

# The surface structure of an organic conductor (BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> observed by scanning tunneling microscopy

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The bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecules in the surface cation layer of the (BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> crystal were observed by scanning tunneling microscopy (STM). The obtained arrangement of BEDT-TTF was in good agreement with that expected from the structure determined by X-ray diffraction. In addition, some subsidiary images were observed around the K and Hg ion positions. The STM image of the BEDT-TTF molecules was influenced by the structure of the anion layer on them, and they showed a strong bias dependence.

## 1. Introduction

Organic superconductors have received considerable attention because of their high potential designability. Among the organic superconductors, some of the bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) compounds have shown the high  $T_c$  (for example,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> shows the highest  $T_c$  (10.4 K)). The crystals consist of alternating stack of the cation layer of

(BEDT-TTF) and an anion layer, the Cu(NCS)<sub>2</sub> layer for example. The BEDT-TTF salts have a nearly two-dimensional character, as do the high  $T_c$  inorganic superconductors [1–5]. Regarding the superconductivity which appears in the two-dimensional BEDT-TTF salts, the anion layer thickness is known to have an important role when the anions form a rigid polymer in a bridged anion sheet [6]. Since the KHg(SCN)<sub>4</sub> layer is rather thick, about 0.7 nm, compared with other anion layers, it is interesting to compare the electronic structure of the (BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> with the other BEDT-TTF compounds such as  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> [6–10].

Since the surface of (BEDT-TTF) compounds have a layer structure and their surfaces are very

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stable, investigation of the surface structure by STM (scanning tunneling microscopy) is expected to offer useful information for our understanding of the bulk electronic structure.

In this paper, we report the surface structure of  $(\text{BEDT-TTF})_2\text{KHg}(\text{SCN})_4$  observed by STM.

## 2. Crystal structure

In the  $(\text{BEDT-TTF})_2\text{KHg}(\text{SCN})_4$  crystal, BEDT-TTF molecules form conductive two-dimensional sheets in the  $ac$ -plane which are sandwiched by the insulating layers of the anion,  $\text{KHg}(\text{SCN})_4$ , along the  $b$ -axis (figs. 1(a) and (b)). The crystal has a triclinic structure;  $a = 1.0082$  nm,  $b = 2.0565$  nm,  $c = 0.9933$  nm,  $\alpha = 103.70^\circ$ ,  $\beta = 90.91^\circ$ ,  $\gamma = 93.06^\circ$ ,  $V = 1.997$  nm<sup>3</sup>. The BEDT-TTF molecules are not dimerized in this crystal as is the case in the  $\kappa$ - $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  crystal. There are four BEDT-TTF molecules in the unit cell. The BEDT-TTF molecules array linearly along the crystal  $c$ -axis. An anion layer consists of a triple-sheet parallel to (010). The bottom and top sheets are made of zigzag arrays of linearly arranged SCN molecules. The middle sheet contains both K and Hg ions, where one of the two K ions in the unit cell is electrostatically linked to four SCN groups in the bottom sheet with nitrogen atoms to form a pyramid. The other K ion forms a pyramid in the same way with the SCN ions in the top sheet (fig. 1(b)). The Hg ions are coordinated to four SCN

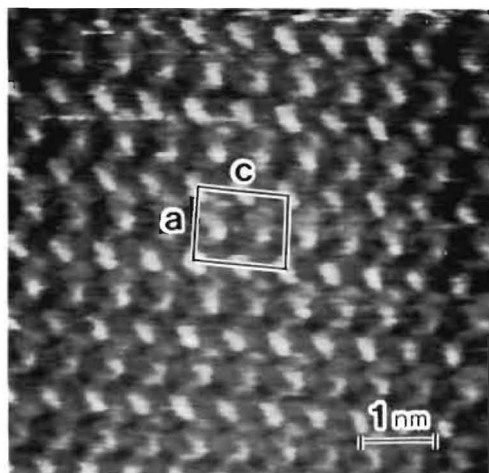


Fig. 2. A  $6.5 \times 6.5$  nm<sup>2</sup> image of the  $(\text{BEDT-TTF})_2\text{KHg}(\text{SCN})_4$  surface obtained over the  $ac$ -plane at the sample bias of 18.3 mV. A unit cell is drawn.

ions, two of them in the bottom and the others in the top sheet, with sulfur atoms to form tetrahedra (fig. 1(b)). Since the surface stability of this crystal can be realized by the  $\text{KHg}(\text{SCN})_2$  anions which frame the BEDT-TTF molecules, the topmost surface layer of the stably observed specimen is considered to be the insulation layer.

