



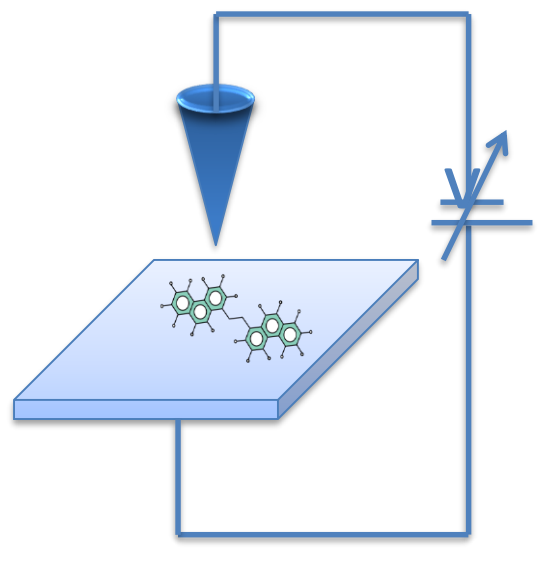
Growth and Electronic Properties of Functionalized DAE Molecules on Au(111)/Ag(111) studied by STM/STS

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STM @ 77 K IN UHV



Introduction:

Comparative study of two diarylethene (DAE) derivatives functionalized for coupling reactions: Cl-DAE and Br-DAE.

Background

- Reversible light-induced switching between open and closed states.

Molecular structure

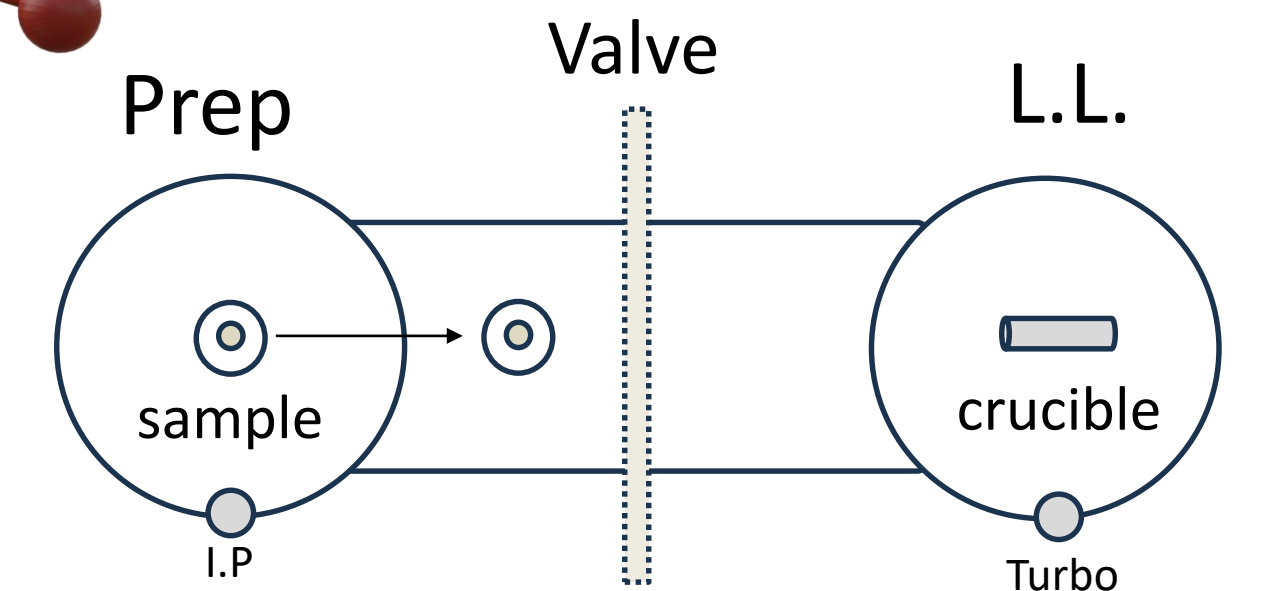
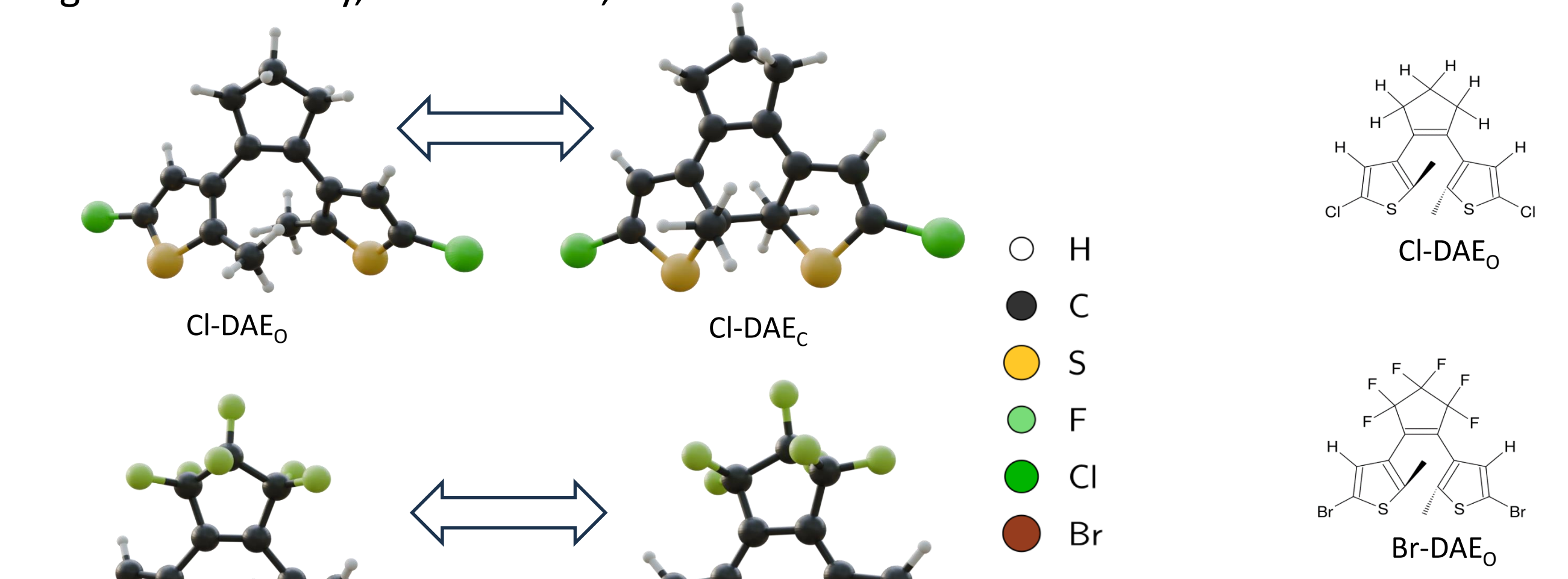
- Same diarylethene photo-switch core.
- Different bridge: cyclopentene (-CH₂-) vs perfluorocyclopentene (-CF₂-).
- Different halogen substituents on the thiophene rings: Cl- vs Br-substituted derivative.

