

Modulation of β -(BEDT-TTF) $_2$ PF $_6$ crystal surface structure induced by charge redistribution in surface layers

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Abstract

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) were used to characterize the surface superstructures of a quasi-one-dimensional organic conductor, β -(BEDT-TTF) $_2$ PF $_6$ [where BEDT-TTF denotes bis(ethylenedithio)-tetrathiafulvalene]. The existence of periodic modulation formed by alternate missing rows of PF $_6$ molecules, which was previously observed by STM on the PF $_6$ top layer, was confirmed using AFM. For a surface with a BEDT-TTF top layer, periodic modulation was observed to be formed by the combination of molecular and electronic structural changes in the surface layer. The phenomena observed are comprehensively explained by the charge-compensation model. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is well known that the structure of material surfaces is unstable due to symmetry breaking, which induces surface relaxation/reconstruction in the surface layers. Understanding the surface reconstruction is essential from both fundamental and practical points of view, and has been studied extensively by scanning tunneling microscopy (STM) and atomic force microscopy (AFM) on an atomic scale. Non-stoichiometry often occurs on polar surfaces of ionic crystals such as the

(111) surface, resulting in a reduction of charge imbalance in the surface layers. Similarly, charge redistribution in the surface layers induced by the formation of ordered defects with an excess or deficient charge has been observed to stabilize the surface structure of compound semiconductors [1]. In the case of silicon surfaces, an example is the buckling of silicon dimers of the Si(100) which induces a charge redistribution that stabilizes the surface structure.

It has been thought that organic materials do not show the surface reconstruction described above. However, recently a structural modulation involving a drastic change in the molecular arrangement was observed by STM on the surface of a β -(BEDT-TTF) $_2$ PF $_6$ crystal [where BEDT-

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TTF denotes bis(ethylenedithio)-tetrathiafulvalene]. Previous work concluded that this arose from alternate missing rows of PF₆ molecules forming the outer layer [2]. A similar but less drastic modulation was also observed on the surface with a BEDT-TTF top layer [3–6]. If the observed surface modulations can be explained by the charge-compensation mechanism, i.e., by charge and molecular rearrangements to reduce the charge imbalance in the surface layers, surface reconstruction of these organic surfaces can be systematically understood.

In order to clarify the mechanism of the structural modulations observed on the β -(BEDT-TTF)₂PF₆ surface, we performed STM and AFM measurements on the surface.

2. Experimental

Fig. 1 shows the crystal structure of β -(BEDT-TTF)₂PF₆ determined by X-ray diffraction [7]. The crystal *c*-axis corresponds to the one-dimensional conductive axis of the crystal. Single crystals of β -(BEDT-TTF)₂PF₆ were grown by the standard electrochemical oxidation method and fixed to metallic plates with a conductive silver epoxy. STM and AFM images were taken over the crystal *a*-*c* plane with a mechanically sharpened Pt/Ir tip and a pyramidal Si₃N₄ tip, respectively. All images reported in this paper are the topographic images taken under ambient temperature and pressure conditions.

3. Results and discussion

Since BEDT-TTF (cation) and PF₆ (anion) sheets are alternately stacked along the crystal *a*-axis, two types of surface with a BEDT-TTF or a PF₆ top layer can be observed on the *a*-*c* plane. The BEDT-TTF and PF₆ molecular layers are 1.3 and 0.3 nm thick, respectively, and are quite different from one another. Therefore, we can identify and observe each layer selectively by checking the step height of the layers on the surface. First, let us examine the surface structure of the PF₆ top layer.

Fig. 2 shows STM (a) and AFM (b) images obtained on the surface. As is shown in Fig. 2a, alternate missing rows of PF₆ molecules in the direction of the crystal *a*-axis exist on the surface as indicated by the white arrows. Similar structure was also observed by AFM as shown in Fig. 2b. Since the AFM image should reflect the structure related to the total electron density, i.e., the atomic positions, the results obtained strongly indicate that the surface modulation is actually formed by the ordered missing molecular rows.

Next, let us examine the structure of a BEDT-TTF top layer. Fig. 3a is an STM image obtained on the surface. The surface unit cell consists of four BEDT-TTF molecules forming dimers A–B and C–D as shown in Figs. 1 and 3c. If the surface has an ideal structure, upper molecules of each dimer should be observed with the same brightness by STM because they are at the same distance from the STM tip. However, only one molecule in a unit cell (A or C) was brightly imaged as clearly shown in the cross-sectional profile along the *a*-axis. The periodic modulation on the surface was also observed by AFM as shown in Fig. 3b. In consideration of the fact that an AFM image reflects the structure of the total electron density, close to the atomic position, we conclude that not only a change in the electronic structure but also a molecular rearrangement occurred on this surface as has been observed in inorganic crystal surfaces.

