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Effect of solvent-induced phase separation on performance of carboxylic indoline-based small-molecule organic solar cells



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ABSTRACT

In this study, we investigate a carboxyl indoline dye named D205 with deep highest occupied molecular orbital energy level of -5.4 eV as donor material together with [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₀BM) as acceptor material in solution-processed bulk heterojunction solar cells. We employ chloroform (CF) and chlorobenzene (CB) as different solvents to investigate the influence of which on the active layer phase separation. The morphologies of D205:PC₇₀BM with CB as solvent seem to be stable as the ratio of PC₇₀BM increasing while it shows obvious change when processed by CF. The root-mean-square (RMS) values processed in CB change from 1.2 nm (D205:PC₇₀BM = 1:2) to 0.8 nm (D205:PC₇₀BM = 1:19). While the RMS values processed in CF change from 1.1 nm (D205:PC₇₀BM = 1:2) to 13 nm (D205:PC₇₀BM = 1:19). This may originate from that the rapid volatilization of CF solvent, leading to the aggregation behavior of the blending layer especially the aggregates of PC70BM. A proper RMS value leads to a better phase separation and thus can prompt balanced holes and electrons transportation. This can eventually benefit the short-circuit current. By regulating the ratio of D205:PC70BM as 1:4 in CB, an optimized power conversion efficiency(PCE) of 3.0% was reached after device annealing at 90 °C for 1 min under standard AM 1.5100 mW/cm² sunlight.

1. Introduction

Organic solar cells (OSCs) have been considered as one of the most promising alternatives to traditional silicon-based solar cells owing to their low cost, light weight as well as flexibility [1-5]. Compared to polymer solar cells, small molecule-OSCs (SM-OSCs) have attracted much attention since they are easier to synthesize and purify as well as better to form a well ordered self-assembly domain growth [6-8].

SM materials based on oligothiophene [9], benzodithiophene [10], dithienosilole [11], and indoline [12,13] as well as squaraine [14-16] have been reported as donors in OSCs. Among which, indoline-based small molecules have been well known as organic sensitizers in dyesensitized solar cells (DSSCs) [17-21]. In particular, indoline dyes D149 and D205 showed high power conversion efficiencies (PCE) in DSSCs (D149, PCE = 9.03% [22], D205, PCE = 9.52% [23]) due to their significantly high molar extinction coefficients and their potential of efficient photocurrent generation. The superior performance of D205 is attributed to reduced dye aggregation by the substitution of n-octyl chain onto the rhodanine ring of D149 [23]. However, liquid electrolytes in DSSCs contain volatile organic solvents reducing the stability of the devices and giving rise to other problems and thus bring difficulties

in practical applications for the organic sensitizers [24–27]. Previous study showed that D149 blended with [6,6]-phenyl C71 butyric acid methyl ester (PC70BM) for solution-processed OSCs displayed a PCE of 2.28% [28]. Given that D205 showed higher performance in DSSCs and enhanced solubility owing to n-octyl chain in comparison with D149, a higher efficiency using D205 as donor in solution-processed OSCs is envisaged.

In solution-processed OSCs, different solvents could influence the aggregate structure of active material in the solution. And this can influence the phase separation and ultimately form diverse surface structures when they are spin-coated onto solid films as the volatilization speeds and polarity of the solvents are different. The morphology of active layer acts as a key factor to determine the final photovoltaic performance for the reasons that the morphology of blending layer could influence the balance of holes and electrons transportation as well as the amounts of blending interface.

In this paper, we attempt to introduce D205 as donor material into OSCs together with PC70BM as accepter for solution-processed bulk heterojunction (BHJ) solar cells. We also investigate the impacts of different solvents (chloroform (CF) and chlorobenzene (CB)) as well as the blend ratio on the blending layer morphology.

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Fig. 2. The AFM height images of D205:PC70BM blending films processed by CB and CF with different blending ratios.

2. Experimental section

2.1. Materials

D205 was synthesized as reported before [23]. The indium-tin oxide (ITO) were purchased from Dongguan City Everest Display Technology Co. Ltd. MoO₃ and Sublimated 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was purchased from Wako Chemicals Ltd. PC70BM which were purchased from Hangzhou Perovs Optoelectronic Technology Co. Ltd.

2.2. Device fabrication

BHJ solar cells were fabricated with the following structures: ITO/ MoO₃ (5 nm)/D205:PC₇₀BM (70 nm)/BCP (8 nm)/Al (100 nm). D205:PC70BM (1:2-1:19 wt%, 20 mg/ml of the blends) are prepared both in CF and CB. The ITO substrates were precleaned with detergent, deionized water, acetone and isopropyl alcohol in an ultrasonic bath for 20 min in sequence and then exposed in ultraviolet-ozone for 30 min. After that the substrates were transferred into the vacuum chamber to deposit 5 nm MoO₃ in the vacuum about $4*10^{-4}$ Pa. Then the blending layer was spin coated onto the MoO3 modified substrates with the D205:PC70BM (1:2-1:19 wt%, 20 mg/ml of the blends in CB or CF) to get different thickness by changing the rotational speed of the spin coater in the glove box. Then BCP and Al were thermally deposited in high vacuum with an active area of 0.09 cm² controlled by a metal mask. The final photovoltaic performance is averaged by four independent devices.

2.3. Material characterization

Electronic absorption spectra of D205 on the solid film and in tetrahydrofuran (THF) solution as well as the PC70BM film were measured using a UV-1800 spectrophotometer (Shimadzu). The highest occupied molecular orbital (HOMO) levels of D205 were measured by a photoelectron spectrophotometer in air (Model AC-3, Riken Keiki).

2.4. Device characterization

The thickness of every film was measured by a Dektak 8 stylus profiler (Veeco). Surface roughness profiles of D205 were measured with AFM (Veeco). PCE of photovoltaic cells were carried out on a CEP-2000 integrated system (Bunkou Keiki) under standard measurement conditions. Incident photon-to-electron conversion efficiency (IPCE) were carried out using a commercial IPCE setup equipped with a 100Q Xe arc lamp, filter wheel, and monochromator. (CrowntechOTest Station 1000AD, SOFN INSTRUMENTS SO., LTO) Monochromated light chopped at a frequency of 80 Hz and photocurrents were measured using a lock-in amplifier.

3. Results and discussion

Fig. 1a shows the molecular structure of D205 and PC₇₀BM that used in our investigation. D205 composes a pair of electronic pushing and drawing substituents. The indoline group acts as electron pushing moiety while the carboxyl functioned double rodanine ring acts as electron withdrawing group. Besides, the carboxyl group of the double

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