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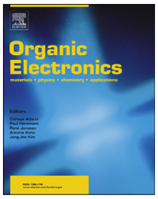

Carbazole-based small molecules for vacuum-deposited organic photovoltaic devices with open-circuit voltage exceeding 1 V

Yuan Jay Chang [a, **], Jung-Lien Hsu [a], Yi-Hua Li [b], Sajal Biring [b], Tzu-Hung Yeh [b, c], Jhih-Yan Guo [b], Shun-Wei Liu [b, *]

[a] *Department of Chemistry, Tunghai University, Taichung 40704, Taiwan*
[b] *Department of Electronic Engineering and Organic Electronics Research Center, Ming Chi University of Technology, New Taipei City 24301, Taiwan*
[c] *Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan*

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ABSTRACT

Fabrication of vacuum deposited small molecules organic solar cell with open-circuit voltage (V_{oc}) exceeding 1 V is crucial in advancing the applications of organic photovoltaics (OPVs). Here, a novel carbazole-based donor-π bridge-acceptor (D-π-A) of p-type material (F-series) in combination with fullerene derivative C_{60} or C_{70} as n-type material for bulk-heterojunction OPVs with the structure of ITO/MoO_3 (15 nm)/F-series donor: C_{60} or C_{70} (40 or 80 nm)/BCP (7 nm)/Ag (120 nm) have been proposed. The vacuum deposited small molecules OPV with the donor layer consisting of F1 combined with the electron acceptor C70 exhibits a high power conversion efficiency (PCE) of 4.93%. The higher PCE of the OPV is attributed to the large V_{oc} value of 1.02 V. The analysis of photophysical properties using a time-dependent density functional theory model and the B3LYP functional corroborates the experimental results and provides the evidence on increasing the V_{oc} of OPVs.

1. Introduction

The global energy demand is raised rapidly in current year [1,2]. Combustion of fossil fuels produces large quantities of greenhouse gases, which may have catastrophic consequences resulting in global warming. Therefore, there is an urge to investigate and develop renewable and environmental friendly energy source. Especially solar energy has tremendous potential as alternative energy resource. In the past two decades, compared with silicon-based photovoltaic devices, the organic photovoltaics (OPVs) have received considerable attention due to its ease of fabrication, extended absorption range by tuning structure, colorful transparency, compatibility with flexible substrates, large area processing, and low fabrication cost of device [3–5]. A general notion in OPVs research field regarding the successful improvement of power conversion efficiency (PCE) is to use a p-type conjugated polymer as a donor and the fullerene derivative PC61BM as an acceptor. Currently, PCE of polymer-based solar cells have been reached over 10% using solution processed bulk-heterojunction (BHJ) with tandem cell structure [6–8].

The small molecules can receive the predominant advantages over the polymeric materials having well-defined molecular structures, easier purification, higher reliability and better reproducibility. Therefore, enormous research works have been carried out with small-molecule OPVs, which exhibit appreciable PCEs of >6% using vacuum-deposition fabrication techniques [9–11]. Although, in general, the solution processing is considered to be more cost-effective compared to vacuum deposition, but solution processing creates leakage paths between anode and cathode due to either p-type or n-type phase continuity arising from spin-coating of the solvent to form the film [12,13]. On the other hand, vacuum deposition technique of OPVs shows higher potential availing the advantage of easy fabrication of multilayered tandem architectures. Of late, a tandem cell of OPV device with a PCE of up to 11% has been reported [14].

Recently, researches on new small molecule-based p-type material in OPVs have developed a large variety of promising organic materials with different donor-acceptor moiety combinations. For example, symmetrical acceptor-donor-acceptor (A-D-A) [15–19], donor-acceptor-donor (D-A-D) [20–22], unsymmetrical D-A [23–25], and D-A-A′ [9,10,26,27] systems have been synthesized

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* Corresponding author.
** Corresponding author.

