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A Novel Oligomer Poly(Phenylene Vinylene) Derivative Containing Oxadiazole Segment *

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A novel oligomer PPV derivative (OPPV) is reported, which is designed to contain the oxadiazole function segment in the main chain. Photoluminescence of the OPPV thin film originates from aggregated states. In a double layer device consisting of poly phenylene vinylene (PPV) and OPPV, emission only from PPV layer was observed and the efficiency of the device was improved by about one order of magnitude compared with the single layer PPV device, this indicates the electron transport characteristic of OPPV. In the OPPV/Tb complex device, OPPV functions as the hole transport layer. A possible explanation is proposed.

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Since the first polymer electroluminescence device (PELD) was reported by Burroughes *et al.*,¹ research in this field has developed rapidly on account of the unique virtues of polymers, namely easy processability, low cost and the possibility of chemical tailoring to realize desired properties comparing with the inorganic counterpart.^{2,3} Single layer PPV devices have relatively low efficiency due to unbalanced carrier injection and transport (mainly deficiency of electrons). Generally, two methods have been adopted to improve the efficiency of the device: (1) Utilizing a low work function metal such as calcium to facilitate electron injection from the cathode.⁴ (2) Inserting an additional electron transport layer to improve electron injection. Because of the reactivity of low work function metals, it is highly desirable to fabricate PELDs with a relatively high work function metal. Greenham *et al.*⁵ reported that cyano substituted PPV (CN-PPV) increased the electron affinity potential of the material and reduced the electron injection barrier, while the band offset at the PPV/CNPPV layer interface redistributed the electric field, thus improving the electron injection and efficiency of the device. However, due to the relatively smaller band gap of the CN-PPV, emission comes from the CN-PPV layer. Here we report an oligomer PPV derivative with the oxadiazole function segment in backbone, namely [poly(2,5-diphenylene-1,3,4-oxadiazole)-4,4'-vinylene] (OPPV). The photoluminescence (PL) and electroluminescence (EL) characteristics of this material have been studied, and the carrier transport characteristics of OPPV was discussed in the double layer devices consisting of OPPV and a hole transport layer or electron transport layer.

Figure 1(a) shows the molecular formula of OPPV; its structure was identified by IR spectra and nuclear magnetic resonance. The average molecular weight was determined to be 1000. OPPV was dis-

solved in chloroform and the concentration of the solution was 5 mg/ml. PPV thin film was fabricated in the standard precursor way.¹ The single layer OPPV and PPV/OPPV double layer devices were built by spin-casting OPPV chloroform solution on precleaned indium-tin-oxide (ITO) glass or precoated PPV layer, respectively. Tb(acetylacetonato)₃-(monophenanthroline) [Tb(AcAc)₃Phen] as discussed in Ref.6 and aluminum were thermally evaporated. The PL and EL spectra were measured by a Hitachi F-4000 spectrometer, the room temperature optical absorption spectrum was measured by a UVKON810 absorption spectrometer, and the luminescence lifetime of the OPPV solid-state film was obtained by an SLM4800S multi-frequency lifetime spectrometer. The brightness of the device was measured by the radiance.

The optical characteristics of OPPV are shown in Figs. 1(b) and 1(c). For OPPV film, the absorption spectrum peaks at 295 nm, and the PL peak lies at 508 nm. Comparing with the PPV oligomer with the same conjugated length, the relative large Stokes shift and broad structureless emission profile may imply that emission comes from aggregated states. We dispersed OPPV into polyethyleneoxide matrix, and found that the emission spectra blueshifted with decreasing concentration of OPPV. When the concentration ratio by weight is 0.5%, the emission spectrum peaks at 416 nm and does not shift any more similar with the PL spectrum of diluted OPPV solution (1 mg/L). From the molecular structure we can see there is no bulky substitution in this material, so molecules may have the relatively large possibility to stack upon each other, and aggregated states are easily formed. This assumption is further proved by time-resolved luminescence experiment, the decay time constants of luminescence are 1 and 8 ns in the film samples. Based on the above discussion we believe that

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emission originates from the charge transfer states.⁷

The EL spectrum of the single layer OPPV device (ITO/OPPV(70 nm)/Al) is basically identical to the PL of OPPV film, as shown in Fig. 1(c). The turn-on voltage of this device was about 5 V, the current-voltage characteristic curve of the device had obvious diode rectifying properties and the rectification ratio at 5 V was about 100. Under the same injection current, the brightness of the single layer OPPV device was about 3–5 times higher in comparison to the single layer PPV device. However, we believe the apparent increment of the efficiency of the OPPV device may be related to the insertion of the oxadiazole segment, but cannot be simply assigned to one particular aspect such as carrier transport characteristics, which we will discuss below. This is because the luminescence efficiency of PLED is related to many factors such as PL efficiency, carrier injection and recombination efficiency.

