ORDERED SUPRAMOLECULAR POLYTHIOPHENE STRUCTURES ON PASSIVATED SILICON SURFACES

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Background

- The functionalization of semiconductor surfaces with organic molecules is a necessary step in the development of hybrid organic-semiconductor structures.

- A significant challenge to organic layer formation is the fact that semiconducting surfaces exhibit a large number of dangling bonds which suppress the diffusivity of adsorbed molecules and can even break the molecules apart via the formation of Si-C bonds.

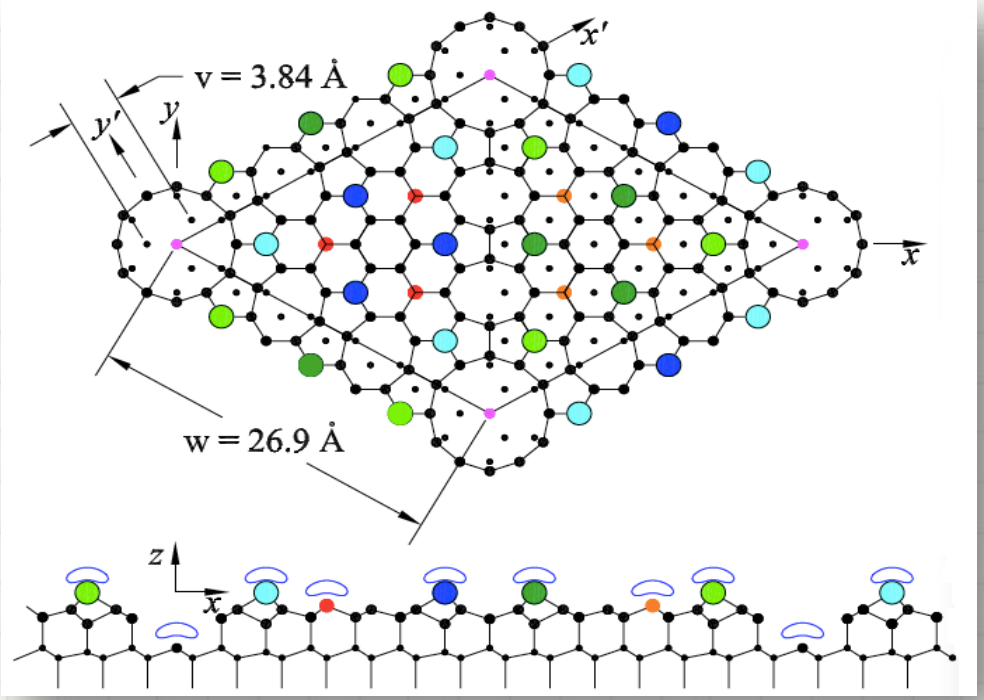
- Recently it has been shown that these problems can be overcome by depositing the molecules onto a passivated surface.*

*Suzuki et al. Phys. Chem. Chem. Phys., 2009, 11, 6498–6504

Silicon Substrate

Si(111) has a complex stable 7 × 7 reconstruction, which reduces the number of dangling bonds from 49 to 19 for each 7 × 7 unit cell.

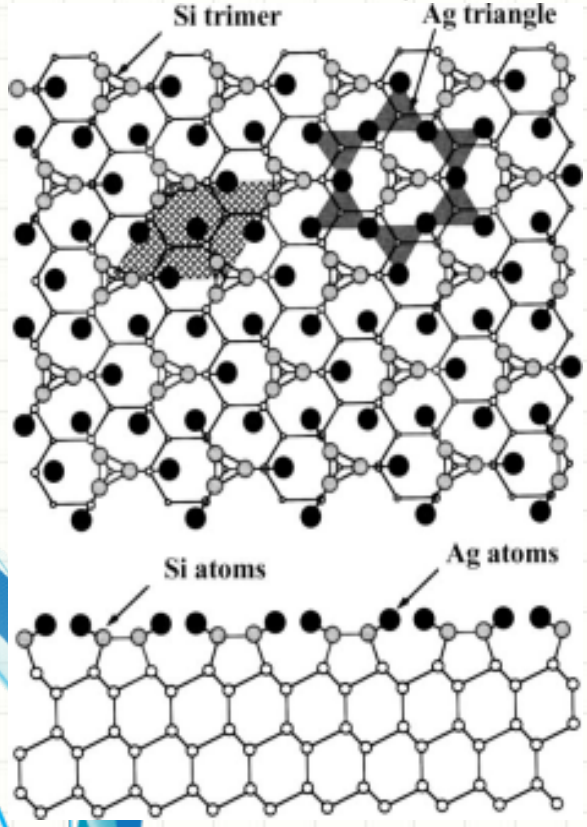
Still not good enough! Can't provide a surface with enough mobility for molecule diffusion.



