## Effect of Oxygen-Containing Functional Side Chains on the Electronic Properties and Photovoltaic Performances in a Thiophene–Thiazolothiazole Copolymer System

Masahiko Saito,<sup>1</sup> Itaru Osaka,<sup>1,2</sup> Tomoyuki Koganezawa,<sup>3</sup> and Kazuo Takimiya<sup>1,2</sup>

<sup>1</sup>Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8527, Japan

<sup>2</sup>Emergent Molecular Function Research Group, RIKEN Center for Emergent Matter Science, Wako, Saitama 351-0198, Japan

<sup>3</sup>Japan Synchrotron Radiation Research Institute, Sayo-gun, Hyogo 679-5198, Japan

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ABSTRACT: We report the synthesis and characterization of new thiazolothiazole-based semiconducting polymers with alkoxy and/or ester groups as the side chain. An introduction of the alkoxy groups raised the HOMO energy level of the polymers, whereas the introduction of the ester groups lowered the LUMO energy level. It is found that, interestingly, in the monomers the electronic effect of the ester group was more significant than that of the alkoxy groups, whereas in the polymers the effect of the alkoxy group was more significant. PTzBT-oBOeHD with both the alkoxy and ester groups gave the most redshifted absorption spectrum compared to the polymers with the alkyl and alkoxy groups (PTzBT-oBOHD) and with the alkyl and ester groups (PTzBT-BOeHD). Solar cells using *PTzBT-oBOeHD* gave the highest power conversion efficiencies of up to 4.5% with the highest short-circuit current density  $(J_{SC})$  of 10.9 mA/cm<sup>2</sup> among those with the newly synthesized polymers. © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 25:556–564, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21196

## **INTRODUCTION**

Bulk heterojunction (BHJ) solar cells using semiconducting polymers as the p-type photoactive materials together with fullerene derivatives as the n-type materials are of great interest for the development of low-cost, flexible, and large area renewable energy sources [1]. During the last decade, a number of new semiconducting polymers have been reported, and the power conversion efficiencies (PCEs) of polymerbased BHJ solar cells have rapidly improved [2]. To develop high-efficiency solar cells, semiconducting polymers are required to have a wide absorption range, namely a narrow bandgap, to absorb as much sunlight as possible [3]. They also need to form a highly ordered structure in thin films to ensure high charge carrier transport to efficiently collect the generated charge carriers.

*Correspondence to*: Itaru Osaka; e-mail: itaru.osaka@riken.jp. Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

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FIGURE 1 Chemical structure of thiophene-thiazolothiazole copolymers. PTzBT-BOHD: the previously reported polymer; PTzBT-oBOHD, PTzBT-BOeHD, PTzBT-oBOeHD: newly synthesized in this work.





Among the many polymer systems studied so far, polymers with thiazlothiazole (TzTz) is a promising system that provides highly ordered structures and thus high charge carrier mobilities [4]. In fact, several groups have reported on the synthesis of TzTz-based polymers incorporating various donor units in the backbone, which showed good PCEs of  $\sim 5.8\%$  [5]. Independently, we have also reported a series of TzTz-based polymers with alkylthiophenes as the counit and demonstrated that one of the polymers (PTzBT-BOHD, Fig. 1) showed quite high PCEs of 6-7.5% in conventional single-junction cells depending on the ntype material and the active layer thickness [6]. However, the relatively narrow absorption range of ~680 nm for PTzBT-BOHD limited the light harvesting property, and thus broadening the absorption range, i.e., narrowing the bandgap, has been an issue for the further improvement of the performances.

In this work, we introduced the electrondonating alkoxy and/or electron-withdrawing ester groups on the thiophene moieties instead of the alkyl groups introduced in the side chain of PTzBT-BOHD while using the same backbone system (PTzBT-oBOHD, PTzBT-BOeHD, and PTzBToBOeHD; Fig. 1), since the backbone has been proven to offer highly ordered structures [5]. It is expected that the combination of these two functional groups with different electronic natures would allow us to have polymers with narrow bandgaps with various HOMO and LUMO levels. We here describe the synthesis, electronic structures, and the ordering structures of new thiophene-TzTz polymers with alkoxy and/or ester groups as the side chain and their solar cell performances.



polymerization conditions: Pd<sub>2</sub>(dba)<sub>3</sub>, P(o-Tol)<sub>3</sub> / chlorobenzene, 200, °C, µW

SCHEME 2 Synthesis of PTzBT-oBOHD, PTzBT-BOeHD, and PTzBT-oBOeHD.

