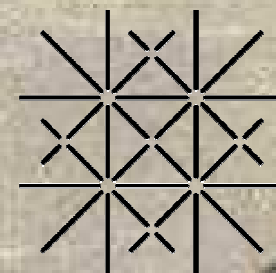
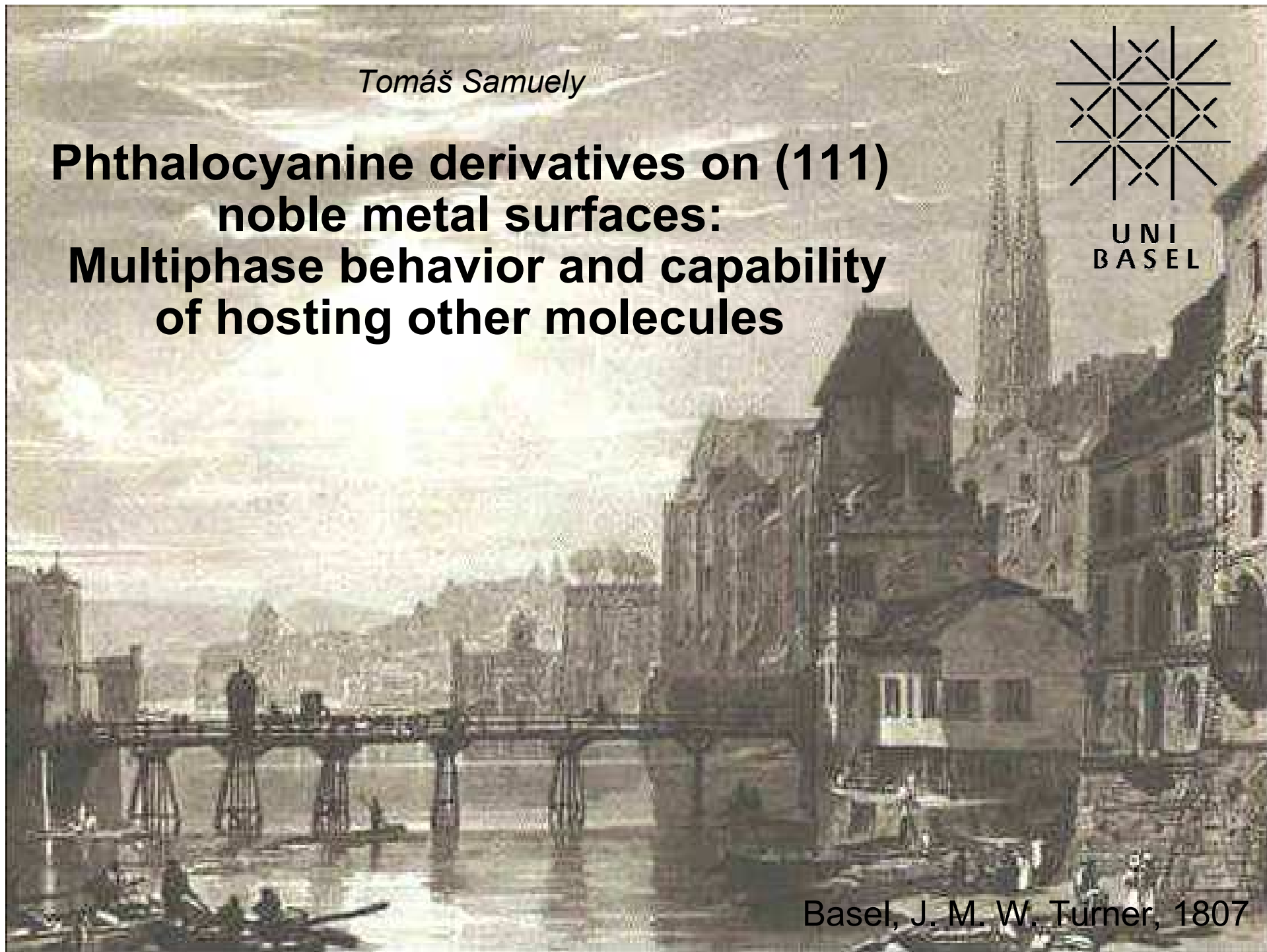


*Tomáš Samuely*

**Phthalocyanine derivatives on (111)  
noble metal surfaces:  
Multiphase behavior and capability  
of hosting other molecules**



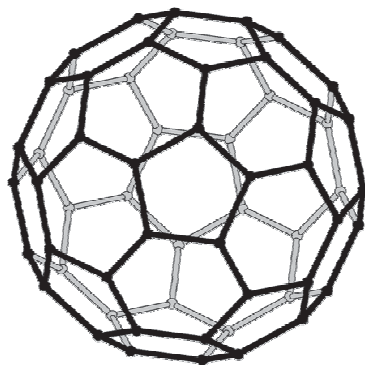
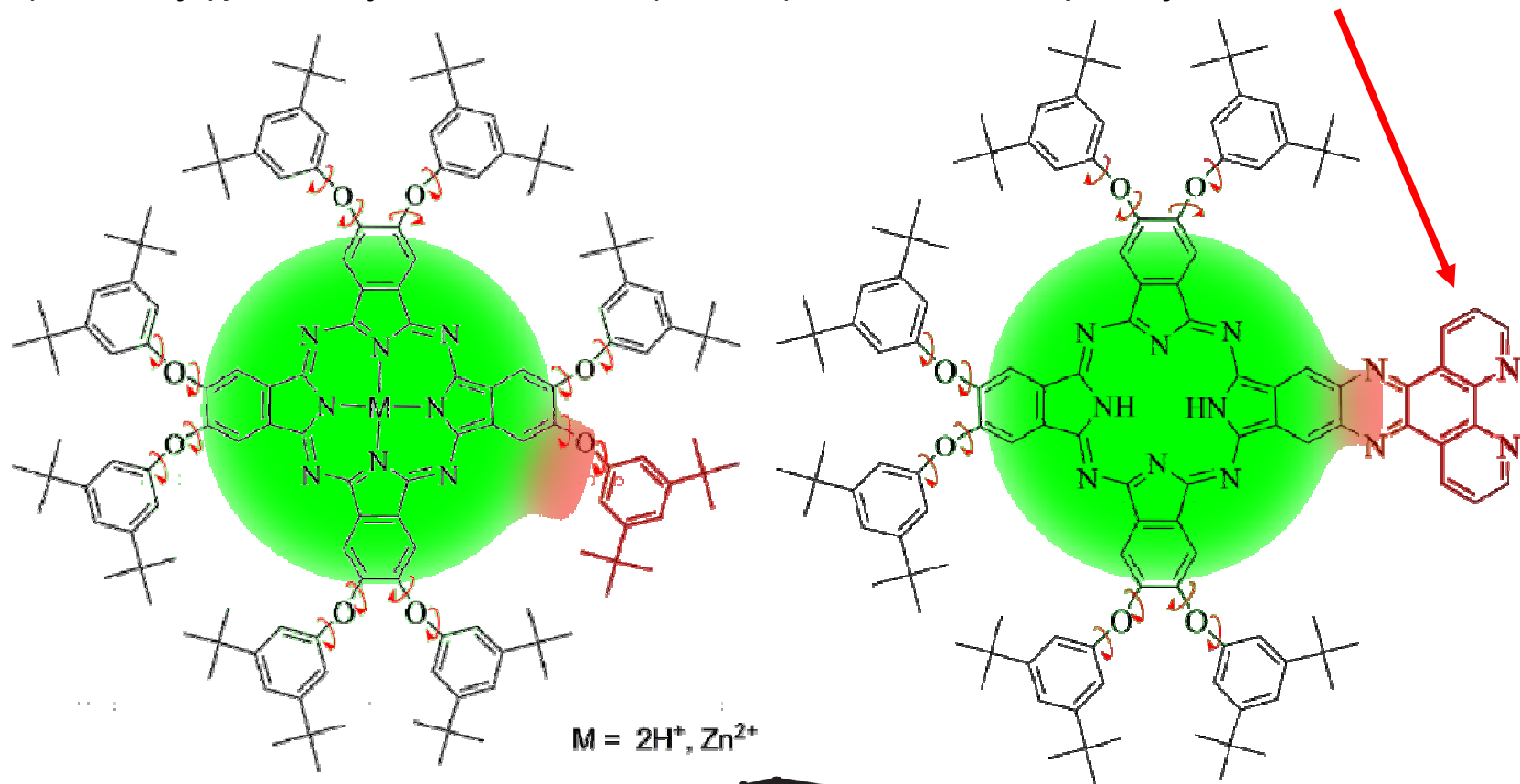
UNI  
BASEL



