Abstract: In-situ low-temperature scanning tunneling microscopy (LT-STM) has been used to systematically investigate the epitaxial growth behaviors of monolayer Chloro-aluminum phthalocyanine-copper (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.

2. ClAlPc assembly on HOPG

3. Monolayer ClAlPc on Au(111)

4. Monolayer ClAlPc on Ag(111)

5. ClAlPc on solid state surfaces

Summary

Sub-monolayer ClAlPc on different substrates

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Cl-up</th>
<th>Cl-down</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>97%</td>
<td>3%</td>
</tr>
<tr>
<td>Au(111)</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>1 ML Au(111) (annealing)</td>
<td>60% (95%)</td>
<td>40% (5%)</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>50%</td>
<td></td>
</tr>
</tbody>
</table>

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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