Investigation of Supramolecular Coordination Self-Assembly and Polymerization Confined on a Au(111) Surface Using Scanning Tunneling Microscopy

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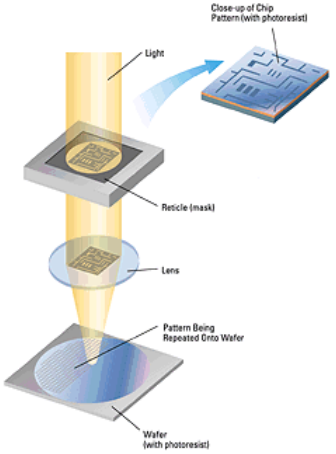
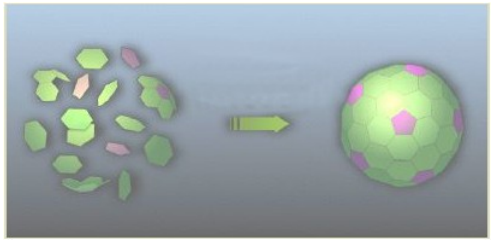
Introduction: Nano Devices

top-down (photolithography, …)
size-limitation, high-cost



bottom-up
organic molecules: building blocks for nano-devices
interaction: non-covalent / covalent



@ a single-molecule level

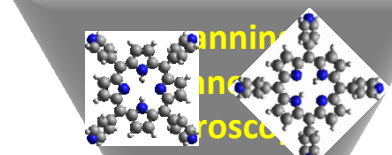
- **structural information**
- **electronic / magnetic properties**

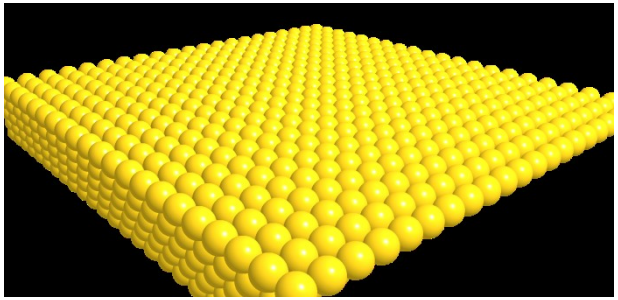
a) *Prog. Surf. Science* **2003**, *71*, 95-146.
b) http://www.just2good.co.uk/cpuSilicon.php
c) Makoto FUJITA's homepage

Introduction: Low-Dimensional Systems

3D to low-dimensional systems
→ single molecule level

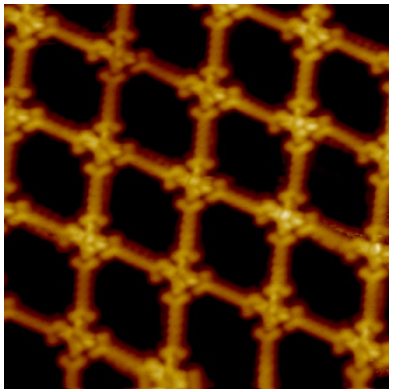
surface sensitive techniques

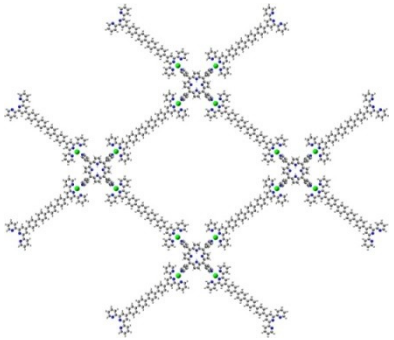




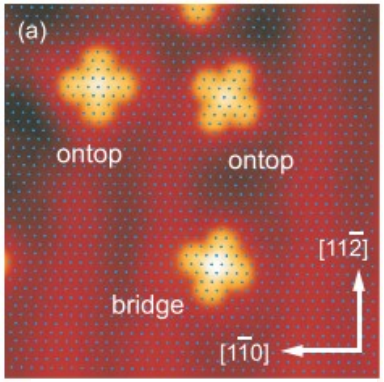
well-defined metal surfaces
(e.g. the Au(111) surface)

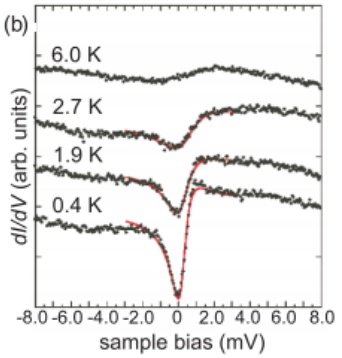
structural information



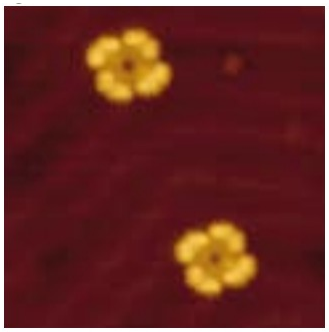


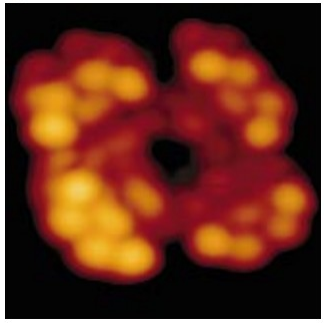
electronic / magnetic properties

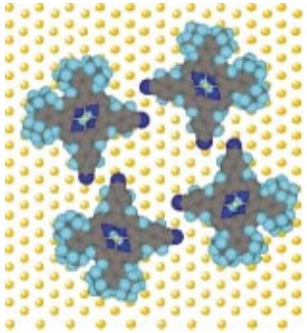




effects of substrate

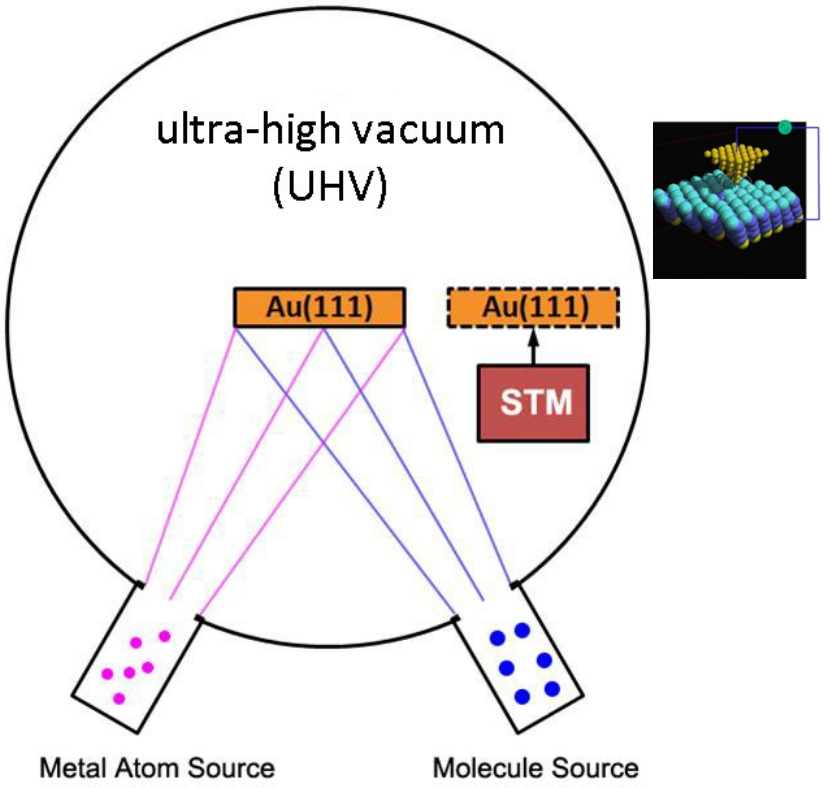






a) Phys. Rev. Lett. **2011**, *106*, 187201.
b) *Nature* **2001**, *413*, 619-621.

Introduction: Experimental Setup



- **Sample preparation:**

1. organic molecule source
2. metal atom source

- **Characterization:**

1. STM: structural information
2. STS: electronic structure

Outline

1. On-surface supramolecular coordination self-assembly

- systems exhibiting different dimensionalities
- networks containing out-of-plane dinuclear Fe centers
- supramolecular coordination polygons
- networks containing bi-functional porphyrin ligands

2. On-surface polymerization

- metal-catalyzed Ullmann coupling reactions

3. A combination of coordination bonds and covalent bonds

- metal-directed template to control polymerization process
- large porous networks via a two-step approach

Outline

1. On-surface supramolecular coordination self-assembly

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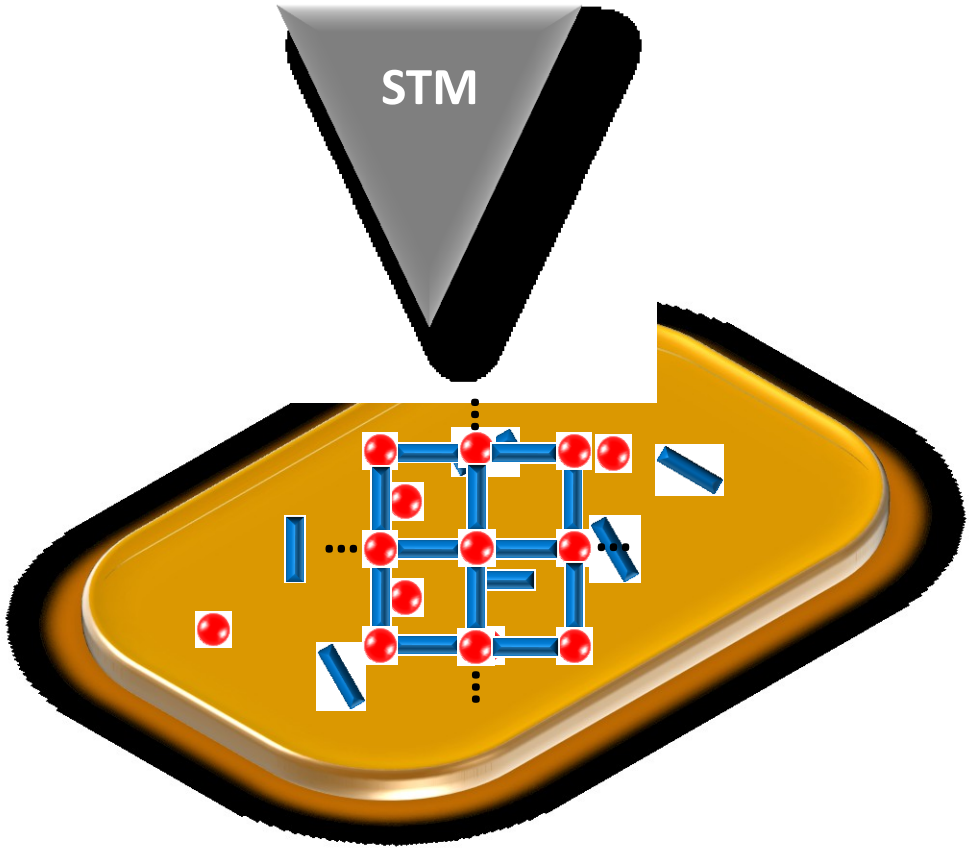
- metal-directed template to control polymerization process

On-surface Supramolecular Coordination Self-Assembly

Building blocks:

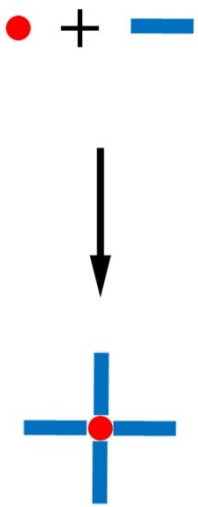
organic ligands

metal atoms

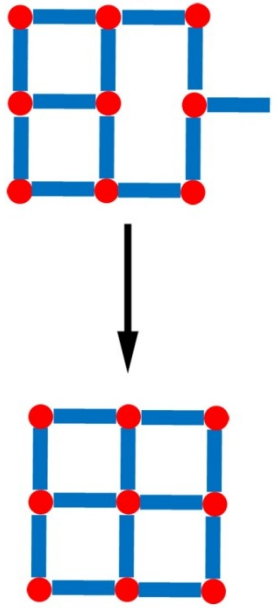


metal-organic coordination bond:

preferred bonding geometries ↓ recognition



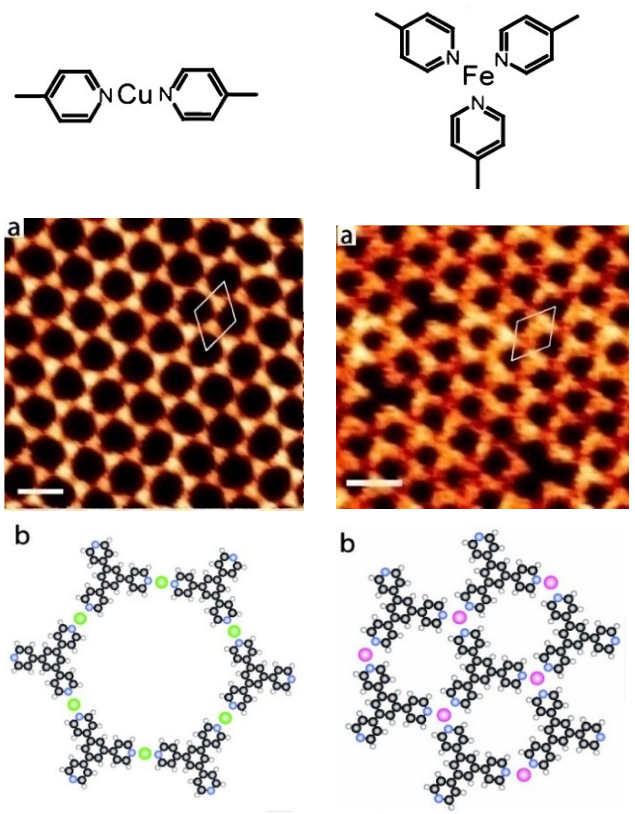
reversibility ↓ self-correction



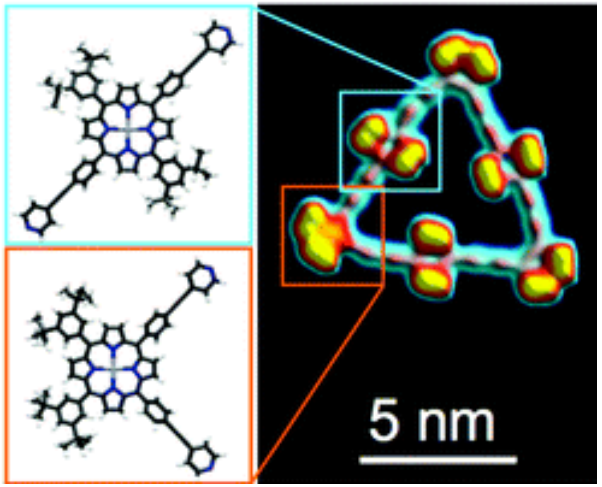
Supramolecular System

2D Extended Networks

0D Discrete Structures



... ...



2D structures: easy
0D structures: difficult

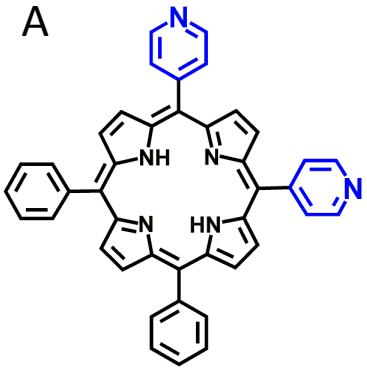
↔

dimensionality?

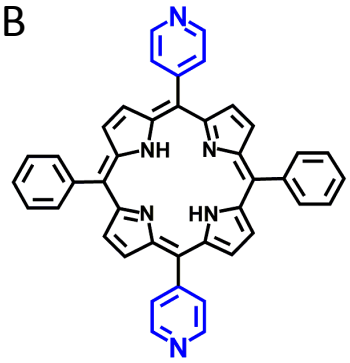
a) *J. Am. Chem. Soc.* **2011**, *133*, 6150; b) *Nano Lett.* **2010**, *10*, 122.

