New Oxadiazole-Containing Conjugated Polymer for Single-Layer Light-Emitting Diodes

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Poly(phenylenevinylene)s (PPVs) containing rigid oxadiazole units as main chain substituents were synthesized. The electron-deficient oxadiazole moieties are directly attached to the phenyl rings of PPVs to increase the electron-injection properties of the polymers. In addition, the near-orthogonal arrangement of the PPV backbone and the oxadiazole units helps to limit the π-stacking of the emissive units, thus increasing the radiative decay quantum yield and photostability of the polymer. These polymers have shown good electron injection/transport ability and luminescence properties. Single-layer LED devices with the configuration ITO/polymer/Al show external quantum efficiencies up to 0.045%.

Introduction

The discovery of polymer light-emitting diodes (LEDs) in 1990[1] has stimulated an enormous amount of research in the field of polymer LEDs.[2−6] Compared to conventional semiconductor LEDs, polymer LEDs offer a variety of advantages, such as low fabrication cost, excellent mechanical properties, and tunable emission colors. It is widely expected that polymer LEDs will have a significant impact on display technologies.

The light emission from a polymer LED comes from the radiative decay of excitons resulting from the recombination of electrons and holes injected from the electrodes. An efficient LED device thus requires balanced injection and transport of both electrons and holes. However, most of the conjugated polymers developed so far transport electrons much less efficiently than holes,[7,8] which significantly decreases the efficiency of the device. Although a multilayer device structure, comprised of an emissive polymer layer plus separate layers to facilitate electron and hole transport, does significantly improve the device efficiency,[1,9−13] fabrication of such a multilayer device is often tedious, difficult, and may be significantly more expensive than single-layer devices. An alternative approach, using polymer blends to balance the charge injection and transport, is rather successful in fabricating efficient single-layer devices.[14] However, the immiscibility of different components often results in phase separation and reduces the device lifetime.

It has been reported that introduction of oxadiazole units into the side chain[15] or the main chain[16,17] of poly-(phenylenevinylene)s (PPVs) could significantly improve their LED device efficiency. In our recent studies, we have designed and synthesized PPVs containing rigid oxadiazole units as main chain substituents. The oxadiazole moieties were directly linked to the phenyl rings of a PPV so that the electron affinity of the polymer could be improved.[18,19] In addition, the near-orthogonal arrangement of the rigid oxadiazole units and the PPV backbone may limit the π-stacking, thus increasing the radiative decay quantum efficiency and photostability of the polymers.[19,20]

Experimental Section

The *p*-divinylbenzene[21] and 2,5-didodecyloxy-1,4-diiodobenzene[22] were synthesized according to the literature procedures. All of the other chemicals were purchased from the Aldrich

