

# Self-assembly of Dipole-Phthalocyanines on Surfaces: Construction of Dipole Dot Arrays and Substrates Effect on Ordering

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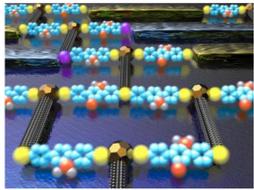
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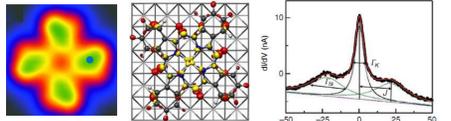
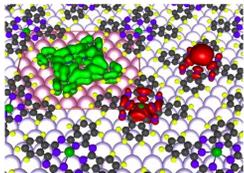
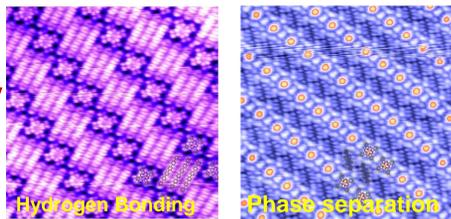
## Introduction

Molecular Electronics  
Circuit, Diodes, transistors

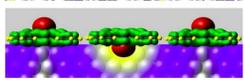


Bottom-up;  
Self-Assembly

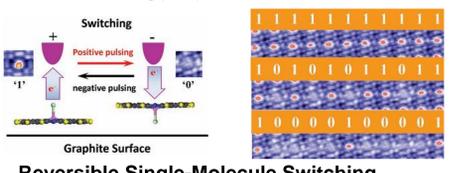
Two-Dimensional Molecular Array



Spin coupling and relaxation  
CuPc-Ag(110) *Nature comm.* 2011, 2, 490.

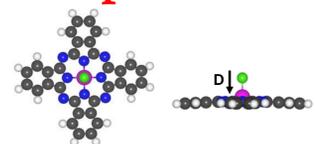


Substrate Effects on the  
Order/ disorder Packing  
*Nature Physics* 5, 153 (2009)

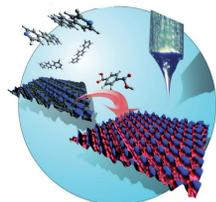


Reversible Single-Molecule Switching

## Experiment



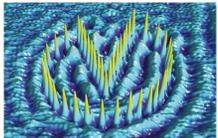
Non-planar Dipole-Phthalocyanine  
Chloride Aluminum Pc (CIAIPc)  
Vanadyl Phthalocyanine (VOPc)



