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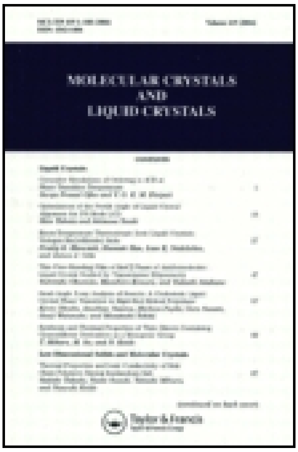

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Synthesis and Photovoltaic Properties of Low-Band Gap Copolymers Containing Perylene Diimide Derivatives

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Two kinds of low-band gap polymers, poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{1,7-di(4-tert-butylphenyloxy)-3,4,9,10-perylenebis(dicarboximide)-N,N′-di(2,6-dimethyl-phenyl-4-yl)}] poly(Cvz-PDIMEP) and poly{[N,N′-di(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide-1,7-diyl]-alt-(9-heptadecyl)-9H-carbazol-2-yl)} poly (Cvz-PDIC9), 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 short-circuit current density, open-circuit voltage, fill factor, and power conversion efficiency of 0.85 mA/cm^2, 0.32 V, 0.27, and 0.073% under AM 1.5 irradiation (100 mW/cm^2), respectively.

Keywords Bulk heterojunction solar cells; low-band gap polymers; perylene diimide; π-conjugated polymer

Introduction

Bulk heterojunction (BHJ) solar cells offer solar energy harvesting characterized by low cost, ease of processing, physical flexibility, and large area coverage [1,2]. Current progress on BHJ solar cells from the standpoint of increasing power conversion efficiency (PCE) is mainly attributed to the bulk heterojunction structure, which enables an efficient charge separation due to the increased photoactive interface area of p-n junction. The BHJ is typically attained by blending an electron donor (p-type) and an acceptor (n-type) molecule. The search of new materials with good photovoltaic performance as well as the improvement in the device fabrication has been a subject of importance.

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In order to increase the PCE of BHJ solar cells, many aspects should be taken into account, such as the absorption coefficients of the materials, the exciton dissociation rates and the charge carrier mobilities. We are interested in perylene diimide derivatives (PDIs), because PDIs have large molar absorption coefficients, good electron accepting properties [3] and possible generation of highly conducting direction along the π-π stacking axis [4–6], in addition to the other merits, like robust, thermally stable, and inexpensive. Up to date, most of the applications for PDIs were performed to dye-sensitized solar cells [7]. This paper reports the synthesis and characterization of a low-band gap polymers, poly{[1,7-di(4-tert-butylphenyloxy)-3,4,9,10-perylenebis(dicarboximide)-N,N′-di(2,6-dimethylphenyl-4-yl)]-alt-(9-heptadecyl)-9H-carbazol-2-yl)}, poly(Cvz-DIMEP) and poly{[N,N′-di(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide-1,7-diyl]-alt-(9-heptadecyl)-9H-carbazol-2-yl)}, poly(Cvz-PDIC9) and their characterization of photovoltaic properties of bulk heterojunction solar cells.

Experimental

1,7-Dibromoperylene-3,4,9,10-tetracarboxylic acid dianhydride and N,N′-di(heptadecanyl)perylene-3,4,9,10-bis(dicarboximide) were synthesized according to the literature [8]. N-(Heptadecanyl)-2,7-bis(4,4,5,5,-tetrametyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole was purchased from Lumtec Co.

Synthesis of N,N′-di(4-bromo-2,6-dimethylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (1)

1,7-Dibromoperylene-3,4,9,10-tetracarboxylic dianhydride (0.7 g, 1.272 mmol) and 4-bromo-2,6-dimethylaniline (2.54 g, 12.7 mmol) were added to propionic acid (11 mL) and purged with nitrogen. The reaction mixture was refluxed at 155°C for 72 h under a nitrogen atmosphere. To the cold reaction mixture, methanol (35 mL) was added. The precipitated product was isolated by filtration, and washed with methanol until the filtrate was colorless. The crude product was dried for 24 h at 50°C under vacuum. The compound was purified by column chromatography on silica gel using chloroform as an eluent afforded 0.81g of a red solid (70%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 2.18 (s, 12H), 7.42 (s, 4H), 8.8 (d, 2H), 9.0 (s, 2H), 9.58 (d, 2H),

