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Europe/Paris timezone

Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

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Les Houches
Bologna

Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

Area della Ricerca di Bologna

- **Chemistry**
- **Micro-electronics**
- **Material science**
- **Astrophysics**
- **Agronomy**

Etc.

ISOF: Istituto per la Sintesi Organica e la Fotoreattivita'

- New methodologies of organic synthesis
- New photoluminescent organic molecules: synthesis and assembling into functional nanostructures
- Bio-organic processes
- New materials and nanotecnology

- Supramolecular systems
- Photochemistry and catalisist
- Radical reaction chemistru
- Macromolecular systems

Nanochemistry Lab

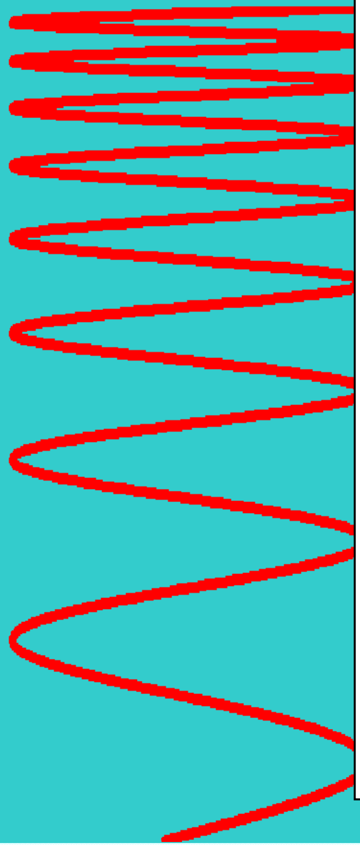
WHY?

WHAT?

HOW?

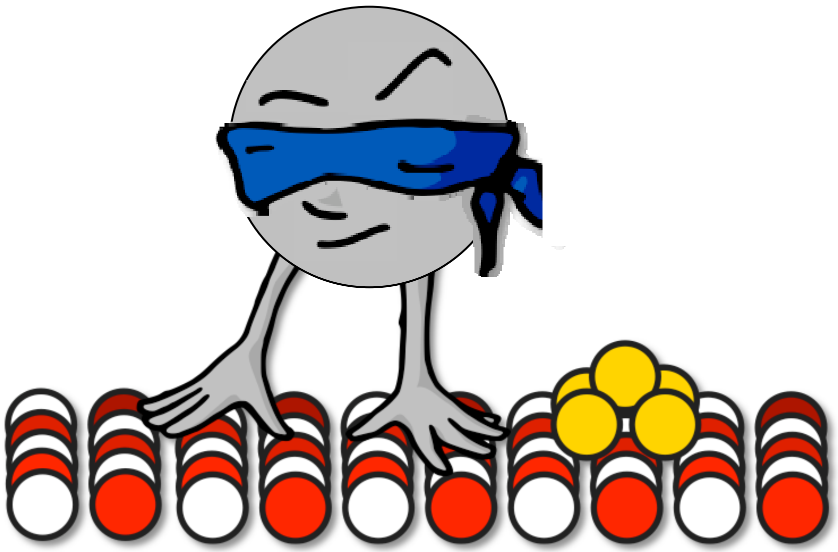
WHY?

de Broglie wavelength (λ_{dB})



Temperature (K)	E... (meV)	Velocity	λ... (nm)

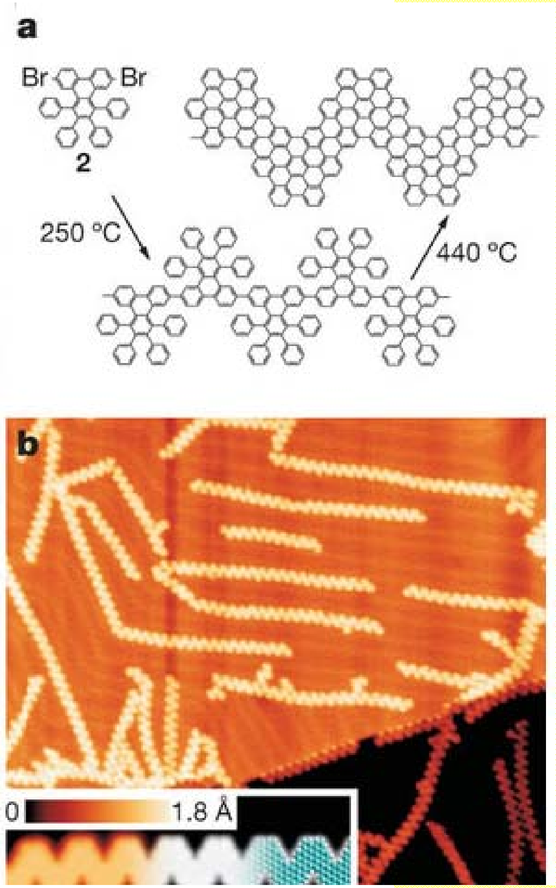
UCNs feel nanoscale world



WHAT?

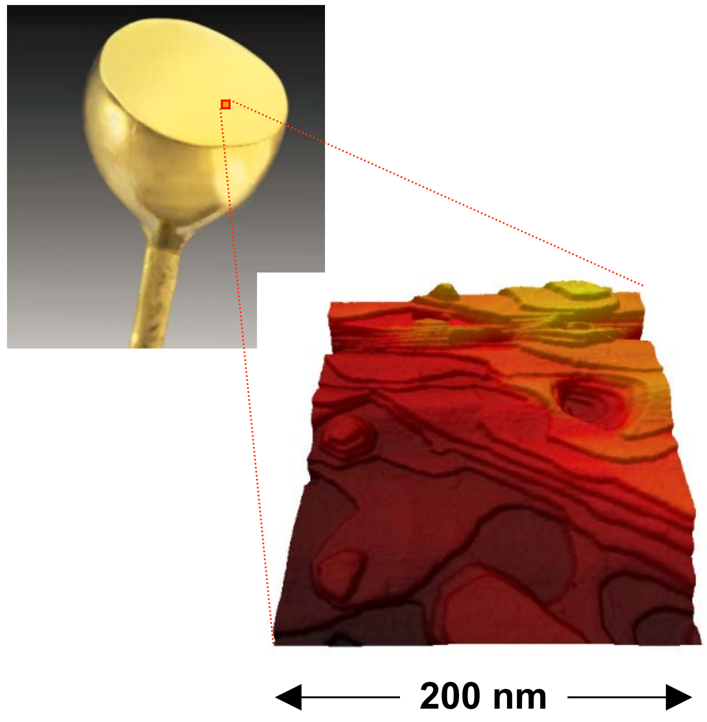
Nanoscale

Nano-objects



Cai J. et al., Nature 466, 470–473 (2010)

Nanoscaled-objects



http://www.specs.de/cms/upload/PDFs/ApplNotes/AFM/AN_NCAFM_AtomicResolution_Au111.pdf

HOW?

Electron microscopy (TEM, SEM)

Lat Res: 1 Å

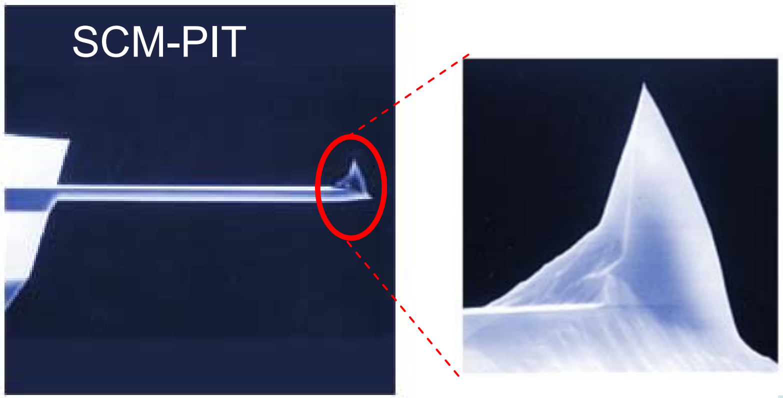
Vacuum
(10^{-9} mbar)

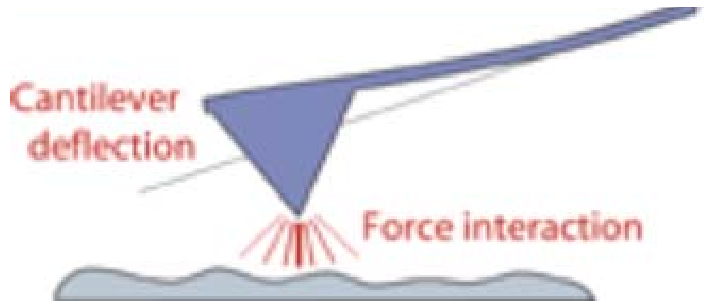
Scanning Probe Microscopy (SPM)

Lat Res: 1 Å – 1 nm

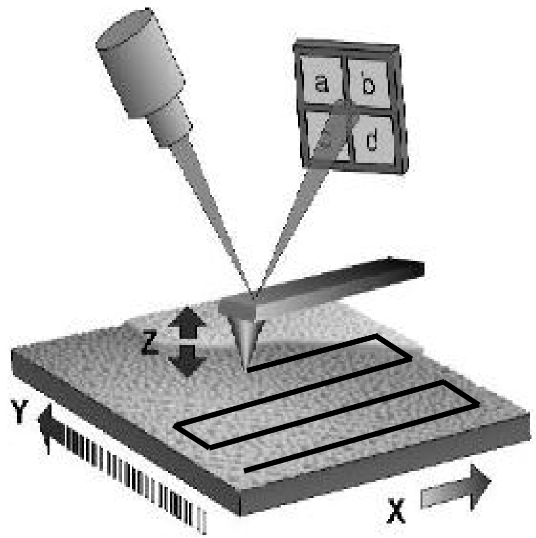
Slow tecnique
(μm^2 / min)

SPM technique, image acquisition





- Tip at free end of a flexible cantilver
- Deflection due to the tip-sample forces
- Cantilever raster scanned over the sample
- Measurement of the Z-adjustment



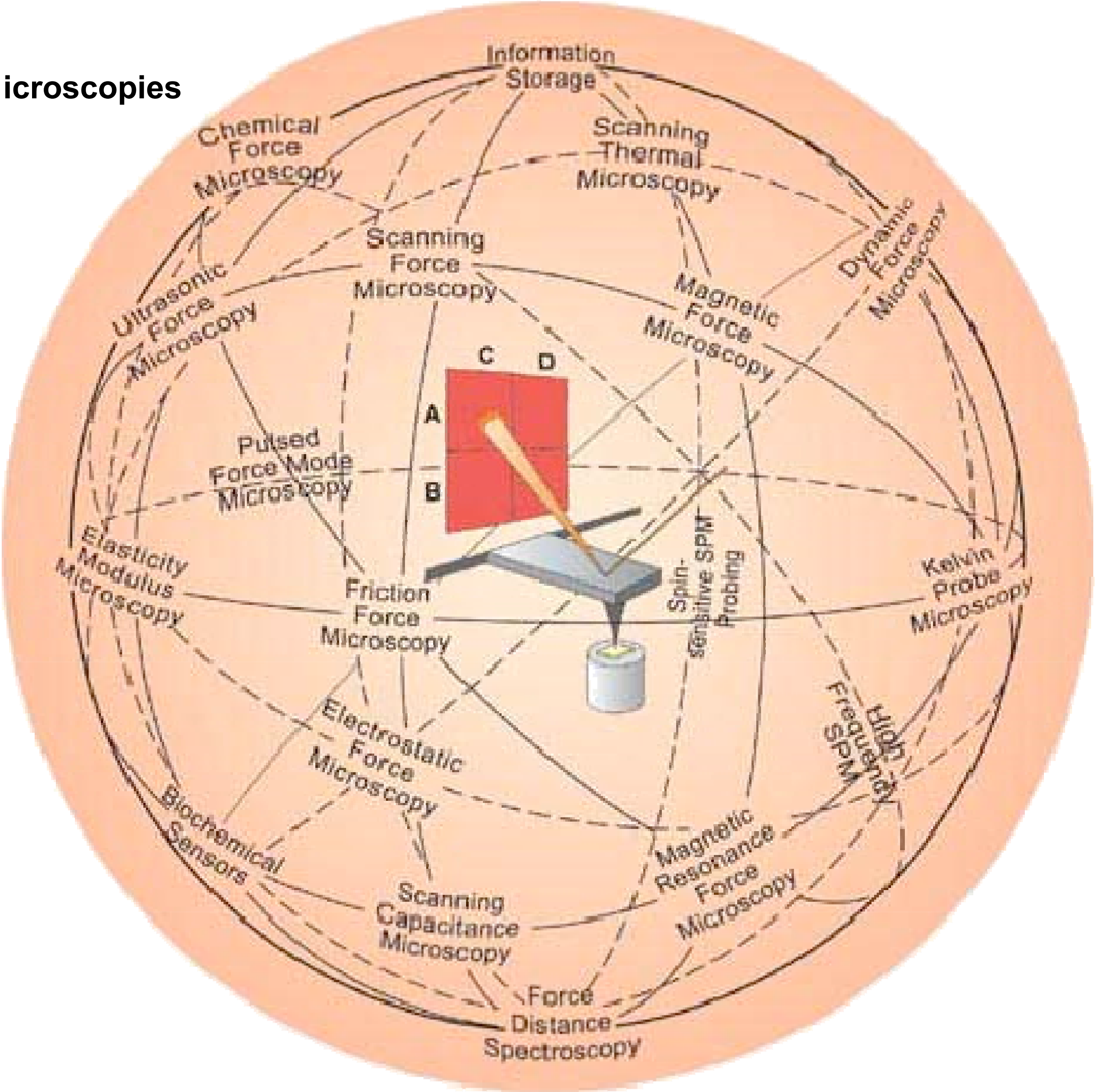
Surface topography
n$\times$m matrix

Scanning PROBE Microscopies

FORCE

Interactions:

- Van der Waals
- Electrostatic
- Magnetic
- Capacitive
- Frictional
- etc...

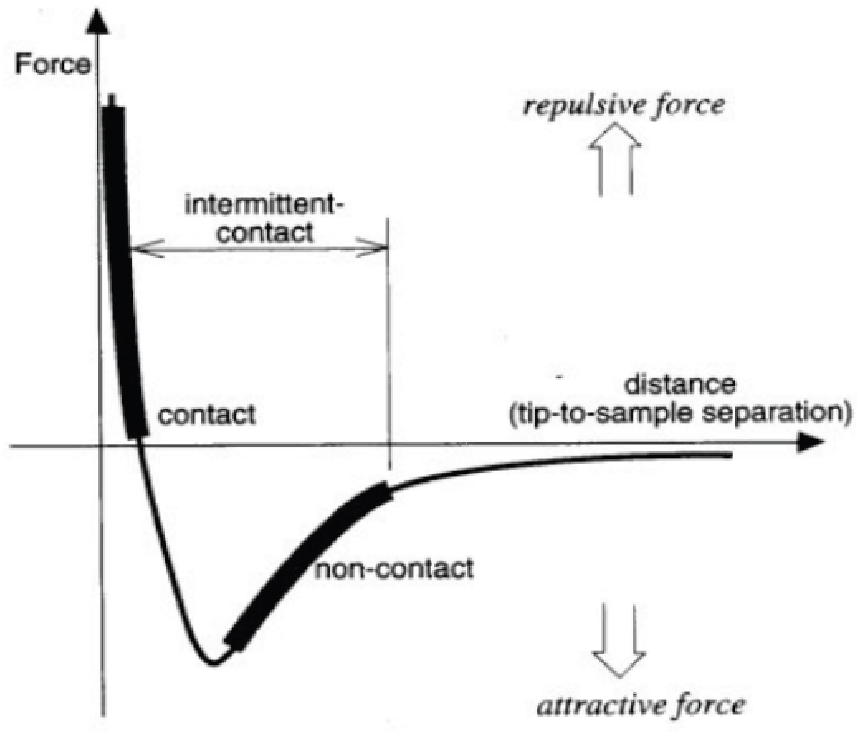


1986. First AFM microscope

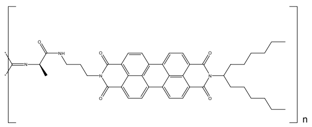
Gerd Binnig, Calvin Quate, Christoph Gerber

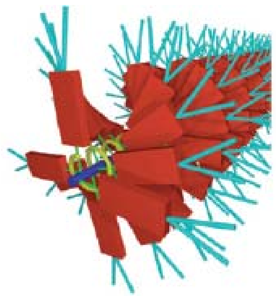
Atomic Force Microscopy (AFM)

