

Photoluminescence and electroluminescence properties of a new PPV derivative containing oxadiazole segments

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Abstract

The synthesis of a new PPV derivative (poly[(2,5-diphenylene-1,3,4-oxadiazole)-4,4'-vinylene] (O-PPV) oligomer) and the investigation of the absorption and photoluminescence (PL) properties of O-PPV in the forms of solution and solid-state film are reported. Our results showed that the PL in the case of solid-state originates from an excimer or interchain charge transfer complex. To understand the nature of carrier transport, two types of devices: ITO/PPV/O-PPV/Al and ITO/O-PPV/Tb(AcAc)₃Phen/Al were fabricated. Their electroluminescence result indicates that O-PPV has both hole and electron transport abilities. As a result, the EL efficiency of the single layer O-PPV device is higher compared with that of the single layer PPV due to the balance of charge injection and transport. The electron transport property is attributed to the property of excimers. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since the discovery of polymeric electroluminescence (PEL) by a Cambridge group [1], an increasing amount of research has been devoted towards the understanding of the electroluminescence mechanism, the performance and the efficiency of the PEL devices. Single layer PPV (polyphenylene vinylene) devices have relatively low efficiency, because the injection and transport of holes is preferential and recombination occurs between imbalanced carriers. Electron injection may be enhanced by the use of cathode with low work function [2] or by choosing polymer with large electron affinity [3]. An alternative method is inserting an electron transport layer [4] but in multilayer devices, the interface between electron transport and hole transport layers will influence the device performance. Recently, attempts have been made to combine two or three functional groups into a single molecule or polymer to form the combined electron transport segment, hole transport segment and emitter so that the system will have balanced charge transport properties between electrons and holes [5–7]. To improve the balance of hole and electron transport in a single molecule, we introduced the oxadiazole molecule into the PPV backbone, and synthesized poly[(2,5-diphenylene-1,3,4-oxadiazole)-4,4'-vinylene] (O-PPV) (Fig. 1)

oligomers. From the EL characteristics of double-layer devices consisting of O-PPV and hole or electron transport layer respectively, the O-PPV shows both hole and electron transport properties. The electron transporting characteristics in O-PPV is attributed to the formation of excimers.

2. Experiment

We synthesized soluble O-PPV oligomers according to the HORNER reaction. The molecular structure of O-PPV is investigated by means of IR spectrum and NMR with a Nicolet 50 × FTIR spectrometer and a Varian Unity Plus-400 spectrometer. The molecular weight was determined in THF by WATERS 510 gel permeation chromatography to be $M_w = 1000$ and $M_n = 855$. This result indicated that O-PPV oligomer had roughly four repeating units [8]. PPV thin film was fabricated by a standard precursor method [1]. The single O-PPV and PPV/O-PPV double layer devices were made by spin coating from O-PPV chloroform solution of 5mg/ml on ITO glass or precoated PPV layer. The Tb complex (Tb(acetylacetonato)₃-(monophenanthroline)) (Tb(AcAc)₃Phen) (Fig. 1) was thermally evaporated in a vacuum of 10^{-5} Torr. The PL and EL spectra were measured by a Fluorolog3 spectrometer. The optical absorption spectra were measured by UVKON810 spectrometer.

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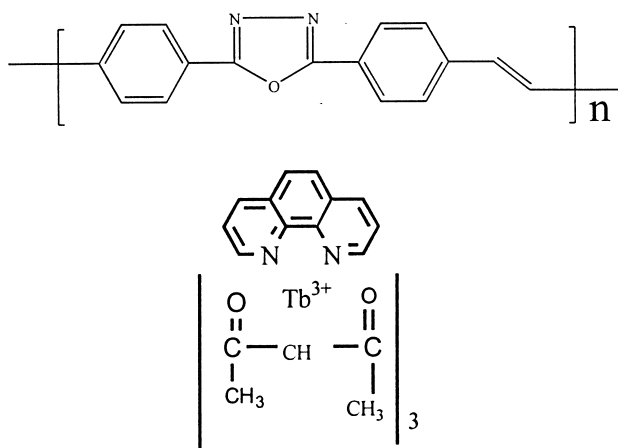


Fig. 1. The molecular structures of O-PPV and $\text{Tb}(\text{AcAc})_3\text{Phen}$.

3. Results and discussion

The optical absorption spectra of O-PPV in dilute solution and solid-state film are shown in Fig. 2. We noted that there are some vibronic structures in dilute solution spectrum with the peak at 350 nm and the absorption edge locating at 420 nm. For solid-state film, the absorption peak is at 300 nm and its absorption edge is at 460 nm. The PL spectra of dilute solution and solid-state film O-PPV are shown in Fig. 3. It is noted that their PL spectra are different. The solution spectrum has vibronic structures, while the film spectrum is featureless, broad and red-shifted shape with a peak at 506 nm. The change in film spectrum is attributed to the formation of excimers [8,9].