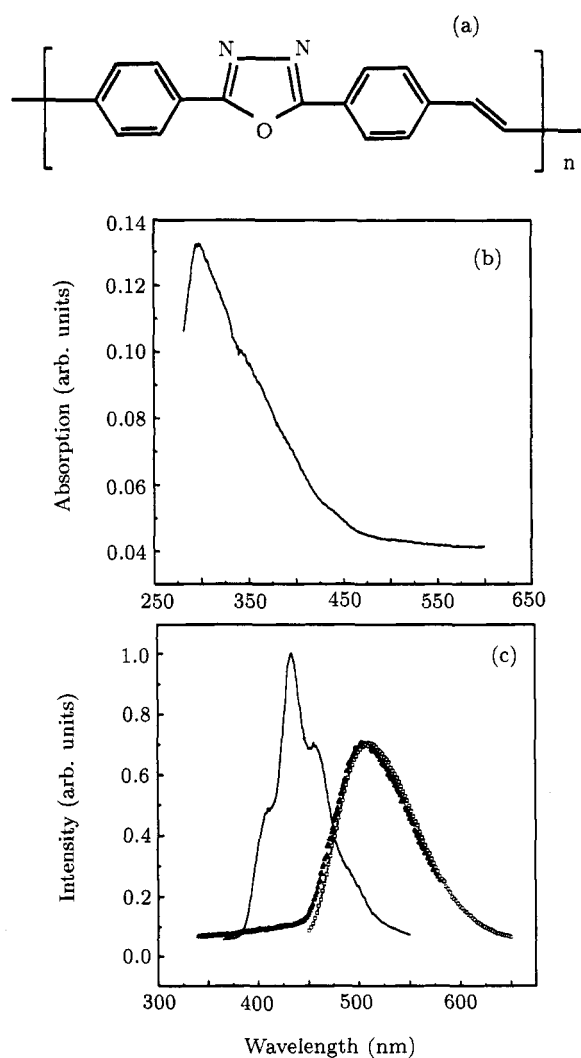


Fig. 1. (a) Molecular formula of OPPV, (b) absorption spectrum of OPPV film, (c) PL and EL spectra of OPPV. Solid line: PL spectrum of OPPV diluted solution, triangles: PL spectrum of OPPV film, squares: EL spectrum of single layer OPPV device.

We identified OPPV as having better electron transport ability, due to the presence of the electron deficient nitrogen containing oxadiazole segment,⁸ which was our initial goal in synthesizing these kinds of material. To test this we fabricated the double layer device: ITO/PPV(70 nm)/OPPV(30 nm)/Al (type I device) as well as the single layer PPV device for comparison. The turn-on voltage of all these devices was about 6–7 V. In the double layer device emission only from the PPV layer was observed, and from our initial results the brightness of the device reached 230 cd/m² at high current density (about 110 mA/cm²), while in the single layer PPV device at the same driven current density the brightness was only about 10–20 cd/m², indicating efficiency of the double layer device was improved by about ten times. The current–voltage and brightness–voltage characteristics of the devices are presented in Fig. 2.

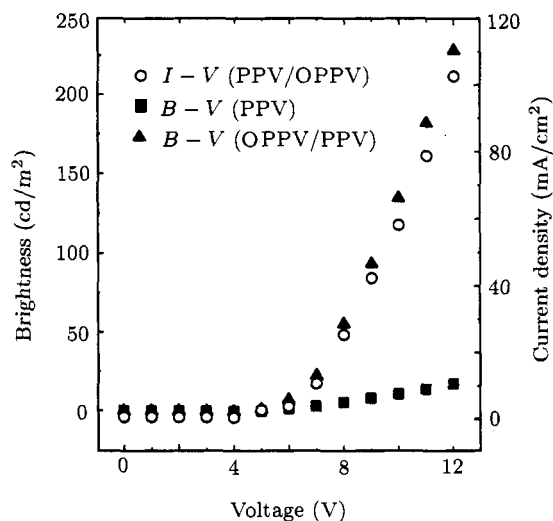


Fig. 2. Current–voltage characteristic and brightness–voltage characteristic of PPV/OPPV double layer device. Brightness–voltage characteristic of single layer PPV device is also presented for comparison.

