Noncontact Atomic Force Microscopy of Perfect Single Crystals of Pentacene Prepared By Crystallization from Solution

Kazuya Sato,† Takahiro Sawaguchi,§ Masafumi Sakata,§ and Kingo Itaya*†‡§

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Sendai 980-8579, Japan, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Central 6, Tsukuba, Ibaraki 305-8566, Japan, and Core Research Evolutional Science and Technology organized by Japan Science and Technology Agency (CREST-JST), Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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Nearly perfect single crystals of pentacene were grown from trichlorobenzene solution. The surface structure of pentacene single crystals has been investigated by frequency modulation atomic force microscopy. Molecularly flat and extraordinarily wide terraces, extended over the width of more than a few micrometers with monomolecular steps, were consistently observed, suggesting that those pentacene crystals were nearly perfect single crystals. Molecular packing arrangements were revealed by FM-AFM for the first time.

Recently, several research groups successfully performed atomic and molecular resolution imaging using noncontact atomic force microscopy (NC-AFM).1 Particularly, frequency modulation atomic force microscopy (FM-AFM) is highly advantageous for imaging nonconductive organic materials with molecular resolution even on insulators. Yamada’s group has demonstrated that FM-AFM yields molecular resolution images of the self-assembled monolayer of alkanethiol in ultrahigh vacuum (UHV)2 and in air3 and that of polydiacetylene in water.4 Those results encouraged us to apply FM-AFM to the investigation of organic semiconductors such as pentacene and rubrene, although scanning tunneling microscopy (STM) has been used for investigating pentacene thin films formed on Au(111) in UHV.5−7 A recent paper reported that the flat-lying pentacene monolayer seeds and promotes the layer-by-layer growth of a multilayer polycrystalline film.5 However, in general, STM is not applicable to thick nonconductive films or bulk crystals of organic materials because of their low electrical conductivity.

Pentacene is one of the most intensively investigated organic semiconductors for organic field effect transistors (OFETs).8,9 The vacuum evaporation technique has long been used for the preparation of thin films of pentacene.9−14 It is commonly recognized that the carrier mobility in organic semiconductors depends strongly on their crystal structure.14 Grazing-angle incidence X-ray diffraction (GIXD) has been widely utilized for the characterization of microstructure of pentacene thin films.12,13 Atomic force microscopy (AFM) in the tapping mode has also been used to determine surface topographies of monolayers and multilayers of pentacene evaporated on a-SiO2 in air.7−11 It is of interest to note that pentacene molecules, even in the first monolayer, usually stand nearly vertically on substrates such as SiO2, because the intralayer pentacene−pentacene interaction is stronger than the pentacene−substrate interaction. An AFM image reported by Fritz et al. demonstrated that the pentacene monolayer on a-SiO2 was composed of relatively large domains with a thickness of 1.6 nm, which was slightly smaller than the estimated length of 1.64 nm for a pentacene molecule.12 More recently, single crystals of organic semiconductors such as rubrene15 and pentacene16 are attracting great interest as materials to be used for OFETs, because single crystals are expected to possess a higher mobility than their polycrystalline counterparts. Intrinsic electronic properties of organic semiconductors cannot be evaluated by examining evaporated films, because of the presence of a large number of defects in the film. Most single crystals for OFETs have been prepared by the so-called physical vapor transport method.15

With these previous works in mind, we attempted to develop a chemical method for the preparation of well-defined single crystals of pentacene. We believed that classical methods should be more suitable as a general technique for the preparation of nearly perfect single crystals of organic semiconductors for the application of OFETs. Because of the easy oxidation of pentacene in air,17 well-defined single crystals of pentacene for OFETs have not been prepared successfully so far by crystallization from solution. However, it was reported that single crystals of dithiophene tetrathiafulvalene (DT-TTF) and its derivatives were grown from solutions, and their hole mobilities have been evaluated from FET characteristics.18,19 Although crystals of...
5-chlorotetraacene were selectively grown on self-assembled monolayers, the quality of the crystals appeared to be unsatisfactory as a material for FET with high mobility.\textsuperscript{19} It is noteworthy that a method called the floating-drop technique has been used for the preparation of high-quality single crystals of quaterthiophene.\textsuperscript{21} The quality of the samples has been assessed by conventional AFM.

Pentacene (Tokyo Kasei) was purified by repeating temperature-gradient vacuum sublimation at a pressure lower than $10^{-6}$ Pa several times. Purified pentacene was placed in a Pyrex glass tube connected to a standard vacuum line.\textsuperscript{22} Triply distilled trichlorobenzene was completely degassed by repeating five freezing–pumping–thawing cycles. Extreme care was exercised in the preparation of high-quality single crystals of pentacene. It should be noted that pentacene is very easily oxidized in solution in the presence of oxygen.\textsuperscript{17} In trichlorobenzene, the absorption bands in the UV–visible region disappeared almost totally in air-saturated solution within 20 min. However, it was found in this study that pentacene is very stable in the completely degassed solution prepared by the freezing–pumping–thawing cycles. No change in absorption spectra was found for several days or even for months. UV–visible adsorption data are included in Supporting Information. Such long-term stability allowed us to prepare well-defined, high-quality single crystals. The concentration of pentacene was typically 2–3 mg/mL. The glass tube with degassed pentacene solution was sealed off from the vacuum line. The glass tube was placed in a temperature-controlled oil bath and heated up to 200 °C, followed by cooling down slowly (10 °C/h) by using a programmable temperature controller. Evaporated pentacene films were also prepared on a-SiO$_2$ on Si(100) at the rate of ca. 0.03 nm/s under $10^{-7}$ Pa. Freshly prepared single crystals and evaporated films were quickly transferred into a main UHV chamber ($10^{-9}$ Pa) for AFM measurements.

