

Largely Enhanced Efficiency with a PFN/Al Bilayer Cathode in High Efficiency Bulk Heterojunction Photovoltaic Cells with a Low Bandgap Polycarbazole Donor

Zhicai He, Chen Zhang, Xiaofeng Xu, Lianjie Zhang, Liang Huang, Junwu Chen,*
Hongbin Wu,* and Yong Cao

Polymeric photovoltaic cells (PVCs) have attracted considerable attention over the past several years because of their unique advantages of low cost, light weight, and great potential for the realization of flexible and large-area devices.^[1,2] Typically, bulk heterojunction (BHJ) PVCs, a promising device configuration for high power conversion efficiency (PCE), involve the use of a phase-separated blend of an electron-donating conjugated polymer and an electron-accepting fullerene derivative as the active layer.^[3–10] Judicious design of a polymer donor and selection of a fullerene acceptor have realized high efficiency BHJ PVCs with PCE values over 5%.^[11–16] Tremendous efforts have also been made to optimize the active layer formation and the device configuration. Many optimization methods, such as using different solvents to fabricate the active layer,^[4] thermal annealing of the active layer or the device,^[17] film forming speed,^[18] the addition of additives to the active layer,^[19] the use of an optical spacer,^[15] a tandem structure,^[20] an inverted configuration,^[21,22] a cathode interfacial layer,^[23] etc., have demonstrated effective improvements in the photovoltaic performance of BHJ PVCs.

There are several examples of cathode interfacial layers in BHJ PVCs. Inserting insulating LiF as the interfacial layer between a poly(2-methoxy-5-(3',7'-dimethyl-octyloxy))-p-phenylene vinylene:(6,6)-phenyl-C₆₁-butyric acid methyl ester (MDMO-PPV:PCBM) active layer and Al cathode was an early test, which showed an increase of the PCE of over 20%, attributable to the improvements of the open circuit voltage (V_{oc}) and fill factor (FF).^[23] Application of carboxylic acids as a self-assembled monolayer on top of ZnO could modify the interfacial property of ZnO/metal bilayer cathodes, from which photovoltaic performances of poly(3-hexylthiophene) (P3HT)-based PVCs with different metal contacts were largely improved.^[24] Some reports also described the potential of using alcohol/water-soluble polymers as the interfacial layer. It is the alcohol/water solubility of the polymers that avoids intermixing between the active layer and the subsequently deposited interlayer, and favors fabrication of all-solution-processed devices. Using

poly(ethylene oxide) (PEO) as the cathode interfacial layer for PVCs with a polyfluorene copolymer as the donor elevated the PCE from 1.2% to 1.8%, mainly because of an increase in V_{oc} .^[25] Water-soluble polyfluorenes with alkyl-phosphonates and alkyl-amine salts on the side chains were found to be very effective for the elevation of V_{oc} for PVCs with P3HT as the donor.^[26,27] It should be noted that all the above-mentioned modifications of P3HT-based PVCs could realize PCE values up to 4.21%.

