

Electronic modification of coronene monolayer by K-doping

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1 Introduction

Modification of the electronic properties of organic materials by doping with foreign metals or molecules is one of the key technologies used in next-generation organic electronics [1]. In general, microscopic structural information is essential for understanding the mechanisms underlying doping. However quite few number of investigations have addressed the microscopic structural features with respect to doping, mainly due to difficulties in the measurement of inhomogeneous samples.

In the present study, we focus on metal-intercalated aromatic superconductors, which are a recent and interesting topic relevant to the field of metal-doped organic molecules. Superconductivity in the metal-intercalated aromatic hydrocarbons was initially discovered in K-doped picene crystals in 2010, providing a new class of organic superconductors [2]. Until now, similar superconductivity has been reported for four different aromatic molecules including coronene [3]. However, basic information about the crystalline structures and electronic ground states of these doped aromatic molecules is not fully understood.

We have revealed the structural changes in the coronene monolayer on Au(111) upon K-doping by means of scanning tunneling microscopy (STM) measurement as shown in Fig. 1. At the same time, we have investigated the modification of electronic state of coronene monolayer on inert substrate associated with the structural change upon K-doping.

2 Experiment

The coronene monolayers were prepared on Au(111) or highly oriented pyrolytic graphite (HOPG) using vacuum deposition by a homemade Knudsen cell. Formation of the monolayer was confirmed by LEED observations. K was then deposited on the monolayer from alkali

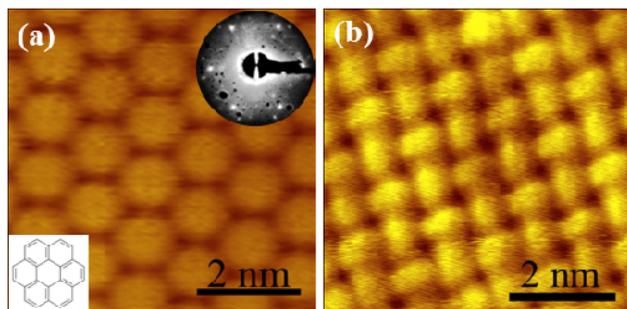


Fig. 1 $5.9 \times 5.9 \text{ nm}^2$ -STM image of (a) pristine and (b) K-doped coronene monolayer on Au(111). Measurement conditions; (a) $V_s = -1.0 \text{ V}$, $I_t = 0.2 \text{ nA}$, (b) $V_s = -1.4 \text{ V}$, $I_t = 0.1 \text{ nA}$.

dispensers (SAES getters). The deposition rate was monitored in-situ using a quartz microbalance (QCM). Photoemission spectroscopy were conducted at the Beam Line 13B, Photon Factory (PF-13B). Core level spectra were obtained with an incident light of 340 eV in the normal emission geometry. To measure the work function, the high-binding-energy cutoff of the photoelectron spectrum was measured using the light with energy of 30 eV with a DC sample bias of 9.9 eV. The resolution of the VB measurement was determined to be approximately 70 meV based on the Fermi edge of clean Au(111).

3 Results and Discussion

Fig. 2 shows the change in the C 1s core-level spectra of the coronene monolayer following K-doping. With increasing K adsorption, the intensity of the original peak at 284.7 eV significantly decreased, and a shifted and broadened peak appeared at 285.6 eV. At a doping level of approximately 3.2-K atoms per coronene molecule, the original peak vanishes. Thus, the shifted C 1s peak found in the doped phases can be attributed to emission from the doped region. The broadening of the C 1s spectrum from the K-doped region indicates the inhomogeneity in the surrounding environment for C atoms within the molecules due to dopants. Here it is important to note that, upon K-doping, the portion of the peak originating from the doped region simply increases. This observation indicates that only one type of doped phase exists, and the area of the doped phase increases with greater alkali coverage. this conclusion appears consistent with our STM

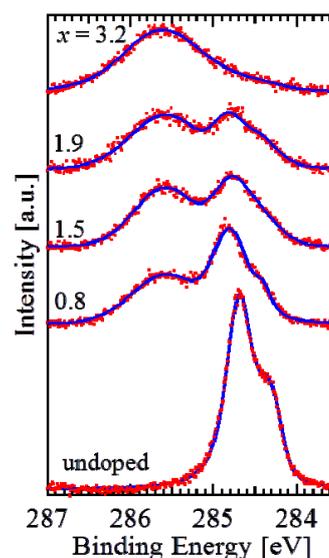


Fig. 2 C 1s core level photoemission spectra of K-doped coronene monolayer on Au(111) as a function of the alkali content per one molecule, x .

