New Low Bandgap Conjugated Polymer Derived from 2, 7-Carbazole and 5, 6-Bis(octyloxy)-4, 7-di(thiophen-2-yl) Benzothiadiazole: Synthesis and Photovoltaic Properties

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ABSTRACT: To develop conjugated polymers with low bandgap, deep HOMO level, and good solubility, a new conjugated alternating copolymer **PC-DODTBT** based on *N*-9′-heptadecanyl-2,7-carbazole and 5, 6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole was synthesized by Suzuki cross-coupling polymerization reaction. The polymer reveals excellent solubility and thermal stability with the decomposition temperature (5% weight loss) of 327°C. The HOMO level of **PC-DODTBT** is -5.11 eV, indicating that the polymer has relatively deep HOMO level. The hole mobility of **PC-DODTBT** as deduced from SCLC method was found to be 2.03×10^{-4} cm^2/Versus Polymer solar cells (PSCs) based on the blends of **PC-DODTBT** and [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) with a weight ratio of 1:2.5 were fabricated. Under AM 1.5 (AM, air mass), 100 mW/cm^{-2} illumination, the devices were found to exhibit an open-circuit voltage (V_{oc}) of 0.73 V, short-circuit current density (J_{sc}) of 5.63 mA/cm^{-2}, and a power conversion efficiency (PCE) of 1.44%. This photovoltaic performance indicates that the copolymer is promising for polymer solar cells applications. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 99–107, 2012

Key words: low bandgap; poly(2,7-carbazole); benzothiadiazole; polymer solar cells

INTRODUCTION

Solar cells are very important for solving world energy problem. Among all of solar cells, polymer solar cells (PSCs) are being increasingly attractive from both academic and industrial laboratories due to their ease of processing, large area fabrication, flexibility, and low costs.[1,2] In the past two years, the research of bulk heterojunction (BHJ) polymer solar cells has made great progress,[3–5] but improving the power conversion efficiency (PCE) of the BHJ polymer solar cells is still a big challenge towards commercialization.

To enhance the PCE of PSCs, an effective method is to develop donor polymers with low bandgap and suitable energy level to facilitate the generation, separation, transport, and collection of charge carriers. Up to date, the approach of using the donor-acceptor (D-A) framework is proved to be the most efficient strategy for obtaining low bandgap polymers and for modulating the polymer electronic properties. During the past few years, the 2,1,3-benzothiadiazole(BT) and 4,7-dithienyl-2,1,3-benzothiadiazole (DTBT) units were widely used as electron accepting moieties for the design and synthesis of low bandgap copolymers. A series of low bandgap benzothiadiazole (BT)-based polymers have been reported by Mario Leclerc et al.[6,7] and Yong Cao et al.[8,9] These BT-based conjugated polymers have demonstrated excellent photovoltaic properties. Recently, our group synthesized a planar alternating copolymer-**PBDT-DODTBT** from benzodithiophene (BDT) and 5, 6-bis(octyloxy)-4, 7-di(thiophen-2-yl)benzothiadiazole (**PBDT-DODTBT**), which shows an impressive PCE of 4.02% without annealing and additives.[10] Two octyloxy lateral chains made the polymer highly soluble in common organic solvents, and meanwhile the polymer shows a planar conformation. This indicates that 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole(DODTBT) is a good electron accepting building block for constructing highly soluble polymer photovoltaic materials. Therefore we have tested different electron-donor

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units copolymerized with the DODTBT unit to obtain low bandgap conjugated polymers with good photovoltaic performance.

Poly(2,7-carbazole) derivatives are excellent candidates for BHJ solar cells with the potential PCE up to 10%. In 2009, Bo et al.[11] reported an alternating copolymer-HXS-1 with limited solubility, which shows a promising PCE of 5.4% using 1,8-diiodooctane as the additive. As an electron-donor, 2,7-carbazole is perfect for the development of the D-A polymers. However, poly(2,7-carbazole) derivatives generally were poorly soluble and showed a lack of orderness in morphology.[7]

Therefore, if we could introduce a secondary alkyl side chain on the nitrogen atom of the carbazole unit, the Y-shape long alkyl chain in the carbazole unit could make the polymer highly soluble, even if the polymer has relative high molecular weight. As a result, improved photovoltaic properties could be achieved. On the basis of above rationalization, using DODTBT as an electron-acceptor moiety and 2,7-carbazole as an electron-donor moiety, we synthesized a new low bandgap copolymer with high solubility-poly(*N*-9′-heptadecanyl-2,7-carbazole-*alt*-5, 5-(4′, 7′-di-2-thienyl-5′, 6′-bis(octyloxy)-2, 1, 3-benzothiadiazole) (**PC-DODTBT**). This manuscript describes the synthesis and detailed characterization of this polymer with respect to optical, thermal, electrochemical properties. Photovoltaic devices were fabricated using its blend with $PC_{71}BM$, and the relationship between structure and photovoltaic properties was also investigated and discussed.

