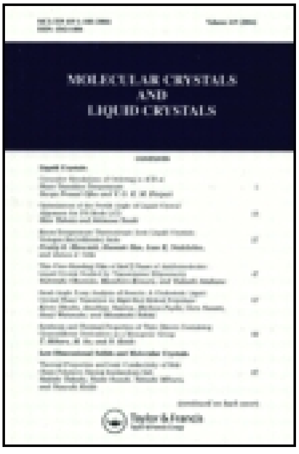

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Scanning Tunneling Microscopy Study of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and α(BEDT-TTF)$_2$I$_3$

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Version of record first published: 24 Sep 2006.

Mol. Cryst. Liq. Cryst., 1991, Vol. 196, pp. 161–165
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Printed in the United States of America

Scanning Tunneling Microscopy Study of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ and α-$(BEDT\text{-}TTF)_2I_3$

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(Received August 16, 1990; in final form September 28, 1990)

Scanning tunneling microscopy (STM) measurements were performed for bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF)-based radical salts, κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ and α-$(BEDT\text{-}TTF)_2I_3$. Each STM image agreed well with the corresponding bulk structure determined by X-ray diffraction method.

Keywords: Scanning tunneling microscopy; superconductors; bis(ethylenedithio)tetrathiafulvalene; κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$; α-$(BEDT\text{-}TTF)_2I_3$

INTRODUCTION

The organic compound bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is known to form a large variety of charge transfer salts with transport properties ranging from semiconducting, to metallic, to superconducting.[1] The κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ crystal undergoes a superconducting transition at 10.4 K.[2] On the other hand, α-$(BEDT\text{-}TTF)_2I_3$ undergoes a metal-insulator transition at 135 K.[3] The superconducting transition is observed at 6 K for the thermally annealed samples (α_t-$(BEDT\text{-}TTF)_2I_3$).[4]

Scanning tunneling microscopy (STM) is a powerful tool for investigating geometrical and electronic structures of the surface of organic metals.[5–8] The surface structure can differ from the bulk structure considering that the surface is in conditions different from the rest. The observation of the surface structure of crystals with various polymorphs such as (BEDT-TTF)-based radical salts is therefore an interesting subject.

In this study, the surface structure of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ and α-(BEDT-

TTF)$_2$I$_3$ crystals are examined by STM to clarify the relationship between the surface and the bulk structures.

EXPERIMENTAL

Measurements were carried out with a commercial STM (NanoScope II, Digital Instruments Inc.) in air at ambient temperature and pressure. Mechanically polished Pt-Ir tips were used for the STM observations. All the STM observations were performed with constant current mode. The lateral distance scale was not corrected for the piezo drift. We estimate an accuracy of 10% in distance from repeated measurements.

Typical crystal dimensions of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and α-(BEDT-TTF)$_2$I$_3$ were $0.1 \times 1 \times 2$ mm^3 and $0.1 \times 2 \times 2$ mm^3, respectively. The bc plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and the ab plane of the α-(BEDT-TTF)$_2$I$_3$ were identified based on their crystal shapes. Crystals were mounted on aluminum-coated glass substrates with silver paint. STM scans were taken over the crystal faces with the largest area, which are the bc plane and the ab plane for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and α-(BEDT-TTF)$_2$I$_3$, respectively. Scan area of the measurements was 6 nm × 6 nm for each crystal.

RESULTS AND DISCUSSION

Figure 1(a) shows a typical STM image of the bc plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ with a tunneling current of 1.1 nA and a tip bias of +294 mV. This crystal is monoclinic with lattice constants a = 1.6248, b = 0.8440, c = 1.3124 nm, β = 110.3°.[9] In Figure 1(a), a regular array of corrugations with 0.8- and 1.3-nm repeats is seen. The repeat distances are very close to the b and c lattice constants, respectively. Further, all the bumps in the drawn unit cell of the STM image agree well with the two-dimensional network of BEDT-TTF molecules projected onto its bc plane, as shown in Figure 1(b). Thus the 0.8- and 1.3-nm repeat distances can be identified with the b and c lattice constants, respectively.

Furthermore, the images attributed to BEDT-TTF molecules at particular sites, as indicated by arrows in Figure 1(a), are rather dark and small, which was reproducible for different scans. The study is now in progress on the relationship between this phenomenon and the electronic structure of each BEDT-TTF molecule.

