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Reordering and disordering of copper hexadecafluorophthalocyanine (F16CuPc) monolayer by K dopings

Yuri Hasegawa, Yoichi Yamada*, and Masahiro Sasaki
Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, 305-8577, Japan

1 Introduction

Electron injection by metal- or molecular doping plays a key role to modify the electronic properties of organic semiconductor materials. Among them, potassium (K)-doped phthalocyanine (Pc) has been attracted much attentions because of its characteristic change of electric conductivity depending on the K concentration. The conductivity of Pc increases when K concentration is one to two atoms per molecule and further doping causes a rapid decrease in the conductivity. These observations have led to the assumption of the insulator-metal-insulator transition[1]. On the other hand, x-ray photoemission spectroscopy (XPS) investigations have not revealed any evidence of the formation of the metallic state with alkali-metal-doping at any doping level[2]. This contradiction indicates that the mechanism of the alteration in the conductivity of K-doped Pcs has not yet been completely clarified.

In order to clarify the mechanism of doping, it is necessary to reveal structural and electronic modification using well-defined system such as a monolayer on an inert substrate. In this study, therefore, we have investigated the structural and electronic modification of K doped F_{16}CuPc monolayer on $Cu_3Au(001)$ surface by Scanning Tunneling Microscopy (STM) and Photoelectron Spectroscopy (PES).

2 Experiment

All experiments were carried out under ultra-high vacuum (UHV) condition at room temperature. F_{16}CuPc monolayer was prepared by vacuum deposition using a home-made Knudsen-cell. Potassium was deposited in several steps onto the F_{16}CuPc monolayer from a SAES getter source. The deposited amount was determined by QCM. The structural changes in the F_{16}CuPc monolayer with K doping were observed by STM. PES measurements were conducted at BL-3B.

3 Results and Discussion

Fig. 1(a) shows an STM image of a F_{16}CuPc monolayer on the Cu3Au(001) surface. The F_{16}CuPc monolayer exhibits a large domain with small population of domain boundaries. This is likely owing to the four-fold symmetrical structure of the Cu3Au(001) surface, which matches the symmetry of the monolayer.

Fig. 1(b) shows an STM image of two types of reconstructed structure of monolayer found in the initial doping stage. When K was doped approximately one atom per molecule, one-dimensional structure (1:1 phase) was formed, and further reordering with square unit cell was formed when the concentration is two atoms per molecule (1:2 phase). In these cases, adsorption of K atoms into the aza-bridging nitrogen sites brings about reconstruction of the molecular arrangement as illustrated in schematic image in Fig.1. It has been revealed recently by DFT calculations that stable adsorption of alkali (Li) atom occurs at next to an aza-bridging nitrogen atom in the case of single CuPc molecule on the Ag(100) surface.

When K coverage exceeds two K atoms per molecule, on top adsorption of K atom appeared. The on-top adsorption of K causes a disorder in the molecular arrangement such as small protrusions and bright, rotated molecules, as shown in Fig. 1(c). This phenomenon may cause a further decoupling of the molecule from the substrate due to excess charge transfer. An alkali-induced disordering of the Pc layer has already been suggested for doping levels of approximately 4 K atoms per molecule, although indirectly, for thick films of ZnPc and H2Pc. Therefore, it is considered that the F_{16}CuPc monolayer, to a certain extent, can model the properties of thicker film systems.

Next, we discuss the electronic modification upon reconstruction of the alkali-metal-doped F_{16}CuPc monolayer by means of UPS. Fig. 2(a) shows the valence-band spectra of the doped F_{16}CuPc monolayer on Cu3Au(001) surface as a function of the doping level, x. The bottom spectrum in Fig. 2(a) is taken from the Cu3Au(001) surface. After the formation of a F_{16}CuPc monolayer, new components located between 13 and 8eV were observed. These should originate from the molecular

