

# Synthesis, Photo-, and Electroluminescent Properties of the Soluble Poly[(2,5-diphenylene-1,3,4-oxadiazole)-4,4'-vinylene]

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**ABSTRACT:** A novel soluble conjugated polymer, poly[(2,5-diphenylene-1,3,4-oxadiazole)-4,4'-vinylene] (O-PPV), containing an electron-transporting group on the main chain of PPV, was synthesized according to HORNER mechanism. The oligo-polymer with  $M_w = 1000$  and  $T_d = 270^\circ\text{C}$  is soluble in chloroform and tetrahydrofuran. The photoluminescent (PL) properties were investigated using different concentrations of solid-state O-PPV/PEO blends absorption and selective excitation measurements. The results show that PL arises from interchain charge-transfer states in solid-state O-PPV. Compared with the analogous single-layer device constructed with PPV (ITO/PPV/Al), which emits two peaks at  $\lambda = 520$  nm and 550 nm (shoulder), the electroluminescence (EL) spectrum of the device [ITO/O-PPV (80 nm)/Al] is a broad peak at  $\lambda_{\text{max}} = 509$  nm. The quantum efficiency (0.13%) of the device ITO/O-PPV/Al is much higher than that of the device ITO/PPV/Al, due to the introduction of the electron-transporting group—oxadiazole units in the main chain of PPV. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3535–3540, 1999

**Key words:** PPV oligo-polymer; organic electroluminescence; electron-transporting layer; hole-transporting layer

## INTRODUCTION

Since the first discovery of electroluminescence (EL) in poly(1,4-phenylene vinylene) (PPV) in 1990 by Burroughes et al.,<sup>1</sup> there has been tremendous interest in conjugated polymer light-emitting diodes (LEDs) due to the strong potential for applications in displays and lighting. PPV

is a conjugated polymer with high chemical and thermal stability, which allows the fabrication of large area, long operating period (>4000 h), low-onset voltage (2 ~ 3 V), and flexible LEDs.<sup>2,3</sup> Despite this great progress, PPV LEDs still have some disadvantages. PPV is almost insoluble in organic solvents because the main chain of the conjugated polymer is a rigid structure. Thus, in order to form the polymeric thin film for fabricating the device, it needs to use a soluble precursor or attach a long side-chain group to the main chain. Furthermore, the injection and the transport of holes are strongly favored compared to electrons in PPV and, consequently, only moderate external quantum efficiencies of about 0.001%

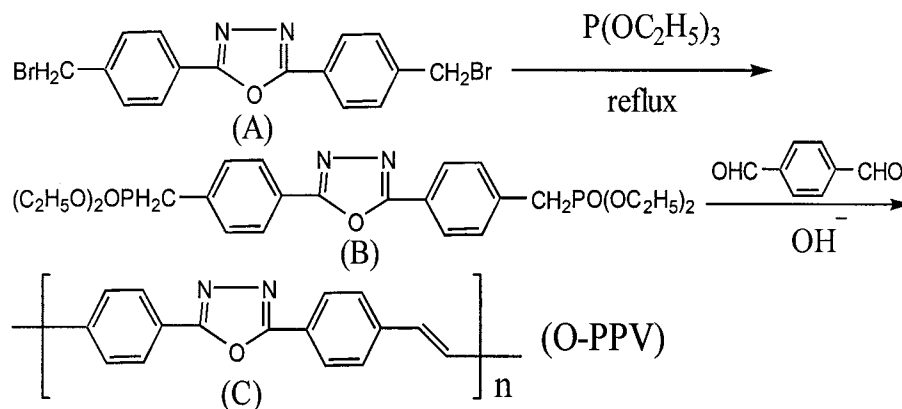
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Scheme 1

for PPV LEDs with Al electrode are measured.<sup>4</sup> To increase the quantum efficiency in these devices, low work function metals like Ca and Mg<sup>2</sup> can be used as cathode. However, these metals are extremely unstable in atmosphere. In recent years, many small molecular oxadiazole derivatives have been reported<sup>5</sup> as efficient materials for facilitating electron transport and injection in bilayer PPV LEDs to increase the quantum efficiency. But as a consequence of their low glass transition temperature, they usually have a strong tendency to crystallize during operation.

