Wiederholung

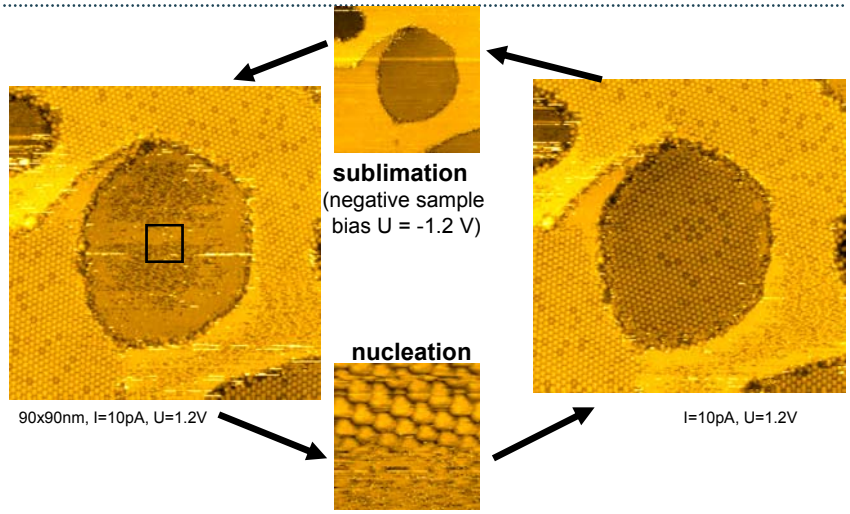
Diffusionsexperimente und Wachstumseigenschaften

STM: ‘Mikroskopie und Experimente’
Experimente mit Kraeften, Atomen und Molekuelen

AFM: Kraefte abbilden, damit experimentieren und (auch) elektronische Eigenschaften vermessen.

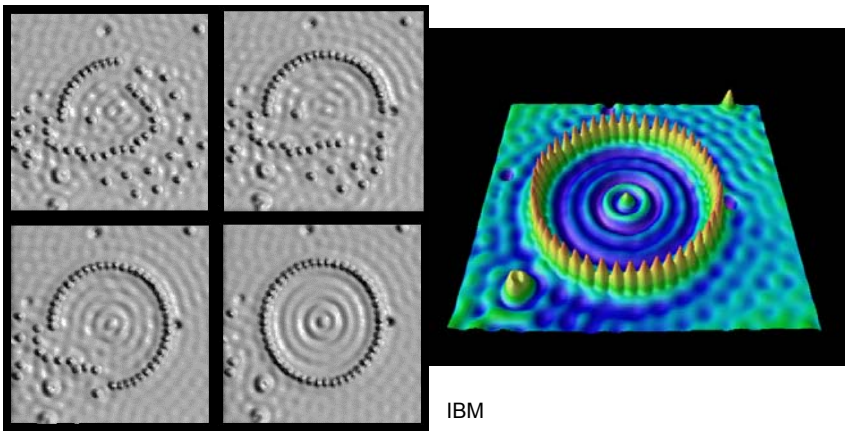
Reibung, KelvinProbe, Bruch, SCFM, SSRM, contact / non-contact, ….

Reversible 2D Phase Transition controlled by the STM tip



Controlled phase transition 2D fluid <=> 2D solid

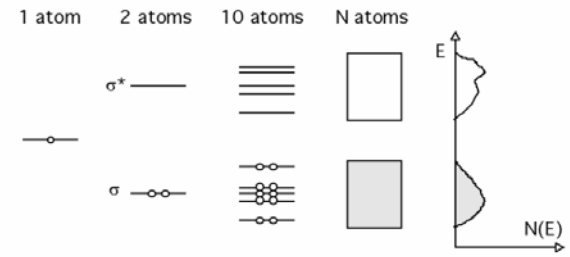
Quantum Corral



IBM

STS (scanning tunneling spectroscopy)

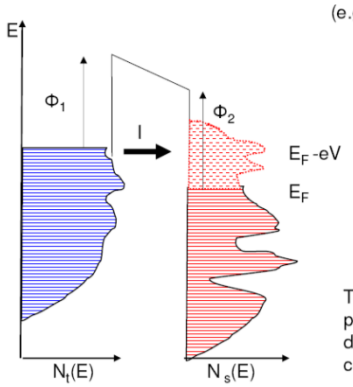
Density of States (DOS)



Density of States (DOS), N(E) is the number of energy levels bewteen E and E+dE (states per eV)

States can have s,p,d,f or mixed (hybrid) character
Bands may be separated by band-gaps E_g

Voltage dependence of tunneling current



By changing the voltage, the density of states can be recorded as function of the voltage (e.g., band structure of semiconductors)

$$I \propto \int_0^{eV} N_1(E) N_2(E - eV) T(E,V) dE$$

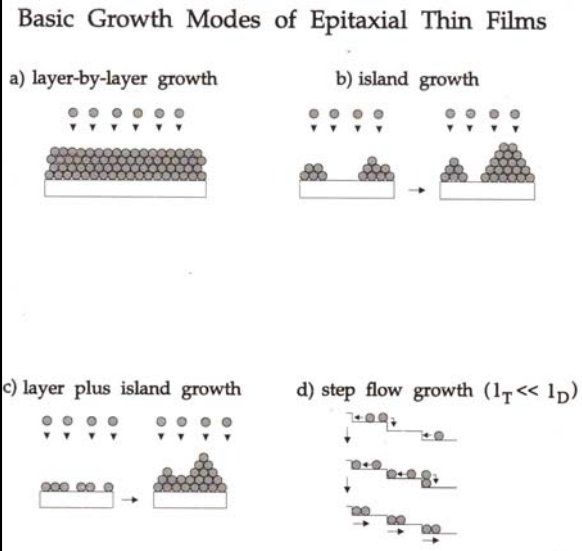
where N_1 N_2 are the densities of states at the Fermi niveau and T(E,V) the transmission probability.

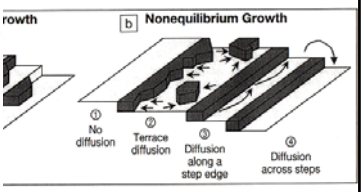
$$T(E,V) = \exp\left\{-2s\left[\phi - E + \frac{eV}{2}\right]^{1/2}\right\}$$

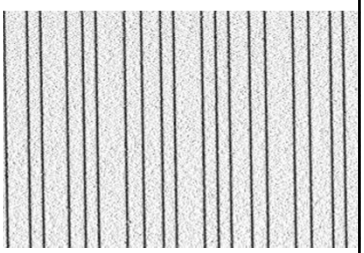
The contribution of the states to the tunneling process decays exponentially with their energetic distance to the Fermi niveau. Core levels do not contribute at all.

'Physical' Self Assembly of e.g. Nanowires

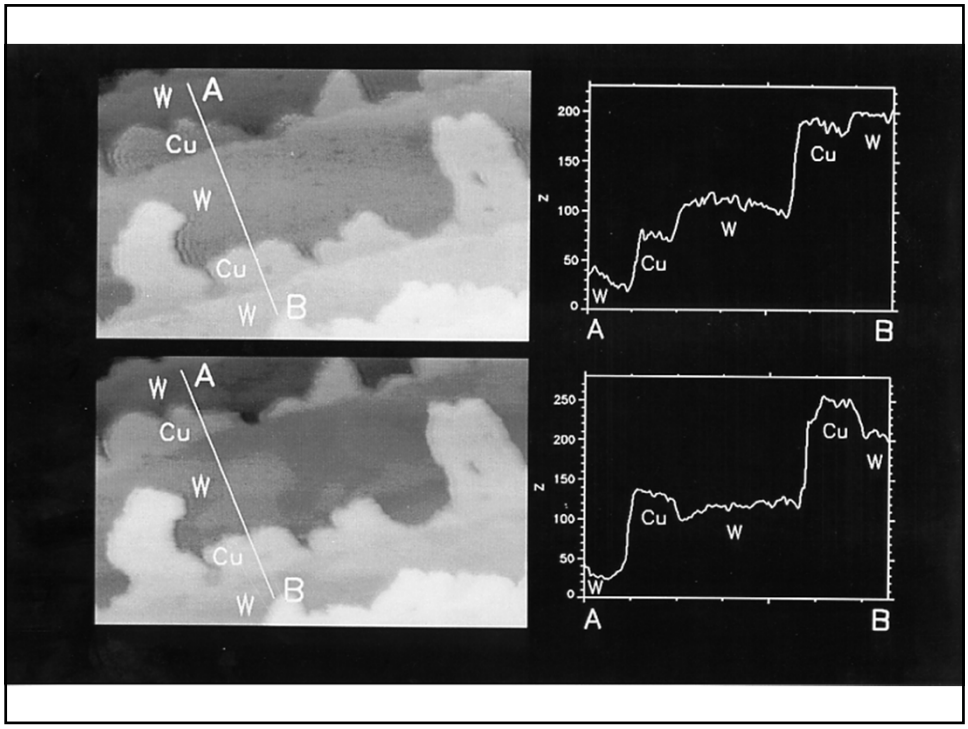
jumping from 3D to 2D



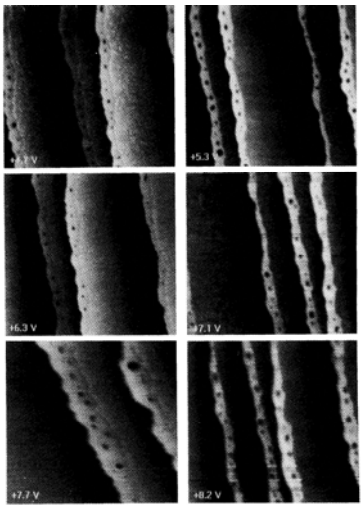


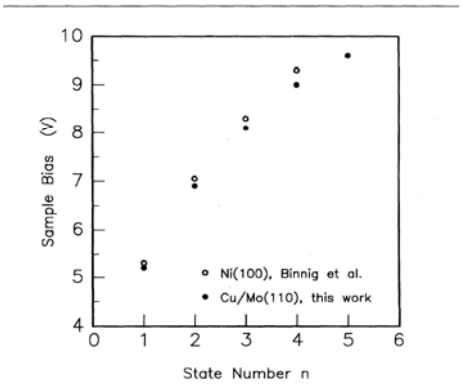


Th. Jung et al.
n **24**, 20--24 (1999).



Chemical Sensitivity in STM: surface states vs image states

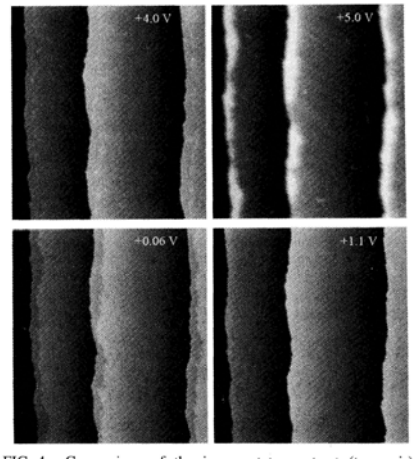




Periodic Contrast Change in U_{gap}: Image Resonant Enhancement !

T. Jung et al. Phys. Rev. Lett. 74, 1641 (1995)

Chemical Sensitivity in STM: surface states vs image states



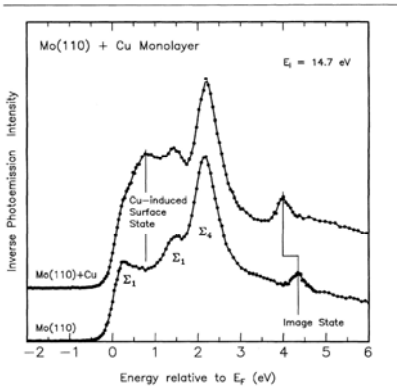
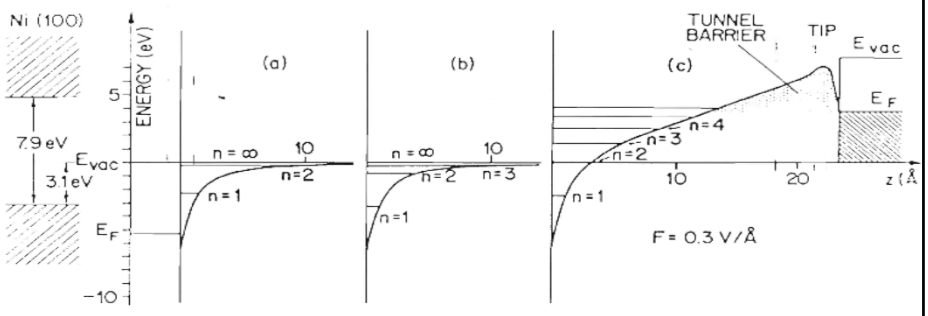


Image State Contrast >>> Surface State Contrast

T. Jung et al. Phys. Rev. Lett. 74, 1641 (1995)

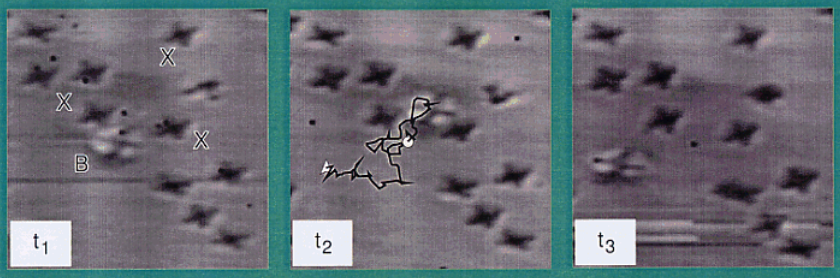
Bildladungspotential ueber leitender Oberflaeche



a) idealer Leiter
b) hohe Stufendichte
c) Potentialverschiebung im STM

Molecular Motion Constrained to Two Dimensions

co-evaporation of Cu-tetraphenyl porphyrin (pins, X) and
Cu-tetra-di-t-butyl-phenyl porphyrin (balls, B)



Molecular structure influences: **STM - Contrast**
DE Adsorption
Mobility

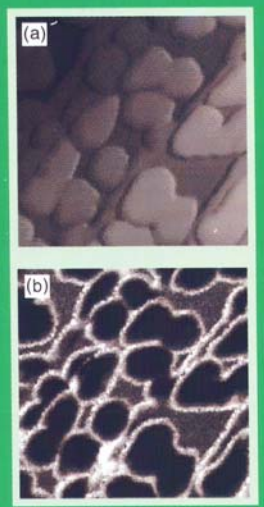
IBM

T.A. Jung, R.R. Schlittler and J.K. Gimzewski
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

•T. A. Jung SPM Tutorial

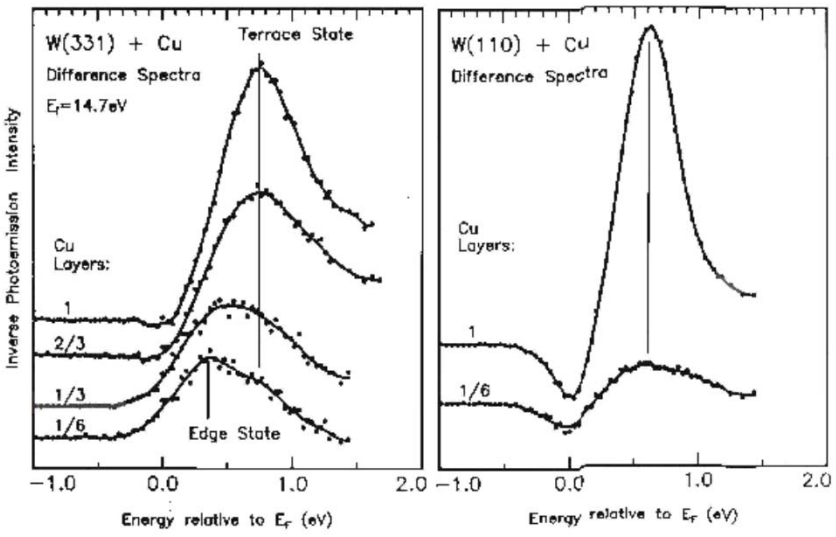
Chemical Information from SPM / Spectroscopy

Spectroscopic Changes at the Edge of Fe Islands on W(110)

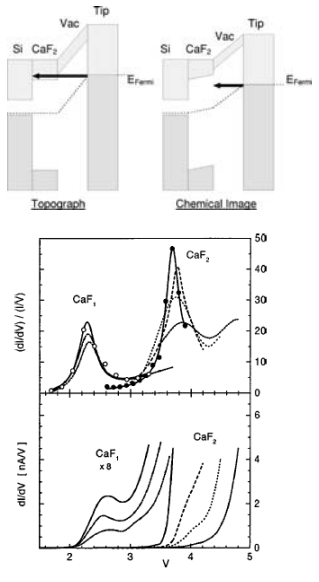


(a) From Bode et al., Phys. Rev. B 54, R 8385 (1996);
(b) From Wiesendanger et al., J. Vac. Sci. Technol. A 14, 1161 (1996).