Basel, J. M. W. Turner, 1807

# What

8 di-(tert-butyl)phenoxy substituents (DTPO)    tetraazatriphenylene substituent (TATP)



## Why

Charge transfer complexes including phthalocyanines are widely studied for various reasons:

- they mimic porphyrins involved in processes such as photosyntheses or breathing
- they are used in solar cells due to their broad absorption range – in fact, the most efficient molecular photovoltaic device reported to date has been fabricated using a heterojunction based on copper phthalocyanine and  $C_{60}^*$ .
- possible candidates for nanoelectronic devices

\*S. Heutz et al., Sol. Energy Mater. 2004, 83, 229 & P. Peumans et al., Appl. Phys. Lett. 2001, 79, 126.

## How

- homebuilt STM + Omicron LT STM
- UHV with a base pressure of  $2 \cdot 10^{-10}$  mbar

substrate preparation:

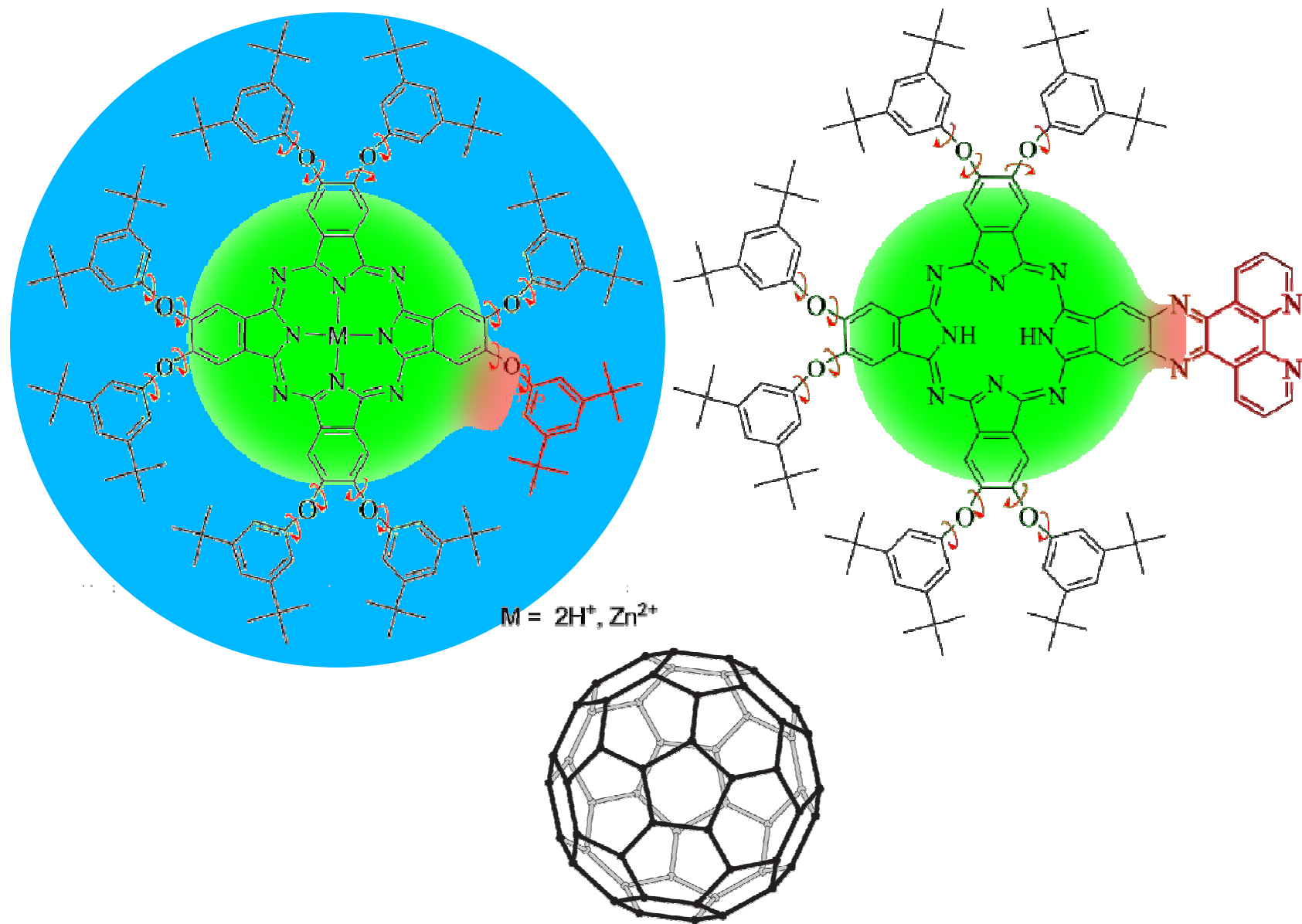
- Ag(111), Au(111) and Cu(111) single crystals were cleaned by cycles of sputtering and annealing

preparation of the molecular films:

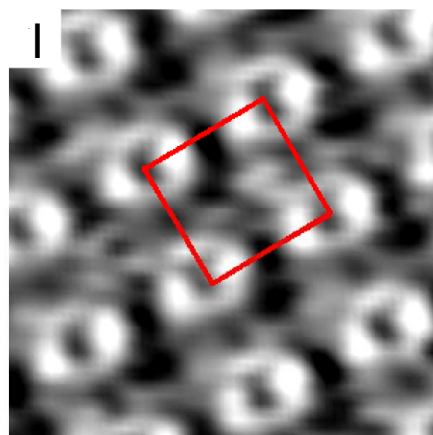
- thermal evaporation
- rate was controlled with a quartz crystal microbalance
- possibility to anneal the molecular films

• the underlying metal as well as the central atom of the Pc derivatives didn't induce any observable differences

