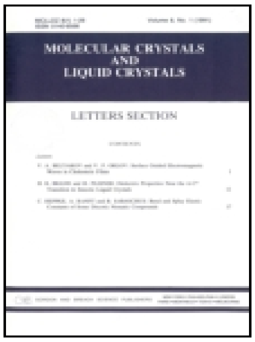

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Orientation of Rod-Shape Molecule, 2,2′-Bis[4-(Trifluoromethyl)Phenyl]-5,5′-Bithiazole in Films Deposited in a Vacuum on Oriented α-Sexithiophene Films

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We demonstrated orientation control of n-type rod-shape, 2,2′-Bis[4-(trifluoromethyl)phenyl]-5,5′-bithiazole (BTMPB) molecules when deposited on the in-plane oriented polythiophene (PT) and α-sexithiophene (6T)/PT films in vacuum. The results showed that the π-π stacking direction of BTMPB molecules on the PT and 6T/PT films is perpendicular to the substrate plane. In addition, a molecular long axis of BTMPB oriented parallel to the friction direction of the PT. Moreover, in-plane orientation of BTMPB was more enhanced by in-plane oriented 6T molecules than in-plane oriented PT underneath. On the other hand, the molecular long axis of BTMPB deposited on the substrates stood on the substrates.

Keywords Friction Transfer; Conductive Polymer; Polythiophene; α-sexithiophene; rod-shape molecule; Orientation

1. Introduction

Molecules of π-conjugated rod-shape molecules are promising materials for application in organic opto-electronic devices like field-effect transistor (FETs) [1] and organic photovoltaic cells (OPVs) [1, 2]. Control of molecular orientation is a key issue to improve the performance of these FETs and OPVs based on films of the rod-shape molecules because molecular orientation has been reported to significantly affect the performance of these devices. For organic photovoltaic (OPV) devices, the increase in mobility in the direction perpendicular to the substrate should lead to improved power conversion efficiency. This can be achieved if these molecules are lying horizontally on the substrate, which allows π electrons overlap, such as herringbone or cofacial π stacking, in the vertical direction [3, 4]. However, rod-shape molecules tend to lie on oxide substrates like SiO_2, quartz and ITO [5]; therefore, orientation control of these molecules is required. There are some reports about

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the improvement of performance of OPV devices consisting of p-type oligothiophenes lying on the substrate by controlling orientation of these molecules [3, 4].

We have reported the formation of OPV devices consisting of α-sexithiophene (6T) layers, which act as the p-type semiconductor, where the 6T molecules lie on the substrates by depositing 6T on oriented PT films, [5] and evaluation of the OPVs performance [6]. The OPV performance of devices based on the lying 6T films was confirmed to be higher than that of those based on standing 6T films [6].

N-type rod-shape molecules, which have been used as n-type organic FETs [7–12], are also expected to be suitable for the OPV application instead of typical n-type semiconductor, like fullerene, and its derivatives; however, there are no reports on OPV devices consisting of n-type rod-shape molecules. This may be because these n-type rod-shape molecules stand on the substrate by vacuum deposition; therefore, it is expected to achieve in-plane orientation of the molecular long axis of these molecules. OPVs based on these in-plane oriented molecules could show higher OPV performance due to its higher electron transport property.

In this study, we succeeded in the formation of in-plane oriented films of n-type rod-shape molecules, 2,2′-bis[4-(trifluoromethyl)phenyl]-5,5′-bithiazole [7], by depositing the molecules in a vacuum on the in-plane oriented PT and 6T/PT films formed by the method reported previously [5, 6].

2. Materials and Methods

PT (Lot No. 12911DH) and 2,2′-bis[4-(trifluoromethyl)phenyl]-5,5′-bithiazole (BTMPB) were purchased from Aldrich Chemical Co., Inc. 6T was purchased from Tokyo Chemical Industry Co., Ltd. These materials were used without further purification. Chemical structures of these materials are shown in Figs. 1(a), (b) and (c).

The friction transfer process was carried out by squeezing and drawing this PT pellet on the substrates [5, 6]. The PT thickness was about 4 nm.

