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Bulk-Heterojunction Solar Cells with Benzotriazole-Based Copolymers as Electron Donors: Largely Improved Photovoltaic Parameters by Using PFN/Al Bilayer Cathode

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ABSTRACT: Three benzotriazole (BTA)-based conjugated polymers PF-DTBTA, PCz-DTBTA, and PPh-DTBTA, with electron-donating segments of fluorene, carbazole, and dialkoxybenzene, respectively, were successfully synthesized as new polymeric donors in bulk-heterojunction (BHJ) photovoltaic cells (PVCs). All the copolymers exhibited good solubility in common organic solvents and good thermal stability. The optical band gaps for PF-DTBTA, PCz-DTBTA, and PPh-DTBTA are 2.24, 2.18, and 1.87 eV, respectively. The HOMO levels for PF-DTBTA, PCz-DTBTA, and PPh-DTBTA are −5.67, −5.54, and −5.20 eV, respectively, which were determined by the electron-donating segments. The LUMO levels for PF-DTBTA, PCz-DTBTA, and PPh-DTBTA are −3.43, −3.36, and −3.33 eV, respectively, which were mainly dominated by the BTA unit. For a blend ratio of polymer:PCBM = 1:2, BHJ PVCs with Al cathode displayed power conversion efficiencies (PCE) of 0.9%, 1.51%, and 1.16% for PF-DTBTA, PCz-DTBTA, and PPh-DTBTA, respectively. Alcohol-soluble poly[(9,9-dioctyl-2,7-fluorene)-*alt*-(9,9-bis(3′-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)] (PFN) was selected for cathode modification. For BHJ PVCs with PF-DTBTA and PCz-DTBTA as the donors, open-circuit voltages (V_{oc}) of the PVCs could all be elevated with the PFN/Al bilayer cathode, whereas no such improvements were found for PVCs with PPh-DTBTA as the donor. The behaviors could be attributed to the different V_{oc} losses when using Al cathode. Using PFN/Al bilayer cathode could also improve short-curcuit current and fill factor for the three BTA-based copolymers. The *N*−*N* interactions between the BTA-based polymers and the PFN may modify interfacial contact, resulting in enhancement of the electron extraction from the acceptor phase to the cathode and decreasing hole−electron recombination in the active layer. Consequently, PFN/Al bilayer cathode elevated PCE values to 1.3%, 2.75%, and 1.39% for PF-DTBTA, PCz-DTBTA, and PPh-DTBTA, respectively. The most significant increasing of PCE with a calculated value of 80% was found for PCz-DTBTA as the donor, and this might be related to the additional *N*−*N* interactions between the carbazole segments and the PFN. The results would supply useful information to understand the contribution of an interfacial layer on the photovoltaic performance. Our results also suggest that the bilayer cathode would have great potential to elevate PCE of BHJ PVCs.

Introduction

Organic photovoltaic technology, a low-cost, lightweight, and flexible thin film device toward inexhaustible renewable clean energy, has received great attention during the past years.[1] Polymeric bulk-heterojunction (BHJ) PVCs, whose photoactive layer is composed of a blend of bicontinuous and interpenetrating donor and acceptor, can maximize interfacial area between the donor and the acceptor.[2] The low band gap feature to match the solar spectrum, fast hole mobility, and suitable energy levels are basic requirements to design an ideal polymer donor.[3,4]

Combinations of electron-donating (D) units and electron-accepting (A) heterocycles have become an attractive methodology to construct D−A polymer donors for high-efficiency BHJ PVCs.[5] Fluorene,[6] carbazole,[7] and dibenzosilole[8] are the typical D-type units for polymer donors with high open-circuit voltage (V_{oc}). 2,1,3-Benzothiadiazole (BT) is an early and widely utilized example of A-type heterocycles.[6,7a,8−14] Recently, D−A copolymers with thieno[3,4-*b*]pyrazine,[15] quinoxaline,[16] silole,[17] and diketopyrrolopyrrole (DPP)[18] as A-type heterocycles are also promising for their notable performances in BHJ PVCs.

Benzotriazole (BTA) is an electron-deficient A-type heterocycle.[19] Particularly, 2-alkylbenzotriazole is a close analogue to BT, in which the 2-alkyl substitution of BTA is very helpful for the construction of a conjugated polymer with better solubility, in comparison with the incorporation of BT. The good solubility of a conjugated polymer is crucial for its purification and the deposition of high-quality film for efficient optoelectronic devices. Several reports have described the light emissions of BTA-based conjugated polymers.[19,20] Moreover, BTA-based conjugated polymers also showed excellent electrochromic property.[21] However, incorporation of BTA to construct a polymer donor for BHJ PVCs receives less attention. Very recently, photovoltaic performances with a relatively low power conversion efficiency (PCE) were reported for poly(2-dodecyl-4,7-bis(4-hexylthiophen-2-yl)benzotriazole), a polymer prepared using $FeCl_3$ as the oxidizing agent.[22]

In this work, three BTA-based conjugated polymers (Chart 1), poly[9,9-dioctyl-2,7-fluorene-*alt*-(4,7-bis(2′-thienyl)-2-dodecyl-2,1,3-benzotriazole)] (PF-DTBTA), poly[(*N*-9′-heptadecanyl-2,7-carbazole)-*alt*-(4,7-bis(2′-thienyl)-2-dodecyl-2,1,3-benzotriazole)] (PCz-DTBTA), and poly[(2,5-dioctyl-1,4-phenylene)-*alt*-(4,7-bis-(2′-thienyl)-2-dodecyl-2,1,3-benzotriazole)] (PPh-DTBTA), were synthesized as new polymeric donors for photovoltaic cells.