Next, let us discuss the surface modulation produced by the charge-compensation mechanism [8,9]. In the surface layer of the BEDT-TTF compounds, a half amount of the ionic charge should be reduced. As shown in Fig. 4a, the PF₆ molecular rows are alternately desorbed from the surface and each surface PF₆ molecule can have the favorable valence state (PF₆⁻). Since the interaction between PF₆ molecules is weak because of their large intermolecular distance in the anion sheet, the PF₆ molecules are considered to be removed relatively easily.

On the other hand, since BEDT-TTF molecules in the cation sheet strongly interact with each other, it is difficult for them to be desorbed from the surface. Therefore, only structural modulation, which induces charge redistribution, occurs on the

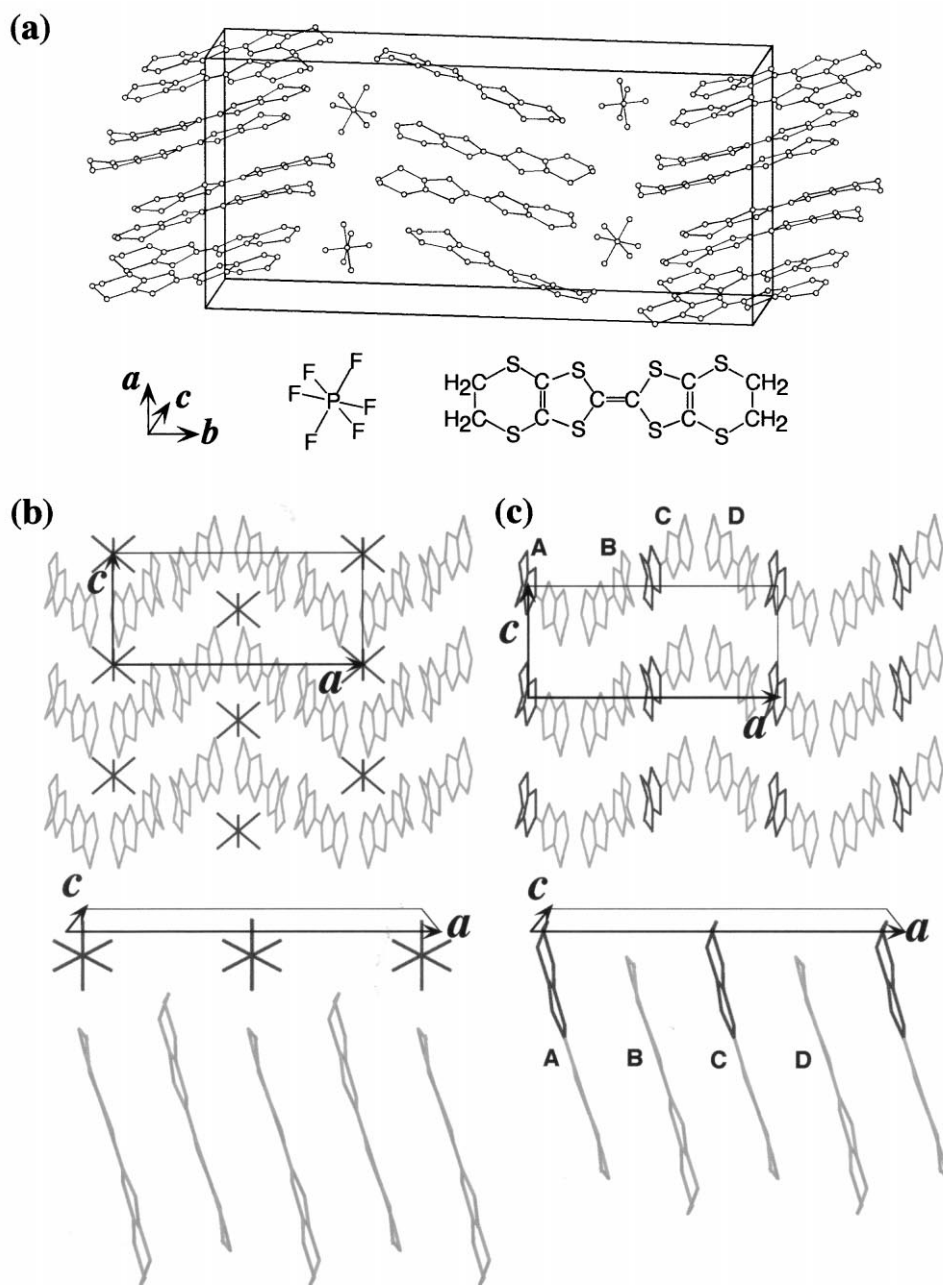


Fig. 1. (a) Crystal structure of β -(BEDT-TTF) $_2$ PF $_6$ ($a=1.4960$, $b=3.2643$, $c=0.6664$ nm), and molecular arrangements of its anion (b) and cation (c) layers.