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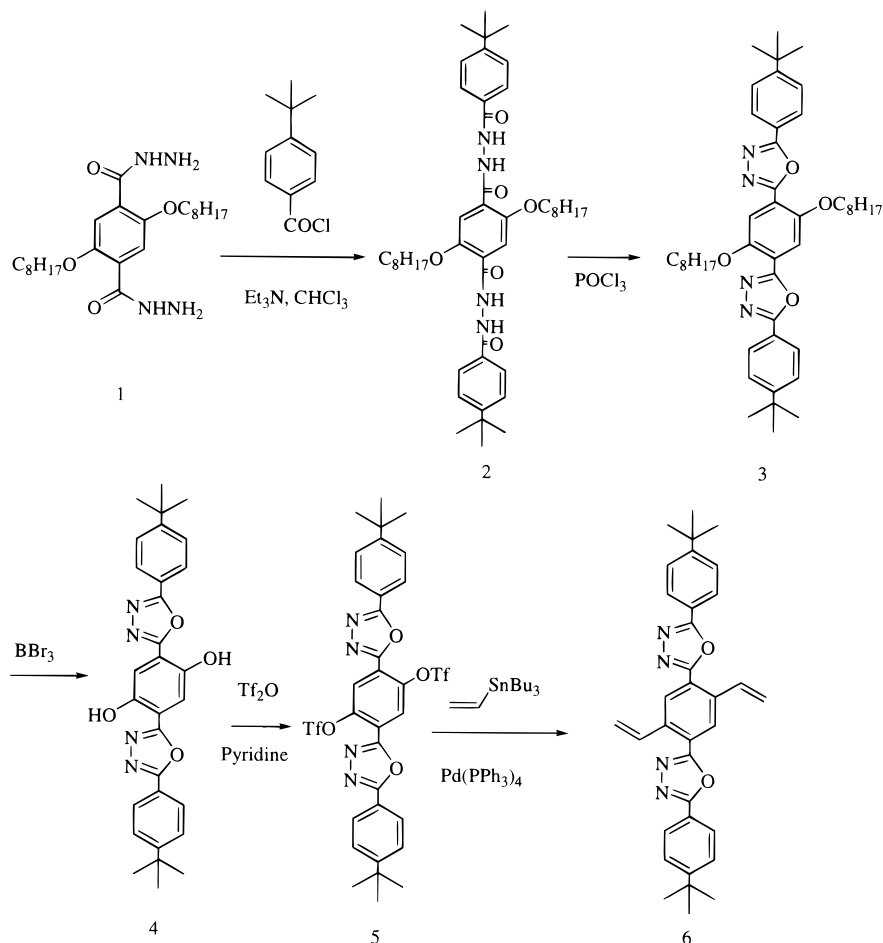
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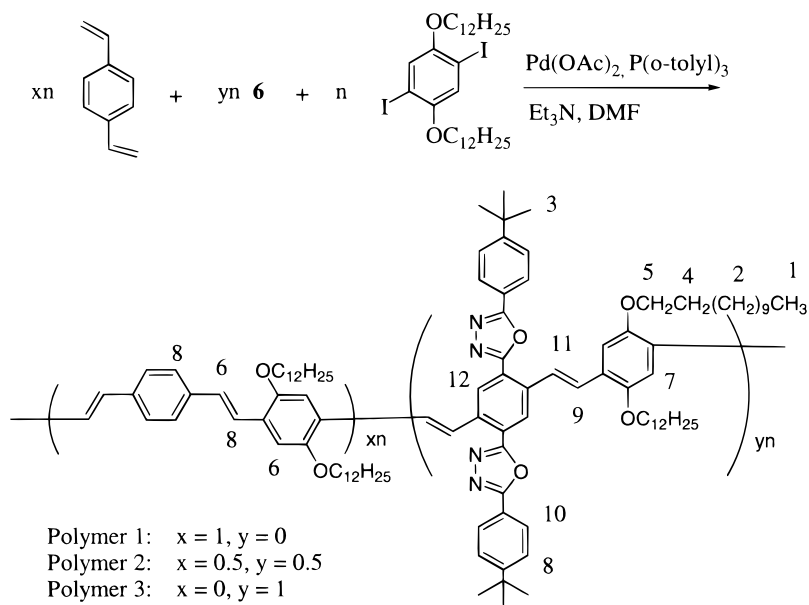
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Scheme 1. Synthesis of the Monomer

Scheme 2. Syntheses of the Polymers

Polymer 1:   x = 1, y = 0
Polymer 2:   x = 0.5, y = 0.5
Polymer 3:   x = 0, y = 1

Chemical Co. and were used as received unless otherwise stated. The synthetic schemes for the monomer and polymers are shown in Schemes 1 and 2.

Compound 1 was synthesized according to a literature procedure.[23] Mp: 99−99.5 °C. ^{1}H NMR (CDCl$_3$, ppm): δ 0.88 (t, J = 6.77 Hz, 6 H, CH$_3$), 1.33 (m, 16 H, aliphatic protons),

1.47 (t, J = 7.53 Hz, 4 H, aliphatic protons), 1.88 (t, J = 7.33 Hz, 4 H, aliphatic protons), 4.17 (t, J = 6.72 Hz, 8 H, OCH$_2$ and NH$_2$), 7.84 (s, 2H, aromatic protons), 9.21 (s, 2 H, CONH).

