

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

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ABSTRACT: Two new poly(*p*-phenylenevinylene) (PPV) derivatives containing oxadiazole moiety (OXA-PPV1 and OXA-PPV2) were synthesized by the Wittig condensation polymerization reaction. Their thermal and light-emitting properties were investigated. The single- and triple-layer electroluminescent (EL) devices with configurations of ITO/polymer/Al and ITO/polymer/OXD-7/Alq₃/Al were fabricated. They exhibited blue emission at 470 nm for OXA-PPV1 and green emission at 560 nm for OXA-PPV2. The turn-on voltages of triple-layer device were 11 V for OXA-PPV1 and 8 V for OXA-PPV2. The triple-layer EL devices showed much better performance than did the single-layer devices. The spectra indicated energy transfer occurred from segments of side chain to polymer backbone. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 422–428, 2002

Key words: heteroatom-containing polymers; light-emitting diode; oxadiazole moiety; electroluminescent device

INTRODUCTION

Since the first light-emitting diodes (LEDs) based on poly(*p*-phenylenevinylene) (PPV) were reported by Holmes,¹ tremendous progress has been made in the discovery of new polymers and in the performance of the related LED devices.^{2–5} Multicolor-display applications require at least three basic colors: red, green, and blue. Because blue electroluminescence 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.^{6–9} An approach to achievement of short-

wavelength light-emitting polymers is to introduce well-defined lumophores to the polymer main chains.¹⁰ To prevent the higher turn-on voltage, an alternative approach is to incorporate nonconjugated rigid spacer into a rigid conjugated polymer backbone.^{11,12}

In this study 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. The oxadiazole is known to be an electron-transporting material as well as a thermally, hydrolytically, and photolytically stable material and many oxadiazole-containing polymers with en-

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hancing EL efficiencies have been investigated.^{13–16} The use of 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

Materials and Measurements

¹H-NMR spectra were obtained on a Bruker ARX 400 spectrometer (Bruker Instruments, Billerica, MA). FTIR spectra were measured on a VG-ZAB-HS spectrometer (VG Scientific). The UV-Vis and fluorescence spectra were obtained on an HP8453 (Hewlett-Packard, Palo Alto, CA) and Hitachi 4500 spectrometer (Hitachi, Tokyo, Japan), respectively. DSC was run on a DuPont DSC 2010 analyzer (DuPont, Wilmington, DE). 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 CHCl₃-DMF solution containing polymers. 1,3-Bis(4-*tert*-butylphenyl)-1,3,4-oxadiazole-phenylene (OXD-7) and tri(8-hydroxyquinoline) aluminum (Alq₃) or aluminum (Al) were deposited on the top of polymer films by vacuum evaporation at a pressure below 399.9×10^{-5} Pa, yielding an active area of 12.5 mm². Alq₃, 3,4-dihydroxy-benzaldehyde, 1,3-dibromopropane, and 33 wt % HBr in acetic acid were commercially obtained from Aldrich (Milwaukee, WI). 2,5-Bis(3-bromomethyl-phenylene)-1,3,4-oxadiazole,¹⁷ 2,5-bis[(4-triphenylphosphonium-methyl)phenylene]-1,3,4-oxadiazole bis-bromine,¹⁶ and 1,4-bis(pentoxyl)-phenylene **5**¹⁸ were prepared according to processes detailed in the literature.

Monomer Synthesis

Compound 2

A mixture of 3,4-dihydroxy-benzaldehyde (2.76 g, 0.02 mol), 1,3-dibromopropane (1.02 mL, 0.01 mol), and K₂CO₃ (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 H₂O. After filtration, recrystallization from DMF/H₂O, and drying, a white crystal of 0.81 g (25.6%) was obtained (m.p. 217–218°C).

¹H-NMR (DMSO-*d*₆, ppm) δ 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 3

A mixture of compound **2** (79 mg, 0.25 mmol), 2,5-di(*m*-bromomethyl-phenylene)-1,3,4-oxadiazole (102 mg, 0.25 mmol), and K₂CO₃ (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 H₂O. After filtration, recrystallization from CHCl₃/EtOH, and drying, a white powder of 55 mg (39.2%) was obtained (m.p. 278–280°C).

IR (ν /cm⁻¹): 2720 (H—C=O), 1686 (C=O); ¹H-NMR (CDCl₃, ppm) δ 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 C₃₃H₂₆N₂O₇·1.5H₂O: C, 67.23%; H, 4.96%; N, 4.75%. Found: C, 67.06%; H, 4.97%; N, 5.22%.

