Contents lists available at ScienceDirect

Organic Electronics

An efficient nonfullerene acceptor for all-small-molecule solar cells with versatile processability in environmentally benign solvents

Oh Kyu Kwon, Jung-Hwa Park, Soo Young Park[*]

Center for Supramolecular Optoelectronic Materials, Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, South Korea

ABSTRACT

A new structure of dicyanodistyrylbenzene-naphthalimide-based nonfullerene acceptor NIDCSN was synthesized and characterized to have a favorable electron accepting property and versatile processability in various organic solvents. The nonfullerene all-small-molecule solar cells comprising p-DTS(FBTTh$_2$)$_2$ as the donor and NIDCSN as the acceptor exhibited a maximum power conversion efficiency of 3.45% with a remarkable open-circuit voltage of 1.04 V, together with similar device performances when fabricated in five different solvents including environmentally benign non-halogenated ones.

1. Introduction

In the past decade, bulk-heterojunction (BHJ) organic solar cell research has made great leap forward with the development of efficient organic photoactive materials, currently exhibiting power conversion efficiencies (PCEs) exceeding 10% [1]. Until now, such material developments have focused mostly on the high-performance donor materials because fullerene-based [6,6]-phenyl-(C$_{61}$ or C$_{71}$)-butyric acid methyl ester (PC$_{61}$BM or PC$_{71}$BM) molecules which have outstanding electron accepting and transporting abilities have been exclusively utilized as the acceptor material in the BHJ devices. While these PCBM-based devices have shown successful results, some drawbacks of the PCBM, such as weak visible light absorption and difficulty of energy level control, limit the further improvement of the device efficiency. In this respect, nonfullerene electron acceptors are considered potential alternatives to the conventional fullerene-based acceptor in recent years [2,3]. With the diverse and versatile molecular design, however, the nonfullerene acceptors could have enhanced light harvesting abilities and finely tuned frontier molecular orbital energy levels, providing possibilities of enhanced device efficiencies,

especially in increased open-circuit voltages (V_{oc}). Very recently, a variety of nonfullerene small molecule/polymeric acceptors have been reported in combination with several high-performance donor materials to have PCEs of 6.0–7.7% [4–15].

Attaining favorable donor–acceptor blend morphologies to facilitate efficient charge separation and transport is an important goal for high-performance organic solar cells. Because the film characteristics are affected mainly by processing solvent properties like boiling point, viscosity, and so on, selection of a suitable solvent system is the most critical in the device optimization process. Thus far, halogenated and/or aromatic solvents such as chloroform (CF), chlorobenzene (CB), and o-dichlorobenzene (o-DCB) have been used commonly in a large number of devices due to their high solubility for active materials [16,17]. However, such halogenated ones have to be avoided in application for practical large-scale manufacturing due to their environmentally harmful nature [18,19]. Therefore, the need for using environmentally benign solvents, such as n-butanol (n-BuOH) [20], 2-methyltetrahydrofuran (2-MeTHF) [21], N-methyl-2-pyrrolidone (NMP) [22], and non-halogenated aromatic ones [23–25], has been growing in recent years. Nonetheless, low solubility of the PCBM acceptor as well as the donor materials in non-halogenated solvents has limited their extensive applications in various processing conditions. In this regard, nonfullerene acceptors could be promising materials well compatible with various organic solvents because their solubility

---

* Corresponding author.
E-mail address: parksy@snu.ac.kr (S.Y. Park).

characteristics could be controlled easily by modifying molecular structures. In spite of potential applications of the nonfullerene acceptors including large area roll-to-roll processing [26,27], there have been only few reports of high-performance nonfullerene solar cells with unconventional environmentally benign processing solvents [15,28,29].

Recently, we developed dicyanodistyrylbenzene-naphthalimide (DCS-NI) type molecular acceptors, which show outstanding electron accepting and transporting properties with a balanced self-assembly behavior that suppress undesirable aggregations in films. The resulting DCS-NI acceptor-based solar cells showed maximum 2.7% and 5.4% PCEs with a polymer poly(3-hexylthiophene) (P3HT) and a small molecule 7,7'-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole) (*p*-DTS(FBTTh$_2$)$_2$) as the donor, respectively [30,31]. Unfortunately, although these combinations yielded successful results for solar cells, these devices had to fabricated using only CF as a processing solvent due to unfavorable film formation features in other aromatic solvents. This difficulty for favorable film formation in non-halogenated solvents may limit the broad applications in nonfullerene solar cells, so improving processability of DCS-NI acceptors in various processing conditions remained challenging.

