Towards the rational design of functional nanostructures from molecular building blocks

FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG

Hubertus Marbach

Microscopy and Nanolithography Group

PC-II

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Fabrication/Nanotechnology

Functional Nanostructure

X nm

(x < 100)

top-down approach

bottom-up approach

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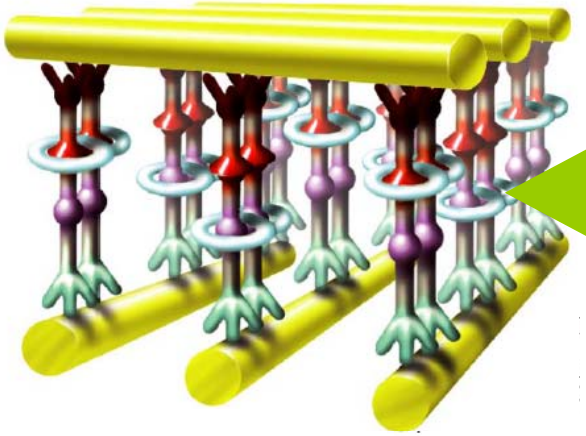
BREAKTHROUGH OF THE YEAR

In 2001, scientists assembled molecules into basic circuits, raising hopes for a new world of nanoelectronics

Molecules Get Wired



Good connections. Molecules can now be crafted into working circuits. Constructing real molecular chips will be a big challenge.

21 DECEMBER 2001 VOL 294 SCIENCE

top-down approach

bottom-up approach

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Observation/Microscopy

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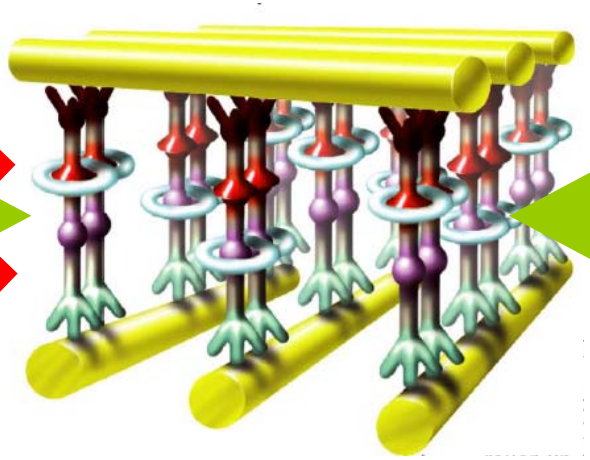
top-down approach

bottom-up approach

Next-Generation Technology Hits an Early Midlife Crisis

Researchers had hoped that a new revolution in ultraminiaturized electronic gadgetry lay almost within reach. But now some are saying the future must wait



Turnoff. Models like this one for rotaxanes are "somewhere between naïve and misleading," Paul Weiss says.

24 OCTOBER 2003 VOL 302 SCIENCE

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Observation/Microscopy

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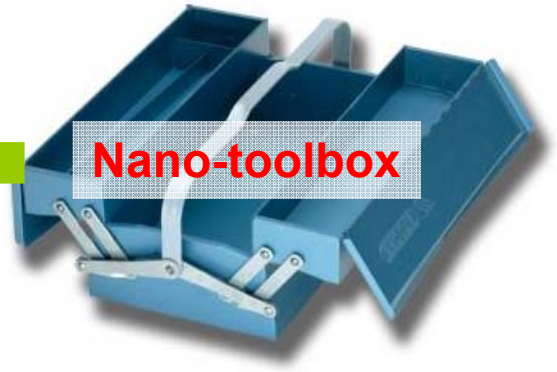
Functional Nanostructure

top-down approach



bottom-up approach

X nm

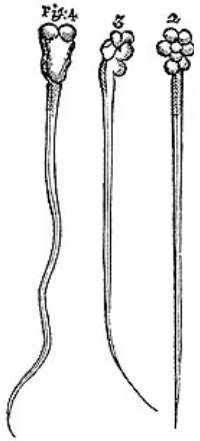
(x < 100)

A pioneer of microscopy: Antonie van Leeuwenhoek

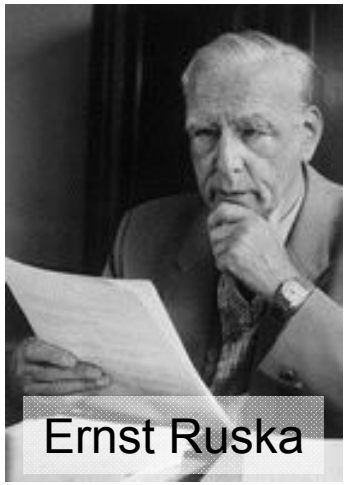
(1632-1723)

Correction
A v L 1702

Homunculi proposed by Dalenpatius based on microscopic investigations



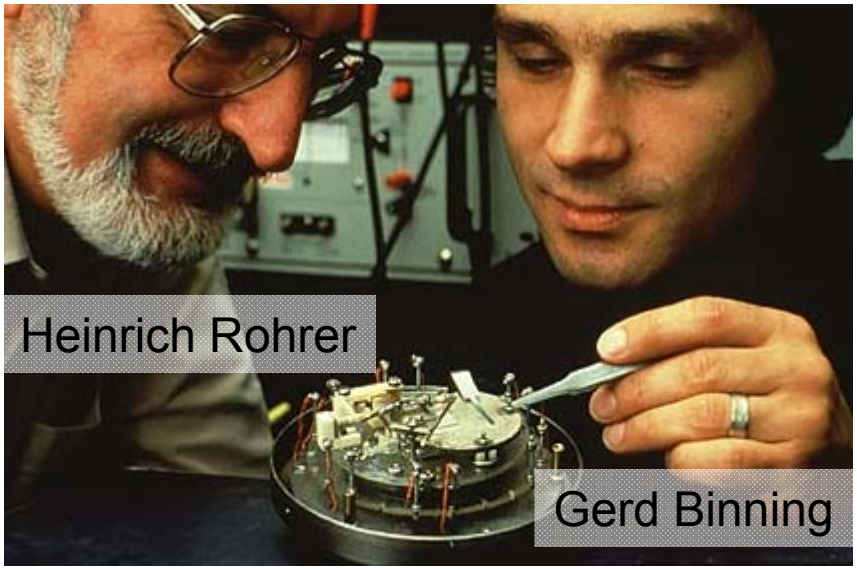
Pushing resolution in microscopy: the Nobelprice 1986



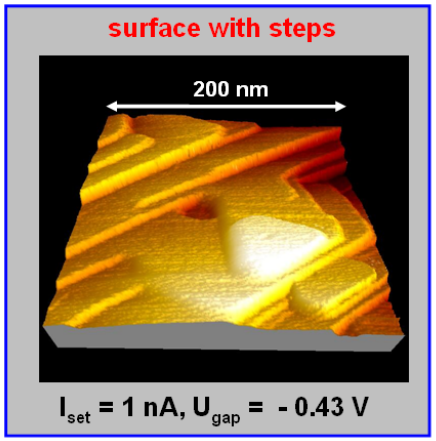
Concept: smaller wavelength of illuminating radiation, e.g., electrons

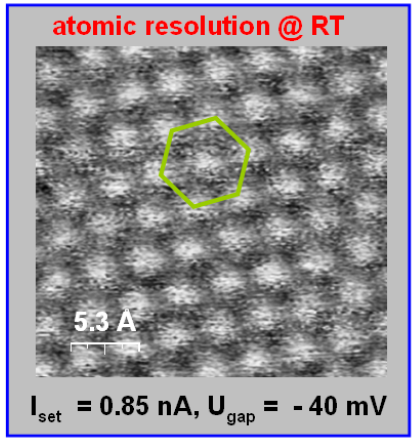
-transmission electron microscope (TEM)
-scanning electron microscope (SEM)

Concept: Sensing with sharp probes based on near field interactions

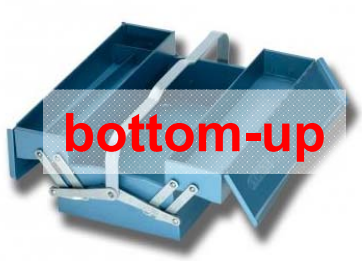


-Scanning tunneling microscope (STM)
-Atomic force microscope (AFM)

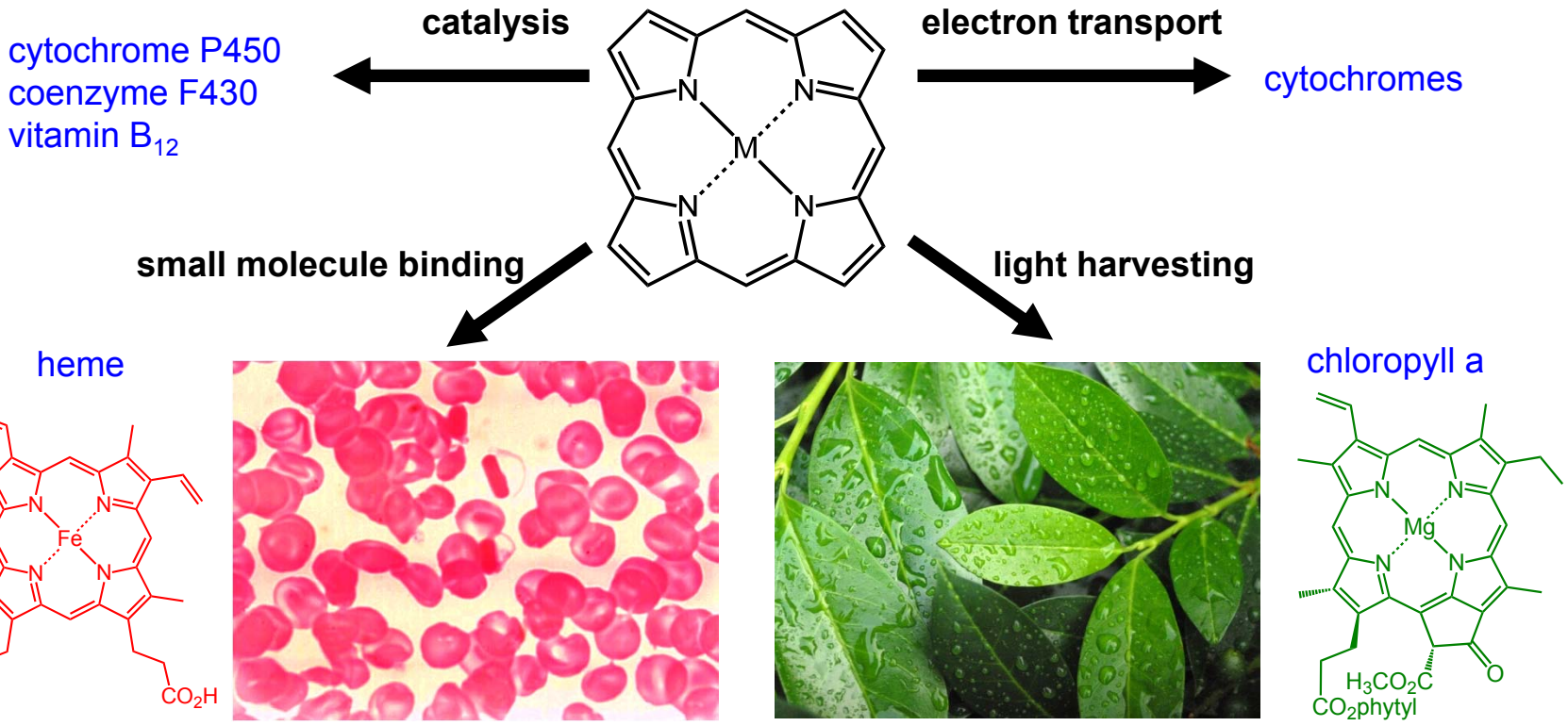




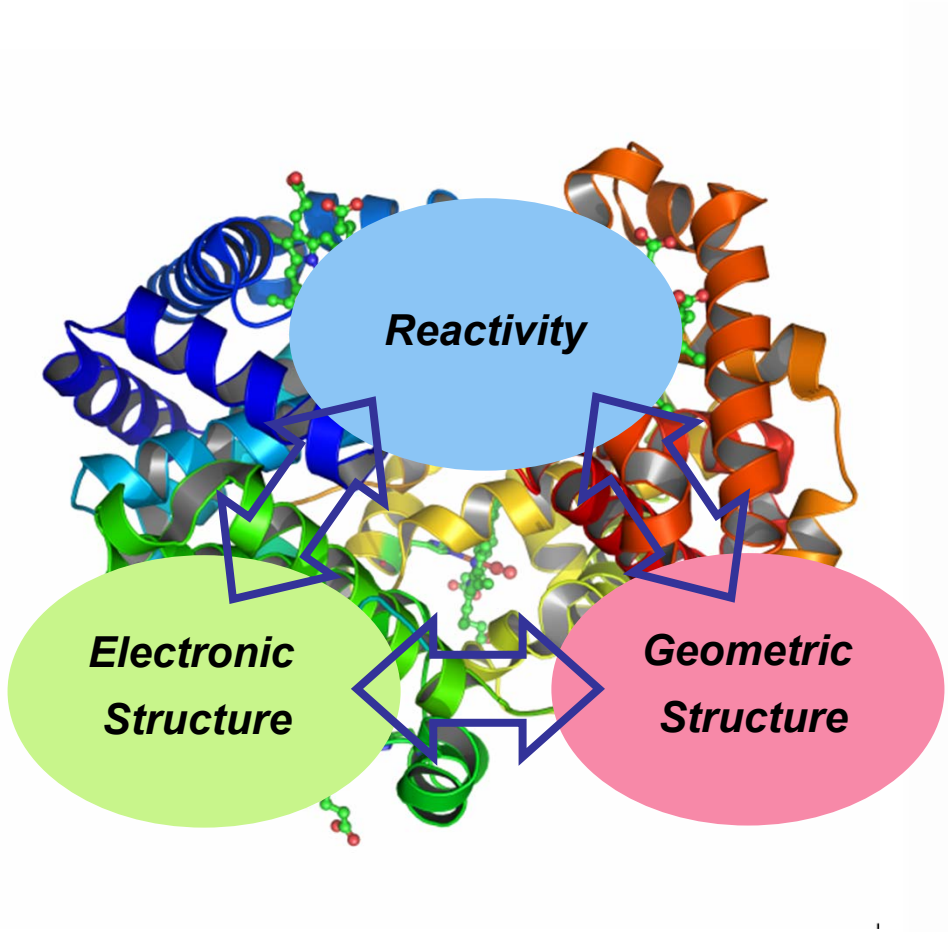
1st part:

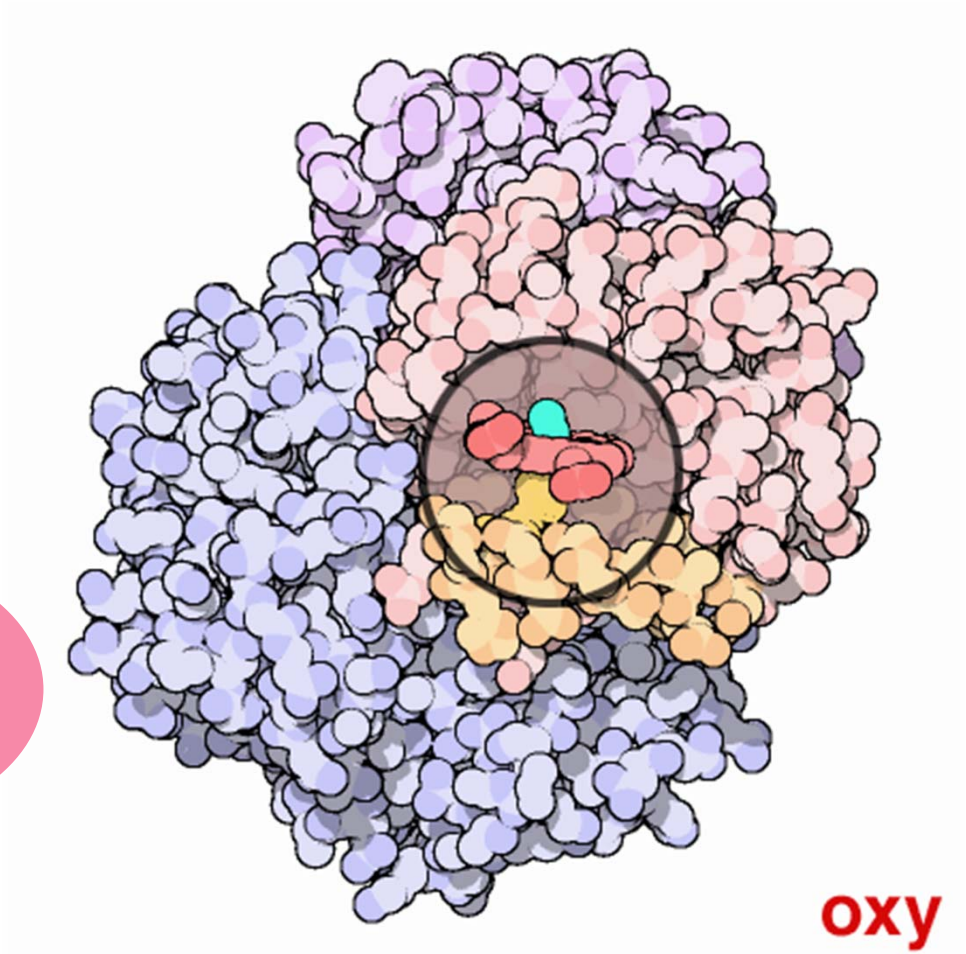


STM investigations of porphyrins on single crystal metal surfaces as prototypes for functional molecules



Haemoglobin: conformational adaption upon O_2 coordination





M. Paoli et al., J. Mol. Biol., 256:775-792, 1996

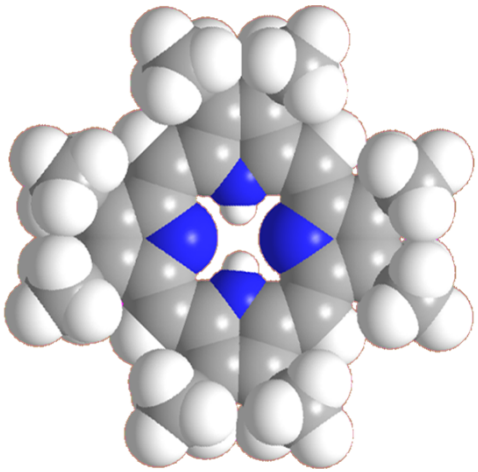
G. Fermi et al., J Mol Biol, 175: pp. 159, 1984

The ingredients

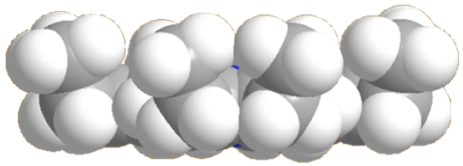
M= metal (e.g.: Zn, Co, Fe)

