



Vertical Electronic Interaction in DB6P on Ag(111)

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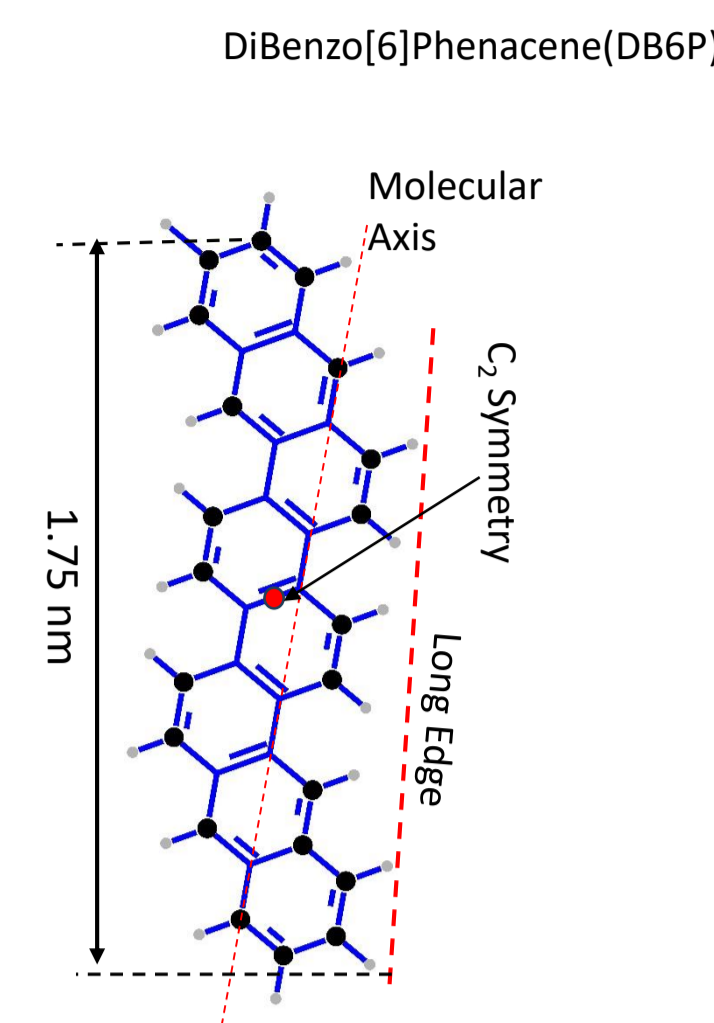
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Introduction:

