Emission from Charge-Transfer States in Bulk Heterojunction Organic Photovoltaic Cells Based on Ethylenedioxythiophene-Fluorene Polymers

TAKESHI YASUDA[1,*], JUNPEI KUWABARA[2], LIYUAN HAN[1], AND TAKAKI KANBARA[2]

[1]Photovoltaic Materials Unit, National Institute for Materials Science (NIMS), Japan

[2]Tsukuba Research Center for Interdisciplinary Materials Science (TIMS) and Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan

*Address correspondence to T. Yasuda, Photovoltaic Materials Unit, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, 305-0047, Japan, Tel.: +81-29-859-2850, Fax: +81-29-859-2101, E-mail: YASUDA.Takeshi@nims.go.jp

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ABSTRACT

We investigated the electroluminescence (EL) from charge-transfer (CT) in the interface state of PEDOTF/PC$_{70}$BM, known to be empirically related to V_{oc}, to elucidate a difference in V_{oc} of 0.24 V in bulk heterojunction (BHJ) organic photovoltaic cells (OPVs) based on two polymers (H-PEDOTF and S-PEDOTF with a high and low molecular weight, respectively)

having almost the same HOMO energy levels. The difference in the energies of CT EL peaks is relatively small (0.06 eV) compared to the difference in the V_{oc}s. Consequently, we mainly attribute the excessive loss of V_{oc} in S-PEDOTF-based OPVs to a trap assisted recombination mechanism.

Keywords bulk heterojunction; organic; photovoltaic; polymer; electroluminescence

INTRODUCTION

Power conversion efficiency (PCE) of bulk heterojunction (BHJ) organic photovoltaic cells (OPVs) has markedly improved in recent years [1-5]. The open-circuit voltage (V_{oc}) is one of the important parameters that determines the PCE. It is widely believed that the V_{oc} correlates well with the energy difference between the lowest unoccupied molecular orbital (LUMO) of the acceptor and highest occupied molecular orbital (HOMO) of the donor. Lowering the HOMO energy levels of the donor has been regarded as an effective way to increase V_{oc} [6,7]. In contrast, in a previous study, we found BHJ OPVs based on two alternating conjugated polymers consisting of ethylenedioxythiophene and fluorene (PEDOTF), shown in Fig. 1(a), with almost identical HOMO energy levels of –5.2 eV exhibited significantly different V_{oc}s: V_{oc} of 0.83 V for H-PEDOTF with a high molecular weight and 0.59 V for S-PEDOTF with a low molecular weight [8]. In the present study, to elucidate the difference of V_{oc}s in these BHJ OPVs in detail, we investigated the electroluminescence (EL) from charge-transfer (CT)

states between the HOMO of PEDOTF (donor) and the LUMO of $PC_{70}BM$ (acceptor), which is directly related to V_{oc}s [9]. Figure 1(b) shows the conceptual energy diagram of this study.

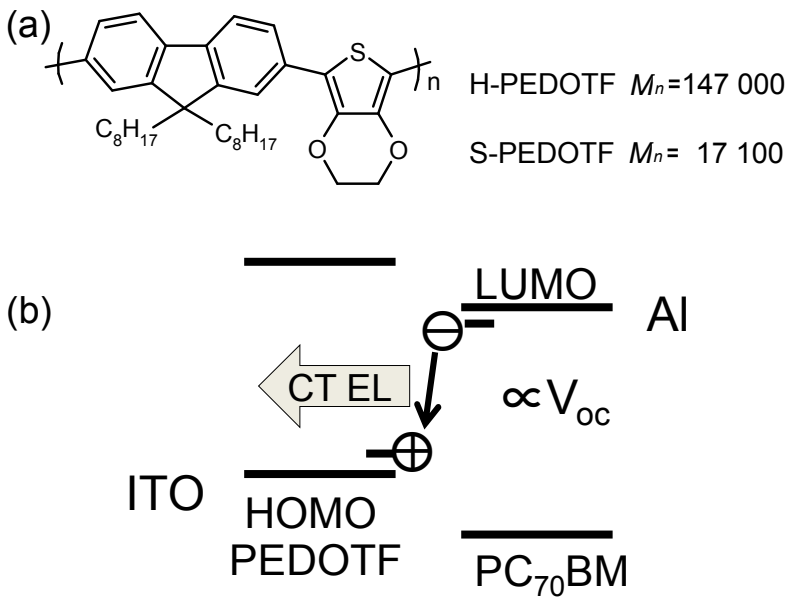

FIGURE 1 (a) Chemical structure of PEDOTF. H-PEDOTF with M_n of 147,000 prepared via direct C-H arylation and S-PEDOTF with M_n of 17,100 prepared via the Suzuki-Miyaura cross-coupling reaction. (b) Conceptual energy diagram of this study.

EXPERIMENTAL

Two kinds of PEDOTF were prepared – H-PEDOTF via dehydrohalogenative cross-coupling reaction (so-called direct C-H arylation [10,11]) and S-PEDOTF via the Suzuki-Miyaura cross-coupling reaction [8]. The resultant H-PEDOTF polymer had a higher number-average molecular weight (M_n) of 147,000 compared to S-PEDOTF with a M_n of 17,100.