2H-OEP

2H- 2,3,7,8,12,13,17,18-Octaethylporphyrin

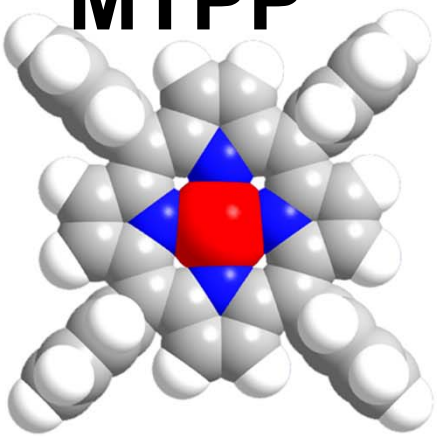


1,52 nm

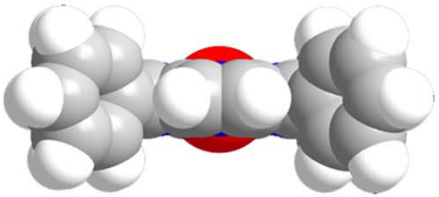


MTPP

M(II)- 5,10,15,20-Tetraphenylporphyrin

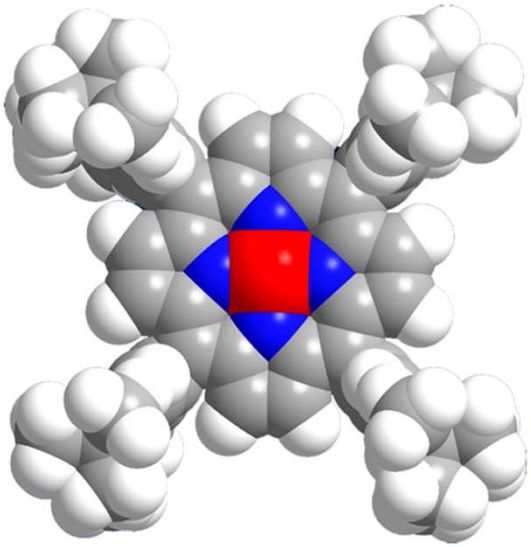


1,35 nm

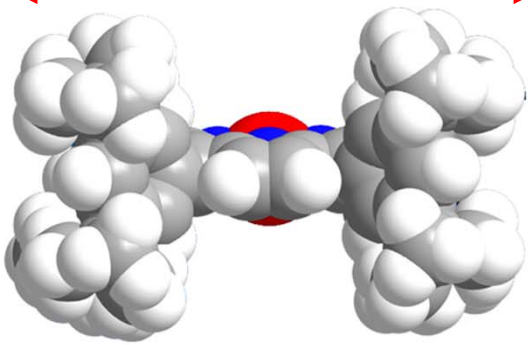


MTTBPP

M(II)- 5,10,15,20-Tetrakis-(3,5-di-*tert*-butyl)-phenylporphyrin

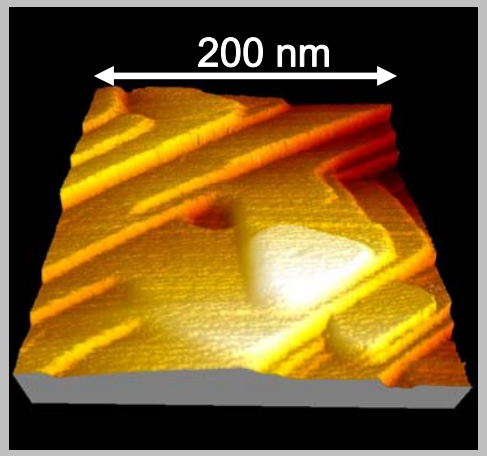


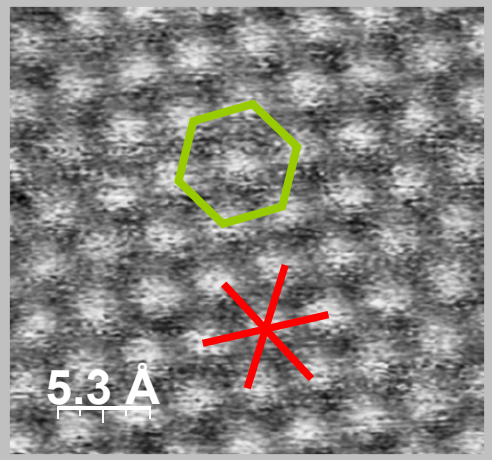
1,6 nm



The ingredients

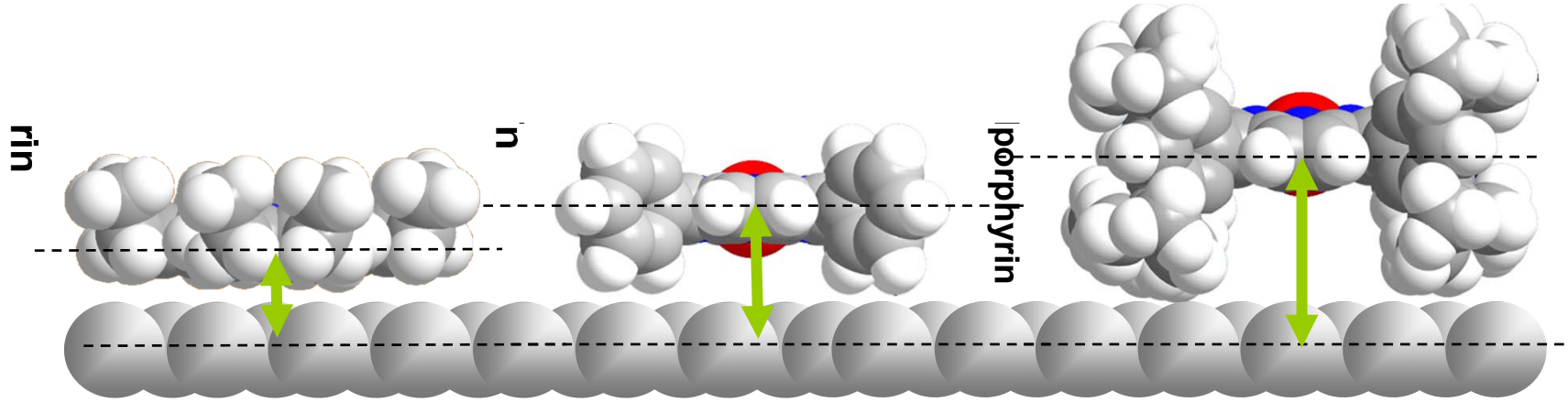
The Substrate Ag(111) in STM @ RT





I_{set} = 1 nA, U_{gap} = - 0.43 V

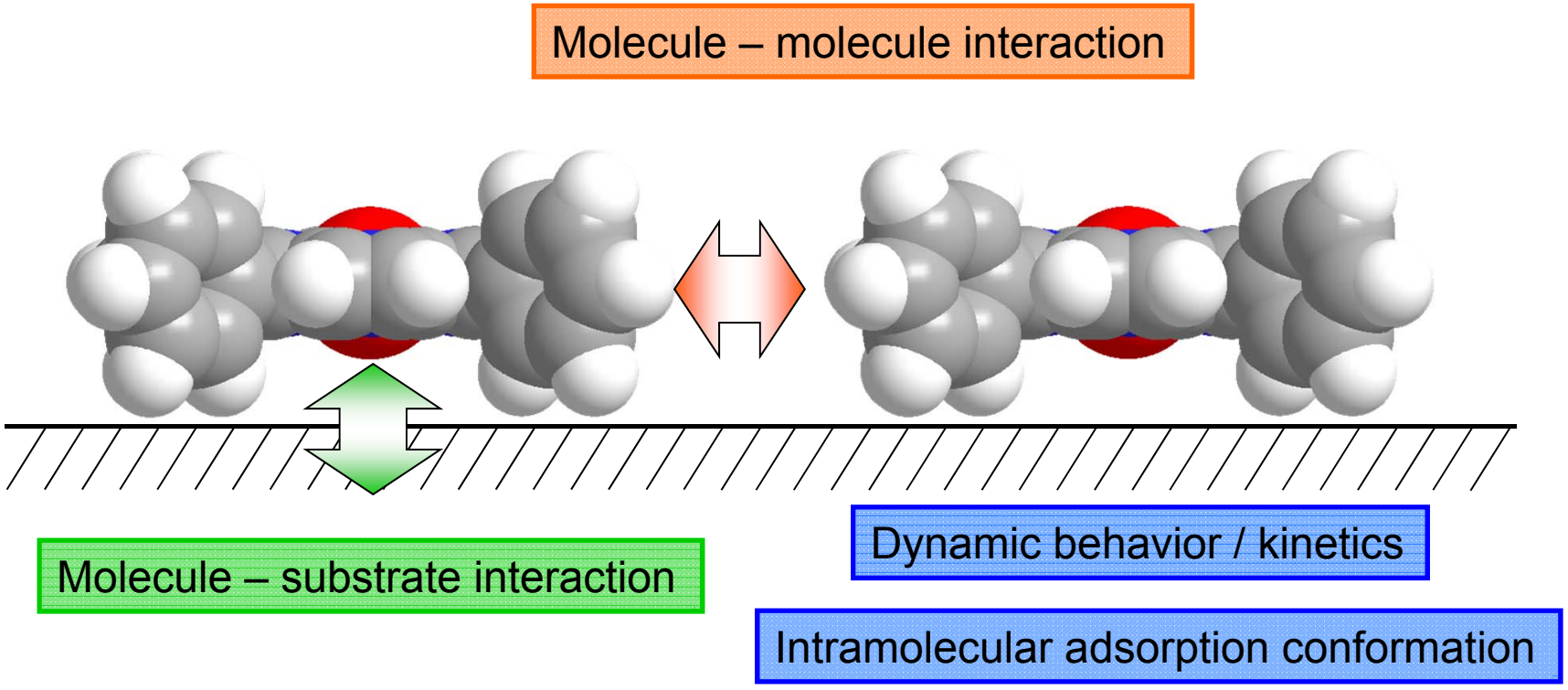
I_{set} = 0.85 nA, U_{gap} = - 40 mV



Controlling the reactivity of the metal center by interaction with the substrate

Molecular arrangement on surface: general considerations

How do the different interactions contribute to the arrangement?
And can we exploit them to tailor molecular architechtures?



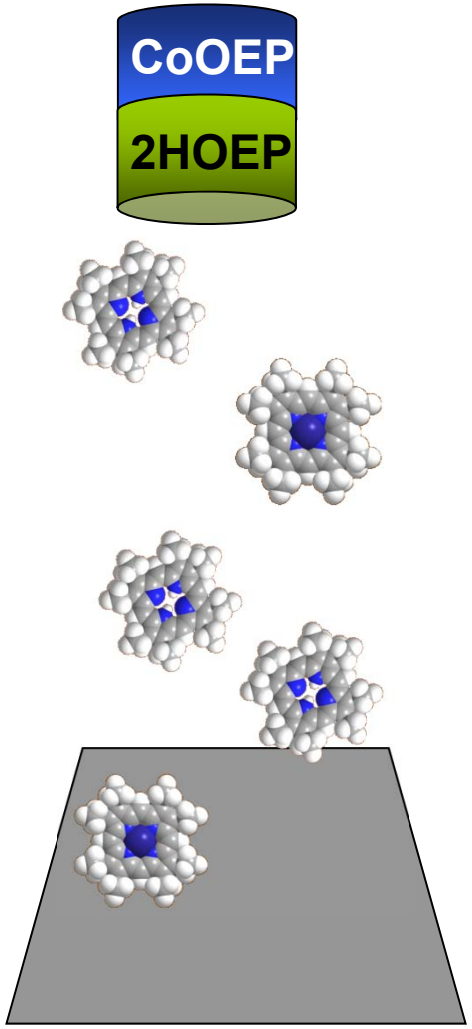
<u>Factors expected to influence the arrangement:</u>

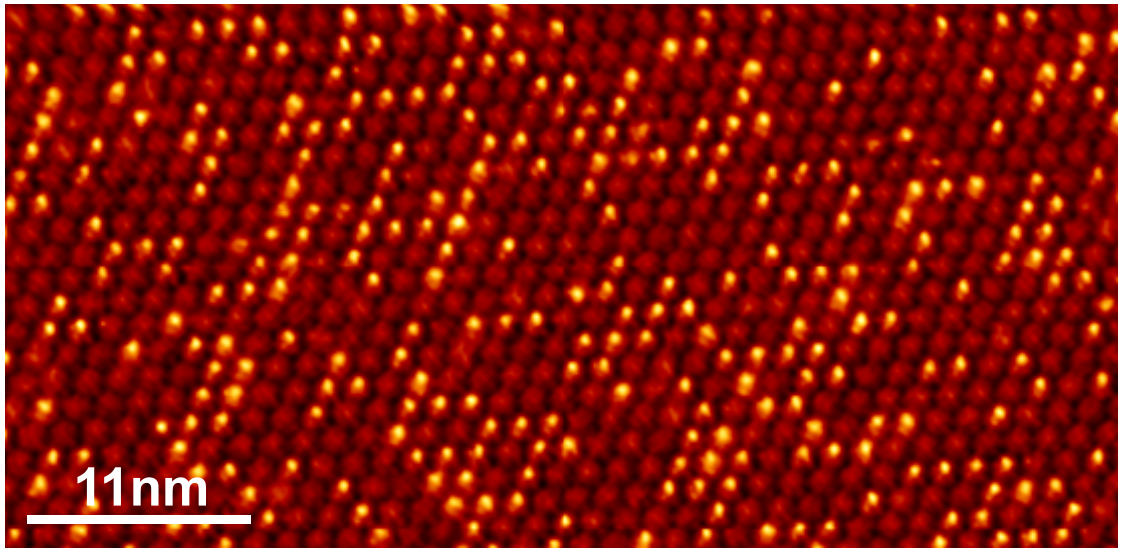
-choice of the actual porphrin derivative (e.g. different ligands and metal centers)

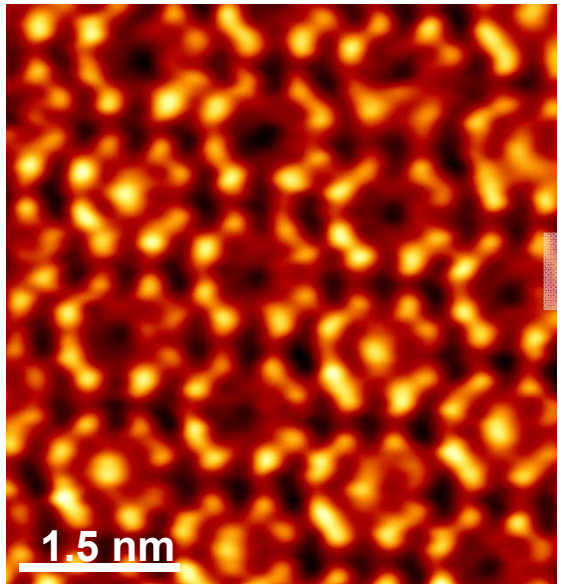
-choice of the substrate

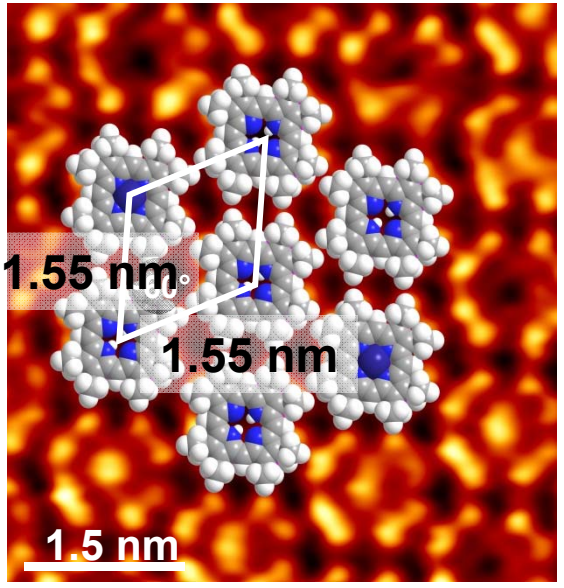
Mixture of 2HOEP and CoOEP on Ag(111)

I set = 37 pA, Ugap = -0.2 V



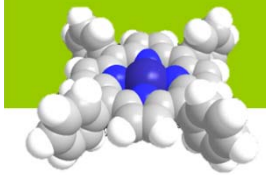


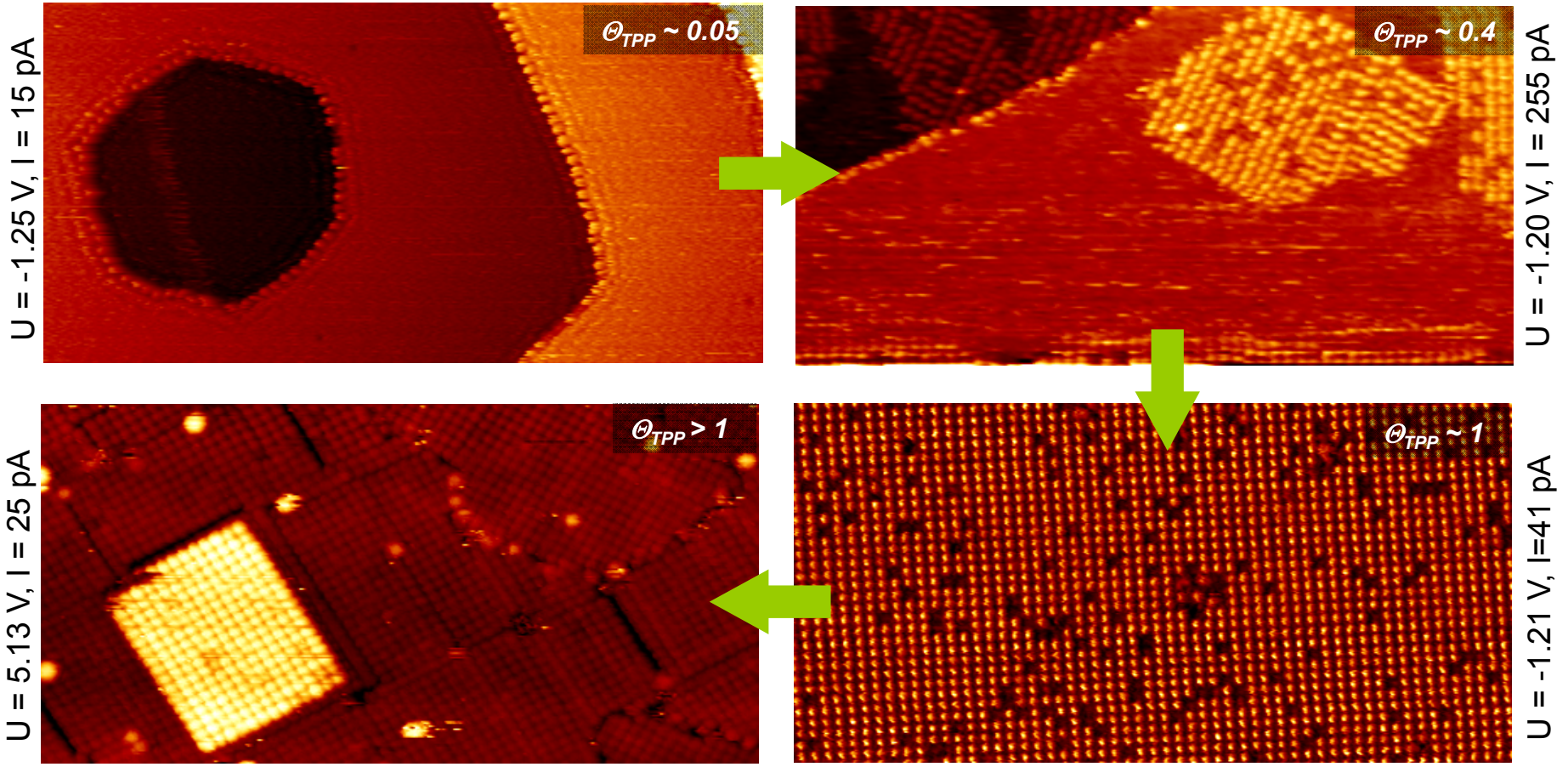




Y. Bai, F. Buchner, I. Kellner, M. Schmid, F. Vollnhals, H.P. Steinrück, H. Marbach, J.M. Gottfried, **New Journal of Physics**, 11 (2009) 125004

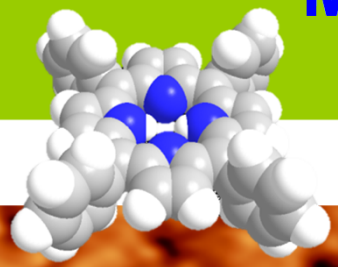
From submonolayer coverage to the multilayer regime: CoTPP on Ag(111)

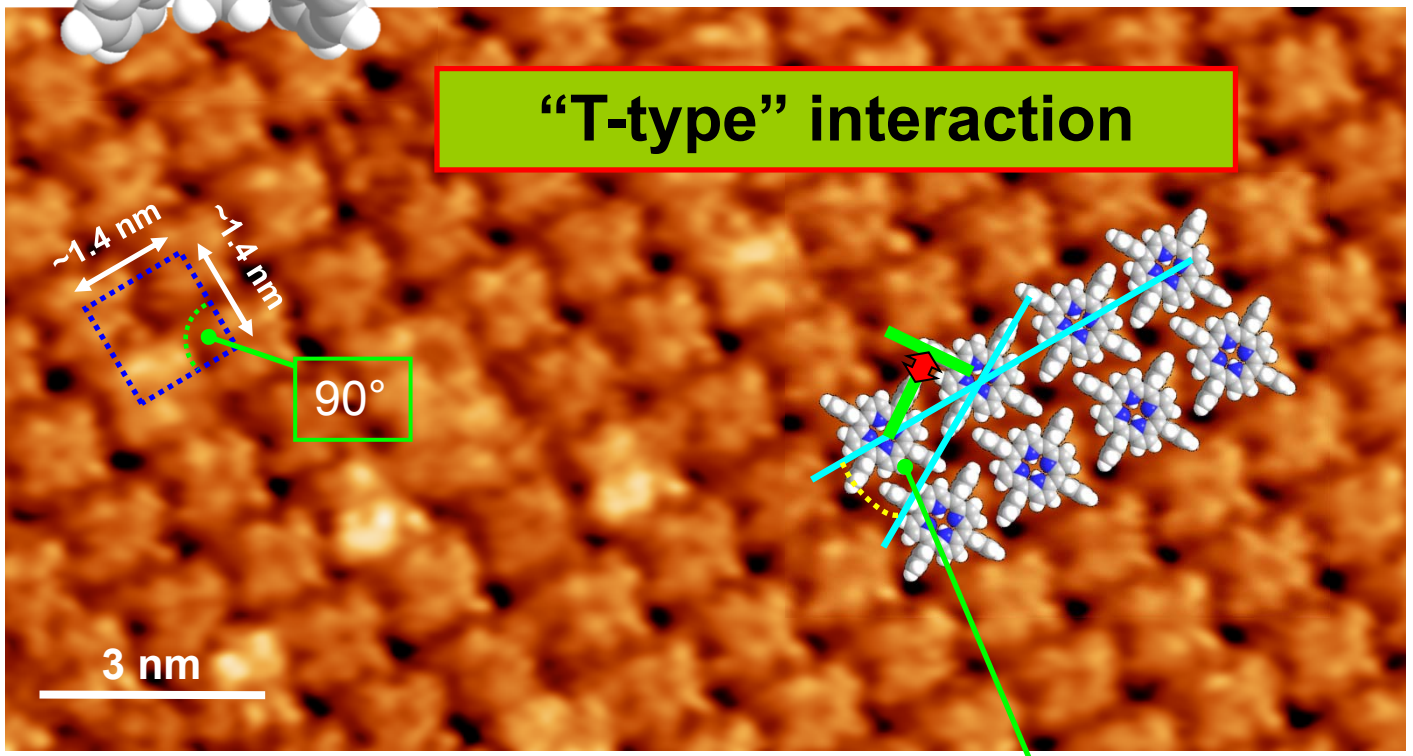




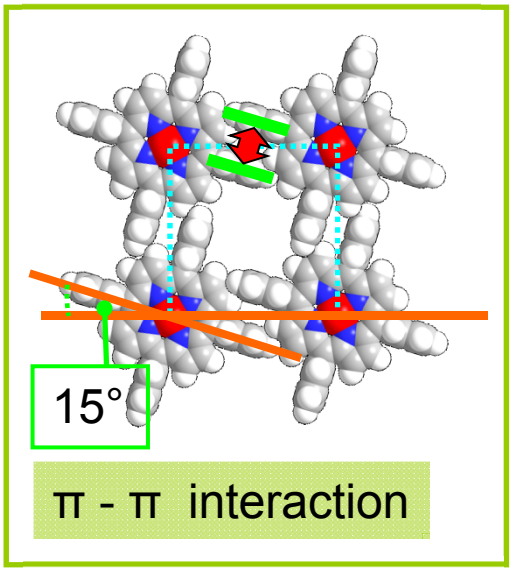
F. Buchner, I. Kellner, W. Hieringer, A. Görling, H.-P. Steinrück and H. Marbach
PCCP 12 (2010) 13082.

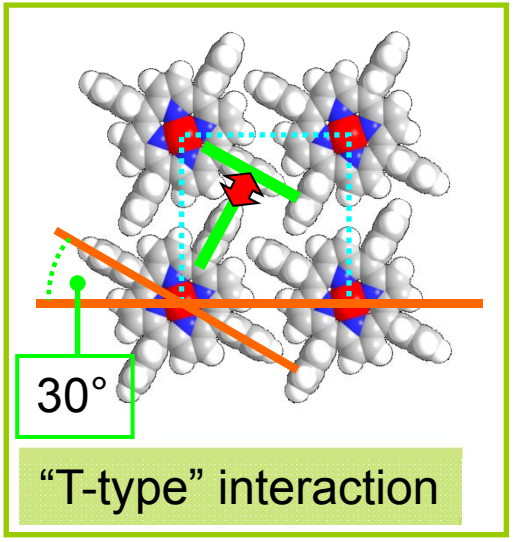
Molecular arrangement of 2HTPP on Ag(111)





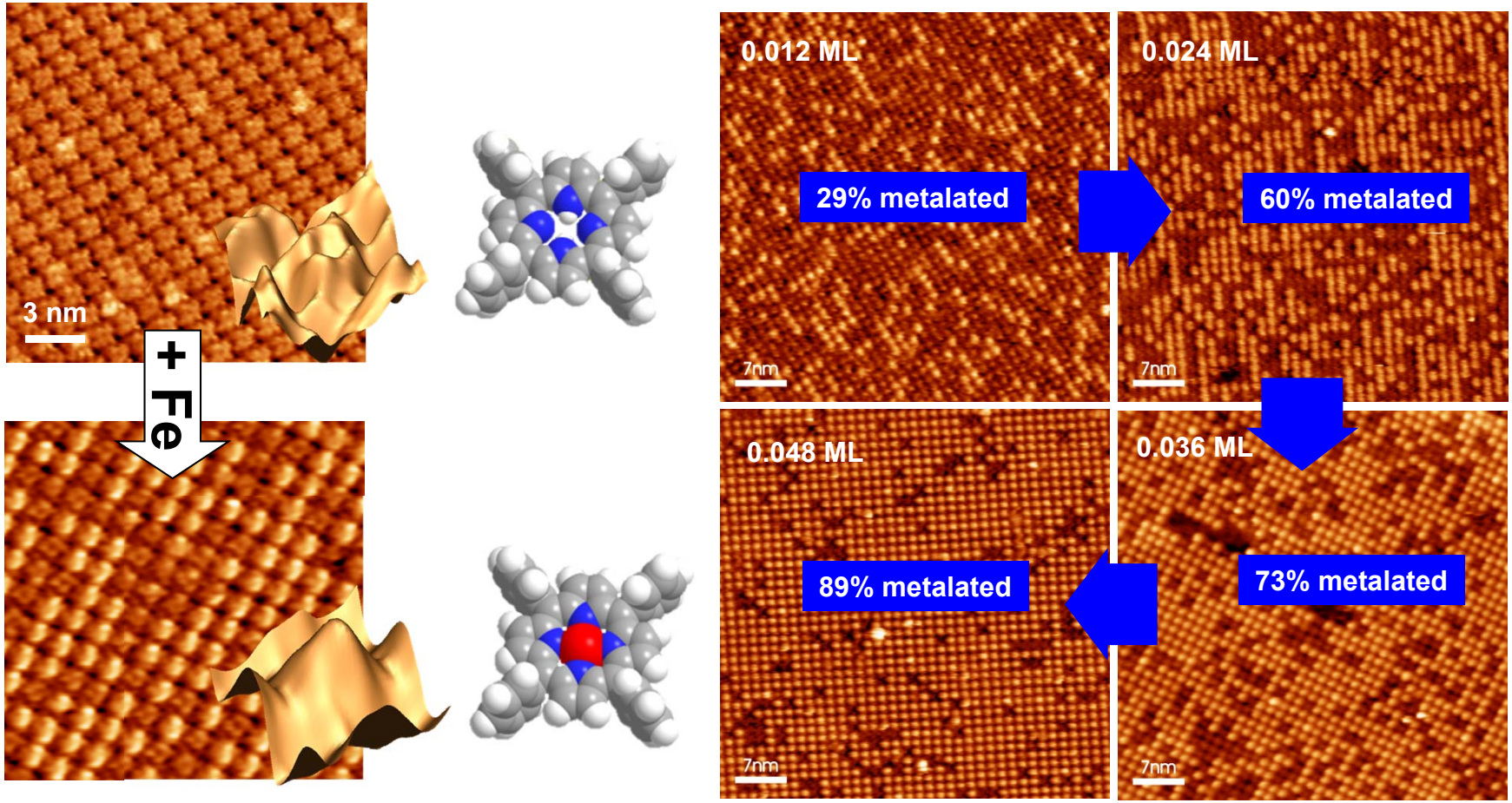
Same arrangement also for CoTPP, ZnTPP and FeTPP





F. Buchner, I. Kellner, W. Hieringer, A. Görling, H.-P. Steinrück and H. Marbach, **PCCP** 12 (2010) 13082.

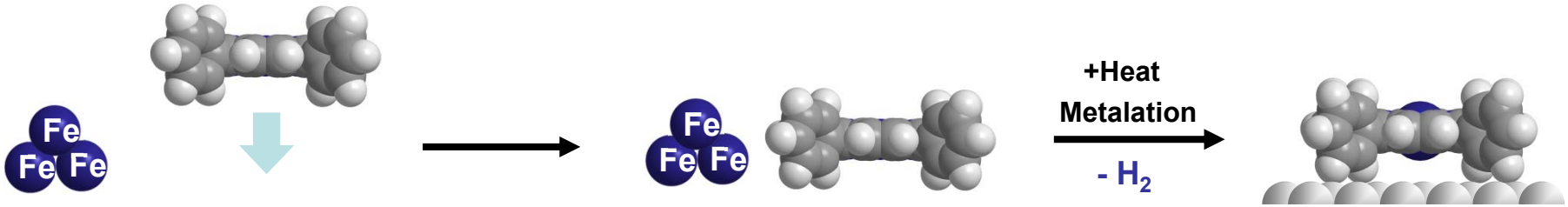
In situ metalation (functionalization) of 2HTPP

