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Bis-adducts of benzocyclopentane- and acenaphthene-C_{60} superior to mono-adducts as electron acceptors in polymer solar cells

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ABSTRACT

Four fullerene derivatives, benzocyclopentane-C_{60} mono-adduct (BPCMA) and its bis-adduct (BPCBA), acenaphthene-C_{60} mono-adduct (ACMA) and its bis-adduct (ACBA), were synthesized by cyclopropanation reaction. Geometrical structures and molecular packing of the mono-adduct compounds (BPCMA and ACMA) were identified by X-ray crystallography. As measured by cyclic voltammetry, LUMO energy levels of BPCBA and ACBA are about 0.08 and 0.09 eV higher than their corresponding mono-adducts. Even though the power conversion efficiency remains to be improved, the polymer solar cells (PSCs) incorporating P3HT as donor and BPCBA (or ACBA) as acceptor exhibit open-circuit voltage (V_{oc}) of 0.67 V (or 0.68 V), which is about 0.22 V (or 0.23 V) higher than the PSCs with the mono-adduct BPCMA (or ACMA) as electron acceptor. In addition, the short-circuit current density (J_{sc}) of the PSCs involving bis-adducts (BPCBA and ACBA) are obviously higher than those based on BPCMA and ACMA. The photovoltaic difference between mono- and bis-adducts can be rationalized by their different behaviors in LUMO energy and molecular packing.

1. Introduction

Bulk-heterojunction (BHJ) polymer solar cells (PSCs) have attracted much attention because of their advantages of light weight, solution process and the possibility of fabrication in large scale at low cost [1–4]. In recent years, the power conversion efficiency (PCE) of BHJ PSC has witnessed a rapid development in an average rate of ~0.7% per year [5–12]. To further improve the PCE of PSCs it heavily depends on optimization of the device as well as the performance of the photoactive layer, which is typically comprised of a blend film with a conjugated polymer donor and a fullerene derivative acceptor. Research efforts have been paid toward designing and synthesizing of novel donor materials with low band gap, broad absorption, optimal energy level [13–16] and, in parallel, paid to device optimizations [17–23]. In contrast to the donor materials or the device optimizations, however, the electron acceptors of fullerene derivative attracted less attention previously. Up to now, [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) and its analog $PC_{71}BM$ are still the acceptor materials predominantly used in most PSC devices [24–26]. Some PCBM-analogues with modified substitution groups have been investigated as electron acceptors. Most of them, however, exhibited poorer photovoltaic performance [27–31]. More recently, many 56-π-electron C_{60} bis-adducts with higher LUMO energy levels have been developed as acceptors in PSCs [32–53]. Better than those involving mono-adducts, the devices based on P3HT as donor and C_{60} bis-adducts as acceptors have exhibited higher PCE in corresponding PSCs system, especially exemplified with indene-C_{60} bis-adduct (ICBA), OXCBA, DMPCBA, OQMF and Bis-MDNC [34,39,41,47,51]. However, influence of the substitution groups on the bis-adducts-based PSCs performance is still unclear. Therefore, to explore novel structures of fullerene bis-adducts and to reveal fundamental principles that underlie their structure–property relationship are highly desired.

Very recently, an indan-C_{60} and an indan-$PC_{61}BM$ derivative were synthesized for photovoltaic application by Yam's group [54]. The later one was used as electron acceptor better than the pristine $PC_{61}BM$, typically with PCE of ca. 4% in poly (3-hexylthiophene) (P3HT) and $PC_{61}BM$ photovoltaic system. However, bis-adduct of the indan-C_{60} has not been investigated yet. Here we report such a bis-adduct of the indan-C_{60} [Note that the indan-C_{60} bis-adduct might be briefed as 'ICBA' but apparently confused with the well-known abbreviation of indene-C_{60} bis-adduct [34]. The compound of indan-C_{60} bis-adducts is thus specified as an equivalent name of benzocyclopentane-C_{60} bis-adduct (BPCBA) to make a distinction from the well-known abbreviation of ICBA] and acenaphthene-C_{60} bis-adducts (ACBA) as well as their mono-adducts (BPCMA and ACMA) (see Schemes 1 and 2). The four fullerene derivatives, with

