Surface reconstruction formed by ordered missing molecular rows observed on the quasi-one-dimensional organic conductor β-(BEDT-TTF)$_2$PF$_6$

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The surface structure of a quasi-one-dimensional organic conductor β-(BEDT-TTF)$_2$PF$_6$ crystal [BEDT-TTF is bis(ethylenedithio)-tetrathiafulvalene] was studied by scanning tunneling microscopy (STM). Twofold periodic modulation along the crystal a axis was observed on the crystal a-c plane with a PF$_6$ top layer, similarly as the previous result obtained for the surface with a BEDT-TTF top layer. With the analysis using high-resolution STM images including the second BEDT-TTF molecular layer, the surface superstructure was found to be formed by alternate missing rows of PF$_6$ molecules. To our knowledge, this is the first observation of an organic surface reconstruction involving such a drastic change in the molecular arrangement, which was comprehensively explained using a proposed model based on the charge balance in the surface layers. [S0163-1829(97)02408-9]

It is well known that material surfaces induce reconstructions to stabilize their surface structures by reducing surface energy. With the progress of the techniques of surface physics, surface reconstructions have been studied extensively to clarify the mechanism for the processes, however, which have been subjected to only inorganic materials for a long time. Recently, thin films of TTF-TCNQ [tetrathiafulvalene-tetracyanoquinodimethane] and β-(BEDT-TTF)$_2$I$_3$ [BEDT-TTF: bis(ethylenedithio)-tetrathiafulvalene] have been found to have different phase transition properties in contrast with those of the bulk crystals; critical temperatures of phase transition became higher for the thin films, and the important role of the surface effect has also been identified for the organic materials.[1,2] In addition, according to the recent scanning tunneling microscopy (STM) studies, surface superstructures were actually confirmed to exist on the materials such as β-(BEDT-TTF)$_2$I$_3$ and β-(BEDT-TTF)$_2$PF$_6$.[3–6] However, the observed structures could be understood as a change mainly in the electronic structures, and no drastic structural change with reconstruction of elemental molecules in the surface of organic materials has been observed until now.

In this work, we present the STM observation of a surface reconstruction which consists of missing molecular rows in an organic material surface of β-(BEDT-TTF)$_2$PF$_6$ crystal. In consideration of the electronic structure including second layer molecules, the observed reconstruction is concluded to be caused by charge redistribution in the surface layers.

β-(BEDT-TTF)$_2$PF$_6$ is the first organic conductor in which quasi-one-dimensional conductivity has been observed in the direction parallel to the molecular plane, along the c axis. The crystal structure of β-(BEDT-TTF)$_2$PF$_6$ determined by x-ray diffraction is shown in Fig. 1. The crystal structure is orthorhombic with space group $Pnna$, and $a=1.4960(4)$, $b=3.2643(7)$, $c=0.6664(2)$ nm and $V=3.2546$ nm^3. The structure consists of a stack of alternate BEDT-TTF layers and PF$_6$ layers parallel to the b axis.

According to calculations based on the Hückel method, strong dimerization of BEDT-TTF molecules is expected to result in uniform half-filled metallic chains along the c axis

above T_c, and metal-insulator transition caused by low dimensionality has been observed at $\sim$297 K ($=T_c$).[7] Since charge density waves (CDW's) cause modulation along the conductive axis in one-dimensional conductors, the lattice constant along the c axis is expected to be doubled below T_c due to the corresponding $2k_F$ CDW. However, according to the results of recent STM measurements, the surface most often observed showed twofold charge modulation along the a axis, which remained, even in the image of a sample considered to be in the CDW phase.[5] Since this material is a charge transfer salt, which is not balanced in the top layer, the observed modulation is expected to be related to a mechanism in which the surface structure is stabilized by charge redistribution.

β-(BEDT-TTF)$_2$PF$_6$ crystals were grown using the electrochemical oxidation method via a layer-by-layer mechanism. They are black, flake-shaped, and elongated along the conductive c direction. For STM observation, the crystals were fixed onto copper plates using conductive silver epoxy resin, and STM observations were performed at room temperature in air. All images were taken by the constant current mode.