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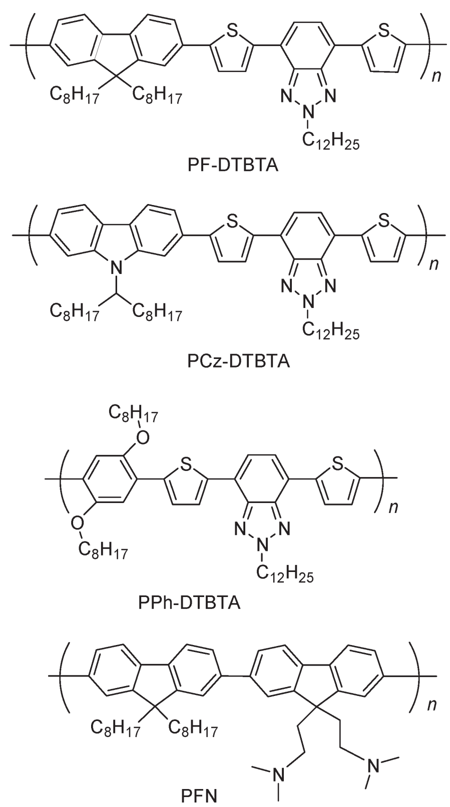
Chart 1



We selected the Suzuki coupling reaction to prepare the BTA-based conjugated polymers. It might be expected that the resulting polymers would have better purity control than the reported $FeCl_3$-catalyzed polymer, which was an important control for high-efficiency BHJ PVCs. The UV−vis absorptions, energy levels, and photovoltaic performances of the three copolymers were evaluated to understand the relationships between their structures and properties. With [6,6]-phenyl C61 butyric acid methyl ester (PCBM) as the electron acceptor of BHJ PVCs, the highest PCE of 1.51% was realized with PCz-DTBTA as the polymer donor in a routine device configuration of ITO/PEDOT/active layer/Al. With alcohol-soluble poly[(9,9-dioctyl-2,7-fluorene)-*alt*-(9,9-bis(3′-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)] (PFN, Chart 1) as the cathode modification layer,[23,24] BHJ PVCs of the three copolymers all showed obvious improvements of photovoltaic performances. The most significant increasing of PCE to 2.75% was also found for PCz-DTBTA, a nitrogen-atom-abundant polymer, in which V_{oc}, short-circuit current (I_{sc}), and fill factor (FF), the three photovoltaic parameters, could be elevated in the meantime, giving an overall PCE improvement of 80%. The influences of the PFN layer on the photovoltaic parameters of the BHJ PVCs were discussed.

Experimental Section

Materials. All reagents and solvents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and were used as received. Anhydrous tetrahydrofuran was distilled over sodium/benzophenone under N_2 prior to use. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. 4,7-Dibromo-2-dodecyl-2,1,3-benzotriazole,[25] 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctylfluorene,[26] 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-9-heptadecanylcarbazole,[26] and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene[27] were synthesized similar to already published procedures. Poly[(9,9-bis(3′-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-9,9-dioctyl-2,7-fluorene)] (PFN) was prepared according to a previous report.[28] Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was recrystallized twice from a 50:50 mixture of methanol/water and dried at 60 °C under vacuum.

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 spectrometer with tetramethylsilane (TMS) as the internal reference. Molecular weights of the polymers were obtained on a Waters GPC 2410 using a calibration curve of polystyrene standards, with tetrahydrofuran as the eluent. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). Thermogravimetric (TGA) measurements were carried out with a NETZSCH (TG209F1) apparatus at a heating rate of 20 °C/min under a nitrogen atmosphere. UV−vis absorption spectra were recorded on a HP 8453 spectrophotometer. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV/s against a saturated calomel reference electrode with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). The deposition of a copolymer on the electrode was done by the evaporation of a dilute chlorobenzene solution.

4,7-Bis(2′-thienyl)-2-dodecyl-2,1,3-benzotriazole (1). In a pressure vessel, 4,7-dibromo-2-dodecyl-2,1,3-benzotriazole (2.225 g, 5 mmol) and tributyl(2-thienyl)stannane (4.67 g, 12.5 mmol) were dissolved in anhydrous THF (100 mL). The solution was purged with argon for 30 min, and dichlorobis-(triphenylphosphine)palladium(II) (25 mg) was added at room temperature under an argon atmosphere. The mixture was heated up to 85 °C for 3 days. The solvent was evaporated under a vacuum, and the crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 20:1, as eluent) to yield 1.69 g (75%) of the product as green-yellowish crystals. ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.11 (dd, $J = 1.05$ Hz, 2H), 7.66 (s, 2H), 7.41 (dd, $J = 1.08$ Hz, 2H), 7.21 (m, 2H), 4.84 (t, $J = 7.23$ Hz, 2H), 2.27 (m, 2H), 1.29 (m, 18H), 0.91 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): 142.1, 139.9, 128.0, 126.9, 125.5, 123.6, 122.7, 56.8, 36.6, 31.9, 30.0, 29.6, 29.5, 29.4, 29.3, 29.0, 26.5, 22.6, 14.1. Anal. Calcd (%) for $C_{26}H_{33}N_3S_2$: C 69.14; H 7.36; N 9.30; S 14.20. Found: C 68.77; H 7.20; N 9.26; S 14.77.

