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

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b) [http://www.just2good.co.uk/cpuSilicon.php](http://www.just2good.co.uk/cpuSilicon.php)
c) Makoto FUJITA’s homepage
Introduction: Low-Dimensional Systems

3D to low-dimensional systems \(\rightarrow\) single molecule level

structural information

electronic / magnetic properties

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

effects of substrate

surface sensitive techniques

- scanning tunneling microscopy (STM)

3D to low-dimensional systems

- single molecule level

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

- electronic / magnetic properties

- effects of substrate

- scanning tunneling microscopy (STM)

- surface sensitive techniques

- 3D to low-dimensional systems

References:

Introduction: Experimental Setup

- **Sample preparation:**
  1. organic molecule source
  2. metal atom source

- **Characterization:**
  1. STM: structural information
  2. STS: electronic structure
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
1. On-surface supramolecular coordination self-assembly
   - systems exhibiting different dimensionalities
   - networks containing out-of-plane dinuclear Fe centers

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   - metal-directed template to control polymerization process
Building blocks:

- organic ligands
- metal atoms

Metal-organic coordination bond:

- preferred bonding geometries
- recognition
- reversibility
- self-correction

On-surface Supramolecular Coordination Self-Assembly
Supramolecular System

2D Extended Networks

2D structures: easy

0D Discrete Structures

0D structures: difficult

dimensionality?

Molecules

A. B. E. 

C. D. 

@Au(111) by RT-STM
Experimental Results

0D

1D

Quasi-2D

2D

size: 20*20 nm²

65°
Experimental Results

<table>
<thead>
<tr>
<th>Size: 100*100 nm²</th>
<th>0D</th>
<th>1D</th>
<th>Quasi-2D</th>
<th>2D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_a = 300K$</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
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<tr>
<td>$T_a = 400K$</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
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<tr>
<td>$T_a = 450K$</td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image10" alt="Image" /></td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
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<tr>
<td>$T_a = 480K$</td>
<td><img src="image13" alt="Image" /></td>
<td><img src="image14" alt="Image" /></td>
<td><img src="image15" alt="Image" /></td>
<td><img src="image16" alt="Image" /></td>
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<tr>
<td>$T_a = 540K$</td>
<td><img src="image17" alt="Image" /></td>
<td><img src="image18" alt="Image" /></td>
<td><img src="image19" alt="Image" /></td>
<td><img src="image20" alt="Image" /></td>
</tr>
</tbody>
</table>
Simulation Results (Monte Carlo)

hopping with/without configuration changes:

\[ \text{compare energy differences:} \]

\[ P_{\text{acc}} = \min(1, e^{\frac{\Delta U}{kT}}) \]
\[ r \in (0,1) \]
\[ r < P_{\text{acc}}, \text{ accepted} \]
\[ r > P_{\text{acc}}, \text{ rejected} \]

Eb=0.2eV, MCstep=10^9

\text{Eb=0.2eV, MCstep=10^9}

\text{J. Am. Chem. Soc. 2013 135, 6942-6950.}
Kinetic trapped at RT

Equilibrium states at RT

- 0D
- 1D
- Quasi-2D
- 2D

free

Kinetic trapped at RT

- substrate trapped

$T_a = 300K$

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)

<table>
<thead>
<tr>
<th></th>
<th>0D</th>
<th>1D</th>
<th>Quasi-2D</th>
<th>2D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>350K</td>
<td>325K</td>
<td>400K</td>
<td>525K</td>
</tr>
</tbody>
</table>

0D, 1D, Quasi-2D: broad & low
2D: sharp & high
Simulation Results (Monte Carlo)

**molecular architectures** → **gas phase**

(randomly distributed)

**Specific Heat (eV/K•N)**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
</tr>
<tr>
<td>200</td>
</tr>
</tbody>
</table>

- **0D**
- **2D**

**not sharp transition**

**sharp transition**

\[ T_c - 20K \]

\[ T_c \]

\[ T_c + 20K \]
Discussion (Fe in 0D)

- **@300K**: Fe island or (dive into substrate)
- **@450K**: Fe island or (dive into substrate)
- **@480K**: Fe island or (dive into substrate)

**Size**: 100*100 nm²
Discussion (Fe in 2D)

![Graph showing specific heat vs temperature with 0D and 2D curves.]

- @300K: Fe island (dive in substrate)
- @480K: Fe island
- @540K: Fe island

size: 100*100 nm²
Conclusion

- supramolecular coordination systems with different dimensionality
  1. 0D, 1D, Quasi-2D: kinetic trapping, Fe atoms
  2. 2D: annealing treatment

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
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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

---

Experimental Setup

- Ultra-high vacuum (UHV)
- Metal Atom Source
- Molecule Source
- STM
- Au(111)
- TPyP
- Fe

- on Au(111) surface
- @RT or LHe
Structural Results

without Fe

Size is 25×25 nm²

with Fe

Size is 40×30 nm²

Ag(111)

a) Chemphyschem 2007, 8, 250.
Structural Results

Size is $6 \times 6 \text{ nm}^2$

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

Fe-N: 0.25nm

Kondo resonance

magnetic impurity
Structural Results

- **Fe-N**: 0.25 nm

**Size**
- Type I: 40×30 nm²
- Type II: 7.5×7.5 nm²

**Side View**

- **Type I** (four-lobe)
  