Application

- Molecular switches with high-speed switching.
- Molecular memory.

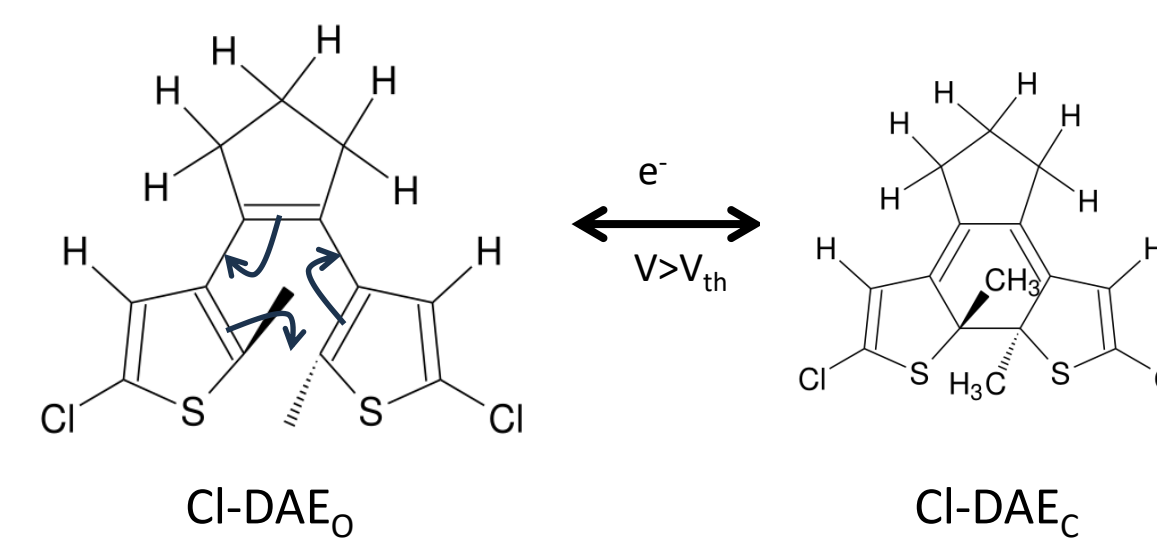
Goal

- Realization of reversible molecular switching
- Thermal on-surface polymerization.

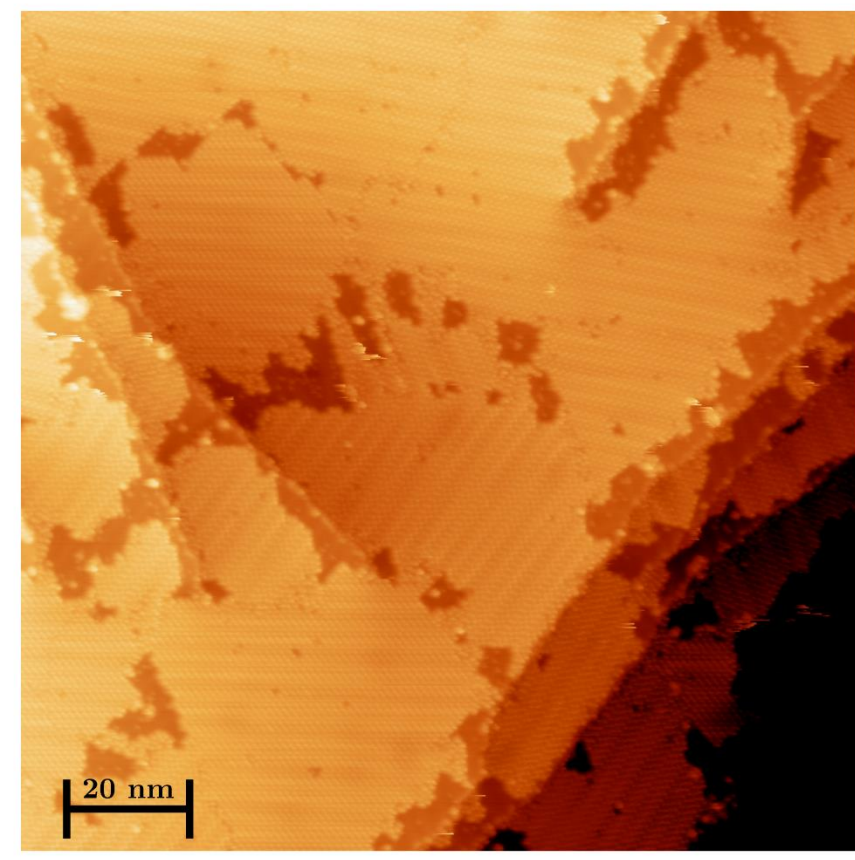


Preparations

- Both molecules have room temperature sublimation.
- Load lock deposition on Au(111) and Ag(111).
- 0.5 to 0.6 ML in 35 seconds in high vacuum.

