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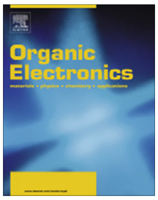

Structural control of bulk heterojunction films based on oligothiophene with sterically-bulky groups

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ABSTRACT

Organic photovoltaic solar cells based on oligothiophene and fullerene have been investigated intensively. Until now, the morphologies of bulk heterojunction (BHJ) structures based on oligothiophene and fullerene have been difficult to control because the oligothiophene molecules have lacked substituent groups and therefore have interacted strongly with one another to the point of aggregating into microfibril structures.

We succeeded in fabricating homogeneous oligothiophene:C_{60} BHJ films by adding sterically-bulky groups to oligothiophene in order to control the extent of aggregation. We found that the aggregation onset and maximum fill factor occurred at higher oligothiophene concentrations in BHJ films with C_{60} for the substituted molecules – the ratio that provides as much oligothiophene as possible for good photovoltaic performance but not so much as to incur aggregation-fill factor was improved. Here in, we report the morphologies and photovoltaic performances of single-component oligothiophene films and BHJ films based on oligothiophenes.

1. Introduction

The power conversion efficiency (PCE) of organic photovoltaic (OPV) solar cells based on small molecules improves significantly when the cells contain bulk heterojunction (BHJ) structures that blend donor molecules and acceptor molecules [1–5]. In particular, BHJ cells based on the donor molecule oligothiophene (especially α-sexithiophene (**α-6T**)) and the acceptor molecule fullerene (C_{60}) have been studied intensively [6–8]. The **α-6T** molecules were used as organic field-effect transistors (OFETs) because of their highly-ordered crystalline structures [9,10]. The presence of oligothiophenes in OPVs is advantageous for two main reasons: First, they enable easy control of redox energy level and crystallinity by chemical modification [11,12]. Second, they promise high open-circuit voltages (V_{oc}) because of their deep HOMO levels; for example, **α-6T** has a HOMO level of 5.2 eV [13]. The OPV performance of a BHJ solar cell based on **α-6T** and C_{60} depends strongly on the volume ratio of **α-6T** to C_{60} in the film [6]. At an equal volume ratio (**α-6T**:C_{60} = 1:1), performance is poor because **α-6T** molecules form aggregation structures having microfibril shape with extremely rough surface. At volume ratios of **α-6T** less than 50%, both favorable and unfavorable results are considered. On the favorable side, with less **α-6T** present, aggregation of microfibrils does not occur, which enhances cell performance. On the unfavorable side, with less **α-6T** available to absorb light, light-absorption efficiency decreases and hole-transport capability narrows.

However, the effect of donor volume ratio on BHJ-type OPV device remains unclear. To achieve higher OPV performance, it was necessary to expand interface area between

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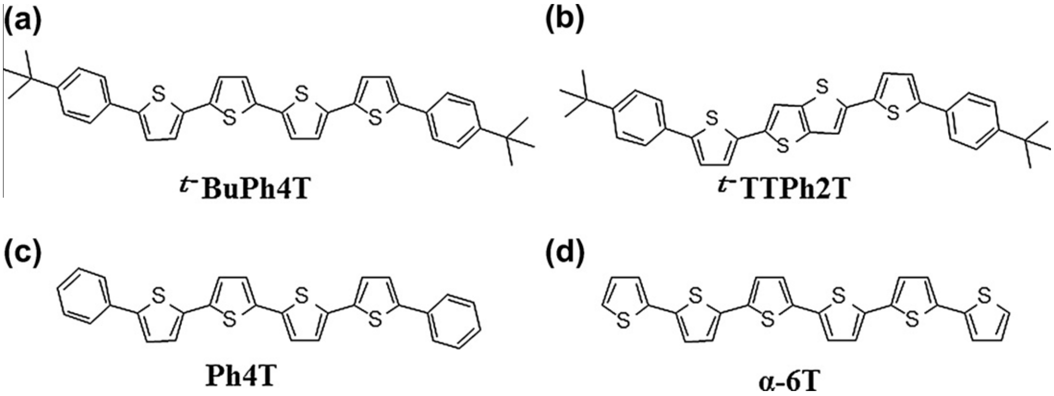

Fig. 1. Structures of oligothiophene derivatives: (a) ***t*-BuPh4T**, (b) ***t*-TTPh2T**, (c) **Ph4T**, (d) **α-6T**.

donor and acceptor [14]. These findings suggest that non-uniform composition in the BHJ film leads to low separation efficiency of electron–hole pairs. There is a possibility of limited photocurrent densities and fill factors in BHJ-type devices based on **α-6T** and C_{60}. Unless the strong interactions among oligothiophenes can be suppressed, the performance of BHJ cells based on oligothiophene and C_{60} will remain limited.