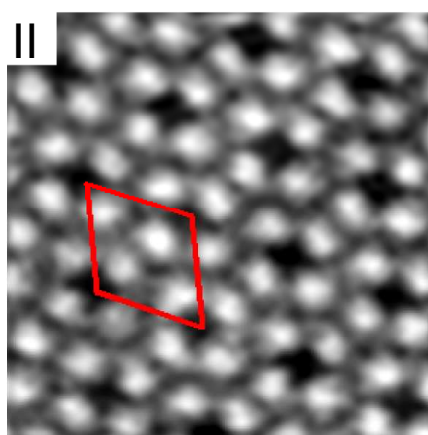
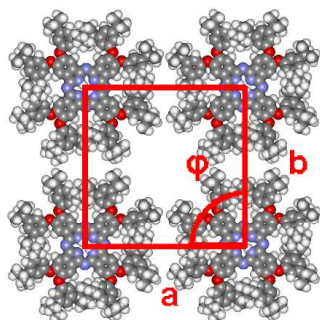
# Symmetric Pc derivative



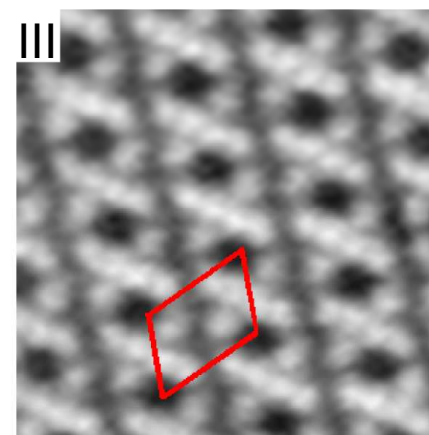
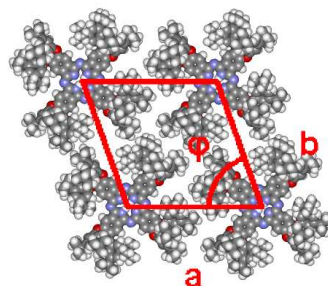
# Symmetric Pc derivative on Ag(111)



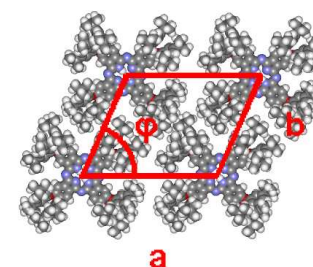
10x10nm<sup>2</sup>



10x10nm<sup>2</sup>



10x10nm<sup>2</sup>

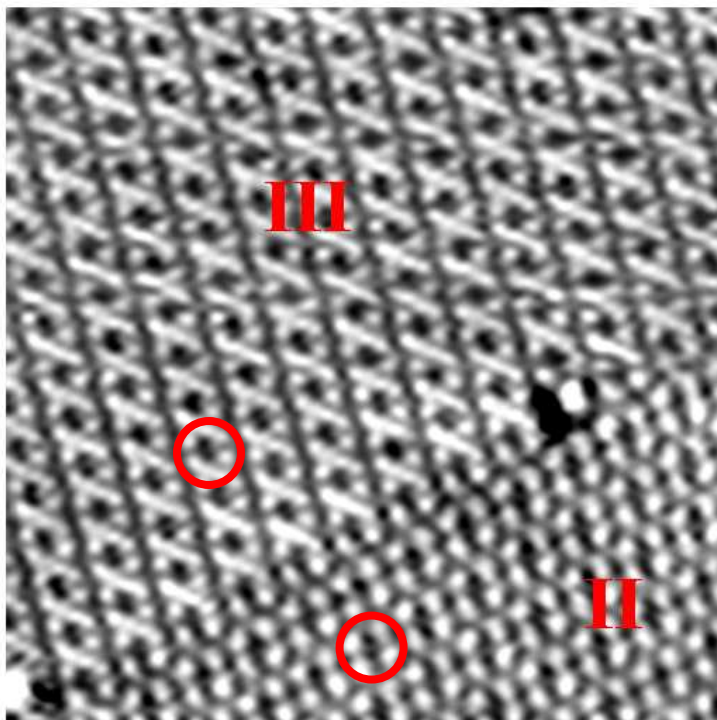


density & probability increases: dominant  $\pi$ - metal interaction



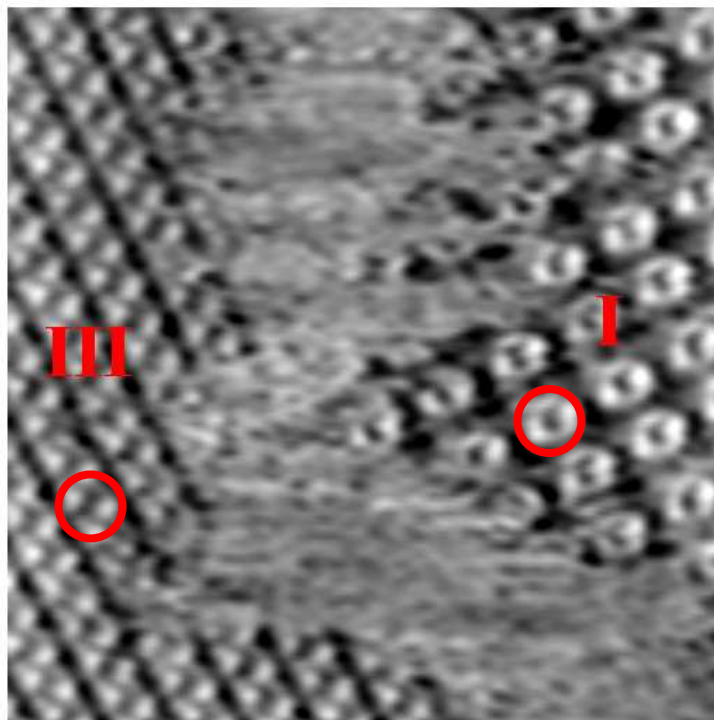
Phase	$a$ [nm]	$b$ [nm]	$\phi$ [ $^\circ$ ]	$\rho$ [molecules/nm <sup>2</sup> ]
I	$3 \pm 0.15$	$3 \pm 0.15$	$90 \pm 3$	0.11
II	$2.5 \pm 0.13$	$2.5 \pm 0.13$	$67 \pm 3$	0.17
III	$2.5 \pm 0.13$	$2 \pm 0.1$	$73 \pm 3$	0.21

# Symmetric Pc derivative



50x50nm<sup>2</sup>

H<sub>2</sub>Pc on Au(111)