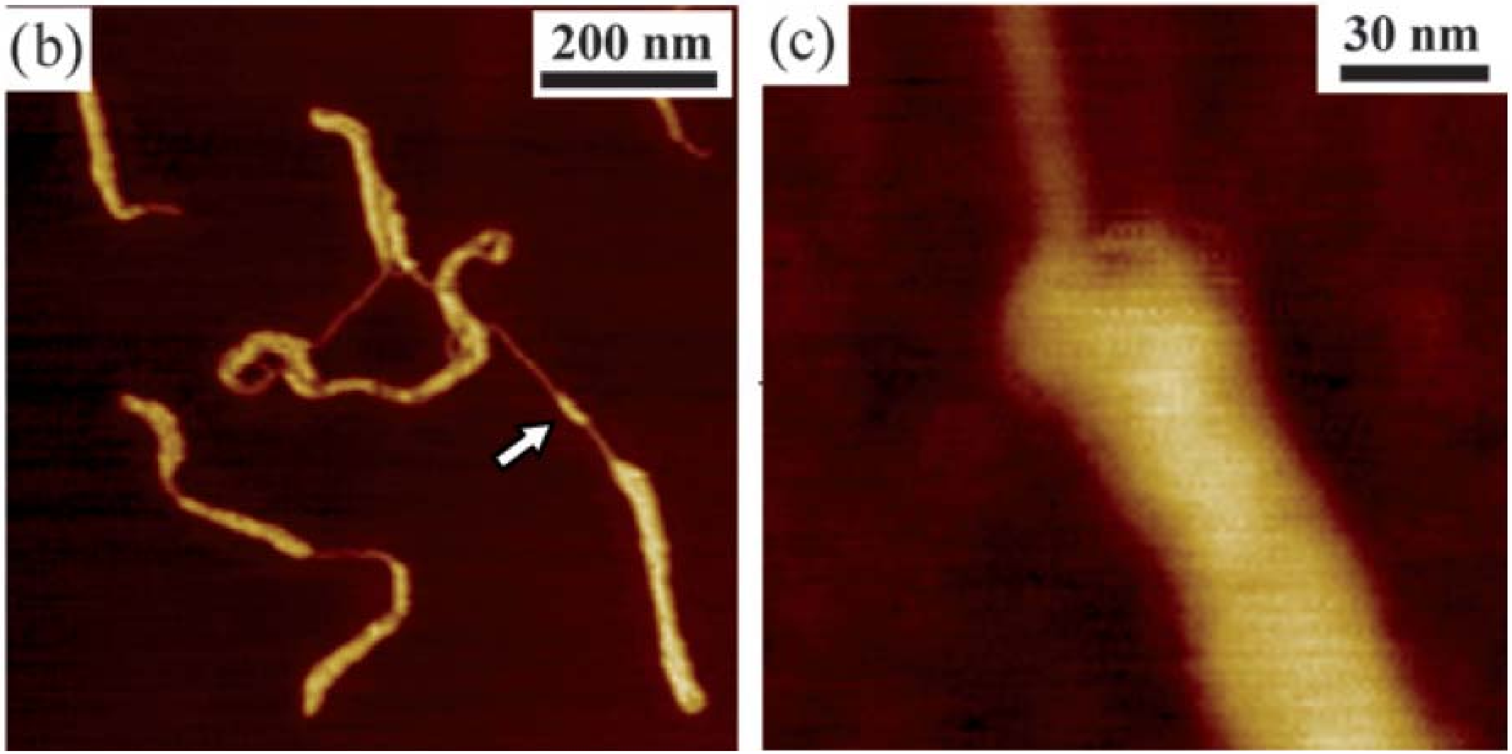
Probe = vdW FORCE



AFM, high resolution in air







Z range = 5 nm

Z range = 5 nm

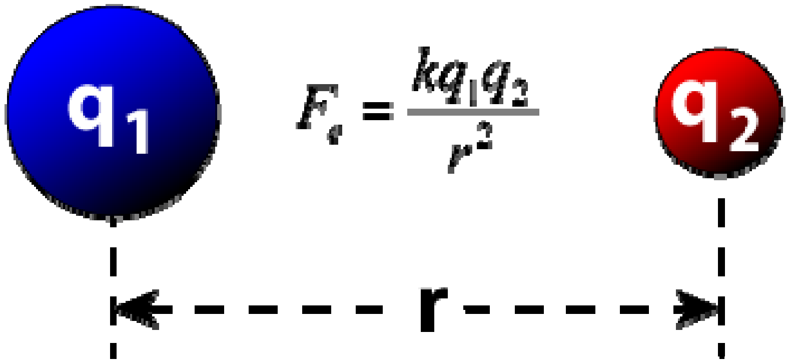
Palermo V., Schwartz E., Liscio A., Otten M.B.J, Müllen K., Nolte R.J.M., Rowan A.E., Samorı` P., *Soft Matter* (2010) **5**, 4680–4686

1991. First KPFM microscope

N Nonnenmacher et al., *APL* **58**, 2921

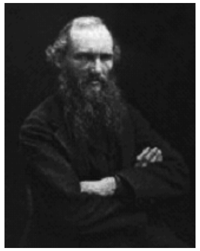
Kelvin Probe Force Microscopy (KPFM)

Probe = Electrostatic FORCE



$$F_e = \frac{kq_1q_2}{r^2}$$

Kelvin Probe FORCE Microscopy



William Thomson,
a.k.a. Lord Kelvin, 1898

Work function measurement
of metallic and semi-conductive samples

Vibrating capacitor
Zisman method (1932)

$$i\,(t) = (V - V_{cpd})\,\frac{dC}{dt}$$

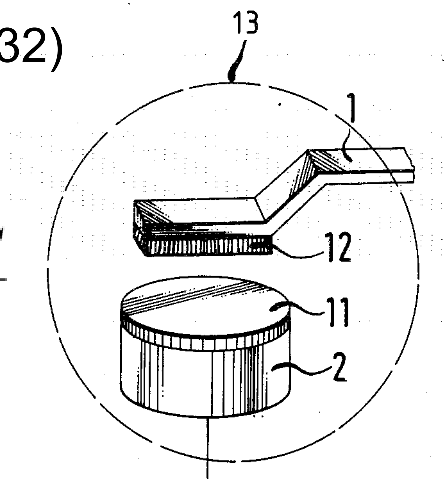
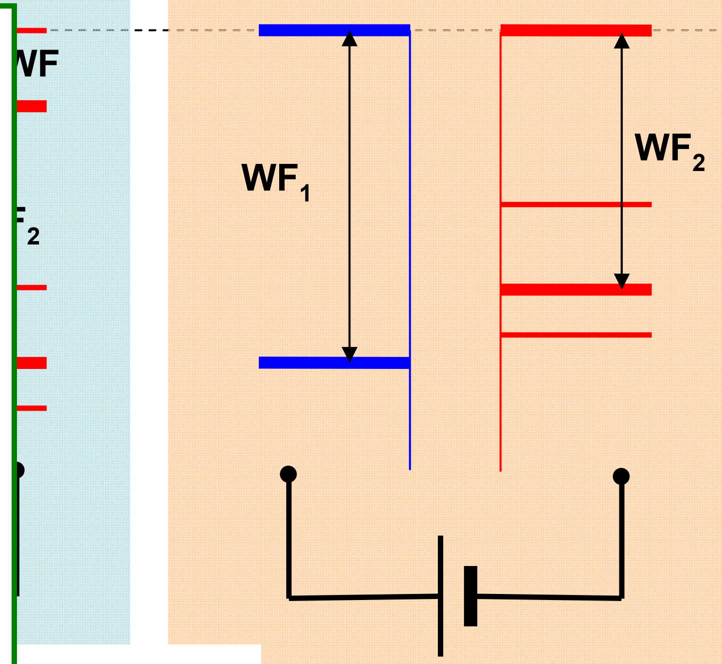


FIG. 1A

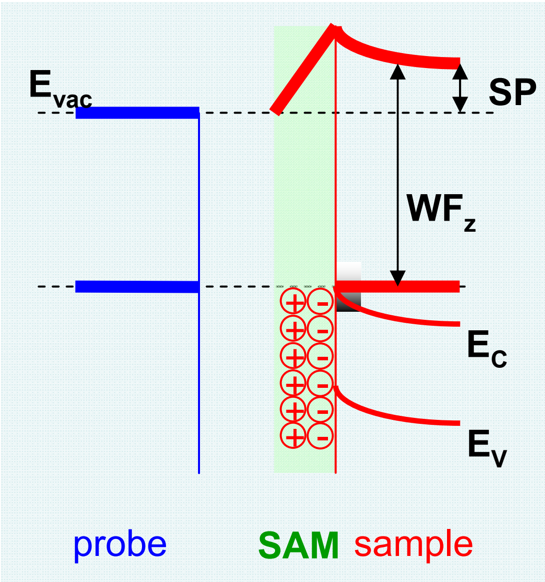
U.S. Patent



a.k.a. CPD
a.k.a. SP

$V_{bias} = \Delta WF$

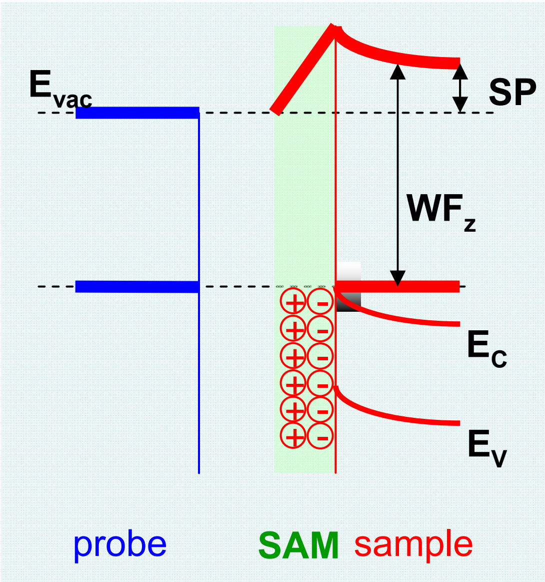
Kelvin Probe FORCE Microscopy



Measurements on SAM and thin film

- tip-sample work function difference (ΔWF)
- thin film dipole (μ_{SAM})
- band-bending
- interface bonding
- fixed charges

Kelvin Probe FORCE Microscopy



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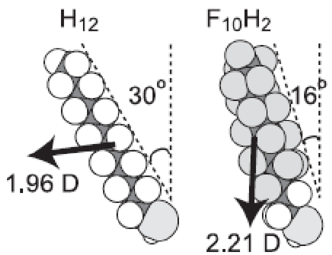
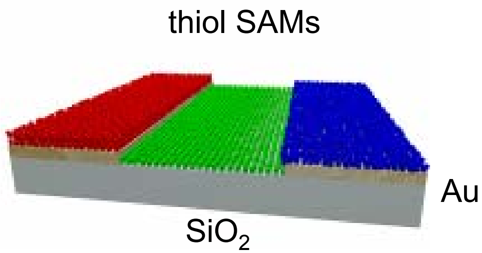


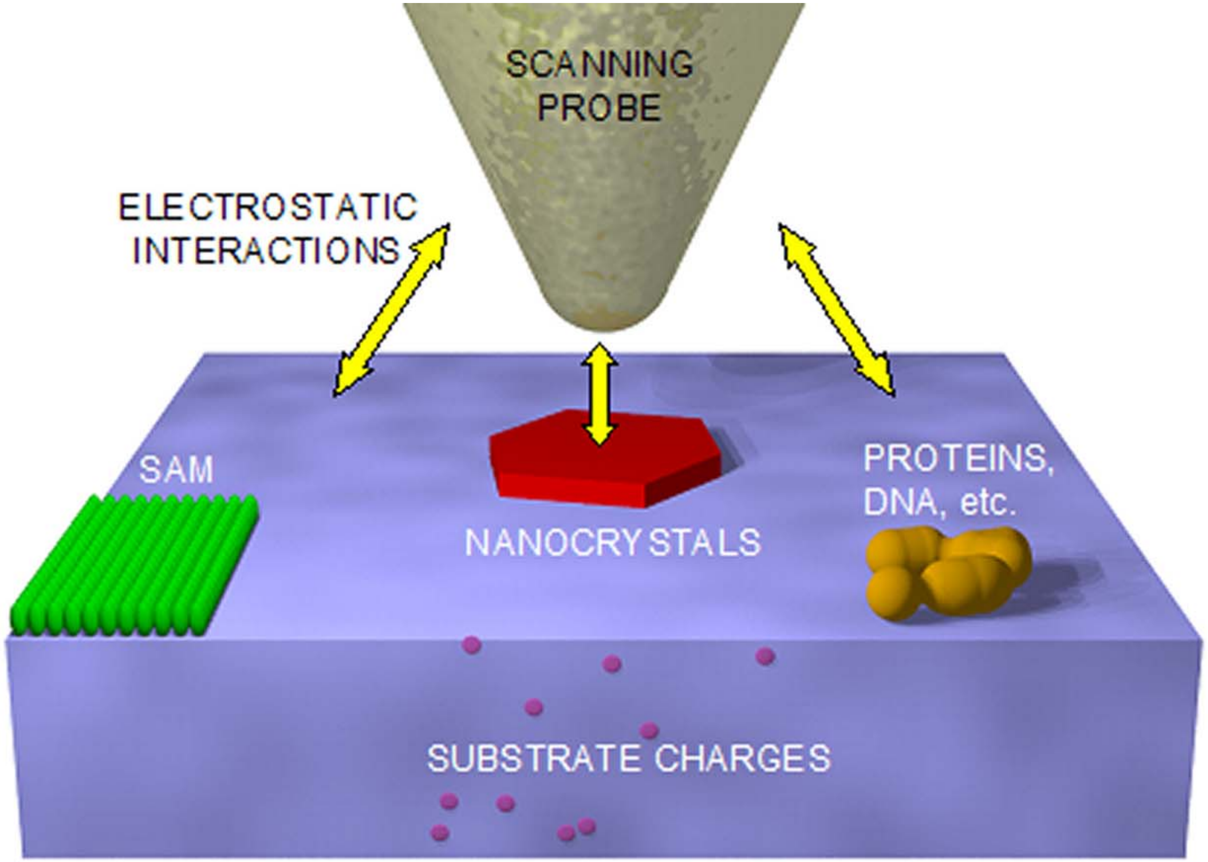
Alkanethiol (H_{12})
Fluoroalkanethiol ($F_{10}H_2$)



$$SP_{SAM/Au} = WF_{Au} + A \cdot \mu_{thiol,\perp} / \varepsilon_{thiol}$$

[KP] Alloway D.M. et al. *Journ. Phys. Chem. B* **107** (2003), 11690-11699
[KPFM] Saito N. et al., *Surf. Interface Anal.* **34** (2002), 601-605
[KPFM] Liscio A. et al., *Adv. Mat.* **22** (2010), 5018-5023

Kelvin Probe FORCE Microscopy



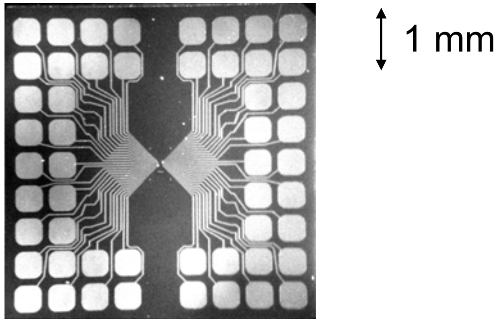
AFM setup

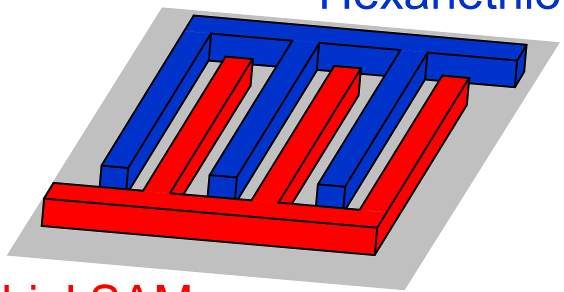
• Metals
• Semiconductors
• Thin insulators

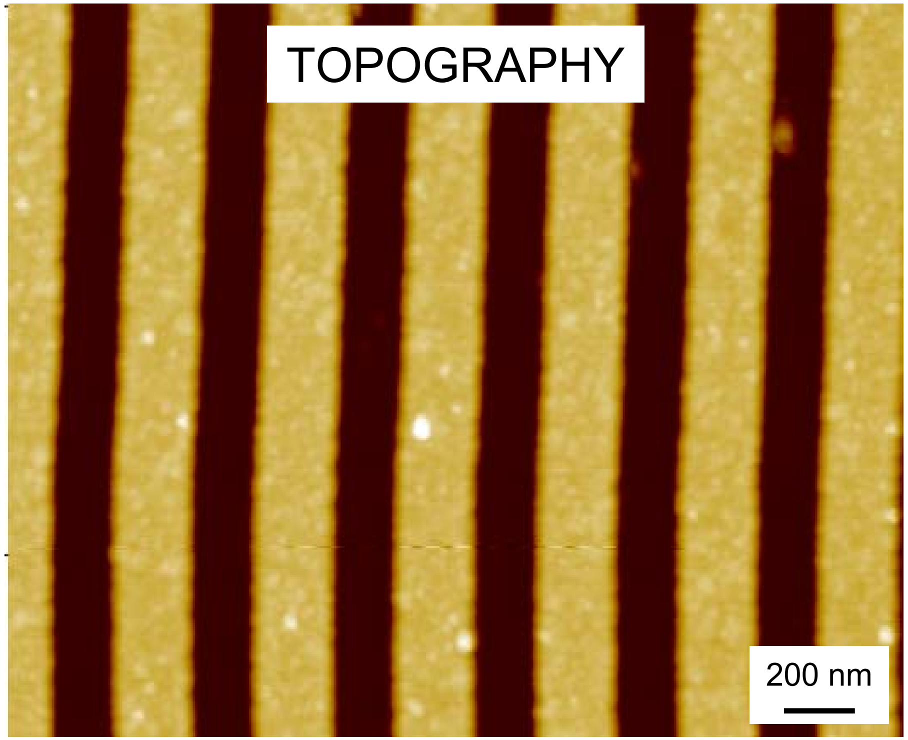
Morphology &
Surface Potential
<u>simultaneously</u>

