

Synthesis and Photovoltaic Properties of Dithienyl Benzotriazole Based Poly(phenylene vinylene)s

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ABSTRACT: Two new alternating copolymers based on dithienyl benzotriazole segment and phenylene vinyl unit were synthesized by Heck cross coupling method. The polymers exhibited broad absorption bands (from 300 nm to 752 nm for P1, and from 300 nm to 654 nm for P2) in the UV-visible region with optical bandgap ranging between 1.6 and 1.9 eV and proper electronic energy levels measured by cyclic voltammetry. The photovoltaic properties of the polymers as electron donors with 6,6-phenyl C61-butyric acid methyl ester as the electron acceptor in a bulk heterojunc-

tion structures were reported. Preliminary results showed moderate power conversion efficiency of 0.36% and 0.4%, respectively, under the illumination of AM 1.5, 100 mW/cm² with a device structure of ITO/PEDOT : PSS/polymer : PC₆₀BM (1 : 3)/Ca/Al. Furthermore, the side chain effect on properties has also been investigated. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2534–2542, 2011

Key words: charge transport; conducting polymers; conjugated polymers; UV-vis spectroscopy

INTRODUCTION

In the last few years, significant progress in polymer solar cells (PSCs) has been made.^{1,2} PSCs show many attractions such as low cost, lightweight, flexibility, and easy processability.³ However, the efficiency and stability are needed to be further improved for commercialization. For these reasons, considerable efforts have been devoted to develop new conjugated polymers.^{4–8} Among them, polythiophenes (PTs) and poly(phenylene vinylene)s (PPVs) have shown the good power conversion efficiencies (PCEs).^{9–11} Although promising features have been demonstrated, the absorption spectra of these polymers have poor overlap with the solar emission spectrum with onset at ~ 1.9 and 2 eV, respectively. To overcome this problem, low bandgap materials are engineered to improve the sunlight-harvesting.

Low bandgap polymers can be obtained by the synthesis of copolymers made of alternating electron donating (D) and electron accepting (A) units. Following this synthetic strategy, many low bandgap polymers have been synthesized.^{12–16} Among these polymers, 2,1,3-benzothiadiazole (BT) and 4,7-dithienyl-2,1,3-benzothiadiazole (DTBT) units are widely used acceptors for the synthesis of D-A copolymers. For example, copolymers of DTBT with fluorene,¹⁷ silafluorene,¹⁸ carbazole,¹⁹ dithienylsilole,²⁰ and dithienylpyrrole²¹ were synthesized and applied in PSCs, exhibiting promising PCEs.

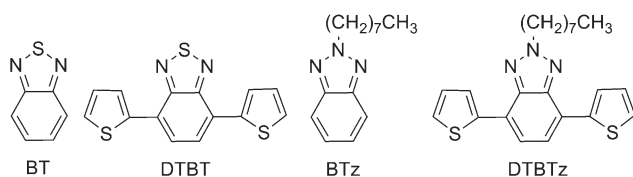
1,2,3-benzotriazole (BTz) is a known heteroaromatic compound similar to 2,1,3-benzothiadiazole with a high electron accepting feature because of two electron withdrawing imine (C=N) nitrogens, furthermore, easy modification of N–H bond of BTz unit can allow us to tune the structural and electronic properties for BTz-containing polymers. However, this attractive unit is missing in the chemical inventory. To the best of our knowledge, only there are few reports about BTz based homopolymers and copolymers, which have been only applied in light emitting or the electrochromic devices. For example, Tanimoto and Yamamoto^{22,23} reported the synthesis and optical properties of BTz-containing homopolymers and copolymers. Cao and coworkers²⁴ applied the copolymers from fluorene and BTz units into the blue light emitting diodes. Gong and coworkers²⁵

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Scheme 1 Chemical structures of the comonomer units.

copolymerized BTz segment with phenothiazine vinylene unit to obtain orange-red light emitting copolymers. Recently, Toppare and coworkers²⁶ copolymerized BTz unit with 3,4-ethylenedioxythiophene segment to construct the D-A polymers which showed enhanced electrochromic properties compared with PEDOT. Almost at the same time, the same group²⁷ obtained the copolymer from BTz unit with thiophene comonomer, which exhibited some interesting and promising electrochromic properties.

On the basis of these informations, our group became interested in the replacement of sulfur atom in the BT unit with nitrogen. Furthermore, we have decided to put thiophene units next to the BTz moiety to minimize the steric hindrance and to lower the band gaps. For the first time, we synthesized 4,7-dibromothiényl-2-alkyl-1,2,3-benzotriazole. To shed light on the potential of this new unit-dithienyl-1,2,3-benzotriazole (DTBTz, shown in Scheme 1) on the properties of the copolymers, combined with different side chains exerting different effects on the optoelectronic performance,²⁸ we synthesized DTBTz containing low bandgap polymers with different side chains by using this new monomer as electron deficient unit copolymerizing with two different electron rich phenyl vinyl (PV) blocks. Herein, we describe the synthesis, optical and electronic properties of the two low bandgap polymers. Moreover, the processable DTBTz-containing polymers have been firstly applied in solar cells, exhibiting moderate photovoltaic performance.

EXPERIMENTAL

Materials

Pd(PPh₃)₄, Pd(AcO)₂, P(*o*-tol)₃, PPh₃, thiophene-2-boronic acid were obtained from Alfa Asia Chemical Co, and they were used as received. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification.

