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Quinoxaline-based π -conjugated donor polymer for highly efficient organic thin-film solar cells

Daisuke Kitazawa,^{a)} Nobuhiro Watanabe, Shuhei Yamamoto, and Jun Tsukamoto

Electronic and Imaging Materials Research Laboratories, Toray Industries, Inc., 3-2-1 Sonoyama, Otsu, Shiga 520-0842, Japan

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A quinoxaline-based π -conjugated donor polymer, poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5-(5',8'-di-2-thienyl-2',3'-diphenylquinoxaline)] (N-P7), was synthesized to achieve a high power conversion efficiency (PCE) of bulk heterojunction (BHJ)-based solar cells. The optical band-gap and highest occupied molecular orbital level of N-P7 were 1.95 and -5.37 eV, respectively. BHJ-based solar cells using N-P7 as a donor and phenyl C₇₁ butyric acid methyl ester as an acceptor gave a PCE as high as 5.5% under AM 1.5G 100 mW/cm² illumination. We also investigated the effects of substituent groups of quinoxaline-based polymers on the morphology of the BHJ layer. © 2009 American Institute of Physics. [DOI: 10.1063/1.3202393]

Organic thin-film solar cells (OSC) have potential advantages of low cost by use of printing or vacuum-sublimation technologies.¹ However, OSC have not yet reached the level of practical use due to their low power conversion efficiency (PCE). One possible way to improve the efficiency is to introduce the bulk heterojunction (BHJ) structure, which is effective to separate carriers from exciton state because the BHJ structure has a three-dimensional donor/acceptor network and a large contact area between the donor and acceptor.² A number of polymer-based donor materials have been developed for use in BHJ-based polymer solar cells.^{3–8} The PCE of BHJ-based polymer solar cells has reached 3%–5% using π -conjugated polymers as a donor material, such as regioregular poly(3-hexylthiophene) (P3HT).⁹

Control of the BHJ structure and the development of new donor materials are also important to enhance the PCE of the solar cells. For example, thermal annealing,⁹ slow vaporization,¹⁰ and the addition of alkane dithiol¹¹ are known as methods for controlling the BHJ structure. It is also effective to change the substituents of the polymer as a method to change the BHJ morphology.¹² Within the class of polymer-based organic semiconductors, quinoxaline-based polymers are active materials for OSC.^{7,13} The quinoxaline unit is an attractive structure from the viewpoint of controlling the morphology because it has the advantage of introducing the substituent groups easily on the two and three positions of quinoxaline. In this study, we synthesized and characterized the quinoxaline-based donor polymer, poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5-(5',8'-di-2-thienyl-2',3'-diphenylquinoxaline)] (N-P7), to achieve a high PCE of BHJ-based solar cells by controlling the morphology of the BHJ active layer.

Phenyl C₇₁ butyric acid methyl ester ([70]PCBM) was purchased from Advanced Technology Research and used without any purification. The quinoxaline-based donor polymer, N-P7, was synthesized palladium-catalyzed coupling reactions as shown in Fig. 1. The monomer **1** was synthesized following the previously reported procedure.¹⁴ The monomer **2** was purchased from Aldrich Chemical Co., Inc., and used

without further purification. Polymerization was carried out with equivalent amounts of the two monomers (**1** and **2**) and the chloroform (CF) soluble fraction was isolated. For comparison, poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5-(5',8'-di-2-thienyl-(2',3'-bis-(3'-octyloxyphenyl)-quinoxaline))] (APFO-15), which has a structure similar to N-P7 and has been reported to show a PCE as high as 3.7%, was synthesized as described.¹³ The molecular weights of polymers were measured by gel permeation chromatography (HLC-8220GPC; Tosoh Corp.) using CF as the eluent and polystyrene as a standard. UV-visible absorption spectra of the polymer thin films (approximately 60 nm thick) were measured using a Hitachi U-3010 UV-vis spectrophotometer. The optical band-gap (E_g) of the polymer thin films was estimated from the equation $E_g(\text{eV}) = \lambda_{\text{onset}}(\text{nm}) / 1240$, where λ_{onset} is the wavelength at the onset of absorption of the UV-visible spectra. The highest occupied molecular orbital (HOMO) level of the polymers was measured by the method of photoelectron spectroscopy in air using AC-2 (Riken Keiki Co., Ltd.). The surface morphology of BHJ active layers (approximately 100 nm thick) composed of polymer (N-P7 or APFO-15) and [70]PCBM (1:4, w/w) was measured by atomic force microscopy (AFM). These BHJ active layers were prepared in chlorobenzene (CB) and spin-coated on top of the glass substrates.

Fabrication and characterization of the BHJ-based solar cells were performed as follows. The buffer layer was

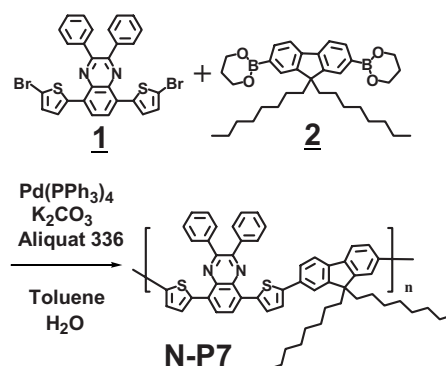


FIG. 1. Synthesis of N-P7.

