

Imaging of an organic superconductor $(\text{BEDT-TTF})_2(\text{NH}_4)\text{Hg}(\text{SCN})_4$ surface structure by scanning tunneling microscopy

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The STM image of the two-dimensional organic superconductor $(\text{BEDT-TTF})_2(\text{NH}_4)\text{Hg}(\text{SCN})_4$ [BEDT-TTF:bis(ethylenedithio)tetrathiafulvalene] crystal showed a periodic structure, which is in good agreement with the molecular arrangement with the conductive BEDT-TTF layer in the crystal. The influence of the top anion layer on the STM image was observed, as was previously shown for the $(\text{BEDT-TTF})_2\text{KHg}(\text{SCN})_4$ crystal. The high stability of this surface has also been revealed.

I. INTRODUCTION

The second-generation organic superconductors of the BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] family have layer structures and consist of the alternating stacking structure of BEDT-TTF cation layers and anion layers such as $\text{Cu}(\text{NCS})_2$, I_3 , and $\text{KHg}(\text{SCN})_4$.¹⁻³ It is known that the critical temperature (T_c) of the superconductivity of these materials depends strongly on the structure of the anion layers. For example, β - $(\text{BEDT-TTF})_2\text{I}_3$ shows various phases with different T_c due to the instability of its anion layers.⁴ According to the STM (scanning tunneling microscopy) study of this material,⁵ there are many vacancies of BEDT-TTF molecules, and the surface is reconstructed. Since the anion layer of $(\text{BEDT-TTF})_2(\text{NH}_4)\text{Hg}(\text{SCN})_4$ has a quasi-three-dimensional framework structure and the BEDT-TTF molecules are sandwiched by these anion networks, imaging of the surface structure with very few defects can be expected by STM observation, as is the case for the $(\text{BEDT-TTF})_2\text{KHg}(\text{SCN})_4$ crystal.⁶ In this paper, we report the result of the observation of the surface of an organic superconductor, $(\text{BEDT-TTF})_2(\text{NH}_4)\text{Hg}(\text{SCN})_4$, by STM. The STM image corresponding to the molecular structure of the BEDT-TTF layer, which was arranged perfectly in a wide range, was observed.

II. CRYSTAL STRUCTURE

The crystal of $(\text{BEDT-TTF})_2(\text{NH}_4)\text{Hg}(\text{SCN})_4$ has triclinic structure and the crystal data are as follows: $a = 1.0091$ nm, $b = 2.0595$ nm, $c = 0.9963$ nm, $\alpha = 103.65^\circ$, $\beta = 90.53^\circ$, $\gamma = 93.30^\circ$, $V = 2.0081$ nm³.⁷ Figure 1 shows the crystal structure viewed from the crystal ab -plane. The BEDT-TTF layer is framed by that of $(\text{NH}_4)(\text{SCN})_4$ and $\text{Hg}(\text{SCN})_4$ molecules which consist of a quasi-three-dimensional network of about 0.7 nm in thickness. The BEDT-TTF molecules are tilted by about 13° from the ac -plane. The electron transfer from the BEDT-TTF layer to the $(\text{NH}_4)\text{Hg}(\text{SCN})_4$ layer makes the former layer

conductive and the latter insulative. The topmost layer is expected to be the anion layer, as was determined for the $(\text{BEDT-TTF})_2\text{KHg}(\text{SCN})_4$ crystal.⁶ Figure 2 shows the molecular arrangement of the BEDT-TTF viewed from the ac -plane, where the positions of NH_4 and Hg ions in the anion layer are also overlapped. Four BEDT-TTF molecules (A, B, C, and D) with different shapes exist in the unit cell drawn in the figure. Two of these (C and D) have the NH_4 or Hg ion on them, while the others (A and B) are positioned between the ions. The STM images of molecules C and D are influenced by the ions on them.

III. EXPERIMENT

The single crystal of $(\text{BEDT-TTF})_2(\text{NH}_4)\text{Hg}(\text{SCN})_4$ used in this study was prepared by the conventional electrochemical oxidation of BEDT-TTF in the presence of $(\text{NH}_4)\text{SCN}$, $\text{Hg}(\text{SCN})_2$ and 18-crown-6 ether in 1,1,2-trichloroethane (TCE) and ethanol.⁷ The dimensions of the sample obtained were $1 \times 2 \times 0.3$ mm.³ The sample was at-

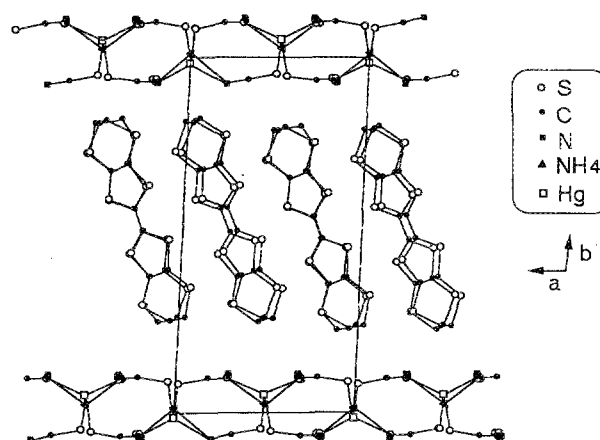


FIG. 1. The crystal structure of $(\text{BEDT-TTF})_2(\text{NH}_4)\text{Hg}(\text{SCN})_4$.