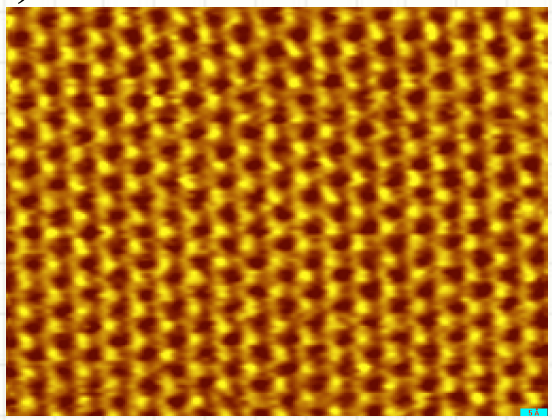
Graph reproduced from Ann. Phys. 10 (2001) 11—12

√3 surface

Compared to the highly reactive Si(111) (7 × 7) surface, a monolayer Ag layer passivates the surface which allows the supramolecular ordering of TPA on Si(111).*



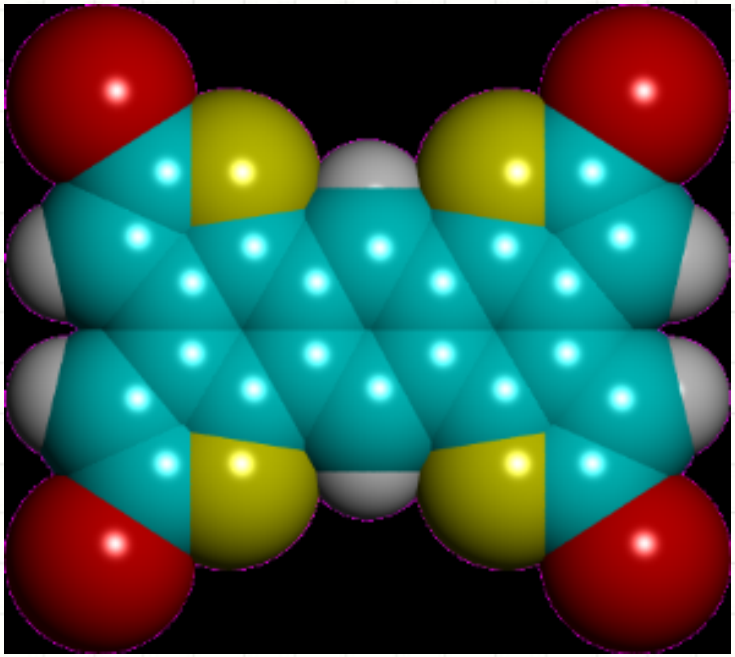
Atomic structure of √3 Ag reconstruction.
Reproduced from X. Tonga et al.;
Applied Surf. Sci. 190,121 (2002).



STM image of the √3-Ag surface.
100Å×100Å

*Suzuki et al. Phys. Chem. Chem. Phys., 2009, 11, 6498–6504

Thiophene Deposition



Tetrabromo-tetrathienoanthracene (TBTTA)
Red: Bromine
Blue: Carbon
Yellow: Sulfur
White: hydrogen

