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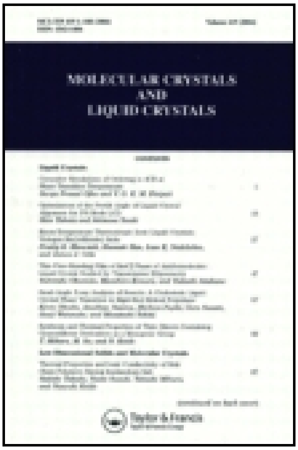

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Low Temperature Scanning Tunneling Spectroscopy of Phthalocyanine Molecules on Metal Surfaces

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We studied the electronic structure of cobalt-phthalocyanine (CoPc) molecules on an Au(111) surface by scanning tunneling microscopy and spectroscopy at 5 K. The differential conductance (dI/dV) spectrum measured on the Co atom showed a peak related to the d orbital of the Co atom, whereas that measured on the Pc ring showed three peaks related to the highest occupied molecular orbital (HOMO), HOMO-1 and the lowest unoccupied MO (LUMO). The current-voltage characteristics showed dependence on the position measured within the molecule, indicating that the intramolecular position of the contact between the molecule and the electrode made influence on carrier transport through a single molecule.

Keywords: current-voltage characteristics; dI/dV spectroscopy; low temperature scanning tunneling microscopy; phthalocyanine

INTRODUCTION

Carrier transport properties through a single molecule have been intensively studied molecular-scale electronic devices [1,2]. Simple molecular devices consisting of a single molecule between two metal electrodes have been demonstrated by several groups [3–7]. Although various carrier transport properties, such as current rectification [3], coulomb blockade [4], negative differential resistance [5] and Kondo

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effect [6,7], have been reported, there are still many arguments on the effects of the contacts between molecules and electrodes onto carrier transport properties. In order to understand this issue, it is necessary to elucidate the electronic structures of the interfaces between the molecules and the electrodes.

Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are useful to investigate the electronic structures of surfaces in real space with an atomic resolution. Differential tunneling conductance (dI/dV) spectroscopy makes it possible to obtain information about the local density of states [8,9]. Since integrals of dI/dV spectra correspond to current (I)-voltage (V) characteristics, it is possible to understand both the electronic structures and the carrier transport properties at the interface. Since it is difficult to elucidate the spatial distribution of dI/dV spectra within a single molecule at room temperature mainly due to thermal drift and mobility of molecules, the electronic structures and carrier transport properties of molecules have been discussed on the basis of spatially averaged I-V characteristics in previous reports [10–13]. One of the promising ways of overcoming this difficulty is to keep the specimen at low temperature during STM observation. In the present study, we report the electronic structure of cobalt-phthalocyanine (CoPc, Fig. 1) on Au(111) surfaces on the basis of STM, dI/dV spectroscopy and I-V characteristics at 5 K and discuss the interface properties between molecules and electrodes.

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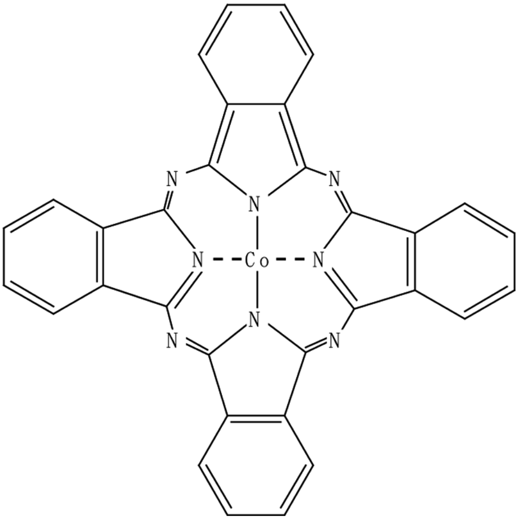

FIGURE 1 Molecular structure of CoPc.

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EXPERIMENTAL

Experiments were carried out using a low-temperature STM system, which consists of three differentially pumped ultrahigh-vacuum chambers used for load-lock, preparation, and STM observation. An Au(111) surface grown on mica was cleaned by Ar^+ sputtering and annealing at 850 K in the preparation chamber. CoPc (Aldrich) was purified by vacuum sublimation and deposited onto the Au(111) surfaces kept at room temperature. The specimen was then transferred into the STM chamber and cooled to 5 K. A Pt/Ir tip was used and dI/dV spectra were measured by the lock-in detection.

RESULTS AND DISCUSSION

Figure 2 shows the STM image of CoPc molecules on the terraces of the Au(111) surface. Five CoPc molecules are recognized in Figure 2. Each CoPc molecule appeared as a cross shape with a bright center. CoPc molecules stayed with their molecular planes parallel to the surface.

