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Blue photo- and electroluminescence from a novel poly (phenelene vinylene) derivative containing oxadiazole segment in main and side chains

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Abstract

Optical and electroluminescent properties of a novel PPV derivative (OPPV) which contains oxadiazole segments in main and side chains were studied. Both the single-layer EL device and the triple-layer EL devices fabricated with OPPV as the active layer emitted blue light from OPPV with a peak of spectrum at around 460 nm. The device structure: ITO/PVK + OPPV(2:1 weight ratio)/OXD(40 nm)/Alq(20 nm)/Al, was fabricated, which showed much better performance than the single-layer EL device and the triple-layer EL device without PVK in the emitter material. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since the first polymer electroluminescence devices (PELDs) fabricated using poly(p-phenylene vinylene) was reported by Cambridge group [1], research on PELDs has been developed rapidly for the unique virtues of polymer, namely low cost, easy processing and the possibility of chemical tailoring to realize desired properties. It is specially interest that the emission of PELDs based on a variety of polymers may cover the visible spectral range.

The realization of blue EL is urgently necessary for possible application of conjugated polymers in flat-panel color displays. Poly(p-phenylene) (PPP) was the first conjugated polymer from which blue-emitting diodes were realized [2]. Since then, blue EL has been reported from different conjugated polymers such as PPP-type ladder polymers [3], poly(pyridine) [4], poly(alkylfluorene) [5], non-conjugated polymers like poly(N-vinyl carbazole) [6], polymer blends [7] and copolymers [8,9].In this paper we report the blue photoluminescence and electroluminescence properties of poly (p-phenylene vinylene) derivative OPPV. In fact, OPPV contains oxadiazole segments in backbone and side chains and forms a conjugated/non-conjugated multiblock copolymer. The non-conjugated segments in the backbone reduce conjugation of intra-chains and localize the excited state wave functions within a limited conjugated segment of a single polymer chain. Therefore, this is expected to constrain exciton motion and protect it from quenching sites [10,11].

2. Experiment

The chemical structure of OPPV is shown in Fig. 1. We mixed the solvent of N,N-Dimethylformamide (DMF) and chloroform and then put in O-PPV as solute. Then, the solution of O-PPV was spin coated onto quartz substrates for PL experiment. PELDs were fabricated using OPPV as the emissive material, indium-tin-oxide (ITO) as the anode material and vacuum-evaporated aluminum as the cathode. The organic emissive layer was deposited by spin coating from the solution. The electron transport layer and buffer layer were evaporated at a deposition rate of 1–3 Å/s at 10^{-5} Torr, respective. Photoluminescence, photoluminescence excitation and electroluminescence spectra measurements were carried out using a Spex Fluorolog-3 fluorescence spectrometer. Absorption spectrum was taken with the

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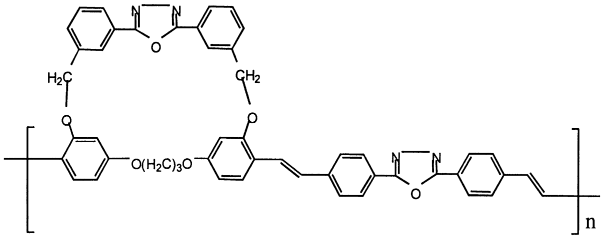

Fig. 1. Molecular structure of OPPV.

UV-3101C spectrophotometer. All spectra were measured at room temperature and in air.