## 3. Experimental results and discussion

A single crystal with a distorted hexagonal shape (2 mm  $\times$  1 mm  $\times$  0.2 mm) was prepared by

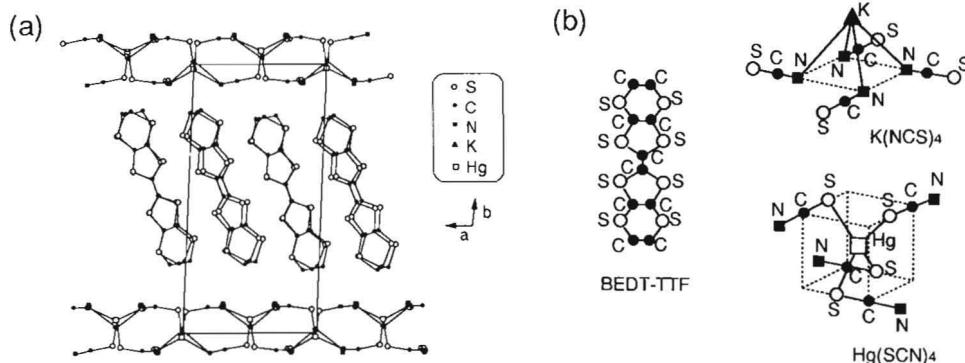


Fig. 1. (a) Crystal structure of  $(\text{BEDT-TTF})_2\text{KHg}(\text{SCN})_4$  determined by X-ray diffraction. (b) Molecular structure of BEDT-TTF,  $\text{K}(\text{NCS})_4$  and  $\text{Hg}(\text{SCN})_4$ .

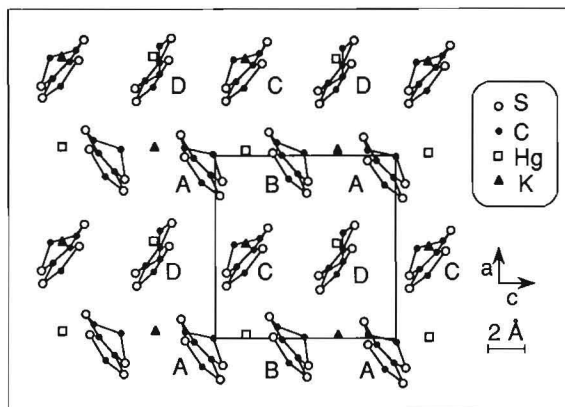


Fig. 3. The arrangement of the upper half of the BEDT-TTF molecules projected onto the crystal  $ac$ -plane. The K and Hg ion positions are also marked.

the electrocrystallization of BEDT-TTF in the presence of  $Hg(SCN)_2$ , KSCN and the crown in 1,1,2-trichloroethane and 10 vol.% ethanol under 1  $\mu A$ . The STM observation was performed in air and at room temperature over the crystal  $ac$ -plane using a Pt-Ir tip. No particular surface treatment was carried out except rinsing in deionized water.

Fig. 2 shows a current image taken at the sample voltage of 18.3 mV. A periodic zigzag structure was observed along the crystal  $a$ -axis,

which consisted of alternate protrusions with different shapes and brightness. Since almost the same image was obtained for the inverse tunneling voltage ( $-18.3$  mV), the electronic structure of the surface obtained was revealed to be metallic. These results also suggest that the STM image reflects not the structure of the  $KHg(SCN)_4$  insulating layer but the structure of the BEDT-TTF conductive layer. Fig. 3 shows the top view of the BEDT-TTF cation layer, where the positions of the K and Hg ions in the top anion layer are also marked. The four BEDT-TTF molecules in a unit cell are labelled as A to D. They have different shapes and the molecules labeled C and D have the K or Hg ion on them. The STM image of protrusions C and D are expected to be modified by the existence of those K and Hg ions. According to the result of the *ab initio* calculation [11], the highest occupied molecular orbital of the BEDT-TTF molecule has big lobes around the S atoms, and they stand perpendicular to the molecular plane. Since the STM image mainly reflects the surface structure, it is sufficient to only consider the lobes which stand out from the top ring closest to the surface anion layer (fig. 1(a)). When the molecular plane is tilted from the normal axis to the  $ac$ -plane, the STM image becomes asymmetric. The calcula-