6T films with 20 nm thickness were deposited onto these PT films, under vacuum better than 4×10^{-4} Pa [6]. Then, BTMPB was deposited at a deposition rate between 0.1 and 0.2 nm/s onto these 6T/PT films.

X-ray diffraction (XRD) measurements were carried out with a SHIMADZU LabX XRD-6000 X-ray diffractmeter system with CuKα radiation as an X-ray source.

UV-vis absorption spectra were measured using a Shimadzu UV-3150 spectrophotometer with a Glan-Taylor polarizing prism.

3. Results and Discussion

To determine the molecular long axis direction of BTMPB perpendicular and/or parallel to the substrate plane, XRD measurement was performed. Figs. 2 (a) and (b) show XRD results of a BTMPB/glass and a BTMPB/PT/glass. The 020, 200, 400 and 600 reflections of BTMPB [7] were observed from the BTMPB/glass. The 020 reflection of BTMPB derived from BTMPB crystallites whose *b*-axis was oriented perpendicular to the substrate plane. In the unit cell of BTMPB crystallite, molecular planes of BTMPB were almost perpendicular to the *b*-axis (see Fig. 2(d) [7]); therefore, molecular long axis was oriented parallel to the substrate and "π-π stacking" direction of BTMPB was perpendicular to the substrate. The 200, 400 and 600 reflections of BTMPB derived from BTMPB crystallites whose *a*-axis was oriented perpendicular to the substrate plane; *i.e.*, the molecular long axis of BTMPB

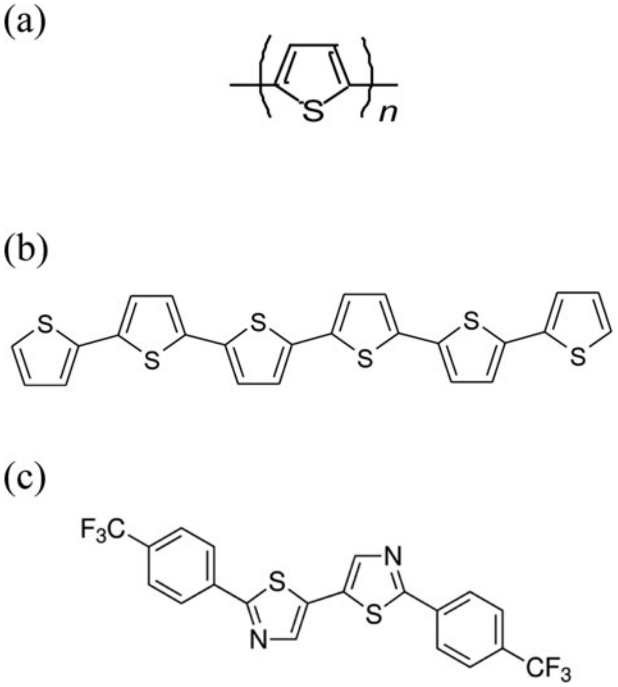

Figure 1. Chemical structure of (a) PT, (b) 6T and (c) BTMPB.

molecules stood on the substrate (see Fig. 2(d)). Therefore, this result indicates that some BTMPB molecules deposited on the glass substrate lay on the substrate, while the molecular long axis of some molecules stood on the substrate in the film. On the other hand, strong 020 reflection of BTMPB was observed from the BTMPB/PT/glass, which shows that *b*-axis of most BTMPB crystallites oriented perpendicular to the substrate plane. In this case, the high electron mobility is in the direction perpendicular to the π-π stacking direction, of crystalline films of BTMPB. Therefore, devices produced with oriented BTMPB whose π-π stacking direction perpendicular to the substrate are expected to show increased current density through the films.

For the fabrication of p-n planer heterojunction OPVs, these oriented BTMPB molecules parallel to the substrate planes on p-type semiconductor 6T films are required. Fig. 2(c) shows XRD results of a BTMPB/6T/PT/glass. Dislike the result of the BTMPB/PT/glass, only the 020 reflection of BTMPB [7] and 12 00 reflection of 6T [13] was observed, which shows that *b*-axis of almost all the BTMPB crystallites oriented perpendicular to the substrate plane. This result indicates that 6T molecules strongly enhance orientation of BTMPB molecules; therefore, just (020) reflection was observed from the BTMPB/6T/PT/glass.

