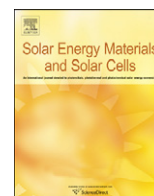




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Indolinone-substituted methanofullerene—A new acceptor for organic solar cells

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ABSTRACT

Indolinone-substituted methanofullerene, 1-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3-(3-cyclopropane[1,9](C₆₀-I_h)[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/cm²) 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-C₆₁-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 π -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](C₆₀-I_h)[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 CH_2Cl_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 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 Bu_4NBF_4 (0.1 M). The potential sweep rate was 50 mV s^{-1} . A silver electrode Ag/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°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°C for 15 min. Polymer and fullerene (PCBM and HBIM) were separately dissolved in DCB at a concentration of 20 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 mm^2 . Post-thermal treatment of the devices (annealing) was performed on a hotplate at 140°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 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 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 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 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

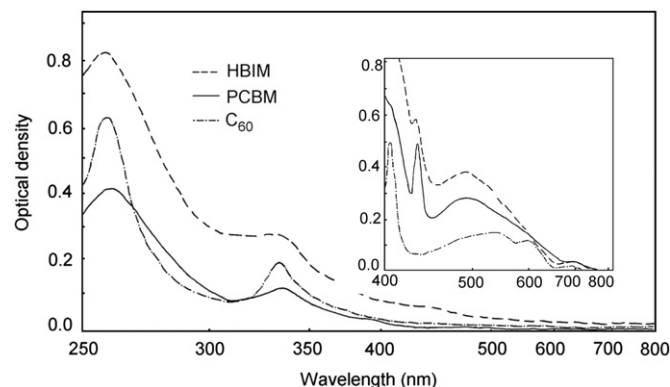


Fig. 2. Absorption spectra of HBIM, PCBM, and C_{60} in CH_2Cl_2 ($2 \times 10^{-5} \text{ mol L}^{-1}$, the cell thickness $d = 2 \text{ mm}$). Inset shows the absorption spectra at $d = 10 \text{ mm}$.

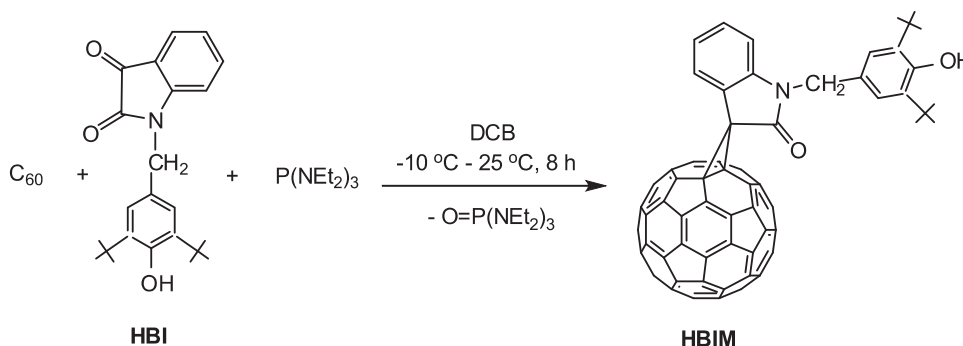


Fig. 1. Synthesis procedure for HBIM.

Table 1
Peak potentials (E_p^{red}) of C_{60} , HBIM, and HBI.

Compound	Concentration (M)	E_p^{red} (V) ^a				
		C ₁	C ₂	C ₃	C ₄	C ₅
C_{60}	$5.0 \cdot 10^{-3}$	-0.83	-1.24	-1.70	-2.16	-
HBIM	$5.7 \cdot 10^{-3}$	-0.93	-1.33	-1.54	-1.75	-1.92
HBI	$4.8 \cdot 10^{-3}$	-1.30	-1.62	-1.91	-	-

^a Potential values are versus Ag/Ag⁺ reference electrode.

