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Synthesis and photovoltaic properties of low-bandgap polymers based on *N*-arylcarbazole

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ABSTRACT

Low-bandgap poly(2,7-carbazole) derivatives with variable *N*-substituent of ethyl (**PEtCzBT**), phenyl (**PPhCzBT**) and 4-diphenylaminophenyl (**PTPACzBT**) on the carbazoles, were synthesized through Suzuki coupling reaction. The polymers show excellent solubility in organic solvents (readily soluble in chloroform, THF and toluene etc.), good thermal stability (5% weight loss temperature of more than 417 °C), and electrochemical properties (reversible redox process with narrow bandgap), and deep HOMO energy levels (~5.1 eV), allowing them promising candidates in the solar cell fabrication. Bulk-heterojunction solar cells with these polymers as electron donor and (6,6)-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as electron acceptor exhibit high V_{oc} (0.91–0.95 V) and good power conversion efficiency (PCE) of 1.69% for **PEtCzTB**, 2.01% for **PPhCzTB,** and 2.42% for **PTPACzTB**.

1. Introduction

Polymer solar cells (PSCs) have been attracting considerable attention in recent years due to their unique features of low cost, light weight, and potential application in flexible large-area devices [1–3]. The most common device structure for efficient PSCs is based on the bulk-heterojunction (BHJ) concept which involves a thin film blend of conjugated polymer as the electron donor and a fullerene derivative as the electron acceptor. In order to obtain high-performance PSCs, it is necessary to design and synthesize conjugated polymers with desired properties, such as low-bandgap (LBG), broad absorption range, high carrier mobility, and appropriate molecular energy levels [4]. In the past decade, LBG conjugated polymers have been developed and used in PSCs, and high power conversion efficiencies of over 6% have been achieved due to their absorption often correspond to the maximum photon flux of sunlight spectrum [5]. However, LBG polymers often show better absorption at a long-wavelength range, while other parts of sunlight spectrum are being sacrificed. Meanwhile, the donor-acceptor systems in the LBG polymers cause partial intramolecular charge transfer (ICT) that enables manipulation of the electronic structure (HOMO/LUMO levels) and benefits for charge-separation, but the transport capabilities will be compromised due to the space charge limitation [6]. Therefore, development of new LBG polymers with broad and intense absorption and excellent charge transport is still required.

Poly(2,7-carbazole) derivatives, as a type of LBG photoactive donor materials by incorporation of electron-withdrawing group in the main chain, have been well studied by Leclerc [7], Bo [8], and Hashimoto [9] et al., and exhibited great promise when used with PCBM in bulk-heterojunction photovoltaic cells. In a most recent publication, excellent power conversion efficiency of 6.1% has been reported by Heeger, Leclerc and co-workers [10]. In our research, we presented a highly crystalline alternative copolymer of indolocarbazole and benzothiadiazole-cored oligothiophenes with a good power conversion efficiency of 3.6% [11]. We also developed new random copolymers of tertiary benzothiadiazole-cored oligothiophene, 2,2′-bithiophene and 2,7-dibromocarbazole, which provides us an opportunity to fine tune the optoelectronic properties of the molecular system and thus, a broad and strong absorption spectrum was achieved from a single polymer chain [12]. Almost all the work including just mentioned is based on poly(*N*-alkyl-2,7-carbazole)s. Examples of poly(*N*-aryl-2,7-carbazole)s in the application to PSCs were scarce [13], although they were frequently used as light-emitting and hole-transporting materials in organic light-emitting diodes [14]. In this study, we wish to explore the photovoltaic performance of LBG polymers based on *N*-aryl-2,7-carbazole. It was known that carbazole-based polymers

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generally exhibit deep-HOMO energy level [15], so high open-circuit voltage is expected. Thus, polymer incorporating benzothiadiazole-centered quarterthiophene and *N*-phenyl-2,7-carbazole was designed and synthesized. Furthermore, a 4-diphenylaminophenyl group was introduced to the *N*-atom of the carbazole moiety for further improving the hole-transporting ability of the resulting polymer to compensate the influence of space charge limitation in the polymer main chain [16]. Additionally, a poly(*N*-ethyl-carbazole) was also synthesized. The molecular structures of the three copolymers were shown in Scheme 1. The thiophene segments in the backbone of the copolymers may help to tune the absorption spectrum by elongation of the π conjugation and the alkyl chain on the thiophene rings would ensure good solubility.

