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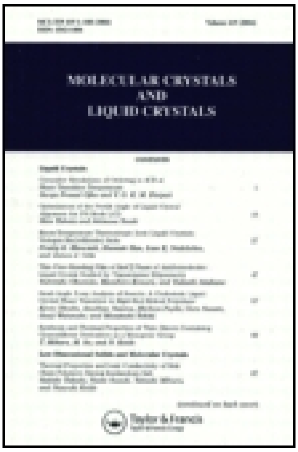

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Study on Low-Band Gap Polymers Based on Diketopyrrolopyrrole for Organic Photovoltaic Applications

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Study on Low-Band Gap Polymers Based on Diketopyrrolopyrrole for Organic Photovoltaic Applications

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Two kinds of low-band gap polymers, poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{3,6-bis(phenylene-1,4-diyl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo[3,4]pyrrole-1,4-dione}], poly(Cvz-PhDPP) and poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{3,6-bis(pyridinyl-5-yl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo[3,4]pyrrole-1,4-dione}], poly(Cvz-PyDPP), were synthesized by palladium-catalyzed Suzuki polymerization. Bulk heterojunction solar cells with an ITO/PEDOT/polymer:PC$_{71}$BM/LiF/Al configuration were fabricated, which shows open-circuit voltage, short-circuit current density, fill factor, and power conversion efficiency of 0.76 V, 4.01 mA/cm^2, 0.35, and 1.07% under AM 1.5 irradiation (100 mW/cm^2), respectively.

Keywords π-conjugated polymer; diketopyrrolopyrrole; organic photovoltaics

Introduction

Since the first organic photovoltaics (OPVs) were developed in 1985 [1], the study about OPVs have been continued steadily and the efficiencies of OPVs have dramatically increased for last two decades. OPVs have many advantages such as low cost, low weight, possibility of solution processing, and a realizable possibility of flexible displays by using flexible substrates. The power conversion efficiency (PCE) of OPVs above 8% were reported recently [2] and it is expected to reach the efficiency about 15% in the near future. To enhance the PCE, various efforts were tried such as synthesis of new electron acceptors and donors [3], changing the type of active layer [4], device structure [5], and also developing the charge transport materials.

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One of the important factors for increasing the PCE is regarded as developing the electron donors, which absorb the light directly. Various π-conjugated polymers have been used for electron donors such as polythiophenes, polycarbazoles [6] and diketopyrrolopyrrole (DPP) [7] and etc.

Among the π-conjugated polymers, DPP derivatives have attracted great attention and have been used various molecular electronics such as OPVs, organic thin film transistor and organic light-emitting diodes. DPP unit is composed of two lactam units and their electron withdrawing effect causes the chromophore to have a high electron affinity. Lots of articles reported DPP derivatives, which have thiophene [8], furan [9] and benzene [10] as π-conjugation moiety and especially DPP unit introduced thieno[3,2-b]thiophene showed the PCE of 5.4% recently [11].

This paper reports the synthesis and characterization of a novel low-band gap polymers, poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{3,6-bis(phenylene-1,4-diyl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo[3,4]pyrrole-1,4-dione}], poly(Cvz-PhDPP) and poly [{N-(1-octyldecyl)-2,7-carbazole)}-alt-{3,6-bis(pyridinyl-5-yl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo[3,4]pyrrole-1,4-dione}], poly(Cvz-PyDPP) and their characterization of photovoltaic properties of bulk heterojunction solar cells.

Experimental

Materials

1,4-Diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 1,4-diketo-2,5-di(1-octyldecyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole (PhDPP), 9-heptadecanol, and 9-heptadecane p-toluenesulfonate were synthesized according to the literature [12,13]. 9-(Heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole was purchased from Luminescence Technology Corp.

