Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 17 Oct 2011

To cite this article: Hideyuki Tanaka, Takeshi Yasuda, Katsuhiko Fujita & Tetsuo Tsutsui (2006): Highly-Oriented Organic Thin Films and Application for Photovoltaic Device, Molecular Crystals and Liquid Crystals, 462:1, 67-73

To link to this article: http://dx.doi.org/10.1080/15421400601010631

Mol. Cryst. Liq. Cryst., Vol. 462, pp. 67–73, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601010631

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Highly-Oriented Organic Thin Films and Application for Photovoltaic Device

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We fabricated highly-oriented thin films of 3,4,9,10-perylenetetracarboxylic-bis-benzimidazole (PTCBI), poly(9,9-dioctyl-fluorene) (PFO) and regioregular poly(3-hexylthiophene) (P3HT). Each material was aligned by the rubbing process, and high dichroic ratio of 4–6 was achieved. We also investigated application for organic p-n heterojunction type photovoltaic devices, which include the aligned layer. Aligned-PTCBI (n-type) stacked with unaligned-TiOPc (p-type) showed good photovoltaic performance equal to the conventional unaligned stacked devices. High power conversion efficiency of 0.8% was achieved.

Keywords: aligned film; organic photovoltaic device; perylenetetracarboxylic-bis-benzimidazole; polarization-sensitive photo-detectors; rubbing method

INTRODUCTION

One of the fascinating aspects of organic semiconductors is utilization of optical and electronic anisotropy originated from anisotropic shape of organic molecules. Various organic polarized light-emitting diodes and field-effect transistors with large charge transport anisotropy have been reported [1–3]. A few organic photovoltaic devices using oriented thin films were also reported [4]. The quantum efficiency and power-conversion efficiency of those photovoltaic devices, however, are much lower than those of recent multiplayer p-n junction

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type or bulk heterojunction photovoltaic devices. In this letter, for the purpose of achieving high power conversion efficiency in photovoltaic devices, we introduce orientation of the various organic thin films, and investigated polarization-sensitive photovoltaic devices made of p-n hetero-junction of oriented organic layer. Highly-oriented thin films of 3,4,9,10-perylenetetracarboxylic-bis-benzimidazole (PTCBI), poly(9,9-dioctyl-fluorene) (PFO) and regioregular poly(3-hexylthiophene) (P3HT) can be produced by the rubbing method. Aligned-PTCBI stacked with titanyl phthalocyanine (TiOPc) showed good photovoltaic performance equal to the conventional organic photovoltaic devices.

EXPERIMENTAL

First of all, the fabrication of the aligned-PTCBI films and the photovoltaic devices with high molecular orientation were tested. A 10-nm-thick PTCBI layer was vacuum deposited on a glass substrate. The surface of the PTCBI layer was gently rubbed ten times with a velvet cloth in an ambient atmosphere and the PTCBI layer was grown at a deposition rate of 0.3 nm/min on the rubbed substrate [5]. Figure 1 shows the absorption spectra of the PTCBI layer, when parallel and perpendicularly polarized light beams along the rubbing direction were irradiated. The dichroic ratio of optical absorption was 4.7 at the peak wavelength of 540 nm. Moreover, we introduced the aligned-PTCBI layer into photovoltaic devices. The configuration of the devices was ITO/In/aligned-PTCBI/TiOPc/PEDOT-PSS/Au (using aligned-PTCBI). A thin indium (In) metal layer was vacuum deposited onto a precleaned transparent indium-tin-oxide (ITO) substrate, followed by deposition of a 20-nm-thick aligned PTCBI layer (n-type) by the procedure mentioned above. Then, a 20-nm-thick TiOPc layer (p-type) was formed at a deposition rate of 0.05 nm/s. On top of TiOPc layer, a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron 4083) layer was formed by spin coating followed by a heat treatment at 120°C for 5 min in a N_2 glove box. A 20-nm thick of Au electrode was deposited through a shadow mask.