In this study, we synthesized soluble poly(2,5-diphenylene-1,3,4-oxadiazole-4,4'-vinylene) (O-PPV) containing an electron-transporting group on the main chain of PPV. The photoluminescence properties were investigated using absorption and selective excitation measurements. The results showed that PL arises from inter-chain charge-transfer states in solid-state O-PPV. The EL spectrum of the device [ITO/O-PPV (80 nm)/Al] and the quantum efficiency were also discussed.

## EXPERIMENTAL

### Measurements

The molecular structures were proved by IR (Bio-Rad, USA) and NMR (Varian, USA) spectra with a Bio-Rad FTS 135 spectrometer and a Varian Unity Plus-400 spectrometer, respectively. The molecular weights were determined in THF by a Waters510 gel permeation chromatography (GPC, Waters, USA) using polystyrene as the standard sample. Photoelectron spectra (PE, USA) were recorded using a Perkin-Elmer

PHI1600 ESCA system. Fluorescence spectra were obtained on a Fluorolog3 (SPEX Industries, USA) spectrometer. Room-temperature optical absorption was measured with a Uvikon810 absorption spectrometer. DSC (PE, USA) analysis was measured by Perkin-Elmer 7C. PEO (poly ethylene oxide) was purchased from ACROS and a weight-average molecular weight was 100,000. O-PPV was blended with PEO in chloroform under different concentrations of O-PPV and the ratio of weight to volume in solution was 5 mg/mL for all samples.

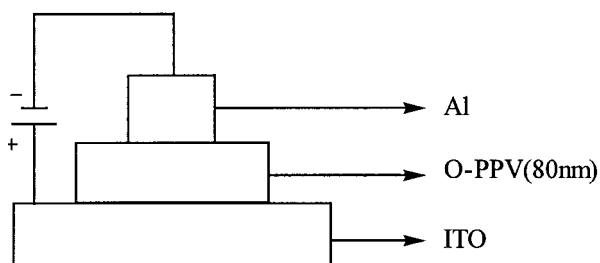
### Synthesis of O-PPV

The pathway of synthesis of poly(2,5-diphenylene-1,3,4-oxadiazole-4,4'-vinylene) (O-PPV) is shown in Scheme 1.

### Preparation of Monomer

2,5-bis(*p*-Bromomethylphenyl)-1,3,4-oxadiazole (A) was prepared according to a previously reported synthetic method.<sup>6</sup> 2,5-bis[4-[(Diethoxyphosphinyl)methyl]phenyl]-1,3,4-oxadiazole (B) can be prepared by the following procedure: To a stirred triethyl phosphite solution (400 ml) was added 2,5-bis(*p*-bromomethylphenyl)-1,3,4-oxadiazole (A) (81.6 g, 0.2 mol). The reaction mixture was then heated under reflux for 4 h. After cooling, white crystalline precipitate was formed, then filtered out and washed with 50 mL *n*-hexane to yield 80.6 g product (15.4%); m.p. 107–109°C.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.6, 8.1 (4H, s, phenyl), 4.6 (4H, s, CH<sub>2</sub>-P), 3.2 (8H, m, P-CH<sub>2</sub>-CH<sub>3</sub>), 2.6 (12H, t, P-CH<sub>2</sub>-CH<sub>3</sub>). ANAL. calcd. for C<sub>24</sub>H<sub>32</sub>P<sub>2</sub>O<sub>7</sub>N<sub>2</sub>:



**Figure 1** The device structure of O-PPV.

C, 55.13; H, 6.12; N, 5.40; P, 11.92. Found: C, 55.17; H, 6.13; N, 5.36; P, 11.88%.