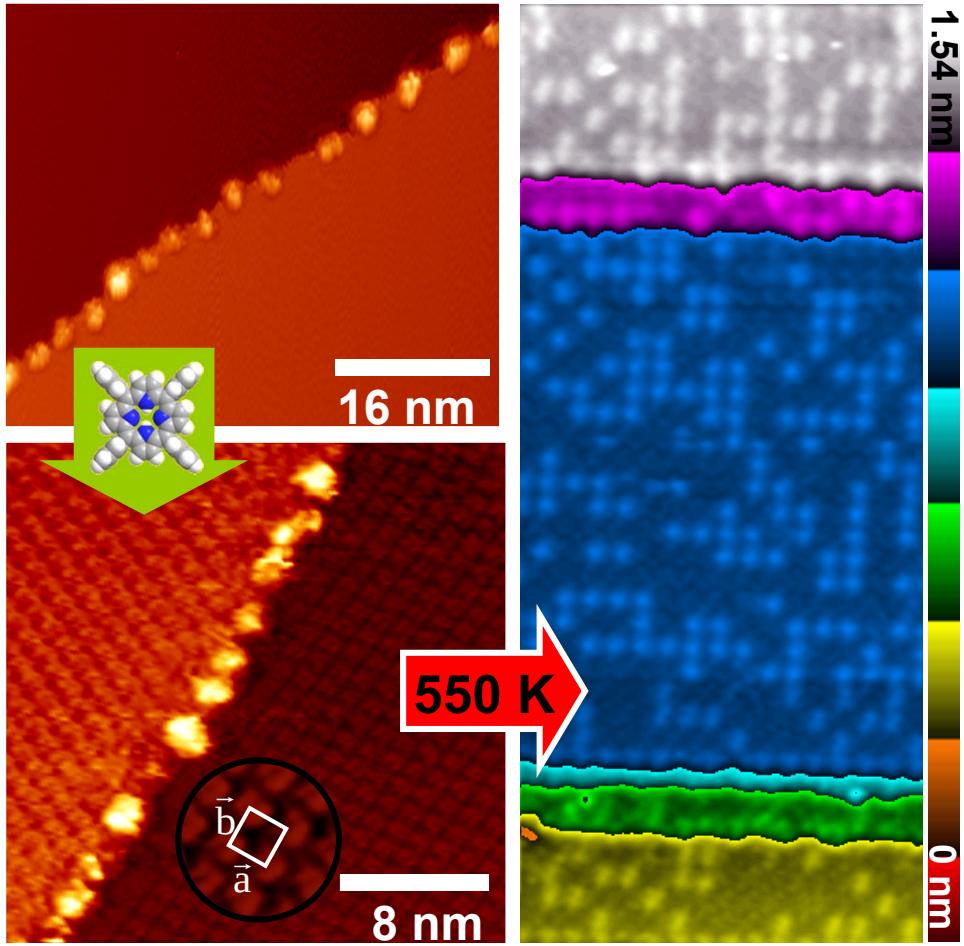


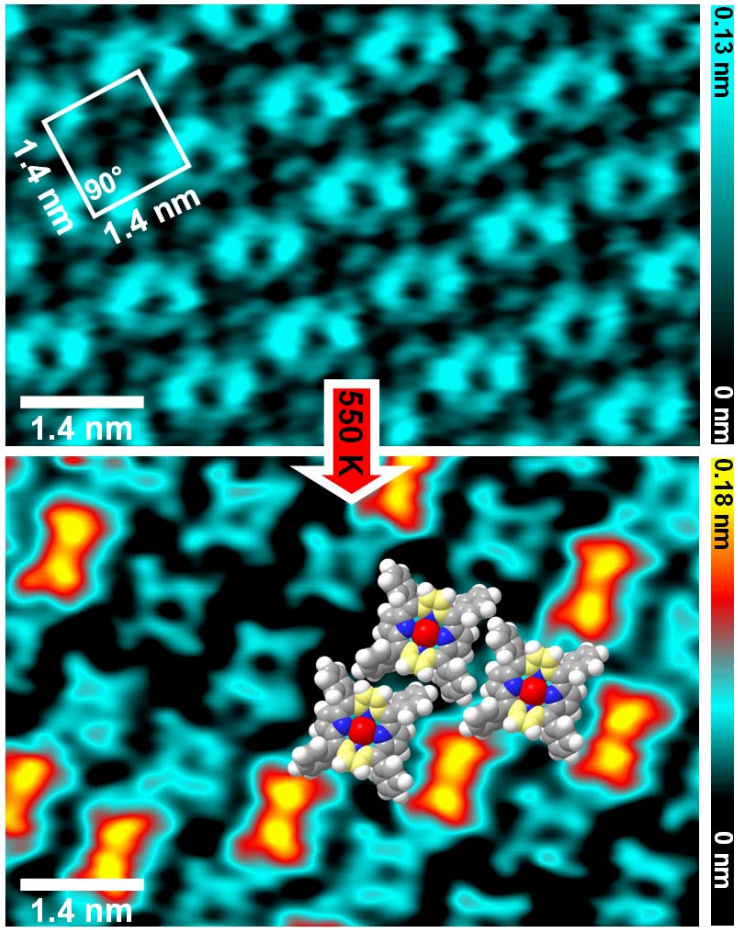
STM: F. Buchner, V. Schwald, K. Comanici, H.-P. Steinrück and H. Marbach, **ChemPhysChem.** 8 (2007)
XPS/STM: F. Buchner, K. Flechtner, Y. Bai, E. Zillner, I. Kellner, H.P. Steinrück, H. Marbach, and J.M. Gottfried **,** **J. Phys. Chem. C** 112(2008) 15458

-Co/2HTPP-XPS: J. M. Gottfried, K. Flechtner, A. Kretschmann, T. Lukasczyk, H.-P. Steinrück, *J. Am. Chem. Soc.* 128 (2006) 5644
-Fe/2HTPyP-STM: W Auwärter, A Weber-Bargioni, S Brink, A Riemann, A Schiffrin, M Ruben, J V Barth, 2007 *ChemPhysChem* , 8, 250
-Co/2HTPP-XPS/STM/Theo:T. E. Shubina, H. Marbach, K. Flechtner, A. Kretschmann, N. Jux, F. Buchner, H.-P. Steinrück, T. Clark and J. M. Gottfried, *J. Am. Chem. Soc.* 129 (2007) 9476
-Fe/2HPc-STM/XPS: Y. Bai, F. Buchner, M. T. Wendahl, I. Kellner, A. Bayer, H.-P. Steinrück, H. Marbach and J. M. Gottfried, *J. Phys. Chem. C* 112 (2008) 6087

Metalation of 2HTPP with predepositied Fe





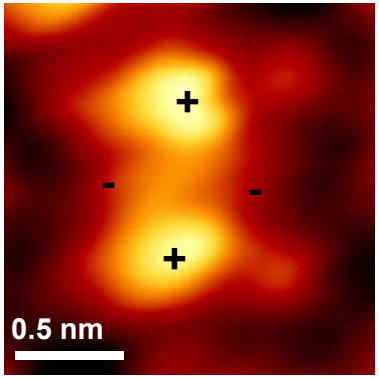


F. Buchner, K. Flechtner, Y. Bai, E. Zillner, I. Kellner, H.P. Steinrück, H. Marbach, and J.M. Gottfried , *J. Phys. Chem. C* 112(2008) 15458

Submolecularly resolved appearance of TPP molecules

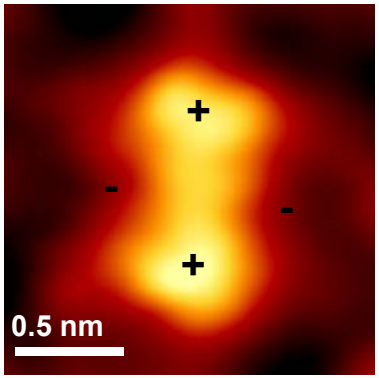
FeTPP

U = -1.25 V
I = 15 pA



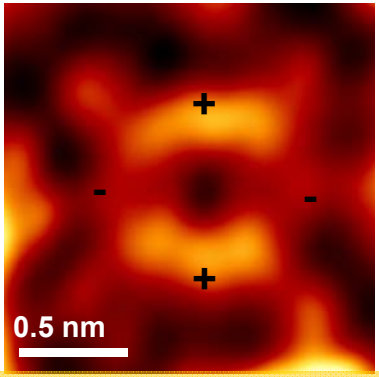
CoTPP

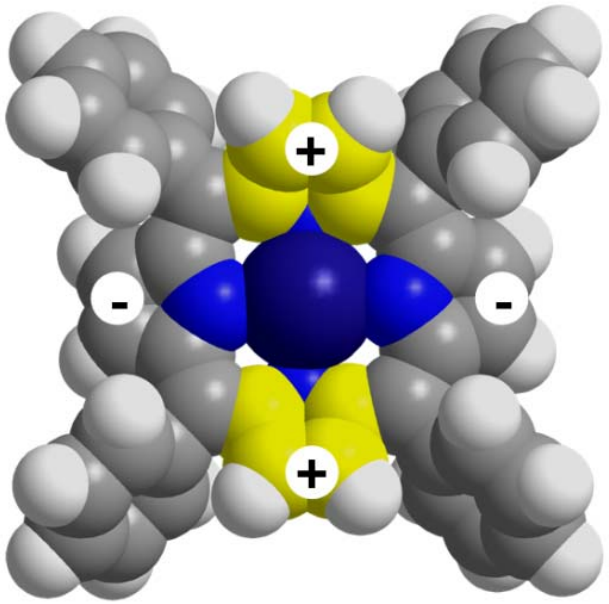
U = -1,18 V
I = 58 pA

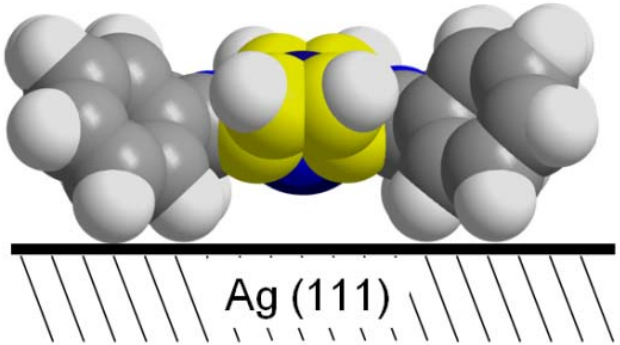


2HTPP

U = -7 mV
I = 54 pA.





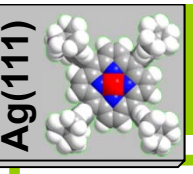


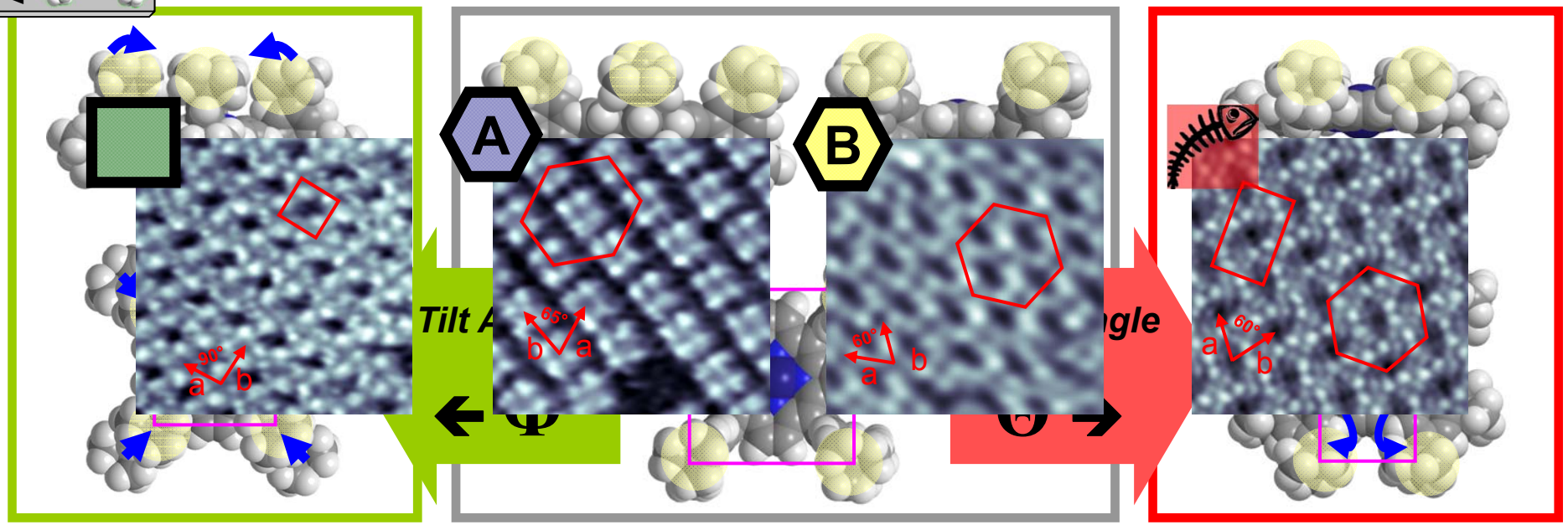
➔ **Conformational adaption upon adsorption – saddle-shaped macrocycle**

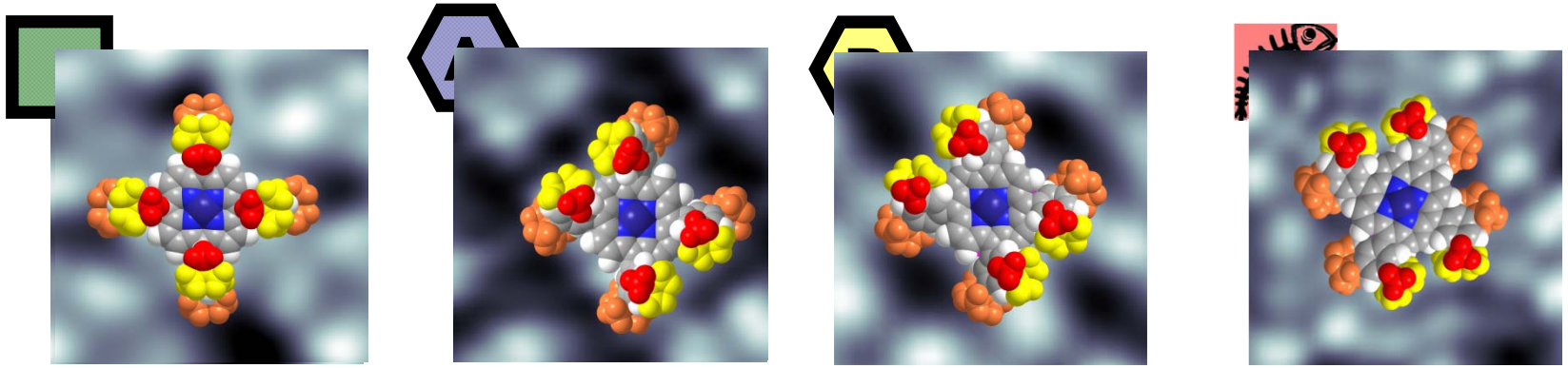
F. Buchner et al., **ACS Nano**, 2009. **3**(7): p. 1789-1794

F. Buchner et al., **PCCP**. 12 (2010) 13082

Polymorphism of CoTTBPP on Ag(111)



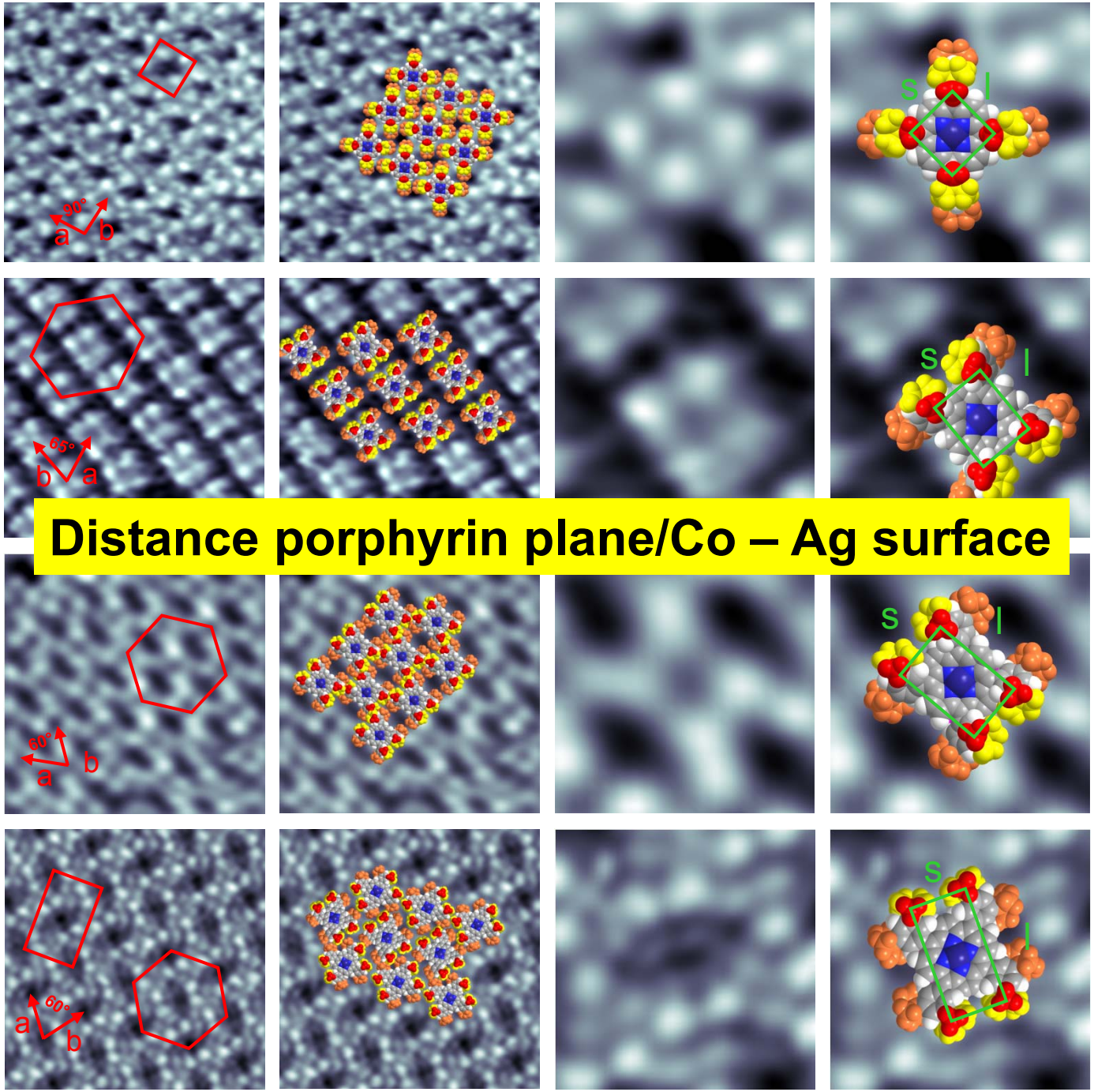




I/s ~1.0	I/s ~1.3	I/s ~1.6	I/s ~2.0
Θ ~ 90°	Θ ~ 60°	Θ ~ 45°	Θ ~ 20°
Φ ~ 30°	Φ ~ 20°	Φ ~ 15°	Φ ~ 5°

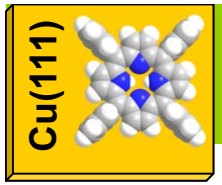
F. Buchner, K. Comanici, N. Jux, H.-P. Steinrück and H. Marbach, **J. Phys. Chem. C**, 111 (2007) 13531

Phase ⇩	Θ [°]	Φ [°]
Square	90	25
	0,42 nm	
Hex A	60	20
	0,39 nm	
Hex B	45	15
	0,39 nm	
Herring-bone	20	5
	0,36 nm	

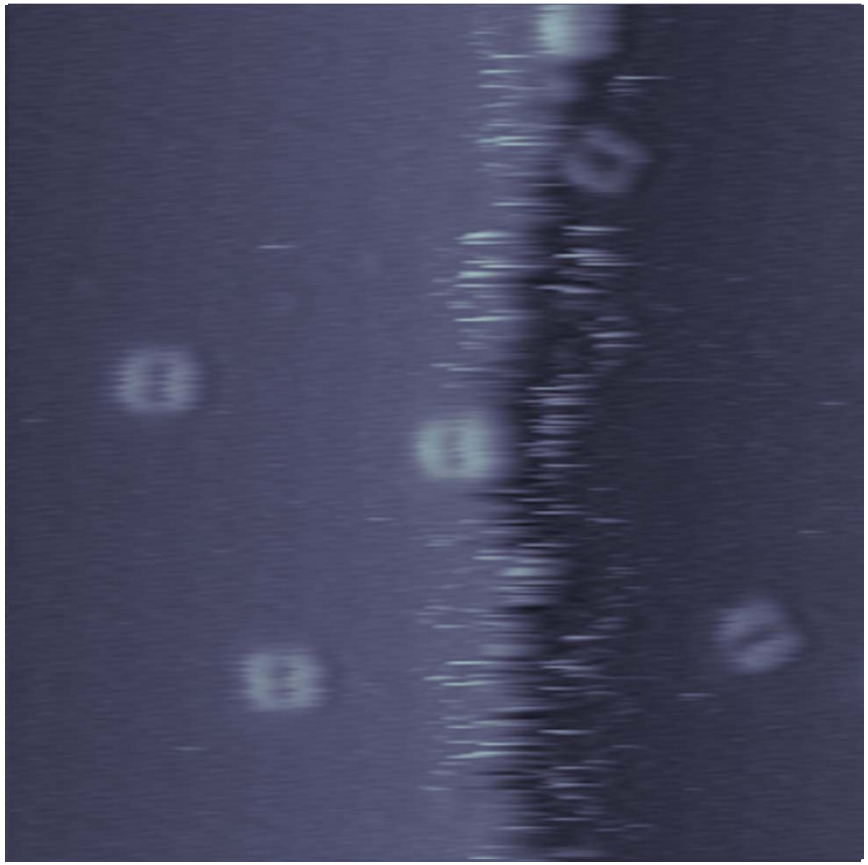


Distance porphyrin plane/Co – Ag surface

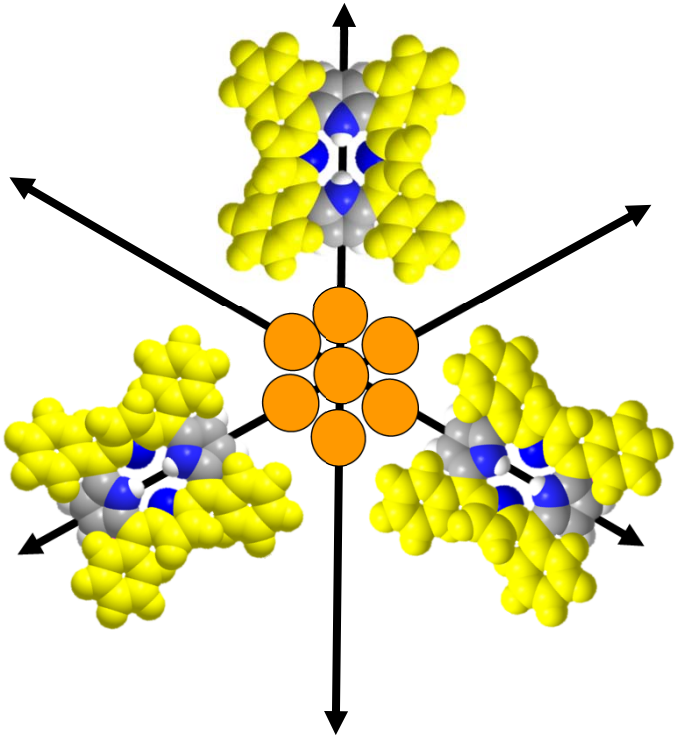
F. Buchner, K. Comanici, N. Jux, H.-P. Steinrück and H. Marbach, **J. Phys. Chem. C**, 111 (2007) 13531



Individual 2HTPP on Cu(111)



