La microscopie à effet tunnel à basse température : Un outil de choix pour observer les molécules

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Outline

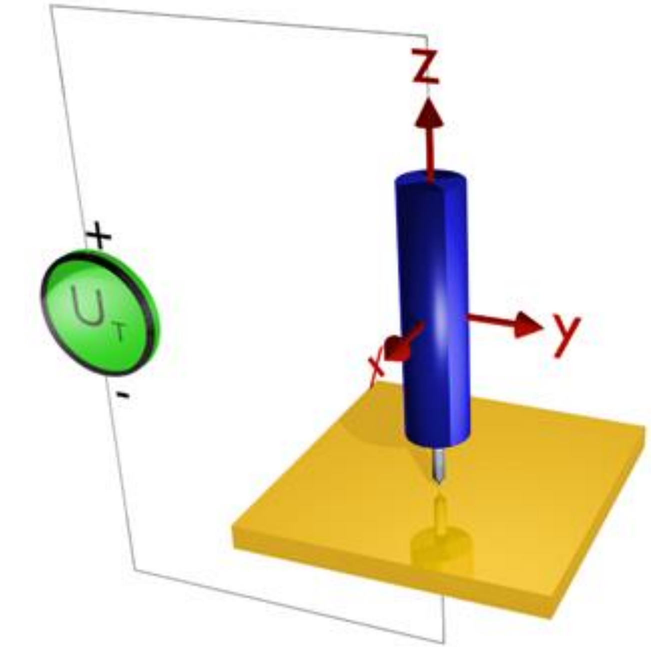
- Quick reminder of Scanning Tunneling Microscopy (STM)

- Why we need and how we reach Low Temperature (LT) ?

- Examples of molecules on surface and what can be achieved with STM and LT.

- Focus on the elaboration of p-n junctions on N-doped graphene

Scanning Tunneling Microscopy (STM)



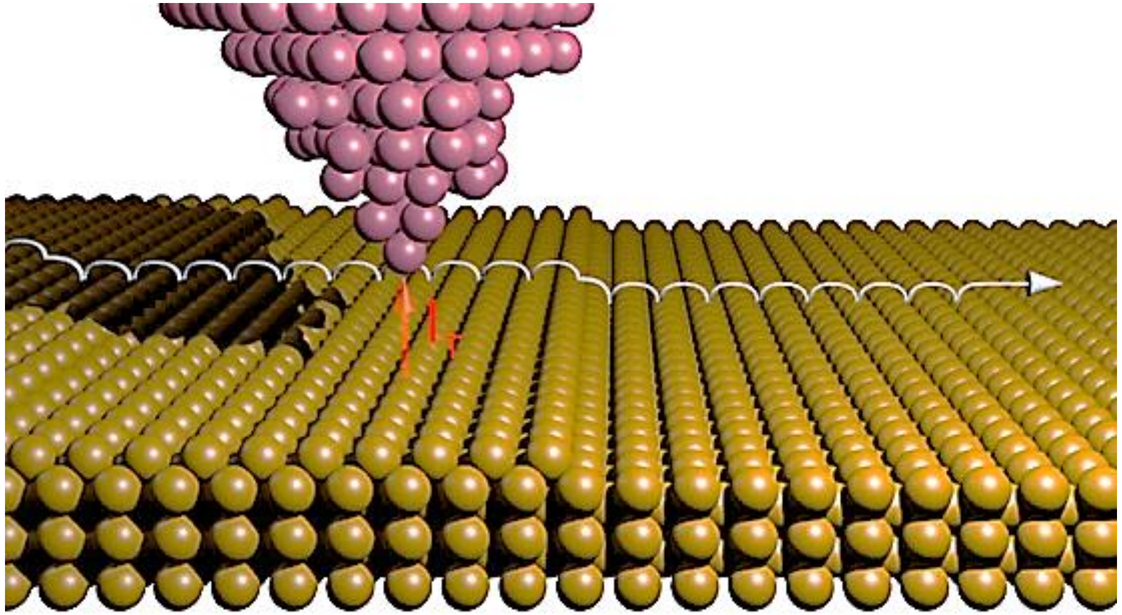


Photo from the Nobel Foundation archive.
Gerd Binnig

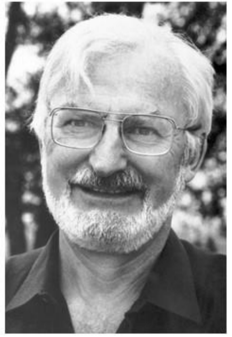
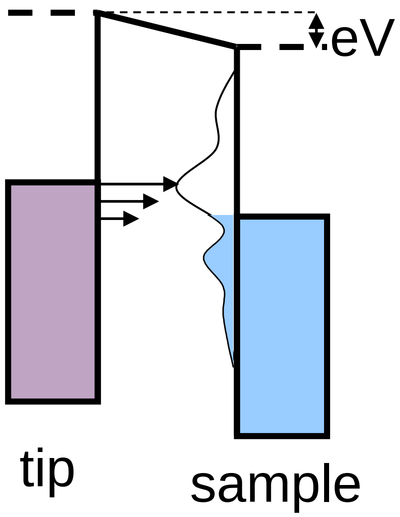


Photo from the Nobel Foundation archive.
Heinrich Rohrer



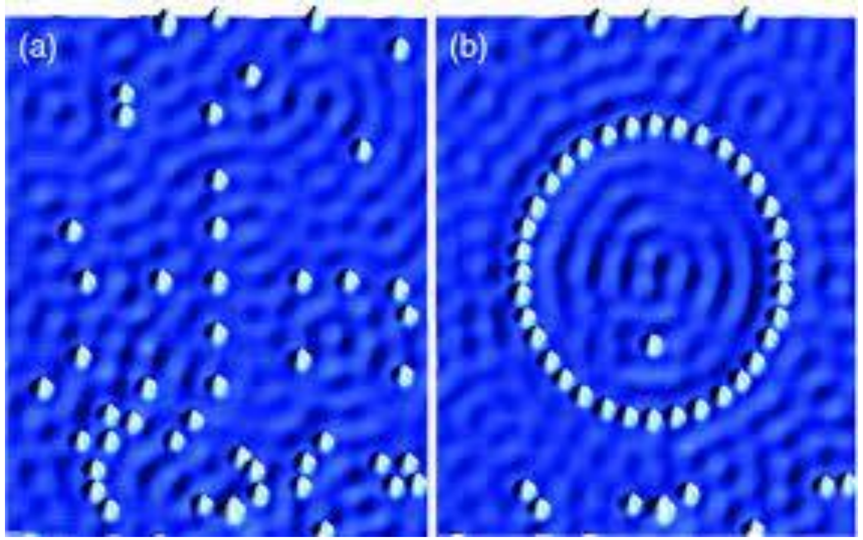
$$I \propto e^{-\alpha z}$$

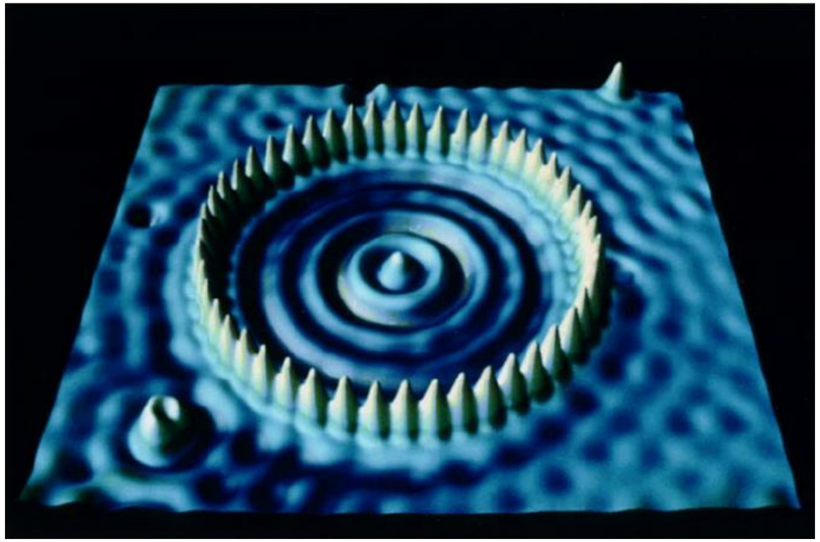
Exponential dependence of the tunnel current with the tip-sample distance **-> STM**

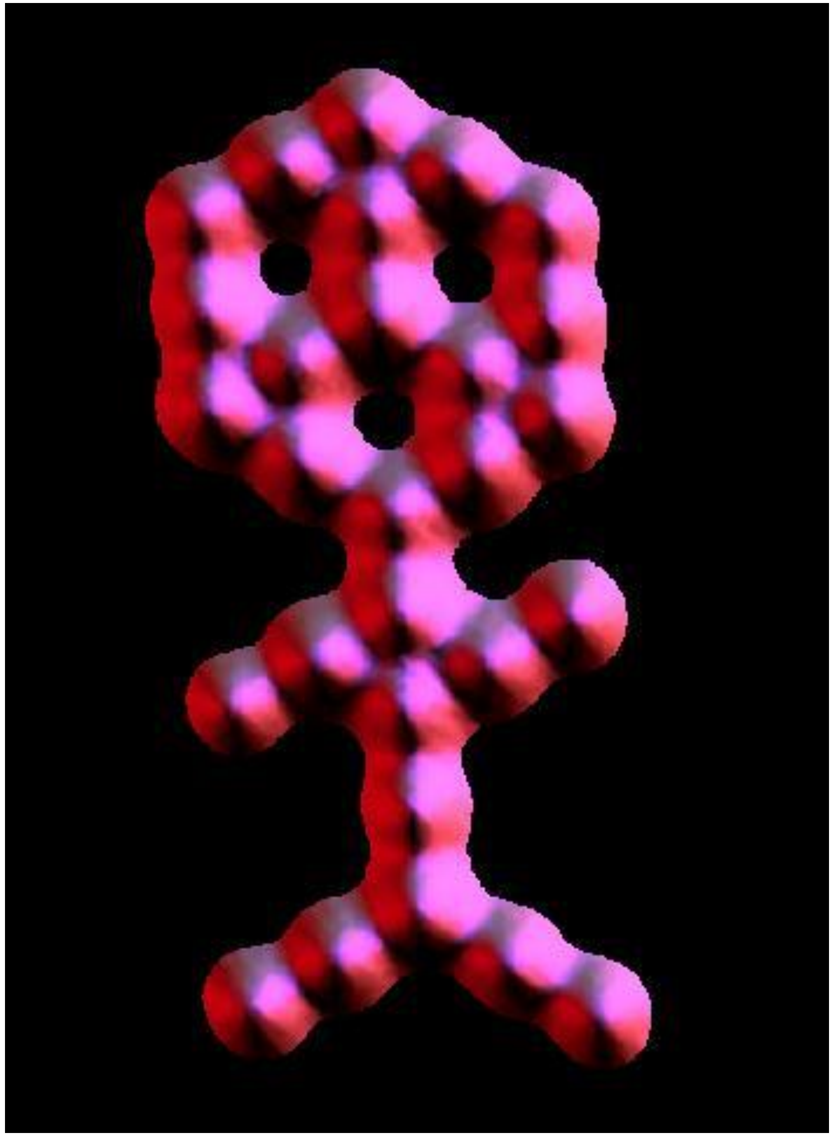
$$\frac{dI}{dV} \propto \rho_s(\vec{r}_0, eV)$$

ρ_s : Local density of states of the sample **-> STS**

Scanning Tunneling Microscopy (STM)







Quantum Corral

Artificial ring of 48 iron atoms on a Cu(111) surface
Confined states du to the electron-trapping effect

Carbon monoxide man

28 CO molecules on Pt(111)

IBM Research Center, Almaden, CA (D. Eigler and P. Zeppenfeld)

Why we need Low Temperature (LT)

- UHV conditions: If the microscope is incorporated in a cryostat that acts as an effective cryopump, surfaces are kept free

- Physical properties can be studied as a function of temperature or physical effects can be examined that occur only at low temperatures

- Small thermal broadening at the Fermi energy is a necessary condition for spectroscopic investigations with high-energy resolution

- Individual adsorbates can be manipulated with the STM to qualitatively probe their interaction with the substrate.

- Thermal diffusion of adsorbates and defects is suppressed.

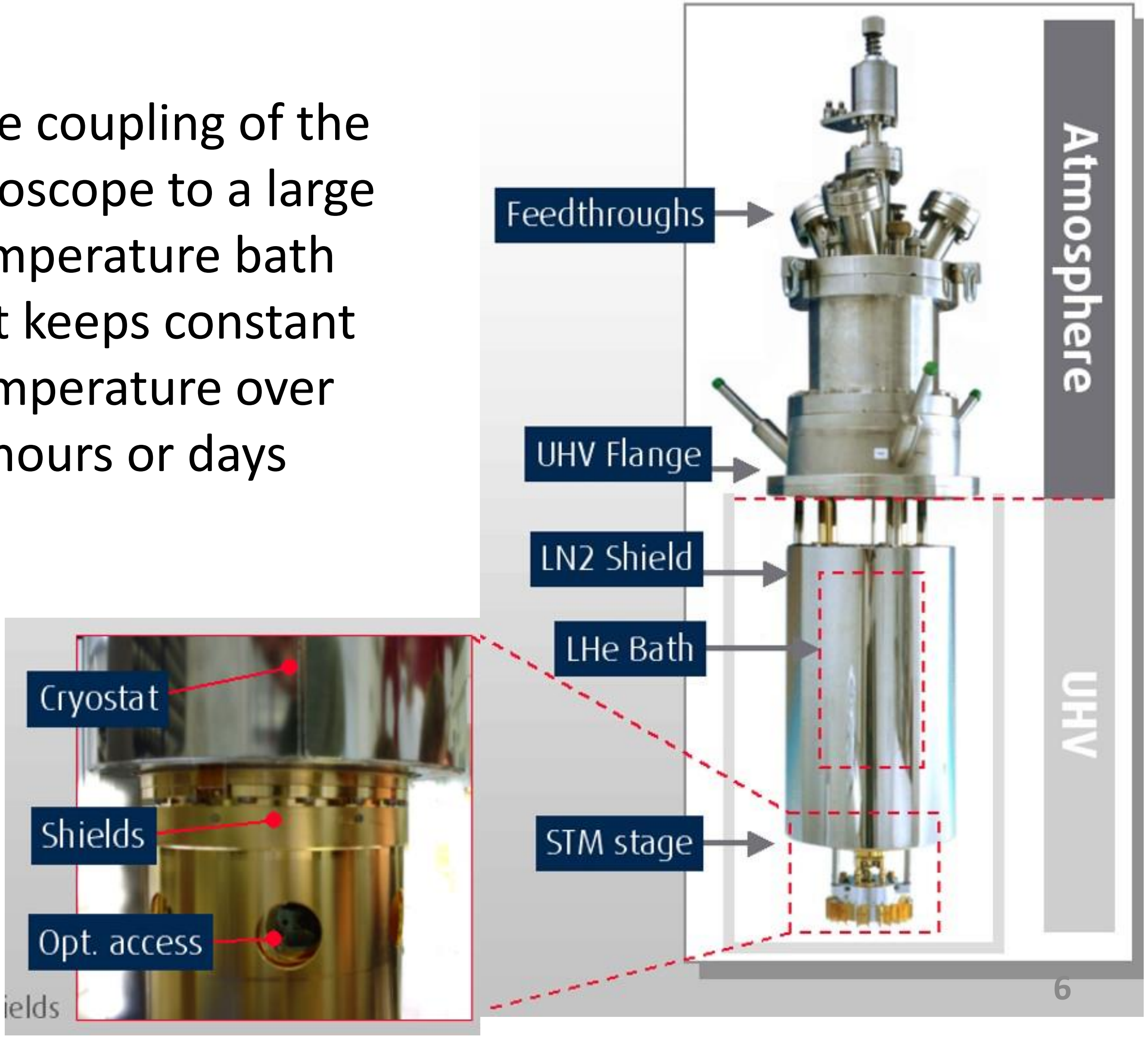
- Reduction of thermal drift and allows long-term measurements.