E-mail addresses: jaychang@thu.edu.tw (Y.J. Chang), swliu@mail.mcut.edu.tw (S.-W. Liu).

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with PCE approaching those of polymeric system. A wide variety of prominent chemical structures of photovoltaic materials with vacuum processed deposition have been reported in the literature including the oligothiophene [15,28,29], phathalocyanines (Pc) [30], subphathalocyanines (SubPc) [31–34], squaraine [35–37], and triarylamine [38–40].

Although the device performance is improved continuously by using unique property of materials and fabrication architectures of device, but it is still inadequate in meeting commercial requirements [41,42]. The previous reports have focused on the panchromatic absorption range and photocurrent output using various active materials [38,43–45] and device structures [46–48]. However, one of the crucial limitations for device performance is the low value of open-circuit voltage (V_{oc}). Carbazole structure possesses weak electron donating ability which is one of curial factors for designing higher HOMO energy level of p-type material in order to achieve high V_{oc} value in organic photovoltaics devices.

To date, most of the previous publications have reported V_{oc} value in solution processed devices using the symmetry structure based on carbazole core as p-type or n-type materials [49–54]. In this work, we have used carbazole as electron donating moiety with four acceptors applying D-π-A dipolar system as p-type material in photovoltaic solar cells. We have fabricated a highly efficient OPVs device with ITO/MoO_3/Active layer/BCP/Ag by vacuum deposition technique. The active layer consisting of **F1** combined with the electron acceptor C_{70} exhibits a high PCE of 4.93%, which is attributed to the higher V_{oc} value of 1.02 V.

2. Experimental section

2.1. General information

All reactions and manipulations were performed in a nitrogen atmosphere. Solvents were distilled freshly according to standard procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker (AV 400/AVIII HD 400/AV 500 MHz) spectrometer, and $CDCl_3$ was used as solvents. Chemical shifts were reported on the δ scale downfield from the tetramethylsilane peak. Absorption spectra were recorded on a SHIMADZU UV-1800 and Jasco V-630 spectrophotometer, and emission spectra were obtained using a Hitachi F-4500 spectrofluorimeter. Emission spectra in solutions were measured using a spectral grade solvent and right-angle detection. For material analysis, the photoelectron spectrometer (AC-2, Riken Keiki) was used to measure the ITO work function and the HOMO level of the organic materials. Mass spectra were recorded on a JEOL JMS-700 double-focusing mass spectrometer. The surface morphology of the materials was characterized by the non-contact mode atomic force microscopy (AFM). Thermogravimetric analysis (TGA; Pyris 1 TGA Lab system) measurements were carried out with heating rate of 10 °C/min under a nitrogen gas atmosphere.

The chemicals *N*-Bromosuccinimide (NBS), *trans*-Dichlorobis(-triphenylphosphine) palladium(II) ($PdCl_2(PPh_3)_2$), 2-(Tributylstannyl)thiophene, n-Butyllithium (1.6 M in hexane), *N,N′*-Dimethylformamide, 4-Bromobenzaldehyde, tri-n-Butyltin chloride, Malononitrile, 1,3-Indandione, Ammonium acetate, and Piperidine were purchased from Acros, Alfa, Merck, Lancaster, TCI, Sigma-Aldrich, and Showa, separately, and purified when necessary. Chromatographic separations were performed using silica gel from Merck (Kieselgel Si 60; 40–63 μm).