4,7-Bis(2′-(5′-bromothienyl))-2-dodecyl-2,1,3-benzotriazole (2). To a stirred solution of 4,7-bis(2′-thienyl)-2-dodecyl-2,1,3-benzotriazole (**1**) (1.58 g, 3.5 mmol) in dimethylformamide (DMF) (30 mL) was added *N*-bromosuccinimide (NBS) (1.44 g, 8.05 mmol) in darkness. The mixture was stirred at room temperature for 9 h, and water was added. The product was extracted with ethyl acetate, and the organic phase was washed with saturated sodium chloride and water successively and dried over Na_2SO_4. The solvent was removed to afford the product as yellow crystal that was recrystallized from hexane to afford 1.562 g of pure compound (87.7%). ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 7.84 (d, $J = 3.96$ Hz, 2H), 7.53 (s, 2H), 7.15 (d, $J = 4.68$ Hz, 2H), 4.84 (t, $J = 7.26$ Hz, 2H), 2.22 (m, 2H), 1.29 (m, 18H), 0.91 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): 141.7, 141.2, 130.8, 126.9, 122.9, 122.1, 113.1, 56.9, 36.6, 31.9, 30.0, 29.6, 29.5, 29.4, 29.3, 29.0, 26.5, 22.6, 14.1. Anal. Calcd (%) for $C_{26}H_{31}N_3S_2Br_2$: C 51.24; H 5.13; N 6.89; S 10.52. Found: C 51.25; H 5.12; N 6.95; S 11.16.

Polymerization. All of the polymerizations were carried out by palladium(0)-catalyzed Suzuki coupling reactions with equivalently molar ratio of a diboronic ester monomer to the dibromo monomer **2** under argon protection. The purifications of the polymers were conducted in air. A typical procedure for the copolymerization and the characterizations for the three alternating copolymers are given below.

Table 1. Molecular Weights, Elemental Analyses, and Decomposition Temperatures of the Copolymers

			elemental analysis[b]				
polymer	M_w[a] (kDa)	M_w/M_n[a]	C	H	N	S	T_d[c] (°C)
PF-DTBTA	20.2	2.32	78.08 (78.79)	8.63 (8.51)	4.56 (5.01)	7.88 (7.65)	405
PCz-DTBTA	296	2.76	77.66 (77.41)	8.77 (8.50)	6.34 (6.57)	7.39 (7.51)	410
PPh-DTBTA	18.3	2.11	73.37 (73.70)	9.05 (8.63)	5.02 (5.37)	7.84 (8.20)	375

[a] Estimated by GPC in THF on the basis of a polystyrene calibration. [b] Data given in the parentheses are contents in the feed compositions. [c] Temperature for 5% weight loss measured by TGA at a heating rate of 20 °C/min under nitrogen.

Poly[9,9-dioctyl-2,7-fluorene-*alt*-(4,7-bis(2′-thienyl)-2-dodecyl-2,1,3-benzotriazole)] (PF-DTBTA). Carefully purified 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctylfluorene (231 mg, 0.36 mmol), 4,7-bis(2′-(5′-bromothienyl))-2-dodecyl-2,1,3-benzotriazole **2** (183 mg, 0.36 mmol), $(PPh_3)_4Pd(0)$ (3 mg, 0.0025 mmol), and Aliquat 336 (three drops) were dissolved in a mixture of toluene (10 mL) and aqueous 2 M Na_2CO_3 (1.2 mL). The solution was refluxed with vigorous stirring for 48 h. At the end of polymerization, a small amount of bromobenzene was added as a monofunctional end-capping reagent to remove boronic ester end group, and phenylboronic acid was added as a monofunctional end-capping reagent to remove bromine end groups. The mixture was then poured into vigorously stirred methanol. The precipitated solid was filtered and washed with acetone and then hexane to remove oligomers and catalyst residues. Orange polymer powder was dried in vacuum at 50 °C for 2 days to give 192 mg of final product (72.7%). GPC: M_w 20.2 kDa; M_w/M_n 2.32 (Table 1). ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.17 (br, 2H), 7.86−7.69 (m, 8H), 7.51 (br, 2H), 4.91 (br, 2H), 2.36−2.00 (m, 6H), 1.39−0.64 (m, 51 H). Anal. Calcd (%) for $(C_{55}H_{71}N_3S_2)_n$: C 78.79; H 8.51; N 5.01; S 7.65. Found: C 78.08; H 8.63; N 4.56; S 7.88.

Poly[(*N*-9′-heptadecanyl-2,7-carbazole)-*alt*-(4,7-bis(2′-thienyl)-2-dodecyl-2,1,3-benzotriazole)] (PCz-DTBTA) was prepared similarly with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-9-heptadecanylcarbazole as the diboronic ester monomer. A red powder of PCz-DTBTA was isolated in 60% yield (159 mg). GPC: M_w 296 kDa; M_w/M_n 2.76 (Table 1). ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.22−8.14 (m, 4H), 7.9−7.53 (br, 8H), 4.91 (br, 2H), 4.71 (br, 1H), 2.44−1.87 (m, 6H), 1.48−0.78 (m, 51H). Anal. Calcd (%) for $(C_{55}H_{72}N_4S_2)_n$: C 77.41; H 8.50; N 6.57; S 7.51. Found: C 77.66; H 8.77; N 6.34; S 7.39.

