

# Synthesis and Light-Emitting Properties of New Poly(*p*-phenylenevinylene) Derivatives Containing Oxadiazole Moiety

Shu Wang,<sup>1</sup> Wenting Hua,<sup>1</sup> Xiaohong Chen,<sup>2</sup> Yanbing Hou<sup>2</sup>

<sup>1</sup> Department of Chemistry, Peking University, Beijing 100871, People's Republic of China

<sup>2</sup> Institute of Optoelectronic Technology, Northern Jiaotong University, Beijing 100044, People's Republic of China

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**ABSTRACT:** Two new poly(*p*-phenylenevinylene) (PPV) derivatives containing the oxadiazole moiety (OXA-PPV1 and OXA-PPV2) were synthesized by the Wittig condensation polymerization reaction and their thermal and light-emitting properties were investigated. The single-layer and triple-layer electroluminescent (EL) devices with configurations of ITO/OXA-PPV1/Al and ITO/OXA-PPV1/OXD/Alq<sub>3</sub>/Al were fabricated. They both exhibited blue emission at 460 nm. For comparison, the PPV derivative containing the oxadiazole moiety only in the side chains (OXA-PPV2) was also synthesized. Both single-layer and triple-layer EL

devices with OXA-PPV2 as the emissive layer emitted green-light at 560 nm. The turn-on voltages of the triple-layer device was 11 V for OXA-PPV1 and 8 V for OXA-PPV2. The triple-layer EL devices showed much better performance than that of the single-layer devices. The spectra indicated that energy or electron transfer occurred from the side-chain oxadiazole to the main-chain styrene unit. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2424–2428, 2002

**Key words:** poly(*p*-phenylenevinylene) derivatives; oxadiazole; electroluminescence

## INTRODUCTION

Since the first light-emitting diodes (LEDs) based on poly(*p*-phenylenevinylene) (PPV) were reported by Holmes et al.,<sup>1</sup> tremendous progress has been made in the discovery of new polymers and in the performance of the related LED devices. Multicolor display applications require at least three basic colors: red, green, and blue. Because blue electroluminescence (EL) is difficult to achieve with inorganic semiconductors, recent material research has been focused on the synthesis of polymers with large energy band gaps to emit blue light. An approach to the achievement of short-wavelength light-emitting polymers is to introduce well-defined lumophores to the polymer main chains. To prevent higher turn-on voltage, an alternative approach is to incorporate a nonconjugated rigid spacer into a rigid conjugated polymer backbone. In this article, we report on the synthesis of a new blue light-emitting polymer, OXA-PPV1, containing a macrocycle unit as a rigid spacer group. The oxadiazole moieties are included in the conjugated PPV main and side chains. For comparison, a similar green light-emitting polymer, OXA-PPV2, containing no oxadiazole moiety in the main chain, was also synthesized. Oxadiazole is known to be an electron-transporting

material as well as a thermally, hydrolytically, and photolytically stable material. In comparing OXA-PPV1 with OXA-PPV2, the use of the oxadiazole moiety in the main chain can shorten the effective conjugation length between a benzene ring and a vinyl double bond, which results in a blue shift in emission. Thus, we can effectively control the conjugated length of the polymer to tune the emitting color.

