

Comparison of the Symmetry Breaking in the Surface Molecular Structures of One- and Two-Dimensional Bis(ethylenedithio)tetrathiafulvalene Compounds

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Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) were performed on the cationic molecular surfaces of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)-based organic conductors with one-dimensional (β -BEDT-TTF)₂AsF₆) and two-dimensional (κ -BEDT-TTF)₂Cu(NCS)₂) conductivity. For the β -BEDT-TTF)₂AsF₆ surface, highly similar STM/AFM images to those of β -BEDT-TTF)₂PF₆ were observed. Two types of alternately aligned molecular rows existed in the direction of the crystal *a*-axis; one is characterized by bright and distinct protrusions, and the other is a little darker with less distinct rows forming a zigzag structure. On the other hand, in the case of κ -BEDT-TTF)₂Cu(NCS)₂, similar one-dimensional modulation was confirmed by AFM for the first time in addition to the STM observation. However, the observed difference in the molecular images was only in their brightness, and their shapes were quite similar. Since the surface structures were confirmed by both STM and AFM, the obtained results indicate that the observed modulations are associated with the structural changes in the surface molecular arrangements. The modulations were discussed in relation to the crystal structures.

KEYWORDS: scanning tunneling microscopy, atomic force microscopy, bis(ethylenedithio)tetrathiafulvalene, surface structure, surface reconstruction, surface relaxation, molecular crystal, charge transfer salt

1. Introduction

On the surface of inorganic crystals, it is well known that the structures are modulated from the ideal ones due to surface reconstruction or surface relaxation. Generally, the total energy of the ideal surfaces is increased by the occurrence of chemical bond breaking, and marked changes such as atomic arrangement or modulation of the periodicity are induced, in order to reduce the surface energy. From this standpoint, structures that do not undergo chemical bond breaking on the surface, such as molecular crystals or layered materials, are considered to be stable. In fact, in contrast with inorganic crystals, most of the other materials actually exhibit less changes in the surface from the ideal structure.¹⁾ However, recently, using scanning tunneling microscopy (STM) and atomic force microscopy (AFM),²⁻⁸⁾ structural modulation introduced by surface relaxation and surface reconstruction has been observed on the surfaces of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) based low-dimensional organic conductors such as β -BEDT-TTF)₂PF₆⁶⁻⁸⁾ and κ -BEDT-TTF)₂Cu(NCS)₂.⁵⁾ In particular, in the case of β -BEDT-TTF)₂PF₆, a marked change is induced by the formation of ordered missing molecular rows. These results indicate that the ideal surface is not stable even for organic materials. The origin of the observed surface structures is related to the characteristics of these surfaces, such as polarity and charge transfer,^{9,10)} and the modulations were explained comprehensively by the same mechanism such as that used to describe the surface structures of inorganic material surfaces such as GaAs(111),¹¹⁾ MnO(111),¹²⁾ Si(001)¹³⁾ and GaAs(001).¹⁴⁾

However, some uncertainty still remains. In the case of β -BEDT-TTF)₂PF₆, which has one-dimensional (1D) conductivity, 1D characteristic modulation was observed by STM and AFM.⁶⁻⁸⁾ There exist two types of molecular rows alternately aligned in the direction perpendicular to the quasi-

1D axis (*c*-axis). One is characterized by the bright and distinct protrusions, and the other is a little darker and features less distinct rows forming a zigzag structure. On the other hand, in the case of κ -BEDT-TTF)₂Cu(NCS)₂, for example, which has two-dimensional (2D) conductivity, the existence of the modulation is still a topic of controversy.³⁻⁵⁾ One-dimensional modulation formed by the two types of ET molecular rows alternately aligned was pointed out by Shigekawa *et al.*,⁵⁾ however, according to Yoon *et al.*, modulation was observed for the surface terminated with the anion layer, and no structural change occurred on the surface terminated with ET molecules.^{3,4)}

As is well known, ET compounds are formed by the alternate stacking of two-dimensional (2D) cation and anion molecular layers, and through the charge transfer of 0.5 electrons from each ET molecule to the anion layers, ET and anion layers become conductive and insulating, respectively. The conductive cation (ET) layers govern the electronic properties of the materials, such as conductivity and phase transitions,¹⁵⁾ and their characteristic properties are strongly related to the molecular structure of the ET layers. Therefore, it is very important to study the molecular and electronic structures of the ET layers on an atomic scale. In consideration of the fact that the conductivity of the materials is 1D and 2D for β -BEDT-TTF)₂PF₆ and κ -BEDT-TTF)₂Cu(NCS)₂, respectively, the observed difference in modulation may be related to the dimension of the material conductivity.

