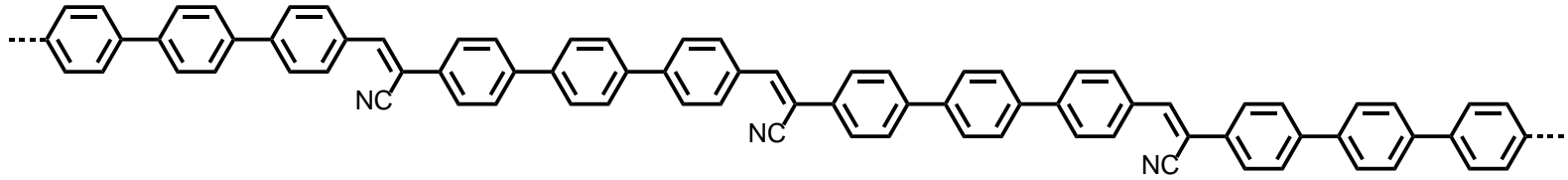


# On-surface synthesis investigated by UHV-LT-STM: Knoevenagel condensation PKL-2-Lin on Au(111)

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Collaborative Research Centre 1415

Chemistry of Synthetic  
Two-Dimensional Materials



# Two preparation strategies

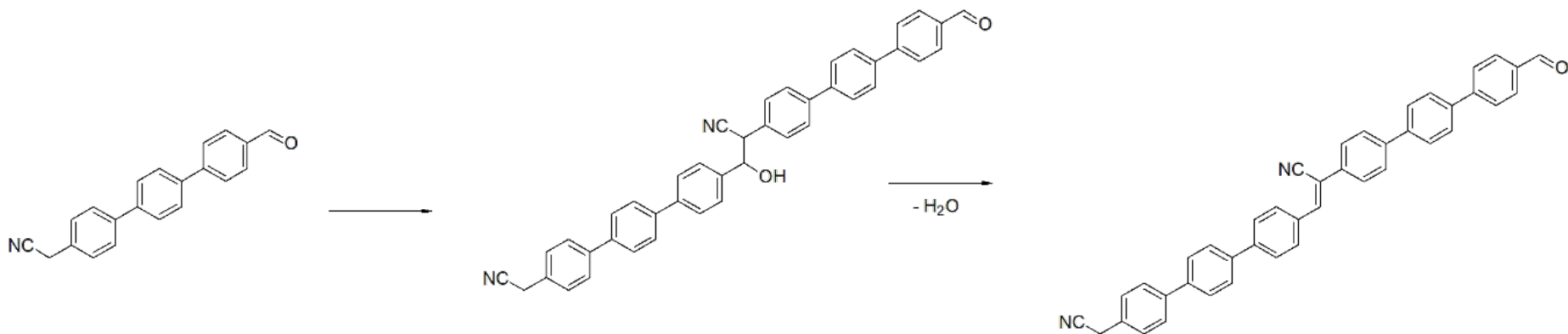
## 1. Deposition on RT Au(111) surface, then stepwise increase annealing temperature