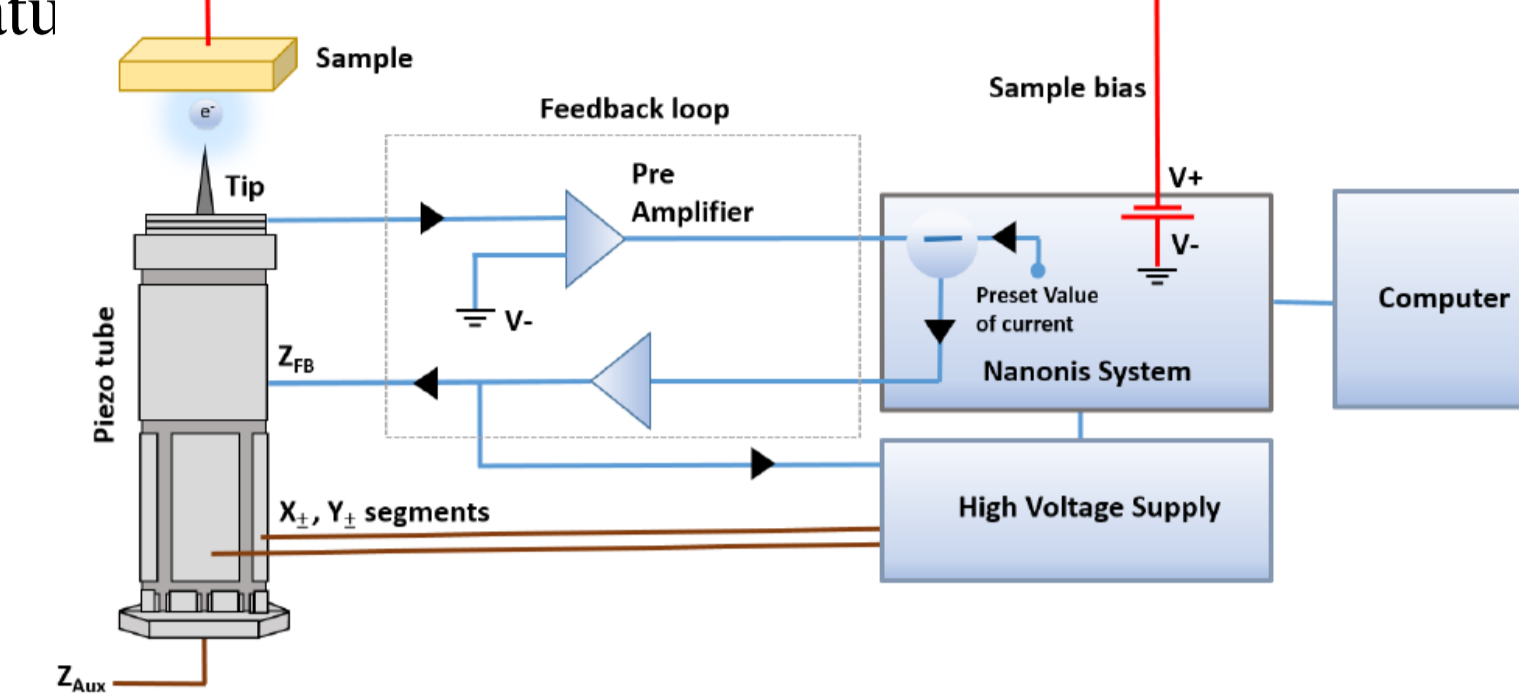
This research focuses on DiBenzo[6]Phenacene (DB6P), a [6]Phenacene derivative extended with benzene rings, for its potential use in organic field-effect transistors. Using scanning tunneling microscopy and spectroscopy, the study investigates DB6P's growth and electronic properties on a Ag (111) surface. The findings show that in the first layer, DB6P forms a uniform, row-wise pattern with the molecules parallel to the surface. In the second layer, growth continues in rows but with dimerized, unevenly tilted molecules. A significant finding is that the alignment of rows changes between the layers, which affects the electronic states of the molecules. This behavior, different from standard [n]Phenacenes, suggests a pinning effect in molecular states due to vertical electronic interactions. The study presents these experimental results and offers interpretations of these phenomena.

Molecular Structure:

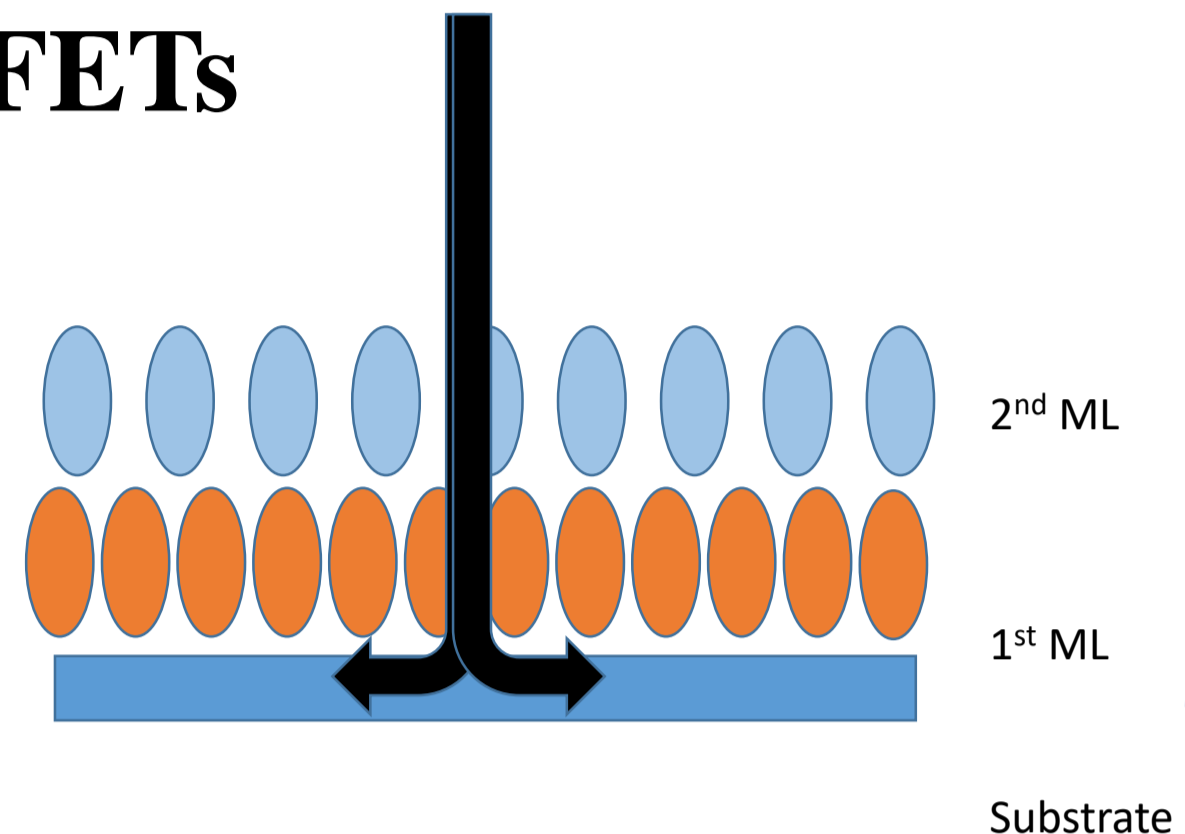


Experimental Method

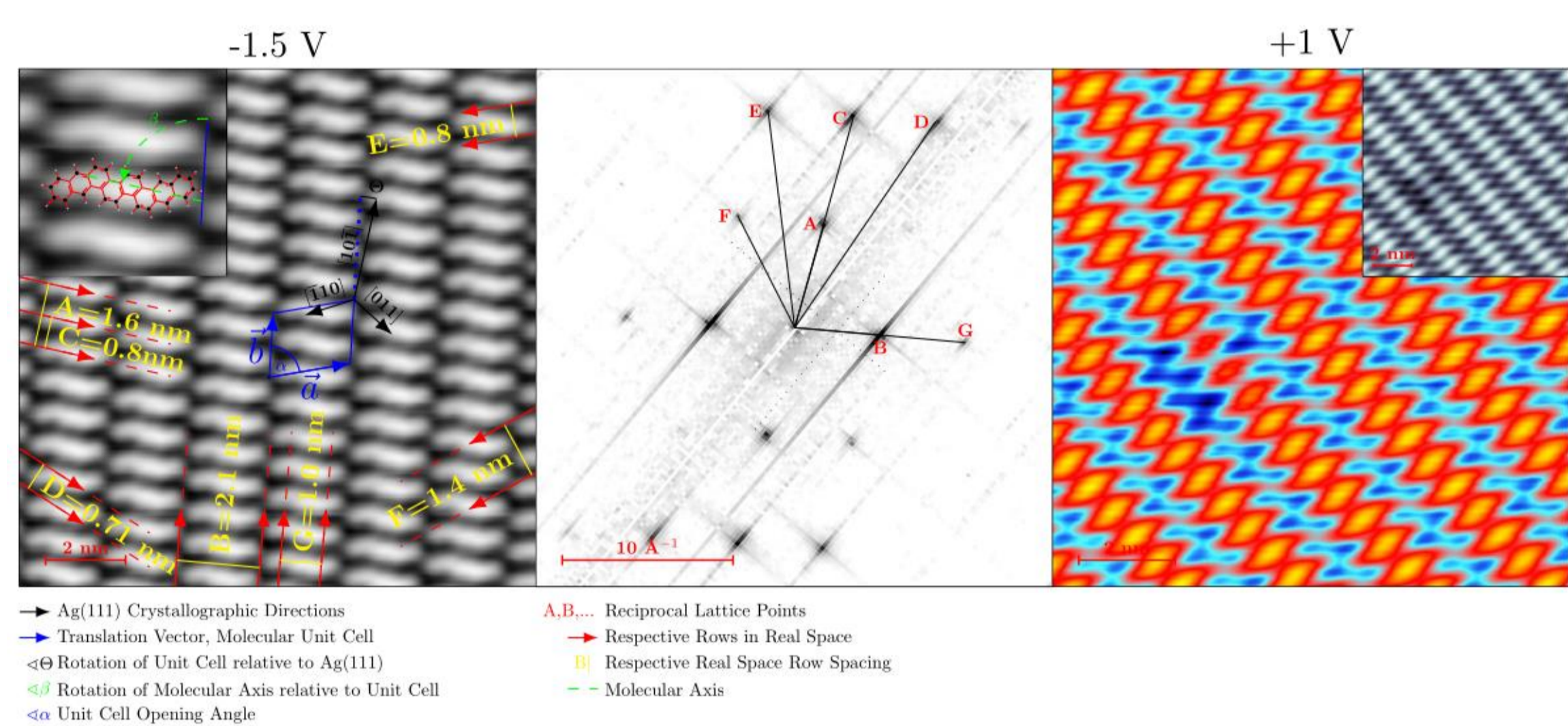
We use STM for experiments in ultra-high vacuum at 77K. Molecular films are prepared by thermal deposition with the sample kept at room temperature



