Adsorption of Thiophene-Based Molecules at Passivated Silicon Surfaces

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Introduction

- we present our STM experiments on the adsorption of Tetrabromo-tetrathienoanthracene (TBTTA) onto the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag and $\sqrt{3}\times\sqrt{3}$-B surfaces
- a significant challenge to forming organic layers on silicon surfaces is the large number of dangling bonds which can suppress the diffusivity of adsorbed molecules and even break the molecules apart (form Si-C bonds)
  - has been shown that these problems can be overcome by depositing the molecules onto a passivated surface
    - TPA on Si(111)$\sqrt{3}\times\sqrt{3}$-Ag (Suzuki et al. *Phys. Chem. Chem. Phys.* **11**, 6498 (2009))
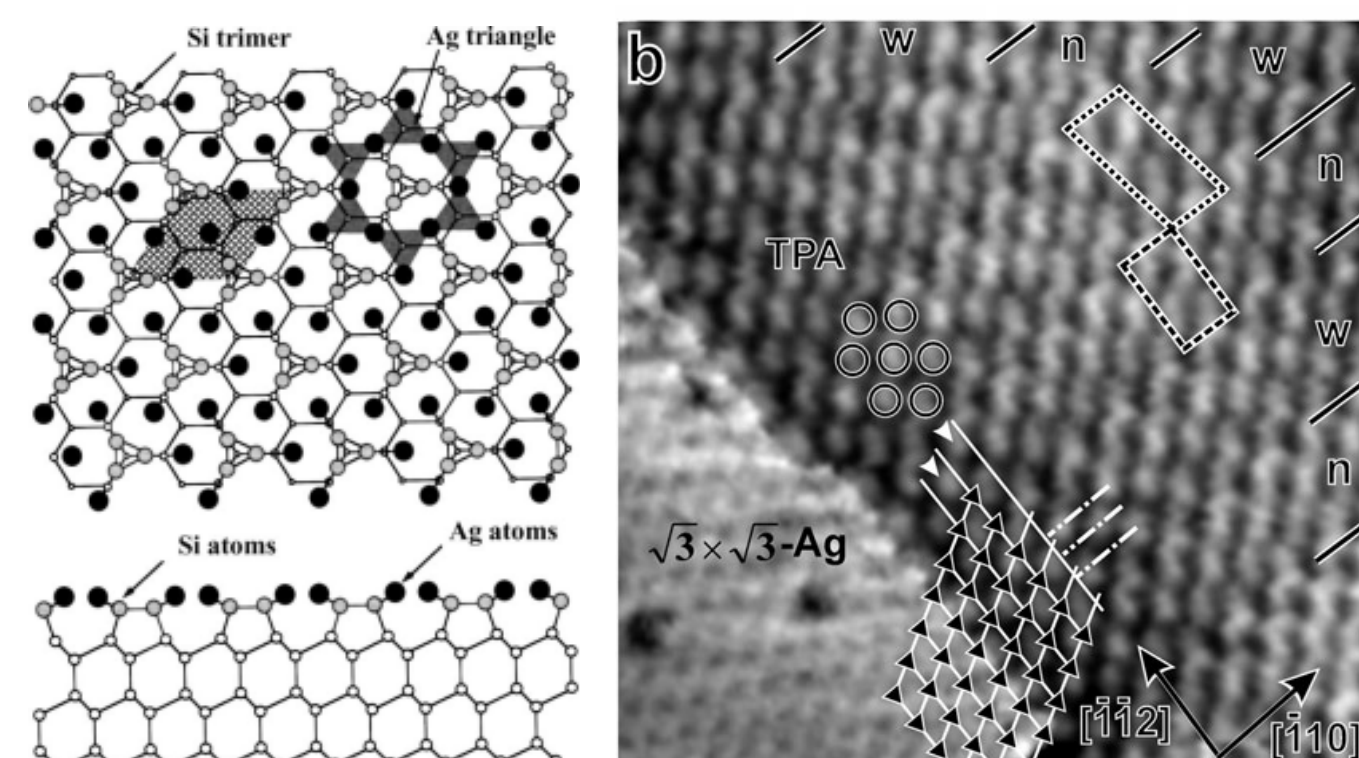   - DBT on Si(111)$\sqrt{3}\times\sqrt{3}$-B (Makoudi et al., *Chem. Commun.* **50**, 5714 (2014))