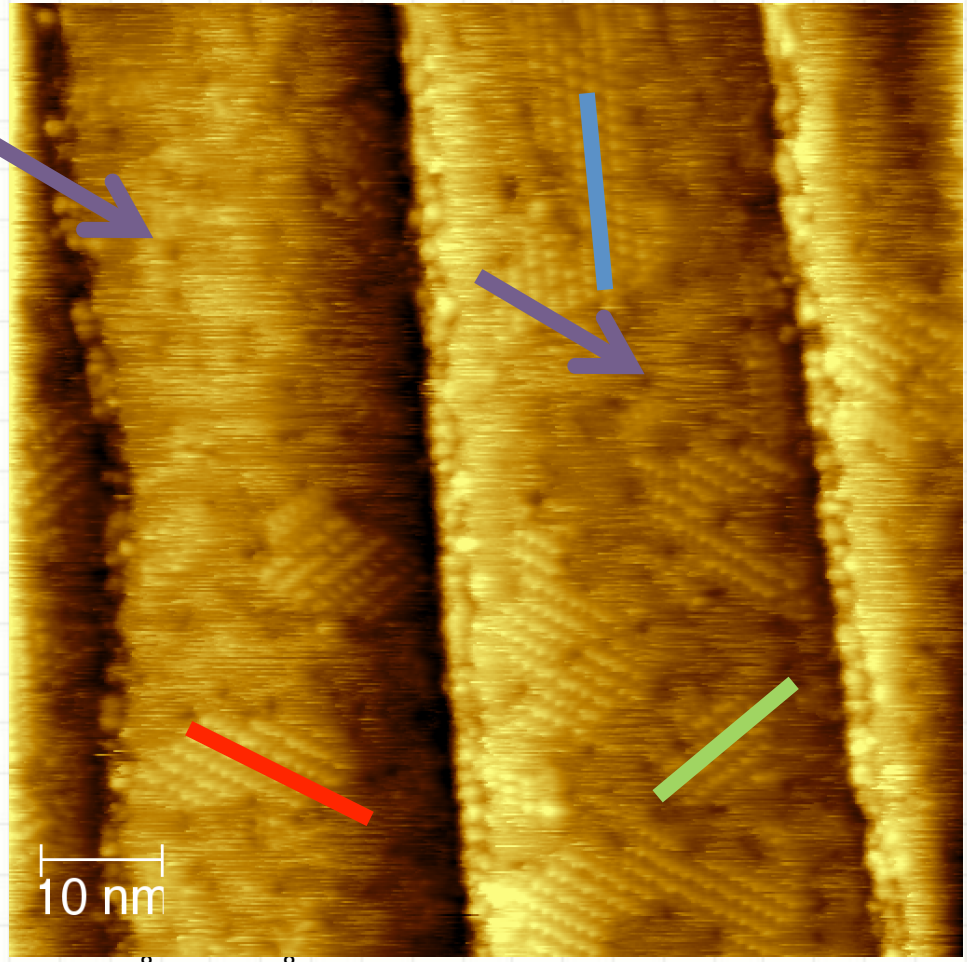
- Thiophene based molecules are of considerable interest in organic semiconductor research due to their efficient conjugation and the chemical stability.
- Thiophene thin films exhibit reasonably high mobilities ($\mu_h \sim 2\ cm^2\ V^{-1}\ s^{-1}$)*
- In addition to non-conjugated layers, thiophene based molecules have been used as precursors in surface-confined polymerization experiments.

*Takimiya et al., J.AM.CHEM.SOC.128, 2006 12605

Experiment

- All measurements are performed in UHV system with a base pressure ~2×10^{-10} Torr.
- Si(111) wafers use a annealing sequence to attain 7×7 reconstruction.
- The √3 surface is formed by deposition of one monolayer of silver onto the clean Si surface at 580 °C. Layer formation confirmed with low energy electron diffraction (LEED).
- TBTTA molecules deposited and Auger electron spectroscopy (AES) was used to verify the coverage.

