Déposition de molécules organiques par électrospray

Hinaut Antoine, Rémy Pawlak, Thilo Glatzel et Ernst Meyer

Department of Physics, University of Basel, CH-4056 Basel

https://nanolino.unibas.ch

UNI BASEL

SNI SWISS NANOSCIENCE INSTITUTE

SWISS CONTRIBUTION

Introduction

Etude locale de molécules → Electronique moléculaire, Photovoltaïque organique → Taille importante

Etude locale de molécules → Géométrie d'adsorption, Propriétés électroniques → UHV, surface isolante → ncAFM

Introduction

Etude locale de molécules → Electronique moléculaire, Photovoltaïque organique → Taille importante

Etude locale de molécules → Géométrie d'adsorption, Propriétés électroniques → UHV, surface isolante → ncAFM

- Evaporation thermique : Technique la plus utilisée
  T° sublimation vs T° fragmentation
- Plusieurs solutions :

Vanne pulsée, Droplet Casting ou Electrospray par Ionisation (ESI).

Tanaka et al., Surface Science (1999)
Zambelli et al., Int. J of Nanoscience (2004)

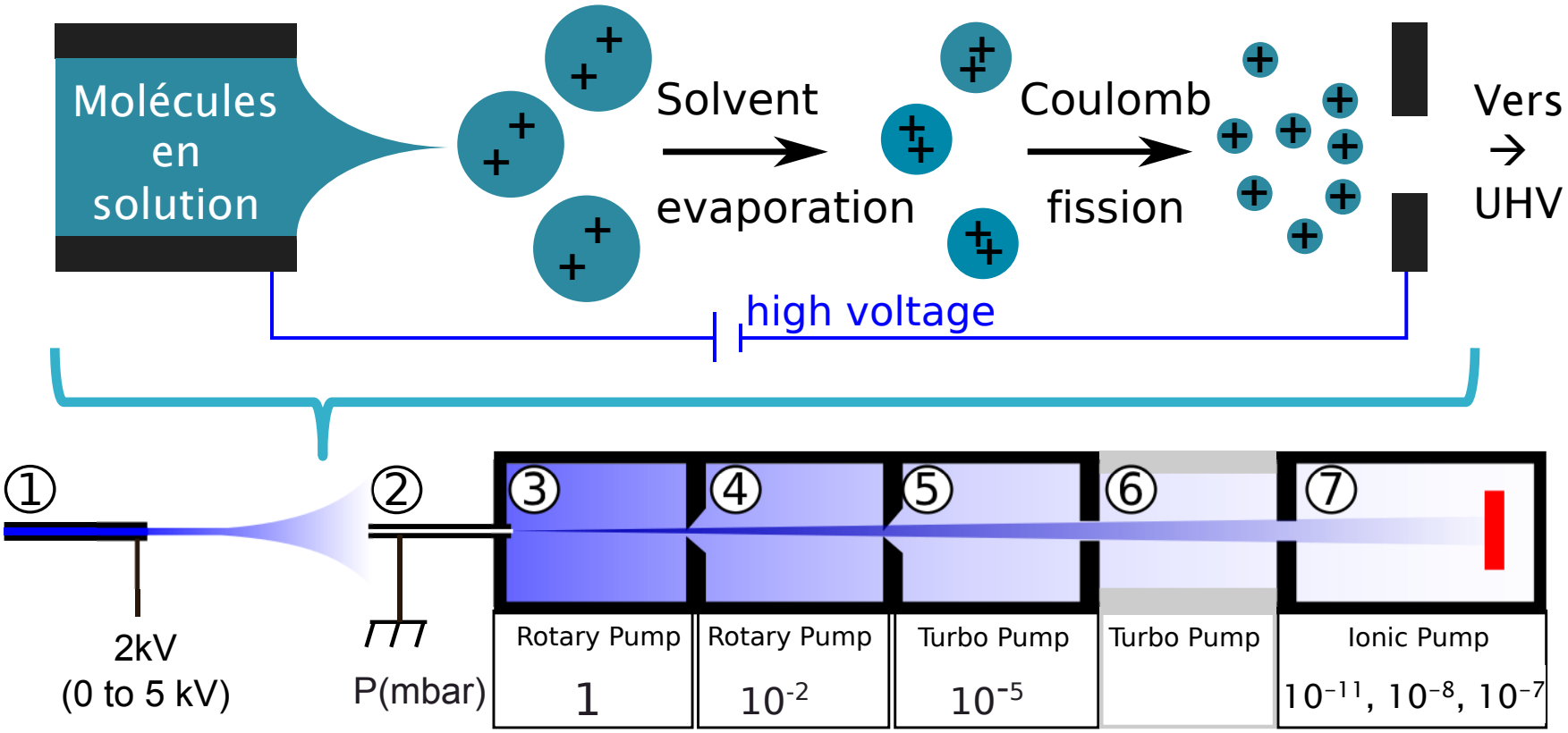
Introduction de protéines sous vide pour leur étude par spectroscopie de masse.

J.B Fenn et al. (1989), Science 246

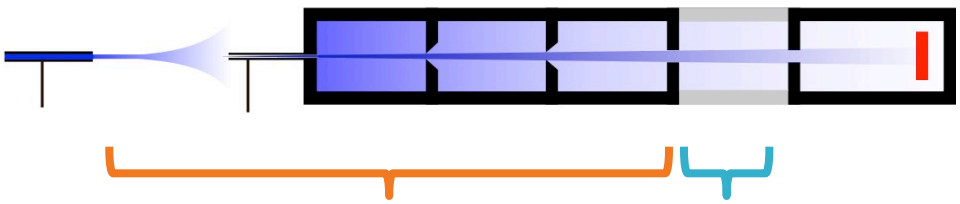
ESI pour déposer des molécules.

ElectroSpray Ionisation (ESI)

→ Technique non destructive pour l'introduction sous UHV.
→ Orienté vers un échantillon pour le dépôt de molécules.



Dispositifs :



Dispositifs avec sélection et tri des ions, soft landing :

S. Rauschenbach et al. (2006), Small, vol. 2.
C. Hamann et al. (2011), RSI, vol. 82.
A. Bodin et al. (2013), RSI, vol. 84.

Molecularspray :

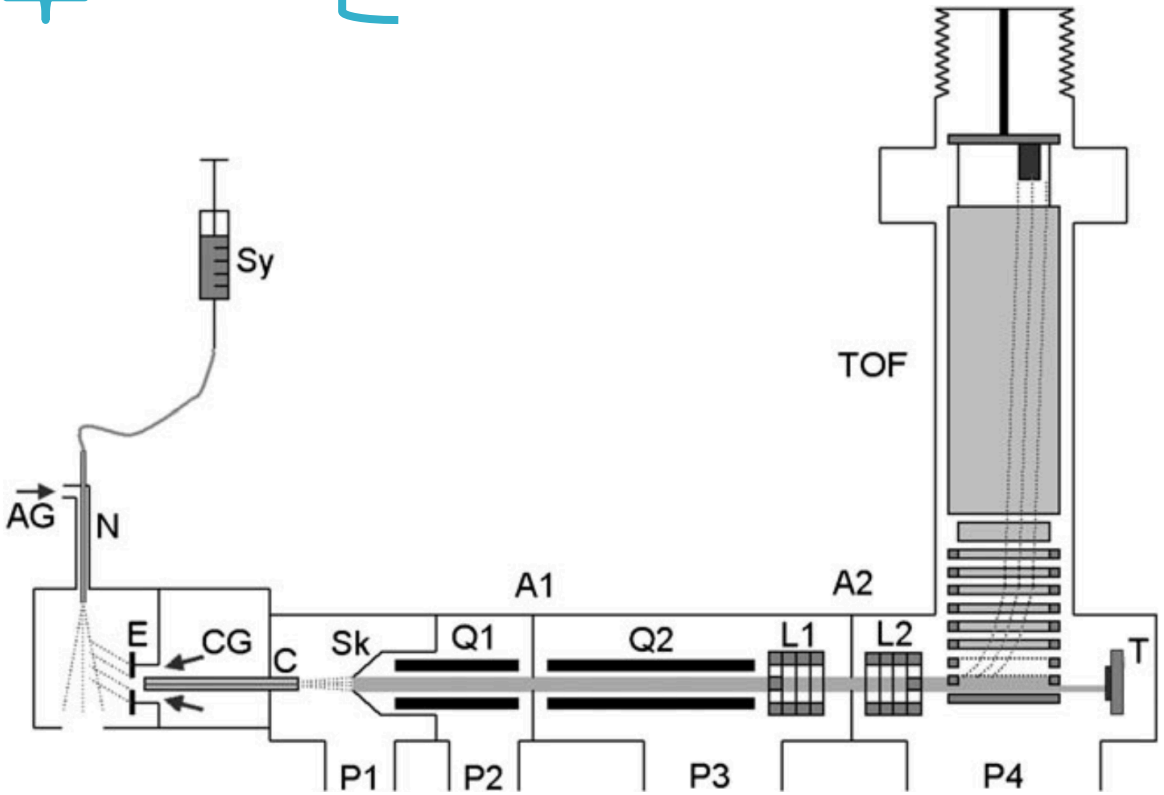
Saywell et al,. Angewandte Chemie 49 (2010)