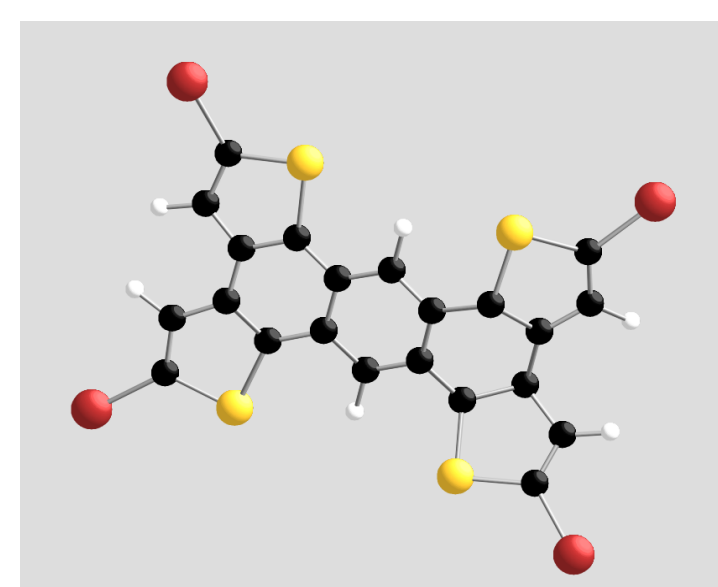**Figure 1: $\sqrt{3}$-Ag structure (left) and TPA on $\sqrt{3}$-Ag (Suzuki et al.)**

Figure 2: TBTTA

TBTTA

- molecule of interest, TBTTA (Figure 2)
- TBTTA has been used as precursor molecule in surface-confined polymerization experiments (Figure 3)
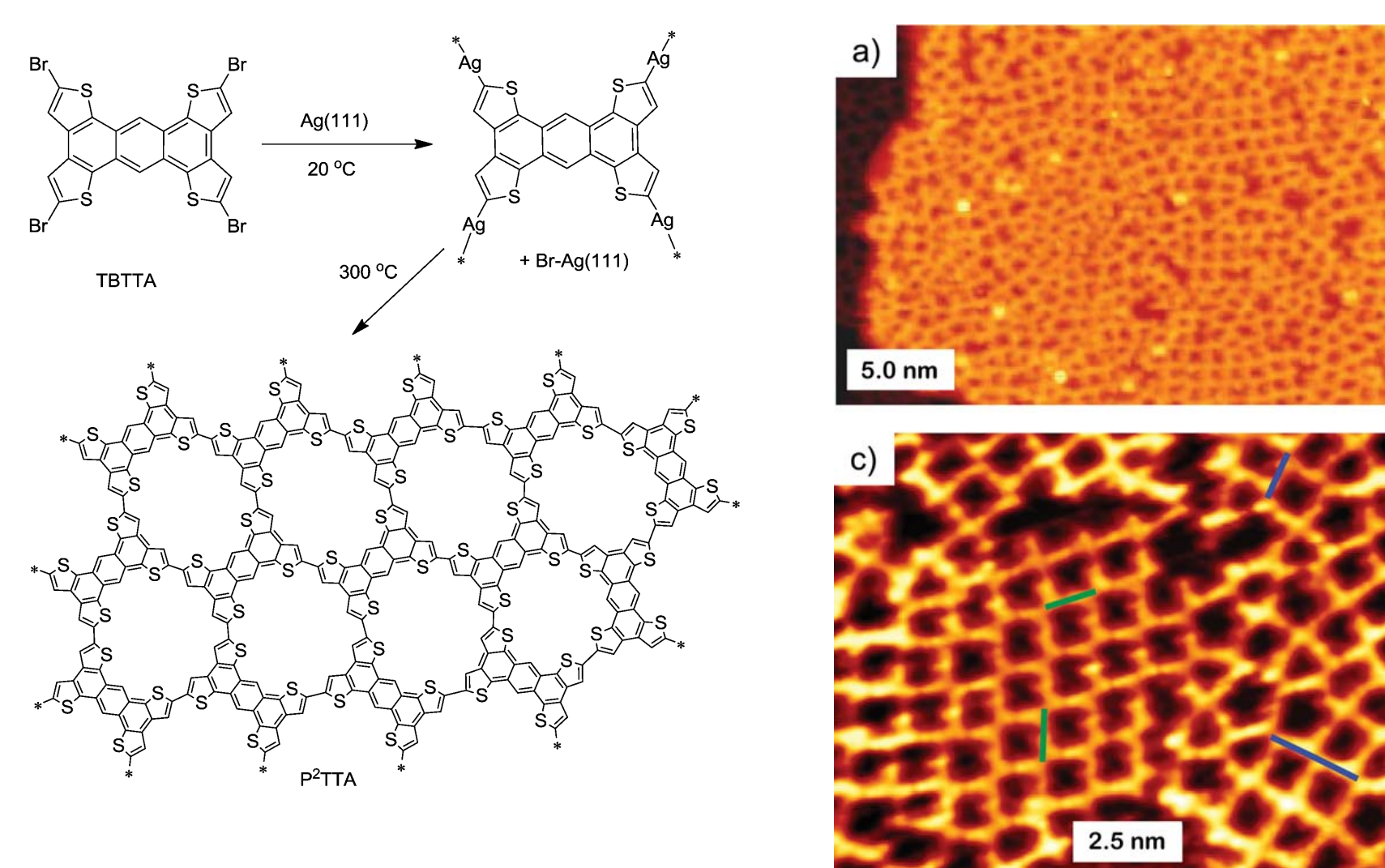