3. Results and discussion

Fig. 2 shows the absorption, PLE and PL spectra of a thin OPPV film. In the film there are absorption maxima at 373, 290 and 200 nm. By extrapolating the absorption spectrum, the optical gap between (lowest unoccupied molecular orbital) LUMO and (highest occupied molecular orbital) HOMO was estimated to be 2.77 eV. The PLE spectrum monitored by the PL peak at 460 nm was measured, which locates at 370 and 300 nm (shoulder) and is roughly similar to absorption spectrum. This shows that the PL spectrum with excitation at 370 nm is much more efficient than that at 300 nm. According to the absorption spectrum and PLE spectrum, we think that the shoulder peak (300 nm) of PLE spectrum is related to the oxadiaole side chain of O-PPV. To elucidate this problem, we studied the optical properties of the pure film and the solution of a similar molecule PBD(2-(4-Biphenyl)-5)4-tert-butylphenyl)-1,3,4-oxadiazole) for comparison. Because the chemical structure of luminary segment in PBD is similar to that of the luminary segment of O-PPV in side chain. The PL spectrum peak of pure film of PBD lies at 392 and 377 nm (shoulder) and the PL peak of the diluted solution locates at 360 and 377 nm(shoulder). In addition, the solid film of PBD and the diluted solution show absorptions at 260–340 nm. The PL spectrum of the oxadiazole side groups of O-PPV overlapped with the absorption spectrum of the conjugated segments in backbone chains. The energy of the segments of side chains possibly transfers to the segments of backbone chains. The PL spectrum for the solid film of OPPV is very similar to that of the solution but the spectral peak is slightly red-shifted. This indicates that the emission spectrum of OPPV is characteristic of an isolated polymer chain because the introduction of oxadiazole segments in side groups makes interactions of inter-chains weak [12,13].

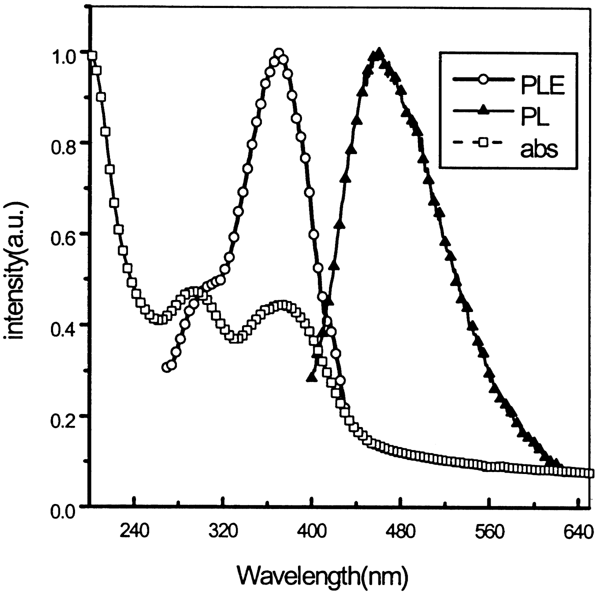

Fig. 2. Absorption, PLE, and PL spectra of an OPPV film. The excitation wavelength for the PL spectrum is $\lambda_{ex} = 370$ nm and the emission wavelength for the PLE spectrum is $\lambda_{em} = 460$ nm.

Single-layer PELDs were fabricated with OPPV as the emissive layer. When PELDs were forward biased with the ITO electrode at positive polarity, blue EL was observed. However, the brightness of these devices was low and the EL was only visible in a dimly lit room. To improve the diodes parameters, polymer blends were used and the transport layer and buffer layer were introduced. The structures of devices were fabricated: ITO/OPPV/OXD(40 nm)/Alq(20 nm)/Al and ITO/PVK + OPPV(2:1 weight ratio)/OXD(40 nm)/Alq(20 nm)/Al, where PVK is poly(N-vinyl carbazole), OXD-7 is 1,3-bis(4-tert-butylphenyl-1,3,4-oxadiazoyl) phenylene, Alq is tris(8-quinolinolato)aluminum. We use PVK since it is a hole transport material and its PL spectrum overlaps with the PLE spectrum of OPPV enabling efficient energy transfer from PVK to the emitter OPPV. As an electron transport material, OXD-7 has a high glass transition temperature and good film forming properties and better ability of blocking hole carriers. The introduction of the buffer layer (Alq) is to improve the contact between the electron-transport layer and Al electrode because deposition of Al electrode directly on OXD appears gray-white color.

