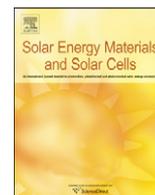




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Electrochromic device and bulk heterojunction solar cell applications of poly 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo[1,2,3]triazole (PBEBT)

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ARTICLE INFO

Article history:

Received 12 February 2010

Received in revised form

20 May 2010

Accepted 22 May 2010

Available online 16 June 2010

Keywords:

Electrochromic device

Bulk heterojunction

Organic solar cells

Benzotriazole

ABSTRACT

4,7-Bis(2,3-dihydrothieno [3,4-b] [1,4] dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] triazole (BEBT) was polymerized both electrochemically (ePBEBT) and chemically (cPBEBT). Since chemical polymerization enabled a soluble polymer in common organic solvents, a single layer electrochromic device of ePBEBT was constructed. The polymer cPBEBT was also used in bulk heterojunction (BHJ) solar cells as the active layer in combination with a soluble fullerene derivative, 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₁ PCBM.

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1. Introduction

The ability to sense or respond to a controllable external stimulus classifies conjugated polymers as candidates for smart materials [1]. Applications of these materials to low cost optoelectronic devices will be possible using solution processable conjugated polymers with promising electrical and physical properties. Recent worldwide research interest is focused on organic solar cells (OSCs) [2–5] and electrochromic devices (ECDs) [6]. Polymers that are applicable to many fields are regarded as multi-purpose smart materials for organic electronics [7].

Conjugated polymers allow fine tuning in optical properties via structural modifications and, in principle, highly efficient devices can be obtained by design of low band gap polymers. However, the performance of polymer based solar cells is quite low compared with those of their inorganic counterparts due to restricted charge transport and limited exciton diffusion lengths. [8].

Among conjugated polymers, poly-3,4-ethylenedioxythiophene is proven to be an excellent candidate for optoelectronic applications [9] and known as the blue component of ECD-based display devices [10,11]. Our previous study on the integration of benzotriazole moiety to PEDOT chains resulted in enhancement

of optical properties of the resultant polymer [11]. The contrast was improved (53%) compared with those of PEDOT (44%) with a much shorter switching time (1.1 s compared with 2.2 s for PEDOT) and higher coloration efficiency (211 cm²/C vs 183 cm²/C). Although the pendant alkyl chain on benzotriazole moiety provided high solubility to the monomer (4,7-bis(2,3-dihydrothieno [3,4-b] [1,4] dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] triazole (BEBT)), high electroactivity of the oligomers and the polymer resulted in the electrodeposition of insoluble chains on ITO. However, its chemical polymerization succeeded in the production of a soluble polymer. Here we highlight the photovoltaic and electrochromic device applications of PBEBT as the active layer. The ability to play with the structure of the active component will enable one to improve the performance of polymer/organic based devices compared with their inorganic counterparts.

2. Experimental

2.1. General

Propylene carbonate (PC), tetrabutylammonium hexafluorophosphate (TBAPF₆), poly(methylmethacrylate) (PMMA) and acetonitrile (AN; Merck) were purchased from Aldrich and used without further purification. BEBT was synthesized according to the reported procedure [11]. All electrochemical studies were performed under ambient conditions using a Voltalab 50

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potentiostat. Average molecular weights were determined by gel permeation chromatography (GPC) using a Polymer Laboratories GPC 220. All current–voltage (I – V) characteristics for the photovoltaic devices were measured using a Keithley SMU 236 under nitrogen in a dry glove box. A Steuernagel solar simulator, AM 1.5, was used as the excitation source with an input power of 100 mW/cm^2 white-light illumination, which was calibrated using a standard crystalline silicon diode. The solar cells were illuminated through the ITO side. The spectrally resolved photocurrent (IPCE) was measured with an EG&G Instruments 7260 lock-in amplifier. The samples were illuminated with monochromatic light (xenon). Fluorescence measurements were conducted using a Varian Eclipse spectrofluorometer. A Varian Cary 5000 UV–vis spectrophotometer was used to perform the spectroelectrochemical studies of the polymer.