Figure 2(a) shows a STM image of the crystal a-c plane. As shown in Fig. 2(a), there are two terraces separated by a step. A cross section along A-B in Fig. 2(a) is shown in Fig. 2(b). The height difference between the two terraces is about 1.3 nm, which is close to half of the lattice parameters in the direction of the crystal b axis, 1.6 nm. Since the crystal con-
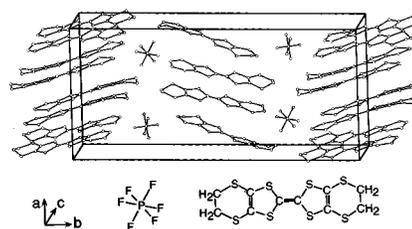
FIG. 1. Crystal structure of β-(BEDT-TTF)$_2$PF$_6$ determined by x-ray diffraction.

(a)

(b)
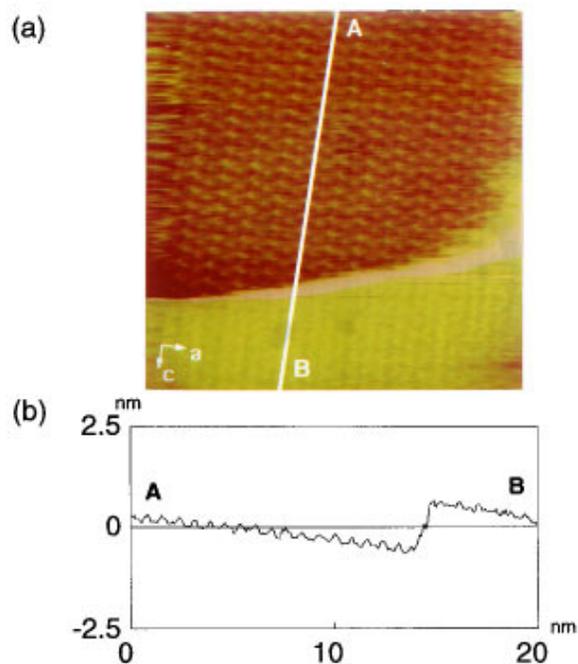
FIG. 2. (a) (Color) STM image of the a-c plane of β-(BEDT-TTF)$_2$PF$_6$ (20×20 nm^2, $V_s = -100$ mV, $I_t = 2.1$ nA). (b) Cross section along A-B in (a).

sists of alternate BEDT-TTF and PF$_6$ molecular layers stacked along the b axis, i.e., normal to the surface as shown in Fig. 1, the present result indicates that the crystal growth occurs via a layer-by-layer mechanism, as expected.

When the crystal is grown layer by layer, the surface has both BEDT-TTF- and PF6-terminated areas. Figure 3(a) shows a STM image of a terrace shown in Fig. 2(a), where two domains with different structures exist. The domain boundary is indicated by white dashes in Fig. 3(a), and the unit cells in both areas are indicated by U_{ET} and U_{PF}, respectively. Both the two unit cells in Fig. 3(a) have dimensions of 1.6 nm×0.62 nm, which agree well with the dimensions in Fig. 1, obtained by x-ray diffraction, of 1.4960(4) ×0.6664(2) nm. Cross sections along A-B and C-D in Fig. 3(a) are shown in Fig. 3(b). The step height is about 0.1 nm, which is comparable to the height of one PF$_6$ layer $\sim$0.2 nm. Therefore, the two domains separated by a small step on a terrace are probably surfaces with BEDT-TTF and PF$_6$ molecular top layers.

A schematic structure for the surface in Fig. 3(a) is shown in Fig. 3(c). The upper half shows a schematic structure of a BEDT-TTF layer projected onto the crystal a-c plane. In the lower half, a PF$_6$ molecular layer overlaps the BEDT-TTF layer. For the BEDT-TTF molecules, the upper two rings of the molecules, which are closer to the surface, are shown. Since the lobes of the highest occupied molecular orbital (HOMO) around the S atoms in the hexagonal ring are large according to *ab initio* calculations, and alternate BEDT-TTF molecules along the a axis are about 0.1 nm from the surface, the positions of the HOMO lobes of the S atoms in the uppermost rings of alternate BEDT-TTF molecules are indicated by ellipses in the direction of the a axis, which should be compared with the STM image obtained. On the other hand, since top-layer PF$_6$ molecules are considered to occupy

(a)

(b)