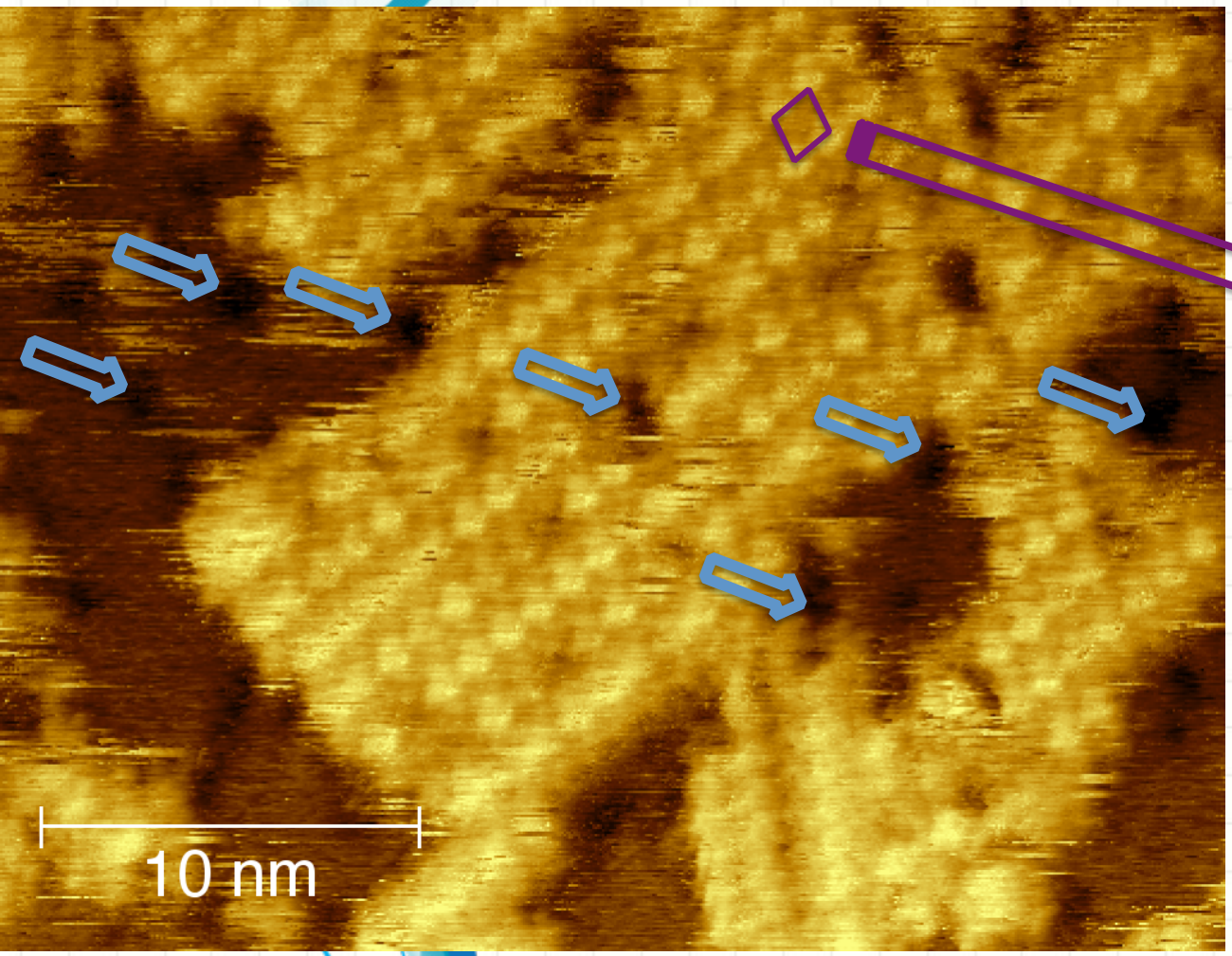
Supermolecular structures at RT

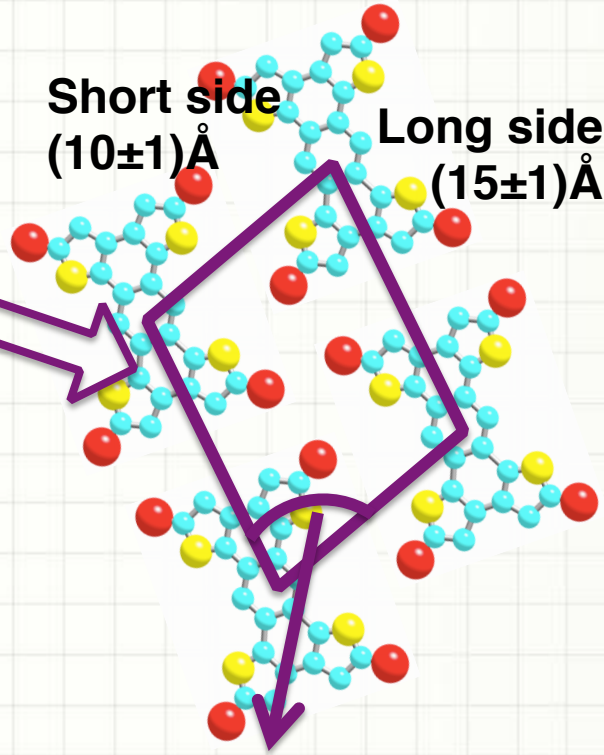


770Å×770Å (-1.2 V 110 pA)

- Three supramolecular domains consistent with the 3-fold symmetry of √3 lattice
