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Bulk heterojunction solar cells based on a low-bandgap carbazole-diketopyrrolopyrrole copolymer

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Bulk heterojunction (BHJ) solar cells fabricated with a phase separated nanomaterial comprising a carbazole-diketopyrrolopyrrole copolymer (**PCBTDDP**) and [6,6]-phenyl C₇₀-butyric acid methyl ester (PC₇₀BM) are demonstrated with power conversion efficiency > 3.5%. The **PCBTDDP**:PC₇₀BM BHJ nanomorphology was controlled by changing the length of the alkyl side-chain of the polymer and by utilizing processing additives. © 2010 American Institute of Physics. [doi:10.1063/1.3508951]

Organic solar cells have attracted attention as an opportunity for low cost conversion of sunlight into electricity. In particular, bulk heterojunction (BHJ) polymer solar cells have emerged as a promising technology because they can be manufactured by solution-based coating methods.^{1–5} Despite a continuing increase in the power conversion efficiency (PCE) during the past few years, due mostly to the development of novel polymer materials,^{6–9} the relatively poor device performance remains a problem.

Recently, a low-bandgap copolymer based on carbazole and diketopyrrolopyrrole, poly[*N*-9'-heptadecanyl-2,7-carbazole-alt-3,6-bis(thiophen-5-yl)-2,5-diocetyl-2,5-dihydropyrrolo[3,4-*b*]pyrrole-1,4-dione] (**PCBTDDP**), was introduced as a promising candidate for use in BHJ solar cells.¹⁰ Although this polymer has a high hole-mobility, a deep HOMO energy, and a relatively small band gap, solar cells fabricated from **PCBTDDP**:PC₇₀BM showed relatively low performance (PCE=1.6%) owing to poor BHJ morphology. In this report, we demonstrate **PCBTDDP**:PC₇₀BM solar cells with PCE>3.5%. The BHJ nanomorphology was improved using two different methods: i) chemically modifying the polymer by changing the length of the alkyl side-

chains and ii) controlling the BHJ phase separation by using processing additives.

The effects of changing the alkyl chains of the semiconducting polymer on the performance of BHJ solar cells have been investigated by several research groups.^{11–13} For the poly(3-alkylthiophenes), longer alkyl chains enhance the mobility of the PCBM molecules and lead to larger-scale phase separation in the composite film. The BHJ nanomorphology can also be modified by incorporating a small amount of processing additives to the solution during device fabrication.^{14,15} Herein, we report that each of these methods can be used to enhance the performance of **PCBTDDP**:PC₇₀BM BHJ solar cells.

The molecular structure and energy level diagram of **PCBTDDP** are shown in Fig. 1(a). **PCBTDDP** was synthesized using copolymerization through the Suzuki coupling reaction between two monomers, as reported previously.¹⁰ In addition, we synthesized a series of copolymers with different alkyl chain lengths in positions R₁ and R₂ as shown in Fig. 1(a). To evaluate the effect of different alkyl chains on the evolution of BHJ nanomorphology and the change in the device performance of **PCBTDDP**:PC₇₀BM BHJ solar cells, two types of copolymer were selected: R₁=R₂=C₈H₁₇ (des-

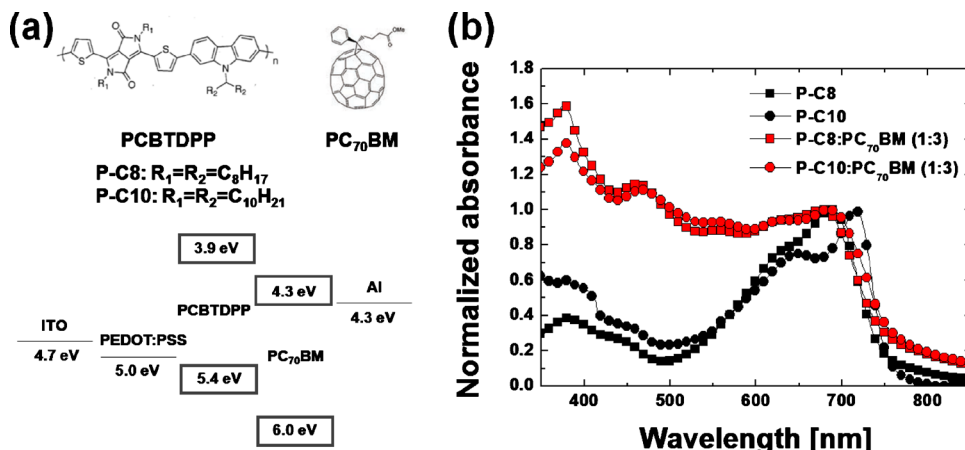


FIG. 1. (Color online) (a) Molecular structures and energy level diagram of **PCBTDDP** and PC₇₀BM, and (b) UV-Vis absorption spectra of the pristine and composite films.

