



	Experiment title: Structural investigations of the adsorption of large organic molecules on metal surfaces	Experiment number: SI-1820
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Report:

The topics of our ongoing series of ESRF beamtime projects are geometric and electronic properties of organic-inorganic interfaces, in particular, the adsorption behavior of pi-conjugated organic molecules on metal surfaces. A number of publications in highly ranked journals are the result of this work, the most prominent being Nature Physics, Vol. **5**, 153 (2009). This work was also selected for the ESRF Highlights 2008.

In these publications we report on a family of organic molecules exhibiting a very unusual behaviour upon adsorption on a Ag(111) surface. Along with the example of Sn-Phthalocyanine (SnPc) we show that a repulsive intermolecular interaction occurs when the molecules are deposited on a Ag(111) surface in very thin films (coverage below one layer). Other molecules (CuPc, TiOPc and H₂Pc) show the same phenomenon which is very unusual since molecules usually “cluster” on such surfaces and form islands which grow larger and larger when the coverage is increased. However, in the case of the metal-Pcs the molecules always cover the entire surface homogeniously since they maximize the distance to their neighbors. A continuous rearrangement during increasing of coverage is the consequence. At coverages close to a close-packed layer this even occurs in a series of long-range ordered incommensurate phases, the structural parameters of which change continuously. This effect is caused by a substrate-mediated repulsive inter-molecular interaction between the molecules exceeding van-der-Waals and other attractive forces.

Thanks to x-ray standing waves (XSW), photoemission (PES) and high-resolution low energy electron diffraction measurements (SPA-LEED) the effect is basically understood. An exchange of electronic charge (donation/backdonation) was found and confirmed by density

functional theory (DFT) calculations. The effect is illustrated in Fig. 1. Electron donation to the substrate just below the molecules (yellow area) displaces Ag electrons to the vicinity (blue). Backdonation to unoccupied orbitals of the molecule cannot completely compensate for this effect. Therefore neighbouring molecules – if they are identically oriented in “tin-down” position and located close to each other as it is the case at high coverages (Fig. 1a) – compete for the donation/backdonation effect which causes repulsion between the molecules. At lower coverages the repulsion is reduced by the mixed “tin-up”/“tin-down”-orientation, but at room temperature (disordered phase) it still remains dominant. Only upon cooling the influence of the substrate overcomes the repulsion and an ordered structure is formed (Fig. 1b).

Consequently we started to investigate the adsorption of MePc molecules on other (noble) metal surfaces. On Au a very much weaker interaction between molecules and surface was found in the first experiments. CuPc/Au(111), e.g., exhibits a significantly larger adsorption height above the surface (obtained from XSW experiments) and no clear signs for charge transfer in PES. The consequence is a much weaker (possibly completely vanished) intermolecular repulsion between the molecules. In contrast, on Cu a stronger interaction is expected. This should – on the one hand – increase the region of coverage in which incommensurate structures prevail intermolecular repulsion, and on the other hand make the interaction to the substrate more site specific. The question which of these effects is dominant and how the phase diagram and interaction mechanisms change upon the changed interaction strength is proposed to be addressed in our future investigations.

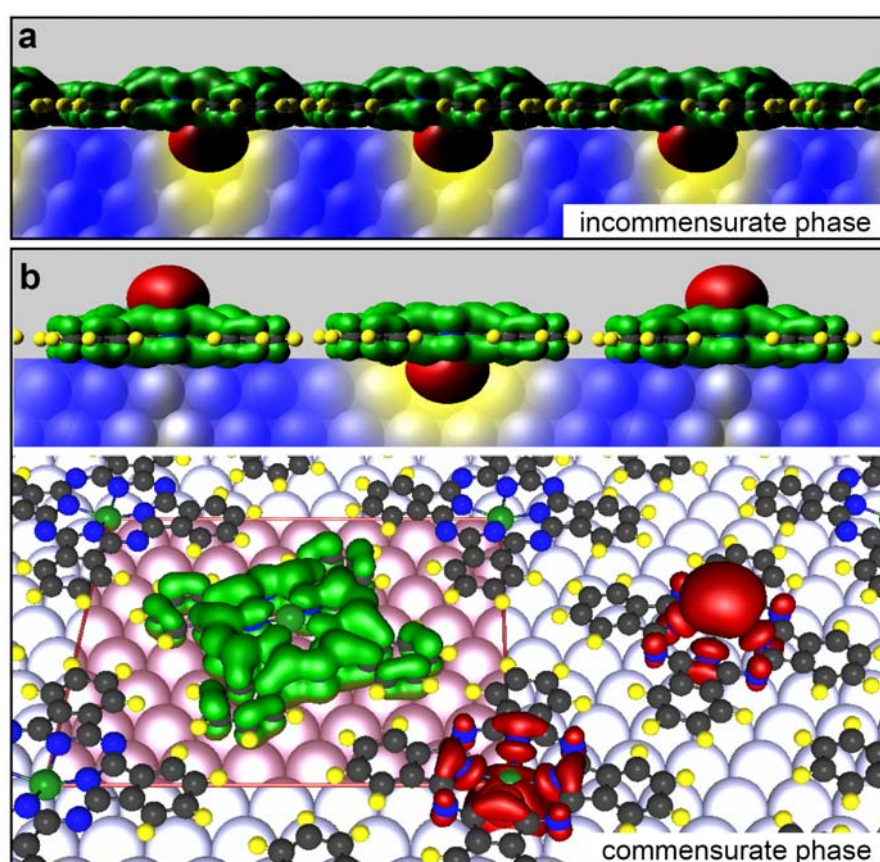


Fig. 1: Structural model and illustration of the donation/backdonation effect: (a) Side view of the incommensurate monolayer structure. (b) Side and perspective view of the commensurate LT structure. Molecular orbitals (HOMO-1 and LUMO) are drawn in red and green colour, respectively.