From these points of view, we performed STM/AFM observation on the cationic molecular surfaces of β -BEDT-TTF)₂AsF₆¹⁶⁾ which has 1D conductivity like β -BEDT-TTF)₂PF₆,¹⁷⁾ and κ -BEDT-TTF)₂Cu(NCS)₂,¹⁸⁾ the structure of which is still controversial as described above.

2. Experimental and Results

2.1 Experimental

Single crystals of β -BEDT-TTF)₂AsF₆ and κ -BEDT-TTF)₂Cu(NCS)₂ were grown by the standard electrochemical oxidation method and fixed onto metallic plates with conduc-

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tive silver epoxy. STM/AFM measurements were performed on the surfaces terminated with the ET layer, in the topographic mode under ambient conditions using a mechanically sharpened Pt/Ir tip and a pyramidal Si₃N₄ tip, respectively. β -(BEDT-TTF)₂AsF₆¹⁶⁾ has a crystal structure and physical property similar to those of β -(BEDT-TTF)₂PF₆¹⁷⁾; conductivity is 1D and metal-insulator transition occurs at \sim 264 K. But its conductivity is more isotropic in the ET layers, because of the stronger interaction between 1D chains which is induced by the larger difference in the lattice parameters caused by As substitution. On the other hand, κ -(BEDT-TTF)₂Cu(NCS)₂ is one of the typical ET compounds with 2D conductivity and shows normal-superconducting phase transition at 10.4 K. Molecular arrangements in the ET layers of these crystals are schematically shown in Fig. 1.

2.2 Results of the β -(BEDT-TTF)₂AsF₆ surface

Figure 2(a) shows a topographic STM image obtained over the *a-c* plane of β -(BEDT-TTF)₂AsF₆ terminated with the ET layer. Dimensions of the unit cell estimated from the STM image, $a = 0.66$ nm, $c = 1.56$ nm, are in good agreement with the lattice parameters determined by the X-ray diffraction measurement, $a = 0.67$ nm, $c = 1.51$ nm.¹⁹⁾ No bias dependence was observed, reflecting the fact that no other molecular orbital contributes to the energy levels near the Fermi level, except for the highest occupied molecular orbital