Poly[(2,5-dioctyl-1,4-phenylene)-*alt*-(4,7-bis(2′-thienyl)-2-dodecyl-2,1,3-benzotriazole)] (PPh-DTBTA) was prepared similarly with 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene as the diboronic ester monomer. A deep red powder of PPh-DTBTA was isolated in 61% yield (142 mg). GPC: M_w 18.3 kDa; M_w/M_n 2.11 (Table 1). ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.18 (br, 2H), 7.71−7.62 (br, 4H), 7.38 (br, 2H), 4.91 (br, 2H), 4.21 (br, 4H), 2.26−2.04 (m, 10H), 1.44−0.89 (m, 43H). Anal. Calcd (%) for $(C_{48}H_{67}N_3O_2S_2)_n$: C 73.70; H 8.63; N 5.37; S 8.20. Found: C 73.37; H 9.05; N 5.02; S 7.84.

PVC Fabrication and Characterization. Patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 15−20 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 5 min, a 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in a vacuum oven at 80 °C for overnight. The active layer, with a thickness in the 70−80 nm range, was then deposited on top of the PEDOT:PSS layer by casting from a chlorobenzene solution. The PFN solution in methanol was spin-coated on the top of the obtained active layer to form a thin interlayer of 5 nm. The thickness of the PEDOT:PSS and active layer were verified by a surface profilometer (Tencor, Alpha-500). Determination of the thickness of the interlayer followed a previously published paper.[23] Finally, a 100 nm aluminum layer was thermally evaporated with a shadow mask at a base pressure of 3×10^{-4} Pa. The overlapping area between the cathode and anode defined a pixel size of 0.15 cm^2. The thickness of the evaporated cathodes was monitored by a quartz crystal thickness/ratio monitor (model: STM-100/MF, Sycon). Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen drybox (Vacuum Atmosphere Co.) containing less than 10 ppm oxygen and moisture. The power conversion efficiencies of the resulting polymer solar cells were measured under 1 sun, AM 1.5G (air mass 1.5 global) spectrum from a solar simulator (Oriel model 91192) (100 mW/cm^2). The current density−voltage ($J-V$) characteristics were recorded with a Keithley 2410 source unit.

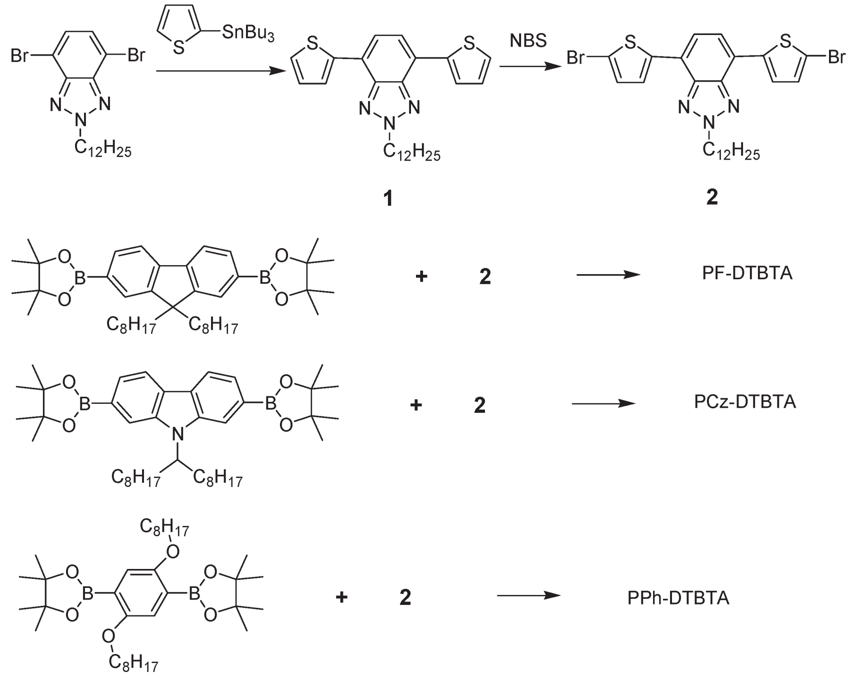
Results and Discussion

Synthesis of Monomers and Polymers. The synthesis of the BTA-based monomer **2** is shown in Scheme 1. 4,7-Dibromo-2-dodecyl-2,1,3-benzotriazole, the starting compound, was prepared similarly according to a previous report.[25] The Stille coupling reaction of the starting compound with tributyl(2-thienyl)stannane gave 4,7-bis(2′-thienyl)-2-dodecyl-2,1,3-benzotriazole (**1**) with a good yield of 75%. Further bromination of **1** with *N*-bromosuccinimide (NBS) in darkness afforded the target monomer **2** in a high yield of 87%. The chemical structure of **2** was confirmed by ^1H NMR, ^{13}C NMR, and elemental analysis (see Experimental Section for details). The three diboronic ester monomers were prepared according to published procedures.[26,27]

The BTA-based conjugated polymers PF-DTBTA, PCz-DTBTA, and PP-DTBTA were prepared by palladium(0)-catalyzed Suzuki coupling reactions with an equivalently molar ratio of the diboronic ester monomers to the BTA-based monomer **2** (Scheme 1). The alternating copolymers are quite soluble in common solvents such as chloroform, toluene, chlorobenzene, and tetrahydrofuran, etc., showing the special contribution of the 2-alkyl substitution on BTA to the solubility of the copolymers. The molecular weights of the copolymers are listed in Table 1. The M_w values of PF-DTBTA and PPh-DTBTA are around 20 kDa with polydispersity index (M_w/M_n) between 2.11 and 2.32. PCz-DTBTA possesses a high M_w of 296 kDa and a M_w/M_n value of 2.76. The elemental analyses of the copolymers are also listed in Table 1. The C, H, N, and S contents for the three alternating copolymers are very close to those calculated from the feed compositions. Thermal stability of the polymers was investigated with thermogravimetric analysis (TGA). PF-DTBTA and PCz-DTBTA possess comparable decomposition temperatures over 400 °C, higher than that of PPh-DTBTA (375 °C).