#### **RESULTS AND DISCUSSION**

#### Synthesis

The synthetic routes to the monomer with the alkoxy groups [7] and the ester groups [8] are shown in Scheme 1. The dithienyl-TzTz with the alkoxy groups on the thiophene rings (2) was prepared by heating the mixture of **1** and dithiooxiamide. Compound **2** was then dibrominated using N-bromosuccinimide (NBS) to give 3, which was then stannylated via the treatment of *n*-BuLi followed by the addition of trimethyltin chloride, giving the alkoxy monomer (4). As for the dithienyl-TzTz with the ester groups on the thiophene rings (8), 5-bromothiophene-3carboxylic acid (5) was first formylated at the 2 position by the treatment of *N*,*N*'-dimethylformamide (DMF) through lithiation with lithium diisopropylamide (LDA) to yield 6. However, this reaction gave the 4-formyl-3-thiophene-carbxylic acid as a byproduct, which could not be removed by column chromatography. The crude of 6 was thus subjected to esterification with 2-hexy-1-bromodecane to afford 7, which was successfully isolated by column chromatography. The ester monomer (8) was prepared by the reaction of **7** and dithiooxamide in DMF.

All polymers were synthesized via the Stille coupling reaction using a microwave reactor (Scheme 2). The alkoxy monomer (4) was copolymerized with the dibrominated alkyl monomer (9) and the ester monomer (8) to give PTzBT-oBOHD and PTzBT-BOeHD, respectively. Compound 8 was also copolymerized with the distannylated alkyl

 TABLE 1
 Polymerization Results<sup>a</sup>

Polymer	M <sub>n</sub> (kDa)	M <sub>w</sub> (kDa)	PDI	
PTzBT-oBOHD	32	132	4.0	
PTzBT-BOeHD	25	115	4.8	
PTzBT-oBOeHD	29	235	8.2	
PTzBT-BOHD <sup>b</sup>	35	110	3.1	

Abbreviation: PDI, polydispersity indice.

<sup>a</sup>Determined by GPC using polystyrene standard and *o*dichlorobenzene as the eluent at 140°C.

<sup>b</sup>From [6b].

monomer (10) to give PTzBT-oBOeHD. All polymers were soluble in warm chloroform (CF) and chlorobenzene (CB), and the molecular weight of polymers evaluated by gel permeation chromatography (GPC) at 140°C were mostly above 30 kDa ( $M_n$ ) (Table 1). Polydispersity indices of the polymers synthesized here were relatively large (>4), owing to the bimodally appeared signal in the chromatograph (Fig. S14 in the Suporting Information). This is likely because the polymers with the alkoxy and ester groups have higher tendency to aggregate, resulting in the bimodal signals.

### Physicochemical Properties of the Polymers

To confirm the electronic effect of the side chains, cyclic voltammetry (Fig. 2a) and UV–vis absorption spectroscopy (Fig. 2b) of dithienyl-TzTzs with the alkyl (TzBT-HD, **9**), alkoxy (TzBT-oBO, **3**), and ester groups (TzBT-eHD, **8**) were carried out in



FIGURE 2 Cyclic voltammograms (a) and UV-vis absorption spectra (b) of the monomers in the solution.

