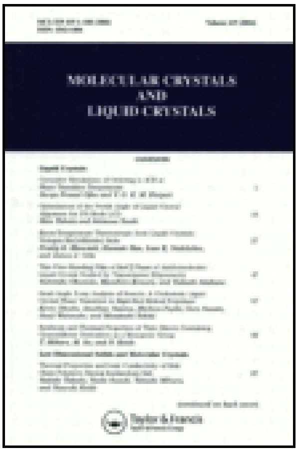

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Photovoltaic Properties of Poly(Carbazolyl-2,7-vinylene) Derivatives by Optimization of Cathode Structures

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Photovoltaic Properties of Poly(Carbazolyl-2,7-vinylene) Derivatives by Optimization of Cathode Structures

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The novel π-conjugated polymer, poly[N-(3,4-bis(decyloxy)phenyl)carbazolyl-2,7-vinylene)-co-*{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene}] (PCzV*-co-*MEH-PPV) was synthesized by using the Gilch polymerization method and used for the fabrication efficient photovoltaic cells. Bulk heterojunction photovoltaic cells, ITO/PEDOT:PSS/polymer:$PC_{61}BM$ (1:3, 1:4, 1:5 and 1:6 wt/wt)/Ca/Al configurations, were fabricated by blending of the PCzV*-co-*MEH-PPV with the fullerene derivative [6,6]-phenyl C61 butyric acid methyl ester (PCBM) were found to have a power conversion efficiency of up to 1.33%, measured using an AM 1.5 G solar simulator at 100 mW/cm^2 light illumination.*

Keywords Poly[N-(3,4-bis(decyloxy)phenyl)carbazolyl-2,7-vinylene)-*co*-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene}]; Bulk-heterojunction solar cell; Gilch polymerization; π-Conjugated polymers; PCBM

Introduction

The limited supply of main energy sources such as oil, coal and uranium will focus to replace most of the currently used power plants with renewable energy sources [1]. Organic photovoltaic cells have advantages over the inorganic thin film photovoltaic cells such as reduced material cost, possibility to make in large area cells, lightweight and low temperature solution process [2]. Recent advances in organic photovoltaic cells have allowed significant increase in the power conversion efficiency (PCE),

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which makes them economically interesting. Therefore, organic photovoltaic cells offer great technological potential as a renewable and alternative source for electrical energy. Organic photovoltaic cells are divided as bilayer heterojunction [3] and bulk heterojunction photovoltaic [4] cells by photoinduced electron transfer from optically excited π-conjugated polymers to the C_{60} derivatives. The essence of the bulk heterojunction photovoltaic cell is mixing donor and acceptor components in a bulk volume intimately so that each donor–acceptor interface will be within a distance less than the exciton diffusion length of each absorbing site. The interface dispersed throughout the bulk makes the exciton diffusion length small, which makes all excitons dissociated within their lifetime [5]. In this conception, the charges are also separated within the different phases. Hence, recombination is reduced to a large extent and the photocurrent often follows the light intensity linearly or slightly sublinearly. Therefore, the bulk heterojunction photovoltaic cells are much more sensitive to the nanoscale morphology in the blend. Another problem of π-conjugated polymers is that electron injection into cathode is much more difficult than hole injection due to the high LUMO energy level, resulting in an imbalance between the rates of electron and hole injection into the negative and positive electrodes [6]. Balancing the rates of injection of electrons and holes into opposite electrodes is crucial to achieve high photovoltaic performance. The use of low work function metal such as calcium, magnesium, or lithium as the cathode can lower the charge injection barrier at the cathode, which improves the photovoltaic performance by increasing the current density and fill factor. In this work, we studied the effect of different cathode structures on PCzV-co-MEH-PPV with PCBM. Different process parameter such as ratio of electron donor to electron acceptor ratio on the photovoltaic performance is also studied.

