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Optical properties of Poly-[2-methoxy-5-(2-ethyl-hexyloxy)-phenylene vinylene and its application in photovoltaic cells

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ABSTRACT

A conjugated polymer poly[2-methoxy-5-(2-ethyl-hexyloxy)-phenylene vinylene] (MEH-PPV) exhibits unique absorption band in the visible region due to electron transitions between non-localized bands and emits light in three different wavelength regions. Doping of iodine increases absorption in the visible region of polymer. MEH-PPV is used as a hole-conductor and a sensitizer in titana based solid-state photovoltaic cells. Maximum photocurrent of 1.3 $mAcm^{-2}$ and voltage of about 543 mV are observed for a photovoltaic cell with the polymer sensitizing layer. However, slightly higher photocurrent (2.4 $mAcm^{-2}$) with a decrement of voltage (465 mV) is observed for a solid-state cell with a configuration of TiO_2|dye|MEH-PPV|I_2, under AM 1.5 conditions. Incident light to power conversion efficiency of these cells is about 0.6 %.

1. INTRODUCTION

Conjugated polymers have aroused blooming attraction due to their peculiar properties of higher absorption co-efficient, luminescent and sufficiently fast carrier mobility. For examples, poly phenylene vinylene (PPV) and its derivatives exhibit luminescence at red region of the visible spectrum [1,2]. An efficient separation of excitons is observed in combination of MEH-PPV with a material which has low electron affinity function [3]. In

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addition, sufficient fast hole conductivity is observed in MEH-PPV [4,5]. These properties suggest capability of utilization of PPV and its derivatives in solid-state devices. We have made an attempt to utilize MEH-PPV as a sensitizer and a hole-conductor, in titana based photovoltaic cells. Photo-properties of TiO_2|MEH-PPV|electrolyte and TiO_2|dye|MEH-PPV|I_2|graphite cells are studied and our primary observations are discussed.

2. EXPERIMENTAL

Meso-porous TiO_2 films with thickness of ~ 10 μm were prepared by applying a colloidal solution of hydrolyzed titanium isopropoxide which contains TiO_2 powder (P-25 Degussa, Japan) on preheated conducting glass plates (FTO) as descried elsewhere [6].

2.1. Fabrication of photo-voltaic cells with MEH-PPV sensitizing layer

MEH-PPV was embedded in porous matrix of TiO_2 by a slow solvent evaporation technique. MEH-PPV in $CHCl_3$ was used as the coating solution. TiO_2|MEH-PPV electrodes were allowed to dry at room temperature. An FTO electrode was attached to TiO_2|MEH-PPV electrode as the counter electrode. The electrolyte was spread in between two electrodes by capillary action. Standard $I^-|I_3^-$ (E_o = 0.53 V vs NHE, [7]) redox-couple in acetonitrile was used as the electrolyte.

2.2. Fabrication of photo-voltaic cells with MEH-PPV hole-conducting layer

Dye [cis dithiocyanate-bis (2,2′-bipyridyl 4, 4′-dicarboxylate) ruthenium (II)] (hereafter abbreviated as N3) was coated on dried TiO_2 electrodes by dipping in a dye solution of $3x10^{-3}$ M, (in ethanol at 40ºC). Dye coated TiO_2 electrodes were dried in a hot air stream followed by washing with ethanol. A thin layer of MEH-PPV was coated on sensitized TiO_2 films as described in the previous section. TiO_2|N3|MEH-PPV electrodes were allowed to dry at room temperature and then a thin layer of graphite was applied on the MEH-PPV layer followed by doping of iodine in the polymer film. An FTO electrode was attached to the graphite surface as the back contact of the cell. Cells were characterized under illumination of monochromatic and polychromatic light (100 mWcm^{-2}).
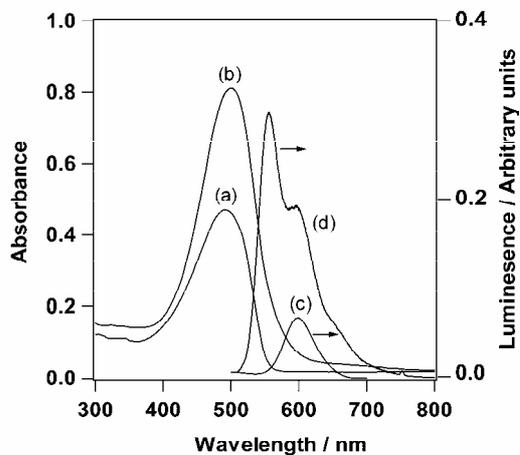
Fig. 1 Absorption spectrum of a MEH-PPV solution in chloroform (a) as obtained (without iodine treatment, 10^{-3} M), (b) after doping iodine in same solution, and emission spectra for MEH-PPV in chloroform different concentrations (c) 10^{-3} M and (d) 10^{-5} M

