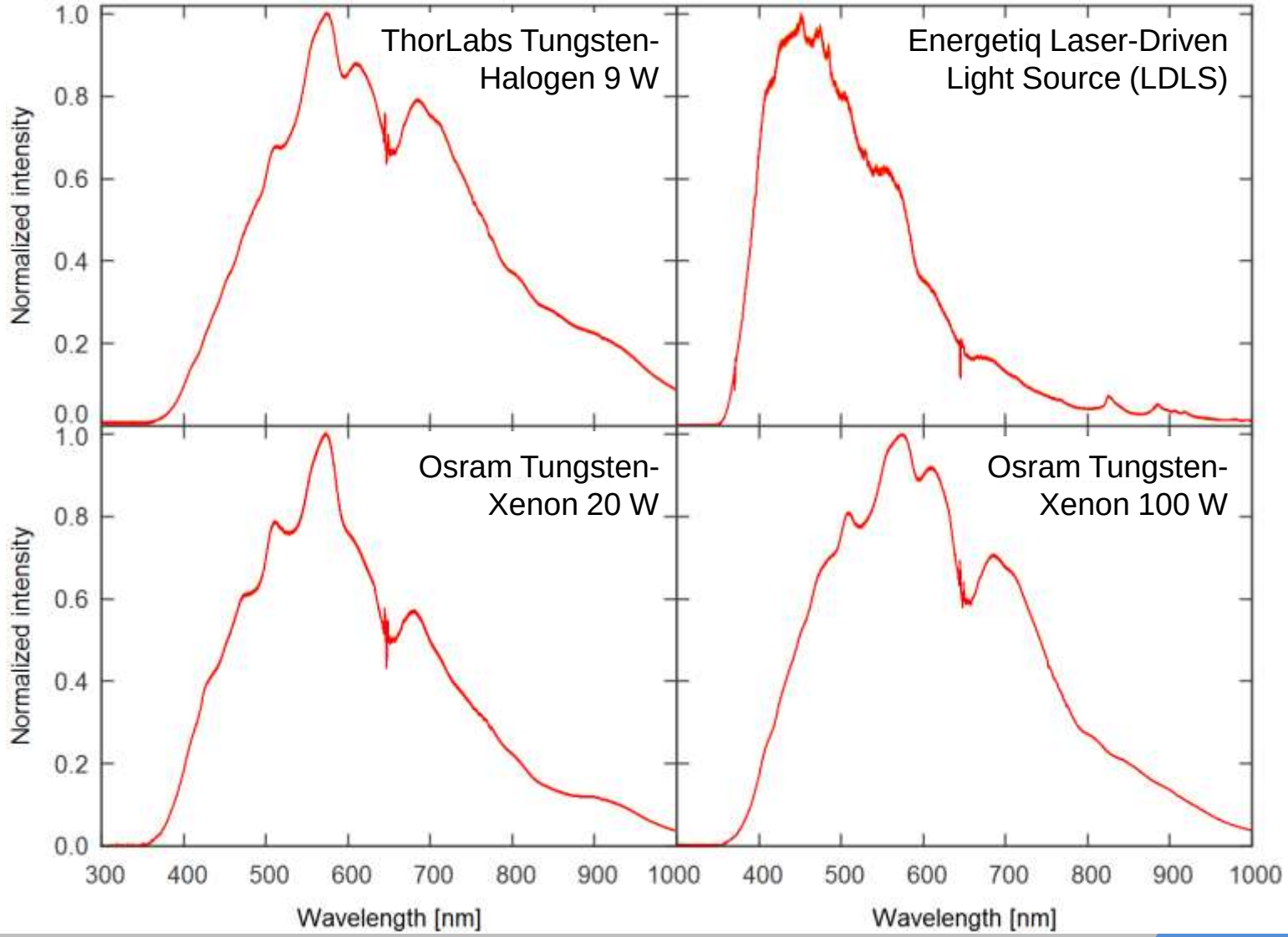
↓

Old software
2 s/scan

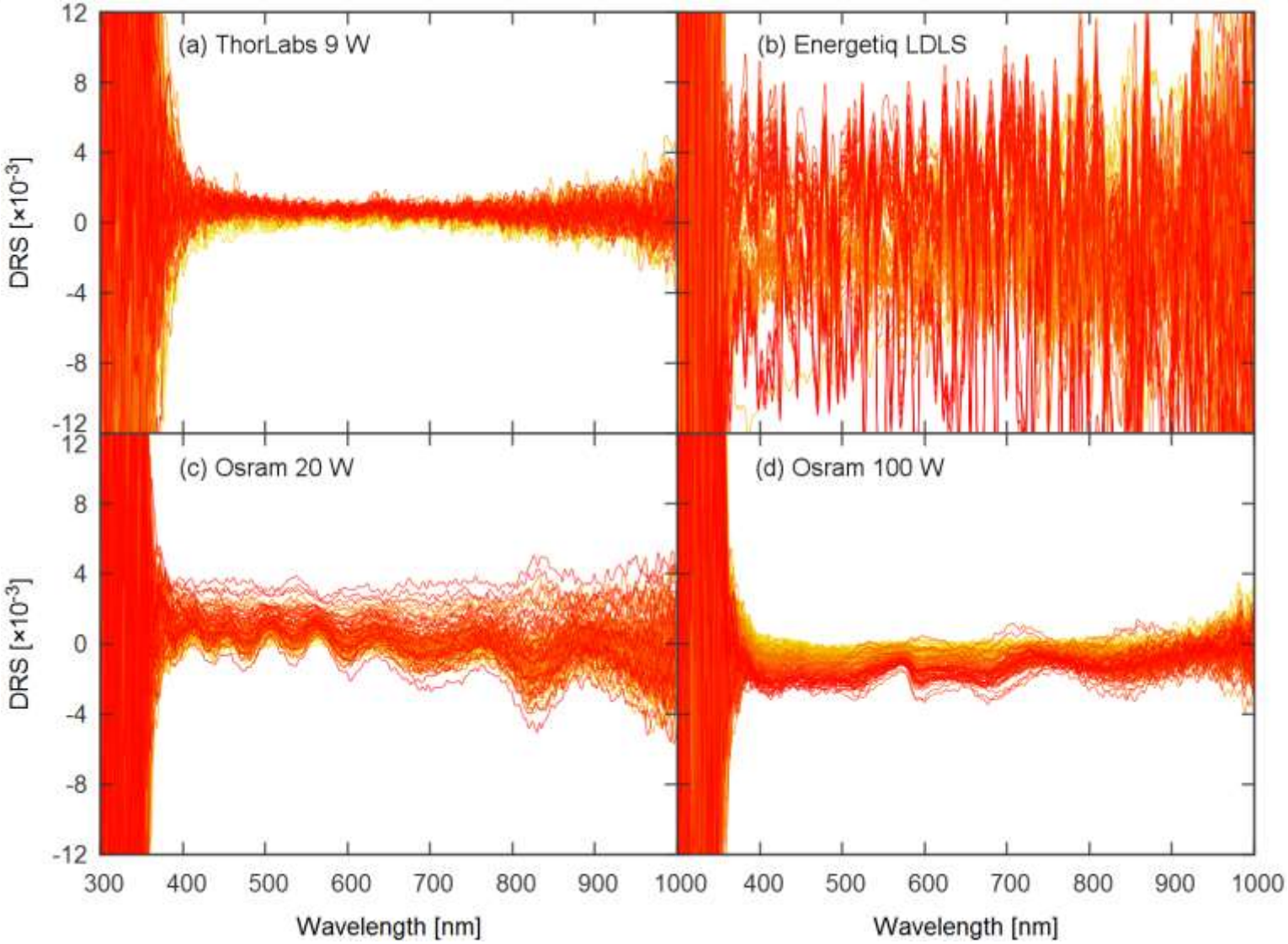
→ 100x faster

Current software
16 ms/scan

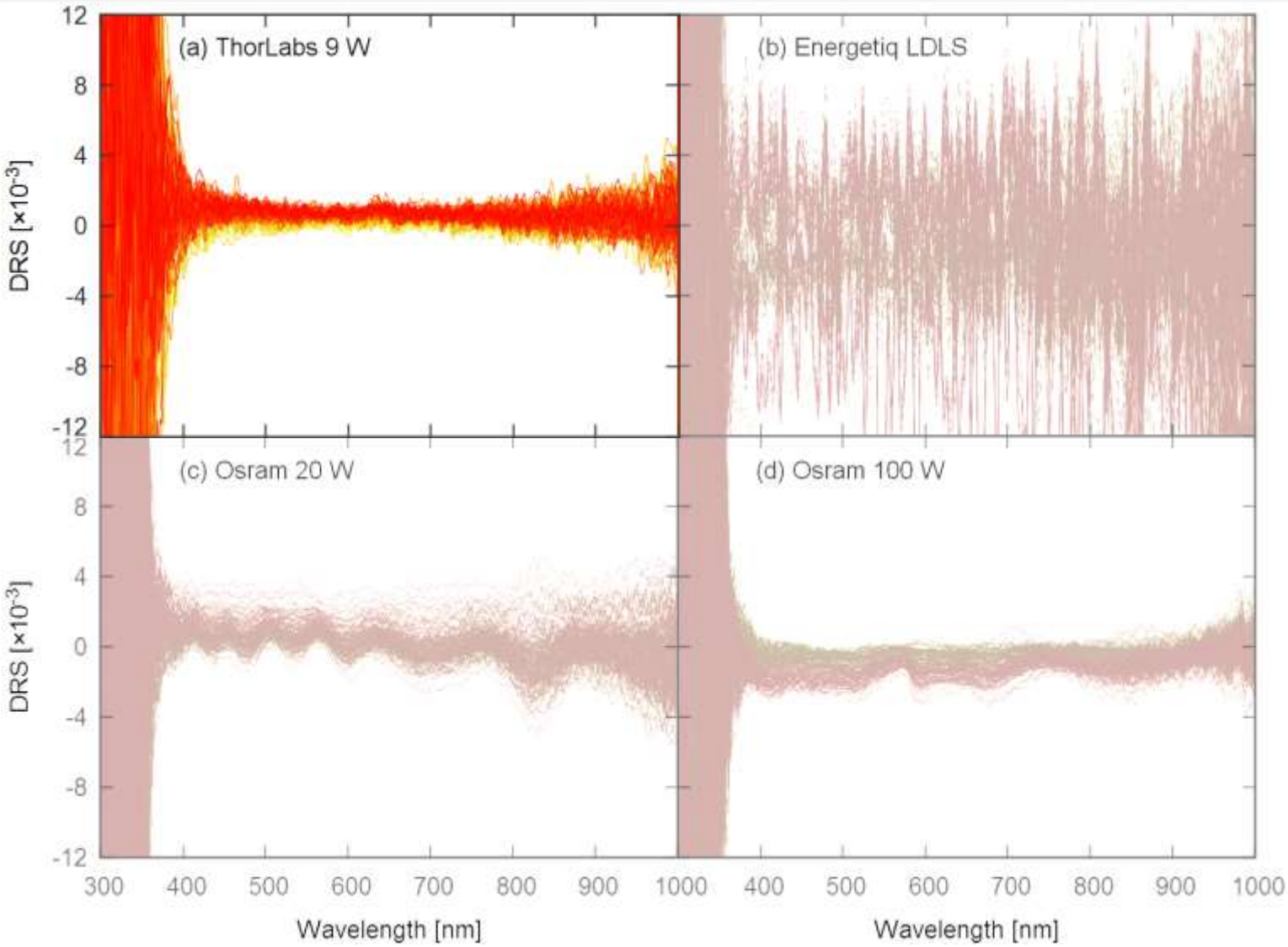
2. Stability – Light sources



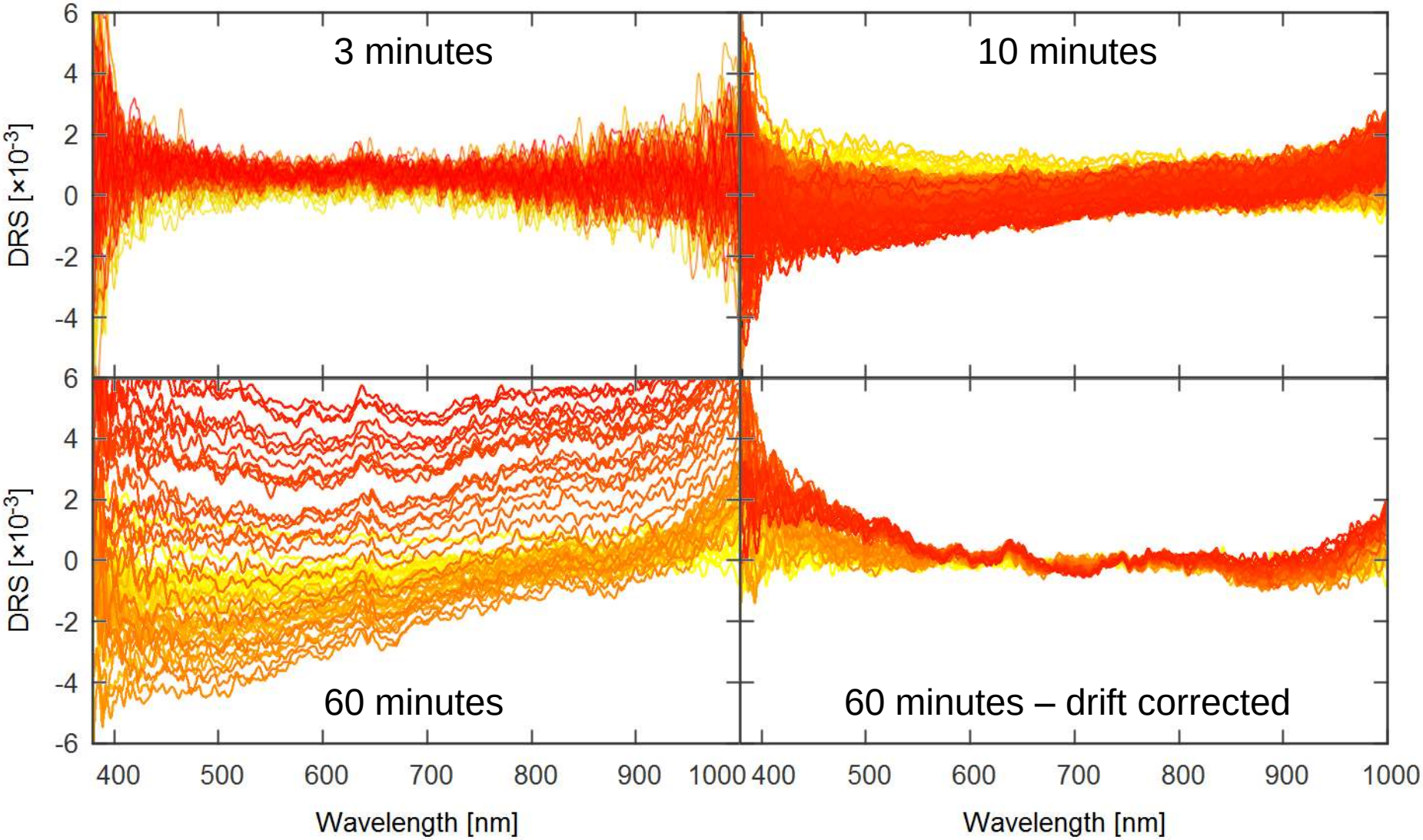
2. Stability – 3 minutes



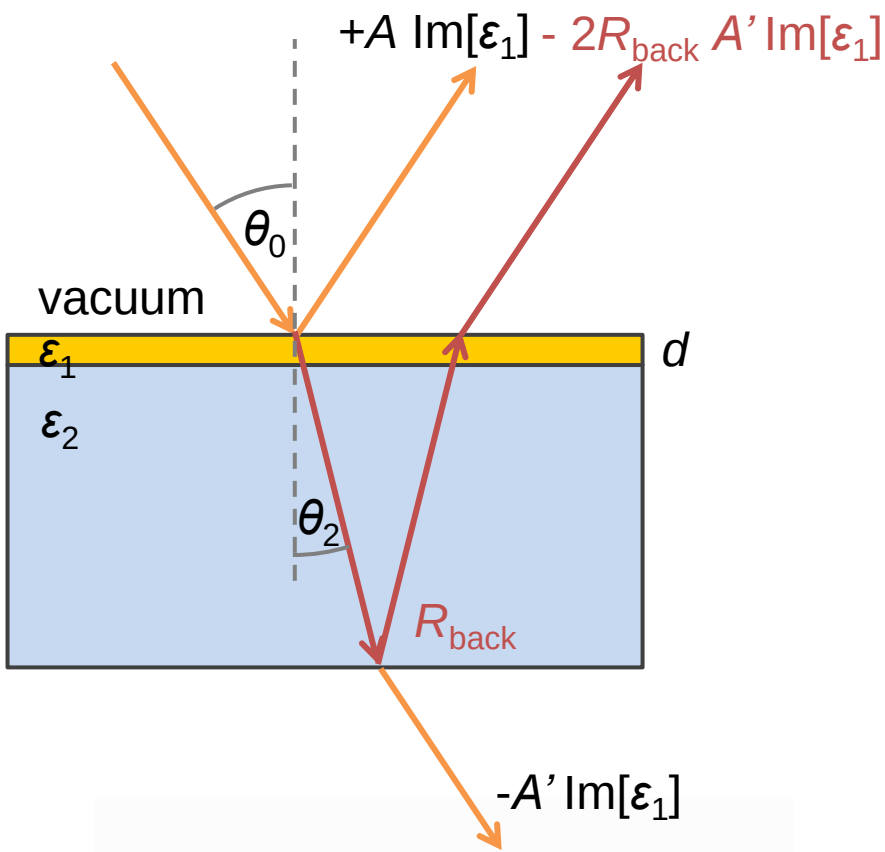
2. Stability – 3 minutes