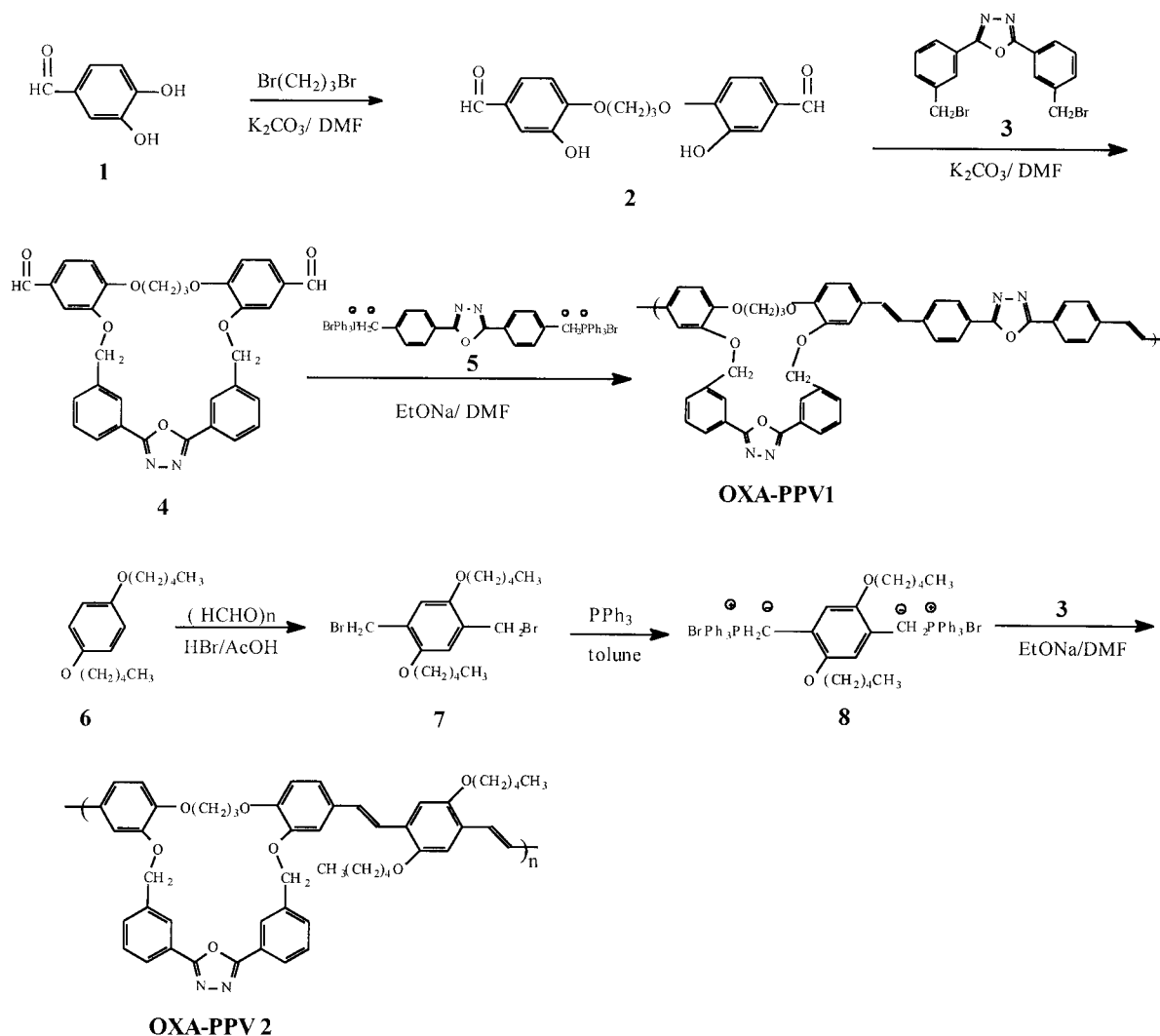
## EXPERIMENTAL

<sup>1</sup>H-NMR spectra were collected on a Bruker ARX 400 spectrometer. FTIR spectra were measured on a VG-ZAB-HS spectrometer. The UV-vis and fluorescence spectra were obtained on an HP8453 and Hitachi 4500 spectrometer, respectively. DSC was run on a DuPont DSC 2010 analyzer. GPC analyses were conducted with a Walter 2410 Model 515HPLC system using polystyrene as the standard and DMF as the eluant. The polymer films were prepared by spin casting from a chloroform solution containing polymers. OXD, Alq<sub>3</sub>, or Al was deposited on the top of the polymer films by vacuum evaporation at a pressure below  $3.0 \times 10^{-5}$  Torr, yielding an active area of 12.5 mm<sup>2</sup>. 2,5-Di(*m*-bromomethylphenylene)-1,3,4-oxadiazole 3,<sup>11</sup> compound 5,<sup>7</sup> and compound 6 (ref. 12) were prepared according to the literature processes.

## Compound 2

The mixture of 3,4-dihydroxybenzaldehyde (2.76 g, 0.02 mol), 1,3-dibromopropane (1.02 mL, 0.01 mol),

Correspondence to: W. Hua.



Scheme 1

and  $K_2CO_3$  (1.38 g, 0.01 mol) in 30 mL of DMF was refluxed under stirring for 8 h and then cooled to room temperature. The resulting mixture was poured into 100 mL of  $H_2O$ . After filtration, recrystallization from DMF/ $H_2O$ , and drying, a white crystal of 0.81 g (25.6%) was obtained; mp 217–218°C.

$^1H$ -NMR (DMSO- $d_6$ , ppm):  $\delta$  9.75 (d,2H), 9.49 (s,2H), 7.39 (q,2H), 7.27 (s,2H), 7.16 (d,2H), 4.29 (t,4H), 2.26 (t,2H); MS (EI): 316 ( $M^+$ ).