V. Palermo, M. Palma and P. Samorì, *Adv. Mater.* (Review Article) **2006**, *18*, 145-164
A. Liscio, V. Palermo and P. Samorì, *Acc. Chem. Res.* **2010**, *43*, 541-550

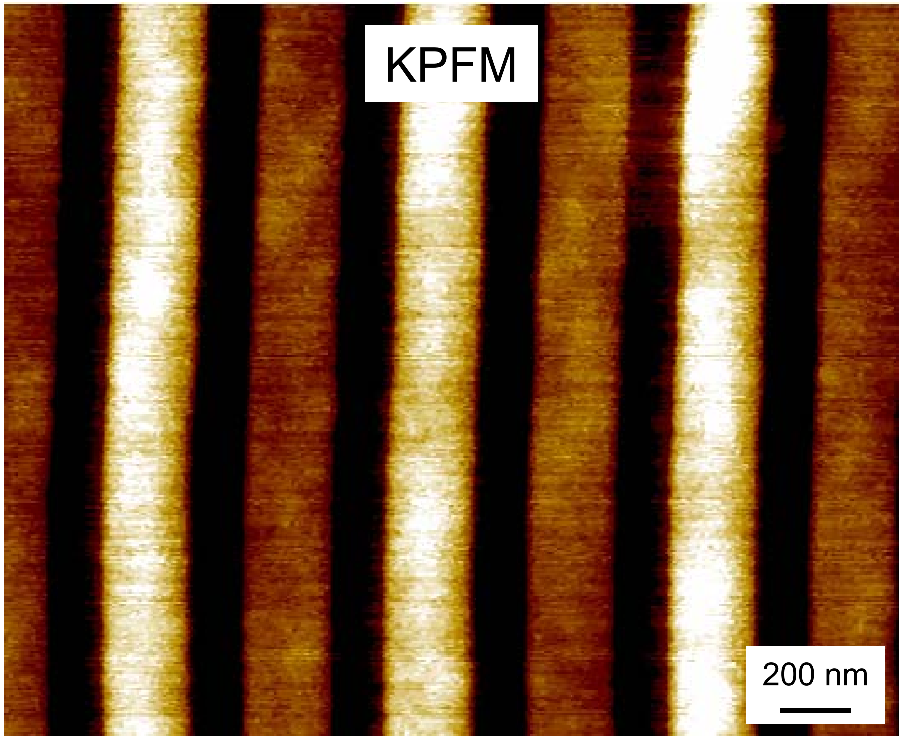
Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies







Z range = 50 nm



Z range = 40 mV

Theory of KPFM

1. $$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}\left(V_{tip} - V_{sample}\right)^2 = F_0 + F_\omega + F_{2\omega}$$

2. $$F_0 = -\frac{1}{2}\frac{\partial C}{\partial z}\left[\left(\Delta SP - V_{DC}\right)^2 + \frac{V_{AC}^2}{2}\right]$$

3. $$F_\omega = -\frac{\partial C}{\partial z}\left(\Delta SP - V_{DC}\right)\cdot V_{AC}\sin\left(\omega \cdot t\right)$$

4. $$F_{2\omega} = \frac{1}{4}\frac{\partial C}{\partial z}V_{AC}^2\cos\left(2\omega \cdot t\right)$$

$$V_{tip} = V_{DC} + V_{AC}\sin\left(\omega \cdot t\right)$$

$$V_{sample} = V_0 + \Delta SP$$

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$$V_{sample} = V_0 + \Delta SP$$

$$\boxed{F_\omega = 0 \quad \Rightarrow \quad \Delta SP = V_{DC}}$$

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$$V_{sample} = V_0 + \Delta SP$$

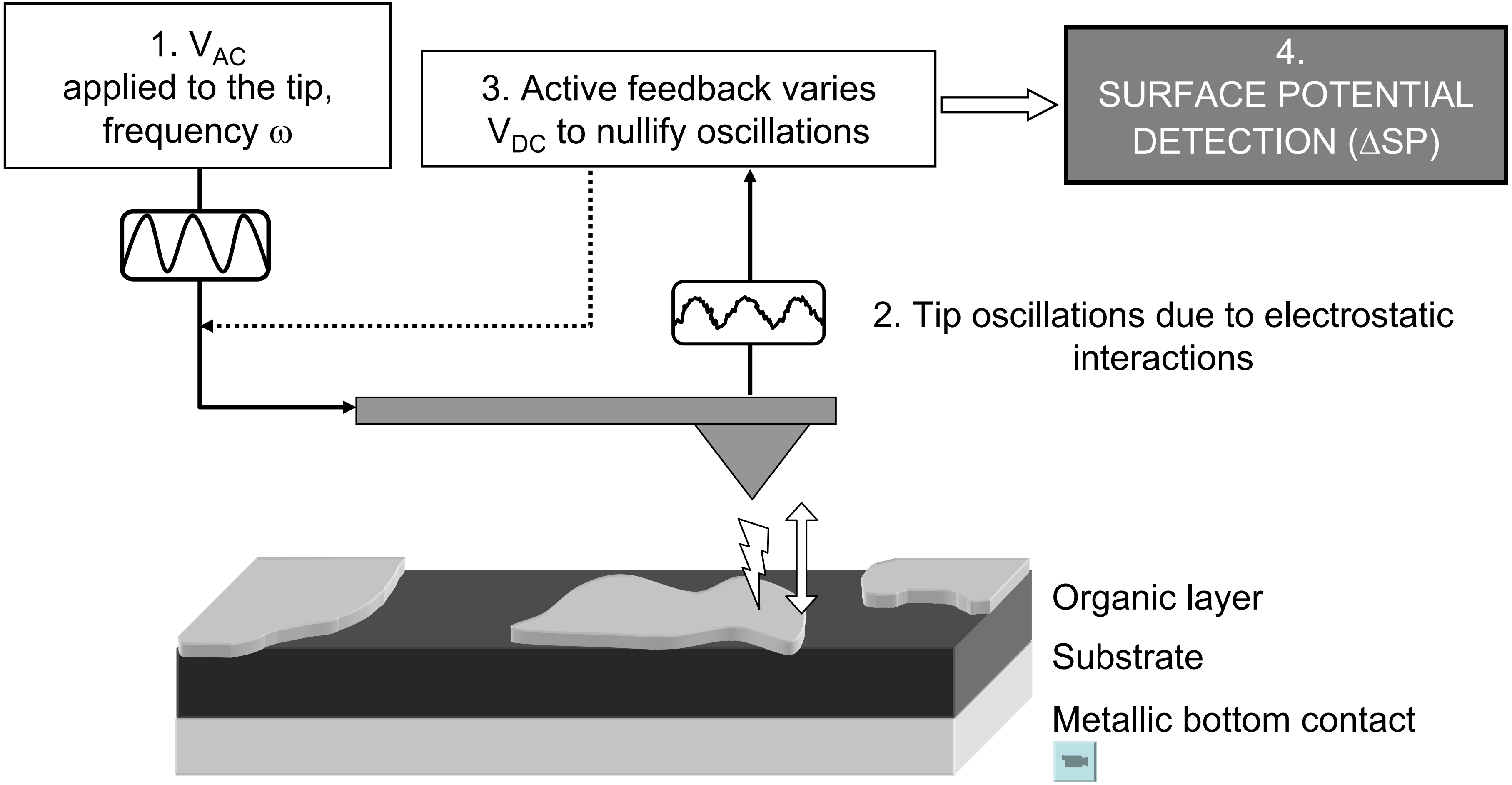
$$\boxed{F_\omega = 0 \quad \Rightarrow \quad \Delta SP = V_{DC}}$$

Metallic samples	$\Delta SP = WF_{sample} - WF_{tip}$
Monolayer (few nm)	$\Delta SP = WF_{sub} + \mu_{film}/\varepsilon_r - WF_{tip}$
Semiconductive films (< 100 nm)	$\Delta SP = WF_{sub} + WF_{film} + surf\ dipoles + band\ bending + ...$
Dielectrics thick films (> 100 nm)	$\Delta SP =\ surf\ dipole\ layer + charge\ density$

Shen Y. et al., *Rev. Sci. Instrum.* **79,** (2008) 023711

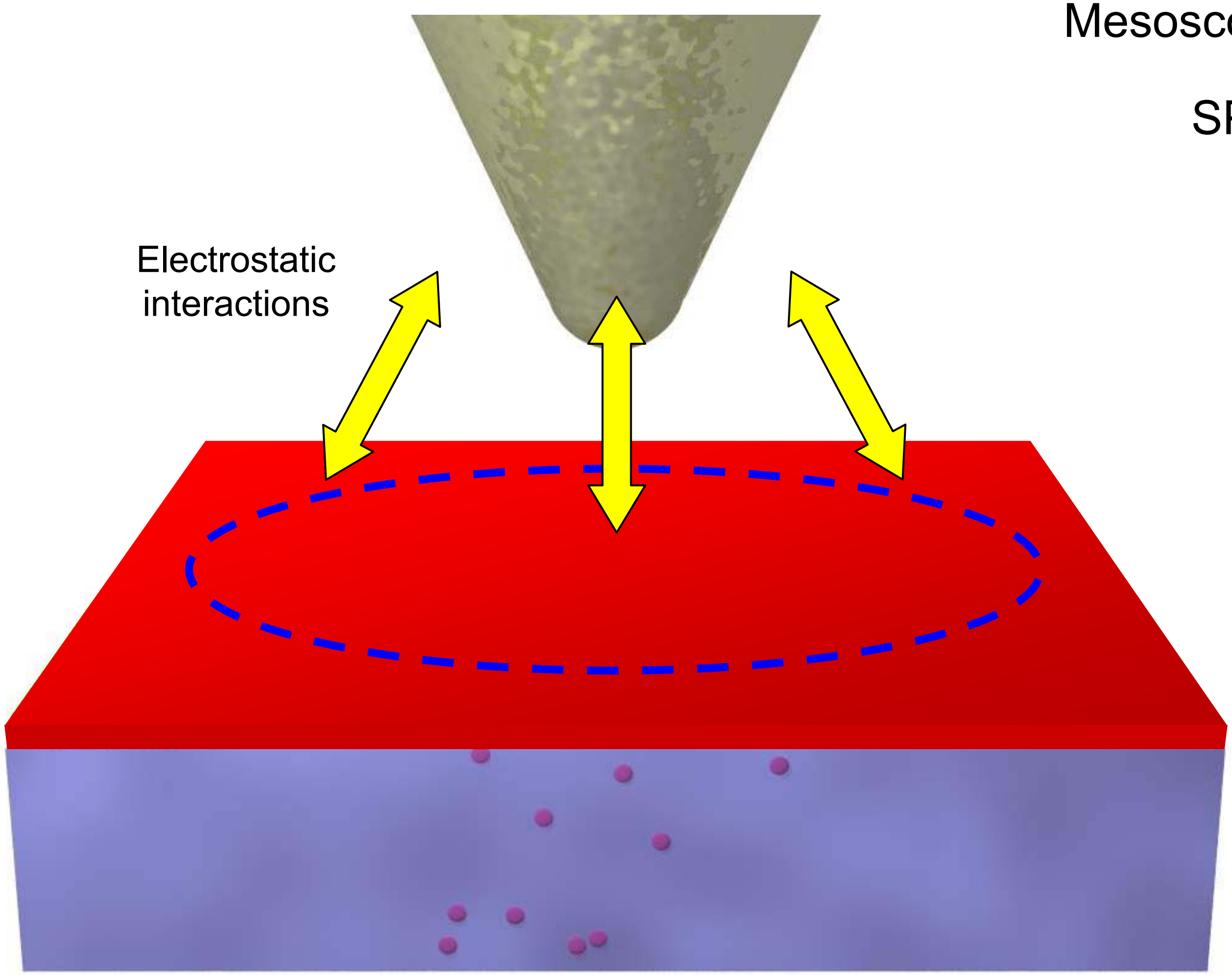
KPFM

Vibrating capacitor, essential features



Zisman W.A., *Rev. Sci. Instrum.* **3** (1932), 367; Palermo V., Palma M. and Samorì P., *Adv. Mater.* (Review Article) **18** (2006), 145-164

Going into the nanoscale...

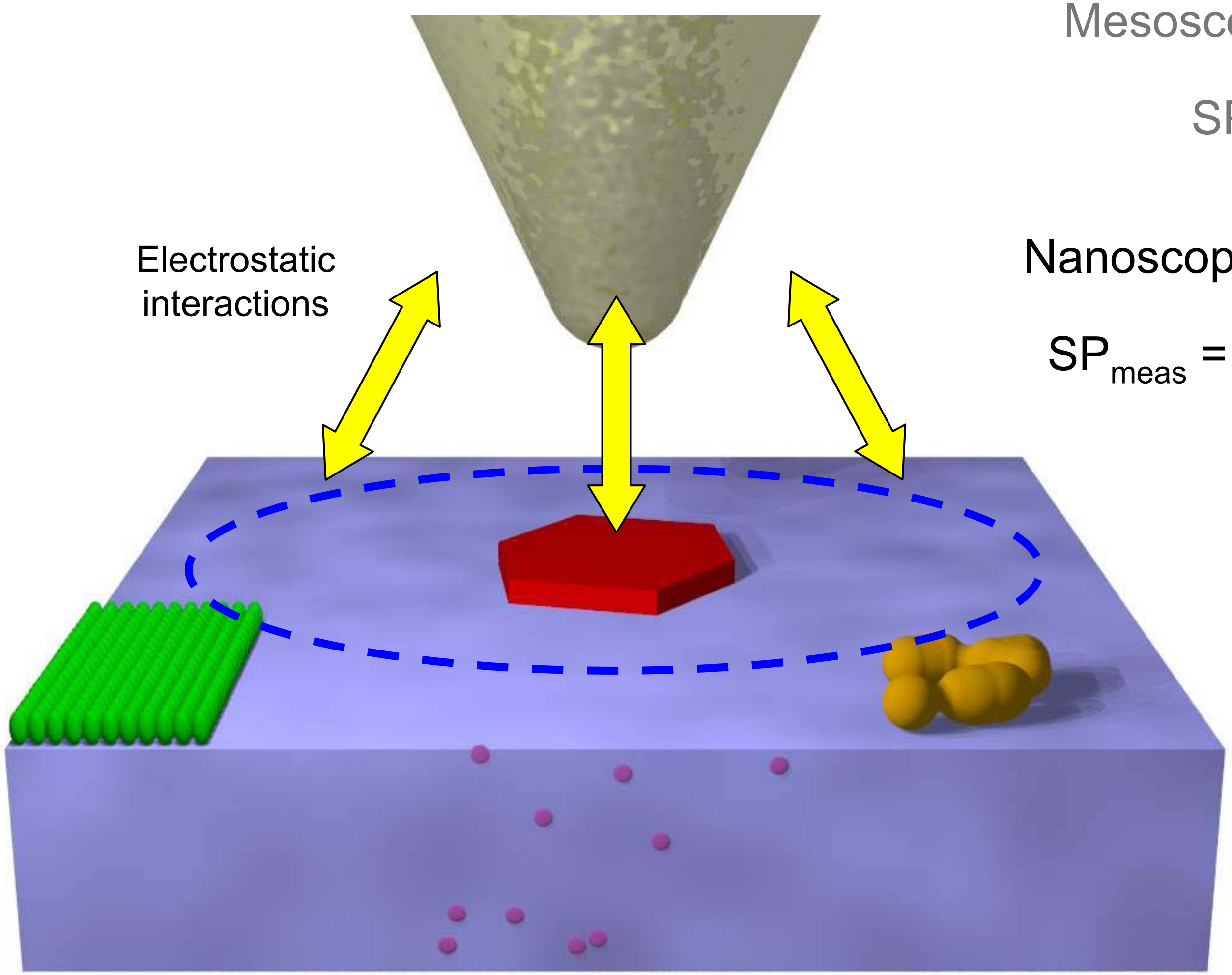


Mesoscopic scale (size > μm)

$$SP_{meas} = SP_{object}$$

Liscio A, Palermo V. Samorì P., *Accounts of Chemical Research* **43** (2010), 541

Going into the nanoscale...