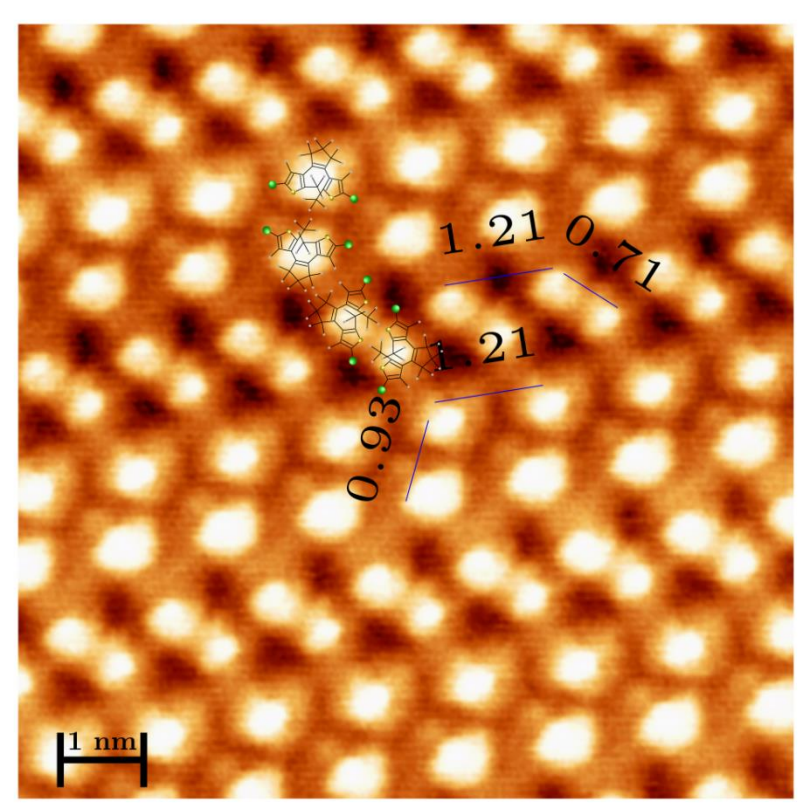
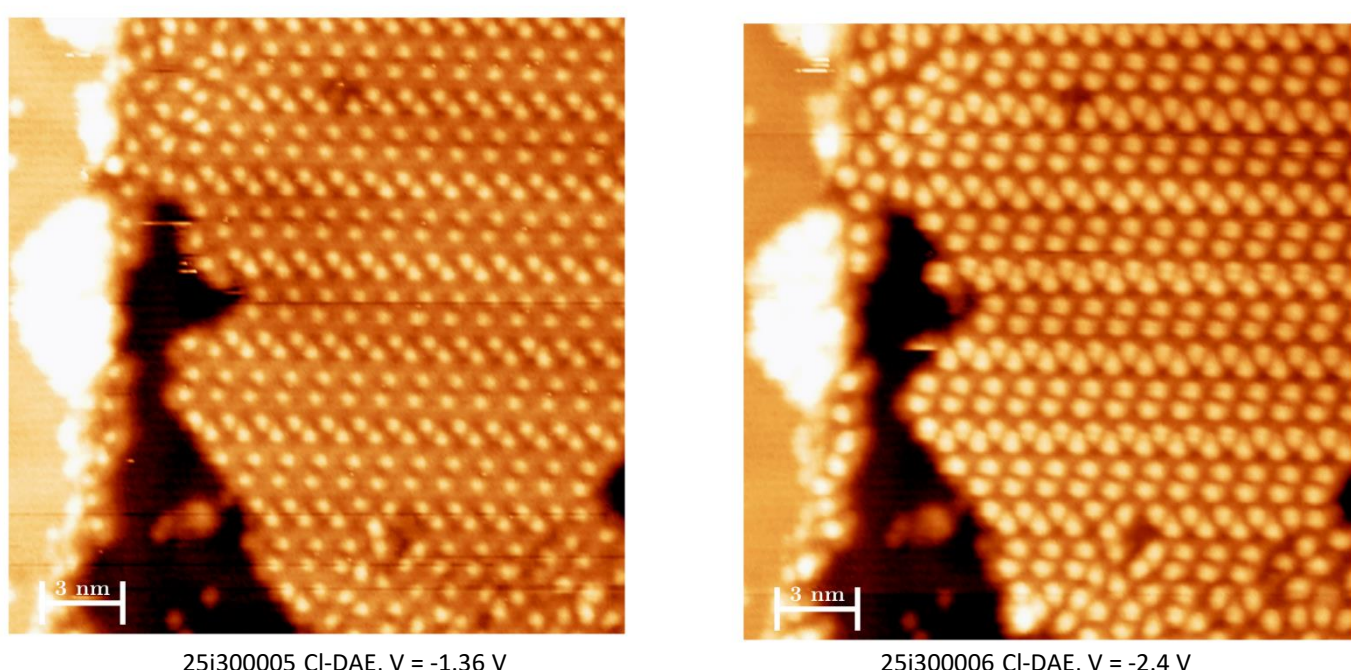


Molecular Self-Assembly on Thermally Relaxed Noble Metal Surfaces



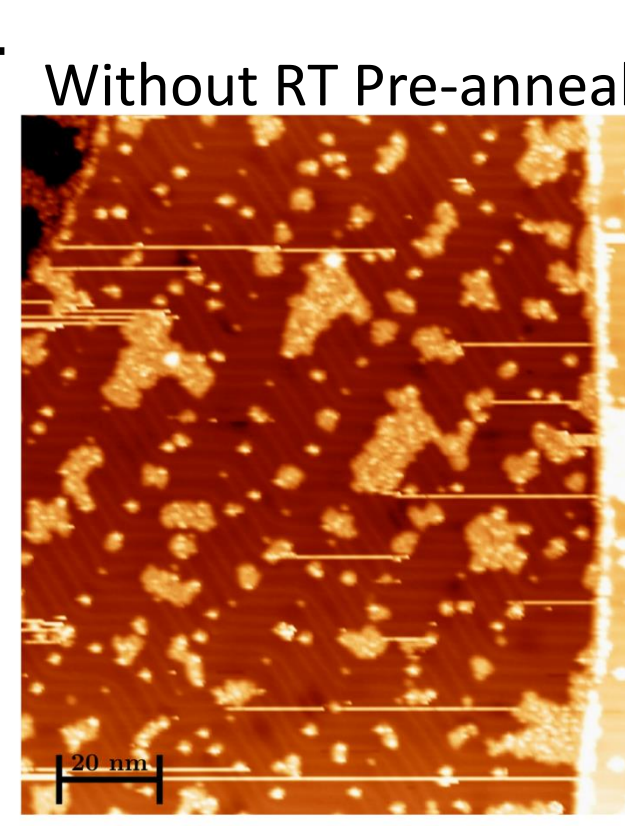
- Molecule lands intact.
- Similar self-assembly with and without RT Pre-anneal.

