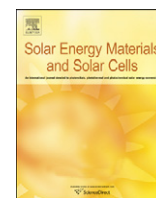




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## Solar Energy Materials &amp; Solar Cells

journal homepage: [www.elsevier.com/locate/solmat](http://www.elsevier.com/locate/solmat)

## Indolinone-substituted methanofullerene—A new acceptor for organic solar cells

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## ARTICLE INFO

## Article history:

Received 13 February 2012

Received in revised form

5 April 2012

Accepted 6 April 2012

Available online 3 May 2012

## Keywords:

Polymer solar cells

Fullerene derivatives

Indolinone-substituted methanofullerene

Thin films

## ABSTRACT

Indolinone-substituted methanofullerene, 1-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3-(3-cyclopropane[1,9](C<sub>60</sub>-I<sub>h</sub>)[5,6]fullerene-3-yl)-indolin-2-one (HBIM), has been studied as an electron acceptor for polymer–fullerene solar cells. HBIM is easier to synthesize and purify than the standard fullerene derivative for polymer solar cells, PCBM. Optical absorption, solubility, and electrochemical properties of HBIM are reported. Solar cells with the device configuration ITO/PEDOT:PSS/P3HT:HBIM/CaAl have been investigated with the reference cells based on the P3HT:PCBM blend. We study the effect of thermal annealing on the device performance and the surface morphology of the active layer. The power conversion efficiency of P3HT:HBIM devices with a weight ratio of 1:1 is about 2% under illumination by AM1.5G (100 mW/cm<sup>2</sup>) radiation. The P3HT:HBIM devices show the same open-circuit voltage as the P3HT:PCBM ones, but the short-circuit current and the fill factor are considerably less.

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### 1. Introduction

For the last few years, the best laboratory polymer solar cells have demonstrated a considerable increase in efficiency that has exceeded 8% [1,2]. The active layer of a typical polymer solar cell is a blend of highly soluble conjugated polymer and fullerene derivative. Many efforts have been done in the development of novel conjugated polymers for organic photovoltaic cells (OPVs) [3], whereas much less attention has been paid to the fullerene derivatives [4]. Methanofullerenes are the most studied fullerene derivatives in polymer solar cells. Among them PCBM is a standard fullerene derivative in OPV, and the polymer–PCBM solar cells have shown the highest efficiency among the solution-processed solar cells [5]. In the near future, scaling of OPVs technologies is expected, and low cost of OPVs materials becomes challenging [6]. From the viewpoint of low production cost, the PCBM-type fullerenes seem to be far from optimal. Indeed, the synthesis of [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM)-type fullerenes is a multi-stage process requiring the synthesis of a diazo-compound, and the reaction needs heating [7]. In addition, the reaction gives two monoadducts, [5,6]-open (homofullerene) and [6,6]-closed (PCBM). To enhance the PCBM yield, the homofullerene is thermally converted to PCBM, and this requires additional heating of the reaction mixture as well.

The presence of homofullerene also complicates the PCBM separation by the column chromatography. Because of this, methanofullerenes synthesized at low-temperature with high yield and minimal number of the synthetic steps and without byproducts are promising as their production cost could be decreased.

In this paper, we report first organic solar cells based on a recently synthesized indolinone-substituted methanofullerene, HBIM. This compound was obtained by the reaction in a three-component system, fullerene-dicarbonyl compound–hexaethyltri-aminophosphine [8]. In contrast to the PCBM and other types of methanofullerenes [9,10], the three-component system requires neither heat nor irradiation and results in only 6,6-closed monoadduct, indolinone-substituted methanofullerene. The yield of this methanofullerene with respect to the initial fullerene is about 50% even in non-optimized conditions. Another common disadvantage of fullerenes in OPVs is their low optical absorption of the solar radiation. In this regard, the indolinone-substituted methanofullerenes could also be attractive as the fullerene  $\pi$ -conjugated addend could increase light harvesting. Below we present the optical and electrochemistry data on HBIM, morphology data on P3HT:HBIM blends, and results of characterization of P3HT:HBIM solar cells. As a reference, P3HT:PCBM blends are used.