Figure 3: TTA on Ag(111) Cardenas et al., *Chem. Sci.*, 4 3263 (2013)

RESULTS

♦ TBTTA on $\sqrt{3}$-Ag

- monomers are highly mobile, readily migrating to substrate steps and defects on the surface
- at higher coverage supramolecular domains are formed. Three orientational domains consistent with C3 symmetry of $\sqrt{3}$ substrate (Figure 4)
- "raster noise" in many images suggest additional molecules moving on the surface

♦ Domain Stability

- structures are sensitive to changes in STM bias conditions
  - often decompose when imaged under high (|V| > 2V), or low (|V| < 0.7 V) bias conditions
- also observe time dependent dissolution and enlargement of domains (Figure 5)

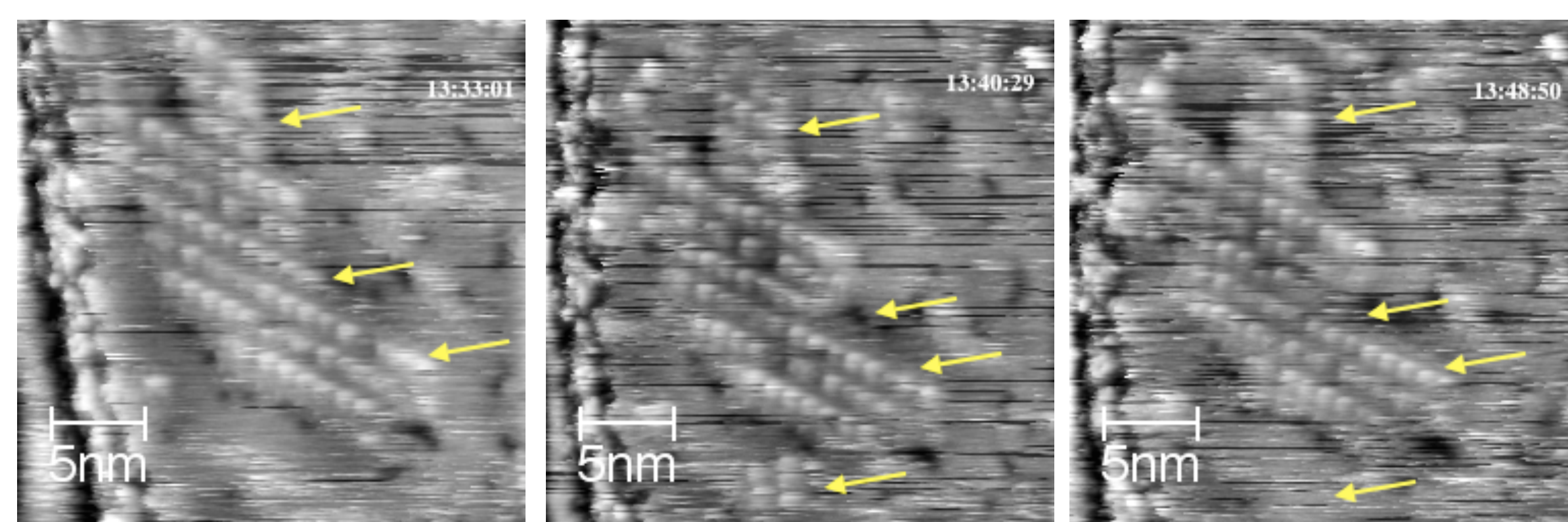**Figure 4: 320Å × 270Å (-1.11 V, 497 pA)**