2.2. Synthesis of poly 4,7-bis(2,3-dihydrothieno[3,4- b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo[d][1,2,3]triazole

200 mg BEBT was dissolved in 10 mL of CHCl_3 under argon atmosphere. FeCl_3 (227 mg) was suspended in 30 mL of nitromethane and slowly added to the monomer solution. The yellow solution slowly turned to light blue. The mixture was stirred for 15 min and then poured into 200 mL methanol. The precipitate was dissolved in CHCl_3 and extracted several times with water. The organic phase was evaporated and the residue was dissolved in 50 mL THF, 50 mL hydrazine monohydrate added and the mixture was stirred for 12 h, where during this period the solution turned to deep blue. THF was evaporated, chloroform was added to the residue and the organic phase was extracted with water. The solvent was evaporated and the residue was stirred in acetone overnight to remove unreacted monomers. The polymer was filtered and dried under vacuum to give PBEBT as a blue solid. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 7.90 (benzotriazole), 4.5 (O– CH_2), 4.6 (N– CH_2), 2.0–0.8 (pendant alkyl chain).

2.3. Preparation of the gel electrolyte

Gel electrolyte was prepared using TBAPF_6 :AN:PMMA:PC in the ratio of 3:70:7:20 by weight. After TBAPF_6 was dissolved in AN, PMMA was added to the solution. In order to dissolve PMMA, vigorous stirring and heating are required. Propylene carbonate (PC), as the plasticizer, was introduced into the reaction medium after all PMMA was completely dissolved. The mixture was stirred and heated until a highly conducting transparent gel electrolyte was produced [12].

3. Results and discussion

3.1. Synthesis

Synthesis of 4,7-bis(2,3-dihydrothieno[3,4- b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo[1,2,3] triazole (BEBT) was performed

according to the published procedure [11] Monomer, BEBT, was polymerized either electrochemically (ePBEBT) or chemically (cPBEBT; Scheme 1). However, the polymer was soluble only in the case of chemical polymerization. For electrochemical polymerization indium tin oxide coated glass slide (ITO) was used as the working electrode. The monomer was electrochemically deposited on ITO in a TBAPF_6 /AN solution. Iron (III) chloride (FeCl_3) in nitromethane:chloroform(1:1) mixture was used as the catalyst for chemical polymerization. The polymer was then reduced with hydrazine, precipitated in methanol and washed with acetone several times to remove the catalyst and the unreacted monomer. The GPC results are given in Table 1.

3.2. Construction of electrochromic and photovoltaic devices

Homopolymer of BEBT was utilized as the cathodically coloring material in a single layer device. As a result of electrochemical polymerization, ePBEBT was deposited on ITO (Delta Technologies, $7 \times 50 \times 0.7 \text{ mm}^3$) via cyclic voltammetry. ECD was built by arranging the polymer coated ITO and the free ITO facing each other separated by a gel electrolyte.

cPBEBT was used as the electron donor component in bulk heterojunction solar cells in combination with a soluble fullerene derivative, 1-(3-methoxycarbonyl)-propyl-1-1-phenyl-(6,6) C_{60} PCBM. Photovoltaic devices were prepared by spin coating (ca. 90 nm) the blend from a chlorobenzene (CB) solution on a PEDOT:PSS (polyethylenedioxythiophene:poly styrenesulfonate) coated ITO glass substrate. As the metal contact, Al was deposited under vacuum. It has been shown in the literature that solar cell efficiency can be enhanced by varying the polymer to PCBM ratio [13]. Thus, composition of the blends was varied as 1:1, 1:2, 1:3 and 1:4 (w:w, 5 mg cPBEBT:10 mg PCBM for 1:2). These blends containing active layer were spin cast from CB onto freshly prepared ITO/PEDOT:PSS substrates. Thicknesses of the active layers were measured by AFM data of the substrates (Table 2). The

Table 1

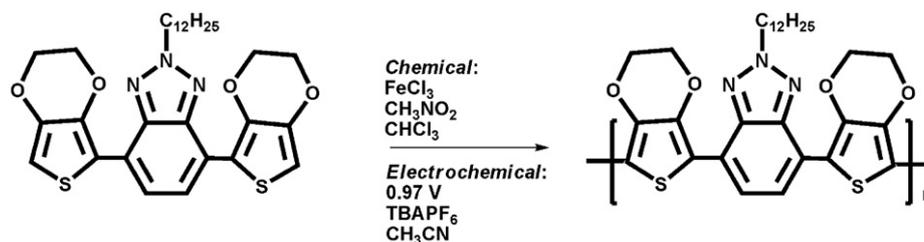
Average molecular weight of PBEBT calculated from GPC result.

