



Facile synthesis of isomeric fullerene derivatives as acceptors for high performance organic photovoltaic



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ABSTRACT

Two new isomeric fullerene derivatives, {6}-1-(3-(Benzoyl)propyl)-{5}-1-phenyl [5,6] C₆₁ and 1-(3-(Benzoyl)propyl)-1-phenyl[6,6] C₆₀, have been synthesized efficiently through a 1,3-dipolar cycloaddition of a tosylhydrazone to provide relatively high photovoltaic performances. A systematic study on the optical, electrochemical and photovoltaic properties of the fullerene derivatives has been performed. In particular, the polymer solar cell (PSC) based on {6}-1-(3-(Benzoyl)propyl)-{5}-1-phenyl [5,6] C₆₁ and poly(3-hexylthiophene) showed a power conversion efficiency of 2.81%, which is higher than that of PCBM (2.53%) under the same device conditions.

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1. Introduction

Organic solar cells have been attracting much attention around the world within recent years. The first semiconducting polymer-fullerene bulk heterojunction (BHJ) solar cell was reported in 1993, which gave a power conversion efficiency (PCE) of 0.04%.¹ Since then, the power conversion efficiency of single and tandem BHJ solar cells had achieved a significant 9.2%² and a remarkable 10.6%,³ respectively, which was mainly ascribed to the design and synthesis of novel polymer donors^{4–6} and fullerene acceptors,^{7–11} the improvement of device processing^{12,13} and architectures.^{14,15}

Due to their high electron affinity and high electron mobility, and tunable solubility, energy level and packing structure, numerous fullerene derivatives have been synthesized as acceptors for BHJ solar cells in the past decade. Since Hummelen et al. firstly synthesized [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) in 1995,¹⁶ PCBM is still the most commonly used fullerene acceptor in the photovoltaic solar cells, which offer good solubility and high electron mobility. The structural modification on the substituent of PCBM could be a way to design various fullerene derivatives for investigating the relationship between the molecular structure of fullerene acceptor and photovoltaic properties in the BHJ solar cells.

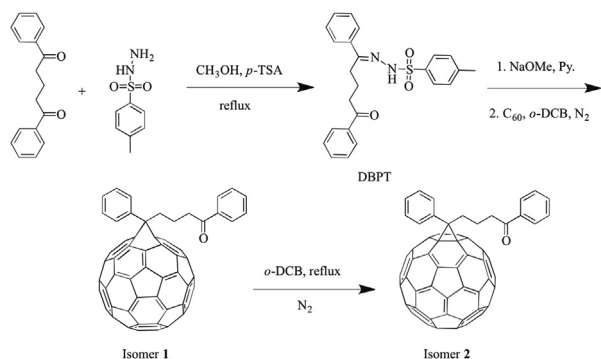
The substituent of PCBM can normally be divided into four parts, a phenyl ring, a middle butyl chain, an ester group and a methyl end group. Hummelen et al. replaced the phenyl ring with a series of electron-donating or electron-withdrawing substituents, and indicated that raising the lowest unoccupied molecular orbital (LUMO) level of the acceptor fullerene does give a higher open-circuit voltage (V_{oc}) in BHJ solar cell devices.¹⁷ Yang et al. reported the alkyl chain length on the side chain of the PCBM-like molecules significantly influence the photovoltaic performance of the fullerene derivatives.¹⁸ More researches focused on replacing the methyl end group with other groups such as octadecyl group¹⁹ or amine moiety,²⁰ which was expected to result in better solubility, stronger absorption of the fullerene derivatives. However, research on replacing the ester group with other groups has been rarely reported. Li et al. converted the ester group into amide, which resulted in the ordered molecular aggregates because of the hydrogen-bonding interaction among amides and improved the performance of the PSCs.²¹ Echegoyen et al. recently described the synthesis of bisadducts of C₆₀ and C₇₀ using the same original substrate dibenzoyl propane. All synthesized bisadducts show higher LUMO level between 200 and 300 mV compared to the corresponding values for the pristine fullerenes, however their properties for the polymer solar cell is not investigated.²² Research on the relationship between structures and functions of fullerene derivatives provided new ideas for designing more efficient and stable organic photovoltaic devices.

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In this report, by replacing the ester group on PCBM with benzoyl to get a more symmetrical fullerene acceptor, two isomeric fullerene derivatives, {6}-1-(3-(benzoyl)propyl)-{5}-1-phenyl[5,6]C₆₀ (isomer 1) and 1-(3-(benzoyl)propyl)-1-phenyl[6,6]C₆₀ (isomer 2), were synthesized through a 1,3-dipolar cycloaddition of a tosylhydrazone. Their optical and electrochemical properties were reported. The P3HT based BHJ solar cells were fabricated. The influence of isomers, the composition ratios of donor and acceptor, the thickness of BHJ films and additive on the photovoltaic properties was investigated with these fullerene derivatives.

2. Results and discussion

The structure and synthesis of isomeric fullerene derivatives including intermediates were shown in Scheme 1. HPLC-spectra of two isomers on Buckyprep column show difference in retention time, which could be seen in Fig. S1. The FTIR spectra of isomer 1 and 2 had the C=O stretching band and the NMR data clearly showed the presence of the carbonyl carbon, which meant that the derivative group has been connected to C₆₀. Isomer 1 showed 4 sp³-carbons, and isomer 2 showed 6 sp³-carbons, which meant that isomer 1 was 5,6 adduct, and isomer 2 is 6,6 adduct. The functional C₆₀ derivative isomers processed high solubility in toluene, chlorobenzene and *o*-dichlorobenzene (*o*-DCB), and could stable in air for a few months when stored away from light.



