# Layer-by-layer growth of precisely controlled hetero-molecular multi-layers and superlattice structures

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## ARTICLE INFO

## ABSTRACT

We demonstrate a technique for growing fine molecular films on a monolayer scale. We achieve layer-by-layer growth under thermally equilibrium condition by precisely controlling the conditions of an ultra-slow deposition technique. This technique is applicable to various kinds of p-type and n-type organic semiconductors and makes it possible to form a hetero-molecular interface (p-n junction) with molecular level flatness. The technique was used to produce a molecular superlattice, which enables the well-controlled design of energy level alignments in organic semiconductors.

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## 1. Introduction

Various organic opto-electronic devices have been developed in the last decade [1–4]. For example, organic light emitting diodes have reached the practical application stage [5–7], and organic solar cells have improved considerably in terms of convergent efficiency [8–10]. For these applications, donor–acceptor interfaces, which are p-n junctions when related to semiconductors, should be well designed. This is because carrier processes, including carrier recombination, exciton dissociation and charge transfer, take place at hetero-interfaces. Kahn et al., have reported that charge transfer occurs at a hetero-molecular interface and, as a result, shifts are induced in the energy levels of the molecules. This charge transfer is explained in terms of charge neutral levels [11–13]. Such energy level shifts have made it difficult to achieve precise control of the energy level alignment at the hetero-interface of organic materials. However, the molecular orientations and flatness of the interface were not taken into account in these previous studies. Meanwhile, we have shown that no charge transfer or energy shift could be observed when the molecular orientations were well-controlled. The perpendicular orientation of the molecules and a flat interface on a monolayer level prevented both π-electron interaction and charge transfer, allowing the precise control of energy level alignments [14]. Namely, we must develop a technique for growing fine molecular layers if we are to realize energy level engineering in organic semiconductors [15–18].

The purpose of this study is to establish a technique for preparing a hetero-molecular interface with molecular level flatness and a well-controlled orientation. To achieve this goal, we employed the ultra-slow "hot-wall" deposition technique. We demonstrate well-ordered hetero-interfaces were produced by various p- and n-type organic semiconductors, and finally supperlattice structure was prepared. These fundamental techniques revealed the potential for molecular functionalities, such as the Mott transition, the Dirac fermion state, giant magnetic resistance and tunneling transistors.

## 2. Experimental details

Si wafers with thermally oxidized surface layers ($SiO_2$) were used as substrates. A terylene tetracarboxylic di-imide derivative ($TTCDI-C_{12}$) was chemically synthesized and purified using high performance liquid chromatography [16]. The other organic materials (pentacene, quaterrylene (QT), perylene tetracarboxylic di-imide derivatives ($PTCDI-C_8$), and α, ω-diperfluorohexyl-quaterthiophene (DFH-4T)) were commercially obtained and used as received. After ultrasonication in acetone and isopropyl alcohol, the $SiO_2$/Si substrates were cleaned by $UV/O_3$ treatment, and were introduced into a vacuum chamber with a background pressure of $10^{-7}$ Pa. The ultra-slow deposition technique was utilized for QT, $PTCDI-C_8$, $TTCDI-C_{12}$ and DFH-4T to achieve precise control of monolayer growth and well-defined molecular packing. The vacuum pressure was kept on the order of $10^{-6}$ Pa during deposition. A conventional Knudsen effusion cell was used as the source evaporator for pentacene deposition because the ultra-slow deposition technique was not effective for pentacene owing to its low partial pressure compared with the other molecules. In this case, the distance between crucible and substrate is about 160 mm. The deposition rate was calibrated by a quartz thickness monitor and was kept at less than 0.03 molecular layers per minute in each deposition process. Accurate optimization of the substrate temperature ($T_s$) is crucial to achieve layer-by-layer