$(18\ nm)^2$; 39 images x 20s = 13 min

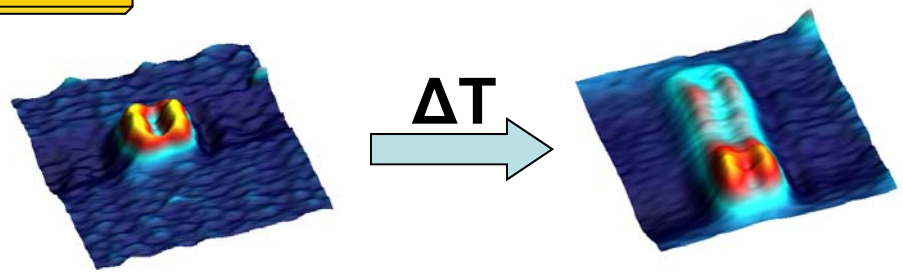


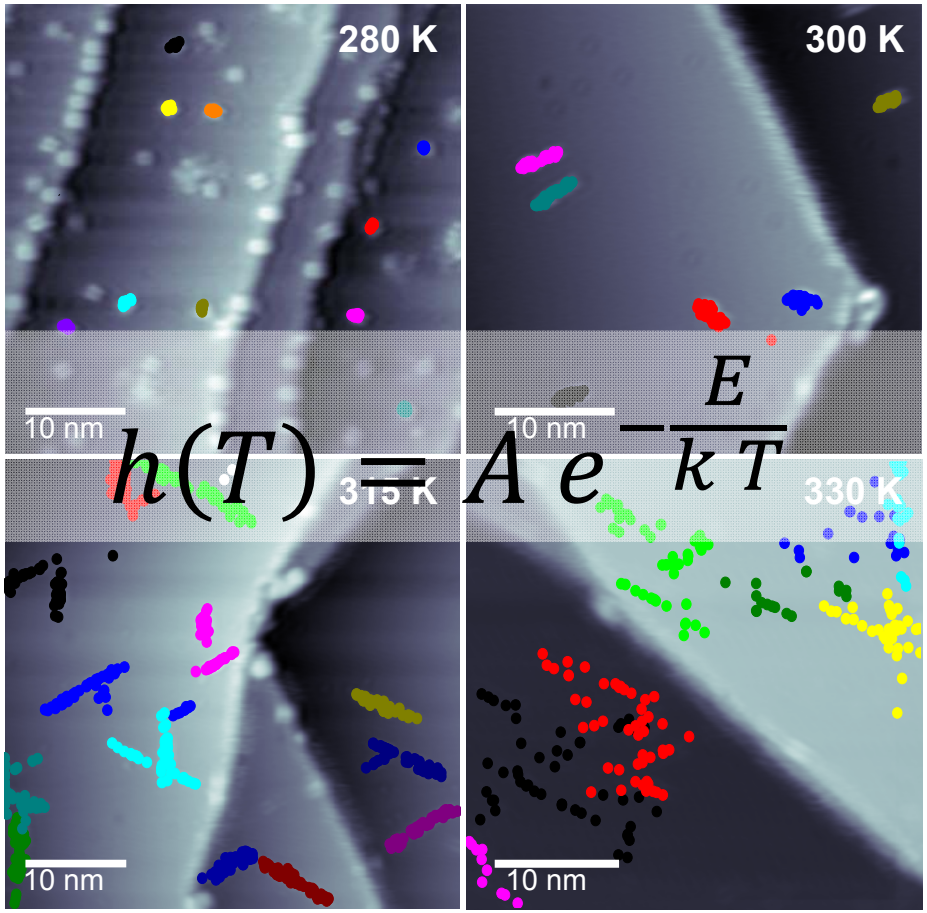
→ 1D-diffusion in preferential direction of the substrate

→ Interaction between Cu and nitrogens of macrocycle

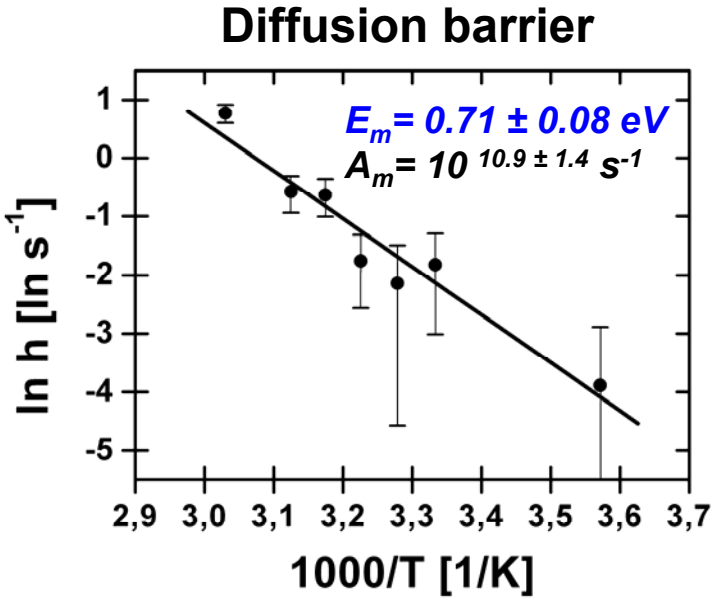
F. Buchner et al., J. Phys. Chem. C, *115* (2011) 24172

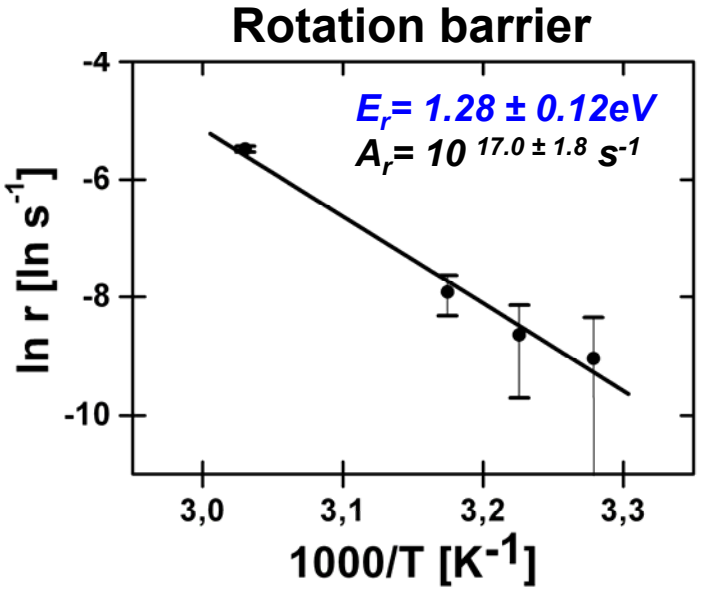
2HTPP on Cu(111): temperature dependent dynamics





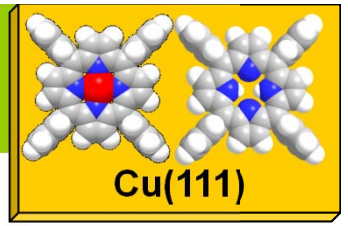
$$h(T) = A\, e^{-\frac{E}{k\,T}}$$



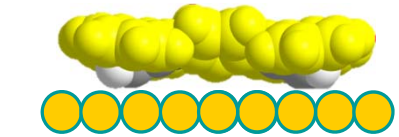


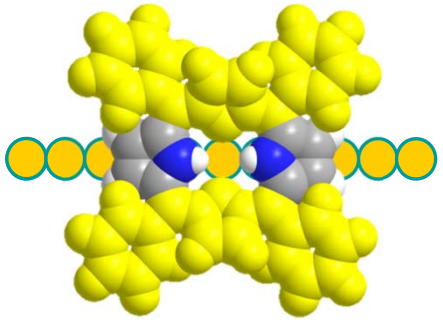
F. Buchner et al., J. Phys. Chem. C, *115* (2011) 24172

Separation of CoTPP and 2HTPP on Cu(111)

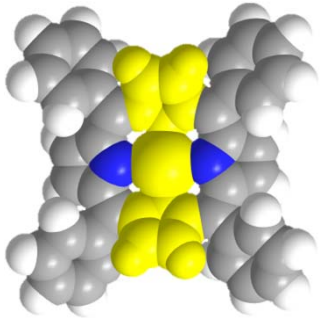


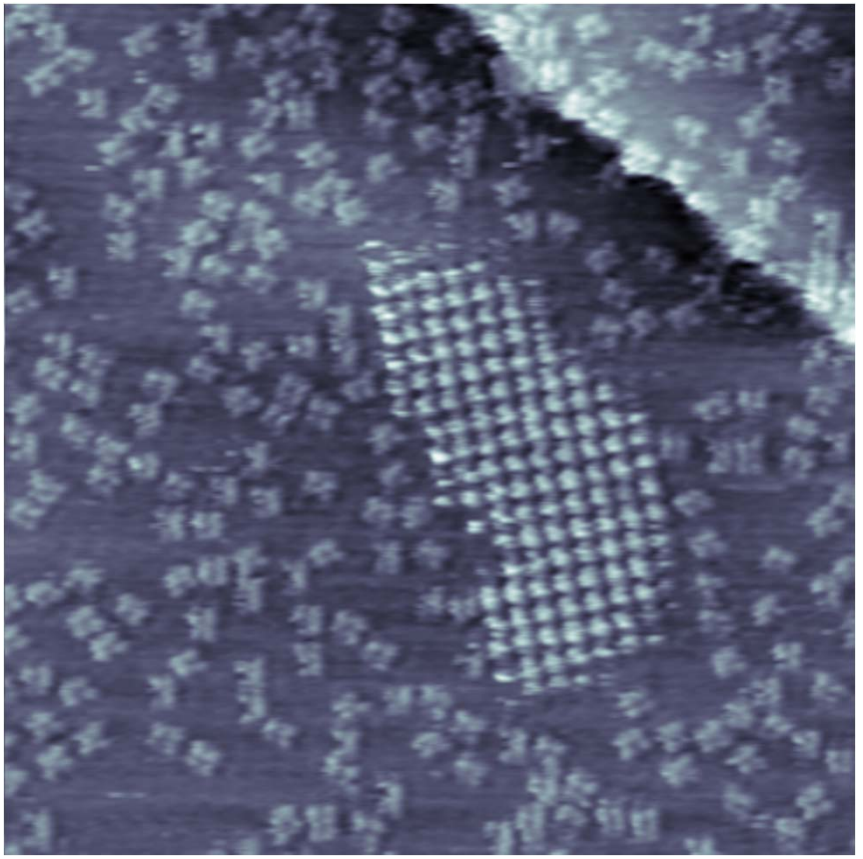
For **2HTPP** a strong interaction of the iminic nitrogen with the close packed Cu rows is proposed





For, e.g. **CoTPP** all nitrogens are coordinated to Co





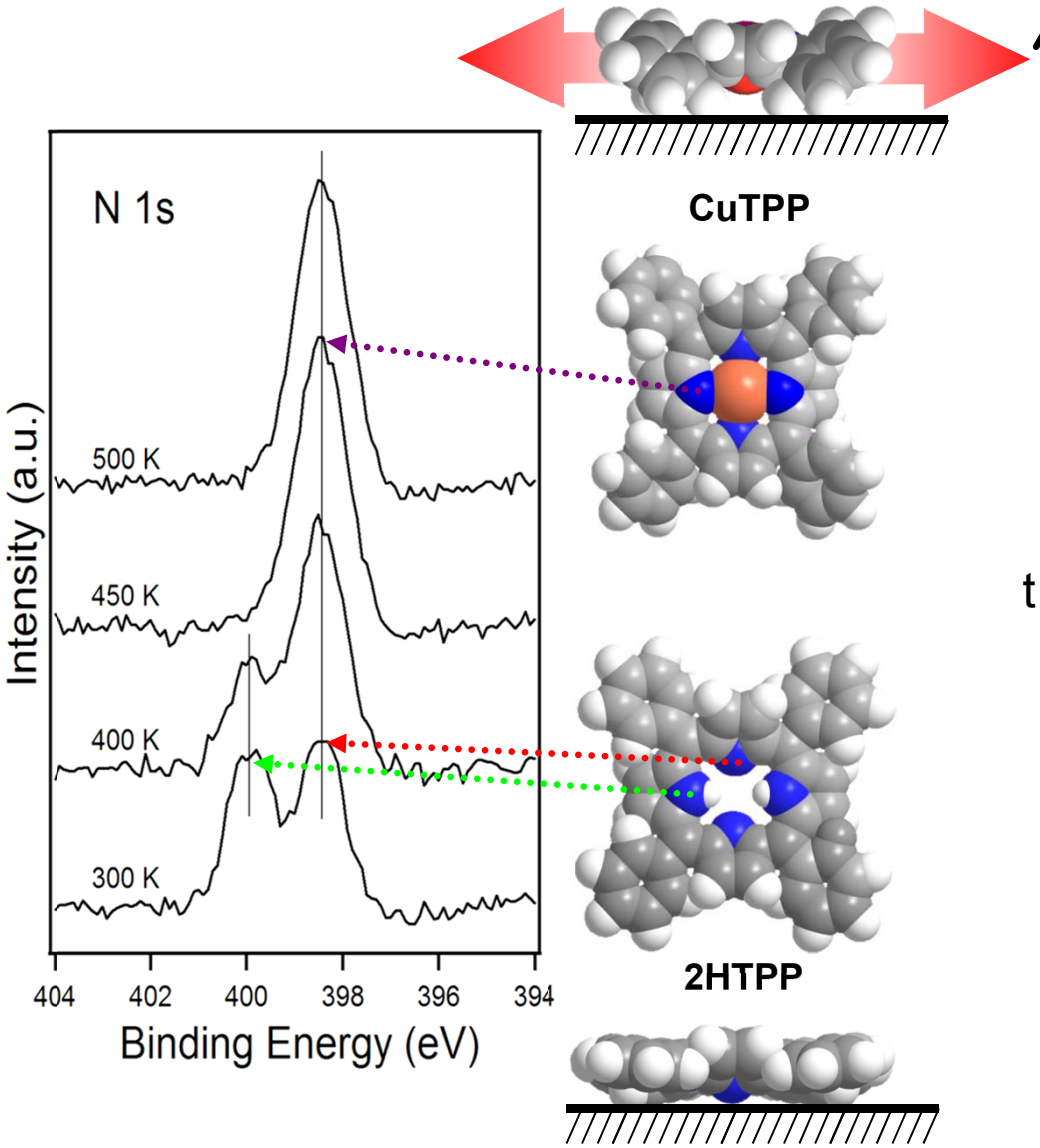
Iset = 30 pA, Ubias = -1.35 V

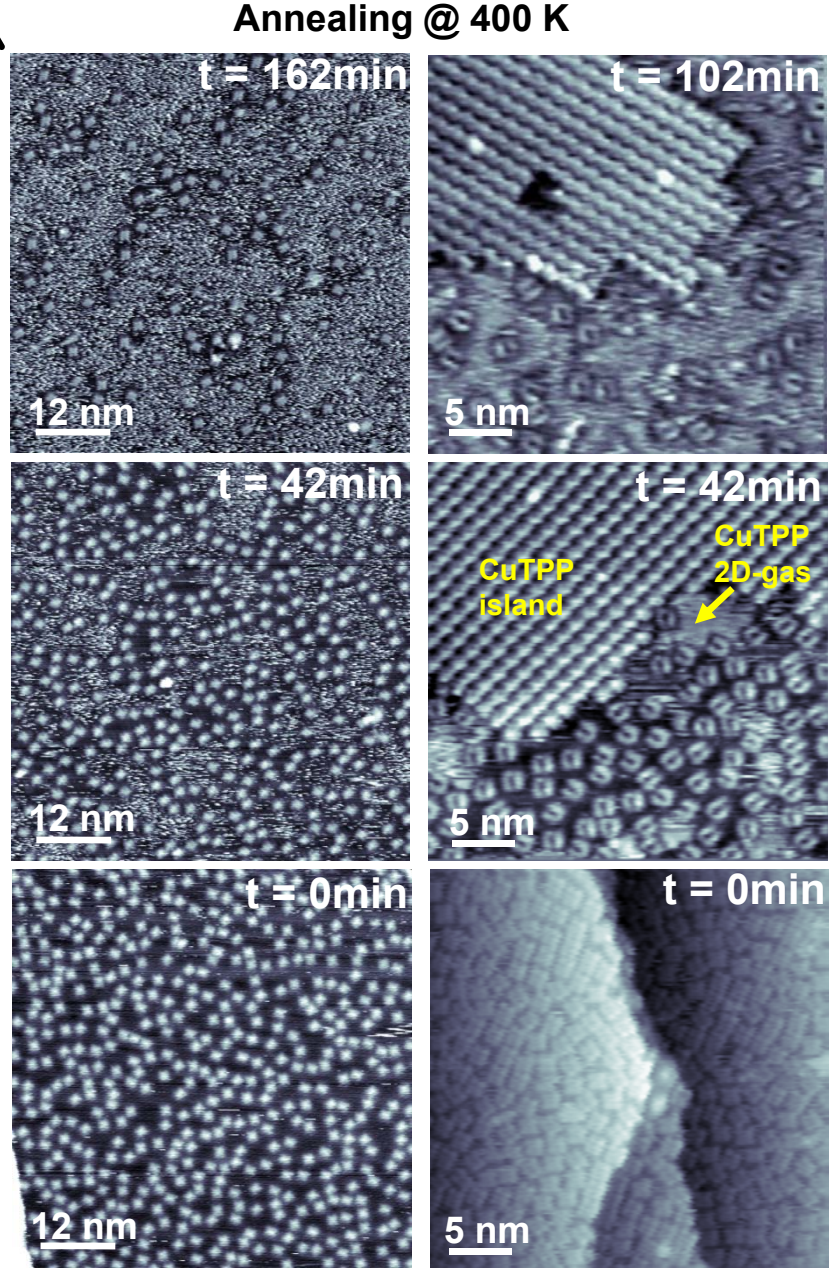
(44 nm)^2; 26 images x 48s = 21 min

Sample @ RT

F. Buchner, E. Zillner, M. Röckert, S. Gläßel, H.-P. Steinrück and H. Marbach**, Chem. Eur. J.** 17 (2011) 10226

In situ metalation of 2HTPP on Cu(111): XPS &STM

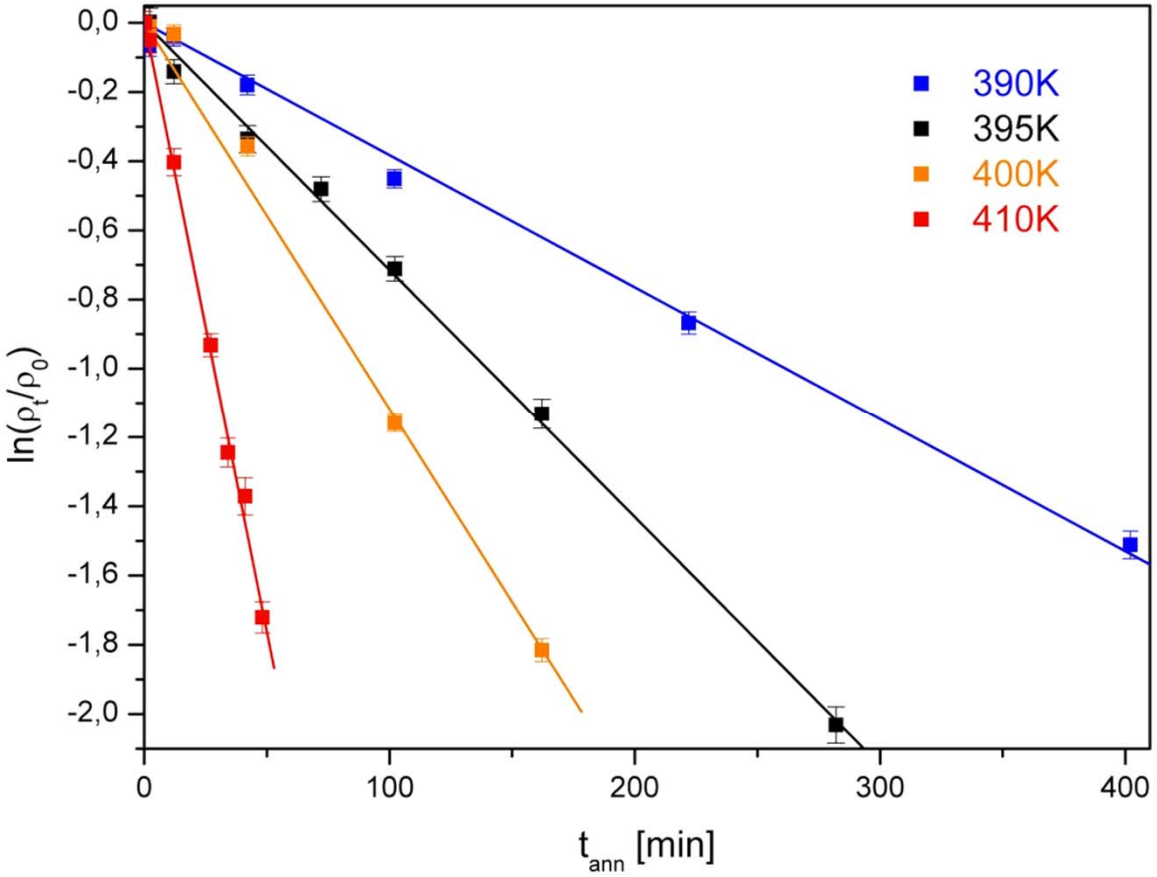




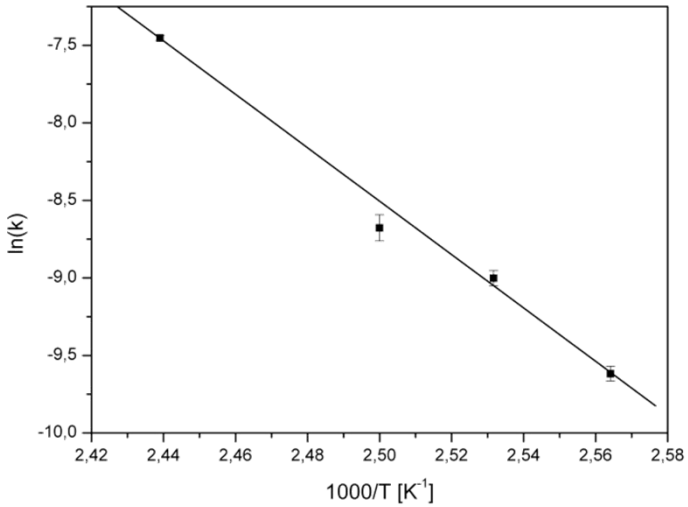
Xiao and Ditze et al., JPCC 116 (2012) 12275

Diller et al.,J. Chem. Phys. 136 (2012) 014705

Metalation of 2HTPP on Cu(111): analysis of STM data



Arrhenius analysis:



$$k(T) = Ae^{\frac{-E_A}{k_B T}}$$

E_A [eV]	A [1/s]
1.48 ± 0.03	$10^{15 \pm 0.4}$

Reaction pseudo-first order:

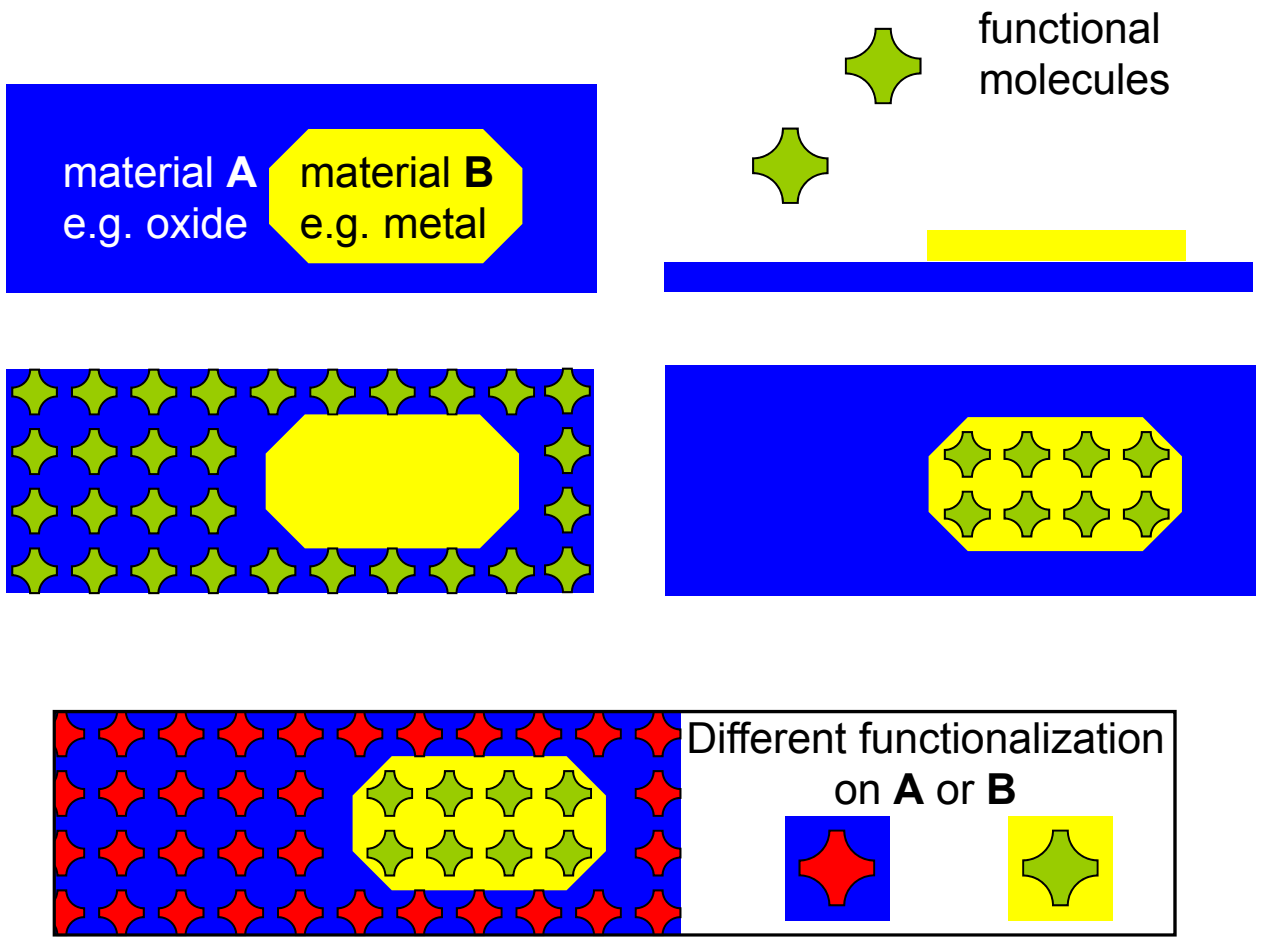
$$\frac{\rho_t}{\rho_0} = e^{-kt}$$

DFT calculations yield:
1.03 eV (B3LYP/6-31G(d)) and
1.69 eV (B3LYP/6-31G(d,p)+LANL2DZ)

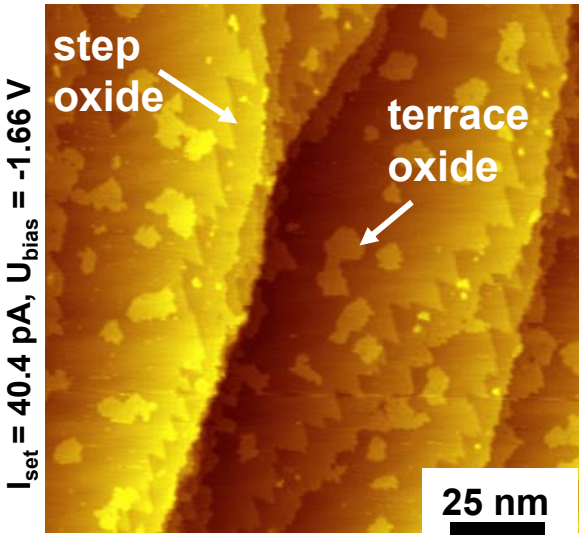
Shubina, T. E. *J. Am. Chem. Soc.* **2007**, *129*, 9476.

