



A new anodic buffer layer material for non-mixed planar heterojunction chloroboron subphthalocyanine organic photovoltaic achieving 96% internal quantum efficiency

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ABSTRACT

Nonmixed planar heterojunction (PHJ) small-molecule organic photovoltaics (OPVs) with 96% internal quantum efficiency (at 595 nm) and 4.77% power conversion efficiency (PCE) have been demonstrated. In addition to boron subphthalocyanine chloride (SubPc) and C₆₀ as electron donor and acceptor materials, respectively, PHJ OPVs contain an ultrathin (2 nm) buffer layer of bis-(naphthylphenylaminophenyl) fumaronitrile (NPAFN) between the indium tin oxide (ITO) anode and the donor layer (SubPc). Compared with copper phthalocyanine (CuPc) or α -naphthylphenylbiphenyl diamine (NPB) buffer layers, the NPAFN buffer layer blocks the exciton diffusion from the SubPc electron donor layer to the ITO anode more effectively and considerably improves the short circuit current (J_{sc}) from 5.96 (without an NPAFN layer) to 7.70 mA/cm² (with a 4-nm-thick NPAFN layer). In addition, experimental results indicated that the NPAFN buffer layer reduces the crystallization, or stacking, of the SubPc electron donor, thereby limiting the reverse saturation current and elevating the open circuit voltage (V_{oc}) from 1.01 (without an NPAFN layer) to 1.08 V (with a 2-nm thick NPAFN layer). However, series resistance (R_s) of the OPV monotonically increases with increasing NPAFN layer thickness. The performance of the OPV is optimized when the NPAFN buffer layer thickness is 2 nm. Compared with a SubPc–C₆₀ PHJ OPV without an NPAFN buffer layer, the PCE of a OPV with a buffer layer increases by 22% from 3.96% to 4.77%, with a concurrent increase in J_{sc} (from 5.96 to 7.02 mA/cm²) and V_{oc} (from 1.01 to 1.08 V). However, a decrease in R_s (from 10.21 to 14.95 Ω cm²) and in fill factor (from 65% to 63%) is also observed.

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1. Introduction

Organic photovoltaic (OPV) devices have been extensively studied because of their enormous potential and simple fabrication process

[1–4]. In polymeric systems, a power conversion efficiency (PCE) of more than 9% has been achieved through the optimization of materials used in polymer-based bulk heterojunction (BHJ) inverted and/or tandem structures [5–8]. However, their low reproducibility and complicated purification procedure hamper their commercial application [9]. Compared with polymer BHJ solar cells, a multilayer planar heterojunction (PHJ) device fabricated using small molecules through a vacuum process suffer from a low photocurrent and short circuit current (J_{sc}), mainly because of the limited exciton

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dissociation interface and insufficient sunlight absorption by the materials [10,11]. Recently, a series of materials – mainly phthalocyanine-type chromophores such as copper-Pc (CuPc), zinc-Pc (ZnPc), tin-Pc (SnPc), chloroaluminum-Pc (ClAlPc), titanium-Pc (TiOPc), and subphthalocyanine (SubPc) – with the ability to absorb long wavelengths in the visible spectrum and even extend to the near infrared range, exhibit wide spectral coverage when used with fullerene materials [12–18]. Cnops et al. even investigated the efficient fullerene-free cascade structure with SubNc and SubPc as the electron acceptor, showed the long absorption range from visible to near-infrared spectrum and extreme high efficiency of 8.4% [19]. These phthalocyanine-type chromophores not only extend the absorption range of the device efficiently, but also exhibit changes in the molecular packing, orientation, and even the energy level with regard to distinct deposition methods, resulting in distinct optical and electrical characteristics [20–22]. In addition to phthalocyanine materials, numerous amorphous hole-transporting materials with a planar structure and high hole mobility are also widely applied as a donor material in OPV devices because of their isotropic optical and charge-transporting properties [23–25]. The energy level offset between the donor materials and fullerene heterojunction structure, resulting in varying device performance because of the trade-off between the open circuit voltage (V_{OC}) and charge-separation efficiency of the OPV device, have also been widely discussed [12,26]. However, the low external quantum efficiency (EQE) indicates that the photocurrent output of these devices requires improvement. The construction of a BHJ device structure through co-evaporation of small-molecule materials in a vacuum has also been explored because the considerable dissociation interface in the structure can substantially improve the photocurrent [27–29]. However, compared with the polymeric counter-

