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Molecular and electronic properties of β-(BEDT-TTF)$_2$PF$_6$ studied by scanning tunneling microscopy

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Two different structures based on one-dimensional molecular rows were observed by scanning tunneling microscopy (STM) in the β-(BEDT-TTF)$_2$PF$_6$ crystal surface. The temperature dependence of tunneling current-bias voltage curves showed the property of a metal-insulator phase transition. However, metallic electronic states were observed even at ~230K between the energy gap, indicating fluctuation of the charge density wave. The metallic property was recovered when the STM tip was softly brought into contact with the sample surface, where the charge density wave is considered to be formd.

Figure 1(a) shows a current scanning tunneling microscope (STM) image obtained over the a-c plane of a one-dimensional organic conductor, β-(BEDT-TTF)$_2$PF$_6$ (BEDT-TTF: bis(ethylenedithio)-tetrathiafulvalene), which has a metal-insulator transition at 297K. The observed size of the unit cell in Fig. 1(a), 0.71nm x 1.46nm, agrees well with that determined by X-ray diffraction, 0.664nm x 1.496nm.[1,2] A schematic of the structure of the crystal a-c plane is shown in Fig. 1(b), where the upper two rings of the BEDT-TTF molecules which are closer to the crystal surface are drawn together with the anions, similarly to those reported in refs. 3-5. Ellipses indicate the lobes of the highest occupied molecular orbital (HOMO) around the S atoms, and BEDT-TTF molecules with the ellipses are about 0.1nm higher than other molecules along the b-axis in the a-c plane. Therefore, STM images are expected to reflect the arrangement of the ellipses which are equivalent to each other.

The obtained molecular arrangement agrees well with that of the crystal: however, molecular rows along the c-axis are alternately bright and dark, as indicated by a-b and c-d in Fig. 1(a). A similar structure was observed previously on a TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) crystal surface below its critical temperature for a charge density wave (CDW) formation. The double lattice constant was formed by bright molecular rows with twofold periodicity, however, the twofold periodicity, which is expected to appear along the molecular rows, was not observed.[6]

Figure 2 shows a series of I-V (tunneling current - bias voltage) curves measured at (a) 304K, (b) 230K, and (c) 202K, under the conditions of (Vt, Is) (a) (50mV, 1.0nA), (b) (200mV, 0.5nA), and (c) (200mV, 0.5nA). As shown in Fig. 2,

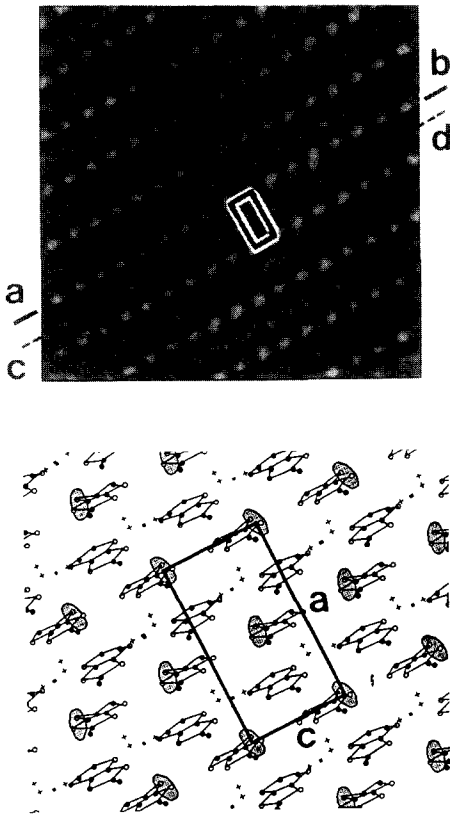

Fig. 1. (a) STM image obtained over the a-c plane of β-(BEDT-TTF)$_2$PF$_6$ crystal at ~280K (Vt=-40.0mV, Is=0.9nA, 11nm x 11nm), (b) molecular arrangement of the crystal projected on the crystal a-c plane (■:P, +: F, ○: S, ●: C).