2. Stability


3 minutes
10 minutes
60 minutes
60 minutes – drift corrected
DRS [×10⁻³]
DRS [×10⁻³]
6
4
2
0
-2
-4
-6
400
500
600
700
800
900
1000
Wavelength [nm]
Wavelength [nm]

3. Back surface reflection



- Unwanted signal from back surface
- Roughen back surface can eliminate this effect
- Beckmann reflection model [1-2]

$$R_{\text{back}} = R_{\text{rough}}\, R_F$$

$R_{\text{rough}} \rightarrow e^{-g^2}$

$g = 4\pi\sigma_h \cos\theta_2 / \lambda \rightarrow$ height roughness

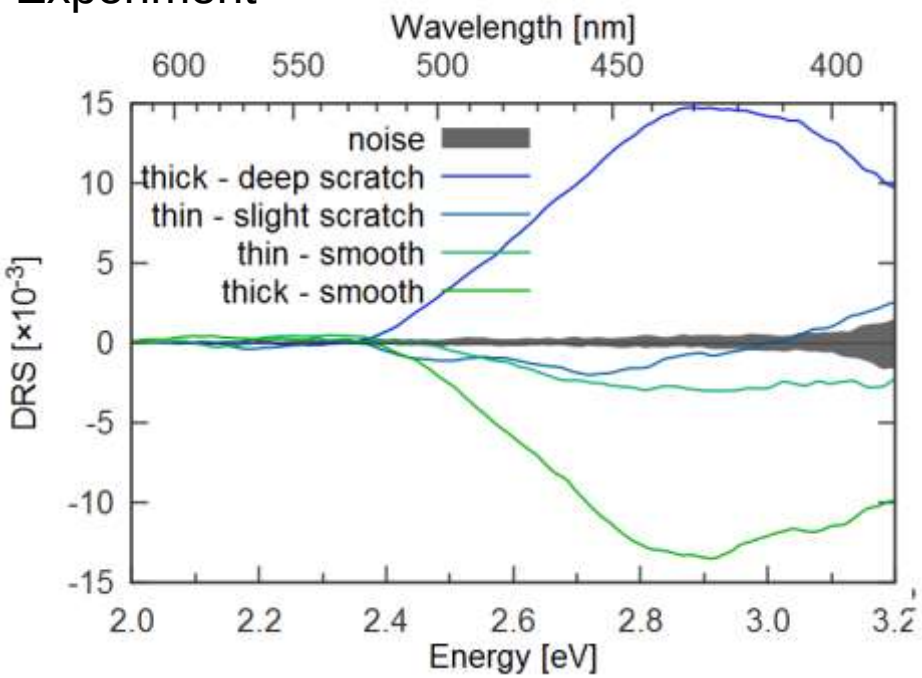
$R_F \rightarrow$ Flat Fresnel reflection

[1] P. Beckmann and A. Spizzichino, Pergamon Press, 1963.
[2] S. K. Nayar, K. Ikeuchi and T. Kanade, *IEEE Trans. PAMI* **13**, 611 (1991).