(c)
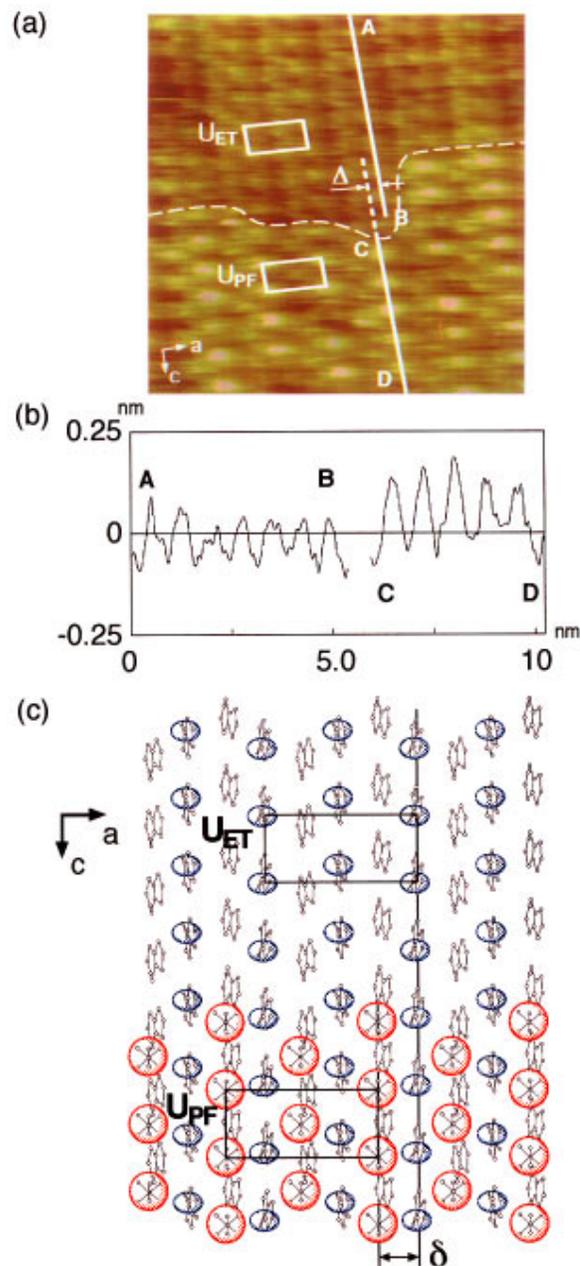
FIG. 3. (a) (Color) STM image of a terrace in Fig. 2(a) (10×10 nm^2, $V_s = -44$ mV, $I_t = 0.53$ nA). (b) Cross sections along A-B and C-D in (a). (c) (Color) Schematic structure of surface shown in (a). BEDT-TTF and PF$_6$ molecules are colored by blue and red, respectively.

equivalent sites, all of them in the lower half of the schematic diagram are indicated by the same circles. The observed image of PF$_6$ molecules is in fact similar to that obtained on the surface of (TMTSF)$_2$PF$_6$ crystal.[8] Here, twofold modulation of the surface, which was previously observed,[5] is not taken into account. The two unit cells indicated by U_{ET} and U_{PF} in Fig. 3(a) are shifted by an amount of Δ. The observed value of Δ was about 0.4 nm, which agrees well with the value determined by x-ray diffraction, $\delta = 0.37$ nm, shown in Fig. 3(c). The agreement between the observed image and the structure shown in Fig. 3(c) is excellent.

