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THE HETEROEPITAXIAL GROWTH OF π-CONJUGATED ORGANIC MOLECULES ON INORGANIC SINGLE CRYSTAL SAPPHIRE SUBSTRATE

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Abstract

The structure of organic semiconductor layers strongly affects the performance of the organic semiconductor-based devices such as organic thin film transistors (OTFTs), organic field effect transistors (OFETs), organic light emitting diodes (OLEDs) and organic photovoltaic cells (OPVs). The layer structure such as preferred orientation is controlled by the heteroepitaxial growth of organic molecules on different type of substrates. The π-conjugated organic semiconductor materials were deposited on single crystal sapphire substrate by vacuum thermal evaporation. The heteroepitaxial growth of π-conjugated n-type semiconductor of N, N'-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8) and p-type semiconductor of 2,7-dioctyl [1] benzothieno [3,2-b][1] benzothiophene (C8-BTBT) on single crystal Al_2O_3 sapphire substrates were investigated by X-ray diffraction analysis and atomic force microscopy observation. The (001) out-of-plane orientation of organic layers were developed on single crystal sapphire substrates for all prepared samples irrespective of the deposited organic materials we used in this research. The needle-shape PTCDI-C8 grains and layer-by-layer islands growth of C8-BTBT layers on (0001) C-sapphire substrate were observed in AFM observation. The PTCDI-C8 and C8-BTBT layers showed characteristic of its absorption spectra.

Keywords: π-conjugated organic molecules, heteroepitaxial growth, sapphire substrate, vacuum thermal evaporation

Introduction

The organic semiconductors have been successfully employed in electronics and optoelectronic devices such as organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), and organic photovoltaic cells (OPVs). (C.D. Dimitrakopoulos, et al, 2001, 2002) (A. Facchetti, et al 2007), (C.W. Tang, et al, 1989), (H. Hoppe, et al, 2004), (T. Uemura, et al, 2009). In addition to that of devices, it is possible to be applied in application such as magnetoresistance devices. (F. Sawano, et al, 2005), (S. Sakai, et al, 2006). The device performance mainly relies on the crystal structure including the orientation and grain structure of the prepared-organic layers. (H.N. Tsao, et al, 2009), (F. Dinelli, et al, 2016). The structure has been controlled by optimizing the type of substrate materials as flexible substrates or metal substrates, in addition to orientation controlled substrates, (H. Huang, et al, 2016), (E.J. Kintzel, et al, 2006), and the growth containing the preparation processes and conditions such as substrate temperature, deposition rate, vacuum pressure and layer thickness. (L.Zhang, et al, 2015) (A. Andreev, et al, 2003).

Perylene derivatives of N, N'-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8) was potential material to fabricate in molecular based devices due to its mobility up to 0.6 $cm^2V^{-1}s^{-1}$. (P.R.L. Malenfant, et al, 2002). The 1D-PTCDI-C8 nanoribbons were prepared by a rapid transfer method, and the optical properties of this material made it possible to be utilized in

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optoelectronic circuitry and laser resonator. (C.O.N. Spectus, et al, 2008), (T. Abhijith, et al, 2015). The unit cell of the PTCDI-C8 was reported by the group of A.L. Briseno, et al, 2007 and (T.N. Krauss, et al, 2008) and it has triclinic lattice structure with two different values of lattice constants for the bulk and films of PTCDI-C8.

One of the BTBT derivatives of acceptor material, 2,7dioctyl [1] benzothieno [3,2-b][1] benzothiophene, is one of the promising materials to be used in photovoltaic and optoelectronic devices. It has been reported that high charge carrier mobility of ~ 43 $cm^2 V^{-1} s^{-1}$ were achieved in solution-based organic field effect transistor. We have reported that the (001)-2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) layers were grown on aluminium oxide Al_2O_3 and magnesium oxide MgO single crystal substrates and the electrical resistivity related the grain structure of C8-BTBT layers. (A.M. Moh, et al, 2018).

In this paper, we investigated the effect of substrate orientation of (0001) and type (single crystal aluminium oxide) on the growth and orientation of vacuum thermal evaporated-PTCDI-C8 and C8-BTBT layers, and also investigated the heteroepitaxial growth of π-conjugated organic semiconductor materials on (0001) C-Sapphire substrate with X-ray diffraction (XRD), atomic force microscopy (AFM), and optical absorption spectra measurement.

