香港科技大學
THE HONG KONG UNIVERSITY OF SCIENCE AND TECHNOLOGY

Thesis Defense

Structural and Chemical Control of Supramolecular Coordination Self-Assembly Confined on Metal Surfaces

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Rm. 4503, Academic Building, HKUST
10:00am, 09 August 2012

OUTLINE

2. Structural and chemical controls through

   a) modifying the chemical states of the organic components;

      TPyP on Au(111), TPyP-Cu on Au(111)

   b) tuning the external environments;

      TPyP-PBTP

   c) controlling the thermodynamic and kinetic process;

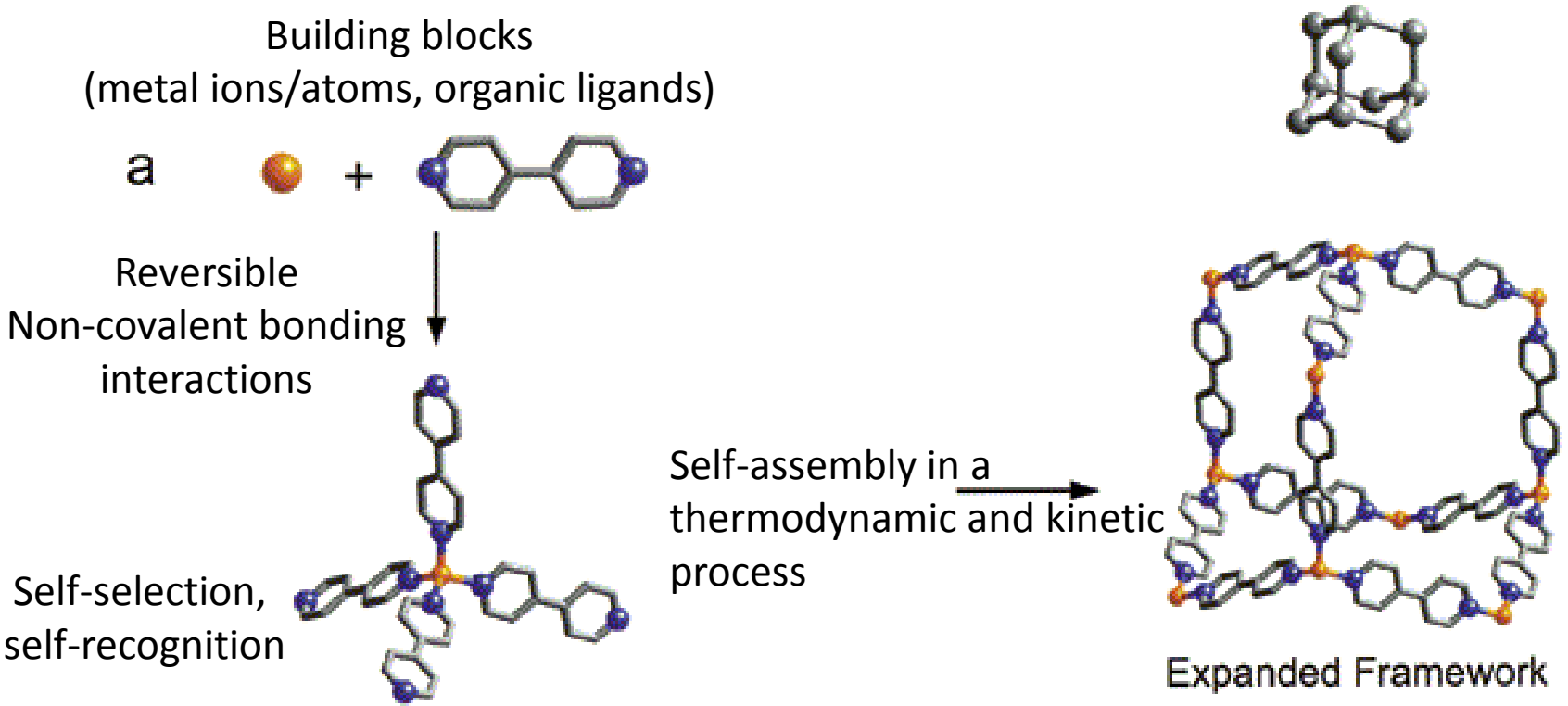
      TPyB-Cu and TPyB-Fe

3. Electronic states of artificial “quantum dots”

      TPyB-Cu on Au(111), TPyB-Cu on Cu(111)

Introduction - Principles

- Bottom-up
  - The supramolecular self-assembly in 3-dimensions (3D)

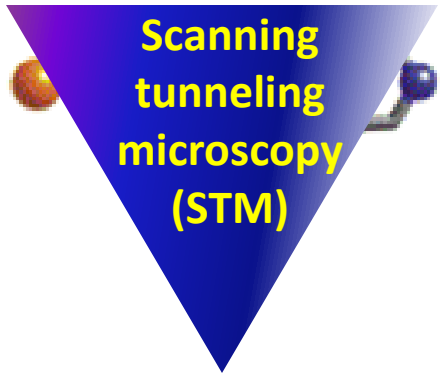


O. Yaghi et al. Nature 423, 705 (2003)

Introduction - Principles

- From 3D to reduced dimensions
  - Supramolecular self-assembly confined on metal surfaces

Surface sensitive techniques

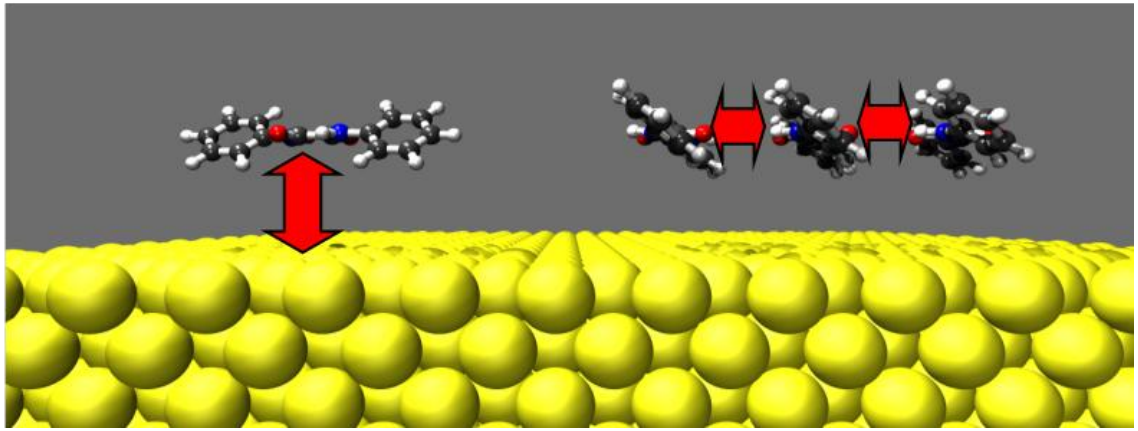


Well-defined metal surfaces
(e.g. the Au(111) surface)

New aspects of 2D systems

molecule/atom-substrate interaction

molecule-molecule/atom interaction

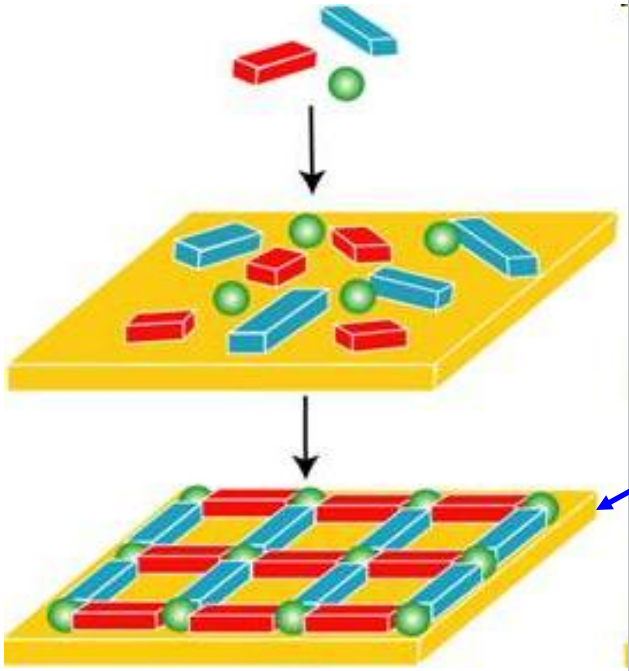


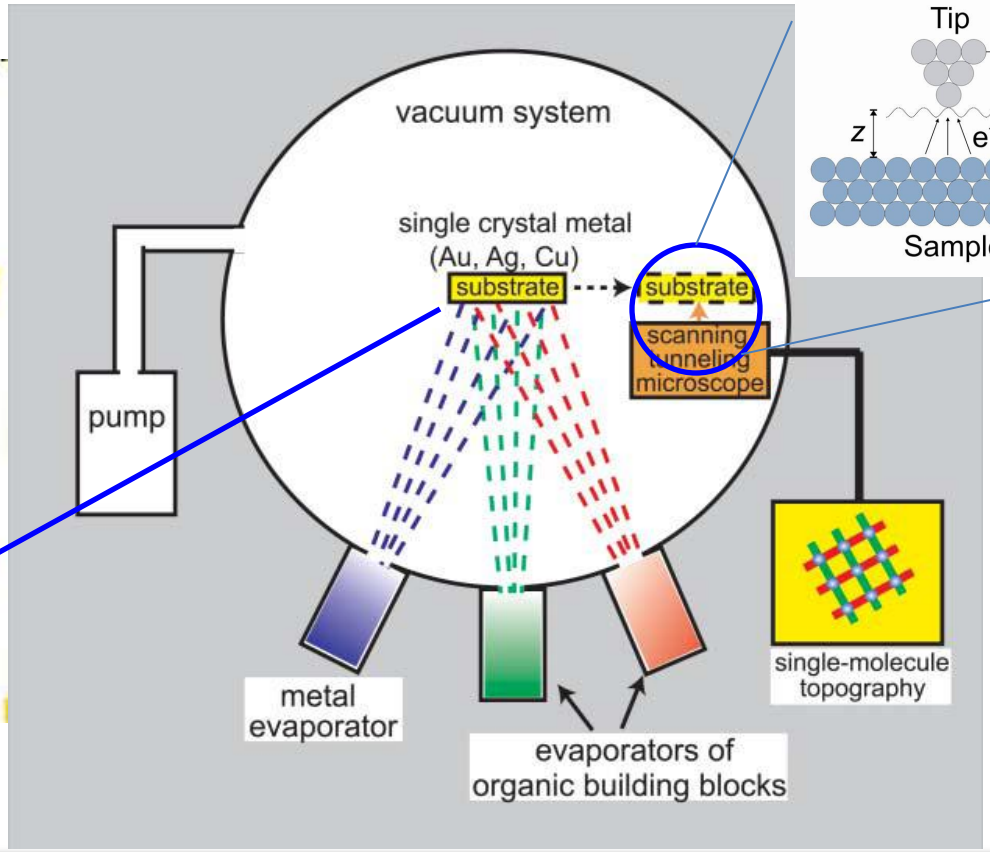
effects on ordering, conformation, electronic levels of the adsorbates and the patterned surface

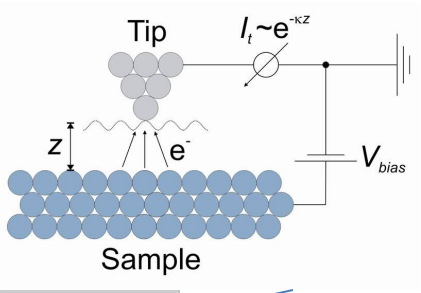
F. Klappenberger, presentation in visiting HKUST (2009)

Introduction – Methodology

- Studies of 2D supramolecular self-assemblies in ultra-high vacuum environment (pressure ~ 1.0E(-10) mbar)







N. Lin et al., Dalton Trans., 2006, 2794–2800.

2. Structural and chemical controls through

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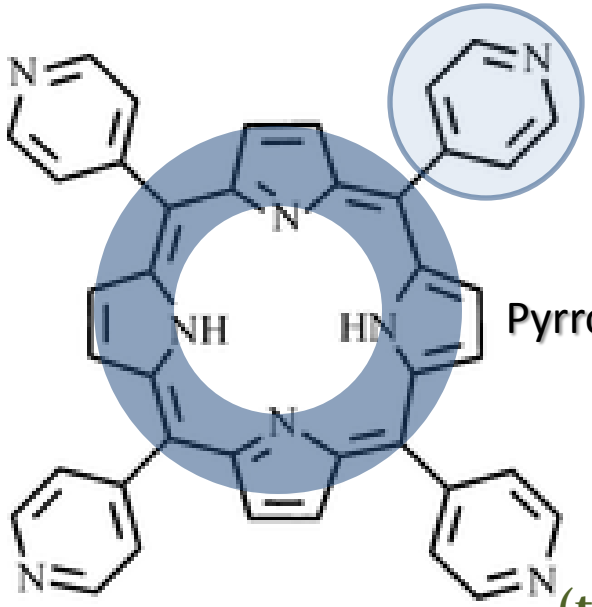
3. Electronic states of artificial "quantum dots"

TPyB-Cu on Au(111), TPyB-Cu on Cu(111)

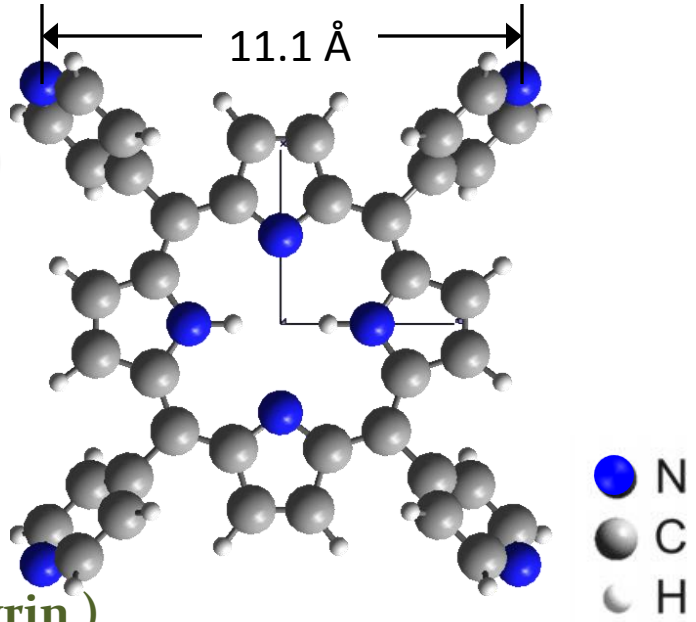
TPyP on Au(111)

- The bifunction of the TPyP molecule

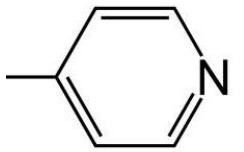


Pyridyl end-group (py)

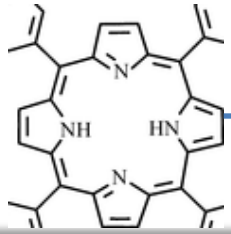
Pyrrolic macrocycle



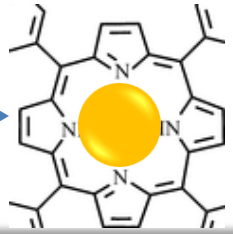
TPyP
(tetra-pyridyl-porphyrin)



+ metal (Cu, Fe, …)



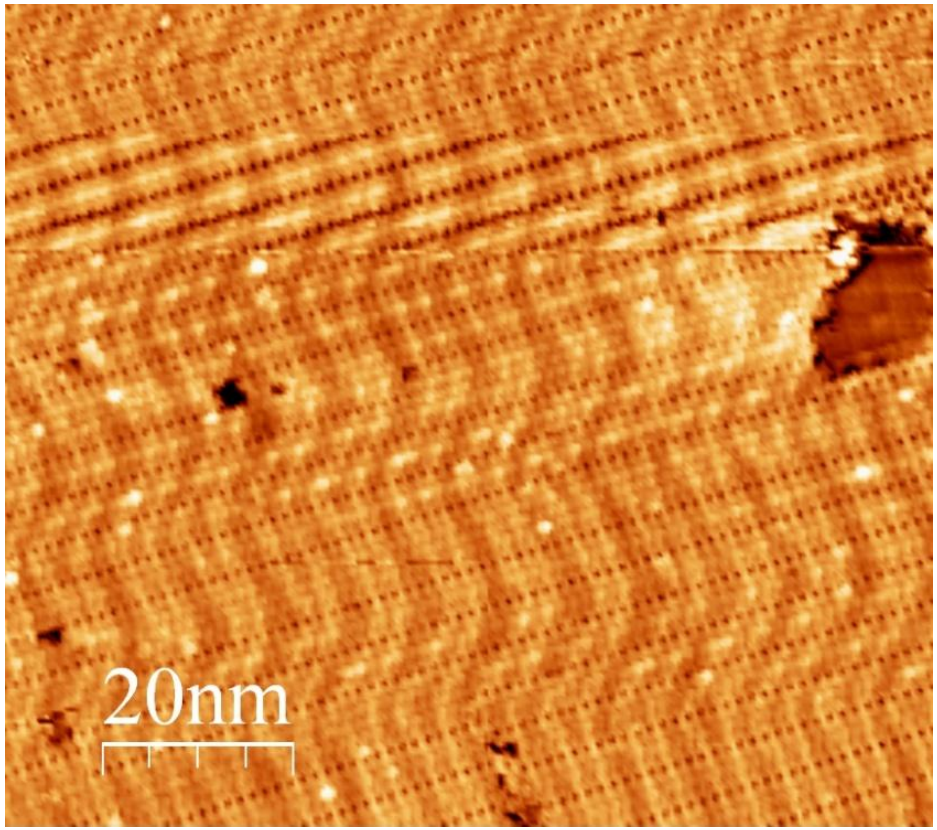
e.g. react with
metal (Cu, Zn, …)

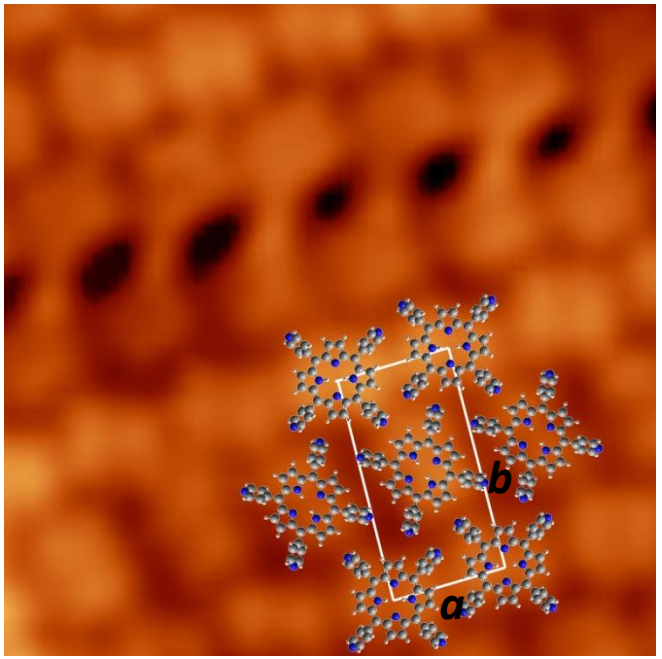


W. Auwärter, et al., J. Chem. Phys. 2006, 124, 194708.

TPyP on Au(111)

- Deposition of TPyP on Au(111)



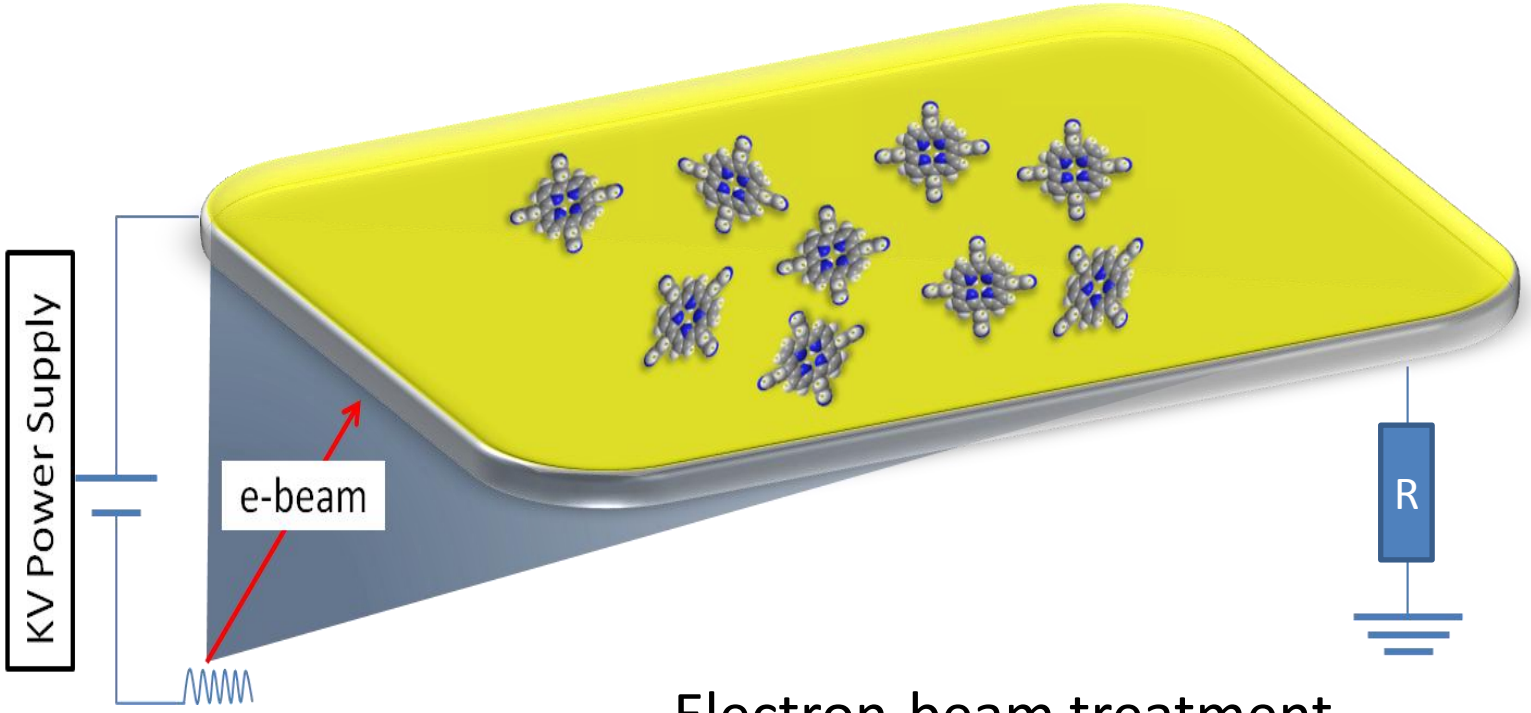


a= 1.39 nm
b = 2.74 nm
∠ *ab* = 93 °

Weak intermolecular interaction
(e.g. H-bond, Van der Waals, etc.)

