

## Study of surface photovoltage spectra of MEH-PPV

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### Abstract

Surface photovoltage spectra studies are performed on thin films of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] in order to determine its photoelectric properties. We find that a localized subgap electronic transition causes the photovoltaic response with polarity opposite to that from the band-to-band electronic transition ( $\pi-\pi^*$ ). This transition is from the valence band to a local state in the conduction band. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** MEH-PPV; Surface photovoltage; Local state; Electron transition

### 1. Introduction

Light-emitting diodes fabricated with poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) have attracted attention due to its potential for use in display technology [1], photocells [2,3] and lasers [4]. As kind of poly(1,4-phenylene vinylene) (PPV) derivative (Fig. 1), MEH-PPV exhibits an external quantum efficiency for electroluminescence of  $\sim 1\%$  photons/electrons (ph/el) under forward bias and a quantum yield of  $>10\%$  electrons/photons (el/ph) under reverse bias [1]. In comparison with PPV, MEH-PPV is soluble in common organic solvents, thereby enabling relatively simple device fabrication by processing the active layer from solution with no subsequent processing or heat treatment required [1–5]. MEH-PPV can be used as the active element in a light-emitting diode with a sandwich device configuration of AL/MEH-PPV/ITO. The same device, under reverse bias, exhibits excellent sensitivity as a photodiode.

MEH-PPV is one of the family of conjugated polymers; these quasi-one-dimensional conjugated polymers have relatively broad  $\pi$  (valence) and  $\pi^*$  (conduction) bands, and they can be doped, with resulting properties that span the full range from insulator to metal [6]. MEH-PPV is a weak donor (as are many other conjugated polymers) which can be oxidized with relative ease [7].

Extensive studies of the EL and PL from spin-cast films of MEH-PPV reveal the result of the radiative decay of the self-localized intra-chain exciton (alternatively described as a neutral bipolaron) formed by the recombination of a negative polaron with a positive one [8]. It has been found that the luminescence efficiency can increase significantly by introducing local state that can act as an exciton trap and reduce motion to quenching sites, by synthesizing copolymers that have regions of different  $\pi-\pi^*$  gap within a single chain [9]. We consider that the existing local states (trap levels) play a key role in radiative efficiency. In other words, states localized on the molecular units produce a sequence of excited states in which positive and negative charges can be separated further at higher energies, as the mobility and lifetime of the photoexcited carriers are dominated by the effective radiation or quenching.

To study the possible localized states in photoexcited MEH-PPV, we use the surface photovoltage spectra technique. A localized transition is found which is assigned to an electronic transition from the valence band to a localized state in the conducting band.

### 2. Experimental details

#### 2.1. Preparation of MEH-PPV thin films

MEH-PPV was synthesized in this laboratory according to

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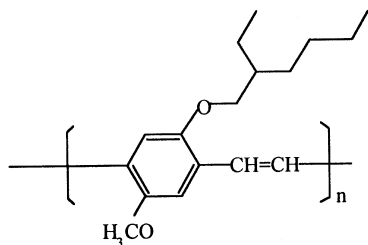


Fig. 1. Structure of MEH-PPV.

the reported method [10]. Polymer films were fabricated by spin casting MEH-PPV from a tetrahydrofuran (THF) solution. Films spin-cast from THF showed lower pump-energy thresholds for gain narrowing and narrower widths above threshold than films spin-cast from other solvents, such as chlorobenzene (CB) or P-xylene [11]. The MEH-PPV thin film was homogeneous and dense showing a orange–red color.

**2.2. Special measurements**

Surface photovoltage spectra were measured with a surface photovoltage spectrometer. ITO were used as the transparent front or back electrodes. Field-induced surface photovoltage spectra were obtained with the aid of a DC bias applied to the two sides of the sample cell. To avoid a possible dielectric breakdown, a contactless measurement method was used, in which a thin insulator layer was sandwiched between the film and the back ITO electrode. When the external electric field was directed from the bulk to the ITO electrode, the applied bias was called positive [12].