EXPERIMENTAL

Materials

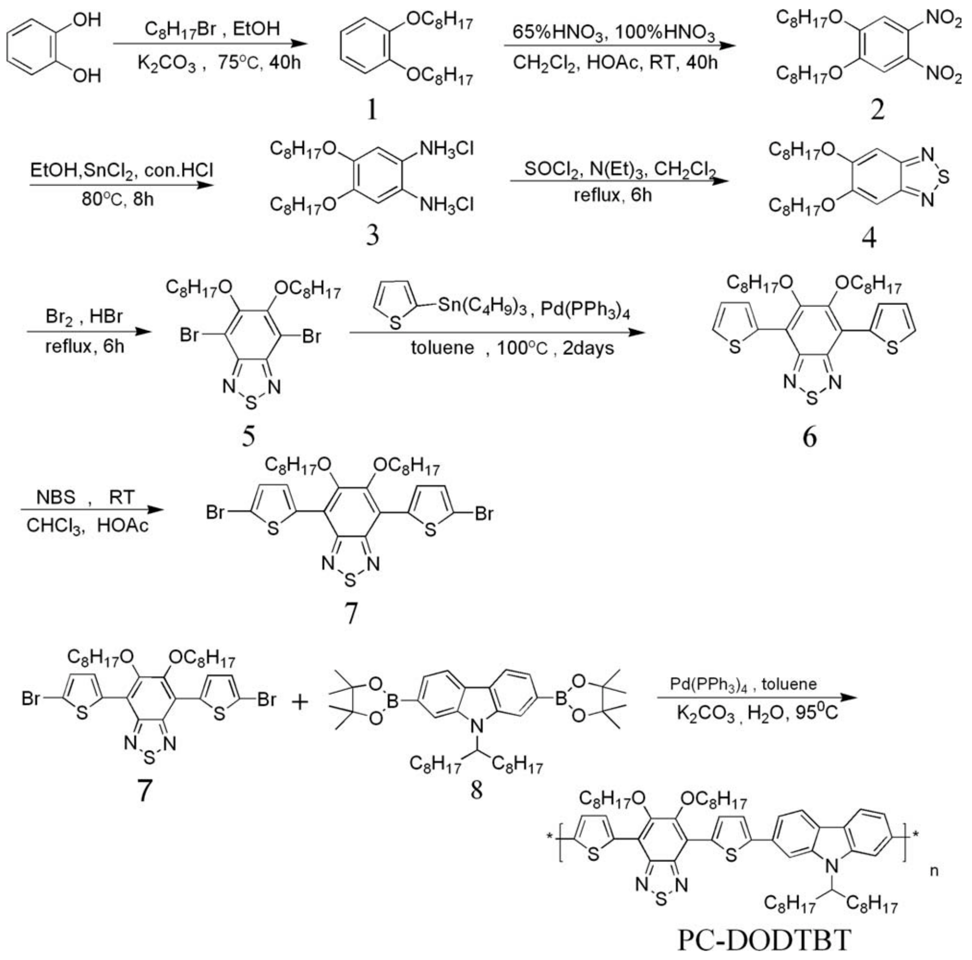
$Pd(PPh_3)_4$, 2-(tributylstannyl)thiophene, catechol were obtained from Alfa Asia Chemical, and they were used as received. Toluene was dried over Na/benzophenone ketyl and freshly distilled prior to use. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification. Column chromatography was carried out on silica gel (size: 200–300 mesh). 2,7-Bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolane-2′-yl)-*N*-9′-heptadecanyl-carbazole(**8**) was prepared according to the literature.[6]

Characterization

^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AV-400 spectrometer in deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane(TMS) standard. Elemental analyses were performed on a Flash EA 1112 analyzer. 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 eluent 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 20°C/min under a nitrogen atmosphere. The temperature of degradation (T_d) corresponds to a 5% weight loss. 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 spectra. X-ray diffraction (XRD) measurements of the polymer thin film were carried out with a 2-kW Rigaku X-ray diffraction system. XRD patterns were obtained using Bragg-Brentano Geometry (θ–2θ) with Cu Kα radiation as an X-ray source in the reflection mode at 45 kV and 300 mA. The cyclic voltammogram was recorded with a Zahner IM6e electrochemical workstation (Germany) using polymer film on platinum disk as the working electrode, platinum wire as the counter electrode and Ag/Ag^+ (0.1*M*) as the reference electrode in a nitrogen-saturated acetonitrile (CH_3CN) solution containing 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6). Hole mobility of the polymer was measured by the space-charge-limited current (SCLC) method with a device structure of ITO/PEDOT:PSS/polymer/Au.

Fabrication of photovoltaic device and testing

The organic photovoltaic cells, with the sandwiched structure of Glass/ITO/PEDOT: PSS/Polymer: $PC_{71}BM$(1: 2.5)/Ca(or LiF or without)/Al, were prepared on commercial (ITO)-coated glass substrate (15 × 15 mm^2) with a sheet resistance of $\leq$10 Ohms/sq (Prazisions Glas and Optic GmbH, Germany). Each substrate was patterned using photolithography techniques before ITO was etched using hydrochloric acid for 20 min and resin was finally removed. Prior to use, the substrates were cleaned with detergent and deionized water. Then, they were ultrasonicated in acetone and in isopropanol for 20 min, respectively. A thin layer of poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS, Baytron P, H. C. Starck) was spin-coated on the ITO glass and dried at 150°C for 15 min in a glove box. The thickness of the PEDOT: PSS layer was ~ 40 nm determined by a surface profilometer (XP-2, USA). Subsequently, the active layer was prepared by spin coating the *o*-dichlorobenzene(ODCB) solution of polymer: $PC_{71}BM$ (1:2.5, w/w)



Scheme 1 Synthesis of comonomers and **PC-DODTBT**.

on the top of the PEDOT: PSS layer. Then the top metal electrode, which is made up of Ca(10 nm) or LiF (0.5nm) and Al (100 nm), was deposited on the active layer by vacuum evaporation ($\approx 5 \times 10^{-5}$ Pa). Solar cells were fabricated with an effective area of 0.12 cm^2. Current versus potential curves (*J-V* characteristics) were measured with a Keithley 2400 Digital Source Meter under acollimated beam. Illumination of the cells was done through the ITO side using light from 150 W Oriel Instruments Solar Simulator and xenon lamp with AM1.5G filter (No. 81094) to provide an intensity of 100 mW/cm^{-2}. All fabrications after cleaning ITO substrates and characterizations were performed in a glove box.