ADCAP Vacuum Technology :

Yokoyama et al., JPCC 117, 36 (2013)

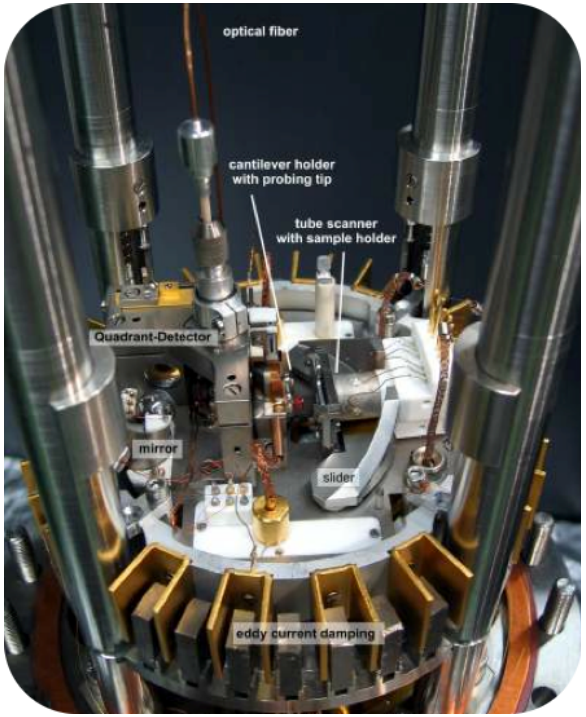
Nouvel étage de pompage :

A. Hinautet al., BJ Nano 6 (2015).
P. Erler et al., ACS Nano 15 (2015).

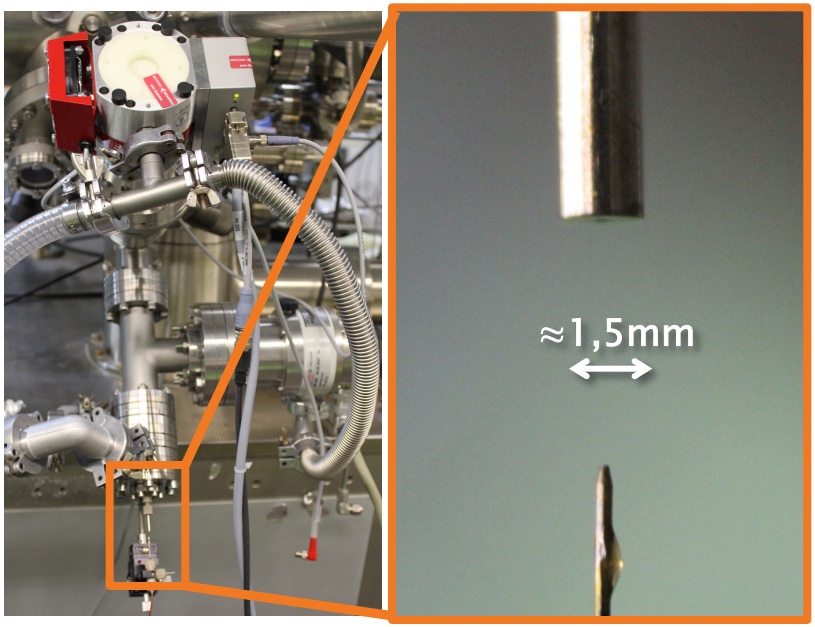


Molecularspray

Chambre d'analyse ncafm	Chambre de préparation	Sas d'introduction rapide
10^{-11}mbar	10^{-10}mbar	

