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Molecular Nanocrystals on Ultrathin NaCl Films on Au(111)

Yongfeng Wang,*,† Jörg Kröger,† Richard Berndt,† and Hao Tang‡

Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität, D-24098 Kiel, Germany, and CNRS, CEMES, BP 94347, 29 rue J. Marvig, and Université de Toulouse, UPS, F-31055 Toulouse, France

Received June 11, 2010; E-mail: yfwang@physik.uni-kiel.de

Abstract: Direct comparison of SnPc growth on a metal and a nearly insulating surface was achieved by adsorption of SnPc on Au(111) partially covered with NaCl. While on Au(111), SnPc lies flat and grows in a Stranski−Krastanov mode; on NaCl, Volmer−Weber growth of three-dimensional molecular nanocrystals occurs. On NaCl, intermolecular interactions dominate over the molecule−NaCl coupling and result in a tilted adsorption configuration.

Organic thin film devices receive great attention because of advantages such as low cost, diversity, and flexibility. Electronic and optoelectronic properties of such films depend on the specific molecular arrangement within the film and at its interface to a substrate.[1] Understanding and controlling the growth of molecular films on surfaces is crucial for optimizing their performance. In this context, growth of phthalocyanine molecules on surfaces has been intensively studied by various surface science techniques, especially scanning tunneling microscopy (STM),[2] for its submolecular resolution capability in real space.[3] On metals and semiconductors, phthalocyanine molecules prefer to lie parallel to substrates due to large molecule−substrate interactions and grow in a layer-island (Stranski−Krastanov) mode.

Little is known about the detailed structure of phthalocyanines on insulators because they cannot be investigated by STM. This problem can be circumvented with ultrathin NaCl films as these films partially decouple the molecular electronic structure from substrates and still allow current flow to enable STM measurements.[4] Volmer−Weber growth of tin phthalocyanine (SnPc, Figure 1a) on a NaCl double-layer film adsorbed on Au(111) is reported here. Molecules form dispersed three-dimensional islands on the NaCl film. Within the islands, the molecular planes are tilted by 67° with respect to the surface normal. On bare Au(111), however, SnPc exhibits a flat adsorption configuration and Stranski−Krastanov growth. Molecular mechanics (MM) calculations[5] were carried out to model SnPc structures on both Au(111) and the NaCl film.

Experiments were performed with a home-built STM at 7 K and in ultrahigh vacuum. Chemically etched W tips and Au(111) surfaces were cleaned by Ar$^+$ bombardment and annealing. NaCl was thermally evaporated onto Au(111) surfaces held at room temperature. SnPc was subsequently deposited onto partially NaCl-covered Au(111).

Figure 1b shows a constant-current STM image of Au(111) partially covered with double-layer NaCl with an apparent height of 0.4 nm. Its schematic structure was shown as an inset in the figure. The characteristic herringbone reconstruction of Au(111) is also visible on the NaCl film, which indicates that the NaCl film hybridizes weakly with the metal substrate and, therefore, retains most of its genuine properties.

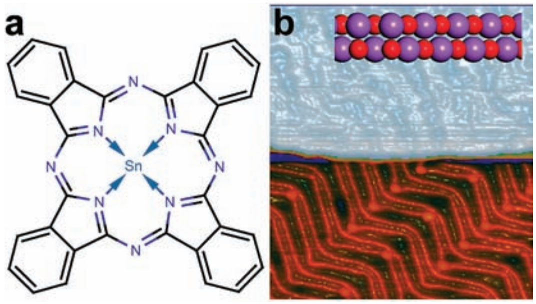

Figure 1. (a) Scheme of SnPc. (b) STM image of Au(111) partially covered by a NaCl double layer with schematic structure as an inset (61 × 71 nm^2; −1.0 V, 0.09 nA).

Subsequent deposition of SnPc on NaCl-covered Au(111) leads to the preferential adsorption of the molecules on the metal surface. Individual molecules adopt a flat adsorption geometry to maximize the interaction between their π electron system and Au(111). The shuttlecock geometry of the molecule, which is determined by the central Sn atom sticking out of the molecular plane, gives rise to STM images with a depression (Sn atom pointing toward the surface, SnPc-down) or a protrusion (Sn atom pointing toward vacuum, SnPc-up) at the molecular center.[6] Similar behavior was observed for SnPc adsorption on Ag(111).[6] The molecules arrange in a square lattice with a unit cell width of 1.4 nm. Figure 3a shows the optimized molecular arrangement on Au(111), which turns out to match the experimental data.

Increasing the amount of deposited SnPc first leads to an occupation of available metal sites. Then molecules likewise adsorb on the first molecular layer (Figure 2b) and on the NaCl film (Figure 2d). On the molecular layer, SnPc islands form, which exhibit a uniform molecular configuration (either SnPc-up or SnPc-down). A uniform orientation of the molecules is favored to optimize intermolecular C−H...N hydrogen bonds.[7] The first molecular layer efficiently decouples the additionally adsorbed molecules from the metal, and Figure 2b shows the spatial distribution of the highest occupied molecular orbital (HOMO). A further hint to decoupling may be the dI/dV spectrum of SnPc-up in the second layer (Figure 2f), which shows clear vibronic excitation. The peak spacing of 150 meV corresponds to C−C and C−N stretch vibrations.[8] In contrast, this vibronic progression is not discernible in the spectrum of SnPc-up in the first layer (Figure 2c) due to the strong electronic coupling of the molecule and substrate.