Figure 2(a) shows an STM image of the ab plane of α-(BEDT-TTF)$_2$I$_3$ surface with a tunneling current of 0.42 nA and a tip bias of +105 mV. Since both α-(BEDT-TTF)$_2$I$_3$ and β-(BEDT-TTF)$_2$I$_3$ crystals grow simultaneously in an electrochemical cell,[10] α-(BEDT-TTF)$_2$I$_3$ crystals were collected by X-ray diffraction method. The α-(BEDT-TTF)$_2$I$_3$ crystal is triclinic with lattice constants a = 0.9183 nm, b = 1.0804 nm, c = 1.7442 nm, α = 96.96°, β = 97.93, γ = 90.85°.[3] The 0.9- and 1.0-nm repeat units, seen in Figure 2(a), are close to the a and b lattice constants, respectively. Further, the regular array of the bumps in the tunneling image agrees with the projection of BEDT-TTF molecules onto its ab plane, as shown in Figure

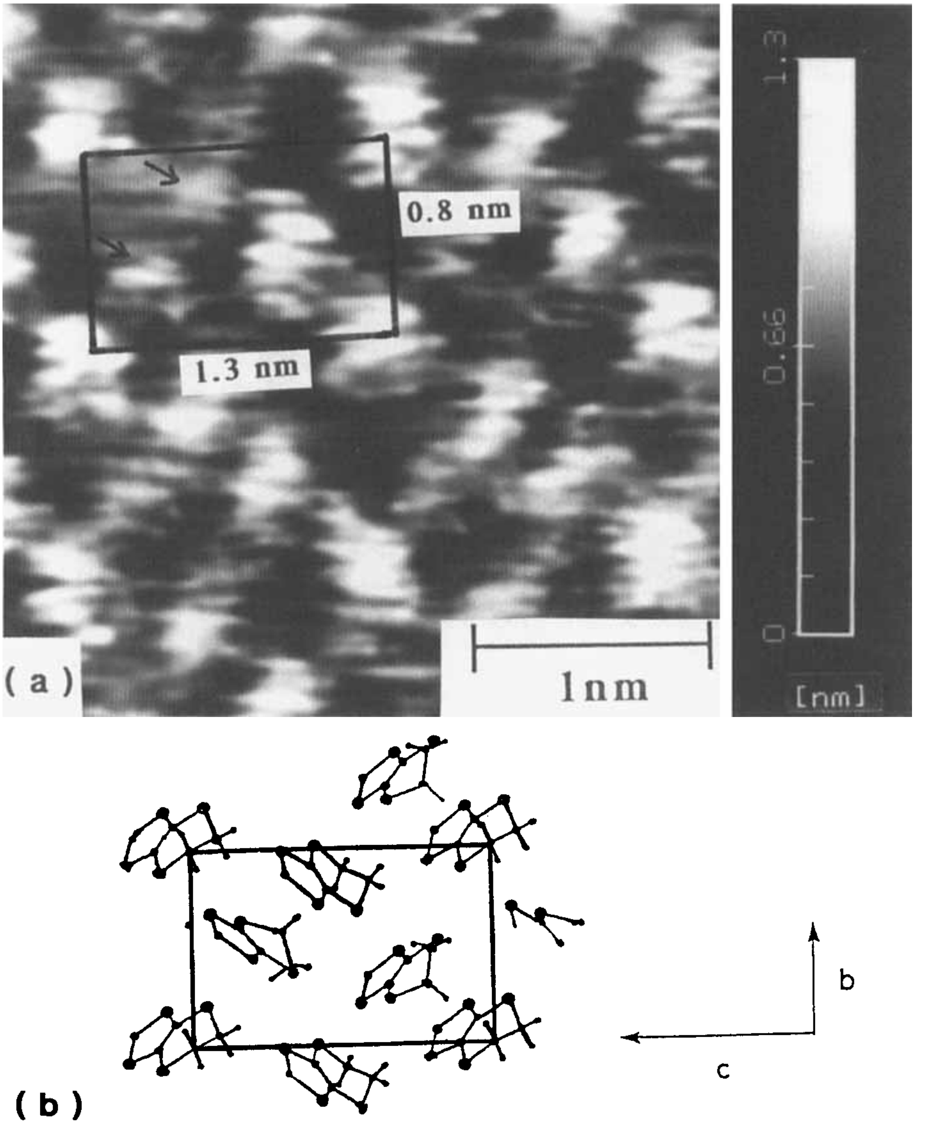

FIGURE 1 (a) Gray scale image of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ surface of an area 2.8 nm × 2.8 nm. The unit cell is indicated by a square of 0.8 nm × 1.3 nm. (b) The projection of BEDT-TTF molecules of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ crystal onto bc plane. The dimension of the drawn unit cell is 0.84 nm × 1.31 nm. The upper halves of the BEDT-TTF molecules are shown.

2(b). Therefore the 0.9- and 1.0-nm repeat distances can be identified with the b and c lattice constants, respectively. No structure is seen which is assignable to other crystal phases of $(BEDT\text{-}TTF)_2I_3$.