^{a)}Electronic mail: daisuke_kitazawa@nts.toray.co.jp.

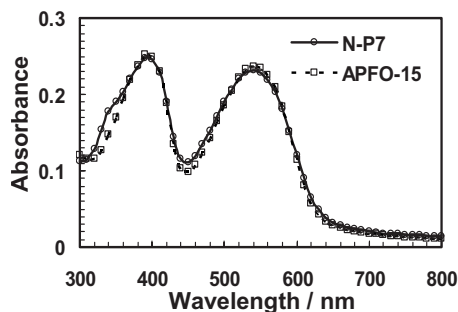


FIG. 2. UV-visible absorption spectra of the polymer thin films (approximately 60 nm thick).

formed by spin-coating poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; approximately 60 nm thick) on precleaned indium-tin-oxide (ITO) anode/glass substrates. A solution of polymer (N-P7 or APFO-15) and [70]PCBM (1:4, w/w) was spin-coated on top of the PEDOT:PSS layer to form the BHJ-based active layers (approximately 100 nm thick). CB and/or CF were used as solvents. Aluminum (Al, 80 nm thick) was thermally evaporated on top of the BHJ-based active layers with a shadow mask to form a cathode. The active area (intersection area of the ITO anode and the Al cathode) of the device was 25 mm². Current density–voltage (*J*-*V*) measurements in the dark and under AM 1.5G 100 mW/cm² illumination using a solar simulator (YSS-E40; Yamashita Denso Corp.) were performed with a Hewlett-Packard 4140B pA Meter/DC Voltage Source in air at ambient temperature. The incident photon-to-current efficiency (IPCE) spectra of BHJ-based solar cells were measured under illumination with high power monochromatic light from a Xe lamp (1–7 mW/cm² at each wavelength, SM-25; Bunkoh-Keiki Co., Ltd.) at room temperature. IPCE was calculated from the equation $\text{IPCE}(\%) = 1240J_{\text{SC}}/(\lambda I_p)$, where J_{SC} is the short-circuit current density, λ and I_p are the wavelength and the intensity of incident monochromatic light, respectively.

The synthesized N-P7 had a yield of 78% and molecular weights of $M_n = 16\,600$ and $M_w = 39\,500$. APFO-15 had a high yield (91%) due to good solubility. On the other hand, the molecular weights of APFO-15 were slightly lower ($M_n = 15\,300$ and $M_w = 33\,000$) than those of N-P7. The UV-visible absorption spectra of thin films of N-P7 and APFO-15 are shown in Fig. 2. The absorbance properties of these polymers were almost the same. The optical band-gap (E_g) and HOMO level of N-P7 were 1.95 and -5.37 eV, respectively, and in the case of APFO-15, E_g and HOMO level were 1.96 and -5.36 eV, respectively. Thus, the UV-visible absorbance properties and HOMO level were almost independent of the substituent groups of the donor polymers.

The surface topographies of BHJ active layers composed of donor polymers and [70]PCBM (1:4, w/w) by AFM are shown in Fig. 3. A marked difference in surface morphology between these films was observed. The surface topography of BHJ film of N-P7 [Fig. 3(a)] showed only small phase separation (<100 nm). In contrast, BHJ film of APFO-15 [Fig. 3(b)] was composed of domains with lateral dimensions of several hundreds of nanometers. These results suggested that the substituent groups attached to the quinoxaline unit affect the morphology of the BHJ structure. The substituents of the quinoxaline unit were phenyl groups for N-P7. On the

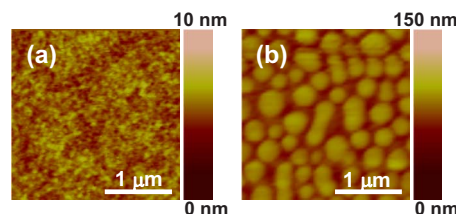


FIG. 3. (Color online) Surface topography of the BHJ-based active layer (approximately 100 nm thick) composed of polymers [(a) N-P7 and (b) APFO-15] and [70]PCBM (1:4, w/w) measured by AFM.

other hand, the substituents of the quinoxaline unit of APFO-15 were octyloxy-substituted phenyl groups. One possible explanation for the difference in surface morphology is that the substituent groups attached to the quinoxaline unit not only change the solubility of the polymer but also influence the compatibility of the polymer and [70]PCBM.

