Study on Interactions among *ortho*-Biphenyl Groups in Oligothiophene for Structural Control of Bulk Heterojunction Films

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Abstract

To elucidate the optimal bulk heterojunction (BHJ) film for high-performance organic photovoltaics, structural control of BHJ films based on small molecules is one of great challenges. A homogeneous BHJ structure based on oligothiophene and fullerene has been fabricated by means of terminal modification using the sterically bulky *t*-butyl group. However, the suppression of interaction among the oligothiophene molecules produces a low fill factor. Molecular design of donor material in order to obtain good fill factor was not clear.

Herein, we synthesized oligothiophene with sterically bulky *o*-biphenyl groups possessing molecular flexibility. We achieved balance between the morphological control of BHJ films and improvement of the fill factor. In this study, we suggest that improvement of fill factor is attributed to increasing hole mobility and crystallinity by *ortho*-biphenyl group.

1. Introduction

Extensive studies on organic photovoltaics (OPVs) based on small molecules have recently been carried out because of their low cost, easy manufacturing process, and realization of tandem-structure devices [1-3]. For high OPV performance, a bulk heterojunction (BHJ) structure comprising a mixture of electron donor and acceptors, fabricated by the co-deposition method, was suggested in 1991 [4]. The BHJ structure is well known as an advanced three-dimensional structure used for the construction of wide interfaces between donors and acceptors. For BHJ-type OPV devices based on small molecules, oligothiophenes as donor materials have been intensively investigated [5-7]. The advantages of using oligothiophenes are the simply control of redox energy level and/or deep the highest occupied molecular orbital (HOMO) level, as well as crystallinity by chemical modifications [8, 9]. As long as highly ordered oligothiophene molecules are applied to the co-deposition films, the appearance of microaggregates significantly deteriorates the BHJ-type device performance [5].

We previously investigated the OPV performance using terminally-modified oligothiophene molecules, such as quarterthiophene (Ph4T) with *t*-butylphenyl endcaps (*t*-BuPh4T, shown in Fig. 1.), and Ph4T (without terminal modification) [10]. We demonstrated that suppression of interaction among oligothiophene molecules enabled

the control of the microaggregates in oligothiophene volume ratio of 50 %. The terminally-modification oligothiophene are useful for fabrication homogeneous BHJ films. However, the fill factor (FF) of these devices is lower than that of devices with highly ordered oligothiophenes such as α -sexithiophene (α -6T) and phenyl endcapped **Ph4T**. Regardless of the reports that FF is strongly dependent on carrier mobility [11] and parallel resistance [12], the molecular design rule of a suitable oligothiophene for superior FF in BHJ-type devices was not established.

Then, we focused on the balance between the morphological control of oligothiophene:fullerene BHJ films and the improvement of FF. The ***t*-BuPh4T** moieties are recognized as rigid groups because of highly symmetric structure. In contrast, sterically bulky *o*-biphenyl groups have rotatable flexibility. Generally, molecular interaction between phenyl rings is strong. Thin films of 2,5-bis(4-biphenyl) bithiophene (BP2T) and pentacene with some phenyl rings exhibit large crystal domains and good carrier mobility [13, 14]. Oligothiophene, possessing both strong interaction and flexibility, is expected to show some degree of π -conjugation due to intramolecular π -conjugation and π - π overlap. Therefore, there is possibility that the *o*-biphenyl group can provide a balance between stronger interaction than that exhibited in the ***t*-BuPh4T** molecule and the morphological control of the

oligothiophene:fullerene BHJ films.

Accordingly, we designed terminally-modified oligothiophene molecules with *ortho*-biphenyl groups (***o*-BiPh4T**), as shown in Fig.1. Here, we report on the film morphology and crystallinity, OPV performances, and carrier mobility of ***o*-BiPh4T** molecules. The ***t*-BuPh4T** was prepared as reported reference [10]. To discuss the effects of molecular interaction among oligothiophene molecules on photovoltaic characteristics, the characteristics of ***t*-BuPh4T** possessing weak molecular interaction are used as a comparison.

Fig. 1. Structure and calculated molecular length of (a) ***o*-BiPh4T** and (b) ***t*-BuPh4T**. Molecular length was calculated from density functional theory (DFT) for the B3LYP/6-31G(d) level.