- "Raster noise" in many images suggest additional molecules moving on the surface
- Structures only stable under certain bias conditions

Unit Cell

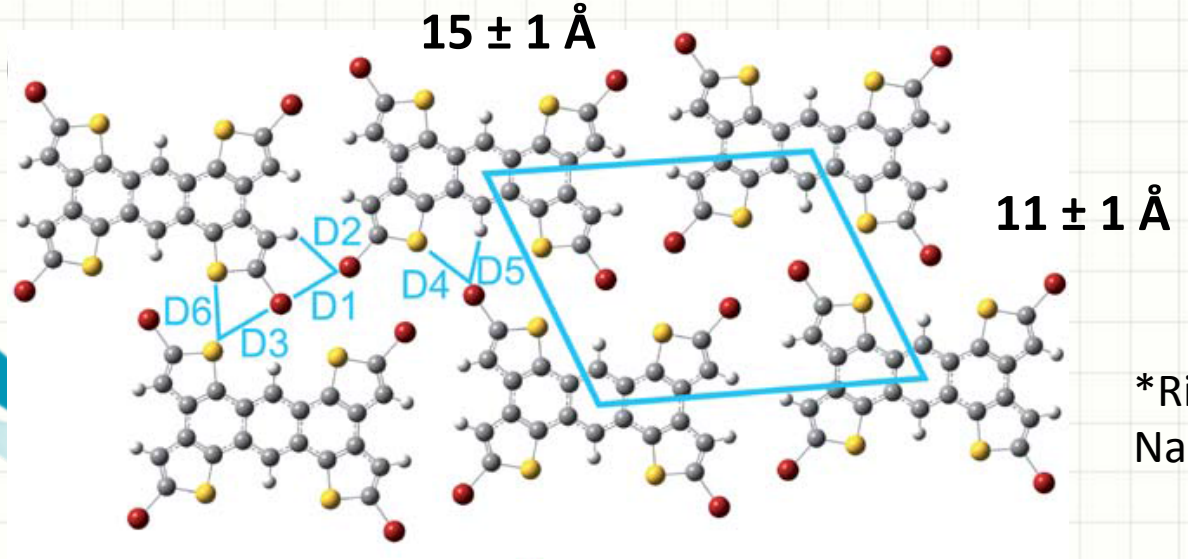




320Å×320Å (-1.11 V 500 pA)