Another type of double layer device: ITO/OPPV (70 nm)/Tb(AcAc)₃Phen(40 nm)/Al (type II device) was fabricated to examine whether OPPV still had hole transport ability, and a single layer Tb(AcAc)₃Phen device was also fabricated for comparison. We argue that, if OPPV has hole transport ability or functions as the hole transport layer in the device, the carrier recombination zone of the type II device should be located at the interface of the OPPV and Tb(AcAc)₃Phen layers since Tb(AcAc)₃Phen was reported to be an electron transport material,⁶ otherwise emission from OPPV layer should mostly be observed as it is generally accepted that for electron transport material carrier recombination zone is located near the anode. Figure 3 shows the EL spectra of the type II device under different operating voltage. Under a lower operating voltage of 8 V, the EL spectrum consisted of the characteristic emission of Tb³⁺ from Tb(AcAc)₃Phen layer. When the operating voltage was higher (14 V), emission from the OPPV layer

contributed to the total light emission. However, in the single $\text{Tb}(\text{AcAc})_3\text{Phen}$ layer device no emission or very faint and unstable emission was observed under a rather large current density up to 50 mA/cm^2 , which suggests almost unipolar carrier injection.

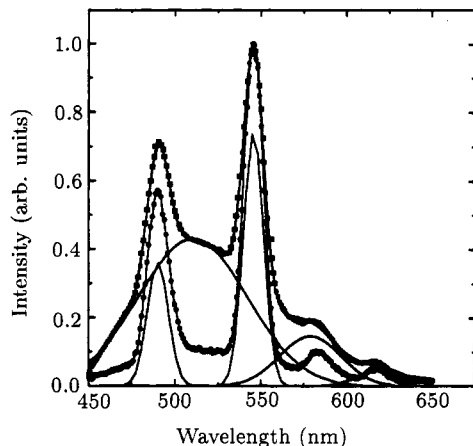


Fig. 3. EL spectra of OPPV/ $\text{Tb}(\text{AcAc})_3\text{Phen}$ device under different driven voltage, which are normalized by the peak at 544 nm (corresponding ${}^5D_4 - {}^7F_5$ transition of Tb^{3+}). Solid circles: EL spectrum under low operating voltage, squares: EL spectrum under high operating voltage. Solid lines: decomposition result of EL spectrum of the device under high driven voltage (four sharp peaks correspond the emission of Tb^{3+} , the broad peak corresponds the emission of OPPV).

The EL spectra of type I device are characteristic spectra of PPV, indicating that carrier recombination occurs in the PPV layer. The improved efficiency of the device illustrates that OPPV may have the effect of facilitating electron injection, and as result the recombination ratio of holes and electrons is greatly enhanced. In the type II device the improved luminescence characteristics of Tb^{3+} and the carrier recombination zone indicate that the OPPV layer functions as the hole transport layer in this case. Based on the above discussion we believe that by inserting the electron accepting oxadiazole function segment, we can balance the carrier transport ability of the material. In other words, OPPV is a kind of bipolar carrier transport material.

An investigation to explain the bipolar carrier transport characteristics is now under way. We believe that since there is little difference between the lowest unoccupied molecular orbital level of PPV and 2-(4-biphenyl)-5-(4-tert-butyl phenyl)-1,3,4 oxadiazole (PBD) (a kind of typical electron transport material containing oxadiazole segment), intrachain charge transfer should not be important in this case, which we believe is crucially important for the synthesis of this kind of material, otherwise the PL efficiency of

OPPV would be drastically reduced due to the effective quenching of excitation by charge transfer as suggested by Grunier *et al.*⁹ These authors incorporated PBD segments into the ladder (para-phenylene) compound, and found that hole transportation was not decreased and ascribed this to hole transport preferentially taking place along ladder units or spacer groups, having PBD units bypassed via interchain hopping. However, we notice that the PBD concentration was relatively small in their experiment. We also note a report about a similar p-n type diblock material by Huang Wei *et al.*¹⁰ in which they inserted oxadiazole segment into polythiophene main chain. They observed that it was the highest occupied molecular orbital level that was sensitive to the number of thiophene rings. This may imply that holes mainly transport through the thiophene segment. From our experiment we may infer that there is a possibility that electrons hop between these oxadiazole segments while holes pass through the PPV segment. On the other hand, study of the PL characteristics of OPPV indicates that aggregated states are responsible for the PL behavior of OPPV solid film, and aggregated state formation may mean relatively stronger interaction among different molecules. We believe this can partially strengthen the phenomena of carriers hopping among different molecules following different sites, and be partially responsible for the carrier transport characteristics of OPPV.

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