Growth of dipolar molecule ClAlPc on solid state surfaces

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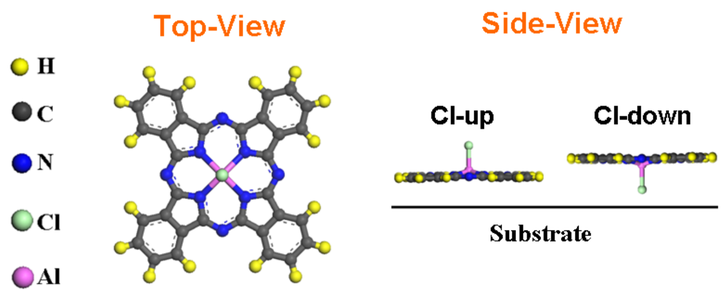
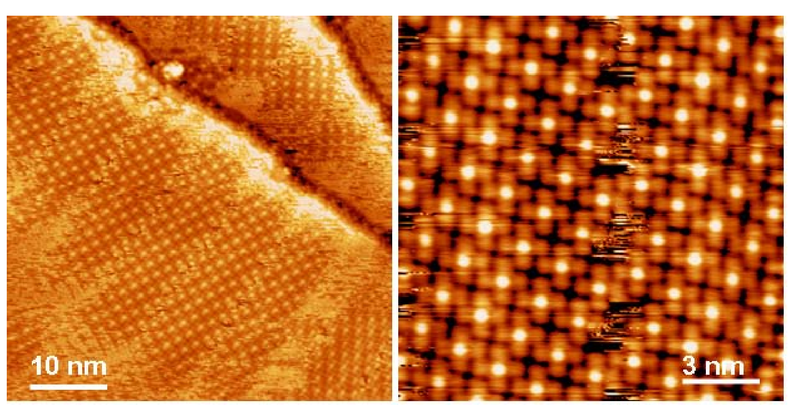
Abstract: *In-situ low-temperature scanning tunneling microscopy (LT-STM) has been used to systematically investigate the epitaxial growth behaviors of monolayer Chloro-aluminum phthalocyaninecopper (ClAlPc) on different substrates, including highly oriented pyrolytic graphite (HOPG), Au(111) and Ag(111). The ClAlPc molecule can be adsorbed in two different packing geometries, namely 'Cl-up' or 'Cl-down' configurations with the central Cl atom pointing out-of or into the substrate. The adoption of the ClAlPc orientation is largely depended on its supporting surface as well as the molecular coverage. The complicated growth behaviors of the monolayer ClAlPc are attributed to the subtle competition between the intermolecular dipole-dipole interactions and molecule-substrate interactions.*

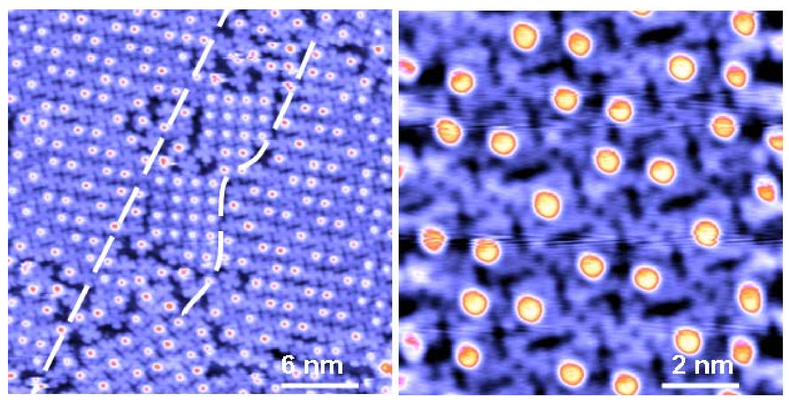
1. ClAlPc molecular structure and adsorbed geometries.