Synthesis of 2-cyano-5-bromopyridine (1)

2,5-Dibromopyridine (5.00 g, 21.11 mmol) was dissolved in DMF (50 mL) and sodium cyanide (0.85 g, 17.34 mmol) and copper cyanide (1.5 g, 16.75 mmol) were added to this solution. The reaction mixture was heated to reflux for 6 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using methylene chloride/ethyl acetate/hexane (1:1:8) as an eluent to give 1 as a white solid (1.9 g, 49%). ^{1}H-NMR ($CDCl_3$, δ ppm): 8.80 (s, 1H), 8.00 (d, 1H), 7.60 (d, 1H). ^{13}C-NMR ($CDCl_3$, δ ppm): 152.5, 140.0, 132.1, 129.4, 125.0, 116.9

Synthesis of 3,6-di(3-bromopyridin-6-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (2)

2-Cyano-5-bromopyridine (1) (8 g, 43.71 mmol), potassium tert-butoxide (10.79 g, 96.17 mmol) and tert-amyl alcohol (40 mL) in a three neck flask (100 mL) were heated to 100°C. When the temperature reached, a solution of diisopropyl succinate (3.536 g, 17.49 mmol) in tert-amyl alcohol (10 mL) was added dropwise. The reaction mixture was stirred at 100°C for 24 h and cooled to 65°C. After added the acetic acid (17 mL), the reaction mixture was heated to the reflux for 1 h, the residue was filtered and washed with water and methanol and dried under vacuum to give red-brown solid (5.1 g, 65%). The product was used in the next step without further purification. Elemental analysis: calcd for $C_{16}H_8Br_2N_4O_2$: C, 42.89; H, 1.80; N, 12.50; found : C, 43.28; H, 1.83; N, 12.46

Synthesis of 3,6-di(3-bromopyridin-6-yl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo[3,4] pyrrole-1,4-dione (PyDPP)(3)

To a solution of 3,6-di(3-bromopyridin-6-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (2) (2.50 g, 5.579 mmol) in NMP (45 mL), potassium tert-butoxide (1.56 g, 13.95 mmol) was added and the reaction mixture was heated to 60°C. 9-Heptadecane p-toluenesulfonate (6.87 g, 16.74 mmol) in NMP (20 mL) was slowly added and the reaction mixture was stirred at 60°C for 24 h. After cooling to room temperature, it was poured into water (300 mL) and extracted with toluene (150 mL) with 3 times. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica using methylene chloride/hexane (1:1) as an eluent to give 3 (0.57 g, 11%).

^{1}H-NMR ($CDCl_3$, δ ppm): 8.76 (s, 2H), 8.49 (d, 2H), 8.01 (d, 2H), 4.87 (m, 2H), 2.91 (m, 4H), 1.70 (m, 4H), 1.19(m, 48H), 0.85(t, 12H). ^{13}C-NMR ($CDCl_3$, δ ppm): 163.3, 147.8, 146.78, 143.2, 140.1, 135.6, 118.4, 107.9, 45.2, 37.3, 34.5, 30.2, 29.9, 29.4, 28.2, 14.4

Synthesis of poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{3,6-bis(pyridinyl-5-yl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo[3,4]pyrrole-1,4-dione}], poly(Cvz-PyDPP) using Suzuki Reaction

3,6-Di(3-bromopyridin-6-yl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo[3,4]pyrrole-1,4-dione (3) (0.28 g, 0.304 mmol), 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetr-amethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (0.204 g, 0.304 mmol), palladium(II) acetate (6.83 mg, 0.0304 mmol), and tricyclohexyl phosphine (17.06 mg, 0.068 mmol) were added into round bottom flask (25 mL). Freshly distilled toluene (2 mL) was added and the reaction mixture was stirred at 90°C for 5 min. Then tetraethylammonium hydroxide (1 mL) was injected slowly into the reaction mixture and stirred for 48 h. After cooling the mixture to room temperature, it was poured into methanol for precipitation. A solid was obtained by filteration. The polymer was further purified by stirring in methanol and acetone for 24 h and passed through celite to remove oligomers and catalyst residues. After precipitating the resulting product in methanol, it was dried under reduced pressure to give dark red polymer. ^{1}H-NMR ($CDCl_3$, δ ppm): 8.27–7.40 (br, 14H, aromatic protons), 4.85–4.67 (br, 1H, methylene protons next to nitrogen of carbazole), 3.78–4.00 (br, 4H, methylene protons next to nitrogen of diketopyrrolopyrrole), 2.41–2.02 (br, 4H, methylene protons), 1.58- 1.02 (br, 48H, aliphatic protons), 0.92–0.75 (br, 12H, methyl protons). ^{13}C-NMR ($CDCl_3$, δ ppm): 163.1, 148.3, 145.2, 143.3, 140.0, 138.2, 129.4, 128.1, 127.0, 121.8, 118.7, 110.1, 106.5, 44.8, 39.2, 37.3, 34.6, 32.9, 32.1, 31.9, 29.9, 29.5, 29.3, 27.3, 22.9, 22.8, 19.9, 14.3, 11.6.

The poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{3,6-bis(phenylene-1,4-diyl)-2,5-di (1-octyldecyl)-2,5-dihydropyrrolo[3,4]pyrrole-1,4-dione}], poly(Cvz-PhDPP) was synthesized by using the same method of poly(Cvz-PyDPP). ^{1}H-NMR ($CDCl_3$, δ ppm): 9.09 (br, 2H, aromatic protons), 8.76 (br, 2H, aromatic protons), 8.24 (br, 4H, aromatic protons), 7.87–5.58 (br, 4H, aromatic protons), 5.24 (br, 2H, methylene protons next to nitrogen of diketopyrrolopyrrole), 4.70 (br, 1H, methylene protons next to nitrogen of carbazole), 2.34–2.03 (br, 4H, methylene protons), 1.63–1.16 (br, 80H, aliphatic protons), 0.85 (br, 18H, methyl protons). ^{13}C-NMR ($CDCl_3$, δ ppm): 163.4, 147.8, 146.5, 143.5, 140.1, 138.4, 135.4, 127.8, 125.7, 124.0, 122.7, 121.6, 118.6, 111.8, 107.9, 45.0, 39.3, 37.3, 34.5, 33.0, 32.2, 30.3, 29.9, 29.6, 28.2, 27.3, 24.7, 22.9, 22.8, 19.9, 14.3, 11.7.

Fabrication of Organic Photovoltaic Cells

Each glass substrate was coated with a transparent ITO electrode (110 nm thick, 10–15 Ω/square). The ITO-coated glass substrates were ultrasonically cleaned with detergent, distilled water, acetone, and isopropyl alcohol (IPA). The layer of 40 nm thick PEDOT:PSS (Baytron P) was spin-coated onto the pre-cleaned and UV-ozone treated ITO substrates. And then, spin-coated film baked in air at 150°C for 30 min. The poly(Cvz-PhDPP):$PC_{71}BM$ and poly(Cvz-PyDPP):$PC_{71}BM$ were dissolved in 1:1 weight ratio of chloroform and o-dichlorobenzene cosolvent system. The polymer solutions used in the device fabrication were filtered with 0.45μm PTFE syringe filter. Both poly(Cvz-PhDPP):$PC_{71}BM$ and poly(Cvz-PyDPP):$PC_{71}BM$ were blended at the different weight ratio from 1:1 to 1:5 and allowed to stir for 24 h. The active layer (80–90 nm) was spin-coated and dried at room temperature for 40 min. The LiF (0.5 nm) and Al cathode (120 nm) were deposited on the top of the active layer under vacuum less than $5.0 \times 10^{–6}$ torr, which yields a 9 mm^2 of active area per each pixel. The film thickness was measured with an α-Step IQ surface profiler (KLA Tencor, San Jose, CA). The performance of OPVs were measured using a calibrated AM1.5G solar simulator (Oriel$^{®}$ Sol3A^{TM} Class AAA solar simulator, models 94043A) with a light intensity of 100 mW/cm^2 adjusted using a standard PV reference cell (2 cm × 2 cm monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA) and a computer-controlled Keithley 236 source measure unit. Incident photon to current conversion efficiency (IPCE) spectrum was measured using Oriel$^{®}$ IQE-200^{TM}.