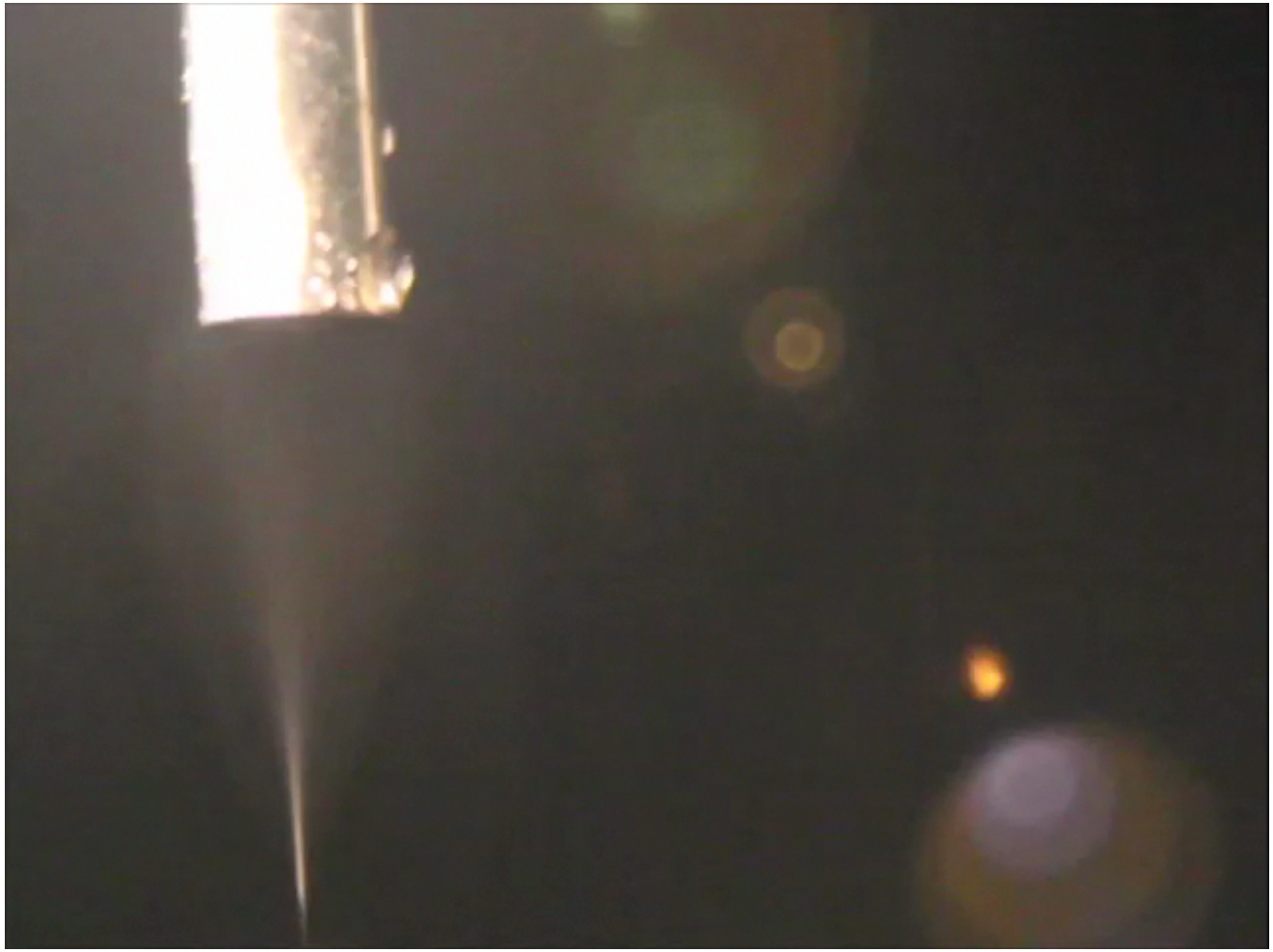


ncAFM room temperature, home built



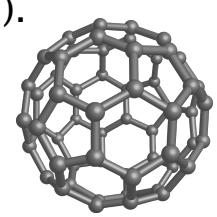
Spray

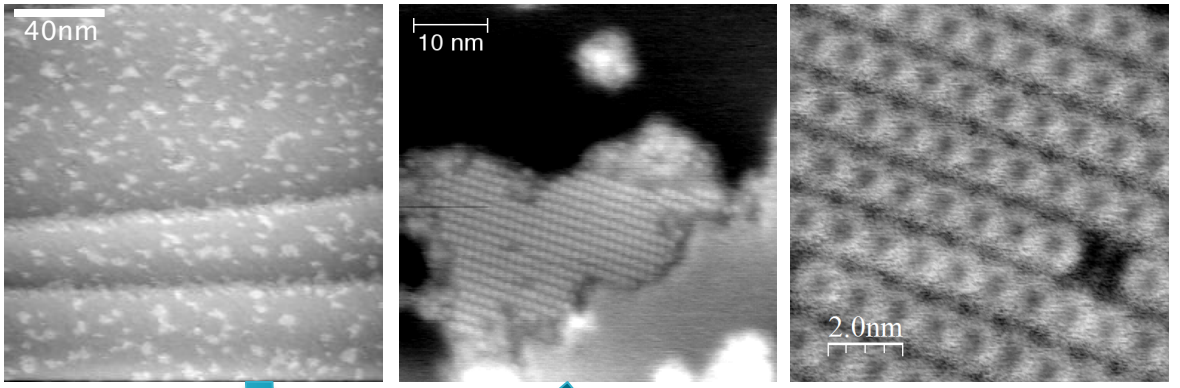
≈1,5mm



Dispositif : MolecularSpray

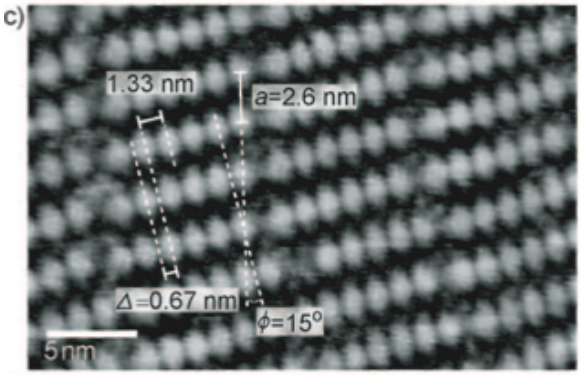
C_{60}/Cu(111)
Spray deposition = 3min.
Dichloromethane et
Acetonytrile (4:1).



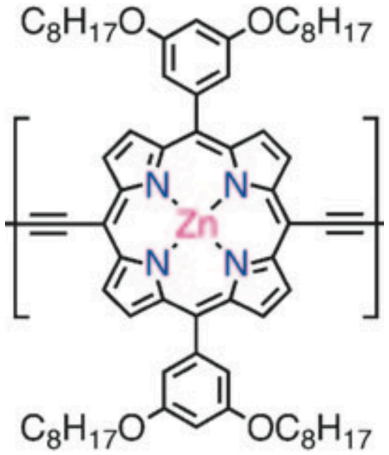


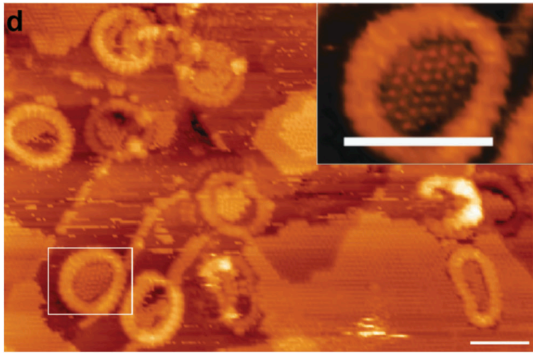
150°C 1h

Porphyrin chain/Au(111),
chauffage 100°C.



A. Saywell et al., Angewandte chemie, 49 (2010)

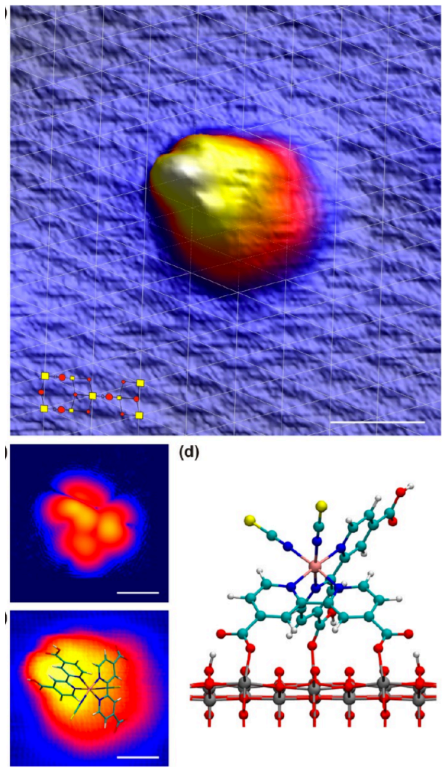




M.B. Wieland et al., Chem. Commun., 50 (2014)

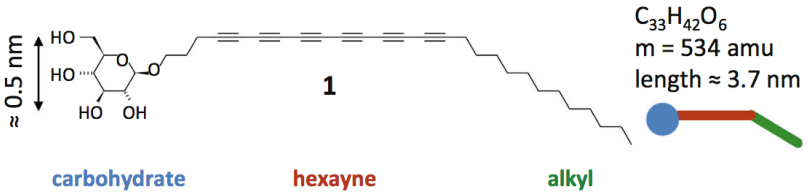
ESD avec sélection :

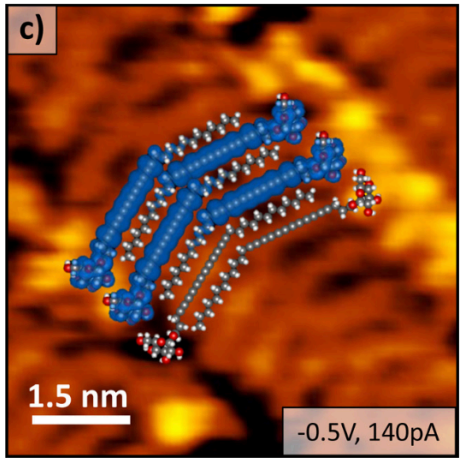
N3 Dye/TiO_2 anatase



Kley C. S. et al., Nano Letters 14 (2014)
Groupe Klaus Kern

Glycosylated hexayne/Au(111)



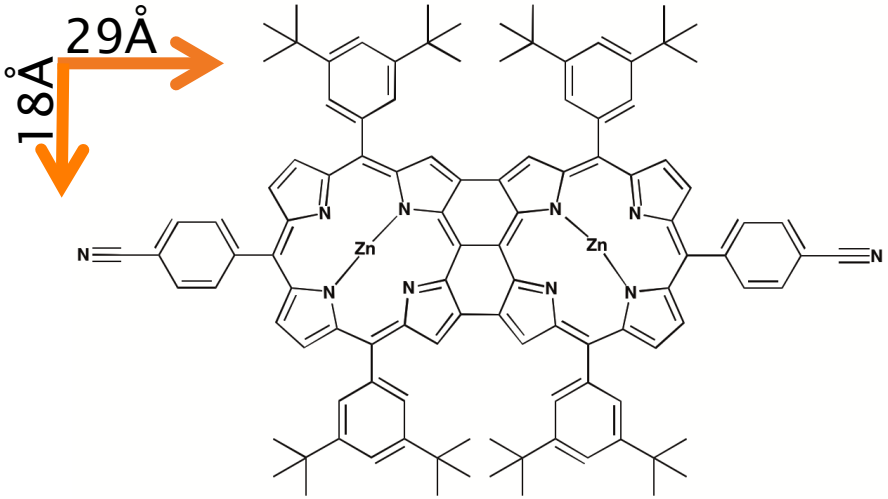


Quadrupole
&
Soft landing

Rinke G. et al., International Journal of Mass Spectrometry (2015)
Groupe Richard Berndt

Molécules et surface

Double porphyrine



Synthèse par F. Diederich, ETH Zurich.
2 groupes CN : ancrage sur la surface

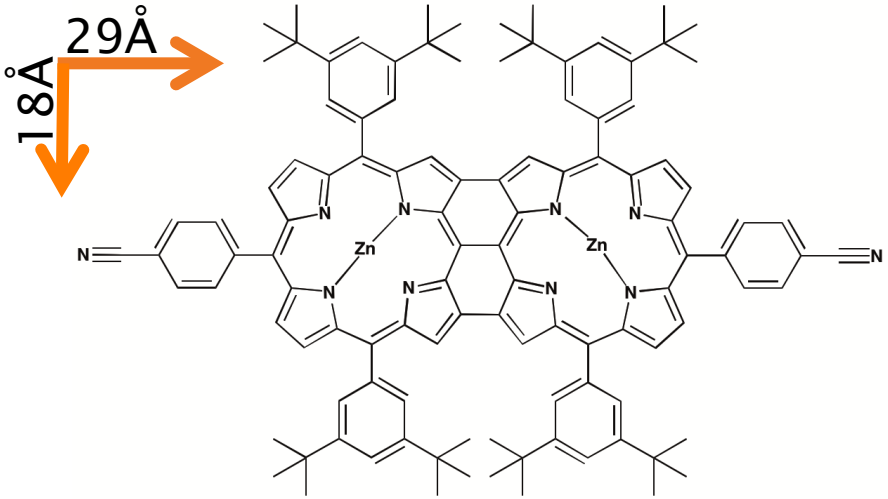
B. Such et al. (2010), ACS Nano 4.