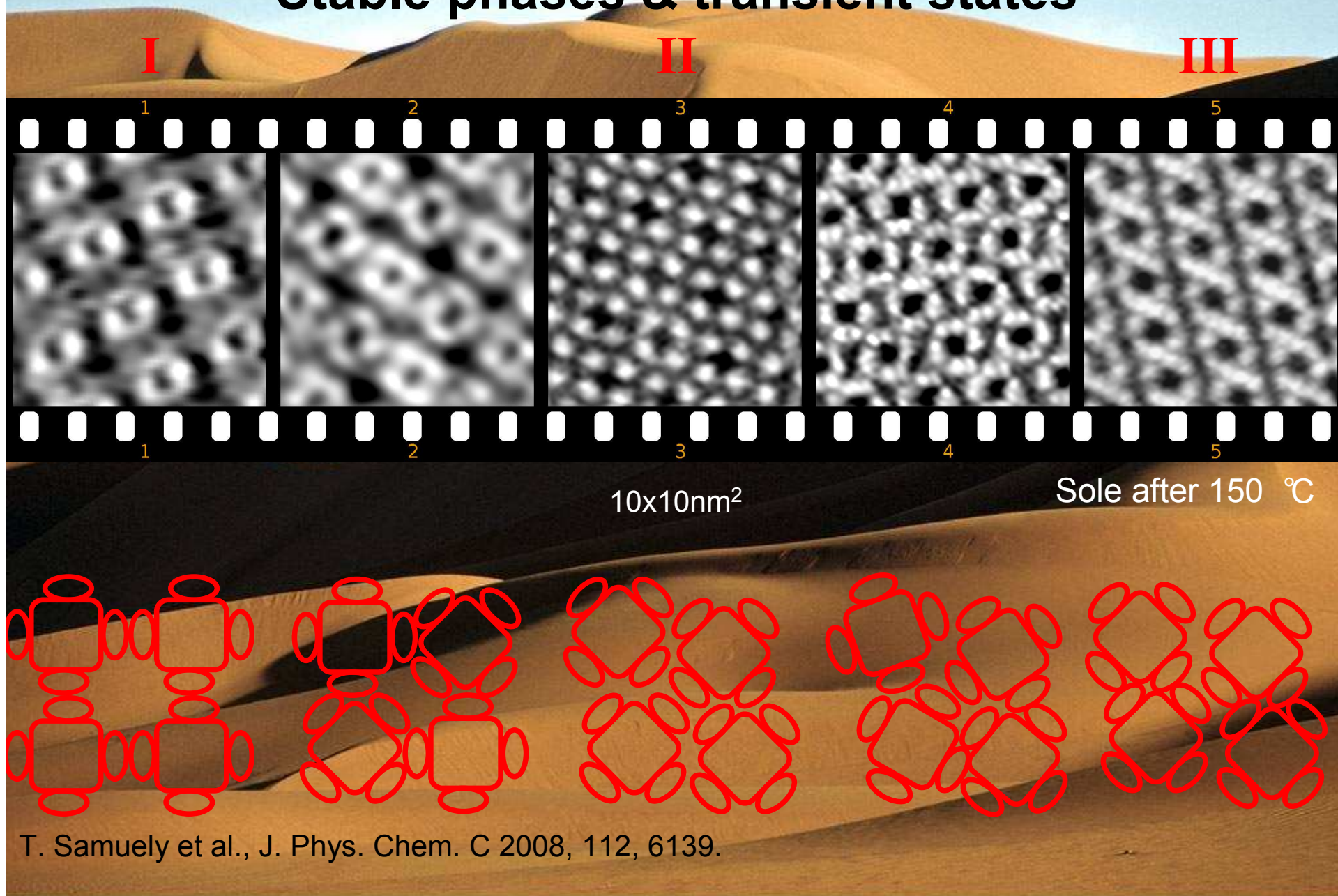
50x50nm<sup>2</sup>

H<sub>2</sub>Pc on Ag(111)

The phases coexist due to the retardation of the conformational optimization in consequence of the steric entanglement of the substituents.

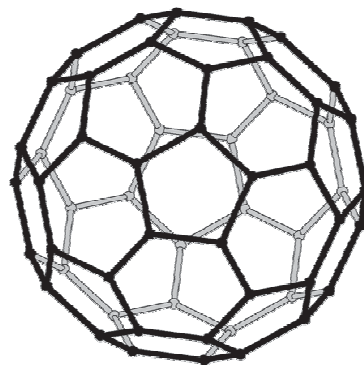
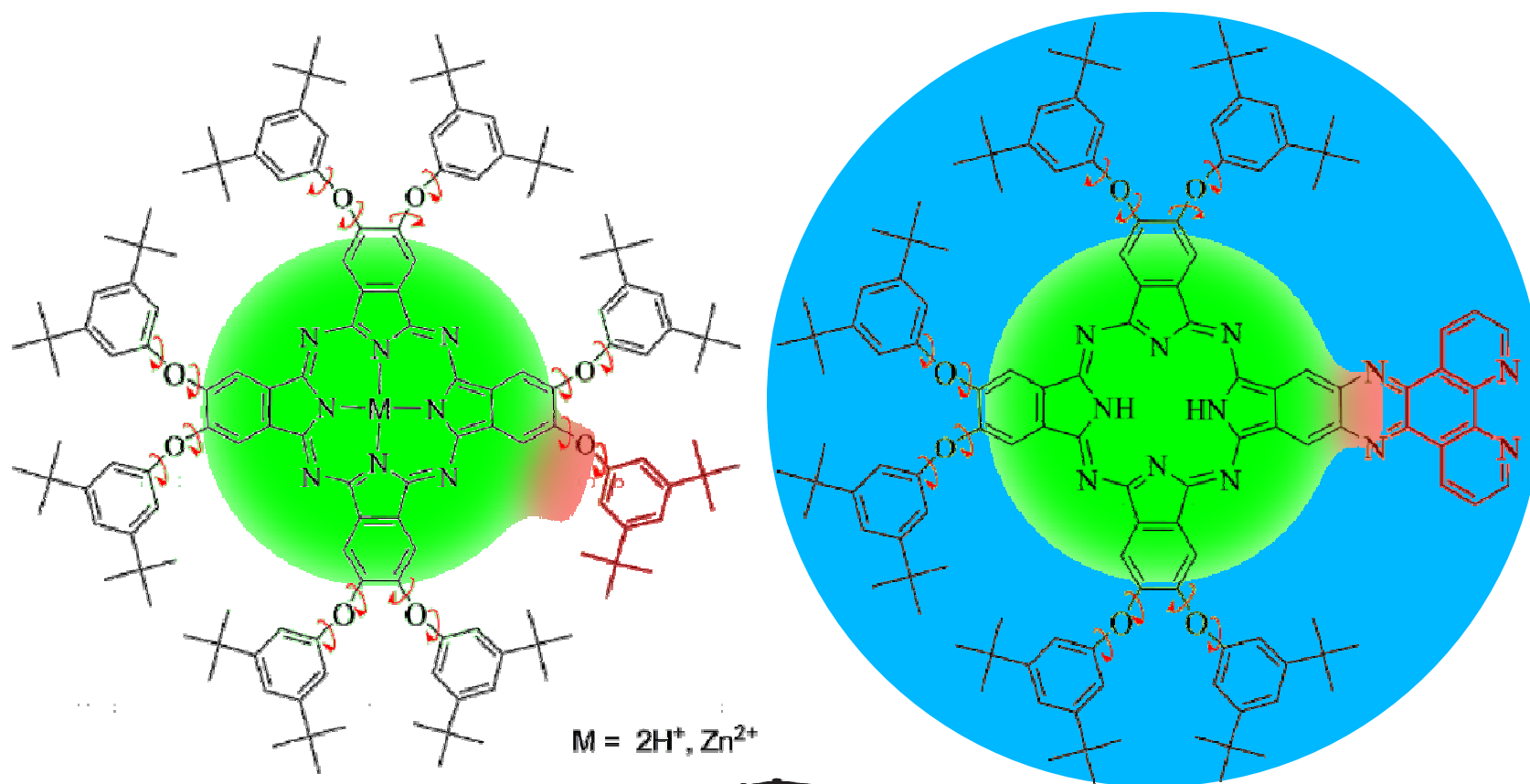
# Complex energy surface of the conformational space