Experimental Details

The annealing was carried out in air for 1 hr at 1200 °C for (0001)- Al_2O_3 (C-Sapphire) sapphire substrates before deposition of organic semiconductor layers. (0001)-Al_2O_3 (C-Sapphire) substrate were cleaned with acetone, ethanol and deionized water for 15 min each in ultrasonic bath. After cleaning the substrates, it is dried at room temperature. After cleaning the substrates, the 100-nm-thick PTCDI-C8 and C8-BTBT layers were deposited at substrate temperature of 100 °C at a pressure around 4×10^{-5} Pa on single crystal substrates of (0001)-Al_2O_3 (C-Sapphire) substrate by a vacuum thermal evaporation system (ULVAC, VTS-350 ERH/M) connected with turbo molecular pump and oil-free scroll vacuum pump. The deposition rate 0.1 nm/s was controlled by a quartz crystal deposition control system (ULVAC, CRTM-6000G).

To characterize the heteroepitaxial growth of PTCDI-C8 and C8-BTBT layers, vacuum evaporated 100 nm-thick-semiconductor layers were prepared on C-Sapphire substrate at substrate temperature 100 °C. The thickness of the organic layers was determined by a surface profiler system (ULVAC, Dek Tak 150). The out-of-plane X-ray diffraction were performed at 2θ value from 5 degrees to 30 degrees by a $\theta/2\theta$ scanning technique using Rigaku RINT 2500 X-ray diffractometer at monochromatic CuKα radiation operated at 40 kV, 100 mA with a wavelength (λ = 0.154059 nm). Surface morphologies were observed by an atomic force microscopy (AFM, Shimadzu, SPM-9700 Kai) in dynamic mode in air. Absorption spectra measurements were performed using a UV-VIS-NIR spectrophotometer (HITACHI, U4100) with a reference of (0001) C-Sapphire bare substrate.

Results and discussion

X-ray diffraction method was performed to analyse the structure and orientation of the vacuum thermal-evaporated semiconducting layers prepared on (0001) C-sapphire substrate. The PTCDI-C8 possesses a triclinic lattice with a = 0.900 nm, b = 0.489 nm, c = 2.165 nm, α = 95.0 degree, β = 100.7 degree, and γ = 112.8 degree, and the lattice parameters varied depending on the type of the PTCDI-C8 such as powder type and layer type. (A.L. Briseno, et al, 2007), (T.N. Krauss, et al, 2008), (T.N. Krauss, et al 2009). The Al_2O_3, C-sapphire substrate possesses a hexagonal lattice with a = 0.47589 nm, and c = 1.2991 nm. The lattice mismatch was estimated to be approximately 0.58% for a-axis and 2.68% for b-axis of PTCDI-C8 for the lattice relationship of $(001)_{PTCDI\text{-}C8}$ is parallel to the substrate of single crystal C-Sapphire (0001)Al_2O_3. Although the lattice mismatch varied in wide range between the substrate material of Al_2O_3 sapphire substrate and PTCDI-C8, but the lattice mismatch between the molecule of PTCDI-C8 and substrate did not affect the out-of-plane orientation of the PTCDI-C8 layers by the X-ray diffraction patterns.