surface. When the structure of the BEDT-TTF molecular layer is relaxed on the surface, the degenerated energy levels of the molecules must

split, and charge transfer is expected to be induced. In such a case, ionic interactions between the surface BEDT-TTF molecules and PF $_6$ molecules

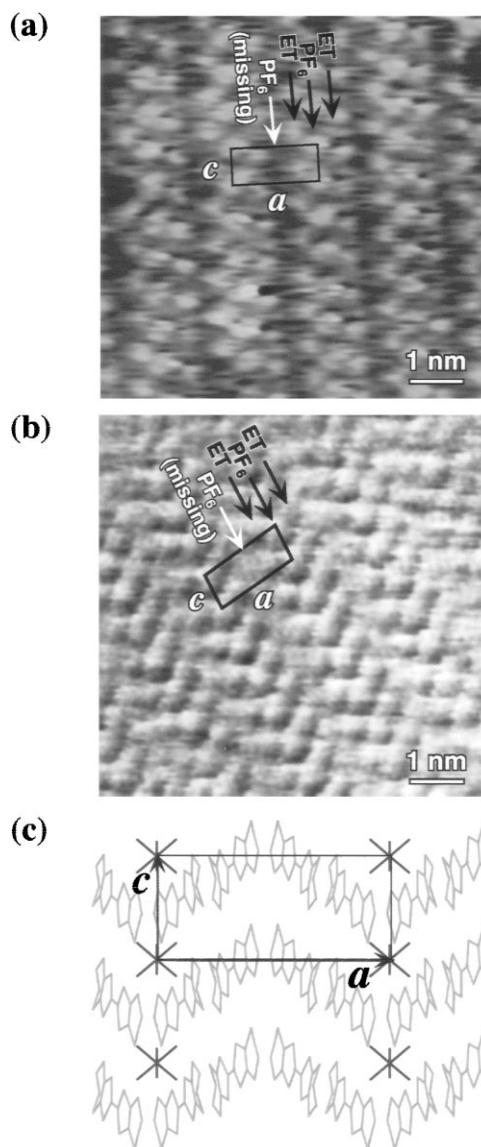


Fig. 2. (a) STM image ($7 \text{ nm} \times 7 \text{ nm}$, $V_s = 30 \text{ mV}$, $I_t = 0.46 \text{ nA}$, ET: BEDT-TTF) and (b) AFM image ($7 \text{ nm} \times 7 \text{ nm}$, $F_{\text{REF}} = 9.7 \text{ nN}$) of the β -(BEDT-TTF) $_2$ PF $_6$ surface with a PF $_6$ top layer. (c) Molecular arrangement of the PF $_6$ layer.

in the underlying layer are no longer uniform, and BEDT-TTF molecules that have greater charge (holes) must be pulled towards the PF $_6$ layer due to the ionic interactions.

On the basis of the experimental results shown in Fig. 3, a model can be constructed where BEDT-