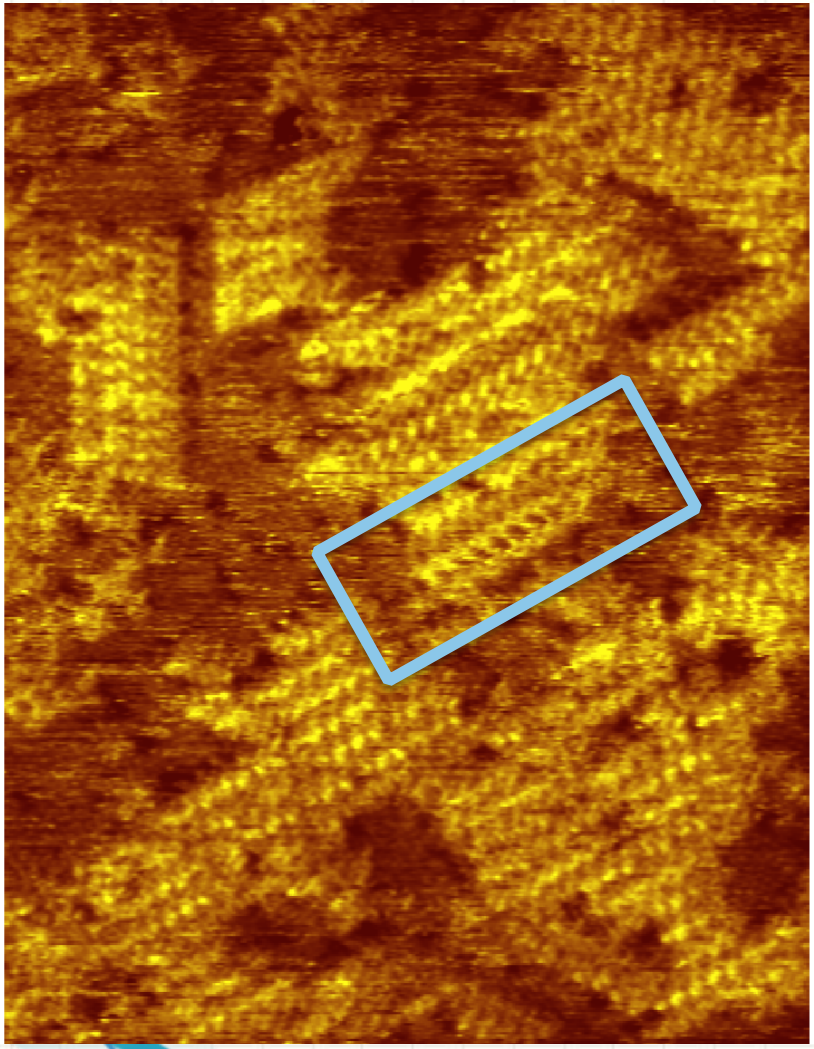
Intermolecular Interactions

- TBTTA on Highly oriented pyrolytic graphite (HOPG) exhibits very similar unit cell*
- On HOPG, DFT calculations indicate ordering determined entirely by Van der Waals interactions between molecules.



