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Efficient bulk heterojunction solar cells based on D–A copolymers as electron donors and $PC_{70}BM$ as electron acceptor

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ABSTRACT

Two low band gap conjugated polymers **P1** (alternating phenylenevinylene containing thiophene and pyrrole rings) and **P2** (alternating phenylenevinylene with dithenyl (thienothiadiazole) segments) having optical band gap 1.65 eV and 1.74 eV, respectively, were used as electron donor along with the $PC_{70}BM$ as electron acceptor for the fabrication of bulk heterojunction solar cells. The power conversion efficiency (PCE) of BHJ devices based on **P1**:$PC_{70}BM$ and **P2**:$PC_{70}BM$ cast from THF solvent is about 2.84% and 2.34%, respectively, which is higher than the BHJ based on PCBM as electron acceptor. We have investigated the effect of mixed (1-chloronaphthalene (CN)/THF) solvent, modification of PEDOT:PSS layer and inserting of TiO_2 layer, on the photovoltaic performance of polymer solar cell. We have achieved power conversion efficiency of 5.07% for the polymer solar cells having structure ITO/PEDOT:PSS (modified)/**P1**:$PC_{70}BM$ (CN/THF cast)/TiO_2/Al. The effect of solvent used for spin coating, modification of PEDOT:PSS layer and inclusion of TiO_2 layer has been discussed in detail.

1. Introduction

Polymer solar cells (PSCs) recently have attracted a great deal of attention because of the low cost, light weight, and mechanical flexibility [1–6]. The most efficient device structure of PSCs was based on the concept of bulk heterojunction (BHJ) [7,8], which consists of a blend of conjugated polymers and fullerene derivatives as electron donors and acceptors, respectively. Poly(3-hexylthiophene) (P3HT) has been used as electron donor along with the [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) for the single BHJ polymer solar cells and has reached power conversion efficiency (PCE) between 4 and 5% [9,10]. However, the relatively large band gap and higher position of highest occupied molecular orbital (HOMO) energy level (in between −4.8 and −4.9 eV) of P3HT [11] significantly limit the short circuit current (J_{sc}) and open circuit voltage (V_{oc}) of the BHJ polymer solar cells, respectively, based on P3HT:PCBM. The mismatch of absorption spectra of P3HT with the solar spectrum significantly limits the photovoltaic performance of the BHJ solar cells. In order to improve the visible absorption and decrease the HOMO energy level of conjugated polymers, design and synthesis of donor–acceptor (D–A) copolymers had been proven to be the most successful strategy to reduce the band gap [12–15]. Research efforts to design this group of conjugated polymers have recently focused on developing low band gap intramolecular charge transfer (ICT) copolymers using donor (D) and acceptor (A) units [16–19]. Significant progress had been made in this field and the PCEs of solution processed polymer solar cells have reached 7–8%, primarily due to the development of new low band gap conjugated polymers [20–23] and the better control of the nanoscale morphology of the interpenetrating networks. To date, the PCEs of conjugated polymer solar cells based on D–A structure have reached high up to 8.13% by Solarmer [24] and 8.3% by Konarka [25].

A literature survey revealed that certain copolymers containing thiophene and pyrrole rings had been recently synthesized and used as donor components for BHJ polymer solar cells and the PCE of these devices ranged from 0.18% to 2.8% [26,27]. Recently, our group has designed two low band gap soluble phenylenevinylene copolymers with cyanovinylene 4-nitrophenyl segments and achieved a PCE up to 4.06% using these copolymers as electron donor along with PCBM as electron acceptor for BHJ solar cells [28].

In this paper, we report the photovoltaic effect of the BHJ devices based on **P1**:$PC_{70}BM$ and **P2**:$PC_{70}BM$ blends. **P1** is the D–A

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copolymer having optical band gap of 1.65 eV, in which dihexyloxyphenylene, thiophene and pyrrole groups behave as electron donor and the cynovinylene 4-nitrophenyl group behaves as an acceptor unit [29]. **P2** is another D–A copolymer having optical band gap about 1.74 eV, in which hexyloxyphenylene and dithenyl (thienothiadiazole) cyanovinylene nitrophenyl units as electron donor and acceptor, respectively [30]. We have already reported that the PCE of BHJ devices based on **P1**:PCBM and **P2**:PCBM is about 1.50% and 1.40%, respectively [29,30]. However, the PCE of the photovoltaic devices based on **P1**:$PC_{70}BM$ and **P2**:$PC_{70}BM$ cast from THF solvent is about 2.84% and 2.34%, respectively. The enhanced PCE for the device based on $PC_{70}BM$ is attributed to the improvement of both J_{sc} and V_{oc} as compared to the device based PCBM. The increase in the J_{sc} is attributed to the strong absorption by the $PC_{70}BM$ as compared to PCBM in the wavelength region below 500 nm. Moreover, the difference in the HOMO level of copolymer and LUMO level of the $PC_{70}BM$ is higher than that for the BHJ active layer based on PCBM, resulted higher value of V_{oc}. The overall PCE of the BHJ active layer processed from a mixed solvent (CN/THF) is about 4.12% and 3.3% for **P1**:$PC_{70}BM$ and **P2**:$PC_{70}BM$ BHJ active layer, respectively. This improved PCE has been attributed to the increased crystalline nature of copolymer and hole mobility in the blend, resulting in balanced charge transport. We have used the modified PEDOT:PSS electrode to improve the photovoltaic performance of the devices and achieved overall PCE of 3.54% and 4.4% with **P2**:$PC_{70}BM$ and **P1**:$PC_{70}BM$ blends cast from the CN/THF solvents. Further the overall PCE of the PSCs has been improved up to 4.14% and 5.07% for **P2**:PC70BM and **P1**:PC70BM blends, respectively, cast from CN/THF solvent, with the incorporation of a TiO_2 layer in between the active layer and Al electrode.