Molecules

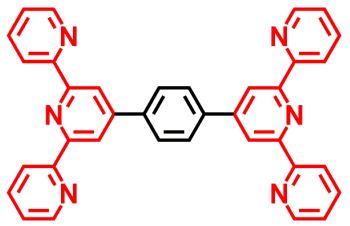
A



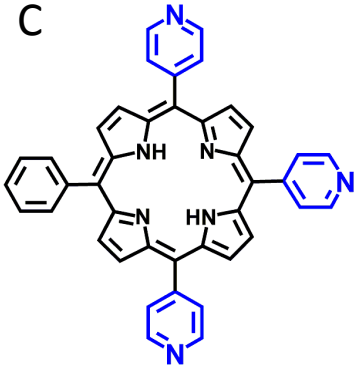
B



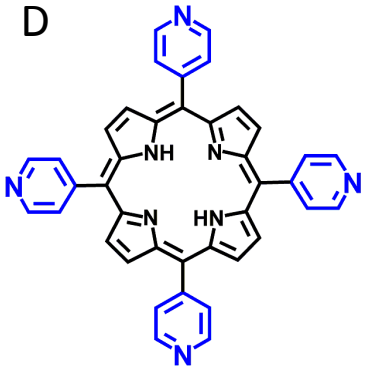
E

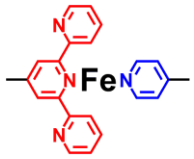


C



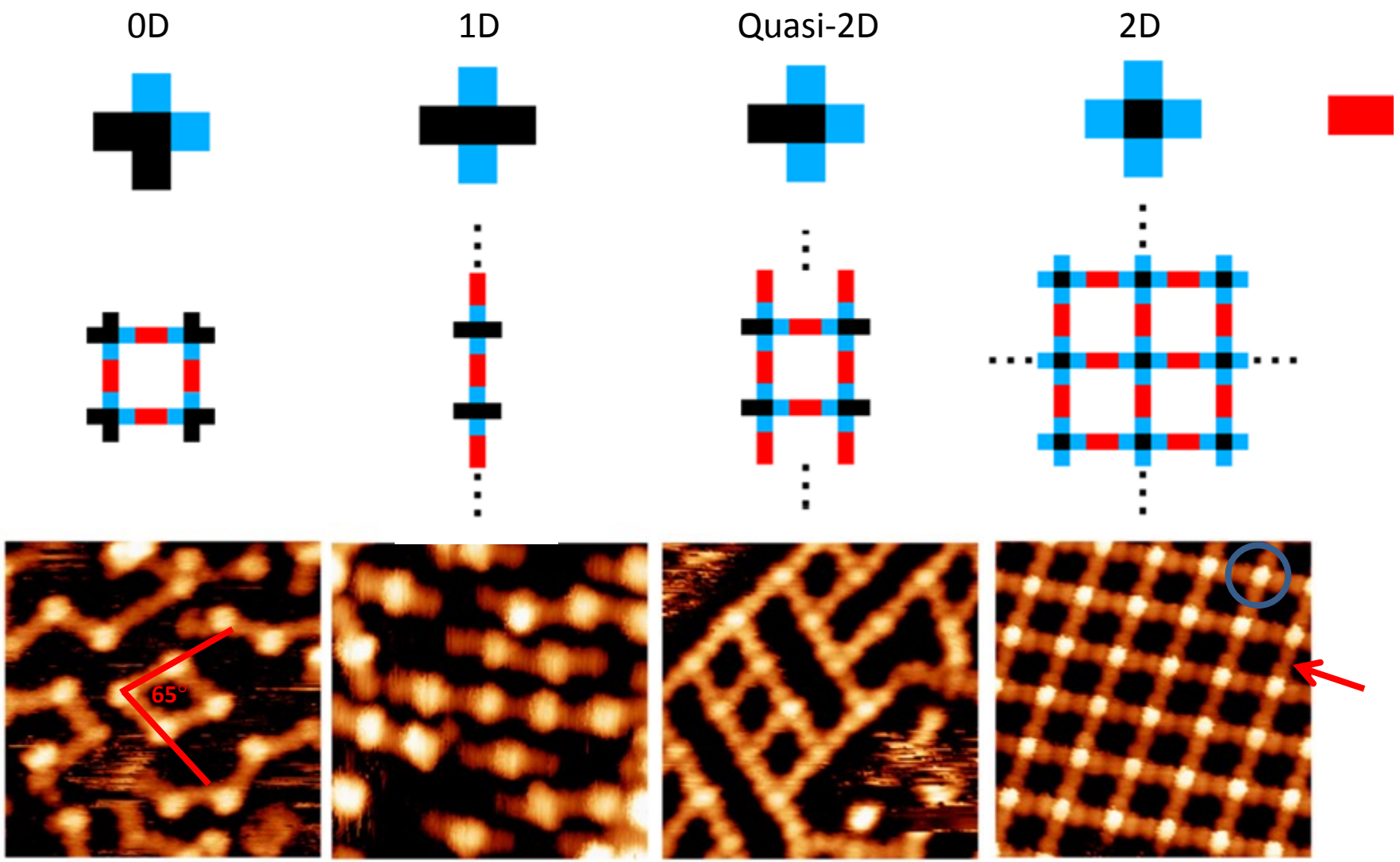
D





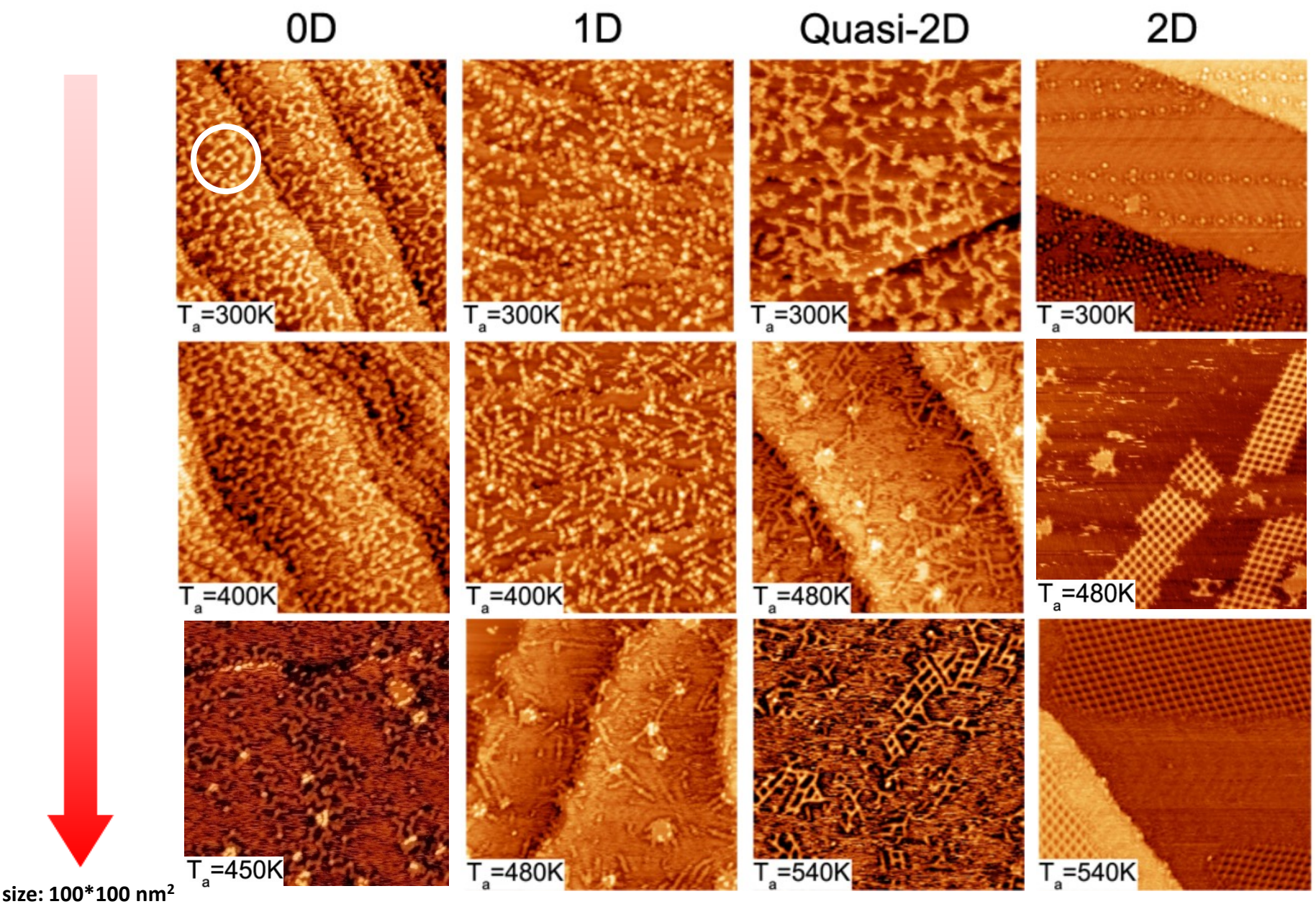
@Au(111) by RT-STM

Experimental Results



size: 20*20 nm^2

Experimental Results

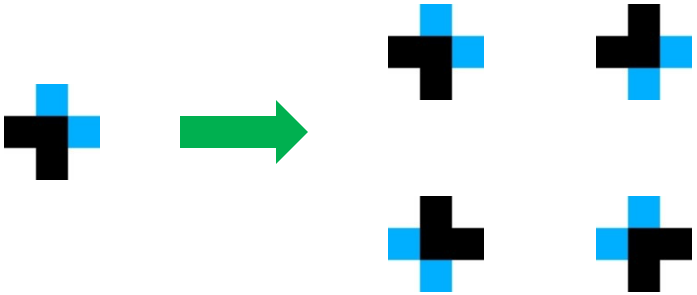


Simulation Results (Monte Carlo)

0D

Eb=0.2eV, MCstep=10^9

hopping with/without configuration changes:



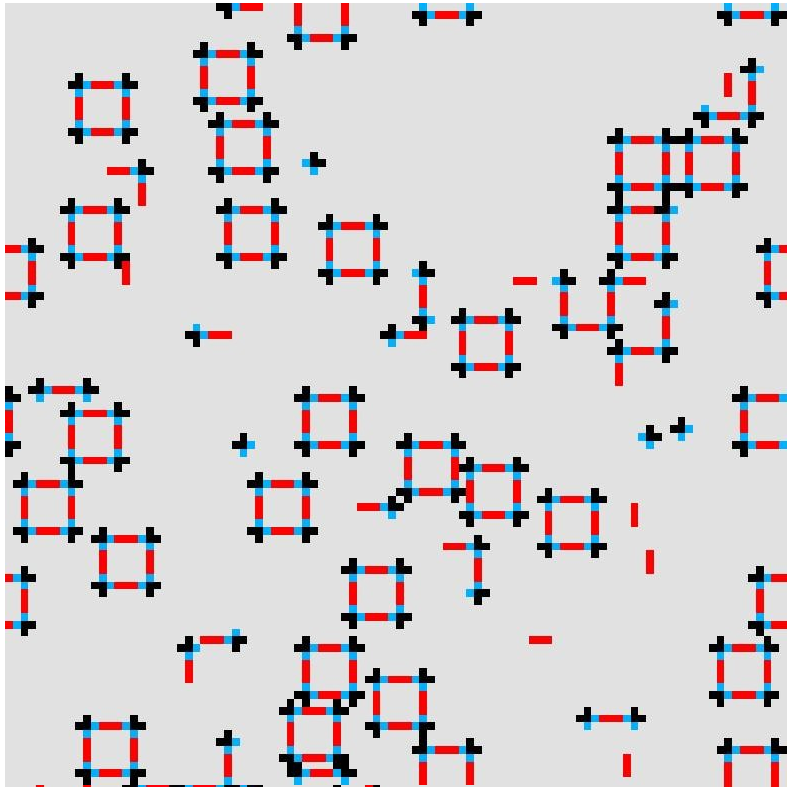
compare energy differences:

$$P_{acc} = \min(1, e^{\Delta U/kT})$$

$$r \in (0,1)$$

r<P_{acc}, accepted

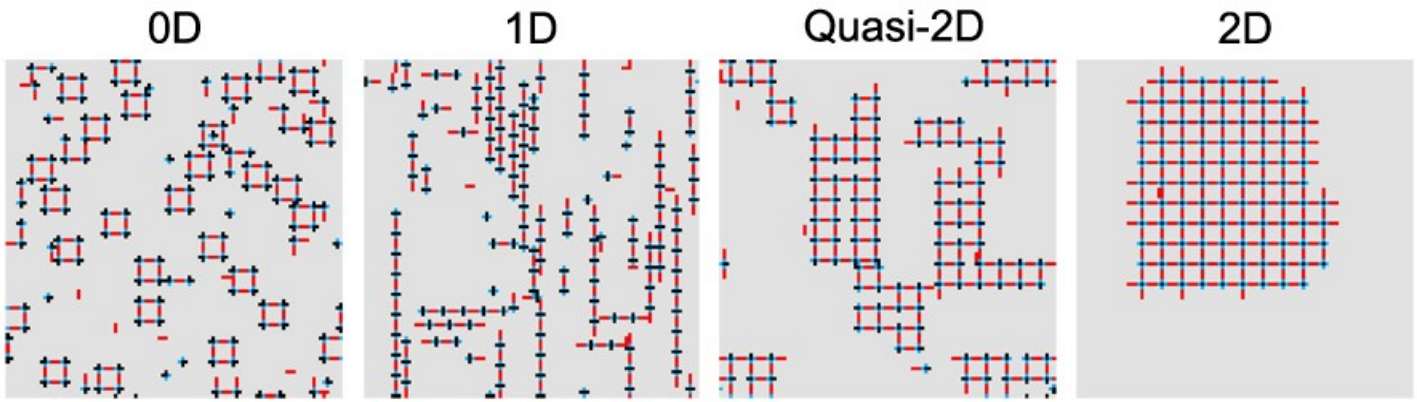
r>P_{acc}, rejected



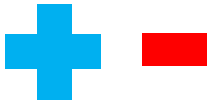
a) *J. Am. Chem. Soc.* **2013** *135,* 6942-6950.

Kinetic trapped at RT

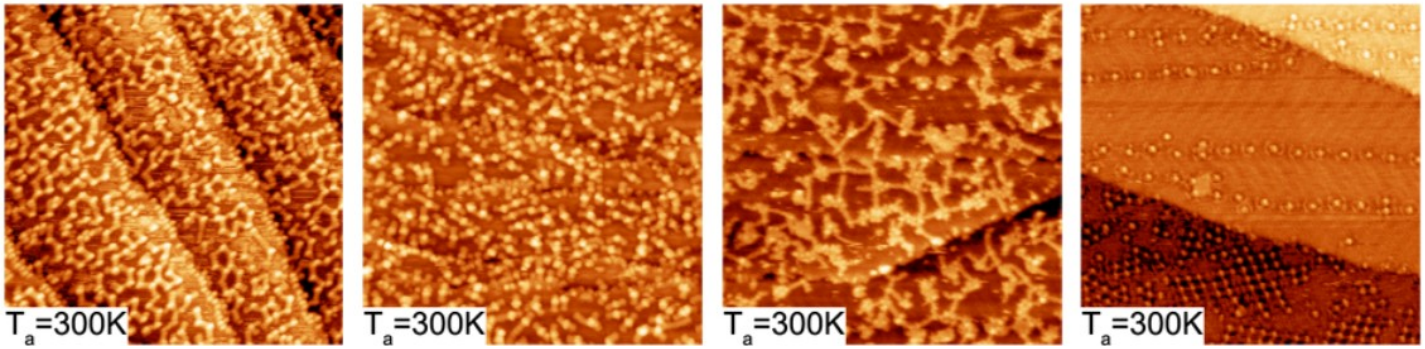
Equilibrium states at RT



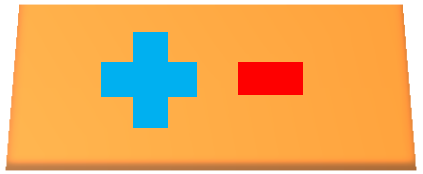
free



Kinetic trapped at RT



substrate trapped



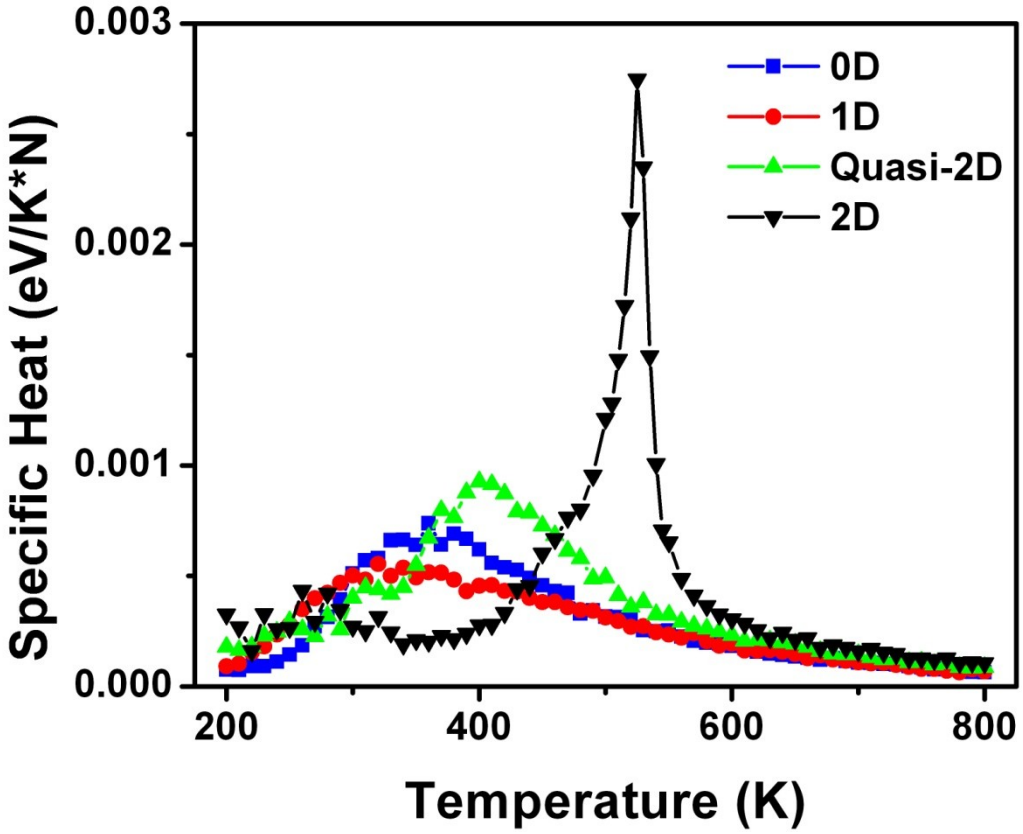
size: 100*100 nm^2

Simulation Results (Monte Carlo)

energy fluctuations to derive specific heat

$$c_v = \frac{\langle U^2 \rangle - \langle U \rangle^2}{N \times kT^2}$$

U is the total energy of each system
***N* is the total number of molecules in each system**

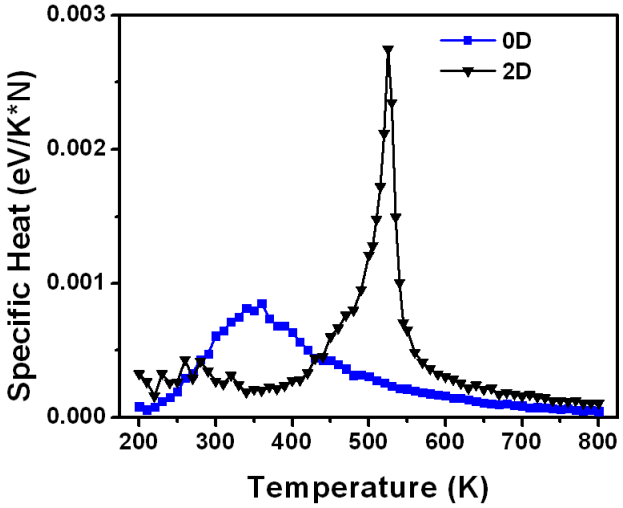


Peak Position (Tc)

0D	1D	Quasi-2D	2D
350K	325K	400K	525K

0D, 1D, Quasi-2D: broad & low
2D: sharp & high

Simulation Results (Monte Carlo)



molecular architectures→ gas phase

(randomly distributed)

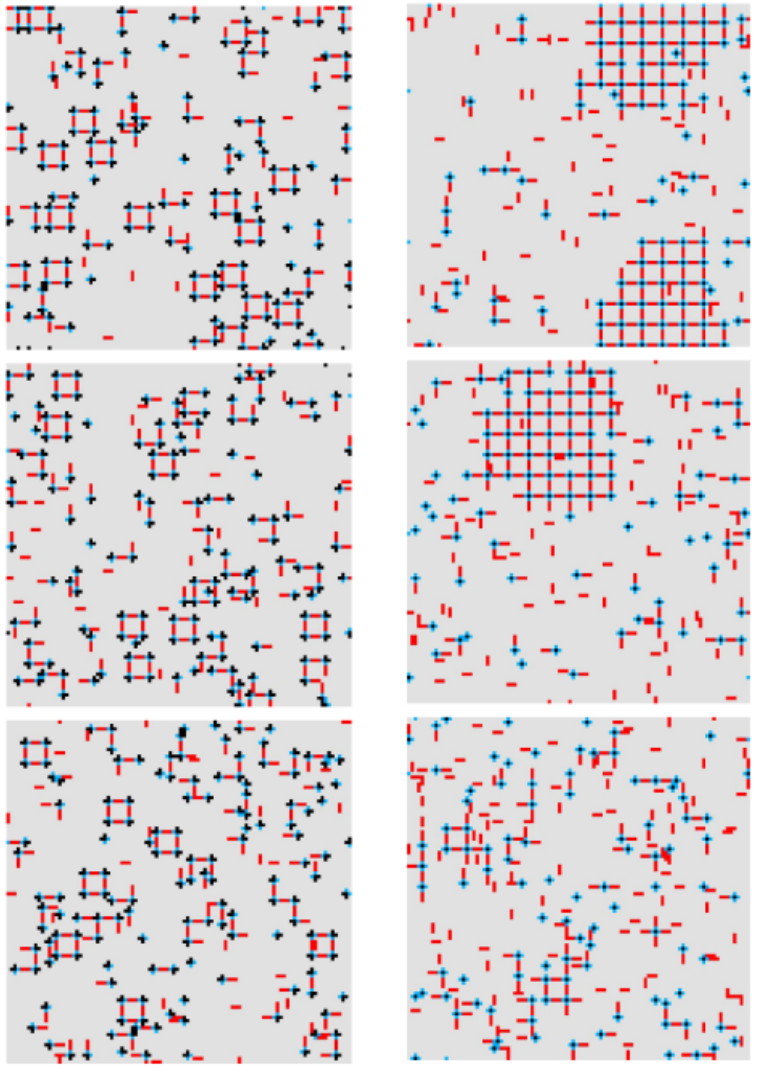
not sharp transition **sharp transition**

0D 2D

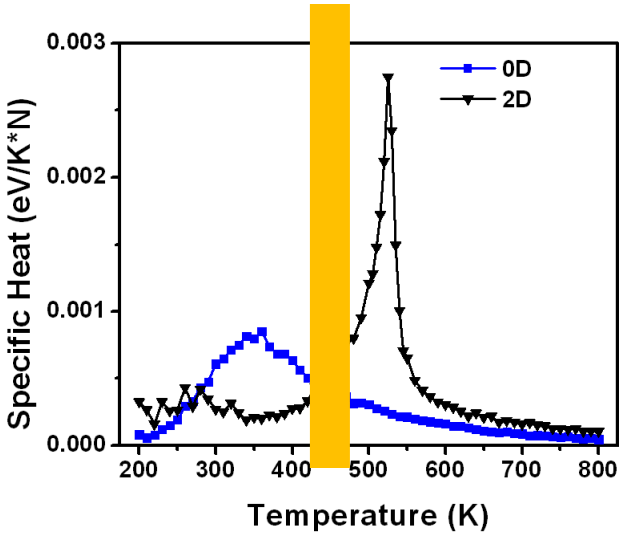
T_c-20K

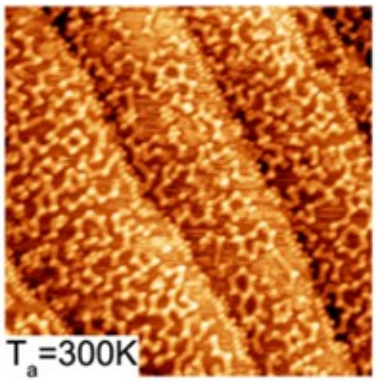
T_c

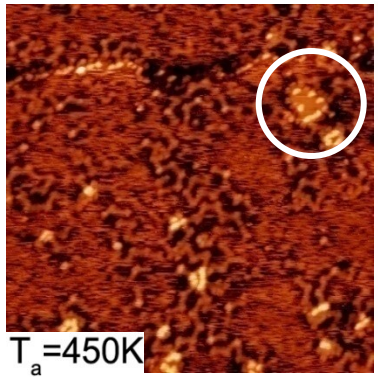
T_c+20K

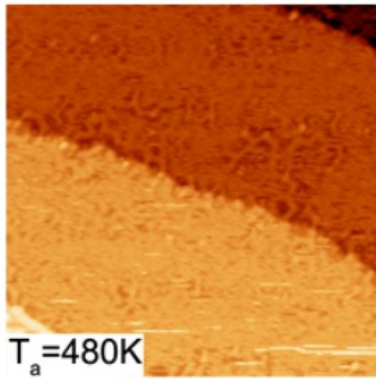


Discussion (Fe in 0D)









Fe

Fe island or
(dive into substrate)