## 2. Slow (140°C) thermal deposition on **HOT** surface @240°C for 30mins, then further anneal for 10min



# Overview (Chemical) - Knoevenagel condensation



# Overview & close-up

Deposition  
@170°C

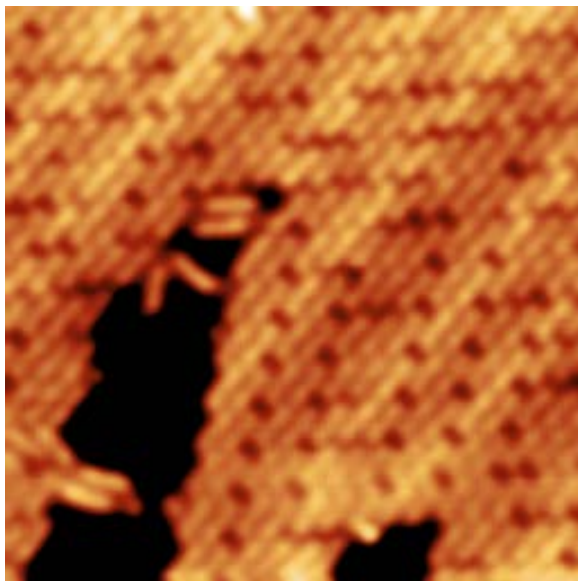
Anneal  
@200°C

Anneal  
@220°C

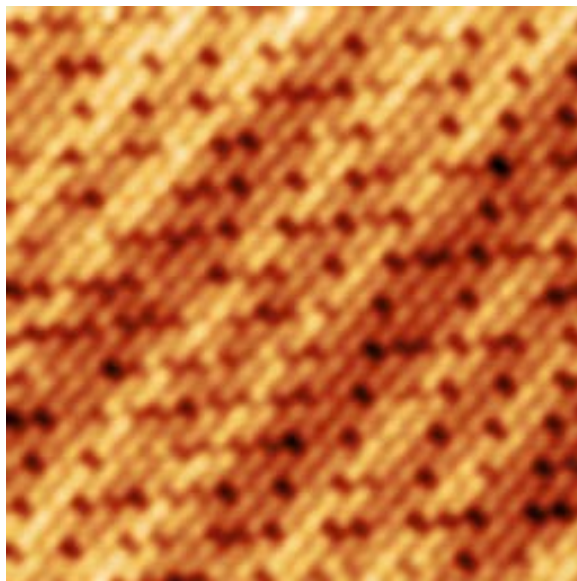
Anneal  
@230°C

Anneal  
@240°C

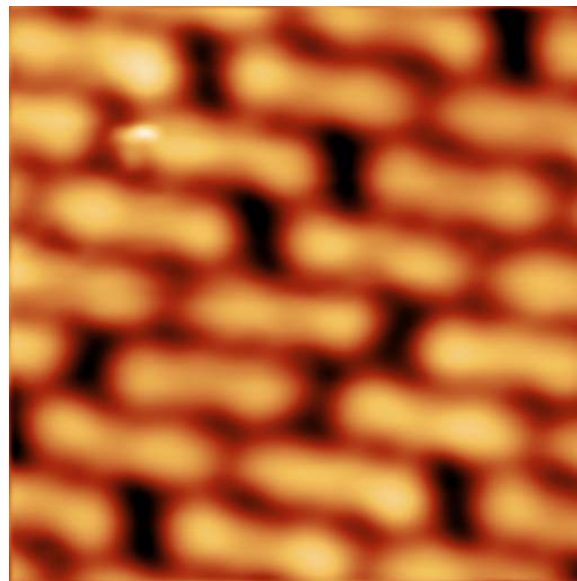
Anneal  
@250°C



(20 nm)<sup>2</sup> 300 mV, 3 pA



(20 nm)<sup>2</sup> 300 mV, 3 pA



(6 nm)<sup>2</sup> 1 V, 10 pA

- Patterned/packed ML
- >90% coverage

# Overview

Deposition  
@170°C

Anneal  
@200°C

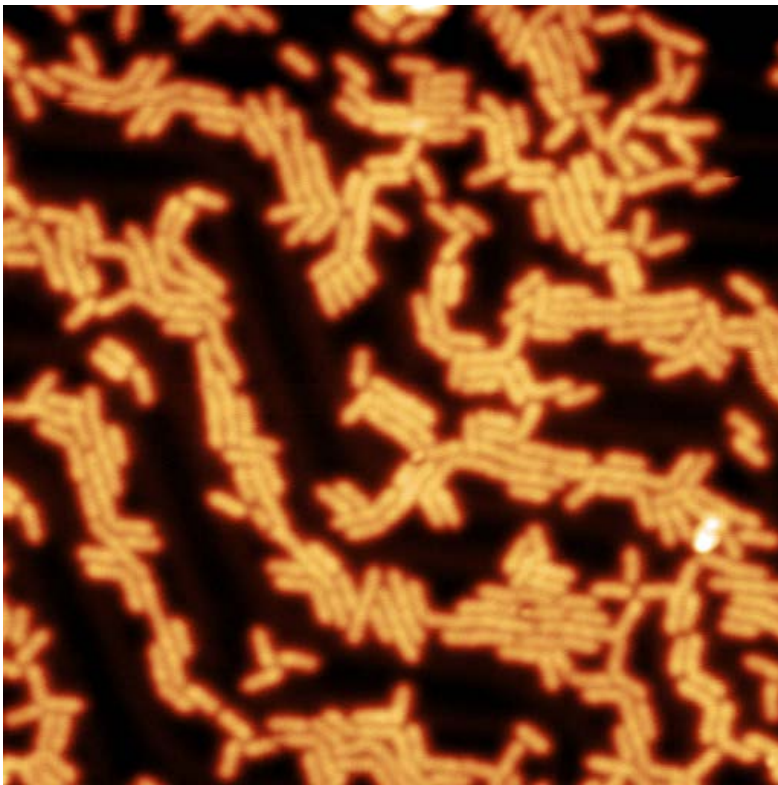
Anneal  
@220°C

Anneal  
@230°C

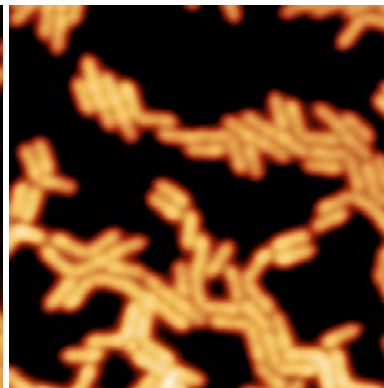
Anneal  
@240°C

Anneal  
@250°C

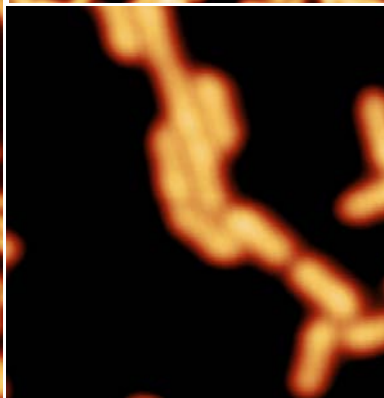
~45% coverage



$(40 \text{ nm})^2$  500 mV, 5 pA



$(20 \text{ nm})^2$  500 mV, 5 pA



