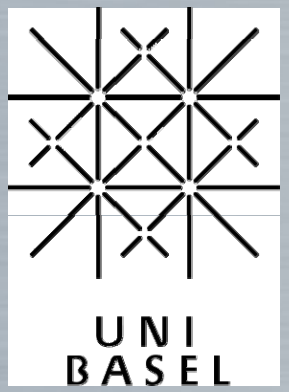
Electronic confinement and band formation originating from a supramolecular Porous Network

J. Lobo-Checa , M. Matena, K. Müller, J.H. Dil, F. Meier, L. H. Gade , T. A. Jung, M.Stöhr



- Outline:
- Motivation: Electronic confinement in nanostructures
- Characterization of the molecular adlayer: STM, LEED
- Electronic structure: STS + ARPES
- Conclusions

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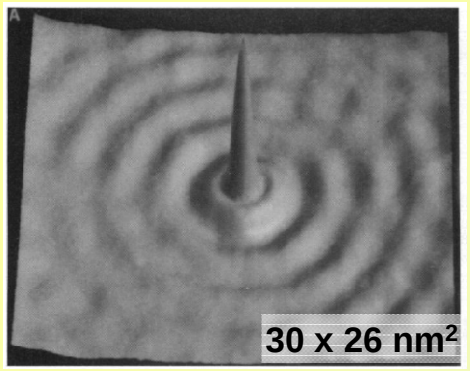
TNT2009. September 2009

Electronic confinement on surfaces

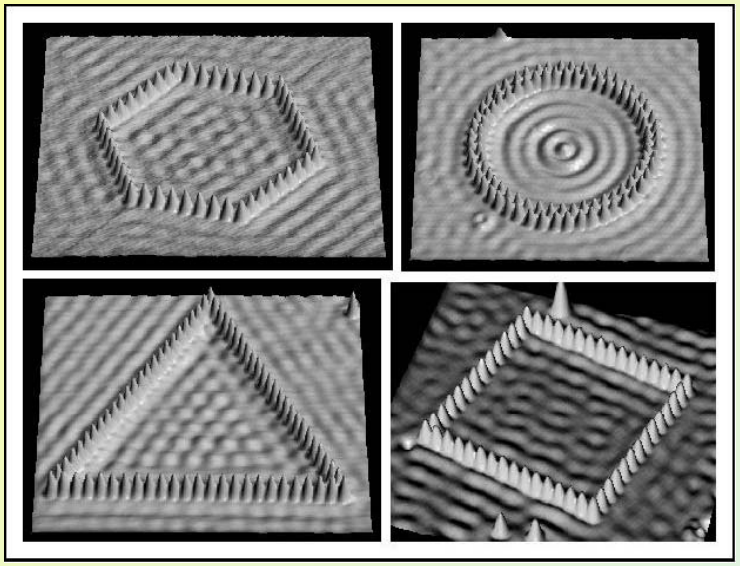
CIN2

Surface state in noble metals are 2D quasi-free electron gas

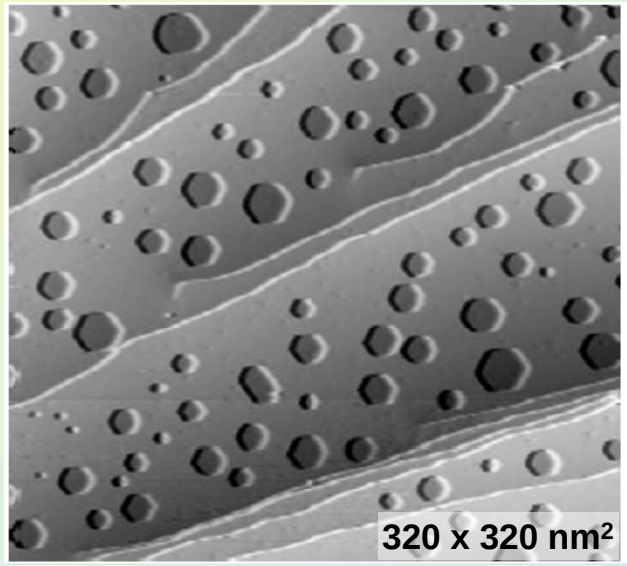
Fe /Cu(111)



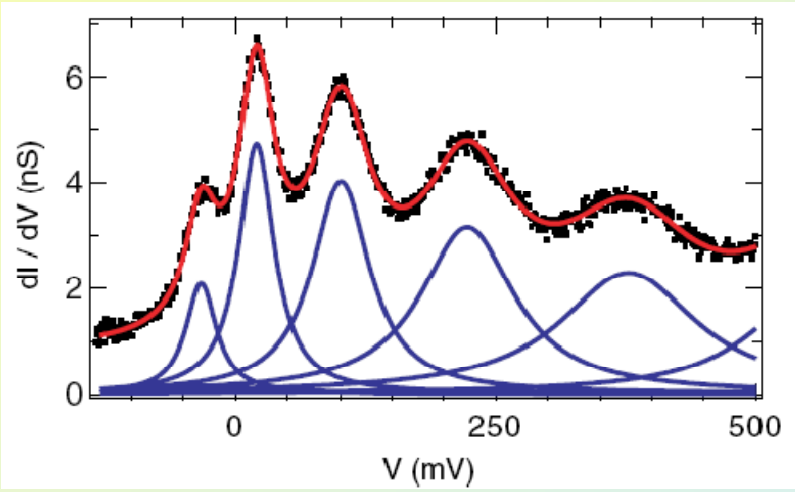
M.F. Crommie, *et al.*,
Science **262,** 218 (1993)



Atomic manipulation (D. Eigler *et al.*, IBM)



Nano-Islands on Ag(111)
J. Li *et al.*, PRL **80**, 3332 (1998)



STS of a Vacancy island on Ag(111)
J. Kröger, *et al.*, Prog. in Surf. Sci., **82,** 293 (2007)

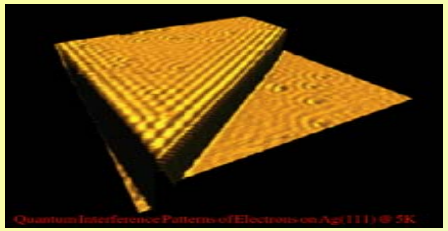
Characteristic **imperfect confinement.**

'Lossy scattering' is dominant with respect to electron-electron and electron-phonon scattering.

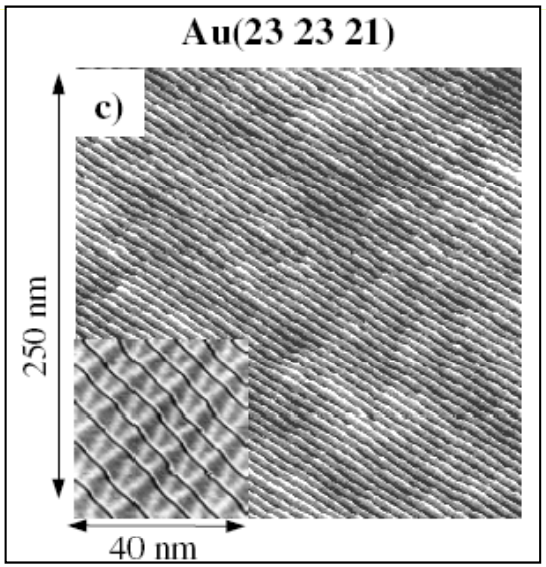
H. Jensen, *et al.*, PRB **71,** 155417 (2005)

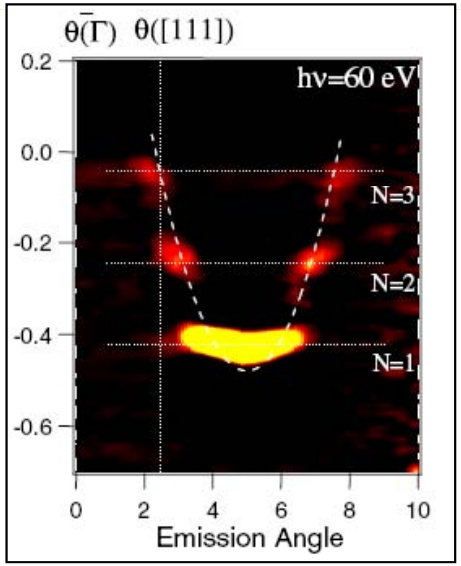
No electronic band structure

1D electronic confinement on surfaces



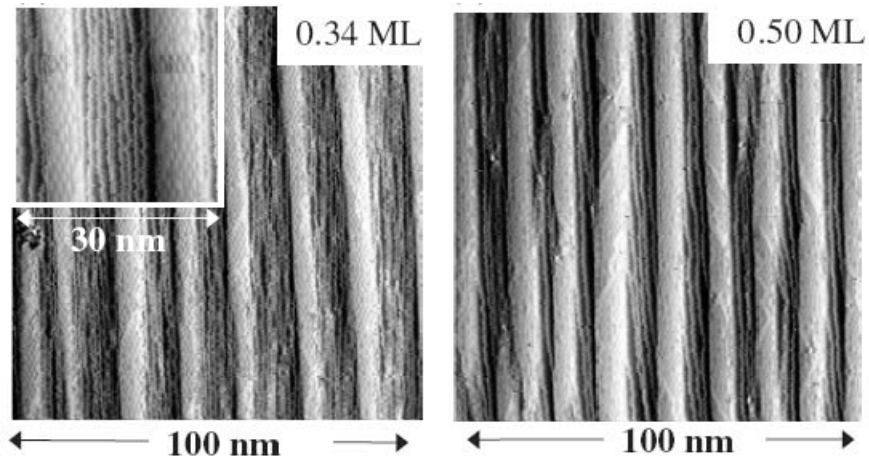
Scattering by steps and other surface defects
(H. Brune et al., EPFL)