Characterization

¹H-NMR spectra were recorded using a Bruker AM-400 spectrometer, with tetramethylsilane (TMS) as the internal reference, chemical shifts were recorded

in ppm. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene as standard (Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)) using THF (HPLC grade) as eluant at a flow rate of 1.0 mL/min at 35°C. Thermogravimetric analysis (TGA) was conducted on a Shimadzu DTG-60 thermogravimetric analyzer with a heating rate of 10 K/min under a nitrogen atmosphere. The UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. For solid state measurements, polymer solution in chloroform was drop-cast on quartz plates. Optical bandgap was calculated from the onset of the absorption band. The cyclic voltammogram was recorded with a computer controlled Zahner IM6e electrochemical workstation (Germany) using polymer film on platinum disk as the working electrode, platinum wire as the counter electrode, and Ag/Ag⁺ (0.1M) as the reference electrode in an anhydrous and argon-saturated solution of 0.1M of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile.

Fabrication and characterization of polymer solar cell

The PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass positive electrode and a metal negative electrode. Patterned ITO glass with a sheet resistance of 10 Ω/□ was purchased from CSG HOLDING Co., LTD. (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company) for 20 min. Then PEDOT:PSS (poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)) (Baytron P 4083, Germany) was filtered through a 0.45 μm filter and spin coated at 2000 rpm for 60 s on the ITO electrode. Subsequently, the PEDOT:PSS film was baked at 150°C for 15 min in the air to give a thin film with a thickness of 40 nm. A blend of polymer and PCBM (1 : 3 w/w, 10 mg/mL for polymers) was dissolved in *ortho*-dichlorobenzene (ODCB) with heating at 60°C for 2 h, and spin-cast at 3000 rpm for 45 s onto the PEDOT:PSS layer. The substrates were then dried at 70°C for 15 min. The thickness of the photoactive layer is in the range of 50–70 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisted of Ca (~ 20 nm) capped with Al (~ 60 nm) was thermal evaporated under a shadow mask in a base pressure of ~ 10⁻⁵ Pa. The device active area of the PSCs is 3.8–4 mm². Device characterization was carried out under AM 1.5 G

irradiation with the intensity of 100 mW/cm² (Oriol 67005, 500 W) calibrated by a standard silicon cell. *I*-*V* curves were recorded with a Keithley 236 digital source meter.

Synthesis

The synthetic route of the monomers and polymers are shown in Scheme 2. The detailed synthetic procedures were as follows:

2-Octylbenzotriazole (1)^{26,27}

1,2,3-Benzotriazole (5.0 g, 42 mmol), potassium hydroxide (5.6 g, 100 mmol), and 1-bromooctane (9.5 g, 49 mmol) were dissolved in methanol (50 mL). The reaction mixture was refluxed for 24 h and monitored by TLC. After removal of the solvent by evaporation, the residue was dissolved in 200 mL of CHCl₃ and washed with water twice. The organic extraction was dried over anhydrous MgSO₄ and the solvent was evaporated under reduced pressure. Column chromatography on silica gel was performed to obtain 2-octylbenzotriazole as a colorless oil with a 30% yield.

¹H-NMR (400 MHz, CDCl₃, ppm): 7.87 (m, 2H), 7.37 (m, 2H), 4.72 (t, 2H), 2.12 (m, 2H), 1.34–1.22 (m, 10H), 0.86 (t, 3H).

4,7-Dibromo-2-octylbenzotriazole (2)

Compound 1 (2.9 g, 12.6 mmol) and an aqueous HBr solution (5.8 mol/L, 14.4 mL) were added to a flask, and the mixture was stirred for 1 h at 100°C. Bromine (5.5 g, 34.6 mmol) was added drop wise, and the reaction mixture was stirred for 12 h at 135°C. After cooling the mixture to room temperature, an aqueous solution of NaHCO₃ was added and then was extracted with CHCl₃. The organic layer was dried over anhydrous MgSO₄ and the solvent was evaporated under reduced pressure. Compound 2 was obtained as a light yellow oil by column chromatography in a 75% yield.

¹H-NMR (400 MHz, CDCl₃, ppm): 7.43 (s, 2H), 4.78 (t, 2H), 2.15 (m, 2H), 1.40–1.25 (m, 10H), 0.87 (t, 3H).

2-Octyl-4, 7-di (thiophen-2-yl)-2H-benzo[d][1,2,3] triazole (DTBTz) (3)

Compound 2 (3.5 g, 9 mmol) and thiophene-2-boronic acid (3.0 g, 23.4 mmol), and Pd(PPh₃)₄ (208 mg, 0.18 mmol) were dissolved in 80 mL of 1,2-dimethoxyethane, following by the addition of aqueous sodium bicarbonate (Na₂CO₃, 1.0 mol/L, 90 mL). The reaction mixture was vigorously stirred at 90°C for 12 h under a nitrogen atmosphere. After cooling, the reaction solution was extracted with methylene chloride for three

times, the combined organic layers were washed with 1 mol/L of NaOH aqueous solution, dried over anhydrous MgSO₄, and then concentrated under reduced pressure. Further purification was performed using silica gel column chromatography (petroleum ether/EtOAc = 50 : 1 as eluent), yellow-green crystals were obtained. The yield was 82%.