$(10 \text{ nm})^2$  500 mV, 5 pA

# Manipulations

Deposition  
@170°C

Anneal  
@200°C

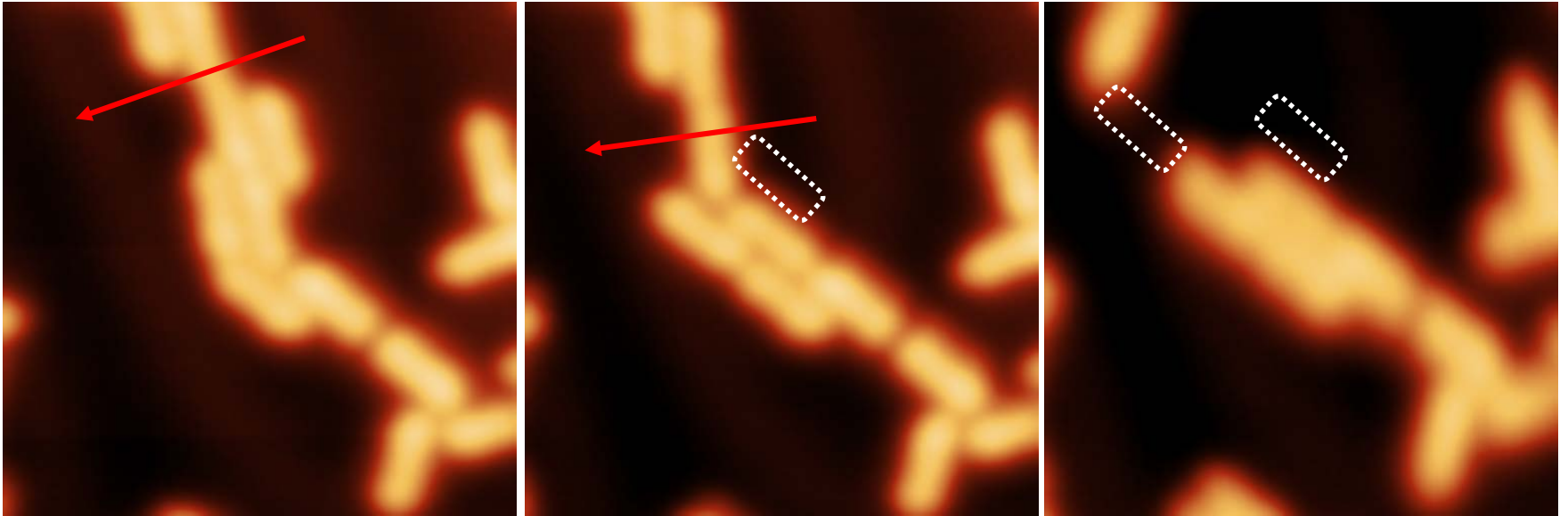
Anneal  
@220°C

Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C

(10 nm)<sup>2</sup> 500 mV, 5 pA  
Manipulations: 10 mV, 1 nA



- Picked up molecules (see white dashed)
- Also destroyed the wire

# Overview

Deposition  
@170°C

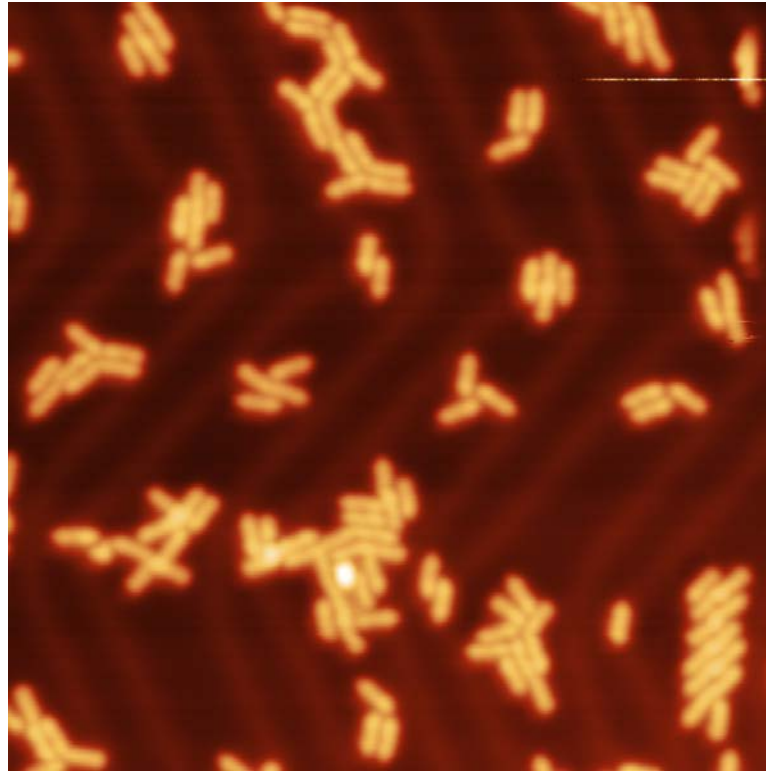
Anneal  
@200°C

Anneal  
@220°C

Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



~17% coverage

(40 nm)<sup>2</sup> 500 mV, 10 pA

- Coverage decreases
- No longer chain more than 3 units
- “Dimers” still exist

# Overview

Deposition  
@170°C

Anneal  
@200°C

Anneal  
@220°C

Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



- Coverage ~11%: Good for tip form and picking CO
- Possible to find longer wire
- “Dimers” still exist –  
A-B  $\leftrightarrow$  B-A? A-B  $\leftrightarrow$  A-B?