Figure 5: dissolution and growth of molecular structures

- bias dependence and temporal changes suggest relatively weak intermolecular interactions

♦ Supramolecular Unit Cell

- domains characterized by an oblique unit cell (Figure 6)
- expressed in matrix form:

$$\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} 3 & 2 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} a_{\sqrt{3}} \\ b_{\sqrt{3}} \end{pmatrix}$$
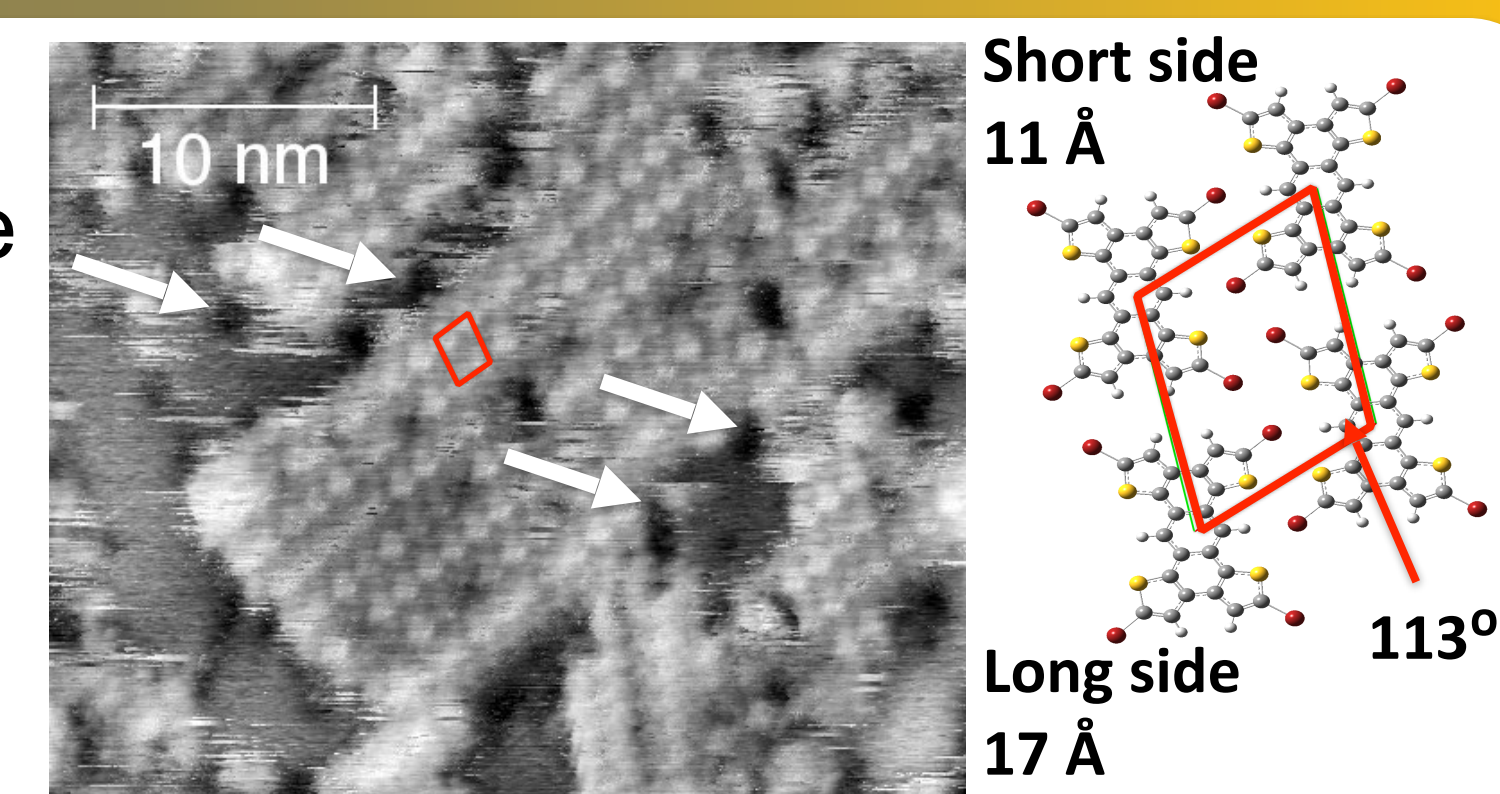