UV Absorption and Energy Level. The UV−vis absorption spectra of thin solid films of PF-DTBTA, PCz-DTBTA, and PPh-DTBTA are shown in Figure 1. PF-DTBTA shows absorption maximum at 481 nm and a right shoulder peak at 511 nm. There is no strong absorption at ~385 nm resulting from the fluorene segments.[6] The absorption edge of PF-DTBTA is at 554 nm. A similar absorption spectrum was also found for PCz-DTBTA, but showing slight red

Scheme 1



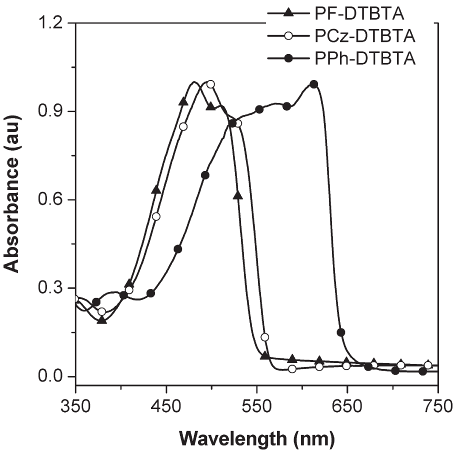


Figure 1. Normalized UV−vis absorption spectra of thin solid films of PF-DTBTA, PCz-DTBTA, and PPh-DTBTA.

shift. The main and shoulder peaks are at 495 and 523 nm, respectively, while the absorption edge is at 568 nm. The absorption spectra of PF-DTBTA and PCz-DTBTA indicate that the electronic configurations of electron-donating segments (fluorene, carbazole, and thiophene) and the electron-accepting unit (BTA) in the alternating copolymers are mixed and BTA-dominant. It should be noted that the absorption behaviors of PF-DTBTA and PCz-DTBTA are quite different from two separate absorption peaks of the already reported benzothiadiazole-based alternating copolymers with fluorene and carbazole as the donating segments.[6,7] The absorption spectrum of PPh-DTBTA is much more red-shifted, compared with those of PF-DTBTA and PCz-DTBTA. PPh-DTBTA shows absorption maximum at 612 nm and a left shoulder peak at 570 nm. Its absorption edge moves to 662 nm. Our results suggest that changing donating segment of a BTA-based copolymer would largely tune its absorption behavior, which is very useful for the design of the photovoltaic materials.

Table 2. Optical Band Gaps and Electrochemical Properties of the Films of Copolymers

copolymer	optical band gap[a] (eV)	E_{ox} (V)	HOMO[b] (eV)	LUMO[c] (eV)
PF-DTBTA	2.24	1.27	−5.67	−3.43
PCz-DTBTA	2.18	1.14	−5.54	−3.36
PPh-DTBTA	1.87	0.80	−5.20	−3.33

[a] Estimated with the absorption edges of thin solid films. [b] Calculated according to HOMO = $-e(E_{ox} + 4.4)$. [c] Calculated from HOMO level and the optical band gap.

The optical band gaps of the films of the copolymers estimated with the absorption edges of thin solid films are listed in Table 2. Their optical band gaps are between 2.24 and 1.87 eV. The HOMO levels of the copolymers were obtained from the onsets of oxidation potentials (E_{ox}) during cyclic voltammetry (CV) measurements. Their HOMO levels are at −5.67 eV for PF-DTBTA, slightly up-lying to −5.54 eV for PCz-DTBTA, and further up-lying to −5.20 eV for PPh-DTBTA (Table 2). The results indicate that the HOMO levels of the BTA-based polymers are mainly determined by the different electron-donating segments. The LUMO levels of the copolymers were calculated from the HOMO levels and resulting optical band gaps. The copolymers possess comparable LUMO levels between −3.43 and −3.33 eV, demonstrating that the LUMO levels of the BTA-based polymers are mainly dominated by the BTA unit.

Photovoltaic Properties. In the fabrication of BHJ PVCs, PCBM is the typical electron acceptor.[1] The HOMO and LUMO levels of PF-DTBTA, PCz-DTBTA, and PPh-DTBTA also match that of an electron donor for BHJ PVCs with the PCBM acceptor (Figure 2). Two device configurations of ITO/PEDOT (40 nm)/active layer (~75 nm)/Al (100 nm) and ITO/PEDOT (40 nm)/active layer (~75 nm)/PFN (5 nm)/Al (100 nm) were utilized to evaluate the photovoltaic performances of PVCs with the BTA-based conjugated copolymers as the donors. Our selection of PFN/Al, the bilayer cathode, in comparison with routine Al cathode, is to find the potential of the bilayer cathode in the photovoltaic device modifications. The PFN, a typical