TPyP on Au(111)

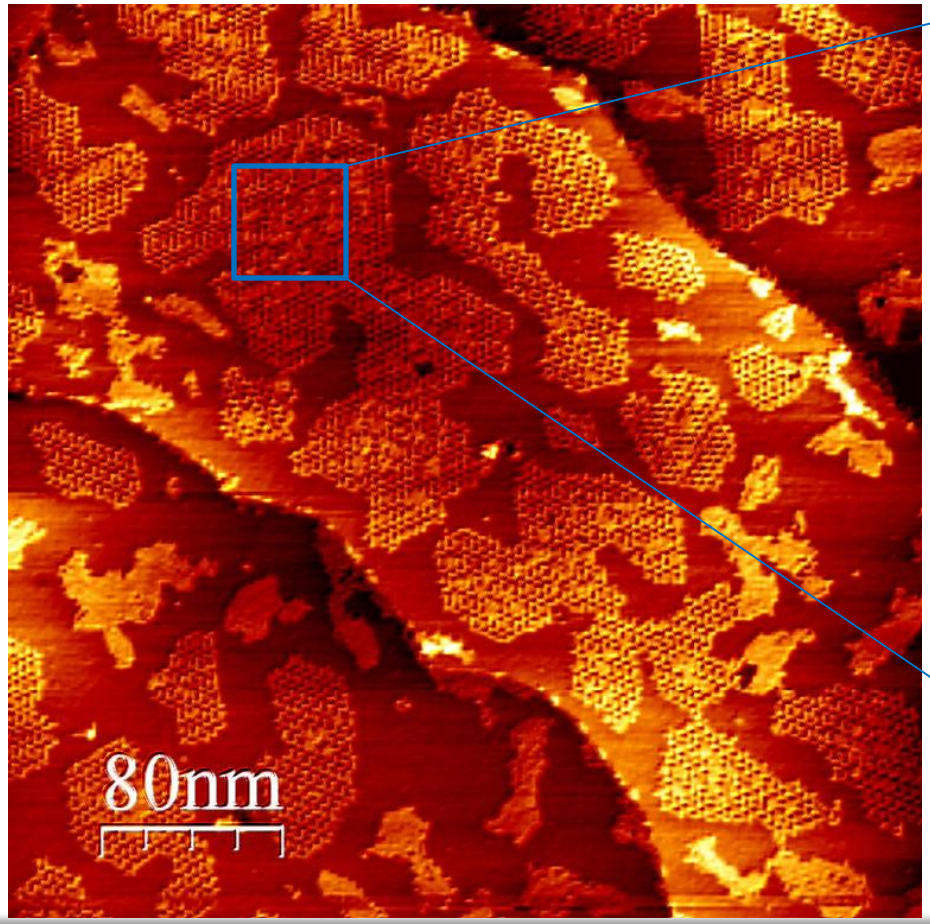
- Charging the sample to modify the chemical state of the TPyP macrocycle

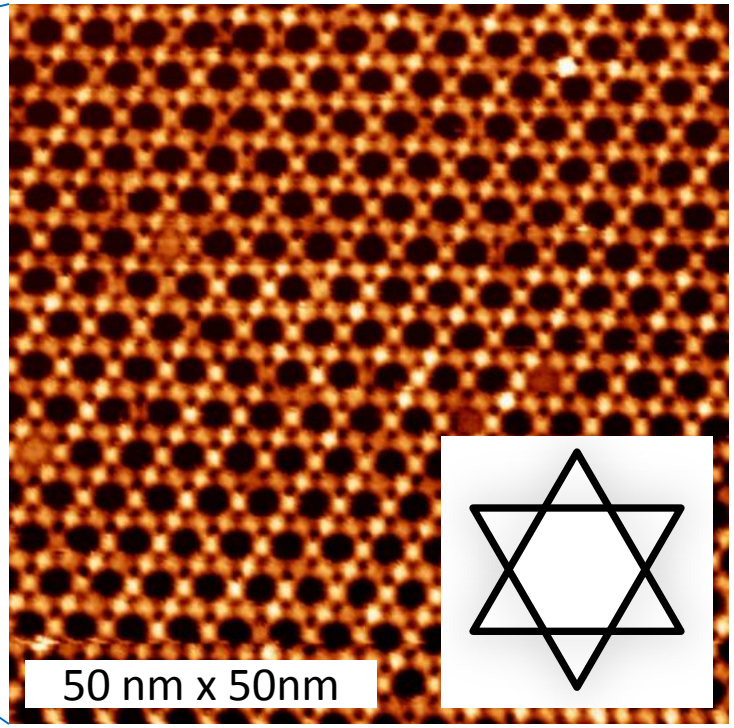


Electron-beam treatment (EBT)

TPyP on Au(111)

- The emergence of the network structure after EBT



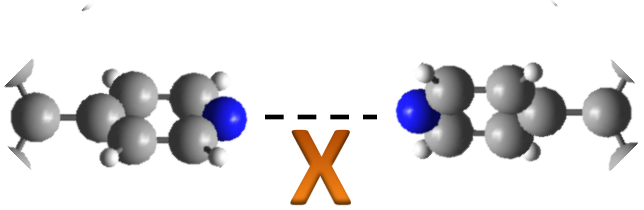


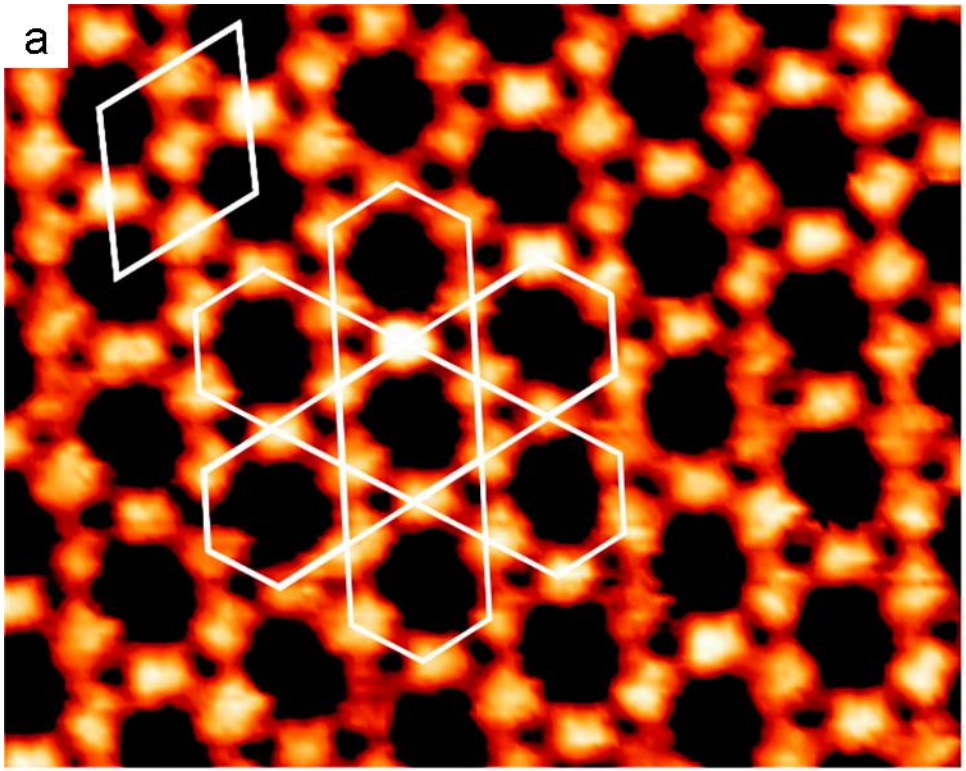
Kagome network

η (network) / η(close-packing) = 4.0

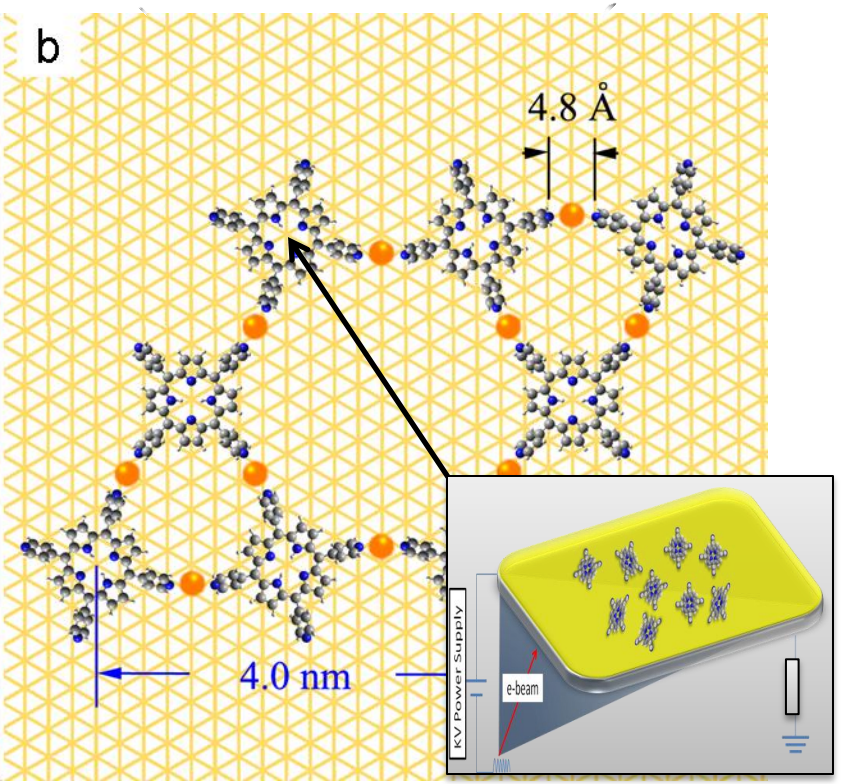
TPyP on Au(111)

- TPyP-Au Kagome network



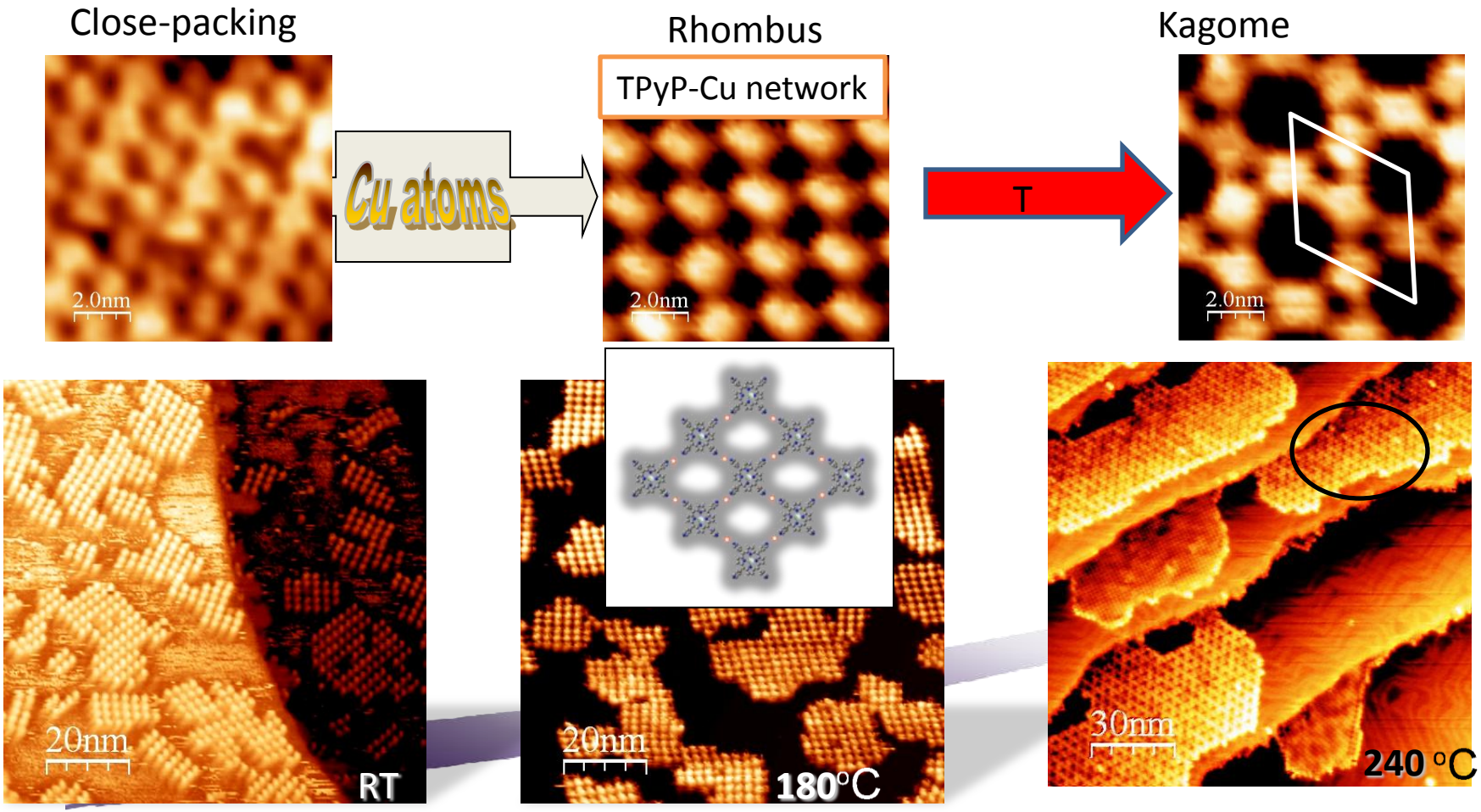


Side length of the rhombus = 4.1 nm



Au-py coordination bonding

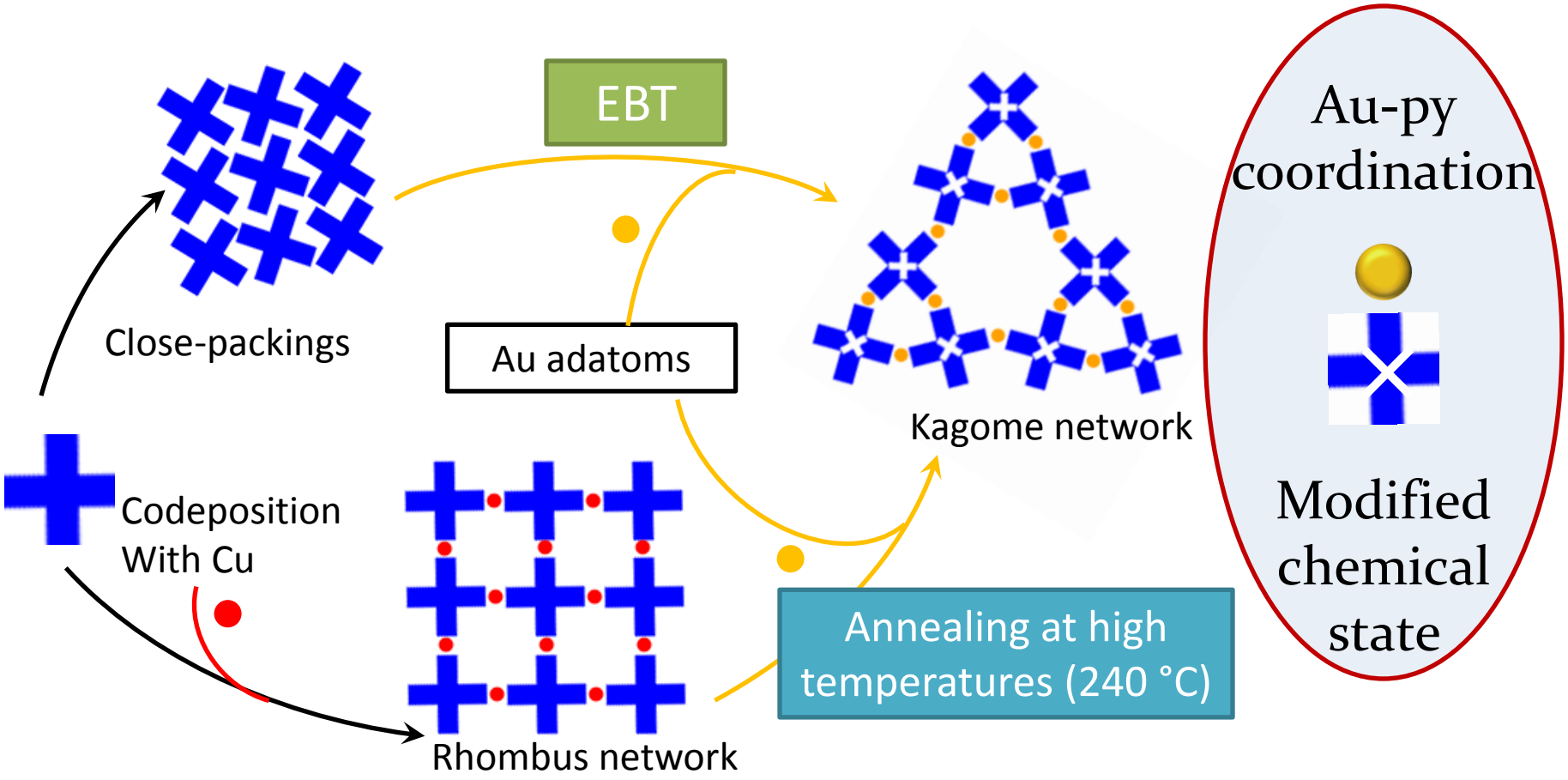
Co-deposition of TPyP and Cu on Au(111)



Post-annealing temperatures increase

TPyP and TPyP-Cu on Au(111)

- Modification of building blocks via two methods



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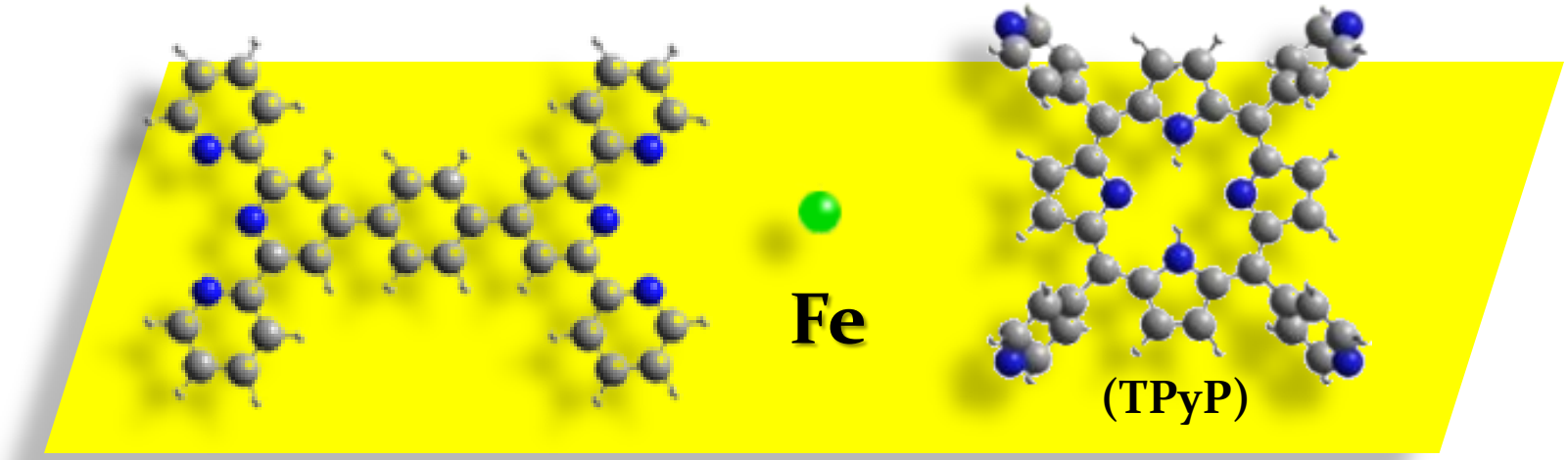
TPyP-PBTP bicomponent system