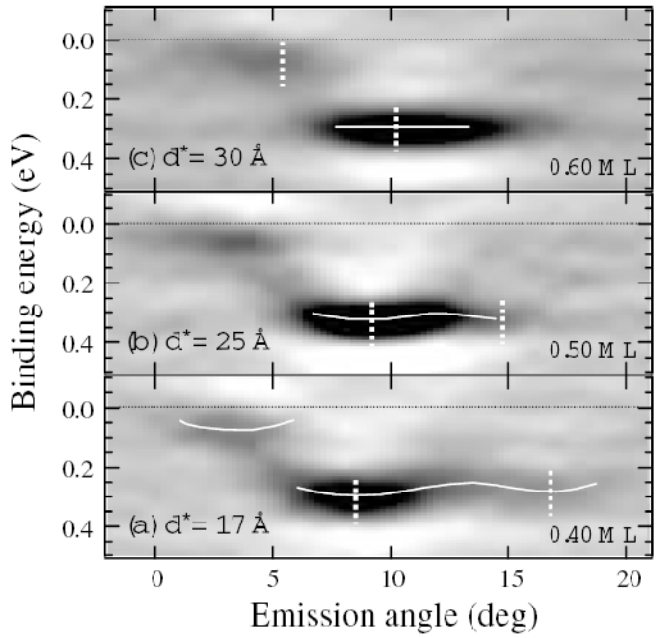


A. Mugarza, J.E. Ortega, J. Phys.- Cond. Matt. **15,** S32811 (2003)

The step periodicity induces 1D states perpendicular to steps

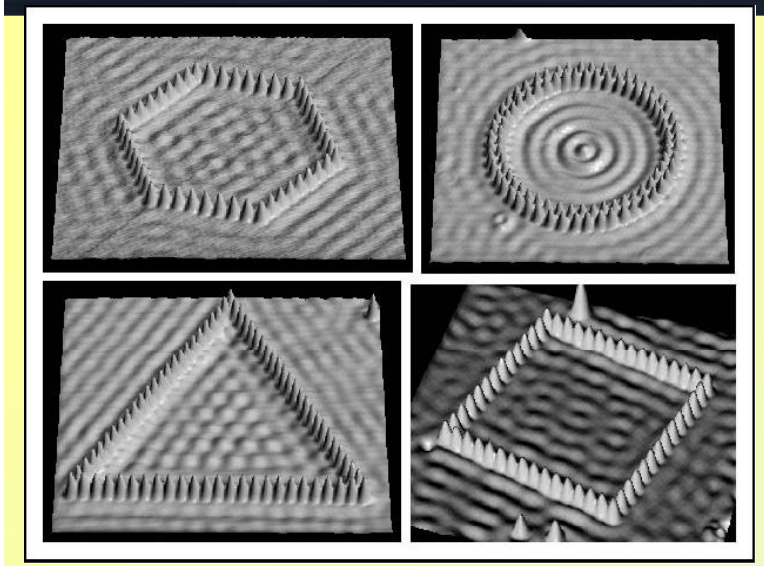


Ag/Cu(223)



A.R. Bachmann, *et al.*,J. Phys.- Cond. Matt. **15,** S3337 (2003)
J. Lobo, *et al.*, PRL **93,** 137602 (2004)

Periodic 0D electronic confinement on surfaces



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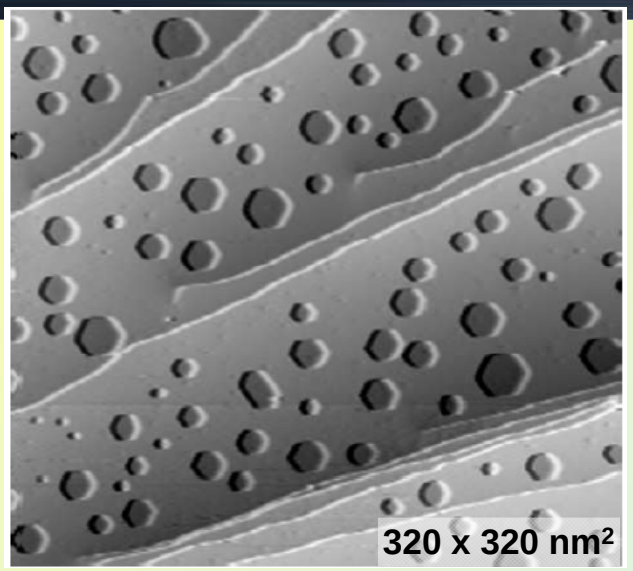


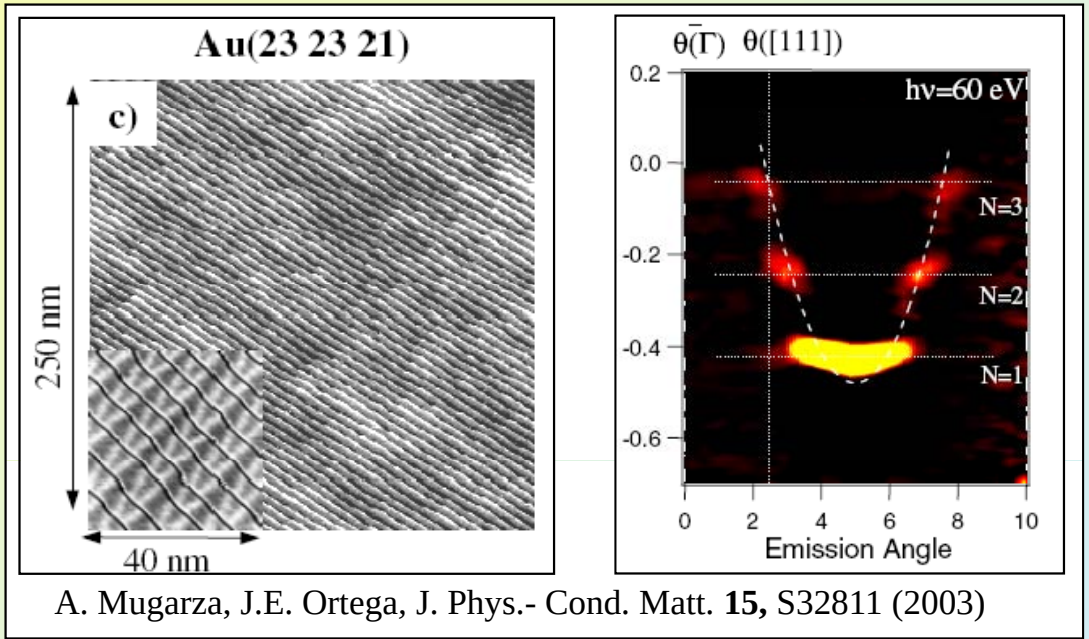
Nano-Islands on Ag(111)
J. Li *et al.*, PRL **80**, 3332 (1998)

Periodic 0D confinement on the surface is elusive

Difficulty to produce regular nanostructures capable of trapping the electronic states.

Size of confining entities ≥ ~2 nm (lateral coherence length of 1D surface state electrons)

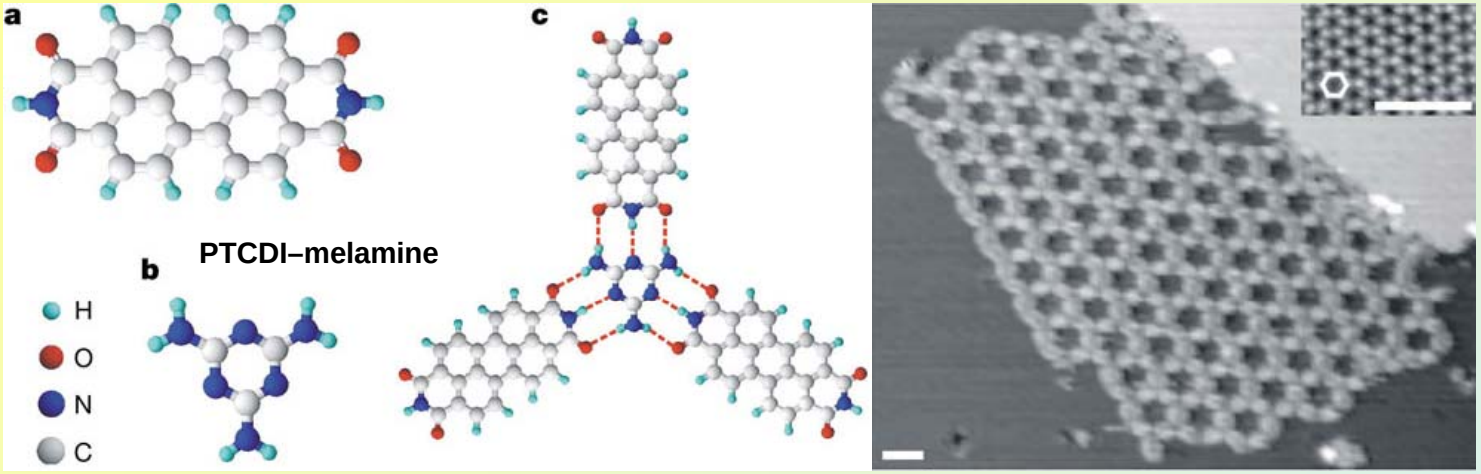
Can ***molecules*** be used for this purpose?