## Stable phases & transient states

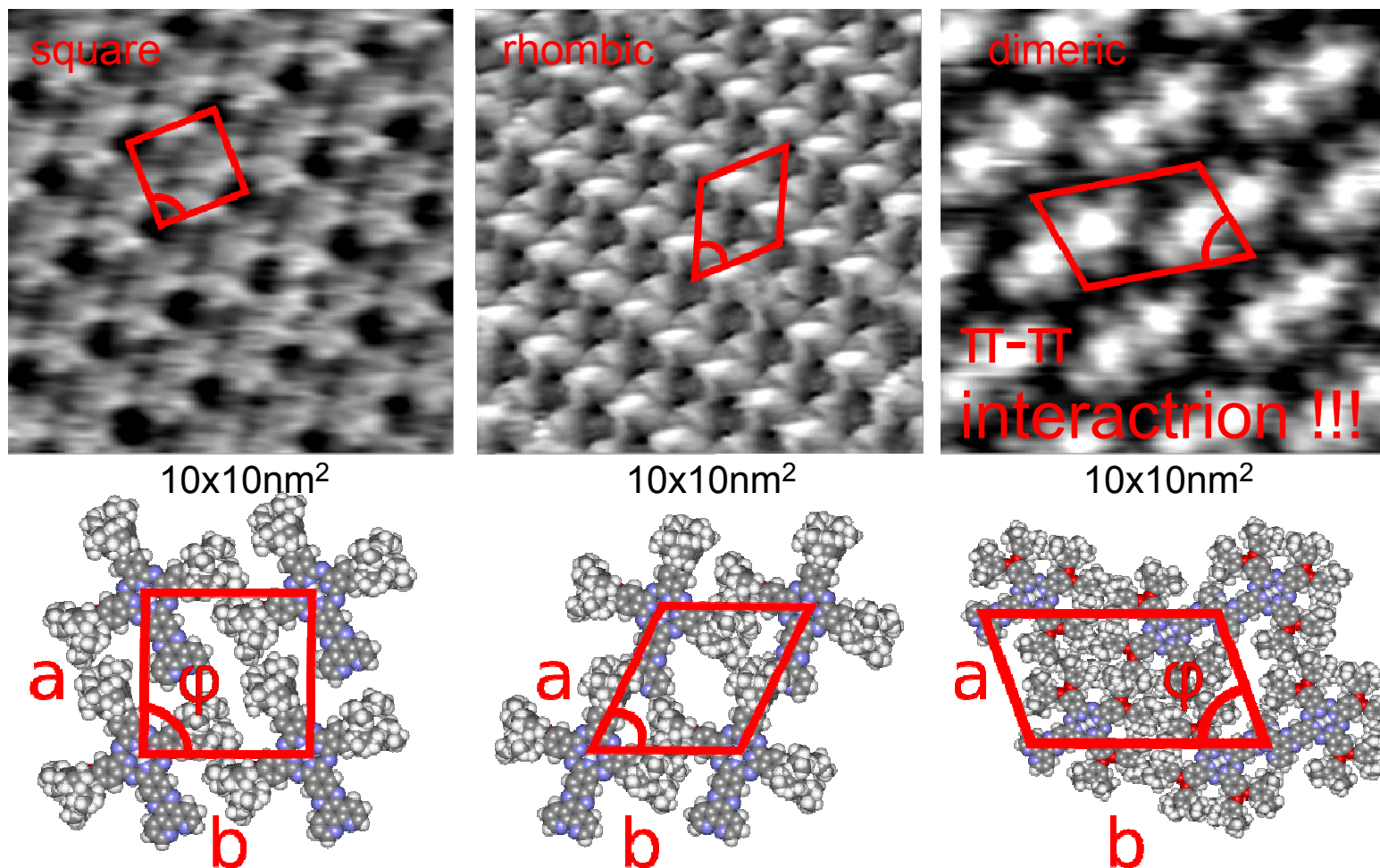




# Asymmetric Pc derivative



# Asymmetric Pc derivative on Cu(111)

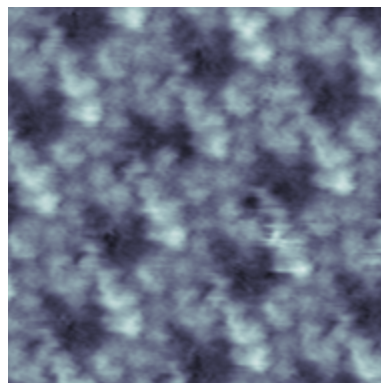


Reduced steric entanglement – higher surface density.

Phase	$a$ [nm]	$b$ [nm]	$\phi$ [ $^\circ$ ]	$\rho$ [molecules/nm <sup>2</sup> ]
square	$2 \pm 0.10$	$2 \pm 0.10$	$90 \pm 3$	0.25
rhombic	$2 \pm 0.10$	$2 \pm 0.10$	$65 \pm 3$	0.27
dimeric	$2.5 \pm 0.13$	$3.5 \pm 0.18$	$68 \pm 3$	0.25

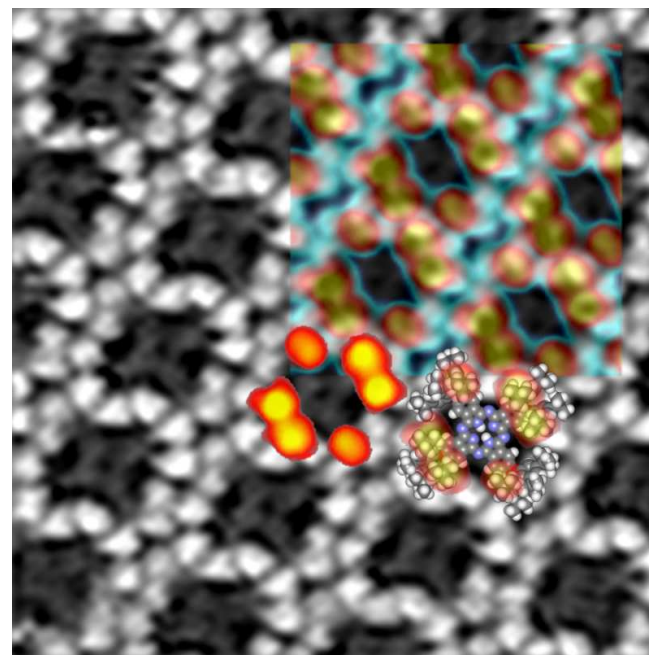
# Various imaging modes help to identify conformation

**symmetric Pc derivative**



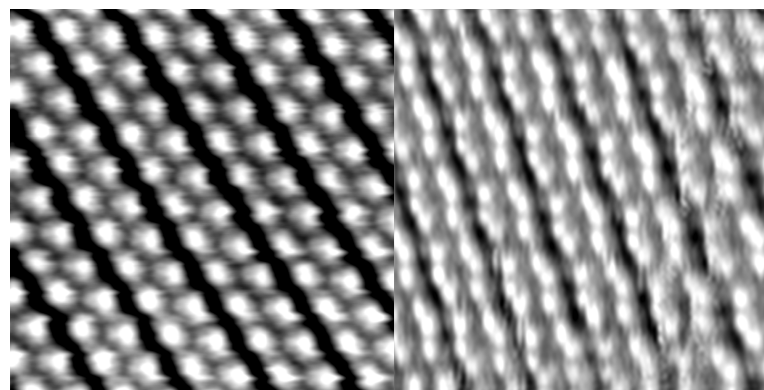
7.4x7.4nm<sup>2</sup>, 7pA

Bias voltage was  
changed from 0.7V to  
2.2V in 0.1V steps.



