Microscopic Structure of K-Doped Organic Monolayers*

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Potassium (K) adsorption on coronene, picene and [6]phenacene monolayers, which serves as a model system for the metal-intercalated aromatic superconductors, was studied in a molecular scale. Scanning tunneling microscopy (STM) on the K-doped monolayers revealed drastic rearrangements of the molecular layers. Besides the overall similarity of the molecular arrangement in the doped phase, fine structures and unit cell sizes were different, depending on the host molecules. The overall similarity in the structures of the K-doped monolayers should be in close relation to the superconductivity on these systems. [DOI: 10.1380/ejssnt.2014.330]

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I. INTRODUCTION

Metal-doping to organic molecules has been known to be a key technology to modify the electronic properties of organic materials. Especially, alkali-doping has been effective for drastic modification of the electronic states[1–5]. One of the recent impressive examples of alkali metal-doping to organic materials has been the finding of the superconductivity of the alkali-doped aromatic hydrocarbons, called “metal-intercalated aromatic superconductors” [6]. The superconductivity has been firstly discovered in K-doped picene crystals with a $T_c$ of 18 K [6–9]. Subsequently, similar superconductivity has been reported for four different aromatic molecules [6–11]. Until present, basic informations such as crystalline structure and electronic ground state have not been completely settled yet. As for the electronic structures of these materials, various research groups have investigated using film samples by means of photoemission [12–15] and electron-loss spectroscopy [16, 17]. However, these groups have reported contradicting results for the normal electronic state of these materials, from insulating [13–15] to metallic state [12]. These discrepancies may originate from various film structures due to different substrates and different thicknesses. Furthermore, structural information has been lacked due to difficulties in measuring inhomogeneous samples. Therefore, settlement of the structure of the doped molecular layer is essential for understanding the mechanisms of doping. To do so, it is obviously necessary to focus on a well-defined system.

In our previous work, we investigated K adsorption on the well-defined coronene monolayer [18]. We observed that the geometric and electronic structure of coronene monolayer significantly changed upon K adsorption as shown in Fig. 1. Furthermore, photoemission spectroscopy and X-ray absorption spectroscopy (XAS) indicated the presence of the hybridization and charge transfer, between coronene and K. On the other hand, STM and photoemission spectroscopy indicated that the interaction of molecular layer with substrate is weak. Since these results suggest that the interaction between coronene and K dominates the structure and electronic properties of doped monolayer, even the monolayer system might reflect the nature of bulk system, although not perfectly.

In this paper, we examine the K adsorption on picene monolayer on Au(111) and compare them with the case of coronene monolayer, in order to elucidate any similarities and differences to the case of coronene. Note that the K-induced superconductivity has been reported both for K-doped coronene [7] and picene [6–9]. We also examine K-doping to [6]phenacene, which shows similar molecular shape to picene. We observed structural rearrangement of the molecular layer upon K-adsorption for all monolayers. Although similarity in the molecular arrangement was observed in the doped phases, the unit cells and fine structures were different, depending on the host molecules. From the results, we discuss the electronic properties of the K-doped aromatic molecules.

II. EXPERIMENTAL

All the experiments were performed by means of an ultra-high vacuum (UHV) STM at room temperature. The Au(111) single crystalline substrate surface was pre-

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FIG. 1: (a) 5.9 × 5.9 nm²-STM image of coronene monolayers on Au(111) observed with $V_{sample} = +1.1$ V, $I = 0.1$ nA. (b) 5.9 × 5.9 nm²-STM image of the K-doped coronene monolayer on Au(111) observed with $V_{sample} = -1.4$ V, $I = 0.1$ nA.
pared with conventional cycles of Ar+ ion sputtering and subsequent annealing. The quality of the substrate surface was examined by low-energy electron diffraction (LEED) and direct observation with STM. The monolayers of picene and [6]phenacene were then prepared by means of vacuum deposition using a homemade Knudsen cell. K was deposited on the monolayers from alkali dispensers (SAES getters). The deposition rate was monitored in situ using a quartz microbalance (QCM).