Polymer	M_n (g/mol)	M_w (g/mol)	PDI	Avg. no. rep. un.
PBEBT	95,800	152,000	1.6	168

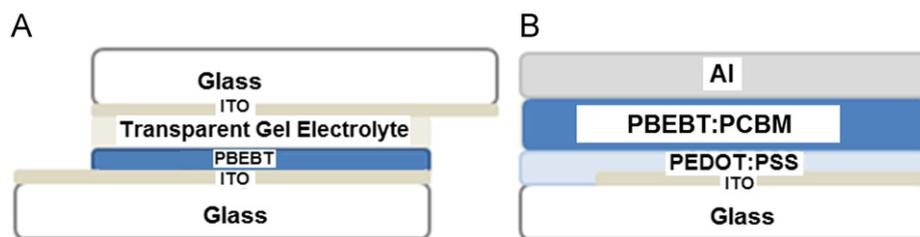
Table 2

Thicknesses of the active layers with varying PBEBT:PCBM ratios.

	Thickness (nm)
Pristine PBEBT	30
PBEBT:PCBM(1:1)	50
PBEBT:PCBM(1:2)	60
PBEBT:PCBM(1:3)	80
PBEBT:PCBM(1:4)	100



Scheme 1. Synthetic routes for ePBEBT and cPBEBT.



Scheme 2. Schematic representation of (A) electrochromic device (B) BHJ solar cell.

Table 3

HOMO, LUMO, electronic (E_g^{CV}) and optical (E_g^{UV}) band gap of the PBEBT.

	HOMO (eV)	LUMO (eV)	E_g^{CV} (eV)	E_g^{UV} (eV)
cPBEBT	-4.5	-3.3	1.2	1.6
ePBEBT	-4.7	-3.4	1.3	1.6

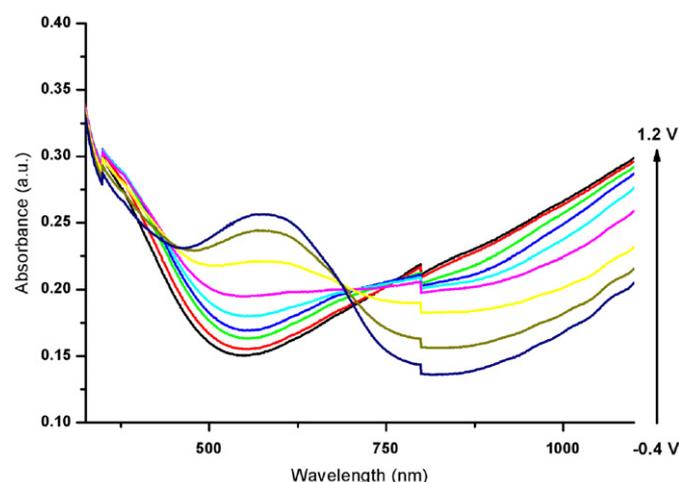


Fig. 1. Electronic absorption spectra for the device on doping in the range between -0.4 and 1.2 V.

configurations of the single layer device and BHJ solar cell are depicted in Scheme 2.

3.3. Cyclic voltammetry

According to the band theory, oxidation onset obtained from cyclic voltammetry (CV) revealed information on HOMO band energy. Also LUMO energy of the polymers can be obtained from the onset of reduction potential. The cyclic voltammogram of BEBT was taken according to a previous report using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) and 1×10^{-2} M BEBT solution while sweeping potentials between -0.5 V and +1.1 V (scan rate: 100 mV/s) vs Ag/AgCl reference electrode. CV of ePBEBT was studied in a monomer free TBAPF₆/AN solution in order to determine the redox properties.

Similar data for cPBEBT were obtained using 0.1 M TBAPF₆ in AN. Polymer was drop cast onto a Pt foil. Three-electrode cell consisting of Pt as the counter, ITO as the working electrode and a Ag/AgCl pseudo-reference electrode was used. Electrodes were calibrated with respect to Fc/Fc⁺. Assuming a value of -4.75 eV vs. vacuum level for the NHE, the band edges for the HOMO and the LUMO were estimated. The HOMO-LUMO values, electronic band gap and optical band gap of the polymer are summarized in Table 3. The difference between the electrochemical and optical