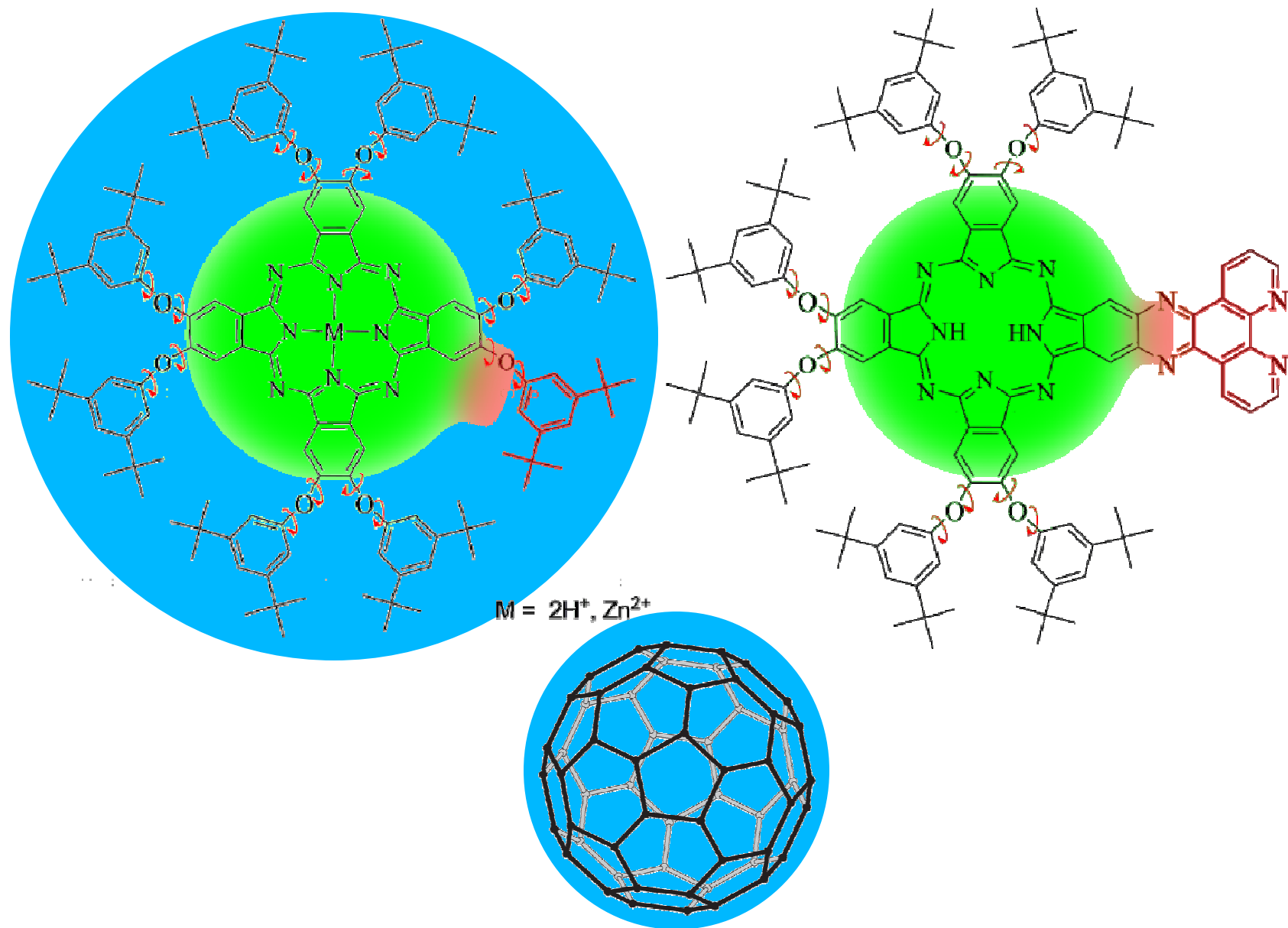
10x10nm<sup>2</sup>, 0.8V, 63pA

**asymmetric Pc derivative**

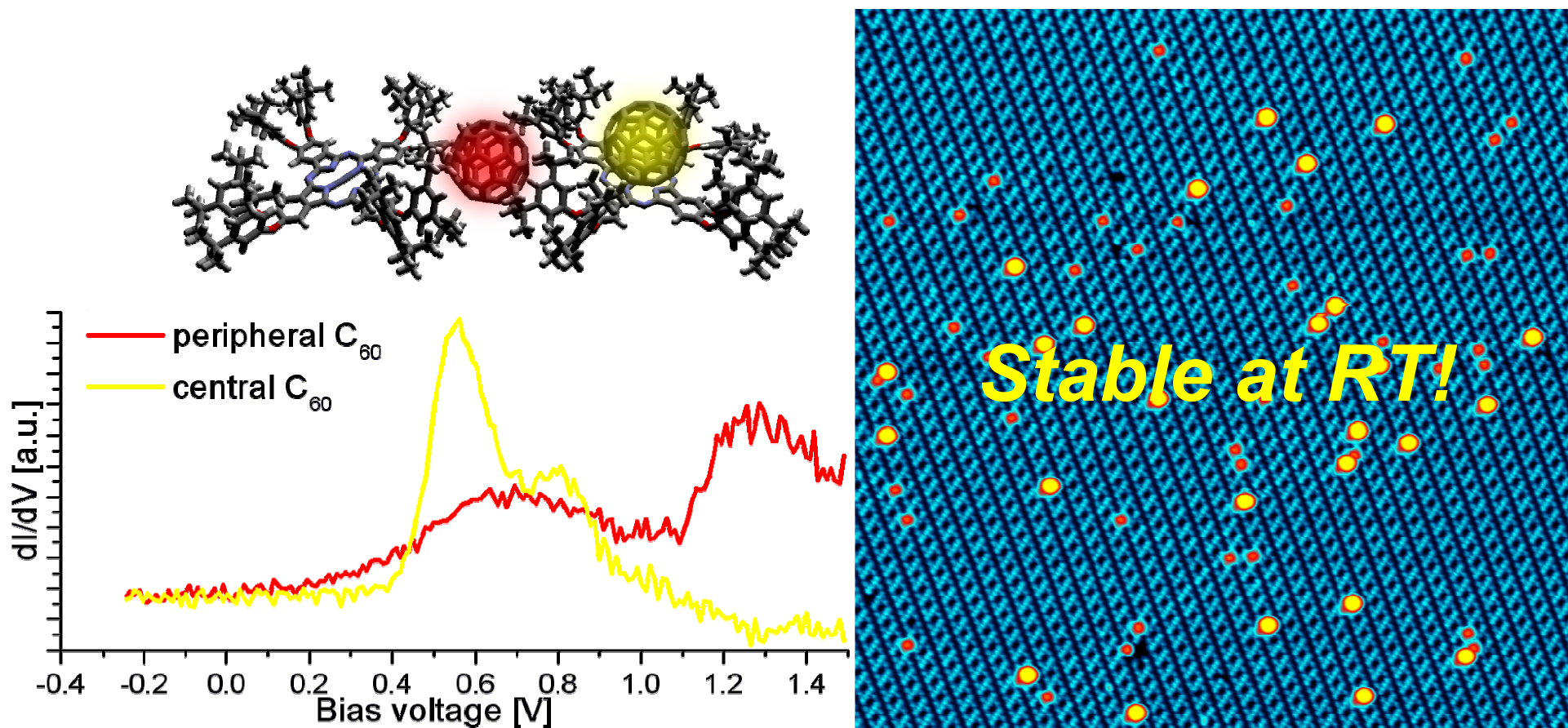


10x10nm<sup>2</sup>, 2 V, 10 pA

# $C_{60}$ on symmetric Pc derivative



# C<sub>60</sub> on symmetric Pc derivative



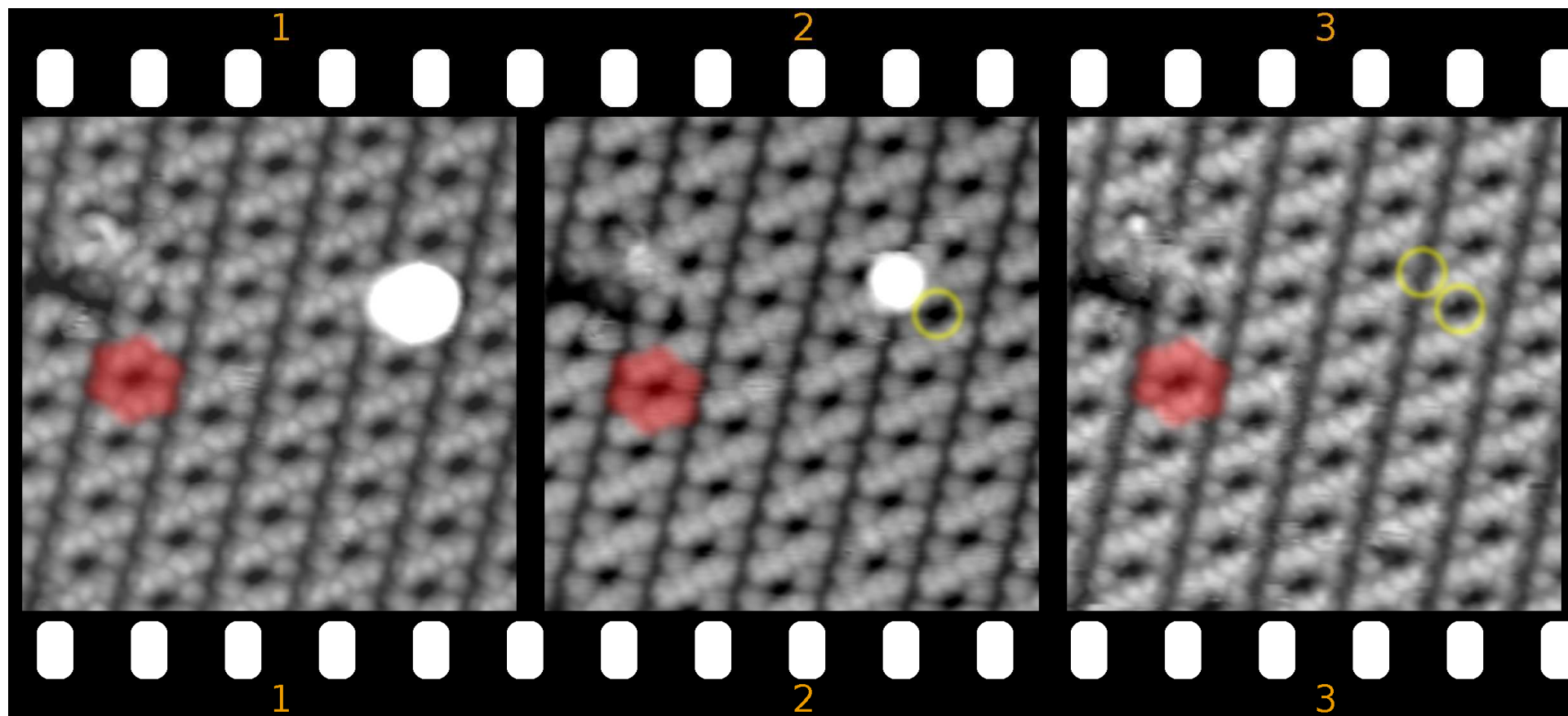
Ag(111) 80x80 nm<sup>2</sup>, 77 K

Red peaks coincide with the calculated LUMO and LUMO+1 positions of the C<sub>60</sub> on Ag(111)\* as well as the corresponding peaks of the dI/dV spectrum measured for C<sub>60</sub> on Ag(100)\*\*

\*M. De Menech et al., Phys. Rev. B 2006, 73, 155407.

\*\*X. H. Lu et al., Phys. Rev. Lett. 2003, 90, 096802.

# $C_{60}$ on symmetric Pc derivative



14x14 nm<sup>2</sup>, 77 K

After removing the C<sub>60</sub> from each of its binding sites, the underlying ordered layer of the ZnPc-DTPOs remains intact.

# Summary

Additional rotational degrees of freedom of phenoxy substituents allow:

- three different coexisting phases
- interaction of the Pc core with the metal substrate
- bowl-like shape

Their sterical entanglement allows the phases to coexist.

Rigid TATP substituent:

- reduces the sterical entanglement of adjacent phenoxy substituents
- Increases surface density
- Allows  $\pi$ - $\pi$  interaction between adjacent TATP substituents

$C_{60}$  spontaneously binds either to the Pc core or in between two symmetric Pc derivatives

Peripheral  $C_{60}$  exhibits electronic properties of  $C_{60}$  adsorbed on plain Ag(111) surface, whereas the electronic properties of the central  $C_{60}$  differ significantly.

