Organic Photovoltaics Based on Poly(3,4-phenylenedioxy-2,5-thienylenevinylene)s

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ABSTRACT

Poly(3,4-phenylenedioxy-2,5-thienylenevinylene)s with a fluorine substituent at the phenylene moiety (PPhDOTFV) and without the substituent (PPhDOTV) were synthesized by Stille coupling polymerization. They exhibited good solubility in common organic solvents owing to a branched alkyl chain at the phenylene moiety and a narrow optical bandgap of 1.66 eV due to an increased conjugated length caused by the vinylene bridge. Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of PPhDOTFV were 0.2 eV deeper than those of PPhDOTV. Organic photovoltaic cells (OPVs) using PPhDOTV:PC₇₀BM exhibited a short-circuit current density (J_{sc}) of 3.30 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.52 V, and a power conversion efficiency of 0.91%, as compared to 1.62 mA cm⁻², 0.68 V, and 0.45%, respectively, for OPVs using PPhDOTFV:PC₇₀BM. The J_{sc} value of PPhDOTV-based OPVs was higher than that of PPhDOTFV-based OPVs because of a large LUMO energy offset between PPhDOTV and PC₇₀BM. On the other hand, the V_{oc} value of PPhDOTV-based OPVs was lower than that of PPhDOTFV-based OPVs because of a small energy difference between the HOMO level of PPhDOTV and the LUMO level of PC₇₀BM.

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Keywords : Phenylenedioxythiophene, Thienylenevinylene, PEDOT, Solar Cell

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is known as one of the most successful conducting polymers and has high conductivity, a narrow bandgap (E_g), and good environmental stability.^{1–5} Owing to their outstanding characteristics, many PEDOT derivatives have been developed and applied to printed electronic devices such as organic photovoltaic cells (OPVs) and organic field-effect transistors.^{6–9} For example, Roquet and co-workers have designed 3,4-phenylenedioxythiophene (PhDOT), which has a planar structure, by replacing the ethylene bridge of ethylenedioxythiophene with a phenylene unit and synthesized poly(PhDOT) (PPhDOT).^{10,11} PPhDOT is expected to be an alternative to PEDOT because it exhibits a smaller E_g and better conductivity than PEDOT. However, it has low solubility in common organic solvents, which limits its practical use for various organic devices fabricated by a solution process.¹² To solve this problem, a highly soluble PPhDOT derivative, shown in Fig. 1, was developed in our previous work by introducing an asymmetric alkyl substituent.¹³ Spin-casting of the resultant polymer from a chloroform solution yielded a continuous film with an E_g value of 1.85 eV and good hole transport. Furthermore, it was found that introducing fluorine into the phenylene part of PhDOT can effectively lower the highest occupied molecular orbital (HOMO) of the polymer without a large change in E_g . Hence, the fluorinated PhDOT-based polymer might be a good electron-donating polymer for bulk heterojunction (BHJ) OPVs because the HOMO level of the polymer should be low in order to obtain a high open-circuit voltage (V_{oc}).^{14,15}

Figure 1. Chemical structures of π -conjugated polymers: PPhDOT (reference material), PPhDOTV, and PPhDOTFV.

In this study, we developed highly soluble PhDOT-based polymers, poly(3,4-phenylenedioxy-2,5-thienylenevinylene)s (PPhDOTV and PPhDOTFV, Fig. 1), with a more red-shifted onset of absorption by introducing a vinylene unit between PhDOTs to reduce the amount of steric hindrance between them.^{16,17} As we expected, these new polymers had an absorption edge at longer wavelengths, up to 747 nm (an optical E_g value of 1.66 eV) than PPhDOT (1.85 eV). The light absorption properties of conjugated polymers in the near-infrared region are desirable for a high short-circuit current (J_{sc}) in BHJ OPVs. PPhDOTV and PPhDOTFV differ only in the presence of the fluorine atom on PhDOT. Thus, their optical properties and energy levels were investigated, and their photovoltaic performances were compared.