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS P VP AI 4083) was purchased from Heraeus. [6,6]-Phenyl C71 butyric acid methyl ester ($PC_{70}BM$) (purity 99%) was purchased from Solenne. The HOMO energy levels of the materials were estimated using photoelectron yield spectroscopy (PYS) with an AC-3 spectrometer (Riken Keiki).

The OPV cells were fabricated in the following configuration: ITO/PEDOT:PSS/BHJ layer/LiF/Al. The patterned indium tin oxide (ITO) glass (conductivity: 10 Ω/square) was pre-cleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin-coated onto the ITO at 3000 rpm and air-dried at 110°C for 10 min on a hot plate. The substrate was then transferred to a N_2-filled glove box where it was re-dried at 110°C for 10 min on a hot plate. An *o*-dichlorobenzene solution of the PEDOTF and $PC_{70}BM$ blended in a 1:4 weight ratio was subsequently spin-coated onto the PEDOT:PSS surface to form the BHJ layer. The substrates with the BHJ layers were dried for 10 min at 110°C. LiF (1 nm) and Al (80 nm) were then deposited onto the active layer with conventional thermal evaporation at a chamber pressure lower than 5×10^{-4} Pa, which provided the devices with an active area of 2×2 mm^2. The current density–voltage (*J*-*V*) curves were measured using an ADCMT 6244 DC voltage current source/monitor under AM 1.5G solar-simulated light irradiation of 100 mW cm^{-2} (OTENTO-SUN III, Bunkoh-Keiki Co., Ltd.).

Organic light-emitting diodes (OLEDs) were fabricated in the following configuration: ITO/PEDOT:PSS/light emitting (PEDOTF or $PC_{70}BM$ or BHJ) layer/LiF/Al. The fabrication method of OLEDs is the same as that of BHJ OPVs with the exception of the spin-coated $PC_{70}BM$ layer; a chloroform solution of $PC_{70}BM$ was subsequently spin-coated onto the PEDOT:PSS. By applying a positive bias voltage to the ITO electrode with respect to Al, electrons from Al and holes from ITO can be injected into OLEDs or BHJ OPVs. The resultant EL spectra from OLEDs or BHJ OPVs were measured using an array spectrometer (MCPD-9800-311C, Otsuka Electronics Co, Ltd.). The spectrometer was calibrated in wavelength and intensity.

TABLE 1 Photovoltaic parameters for BHJ OPV based on PEDOTF:$PC_{70}BM$(1:4), HOMO energy levels, hole mobility values cited from Ref. 8, and calculated values of V_{oc}.

Polymer	PCE (%)	J_{sc} ($mAcm^{-2}$)	FF	V_{oc} (V)	HOMO (eV)	Hole mobility ($cm^2V^{-1}s^{-1}$)[a]	Cal. V_{oc} (V)[b]
H-PEDOTF	4.08	9.41	0.52	0.83	−5.19	1.2×10^{-3}	0.77
S-PEDOTF	0.48	2.58	0.31	0.59	−5.26	3.2×10^{-5}	0.71

[a] Estimated from the measurement of field-effect transistors

[b] Calculated from the empirical equation, V_{oc} = CT EL peak energy/e − 0.4 V [9]

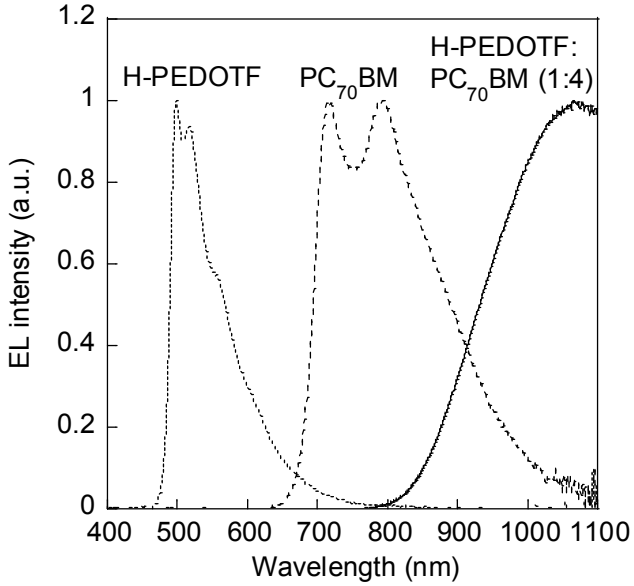

FIGURE 2 EL spectra from OLEDs with H-PEDOTF, $PC_{70}BM$, and the H-PEDOTF:$PC_{70}BM$ (1:4) blended (BHJ) layer.