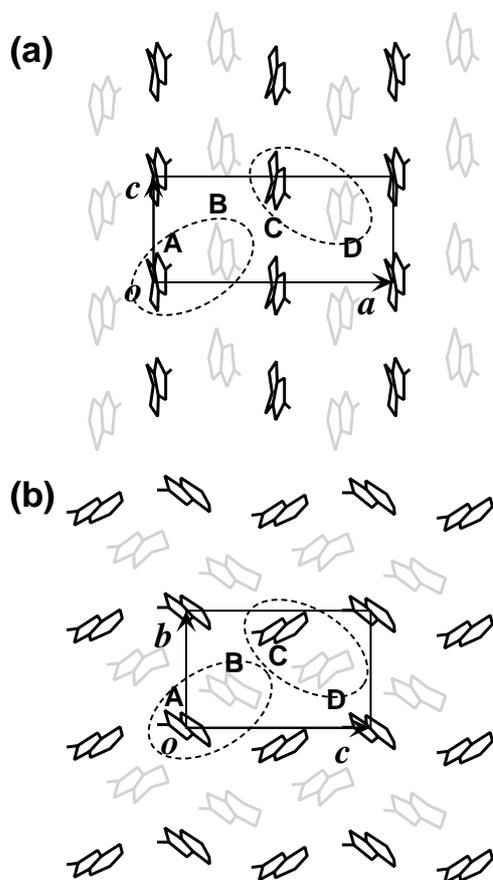


Fig. 1. Molecular arrangements of the ET layers of (a) β -(BEDT-TTF)₂AsF₆ and (b) κ -(BEDT-TTF)₂Cu(NCS)₂. The upper two rings in the ET molecule, which are closer to the surface, are shown in these models. Dotted circles indicate dimerization of the molecules in a unit cell. Molecules depicted by dotted lines are about 0.2 nm lower from the surface compared to the other molecules.

of ET which forms the conduction band of this material. A cross section along A-B is shown in the lower part of Fig. 2(a). Since the molecules are not aligned in a straight line along the crystal *a*-axis, the values were averaged over the unit cells in the square represented by the white dots in the figure.

As is shown in Fig. 2(a), the STM image is remarkably similar to that of β -(BEDT-TTF)₂PF₆. There are two types of molecular rows alternately aligned in the direction perpendicular to the quasi-1D axis (*c*-axis). One is characterized by bright and distinct protrusions (represented by open circles), and the other is a little darker and features less distinct rows

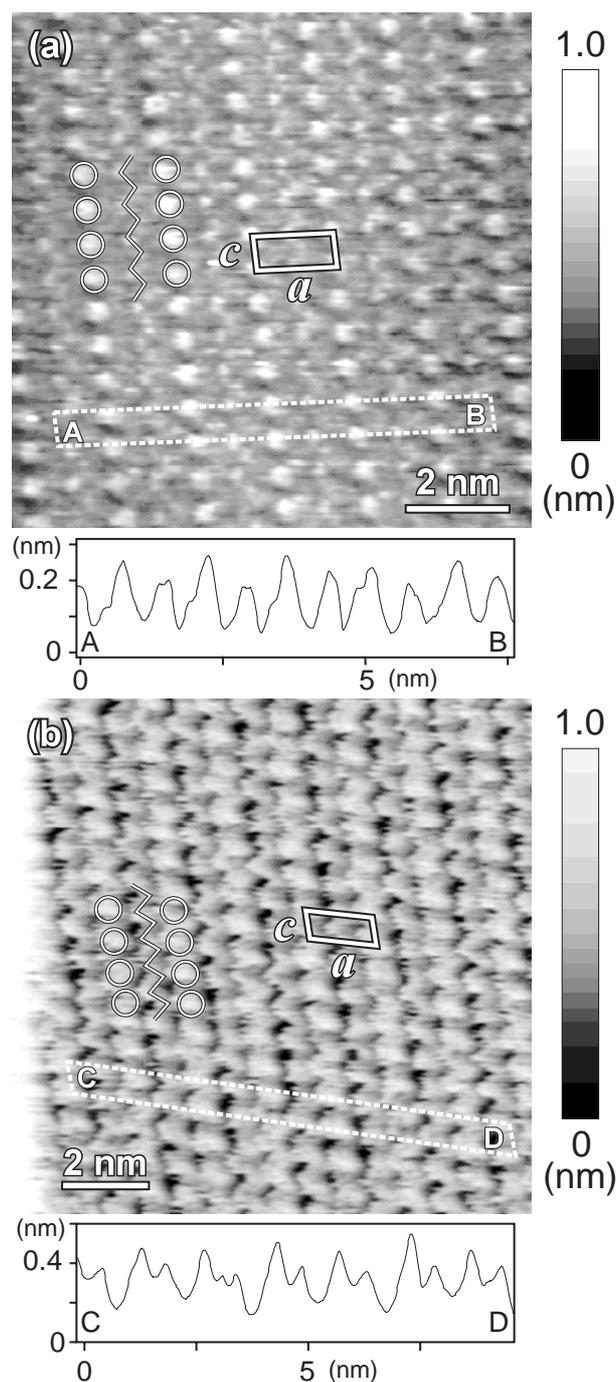


Fig. 2. (a) A topographic STM image obtained over the *a-c* plane of β -(BEDT-TTF)₂AsF₆ ($V_s = 40$ mV, $I_t = 0.3$ nA). Two types of molecular images are denoted by circles and a zigzag line. (b) A topographic AFM image obtained over the *a-c* plane of β -(BEDT-TTF)₂AsF₆ ($F_{REF} = 0.39$ nN). Two types of molecular images were also observed.

forming a zigzag structure, as shown in the figure. Since the STM image is strongly influenced by the electronic structure near the Fermi level, we performed AFM observation on this surface.