2. Experimental

2.1 Measurements

^1H NMR spectra were measured using a JEOL JM-ECS 400 instrument at a resonance frequency of 400 MHz for ^1H at room temperature. Ultraviolet–visible (UV–vis) spectra were measured on a HITACHI U-3010 spectrometer. Elemental analysis of the polymers was performed using a PerkinElmer 2400CHN Elemental Analyzer for C and H determination. The average molecular weight and polydispersity index (PDI) of the polymers were determined by gel permeation chromatography calibrated with polystyrene standards using tetrahydrofuran as an eluent. Thermogravimetric analysis (TGA) of the polymers in the solid state was performed under Ar at a heating rate of $10^\circ\text{C min}^{-1}$ using a Seiko EXSTAR7000. The HOMO levels of the polymers were estimated by photoelectron yield spectroscopy using an AC-3 spectrometer (Riken Keiki). The thickness of the films was determined using an automatic microfigure measuring instrument (SURFCORDER ET200, Kosaka Laboratory, Ltd.). The surface morphologies of the films were observed using an atomic force microscope (AFM) (Hitachi High-Tech Science 5100N).

2.2 Materials

All the chemicals were purchased from Kanto Chemical Co., Inc.; Tokyo Chemical Industry Co., Ltd.; Nacalai Tesque Inc., or Sigma-Aldrich Co., LLC and were used without further purification unless otherwise stated. Toluene was refluxed over sodium and distilled. PPhDOT, 2,5-dibromo-1,4-[4-(2-hexylundecyl)phenylene]dioxithiophene (M1 in Scheme 1), and 2,5-dibromo-1,4-[4-fluoro-5-(2-heptylundecyl)phenylene]dioxithiophene (M2 in Scheme 1) were synthesized according to literature methods.¹³

2.3 Synthesis of PPhDOTV

In a two-necked flask, M1 (141 mg, 0.23 mmol), trans-1,2-bis(tributylstannyl)ethylene (142 mg, 0.23 mmol), dry toluene (3.5 ml), and tetrakis(triphenylphosphine)palladium(0) [$\text{Pd}(\text{PPh}_3)_4$] (11.7 mg) were mixed and refluxed for 5 h under Ar atmosphere. After cooling to room temperature, the polymeric products were precipitated from methanol. The precipitates were successively extracted with methanol, acetone, hexane, and chloroform by Soxhlet extraction. The chloroform extract was again precipitated from methanol. PPhDOTV was obtained as a black-purple solid (70 mg, 64% yield). ^1H NMR (400 MHz, CDCl_3) 6.70 (br 5H), 2.45 (br, 2H), 1.30 (br, 29H), 0.90 (br 6H). Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{O}_2\text{S}$: C, 77.20; H, 9.07. Found: C, 74.89; H, 9.29.

2.4 Synthesis of PPhDOTFV

PPhDOTFV was synthesized from M2 using the method adopted for PPhDOTV. PPhDOTFV was obtained as a black-purple solid (80% yield). ^1H NMR (400 MHz, CDCl_3) 6.64 (br 4H), 2.46 (br, 2H), 1.28 (br, 29H), 0.89 (br 6H). Anal. Calcd for $\text{C}_{30}\text{H}_{41}\text{FO}_2\text{S}$: C, 74.34; H, 8.53. Found: C, 73.63; H, 8.42.

Scheme 1. Synthesis of PPhDOTV and PPhDOTFV.

2.5 Fabrication and measurement of BHJ OPVs

BHJ OPVs were fabricated in the following configuration: indium tin oxide (ITO)/PEDOT: polystyrene sulfonate (PSS)/BHJ layer/LiF/Al. Patterned ITO glass (conductivity: $10 \Omega/\text{square}$) was precleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin-coated onto the ITO at 3000 rpm and air-dried at 110°C for 10 min on a hot plate. The substrate was then transferred to a N_2 -filled glove box where it was re-dried at 110°C for 10 min on a hot plate. A chloroform solution of PC₇₀BM blended with PPhDOTV or PPhDOTFV was subsequently spin-coated onto the PEDOT:PSS surface to form the BHJ layer. The substrates with the BHJ layers were dried for 10 min at 110°C . LiF (1 nm) and Al (80 nm) were then deposited on the BHJ layer by conventional thermal evaporation at a chamber pressure lower than 5×10^{-4} Pa, which provided the devices with an active area of $5 \times 2 \text{ mm}^2$. The current density–voltage (J – V) curves were measured using an ADCMT 6244 DC voltage current source/monitor under AM 1.5G solar-simulated light irradiation at 100 mW cm^{-2} (OTENTO-SUN III, Bunkoh-Keiki Co., Ltd.). The incident-photon-to-current conversion efficiency (IPCE) was measured using an SM-250 system (Bunkoh-Keiki Co., Ltd.).

