Dealkylation and Metallation of a Hydrocarbon in On-Surface Synthesis

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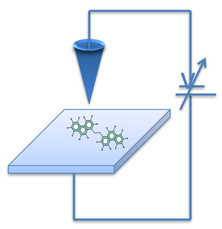
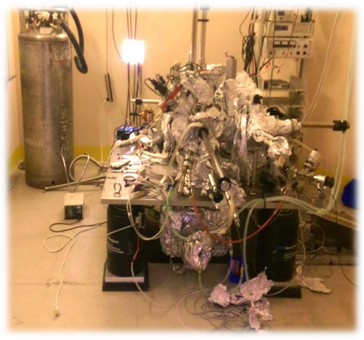
STM @ 77 K IN UHV





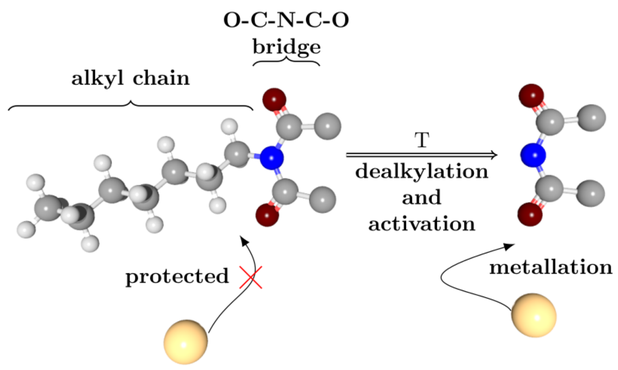
Introduction: We demonstrate temperature-controlled cleavage and desorption of alkyls from carboxyl diimide picenes (*C_{12}PicDI) on Au(111).* The initially alkyl-passivated diimide group is activated and available for metal coordination.

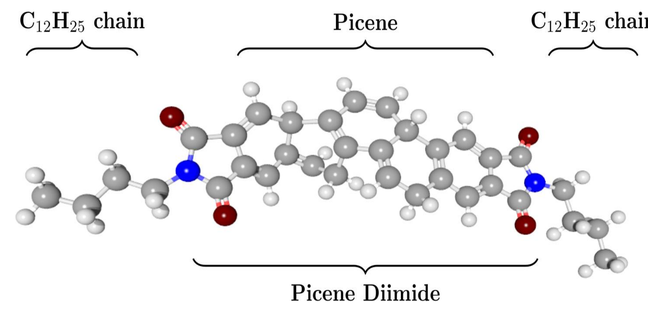
Background
- Imide groups supports metal ion coordination [1]
- [5]Phenacene (known as picene): polycyclic aromatic hydrocarbon

Molecular structure of *C_{12}PicDI*
- Picene core with imide functionalities at both ends
- Dodecyl-chain-passivated imide groups

Applications
- Organic semiconductor with high electron mobility [2a] for organic n-channel FET devices[2b,3]

