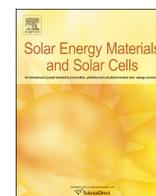




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journal homepage: www.elsevier.com/locate/solmatAll-polymer solar cells with *in-situ* generated n-type conjugated polymer nanoparticlesHyena Lee^a, Jaehoon Jeong^a, Hyemi Han^a, Sungho Nam^a, Hwajeong Kim^{a,b}, Youngkyoo Kim^{a,*}^a Organic Nanoelectronics Laboratory, Department of Chemical Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea^b Research Institute of Advanced Energy Technology, Kyungpook National University, Daegu 702-701, Republic of Korea

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ABSTRACT

We report all-polymer solar cells with new electron-accepting (n-type) polymer nanoparticles, poly(2,7-bis(4-hexylthiophen-2-yl)-9H-fluoren-9-one-co-benzothiadiazole) (BHTF-co-BT), which were *in-situ* generated during polymerization reaction. The size of the BHTF-co-BT nanoparticles was ca. 5–15 nm with a particular single X-ray diffraction peak (d-spacing=1.3 nm), indicative of a highly ordered crystalline state, while their glass transition temperature was ~ 140 °C. Their band gap energy and ionization potential were 1.8 eV and 5.7 eV, respectively. The possibility of the BHTF-co-BT nanoparticles as an electron acceptor for both normal-type and inverted-type all-polymer (polymer:polymer) solar cells was examined by employing poly(3-hexylthiophene) (P3HT) as an electron donor. The normal-type P3HT:BHTF-co-BT solar cells exhibited promising open circuit voltage (V_{oc} =0.67–0.73 V) and fill factor (FF=51.3%), while a three-fold improved short circuit current density and higher V_{oc} (0.77 V) were achieved for their inverted-type solar cells.

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1. Introduction

Organic solar cells (OSCs) have recently attracted keen attention because of their strong competitiveness against conventional inorganic solar cells in terms of viable low-cost fabrication of ultra-thin flexible solar modules [1–3]. Although small molecule-based OSCs exhibited improved efficiency, most of researches have been concentrated on polymer-based OSCs owing to the practical viability of using wet-coating processes at room temperature under atmospheric pressure without using expensive vacuum systems [1–4]. The advancement in the polymer-based OSCs (mostly polymer:fullerene solar cells) has been fueled by series of in-depth researches on the bulk heterojunction nanomorphology as well as invention of new materials (conjugated polymers and soluble fullerenes) [5–14]. In addition to the efficiency improvement, a variety of applied researches have been carried out in order to overcome stability (lifetime) issues, to improve coating processes, and to develop sophisticated module structures [15–20].

Because polymers have in principle strong advantages over small molecules for better flexibility and toughness, all-polymer (i.e., polymer:polymer) solar cells have been persistently studied by replacing a soluble fullerene (in polymer:fullerene solar cells)

with an electron-accepting (n-type) polymer [21–31]. In particular, compared to the limited solar light absorption of fullerenes (electron acceptor) for the polymer:fullerene solar cells, the polymer:polymer solar cells have an additional advantage in enhancing the light harvesting efficiency because electron-accepting polymers can be tuned to absorb more solar light up to 1000 nm (wavelength) [32,33].

However, the power conversion efficiency (PCE) of polymer:polymer solar cells (2–2.8%) is still far behind that of the well-optimized polymer:fullerene solar cells, although a couple of new approaches have been attempted such as a nano-mold technique that makes a polymer bilayer structure to make well-organized large p–n junction interfaces for overcoming the charge blocking resistance that is one of major limiting factors in the bulk heterojunction type polymer:polymer solar cells [23,34–38]. The previous studies inform that the proper control of charge percolation paths (nanomorphology) to overcome the undesirable morphological characteristics (randomly interspersed donor/acceptor phases) is still a crucial factor to improve the performance of polymer:polymer solar cells [28,39–43]. Basically, however, the nanomorphology control is much more difficult for the polymer:polymer bulk heterojunction films than for the polymer:fullerene bulk heterojunction films because of long polymer chains in contrast to the crystallizable fullerene molecules [39–41].