A. Hinaut et al. (2012), Beilstein J Nanotechnol 3.

Solvants type chromasolv
Toluène et isopropanol (2:1)

Molécules et surface

Double porphyrine



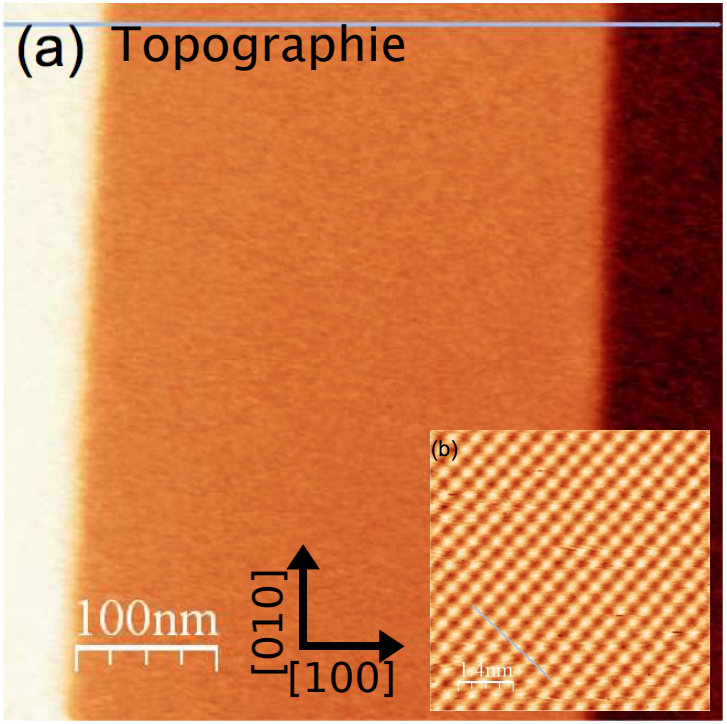
Synthèse par F. Diederich, ETH Zurich.
2 groupes CN : ancrage sur la surface

B. Such et al. (2010), ACS Nano 4.

A. Hinaut et al. (2012), Beilstein J Nanotechnol 3.

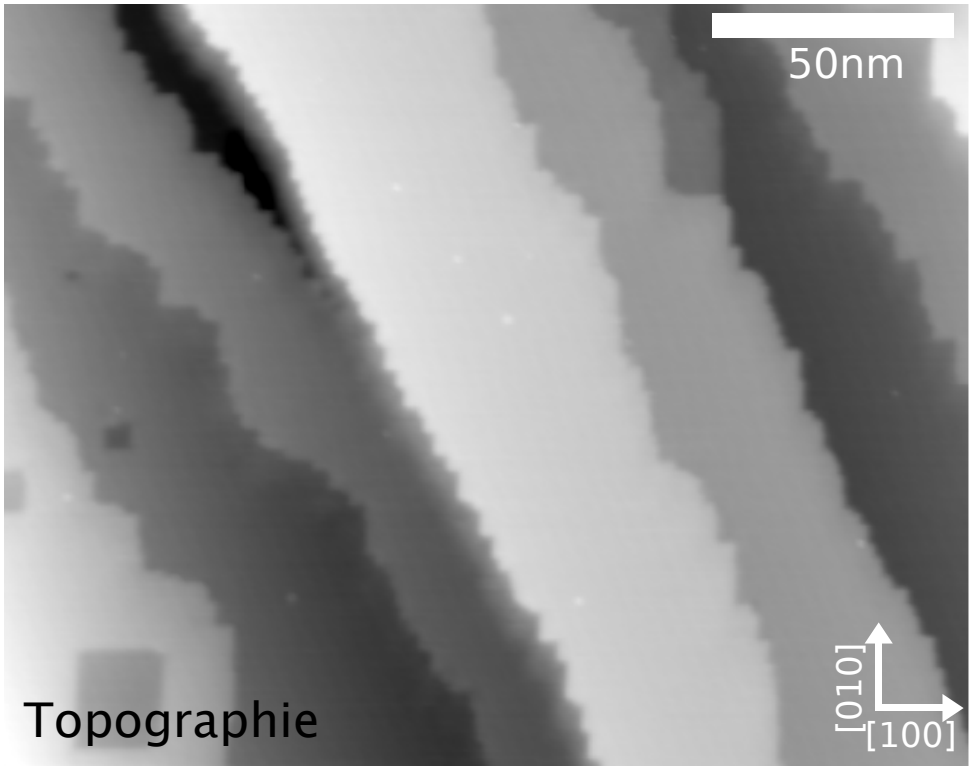
Solvants type chromasolv
Toluène et isopropanol (2:1)

KBr(001)

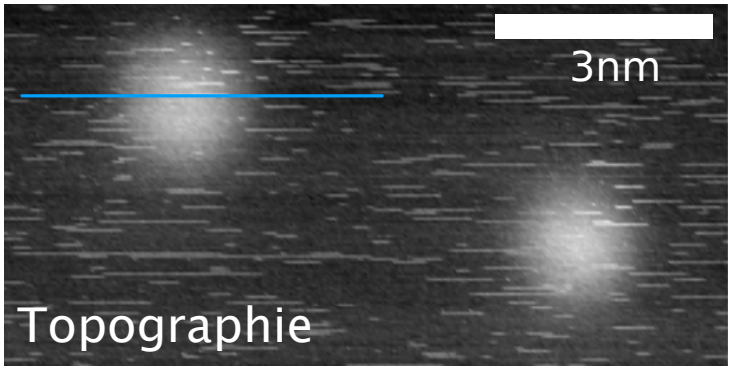


Clivage air ou UHV.
→ Chauffage 1h @ 150°C.
→ -1V < Bias <1V

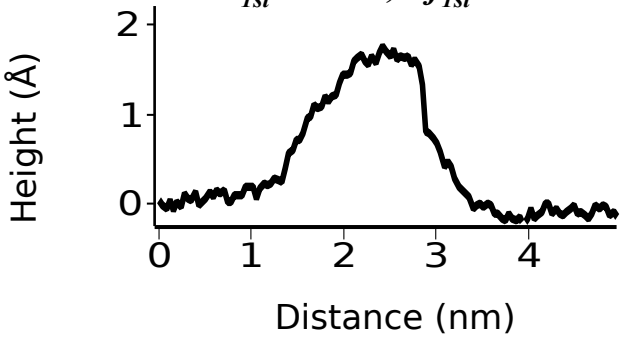
ESI : Solvant seul



$A_{1st} = 5\ nm,\ \Delta f_{1st} = -10Hz$



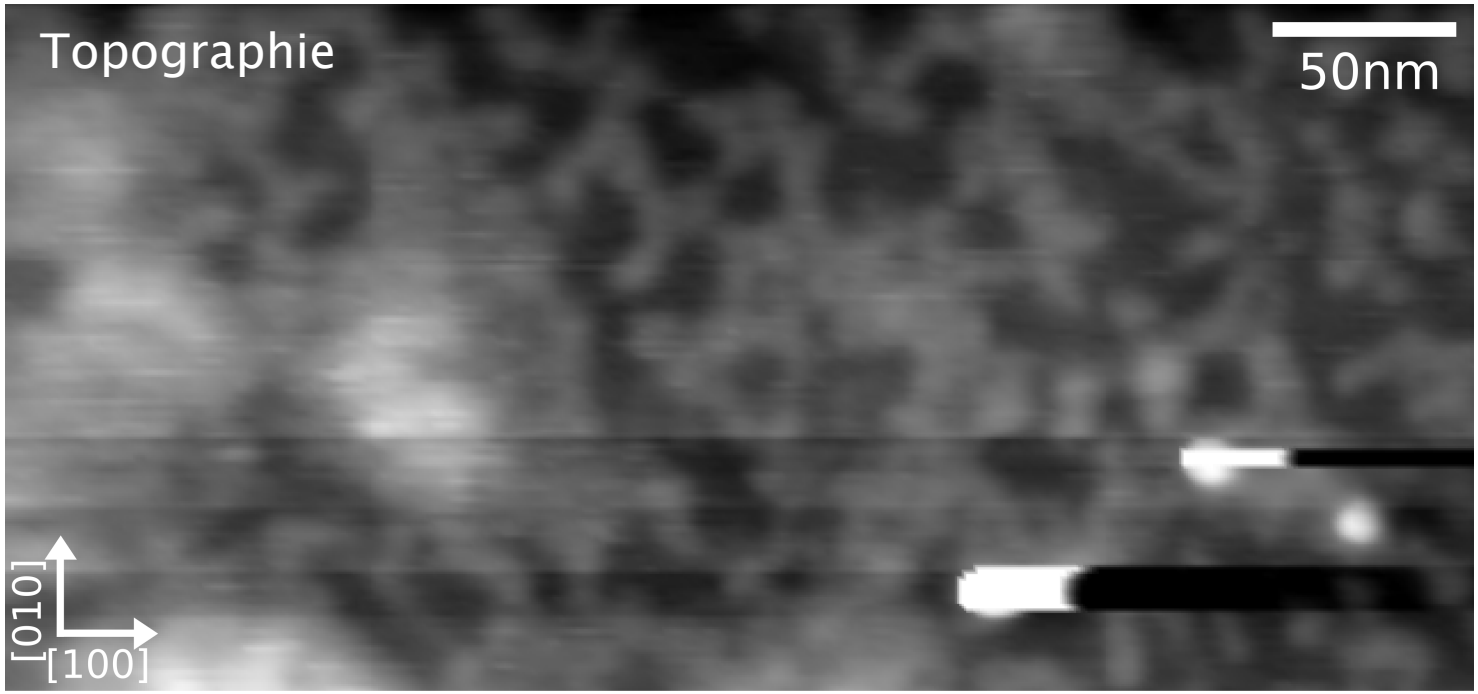
$A_{1st} = 2\ nm,\ \Delta f_{1st} = -25Hz.$