Goal
- Controlled imide activation for metal coordination

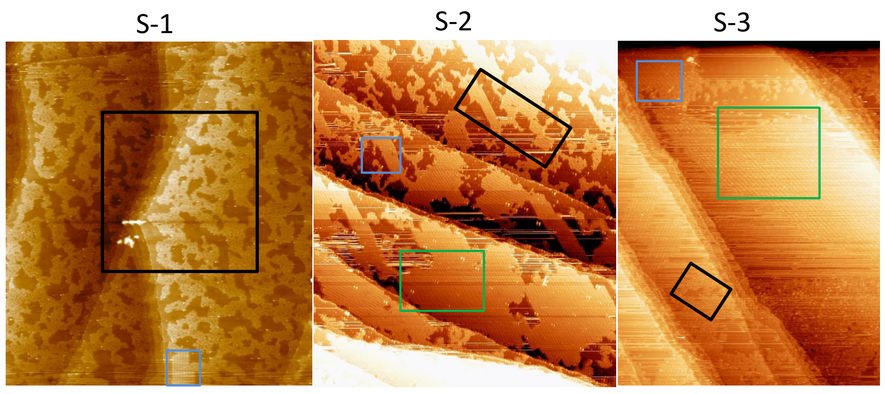




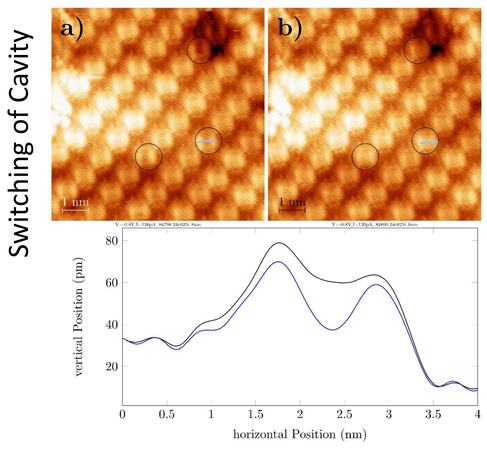
Preparations
- Three Au(111) samples prepared
- S-*1*: 0.45ML, surface defect density: High
- S-*2*: 0.50ML, surface defect density: Low
- S-*3*: 0.40ML, surface defect density: High

Room-Temperature preparation of C_{12}PicDI

**All measurements are performed at 77K*

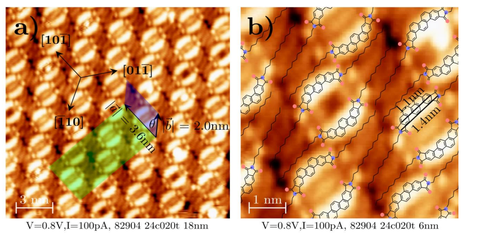


Observation:
- Molecules absorb intact on surface
- Three distinct structures (A, B, C)
- Structure A: Cavity-like structure
- Structure B: Alternatingly rotated against each other
- Structure C: Disordered
- Structure A, B: oriented in crystallographic direction => indicates strong Molecule-Substrate interaction



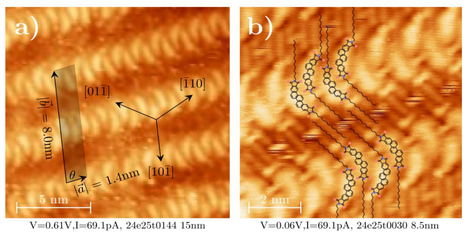
Switching of cavity:
- three kinds of cavities
  - white dot at centre (S1-S2-S3)
  - elongated central structure (S1)
  - empty (S1)
- Switching of the cavity is seen in line sections after continuous scan
- Black= bright cavity, Blue= dark cavity

Structure A



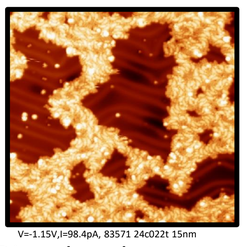
Row structure (2 Molecules / unit cell)

Structure B



Banana structure (4 Molecules / unit cell)

Structure C



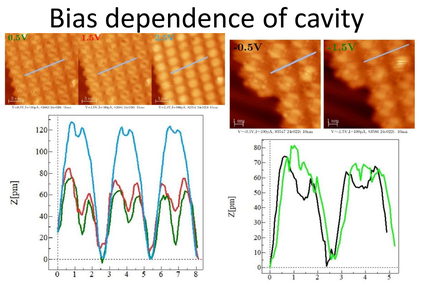
Disordered structure

Structure C shows diffuse/disordered structure

Bias dependence of cavity:

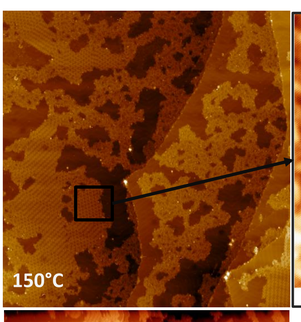
Left graph +ve V/Right graph –ve V
- Double peak around +0.5V,+1.5V
- Lower depth of holes at +2.5V
- Picene cores widen with increasing bias voltage

Bias dependence of cavity

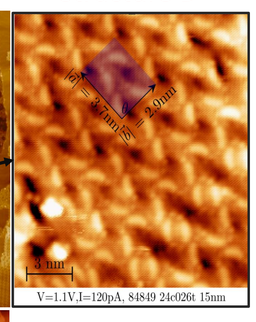


Structural Reorganization at Mild-Heating (< 320°C)