In this work, we attempted to synthesize electron-accepting polymer nanoparticles that can be dispersed on a nanoscale in the electron-donating polymer matrix leading to better charge

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percolation morphologies (than the thread-like polymer chains) in the polymer:polymer bulk heterojunction films. For this purpose, we employed an *in-situ* nanoparticle generation technology during polymerization reaction on the basis of the fact that the solubility of a particular polymer from its constituent monomers with a limited solubility in organic solvents becomes poor so that the polymer chains are subject to shrink and stack each other leading to an aggregate on a nanoscale. To realize this idea, 2,7-bis(4-hexylthiophen-2-yl)-9H-fluoren-9-one (BHTF) was synthesized because it has both high solubility unit (hexylthiophene) and poor solubility unit (fluorenone – a polar carbonyl group leading to unfavorable solubility) in organic solvents. After bromination reaction of BHTF, the target electron-accepting polymer nanoparticles, poly(2,7-bis(4-hexylthiophen-2-yl)-9H-fluoren-9-one-co-benzothiadiazole) (BHTF-co-BT), were *in-situ* synthesized during polymerization in solution. To examine the performance of the BHTF-co-BT nanoparticles, both normal-type and inverted type all-polymer (polymer:polymer) solar cells were fabricated using bulk heterojunction films of poly(3-hexylthiophene) (P3HT) (donor) and BHTF-co-BT nanoparticles (acceptor).

2. Experimental

2.1. Materials and synthesis

To synthesize 2,7-bis(3-hexylthiophen-2-yl)-9H-fluoren-9-one (BHTF), 2,7-dibromo-9H-fluoren-9-one (DBF) and 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (or 3-hexylthiophene-2-boronic pinacol ester, B-3HT) were used as received from Sigma-Aldrich. DBF and B-3HT were dissolved in a mixture of tetrahydrofuran (THF, 5 ml) and deionized water (2 ml) for 20 min, followed by adding tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄, 0.015 g). Then this solution was heated and kept at 85 °C for 16 h. After terminating the coupling reaction, methanol (Aldrich, 99.8%) was added to the reacted mixture for precipitation. The unreacted starting materials were washed out and then the final precipitates were subjected to centrifugation and filtration processes. Next, additional purification processes (column chromatography etc.) were carried out before drying in vacuum oven for 24 h. The synthesized BHTF (yield = 87%) showed its exact mass (FW = 512) from matrix-assisted laser desorption/ionization-time of flight-mass spectrum (MALDI-TOF-MS) (see Fig. S1), which was also confirmed by conventional elemental analysis (EA) (less than 5% deviation depending on samples) and nuclear magnetic resonance (¹³C-NMR) spectroscopy measurement (see Fig. S2). The bromination reaction of BHTF was carried out using N-bromosuccinimide (NBS) in THF (5 ml). The mixture solution of BHTF (0.1 g) and NBS (0.07 g) in THF (5 ml) was refluxed for 5 h. This reaction was terminated after cooling, followed by adding deionized water and dichloromethane. The brominated BHTF, 2,7-bis(5-bromo-3-hexylthiophen-2-yl)-9H-fluoren-9-one (Br-BHTF), was characterized and confirmed by MALDI-TOF-MS measurements (see Fig. S3). To synthesize poly(2,7-bis(3-hexylthiophen-2-yl)-9H-fluoren-9-one-co-benzothiadiazole) (BHTF-co-BT) nanoparticles, Br-BHTF (0.08 g) was mixed with 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]-thiadiazole (or 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester)-BisBA-BT) (0.092 g) in a solvent mixture of THF (5 ml) and deionized water (2 ml). After adding catalysts, potassium carbonate (K₂CO₃) (0.0165 g) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (0.004 g), the reaction mixture was stirred at room temperature for 48 h. Then the temperature was increased up to 85 °C and the reaction was kept for 20 min. During polymerization reaction, tiny nanoparticles were generated and the population of these nanoparticles became enriched with time. After cooling down, the polymerization reaction