*Rico Gutzler et al. Nanoscale, 2012, **4**, 5965–5971

Type II structures at RT

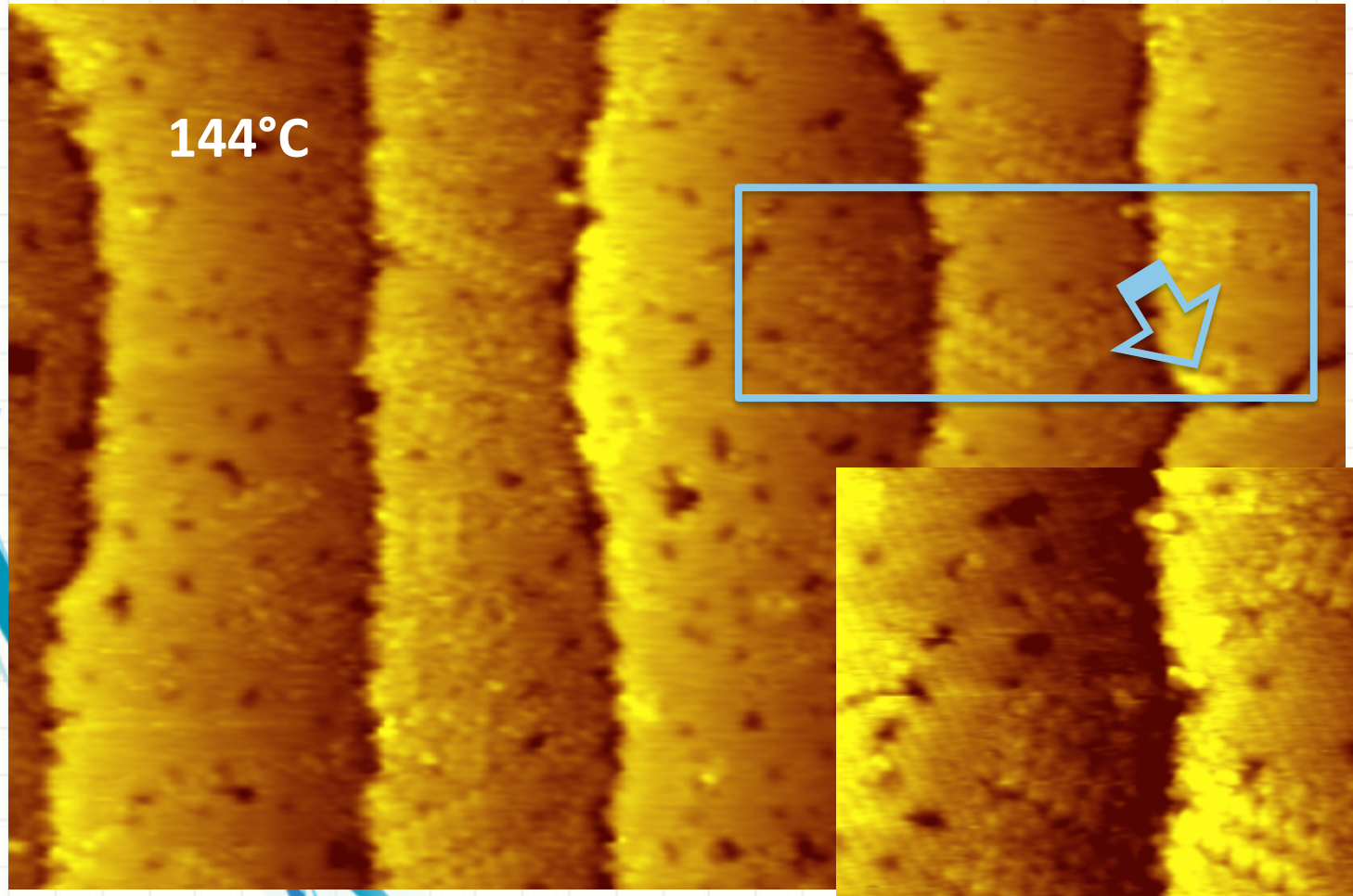


350Å×500Å (1.03 V 480 pA)

- Do observe second (type II) structures at RT
- The periodicity is (9±0.5)Å
- More stable under range of bias conditions

Effect of annealing

- Silver layer limits temperature to 400°C
- Above 160°C molecular layer decomposes



640Å×425Å (1.2 V 300 pA)

Auger indicates no stoichiometric change after anneal at this temperature.

300Å×150Å (1.2 V 300 pA)

Summary:

- The √3 surface does provide a high mobility template for TBTTA adsorption.
- Molecules form 2-d structures on √3 surface at RT. Structures are quite fragile and can decompose readily under STM imaging.
- Size and symmetry of unit cell suggests Van der Waals interaction the driving force.
- Defects in √3 structure can limit the size of domains.
- Another (type II) structure observed at room temperature.
- Do see changes after annealing.

THANK YOU
FOR YOUR ATTENTION!