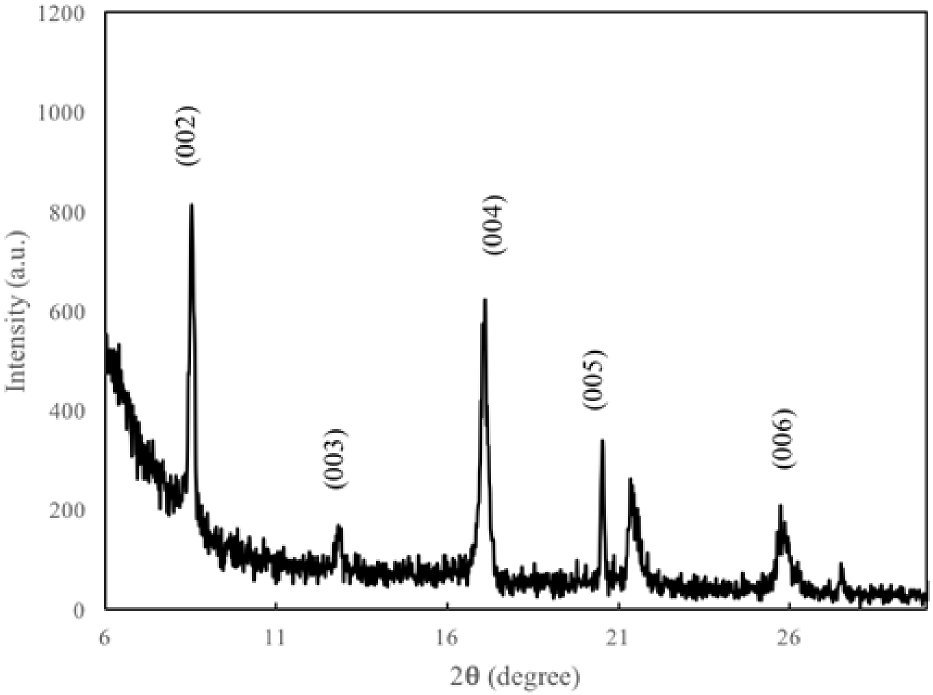

Figure 1 X-ray diffraction pattern of PTCDI-C8 layers prepared on C-sapphire substrate at 100 °C.

Figure 1 shows out-of-plane X-ray diffraction patterns for 100-nm-thick PTCDI-C8 layers prepared at substrate temperature 100 °C. The diffracted X-ray peaks could be observed from 8.4 degrees and each approximately 4.2 degrees, and these peaks were assigned as (002), (003), (004), and (005) planes, respectively. The peak at around 21 degrees which was originated from the single crystal C-sapphire substrate. The interlayer spacing d of the (002) plane of 100 nm thick vacuum thermal evaporated-PTCDI-C8 layers could be estimated to be 1.03 nm, which was close to 0.98 nm calculated from the lattice parameters mentioned above. It was confirmed from the out-of-plane X-ray diffraction patterns that PTCDI-C8 layers possessed the (001)-out-of-plane orientation, in which PTCDI-C8 molecules with almost upright standing position were preferably to grow on C-sapphire substrate. The lattice relationship between PTCDI-C8 layers and substrate materials could be identified as; $(001)_{PTCDI\text{-}C8}$ is parallel to the $(0001)_{Al2O3}$.

