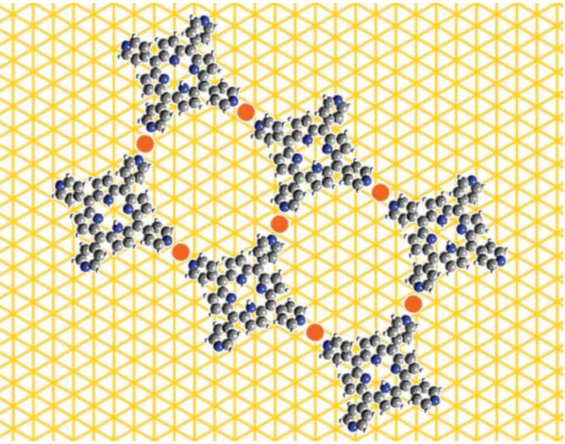
Hong Kong University of Science and Technology
Defense for MPhil in Physics

Kinetics and Functionality of Cu-coordinated Pyridyl-porphyrin Supramolecular Self-assembly on a Au(111) Surface



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2012-08-08

→Outline

1. Introduction

What is Supramolecular Self-assembly

2. Kinetics

2D porphyrin network growth

3. Design

Internal molecular codes & external variables

4. Functionality

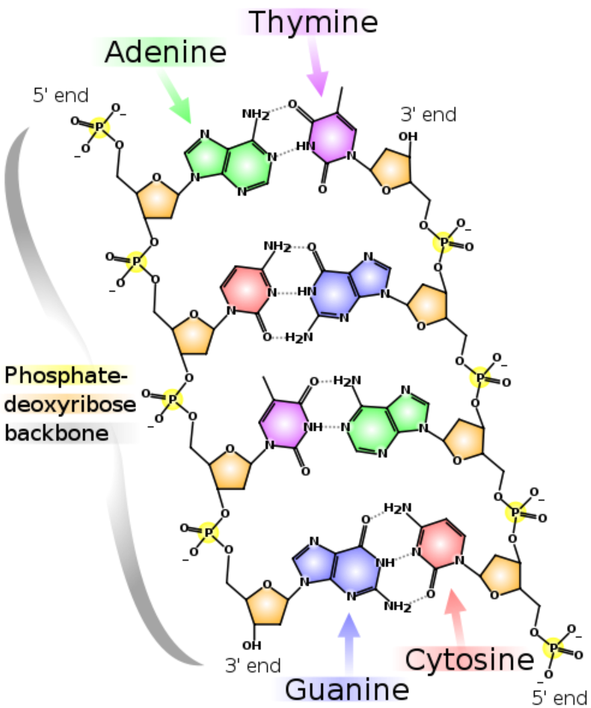
Coordination and metalation bifunctionality