The EL spectrum of single layer device with O-PPV (ITO/O-PPV(70 nm)/Al) is identical to its PL, and is independent on driving voltage. The turn-on voltage of the device is about 5 V, and the device has obvious rectification. Under the same current density, the brightness of O-PPV

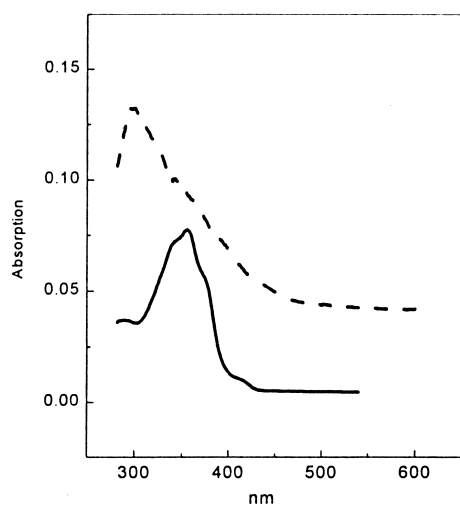


Fig. 2. The optical absorption spectra of O-PPV in dilute chloroform solution of 12.5 mg/l (solid line) and solid-state film (dashed line).

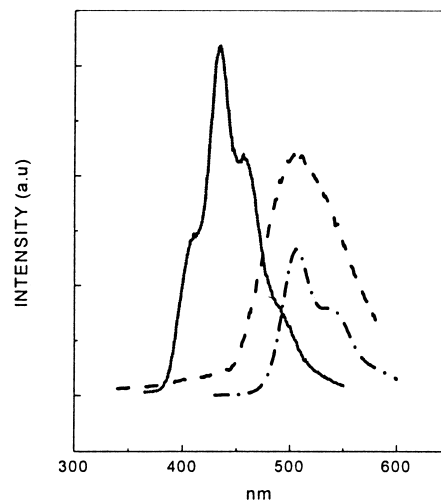


Fig. 3. The PL spectra of O-PPV in dilute chloroform solution of 12.5 mg/l (solid line) and solid-state film (dashed line), and EL spectra of ITO/PPV/O-PPV/Al device (dash-dot line).

device is higher than that of single layer device of PPV. Although there are many reasons for improved EL efficiency, we believe that the main effect is the balance of charge injection and transport. The reason is that the PL of solid-state O-PPV is from an excimer, whose PL efficiency is usually very low [10]. So we think that the injection and transport of electrons and holes may be balanced in single layer O-PPV device due to the introduction of oxadiazole into PPV backbone to maintain conjugation between the oxadiazole and PPV segment. As a result, the electron transporting properties of O-PPV may be improved. In order to investigate the carrier transport characteristics of O-PPV, we made double-layer devices and study their EL properties.

The EL properties of ITO/PPV(70 nm)/O-PPV(30 nm)/Al device are shown in Fig. 4. The light emission of this device is only from PPV, and the onset of turn-on voltage is at 5 V.

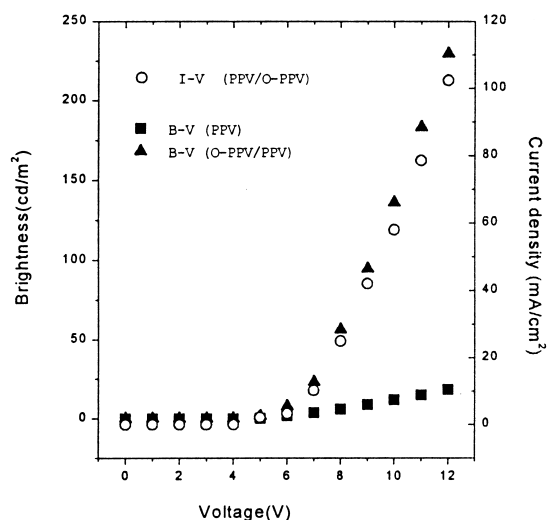


Fig. 4. The EL properties of ITO/PPV/Al and ITO/PPV/O-PPV/Al devices.