TABLE 2 Electronic Properties of the Monomers and Polymers

Compound	λ <sub>max</sub> (nm)	$\lambda_{edge}$ (nm) / $E_g^{opt}$ (eV) <sup>a</sup>	Е <sub>номо</sub> (eV) <sup>ь</sup>	E <sub>LUMO</sub> (eV) <sup>c</sup>	
TzBT-HD (9)	403	448/2.77	-5.59	-2.82	
TzBT-oBO (3)	415, 440	457/2.71	-5.29	-2.58	
TzBT-eHD (8)	432	481/2.58	-5.80	-3.22	
PTzBT-BOHD	573, 624	685/1.81	-5.23	-3.42	
PTzBT-oBOHD	600, 653	709/1.75	-5.02	-3.27	
PTzBT-BOeHD	578, 633	700/1.77	-5.28	-3.51	
PTzBT-oBOeHD	621, 675	730/1.70	-5.08	-3.38	

<sup>*a*</sup> $\lambda_{edge}$ : absorption edge,  $E_{g}^{opt}$ : bandgaps calculated with  $\lambda_{edge}$ .

<sup>b</sup>HOMO energy levels; cyclic voltammetry and photoelectron spectroscopy in air (PESA) were used to evaluate them for the monomers and polymers, respectively.

<sup>c</sup>LUMO energy levels estimated by adding the band gap ( $E_g^{opt}$ ) to  $E_{HOMO}$ .

the dichloromethane solution.  $E_{\text{HOMO}}$  of TzBT-BO, TzBT-oBO, and TzBT-eHD were estimated from the onset oxidation potentials. E<sub>HOMO</sub> of TzBT-oBO was higher by 0.3 eV (-5.29 eV) and that of TzBT-eHD was lower by 0.21 eV (-5.80 eV) than that of TzBT-BO (-5.59 eV) (Table 2). These results are consistent with what is expected from the electron-donating and electron-withdrawing nature of the alkoxy and the ester groups.  $E_{LUMOS}$  were estimated by the addition of  $E_{\rm g}$  determined from the absorption onset. As is the case in  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  of TzBT-oBO (-2.58 eV) was higher by 0.24 eV and that of TzBT-eHD (-3.22 eV) was lower by 0.40 eV than that of TzBT-BO (-2.82 eV) (Table 2). These results indicate that the alkoxy group affects  $E_{\text{HOMO}}$  and the ester group affects  $E_{\text{LUMO}}$  more strongly. The absorption maxima ( $\lambda_{max}$ ) of both TzBT-oBO (415 nm) and TzBTeHD (430 nm) were redshifted as compared to that of TzBT-BO (403 nm). The more significant redshift in TzBT-eHD than in TzBT-oBO might be due to the resonance effect of the ester groups.

 $E_{\text{HOMOS}}$  of the polymers were evaluated by photoelectron spectroscopy in air using the polymer thin films (Fig. 3a).  $E_{\text{HOMOS}}$  of PTzBT-oBOHD

and PTzBT-oBOeHD with the alkoxy groups were -5.02 and -5.08 eV, respectively, which were about 0.15–0.2 eV higher than that of PTzBT-BOHD (-5.23 eV) (Table 2), owing to the electron-donating nature of the alkoxy group. Slightly lower  $E_{HOMO}$ of PTzBT-oBOeHD compared to PTzBT-oBOHD is likely due to the electron-withdrawing nature of the ester group.  $E_{HOMO}$  of PTzBT-BOeHD (-5.28 eV) was slightly lower than that of PTzBT-BOHD (Table 2), which is also attributed to the electronwithdrawing nature of the ester groups. It should be noted that the downward shifts of  $E_{\text{HOMO}}$  by the introduction of the ester group, i.e., shifts from PTzBT-BOHD to PTzBT-BOeHD and from PTzBT-oBOHD to PTzBT-oBOeHD, were 0.05-0.06 eV, which was far less than the upward shift by the alkoxy group.

 $E_{\rm LUMO}$  of the polymers were estimated by adding the band gap ( $E_{\rm g}^{\rm opt}$ ), which was determined from the absorption onset in the film, to  $E_{\rm HOMO}$  (Table 2). In PTzBT-oBOHD,  $E_{\rm LUMO}$  was elevated to -3.28 eV from that in PTzBT-BOHD (-3.42 eV), being affected by the alkoxy group. On the other hand,  $E_{\rm LUMO}$ of PTzBT-BOeHD was lower (-3.51 eV) than that of PTzBT-BOHD owing to the electron-withdrawing



FIGURE 3 Photoelectron spectra (a) and UV-vis absorption spectra (b) of the polymer thin films.

nature of the ester group. In PTzBT-oBOeHD, despite having the ester groups,  $E_{LUMO}$  was -3.38 eV that is almost the same as that in PTzBT-BOHD. This implies that the electronic effect of the ester groups on the  $E_{LUMO}$  is compensated by the effect of the alkoxy groups. These perturbations of  $E_{HOMO}$  and  $E_{LUMO}$  suggest that the electronic effect of the alkoxy group was more significant in this system.