S -1



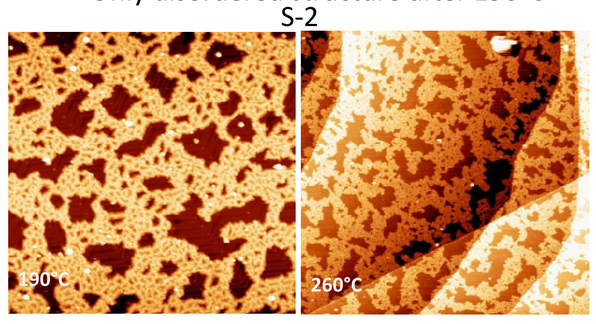
Structure D



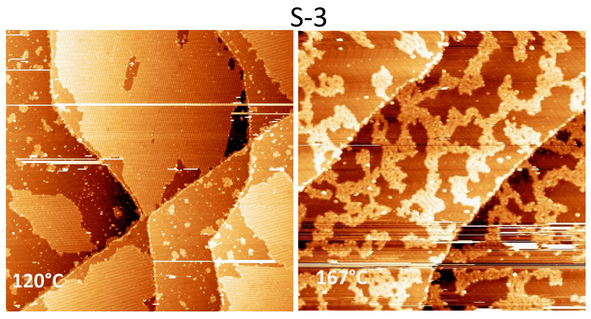
Observation (S-1):
- New net structure after 150°C
- Ordering increases up to 317°C

Observation (S-2):
- Only disordered structure after 190°C

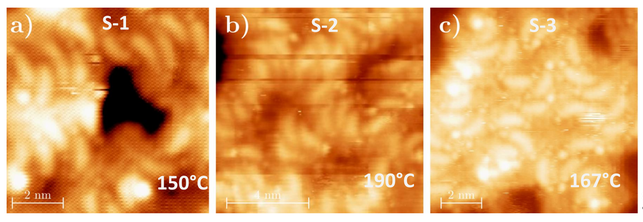
S-2



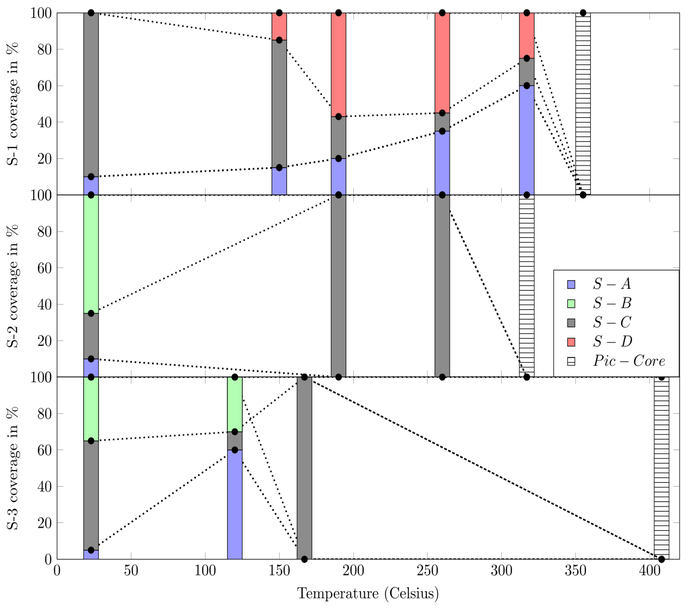
S-3



Observation (S-3):
- Ordering increases up to 120°C
- Only disordered structure after 167°C