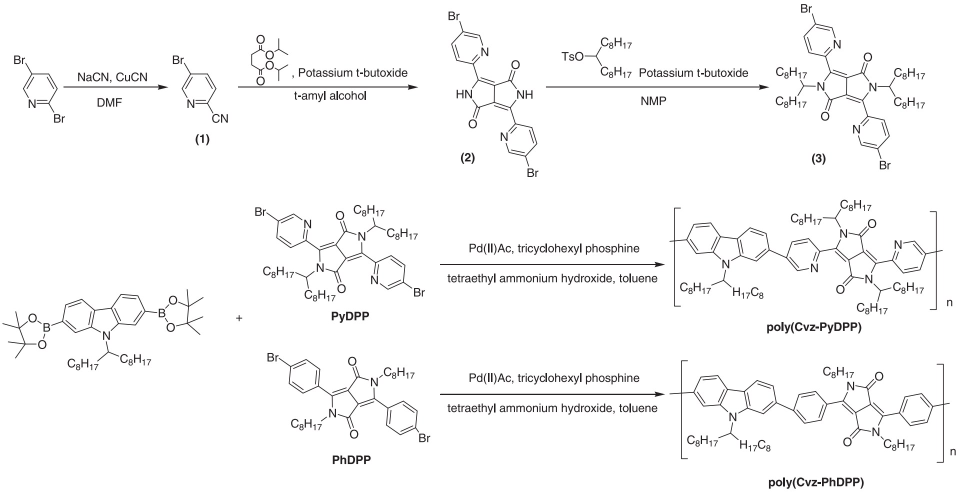
The PCE (η) of a solar cell given by

$$\eta = P_{out}/P_{in} = (J_{sc} \times V_{oc}) \times FF/P_{in}$$

with $FF = P_{max}/(J_{sc} \times V_{oc}) = (J_{max} \times V_{max})/(J_{sc} \times V_{oc})$, where P_{out} is the output electrical power of the device under illumination, and P_{in} is the intensity of incident light (e.g., in W/m^2 or mW/cm^2). V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, and fill factor (FF) is calculated from the values of V_{oc}, J_{sc}, and the maximum power point, P_{max}. All fabrication steps and characterization measurements were carried out in an ambient environment without a protective atmosphere. While measuring the current density-voltage (J-V) curves for OPVs, a black mask was used and only the effective area of the cell was exposed to light irradiation. The data reported in this paper was obtained by meaurements on five or more independently constructed devises.

Results and Discussion

Scheme 1 shows the synthetic routes for the monomer (PyDPP) and polymers. 2-Cyano-5-bromopyridine (1) was synthesized by Rosenmund-von Braun reaction [14] and then reacted with the diisopropyl succinate to give a 3,6-di(3-bromopyridin-6-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (2) and followed by alkylation with 9-heptadecane p-toluenesulfonate to give a 3,6-di(3-bromopyridin-6-yl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo[3,4]pyrrole–1,4-dione (3) (PyDPP) was obtained. These monomers, PhDPP



Scheme 1. Synthetic process of the poly(Cvz-PhDPP) and poly(Cvz-PyDPP).

and PyDPP, were copolymerized with 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole by Suzuki coupling polymerization. The resulting low-band gap polymers, poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{3,6-bis(phenylene-1,4-diyl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo [3,4]pyrrole-1,4-dione}], poly(Cvz-PhDPP) and poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{3,6-bis(pyridinyl-5-yl)-2,5-di(1-octyldecyl)-2,5-dihydropyrrolo [3,4]pyrrole-1,4-dione}], poly(Cvz-PyDPP), were completely soluble in various organic solvents such as chloroform, chlorobenzene, toluene, xylene, and THF. The molecular structures and thermal properties of the monomer and the polymers were identified by ^{1}H, ^{13}C NMR, UV-visible spectra, DSC, and TGA thermograms. The weight average molecular weight (Mw) and polydispersity index (PDI) were 77000, 2.4 for poly(Cvz-PhDPP) and 21000, 2.1 for poly(Cvz-PyDPP), respectively.

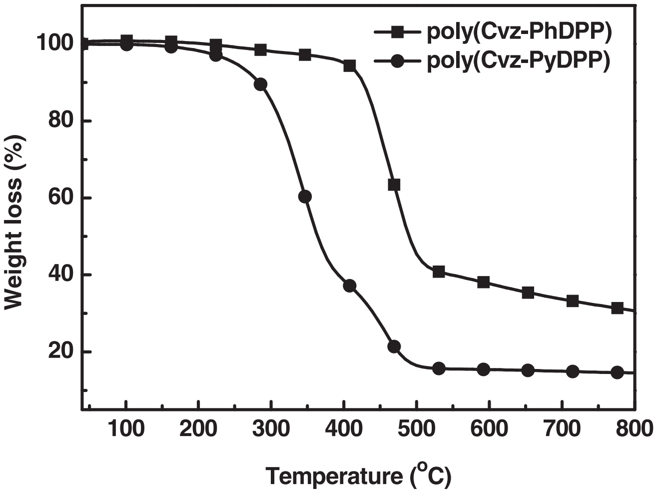


Figure 1. TGA thermograms of poly(Cvz-PhDPP) and poly(Cvz-PyDPP).