Stufenzustaende und Oberflaechenzustaende auf W(331)

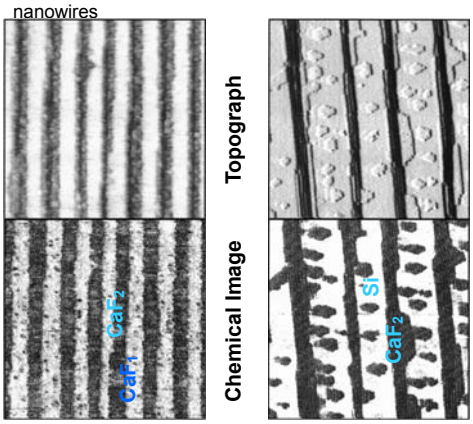


Scientific Background: Chemical Imaging



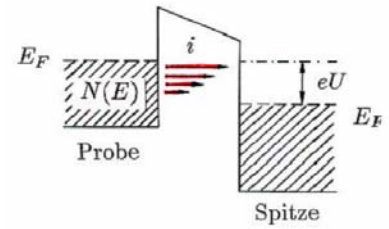
CaF_1 / CaF_2 nanowires

CaF_2 on Si(111)



Chemical imaging of insulators by STM
J. Viernow et al., *Phys Rev. B 59 (1999) 10356*

Spektroskopie



Spektroskopie

Lokale Messung der I/U-Charakteristik bei $x, y, z = const$ (R.J. Hamers, R.M. Tromp and J.E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986))

Information über lokale elektronische Zustandsdichten N(E) enthalten in

$$I/U$$

$$dI/dU$$

$$\frac{dI}{dU}/\frac{I}{U} = \frac{d\ln I}{d\ln U}$$

CCT's mit $+U$ und $-U$

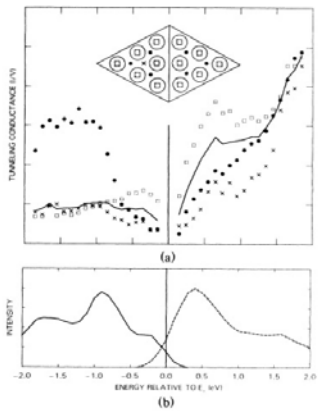
Stabilisierungsspannung U_0 und U sind Parameter

Zustandsdichte der Wolframdichte im Bereich der Fermienergie ändert Sich wenig, d.h. es wird primär die Zustandsdichte der Probe beobachtet (+; unbesetzte Zustände, -, besetzte Zustände)

Tunnelspektroskopie von Si(111)7x7

I(V)/V

UPS/IPS



R. Hamers,
Phys. Rev. Lett. 56, 1972 (1986)

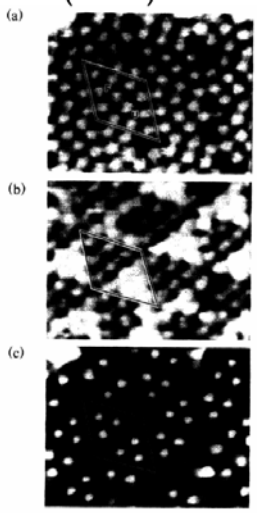


FIG. 1. Simultaneously acquired topograph and current images: (a) STM topograph with +2 V applied to the sample, and current images with (b) +1.45 V and (c) −1.45 V applied to the sample.

Tunnelspektroskopie von GaAs(110)

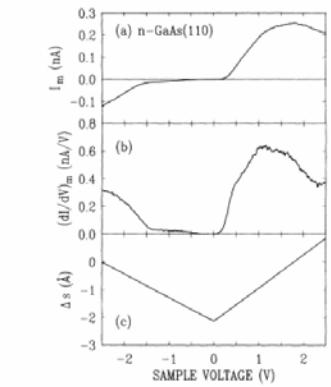


FIG. 1. Raw data from an *n*-type GaAs(110) surface, showing the (a) measured tunnel current and (b) measured conductance, as a function of sample voltage. The applied variation in tip-sample separation is shown in (c).

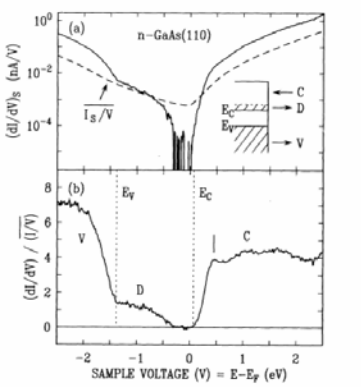


FIG. 3. Analyzed spectral data for *n*-type GaAs(110), showing (a) the differential conductance at constant tip-sample separation, and (b) the ratio of differential to total conductance. The dashed line in (a) shows the total conductance, broadened over a voltage width of 1.5 V. The components of the spectrum are indicated in the inset: *C*—conduction band, *V*—valence band, and *D*—dopant induced. Valence- and conduction-band edges are indicated by dotted lines, labeled E_V and E_C, respectively. The thin vertical line at 0.45 V marks a surface-state feature.

R. Feenstra et al., Phys. Rev. B 50, 4561 (94)

Tunnelspektroskopie auf Supraleitern

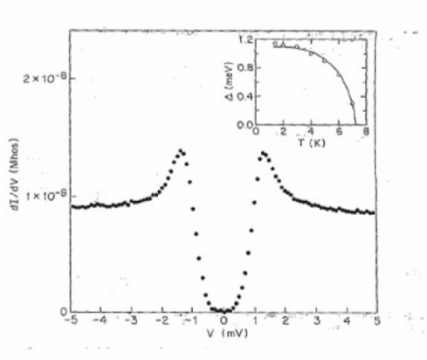


Fig. 2.7. dI/dV vs. bias voltage V for $NbSe_2$ at 0T applied magnetic field used to determine the gap at 1.45K. Inset: The gap vs. temperature and the corresponding BCS-fit. From [35].

H.Hess et al., Phys.Rev. Lett. 62(2), 214(1989)

Inelastic Tunneling Spectroscopy

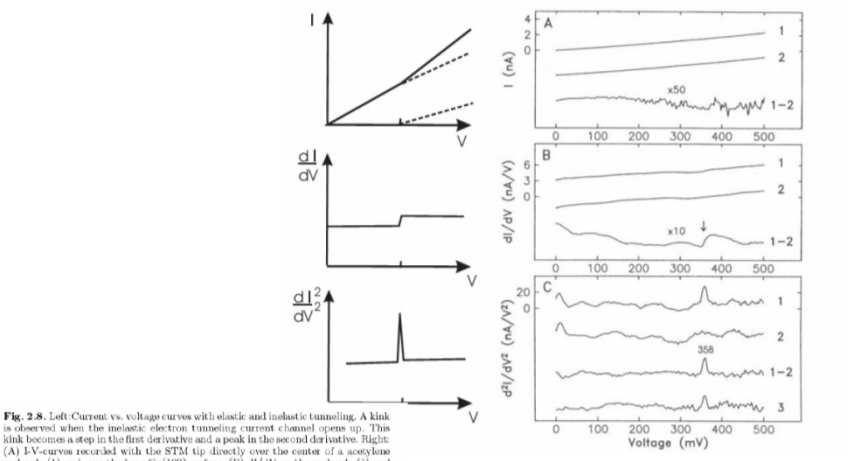


Fig. 2.8. Left-Current vs. voltage curves with elastic and inelastic tunneling. A kink is observed when the inelastic electron tunneling current channel opens up. This kink becomes a step in the first derivative and a peak in the second derivative. Right: (A) I-V-curves recorded with the STM tip directly over the center of a acetylene molecule (1) and over the bare Cu(100) surface. (B) dI/dV on the molecule (1) and on the substrate (2). (C) d^2I/dV^2 on the molecule (1) and on the substrate (2). The difference spectrum (1-2) shows a peak at 358mV. (3) is an average of 279 scans. From [41].

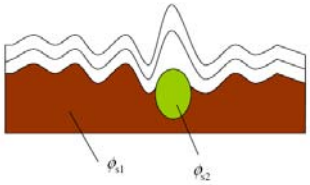
B.Stipe,M.Rezaei,W.Ho:Science 280, 1732 (1998)

Constant current mode

$$\ln(I) = \text{konst.} \Rightarrow \sqrt{\phi}\, s = \text{konst.}$$

If barrier height constant ⇨ **s=constant**

If barrier height varies ⇨ **ϕ(x,y), s(x,y) affect topography z(x,y)**



**Contour z(x,y)
at constant current**

Chemical contrast in an alloy

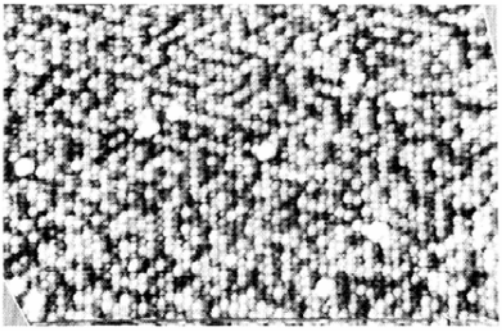
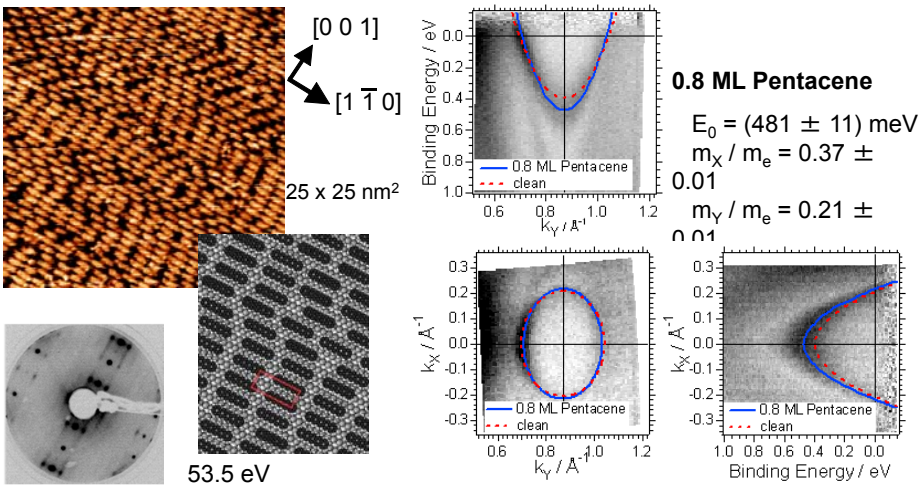


Fig. 2.14. STM image of the (111) surface of a $Pt_{25}Ni_{75}$ single crystal. A voltage of 5mV and current of 16nA were applied. A rather strong "chemical" contrast is observed, where the dark species is attributed to Pt und the bright features to Ni. The contrast is related to the interaction between tip adsorbates and the surface. Image size is 125Åx 100Å. From [50].

PAUL SCHERRER INSTITUT

Modification of the Cu(110) Surface State by Adsorption of 0.8 ML of Pentacene



0.8 ML Pentacene

E_0 = (481 ± 11) meV
m_X / m_e = 0.37 ± 0.01
m_Y / m_e = 0.21 ± 0.01

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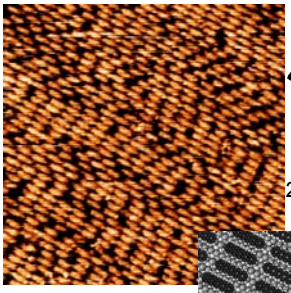
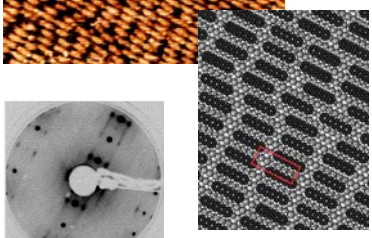
A. Scheybal et al. Physical Review B **79**, 115406 (2009)

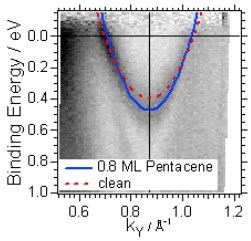
PAUL SCHERRER INSTITUT

Modification of the Cu(110) Surface State by Adsorption of 0.8 ML of Pentacene



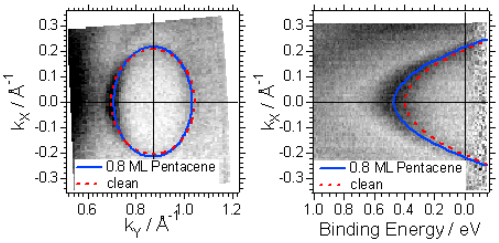


53.5 eV



0.8 ML Pentacene

E_0 = (481 ± 11) meV
m_X / m_e = 0.37 ± 0.01
m_Y / m_e = 0.21 ± 0.01



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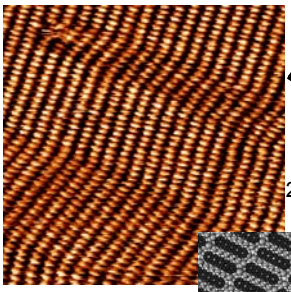
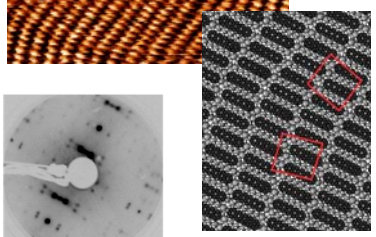
A. Scheybal et al. Physical Review B **79**, 115406 (2009)