High-resolution FM-AFM images were obtained in the constant frequency shift mode using a frequency modulation (FM) detection method. Molecular-scale images were obtained with a commercial UHV–AFM instrument (JEOL JSPM-4610A) with an easyPLL plus (Nanosurf, Inc., Switzerland) in order to maintain a constant cantilever oscillation amplitude. Cantilevers used were ULTRASHARP Silicon (NSC35AIBS, MaicroMasch, Spain). The typical resonance frequency and spring constant of the cantilever (type B) were 300 kHz and 14 N m$^{-1}$, respectively.

It was found in the present study that evaporated pentacene films were composed of many islands measuring 100–300 nm. Terraces were found to be flat at the molecular level, and the averaged terrace widths were in the range of 10–30 nm, depending on the evaporation rate. All steps observed in the images were monomolecular steps measuring ca. 1.3–1.4 nm in height. Similar images were previously reported by contact-mode and tapping-mode AFM measurements performed in air.\textsuperscript{9–11}

Figure 1 shows an FM-AFM image of a single crystal of as-prepared pentacene acquired in a larger area ($5 \times 5 \, \text{nm}^2$). The negative shift of the cantilever ($\Delta f = -110.5 \, \text{Hz}$) was kept constant during FM-AFM. The vibration amplitude of the cantilever ($A$) was set at 10 nm. It was surprising to us to find extraordinarily wide terraces extended over a few micrometers or even more. Although we investigated surface morphologies of various single crystals of metals and semiconductors, we have not observed such flat surfaces in our previous studies.\textsuperscript{18} It is noteworthy that no island was found on the terraces in Figure 1. The appearance of the wide terraces with no islands suggests strongly that the single crystals prepared from the solutions were nearly perfect with essentially no defects.

Figure 2a shows the first molecular image acquired on the surface of a single crystal of pentacene on a flat terrace shown in Figure 1. The piezo-electric tube was calibrated by the Si-(111)-(7 $\times$ 7) structure for the $x$ and $y$ directions and for the step-height in the $z$ direction. Corrugation heights for bright spots were in the range 0.5–0.6 nm, which were surprisingly larger than those commonly observed in scanning tunneling microscopy (STM) of organic molecules adsorbed on single-crystal metal electrodes.\textsuperscript{18} Figure 2b,c shows, respectively, the side and top views of the layered structure of a bulk single crystal of pentacene.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image1.png}
\caption{FM-AFM image of a single crystal of as-prepared pentacene acquired in a larger area ($5 \times 5 \, \text{nm}^2$). $\Delta f = -110.5 \, \text{Hz}, A = 10 \, \text{nm}$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image2.png}
\caption{(a) FM-AFM molecular image of a single crystal of as-prepared pentacene. $6.9 \times 6.9 \, \text{nm}^2$, $\Delta f = -173.3 \, \text{Hz}, A = 12.5 \, \text{nm}$. (b) and (c) show, respectively, the side and top views of the layered structure of a bulk single crystal of pentacene.}
\end{figure}

In the unit cell of the topmost layer shown in Figure 2c, four molecules at the corners have an identical configuration, and the molecule at the center of the unit cell has a different configuration. In the FM-AFM image shown in Figure 2a, the corresponding unit cell is seen as a rhombus. The average lengths of the unit cell were 0.69 ± 0.02 nm and 0.80 ± 0.02 nm for the directions of \( a \) and \( b \), respectively. We also succeeded in achieving molecular resolution on an evaporated film of pentacene. Essentially identical molecular images were consistently observed on flat terraces within experimental error. Although a small thermal drift during the acquisition of the image always prevented to determine accurate lattice parameters, the values obtained from the FM-AFM image seem to be consistent with literature values obtained by X-ray diffraction.\(^{23}\) Finally, it is noteworthy that pentacene crystallizes in different morphologies with different \( d\)(001) spacings of 1.41, 1.45, 1.50, and 1.54 nm. However, Palstra et al. reported that both single crystals of pentacene grown by vapor transport and from solution have a \( d\)-spacing of 1.41 nm.\(^{23,24}\) Although small differences in the lattice parameters could not be determined accurately by the present FM-AFM technique, a further investigation is needed to study the crystal structure of the single crystal grown from the solution.

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**Supporting Information Available:** Stability of solutions, crystallity of crystal, and FM-AFM images of evaporated films. This material is available free of charge via the Internet at http://pubs.acs.org.

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