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## Effect of replacing proton with alkoxy side chain for donor acceptor type organic photovoltaics

Kwan Wook Song<sup>a</sup>, Min Hee Choi<sup>a</sup>, Ho Jun Song<sup>a</sup>, Soo Won Heo<sup>a</sup>, Jang Yong Lee<sup>b</sup>, Doo Kyung Moon<sup>a,\*</sup><sup>a</sup> Department of Material Chemistry and Engineering, Konkuk University, Seoul 143-701, Republic of Korea<sup>b</sup> Energy Materials Research Center, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, Republic of Korea

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## ABSTRACT

Poly(quarterthiophene-alt-benzothiadiazole), PQT12oBT and PQT12BT, were synthesized through the Stille coupling reaction. The UV-visible absorption spectrum of PQT12oBT showed peaks at 535 nm; moreover, it exhibited a higher molar absorption coefficient ( $\epsilon=44,000 \text{ M}^{-1} \text{ cm}^{-1}$  at 535 nm) than PQT12BT ( $3300 \text{ M}^{-1} \text{ cm}^{-1}$ ) in chloroform solution. The optical band gap of PQT12oBT was calculated 1.74 eV in solid state. The HOMO and LUMO energy levels of PQT12oBT were  $-5.18$  and  $-3.44$  eV, respectively. From the results of X-ray diffraction measurements, the lamellar d-spacing of PQT12oBT in out-of-plane direction was determined to be 21.6 Å, and the  $\pi$ - $\pi$  stacking distance between layers was found to be 4.09 Å, with a slight edge-on orientation. Bulk heterojunction-type polymer solar cells were fabricated. With a 1:1 ratio of PQT12oBT and PC<sub>71</sub>BM, the values of open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), fill factor (FF), and power conversion efficiency (PCE) were found to be 0.77 V, 8.9 mA  $\text{cm}^{-2}$ , 62.4%, and 4.2%, respectively. In addition, PCE was increased up to 4.4% by the addition of 1-bromonaphthalene (1-BrNT) to the active layer.

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## 1. Introduction

Organic electronic devices such as organic light-emitting diodes (OLEDs) [1–5], organic photovoltaic cells (OPVs) [6–10], and organic thin-film transistors (OTFTs) [11–14] have attracted significant attention owing to their easy manufacturing based on solution processes. As a result, good solubility, oxidative stability, and high charge-carrier mobility represent important properties required in active materials. OPVs have lately been gathering attention as a major research section since the introduction of the advanced molecular engineering technology of  $\pi$ -conjugated polymers. However, the low power conversion efficiency (PCE) of OPVs is a major obstacle. In order to increase the PCE, it is necessary to tune the optoelectronic properties of the photoactive material, i.e., the  $\pi$ -conjugated polymer. Methods of tuning these properties include (1) a lowering of the energy level of the highest occupied molecular orbital (HOMO) to achieve a high open-circuit voltage ( $V_{oc}$ ), (2) decreasing the band gap to extend the absorption region, and (3) increasing the molecular weight [15].

One of the promising  $\pi$ -conjugated polymers in the field of organic solar cells was poly(3-hexylthiophene) (P3HT) because of its beneficial properties such as a high hole mobility ( $0.10 \text{ cm}^2/\text{V s}$ ) [16], enhanced photostability [17], and an improved optical

absorption in the visible region. Recently, solution processable regioregular poly(3,3'-didodecylquaterthiophene) (PQT-12) was reported to have a lower HOMO level ( $\text{HOMO}_{\text{PQT-12}} = -5.24$  eV,  $\text{HOMO}_{\text{P3HT}} = -5.00$  eV), better oxidative stability and faster transistor mobility ( $0.18 \text{ cm}^2/\text{V s}$ ) [18–22] than P3HT. In spite of these merit, the PCEs of PQT-12 and its derivatives were reached up to 3.2% [22–26]. Especially, these polymers like PQT-12 and PBTBT [12] had unsubstituted conjugated moieties as bithiophene and thienothiophene in backbone resulted in much better oxidative stability and hole mobility. These moieties promoted favorable interdigitation of side chains. Because of interdigitation, well-organized intermolecular 3D ordering and large crystalline domains would be available [27].