Synthesis

The synthetic routes of the monomers and polymer are shown in Scheme 1. The detailed synthetic processes are shown as follows.

1, 2- dioctyloxybenzene (1)

Bromooctane (10 g, 90.8 mmol) was added to a vigorously stirred solution of catechol (35 g, 181.6 mmol) and potassium hydroxide (10 g) in ethanol (400 mL) under nitrogen. The reaction mixture was stirred under reflux for 40 h and filtered through Celite with copious washings of ethanol. The filtrate was concentrated *in vacuo* and subjected to column chromatography on silica, eluting with 1:1 dichloromethane: light petroleum ether to give the product as a pale yellow oil. Yield: 23.6 g (78%). ^{1}H NMR (CDCl$_3$): δ = 6.88 (s, 4 H), 3.98 (t, 4 H), 1.89-1.26 (m, 24H), 0.90 (t, 6H). ^{13}C NMR (CDCl$_3$): δ = 149.32, 121.04, 114.25, 69.34, 31.92, 29.68, 29.48, 29.36, 26.08, 22.69, 14.10.

1,2-dinitro-4,5-bis(octyloxy)benzene (2)

To a three-necked round-bottom flask containing dichloromethane (140 mL), acetic acid (140 mL), and 1, 2-bisoctyloxybenzene (6.68 g, 20 mmol), with cooling to 10°C, was added dropwisely 65% nitric acid (20 mL). The reaction was allowed to warm to room temperature and stirred for 1 h. The mixture was again cooled to 10°C and 100% nitric acid (50 mL) was added dropwisely. The mixture was allowed to warm to room temperature and the mixture was stirred for 40 h. After the completion of the reaction, the reaction mixture was poured into ice-water, and the dichloromethane layer was separated. The water phase was extracted with dichloromethane. The combined organic phase was washed with water and sat. $NaHCO_3$ (aq), and brine and dried over $MgSO_4$. Concentration under reduced pressure gave the crude product, then the final product was obtained as a yellow solid by recrystallization from ethanol. Yield: 6.7 g (79%). *Mp* = 87-87.5°C. ^{1}H-NMR ($CDCl_3$): δ = 7.30 (s, 2H), 4.12(t, J = 6.5 Hz, 4H), 1.95-1.82 (m, 4H), 1.57-1.18(m, 20H), 0.89 (t, J = 6.6 Hz, 6H). ^{13}C-NMR ($CDCl_3$): δ = 151.80, 136.52, 107.95, 70.21, 31.92, 29.72, 29.48, 29.14, 25.87, 22.69, 14.10.

4, 5-bis(octyloxy)benzene-1,2-diaminium chloride (3)

A mixture of 1,2-dinitro-4,5-bis(octyloxy)benzene[12] (1.43 g, 3.37 mmol) and Sn(II)Cl_2 (26.9 mmol, 5.1 g) in ethanol (50 mL) and conc. HCl (20 mL) was heated to 85°C overnight. After cooled to room temperature, the product was filtered and washed with water and methanol. Finally it was dried at RT under a stream of argon and used directly (unstable). Yield: 1.3 g (88%), off-white solid.

5, 6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (4)

To a mixture of 4, 5-bis(octyloxy)benzene-1,2-diaminium chloride[13] (7.87 g, 18 mmol) and triethylamine (186.4 mmol, 26 mL) in 270 mL dichloromethane, was slowly added a solution of thionyl chloride (123.3 mmol, 9 mL) in 35 mL dichloromethane. After addition, the mixture was heated to reflux for 20 h under argon. The cooled solution was concentrated in vacuum followed by titration with water. After stirring for 30 min, the mixture was filtered and purified on a silica gel column eluting with petroleum ether. Yield: 1.9 g (27%), off-white solid. M_p = 97.1-97.5°C.^{1}H-NMR ($CDCl_3$): δ = 7.14 (s, 2H), 4.10 (t, *J* = 6.5 Hz, 4H), 2.04-1.78 (m, 4H), 1.58-1.15 (m, 20H), 0.95-0.84 (m, 6H). ^{13}C NMR ($CDCl_3$): δ = 154.16, 151.42, 98.45, 69.15, 31.92, 29.71, 29.36, 28.85, 26.02, 22.68, 14.10.

4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5] thiadiazole (5)

To a solution of **4** (3.92 g,10 mmol) in a mixture of dichloromethane (250 mL) and acetic acid (120 mL), was added bromine (3.8 mL, 72 mmol), and the resulting mixture was stirred in the dark for ~ 48 h at room temperature. The mixture was then poured in water (500 mL), extracted with dichloromethane, sequentially washed with water, saturated $NaHCO_3$ (aq), and 1*M* Na_2SO_3 (aq), and the solvents are evaporated under reduced pressure. The crude product was purified on a silica gel column eluting with petroleum ether to give needle-like microcrystals. Yield: 5.06 g (92%). *Mp* = 44.5-45.6°C. ^{1}HNMR ($CDCl_3$): δ = 4.16 (t, *J* = 6.6 Hz, 4H), 1.96-1.82 (m, 4H), 1.62 - 1.46 (m, 4H), 1.46 - 1.20(m, 20H), 0.89 (t, *J* = 6.6 Hz, 6H). ^{13}C-NMR ($CDCl_3$): δ = 154.52, 150.39, 106.24, 75.14, 31.92, 29.73, 29.43, 29.26, 26.00, 22.70, 14.11.