parts, the difficulty of controlling small-molecule morphology during the co-evaporation of multi-sources reduces the fill factor (FF) in the structure [30–33]. To improve the exciton dissociation efficiency, a material of substantial exciton diffusion length is essential for facilitating exciton diffusion at the interface for charge (or exciton) dissociation [23,34–37]. The incorporation of an exciton blocking layer (EBL) is an alternative approach to improving the exciton dissociation efficiency [38–41]. In addition, efforts have been made to develop an anodic buffer or two-donor cascade OPV device to improve the device performance [42–47]. By inserting a buffer layer between the anode and the electron donor layers, hole extraction at the anodic interface could be considerably enhanced, resulting in enhanced charge collection efficiency, EQE, and device performance. An anodic EBL can also prevent the excitons from quenching by the highly conductive electrode, thereby increasing the exciton dissociation efficiency [48,49]. Hirade and Adachi demonstrated a PCE of up to 5.24% in a small-molecule PHJ OPV with an EBL at the anode-donor interface [50]. Barito et al. further investigate the alternative concept which introduced the transparent buffer layer, α -NPD, as the exciton dissociation layer (EDL) to provide an additional interface for exciton dissociation and result in a 27% increase in short-circuit current (J_{SC}) from 3.94 to 4.90 mA/cm² [51]. However, even though a PCE of 5.24% is among the highest for nonmixed PHJ OPVs, the EQE of such devices is still less than 60%.

In this paper, we fabricated an OPV device based on a SubPc-C₆₀ PHJ structure with an extremely high internal quantum efficiency (IQE) of 96%, by inserting bis-(naphthylphenylamino-phenyl)fumaronitrile (NPAFN) as the anode buffer layer between the ITO and SubPc layers [52]. In addition to the influence on OPV exciton, IQE, and J_{SC} , as indicated by the experimental results, introduction of the NPAFN anode buffer layer also affects the crystallization (or molecular stacking) of the electron donor material SubPc; this reduces the intermolecular interaction and

the reverse saturation current, improving the V_{OC} and overall PHJ OPV performance.

2. Experimental

The PHJ OPV devices based on SubPc-C₆₀-BCP structure were fabricated on patterned indium tin oxide (ITO) substrates with a sheet resistance of 40 Ω /sq. Prior to device fabrication, the substrates were cleaned using various solvents and treated with O₂ plasma (40 W) for 5 min to increase the work function of the ITO from 4.70 ± 0.05 eV (un-treat) to 5.65 ± 0.05 eV (after the O₂ plasma treatment) [22]. After surface treatment, the substrates were transferred to the high vacuum chamber of the thermal evaporator and the organic hole-transporting material was deposited to create donor buffer layers of various thicknesses. After the donor buffer layers were deposited, organic active materials were deposited in the sequence of SubPc (15 nm)-C₆₀ (55 nm)-BCP (5 nm) at a pressure of 6×10^{-6} Torr simultaneously to prevent variations in the active materials of each device. The deposition rate of each organic material was maintained in the range of 0.1 to 0.2 nm/s. A 100-nm Al cathode was placed in the same chamber through a shadow mask and the 4 mm² active regions of the devices were defined as the overlapping area between ITO-organic layer-Al. Except the NPAFN, all the organic material was purchased from Lumtec Co. and the SubPc was purified two times with gradient sublimation prior to use [53]. After the evaporation process, the devices were transferred to a glove box and encapsulated in an N₂ environment to prevent damage from oxygen and water molecules. The single buffer layer or buffer-SubPc bilayer thin films were deposited on the ITO substrates in the same sequence for material analysis.

The J - V characteristics of the OPV devices were measured using an I - V source meter (Keithley 2400) both in the dark and under the illumination of a 1-sun AM 1.5 G solar simulator, which was calibrated using a Si reference cell. The AM 1.5 G solar simulator was used to generate the bias light for measuring the IPCE spectra. A monochromator, which was calibrated using a photodiode and chopped at 250 Hz, was used to select wavelengths between 350 and 800 nm for illuminating the OPV. The photocurrent from the OPV was measured through the lock-in amplifier, which was referenced to the chopper frequency. During measurement, the OPV device was covered with a 1 mm² aperture to eliminate the extrinsic effect. The measurements of the IPCE spectra were integrated to calculate the J_{SC} of the devices and subsequently compared with the J_{SC} measured under the illumination of the solar simulator. The inaccuracy between the measured J_{SC} and the J_{SC} calculated from the IPCE spectrum was under 3% for each device. Furthermore, the IQE of the devices were calculated from the EQE spectrum and the absorption efficiency of the devices. The absorption efficiency could be calculated from the equation $A(\lambda) = 100\% - T(\lambda) - R(\lambda)$, where $A(\lambda)$, $T(\lambda)$, and $R(\lambda)$ are the absorption efficiency, transmission efficiency, and the reflection efficiency, respectively. The transmission and the reflection efficiency of the devices were measured by the spectrophotometer (V-630, Jasco) with the integration sphere. After the absorption efficiency of the devices was determined, the IQE could be calculated by divide the EQE spectrum with absorption efficiency in each wavelength.

For the material analysis, the photoelectron spectrometer (AC-2, Riken Keiki) was used to measure the work function of ITO and the highest occupied molecular orbital (HOMO) level of the organic materials, and the absorption spectra of the materials were measured using UV-visible spectroscopy. The surface morphology of the materials was characterized through noncontact-mode atomic force microscopy (AFM) and the synchrotron X-ray diffraction (SR-XRD) measurements were recorded at the beam line BL-4C in the KEK

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