Mesoscopic scale (size > μm)

$$SP_{meas} = SP_{object}$$

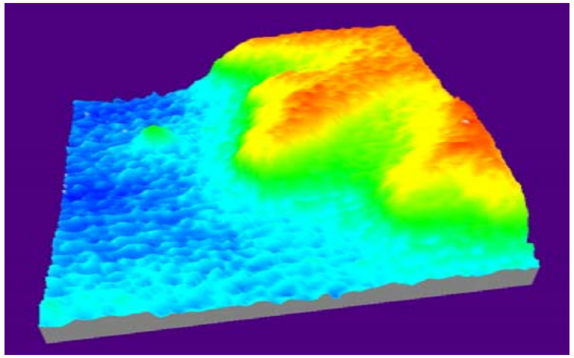
Nanoscopic scale (size < 10^2 nm)

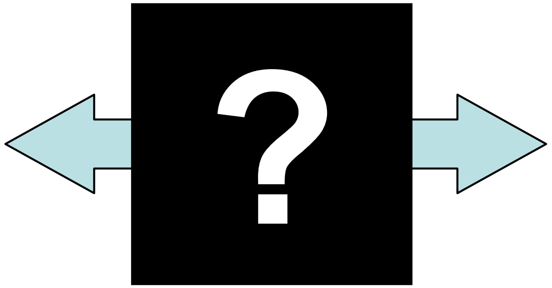
$$SP_{meas} = SP_{object} \oplus SP_{sorrounding}$$

Liscio A, Palermo V. Samorì P., *Accounts of Chemical Research* **43** (2010), 541

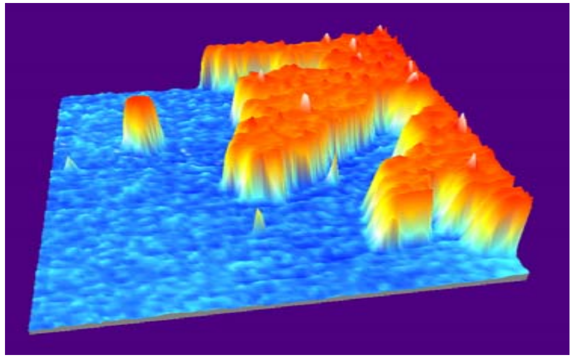
Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

Measured KPFM image

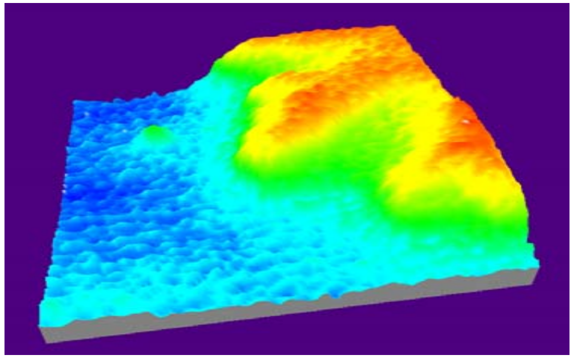


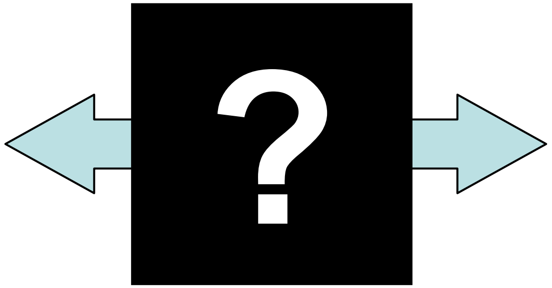


“Real” KPFM image

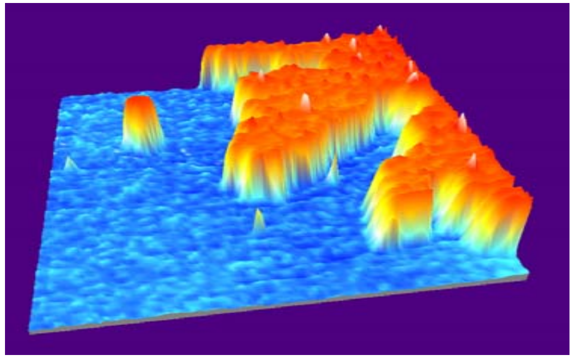


Measured KPFM image





"Real" KPFM image



Transfer function representation

$$SP_{meas}\left(r_{//}\right)=\int_{surface} d\,r'_{//}\int_{0}^{\infty}\Gamma\left(r'_{//}-r_{//},z'\right)\cdot SP_{0}\left(r'_{//},z'\right)d\,z'$$

$$\boxed{\Gamma\left(r'_{//}-r_{//},z'\right)\propto\lim_{\Delta r'_{//},\Delta z'\to 0}\frac{\left|\mathrm{E}\left(r'_{//}-r_{//},z'\right)\right|^{2}}{W\left(\Delta r'_{//},\Delta z'\right)}}$$

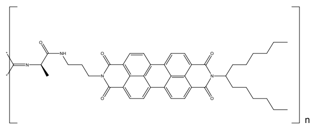
E electric field

W electrostatic energy

Artifacts are mainly due to the tip-sample electrostatic interactions

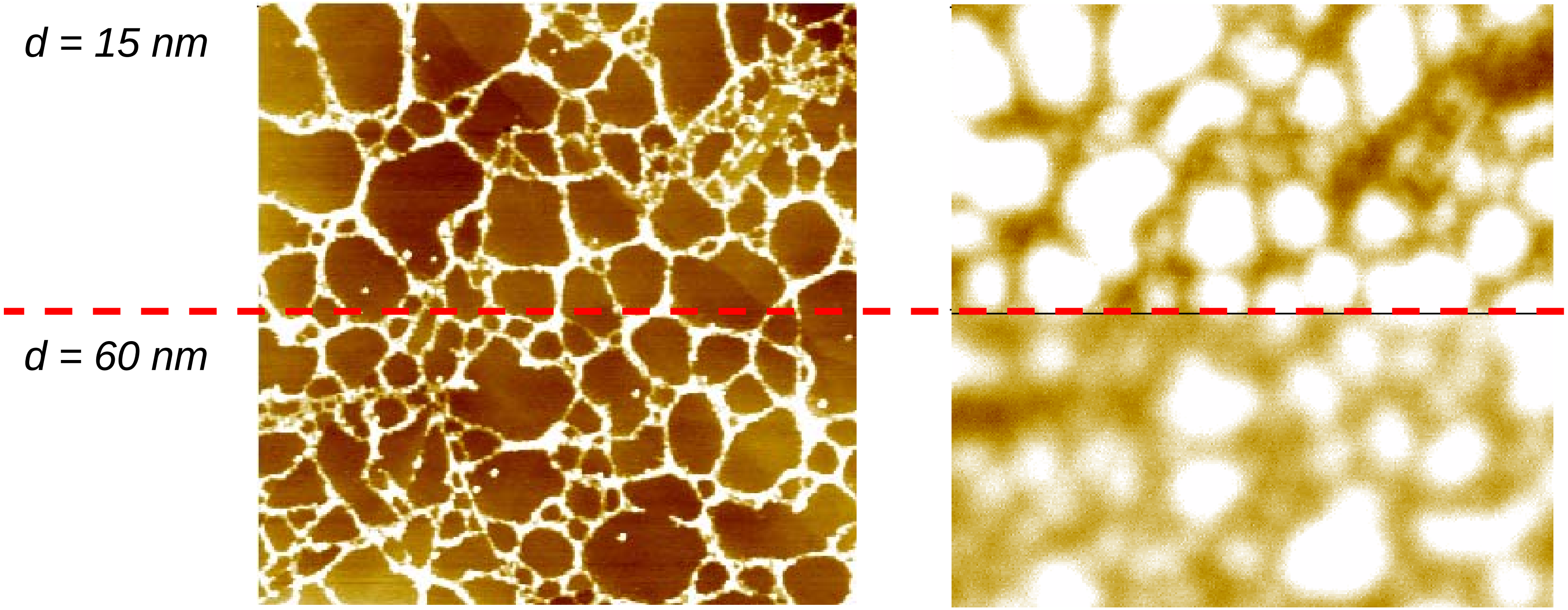
♣ Liscio et al., *Adv. Funct. Mater*. **16**, (2006), 1407, ♣ Liscio et al., *Adv. Funct. Mater.* **18**, (2008), 907,
♣ Liscio et al., *J. Phys. Chem. C* **112**, (2008), 173698, ♣ Liscio et al., *Acc. Chem. Res.* **43**, (2010), 541, Liscio et al., *Small* **7**, (2011), 634

Effect of tip-sample distance (*d*) in AFM and KPMF images



AFM

KPFM



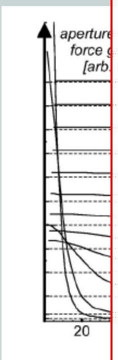
Size: 5.12 x 5.12 μm^2
Z-range: 4 nm

Size: 5.12 x 5.12 μm^2
Z-range: 100 mV

?

Models used to describe the tip-sample geometry

Tip shape



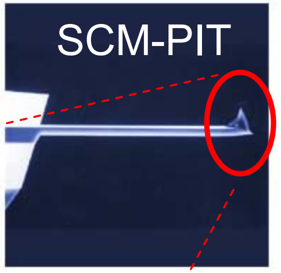
Colchero et al., *Phys. Rev. B* 64 (2001)

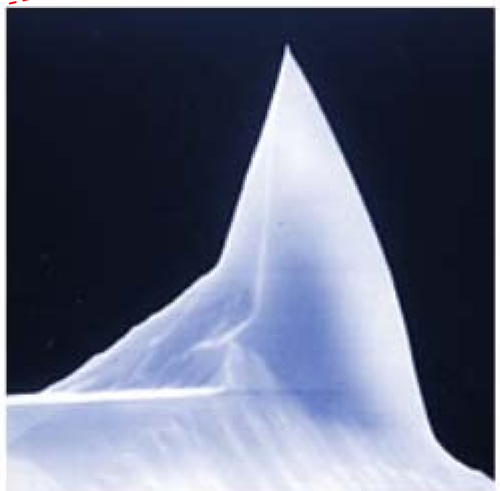
...ser et al., *Appl. Surf. Science* **210** (2003), 32

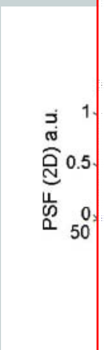
Tip Specification

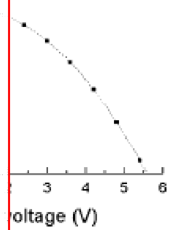
The Pt/Ir front side coating provides a metallic electrical path from the cantilever die to the apex of the tip. The iridium alloy is used to increase the durability of the film.

Geometry:	Anisotropic
Tip Height (h):	10 - 15µm
Front Angle (FA):	25 ± 2.5°
Back Angle (BA):	15 ± 2.5°
Side Angle (SA):	22.5 ± 2.5°
Tip Radius (Nom):	20nm
Tip Radius (Max):	25nm
Tip SetBack (TSB)(Nom):	15µm









Strassburg et al., *Rev. Sci. Instrum* **76** (2005), 083705

Charrier et al., *ACSNano* **2** (2008), 621

Γ: an operative definition

1. SP broadening or simplified geometry → 2. $\Gamma\left(r_{//}, z\right)$

3. $$SP_{meas} = \Gamma \otimes SP_{real}$$

♣ Liscio et al., *Adv. Funct. Mater*. **16**, (2006), 1407, ♣ Liscio et al., *Adv. Funct. Mater.* **18**, (2008), 907,
♣ Liscio et al., *J. Phys. Chem. C* **112**, (2008), 173698, ♣ Liscio et al., *Acc. Chem. Res.* **43**, (2010), 541, Liscio et al., *Small* **7**, (2011), 634

Γ: an operative definition

1. SP broadening or simplified geometry → 2. $\Gamma\left(r_{//}, z\right)$

3. $$SP_{meas} = \Gamma \otimes SP_{real}$$

inversion

4. $$SP_{real} = \Gamma^{-1} \otimes SP_{meas}$$

♣ Liscio et al., *Adv. Funct. Mater*. **16**, (2006), 1407, ♣ Liscio et al., *Adv. Funct. Mater.* **18**, (2008), 907,
♣ Liscio et al., *J. Phys. Chem. C* **112**, (2008), 173698, ♣ Liscio et al., *Acc. Chem. Res.* **43**, (2010), 541, Liscio et al., *Small* **7**, (2011), 634

Γ: an operative definition

1. SP broadening
or simplified geometry

→

2. $$\Gamma\left(r_{//}, z\right)$$

3. $$SP_{meas} = \Gamma \otimes SP_{real}$$

5. $$SP_{simul} = \left(\Gamma^{-1}\right)^{-1} \otimes SP_{real}$$

inversion

simulation

4. $$SP_{real} = \Gamma^{-1} \otimes SP_{meas}$$

♣ Liscio et al., *Adv. Funct. Mater*. **16**, (2006), 1407, ♣ Liscio et al., *Adv. Funct. Mater.* **18**, (2008), 907,
♣ Liscio et al., *J. Phys. Chem. C* **112**, (2008), 173698, ♣ Liscio et al., *Acc. Chem. Res.* **43**, (2010), 541, Liscio et al., *Small* **7**, (2011), 634

Γ: an operative definition

1. SP broadening or simplified geometry

2. $\Gamma(r_{//}, z)$

3. $SP_{meas} = \Gamma \otimes SP_{real}$

inversion

4. $SP_{real} = \Gamma^{-1} \otimes SP_{meas}$

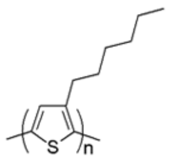
simulation

5. $SP_{simul} = \left(\Gamma^{-1}\right)^{-1} \otimes SP_{real}$

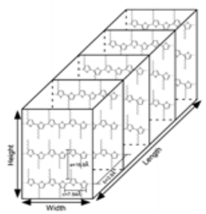
♣ Liscio et al., *Adv. Funct. Mater*. **16**, (2006), 1407, ♣ Liscio et al., *Adv. Funct. Mater.* **18**, (2008), 907,
♣ Liscio et al., *J. Phys. Chem. C* **112**, (2008), 173698, ♣ Liscio et al., *Acc. Chem. Res.* **43**, (2010), 541, Liscio et al., *Small* **7**, (2011), 634

Quasi 1D-systems:

P3HT nanofibres on HOPG

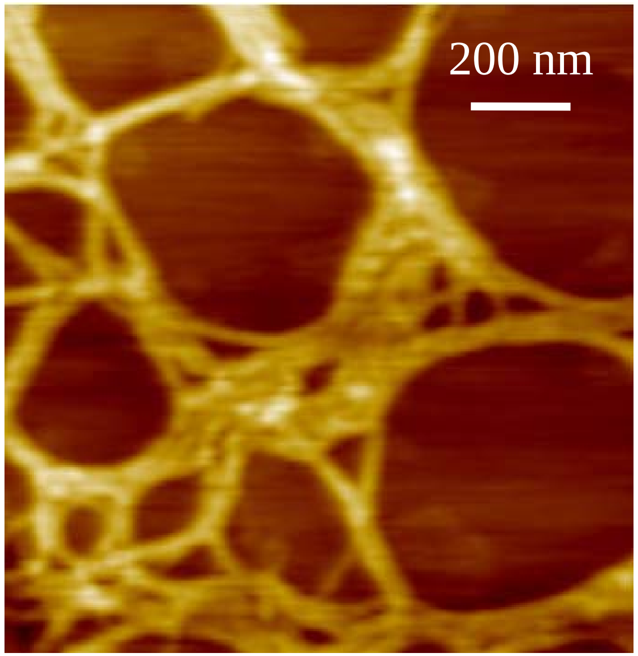


Poly-3-hexylthiophene
(P3HT)



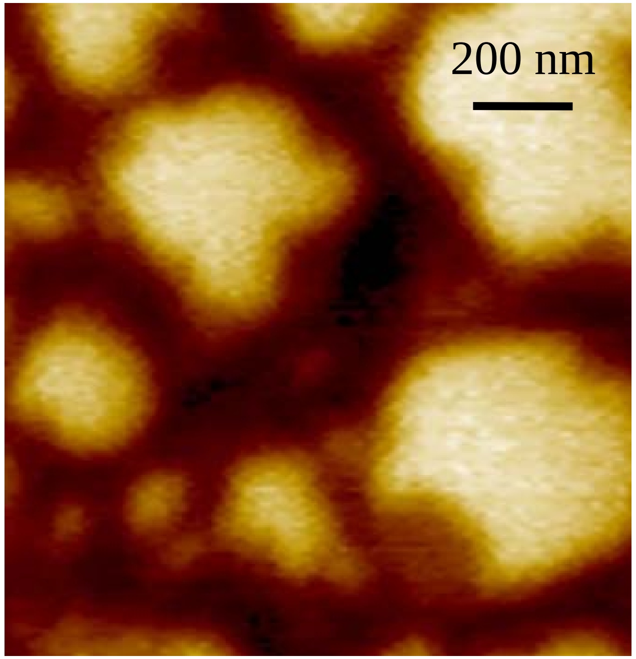
Merlo J.A. et al.,
J. Phys. Chem. **108** (2004), 19169