5, 6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[c] [1,2,5]thiadiazole (6)

To a solution of **5** (2.2 g, 4 mmol), $Pd(PPh_3)_4$ (0.51 g, 0.44 mmol) in dry toluene (100 mL) was added 2-(tributylstannyl)thiophene (4.5 g, 12 mmol), and the reaction mixture was heated to reflux for 48 h under argon. The reaction mixture was concentrated directly on celite under reduced pressure. The residue was chromatographically purified on a silica gel column eluting with CH_2Cl_2/hexane (1:10, *v*:*v*) to afford **6** as a yellow oil (2.0 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46-8.45 (d, 2H), 7.52-7.51 (d, 2H), 7.25-7.22 (t, 2H), 4.12-4.10 (t, 4H), 1.95-1.88 (m, 4H), 1.43-1.30 (m, 20H), 0.92-0.90 (t, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.98, 149.05, 132.18, 128.61, 125.34, 124.80, 115.68, 72.42, 29.92, 28.45, 27.63, 27.36, 24.05, 20.75, 14.21. Anal. Calcd. for $C_{30}H_{40}N_2O_2S_3$: C, 64.71; H, 7.24; N, 5.03. Found: C, 62.83; H, 7.18; N, 4.80.

4, 7-Bis(5-bromothiophen-2-yl)-5, 6-bis(octyloxy)benzo-[c][1,2,5]- thiadiazole (7)

A mixture of **6** (2.56 g, 4.6 mmol), *N*-bromosuccimide (NBS) (1.83 g, 10.2 mmol), glacial acetic acid (100 mL) and chloroform (100 mL) was stirred at room temperature in dark for 24 h. The solvent was removed under reduced pressure, the residue was chromatographically purified on silica gel column eluting with CH_2Cl_2/hexane (1:10, *v* : *v*) to afford **7** as an orange crystal (2.56 g, 78%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.38-8.36 (d, 2H), 7.18-7.16 (d, 2H), 4.12-4.09 (t, 4H), 1.97-1.92 (m, 4H), 1.47-1.24 (m, 20 H), 0.91-0.89 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.45, 150.36, 135.67, 130.98, 129.65, 116.96, 115.43, 74.56, 31.82, 30.25, 29.45, 29.39, 25.92, 22.68, 14.17. Anal. Calcd. for $C_{30}H_{38}Br_2N_2O_2S_3$: C, 50.42; H, 5.36; N, 3.92. Found: C, 50.82; H, 5.48; N, 3.91.

Poly(*N*-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-5′,6′-bis(octyloxy)-2,1,3-benzothiadiazole) (**PC-DODTBT**).

A mixture of **7** (92.8 mg,0.13 mmol), 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolane-2-yl)-*N*-9′-heptadecanylcarbazole (**8**) (85.5mg, 0.13 mmol), H_2O (1.6 mL), toluene(7.0 mL) and K_2CO_3(0.43 g, 3.12 mmol) was carefully degassed before and then $Pd(PPh_3)_4$ (8 mg, 6.4 μmol) was added. The polymerization reaction was heated to 95°C, and the mixture was stirred for four days under argon. The mixture

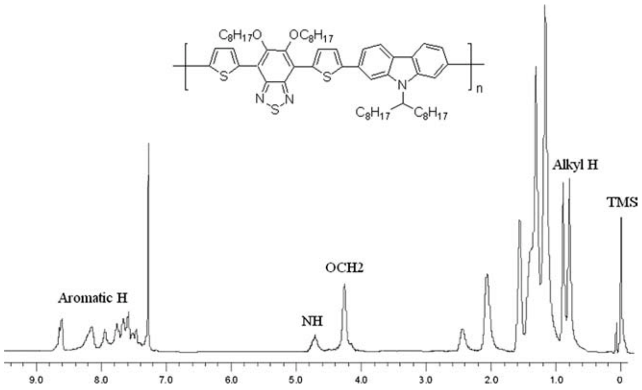


Figure 1 ^{1}H NMR spectrum of **PC-DODTBT** in CDCl$_3$.

was cooled to room temperature and poured slowly in methanol (20 mL), and the resulting precipitate was collected by filtration. The crude polymer was washed with methanol and hexane by a soxhlet apparatus to remove the oligomers and catalyst residue. Finally the polymer was extracted with chloroform. The polymer solution was condensed to ~ 20 mL and slowly poured in methanol (100 mL). The precipitate was collected by filtration and dried under high vacuum to afford **PC-DODTBT** as a black solid (92 mg, 75%).^{1}H-NMR (400 MHz, CDCl$_3$): δ = 8.67-8.60 (d, 2H), 8.16-8.25 (d, 2H), 7.95-7.94 (br, 2H), 7.76-7.74 (br, 2H), 7.62-7.58 (d, 2H), 4.75-4.74 (br, 1H); 4.12-4.09 (t, 4H), 2.43-2.38 (br, 4H), 2.05-1.96(m,4H), 1.23-1.02 (m, 44H), 0.90-0.72 (t, J = 6.8Hz, 12H). GPC (THF): $M_w = 64800$, PDI = 2.58.

