Supplementary Information

Subphthalocyanine-Based Nanocrystals

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1. Discussion on the adsorption geometry of chlorosubphthalocyanine on Cu(111)

We have assigned the adsorption geometry of Chlorosubphthalocyanine on Cu(111) on the basis of both our and previously reported experimental data, and the STM image simulations of gas-phase SubPc molecules. Nevertheless there is still room for interpretation. For example, another possibility is that the minority trefoil SubPc molecules are not chemically intact. Given the very high stability of aromatic macrocycles such as the SubPc one, the most likely reaction to occur is the breaking of the boron-chlorine bond, which might also explain the difference in overall height between the trefoil and protrusion-like molecules, the trefoil molecules being on the average darker than the protrusion-like ones. However, UPS experiments on silver do not show any sign of such decomposition, and the calculated energy that should be provided to the molecule to break this bond is of about 5.6 eV. Furthermore, the amount of reacted trefoil molecules should either decrease with decreasing substrate temperature (if the decomposition of the molecule were thermally activated) or remain the same (if such reaction were spontaneous in the presence of the metal surface). However, the ratio of trefoil to protrusion-like molecules is larger for low temperature deposition, showing that the thermodynamically stable situation is that represented by the protrusion-like molecules.

The previous discussion might suggest that the bright protrusion molecules are the ones corresponding to the reacted molecules, i.e. molecules without the Cl atom. However, the high energy barrier for chlorine detachment implies that such should be completely suppressed by keeping the substrate temperature low during deposition. Such experiment was carried out (substrate temperature about 200 K), with no significant difference in the ratio bright-protrusion versus trefoil molecules as compared to that at RT deposition. It seems unlikely that a change of 100 K in the temperature should have no noticeable effect on the reactivity of the molecules. More exotic explanations for the different molecular appearances can be possibly put forward, but it does not seem to be necessary as the model of having the molecules adsorbed both with the chlorine atom pointing outwards and inwards explains the submolecular features observed in the STM images.27-29
**Figure S1.** STM image (9×7 nm$^2$, $I = 0.37$ nA, $Bias = -2.5$ V) showing the trefoil appearance of one defective site and the protrusion-like appearance of the majority of SubPc molecules in the honeycomb network. Such trefoil appearance is consistent with calculated STM images for a Cl-down adsorption geometry. The bight-protrusion at the center of the molecule is however expected for Cl-up configurations.

2. **Determination of the orientation of the SubPc molecules in the first layer in the triangular nanocrystals**

The orientation of the trefoil-shaped Cl-down molecules on the 2$^{\text{nd}}$ layer around their $C_3$ axis with respect to the substrate lattice can be determined from our STM images. On the other hand, these images do not offer any clue as to the orientation of the underlying 1s-layer, Cl-up molecules. In order to propose a structural model for the bilayer islands, we have performed theoretical calculations of a 4-molecule cluster in the gas phase (molecular mechanics calculations with the MM+ force field from the HyperChem 7.0 package software). In this cluster we have placed three Cl-down molecules forming an equilateral triangle of 1.58 nm: Each of the Cl-down molecules is aligned with the direction of the supramolecular triangle, as observed for 2$^{\text{nd}}$ layer Cl-down molecules in our STM images (see Figure S2a). A Cl-up molecule (representing one of the molecules in the 1$^{\text{st}}$ layer of the triangular islands) is placed along the axis defined by the triangle’s baricenter and the dipole moment of the SubPc molecules. In the calculation the distance ($z$) between the Cl atom of the Cl-up molecule, and the plane determined by the topmost hydrogen atoms of the 2$^{\text{nd}}$ layer, Cl-down molecules, is changed from 0 nm to 0.3 nm. We have calculated the bonding energy of the system as a function of the molecular orientation of the 1$^{\text{st}}$ layer with respect to the 2$^{\text{nd}}$ (as determined by the angle $\theta$ defined in Figure S2a) for different
interlayer distances $z$, and the resulting energy landscapes are plotted in Figure S2b. Calculations for bigger clusters gave similar results.

**Figure S2.** a) Gas-phase model cluster for Molecular Mechanics calculations. In this schematic representation, light-gray triangles with a central white dot represents Cl-up molecules, whereas black triangles represent Cl-down molecules, the green circles representing the peripheral phenyl rings. The configuration of the 2nd layer Cl-down molecules is kept fixed to the experimentally observed configuration, whereas both the interlayer distance and the molecular orientation of the 1st layer Cl-up molecule is changed systematically in order to obtain the energy landscape. b) Angular dependence of the cluster’s bonding energy for different interlayer distance. All the curves show the $C_{3v}$ symmetry of the original cluster. The configurations of the maxima and minima in the curves are shown as insets. c) Structural model for the triangular nanocrystallites based on experimental STM images and the cluster calculations described in a) and b).
3. Other Triangular Nanocrystals

55.8 x 65.4 nm$^2$, ($I_t = 0.15$ nA, $V_{bias} = 1.25$ V)

16.7 x 19.6 nm$^2$, ($I_t = 0.12$ nA, $V_{bias} = 1.25$ V)

22.3 x 26.1 nm$^2$, ($I_t = 0.15$ nA, $V_{bias} = 1.25$ V)

167.0 x 196.0 nm$^2$, ($I_t = -0.90$ nA, $V_{bias} = -2.15$ V)
**Figure S2.** STM images of triangular nanocrystals.
4. Vacuum deposition and STM imaging

The experiments were carried out in an ultra-high vacuum chamber (base pressure of $10^{-10}$ mbar) equipped with a variable temperature scanning tunneling microscope (STM). Cu(111) clean surfaces were prepared by cycles of Ar$^+$ sputtering (500 eV) and annealing at 850 K. SubPc molecules were deposited in situ by thermal sublimation (420 K) on the clean copper surface, which was held at room temperature. STM measurements were performed at 150 K.