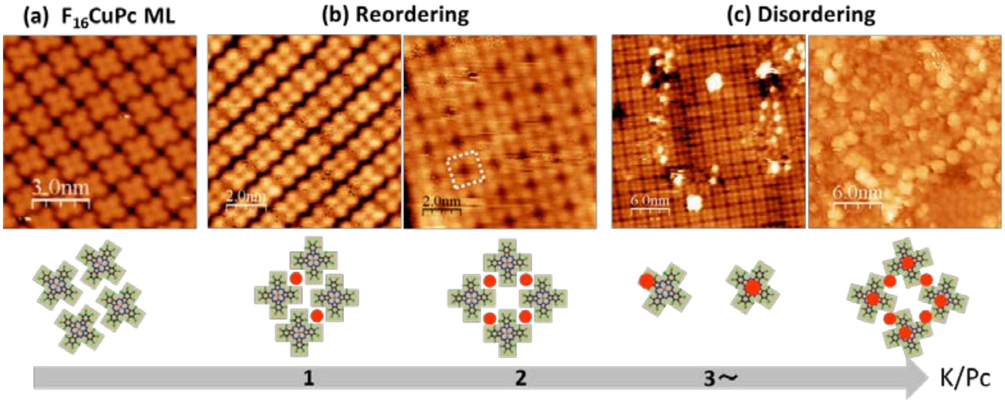

Fig.1
STM images of (a) F_{16}CuPc monolayer and (b, c) K-doped F_{16}CuPc monolayer on Cu3Au(001) substrate

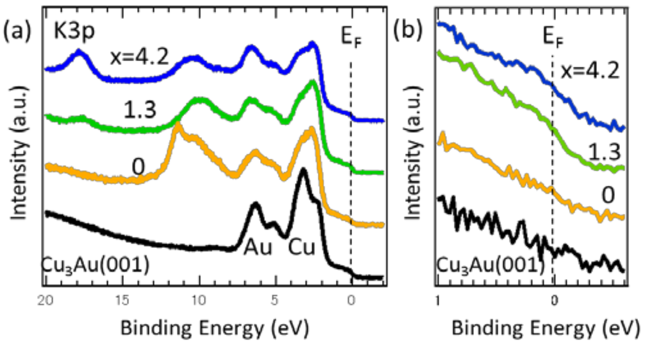

Fig.2 UPS spectrum of K-doped F16CuPc monolayer

orbitals below the highest occupied molecular orbital (HOMO). After deposition of K on the F$_{16}$CuPc monolayer, the K3p peak (labeled H) appeared, and its intensity increased as a function of the deposition. A slight shift of this peak is observed at the higher coverage. This indicates that different chemical conditions exist for the K atoms depending on the coverage, which appears to be consistent with the STM observations. At the initial stages of K deposition, the molecular peak G disappeared and F shifted toward a higher binding energy. This behavior indicates the interaction between the molecule and the K atoms. Note also that the substrate peaks remain unchanged with K doping, although their intensity decreased. These observations indicate that the deposited K atoms do not interact with the substrate, but form compounds with the molecules.

Finally, we discuss the electronic modifications around the Fermi level. Fig. 2(b) shows the evolution of photoelectron spectra around the Fermi level with increasing K coverage, taken with an emission angle of 60°. The bottom two spectra are taken from the Cu3Au(001) surface and the F16CuPc monolayer. The Fermi edge is not clear in either case. After K deposition, a new DOS appears immediately below the Fermi level. Note that the appearance of the new DOS has not been observed previously in the thick film systems. It is considered that this feature, close to the Fermi level, is sensitive to molecular arrangements in the layer. However, this observation also suggests that the system is not metallic, which is in agreement with previous studies.

It is considered that both observations, the change in the ordering of the monolayer and the formation of the new state around the Fermi level after K doping of the F$_{16}$CuPc monolayer, are related to the reported alteration in the conductivity of the Pc films. The present STM images of the reordered F$_{16}$CuPc suggest that the molecules are "connected" via alkali metals. This observation implies that the coupling of the wave functions of the F$_{16}$CuPc molecule and alkali metals becomes significant in the reordered phase. This hybridization may cause the formation of the new DOS near the Fermi level, and increase the electric conductivity via enhancing hopping provability. On the other hand, a significant decrease in electric conductivity has been reported for doping in excess of three atoms per molecule. Since we observed disordering of the F$_{16}$CuPc monolayer after further doping of K above approximately three atoms per molecule, a close relationship between the decrease in conductivity and disordering can be suggested[3].

Acknowledgement

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* yamada@bk.tsukuba.ac.jp