RESULTS AND DISCUSSION

Synthesis and characterization of PC-Dodtbt

The general synthetic routes of the monomers and the copolymer are outlined in Scheme 1. Compound **5**[12] and Compound **8**[6] were prepared according to the known literatureprocedures. Compound **5** took a Stille coupling reaction with 2-(tributylstann-yl)thiophene to obtain the compound **6**, this step revealed a quite satisfactory yield. A dibromination step of compound **6** using NBS as the brominating agent to get comonomer **7** in 78% yield. Compound **7** copolymerized with compound **8** through Stille coupling reaction to afford the target polymer-**PC-DODTBT.** The polymer was 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 black solid. The chemical structure of the polymer was verified by ^{1}H-NMR as shown in Figure 1. The copolymer displayed excellent solubility in common solvents such as THF, CHCl$_3$, dichlorobenzene, and so forth. The molecular weight of the polymer was determined by GPC in tetrahydrofuran (*THF*) solution relative to polystyrene standards. The weight average molecular weight (M_w) and number average molecular weight (M_n) are 64800 and 25100, respectively, with a PDI of 2.58.

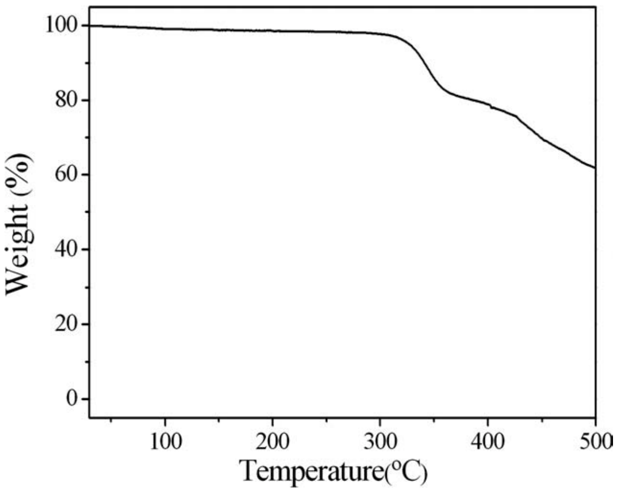


Figure 2 TGA curve of **PC-DODTBT** with a heating rate of 20°C/min.

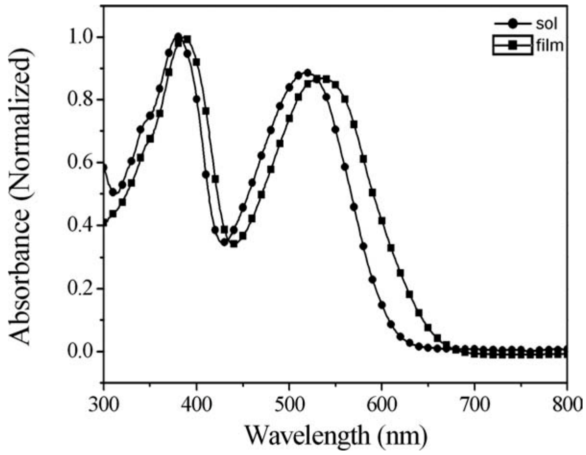


Figure 3 The absorption spectra of **PC-DODTBT** in CHCl$_3$ and in thin film spinning from CHCl$_3$, respectively.

Thermal Stability

Thermal stability of the polymer was investigated using thermogravimetric analysis (TGA) as shown in Figure 2. The TGA thermogram reveals that, the 5% weight loss temperatures (T_d) of **PC-DODTBT** was found to be 327°C under the protection of an inert atmosphere, mainly due to the removal of the alkoxy or alkyl groups. The thermal stability of the polymer is high enough for its application in PSCs and other optoelectronic devices.

Optical properties

The photophysical characteristics of **PC-DODTBT** was investigated by UV-Vis absorption spectra in

TABLE I
The Optical and Electrochemical Properties of PC-DODTBT

	Absorption spectra				Cyclic voltammetry (vs. Ag/Ag$^+$)	
	Solution	Film				
Polymer	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	E_{on}^{ox}/HOMO (V)/(eV)	LUMO (eV)
PC-DODTBT	520	537	682	1.82	0.4/-5.11	-3.29

dilute chloroform solution and in solid film spinning-coated on a quartz substrate. Figure 3 shows the UV-Vis absorption spectra of the polymer solution and the polymer film, respectively. The related optical data are listed in Table I. The polymer shows two absorption peaks both in chloroform solution and in thin film, which are in accordance with other D-A copolymers.[14] The absorption peak at long wavelength is attributed to the intramolecular charge transfer (ICT) transition in the backbone, while the absorption peak at short wavelength is the result of the π-π* transition of carbazole units.[15–19] We noted that the absorption peak of the film is red-shifted 17 nm as compared with that in solution, as a result of the intermolecular interaction in solid state.[20] The optical bandgap of the polymer is 1.82 eV, deduced from the absorption onset of the film at 682 nm.

Electrochemical properties

To investigate the electrochemical properties of **PC-DODTBT** i.e., to estimate its the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, cyclic voltammetry (CV) was carried out in a 0.1*M* solution of Bu_4NPF_6 in CH_3CN at room temperature under argon with a scanning rate of 50 mV/s. All the potentials are reported versus Ag/Ag$^+$ with the ferrocene/ferrocenium couple as an internal standard. CV curve of the polymer is shown in Figure 4. The curve from the negative potential scanning is not observed. The related electrochemical data are listed in Table I.