@300K

Fe

Fe island

@450K

Fe

Fe island

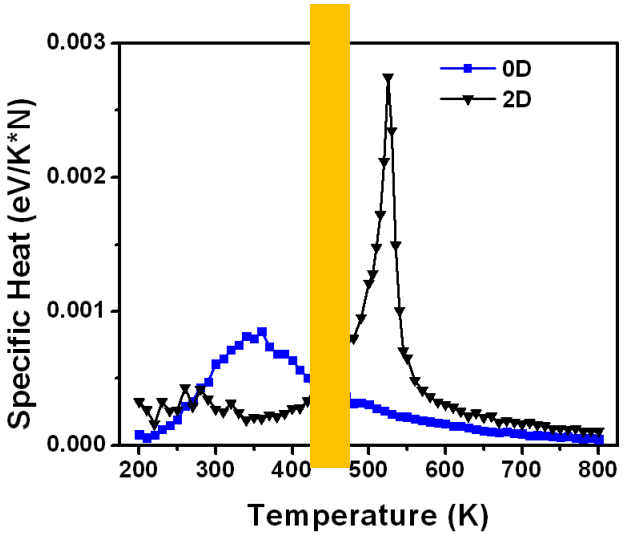
@480K

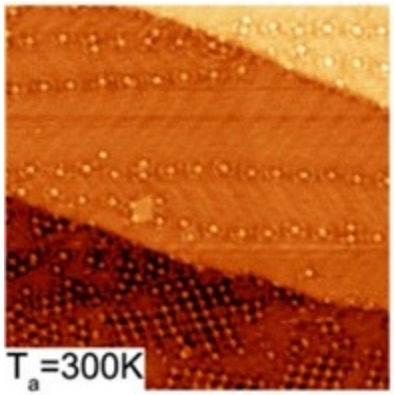
Fe

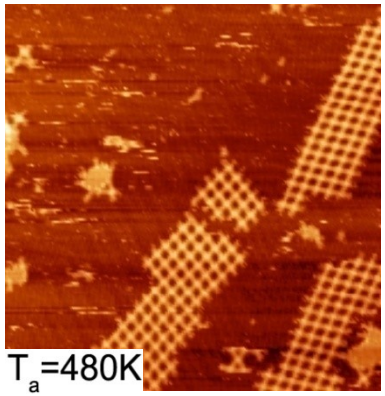
Fe island

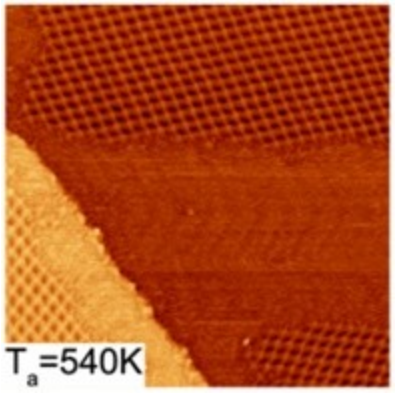
size: 100*100 nm^2

Discussion (Fe in 2D)









@300K

@480K

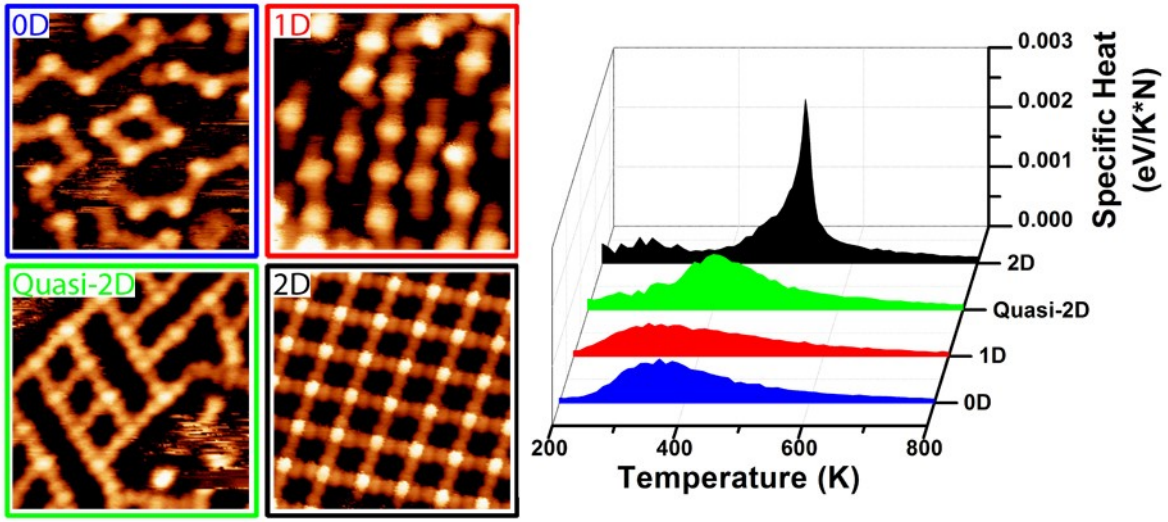
@540K

size: 100*100 nm^2

Conclusion

- supramolecular coordination systems with different dimensionality

1. 0D, 1D, Quasi-2D: kinetic trapping, Fe atoms
2. 2D: annealing treatment



T. Lin, Q. Wu, J. Liu, Z. Shi, P. N. Liu, N. Lin Thermodynamic versus Kinetic Controls in Self-Assembly of Metal-Organic Coordination Systems Exhibiting Different Dimensionalities, in preparation.

Outline

1. On-surface supramolecular coordination self-assembly

- systems exhibiting different dimensionalities
- networks containing out-of-plane dinuclear Fe centers

2. On-surface polymerization

- metal-catalyzed Ullmann coupling reactions

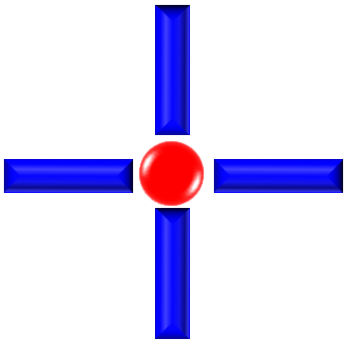
3. A combination of coordination bonds and covalent bonds

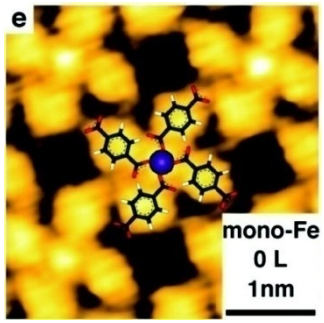
- metal-directed template to control polymerization process

Examples of On-Surface Coordination System

one single atom

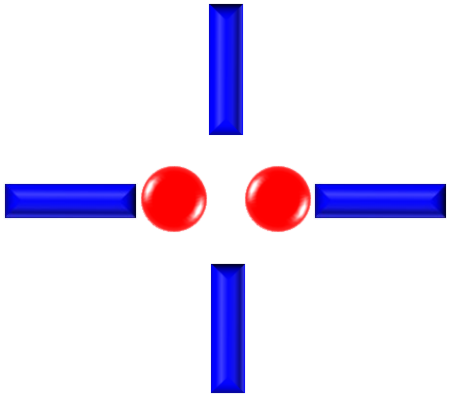
top view

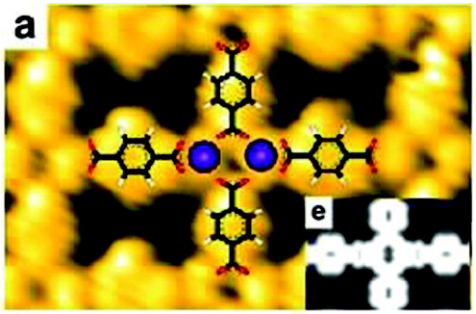




two atoms in-plane

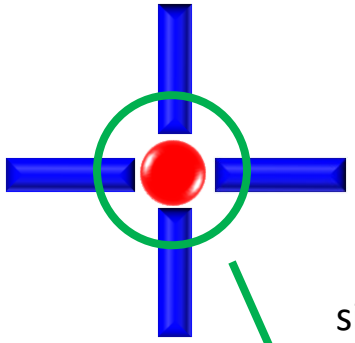
top view



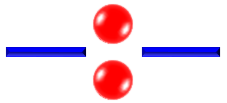


two atoms (vertically aligned)

top view

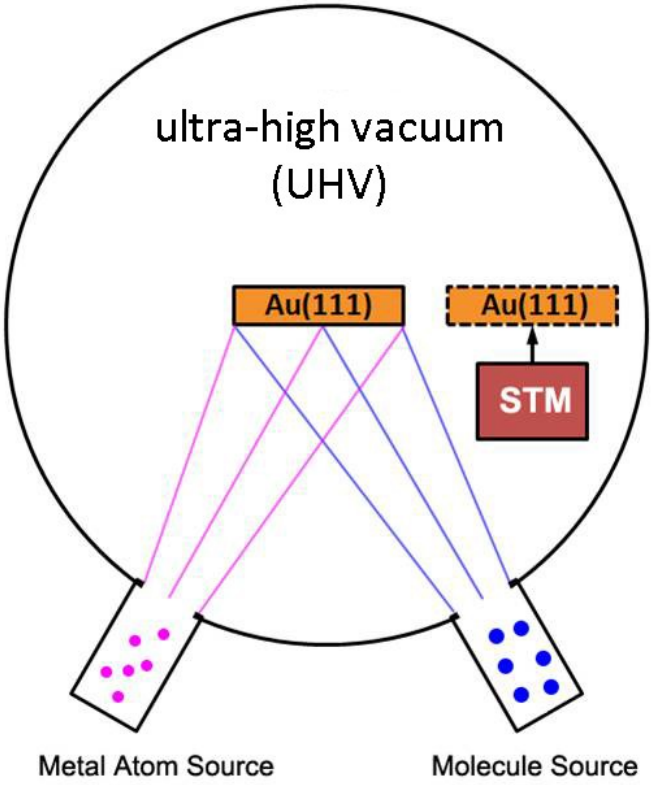


side view

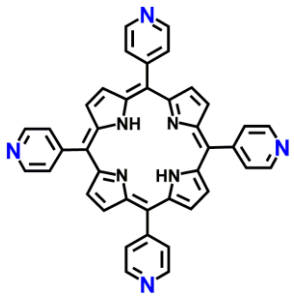


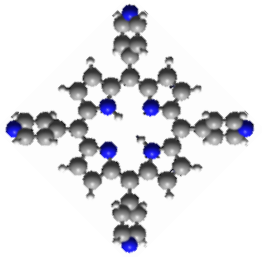
a) *Nano Lett.* **2011**, *11*, 5414.

Experimental Setup



TPyP



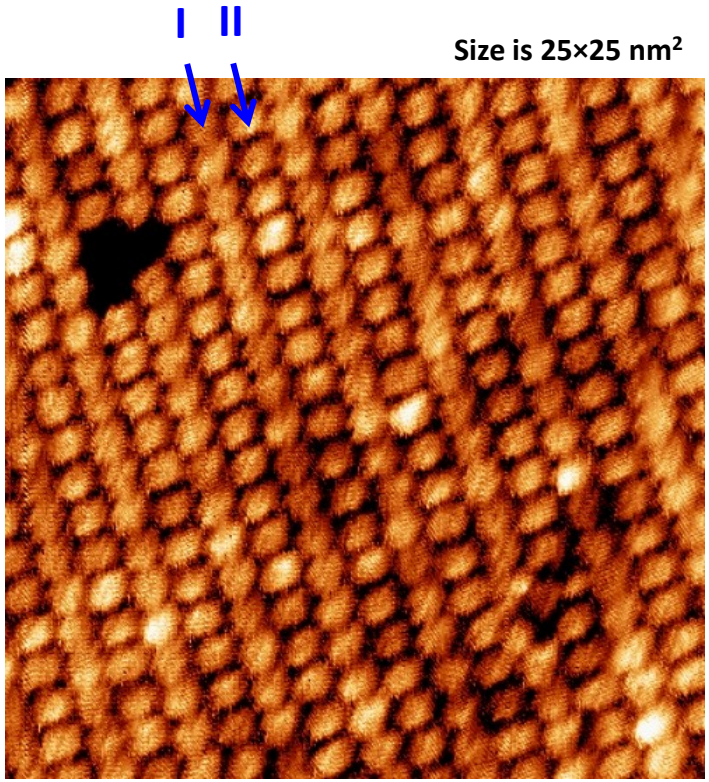


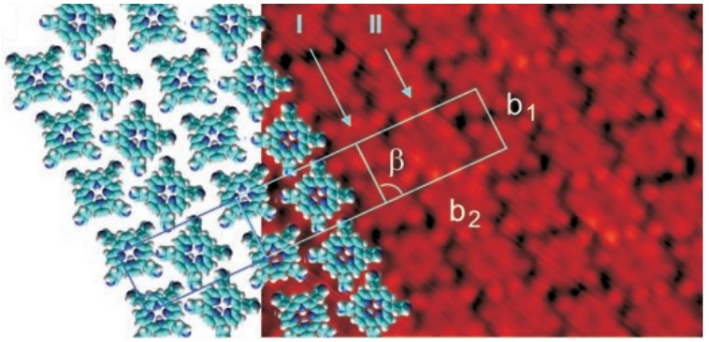
Fe

on Au(111) surface
@RT or LHe

Structural Results

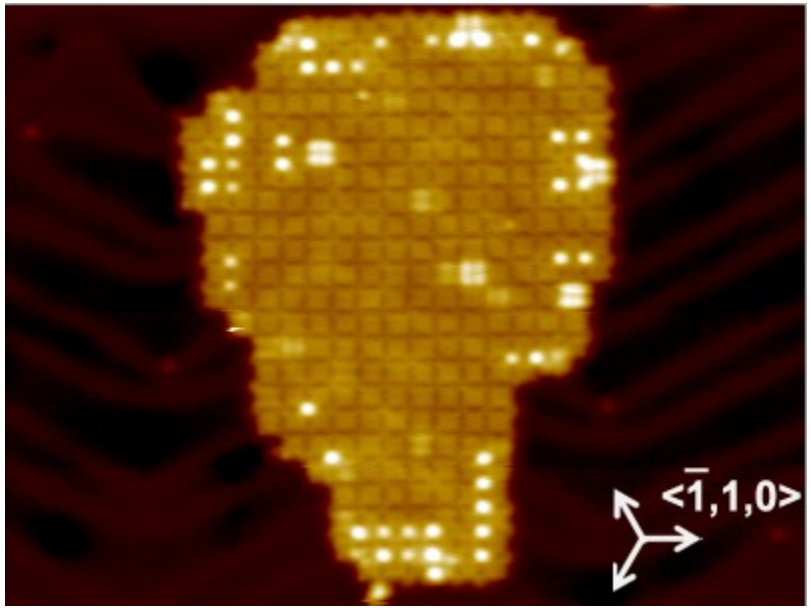
without Fe





Ag(111)

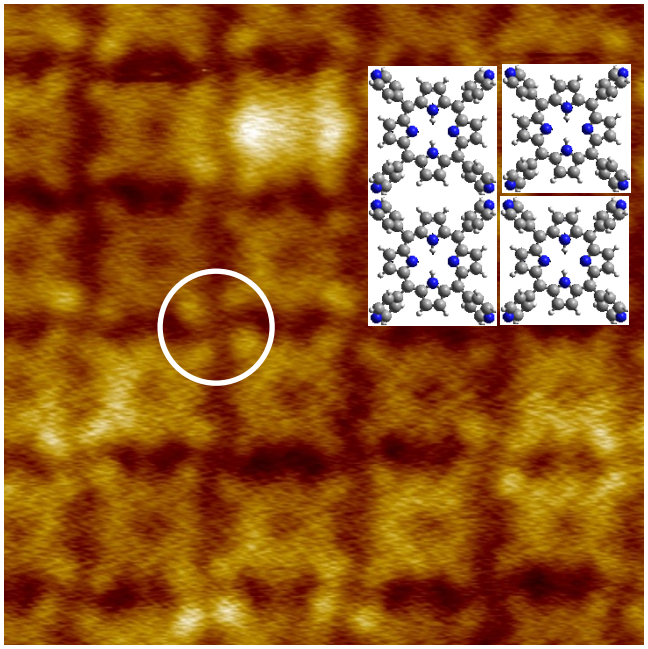
with Fe



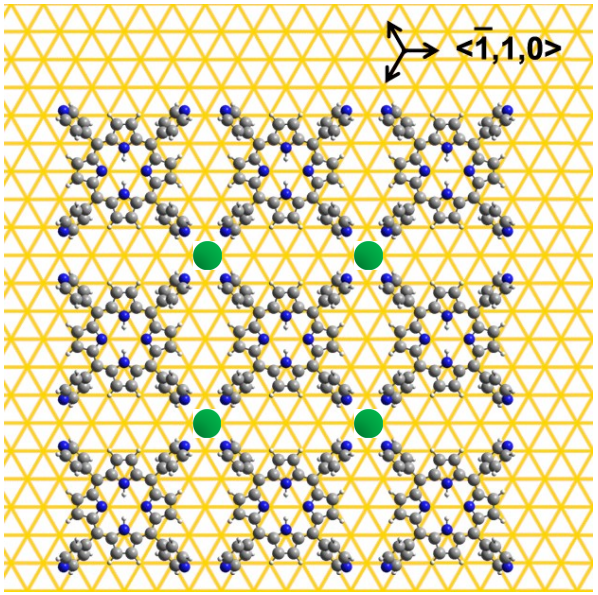
Size is 40×30 nm²

a) *Chemphyschem* **2007**, *8*, 250.

Structural Results

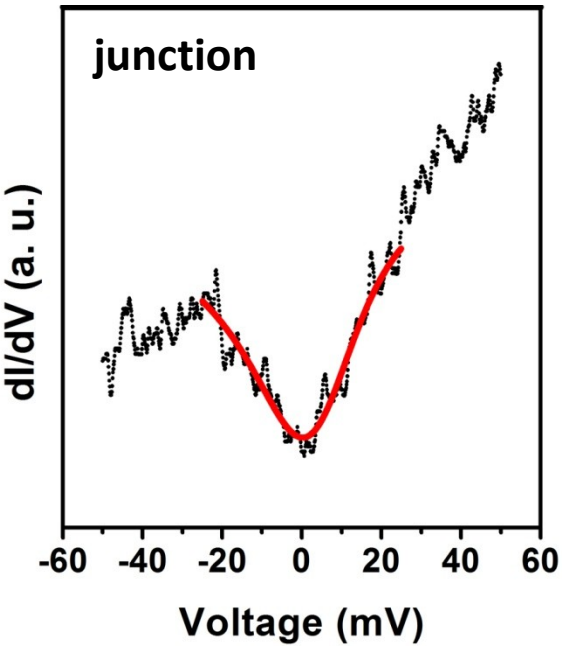


Size is 6×6 nm^2



Fe-N: 0.25nm

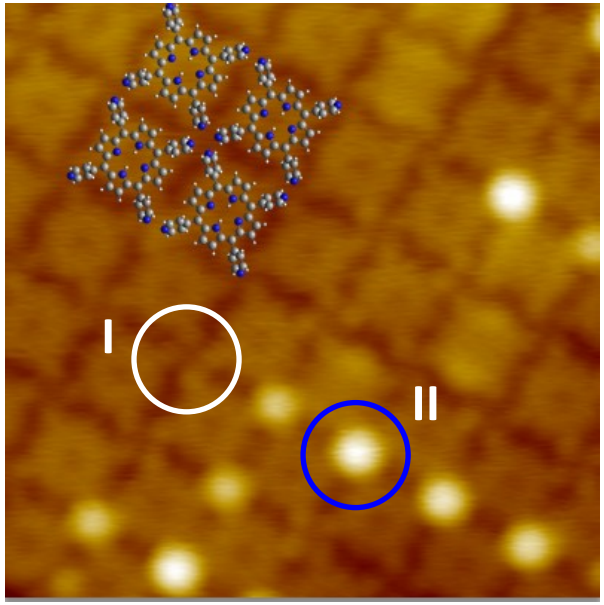
$$f(x) = \mathrm{A} \times \frac{[\mathrm{q} + (\mathrm{x} - \epsilon_0)/\Gamma]^2}{1 + [(\mathrm{x} - \epsilon_0)/\Gamma]^2} + \mathrm{B}$$



