Communications

Enhancement of Power Conversion Efficiency of Photovoltaic Cell Fabricated with 1,2,4,5-Tetra(6-hexyl-2-vinyl-dithieno [3,2-b;2',3'-d]thiophene)-benzene and Methanofullerene [6,6]-phenyl C61-butyric acid Methyl Ester

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Introduction

With regard to the application of organic semiconductors in electronic and optoelectronic devices, the organic photovoltaic cell (OPV) in particular is an important device for developing future energy resources.1-6

Recently, organic photovoltaic devices employing conjugated polymer-fullerene heterojunctions have been shown to have a power conversion efficiency approaching 5.0-6.0%. This range of value is obtained by introducing variations in the processing techniques. Oligothiophenes are also well-known as good hole-transport materials and by changing the number of thiophene rings and making chemical modifications or substitutions, its characteristics relevant to PV applications can be controlled. However, most of the linear oligothiophenes are not well soluble in organic solvents. Compared with linear organic conjugated oligomers and polymers used in organic field-effect transistors (OFETs) or OPVs, multi-branched molecules have a number of advantages, including the ability to spatially control the active components, and thus, the interlayer carrier mobility properties owing to ready crystallization.7-12

In this work, we demonstrated new organic photovoltaic devices fabricated with 1,2,4,5-tetra(6-hexyl-2-vinyl-dithieno [3,2-b;2',3'-d]thiophene)-benzene (HPDTT). In our previous report, a similar molecule of 1,2,4,5-tetakis((E)-2-(5-hexyl-2,2-bithiophen-5-yl)vinyl)benzene (HPBT) having bithiophene peripheral groups was employed to PV device, it exhibits power conversion efficiency (PCE) of around unity. HPDTT is also well mixed with methanofullerene [6,6]-phenyl C61-butyric acid methyl ester (PCBM) for fabricating bulk heterojunction PV devices. The device properties were investigated and compared with those of the device fabricated with HPBT and PCBM.

Experimental

HPDTT was synthesized by following our previous method.12 PCBM was purchased from Nano-C. The redox properties of HPDTT were examined by using cyclic voltammetry (Model: EA161 eDAQ) followed by our previous report.12 Atomic force microscopy (Digital Instruments Multimode equipped with a nanoscope IIIa controller) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the samples. The film samples were fabricated by spin-coating (1,500 rpm) on PEDOT:PSS coated silicon wafer followed by drying at 60 °C under vacuum.

In order to study absorption behavior, the solutions of HPDTT and HPDTT:PCBM (1:1) were prepared in chloroform. Thin films were fabricated on quartz substrates using the solution (2.5 wt%) of each molecule in monochlorobenzene. Absorption spectra of film samples were obtained...
using a UV-VIS spectrometer (HP 8453, photodiode array type) in the wavelength range of 190-1,100 nm.

The PV device fabrication and characterization was performed by following the previously reported method.\textsuperscript{3}

### Results and Discussion

We recently reported the facile and high-yield synthesis of new p-type thiophene-based multi-branched semiconducting molecules.\textsuperscript{12,13} Figure 1 illustrates the structure of the p-type multi-branched semiconducting molecule, HPDTT and PCBM. The four-armed crystalline star-shaped molecule contains thienothiophene as the dendritic wedge. A hexyl group is attached to dithienothiophenyl using 1-bromohexane via cold lithiation. Horner-Emmons coupling of [1,2,4,5-tetra-(diethoxy-phosphorylmethyl)-benzyl]-phosphonic acid diethyl ester and thiophene-based carbaldehyde produces HPDTT with a yield of 70%. They were found to have good self-film forming properties and were well soluble in various organic solvents such as chloroform, xylene, chlorobenzene, and THF.

HOMO and LUMO energies are quite important to facilitate the photoinduced electron transfer in the bulk heterojunction state after blending PCBM with HPDTT.

Cyclic voltammograms were recorded on a film sample and the potentials were obtained relative to an internal ferrocene reference (Fc/Fc\textsuperscript{+}). These CV scans in the range of -2.0 V to +2.0 V (vs Ag/AgCl) range show quasi-reversible oxidation peaks. In order to determine the LUMO levels, we combined the oxidation potential in CV with the optical energy bandgap ($E_{\text{g opt}}$) resulting from the absorption edge in the absorption spectrum. Voltammograms of HPDTT in the film state showed that their lowest oxidative waves were at +0.86 eV.

HPDTT has HOMO level of -5.26 eV which is relatively deeper HOMO level compared to that of HPBT ($E_{\text{HOMO}} = -5.20$ eV). It should endow the material with better environmental stability. In addition, HPDTT has LUMO energy levels of -3.06 eV, determined by using the optical bandgap energies ($E_{\text{g opt}}$). When we draw the energy diagram (see Figure 1) of the bulk heterojunction OPV devices, we can expect efficient photoinduced electron transfer between the donor and acceptor.

