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Horizontally oriented molecular thin films for application in organic solar cells

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ABSTRACT

The authors investigate the influence of molecular orientation of *p*-type molecules of alpha-sexithiophene (α-6T) and *n*-type molecules of 3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI) on organic solar cell (OSC) performance. Deposition of α-6T and subsequently PTCBI on an α-6T buffer surface rubbed with a nylon cloth allows their horizontal orientations to be formed in separate layers. Power conversion efficiency and operation stability of a rubbed OSC are markedly improved when compared with an unrubbed OSC. The improved OSC performance is confirmed to be due to increases in light absorption, exciton diffusion length, energy difference between the *p*-type and *n*-type layers, and carrier collection by electrodes, which are caused by the rubbing-induced double horizontal orientations.

1. Introduction

Performance of organic (opto)electronic devices, such as organic light-emitting diodes (OLED), organic solar cells (OSC), and organic thin-film transistors (OTFT), has rapidly progressed through synthesis of new organic materials, exploration of new device architectures, and elucidation of device working mechanisms. In addition, considerable effort has recently been devoted to control molecular orientation to achieve higher device performance. It is known that for OTFTs a vertical orientation of molecules with their molecular axes stacked parallel to each other on a substrate surface enhances carrier mobility in the stacking direction due to enhanced π coupling between neighboring molecules [1,2]. For standard OLEDs and OSCs where a current flow takes place normal to the substrate plane, a horizontal orientation of molecules with respect to the substrate plane is more desirable for a current flow than the vertical orientation [3,4]. The horizontal orientation increases light out-coupling efficiency of OLEDs [5] and light-harvesting efficiency of OSCs [6] due to alignment of molecular electronic transition moments parallel to the substrate plane. Moreover it is known that ionization potential energy (IP) and electron affinity (EA) of organic films are dependent by several hundred meV upon molecular orientation [7–10], indicating that a charge injection barrier at metal/organic and organic/organic heterojunction interfaces as well as an energy difference between a highest occupied molecular orbital (HOMO) level of a *p*-type material and a lowest unoccupied molecular orbital (LUMO) level of an *n*-type material, which is correlated to open-circuit voltage of OSCs [11], are controllable by molecular orientation. We have recently demonstrated that a rubbing-induced horizontal orientation of alpha-sexithiophene (α-6T) markedly reduces a driving voltage of OLEDs due to a reduced hole injection barrier [10,12]. Thus, the appropriately controlled molecular orientation is very advantageous to improve device performance.

Deposition of an organic film on a specific surface (e.g., a KCl single-crystal surface [3], a copper iodide (CuI)-coated substrate surface [13], an oriented molecular surface [4], and a periodic groove surface [14]) has been used to control molecular orientation. Besides, quasi-homoepitaxial growth of organic molecules on a surface, where the same or a different kind of molecule is preoriented by a rubbing technique, is also possible to obtain a horizontal orientation of organic molecules [6,15–17]. Unique OLED and OSC characteristics have been realized by using the oriented molecular films. For examples, Videlot et al. fabricated the Schottky cells based on octithiophene (8T) and showed a substantial increase in photocurrent by aligning 8T molecules horizontally and parallel to each other on a substrate by means of a rubbing technique [6]. Era et al. used quasi-homoepitaxial growth of *p*-sexiphenyl (6P) on a rubbed 6P surface to obtain an uniaxially and horizontally oriented 6P film, resulting in the observation of polarized electroluminescence from the oriented 6P film although performance

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of the rubbed OLED was the same as that of an unrubbed OLED [16]. Yanagi et al. constructed OLEDs by depositing 6P and additional layers on a KCl (001) surface and transferring the multilayer structure to an indium tin oxide (ITO)-coated substrate [3]. A horizontal orientation of 6P, deposited at a lower temperature, resulted in a lower drive voltage than a vertical orientation. Tanaka et al. obtained uniaxially and horizontally oriented PTCBI by depositing PTCBI on a rubbed PTCBI surface. They used the oriented PTCBI film to fabricate an image sensor that works under polarized light irradiation by utilizing a difference in photocurrent [17]. Chen et al. found that copper phthalocianine (CuPc) molecules were horizontally oriented on a CuI surface although CuPc molecules were vertically oriented on a bare glass substrate [13]. OSC performance was higher when using the horizontally oriented CuPc than the vertically oriented CuPc. Moreover Yokoyama et al. demonstrated that planar-shaped long organic molecules in vacuum-deposited amorphous films were horizontally oriented by themselves without any influence of substrate surfaces [18], enabling higher-performance OSCs to be realized [19]. However in the above-mentioned reports, horizontally oriented molecules were formed in a single organic layer, so that the enhancing effect of the single horizontal orientation on the device performance is limiting. If both *p*-type and *n*-type molecules can be horizontally oriented in each layer of a multilayer structure simultaneously, OSC performance will be further enhanced because the enhancing effect caused by two kinds of horizontal orientation in the separate *p*-type and *n*-type layers becomes doubled when compared with the case of the single horizontal orientation.