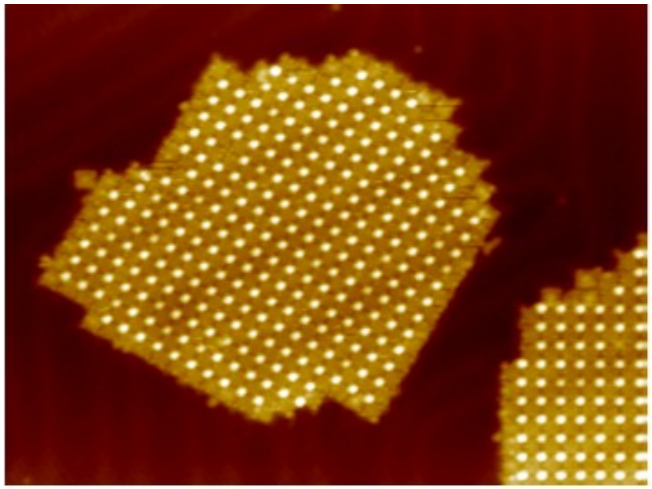
Kondo resonance

magnetic impurity

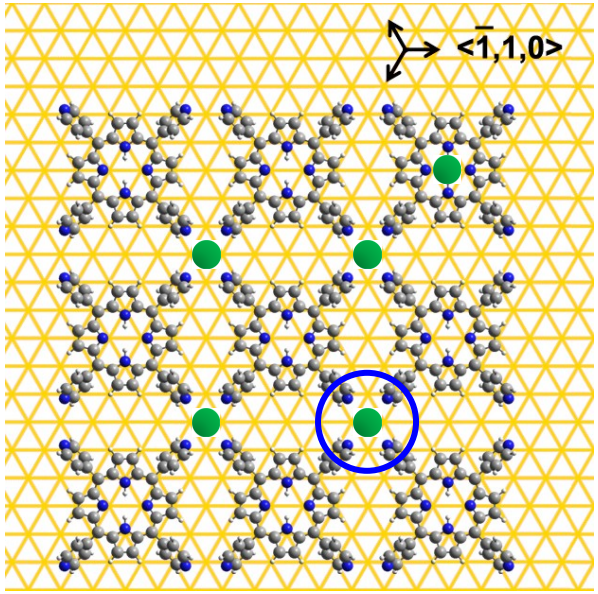
Structural Results



Size is 7.5×7.5 nm^2



Size is 40×30 nm^2



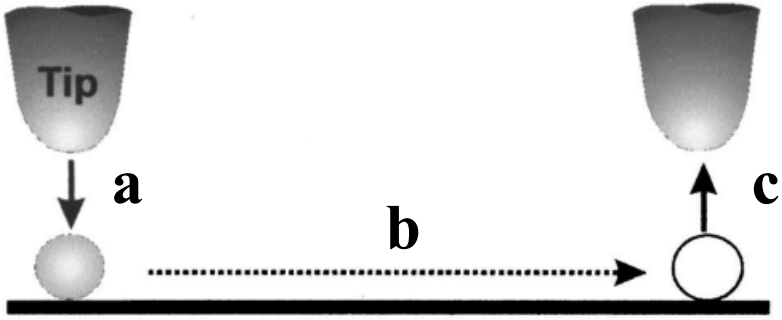
Fe-N: 0.25nm

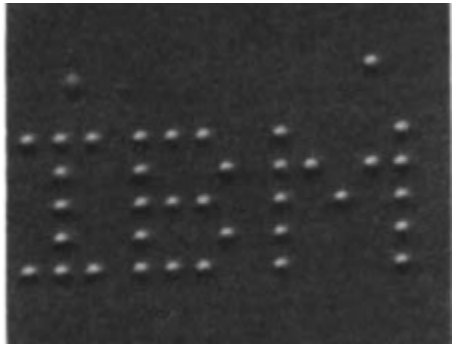
Side View

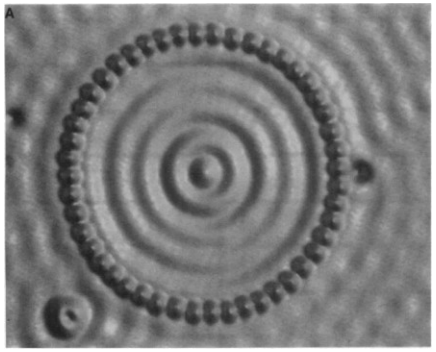
Type I **(four-lobe)**

Type II **(bright-dot)**

Lateral Manipulation





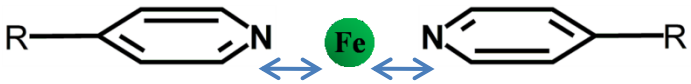


no example of large coordination network moved by STM tips without break

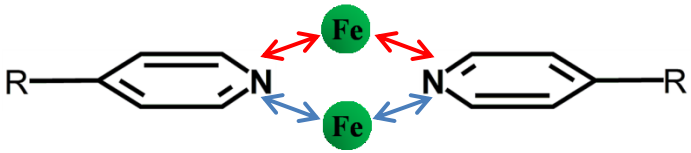
a) *Nature* **1990**, *344*, 524; b) *Science* **1993**, *262*, 218; c) *J. Vac. Sci. Technol. B* **2005**, *23*, 1351

Lateral Manipulation

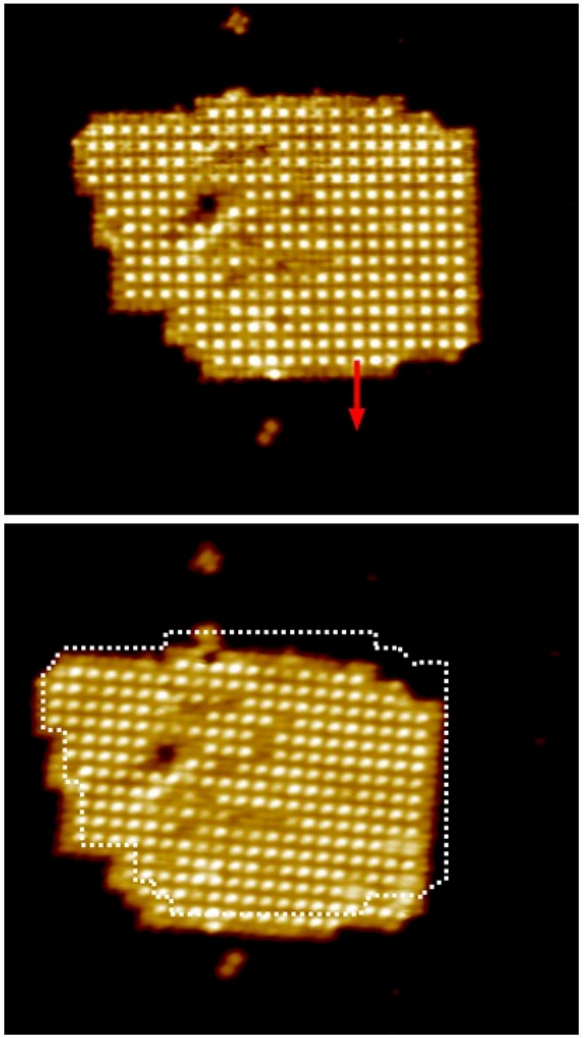
Type I



Type II

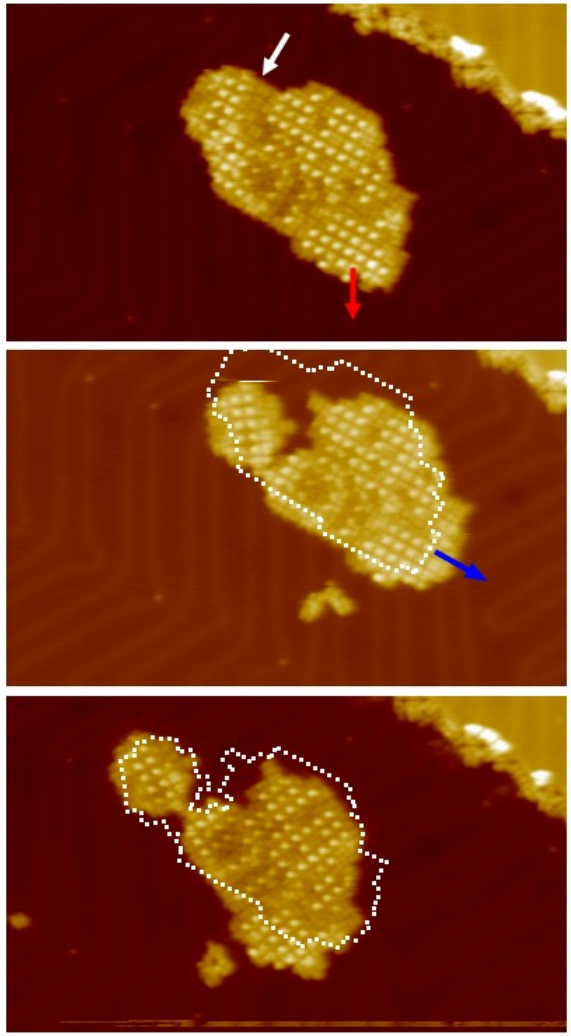


Type II (~ 300 molecules)



Size is 40×35.5 nm^2

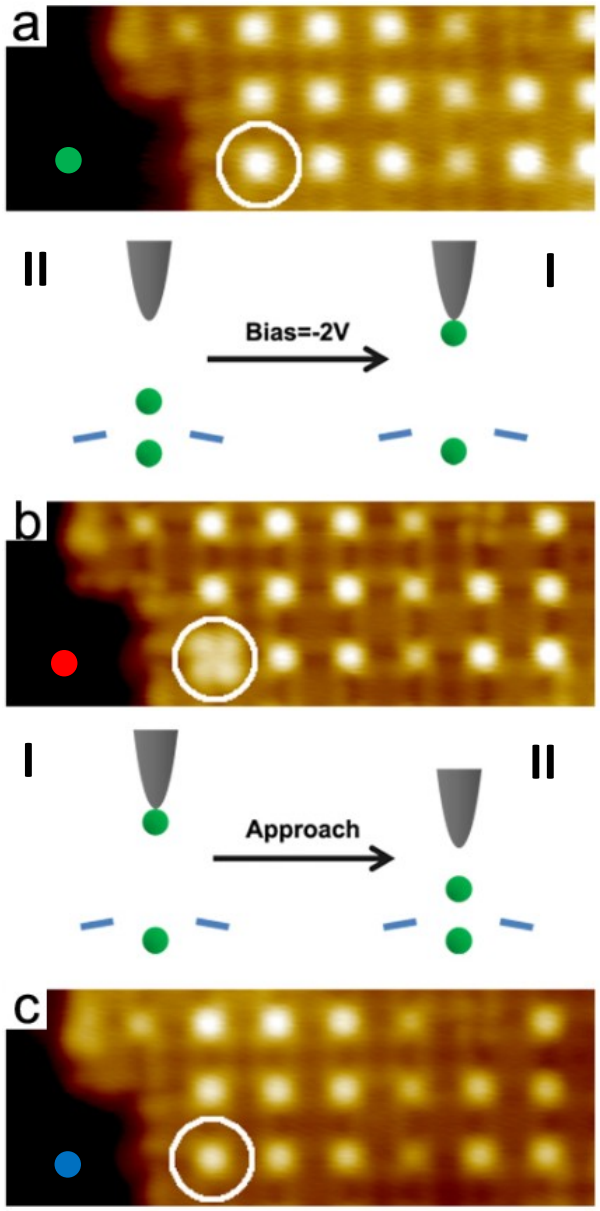
Type I chain



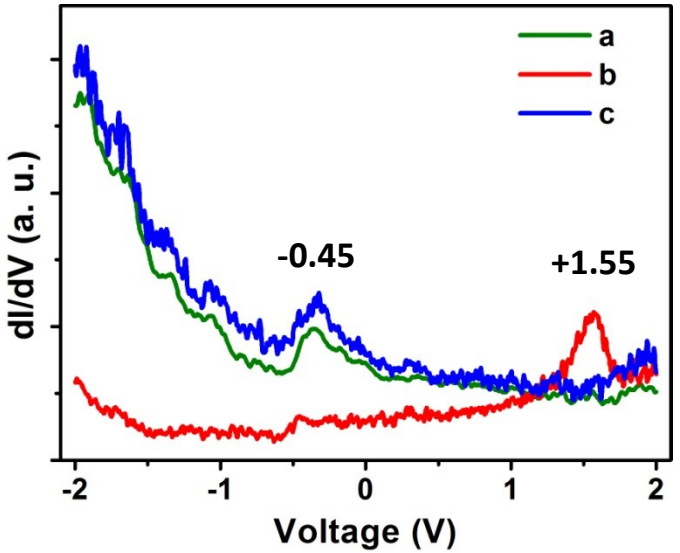
Size is 50×30 nm^2

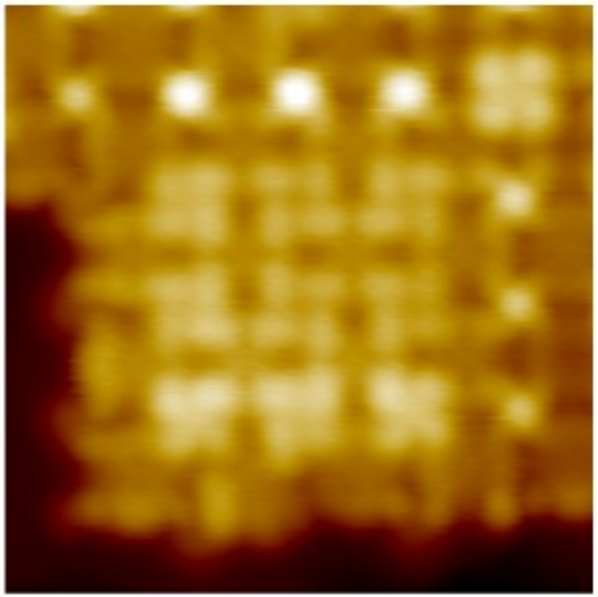
Vertical Manipulation

size is 10.5×3.6 nm^2



dI/dV represents LDOS

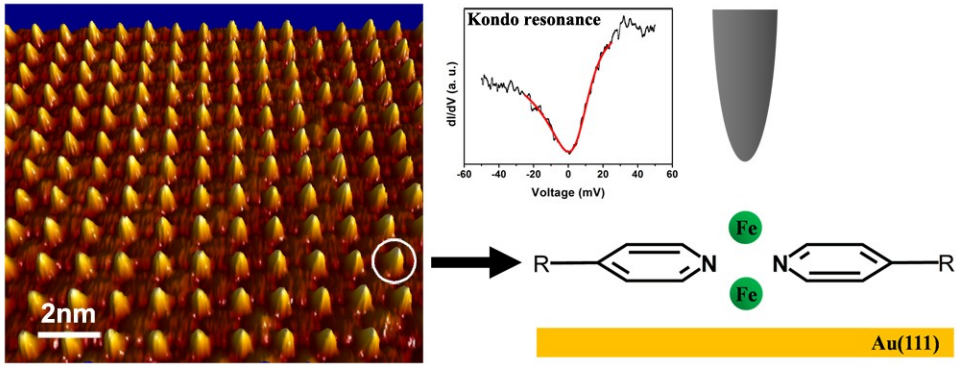




size is 6.5×6.5 nm^2

Conclusion

- first example of out-of-plane dinuclear coordination network
- study the properties of this network
  1. STM lateral manipulation
  2. STM vertical manipulation
  3. Kondo resonance



T. Lin, G. Kuang, W. Wang, N. Lin Two-Dimensional Lattice of Out-of-Plane Dinuclear Iron Centers Exhibiting Kondo Resonance ***ACS Nano*** **DOI:** 10.1021/nn502765g.

Outline

1. On-surface supramolecular coordination self-assembly

- systems exhibiting different dimensionalities
- networks containing out-of-plane dinuclear Fe centers

2. On-surface polymerization

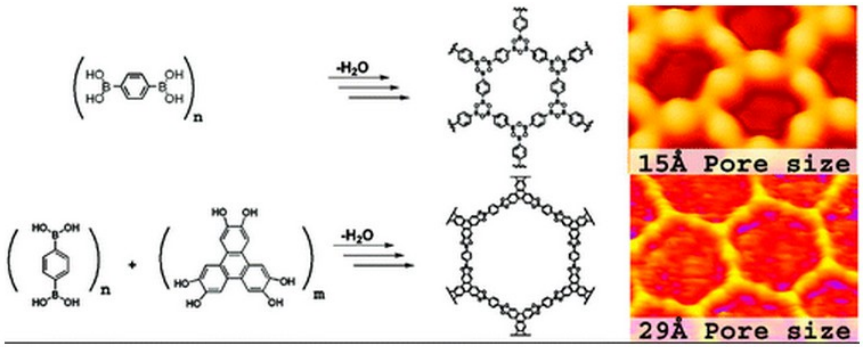
- metal-catalyzed Ullmann coupling reactions

3. A combination of coordination bonds and covalent bonds

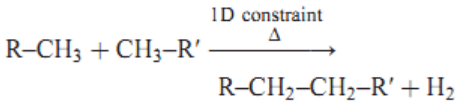
- metal-directed template to control polymerization process

On-Surface Polymerization

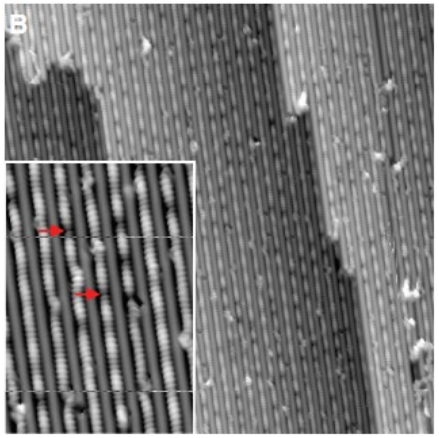
Enhanced Stability



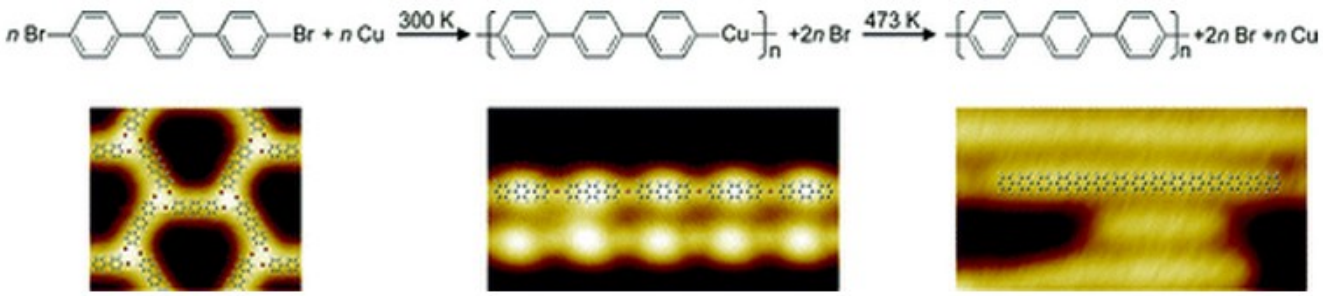
More Accessibility



Alkane Polymerization



Surface as a catalyst



a) Science **2011**, 334, 213; b) J. Am. Chem. Soc. **2008**, 130, 6678; c) J. Am. Chem. Soc. **2011**, 133, 13264.

On-Surface Polymerization

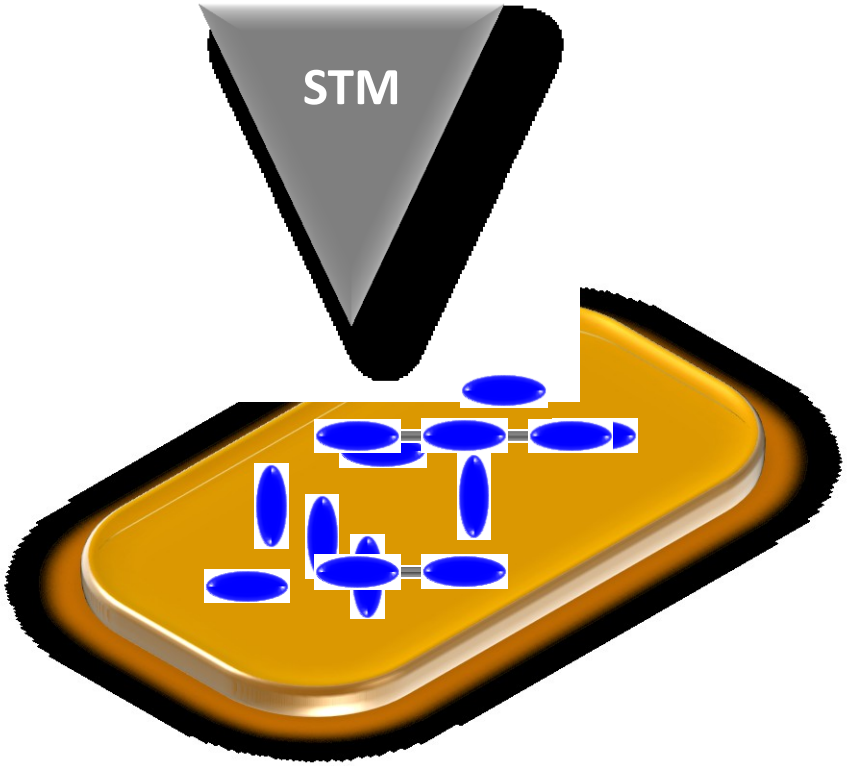
Precursor
(small monomer)

heating

Chemical Reaction

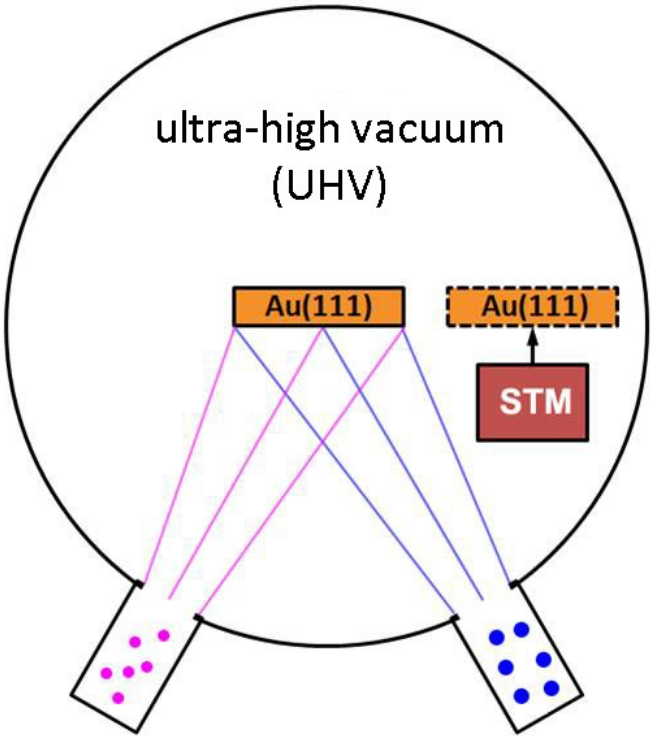
Macromolecular
System (covalent)

... ...