was terminated by adding deionized water. The solution was filtered and dried under vacuum for 24 h. A fine powder-like product (BHTF-co-BT) was obtained (yield = 78%). Because the BHTF-co-BT nanoparticles were not dissolved in common organic solvents (toluene, chlorobenzene, chloroform etc.), we attempted to characterize them by employing a solid-state ¹³C-NMR. As shown in Fig. S4, the proper covalent bond between 3-hexylthiophene and benzothiadiazole was confirmed to be successfully formed: New peak at 125 ppm was made by the C–C bond formation between the hexylthiophene part of BHTF and the benzene ring of BT, while the C–Br peak at 116 ppm existed in the 3-hexylthiophene of the Br-BHTF disappeared (note that the peaks are quite broad because of the intrinsic nature of solid-state NMR measurement).

2.2. Film and device fabrication

The BHTF-co-BT nanoparticles were dispersed in THF and spread on quartz or glass substrates for various measurements (SEM images, UV–vis spectra, XRD, and PEYS spectra). Note that the BHTF-co-BT nanoparticles were spread on a gold grid mesh (400 mesh) for HRTEM measurements. For the fabrication of solar cells, the BHTF-co-BT nanoparticles were mixed with P3HT in chlorobenzene, followed by vigorous stirring for well dispersion of the nanoparticles (P3HT:BHTF-co-BT = 1:0.7 and 1:1 by weight). Prior to spin-coating step, indium–tin oxide (ITO)-coated glass substrates (sheet resistance = 10 Ω/□) were patterned to have 12 mm × 8 mm using a photolithography/etching system. The ITO-glass substrates were cleaned with wet (acetone and isopropyl alcohol) and dry (UV–ozone) processes. For the fabrication of normal-type solar cells, the hole-collecting buffer layer was spin-coated on top of the cleaned ITO-glass substrates at 2500 rpm for 1 min using a conducting polymer solution (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, PH500, HC Starck)), followed by annealing at 230 °C for 15 min. Then the P3HT:BHTF-co-BT film (thickness = ca. 75 nm) was spin-coated on the PEDOT:PSS layer. The active layer (P3HT:BHTF-co-BT)-coated samples were soft-baked at 50 °C for 30 min. These samples were loaded into a vacuum chamber inside an argon-filled glove box. After pumping down the chamber pressure to ~1 × 10^{−6} Torr, aluminum (Al, *t* ≅ 100 nm) top electrodes were deposited by thermal evaporation. The active area of the P3HT:BHTF-co-BT solar cells was 3 mm × 3 mm. Then these solar cells were subject to thermal annealing (130 °C or 140 °C for 30 min) inside the same glove box system and stored before measurement for avoiding any attack from oxygen and/or moisture that can possibly degrade the device performance. Before fabricating the inverted-type solar cells, we prepared zinc oxide (ZnO) precursor solutions by dissolving zinc acetate dihydrate (Aldrich) and ethanolamine (Aldrich) in 2-methoxyethanol (Aldrich). This ZnO precursor solution was subjected to vigorous stirring at ~80 °C for the desirable reaction and then was spin-coated on the cleaned ITO-glass substrates at 2000 rpm 30 s. After spin-coating, the ZnO-coated ITO-glass substrates were thermally annealed at 200 °C for 15 min in air. Next, the P3HT:BHTF-co-BT (1:1) film was deposited on the ZnO-coated ITO-glass substrates by spin-coating the corresponding solution. After soft-baking at 50 °C for 30 min, the PEDOT:PSS layer was spin-coated on the P3HT:BHTF-co-BT layer using the PEDOT:PSS solution that is diluted with isopropyl alcohol. These samples were loaded into the vacuum chamber for the deposition of silver (Ag, 60 nm) top electrodes. The active area of the inverted-type solar cells was the same as for the normal-type solar cells. Finally, the inverted-type solar cells were subjected to thermal annealing at 130 °C for 30 min inside the same glove box.

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