EPITAXIAL GROWTH OF ORGANIC NANOCRYSTALS WITH ANTIFERROELECTRICAL STACKING

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Organic nanoparticels display size-dependent absorption and fluorescence bands and single photon emission. The detailed understanding of these effects is hindered by the difficulty in the synthesis of organic nanocrystals, i.e. organic nanoparticles with an ordered molecular arrangement. A possibility that remains mostly unexplored is the synthesis of such nanocrystals on solid surfaces. In the same way in which crystalline inorganic nanodots can be epitaxially grown on suitable substrates under conditions in which 3D Volmer-Weber growth takes place, an organic system could in principle be devised such that the growth of crystalline 3D islands sets in before the completion of the first monolayer. In practice, however, for organic adsorbates deposited on inorganic substrates intermolecular interactions are much weaker than molecule-substrate interactions, thus promoting a layer-by-layer mode, and preventing the fabrication of isolated 3D nanocrystal.

Here we show that, upon deposition of cone-shaped subphthalocyanine (SubPc) molecule (See Figure 1)on Cu(111), isolated triangular nanocrystallites up to 3 ML appear on the surface before the completion of the firs monolayer (See Figure 2). The different molecular layers show an alternating or antiferroelectric (AF) stacking of the molecular dipole moments. The structure of such nanocrystals can be explained by the joint effect of electrostatic (dipole-dipole) and dispersive (JI-JI) interactions. Although 1 ML-thick islands can also be found on the surface, the molecular arrangement in these areas is different from the geometry of the firsT layer molecules in the crystallites. We suggest that the formation mechanism of the organic nanocrystals is related to the existence of two different adsorption geometries, cone-up and cone-down, each of which sits on different molecular layers placed at different distances from the surface upon crystallite formation.

References:

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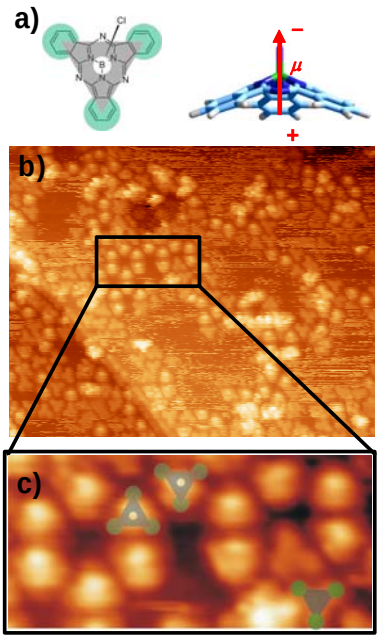

Figure 1. a) Chemical structure of the chlorosubphthalocyanine molecules and side view of its 3D structure showing the dipole moment. The molecules will be sketched as gray triangles with green circles at the outermost benzene rings. They will display a white dot at the centre when the Cl atoms points up (sticking out of the surface); the lack of such a white dot indicates that the Cl atoms points towards the surface. b) 33.4 × 26.5 nm^2 STM image of 0.2 ML SubPc/Cu(111) (I_t = -0,380nA; V_{bias} = -2,1V). c) Zoom-in (10.8 × 5.5 nm^2) showing the two types of STM images associated with the adsorption of SubPc: a bright protrusion and a trefoil shape. We interpret these features as corresponding to the coexistence of Cl-up and Cl-down adsorption geometries.

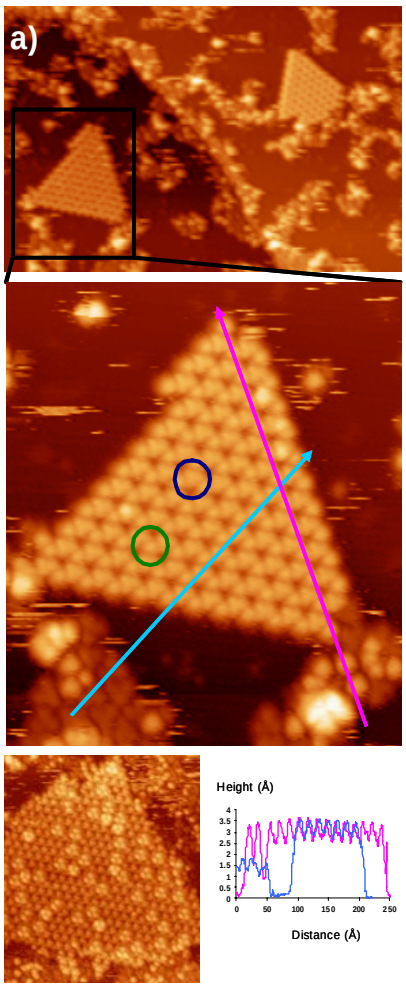

Figure 2. a) 62.4 × 41.6 nm^2 STM image of 0.4 ML SubPc/Cu(111) (I = -0,8 nA; V = -2,9 V). Two triangular islands can be found. As for the 1 ML thick islands, high resolution STM images such as (b, 22.3 × 26.1 nm^2) show two different molecular features, bright protrusions (green circles) and trefoil shapes (blue circles). The bright protrusions are identical in shape and size to the Cl-up molecules identified in Figure 2, but the trefoil features are 0.2 nm higher (c). Even thicker islands can be found upon further deposition (d, 33.4×39.2 nm^2).