### 3. Results and discussion

#### 3.1. Photoinduced charge separation properties of MEH-PPV thin films

Surface photovoltage spectroscopy (SPS) is based on the

detection and measurement of changes of the surface electric charge induced by incident light [13,14]. Different from optical absorption spectroscopy, it can distinguish localized photoexcited electronic transitions from the delocalized ones, by changes of the surface potential of the measured sample caused by illumination [12]. Fig. 1 shows the surface photovoltage spectrum of MEH-PPV thin film. The photovoltage response curve ranged from 300 to 600 nm, their threshold value of transition energy is about 580 nm, therefore it can be assigned to the band-to-band transition, i.e. photoinduced electronic transition from the bonding  $\pi$  orbital to the antibonding  $\pi^*$  orbital. The dominant electronic excitation created by photoexcitation across the  $\pi$ – $\pi^*$  energy gap is a singlet exciton that can execute a random walk among the chain segments.

Surface photovoltage measures the change of the surface potential of the sample on illumination. The surface potential arises from charge population in the space charge region (SCR), so the surface photovoltage gives information about the change of charge population in SCR [12].

In Fig. 2, the surface photovoltage response shows a broad band, so we obtained external field-induced surface photovoltage spectra of the MEH-PPV thin film in order to distinguish the localized photoexcited electronic transition from the delocalized one.

#### 3.2. Field-induced surface photovoltage spectra and the determination of a local state

Surface photovoltage results from the separation of photoinduced electron-hole pairs which results in the change of charge population in SCR. Under the built-in electric field, the minority carriers move towards the surface, and the majority carriers towards bulk. For the band-to-band transition, the application of the external electric field changes the strength of the built-in field and the

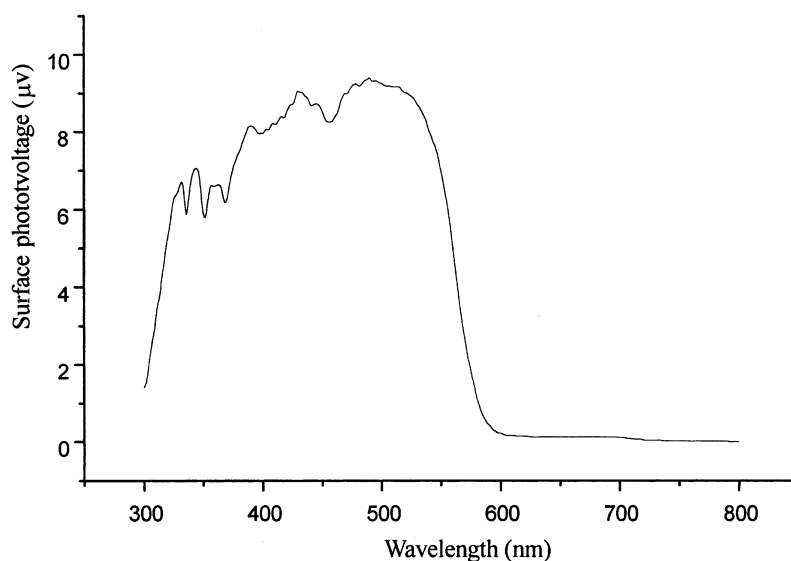


Fig. 2. Surface photovoltage spectrum of the MEH-PPV thin film.

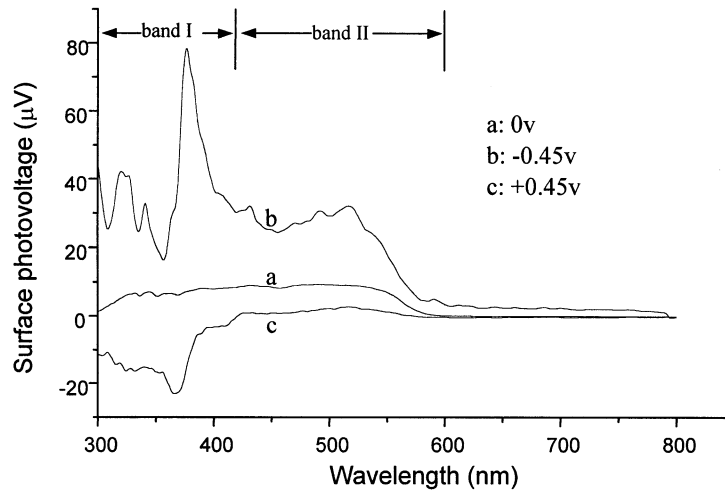


Fig. 3. External field-induced surface photovoltage spectra of the MEH-PPV thin film.

