Benzooxadiazole-based donor/acceptor copolymers imparting bulk-heterojunction solar cells with high open-circuit voltages

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ABSTRACT

In this study we used Suzuki cross-coupling to synthesize three new donor/acceptor copolymers—**PFTBO**, **PAFTBO**, and **PCTBO**—featuring soluble alkoxy-modified 2,1,3-benzooxadiazole (**BO**) moieties as acceptor units and electron-rich building blocks—dialkyl fluorene (**F**), alkylidene fluorene (**AF**), and carbazole (**C**), respectively—as donor units. These polymers, which we characterized using gel permeation chromatography, thermogravimetric analysis, NMR spectroscopy, UV–Vis absorption spectroscopy, and electrochemical cyclic voltammetry, exhibited good solubility, low-lying energy levels for their highest occupied molecular orbitals, excellent thermal stability, and air stability. Using these polymers, we fabricated bulk-heterojunction solar cell devices having the structure indium tin oxide/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate/polymer:[6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) (1:1, w/w)/Ca/Al. Under AM 1.5G illumination (100 mW cm^{-2}), the solar cell incorporating **PFTBO** exhibited a high value of V_{oc} of 1.04 V and that based on **PCTBO** provided a power conversion efficiency of 4.1% without the need for any post treatment.

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1. Introduction

Polymer solar cells (PSCs) are attracting growing interest as a potential renewable energy technology because they can be manufactured at low cost with the capability of being used in flexible large-area devices [1–3]. To date, bulk-heterojunctions (BHJs), in which the active layer consists of a blend of electron-donating conjugated polymers and electron-accepting fullerene derivatives, have been the most prevalent active layer structures in polymer solar cells exhibiting high power conversion efficiencies (PCEs). Several conjugated polymers have been developed featuring electron donor/acceptor (D/A) units in main chain—conjugated configurations [4–15] and side chain—attached architectures [16–20]. Recently, BHJ solar cells based on blends of some D/A low-band gap polymers and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) or $PC_{71}BM$ have been investigated extensively, providing PCEs as high as 7% [21–27].

The PCE of a solar cell device is essentially determined by short-circuit current density (J_{sc}), the fill factor, and the open-circuit voltage (V_{oc}). The relatively low open-circuit voltage (ca. 0.6 V) obtained in some thiophene-polymer based BHJ devices will limit their PCEs. In a BHJ-structured active layer, the open-circuit voltage is typically proportional to the difference in energy between the highest occupied molecular orbital (HOMO) of the polymer and the lowest unoccupied molecular orbital (LUMO) of the fullerene, although some other characteristics of the device structure (e.g., the type of cathode material, the active layer morphology, or exciton non-radiative recombination) can also affect the values of V_{oc} of BHJ PSCs [28–31]. Therefore, the value of V_{oc} can be increased either by elevating the LUMO energy level of the fullerene or depressing the HOMO energy level of the polymer while keeping its counterpart unchanged. Low-band gap polymers that provide efficient absorption of the solar spectrum, however, tend to have high-lying HOMOs and low-lying LUMOs; the difference in the energy levels between the low-lying LUMOs of the polymers and the LUMO of the fullerene frequently result in inefficient charge separation, leading to a smaller enhancement of J_{sc}. On the other hand, the combination of a high-lying HOMO in a low-band gap polymer and a fixed LUMO in fullerene will also provide a lower value of V_{oc}. Therefore, fine tuning of the band gap and the energy levels such as lowering the HOMO and LUMO of the polymer simultaneously but with a larger decrease in the LUMO while maintaining its value 0.3 eV above that of the fullerene is required to obtain BHJ PSCs with high values of V_{oc} and J_{sc} [32–34]. Currently, the highest open-circuit voltages obtained from BHJ PSCs (ca. 1 V) have required polymers possessing medium-sized band gaps (ca. 2 eV) [35–38].