¹H-NMR (400 MHz, CDCl₃, ppm): 8.01 (d, 2H), 7.52 (s, 2H), 7.28 (d, 2H), 7.09 (t, 2H), 4.60 (t, 2H), 2.10 (m, 2H), 1.35–1.17 (m, 10H), 0.80 (t, 3H).

2-Octyl-4, 7-di (5-bromo-thiophen-2-yl)-2H-benzo[d][1, 2, 3]triazole (M1)

Under the darkness, compound 3 (2.37 g, 6 mmol) was dissolved in the mixture of CHCl₃ (60 mL) and HOAc (60 mL), after cooling the mixture to 0°C, NBS (2.35 g, 13.2 mmol) was added in portions. After 12 h, the reaction mixture was extracted with CH₂Cl₂ and washed by water twice, and then combined organic extractions were dried over anhydrous Na₂SO₄. The organic solvent was evaporated. The crude product was purified by recrystallization using dimethyl formide (DMF), yellow crystals were obtained with 75% yield.

¹H-NMR (400 MHz, CDCl₃, ppm): 7.79 (d, 2H), 7.51 (s, 2H), 7.13 (d, 2H), 4.80 (t, 2H), 2.18 (m, 2H), 1.41–1.27 (m, 10H), 0.87 (t, 3H).

¹³C-NMR(100 MHz, CDCl₃, ppm) : 141.69, 141.23, 130.86, 126.93, 122.98, 122.16, 113.16, 59.91, 31.75, 30.03, 29.10, 28.97, 26.58, 22.62, 14.07.

1-Methoxy-4-octoxylbenzene (4a)²⁹

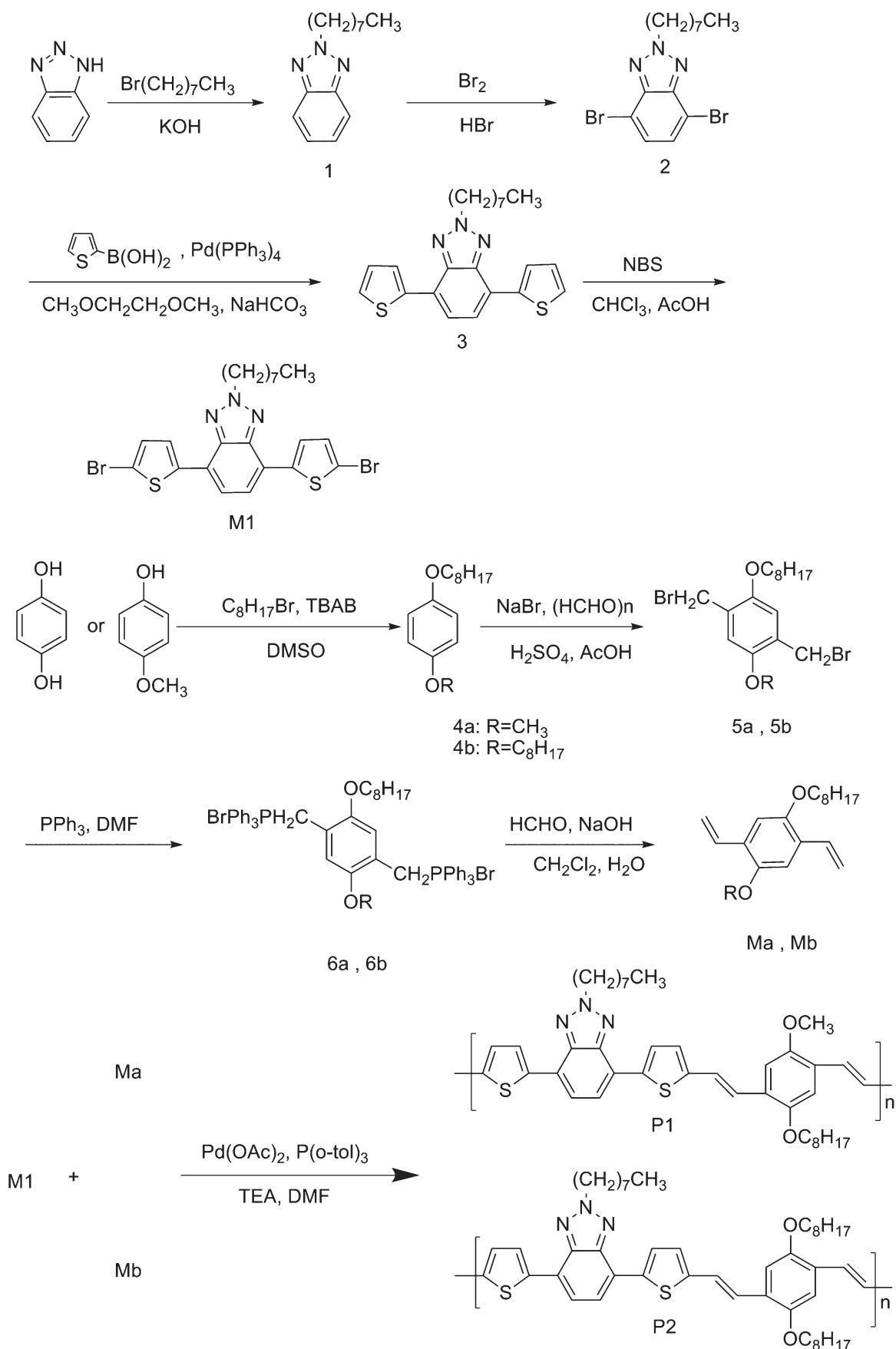
A solution of 4-methoxyphenol (2.48 g, 20 mmol), 1-bromooctane (3.86 g, 20 mmol), and potassium carbonate (3.04 g, 22 mmol) in 60 mL of DMSO was stirred and heated at 140°C under nitrogen overnight. The mixture was then poured into 200 mL of distilled water after being cooled to room temperature. The crude product was washed several times with aqueous sodium carbonate solution (2 mol/L) and extracted by chloroform for three times. The combined organic extractions were evaporated. The residue was then recrystallized from isopropanol. A white flake-like crystal was obtained with 87% yield. mp: 34–35°C.