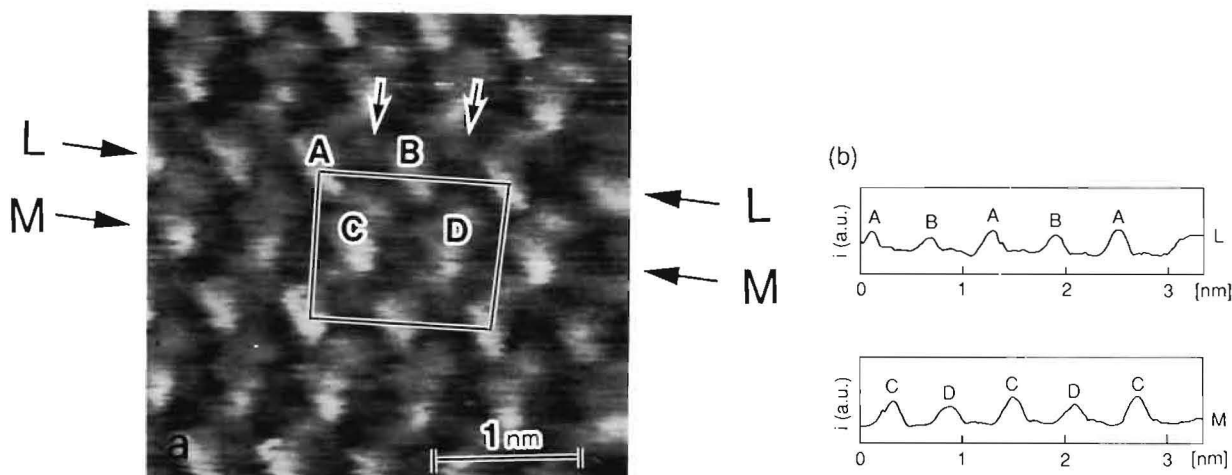


Fig. 4. (a) A magnified image ( $3.5 \times 3.5$  nm<sup>2</sup>) obtained at the sample voltage of 18.3 mV. Labels A to D correspond to those drawn in fig. 3. The arrays show the position of the subsidiary protrusion. (b) The cross sections along line L and M in fig. 4(a)

tion also showed that the size of the lobe increases with the degree of distortion of the hexagonal ring in the molecule. Regarding molecules A and B, the top hexagonal ring in molecule A has a bigger tilt angle and is more distorted. Also, the S atom in the top hexagonal ring of the BEDT-TTF molecule A is closer to the surface. Therefore, the STM image of molecule A is expected to be brighter and more asymmetric in shape and brightness.

Fig. 4(a) shows the magnified image and fig. 4(b) shows the line profiles of the protrusions on lines L and M in fig. 4(a). Four types of protrusions with different shapes and brightness can be observed; as is shown in fig. 4(a), the images on L are much sharper, while the image on M is rather distorted, and STM images of the protrusions on both lines are alternately bright and less bright (fig. 4(b)). According to the molecular structure written above, we attribute those four images to molecules A to D in fig. 3, as shown in fig. 4(a).

The stronger asymmetry in the brightness of the STM images observed for molecules A (fig. 4(a)) is in good agreement with the electronic structure expected from their bigger tilt angle as written above. The unit cell size obtained (fig. 4(a)) is  $0.98 \text{ nm} \times 1.2 \text{ nm}$  and is very close to that determined by X-ray diffraction ( $1.0082 \text{ nm} \times 0.9933 \text{ nm}$ , fig. 3). The difference in the brightness of the STM images between the molecules labeled C and D is supposed to be due to the difference in the anion structure on them. In addition, as is marked in fig. 4(a), some subsidiary images are observed at the positions of K and Hg ions between molecules A and B.