A. Mugarza, J.E. Ortega, J. Phys.- Cond. Matt. **15,** S32811 (2003)

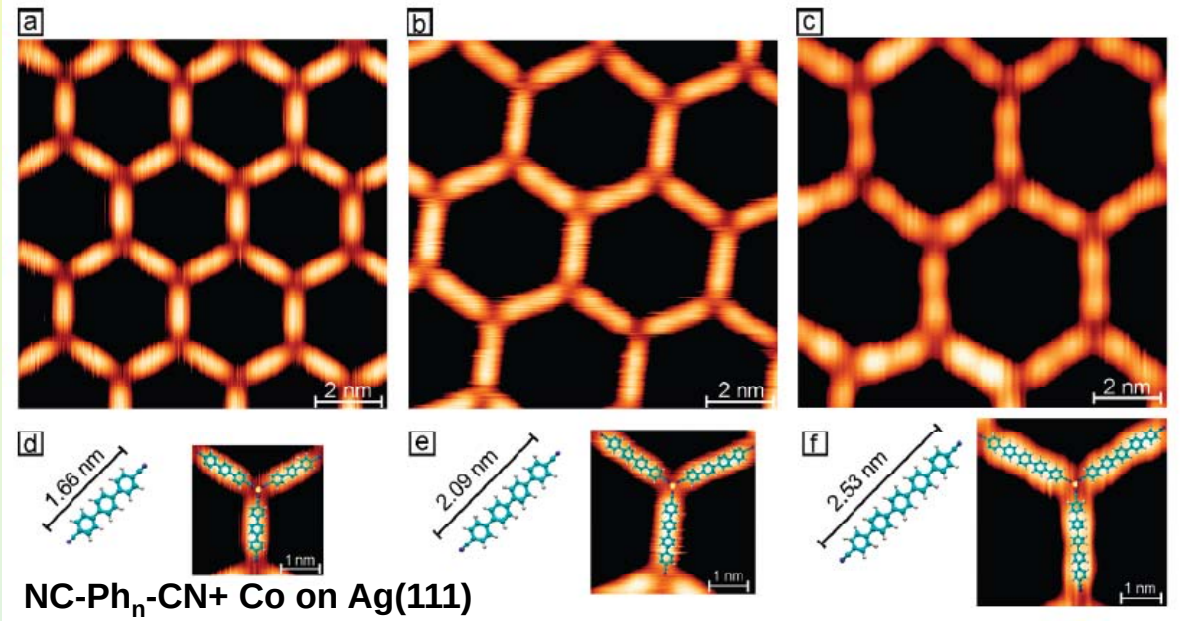
Supramolecular self-assembly

Supromolecular porous networks are a possible alternative to confine the electronic states within the existing pores.



Hydrogen bond networks

J.A. Theobald *et al.*,
Nature **424,** 1029 (2003)



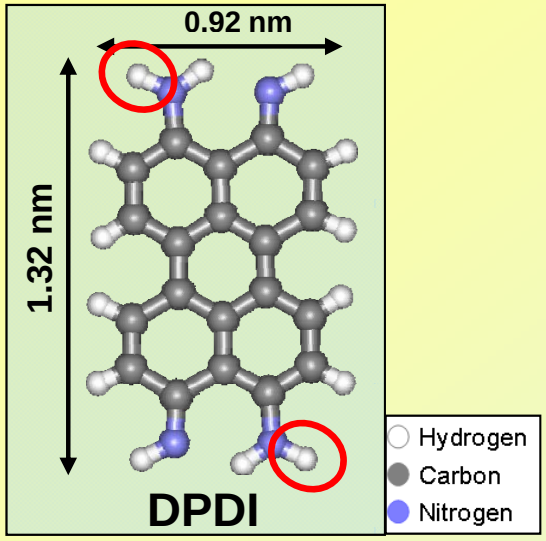
NC-Ph$_n$-CN+ Co on Ag(111)

Metal coordination networks

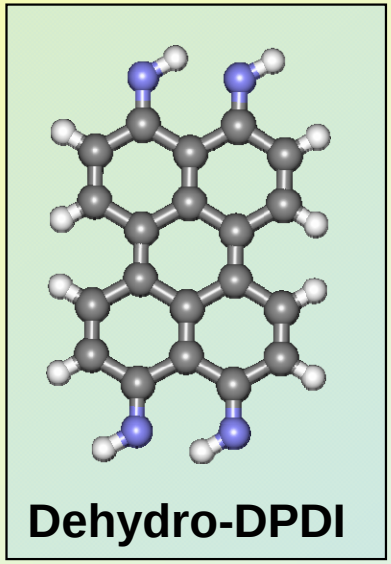
U. Schlickum, *et al.*,
Nano Lett. **7,** 3813 (2007)

Nanoporous Network: DPDI/Cu(111)

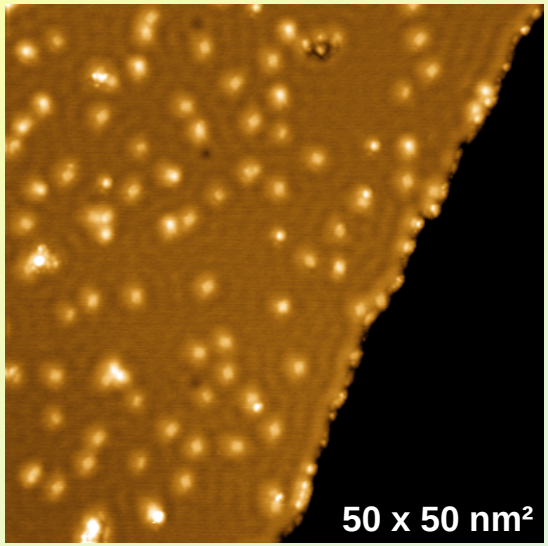
DPDI
(4,9-diamino-perylenequinone-3,10-diimine)



$-H_2$ 500 K

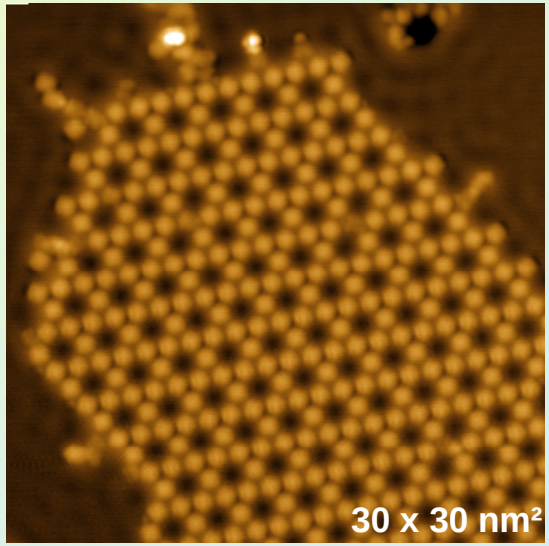


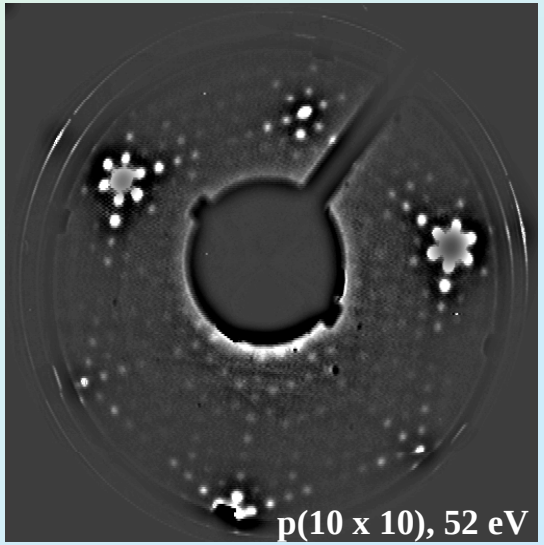
DPDI/Cu(111) imaged at 5 K



Below 0.7 ML observed porous network

It is commensurate with substrate

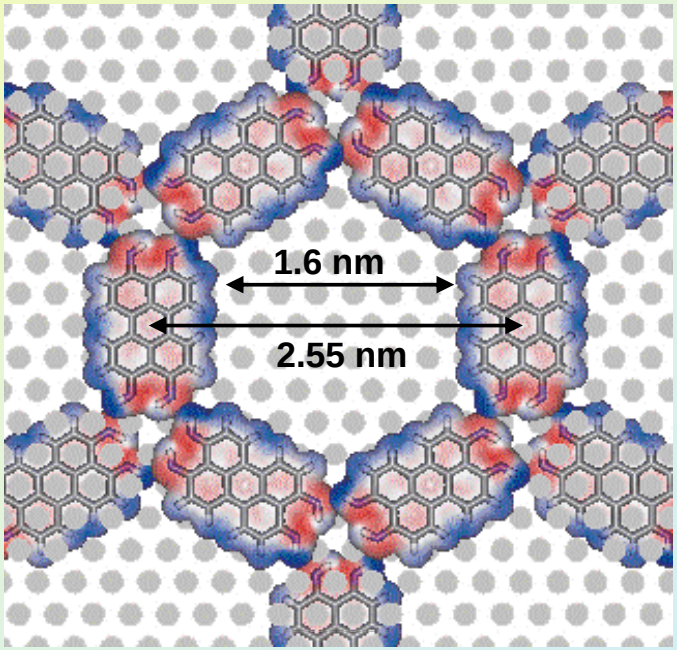


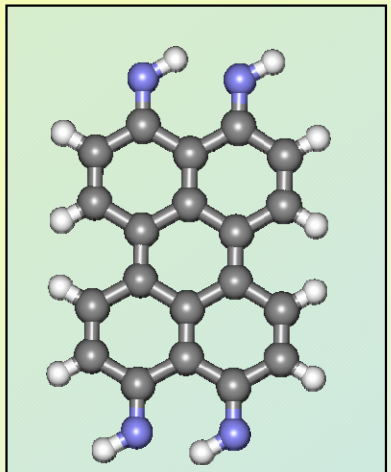


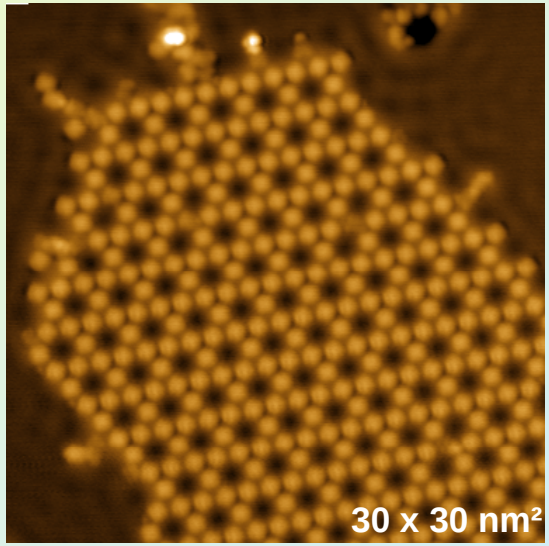
M. Stöhr *et al.*, Angew. Chem. Int. Ed., **44**, 7394 (2005)