#### Macrocycle 4

The mixture of compound 2 (79 mg, 0.25 mmol), 2,5-di(*m*-bromomethylphenylene)-1,3,4-oxadiazole 3 (102 mg, 0.25 mmol), and  $K_2CO_3$  (35 mg, 0.25 mmol) in 30 mL of DMF was refluxed under stirring for 8 h and then cooled to room temperature. The resulting mixture was poured into 100 mL of  $H_2O$ . After filtration, recrystallization from  $CHCl_3$ /EtOH, and drying, a

white powder of 55 mg (39.2%) was obtained; mp 276–280°C.

IR ( $\nu/cm^{-1}$ ): 2720 (H—C=O), 1686 (C=O).  $^1H$ -NMR ( $CDCl_3$ , ppm):  $\delta$  9.92 (s,1H), 9.79 (s,1H), 8.11 (s,1H), 7.83–7.93 (d,2H), 7.59–7.68 (m,4H), 7.36–7.51 (m,3H), 7.00 (d,1H), 6.83 (d,1H), 5.72 (s,2H), 4.23 (br,2H), 4.01 (t,2H), 2.39 (t,2H); MS (FAB):563 ( $M+1$ ).

ANAL. Calcd for  $C_{33}H_{26}N_2O_7 \cdot 1 \cdot 5H_2O$ : C, 67.23%; H, 4.96%; N, 4.75%. Found: C, 67.06%; H, 4.97%; N, 5.22%.

#### Compound 7

To a mixture of compound 6 (3.8 g, 15.1 mmol) and paraformaldehyde (0.93 g, 31 mmol) in 50 mL of acetic acid, 33 wt % HBr in acetic acid (5.5 mL 32.2 mmol) was added dropwise under stirring. Subsequently, the mixture was stirred at 60–70°C for 2 h and then cooled to room temperature. The resulting solution was

poured into 400 mL of H<sub>2</sub>O, and a saturated solution of K<sub>2</sub>CO<sub>3</sub> was added to adjust the pH value in the range of 5–6. After filtration, washing with H<sub>2</sub>O, and recrystallization from EtOH, a slight yellow crystal of 5.03 g was obtained (76.0%): mp 79–80°C.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): δ 6.85 (s,2H), 4.53 (s,4H), 3.98 (t,4H), 1.81 (q,4H), 1.47 (m,4H), 1.36 (m,4H), 0.93 (t,6H).

### OXA-PPV 1

To a solution of compound 5 (326 mg, 0.36 mmol) in 30 mL of DMF was added, dropwise, an excess fresh solution of EtONa/EtOH. The mixture was stirred at room temperature for 0.5 h, and then the macrocycle 4 (200 mg, 0.36 mmol) was added batchwise. The mixture was refluxed under stirring for 6 h and then cooled to room temperature. The resulting solution was poured into 100 mL of H<sub>2</sub>O, and a 2N HCl solution was added to adjust the pH value in the range of 5–6. The precipitate was filtered and washed with H<sub>2</sub>O. The crude polymer was redissolved in 30 mL of DMF and poured into 100 mL of MeOH. The yellow solid was filtered, washed with MeOH, and dried at 40°C for 2 days. The polymer yield was 200 mg (71.6%).

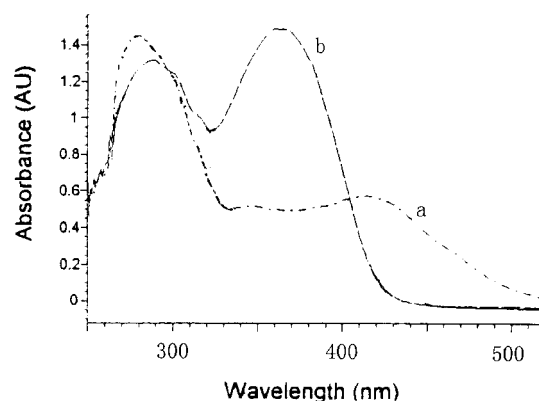
IR ( $\nu$ /cm<sup>-1</sup>): 1596 (C=N), 962 (*trans*-CH=CH). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, ppm): δ 6.65–8.09 (br,18H), 4.80–5.60 (br,4H), 2.17–2.33 (br,2H).

ANAL. Calcd for C<sub>49</sub>H<sub>36</sub>N<sub>4</sub>O<sub>6</sub>: C, 75.76%; H, 4.67%; N, 7.21%. Found: C, 69.67%; H, 4.80%; N, 7.32%.