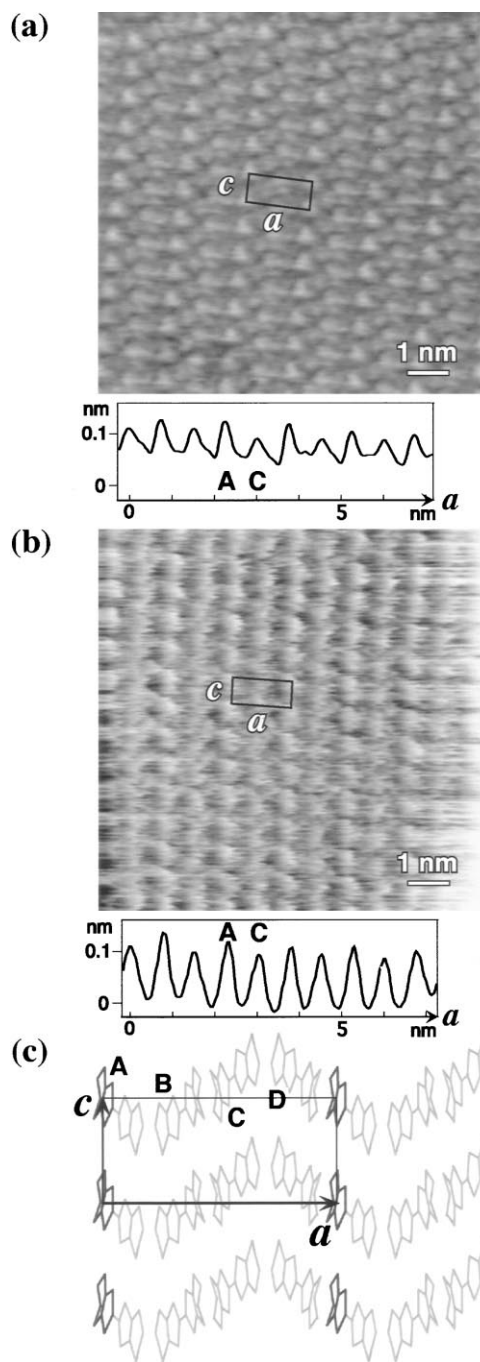


Fig. 3. (a) STM image ($9 \text{ nm} \times 9 \text{ nm}$, $V_s = -10 \text{ mV}$, $I_t = 0.25 \text{ nA}$) and (b) AFM image ($9 \text{ nm} \times 9 \text{ nm}$, $F_{\text{REF}} = 0.5 \text{ nN}$) of the β -(BEDT-TTF) $_2$ PF $_6$ surface with a BEDT-TTF top layer. (c) Molecular arrangement of the BEDT-TTF layer.

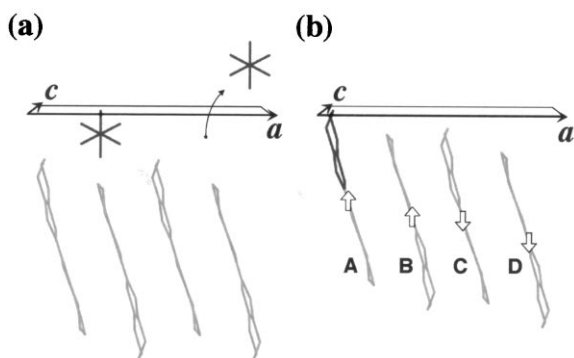


Fig. 4. Schematic model of the surface modulation for the surface with a (a) PF_6 and (b) BEDT-TTF top layers.

TTF molecules are rearranged in the dimer unit as shown schematically in Fig. 4b. Since the positional change observed is about 0.02 nm, upper dimers are expected to be imaged brightly. However, as described above, charge (holes) is considered to be transferred from the lower to the upper dimers. Therefore, when the charge transfer is completed, the upper dimers are ideally considered to become semiconductive.

The results obtained suggest that the surface modulation is governed not only by the charge compensation, but also by some other factor such as the elastic energy change induced by the modulation. This mechanism is generally accepted for the surface reconstruction in inorganic materials.

β -(BEDT-TTF) $_2$ PF $_6$ is known to show a metal–insulator transition with a charge density wave (CDW) at ~ 297 K [10]. Characteristic properties of CDW phase, such as periodicity of superstructures and critical temperature, depend on the amount of electronic charge and the dispersion of phonon modes. Since molecular arrangement must strongly influence the electronic and vibrational structures, the metal–insulator transition and related properties such as the formation of charge density wave may show new characteristics on this surface.

In summary, periodic modulation formed by

the alternate missing rows of PF_6 molecules was confirmed to exist on the anion layer of the β -(BEDT-TTF) $_2$ PF $_6$ surface. For the surface with a BEDT-TTF top layer, similar periodic modulation was observed to be formed by the combination of molecular and electronic structural changes. The observed surface modulations can be understood in terms of a charge-compensation mechanism similar to that found for surface reconstruction of inorganic surfaces.

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References

- [1] D.K. Biegelsen, R.D. Bringans, J.E. Northrup, L.-E. Schwarz, Phys. Rev. Lett. 65 (1990) 452.
- [2] M. Ishida, K. Hata, T. Mori, H. Shigekawa, Phys. Rev. B 55 (1997) 6773.
- [3] H. Shigekawa, K. Miyake, A. Miyauchi, M. Ishida, H. Oigawa, Y. Nannichi, R. Yoshizaki, T. Mori, Phys. Rev. B 52 (1995) 16361.
- [4] M. Ishida, K. Hata, T. Mori, K. Nakamoto, M. Iwatsuki, R. Yoshizaki, H. Shigekawa, Jpn J. Appl. Phys. 36 (1997) 3894.
- [5] S.N. Magonov, G. Bar, A.Y. Gorenberg, E.B. Yagubskii, H.-J. Cantow, Adv. Mater. 5 (1993) 453.
- [6] S.N. Magonov, G. Bar, H.-J. Cantow, J. Paradis, J. Ren, M.-H. Whangbo, E.B. Yagubskii, J. Phys. Chem. 97 (1993) 9170.
- [7] T. Mori, A. Kobayashi, Y. Sasaki, R. Kato, H. Kobayashi, Solid State Commun. 53 (1985) 627.
- [8] R.W. Nosker, P. Mark, Surf. Sci. 19 (1970) 291.
- [9] M. Tsukada, T. Hoshino, J. Phys. Soc. Jpn 51 (1982) 2562.
- [10] H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, H. Inokuchi, Chem. Lett. 1983 (1983) 759.