- Piezo nonlinearities and hysteresis (creep) affecting the piezoelectric scanners of the STM decrease substantially at low temperatures

How do we reach Low Temperature

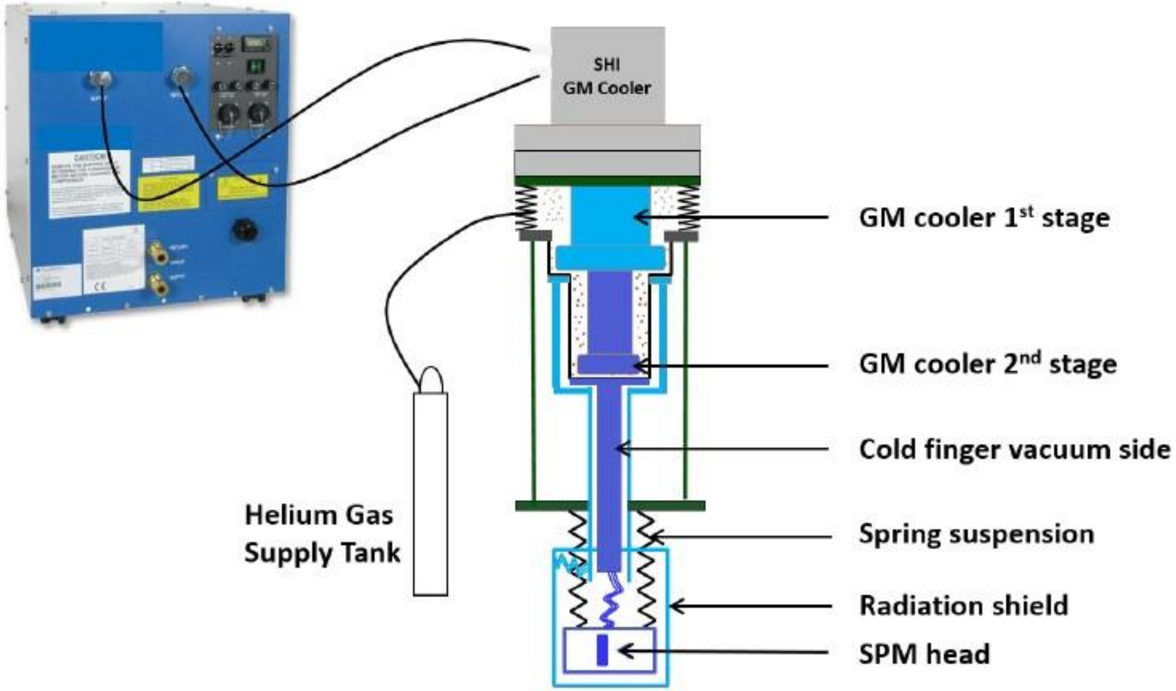
The most conventional LT-STM instrument : down to 4 K on the sample stage

Close coupling of the microscope to a large temperature bath that keeps constant temperature over hours or days



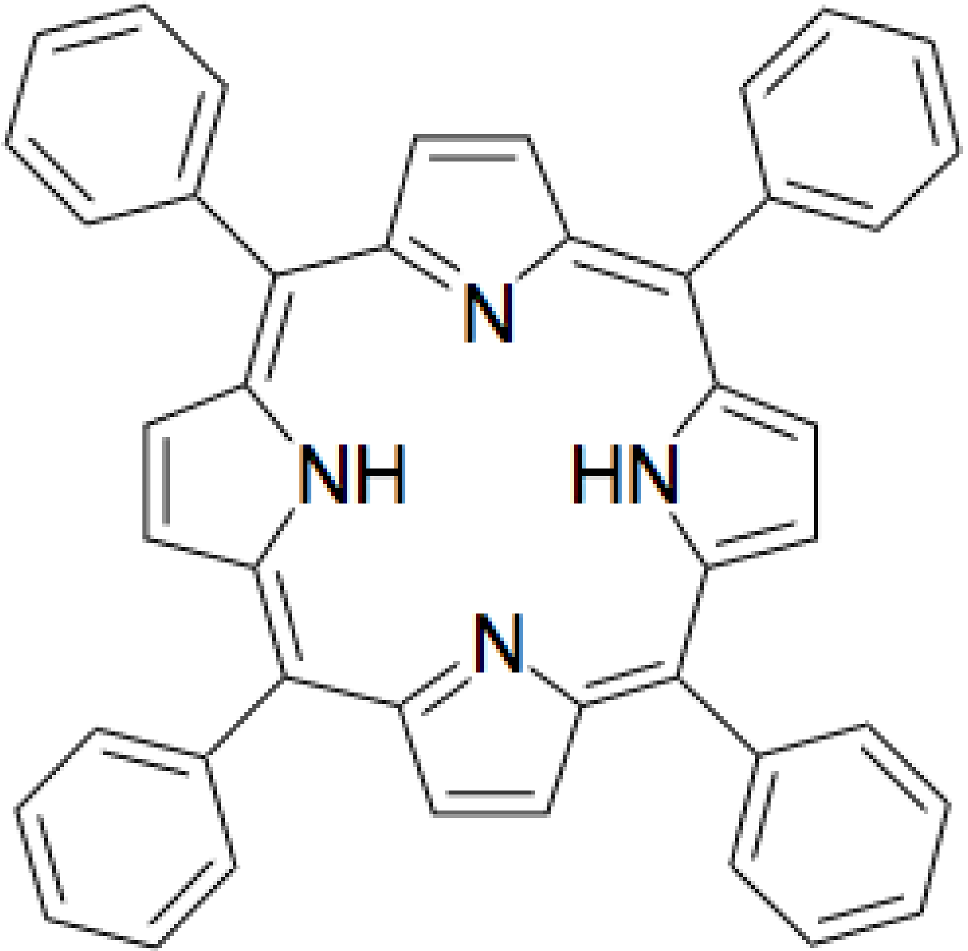
How do we reach Low Temperature

More recently : The LT-STM instrument coupled to a **Gifford-McMahon Cryocooler** down to 9 K on the sample stage



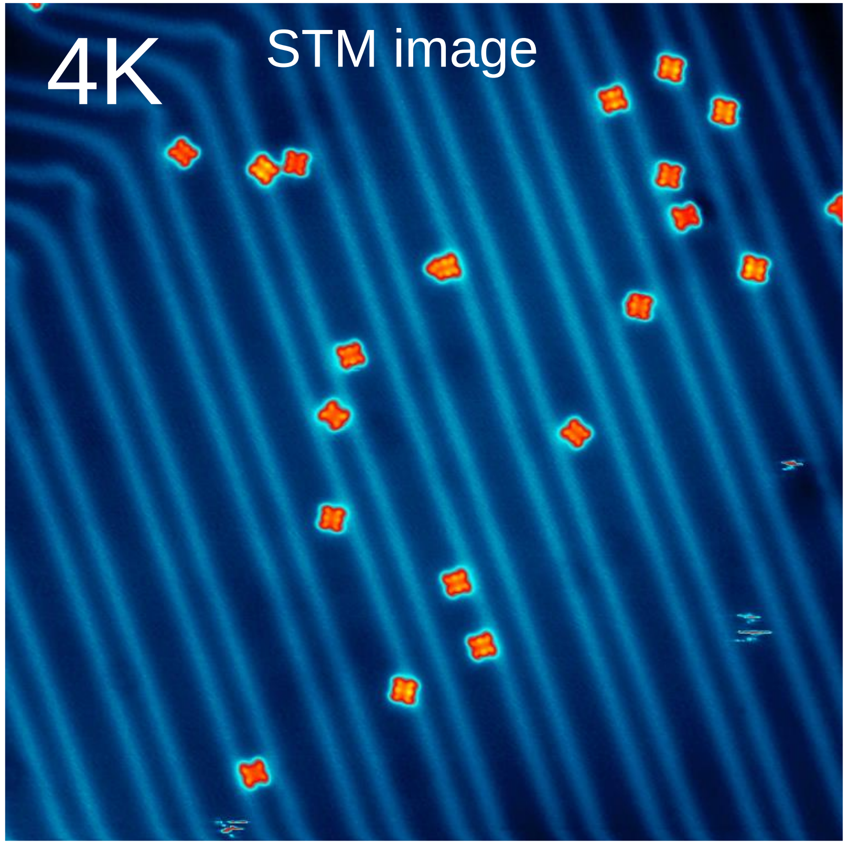
Examples of molecules on surface : H_2TPP

Tetraphenylporphyrin



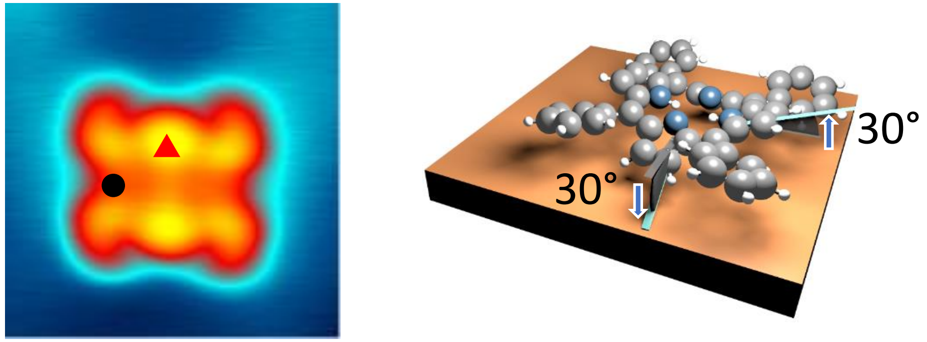
Examples of molecules on surface : H_2TPP on Au(111)

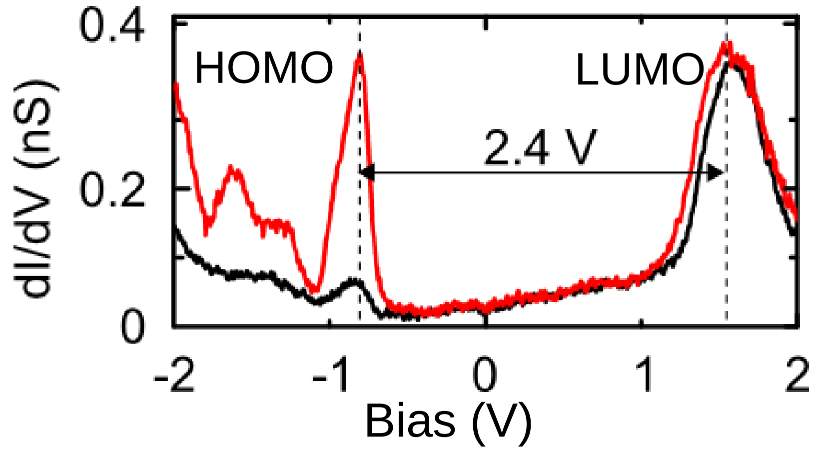
Tetraphenylporphyrin

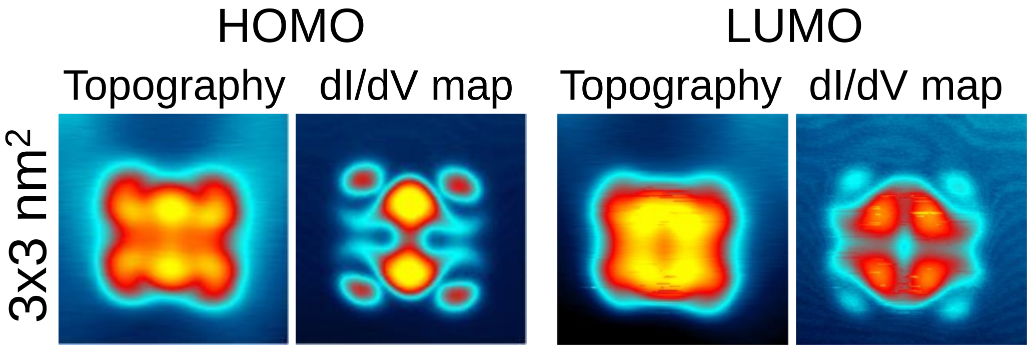


100 nm, -0.8V, 120 pA

V. D. Pham et al., J. Phys. Chem. Lett. 7, 1416 (2016)





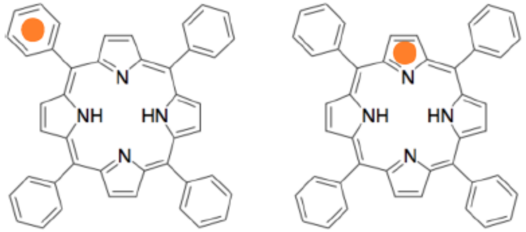


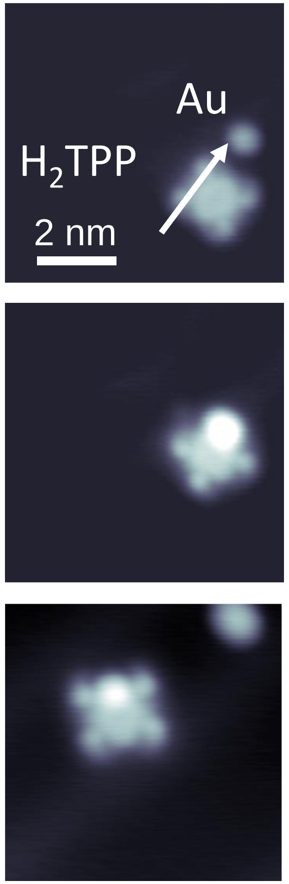
V_b= -0.8V V_b= +1.6V

Examples of molecules on surface : H_2TPP on Au(111)