UV-vis absorption spectra of the polymers in the film are shown in Fig. 3b. As expected, all the polymers synthesized here exhibited redshifted spectra compared to that of PTzBT-BOHD with  $\lambda_{max}$ of 624 nm. PTzBT-oBOeHD with both the alkoxy and ester groups had the most redshifted absorption spectra with  $\lambda_{max}$  of 675 nm and the smallest optical bandgap ( $E_{g}^{opt}$ ) of 1.70, which was reduced by ca. 0.1 eV compared to that of PTzBT-BOHD (Table 2). It was interesting that  $\lambda_{max}$  of PTzBT-BOeHD (633 nm) was located at the shorter wavelength region than  $\lambda_{max}$  of PTzBT-oBOHD (653 nm) (Table 2), which sharply contrast to the result in the monomer system. This suggests that the electronic effect of the alkoxy group is more significant than the ester group in the polymers, as also observed in perturbation of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ . These phenomena could be explained as follows. In the monomers, the  $\pi$ -electron system of the molecule is limited to three aromatic heterocyles and thus the electronic state is strongly reflected by the resonance effect of the ester groups. However, in the polymers where the  $\pi$ -electron system is well developed along the backbone, the resonance effect of the ester groups might be weakened.

#### Solar Cell Characteristics

Solar cells were fabricated by spin coating the solutions of polymer and [6,6]-phenyl-C<sub>61</sub>-butyric acid

methyl ester ( $PC_{61}BM$ ) with the weight ratio of 1:2 in CB onto the PEDOT:PSS spin-coated indium tin oxide (ITO) glass, followed by vacuum deposition of Ca/Al as the cathode. The current density (J)-voltage (V) curves and the external quantum efficiency (EQE) spectra of the cells under 1 Sun of simulated AM 1.5G solar irradiation (100 mW/cm<sup>2</sup>) are displayed in Figs. 4a and 4b, respectively, and photovoltaic parameters are summarized in Table 3. Although only the PTzBT-oBOeHD-based cell gave higher short-circuit current density  $(J_{SC})$ of 10.9 mA/cm<sup>2</sup> than the PTzBT-BOHD-based cell (10.1 mA/cm<sup>2</sup>), all the cells using the new polymers (PTzBT-oBOHD, PTzBT-BOeHD, and PTzBToBOeHD) showed photoresponse in wider spectral ranges compared to that with PTzBT-BOHD, as expected from the absorption spectra. Owing to the lower lying  $E_{\text{HOMO}}$  of PTzBT-BOeHD, its cell showed slightly but higher open-circuit voltage ( $V_{OC}$ ) of 0.92 V than PTzBT-BOHD-based cell (0.91 V). In the cells with PTzBT-oBOHD and PTzBT-oBOeHD, Vocs were lower by more than 0.1 V than the cell with PTzBT-BOHD, reflecting their higher lying  $E_{\text{HOMO}}$ . All the cells with the new polymers showed lower fill factors of below 0.60 than that of the cell with PTzBT-BOHD (0.68). This is likely due to the lower hole mobility of the new polymers. As revealed by the hole-only device characterization, the hole mobilities for PTzBT-oBOHD, PTzBT-BOeHD, and PTzBToBOeHD (5–9  $\times$  10<sup>-5</sup> cm<sup>2</sup>/Vs) calculated as the space charge limited current model were about one order of magnitude lower than that for PTzBT-BOHD (4.8  $\times$  10<sup>-4</sup> cm<sup>2</sup>/Vs) (Fig. S16 in the Suporting Information). Although the PCEs of the new polymer-based cells (3.8-4.5%) were lower than that of PTzBT-BOHD (6.1%), the cell using PTzBT-oBOeHD with the most redshifted absorption showed the highest PCE of 4.5% among the cells using new polymers.