Compound 2. An 18.33 g portion of 4-*tert*-butylbenzoyl chloride (0.0932 mol) in CHCl$_3$ (50 mL) was added dropwise into a CHCl$_3$ solution (250 mL) of compound **1** (21.00 g, 0.0466 mol) and triethylamine (9.41 g, 0.0932 mol) at room temperature. The resulting mixture was stirred for 1 h. The solvent was then stripped off. After washing with water, the residue

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solid was collected by filtration and recrystallized from methanol/CHCl₃ to yield 34.00 g of product (95%, mp 147.5−148 °C). ¹H NMR (CDCl₃, ppm): δ 0.85(t, J = 6.62 Hz, 6 H, CH₃), 1.33 (m, 34 H, aliphatic protons), 1.51 (t, J = 7.61 Hz, 4 H, aliphatic protons), 2.06 (t, J = 7.20 Hz, 4 H, aliphatic protons), 4.23 (t, J = 6.75 Hz, 4 H, OCH₂), 7.47 (d, J = 8.42 Hz, 4 H, aromatic protons), 7.82 (d, J = 8.35 Hz, 4 H, aromatic protons), 7.86 (s, 2 H, aromatic protons), 9.71 (t, J = 7.74 Hz, 2 H, CONH), 11.36 (d, J = 7.78 Hz, 2H, −CO−NH-).

Compound 3. A mixture of compound **2** in 300 mL of POCl₃ was refluxed for 6 h. The resulting clear greenish solution was distilled to strip off the excess POCl₃. The residue solid was filtered and washed first with 1 M NaOH solution and then with water. It was further purified by recrystallization from CHCl₃/MeOH (25.2 g, colorless plate crystal, 94.4%, mp 173−174 °C). Anal. Calcd for C₄₆H₆₂N₄O₄: C, 75.16; H, 8.50; N, 7.62. Found: C, 74.93; H, 8.53; N, 7.49. ¹H NMR (CDCl₃, ppm): δ 0.86 (t, J = 6.73 Hz, 6 H, CH₃), 1.28 (m, 16 H, aliphatic protons), 1.40 [s, 18 H, (CH₃)₃], 1.57 (m, 4 H, aliphatic protons), 1.98 (t, J = 7.49 Hz, 4 H, aliphatic protons), 4.31 (t, J = 6.19 Hz, 4 H, OCH₂), 7.66 (d, J = 8.46 Hz, 4 H, aromatic protons), 7.92 (s, 2 H, aromatic protons), 8.17 (d, J = 8.46 Hz, 4 H, aromatic protons).

Compound 4. BBr₃ (75 mL) was added dropwise to a solution of compound **3** (14 g, 19 mmol) in 70 mL of CH₂Cl₂ at −75 °C. The resulting solution was stirred at room temperature for 3 h. The initial suspension changed to clear orange solution shortly after the addition of BBr₃. Yellow solid started to precipitate out after stirring about half an hour at room temperature. Water was added slowly to the reaction mixture. The crude product was collected by filtration and purified by recrystallization from CHCl₃/MeOH to give 7.0 g of product, a light yellow powder (72%, melting not observed up to 300 °C). Anal. Calcd for C₃₀H₃₀N₄O₄: C, 70.57; H, 5.92; N, 10.97. Found: C, 68.40; H, 5.88; N, 10.51. ¹H NMR (CDCl₃, ppm): δ 1.39 [s, 18 H, (CH₃)₃], 7.60 (d, J = 7.61 Hz, 4 H, aromatic protons), 8.15 (d, J = 8.35 Hz, 4 H, aromatic protons), 8.49 (s, 2H, aromatic protons).