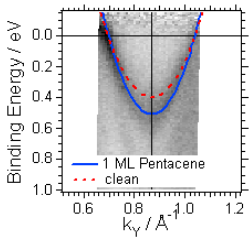
PAUL SCHERRER INSTITUT

Modification of the Cu(110) Surface State by Adsorption of 1 ML of Pentacene



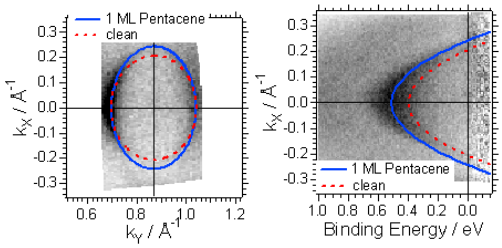


63.0 eV



1 ML Pentacene

E_0 = (515 ± 7) meV
m_X / m_e = 0.42 ± 0.02
m_Y / m_e = 0.22 ± 0.01



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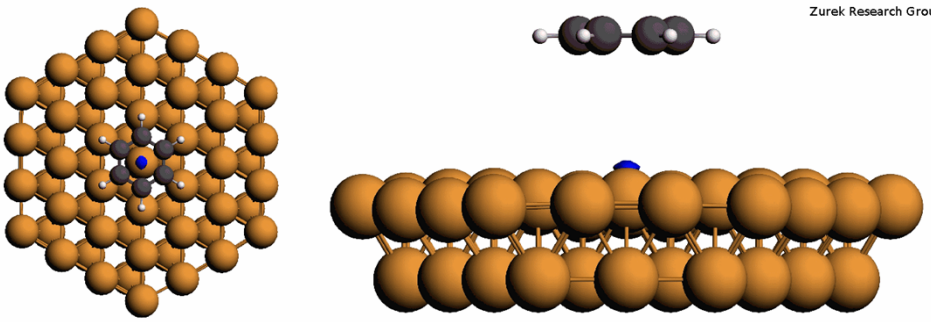
A. Scheybal et al. Physical Review B **79**, 115406 (2009)

Pillow Effect vs. Bond Formation



Animation of the formation of the pillow effect of surface charges as a benzene approaches a Cu(111) surface.
Calculations: E. Zurek and S. Simpson, SUNY Buffalo.
http://physics.unl.edu/enders/research#tab2

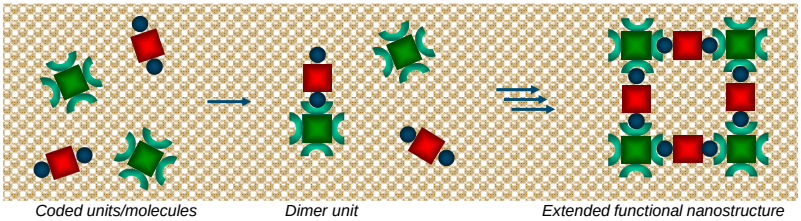
Surface Supported Supra Molecular Assemblies

Functionality by Host-Guest Assembly

Molecular self-assembly

Known from biochemical processes / supra-molecular chemistry

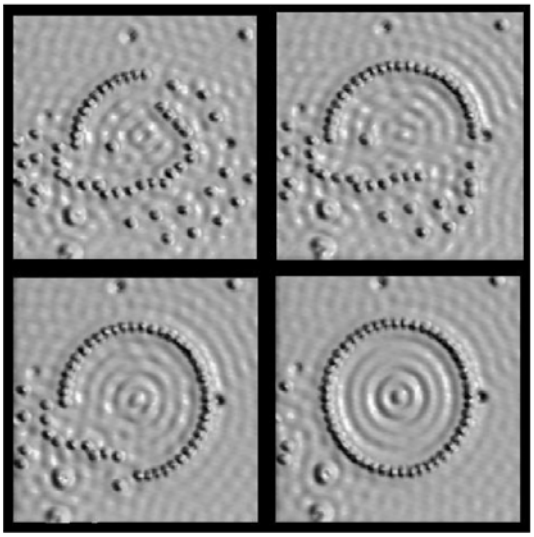
- Coded building blocks (molecules)
- Spontaneous structure formation („bottom-up“)
- Advantages
  - Parallel processing (fast)
  - Systems tunable by coding of units
  - Sub-nanometer precision, high reproducibility



Coded units/molecules *Dimer unit* *Extended functional nanostructure*

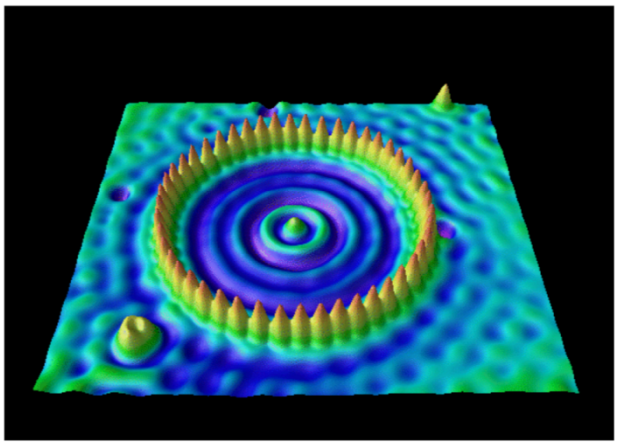
Challenge: Solvent free, modified by surface potential

Surface state scattering



M.F. Crommie, C.P. Lutz and D.M. Eigler, *Nature* 363 (1993)

Quantum corral



M.F. Crommie, C.P. Lutz and D.M. Eigler, *Nature* 363 (1993)

Oberflächenzustände auf Cu(111)

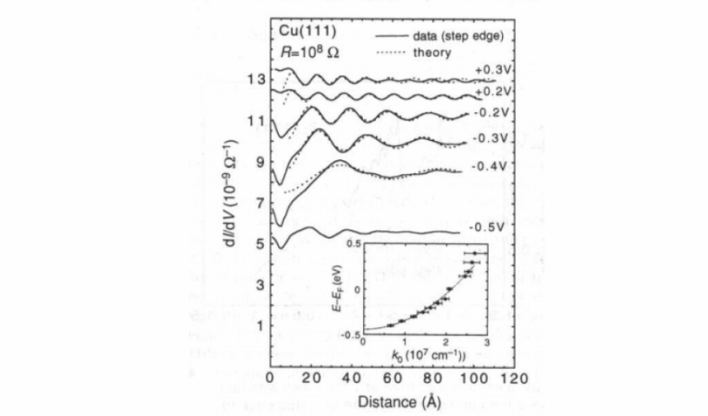


Fig. 2.16. Spatial dependence of dI/dV across a step edge on Cu(111) at 4K. For details see text. From [80].

„Confined electrons“

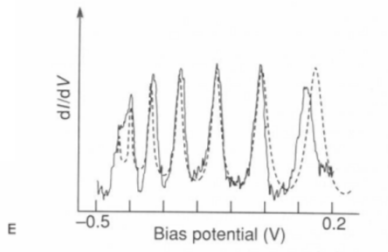
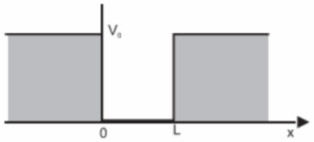


Fig. 2.18. The experimental (solid line) and theoretical (dashed line) voltage dependence of dI/dV, with the top of a STM located at the center of a 88.7Å diameter, 60-atom circle of Fe atoms on a Cu(111) surface. From [84].



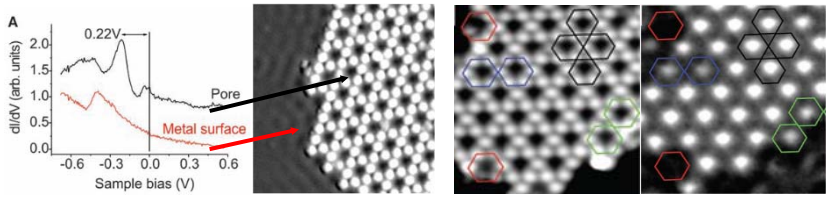
$$E_n = \frac{h^2}{8mL^2}n^2$$

E.Heller,M.Crommie,C.Lutz,D.Eigler:Nature 369, 464 (1994)

2D bandstructure

Detection of confined states in a porous supramolecular network

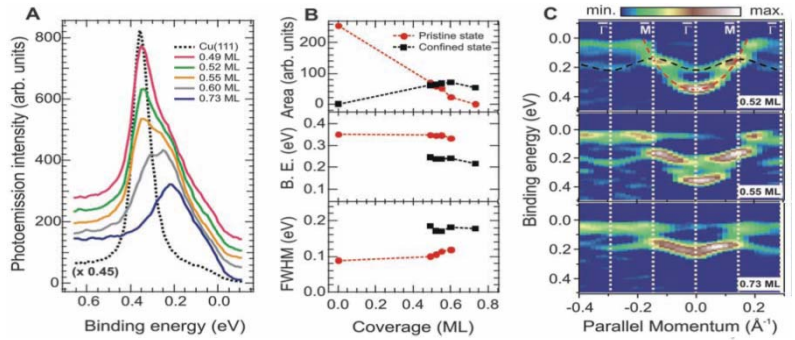
STS is a powerful tool to probe the local electronic density of states (LDOS) of a quantum entity.
STS performed inside the hexagonal DPDI pores shows, in the corresponding dI/dV curve, a confined electronic state at -0.22V (black curve).
No peak is seen on the metal surface for the same voltage (red curve).



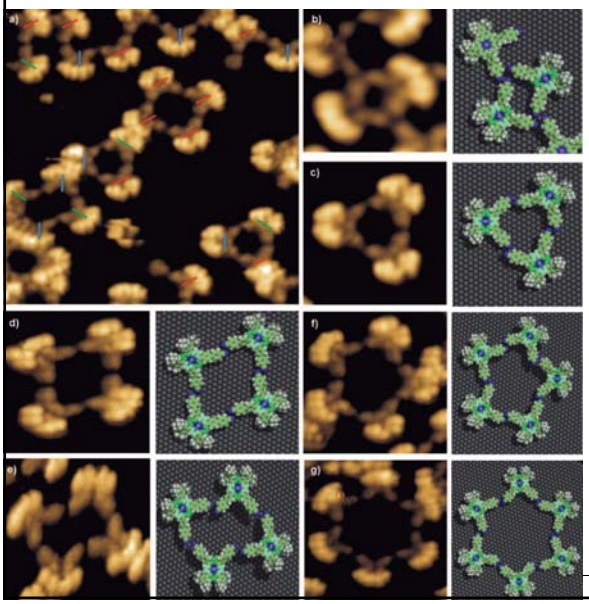
J.Lobo-Checa et al, Science, 325,300 (2009).

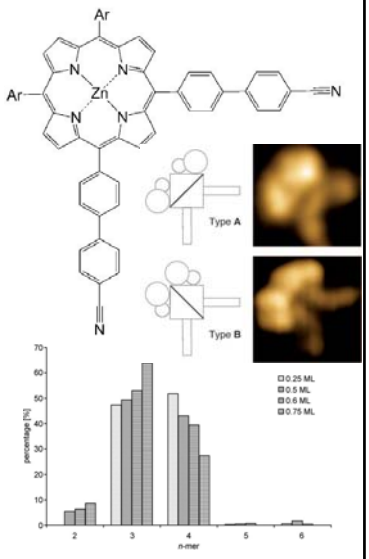
2D bandstructure (STS+ARPES)

ARPES is a surface analytical technique that helps us to identify the binding energy of the confined electrons with respect to their momentum.
The red dotted line in fig c shows the E(k) relation of the free surface electrons and the black line (first sub-band) corresponds to the first confined state.
The energy gap between the sub-bands is ~90 eV.
With increasing molecular coverage, the number of the confined states increases and the surface state forms a continuous band in 2D supramolecular structure.



Supramolecular Assemblies: CN-di-phenyl-porphyrin Macrocycles

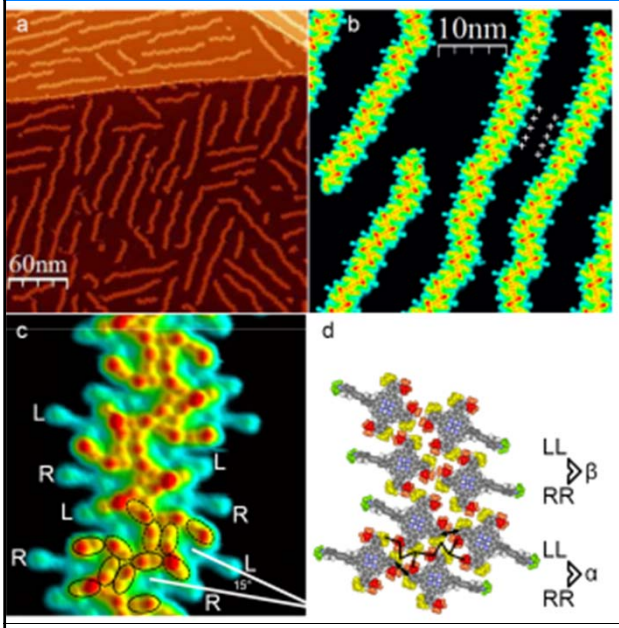




CN-phenyl → only tetramers
Yokoyama et al. Nature 2001

L.-A. Fendt et al., Chem. Eur. J. 15, (2009) 1139

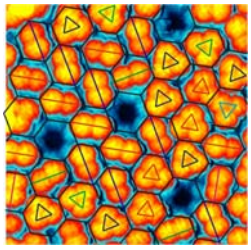
Controlling the Dimensionality and Structure of Supramolecular Acetylene-appended Porphyrin Assemblies

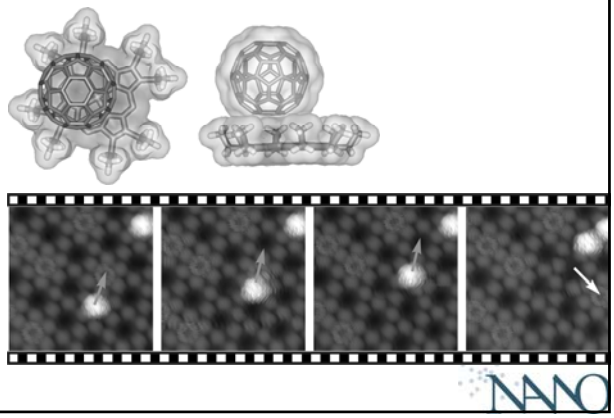


Staged Self Assembly
→ Cristian, Saranyan

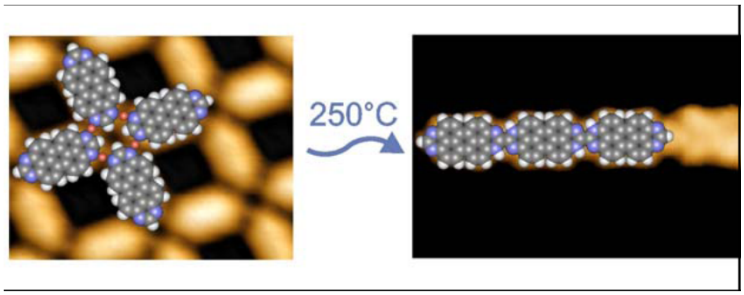
Engineering of Donor / Acceptor Layers and Chromophores for light harvesting

- Donor (Octa-ethylporphyrin) and Akzeptor (C60) complexes
- self-assembly and STM positioning