To obtain information about in-plane orientation of BTMPB on substrates, polarized UV-vis measurement was performed. Fig. 3 shows the polarized UV-vis spectra derived from the 40-nm-thick BTMPB films after subtracting the spectra of PT/quartz and quartz substrates [5, 6] from the spectra of the BTMPB/PT/quartz and the BTMPB/quartz substrates, respectively. Optical polarization parallel (red and green lines) and orthogonal (black and blue lines) to the friction direction are shown. The spectra of the BTMPB/PT/quartz show that absorbance of a peak around 440 nm, in parallel polarization, was larger than that

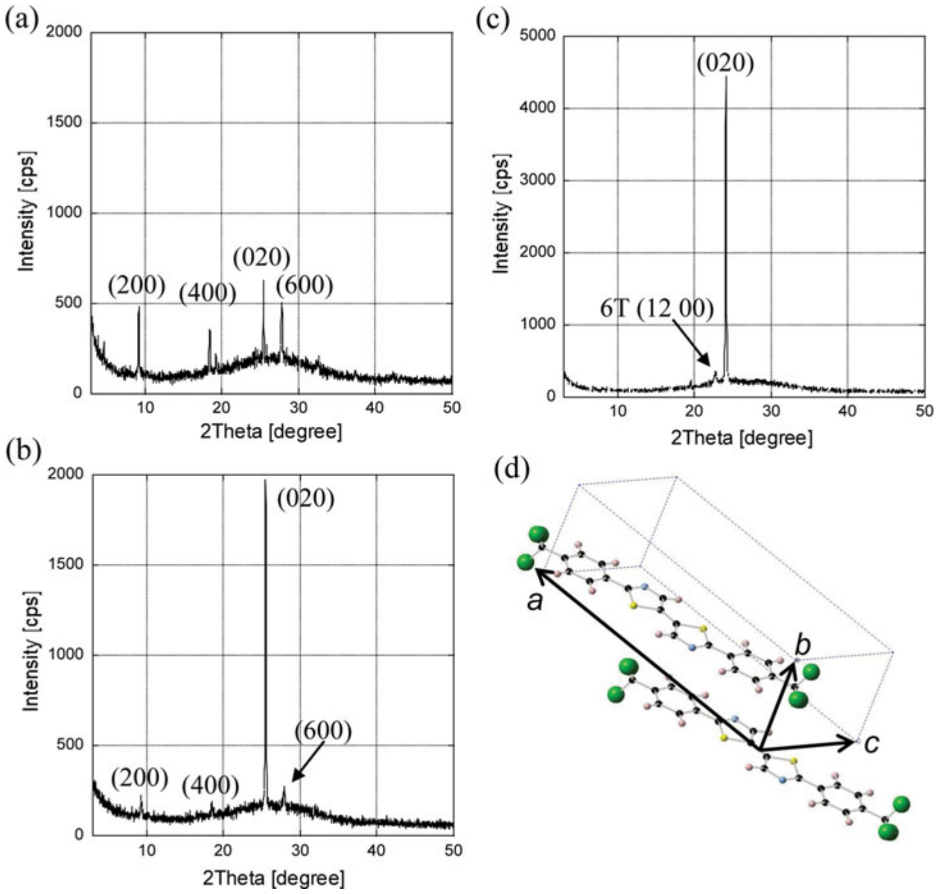

Figure 2. XRD profiles of 50-nm-thick BTMPB on glass (a), on PT/glass (b) and on 20-nm-thick-6T/PT/glass (c). (d) shows molecular structure of BTMPB.

in orthogonal polarization, whereas absorbance of a peak around 320 nm, in orthogonal polarization, was larger than that in parallel polarization. Absorbance maximum wavelength of BTMPB in chloroform was around 360 nm (thick dashed line), which is much different from that of the BTMPB films. This change is probably derived from molecular orientation and/or intermolecular interaction of BTMPB in the films. The polarized UV-vis spectra provide information about the anisotropy of the absorption process of BTMPB molecules. In this case, the large anisotropy was observed from the BTMPB/PT/quartz, which is due to the in-plane orientation of BTMPB molecules.