5. Conclusions & Perspectives

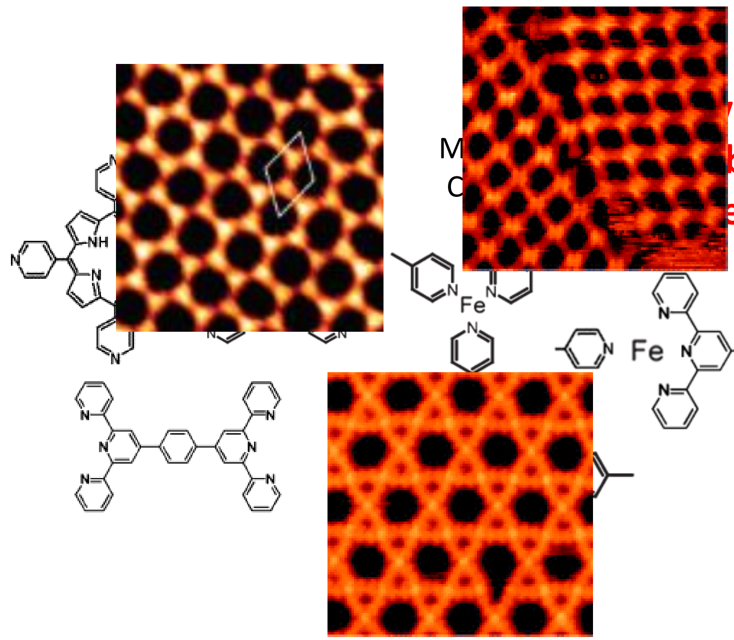
→1. Introduction

1.1 Supramolecular self-assembly

DNA double helix



Metal-organic networks



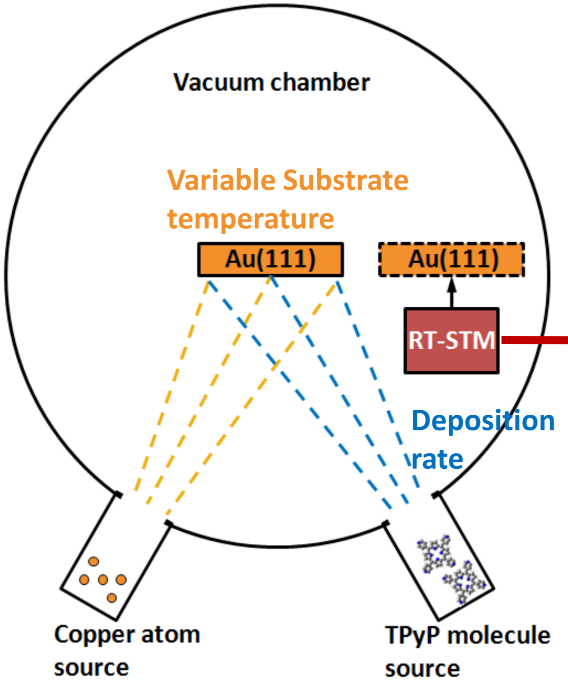
M
C

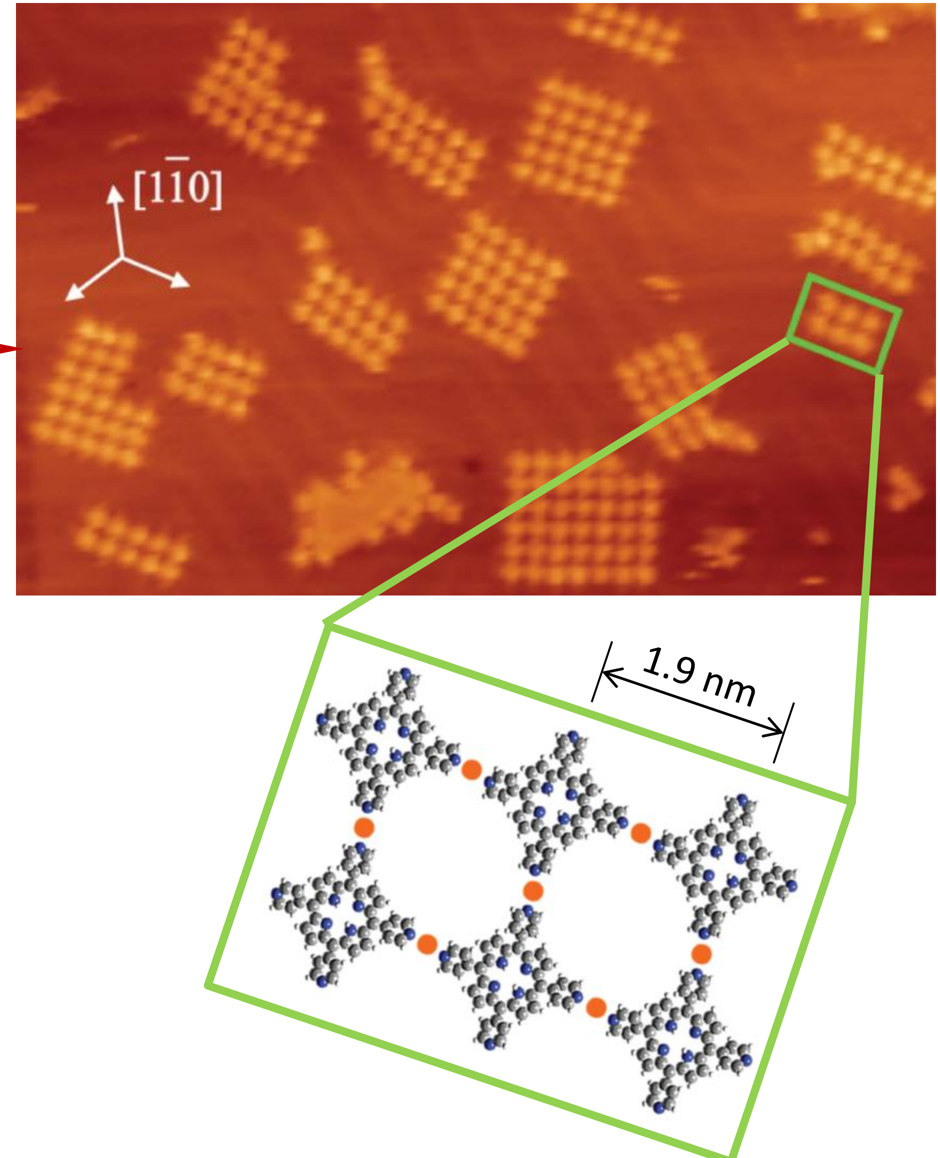
versible
ble (>H bond)
ectional

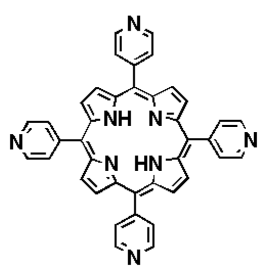
http://en.wikipedia.org/wiki/DNA
Ziliang Shi *et al.*, *J. Am. Chem. Soc.* **131**, 5376 (2009); **132**, 10756 (2010); **133**, 6150 (2011);

→1. Introduction

1.2 experimental setup & the system that we studied





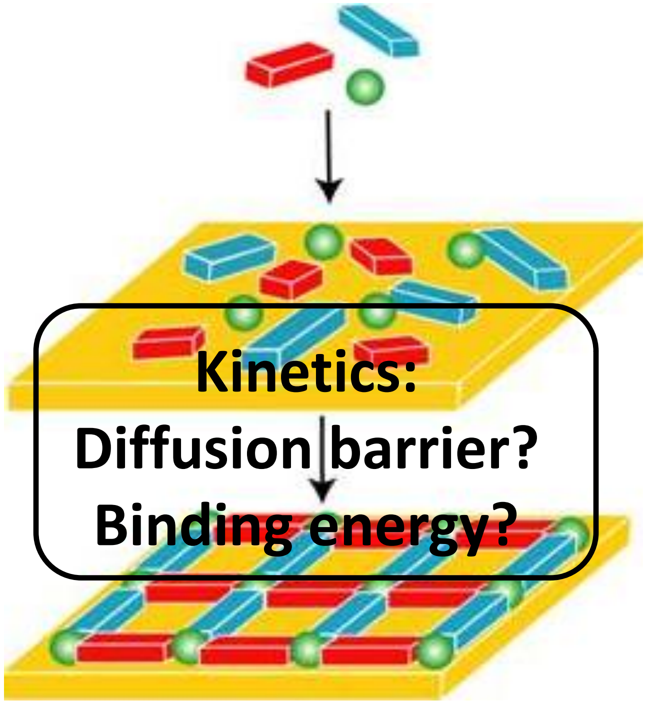


TPyP
(tetra-pyridyl porphyrin)

Metal-organic coordination network

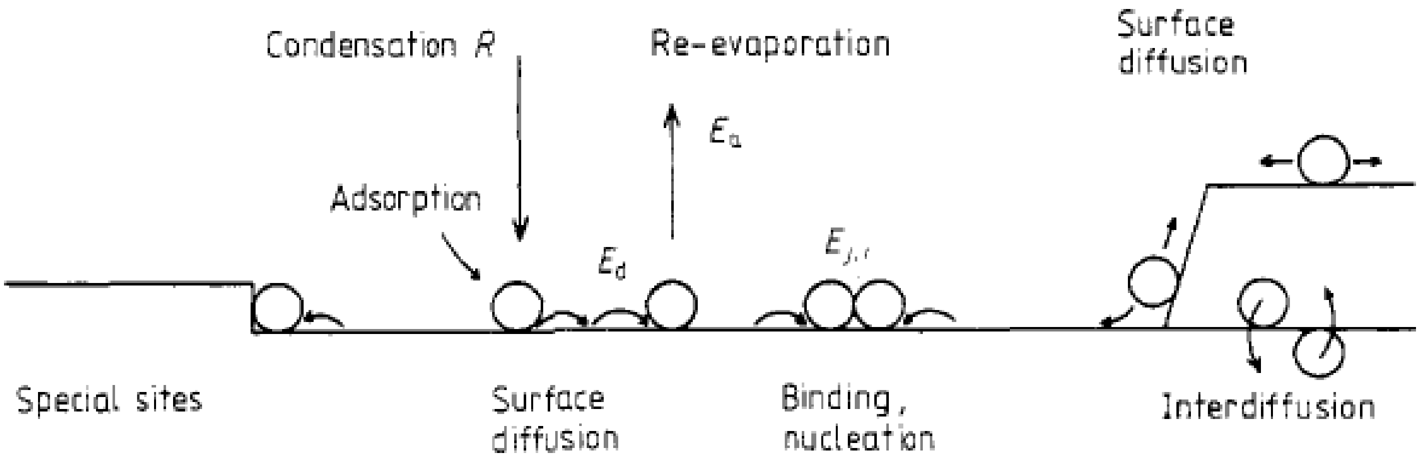
→2. Kinetics

Kinetics of Cu-coordinated pyridyl-porphyrin supramolecular self-assembly on Au(111) surface



→2. Kinetics

2.2 Nucleation & Growth Theory in atomic epitaxy



-Critical nucleus size i (size of smallest stable island)

-Binding energy E_b (involved in E_i, total binding energy of one island with size=i)

-Diffusion barrier E_d

$$n_x \sim \eta(\theta, i) \left(\frac{R}{\nu_0}\right)^{\frac{i}{i+2}} \exp\left(-\frac{1}{kT}\frac{E_i + iE_d}{i+2}\right)$$

