

High-resolution molecular images of rubrene single crystals obtained by frequency modulation atomic force microscopy

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Frequency modulation atomic force microscopy (FM-AFM) was employed to study molecular structures of rubrene single crystals in ultrahigh vacuum. Molecularly flat and extraordinarily wide terraces were extended over the width of more than a few micrometers with monomolecular steps. Molecular packing arrangements and internal structures were revealed by FM-AFM. The unit cell determined by FM-AFM was consistent with the lattice parameters of bulk crystal within the experimental error, suggesting that the surface structure of rubrene is not reconstructed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3184770]

Single crystals of pentacene and rubrene are of great interest as promising materials for organic field effect transistors (OFETs).^{1–6} Our recent papers demonstrated that nearly perfect single crystals of pentacene can be grown from solutions and that their molecular packing arrangement can be clearly observed by the frequency modulation atomic force microscopy (FM-AFM) in ultrahigh vacuum (UHV).^{7,8} We also demonstrated that the field effect mobility in a nearly perfect single crystal of pentacene is in the range of 0.4–0.6 cm²/Vs, which is comparable to that of OFETs fabricated with pentacene single crystals prepared by a physical vapor-phase growth method.⁹ These results strongly encouraged us to apply FM-AFM to the characterization of surface structures of single crystals of organic semiconductors.¹⁰

Although scanning tunneling microscopy (STM) is not easily applicable to thick nonconductive films or bulk crystals in general, Wagner *et al.*¹¹ succeeded in achieving molecular resolution on bulk crystals of 3,4,9,10-perylenetetracarboxylic-dianhydride using an STM operated at very low tunneling currents in the range of a few picoamperes in UHV. Note that a recent paper reports that the molecular packing arrangement of rubrene can be seen on a bulk single crystal by using STM even in air, although the surface of single crystal of rubrene was reported to be oxidized upon exposure to ambient atmospheres, resulting in a decrease in stability and lifetime of organic devices.¹²

It is very important to evaluate surface structures of rubrene single crystals because of the fact that the electrical performance of OFETs depends strongly on crystal structure and morphology of the organic active layer.³ In the present investigation, therefore, we report high-resolution FM-AFM images of rubrene single crystals in UHV, not in air, in order

to avoid oxidation and contamination of the surface of rubrene crystals.

Single crystals of rubrene were prepared by a physical vapor transport method in purified argon stream as well as by crystallization from solution.¹³ Because of the relative ease of oxidation of rubrene, well-defined single crystals were prepared by crystallization from completely degassed *n*-decane solution. This method is similar to the procedure described previously for the preparation of pentacene.⁷ The stability of rubrene solutions was investigated by UV-visible absorption spectroscopy. The data are included in the supporting information.¹³

High-resolution FM-AFM images were obtained by using a UHV-AFM instrument (JEOL JSPM-4610A). We used commercial ultra sharp cantilevers (type NSC35/AIBS from μ Masch). A typical resonance frequency used was 400 kHz.

Large rectangular single crystals were relatively easily obtained by either method. The lattice parameters and the directions of *a*, *b*, and *c* crystal axes were determined by x-ray diffraction (Bruker Co., Smart APEXII). It was found in this study that all crystals grown by physical vapor transport had very similar lattice dimensions: *a*=1.42 nm, *b*=0.72 nm, and *c*=2.68 nm.¹³ These values are consistent with the literature values.^{12,14,15} The crystal axes of *a*, *b*, and *c* are defined here in the same way as in the paper describing STM images for the purpose of direct comparison between the two sets of data.¹² To avoid the oxidation of rubrene in air, the prepared single crystals were separated and mounted on an AFM sample holder, and they were quickly transferred into an UHV chamber for FM-AFM measurements. The base pressure of the UHV system was approximately 5×10^{-11} torr.