To overcome these problems, we focused on controlling the BHJ film structure using sterically-bulky substituent oligothiophenes that inhibit microfibril growth in the films.

In the field of organic light-emitting diodes (OLEDs), it was reported that the molecules having *tert*-butyl groups formed amorphous-like films [15–17]. The *tert*-butyl group has the effect of breaking the molecular stacking.

Accordingly, we synthesized the novel oligothiophene derivatives ***t*-BuPh4T** and ***t*-TTPh2T** having the sterically-bulky group *tert*-butyl (Fig. 1a and b). For a reference, we also synthesized bisphenyl-quarterthiophene (Fig. 1c, **Ph4T**) having a sterically rigid group so that we could compare the performance of oligothiophenes having sterically-bulky and sterically-rigid groups. In addition, we synthesized thienothiophene having a *tert*-butyl groups on its backbone (Fig. 1b, ***t*-TTPh2T**) so that we could investigate the effect of this configuration on BHJ film morphology.

2. Experimental

2.1. Fabrication of OPV device

OPV devices were fabricated by the following steps. (1) Glass substrates coated with indium–tin-oxide (ITO, purchased from Sanyo Vacuum Industries Co., Ltd.) film were cleaned by oxygen plasma for 30 min. ITO film thickness was 150 nm; sheet resistance was about 15 Ω/sq. (2) A molybdenum oxide (MoO_3; ca.15 nm) was deposited onto the ITO film by vacuum vapor deposition. The vacuum pressure was 10^{-5} Pa. (3) A BHJ layer consisting of oligothiophene (***t*-BuPh4T**, ***t*-TTPh2T**, **Ph4T**, or **α-6T**) and C_{60} (purchased from Frontier Carbon Corp.) was deposited onto the MoO_x layer by vapor deposition. The thickness of the BHJ layer was 50 nm. The volume ratio of the BHJ layer was controlled by adjusting the deposition rates of oligothiophene and C_{60}, which were monitored by quartz crystal microbalance. (4) An electron-transporting layer of C_{60} (30 nm) was deposited onto the BHJ layer. (5) An exciton-blocking layer of bathocuproine (BCP; 6 nm) was deposited onto the C_{60} layer. (6) Finally, a thick cathode contact layer of aluminum (Al; 80 nm) was deposited onto the BCP layer. Therefore, our fabricated BHJ-type device structure is ITO/MoO_x(15 nm)/oligothiophene:C_{60} (50 nm)/C_{60} (30 nm)/BCP (6 nm)/Al (80 nm) as shown in Fig. 2. The active area of our fabricated devices was 0.04 cm^2.

2.2. Measurement

OPV characteristics were measured under an Air Mass 1.5 Global (AM1.5G) solar simulator light source, calibrated at 100 mW/cm^2 using an amorphous silicon reference cell with an amorphous silicon optical filter (Bunko Keiki BS520). *J–V* characteristics were measured with a source meter (KEITHLEY 2400 series). Photovoltaic characteristics were measured under N_2 atmosphere at room temperature without exposure to ambient air.

Ionization potentials were measured by photoelectron spectroscopy (Bunko Keiki BIP-KV200) under a N_2 atmosphere. Atomic force microscopic images were taken by SII nanotechnology, Nanonavi/E-sweep, dynamic force microscopy (DFM-mode; scanning with tapping). The

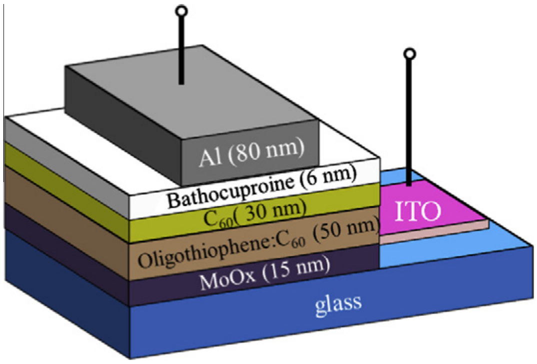

Fig. 2. Schematic of our fabricated BHJ-type device structure.