Here we present a new DCS-NI type acceptor, (2E,2'E)-3,3'-(1,5-bis(hexyloxy)naphthalene-2,6-diyl)bis(2-(5-(4-(N-(2-ethylhexyl)-1,8-naphthalimide)yl)thiophen-2-yl)acrylonitrile) (NIDCSN), with remarkable processability in various organic solvents. This compound was designed by replacing a phenyl unit on the core of our previously published high-performance DCS-NI compounds [30,31] with a naphthalene unit, showing highly enhanced solubility in various solvents with uniform film formation characteristics. In addition, as for a donor material selection of the solar cell devices, the high-performance small molecular donor *p*-DTS(FBTTh$_2$)$_2$ [31,32] (Fig. S1 in Supplementary material) was also adopted in this work because small molecular systems have an advantage of superior solubility in most of solvents over polymeric systems as well as circumvent batch-to-batch variation issues caused by molecular weight distribution of synthetic polymers. The resulting all-small-molecule solar cells fabricated using *p*-DTS(FBTTh$_2$)$_2$ as the donor and NIDCSN as the acceptor in five different solvents, such as CF, CB, tetrahydrofuran (THF), toluene, and *o*-xylene, all exhibited similar device performances at a 110 °C annealing condition with a best PCE of 3.45% and remarkable V_{oc} values of 1.04–1.08 V. The detailed blend characteristics in all of the processing conditions were examined by optical, morphological, and electrical analyses.

2. Materials and methods

2.1. Synthesis

2.1.1. (2E,2'E)-3,3'-(1,5-bis(hexyloxy)naphthalene-2,6-diyl)bis(2-(5-(4-(N-(2-ethylhexyl)-1,8-naphthalimide)yl)thiophen-2-yl)acrylonitrile) (NIDCSN)

Compound (1) [33] and (2) [30] were synthesized using the procedure reported elsewhere. Compound (1) (0.10 g, 0.26 mmol) and (2) (0.24 g, 0.56 mmol) were dissolved in MeOH (30 mL) and stirred at 50 °C. Potassium *tert*-butoxide (*t*-BuOK, 20 wt% solution in THF) (0.41 mL, 0.65 mmol) was then injected into the mixture followed by stirring for 6 h. After cooling to room temperature, the orange precipitate was collected by filtration and washed with MeOH. Flash silica gel and alumina column purification in THF, followed by recrystallization with EtOAc, gave an orange powder (0.27 g, yield = 86%). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.69 (d, J = 7.3 Hz, 2H; Ar H), 8.66 (d, J = 8.3 Hz, 2H; Ar H), 8.65 (d, J = 7.5 Hz, 2H; Ar H), 8.42 (d, J = 9.0 Hz, 2H; Ar H), 8.04 (s, 2H; vinyl H), 8.02 (d,