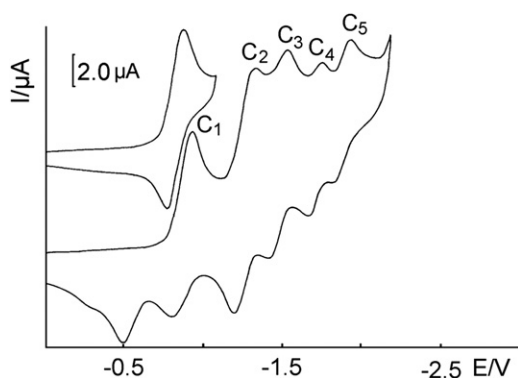


Fig. 3. Cyclic voltammetry curves in *o*-DCB/MeCN (3:1 by volume) solution of HBIM.

radical. Note that the first electron transfer to HBI is observed in the same potential range as that of the second reduction peak of C_{60} . Four standard reversible one-electron reduction peaks are observed for C_{60} . Fig. 3 presents CV curves of HBIM. Its reduction is more complicated, and the CV data exhibits five reduction peaks in the potential range from -0.93 to -1.92 V. The first and the second reduction peaks are reversible for the potential reverse at the end of the second reduction wave. The first step of the methanofullerene reduction (C₁) involves electron transfer onto the fullerene sphere as follows from the potentials for C_{60} , HBI, and HBIM given in Table 1. The second reduction peak (C₂) and the other cathodic peaks (C₃ and C₄) of HBIM correspond to reduction of the fullerene sphere and the attached polycyclic addend. The data in Table 1 show that the HBIM first reduction potential is shifted by 100 mV to the cathodic region as compared with that of C_{60} . This can be attributed to the opening of one C=C fullerene bond decreasing the fullerene sphere electrophilicity. Note that the first reduction peaks of PCBM and other methanofullerenes are also shifted with respect to that of C_{60} by about 100 meV [7,13]. Therefore, as the open-circuit voltage V_{oc} in organic solar cells depends on the LUMO energy of the acceptor material, one can expect that HBIM can provide the open-circuit voltage close to that of PCBM.

The solubility of fullerene derivatives is an important parameter that influences the morphology of polymer–fullerene blends and hence their photovoltaic performance. The optimal solubility of fullerene derivatives in chlorobenzene, which is a typical solvent for fabrication of P3HT–fullerene solar cells, is reported to be in the range 30 – 80 mg mL⁻¹ at room temperature [13]. The HBIM solubility in chlorobenzene was evaluated to be 15 mg mL⁻¹. The HBIM solubility in DCB was found to be higher (31 mg mL⁻¹) and is expected to be sufficient to realize the optimal morphology in polymer–fullerene blends.

HBIM and PCBM were used as acceptors for P3HT–fullerene solar cells, with the P3HT:PCBM cells being used as a reference. As the optimal preparation protocol for P3HT:HBIM solar cells is *a priori* unknown, we used that of P3HT:PCBM as a starting point.

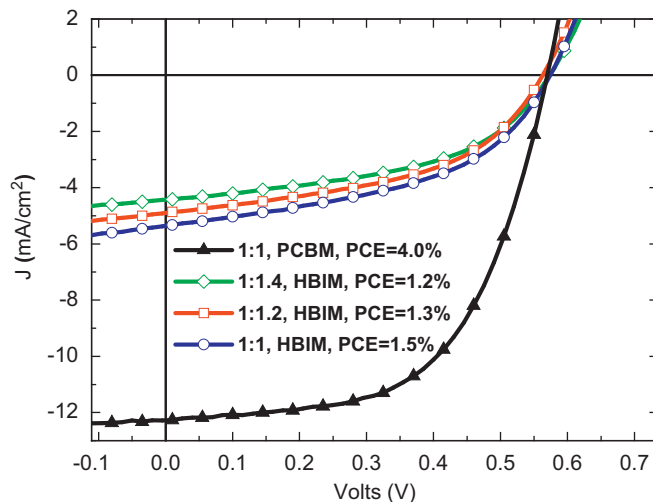


Fig. 4. J - V characteristics of P3HT:HBIM devices with blend ratios of 1:1, 1:1.2 and 1:1.4 in comparison with the optimized P3HT:PCBM device.