Because of harvesting visible and near infrared wavelength photons, low band-gap conjugated materials have been interested. To make low band gap materials is the incorporation of strong electron donating and electron accepting moieties along the conjugated backbone. Typical acceptor units are 2,1,3-benzothiazole (BT). Geng et al. reported on the polymers, poly(oligothiophene-alt-benzothiadiazole) (PT<sub>n</sub>BT) ( $n=2-6$ ) which include oligothioephen and BT, with a PCE of 0.93–2.23% [28]. Many studies have focused on increasing the molecular weight and solubility by using DTBT derivatives in which side chains are introduced [29–36].

In this work, we synthesized low band-gap polymer, poly(quarterthiophene-alt-benzothiadiazole) (PQT12oBT), with octyloxy chains in the benzothiadiazole (oBT). Due to the introduction of octyloxy chain, the molecular weight and the solubility of PQT12oBT

\* Corresponding author. Tel.: +82 2 450 3498; fax: +82 2 444 0765.

E-mail address: [dkmoon@konkuk.ac.kr](mailto:dkmoon@konkuk.ac.kr) (D.K. Moon).

were increased rather than those of PQT12BT. A number-average molecular weight of 43 kg/mol and molar absorption coefficient ( $\epsilon = 4.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 535 nm) of PQT12oBT was confirmed.