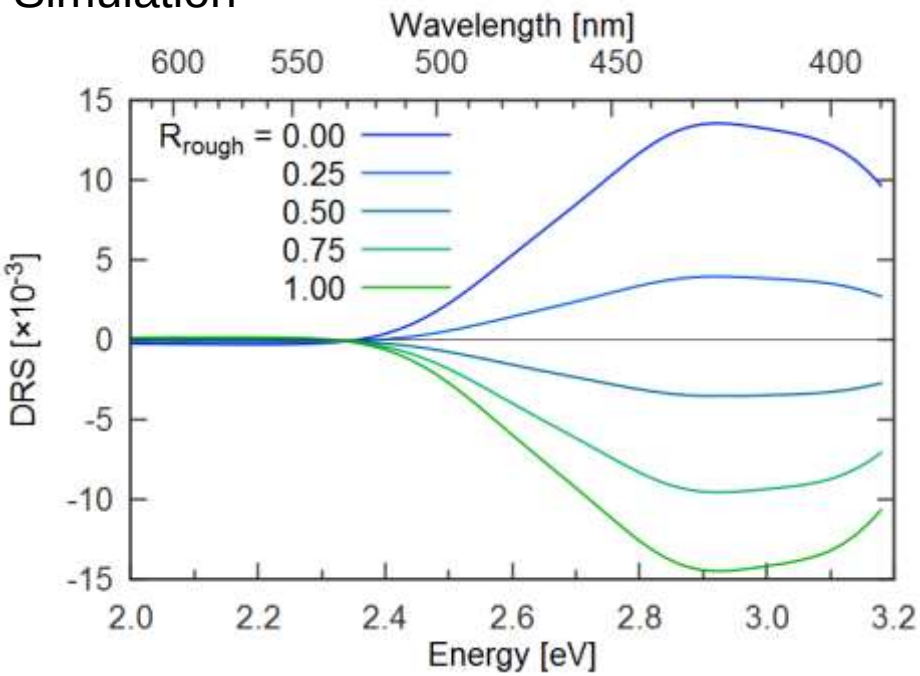
3. Back surface reflection

- Experiment with 1 ML pyr8 on glass
- Different amount of scratch on back surface
- Roughening by rasp is an effective way

Experiment



Simulation

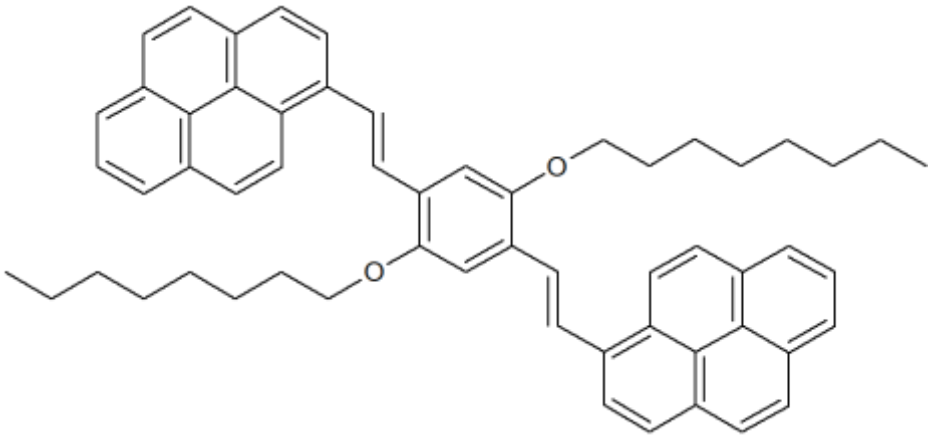


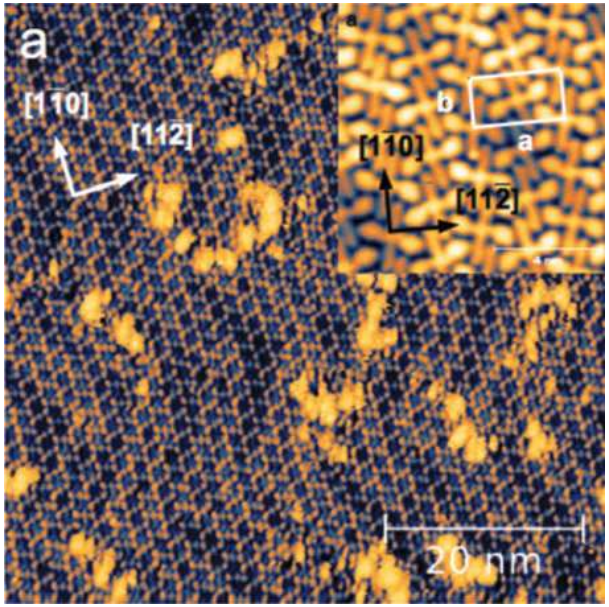
Results and Discussions

- Test measurement
  1. Software development
  2. Stability test
  3. Back surface reflection
- Real measurement
  1. Pyrene: pyr8
  2. Porphyrin: CKRS16

Pyr8

- 1,4-di-n-octyloxy-2,5-bis(pyren-1-ylethenyl)benzene
- Two pyrene linked by ethenyl bridge to benzene ring
- Synthesized at the CINaM, Marseille
- Organized layer on Au(111) [1]

