Fabrication of Highly Oriented Multilayer Films of Picene and DNTT on Their Bulklike Monolayer

Chunyang Zhang,‡ Hiromu Tsuboi,‡ Yuri Hasegawa,∥ Masato Sasaki,‡ Yutaka Wakayama,§ Hiroyuki Ishii,† and Yoichi Yamada†,‡

‡Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan
∥Tsukuba Research Center for Energy Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan
§International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

ABSTRACT: Highly oriented, multilayer molecular films of picene and dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT) molecules with the long axis parallel to the substrate (parallel configuration, hereafter) were fabricated on their characteristic bulklike monolayer. These molecules form a dense monolayer with a bulklike molecular arrangement on metal surfaces such as Au(111), which allows further stacking of parallel molecules. Indeed, upon adsorption of picene and DNTT on these dense monolayers, growth of straight islands of multilayer without the dendritic layer was observed. Particularly, in the case of picene, one-dimensional islands with lengths over 100 μm were formed and aligned in 3-fold symmetric directions of the substrate, which was not observed in the case of DNTT. X-ray diffraction measurements revealed the presence of [201] and [211] planes and the absence of the [001] diffractions, indicating that the one-dimensional islands of picene indeed consist of parallel molecules. The formation of huge crystalline islands in the case of picene, in contrast to the case of DNTT, is likely induced by the stronger intermolecular force, as suggested from the calculation of the vibrational energy.

1. INTRODUCTION

Small organic semiconductors with enhanced intermolecular interaction, such as phenacenes and thienoacenes, have been attracting attention because high-quality single crystals or thin films are expected. In this study, we focused on picene and dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT) (as shown in the insets of Figure 1a,d) as model molecules of phenacenes and thienoacenes, respectively. Indeed, the single-crystalline picene shows significant dispersion of the highest occupied molecular orbital,1,2 and organic field-effect transistors (OFETs) utilizing the single-crystalline picene exhibit high carrier mobility of more than 1 cm2 V−1 s−1.3 Theoretical calculations have suggested that the single-crystalline picene can exhibit a maximum mobility up to 2.6 cm2 V−1 s−1 along the π−π stacking direction.4 OFETs based on single-crystalline DNTT have shown mobility as high as 10 cm2 V−1 s−1.5 However, OFETs utilizing the thin films of these molecules have exhibited much lower hole mobility, such as 0.1−0.3 cm2 V−1 s−1 for picene2 and 2.9 cm2 V−1 s−1 for DNTT.7 These facts suggest that further optimization of the thin-film structure of these organic semiconductors is required.

There have been common problems in the growth of the multilayer film of these π-conjugated planar molecules; the monolayers of these molecules on the flat substrates usually take a “flat-lying” or “face-on” conformation due to significant coupling between π orbital of molecules and the surface electronic states, whereas the second layer does not usually follow the configuration of the monolayers and tends to “stand up”. This mechanism usually leads to a dendritic growth of the multilayer with a complicated morphology and small domain sizes.8−11 Even in the case of a carefully optimized deposition utilizing the supersonic molecular beam deposition of picene, the reported grain size of the film is in the range of several micrometers.12 We focus here on the morphology of the monolayer, which is known to be one of the key features determining the structure of multilayer films of organic semiconductors.13 We have recently reported that the careful deposition of picene and DNTT on flat surfaces can form a corrugated monolayer in which half of the molecules take a “side-on” geometry.14 The same growth feature can also be seen in other phenacenes.15 The molecular ordering of the monolayer resembles the (110) plane of the bulk crystal, although they are not identical, which is distinct from the case of the similar π-conjugated molecules such as pentacene, and...
this phenomenon should reflect the strong intermolecular interaction of these molecules. The bulklike monolayers could be useful for further stacking of parallel molecules on it, which can potentially yield a high-quality multilayer film.

Therefore, in this work, we have tried to grow the multilayer picene and DNTT on their peculiar monolayer. We indeed demonstrated here that the careful fabrication of the bulklike monolayers and further slow deposition of molecules resulted in formation of extremely long (more than 100 μm in the case of picene) and unidirectional islands consisting of parallel molecules. We will emphasize that much better crystalline structure of these molecules. We note here that, in the analysis of the normal vibrational modes of the single-molecule, which is particularly effective for small molecules with enhanced intermolecular interaction such as phenacenes, will be beneficial not only for the applications in organic electronics devices but also in the basic research of the structure–function relationship of organic semiconductors.