-island density

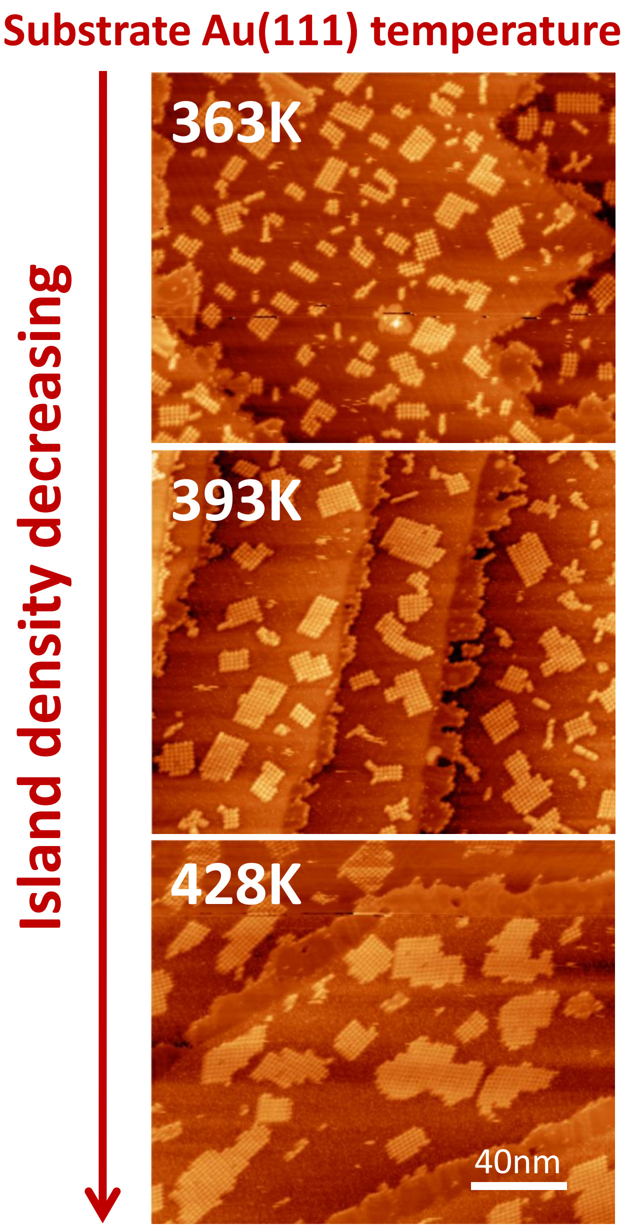
-Deposition rate R

-Substrate temperature T

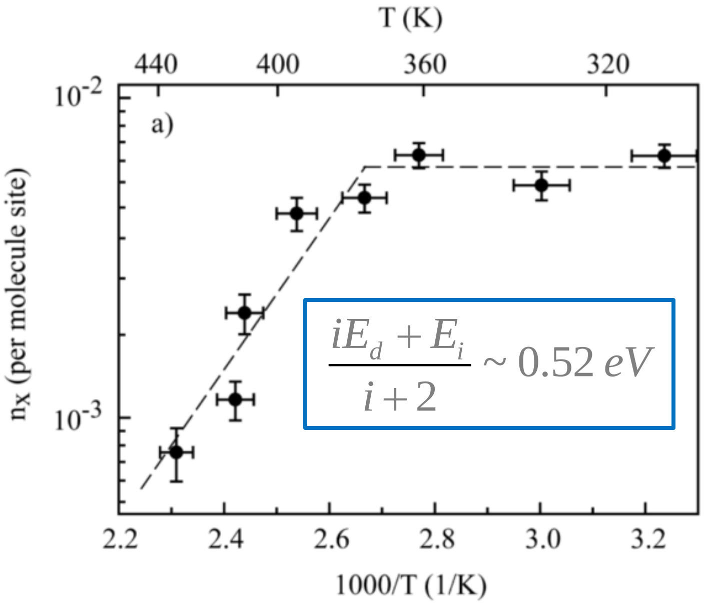
Venables JA *et al.*, *Rep. Prog. Phys.* **47**, 399-459 (1984); Bert Müller *et al.*, *Phys. Rev. B* **36**, 4153 (1987)

→2. Kinetics

2.3 Island density vs. substrate temperatures



$$n_x \sim \eta(\theta, i)\left(\frac{R}{\nu_0}\right)^{\frac{i}{i+2}} \exp\left(-\frac{1}{kT}\frac{E_i + iE_d}{i+2}\right)$$



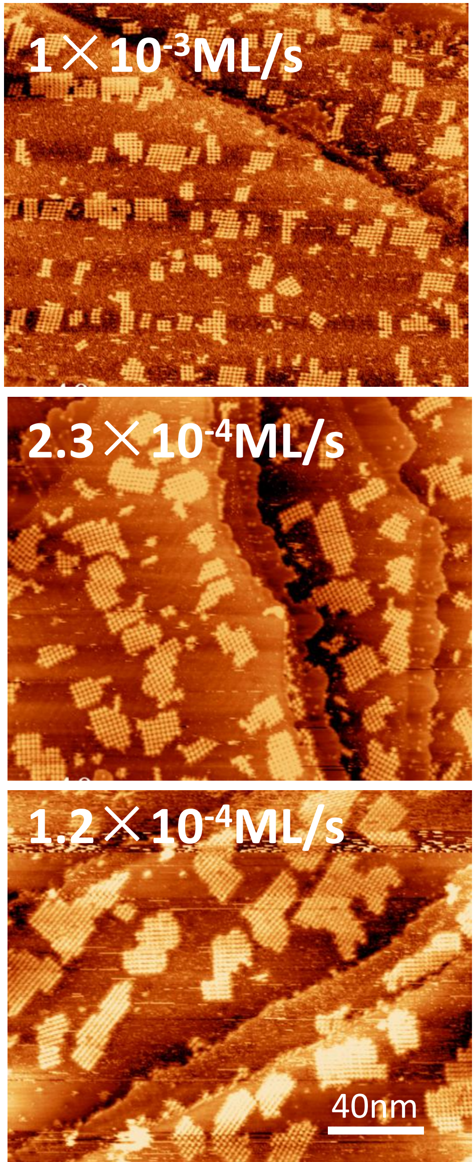
$$\boxed{\frac{iE_d + E_i}{i+2} \sim 0.52\ eV}$$

→2. Kinetics

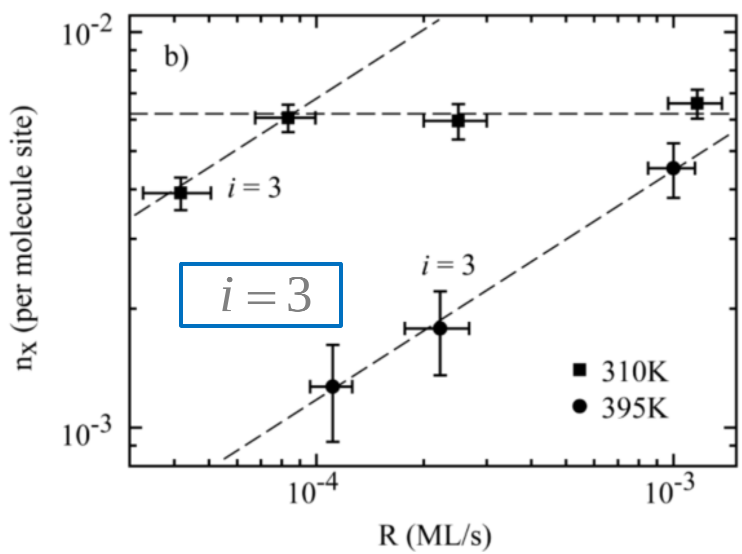
2.3 Island density vs. deposition rate

Molecule deposition rate

Island density decreasing



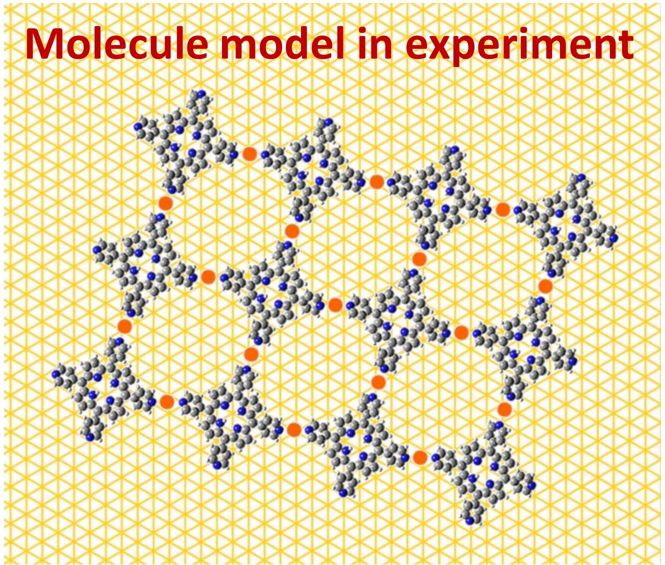
$$n_x \sim \eta(\theta, i)\left(\frac{R}{\nu_0}\right)^{\frac{i}{i+2}} \exp\left(-\frac{1}{kT}\frac{E_i + iE_d}{i+2}\right)$$