ESI : Toluène et isopropanol (2:1) pendant 30 min
1kV < U < 2,5kV

ESI : Double porphyrine

ESI : Double porphyrines dans toluène et isopropanol (2:1) pendant 5 min

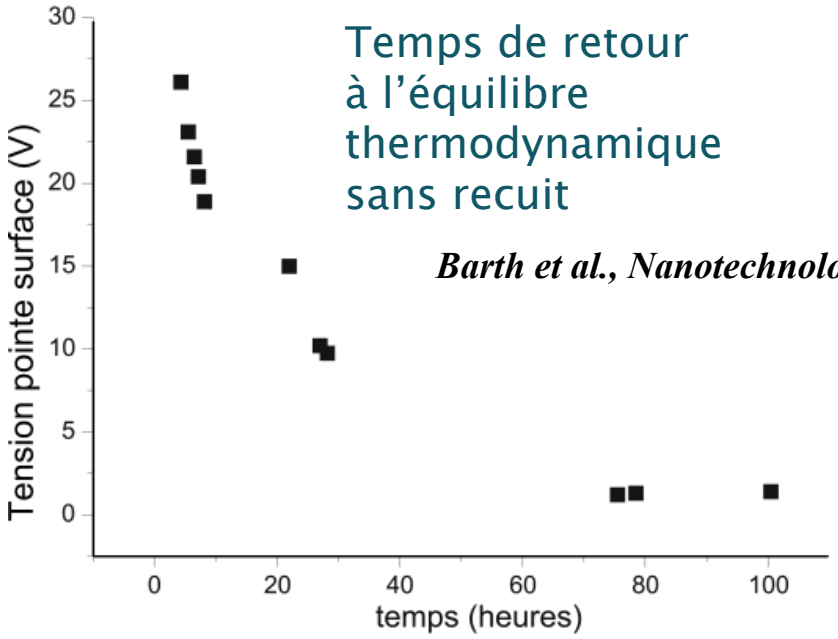


A_{1st}=2nm, Δf_{1st}= -15Hz

U< -30V (-10V appliqués).

Cristaux ioniques et charges

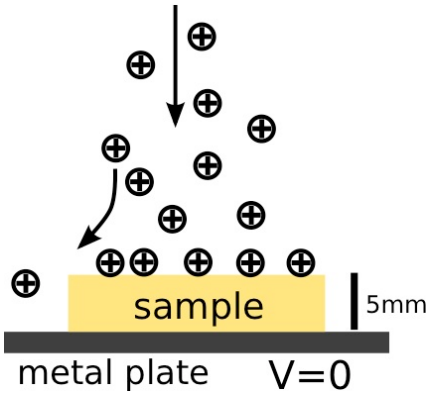
Clivage sans recuit



Temps de retour
à l'équilibre
thermodynamique
sans recuit

Barth et al., Nanotechnology 17 (2006)

ESD sur isolant bulk :

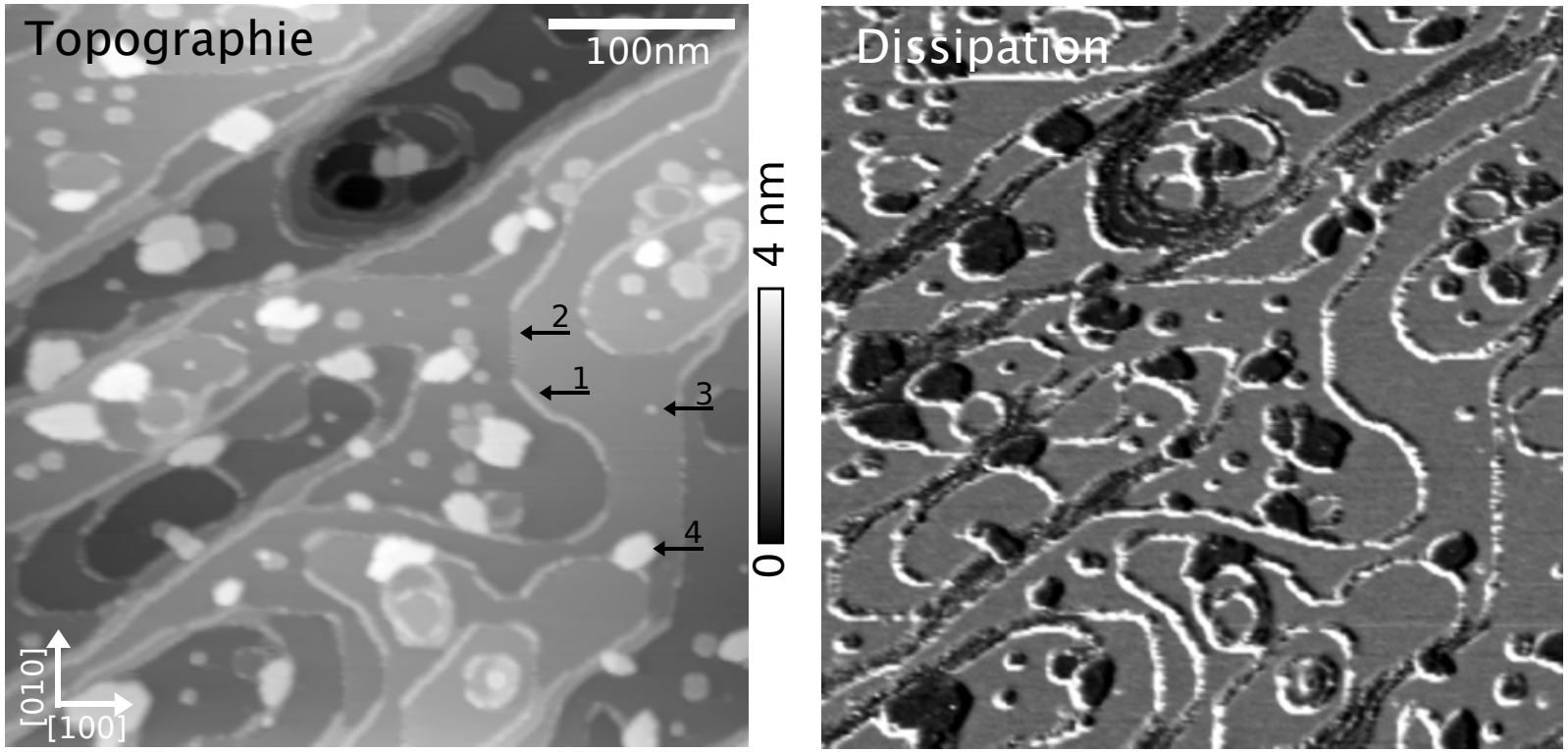


Répulsion électrostatique
→ taux de couverture limité.

→ Chauffage de l'échantillon Double porphyrine/KBr(001)
1h @ 350K

Double porphyrine : Recuit

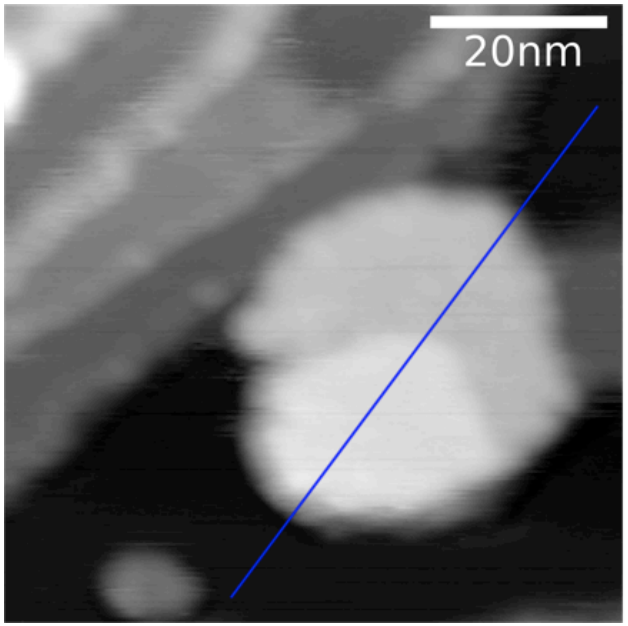
Chauffage échantillon : 1h @ 350K.