Compound 6

To a mixture of compound **5** (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 H₂O, and a saturated solution of K₂CO₃ was added to adjust the pH value in the range of 5 to 6. After filtration, washing with H₂O, and recrystallization from EtOH, a slightly yellow crystal of 5.03 g was obtained (76.0%) (m.p. 79–80°C).

¹H-NMR (CDCl₃, 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).

Polymer Synthesis

OXA-PPV1

To a solution of compound **4** (326 mg, 0.36 mmol) in 30 mL of DMF was added an excess fresh solution of EtONa/EtOH dropwise. The mixture was stirred at room temperature for 0.5 h, and then macrocycle **3** (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 H₂O, and 2N HCl solution was added to adjust the pH value in the range of 5 to 6. The precipitate was filtered and washed with H₂O. 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 (ν/cm^{-1}): 1596 (C=N), 962 (*trans* CH=CH); ¹H-NMR (DMSO-*d*₆, ppm) δ 6.65–8.09 (br, 18H), 4.80–5.60 (br, 4H), 2.17–2.33 (br, 2H). ANAL. calcd for C₄₉H₃₆N₄O₆: C, 75.76%; H, 4.67%; N, 7.21%. Found: C, 69.67%; H, 4.80%; N, 7.32%.

OXA-PPV2

A solution of compound **6** (87.2 mg, 0.2 mmol) and Ph₃P (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 get a red solution. To this solution, 80% EtONa (34 mg, 0.5 mmol) was added and stirred for 0.5 h, and then macrocycle **3** (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 again into 80 mL of MeOH. 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 (ν/cm^{-1}): 1600 (C=N), 964 (*trans* CH=CH); ¹H-NMR (DMSO-*d*₆, 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). ANAL. calcd for C₅₁H₅₂N₂O₇: C, 76.10%; H, 6.51%; N, 3.48%. Found: C, 72.82%; H, 6.97%; N, 3.57%.

RESULTS AND DISCUSSION

Syntheses and Characterizations

The synthetic approach to title copolymers is depicted in **Scheme 1**. 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*-bromomethyl-phenylene)-1,3,4-oxadiazole in the presence of K₂CO₃. The copolymers were synthesized by the Wittig reaction. OXA-PPV2 was soluble in common organic solvents such as CHCl₃ and THF. The OXA-PPV1 was partially soluble in these convenient sol-

vents, but it was completely soluble in DMF. The attachment of a pendent with a long alkoxy chain made the OXA-PPV2 soluble and processable.

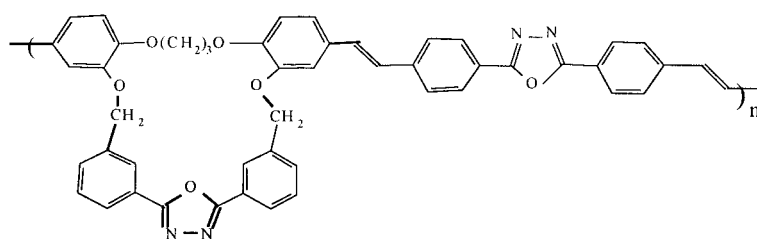
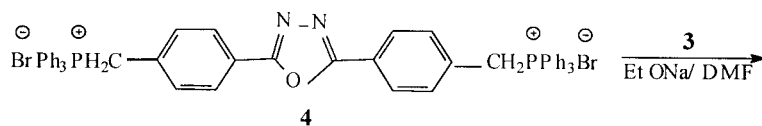
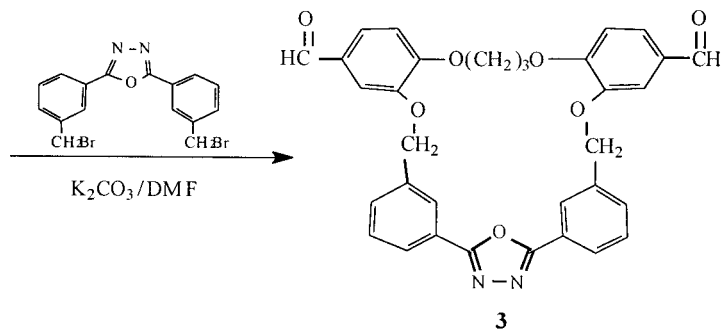
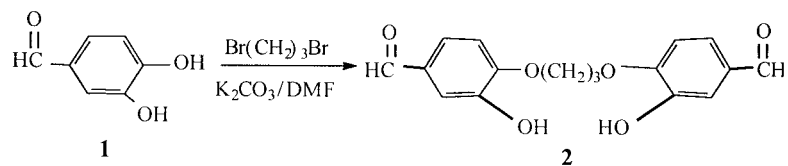
Comparison of the FTIR spectra of OXA-PPV1 and OXA-PPV2 to that of monomer macrocycle **3** showed that the peaks at 1686 cm⁻¹ corresponding to the aldehyde carbonyl stretching decreased sharply, and weak new peaks at 962 cm⁻¹ (OXA-PPV1) and 964 cm⁻¹ (OXA-PPV2) corresponding to the *trans*-vinylene out-of-plane bending appeared. This indicated that the polymerization reaction was successful. The molecular weights of the polymers were determined by GPC using polystyrene as standards in DMF. OXA-PPV1 had a weight-average molecular weight (*M*_w) of 40,900 with a polydispersity of 1.61, and OXA-PPV2 had *M*_w of 38,600 and a polydispersity of 1.73. OXA-PPV1 and OXA-PPV2 showed highly thermal stabilities below 300°C; the DSC results indicated their glass-transition temperatures 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 oxadiazole moiety in the polymer main chain increased the rigidity of the polymer.