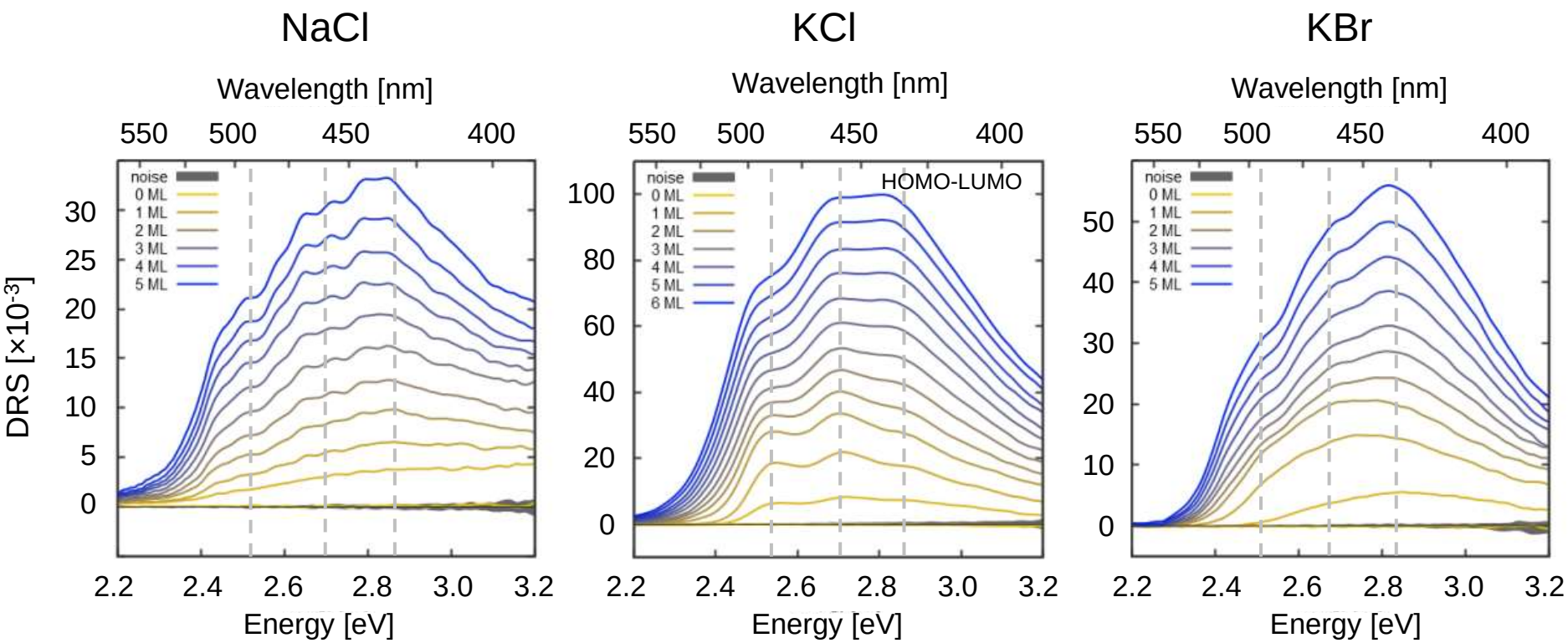




[1] Tony Lelaidier et al., *Phys. Chem. Chem. Phys.* **18**, 5299 (2016).

Pyr8 - DRS

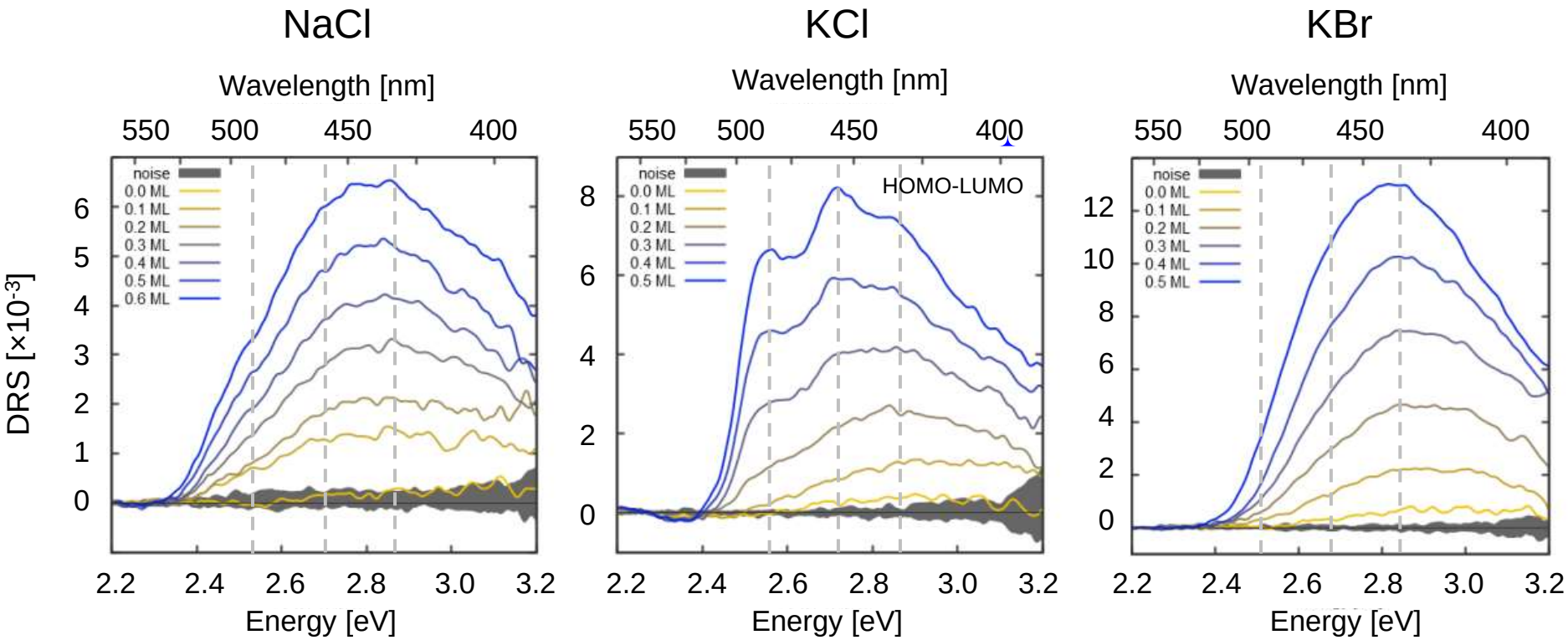
- DRS of 5 monolayer (ML) coverage of pyr8 on salts
- Deposition rate 0.11 ML/min



Similar spectra for all substrates after 5 ML

Pyr8 - DRS

- DRS of 0.5 monolayer (ML) coverage of pyr8 on salts
- Deposition rate 0.11 ML/min