2. Experimental Details

2.1. Device Fabrication

The devices were fabricated in vacuum deposition chamber at a pressure of 10^{-5} Pa at room temperature. The materials of *o*-BiPh4T and *t*-BuPh4T were repeatedly purified by a vacuum sublimation system. The fullerene C₆₀ (purity 99.999 %) as electron acceptor and bathocuproine (BCP) as the exciton blocking material [15] were purchased from Frontier Carbon Corporation and Dojindo Co.,Ltd., respectively. The device fabrication procedures were as follows. (1) An indium tin oxide (ITO) coated glass substrate of 150 nm thickness was cleaned by oxygen plasma treatment for 30 min. (2) After that, the 15 nm thick of molybdenum oxide (MoO₃ purchased from Niraco Corp.) was deposited onto the ITO. (3) To fabricate BHJ film, the oligothiophene *o*-BiPh4T or *t*-BuPh4T and fullerene were simultaneously deposited. The oligothiophene volume ratio was controlled by the quartz crystal microbalances. (4) C₆₀ (30 nm thick), BCP (6 nm thick), and aluminium electrode (80 nm thick) were employed as an electron transport layer, an exciton blocking layer, and a metal electrode, respectively. The BHJ-type device configuration was ITO/MoOx(15 nm)/oligothiophene:C₆₀ BHJ layer (X nm)/C₆₀ (30 nm)/BCP (6 nm)/Al (80nm). The effective device area was 0.04 cm². To

measure the oligothiophene mobility in space-charge-limited-current (SCLC) region and the dielectric constant of ***o*-BiPh4T** and ***t*-BuPh4T**, we fabricated samples of ITO/MoOx (15 nm)/oligothiophene (150 nm)/Au (50 nm) and ITO/MoOx(15 nm)/oligothiophene:C₆₀=1:1 (120 nm)/Au (50 nm) as hole-only devices.

2.2. Measurement

The **current density-voltage (*J-V*)** characteristics and SCLC were measured by using KEITHLEY 2400 and 2600 series source meters (Keithley Instrument Inc.), respectively. Impedance spectroscopy (IS) of single-component oligothiophene films was conducted using a Solartron 1260 impedance analyzer with an **frequency-response-analyzer (FRA)** system and a Solartron 1296 dielectric interface unit (TOYO technical corp.). The applied **direct current (DC)** bias and **alternating current (AC)** signal were 0 and 30 mV, respectively. The frequency range was varied from 1 MHz to 0.1 Hz. Impedance (*Z*) plots obtained from IS measurement were converted into modulus plots. “Modulus (**M**)” is defined as $M \equiv j\omega Z$, where *j* and ω are imaginary unit and angular frequency, respectively. The obtained modulus plots was fitted to the equivalent circuit model using the Scriber Associates software “Z-view”. Electrical measurements of *J-V*, SCLC, and IS were carried out under N₂ atmosphere at

room temperature without exposure to ambient air. For J - V characteristics, Air Mass 1.5 Global (AM1.5G) solar simulator light source calibrated at $100\text{mW}/\text{cm}^2$ using an amorphous silicon photodiode (Bunko Keiki BS-520) was used. Surface images were taken by atomic force microscope (AFM; SII nanotechnology, Nanonavi/E-sweep, dynamic force microscopy (DFM) scanning in tapping mode). Out-of-plane and in-plane X-ray diffraction (XRD) measurements were performed at diffractometer equipped with Cu-K α source (Rigaku Co.,Ltd. Smart-Lab). The wavelength of the irradiated X-ray was 0.154 nm. UV/Visible spectra of oligothiophenes in CHCl_3 solution was measured by SHIMAZU-UV3101. Ionization potentials of oligothiophene films on ITO /MoOx substrate were measured with photoelectron yield spectroscopy (PYS, BIP-KV200 Bunko Keiki Co.,Ltd) in vacuum.

2.3. Synthesis scheme of *o*-BiPh4T molecule

The synthesis procedures of oligothiophene “*o*-BiPh4T” are as follows. The *o*-BiPh4T was synthesized in 4 steps from 2-Bromobiphenyl. The purification of *o*-BiPh4T was employed vacuum sublimation. Differential scanning calorimetry measurement showed a sharp melting-endotherm peak at 214.6 °C. (Synthesis procedures of *t*-BuPh4T and compound **1** are described in the reference [10].)