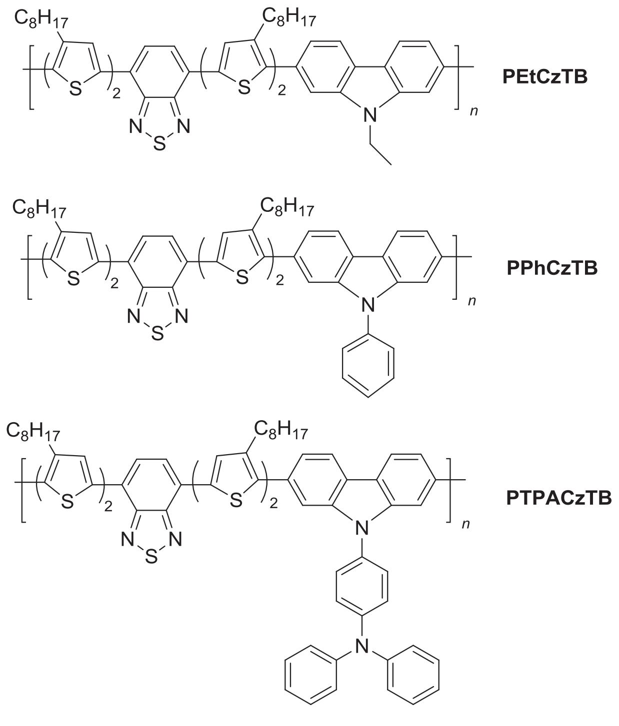
2. Experimental section

2.1. Materials

4,7-dibromo-2,1,3-benzothiadiazole [17], 2,7-dibromocarbazole (**1**) [18], 2,7-dibromo-9*H*-(ethyl)-9*H*-carbazole (**2**) [19],2,7-dibromo-9-(4-nitrophenyl)-9*H*-carbazole (**3**) [20], 4-(2,7-dibromo-carbazol-9-yl)phenylamine (**4**) [21], 2,7-dibromo-9-(4-phenyl)-9 *H*-carbazole (**5**) [20] and *N*-(4-(2,7-dibromo-9*H*-carbazol-9-yl) phenyl)-*N*-phenylbenzenamine (**6**) [22] were prepared according to the reported methods. All reagents and solvents were purchased from JK chemicals and Alfa Chemicals. Anhydrous tetrahydrofuran was distilled over sodium/benzophenone under Ar prior to use.

2.2. Measurement and characterization

NMR spectra were recorded on a Varian 500 or Bruker 400 spectrometer using tetramethylsilane as internal references. Number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters 410 instrument equipped with Waters HT4 and HT3 column assembly using polystyrene as standards and THF as eluent. UV–vis spectra were measured using a PerkinElmer Lambda 900 UV-vis-NIR Spectrometer. Thermal properties of the polymers were analyzed with a Perkin-Elmer-TGA 7 instrument under nitrogen at a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was carried out using TA instruments TGA Q500 in air. Cyclic voltammetry experiments were carried out on an EG&G Princeton Applied Research potentiostat/galvanostat (model 2273) in an electrolyte solution of 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) in acetonitrile at 50 mV s^{-1}. A three-electrode cell was used in all experiments, wherein platinum wires act as the working and counter electrode and Ag/AgCl electrode as the reference. The reference electrode was calibrated with an internal standard of ferrocene. Polymer thin films were formed by drop-casting 1.0 mm^3 of polymer solutions in chlorobenzene (1 mg/mL) on the working electrode and were then dried in air.



Scheme 1. *N*-arylcarbazole-based low-bandgap deep HOMO polymers reported in this work.

2.3. Photovoltaic device fabrication and testing

Glass slides patterned with ITO (Colorado Concept Coatings LLC) were cleaned by sonicating sequentially in detergent, water, 1,1,1-trichloroethane, acetone, and methanol, followed by treatment in a low power air plasma for 15 min with a Harrick PDC-32G plasma sterilizer. Thereafter, the ITO-coated slides were spin-coated (500 rpm for 5 s, then 4000 rpm for 60 s) with a filtered (0.45 μm NYL w/GMF syringe filter) aqueous solution of poly(ethylene dioxythiophene) doped with polystyrene sulphonic acid, PEDOT:PSS (Baytron P, H.C. Starck) and then transferred to a dry box. The resulting thin PEDOT:PSS layer (~35 nm) was dried in an oven under a mild N_2 purge at 120 °C for 1 h. A chlorobenzene solution of polymer and $PC_{71}BM$ with different weight ratio of 1:1 and 1:3 for each cell was stirred at 50 °C for 16 h and then spun-cast on the PEDOT:PSS-coated slides for 90 s. LiF/Al cathode was deposited at a vacuum level of 4×10^{-4} Pa. The thicknesses of the LiF and Al layers are 1 and 100 nm, respectively. The effective area of the unit cell is 12 mm^2. The thickness of organic layer is determined by DEKTAK 6M Stylus profiler. Preliminary testing of each of the ten pixels was performed to select the most promising pixel prior to full solar simulated analysis. The best performing pixel then underwent V_{oc}, I_{sc}, dark and illuminated *I*–*V* studies using an Oriel 300 W solar simulator with appropriate filters to provide AM 1.5G (100 mW/cm^2). The fill-factor (*FF*) was determined from the illuminated *I*–*V* and is the maximum power delivered divided by the product of V_{oc} and I_{sc}. The EQE was measured at a chopping frequency of 280 Hz with a lock-in amplifier (Stanford, SR830) during illumination with the mono-chromatic light from a Xenon lamp. Current–voltage (*I*–*V*) characteristics were recorded using a computer-controlled Keithley 236 source meter in the dark and under white light (CHF-XM 500W Xenon lamp) illumination.