Motivation: OFETs



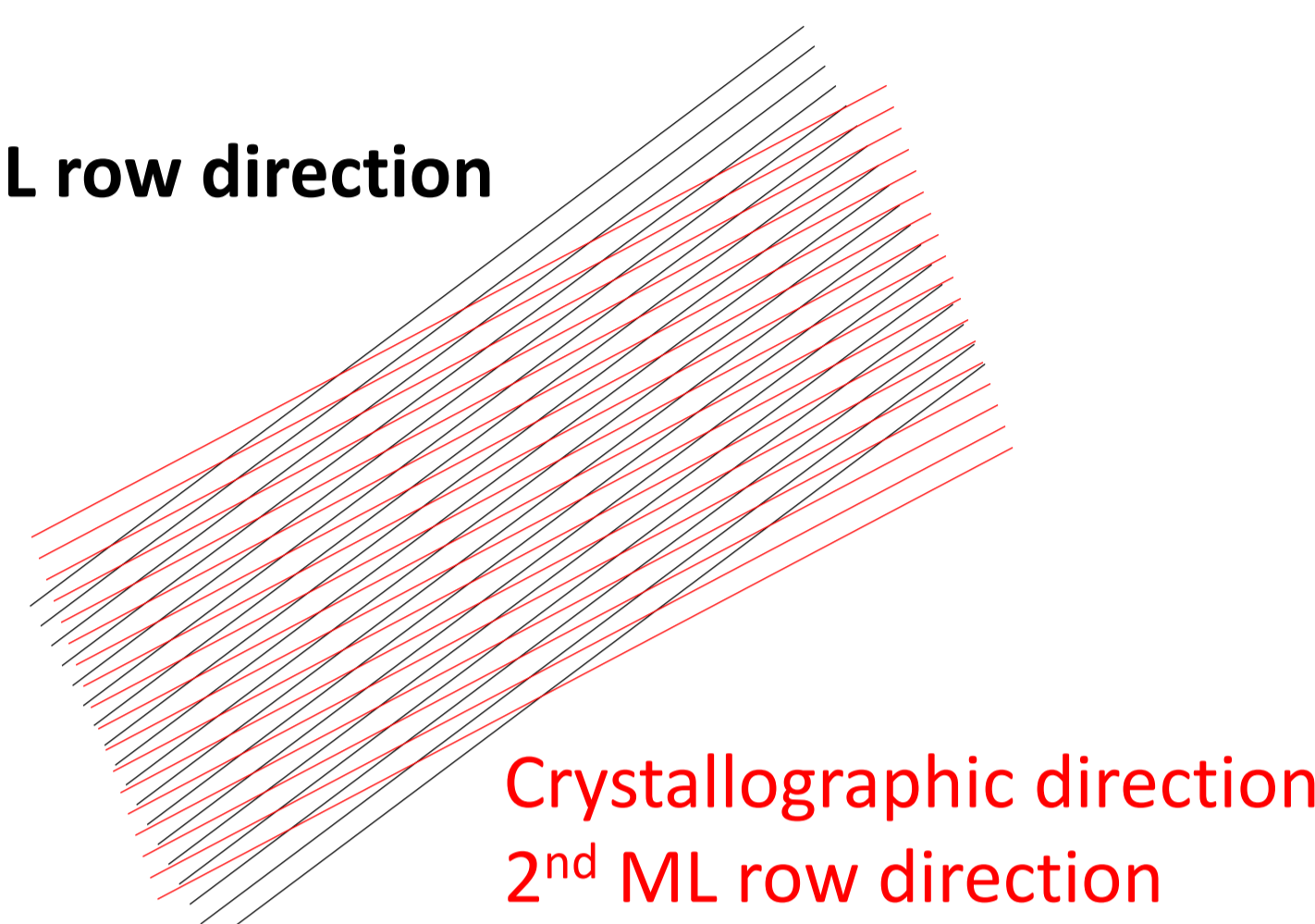
First Monolayer Structure:



- DB6P forms a regular network of rows on Ag(111) which is rotated by $\Theta=9^\circ$ to Crystallographic direction.
- We find six different domain orientations
 - Three domains have anticlockwise orientation of molecule with $\Theta=9^\circ$
 - Three domains have clockwise orientation of molecule with $\Theta=-9^\circ$
- DB6P molecular Axis rotated by 81° to row direction.
- DB6P forms two-molecule unit cell ($a \times b = 2.08 \times 1.68 \text{ nm}^2$, $\alpha = 77^\circ$)
 - Clearly resolved at positive polarity
 - At negative polarity only clear contrast in FFT