Bias Dependence

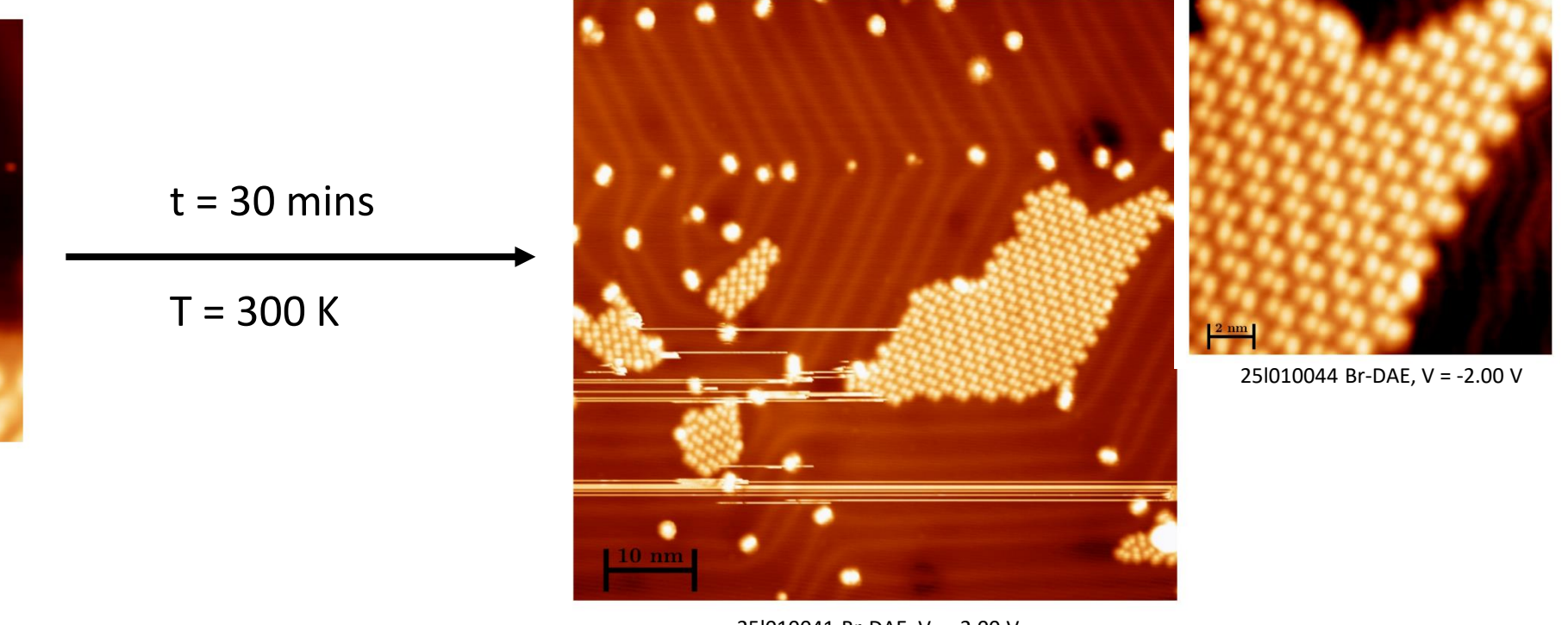
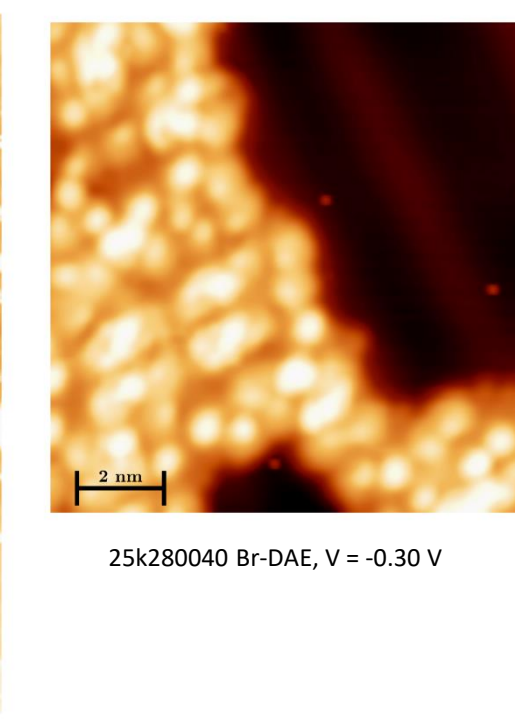


- Scaled overlay illustrating plausible geometry.
- Non-rectangular, oblique unit cell symmetry.
- Lattice Periodicity: Uniform 1.21nm.
- Adjacent rows has asymmetric NN distances.

Au(111)



Thermally Activated Self-Assembly of Br-DAE

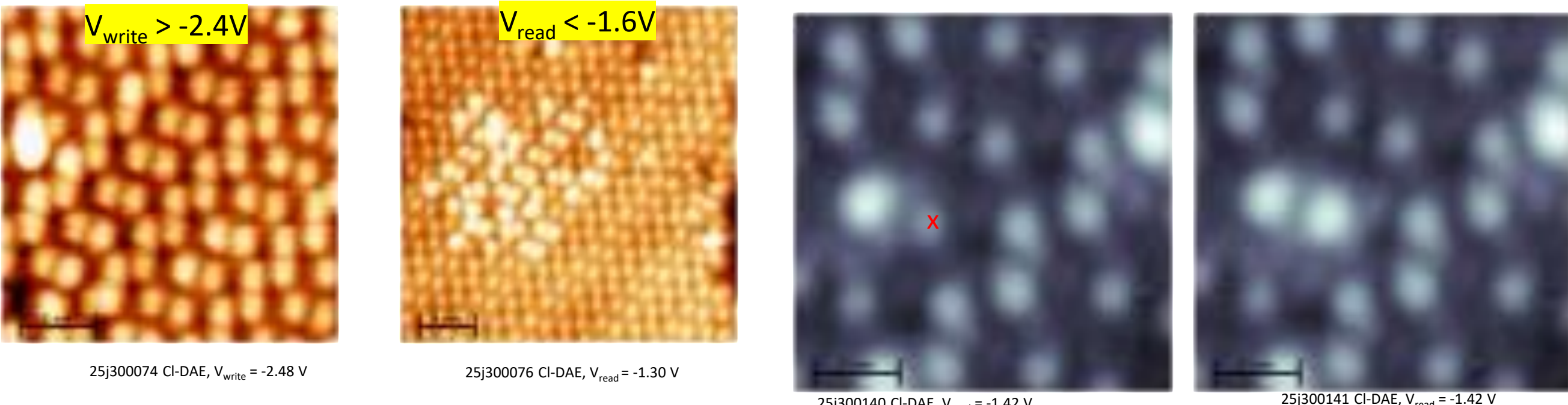


- kinetically trapped disordered clusters.

