

# Electron Accepting Benzodithiophene-4,8-dicarboxylate Designed for New Type D-A Narrow Bandgap Copolymers

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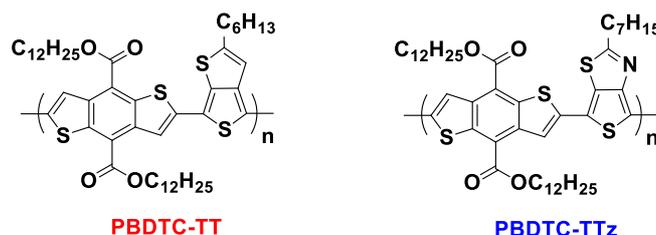
**Keywords:** benzodithiophene, thienothiazole, donor-acceptor conjugated polymer

**Abstract.** An acceptor (A) unit of benzodithiophene-4,8-dicarboxylate (**BDTC**) was combined with a donor (D) unit of thieno(3,4-*d*)thiazole (**TTz**) to synthesize a D-A type conjugated polymer, **PBDTC-TTz**. Bandgap of **PBDTC-TTz** was narrow, estimated to be 1.57 eV. The  $\pi$ -stacking distance observed by XRD was small value to be 3.55 Å. The energy level of the highest occupied molecular orbital was estimated to be -5.03 eV, which was deeper than that another D-A type copolymer composed of **BDTC** and thieno(3,4-*b*)thiophene, previously synthesized.

## 1. Introduction

Recently, we have developed a new type donor-acceptor (D-A) polymer, poly[4,8-benzo(1,2-*b*:4,5-*b'*)dithiophenedicarboxylate-*alt*-thieno(3,4-*b*)thiophene] (**PBDTC-TT**) composed of an electron accepting benzodithiophene-4,8-dicarboxylate (**BDTC**) and an electron donating thieno(3,4-*b*)thiophene (**TT**), as shown in Figure 1.<sup>[1]</sup> **PBDTC-TT** exhibited narrow bandgap nature (1.5 eV) and broad photoabsorption owing to strong intermolecular charge transfer (ICT) between the **BDTC** and the **TT** units. The bulk heterojunction (BHJ) organic photovoltaic cell (OPV) based on **PBDTC-TT** showed the power conversion efficiency (PCE) of 3.0% and efficient sensitization in the range of visible light and near infrared as far as 900 nm. These results indicated that the **BDTC** unit is a promising A-type building block to construct narrow bandgap copolymers. However, **PBDTC-TT** was revealed to have shallow energy level of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) (-4.80 eV), which would limit further improvement of PCE on OPV.

In this work, **BDTC** was combined with thieno(3,4-*d*)thiazole (**TTz**) that has been known to possess weaker electron donating ability than that of **TT**, constructing the D-A type copolymer, poly[4,8-benzo(1,2-*b*:4,5-*b'*)dithiophene dicarboxylate-*alt*-thieno(3,4-*d*)thiazole] (**PBDTC-TTz**), as shown in Figure 1. The effect of the electron donating **TTz** on  $E_{\text{HOMO}}$  of the **BDTC** based polymers was investigated in order to achieve narrow bandgap nature and deep  $E_{\text{HOMO}}$  for OPVs.