From the onset oxidation potential (E_{on}^{ox}), we calculated the HOMO level of the polymer according to the equation[21]:

$$E_{\mathrm{HOMO}} = -e(E_{\mathrm{on}}^{\mathrm{ox}} + 4.71)(\mathrm{eV}) \qquad (1)$$

The highest occupied molecular orbital (HOMO, ca. −5.11 eV; $E_{on}^{ox} = 0.4$ V versus Ag/Ag$^+$) and lowest unoccupied molecular orbital (LUMO, ca. −3.29 eV) energy levels calculated from these optical gap measurements are close to the required electronic levels (E_{HOMO} level between 4.9–5.5 eV; E_{LUMO} level between 3.4 and 3.7 eV here assuming SCE −4.4 eV).[22]

Theoretical calculations

The optimal geometries and electronic state wavefunction distribution of HOMO and LUMO of the D-A model compound were obtained at the DFT (B3LYP/6-31G*) level using the Gaussian 03 program suit (Fig. 5). To simplify the calculations, all of the alkyl chains were replaced by $-CH_3$ groups. The

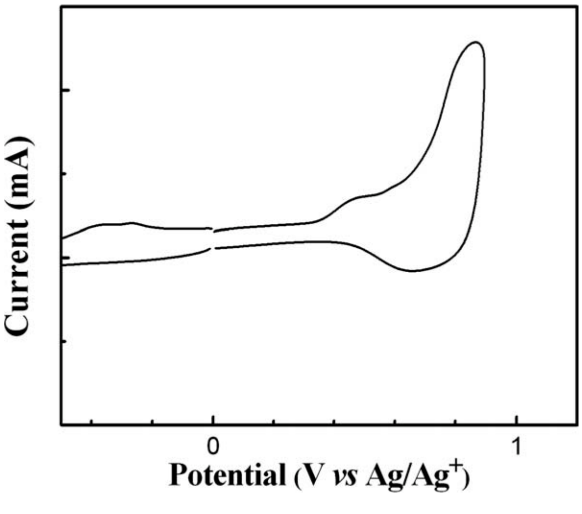


Figure 4 Cyclic voltammogram of **PC-DODTBT** in CH_3CN solution of 0.1 mol Bu_4NPF_6.

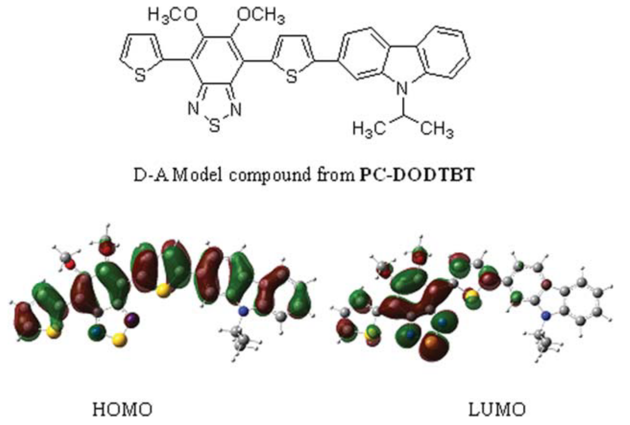


Figure 5 Molecular orbital isosurfaces of HOMO and LUMO of the model compound for **PC-DODTBT**, calculated at the DFT (B3LYP/6-31G*) level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

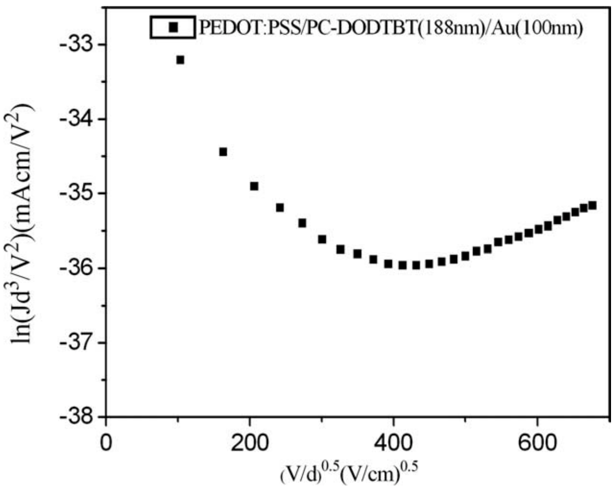


Figure 6 $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ plot of **PC-DODTBT** for the measurement of hole mobility by the SCLC method.

DFT(B3LYP/6-31G*) method has been found to be an accurate method for calculating the optimal geometry and electronic structures of many molecular systems. *Ab intitio* calculations on the model compound for **PC-DODTBT** show that it is a planar molecule, which enables the electrons to be delocalized within the entire molecule due to the π-conjugation. For **PC-DODTBT**, the electronic wavefunction of the HOMO was distributed entirely over the conjugated molecules, which is beneficial for obtaining high hole mobility[23]; however, the electronic wavefunction of LUMO was mainly localized on the DOTBT part. Thus, the incorporation of the DOTBT segment effectively reduces the bandgap due to the low LUMO energy level of the DOTBT unit. From the DFT B3LYP/6-31G* level calculations combined with the formula provided by Leclerc group[7] (here, SCE level is assumed to be −4.4 eV). The HOMO, LUMO engery levels and energy gap of **PC-DODTBT** are −5.12 eV, −3.23 eV, and 1.89 eV, respectively, which are in good agreement with the experimental values. Therefore, the DFT calculations performed here on the repetitive units can indeed provide good estimations of the HOMO, LUMO, and bandgap energy trends, thus allowing a rapid screening of the most promising polymeric structures.