Absorption and Fluorescence Spectra

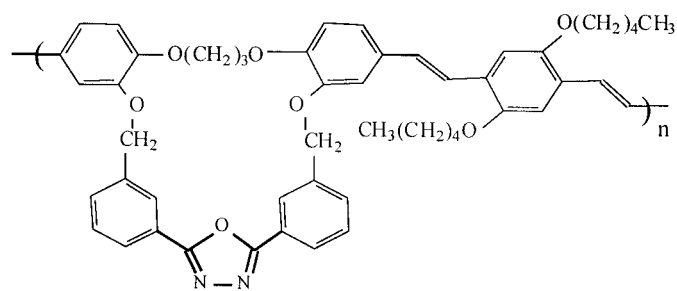
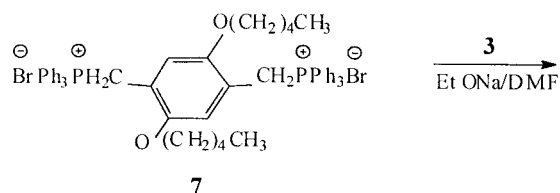
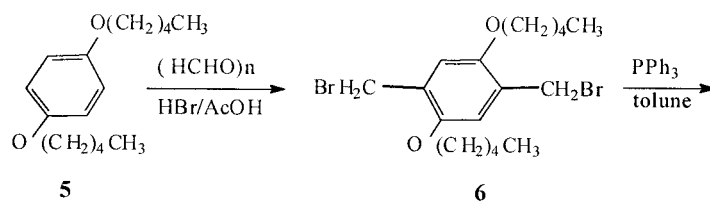
Figure 1 shows the UV-Vis absorption spectra of OXA-PPV1 and OXA-PPV2 in DMF, with the maximum absorption wavelength (λ_{max}) at 365 and 414 nm, respectively. The maximum absorption peak of OXA-PPV1 was more blue-shifted compared to that of OXA-PPV2, which was attributed to the introduction of oxadiazole moiety in the polymer main chain. The use of oxadiazole moiety in the main chain can shorten the effective conjugation length between a benzene ring and a vinyl double bond.

The π - π^* band gaps of OXA-PPV1 and OXA-PPV2 were 2.82 and 2.48 eV, respectively, obtained from their film UV-Vis absorption spectra (Fig. 2). This showed that the use of oxadiazole moiety in the main chain could enlarge the energy band gap.

The fluorescence spectra of OXA-PPV1 and OXA-PPV2 in 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-PPV1



OXA—PPV1



OXA—PPV2

Scheme 1

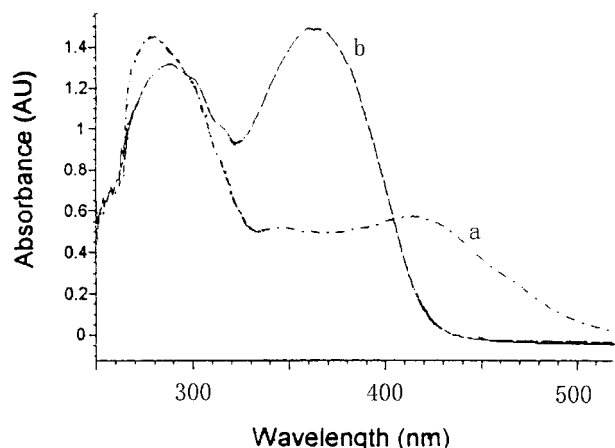


Figure 1 UV-Vis spectra of (a) OXA-PPV2 and (b) OXA-PPV1 in DMF.