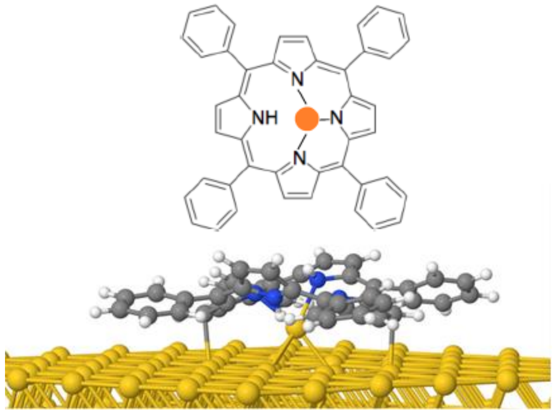
Atom trapping chemistry: H_2TPP+adatom

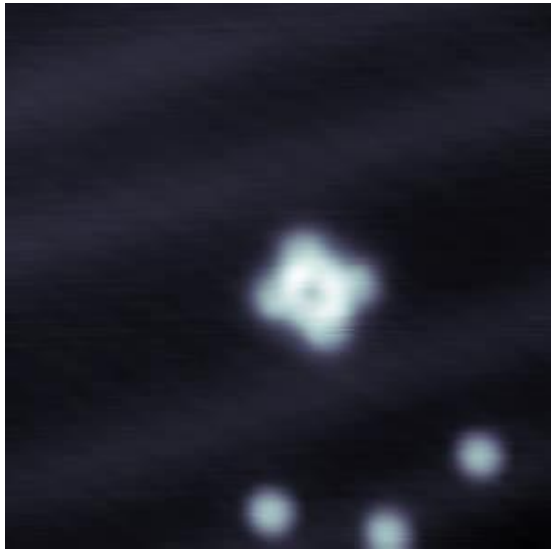
Doping





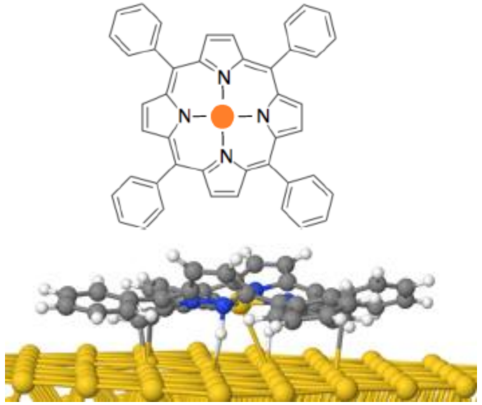
Rotor

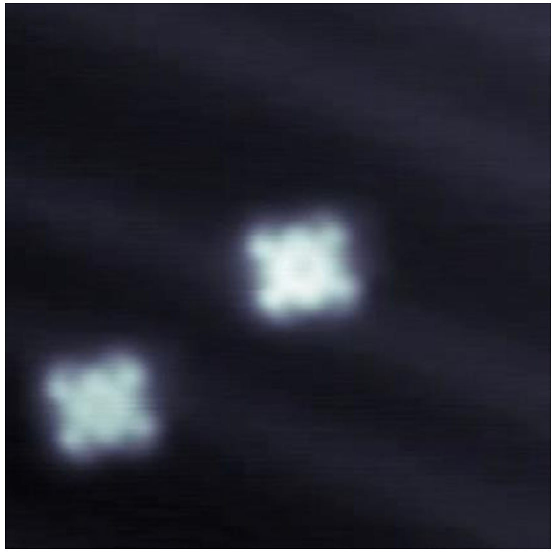




10 nm x 10 nm, 1V, 100 pA

Jumper

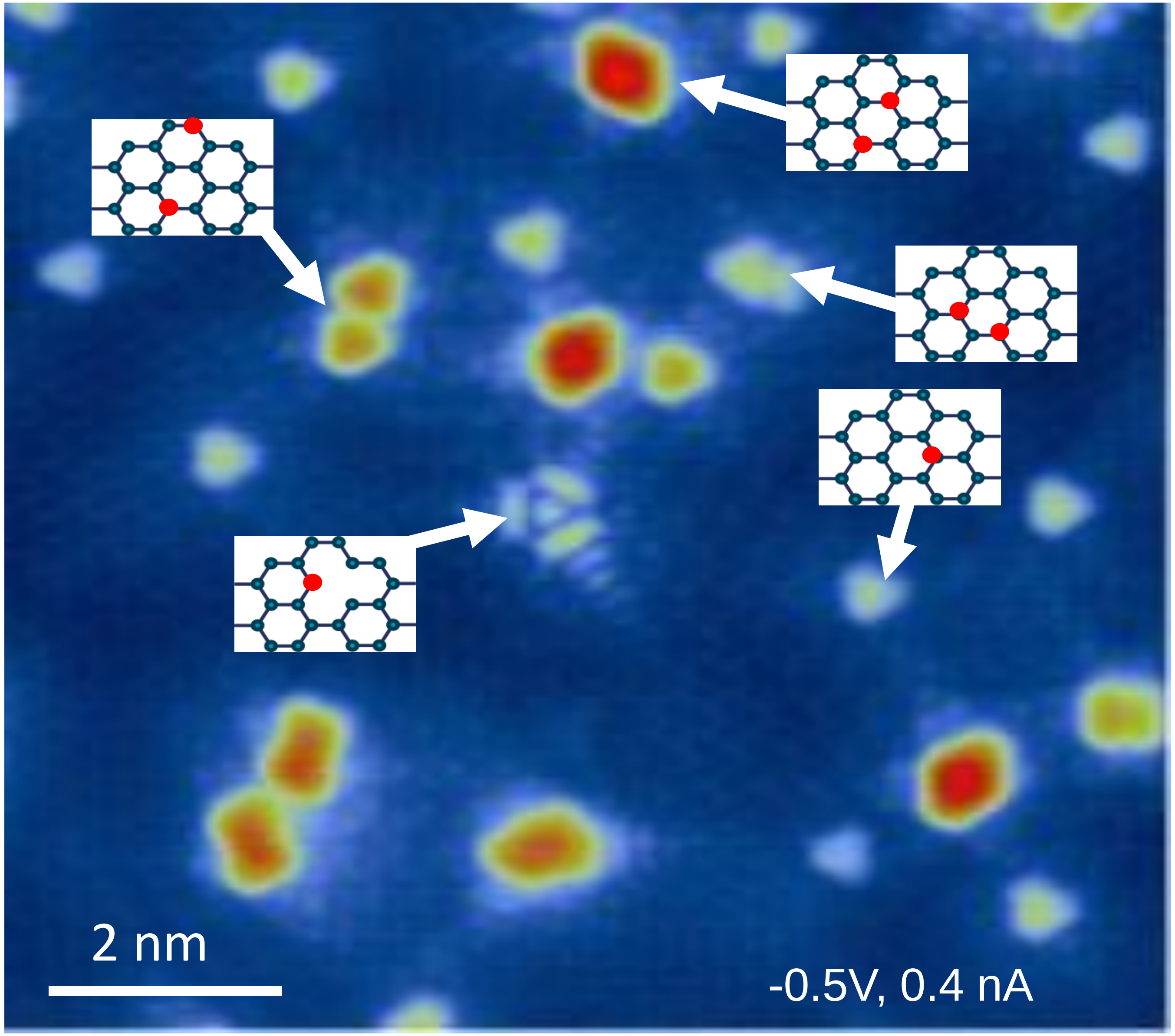




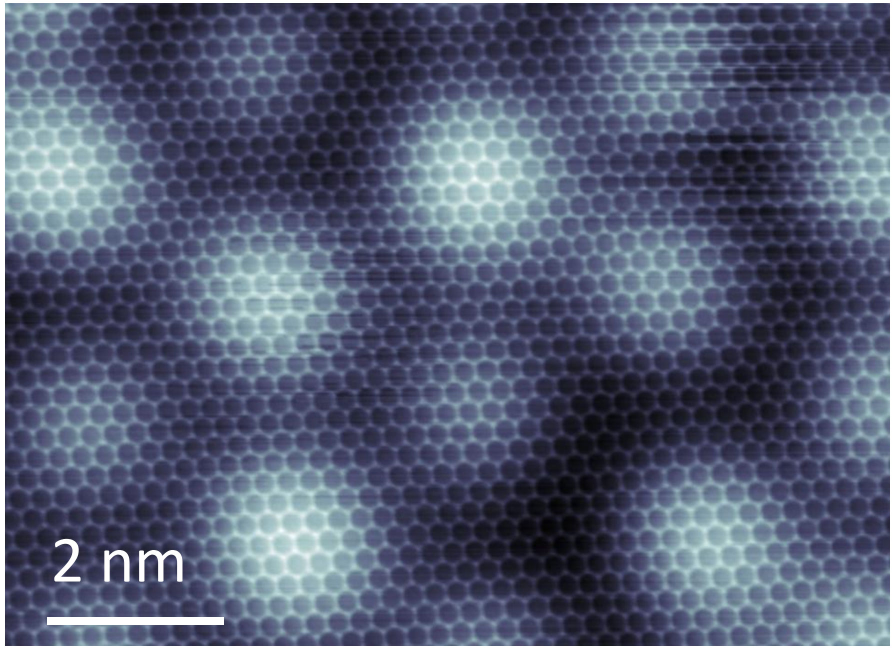
10 nm x 10 nm

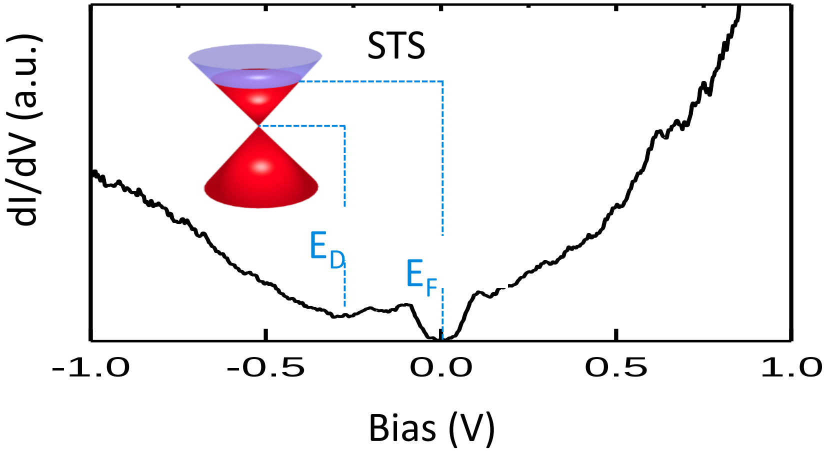
V. D. Pham et al., *ACS Nano* 11, 10742 (2017)

Examples of molecules on surface : H_2TPP on (N dopped)Graphene



Post-synthesis Nitrogen-doping, exposure to N_2 plasma

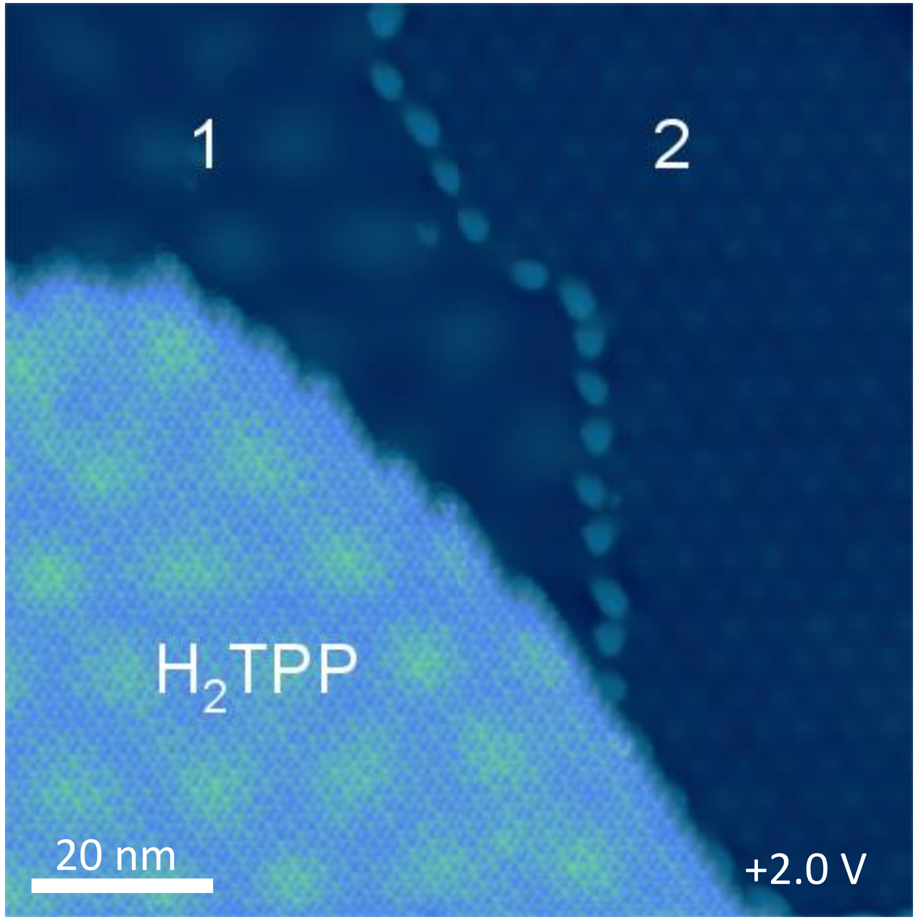




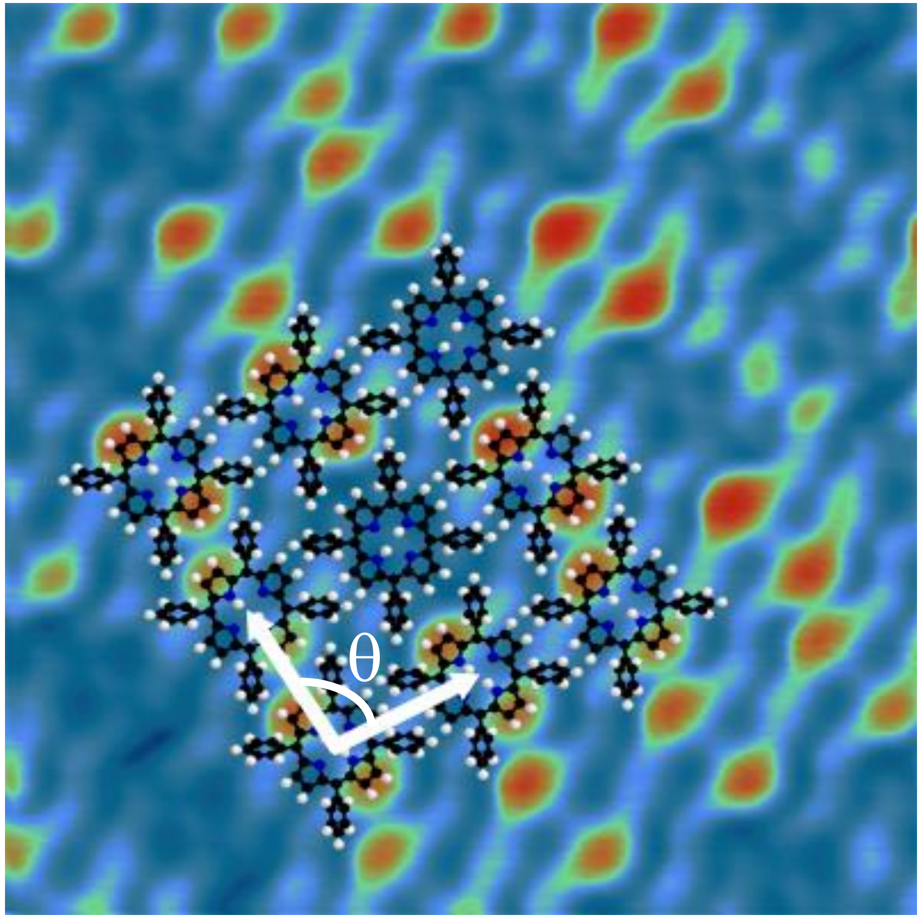
Y. Tison et al., *ACS Nano* 9, 670 (2015)

Examples of molecules on surface : H_2TPP on (N dopped)Graphene

H_2TPP island on graphene



Molecular lattice

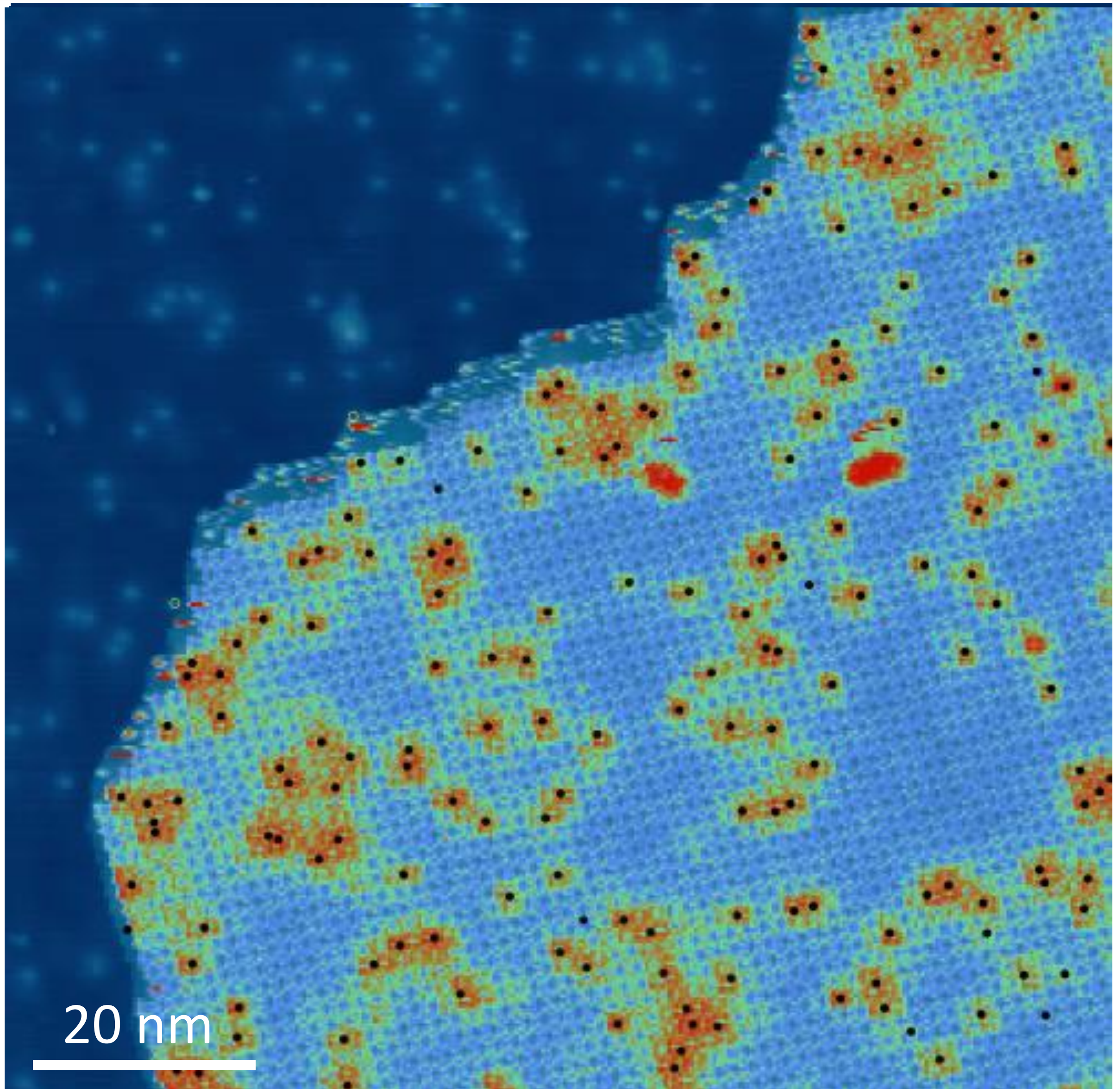


-1.5 V, 20 pA V

- Molecular network after RT annealing
- Lattice not following the symmetry of graphene, molecule-molecule interaction stronger than molecule-graphene