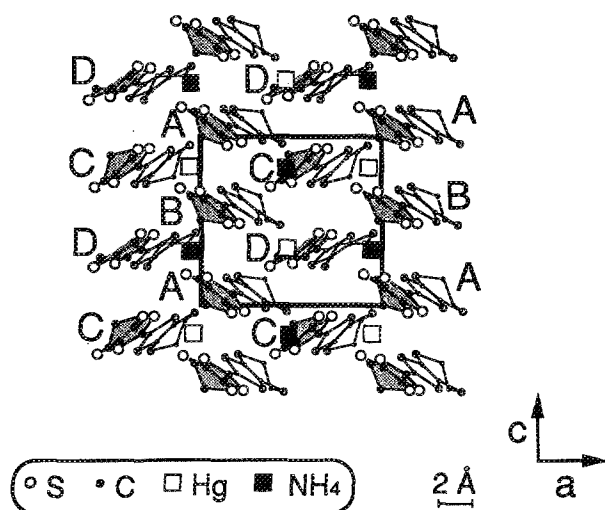


FIG. 2. The top view of the BEDT-TTF molecular arrangement in the ac -plane. The positions of Hg and NH_4 ions in the anion layer are also marked.

tached to a copper plate with conductive silver epoxy after rinsing in deionized water. The STM measurement was performed in air and at room temperature. A platinum-iridium tip was used for probing the tunneling current from/to the surface of the sample.

IV. RESULTS AND DISCUSSION

Figure 3(a) shows a topographic image over a wide $120 \times 120 \text{ nm}^2$ area at a sample voltage of 50 mV and a constant current of 4.1 nA. Step structures were observed along

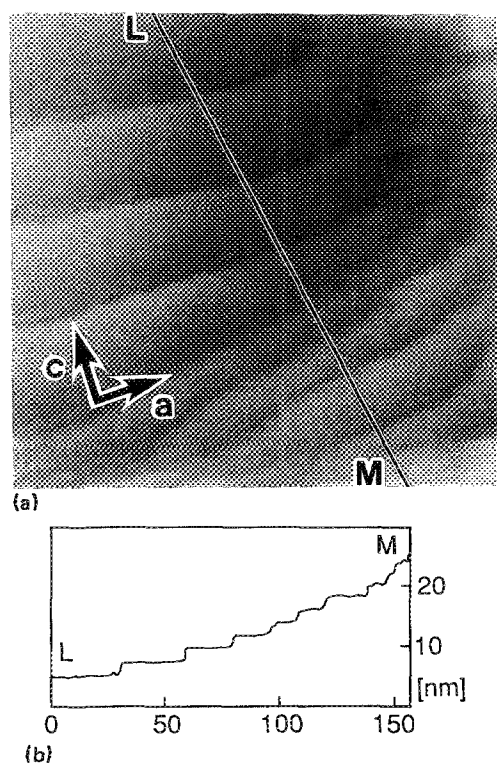


FIG. 3. (a) A $120 \times 120 \text{ nm}$ topographic image over the crystal ac -plane (50.0 mV, 4.1 nA); (b) the cross section along the line LM drawn in (a).

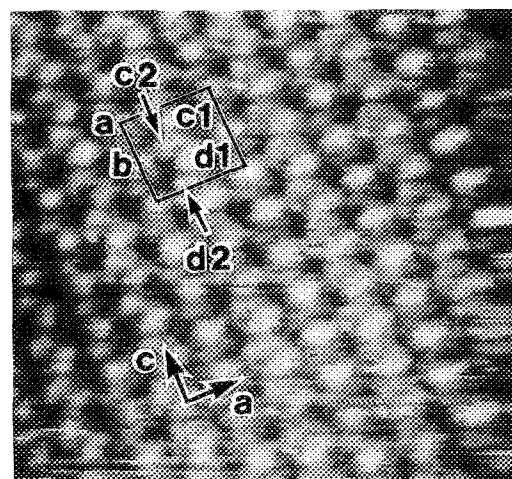


FIG. 4. A $6 \times 6 \text{ nm}$ current image at a sample voltage of 40.2 mV. The unit cell is drawn.

the a -axis. Steps along the c -axis were not observed in all of the images. This may indicate that the interaction between the BEDT-TTF molecules is stronger along the c -axis. This is in good agreement with the result of the tight binding calculation of the HOMO overlap integrals⁷ where the interactions A-D and B-C are stronger than those of other couplings.