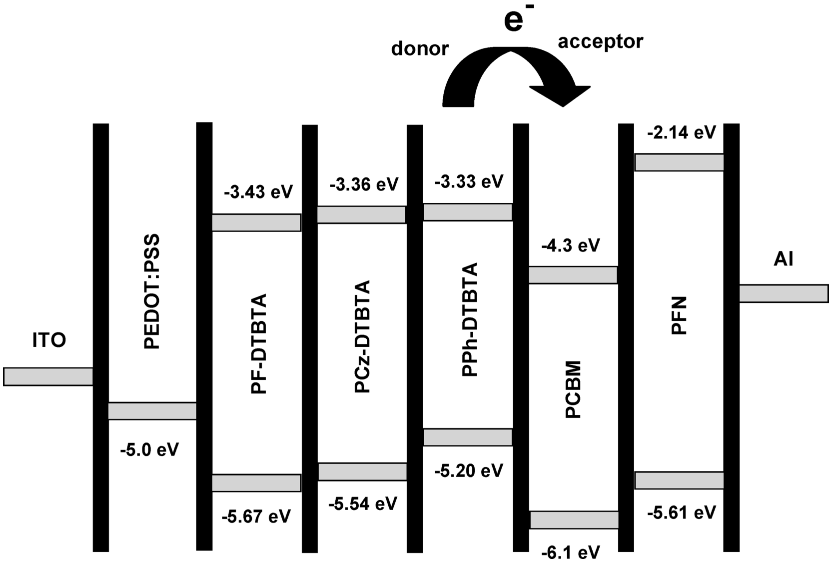


Figure 2. Energy level diagrams for the copolymers as the donors in photovoltaic cells.

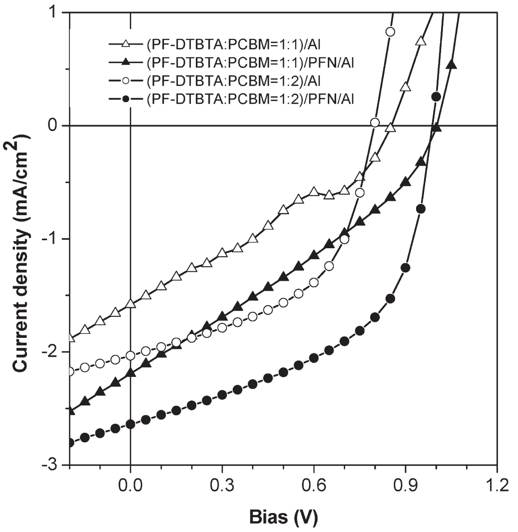


Figure 3. $I-V$ curves of photovoltaic cells based on PF-DTBTA using different cathodes (under illumination of AM1.5G at 100 mW/cm^2).

example of fluorene-based water/alcohol-soluble conjugated polymers, has shown excellent electron-injection ability in combination with high work-function metals such as Al, Ag, and even Au, in light-emitting diodes.[23,29−31] The fluorene-based water/alchohol soluble conjugated polymers also exhibited special improvements of carrier injections in *n*-channel thin-film transistors (TFTs).[32] The modifications of BHJ PVCs with the bilayer cathode have shown great reliance on the chemical structures of the polymer donors and the fluorene-based water/alcohol polymers.[24,33,34] Water-soluble polyfluorenes with alkylphosphonates and alkylamine salts on the side chains were found very effective for the elevations of V_{oc} for BHJ PVCs with poly(3-hexylthiophene) (P3HT) as the donor,[33,34] whereas almost no changing of V_{oc} was encountered for some other water-soluble polyfluorenes in P3HT-based BHJ PVCs.[24] The BTA-based conjugated polymers with different chemical structures, synthesized in this work, would supply useful information to understand the contribution of PFN on the photovoltaic performances.

The measurements of the photovoltaic performances of the BTA-based conjugated polymers as donors in BHJ PVCs with the two device configurations were carried out under illumination of AM1.5G simulated solar light at 100 mW/cm^2. Figure 3 shows the current density−voltage characteristics of BHJ PVCs with PF-DTBTA as the donor. Their PVC parameters are summarized in Table 3. For a PF-DTBTA: PCBM ratio of 1:1, the PVC with Al cathode showed V_{oc}, I_{sc}, and FF of 0.85 V, 1.58 mA/cm^2, and 30.2%, respectively. The PCE for the PVC is 0.4%. Using PFN/Al bilayer cathode obviously improved V_{oc} to 1 V and I_{sc} to 2.19 mA/cm^2. Despite the slight increase of FF, the PCE of the device (0.69%) showed a 70% increase in comparison with that of Al cathode. A PF-DTBTA:PCBM ratio of 1:2 was better for photovoltaic performance. The PVC with Al cathode showed V_{oc}, I_{sc}, and FF of 0.8 V, 2.03 mA/cm^2, and 51.2%, respectively, corresponding to PCE of 0.9%. Using PFN/Al bilayer cathode elevated V_{oc} to 1 V and I_{sc} to 2.64 mA/cm^2. The FF of the device almost did not change and the calculated PCE was 1.3%, with an increase of over 40%.

The current density−voltage characteristics of BHJ PVCs with PCz-DTBTA as the donor are shown in Figure 4. For a PCz-DTBTA:PCBM ratio of 1:1, the PVC with Al cathode showed V_{oc}, I_{sc}, and FF of 0.85 V, 3.96 mA/cm^2, and 38.5%, respectively, corresponding to a PCE of 1.29%, obviously higher than the case of PF-DTBDT (Table 3). Using PFN/Al bilayer cathode was found effective, showing improvements of V_{oc}, I_{sc}, and FF in the meantime, and the calculated PCE of 1.94% corresponded to an increase of 50%. A PCz-DTBTA:PCBM ratio of 1:2 showed better photovoltaic performances. The PVC with Al cathode displayed a PCE of 1.51%. Introducing PFN/Al bilayer cathode also largely enhanced the photovoltaic performance. The V_{oc} showed an increase of over 10% and the I_{sc} displayed an increase of 20%. The over 30% increase of FF to a value of 65.3% was more notable. The improvements of the three photovoltaic parameters gave a PCE of 2.75% for the PVC with PFN/Al bilayer cathode, which corresponded to a PCE increase of 80% in comparison with the case of Al cathode.