Compound 5. Trifluoromethanesulfonic anhydride (5.60 g, 19.8 mmol) was added dropwise into a pyridine solution (10 mL) of compound **4** (4.00 g, 7.83 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 3 h and then poured into water. The crude product was collected by filtration and purified by recrystallization from CHCl₃/MeOH to yield 5.30 g of product, colorless needle crystals (85%, mp 234−235 °C). Anal. Calcd for C₃₂H₂₈N₄O₈S₂F₆: C, 49.61; H, 3.64; N, 7.23. Found: C, 49.27; H, 3.73; N, 7.06. ¹H NMR (CDCl₃, ppm): δ 1.39 [s, 18 H, (CH₃)₃], 7.60 (d, J = 7.61 Hz, 4 H, aromatic protons), 8.15 (d, J = 8.35 Hz, 4 H, aromatic protons), 8.49 (s, 2 H, aromatic protons).

Compound 6. The mixture of compound **5** (5.30 g, 7.61 mmol), tributyl(vinyl)tin (5.00 g, 15.8 mmol), Pd(PPh₃)₄ (0.36 g, 0.31 mmol), LiCl (1.94 g, 45.8 mmol), and dioxane (30 mL) was stirred at 90 °C for 9 h. After cooling to room temperature, the mixture was poured into water. The aqueous layer was decanted and the sticky residue was dissolved in CH₂Cl₂. After washing with water three times, the organic layer was collected, dried with MgSO₄, and concentrated by evaporation of the solvent. Product precipitates out after addition of methanol to the concentrated solution. The product was collected by filtration and purified by recrystallization from CHCl₃/MeOH to yield 2.40 g of pure product, a light yellow powder (66%, mp 244−245 °C). Anal. Calcd for C₃₄H₃₄N₄O₂: C, 76.95; H, 6.46; N, 10.56. Found: C, 77.03; H, 6.48; N, 10.44). ¹H NMR (CDCl₃, ppm): δ 1.39 [s, 18 H, (CH₃)₃], 5.59 (d, J = 11.44, 2 H, vinyl protons), 5.95 (d, J = 16.90 Hz, 2 H, vinyl protons), 7.60 (d, J = 8.59 Hz, 4 H, aromatic protons), 7.75 (dd, 2 H, vinyl protons), 8.10 (d, J = 8.48 Hz, 4 H, aromatic protons), 8.36 (s, 2 H, aromatic protons).

Polymerization. A typical polymerization procedure is exemplified by that of polymer **2**.[23,25,26] A mixture of compound

6 (0.3000 g, 0.5653 mmol), *p*-divinylbenzene (0.0736 g, 0.5653 mmol), 2,5-didodecyloxy-1,4-diiodobenzene (0.7896 g, 1.1306 mmol), Pd(OAc)₂ (0.010 g, 0.0445 mmol), tri-*o*-tolylphosphine (0.0680 g, 0.2234 mmol), triethylamine (0.4 mL), and DMF (10 mL) was stirred at 85 °C for 5 h. The hot solution was poured into methanol and the polymer precipitated as a red solid. The polymer was collected by filtration. To purify the polymer, it was redissolved in hot THF. After filtration, the filtrate was poured into methanol. The polymer was collected by filtration and dried under vacuum at 50 °C overnight. ¹H NMR (CDCl₃, ppm, the numbering refers to Scheme 2): δ 0.87 (b, H₁), 1.26 (b, H₂), 1.36 (b, H₃), 1.85 (b, H₄), 4.00 (b, H₅), 5.50 (d, vinyl protons), 5.59 (d, vinyl protons), 7.10 (b, H₆), 7.26 (b, H₇), 7.48 (b, H₈), 7.70 (m, H₉), 8.10 (b, H₁₀), 8.22 (m, H₁₁), 8.50 (m, H₁₂). Anal. Calcd for C₅₂H₇₂N₂O₃: C, 80.78; H, 9.39; N, 3.62. Found: C, 77.33; H, 8.79; N, 3.46.