On rubrene crystals, molecularly flat and extraordinarily wide terraces were always extended over the distance of several micrometers, as shown in Fig. 1(a). It is also noteworthy that no islands and pits were found on the terraces in Fig. 1. Such extraordinarily wide terraces were found on a single

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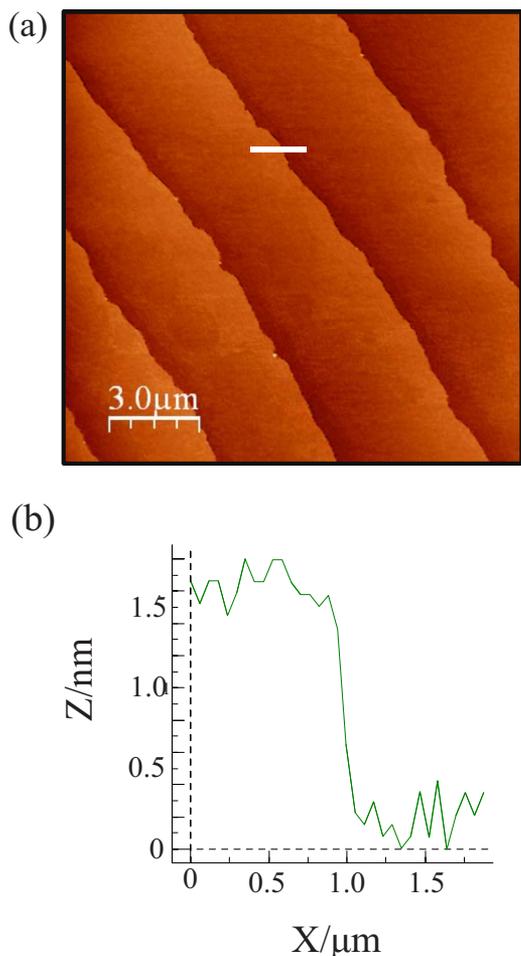


FIG. 1. (Color online) (a) An AM-AFM image of a rubrene single crystal prepared by a physical vapor transport method acquired at $15 \times 15 \mu\text{m}^2$. (Resonant frequency=146 kHz.) (b) Line profile along the white line in (a).

crystal of pentacene prepared from a trichlorobenzene solution as described in our previous paper.⁹ The appearance of the wide terraces with no islands and pits suggests strongly that the single crystals of rubrene were nearly perfect with essentially no defects. All steps are monomolecular in height (1.3–1.4 nm, one half of the length of c -axis), as shown in Fig. 1(b), and their orientations are nearly parallel to each other. It is also important to note that the step lines seem to be nearly parallel to the longer side of the crystal (b -axis), which is in agreement with the direction of stacking of the rubrene crystal (see supporting information¹³). This suggests that the crystal growth proceeded preferentially along the direction of b -axis. Crystal growth processes with a molecular scale are of special interest to us.

High-resolution FM-AFM imaging was conducted on molecularly flat terraces. The image shown in Fig. 2(a) was acquired in an area of $10 \times 10 \text{ nm}^2$ where bright molecular rows can be clearly seen. The same packing feature was consistently found to be extended over wide molecularly flat terraces. Figure 2(b) presents a FM-AFM image acquired in an area of $5 \times 5 \text{ nm}^2$ showing a more detailed internal structure. We observed molecular packing arrangement of rubrene molecules at the surface of single crystal by FM-AFM. It is important to note that Fig. 2(b) clearly shows that the unit cell were 1.4–1.5 and 0.7–0.9 nm in the directions of a and b , respectively. These values appear to be consistent with the