was more blue-shifted compared to that of OXA-PPV2, also resulting from the introduction of oxadiazole moiety in the main chain. Thus, we can effectively control the conjugated length of the polymer to tune the emitting color. The fluorescence spectra for the solid films of OXA-PPV1 were very similar to those of the solutions. This indicated that the emission spectrum of OXA-PPV1 was characteristic of an isolated polymer chain because the introduction of oxadiazole moi-

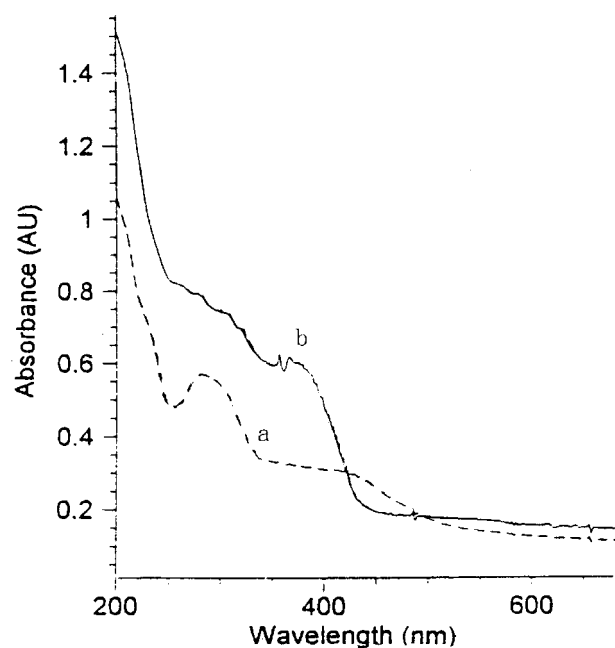


Figure 2 UV-Vis spectra of (a) OXA-PPV2 and (b) OXA-PPV1 thin film.

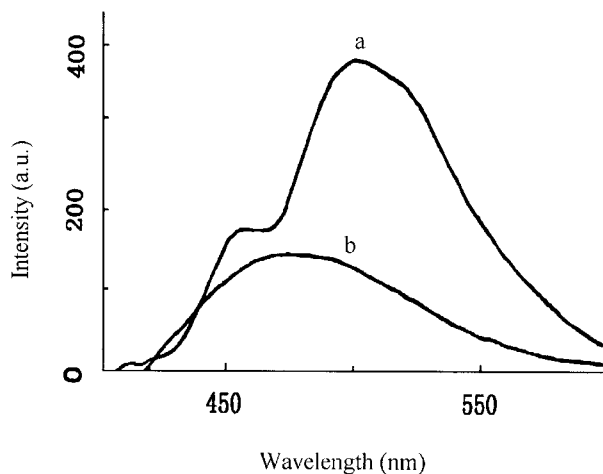


Figure 3 Fluorescent spectra of (a) OXA-PPV2 and (b) OXA-PPV1 in DMF.

eties in the side chain was expected to suppress chain aggregation in the solid states.¹⁹

We noted that when 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 OXA-PPV2 side chain was similar to that of the luminary segment in 2,5-di(3-methylphenylene)-1,3,4-oxadiazole. However, in the fluorescence spectrum of OXA-PPV2 solution, there was no emission band. Nearly identical emission spectra were obtained from OXA-PPV2 in DMF solution excited at 321 or 429 nm; the same result was obtained from OXA-PPV1. These results indicated that the energy of the side chain segments possibly transfers to the polymer backbone segments. This energy transfer could be expressed in eq. (1). Here, St and Oxa represent the styrene unit in the main chain and the side chain oxadiazole moiety, respectively.

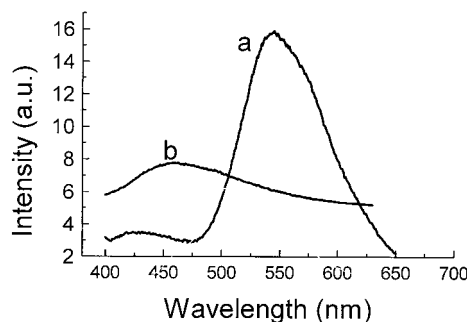


Figure 4 Fluorescent spectra of (a) OXA-PPV2 and (b) OXA-PPV1 thin films.