S. Ditze, M. Stark, M Drost, F. Buchner, H.P. Steinrück, and H. Marbach, **Angew. Chem Int. Ed.**, 2012 in press.

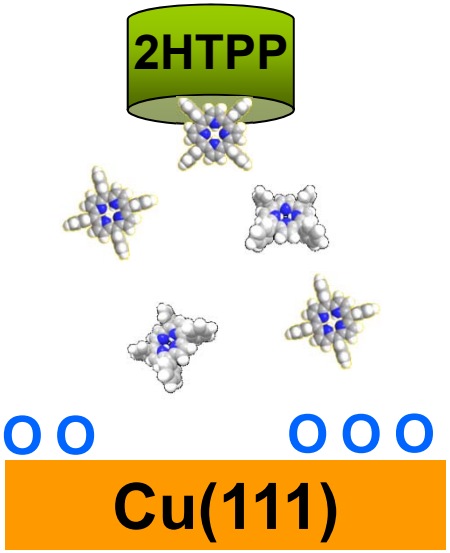
Composite surfaces a template for molecular architectures?

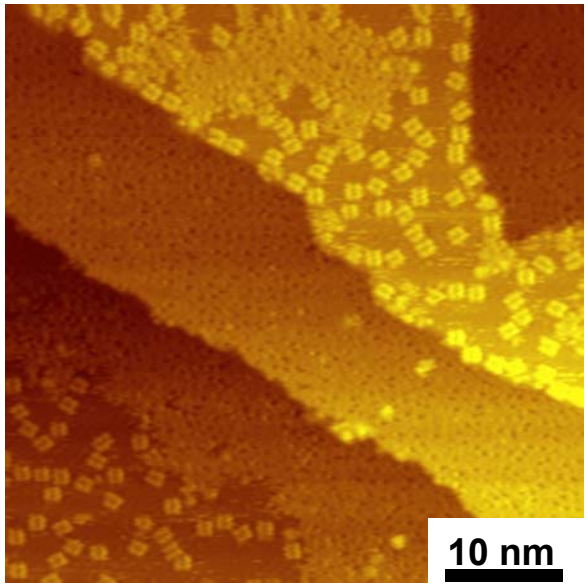


2HTPP and CoTPP on Cu(111) precovered with oxygen islands

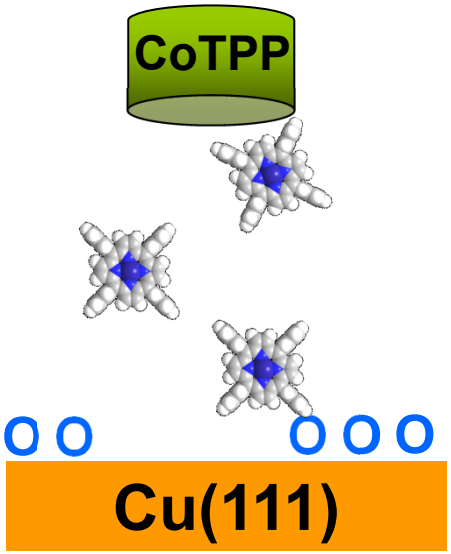


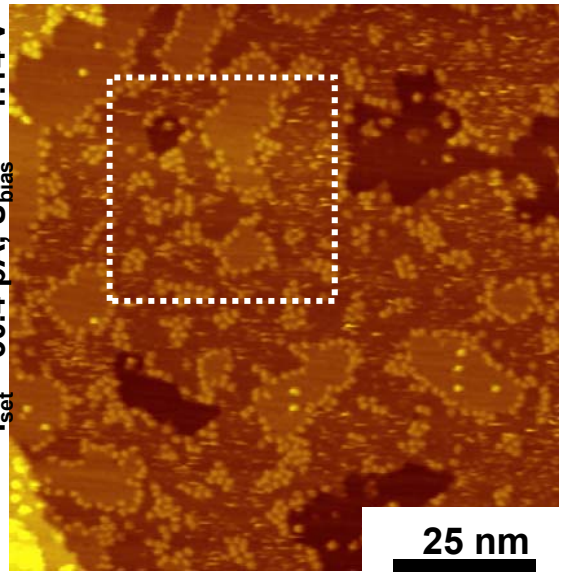
I_{set} = 40.4 pA, U_{bias} = -1.66 V



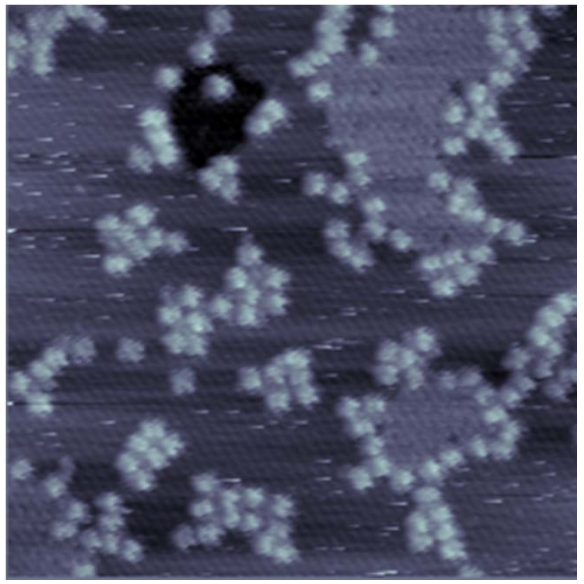


I_{set} = 21.3 pA, U_{bias} = -1.01 V





I_{set} = 30.4 pA, U_{bias} = -1.14 V

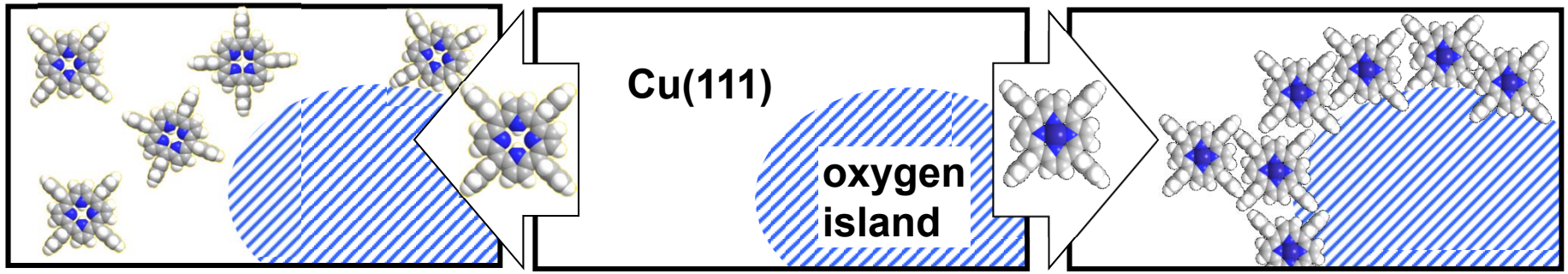


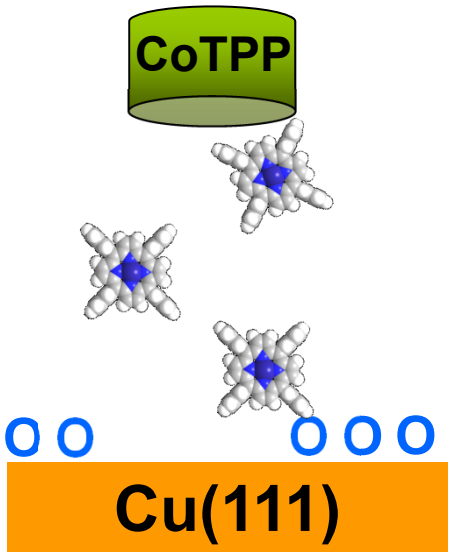
I_{set} = 30.4 pA, U_{bias} = -1.14 V

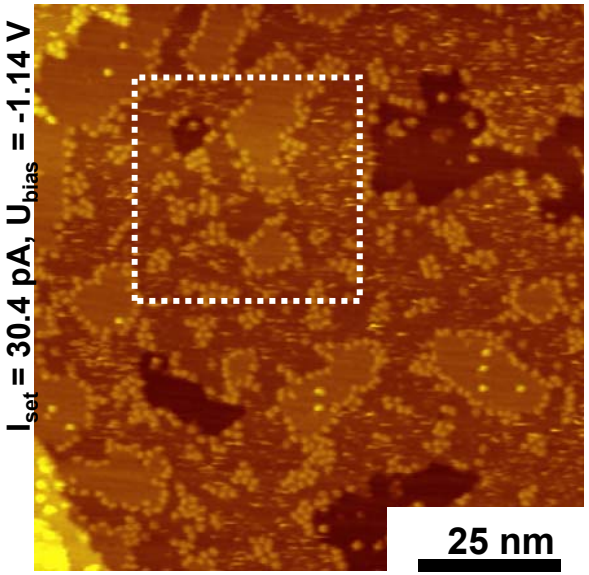
52x114s

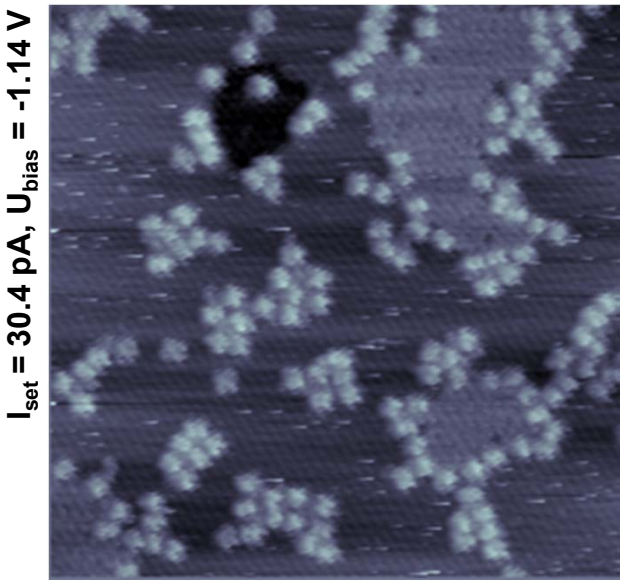
(43 nm)²

2HTPP and CoTPP on Cu(111) precovered with oxygen islands

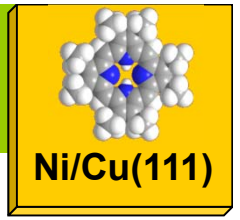


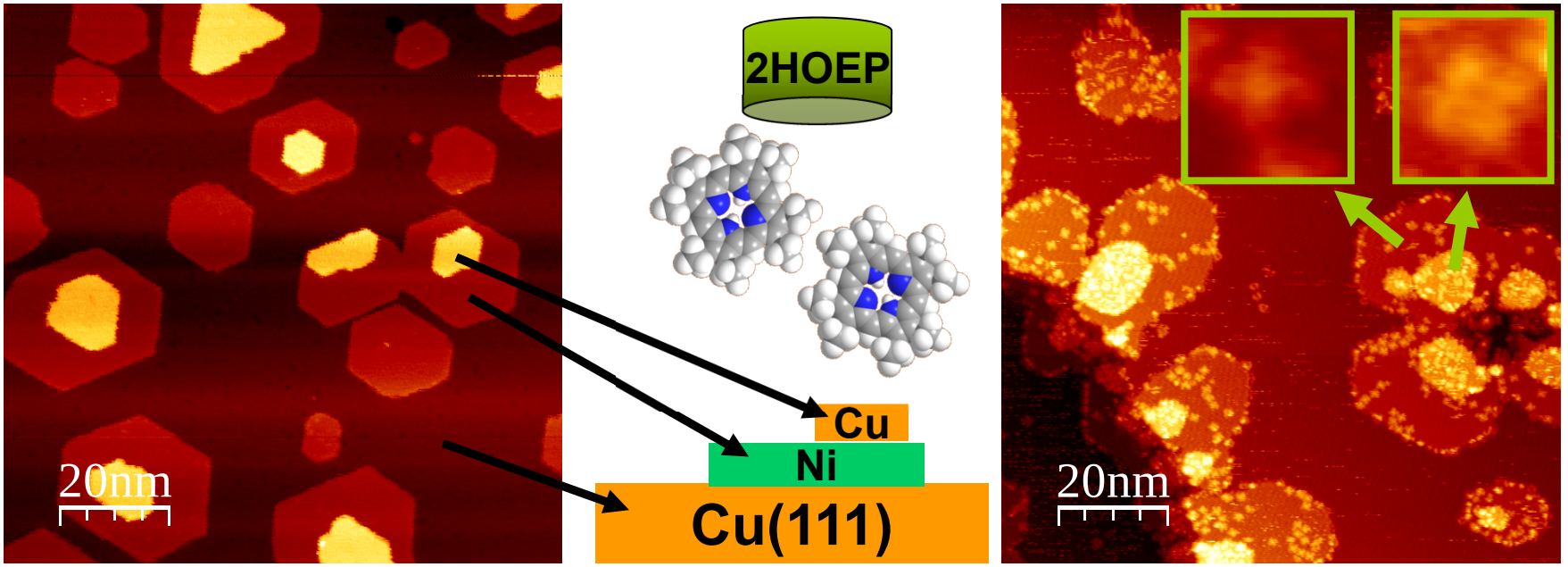


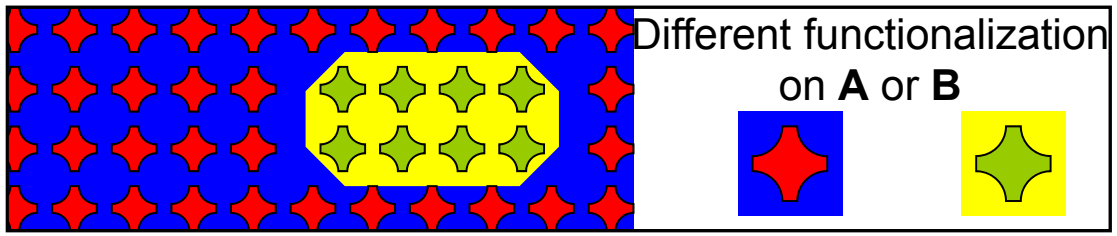




Prestructured surfaces for molecular architectures

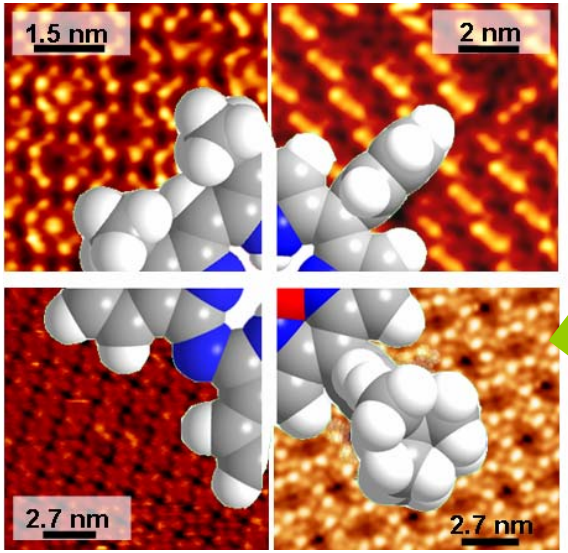




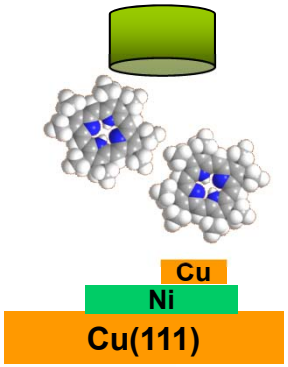


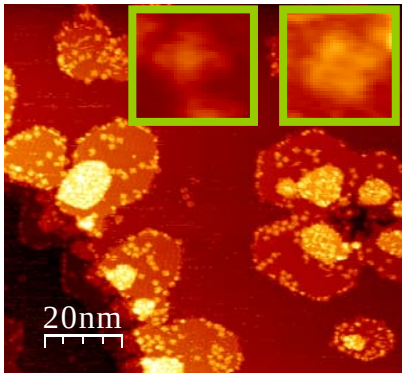
The bottom-up porphyrin toolbox

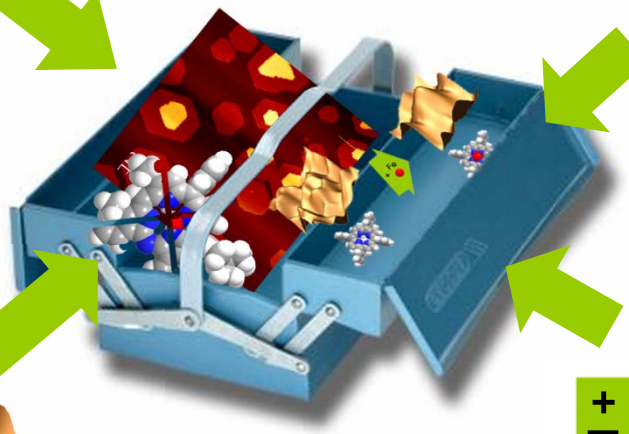
Choice of peripheral ligands



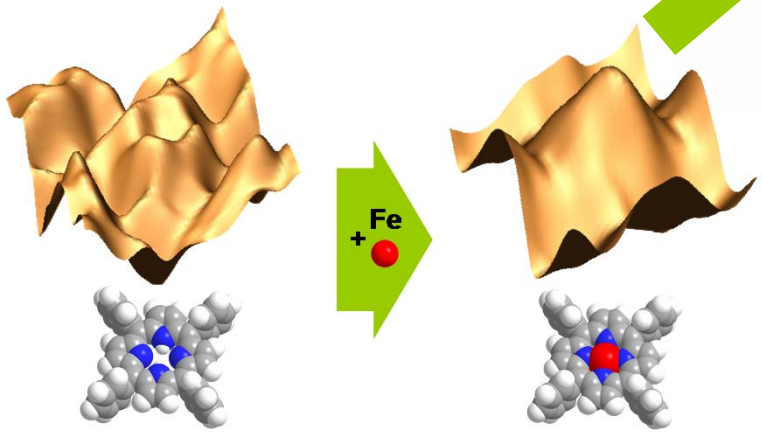
Choice of (prestructured) substrate



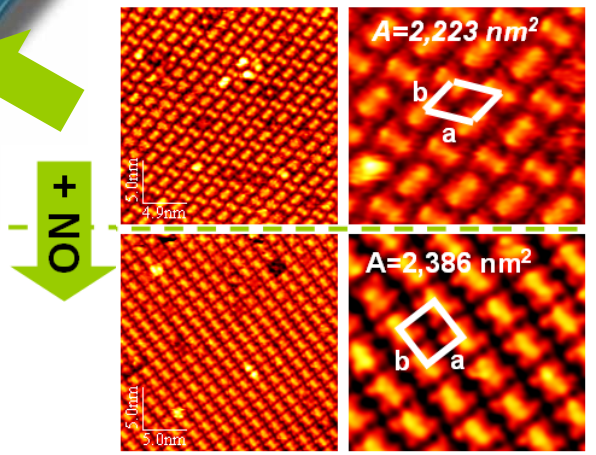




Metalation of 2H porphyrins



CoTPP/Ag(111) + NO

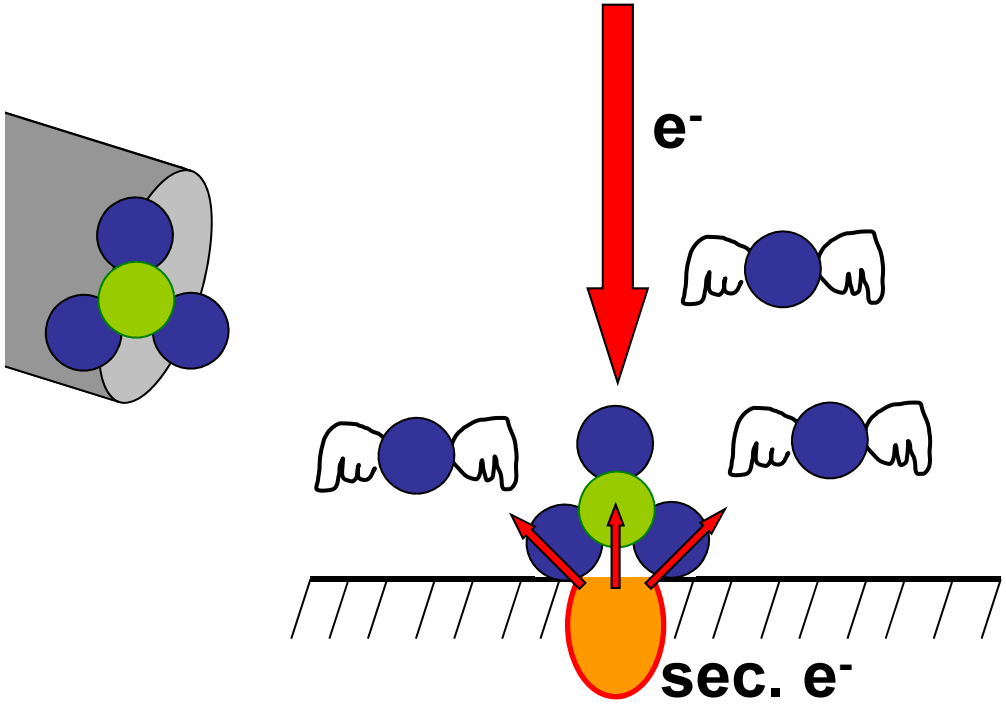


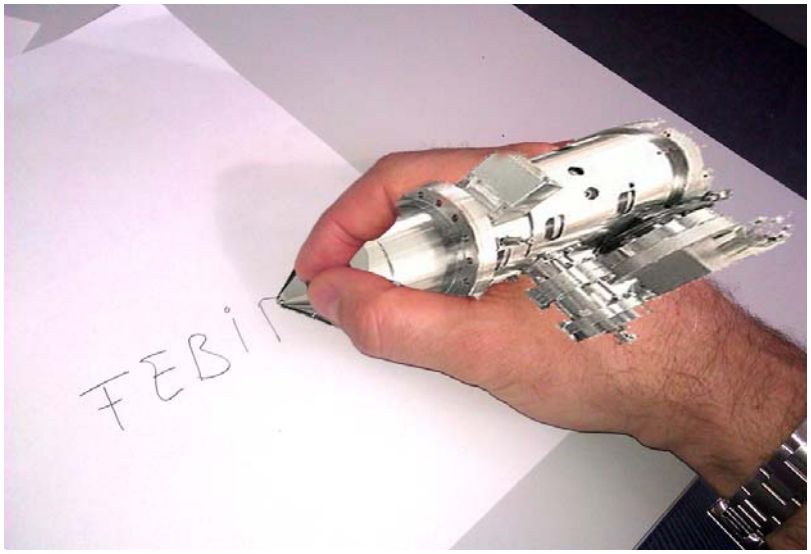
F. Buchner, K. Seufert, W. Auwärter, D. Heim, J.V. Barth, K. Flechtner, J.M. Gottfried, H.P. Steinrück, and H. Marbach, **ACS Nano**, 2009. **3**(7): p. 1789-1794

2nd part:

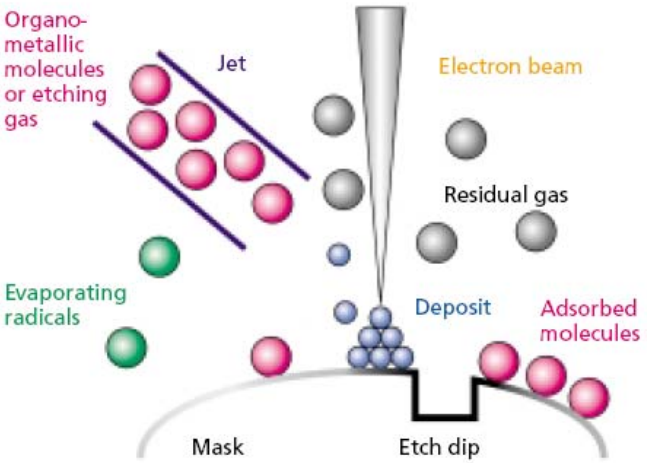
Fabrication and characterization of nanostructures by means of a highly focused electron beam in UHV

➔ *Writing nanostructures via Electron Beam Induced Deposition (EBID)*

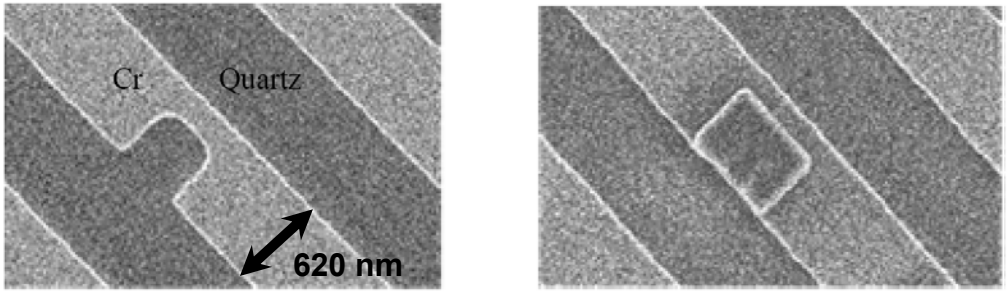




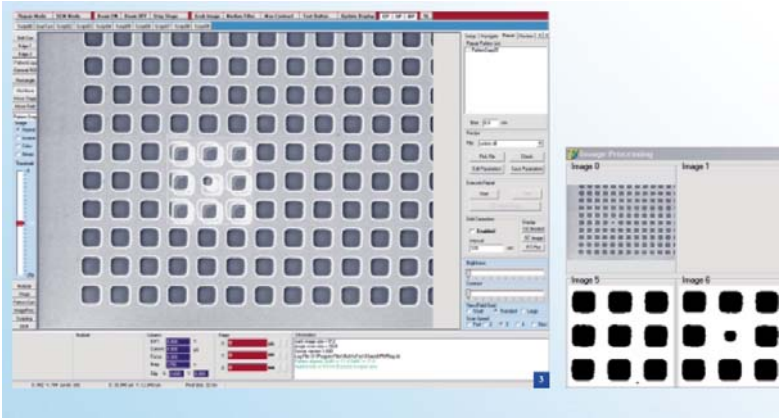
FEPIP application: state-of-the-art mask repair tool



ZEISS, Mask repair tool



T. Liang, et al. Intel Corporation;
Boegli, et al. NaWoTec GmbH,



Why UHV ?