Figure 5 shows the current density−voltage characteristics of BHJ PVCs with PPh-DTBTA as the donor. For a PPh-DTBTA:PCBM ratio of 1:1, the PVC with Al cathode showed a low V_{oc} of 0.55 V (Table 3) due to the up-lying HOMO level of PPh-DTBTA. The I_{sc} and FF were 3.12 mA/cm^2 and 38.7%, respectively, giving a PCE of 0.66%. Using

Table 3. Photovoltaic Performances Based on the Copolymers Using Different Cathodes (Under Illumination of AM1.5G at 100 mW/cm^2)

active layer	cathode	V_{oc} (V)	I_{sc} (mA/cm^2)	FF (%)	PCE (%)	R_s[a] (Ω cm^2)
PF-DTBTA:PCBM = 1:1	Al	0.85	1.58	30.2	0.40	238
	PFN/Al	1.00	2.19	31.5	0.69	11.2
PF-DTBTA:PCBM = 1:2	Al	0.80	2.03	51.2	0.90	25.7
	PFN/Al	1.00	2.64	51.5	1.30	9.44
PCz-DBTA:PCBM = 1:1	Al	0.85	3.96	38.5	1.29	7.79
	PFN/Al	0.95	4.50	45.5	1.94	5.09
PCz-DBTA:PCBM = 1:2	Al	0.80	3.91	48.4	1.51	6.41
	PFN/Al	0.90	4.68	65.3	2.75	2.87
PPh-DBTA:PCBM = 1:1	Al	0.55	3.12	38.7	0.66	11.2
	PFN/Al	0.55	3.63	44.1	0.88	3.56
PPh-DBTA:PCBM = 1:2	Al	0.55	4.35	48.4	1.16	7.75
	PFN/Al	0.55	4.50	56.1	1.39	3.12

[a] Series resistance deduced from the inverse slope near V_{oc} in the $I-V$ curve.

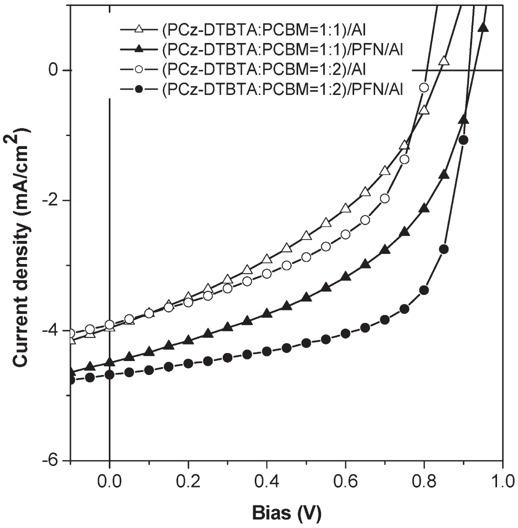


Figure 4. $I-V$ curves of photovoltaic cells based on PCz-DTBTA using different cathodes (under illumination of AM1.5G at 100 mW/cm^2).

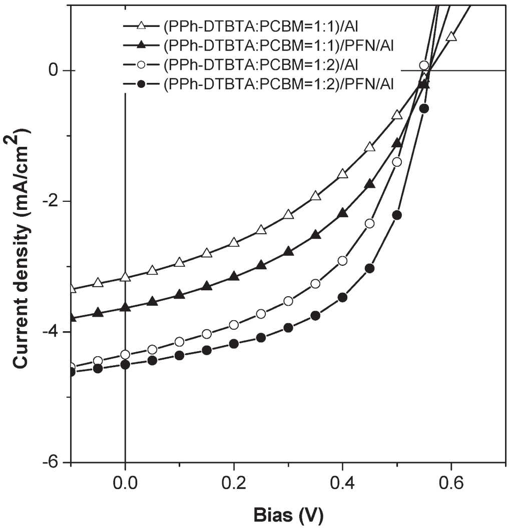


Figure 5. $I-V$ curves of photovoltaic cells based on PPh-DTBTA using different cathodes (under illumination of AM1.5G at 100 mW/cm^2).

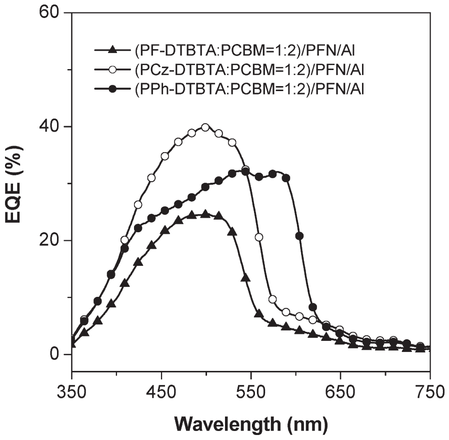


Figure 6. EQE curves of the photovoltaic cells with (polymer:PCBM = 1:2) as the active layer using PFN/Al bilayer cathode.

PFN/Al bilayer cathode showed no improvement to the V_{oc}. The elevations of I_{sc} and FF enhanced the PCE to 0.88%, with an increase of 30% relative the case of Al cathode. For a PPh-DTBTA:PCBM ratio of 1:2, BHJ PVC with Al cathode displayed V_{oc} of 0.55 V, I_{sc} of 4.35 mA/cm^2, and FF of 48.4%, corresponding to a PCE of 1.16%. No improvement of the V_{oc} was also found for the PFN/Al bilayer cathode. The slight increase of I_{sc} and FF enhanced the PCE to 1.39%, only showing an increase of 20% relative the case of Al cathode.