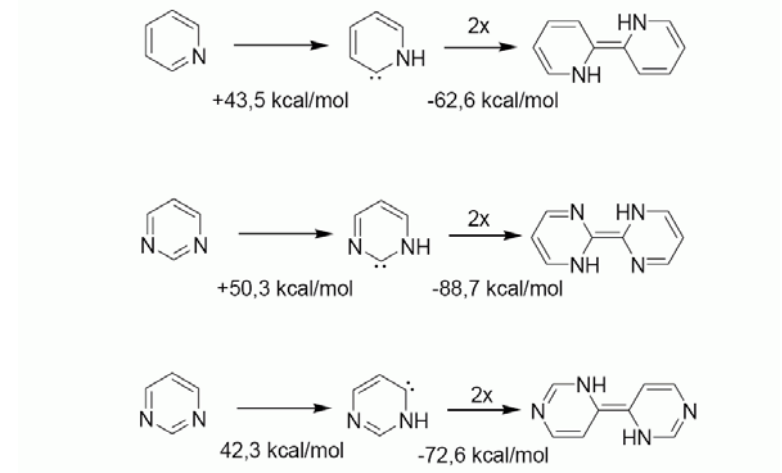


Transforming surface coordination polymers into covalent surface polymers:



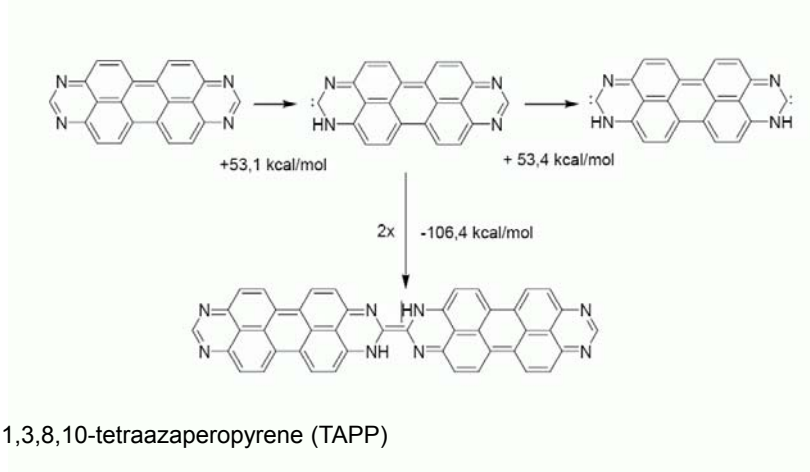
M. Matena et al. Angew. Chem. Int. Ed. 2008, 47, in print

Transforming surface coordination polymers into covalent surface polymers:



M. Matena et al. Angew. Chem. Int. Ed. 2008, 47, in print

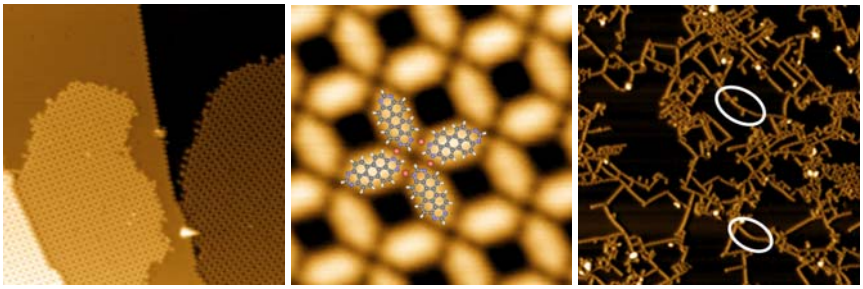
Transforming surface coordination polymers into covalent surface polymers:



1,3,8,10-tetraazaperopyrene (TAPP)

M. Matena et al. Angew. Chem. Int. Ed. 2008, 47, in print

Transforming surface coordination polymers into covalent surface polymers:

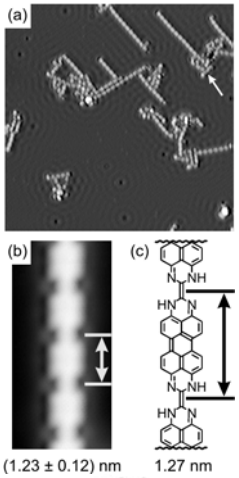


- TAPP: Coordination polymer formation @ 150 C
- lattice registry and metal coordination
- Transformation @ 250 C
- Curvature suggest lifting of lattice registry

M. Matena et al. Angew. Chem. Int. Ed. 2008, 47, in print

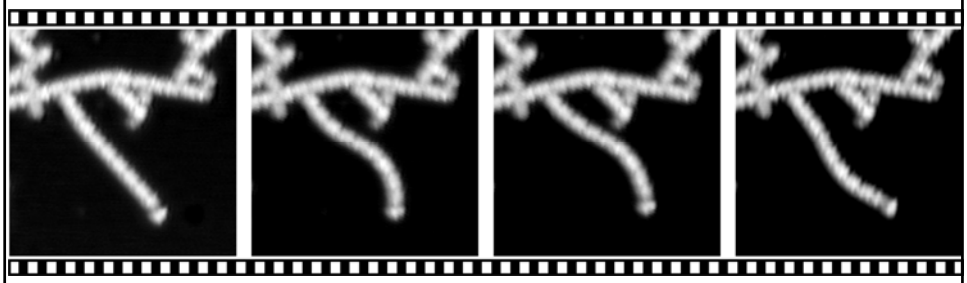
Transforming surface coordination polymers into covalent surface polymers:

- Temperature (250 C) induced
- Tautomerisation in surface potential
- Delocalised electron system across polymer
- electronically and optically novel system can be positioned



M. Matena et al. Angew. Chem. Int. Ed. 2008, 47, in print

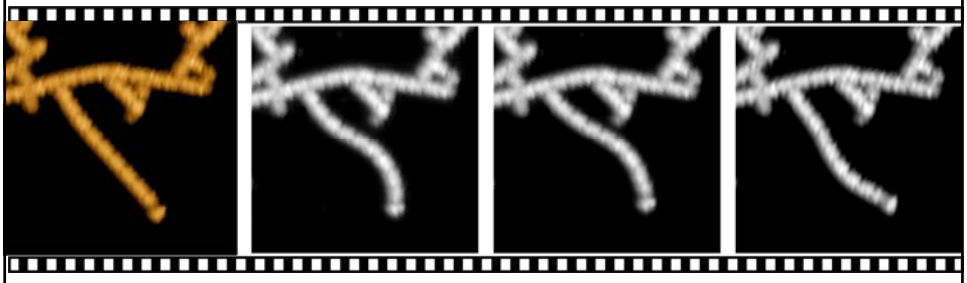
Transforming surface coordination polymers into covalent surface polymers:



- STM positioning: Flexible molecular chains can be flexed
- irrespective of lattice registry
- no rupture of covalent chains

M. Matena et al. Angew. Chem. Int. Ed. 2008, 47, in print

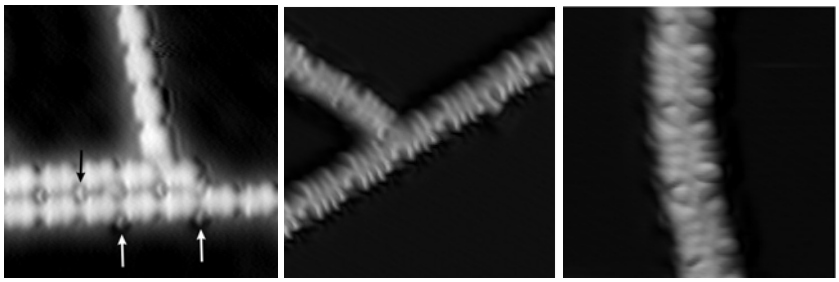
Transforming surface coordination polymers into covalent surface polymers:



- STM positioning: Flexible molecular chains can be flexed
- irrespective of lattice registry
- no rupture of covalent chains

M. Matena et al. Angew. Chem. Int. Ed. 2008, 47, in print

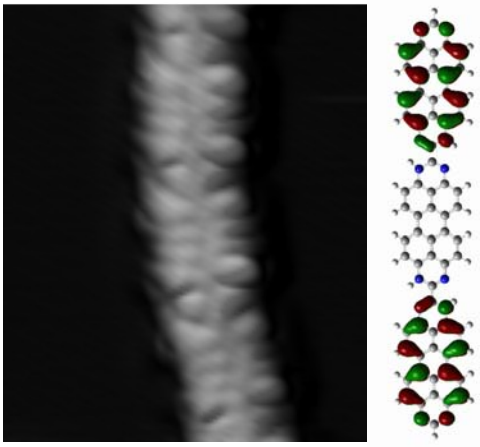
Transforming surface coordination polymers into covalent Surface polymers:



- planar polymer, covalent interlinking of chains
- metal conjugation between chains

M. Matena et al. Angew. Chem. Int. Ed. 2008, 47, in print

Transforming surface coordination polymers into covalent Surface polymers:



- planar polymer, covalent interlinking of chains
- sub-molecular contrast
- Homo-calculation for trimer – good agreement
- Lumo: see Suppl. Inf.

M. Matena et al. Angew. Chem. Int. Ed. 2008, 47, in print

Self – Assembly / Self – Organisation

Tuning forces between atoms and molecules.

- Covalent backbone (Protein, DNA, etc …)
- Steric interactions within molecular chains (e.g. α–helix former / blocker)
- 'Sticky functional groups'
  a) covalent: (R – SH) 'disulfide bridges'
  b) non-covalent: Hydrogen – and other – polar bridges
- 2D/3D Complexation (Heme-porphyrin, etc.)
- Conformational Flexibility / Conformational Dynamics
- Selective use of Chirality / Enantioselective Interactions
- Molecular Solvent interaction: Formation of Hydrophilic / Hydrophobic pockets and anchoring in lipids etc.

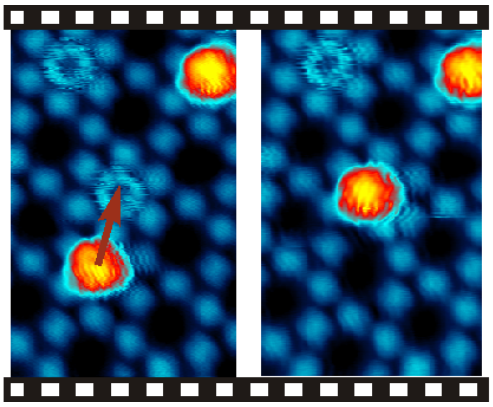
Solvent Free Supra-Molecular Chemistry at Surfaces

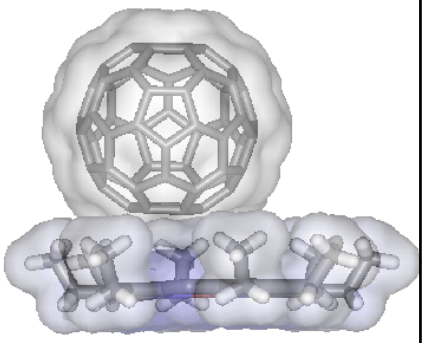
- Surface interaction → often unprecedented behaviour
- No TD equilibrium for desorption / re-adsorption
- Molecular orientation dynamics retarded by surface molecular interaction
- Molecular conformation dynamics retarded by confinement, surface molecular interaction
- No collisions with 'small and fast' solvent molecules,
  → modified behaviour in response to entropy / enthalpy balance
- Synthon / Tecton concept transferrable --- not always

→ Phase space for molecular libration and motion strongly modified
→ Chemical reaction channels modified, mechanistic differences, steric accessibility modified
→ Polar / apolar pockets, nanophases, domains rather than hydrophilic / hyrdophobic interaction

→ modifed chemical, physico-chemical behaviour which is in progress to be understood

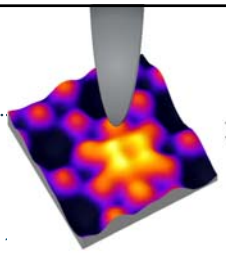
Supra – molecular assembly of donor-acceptor system

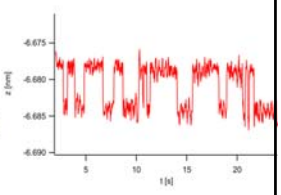




M. Stoehr et al. small 2007, 3, No. 8, 1336 – 1340

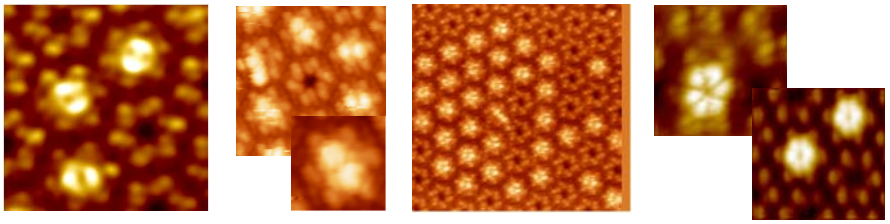
Molecular Rotors





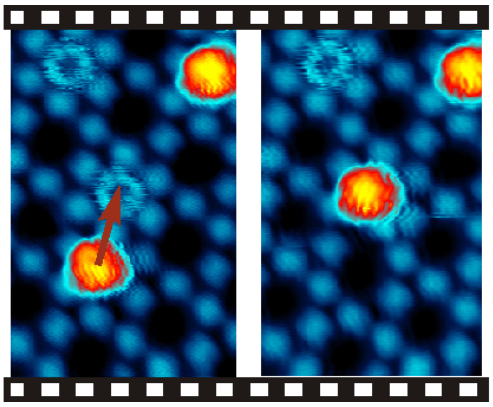
Temperature dependence

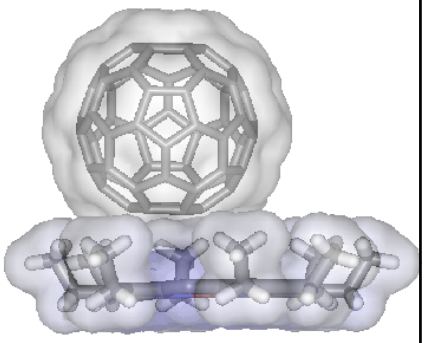
- Trapped porphyrins inside pores
  - Stable up to ~110 K
  - Thermally activated rotary motion above



77 K *112 K* *116 K* *150 K* *300 K*

Supra – molecular assembly of donor-acceptor system





M. Stoehr et al. small 2007, 3, No. 8, 1336 – 1340

NANO

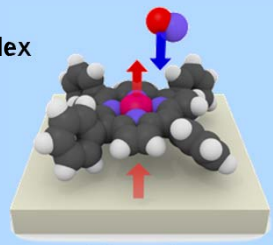
PAUL SCHERRER INSTITUT PSI

Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut

Surface Science in Increasingly Complex Systems

N. Ballav, Th. Jung et al.



•EPFL •13/05/2013

Molecular Nanoscience

Laboratory for Micro and Nanotechnology
Paul Scherrer Institute

Nanolab @ UniBasel

Dorota Siewert,*
Tatjana Haehlen,*
Harald Rossmann*
Christian Waeckerlin
Milosz Baljozovic+