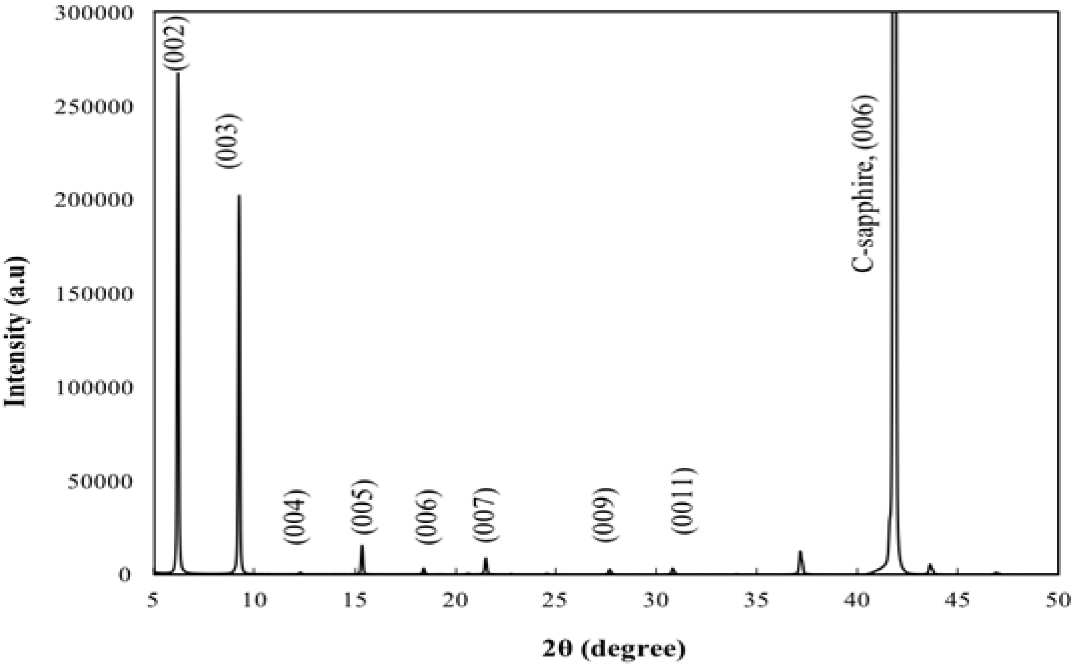

Figure 2 X-ray diffraction pattern of C8-BTBT layers prepared on C-sapphire substrate at 100 °C.

Figure 2 shows the X-ray diffraction pattern of 100 nm thick thermally evaporated- π-conjugated C8-BTBT molecules on C-sapphire substrate at substrate temperature 100 °C. Series of peaks could be assigned as (002), (003), (004), (005) etc, and planes of the C8-BTBT layer with the characteristic monoclinic lattice. The lattice mismatch was estimated to be approximately -24 and 4% on the a- and b-axes of C8-BTBT for the lattice relationship $(001)_{C8\text{-}BTBT}$ is parallel to that of the substrate material of $(0001)_{Al2O3}$. The growth mechanism governs by the strong π–π stacking between the molecules. Since the preferred orientation of the organic semiconducting molecules on C-sapphire substrate was (001) orientation without depending on the type of substrate.

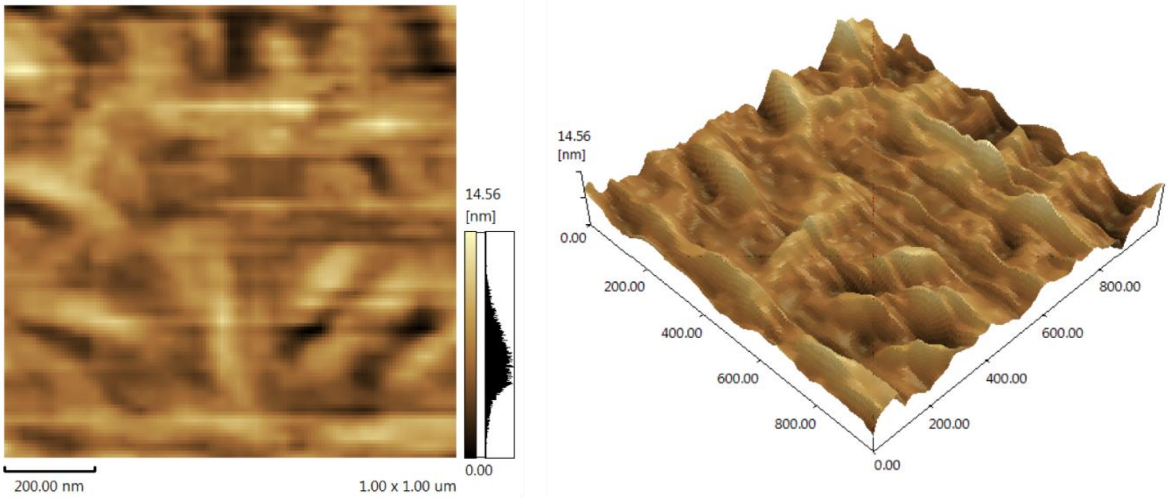

Figure 3 AFM images for 100-nm-thick-PTCDI-C8 layers prepared at substrate temperature of 100 °C.