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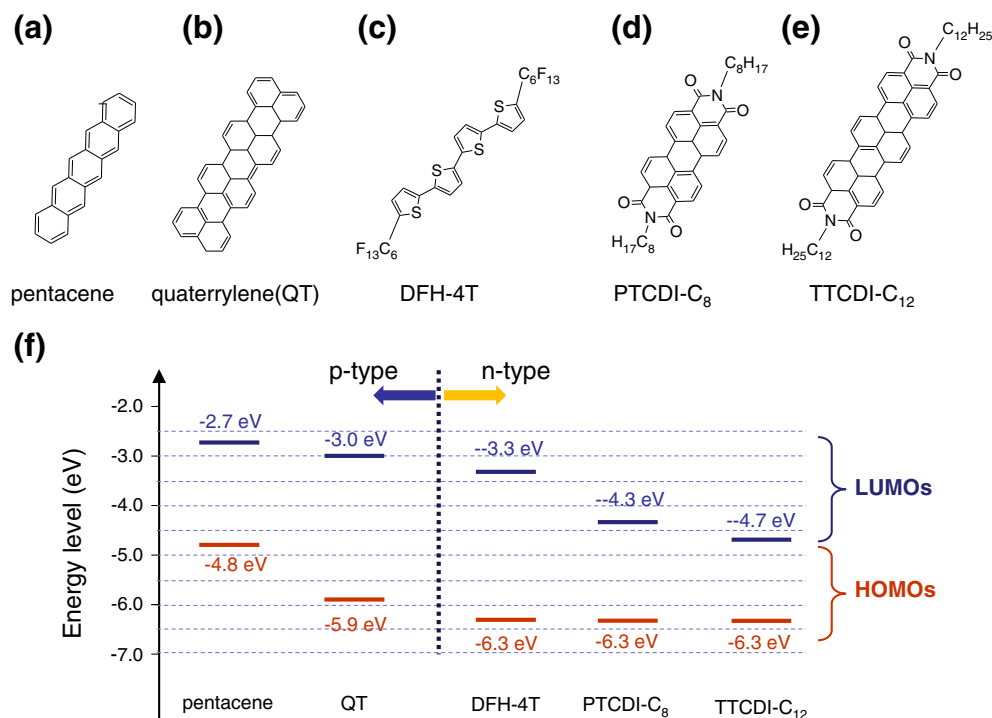E-mail address: WAKAYAMA.Yutaka@nims.go.jp (Y. Wakayama).

Fig. 1. Molecular structures of (a) pentacene, (b) quaterrylene (QT), (c) DFH-4T, (d) PTCDI-C$_8$ and (e) TTCDI-C$_{12}$. (f) LUMO and HOMO of molecules.

growth. For this purpose, the molecular layers were grown at different $T_s$ values ranging upwards from room temperature in 3°C steps. Thin film growth processes were examined using atomic force microscopy (AFM, SII NanoTechnology Inc., SPI-4000 E-sweep) measurements performed with a dynamic force microscope.

## 3. Results and discussion

Fig. 1(a) to (e) show the molecular structures considered in this study. Pentacene and QT are known to work as p-type semiconductors. Meanwhile, the other compounds (DFH-4T, PTCDI-C$_8$ and TTCDI-C$_{12}$)

act as n-type semiconductors. This organic semiconductor polarity can be defined in terms of the energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). For pentacene and QT, holes are injected from electrodes (Au) into the HOMOs to make them p-type semiconductors. On the other hand, the strong electron affinities of fluorine atoms and carboxylic imides lowered the LUMOs for the other three compounds thus allowing electron injection into the LUMOs to make them n-type semiconductors. The LUMOs and HOMOs of these compounds vary in an orderly sequence as illustrated in Fig. 1(f) [14,19,20]. We anticipate that if well-defined hetero-interfaces are formed by these materials,
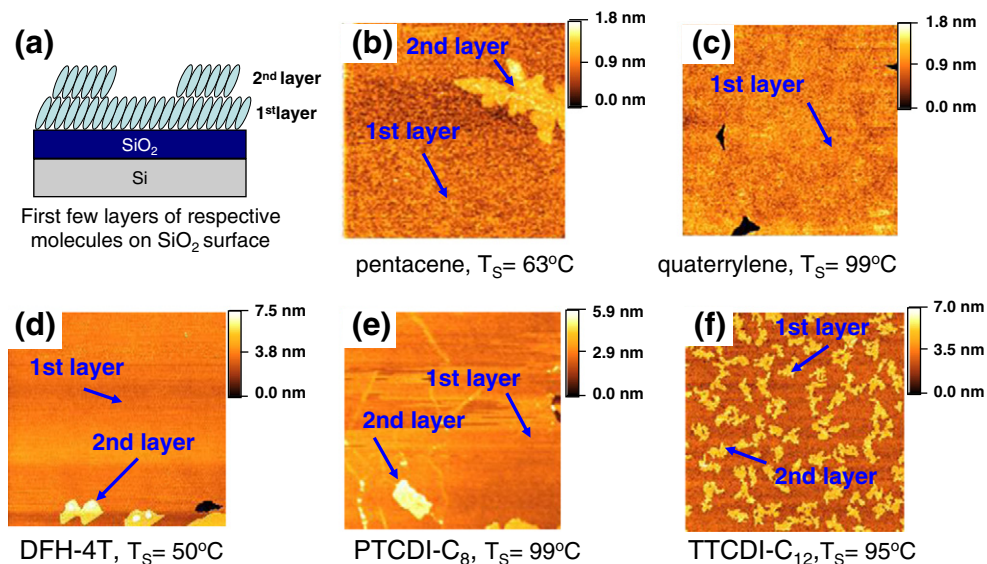


Fig. 2. (a) Schematic illustration of layers with a single component. AFM images of first few layers of (b) pentacene, (c) quaterrylene (QT), (d) DFH-4T, (e) PTCDI-C$_8$ and (f) TTCDI-C$_{12}$. Scanning areas are 5 μm × 5 μm for all images.