SEM in a High Vacuum Environment (HV):

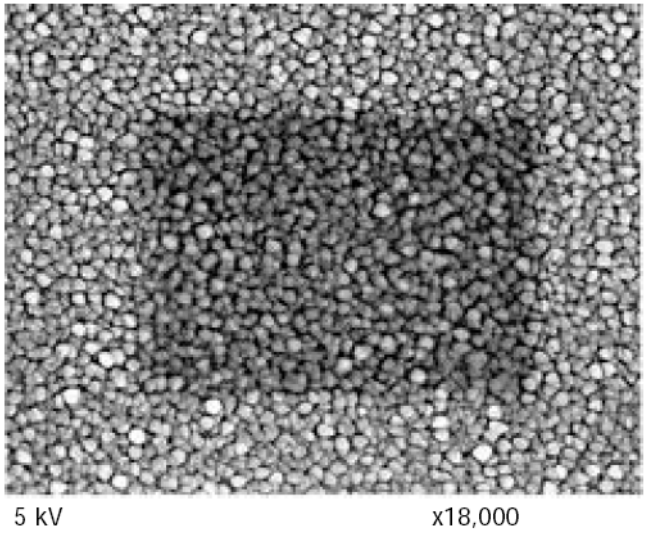


Image from: "A guide to Scanning Microscope Observation", Jeol

-electron induced deposition of adsorbats

-in HV systems mainly hydrocarbons (pump oil)

-most commercial SEMs are housed in HV

Goals

Shape:
-defined form
-ultimative size

Chemical Composition:
-targeted material
-cleanliness

Results for EBID in a High Vacuum Environment (HV) from Literature:

Typical metal content of HV-EBID deposits [1-3]:

≈ 15 - 60 % metal

[1] H. W. P. Koops et. al., *J. Vac. Sci. Technol. B*, 1988, 6, p. 477; [2] Y. M. Lau et. al., *J. Vac. Sci. Technol. A*, 2002, 20, p. 1295; [3] I. Utke et al., Applied Physics Letters (2002), 80, 4792-4794. .

Why UHV ?

SEM in a High Vacuum Environment (HV):

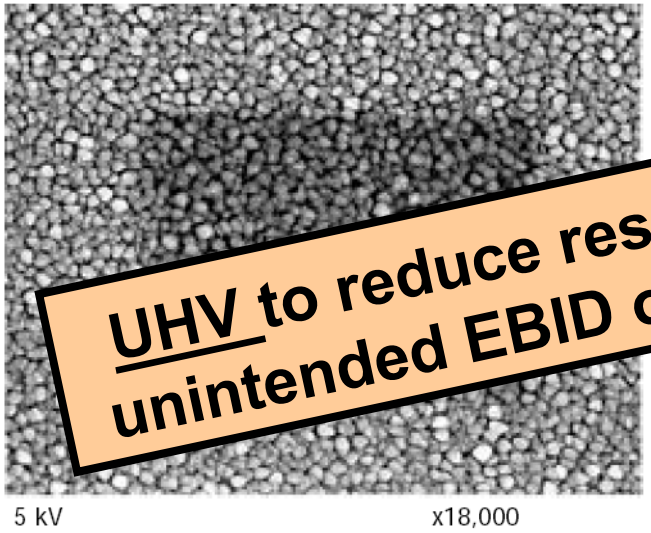


Image from: "A guide to Scanning Microscope Observation", Jeol

UHV to reduce residual gases and thus to minimize unintended EBID of molecules from the residual gas

-electron induced

dep

(pump oil)

-most commercial SEMs are housed in HV

-defined form
-ultimative size

Goals

Chemical Composition:
-targeted material

Re
E

Processes involved: adsorption, desorption, diffusion....detailed understanding in the field of Surface Science = UHV

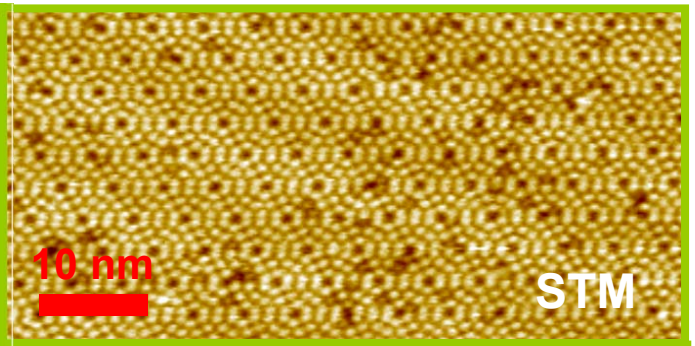
Typical metal content of HV-EBID deposits [1-3]:

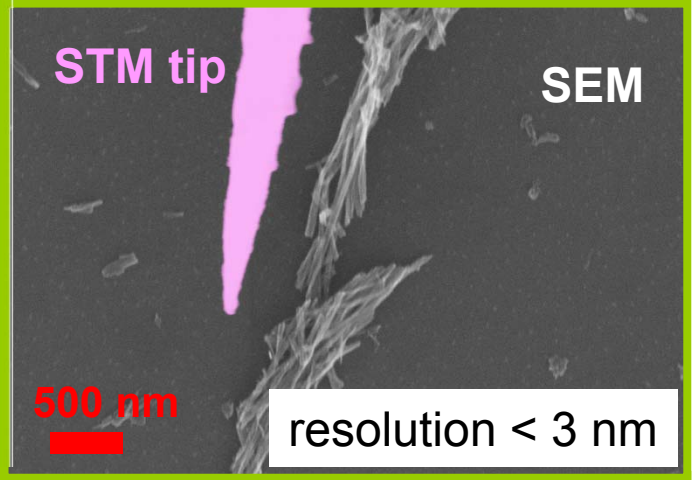
≈ 15 - 60 % metal

[1] H. W. P. Koops et. al., *J. Vac. Sci. Technol. B*, 1988, 6, p. 477; [2] Y. M. Lau et. al., *J. Vac. Sci. Technol. A*, 2002, 20, p. 1295; [3] I. Utke et al., Applied Physics Letters (2002), 80, 4792-4794. .

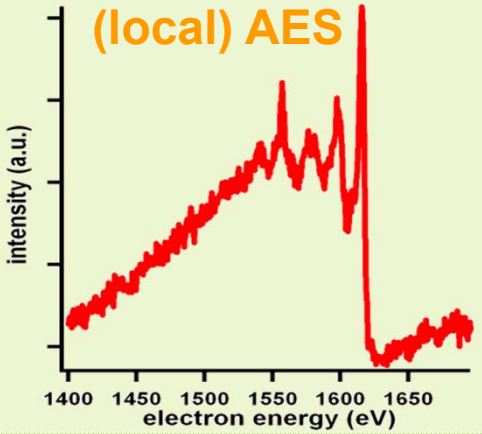
The UHV Instrument

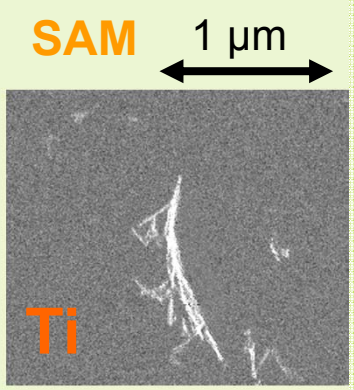
base pressure ~ $2 \cdot 10^{-10}$ mbar





resolution < 3 nm

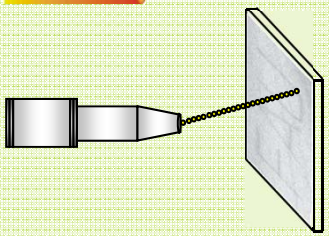




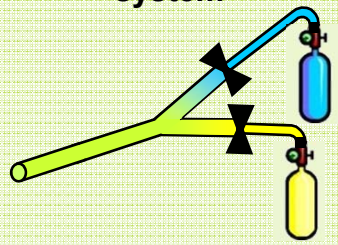
EBID specific attachments

Raith

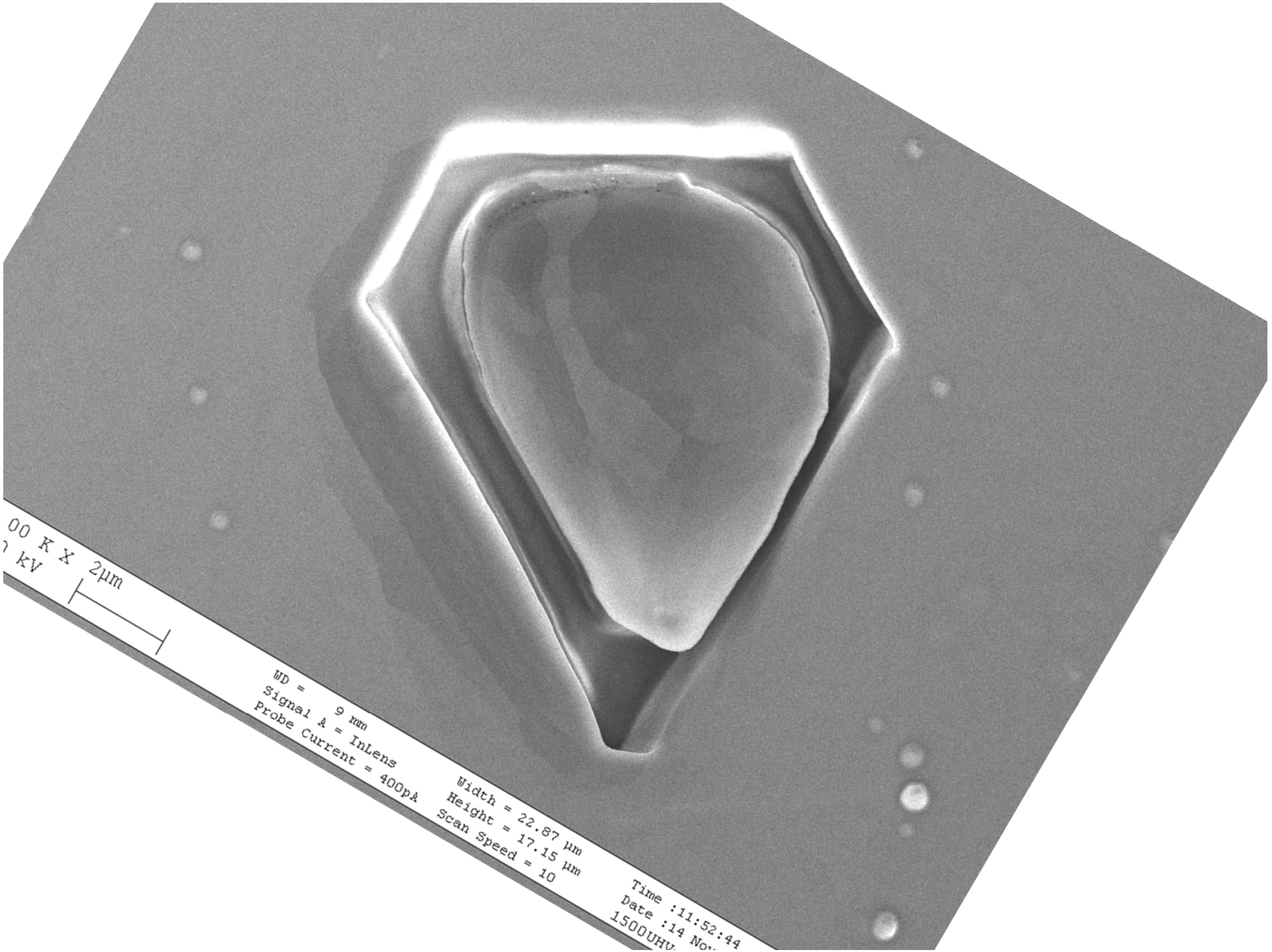
Lithographic attachment

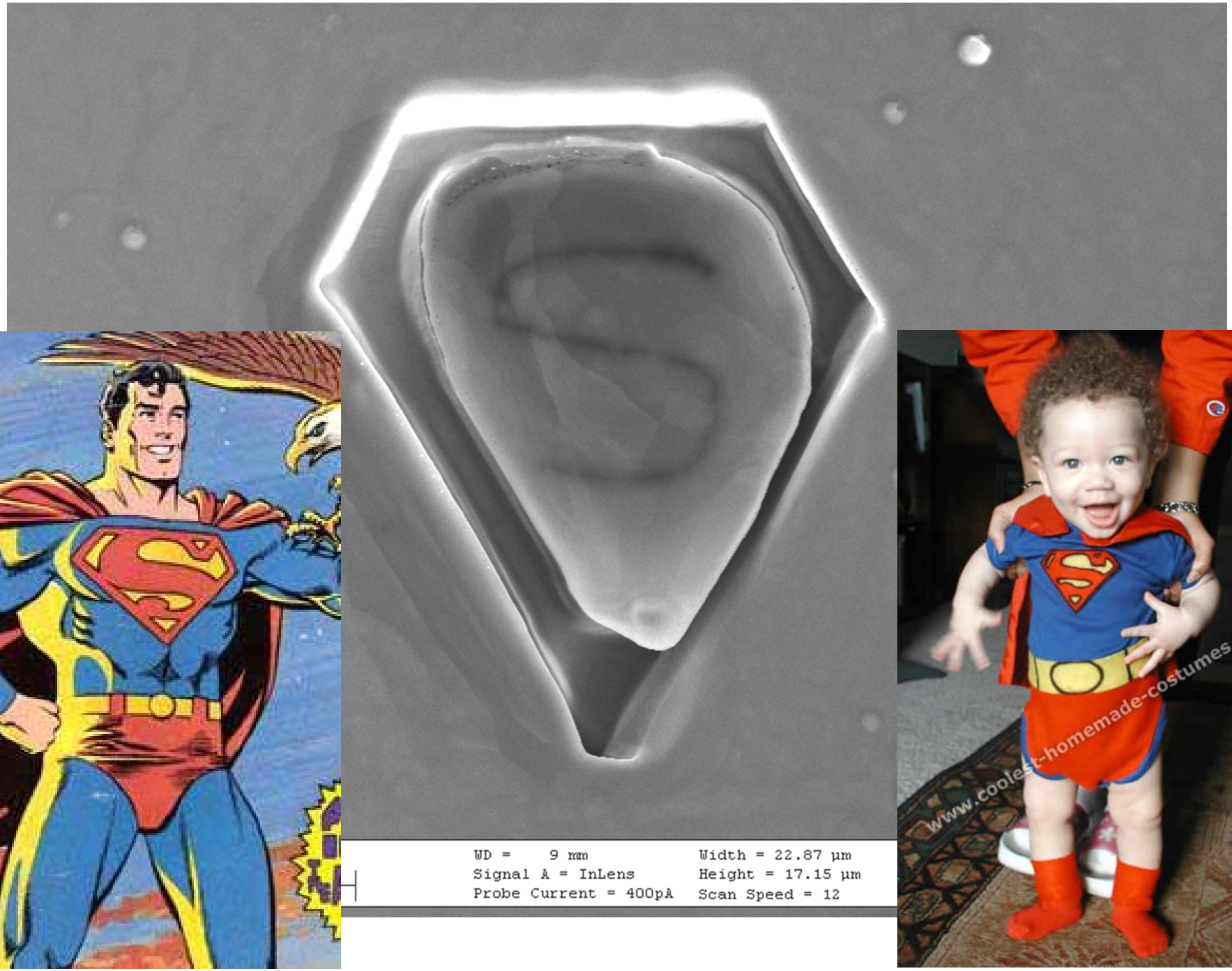


Heatable gas dosage system

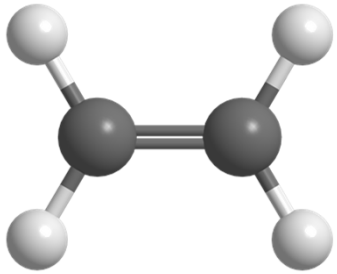


TiO_2 nanotubes supplied by Dr. Oliver Diwald, TU Wien

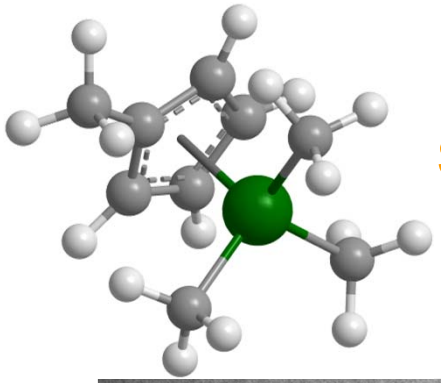

00 K X 2µm
kV
WD = 9 mm
Signal A = InLens
Probe Current = 400pA
Width = 22.87 µm
Height = 17.15 µm
Scan Speed = 10
Time :11:52:44
Date :14 Nov
1500UHV


WD = 9 mm
Signal A = InLens
Probe Current = 400pA
Width = 22.87 µm
Height = 17.15 µm
Scan Speed = 12
www.coolest-homemade-costumes.com

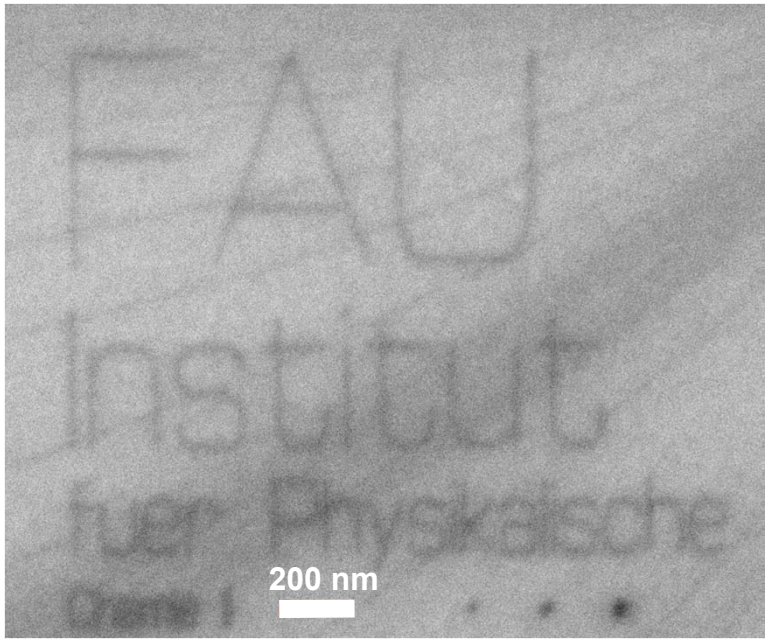
Lithographic control: EBID with different molecules



Si(111)

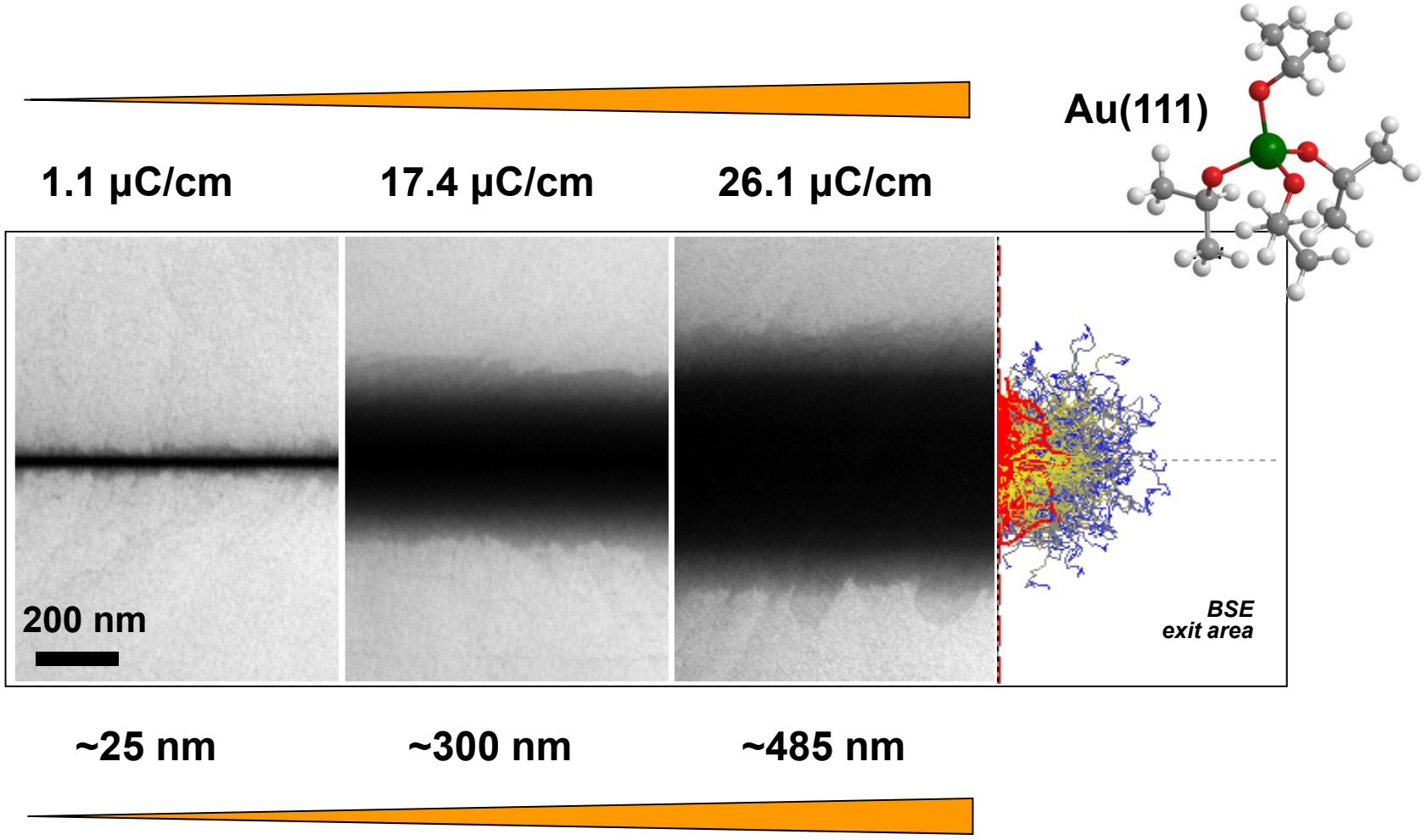


Si(111)