Jan Girovsky
Jan Nowakowski
Rolf Schelldorfer
Thomas Jung

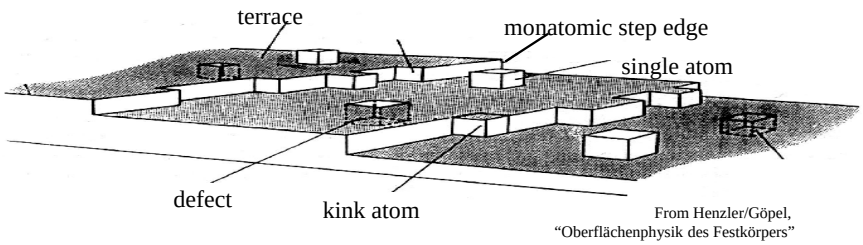
Nirmalya Ballav#

and many research partners

Sylwia Nowakowska,
Susanne Martens,
Aneliia Schyrba
Toni Ivas
Marco Martina

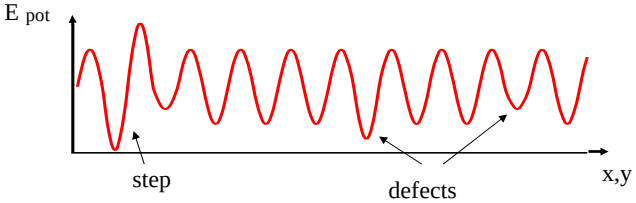
UHV-STM
(4K –RT)

Surface Science --- Atomic Concepts



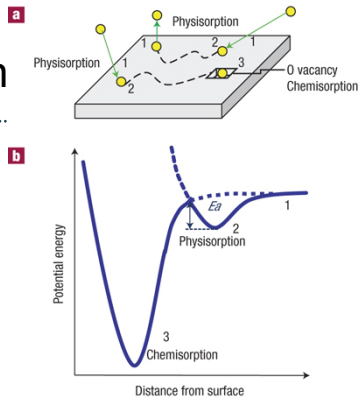
From Henzler/Göpel,
"Oberflächenphysik des Festkörpers"

Steps, defects => modification of the surface potential



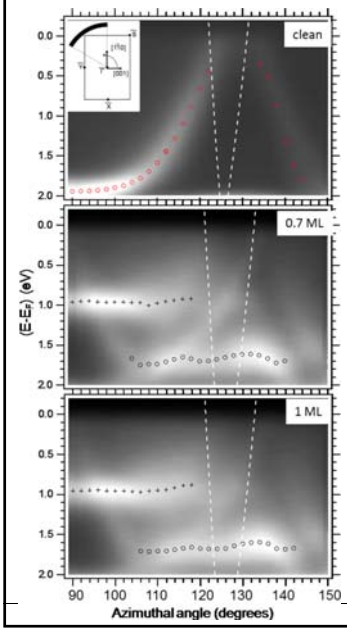
=> steps, defects may act as pinnig centers for adsorbates

Physisorption vs. Chemisorption



Forces of attraction are van der Waals' forces	Forces of attraction are chemical bond forces
Low enthalpy of adsorption (20 - 40 k.J/mole)	**High** enthapy of adsorption (200 - 400 k.J/mole)
This process is observed under conditions of low temperature	This process takes place at high temperatures
It is not specific	It is highly specific
Multi-molecular layers may be formed	Generally, monomolecular layer is formed
This process is reversible	This process is irreversible

ARPES: Molecule Derived Bands



Molecule Derived Bands

@0.96 eV & 1.67 eV

→ hybridized states
HOMO, HOMO-1

Pentacene as a Model for a 'simple' large molecule

Considerable modifications:
(1) reduced *structural* & *electronic* integrity, substantial bending of molecule,
(2) buckling of the substrate top layers

Molecular bending: → reduced number of C-Cu bonds @ interface
→ Nonequivalent bonding of adsorbate atoms
→ "energy per atom" not equal to bond strength

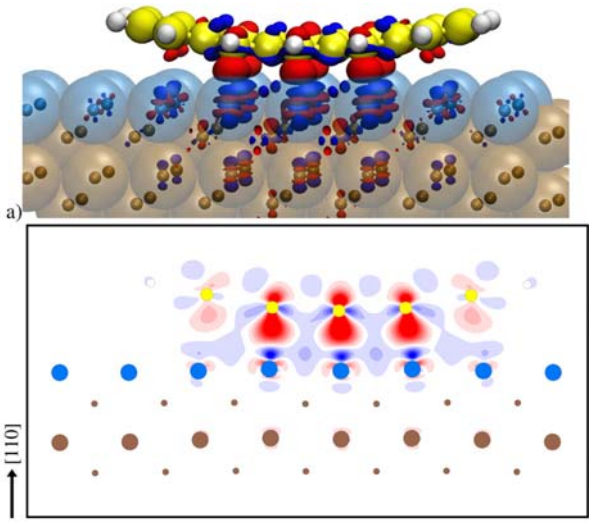
Note: for *non-covalent* bonding

Electronics @ Interface:
(1) Hybridization at the vicinity of the Fermi level
(2) Charge redistribution between substrate and molecule,
→ Structural distortion
→ unambiguous evidence for stronger adsorption than typical for vdW/ physisorption

→ chemisorption-like interaction: large organic molecules @ metal
also in absence of covalent bond

Important for: charge injection in organic electronic devices,
→ more detailed insight needed.

Electronic Structure of an Organic/Metal Interface: Pentacene/Cu(110)

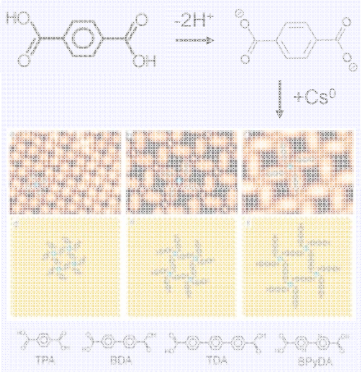


K. Mueller et al. J. Phys. Chem. C 2012, 116, 23465−23471

Motivation – formation 2D structures on surface

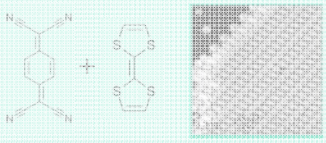
Self-assembly | Ionic networks | Covalent bond formation

"Molecule + Metal"
i.e. TPA + Cs^0



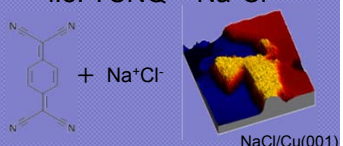
S. Stepanow et al. *ACS Nano* 4, 1813-1820 (2010)

"Molecule + Molecule"
i.e. TCNQ + TTF



I. Fernández-Torrente et al. *J. Phys. Rev. Lett.* **101** (2008)

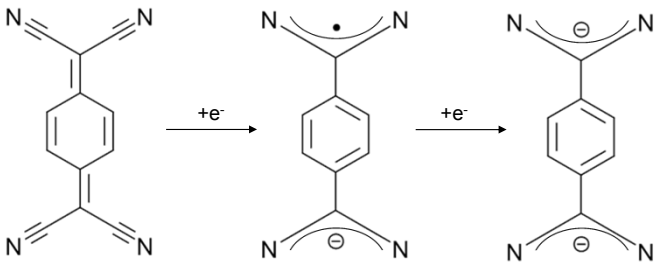
"Molecule + Salt"
i.e. TCNQ + Na^+Cl^-



→ The topic of this contribution

TCNQ – a strong electron acceptor

7,7,8,8-Tetracyano-p-quinodimethane (TCNQ)



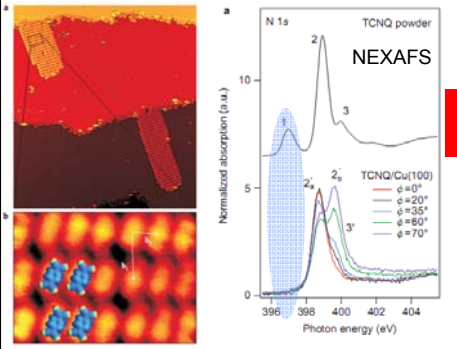
$TCNQ^0$ $TCNQ^-$ $TCNQ^{2-}$

TCNQ: L.R.Melby, et al, *J. Am. Chem. Soc.* **84**, 3374-3387 (1962)

TCNQ + Metal – 1/2

TCNQ/Cu(001)

TCNQ

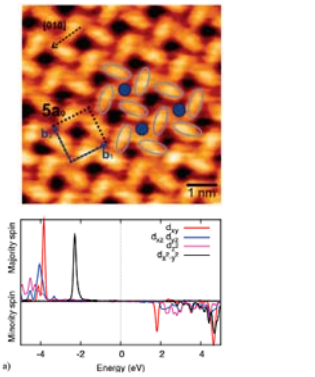


→CT from substrate to molecule
→TCNQ leads to a rearrangement of Cu atoms

+Mn⁰

TCNQ/Cu(001) +Mn

M→TCNQ



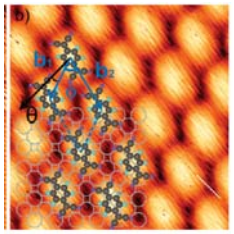
TCNQ/Cu(001) + Mn⁰
→CT from Mn to TCNQ
→ionic network

T.-C. Tseng et al. *Nat. Chem.* **2** (2010); X.Q. Shi et al. *J. Phys. Chem. C* **114** (2010)

TCNQ + Metal – 2/2

TCNQ/Ag(001)

TCNQ

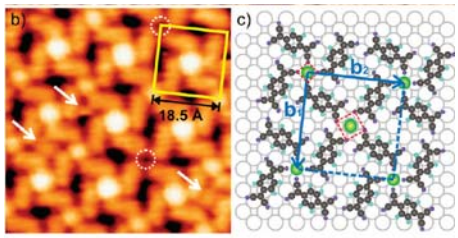


TCNQ/Ag(001)
→Substrate to molecule CT?

+Ni⁰

TCNQ/Ag(001) +Ni⁰

M→TCNQ

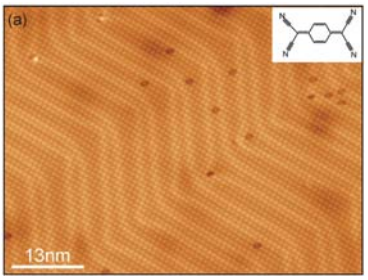


TCNQ/Ag(001) + Ni⁰
→CT from Ni to TCNQ
→ionic network

T.-C. Tseng et al. K. *J. Phys. Chem. C* (2011)

TCNQ + TTF (a molecular electron donor)

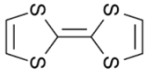
TCNQ/Au(111)

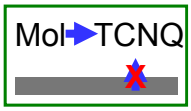


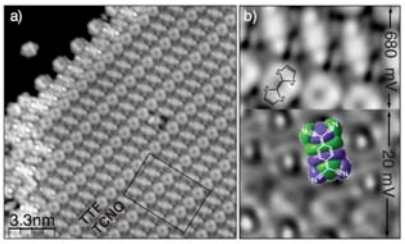
TCNQ/Au(111)
→No CT with Au(111)
→TCNQ neutral
(concluded from STM, STS)

+TTF^0

TCNQ/Au(111)
+TTF



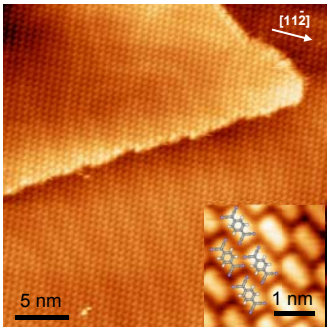




TCNQ+TTF/Au(111)
→CT from TTF into TCNQ

I. Torrente, *Int. J. Mass. Spectrom.* **277** (2008); J. *Phys. Rev. Lett.* **101** (2008)

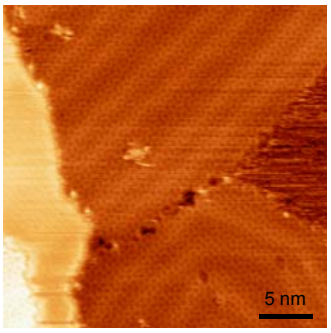
TCNQ + alkali-halides – a novel approach

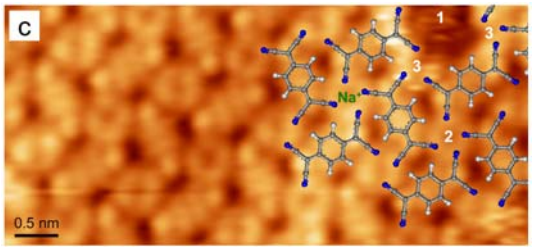


TCNQ/Au(111)
→neutral TCNQ

+ Na^+Cl^-

TCNQ/Au(111)
+NaCl
→ionic network





C. Wäckerlin et al, manuscript under review

Na^0 and Na^+Cl^-

Sodium metal

- Na^0: [Ne]$3s^1$
- highly reactive
- workfunction: 2.4 eV

→Na^0 (alkali-metals and most metals in general) should easily undergo CT with a strong electron acceptor like TCNQ

→Na^+TCNQ^-

Sodium chloride

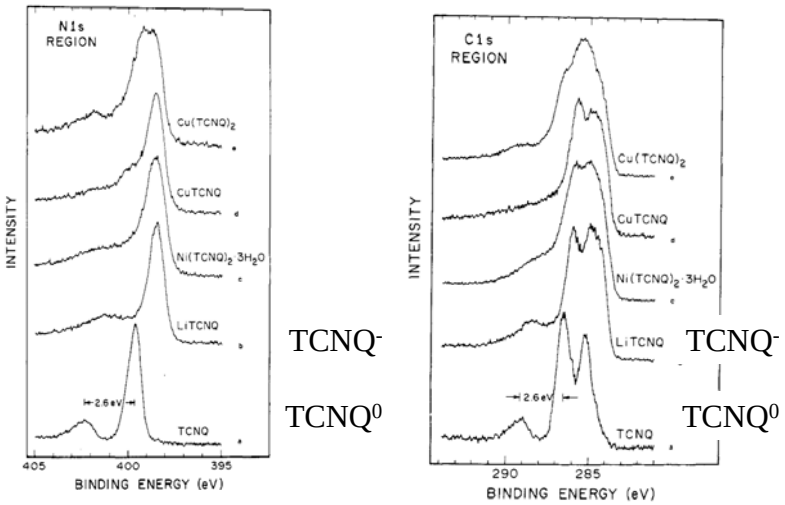
- Na^+: [Ne]
- Cl^-: [Ar]
- inert

→Na^+ and Cl^- are both in the noble gas electronic configuration and thus halides in general are quite inert

"Who gives the electron to TCNQ?"
A: the substrate
B: $Na^+ \rightarrow Na^{2+} + e^-$: I_E ~47 eV
C: $Cl^- \rightarrow Cl + e^-$: E_A ~ 3.6 eV

Photos: http://en.wikipedia.org/wiki/File:Nametal.JPG.jpg; http://upload.wikimedia.org/wikipedia/commons/e/ea/Halit-Kristalle.jpg

XPS on TCNQ and M^+TCNQ^- in bulk



$TCNQ^-$

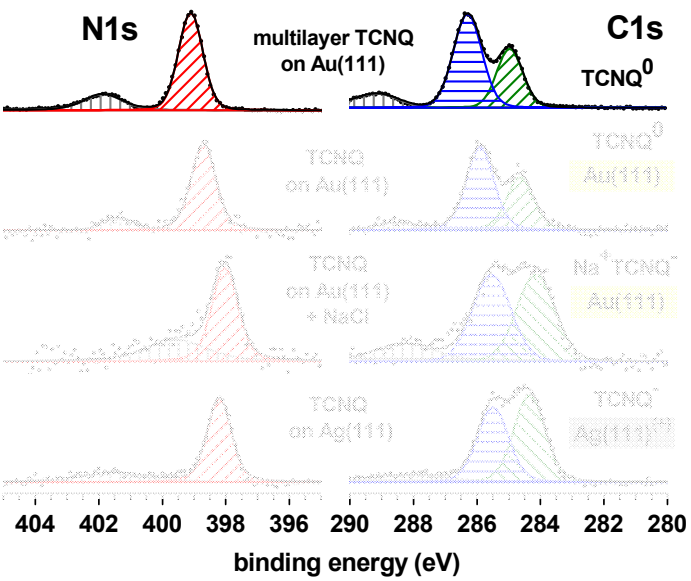
$TCNQ^0$

$TCNQ^-$

$TCNQ^0$

J. M. Lindquist et al, *Chem. Matr.* **1**, 72-78 (1989).

X-ray photoelectron spectroscopy

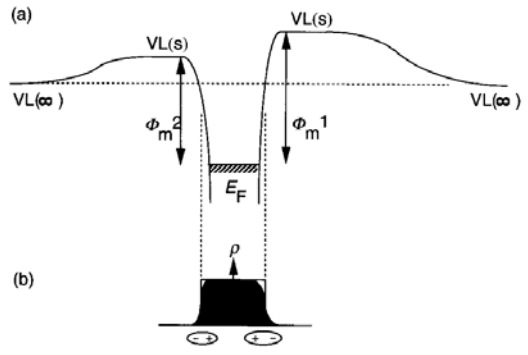


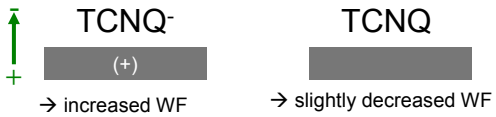
on Au(111):
→**TCNQ⁰**

+NaCl:
→**TCNQ⁻**

on Ag(111)
(no NaCl)
→**TCNQ⁻**

UV photoelectron spectroscopy → work function





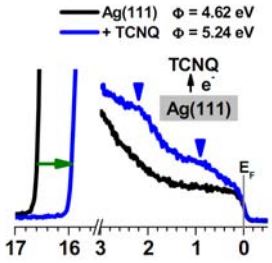
→ increased WF

→ slightly decreased WF

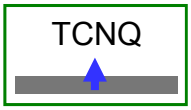
review paper on UPS/WF: H. Ishii, H., *Adv. Mater.* **11**, 605-625 (1999).