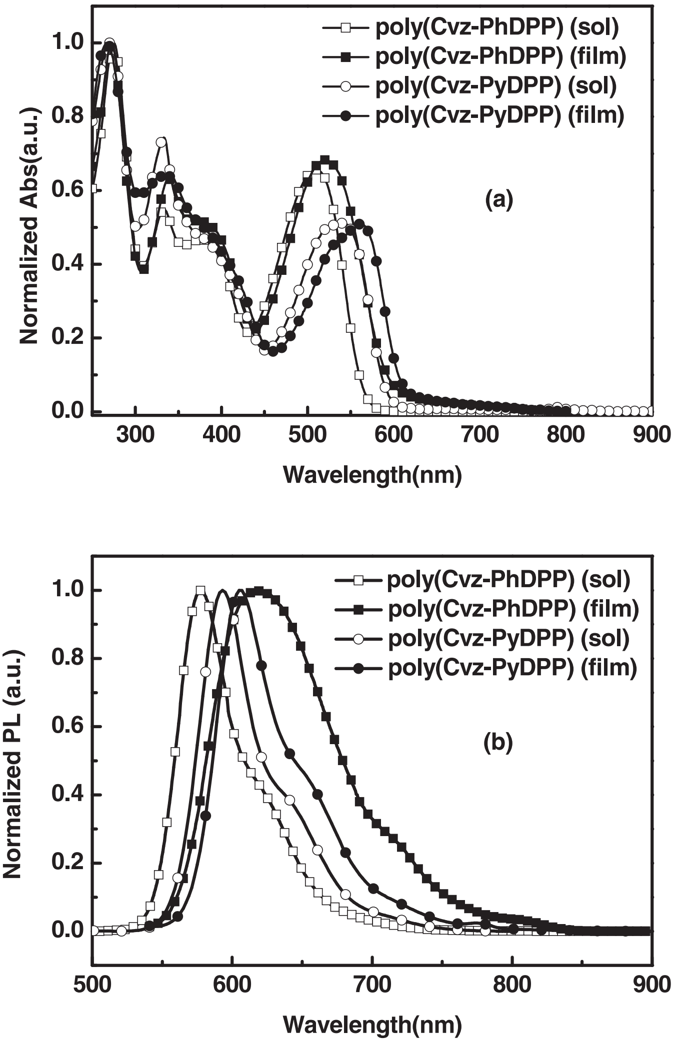


Figure 2. UV-visible absorption and PL spectra of poly(Cvz-PhDPP) and poly(Cvz-PyDPP).

The TGA results for poly(Cvz-PhDPP) and poly(Cvz-PyDPP) are shown in Fig. 1. The temperature of 5% weight loss and the glass transition temperatures were 398°C, 113°C for poly(Cvz-PhDPP) and 246°C, 30°C for poly(Cvz-PyDPP), respectively. Due to the introduction of longer alkyl chains in poly(Cvz-PyDPP), the thermal stability of poly(Cvz-PyDPP) is lower than that of poly(Cvz-PhDPP).

Fig. 2 shows the normalized UV-visible and PL spectra of the poly (Cvz-PhDPP) and poly(Cvz-PyDPP) in dilute chloroform solution and film state. The absorption spectra of the polymers contain two broad peaks at about 343 nm and 514 nm for poly(Cvz-PhDPP) and 334 nm and 548 nm for poly(Cvz-PyDPP) in solution and film states, respectively. These characteristics vibronic features can be attributed to the $\pi-\pi^*$ transitions of the carbazole and DPP segments. The energy band gaps (E_g) of the poly(Cvz-PhDPP) and poly(Cvz-PyDPP) estimated from the absorption edge of the film state is 2.05 and 2.03 eV, respectively. The PL spectrum of poly(Cvz-PhDPP) and poly(Cvz-PyDPP) has maxima at 619 and 606 nm with a shoulder at 652 and 708 nm in film state, respectively.