FIGURE 4 J-V curves (a) and EQE spectra (b) of the solar cells based on PTzBTs.

TABLE 3 Photovoltaic Properties of the Solar Cells Based on PTzBTs

Polymer	J <sub>SC</sub> (mA/cm²)	V <sub>OC</sub> (V)	FF	PCE <sub>max</sub> [PCE <sub>ave</sub> ] (%) <sup>a</sup>
PTzBT-BOHD	10.1	0.91	0.68	6.1 [5.8]
PTzBT-oBOHD	9.4	0.71	0.57	3.8 [3.5]
PTzBT-BOeHD	8.1	0.92	0.57	4.2 [4.0]
PTzBT-oBOeHD	10.9	0.78	0.53	4.5 [4.2]

Abbreviations:  $PCE_{max}$ , maximum power conversion efficiencies;  $PCE_{ave}$ , average power conversion efficiencies; FF, fill factor.

#### Thin Film Structure and Morphology

To further understand the photovoltaic performances of the cells, polymer ordering structures in the thin film were investigated by X-ray diffraction studies. Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) images of the polymer/PC<sub>61</sub>BM blend films on the PE-DOT:PSS/ITO substrate are shown in Fig. 5a. In all cases, diffractions assignable to the  $\pi - \pi$  stacking structures ( $q \approx 1.7$  Å<sup>-1</sup>) appeared along the  $q_z$ axes (out of plane), indicating that the polymers formed face-on orientation on the substrate surface [9], which would facilitate the out-of-plane charge transport and thus are ideal for the solar cells.  $\pi - \pi$ Stacking distances were estimated to be ca. 3.5 Å for all the polymers, suggesting that the alkoxy and ester groups are not detrimental to the  $\pi - \pi$  stacking order.



FIGURE 5 2D-GIXD patterns (a) and AFM images (b) of the polymer/PC<sub>61</sub>BM blend films.

We also investigated the morphology of the polymer/PC<sub>61</sub>BM blend films by the atomic force microscopy (AFM) (Fig. 5b). The polymers with the ester groups (PTzBT-BOeHD and PTzBT-oBOeHD) showed needle-like textures that are slightly different from the nodule-like textures observed in other polymers. Nevertheless, all the films seem to have formed well phase separated morphologies, which would ensure the charge generation. On the other hand, the surface roughness (rms) of the blend of PTzBToBOHD, PTzBT-BOeHD, and PTzBT-oBOeHD is larger than that of PTzBT-BOHD, which means that the blend films of PTzBT-oBOHD, PTzBT-BOeHD, and PTzBT-oBOeHD are less uniform compared to that of PTzBT-BOHD, which could be a reason for the lower hole mobility and the lower solar cell performances of the new polymers. We believe that the solar cell performances of the new polymers could be improved by optimizing the film morphology.

#### Summary

New thiazolothiazole-based semiconducting polymers with the alkoxy and/or ester groups as the side chain have been synthesized and investigated. As expected, the introduction of the alkoxy groups raised the HOMO energy levels of the polymers, and the introduction of the ester groups lowered the LUMO energy levels. Interestingly, the electronic effect of the alkoxy group was more significant compared to the ester group in the polymers, which was in sharp contrast to what was observed in the monomers. This is likely because the electronic effect of the ester group is dominated by the resonance effect, which is weakened in the polymers with well-developed  $\pi$ -conjugation. Having both the alkoxy and ester groups, PTzBT-oBOeHD gave the most redshifted absorption spectrum among the polymers studied here. Although the overall efficiencies were lower for the cells using the new polymers compared to the polymer with all alkyl groups, all the cells using new polymers showed photoresponse in wider spectral regions. Further device optimization might lead to the improvement of the efficiency.