¹H-NMR (400 MHz, CDCl₃, ppm): 6.71 (m, 4H), 3.80 (t, 2H), 3.62 (s, 3H), 1.76 (m, 2H), 1.42–1.28 (m, 10H), 0.90 (t, 3H).

Anal. Calcd for C₁₅H₂₄O₂: C, 76.23; H, 10.24. Found: C, 76.12; H, 10.25.

1,4-Dioctoxybenzene (4b)

The synthetic procedure for 4b was similar to that for 4a, giving a white flake-like crystal. Yield: 80%.



Scheme 2 Synthetic routes of the monomers and polymers.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 6.76 (s, 4H), 3.93 (t, 4H), 3.8–3.75 (t, 8H), 1.72–1.40 (m, 16H), 0.93 (t, 6H).

Anal. Calcd for $\text{C}_{22}\text{H}_{38}\text{O}_2$: C, 78.89; H, 11.45. Found: C, 78.90; H, 11.47.

1,4-Bis(bromomethyl)-2-methoxy-5-octoxybenzene (5a)

A three-necked flask containing compound **4a** (2.36 g, 10 mmol), paraformaldehyde (1.05 g, 35 mmol), sodium bromide (3.50 g, 34 mmol), and glacial acetic acid (15 mL) was placed in an ice bath. Then sulfuric acid (3.3 mL, 33 mmol) and isochoric glacial acetic acid (50%, V/V) were carefully added into this flask, and the mixture was stirred for 24 h at 60–70°C. The pale yellow solid was precipitated in water and recrystallized from hexane twice to obtain compound **5a** as a white crystal with 78% yield. mp: 82–83°C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 7.00 (s, 2H), 4.72 (s, 4H), 4.06 (t, 2H), 3.84 (s, 3H), 1.80–1.64 (m, 2H), 1.38–1.25 (m, 10H), 0.90 (t, 3H).

Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{Br}_2\text{O}_2$: C, 48.36; H, 6.21. Found: C, 48.40; H, 6.25.

1,4-Bis(bromomethyl)-2,5-octoxylbenzene (5b)

The synthetic procedure for **5b** was similar to that for **5a**, giving a white crystal. Yield: 75%.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 7.01 (s, 2H), 4.61 (s, 4H), 4.06 (t, 4H), 1.86 (m, 4H), 1.55 (m, 4H), 1.36–1.32 (m, 16H), 0.96 (t, 6H).

Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{Br}_2\text{O}_2$: C, 55.39; H, 7.75. Found: C, 55.42; H, 7.79.

2-Methoxy-5-octoxy-1,4-xylene-bis(triphenyl phosphonium bromine) (6a)

The synthetic procedure of **6a** was similar to **6b**, giving a white crystal. Yield: 85%.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 7.57–7.78 (b, 32H), 5.21 (d, 4H), 4.02 (t, 2H), 3.80 (s, 3H), 1.70–1.64 (m, 2H), 1.47–1.21 (m, 10H), 0.89 (t, 3H).

2,5-Dioctoxyl-1,4-xylene-bis(triphenyl phosphonium bromine) (6b)³⁰

A mixture of compound **5b** (2.6 g, 5 mmol), triphenyl phosphine (3.93 g, 15 mmol), and 10 mL of freshly distilled DMF was heated to 95°C, and the reaction proceeded under the temperature while stirring for 24 h. The resulting mixture was poured into diethyl ether. The white solid was filtered and washed with diethyl ether repeatedly to remove the by-products, dried under vacuum to afford a white powder. Yield: 91%, mp >200°C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 7.92–7.69 (m, 30H), 7.11 (s, 2H), 5.41–5.38 (d, 4H), 3.18–3.15 (t, 4H), 2.05 (m, 6H), 1.30–1.11 (m, 18H), 0.85–0.83 (t, 6H).

2-Methoxy-5-octoxy-1,4-divinylbenzene (Ma)

The synthetic procedure of **Ma** was similar to **Mb**. The yield was 58%.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 7.00–7.10 (d, 2H), 6.98 (s, 2H), 5.75–5.71 (d, 2H), 5.26–5.24 (d, 2H), 4.06 (t, 2H), 3.84 (s, 3H), 1.80–1.64 (m, 2H), 1.57–1.31 (m, 10H), 0.90 (t, 3H).