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In recent years, 9,9-dialkylfluorenes have emerged as attractive donor candidates for D/A polymer photovoltaics because of their good processability, high absorption coefficients, and considerable values of V_{oc} [39,40]. By changing the sp^3-hybridized carbon atom at the 9-position of 9,9-dialkylfluorene to an sp^2-hybridized atom, the resulting alkylidene fluorene permits the alkyl chains to adopt a coplanar conformation relative to the polymer backbone, thereby facilitating cofacial $\pi-\pi$ stacking, which can lead to very short intermolecular distances (<4 Å) in crystalline or liquid crystalline states and, accordingly, enhanced charge carrier transportation [41]. Unlike a C-bridged fluorene, the corresponding N-bridged carbazole moiety is fully aromatic, providing superior chemical and environmental stability. Poly(N-alkyl-2,7-carbazole) derivatives have been applied successfully in polymer light emitting diodes [42] and organic field-effect transistors [43], demonstrating good p-type transport properties.

On the other hand, BHJ devices based on main chain D/A polymers containing alkoxy benzooxadiazole (BO) units as acceptors and several thiophene-based building blocks as donors have exhibited relatively high values of V_{oc} [44,45]; therefore, combining a strongly electron-withdrawing acceptor with a weakly electron-donating donor can be a very effective means of lowering the HOMO energy level in the D/A polymer and, ultimately, enhancing the value of V_{oc} of the resulting PSC [46]. Those studies inspired us to further explore the possibility of copolymerizing alkoxy-modified BO derivatives with weakly electron-donating units to synthesize copolymers exhibiting high values of V_{oc}. In this study, we prepared a series of new D/A alternating polymers—**PFTBO**, **PAFTBO**, and **PCTBO**—based on 9,9-dialkylfluorene (**F**), alkylidene fluorene (**AF**), and N-alkyl-2,7-carbazole (**C**) units, respectively, as weak electron donors and alkoxy-modified BO (**BO**) units as electron-deficient acceptors; conjugation of the electron-withdrawing BO units to the weakly electron-donating units provided polymers with deep HOMO energy levels and medium-sized band gaps. These desirable features provided **PFTBO**, **PAFTBO**, and **PCTBO** with good hole mobilities and high values of V_{oc}, making them suitable for photovoltaic applications.

2. Experimental section

2.1. Materials and synthesis

The synthesis of 4,7-bis(5-bromothiophen-2-yl)-5,6-bisoctyloxybenzo[c][1,2,5]oxadiazole (**M1**) [44] has been reported elsewhere.

4,4,5,5-Tetramethyl-2-[2-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-9,9-dioctyl-9H-fluoren-7-yl]-1,3-dioxolane (**M2**) [47], 2-[9-(heptadecan-9-ylidene)-2-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-9H-fluoren-7-yl]-4,4,5,5-tetramethyl-1,3-dioxolane (**M3**) [41], and 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-9H-carbazole (**M4**) [48] were prepared according to reported procedures. PC$_{61}$BM was purchased from Nano-C. All other reagents were used as received without further purification, unless stated otherwise.

2.2. General procedure for Suzuki polymerization: alternating polymer PFTBO

A mixture of **M1** (105 mg, 0.150 mmol), **M2** (96.3 mg, 0.150 mmol), Aliquat 336 (ca. 20 mg), K$_2$CO$_{3(aq)}$ (2 M, 1.5 mL), and chlorobenzene (CB) 4 mL were degassed under N$_2$ at 60 °C for 15 min. Pd(PPh$_3$)$_4$ was added to the mixture, which was then heated at 130 °C for 48 h. Phenylboronic acid (49.9 mg, 0.300 mmol) was added and then the mixture was stirred 6 h.