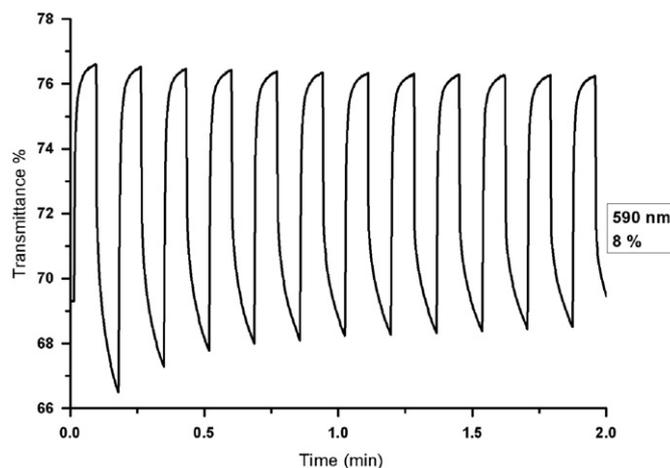


Fig. 2. Optical transmittance changes of ePBEBT device monitored at 590 nm while switching the potentials between the oxidized and reduced states.

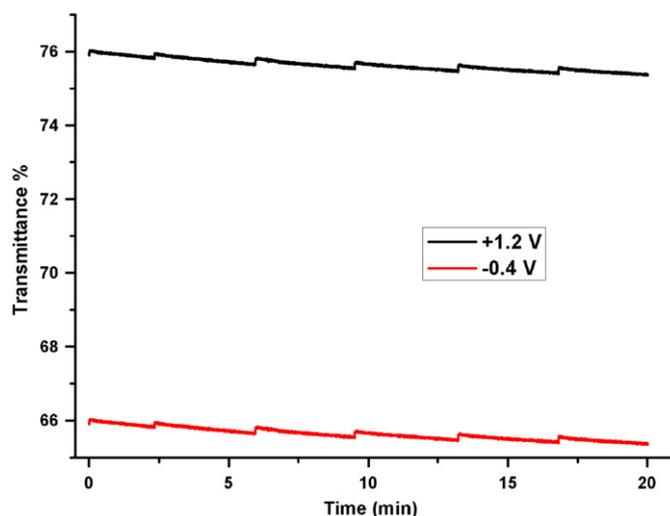


Fig. 3. Open circuit memory of an ePBEBT device monitored by single-wavelength absorption spectroscopy at 590 nm.

band gap can be attributed to the creation of free ions in the electrochemical experiment compared with the one measured through UV experiments, which refers to a neutral state [14].

3.4. Characterization of electrochromic device

3.4.1. Spectroelectrochemistry

We examined the changes in optical absorption of the polymer backbone using spectroelectrochemistry. Optical studies of

electrochromic devices were performed using a UV–vis spectrophotometer coupled to cyclic voltammetry. To observe the behavior on doping, BEBT was polymerized (as stated in the cyclic voltammetry section) and immersed into a monomer free solution containing AN and TBAPF₆ as the solvent–electrolyte couple. Optoelectrochemical spectra of the single layer device are

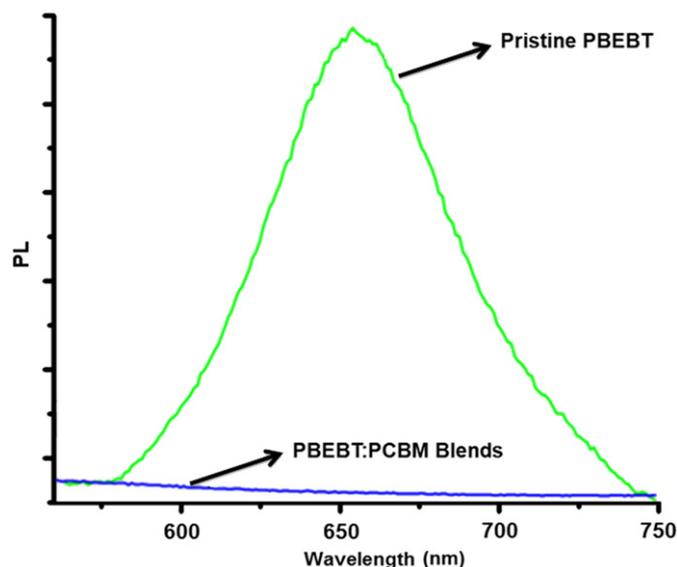


Fig. 4. PL quenching in cPBEET:PCBM blends.

shown in Fig. 1. Due to the $\pi \rightarrow \pi^*$ transition there is a maximum absorption at 590 nm, revealing a blue color in the neutral state of the device. On increasing the potential in oxidative direction, a gradual decrease was observed in the peak intensity at 590 nm, accompanied by an increase in absorption beyond 900 nm due to the formation of charge carriers (i.e. polaron bands). The disappearance of the absorption in the visible region at high potentials resulted in a transparent regime for the device.