Topography



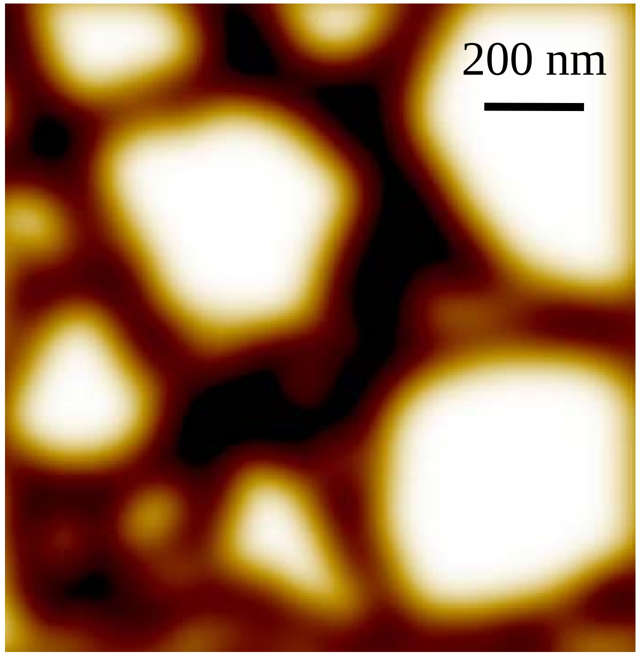
Z range = 10 nm

Measured KPFM



Z range = 180 mV

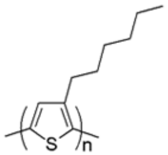
Simulated KPFM



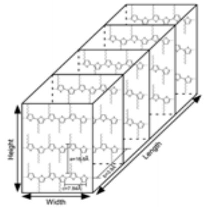
Z range = 180 mV

Quasi 1D-systems:

P3HT nanofibres on HOPG

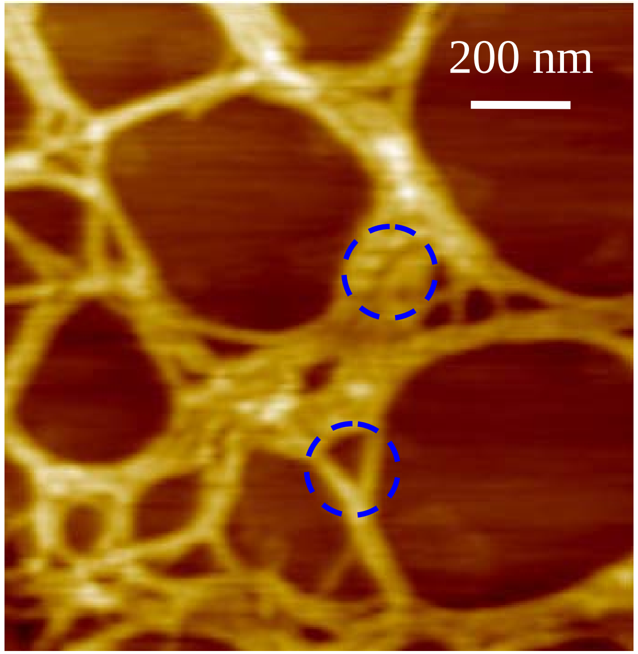


Poly-3-hexylthiophene
(P3HT)



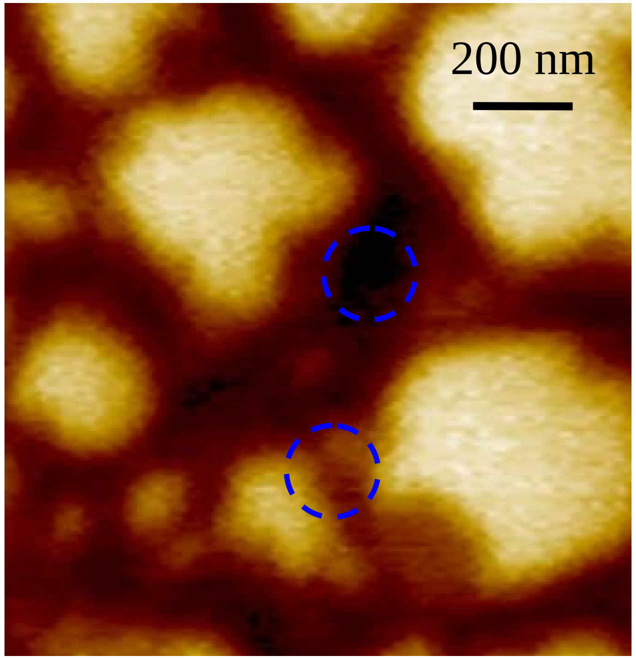
Merlo J.A. et al.,
J. Phys. Chem. **108** (2004), 19169

Topography



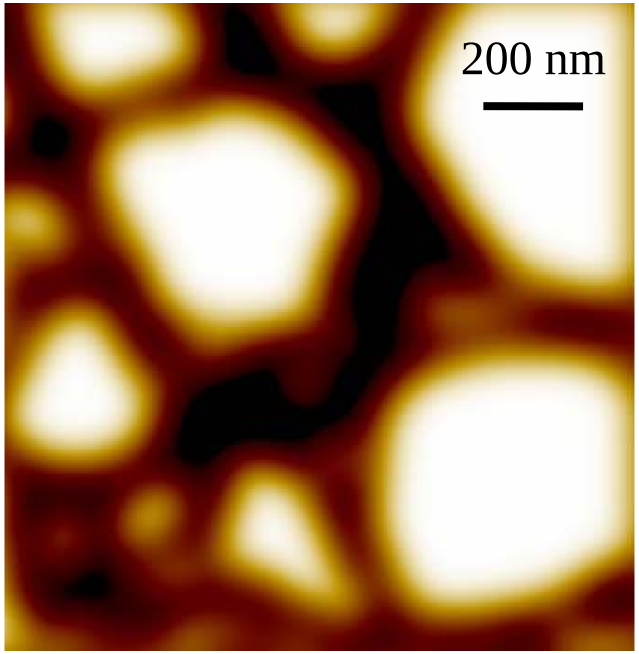
Z range = 10 nm

Measured KPFM



Z range = 180 mV

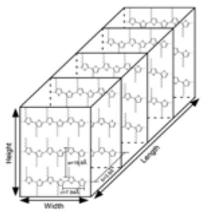
Simulated KPFM



Z range = 180 mV

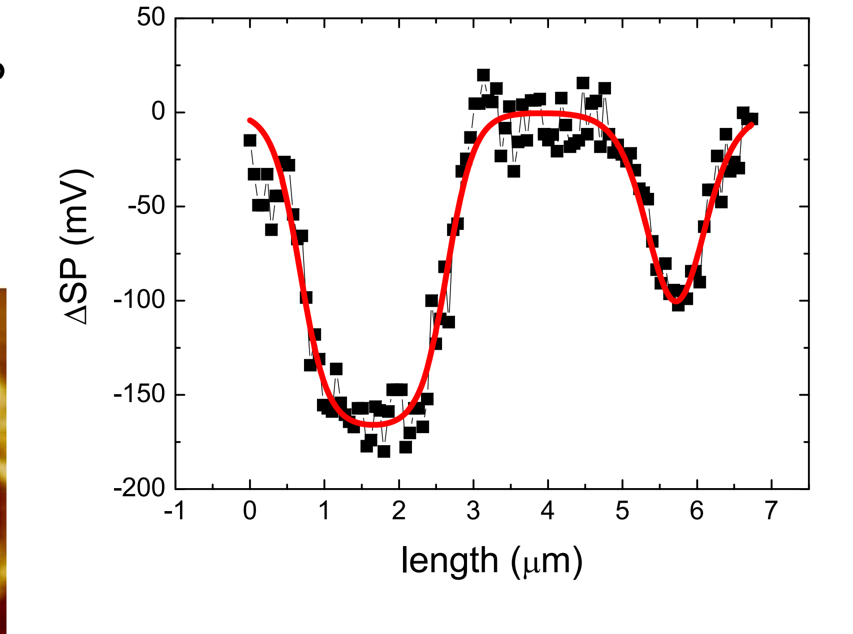
Quasi 1D-systems:

bres on HOPG



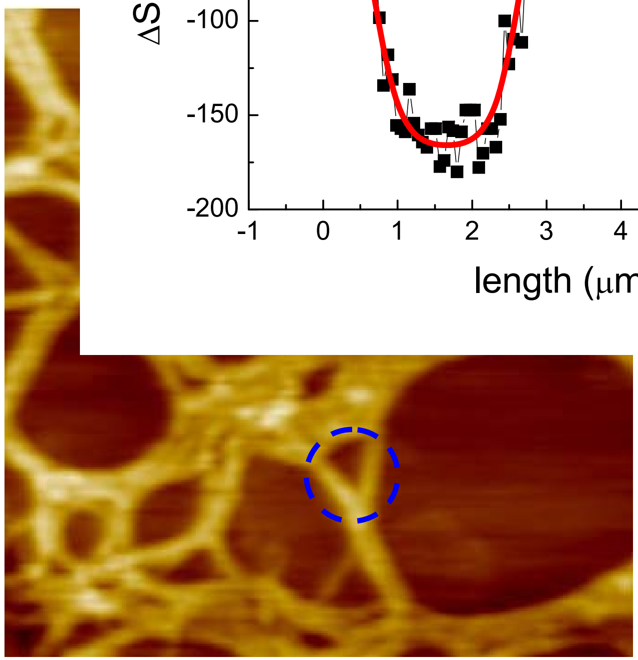
Merlo J.A. et al.,
J. Phys. Chem. **108** (2004), 19169

P

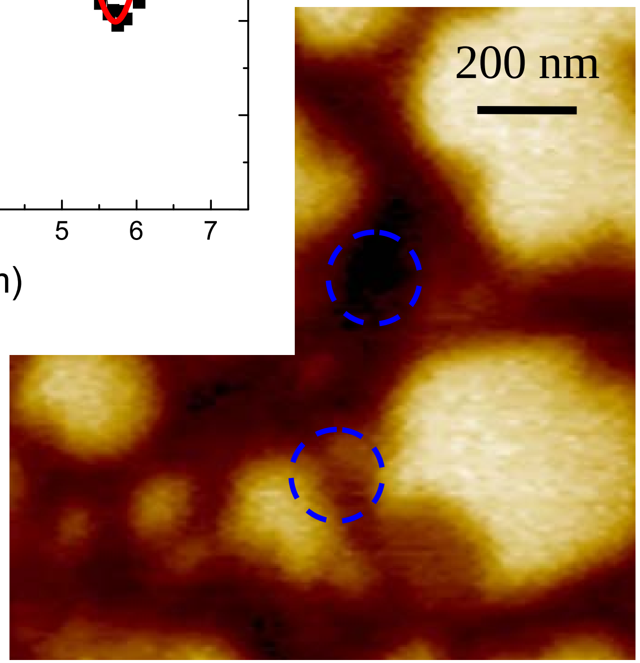


ed KPFM

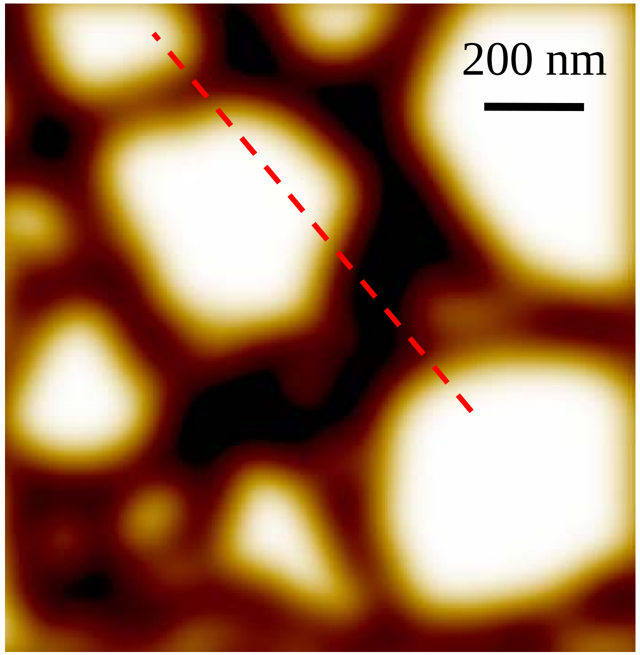
Simulated KPFM



Z range = 10 nm

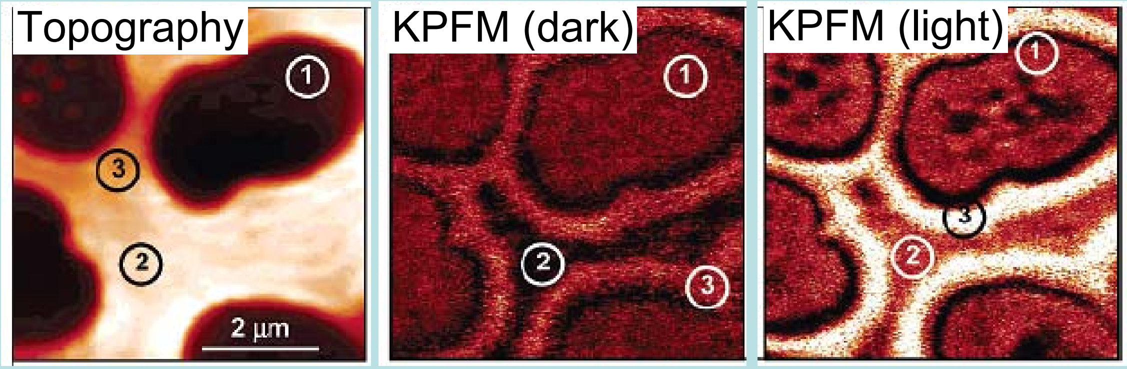


Z range = 180 mV



Z range = 180 mV

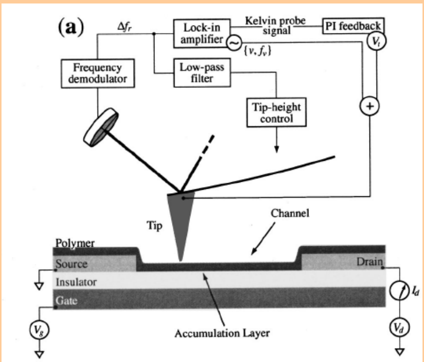
Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

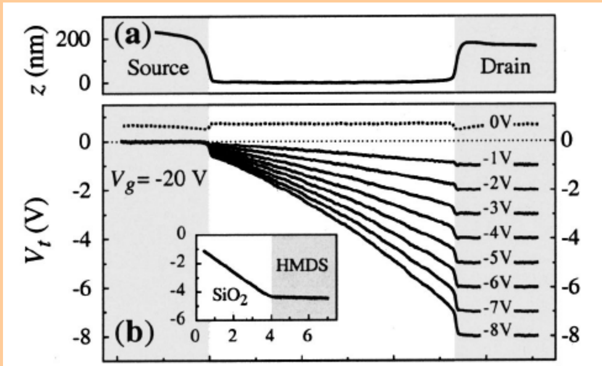


Photovoltaic

F8BT/PFB blends

M. Chiesa, L. Burgi, J. Kim, R.H. Friend, H. Sirringhaus,
NanoLetters **5** (2005), 559

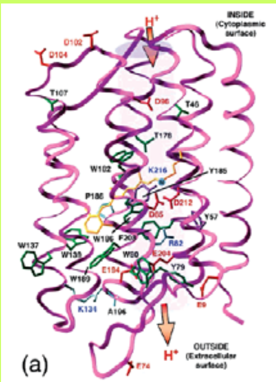


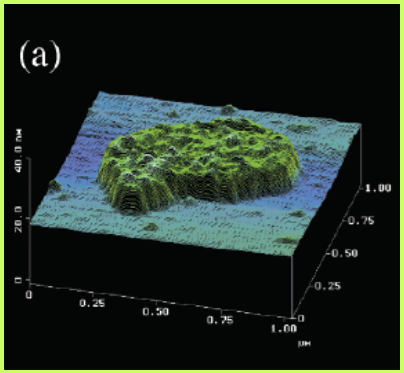


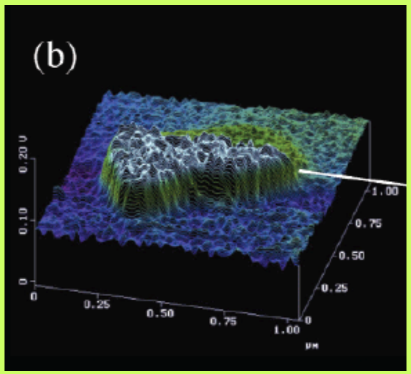
Working FET

P3HT thin film

L. Bürgi, H. Sirringhaus, R.H. Friend,
Appl. Phys. Lett. **80** (2002,) 2913





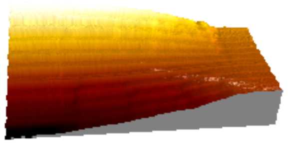


Biology

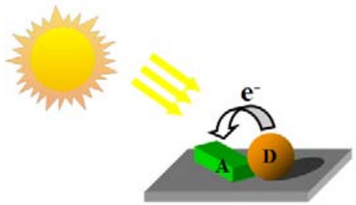
Bacteriorhodopsin Mutant D96N

I. Lee, E. Greenbaum, S. Budy,
J.R. Hillebrecht, R.R. Birge, J.A. Stuart,
J. Phys. Chem. B **110** (2006), 10

What we can measure?