Next, the fabrication of the aligned-PFO films and the photovoltaic devices with high molecular orientation were tested. An aqueous solution of precursor-PPV was spin coated on a glass substrate, and thermally polymerized to PPV. The surface of PPV was rubbed ten times with a velvet cloth in an ambient atmosphere. Spin coated PFO onto rubbed PPV was induced orientation followed by a heat treatment at 60°C for 10 min and at 210°C for 30 min in a N_2 glove box [6].

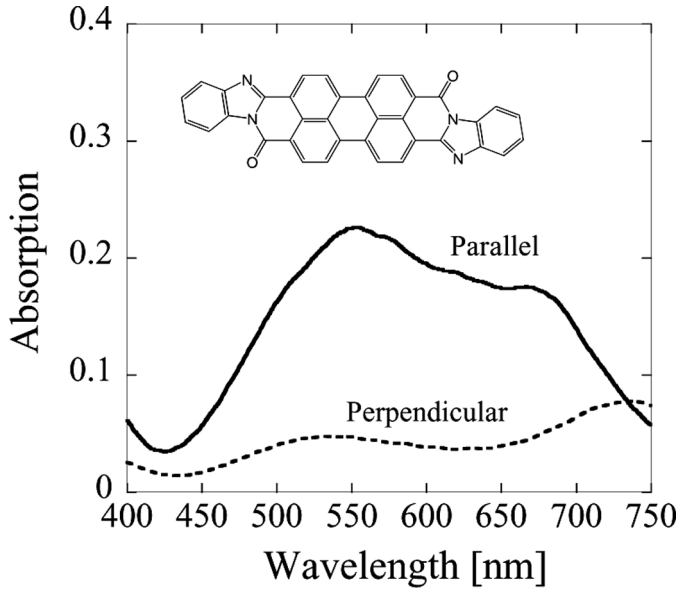

FIGURE 1 Absorption spectra of aligned-PTCBI layer when light is polarized parallel and perpendicular to molecular orientation axis of PTCBI. The inset shows the chemical structure of PTCBI.

Figure 2 shows the absorption spectra of the PFO layer, when parallel and perpendicularly polarized light beams along the rubbing direction were irradiated. The dichroic ratio was 4.2 at the peak wavelength of 395 nm. We tried to introduce the aligned-PFO layer into photovoltaic devices. The configuration of the devices was ITO/PPV/aligned-PFO/C_{60}/Al (using aligned-PFO). Less than 40 nm thick aligned PFO layer (p-type) was formed onto a precleaned ITO substrate by the procedure mentioned above, followed by deposition of a 20-nm-thick C_{60} layer (n-type). On top of C_{60} layer, a 80-nm thick of Al layer was deposited.

The aligned-P3HT films and the photovoltaic devices with high molecular orientation were also tested. Spin coated P3HT films were obtained on glass substrate by a solution (6 mg/ml) in chloroform. A P3HT film was heated at 100°C for 30 min, after that, the surface of P3HT was directly rubbed ten times with a cloth (kimwipe) at 100°C in a N_2 glove box [3]. Figure 3 shows the absorption spectra of the P3HT layer when parallel and perpendicularly polarized light beams along the rubbing direction were irradiated. The dichroic ratio was 4.3 at the peak wavelength of 560 nm. Photovoltaic devices composed

