



Dihydrobenzofuran- C_{60} bisadducts as electron acceptors in polymer solar cells: Effect of alkyl substituents



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ABSTRACT

A series of novel dihydrobenzofuran- C_{60} bisadducts, denoted by BFCBA (without side chain substituent) and C_n -BFCBA (n represents the number of carbon atoms on side chain substituent, and varies as 1–5), were synthesized by a facile method and utilized as acceptor materials in polymer solar cells (PSCs). These fullerene bisadducts were found to possess similar optical, electrochemical properties but the PSCs based on them as acceptors present very diverse photovoltaic performance as the variation of n . Compared to the PSC based on BFCBA, device performances were significantly improved by the application of alkyl chain substituted dihydrobenzofuran- C_{60} bisadducts (C_n -BFCBA). In particular, when $n = 4$, i.e. *tert*-butyl used as substituent, PCE of the corresponding device reached to a summit of 3.40%. This result is comparable to that of the device based on $PC_{61}BM$ as acceptor. The morphology studied by AFM and electron mobility investigated by the space charge limited current (SCLC) method further revealed that C4-BFCBA shows a reasonably well miscibility with P3HT and a significantly higher electron mobility. These properties might account for its optimal photovoltaic performance among these series of the fullerene bisadducts. For comparison, dihydrobenzofuran- C_{60} monoadduct and trisadduct based on *tert*-butyl substituents were also synthesized. The corresponding PSC device test results showed that C4-BFCBA present much better photovoltaic performance than its corresponding monoadduct (C4-BFCMA) and trisadduct (C4-BFCTA) as well as BFCBA.

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1. Introduction

Polymer solar cells (PSCs) have been regarded as a promising alternative solution to silicon-based solar cells due to their advantages of low cost, easy fabrication, light weight and flexibility [1–3]. A PSC is generally composed of a bulk heterojunction (BHJ) structure, i.e. a blend layer of electron-donor and electron-acceptor sandwiched between anode and cathode [4]. Many efforts have been devoted to enhance the power conversion efficiency (PCE) of PSCs via design of new donor or acceptor materials [1,5–16], optimization of device construction and device fabrication processing [17–25].

Fullerene derivatives have been often used as electron acceptors in PSCs due to their excellent charge mobility and electron affinity [26]. $PC_{61}BM$ [27] and $PC_{71}BM$ [28], which was first reported in 1995 and 2003, are still predominantly used in

today's PSC research. Efforts of modifying fullerene aiming at better performance in PSCs have been made. However, most of them exhibited even poorer photovoltaic performance than $PC_{61}BM$ [12,29–31]. Recently, the C_{60} bisadducts, with higher LUMO energy level, became the focus on the effort of searching for better fullerene-based acceptors. The second attached functional group on the fullerene cage further reduced the π -conjugation as well as electron delocalization in the fullerenes. This electron structure intends to yield a higher LUMO energy level and in turn, give rise to an enhanced photovoltaic performance. Indene- C_{60} bisadduct ($IC_{60}BA$) and its C_{70} analogue ($IC_{70}BA$) are the representative fullerene bisadduct reported so far and the PCE values of PSCs based on P3HT/ $IC_{60}BA$ increased 40% in comparison to that of the PSCs based on P3HT/ $PC_{61}BM$ [32,33]. Recently, a series of fullerene bisadducts with excellent PSC performance were developed [5,10,27,34,35]. Devices based on these compounds generally achieved comparable or even higher V_{oc} and PCE than $PC_{61}BM$. Fullerene bisadducts thus made preferable candidates as fullerene electron acceptors in PSCs. However, besides all these efforts [36–43], compared to the extensive studies on the electron donor materials, especially for polymers donors, the study on molecular

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design of fullerene acceptors are still deficient. Thus, the exploration on the new acceptors based on fullerene derivatives is desirable, and there is still a considerable need for a fundamental understanding of how the structural modification of fullerene derivatives can affect the solar cell performance.

Side chain modification is a common method adopted to structurally alter the fullerene derivatives as size-suitable addends can assist close contacts between fullerene balls and help the derivatives achieve better solubility [44]. However, although this method was demonstrated to be efficient in several cases with the modification of fullerene-monoadduct acceptors, devices based on the most of side chain modified fullerene-bisadduct acceptors often failed to achieve better performance [5,6]. For instance, when NCBA-based PSC present high efficiency of 5.3%, the side chain modified NCBA derivatives-based devices suffered inferior PCE ranging from 0.9% to 4.1% [26,36,43]. Hence, the further investigations of the effect of the side chain substituents on fullerene-bisadduct-based PSC performances are needed.

In this paper, we thus designed and prepared a series of dihydrobenzofuran- C_{60} bisadducts (denoted by BFCBA (without side chain substituent) and C_n -BFCBA (n represents the number of carbon atoms on side chain substituent, and varies as 1–5) and used them as acceptor materials in PSCs. The results show that the side chain substituents play an important role on the related photovoltaic performance of devices. Compared to the PSC based on BFCBA, device performances were significantly improved by the application of alkyl chain substituted dihydrobenzofuran- C_{60} bisadducts (C_n -BFCBA). In particular, a summit PCE as high as 3.40% was achieved when using *tert*-butyl as substituent. This value is comparable to the PCE of $PC_{61}BM$ -based PSCs. For comparison, dihydrobenzofuran- C_{60} monoadduct and trisadduct based on *tert*-butyl substituents were also synthesized. The corresponding PSC device test results showed that C4-BFCBA present much better photovoltaic performance than its corresponding monoadduct (C4-BFCMA) and trisadduct (C4-BFCTA).

