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

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Introduction
Molecular Electronics
Circuit, Diodes, transistors

Two-Dimensional Molecular Array

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

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

Ultra-high vacuum low temperature scanning tunneling microscopy
UHV-LT-STM

Results and Discussion
Tunable Two-dimensional Molecular Dipole Dot Array

Unidirectionally Aligned Molecular Dipole Dot Arrays

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
Authors acknowledge the support from Singapore ARF grant R143-000-440-112, R143-000-505-112, R143-000-530-112, and NUS YIA grant R413-000-452-101

Results and Discussion

Figure 1. Molecular resolved STM images of the ClAlPc dipole dot arrays with tunable dipole density as a function of the relative ratio of ClAlPc:F₄CuPc on HOPG surface.

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 1with purely composed of O-down VOPc; (F) Pattern 2 with mixed O-up and O-down VOPc molecules

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.