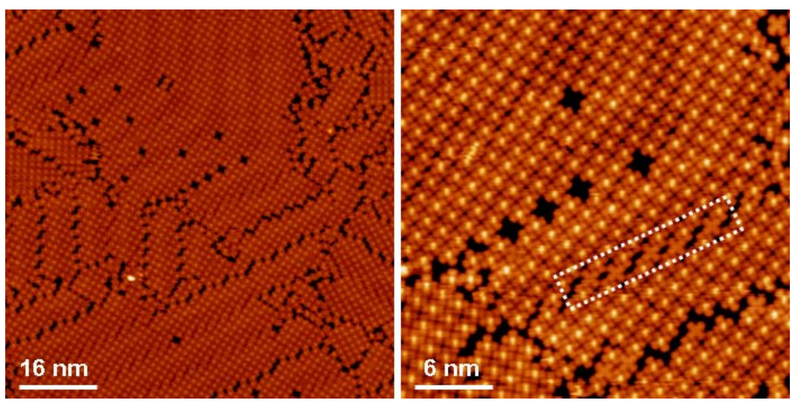
3. Monolayer ClAlPc on Au(111)



0.7 ML ClAlPc on Au(111) with Cl-up configuration. Loose-packing structure with intermolecular space of ~1.59 nm.

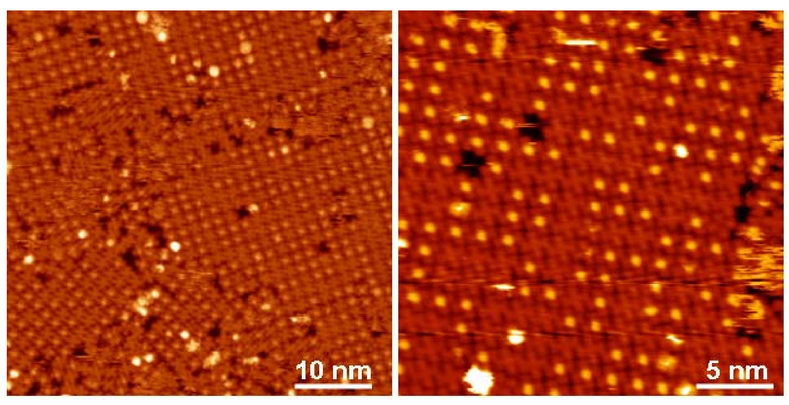


Monolayer ClAlPc on Au(111) with 60% molecules in Cl-up configuration and 40% molecules in Cl-down configuration. Regimes with short-range ordering are observed, formed by Cl-up (Cl-down) pairs alternating with Cl-down (Cl-up) single molecules.



Monolayer ClAlPc on Au(111) after annealed at 200°C. The population of the Cl-down molecules is reduced to 5%. Vacancies are also observable. The intermolecular distance is about 1.40 nm.

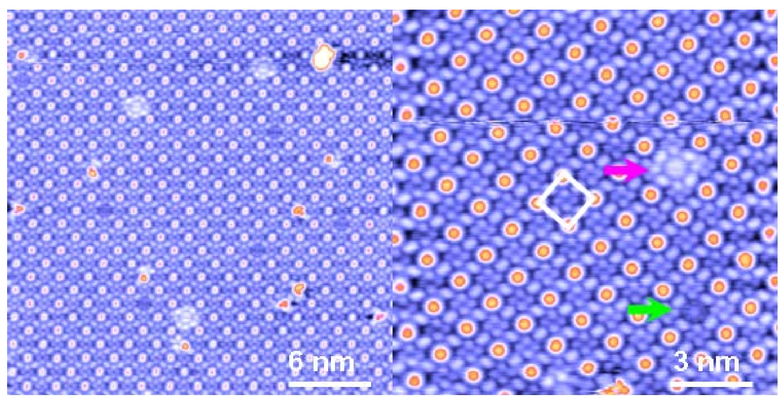
4. Monolayer ClAlPc on Ag(111)