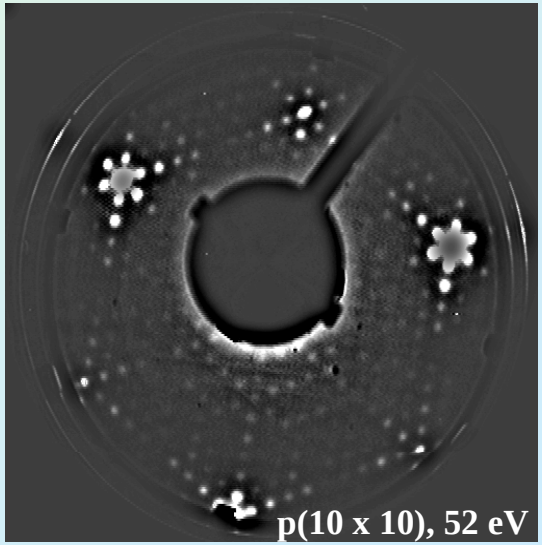
Nanoporous Network: DPDI/Cu(111)

- Temperature induced dehydrogenation of DPDI
- Most stable structure is the H-bonded network for coverage < 0.7 ML
- Oxidized form can act both as H-bond donor and acceptor
- The molecules are in registry with the underlying substrate
- structure is highly stable (up to 600 K)




Dehydro-DPDI





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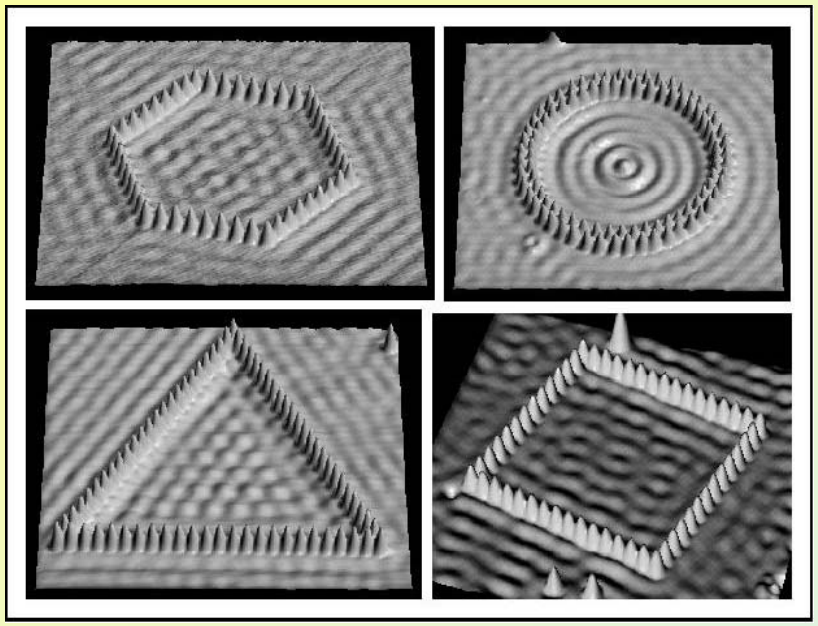
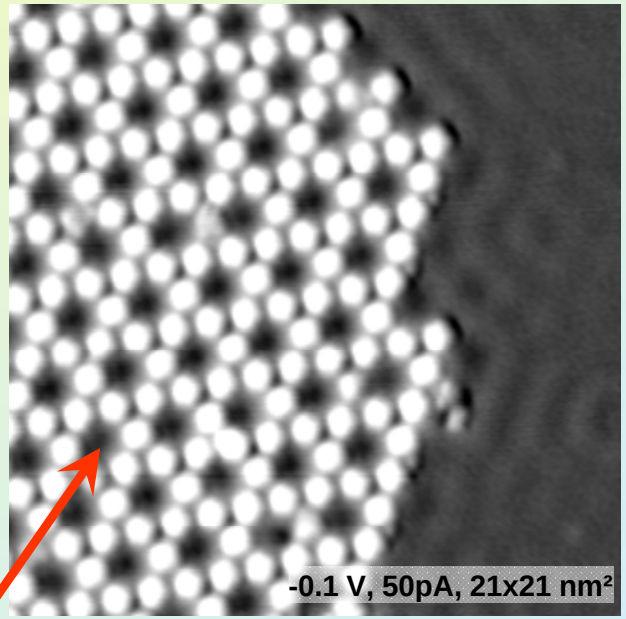
Confinement of the Cu(111) surface state

- Surface state electrons considered as 2D free electron gas
- Surface state interacts with network ⇒ Standing wave pattern



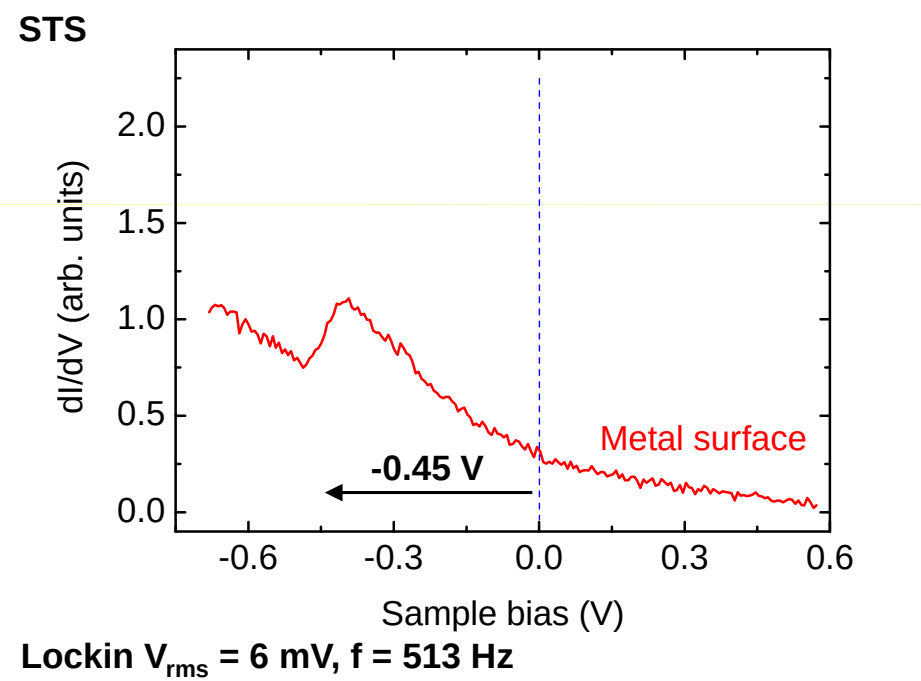
D. Eigler et al. (IBM)

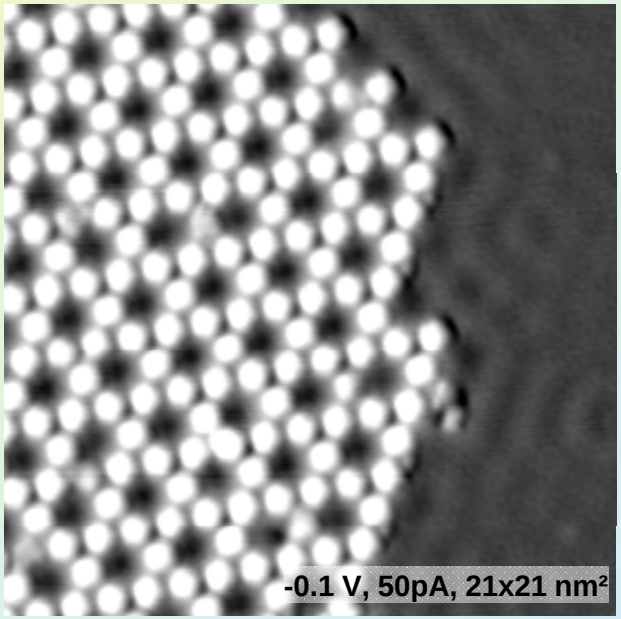


Confinement inside a pore?