3. RESULTS AND DISCUSSION

MEH-PPV absorbs visible light in the wavelength region of 400-575 nm with an optimal at 500 nm (curve a, Fig. 1). Electron transitions between non-localized bands ($\pi \rightarrow \pi^*$) are responsible for this unique absorption band [8,9]. The onset of absorption mimics that band gap of MEH-PPV is 2.2 eV. This value agrees with Daoud et al′s observations [5]. A clear enhancement of absorbance is observed by doping iodine in the polymer (curve b). Almost similar shapes in absorption spectra reveal that light doping does not make any significant influence in disordering of polymer chain. Similar result has been observed by introducing polystyrene in MEH-PPV [9]. It is known that MEH-PPV exhibits a strong emission band in the red portion of the visible spectrum. Luminescence spectrum of a solution of MEH-PPV (10^{-3} M) is also shown in Fig. 1 (curve c). This luminescence band is associated with single-chain excitons [10]. In addition, two other emission bands (with maxima at 550 and 660 nm) are observed by diluting the stock solution (10^{-3} M) from CHCl$_3$ (curve d). Luminescence band with the maximum at 550 nm is associated with reduction of interaction between adjacent chains caused due to diluting effect [11]. Vibrational modes are responsible for the remaining band at 660 nm [12]. Only this luminescence band is slightly red shifted compared to previously reported luminescence bands by Yan *et al* and Lui *et al* [10,13]. Excimer species in the polymer are responsible for this red shift [9].
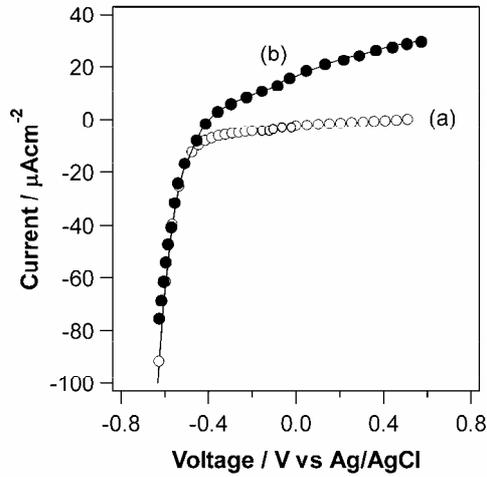
Fig. 2. Current voltage characteristics of a MEH-PPV|TiO$_2$ electrode (a) at dark and (b) under illumination, in aqueous poly-iodide electrolyte (I$^-$:I$_2$=10^5:1), under three electrode configuration
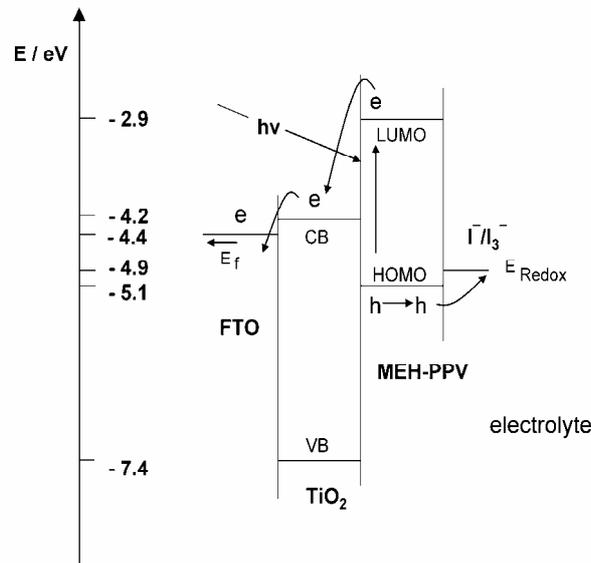

Fig. 3. Band diagram of MEH-PPV|TiO$_2$|FTO electrode in polyiodide electrolyte under illumination with flat band concept. Where E$_f$– Fermi Level of FTO, HOMO – highest occupied level of polymer, LUMO – lowest occupied level of polymer, CB – Conduction band of TiO$_2$, VB –Valance band of TiO$_2$ and E$_{redox}$ – redox potential of poly iodide electrolyte