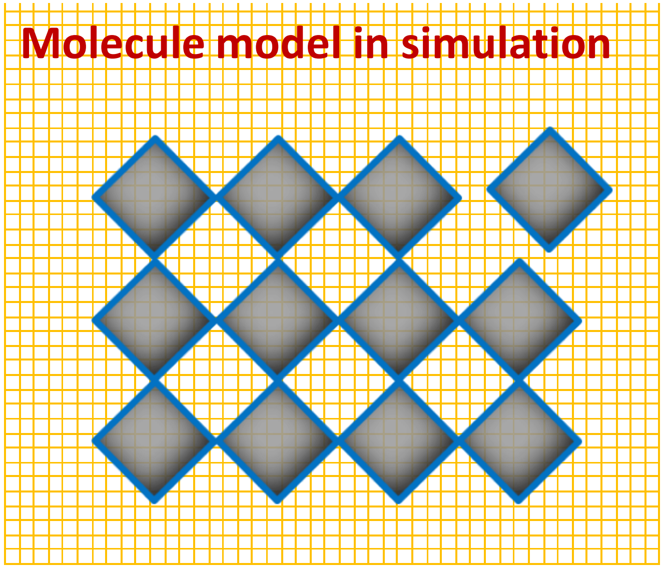


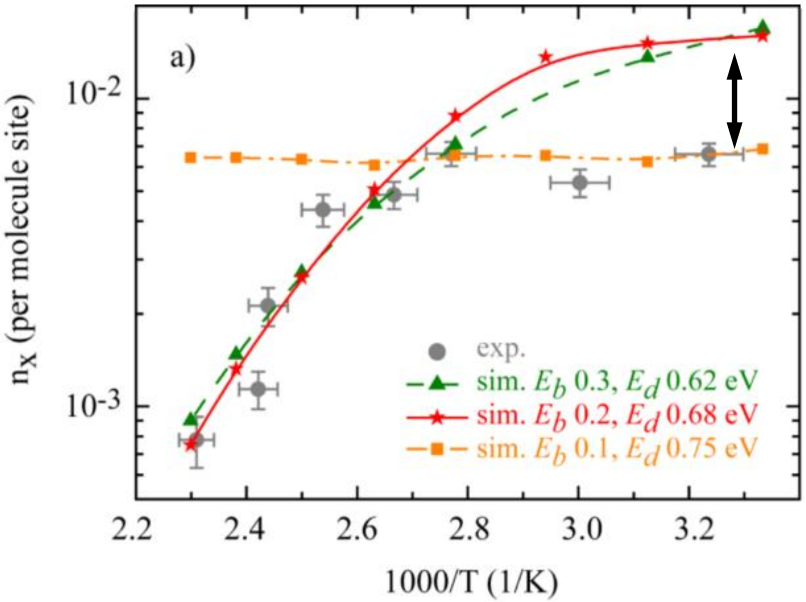
$$\boxed{3E_d + 2E_b \sim 2.6\, eV}$$

→2. Kinetics

2.4 Kinetic Monte Carlo simulation







Porphyrin dimers diffuse more rapidly than monomer.

*M. Eichberger *et al.*, *Nano Lett.* **8**, 4608 (2008)

→2. Kinetics

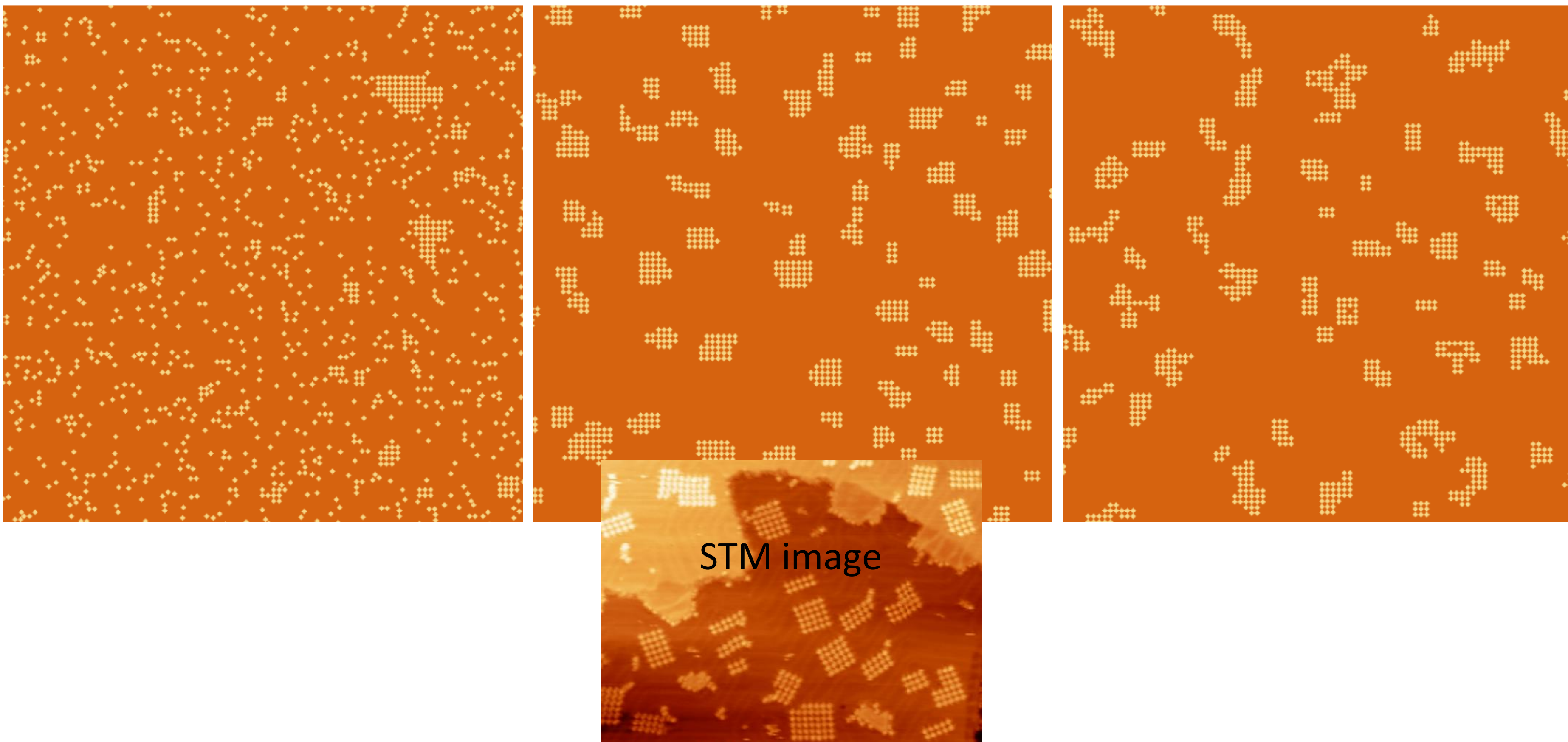
2.4 Kinetic Monte Carlo simulation

Simulated topographies with different energies:

E_b=0.10eV
E_d=0.75eV

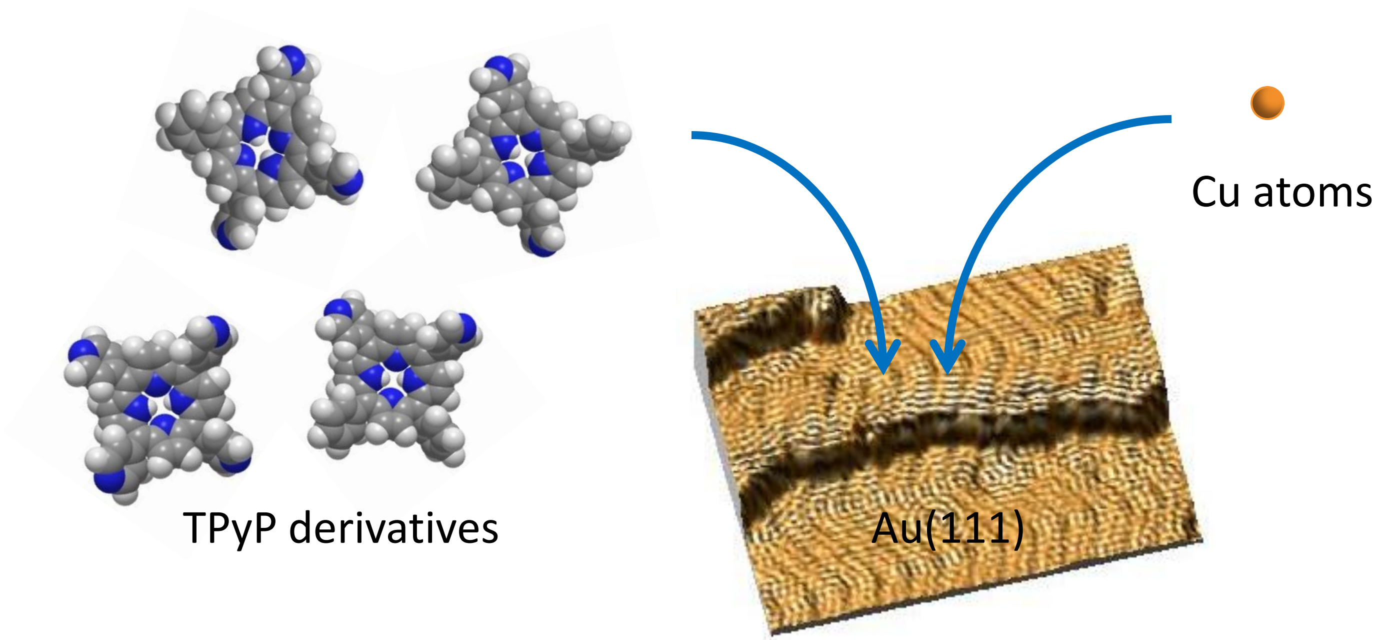
E_b=0.20eV
E_d=0.68eV

E_b=0.30eV
E_d=0.62eV



→3. Design

Revealing supramolecular self-assembly regulated by internal molecular codes and external variables

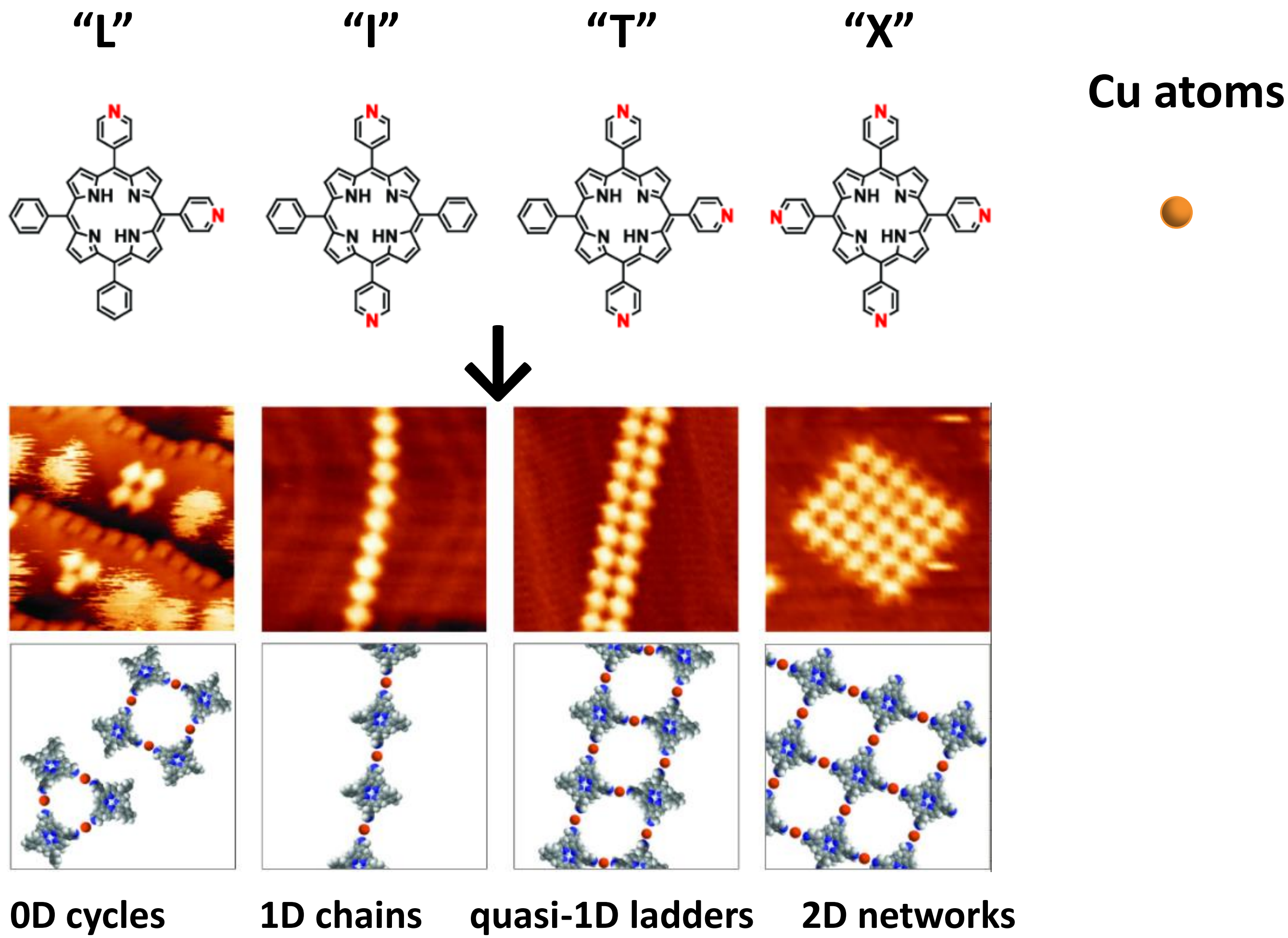


Can we design and build nanostructures in low dimension?

→3. Design

3.2 Internal molecular code

Implant information into building blocks:

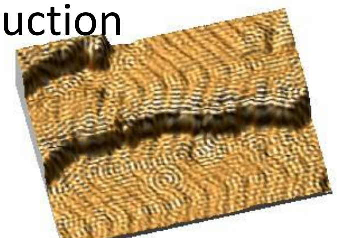


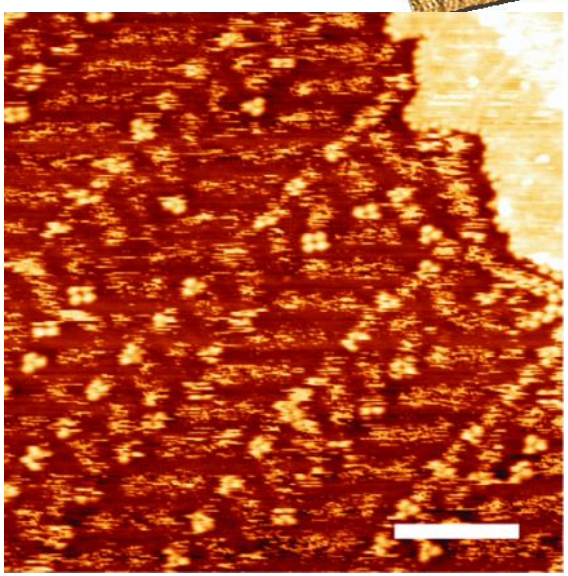
→3. Design

3.3 External substrate ragulation

molecule “L” - nucleate at elbow site:

Substrate - Au(111) with steps
& herringbone reconstruction

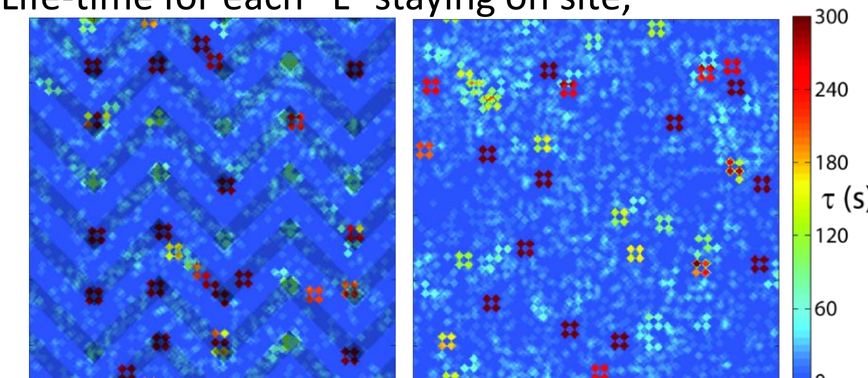




STM image/Room Temperature

KMC simulation at Room Temperature, (1h in 1min movie)

Life-time for each “L” staying on site,

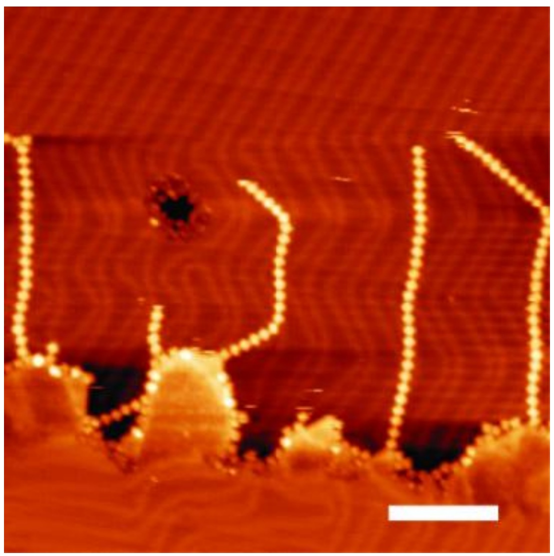


Kinetic Monte Carlo Simulation (patterned diffusion barrier on substrate, $E_{diff,\ elbow} > E_{diff,\ ribbon} > E_{diff,\ other}$)

→3. Design

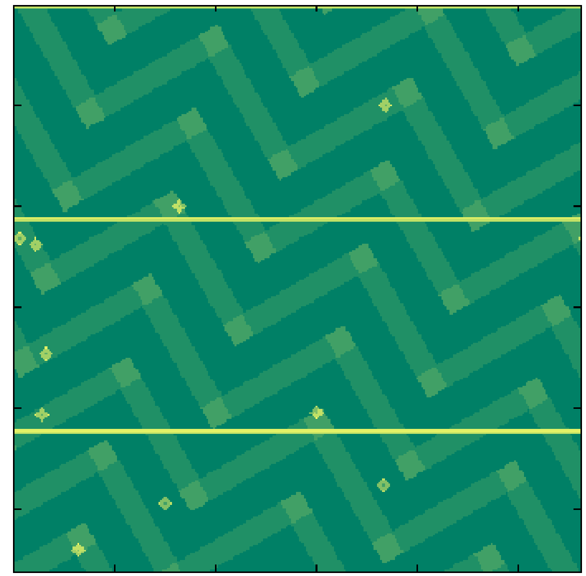
3.3 External substrate ragulation

molecule “I” - grow from atomic steps:

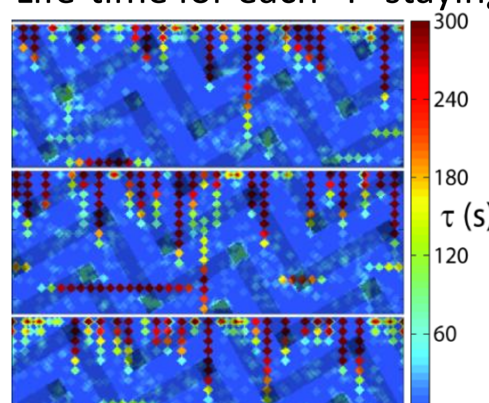


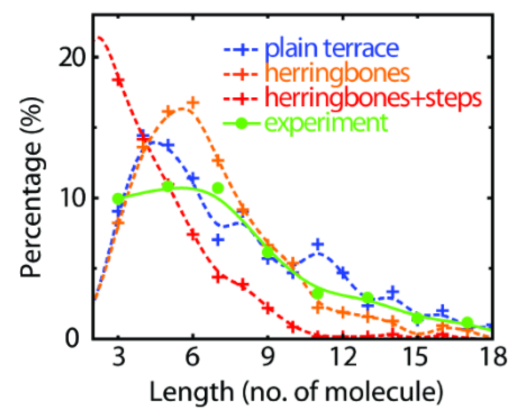
STM image/Room Temperature

KMC simulation at Room Temperature, (1h in 1min movie)



Life-time for each “I” staying on site/length distribution,



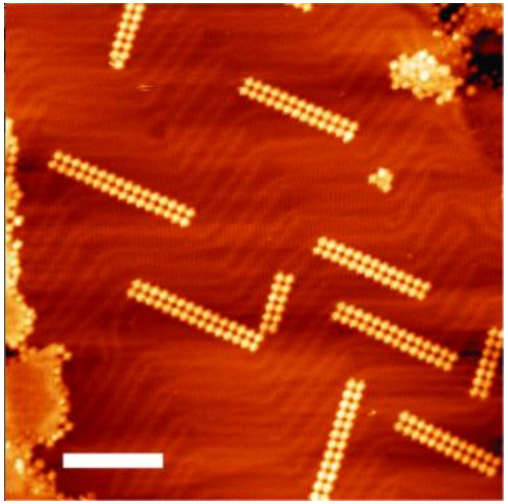


→3. Design

3.3 External substrate ragulation

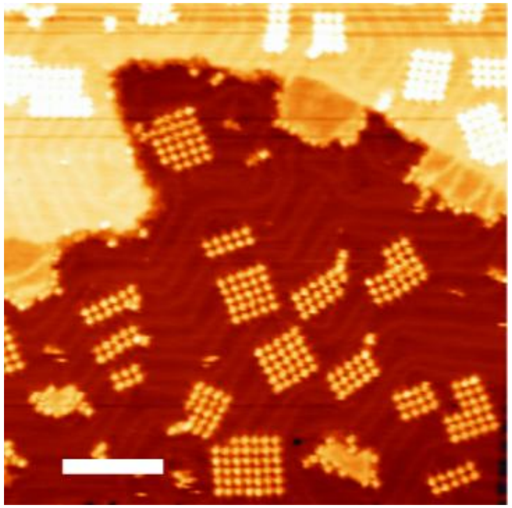
molecule “T” & “X” - substrate influents less:

“T”

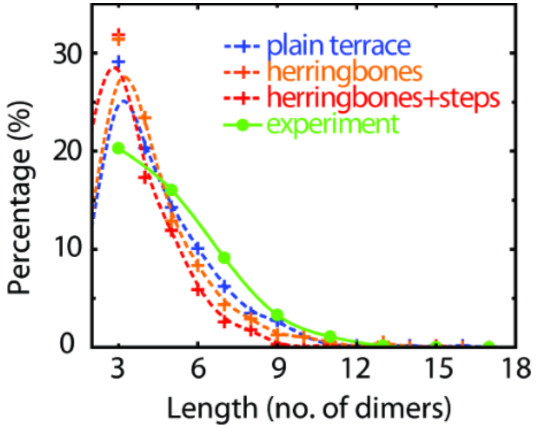


STM image/Room Temperature

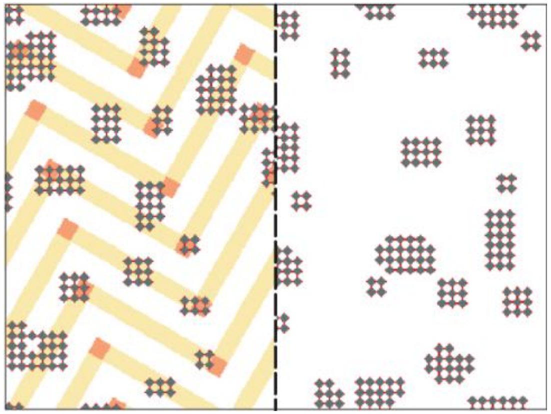
“X”