### HORNER Condensation Polymerization

A mixture of *p*-phthalaldehyde (1.34 g, 10 mmol) and 2,5-bis{4-[(diethoxyphosphinyl)methyl]phenyl}-1,3,4-oxadiazole (B) (5.22 g, 10 mmol) in 60 mL methanol was stirred at room temperature until dissolution was complete. The methanol solution (10 mL) of sodium methylate (25 mmol) was added in one portion, then the mixture was heated at 60°C for 3 h. A pale yellow precipitate was formed; after cooling the polymer product was filtered and washed with water to neutralization. The polymer was extracted with methanol in Soxhlet extractor for 10 h, then redissolved in chloroform and reprecipitated in alcohol.

### LED Device Preparation

Indium-tin oxide (ITO)-coated glass (30 Ω/□) was repeatedly washed three times in isopropyl alcohol by a supersonic cleaner for 50 min, because the cleanliness of the ITO substrates influences the performance of the EL devices due to a generation and increment of dark spots. A layer of polymer was then deposited by spin-coating onto the ITO electrode with a thickness of 80 nm, and finally Al was evaporated onto the polymer used as the negative electrodes in the vacuum of  $2 \times 10^{-5}$  MPa, as shown in Figure 1.

## RESULTS AND DISCUSSION

### Characterizations of Synthesis

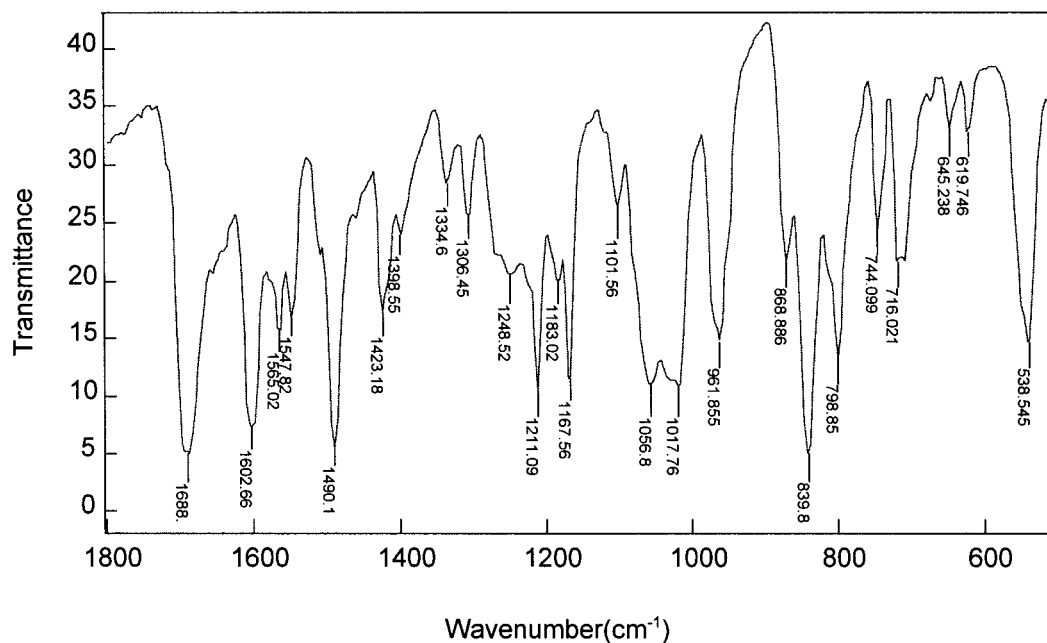
The synthetic strategy is based on step-growth polymerization through dialdehyde with primary bis(phosphonates) (HORNER reaction). This route is extremely flexible and allows a lot of PPV-type copolymers to be synthesized. The monomers required for HORNER polymerization,