Experimental

Materials

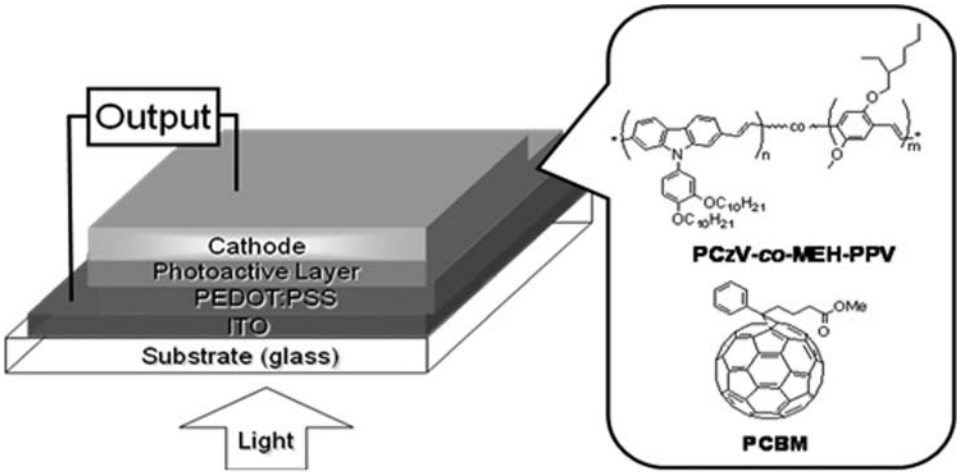
9-(3,4-Bis(decyloxy)phenyl)-2,7-bis(chloromethyl)carbazole and 1,4-bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxybenzene and the polymers were prepared according to the reported procedures [7, 8]. Soluble fullerene derivative [6,6]-phenyl C61 butyric acid methyl ester (PCBM) was synthesized using the procedure published earlier [9].

Bulk Heterojunction Photovoltaic Cell Fabrication and Measurements

Bulk heterojunction photovoltaic cells used to measure photovoltaic properties were constructed as follows. Each glass substrate was coated with a transparent ITO electrode (110 nm thick, 10–20 Ω/sq sheet resistance). The ITO-coated glass substrates were ultrasonically cleaned with detergent, deionized water, acetone, and isopropyl alcohol. The layer of 40 nm thick PEDOT:PSS (H.C.Stack, PH500) was spin-coated onto the pre-cleaned and UV-ozone treated ITO substrates. The spin-coated film was baked in air at 150°C for 30 min. For fabrication of the active layers composed of interconnected networks of electron donor and acceptor, 1,2-dichlorobenzene and chloroform (1:1 wt%) solutions of the synthesized polymer (10 mg/mL) and PCBM (15 mg/mL) were shaken at room temperature for 12 h. The polymer and PCBM blends was then prepared by mixing the two solutions and subsequent shaking for 12 h. Filtration using a 0.45 μm PTFE (hydrophobic) syringe filter gave the polymer blends with a ratio of the PCzV-*co*-MEH-PPV as an electron donor to the PCBM as an electron acceptor of 1:3, 1:4, 1:5, and 1:6 wt/wt, respectively. The bulk heterojunction photovoltaic cell structure was completed by depositing Ca (5 nm)/Al (100 nm) cathode as a top electrode under the pressure less than 3.0×10^{-6} torr in the vacuum evaporator attached with glove box onto the polymer active layer. The top metal electrode area, comprising the active area of the solar cells, was found to be 4 mm^2. Performance of the bulk heterojunction photovoltaic cells were measured using a AM 1.5G solar simulator (Oriel 300 W) at 100 mW/cm^2 light illumination after adjusting the light intensity using Oriel power meter (model No. 70260 which was calibrated using laboratory standards that are traceable to the National Institute of Standards and Technologies USA). Current density-voltage (I-V) curves were recorded using a standard source measurement unit (Keithley 236). All fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere. Thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ± 1 nm.

Results and Discussion

Scheme 1 represents the molecular structure of PCzV-*co*-MEH-PPV and the device configuration of the bulk heterojunction photovoltaic cell fabricated in this study. The polymer were found to be completely soluble in organic solvents such as chloroform, 1,2-dichlorobenzene, and THF. The high solubility of polymer is an important requirement for device fabrication. To improve photovoltaic performance, the resulting polymer was purified by using Soxhlet extraction with different solvents, including methanol, acetone and finally chloroform, in order to remove the unreacted monomers, impurities, and oligomers. The composition ratio of PCzV-*co*-MEH-PPV is calculated from the integration ratios of the 8.19–6.70 ppm and 4.26–3.29 ppm peaks in the ^{1}H-NMR. ^{1}H-NMR peak area calculations show that the actual composition of PCzV-*co*-MEH-PPV is 30:70 wt%. The weight-average molecular weight (M_w) and the polydispersity of the PCzV-*co*-MEH-PPV were found to be 79,900, 2.05, respectively. The thermal behaviors of the polymer were investigated by using DSC and TGA thermograms. PCzV-*co*-MEH-PPV has glass transition temperatures (T_g) of 78°C and this polymer has good thermal stabilities with a 5% weight loss temperature at 377°C under N_2 atmosphere. The high T_g value and thermal stability of PCzV-*co*-MEH-PPV indicate that this polymer can be used for the fabrication of bulk heterojunction photovoltaic cells



Scheme 1.