2.3.1. Monomer and polymer syntheses

The dibromonated monomer **M1** was synthesized from 2,1,3-benzothiadiazole via a divergent method according to our recent publication [23]. 2,7-Di(1,3,2-dioxaborinan-2-yl)-9-ethyl-9*H*-carbazole (**M2**) was prepared according to the reported method [24].

2,7-di(1,3,2-dioxaborinan-2-yl)-9-phenyl-9H-carbazole (***M3***) [24]. To a solution of **5** (4.02 g, 10 mmol) in THF (50 mL) at −78 °C was added dropwise 2.5 M *n*-BuLi in hexane (8.4 mL, 21 mmol) over 15 min. The resulting mixture was stirred for 1 h while maintaining the temperature at −78 °C, after which trimethylborate (4.36 g, 42 mmol) was added and the mixture was stirred at −78 °C for an additional hour. The reaction mixture was then allowed to warm to room temperature and stirred for 15 h. The mixture was then cooled to 0 °C and 2 mol/L HCl (40 mL) added. After the mixture was stirred for 30 min, the organic layer was separated using ether, washed with brine three times, and finally dried over $MgSO_4$. After filtration and evaporation of the solvents, a light yellow viscous liquid was obtained. Dissolving this liquid in THF followed by precipitation to hexane gave a white solid. The solid was filtered, washed with hexane three times, and dried briefly (30 min) under vacuum at room temperature. The resulting compound, 9-phenyl-9*H*-carbazole-2,7-diyldiboronic acid, was mixed with toluene (100 mL) and 1,3-propylene glycol (2.28 g, 30 mmol). The mixture was heated to reflux for 3 h; meanwhile, the water produced was removed using a Dean–Stark trap. The mixture was cooled and the solvent was removed. The residue was purified by column chromatography (ethyl acetate/petroleum ether, 1/30, v/v) on silica gel. Recrystallization from hexane gave the product as colorless crystals. Yield: 3.08 g (75%). ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 8.13 (d, 2H, J = 8.0 Hz), 7.81(s, 2H), 7.69 (d, 2H, J = 8.0 Hz), 7.60 (m, 4H), 7.46(d, 1H, J = 7.0 Hz), 4.17 (t, 8H, J = 5.5 Hz), 2.06 (m, 4H). Anal. Calcd. (%): C, 70.12; H, 5.64; N, 3.41. Found (%): C, 70.33; H, 5.66; N, 3.45. MS (*m*/*z*): calcd. for $C_{24}H_{23}B_2NO_4$, 411.07; found, 412.31.

N-(4-(2,7-di(1,3,2-dioxaborinan-2-yl)-9H-carbazol-9-yl)phenyl)-N-phenylbenzenamine (***M4***) [25]. To a solution of **6** (5.68 g, 10 mmol) in THF (50 mL) at −78 °C was added dropwise 2.5 M *n*-BuLi in hexane (8.4 mL, 21 mmol) over 15 min. The resulting mixture was stirred for 1 h while maintaining the temperature at −78 °C, after which trimethylborate (4.36 g, 42 mmol) was added and the mixture was stirred at −78 °C for an additional hour. The reaction mixture was then allowed to warm to room temperature and stirred for 15 h. The mixture was then cooled to 0 °C and 2 mol/L HCl (40 mL) added. After the mixture was stirred for 30 min, the organic layer was separated using ether, washed with brine three times, and finally dried over $MgSO_4$. After filtration and evaporation of the solvents, a light yellow viscous liquid was obtained. Dissolving this liquid in THF followed by precipitation to hexane gave a white solid. The solid was filtered, washed with hexane three times, and dried briefly (30 min) under vacuum at room temperature. The resulting compound, 9-(4-(diphenylamino)phenyl)-9*H*-carbazole-2,7-diyldiboronic acid, was mixed with toluene (100 mL) and 1,3-propylene glycol (2.28 g, 30 mmol). The mixture was heated to reflux for 3 h; meanwhile, the water produced was removed using a Dean–Stark trap. The mixture was cooled and the solvent was removed. The residue was purified by column chromatography (ethyl acetate/petroleum ether, 1/30, v/v) on silica gel. Recrystallization from hexane gave the product as colorless crystals. Yield: 4.34 g (75%). ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 8.12 (d, 2H, J = 7.5 Hz), 7.84 (s, 2H), 7.69 (d, 2H, J = 8.0 Hz), 7.39 (d, 2H, J = 8.5 Hz), 7.32 (m, 4H), 7.25 (d, 2H, J = 7.0 Hz), 7.08 (d, 1H, J = 7.0 Hz), 4.19 (t, 8H, J = 5.0 Hz), 2.05 (m, 4H). Anal. Calcd. (%): C, 74.77; H, 5.58; N, 4.84. Found (%): C, 74.98; H, 5.59; N, 4.86. MS (*m*/*z*): calcd. for $C_{36}H_{32}B_2N_2O_4$, 578.25; found, 579.11.