3.1. Characteristics of photo-voltaic cells with MEH-PPV as a sensitizer

A feeble cathodic photocurrent was observed on MEH-PPV|FTO electrode, under illumination. Localization of pseudo Fermi level of MEH-PPV close to the ionization
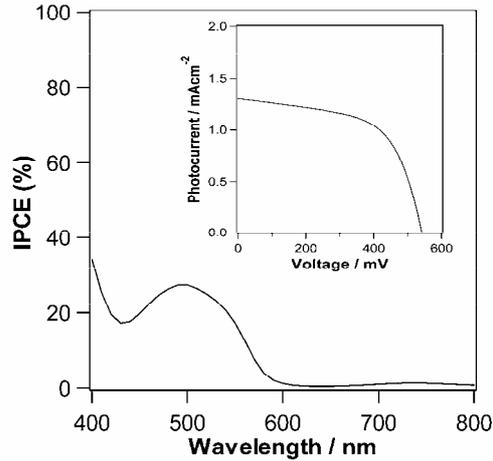
32

Fig. 4 IPCE spectrum of TiO$_2$|MEH-PPV|polyiodide cell, Insert shows the current voltage characteristics of the same cell, light intensity is maintained as 100 mWm^{-2}, at the electrode surface

potential (energy of HOMO level) is a reason for the generation of a cathodic photocurrent on MEH-PPV|FTO electrode [3,14]. It seems that the photocurrent generation takes place at polymer|electrolyte interface for MEH-PPV films and the photo-generated electrons tunnel into the electrolyte while the holes migrate toward the back contact of the electrode. However, MEH-PPV|TiO$_2$ electrodes exhibit anodic sensitized photocurrent (Fig. 2). This result indicates that charge separation takes place at polymer|TiO$_2$ interface and electrons are injected into lower lying conduction band of TiO$_2$ and holes migrate toward the polymer|electrolyte interface, under illumination. The LUMO level of MEH-PPV lies at a higher energy level than the conduction band of TiO$_2$. Therefore, the charge injection form LUMO level to the conduction band of TiO$_2$ is thermodynamically allowed [3]. The mechanism of charge generation of the MEH-PPV|TiO$_2$ electrode is energetically illustrated in Fig. 3, using flat band concept. Values of work functions of TiO$_2$, MEH-PPV, FTO and redox potential of I$^-$/I$_3^-$ are adopted from literature [4,15,7]. A significant enhancement in the photocurrent is observed when electrolyte sandwiches in between MEH-PPV|TiO$_2$ and FTO electrodes. Incident-photon-to-current conversion efficiency (IPCE) of such a TiO$_2$|MEH-PPV|I$^-$/I$_3^-$ cell is shown in Fig. 4. Close resemblance absorption spectrum (curve a, Fig. 1) with IPCE spectrum in the visible region implies that the charge generation is by MEH-PPV in the cell. The maximum incident photon-to-current conversion efficiency (IPCE) of the cell is evaluated as 30% at 550 nm. The decrease of IPCE of the in wavelength region 490-425 nm is attributed to the difference in the excitation depth profiles in the polymer layer [3]. The gradual increase of IPCE in shorter wavelengths than 425 nm is attributed to the band gap excitation of TiO$_2$. An

efficient recombination of photo-generated carriers via radioactive processors (intersection of absorbance and emission spectra of MEH-PPV, Fig. 1) could be one of the reasons for observed lower conversion efficiency of the cell. Non radioactive processors also decrease performance of the cell. Current-voltage characteristics of $TiO_2|MEH$-$PPV|I^-/I_3^-$ cell are also shown in the inset of the Fig. 4. The maximum short circuit photocurrent of 1.3 mAcm^{-2} and open circuit voltage of about 543 mV are observed for this cell, under AM 1.5 conditions.
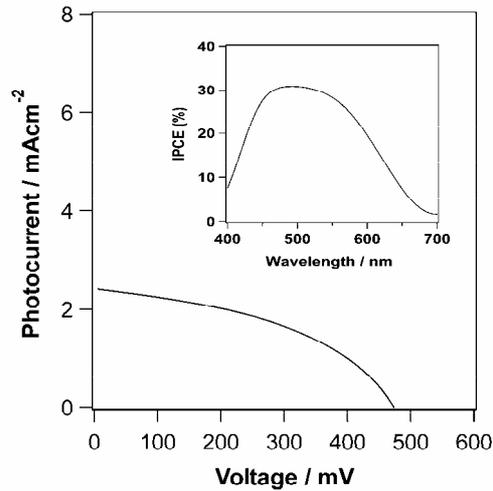

Fig. 5   Current voltage characteristics of $TiO_2|N3|MEH$-$PPV|I_2|$graphite cell under illumination of 100 mWm^{-2}. Insert shows the IPCE spectrum of $TiO_2|N3|MEH$-$PPV|I_2|$graphite cell