Organic molecular beam epitaxial (OMBE)  
Characterized by STM

Ultra-high vacuum low temperature scanning tunneling microscopy

UHV-LT-STM



## Results and Discussion

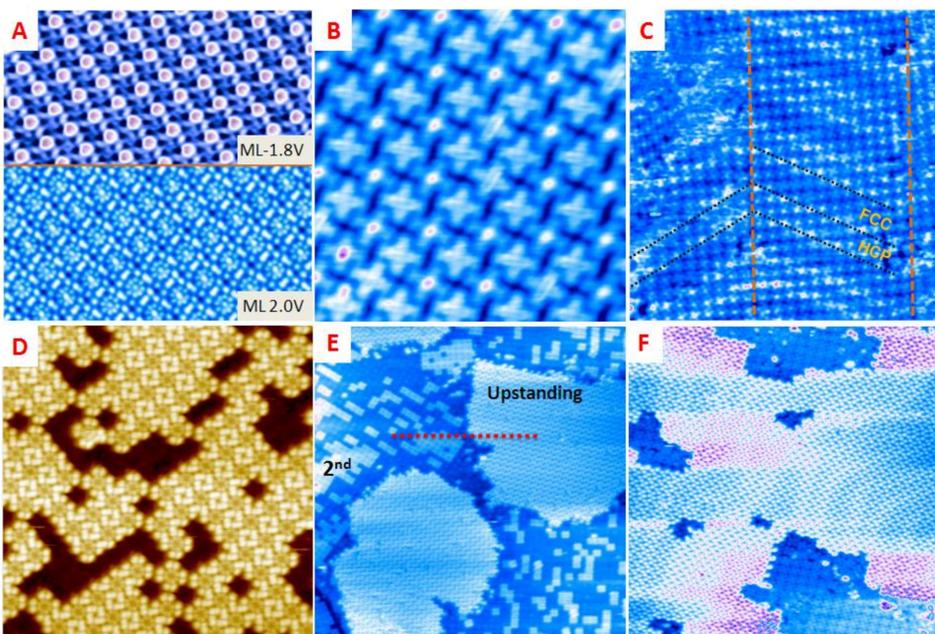


Figure 5. The packing structure of VOPc on different substrates at different coverages. Monolayer VOPc on (A)HOPG; (B) Ag(111) and (C) Au(111); Further increasing the coverage on these monolayer structures can induce (D) flat-lying bilayer on HOPG; (E) co-existence of flat lying VOPc and the up-standing islands; (F) large area Up-standing islands.

## Conclusion

- Two methods are reported to construct molecular dipole dot arrays: binary networks; site-specific adsorption on the artificial reconstructed substrates;
- Substrates effects on the ordering of dipole VOPc : weak physisorption (HOPG, Au) ; weak chemisorption (Ag) and strong chemisorption(Cu)
- Flat-lying; unidirectionally aligned dipole; molecular ordering on HOPG
- Upstanding islands on Au(111) and Ag(111)
- Purely O-down monolayer and mixed monolayer on Cu(111)

## Acknowledgement

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## Results and Discussion

### Tunable Two-dimensional Molecular Dipole Dot Array

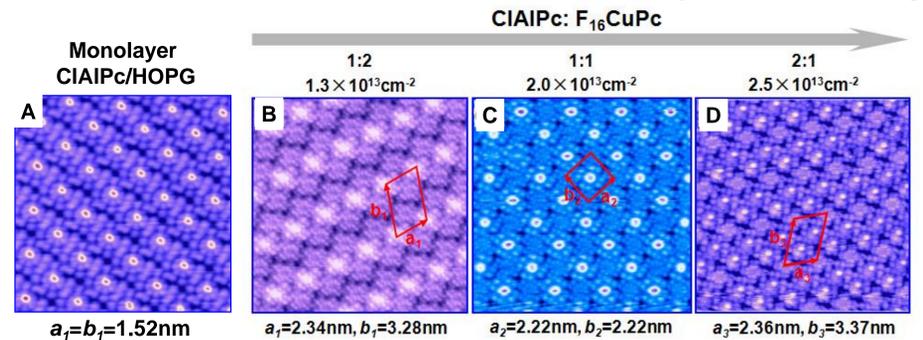


Figure 1. Molecular resolved STM images of the CIAIPc dipole dot arrays with tunable dipole density as a function of the relative ratio of CIAIPc:F<sub>16</sub>CuPc on HOPG surface.

### Unidirectionally Aligned Molecular Dipole Dot Arrays

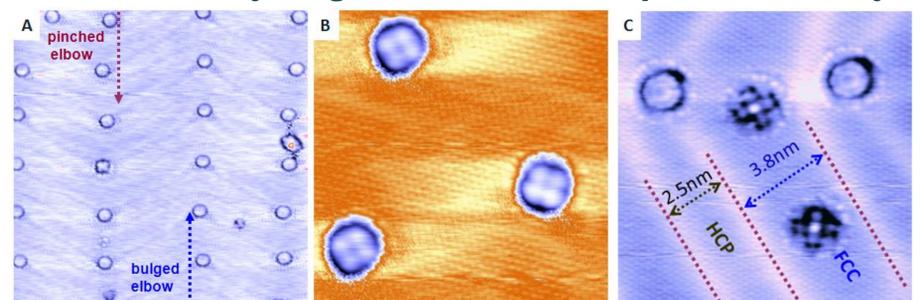


Figure 2. (A) STM image of large scale unidirectionally aligned molecular dipole dot arrays of VOPc on the reconstructed Au(111) surface. (B) Molecularly resolved STM image shows the O-down oriented single VOPc molecules at bulged and pinched elbow sites. (C) The VOPc molecules adopt O-down configuration at the elbow sites, it oriented with O-up configuration at the FCC region