The performance of the solar cells may be influenced by the solvent used for preparation of the active layer. Therefore, we investigated the effects of solvent blend ratio with CB and CF. Figure 4 shows the normalized values of the parameters [short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and PCE] of BHJ-based solar cells fabricated with N-P7 and [70]PCBM as a function of solvent blend ratio [CB/(CB+CF), v/v]. The open-circuit voltage and FF were almost independent of the blend ratio. In contrast, the short-circuit current density was considerably affected by the blend ratio. The short-circuit current density increased gradually when the blend ratio was changed from 0 to 0.6 and decreased slightly when this ratio was changed from 0.6 to 1. As a result, the highest PCE was obtained when the blend ratio was 0.6. However, no changes in the surface topography features at the micrometer-scale were observed by AFM for different solvent blend ratios. The CB/CF ratio is thought to influence the nanometer-scale phase separation and mixed solvent at a blend ratio of 0.6, forming a favorable network of donor and acceptor.

Based on the above results, we fabricated a device using this mixed solvent system [CB/(CB+CF), ratio=0.6], combined with insertion of a lithium fluoride (LiF) layer between the BHJ active layer and the Al cathode. The device structure was glass/ITO/PEDOT:PSS (approximately 60 nm thick)/N-P7 and [70]PCBM (1:4, w/w, approximately 100 nm thick)/LiF (0.1 nm)/Al (80 nm), and the active area of the device was 25 mm². This device gave a short-circuit current density of 9.72 mA/cm², an open-circuit voltage of 0.990 V, a FF of 0.574, and a PCE of as high as 5.5% under AM 1.5G

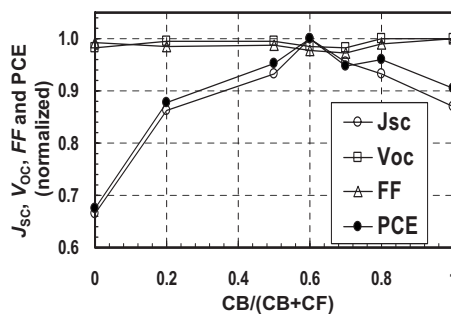


FIG. 4. Normalized values of J_{SC} , V_{OC} , FF, and PCE of BHJ-based solar cells fabricated with N-P7 and [70]PCBM (1:4, w/w) as a function of CB/(CB+CF) (v/v) blend ratio.

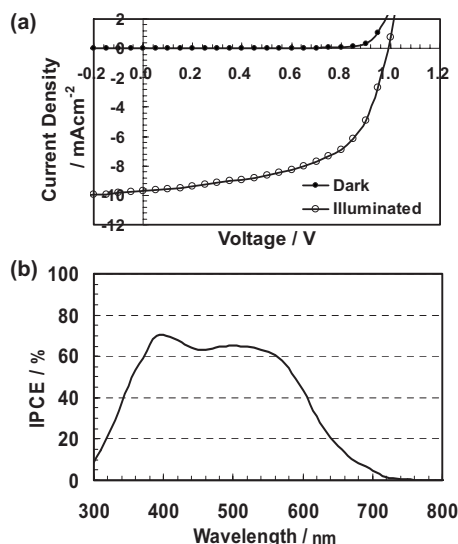


FIG. 5. (a) Current density–voltage (J - V) characteristics under AM 1.5G 100 mW/cm^2 illumination and (b) IPCE spectrum of the BHJ-based solar cell (active area: 25 mm^2) fabricated with N-P7 and [70]PCBM (1:4, w/w).

100 mW/cm^2 illumination, as shown in Fig. 5(a). The J - V measurement of the device was conducted in air without any passivation. The N-P7 device seems to be more stable in the atmosphere than the P3HT device because N-P7 has a deeper HOMO level than that of P3HT (HOMO levels of P3HT and N-P7 measured by AC-2 were -4.72 and -5.37 eV, respectively). The IPCE spectrum of the N-P7 device exhibited a considerably high IPCE value with a peak at $\sim 70\%$, as shown in Fig. 5(b). This value is considerably higher than the reported external quantum efficiency of $\sim 43\%$ in the case of APFO-15.¹³

BHJ-based solar cells were fabricated with APFO-15 using the same conditions [CB/(CB+CF), ratio=0.6, thickness of LiF=0.1 nm] for comparison. The PCE of this device was 1.74% ($J_{\text{SC}}=4.05$ mA/cm^2 , $V_{\text{OC}}=0.910$ V, and $\text{FF}=0.471$). The high PCE for N-P7 may be attributed to the nanometer-scale phase separation of the BHJ active layer, as shown in Fig. 3(a).

In summary, we have synthesized a quinoxaline-based π -conjugated donor polymer, N-P7, to achieve a high PCE of BHJ-based solar cells by controlling the morphology of the BHJ active layer. The UV-visible absorbance properties

and HOMO level were almost independent of the donor polymer substituent groups. However, the surface morphology of the active layer measured by AFM was considerably affected by the substituents. We obtained favorable morphology of the BHJ active layer by attachment of unsubstituted phenyl groups to the quinoxaline unit of the polymer. Combined with use of a CB/CF mixed solvent system, N-P7 gave a PCE as high as 5.5% under AM 1.5G 100 mW/cm^2 illumination.

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