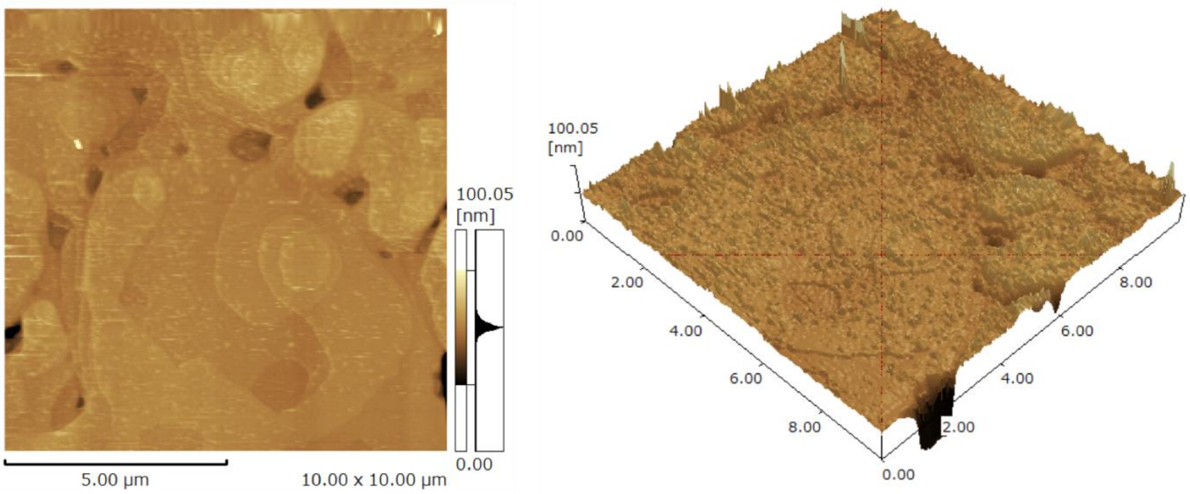

Figure 4 AFM images C8-BTBT layers prepared at 100 °C with the thickness of 100 nm.

The surface morphology of 100 nm-thick PTCDI-C8 and C8-BTBT layers prepared at 100 °C was observed by AFM. **Figure 3** shows AFM images for 100-nm-thick-PTCDI-C8 layers prepared at substrate temperature of 100 °C. Elongated needle-shape grains were formed over the C-sapphire substrate surface, and the grain length was estimated to be around 242 nm. The PTCDI-C8 layers possessed a relatively smooth surface with surface roughness (Ra) about 1.65 nm for prepared samples on (0001) C-sapphire substrate. The observed values show that the needle-shape grains grew with the smooth surface on growth of single crystal substrate. The needle-shape islands with the (001)-out-of-plane orientation were formed on the substrate by governing the π–π stacking. According to the experimental results, molecule-substrate interaction is weak and interaction between molecule-molecule is prominent.

Figure 4 shows AFM images of C8-BTBT layers prepared at 100 °C with the thickness of 100 nm. The layer by layer growth with several small islands were nucleated onto the early stage growth of continuous layers and the formation of continuous layer with several micro-meters wide, although some pores could be located between the coalescence islands. The surface roughness Ra could be estimated as 9.2 nm.

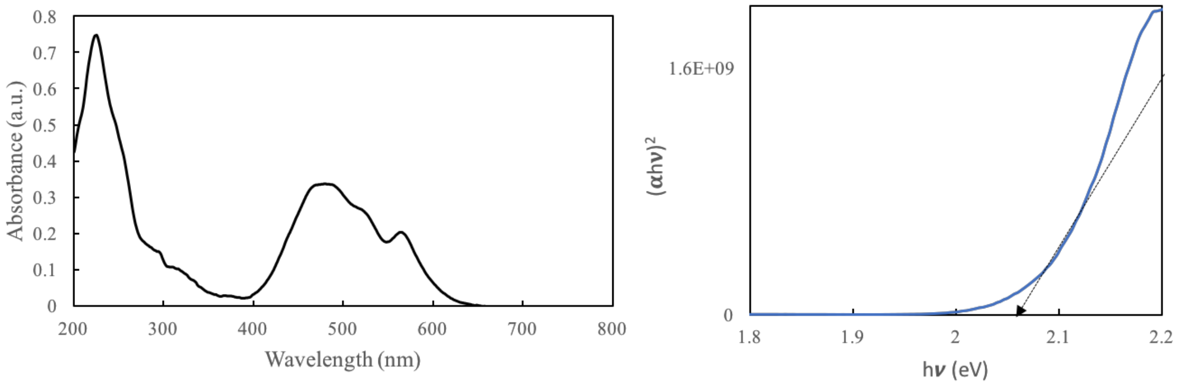

Figure 5 The optical absorption spectra for 100-nm-thick-PTCDI-C8 layers at 100 °C