Figure 6: 320 Å × 270 Å (-1.11 V, 497 pA)

- previous DFT calculations (Gutzler et al., *Nanoscale*, **4** (19): 5965-5971(2012)) on a free standing TBTTA layer predict oblique cell of dimensions 14 Å × 11 Å with an angle of 114°, consistent with the unit cell we find on $\sqrt{3}$-Ag.
- similarity suggests our domains consist of intact TBTTA molecules held together by relatively weak halogen intermolecular bonding

♦ Influence of Defects

- As domains grow extent can be limited by defects in the underlying $\sqrt{3}$ layer (indicated by yellow arrows in Figure 6)

Si(111) $\sqrt{3}\times\sqrt{3}$-B Surface

- heating (950°C) highly boron doped silicon wafer leads to surface segregation of boron
- boron atom actually sits below the surface under a three fold coordinated silicon adatom and resultant $\sqrt{3}$ surface is passivated (Figure 7)
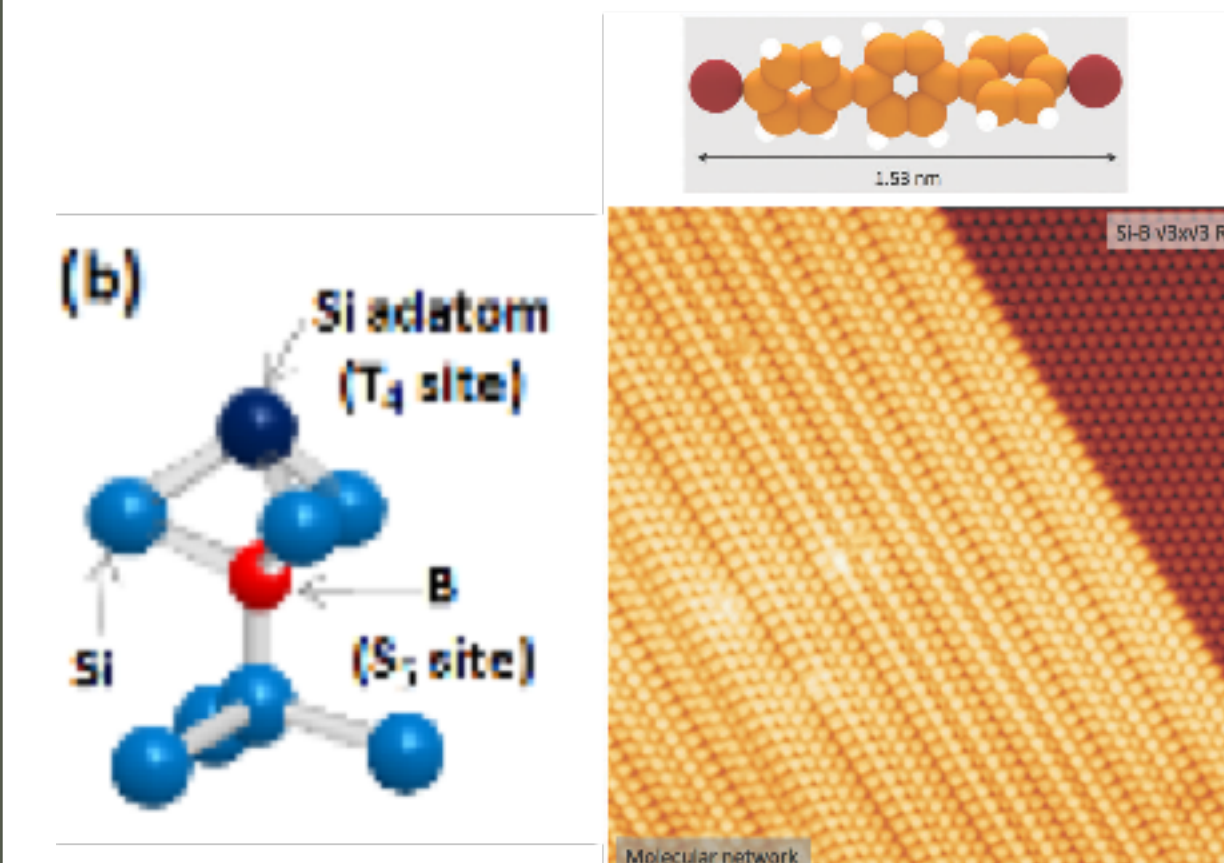