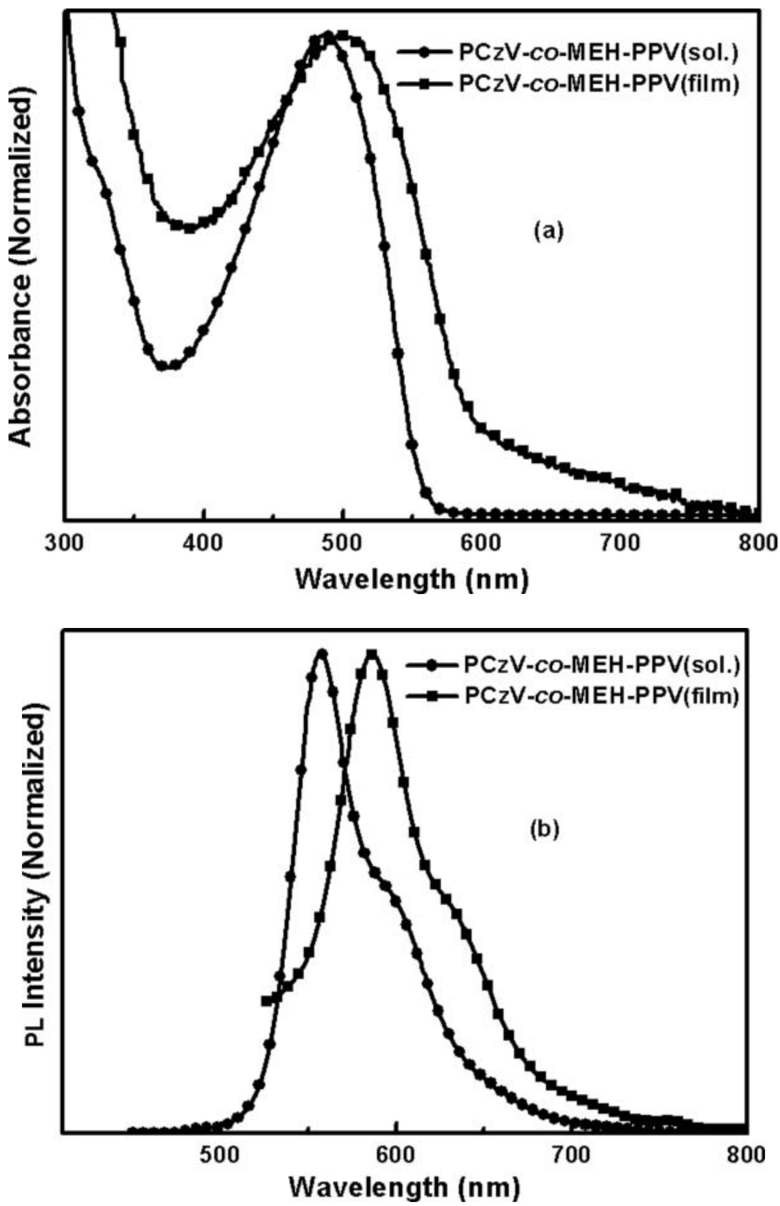


Figure 1. UV-visible absorption (a) and PL emission (b) spectra of PCzV-*co*-MEH-PPV.

without complications associated with deformation or degradation during operation of the solar cells.

In Figure 1a are shown the normalized UV-visible absorption spectra (Fig. 1a) of the PCzV-*co*-MEH-PPV in chloroform and in thin film state. The absorption spectrum of the PCzV-*co*-MEH-PPV has a maximum at 489 nm in the solution state and at 499 nm in the thin film state. Absorption band in thin film state is slightly red-shifted by *ca.* 10 nm compared to the solution state owing to interactions between the polymer chains. The optical band gap (E_g), calculated from the onset of the absorption of the PCzV-*co*-MEH-PPV, is 2.07 eV.