Fig. 4 demonstrates J - V characteristics of as-prepared P3HT:HBIM solar cells for various polymer:fullerene weight ratios. The data for an annealed reference P3HT:PCBM device are also plotted in Fig. 4. The reference device shows the power conversion efficiency (PCE) 4.0% and the short-circuit current density $J_{sc} = 12$ mA/cm². The HBIM-based devices demonstrate the same open-circuit voltage (0.57 V) as that of the PCBM-based device, and this is in accordance with our electrochemical data (see above). Nevertheless, due to a lower short-circuit current and a lower fill factor (FF), their PCE is only around 1.3%. Increasing the HBIM content in the blend decreases the PCE from 1.5% (for 1:1) down to 1.2% (for 1:1.4). The corresponding J_{sc} values decrease from 5.4 to 4.4 mA/cm²; while V_{oc} and FF are almost the same. For the HBIM content lower than 1:1, J_{sc} gradually decreased upon decreasing the HBIM. As a result, we conclude that the weight ratio 1:1 is close to the optimal one for P3HT:HBIM blends.

Thermal annealing is known to be an efficient post-treatment step for polymer:fullerene solar cells. We used thermal annealing to improve the device performance with conditions typically used for P3HT:PCBM solar cells, i.e. annealing at 140 °C for 15 min [14]. Fig. 5 compares J - V (a) and EQE (b) characteristics of the as-casted and annealed P3HT:HBIM devices. For the annealed device, J_{sc} increased by 40%, i.e. from 6.5 to 9.1 mA/cm²; however, FF decreased from 0.48 to 0.39 . As a result, the PCE increased from 1.7% to 2.0%. The V_{oc} was 0.55 V and did not change after annealing. Therefore, the annealing protocol used for P3HT:PCBM solar cells is hardly close to the optimal one for the P3HT:HBIM ones. This conclusion is supported by the external quantum efficiency (EQE) data presented in Fig. 5(b). Indeed, the EQE is increased by 76% after annealing, i.e. from 25% to 44% (Fig. 5b), and this increase is about two times higher than that of J_{sc} . Fig. 5(b) also compares the EQE spectra for P3HT:HBIM and P3HT:PCBM blends. One can see that the EQE in the former is about 10% less than in the latter. Accordingly, charge generation and collection in P3HT:HBIM blends can be quite close to those in P3HT:PCBM blends. However, at solar intensities, charge recombination probably limits the performance of P3HT:HBIM blends, and this could be assigned to non-optimized morphology. In addition, the EQE is flatter in the range 400 – 500 nm for the as-prepared P3HT:HBIM device as compared to the reference P3HT:PCBM one. This is in parallel with higher optical absorption of HBIM (see Fig. 1) and could indicate more efficient charge generation via fullerene–polymer hole transfer. Nevertheless, the annealed P3HT:HBIM device does not show evidence of improved

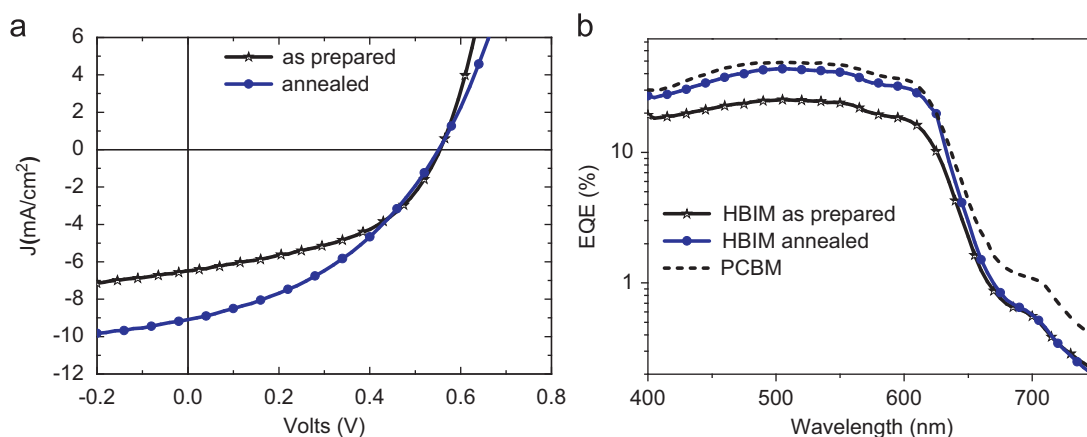


Fig. 5. *J*-*V* characteristics (a) and EQE (b) of 1:1 P3HT:HBIM devices for as-prepared and annealed devices. EQE for the annealed P3HT:PCBM blend is also shown for comparison.