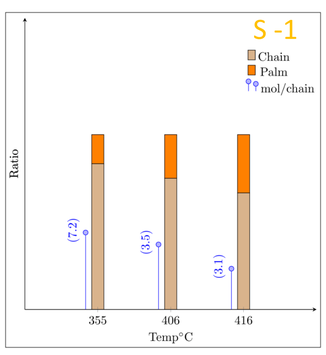


Similar diffuse structures seen for all samples

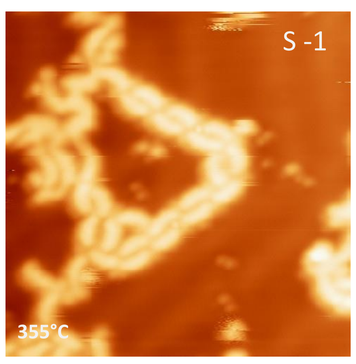


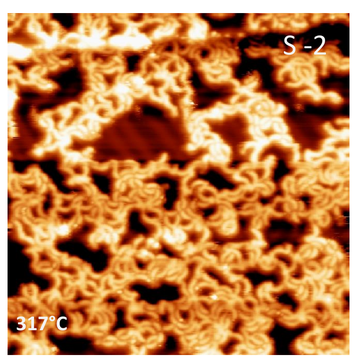
The ratio between the structures for the three samples

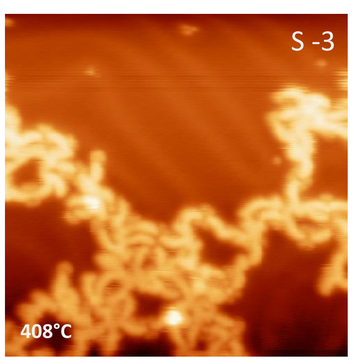
Dealkylation at High-Heating Treatment (≥ 317°C)

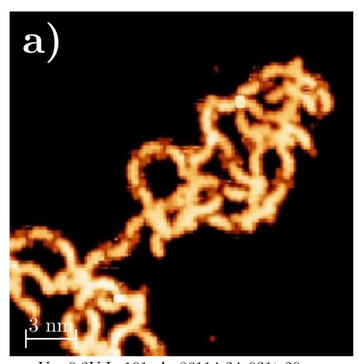


Ratio of chain to palm

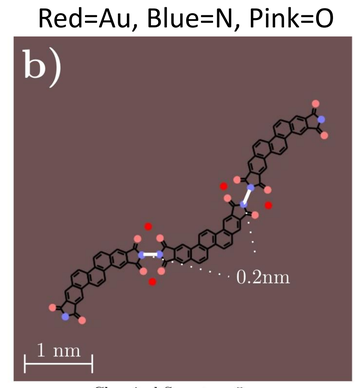


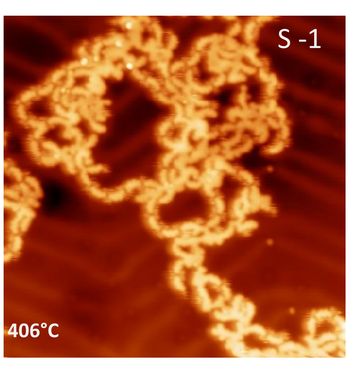






Red=Au, Blue=N, Pink=O





Observations (S-1, S-2, and S-3):
- **Intact diimide picenes cores without alkyl chains for all 3 samples**
- **Molecule-metal bonds observed as cloud-like blobs**
- Alkyl chains detachment: S-1 at 355°C
  S-2 at 317°C
  S-3 at 408°C
- Dealkylated PicDI cores show two new structures:
  - Linear chains (lower population in S-2 and S-3)
  - 2D palm tree-shape (increases with temperature)
- N-N distance of 0.2nm for linear chains (agrees with Ref. [1])
- Four circular protrusions are seen at and between the imide head groups
- The number of molecules per chain decreases with temperature
- Alkyl chains desorb from the surface [4]

Interpretation:
- Our results align with previous work[1] regarding molecule-molecule distance and circular protrusion shape
- Au atoms are extracted and are involved in the chain formation process

Summary

- Sample variations may stem from deposition temperature differences, cleanliness, and heating rates due to filament change after initial preparation
- Mild heating induces structural changes, with intact molecules still present on the surface
- Diimide picene cores remain intact even after high-temperature treatment
- We've shown that the alkyl chain can be removed without damaging the picene diimide core, potentially enabling the creation of high-performance n-channel organic semiconductors through on-surface synthesis

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Reference

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