namely the primary or secondary bis(phosphonates), and the substituted dialdehydes, can easily be prepared by conventional organic reactions. As shown in the reaction route, the polymerization was carried out in methanol solution using sodium methylate as the condensing agent to give yellow solid product. The polymer determined in THF by a Waters510 gel permeation chromatography is proved to be low molecular weight ( $M_w = 1000$ ; oligo-polymer), which is insoluble in alcohol solutions. This oligo-polymer formed in the HORNER reaction may be due to the *trans*-vinylene rigid structure and no flexible groups such as the *long* alkyl or alkoxy side-chains attached to the central benzene ring. The solubility of this oligo-polymer is not at all remarkable, as in chloroform and tetrahydrofuran the solubility is only about 5 mg/mL. On the other hand, the decompose temperature of this oligo-polymer is relatively high (270°C) due to the rigid structure, and the polymer has less tendency to crystallize during operation.

HORNER polymerization between dialdehydes and primary bis(phosphonates) provides vinylene double bonds in all *trans*-configuration (*E*), as provided by IR spectroscopy (peak at  $962 \text{ cm}^{-1}$ ) shown in Figure 2 and  $^1\text{H-NMR}$  spectroscopy (no signal in the range of approximately 5.5 to 7.0 ppm as expected for *cis*-vinylene). So, there are three major advantages of the HORNER reaction to synthesize PPV-type polymer over the synthetic method reported by Wessling<sup>7</sup>: (1) there is a better access of the monomers from commercial chemicals [dialdehydes/diketones and bis(phosphonates)]; (2) Wessling's method provides both *trans*(*E*) and *cis*(*Z*) configuration of double bonds in PPV structure, but HORNER's polymer reaction provides vinylene double bonds in all-*trans*; and (3) the purity of PPV-type polymers may be much more easily controlled by HORNER's method than that of Wessling's reaction.

### PL Properties of O-PPV

Figure 3 shows the room-temperature solid-state optical absorption spectra for pristine O-PPV and blends of O-PPV with PEO. The position of absorption edge is at 450 nm in pristine O-PPV; however, the absorption edge blueshifts with a decrease in the weight ratio of O-PPV to PEO, and finally moves to 390 nm. The difference indicates that the ground states of polymer couple with each other on solid-state pristine O-PPV. The result further shows that electrons or holes in the

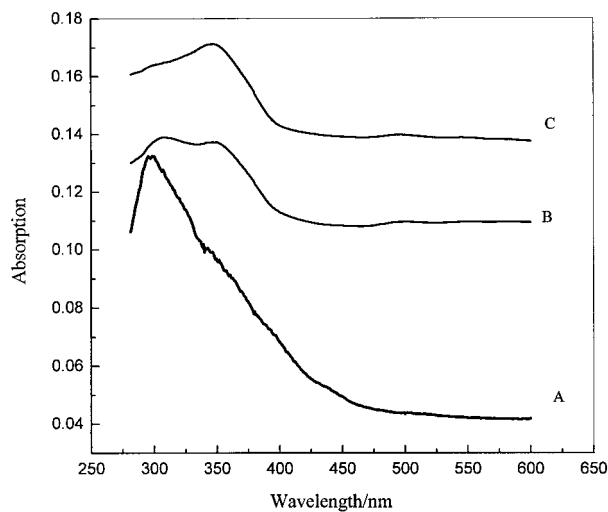


**Figure 2** IR spectrum of O-PPV.

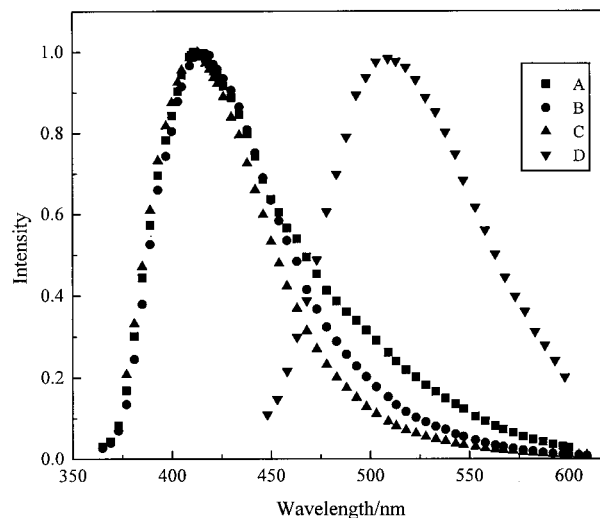
intrachain have opportunity to go to the neighbor polymer chains; in other words, the electron wavefunctions couple on the ground states of polymers, so that the absorption edge is shifted to lower energy. The phenomenon arises from the interaction of interchain due to close packing.