(100 nm)<sup>2</sup> 500 mV, 5 pA



# Close-up

Deposition  
@170°C

Anneal  
@200°C

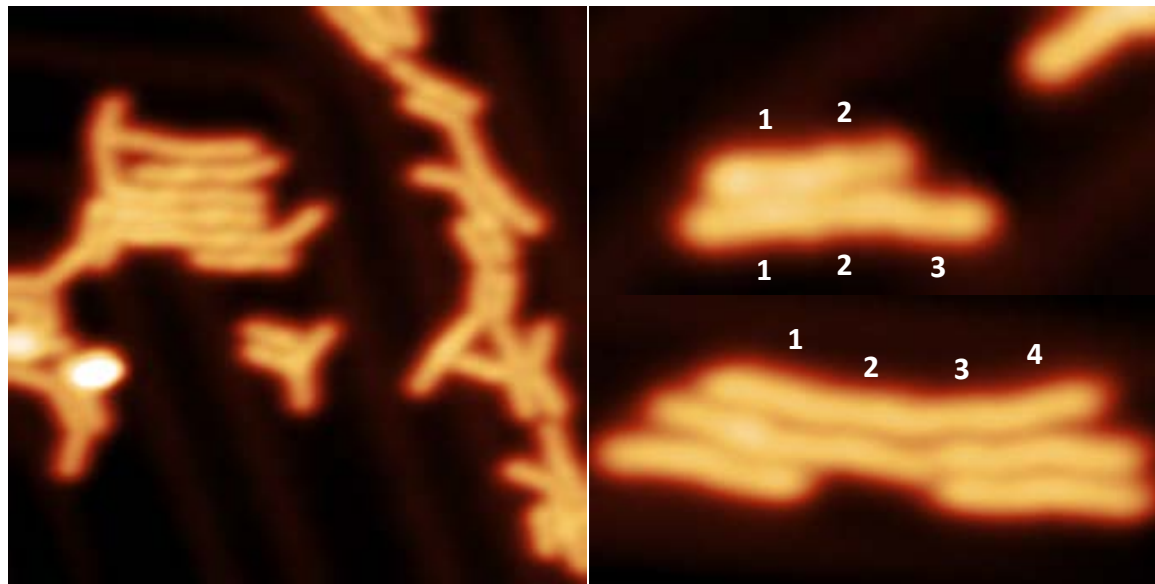
Anneal  
@220°C

Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C

10 x 5 nm<sup>2</sup> 500 mV, 5 pA



20 x 20 nm<sup>2</sup> 500 mV, 5 pA

10 x 5 nm<sup>2</sup> 500 mV, 5 pA

# Manipulations

Deposition  
@170°C

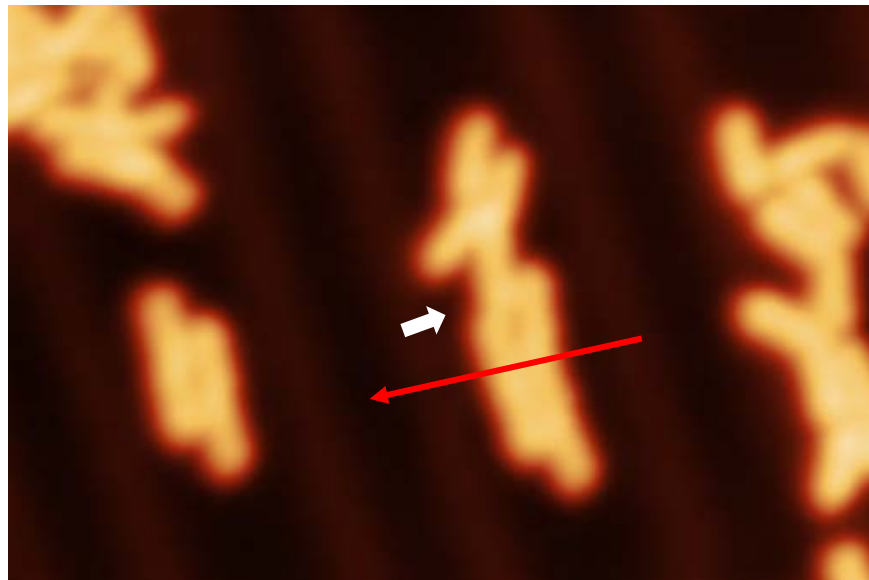
Anneal  
@200°C

Anneal  
@220°C

Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



20 x 20 nm<sup>2</sup> 500 mV, 5 pA  
Manipulations: 10 mV, 2 - 2.7 nA

# Manipulations

Deposition  
@170°C

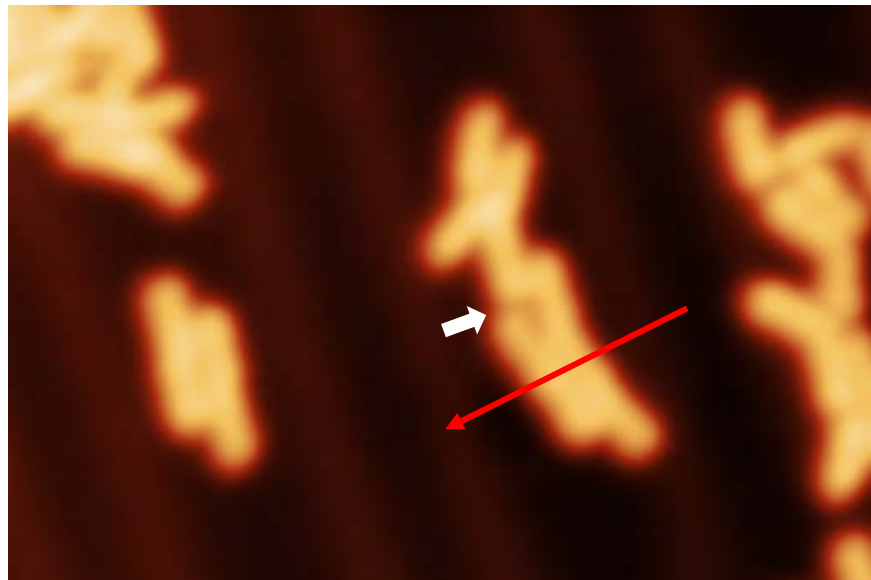
Anneal  
@200°C

Anneal  
@220°C

Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



20 x 20 nm<sup>2</sup> 500 mV, 5 pA  