Central Finding

1st ML row direction



Rotation of 1st ML relative to crystallographic axis and 2nd ML

Assumption:

- 1st ML is not affected by growth of 2nd ML

Consequence:

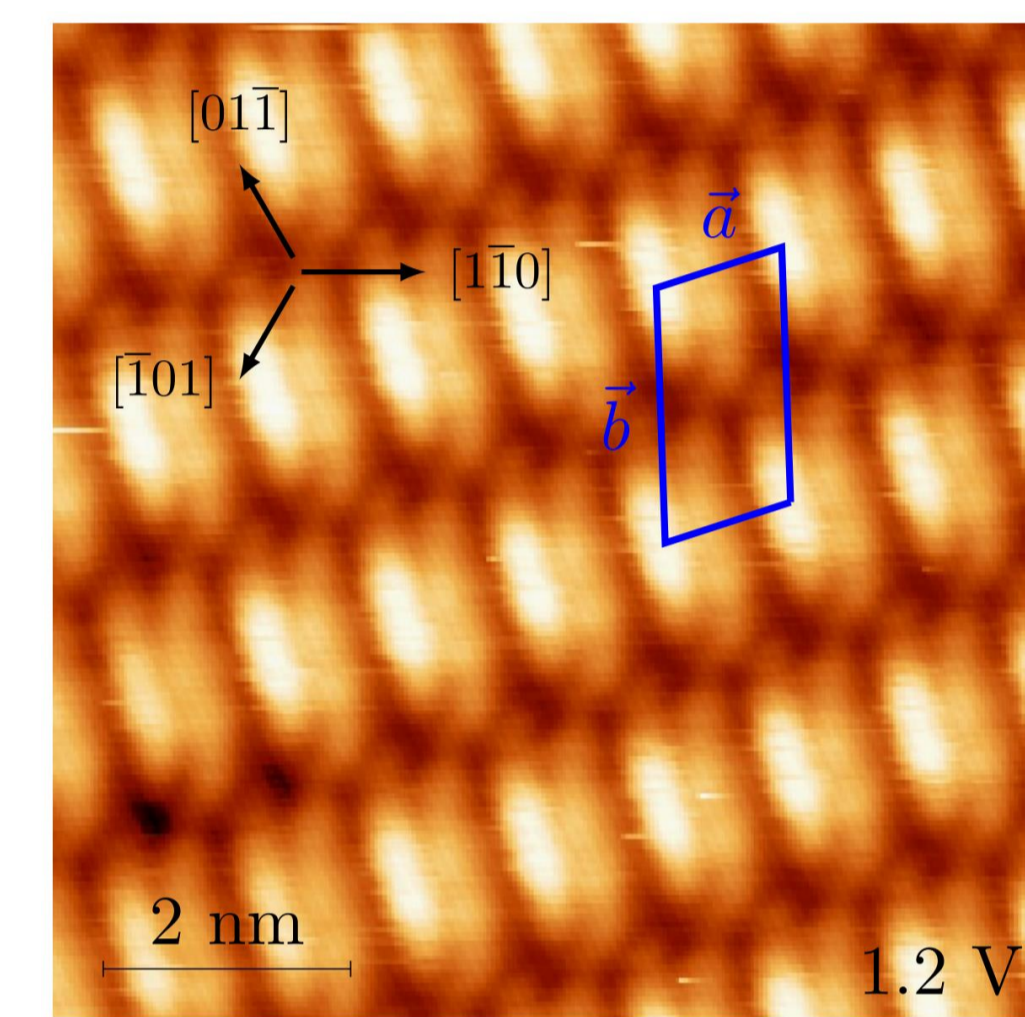
- Each 2nd ML molecule experiences a different local environment

Challenges:

- Can we proof the changed environment ?
- How does the changed environment alter molecular properties ?