To explore the interchain interaction, a series of PL spectra are measured for the solid state of

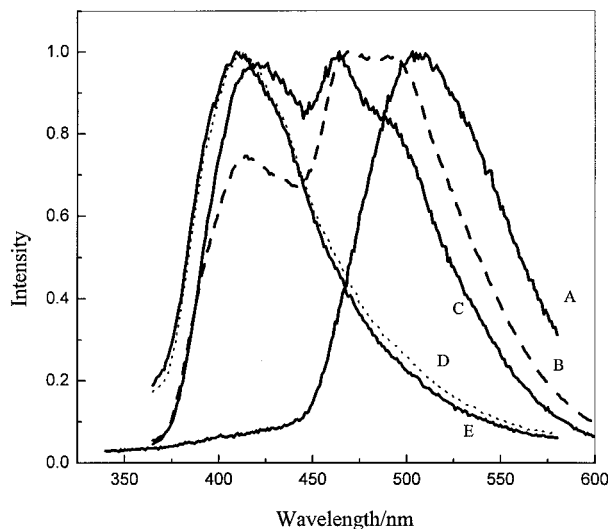
pristine O-PPV and O-PPV/PEO blends under the excitation wavelength of 300 nm and 350 nm, respectively. It is shown in Figure 4 that PL spectrum of pristine O-PPV is different from that of O-PPV/PEO blends. By decreasing the concentration of O-PPV in blends, the PL peak gradually moves to higher energy and finally stops at 416



**Figure 3** The solid-state optical spectra for pristine O-PPV and blends of O-PPV/PEO under the different weight ratios of O-PPV to PEO. (A) O-PPV; (B) O-PPV/PEO = 1 : 200; (C) O-PPV/PEO = 1 : 300.



**Figure 4** The normalized EL and PL spectra of O-PPV or O-PPV/PEO blends at 350 nm. (A) PL (O-PPV/PEO = 1 : 100); (B) PL (O-PPV/PEO = 1 : 200); (C) PL (O-PPV/PEO = 1 : 300, 1 : 400, 1 : 500); (D) EL (O-PPV).



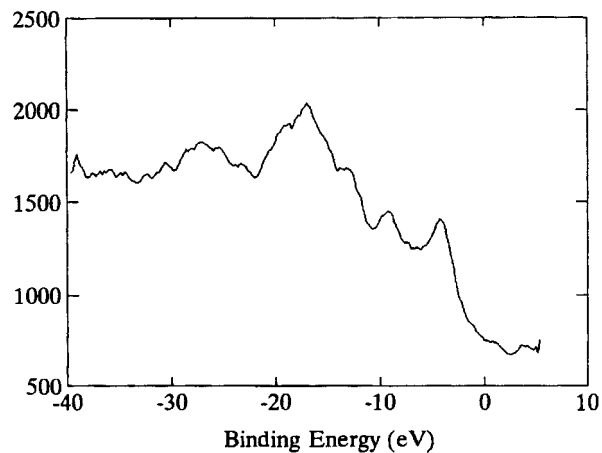
**Figure 5** Solid-state PL spectra normalized for ease of comparison at 300 nm under different weight ratios of O-PPV to PEO. (A) Pristine O-PPV; (B) O-PPV/PEO = 1 : 100 (dash); (C) O-PPV/PEO = 1 : 200; (D) O-PPV/PEO = 1 : 300 (dot); (E) O-PPV/PEO = 1 : 400 and 1 : 500.