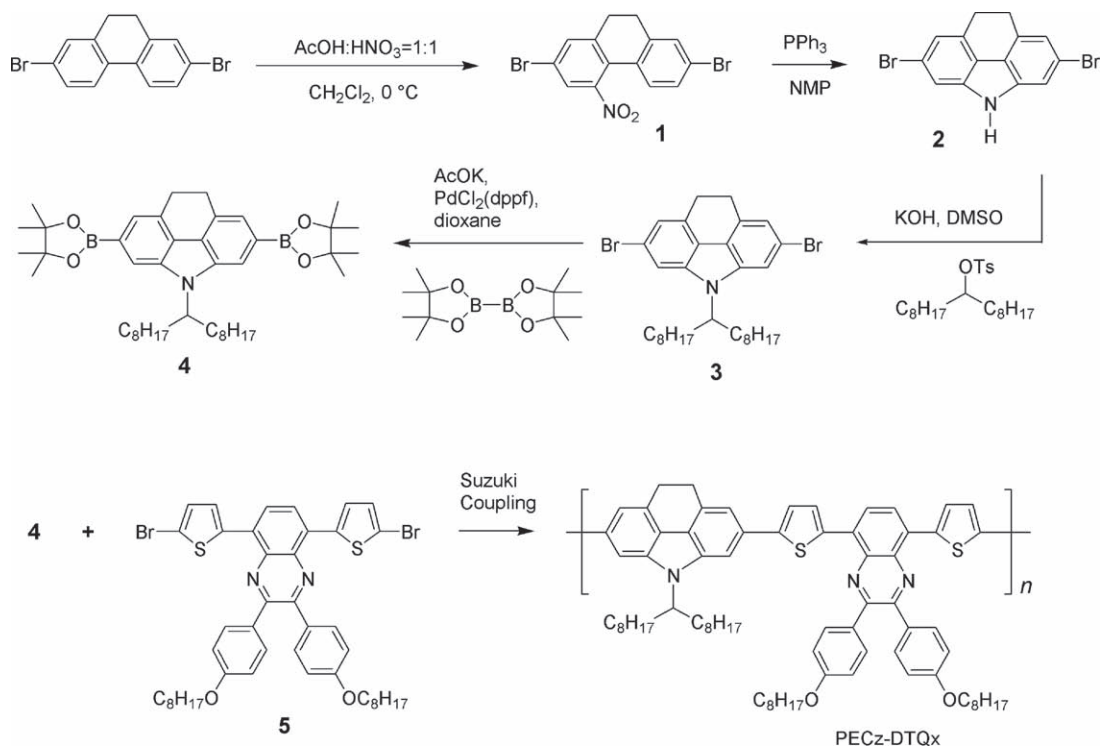
We are interested in introducing alcohol-soluble polymers as the interfacial layer in optoelectronic devices.^[28,29] Delighted by the excellent electron-injection ability of the alcohol-soluble polyfluorenes in combination with high work-function metals such as Al, Ag, and even Au, in light-emitting diodes,^[28] we have introduced different alcohol-soluble polymers as the cathode interfacial layer in PVCs.^[30–32] It was found that PCE improvements had great reliance on the chemical structures of the polymer donors and the alcohol-soluble polymers.^[31,32] Poly[(9,9-dioctyl-2,7-fluorene)-*alt*-(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)] (PFN), a typical example among alcohol-soluble polyfluorenes, was ineffective in P3HT and PPV-based PVCs, however, the PFN interlayer could elevate the PCE of a group of *N*-heterocycle-containing polymer donors.^[31,32] In particular, the most powerful improvement of the PCE of 80% was achieved with a PFN interlayer in a PVC with the benzotriazole-containing polycarbazole as the polymer donor, from which modified layer–layer contacts and N–N interactions between the polymer donor and the PFN interlayer were proposed for the recovery of V_{oc} loss existing in PVCs with a sole Al cathode as well as the improvements of short-circuit current (I_{sc}) and FF.^[32] So far, the final PCE values of PVCs with a PFN/Al bilayer cathode are still lower than 3%.

It would be more attractive if the modification with a cathode interlayer could be effective in high efficiency PVCs. In this communication, a low bandgap quinoxaline-containing poly(4,5-ethylene-2,7-carbazole) (PECz-DTQx) was synthesized. With PECz-DTQx:[6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM) in a ratio of 1:4 as the active layer, the PVC with an Al cathode displayed a good PCE of 3.99%. With PFN as the cathode interlayer, a high PCE of 6.07% was realized mainly as a result of obvious elevations of I_{sc} and FF. The increase of PCE with the bilayer cathode was 52%. The PCE with a PFN/Al bilayer cathode was also remarkably higher than that of 4.52% for a Ca/Al cathode that has been utilized in some high efficiency solar cells.^[10,12,16]

The 4,5-ethylene-2,7-carbazole is a new member of the carbazole family,^[8] and the 4,5-ethylene linkage enlarges the skeleton

Z. He, C. Zhang, X. Xu, L. Zhang, L. Huang, Prof. J. W. Chen,
Prof. H. B. Wu, Prof. Y. Cao
Institute of Polymer Optoelectronic Materials and Devices
State Key Laboratory of Physics and Chemistry of Luminescence
South China University of Technology
Guangzhou 510640, P. R. China
E-mail: psjwchen@scut.edu.cn; hbwu@scut.edu.cn

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Scheme 1. Synthetic procedures for PECz-DTQx.