Synthesis of N,N′-di(4-bromo-2,6-dimethylphenyl)-1,7-di[4-tertbutyl) phenoxy]perylene-3,4,9,10-tetracarboxydiimide (2)

N,N′-di(4-bromo-2,6-dimethylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (1 g, 1.09 mmol), 4-tertbutylphenol (0.54 g, 3.61 mmol) and potassium carbonate (0.25 g, 1.8 mmol) were added to NMP (20 mL), and purged with nitrogen. The reaction mixture was stirred for 48 h at 80°C. After cooling to room temperature, the mixture was poured into a hydrochloric acid (10%, 36 mL) and methanol (54 mL). The precipitated product was isolated by filtration, washed with 150 mL of a methanol/water mixture (3:2) and dried for 24 h at 50°C under vacuum. Column chromatography on silica gel with chloroform as an eluent afforded 0.64 g of a red solid (55%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 1.36 (s, 18H), 2.18 (s, 12H), 7.1 (d, 4H), 7.38 (m, 4H), 7.5 (d, 4H), 8.4 (d, 2H), 8.7 (m, 2H), 9.7 (m, 2H).

Synthesis of 1,7-dibromo-N,N′-di(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide (4)

N,N′-di(10-nonadecyl)perylene-3,4,9,10-bis(dicarboximide) (1.4g, 1.51 mmol) was dissolved in methylene chloride (30 mL). After raising the temperature until 60°C, bromine (5.28 mL, 0.103 mol) was added and stirred at 60°C for 4 h. The reaction mixture was allowed to reach the room temperature. After removing the excess of bromine by air bubbling, the solvent was removed under vacuum. Column chromatography on silica gel with chloroform/hexane (2:3) as an eluent afforded 1.47g of a deep red solid (90%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 0.85 (t, 12H), 1.25 (m, 56H), 1.85 (m, 4H), 2.25 (m, 4H), 5.20 (m, 2H), 8.70 (br, 2H), 8.91 (br, 2H), 9.52 (d, 2H).

Synthesis of poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{1,7-di(4-tert-butylphenyloxy)-3,4,9,10-perylenebis(dicarboximide)-N,N′-di(2,6-dimethylphenyl-4-yl)}] poly(Cvz-PDIMEP)

Compound **2** (0.32 g, 0.304 mmol), N-(heptadecanyl)-2,7-bis(4,4,5,5,-tetrametyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (0.2 g, 0.301mmol), palladium acetate (6 mg, 0.0267 mmol), and tricyclohexyl phosphine (17 mg, 0.06 mmol) were dissolved in toluene (1 mL). The mixture was stirred at 90°C for 5 min. Aqueous solution of tetraethyl ammonium hydroxide (1 mL, 20%w/w) was then added to the reaction mixture. The polymerization proceeded at 90°C for 72 h and was end-capped with bromobenzene and phenylboronic acid. The reaction mixture was cooled to room temperature and added to vigorously stirred methanol (400 mL). The polymer was further purified by Soxhlet extraction with methanol, acetone and THF to remove the oligomers. After precipitation, the final polymer was obtained after drying at 50°C in vacuum.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 9.70–9.73 (m, 2H), 8.73 (m, 1H), 8.38–8.47 (m, 2H), 8.12–8.15 (br, 1H), 7.76 (br, 1H), 7.60 (br, 1H), 7.48–7.51 (br, 12H), 7.15–7.16 (br, 4H), 4.64–4.68 (br, 1H), 2.40–2.53 (br, 4H), 2.25–2.28 (br, 4H), 1.05–1.15 (br, 12H), 1.15–1.69 (m, 20H), 0.80–0.87 (br, 24H). ^{13}C-NMR (600 MHz, $CDCl_3$): δ (ppm) 163.07, 162.72, 155.93, 152.65, 148.56, 143.46, 143.17, 139.79, 135.85, 134.23, 132.66, 130.93, 129.29, 128.31, 128.22, 127.72, 125.95, 124.41, 124.09, 122.46, 120.65, 120.45, 119.39, 119.18, 118.85, 110.75, 109.70, 108.00, 39.64, 39.28, 37.66, 37.32, 36.87, 34.78, 32.14, 30.26, 29.46, 26.96, 23.27, 22.81, 19.98, 19.78, 18.44, 17.38, 14.26, 11.62.