Figure 2(b) shows an example of the AFM image. As in Fig. 2(a), a cross section C-D, along the crystal *a*-axis, averaged over the unit cells, is shown. Dimensions of the obtained unit cell are $a = 0.66$ nm and $c = 1.50$ nm. The 1D modulation appearing in the STM image (Fig. 2(a)) was also observed by AFM, as shown in Fig. 2(b). If the ET surface retains its ideal structure, two molecular rows are expected to appear with the same height and shape in the AFM image. Therefore, the observed differences in the brightness and shape indicate direct evidence of a structural difference between the two types of molecular rows.

2.3 Results of the κ -(BEDT-TTF)₂Cu(NCS)₂ surface

Figure 3(a) shows a topographic STM image obtained over the *b*-*c* plane of κ -(BEDT-TTF)₂Cu(NCS)₂. Dimensions of the obtained unit cell are estimated as $b = 1.31$ nm, $c = 0.83$ nm, and agree well with the lattice parameters, $b = 1.31$ nm, $c = 0.84$ nm, determined from the X-ray diffraction patterns. An interesting characteristic of this image is that the four molecules in a unit cell (denoted in the inset) are observed with almost identical shape, but their brightness differs. The observed difference of the four molecules in the unit cell is quite similar to the previous results obtained by Yoshimura *et al.*,²²⁾ as opposed to the results of Yoon *et al.*,⁴⁾ in which the two dimers in a unit cell were imaged similarly. As a result of the modulated brightness, 1D modulation along the *b*-axis appears in spite of its 2D crystal structure. In order to confirm the observed modulation, we performed AFM observation on this surface.

Figure 3(b) shows a typical topographic AFM image of the surface. Dimensions of the unit cell were estimated to be $b = 1.30$ nm, $c = 0.93$ nm. Contrary to the result of Yoon *et al.*,⁴⁾ the obtained AFM image in Fig. 3(b) shows a striking similarity to the STM image in Fig. 3(a), not only in the arrangement of the protrusions but also in the modulated 1D structure. We confirmed the reproducibility of this structure through observations of a mica surface using the same AFM tip.

The height difference of the four molecules observed by STM/AFM is summarized in Fig. 3(c). They are the values acquired at the highest positions on each of the four molecules, which were averaged over the unit cells in the STM/AFM images. This result indicates that the modulated 1D structure in this 2D material also includes a structural change similar to that observed for the ET surface with 1D conductivity, β -(BEDT-TTF)₂AsF₆. However, in the case of κ -(BEDT-TTF)₂Cu(NCS)₂, the observed breaking of symmetry in the molecular structure was recognized only by the brightness of the protrusions. The additional modulation in the molecular shape that appeared in the case of β -(BEDT-TTF)₂AsF₆ was not observed.

3. Discussion

From the STM and AFM investigations of the surfaces of the ET compounds with different anisotropy, β -(BEDT-TTF)₂AsF₆ and κ -(BEDT-TTF)₂Cu(NCS)₂, the 1D modulation consisting of two types of ET dimers appears to be a common characteristic of typical ET-surface structure. The mod-