2,5-Dioctyl-1,4-divinylbenzene (Mb)

A mixture of **6b** (1.93 g, 1.85 mmol), 27 mL of methylene chloride, and 7.2 mL of formalin solution was added into 100 mL flask, then 20% sodium hydroxide aqueous solution was slowly dropped into the flask at 0°C for 1 h. The reaction proceeded for 24 h at room temperature. Pouring the reaction mixture into 50 mL of water and then the mixture was extracted by methylene chloride, the organic layer was collected, dried with anhydrous MgSO_4 , and the solvent was removed through rotary evaporator. The crude product was recrystallized twice from 20% ethanol to give 0.71 g of white crystal with 95% Yield. mp: 42–43°C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 7.11 (s, 2H), 5.75–5.71 (d, 4H), 5.26–5.24 (d, 2H), 3.99–3.96 (m, 4H), 1.82–1.76 (m, 4H), 1.57–1.31 (m, 20H), 0.91–0.89 (t, 6H).

Poly[2-methoxy-5-octoxy-1,4-divinylbenzene-co-2-octyl-4,7-dithiophen-2'-yl-2H-benzo[d][1,2,3]triazole] MOPPV-DTBTz (P1)^{31,32}

Under nitrogen, **M1** (277 mg, 0.5 mmol), **Ma** (144 mg, 0.5 mmol), $\text{P}(o\text{-toly})_3$ (37 mg, 0.12 mmol), DMF (6 mL), triethyl amine (TEA) (2 mL) were put into a two-necked flask. After 10 min of flushing with nitrogen, $\text{Pd}(\text{OAc})_2$ (4.5 mg, 0.02 mmol) was added. After being flushed with nitrogen for another 20 min, the mixture was stirred at 90°C for 24 h and then stirred at 110°C for 24 h. After the mixture was cooled to room temperature, CH_3OH (30 mL) was added to the two-necked flask, the dark red precipitate was filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with CH_3OH , hexane, and CHCl_3 . The polymer of MOPPV-DTBTz (**P1**) was recovered from the CHCl_3 fraction by rotary evaporation. The solid was dried under vacuum for 24 h at 60°C, dark red solid was obtained (0.12 g, 34%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 8.20 (br, 2H), 7.62 (br, 4H), 7.50–7.03 (br, 6H), 4.84 (br, 2H), 4.10–3.8 (br, 5H), 1.99–1.05 (m, 24H), 0.86 (br, 6H).

Poly[2,5-dioctyl-1,4-divinylbenzene-co-2-octyl-4,7-dithiophen-2'-yl-2H-benzo[d][1,2,3]triazole] DOPPV-DTBTz (P2)

The synthetic procedure for **P2** was similar to that of **P1**, giving a dark red solid (0.11g, 27% yield).