Figure 3(a) shows the dI/dV spectra measured at two different points of one CoPc molecule located on the terrace of the Au(111) surface. The spectrum (1) measured on the Co atom has one peak at the sample bias of −0.3 V indicated as D. The spectrum (2) measured on the Pc ring has three peaks at the sample biases of −0.8 V, −0.5 V and +1.1 V indicated as H-1, H and L, respectively. Since the spectrum of the bare Au(111) surface did not show these features, these peaks were

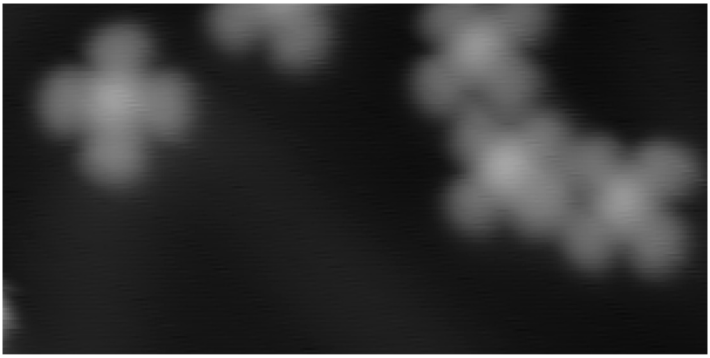

FIGURE 2 STM image of CoPc molecules adsorbed on the Au(111) surface taken at sample bias of −0.5 V and tunneling current of 0.1 nA at 5 K. The scan size was 7.8 nm × 3.9 nm.

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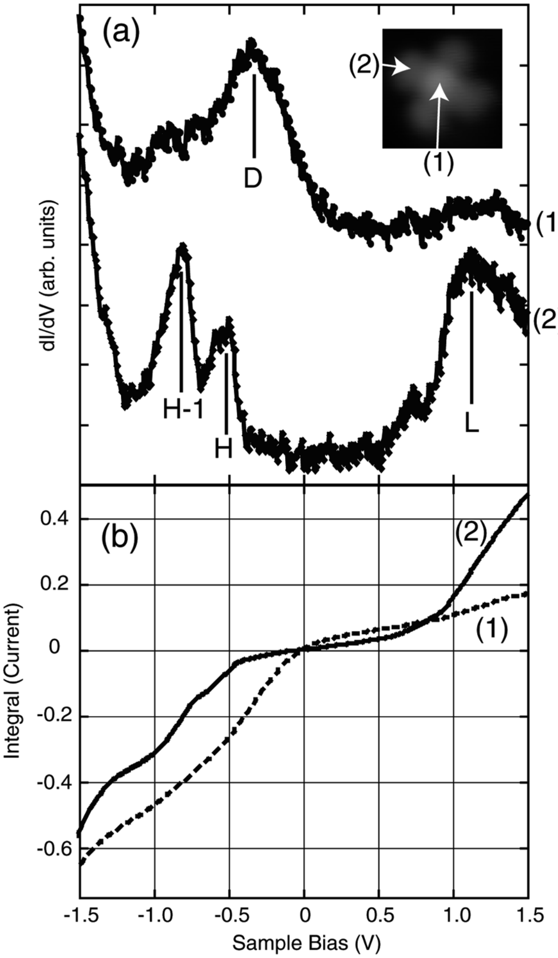

FIGURE 3 (a) dI/dV spectra of a single CoPc molecule on the Au(111) surface at 5 K. The spectra were measured at indicated spots on the inset image. (b) I-V characteristics of a single CoPc molecule. The curves were integrated numerically from the dI/dV spectra (1) and (2).

attributed to the electronic structures of CoPc on the Au(111) surface. The difference between the dI/dV spectra (1) and (2) is thought to arise from the spatial inhomogeneity of the electronic structure within a single CoPc molecule. Peaks D, H-1, H and L are assigned as d orbital of Co atom, HOMO-1, HOMO and LUMO, respectively. The detailed discussion of the peak assignment was published elsewhere [14].

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Figure 3(b) shows I-V curves calculated from the dI/dV spectra of Figure 3(a). The offset was subtracted from the dI/dV spectra obtained prior to the integration of the values. It is recognized that two curves are different from each other, indicating that the spatial inhomogeneity of the electronic structure within a single molecule makes influence on I-V characteristics of the interface between the molecule and metal electrodes. It is concluded that carrier transport properties at the interface between a single molecule and an electrode strongly depends on the intramolecular position where the molecule is in contact with the electrode.

CONCLUSIONS

We studied the electronic structure of CoPc molecules on the Au(111) surface using STM and STS at 5 K. The dI/dV spectra of CoPc molecules on the Au(111) surface showed four peaks corresponding to the HOMO-1, HOMO, LUMO and d orbital of the Co atom. I-V characteristics integrated numerically from the dI/dV spectra showed dependence on the position within a single CoPc molecule, which indicated that intramolecular positions of the contacts made between the molecule and the electrodes had strong influence on carrier transport properties through the single molecule.

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