Manipulations: 10 mV, 2 - 2.7 nA

# Manipulations

Deposition  
@170°C

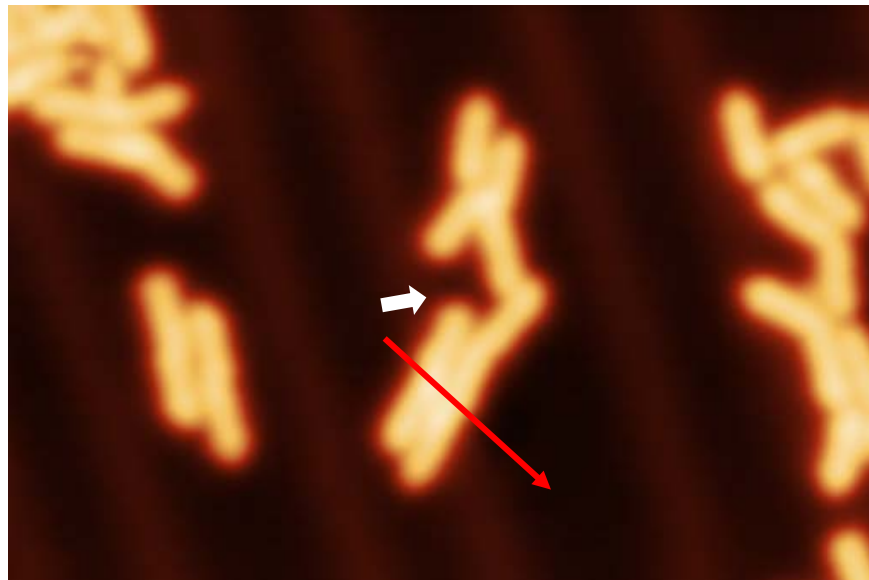
Anneal  
@200°C

Anneal  
@220°C

Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



20 x 20 nm<sup>2</sup> 500 mV, 5 pA  
Manipulations: 10 mV, 2 - 2.7 nA

# Manipulations

Deposition  
@170°C

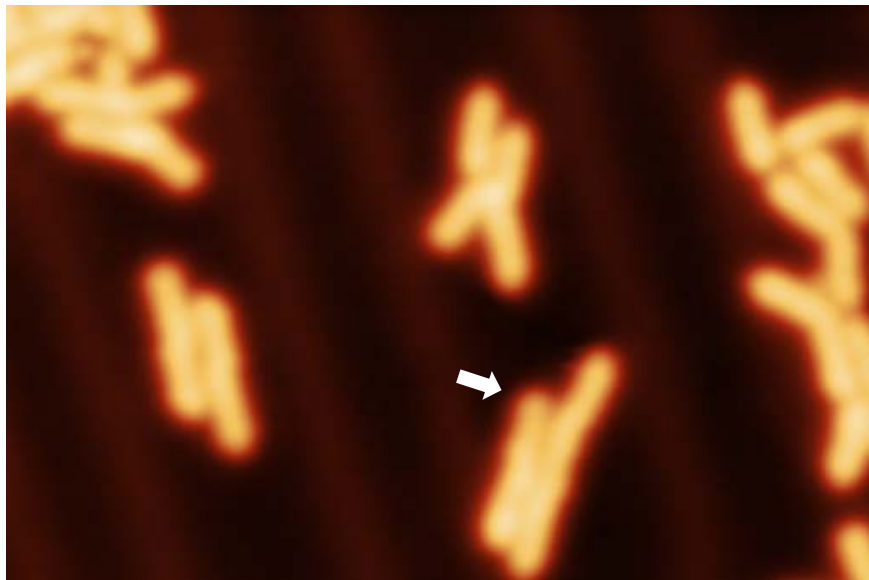
Anneal  
@200°C

Anneal  
@220°C

Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



The other parts do not break, confirming the reaction occurs

20 x 20 nm 500 mV, 5 pA  
Manipulations: 10 mV, 2 - 2.7 nA

# Analysis by linescan

Deposition  
@170°C

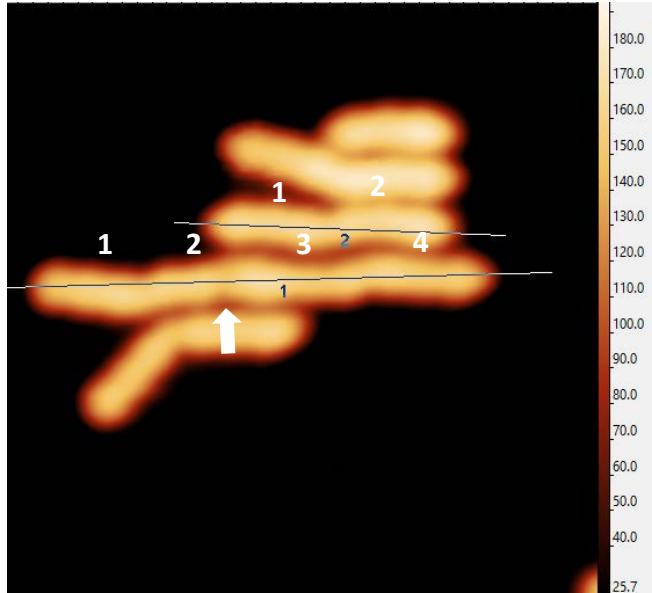
Anneal  
@200°C

Anneal  
@220°C

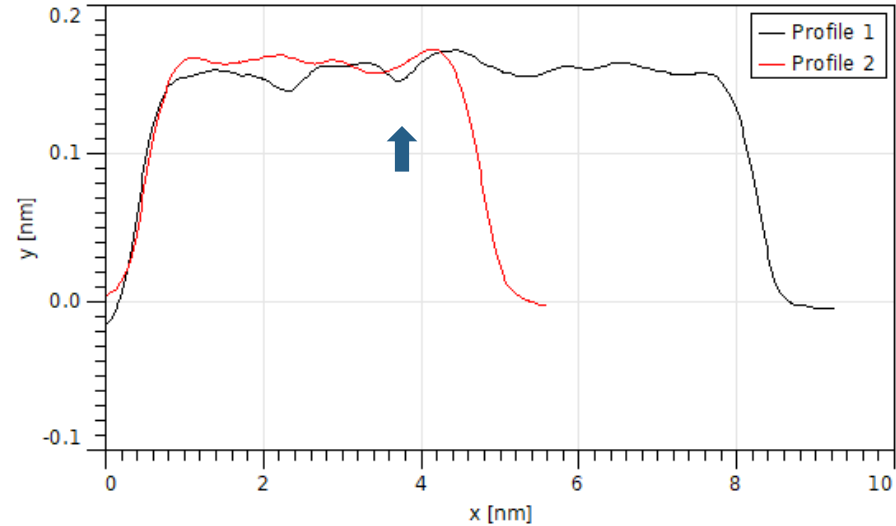
Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