The cross section along the line L-M is shown in Fig. 3(b). The step height is about 2.0–2.2 nm and is close to the value of the lattice parameter along the b^* -axis (perpendicular to the ac -plane), 1.9975 nm. This shows that the step structure in the image consists of a monolayer step of the $(\text{BEDT-TTF})_2 (\text{NH}_4)\text{Hg}(\text{SCN})_4$ crystal.

Figure 4 shows a $6 \times 6 \text{ nm}^2$ current image at a sample voltage of 40.2 mV scanned over the crystal ac -plane. A periodic structure can be observed. There are four kinds of bright protrusions (a , b , $c1$, and $d1$) and two less bright ones ($c2$ and $d2$) in the unit cell, as is drawn in Fig. 4. The brightness of a and b is almost the same, while $c1$ is brighter than $d1$. The observed size of the unit cell is $1.18 \times 1.09 \text{ nm}^2$. This is in good agreement with that in the crystal ac -plane. According to the *ab initio* calculation on the BEDT-TTF molecule,⁸ the highest occupied molecular orbital (HOMO),

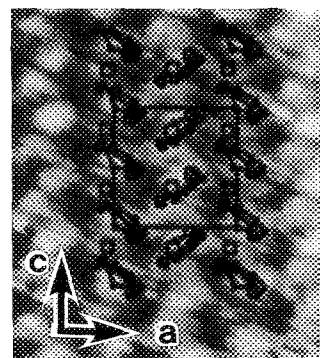


FIG. 5. A magnification image superposed with the corresponding arrangement of BEDT-TTF molecules and ions in the anion layer.

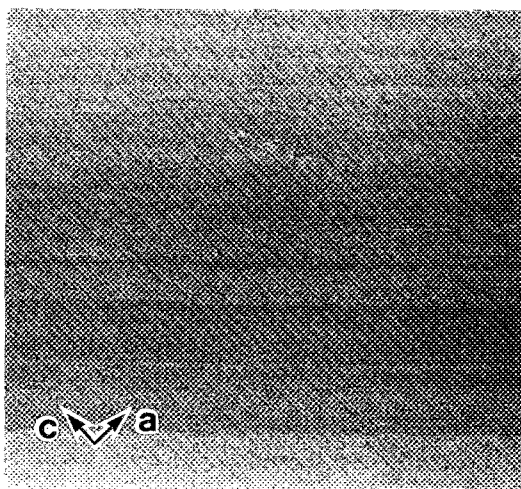


FIG. 6. A 50×50 nm high-resolution topographic image (40 mV, 4.1 nA).

which will contribute to the tunneling current, is concentrated on the eight sulfur atoms and six carbon atoms of the central TTF part. Since we scanned over the *ac*-plane, the electronic structure of the two sulfur atoms of the top hexagonal ring of the BEDT-TTF molecule nearest to the surface most affects the tunneling current. When the tilt angle of the molecules is larger, the lobes from S atoms become closer to the surface and their STM image must be brighter.

Since the difference in the tilt angle of molecules A and B is very small and those molecules have no anions on them, the STM images of those molecules are expected to be similar. However, for molecules C and D, as the tilt angle of molecule D is much smaller than that of molecule C, the STM image of molecule D is expected to be darker than that for C. Besides, as molecules C and D have ions on them, the STM images of those molecules must have some modification in their shape.

Taking the above molecular conditions into account, we assign the protrusions *a*, *b*, *c*1, and *d*1 observed in the image to molecules A through D in Fig. 2, respectively (Fig. 5). In addition, we consider that protrusions *c*2 and *d*2 result from molecules C and D due to the modification by the anions on them.

Figure 6 shows a wide-scan high-resolution image obtained at a sample voltage of 40 mV and a constant current of

4.1 nA (50×50 nm²) and without any image processing. Individual BEDT-TTF molecules are clearly observed without any defects. The lines along the horizontal axis are tip artifacts. This stable structure is in contrast to the image of β -(BEDT-TTF)₂I₃, in which many vacancies of BEDT-TTF molecules were observed.⁵ The stability of the surface structure is considered to be realized by the stable anion structure which frames the BEDT-TTF molecules. In the case of β -(BEDT-TTF)₂I₃, the I₃ molecules are weakly bonded to each other, forming the one-dimensional thin polymer structure, while the rigid quasi-three-dimensional structure of anion molecules are formed in a (BEDT-TTF)₂(NH₄)Hg(SCN)₄ crystal.

V. CONCLUSIONS

The surface structure of the (BEDT-TTF)₂(NH₄)Hg(SCN)₄ crystal was observed by scanning tunneling microscopy. The image obtained had a periodic structure and was in good agreement with the bulk arrangement of BEDT-TTF molecules. It was confirmed that the topmost layer of this crystal was the insulative anions of (NH₄)Hg(SCN)₄ and influenced the STM image. A stable surface without any defects was also observed over a wide scan range, reflecting the stability of the anion layer located on the top of the surface.

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