Figure 7: $\sqrt{3}$-B stucture (left) and DBT layer (right) (Makoudi et al.)
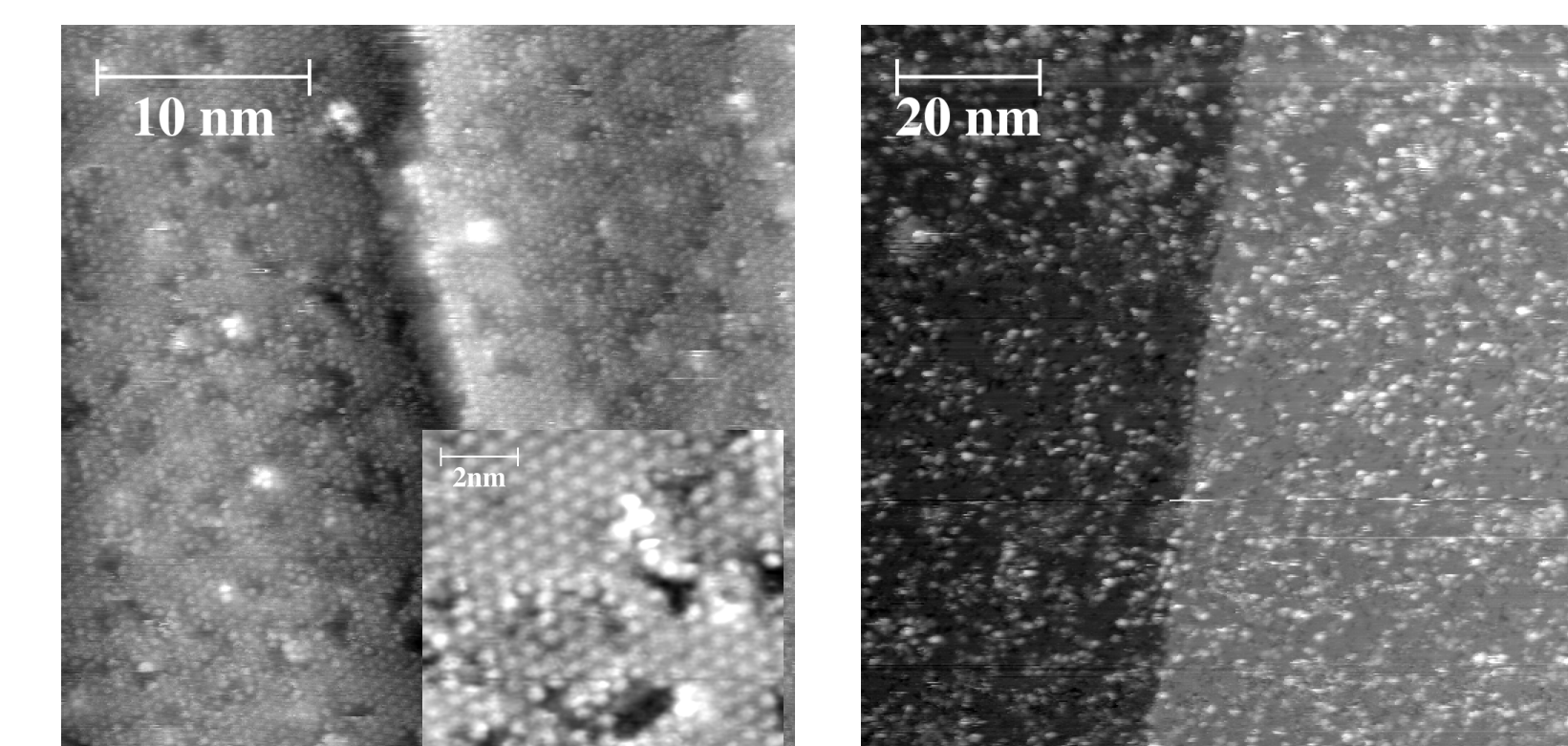

Figure 8: $\sqrt{3}$-B surface (left) TBTTA on $\sqrt{3}$-B (right)

- to date we have found TBTTA does not form ordered superstructures on the $\sqrt{3}$-B surface (Figure 8)