Photoluminescent (PL) spectrum of the PCzV-*co*-MEH-PPV has maxima at 556 nm and 596 nm in the solution state and at 585 nm and 631 nm in the thin film state as shown in Figure 1b. The disappearance of PL emission from PCzV in the PCzV-*co*-MEH-PPV copolymer indicates that efficient energy transfer takes place from the wide band gap PCzV segment to the small band gap MEH-PPV segment. Thus, the transfer of exciton energy from the PCzV segment to the MEH-PPV segment occurs mainly along the polymer chain and intermolecular energy transfer occurs in the PCzV-*co*-MEH-PPV.

To investigate the charge injection and transport property of PCzV-*co*-MEH-PPV and to determine the energies of their highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, redox measurements were carried using CV. The HOMO energy of PCzV-*co*-MEH-PPV for the standard ferrocene/ferrocenium (4.8 eV) is 5.34 eV. The respective LUMO energy, calculated based on the HOMO energy and the band gap determined by using UV spectroscopic analysis spectrum, for PCzV-*co*-MEH-PPV is 3.27 eV. The energy band diagrams of PCzV-*co*-MEH-PPV and PCBM are shown in Figure 2. The energy of this electron donor is well-matched to that of PCBM as an electron acceptor. Bulk heterojunction photovoltaic cells were fabricated using PCzV-*co*-MEH-PPV as electron donor and PCBM as an electron acceptor. Proper choice of the cathode is one of the important parameters in photovoltaic cell, because the barrier height between the metal cathode and the photoactive layer will affect the injection of charge separated electrons into the cathode electrode and thus the power conversion efficiency (PCE). In this paper, we chosen Ca/Al cathode instead of a pristine Al cathode in order to guarantee a good photovoltaic performance of bulk heterojunction solar cells. The bulk heterojunction photovoltaic cell structures are as follows: ITO/PEDOT:PSS/PCzV-*co*-MEH-PPV:PCBM/Ca (5 nm)/Al (100 nm). Many research groups have obtained best photovoltaic performances through optimization of the ratios of electron donor polymer to the electron acceptor PCBM

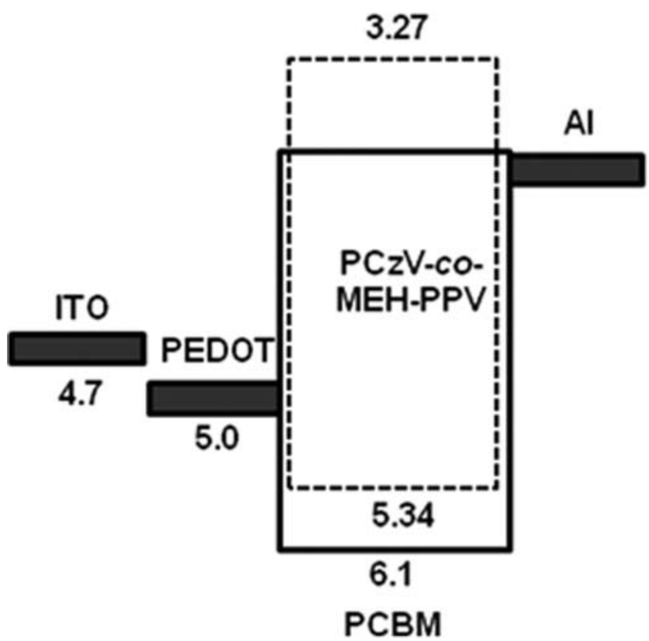


Figure 2. Energy level diagram of the components of the bulk-heterojunction photovoltaic cell.