2.3.2. *General procedure for the preparation of the polymers [7b,25]*

To a 50 mL one-necked flask was added tricaprylylmethylammonium chloride (Aliquat 336) (20 wt% based on monomers), the appropriate diboronate (0.4 mmol), the appropriate dibromide (0.4 mmol), and toluene. Once all the monomers were dissolved, 2 M Na_2CO_3 (1.32 mmol) aqueous solution 0.66 mL was added. The flask equipped with a condenser was then evacuated and filled with argon three times to remove traces of air. $Pd(PPh_4)_3$ (0.002 mmol) was then added under an argon atmosphere. The flask was again evacuated and filled with argon three times. The mixture was then heated to reflux and maintained for 72 h under argon. The reaction mixture was then cooled to room temperature and the organic layer was separated, concentrated, and precipitated into methanol. The polymer was purified by precipitation in methanol/water (10:1), filtered through 0.45 μm nylon filter and washed on Soxhlet apparatus with acetone and hexanes. The resultant polymer was collected, dried, and further purified by passing through a short silica gel column to remove the catalyst residues. The resulting copolymer solution was collected, concentrated, and precipitated into methanol. The black solid obtained was dried overnight under vacuum at 50 °C.

PEtCzTB: 309 mg, 69% yield. GPC: M_n: 9600, M_w/M_n = 1.30 (relative to polystyrene standards). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.14 (br, 2H); 8.03 (br, 2H); 7.85 (br, 2H); 7.52 (br, 2H); 7.39 (br, 2H); 7.20 (br,2H); 4.44 (br, 2H); 2.94 (br, 4H); 2.85 (br, 4H); 1.81 (br, 4H); 1.73 (br, 4H); 1.53 (br, 2H); 1.48 (br, 3H); 1.26–1.39 (br, 38H); 0.86 (br, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 152.52, 140.57, 140.13, 139.13, 136.49, 134.20, 132.87, 131.99, 130.71, 128.51, 125.31, 125.02, 122.07, 120.75, 120.43, 109.03, 31.90, 31.14, 31.65, 30.51, 30.45, 29.68, 29.48, 29.36, 29.33, 29.05, 22.69, 14.11, 13.89, 1.01; Anal. Calcd. for $(C_{69}H_{89}N_3S_5)_n$ (%):C, 73.94; H, 8.00; N, 3.75; Found (%): C, 74.16; H, 8.06; N, 3.79.

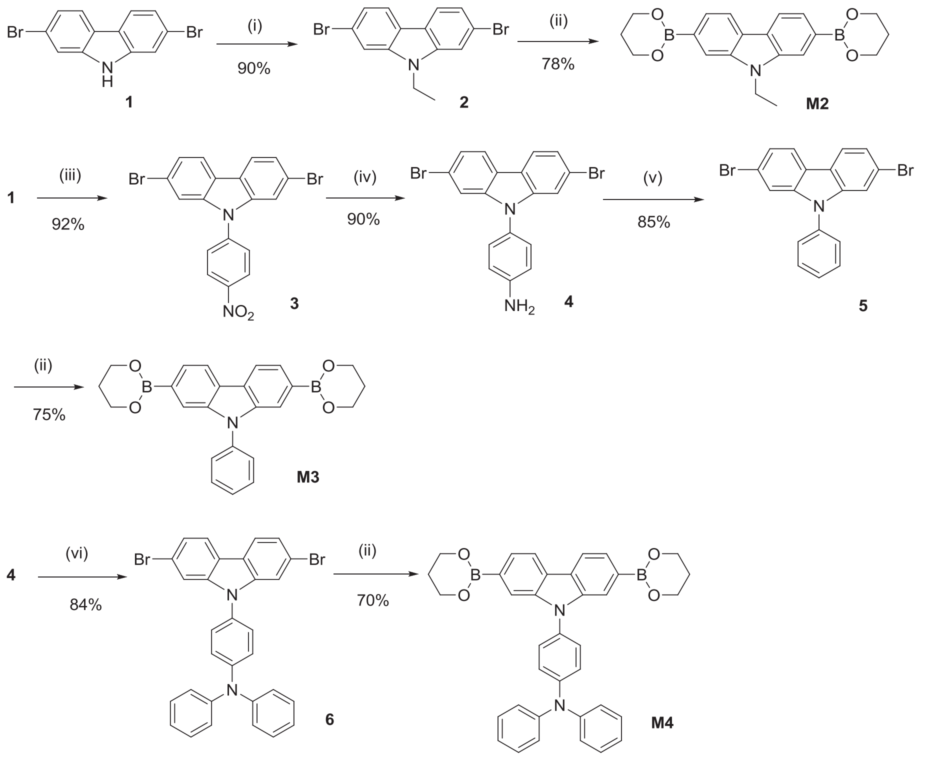
PPhCzTB: 280 mg, 60% yield. GPC: M_n: 10600, M_w/M_n = 1.40 (relative to polystyrene standards). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.18 (br, 2H); 7.98 (br, 2H); 7.83 (br, 2H); 7.63 (br, 4H); 7.51 (br, 2H); 7.45 (br, 3H); 7.14 (br, 2H); 2.86 (br, 4H); 2.70 (br, 4H); 1.75 (br, 4H); 1.65 (br, 4H); 1.46 (br, 4H); 1.36–1.25 (br, 36H); 0.87 (br, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 152.43, 140.54, 140.06, 139.08, 136.45, 134.23, 132.83, 131.97, 130.66, 128.45, 125.19, 124.92, 122.04, 120.73, 120.41, 108.96, 31.90, 31.14, 30.62, 30.50, 30.43, 29.70, 29.48, 29.34, 29.07, 22.68, 14.11, 13.87; Anal. Calcd. for $(C_{73}H_{89}N_3S_5)_n$ (%): C, 75.01; H, 7.67; N, 3.60; Found (%): C, 75.24; H, 7.69; N, 3.66.