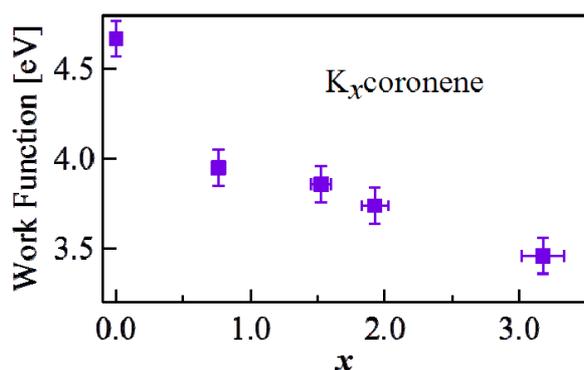


Fig. 3 work function change in the K-doped coronene monolayer on Au(111) as a function of the K content per one molecule, x .

observations, wherein we also found only one type of doped region, and its area increased with increasing alkali deposition. Note also that the direction of the apparent chemical shift of the acceptor in the present system is opposite to the case of usual donor-acceptor system. The shift of the C 1s level toward high binding energy side can be interpreted from the perspective of filling the lowest unoccupied molecular orbital (LUMO) because of both charge transfer [4]. This phenomenon shifts all molecular levels toward higher binding energy, which also results in the downward shift of the local vacuum level at the doped region [5]. We indeed confirmed the shift in the vacuum level by measuring the work function. Fig. 3 shows the change in the work function of this system measured using the high-binding-energy cutoff of the photoelectron spectrum. We observe that the adsorption of K causes a decrease in the work function, i.e., the shift down of vacuum level. The maximum decrease in the work function for K adsorption is approximately 1.0 ± 0.1 eV, which corresponds to the shift observed in the C 1s core level. It is notable that the approximately identical amount of shift in the vacuum level and core levels suggests that the band structure remains rather rigid after undergoing doping.

Fig. 4 shows the change in the photoemission spectra near the Fermi level for K-doped coronene monolayer on HOPG. With increasing doping, we observed a new density of states appearing near the Fermi level forming apparent Fermi edge. Note that a similar increase in the intensity near the Fermi level has also been observed previously for thick picene film on HOPG [6]. This similarity ensures the perspective that the well-defined monolayer can be a model for the doped aromatic hydrocarbons crystals. Therefore, the molecular structure determined from the doped phase can be utilized as input for further detailed investigations including theoretical calculations.

References

- [1] B. Lüssem *et al.*, *Phys. Status Solidi* **210**, 9 (2013).
- [2] R. Mitsuhashi *et al.*, *Nature* **464**, 76 (2010).
- [3] Y. Kubozono *et al.*, *Phys. Chem. Chem. Phys.* **13**, 16476 (2011).
- [4] B. Mahns *et al.*, *J. Chem. Phys.* **136**, 134503 (2012).
- [5] S. Yoshimoto *et al.*, *J. Electroanal. Chem.* **532** (2002).

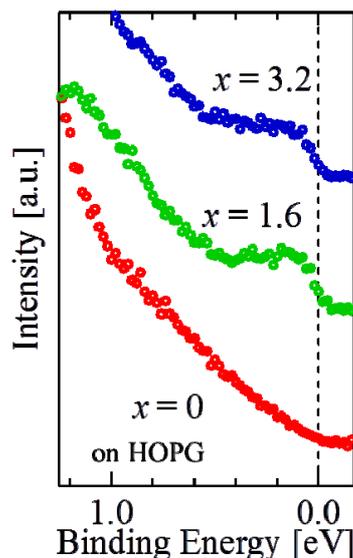


Fig. 4 Photoemission spectra around Fermi level of coronene monolayer as a function of the K content per one molecule, x .

[6] H. Okazaki *et al.*, *Phys. Rev. B* **88**, 245414 (2013).

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