3.4.2. Electrochromic switching

For electrochromic applications, the response time of the electrochromic devices is very significant. This is defined as the time required to perform a switching between the two states (oxidation and reduction). For this purpose double potential step chronoamperometry coupled with optical spectroscopy was carried out by stepping potentials between -0.4 and 1.2 V with a residence time of 5 s. During the switching studies the percent transmittance difference ($\Delta T\%$) at the wavelength of maximum contrast (590 nm) was measured. For the device, the maximum contrast at 590 nm was measured as 8% with a 2.4 s switching time (Fig. 2). The transparency of the device decreased with time since in this single layer device there is no anodically coloring counterpart. In electrochromic devices, while one part of the device gets oxidized (anodically coloring polymer), the other part gets reduced (cathodically coloring polymer), resulting in a color change. However, in single layer devices, since either the cathodically or the anodically coloring component reveals color, the ITO electrode itself gets either oxidized or reduced, which leads to a short life-time for an electrochromic device.

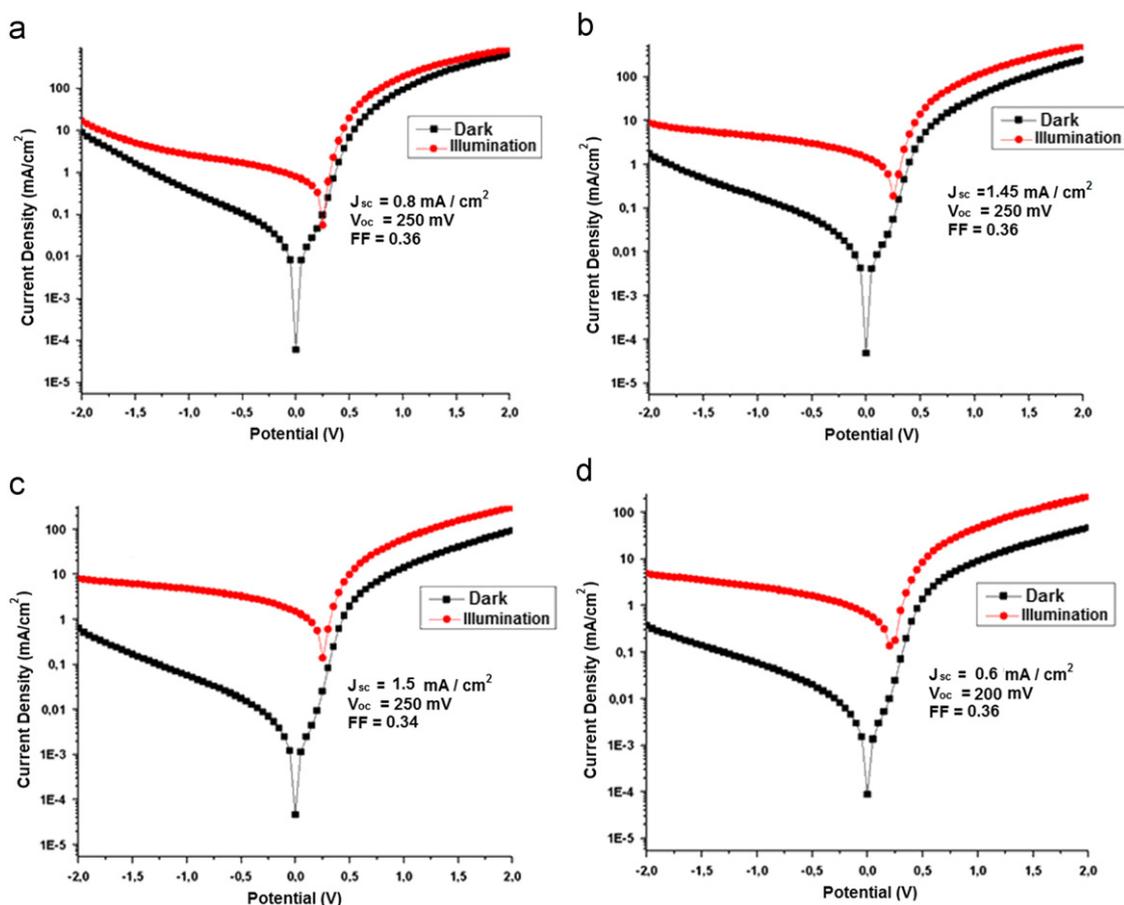


Fig. 5. Current–voltage (I – V) characteristics of solar cells. cPBEET/PCBM (w/w) blends: (a) 1:1, (b) 1:2, (c) 1:3 and (d) 1:4.