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TABLE I. Performance parameters obtained from J - V curves shown in Fig. 2.

Active layer	Additives	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
P-C8:PC ₇₀ BM	None	0.76	8.02	40	2.45
	DIO	0.78	8.58	44	2.97
	CN	0.78	9.39	45	3.28
P-C10:PC ₇₀ BM	None	0.77	9.03	52	3.64
	DIO	0.68	4.78	59	1.93
	CN	0.76	8.10	56	3.42

ignated **P-C8** in this communication) and C₁₀H₂₁ (**P-C10**).

The BHJ solar cell devices were fabricated on indium tin oxide (ITO)-coated glass substrates. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron PH) was spin-cast onto the ITO-coated glass and then baked at 140 °C for 10 min in air. After transferring to a N₂-filled glove box, the blend solution (0.8 wt %) **PCBTDP**:PC₇₀BM (1:3 ratio by weight) was spin-cast from 1,2-dichlorobenzene onto the PEDOT:PSS layer. The thickness of the BHJ layer (~70 nm) was determined by profilometry. After transferring into a vacuum chamber without exposing the films to air, an Al electrode (100 nm) was deposited on top of the BHJ layer by thermal evaporation under high vacuum ($<3 \times 10^{-6}$ torr). Current density-voltage (J - V) characteristics were measured inside a N₂-filled glove box using a Keithley 2400 source measurement unit. The solar cells were illuminated through an aperture (12.38 mm²) with 100 mW/cm² using an AM 1.5G filter. The incident photon-to-current conversion efficiency (IPCE) spectra were obtained with the samples by using a QE measurement system (PV measurements, Inc.).

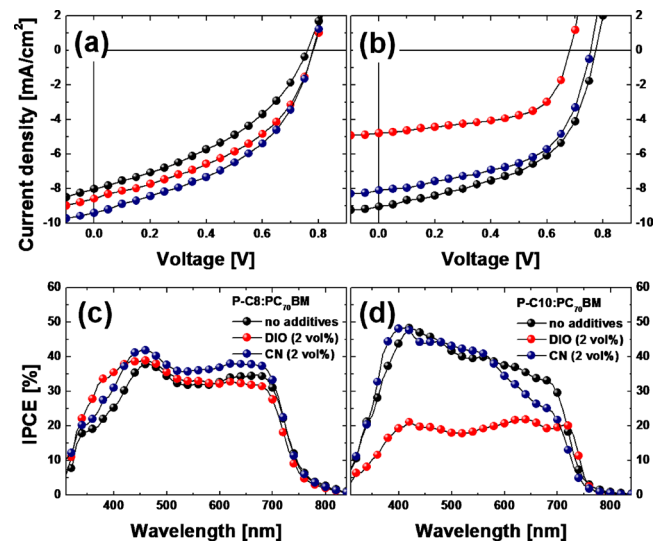


FIG. 2. (Color online) J - V curves [(a) and (b)] and IPCE spectra [(c) and (d)] of BHJ solar cells based on the **P-C8**:PC₇₀BM [(a) and (c)] and **P-C10**:PC₇₀BM [(b) and (d)] composites treated with different processing additives: 1,8-diiodooctane (DIO) and 1-chloronaphthalene (CN).

As shown in Fig. 1(b), the UV-Vis absorption spectrum of **P-C10** film shows a clearer vibronic shoulder than observed in the spectrum of **P-C8**, and the absorption maximum occurs at a wavelength longer than that of **P-C8**. Similarly, the absorption spectrum of **P-C10**:PC₇₀BM composite film shows a slight red-shift with respect to the **P-C8**:PC₇₀BM absorption spectrum, with maximum near 700 nm suggesting ordered stacking of the polymer chains.^{16,17} As shown in Fig. 2, the **P-C10**:PC₇₀BM device exhibited better performance with PCE, J_{sc} , and FF superior to those of the **P-C8**:PC₇₀BM device.