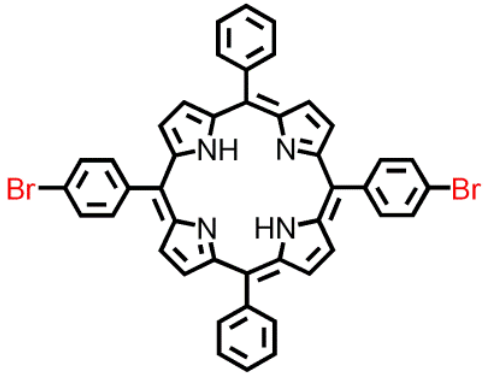


- metal as catalyst?
- activation energy?

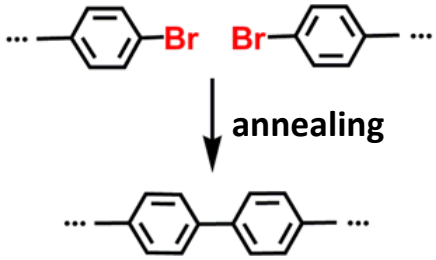
On-Surface Polymerization



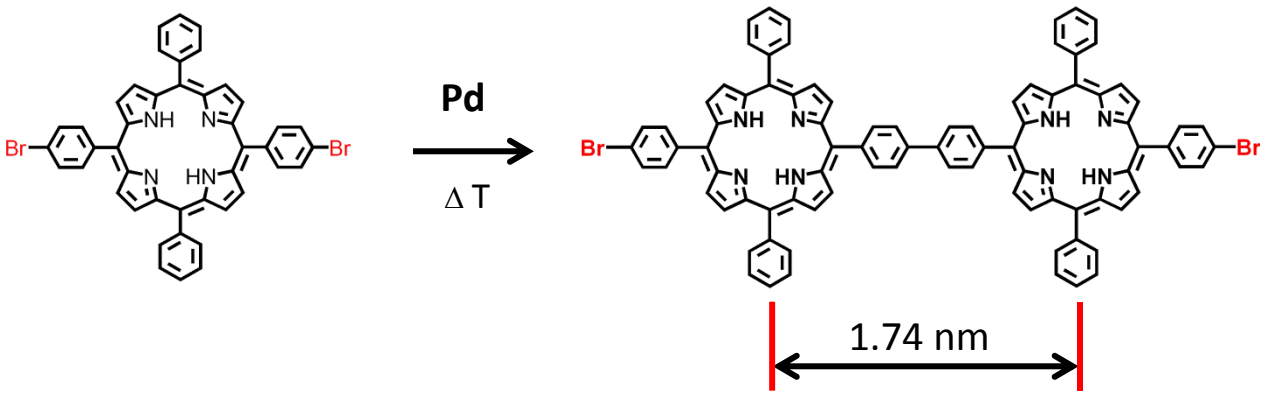
Pd/Cu **molecule**



Ullmann reaction

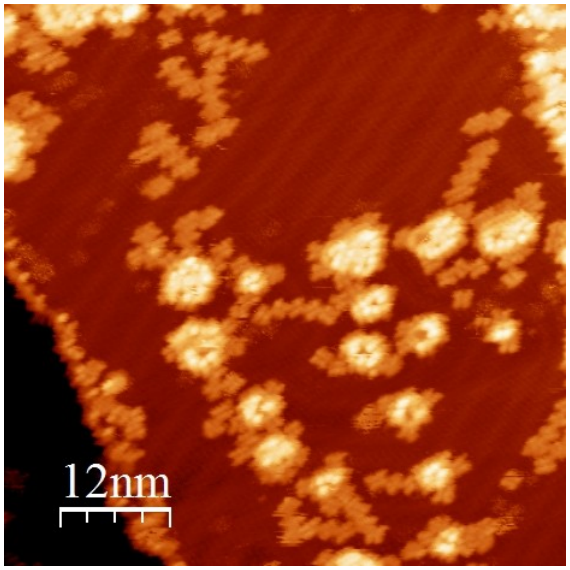


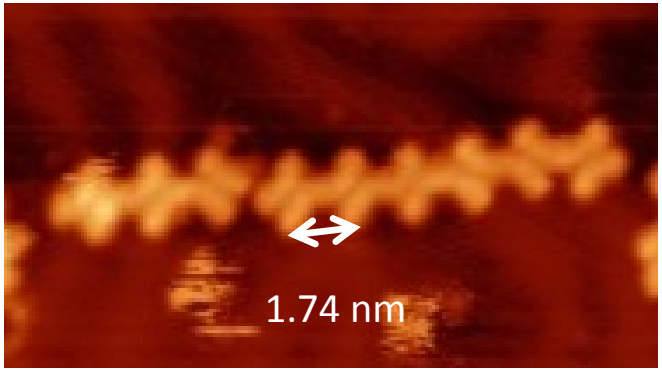
Pd as Catalyst



on pure Au(111) ~**500K**

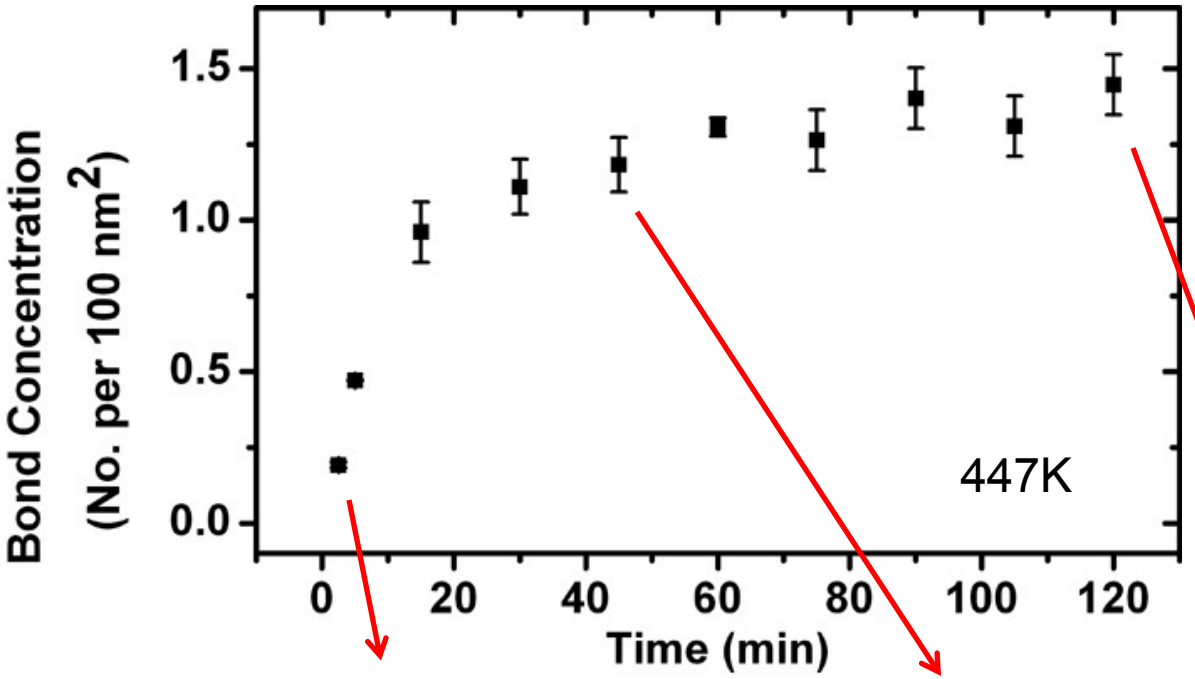
411K

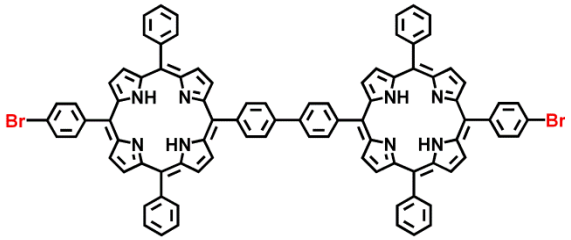


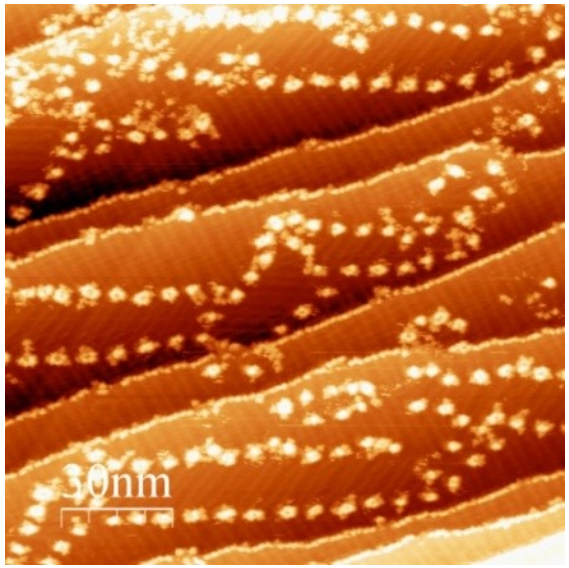


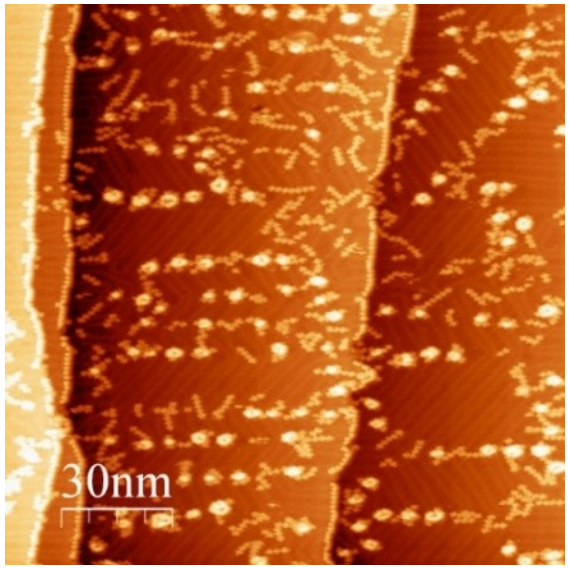
a) *Nat. Chem.* **2012** *4,* 215-220. b) *Nature* **2010** *466,* 470-473.

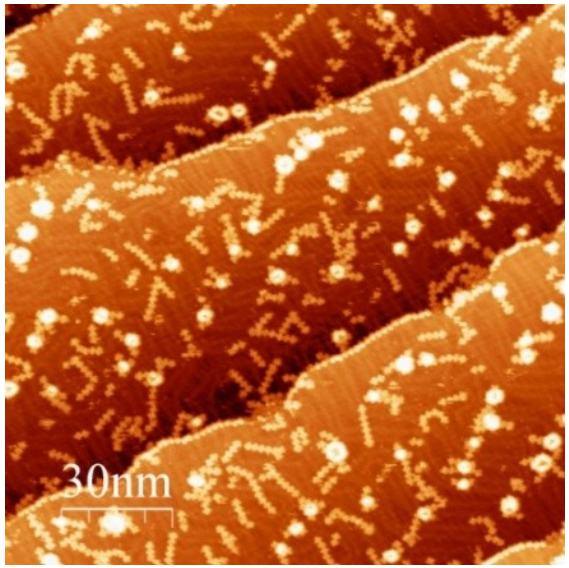
Annealing Process



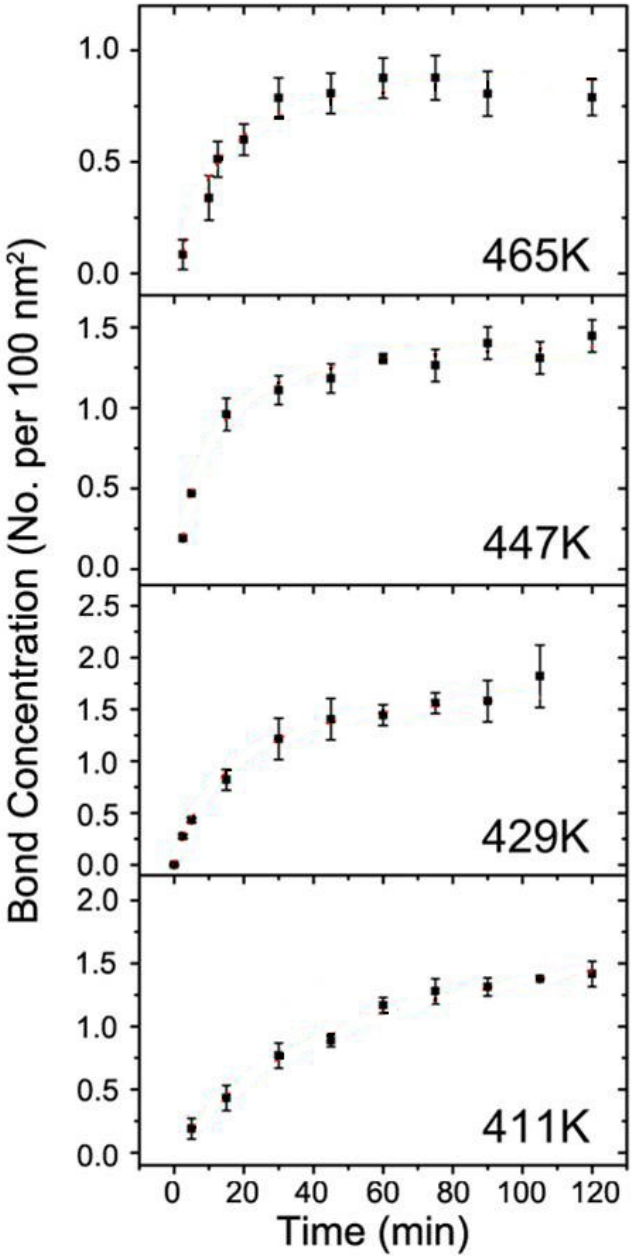


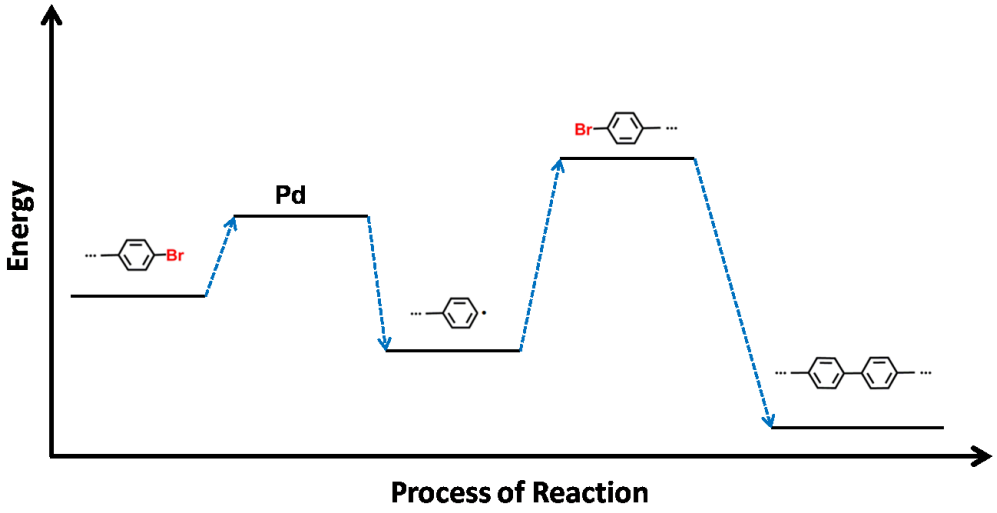


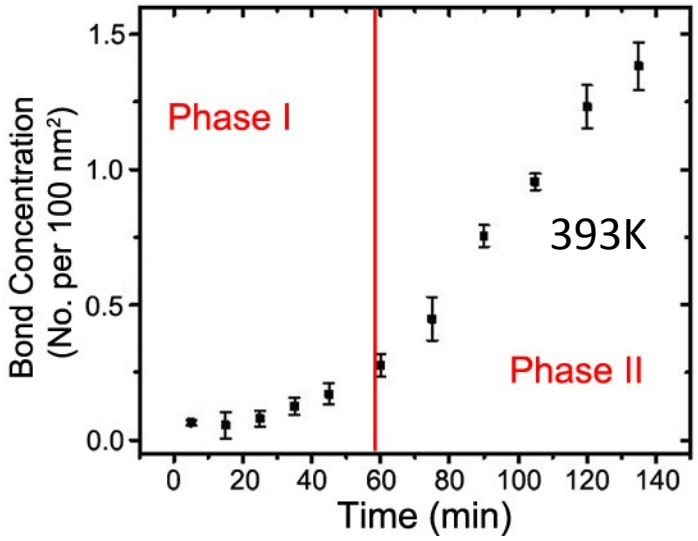




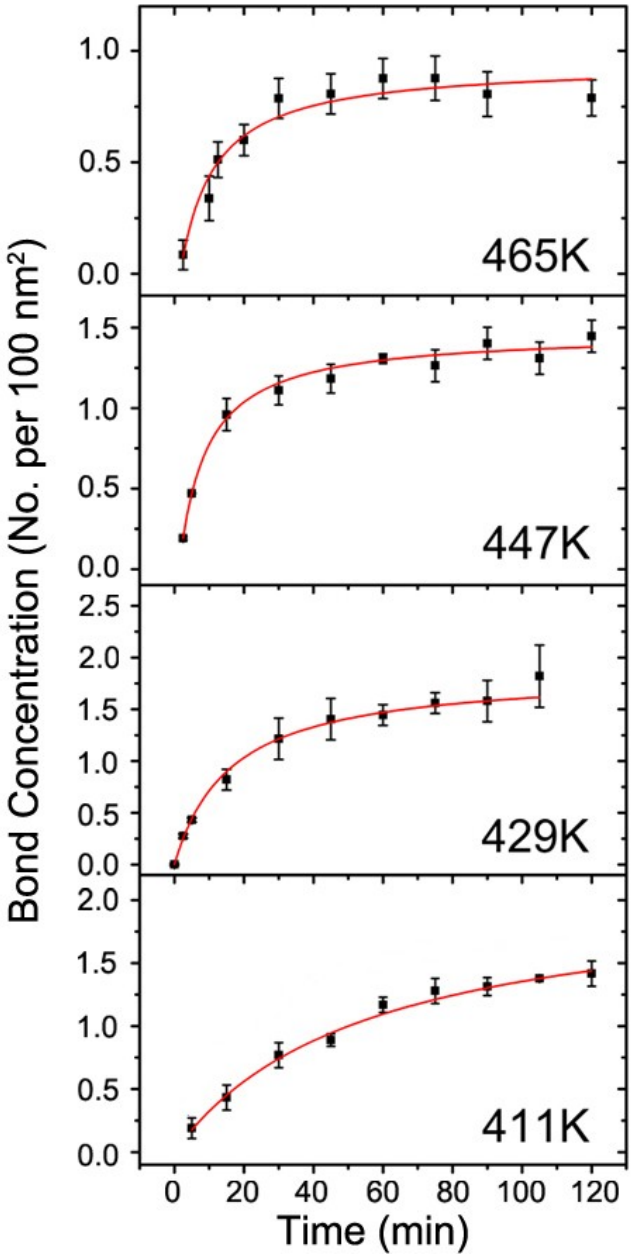
Varying Annealing Temperature

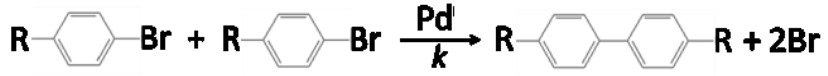






Varying Annealing Temperature



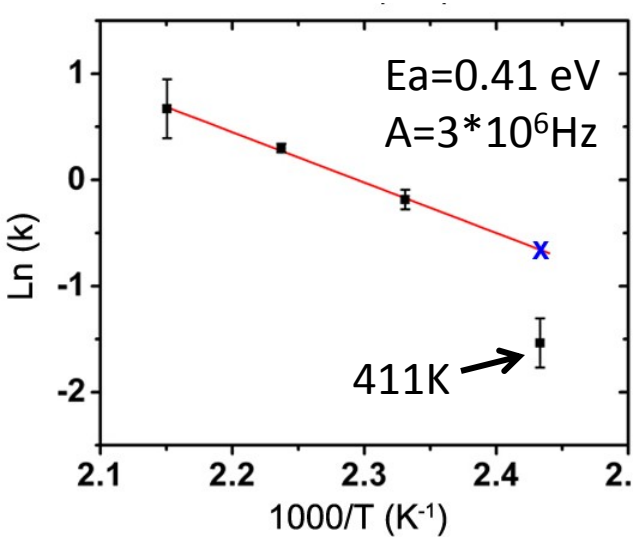


$$\frac{d[Br]}{dt} = -2 \times k[Br]^2$$

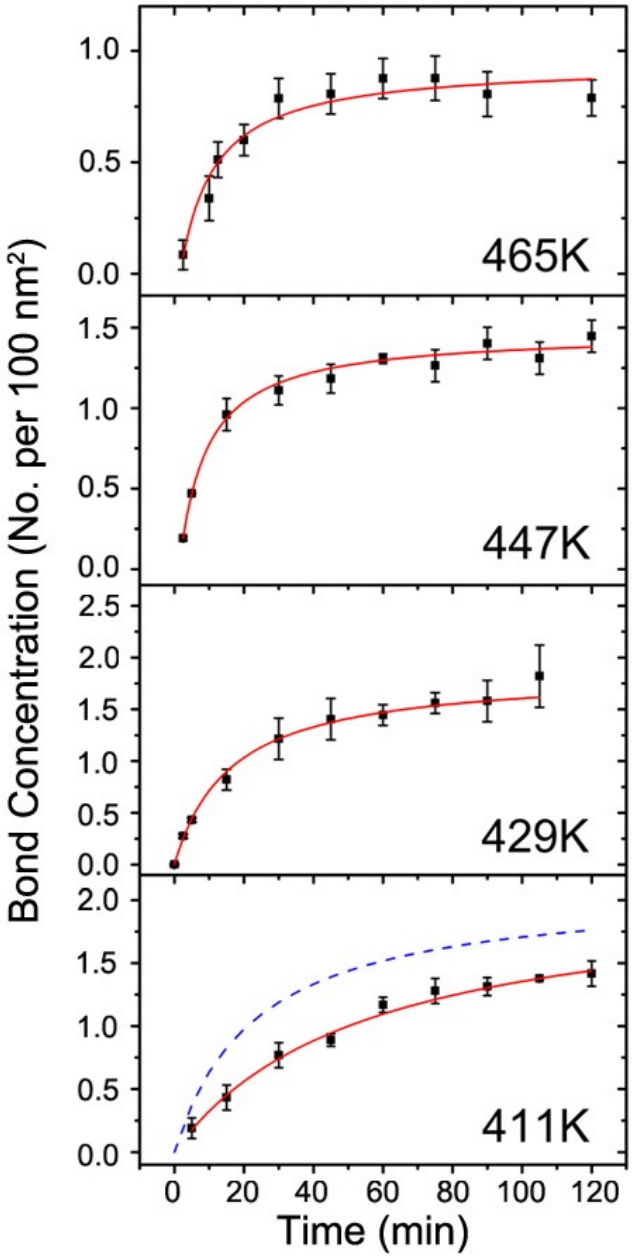
$$\frac{d[Bond]}{dt} = k[Br]^2$$

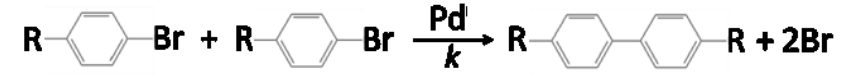
$$[Bond] = \frac{kt[Br]_0^2}{1 + 2 \times kt[Br]_0^2}$$