separation efficiency of photoinduced electron-hole pairs, leading to the change in surface photovoltage. When the external field is in the direction of the built-in field, the latter is enhanced. Consequently, the value of surface photovoltage is positive and increased. Alternatively, when the external field is in the direction opposite to the built-in field, and the latter is reduced, the value of surface photovoltage is negative and increased. Therefore, field-induced surface photovoltage can be used to determine the direction of the built-in field and the mobile direction of photoinduced carriers. On the other hand, because of the different influence of the external field on the mobile direction and diffusive distance of the delocalized and localized photoinduced carriers, the corresponding photovoltaic responses will change in different ways. Thus, with the help of the external field, the photoinduced charge transfer process can be detected clearly [12].

Fig. 3 shows the field-induced surface photovoltaic responses of a MEH-PPV thin film. The photovoltage response curve can be divided into two regions with variation of strength: band I ranged from 350 to 420 nm, and band II ranged from 420 to 600 nm. We analyze the transition corresponding to band II in Fig. 3. When a positive bias was applied to the sample, the value of surface photovoltage was positive, and the response strength of band II decreased. On the contrary, when the negative bias was applied, the value of surface photovoltage was positive, and the response strength increased. From the response behavior of band II, band II can be inferred to belong to the  $\pi-\pi^*$  transition, which may be delocalized at the conjugative main chain.

The field-induced photovoltage spectra indicates that when the applied external field is positive (or negative), the built-in field of MEH-PPV thin film is reduced (or enhanced). Therefore, the built-in field in the SCR is directed from the bulk to the surface, and the photovoltaic response of the band-to-band transition arises from the following processes: the photoinduced electrons drift towards the bulk and holes, towards the surface under the

built-in field, resulting in the decrement of positive-charge population in SCR. We consider the MEH-PPV behaves as a n-type semiconducting polymer.

Next we analyzed the transition corresponding to band I in Fig. 3. When a positive bias was applied to the sample, the value of surface photovoltage is negative, and the response strength of band I increased strikingly. From the discussion above, band I indicates that this localized transition results in increased negative charge population in SCR. There seem to be two possible transition processes: one from a local state in the valence band to the conduction band, and another from the valence band to a local state in the conduction band. In the first process, the photogenerated  $\pi$  electrons in the conduction band will drift to the bulk, and the positive charge center is localized, resulting in a decrement of negative charges in SCR. Therefore, this process does not explain the observed behavior of band I. In the second process,  $\pi$  electrons are trapped at the local state, which will result in the increase of negative charges in SCR as a total effect, due to the much higher mobility of the holes (although the photogenerated holes in the valence band are delocalized and can drift towards the surface). Hence, we can determine that this transition is from the valence band to a local state lying in the conduction band. Fig. 4 shows the relative energy level position of the local state and photoinduced charge separation models. We believe that the transition may be localized at a benzene ring.

From Fig. 3, we find that the response strength of band I increase strikingly with the external field. These phenomena can be explained well with the determined local state and corresponding transition (see Fig. 4): the photogenerated holes are drawn towards the surface under the positive field, increasing the probability of them recombining with the photoinduced electrons trapped at this local state, thus band I decreases strikingly. The photogenerated holes are drawn towards the bulk under a negative field, reducing the probability of interaction with the trapped electron. As a

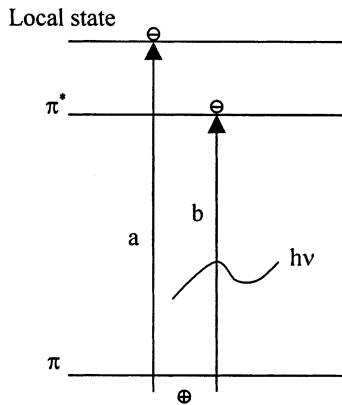


Fig. 4. Schematic of relative energy-level positions and photoinduced charge separation models: (a) band-to-band transition; (b) the determined localized transition.

result, more positive charges are obtained in SCR, and band I increases strikingly.

The determined local state may play a key role for the radiative decay. A positive voltage needs to be applied to the ITO electrode of the LED in order to obtain EL.

#### 4. Conclusion

These results have more general implications for the understanding of the photoelectric properties of MEH-PPV thin films. A local state in the conduction band is considered to be responsible for this localized transition.

#### Acknowledgements

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