- The TPyP, PBTP molecules

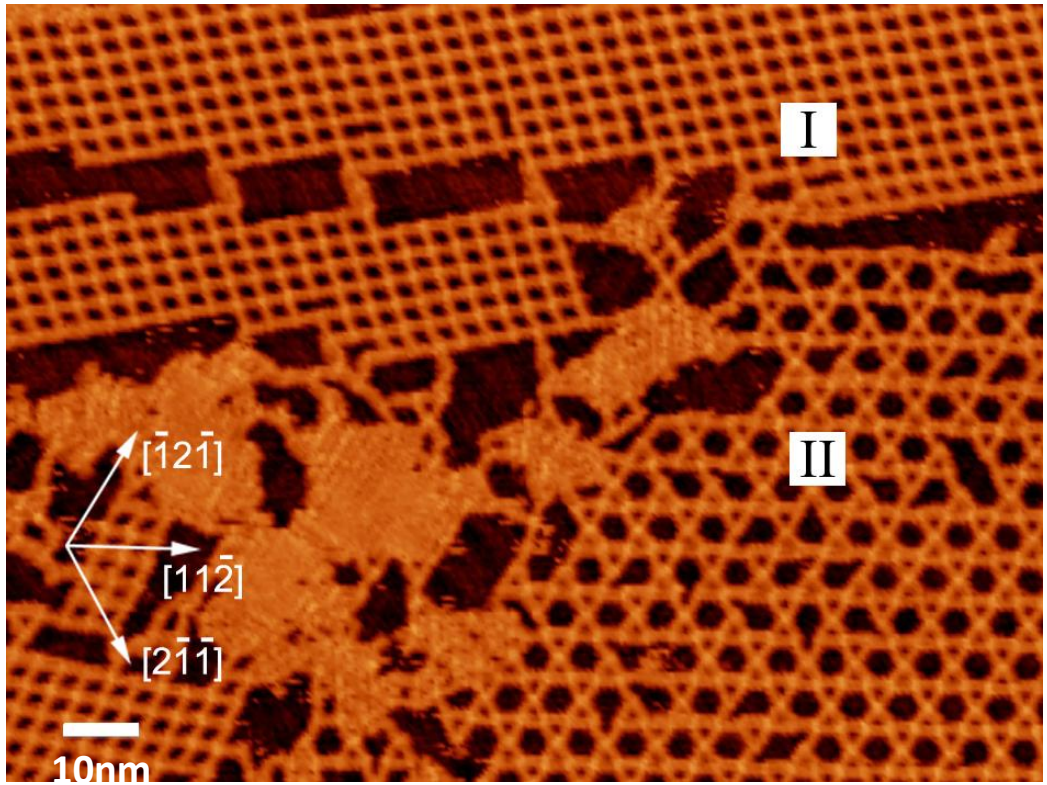


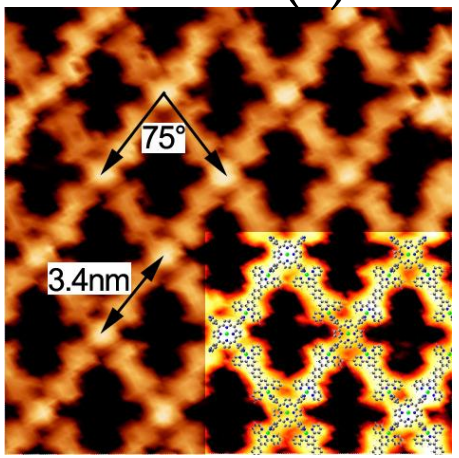
4′,4′′′′-(1,4-phenylene)bis(2,2′:6′,2′′-terpyridine)
(PBTP)

Au(111) surface

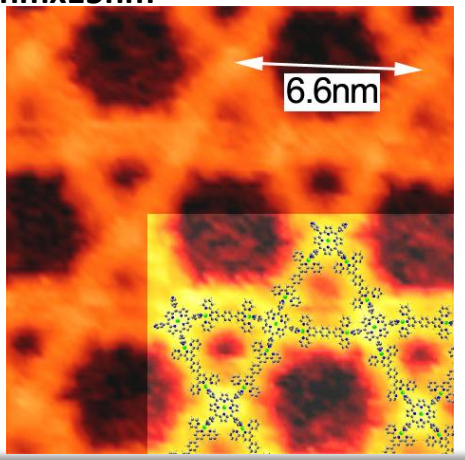
Co-deposition of PBTP, TPyP and Fe

- Mixtures of two types of networks- rhombus (I) and Kagome (II)



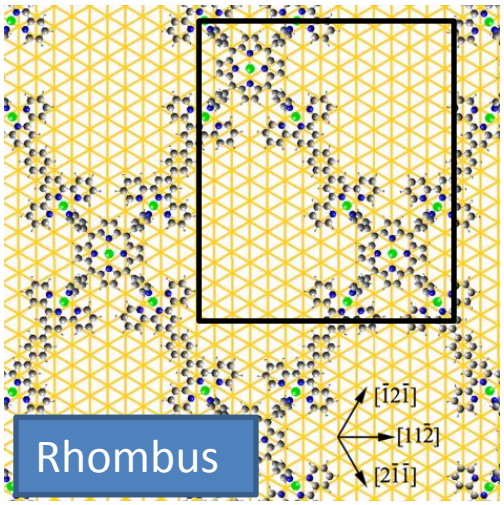


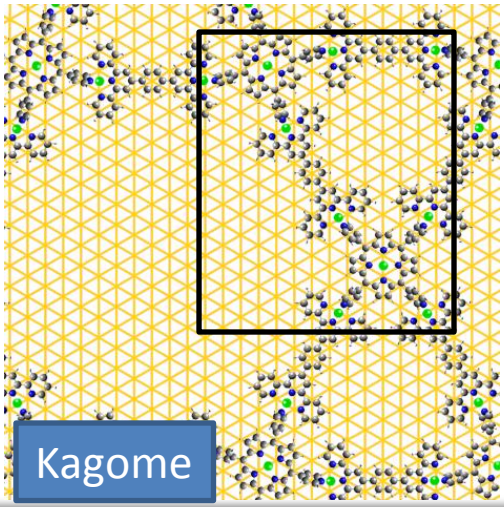
15nmx15nm

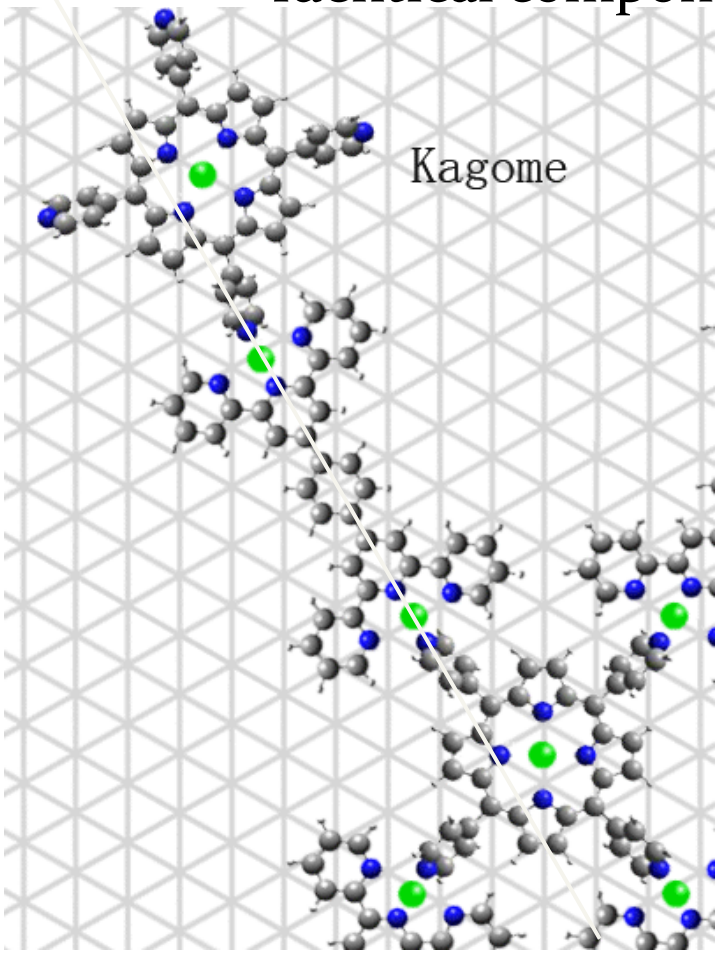


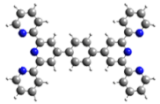
Structure models

- Identical adsorption sites
- Identical coordination configuration
- Identical component ratio

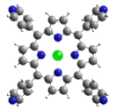








PBTP



TPyP(iron metalated)

PBTP/TPyP

= 2:1

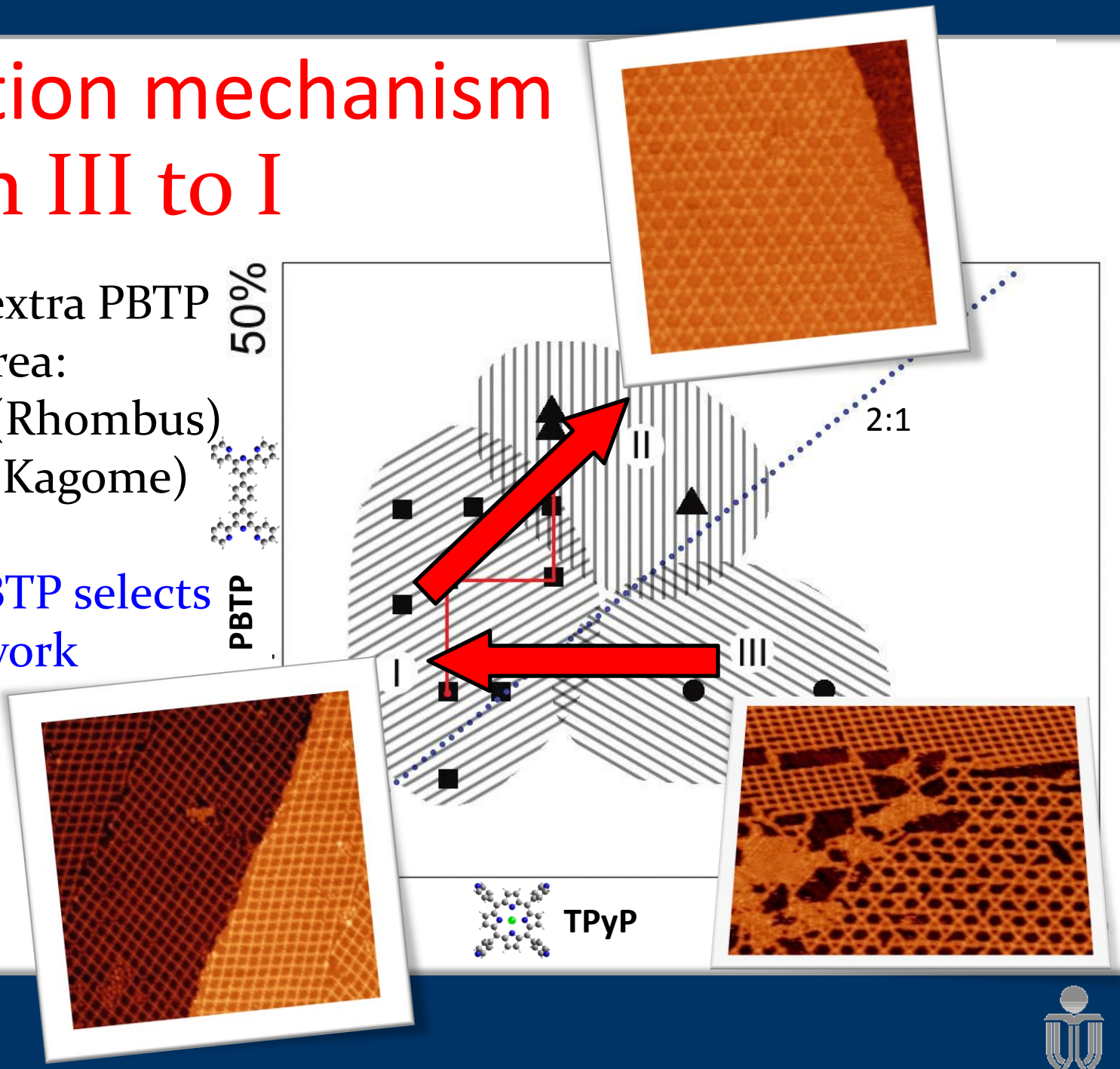
Transition mechanism - From III to I

- Gas phase of extra PBTP
- Occupation area:

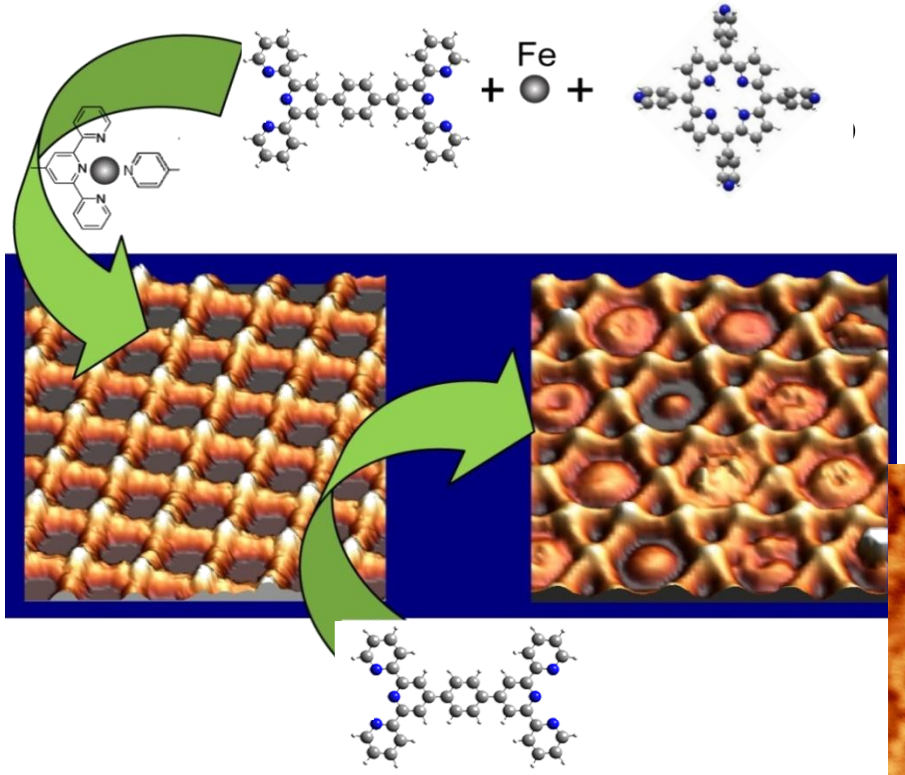
10 nm²/TPyP (Rhombus)

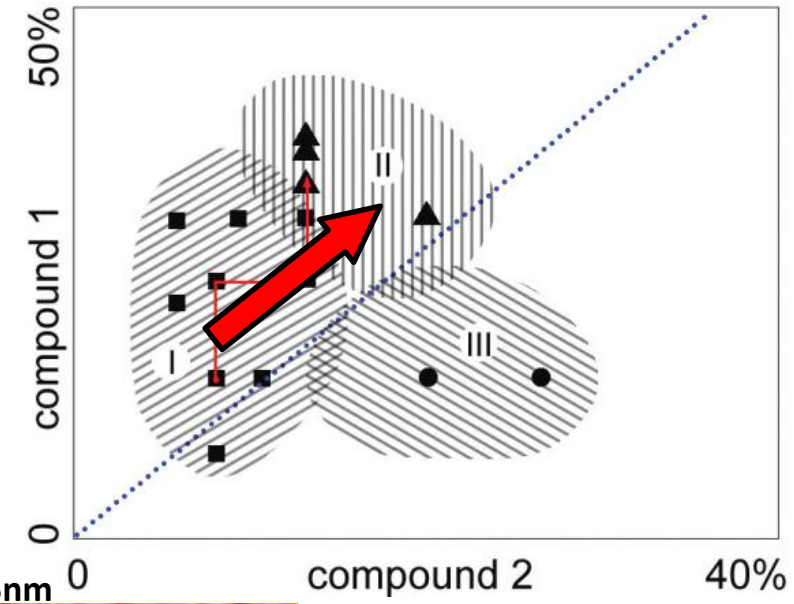
12 nm²/TPyP (Kagome)

- Gas-phase PBTP selects Rhombus network

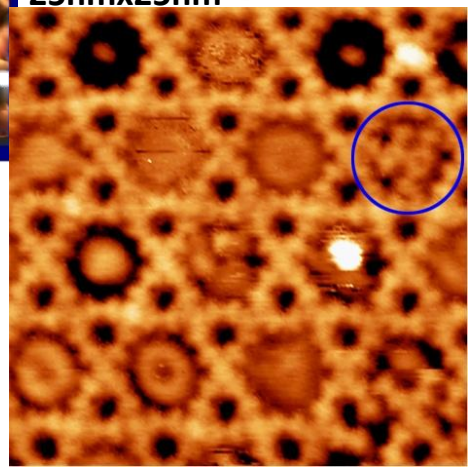


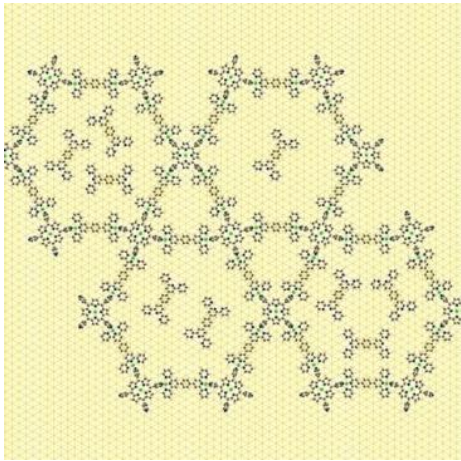
Transition mechanism - From I to II





25nmx25nm





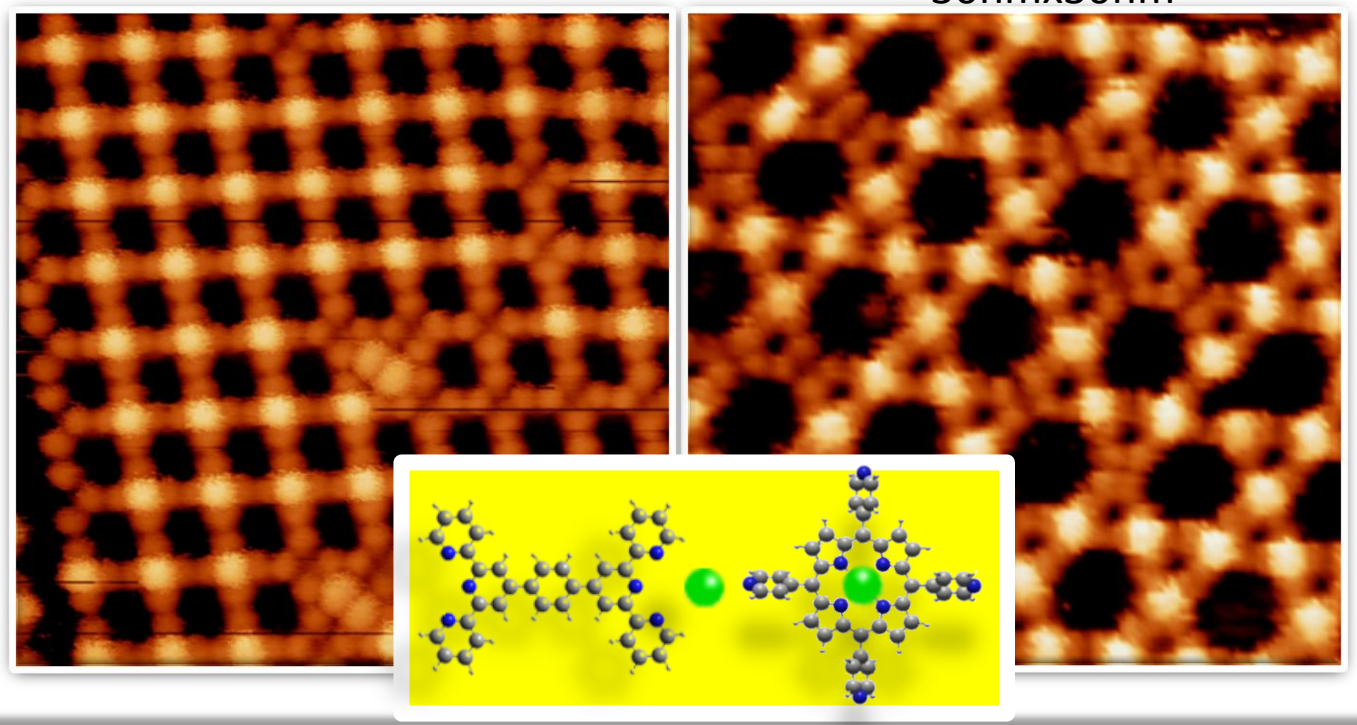
- Inclusion of PBTP selects Kagome network

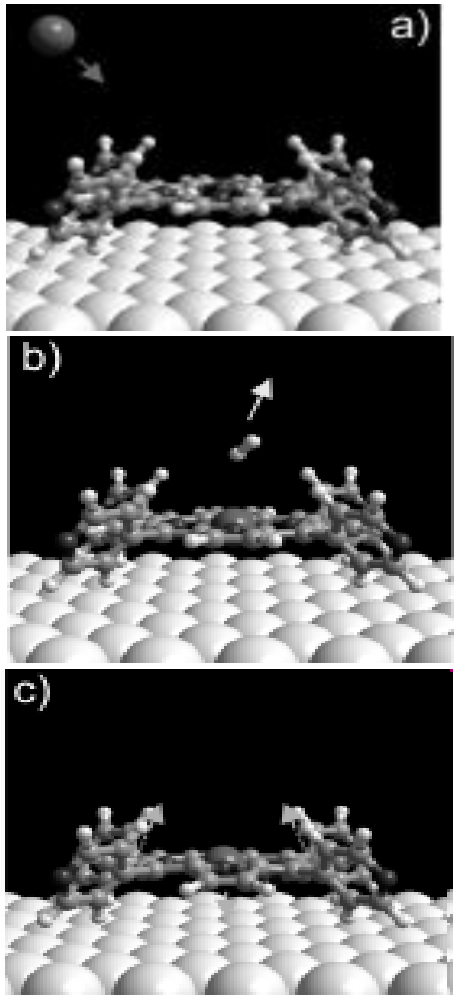
Chemical control

- Chemical diversity:

Dark/bright (intrinsic / iron-metallated) TPyPs distribute randomly in both types of networks.