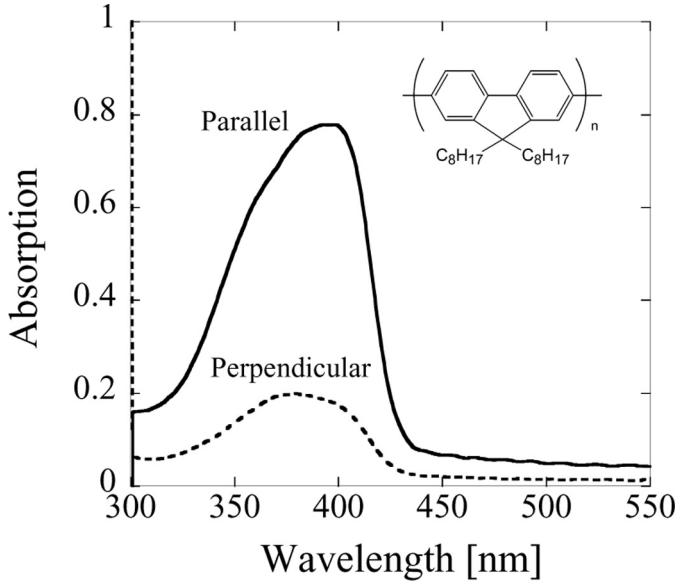

FIGURE 2 Absorption spectra of aligned-PFO layer when light is polarized parallel and perpendicular to molecular orientation axis of PTCBI. The inset shows the chemical structure of PFO.

of the aligned-P3HT layer was fabricated. The configuration of the devices was ITO/PEDOT:PSS/aligned-P3HT/C_{60}/BCP/Al (using aligned-P3HT). Less than 40 nm-thick aligned P3HT layer (p-type) were formed onto a PEDOT:PSS coated ITO substrate by the procedure mentioned above, followed by deposition of a 20-nm-thick C_{60} layer (n-type). On top of C_{60} layer, a 15-nm thick BCP and a 80-nm thick Al layer was deposited.

Polarized white light provided from an AM1.5 solar simulator with the intensity of 45 mW/cm^2 was used for the estimation of power conversion efficiency of the photovoltaic devices. Polarized light was irradiated onto the devices through the ITO electrode with the polarization parallel or perpendicular to the orientation-direction of the aligned layer. Current-voltage characteristics were measured with a Keithley 238 source measure unit.

RESULTS AND DISCUSSION

Highly-ordered organic thin films were successfully produced in PTCBI, PFO and P3HT. However, the characteristics of photovoltaic

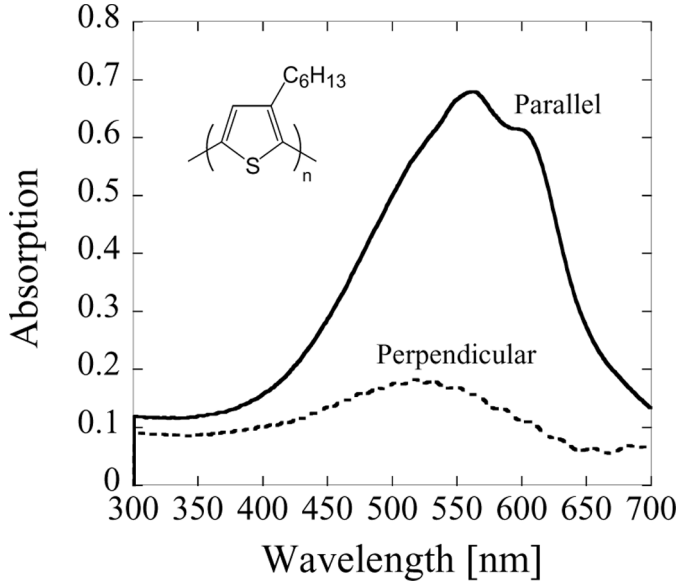

FIGURE 3 Absorption spectra of aligned-P3HT layer when light is polarized parallel and perpendicular to molecular orientation axis of PTCBI. The inset shows the chemical structure of P3HT.

devices with each material showed a large difference. Table 1 shows photovoltaic performances of each device. An aligned-PTCBI stacked with TiOPc showed good photovoltaic performance equal to the conventional stacked devices and large photocurrent anisotropy, whereas poor efficiencies were observed in the devices with aligned-PFO or P3HT layers.