Figure 5 shows the optical absorption spectra for 100-nm-thick-PTCDI-C8 layers at 100 °C. The PTCDI-C8 layers possessed three absorption peaks at the wavelength of 565 nm, 480 nm, and 228 nm and a weak shoulder at 525 nm. The spectra were almost the same in profile as that already reported for the PTCDI-C8 layer. (B. Mukherjee, et al, 2015). Since the C-sapphire substrate showed no absorption at wavelength from 200 to 700 nm, the absorption peaks at the wavelength of 228 nm also was originated from the PTCDI-C8 layers. The PTCDI-C8 layers showed an absorption edge at wavelength of 610 nm corresponding to the photon energy of 2.03 eV. The absorption edge wavelength was determined by extrapolating the linear line. The absorption coefficient was calculated from the absorbance at the wavelength of 228 nm and thickness, and value of 8.9×10^4 cm^{-1} for 100-nm-thick-PTCDI-C8 layers.

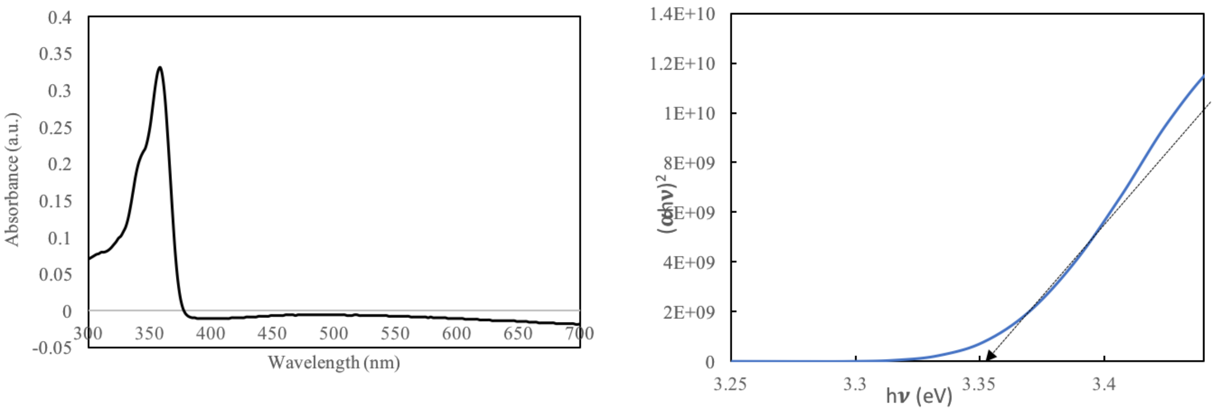

Figure 6 The optical absorption spectra for 100-nm-thick- C8-BTBT layers at substrate temperature 100 °C.

Figure 6 shows the optical absorption spectra for 100-nm-thick- C8-BTBT layers at substrate temperature 100 °C. The maximum absorption peak at the wavelength of 358 nm and a weak shoulder at the wavelength of approximately 340 nm could be estimated from absorption spectrum of prepared C_8-BTBT layer. The optical band gap energy of C8-BTBT layers was estimated to be 3.36 eV.

There was no effect of the atomic arrangement and lattice mismatch of (0001) Al_2O_3 C-Sapphire on the growth of the PTCDI-C8 layers, and C8-BTBT layers, the preferred orientation of (001) due to molecule-molecule interaction is stronger than those of molecule-substrate interaction. The growth of the PTCDI-C8 layers showed the similar growth to that of C8-BTBT layers.

Conclusions

π-conjugated organic semiconductors PTCDI-C8 and C8-BTBT layers were deposited on single crystal (0001) Al_2O_3, C-sapphire substrates by vacuum thermal evaporation technique. The (001)-out-of-plane orientation was developed on substrate material although there are large differences in the lattice mismatch. The needle-shape PTCDI-C8 grains and layer-by-layer of C8-BTBT islands growth were formed on C-Sapphire substrate. The optical band gap energy 2.03 eV of PTCDI-C8 and 3.36 eV of C8-BTBT were estimated from the absorption spectra of vacuum evaporated organic semiconductor layers. The results found in this experiment support the heteroepitaxial growth of organic semiconductors on the single crystal substrate without changing the orientation of deposited PTCDI-C8 and C8-BTBT, (001) preferred orientation on substrate which suggest that strong π-π bonding between molecules.

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