PTPACzTB: 379 mg, 71% yield. GPC: M_n: 16800, M_w/M_n = 1.81 (relative to polystyrene standards). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.17 (br, 2H); 8.01 (br, 2H); 7.86 (br, 2H); 7.54 (br, 2H); 7.45 (br, 2H); 7.33–7.21 (br, 10H); 7.16 (br, 2H); 7.08 (br, 2H); 2.91 (br, 4H); 2.73 (br, 4H); 1.79 (br, 4H); 1.67 (br, 4H); 1.46 (br, 4H); 1.32–1.21 (br, 36H); 0.89 (br, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 152.57, 147.43, 141.78, 140.20, 139.23, 139.03, 136.55, 134.19, 132.82, 132.20, 130.72, 129.47, 128.51, 127.77, 125.39, 125.11, 124.94, 123.70, 123.53, 122.30, 121.68, 120.31, 110.42, 31.87, 31.08, 30.64, 29.66, 29.43, 29.32, 28.99, 22.66, 14.09; Anal. Calcd. for $(C_{86}H_{99}N_3S_5)_n$ (%):C, 77.37; H, 7.47; N, 3.15; Found (%): C, 77.60; H, 7.51; N, 3.16.

3. Results and discussion

3.1. *Synthesis and characterization*

The synthetic route towards monomers **M1**–**3** was given in Scheme 2. Compounds **1**–**6** were prepared according to reported methods [17–22]. It was noteworthy that one of the key intermediates, 2, 7-dibromo-9-(4-nitrophenyl)-9*H*-carbazole (**3**) was readily prepared with a modified literature procedure [20]. As a result, the reaction of **1** with 1.1 equiv of 4-fluoronitrobenzene in DMF at 60 °C afforded compound **3** in 92% yield. While the reaction reported by Jian et al. needs to perform in DMF at reflux using excess 4-fluoronitrobenzene (4.0 equiv.) and compound **3** was obtained in 86% yield [20]. Three new alternating copolymers **PEtCzTB**, **PPhCzTB** and **PTPACzTB** based on 2,7-linked carbazole, 2,1,3-benzothiadiazole and 3-octylthiophene were synthesized via the Suzuki coupling reaction. The general synthetic routes of the polymers are shown in Scheme 3. Their chemical structures were verified by ^1H NMR, ^{13}C NMR and elemental analysis (for details, see supporting information). All the copolymers were obtained as a dark-brown powder and are readily soluble in common organic solvents such as chloroform, THF and toluene etc.



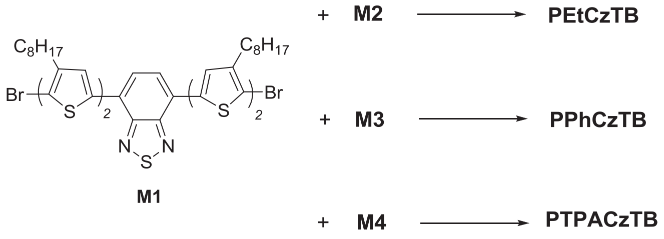
Scheme 2. Reagents and conditions: (i) C_2H_5Br, K_2CO_3, DMF, rt. (ii) (a) *n*-BuLi, THF, −78 °C; (b) $B(OMe)_3$, −78 °C; (c) 1 M HCl, 0 °C; (d) 1,3-propylene glycol, toluene, reflux; (iii) 4-F-$C_6H_4NO_2$, K_2CO_3, DMF, 60°C; (iv) Sn, HCl, EtOH, reflux; (v) (a) HCl, $NaNO_2$, CH_3CN, 0 °C; (b) H_3PO_2, 80 °C; (vi) PhI, CuCl, 1,10-phenanthroline, KOH, toluene, reflux.

3.2. Thermal properties

The thermal properties of the copolymers were determined by DSC and TGA under a nitrogen atmosphere. As shown in Fig. 1 and Table 1, polymers **PEtCzTB**, **PPhCzTB** and **PTPACzTB** exhibited 5% weight-loss temperatures (T_d) of 447, 417 and 439 °C, respectively. No glass transition was observed for polymers **PEtCzTB** and **PPhCzTB** in the DSC curves, while polymer **PTPACzTB** gave a distinct glass transition temperature (T_g) at 67 °C, most probably due to the introduction of the triphenylamine moiety onto the polymer side chain (see supporting information). No melting or crystallization peak was observed in further heating and cooling cycles. The good thermal stability of the polymers is desirable for their application in PSCs.