Ladder Length distribution on different substrates (KMC simulation),



Comparison (with/without substrate),



KMC Simulation

→3. Design

3.4 Summary of the different structures & the influence of the substrate

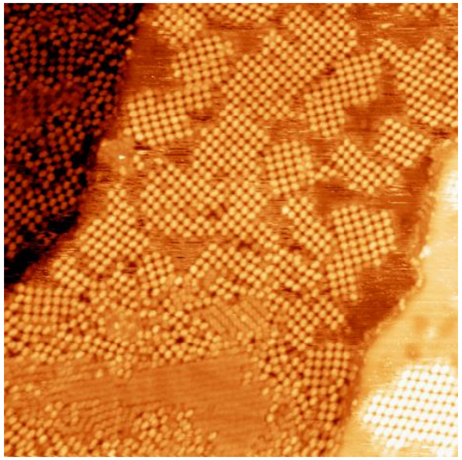
	No. of binding site	Assembled structure	Bonding configuration	Room-temperature stability	Influence of step edges	Influence of herringbone
"L"	**2**	0D close cycles	flexible	unstable	N.A.	strong
"I"	**2**	1D chain	flexible	less stable	strong	weak
"T"	**3**	Quasi-1D ladder	rigid	stable	no	weak
"X"	**4**	2D network	rigid	stable	no	no

→4. Functionality

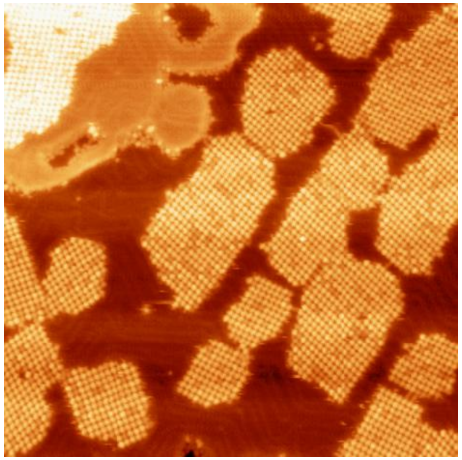
Coordination and metalation bifunctionality of 2D porphyrin networks: Towards a mixed-vance 2D coordination network

TPyP + Cu @ Au(111) postannealed at three temperatures:

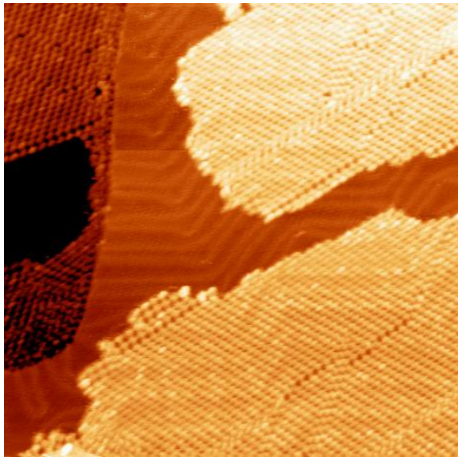
300K



450K



570K

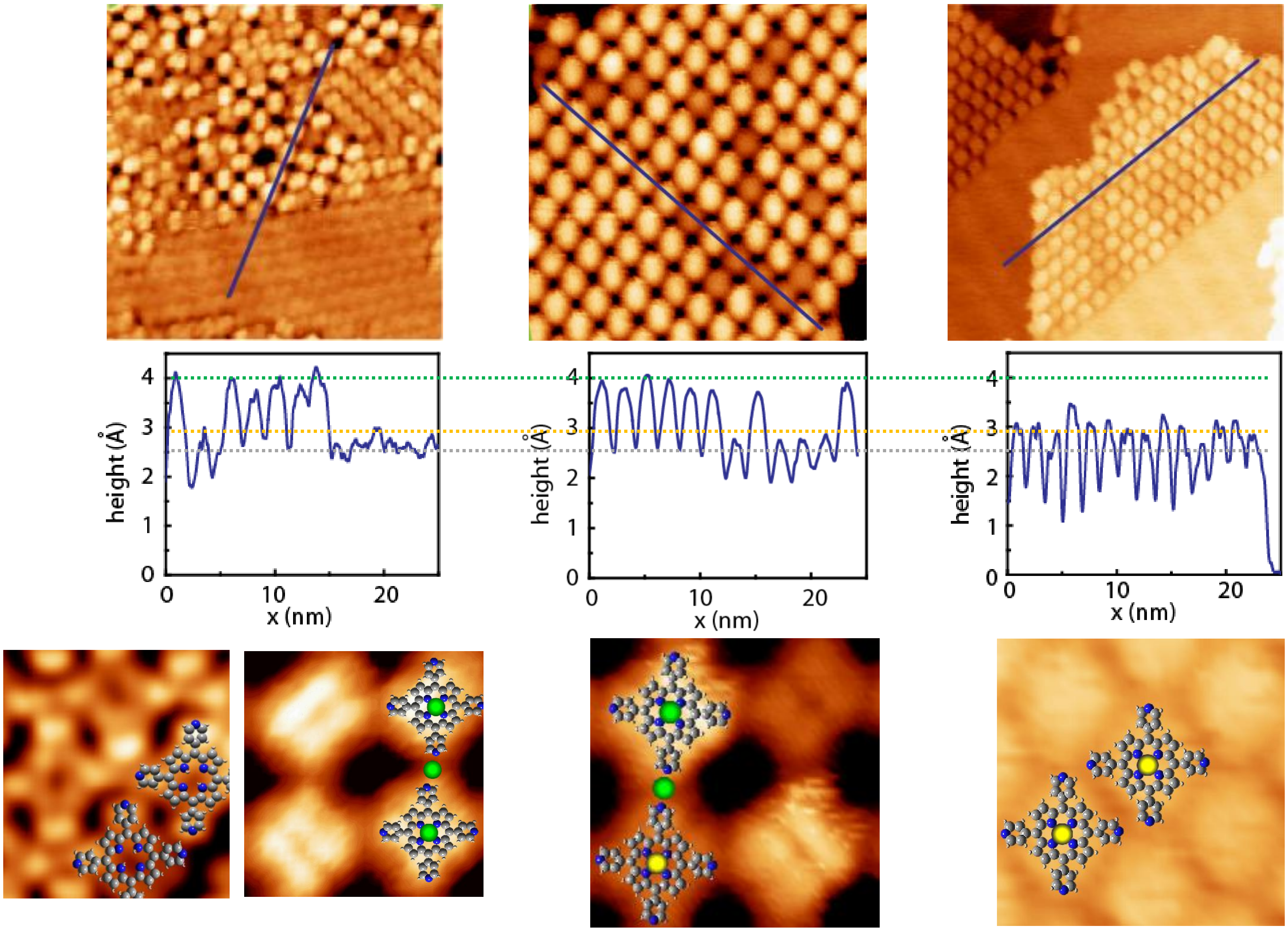


Why does the system show different contrast?