30nmx30nm

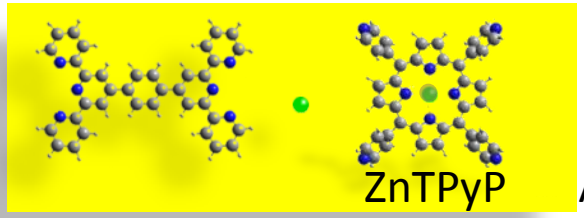




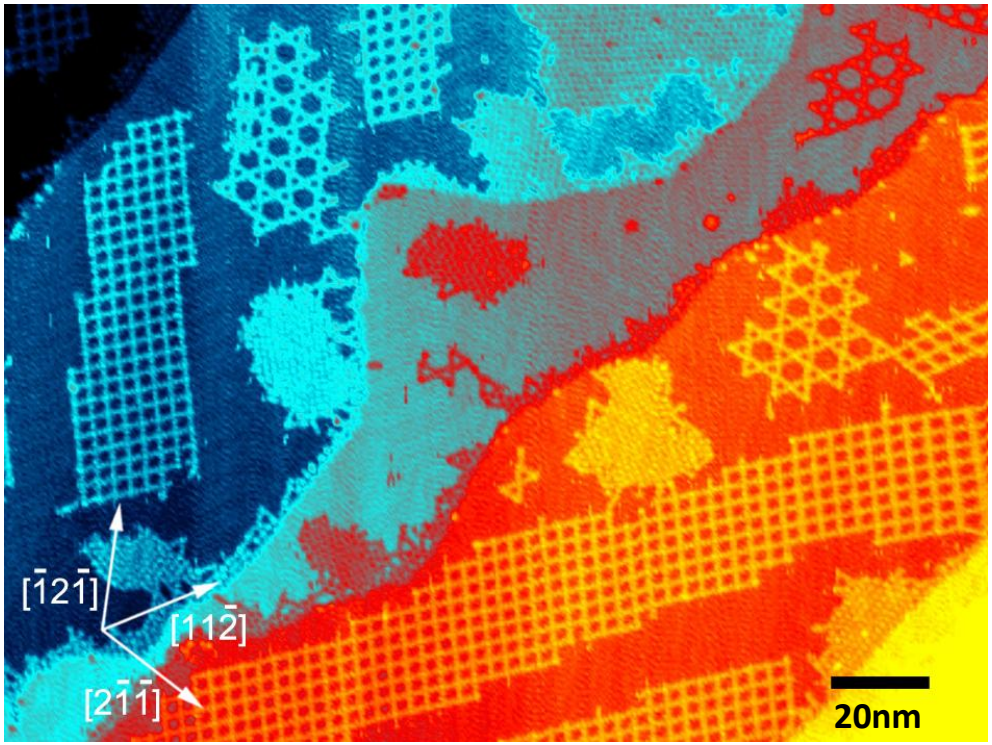
Process of the metallation of TPyP on surfaces

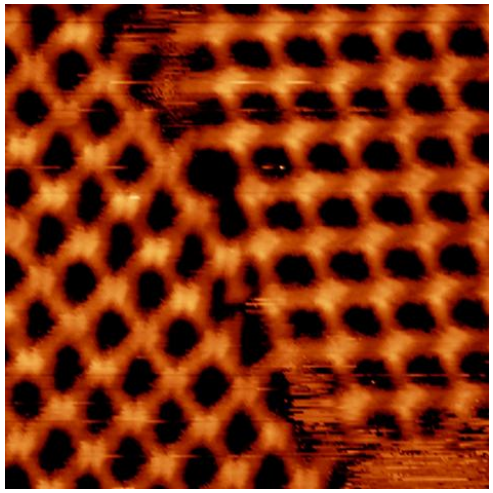
W. Auwärter, et al, ChemPhysChem 2007, 8, 250 – 254.

Chemically pure phase of networks

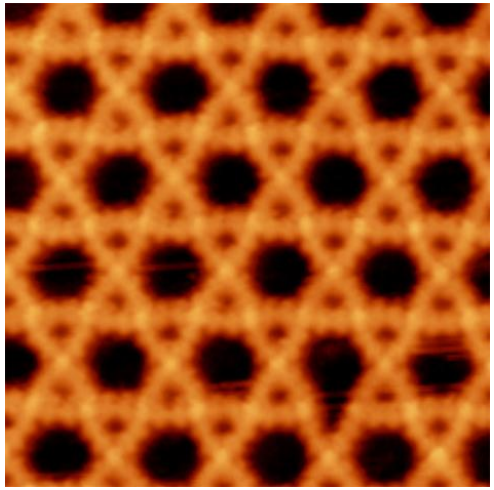


Au(111)

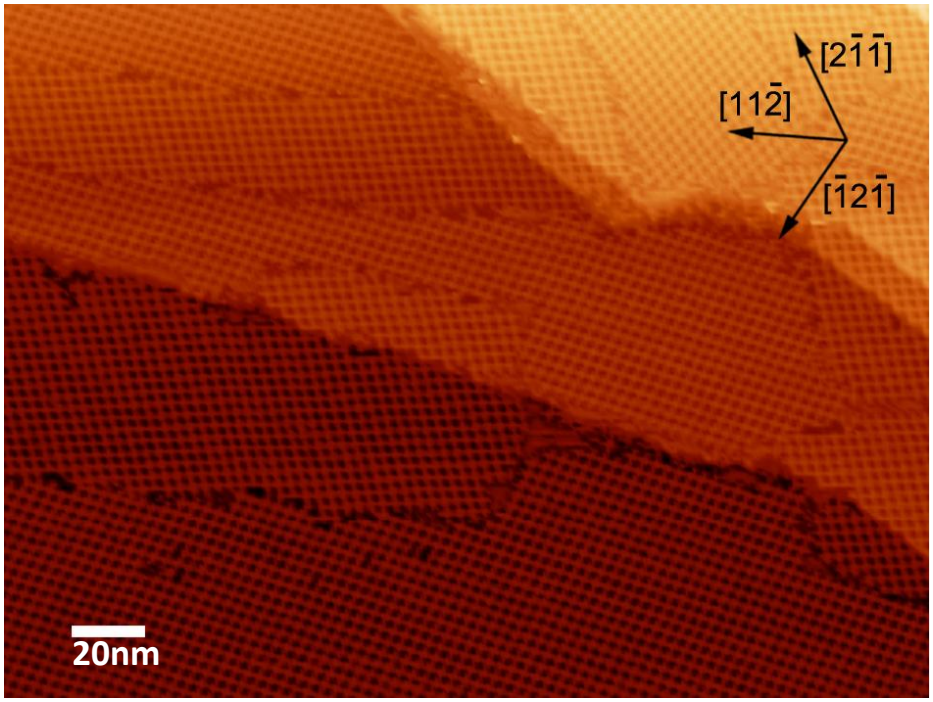


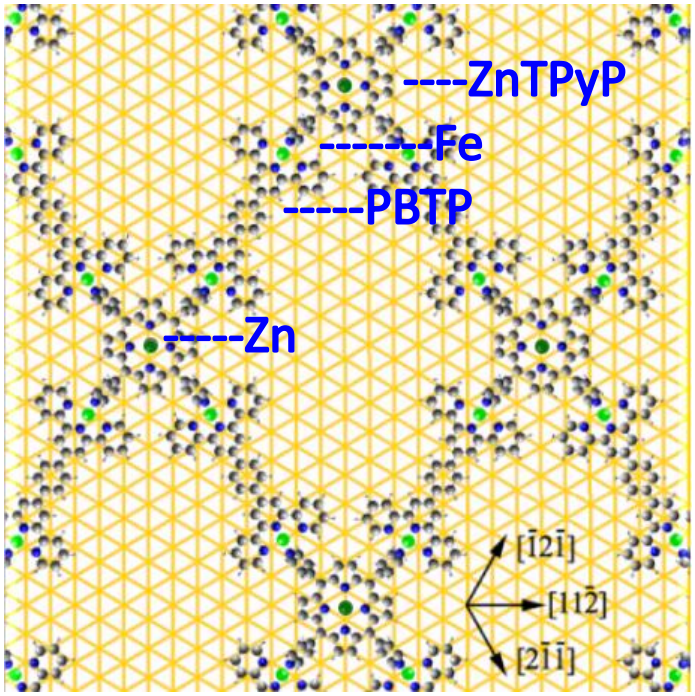


30nmx30nm



Pure structural and chemical phase





The rhombus network with bi-organic(PBTP and ZnTPyP) and bi-metallic(Zn and Fe) components covers an entire surface.

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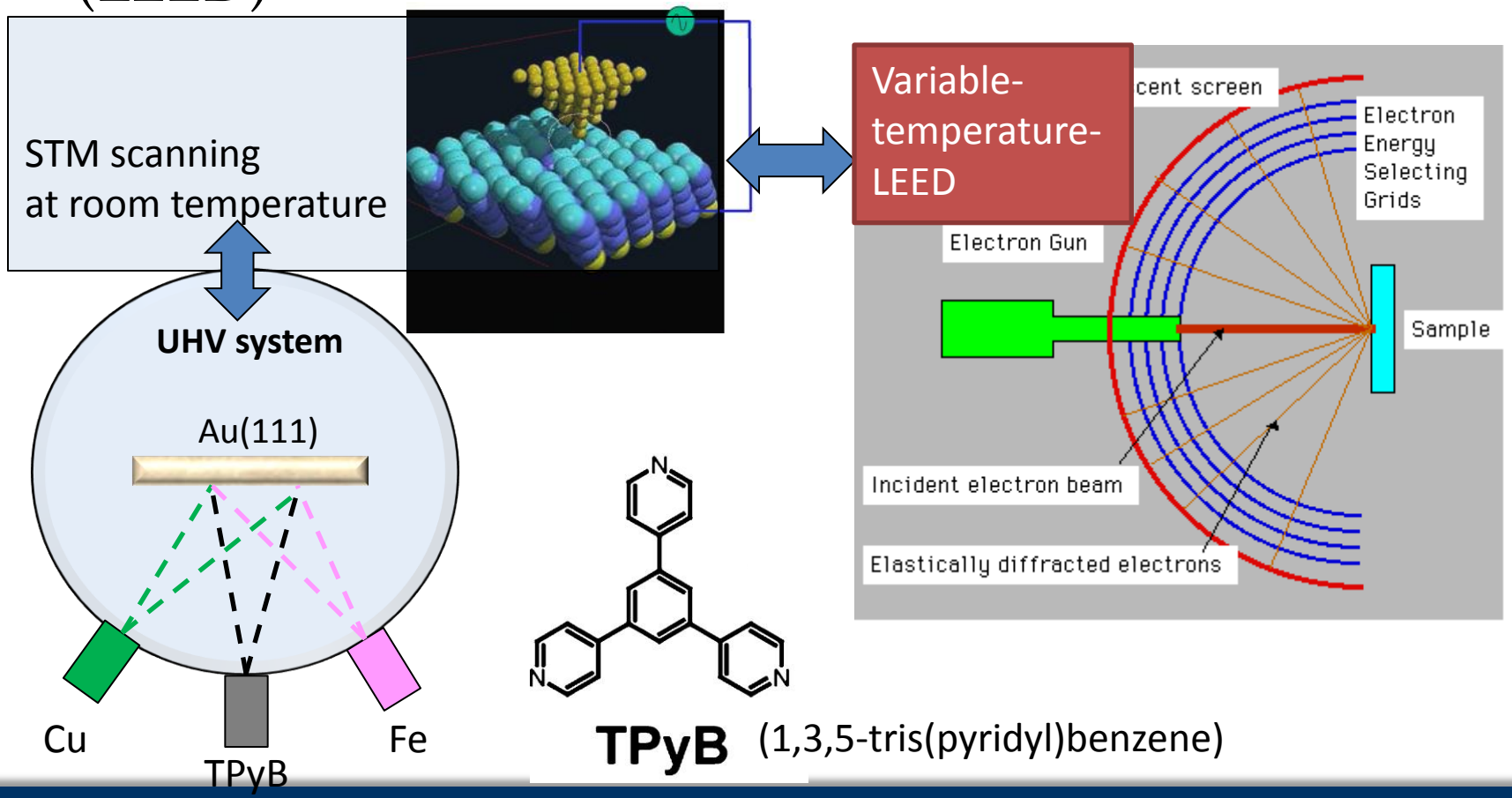
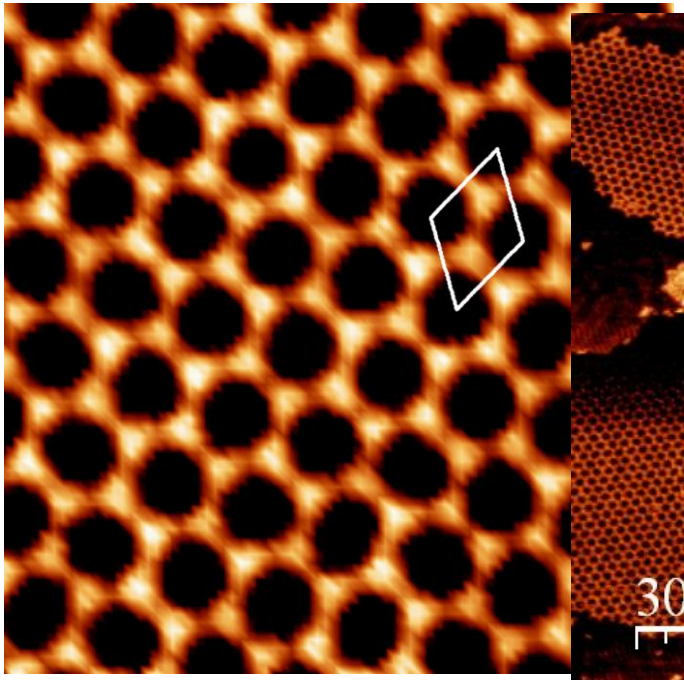
TPyB coordination system

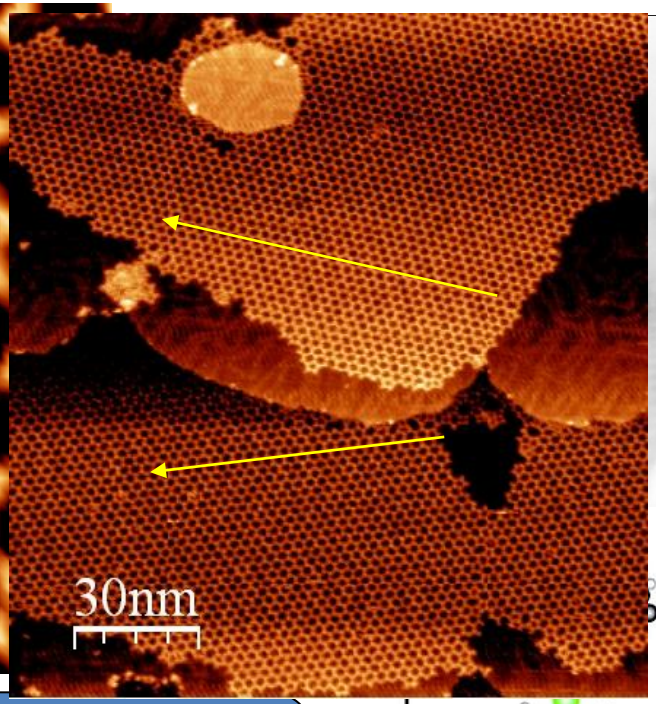
- Method – STM and low-energy electron diffraction (LEED)

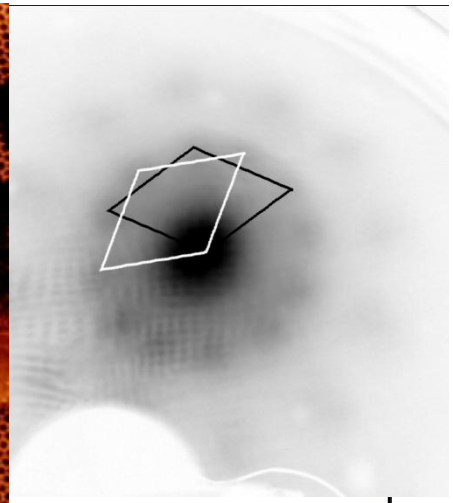


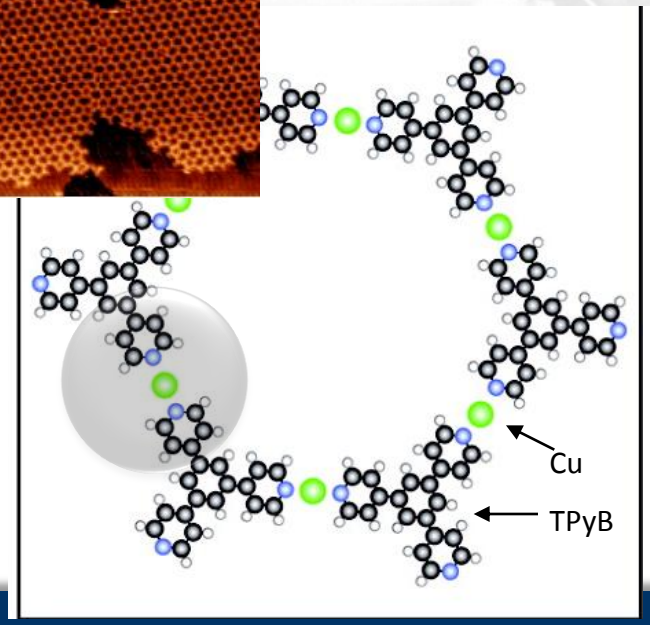
- *STM illustration is derived from http://nanohub.org/topics/AQME/Image:pic3_stm.png*
- *LEED illustration is derived from http://www.chembio.uoguelph.ca/thomas/oldthom/LEED001.GIF*

TPyB-Cu coordination network





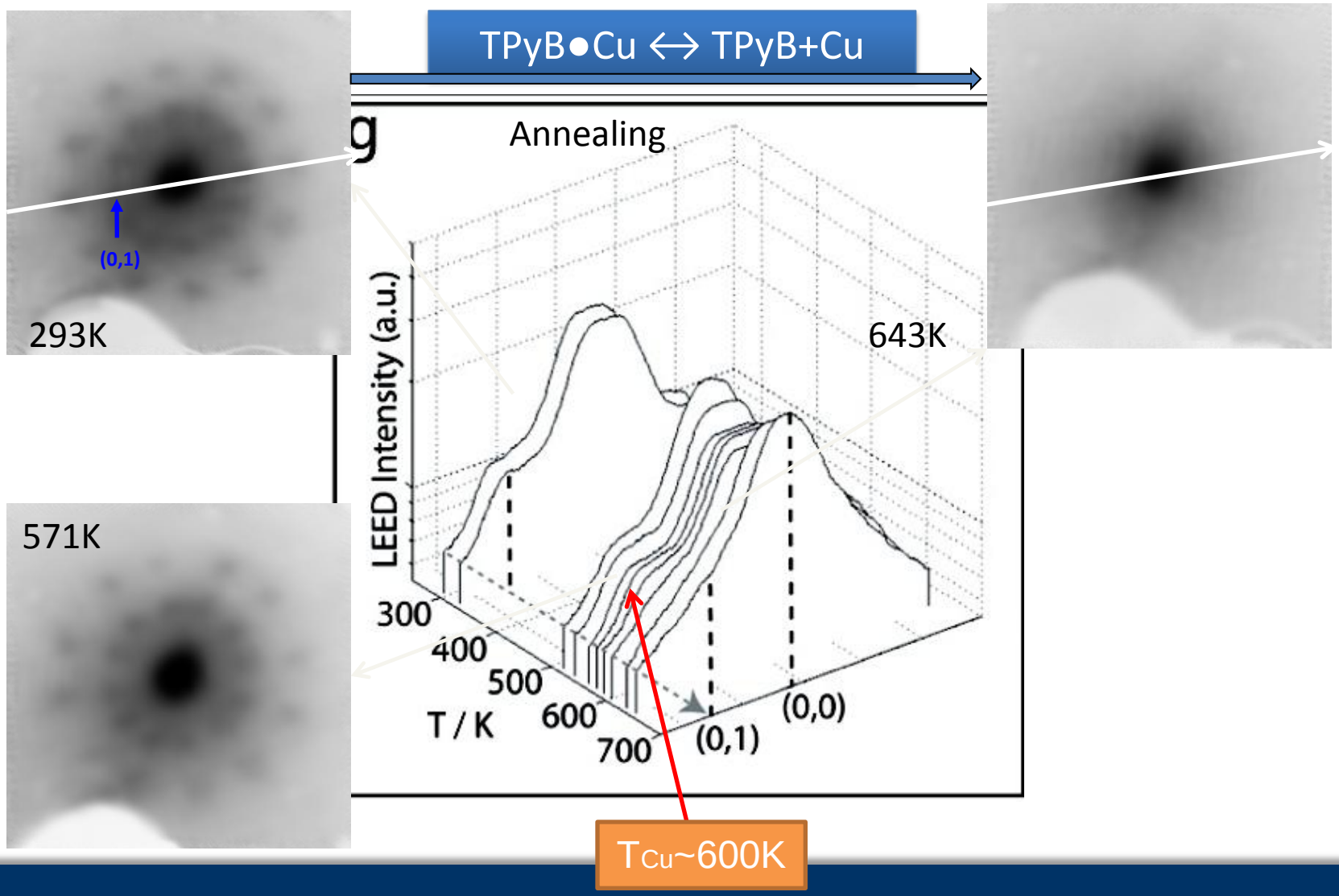




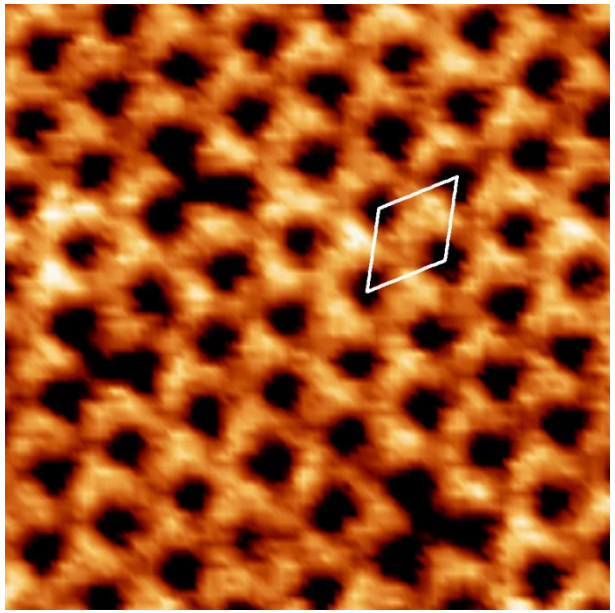
- STM(20nmx20nm)
  TPyB-Cu Honeycomb network,
- Lattice const.=2.73nm(±0.05nm)
- 2-fold Cu-py coordination bond
- Domain orientation difference: 28 degrees