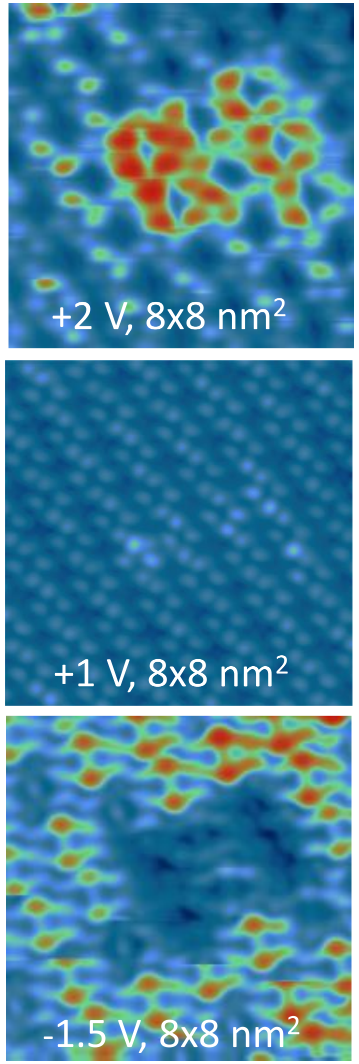
a = 1.41±0.01 nm
θ= 96.8°

Examples of molecules on surface : H_2TPP on (N dopped)Graphene



2V, 50 pA

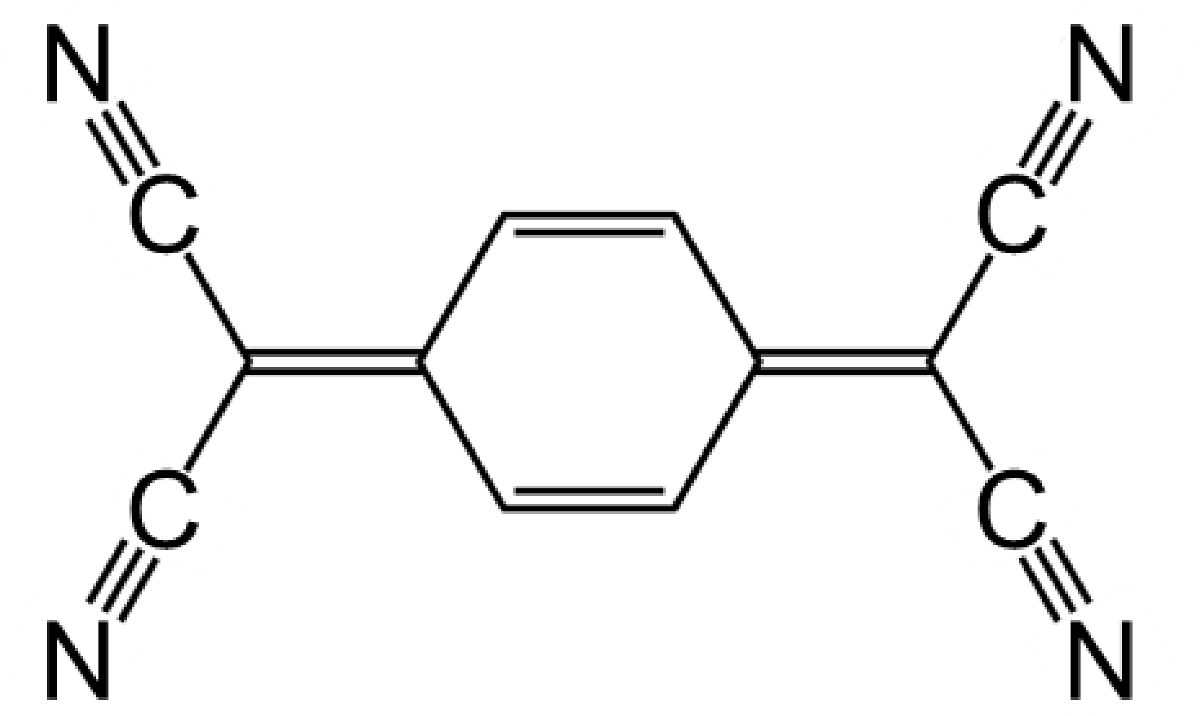
Voltage dependent contrast



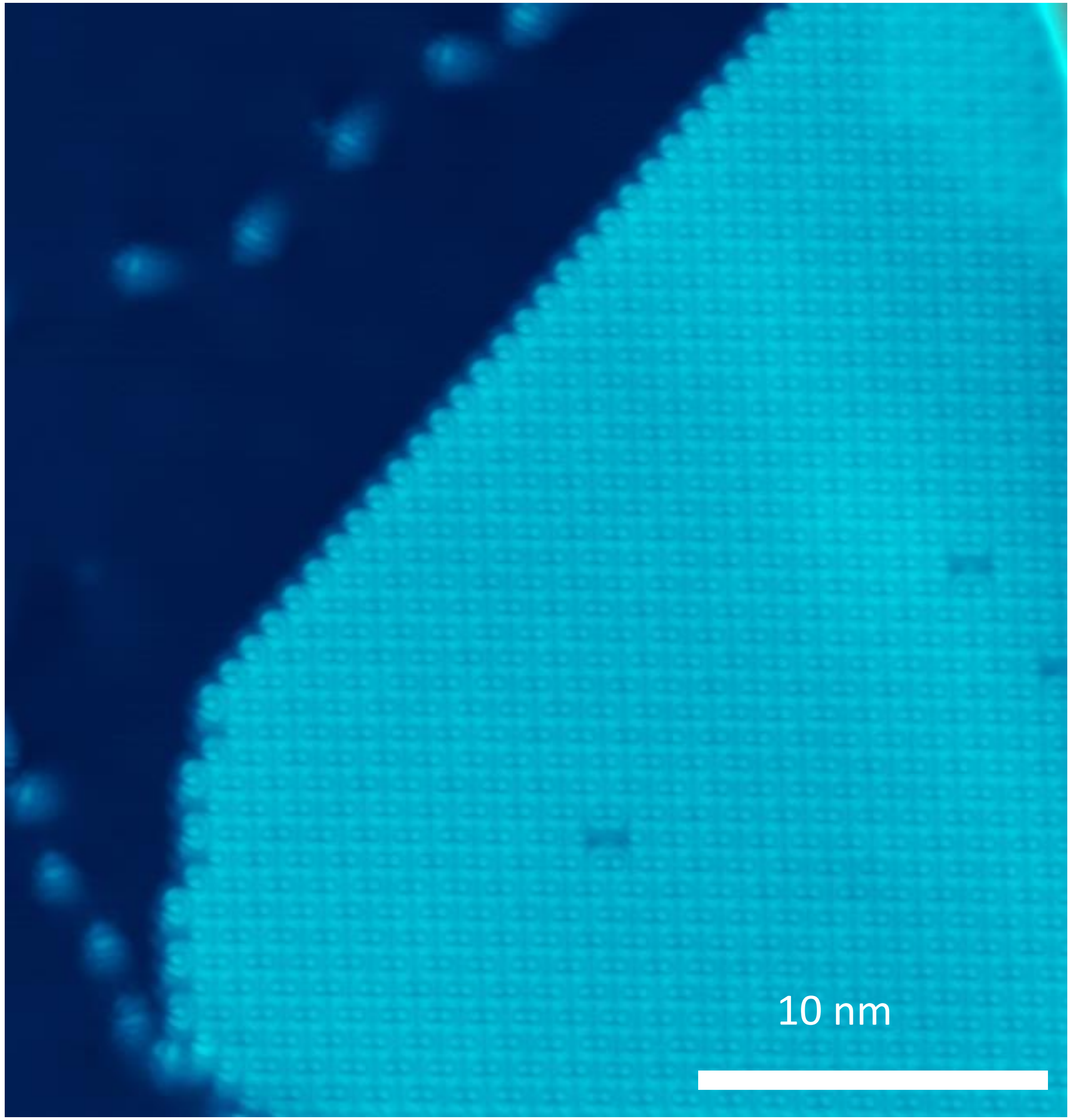
V. D. Pham et al *Sci. Rep.* 6, 24796, (2016)

Examples of molecules on surface : TCNQ

Tetracyanoquinodimethane



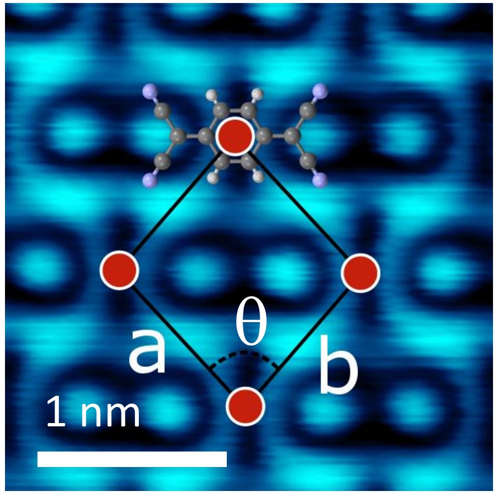
Examples of molecules on surface : TCNQ on (N dopped)Graphene



30×30 nm^2 1V, 30pA

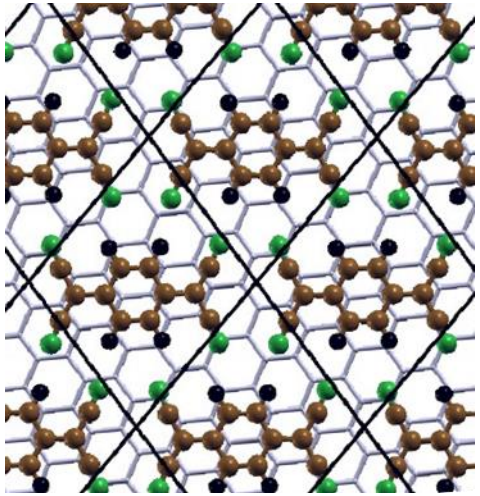
- Molecular network after RT annealing

Exp



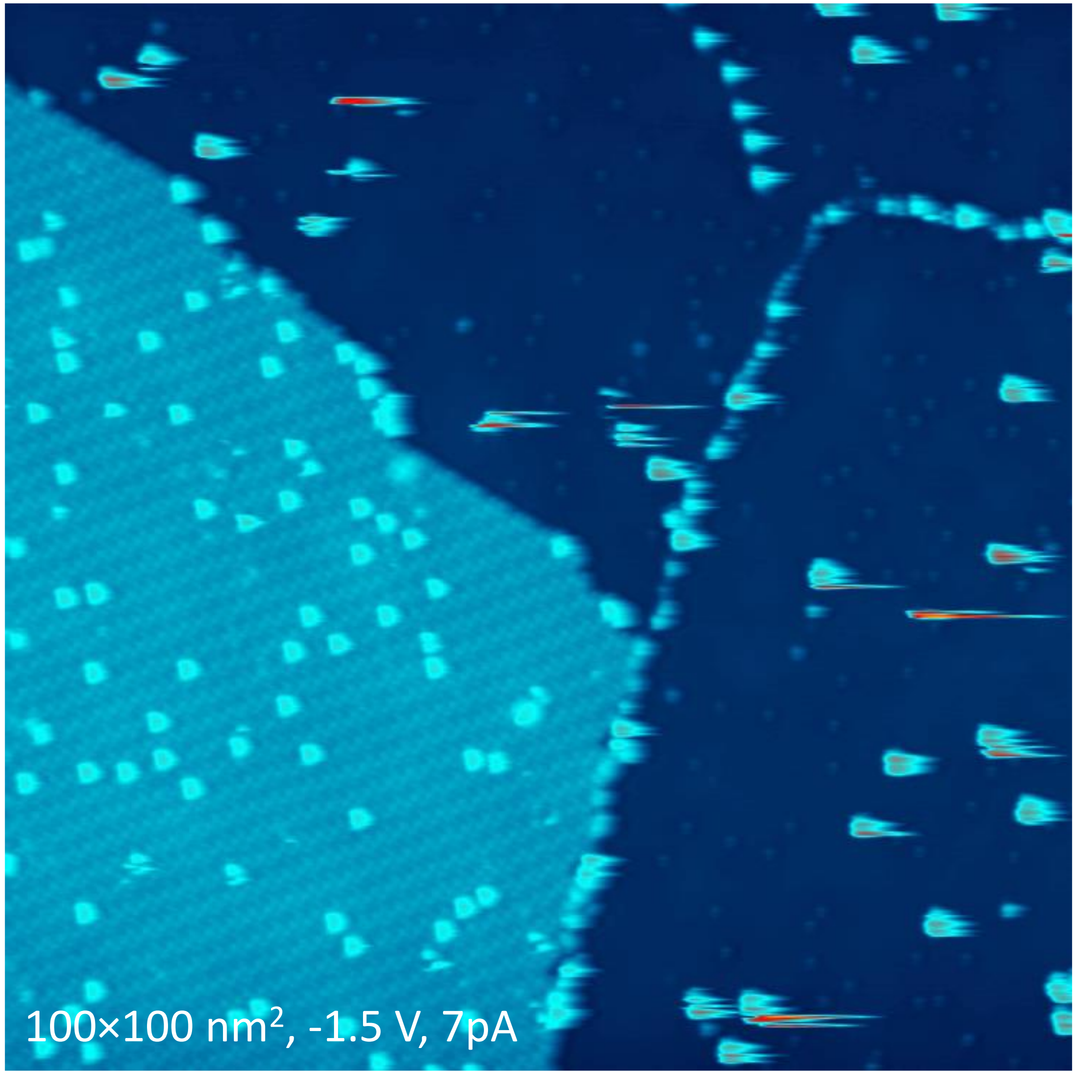
a = 0.93 ± 0.01 nm
b = 0.89±0.02
θ = 85 ± 2°

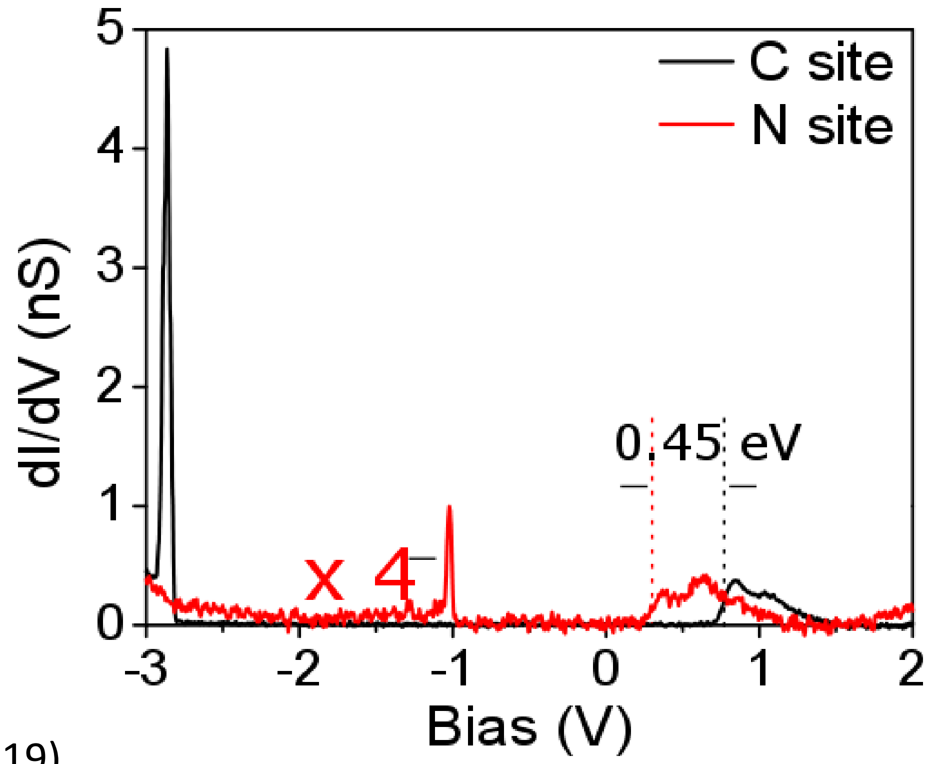
DFT



DFT:
Nearly square lattice.
Stabilization energy due to hydrogen bond
-0.31 eV / molecule