of carbazole. Moreover, the 4,5-ethylene group has the possibility of being converted into a double bond, from which a novel carbazole with enhanced aromaticity and larger conjugation extent might be afforded. The synthetic procedures for PECz-DTQx are shown in **Scheme 1**. The nitration of 2,7-dibromo-9,10-dihydrophenanthrene with a mixture of fuming nitric acid and acetic acid readily gave compound **1**.^[33] Catalyzed by PPh_3 , heating a mixture of **1** in *N*-methyl-2-pyrrolidone at 190°C afforded the 4,5-ethylene-2,7-dibromocarbazole **2** in an 88% yield.^[33] The next alkylation reaction, toward *N*-9'-heptadecanylethylcarbazole **3**, was prepared according to a report by Leclerc et al.,^[34] with a yield of 62%. The diboronic ester **4** with a total yield of 55% after recrystallization in ethanol was synthesized by Miyaura coupling of **3** and bis(pinacolato)diboron, with $\text{PdCl}_2(\text{dppf})$ as the catalyst. The Suzuki coupling reaction of **4** and 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-octyloxyphenyl)quinoxaline **5** afforded the PECz-DTQx with a weight-average molecular weight, M_w , of 50.7 kDa and M_w/M_n of 2.09, where M_n is the number-average molecular weight, which showed good solubility at room temperature in chloroform, tetrahydrofuran (THF), chlorobenzene, and 1,2-dichlorobenzene.

UV-vis absorption spectra of PECz-DTQx are shown in **Figure 1**. The THF solution of PECz-DTQx displayed absorptions from the 4,5-ethylenecarbazole and 5,8-dithienylquinoxaline^[35] units at 391 and 535 nm, respectively. The photoluminescence (PL) spectrum of the solution (**Figure 1**) showed a red emission with a peak at 633 nm. A slight red-shift could be found from the absorption spectrum of the thin solid film of PECz-DTQx. The corresponding absorptions of the two building blocks were at 401 and 557 nm, respectively. The 4,5-ethylene linkage of the 2,7-carbazole generates slight red-shifts of absorptions

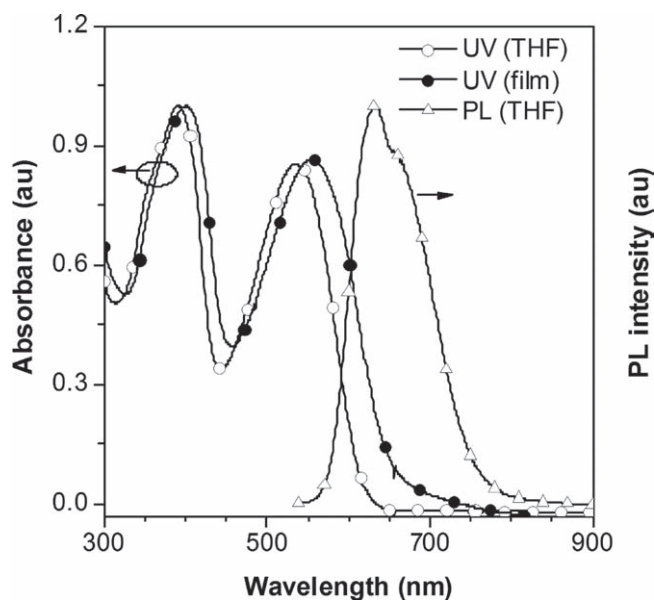


Figure 1. Normalized UV-vis absorption spectra of a THF solution and thin solid film of PECz-DTQx and a PL spectrum of PECz-DTQx in THF.

in solution and in a film, in comparison to those of a classic 2,7-carbazole in polymers.^[34] The absorption edges also moved from 650 nm in solution to ≈ 730 nm in a film. The optical bandgap of PECz-DTQx, calculated from the onset of the film absorption, was 1.7 eV. The highest occupied molecular orbital (HOMO) level of PECz-DTQx, obtained from the onset of oxidation potential during cyclic voltammetry (CV) measurement,

was -5.15 eV. The lowest unoccupied molecular orbital (LUMO) level of -3.45 eV for the polymer was calculated from the HOMO level and the optical bandgap.

Typically, two device configurations of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (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 PECz-DTQx as the donor and PC₇₁BM as the acceptor. The photovoltaic performances of the PVCs with three blend ratios (PECz-DTQx:PC₇₁BM) from 1:1 to 1:4 were investigated under illumination of AM1.5G simulated solar light at 100 mW cm^{-2} (Table 1). The active layers were spin-coated from chlorobenzene solutions while the PFN interlayer was spin-coated from its methanol solution. In addition, a PVC with a Ca/Al cathode was fabricated for the active layer of PECz-DTQx:PC₇₁BM = 1:4 for comparison.