- RT thermal anneal activates mobility.
- Thermodynamic ordered assembly.

- Near-rectangular symmetry.
- Pi-Pi stacking along mol. long axis.
- Likely Br-driven directional assembly.

Electronic Fingerprinting of the Selective Switched State

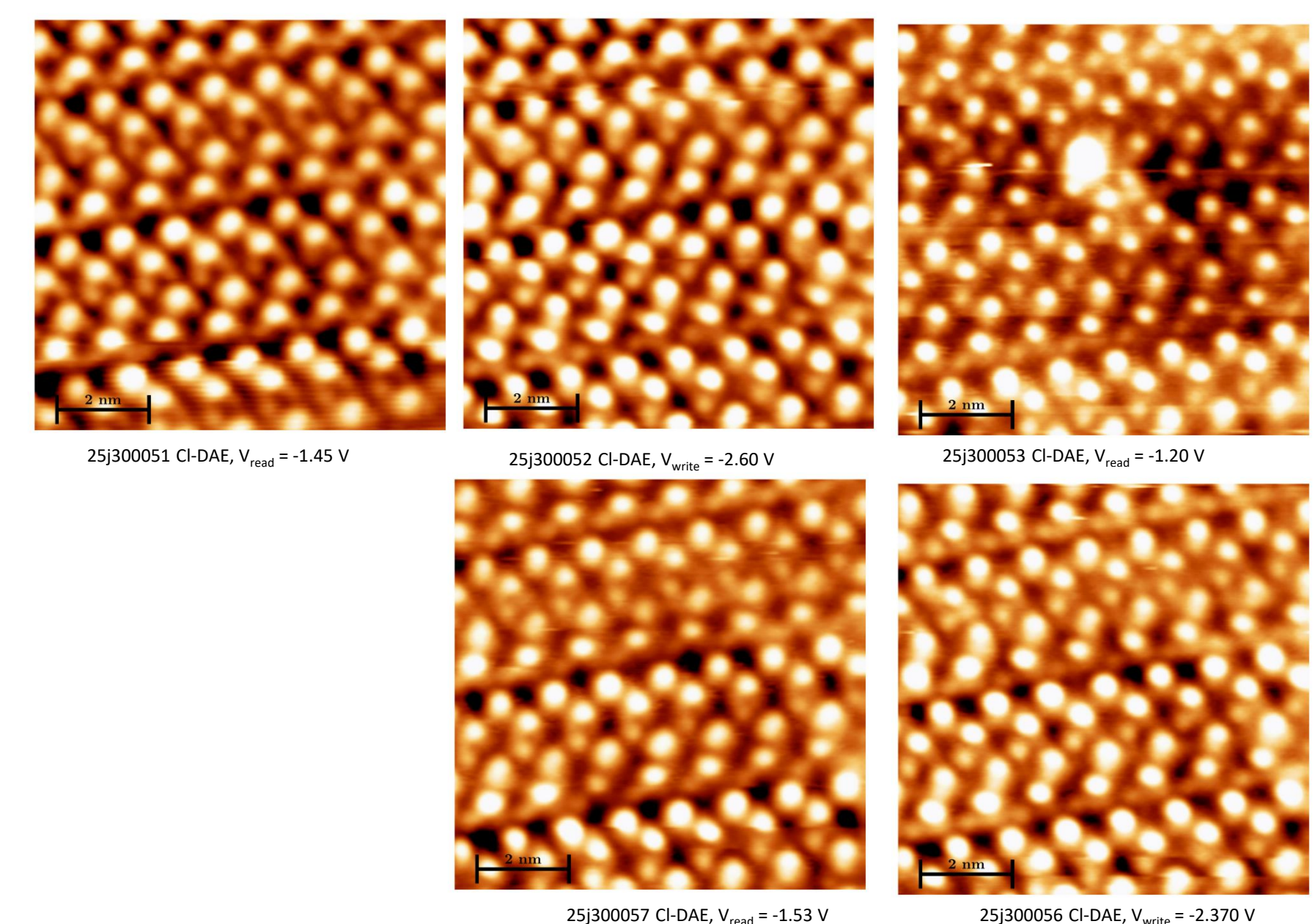


Collective switching (Color Images)

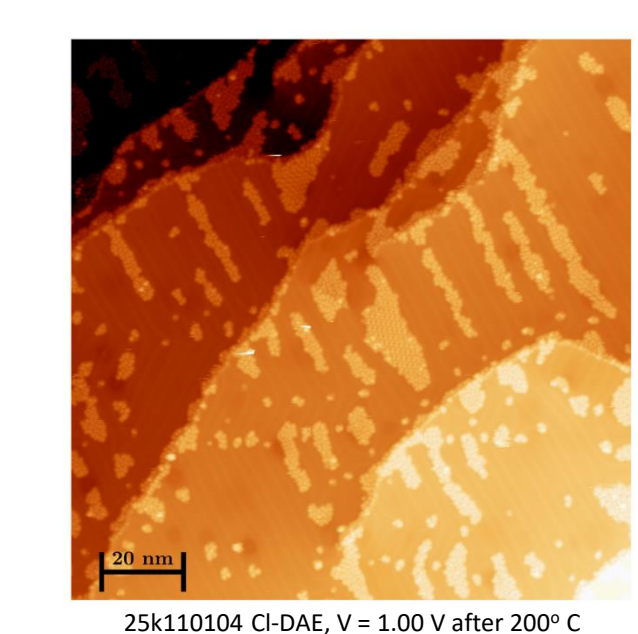
- A defined sub-region scanned at V_{write}.
- Large-area imaging at a low bias, V_{read}.
- Rectangular high-conductance domain.