Confinement of the Cu(111) surface state

- Surface state electrons considered as 2D free electron gas
- Surface state interacts with network ⇒ Standing wave pattern





Confinement of the Cu(111) surface state

- Surface state electrons considered as 2D free electron gas
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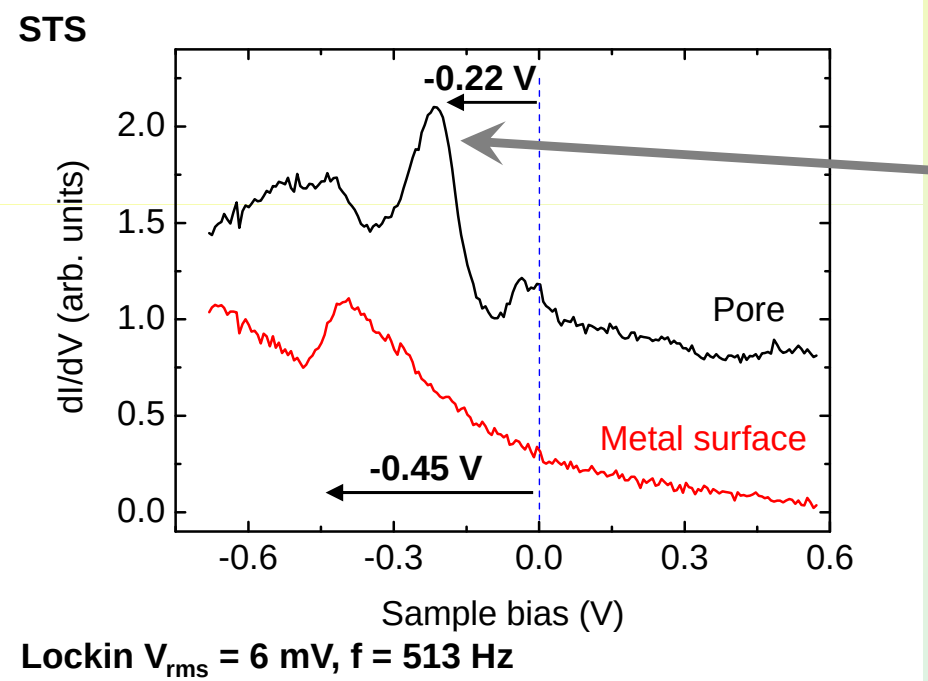
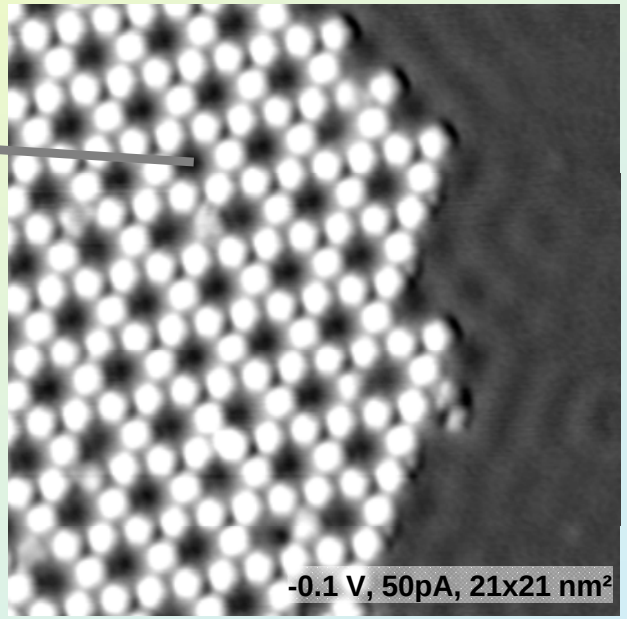
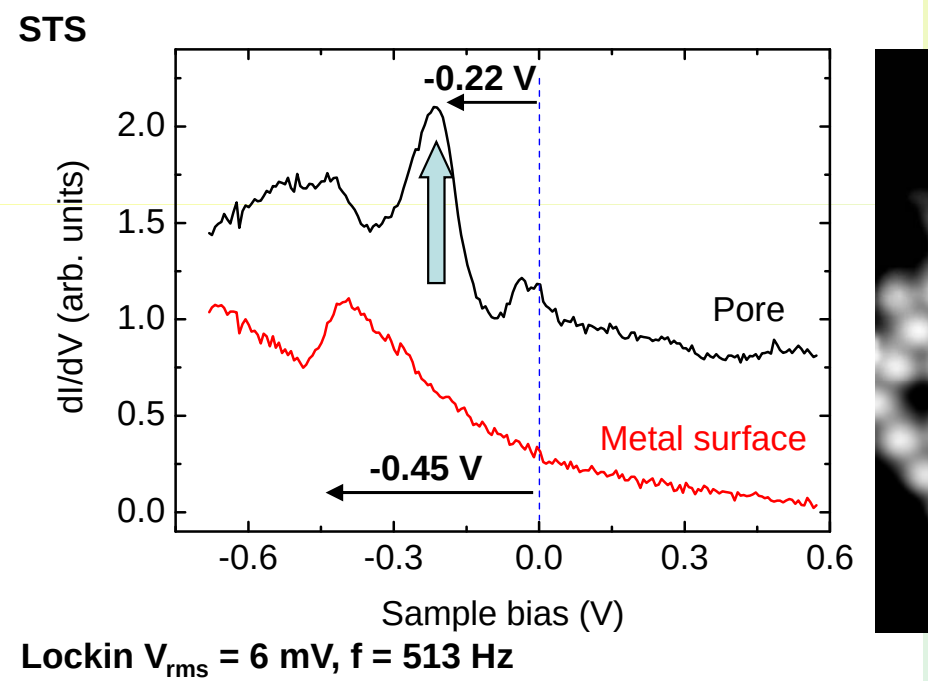




New Peak at -0.22 eV.
The Surface State feature disappears.
Is it a confined state?

Surface State confinement: STM + dI/dV map

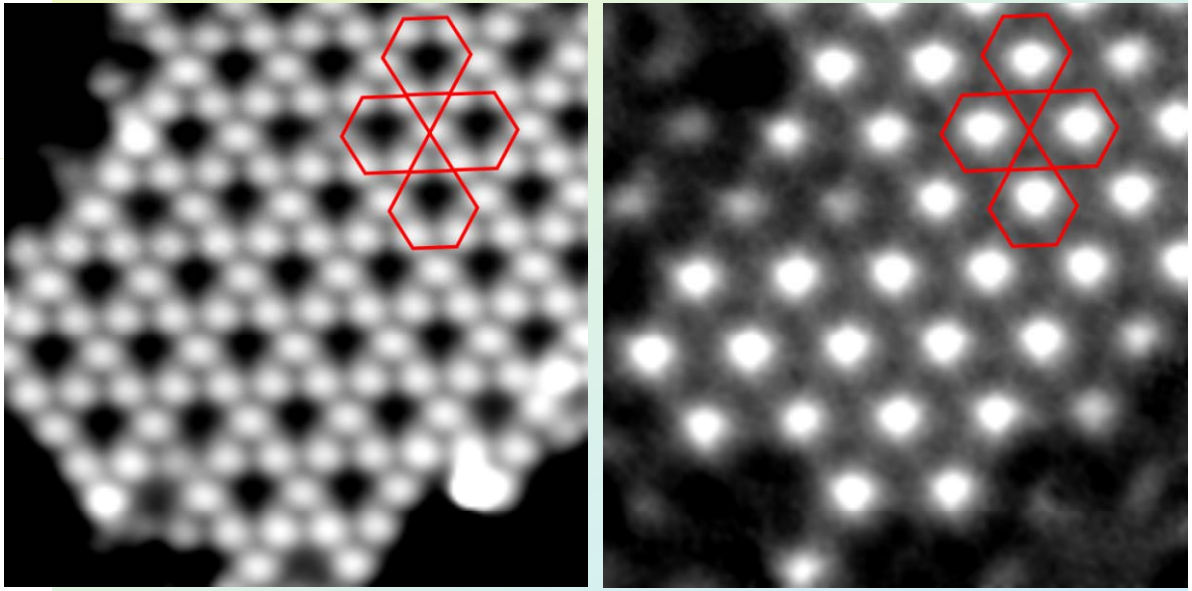
dI/dV map shows in a first order the state's local distribution



Lockin V_{rms} = 6 mV, f = 513 Hz

Topography

dI/dV map



-0.22 V, 70pA, 13.6x13.6 nm², Lockin V_{rms} = 8 mV, f = 513 Hz

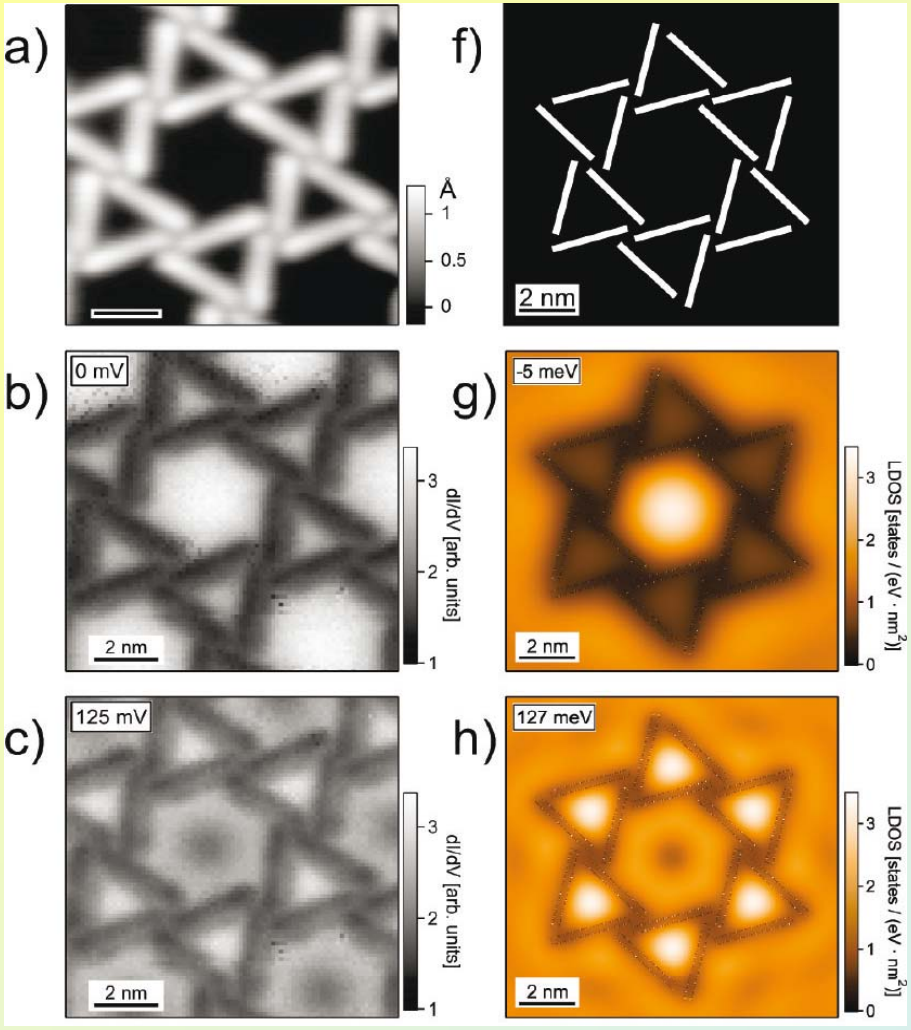
Confined electronic states into the pores!