Scheme 1. Synthetic route of **o-BiPh4T**.

Preparation of 2-([1,1''-biphenyl]-2'-yl)thiophene (**2**). Under N_2 atmosphere, 2-Bromobiphenyl (2.73 g, 11.7 mmol), 2-(tributylstanyl)thiophene (4.40 g, 12.8 mmol), and $\text{Pd(PPh}_3)_4$ were dissolved in toluene 15 ml. The mixture was refluxed for 10 h. After cooling to r.t., solvent was removed by evaporator, and mixture was extracted with ethyl acetate, and organic layer was washed with saturated NaCl aq, and dried over by MgSO_4 . After removed the solvent, residue was purified by column chromatography (SiO_2 , elute; hexane). Compound **2** was further purified by high pressured liquid chromatography (SiO_2 , elute; hexane) to give a **2** (2.30 g, 83 %) as a colorless solid.

$^1\text{H-NMR}$ (acetone- d_6) δ : 7.58-7.54 (m, 1H), 7.45-7.41 (m, 2H), 7.39-7.36 (m, 1H), 7.34-7.29 (m, 4H), 7.23-7.22 (m, 2H), 6.90 (d/d, 1H, $J = 5.1, 3.6$ Hz), 6.73 (d/d, 2H, $J = 3.6, 1.2$ Hz). $^{13}\text{C-NMR}$ (acetone- d_6) δ : 144.00, 142.60, 141.94, 134.12, 131.76, 131.49, 130.52 (2C), 129.09 (2C), 128.93, 128.73, 128.03, 127.95, 127.93, 126.83.

Preparation of 2-([1,1'-biphenyl]-2-yl)-5-bromothiophene (**3**). Compound **2** (2.30 g, 9.73 mmol) was dissolved in acetic acid (15 ml) and CHCl_3 (15 ml). The mixture was cooled by ice-water bath. NBS (1.81 g 10.1 mmol) was added in one portion. The reaction mixture was slowly warm to r.t. and then stirred for 16 h at r.t.. The reaction mixture was cooled by ice-bath and basified with NaOH aq. aqueous layer was extracted with CH_2Cl_2 . The CH_2Cl_2 fraction was combined and dried over by MgSO_4 , and then the solvent was removed by evaporator. The residue was purified by column chromatography (SiO_2 , elute; hexane) to give a compound **3** (2.89 g, 94%) as a colorless solid. $^1\text{H-NMR}$ (acetone- d_6) δ : 7.57-7.52 (m, 1H), 7.47-7.41 (m, 2H), 7.39-7.31 (m, 4H), 7.28-7.23 (m, 2H), 6.95 (d, 1H, $J = 3.8$ Hz), 6.63 (d, 1H, $J = 3.8$ Hz). $^{13}\text{C-NMR}$ (acetone- d_6) δ : 145.86, 141.90, 141.65, 132.93, 131.67, 130.99, 130.97, 130.38 (2C), 129.26, 129.10 (2C), 128.73, 128.22, 128.19, 112.38

Preparation of 5-(1,1'''-biphenyl-2''-yl)thiophen-2-yl-tributylstannane (**4**). Under N₂ atmosphere, Compound **3** (1.40 g, 4.44 mmol) was dissolved in anhydrous THF (40 ml). After cooling to -80 °C, a solution of n-butyllithium in hexane (added 1.1 eq, 1.65 mol/l solution, 3.0 ml) was slowly added via a syringe. The mixture was stirred at -80 °C for 0.5 h, after which tributyltin chloride (1.60 g, 4.92 mmol) was added in one portion, and then stirred at r.t. for 4 h. The solvent was removed by evaporator, mixture was extracted with hexane, and organic layer was washed with saturated NaCl aq, and dried over by MgSO₄. After removed a solvent by evaporator, the residue was purified by column chromatography (Al₂O₃, elute; hexane) to give a compound **4** (2.24 g, 96% crude: **3** is mixed) as an oil. Compound **4** was used without further purification.