Single-Molecule Manipulation (Grey Images)

- Using STS pulse (0 → -2.6V)
- Distinguishable LDOS for switched (bright) and pristine(dim) molecule



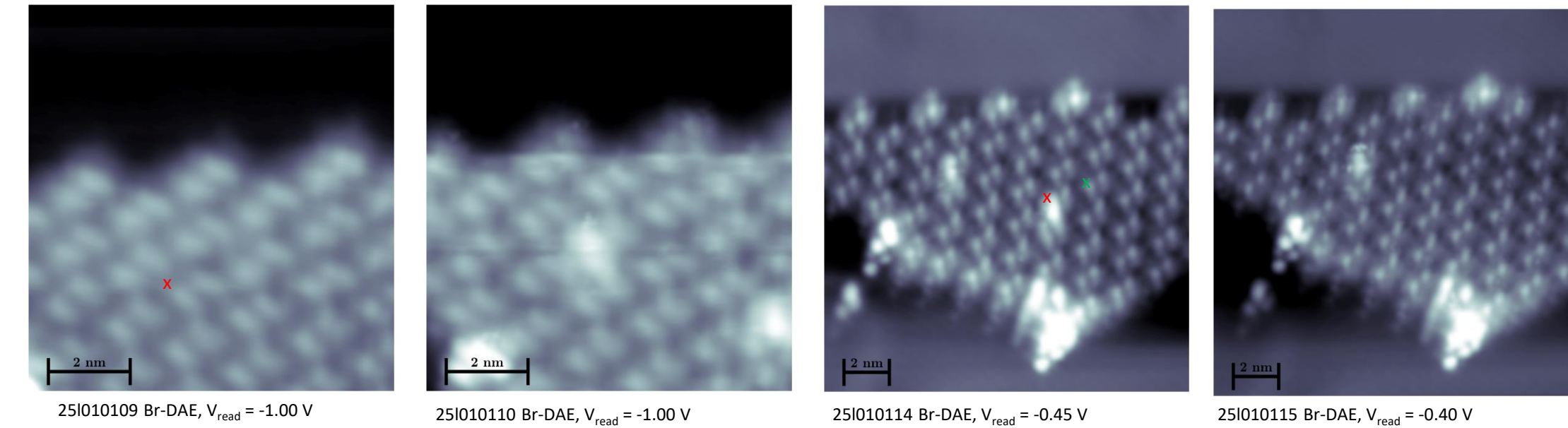
Bi-directional Switching via STM Scanning



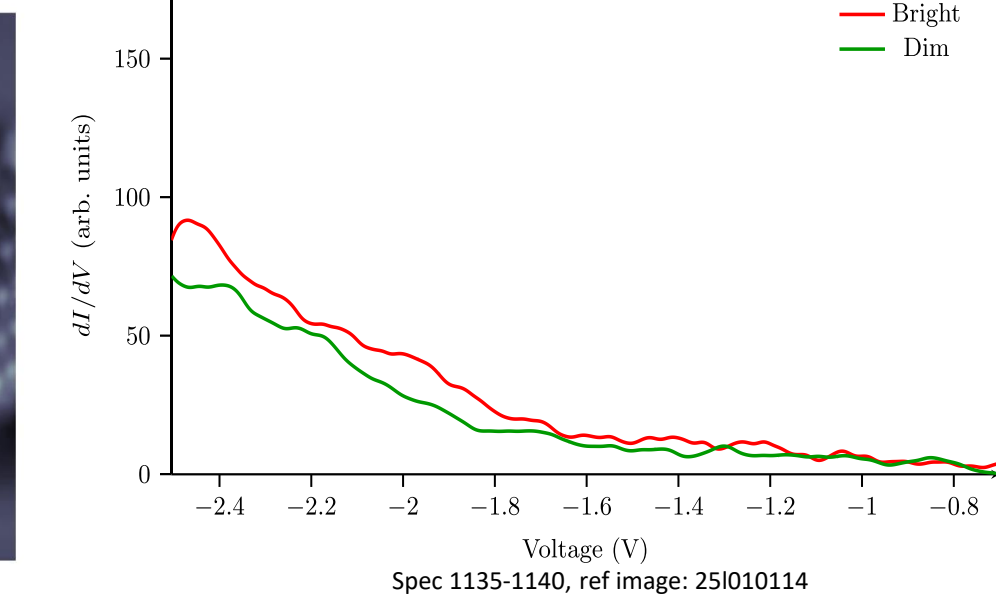
- Annealing at 200°C → lower coverage
- More disordered structure
- Emergence of new structures

Reversible Switching

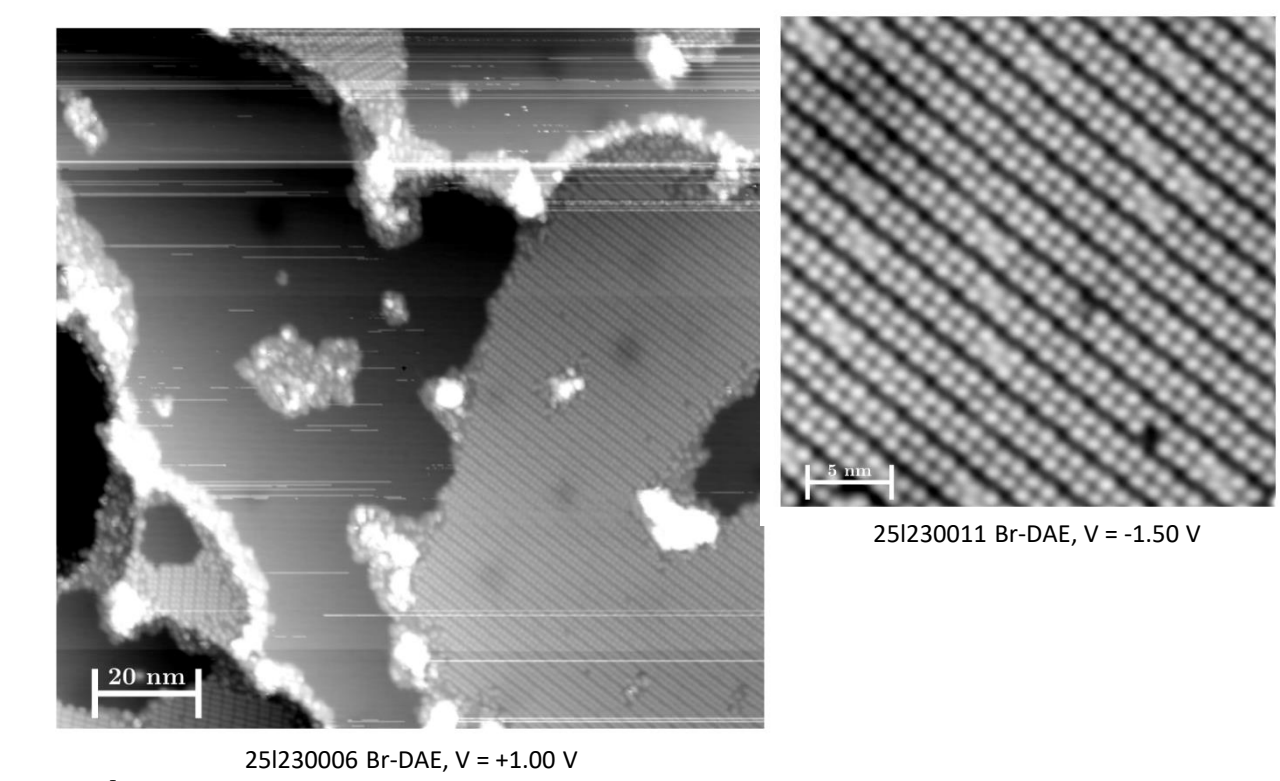
Preliminary Evidence of Reversible Switching