Figures 4(a) and 4(c) show high-resolution STM images
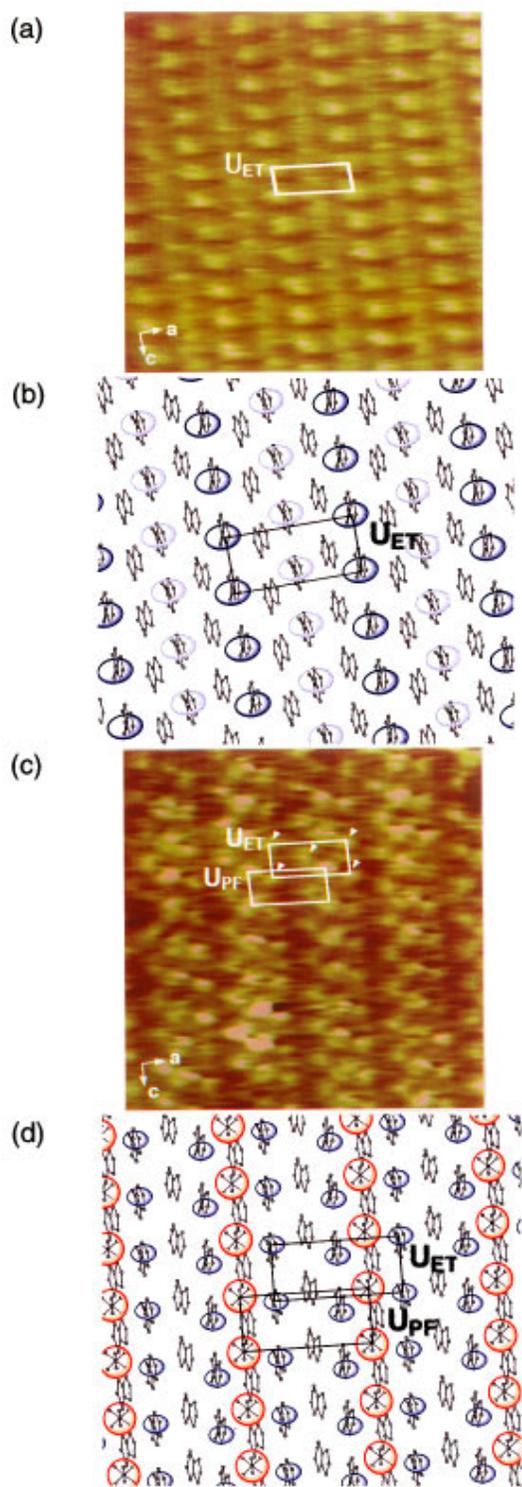
FIG. 4. (Color) High-resolution STM images of β-(BEDT-TTF)$_2$PF$_6$ surface with a top layer consisting of (a) BEDT-TTF, and (c) PF$_6$ layers (8×8 nm^2, $V_s=-30$ mV, $I_t=0.46$ nA). Schematic structures corresponding to STM images (a) and (c) are shown in (b) and (d), respectively, where BEDT-TTF and PF$_6$ molecules are colored by blue and red.

of the structures on the upper and lower terraces in Fig. 3(a), respectively. The structure in Fig. 4(a) is the same as that observed for the surface with a BEDT-TTF molecular top layer. A schematic of a BEDT-TTF layer in the a-c plane is shown in Fig. 4(b). Here, twofold modulation in the surface

electronic structure along the crystal a-axis is taken into account, and alternate ellipses in the direction are indicated by dark ellipses. The molecular arrangement in Fig. 3(a) agrees well with the structure shown in Fig. 3(b).

The STM image of the PF$_6$ terminated surface in Fig. 4(c) is considered to show a superposition of the PF$_6$ and the second BEDT-TTF molecular layers, the unit cells of which are indicated by U_{ET} and U_{PF}, respectively. As shown in Fig. 4(c), the observed PF$_6$ molecules have similar, but different twofold periodic modulation along the crystal a axis. The unit cell of the PF$_6$ layer in the crystal has centered symmetry, as indicated in the schematic shown in Fig. 3(b). In Fig. 4(c), however, the molecular rows of PF$_6$ are at intervals twice as large as those in the schematic, and alternate rows are completely absent. For the BEDT-TTF molecules shown in Fig. 4(a), alternate rows of BEDT-TTF are darkened, but never disappear. For the PF$_6$ molecules, no protrusion is observed at the center of the unit cell, U_{PF}. The height difference between the BEDT-TTF and PF$_6$ molecules in Fig. 4(c) is about ~0.1 nm, which is similar to the value obtained from Fig. 3(b). Since this characteristic was observed for all surfaces with PF$_6$ top layers, regardless of the polarity of the bias voltage applied to the sample, we conclude that the surface superstructure is formed by alternately ordered missing PF$_6$ molecular rows. A schematic structure of the surface in Fig. 4(c) is shown in Fig. 4(d).