Arrhenius relation: $$k = A \times \exp\left(-\frac{E_a}{kT}\right)$$



Varying Annealing Temperature





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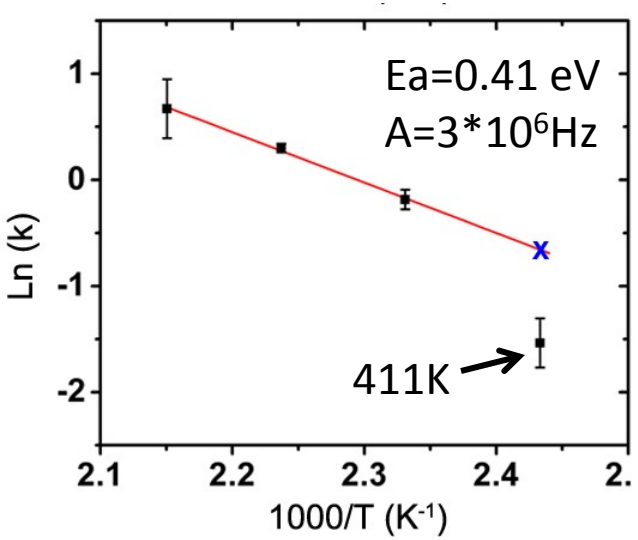
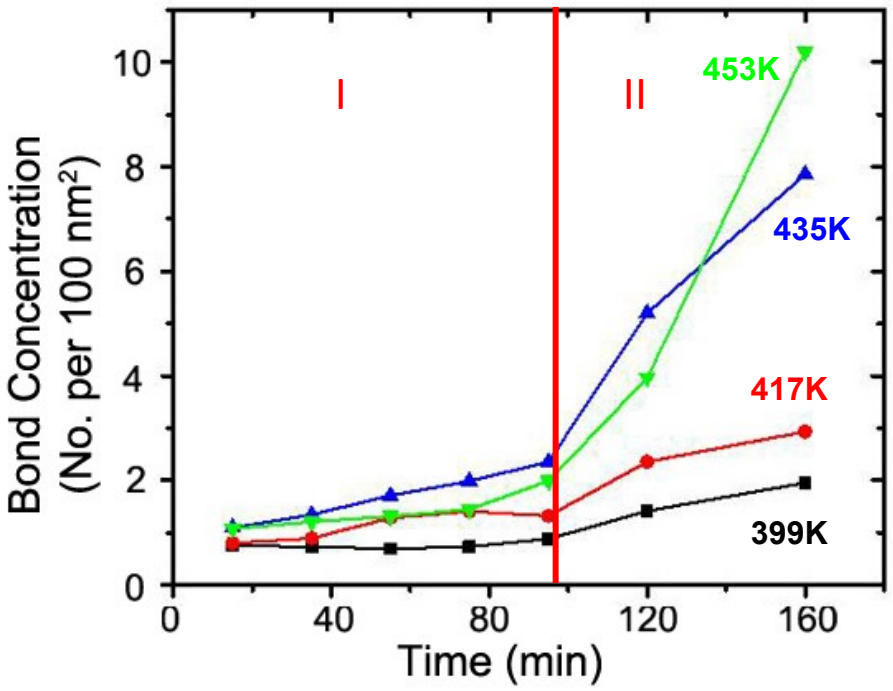
$$\frac{d[Bond]}{dt} = k[Br]^2$$

$$[Bond] = \frac{kt[Br]_0^2}{1 + 2 \times kt[Br]_0^2}$$

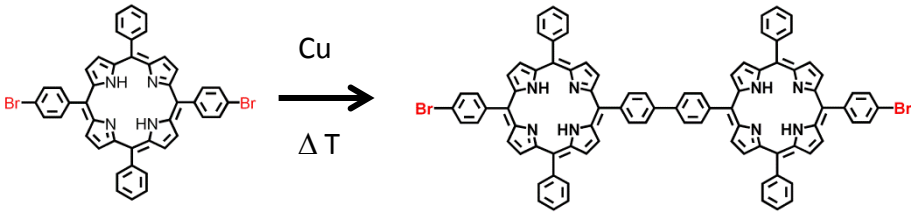
Arrhenius relation: $$k = A \times \exp\left(-\frac{E_a}{kT}\right)$$