Polymer 3. ¹H NMR (CDCl₃, ppm): δ 0.87 (b, H₁), 1.26 (b, H₂), 1.36 (b, H₃), 1.85 (b, H₄), 4.00 (b, H₅), 5.50 (d, vinyl protons), 5.59 (d, vinyl protons), 7.26 (b, H₇), 7.48 (b, H₈), 7.70 (m, H₉), 8.10 (b, H₁₀), 8.22 (m, H₁₁), 8.50 (m, H₁₂). Anal. Calcd for C₆₄H₈₄N₄O₄: C, 78.97; H, 8.70; N, 5.76. Found: C, 75.79; H, 8.32; N, 5.68.

Polymer 1. ¹H NMR (CDCl₃, ppm): δ 0.87 (b, H₁), 1.35 (b, H₂), 1.85 (b, H₄), 4.05 (b, H₅), 7.10 (b, H₆), 7.48 (b, H₈). Calcd. for C₄₀H₆₀O₂: C, 83.86; H, 10.56. Found: C, 82.76; H, 10.12.

Results and Discussion

The key monomer to synthesis of the targeted polymers is the oxadiazole compound with divinyl functional groups. The synthesis of this compound is shown in Scheme 1. Starting from cCompound **1**, which was synthesized according to a literature procedure,[24] compound **3** was synthesized using traditional synthetic procedures to yield 1,3,4-oxadiazoles. After obtaining compound **4**, which possesses two hydroxy groups, compound **5** was then synthesized by converting the two hydroxy groups to two triflates. The desired monomer **6** is finally obtained using the Stille coupling reaction. Good yields are obtained in each step. The overall yield of the synthesis of compound **6** is over 35%, starting from compound **1**. It is worth mentioning that compound **5** is also a valuable monomer that can be used to synthesize other conjugated polymers such as poly-(phenylenethiophene)s.[27]

The syntheses of the polymers are shown in Scheme 2. Three polymers were synthesized. Polymers **1** and **3** are homopolymers while polymer 2 is a random copolymer. All these polymers are soluble in common organic solvents such as chloroform, THF, and DMF. Gel permeation chromatography (GPC) measurements, which were performed at 30 °C using polystyrene as standard and THF as the eluent, indicated that polymers **1**−**3** have number-average molecular weights of 23K, 16K, and 25K Da with polydispersities of 2.35, 3.21, and 2.97, respectively. Polymers **2** and **3** are red-colored, while polymer **1** is yellowish-brown.

The UV−vis spectra of these polymers are shown in Figure 1. Polymers **2** and **3** show two strong absorption peaks: the one at ca. 465 nm is the absorption of the PPV backbone, while the other absorption peak at 320 nm can be assigned to the conjugated oxadiazole unit (the phenyl−oxadiazole−phenyl−oxadiazole−phenyl con-