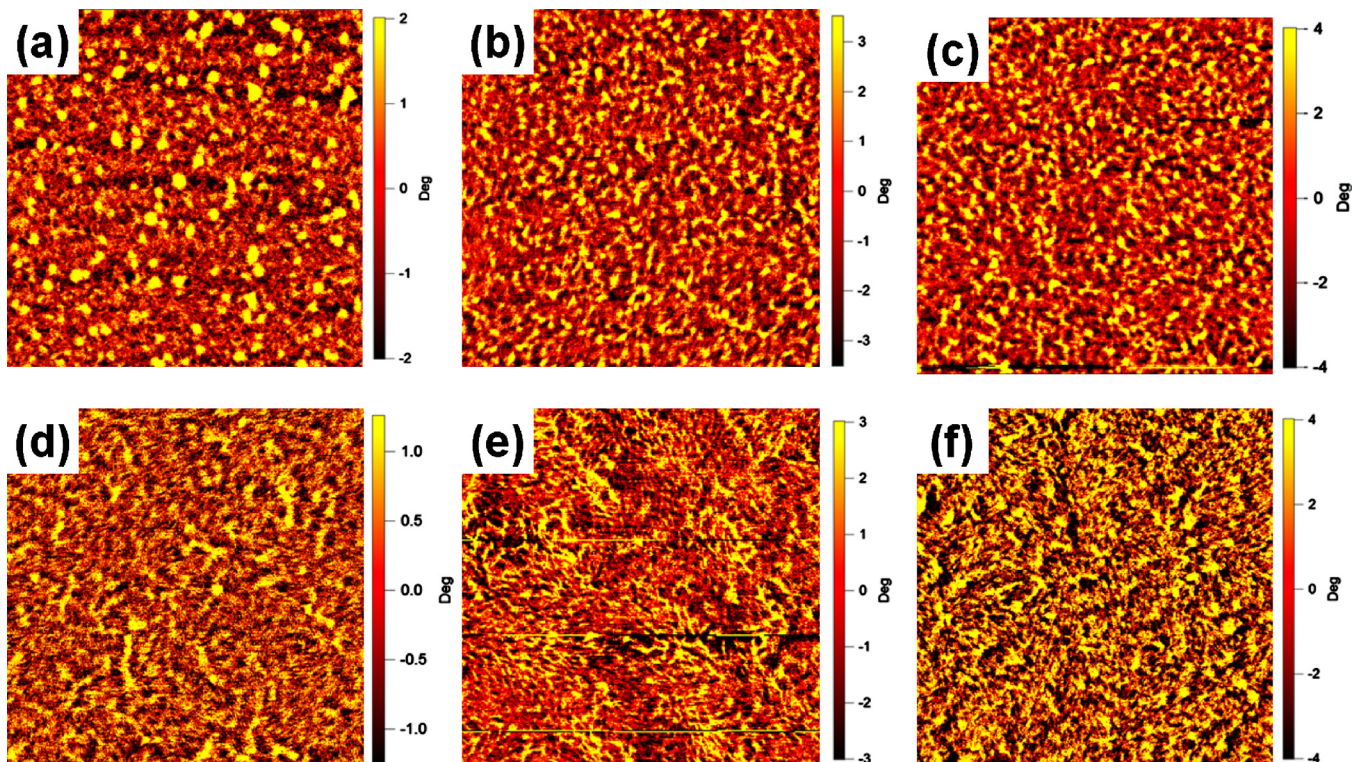


FIG. 3. (Color online) AFM phase images (surface scan area: $5 \times 5 \mu\text{m}^2$) of the **P-C8**:PC₇₀BM [(a), (b), and (c)] and **P-C10**:PC₇₀BM [(d), (e), and (f)] composite films treated without [(a) and (d)] and with DIO [(b) and (e)] or CN [(c) and (f)].