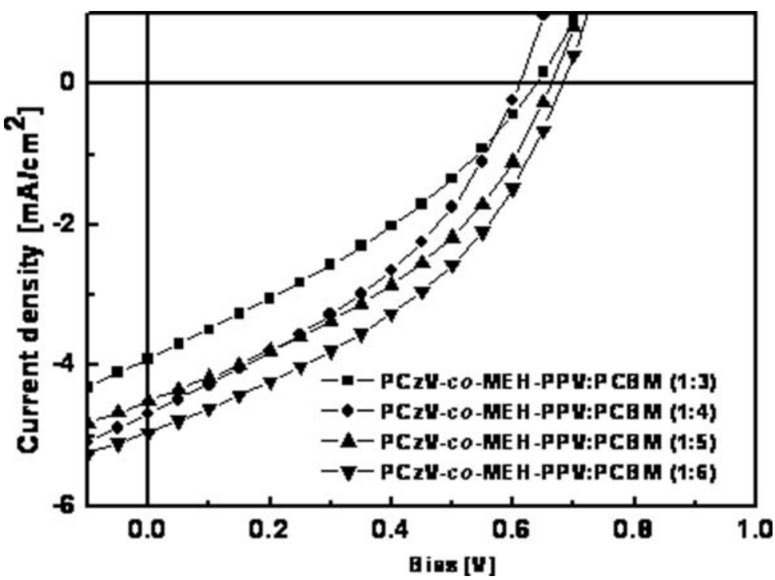


Figure 3. Current density-voltage characteristic of PCzV-*co*-MEH-PPV bulk-heterojunction photovoltaic cells containing different ratios of $PC_{61}BM$.

[10, 11]. The charge balance generally depends on the thickness of the active layer and the amount of PCBM in the polymer blended active layer. In this effort, we probed the effect of the ratios of PCzV-*co*-MEH-PPV and PCBM on photovoltaic performance using a 1,2-dichlorobenzene and chloroform mixed solvent system. The current density-voltage (J-V) characteristics of bulk heterojunction photovoltaic cells, fabricated with 1:3, 1:4, 1:5, and 1:6 ratios of PCzV-*co*-MEH-PPV to PCBM, under AM 1.5G illumination, are shown in Figure 3 and summarized in Table 1.

Open-circuit voltages (V_{oc}) of bulk heterojunction solar cells are closely related to the energy difference between the HOMO level of the electron donor and the LUMO level of the electron acceptor. The V_{oc} of all bulk heterojunction photovoltaic cells we constructed are almost identical, but higher short-circuit current densities (J_{sc}) and a higher fill factors

Table 1. Solar cell performance of PCzV-*co*-MEH-PPV as electron donor sand PCBM as the electron acceptor in ITO/PEDOT:PSS/PCzV-*co*-MEH-PPV:PCBM/Ca/Al devices

Active layer	V_{oc} (V) [a]	J_{sc} (mA/cm^2)[b]	FF (%)[c]	PCE (%)[d]
PCzV-*co*-MEH-PPV: PCBM (1:3 wt/wt)	0.64	3.91	32	0.81
PCzV-*co*-MEH-PPV: PCBM (1:4 wt/wt)	0.61	4.70	37	1.05
PCzV-*co*-MEH-PPV: PCBM (1:5 wt/wt)	0.66	4.51	39	1.15
PCzV-*co*-MEH-PPV: PCBM (1:6 wt/wt)	0.68	4.95	40	1.33

[a]V_{oc}: open-circuit voltage.
[b]J_{sc}: short-circuit current density.
[c]FF: fill factor.
[d]PCE: power conversion efficiency.

(FF) are observed with increasing $PC_{61}BM$ content in the blended active layer. The best photovoltaic performance of 1.33% was seen for a solar cell fabricated using a 1:6 ratio of PCzV-*co*-MEH-PPV:PCBM. For reference, the PCE of a bulk heterojunction photovoltaic cells made using a 1:3 ratio of PCzV-*co*-MEH-PPV:PCBM (1:3 wt/wt) is 0.81%.

Conclusions

Novel copolymer composed of poly(N-(3,4-bis(decyloxy)phenyl)carbazolyl-2,7-vinylene) (PCzV) and poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) repeating units was found to have high molecular weight and exhibit good solubility in common organic solvents. Due to the high thermal stability, PCzV-*co*-MEH-PPV is promising material for photovoltaic applications. Bulk heterojunction photovoltaic cells were fabricated using PCzV-*co*-MEH-PPV as donor material. Effect of electron donor to acceptor ratio (1:3, 1:4, 1:5 and 1:6 wt/wt) on the PCE was studied. The bulk heterojunction photovoltaic cells prepared with 100 nm thick photoactive layer and 1:6 donor to acceptor ratio have given the highest PCE. The device prepared PCzV-*co*-MEH-PPV:PCBM (1:6 wt/wt) has given the maximum PCE of 1.33% ($J_{sc} = 4.95$ mA/cm^2, $V_{oc} = 0.68$ V, FF = 40%).

Acknowledgment

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