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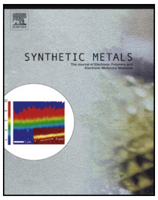

Substituent effect of fulleropyrrolidine acceptors on bilayer organic solar cells

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ABSTRACT

Two fulleropyrrolidine derivatives, Th-C60 and PFTh-C60, as the acceptors are synthesized to investigate the substituent effects on the device performance in bilayer organic solar cells (OSCs). The devices with a configuration of ITO/MoO_3/CuPc/acceptor/BPhen/Ag are optimized by varying the thickness of MoO_3 as the anode buffer layer. Th-C60 based devices have a slightly larger open-circuit voltage (V_{oc}) of 0.47 V than the counterpart C60 of ~0.46 V and PFTh-C60 of ~0.44 V with the same device structures. Th-C60-based devices exhibited a highest V_{oc} of about 0.49 V when the thickness of MoO_3 is 4 nm. In contrast, the bulky phenylfluorenyl moieties (PFMs) of PFTh-C60 deteriorated the device performance with regard to the precursor Th-C60. The maximum power conversion efficiency (PCE) of Th-C60 based device reaches 0.79% with a short-circuit current density (J_{sc}) of 2.65 mA/cm^2, V_{oc} of 0.49 V, and fill factor (*FF*) of 60.5%. The results indicate that there are dramatically different structure–performance relationships and molecular design principles between organic bilayer- and bulk-heterojunction solar cells.

1. Introduction

Over the past two decades, organic solar cells (OSCs) have attracted considerable interest in scientific and industrial fields due to their low cost, large-area, light weight, and flexibility, which will be the most promising next-generation photovoltaic technology to address energy crisis. Since the pioneering work of Tang on donor-acceptor bilayer-planar heterojunction solar cells [1], great progress has been made in terms of the power conversion efficiencies (PCEs) of bulk heterojunction (BHJ) polymer solar cells (PSCs) have reported over 7% [2–11]. In comparison with PSCs, the progress in bilayer small OSCs is still lagging considerably behind, and PCE is unsatisfied [12]. In this context, it is important to uncover molecular structure effect on photovoltaic behaviors in order to improve the performance of bilayer small OSCs.

For organic materials of OSC active layer, exploiting both new donor and acceptor materials are equally important. Current researches mainly focus on designing novel donor materials with a low bandgap and suitable high occupied molecular orbital (HOMO). Nevertheless, less attention has been paid to developing new acceptors and investigating its structure–performance relationships. To develop new fullerene acceptors is an effective approach to obtain improved performance of OSCs. Li et al. reported an indene-C_{60}

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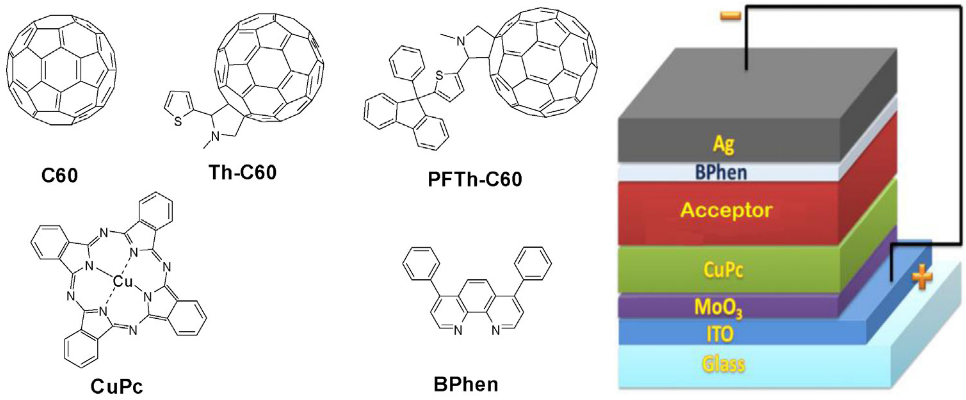

Fig. 1. Chemical structure of active materials and schematic diagram of bilayer OSC.

bisadduct with a lowest unoccupied molecular orbital (LUMO) of −3.74 eV, and its corresponding P3HT-based polymer OSC had a high open-circuit voltage (V_{oc}) of 0.84 V and PCE of 6.48%, which are much higher than those of P3HT/PCBM system [13,14]. The influence of carbon chain length in the substituent of PCBM-like derivatives on absorption intensity, film morphology, electron mobility and photovoltaic properties have been also investigated [15]. Meanwhile, several groups have reported that the influence of mono-, bis- and muti-adduct of fullerene derivatives on LUMOs and BHJ photovoltaic properties, and further confirmed that fullerene bisadduct derivatives have better performance due to their suitable LUMO, solubility, miscibility with donors, and light absorption [13,14,16–18].