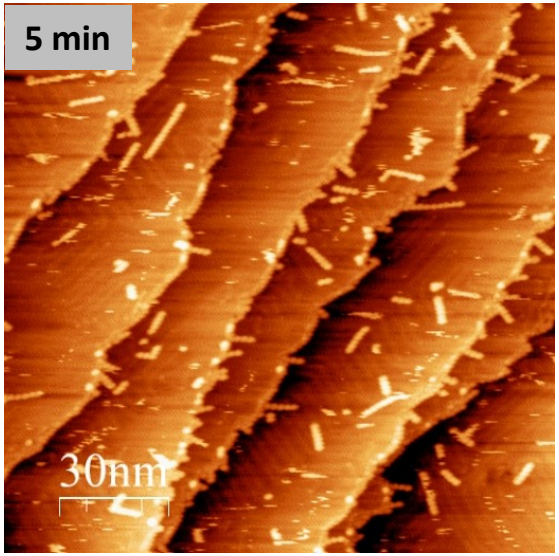
Cu as Catalyst

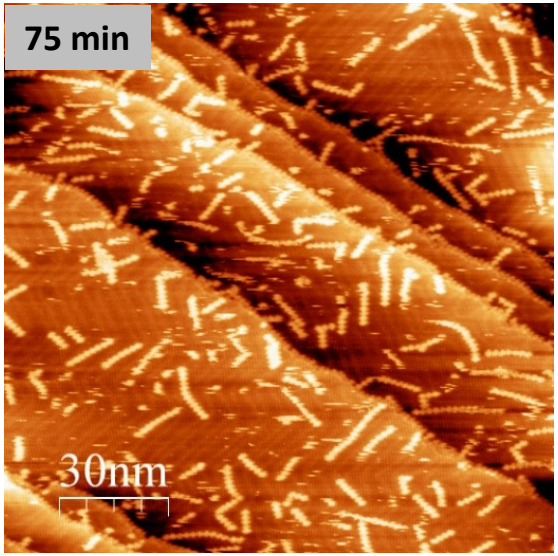


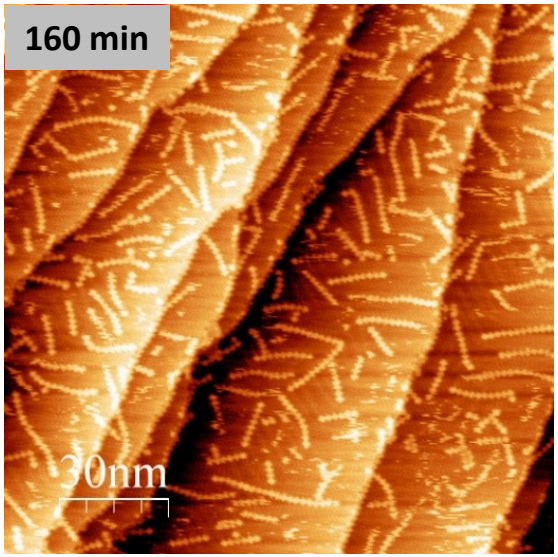
Two-phase



@453K

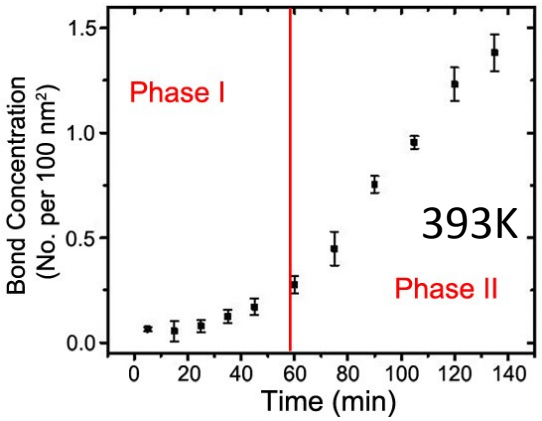


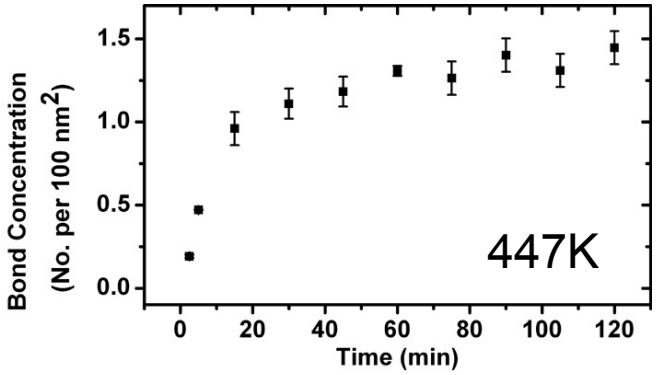




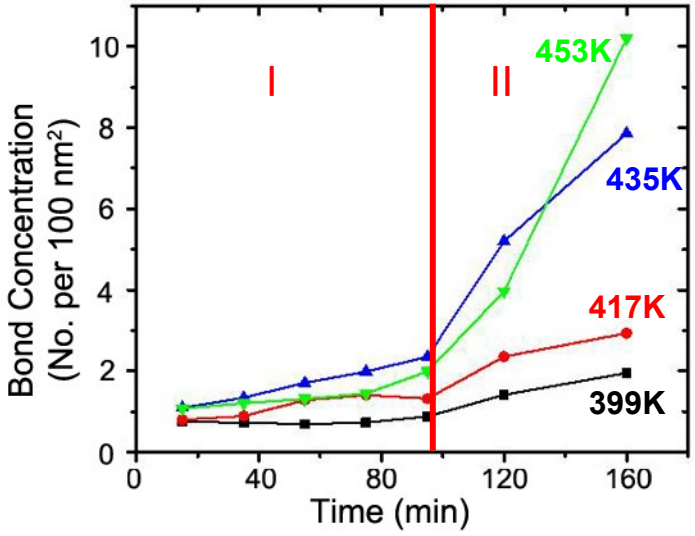
Comparison Pd-Cu

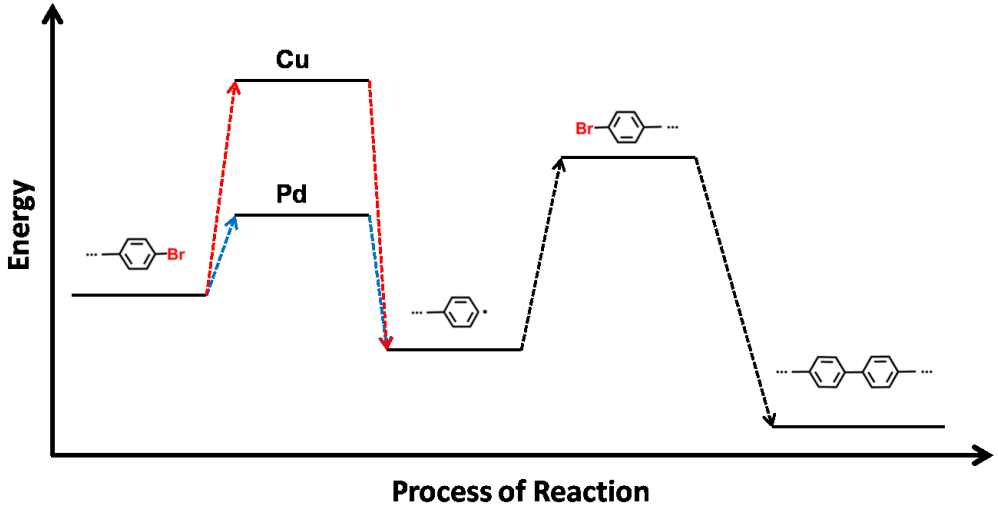
Pd





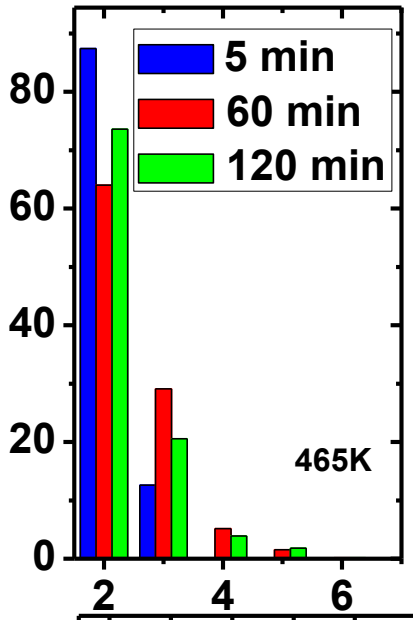
Cu

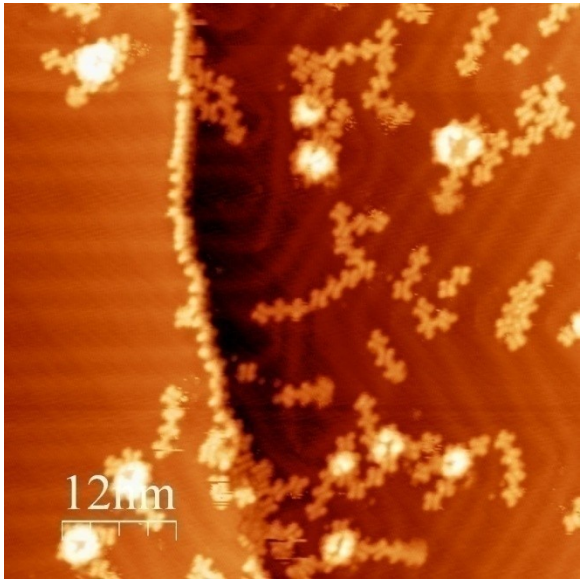


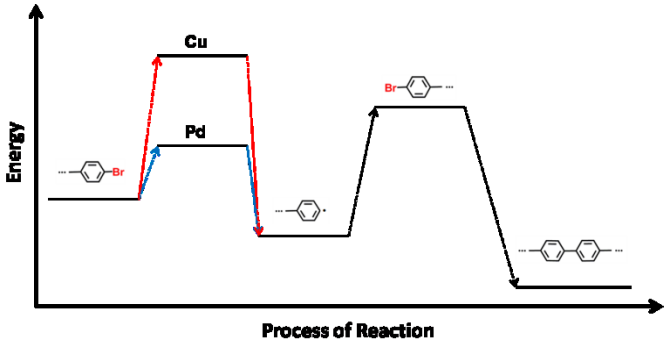


Comparison Pd-Cu

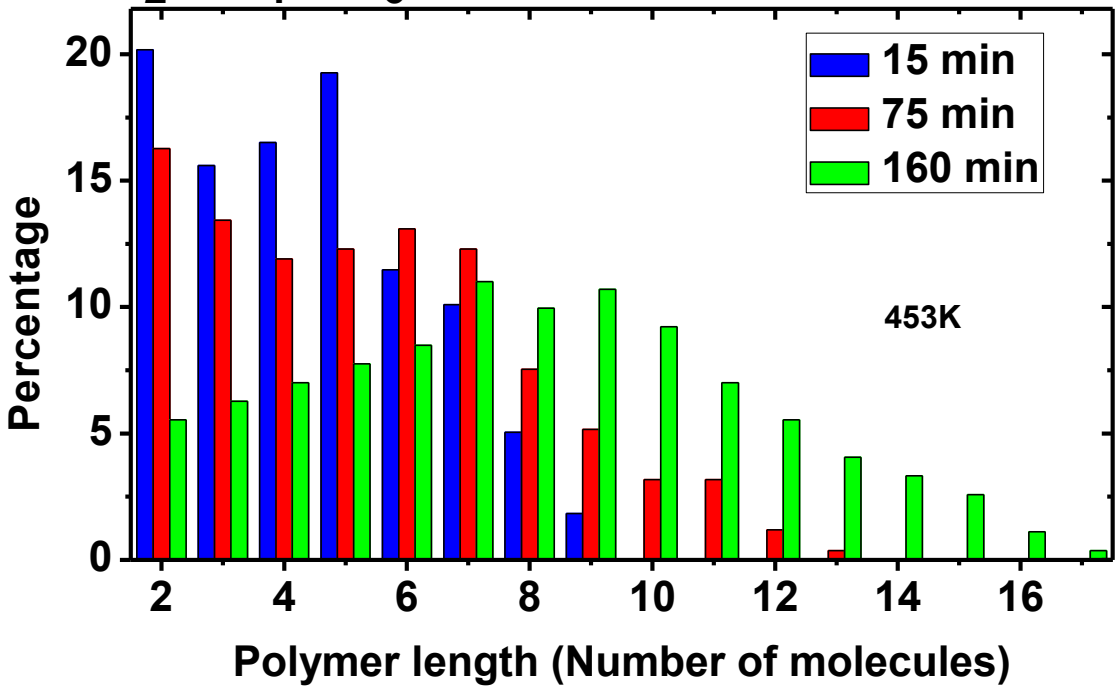
Pd

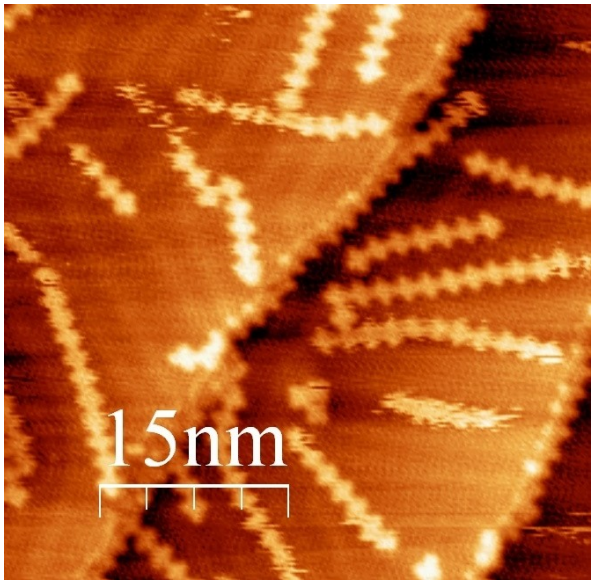




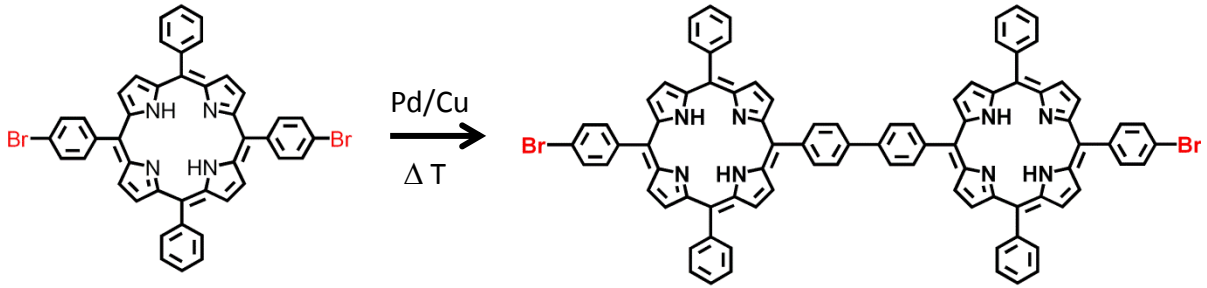


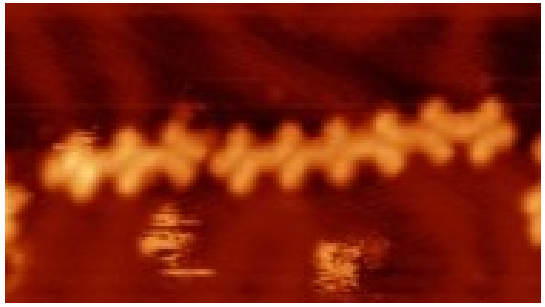
Cu



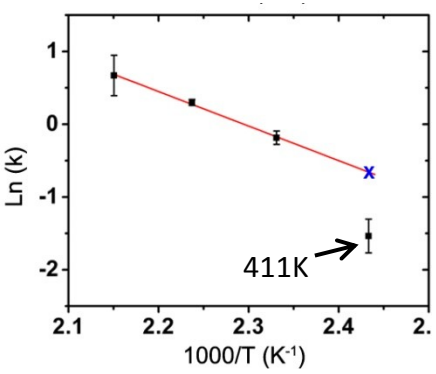


Conclusion

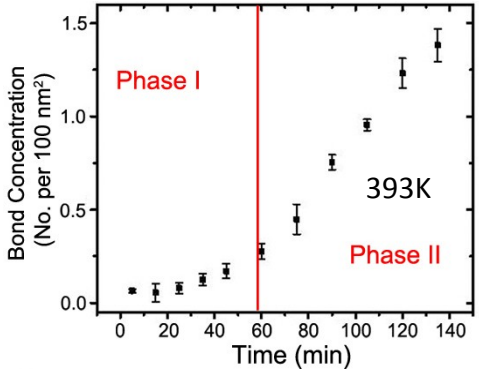




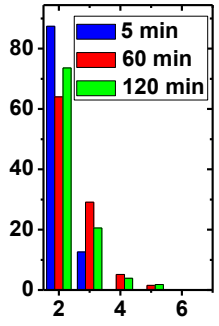
Pd- / Cu-Catalyzed homocoupling

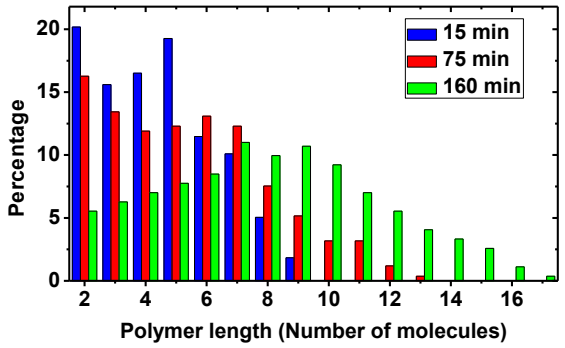


Activation Energy 0.41 eV



2 phases





Comparison

J. Adisoejoso, T. Lin, X. S. Shang, K. Shi, A. Gupta, P. N. Liu, N. Lin, A Single-Molecule Level Mechanistic Study of Pd-Catalyzed and Cu-Catalyzed Homo-Coupling of Aryl Bromide on a Au(111) Surface, ***Chem. Eur. J.*** 20, 4111–4116 (2014).

Outline

1. On-surface supramolecular coordination self-assembly

- systems exhibiting different dimensionalities
- networks containing out-of-plane dinuclear Fe centers

2. On-surface polymerization

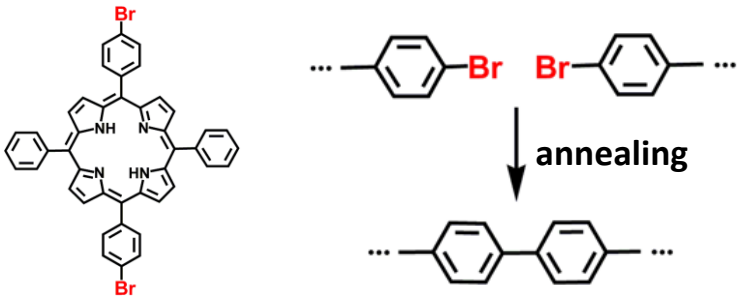
- metal-catalyzed Ullmann coupling reactions

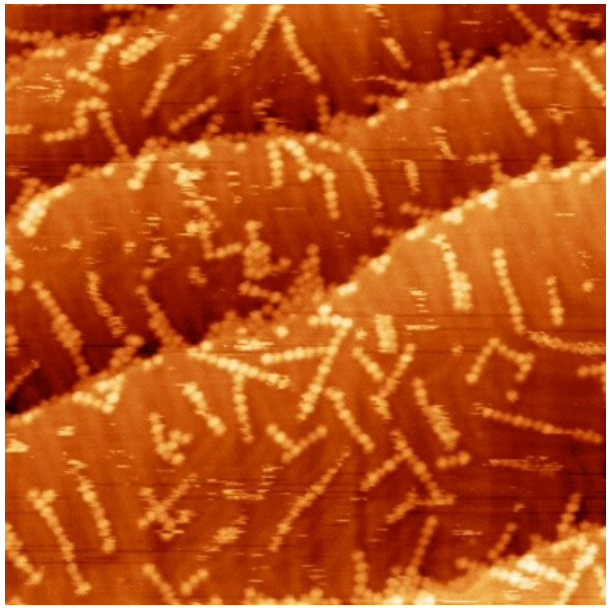
3. A combination of coordination bonds and covalent bonds

- metal-directed template to control polymerization process

1D Polymerization

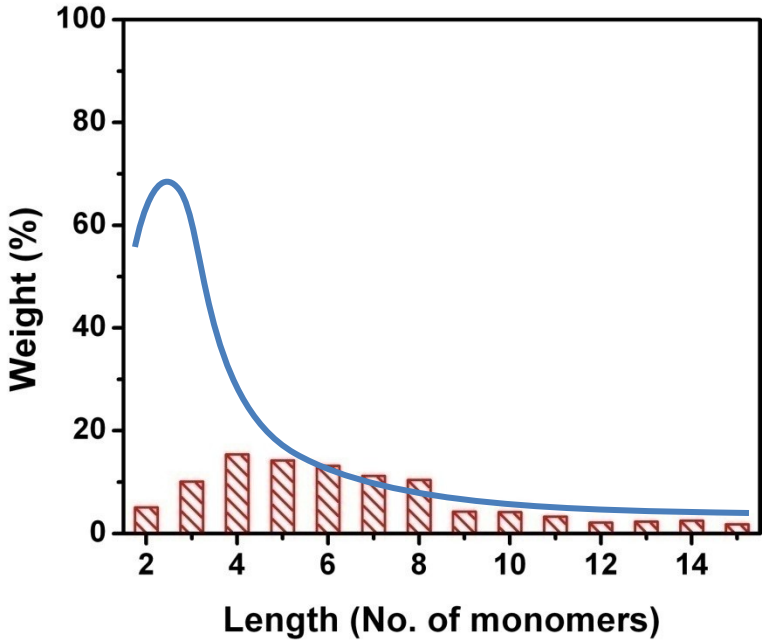
Covalent by Debromination





size: 100*100 nm^2

weight: % of molecule in each config.

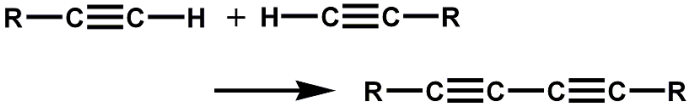


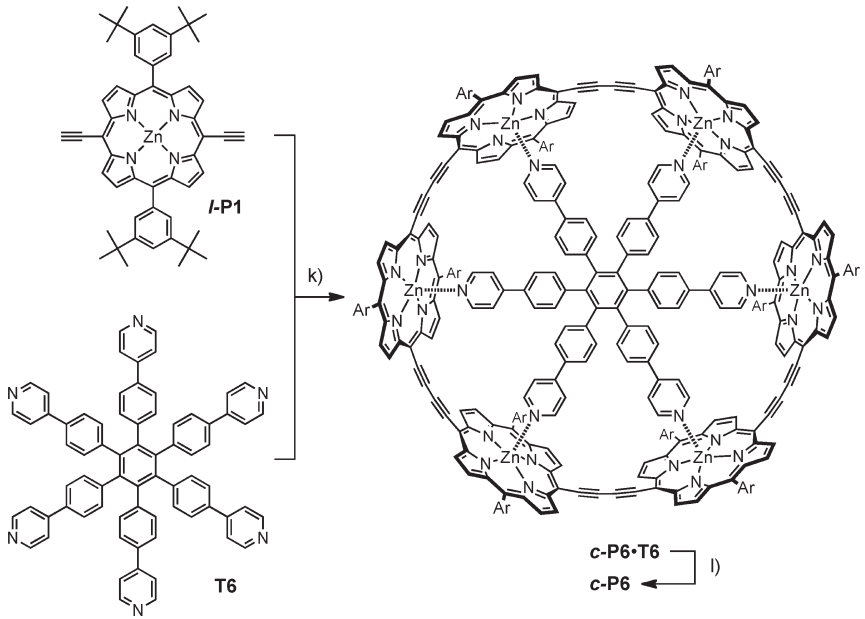
a) Nat. Nanotechnol. **2007,** 2, 687; b) *J. Am. Chem. Soc*. **2013,** 135, 3576. c) Nat. Chem. **2012**, 4, 215.

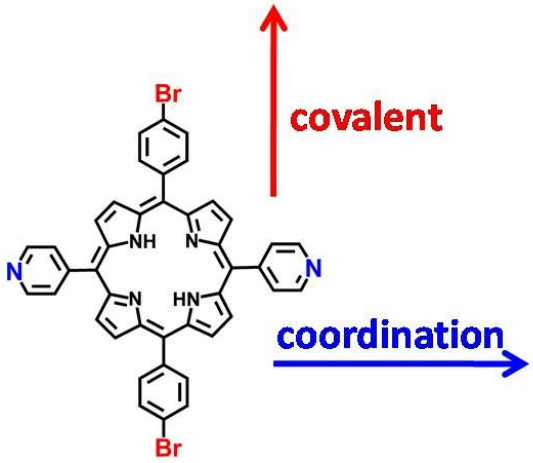
Template Synthesis

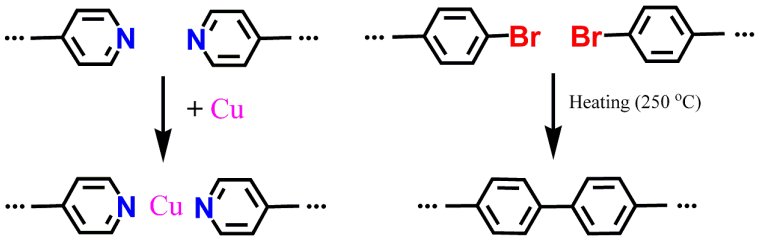
Template Synthesis:
Non-covalent bond to control the formation of covalent products.

Glaser Coupling:







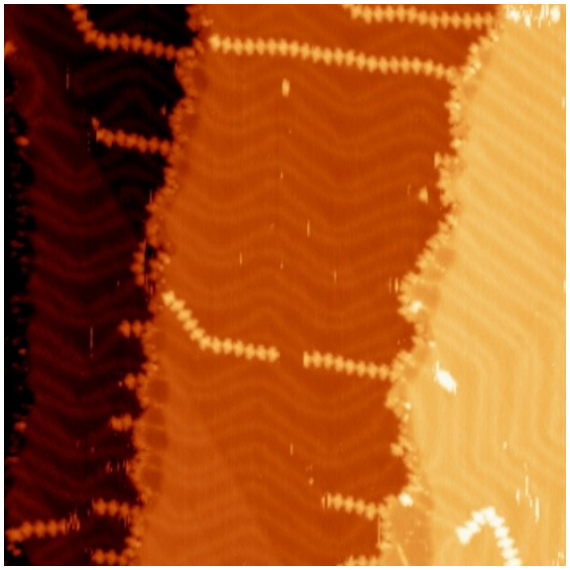


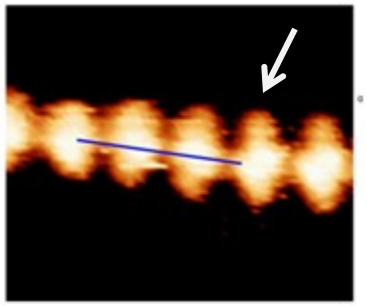
a) Acc. Chem. Res. **1993**, 26, 469; b) J. Am. Chem. Soc. **2011**, 133, 17262.

Experimental Results

+ Cu @Au(111) RT

Single-Row Chains

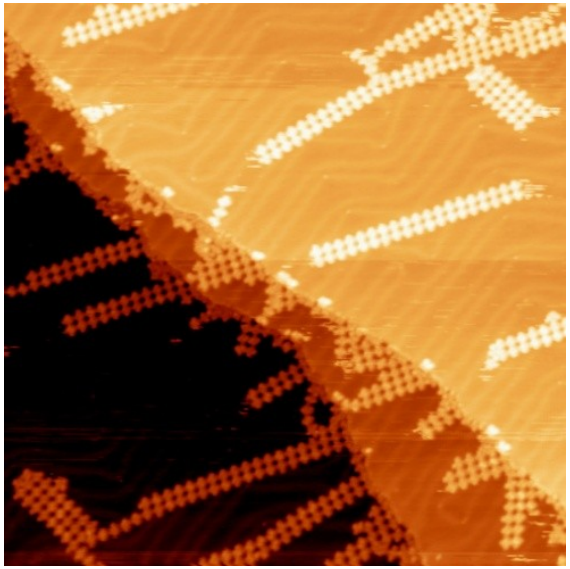




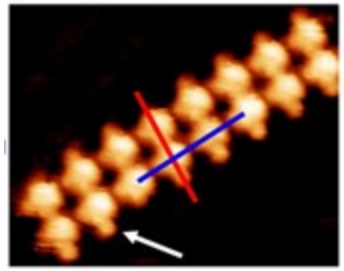
blue: 1.97nm

180°C annealing

Double-Row Chains

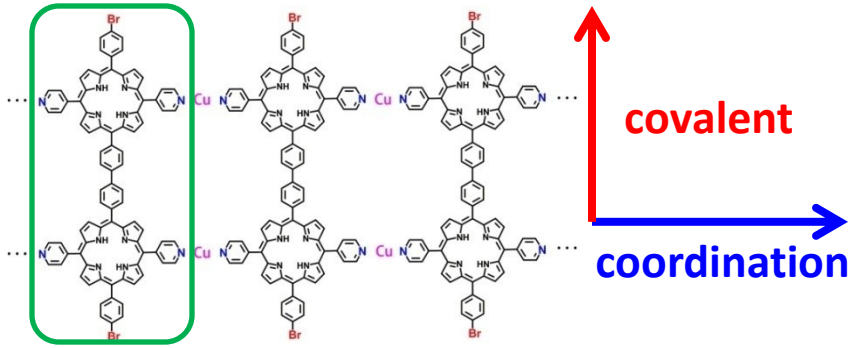


size: 100*100 nm^2

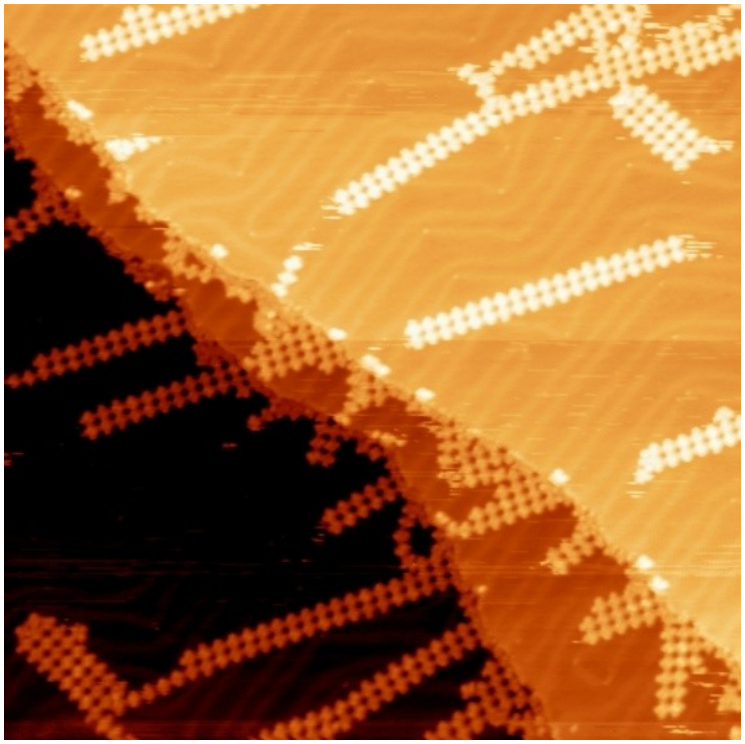


blue: 1.95nm

red: 1.73nm

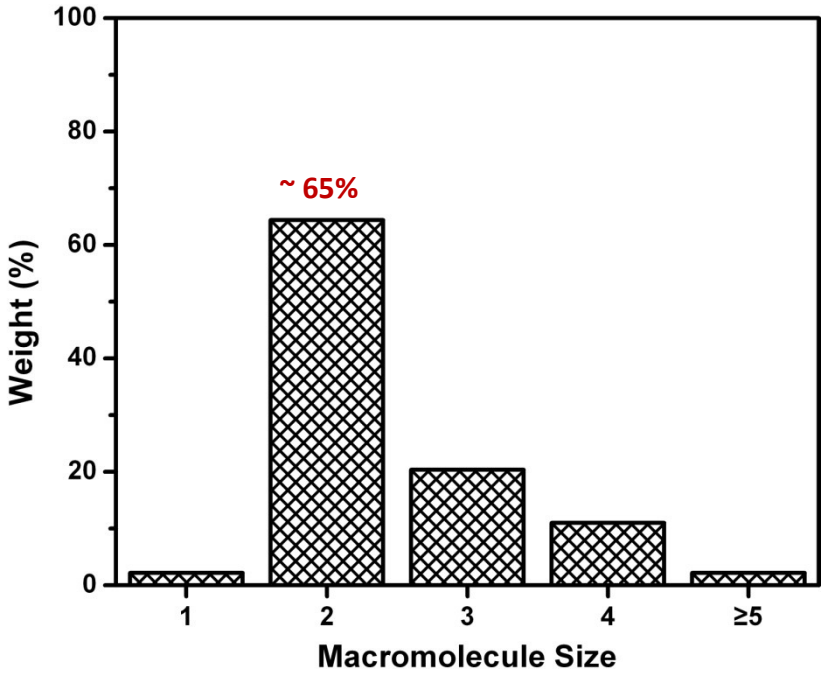


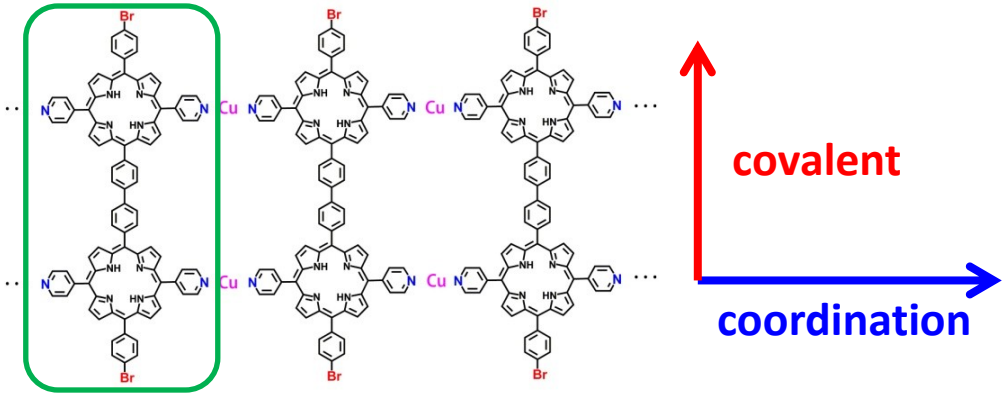
Experimental Results



size: 100*100 nm^2

weight: % of molecule in each config.
Macro. Size: size of covalent structure/width of chain

