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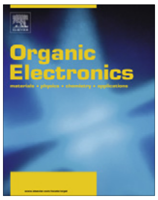

The effect of processing additive on aggregated fullerene derivatives in bulk-heterojunction polymer solar cells

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ABSTRACT

The effects of processing additive on fullerene aggregation in polymer BHJ solar cells were investigated using new fullerene derivatives bearing a thiophene moiety and alkyl groups. Although new fullerene derivatives showed quite similar electronic transport properties in field-effect transistors, the photovoltaic performances were significantly limited by their aggregative nature. Processing with 1% CN additive, however, changed the aggregated morphology of BHJ films to a smoother and homogeneous morphology, improving photovoltaic performance. The result indicates that processing additive not only influences on polymer side, but also significantly affects fullerene acceptor component.

1. Introduction

Bulk heterojunction (BHJ) solar cells have generated strong interest in the field of renewable energy because of their potential to lower manufacturing costs for large-area and lightweight devices [1–3]. Considerable effort has been expended to improve the power conversion efficiency (PCE) by means of new materials design, interface control, and device fabrication [4–8]. Process engineering via thermal annealing, solvent annealing, and solvent additives have been utilized to significantly enhance device performance of these BHJ solar cells [9–11].

One of key factors governing the PCEs is the nano-scale morphology of the blend comprising conjugated polymer donors and fullerene acceptors [9–12]. A desired morphology plays a critical role affecting interfaces for charge separation of photogenerated excitons and continuous pathway for separated charge carrier transport. In 2006, solvent additives were found to be a particularly effective way to influence on the phase separation during film formation [13–16]. This processing additive method is simple and amenable to solution deposition methods and does not require post processing modification such as thermal annealing or solvent annealing.

Two types of processing additive have been used to control nano-scale morphology of BHJ solar cells. One is the method using selective solubility of additive. This type processing additive, such as 1,8-octanedithiol and 1,8-diiodooctane, leads to aggregation of the ‘polymer’ in solution, which results in an increase in the size of the BHJ domains in the film [13,14,17]. The effect of additive using selective solubility, therefore, highly depends on the tendency of polymer to aggregate. This type additive does not effectively work on the high aggregative polymer systems.

A second type of cosoluble additive, 1-chloronaphthalene (CN), has been used in BHJ materials comprising aggregative conjugated polymer donors [15,16]. By using the cosoluble additive, large-scale aggregation of polymer is suppressed and the nanoscale morphology required for high-performance BHJ is achieved.

The use of processing additives in the optimization of the nanoscale morphology of BHJ films has been shown to be effective in many systems. However, the effects of

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processing additives are yet to be fully explored on fullerene acceptor side. In this contribution, we have investigated the effect of additive focused on acceptor side.

2. Experimental

2.1. Materials

The synthetic procedure of C_{60}-fused N-methyl-2-(3-hexylthiophen-2-yl)pyrolidine (C_{60}ThHx) was previously reported in the literature [18,19]. The synthetic approach for C_{60}-fused N-methyl-2-(3-otylthiophen-2-yl) pyrolidine (C_{60}ThOt) is depicted in Scheme 1. All reagents were purchased from commercial sources and used without further purification unless otherwise noted. All solvents were purified and freshly distilled prior to use according to literature procedures.

*2.1.1. Synthesis of 3-octylthiophene (**1**)*

A solution containing thiophene (0.10 mol) in dry THF (120 mL) at −78 °C was treated with 1.6 M of *n*-BuLi (0.12 mol) in hexane and stirred for 1 h. 1-Bromooctane (0.12 mol) in dry THF (20 mL) was slowly added in the solution at −78 °C and the solution was allowed to warm to RT and stirred overnight. The solution was quenched with a saturated NH_4Cl solution and extracted with ether. The combined ether extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting crude product was purified by a flash chromatography on silica gel with an eluent of hexane to give of compound **1** (yield: 80%). ^1H NMR ($CDCl_3$, TMS, ppm): δ 7.07 (d, 1H), 6.86 (t, 1H), 6.73 (d, 1H), 2.81 (t, 2H), 1.69 (m, 2H), 1.30 (m, 10H), 0.83 (t, 3H).