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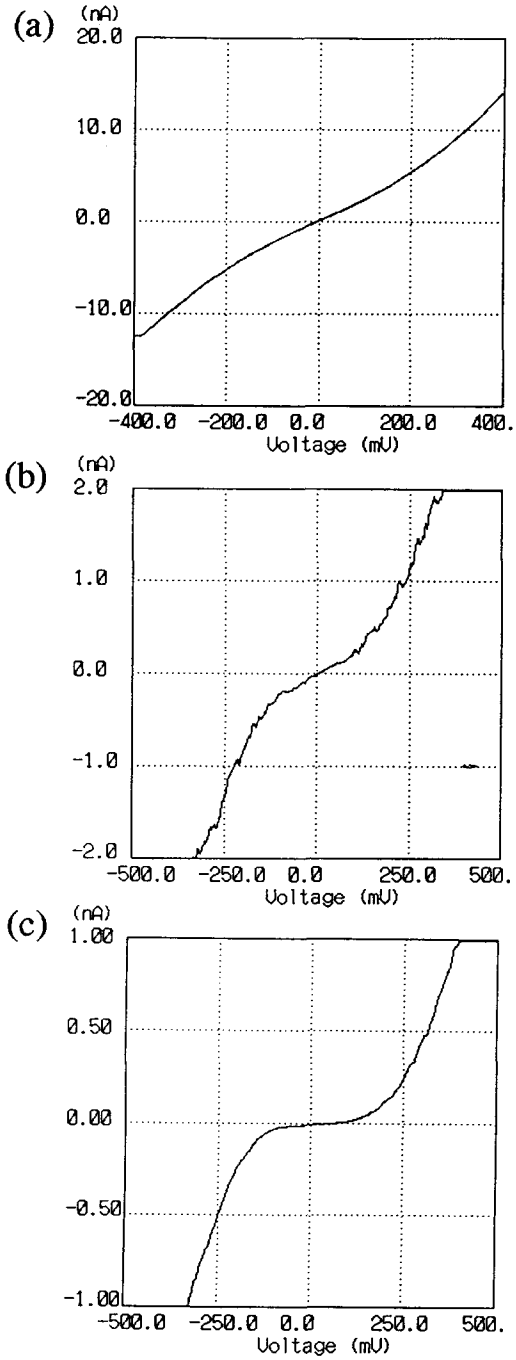

Fig. 2. Series of I-V curves measured at (a)304K, (b)230K, and (C)202K.

the electronic property at 304K is metallic, and conductivity decreased with temperature as expected. However, metallic electronic states partially remained on an atomic scale even at 230K between the energy gap, indicating fluctuation of the CDW. When the STM tip was softly brought into contact with the sample surface at 132K, where CDW was thought to be formed, the metallic character was recovered again, as was observed for the (BEDT-TTF)$_2$ Cu(NCS)$_2$ crystal surface.[5)]

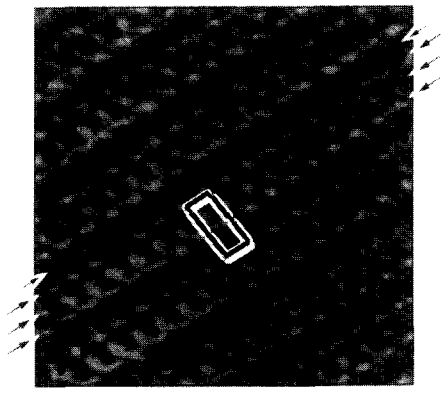

Fig.3 STM image obtained over the a-c plane of β-(BEDT-TTF)$_2$PF$_6$ crystal (Vt=-40.0mV, Is=0.9nA, 11nm x 11nm).

Figure 3 shows another structure observed at ~280K. Here, one dark and three bright molecular rows form a new unit in the modulation, as indicated by two different kinds of arrows in Fig. 3. The observed unit cell is ~0.63nm x ~1.65nm. Rather extensive structural change may be observed in this cell compared to that shown in Fig. 1(a).

In the case of (BEDT-TTF)$_2$Cu(NCS)$_2$, which has two-dimensional conductivity, modulation was observed to form by uniting BEDT-TTF dimers as expected.[5)] Therefore, further study will be necessary in order to understand the detailed properties of the one-dimensional conductive materials on an atomic scale.

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[5] H. Shigekawa, K. Miyake, H. Oigawa, T. Mori, and Y. Saito, to be published. CDW is formed by uniting two BEDE-TTF molecules in (BEDT-TTF)$_2$Cu(NCS)$_2$.

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