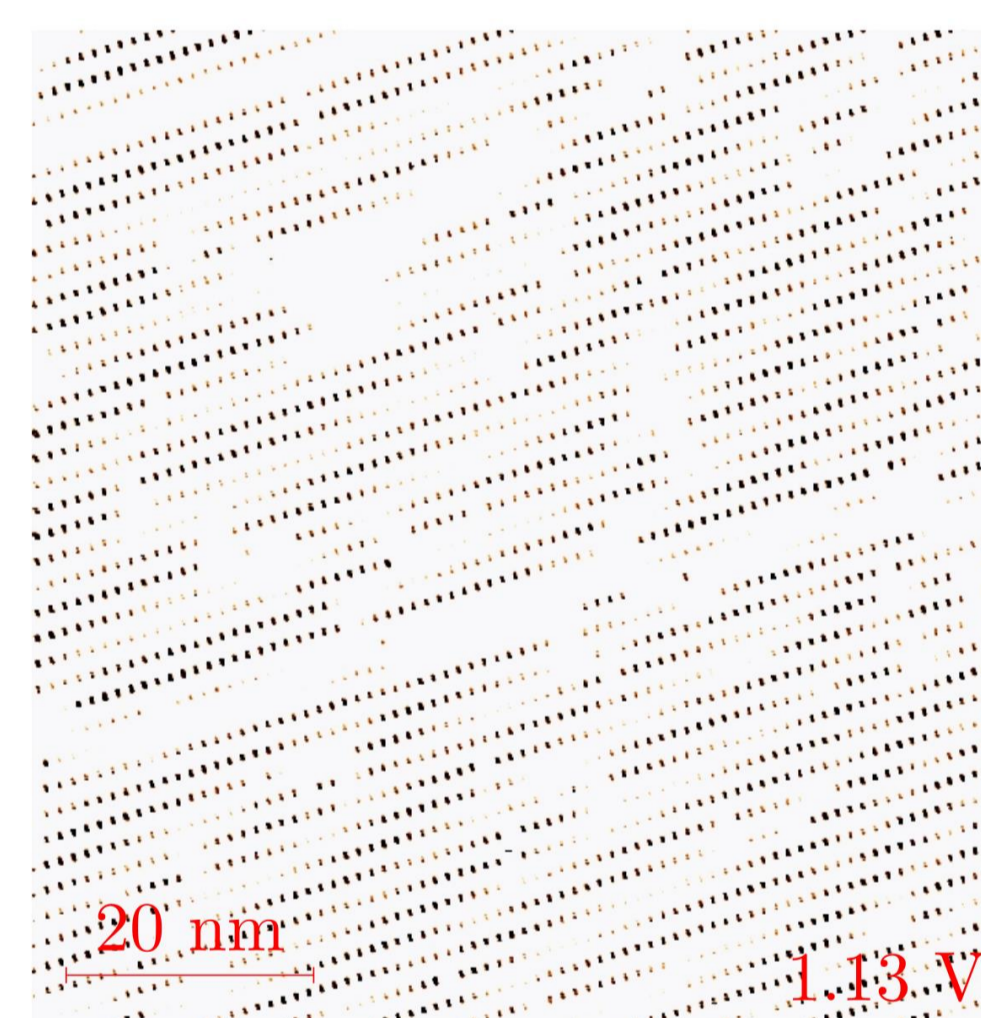
Second Monolayer Structure:

- On the 2nd Monolayer, Dimers of DB6P arranges in rows which are separated by $\sim 1.06 \text{ nm}$ within rows and rows by 1.97 nm .
- Molecular unit cell size is $a = 1.06 \text{ nm}$ and $b = 2.05 \text{ nm}$ and angle between them $\alpha \sim 74^\circ$.