### 2. Experimental details

1-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3-(3-cyclopropane[1,9](C<sub>60</sub>-I<sub>h</sub>)[5,6]fullerene-3-yl)-indolin-2-one (HBIM) was synthesized

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according to Ref. [8]. *N*-1-(3',5'-di-*tert*-butyl-4'-hydroxybenzyl) isatin (HBI) was prepared as described previously [11]. P3HT (Rieke Metals), PCBM (Solenne), poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate), PEDOT:PSS (Baytron P VP Al 4083, H.C. Stark) and 1,2-dichlorobenzene (DCB) were used as received. The HBIM solubility was evaluated from the weight of the HBIM saturated solution and the residue that remained after solvent evaporation.

Absorption spectra were recorded in  $\text{CH}_2\text{Cl}_2$  by using a spectrophotometer (Specord). Atomic force microscopy (AFM) images were obtained with a Smena instrument (NT-MDT).

In cyclic voltammetry (CV) studies, a glassy carbon electrode with a working surface of  $3.14 \text{ mm}^2$  was used as the working electrode. The CV curves were recorded in a three-electrode type electrochemical cell with DCB/MeCN (3:1 by volume) solution in the presence of  $\text{Bu}_4\text{NBF}_4$  (0.1 M). The potential sweep rate was  $50 \text{ mV s}^{-1}$ . A silver electrode  $\text{Ag}/\text{AgNO}_3$  (0.01 M solution in MeCN) was used as the reference electrode ( $E^\circ(\text{Fc}/\text{Fc}^+) = +0.20 \text{ V}$ ). A Pt wire with a diameter of 1 mm served as the auxiliary electrode. The measurements were carried out at  $20^\circ\text{C}$  in nitrogen atmosphere.

The devices were fabricated on ITO-coated glasses (nominal sheet resistance  $15 \Omega/\text{sq.}$ , Kintec) cleaned by sequential ultrasonic treatments in detergent, water, and isopropanol. After drying, a PEDOT:PSS layer was spin-coated at 3000 rpm for 60 s on the ITO electrode. Then the PEDOT:PSS film was heated on a hotplate at  $150^\circ\text{C}$  for 15 min. Polymer and fullerene (PCBM and HBIM) were separately dissolved in DCB at a concentration of  $20 \text{ mg mL}^{-1}$  and stirred for 12 h. Then solutions of polymer and fullerene were mixed in the required concentrations and stirred for 12 h before use. The solutions were spin-coated on top of the PEDOT:PSS layer at 600 rpm for 2 min. The low-work-function electrode, CaAl, with a thickness of  $\sim 100 \text{ nm}$  was thermally deposited on the active layer through a shadow mask with a pixel area of  $5.7 \text{ mm}^2$ . Post-thermal treatment of the devices (annealing) was performed on a hotplate at  $140^\circ\text{C}$  for 15 min in an argon-filled glovebox. The PCBM- and HBIM-based devices were prepared simultaneously (where possible) under the nominally same conditions. Current-voltage ( $J$ - $V$ ) measurements of the devices were conducted with a computer-controlled Keithley 2400 SourceMeter instrument. The devices were illuminated by a 150 W solar simulator (model 9600, Newport) with an AM1.5G filter, the optical power on the sample was set to about  $100 \text{ mW}/\text{cm}^2$  using a bolometric detector. External quantum efficiency (EQE) spectra of the devices were measured under monochromatic light. The photocurrent was measured by a lock-in amplifier, and the optical power was measured by a silicon optical power meter (S120UV, Thorlabs). In the optical studies, the devices were illuminated through a  $3.2 \text{ mm}^2$  circular aperture, which was in contact with the glass side of the device.

### 3. Results and discussion

The HBIM was obtained via the reaction of fullerene  $\text{C}_{60}$  with the HBI in the presence of hexaethyltriamidophosphine. The separation of the reaction products by column chromatography on silica gel gave the unreacted fullerene and non-separated poly-adducts mixture along with the methanofullerene HBIM (Fig. 1) [8].