The poly{[N,N′-di(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide-1,7-diyl]-alt-(9-heptadecyl)-9H-carbazol-2-yl)} poly(Cvz-PDIC9) was synthesized by using the same method of poly(Cvz-PDIMEP). ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 8.81 (br, 2H), 8.17 (br, 2H), 8.00 (br, 2H), 7.84 (br, 4H), 7.50 (br, 1H), 7.41 (br, 1H), 5.14–5.28 (br, 3H), 2.15–2.22 (br, 12H), 1.82 (br, 12H), 1.03–1.20 (br, 64H), 0.81 (br, 18H). 0.72 (br, 2H), 0.59 (br, 2H).

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-PDIMEP):$PC_{71}BM$

and poly(Cvz-PDIC9):$PC_{71}BM$ 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-PDIMEP):$PC_{71}BM$ and poly(Cvz-PDIC9):$PC_{71}BM$ 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 30–40 min. The LiF (0.5 nm) and Al cathode (120 nm) were deposited on the top of the active layer under vacuum less than 5.0×10^{-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™ Class AAA solar simulator, models 94043A) with a light intensity of 100 mW/cm^2 adjusted using a standard PV reference cell (2 cm x 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™.

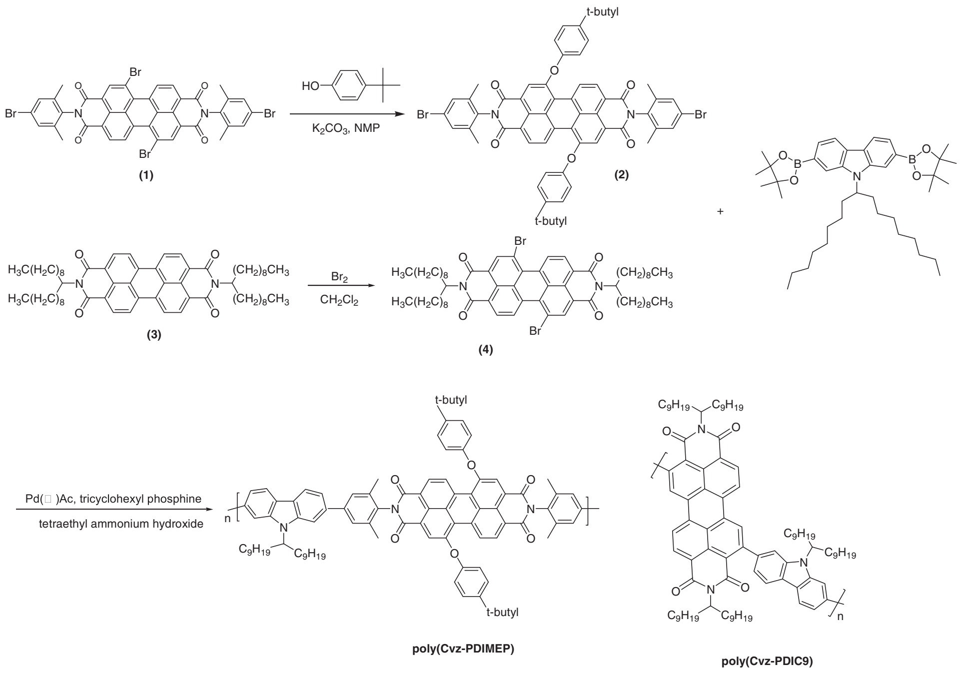
The PCE (η) of a solar cell given by

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

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

Two novel electron donor-acceptor copolymers containing PDI and carbazole derivatives have been designed and synthesized. Scheme 1 shows the synthetic routes for the monomers and polymers. The soluble PDI derivative (2) was synthesized via imidization of 1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid dianhydride with 4-bromo-2,6-dimethylaniline in propionic acid and then reaction with an excess of 4-tertbutylphenol in NMP at 80°C to give monomer (2). 1,7-Dibromo-N,N′-di(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide (4) was synthesized by bromination of N,N′-di(10-nonadecyl)perylene-3,4,9,10-bis(dicarboximide). The polymerization were carried out using palladium(II) acetate, tricyclohexylphosphone and tetraethylammonium hydroxide aqueous solution in toluene under nitrogen atmosphere. The resulting polymers, poly[{N-(1-octyldecyl)-2,7-carbazole)}-alt-{1,7-di(4-tert-butylphenyloxy)-3,4,9,10-perylenebis(dicarboximide)-N,N′-di(2,6-dimethylphenyl-4-yl)}] poly(Cvz-PDIMEP) and poly{[N,N′-di(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide-1,7-diyl]-alt-(9-heptadecyl)-9H-carbazol-2-yl)} poly(Cvz-PDIC9), were completely soluble in chloroform, chlorobenzene and THF etc. Molecular structures of the monomer and the resulting polymers were identified by ^{1}H- NMR. To remove the catalyst, oligomers and raised the device performance, the polymers were further purified by multiple Soxhlet extraction with different solvents including methanol, acetone, and finally chloroform. The solution of polymers were filtered through the methanol precipitation and then