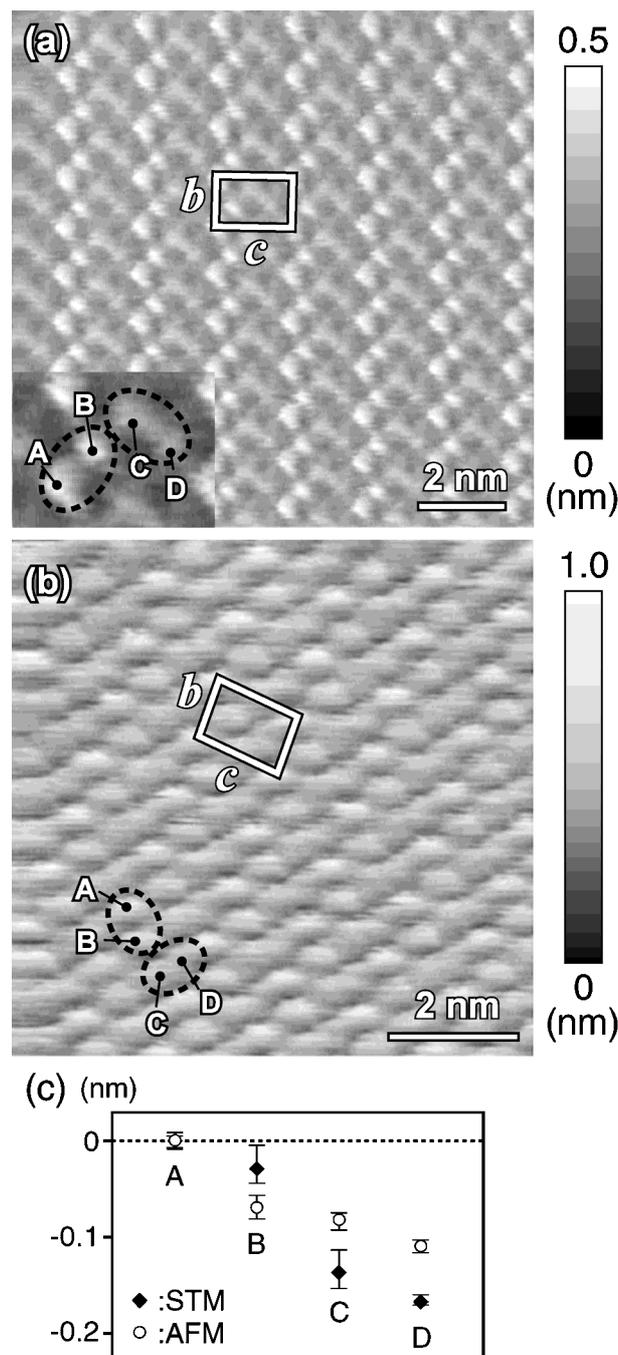


Fig. 3. (a) A topographic STM image obtained over the *b*-*c* plane of κ -(BEDT-TTF)₂Cu(NCS)₂ ($V_s = -30$ mV, $I_t = 0.55$ nA). Four different types of molecules in a unit cell are denoted by A-D in the inset. (b) A topographic AFM image obtained over the *b*-*c* plane of κ -(BEDT-TTF)₂Cu(NCS)₂ ($F_{REF} = 0.27$ nN).

ulations are considered to originate from the breaking of symmetry of the ET dimer structure in a unit cell. However, there exists a noteworthy structural difference between the modulations observed in the two kinds of crystals with 1D- and 2D-conductivity. In the case of the β -(BEDT-TTF)₂AsF₆ surface, the difference between two kinds of dimer rows is not only in the brightness but also in their shape in the molecular image; molecules in the bright dimer rows are imaged as a distinct protrusion, but molecules in the darker rows are imaged as a continuous protrusion along the 1D-axis. The modulation observed here can be seen in the STM images of other previously reported ET compounds with 1D anisotropy, for example, α -(BEDT-TTF)₂I₃,²⁰⁾ (BEDT-TTF)₂TiHg(NCS)₄,²¹⁾ and

β -(BEDT-TTF)₂PF₆.⁶⁻⁸⁾ Taking into account these facts, the observed modulation is considered to be a common phenomenon in the ET-based compounds with 1D anisotropy. On the other hand, in the case of κ -(BEDT-TTF)₂Cu(NCS)₂, the observed breaking of symmetry of the molecular images is recognized only by the brightness of the protrusions.