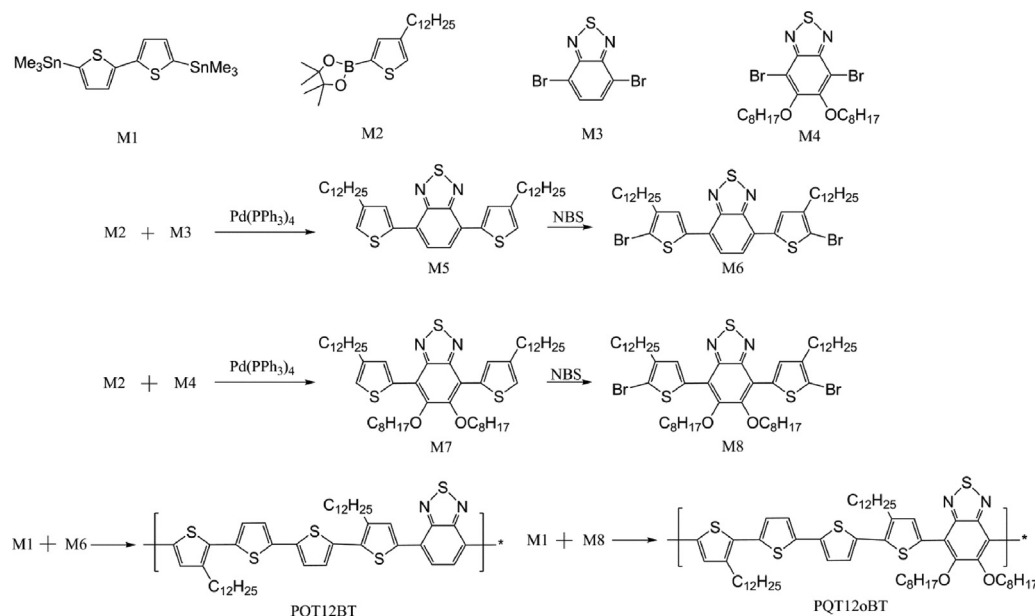
## 2. Results and discussion

Scheme 1 shows the chemical structure and the synthesis process of monomers and polymers. Poly(3,3'-didodecyl-quaterthiophene-5,5'-diyl)-alt-(5,6-octyloxy-2,1,3-benzothiadiazole-4,7-diyl) (PQT12oBT) was polymerized by the Stille coupling reaction using M1 and M8 to introduce octyloxy side chains to BT. Also, poly((3,3'-didodecyl quaterthiophene-5,5'-diyl)-alt-(2,1,3-benzothiadiazole-4,7-diyl)) (PQT12BT) was polymerized by the same method using M1 and M6. PQT12oBT showed a homogeneous phase during polymerization, whereas precipitation occurred after 3 h in case of PQT12BT. The solution was poured into methanol and filtered. The obtained powders were purified using a Soxhlet apparatus with methanol and acetone. Finally, the polymer was recovered from the chloroform soluble fraction and precipitated in methanol. Dark-violet powders were obtained. PQT12oBT showed a high yield (97%), whereas PQT12BT manifested only a low yield (29%). PQT12oBT and PQT12BT could be well dissolved in ordinary organic solvents, such as chlorobenzene and o-dichlorobenzene. The structure of synthesized PQT12oBT has been confirmed by  $^1\text{H}$  NMR (Fig. S1 in the Supporting information).

Gel permeation chromatography (GPC) analysis of the two polymers showed different molecular weight and polydispersity, as listed

in Table 1. PQT12BT was precipitated but PQT12oBT was well-soluble in toluene during polymerization. Thus, the growth of PQT12BT was limited. But, the number of molecular weight of PQT12BT was 43 kg/mol and PQT12oBT showed an unusually high molecular weight distribution (PDI=8.83) with a bimodal distributions due to aggregation. Bo et al. reported that low molecular weight of polymer was probably due to the poor solubility in the organic solvents used in polycondensation and polymer was precipitated from the solvent during the polymerization [33]. Usually, such a weight distribution does not occur in a C–C coupling polymerization reaction between molar equivalents of two divalent monomers [37]. The results of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. S3) revealed that PQT12oBT showed 5% thermal weight loss at 305 °C and a melting temperature of 201 °C [38] corresponding to a high thermal stability.

Fig. 1 shows the UV–visible spectra of the polymers in solution and in normalized films. Maximum absorption peaks (at a corresponding wavelength  $\lambda_{\text{max}}$ ) of PQT12BT and PQT12oBT in  $\text{CHCl}_3$  solution at a concentration of 10  $\mu\text{g}/\text{mL}$  appeared at 548 nm and 535 nm, respectively. The absorption coefficients at the absorption maxima of PQT12BT and PQT12oBT were calculated to  $3.3 \times 10^3$  and  $4.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. In solution, both polymers are red-shifted compared to the UV–visible spectrum of PQT12 ( $\lambda_{\text{max}} \sim 530 \text{ nm}$ ) reported by Sellinger et al. [22]. Due to the introduction of benzothiadiazole derivatives, D–A type polymers were synthesized and the absorption range of polymers was expanded. As shown in Fig. 1(b),  $\lambda_{\text{max}}$  of PQT12BT and PQT12oBT



Scheme 1. Synthesis route to PQT derivatives.

Table 1  
Molecular weight, optical, and electrochemical data for polymers.

	$M_n^a$ [kg/mol]	PDI <sup>a</sup>	UV–visible absorption				Cyclic voltammetry		DFT
			Solution		Film		$E_{\text{onset}}^{\text{ox}}$ (V)/HOMO [eV]	LUMO <sup>c</sup> [eV]	
			$\lambda_{\text{max}}$ [nm]	$\lambda_{\text{max}}$ [nm]	$\lambda_{\text{onset}}$ [nm]	$E_g^{\text{opt}}$ [eV]			
PQT12BT	5.0	1.52	548	577	747	1.66	0.85/–5.11	–3.45	–4.64
PQT12oBT	43.0	8.83	535	581	710	1.74	0.92/–5.18	–3.44	–4.65

<sup>a</sup> Determined by GPC in tetrahydrofuran (THF) using polystyrene standards.

<sup>b</sup> Calculated from the intersection of the tangents at the low energetic side of the absorption spectrum and the baseline.

<sup>c</sup> LUMO = HOMO +  $E_g^{\text{opt}}$ .

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