Line width (e.g. in F): **~ 15 nm**
≈ smallest achievable size

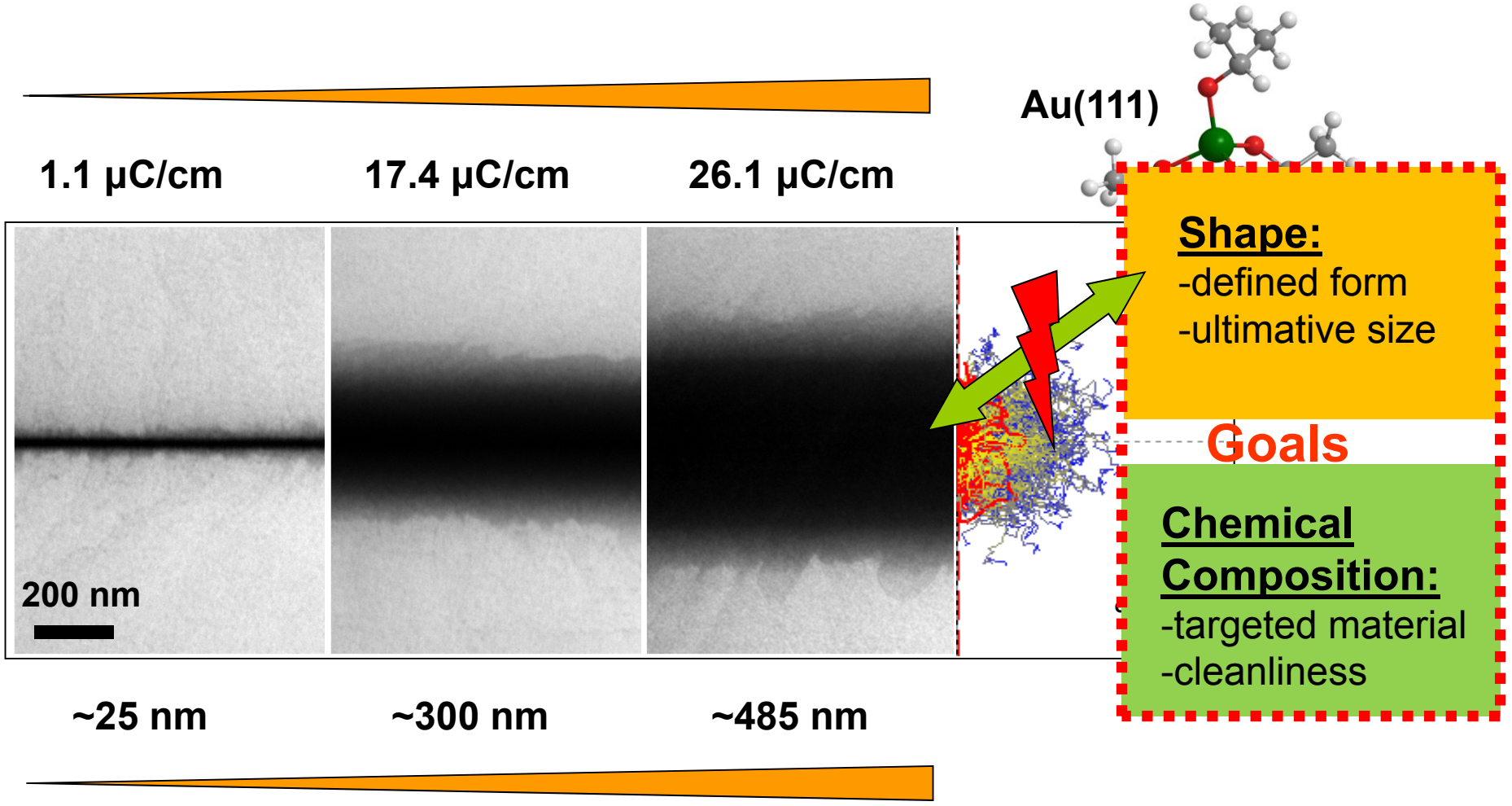
Conventional wisdom: continuous “growth“ of EBID with increasing e^- dose



Simulation with **CASINO V 2.42**

Drouin et al., Scanning (2007), 29, 92

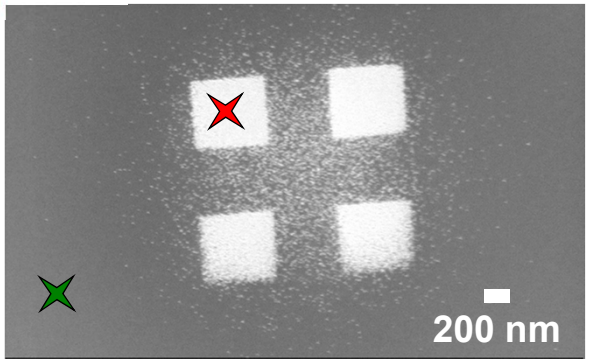
Conventional wisdom:
continuous “growth“ of EBID with increasing e^- dose



Simulation with **CASINO V 2.42**

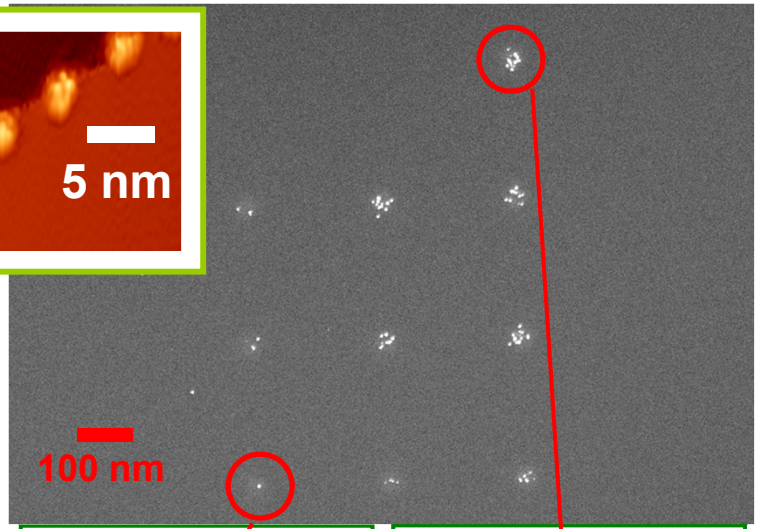
Drouin et al., Scanning (2007), 29, 92

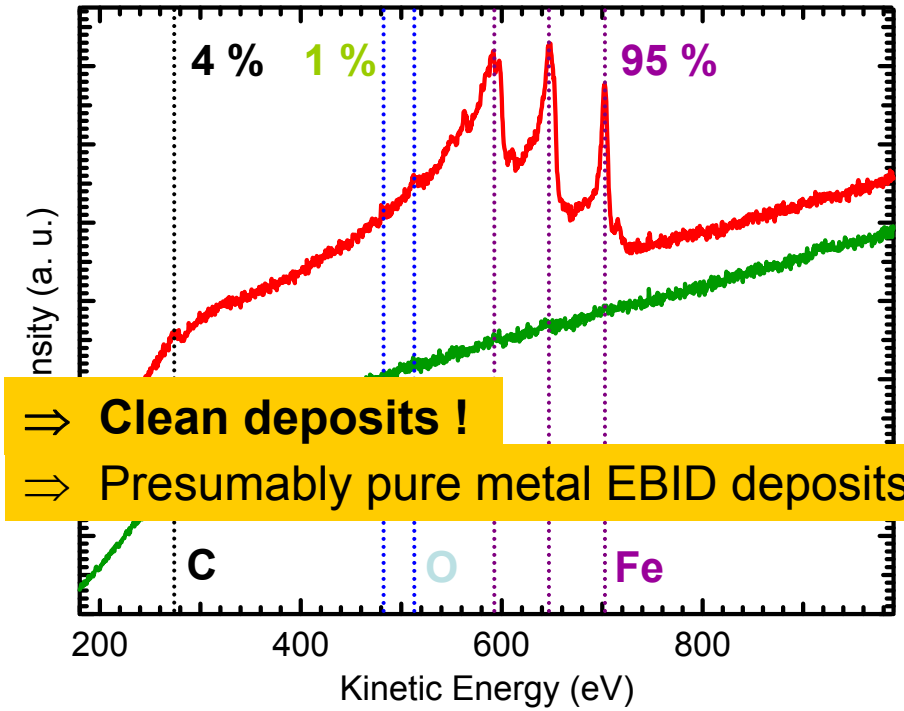
EBID with $Fe(CO)_5$ on clean Si(001)



Increasing exposure time

Increasing e



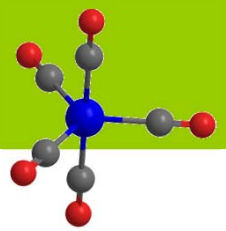


⇒ **Clean deposits !**

⇒ Presumably pure metal EBID deposits

slope of ~1 dot per 0.09 nAs after **offset**

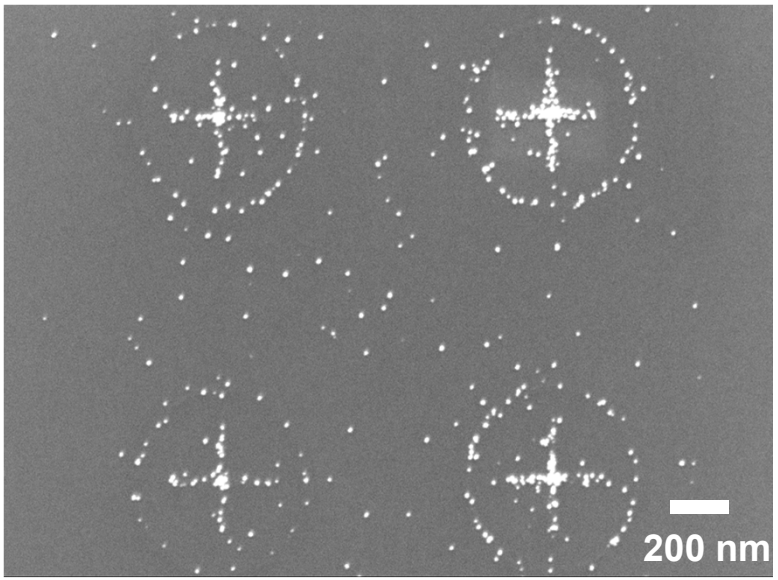
T. Lukasczyk, M. Schirmer, H.-P. Steinrück, H. Marbach, **small 2008,** *4,* No. 6, 841–846



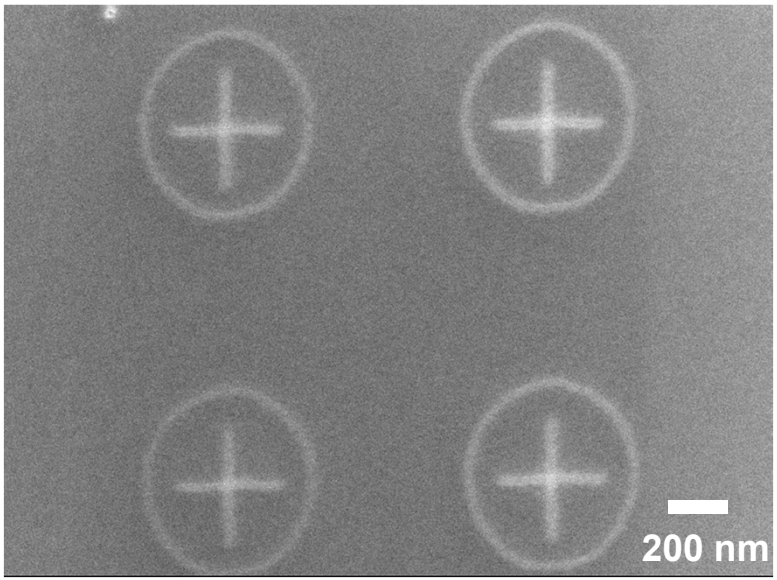
EBID with $Fe(CO)_5$ on clean Si(001)

EBID on a Si(001) sample

at room temperature



EBID at **200 K,** imaging at RT

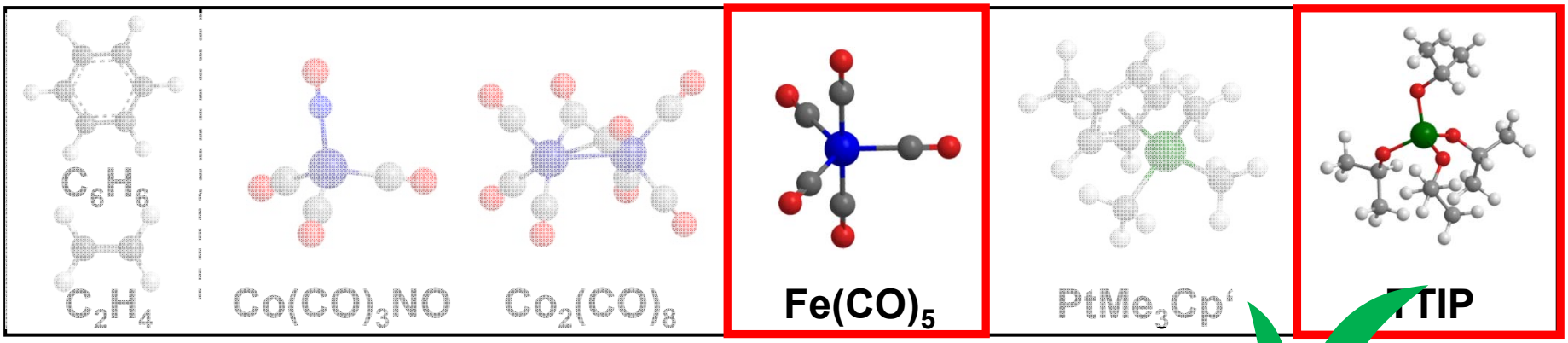


Fabrication of **continuous structures** on a clean Si(001) surface at 200 K

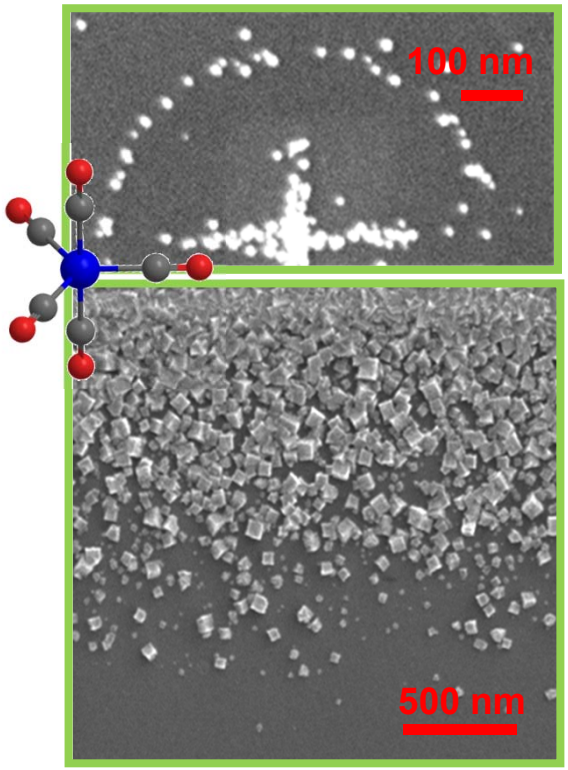
Slightly lower purity of the EBID structures at 200 K

T. Lukasczyk, M. Schirmer, H.-P. Steinrück, H. Marbach, **small 2008,** *4,* No. 6, 841–846

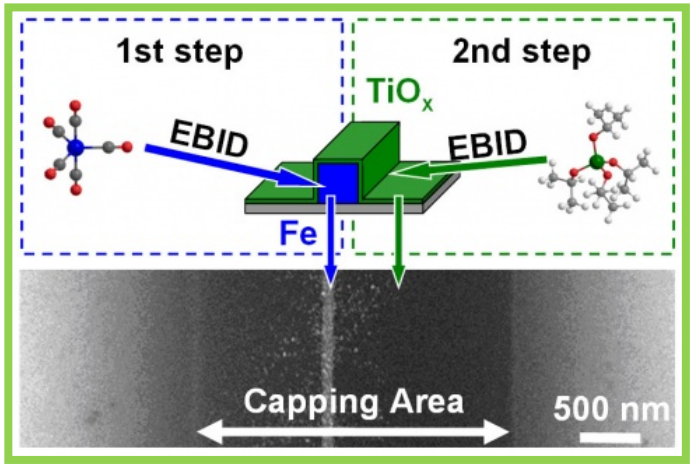
Precursor molecules for FEBIP in our project so far

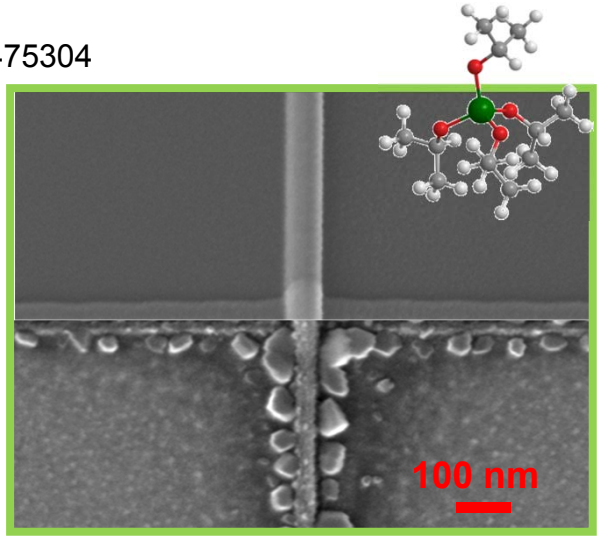


Clean deposits in UHV



M. Schirmer et al., ***Nanotechnology***, 22 (2011) 475304





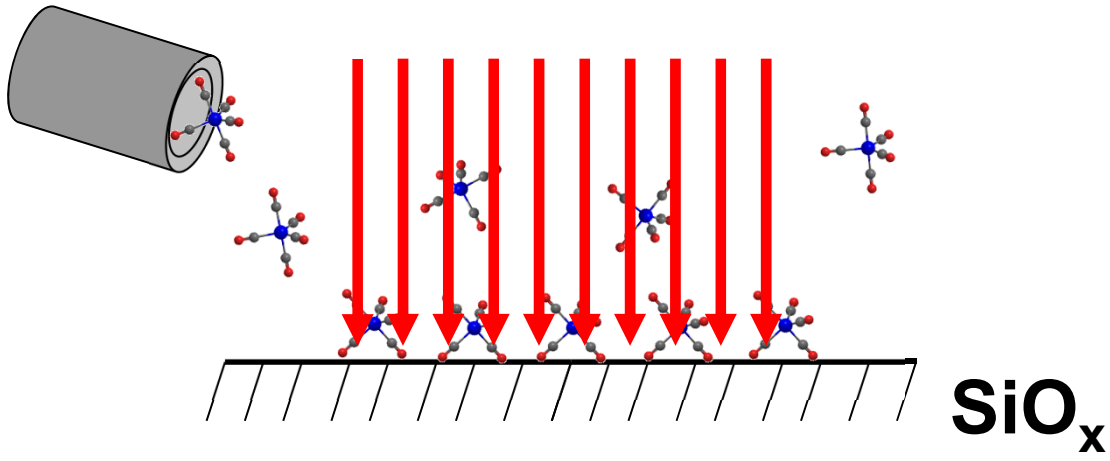
T. T. Lukaschzyk et al.,***Small***, 4 (2008) 841
T. Lukaschzyk et al.,***Langmuir***, 25 (2009) 11930
F. Porrati et al., ***J. Phys. D***, 44 (2011) 425001

M. Schirmer et al., ***Nanotechnology***, 22 (2011) 085301

Separation of irradiation and precursor dosage

Step 1: Irradiate clean surface

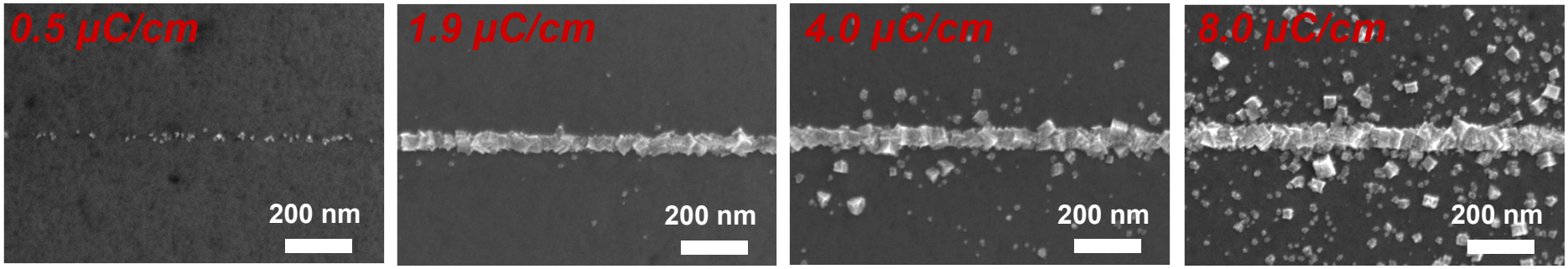
Step 2: Dose $Fe(CO)_5$ for few hours at $p=3x10^{-7}$ mbar

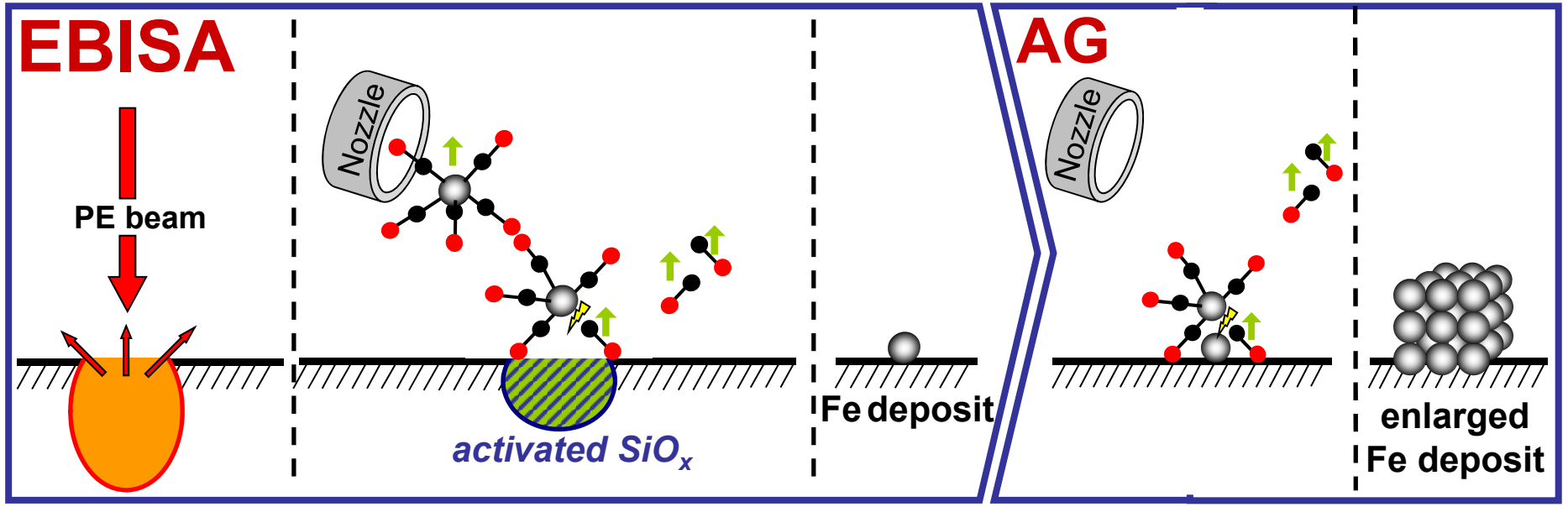


Irradiation without precursor dosage as a seed for structure growth?