*2.1.2. Synthesis of 2-bromo-3-octylthiophene (**2**)*

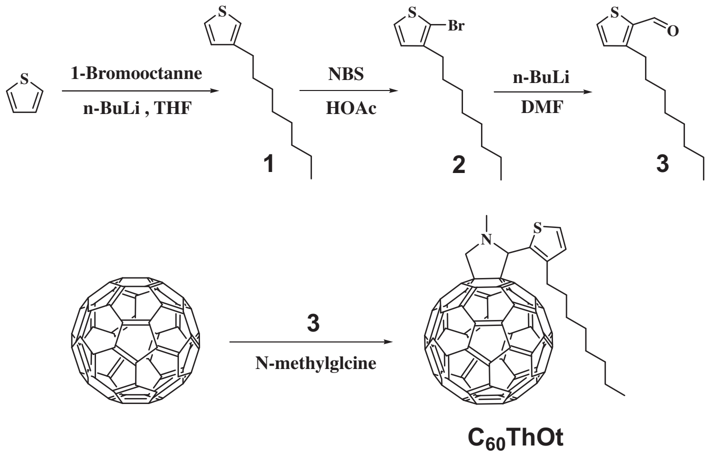
To a solution of 3-octylthiophene (0.05 mol) and 120 mL acetic acid, NBS (0.06 mol) was added in one portion and stirred for 30 min. And then water was added into the resulting solution, and also stirred for 10 min. The mixture was washed with ether, saturated aqueous $NaHCO_3$, and water, and dried with $MgSO_4$. The solvent was removed via rotary evaporation, and 2-bromo-3-octylthiophene (yield: 86%) was obtained. ^1H NMR ($CDCl_3$, TMS, ppm): δ (ppm) 7.17 (d, 1H), 6.80 (d, 1H), 2.59 (t, 2H), 1.60 (m, 2H), 1.35 (m, 10H), 0.93 (t, 3H).

*2.1.3. Synthesis of 3-octylthiophene-2-carbaldedyde (**3**)*

Butyllithium (0.024 mol, 1.6 M in hexane) was added to a stirred solution of 2-bromo-3-octylthiophene (0.02 mol) in THF (25 mL) at −78 °C and the resulting solution was stirred for 15 min. Then, dimethylformamide (0.04 mol) was added and the resulting solution was left to reach room temperature and stirred for additional 30 min at room temperature. An aqueous saturated solution of NH_4Cl (25 mL) was then added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with diethyl ether, the combined organic extracts were dried (Na_2SO_4), the solvent was removed in the rotary evaporator, and the resulting residue was purified by flash chromatography (yield: 70%). ^1H NMR ($CDCl_3$, TMS, ppm): δ (ppm) 10.04 (s, 1H), 7.64 (d, 1H), 7.00 (d, 1H), 2.96 (t, 2H), 1.74 (m, 2H), 1.66 (m, 10H), 0.87 (t, 3H).

2.1.4. Synthesis of C_{60}THOt

A solution of **3** (0.09 mol), fullerene (0.09 mol), and *N*-methylglycine (0.20 mol) in 1,2-dichlorobenzene (30 mL) was refluxed for 48 h. After cooling to RT, the reaction mixture was performed with a flash chromatography on silica gel with a gradient eluent of toluene to 20% hexane in toluene. After the crude product was washed and centrifuged with methanol, recrystallization from 1,4-dioxane yielded the desired product C_{60}THOt (yield: 40%). ^1H NMR ($CDCl_3$, TMS, ppm): δ 7.18 (d, 1H), 6.92 (d, 1H), 5.19 (s, 1H), 5.00 (d, 1H), 4.23 (d, 1H), 2.89 (s, 3H), 2.05 (t, 2H), 1.60 (m, 2H), 1.32 (m, 10H), 0.85 (t, 3H). MALDI-TOF-MS (matrix, 2,5-dihydroxybenzoic acid (2,5-DHB)): calcd for $C_{75}H_{25}NS$ 972.07; found 973.09 $[M^+]$.



Scheme 1. Synthetic routes for C_{60}ThOt.