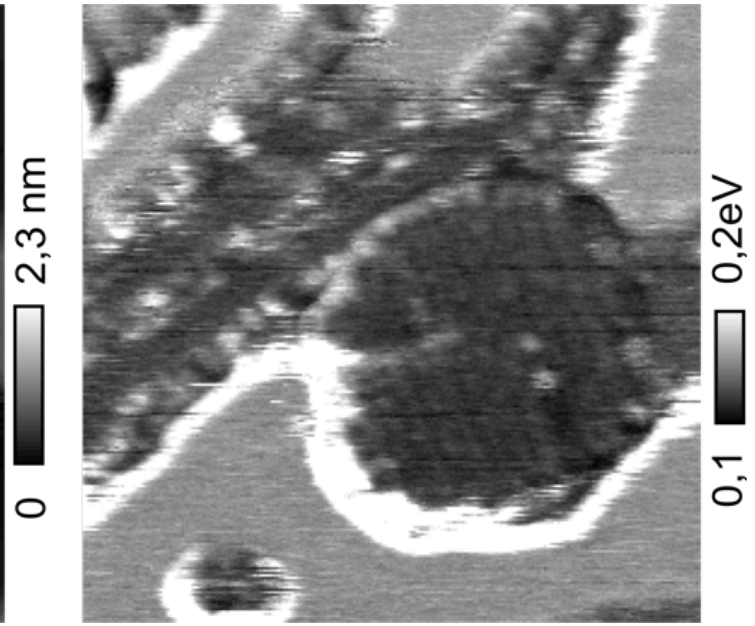


$A_{1st} = 4$ nm, $\Delta f_{1st} = -10$ Hz
$U = -1V$

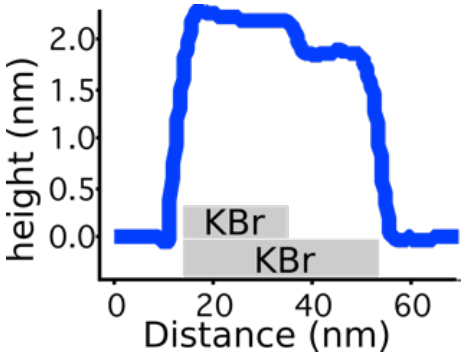
1 : bord de marche avec molécules adsorbées.
2 : bord de marche seul.
3 : petits agrégats.
4 : Ilots.

Double porphyrine : Recuit

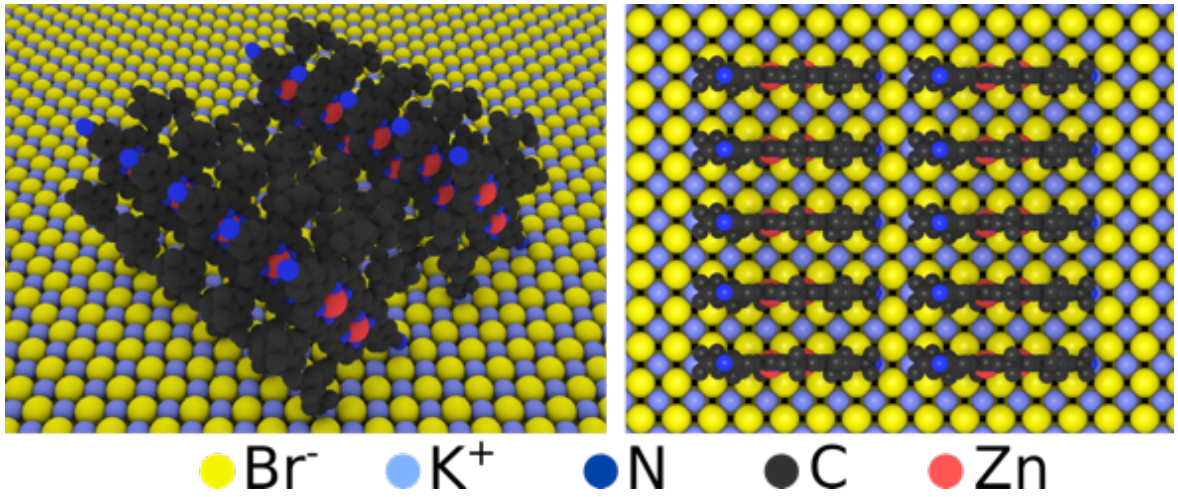


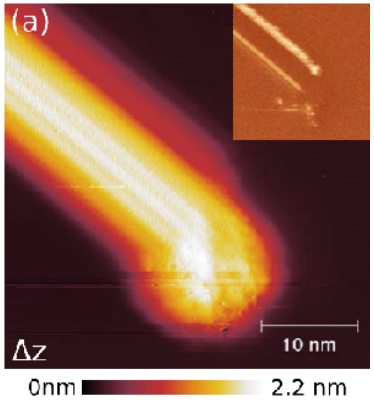


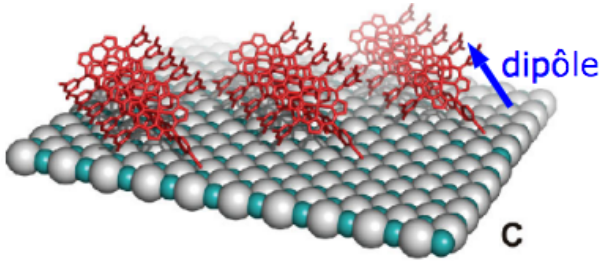
$A_{1st} = 5$ nm, $\Delta f_{1st} = -8$ Hz



Double porphyrine : Recuit





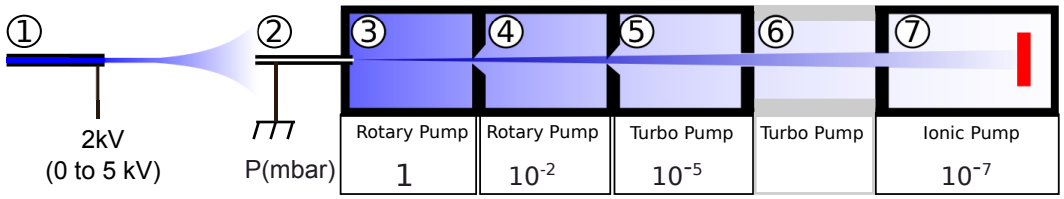


T. Glatzel et al. (2009), Applied Physics Letters 94.
A. Hinaut et al. (2012), Beilstein J Nanotechnol 3.

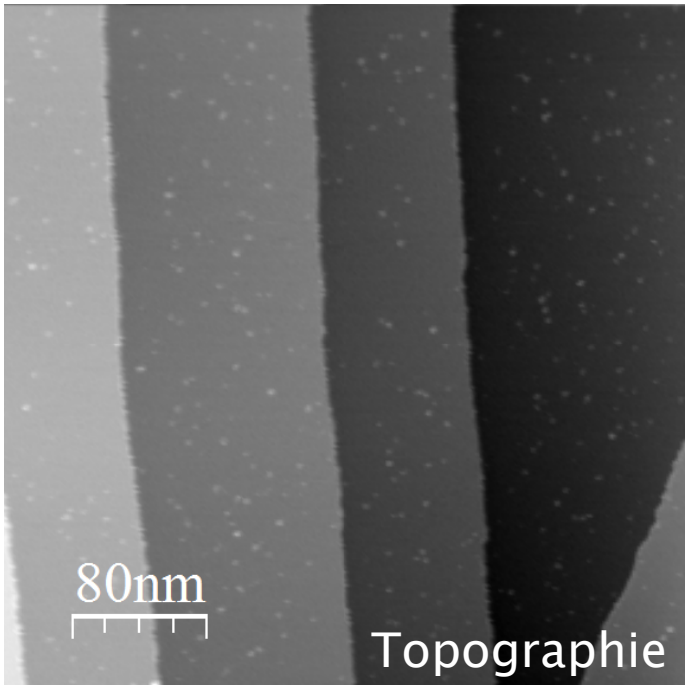
Double Porphyrine : Molécules uniques

Modification du dispositif MolecularSpray.

- Ajout d'un nouvel étage de pompage différentiel.
- Eviter recuit des échantillons.