**Figure 1.** Chemical structures of  $\pi$ -conjugated alternating copolymers, **PBDTC-TT** and **PBDTC-TTz**.

## 2. Experimental

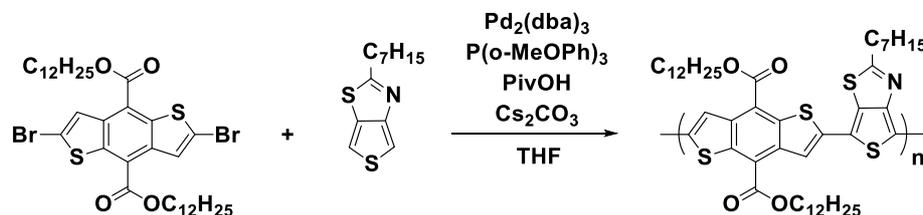
### 2.1. Measurements

$^1\text{H}$  NMR spectrum was obtained with a JEOL JNM-ECS 400 at resonance frequency of 400 MHz for  $^1\text{H}$  in  $\text{CDCl}_3$ . The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity index (PDI) of soluble fraction of the polymers in chloroform were determined by gel permeation chromatography (GPC) calibrated with polystyrene standards using chloroform as an eluent at room temperature. Ultraviolet-visible (UV-vis) spectra of the polymers were measured on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry (CV) of the polymers in a thin film state on Pt was carried out in 0.1 M  $\text{Et}_4\text{NBF}_4$  acetonitrile solution at a scan rate of  $50 \text{ mV s}^{-1}$  under an argon atmosphere by using a Hokuto Denko HB-305 function generator and a HAL3001 potentiostat equipped with a Pt inlay-disk as the working electrode, a Pt plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Ionization potentials (vs vacuum) of the polymers were estimated from the onset of their first oxidation peak ( $E_a^{\text{onset}}$ ) in the cyclic voltammograms on the basis that ferrocene / ferrocenium is 4.8 eV below the vacuum level.<sup>[2]</sup> X-ray diffraction (XRD) measurements of drop-cast polymer films were carried out using a Rigaku MiniFlex600.

### 2.2. Materials

All chemicals were purchased from Kanto Chemical Co., Tokyo Chemical Industry Co., Nacalai Tesque, or Sigma-Aldrich, LLC., and they were used without further purification unless stated. Tetrahydrofuran (THF) was purified by distillation according to common method. 2,6-Dibromo-4,8-benzodithiophenedicarboxylate (**BDTC-Br<sub>2</sub>**) and 2-heptylthieno(3,4-*d*)thiazole were synthesized according to literature methods.<sup>[1,3]</sup>

**Synthesis of PBDTC-TTz.** In a two-necked flask, **BDTC-Br<sub>2</sub>** (80.0 mg, 0.104 mmol), 2-heptylthieno(3,4-*d*)thiazole (24.7 mg, 0.104 mmol), dry THF (1.04 ml), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ( $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ ) (5.38 mg), tris(2-methoxyphenyl)phosphine ( $\text{P}(\text{o-MeOPh})_3$ ) (7.30 mg), pivalic acid (PivOH) (10.6 mg) and cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) (101.1 mg) were mixed with stirring at room temperature. After stirring for 30 min, the reaction mixture was heated at  $80 \text{ }^\circ\text{C}$  for 1 h. 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. **PBDTC-TTz** was obtained as a black solid (41 mg, 46% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ) 0.89-2.50 (br, 59H), 3.07 (br, 2H), 4.64 (br, 4H), 7.69 (br, 2H). Anal. Calcd for  $\text{C}_{48}\text{H}_{69}\text{NO}_4\text{S}_4$ : C, 67.64; H, 8.16; N, 1.64. Found: C, 66.83; H, 7.50; N, 1.72.



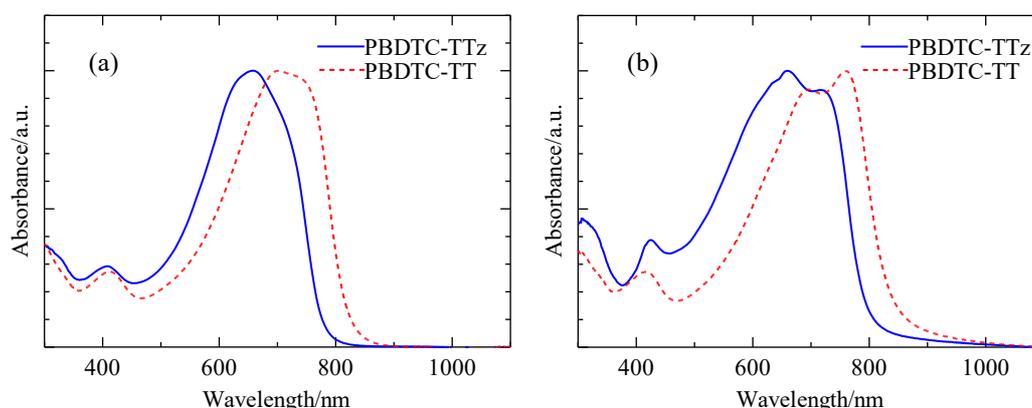
**Scheme 1.** Synthesis of **PBDTC-TTz**. PivOH = pivalic acid, THF = tetrahydrofuran.