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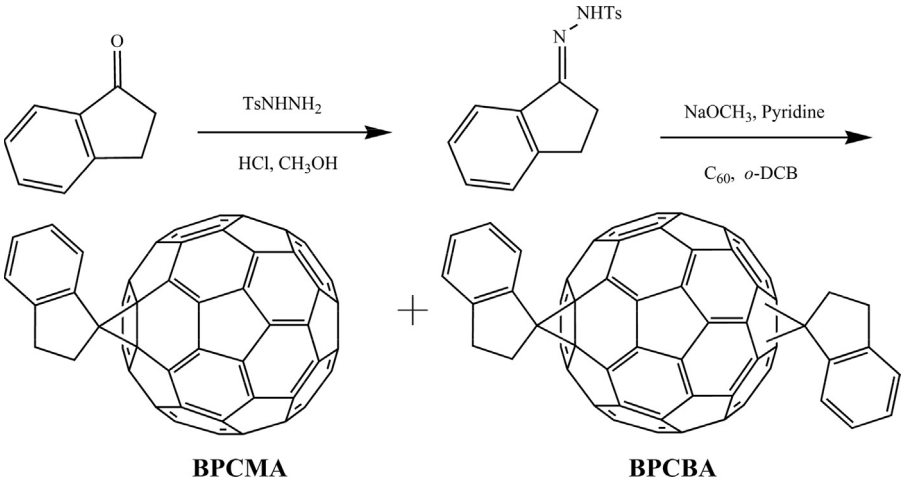
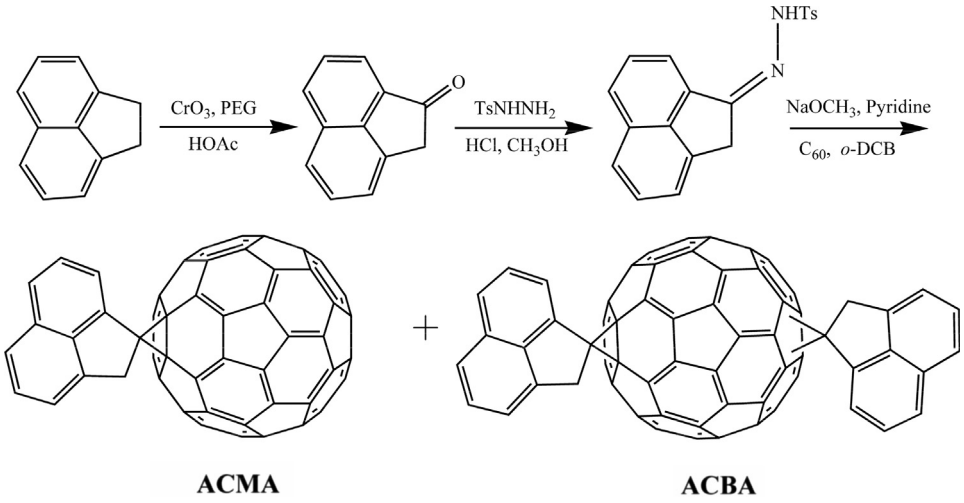


Scheme 1. Synthetic routes and chemical structures of BPCMA and BPCBA.



Scheme 2. Synthetic routes and chemical structures of ACMA and ACBA.

slight alteration in the functional structure, were synthesized by a classic reaction of cyclopropanation [24]. Crystal-packing structure of mono-adduct compounds (BPCMA and ACMA) were unambiguously identified by X-ray crystallography, and electrochemical properties of the four derivatives were studied by cyclic voltammetry. Polymer solar cells based on P3HT as a donor and the derivatives of bis-adduct (BPCBA or ACBA) as acceptors exhibit higher V_{oc} and J_{sc}, whereas BPCMA or ACMA shows poorer photovoltaic performance mainly owing to the lower LUMO level and the easier aggregation for the mono-adduct molecule [55].

2. Experimental section

2.1. Materials

C_{60} (99.5%) was obtained from Puyang Yongxin Fullerene Co., Ltd. P3HT was purchased from Rieke metals. *o*-Dichlorobenzene (*o*-DCB) and acetonitrile were purchased from Sigma-Aldrich and used as received without further purification. Other reagents and chemicals were commercially available as well.

2.2. Measurements

Fullerene derivatives were purified by high performance liquid chromatography (HPLC) with a Shimadzu liquid chromatography modular system consisting of two LC-20AT pumps, an UV Shimadzu SPD-20 A diode array UV detector, and a CBM-20 A system controller. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Biospin Advance III 500 MHz and a Bruker Biospin Advance III 400 MHz spectrometer. Chemical shifts were reported in ppm relative to internal chloroform for ^{1}H and ^{13}C NMR spectroscopy. Mass spectra were recorded on a Bruker Esquire HCT mass spectrometer with an atmospheric pressure chemical ionization (APCI) ion source in the negative ion mode. Cyclic voltammetry was performed on a CHI-660C electrochemical workstation with Pt disk, Pt wire, and Ag/Ag^+ electrode (0.01 M $AgNO_3$, 0.09 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L Bu_4NPF_6 *o*-dichlorobenzene (*o*-DCB)/acetonitrile (5:1) solution with a scan rate of 100 mV/s. UV–vis absorption spectra were obtained on a Varian Cary 5000 UV–vis–NIR spectrophotometer.

2.3. Synthesis of fullerene derivatives

2.3.1. BPCMA and BPCBA

2.3.1.1. Synthesis of 1-indanone p-tosylhydrazone. 1-Indanone *p*-tosylhydrazone was synthesized according to the previous literature [24]. A mixture of 1-indanone (1.32 g, 10 mmol), *p*-toluenesulfonylhydrazide (2.23 g, 12 mmol), methanol (40 ml), and a catalytic amount of concentrated hydrochloric acid was heated at reflux for overnight.