Hole mobility

Hole mobility plays a very important role in the polymer photovoltaic applications. Here, we investigated the hole mobility of **PC-DODTBT** by the space-charge-limited current (SCLC) model with a device structure of ITO/PEDOT: PSS/polymer/Au.[24–26] For the hole-only devices, SCLC is described by

$$J_{\mathrm{SCLC}} = \frac{9}{8}\varepsilon_o\varepsilon_r\mu_o\frac{(V-V_{\mathrm{bi}})^2}{d^3}\exp[0.89\gamma\sqrt{\frac{V-V_{\mathrm{bi}}}{d}}] \quad (2)$$

The result is plotted as ln (Jd^3/V^2) versus $(V/d)^{1/2}$, as shown in Figure 6. Where J is the current density, d is the thickness of the device, and $V = V_{\mathrm{appl}}\text{-}V_{\mathrm{bi}}$ (V_{appl} is the applied potential, and V_{bi} is the built-in potential). According to eq. (2) and Figure 5, the hole mobility is evaluated to be 2.03×10^{-4} $\mathrm{cm}^2/$ Versus Obviously, the hole mobility of **PC-DODTBT** is relatively high as the polymer photovoltaic donor materials in PSCs. The high hole mobility of the polymer is expected to facilitate charge transport and reduce recombination loss in the PSCs, therefore it can lead to an improved device performance.

X-ray analysis

To evaluate the crystallinity of the polymer, X-ray diffraction (XRD) measurements were taken from the spin-coated films on SiO_2 substrate. As shown in Figure 7, XRD pattern of the powdery sample of **PC-DODTBT** exhibits the broad band centered around 28–30°, which indicates the copolymer is an amorphous polymer,

Photovoltaic properties

To explore the photovoltaic properties of **PC-DODTBT**, the bulk heterojunction PSCs using **PC-DODTBT** as the donor and fullerene derivative-$PC_{71}BM$ as the acceptor was fabricated with the structure of ITO/PEDOT: PSS/Polymer: $PC_{71}BM$(1: 2.5, *w*/*w*))/Ca(or LiF or without)/Al. The polymer active layer was spin-coated from a *o*-dichlorobenzene(ODCB) solution and the polymer concentration is 10 mg/mL or 5.0 mg/mL. Furthermore, we selectively added 1,8-diiodooctane(DIO) as the additive. The variations of polymer concentration, the spin-coating speed, the spin-coating time, and the thermal annealing treatment strategies were tested to

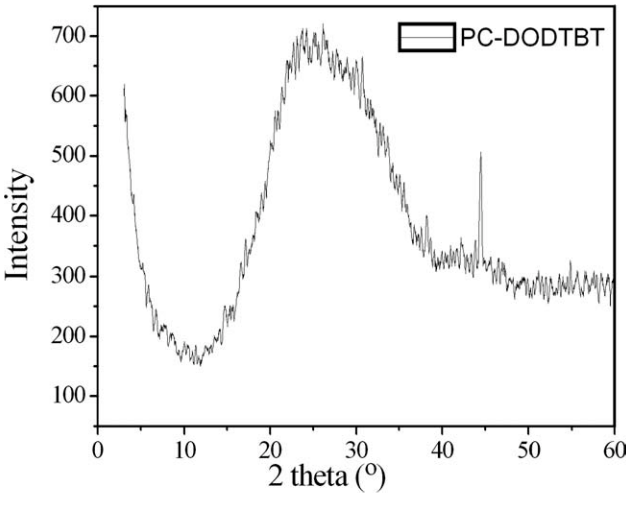


Figure 7 X-ray diffraction pattern of powdery **PC-DODTBT**.

TABLE II
Photovoltaic Performances Based on the PC-DODTBT Using Different Concentration, Cathodes, and Treatments (Under Illumination of AM1.5G at 100 mW/cm^2)

DIO	Conc.	Spin speed	Spin-cast time	Thermal annealing	Cathode		V_{oc}	J_{sc}	PCE	*FF*	Samp-le Name
none	10 mg/mL	800 rmp	2 min	NA	Ca (10 nm)	Al (100 nm)	0.7	−2.14	0.4	26.59	1
							0.69	−2.2	0.41	26.72	2
				110°C (Pre)			0.72	−2.14	0.4	25.86	3
							0.72	−2.23	0.42	25.99	4
		1200 rmp		NA			0.72	−3.53	0.72	28.25	5
				110°C (Pre)			0.73	−3.41	0.7	27.9	6
							0.74	−3.28	0.67	27.7	7
		2000 rmp		NA			0.71	−4.48	1.01	31.78	8
				110°C (Pre)			0.75	−4.44	1.05	31.81	9
2.5 wt %	5 mg/mL	600 rpm	3 min	NA	LiF (0.5 nm)	Al (100 nm)	0.76	−4.37	1.1	33.28	10
							0.72	−4.3	1.05	33.53	11
					Al (100 nm)	0.65	−3.45	0.67	29.94	12	
				150°C (Post)		0.56	−2.93	0.52	32.07	13	
				150°C (Pre)		0.62	−3.83	0.66	27.81	14	
				110°C (Pre)	LiF (0.5 nm)	Al (100 nm)	0.7	−5.62	1.29	32.47	15
		800 rpm		NA			0.71	−4.52	1.17	36.16	16
				0.71			−4.57	1.19	36.31	17	
		110°C (Pre)		0.72			−5.63	1.44	35.58	18	
None		600 rpm		NA			0.63	−5.23	1.05	31.7	19
							0.64	−4.57	0.95	32.44	20
				110°C (Pre)			0.75	−5.24	1.33	33.8	21

NA, none thermal annealing; pre, 10 min preannealing; post, 10 min Postannealing.

optimize the performance of the devices. Under different conditions, the corresponding V_{oc}, J_{sc}, *FF*, and PCE of the devices are summarized in Table II.