2. Experimental

2.1. Material and characterization

C_{60} (99.5%) was purchased from Suzhou Dade Carbon Nanotechnology Co., Ltd. (Diacetoxyiodo) benzene, *p*-toluenesulfonamide, 2,6-lutidine and 4-alkylphenol were purchased from TCI chemicals Co. CuCl and TfOH were purchased from J&K Scientific. KOH and *o*-DCB were purchased from Chinasun speciality products Co., Ltd (China). Methanol (HPLC grade) was bought from ACS chemicals. 1H NMR spectra were obtained using a 600 MHz spectrometer (Agilent, USA). MALDI-TOF MS spectra were recorded on a Bruker ultrafleXtreme instrument. Cyclic voltammetry were measured on a Zahner Zennium electrochemical workstation. Glassy carbon was used as a working electrode whereas platinum and silver served as counter and reference electrodes, respectively. Ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as an internal standard. 0.05 M solutions of *tetra*-*n*-butylammonium hexafluorophosphate (TBAPF6) in *o*-DCB served as supporting electrolyte. UV–vis absorption spectra of the fullerene derivatives were recorded on an Agilent Technologies Cary 5000 UV–vis-NIR spectrophotometer in $CHCl_3$ with a concentration of 10^{-5} M. The surface morphologies of active layer were obtained on a Veeco multimode AFM. Thermal stabilities were investigated on a Discovery TGA (TA, USA).

2.2. Synthesis of C4-BFCBA

A mixture of CuCl (7.13 mg, 0.072 mmol), *o*-DCB (120 mL), and 2, 6-lutidine (16.8 μ L, 0.144 mmol) were added to a flask under a

stream of argon. The mixture was stirring at room temperature for 30 min, then C_{60} (1.3 g, 1.8 mmol) and TsN=IPh (1.68 g, 4.5 mmol) were added and stirred at room temperature for 12 h. A mixture of *N*-tosyl aziridine-fullerene mono-, bis- and multiadduct was obtained from this reaction. The crude product was further purified by a silica gel column chromatography (eluent: toluene/hexane v/v 1/3) to separate the *N*-tosyl aziridine- C_{60} bisadduct from the mixture.

The prepared *N*-tosyl aziridine-fullerene bisadduct (212 mg, 0.2 mmol), 4-*tert*-butylphenol (90.1 mg, 0.6 mmol) and TfOH (0.2 M solution in *o*-DCB, 200 μ L, 0.04 mmol) was dissolved in anhydrous *o*-DCB (60 mL) and stirred under a N_2 atmosphere at 100 °C for 12 h. After the reaction, solvents was removed from the resulting solution under reduced pressure and the crude product was purified by silica gel column chromatography with toluene/hexane (v/v 1/3) as eluent. The obtained product was further washed by methanol for 3 times. Yield: 83%.

1H NMR (600 MHz, ppm, $CDCl_3$): δ 1.34–1.54 (m, 18H, CH_3), 6.67–8.16 (m, 6H, Ar). MALDI-TOF MS: $C_{80}H_{24}O_2$ $[M]^-$ cal. 1016.18 m/z; found 1016.20 m/z.

Synthesis of C4-BFCTA, BFCBA and other C_n -BFCBA (See supplementary material).

2.3. Device fabrication

The BHJ PSCs in a conventional structure (ITO/PEDOT:PSS/P3HT: fullerene/Ca/Al) were fabricated to evaluate the photovoltaic performance of these fullerene derivatives. We optimized the weight ratio of donor to acceptor to 1:1, 18 mg mL $^{-1}$ for each. A layer of poly (ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) was spin-coated on indium tin oxide (ITO)/glass substrates. P3HT and fullerene acceptor were dissolved in *o*-DCB to make a blend solution. An active layer was prepared by spin-coating the blend solution, followed by a solvent annealing process and then thermal annealed at 150 °C for 10 min. A bilayer electrode of Ca layer (~20 nm) and Al layer (~100 nm) were deposited by thermal evaporation under a vacuum of 10^{-4} Pa. The device performance were measured under illumination of AM 1.5G (100 mW cm $^{-2}$).

The space charge limited current (SCLC) devices were fabricated in a configuration of Cs_2CO_3 /active layer/Ca/Al. Firstly, a Cs_2CO_3 layer was prepared by spin-coating the 2-*ehoxyethanol* solution of Cs_2CO_3 (0.2 wt%) on an ITO/glass substrate and annealed at 150 °C for 20 min. Then, the solution of P3HT: fullerene (w/w 1:1) blend was spin-coated on the top of Cs_2CO_3 layer. The active layer was subject to a solvent annealing process and then annealed at 150 °C for 10 min. Finally, the bilayer of Ca and Al were thermally evaporated on the active layer. The current density–voltage (J – V) curves were measured in dark.

3. Results and discussion

3.1. Synthesis of dihydrobenzofuran- C_{60} bisadducts

The synthetic routes for the hydrobenzofuran- C_{60} bisadducts are shown in Scheme 1. The synthesis of TsN=IPh followed the previously reported method by Makoto Okawara et al. [45]. The synthetic routes of C_n -BFCBA ($n = 1–5$) were conducted following the modified method reported by Kenichiro Itami et al. [46]. *N*-tosyl aziridine- C_{60} bisadduct were obtained via the reaction of C_{60} with TsN=IPh at the presence of CuCl and 2, 6-lutidine, then the *N*-tosyl aziridine- C_{60} bisadduct precursor was treated with 4-alkylphenol to afford 5-alkyl-dihydrobenzofuran- C_{60} bisadduct under the catalytic influence of TfOH. The separation process was performed on a silica gel column chromatography with

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