3.3. Optical properties

The optical properties of the polymers were investigated by Ultraviolet–visible (UV–vis) absorption spectroscopy in dilute chlorobenzene (10^{-6} M) solutions and as spin-coated films on quartz substrates. Fig. 2 shows the absorption spectra of the **PEtCzTB**, **PPhCzTB** and **PTPACzTB** in chlorobenzene solution. It was observed that almost identical absorption profiles were observed for the three polymers. The absorption band at shorter wavelength centered at 381 nm corresponds to higher energy transitions such as π–π* transition and the absorption peak located at 536 nm was attributed to the intramolecular charge-transfer (ICT) transition. There is an additional absorption peak at ~ 315 nm for polymer **PTPACzTB**, which obviously arises from the absorption of the pendent triphenylamine segment. The absorption spectra of the polymer films on quartz plate were shown in Fig. 3 and the optical data including the absorption peak wavelength in both solutions and films, absorption coefficients and the optical



Scheme 3. Synthetic routes toward copolymers **PEtCzTB**, **PPhCzTB** and **PTPACzTB**. Reagents and conditions: $Pd(PPh_3)_4$, toluene, Ar, 110 °C.

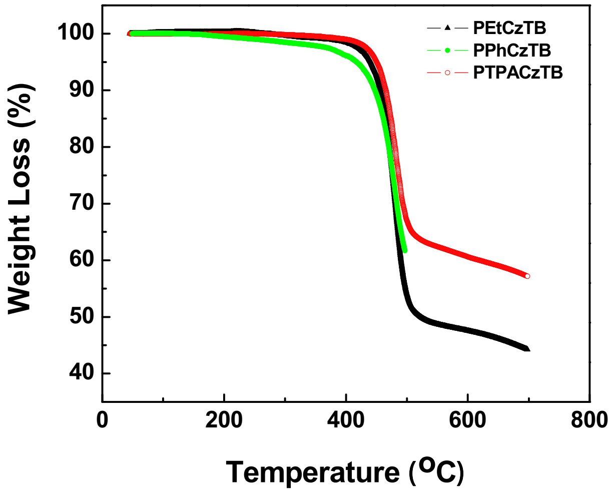


Fig. 1. TGA thermograms of the copolymers, recorded at a heating rate of 10 °C min^{-1} under a N_2 atmosphere.

Table 1
Polymerization data and thermal properties of the copolymers.

Polymers	Yield (%)	M_n (kg mol^{-1})[a]	M_w (kg mol^{-1})[a]	PDI[a]	T_g (°C)	T_d (°C)[b]
PEtCzTB	69	9.6	12.5	1.30	n.d.[c]	447
PPhCzTB	60	10.6	14.8	1.40	n.d.[c]	417
PTPACzTB	71	16.8	30.3	1.81	67	439

[a] Determined by gel permeation chromatography (GPC) in THF against polystyrene standards.
[b] Onset decomposition temperature (5% weight loss) measured by TGA.
[c] Glass transition temperature was not detectable.

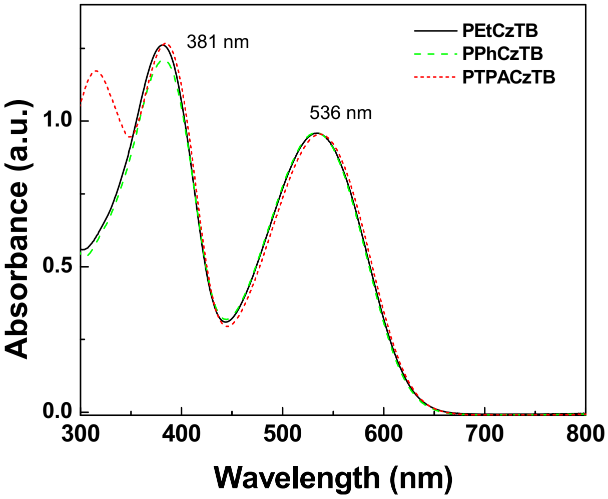


Fig. 2. UV–vis absorption spectra of the polymers in cholorobenzene solution (10^{-6} M).

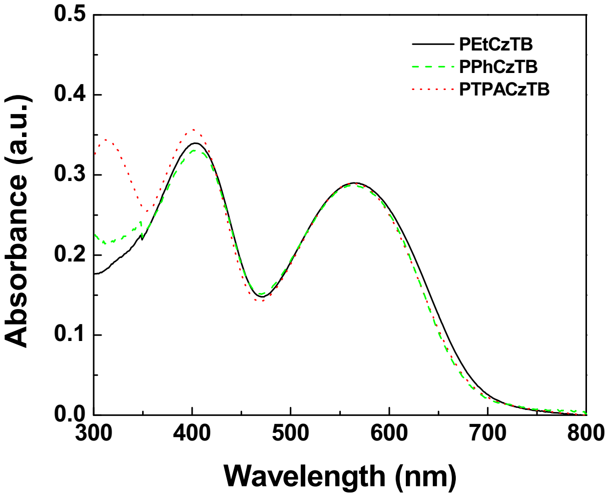


Fig. 3. UV–vis absorption spectra of the polymer films on a quartz plate.

bandgap (E_g^{opt}) are summarized in Table 2. In thin film state, the polymers showed red-shifted and broad absorption bands. The optical band gaps (E_g^{opt}) of the three polymers were calculated from the absorption edges in the films and found to be in the range of 1.78–1.85 eV. Clearly, the photophysical properties and energy levels of the resultant polymers can be slightly tuned by the *N*-substitution of carbazole.