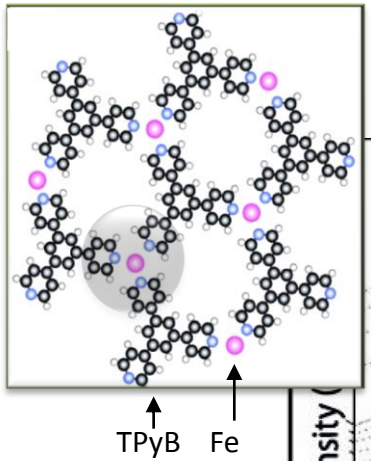
- LEED beam-energy=15.0V
- Lattice const.(derived)=2.76nm(±0.05nm)
- Domain orientation difference: 28 degrees

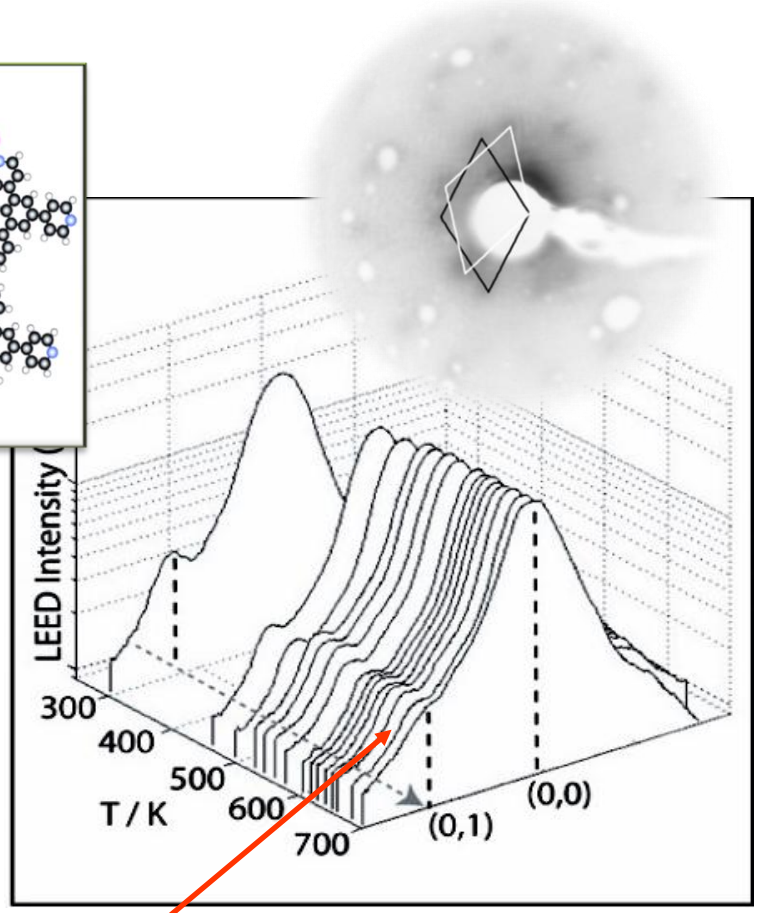
Variable temperature LEED of TPyB-Cu



TPyB-Fe coordination network







- STM (11.1nmx11.1nm)
TPyB-Fe Triangular network
- Lattice const.=1.40 nm(±0.05nm)
- 3-fold Fe-py coordination bond
- Domain orientation difference: 22 degrees

- LEED beam-energy=20.0V
- Lattice const.(derived)=1.38nm(±0.05nm)
- Domain orientation difference: 22 degrees

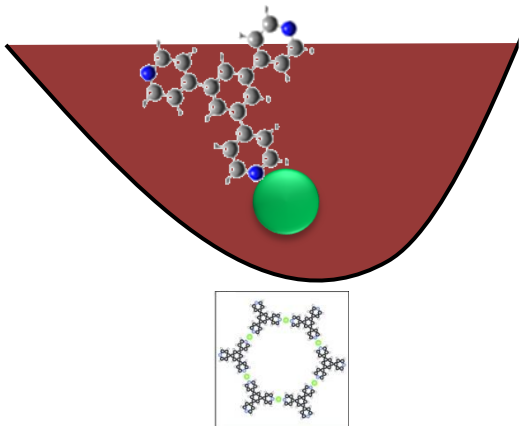
T_{Fe}~680K

T_{Cu}~600K

TPyB●Fe ↔TPyB + Fe

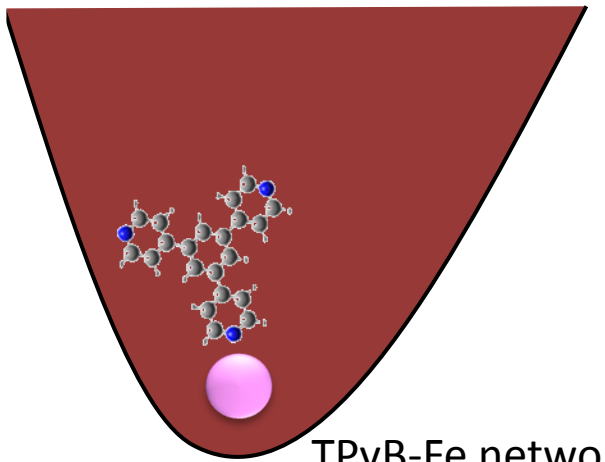
Annealing

T_{Fe}~680K > T_{Cu}~600K



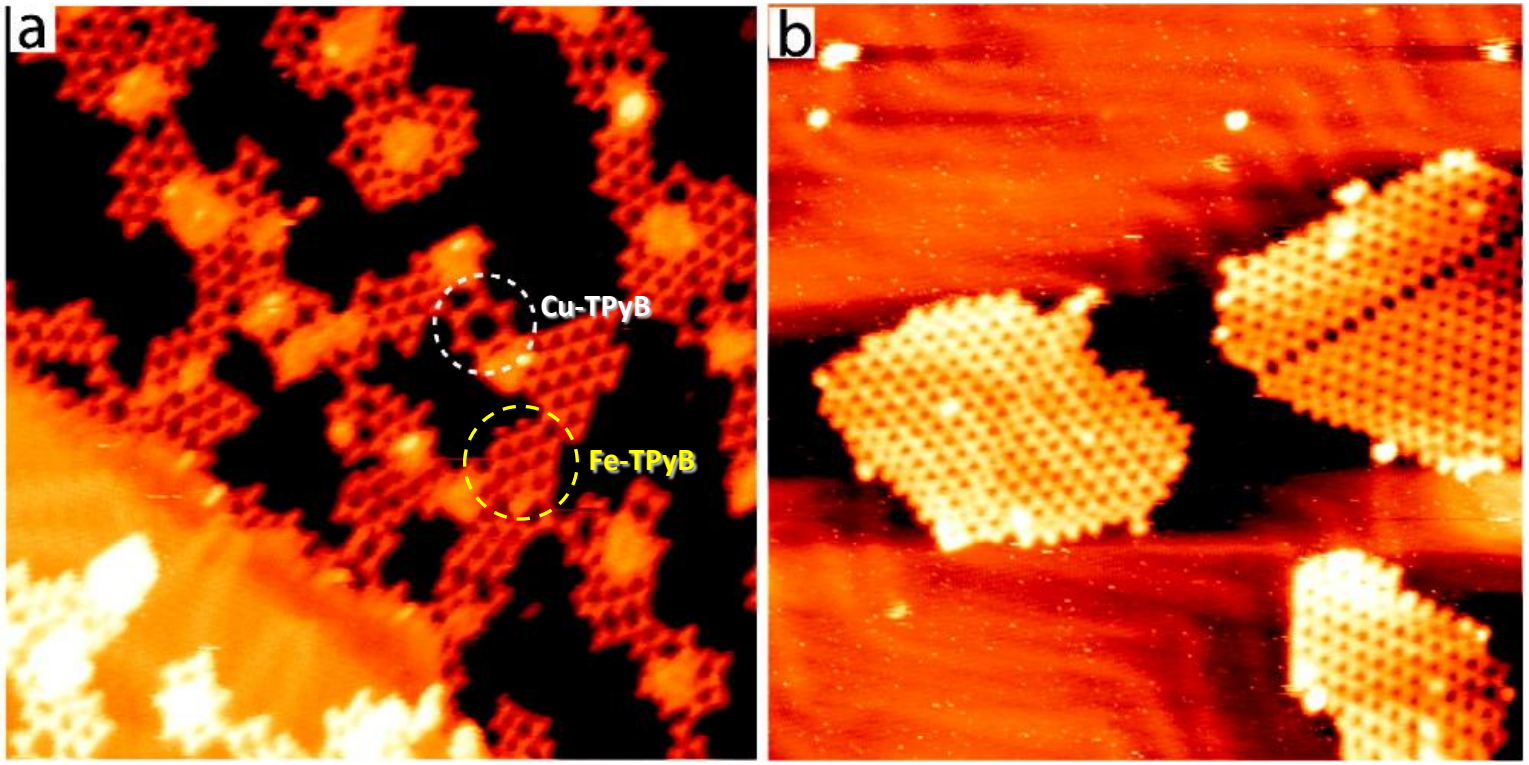
TPyB-Cu network

Fee energy change



TPyB-Fe network

Sequence-I



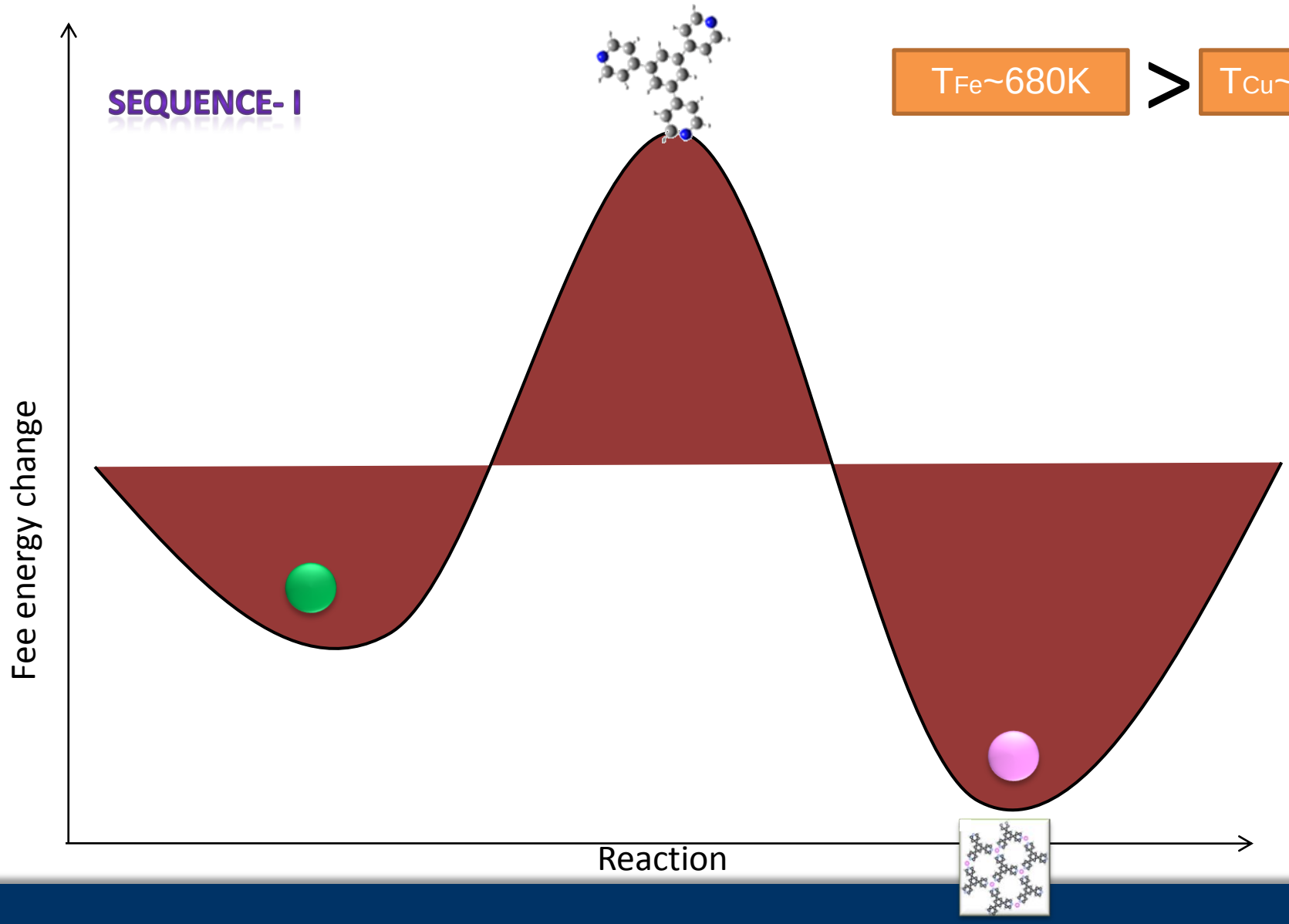
[Fe-py]/ [Cu-py] ~9.0

Only Fe-TPyB networks,
no Cu-TPyB networks observed

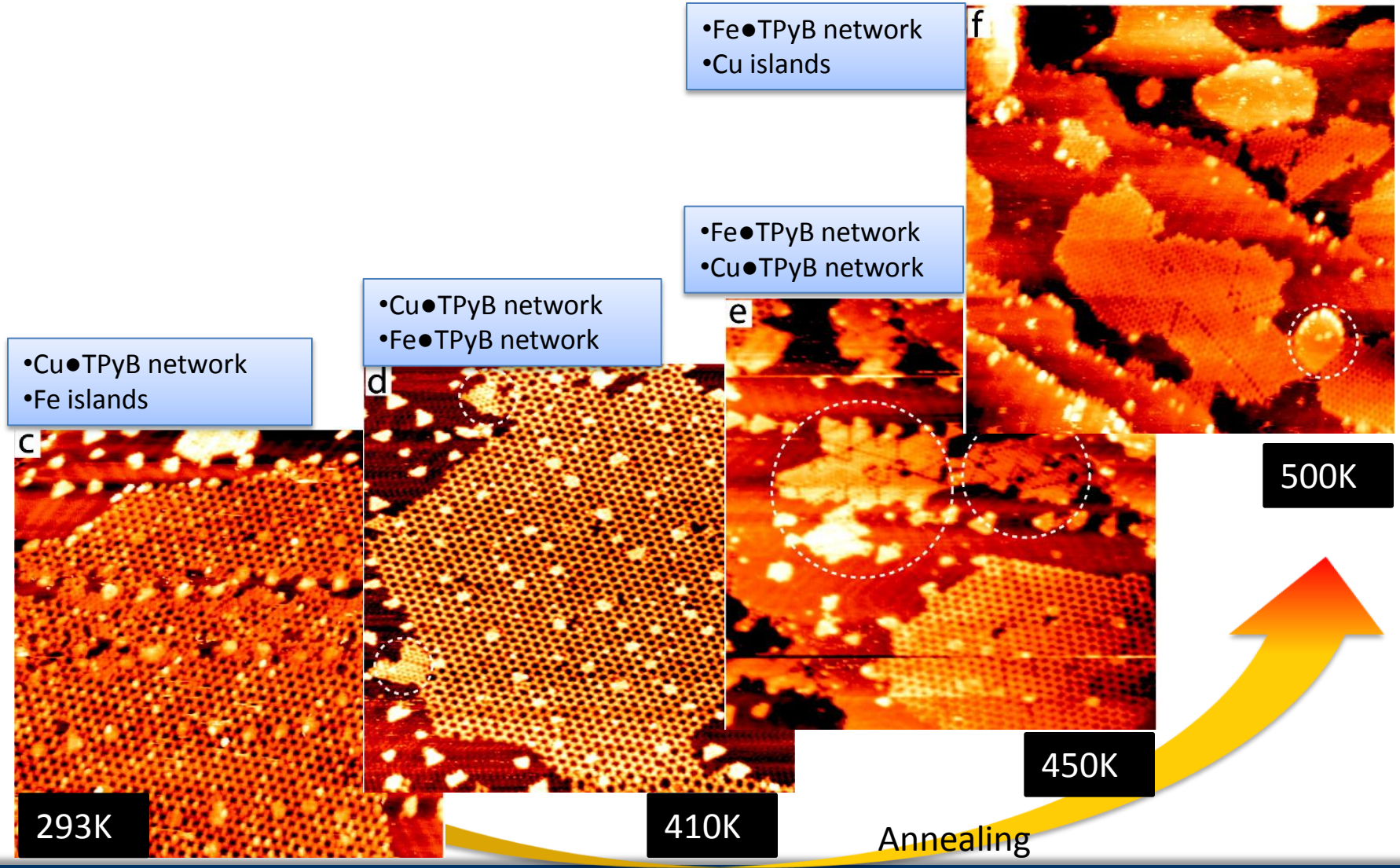
293K → 400K

Annealing

Sequence-I 1. codeposit Fe and Cu; 2. deposit TPyB

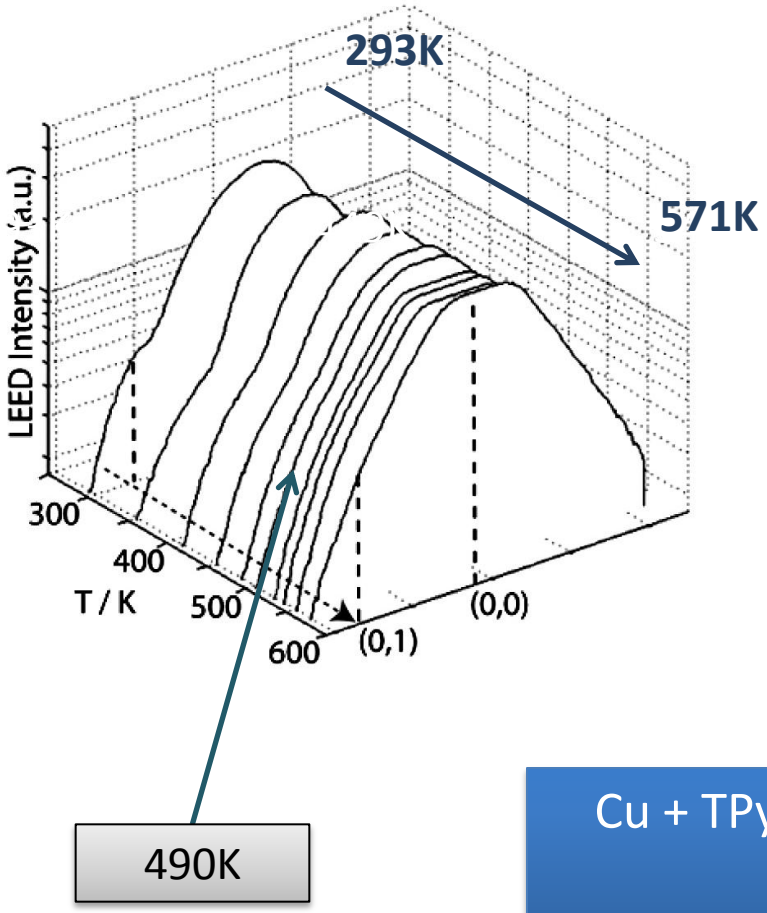


Sequence-II


•Fe●TPyB network
•Cu islands
f
•Fe●TPyB network
•Cu●TPyB network
e
•Cu●TPyB network
•Fe●TPyB network
d
•Cu●TPyB network
•Fe islands
c
500K
450K
410K
293K
Annealing

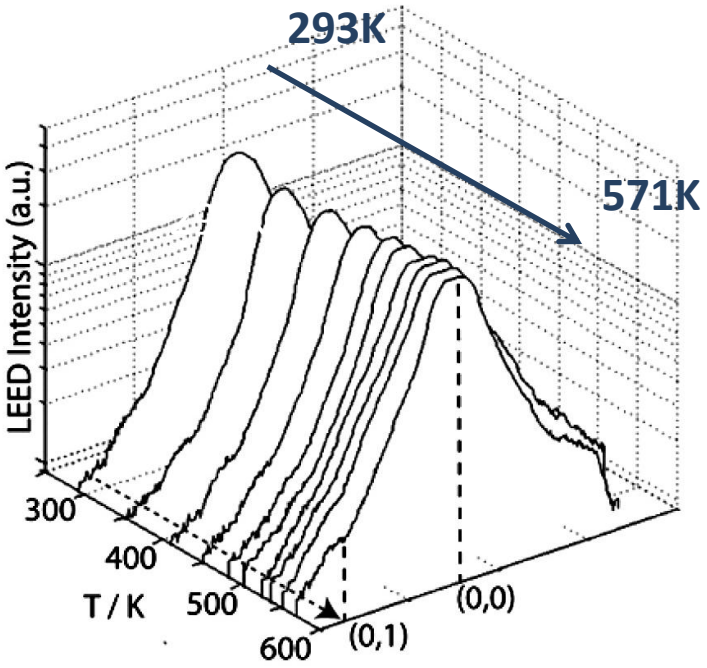
Variable temperature LEED (Sequence-II)