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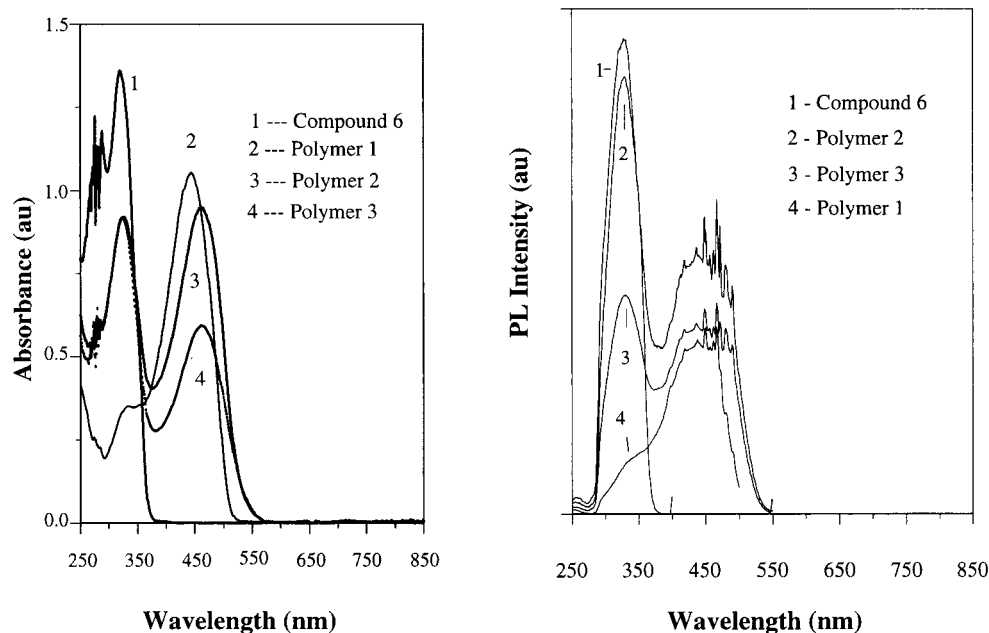(27) Bao, Z.; Chan, W. K.; Yu, L. *Chem Mater.* **1993**, *6*, 2.

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Figure 1. UV–vis (left) and excitation (right) spectra of polymers in dilute THF solutions. The following emission wavelengths were used to obtain the excitation spectra: 400 nm for compound **6**, 520 nm for polymer **1**, and 550 nm for polymers **2** and **3**.

jugated unit). The absorption strength is obviously correlated with the concentration of the oxadiazole moieties in the polymers. Compared to polymer **1**, the absorption maxima of the PPV backbones in polymers **2** and **3** are red-shifted by about 20 nm. The edge of the absorption, however, had larger shifts of 30 and 40 nm, respectively. On the basis of the absorption band edges, the band-gap energies of polymers **1–3** are 2.44, 2.30, and 2.26 eV, respectively. The absorption maxima of the oxadiazole units before and after the polymerization are almost identical. These results imply that, in dilute solutions, the electronic interactions between the oxadiazole units and the PPV backbone are rather limited. Apparently, the oxadiazole rings are twisted away from the plane of the conjugated backbone.

All these polymers are highly fluorescent. When polymer films are excited at 460 nm, both polymers **2** and **3** show one broad emission peak at 640 nm (Figure 2). In dilute THF solutions, both polymers show an emission maximum of 550 nm. Emissions from the oxadiazole unit at 395 nm are not observed, even when polymers are excited at 320 nm, where oxadiazole units absorb strongly. As shown in Figure 1, the excitation spectra of the polymers are almost identical to their absorption spectra, indicating the existence of efficient energy transfer from the oxadiazole moiety to the PPV backbone.

Single-layer LED devices were made by spin-coating the polymer solution (20 mg of polymer in 1 mL of tetrachloroethane, spin rate 1000 rpm) onto ITO-coated glass substrates (sheet resistance of ITO is about 20 Ω). A 1000 Å thick layer of aluminum or 1000 Å of calcium covered with 500 Å of Al was then deposited under vacuum (2×10^{-6} Torr, 5–10 Å/s deposition rate). An HP 4155A semiconductor parameter analyzer with a calibrated silicon photodiode detector was used to measure the LED performance (I–V and EL–V curves). The evaluation of the LED devices was done under ambient conditions. The external quantum efficiency was calculated on the basis of the EL intensity and
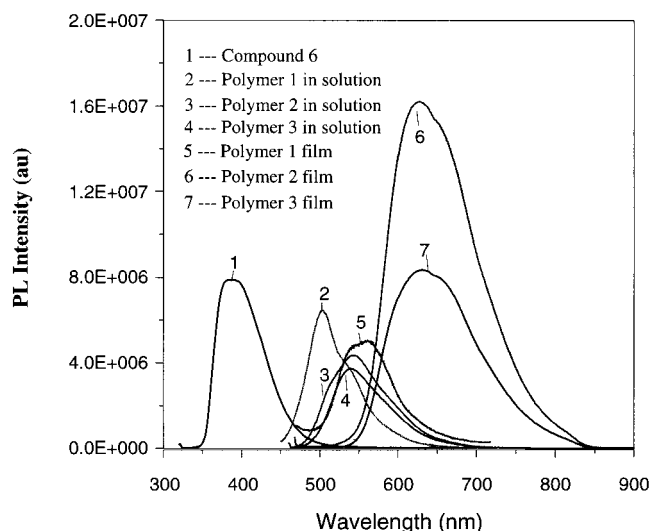