3.4. Electrochemical properties

To investigate the electrochemical properties of the synthesized polymers and estimate their HOMO and LUMO energy levels, cyclic voltammetry (CV) measurement was carried out. The HOMO and the LUMO energy levels of the conjugated polymers were calculated using the empirical equation $E_{\mathrm{HOMO}} = -(E_{\mathrm{ox}}^{\mathrm{on}} + 4.40)$eV and $E_{\mathrm{LUMO}} = -(E_{\mathrm{red}}^{\mathrm{on}} + 4.40)$eV, respectively, where $E_{\mathrm{ox}}^{\mathrm{on}}$ and $E_{\mathrm{red}}^{\mathrm{on}}$ stand for the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively [26]. The cyclic voltammograms of the polymers are shown in Fig. 4. Upon cathodic scan, two couples of reversible reduction peaks were observed, corresponding to the redox process of benzothiadiazole and thiophene units, respectively. In the anodic scan, there is one couple of oxidation peak for polymers **PEtCzTB** and **PPhCzTB**, which is attributed to the redox process of carbazole unit. For **PTPACzTB**, an additional redox peak at 0.6 V from triphenylamine moiety was observed. The HOMO and the LUMO are listed in Table 2. One can see that the polymers gave narrower energy gaps due to the incorporation of electron-withdrawing benzothiadiazole units into the polymer backbone. Meanwhile, the HOMO energy levels **PEtCzTB** and **PPhCzTB** remain low at ~5.10 eV, which are important for achieving the large open-circuit voltage (V_{oc}) and high air stability. The HOMO energy level of **PTPACzTB** was higher (4.95 eV) than the other two polymers, due to the introduction of the triphenylamine group.

3.5. Photovoltaic properties

The potential of these polymers as hole-transporting light-absorbing components in photovoltaic cells were explored. Bulk-heterojunction photovoltaic cells with a device structure of ITO/PEDOT:PSS/polymers:$PC_{71}BM$ (1:1 or 1:3, w/w)/LiF(1 nm)/Al (100 nm) were fabricated. The active layer was spin-coated from chlorobenzene solution using a slow solvent evaporation process. It was found that weight ratio between polymers:$PC_{71}BM$ of 1:3 gave improved photovoltaic performances, but lower than the poly(*N*-alkyl-2,7-carbazole) developed by Leclerc et al. (3.6%) [7c]. Fig. 5 shows the *I*–*V* curves of the devices under AM 1.5 simulated solar illumination of 100 mW/cm^2, and V_{oc}, J_{sc}, *FF*, and PCE data were collected and listed in Table 3. The corresponding power conversion efficiency of the solar cells was 1.69% for **PEtCzTB**, 2.01% for **PPhCzTB,** and 2.42% for **PTPACzTB**. It was observed that the PCE was increased by the replacement of the ethyl group by diphenylaminophenyl group, which may attribute to the enhanced

Table 2
Absorption and electrochemical properties of the copolymers.

Polymer	λ_{abs} (nm)		ε (L mol^{-1} cm^{-1})	E_g^{opt} (eV)[a]	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{ec} (eV)[b]
	Solution	Film					
PEtCzTB	381 536	401 565	3.0×10^5	1.85	−5.12	−3.16	1.96
PPhCzTB	381 536	401 565	2.6×10^5	1.82	−5.18	−3.19	1.99
PTPACzTB	315 381 536	315 401 565	4.7×10^5	1.78	−4.95[c]	−3.16	1.79

[a] Estimated from the absorption edge in film state.
[b] Energy gap = HOMO-LUMO.
[c] E_{HOMO} of **PTPACzTB** was calculated based on triphenylamine moiety.

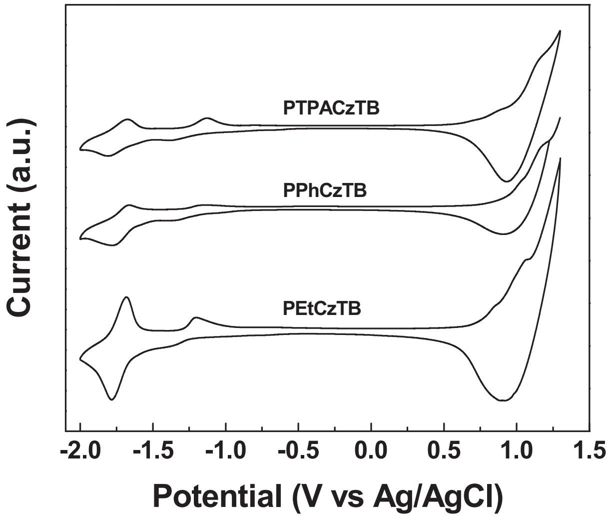


Fig. 4. Cyclic voltammograms of polymer thin films on Pt electrode in 0.1 M Bu_4NClO_4 acetonitrile solution at 50 mV s^{-1}.