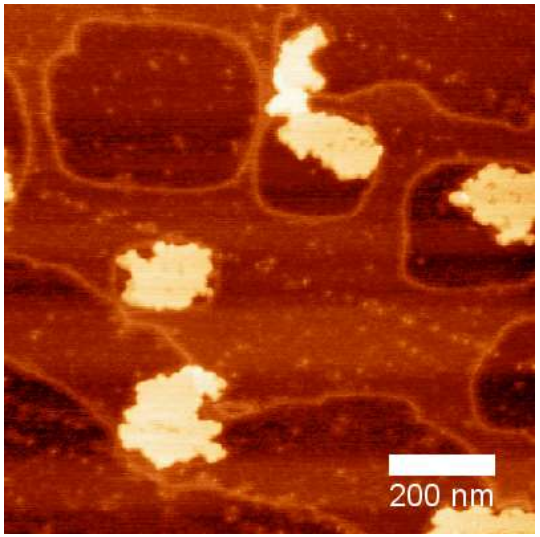


2.54 eV peaks: KCl > NaCl > KBr

Pyr8 assembly

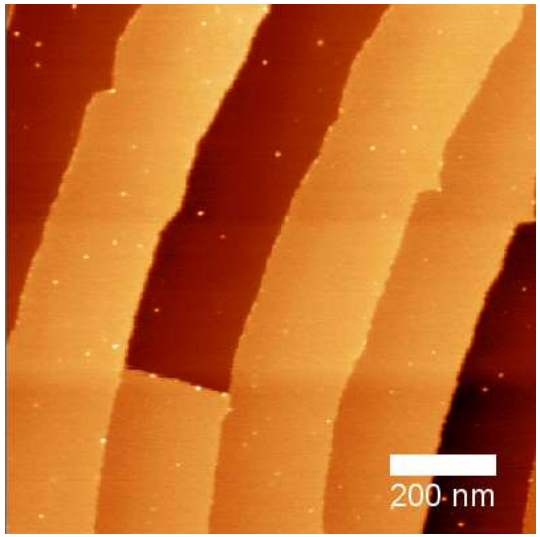
Non-contact AFM images

NaCl



200 × 200 × 3 nm
islands

KCl



0.7 nm
homogeneous layer

Peaks

- 2.54 eV peak
  for ordered assembly
- 2.85 eV peak
  from diffused gas phase
  or HOMO-LUMO

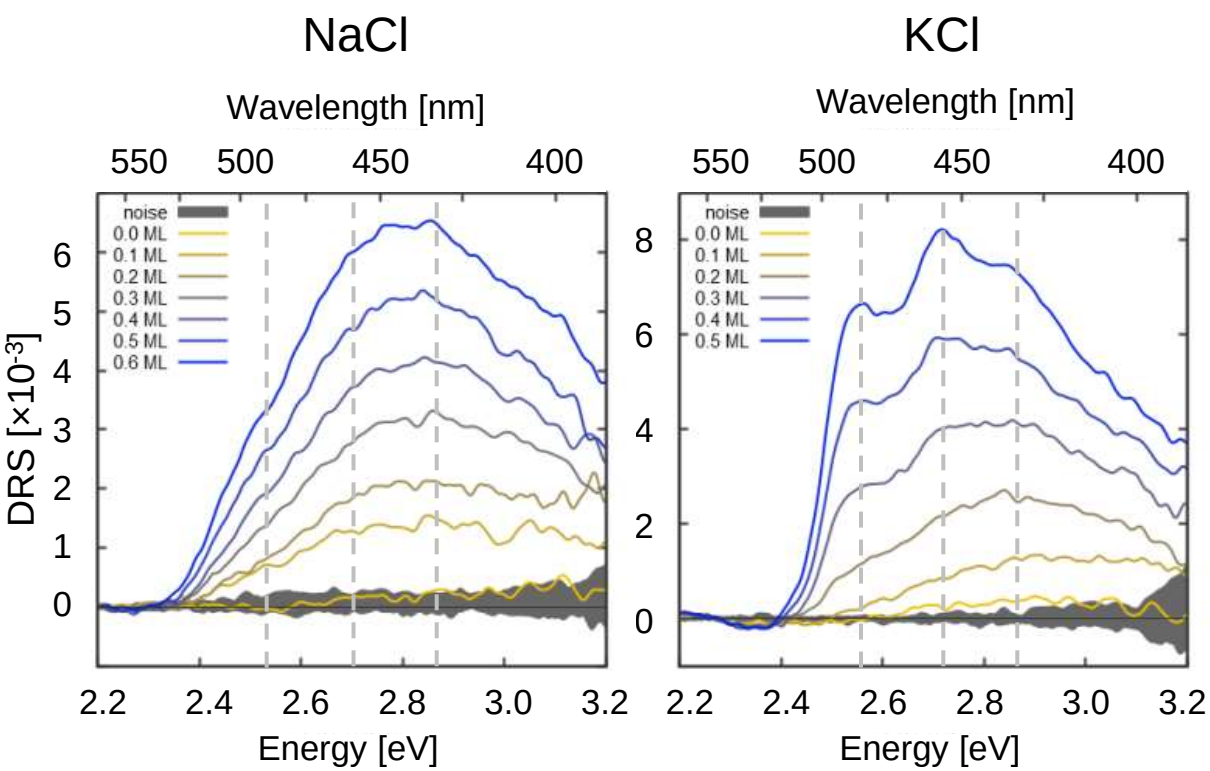
Possible origins

- Davydov splitting[1]
  (molecular exciton)
- 0.16 eV vibronic
  spacing[2]

[1] A. S. Davydov, *Sov. Phys. Usp.* **82**, 393 (1964).
[2] Stephanie Leroy-Lhez et al., *New J. Chem.* **31**, 1013 (2007).

Pyr8 assembly

DRS spectra



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- 2.54 eV peak for ordered assembly
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Possible origins