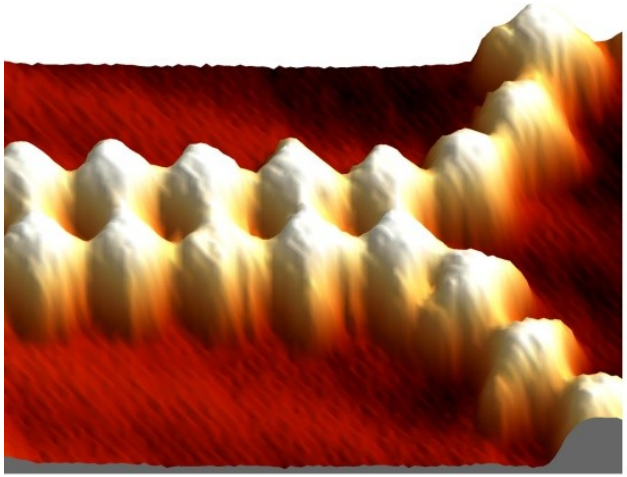


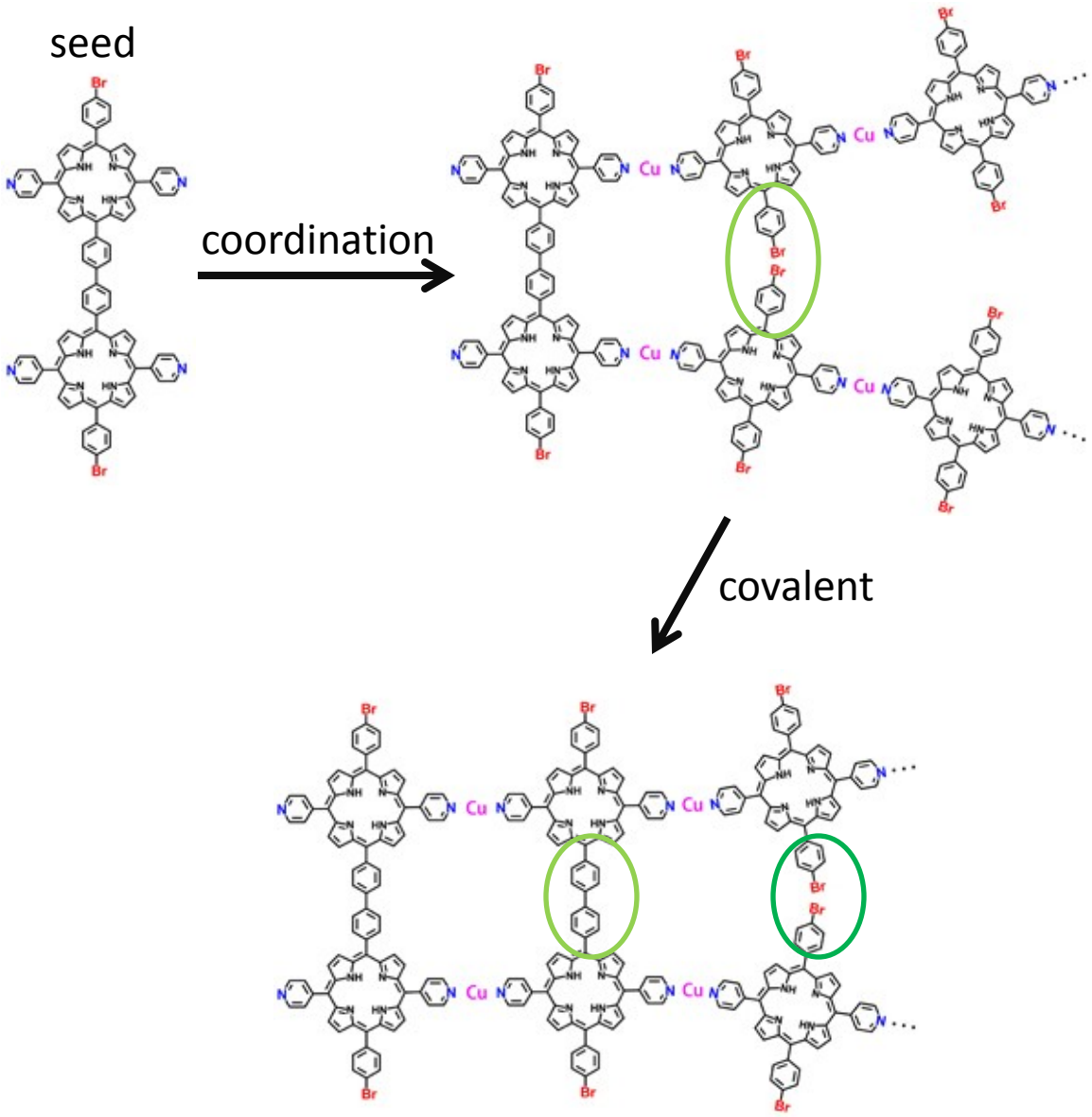


Polymerization: confined into dimer

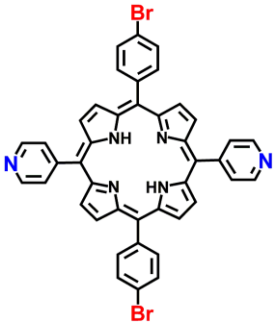
Mechanism

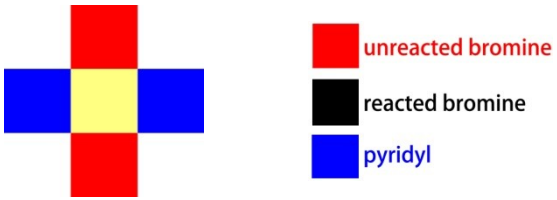
seed-zipper model



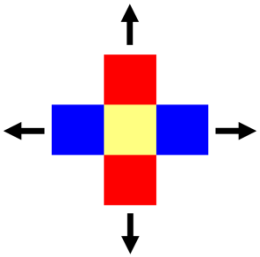


kinetic Monte Carlo Simulation (kMC)

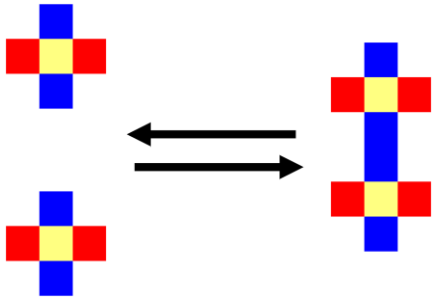




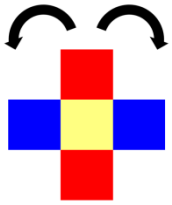
hopping



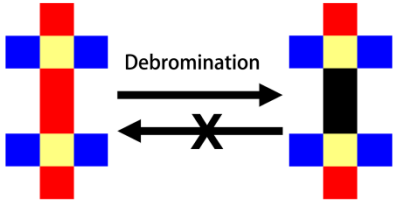
coordination bond



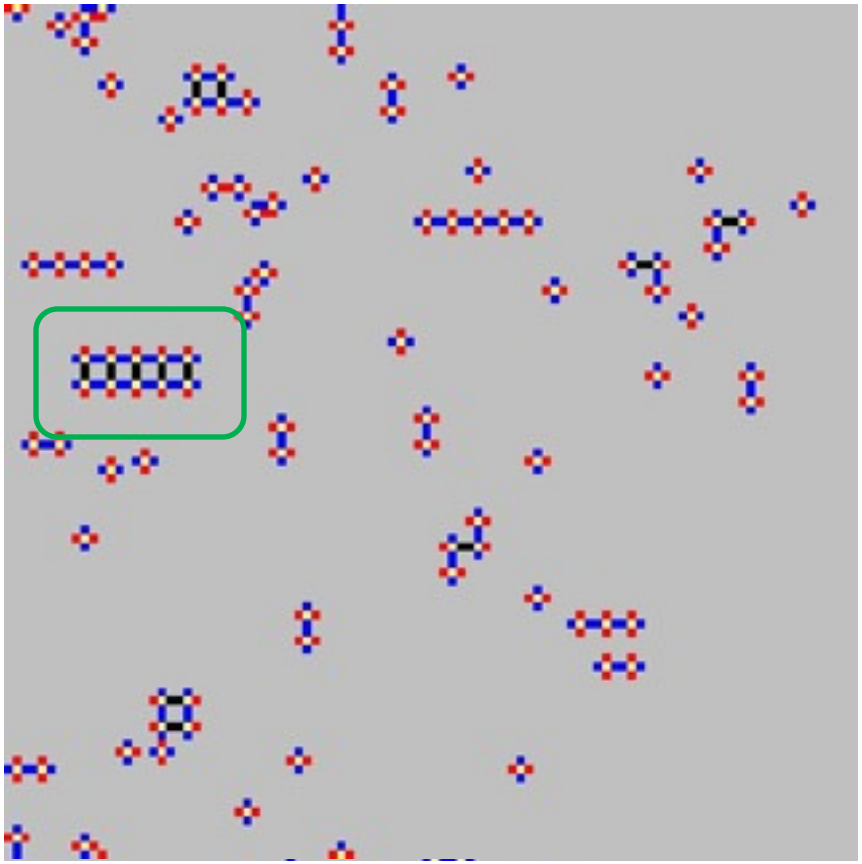
rotation



covalent bond



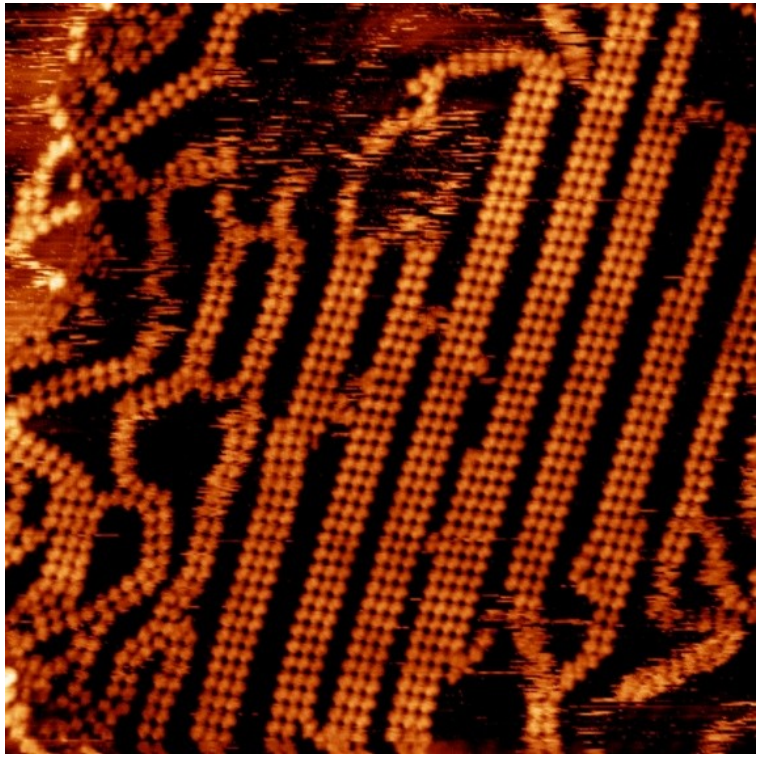
@ 180℃



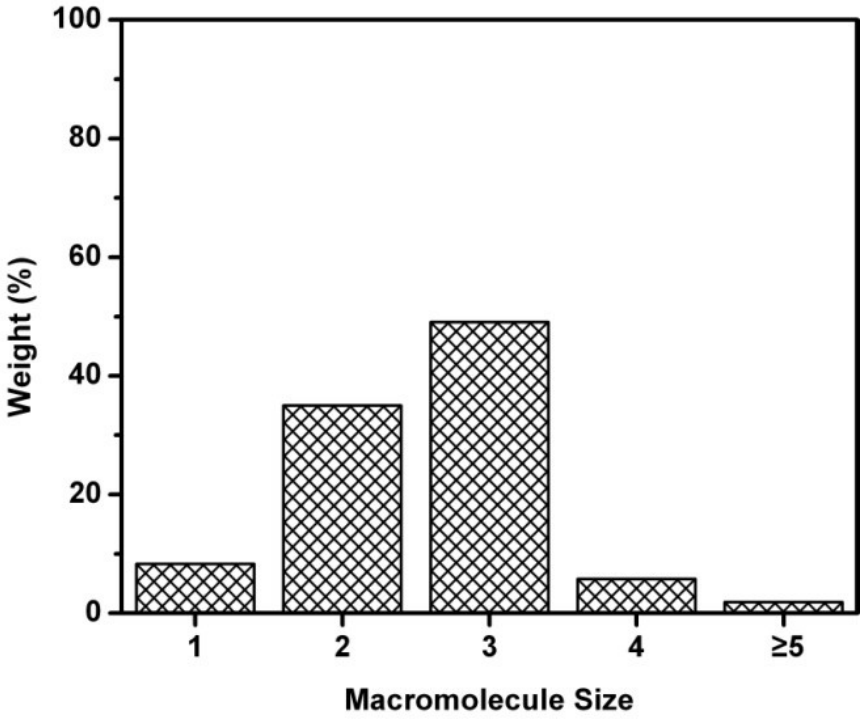
- initial dimer act as seed
- anchored by coordination
- zip along the chain direction

Width Control

deposit onto hot sample with Cu (Temp=240 ℃)



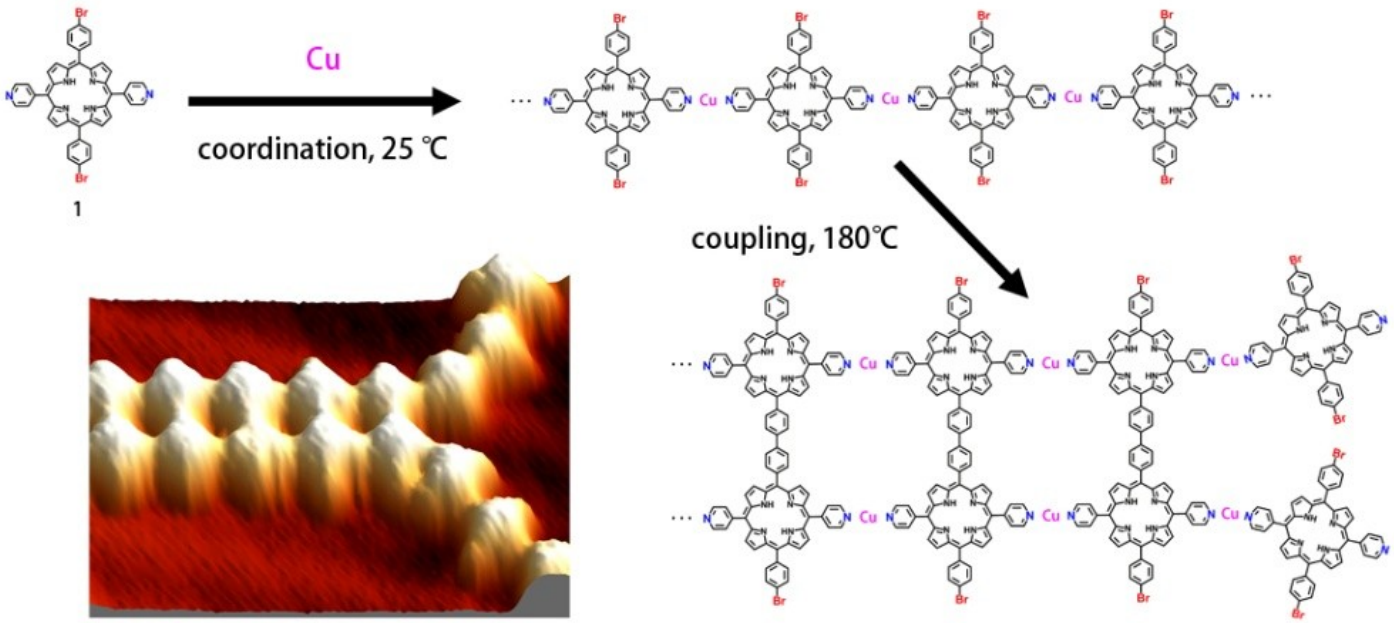
size: 100*100 nm^2



Trimer Seed

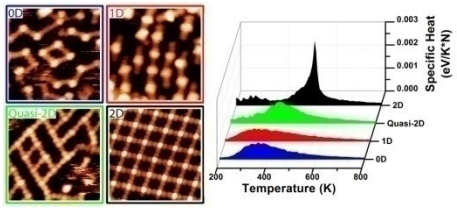
Conclusion

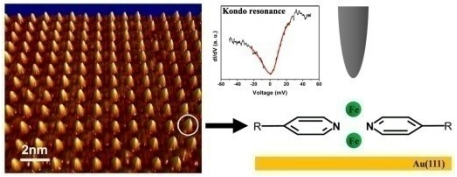
- coordination bond → size-limited polymerization reaction



T. Lin, X. Shang, J. Adisoejoso, P. N. Liu, N. Lin, Steering On-Surface Polymerization with Metal-Directed Template, ***J. Am. Chem. Soc.*** 135, 3576 (2013).

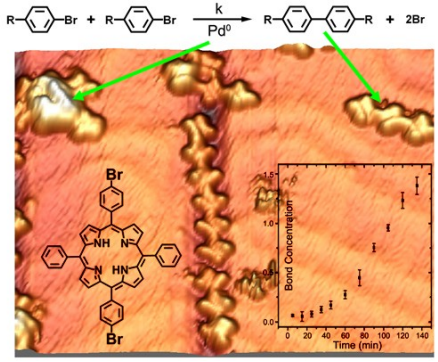
Summary





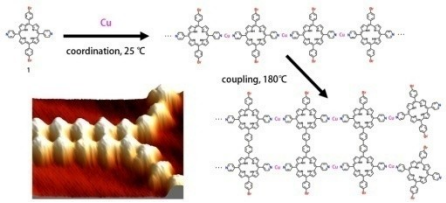
1. On-surface supramolecular coordination self-assembly

- systems exhibiting different dimensionalities
- networks containing out-of-plane dinuclear Fe centers



2. On-surface polymerization

- metal-catalyzed Ullmann coupling reactions



3. A combination of coordination bonds and covalent bonds

- metal-directed template to control polymerization process

Publication

[9] T. Lin, Q. Wu, J. Liu, Z. Shi, P. N. Liu, N. Lin Thermodynamic versus Kinetic Controls in Self-Assembly of Metal-Organic Coordination Systems Exhibiting Different Dimensionalities, in preparation.

[8] T. Lin, G. Kuang, W. Wang, N. Lin Two-Dimensional Lattice of Out-of-Plane Dinuclear Iron Centers Exhibiting Kondo Resonance ***ACS Nano*** **DOI:** 10.1021/nn502765g.

[7] J. Adisoejoso, T. Lin, X. S. Shang, K. Shi, A. Gupta, P. N. Liu, N. Lin, A Single-Molecule Level Mechanistic Study of Pd-Catalyzed and Cu-Catalyzed Homo-Coupling of Aryl Bromide on a Au(111) Surface, ***Chem. Eur. J.*** 20, 4111–4116 (2014).

[6] T. Lin, X. S. Shang, P. N. Liu, N. Lin, Multi-Component Assembly of Supramolecular Coordination Polygons on a Au(111) Surface, ***J. Phys. Chem. C***. 117, 23027 (2013).

[5] X. F. Mao, T. Lin, J. Adisoejoso, Z. Shi, X. S. Shang, P. N. Liu, N. Lin, Coordination self-assembly of bromo-phenyl and pyridyl functionalized porphyrins with Fe on a Au(111) surface, ***Phys. Chem. Chem. Phys.*** 15, 12447 (2013).

[4] T. Lin, X. Shang, J. Adisoejoso, P. N. Liu, N. Lin, Steering On-Surface Polymerization with Metal-Directed Template, ***J. Am. Chem. Soc.*** 135, 3576 (2013).

[3] J. Liu, T. Lin, Z. Shi, F. Xia, L. Dong, P. N. Liu, N. Lin, Structural Transformation of Two-Dimensional Metal-Organic Coordination Networks driven by Intrinsic In-Plane Compression, ***J. Am. Chem. Soc***. 133, 18760 (2011).

[2] Z. Shi, T. Lin, J. Liu, P. N. Liu, N. Lin, Regulating a Two-Dimensional Metallo-Supramolecular Self-assembly with Multiple Outputs, ***CrystEngComm*** 13, 5532 (2011).

[1] Z. Shi, J. Liu, T. Lin, F. Xia, P. N. Liu, N. Lin, Thermodynamics and Selectivity of Two-Dimensional Metallo-supramolecular Self-Assembly Resolved at Molecular Scale, ***J. Am. Chem. Soc*****.** 133, 6150 (2011).

Acknowledgements

- Prof. LIN Nian
- Prof. LIU Peinian
- Current members:
  - Mr. WU Qi
  - Mr. CHEN Shen
  - Mr. CHEN Cheng
  - Mr. KUANG Guowen
  - Mr. LYU Guoqing
  - Dr. DONG Lei
  - Dr. ZHAO Wei
- Former members:
  - Mr. LI Yang
  - Dr. SHI Ziliang
  - Dr. WANG Shiyong
  - Dr. WANG Weihua
  - Dr. ADISOEJOSO Jinne

Acknowledgements

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Prof. WEN Weijia

Prof. HAN Yilong

❖ Chairman

Prof. XIANG Yang

Thanks For Your Attention!