Fig. 3 shows the EL spectrum of the triple layer PELDs, that is ITO/PVK + OPPV (2:1 weight ratio)/OXD/Alq/Al. Blue EL spectra of the triple-layer devices without and with PVK almost overlap with a peak of spectrum at 460 nm. The EL spectrum resembled the PL spectrum of the film of OPPV(Fig. 2). This indicates that the EL and PL originate from the same excited state. Fig. 4 shows the current–applied voltage and brightness intensity–applied voltage characteristics of the latter structure. The emission of the latter started at a driving voltage of 8 V, which was 2 V lower than the former. The triple layer PELDs with the hole-transport material PVK showed better performances than the single layer EL device and triple layer without PVK. According to the structure of OPPV, OPPV contains oxadiazole segment which has better ability of electron-transport than the common PPV derivatives, therefore the electrons pass easily through the emitting layer. It is suggested that in the triple-

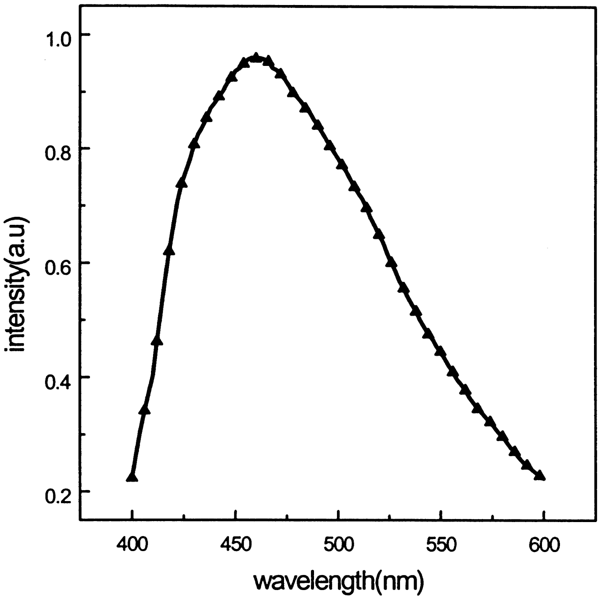

Fig. 3. The EL spectrum of the triple-layer PELD.

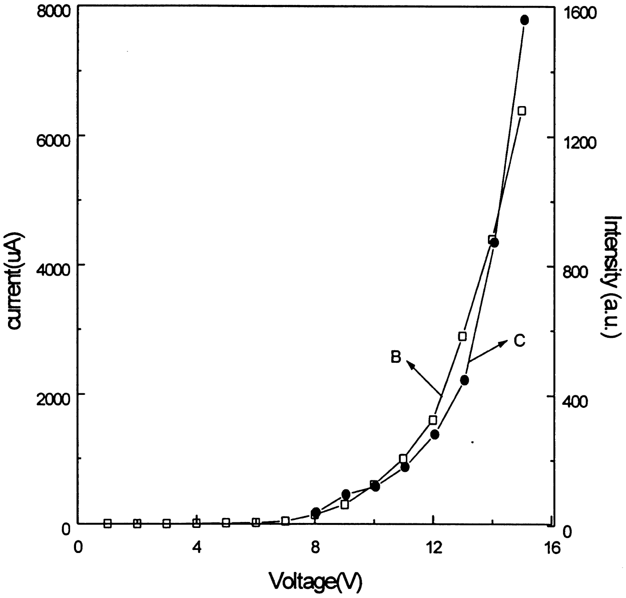

Fig. 4. Current–voltage (B) and brightness intensity–voltage (C) characteristics of a triple-layer PELD with PVK.

layer EL device, the hole injection from the ITO electrode becomes more efficient due to decrease of energy barrier and blockade of the electrons in the presence of the hole transport material PVK, this results in a better balance of a number of holes and electrons injected and helps to displace the recombination zone away from the electrodes, leading to the better performance for the triple layer EL devices.

4. Conclusion

In conclusion, blue EL devices have been successfully fabricated utilizing the novel emitter material OPPV. The triple layer EL device consisting of the emitting layer of OPPV blending with PVK and the electron-transport layer of OXD-7 and the buffer layer of Alq_3 exhibited good performance. The PL spectrum of the oxadiazole side groups of O-PPV overlapped with the absorption of the conjugated segments in backbone, which shows that the energy of the segments of side chains can transfer to the segments of backbone chains. The peak of EL spectrum is 460 nm and the spectrum is similar to that of the PL. It indicates that PL and EL originate from the same excited state.

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