nm. From Figures 4 and 5, we find that the properties of photoluminescence for the solid state of O-PPV/PEO blends have selection for excitation wavelength. The detailed research results about the interaction of interchain will be published in *Chem. Phys. Lett.*

### EL Properties of O-PPV

From Figure 4, it can be seen that the EL spectrum of the device (ITO/O-PPV/Al) fabricated with the oligo-PPV is the same as that of PL, which indicates that the light comes from the same material. The device (ITO/O-PPV/Al) emits green light ( $\lambda_{\max} = 509$  nm), whereas the LED constructed with PPV (ITO/PPV/Al) emits yellow light.<sup>1</sup> The most likely explanation of the difference is that a decrease in the conjugation length of the oligo-PPV increases the bandgap to values higher than that of PPV. XPS experimental result (as shown in Fig. 6) also shows that the energy bandgap of O-PPV is about 4.0 eV, which is higher than that of PPV (3.0 eV) reported by Karasz.<sup>8</sup> This is in agreement with the luminescence results.

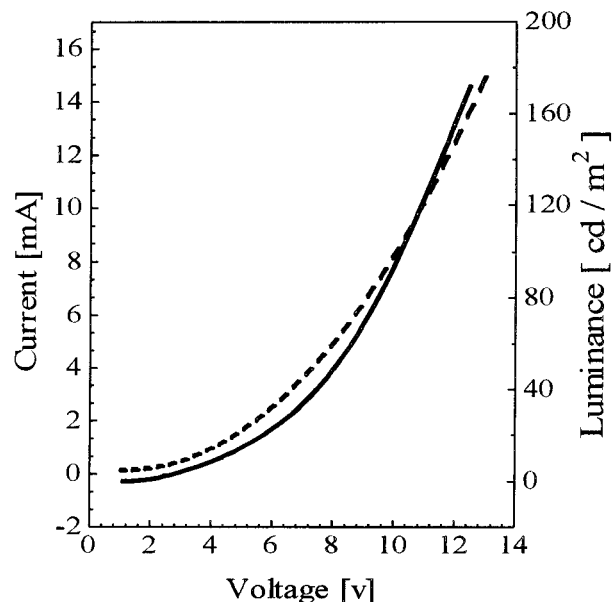
In comparison to the analogous single-layer device constructed with PPV (ITO/PPV/Al), which emits two peaks at  $\lambda = 520$  nm and 550 nm (shoulder),<sup>1</sup> the EL spectrum of the device (ITO/O-PPV/Al) is a broad peak at  $\lambda_{\max} = 509$  nm. The



**Figure 6** XPS spectrum of O-PPV.

difference is that the vinyene double bonds in the oligo-PPV are all *trans*-configuration (*E*), but there are both *trans*(*E*) and *cis*(*Z*) configurations in PPV. Moreover, the PL results have stated that the functions of electron wavefunctions coupled on the ground states of polymers also make the vibration energy be equalization.

From Figure 7, we know that the onset voltage is about 3 V, and the device exhibits an enhanced quantum efficiency (0.13%); thus the efficiency of ITO/PPV/Al is typically 0.001%. This is due to the introduction of electron-withdrawing oxadiazole units in the main chain of PPV, and it is proposed



**Figure 7** I-V (dash line) and B-V (solid line) curve of the device (ITO/O-PPV/Al).

that the electron/hole interactions in the intrachain of the oligo-PPV polymer make more balanced injection of charge carriers.

## CONCLUSIONS

We have reported a novel oligo-polymer in which oxadiazole units are incorporated in the polymer main chain that can be used as an electron transport layer in polymeric LEDs. The polymer is soluble and has good film-forming properties and excellent thermal stability. PL and adsorption results show that the electron interactions are in interchains of the polymer. A considerable increase of the quantum efficiency up to  $\eta = 0.13\%$  has been measured. A relatively balanced injection of charge carriers is suggested.

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