Subsequently, bromobenzene (0.03 mL, 0.3 mmol) was also added to the mixture, which was stirred for another 12 h. After cooling to room temperature, the solution was added dropwise into MeOH (100 mL). The crude polymer was collected, dissolved in CHCl$_3$, and reprecipitated from MeOH. The solid was washed with MeOH, acetone, and CHCl$_3$ in a Soxhlet apparatus. The CHCl$_3$ solution was concentrated and then added dropwise into MeOH. The precipitate was collected and dried under vacuum to give **PFTBO** (100 mg, 72%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.54–8.31 (m, 2H), 8.05–7.88 (m, 2H), 7.80–7.55 (m, 6H), 4.25 (br, 4H), 2.41 (br, 4H), 1.78–1.25 (m, 48H), 0.91 (s, 12H). Anal. Calcd: C, 76.25; H, 8.68; N, 3.01. Found: C, 75.18; H, 8.55; N, 3.15.

2.2.1. Alternating polymer PAFTBO

Using a polymerization procedure similar to that described above for **PFTBO**, a mixture of **M1** (105 mg, 0.15 mmol) and **M3** (98.1 mg, 0.15 mmol) in dry CB (4 mL) was polymerized to give **PAFTBO** (71 mg, 52%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.51–8.29 (m, 2H), 8.17–7.98 (m, 2H), 7.78–7.51 (m, 6H), 4.22 (br, 4H), 2.81 (br, 4H), 1.98–1.56 (m, 48H), 0.83 (s, 12H). Anal. Calcd: C, 76.55; H, 8.57; N, 2.98. Found: C, 74.98; H, 8.42; N, 2.77.

2.2.2. Alternating polymer PCTBO

Using a polymerization procedure similar to that described above for **PCTBO**, a mixture of **M1** (105 mg, 0.15 mmol) and **M4** (98.6 mg, 0.15 mmol) in dry CB (4 mL) was polymerized to give **PCTBO** (120 mg, 85%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.85–8.57 (m, 2H), 8.06–7.83 (m, 2H), 7.68–7.42 (m, 6H), 4.32 (br, 4H), 3.98 (s, 1H), 2.13 (br, 4H), 1.67–1.28 (m, 48H), 0.91 (s, 12H). Anal. Calcd: C, 75.03; H, 8.64; N, 4.45. Found: C, 73.15; H, 8.47; N, 4.56.

2.3. Measurements and characterization

^{1}H NMR spectra were recorded using a Varian UNITY 300-MHz spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 apparatus; the thermal stabilities of the samples were determined under a N$_2$ atmosphere by measuring their weight losses while heating at a rate of 20 °C min^{-1}. Size exclusion chromatography (SEC) was performed using a Waters chromatography unit interfaced with a Waters 1515 differential refractometer; polystyrene was the standard; the temperature of the system was set at 45 °C; THF was the eluent. UV–Vis spectra of dilute samples (1×10^{-5} M) in dichlorobenzene (DCB) were recorded at room temperature (ca. 25 °C) using a Hitachi U-4100 spectrophotometer. Solid films for UV–Vis spectroscopic analysis were obtained by spin-coating the polymer solutions onto a quartz substrate. Cyclic voltammetry (CV) of the polymer films was performed using a BAS 100 electrochemical analyzer operated at a scan rate of 50 mV s^{-1}; the solvent was anhydrous MeCN, containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte. The potentials were measured against a Ag/Ag$^+$ (0.01 M AgNO$_3$) reference electrode; the ferrocene/ferrocenium ion (Fc/Fc$^+$) pair was used as the internal standard (0.09 V). The onset potentials were determined from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammograms. HOMO and LUMO energy levels were estimated relative to the energy level of the ferrocene reference (4.8 eV below vacuum level). Topographic and phase images of the polymer/PC$_{61}$BM films (surface area: 5×5 μm^2) were obtained using a Digital Nanoscope III atomic force microscope (AFM) operated in the tapping mode under ambient conditions. The thickness of the active layer of the device was measured using a Veeco Dektak 150 surface profiler.