Examples of molecules on surface : TCNQ on (N dopped)Graphene





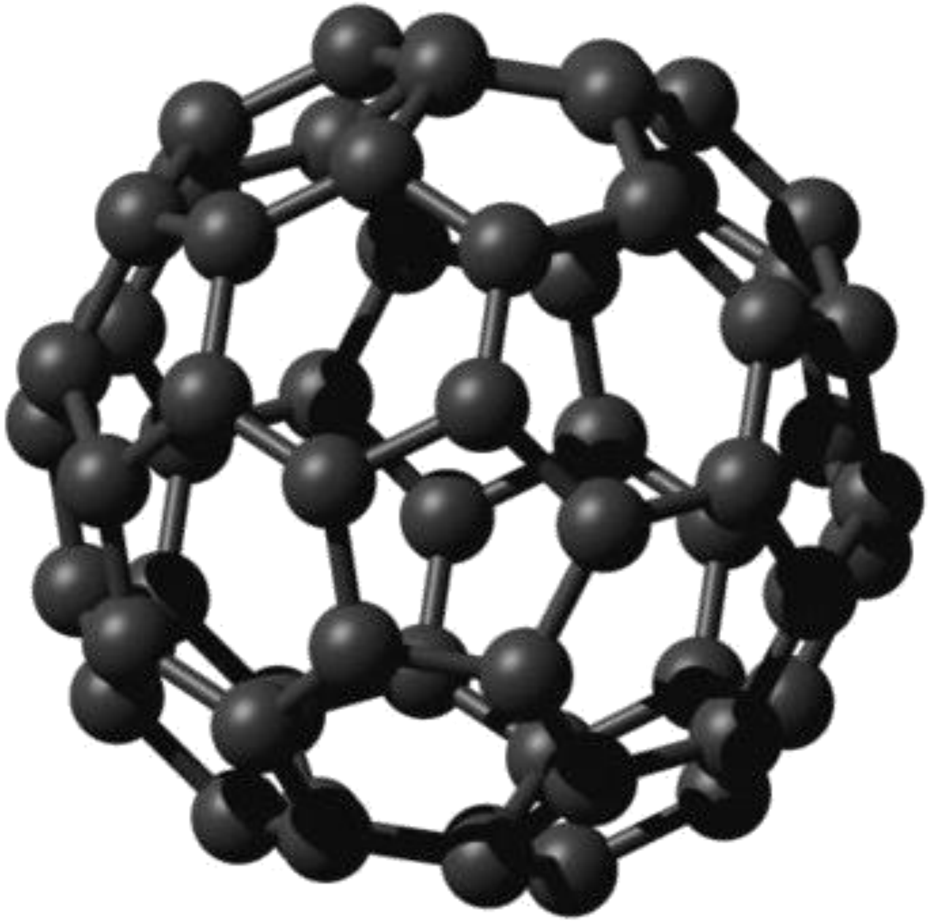
DFT

- Shift of the LUMO state to lower energy
- DFT: charge transfer 0.2 e^- at C site, 0.3 e^- at N site
- Peak at negative bias reveal the shape of the LUMO state in the occupied state region

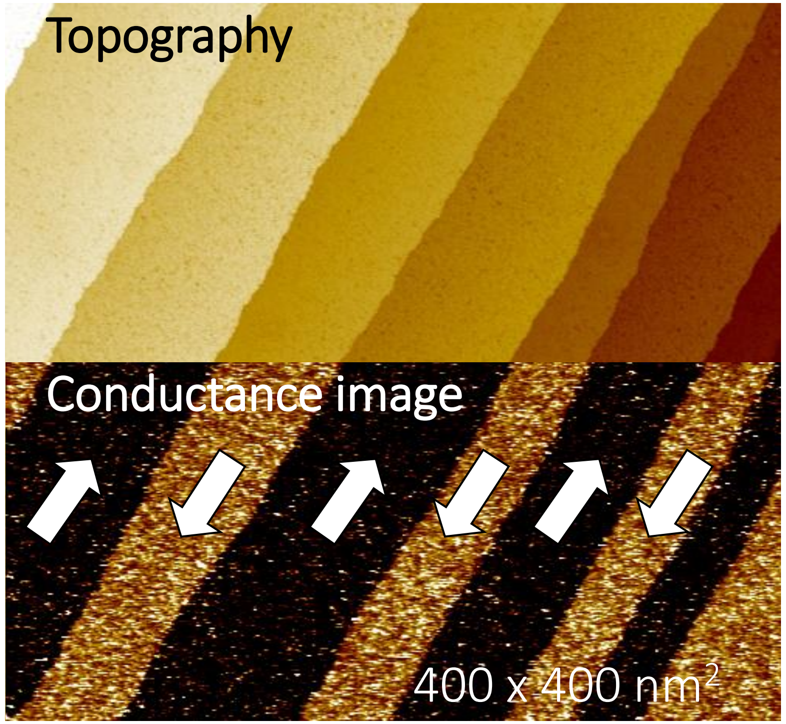
V. D. Pham et al. *npj 2D Materials and Applications* 3, 5 (2019)

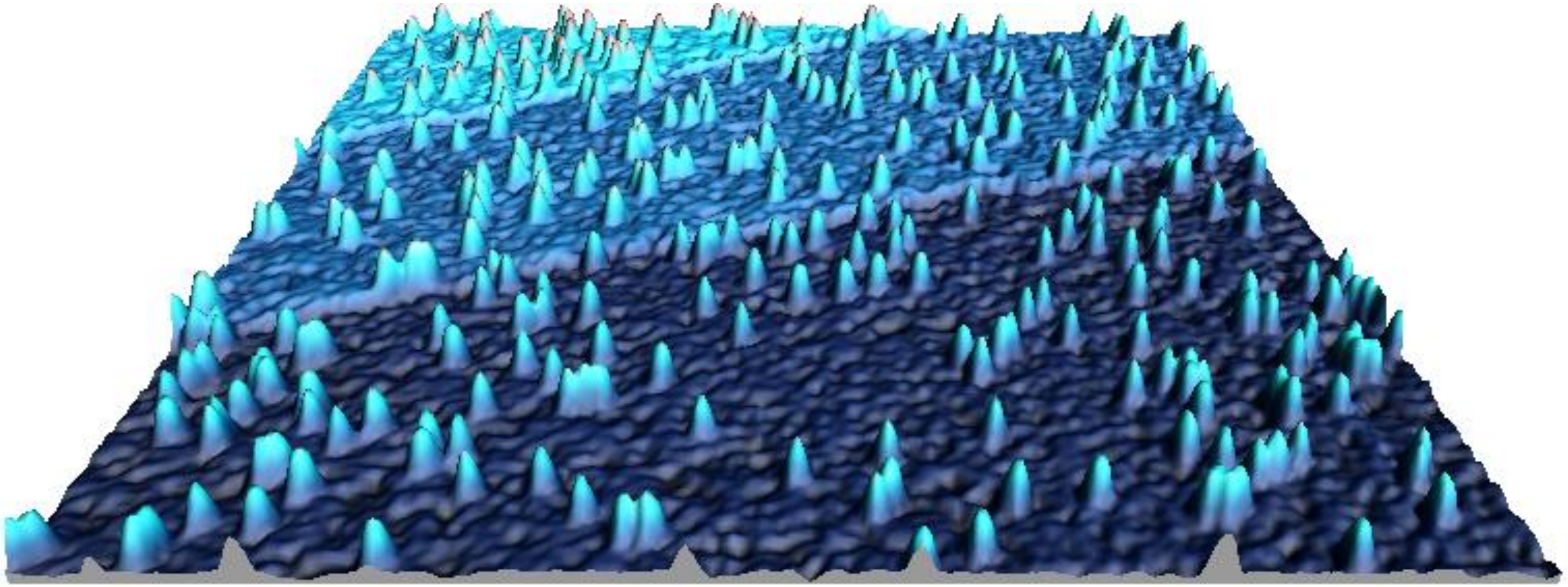
Examples of molecules on surface : C_{60}

fullerene

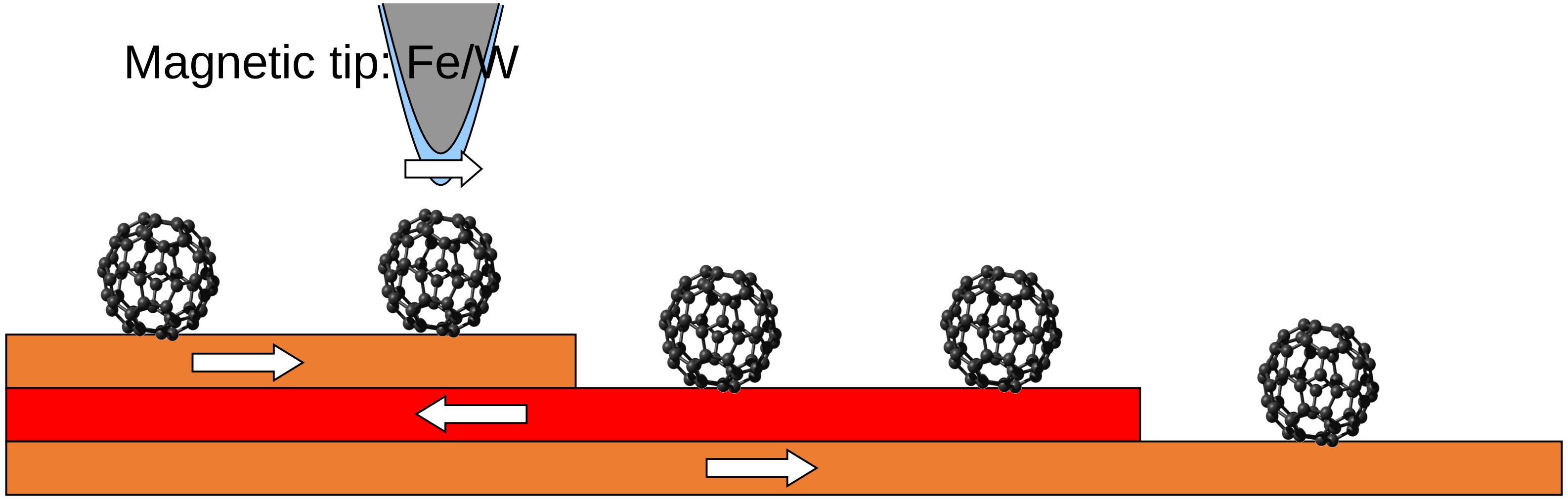


Examples of molecules on surface : C_{60} on Cr(001)





100*100 nm²

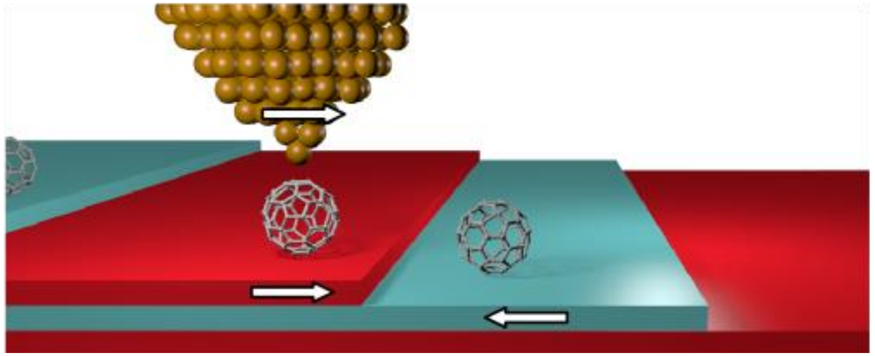


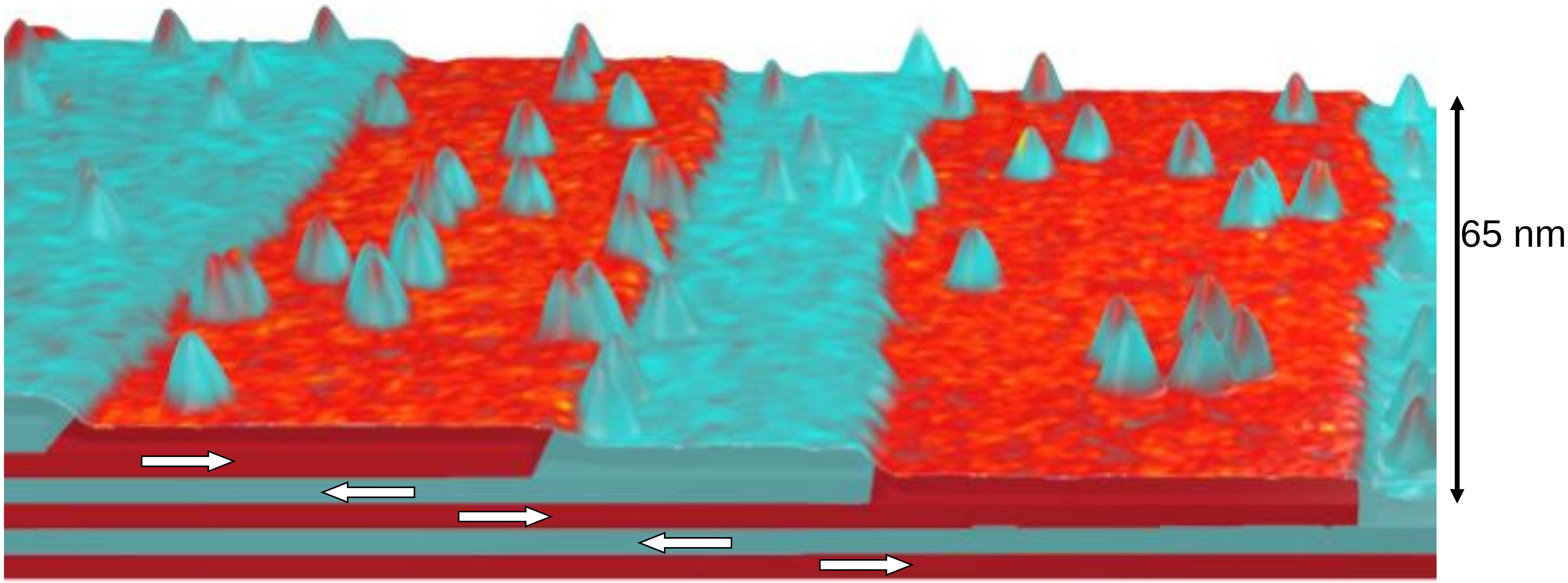
- Deposition of C_{60} at low temperature
- Compare C_{60} on spin up and spin down terraces to measure C_{60} spin polarization

Examples of molecules on surface : C_{60} on Cr(001)