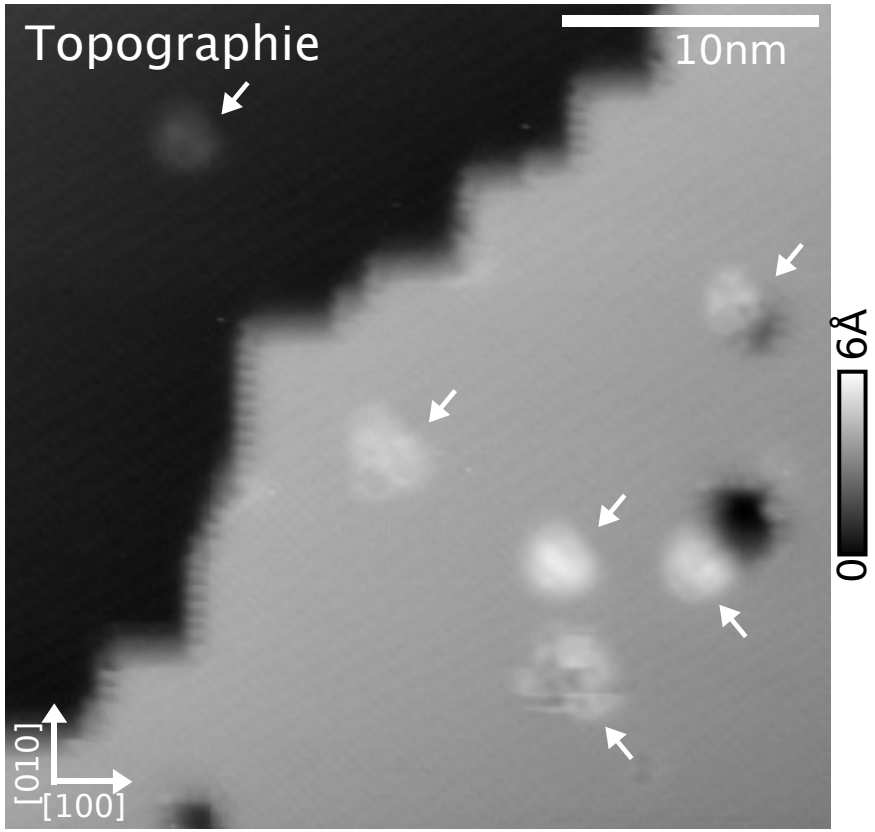


Double porphyrine / KBr(001)
Toluène et isopropanol (2:1)
U<1,5kV
5 min

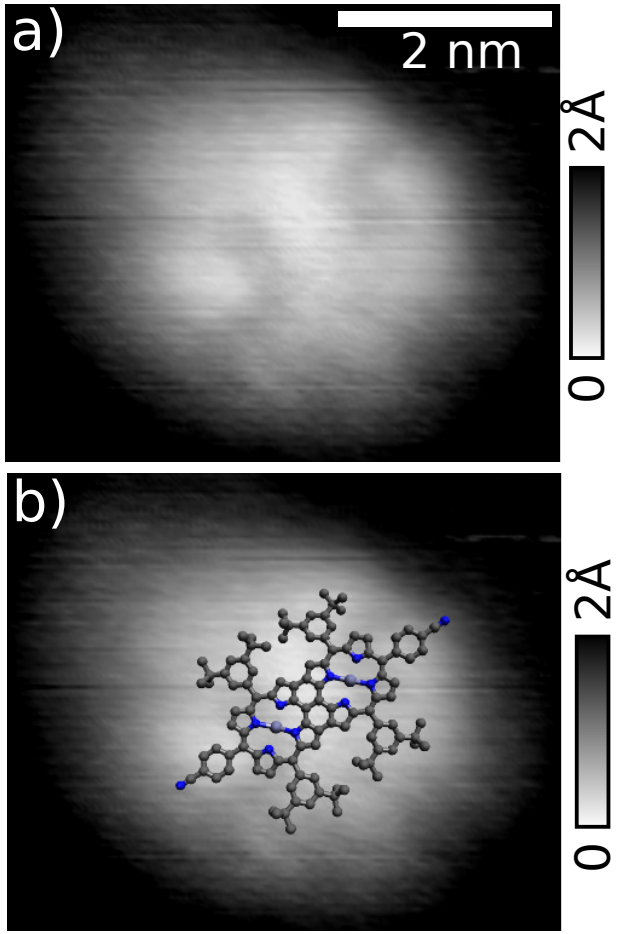


f_2=1017kHz, A_2=400pm, Δf_2=-10Hz.

Double Porphyrine : Molécules uniques

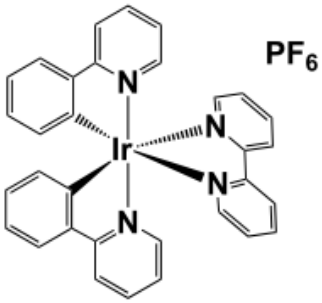


f_{2nd} = 1.02 MHz, A_{2nd} = 400 pm, Δf_{2nd} = -57 Hz

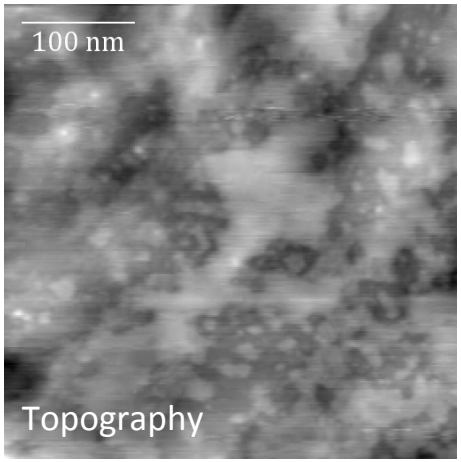


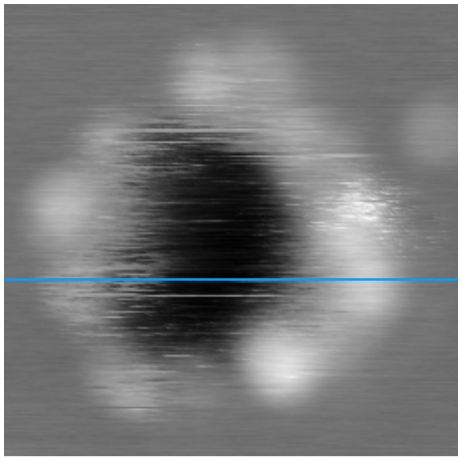
f_{2nd} = 1.02 MHz, A_{2nd} = 400 pm, Δf_{2nd} = -70 Hz

Ir Dye / KBr(001)

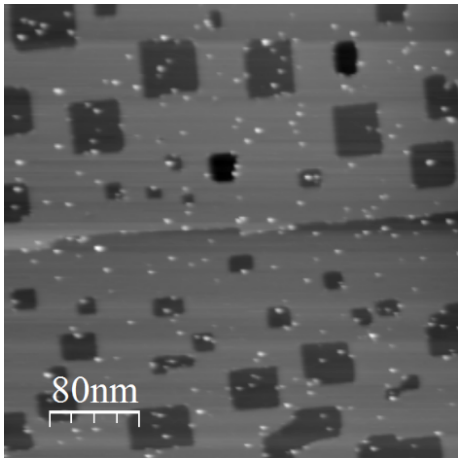


dichloromethane et methanol (1:1)





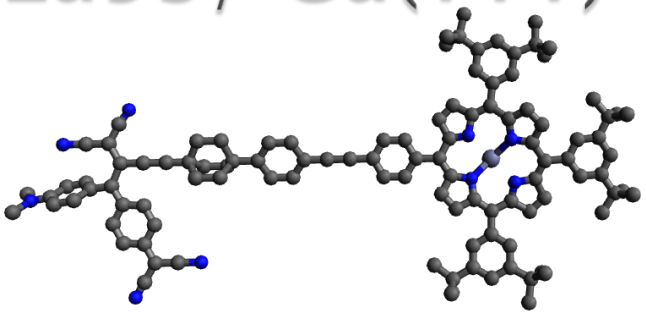
after annealing



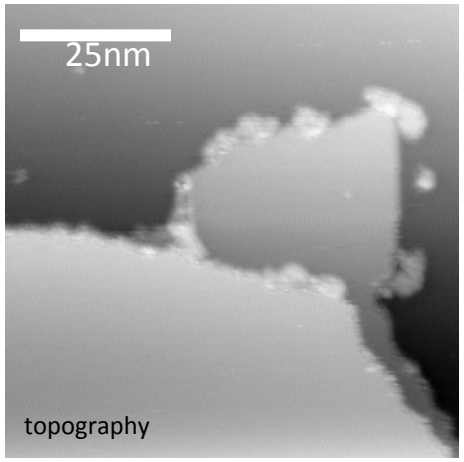
U < 1,5kV

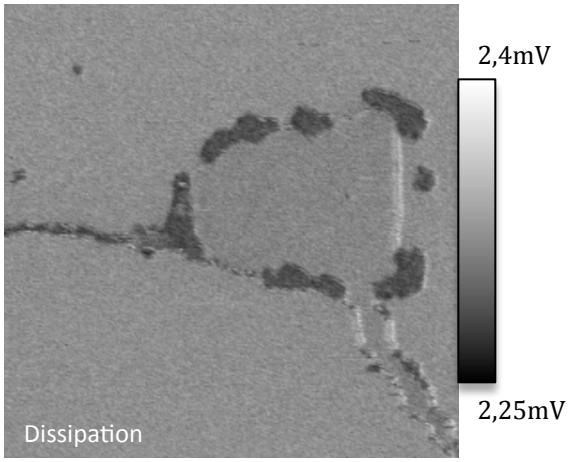
U ≥ 3kV

Lu53/ Cu(111)



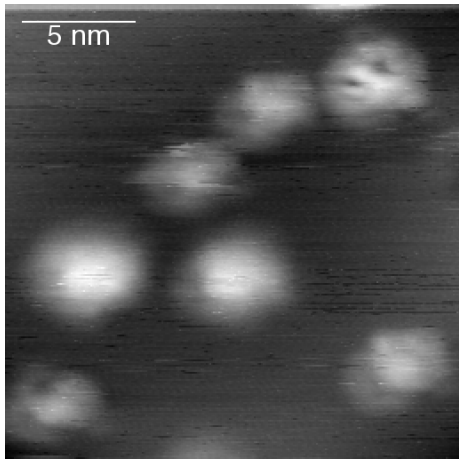
Toluene: isopropanol (2:1).