- **Type II** (bright-dot)
no example of large coordination network moved by STM tips without break

Lateral Manipulation

Type I

Type II (~300 molecules)

Size is 40×35.5 nm²

Type I chain

Size is 50×30 nm²
Vertical Manipulation

Size is $10.5 \times 3.6 \text{ nm}^2$

$dI/dV$ represents LDOS

$\frac{dI}{dV}$

-0.45
+1.55

$\text{Voltage (V)}$

Size is $6.5 \times 6.5 \text{ nm}^2$
• 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

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**On-Surface Polymerization**

**Enhanced Stability**

![Chemical structures and images illustrating enhanced stability](image)

**More Accessibility**

![Chemical reaction and images illustrating more accessibility](image)

**Surface as a catalyst**

![Chemical structures and images illustrating surface as a catalyst](image)

On-Surface Polymerization

Precursor (small monomer) → heating → Macromolecular System (covalent)

STM

• metal as catalyst?
• activation energy?
On-Surface Polymerization

ultra-high vacuum (UHV)

Pd/Cu molecule

Ullmann reaction

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]
Pd as Catalyst

411K

1.74 nm

411K

1.74 nm

on pure Au(111) ~500K

Annealing Process

![Graph showing bond concentration over time](image)

- Bond Concentration (No. per 100 nm²)
- Time (min)

- 447K

![Chemical structures](image)

- 30nm scale bars
Varying Annealing Temperature

- 465K
- 447K
- 429K
- 411K

Process of Reaction

- Phase I
- Phase II

Energy vs. Time (min)

Bond Concentration (No. per 100 nm²)
Varying Annealing Temperature

Arrhenius relation:

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

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

[Bond] = \frac{kr[Br]^2}{1 + 2 \times kr[Br]^2}

Arrhenius relation:

\[
k = A \times \exp \left( -\frac{E_a}{kT} \right)
\]

R –– Br + R –– Br \xrightarrow{Pd/k} R –– R + 2Br

\[
E_a = 0.41 \text{ eV}
\]

A = 3 \times 10^6 \text{ Hz}

411K
Varying Annealing Temperature

**Arrhenius relation:**

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

**Arrhenius relation:**

\[
k = A \times \exp\left(-\frac{E_a}{kT}\right)
\]

- **R** + **R** \(\xrightarrow{Pd} k\) **R** + **R** + 2**Br**

- **Ea=0.41 eV**
  - **A=3*10^6 Hz**

- **411K**
Cu as Catalyst

Two-phase

Bond Concentration (No. per 100 nm²)

Time (min)

5 min

75 min

160 min

30nm

@453K
Comparison Pd-Cu

**Pd**

- Phase I
- Phase II

**Cu**

- 393K
- 435K
- 417K
- 399K
Comparison Pd-Cu

**Pd**
- 5 min
- 60 min
- 120 min

**Cu**
- 15 min
- 75 min
- 160 min

Polymer length (Number of molecules)

Energy

Process of Reaction

Comparison Pd-Cu
Conclusion

Pd- / Cu-Catalyzed homocoupling

Activation Energy 0.41 eV

2 phases

Comparison

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1D Polymerization

Covalent by Debromination

\[
\text{Br} \quad \cdots \quad \text{Br} \quad \text{Br} \quad \cdots
\]

annealing

weight: % of molecule in each config.

\[
\text{weight} = \%
\]

size: 100*100 nm\(^2\)

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

Glaser Coupling:
\[ R\text{C}≡\text{C}H + H\text{C}≡\text{C}R \rightarrow R\text{C}≡\text{C}C≡\text{C}R \]

Experimental Results

+ Cu @Au(111) RT

Single-Row Chains

180°C annealing

Double-Row Chains

blue: 1.97nm

coordination

blue: 1.95nm

red: 1.73nm

covalent

size: 100*100 nm²
Experimental Results

Polymerization: confined into dimer

weight: % of molecule in each config.

Macro. Size: size of covalent structure/width of chain

![Graph showing weight distribution across different macromolecule sizes]

- Covalent Coordination
- Cooperative Coordination
seed-zipper model

Mechanism

seed → coordination

covalent
kinetic Monte Carlo Simulation (kMC)

- **hopping**
  - Diagram showing the hopping process with arrows indicating movement.

- **coordination bond**
  - Diagram showing the coordination bond with a rectangular structure.

- **rotation**
  - Diagram showing the rotation process with a circular structure.

- **covalent bond**
  - Diagram showing the covalent bond with a structure indicating debromination.

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

- Diagram showing the process at 180°C with colored indicators for unreacted and reacted bromine.
Width Control

deposit onto hot sample with Cu (Temp=240 °C)

Trimer Seed
• coordination bond $\rightarrow$ size-limited polymerization reaction

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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

- Thesis Committee Members
  Prof. ZHU Junfa
  Prof. HUANG Xuhui
  Prof. WEN Weijia
  Prof. HAN Yilong
- Chairman
  Prof. XIANG Yang
Thanks For Your Attention!