Cu●TPyB network



490K

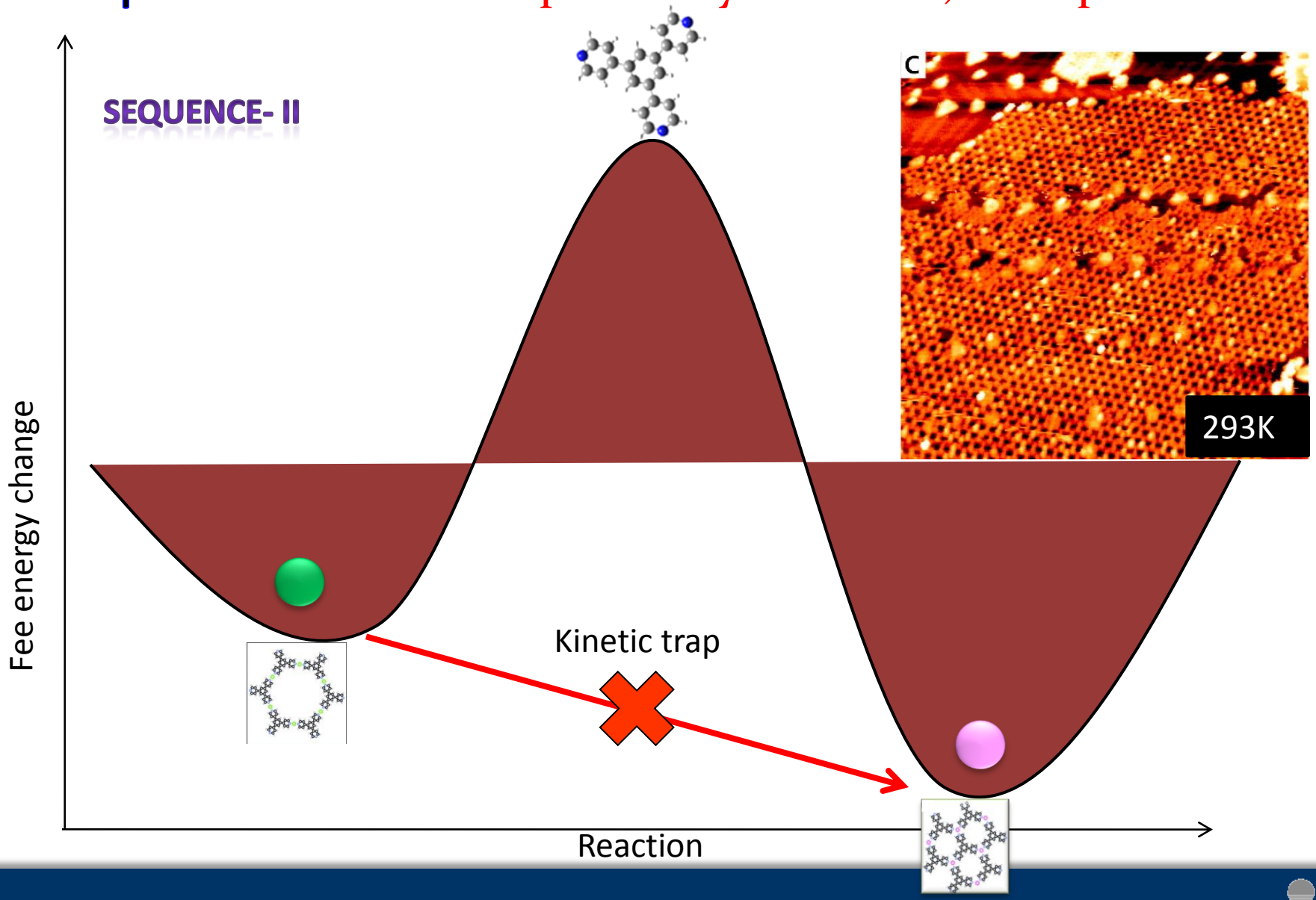
Fe●TPyB network



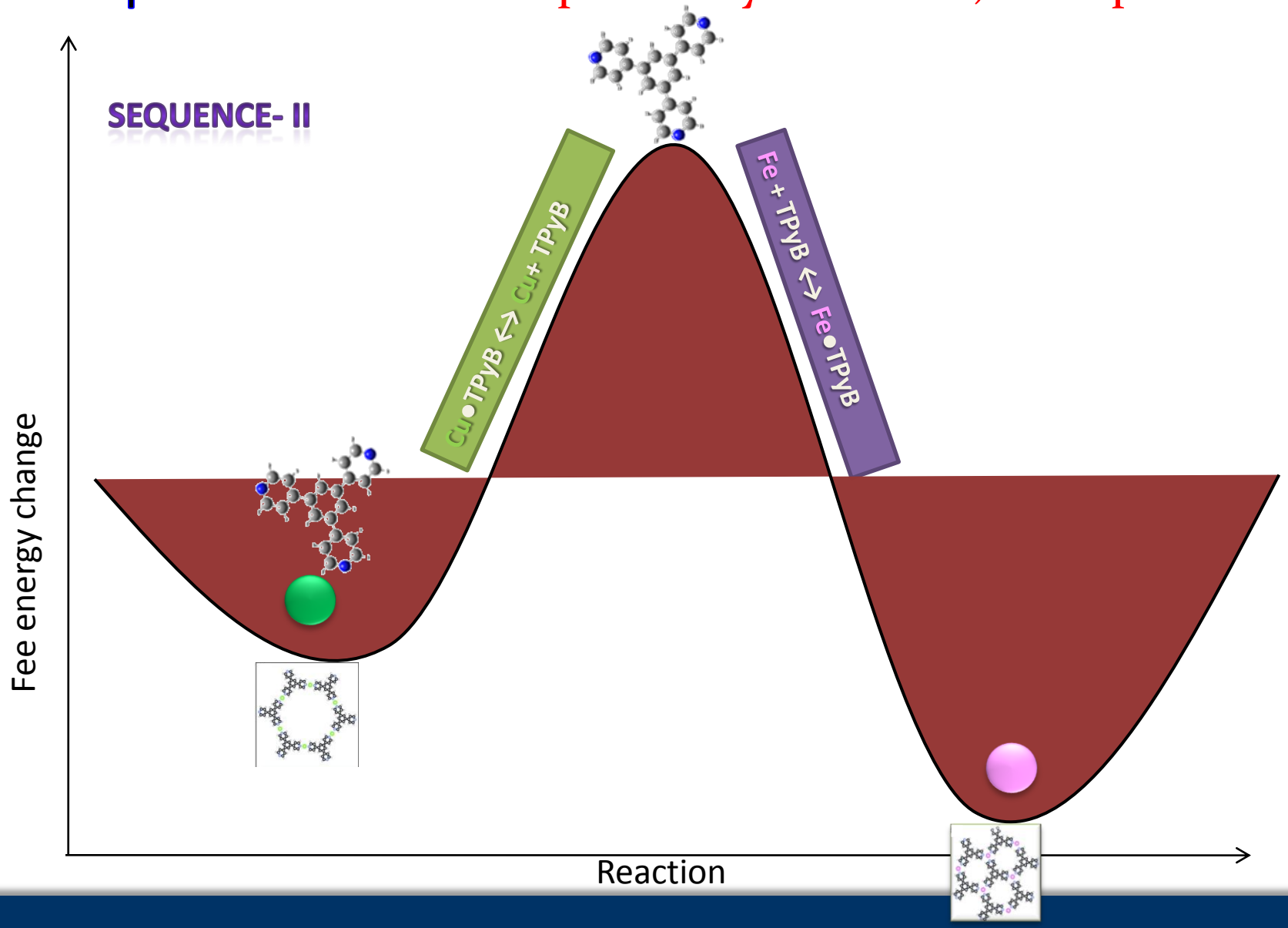
Cu + TPyB ↔ Cu●TPyB

T_{Cu}~600K

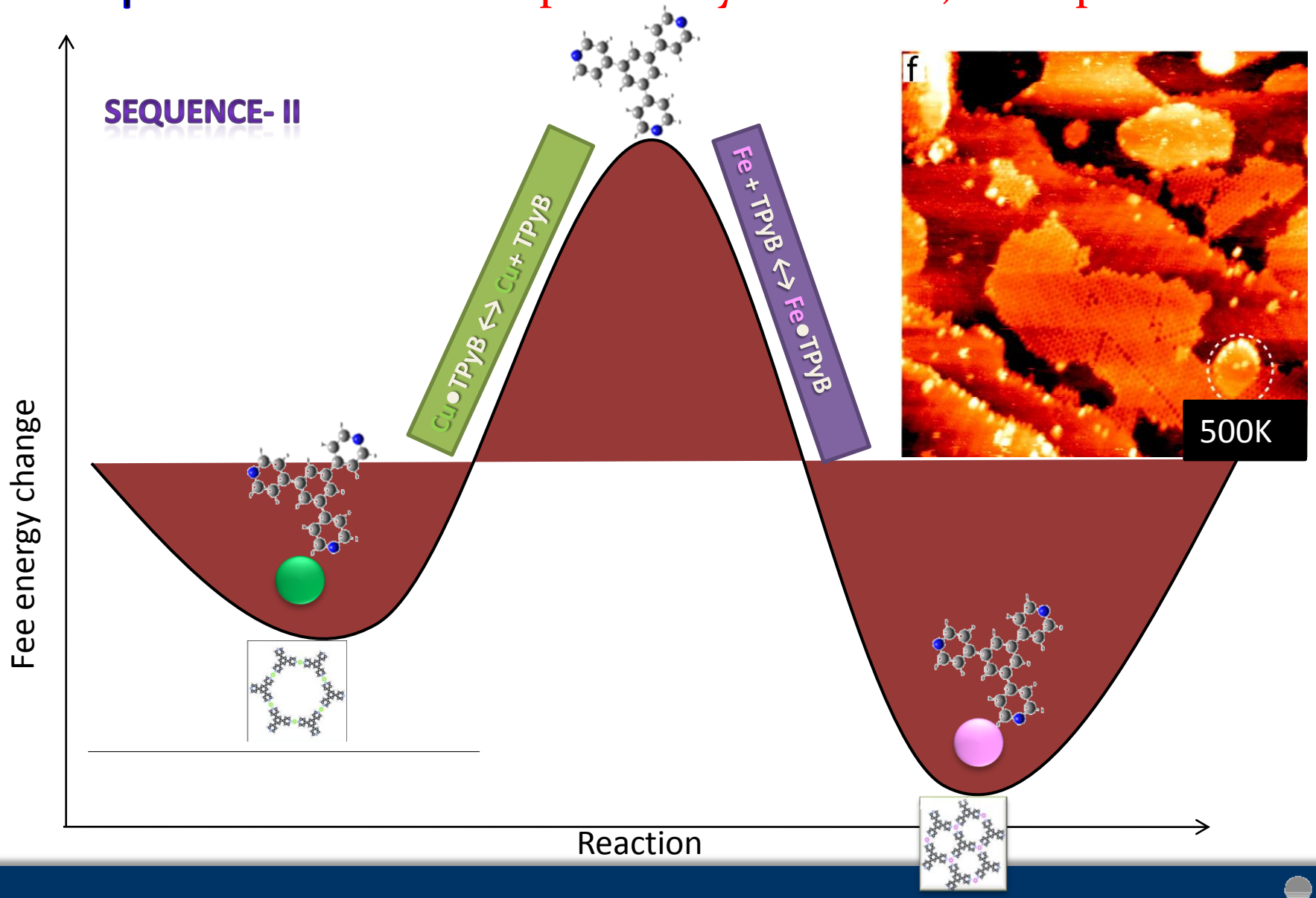
Sequence-II 1. codeposit TPyB and Cu; 2. deposit Fe



Sequence-II 1. codeposit TPyB and Cu; 2. deposit Fe



Sequence-II 1. codeposit TPyB and Cu; 2. deposit Fe



2. Structural and chemical controls through

a) modifying the chemical states of the organic components;

TPyP on Au(111), TPyP-Cu on Au(111)

b) tuning the external environments;

TPyP-PBTP

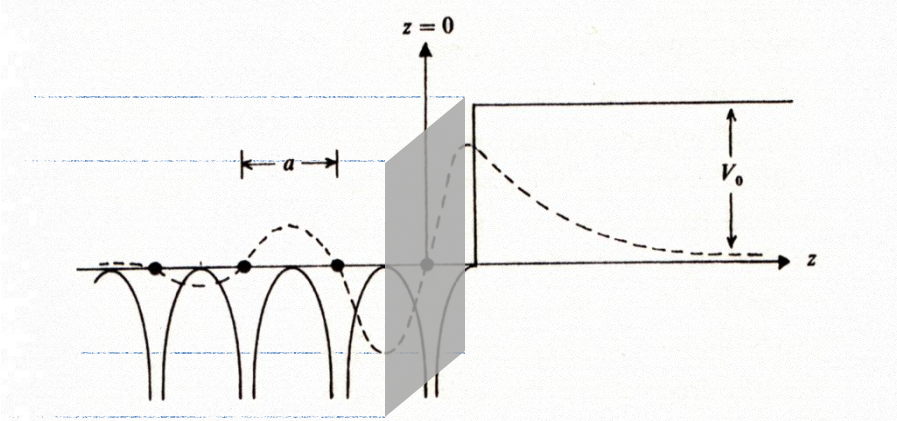
c) controlling the thermodynamic and kinetic process;

TPyB-Cu and TPyB-Fe

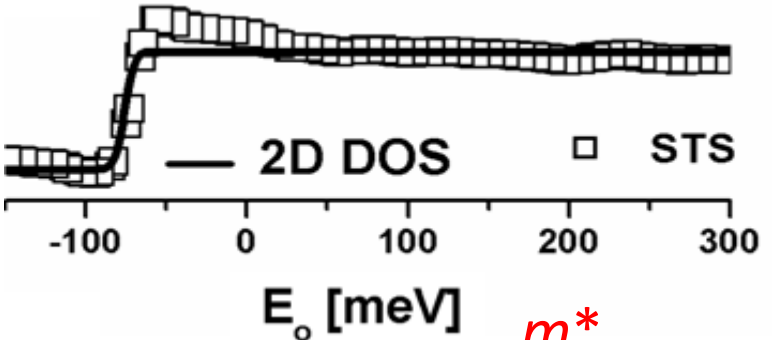
3. Electronic states of artificial "quantum dots"

TPyB-Cu on Au(111), TPyB-Cu on Cu(111)

Surface-electron state of at surface of a crystal

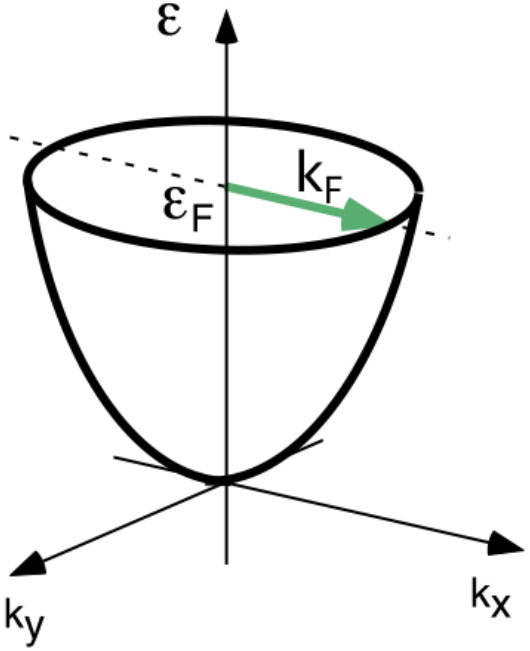


- Scanning tunneling spectroscopy (STS)



$$\rho(E) = \text{const.} = \frac{m^*}{\pi \hbar^2}$$

- Parallel to the surface : plane wave

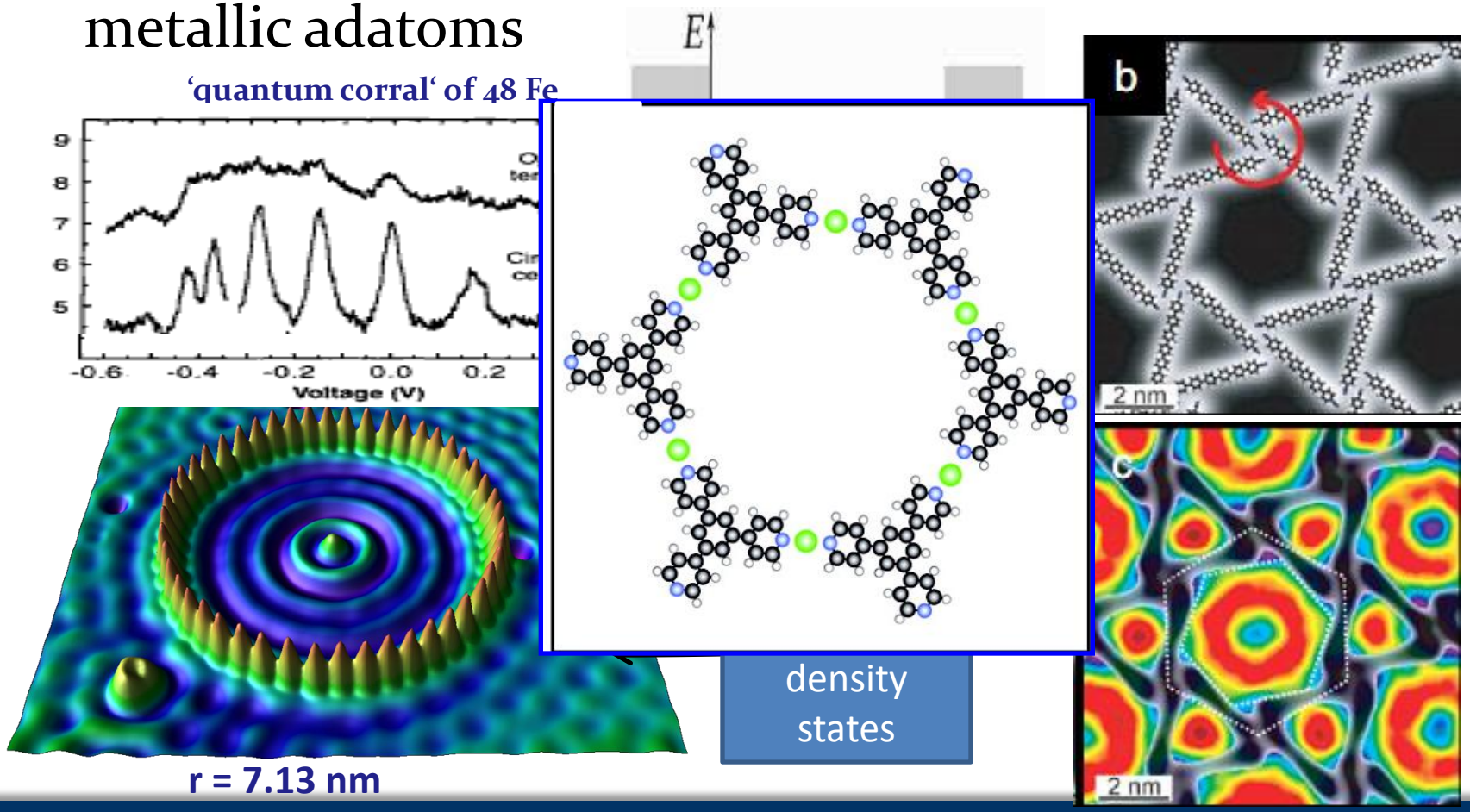


- Near free electrons: Parabolic E~k dispersion

F. Klappenberger, the presentation in visiting HKUST (2009)
Y. Pennec, et al., Nature Nanotech. 2, 99 (2007).

Effective potentials for surface state confinement

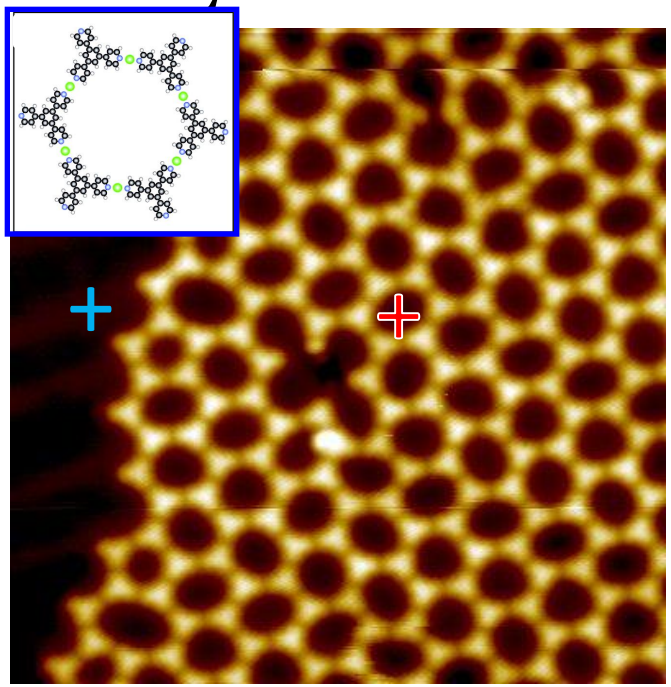
- Quantum corrals of metallic adatoms
- Organic adsorbates

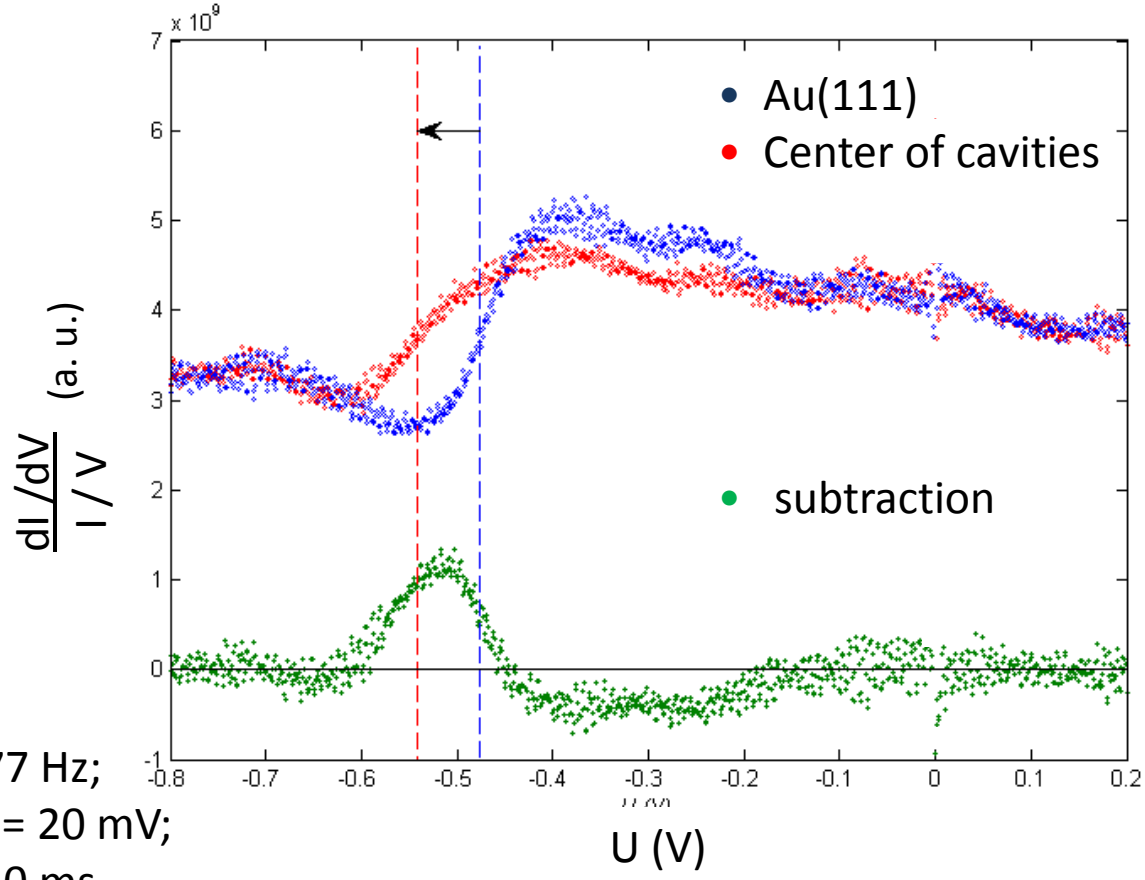


http://plus.maths.org/content/schrodingers-equation-action
*Crommie, Lutz & Eigler, Science **264,** 218 (1993)*
F. Klappenberger, et al. Nano Lett. 9, 3509 (2009)