Each state is confined in all directions ⇒ Periodic array of quantum dots!

Surface State confinement: STM + dI/dV map

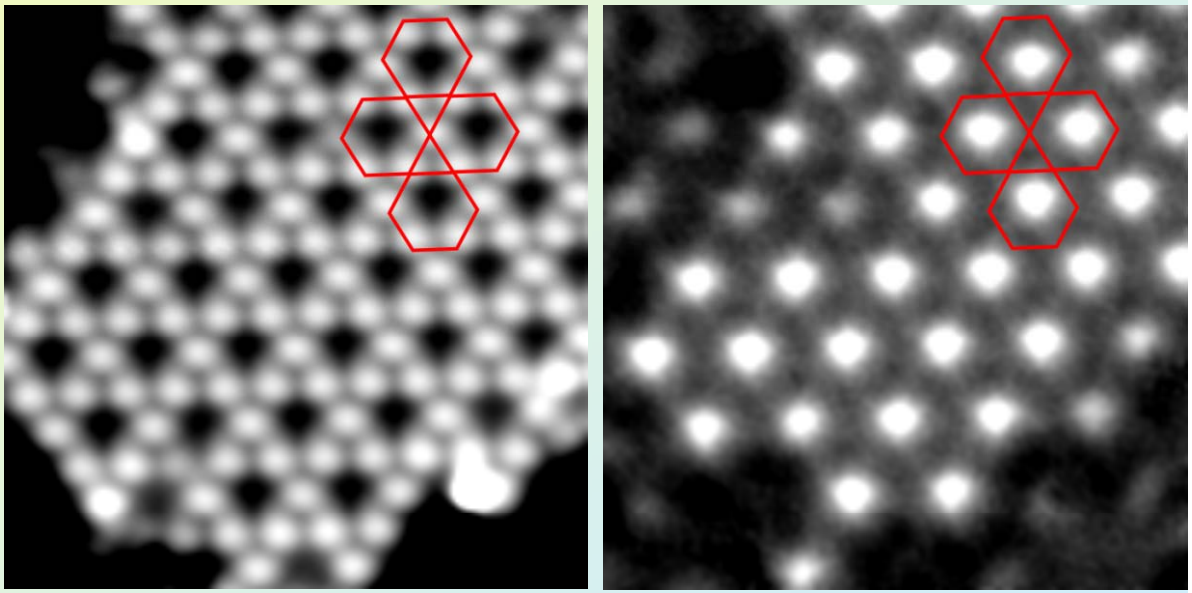
dI/dV map shows in a first order the state's local distribution

~0.4 ML of NC-Ph6-CN / Ag(111)



Topography

dI/dV map



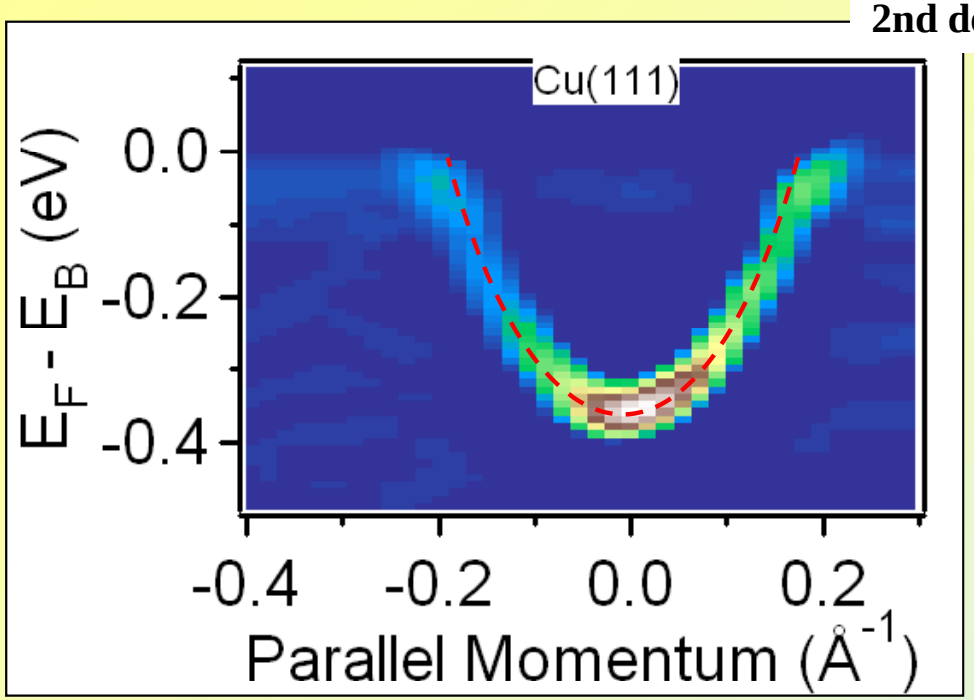
-0.22 V, 70pA, 13.6x13.6 nm², Lockin V_{rms} = 8 mV, f = 513 Hz

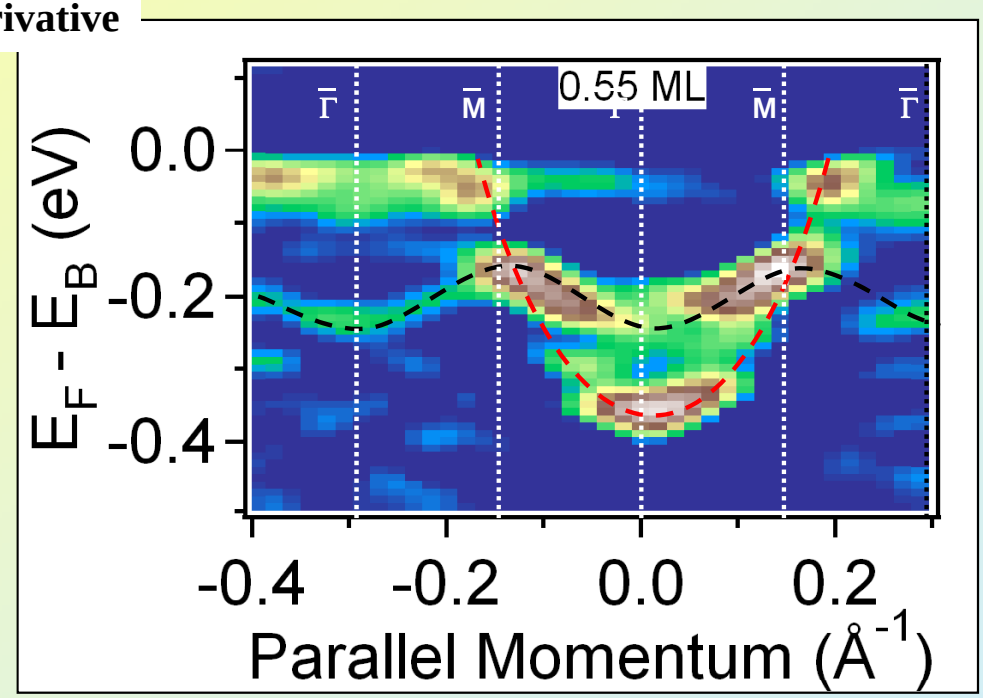
Can the network periodicity induce new electronic bands?