### III. RESULTS AND DISCUSSION

STM images of the picene monolayer on Au(111) are shown in Figs. 2(a) and (b). Two different well-ordered phases were observed, depending on the molecular coverage. In the lower-coverage phase of the picene monolayer, molecules appear to be flat-laying on the Au(111) substrate, as shown in Fig. 2(a). The “W” shape inside the picene molecule is clearly seen in this phase. The unit-cell size of this phase is found to be \(0.9 \times 1.5 \text{ nm}^2\), which is almost the same with the van der Waals size of the picene molecule. In this study, since the STM measurement was performed at room temperature, we need to be aware that there is a possibility to suffer distortion due to thermal drift STM image. We confirmed the distortion is small enough compared to the size of the unit cell, by means of scanning in multiple directions. Furthermore, we also confirmed that the electron diffraction provides the similar periodicity.

The increase in the coverage resulted in a formation of well-ordered one-dimensional rows, shown in Fig. 2(b). The direction of the row follows the atomic directions of substrate. In the row, we observe a dimer-like unit consisting of bright and dim molecules and the period in this direction is 1.2 nm. The size of the unit cell in this phase is \(1.2 \times 1.5 \text{ nm}^2\) and the shape of the unit cell is slightly different from that in the lower-coverage phase. The height difference between bright and dim molecules is approximately 0.3 nm. The apparent arrangement of picene molecules in this phase resemble the ac plane of bulk picene crystal, although the unit-cell size is slightly different (the cell in the ac plane: \(0.8 \times 1.4 \text{ nm}^2\)) [19]. Although the details of the latter phase have not been enough clarified, it is likely that the intermolecular interaction in this phase becomes much stronger and therefore the monolayer interacts more weakly with the substrate. This indicates that the higher-coverage phase is rather close to the bulk than the low-coverage phase. Thus we deposit K atoms on the latter phase.

Figure 2(c) shows the STM image of the picene monolayer with a partial coverage of K atoms. The amount of adsorbed K atoms is 3.5 atoms per picene molecule estimated by QCM. The K-doped phase is consisted of elliptic clusters whose directions varied alternately, forming herringbone-like arrangement. Although the arrangement of clusters resembles that of the molecular sheet in the ab plane of the bulk picene, the dimension of the unit-cell of the doped phase of \(2.8 \times 1.7 \text{ nm}^2\) is considerably larger than that of bulk ab plane which is \(0.8 \times 0.6 \text{ nm}^2\) [19]. Note that the shape of the unit cell is almost rectangular, in contrast to that in the non-doped monolayers. The elliptical cluster in the doped phase consists of two small protrusions, suggesting a dimerization of molecules. On the other hand, the corrugation of the \(23 \times \sqrt{3}\) reconstruction of Au(111) surface is still visible on the K-doped phase. This suggests that the substrate surface is unchanged even after K adsorption and that the K atom directly interacts with the picene molecule. Therefore, the system can be a good model for studying interaction between picene and K atom. In the case of small amount of additional doping, the molecular layer is changed to a disordered structure. Thus the structure shown in Fig. 2(c) can be considered as the maximum-doped phase. It is noted that the recent photoemission studies have reported that, although initial K-doping to the picene film causes an increase in the density of states at the Fermi level, the overdoping causes the decrease of them [20]. Therefore it is suggested that the molecular arrangement is in close relation to the electronic structure of the present system.

A similar experiment was carried out also for [6]phenacene which is similar to picene in shape with one additional benzene ring. Figure 3(a) shows the STM image of the [6]phenacene monolayer on Au(111). The arrangement of the [6]phenacene monolayer is similar to that in the case of picene, reflecting the similar molecular shapes. We observe the formation of the molecular rows with the dimer of the bright and dim molecules. The longer axis of the unit-cell is observed to be elongated by approximately 0.3 nm compared to the picene monolayer.

![Figure 2](image1.png)

**FIG. 2:** \(5.9 \times 5.9 \text{ nm}^2\)-STM images of picene monolayers on Au(111) with (a) “W” shape molecular contrast observed with \(V_{\text{sample}} = -2.0 \text{ V}, I_t = 0.1 \text{ nA}\) and (b) one-dimensional structure observed with \(V_{\text{sample}} = 1.2 \text{ V}, I_t = 0.2 \text{ nA}\). (c) \(5.9 \times 5.9 \text{ nm}^2\)-STM image of the partially K-dope picene monolayer on Au(111), measured with \(V_{\text{sample}} = -2.0 \text{ V}, I_t = 0.1 \text{ nA}\).