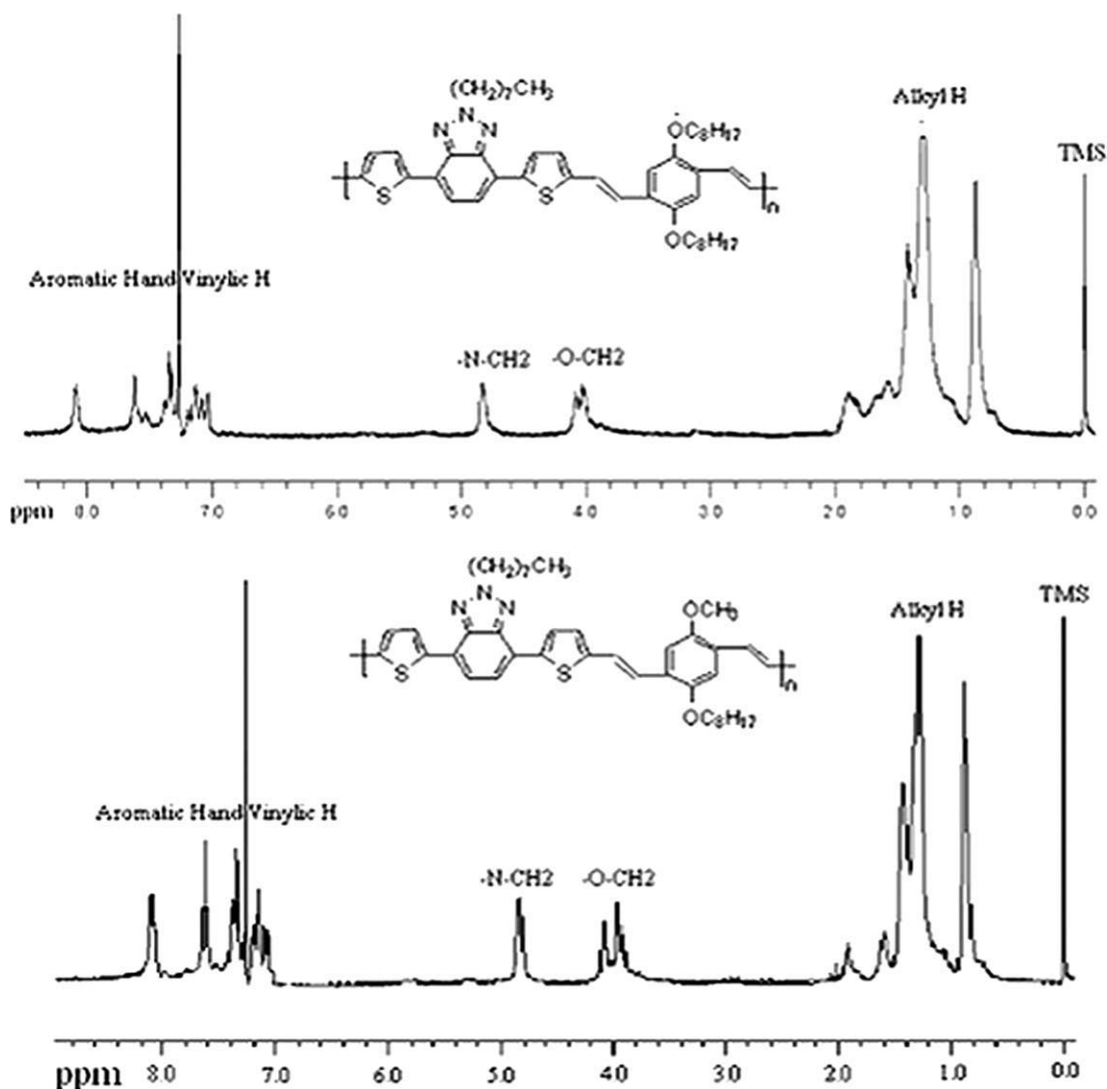


Figure 1 $^1\text{H-NMR}$ spectra of P1 and P2 in CDCl_3 .

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 8.12 (br, 2H), 7.69–7.50 (br, 4H), 7.41–7.0 (br, 6H), 4.84 (br, 2H), 4.10 (br, 4H), 2.0–0.95 (m, 36H), 0.85 (br, 9H).

RESULTS AND DISCUSSION

Synthesis and characterization of the polymers

The comonomer **M1** was synthesized as the following process: Starting from 1,2,3-benzotriazole, an alkylation reaction was performed to get 2-octylbenzotriazole (compound **1**) with a similar yield, in this reaction by using KOH as base instead of *t*-BuOK reported from the literatures.^{26,27} Because of the two possible alkylation sites of the benzotriazole, the desired isomer was isolated in 30% yield in the first step of the reaction sequence. However, this reaction stands as a practical step with relatively cheap starting materials and reagents; hence it can be performed in quite large scales. This step was then fol-

lowed by a dibromination reaction using Br_2/HBr system to yield compound **2** with 75% yield. Compound **2** took a Suzuki coupling reaction with 2-thiophene boronic acid to obtain the compound **3**, this step revealed a quite satisfactory yield. A dibromination step of compound **3** uses NBS as brominating agent to get comonomer (**M1**) in 75% yield. **Ma** and **Mb** were synthesized according to the literature with a little modification. **M1** copolymerized with **Ma** or **Mb** through versatile Heck cross-coupling polymerization to afford the target polymers (**P1** and **P2**), respectively, and the polymers were purified by sequential Soxhlet extraction with methanol, hexane and CHCl_3 . The CHCl_3 fraction was then reduced in volume, precipitated into methanol, and collected by filtration yielding a dark-red solid. The polymers exhibit excellent solubility in common solvents such as THF, CHCl_3 , dichlorobenzene, and so forth.

The $^1\text{H-NMR}$ spectra of the polymers are shown in Figure 1 which shows good agreement with the

TABLE I
Molecular Weight, Polydispersity, and Thermal Properties of Polymers

Polymers	M_n (g/mol)	M_w (g/mol)	PDI ^a	T_d ^b
P1	4600	9398	2.0	378
P2	5282	11,128	1.78	277

^a Polydispersity index.

^b Temperature of 5% weight loss measured by TGA in nitrogen.

polymer structures. The number-average molecular weights (M_n), weight-average molecular weights (M_w), and polydispersity index (PDI) of the copolymers were determined by gel permeation chromatography (GPC) against polystyrene standard using THF as eluant, the data are summarized in Table I, the polymers have low molecular weight, future work we will try different methods to improve that. Thermal stabilities of **P1** and **P2** were investigated with thermogravimetric analysis (TGA), as shown in Figure 2. The TGA analysis reveals that, in nitrogen atmosphere, the 5% weight loss temperatures (T_d) of the **P1** and **P2** are 378 and 277°C, respectively, (Table I), indicating that the stability of the polymer was enough for the fabrication of optoelectronic devices.

Optical properties

The photophysical characteristics of the copolymers were investigated by ultraviolet-visible (UV-vis) absorption spectra in dilute chloroform solutions and in solid films drop-cast on a quartz substrate. Figure 3 depicts the absorption spectra of the polymer solutions and films and the optical data of the polymers are listed in Table II. The absorption peak maxima of **P1** and **P2** films are \sim 549 nm and 500 nm, respectively, (see Fig. 3), which is red-shifted in comparison with those of the polymer solutions (the absorption peaks of **P1** and **P2** solutions are located

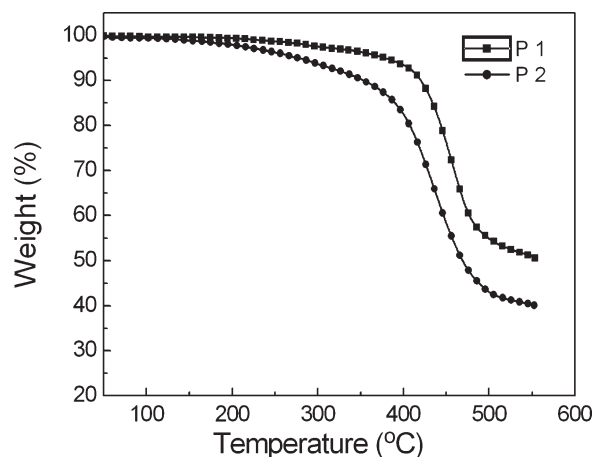


Figure 2 TGA thermograms of **P1** and **P2**.