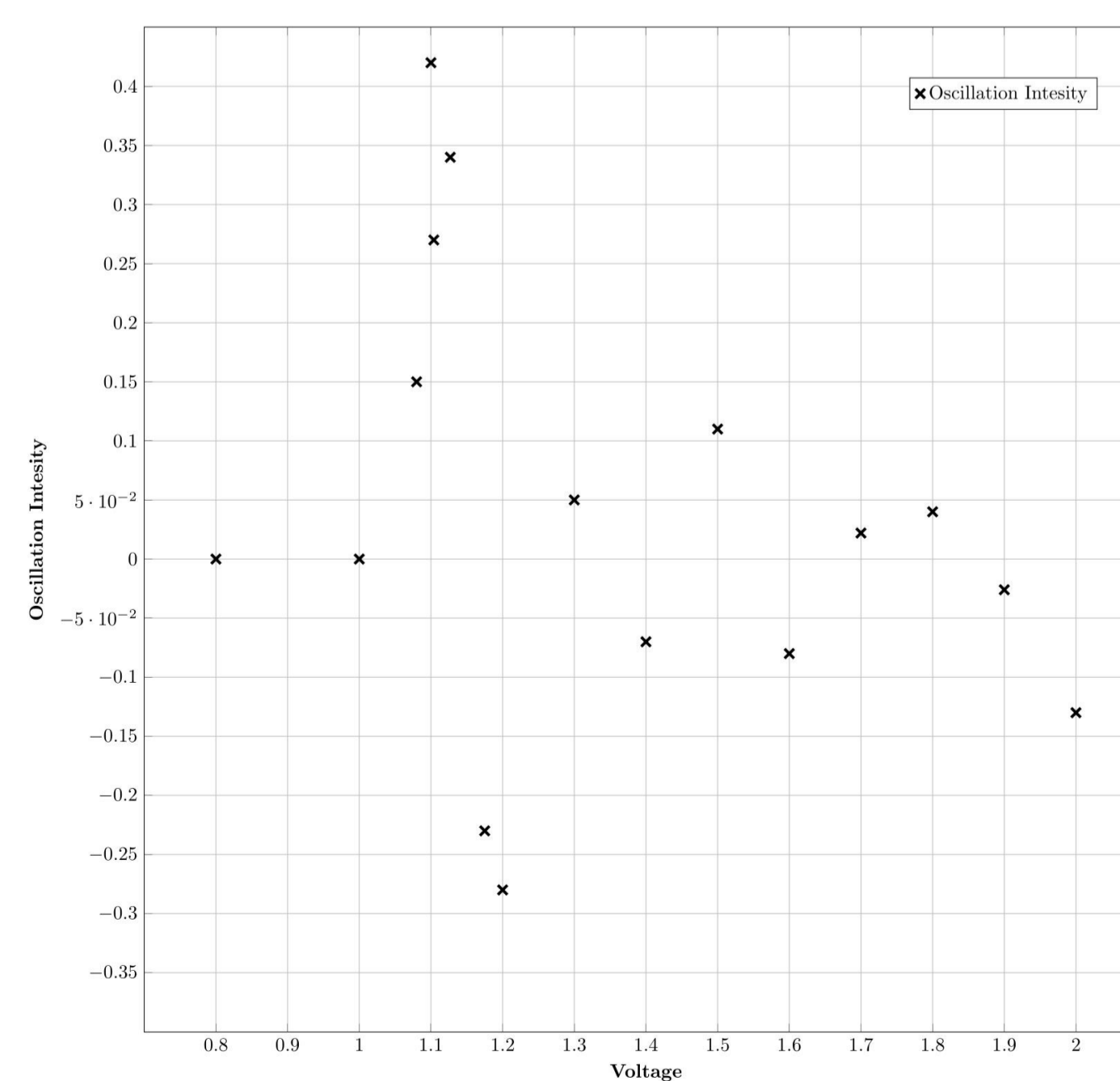


Discussion and comparison to other [n]Phenacene Direction:

- We observe that in the second monolayer, the rows of DB6P molecules are aligned parallel to the Ag(111) substrate but are rotated by approximately $\pm 9^\circ$ relative to the rows in the first monolayer. Conversely, for [n]phenacene, the molecular rows in the second monolayer are parallel to both the first monolayer's molecular rows and the Ag(111) substrate.
- This unequal out-of-plane rotation is due to that In DB6P the molecular axis is not parallel to the rotational axis and the surface. Therefore, The second layer adsorbed on the first disrupts the molecular symmetry of DB6P. Whereas in case of [n] phenacene molecular axis is parallel to both the rotational axis and the surface that's why they are align to each other.