¹H-NMR (acetone-d₆) δ: 7.59-7.56 (m, 1H), 7.37-7.34 (m, 4H), 7.29-7.22 (m), 6.91 (d, 2H, *J* = 3.4 Hz), 6.78(d, 2H, *J* = 3.3 Hz), 1.67-1.59(m), 1.42-1.34 (m), 1.18-1.14(br, t) 0.96-0.92(t). ¹³C-NMR (acetone-d₆) δ: 148.99, 141.87, 140.76, 137.13, 135.38, 133.74, 130.81, 130.47, 129.81 (2C), 128.18, 128.04 (2C), 127.56, 127.50, 126.93, 29.05, 27.34, 13.80, 10.91

Preparation of 5,5'''-di([1,1'-biphenyl]-2-yl)-2,2':5',2'':5'',2'''-quaterthiophene (***o*-BiPh4T**). Under N₂ atmosphere, 5,5'-dibromo-2,2'-bithiophene **1** (600 mg, 1.85

mmol), stannyl reagent **4** (2.42 g, 4.52 mmol), and $\text{Pd(PPh}_3)_4$ (106 mg, 0.092 mmol) were placed in toluene 20 ml. The mixture was refluxed for 48 h, and then cooling to r.t. After cooling to r.t, the solvent was removed by evaporator. Collecting residue was washed with hot hexane and ethanol, and resulting solid was filtered. The crude product was purified by twice train-sublimation. The pure ***o*-BiPh4T** (508 mg, 43 %) was obtained as an orange solid. Mp: 214.6 °C (DSC). $^1\text{H-NMR}$ (acetone- d_6) δ : 7.59-7.55 (m, 2H), 7.41-7.36 (m, 6H), 7.35-7.28 (m, 10H), 7.01 (d, 2H, $J = 3.8$ Hz), 6.97 (d, 2H, $J = 3.8$ Hz), 6.91 (d, 2H, $J = 3.8$ Hz), 6.53 (d, 2H, $J = 3.8$ Hz). $^{13}\text{C-NMR}$ (acetone- d_6) δ : 142.53, 141.44, 140.92, 137.00, 136.46, 135.81, 132.79, 131.10, 130.36, 129.75(2C), 128.34(2C), 128.03, 128.02, 127.78, 127.28, 124.33, 124.19, 123.88. MS (MALDI-TOF) $[\text{M}^+]$: 634. Elemental Analysis ($\text{C}_{40}\text{H}_{26}\text{S}_4$) Calcd. for C, 75.67; H, 4.13; S, 20.20. Found: C, 75.36; H, 4.00; S, 20.48

3. Results and Discussion

3.1. Energy level of *o*-BiPh4T and *t*-BuPh4T

The HOMO levels of *o*-BiPh4T and *t*-BuPh4T were estimated by PYS method (shown in Figure 2). The HOMO level of these materials was determined as follows: *o*-BiPh4T -5.50 eV; *t*-BuPh4T -5.37 eV. In organic photovoltaics, it is well known that the optimal open-circuit voltage (V_{oc}) was determined by the difference between lowest unoccupied molecular orbital (LUMO) level of acceptor molecules and HOMO level of donor molecules [16, 17]. The device of *o*-BiPh4T was expected to exhibit higher V_{oc} than that of *t*-BuPh4T. Also, the LUMO levels of *o*-BiPh4T and *t*-BuPh4T estimated from the HOMO levels and the HOMO-LUMO gaps (calculated from end-absorbance of UV/vis spectra, shown in Figure 3), were as follows: *o*-BiPh4T -2.97 eV; *t*-BuPh4T -2.88 eV.

Fig. 2. Photoelectron yield spectroscopy of oligothiophene films on ITO/MoO_x substrate. Inset: current^{1/3}-energy plots for estimation of HOMO level.

Fig. 3. Light absorption spectra of *o*-BiPh₄T and *t*-BuPh₄T in CHCl₃ solution.