#### EXPERIMENTAL

#### Synthesis

3-((2-Hexyldecyl)oxy)thiophene-2-carbaldehyde (1) [7] and 5-bromothiophene-3-carboxylate (5) [8] were synthesized according to the reported procedure. All chemicals were of reagent grade unless otherwise indicated. All solvents were distilled prior to use. Polymerization was carried out using a microwave reactor (Biotage Initiator, Uppsala, Sweden). Molecular weights were determined by GPC using a TOSOH HLC-8121GPC/HT at 140°C using *o*-dichlorobenzene as a solvent and calibrated with polystyrene standards.

### 2,5-Bis(3-((butyloctyl)oxy)thiophen-2-yl) thiazolo[5,4-d] thiazole (**2**)

Dithiooxamide (1.1 g, 9.2 mmol) and 3-((2hexyldecyl)oxy)thiophene-2-carbaldehyde (1) (6.0 g, 20.2 mmol) were combined in a round-bottom flask and heated at temperature 200°C for 12 h. The crude product was purified by column chromatography on silica gel. Recrystallization from hexane gave pure product as yellow solids (1.8 g, 29%). <sup>1</sup>H NMR  $(400 \text{ MHz}, \text{CDCl}_3) \delta 7.32 \text{ (d, } J = 5.5 \text{ Hz}, 2\text{H}), 6.89 \text{ (d,}$ J = 5.5 Hz, 2H), 4.14 (d, J = 4.8 Hz, 4H), 1.85–1.82 (m, 2H), 1.62–1.49 (m, 8H), 1.40–1.20 (m, 24H), 0.86 (t, J = 7.0 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 159.8, 156.3, 149.9, 126.8, 116.4, 115.5, 74.5, 38.6, 32.0, 31.4, 31.1, 29.8, 29.3, 27.1, 23.2, 22.8, 14.3, 14.3. EI-MS (70 eV) m/z = 674 (M<sup>+</sup>); anal. calcd for C<sub>36</sub>H<sub>54</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>: C, 64.05%; H, 8.06%; N, 4.15%. Found: C, 64.19%; H, 8.36%; N, 4.02%.

#### 2,5-Bis(5-bromo-3-((2-butyloctyl)oxy)thiophen-2-yl)thiazolo[5,4-d]thiazole (**3**)

To a solution of 2,5-bis(3-((2-octyldodecyl)oxy) thiophen-2-yl)thiazolo[5,4-d]thiazole (2) (1.5 g, 2.2 mmol) in  $CHCl_3$  (50 mL) and acetic acid (25 mL) solutions, NBS (870 mg, 4.9 mmol) solution in CHCl<sub>3</sub>/AcOH (20/10 mL) was added dropwise and stirred at 0°C for 2 h. Then, the reaction solution was stirred at room temperature overnight. The mixture was washed with water and brine, and the organic layer was concentrated. Purifications with column chromatography on silica gel and recrystallization from hexane gave pure product as yellow solids (1.57 g, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 6.90 (s, 2H), 4.09 (d, J = 4.9 Hz, 4H), 1.84–1.82 (m, 2H), 1.60-1.49 (m, 8H), 1.35-1.29 (m, 24H), 0.93-0.86 (m, J = 7.0 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) & 158.7, 154.8, 145.0, 119.8, 116.9, 115.5, 74.9, 38.5, 32.0, 31.4, 31.1, 29.8, 29.3, 27.0, 23.2, 22.8, 14.3. EI-MS (70 eV) m/z = 830 (M<sup>+</sup>); anal. calcd for C<sub>36</sub>H<sub>52</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>: C, 51.91%; H, 6.29%; N, 3.36%. Found: C,51.70%; H, 6.19%; N, 3.46%.