Figure 2. Fluorescence spectra of polymers in THF solutions and as solid films. Compound **6** was excited at 320 nm and Polymers **1–3** were excited at 460 nm in both solutions and films.

Table 1. External Efficiencies of Single-Layer Polymer LEDs

polymer	ITO/polymer/Al		ITO/polymer/Ca	
	η, %	$V_{on}/V\,(V_{on}'/V)^a$	η, %	V_{on}/V
1	0.002	15 (10)	0.01	10
2	0.018	10 (8.5)	0.068	7.5
3	0.041	8 (8)	0.066	7.5

^{a} V_{on} is the turn-on voltage of light with V_{on}' the turn-on voltage of current.

electric current running through the device without any correction. Devices of all three polymers were fabricated under the same conditions. The external efficiencies and turn-on voltages of these polymer devices are listed in Table 1.

Devices based on both polymers **2** and **3** show uniform red-orange emission, easily observable under normal room light, under forward bias. As shown in Figure 3,
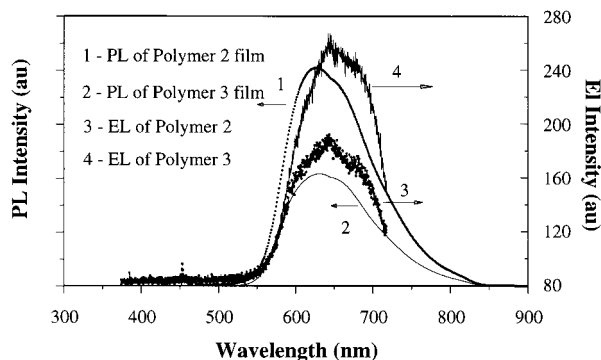
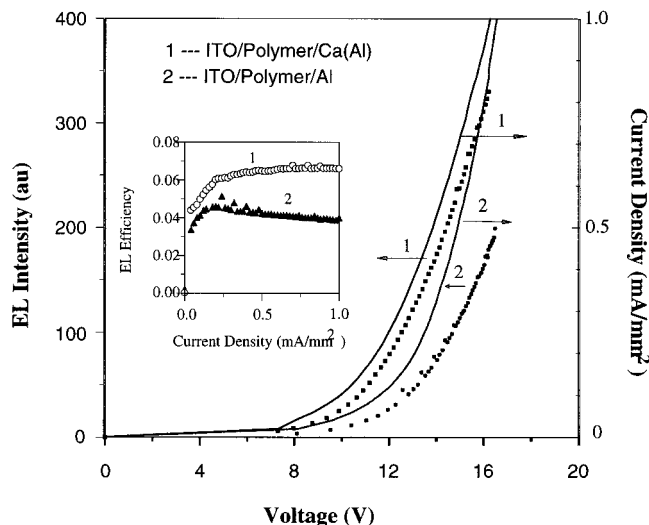**Figure 3.** Electroluminescence spectra of the polymers.