F. Klappenberger *et al.*, Nano Letters (2009).
DOI: 10.1021/nl901700b

Electronic structure of molecular network: ARPES

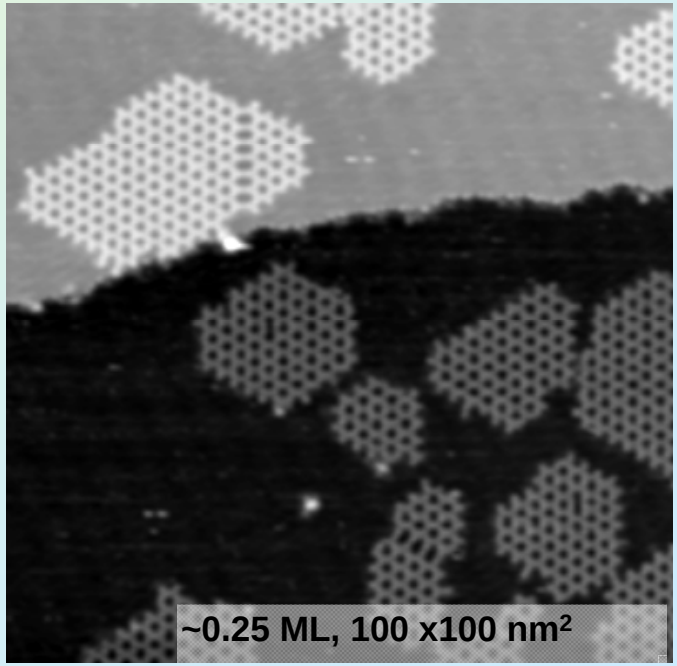
2nd derivative



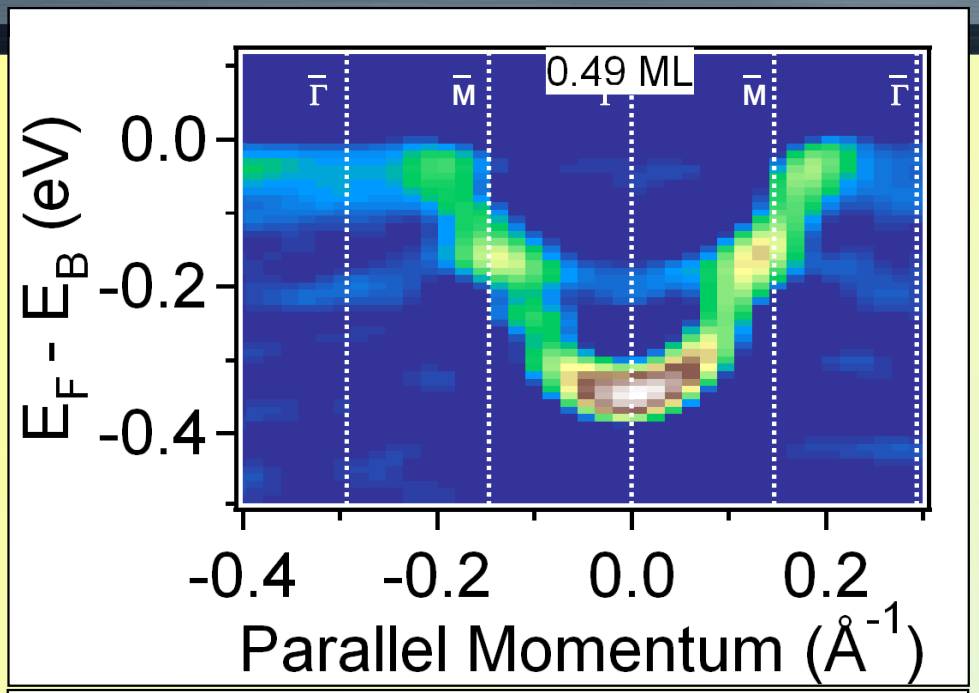


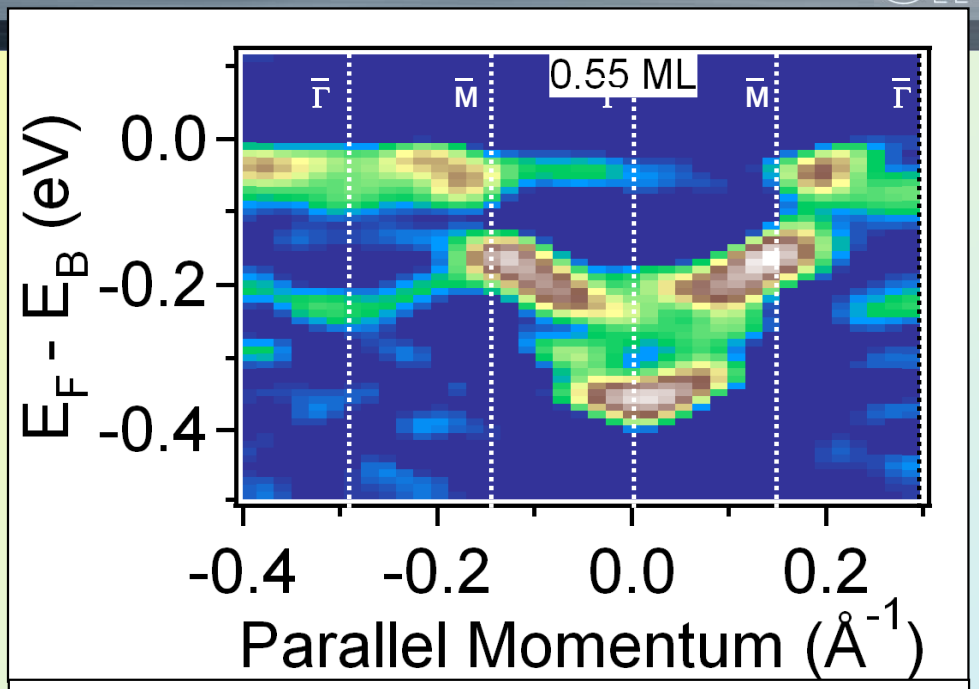
The 2nd derivative enhances the existing features.
The periodicity of the network gives rise to a new band

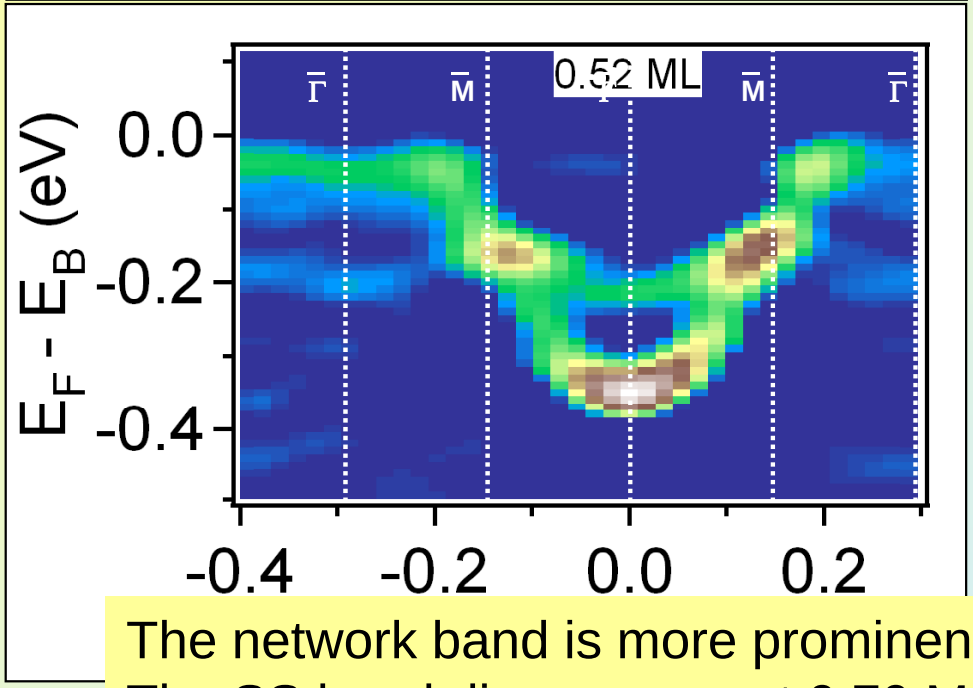
The SS spectral function dominates.
Two bands can be inferred from the EDCs