## 3. Results and discussion

### 3.1. Synthesis and optical properties

A synthetic route for **PBDTC-TTz** is shown in Scheme 1. **PBDTC-TTz** was obtained by direct arylation polymerization according to literature methods.<sup>[4]</sup> **PBDTC-TTz** was highly soluble in common organic solvents such as dichloromethane and chloroform.  $M_n$  and PDI were  $7.4 \text{ kg mol}^{-1}$  and 1.9, respectively.

Figure 2 shows the absorption spectrum of **PBDTC-TTz** with that of **PBDTC-TT** as a reference. The results are summarized in Table 1. The absorption maximum ( $\lambda_{\max}$ ) of **PBDTC-TTz** in chloroform was observed at 659 nm, which was blue-shifted compared with that of **PBDTC-TT** ( $\lambda_{\max} = 702$  nm). The blue shift is due to weak ICT in the **PBDTC-TTz**, which could be interpreted that electron donating ability of **TTz** is lower than that of **TT**. In the film state, **PBDTC-TTz** exhibited two absorption peaks with  $\lambda_{\max}$  at 660 and 716 nm, and the absorption onset ( $\lambda_{\text{onset}}$ ) was almost the same as that in solution. The optical bandgap ( $E_g^{\text{opt}}$ ) of **PBDTC-TTz** determined from  $\lambda_{\text{onset}}$  of the film state was 1.57 eV, which was wider than that of **PBDTC-TT** ( $E_g^{\text{opt}} = 1.50$  eV) but spectral width is much broader than that of the prototype D-A copolymer, **PBDTTTz-1** composed of the D unit of 4,8-dialkoxybenzodithiophene (**BDT**) and the A unit of **TTz** ( $\lambda_{\max} = 625$  nm,  $E_g^{\text{opt}} = 1.8$  eV)<sup>[5]</sup>. ICT interaction in the combination of D-type **TTz** and A-type **BDTC** might be stronger than that in the combination of A-type **TTz** and D-type **BDT**.



**Figure 2.** UV-vis absorption spectra of **PBDTC-TTz** and **PBDTC-TT** (a) in chloroform solution and (b) in the film state.

**Table 1.** Optical properties and energy levels of **PBDTC-TTz** and **PBDTC-TT**.

Polymer	UV – vis absorption		$E_{\text{HOMO}}$ (eV)	$E_g^{\text{opt d}}$ (eV)
	Solution <sup>a</sup>	Film		
	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)		
<b>PBDTC-TTz</b>	659	660, 716	-5.03 <sup>b</sup>	1.57
<b>PBDTC-TT</b>	702	707, 757	-4.88 <sup>b</sup> (-4.80) <sup>c</sup>	1.50

<sup>a</sup> Measured in  $\text{CHCl}_3$ .

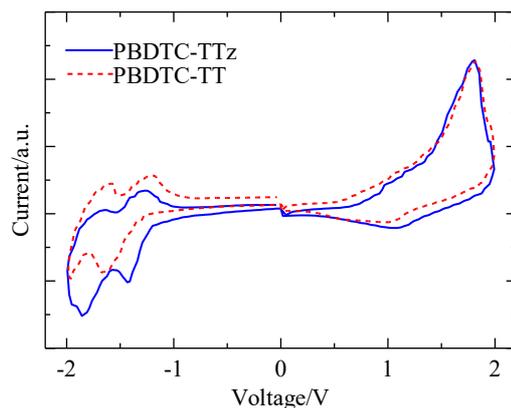
<sup>b</sup> Estimated with CV

<sup>c</sup> Estimated with photoelectron spectroscopy in the atmosphere.