We measured the external quantum efficiency (EQE) of BHJ PVCs that showed the highest PCE for each of the three BTA-based copolymers (Figure 6). The maxima of the EQE are within 24%, 40%, and 32% for PF-DTBTA, PCz-DTBTA, and PPh-DTBTA, respectively. The wavelengths for the maxima of the EQE generally correspond to their UV−vis absorptions, indicating that the spectral responses of the BHJ PVCs are mainly determined by the polymer donors.

For BHJ PVCs with PF-DTBTA and PCz-DTBTA as the donors, V_{oc} values of the PVCs could all be elevated with the PFN/Al bilayer cathode whereas no such improvements were found for PVCs with PPh-DTBTA as the donor. The increased built-in potential due to the establishment of interfacial dipole with the PFN layer could be regarded as the origin of the enhanced V_{oc}. The different V_{oc} changing tendencies for the three BTA-containing polymer donors may also be related to their different V_{oc} losses of the PVC devices. According to an empirical calculation of V_{oc} with $[(|E_{\text{HOMO-donor}}| - |E_{\text{LUMO-PCBM}}|)/e - 0.3]$,[35] the anticipated V_{oc} values are 1.07, 0.94, and 0.6 V for PF-DTBTA, PCz-DTBTA, and PPh-DTBTA, respectively (see Figure 2). Without the PFN interlayer, the V_{oc} values of 0.8−0.85 V for PVCs with PF-DTBTA and PCz-DTBTA as the donors are obviously lower than the corresponding anticipated V_{oc} values. The increased V_{oc} values up to 1 V for PF-DTBTA and 0.9−0.95 V for PCz-DTBTA by inserting the PFN layer indicate that the V_{oc} losses could be recovered. For the cases with PPh-DTBTA as the donor, the V_{oc} values of 0.55 V for Al cathode already close to the anticipated V_{oc} of 0.6 V, meaning a limited V_{oc} loss if the error of its energy level measurement is considered. Therefore, no enhancement of V_{oc} was encountered when inserting the PFN layer.

As shown in Table 3, all the PVCs with the PFN/Al bilayer cathode could show improvements of I_{sc}, and it could be found that FF values could be increased in most cases with the PFN interlayer. Enhancement of the electron extraction from the acceptor phase to the cathode and decreasing hole−electron recombination in the active layer can result in the elevations of I_{sc} and FF. In a previous report, I_{sc} and FF were not improved in most cases with a group of alcohol/water-soluble polyfluorenes, including PFN, as interfacial layers for BHJ PVCs with PFO-DBT35 (a fluorene−BT random copolymer), P3HT, and MEH-PPV as the donors and PCBM as the acceptor.[24] The improvements of I_{sc} and FF in the present study may be related to the BTA heterocycles in the three BTA-based copolymers. A BTA heterocycle has three nitrogen atoms, and PFN also has polar amine groups on the side chains. Here we tentatively attribute elevations of I_{sc} and FF to the *N*−*N* interactions between the BTA-based polymer donors and the PFN. The effect of the *N*−*N* interactions may enhance the contact between the active layer and the PFN. Series resistances (R_s) of the BHJ PVCs, deduced from the inverse slope near V_{oc} in the $I-V$ curve, are summarized in Table 3. Inserting the PFN interfacial layer resulted in obvious decreases of R_s values for all the cases, confirming the modifications of interfacial contacts. It should be noted that the improvements of I_{sc} and FF were the most significant for PCz-DTBTA among the three BTA-based copolymers, especially for the case with PCz-DTBTA:PCBM = 1:2 as the active layer. A carbazole is also a *N*-heterocycle, which may contribute additional *N*−*N* interactions between the polymer donor and the PFN.

Conclusions

In summary, three BTA-based conjugated polymers PF-DTBTA, PCz-DTBTA, and PPh-DTBTA, with electron-donating segments of fluorene, carbazole, and dialkoxybenzene, respectively, were successfully synthesized as new polymeric donors in BHJ PVCs. All the copolymers exhibited good solubility in common organic solvents and good thermal stability. The band gaps and energy levels of the copolymers could be effectively tuned by changing the electron-donating segments on the main chain. The HOMO levels of the copolymers were determined by the electron-donating segments while their LUMO levels were mainly dominated by the BTA unit. For a blend ratio of polymer:PCBM = 1:2, BHJ PVCs with Al cathode displayed PCE values of 0.9%, 1.51%, and 1.16% for PF-DTBTA, PCz-DTBTA, and PPh-DTBTA, respectively. Using PFN/Al bilayer cathode could elevate V_{oc} if V_{oc} loss was encountered when using Al cathode. Using PFN/Al bilayer cathode could also improve I_{sc} and FF for the three BTA-based copolymers, from which *N*−*N* interactions between the BTA-based polymers and the PFN were proposed. Consequently, PFN/Al bilayer cathode elevated PCE values to 1.3%, 2.75%, and 1.39% for PF-DTBTA, PCz-DTBTA, and PPh-DTBTA, respectively. The most significant increasing of PCE with a calculated value of 80% was found for PCz-DTBTA as the donor, and this might be related to the additional *N*−*N* interactions between the carbazole segments and the PFN. The results would supply useful information to understand the contribution of an interfacial layer on the photovoltaic performances. Our results also suggest that the bilayer cathode would have great potential to elevate PCE of BHJ PVCs.

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