# Performance improvement of organic bulk heterojunction solar cells by using dihydroxybenzene as additive*

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We report the enhanced performance of organic solar cells (OSCs) based on regioregular poly(3-hexylthiophene) (P3HT) and methanofullerene [6,6]-phenyl $C_{61}$-butyric acid methyl ester (PCBM) blend by using dihydroxybenzene as additive in the active layer. The effect of the content of the additives on electrical characteristics of the device is studied. The device with 0.2 wt% dihydroxybenzene additive achieves the best power conversion efficiency (PCE) of 4.58% with $J_{sc}$ of 12.5 mA/cm², $V_{oc}$ of 0.65 V, and $FF$ of 66.6% under simulated solar illumination of AM 1.5G (100 mW/cm²), compared with the control device with PCE of 3.39% (35% improvement compared with the control device). The XRD measurement reveals that the addition of additives induces the crystallization of P3HT and establishes good inter-network to increase the contact area of donor and acceptor, and then helps charge to be effectively transferred to the electrode to reduce the chance of recombination. All evidences indicate that the dihydroxybenzene is likely to be a promising new type additive that can enhance the performance of organic bulk heterojunction solar cells.

**Document code:** A  **Article ID:** 1673-1905(2011)04-0246-3

**DOI** 10.1007/s11801-011-1034-7

Recently, organic solar cells (OSCs) have attracted much attention as new renewable energy sources[1-5]. Significant effort has been made for improving the performance of organic solar cells by optimizing the short-circuit current density ($J_{sc}$), the open-circuit voltage ($V_{oc}$), and the fill factor ($FF$)[6-8]. Although the power conversion efficiency (PCE) in the range of 5–8% has been recently reported for BHJ solar cells, the major obstacle to commercialization is still the low PCE of the devices[9-13]. The research in the field of OSCs is focused on achieving PCE in the range of 10-15%[14]. Today, most efficient solar cells are based on an active layer composed of a blend of regioregular (3-hexylthiophene) (P3HT) and the fullerene derivative [6,6]-phenyl $C_{61}$-butyric acid methyl ester (PCBM). There are many factors limiting the PCE of the BHJ solar cells, and the poor exciton/charge transfer and transpor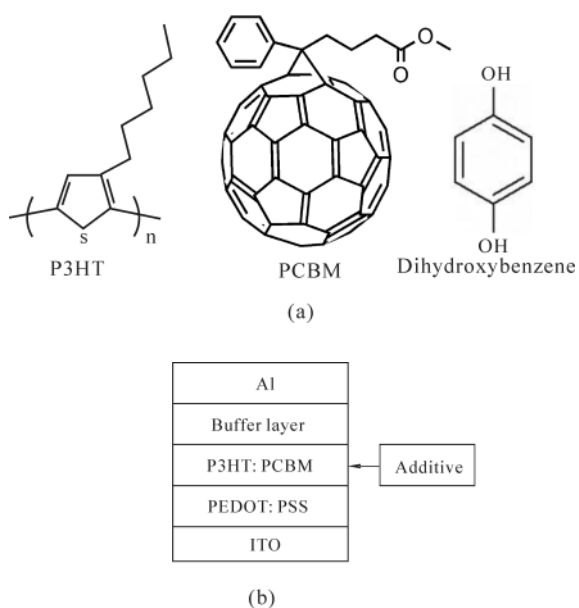t is one of them. To facilitate the exciton/charge transfer and transport, the active layer morphology has been controlled by numerous methods such as thermal, solvent, composition adjustment[15,16]. Recently, a new approach has been reported to control the morphology of the blend film by adding a third non-reacting chemical compound, processing additive, to the donor and acceptor solution. It has been shown that the addition of additive can improve the performance of BHJ solar cells. In this letter, we report the enhanced performance of polymer solar cells based on P3HT: PCBM blend by using dihydroxybenzene as new additives.

The molecular structure of the materials used in the experiment and the schematic device structure (ITO/PEDOT: PSS/P3HT: PCBM: additive /LiF/Al) are shown in Fig.1. The P3HT(4002-E) with purity over 99% is purchased from Rieke Met. Inc. PCBM is purchased from Solenne BV, with purity over 99%. The ITO-coated glass with a sheet resis-

tance of 10 Ω/square is used for device fabrication. The routine cleaning procedure includes ultra-sonication in a solution of detergent, deionized (DI) water, and isopropyl alcohol in sequence. The dihydroxybenzene solution is prepared with concentration of 0.7 mg/mL in ethanol. The active layer solution of P3HT: PCBM (1: 0.8 weight-ratio) is prepared with concentration of 27 mg/mL in o-dichlorobenzene. The additive solution is added into the solution of P3HT: PCBM to obtain the mixture with concentration ranging from 0.1 wt% to 0.7 wt%. The procedure for the solar cell fabrication is described as follows. The PEDOT: PSS layer of about 40 nm is obtained by spin coating at 3000 r/min for 35 s from an aqueous solution (Baytron ® P VP AI 4083) on ITO coated glass substrates, followed by baking at 120 °C for 20 min in a vacuum oven. The mixture solution of active layer is spin coated at 800 r/min for 10 s onto the PEDOT: PSS layer to form a 100 nm-thick active layer. Finally, the 0.7 nm-thick LiF buffer layer and the 100 nm-thick Al cathode are thermally evaporated under a vacuum with a pressure of $1\times10^{-4}$ Pa. The post thermal annealing of the sample is carried out at 160°C for 30 min on a hot plate in an argon-filled glove box. The active layer area of the device is 0.09 cm$^2$ defined by a shadow mask. The current density-voltage (J-V) curves of the devices are measured by a computer-controlled Keithley 2400 source meter in air under 100 mW/cm$_2$ white light illumination. The solar simulator is a 500 W Xe lamp (CHF-XM-500, Beijing Changtuo) with AM1.5G filter. The light intensity is calibrated with a Si photodetector (FZ-A, Photoelectric Instrument Factory of Beijing Normal University). The change in crystallinity of P3HT after add-

ing additive is analyzed at room temperature by XRD using Rigaku D/MAX-2500 diffractometer with Cu K$a$ radiation.