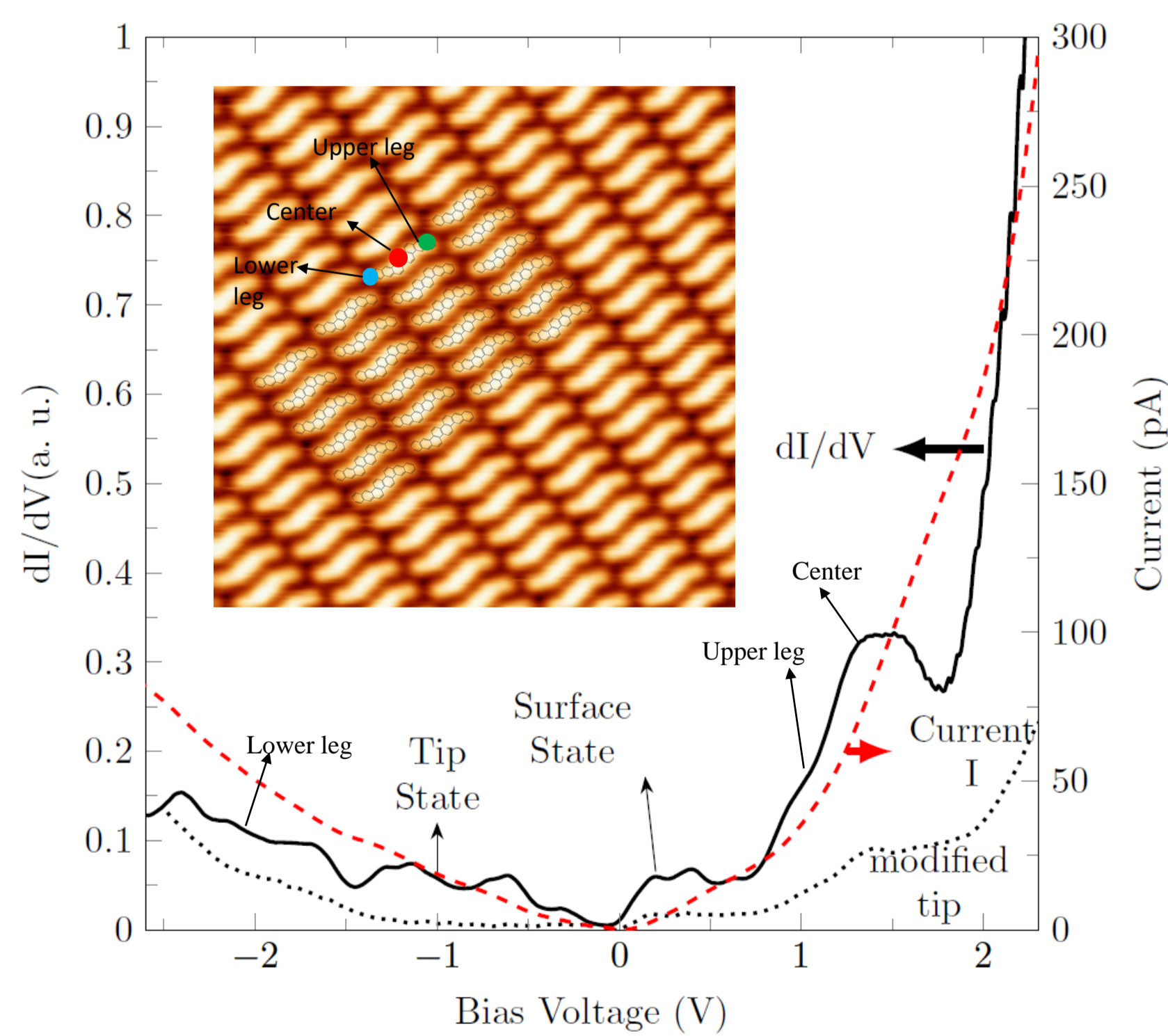
Intensity Vs Voltage Oscillation in di/dv Mapping :



- In di/dv maps we Observe pronounced oscillation of Local Density of State.
- The phase of the oscillations and the respective places of maximum signal strength, fluctuate with energy.
- Here, This graph illustrates the fluctuation of energy with respect to voltage.

STS Measurements:

On 1st ML:



The lowest empty molecular orbitals (LUMO) occur above 0.6 eV, while the highest occupied molecular orbitals (HOMO) occur below approximately -1.5 eV.

Summary:

Here, We studied the growth of DB6P molecule on a metal surface Ag(111) and observed the well-organized molecular rows parallel to each other on 1st ML and this growth continues on 2nd ML but unequal out of plane rotation. we observe that vertical stacking of these two molecular monolayers alters the electronic properties. This interaction can lead to new electronic states, modify the material's band structure, affect charge transport, enhance molecular interactions, and allow for the tuning of the material's properties for various applications in electronics and material science.

References

- [1] Noriko Komura et al. Characteristics of [6]phenacene thin film field-effect transistor. Phys. Lett. 2012,101, 083301.
- [2] Yanting Zhang et al. Photochemical synthesis and device application of acene-phenacene hybrid molecules, dibenzo[n]phenacenes (n = 5-7). Chem. Commun., 2021,57, 4768-477
- [3] Hideki Okamoto et al. Synthesis of the extended phenacene molecules, [10]phenacene and [11]phenacene, and their performance in a field-effect transistor. Science and Reports, 9, 4009.
- [4] Song-Wen Chen, I-Chen Sang, Hideki Okamoto, and Germar Hoffmann The Journal of Physical Chemistry C 2017 121 (21), 11390-11398 DOI: 10.1021/acs.jpcc.7b01806