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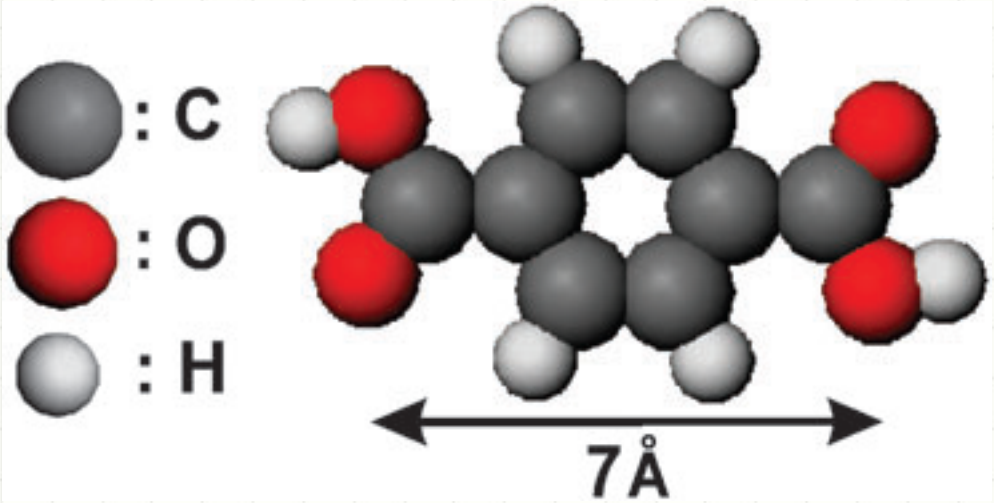
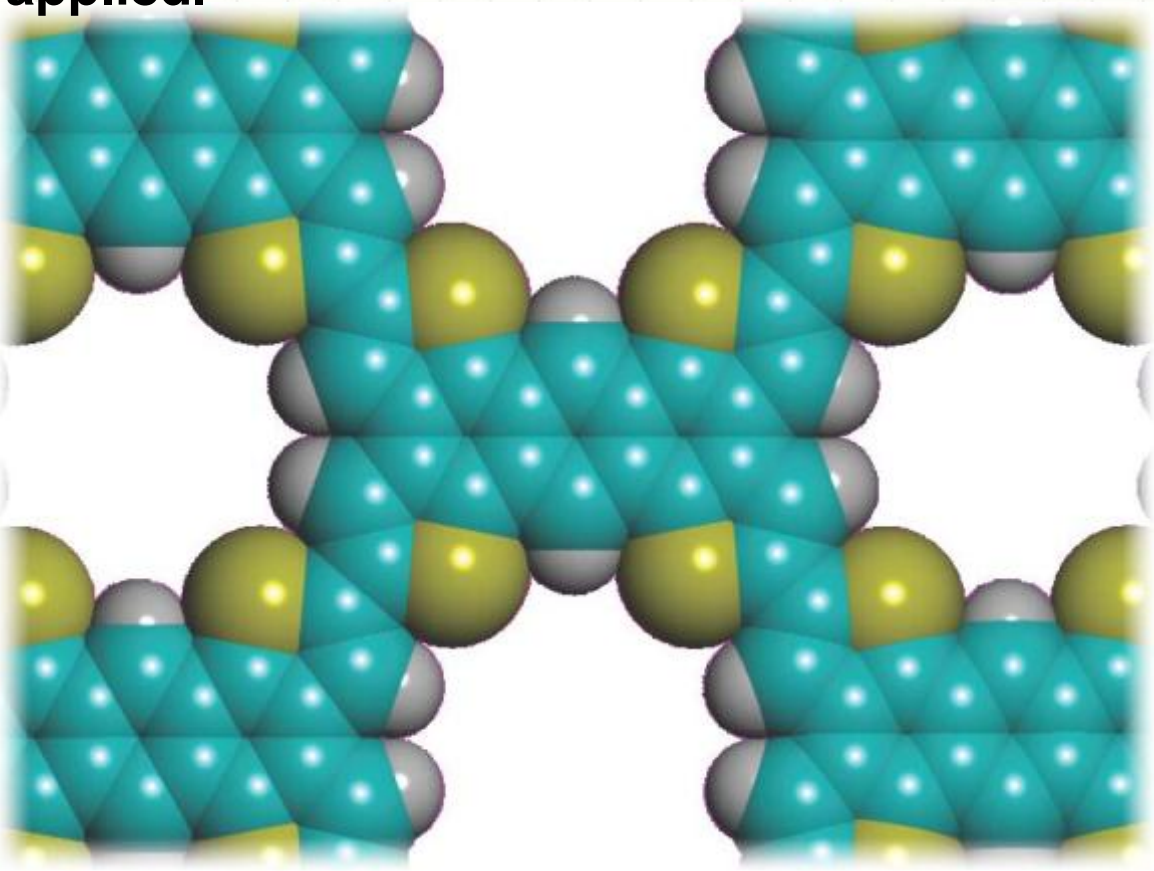


Molecular structure of terephthalic acid (TPA).

Possible covalent structure

A recent research indicated that a Ullman dehalogenation reaction followed with C-C coupling can be performed on Ag(111) surface after the absorption of TBTTA when thermal energy was applied.*



*Nanoscale, 2014, 6, 2660–2668