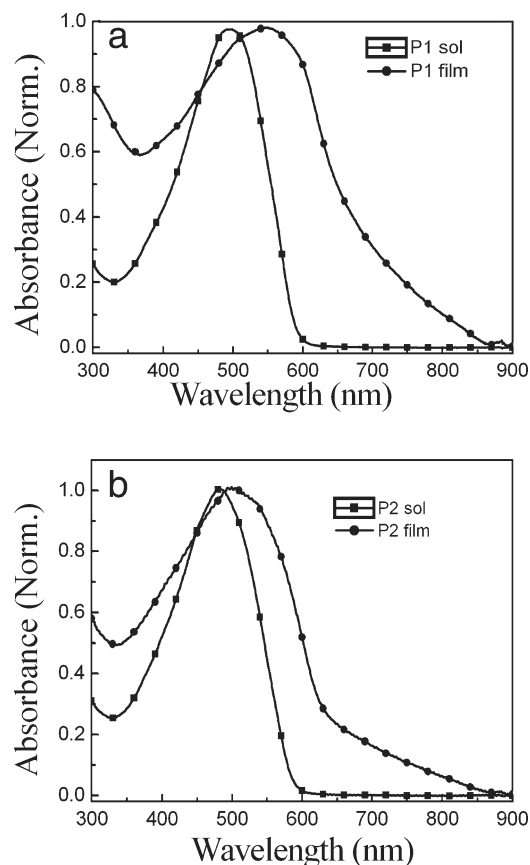


Figure 3 UV-vis absorption spectra of (a) **P1** and (b) **P2** in CHCl_3 and film drop-cast from CHCl_3 solution.

at 493 nm and 482 nm, respectively). This is attributed to a more coplanar configuration formed in solid state. It is worth noting that **P1** exhibits red-shifted absorption and lower optical bandgap than those of **P2**, which indicates that side chains do influence the absorption of the polymers, long side chain hinders the polymer chain closer and has larger steric hindrance than the shorter side chain.³³

Electrochemical properties

To investigate the electrochemical properties of **P1** and **P2** and estimate their HOMO and LUMO energy levels, cyclic voltammetry (CV) was carried out in a 0.1M solution of Bu_4NPF_6 in acetonitrile at room temperature under argon with a scan rate of 50 mV/s.³⁴ All potentials are reported versus Ag/Ag^+ with the ferrocene/ferrocenium couple used as an internal standard. CV curves of **P1** and **P2** are displayed in Figure 4. The related electrochemical data are listed in Table II. **P1** exhibits one reversible oxidation peak while **P2** shows a quasi-reversible oxidation peak, **P1** and **P2** have irreversible reduction peak in the *n*-doping region. In a positive potential region, the onset oxidation potential ($E_{\text{on}}^{\text{ox}}$) is 0.43 V versus Ag/Ag^+ for **P1**. In the negative potential

TABLE II
The Optical and Electrochemical Properties of the Polymers

Polymers	UV-vis-NIR absorption spectra			Cyclic voltammetry(vs Ag/Ag+)				
	Solution ^a		Film ^b	E_g^{optc} (eV)	<i>p</i> -doping		<i>n</i> -doping	
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)		$E_{\text{on}}^{\text{ox}}/\text{HOMO}^{\text{d}}$ (V)/(eV)		$E_{\text{on}}^{\text{red}}/\text{LUMO}^{\text{d}}$ (V)/(eV)	
P1	493	549	752	1.65	0.43/−5.14		−1.18/−3.53	
P2	482	500	657	1.89	0.54/−5.25		−1.26/−3.45	

^a Measured in chloroform solution.

^b Cast from chloroform solution.

^c Bandgap estimated from the onset wavelength of the optical absorption.

^d HOMO = $-e(E_{\text{on}}^{\text{ox}} + 4.71)$ (eV); LUMO = $-e(E_{\text{on}}^{\text{red}} + 4.71)$ (eV).

region, the onset reduction potential ($E_{\text{on}}^{\text{red}}$) is located at -1.18 V versus Ag/Ag⁺ for **P1**. For **P2**, $E_{\text{on}}^{\text{ox}}$ and $E_{\text{on}}^{\text{red}}$ are 0.54 V and -1.26 V, respectively.