Figure 4 shows the current density-voltage characteristics of the aligned-PTCBI device under white light illumination. Short-circuit

TABLE 1 The Performance of each Photovoltaic Devices under Parallel or Perpendicular Polarized Lights

Material	Polarization direction	Jsc [mA/cm^2]	Voc [V]	F. F	η [%]	Current ratio
PTCBI	perpend	0.78	0.52	0.50	0.45	–
	parallel	1.30	0.55	0.49	0.78	1.67
PFO	perpend	45.7×10^{-3}	0.38	0.24	0.0092	–
	parallel	50.0×10^{-3}	0.38	0.25	0.0105	1.09
P3HT	perpend	4.20×10^{-3}	0.63	0.18	0.0011	–
	parallel	6.22×10^{-3}	0.68	0.18	0.0017	1.48

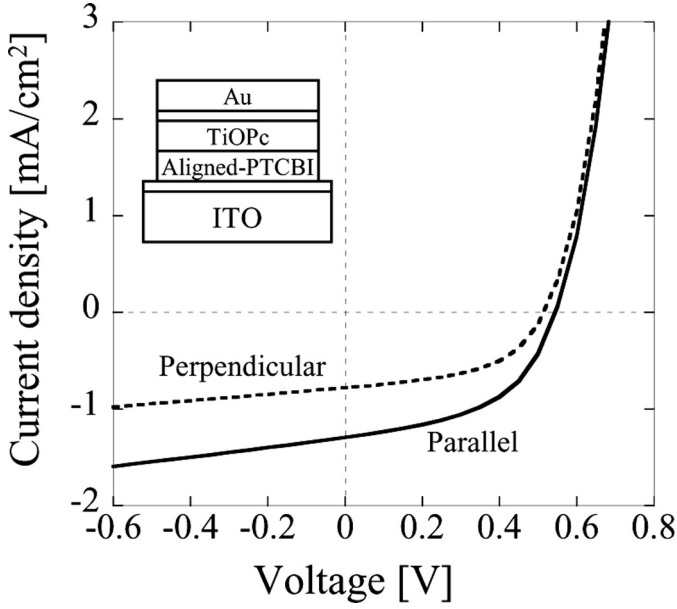

FIGURE 4 Current density vs. voltage curves of ITO/In/aligned-PTCBI/TiOPc/PEDOT:PSS/Au device under irradiation of white light polarized parallel and perpendicular to molecular orientation axis of PTCBI. The power of incident polarized white light is 45 mW/cm^2. The inset shows the device structure.

current density (Jsc), open-circuit voltage (Voc), fill factor (F.F) and the power conversion efficiency (η) under the polarized light parallel to the orientation direction were 1.30 mA/cm^2, 0.55 V, 0.49 and 0.78%, respectively. When polarized light perpendicular to the orientation axis was used, Jsc decreased to 0.78 mA/cm^2 and η was 0.45%. The ratio of short-circuit current of the parallel configuration to that of the perpendicular configuration was 1.67. The surface of the devices has small roughness because of the thin rubbed layer, and spin coated PEDOT:PSS layer gave smooth surface. Therefore, using aligned-PTCBI for photovoltaic devices was suitable, and it is possible effective polarization detection in high power conversion efficiency.

We also confirmed photocurrent anisotropy of 1.09 and 1.48, in the device using an aligned-PFO and -P3HT, respectively. However, these devices had small Jsc value with the order of μA. Electroluminescence and field-effect transistor composed of aligned-PFO were successfully fabricated, whereas tested p-n heterojunction type devices showed low power conversion efficiency, mainly due lower charge generation

efficiency followed by absorption of polarized light, originated from deep ionization potential of PFO. P3HT is currently studied for material of bulk hetero-junction type of photovoltaic devices [7], and P3HT stacked with C_{60} also exhibits good photovoltaic performance. Impurities and defects may be introduced on the rubbed P3HT film surface and this procedure was unsuitable for photovoltaic device, because the p-n interface was most important for photon-to-electron conversion.

In conclusion, we have demonstrated polarization-sensitive photovoltaic devices using oriented thin films of several organic semiconductors. Aligned-PTCBI stacked with TiOPc showed good photovoltaic performance with large anisotropy of the photocurrent.

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