2.2. Fabrication and characterization of bulk-heterojunction OPVs

Devices were fabricated as described using the basic method described in our pervious work [34,55]. The bulk-heterojunction OPVs devices was consisted of **F**-series organic dyes and fullerene derivative C_{60} or C_{70} as the p-type and n-type materials, MoO_3 as hole transporting material, and BCP as the buffer between the n-type material and the cathode. All materials were purified by sublimation before use. The patterned indium-tin-oxide (ITO) substrates as the anode with a sheet resistance of 10 Ω/sq were purchased from Lumtec. The ITO substrates were cleaned by detergent, deionized water, acetone, and isopropanol in sequence, and subsequently the substrates were transferred to a vacuum chamber of the thermal evaporator, and the organic active materials were deposited in the sequence of ITO/MoO_3 (15 nm)/**F**-series donor:C_{60} or C_{70} (40 or 80 nm)/BCP (7 nm)/Ag (120 nm) under the pressure of $6{*}10^{-6}$ Torr. The constant deposition rates of MoO_3 was 0.03 nm/s, and the other organic materials were controlled within 0.1–0.2 nm/s. A cathode material of Ag was deposited in the chamber through a shadow mask to define active regions of the devices (4 mm^2) by the overlapping area between ITO/organic layer/Ag. After the evaporation, the devices were transferred to a grove box and go encapsulation process under the N_2 environment to prevent damage from the oxygen and moisture.

The *J-V* characteristics of the OPVs devices were measured with a current source meter (Keithley 2400) under dark conditions and under the illumination of a 1-sun AM 1.5G solar simulator (91160, Newport), which was calibrated through a Si reference cell. For measuring the external quantum efficiency (EQE) spectra, the AM 1.5G solar simulator was used to generate the bias light. A monochromator, which was calibrated with a photodiode and chopped at 250 Hz, was used to select wavelengths between 350 and 800 nm to illuminate the OPVs. The photocurrent of the OPVs was measured through the lock-in amplifier, which was referenced to the chopper frequency. After measuring the devices, the results of the EQE spectra were integrated to obtain the J_{sc} of the devices and were subsequently compared with the J_{sc}, which were measured under illumination of the solar simulator.

2.3. Synthesis of dyes

The structures of carbazole-based organic dyes and their synthetic sequences are presented in Fig. 1 and Scheme 1.

2.3.1. 9-(4-tert-Butylphenyl)-3-bromo-9H-carbazole (***2a***)

A mixture of **1a** (4.9 g, 16.38 mmol) in dry CH_2Cl_2 was placed in a three-necked flask under a nitrogen atmosphere. Following this, added dropwise NBS (2.91 g, 16.38 mmol) in CH_2Cl_2 to this reaction and stirred 6 h room temperature. The mixture was quenched by adding DI water, and the mixture extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The product was purified by silica gel column chromatograph with hexane as eluent. White solid of **2a** was obtained in 78% yield (4.81 g, 12.77 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.11 (d, 1H, $J = 8.0$ Hz), 7.63 (d, 2H, $J = 8.4$ Hz), 7.51–7.44 (m, 5H), 7.33–7.30 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 141.3, 139.6, 134.4, 128.4, 126.8, 126.6, 126.5, 124.9, 122.9, 122.1, 120.4, 120.1, 112.4, 111.4, 110.1, 34.8, 31.4. MS (FAB, 70 eV): m/z (relative intensity) 377 (M^+, 100); HRMS calcd for $C_{22}H_{20}N^{79}Br$: 377.0779, found 377.0773.

2.3.2. 3-Bromo-9-(4-(dodecyloxy)phenyl)-9H-carbazole (***2b***)

Compound **2b** was synthesized according to the same procedure as that of **2a**. Yellow solid was obtained in 50% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.10 (d, 1H, $J = 7.72$ Hz), 7.44–7.50 (m, 4 H), 7.41 (d, 2H, $J = 8.68$ Hz), 7.33 (d, 1H, $J = 8.44$ Hz), 7.29 (d, 1H, $J = 7.76$ Hz), 7.21 (d, 1H, $J = 8.64$ Hz), 7.12 (d, 2H, $J = 8.76$ Hz), 4.07 (t, 2H, $J = 6.48$ Hz), 1.84–1.90 (m, 2 H), 1.50–1.56 (m, 2 H), 1.32–1.44 (m, 16 H), 0.92 (t, 3H, $J = 6.96$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 141.7, 140.0, 129.5, 128.5, 128.4, 126.5, 124.8, 122.9,