From $E_{\text{on}}^{\text{ox}}$ and $E_{\text{on}}^{\text{red}}$ of the polymers, we calculated the HOMO and LUMO energy levels of the polymer according to the equations:³⁵

$$\text{HOMO} = -e(E_{\text{on}}^{\text{ox}} + 4.71)(\text{eV})$$

$$\text{LUMO} = -e(E_{\text{on}}^{\text{red}} + 4.71)(\text{eV})$$

The E_{LUMO} and E_{HOMO} values of **P1** are -3.53 eV and -5.14 eV, respectively, and the corresponding electrochemical bandgap(E_g^{EC}) is 1.61 eV. The E_{LUMO} and E_{HOMO} values of **P2** are -3.45 eV and -5.25 eV, respectively, and the corresponding E_g^{EC} is 1.80 eV. The HOMO for **P2** is lower than that of **P1**, which verified that side chain plays some role in tuning the bandgap and energy level. The electrochemical bandgap of polymers is consistent with the optical bandgap.

Photovoltaic properties

To investigate the potential use of **P1** and **P2** in polymer solar cells, the bulk heterojunction PSCs

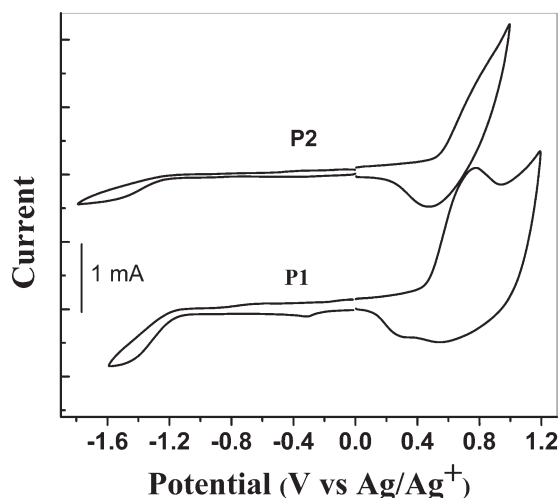


Figure 4 Cyclic voltammograms of **P1** and **P2** films on platinum electrode in 0.1 mol/L Bu_4NPF_6 , CH_3CN solution.

were fabricated with a device structure of ITO/PEDOT:PSS/polymer:PC₆₀BM (1 : 3 w/w)/Ca/Al. PSC device was tested under the illumination of AM 1.5 G, 100 mW cm^{-2} . Figure 5 shows the current density versus voltage (I - V) curves of the devices and the corresponding open-circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF) are listed in Table III.

A PCE of 0.36% and 0.4% is obtained for **P1** and **P2** without annealing. For the similar structures of **P1** and **P2**, **P1** exhibits relatively a little higher I_{sc} , which is probably due to broader absorption and lower bandgap compared with **P2**. However, **P2** has higher V_{oc} (**P2** : 0.6 V) than that of **P1** (V_{oc} : 0.5 V) due to deeper HOMO level of **P2**. Combined with all the factors, **P2** possesses relatively better photovoltaic properties. Based on these primary results, we believe that optimization of the device structures such as donor/acceptor ratio, thickness, annealing, additive, etc., can be expected to increase the PCE of the PSCs.

CONCLUSIONS

In conclusion, dithienyl benzotriazole (DTBTz) unit has been introduced into the polymer backbone.

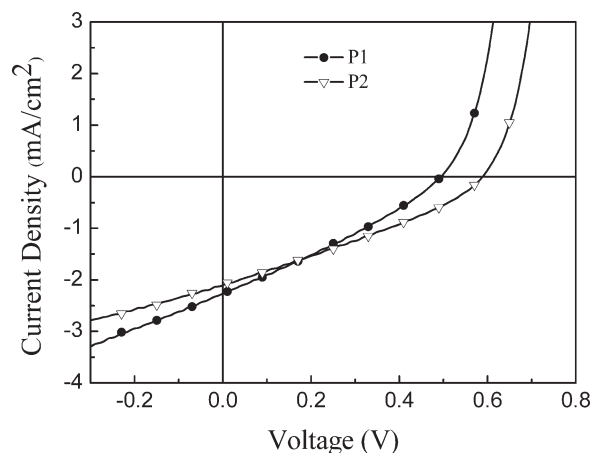


Figure 5 Current-voltage (I - V) curves of the polymer solar cells based on **P1** and **P2** with PC₆₀BM as acceptor.

TABLE III
Photovoltaic Performances of the Polymer Solar Cells
Based on the Copolymers

polymers/ PCBM(1 : 3)	V_{oc} (V)	I_{sc} (mA/cm ²)	FF (%)	PCE (%)
P1	0.5	2.38	30.5	0.36
P2	0.6	2.22	30.6	0.40

Considering the sensitivity of side chain length on properties such as optical property, energy level, device performance, etc., we designed and synthesized two solution processable new D-A copolymers with different side chains by using this unit as the accepting building block and alkoxy phenyl vinylene unit as the donor unit. The polymers were characterized by UV-vis absorption, cyclic voltammetry. The polymers showed broad absorption bands (300–754 nm), low bandgap, and proper electronic energy levels. Furthermore, their photovoltaic properties were investigated using PC₆₀BM as the acceptor. The polymers exhibited moderate photovoltaic properties (0.36% for **P1**, and 0.4% for **P2**). A further improvement in the performance can be expected by increasing the molecular weight of the polymers and optimization of the device. More importantly, the results show that the DTBTz unit can be efficiently utilized to tune the optical and electronic properties of various conjugated polymers and may therefore become an excellent electron accepting building block for the future molecular design for many applications in printed electronics. Detailed investigation on the properties of the two polymers and further synthesis of new DTBTz-containing copolymers are currently in progress and will be reported in due course.

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