Modulation of surface electronic states by 2D coordination networks

- STS of the center of cavities ("quantum dots") of TPyB-Cu network



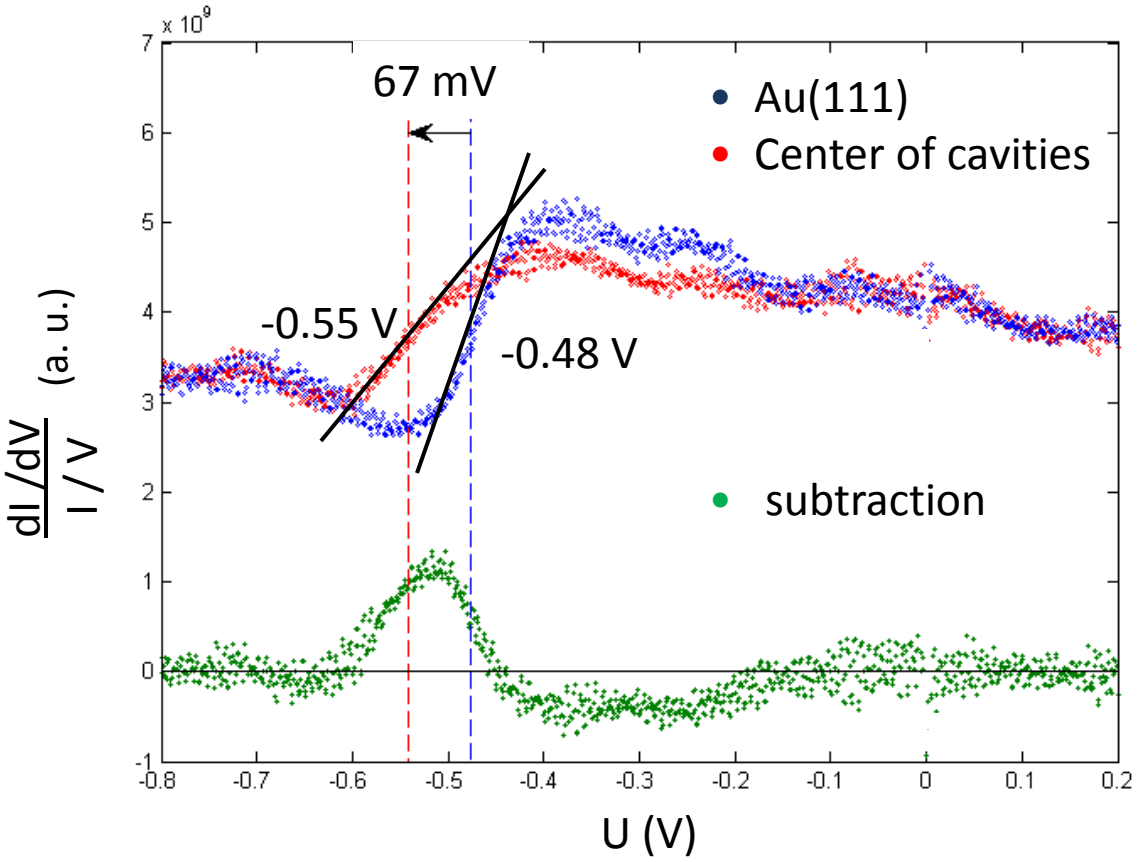


Setpoints: U = +0.1 V, I = 20 pA; 77K.

Lock-in: f = 1777 Hz; V(modulation) = 20 mV; Time const. = 30 ms.

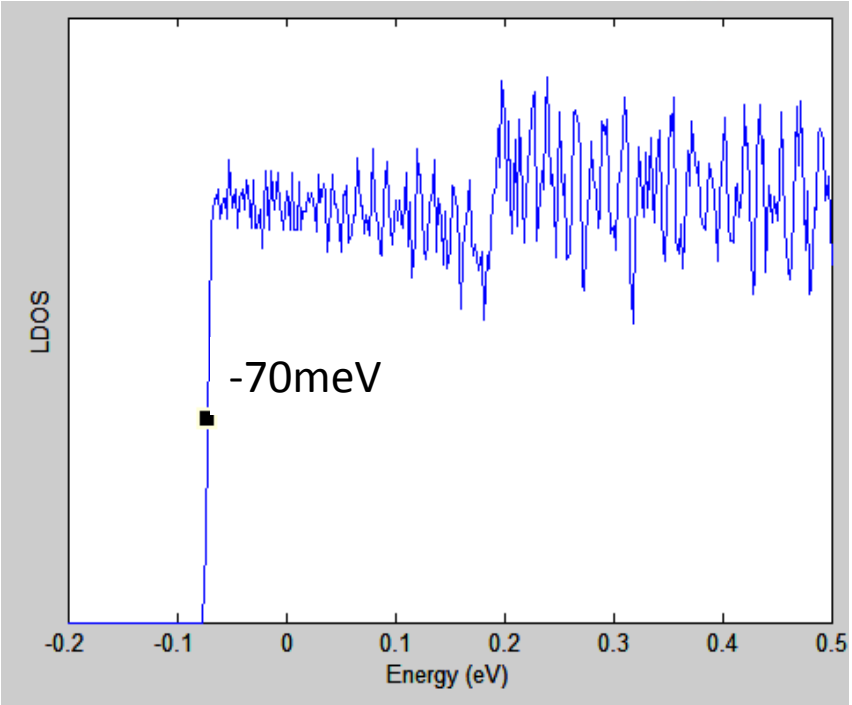
Modulation of surface electronic states by 2D coordination networks

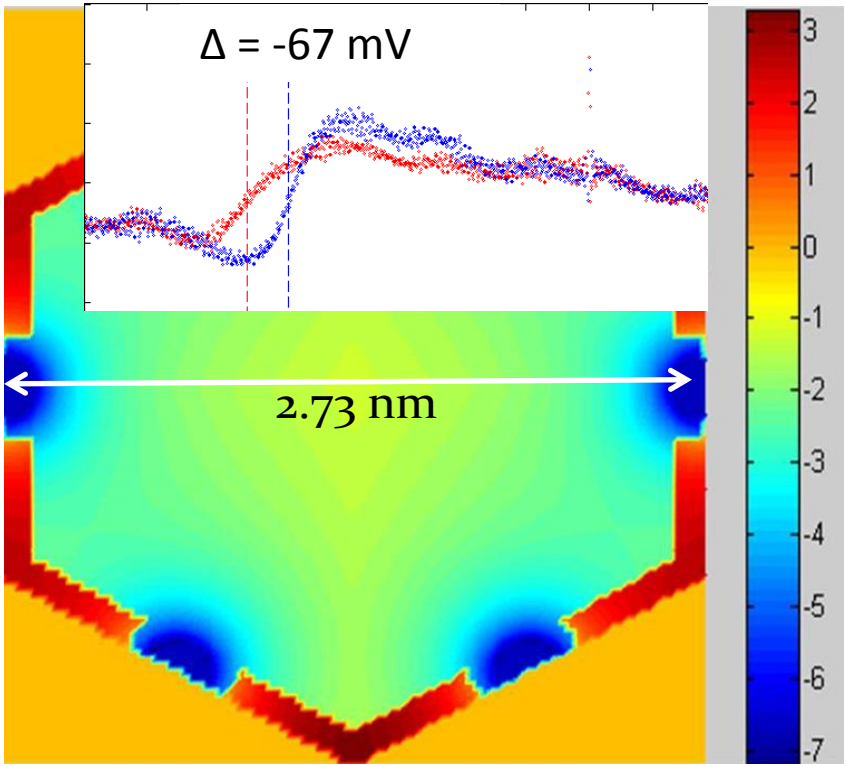
- Downshift of the onset - new states on lower energy levels
- broadening of the slope



Modelling the effective potentials

- Solving the Schrödinger equation of free electrons modulated by a periodic potential



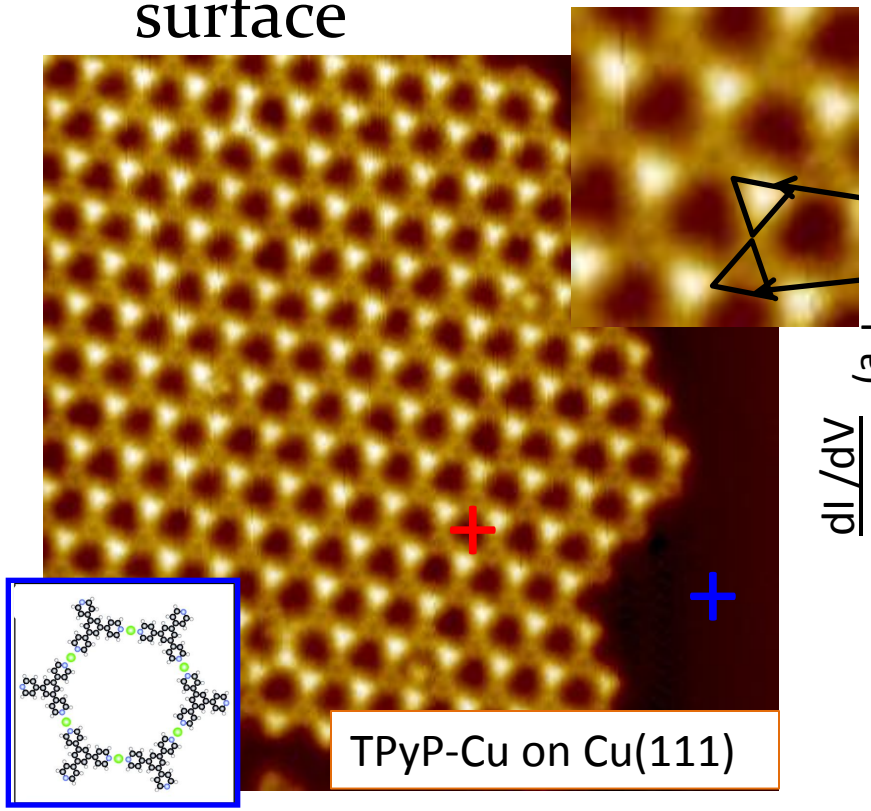


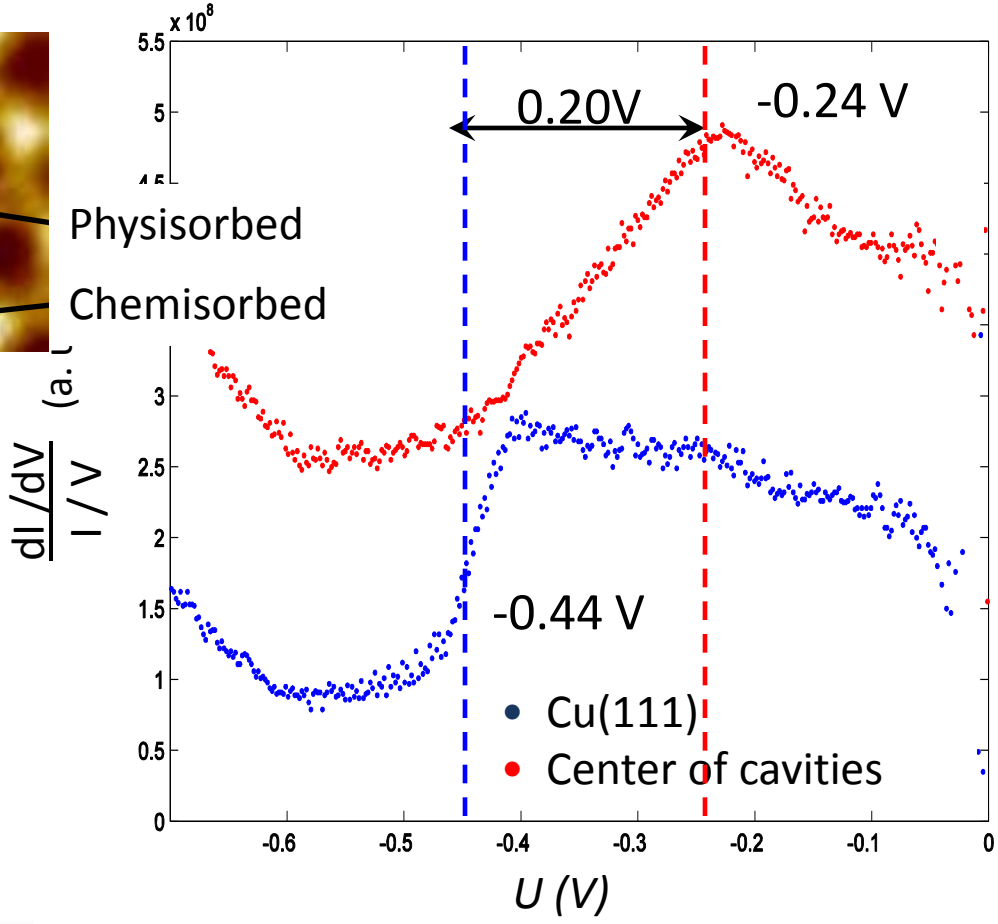
Vm = 100 meV; Vcu = - 220 meV;

The simulations were conducted by Mr. ABRAHAMSSON Richard and Mr. NG Ka Long Gary.

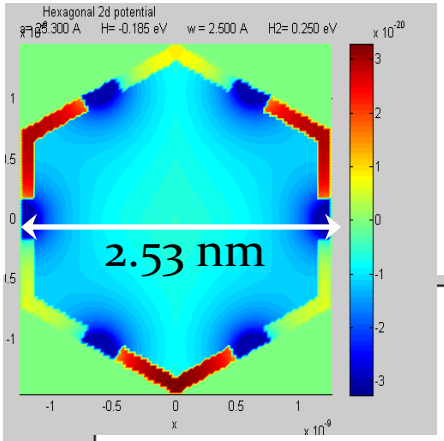
Tailoring the effective potential

- One type of TPyB-Cu coordination networks on Cu(111) surface



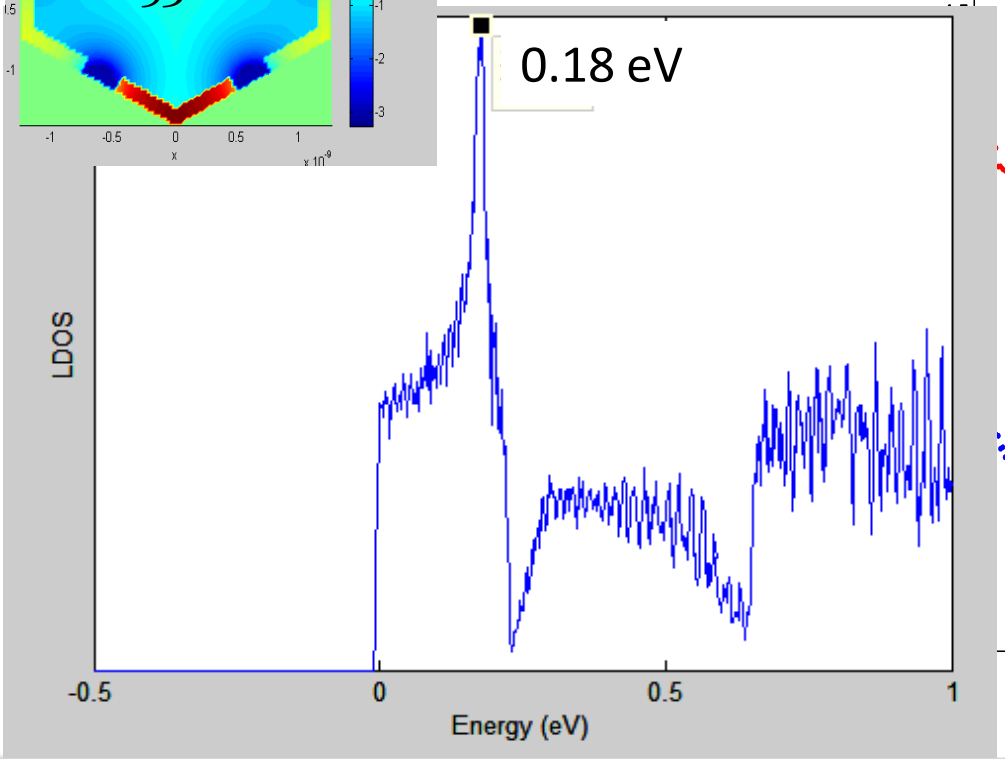


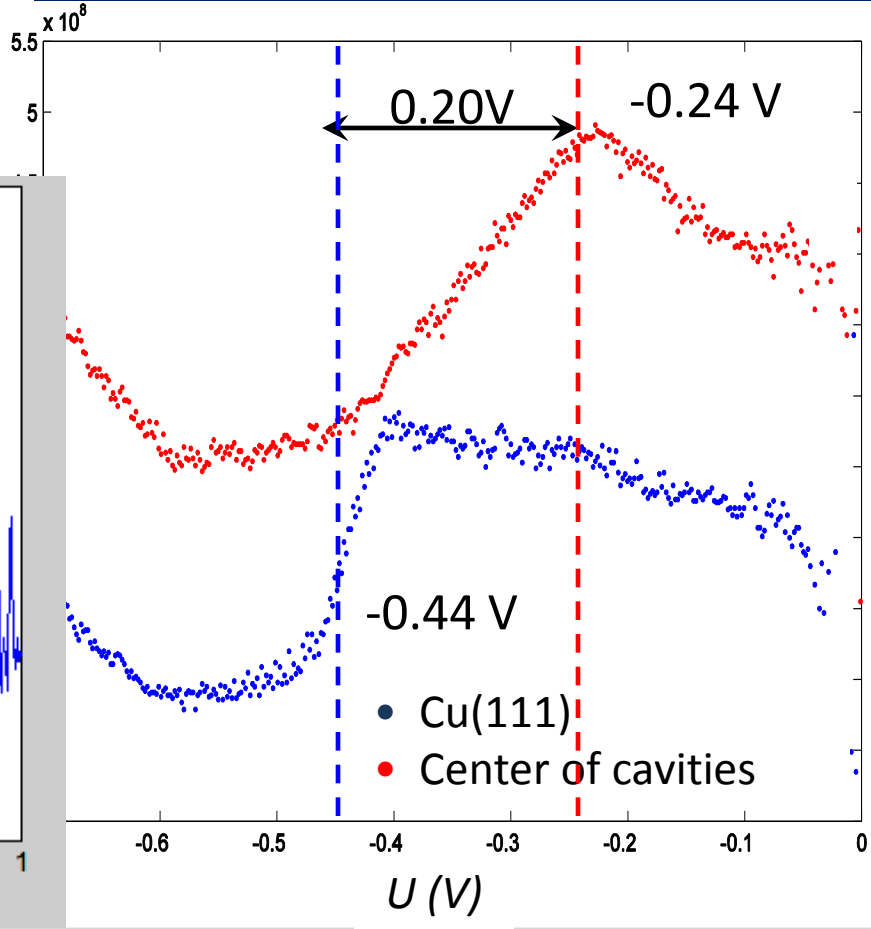
Tailoring the effective potential

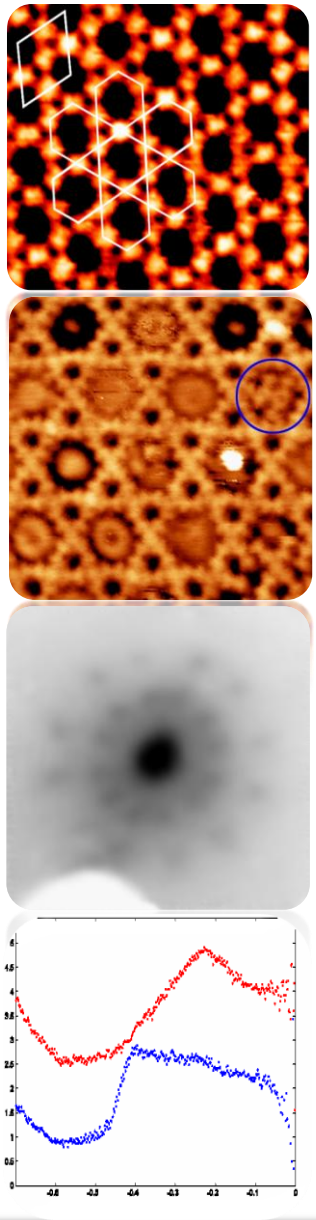


Vm = 100 meV;
(Physisorbed)
Vcu = - 185 meV;

Vm' = 800 meV (Chemisorbed)







SUMMARY

- Controlling supramolecular self-assembly via the strategy of

  a) modifying the chemical states of the organic components;

  b) tuning the external environments

  c) controlling the thermodynamic and kinetic process;

- Electronic states of artificial “quantum dots”

Publications

1. Y. Li, J. Xiao, T. Shubina, M. Chen, Z. Shi, M. Schmid, H-P. Steinrück, M. Gottfried, N. Lin, ***J. Am. Chem. Soc.*** 134, 6401 (2012)
2. J. Liu, T. Lin, Z. Shi, F. Xia, L. Dong, P. N. Liu, N. Lin, ***J. Am. Chem. Soc.*** 133, 18760 (2011)
3. Z. Shi, T. Lin, J. Liu, P. N. Liu, N. Lin, ***CrystEngComm*** 13, 5532 (2011)
4. Z. Shi, J. Liu, T. Lin, F. Xia, P. N. Liu, N. Lin, ***J. Am. Chem. Soc.*** 133, 6150 (2011)
5. Z. Shi, N. Lin, ***J. Am. Chem. Soc.*** 132, 10756 (2010).
6. Z. Shi, N. Lin, ***ChemPhysChem*** 11, 97, (2010)
7. Z. Shi, N. Lin, ***J. Am. Chem. Soc.*** 131, 5376 (2009).
8. Y. Ning, J. Jiang, Z. Shi, Q. Fu, J. Liu, Y. Luo, B. Z. Tang, N. Lin, ***J. Phys. Chem. C***, 113, 26 (2009).