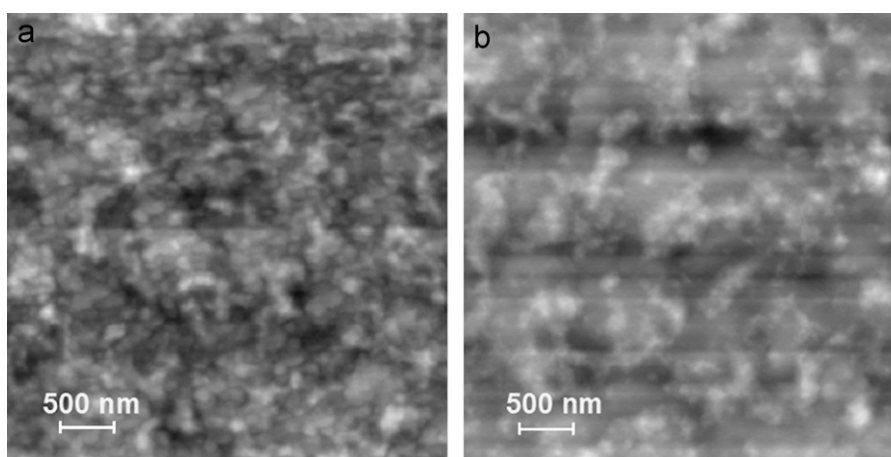


Fig. 6. AFM topography images of as-casted (a) and annealed (b) films of P3HT:HBIM.

hole transfer, i.e. the increased EQE in the spectral ranges 400–500 nm and below the P3HT absorption edge (> 650 nm). In fact, the EQE of the annealed device does not change below the P3HT absorption edge and is less flat in the range 400–500 nm. This suggests that annealing does not enhance hole transfer in P3HT–HBIM blends and probably reflects the non-optimized morphology (see below).

The AFM study shows that the P3HT:HBIM blends are phase separated with the characteristic domain height of about 15–20 nm (see Fig. 2S in SI). Fig. 6 compares AFM images for as-casted and annealed P3HT:HBIM films. One can see that the annealing increases the grain size on the film surface. Similar to P3HT:PCBM blends [15], these grains could be assigned to fullerene domains growing during annealing. Indeed, since the mobility of the fullerene molecules increases with increasing temperature it makes possible for the fullerene molecules to form larger domains with lower surface energy. Note that the reference P3HT:PCBM blends show lower surface roughness with typical domain heights below 10 nm (see Fig. 3S in SI). One can suggest that the coarser surface morphology in P3HT:HBIM blends is a result of fullerene-rich domains, which are too large for the optimal polymer–fullerene phase separation. Possibly, the coarser surface morphology is due to lower solubility of HBIM as compared to PCBM. As a result, the hole transfer efficiency can be reduced due to loss of excitons generated inside the large fullerene domains [16,17]. Note that in our studies of P3HT:HBIM solar cells we have used the device fabrication protocol optimized

for P3HT:PCBM blends. It seems that the performance of P3HT:HBIM solar cells could be improved further by optimizing the fabrication protocol.

4. Conclusion

In summary, for the first time we have studied an indolinone-substituted methanofullerene derivative (HBIM) as a novel acceptor material for bulk heterojunction polymer–fullerene solar cells. Its optical and electrochemical properties are very close to those of PCBM. As the starting device fabrication protocol, we have used that optimized for P3HT:PCBM solar cells. The optimal polymer:–fullerene ratio has been found to be about 1:1 by weight, and the power conversion efficiency was about 2%. However, the fabrication protocol used is hardly to the optimal one for P3HT:HBIM solar cell, and therefore it needs further optimization.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.solmat.2012.04.013>.

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