(10 nm)<sup>2</sup> 500 mV, 10 pA



To prove a successful C-C bond formation,  
>3 molecules as a wire needed

# Longest wire so far (5 units)

Deposition  
@170°C

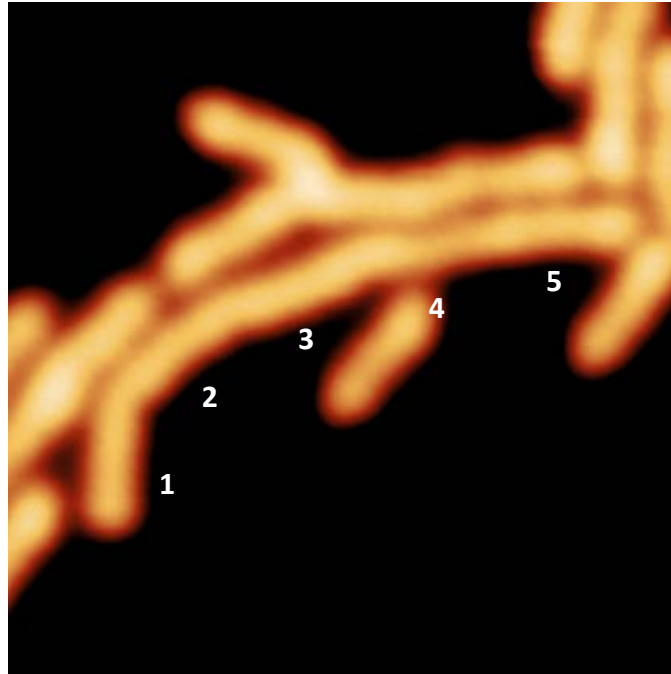
Anneal  
@200°C

Anneal  
@220°C

Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



(10 nm)<sup>2</sup> 500 mV, 5 pA

# Overview

Deposition  
@170°C

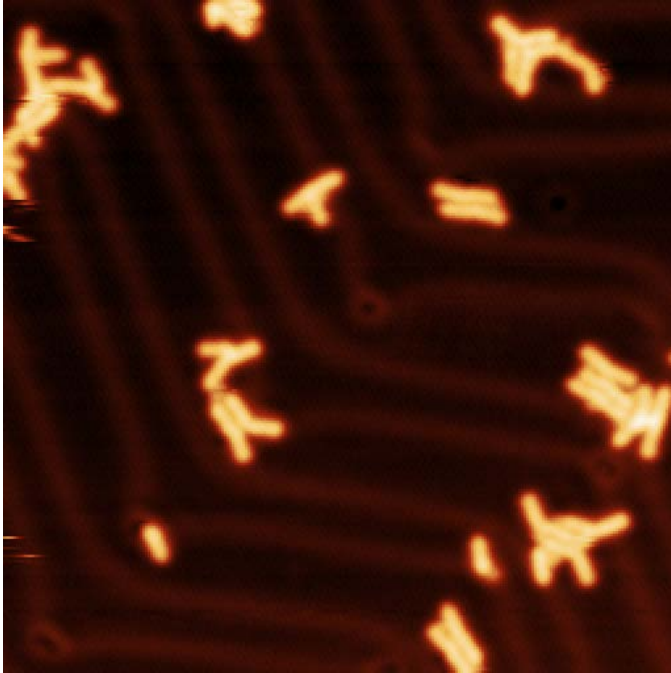
Anneal  
@200°C

Anneal  
@220°C

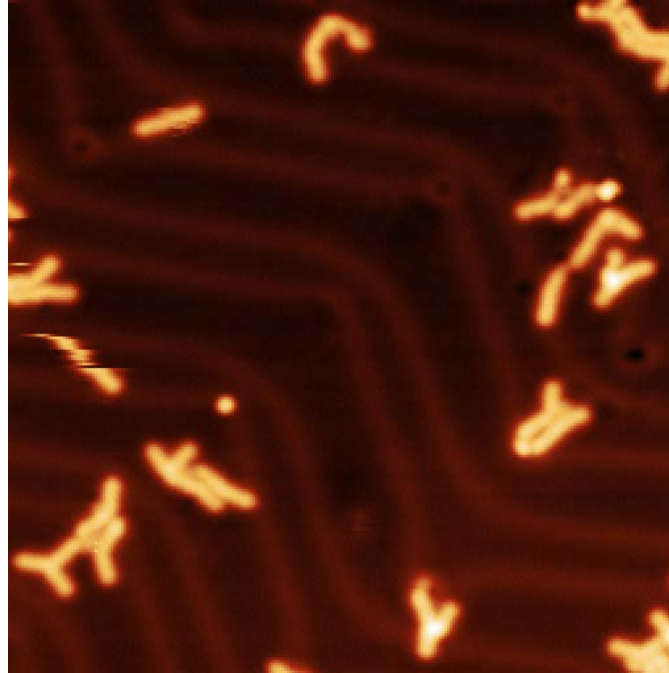
Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