In the case of this work, the surface structures of the organic salts are the same with their bulk structures. Hence STM proves itself to be useful for the crystals

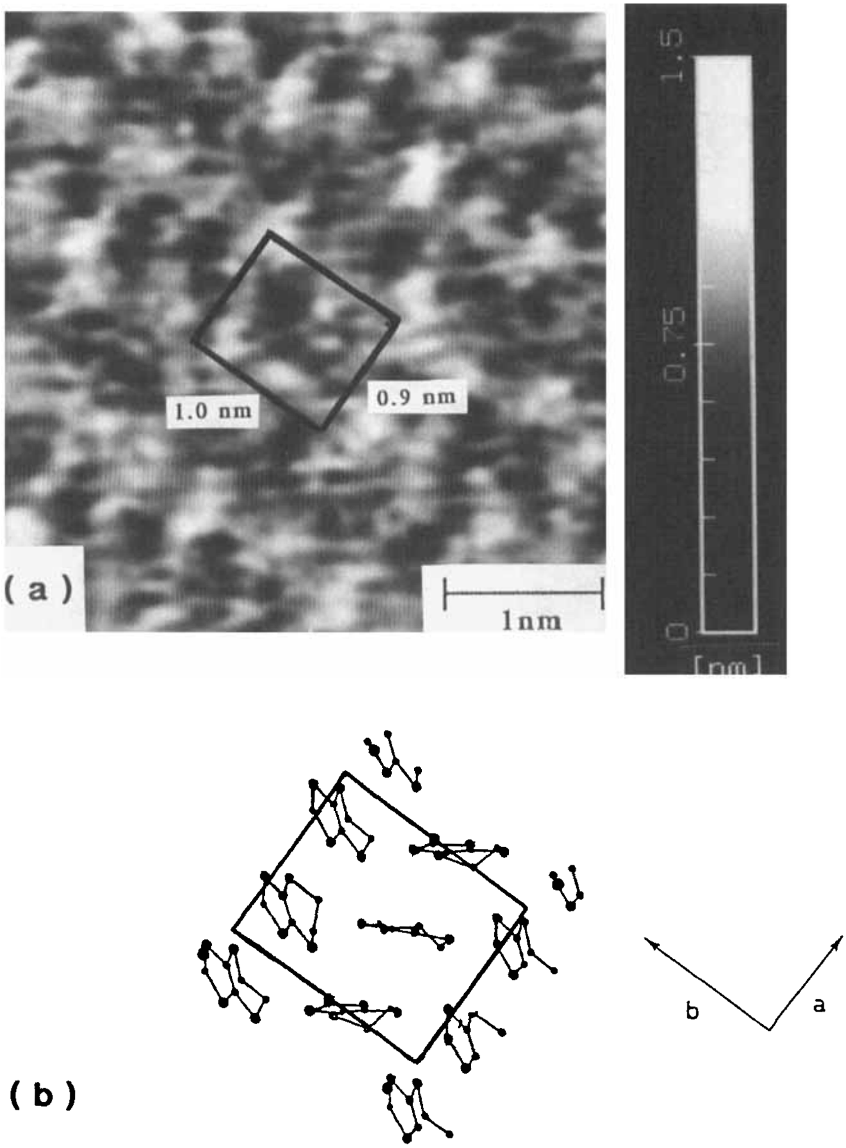

FIGURE 2 (a) Gray scale image of α-$(BEDT\text{-}TTF)_2I_3$ surface of an area 3.9 nm × 3.9 nm. The unit cell is indicated by a square of 0.9 nm × 1.0 nm. (b) The projection of BEDT-TTF molecules of α-$(BEDT\text{-}TTF)_2I_3$ crystal onto ab plane. The unit cell is 0.92 nm × 1.08 nm. The upper halves of BEDT-TTF molecules are shown.

with various polymorphs. In particular, the comparison between STM images of α-$(BEDT\text{-}TTF)_2I_3$ and its new superconducting α_t-phase after tempering is interesting because the latter has a similar structure to its β-phase (Tc = 1.3 K).[9] Further work on the effect of thermal treatments on the surface structure of α-

$(BEDT\text{-}TTF)_2I_3$ will be done by comparing STM images of α-$(BEDT\text{-}TTF)_2I_3$, α_t-$(BEDT\text{-}TTF)_2I_3$, and β-$(BEDT\text{-}TTF)_2I_3$ crystals.

Acknowledgments

We wish to thank Dr. H. Bando of Electrotechnical Laboratory and Drs. K. Honda, H. Hayakawa, and S. Ono for stimulating discussion. We are grateful to Professor G. Saito of Kyoto University for providing the samples.

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