2. EXPERIMENTAL AND THEORETICAL METHODS

Single-crystalline Au(111) was used as a substrate. The substrate was cleaned by several cycles of Ar+ ion sputtering followed by annealing at approximately 400 °C. The cleanliness of the substrate was examined by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) with a constant current mode. Sharp diffraction spots and herringbone reconstruction of the Au(111) substrates were clearly observed by LEED and STM images. The deposition of picene and DNTT molecules on the clean Au(111) substrate was performed in an ultrahigh vacuum (UHV) environment of about 1 × 10−10 Torr with a homemade Knudsen cell, which allows a slow deposition rate of approximately 1 ML/1000 s at room temperature to ensure good crystallinity of the resultant film. The deposition rate was monitored by a quartz crystal microbalance. The distance from the molecule evaporator to the Au(111) substrate was 35 cm. The formation of monolayers of picene and DNTT was confirmed by LEED and STM observation. After that, the multilayers of picene and DNTT were deposited on the well-ordered monolayer at the same rate in UHV. Structural measurements of the multilayer were performed ex situ at room temperature. The morphology of the multilayer was observed by atomic force microscopy (AFM) conducted in the tapping mode under atmospheric pressure and an optical microscope (OM). Crystallographic phase and molecular orientation in the film were characterized by X-ray diffraction (XRD) measurement, which was performed by a Cu Kα source X-ray of λ = 0.15406 nm. The normal vibrational modes of the crystal are obtained from the dynamical matrix constructed by the force field MMFF94s18 using the CONFLEX code.22 Here, the optimization process starts with the experimental structure, and the atomic positions are optimized at fixed lattice constants.

3. RESULTS AND DISCUSSION

First, we confirmed the formation of characteristic corrugated monolayers of picene and DNTT on a clean Au(111) substrate. It was seen that the picene and DNTT molecules adsorb in the flat-lying geometry at low coverage, whereas the geometry transforms into a corrugated arrangement near the monolayer coverage.24 Figure 1b,e shows the monolayer structure of picene and DNTT on Au(111). As seen in the magnified STM image in Figure 1c,f, the molecules in the monolayer show corrugated arrangements with the unit cell sizes of 1.1 × 1.4 nm² for picene and 1.1 × 1.6 nm² for DNTT. For both molecules, it was found that the molecular rows (defined with black arrows in the STM images) of the dense phase were aligned along the symmetric ⟨110⟩ direction of the substrate. Thus, there were three rotational domains, which...
were rotated by 120° from each other. The molecular arrangements and the sizes of the unit cells of the corrugated phases of picene and DNTT are apparently similar to the (110) planes of their single crystals (as illustrated in Figure 1a and d, respectively) although they are not identical. The formation of this type of bulklike monolayer seems to be common for phenacene or thienoacene, with enhanced intermolecular interaction.19,20

The dense monolayers of picene and DNTT with bulklike molecular arrangement as discussed above are promising for enhanced stacking of further molecules in a similar fashion. Therefore, we further deposited the multilayer of picene onto the dense monolayer and observed an abrupt growth of large and straight islands of the multilayer. These islands became so large that they could be clearly seen even with an optical microscope (OM). The OM images of the surface with low and high coverage of the picene islands prepared with the slow deposition of approximately 20 and 70 ML of picene molecules on the dense monolayer are shown in Figure 2a and b, respectively. In the image of the 20 ML coverage, Figure 2a, the formation of the rodlike picene crystalline islands with sharp edges is seen. The typical length, width, and height of the rod are approximately 30 μm, 0.5 μm, and 150 nm, respectively. It was clearly observed that the rods tend to align along three particular directions. The three directions, marked with arrows in Figure 2a, were found to correspond to the three domains of molecular rows of the monolayer on the Au(111) substrate,21 that is, the ⟨110⟩ direction. On increasing the coverage of molecules, as shown in Figure 2b, large-scale crystalline islands with a length of much more than 100 μm were obtained. At the same time, the domain with the aligned islands became as large as 0.5 mm. Figure 2c shows the AFM topography of the top surface of the crystalline picene island, where a step-terrace-like structure was observed. However, most of the steps were with a height of more than 5 nm, as shown in the line scan A in Figure 2c,d, much larger than a single molecular step, possibly due to bunching of the steps. In addition, the terrace morphology was found to be corrugated with amplitude of several nanometers as shown in the line scan B in Figure 2e. It is noted that the AFM measurements were conducted after taking the sample out to the atmospheric environment from a UHV; therefore, some distortion of the crystal surface, such as dewetting or disordering due to water coadsorption, may have occurred in this process. We note here that the structure of the monolayer was not changed on increasing the coverage of the molecule. Therefore, crystalline islands seem to form directly on the monolayer without the wetting layer.