In consideration of the fact that the conductivity of the materials, the observed difference in their surface modulations may be related to the symmetry of the material conductivity. In order to understand this point in further detail, we compare the obtained results with that of β -(BEDT-TTF)₂I₃ with 2D conductivity, reported in previous papers.^{2,23,24)}

In the previous studies on the β -(BEDT-TTF)₂I₃ surface terminated with ET molecules, the existence of surface reconstruction was noted,²⁾ but no 1D-type modulations were observed in contrast to the case of κ -(BEDT-TTF)₂Cu(NCS)₂. The surface reconstruction observed for β -(BEDT-TTF)₂I₃ appears to occur dominantly in the surface plane.^{2,24)} Since both κ -(BEDT-TTF)₂Cu(NCS)₂ and β -(BEDT-TTF)₂I₃ have 2D-conductivity, some other mechanism is required to explain the difference between them. In order to consider this point, let us see the molecular structures of these two crystals.

Figure 4 shows the molecular structures of the ET layer of (a) β -(BEDT-TTF)₂I₃ and (b) κ -(BEDT-TTF)₂Cu(NCS)₂. The arrangement of the ET molecules in β -(BEDT-TTF)₂I₃ appears less isotropic compared to that of κ -(BEDT-TTF)₂Cu(NCS)₂. Therefore, the difference in the structural modulation may be understood as being related to the structural isotropy. Namely, the stronger anisotropic interactions between neighboring molecules may suppress the flexible relaxation of the surface structure. Further study is necessary to clarify the relation between the anisotropic crystal structures and the types of symmetry breaking on the surfaces.

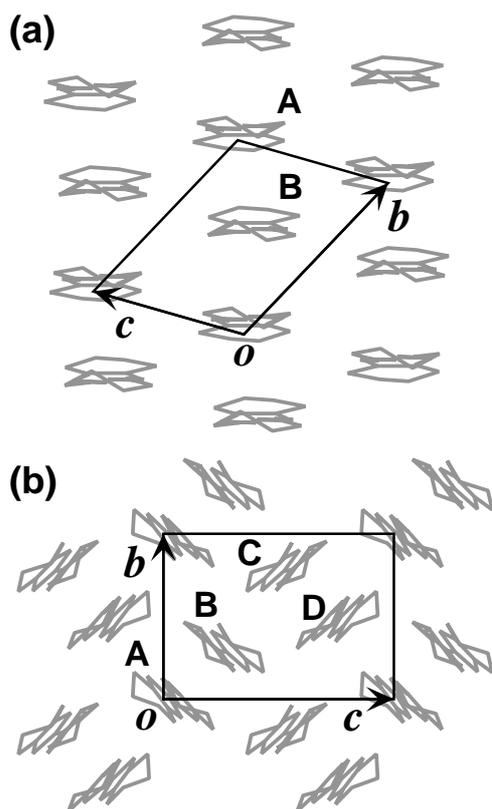


Fig. 4. Molecular arrangements of the ET layers of (a) β -(BEDT-TTF)₂I₃ and (b) κ -(BEDT-TTF)₂Cu(NCS)₂.

4. Conclusion

We performed STM and AFM observations on β -(BEDT-TTF)₂AsF₆ and κ -(BEDT-TTF)₂Cu(NCS)₂, which have 1D and 2D conductivity, respectively. Characteristic 1D structures were observed for both cases, but the details were remarkably different. In the case of β -(BEDT-TTF)₂AsF₆, we found two types of molecular rows alternately aligned in the direction perpendicular to the quasi-1D conductive axis (*c*-axis). One is characterized by bright and features distinct protrusions, and the other is a little darker and less distinct rows forming a zigzag structure. The modulation structure is quite similar to that previously observed on the surface of 1D materials. On the other hand, in the case of κ -(BEDT-TTF)₂Cu(NCS)₂, the modulation was observed only in the brightness of the molecules, and the molecules were imaged in a similar shape. In comparison with the result on the case of β -(BEDT-TTF)₂I₃, molecular arrangement which is related to the anisotropy of the molecular interaction must be taken into account in the case of 2D materials. Further study is necessary.

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