→4. Functionality

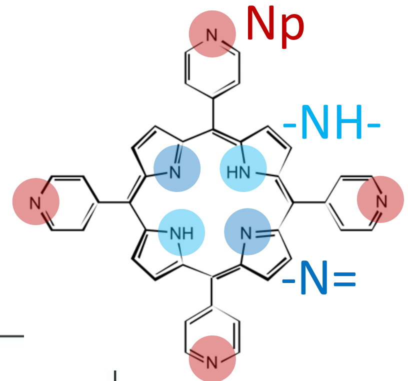
4.2 Coordination & metalation reaction at three temperatures

300K **450K** **570K**

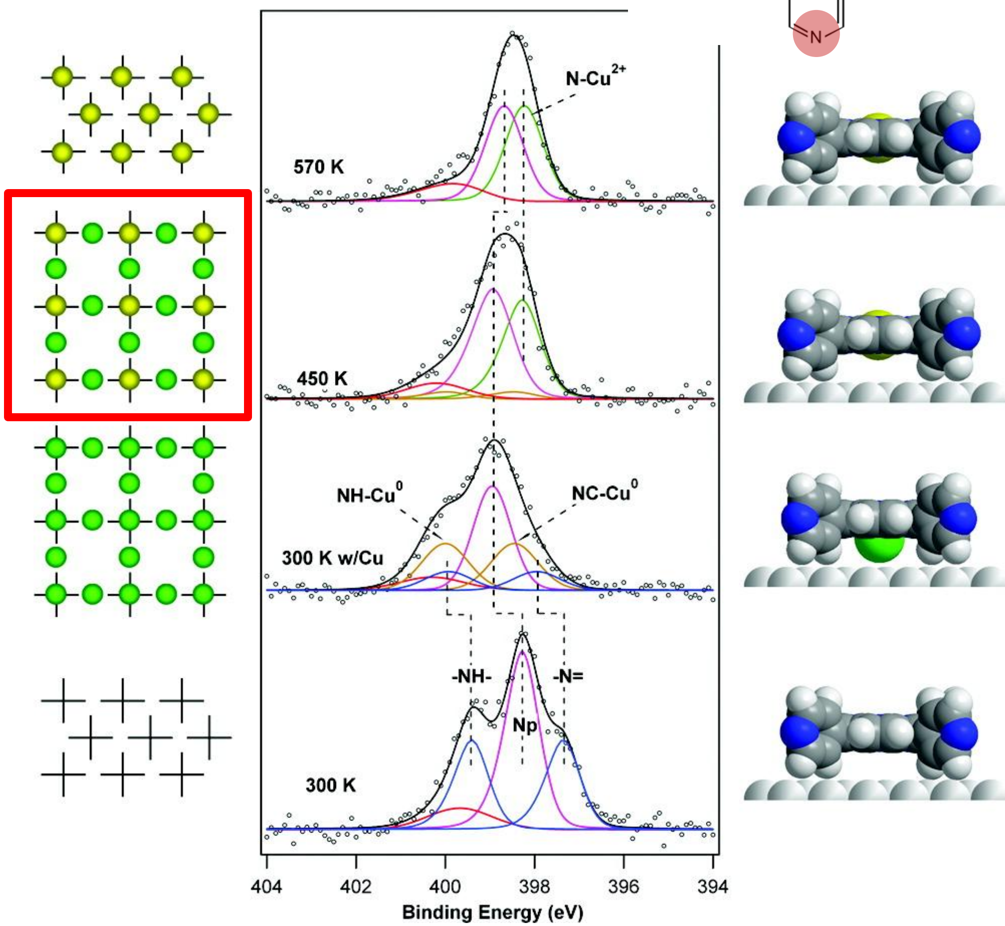


→4. Functionality

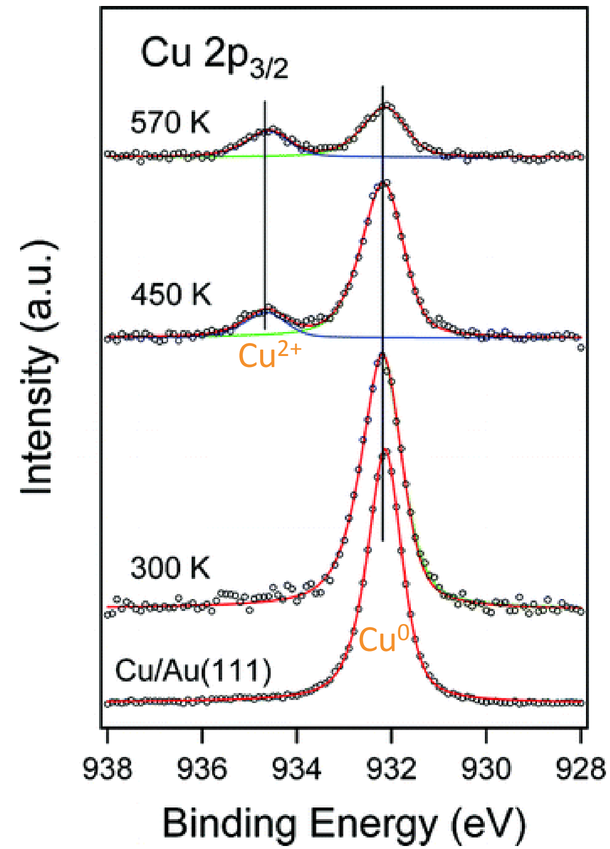
4.3 XPS study



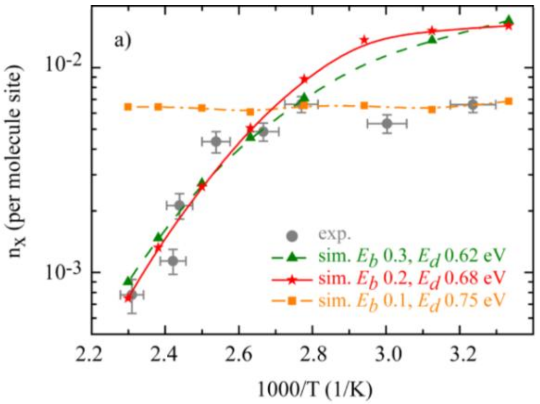
N 1s XP spectra:



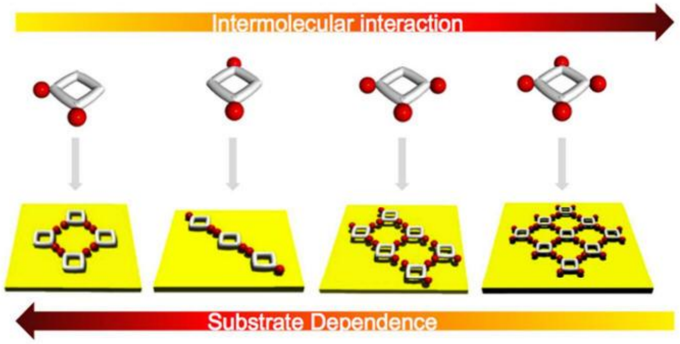
Cu $2p_{3/2}$ XP spectra:



→5. Conclusions

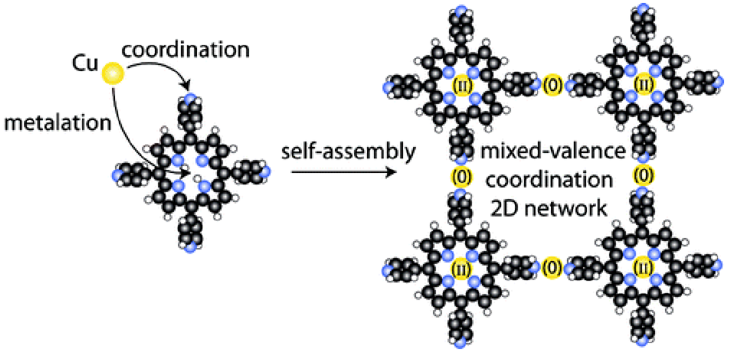


A combined STM and KMC method:
Study the kinetics.[1]



Low dimensional nanostructures:
Internal molecular codes vs. external substrate regulation.[2]

Bifunctional networks:
Coordination and Metalation.[3]



1. Yang Li, Nian Lin, *Phys. Rev. B.* **84**, 125418 (2011).
2. Yang Li, Jinne Adisoejoso, Jun Liu, Pei Nian Liu and Nian Lin, *submitted*.
3. Yang Li, *et al. J. Am. Chem. Soc.* **134**, 6401–6408 (2012).

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Thank you very much!