In this study we show results of OSCs where both *p*-type molecules of α-6T and *n*-type molecules of 3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI) are horizontally oriented in separate layers by growing α-6T quasi-homoepitaxially and subsequently PTCBI quasi-heteroepitaxially on an α-6T buffer layer that is mechanically rubbed with a nylon cloth. We obtain about 3 times improvement of power conversion efficiency (η) by using the rubbing technique. To investigate reasons for the improved η, we analyze the α-6T and PTCBI films with ultraviolet/visible (UV–vis) absorption spectroscopy, atomic force microscopy (AFM), a photoluminescence (PL)-quenching technique [20,21], and photoelectron yield spectroscopy (PYS) and fabricate hole-only α-6T devices and electron-only PTCBI devices. As the results of the analyses, we find that the improved η arises from increases in absorbance, exciton diffusion length, HOMO–LUMO energy difference, and hole and electron collection by respective electrodes, which are caused by the double horizontal orientations of α-6T and PTCBI on the rubbed surface. We believe that the results obtained in this study are very useful for opening a way to design higher-performance OSCs and for clarifying working mechanisms of OSCs as well as basic optical, electronic and electrical characteristics of oriented molecular films.

2. Experimental

2.1. Materials

Fig. 1 shows the molecular structures of α-6T and PTCBI, which were used as model materials for fabrication of OSCs to investigate how their molecular orientations affect OSC performance. A strong intermolecular interaction between these sorts of flat molecule lead to efficient quasi-epitaxial growth [6,17]. α-6T (Aldrich) and

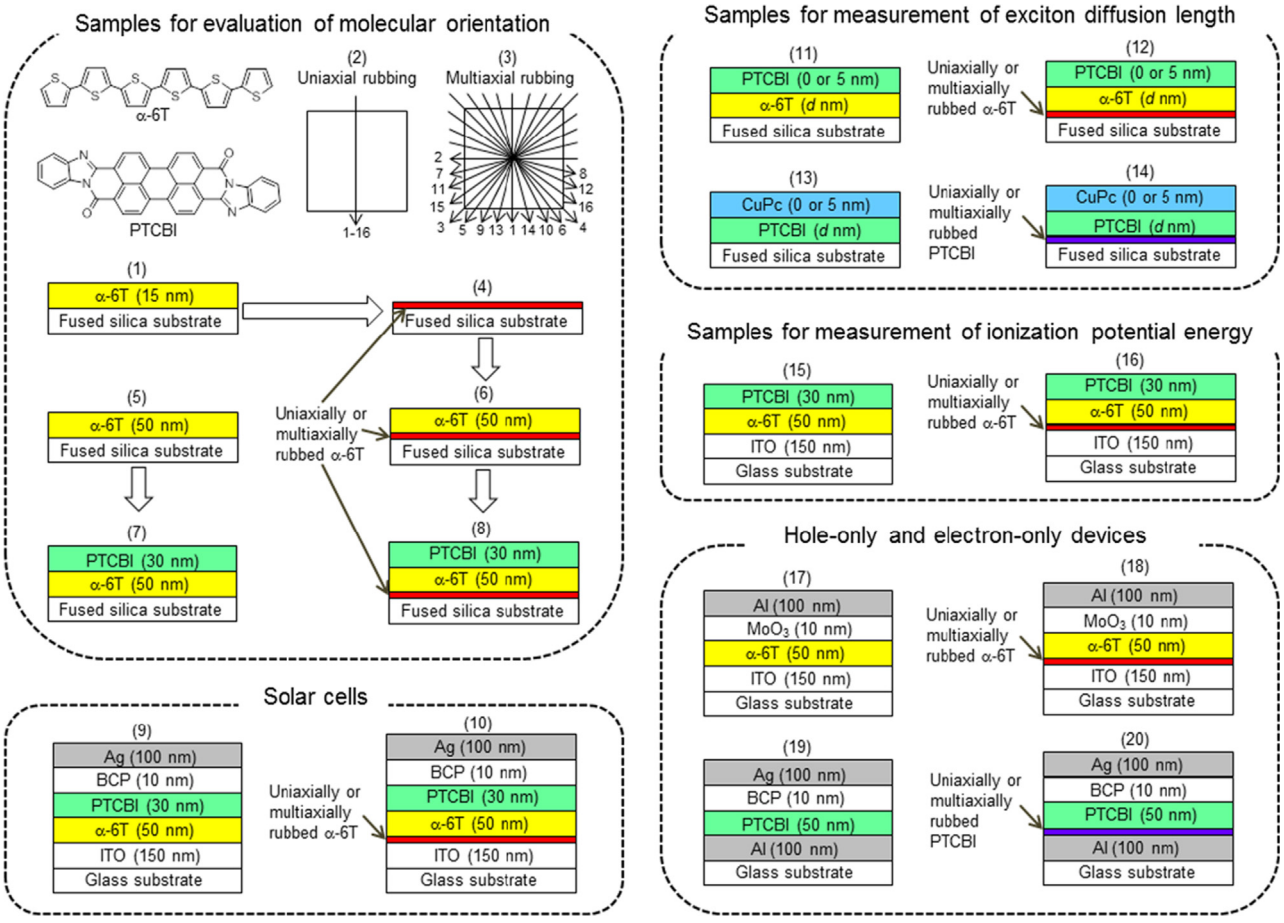

Fig. 1. Chemical structures of α-6T and PTCBI, sample preparation scheme and sample structures used in this study. (2) and (3) represent top views of substrates where arrows with numerals indicate rubbing directions and rubbing orders. For samples (11)–(14), *d* of α-6T was varied from 20 to 50 nm and *d* of PTCBI was varied from 10 to 25 nm.