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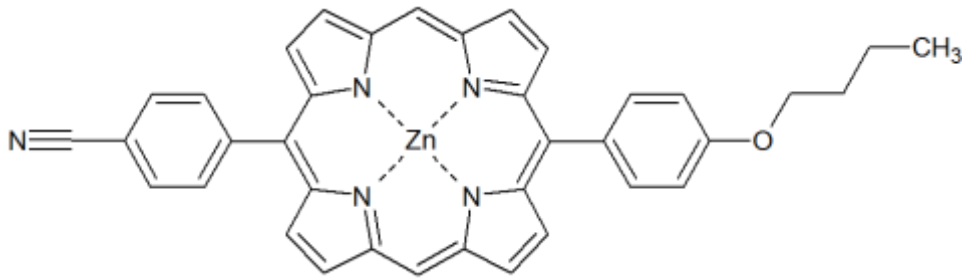
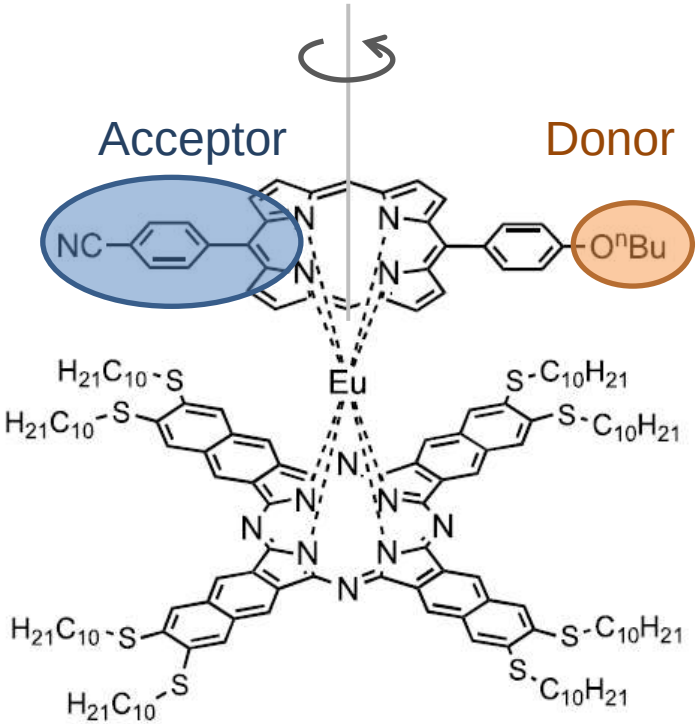
[1] A. S. Davydov, *Sov. Phys. Usp.* **82**, 393 (1964).
[2] Stephanie Leroy-Lhez et al., *New J. Chem.* **31**, 1013 (2007).

CKRS16-Zn

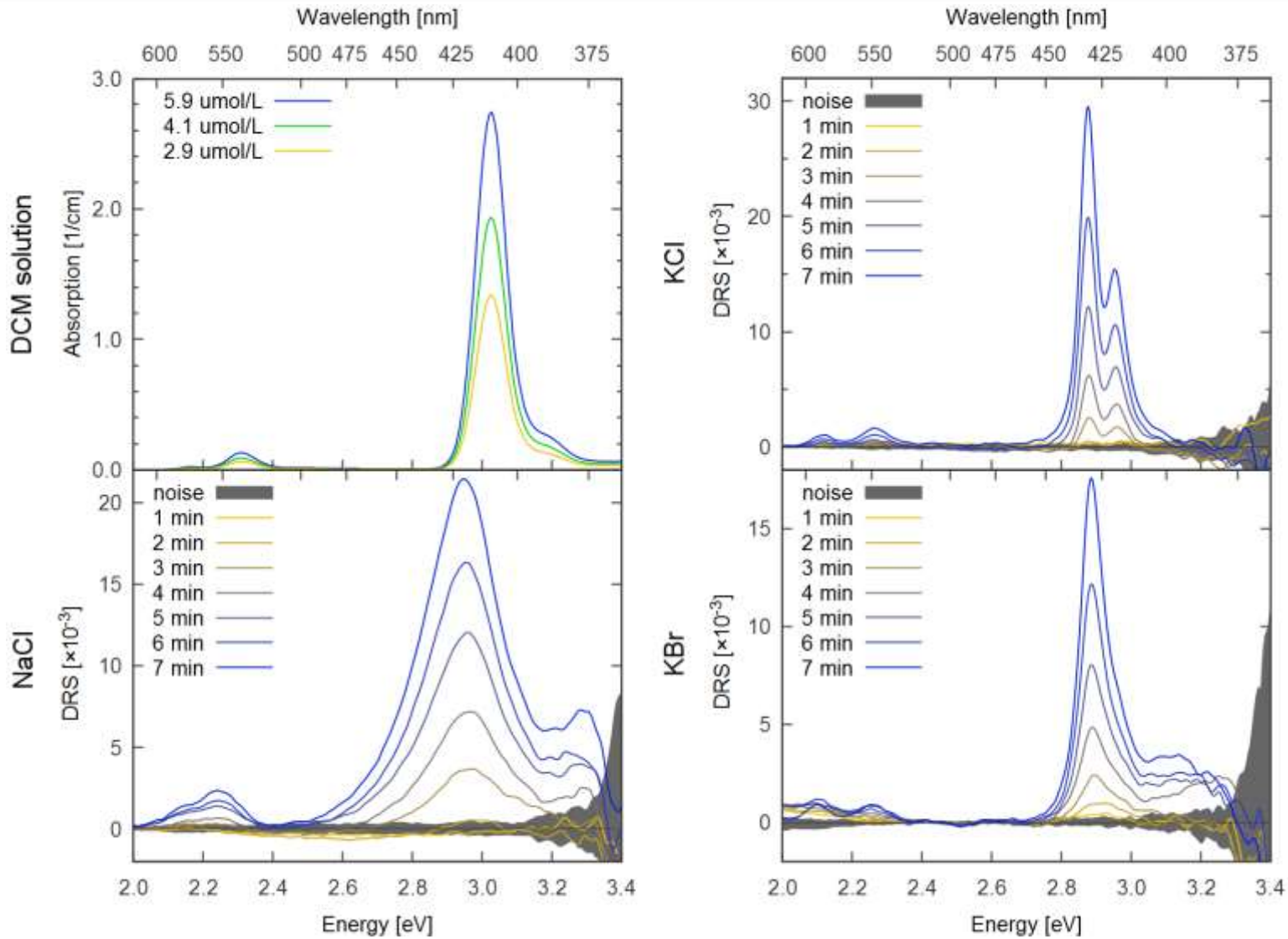
- 5-(4-n-butoxyphenyl)-15-(4-cyanophenyl)porphyrinate zinc complex
- Synthesized at the CEMES, Toulouse
- Donor-acceptor system which can act as rotor[1]





[1] R. Stefak, N. Ramond, and G. Rapenne, *Inorg. Chim. Acta* **380**, 181 (2012).

CKRS16-Zn

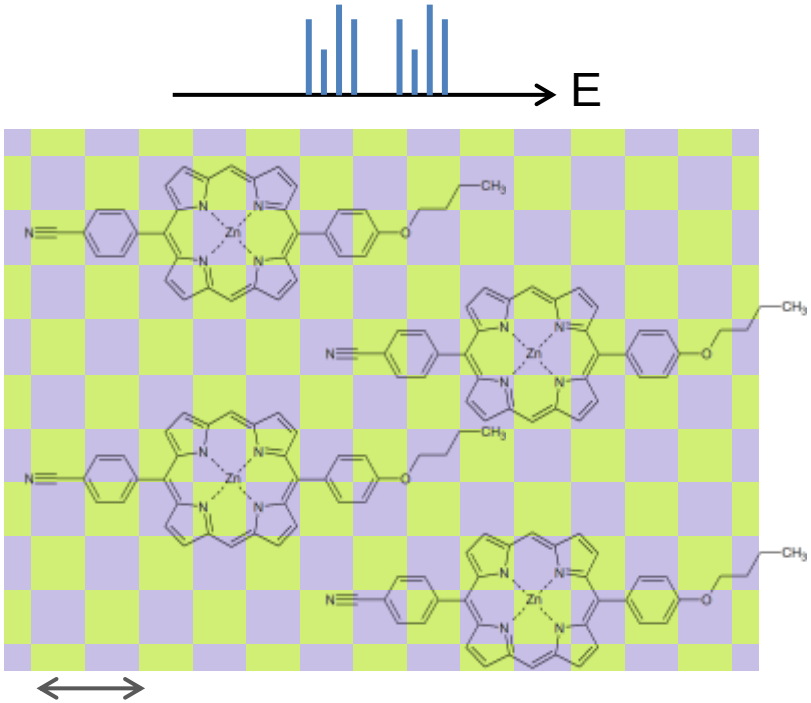


[1] Data from C. Kammerer, CEMES

Spectral narrowing[1]