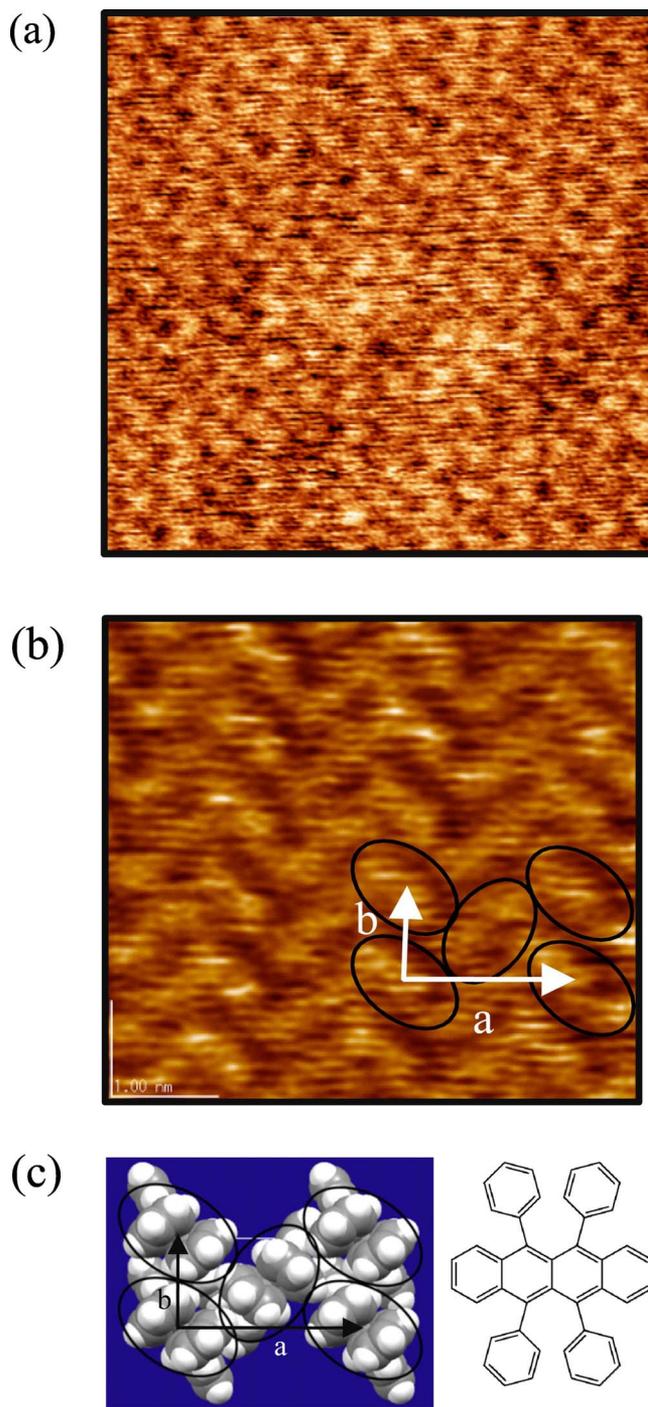


FIG. 2. (Color online) FM-AFM images of a rubrene single crystal acquired at (a) $10 \times 10 \text{ nm}^2$ and (b) $5 \times 5 \text{ nm}^2$. (Resonant frequency=400 kHz, frequency shift=+30 Hz.) (c) Top view of molecular arrangement of rubrene single crystal from c -axis. The angle between the directions of a and b is 90° .

lattice parameters of bulk crystal within the experimental error, suggesting that the surface structure of rubrene is not reconstructed. Figure 2(c) shows a top view of the layered structure of bulk single crystal of rubrene in the plane of a and b .

Although Menard *et al.*¹² reported STM images of rubrene single crystals acquired in air, the reported unit cell determined by STM in air was not rectangular in shape, which is expected from the structure of the a - b plane of the bulk crystal of rubrene (see Fig. 2 in Ref. 12). They also

reported that two molecular rows with different corrugations appeared alternatively along the b -axis.¹² However, as can be seen clearly in the high-resolution AFM image of Fig. 2(b), four molecules at the corners and the molecule at the center of the unit cell appear with a similar brightness, suggesting that all molecules in the a - b plane at the surface are physically identical to each other. It is also noteworthy that the image shown in Fig. 2(b) reveals that each rubrene molecule appears as a set of two spots with a similar intensity. These two spots are believed to correspond to two benzene rings attached to the tetracene ring of rubrene.

In conclusion, we acquired the high-resolution FM-AFM images of rubrene single crystals. The terrace width of the single crystal was greater than several micrometers, suggesting that the samples prepared in this study were nearly perfect single crystals with a low defect density. The high-resolution FM-AFM images revealed the internal shape of each rubrene molecule. Characterization of these single crystals as an organic semiconductor is now in progress.

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