Electron beam induced surface activation (EBISA)

Irradiation of SiO_x without precursor dosage + autocatalytic growth (4h 30min)

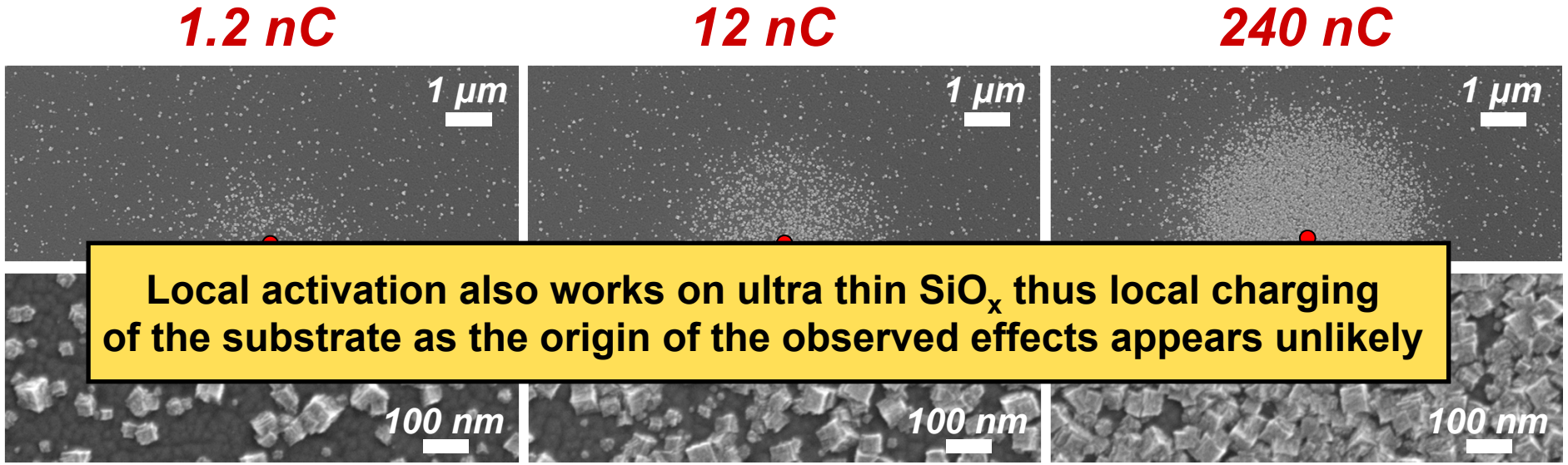




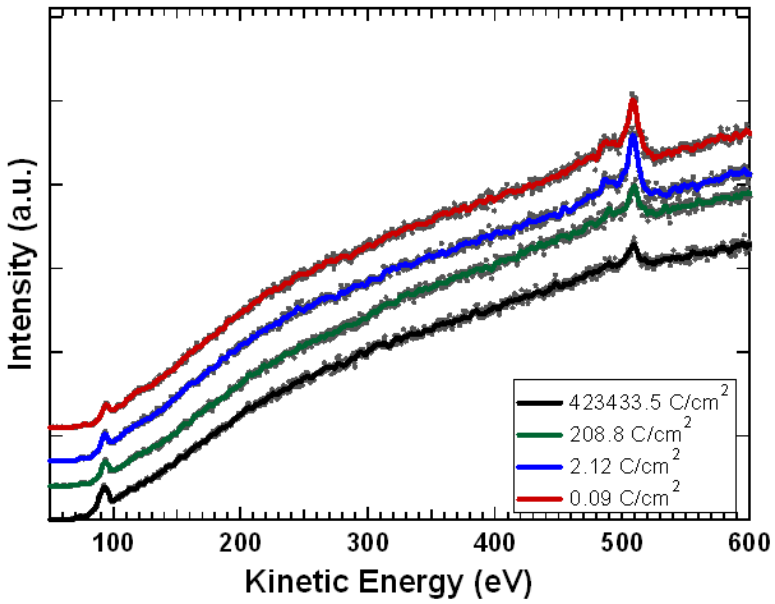
Local electron induced activation of the surface!
Reduction of proximity effects proposed!

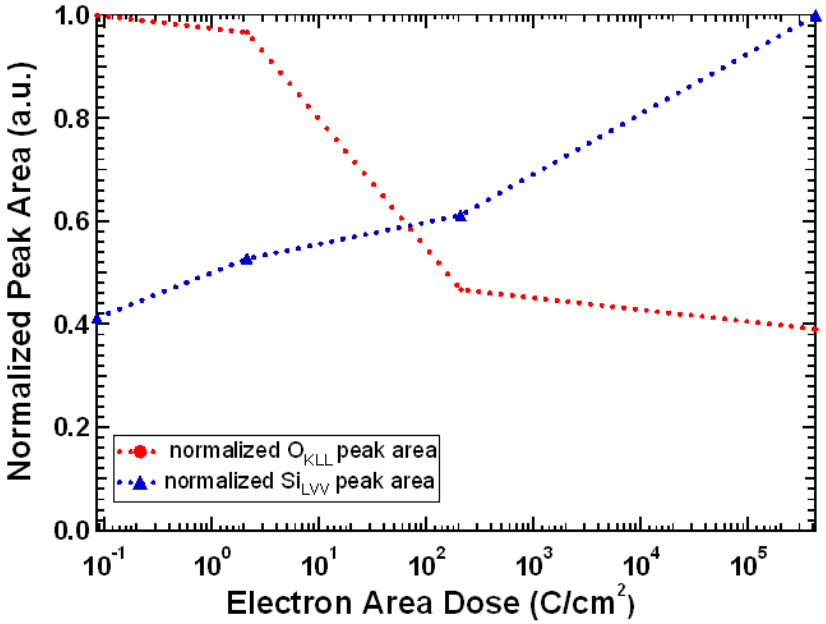
M.-M. Walz, M. Schirmer, F. Vollnhals, T. Lukasczyk, H.-P. Steinrück, H. Marbach, ***Angew. Chem. Int. Ed.***, 49 (2010) 4669.

Does charging account for the catalytic activation?



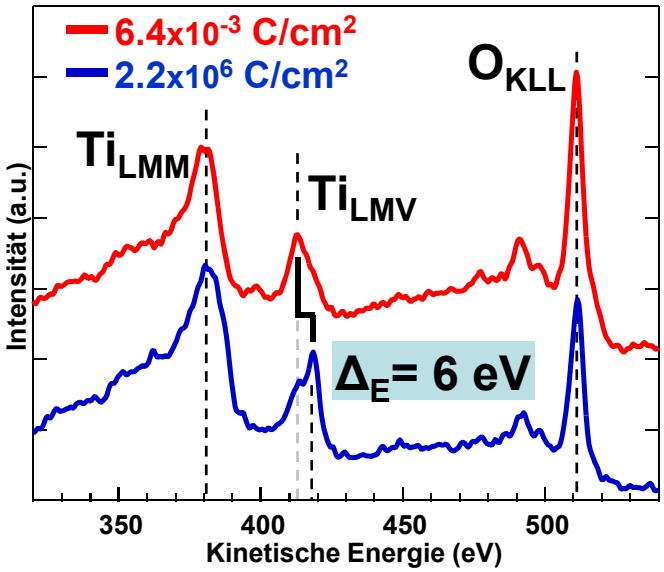
Local activation also works on ultra thin SiO_x thus local charging of the substrate as the origin of the observed effects appears unlikely

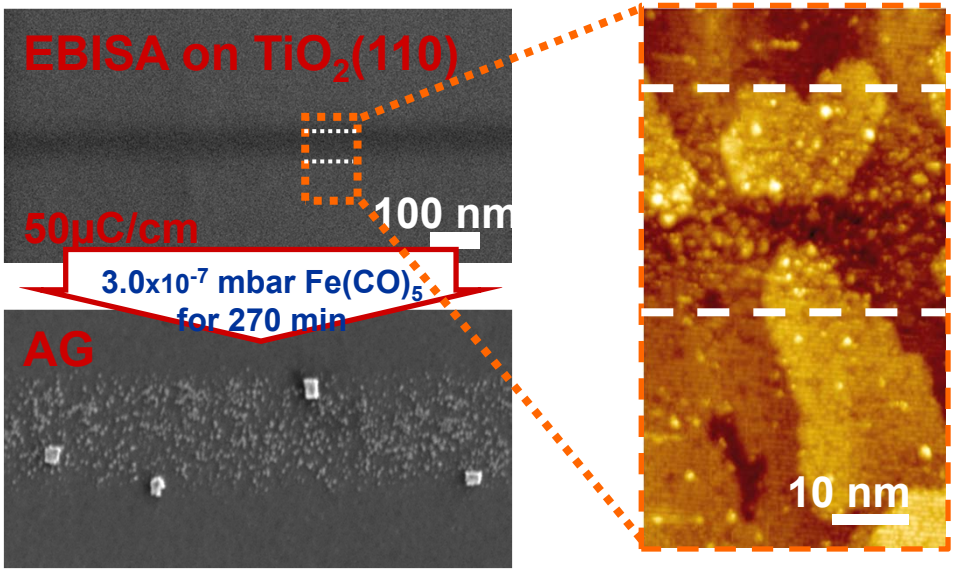




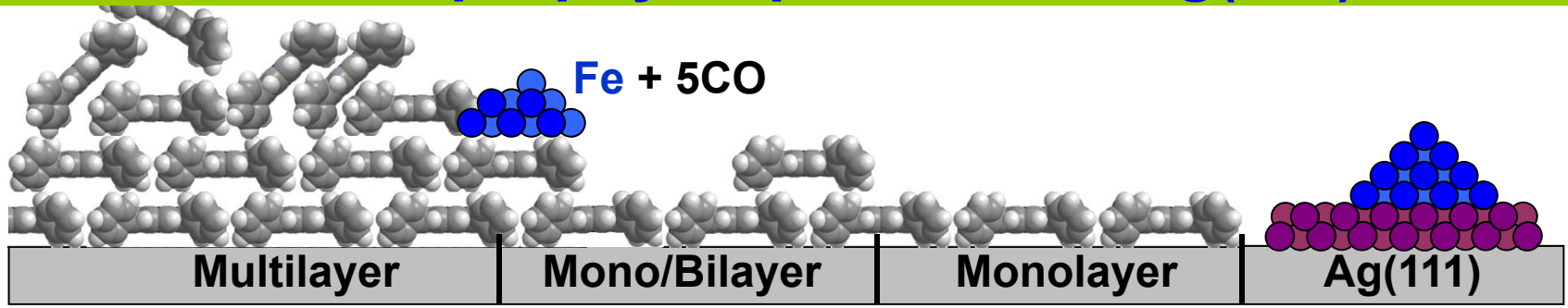
M.-M. Walz, F. Vollnhals, M. Schirmer, H.-P. Steinrück and H. Marbach, PCCP, 13 (2011) 17333

Activation also works on TiO_2…..

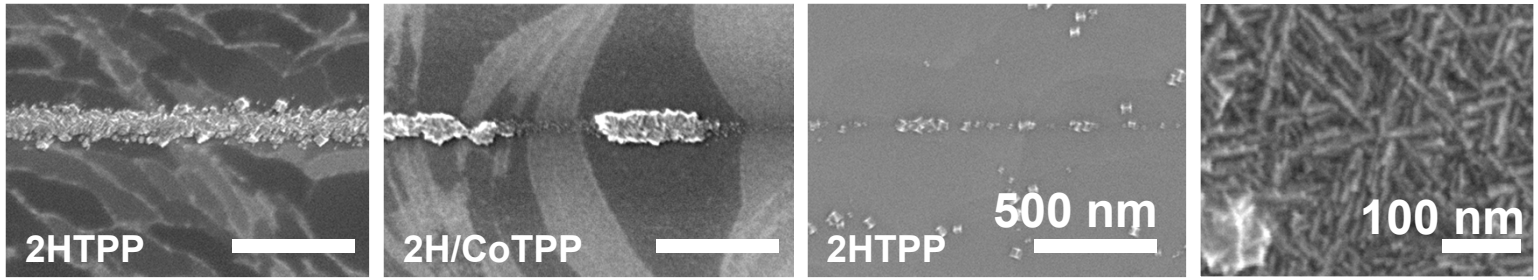




…and on porphyrin precovered Ag(111)

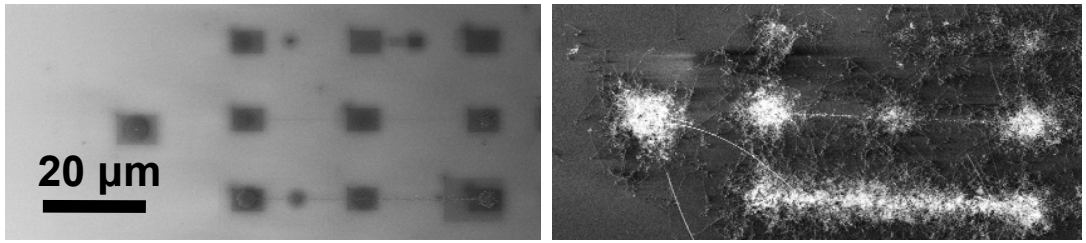


EBID
8µC/cm
~4h gas

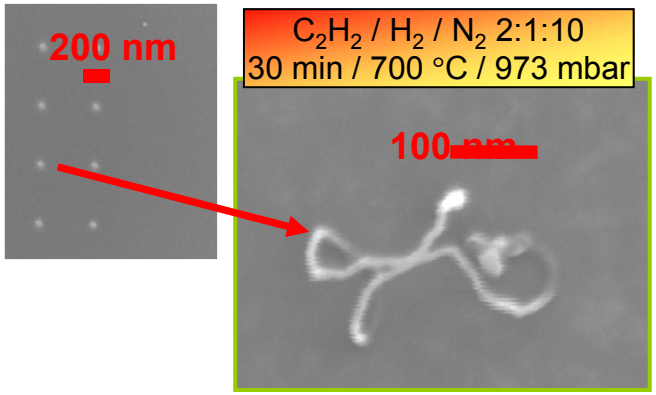


Potential application examples for iron FEBIP nanostructures

FEBIP deposits as seeds for the growth of Nanowires and -tubes

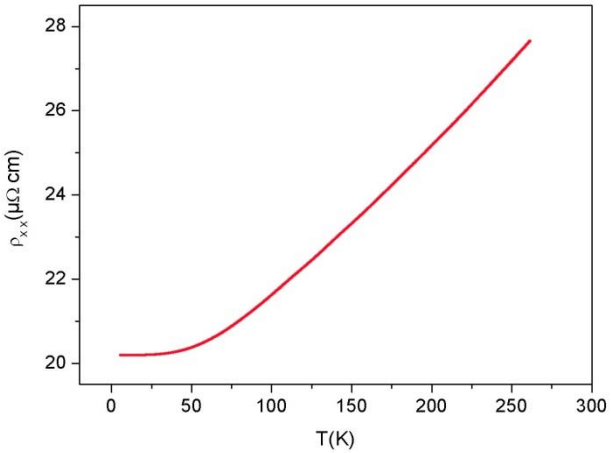


Si nanowire growth: Alois Lugstein, Vienna



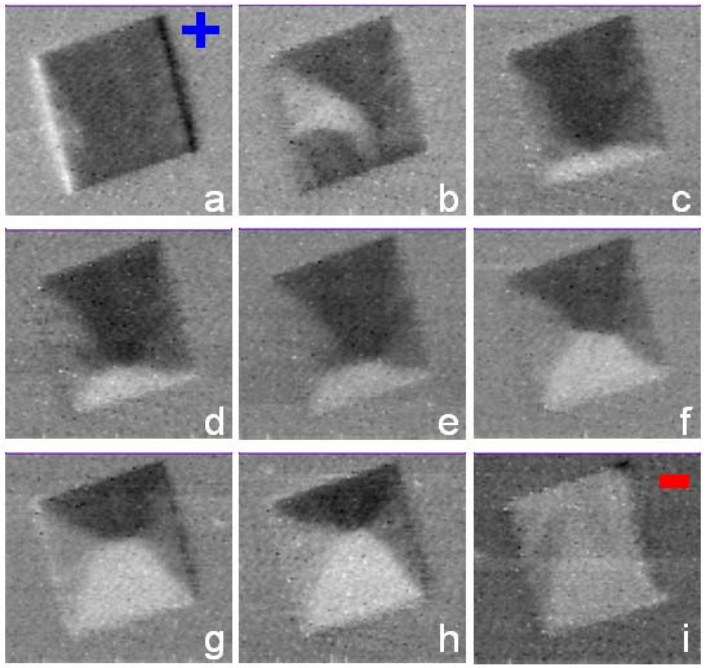
CNT growth: Nadejda Popovska, Erlangen

Exploration of electron transport and magnetic properties

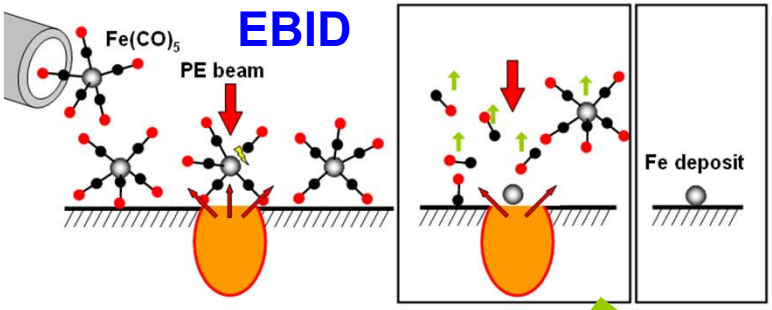


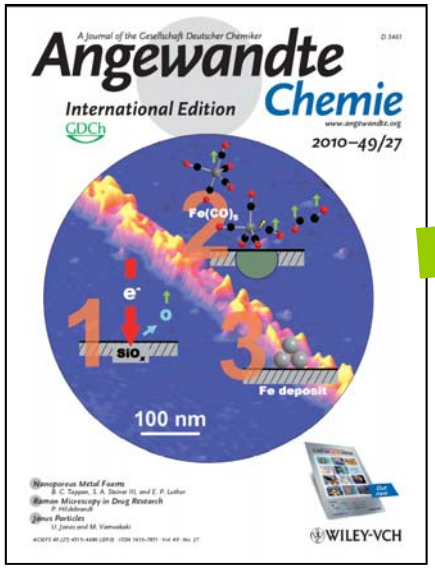
F. Porrati, R. Sachser, M.-M. Walz, F. Vollnhals, H.P. Steinrück, H. Marbach and M. Huth, ***J. Phys. D***, 44 (2011) 425001

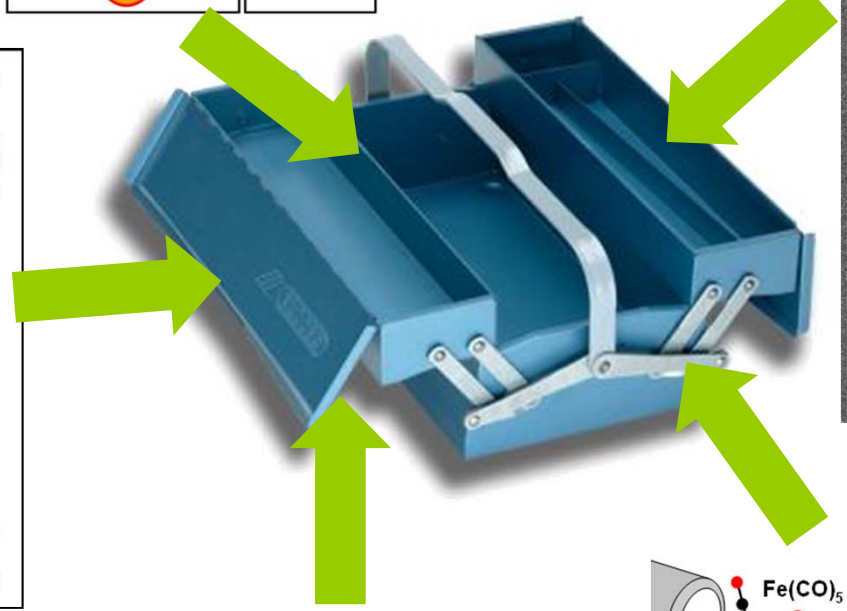
Fe deposits, STXM, XMCD contrast, SLS May 2012

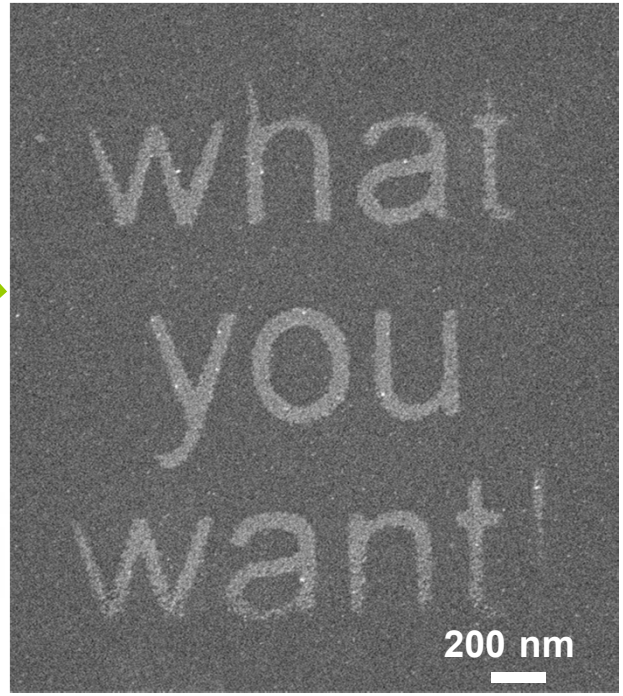


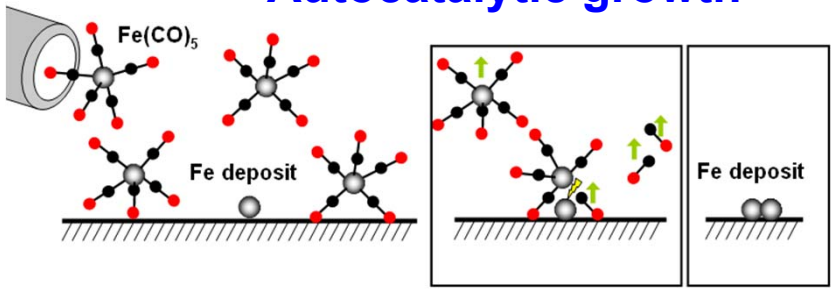
The top-down FEBIP toolbox

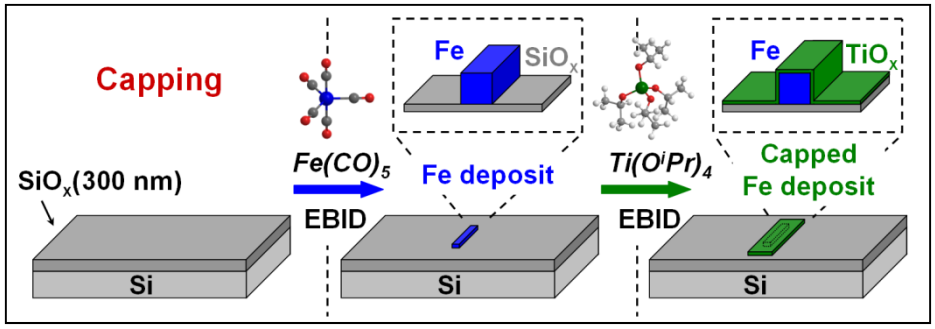






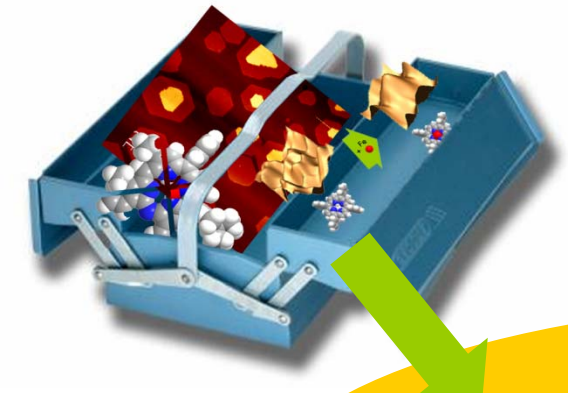






Summary and Outlook

bottom-up approach



...relies on self-assembly of large organic molecules, here porphyrins as prototype examples for functional molecules

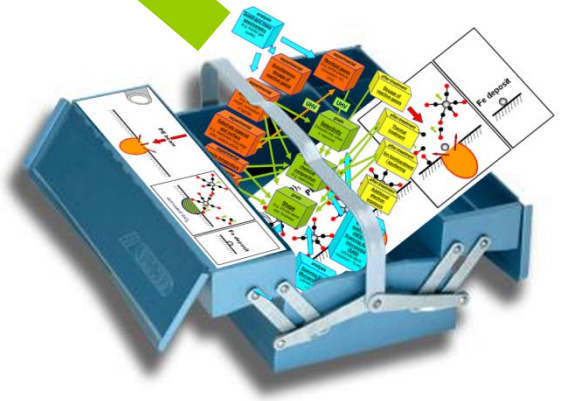
Control through:
-choice of molecule, e.g. attached peripheral ligands
-functionalization by choice of substrate
-*in situ* metalation

FEBIP Structures as template for the assembly and/or functionalization of large organic molecules

Usage of a high
locally modify the sub
to lithographically fabricate nanostructures

Control through:
-lithography
-choice of precursor molecule
- choice of substrate
-catalytic effects

op-down approach



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Veronika Schwald
Ina Kellner
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Marie-Madeleine Walz
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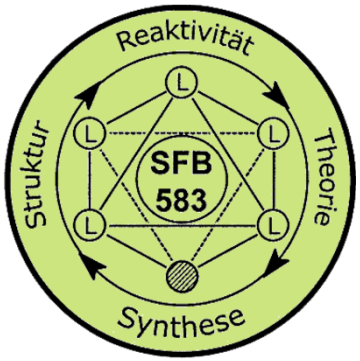

WSxM software:
www.nanotec.es

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Sonderforschungsbereich 583

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Prof. Paul Müller

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Prof. Oliver Diwald and his group

Prof. Michael Huth

Prof. Geoff Thornton

Prof. Janos Kiss

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