3.2. Morphology and Crystal structure of *o*-BiPh4T films

The AFM images and X-ray diffraction data of the vacuum-deposited films with *o*-BiPh4T molecules are shown in Fig. 4. In the single-component *o*-BiPh4T film displayed in Fig. 4 (a), needle-like surface morphology and large root-mean-square (RMS) roughness value were observed. This is attributed to strong interaction between the *o*-BiPh4T molecules. On the other hand, the BHJ film with volume ratio of *o*-BiPh4T 83 % has extensively-branched fibrils [Fig. 4 (b)]. This characteristic structure has already known to possess aggregated oligothiophene molecules [7]. The synthesized *o*-BiPh4T molecules were aggregated by the presence of a few C₆₀ molecules. In contrast, the BHJ film of *t*-BuPh4T with volume ratio of 83 % has nano-sized fibrils and grains [10]. These results imply that the *o*-BiPh4T molecules possess stronger molecular interaction than the *t*-BuPh4T molecules. When the *o*-BiPh4T volume ratio further decreased to 50 % and 17 % [Figs. 4 (c) and (d)], the fibrils disappeared from the surface morphology. Simultaneously, quite smooth surfaces of *o*-BiPh4T:C₆₀ BHJ films were obtained through the control of volume ratio. To analyze the crystal structure of these films, out-of-plane and in-plane X-ray diffraction patterns were measured, as shown in Fig. 5 (a) and (b). The *d*-spacing values calculated from Bragg's equation and full width at half maximum (FWHM) at diffraction peak in

the out-of-plane measurement are summarized in Table 1. Calculated d -spacing values of ***o*-BiPh4T** and ***t*-BuPh4T** are consistent with molecular length demonstrated in Fig. 1. This means that both of ***o*-BiPh4T** and ***t*-BuPh4T** molecules tend to be standing on the ITO/MoOx substrate. In addition, for ***o*-BiPh4T**, FWHM is smaller than that for the ***t*-BuPh4T** film, indicating that terminal modification with *ortho*-biphenyl groups is responsible for strong molecular interaction in the oligothiophene. In particular, the ***o*-BiPh4T** molecules display strong interaction along the in-plane direction (corresponding to the π -stacking structure), as shown in Fig. 5 (c). The π -stacking structure of the ***t*-BuPh4T** molecules was suppressed by the *t*-butyl group. Note that the homogeneous blend films at 50 % oligothiophene volume ratio were obtained in spite of strong molecular interaction among ***o*-BiPh4T**. In next section 3.3, we discuss the relationship between molecular interaction among oligothiophene molecules including investigation of mobility and BHJ-type device performance for ***o*-BiPh4T** molecules.

Fig. 4. AFM images of thin film surface on ITO/MoOx(15 nm), (a) 100 nm thick of single component *o*-BiPh4T (b) *o*-BiPh4T 83% BHJ film (c) *o*-BiPh4T 50 % BHJ film (d) *o*-BiPh4T 17% BHJ film. Thickness of BHJ films is 50 nm.

Fig. 5. X-ray diffraction patterns of films on ITO/MoOx substrate, (a) out-of-plane measurement with $2\theta/\theta$ mode and (b) in-plane measurement with $2\theta/\phi$ mode. The oligothiophene film structure based on XRD patterns is illustrated in (c).

Table 1. Diffraction profile data of oligothiophene single film

Material	2θ (deg)	d (Å)	FWHM (deg)
<i>o</i> -BiPh4T	4.13	21.43	0.24
<i>t</i> -BuPh4T ^[10]	3.90	22.63	0.27

3.3. Relation between BHJ-type Device Performance and mobility

The J - V characteristics of oligothiophene:C₆₀ BHJ-type devices in various compositional ratio and a summary of the photovoltaic parameters estimated from the J - V curves are shown in Fig. 6 (a) and Table 2, respectively. The series resistance (R_s : internal resistance) and shunt resistance (R_{sh} : current leakage) were estimated from light J - V curves. The V_{oc} of ca. 0.9 V in ***o*-BiPh4T**:C₆₀ BHJ-type devices is higher than that in ***t*-BuPh4T**:C₆₀ BHJ-type devices (V_{oc} in BHJ-type devices with ***t*-BuPh4T**: ca. 0.5-0.6V). These results can be attributed to the deeper HOMO level of ***o*-BiPh4T** than that of ***t*-BuPh4T**. In ***o*-BiPh4T** with 83 % volume ratio, the fibril structure leads to a loss of V_{oc} , possibly caused by the formation of discontinuous BHJ films (shown in Fig. 4 (b)). In ***o*-BiPh4T**:C₆₀ BHJ-type devices, power conversion efficiency (PCE) of 1.20 % was achieved at a ratio of ***o*-BiPh4T** 17%. The PCE of ***o*-BiPh4T** 17 % is higher than that of ***o*-BiPh4T** 50 % despite of high R_s and low R_{sh} . The film morphology of ***o*-BiPh4T** 17 % and 50 % was similar, shown in Figure 4 and 5. These results are ascribed to the enhancement of short-circuit current density (J_{sc}) caused by the large light absorption capability of fullerene. Also, the ***o*-BiPh4T** 17% BHJ films (or fullerene-rich BHJ films) leads to low fill factor. The values of R_s and R_{sh} in ***o*-BiPh4T** 17 % BHJ films indicates that low fill factor is attributed to poor carrier transport.