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  - Mr. WANG Shiyong
  - Mr. LIN Tao
  - Mr. CHENG Chen
  - Dr. WANG Weihua
  - Dr. DONG Lei
  - Dr. ADISOEJOSO Jinne
- Former members:
  - Mr. LI Yang
  - Dr. THAKUR Ram-Krishna
  - Dr. NING Yuesheng

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❖ **Collaborators:**

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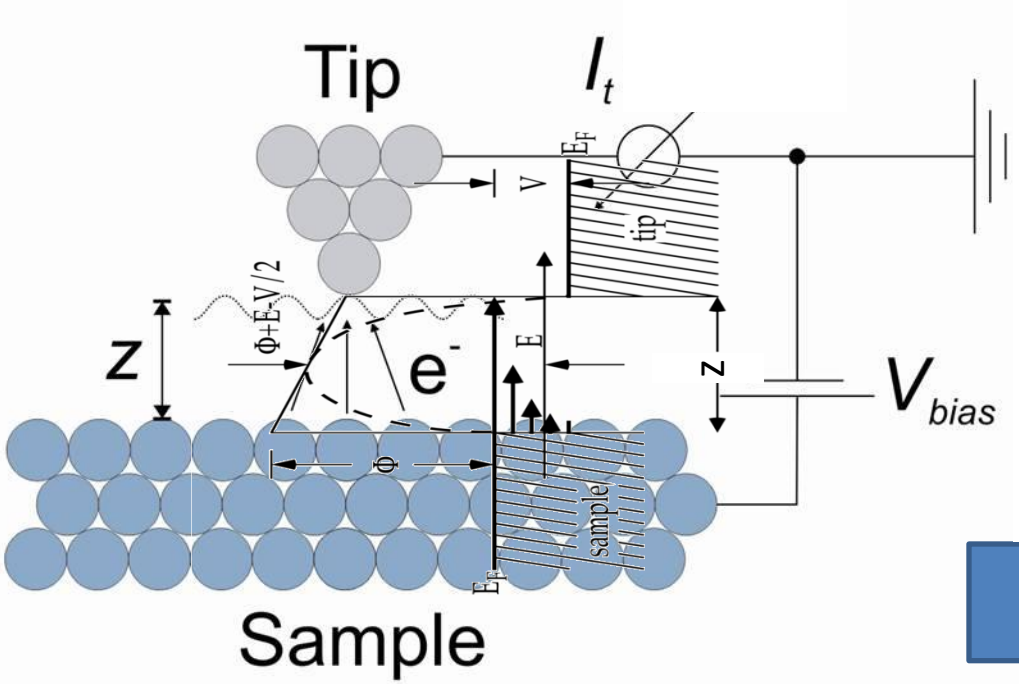
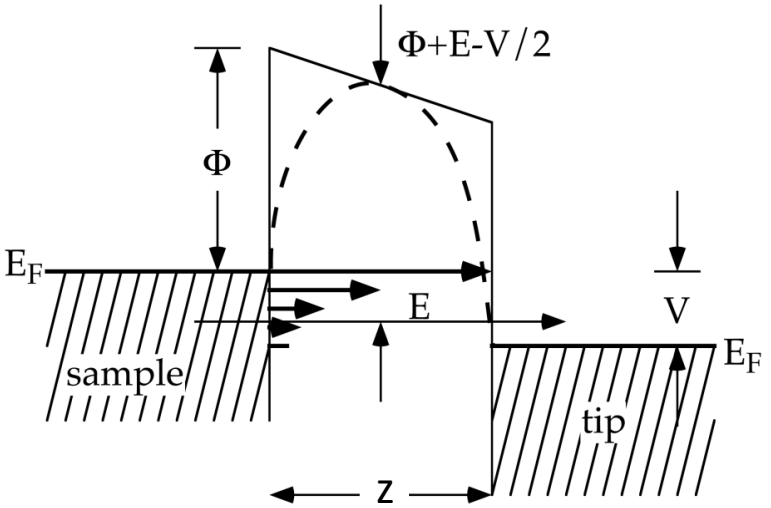
  - Prof. ALTMAN Michael
  - Prof. WEN Weijia
  - Prof. TANG Benzhong
  - Prof. GOTTFRIED Michael
  - Prof. XU Jianbin

Thanks For Your Attention!

STM

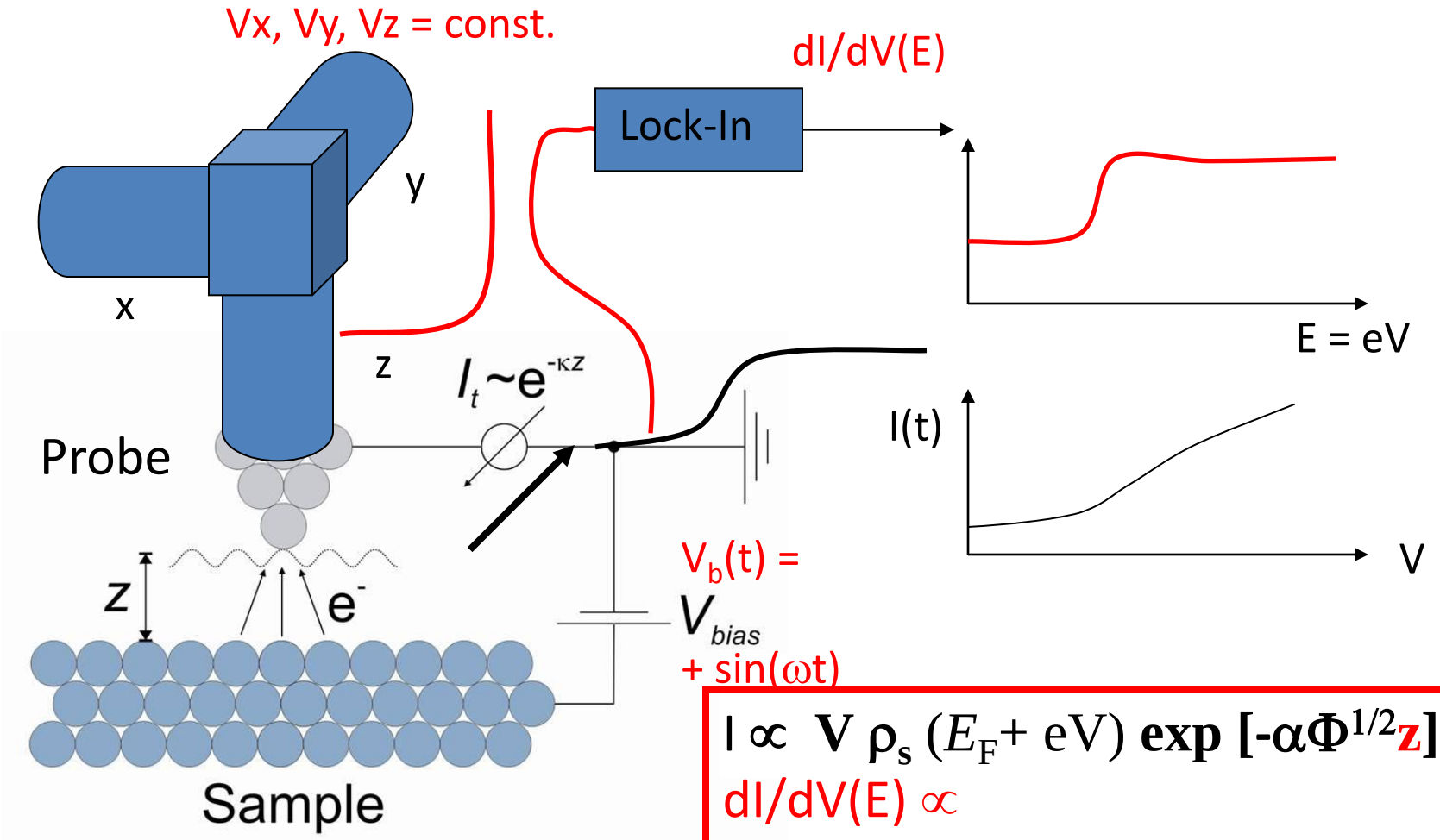
- Scanning tunneling microscopy (STM) on the self-assembly patterned surface





$$I_t \propto V \rho_s(E_F) \exp[-\alpha \Phi^{1/2} z]$$

Low-temperature scanning tunneling spectroscopy (LT-STS)



$$I \propto V \rho_s (E_F + eV) \exp[-\alpha \Phi^{1/2} z]$$

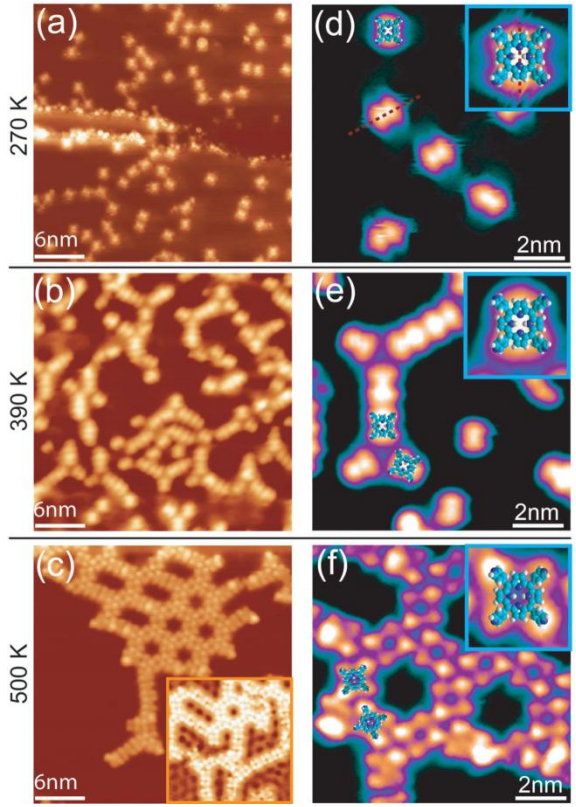
dI/dV(E) ∝ density of states (E)

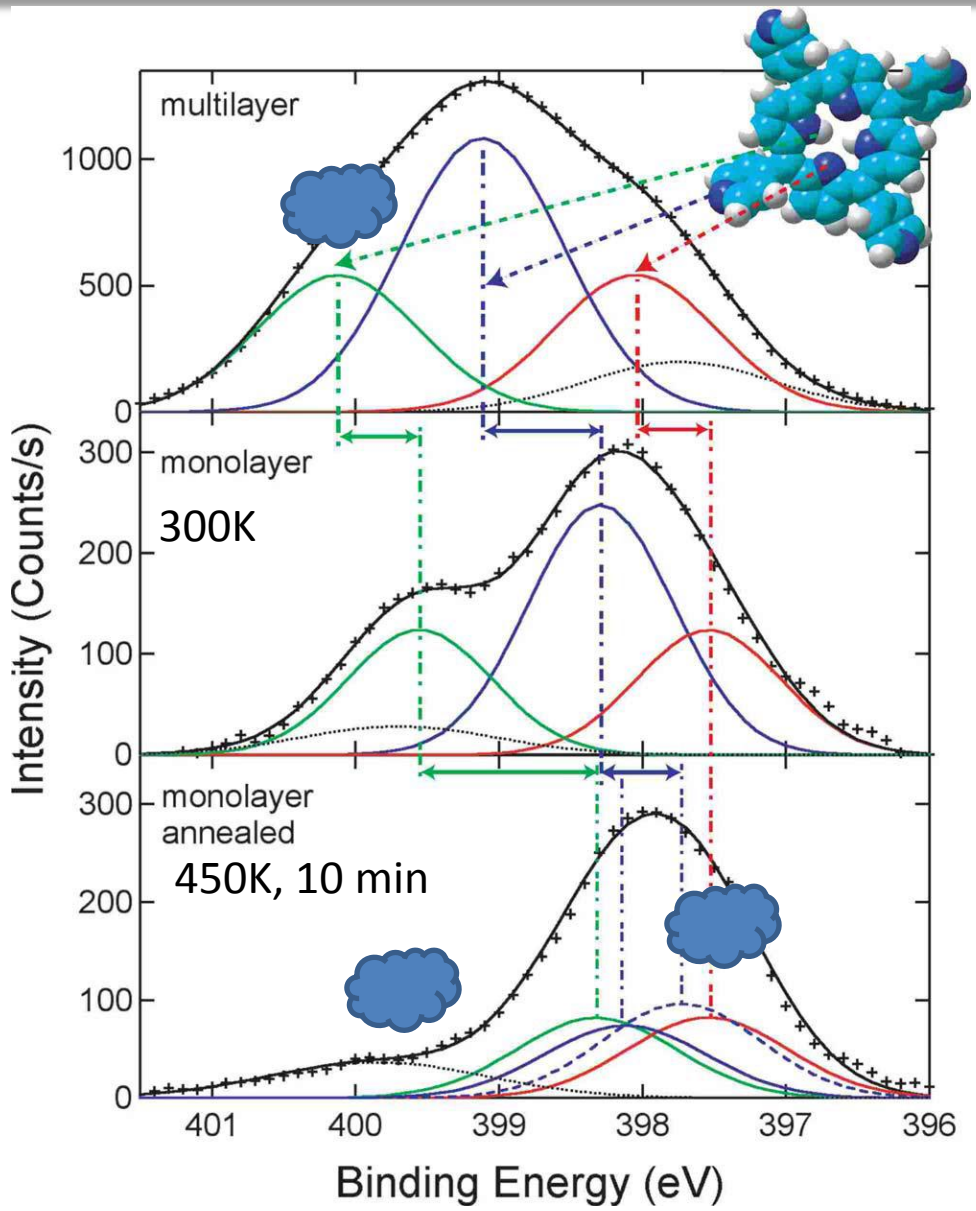
Au-py Kagome models

Since we can address the orientation of the Au (111) lattice by imaging the herringbone reconstruction, in the model, we have slightly adjust the network with a side length 1 angstrom shorter than the stm measurement, so that all TPyP sit on the same sites of the surface, the top sites. This is reasonable considering the externded network might commensurate with the surface lattice. in such a model, Au atoms are put in the middle way of two neighboring nitrogens, this arrangement also allows the Au atoms exactly sit on the bidge sites of the Au surface. here, the Au-py bonds is 2.4 angstrom that lays in the previously reported Au-py lengths in 3D.

TPyP on Cu(111)

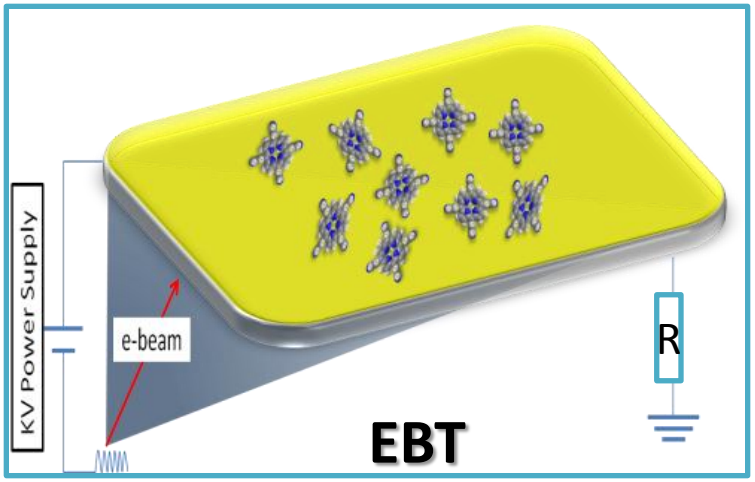
F. Klappenberger, et al., J. Chem. Phys. 2008, 129, 214702.



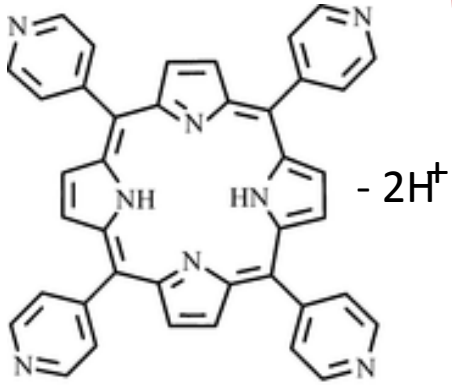


Modification of chemical states

- Proposed mechanism - Deprotonation



Deprotonation



$- 2H^+$

Au-py coordination

Modified chemical state

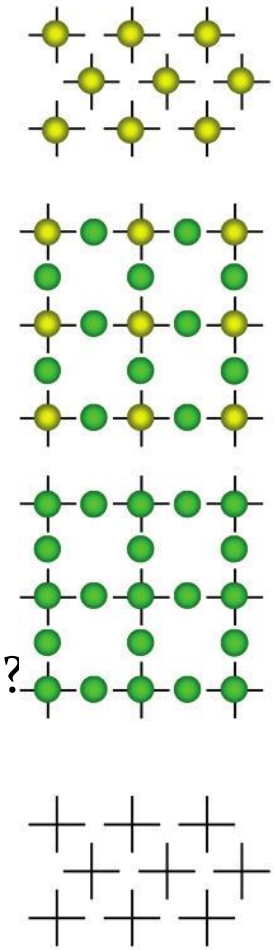
Co-deposition of Cu and TPyP on Au(111) surface

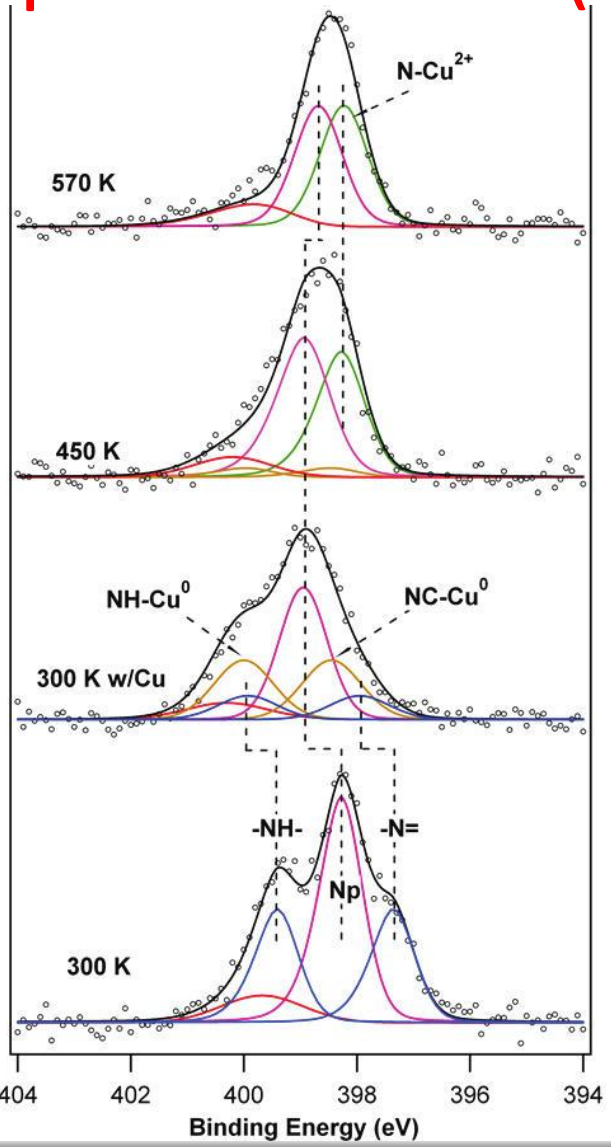
On Cu (111), "*Annealing the sample to high temperatures (500K) leads to a deprotonation of the macrocycle*". [F. Klappenberger et al., 2008].

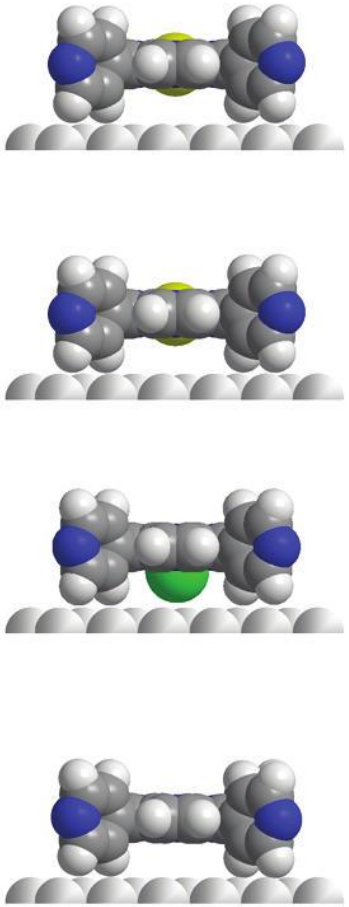
F. Klappenberger, et al., J. Chem. Phys. 2008, 129, 214702.

XPS of TPyP-Cu codepostion on Au(111)

- No deprotonation stage observed
- Small Kagome coverage
- 570K. Deprotonation state not stable?
- No deprotonation?
- Au-metallation?







Y. Li, *et al.*, ***J. Am. Chem. Soc.*** 134, 6401 (2012)

TPyP-Cu on Ag(111) without annealing