J = 9.1 Hz, 2H; Ar H), 7.88 (d, J = 7.6 Hz, 2H; Ar H), 7.83 (dd, J = 8.0, 7.9 Hz, 2H; Ar H), 7.59 (d, J = 3.8 Hz, 2H; Ar H), 7.37 (d, J = 3.8 Hz, 2H; Ar H), 4.20–4.12 (m, 4H; −CH$_2$−), 4.08 (t, J = 6.3 Hz, 4H; −OCH$_2$−), 2.02–1.93 (m, 6H; −CH− and −CH$_2$−), 1.70–1.60 (m, 4H; −CH$_2$−), 1.47–1.25 (m, 24H; −CH$_2$−), 0.95 (t, J = 7.3 Hz, 6H; −CH$_3$), 0.89 (t, J = 6.8 Hz, 6H; −CH$_3$), 0.85 (t, J = 7.0 Hz, 6H; −CH$_3$); ^{13}C NMR (126 MHz, CDCl$_3$, δ): 164.66, 164.40, 156.69, 141.92, 141.12, 137.87, 134.60, 131.94, 131.87, 130.85, 130.71, 130.08, 130.01, 129.14, 128.85, 128.34, 127.81, 124.88, 124.81, 123.41, 122.89, 119.84, 116.77, 106.74, 44.52, 38.17, 31.98, 31.91, 31.00, 30.66, 28.94, 26.33, 24.32, 23.31, 22.89, 14.32, 14.27, 10.90; MALDI-TOF MS (*m/z*): [(M+H)$^+$] calcd for C$_{76}$H$_{80}$N$_4$O$_6$S$_2$: 1208.55, found: 1208.62; EA: calcd (%) for C$_{76}$H$_{80}$N$_4$O$_6$S$_2$: C 75.46, H 6.67, N 4.63, S 5.30; found: C 75.47, H 6.69, N 4.61, S 5.31.

2.2. Characterizations

^{1}H and ^{13}C NMR spectra were obtained on Bruker Avance 300 and Avance 500 spectrometers. Mass spectrum was measured using a Voyager-DETM STR Biospectrometry Workstation, and elemental analysis was performed on a CE Instrument EA1110 instrument. The density functional theory calculation was carried out in gas phase using the Gaussian 09 quantum-chemical package. The geometry optimization of the ground state of the compound was performed using the B3LYP functionals with the 6-31G** basis set. In the calculation, all alkyl chains were replaced with a methyl unit. The UV−vis absorption spectra were obtained on a Shimadzu UV-1650 PC spectrometer. The thermal properties were recorded using DSC and TGA methods under a N$_2$ atmosphere at a heating rate of 10 °C min^{-1} using a PerkinElmer DSC-7 and a TA instruments Q-5000 IR, respectively. CV experiment was carried out using a Princeton Applied Research Potentiostat/Galvanostat Model 273A onto which was configured a three electrode cell assembly including a glassy-carbon working electrode, a platinum wire counter electrode, and a silver wire quasi-reference electrode. After N$_2$-saturation in a one compartment cell, measurements were carried out in 3 mM dichloromethane solution with tetrabutylammonium tetrafluoroborate as the supporting electrolyte with the scan rate of 100 mV s^{-1}. The HOMO/LUMO levels were estimated based on the onset oxidation/reduction potentials (E_{ox}/E_{red}) and each oxidation/reduction potential was calibrated using ferrocene ($E_{Fc/Fc+}$) as a reference (Energy level = −[E_{ox}/E_{red} − $E_{Fc/Fc+}$ + 4.8]). The film thickness was measured using a KLA Tencor Alpha-Step IQ surface profiler. The AFM images were obtained using Multimode with a Nano Scope V Controller (Bruker) in the tapping mode. The TEM images were obtained using FEI Tecnai F20 (200 kV) with EDAX EDS system at Research Institute of Advanced Materials in SNU, Korea. TEM samples were prepared as follows: The blend solutions were spin-coated onto the PEDOT:PSS-coated glass. After annealing, the films were floated off in distilled water, collected on a copper grid, and then dried under a vacuum.

2.3. Solar cell device fabrication and measurements

Solar cells were fabricated with the structure ITO/PEDOT:PSS/*p*-DTS(FBTTh$_2$)$_2$:NIDCSN/Ca/Al. The patterned indium tin oxide (ITO) glass substrate was pre-cleaned in an ultrasonic bath of distilled water, acetone, and isopropanol, and then exposed to a UV-ozone clean for 20 min. A 30−40 nm layer of PEDOT:PSS (Clavious P VP AI 4083) was spin-coated onto the ITO glass (5000 rpm, 30 s) and baked on a hot plate at 150 °C for 20 min. Subsequently, the blend solution of *p*-DTS(FBTTh$_2$)$_2$ and NIDCSN was fully dissolved at 55 °C (for CF, THF) or 70 °C (for CB, toluene, *o*-xylene) for three or more hours before being filtered using 0.50 μm syringe filters and spin-coated at 1800 rpm for 60 s in a N$_2$ glovebox. After drying the