UV photoelectron spectroscopy → work function

on Ag(111)

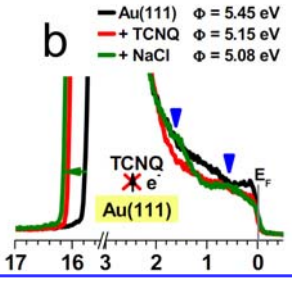


TCNQ/Ag(111)



TCNQ/Ag(111)
→ WF increased
→ Substrate-to-molecule CT

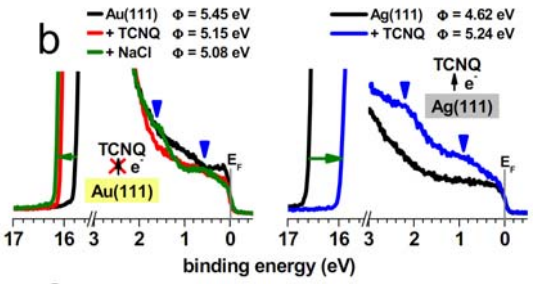
on Au(111)

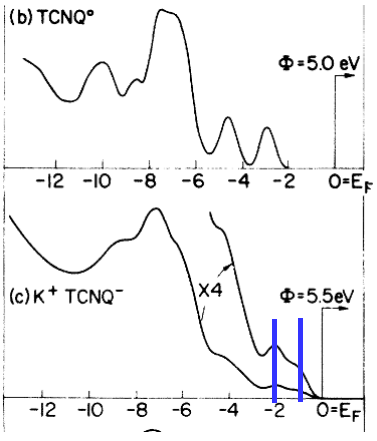


"Who gives the electron to TCNQ?"
A: the substrate
B: $Na^+ \rightarrow Na^{2+} + e^-$: I_E ~47 eV
C: $Cl^- \rightarrow Cl + e^-$: E_A ~ 3.6 eV

TCNQ/Au(111)
→ WF slightly decreased
→Substrate not involved in CT before and after addition of NaCl

UV photoelectron spectroscopy → valence

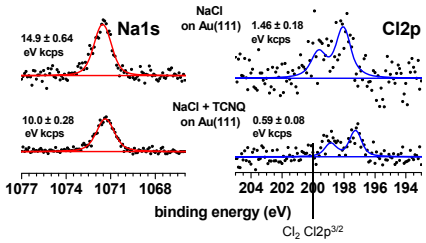




→valence electronic structure gives further evidence towards the presence of $TCNQ^-$ in TCNQ+NaCl/Au(111) and TCNQ/Ag(111)

UPS in bulk: W.D. Grobman, *Phys. Rev. Lett.* **32**, 534 (1974)

Who donates the electron? – oxidation of Cl^-



"Who gives the electron to TCNQ?"
A: the substrate
B: $Na^+ \rightarrow Na^{2+} + e^-$: I_E ~47 eV
C: $Cl^- \rightarrow Cl + e^-$: E_A ~ 3.6 eV

$TCNQ + Na^+Cl^- \rightarrow Na^+TCNQ^- + ½\ Cl_2$

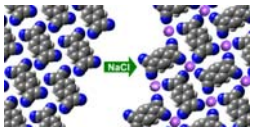
reduction: $TCNQ + e^- \rightarrow TCNQ^-$
oxidation: $Cl^- \rightarrow ½\ Cl_2 + e^-$

addition of TCNQ onto NaCl/Au(111):
→Na/Cl ratio is increased by a factor of **1.67** ± 0.11 after addition of TCNQ
→Cl_2 is not observed in XPS
→**loss of Cl_2 gas**

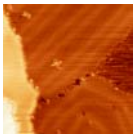
simple experiment:
→TCNQ in ethanol/water
→ + NaCl
→observation of bubbles (Cl_2 gas)
→color change indicates formation of TCNQ-Metal complex (c.f. references)

L.R.Melby, et al, *J. Am. Chem. Soc.* **84**, (1962); J.G Vegter et al, *Phys. Rev. B* **7**, (1973);
X.-L. Mo et al *Thin Solid Films* **436**, (2003)

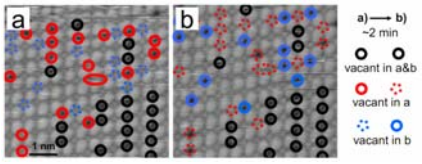
Summary and outlook



- a novel method to create 2D metal-organic layers
  - usage of **metal-halides** instead of metals



- A **well decoupled** layer on Au(111) (herringbone persists, UPS)

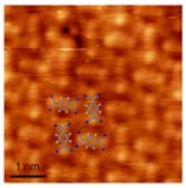


- TCNQ/Ag(111) undergoes CT
  - interesting dynamic vacancies observed

Outlook / Application

- Sublimation of metal halides is very simple
- Excess alkali-metals can strongly affect the substrate (via CT), excess NaCl interacts only weakly
- Usage of other metal halides or salts, i.e.
  - $MgCl_2$, $MnCl_2$, $CoCl_2$
  - Other halides: Br^-, I^-
- Other strongly electron accepting molecules as linker

TCNQ+LiCl/ Au(111) "works"



Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut

Electron and spin states in metal-organic supramolecular materials at surfaces:
Spectro-microscopy correlation experiments

T.A. Jung

Coll.: N. Ballav, F. Diederich, L. Gade, C. Iacovita, T. Ivas, S. Martens, J. Lobo Checa, S. Nowakowska, M. Stohr, M. Persson, P. Oppeneer, A. Schyrba, D. Siewert, C. Thilgen, C. Waeckerlin

Molecular Nanoscience

Laboratory for Micro and Nanotechnology
Paul Scherrer Institute

Nanolab @ UniBasel

Dorota Siewert,*
Tatjana Haehlen,*
Harald Rossmann*
Christian Waeckerlin
Milosz Baljozovic+

Jan Girovsky
Jan Nowakowski
Rolf Schelldorfer
Thomas Jung

Nirmalya Ballav#

and many research partners

Sylwia Nowakowska,
Susanne Martens,
Aneliia Schyrba
Toni Ivas
Marco Martina
Thomas Nijs

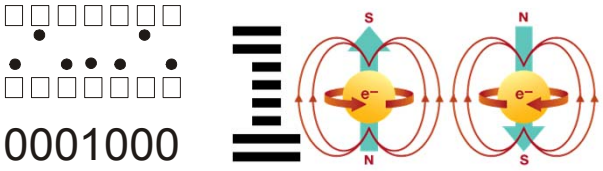
UHV-STM
(4K –RT)

Engineering with Molecules @ Surfaces
→ playing with electrons and spin

- Supramolecular architecturing @ surfaces (cf J. Barth)
- Interaction with contact / environment
- Mechanic, electronic and spintronic Interaction

Engineering with molecules; inspired by nature, but distinctively different

→ adressable molecular architectures,
assembly and function
device like behaviour, logic?

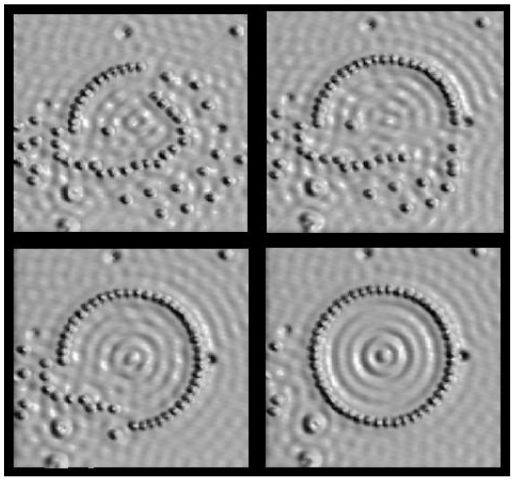


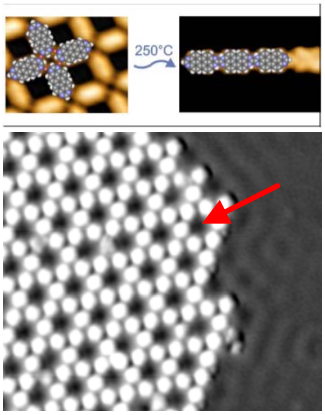
How do we handle Electrons and Spins?

- in the bulk (organic: crystal or polymer)
- or in the single molecule

- contact / environment / architectonics extremely important

Surface States Scattered from Atoms and Molecules





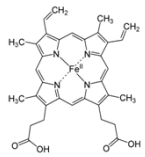
Lobo-Checa et al., *Science* 325, 300 (2009)

M.F. Crommie, C.P. Lutz and D.M. Eigler, *Nature* 363 (1993)

Spectro-Microscopy Correlation

Controlling molecular spins - demonstrated by nature

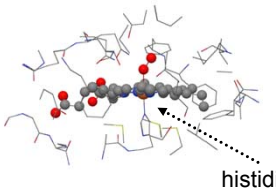
O_2-transport in blood



heme b

Fe-Por + O_2 ⇄ Fe-Por-O_2

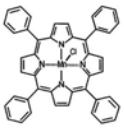
S = 2 **S = 0**

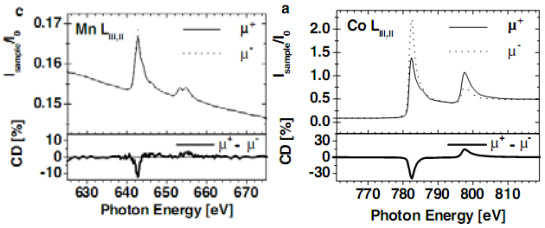


J. M. Friedman, J.M et al. J. Biol. Chem. 258, 10564 (1983)
J. Igarashi et al. J. Biol. Inorg. Chem. 16, (2011).

On ferromagnetic surface:

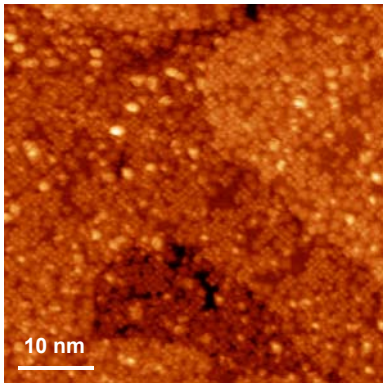
Induced spin in a organo-metallic complex

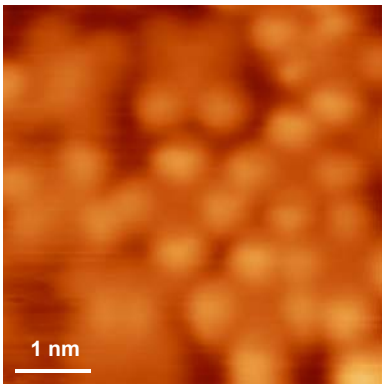




A. Scheybal et al, Chem. Phys. Lett. 411, 214 (2005)

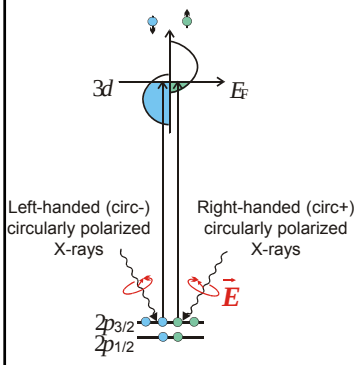
CoTPP/Ni - STM





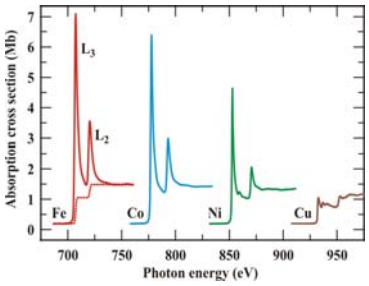
→no self-assembly
→first question:
"is it still magnetic once adsorbed on the surface?"