We also examined the thicker film of DNTT on its bulklike monolayer. Figure 3a shows the OM image of the DNTT thin film with the molecular coverage of 30 ML. Although we observed formation of similar islands with the height of 130 nm (as shown in the line scan in Figure 3c,d) as in the case of picene, their sizes were relatively smaller and the tendency of the alignment of the islands with respect to the substrate was also weaker. At the higher coverage of 70 ML, as shown in Figure 3b, we found a network structure of the island with typical length of several micrometers, which was distinct from the case of the high-coverage picene (Figure 2b). From the AFM image shown in Figure 3c, the surface of the DNTT crystal island is rather rough. These results are consistent with the recent work of Dreher et al.16

We then analyzed the molecular orientation of the crystalline picene film by means of XRD measurements. Figure 4a displays the spectrum of the θ/2θ scan without subtraction of the background signal of an Au substrate. Within the analyzed angular range of 5–30°, two obvious diffraction peaks were observed at 2θ = 22.1° and 2θ = 26.4°. These peaks are assigned to be due to (201) and (211) planes, respectively, in comparison with the powder spectra (Figure 4b). The
schematic images of molecular arrangements of the (201) and (211) planes are illustrated in Figure 4c, which reveals a characteristic orientation of molecules with the long axes parallel to the surface (parallel molecule). Note that the molecular arrangements in the (201) and (211) planes are not identical to the monolayer. This implies that, although the bulklike monolayer can facilitate the further stacking of the parallel molecules, the template effect of the monolayer is not strong enough to realize epitaxial growth of the overlayer. In the case of DNTT, as revealed by the work of Dreher et al., the DNTT island showed a (121) plane in the XRD spectrum, which also shows a similar but distinct molecular arrangement from its monolayer.

Although we demonstrated that both picene and DNTT can form the crystalline islands with parallel molecules, that of picene showed a higher degree of homogeneity of each island, strict orientation with respect to the substrate, and a tendency to form larger domains with single orientation of crystalline islands. Although a microscopic understanding of the crystallization mechanism is still a difficult issue, the different behavior between two molecules may be attributable to the difference in the intermolecular interactions. As the measure of the intermolecular force constant, we examined the vibrational energy of the translational modes with the molecular displacement in the direction of the van der Waals bonding, in the case of the single-crystalline picene and DNTT. Figure 5 shows the translational optic phonon modes at the Γ point, in which the displacements of atoms (indicated by red arrows) are mainly along the π-stacking direction of two adjacent molecules in the a–b plane of the single crystal. The vibrational energies of such modes in the case of picene and DNTT were found to be 10.61 and 8.638 meV, respectively, as indicated in the figure. From the energy of the vibrational modes and masses of the molecule (picene: 2.78 Å × 10⁻¹ kg mol⁻¹; DNTT: 3.40 Å × 10⁻¹ kg mol⁻¹), we estimated the force constant of the intermolecular van der Waals bonding, simply assuming the harmonic oscillation, deducing 30.1 kg s⁻² for picene and 24.3 kg s⁻² for DNTT. Thus, the π–π interaction in picene is found to be stronger than that of DNTT, possibly resulting in the better crystalline morphology of the multilayer. However, since the molecular growth can depend on many other parameters, further detailed examination will surely be required.

It is also noted that the similar straight islands of pentacene and quaterphenyl were previously found on the metal substrate. However, the size of the islands was much smaller than the case of picene or DNTT. This difference is attributable to the difference in the structure of the monolayer, that is, the monolayer of pentacene consists of flat-lying molecules, in contrast to the case of molecules examined in the present study. The characteristic shape of the monolayer with a bulklike molecular arrangement can therefore be considered to stabilize the upper layer with the parallel molecules.

This crystalline film with parallel molecules may exhibit an enhanced π-stacking, and thus it will be beneficial not only for applications in organic electronics, but also for basic research of the structure–property relationships of these types of organic semiconductors.

4. CONCLUSIONS

We fabricated well-defined crystalline films of picene and DNTT on their well-ordered monolayers with a bulklike molecular arrangement. By means of slow deposition of the multilayer on the bulklike monolayer, large-scale crystalline islands having lengths of several hundred micrometers were obtained, especially in the case of picene. XRD measurement revealed that picene crystals consist of planes of (201) and (211), clearly suggesting that the film consists of the parallel molecules which may be stabilized by the peculiar structure of the monolayer.

AUTHOR INFORMATION

Corresponding Author
E-mail: yamada@bk.tsukuba.ac.jp.

ORCID
Chunyang Zhang: 0000-0002-7287-5733
Yutaka Wakayama: 0000-0002-0801-8884
Yoichi Yamada: 0000-0001-8187-3409
The authors declare no competing financial interest.

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