Figure 4. Current−voltage (solid line) and light−voltage (dotted line) characteristics of single-layer LED devices fabricated with polymer **3**. The inset is the curves of external efficiencies over current densities.

their EL spectra are almost identical to their PL spectra, indicating that the same radiative excited states are involved in both EL and PL processes.[28]

Figure 4 shows the current−voltage (solid line) and light−voltage (dotted line) characteristics of single-layer LED devices fabricated with polymer **3**. With Al as the cathode, the devices show external efficiencies of 0.041% at current density of 1 mA/mm^2, which is 20 times higher than that of PPV polymer **1**. The efficiency decreases slightly when the current density increases, as shown in the inset of Figure 4. The highest efficiency of 0.045% was obtained at a current density of 0.3 mA/mm^2. The devices also show similar turn-on voltage (8 V) for both the light and the current, indicating a reasonably balanced charge injection. The device can sustain current densities as high as 10 mA/mm^2 (not shown in the figure), where the brightness of the device is 1160 cd/m^2, calculated on the basis of the EL spectra, the relative sensitivity of a normal eye to light of varying wavelengths, and the measured output light intensity. With Ca as the cathode, a higher efficiency (0.066%) and a slightly lower turn-on voltage were obtained. The external efficiency increases slightly when the current density increases, which is in contrast with the Al devices. This may be related to the different polymer−
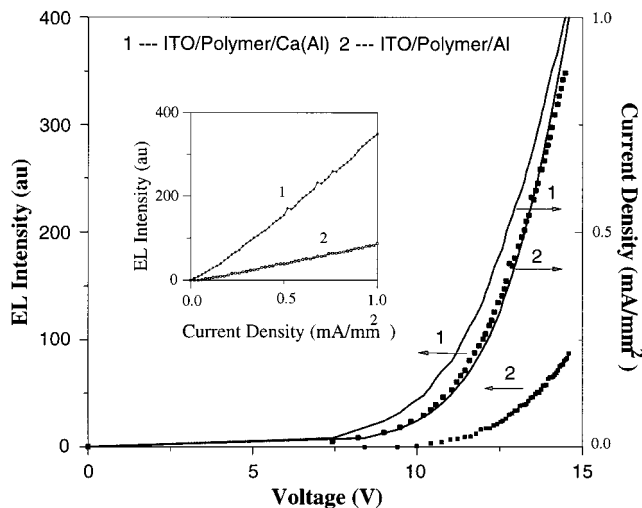

Figure 5. Current−voltage (solid line) and light−voltage (dotted line) characteristics of single-layer LED devices fabricated with polymer **2**. The inset is the light−current plot.

Ca and polymer−Al interlayers.[29,30] The exact reason is unclear at this moment.

Device characteristics of polymer **2** are shown in Figure 5. Polymer **2**, which has half the oxadiazole content as that of polymer **3**, gives less efficient devices (0.018%) when Al is used as the cathode. However, the efficiency is still 1 order of magnitude higher than that of PPV polymer **1**. With Ca as the cathode, polymer **2** shows the same EL efficiency as polymer **3**. From Al cathode to Ca cathode, the improvement in efficiency is 61% for polymer **3** and 280% for polymer **2**. These results indicate two points: (1) The electron injection properties are improved from polymer **1** to **2** and to **3**. (2) The balanced injection of both charge carriers has yet to be achieved even in polymer **3**. This may be due to the limited electronic interactions of the cross-conjugated oxadiazole units with the conjugated backbone. The LED efficiencies of Polymers **2** and **3** are higher than that of side chain oxadiazole PPVs[15] but lower than that of main chain oxadiazole PPVs.[16,17] This seems consistent with the strength of electronic interactions between oxadiazole units and the conjugated backbones in these different types of oxadiazole-containing PPVs.

The number of oxadiazole units in the polymer affects not only the device efficiency but also the turn-on voltages. As shown in Table 1, the turn-on voltage decreases when the number of oxadiazole units in the polymer increases, especially with Al as the cathode. For polymer **3**, similar turn-on voltages were observed for both Al and Ca cathodes.

Conclusions

A new type of oxadiazole-containing conjugated polymer has been synthesized. These polymers possess improved electron injection/transport properties. Efficient single-layer LED devices with Al as the cathode can be fabricated from these polymers.

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CM981087E