- Magnetic contrast and intramolecular resolution

colorscale: conductance map at – 0.025 V

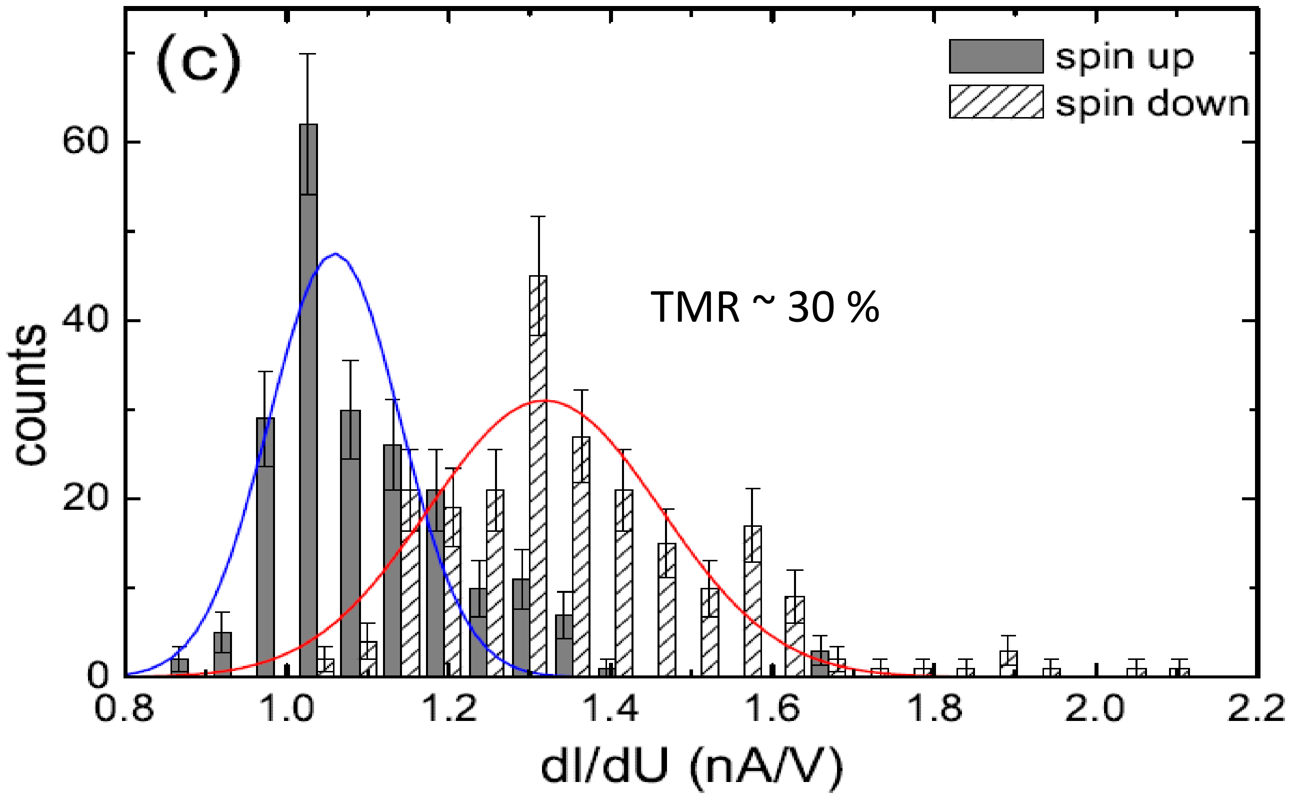




U=1 V, I=300 pA

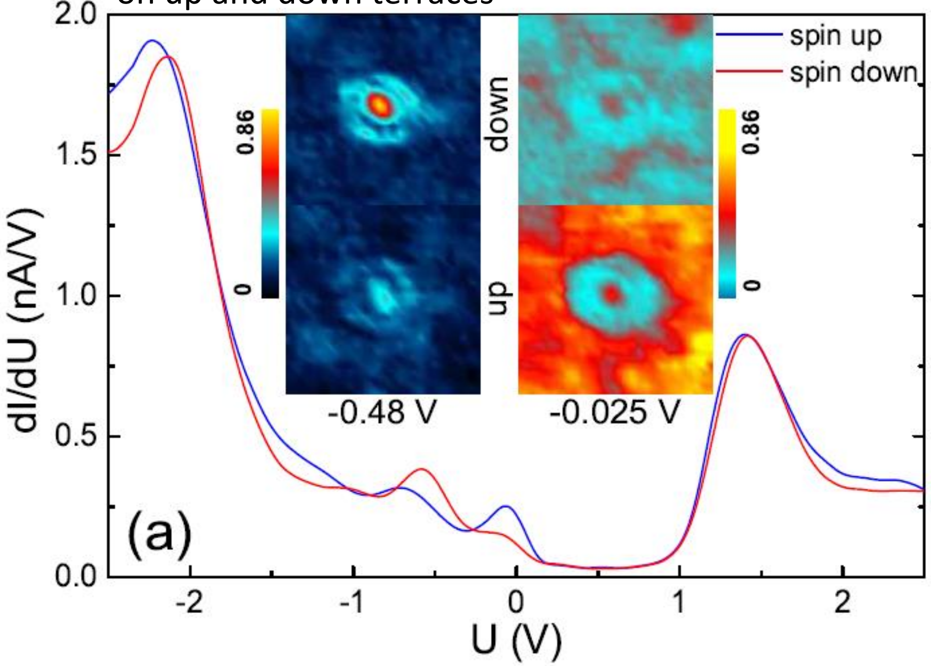
Examples of molecules on surface : C_{60} on Cr(001)

A statistical insight

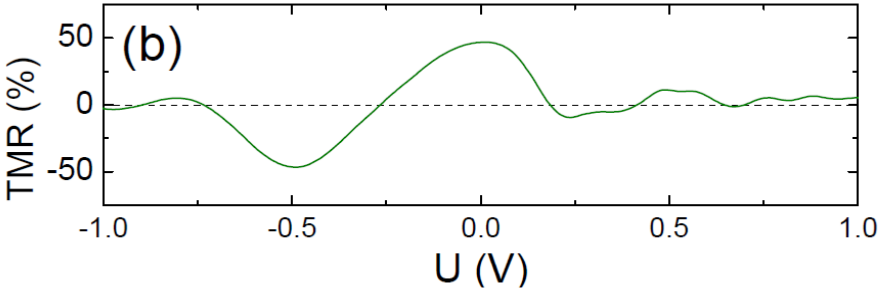


Distribution of the dI/dU values over 427 molecules (~ 50 % on both types of terraces) at -0.5 V

dI/dU spectra above the center of molecules on up and down terraces



Inversion of the TMR as a function of energy



Magnetoresistance :

$$TMR = \frac{G_{\uparrow\uparrow} - G_{\uparrow\downarrow}}{G_{\uparrow\downarrow}}$$

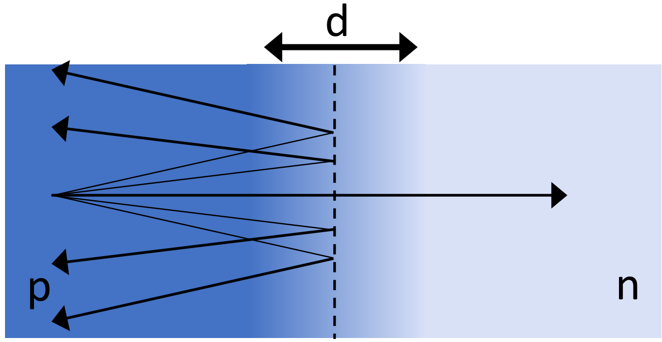
Kawahara, S. L. *et al.*, *Nano letters* (***2012***)

Focus on the elaboration of p-n junctions on N-doped graphene

Focus on the elaboration of p-n junctions on N-doped graphene

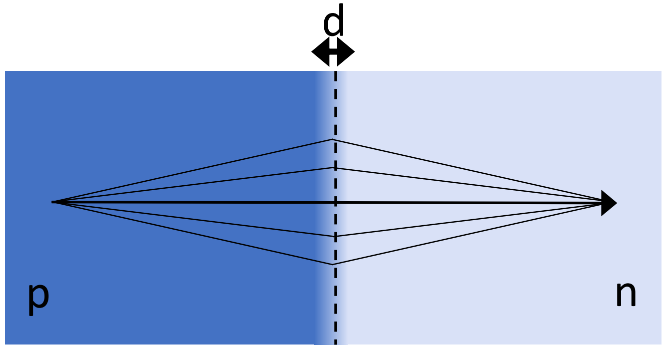
Sharp vs smooth junction

Smooth junction d > λ_F



cf. PRB 74, 041403(R) (2006)

Sharp junction d < λ_F
(d<20 nm)



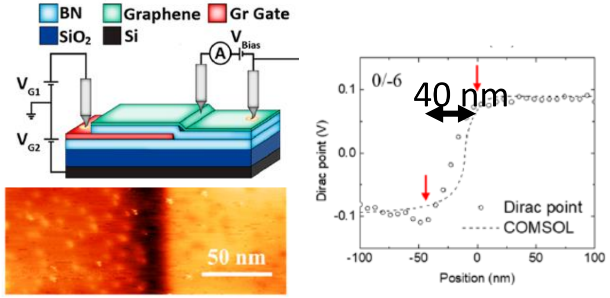
cf. Science 315, 1252 (2007)

Experimental platforms for pn junctions

Pristine graphene

External potential

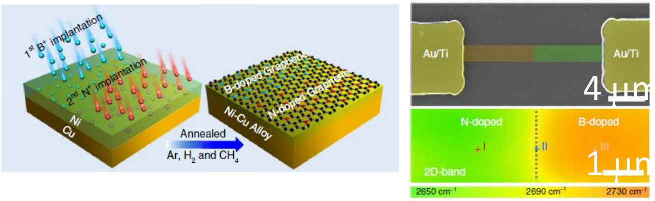
Electrostatic gating



X. Zhou … & A. N. Pasupathy
ACS Nano 13, 2558 (2019)

Doped graphene

CVD on patterned substrate



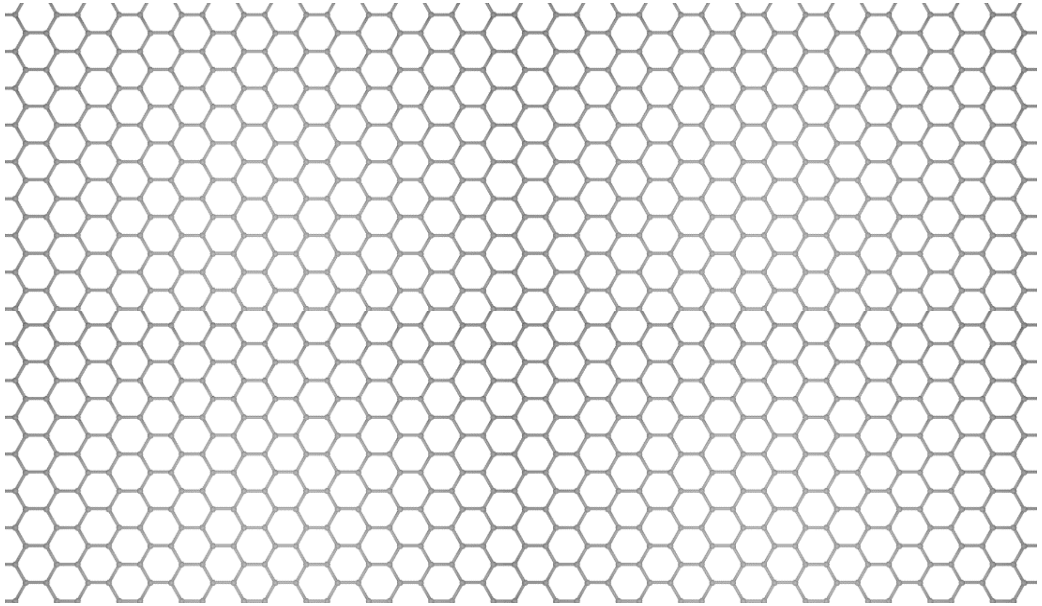
SEM

RAMAN

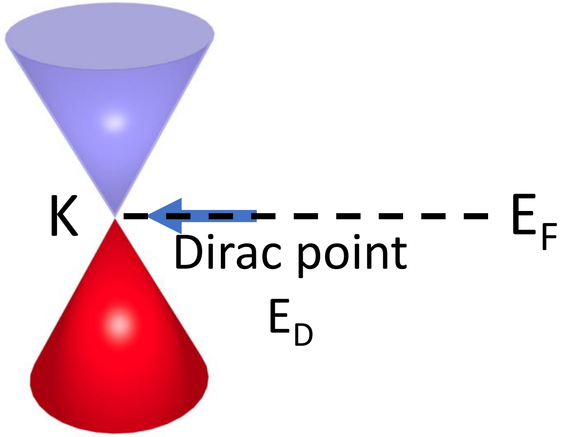
G. Wang et al., Nat. Commun. 9, 1-9 (2018)