3.4.3. Open circuit memory of the ECD

The color persistence of an electrochromic device is also a significant feature since it is directly related with its practical use [15]. The optical memory of an electrochromic device is defined as the time where the material maintains its color without applying a potential [16]. A pulse (-0.4 or 1.2 V) for 1 s was applied and held in open circuit conditions for 200 s while transmittance change ($\Delta T\%$) was monitored as a function of time. Fig. 3 shows the optical spectrum of ePBEBT single layer device at 590 nm where the device retains its contrast up to 99% in 200 s at open circuit conditions.

3.5. Characterization of photovoltaic devices

In order to investigate true photoinduced charge transfer between the donor and acceptor moieties, photoluminescence quenching was studied. As shown in Fig. 4 blending cPBEBT and PCBM resulted in quenching of PL, which indicates the charge transport between cPBEBT and PCBM. [17]

cPBEBT was used as the p type material (electron donor) against [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) as the n type material (electron acceptor). The efficiency of solar cells is given by the product of open circuit voltage (V_{oc}), short-circuit current (J_{sc}) and fill factor FF. J_{sc} is determined by the light absorption ability of the material, charge-separation efficiency and carrier mobility as well as interfacial barriers.

Several solar cells were prepared using cPBEBT–PCBM blends. Performances of the cPBEBT:PCBM blends were evaluated as the possible donor–acceptor materials in organic BHJ solar cells. I – V characteristic curves in dark and illumination under simulated AM 1.5 are shown in Fig. 5. The short-circuit current (J_{sc}) reaches a maximum value of 1.5 mA/cm² when the blend ratio is 1:3.

Induced photon to current efficiency (IPCE) was determined to obtain information on charge generation and the number of photons with different energies that contributes to charge generation in the solar cell. This was done by comparing the spectral response of the solar cell and the optical absorption spectra of the components. Fig. 6 shows the IPCE obtained for 1:1, 1:2, 1:3 and 1:4 blends.

The % IPCE plot exhibits a maximum photocurrent contribution of 7% at around 450 nm. It is noted that the spectrum lies over a wide range of wavelength between 400 and 600 nm.

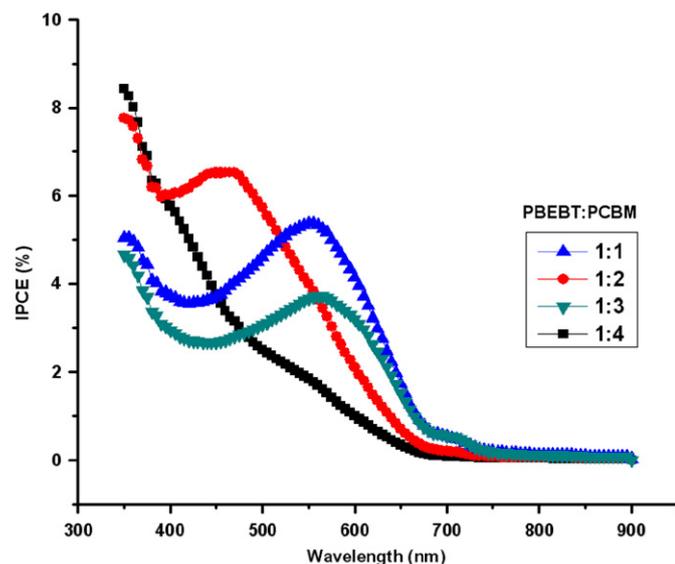


Fig. 6. IPCE spectra of the solar cells PBEBT:PCBM blends.

4. Conclusion

A donor acceptor donor type monomer, BEBT, was polymerized chemically and electrochemically. The resulting polymers, cPBEBT and ePBEBT, were exploited for solar cell and electrochromic device applications, respectively. Although the preliminary results regarding power conversion efficiency are not high, optimization of the conditions may lead to further research on such benzotriazole bearing materials in the near future. Although the photovoltaic results are low, they can be improved by optimization of parameters such as casting solvent and metal contacts.

Acknowledgments

The authors thank European Science Foundation (ESF, ORGANISOLAR Project), TUBA and GÜNAM for financial supports.

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