If the distorted STM images of molecules C and D are due to the influence of the surface anion layer, the degree of modification is expected to be reduced by increasing the tunneling bias. Figs. 5(a) and (b) show the results obtained at the sample voltage of 3.1 mV and 33.9 mV, respectively.

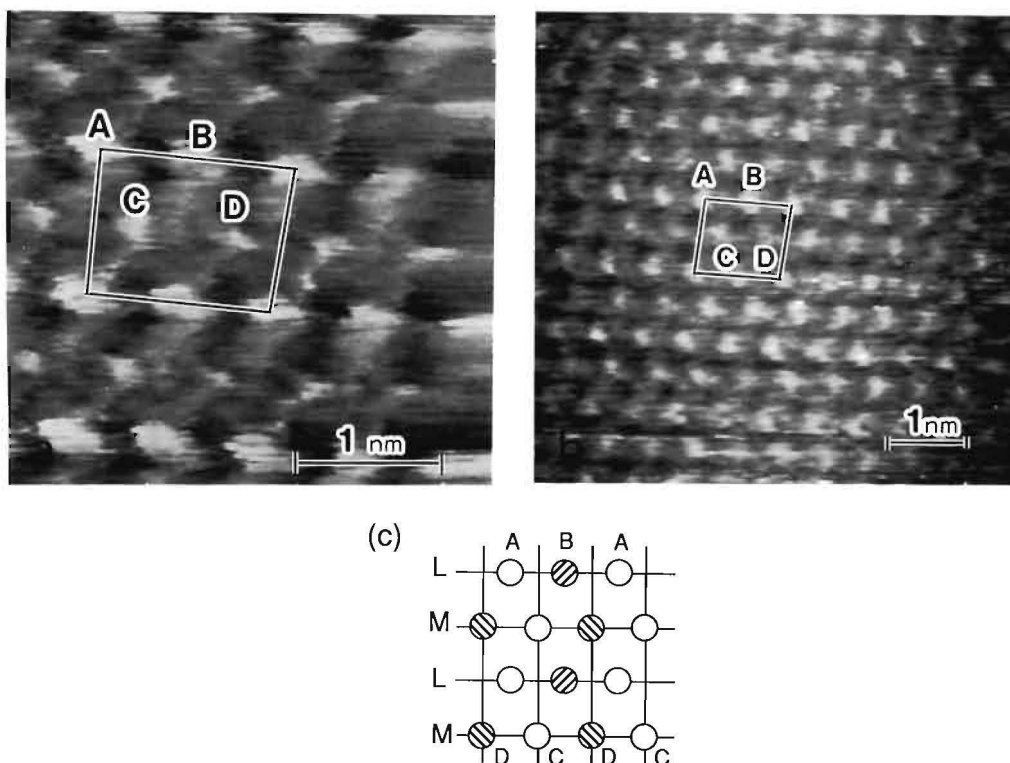


Fig. 5. STM images obtained at; (a) the lower tunneling voltage (3.1 mV) and (b) the higher voltage (33.9 mV). The scan area is: (a)  $3.5 \times 3.5 \text{ nm}^2$ , (b)  $6.5 \times 6.5 \text{ nm}^2$ . (c) Schematic representation of the latticelike structure observed in fig. 5(b).



tively. When the tunneling voltage was decreased, the images lost their sharpness, especially around molecules C and D (fig. 5(a)). For the higher voltage, the zigzag structure along the *a*-axis seemed to disappear and the image became rather simple (fig. 5(b)). Each protrusion had a similar round shape but the difference in brightness was still observed. Some additional structure appeared between the BEDT-TTF molecules, which formed the latticelike structure, as is shown schematically in fig. 5(a). Molecules C and D sit on the cross of the lattice while molecules A and B sit on the line between the crosses (fig. 5(c)).

Theoretical calculations of the electronic structure of the crystal surface are necessary in order to understand the image further.

#### 4. Conclusions

The surface structure of the (BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> crystal was observed by scanning tunneling microscopy. The molecular arrangement observed was in good agreement with the BEDT-TTF molecular structure determined by X-ray diffraction, some of which were strongly influenced by the anion layer on them. In addition to the BEDT-TTF molecules, some subsidiary images were observed at the K and Hg ion positions. A strong tunneling bias voltage dependence of the STM image was also observed.

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