Annealing $\sqrt{3}$-Ag surface

- initial annealing results (~150 °C) indicate more compact and robust "1-d" structures (Figure 9) possible
- periodicity ~10Å along chains, ~10Å between chains, and rotated 30° from $\sqrt{3}$ direction (line d)
- epitaxial relationship to $\sqrt{3}$-Ag → $\sqrt{3}\times\sqrt{3}R30°$

Fig. 9: 640Å×425Å (1.2V, 300pA)
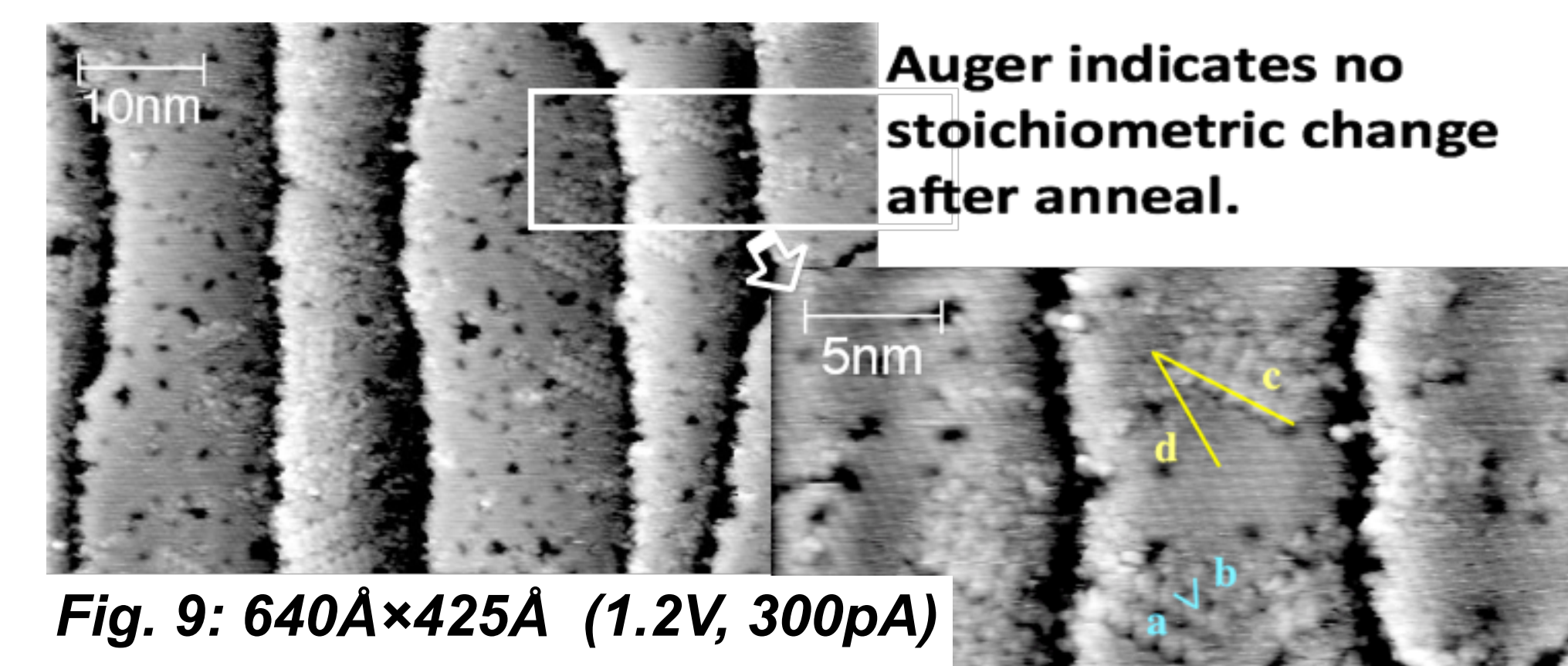
Summary

- the $\sqrt{3}$-Ag surface provides a high mobility template for TBTTA adsorption.
- molecules form 2-d structures on $\sqrt{3}$-Ag surface at RT
  - Structures are quite fragile (decompose readily under STM imaging)
  - Size and symmetry of unit cell suggests intact TBTTA monomers held together by intermolecular halogen bonds.
- no ordered structures observed on the $\sqrt{3}$-B surface
- annealing data (145°C) on $\sqrt{3}$-Ag suggests a more compact and robust structure possible