3. Results and Discussion

3.1 Synthesis and fundamental properties of PPhDOTV and PPhDOTFV

PPhDOTV and PPhDOTFV were obtained by the Stille coupling reaction between dibrominated PhDOT and distannylethylene in the presence of $\text{Pd}(\text{PPh}_3)_4$, as shown in Scheme 1. They were highly soluble in common organic solvents such as chloroform and *o*-dichlorobenzene (*o*DCB). The number average molecular weight (M_n) and PDI of PPhDOTV and PPhDOTFV were 17.4 and 28.6 kg mol^{-1} and 1.7 and 1.6, respectively. TGA of PPhDOTV and PPhDOTFV in Fig. 2 showed that the temperatures of 5 wt% loss were 335 and 336°C , respectively.

Figure 3 shows the absorption spectra in the film state of PPhDOTV, PPhDOTFV, and PPhDOT as a reference material. The absorption peaks of PPhDOTV and PPhDOTFV in the film state were significantly red-shifted compared with that of PPhDOT.¹³ These results indicate that the 2,5-thienylenevinylene structure effectively extends the π -conjugated length of the polymer backbone. Both PPhDOTV and PPhDOTFV exhibited two absorption peaks around 638 and 701 nm. The well pronounced peak at 638 nm is attributed to the main π – π^* electron transitions. The shoulder peak at 701 nm could be attributed to the π -stacking of the planarized individual polymer chains, because the peak is not seen in the absorption spectrum of a hot solution (*o*DCB at 150°C) of the polymers.¹⁸ The optical E_g values of PPhDOTV and PPhDOTFV determined from the absorption onset of the film state were almost the same, 1.66 eV.

Figure 2. TGA curves of the polymers.

Figure 3. UV-vis absorption spectra of PPhDOT, PPhDOTV, and PPhDOTFV in polymer films.

Figure 4. Energy level diagrams for PPhDOTV, PPhDOTFV, and PC₇₀BM. The LUMO energy of PC₇₀BM is taken from the literature.²³

Table 1. Photovoltaic parameters for ITO/PEDOT:PSS (40 nm)/BHJ layer/LiF (1 nm)/Al (80 nm) under AM 1.5G illumination at 100 mW cm⁻². These parameters were calculated as the average of the measured results for four BHJ OPVs.

BHJ layer	Thickness /nm	J_{sc} /mA cm ⁻²	V_{oc} /V	FF	PCE /%
PPhDOTV:PC ₇₀ BM (1:1)	95	3.30	0.52	0.53	0.91 ± 0.04
PPhDOTFV:PC ₇₀ BM (1:1)	100	1.62	0.68	0.41	0.45 ± 0.02

The HOMO levels of PPhDOTV and PPhDOTFV estimated by photoelectron yield spectroscopy were -5.14 and -5.34 eV, respectively, and are summarized in Fig. 4. The lower HOMO energy of PPhDOTFV compared to PPhDOTV originates from the strongly accepting nature of fluorine in the phenylene part of PPhDOTFV, which is beneficial for obtaining a higher V_{oc} in BHJ OPVs.^{19–21} The energy levels of the lowest unoccupied molecular orbital (LUMO) of PPhDOTV and PPhDOTFV estimated from their E_g values and HOMO levels were situated at -3.48 and -3.68 eV, respectively.

3.2 Photovoltaic properties of BHJ layers based on PC₇₀BM and PPhDOTV or PPhDOTFV

To fairly compare PPhDOTV and PPhDOTFV, BHJ OPVs with almost the same device structure consisting of a PPhDOTV:PC₇₀BM or PPhDOTFV:PC₇₀BM layer at a 1:1 mixing ratio with a thickness of approximately 98 nm were prepared using the same fabrication method and characterized. Table 1 lists the average device characteristics of BHJ OPVs with a structure of ITO/PEDOT:PSS (40 nm)/BHJ layer/LiF (1 nm)/Al (80 nm), including the J_{sc} , V_{oc} , fill factor, and power conversion efficiency (PCE) under AM 1.5G illumination at 100 mW cm⁻². Figure 5(a) shows the J - V curves of the OPVs under illumination. The PCE of the PPhDOTV-based OPV (0.91%) was twice that of the PPhDOTFV-based OPV (0.45%). This increase in the PCE is due mainly to the increase in J_{sc} from 1.63 to 3.30 mA cm⁻². We therefore investigated the absorption spectra of each material and the IPCE of the corresponding OPVs. As shown in Fig. 5(b), each of the BHJ films based on PPhDOTV and PPhDOTFV has a slightly different absorption spectrum below 600 nm due to a different PC₇₀BM concentration in each of them. This is because the average PCBM concentration in the film sometimes can remain below the PCBM concentration in the solution, depending on the solution state or the fabrication process of the film.²² On the other hand, BHJ OPVs using PPhDOTV show much higher IPCEs than those using PPhDOTFV at any wavelength [Fig. 5(c)]. The AFM images in Fig. 6(b) and (d) show that the morphologies of both the PPhDOTV:PC₇₀BM and PPhDOTFV:PC₇₀BM layers are very similar with root-mean-square