We noted that ***o*-BiPh4T** molecules led to the homogeneous blend with fullerene at 50 % oligothiophene volume ratio. Then, we investigated the effects of BHJ layer thickness (as a constant of oligothiophene volume ratio 50%) on photovoltaic performance. Figure 6 (b) show the J - V curves dependence on BHJ layer thickness of J - V characteristics in BHJ-type devices. Extracted photovoltaic parameters are summarized in Table 2. The PCE values decreases with increasing BHJ film thickness. This would be attributed to low carrier transport efficiency toward electrodes, such as carrier recombination in BHJ film. Especially, S-shape J - V curve was described in 70 nm thick of ***t*-BuPh4T** 50% devices. The fill factor, R_s , and R_{sh} of ***o*-BiPh4T** BHJ-type devices is better than that of ***t*-BuPh4T**. The difference of these parameters is attributed to molecular interaction among oligothiophene molecules.

Fig. 6. J - V characteristics under light irradiation with AM1.5G, 100mW/cm² for BHJ-type devices of ITO/MoOx (15 nm)/oligothiophene:C₆₀ BHJ film (thickness: X nm)/C₆₀(30 nm)/BCP(6 nm)/aluminium(80 nm): (a) Dependence of o -BiPh4T volume ratio (b) Dependence of BHJ film thickness in oligothiophene volume ratio 50 %.

Table 2. Extracted photovoltaic parameters for BHJ-type devices from J - V curves.

Device	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill Factor	R_s ($\Omega \cdot \text{cm}^2$)	R_{sh} (k $\Omega \cdot \text{cm}^2$)
^{a)} <i>o</i> -BiPh4T 83 %	0.66±0.02	1.94±0.05	0.70±0.01	0.47±0.01	9.7±0.8	2.7±0.2
^{a)} <i>o</i> -BiPh4T 17 %	1.20±0.02	3.93±0.05	0.86±0.01	0.35±0.01	13.0±1.4	1.5±0.2
^{a)} <i>o</i> -BiPh4T 50 %	0.83±0.04	2.31±0.10	0.84±0.03	0.43±0.01	2.4±0.2	1.6±0.2
^{b)} <i>o</i> -BiPh4T X=30 nm	1.16±0.03	2.82±0.04	0.86±0.02	0.48±0.01	2.7±0.8	1.6±0.1
^{b)} <i>o</i> -BiPh4T X=70 nm	0.70±0.01	2.31±0.05	0.80±0.01	0.38±0.01	6.3±1.3	1.4±0.1
^{b)} <i>t</i> -BuPh4T X=30 nm	0.63±0.07	2.74±0.11	0.55±0.01	0.42±0.02	9.6±1.9	2.4±0.2
^{b)} <i>t</i> -BuPh4T X=50 nm	0.42±0.01	2.25±0.04	0.53±0.01	0.35±0.01	10.3±1.3	1.3±0.1
^{b)} <i>t</i> -BuPh4T X=70 nm	0.11±0.01	1.15±0.06	0.47±0.00	0.21±0.01	87.4±26.4	0.9±0.1

a) Thickness X=50 nm, b) oligothiophene volume ratio: 50 %

To investigate the effects of molecular interaction among oligothiophene on carrier transport property in BHJ-type photovoltaic devices, we measured hole mobility (μ_h). The SCLC method determines the trap-free mobility of films [18, 19]. The trap-free carrier mobility μ in SCLC region can be well described by the following equation (1) [20]:

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{d^3} \quad \cdots (1)$$

, where J : current density, ϵ : relative dielectric constant of material, ϵ_0 : dielectric constant of vacuum, V : applied bias and d : thickness. This equation is well known as Mott-Gurney law. To calculate the SCLC mobility, it is necessary to obtain the ϵ value of ***o*-BiPh4T** and ***t*-BuPh4T**, which can be done by impedance spectroscopy [21, 22].