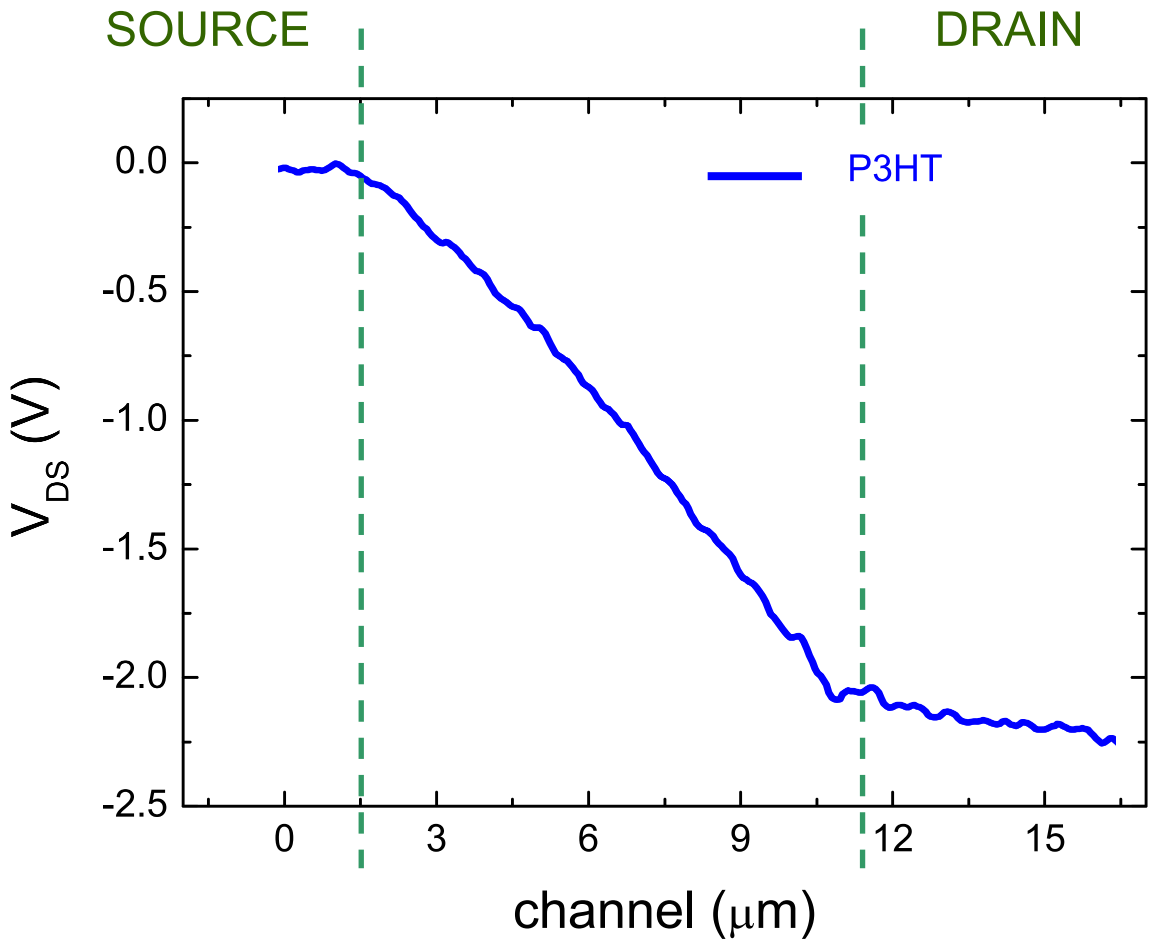
Electrical studies performed on Organic Field-Effect Transistors

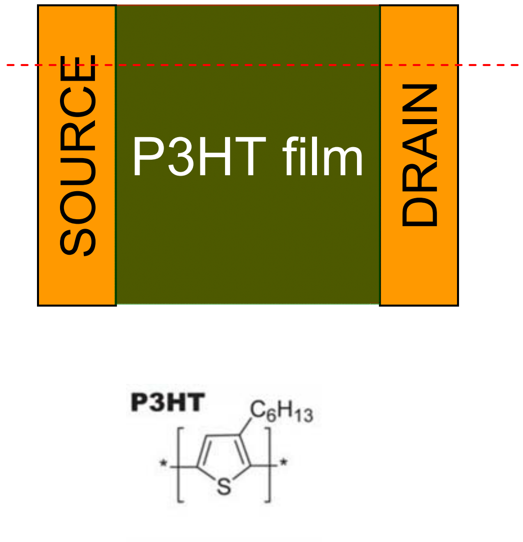


Mapping the photovoltaic activity on the nanometer scale

Gold

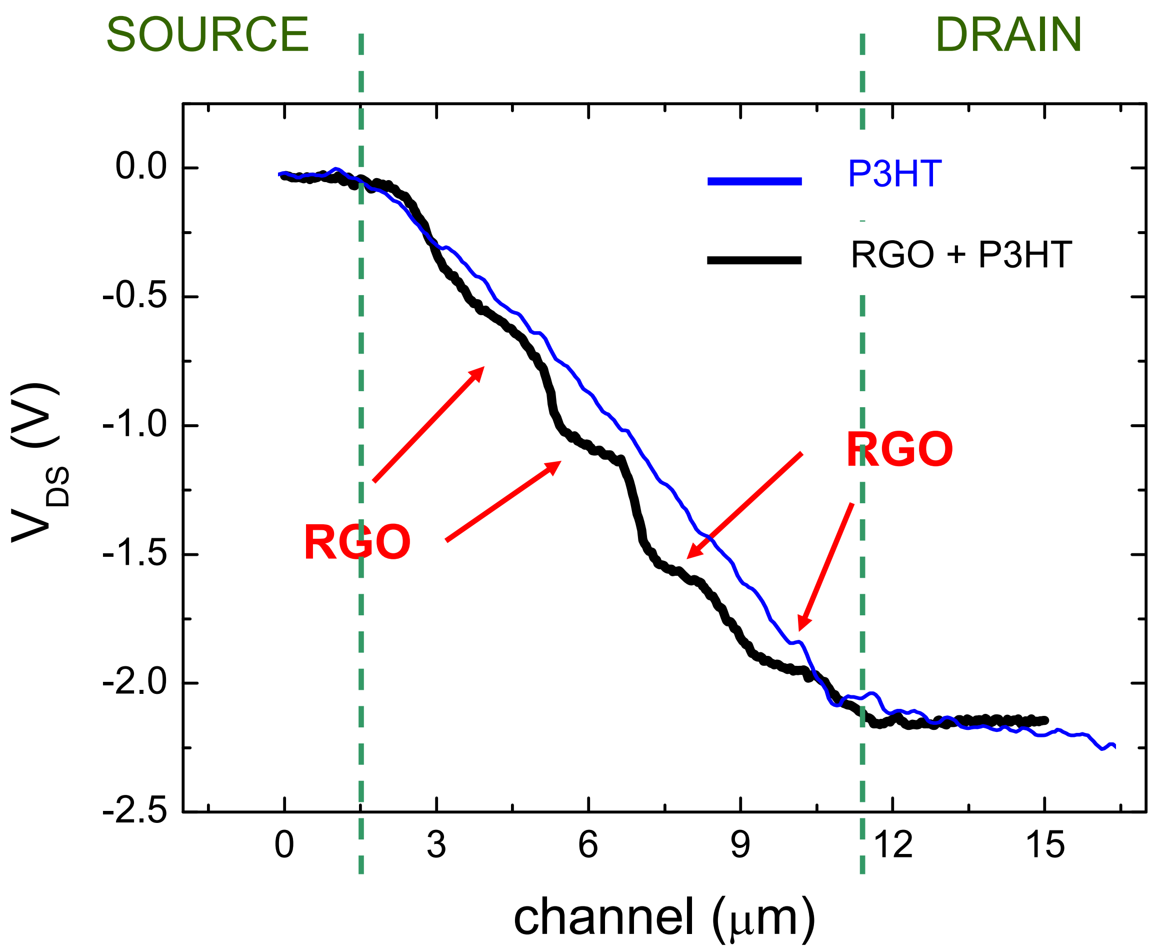
Organic Field-Effect Transistor

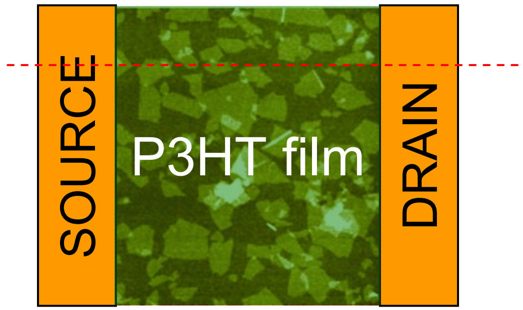


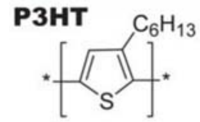


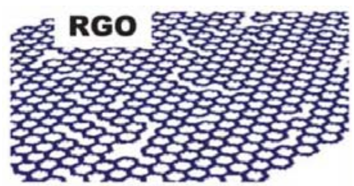
Liscio et al., *J. Mater. Chem.* **21** (2011), 2924

Organic Field-Effect Transistor



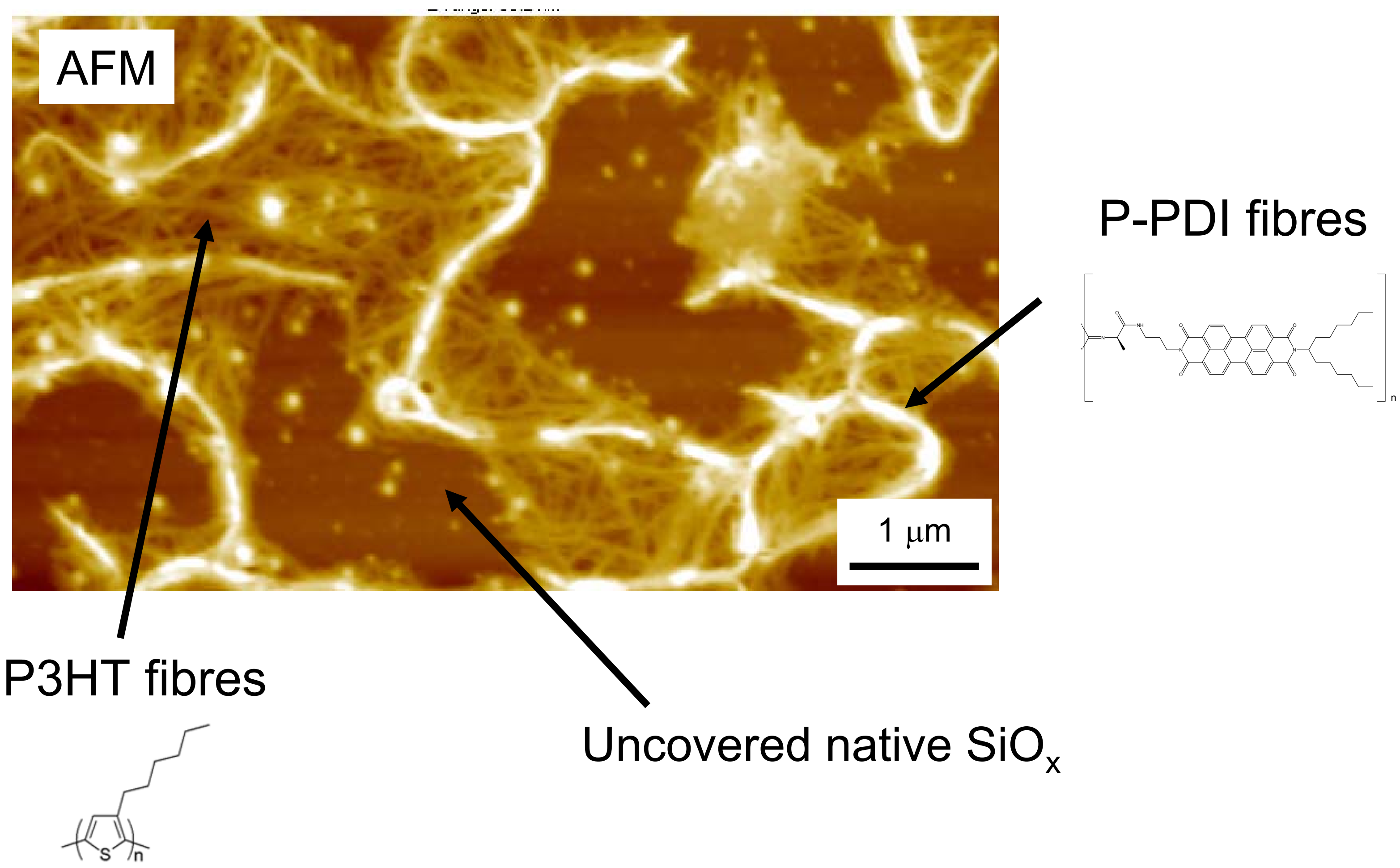






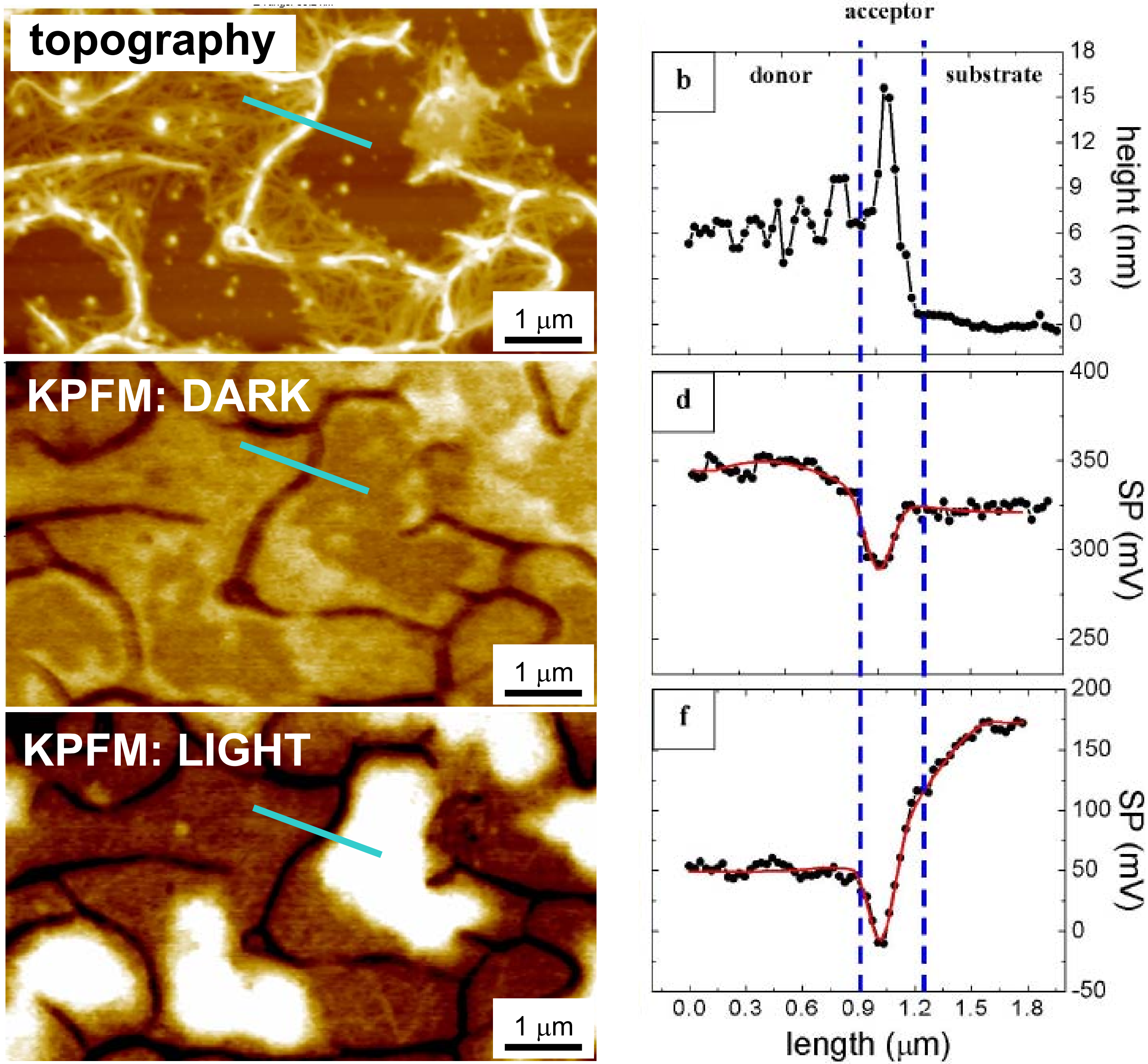
Liscio et al., *J. Mater. Chem.* **21** (2011), 2924