On the other hand, the BTMPB film deposited on the quartz substrates showed no anisotropy (blue and green spectra; overlapped), which shows that molecular axis of BTMPB is not aligned in the substrate plane. The spectra of the BTMPB/quartz show peaks around 320 nm in both parallel and orthogonal polarization, which is the same wavelength of the peak observed when orthogonally polarized light was irradiated to the BTMPB/PT/quartz. The electronic transition probability is maximized when the transition dipole moment of the molecule lies parallel to the direction of the electric vector of the light [14]. From the XRD result, the molecular long axis of some BTMPB molecules on the

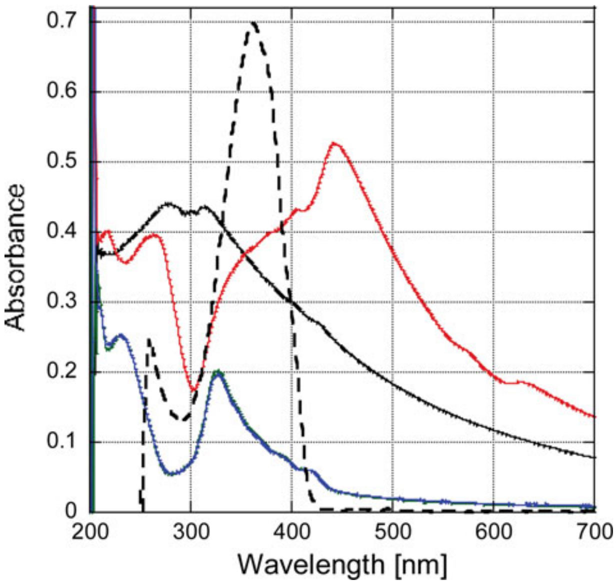

Figure 3. Polarized UV-vis spectra of 40-nm-thick BTMPB obtained by subtracting the spectra of the PT/quartz substrate and the quartz substrate from the spectra of the BTMPB/PT/quartz (red and black lines) and the BTMPB/quartz (blue and green lines) substrates, respectively, for optical polarization parallel (red and green lines) and orthogonal (black and blue lines) to the friction direction. Thick dashed line shows the spectrum of BTMPB in chloroform with the concentration of 2×10^{-4} mol/l.

glass substrate was determined to be nearly perpendicular to the substrate plane. Therefore, these peaks are probably due to the transition dipole moment orthogonal to the molecular long axis of BTMPB. On the other hand, the peak around 440 nm can be derived from the transition dipole moment of BTMPB parallel to the direction of the molecular long axis.

These results show that the molecular long axis of BTMPB in films aligns parallel to the friction direction on the oriented friction-transferred PT films, which is in agreement with previous results that molecular long axis of rod-shape molecules deposited on friction-transferred polymer films tend to be oriented parallel to the friction direction [5, 13, 15].

When BTMPB was deposited on the oriented 6T/PT films, the molecular long axis of BTMPB in the films also aligns parallel to the friction direction (data not shown).

Based on these results, one can expect higher OPV performance by irradiation of polarized light parallel than that orthogonal to the molecular chain of BTMPB and 6T, indicating that the BTMPB/6T/PT OPV devices can also be used as detectors of polarized light [3, 4, 16–18] and in liquid crystal displays as the polarized OPVs [19].

4. Summary

Orientation control of BTMPB was achieved by depositing BTMPB on the in-plane oriented PT and 6T/PT films in vacuum. The results showed that the *b*-axis of the BTMPB on the in-plane oriented PT and 6T/PT films is perpendicular to the substrate plane; *i.e.* π-π stacking direction of BTMPB molecules perpendicular to the substrate. In addition, the molecular long axis of BTMPB was oriented parallel to the friction direction of the PT. Moreover, in-plane orientation of BTMPB was enhanced by in-plane oriented 6T molecules underneath. An improvement of OPV performance based on BTMPB/6T/PT is expected, where BTMPB is used as an n-type semiconductor.

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