From the results of Samples 1–9, we easily found that the thickness of the active layer closely is related to the PCE, which was investigated by controlling the spin speed during the spin-coating process. With the increasing of the spin speed, J_{sc} and *FF* increased significantly, while V_{oc} remained more or less the same. In addition, the PSCs using Al as the cathode showed poorer photovoltaic performance, compared to that using Ca (or LiF) and Al as bilayer cathode. The results of Samples 10–11 and 16–17 showed that the interface between the cathode and the photosensitive layer formed a better ohmic contact after inserted a thin layer of LiF (about 0.5 nm). So the devices based on LiF/Al cathode improved *FF* and V_{oc}, which resulted in the enhancement of PCE. Meanwhile, compared with the results of Samples 10–11 and 19–20, addition of DIO (2.5 wt %) had no apparent effect on the photovoltaic performance. On the basis of the polymer concentration of 10 mg/mL, the PCE did not show improvement by thermal annealing treatment. On the other hand, a 110°C and10 min preannealing treatment optimized the performance of the devices when the polymer concentration is reduced to 5 mg/mL. This phenomenon indicated that the polymer concentration and the thermal annealing treatment played important role in photovoltaic performance of the PSCs.

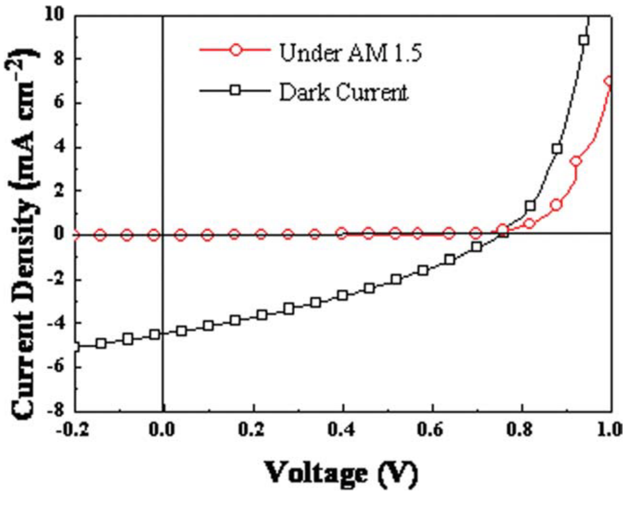


Figure 8 *J-V* curves of the PSCs based on **PC-DODTBT**: PC$_{71}$BM (1:2.5, *w/w*), 1,8-diiodooctane (DIO) concentration in ODCB (2.5%), the polymer concentration (5.0 mg/mL), spin-casting speed (800 rpm), spin-casting time (3 min), and LiF (0.5 nm) and Al (100 nm) as the bilayer cathode, 10 min Preannealing under the illumination of AM 1.5, 100 mW/cm^2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Among the data, the device based on 1,8-diiodooctane (DIO) concentration in ODCB (2.5%), with polymer concentration (5.0 mg/mL), spin-casting speed (800 rpm), spin-casting time (3 min), 10 min preannealing, LiF (0.5 nm) layer, and Al (100 nm) cathode, exhibited the best photovoltaic performance: a PCE of 1.44% with V_{oc} = 0.72 V, an J_{sc} of 5.63 mA/cm^2, and a *FF* of 36%. Figure 8 shows a typical current density-voltage (*J-V*) curve of the polymer solar cells. V_{oc} is found to be 0.72 V, smaller than that of its DTBT analog (**PCDTBT**, E_{HOMO} = -5.50 eV, V_{oc} = 0.89 V, **HXS-1**, $E_{\mathrm{HOMO}} = -5.21$ eV, V_{oc} = 0.81 V).[6,11] The lower V_{oc} in our **PC-DODTBT** devices is probably due to its higher HOMO energy level, since V_{oc} is directly correlated to the difference between the LUMO of the acceptor and the HOMO of the donor. A relatively high current density (J_{sc} = 5.63 mA/cm^{-2}) is related to the strong light absorption and high hole mobility of the polymer. Unexpectedly, the *FF* is not high, indicating that balanced charge transport and the good surface morphology of the active layer were not obtained in this kind of polymer solar cells. Therefore, optimization of PSCs based on **PC-DODTBT** is underway and it is expected that PCE can be further improved under optimized fabrication conditions (such as the blend ratio, film morphology, thickness of active layer, electrode buffer layer, etc.).

CONCLUSIONS

In summary, we have synthesized a new D-A conjugated polymer **PC-DODTBT** containing the donor unit of *N*-9′-heptadecanyl-2,7-carbazole and the acceptor unit of 5, 6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole, by Suzuki cross-coupling polymerization reaction. The polymer combines good thermal stability, high solubility, a broad and strong absorption in the visible region, and air-stability. The hole mobility of **PC-DODTBT** as deduced from the SCLC method was 2.03×10^{-4} cm^2/Versus Studies on photovoltaic cells using the blend of **PC-DODTBT** and PC$_{71}$BM (1:2.5, *w*/*w*, 2.5% DIO) as active layer afforded the best photovoltaic performance with V_{oc} = 0.73 V, J_{sc} = 5.63 mA/cm^{-2}, and a PCE = 1.44%. Optimization of PSCs and synthesis of high purity **PC-DODTBT** with high molecule weight are on the way, we strongly believed that a higher PCE can be anticipated by proper device engineering such as using different blend ratio, additive and thermal annealing treatment.

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