Ultra-thin blend of P-PDI/P3HT on Si



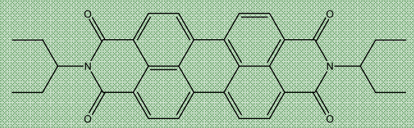
V. Palermo, M.B.J. Otten, A. Liscio et al., *JACS* **130**, 14605 (2008)

Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

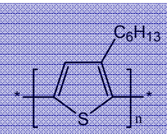


Photovoltaic charge generation visualized at the nanoscale: a proof of principle

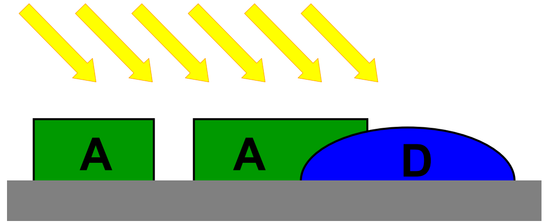
Photovoltaic activity occurring between PDI and P3HT

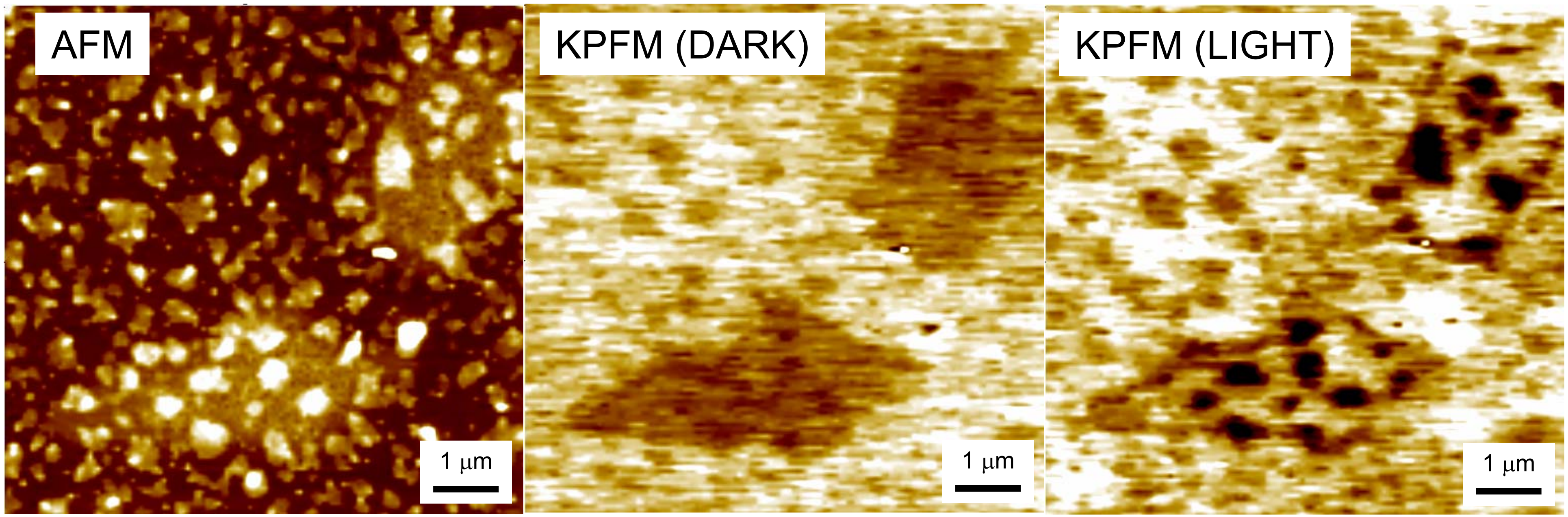


Acceptor (PDI)



Donor (P3HT)





Z range = 40 nm

Z range = 60 mV

Z range = 60 mV

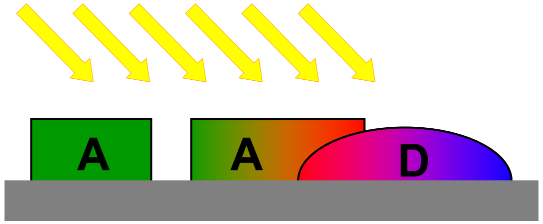
A. Liscio, G. De Luca, F. Nolde, V. Palermo, K. Müllen, P. Samorì, *JACS* **2008**, 130, 780-781

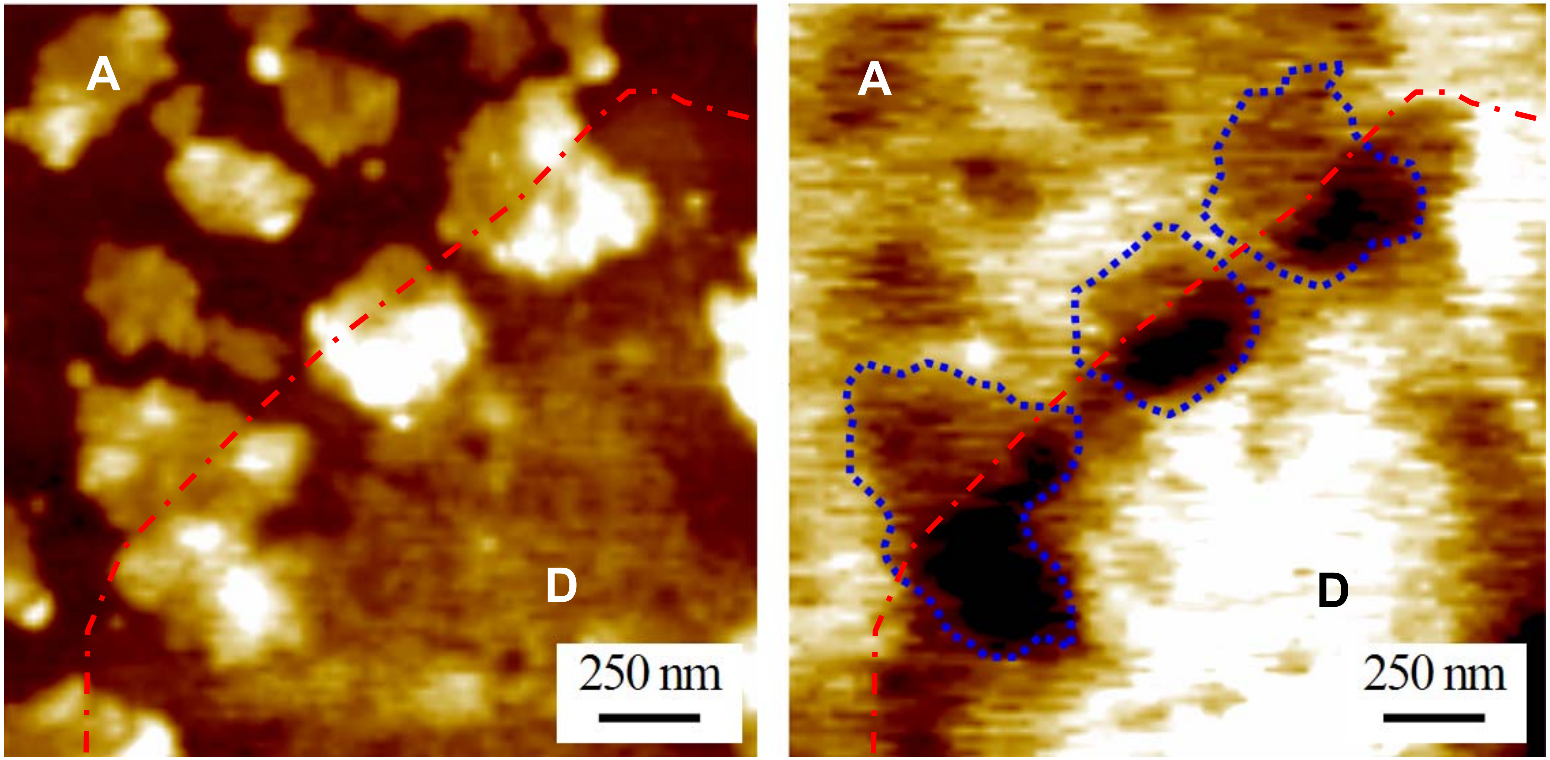
Photovoltaic activity occurring between PDI and P3HT

Table 1. SPs of P3HT and PDI Measured for Sample under Dark and Light Irradiation[a]

	SP (mV)		
	P3HT (type III)	PDI (type II)	PDI (type I)
dark	−30 ± 5	−40 ± 5	−12 ± 4
light	−10 ± 5	−90 ± 10	−32 ± 5
dark − light	−20 ± 7	50 ± 11	20 ± 7

[a] SPs are given as differences with respect to substrate SP. The error bars are the variances obtained by averaging over all the collected measurements.





A. Liscio, G. De Luca, F. Nolde, V. Palermo, K. Müllen, P. Samorì, *JACS* **2008**, 130, 780-781

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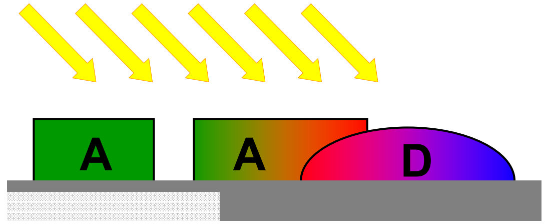
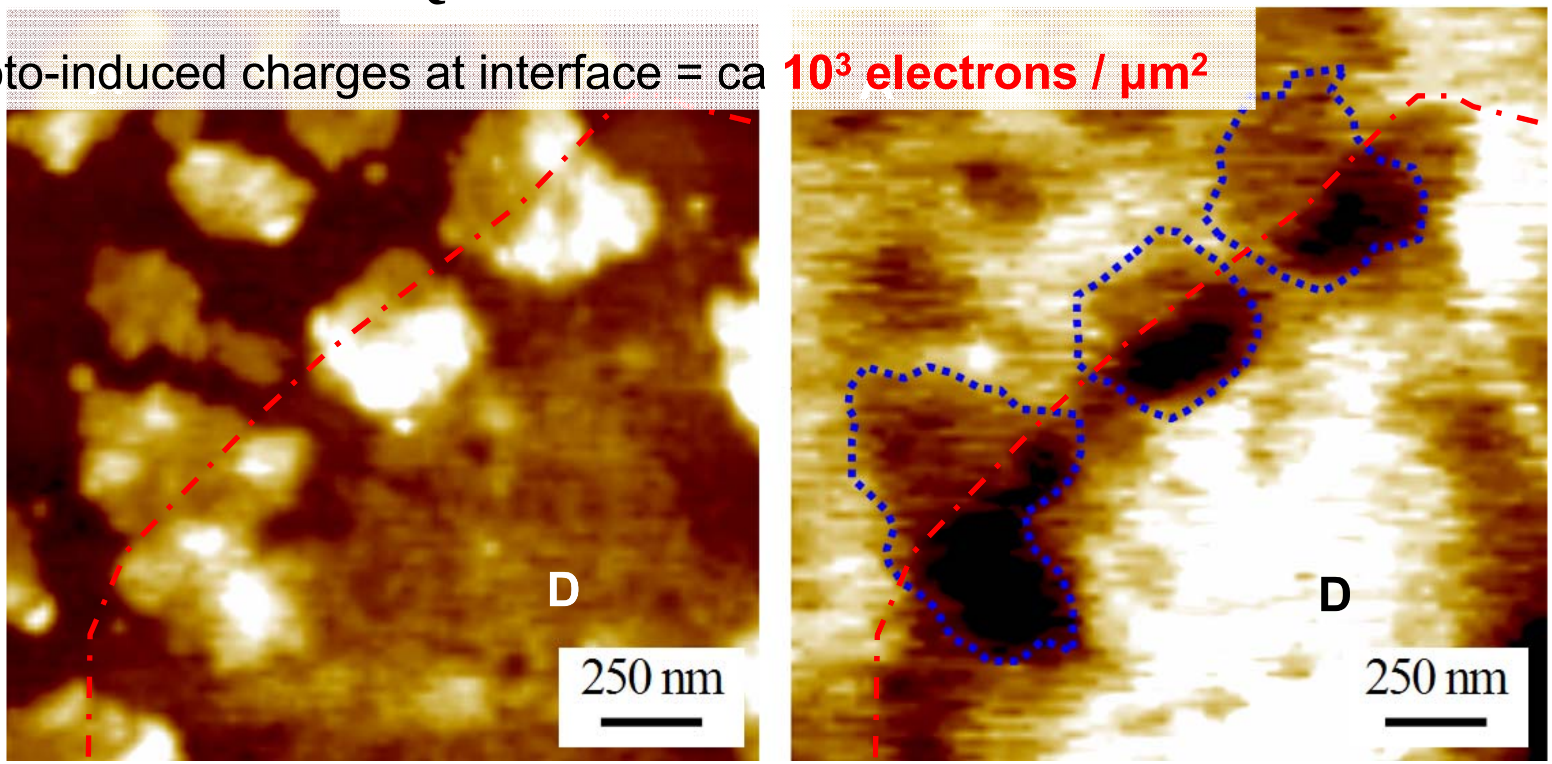
[a] SPs are given as differences with res... bars are the variances obtained by ave... measurements.



$$\Delta Q = \pi \varepsilon d \Delta V$$

Photo-induced charges at interface = ca **10^3 electrons / μm^2**



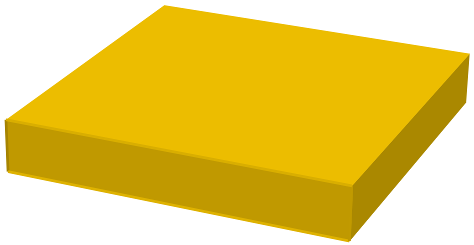
A. Liscio, G. De Luca, F. Nolde, V. Palermo, K. Müllen, P. Samorì, *JACS* **2008**, 130, 780-781

Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

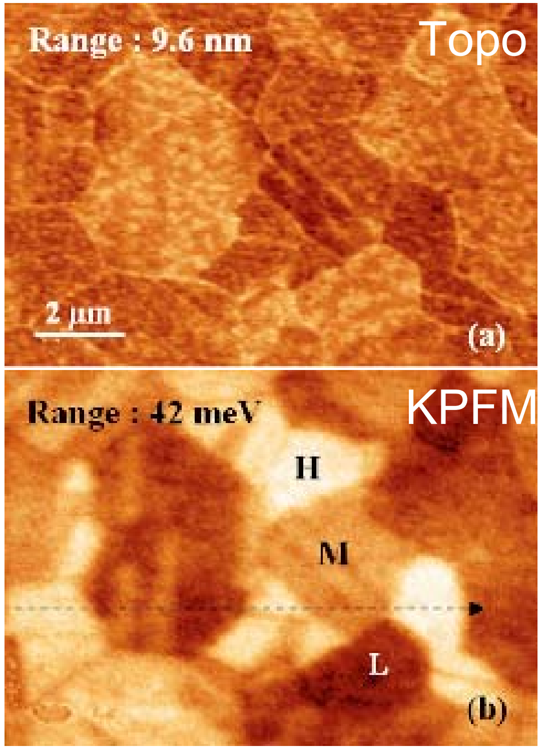
Increasing the complexity

Ideal case



Flat
Perfect reflection
etc

High controlled case



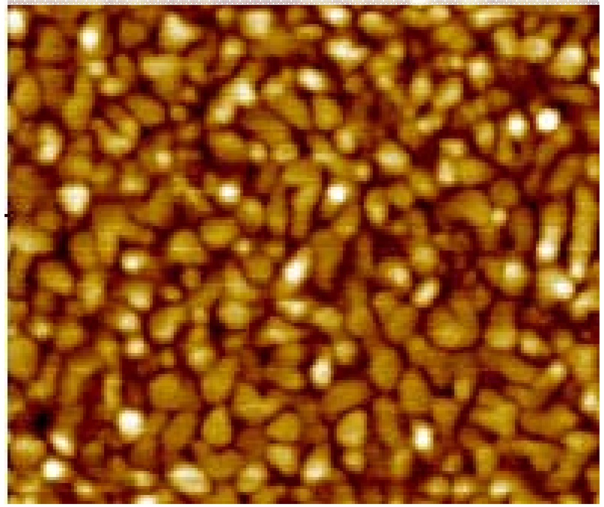
“Typical” case

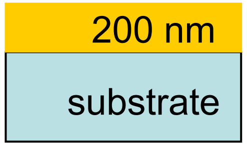
?