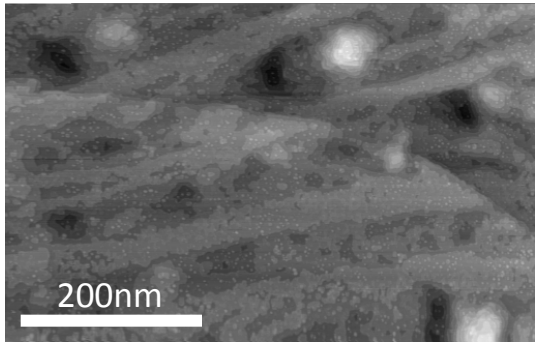


ESD of NanoDiamond

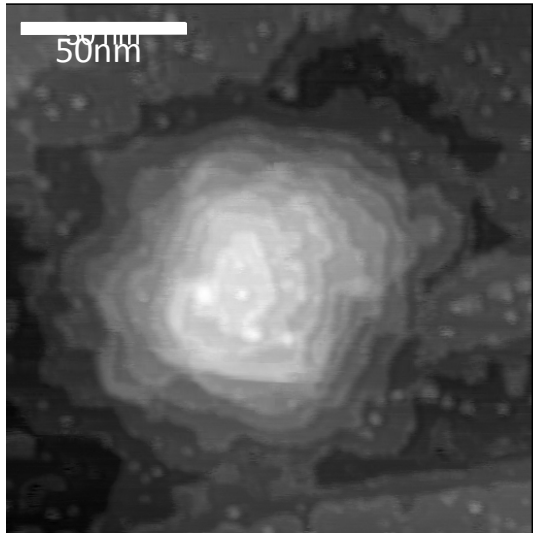
Nanodiamants synthetisés à l'institut de saint louis.
2 solutions acqueuses: 2-5nm et 50nm de diamètre.

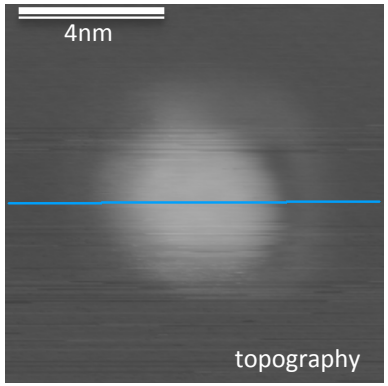


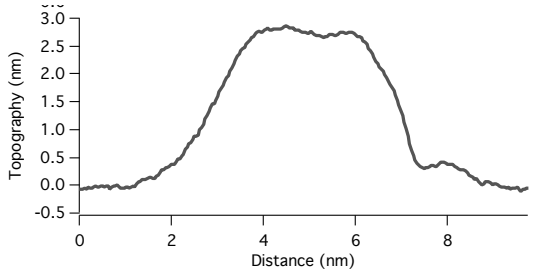
ND 50nm/KBr(001) :



ND 2-5nm/KBr(001)

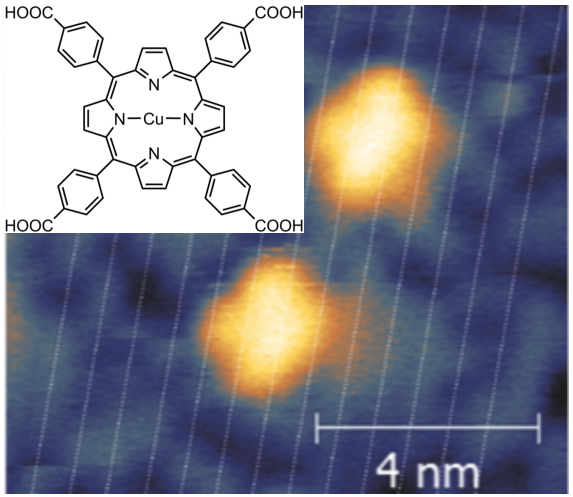






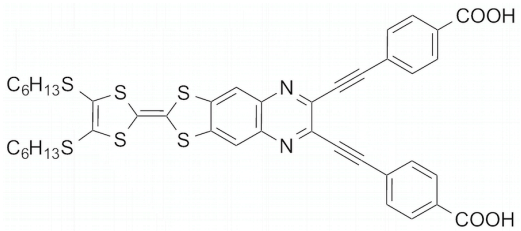
Conclusion

- Dépôt de molécules sur isolants massifs possible par ESI.
- Différents taux de couverture possible.
- → molécules isolées.



Cu-porphyrin/TiO_2 rutile (110)

R. Jöhr et al. *The Journal of Chemical Physics*, 143, 9 (2015)



ESI : TTF–Dye

TiO_2 rutile ou anatase

Acknowledgements

Vielen Dank für Ihre Aufmerksamkeit !!

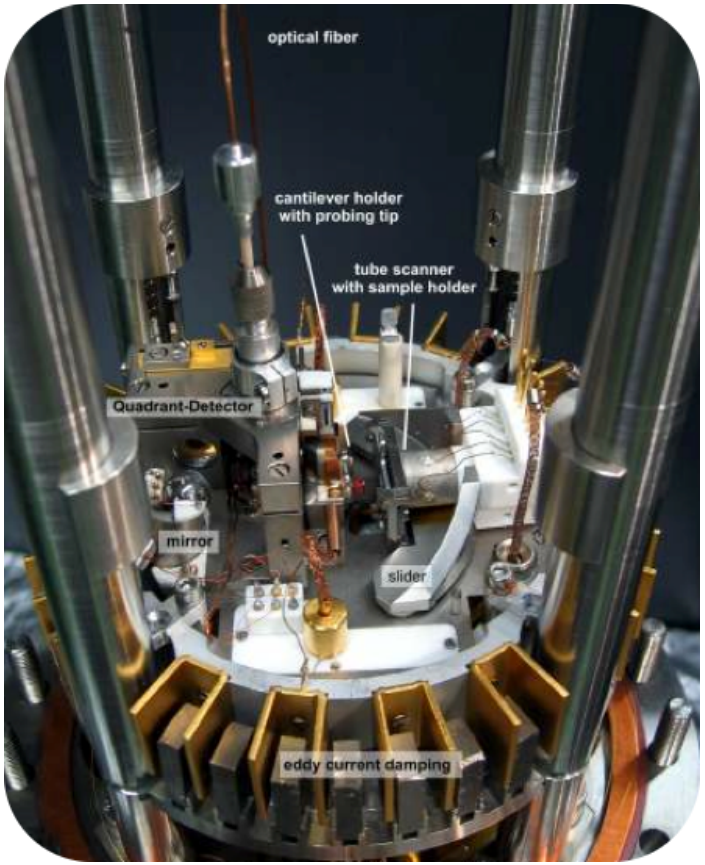
SNI
SWISS
NANOSCIENCE
INSTITUTE

UNI
BASEL

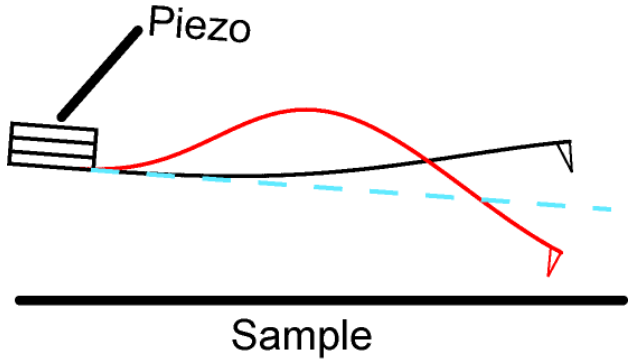
SWISS
CONTRIBUTION

Dispositif et caractérisation

UHV home built RT AFM



ncAFM bimodale



NANONIS SPECS

Cantilever Si : PPP-NCL, chauffage 1h @ 100°C, Sputtering 2min.

f_{1st}=150kHz	f_{2nd}=1MHz	f_{TR}=1.5MHz
Q_{1st}=30000	Q_{2nd}=10000	Q_{TR}=100000

$$k_{2nd} >> k_{1st}$$

S. Kawai, et al., APL 86 193107 (2005)