Actual width of the junction unknown

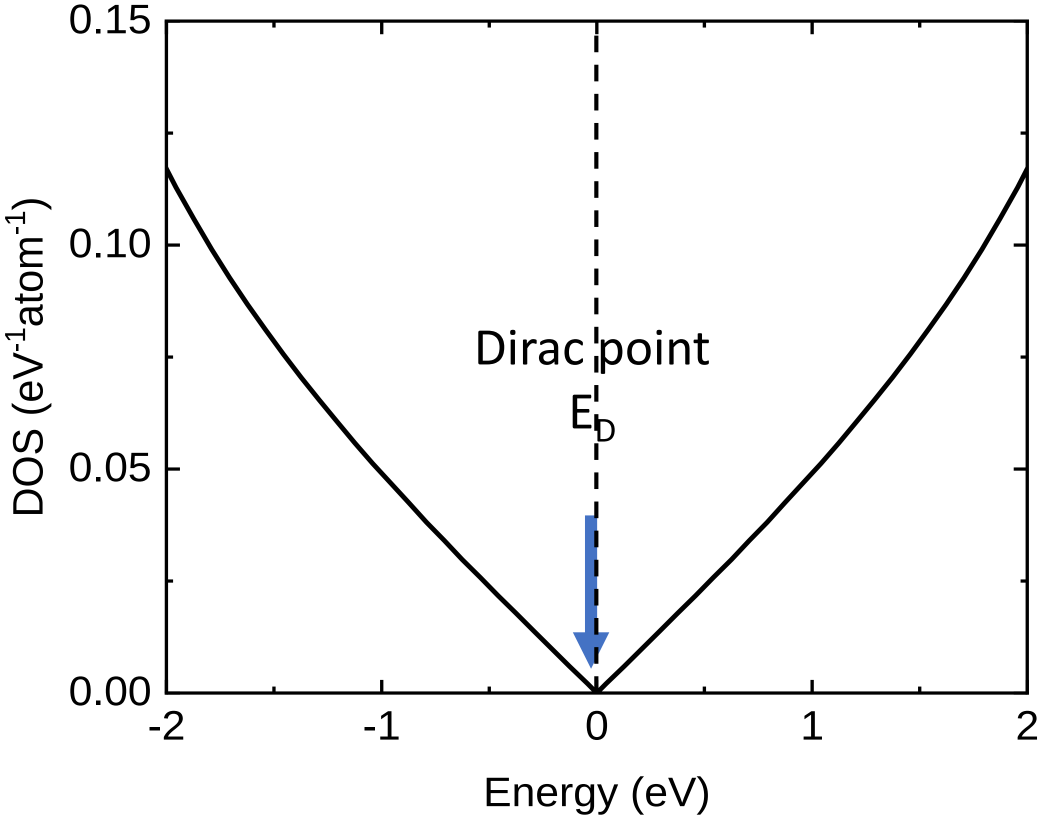
Electronic properties of graphene



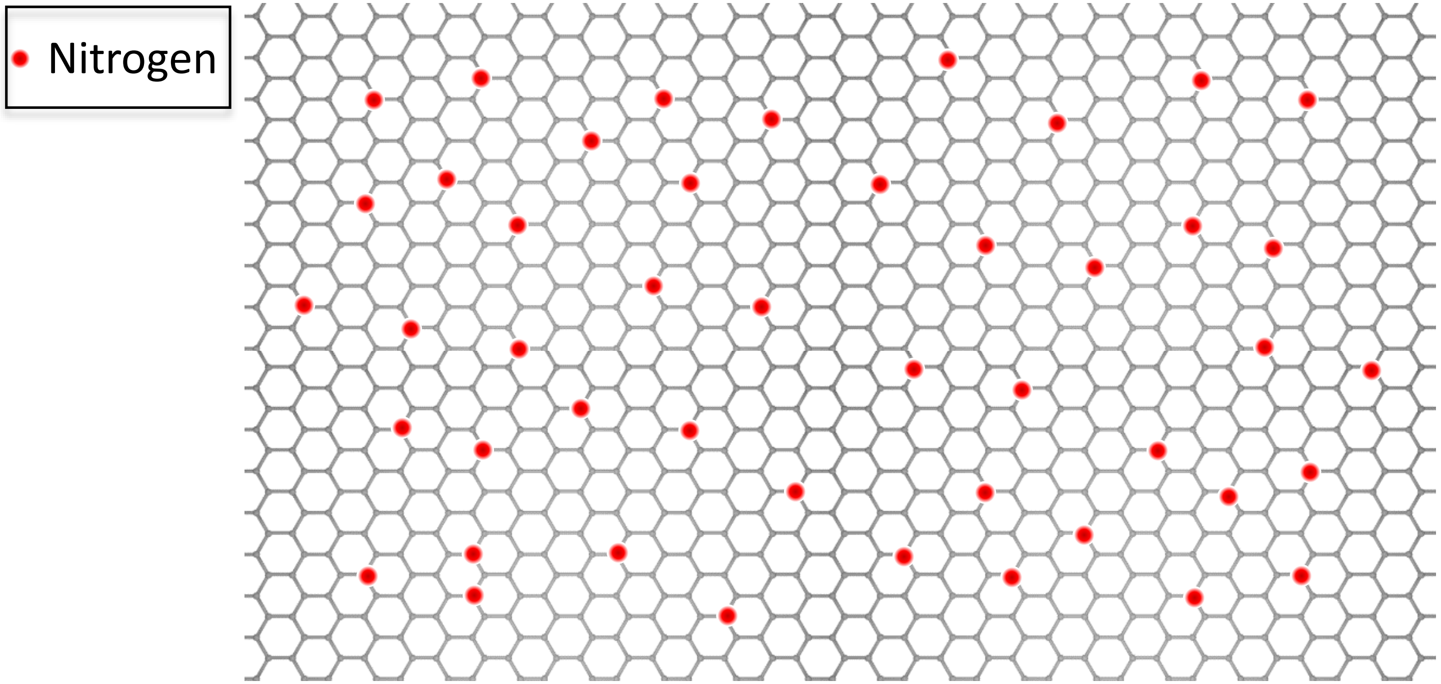
Bandstructure around K point



Density of states



Focus on the elaboration of p-n junctions on N-doped graphene

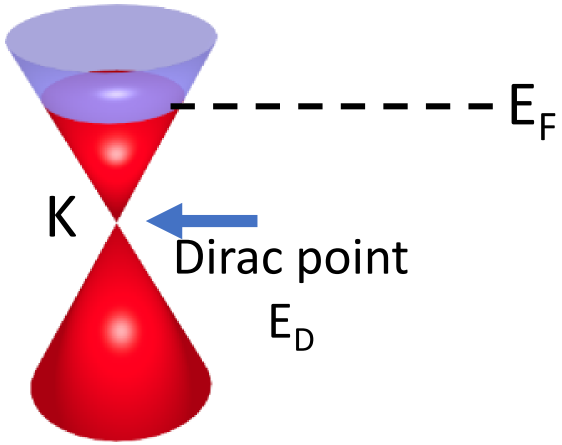


Substitutional nitrogen => n-type doping

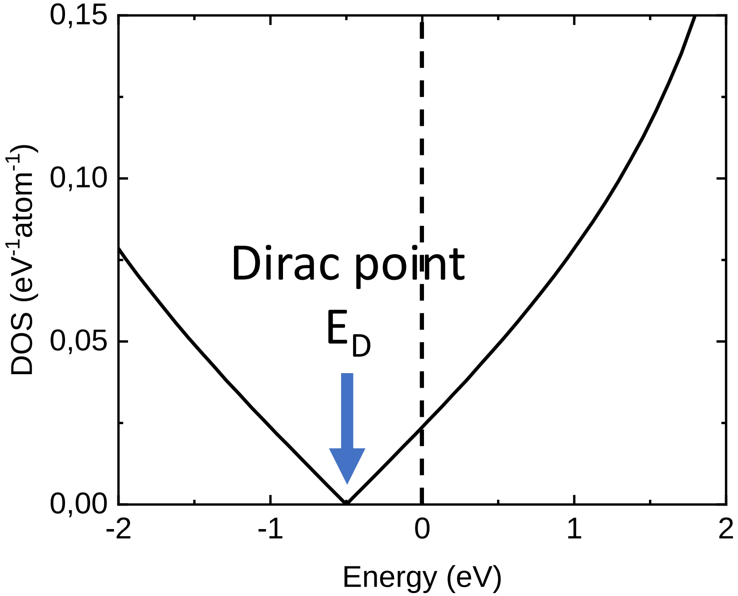
See e.g. F. Joucken et al., Phys. Rev. B 85, 161408(R) (2012)

F. Joucken et al., Scientific Report 5, 14564 (2015)

Bandstructure around K point

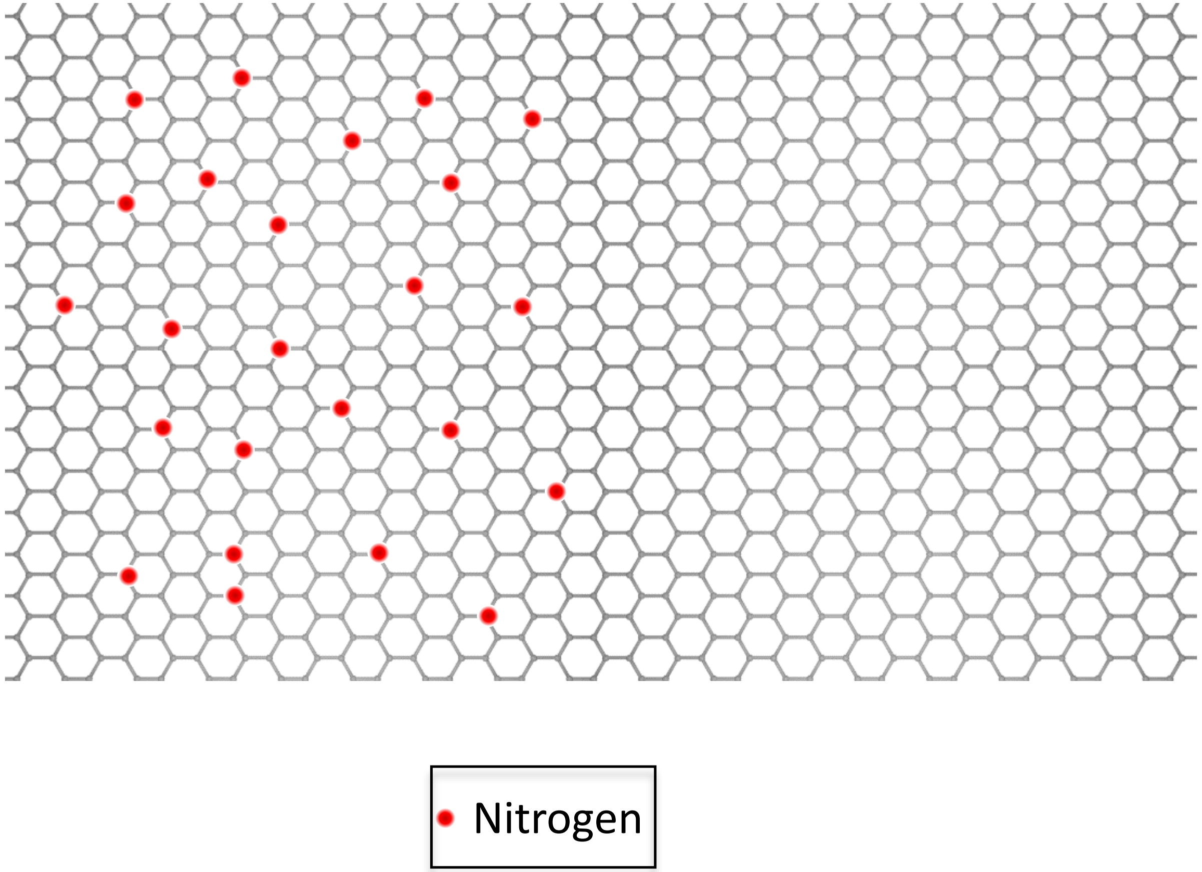


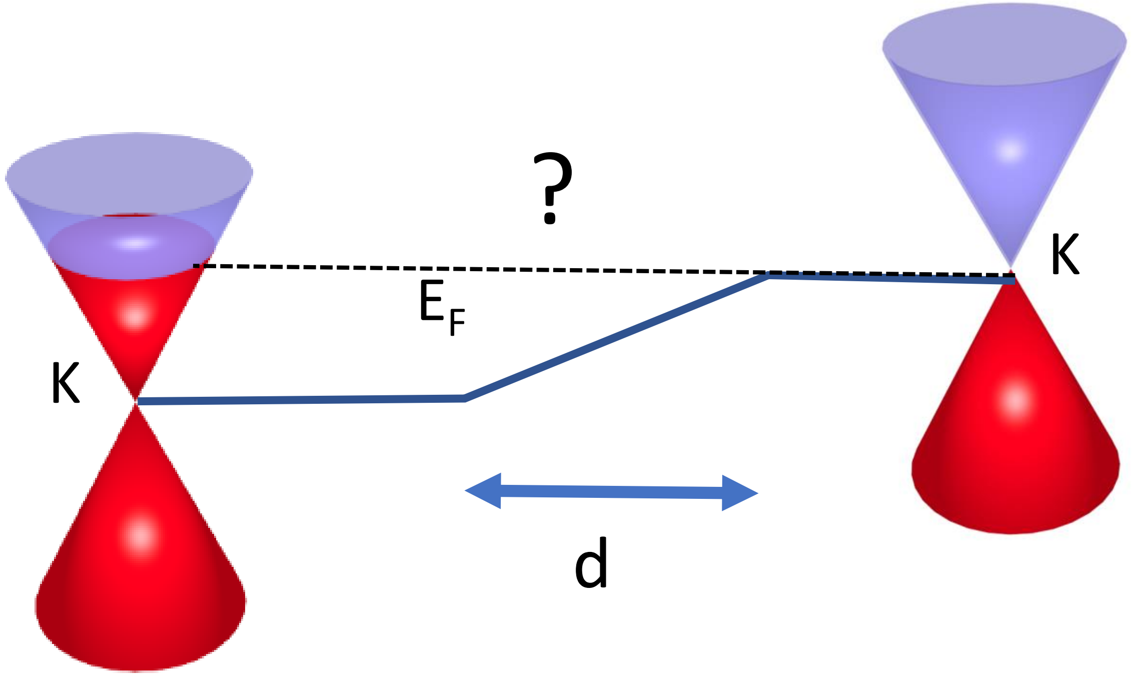
Density of states



Focus on the elaboration of p-n junctions on N-doped graphene

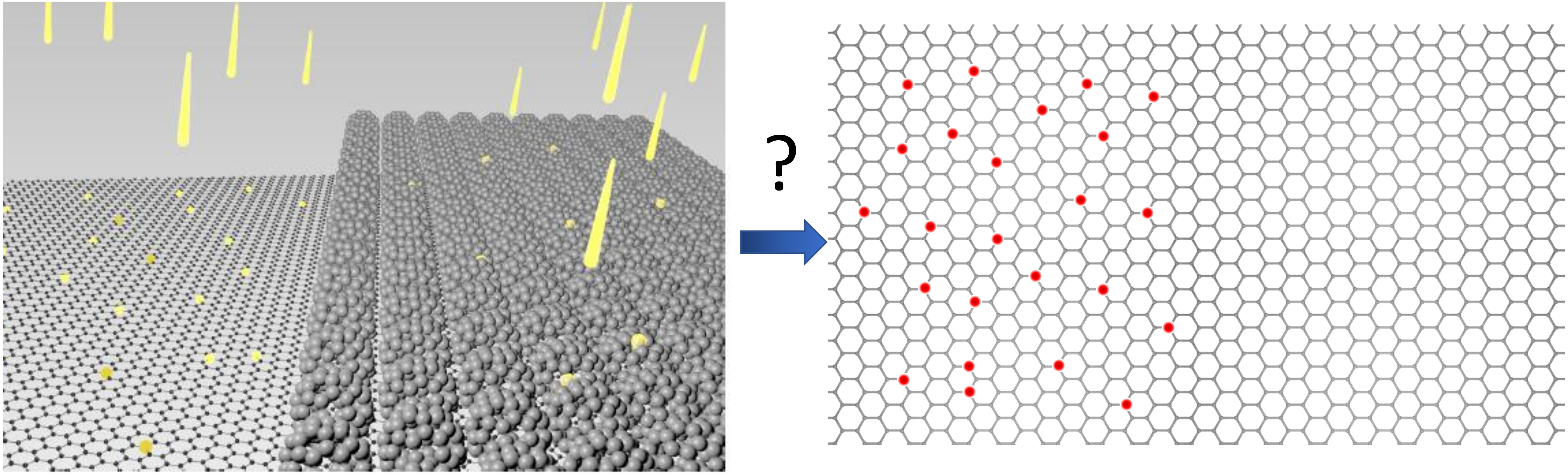
Junction in nitrogen doped graphene





Focus on the elaboration of p-n junctions on N-doped graphene

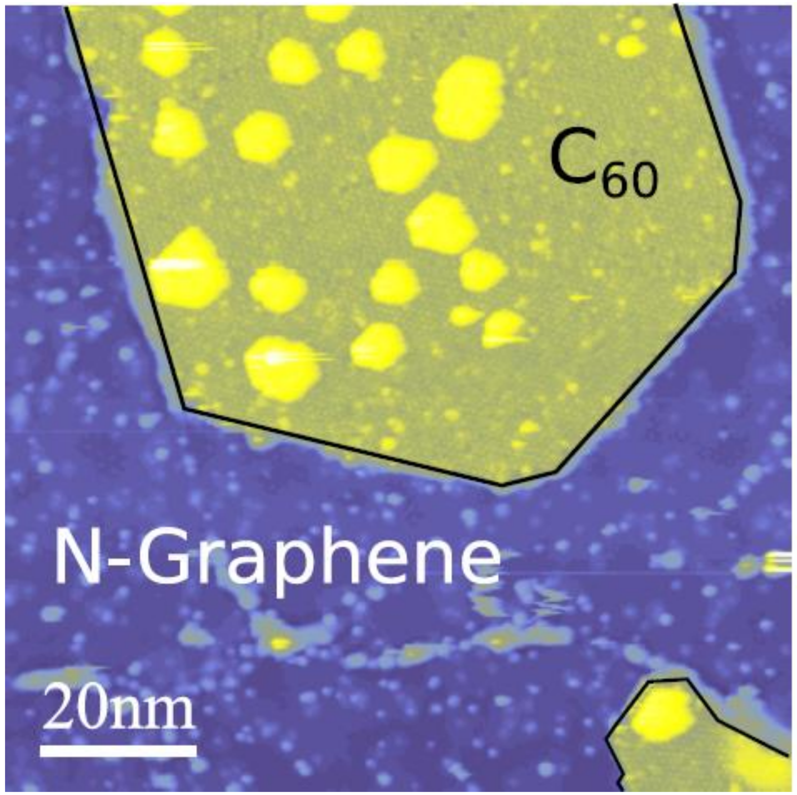
Realization of a junction in nitrogen doped graphene



Focus on the elaboration of p-n junctions on N-doped graphene

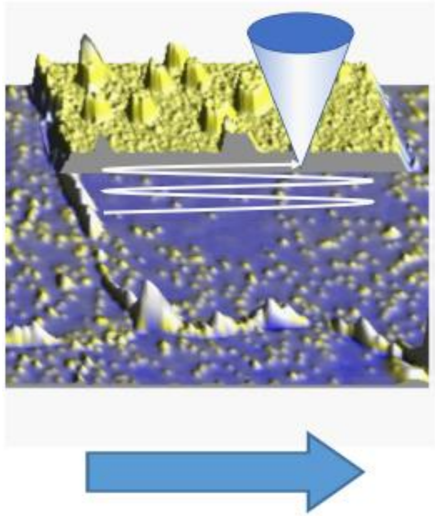
Molecular mask on graphene for nanostructuration of nitrogen doping