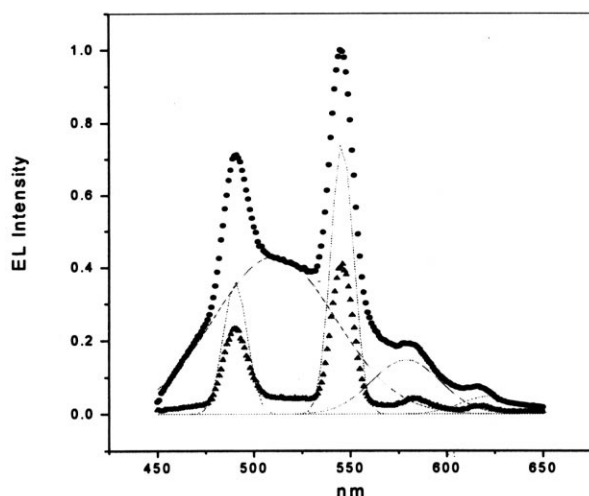


Fig. 5. The EL spectra of ITO/O-PPV/Tb(AcAc)₃Phen/Al at the driving voltage of 6 V (triangle) and 11 V (circle). The EL spectrum at 11 V is decomposed (solid line). The EL spectrum is superposition of O-PPV and Tb(AcAc)₃Phen EL spectra.

Under current density of 150 mA/cm², the EL brightness of double-layer device reaches 230 cd/m². However, the brightness of single layer PPV device is only about 20 cd/m² at the same current density. In the double-layer device, the EL efficiency is improved due to the introduction of the O-PPV layer. Therefore, it indicates O-PPV has electron transport property.

We prepared another device of ITO/O-PPV(70 nm)/Tb(AcAc)₃Phen(40 nm)/Al in order to study the possible hole transport property of O-PPV. The EL spectra under different driving voltage are shown in Fig. 5. It is noted that the Tb emission is mainly observed under low voltage, and the intensity of peak at 510 nm increases with increasing driving voltage. We decomposed the EL spectrum under higher voltage and obtained separate peaks of O-PPV and Tb(AcAc)₃Phen PL emission in the EL spectrum of the double-layer device. The result shows that the recombination occurs in both O-PPV and Tb(AcAc)₃Phen layer, and consequently indicates O-PPV possesses the hole transport property in this device. In the single layer device of Tb(AcAc)₃Phen, the emission is not observed under rather large current density up to 100 mA/cm². The phenomenon is regarded as unipolar carrier injection. Therefore, this provides the evidence that O-PPV possesses both electron and hole transport properties.

From the PL spectra of O-PPV in dilute solution and solid-state film, we note that PL of solid-state film is from an excimer. An excimer can be formed when an exciton on a conjugated polymer chain is stabilized by a charge-transfer interaction with another chain to form an excited-state complex (or it is called an interchain charge-transfer complex alternatively). Because the oxadiazole in the O-PPV main chain is electron deficient, it may accept an electron and act as an acceptor. As O-PPV will closely pack in the solid-state film, the oxadiazole will interact with neigh-

boring chain of O-PPV, then the electron density might shift from the vinyl bonds in a chain of O-PPV to oxadiazole molecules in another chain. This electron shift will delocalize from all single O-PPV chain due to maintaining conjugation between the oxadiazole segment and PPV segment. Therefore the charge-transfer state (excimer) is produced in solid-state film of O-PPV under the photoexcitation. The evidence of O-PPV diffused into PEO (poly ethylene oxide) as a spacer supports the mechanism of interchain charge-transfer excitation [8].

In the EL process, light emission arises from radiative relaxation of the excitons resulting from the recombination of holes and electrons injected from opposite electrodes. It is shown that electrons from cathode may inject and transport in the O-PPV layer. As the oxadiazole segments in O-PPV backbone is an electron acceptor, the electrons injected from cathode may be accepted by oxadiazole. The negative polarons are formed in O-PPV, and will transport between O-PPV chains because there is interchain charge-transfer interaction in solid-state O-PPV. In the blend device with PBD as electron transport material, the electron may inject from cathode into PBD molecule and may hop between PBD molecules since PBD has oxadiazole segment [11]. Consequently the electron may inject from cathode to oxadiazole in O-PPV chain. As O-PPV is fully conjugated between oxadiazole segment and PPV segment, an electron in oxadiazole injected from cathode will delocalize on the entire O-PPV chain, leading to the negative polarons. The electron in negative polaron of O-PPV will transfer into the neighboring chain, as O-PPV possesses interchain charge-transfer effects. At last, we may observe the electron transporting property of O-PPV. As holes (unipolar) are predominant in PPV, the hole transporting property of O-PPV can be easily understood.

4. Conclusion

In summary, we have synthesized an oxadiazole-containing PPV oligomer. From the EL properties of the double-layer devices of ITO/PPV/O-PPV/Al and ITO/O-PPV/Tb(AcAc)₃Phen/Al, we confirm that O-PPV material has both electron and hole transporting properties. The electron mobility originates from oxadiazole segments in O-PPV backbone, and further is a result of interchain charge-transfer interactions in O-PPV. Compared with the single layer EL device of PPV, the EL efficiency of O-PPV is higher due to the balanced injection and transport of electron and hole in O-PPV layer.

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