Gaillard N. Et al., Applied Physics Letters 89, 154101 2006

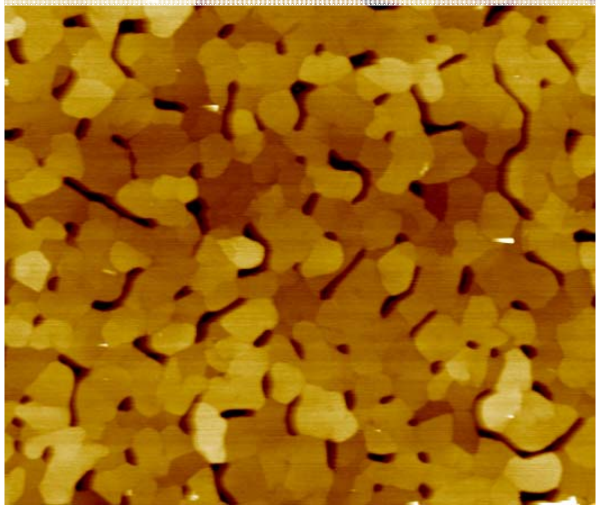
Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

Gold evaporated on glass

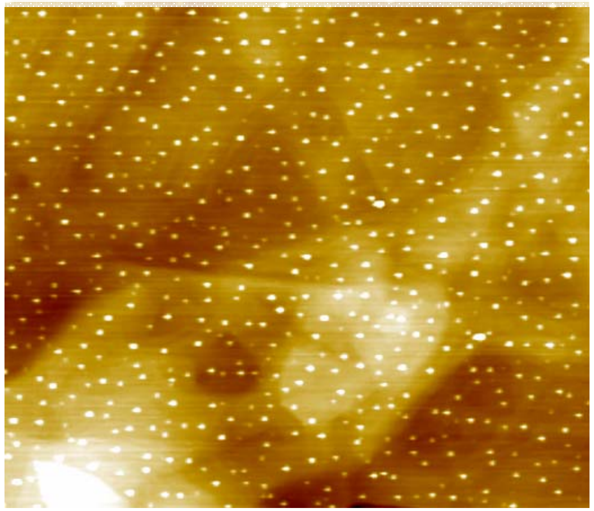




Gold evaporated on glass

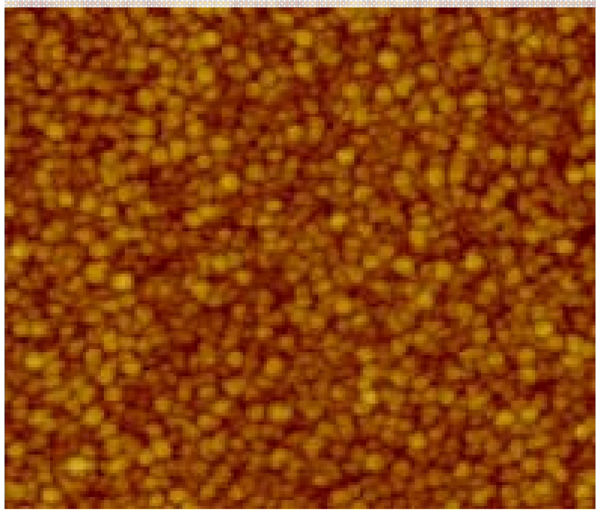


Gold evaporated on mica



AFM size
2.56×2.56 μm^2

Gold sputtered on glass



SURFACE POTENTIAL “ROUGHNESS”

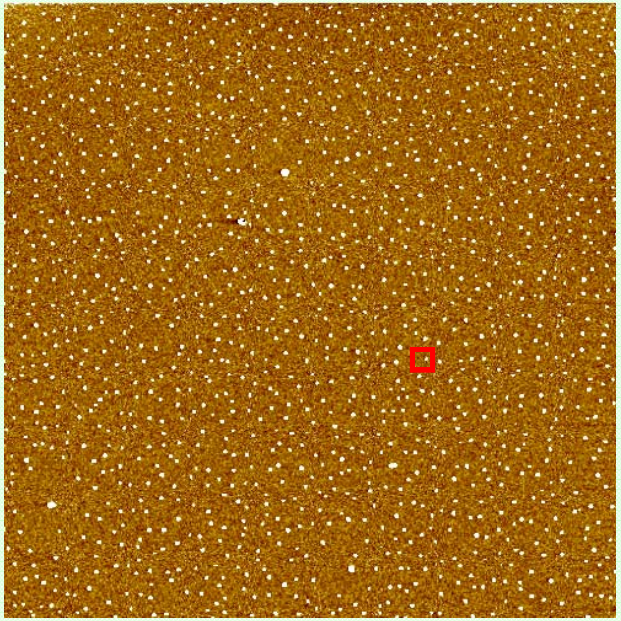
A multi-scale, time-dependent parameter

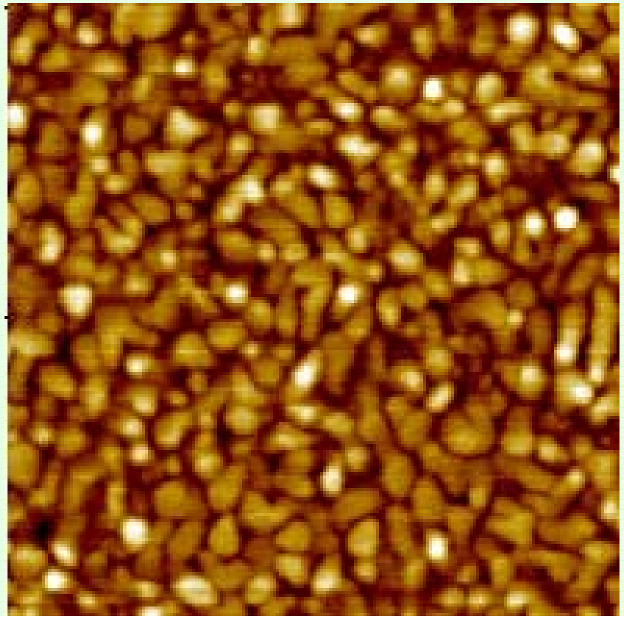
Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

AFM

Lat. size
81.92 µm

Z range
= 12 nm

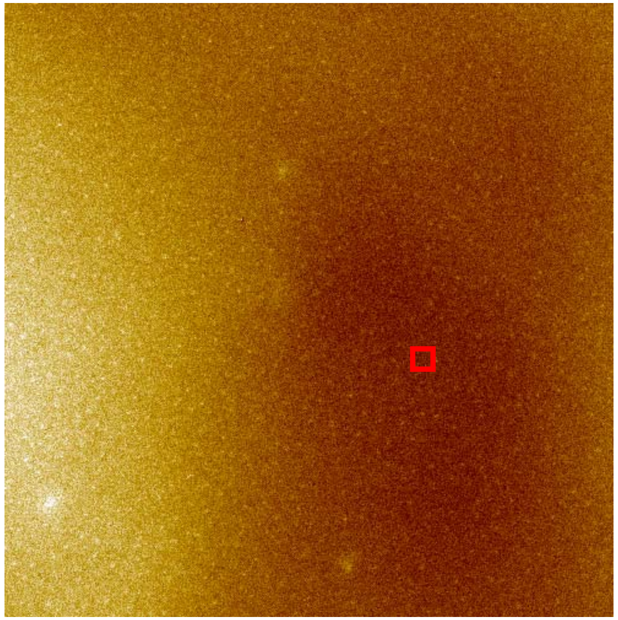




Lat. size
2.56 µm

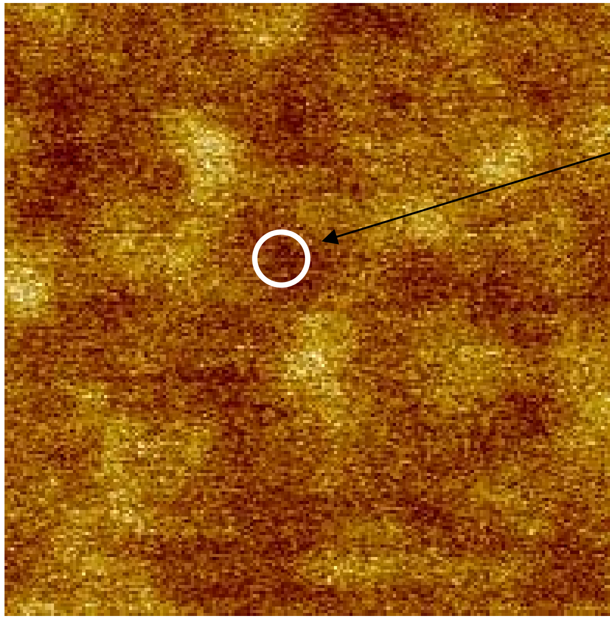
Z range
= 12 nm

KPFM



Lat. size
81.92 µm

Z range
= 50 mV



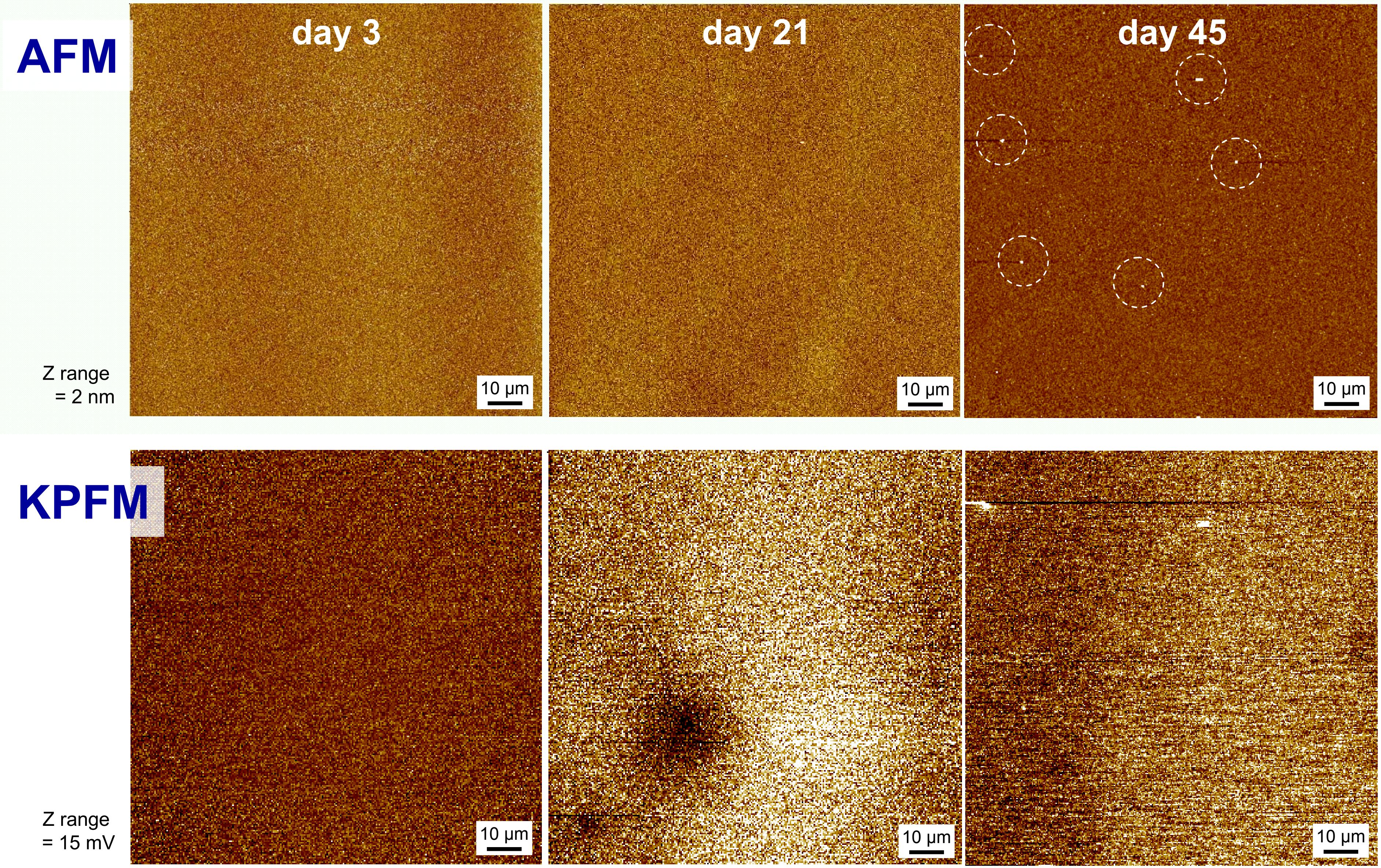
Effective area

Lat. size
2.56 µm

Z range
= 12 mV

AGING EFFECTS

Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies



Electrical characterization and nanoscale surface morphology with Scanning Probe Microscopies

CLUSTERS

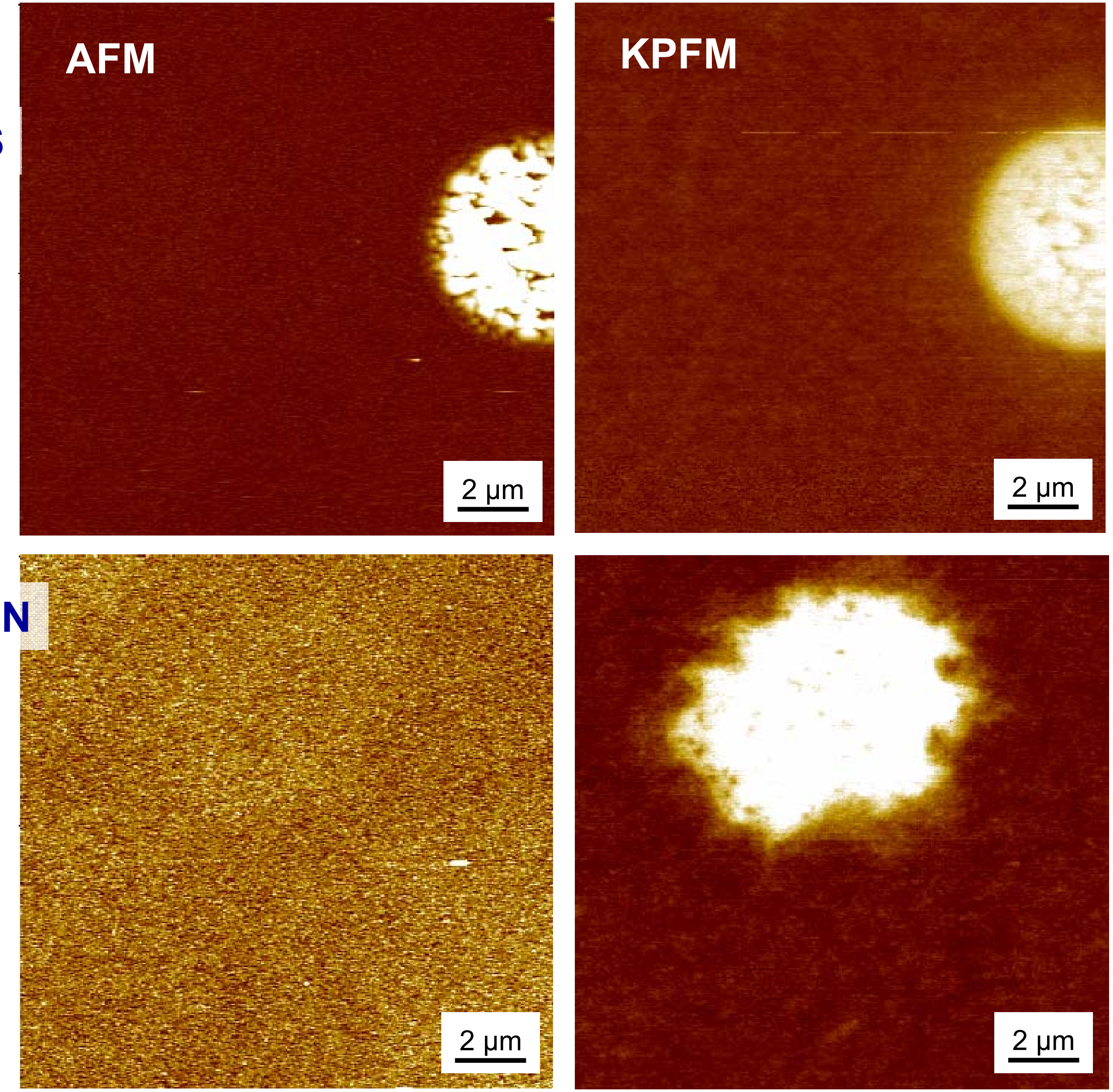
Z-range = 30 nm

Z-range = 160 mV

ADSORPTION

Z-range = 10 nm

Z-range = 100 mV



Outlooks

- SPMs are suitable techniques to explore nanoscale
- Quantitative analysis of SPM images: handle with care
- Gold surface example

    One name for several surfaces

    Roughness (and patches) are multi-scale parameters