$(40 \text{ nm})^2$  500 mV, 5 pA



$(40 \text{ nm})^2$  500 mV, 5 pA

- Coverage decreases
- Monomers almost gone
- Dimers and longer wire still exist

~8% coverage



# Overview

Deposition  
@170°C

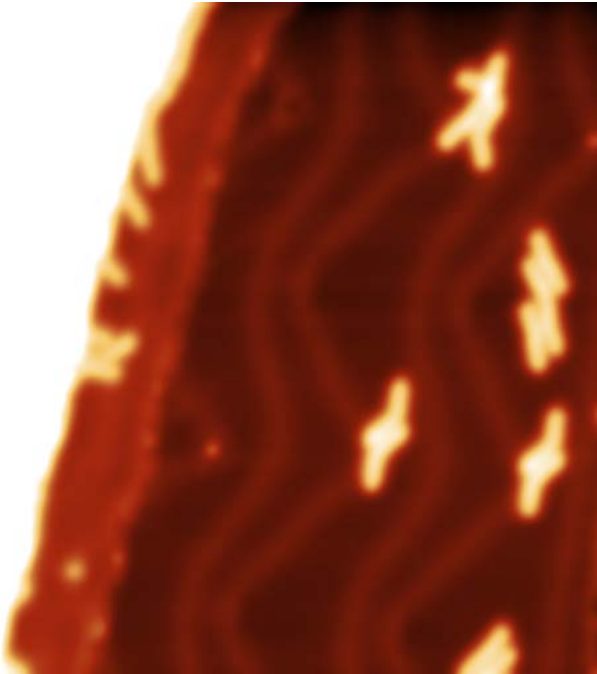
Anneal  
@200°C

Anneal  
@220°C

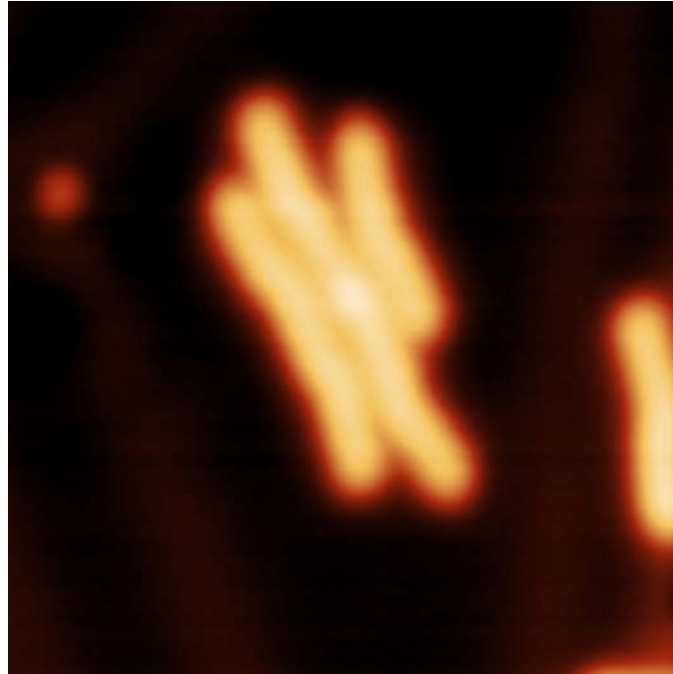
Anneal  
@230°C

Anneal  
@240°C

Anneal  
@250°C



(40 nm)<sup>2</sup> 526 mV, 5.3 pA



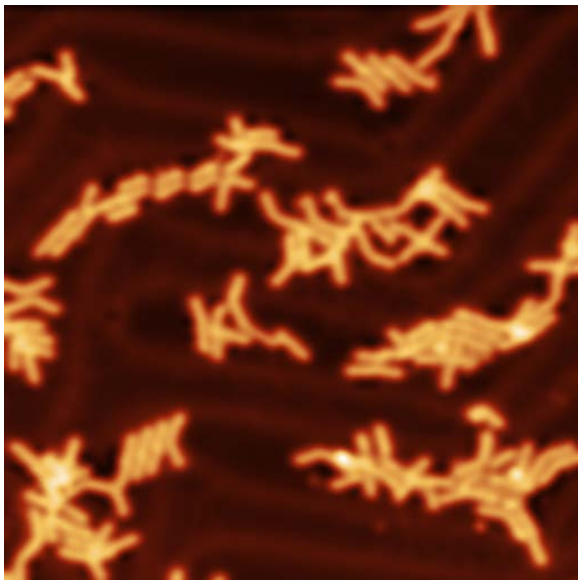
(12 nm)<sup>2</sup> 500 mV, 5.3 pA

- Coverage decreases further
- No longer wire observed

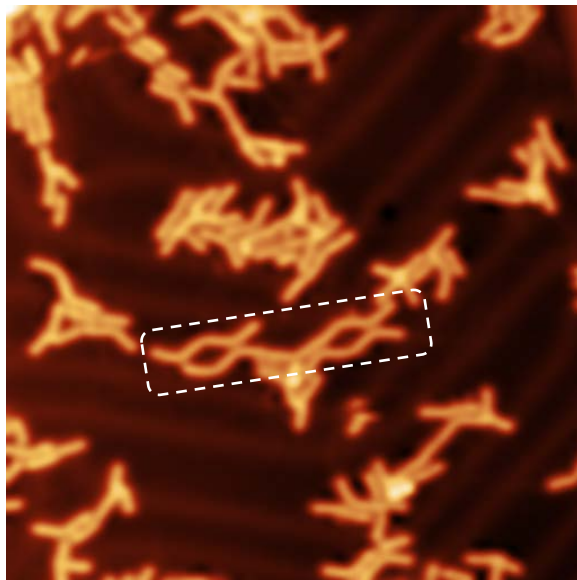
# Overview & close-up

Slow (140°C) thermal deposition on HOT surface @240°C for 30mins

Further anneal @240°C for 10min



(40 nm)<sup>2</sup> 500 mV, 5 pA