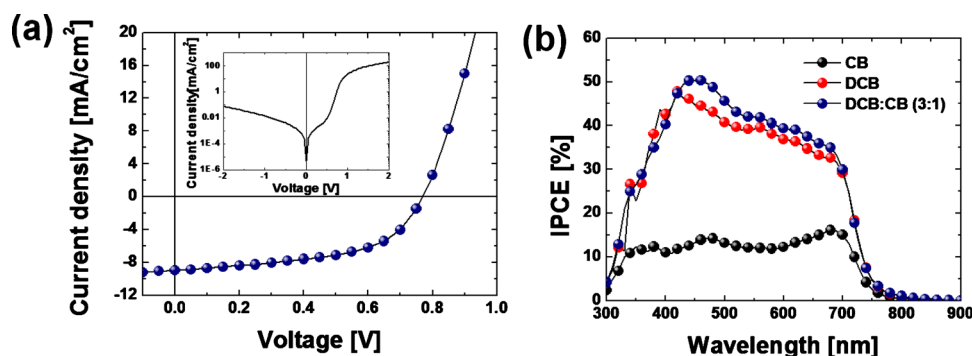


FIG. 4. (Color online) (a) J - V curves, measured in the dark (inset) and under AM 1.5G irradiation ($100 \text{ mW}/\text{cm}^2$) of the best performing BHI solar cell containing a **P-C10**:PC₇₀BM composite. (b) IPCE spectra of devices fabricated with **P-C10**:PC₇₀BM blend solutions based on various solvents: chlorobenzene (CB), 1,2-dichlorobenzene (DCB), and cosolvent.

By using processing additives to control the nanomorphology, BHI solar cells based on various polymer:PCBM composites showed improved device performance.^{7,8,13–15,18} In this report, we investigated the change in BHI nanomorphology and solar cell performance obtained with the use of 1,8-diiodooctane (DIO) or 1-chloronaphthalene (CN) as processing additives. As shown in the J - V curves and IPCE spectra of Fig. 2(a) and 2(c), BHI solar cells based on **P-C8**:PC₇₀BM showed an enhancement in device performance with processing additives of 2% by volume. **P-C10**:PC₇₀BM devices, however, showed reduced performance when processed with the additives (Figs. 2(b) and 2(d)). The performance parameters of all the devices shown in Fig. 2 are summarized in Table I.

Figure 3 shows AFM phase images of **P-C8**:PC₇₀BM and **P-C10**:PC₇₀BM composite films, before and after the incorporation of processing additives (DIO, CN). In the images of **P-C8**:PC₇₀BM composites, randomly distributed islands are connected to each other and evolve into interpenetrating networks after treatment with processing additives (Figs. 3(a)–3(c)). In contrast, **P-C10**:PC₇₀BM composites form interconnecting charge paths without additives [Fig. 3(d)], and show larger segregation of each phase after incorporating additives (Figs. 3(e) and 3(f)). Here, we note that DIO (which has eight carbons) was effective only for improving the morphology of **P-C8**:PC₇₀BM, but not for **P-C10**:PC₇₀BM. This result implies that there may be correlation between the length of alkyl side-chains in polymer and the length of the alkyl chains in additives for optimum control of the nanomorphology.

To obtain the best device performance with the **P-C10**:PC₇₀BM composite, we re-evaluated and optimized the fabrication conditions. Most importantly, we used a cosolvent composed of DCB:chlorobenzene (CB) (3:1 by volume). As shown in Fig. 4(b), the IPCE spectrum showed a particularly high peak in a wavelength range of polymer absorption, while exhibiting reduced peaks in PCBM absorption near 400 nm. This finding is consistent with the result of a previous report demonstrating a solvent effect in a poly(2,7-carbazole) derivative:PC₇₀BM BHI solar cells.⁶

We obtained the highest device performance by using TiO_x as a multifunctional interlayer between the photoactive layer and the Al electrode. Figure 4 shows the J - V curves of an optimized device measured under AM 1.5G irradiation ($100 \text{ mA}/\text{cm}^2$) and dark conditions; its efficiency parameters are as follow: V_{oc} =0.77 V, J_{sc} =9.10 mA/cm², FF=0.55, and PCE=3.80%. The value integrated from the IPCE spectra of the device matches the J_{sc} value within 2% error.

In summary, we report significant improvements in the performance of BHI solar cells based on **PCBTDP**:PC₇₀BM. The BHI nanomorphology was controlled by changing the lengths of the solubilizing alkyl chains of the polymer or incorporating processing additives into the blend. AFM was applied to investigate the BHI nanomorphology of all the composite films. Increasing the length of the alkyl side-chain (C8 to C10) of **PCBTDP** improved the PCE of the device from 2.45% to 3.64%. Optimization using a cosolvent and an interfacial TiO_x layer resulted in an efficiency of 3.80% under AM 1.5G irradiation at an intensity of $100 \text{ mW}/\text{cm}^2$.

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