### Substrate Effect on the Ordering of Dipole Pc

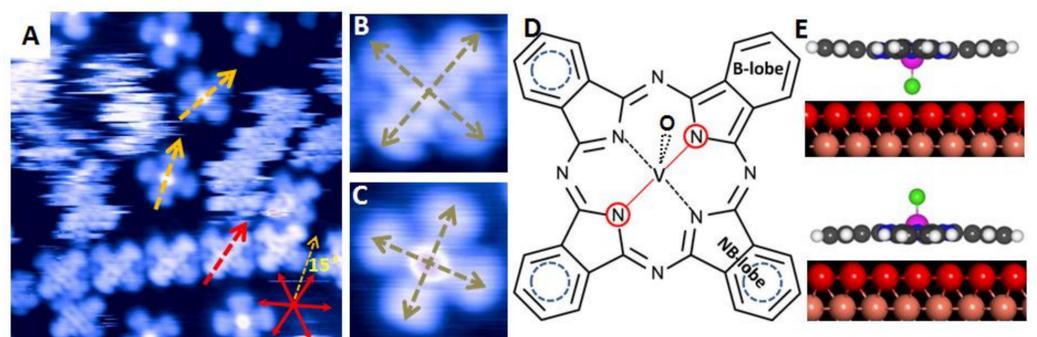


Figure 3. (A) ~0.1 ML VOPc on Cu(111), symmetry-reduction of O-down adsorbed VOPc, and the high diffusion of isolated VOPc-down; (B) and (C) VOPc the two configurations, O-down and O-up; (D) molecular structure of VOPc, two different pairs of lobes; (E) schematic models of O-up and down.

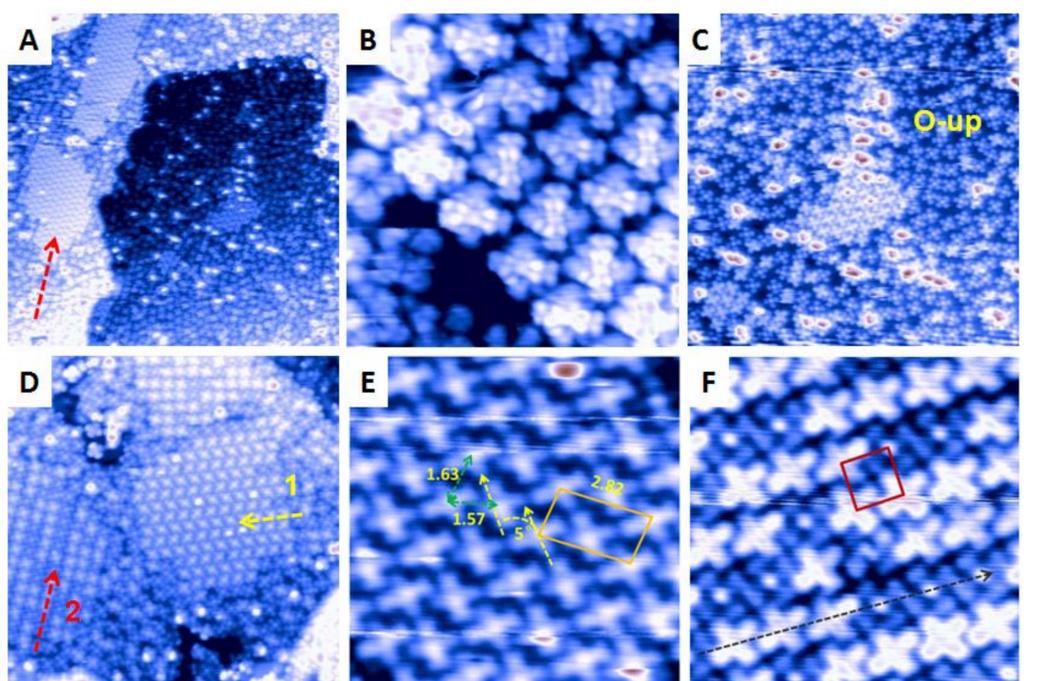


Figure 4. The packing structure of the VOPc molecules with increasing the coverage. (A) ~0.8 ML, the co-existence of ordered pattern and the randomly dispersed phase; (B) ordered pattern composed of purely O-down adsorbed VOPc; (C) O-up adsorbed VOPc molecules randomly dispersed on Cu(111); (D) two close-packed structure after increasing coverage to ~1ML; (E) pattern 1 with purely composed of O-down VOPc; (F) Pattern 2 with mixed O-up and O-down VOPc molecules