For PECz-DTQx:PC₇₁BM ratios of 1:1 and 1:2, PVCs with an Al cathode showed a V_{oc} of 0.7 V, which was elevated to 0.85 V by using the PFN/Al bilayer cathode. The I_{sc} and FF were improved with the PFN/Al bilayer cathode. Thus the PCE values of PVCs with the PFN/Al bilayer cathode were all largely elevated over 60% in comparison with those with an Al cathode. A PECz-DTQx:PC₇₁BM ratio of 1:4 was the best among the studied blend ratios, and the I - V curves of PVCs with the two device configurations are shown in Figure 2a. The PVC with Al cathode showed V_{oc} , I_{sc} , and FF values of 0.78 V, 9.1 mA cm^{-2} , and 56.3%, respectively, corresponding to a good PCE of 3.99%. The PCE is over two times greater in comparison with the efficiency of a polymer analog derived from 5,8-dithienylquinoxaline and a classic 2,7-carbazole (with the same device configuration), possibly because of the difference of solubility of the polymers.^[36] Using a PFN/Al bilayer cathode further modified the three photovoltaic parameters of the PECz-DTQx-based PVC: V_{oc} up to 0.81 V, I_{sc} up to 11.4 mA cm^{-2} , and FF up to 65.8%. The PCE of the solar cell was 6.07%, showing an increase of over 50% in comparison with that with an Al cathode. The averaged PCE of five PVCs was 6%. For the reference PVC with a Ca/Al cathode, a PCE of 4.52% was

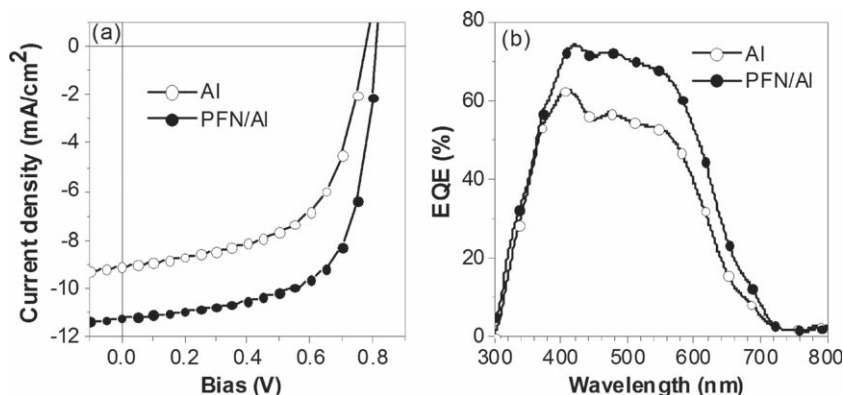


Figure 2. a) I - V curves and b) external quantum efficiency (EQE) curves of solar cells with PECz-DTQx:PC₇₁BM = 1:4 as the active layer when using different cathodes.

obtained, based on V_{oc} , I_{sc} , and FF values of 0.8 V, 9.84 mA cm^{-2} , and 57.4%, respectively. The three photovoltaic parameters were all slightly higher than those of the PVCs with an Al cathode, however, the I_{sc} and FF values were still much lower than those with the PFN/Al bilayer cathode. In order to determine whether methanol, the solvent of PFN, plays a role in the improvement of device efficiency as a result of spin-coating, a control device was fabricated in the same batch of cathode deposition by spin-coating of methanol (without PFN) at the same spin-speed and duration (2000 rpm for 30 s) prior to Al deposition. The device performance of the methanol pretreated device was identical to that without methanol treatment. This fact indicates that solvent alone does not contribute to surface modification in the PECz-DTQx:PC₇₁BM device and the improvements of device parameters were exclusively a result of introducing a thin PFN layer.

Figure 2b shows the external quantum efficiency (EQE) of PVCs with PECz-DTQx:PC₇₁BM = 1:4 as the active layer. The maximum EQE values for the solar cells with an Al cathode and PFN/Al bilayer cathode were 61% and 74% at ≈ 418 nm, respectively. The EQE values for the PVC with the bilayer cathode could be higher than 60% in the wavelength range between 380 and 580 nm.