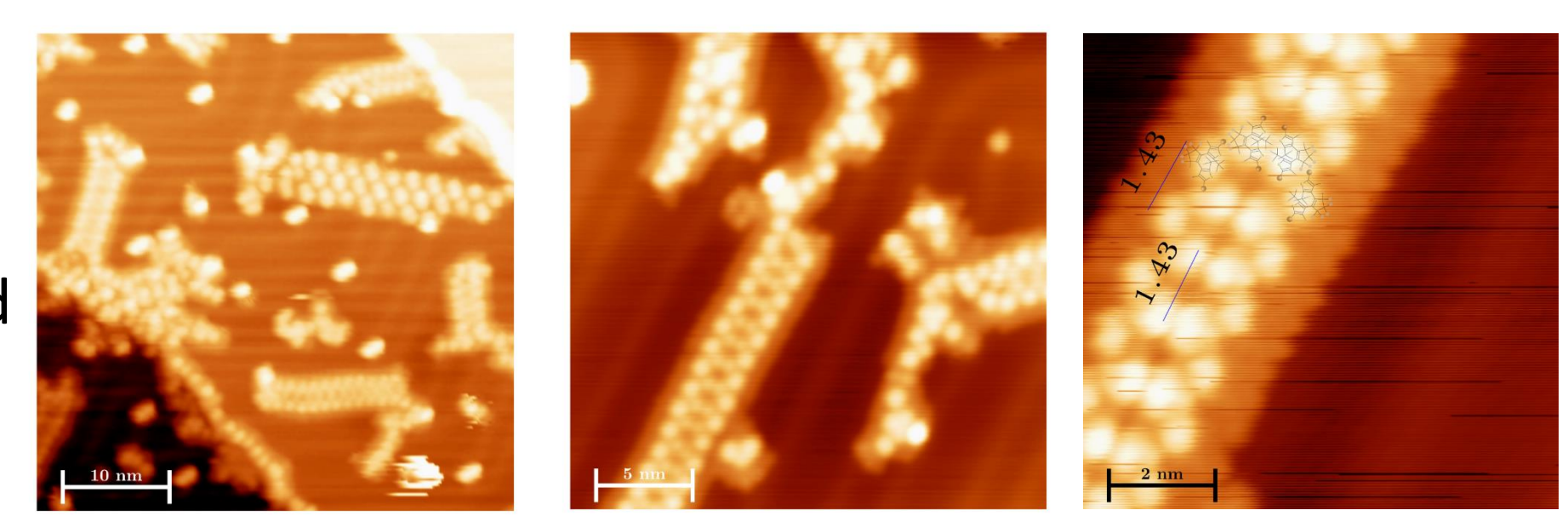
- Proof of Reversibility in dense assemblies.
- Switching event occurs in the vicinity of the target site.
- Using STS pulse (0 → -2.5V)



Ag(111)