The electrochemical behavior of the poly(Cvz-PhDPP) and poly(Cvz-PyDPP) was examined by cyclic voltammetry (CV) in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF4) in anhydrous acetonitrile. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the poly(Cvz-PhDPP) and poly(Cvz-PyDPP) with respect to the ferrocene/ferrocenium (4.8 eV) standard were calculated from the CV and band gap from the optical absorption spectrum. HOMO and LUMO energy levels of poly(Cvz-PhDPP) and poly(Cvz-PyDPP) were −5.32 eV/−3.36 eV and −5.34 eV/−3.35 eV and the electrochemical band gaps were 1.96 eV and 1.99 eV, respectively.

To evaluate the photovoltaic performance of poly(Cvz-PhDPP) and poly(Cvz-PyDPP), we fabricated the OPVs with a structure of ITO/PEDOT:PSS (40 nm)/polymer:$PC_{71}BM$ (80 nm)/LiF (0.5 nm)/Al (120 nm) using poly(Cvz-PhDPP) and poly(Cvz-PyDPP) as an electron donor.

When we fabricated the OPVs by different ratios of poly(Cvz-PhDPP) and $PC_{71}BM$ from 1:1 to 1:5 ratio, the PCE was increased from 0.09% to 0.48%. It was due to the easily transportation of electrons from poly(Cvz-PhDPP) to $PC_{71}BM$. After studying the effect of electron donor to acceptor ratio, OPVs were made with different thickness of active layer and these results are given in Fig. 3 and Table 1. The best PCE of OPV was 1.07% with current density (J_{sc}) of 4.01 mA/cm^2, open-circuit voltage (V_{oc}) of 0.76 V and fill factor (FF) of 35.1%.

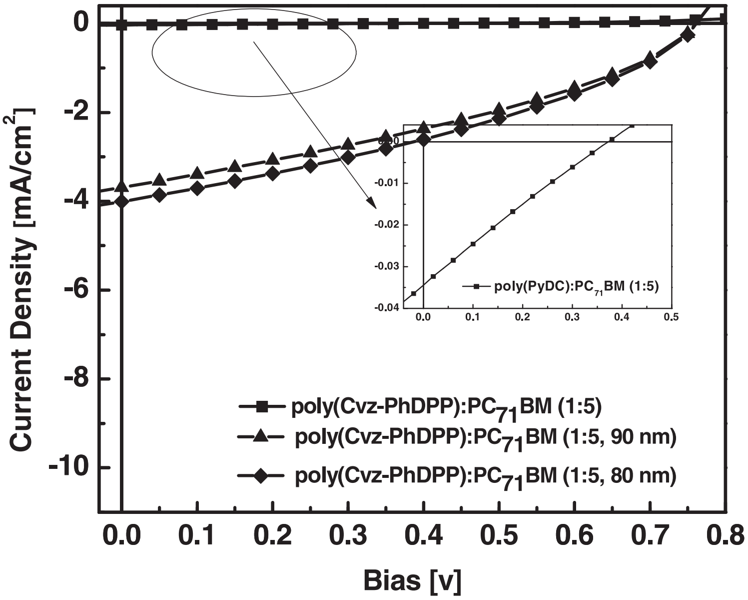


Figure 3. Current density-voltage (J-V) curves for the poly(Cvz-PhDPP):$PC_{71}BM$ (1:5) using different thickness of active layer and poly(Cvz-PyDPP):$PC_{71}BM$ (1:5) (inset).

Table 1. Photovoltaic properties of the devices made with using poly(Cvz-PhDPP) and poly(Cvz-PyDPP)

Active layer (Thickness)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
poly(Cvz-PhDPP) (90 nm)	0.76	3.69	34.6	0.97
poly(Cvz-PhDPP) (80 nm)	0.76	4.01	35.1	1.07
poly(Cvz-PyDPP) (80 nm)	0.37	0.034	23.62	0.003

Conclusions

A new class of low-band gap polymers, poly(Cvz-PhDPP) and poly(Cvz-PyDPP) were synthesized by Suzuki polymerization. Bulk heterojunction photovoltaic cells with an ITO/PEDOT:PSS/polymer:$PC_{71}BM$/LiF/Al configuration were fabricated with poly(Cvz-PhDPP) and poly(Cvz-PyDPP) as an electron donor and $PC_{71}BM$ as an electron acceptor. The maximum PCE of 1.07% (under an AM 1.5 simulated solar light at 100 mW/cm^2) (J_{sc}: 4.01 mA/cm^2, V_{oc}: 0.76 V, FF: 35%) was achieved with poly(PhDC):$PC_{71}BM$ (1:5 wt%).

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