Mismatched lattice

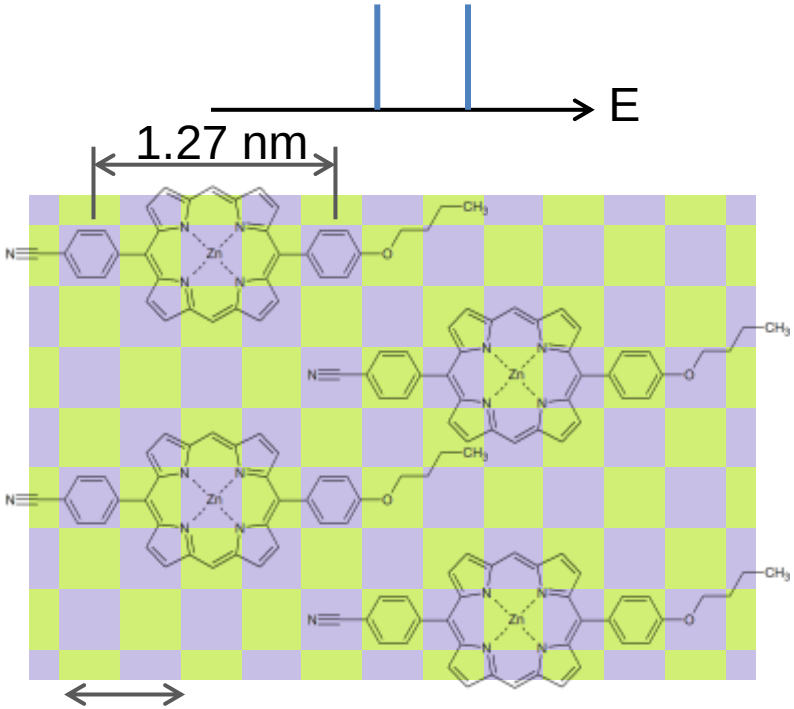
Zn is at random position



NaCl: 0.564 nm

Matched lattice

Zn is at relatively same position



KCl: 0.629 nm

*Only for illustration purpose, real crystal structure is yet to be observed

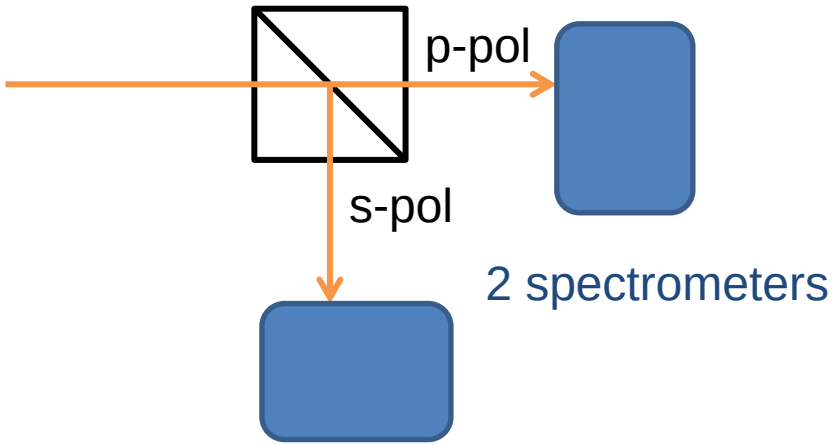
[1] T. Dienel et al., *Adv. Mater.* **20**, 959 (2008).

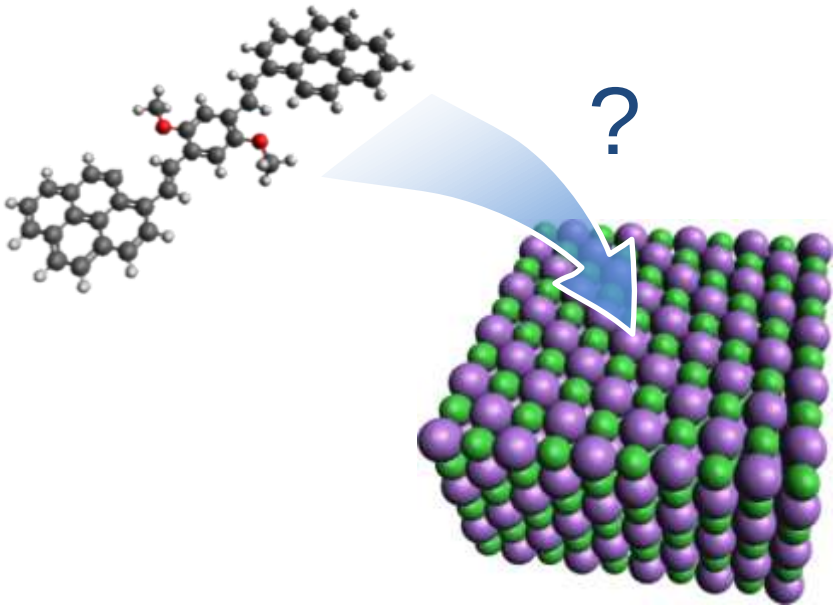
Conclusion

- Achieved DRS with 0.2×10^{-3} in 10 minutes
- Investigated the back surface reflection
- Measured DRS of adsorbed sub-monolayer
- Pyr8 on KCl shows enhanced 2.54 eV peak
  and ordered molecular assembly
- CKRS16-Zn on KCl shows narrow and split peaks
  which hints its ordered molecular assembly

Future work

- Polarization
- Mechanical stability
- More investigation on molecular structures





Thank you for your attention

Acknowledgments:

- Frank Para (IM2NP)
- Tony Lelaidier, Thomas Leoni, Conrad Becker (CINaM)
- Claire Kammerer, Gwenael Rapenne (CEMES)
- Peter Zeppenfeld (Johannes Kepler University Linz)
- Guillaume Demesy (Institut Fresnel)