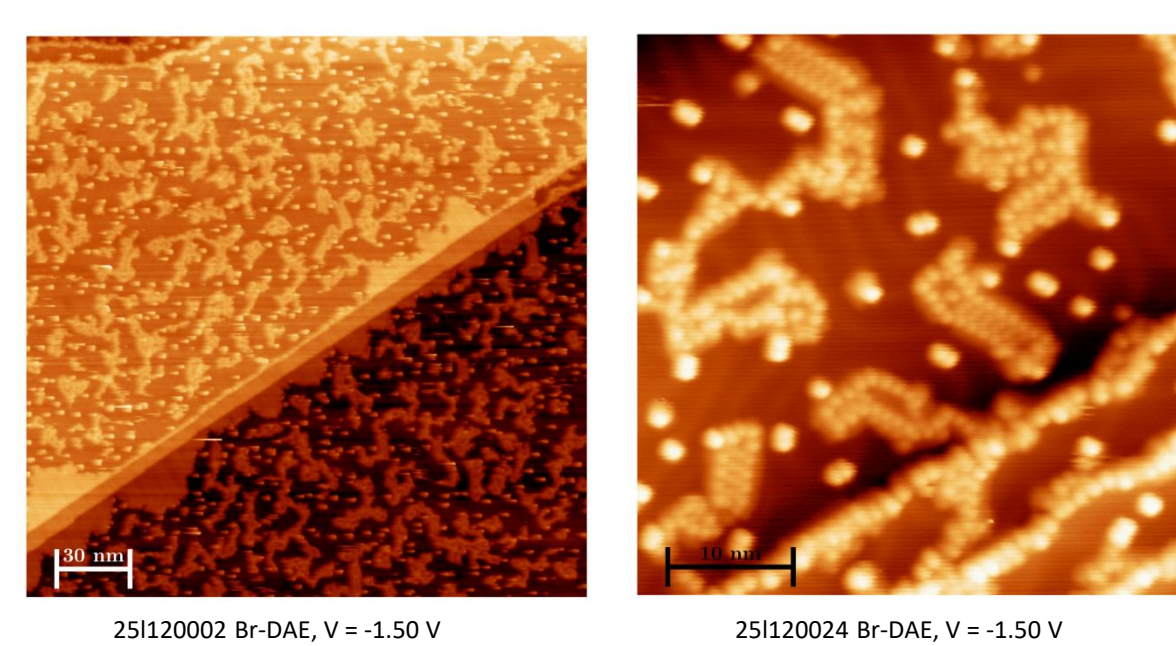


After 100° C anneal

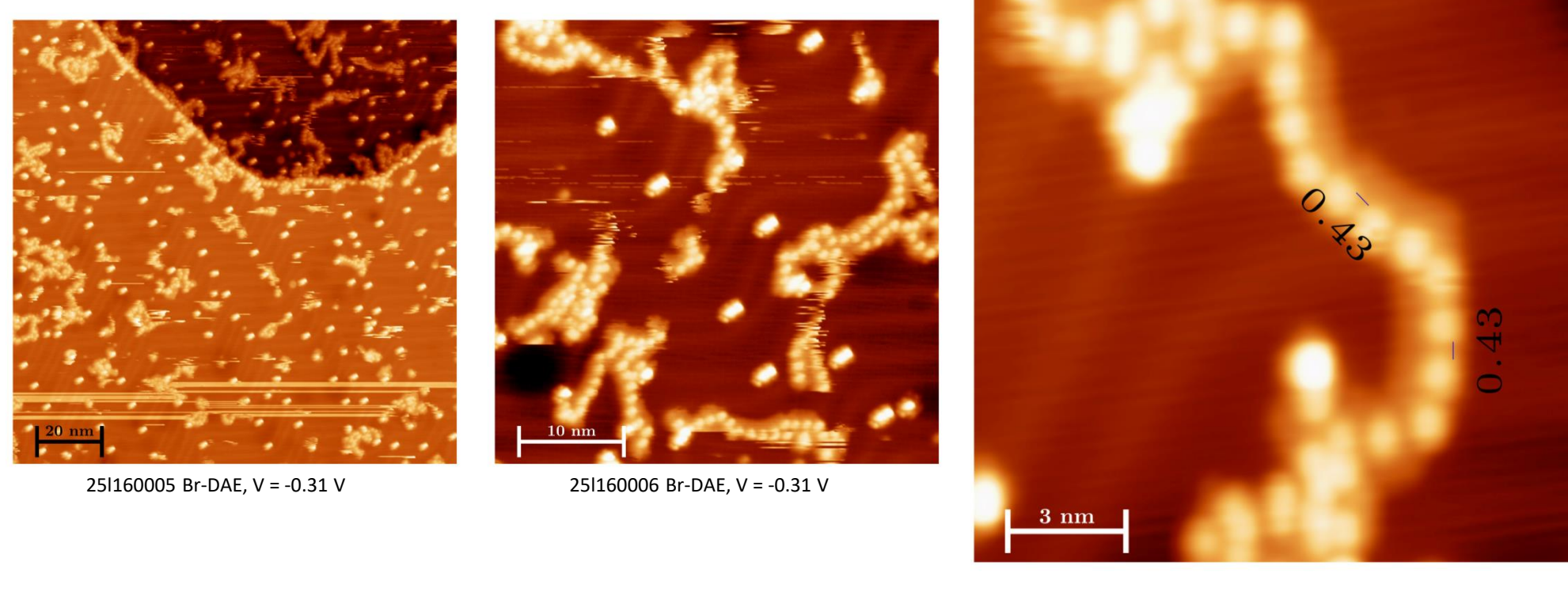


- Minority unresolved dimers or change in adsorption geometry.
- larger periodicity of 1.43 nm.

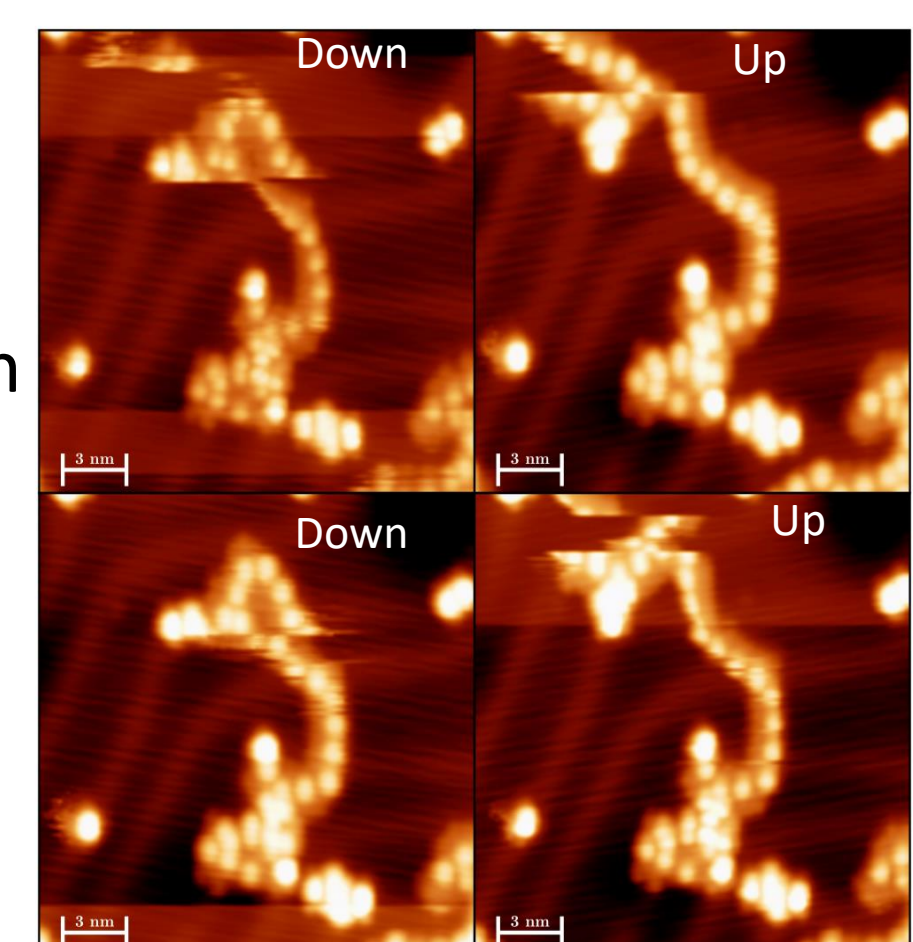
Thermal Evolution



After 200° C anneal



- Linear poly-DAE chains.
- Thermally induced dehalogenation
- Periodicity reduction to 0.43 nm.
- Tip-induced mobility.
- Covalent Coupling.



Conclusions & Outlook

- Future work will distinguish between **current** and **Electric Field-driven** pathways via bias-dependent spectroscopy and mapping.
- Demonstrated preliminary evidence of **STM-induced bi-directional switching**, confirming "Write/Read" capabilities.
- Optimization of pulse parameters (Voltage/Time) aiming for high-fidelity "Write" and "Erase" cycles for molecular memory applications.
- Thermal annealing at 200°C successfully triggered **on-surface polymerization**, confirmed by the lattice contraction to **0.43 nm** (C-C bond formation) and tip-induced chain mobility.

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