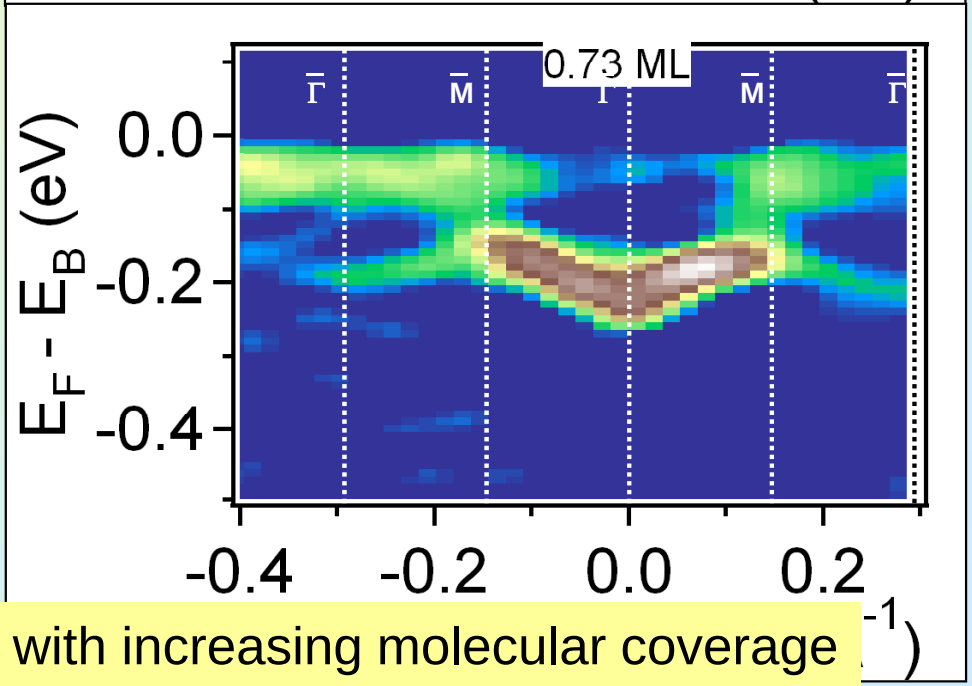


Electronic structure vs molecular coverage



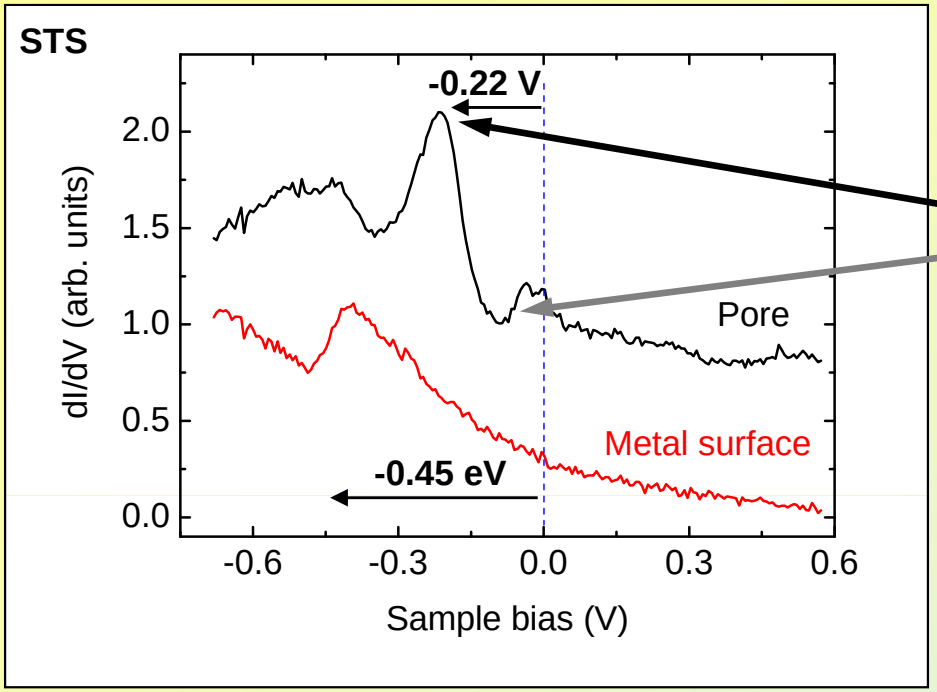


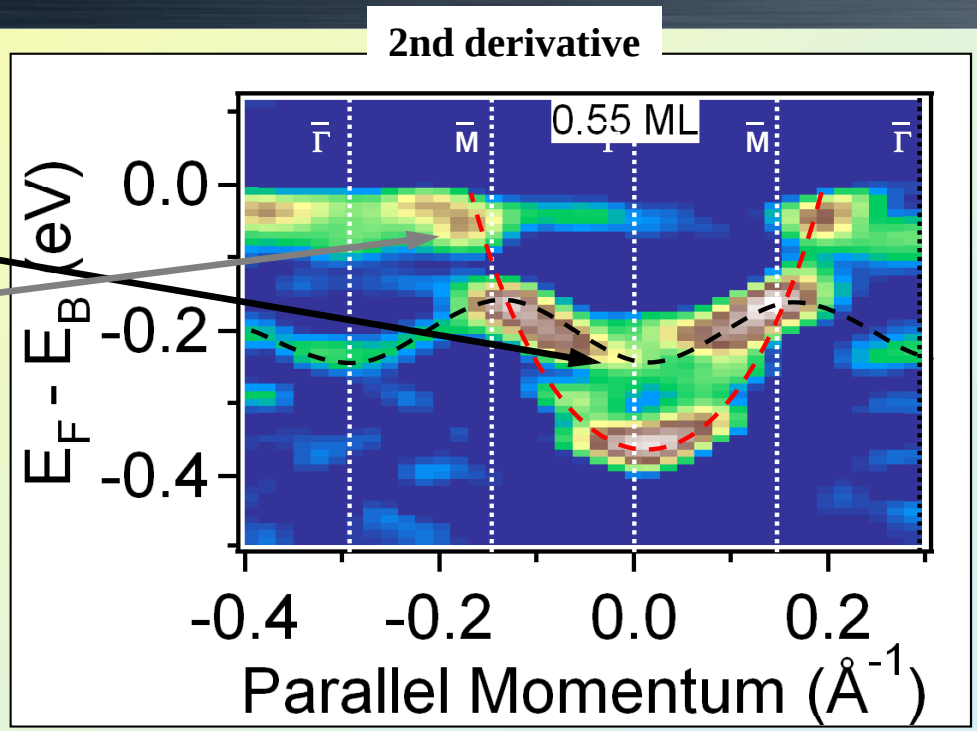




The network band is more prominent with increasing molecular coverage
The SS band dissappears at 0.70 ML (everything covered by network).

Electronic structure: STS vs ARPES



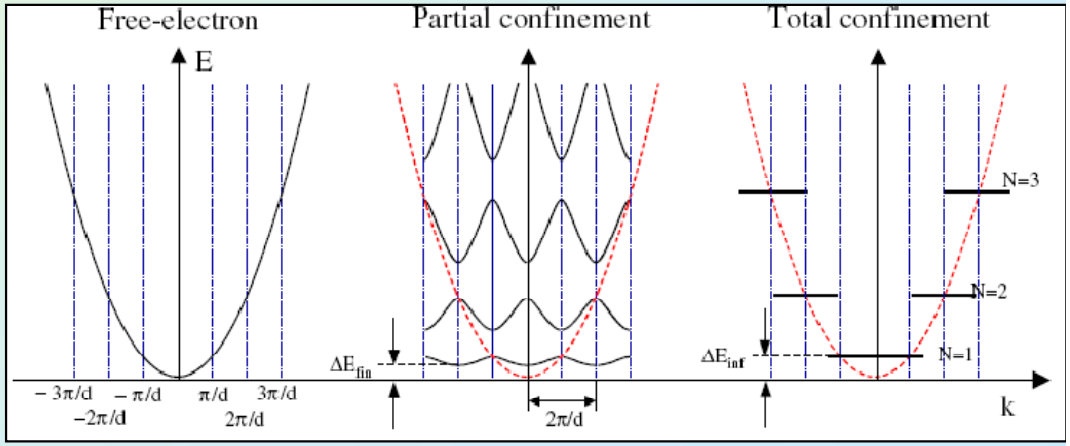


Agreement between STS and ARPES!!!

The band structure = lossy scattering + network periodicity
(Analogy to band structure of solids)

Significant confinement:
- No SS underneath molecules
- Shift of 230 meV
- Band width ~80 meV.
- Energy gap is ~90 meV.

1D Kronnig-Penney model

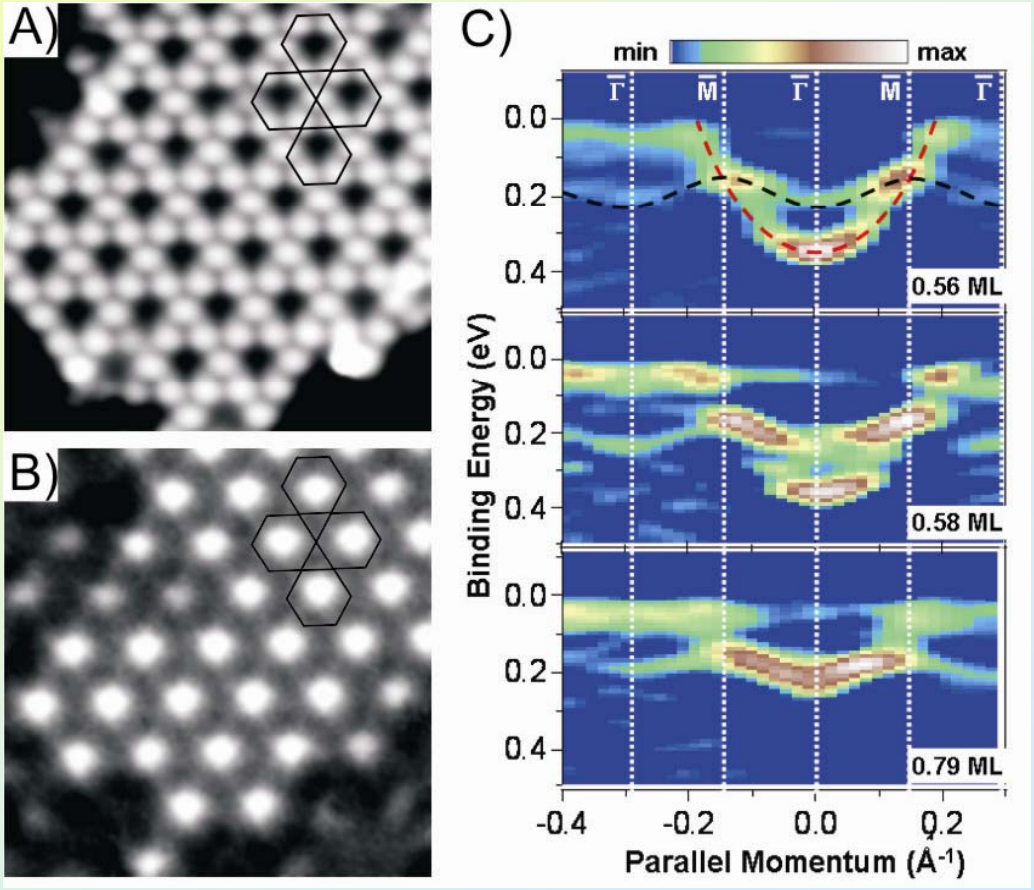


Conclusions

- By means of STM and STS we have observed *periodic* 0D confinement in a supramolecular porous network.

- Because of the periodicity imposed by the network in combination with the lossy confinement at the molecular pores, a band structure is formed, as demonstrated by ARPES.

- Controlling the network dimensions and the coupling between the molecular building blocks with the Surface state, will allow the fabrication of coupled confined electronic systems in analogy to optical 'metamaterials'.



J. Lobo-Checa, M. Matena, K. Müller, J. H. Dil, F. Meier, L.H. Gade, T. A. Jung, M. Stöhr.
"Band structure generated from Coupled Quantum Dots Formed by a Nanoporous Network on a Copper Surface".
Science **325**, 300 (2009)

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Kathrin Müller
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Thomas Greber
Jürg Osterwalder

University of Heidelberg:

Susanne Martens
Till Riehm
Lutz H. Gade

STM control system by

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Thank you for your attention!