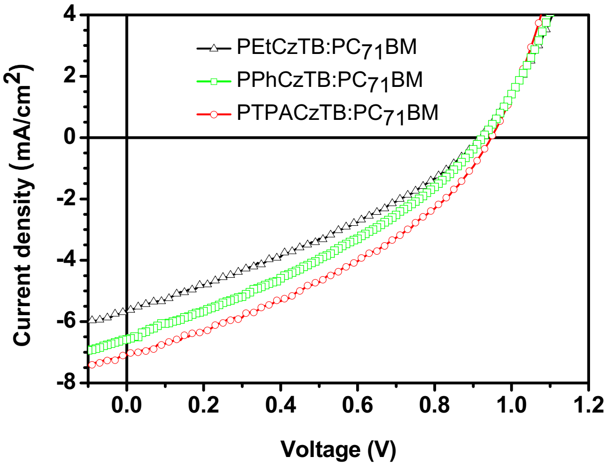


Fig. 5. Current density-voltage characteristics of polymer/$PC_{71}BM$ based devices under AM 1.5 simulated solar illumination of 100 mW/cm^2.

hole-transporting ability of **PTPACzTB** [16], although the intermolecular π–π stacking in **PTPACzTB** is somewhat inhibited by the introduction of triphenylamine moiety.

The open-circuit voltage (V_{oc}) depends on the energetic difference between donor highest occupied molecular orbital (HOMO) and acceptor lowest unoccupied molecular orbital (LUMO). The PSC devices based on the three carbazole-based polymers gave high open-circuit voltages of 0.91 V for **PEtCzTB** and 0.92 V for **PPhCzTB** and 0.95 V for **PTPACzTB**, which are consistent with their deep HOMO energy levels. The high V_{oc} of the three polymers are among the best data (V_{oc} > 0.9 V) of the LBG polymers reported in the literature [27].

Table 3
Photovoltaic properties of polymer solar cells incorporating polymer:$PC_{71}BM$ blends at 1:3 weight ratios.[a,b]

Polymer	Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	PCE (%)
PEtCzTB	75	0.91	5.64	0.33	1.69
PPhCzTB	60	0.92	6.58	0.33	2.01
PTPACzTB	60	0.95	7.08	0.36	2.42

[a] Under simulated AM 1.5 solar illumination at an irradiation intensity of 100 mW/cm^2.
[b] For as-fabricated devices.

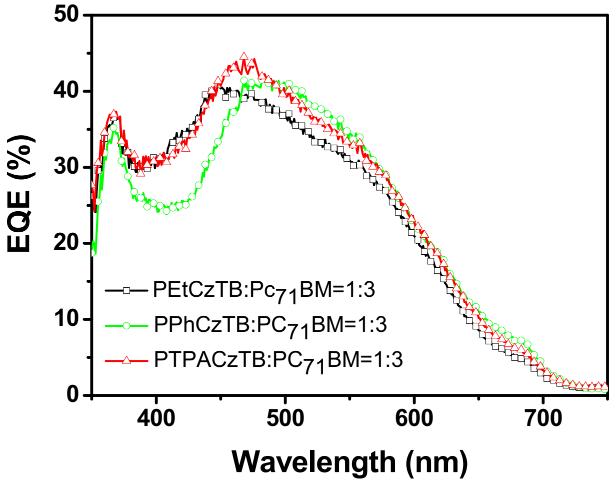


Fig. 6. EQE curves of PSCs incorporating polymer/$PC_{71}BM$ blends, each prepared at a blend of 1:3 (w/w).

The external quantum efficiency (EQE) curves of the PSC devices are plotted in Fig. 6. It is apparent that the device exhibits a broad response range, covering from 350 to 700 nm, but the EQE of the device is within 45% for almost the whole absorption range. If the EQE of the device can be improved by increasing the thickness of the active layer without hampering charge-separation and transport properties, the device performance may be improved.

4. Conclusion

In this paper, we report the synthesis and characterization of two new *N*-aryl-based low-bandgap poly(2,7-carbazole)s, **PPhCzTB** and **PTPACzTB**. Photovoltaic properties of these polymers were investigated by fabricating bulk heterojuntion photovoltaic devices using these polymers as electron donor and $PC_{71}BM$ as the acceptor. High open-circuit voltages of 0.91–0.95 V and moderate power conversion efficiency of 1.69% for **PEtCzTB**, 2.01% for **PPhCzTB,** and 2.42% for **PTPACzTB** were achieved. Of the three polymers, **PTPACzTB** gave best photovoltaic performance under identical conditions, most probably, due to the introduction of triphenylamine moiety increase the hole-transporting ability of the polymer, although the intermolecular stacking may be inhibited to some degree. These results indicate low-bandgap poly(*N*-aryl-2,7-carbazole)s are promising polymer materials for application in polymer solar cells.

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Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2011.02.029.

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