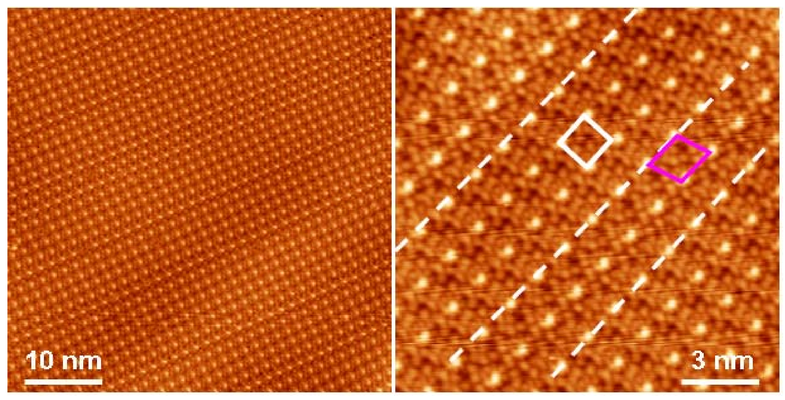


The monolayer ClAlPc on Ag(111) is composed of 50% Cl-up molecules and 50% Cl-down molecules. The distribution of the Cl-up and Cl-down molecules is disordered. It suggests that the interaction of the Ag(111) substrate with the Cl atom is comparable to that with the molecular π plane.

2. ClAlPc assembly on HOPG

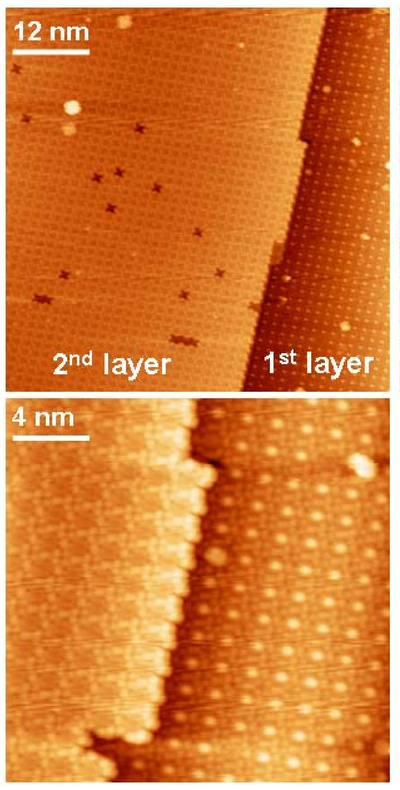
The unidirectional phase of monolayer ClAlPc on HOPG. Most of the ClAlPc molecule adopt the Cl-up configuration. The Cl atom appears as a protrusion at positive scanning bias. Few ClAlPc is packing in Cl-down configuration as noted by the purple arrow. The green arrow marks a defect. The dimension of the square unit cell is 1.52 nm.

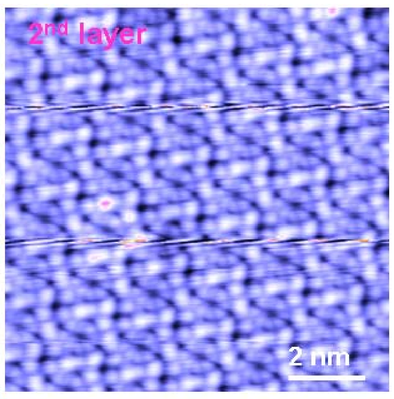




The disordered phase of ClAlPc on HOPG is composed of two different unit cells, as indicated by the white square and pink rhombic. Lattice mismatch between the neighboring molecular stripes is helpful for reducing intermolecular dipolar-dipolar interaction.

The growth of ClAlPc on HOPG is in the layer-by-layer + islanding mode. Before the HOPG surface is full covered with one monolayer ClAlPc, the 2nd layer islands are formed. The 2nd layer ClAlPc is packing in Cl-down configuration. The Cl-down molecule is imaged as four-lobe pattern similar to the other reported Pc molecules. The unite cell of the 2nd layer ClAlPc is a 1.52 × 1.52 nm^2 square the same as the underlying unidirectional phase. Careful analysis of the island edges and incomplete stripes reveals that each 2nd layer ClAlPc molecule adsorbs at the centre of the underlying unit cell.





Summary

Sub-monolayer ClAlPc on different substrates

	HOPG	Au(111)	1 ML Au(111) (annealing)	Ag (111)
Cl-up	**97%**	**100%**	**60% (95%)**	**50%**
Cl-down	**3%**		**40% (5%)**	**50%**

1. Molecule-substrate interactions:

   ClAlPc molecular π plane , Cl interacting with the substrate

   HOPG >

   Au(111) >

   Ag(111) =

2. The roles of dipole-dipole interaction: HOPG, obviously; Au(111), observable at monolayer; Ag(111), confused.

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