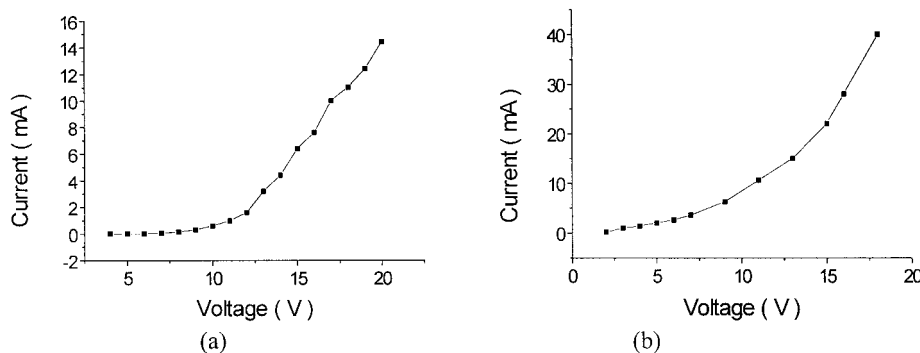
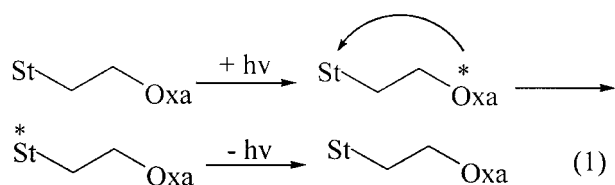


Figure 5 Current–voltage characteristics of ITO/polymer/OXD/Alq₃/Al: (a) OXA–PPV2; (b) OXA–PPV1.



Electroluminescent Properties

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 EL for OXA–PPV1 and green EL for OXA–PPV2 were observed. However, the brightness of these devices was low and the EL was visible only in a dimly lit room. To improve the diode parameters, the triple-layer ITO/polymer/OXD/Alq₃/Al devices were fabricated. As an electron-transport material, OXD-7 had a high glass-transition temperature, good film-forming properties, and better ability of blocking hole carriers. The introduction of the buffer layer Alq₃ was to improve the contact between the electron-transport layer and Al electrode. Figure 5 shows the *I*–*V* characteristics of the triple-layer LEDs, exhibiting typical rectifying diode characteristics. The emissions of the multilayer devices with OXA–PPV1 and OXA–PPV2 as emissive layers started at the driving voltages of 11 and 8 V, respectively. The electroluminescent spectra of triple-layer devices, shown in Figure 6, exhibited EL at 470 nm for OXA–PPV1 and 560 nm for OXA–PPV2, respectively. The EL spectra resembled the solid film PL spectra of OXA–PPV1 and OXA–PPV2, which indicated that the EL and PL originated from the same excited state. The triple-layer EL devices showed better performances than did the single-layer devices. Combining the results of absorp-

tion, fluorescence, and EL spectra, we proposed one possible EL emission mechanism. Under the voltage, electrons from the Al cathode were injected into the π^* orbital (LUMO) of side-chain oxadiazole moiety and holes from the ITO anode were injected into the π orbital (HOMO) of the main-chain styrene unit. Subsequently, an intramolecular energy transfer occurred. The holes and electrons recombined in the styrene unit to form excitons, which led to electroluminescence.

CONCLUSIONS

Two new PPV derivatives containing oxadiazole moiety were synthesized. The single- and triple-layer EL devices were successfully fabricated utilizing the new emissive materials OXA–PPV. The triple-layer EL devices showed much better performance than did the single-layer devices. The introduction of oxadiazole moiety in the polymer

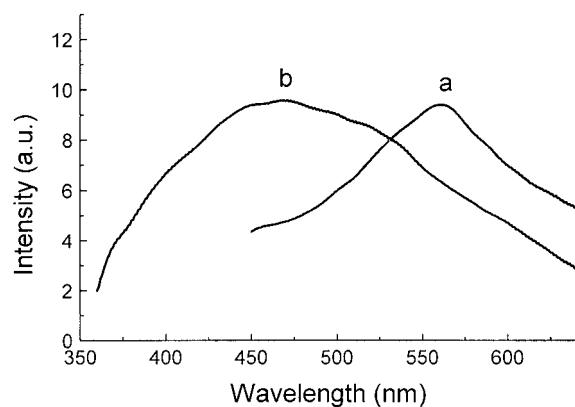


Figure 6 Electroluminescent spectra of ITO/polymer/OXD/Alq₃/Al: (a) OXA–PPV2; (b) OXA–PPV1.

main chain could effectively control the conjugated length of the polymer to tune the emitting color. The spectra indicated energy transfer occurred from segments of side chain to polymer backbone.

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