Scheme 1.

dried in vacuo. From these processes, the highly purified and narrow polydispersity of polymers were obtained. Table 1 summarized the polymerization results, thermal and electrochemical characteristics of the polymers. The weight-average molecular weight (Mw) and the polydispersity of the polymers were in the range of 27000–43000 and 1.6–1.8, respectively. Poly(Cvz-PDIMEP) and poly(Cvz-PDIC9) have glass transition temperatures of 306°C and 210°C, respectively. The TGA results for poly(Cvz-PDIMEP) and poly(Cvz-PDIC9) are shown in Fig. 1. The temperature of 5% weight loss and the glass transition temperatures were 423°C, 306°C for poly(Cvz-PDIMEP) and 415°C, 210°C for poly(Cvz-PDIC9), respectively. Higher thermal stability of the polymers is one of the most critical requirements to operate the organic photovoltaic device.

Figure 2 shows the absorption spectra of the polymers in chloroform solutions and solid films on a quartz substrate. Regardless of polymer structures, polymers exhibited

Table 1. Polymerization results, thermal and electrochemical properties of polymers

Polymer	Mw[a]	PDI[a]	DSC (T_g)[b] (°C)	TGA[c] (°C)	HOMO (eV)	LUMO (eV)	Eg (eV)[d]
poly(Cvz-PDIMEP)	43000	1.6	306	423	-5,51	−3.40	2.12
poly(Cvz-PDIC9)	27000	1.8	210	415	-5.11	−3.3	1.81

[a] Mw and PDI of the polymers were determined by GPC using polystyrene standards.
[b] Determined by DSC at a heating rate of 10°C /min under N_2 atmosphere.
[c] TGA was measured at temperature of 5% weight loss for the polymers.
[d] Band gap estimated from the onset wavelength of the optical absorption.

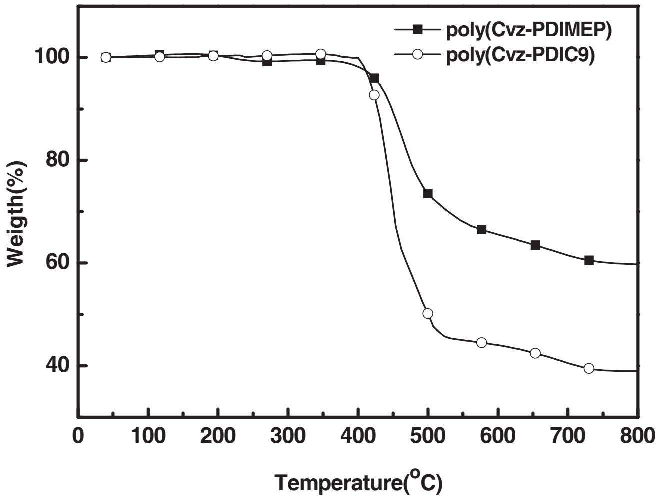


Figure 1. TGA thermogram of poly(Cvz-PDIMEP) and poly(Cvz-PDIC9).

maximum absorption peaks around 300–350 nm, which can be attributed to the carbazole segments in the polymers. The absorption spectrum of poly(Cvz-PDIMEP) displays three absorption bands with peaks at 330 520 and 552 nm, respectively.

The absorption spectra of poly(Cvz-PDIC9) in solution and film are obviously expanded in the visible region and show a broad absorption band that covers from 260 to 680 nm with maximum absorption peak at 558 nm. The absorption spectra of the films were not notably red shifted compared with those in solution, indicating that little intermolecular interaction occurred in the solid state, probably due to the large steric hindrance of the many bulky side chains.

