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Design and synthesis of soluble dibenzosuberane-substituted fullerene derivatives for bulk-heterojunction polymer solar cells

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ABSTRACT

Two new dibenzosuberane-substituted fullerene derivatives, dibenzosuberane-C_{60} mono-adduct (DBSCMA) and bis-adduct (DBSCBA) were synthesized using a classical cyclopropanation reaction via a tosylhydrazone route for application as acceptor materials in polymer solar cells (PSCs). DBSCBA shows good solubility in common organic solvents and both derivatives were characterized by ^{1}HNMR, ^{13}C NMR, MALD-TOF, elemental analysis and UV–vis absorption measurements. The shift of fullerene energy levels induced by the dibenzosuberane substitution was investigated by using theoretical simulations and ultraviolet photoelectron spectroscopy. Bulk-heterojunction PSCs based on poly (3-hexylthiophene) (P3HT) and dibenzosuberane-C_{60} derivatives were fabricated and optimized by adjusting the donor/acceptor ratio and using thermal annealing and solvent additive. The morphologies of the active layers processed under different conditions were also examined by atomic force microscopy. When tested under an illumination of AM 1.5 G at 100 mW/cm^2, the highest power conversion efficiency of the devices using DBSCBA is 3.70% which is superior to that of conventional P3HT:PCBM devices.

1. Introduction

Bulk-heterojunction (BHJ) polymer solar cells (PSCs) have become one of the hottest research fields in recent years because of their unique advantages such as solution process, light weight and the possibility for transparent, flexible devices [1–5]. In a conventional BHJ PSC, the active layer is sandwiched between a transparent indium tin oxide (ITO) anode and a low-work-function metal cathode and comprises of a conjugated polymer as donor and a fullerene derivative as acceptor. One of the most popular compositions in BHJ PSCs is the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid ester (PCBM) [6]. To date, the power conversion efficiency (PCE) of the optimized PSCs based on P3HT/PCBM has exceeded 4% [7,8]. To further improve the device performance, novel conjugated polymers have been synthesized to achieve low bandgap, broad absorption, enhanced electron mobility and optimal energy levels [9–16]. Likewise, the research efforts toward new fullerene derivatives are equally important. As electron acceptor, conventional PCBM has some well-known drawbacks, such as weak absorption in the visible region and a low-lying LUMO (Lowest Unoccupied Molecular Orbital) energy level, leading to significant loss of open circuit voltage (V_{oc}). To address the question, numerous PCBM-like fullerene derivatives have been studied as electron acceptors [17–26], most of which, however, showed poor or just comparable performance to PCBM. Recently, the development of fullerene bis-adduct acceptors for higher V_{oc} PSCs has received considerable attention [27–35]. Successful exam-

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ples such as [6,6]-phenyl-C_{61}-butyric acid methyl ester bis-adduct (bis-$PC_{61}BM$) [27], indene-C_{60}bis-adduct (ICBA) [29], dihydro-naphthyl-C_{60}bis-adduct (NCBA) [30], di(4-methylphenyl)-methano-C_{60}bis-adduct (DMPCBA) [31], bis-adduct thieno-o-uinodimethane-C_{60} (bis-TOQC) [32] have been reported. Although remarkable progress has been made, the influence of multi-adduct functional groups on the photovoltaic performances are still unclear. The exploration of new fullerene derivatives and the investigation of their structure–property relationships are still critical [19]. In this work, we firstly introduced the spiro-structure to three-membered ring group on the fullerene acceptor to investigate the effect of this new structure on the acceptor photovoltaic performance. We designed and synthesized two new acceptors dibenzosuberane-C_{60} mono-adduct (DBSCMA) and its bis-adduct (DBSCBA) through the cyclopropanation reaction (as shown in Scheme 1).Our results showed that the close ring did not interfere with the reaction activity and good yields were obtained. The bis-adduct DBSCBA shows good solubility in common solvents such as chloroform, toluene, chlorobenzol and *o*-dichlorobenzene, while the mono-adduct DBSCMA is less soluble. Their LUMO and HOMO (Highest Occupied Molecular Orbital) energy levels were carefully investigated by using theoretical simulations and ultraviolet photoelectron spectroscopy. When tested under an illumination of AM 1.5 G at 100 mW/cm^2, a high PCE of 3.70% was obtained for the optimized devices using DBSCBA, which is nearly ~10% higher than that of the devices using PCBM.