X-ray magnetic circular dichroism (XMCD)

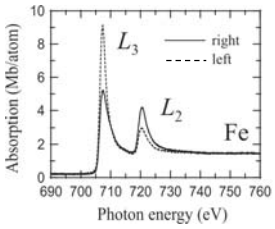


- high sensitivity
- element specific
- fast
  - < 1 h of beamtime for one dataset (molecule & substrate with two directions of magnetization) at the SIM beamline
- usually measuring the sample current (TEY)

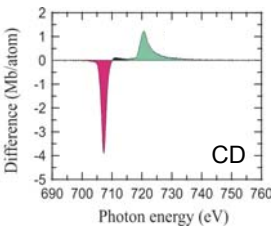
X-ray absorption spectroscopy (XAS)



X-ray absorption spectroscopy (XAS) (with circular polarized light)



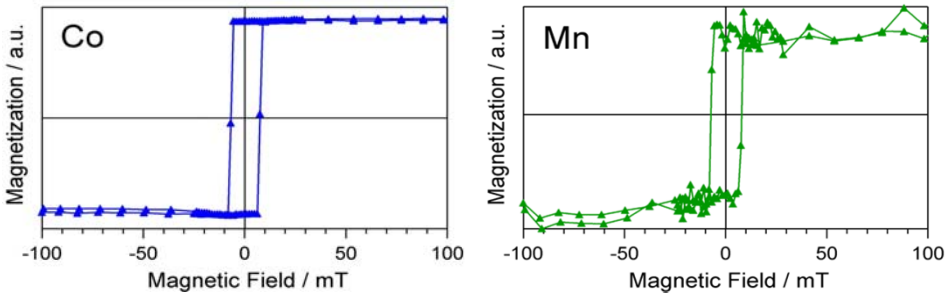
X-ray magnetic circular dichroism (XMCD)



Reiko Nakajima, Doctoral Dissertation (1998)

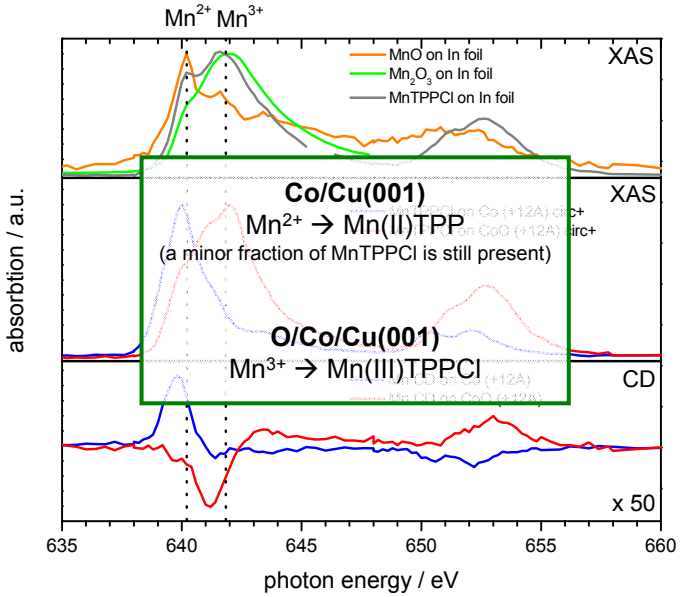
Previous results - element-specific hysteresis curves

	Co	Mn
Coercivity Field:	≈ 7 mT	≈ 7 mT
Saturation Field:	≈ 10 mT	≈ 10 mT



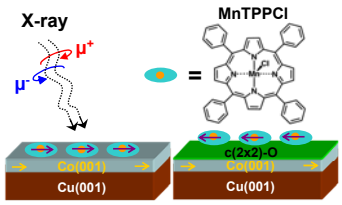
A. Scheybal, et al., Chem. Phys. Lett. (2005)

Mn(III)TPPCl and Mn(II)TPP – oxidation states



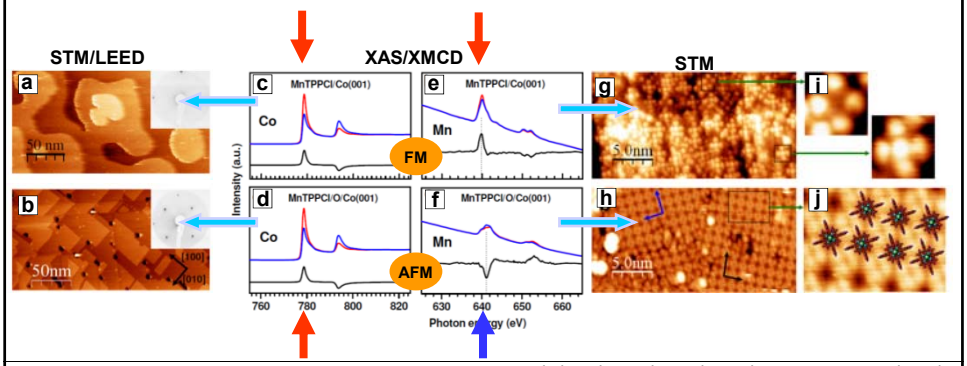
D. Chylarecka et al. *J. Phys. Chem. Lett.* 1 (2010)

Ferromagnetic and Antiferromagnetic Exchange Coupling Spectro-Microscopy Correlation: XAS, XMCD & STM



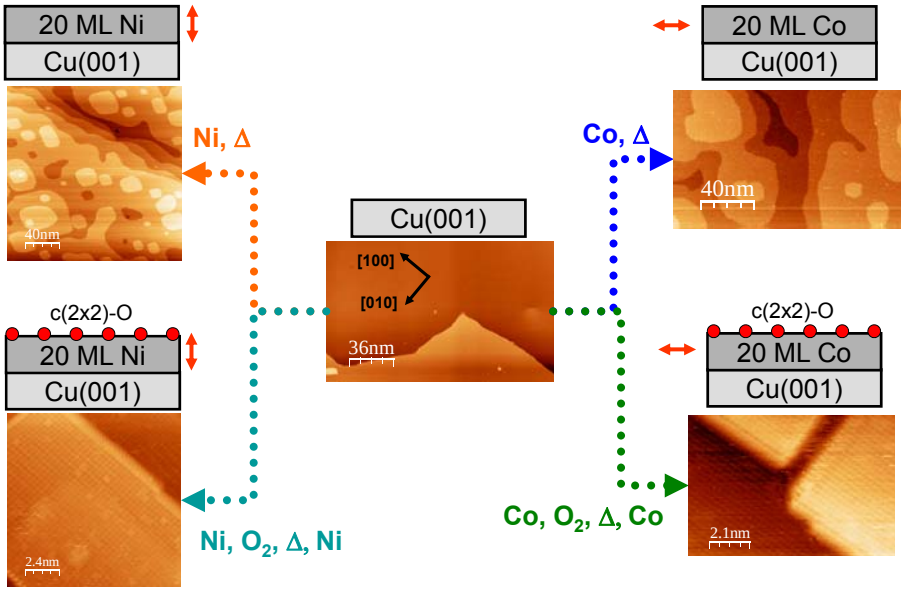
Molecule-Substrate Interface

- FM coupling: molecule substrate
- AFM coupling: molecule–O–substrate
- Random assembly on metal
- Self-assembly on c(2x2)O–metal
- Possible application:
  → Spintronic model interfaces

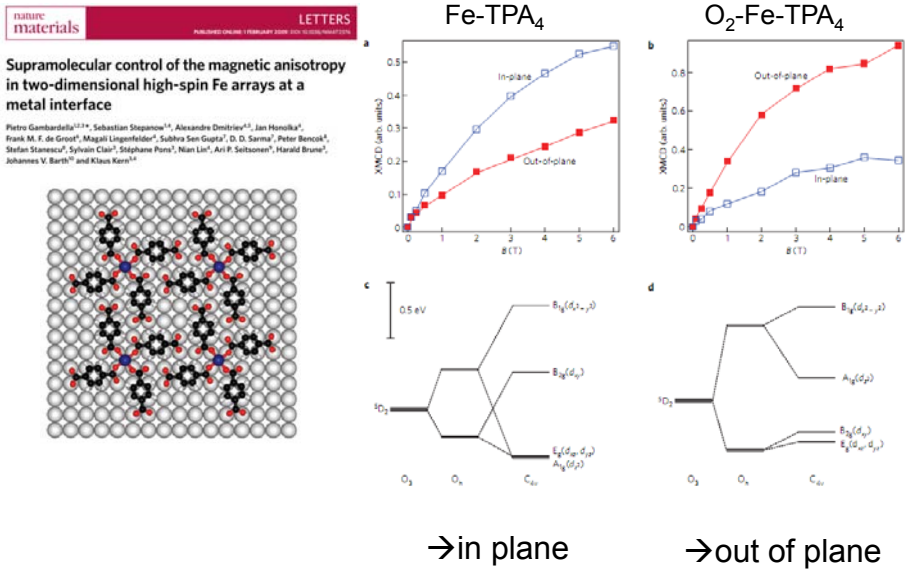


D. Chylarecka et al., *J. Phys. Chem. Lett.* 1, 1408 (2010)

Substrates – ‘native’ and ‘oxygen-reconstructed’

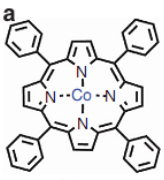


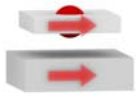
Switching the magnetic anisotropy by O_2



P. Gambardella et al. *Nat Mater* **8**, 189-193 (2009)

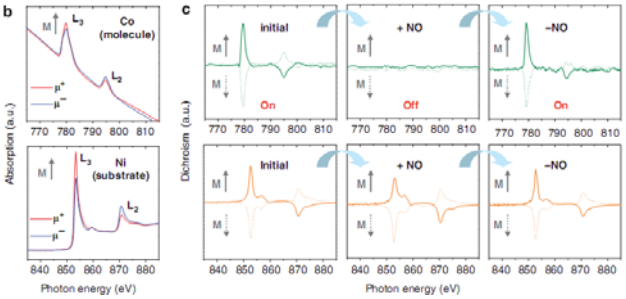
Controlling molecular spins





CoTPP

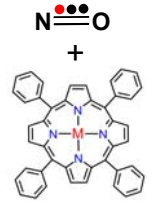
Ni



"spin ON" "spin OFF"

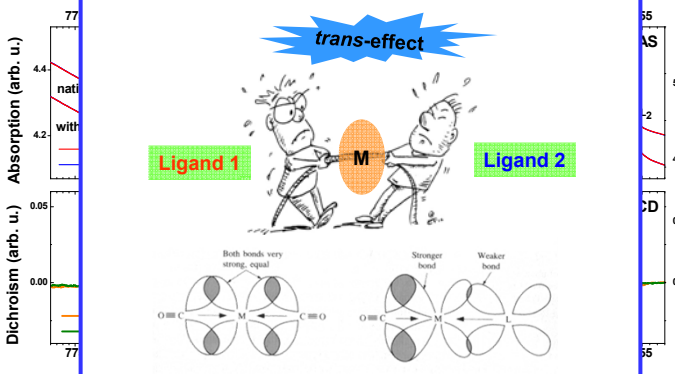
C. Wäckerlin et al, Nat. Commun. 1, 61 (2010)
cf.: J. Miguel et al, J. Phys. Chem. Lett. 2, 1455 (2011)
C. Isvoranu et al, J. Phys.: Cond. Mat. 22, 472002 (2010)

XAS and XMCD of Co, Fe, Mn-TPP



Co^{2+} Fe^{2+} Mn^{2+}

d^7 d^6 d^5

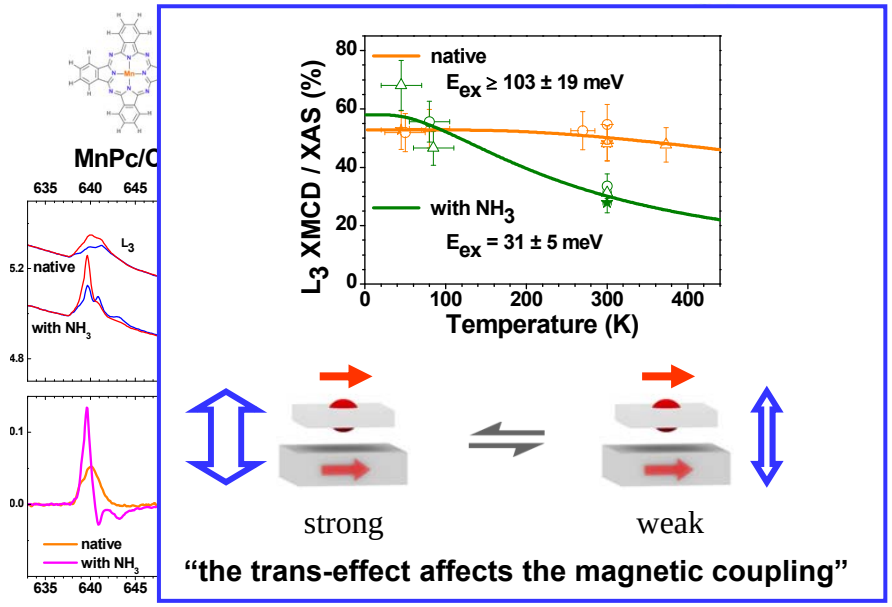


J. Huheey, Inorganic chemistry: principles of structure and reactivity (1993)
F.R. Hartley, Chem. Soc. Rev. 2, 163 (1973)
Lukasczyk et al. JPC C, 111, 3090 (2007)
Flechtner et al. *JACS* 129, 12110 (2007)
W. Hieringer, JACS 133, 6206 (2011)

XMCD				%
DFT+U	0.			μ_B
Change in the distance between the central metal and the substrate (DFT+U)		+0.06 Å	+0.58 Å	+0.30 Å

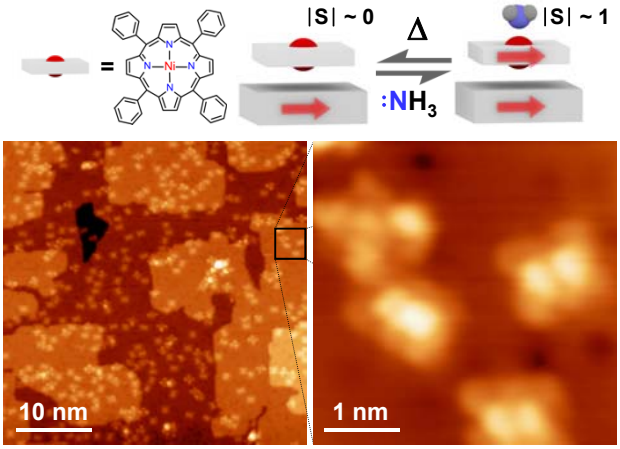
C. Wäckerlin et al, Chemical Science 3, 3154 (2012)

Chemical control over the strength of the exchange coupling



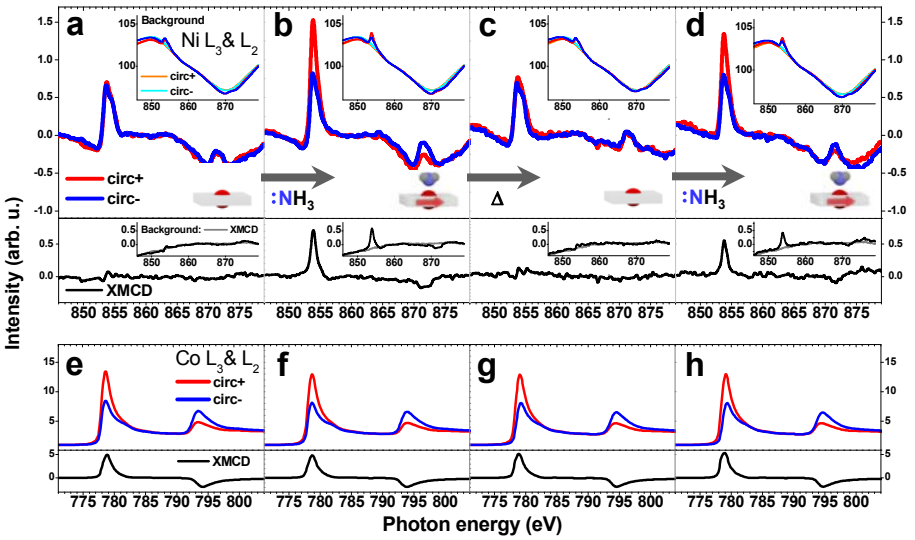
C. Wäckerlin et al, Chemical Science 3, 3154 (2012)

"The On-Switch"