The absorption spectra of HPDTT and their blend sample are illustrated in Figure 2. The wt.-compositions of the blend samples were HPDTT:PCBM = 1:1. The absorption maximum of HPDTT in the solution state is located at 418 nm. We observed a drastic spectral change in the film states of HPDTT, which is attributed to a high degree of intermolecular interaction.\textsuperscript{12} PL emission was completely quenched by electron transfer process in the mixture of HPDTT and PCBM.

When mixing PCBM with HPDTT and annealing the sample, we observed a slight spectral shift to a longer wavelength. Therefore, they are easily associated with each other in order to enhance nano-phase separation in the blended

**Figure 1.** Structures and energy diagram of HPDTT and PCBM used for PV bulk heterojunctions.

**Figure 2.** Absorption and PL spectra of HPDTT and its PCBM blend sample. (a) solution of HPDTT, (b) film of HPDTT, (c) HPDTT:PCBM(1:1) film annealed at 120°C for 10 min, (d) solution of HPDTT, and (e) HPDTT:PCBM(1:1) film. *Solid lines: absorption spectra, dotted lines: PL spectra.

**Figure 3.** Current density versus voltage curves of HPDTT:PCBM. (triangle) 1:1 mixture annealed at 80°C, (circle) 1:1 mixture annealed at 120°C, and (square) HPBT:PCBM (1:2) annealed at 120°C, solar cells under AM 1.5G illumination. *Open symbol: dark current density, *Closed symbol: photocurrent density.
mixture by virtue of thermal annealing.

In Figure 3, the device configuration is well illustrated. First, we fabricated the PV devices using two molecular mixtures with PCBM (HPBT:PCBM=1:2 and HPDTT:PCBM=1:1). In the case of HPDTT-based bulk heterojunction, we selected two annealing temperatures of 80 and 120 °C. The device performances were characterized under identical conditions. For comparison, we adopted our previously reported data of HPBT-based OPV device. The open circuit voltage ($V_{oc}$) of the HPDTT-based cell was 0.79-0.86 V which is higher than that of HPBT-based device ($V_{oc}$=0.64 V). This is attributed to the fact that HPDTT has a deeper HOMO level of -5.26 eV. The energy difference between the HOMO of the donor and the LUMO of the acceptor was found to most closely correlate with the $V_{oc}$ value. Theoretically, if the HOMO levels are identical, different devices having the same components should display the same $V_{oc}$ value. However, the sample of HPDTT:PCBM (1:1) after annealing at 80 °C showed a slightly lower $V_{oc}$ value, which might be attributed to different morphological properties to control the build-up potential. A short-circuit current density ($J_{sc}$) of 4.202-4.382 mA cm$^{-2}$ is also higher than that of HPBT-based device, which is attributed to a higher carrier mobility of HPDTT molecules ($\mu$=2×10$^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ in OFET device). The fill factor, a measure of the squareness of the $J$-$V$ characteristics, is equal to 0.36-0.37. The OPV device made of HPDTT:PCBM exhibited higher PCE and other calculated parameters (see Table I, Figure 3).

Atomic force microscopy (AFM) was used in order to investigate the morphology of the blend sample (HPDTT:PCBM=1:1). These AFM images were collected from samples prepared on PEDOT:PSS coated glass slides. The morphology of the active layer shows a smooth surface with no severe phase separation or roughness (see Figure 4). Both annealed and unannealed films exhibited very smooth surfaces, with a variation in topography of only 1-2 nm across 2 µm.

We observe that there are differences in the topography, such as an aggregated domain structure in an annealed sample. This would suggest the presence of an aggregated region that correlates to the self-association of HPDTT and PCBM. This elucidates the morphology difference between the blend film before annealing and after annealing. This result is encouraging as in general, the exciton dissociation and diffusion for organic semiconductor blended films depends on the grain size, as well as molecular orientation on the substrate. The morphology changes observed on the nanoscale are expected to have significant effects on the photovoltaic performance in OPV cells.

In summary, we have demonstrated that the HPDTT is an efficient p-type semiconducting material for photovoltaic

<table>
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<tr>
<th>Devices</th>
<th>$T_{annealing}$ (°C)</th>
<th>$J_{sc}$/mA·cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>FF</th>
<th>PCE/%</th>
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<td>Devices I</td>
<td>80 °C</td>
<td>-4.202</td>
<td>0.79</td>
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<td>Devices II</td>
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<td>Devices III</td>
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<td>0.64</td>
<td>0.41</td>
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$^{a}$HPDTT:PCBM=1:1, $^{b}$HPBT:PCBM=1:2.

Figure 4. AFM topography of the blend film sample of HPDTT and PCBM (1:1). (A) before annealing and (B) after annealing at 120 °C for 10 min.
cells. The generation of high photocurrents is ascribable to the large hole mobility of HPDTT and $V_{oc}$ increases because of the larger difference of HOMO level of HPDTT and LUMO level of PCBM. When 50 wt% PCBM was blended with HPDTT, the bulk heterojunction PV device exhibits an optimized PCE close to 1.4%, which is the highest data in this class of materials.

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**References**