Sci. Bull. (2016) 61(2):132–138
DOI 10.1007/s11434-015-0979-5

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Article

Chemistry

Stereomeric effects of bis$PC_{71}BM$ on polymer solar cell performance

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Received: 2 November 2015 / Revised: 5 December 2015 / Accepted: 7 December 2015 / Published online: 7 January 2016

Abstract Two stereomers of bisadduct analogues of [6, 6]-phenyl-C_{71}-butyric acid methyl ester (bis$PC_{71}BM$) were synthesized and their geometrical structures with *cis*- or *trans*-configuration were identified by X-ray crystallography. Although both of the bis$PC_{71}BM$ have similar spectrometric and electrochemical properties, the spatial orientation of the two addition groups on C_{70} has impact on crystal packing and molecular assembly of bis$PC_{71}BM$ isomers and, in turn, photovoltaic performance in polymer solar cell based on poly(3-hexylthiophene) (P3HT) (with power conversion efficiency of 1.72 % and 1.84 % for the solar cells involving *cis*- and *trans*-bis$PC_{71}BM$, respectively). Although the power conversion efficiency remains to be improved, this work exemplifies that the photovoltaic properties of fullerene-based electron acceptors are influenced by aggregation of the stereomeric molecules and thus extends the guidelines for rational design of efficient fullerene acceptor.

Keywords Polymer solar cells · Fullerene derivative · Electron acceptor · Stereomeric effects · X-ray crystallography

1 Introduction

Polymer solar cells (PSCs) based on conjugated polymer donor and fullerene acceptor offer opportunities to develop renewable solar energy sources because of their advantages of lightweight, flexible, and large-area fabrication with low cost [1, 2]. The power conversion efficiency (PCE) of state-of-the-art PSC has been improved rapidly [3, 4], largely due to the development of new donor materials of conjugated polymer [5–8]. By contrast, the development of fullerene acceptors is still limited. Among hundreds of fullerene acceptors investigated so far [9–11], incredibly, the most widely used acceptor in PSCs is still the [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) or its analogue $PC_{71}BM$ [12–14]. Obviously, searching for alternative fullerene acceptors superior to PCBMs ($PC_{61}BM$ or $PC_{71}BM$) for next PSCs with landmark PCE is highly desired.

For an efficient fullerene acceptor applicable in PSCs, criteria are usually considered in terms of high electron affinity [15], small reorganization energy [16], high electron mobility [17], wide absorption, good solubility and miscibility with donor, as well as high lowest unoccupied molecular orbital (LUMO) level [8]. The guidelines to design such an efficient fullerene acceptor usually involve the following optimization in turn: (1) type of fullerene core; (2) sort of functional group; (3) number of addend(s);

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Electronic supplementary material The online version of this article (doi:10.1007/s11434-015-0979-5) contains supplementary material, which is available to authorized users.

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(4) regioisomer of fullerene adduct; (5) stereomer of fullerene adduct with different spatial orientation of addend(s). At present, investigation on optimization of fullerene core is insufficient owing to scarcity of new fullerene in macroscopically available quantities [18], and an initial experiment showed that a trimetallic nitride endohedral fullerene of $Lu_3N@C_{80}$ might be superior to C_{60} or C_{70} because of its comparable solubility, miscibility, and electron mobility, as well as higher LUMO level [19]. Numerous pioneer researches have been focused on optimizing functional groups [9–12, 20, 21], but only a few organic groups such as phenyl butyric acid methyl ester [12, 13], indene [22, 23], and silylmethane [24] outstand due to their compatibility with some sorts of organic donors for high efficient solar cells. The number of the organic addend(s) in a fullerene core seems magic for improving LUMO level but lowering electron mobility of fullerene derivatives to some extent [25, 26], and some fullerene bis-addends such as bisPCBM [27], indene-C60 bisadduct (ICBA) [22, 23], dihydronaphthyl-based [60]-fullerene bisadduct (NCBA) [28–31], and bisadducts of thieno-*o*-quinodimethane with C60 (bis-TOQC) [32] have been demonstrated better than their mono-addend analogues for enhancing photovoltaic performance. Regioisomers of fullerene adducts have not been sorted until 2012 when Imahori and co-workers [33] separated dihydronaphthyl-based [60]fullerene bisadduct regioisomers and investigated the effects of fullerene bisadduct regioisomers on solar cell performance. Recently, Meng et al. [34] reported PCEs based on isolated isomers of NCBA or ICBA and showed much different performance for each of the regioisomers. Accordingly, the first four guidelines, i.e., the influences of fullerene core, functional group, addend number, and regioisomer on photovoltaic performance, have been preliminary investigated for design of an efficient fullerene acceptor.