Up to date, there are a few reports on the effect of the substituent fullerene on photovoltaic properties of structure–performance relations in bilayer OSCs. Among fullerene derivatives, fulleropyrrolidine derivatives have attracted considerable interest in the past years due to its good stability of five-member ring, high LUMO energy level, easy preparation, and tunable modification, showing promising n-type acceptor candidates for BHJ PSC [19–23]. Our group proposed the morphology-direct molecular design to investigate the substituent of fullerene derivatives on bulky hetereojuntion and performance [23]. In this paper, in order to investigate the structure–performance relationships, we synthesized two fulleropyrrolidine derivatives, N-methyl-2-(2-thiophenyl) fulleropyrrolidine (Th-C60) and N-methyl-2-(2-(5-(9-phenyl-9-fluorenyl))thiophenyl) fulleropyrrolidine (PFTh-C60) (Fig. 1) as model compounds. We used fulleropyrrolidines as acceptors to fabricate Bilayer OSCs with a configuration of ITO/MoO_3(10 nm)/CuPc(20 nm)/Th-C60 or PFTh-C60/BPhen(9 nm)/Ag. For comparison, we also fabricated OSCs with an unsubstituted fullerene (C60) as acceptor by using the same device structure. The photovoltaic performance of Th-C60-based bilayer OSCs is better than that of PFTh-C60-based ones, which indicates that the prototype phenylfluorenyl moieties (PFMs) of PFTh-C60 obviously has negative influence on the device performance with regard to the precursor Th-C60.

2. Experimental

2.1. Chemicals and materials

C60 was purchased from Yongxin Co. (China). Fulleropyrrolidine derivatives, Th-C60 and PFTh-C60, were synthesized according to our previous report [23].

2.2. Device fabrication and characterization

Indium tin oxide (ITO) coated glass substrates with a sheet resistance of 20 Ω/square were cleaned in an ultrasonic bath with detergent, deionized-water, acetone, and isopropyl alcohol successively for 20 min. After being dried in a laboratory oven, the ITO surfaces were treated by oxygen plasma for 3 min. Molybdenum trioxide (MoO_3), copper phthalocyanine (CuPc), fullerene (C60), N-methyl-2-(2-thiophenyl) fulleropyrrolidine (Th-C60) and N-methyl-2-(2-(5-(9-phenyl-9-fluorenyl))thiophenyl) fulleropyrrolidine (PFTh-C60) were deposited sequentially onto ITO substrate by thermal evaporation in vacuum chamber (8.0×10^{-5} Pa). All materials were used as purchased and synthesized. The layer thickness was monitored by quartz oscillator crystal, located near the substrates. Finally, Ag cathode was thermally evaporated and the active area was about 0.1 cm^2. All measurements were carried out under room temperature in air. The current–voltage (I–V) characteristics were recorded with a Keithley 2400 source meter in dark and under 50, 100, 150 and 200 mW/cm^2 illumination (AM1.5G). The chemical structure of used active materials and schematic diagram of bilayer OSC are shown in Fig. 1.

3. Results and discussions

As showed in Fig. 2, the stability of Th-C60 and PFTh-C60 is similar, which is deteriorated comparison to precursor C60. The optical and electrochemical properties of Th-C60 and PFTh-C60 are similar, because the effect of the substituent on the optical and electrochemical properties can be neglected. Both Th-C60 and PFTh-C60 have a weak featuring absorption peak at c.a. 421 nm, and the only

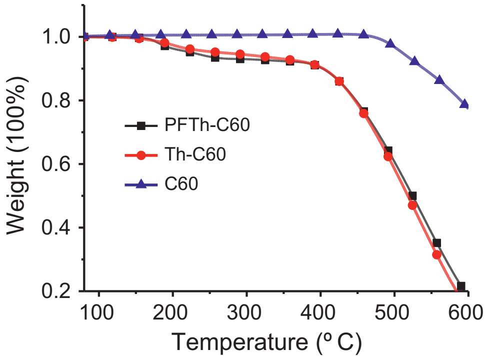

Fig. 2. The TGA curves of C60, Th-C60 and PFTh-C60 (heating rate of 10 °C/min under N_2).