## University of Basel:



Dr. Thomas Jung



Dr. Meike Stöhr



Dr. Jorge Lobo-Checa



Serpil Boz



Manfred  
Matena



Dr. Nikolai  
Wintjes



Mihaela  
Enache



Stefan  
Schnell

## University of Bern:



Prof. Silvio Decurtins



Dr. Shi-Xia Liu



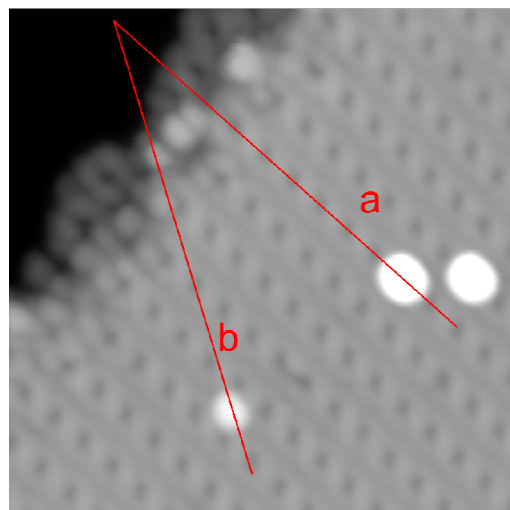
Dr. Marco Haas

STM control system by

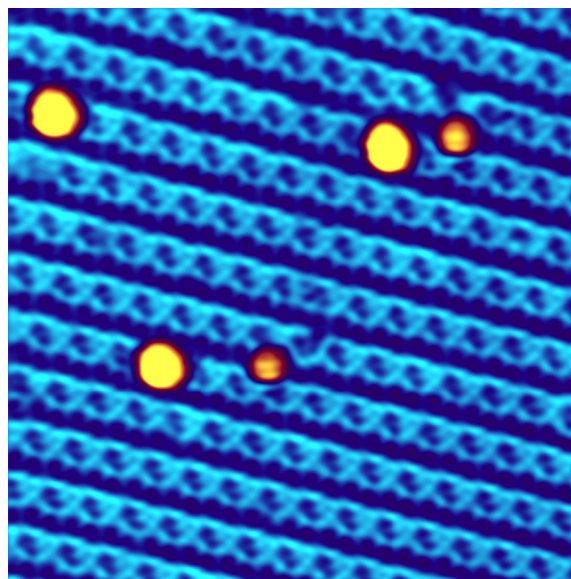
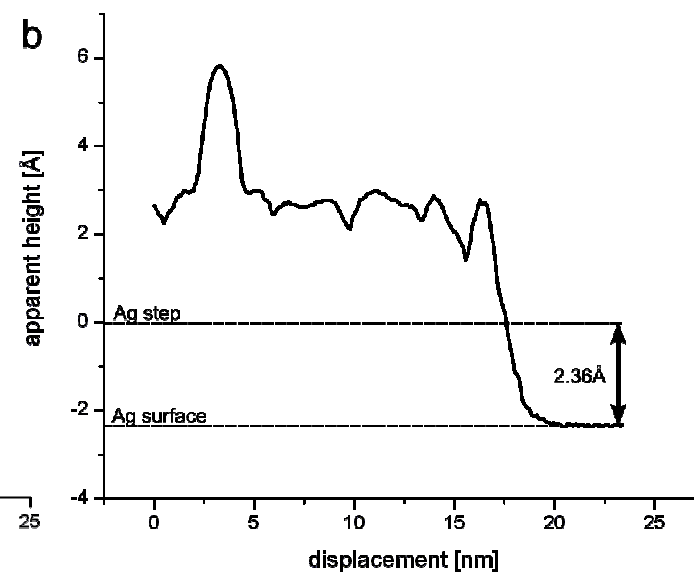
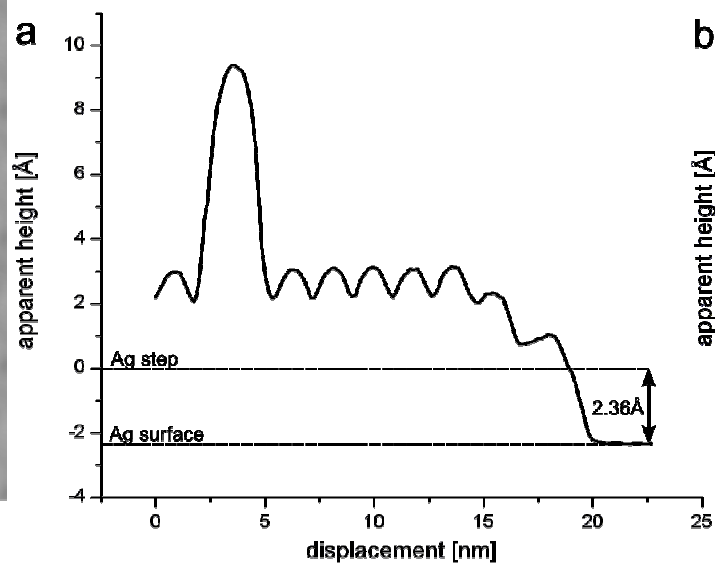




# $C_{60}$ on symmetric Pc derivative

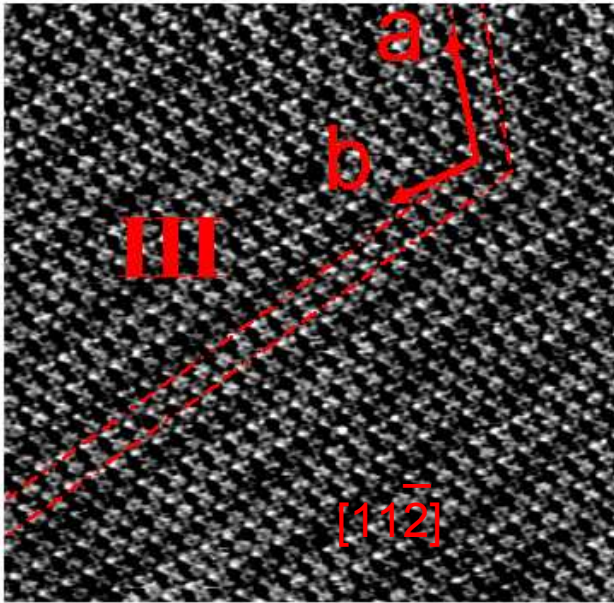


25x25 nm<sup>2</sup>, 77 K



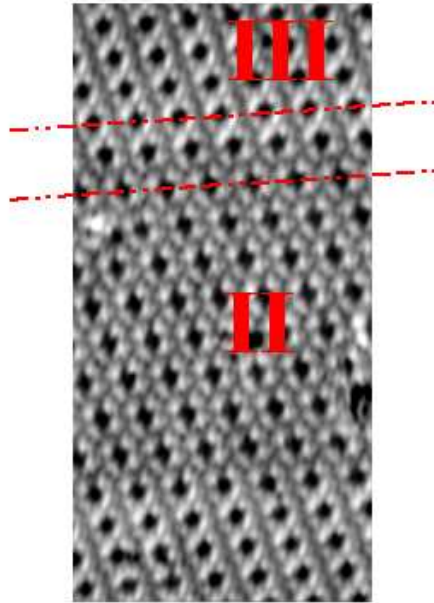
25x25nm<sup>2</sup>

# Orientation of domains

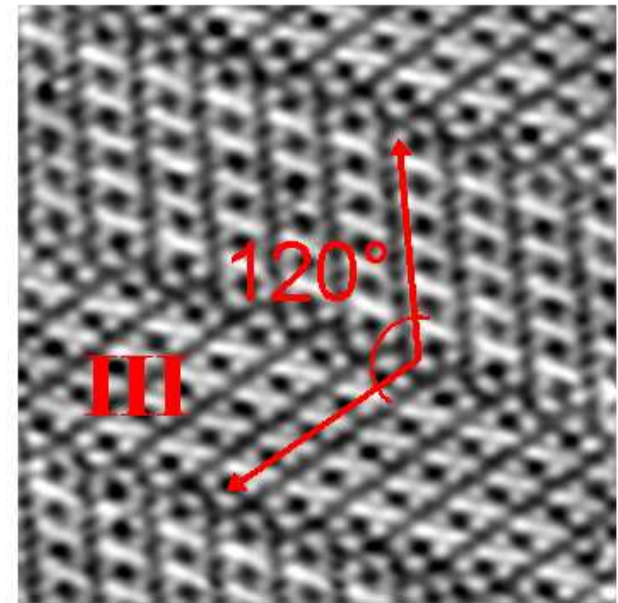


Au(111)  
herringbone reconstruction  
remains intact

50x50nm<sup>2</sup>



37x18nm<sup>2</sup>



25x25nm<sup>2</sup>