![Figure 3](image2.png)

**FIG. 3:** (a) \(5.9 \times 5.9 \text{ nm}^2\)-STM image of [6]phenacene monolayers on Au(111) observed with \(V_{\text{sample}} = 1.0 \text{ V}, I_t = 0.2 \text{ nA}\). (b) \(5.9 \times 5.9 \text{ nm}^2\)-STM image of the K-doped [6]phenacene monolayer on Au(111) observed with \(V_{\text{sample}} = -1.4 \text{ V}, I_t = 0.1 \text{ nA}\).
reflecting longer molecular length. The structure of the monolayer resembles the $bc$ plane of the bulk crystal of [6]phenacene. Upon K adsorption, the appearance of the monolayer is changed significantly, as shown in Fig. 3(b). In this case, the amount of adsorbed K atoms is 2.5 atoms per [6]phenacene molecule estimated by QCM. It is noted that, although the overall appearance of the STM image of the doped phase, the herringbone-like arrangement of the elliptic cluster, is similar to the case of K-doped picene, we have observed several differences in the size and fine structure of the unit-cell. Each cluster now appears to consist of three protrusions, instead of two as in the case of K-doped picene. In addition, the unit-cell is $2.8 \times 2.2 \text{nm}^2$, which is larger than the case of the K-doped picene.

Here we discuss the position of the alkali metal atoms in the doped phase. Although the alkali metal has been reported to intercalate between the herringbone-arranged molecules in the $ab$ plane of bulk crystal [7, 21–23], the formation of the alkali layer on the molecular layer may also be possible. However, the STM appearance of the doped phase has a quite large unit-cell with a rather complicated arrangement of protrusions, which cannot be attributed to the simple alkali overlayers. Furthermore, the different appearance of the doped phase depending on the host monolayer also suggests that the formation of the simple overlayers of alkali metals is less likely. Thus we conclude that the aromatic monolayers are rearranged due to the intercalation of alkali metals. Note that, the obvious observation is found in the case of coronene, where the circular appearance of the flat-laying molecules has completely changed into elliptical shape [18]. In that case, we confirmed that the molecular orientation with respect to substrate has changed from flat to standing configuration, on the bases of the X-ray absorption measurements. So we speculate that similar rearrangement of the molecular monolayer occurs also in the case of the picene and [6]phenacene due to intercalation of the K atoms.

We speculate that the formation of the similar structure of the K-doped coronene, picene, and [6]phenacene are in close relation to the superconductivity on these systems. On the other hand, the fine contrasts of the doped phases differ with different host molecule, possibly resulting in the difference in the electronic structures and $T_c$. By measuring the electronic structure of these phases, we will be able to determine the relation between structure and superconductivity of these systems. Note that we have confirmed, in the case of coronene, that the rearrangement upon K-doping does not depend on the substrate material and that the same rearrangement occurs in the bilayer of coronene [18]. Thus we consider that the rearrangements are not specific to the monolayer.

However, the complex rearrangements of aromatic hydrocarbons upon K adsorption suggest that the mechanisms of K-doping to molecules are not simple. Identification of the position of K atoms is quite important to clarify the origin of the superconductivity of these systems, and therefore further investigation will be required.

IV. CONCLUSIONS

We report STM observations of the K adsorption on the monolayer of coronene, picene, [6]phenacene. The alkali-doping to these molecules does not seem to result in a simple layer formation of alkali metals on the monolayer. For all the cases, molecular rearrangement into herringbone arrangement was observed after K adsorption. Overall similarity of the appearances of the doped phases suggests the significant relation between the rearranged structure and superconductivity of these systems. However, the size and fine structure of the unit-cells were different, depending on the host molecules, which can cause difference in the electronic properties. Further investigation, including the determination of the position of the alkali metals, will be required.

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