### OXA-PPV 2

A solution of compound 7 (87.2 mg, 0.2 mmol) and Ph<sub>3</sub>P (110 mg, 0.2 mmol) in 20 mL of toluene was refluxed under stirring for 5 h. The solvent was removed by evaporation and 20 mL of DMF was added to obtain a red solution. To this solution, 80% EtONa (34 mg, 0.5 mmol) was added and stirred for 0.5 h, and then the macrocycle 4 (110 mg, 0.2 mmol) was added batchwise. The mixture was stirred and heated at 100°C for 8 h and then cooled to room temperature. The resulting solution was poured into 80 mL of MeOH and the crude polymer was filtered. The crude solid was redissolved in 20 mL of DMF and poured into 80 mL of MeOH again. The yellow solid was filtered, washed with MeOH, and dried at 40°C for 2 days. The polymer yield was 110 mg (62.8%).

IR( $\nu$ /cm<sup>-1</sup>): 1600 (C=N), 964 (*trans*-CH=CH). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, ppm): δ 7.87–8.09 (br, 4H), 7.32–7.66 (br, 8H), 6.50–7.25 (br,8H), 5.58–5.72 (br,4H), 3.57–4.26 (br,8H), 1.40–1.98 (br,14H), 0.70–0.93 (br,6H).



**Figure 1** UV-vis spectra of (a) OXA-PPV 2 and (b) OXA-PPV 1 in DMF.

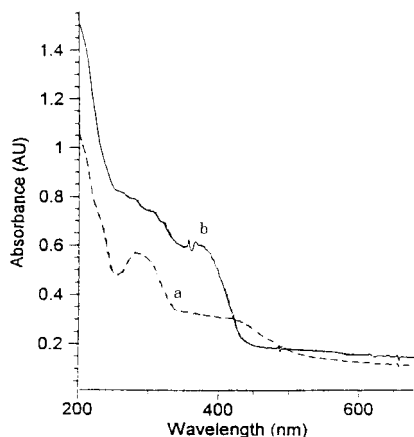
ANAL. Calcd for C<sub>51</sub>H<sub>52</sub>N<sub>2</sub>O<sub>7</sub>: C, 76.10%; H, 6.51%; N, 3.48%. Found: C, 72.82%; H, 6.97%; N, 3.57%.

## RESULTS AND DISCUSSION

The synthetic approach to title copolymers is sketched in Scheme 1. The macrocycle 3 was the key intermediate in the synthesis. It was obtained from a [1+1] cyclization reaction of compound 2 with 2,5-di(*m*-bromomethylphenylene)-1,3,4-oxadiazole in the presence of K<sub>2</sub>CO<sub>3</sub>. The copolymers were synthesized by the Wittig reaction. OXA-PPV2 was soluble in common organic solvents such as CHCl<sub>3</sub> and THF. OXA-PPV1 was partially soluble in these convenient solvents and it was soluble in DMF. The attachment of a pendent with long alkoxy chain made the OXA-PPV2 soluble and processable.

Comparison of the FTIR spectra of OXA-PPV1 and OXA-PPV2 to that of the monomer macrocycle 3 showed that the peaks at 1686 cm<sup>-1</sup>, corresponding to the aldehyde carbonyl stretching, decreased sharply and that weak new peaks at 962 cm<sup>-1</sup> (OXA-PPV1) and 964 cm<sup>-1</sup> (OXA-PPV2), corresponding to the *trans*-vinylene out-of-plane bending, appeared. This indicated that the polymerization reaction was successful. The molecular weight of the polymers was determined by GPC using polystyrene as a standard in DMF. OXA-PPV1 had a weight-average molecular weight ( $M_w$ ) of 40,900 with a polydispersity of 1.01; OXA-PPV2 had an  $M_w$  of 38,600 and a polydispersity of 1.03. OXA-PPV1 and OXA-PPV2 showed highly thermal stabilities below 300°C, and the DSC results indicated that their glass transition temperatures of were 118.8 and 68.1°C, respectively. OXA-PPV1 had a much higher glass transition temperature than that of OXA-PPV2. The results indicated that the introduction of the oxadiazole moiety in the polymer-main chain increased the rigidity of the polymer.