## 2,5-Bis(5-trimethystannyl-3-((2-butyloctyl)oxy) thiophen-2-yl)thiazolo[5,4-d]thiazole (**4**)

To a solution of 2,5-bis(5-bromo-3-((2-butyloctyl) oxy)thiophen-2-yl)thiazolo[5,4-d]thiazole (**3**) (1.2 g,

1.44 mmol) in 50 mL of tetrahydrofuran (THF), 1.6 M solution of *n*-butyllithium in hexane (2.25 mL, 3.6 mmol) was added dropwise at  $-78^{\circ}$ C. The solution was stirred at -78°C for 1 h and trimethyltin chloride (800 mg, 4.0 mmol) was added. After the solution was warmed to room temperature, 50 mL of water and 50 mL of ethyl acetate were added. The organic layer was washed twice with 50 mL of water and dried over magnesium sulfate. After removing the solvent, recrystallization from hexane gave pure product as yellow solids (1.0 g, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.91 (s, 2H), 4.15 (d, J = 4.9 Hz, 4H), 1.84–1.82 (m, 2H), 1.61–1.50 (m, 8H), 1.28-1.24 (m, 24H), 0.87-0.84 (m, J = 7.0 Hz, 12H), 0.41 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 159.5, 157.5, 149.9, 141.2, 123.2, 120.7, 74.3, 38.6, 32.0, 31.4, 31.1, 29.8, 29.8, 29.5, 27.1, 22.8, 14.3. EI-MS (70 eV) m/z = 1002 (M<sup>+</sup>); anal. calcd for C<sub>42</sub>H<sub>70</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>Sn<sub>2</sub>: C, 50.41%; H, 7.05%; N, 2.80%. Found: C, 50.65%; H, 6.88%; N, 2.98%.

# 2-*Hexyldecyl-5-bromo-2-formylthiophene-3-carboxylate* (**7**)

LDA (freshly prepared from diisopropylamine (4.2 mL, 33 mmol) and 1.6 M n-butyllithium (20.1 mL, 33 mmol) in THF (50 mL)) was added dropwise to a THF (50 mL) solution of 5bromothiophene-3-carboxylate (5) (2.07 g, 10 mmol) at -30°C. After stirring the mixture for 1 h, DMF (2.8 mL, 36 mmol) was added to the mixture at  $-30^{\circ}$ C, and then the mixture was warmed to room temperature. The mixture was further stirred for 1 h, and then water (100 mL) was added to the mixture and extracted with ether three times. The organic laver was dried over magnesium sulfate, and the solvent was evaporated under reduced pressure, giving 6 as brown solids (2.2 g). Compound 6 was subjected to the next reaction without further purification. Compound 6 (2.2 g), 2-hexyl-1-bromodecane (3.35 g, 33 mmol), and sodium carbonate (10.5 g, 99 mmol) in DMF (50 mL) were heated to 125°C for 5 h, and then cooled to room temperature. The reaction mixture was poured into water and extracted with dichloromethane. The crude product was purified by column chromatography on silica gel to give 7 as yellow oil (2.4 g, 52% in two steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.48 (s, 1H), 7.51 (s, 1H), 4.26 (d, J = 4.9 Hz, 2H), 1.88-1.78 (m, 1H), 1.62-1.44(m, 4H), 1.34–1.26 (m, 20H), 0.90–0.86 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 183.7, 161.5, 148.7, 137.1, 133.5, 122.7, 68.9, 37.7, 37.5, 32.0, 31.9, 31.5, 31.2, 30.0, 29.7, 29.5, 26.8, 22.8, 14.3. EI-MS (70 eV) m/z = 458 (M<sup>+</sup>); anal. calcd for  $C_{22}H_{35}O_3S$ : C, 57.51%; H, 7.68%. Found: C, 57.36%; H, 7.46%.

2,2'-(Thiazolo[5,4-d]thiazole-2,5-diyl)bis(5-bro*mothiophene-3-carboxylate*). A mixture of **7** (2.02 g, 4.4 mmol) and dithiooxamide (240 mg, 2 mmol) was heated to 140°C for 24 h, and then cooled to room temperature. The reaction mixture was poured into water and extracted with dichloromethane. The combined organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel and recrystallized from hexane to give 8 as yellow solids (220 mg, 11%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (s, 1H), 4.26 (d, J = 4.9 Hz, 4H), 1.78 (m, 2H), 1.60–1.56 (m, 8H), 1.35–1.27 (m, 40H), 0.90–0.86 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.3, 159.6, 153.8, 132.7, 128.8, 115.9, 68.6, 37.5, 32.1, 32.0, 31.5, 30.1, 29.8, 29.7, 29.5, 26.9, 22.9, 22.8, 14.3. EI-MS (70 eV) *m*/*z* = 998  $(M^+)$ ; anal. calcd for  $C_{46}H_{68}N_2O_4S_4$ : C, 55.19%; H, 6.85%; N, 2.80%. Found: C, 54.98%; H, 6.61%; N, 2.91%.