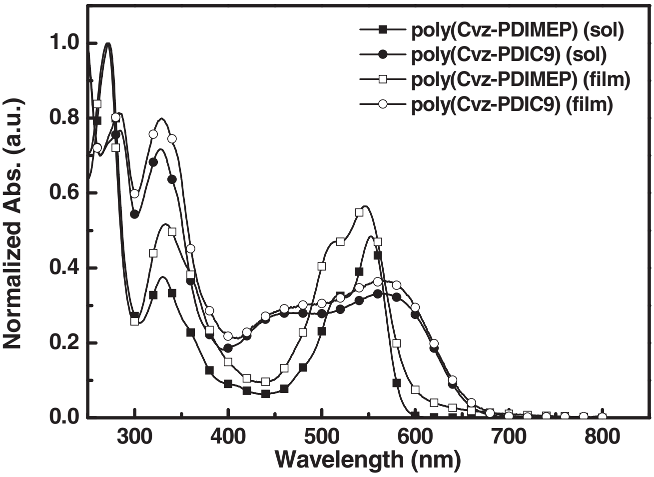


Figure 2. UV-visible absorption spectra of poly(Cvz-PDIMEP) and poly(Cvz-PDIC9).

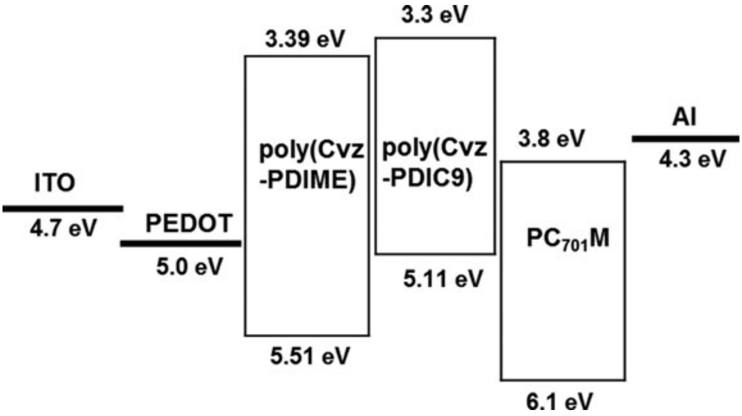


Figure 3. Energy band diagram of the ITO/PEDOT:PSS/polymer:$PC_{71}BM$/LiF/Al.

Oxidation and reduction potentials for the polymers were obtained using cyclic voltammetry (CV) and electrochemical data are summarized in Table 1. The HOMO binding energies of poly(Cvz-PDIMEP) and poly(Cvz-PDIC9) for the standard ferrocene/ferrocenium (4.8 eV) were −5.51 eV and −5.11 eV. The band gaps of poly(Cvz-PDIMEP) and poly(Cvz-PDIC9) obtained from the onsets of the absorption spectrum were 2.11 eV and 1.18 eV. The energy band diagrams and device structure of PDIMEP-Cvz and PDIC9-Cvz are displayed in Fig. 3. Photogeneration of charges in most of π-conjugated polymers is not very efficient since there is always the recombination of two charge carriers involved. However, from these energy band diagram, we predict that the required transfer of charges can be realized at the interface between poly(Cvz-PDIMEP) and poly(Cvz-PDIC9) as an electron donor and $PC_{71}BM$ as an electron acceptor due to the higher LUMO energy levels of poly(Cvz-PDIMEP) and poly(Cvz-PDIC9) and their lower HOMO energy level of $PC_{71}BM$.

Bulk heterojunction solar cells were fabricated using the poly(Cvz-PDIMEP) and poly(Cvz-PDIC9) as an electron donor and $PC_{71}BM$ as an electron acceptor. The photovoltaic cell structure is ITO/PEDOT:PSS/polymer:$PC_{71}BM$/LiF (0.5 nm)/Al (100 nm). All

Table 2. Photovoltaic performance of BHJ solar cells under AM 1.5G illumination (100 mW/cm^2)

Device	J_{sc}^{a} (mA/cm^2)	V_{oc}^{b} (V)	FF^{c} (%)	PCE^{d} (%)
poly(Cvz-PDIMEP):$PC_{70}BM$ (1:1)	0.50	0.30	27	0.041
poly(Cvz-PDIMEP):$PC_{70}BM$ (1:3)	0.68	0.35	28	0.067
poly(Cvz-PDIMEP):$PC_{70}BM$ (1:5)	0.85	0.32	27	0.073
poly(Cvz-PDIC9):$PC_{70}BM$ (1:1)	0.08	0.16	26.62	0.003
poly(Cvz-PDIC9):$PC_{70}BM$ (1:3)	0.12	0.35	30.62	0.013
poly(Cvz-PDIC9):$PC_{70}BM$ (1:5)	0.10	0.59	30.11	0.018