Figure 5. (a) J - V curves of BHJ OPVs based on PPhDOTV:PC₇₀BM (1:1) and PPhDOTFV:PC₇₀BM (1:1) films. (b) Absorption spectra of the BHJ layers. (c) IPCE spectra of the BHJ OPVs.

Figure 6. (Color online) AFM images ($5 \times 5 \mu\text{m}$) of (a) PPhDOTV, (b) PPhDOTV:PC₇₀BM (1:1), (c) PPhDOTFV, and (d) PPhDOTFV:PC₇₀BM (1:1) films.

surface roughnesses of 8.85 and 8.77 nm, respectively. Thus, this increase of IPCEs is due to the large LUMO energy offset (approximately 0.33 eV) between PPhDOTV and PC₇₀BM (LUMO of -3.81 eV)²³ as compared with the offset (approximately 0.13 eV) between PPhDOTFV and PC₇₀BM. A LUMO offset of more than 0.3 eV is generally needed for efficient charge separation from photo-excitons at donor/acceptor interfaces.^{24,25} Thus, the high LUMO energy of PPhDOTV ensured a downhill driving force for charge separation to PC₇₀BM. On the other hand, because the V_{oc} value of BHJ OPVs is determined mainly by the energy difference between the HOMO level of the donor and the LUMO level of the acceptor,^{14,15} the V_{oc} values of the PC₇₀BM-based BHJ OPVs using PPhDOTV (HOMO of -5.14 eV) were lower than those of the BHJ OPVs using PPhDOTFV (HOMO of -5.34 eV).

The obtained PCE, even in BHJ OPVs using PPhDOTV in this study, was relatively low compared with previously reported values.^{26,27} To determine the reason, the surface morphology of the BHJ layers was observed by AFM (Fig. 6). In comparison with a smooth surface of neat polymers [Figs. 6(a) and (c)], BHJ films with the polymer and PC₇₀BM were found to be rougher, indicating substantial phase separation [Figs. 6(b) and (d)]. The pronounced phase separation reduced the heterojunction interface area for exciton dissociation, which generally led to the low J_{sc} values and PCEs of the BHJ OPVs.^{28,29} For improving miscibility in the polymers:PC₇₀BM films, various solvents such as *o*DCB, the mixture of CF and *o*DCB (10 vol%), the mixture of *o*DCB and 1,8-diiodooctane (1.5–3 vol%)³⁰ were used for spin-coating. However, all PCEs of the resultant BHJ OPVs were lower than those listed in Table 1.

4. Conclusion

Dibrominated PhDOT (M1) with a planar structure was polycondensed with 1,2-bis(tributylstannyl)ethylene to obtain PPhDOTV. Similarly, PPhDOTFV having a fluorine substituent at the phenylene moiety of PhDOT was also synthesized. They exhibited good solubility in common organic solvents and thermal stability. Both PPhDOTV and PPhDOTFV exhibited extended π -conjugation along the polymer backbones, which resulted in an

absorption edge at longer wavelengths, up to 747 nm (an optical E_{g} value of 1.66 eV) compared to those of PPhDOT (1.85 eV).¹³ When a fluorine substituent was introduced into the phenylene part of PhDOT, both the HOMO and LUMO energy levels of PPhDOTFV became 0.2 eV deeper than those of PPhDOTV. BHJ OPVs with PPhDOTV exhibited a PCE of 0.91%. The J_{sc} value of PPhDOTV-based BHJ OPVs was higher than that of PPhDOTFV-based BHJ OPVs owing to the large LUMO energy offset between PPhDOTV and PC₇₀BM. On the other hand, the V_{oc} value of PPhDOTV-based OPVs was lower than that of PPhDOTFV-based BHJ OPVs owing to the small energy difference between the HOMO level of PPhDOTV and the LUMO level of PC₇₀BM.

Acknowledgment

We thank the Chemical Analysis Division, Research Facility Center for Science and Technology, University of Tsukuba, for use of the NMR facilities, elemental analysis, and TGA measurements. This work was partly supported by JSPS KAKENHI Grant Number JP16K05899.

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