## General Procedure for Polymerization

To a reaction tube equipped with a stirring bar, stannylated monomer (0.10 mmol), brominated monomer (0.10 mmol),  $Pd_2(dba)_3$  (1.8 mg, 0.002 mmol), P(o-Tol)<sub>3</sub> (2.4 mg, 0.008 mmol), and CB (5 mL) were added. Then, the tube was purged with argon and sealed. The reaction tube was set into a microwave reactor and heated to 200 °C for 10 min. After cooling to room temperature, the reaction solution was poured into 200 mL of methanol containing 5 mL of hydrochloric acid and stirred for 5 h. Then, the precipitated solid was subjected to the sequential Soxhlet extraction with methanol and hexane to remove low molecular weight fractions. The residue was then extracted with CF and reprecipitated in 200 mL of methanol to yield dark purple or dark blue solids (yield = 72-91%).

## Instrumentation

UV–vis absorption spectra were measured using a Shimadzu UV-3600 spectrometer. Cyclic voltammograms were recorded on an ALS Electrochemical Analyzer Model 612D in dichloromethane containing tetrabutylammonium hexafluoride (Bu<sub>4</sub>NF, 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. A Pt counter and working electrodes and a Ag/AgCl reference electrode were used. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple (Fc/Fc<sup>+</sup>:  $E^{1/2} = +0.43$  V measured under identical conditions). Photoelectron spectra were measured by using a photoelectron spectrometer, model AC-2, in air (Riken Keiki, Tokyo, Japan). The dynamic force mode AFM study was carried out on a Nanocute scanning probe microscope system (SII Nanotechnology). 2D-GIXD experiments were conducted at the SPring-8 on the beamline BL19B2. The sample was irradiated at a fixed incident angle on the order of  $0.12^{\circ}$  through a Huber diffractometer. The X-ray energy of 12.39 keV ( $\lambda = 1$  Å) of the 2D-GIXD patterns was recorded using a 2D image detector (Pilatus 300K, Dectris, Baden, Switzerland). Samples for the X-ray measurements were prepared by spin casting the polymer and polymer/PC<sub>61</sub>BM solution on the ITO substrate.

#### Solar Cell Fabrication and Measurement

ITO substrates were first precleaned sequentially by sonicating in a detergent bath, deionized water, acetone, and isopropanol at room temperature, and in a boiled isopropanol bath each for 10 min, and then baked at 120°C for 10 min in air. The substrates were then subjected to a UV/ozone treatment at room temperature for 20 min. The precleaned ITO substrates were coated with PEDOT:PSS (Clevios P VP Al4083, Heraeus, Hanau, Germany) by spin coating (5000 rpm for 30 s, thickness:  $\sim$ 50 nm). The photoactive layer was deposited in a glove box by spin coating a CB solution, containing 3–6 g/L of the polymer sample with respective amount of  $PC_{61}BM$ , at 400 rpm for 20 sec and 1500 rpm for 5 sec, in which the solution was kept heated at 100°C. The thin films were transferred into a vacuum evaporator connected to the glove box, and the Ca layer (20 nm) and the Al layers (100 nm) were deposited sequentially. The active area of the cells was  $0.16 \text{ cm}^2$ . J--V characteristics for the cells were measured using a Keithley 2400 source measure unit in nitrogen atmosphere under 1 Sun (AM1.5G) conditions using a solar simulator (XES-40S1, San-Ei Electric, Osaka, Japan). The light intensity for the *J*--*V* measurements was calibrated using a reference PV cell, AK-100 (Konica Minolta, Tokyo, Japan), which was certified at National Institute of Advanced Industrial Science and Technology, Japan. EOE spectra were measured using a spectral response measuring system (S 9241, Soma Optics, Tokyo, Japan).

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