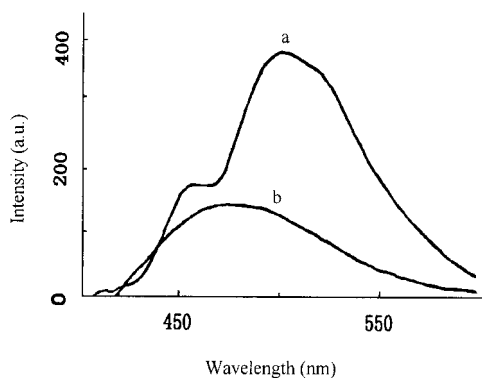
Figure 1 shows the UV-vis absorption spectra of OXA-PPV1 and OXA-PPV2 in DMF. They showed



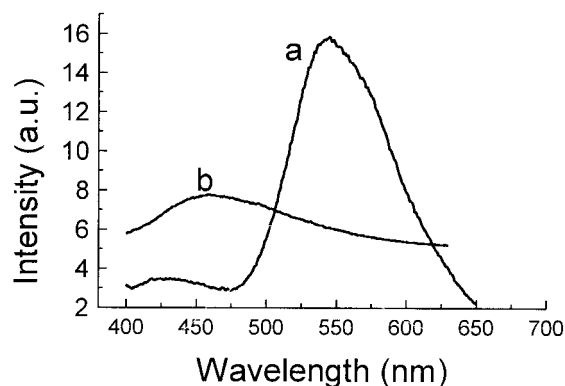
**Figure 2** UV-vis spectra of (a) OXA-PPV 2 and (b) OXA-PPV 1 thin film.

the maximum absorption wavelength ( $\lambda_{\max}$ ) at 365 and 414 nm, respectively. The maximum absorption peak of OXA-PPV2 was more red-shifted compared to that of OXA-PPV1, which was attributed to the introduction of the oxadiazole moiety in the polymer main chain. The  $\pi$ - $\pi^*$  band gaps of OXA-PPV1 and OXA-PPV2 were 2.82 and 2.48 eV, respectively, which were obtained from their film UV-vis absorption spectra (Fig. 2). This showed that the use of the oxadiazole moiety in the main chain enlarged the energy band gap.

The fluorescence spectra of OXA-PPV1 and OXA-PPV2 in the DMF solution exhibited maximum emission peaks at 471 nm (excitation at 417 nm) and 500 nm (excitation at 429 nm), respectively (Fig. 3). The fluorescence spectra of OXA-PPV1 and OXA-PPV2 films exhibited maximum emission peaks at 470 and 540 nm, respectively (Fig. 4). The maximum emission peak of OXA-PPV2 was more red-shifted compared to that of OXA-PPV1, due to the same reason as that in the absorption spectra. The fluorescence spectra for the solid films of OXA-PPV1 and OXA-PPV2 were very similar to those of the solutions except that the spectral



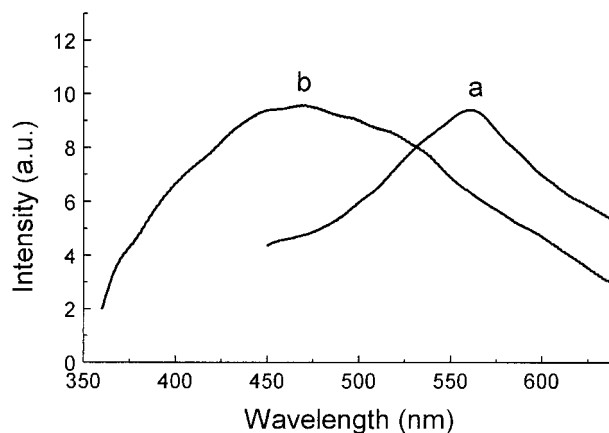
**Figure 3** Fluorescent spectra of (a) OXA-PPV 2 and (b) OXA-PPV 1 in DMF.