In contrast to the synthesis of PCBM [7] or other methanofullerenes [9,10], this reaction proceeds at mild conditions without heating or irradiation. The yield of HBIM was 45–50% with respect to the starting fullerene. It is worth noting that this reaction leads to formation of only one type of adduct, [6,6]methanofullerene. As a result, the synthesis of HBIM is easier than that of PCBM.

Fig. 2 compares absorption spectra of HBIM, PCBM and  $\text{C}_{60}$ . HBIM and PCBM show similar absorption features; however, HBIM is characterized by higher absorption than PCBM in the range 250–600 nm. The higher HBIM absorption could be assigned to the absorption of the indolinone fragment as follows from the HBI absorption (see Fig. 1S in Supporting Information). One could expect that the light harvesting of HBIM in the solar cells could be higher than that of PCBM (Fig. 2).

The reduction peak potentials of HBIM, HBI and  $\text{C}_{60}$  are summarized in Table 1. In contrast to alkyl substituted isatins, which are characterized by two reversible reduction peaks [8], the CV curve of HBI contains three irreversible reduction peaks. This difference is due to the fact that both the polycyclic fragment and benzyl radical in HBI are electroactive. The HBI reduction is reversible for the potential reverse at the end of the first reduction wave. Taking into account the data for the alkyl substituted isatins, the first CV peak of HBI can be attributed to reduction of its heterocyclic fragment [8,12]. The subsequent waves correspond to reduction of the heterocyclic fragment and benzyl

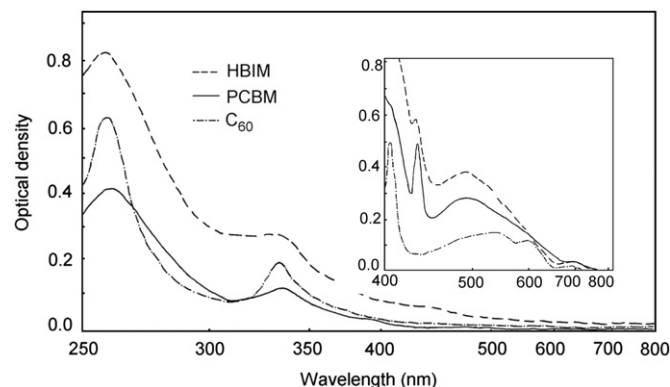


Fig. 2. Absorption spectra of HBIM, PCBM, and  $\text{C}_{60}$  in  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10^{-5} \text{ mol L}^{-1}$ , the cell thickness  $d = 2 \text{ mm}$ ). Inset shows the absorption spectra at  $d = 10 \text{ mm}$ .

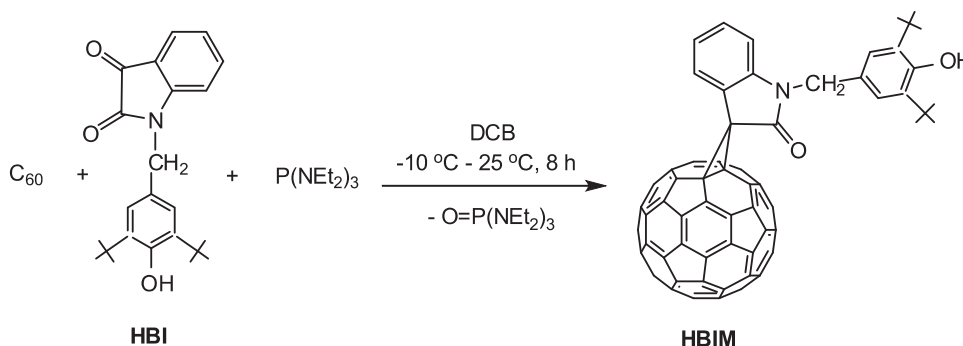


Fig. 1. Synthesis procedure for HBIM.

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