As proposed in a previous report,^[32] PECz-DTQx could supply the necessary N-N interactions at the interface between the polymer donor and PFN. The polar PFN layer could also establish good interface contact with the Al cathode, which was proved by many experimental results in light-emitting diodes.^[29] As listed in Table 1, inserting the PFN layer resulted in an obvious decrease of series resistances (R_s) for all the cases, which confirmed the expected contact modification in the PECz-DTQx-based PVCs. Using PECz-DTQx:PC₇₁BM = 1:4 as the active layer, the R_s value for the PVC with the PFN/Al bilayer cathode was also lower than that with the Ca/Al cathode. The modified contacts by the PFN interlayer could enhance the electron extraction from the acceptor phase to the metal cathode and decrease the hole-electron recombination in the active layer, according to the obvious elevations of I_{sc} and FF when inserting the PFN interlayer. A target PCE of 8–10% had been proposed for the development of PVCs.^[1] Our experimental results, as demonstrated by the PECz-DTQx-based PVCs, suggest that a bilayer cathode would be highly valuable for a device configuration to achieve the target PCE by judicious design of a high-performance polymer donor.

Table 1. Photovoltaic performances of PECz-DTQx using different cathodes (under irradiation of AM1.5G at 100 mW cm^{-2}).

PECz-DTQx: PC ₇₁ BM	Cathode	V_{oc} [V]	I_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	R_s [$\Omega \text{ cm}^2$] ^{a)}
1:1	Al	0.70	5.83	40.9	1.70	13
1:1	PFN/Al	0.85	6.82	49.7	2.94	2.8
1:2	Al	0.70	8.13	45.6	2.60	65
1:2	PFN/Al	0.85	8.32	60.5	4.28	3.6
1:4	Al	0.78	9.10	56.3	3.99	15
1:4	PFN/Al	0.81	11.4	65.8	6.07	7.2
1:4	Ca/Al	0.80	9.84	57.4	4.52	10

^{a)}Series resistance deduced from the inverse slope near V_{oc} in the I - V curve.

In conclusion, 4,5-ethylenecarbazole derivatives, including 2,7-dibromo and 2,7-diboron monomers, have been designed and synthesized for the construction of new polymeric donors in solar cells. The 4,5-ethylene linkage increases the skeleton of a carbazole. An alternating copolymer PECz-DTQx derived from a 4,5-ethylene-2,7-carbazole and a 5,8-dithienylquinoxaline was prepared, which showed good solubility in common solvents at room temperature. With PECz-DTQx:PC₇₁BM = 1:4 as the active layer, solar cells with a PFN/Al bilayer cathode displayed PCEs up to 6.07% due to obvious improvements of I_{sc} and FF, in comparison with those with Al and Ca/Al cathodes. The PFN could establish better interfacial contacts by decreasing the series resistance, resulting in enhanced electron collection at the cathode and decreasing the possibility of hole–electron recombinations in the active layer. A bilayer cathode could be highly valuable for device configurations to achieve a target PCE of 8–10% in combination with a high-performance polymer donor.

Experimental Section

The synthesis and characterization of the monomers and the fabrication of the PVC devices are described in the Supporting Information.

Poly[N-9'-heptadecan-4,5-ethylenecarbazole-alt-5,8-bis(2'-thienyl)-2,3-bis(4-octyloxyphenyl)quinoxaline] (PECz-DTQx): Carefully purified 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,5-ethylene-N-9'-heptadecanecarbazole **4** (342 mg, 0.5 mmol), 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-octyloxyphenyl)quinoxaline **5** (430.4 mg, 0.5 mmol), (PPh₃)₄ Pd⁰ (9 mg, 0.0075 mmol), and Aliquat 336 (two drops) were dissolved in a mixture of toluene (15 mL) and aqueous 2 M K₂CO₃ (2 mL). The solution was refluxed with vigorous stirring for 72 h. At the end of the polymerization, a small amount of bromobenzene was added as a monofunctional end-capping reagent to remove the 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. The deep red polymer powder was dried under vacuum at 50 °C for 2 d to give 525 mg of the final product (93%). Gel permeation chromatography: M_w 50.7 kDa; M_w/M_n 2.09. ¹H NMR (300 MHz, CDCl₃, δ): 8.14 (s, 2H), 7.93 (s, 2H), 7.85 (d, 4H), 7.59 (s, 2H), 7.43 (d, 4H), 6.96 (d, 4H), 4.53 (m, 1H), 4.03 (s, 4H), 3.44 (m, 4H), 2.38 (m, 2H), 2.03 (m, 2H), 1.84 (m, 4H), 1.51 (m, 4H), 1.41–1.15 (m, 44H), 0.90 (m, 6H), 0.77 (m, 6H). Anal. calcd for (C₇₅H₉₁N₃O₂S₂)_n: C 79.53, H 8.28, N 3.71, S 5.66; found: C 78.81, H 7.90, N 3.52, S 5.82.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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