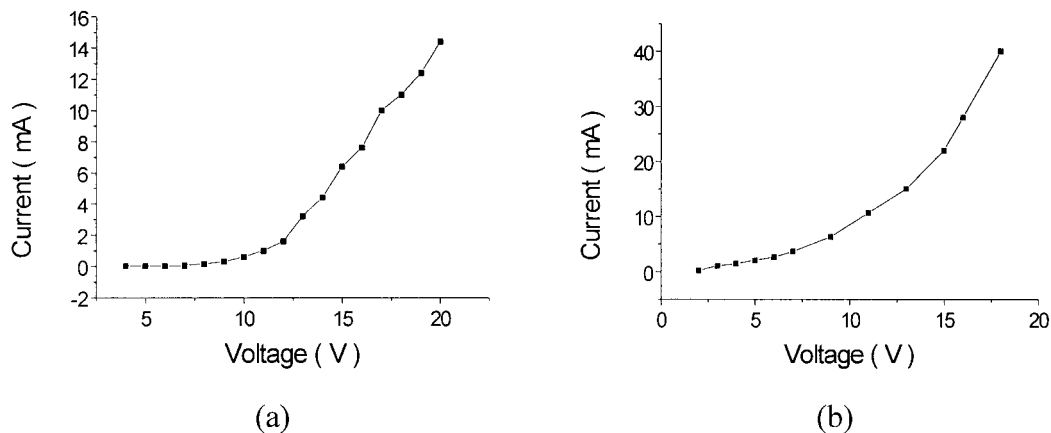
**Figure 4** Fluorescent spectra of (a) OXA-PPV 2 and (b) OXA-PPV 1 thin film.

peak of OXA-PPV2 is red-shifted. This indicated that the emission spectra of OXA-PPV1 and OXA-PPV2 were characteristic of an isolated polymer chain because the introduction of oxadiazole moieties or pendent groups containing a long alkoxy group in the side chain are expected to suppress chain aggregation in the solid states.

We note that the solution of 2,5-di(*m*-methylphenylene)-1,3,4-oxadiazole in DMF was excited at 321 nm; the fluorescence spectrum showed one emission band from 320 to 420 nm. The chemical structure of the luminary segment in the OXA-PPV1 side chain is similar to that of the luminary segment in 2,5-di(*m*-methylphenylene)-1,3,4-oxadiazole. However, in the fluorescence spectrum of the OXA-PPV1 solution, there was no emission band. The almost same emission spectra were obtained from OXA-PPV1 in the DMF solution excited at 321 or 429 nm. The same result was obtained from OXA-PPV2. These results indicated that the energy of the segments of the side chain possibly transfer to the segments of the polymer backbone. This energy transfer can be expressed in eq. (1). Here, Ps and Oxa stand for the styrene unit in

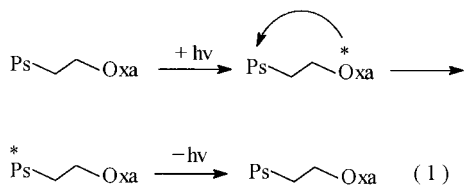


**Figure 5** EL spectra of ITO/polymer/OXD/Alq<sub>3</sub>/Al: (a) OXA-PPV 2; (b) OXA-PPV 1.



**Figure 6** Current–voltage characteristics of ITO/polymer/OXD/Alq<sub>3</sub>/Al; (a) OXA–PPV 2; (b) OXA–PPV 1.

main-chain and side-chain 2,5-diaryl-1,3,4-oxadiazole moiety, respectively:



Single-layer ITO/polymer/Al devices were fabricated with OXA–PPV1 and OXA–PPV2 as the emissive layers. When the devices were forward biased with the ITO electrode at positive polarity, blue and green EL were observed. However, the brightness of these devices was low and the EL was only visible in a dimly lit room. To improve the diode parameters, multilayer ITO/polymer/OXD/Alq<sub>3</sub>/Al devices were fabricated. As an electron-transport material, OXD-7 has a high glass transition temperature and good film-forming properties and a better ability of blocking hole carriers. The introduction of the buffer layer Alq<sub>3</sub> is to improve the contact between the electron-transport layer and the Al electron.

Figure 5 shows the I–V characteristics of the multilayer LEDs. They show typical rectifying diode characteristics. The emissions of the multilayer devices with OXA–PPV1 and OXA–PPV2 as emissive layers start at the driving voltages of 11 and 8 V, respectively. The EL spectra of multilayer devices are shown in Figure 6. They exhibited EL at 470 nm for OXA–PPV1 and at 560nm, respectively. The EL spectra resemble the solid-film PL spectra of OXA–PPV1 and OXA–PPV2. This indicated that the EL and PL originated from the same excited state.

The multilayer EL devices showed better performances than those of the single-layer devices. Combining the results of absorption, fluorescence, and EL spectra, we proposed one possible emission mechanism. Under the voltage, electrons from the Al cathode were injected into the  $\pi^*$  orbital (LUMO) of the side-chain oxadiazole moiety and holes from the ITO anode were injected into the  $\pi$  orbital (HOMO) of the main-chain styrene unit. Subsequently, an intramolecular electron transfer occurred. The holes and electrons recombined in the styrene unit to form excitons, which led to electroluminescence.

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