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Synthesis and characterization of a novel fullerene derivative containing carbazole group for use in organic solar cells

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ABSTRACT

A novel carbazole-group-containing fullerene derivative (CBZ-C_{60}) with good solubility in common organic solvents was synthesized. This derivative was analyzed by using many techniques such as NMR, FAB-MS, FTIR and UV–vis absorption spectroscopy. Further, bulk heterojunction photovoltaic devices were fabricated. Since the LUMO energy level of CBZ-C_{60} was higher than that of fullerene, the open-circuit voltage (V_{oc}) of devices based on CBZ-C_{60} was higher than that of devices based on fullerene. The power-conversion efficiency was highest for devices with composite thin films that have P3HT/CBZ-C_{60} composition ratios of 1:1 and were annealed at 150 °C for 10 min. The maximum V_{oc}, short-circuit current density, and PCE of the best device were 0.64 V, 2.32 mA/cm^2, and 0.48%, respectively.

1. Introduction

Organic solar cells composed of organic electron donor and acceptor composites have been attracting considerable interest as a potential source of renewable energy because they are cost-effective and flexible [1–3]. Many types of low-band-gap conjugated polymers that act as p-type electron donors have been synthesized for use in organic photovoltaic (OPV) devices. However, only a few n-type electron acceptors have been reported for use in OPV devices. Fullerene (C_{60}) has been known to act as an efficient electron acceptor in OPV devices because of its high electron mobility. C_{60} films are usually prepared by evaporation because the solubility of C_{60} in common organic solvents is low. C_{60} is not suitable for preparing composite layers, especially when a bicontinuous-network morphology is desired, because of its strong tendency to crystallize. C_{60} derivatives that exhibit high solubility in common organic solvents and whose solutions do not show phase separation have been developed for use in heterojunction organic solar cells. During the last decade, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), a soluble C_{60} derivative, has been widely used to fabricate bulk heterojunction (BHJ) OPV devices [4–6]. By controlling the HOMO and LUMO energy levels of soluble C_{60} derivatives, the performance of photovoltaic devices could be improved. In this study, we synthesized new C_{60} derivatives with an N-ethylhexylcarbazole moiety via a carbene addition intermediate [7]. It has been reported that an increase in the LUMO energy level of the electron acceptor could result in an increase in the open-circuit voltage (V_{oc}), which in turn would lead to an improvement in the power-conversion efficiency [8]. We expected that the electron-rich carbazole group would increase the LUMO energy level of C_{60} even though it is not directly conjugated with C_{60}. The chemical structure and synthetic route to the novel C_{60} derivative are shown in Scheme 1.

2. Experiment

2.1. Measurements and device fabrication

The ^{1}H NMR and ^{13}C NMR spectrum was recorded using a Bruker AM-400 spectrometer; the absorption spectra, by using a Hitachi spectrophotometer model U-3501; and the Fourier-transform infrared (FTIR) spectra, by using a JASCO FTIR 460 plus spectrometer. EM (EI) was measured by using 7890A-5975C GC/MSD and FAB-MS was measured by using JEOLJMS-DX-303 Mass spectrometer. The cyclic-voltametry (BAS 100) was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10 M) as the electrolyte and material (10^{-3} M) in 1,2-dichlorobenzenen at a scan rate of 50 mV/s at room temperature under argon atmosphere. A glassy carbon electrode (0.3 mm diameter) was used as the working electrode. A Pt and an Ag/AgCl electrode were used as the counter electrode and reference electrode. Composite solutions of P3HT and the synthesized C_{60} derivative were prepared using chlorobenzene as the solvent. The concentration of the composite solution was maintained in the range of 1.0–2.0 wt%.

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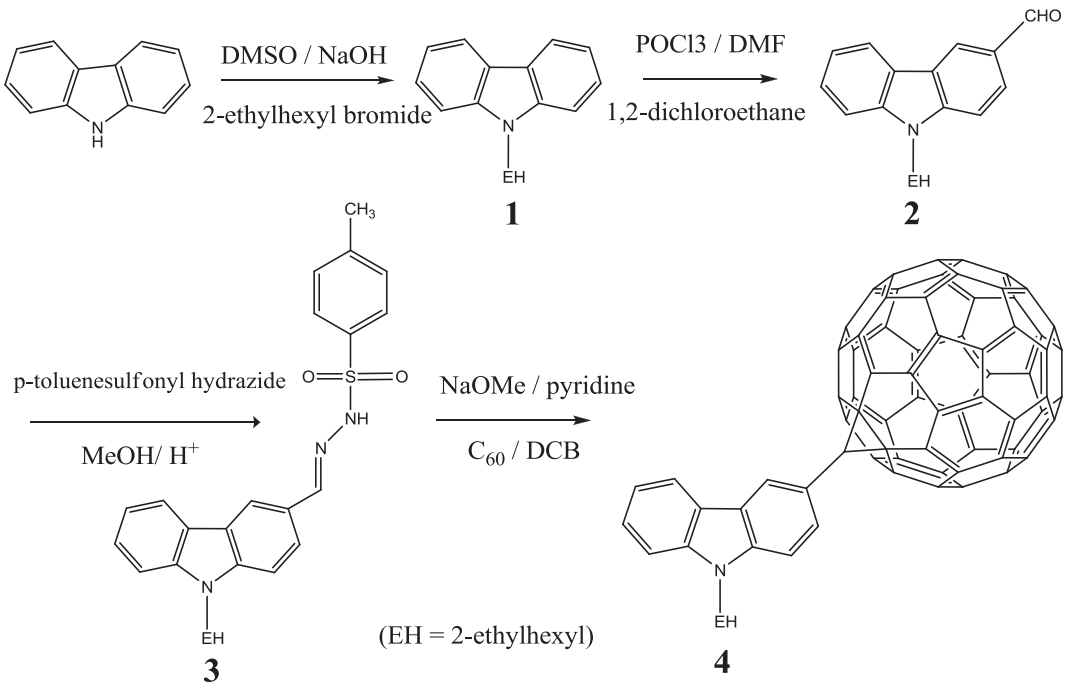