However, little is known about the last guideline, i.e., the effect of the spatial orientation of addend(s) on photovoltaic performance. Although several groups have measured the crystal structures of fullerene acceptors and investigated the relationship between molecular packing of fullerene and solar cell efficiency [21, 34, 35], it is a challenge to obtain single crystals of fullerene stereomers for detailing the spatial effect of fullerene addends on photovoltaic performance. Zhao et al. [35] reported the first experiment on different properties of $IC_{60}BA$ stereomers. A theoretical profile on stereomeric effects of $bisPC_{71}BM$ on photovoltaic performance has been depicted as well [36]. Here we show an unambiguous identification of a pair of $bisPC_{71}BM$ stereomers to exemplify their influence on PSCs in experimental aspect, and provide supplementary guideline for designing an efficient electron acceptor. We pay special attention to $bisPC_{71}BM$ because the stereomers of $bisPC_{71}BM$ are much abundant. Theoretically accessible number of bis-adduct regioisomers of $bisPC_{71}BM$ could be more than 28, even the possibility of enantiomer is ruled out. In addition, the stronger absorption in low-symmetric C_{70} renders its [6,6]-phenyl butyric acid methyl ester derivatives superior to C_{60} (parallel experiments with $PC_{61}BM$ have also been conducted for comparison in this work) and widely useful as the most promising electron acceptors for efficient PSCs as well as perovskite solar cells at the present time [37].

2 Materials and methods

2.1 Materials and characterization

C_{60} (99.9 %) and C_{70} (99.5 %) were purchased from Puyang Yongxin Fullerene Co., Ltd. *o*-Dichlorobenzene (*o*-DCB) was obtained from Alfa-Aesar Company. Photovoltaic performance in polymer poly(3-hexylthiophene) (P3HT) was purchased from FEM Technology Co., Inc. and used as received. Other reagents and chemicals were commercially available.

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Biospin Advance III 400 MHz spectrometer. Chemical shifts were reported in ppm relative to the singlet of residual $CHCl_3$ at 7.26 for ^{1}H NMR and $CDCl_3$ at 77 for ^{13}C NMR, respectively. The NMR spectra were measured in $CDCl_3$ at room temperature unless noted otherwise. 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. The dry gas temperature was set at 250 °C, and the APCI temperature was set at 300 °C. UV–Vis absorption spectra were obtained on a Varian Cary 5,000 UV–Vis–NIR spectrophotometer. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer. Cyclic voltammetry was conducted on a CHI-660C electrochemical workstation with Pt disk, Pt wire, and Ag/Ag^{+} electrode (0.01 mol/L $AgNO_3$, 0.09 mol/L 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*-DCB/acetonitrile (5:1) solution. High-performance liquid chromatography (HPLC) analysis was conducted on a Shimadzu liquid chromatography modular system consisting of two LC-6AD pumps, an UV Shimadzu SPD-20A diode array UV detector, and a CBM-20A system controller.

2.2 Device fabrication and characterization

Polymer solar cells with the configuration of indium tin oxide (ITO)/poly(ethylenedioxythiophene) (PEDOT):