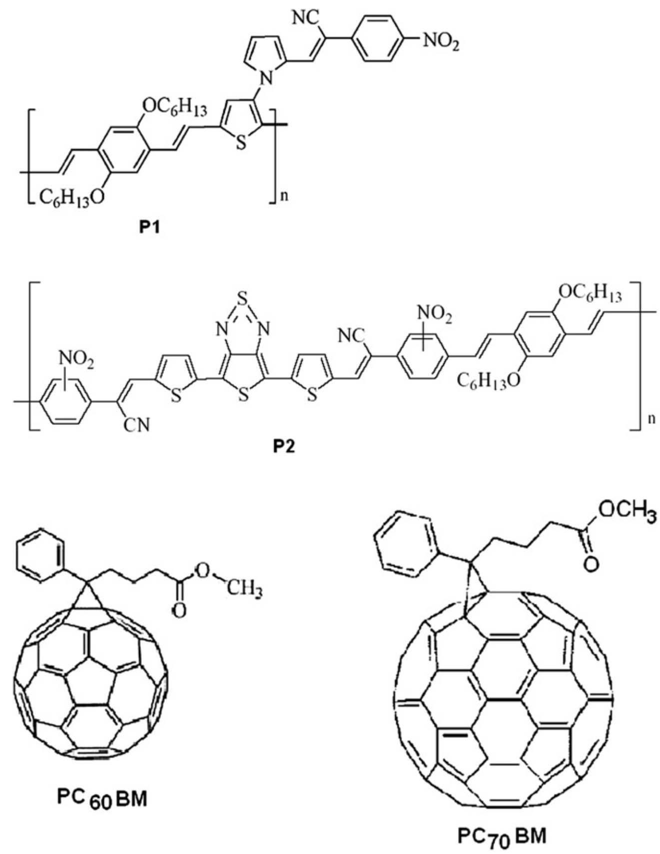

Fig. 1. Chemical structure of **P1**, **P2**, PCBM and $PC_{70}BM$.

2. Experimental details

We have used conjugated copolymers **P1** and **P2** as electron donor and $PC_{70}BM$ as the electron acceptor for the fabrication of BHJ polymer solar cells (chemical structure shown in Fig. 1). The **P1** and **P2** were synthesized as reported earlier [29,30]. $PC_{70}BM$ and 1-chloronaphthalene (CN) were purchased from Aldrich Chemicals. All the reagents and solvents were commercially purchased and were used as supplied. The absorption spectra of the thin films were obtained on a Perkin–Elmer spectrophotometer.

The BHJ PSCs were fabricated having structure of ITO/PEDOT:PSS/**P1** or **P2**:$PC_{70}BM$/Al as follow: The indium tin oxide (ITO) coated glass substrates were cleaned by ultrasonication sequentially in de-ionized water, acetone, detergent, and isopropyl alcohol. After drying the substrate, a thin layer of 60 nm thin layer of poly(3, 4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron) was spin coated (3500 rpm for 30 s) on ITO substrate and subsequently baked at 100 °C for 20 min in air. The blend of **P1** or **P2** with $PC_{70}BM$ in THF under weight ratio 1:1, was spin coated on the top of the PEDOT:PSS layer. In order to investigate the effect of mixed solvent on the performance of the PSCs, a small amount of the high boiling point additive 1-chloronaphthalene (CN) (2% by volume) was added into the blend (in THF) solution. The active layer thicknesses in all devices were approximately 85 (±2 nm) and controlled by changing both the spin coating rate and the concentration of the solution. An aluminum (Al) cathode (100 nm) was then thermally evaporated under vacuum ($\sim 10^{-5}$ Torr) through a shadow mask defining the active device area of 16 mm^2. We have also fabricated separate hole and electron only devices with ITO/PEDOT:PSS/**P1** or **P2**:$PC_{70}BM$/Au and Al/**P1** or **P2**:$PC_{70}BM$/Al structures, respectively, to measure the hole and electron mobility of the BHJ active layer. The current–voltage (J–V) characteristics of the devices were measured using a computer controlled Keithley 238 source meter. A xenon lamp coupled with AM 1.5 solar spectrum filter was used as light source, and the illumination intensity at the surface of device was around 100 mW cm^{-2}.

The incident photon to current efficiency (IPCE) spectra of the devices were measured illuminating the devices through halogen lamp coupled with monochromator and the resulting current was recorded on Keithley electrometer, under short circuit condition. The IPCE at a monochromatic wavelength (λ) was estimated using following expression

$$\mathrm{IPCE}(\lambda) = 1240 J_{sc} \Big/ \lambda P_{in}$$

where J_{sc} is the photocurrent density under short circuit condition and P_{in} is the illumination intensity.

3. Results and discussion

3.1. Optical properties of the BHJ thin films

The absorption spectra of **P1**:$PC_{70}BM$ and **P2**:$PC_{70}BM$ thin films cast from THF and CN/THF mixed solvent are shown in Fig. 2a and b, respectively. The optical absorption spectra of the **P1** and **P2** had also been already reported in our earlier publications [29,30]. It can be seen from these figures that the absorption spectra of the blend show the combination of individual components i.e. **P1** or **P2** and $PC_{70}BM$. The absorption band in the longer wavelength region corresponds to the **P1** or **P2**, which is associated to the interchain π–π^* transition. The absorption spectra of shoulder at 715 nm and 680 nm for **P1** and **P2**, respectively, are related to the interchain interaction and the height of this shoulder indicates the ordering of the chain packing [31]. It can be seen from these figures that optical