C_{60}/graphene after nitrogen plasma

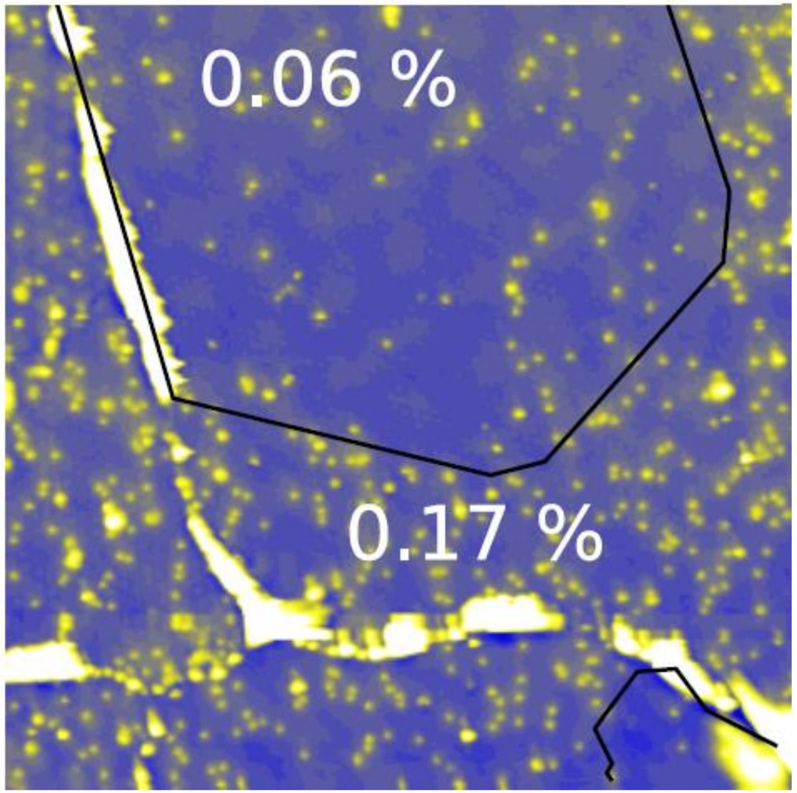


2V, 10 pA

nanoshaving



Nitrogen doping of graphene reduced below the C_{60} island

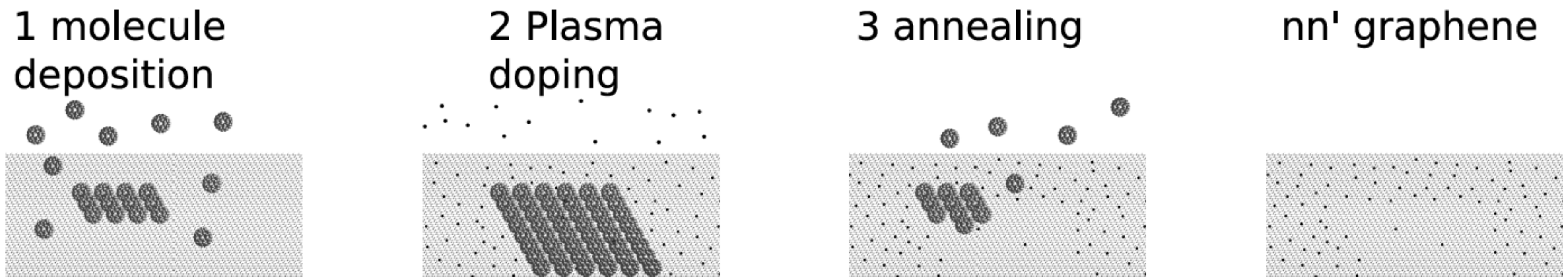


2V, 50 pA

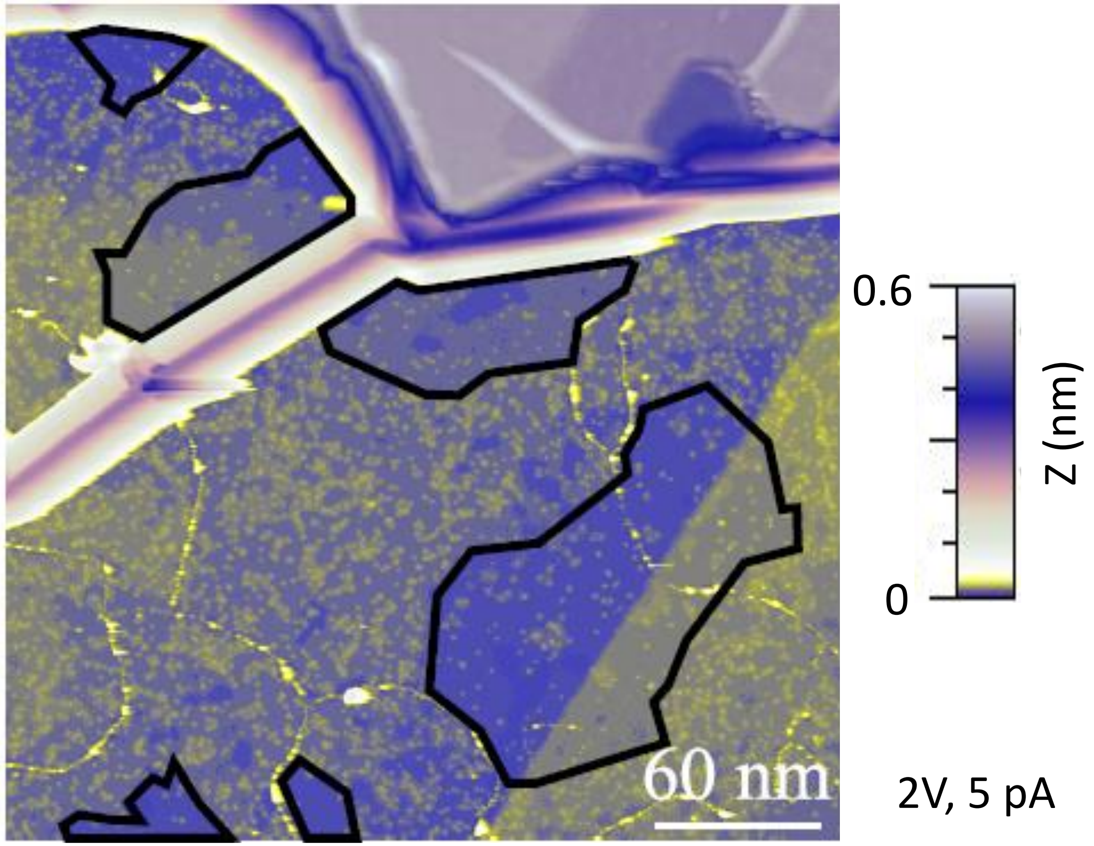
65% of incoming nitrogen species are stopped by the C_{60} monolayer

Focus on the elaboration of p-n junctions on N-doped graphene

Post synthesis 3 steps procedure to produce dopants nanodomains



Large scale STM image



2V, 5 pA

Homogeneous distribution of nanodomains on the sample => suitable for STM studies of junctions

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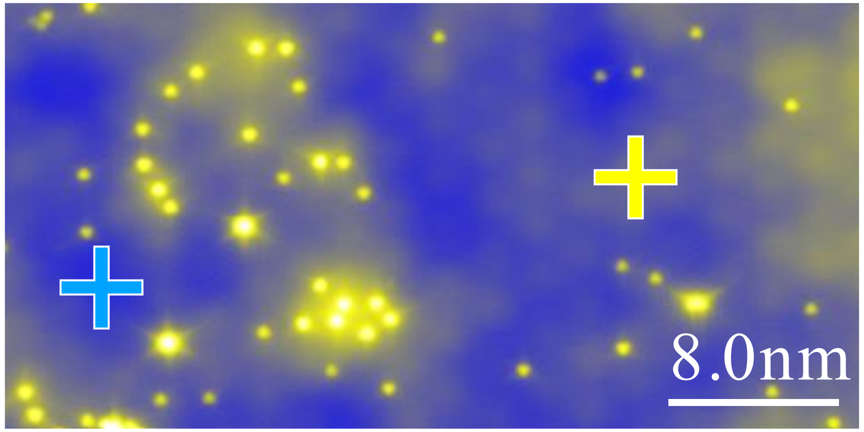
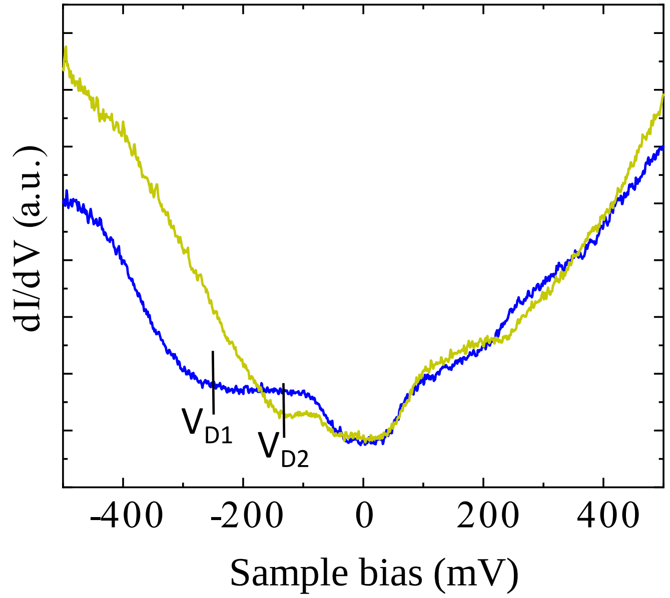
Unipolar nn’ junction in graphene: Dirac point mapping

STM image of nn’ junction



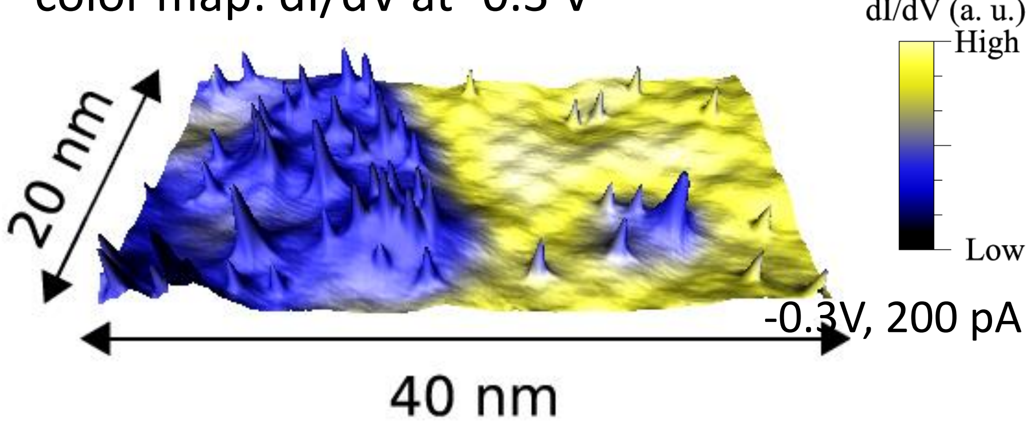
-0.3V, 200 pA

Spectroscopy on both sides of the junction



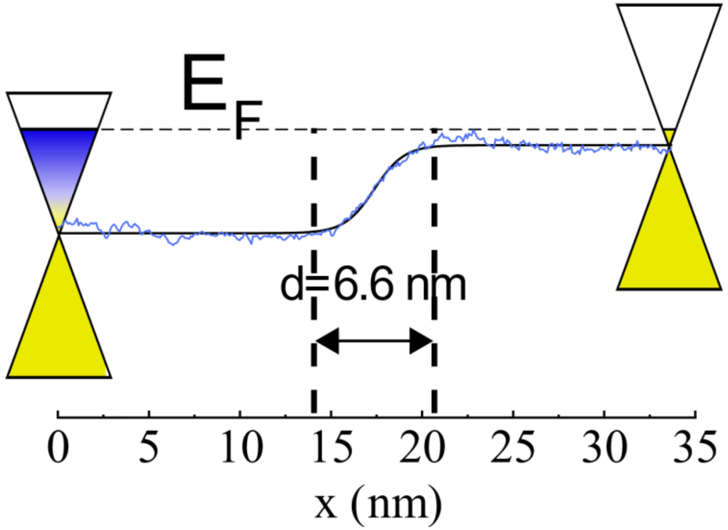
V_{D1} = -0.25 V
V_{D2} = -0.13 V

3D STM topography,
color map: dI/dV at -0.3 V



-0.3V, 200 pA

Linescan of dI/dV map through the junction



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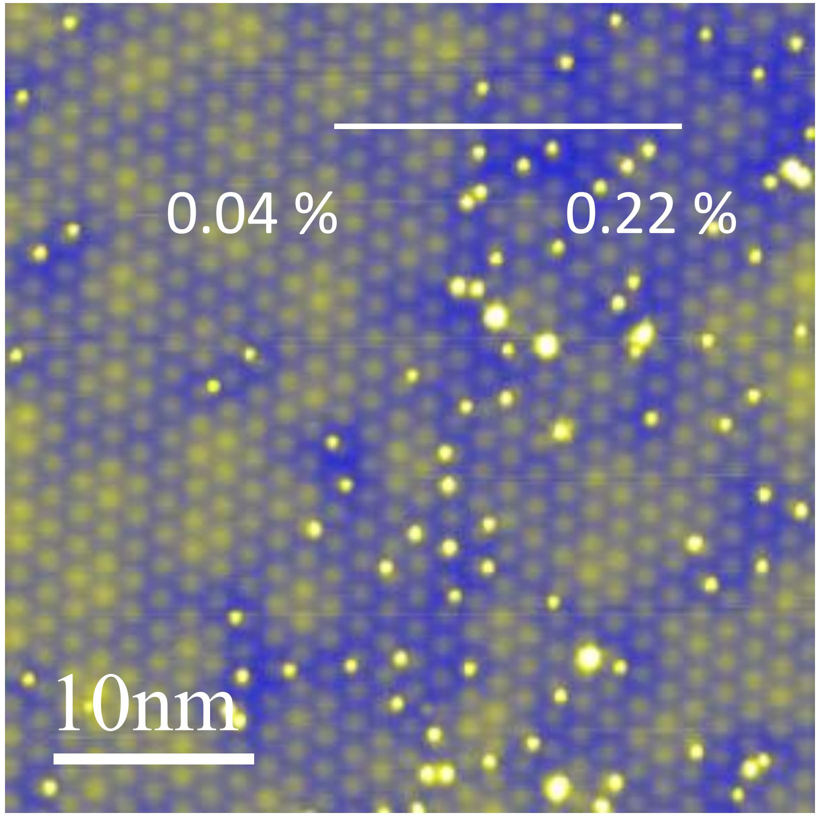
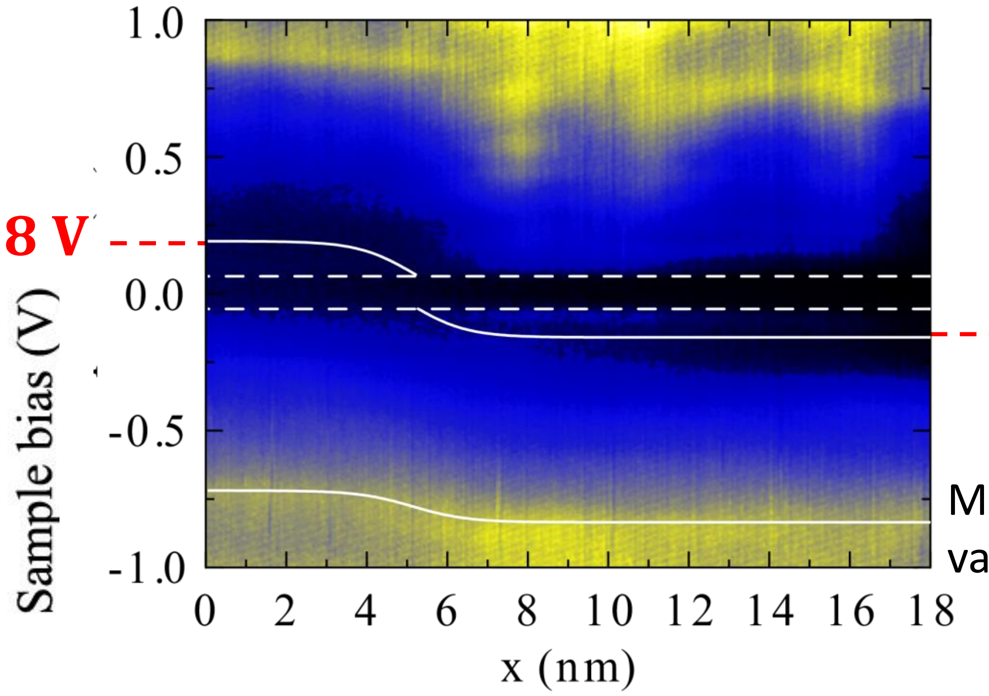
pn junction

Junction on a low doped graphene area



dI/dV along the p-n junction



+0.18 V

−0.2 V

Moiré induced van Hove singularity

On low doping regions, the natural p doping of graphene dominates the n-doping due to nitrogen

⇒ p-n junction is formed on these domains. Width 5.5 nm

Conclusions

Scanning Tunneling Microscopy (STM) and Low Temperature (LT) is a powerful technique in order to :

- See organic molecules and understand for structures on surfaces
- Evidence their electronic properties by combining experimental measurements and theoretical calculations
- Create and understand model systems which allows to imagine future working devices.