One possible explanation for the results obtained for the β-(BEDT-TTF)$_2$PF$_6$ surface is that the reconstruction is caused by electronic deficiency in the surface. It is known that half an electron per BEDT-TTF molecule transfers into the PF$_6$ molecular layers, which makes the BEDT-TTF molecular layers conductive, and the PF$_6$ layers insulating. Since the surface layer has a counter molecular layer only on one side, when the top layer consists of PF$_6$ molecules, they are supplied with only half the number of electrons. On semiconductor surfaces, the symmetry of the surface structure is broken to compensate for the instability due to the charge imbalance. For example, on Si(100) and GaAs(110) surfaces, Si-Si and Ga-As dimers buckle, which induces charge transfer which stabilizes the surface structure.[9,10] In GaAs(100) surfaces, As dimer rows are orderly missing which improves the charge balance in the surface layers.[11] Assuming a similar mechanism, when half of the PF$_6$ molecules are removed, the charge is exactly balanced within the surface layer, resulting in stable surface. The ordering of the alternate missing rows of PF$_6$ molecules may be due to the one-dimensional conductivity in the BEDT-TTF layer along the c axis. In addition, PF$_6$ molecules coordinate most closely along the c axis.

Similar modulation is observed in a BEDT-TTF-terminated surface, as shown in Fig. 4(a). In this case, since the BEDT-TTF molecules strongly interact with the adjacent BEDT-TTF molecules, they are not desorbed and only charge transfer is considered to occur.

When the surface is covered by a reconstructed PF$_6$ molecular layer, the charge of the BEDT-TTF molecules in the second layer is considered to be balanced. Therefore, the electronic structures of the BEDT-TTF molecules in the second layer must be equivalent, unlike those of the BEDT-TTF
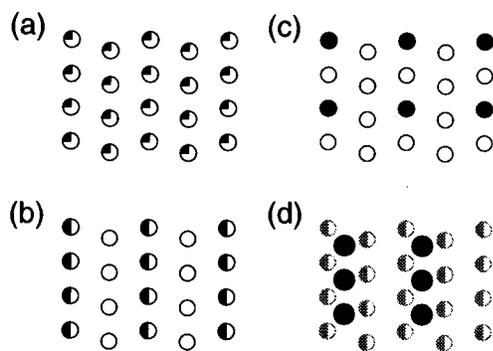
FIG. 5. Schematic of the electronic structures in the surface BEDT-TTF layer: (a) uniform, (b) with twofold periodic modulation along the a axis, (c) CDW phase, and (d) with a top layer of PF_6 molecules: ●, ◐, ◑, and ○ indicate 1, 1/2, 1/4, and 0 holes per BEDT-TTF molecule. The large ● in (d) indicate PF_6 molecules that are completely filled.

molecules in the top layer. In fact, five BEDT-TTF molecules, indicated by arrows in the unit cell, U_{PF}, in Fig. 4(c), are imaged equivalently.

For a BEDT-TTF-terminated surface with a CDW phase, twofold periodicity along the a axis still exists.[5] This can also be explained using our model. A schematic diagram of the charge balance in the BEDT-TTF molecules on the surface is shown in Fig. 5: (a) 1/4-filled uniform metallic phase, (b) with twofold periodic modulation along the a axis, (c) a

CDW phase, (d) with a top layer of PF_6 molecules. The amount of holes introduced into the BEDT-TTF layer is indicated by four different types of circles: ●, ◐, ◑, and ○ for 1, 1/2, 1/4, and 0 holes per BEDT-TTF molecule, respectively. The large ● in Fig. 5(d) indicates PF_6 molecules completely filled. It had been reported in earlier investigations that the transition at T_c is due to $4k_F$ modulation in a highly correlated band. According to the recent band calculation, strong dimerization of BEDT-TTF molecules occurs, which results in a phase transition at T_c associated with $2k_F$ CDW's. Considering the charge balance in our model, the previously observed surface superstructure shown in Fig. 5(c) is considered to support the $2k_F$ interaction in this material instead of $4k_F$.[6]

In conclusion, a superstructure consisting of alternate missing molecular rows was observed in the surface of a quasi-one-dimensional organic conductor, β-(BEDT-TTF)$_2$PF$_6$, with a PF$_6$ top layer. This is the first observation of a surface reconstruction with such a drastic change in the molecular arrangement of the surface. By comparing the electronic structures of the BEDT-TTF molecules in the top and second layers, the charge transfer in the surface layers expected for this crystal structure was confirmed. This charge transfer is considered to play an important role in inducing the observed surface reconstruction.

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