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Effect of asymmetric solubility of diketopyrrolopyrrole-based polymers and PC₇₁BM in a binary solvent system on the performance of bulk heterojunction solar cells

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ABSTRACT

In this study, we demonstrated the effective morphological control of polymer:fullerene blends using three separate solvent systems: chloroform (CF), CF:1,8-diodooctane (DIO), and CF:*o*-dichlorobenzene (ODCB). The polymer:fullerene blends are composed of two diketopyrrolopyrrole (DPP)-based polymers of P(DPP-*alt*-QT) and P(DPP-*alt*-DTBSe) and a fullerene derivative of [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM), i.e., P(DPP-*alt*-QT):PC₇₁BM or P(DPP-*alt*-DTBSe):PC₇₁BM. The CF:ODCB binary solvent exhibited the best photovoltaic performance among the three solvent systems for both polymer-based devices, although the CF:DIO also exhibited an improved performance compared to the CF system. By examining film morphology of the blend films, we found that the CF:ODCB enabled the most optimal nanoscale phase separation and the morphological features were strongly affected by the solubility of each material in the high boiling-point (BP) solvent. Specifically, the polymers have limited but slightly higher solubility in ODCB than in DIO, while the PC₇₁BM molecules have a high solubility in both DIO and ODCB. Therefore, this work highlights that the optimally asymmetric solubility of each photoactive component in the high BP solvent is a critical factor to form the nanoscale, bicontinuous domains in the blend films and thereby to determine the performance of photovoltaic devices.

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1. Introduction

Organic photovoltaics (OPVs) have attracted much attention as promising renewable energy resources because of their advantages in low-cost, printable, light-weight, large-area, and flexible applications [1–13]. Recently, power conversion efficiencies (PCEs) have exceeded 8% from polymer:fullerene bulk heterojunction (BHJ) solar cell devices employing low bandgap (LBG) polymers.

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These LBG polymers were typically organized by an alternating arrangement of electron-rich units and electron-deficient units [14–18]. While the PCEs of OPVs have increased rapidly, it is very important to control the nanoscale morphology of the BHJ-type photoactive layers that are composed of conjugated polymers and fullerenes (typically [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM)). In order to achieve a bicontinuous nanophase-segregated morphology of photoactive layers, they are often treated with thermal annealing [19,20] and solvent annealing processes [21,22]. Alternatively, for high-performance LBG polymer:fullerene blends, the film morphology was effectively controlled by using binary solvent systems where one is a good solvent with a low boiling point (BP) for LBG polymers and fullerenes, and the other is a poor solvent with a high BP [23–26]. The solubility of LBG polymers and fullerenes in each solvent plays a significant role in the formation of bicontinuous nanophase-separated domains of polymers and fullerenes.

According to previous reports, [25,27–30] most LBG conjugated polymers, especially diketopyrrolopyrrole (DPP)-based polymers, are soluble in chloroform (CF), but exhibit a relatively lower solubility in higher BP solvents such as 1,8-diiodooctane (DIO) and *o*-dichlorobenzene (ODCB). Typically, when only CF was used to dissolve polymers and fullerenes, as-spun blend films exhibited large crystalline domains or aggregations. The micro-phase separation led to low short-circuit current densities (J_{sc} s) and PCE values in OPVs [23,25,26]. The addition of a small amount of a high BP solvent additive such as DIO or ODCB into the CF solution induced networked polymer- and fullerene-nanoscale phase separation. This morphology permits (i) the generation of a high interfacial area between polymers and fullerenes, (ii) the suppression of charge recombination, and (iii) the efficient charge transport towards the collecting electrodes [31–34]. As a result, J_{sc} s and PCEs were significantly improved. To further optimize film morphology using a high BP solvent additive, it is important to understand the effect of the solvent system and quantity of high BP solvent additives for polymers and fullerenes.

Herein, we report the solar cell performances of devices made of DPP-based conjugated polymers, P(DPP-*alt*-QT) or P(DPP-*alt*-DTBSe). Using three solvent systems consisting of CF, CF:DIO, and CF:ODCB, we investigated how the choice of solvent systems affected solar cell performances. The CF:ODCB solvent was the best solvent for both polymer:PC₇₁BM blend films because it produced the most optimal nanophase-separated morphology. This result correlated well with the optimal degree of the asymmetric solubility of each component in the high BP solvent. Specifically, we found that higher BP solvents possess considerable solvating power for PC₇₁BMs, whereas they have a limited solvating power for the polymers. Therefore, as the main low BP solvent evaporates, conjugated polymer chains begin to generate networked crystalline domains, and the high BP solvent that evaporates slowly can still retain the fullerene molecules to promote the formation of homogeneously dispersed nanoscale domains of fullerene derivatives.

2. Experimental section

2.1. Materials

The synthesis of P(DPP-*alt*-QT) and P(DPP-*alt*-DTBSe) was reported in our previous publication [35]. PC₇₁BM and poly(3,4-ethylenedioxy thiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevious PVP A14083) were purchased from Nano-C and from H. C. Starck, respectively.