(40 nm)<sup>2</sup> 500 mV, 5 pA

- No wire longer than 4 units seen so far
- Monomers still exist



Not binding to each other?

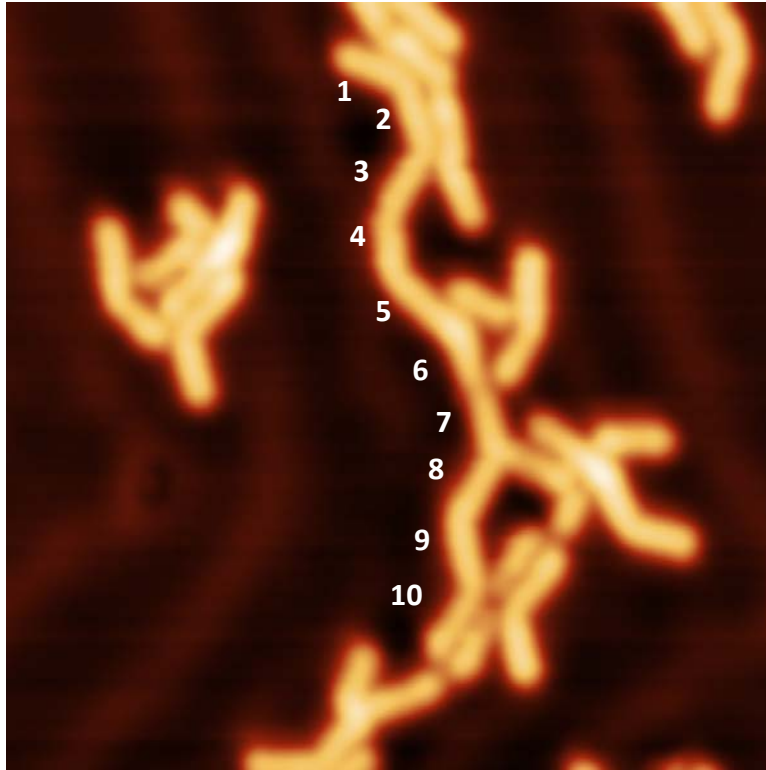
20 x 8.4 nm<sup>2</sup> 500 mV, 5 pA

~22% coverage

# Longest assembly so far

Slow (140°C) thermal deposition on HOT surface @240°C for 30mins

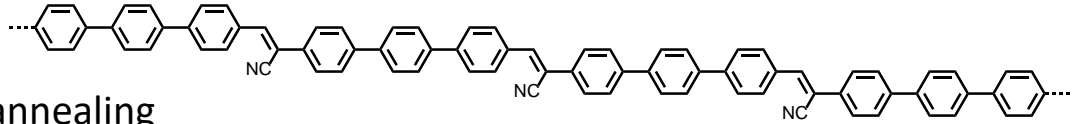
Further anneal @240°C for 10min



(20 nm)<sup>2</sup> 500 mV, 5 pA

10?  
3+3+4?  
3+3+2+2?

# Summary



- Coverage ~50% decrease after each annealing
- Possible up to 5 molecules as a wire
- High-resolution STM images reveal the successful C-C bond formation, and thus Knoevenagel condensation is possible by on-surface synthesis
- Slow deposition on hot surface does not yield longer wire