Scheme 1. Synthesis routes and chemical structures of isomer 1 and isomer 2.

2.1. Optical property

The UV–vis absorption characteristics of isomer 1, 2 and the reference PCBM in CH₂Cl₂ solution with the same concentration of 1 × 10⁻⁵ mol L⁻¹ were depicted in Fig. 1. Isomer 1 showed typical [5,6]-adduct absorption maxima in UV–vis spectroscopy of 337 nm and 426 nm. Nevertheless, isomer 2 showed the characteristic absorption of the fullerene of [6,6]-adduct at 332 nm and 432 nm, similar to [6,6]-PCBM.¹⁶ Compared with isomer 2, the specific absorbing peak of isomer 1 at 337 nm and 426 nm had a red shift of 5 nm and blue shift of 6 nm, respectively. The onset peak of isomer 1, 2 and PCBM (Fig. S2) were calculated to be 750 nm from the UV–vis absorption data, which suggested the similar optical band gap (*E*_g) values for these three fullerene derivatives.²³ The UV–vis absorption data in film, which could be seen in Fig. S3, showed no obviously different with those in solution.

2.2. Electrochemical property

Electronic energy levels (especially the LUMO level) of the fullerene derivatives are crucial for their application in PSCs as acceptor, which can be measured by electrochemical cyclic voltammetry. The cyclic voltammograms of isomer 1, 2 and the

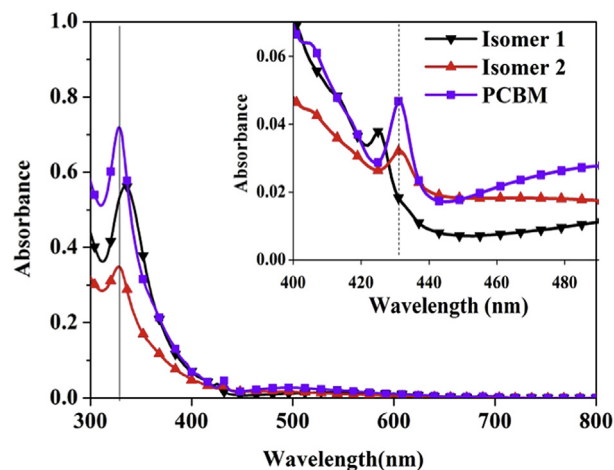


Fig. 1. UV–vis absorption spectra for isomer 1, 2 and PCBM (as the comparison) in CH₂Cl₂ (10⁻⁵ mol L⁻¹).

reference PCBM were shown in Fig. 2. It could be seen that three cyclic voltammograms similarly exhibited three reversible reduction/reoxidation processes over a negative potential range. Reduction potential, LUMO level and highest occupied molecular orbital (HOMO) level for isomer 1, 2 and PCBM were shown in Table 1. The first reduction potential of isomer 2 shifted toward more negative value for ~15 mV with respect to isomer 1, because the two compounds had different numbers of π-electron (60 π-electrons for isomer 1, 58 π-electrons for isomer 2). According to the empirical equation: LUMO level = -(*E*_{1^{red}} + 4.8) eV, HOMO level = LUMO level - *E*_g,²⁴ the LUMO values and the HOMO values of the three structures were calculated from CV data and the optical band gap values. The first reduction potential of isomer 2 shifted toward more negative value of ~30 mV with respect to PCBM, which suggested benzoyl group the higher electron donating ability than the ester group. Both isomers showed higher LUMO level than PCBM, which implied a higher *V*_{oc} in P3HT based BHJ devices.

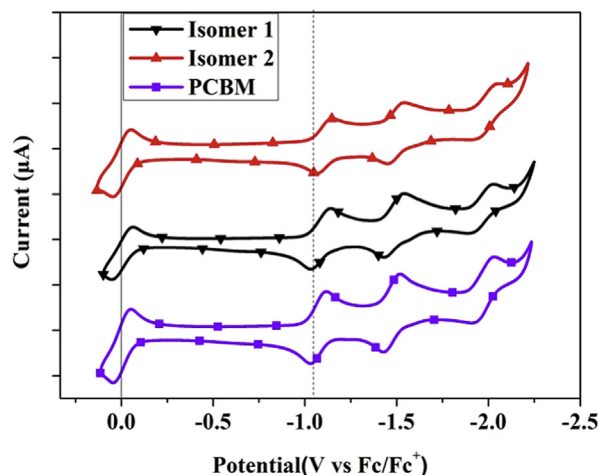


Fig. 2. Cyclic voltammograms of isomer 1, 2 and the reference PCBM in a mixed solvent of *o*-DCB/MeCN (4:1 v/v) with 0.1 M TBAClO₄ as supporting electrolyte at a scan rate of 100 mV/s. Ag/Ag⁺ was used as quasi-reference electrode. Ferrocene was used as an internal standard.

2.3. Photovoltaic properties

To evaluate the photovoltaic potential of the two isomers, PSCs with P3HT as electron donor and two isomeric fullerene isomers 1 or 2 as electron acceptors were fabricated with the structure of ITO/

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