2.2. Measurement of molar extinction coefficients and solubility of materials

For the measurement of the molar extinction coefficients (ϵ), CF solutions of each material with three different concentrations were prepared, and UV–visible absorption spectra on these solutions were obtained. The CF concentrations were 9.8×10^{-6} M, 2.4×10^{-5} M, and 4.9×10^{-5} M for the P(DPP-*alt*-QT) polymer; 6.0×10^{-6} M, 1.2×10^{-5} M, and 3.0×10^{-5} M for the P(DPP-*alt*-DTBSe) polymer; and 8.0×10^{-6} M, 1.6×10^{-5} M, and 3.2×10^{-5} M for PC₇₁BM. The maximum absorbance was measured at 785, 785, and 459 nm for the P(DPP-*alt*-QT), P(DPP-*alt*-DTBSe), and PC₇₁BM, respectively. Then, plots of the UV–visible absorption intensity versus the concentration of the CF solutions were made, and the molar extinction coefficients from the slopes of these plots were extracted (Fig. S1).

The solubility of each material in DIO and ODCB was also determined. The polymers and PC₇₁BM were dissolved in DIO or

ODCB for 24 h under vigorous stirring at room temperature, and filtered through 0.2 μ m-pore diameter Nylon filters. 0.1 mL of the filtered solution was diluted with 2.9 mL of DIO or ODCB to lower the absorbance below 1.0, and UV–visible absorption spectra were obtained (Fig. 7). By using the absorbance of the polymer solutions and the calculated extinction coefficient of each material (on the basis of Beer–Lambert's law), the solubility of each material was estimated.

2.3. Device fabrication and characterization

Indium tin oxide (ITO) glass substrates were cleaned using isopropanol, acetone, and isopropanol again for 10 min each by sonication, and dried under a stream of nitrogen. The ITO substrates were then treated with UV ozone for 20 min. The PEDOT:PSS solution was diluted with methanol to a ratio of 1:1 (by volume) prior to use and spin-coated at a speed of 4000 rpm for 35 s, resulting in a layer with a thickness 30 nm. The PEDOT:PSS-coated ITO substrates were dried in a vacuum oven at 120 °C for 10 min. The blend solution bearing the polymer and PC₇₁BM (1:2, wt ratio) was then spin-coated onto ITO/PEDOT/PSS substrates at 1000 rpm for 35 s, and dried at 70 °C for 20 min. The polymer and PC₇₁BM were then dissolved in three solvent systems, (i) CF, (ii) CF with a small amount of DIO (the DIO portion was 3 vol%, *unless otherwise specified*), and (iii) CF:ODCB (the ODCB portion was 20 vol%, *unless otherwise specified*). The concentration of the polymer:PC₇₁BM blend solution was 10 mg/mL for the CF and CF:DIO solutions, and 7.8 mg/mL for the CF:ODCB solution. The resulting thicknesses of the photo-active layer produced from all the solutions were \sim 90 nm. For the incorporation of a TiO₂ layer, TiO₂ nanoparticles were dispersed in ethanol and spin-coated on top of the photoactive layer at 4000 rpm for 25 s, yielding a 10-nm-thick TiO₂ layer. After transferring ITO/PEDOT:PSS/polymer:PC₇₁BM or ITO/PEDOT:PSS/polymer:PC₇₁BM/TiO₂ films into a vacuum chamber, a 100-nm-thick layer of aluminum was vacuum-deposited through a shadow mask at a base pressure of 2×10^{-6} Torr at a deposition rate of 5 Å/s.

The current density versus voltage (J – V) characteristics were recorded on a Keithley model 2400 source measuring unit in air right after the completion of the device fabrication without encapsulation. A class-A solar simulator with a 1000 W Xenon lamp (Yamashita Denso), equipped with a KG-5 filter, served as a light source. The light intensity was adjusted to AM 1.5 G, 1 sun light intensity, using an NREL-calibrated mono Si solar cell. The external quantum efficiency (EQE) was measured as a function of wavelength from 300 to 1100 nm on incident photon-to-current conversion equipment (PV measurement Inc.). Calibrations were performed using a NIST-calibrated Si photodiode G425 as a standard.

For hole mobility measurements, hole-only devices were fabricated with a structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/Au. Hole mobilities in the polymer:PC₇₁BM blend film were determined from J – V curves in dark by space charge limited current (SCLC) method, [36,37] based on the following equation:

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu_h \frac{V^2}{L^3}$$

where ϵ_0 is the permittivity of free space, ϵ_r is the dielectric constant of the polymer:PC₇₁BM blend film, μ_h is the hole mobility, $V = V_{\text{app}} - V_{\text{bi}} - V_a$ (where V_{app} is the applied bias, V_{bi} is the built-in potential due to the difference in electrical contact work function, and V_a is the voltage drop due to contact resistance and series resistance across the electrodes), and L is the thickness of the photo-active layer. The current density versus voltage characteristics were also recorded on a Keithley model 2400 source measuring unit.

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