Obtained capacitance at applied DC = 0 V means geometric capacitance (C_{geo}). It was reported that oligothiophene derivatives show only p-type operation (hole transport) with gold electrode in organic thin film transistors [23, 24]. This means that the Fermi level of gold electrode is matched to HOMO level of oligothiophene derivatives. For design of hole-only devices, we used Au and ITO as electrode. In order to discuss the hole transport via oligothiophene molecules, we then conducted the impedance measurement of hole-only devices: ITO/MoOx (15 nm)/single-component oligothiophene film (150 nm)/Au (50 nm). The measurement was carried out under dark

condition to estimate the dielectric constant of its film. The impedance plots of single-component oligothiophene film of 150 nm thick and typical equivalent circuit model for the fitting of the impedance data are shown in Fig. 7(a). From the obtained geometric capacitance values, we estimated ϵ by using $C_{\text{geo}} = \epsilon\epsilon_0 S/d$, where S is the electrode area. The estimated C_{geo} and ϵ values listed in Table 3. Here, we used the estimated ϵ values to calculate the hole mobility from SCLC region. The ϵ value of ***t*-BuPh4T** was higher than ***o*-BiPh4T**. The logarithm J - V plots in dark and calculated hole mobility are shown in Fig. 7 (b) and Table 3, respectively. From Mott-Gurney law (equation (1)), the intercept of fitted line with slope of 2 indicates SCLC mobility. Estimated mobility of ***o*-BiPh4T** and ***t*-BuPh4T** was approximately same, ca. $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$. According to SCLC theory, V_t (defined as transition voltage to SCLC region) correlates with amount of carrier's trapping states in solid film [25-26]. In other words, V_t corresponds to carrier trap filled voltage. Kahn et.al reported that the relationship between V_t and trap density can explain as reference [27]. The V_t of ***o*-BiPh4T** was lower than that of ***t*-BuPh4T**. Therefore, we suggest that improvement of FF and carrier transport property (R_s and R_p) in ***o*-BiPh4T** 50% BHJ-type devices can be attributed to the reduction of trap rate of carriers. Thus, molecular design is very important for realization of BHJ-type devices with high performance capabilities. For improvement of

FF value in BHJ-type devices with fullerene, we found that molecular design of donor materials required that balanced between strong molecular interaction and formation of nano-scaled homogeneous blend.

Fig. 7. (a) Modulus plots converted from impedance plots of ITO/MoOx/oligothiophene (150 nm)/Au. Inset: RC parallel equivalent circuit model for curve fitting (b) log-log plots of J - V curves in dark and fitted line for SCLC region.

Table 3. Calculated values from impedance fitting and SCLC measurements.

Sample	C_g (nF)	ϵ	V_t (V)	μ_h (cm ² /Vs)
<i>o</i> -BiPh4T	0.9	3.9	6.1	2.6×10^{-3}
<i>t</i> -BuPh4T	1.2	5.1	8.4	1.9×10^{-3}
<i>o</i> -BiPh4T 50%	—	—	4.4	1.2×10^{-3}
<i>t</i> -BuPh4T 50%	—	—	13.7	1.1×10^{-3}

4. Conclusion

We synthesized terminally-modified oligothiophene with *ortho*-biphenyl groups (*o*-BiPh4T) having deep HOMO level for structural control of bulk heterojunction films. The *ortho*-biphenyl group is useful for balance between strong molecular interaction and homogeneous blend composed of oligothiophene and fullerene. Compared with conventional *t*-BuPh4T molecules, the *o*-BiPh4T molecules lead to improvement of FF and resistance in BHJ-type photovoltaic devices. From the SCLC measurement, it was obvious that interaction among the oligothiophene molecules was necessary for carrier-trap-free photovoltaics. The design of nano-scale donor and acceptor molecules taking into consideration their miscibility will be the next challenges.

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