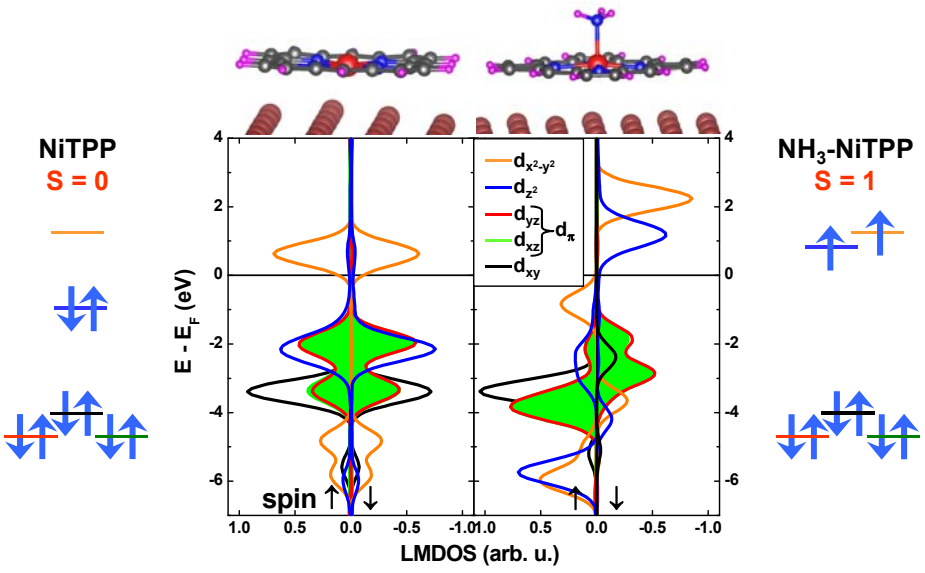
C. Wäckerlin et al, Angewandte Chemie 2013

"The On-Switch"



C. Wäckerlin et al, Angewandte Chemie 2013

"The On-Switch"



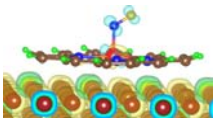
C. Wäckerlin et al, Angewandte Chemie 2013

On-surface magnetochemistry

Coll P. Oppeneer Uni Uppsala, A. Kleibert & F. Notling SLS-SIM

on-switch

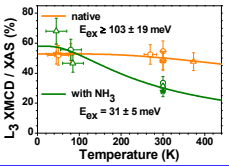
spin-on spin-off



DFT+U: K. Tarafder, P. M. Oppeneer

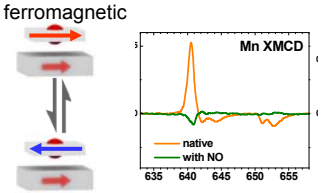
controlling the exchange coupling

strong **weak**



"high spin" "low spin"

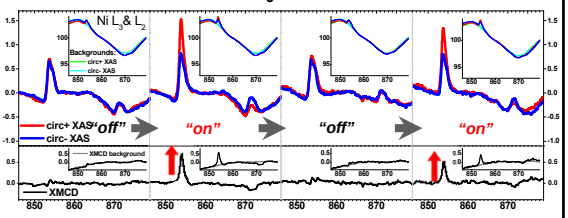
ferromagnetic



antiferromagnetic

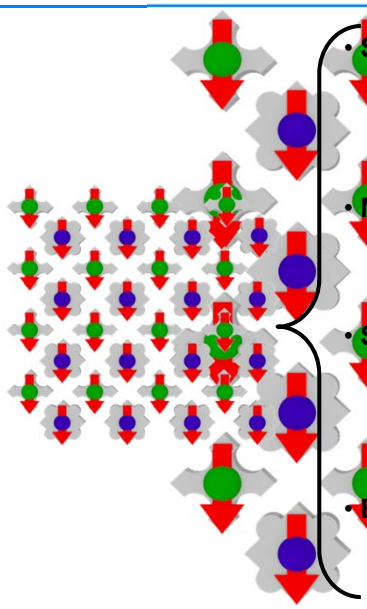
Reverting the *spin-off* switch: **the *spin-on* switch – NiTPP/Co + NH_3**

spin-off spin-on



C. Wäckerlin et al. *Chem. Sci.* 3, 3154 (2012) C. Wäckerlin et al., Angewandte Chemie 2013

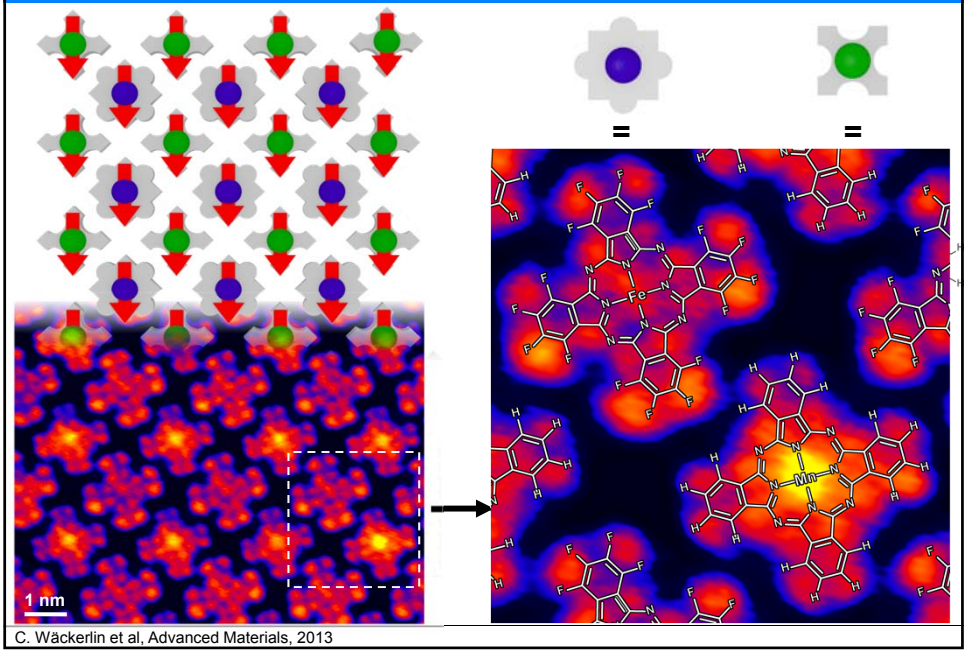
Design of the self-assembled molecular "spin-array"



- **Self-assembly: molecular mobility required**
  - √ Ag(111), Au(111), …
  - X native Co(001) and Ni(001)
  - √ oxygen-reconstructed Co(001) and Ni(001)
- **Magnetic Moments**
  - √ Exchange coupling to FM substrate **(at RT)**
  - √ High magnetic field, very low temperature
- **Supramolecular Assembly**
  - √ using C-F --- H-C hydrogen bonds
    K. W. Hipps, JACS 124, (2002), 2126
  - √ (there are other ways)
- **External control over the spin states**
  - √ Coordination Chemistry

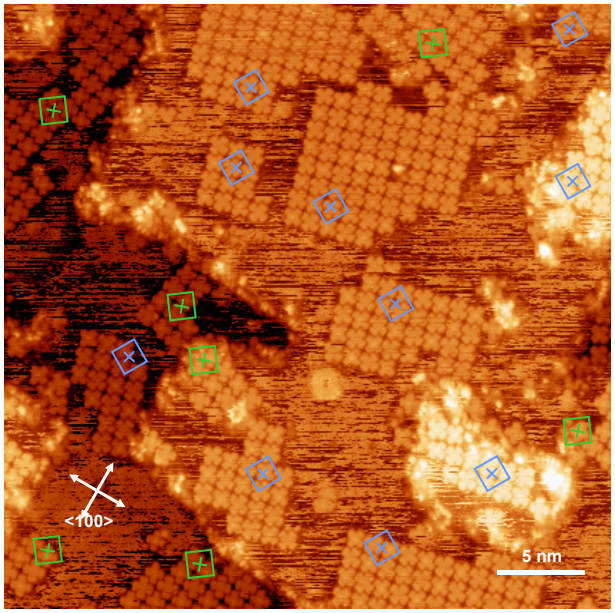
C. Wäckerlin et al, Advanced Materials 2013

Realization of the self-assembled molecular “spin-array”

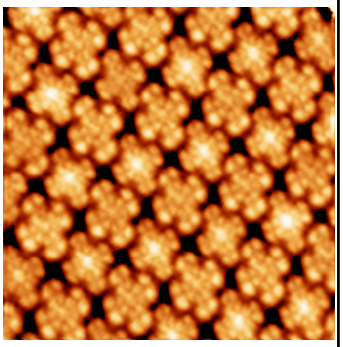


C. Wäckerlin et al, Advanced Materials, 2013

Large scale STM data

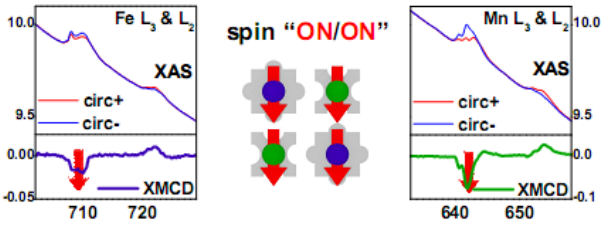


Two mirror domains:



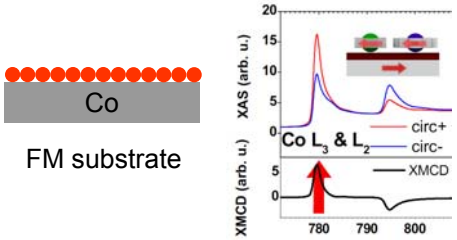
C. Wäckerlin et al, Advanced Materials, 2013

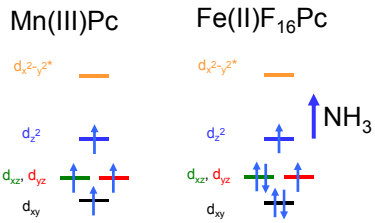
XAS/XMCD reveal electronic/magnetic properties



XMCD:
→ Both Fe and Mn molecules **order AFM** with respect to the O/Co

XAS:
→Fe in FeF16Pc is in 2+ oxidation state
→Mn in MnPc is in 3+ oxidation state

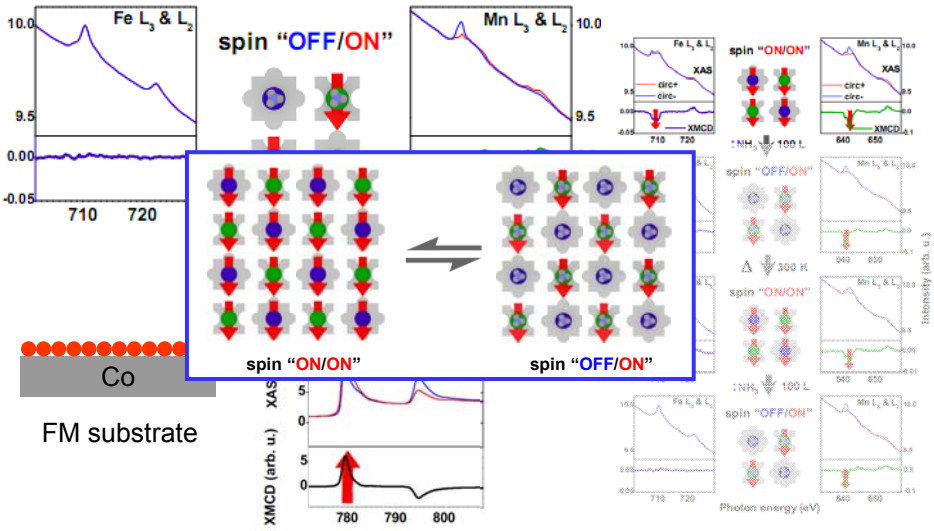




All at 70 K

C. Wäckerlin et al, Advanced Materials 2013; FePc, c.f. C. Isvoranu et al, *J. Phys.: Cond. Mat.* (2010), 472002

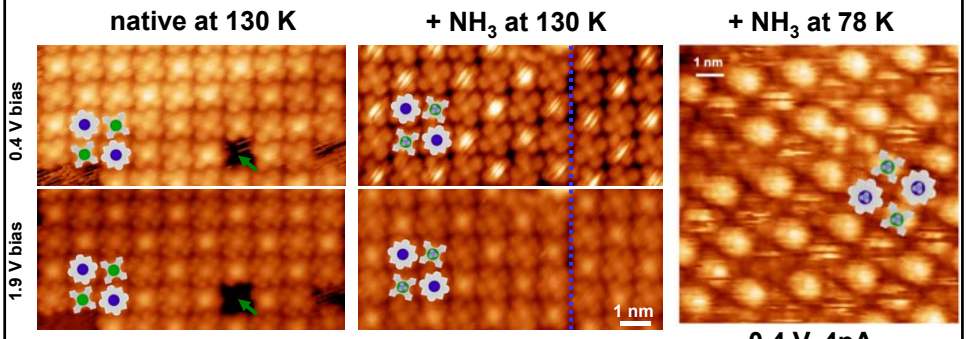
NH_3: Reversible and selective chemical control



All at 70 K

C. Wäckerlin et al, Advanced Materials 2013

STM reveals the NH_3 ligands



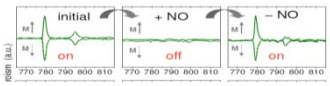
→NH_3 visible at +0.4 V
at 130 K →NH_3 only on MnPc
at 78 K →NH_3 on MnPc and $FeF_{16}Pc$

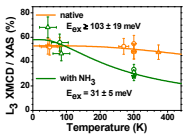
C. Wäckerlin et al, Advanced Materials 2013

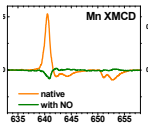
Summary

– FM and AFM coupling on Co and O/Co

– "switching off"



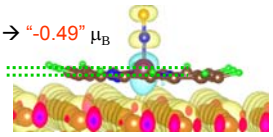




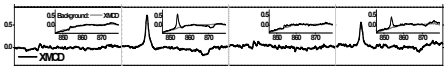
– control the **strength** of the exchange coupling

– control the **sign** of the exchange coupling

4.35 → "-0.49" μ_B

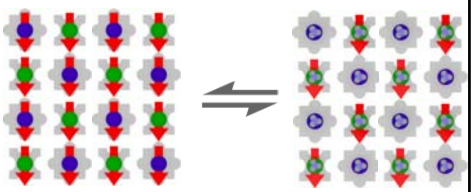


– "switching on"



– the trans-effect on surface affects the spin

– self-assembled spin-arrays and selective control of spin states



spin "ON/ON" spin "OFF/ON"

A. Scheybal et al, Chem. Phys. Lett. 411, 214 (2005)
M. Bernien et al, Phys. Rev. Lett. 102, 47202, (2009)
D. Chylarecka et al, J. Phys. Chem. Lett. 1, 1408 (2010)
C. Wäckerlin et al, Nat. Commun. 1, 61 (2010)
C. Wäckerlin et al, Chemical Science 3, 3154 (2012)

What can we do with it?

- Think more deeply about Electronic and Spin states at Surfaces
  → Quantum Computing ???
- Combine Chemical and Physical concepts to control electrons and spins
  → Organic Electronics and Spintronics,
  Single Molecular Electronics and Spintronics
- Think fundamentally about the limits of a spintronic device and its architecture
  while adressability is maintained

Wishful thinking: on-Surface Spin Architecture

- Design systems with architectured intermolecular coupling while still controlling interaction with ligands / substrate

Spin-switching is reaching to the people ...

ARTICLE

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Controlling spins in adsorbed molecules by a chemical switch

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