Fig.2 shows the current density versus voltage (J-V) characteristics of devices without additive and with various concentrations of additive under 100 mW/cm$^2$ white light illumination. The open-circuit voltage ($V_{oc}$), the short-circuit current ($J_{sc}$), the fill factor (FF) and the power conversion efficiency (PCE) of these devices are also summarized in Tab.1. For the device without additive in the active layer, $J_{sc}$, $V_{oc}$, FF and the PCE are 11.05 mA/cm$^2$, 0.61 V, 50.29% and 3.39%, respectively. With the content of additive increasing from 0.1 wt% to 0.2 wt%, $J_{sc}$, FF and PCE are enhanced accordingly. The performance of the device is greatly optimized at the content of additive of 0.2 wt% with $V_{oc}$ of 0.65 V, $J_{sc}$ of 12.45 mA/cm$^2$ and FF of 56.6%. The calculated PCE is about 4.58%, a 35% improvement compared with the control devices. However, further increasing the content of additive to 0.7 wt% will lead to reduced efficiency for its insulation property. This indicates that the dihydroxybenzene is a promising additive of active layer.
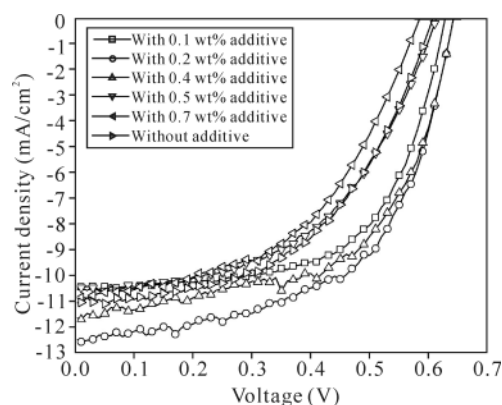


**Fig.2 Current density versus voltage (*J-V*) characteristics of devices with various concentrations of additive in the active layer**

**Tab.1 Device performance with different contents of additive**

| Device | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|---|---|---|---|---|
| Without additive | 11.05 | 0.61 | 50.29 | 3.39 |
| With 0.1 wt% additive | 10.45 | 0.63 | 61.65 | 4.06 |
| With 0.2 wt% additive | 12.45 | 0.65 | 56.60 | 4.58 |
| With 0.4 wt% additive | 11.61 | 0.65 | 57.67 | 4.35 |
| With 0.5 wt% additive | 10.58 | 0.62 | 50.60 | 3.32 |
| With 0.7 wt% additive | 10.84 | 0.59 | 49.42 | 3.16 |

The crystallinity of P3HT in the active layer plays an important role in the hole-transport properties. Mixing additive into the active layer may change the crystallinity property of P3HT. The XRD is employed to detect P3HT crystallinity in the blend containing different amounts of additive. The XRD



**Fig.1(a) Molecular structures of P3HT, PCBM and dihydroxybenzene and (b) the schematic device configuration**

spectra of active layers without and with 0.2 wt%, 0.7 wt% additive are shown in Fig.3. The XRD spectra of P3HT: PCBM active layer with additive show increased intensity at $2\theta \approx 5°$ compared with control device, which means that the addition of additives induces the crystallization of P3HT and establishes good inter-network to increase the contact area of donor and acceptor, and then helps charge to be effectively transferred to the electrode to reduce the chance of recombination.The enhancement of the charge collection efficiency shows improved $J_{sc}$, FF and PCE[17]. However, when too many additives (0.7 wt%) are used, large-scale phase separation may happen, which results in lowered carrier transporation efficiency and lower performance[18].
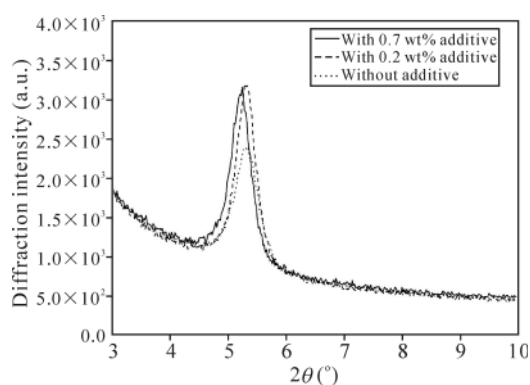


**Fig.3 XRD spectra of active layer without and with additive (0.2 wt% and 0.7 wt%)**

In conclusion, we have shown that the improved performance of polymer solar cells based on P3HT:PCBM blend is obtained by using dihydroxybenzene as active layer additive. A PCE of 4.58% (35% improvement compared with the control device) with $J_{sc}$ of 12.45 mA/cm², $V_{oc}$ of 0.65 V, and FF of 56.6% is obtained for the device with 0.2 wt% additive added in the active layer under simulated AM1.5 G 100 mW/cm² illumination in air. All evidences indicate that the dihydroxybenzene can be used as an effective active layer additive to enhance the polymer BHJ photovoltaic cell efficiency.

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