Scheme 1. Synthetic route for the carbazole-group containing fullerene derivative (CBZ-C_{60}).

Polymer photovoltaic devices with a typical sandwich structure of ITO/PEDOT:PSS/active layer/LiF/Al were fabricated. The ITO-coated glass substrates were cleaned by a routine cleaning procedure that involved sonication in a detergent followed by sonication in distilled water, in acetone, and finally, in 2-propanol. A 45-nm-thick layer of PEDOT:PSS (Baytron P) was spin coated on a cleaned ITO substrate after exposing the ITO surface to ozone for 10 min. The PEDOT:PSS layer was dried on a hot plate at 140 °C for 10 min. The pre-dissolved composite solution was filtered through 0.45 μm syringe filters and an active layer was spin coated over the PEDOT:PSS layer. Finally, a compound cathode (top electrode) consisting of a 0.5-nm thick layer of LiF and a 120-nm thick layer of Al were deposited onto the active polymer layer under vacuum of 3×10^{-6} torr in a thermal evaporator. The current–voltage (*I–V*) characteristics of all the polymer photovoltaic cells were measured under the simulated solar light (100 mW/cm^2; AM 1.5 G) provided by an Oriel 1000 W solar simulator. Electric data were recorded using a Keithley 236 source-measure unit, and characterizations were carried out in an ambient environment. The intensity of the simulated solar light was calibrated by a standard Si photodiode detector (PV measurements Inc.), which was calibrated at

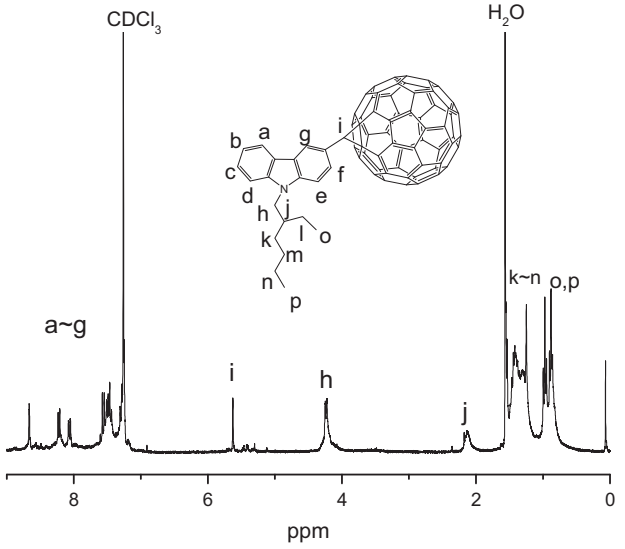

Fig. 1. ^{1}H NMR spectrum for CBZ-C_{60} ($CDCl_3$, 400 MHz).

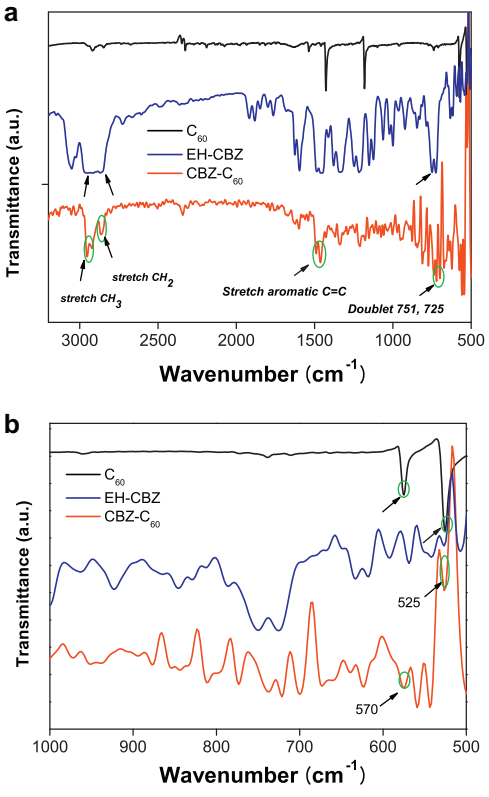

Fig. 2. (a) FTIR spectra of C_{60}, 9-(2-ethylhexyl)-9H-carbazole, and CBZ-C_{60}. (b) FTIR spectra of C_{60}, 9-(2-ethylhexyl)-9H-carbazole, and CBZ-C_{60} in fingerprint region.