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

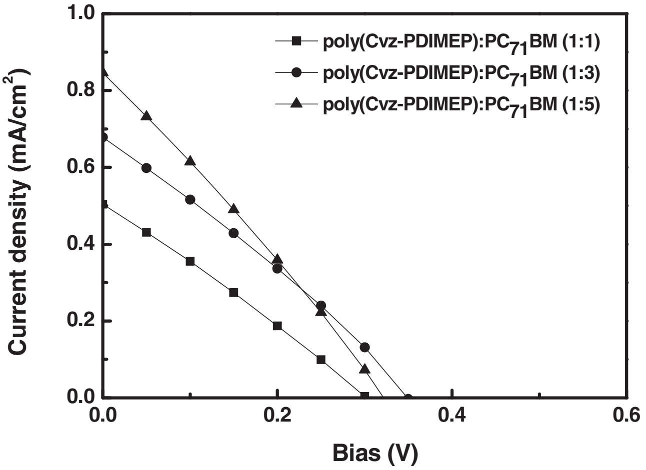


Figure 4. Photovoltaic performance of BHJ solar cells of poly(Cvz-PDIMEP).

devices were optimized with active layer thickness (80 nm) and baking temperature 150°C for 30 min. Table 2 lists the photovoltaic performance of these cells.

When we fabricated the bulk heterojunction solar cells by different ratios of poly(Cvz-PDIMEP) and $PC_{71}BM$ from 1:1 to 1:5 ratio, the PCE was increased from 0.04% to 0.07% as shown in Fig. 4. It was due to the easily transportation of electrons from poly(Cvz-PDIMEP) to $PC_{71}BM$. The device fabricated with poly(Cvz-PDIMEP) showed a higher photovoltaic performance than the devices fabricated with poly(Cvz-PDIC9) giving a J_{sc} of 0.85 mA/cm^2, a V_{oc} of 0.32 V, a FF of 0.27, and a PCE of 0.073%. The lower photovoltaic performance of poly(Cvz-PDIC9) is due to the decreased effective conjugation length than that of poly(Cvz-PDIMEP), which decrease the short-circuit current density.

Conclusions

We synthesized a novel series of polymers, poly(Cvz-PDIMEP) and poly(Cvz-PDIC9), for harvesting of the solar energy more efficiently. Bulk heterojunction photovoltaic cells with an ITO/PEDOT:PSS/polymer:$PC_{71}BM$/LiF/Al configuration were fabricated with poly(Cvz-PDIMEP) and poly(Cvz-PDIC9) as an electron donor and $PC_{71}BM$ as an electron acceptor. The device fabricated with poly(Cvz-PDIMEP) was shown the best performance with the J_{sc} of 0.85 mA/cm^2, V_{oc} of 0.32 V, FF of 0.27, and PCE of 0.073%.

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References

[1] Ling, Y., Wu, Y., Feng, D., Tsai, S. T., Son, H. J., Li, G., & Yu. L. (2009). *J. Am. Chem. Soc.*, *131*, 56.

[2] Hoppe, H., & Sariciftci. N. S. (2004). *J. Mater. Res.*, *19*, 1924.

[3] Jayakannan, M., van Hal, P. A., & Janssen, R. A. J. (2002). *J. Pol. Sci. Part A, Pol Chem*, *40*, 251.

[4] Tang, C. W. (1986). *Appl. Phys. Lett.*, *48*, 183.

[5] Zhan, X. W., Facchetti, A., Barlow, S., Marks, T. J., Ratner, M. A., Wasielewski, M. R., & Marder, S. R. (2011). *Adv. Mater. 23*, 268.

[6] Wang, H., Peng, B., & Wei, W. (2008). *Progress Chem. 2008*, *20*, 1751.

[7] Schmidt-Mende, L., Echtenkeotter, A., Meullen, K., Moons, E., Friend, R. H., & MacKenzie, J. D. (2001). *Science 2001*, *293*, 1119.

[8] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burns, P. L., & Holmes, A. B. (1990). *Nature 34*, 539.