<sup>d</sup> Estimated from the absorption band edge of the films.

### 3.2. Electrochemical properties

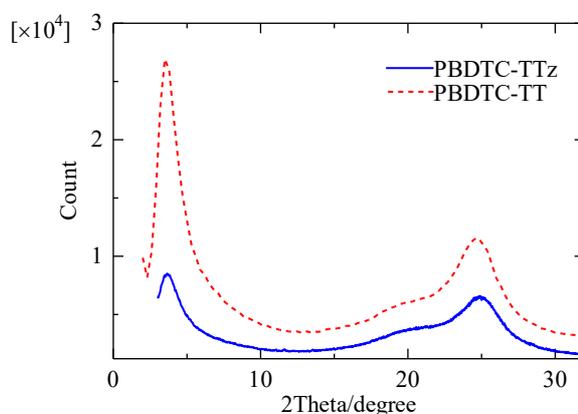
Cyclic voltammogram of **PBDTC-TTz** and **PBDTC-TT** are shown in Figure 3. The  $E_{\text{HOMO}}$  determined by cyclic voltammetry are summarized in Table 1. **PBDTC-TTz** and **PBDTC-TT** exhibited quasi-reversible redox waves. The  $E_{\text{HOMO}}$  of **PBDTC-TTz** estimated from the onset oxidation potential was to be ca. -5.03 eV ( $E_a^{\text{onset}} = 0.66$  V), which was deeper than that of **PBDTC-TT** ( $E_{\text{HOMO}} = -4.88$  eV,  $E_a^{\text{onset}} = 0.51$  V).



**Figure 3.** Cyclic voltammograms of **PBDTC-TTz** and **PBDTC-TT**.

### 3.3. X-ray diffraction analysis

XRD analyses were performed to investigate the structural order of the polymers in the film state. **PBDTC-TTz** showed two diffraction peaks at  $2\theta = 3.64^\circ$  and  $25.1^\circ$  ( $d_1 = 24.3 \text{ \AA}$ ,  $d_2 = 3.55 \text{ \AA}$ ), which are almost the same as those of **PBDTC-TT** ( $d_1 = 24.7 \text{ \AA}$ ,  $d_2 = 3.57 \text{ \AA}$ ) as shown in Figure 4. The former diffractions correspond to the interchain distance between the polymer backbones separated by the side chains, while the latter peaks correspond to the  $\pi$ -stacking distance between the planar polymer backbones. These results indicate that introduction of **TTz** could deepen  $E_{\text{HOMO}}$  of **BDTC** based polymer without increase of the interchain distance and  $\pi$ -stacking distance.



**Figure 4.** X-ray diffraction patterns of the drop cast films of the polymers.

## 4. Conclusions

An alternating D-A type copolymer **PBDTC-TTz** composed of **BDTC** and **TTz** was synthesized and characterized. **PBDTC-TTz** exhibited wider  $E_g$  compared to **PBDTC-TT** due to weaker ICT effect between **BDTC** and **TTz**, but its  $E_g$  was sufficiently narrow to be applicable to OPVs. Incorporation of **TTz** in place of **TT** lowered  $E_{\text{HOMO}}$  of the polymer. The polymer structure of **PBDTC-TTz** evaluated XRD analysis was comparable to that of **PBDTC-TT**. These preliminary studies indicated that  $E_{\text{HOMO}}$  of **BDTC** based polymer could be lowered, which is derived from the weak electron-donating unit with the narrow bandgap nature. Further studies to investigate the effect of the **TTz** unit on the BHJ OPV performance currently are under way.

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