2. Experimental section

2.1. Materials and measurement

C_{60} was purchased from Puyang Yongxin Fullerene Co., Ltd. Other reagents and chemicals were purchased from Alfa-Aesar Co. or Sigma–Aldrich Co. and used as received without further purification. Dibenzosuberone *p*-tosylhydrazone (1) was synthesized according to the literature [17].^{1}H NMR and ^{13}C NMR spectra were measured on a Varian Unity Inova 400 MHz and a Varian NMR system 300 MHz spectrometer with tetramethylsilane(TMS; $\delta = 0$ ppm) as the internal standard, respectively. UV–vis absorption spectra were obtained on a Perkin Elmer model Lambda 750 instrument. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed in a KRATOSULTRA-DLD ultrahigh vacuum surface analysis system. The spectra were measured by using an unfiltered He I (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV. Atomic force microscopy (AFM) was performed with a Veeco Multimode V instrument in tapping mode.

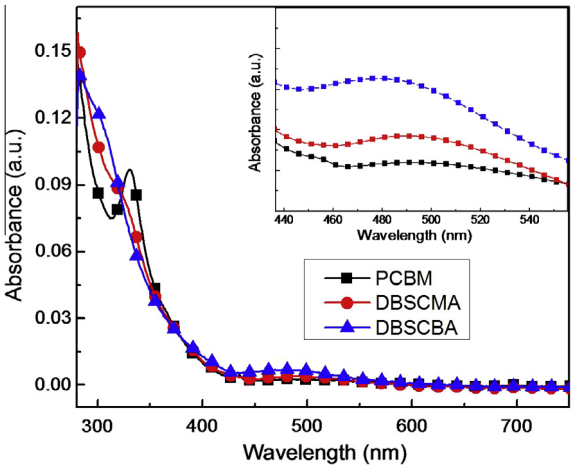
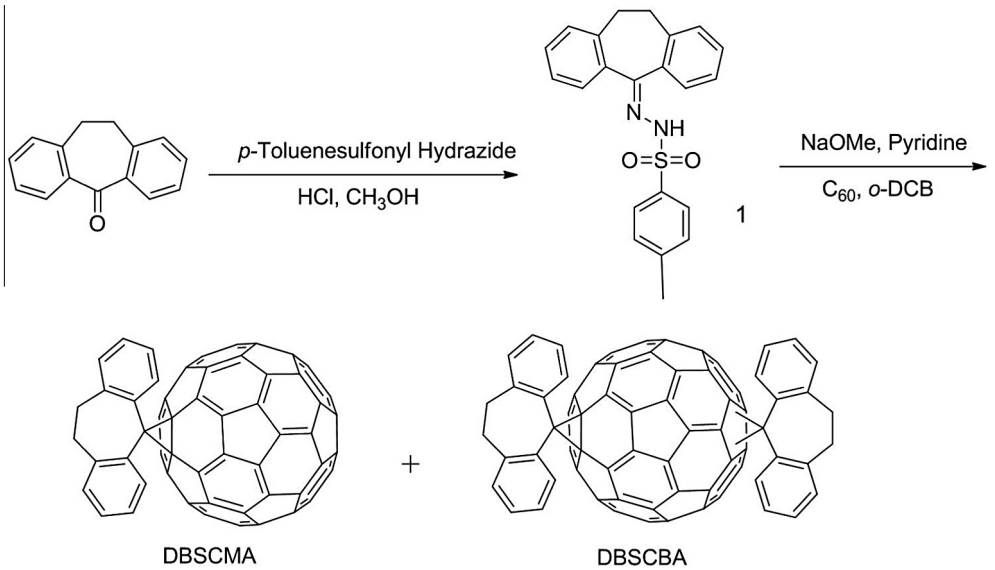


Fig. 1. The UV–vis absorptions spectra of PCBM, DBSCMA and DBSCBA in chlorobenzene solutions. The inset is the enlarged absorption spectra in the visible region from 440 to 550 nm.



Scheme 1. Synthetic routes and chemical structures of DBSCMA and DBSCBA.