3.2. Characteristics of photo-voltaic cells with MEH-PPV as a hole conductor

Negligible photo-properties are observed in solid-state $TiO_2|N3|MEH$-PPV device, under illumination. However, significant enhancement in the photo-voltage is observed after exposing electrodes to iodine vapor. The resulted current is rather low and has to be improved by several fractions. It is known that applying a thin layer of graphite on polymer layer increases the electron collection efficiency of the cell toward the FTO layer [16]. Therefore, a thin layer of graphite was applied on the electrode followed by doping iodine. As expected, an enhancement was observed in the photocurrent. Current-voltage characteristic of the $TiO_2|N3|MEH$-$PPV|I_2|$graphite cell is shown in the Fig.5. A maximum open circuit photovoltage of 465 mV is obtained for the cell. This value is close to 0.4 of attainable maximum photovoltage by this device. Maximum photovoltage of $TiO_2|N3|MEH$-$PPV|I_2|$graphite cell is determined from the energy difference of the conduction band of TiO_2 and HOMO level of the polymer [3]. $TiO_2|N3|MEH$-$PPV|I_2|$graphite cell exhibited maximum photocurrent of 2.4 mAcm^{-2} under AM 1.5

34

conditions. However, thickness of the MEH-PPV film was maintained not to exceed the excitation diffusion length, since this type of cells produces much higher performance when thickness of the film is equal to the magnitude of diffusion length [5]. A drastic decrement in the photocurrent of about 75% was observed in the first 20 seconds in the absence of MEH-PPV film in the cell. This result suggests that enrolment of MEH-PPV layer as an efficient electron donor in the regeneration of dye molecules. However, $TiO_2|N3|MEH-PPV|I_2|graphite$ cell produces moderate photo-performance compared to other dye sensitized systems [6] and much higher performance than other solar cells composed of polymer hole-conducting layer [17]. Photo-properties of hetero-junctions made of polymer-TiO_2 composites or blends have been reported. In these studies, MEH-PPV and other polymers have been used as light harvesting analog or hole conductor it self [3,4]. However, we have not observed any significant performance in the cell in the absence of a sensitizer. It seems that the charge generation of this device takes place via injection of excited dye molecules. $TiO_2|N3|MEH-PPV|I_2|graphite$ cell exhibits maximum IPCE of 35% at 500 nm (inset of Fig. 5). Fig. 6 illustrates the electron-transfer process of $TiO_2|N3|MEH-PPV|I_2|graphite$ cell. Photo-performance of the cell could be further improved by increasing conductivity of the polymer.
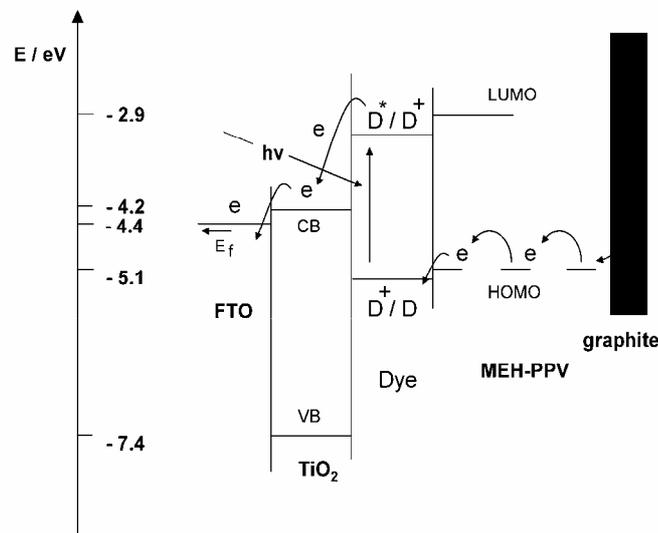

Fig. 6   Electron-transfer process of $TiO_2|N3|MEH-PPV|I_2|graphite$ cell where E_f – Fermi Level of FTO, HOMO – highest occupied level of polymer, LUMO – lowest occupied level of polymer, CB – Conduction band of TiO_2, VB –Valance band of TiO_2, D- ground state of dye molecule, D*- excited state of dye molecule, D^+- dye cation

4. CONCLUSIONS

Poly [2-methoxy-5-(2-ethyl-hexyloxy)-p-phenylene vinylene] exhibits three luminescence bands in the visible region due to electron transitions in between non-localized bands, and interchain - intrachain interaction. Intrinsic and sensitized photocurrent generations are observed in MEH-PPV films when in absence and in contact with titana film. Doping of iodine slight in MEH-PPV was found to increases the conductivity and the absorbance of polymer. Maximum short circuit photocurrent of 2.4 mAcm^{-2} and open circuit voltage of about 543 mV were observed for photovoltaic cells fabricated by using MEH-PPV as a sensitizer and hole-conductor, respectively.

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