Figures 2g shows STM images of SnPc molecules on NaCl with submolecular resolution. A white rectangle indicates that only two isoindole groups of individual molecules are visible as protrusions. This observation indicates a tilted configuration of the molecules on the NaCl film. Further evidence is provided by vacancy sites within the molecular layer (black rectangle in Figure 2f). Here, the characteristic protrusions in STM images are missing. Indeed, supporting calculations reveal that an inclination of the molecular

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† Christian-Albrechts-Universität.
‡ Université de Toulouse.

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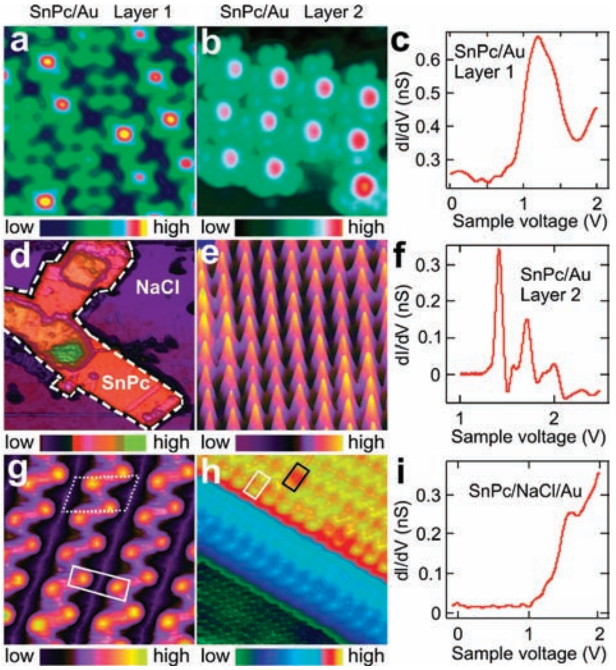

Figure 2. Pseudo-three-dimensional representation of constant-current STM images: SnPc on Au(111) for the first layer (a, (5.3 nm)^2; 1.7 V, 60 pA) and second layer (b, (5.4 nm)^2; 1.5 V, 60 pA), molecular islands of SnPc on NaCl film (d, (62 nm)^2; 2.2 V, 20 pA), atomic resolution image of NaCl (e, (2.9 nm)^2; 0.1 V, 100 pA), submolecular resolution image of SnPc nanocrystal (g, (3.5 nm)^2; 1.86 V, 80 pA), and high resolution image of NaCl and SnPc resolved simultaneously (h, (8.4 nm)^2; 2.2 V, 26 pA). Spectra of dI/dV of unoccupied states of SnPc up in the first layer (c), second layer (f) on Au(111), and SnPc island on NaCl (i).

plane by 65° with respect to the surface normal is the energetically favorable adsorption configuration on the double-layer NaCl film. This angle is also consistent with the apparent height difference between subsequent molecular layers (0.5 nm, cf. Figure 4a) and the lateral size of the molecule in the STM images (1.3 nm), which yield $\arccos(0.5/1.3) \approx 67°$. A unit cell in the top layer is indicated by a dashed parallelogram with dimensions 0.8 nm ×1.3 nm and an angle of 71° between the unit cell vectors (Figure 2g). The optimized structure of SnPc on NaCl (Figure 3b) has a similar size and shape of the unit cell (0.8 nm ×1.4 nm, 73°). Calculation with the program EpiCalc[9] shows that SnPc growth on NaCl is commensurate while it is incommensurate on Au(111). Interestingly, the spectrum of SnPc nanocrystals (Figure 2i) does not show vibronic features; the reason for this is presently not known.

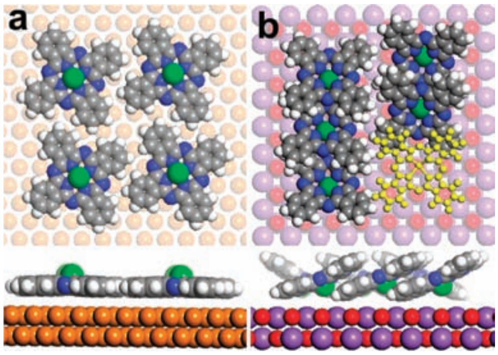

Figure 3. Top and side views of SnPc on Au(111) (a) and on NaCl (b). Structures were optimized with molecular mechanics. In b, one molecule is represented by yellow balls for better conspicuity.

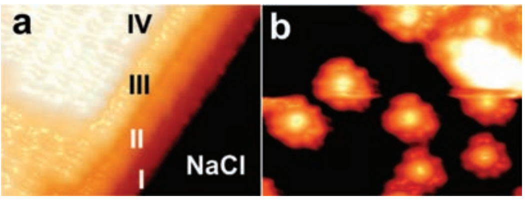

Figure 4. STM image of SnPc nanocrystal on NaCl from first to fourth layer (a, 12.0 × 8.9 nm^2; 2.0 V, 20 pA). SnPc molecules moved from molecular islands lie flat on NaCl (b, 9.5 × 7.0 nm^2; 2.0 V, 310 pA).

According to the molecular mechanics calculations, the molecular tilt is due to strong molecule−molecule interactions within an island. Single molecules, however, prefer to adopt a flat geometry on NaCl. To test this modeling result, individual molecules were moved out of an island and positioned several tenths of nanometers away from the island on the bare NaCl film (Figure 4b). These molecules indeed adsorb with the molecular plane parallel to the surface.

Summarizing, direct comparison of SnPc growth on a metal and a nearly insulating surface was achieved by adsorption of SnPc on Au(111) partially covered with NaCl. While on Au(111), SnPc lies flat and grows in a Stranski−Krastanov mode; on NaCl Volmer−Weber growth of three-dimensional molecular nanocrystals occurs. On NaCl, intermolecular interactions dominate over the molecule−NaCl coupling and result in a tilted adsorption configuration.

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