RESULTS AND DISSCUSION

The reported BHJ OPV performance characteristics, including short circuit current density (J_{sc}), V_{oc}, fill factor (FF), and PCE under AM 1.5G illumination of 100 $mWcm^{-2}$ are listed in Table 1. The V_{oc} in OPVs based on S-PEDOTF (HOMO of –5.26 eV) should be higher than that for OPVs based on H-PEDOTF (HOMO of –5.19 eV), as V_{oc} in BHJ OPVs using $PC_{70}BM$ as an acceptor is mainly determined by the energy difference between the LUMO level of $PC_{70}BM$ (−3.76 eV) [12] and the HOMO level of polymers [6,7]. However, the experimental value of V_{oc} (0.59 V) for the S-PEDOTF-based OPV was lower than that for the H-PEDOTF-based OPV (0.83 V). To understand the origin of this discrepancy in the

experimentally observed V_{oc} values in detail, EL spectra from CT states between the HOMO level of PEDOTFs and LUMO level of $PC_{70}BM$ in BHJ OPVs were measured. The peak energy in the CT EL spectrum is known to have an empirical relationship with V_{oc} expressed as V_{oc} = EL peak energy/e − 0.4 V [9]. Figure 2 shows EL spectra from OLEDs with each single component layer and the PEDOTF:$PC_{70}BM$ blended (BHJ) layer. Three completely different EL spectra are observed in the figure. Hence, we can conclude that EL spectra from the BHJ layer originate from the CT emission in the PEDOTF/$PC_{70}BM$ interface. The observed CT EL peaks were at 1063 nm (1.17 eV) for H-PEDOTF:$PC_{70}BM$ (1:4) and at 1114 nm (1.11 eV) for S-PEDOTF:$PC_{70}BM$ (1:4) as shown in Fig.3. Using the empirical equation mentioned above, the calculated values of V_{oc} are 0.77 V for H-PEDOTF:$PC_{70}BM$ and 0.71 V for S-PEDOTF:$PC_{70}BM$. The difference in the V_{oc} estimated from the empirical equation (0.06 V) is relatively small compared to that estimated from the experimental J-V curves (0.24 V). This result indicates that the S-PEDOTF-based OPV has an excessive V_{oc} loss, compared to H-PEDOTF-based OPV.

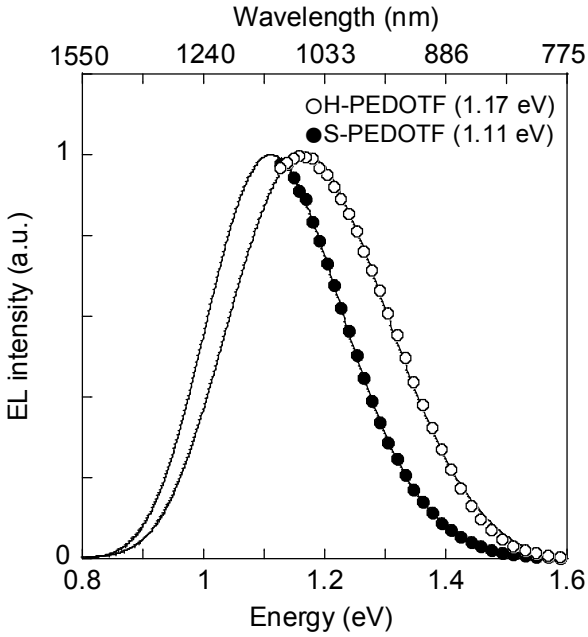

FIGURE 3 CT ET spectra from the BHJ layers of H-PEDOTF:$PC_{70}BM$ and S-PEDOTF:$PC_{70}BM$ (1:4). The values shown in parentheses are the energies of CT EL peaks. The solid lines are Gaussian fitted curves of obtained CT EL spectra.

Two potential factors responsible for the observed difference between the experimentally estimated and calculated V_{oc} values could be as follows: (I) the morphology of the BHJ layer with insufficient percolation path for electrons or holes in the S-PEDOTF-based OPV and (II) the low hole mobility of S-PEDOTF. In our previous study, we found film morphologies for both OPVs based on S- and H-PEDOTF were similar despite significantly different M_n [8]. This rules out the morphology of the BHJ layers as a possible contributing factor for the observed difference in V_{oc}. The hole mobility of S-PEDOTF was reported to be about two orders of magnitude lower than that of H-PEDOTF, i.e., 3.2×10^{-5} $cm^2V^{-1}s^{-1}$ and 1.2×10^{-3} $cm^2V^{-1}s^{-1}$, respectively [8]. The low M_n of S-PEDOTF may contribute to the low mobility

owing to the presence of a high level of terminal units, which are regarded as defects in polymer semiconducting materials. Such defects can also act as traps that increase the probability of charge recombination, leading to reduced values of V_{oc} [13,14]. The present findings suggest that the loss of V_{oc} in S-PEDOTF-based OPVs is potentially due to a trap assisted recombination mechanism rather than the interfacial state of S-PEDOTF/$PC_{70}BM$.

CONCLUSION

By analyzing CT EL spectra from BHJ OPVs based on H-PEDOTF and S-PEDOTF, we investigated the difference in V_{oc}s of these OPVs. We found that a trap assisted recombination mechanism is the most likely origin of the excessive loss of V_{oc} in S-PEDOTF-based OPVs as opposed to any contribution from the interface state of S-PEDOTF/$PC_{70}BM$. We believe that the analysis of CT EL spectra from BHJ OPVs is a powerful tool to evaluate the accuracy of the value of V_{oc} in BHJ OPVs.

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