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## Novel Oxadiazole Side Chain Conjugated Polymers as Single-Layer Light-Emitting Diodes with Improved Quantum Efficiencies

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Tremendous advancement has been achieved in the field of organic and polymeric electronics and optics in recent years.[1,2] Interesting applications, such as thin film field-effect transistors,[3−6] photovoltaics,[7] and light-emitting diodes (LEDs)[8−13] have been demonstrated. The driving force for using soluble polymeric materials in such device applications lies in the ease of fine-tuning material properties and low-cost processing conditions. Unlike the fabrication of inorganic materials, which generally requires high vacuum and high temperature, organic polymer thin films can be obtained by spin-coating, casting, or printing techniques.[6,14,15] Polymer LEDs have been widely studied, and the most efficient devices reported are multilayer devices which comprise a sequence of a hole-transporting layer, an emitting layer, and an electron-transporting layer.[16−18] The emission of such devices comes from the radiative decay of excitons resulting from recombination in the emitting layer of electrons and holes. Balanced injection and transport of holes and electrons is therefore crucial in achieving high quantum efficiency. Multilayer devices have been found to be more efficient than single-layer devices made from one conjugated polymer layer in which hole injection and transport is easier than that for electrons.[18] However, the fabrication of multilayer devices is tedious and requires careful selection of each layer so that the solution of a subsequent layer will not attack the previous one. While metals with low work functions such as Ca can lower the charge injection barrier at the cathodes, these electrodes are air- and moisture-sensitive. To solve this problem, blended materials that contain mixtures of hole transporters, electron transporters, and emitters are often used to form efficient single-layer devices with an external quantum efficiency greater than 1% with air-stable Mg:Ag alloy contact.[19−21] The drawback to this approach

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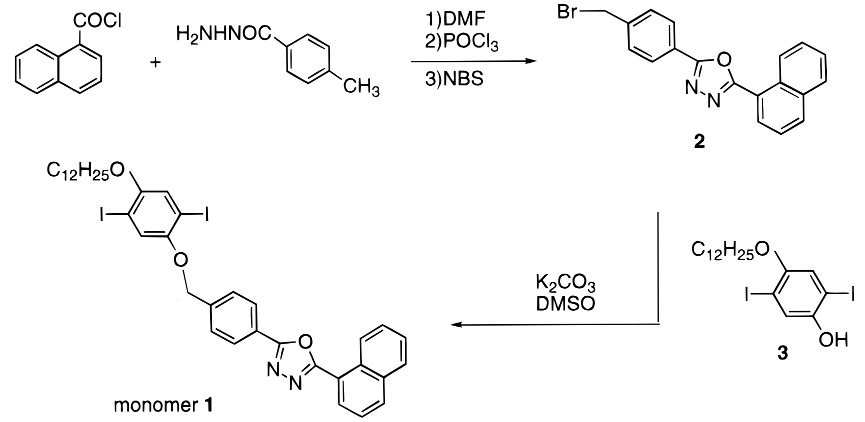
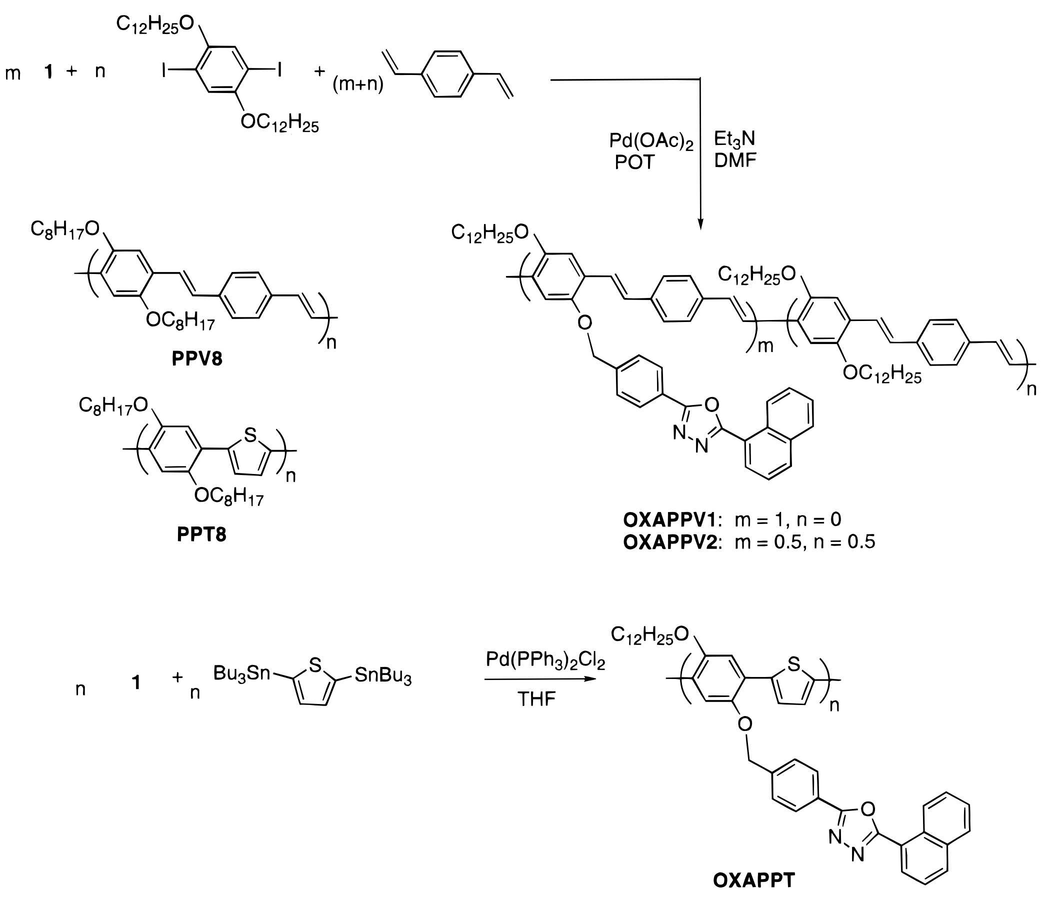
**Scheme 1. Syntheses of Monomer 1**



**Scheme 2. Syntheses of Oxadiazole Side Chain Polymers**



is that phase separation of different components is often problematic and reduces device lifetime.

In our approach, we have designed and synthesized hybrid polymers with electron-transporting oxadiazole side chains attached to a conjugated backbone which is both hole-transporting and light-emitting. Oxadiazole-containing species and polymers have been widely used as electron-transporting and hole-blocking materials in LED devices.[22-24] In our new polymers, we have incorporated the oxadiazole moieties by covalently linking them to a conjugated polymer backbone, i.e., poly(phenylene vinylene) (PPV) or poly(phenylene thiophene) (PPT). The single-layer devices (ITO/polymer/Al) fabricated from these polymers have shown at least 1 order of magnitude increase in quantum efficiency when compared to the corresponding **PPV8** or **PPT8** LEDs.

The synthesis of key monomer **1** used in preparing the oxadiazole side chain PPVs and PPT is shown in Scheme 1.[25-27] The OXAPPV polymers are synthesized

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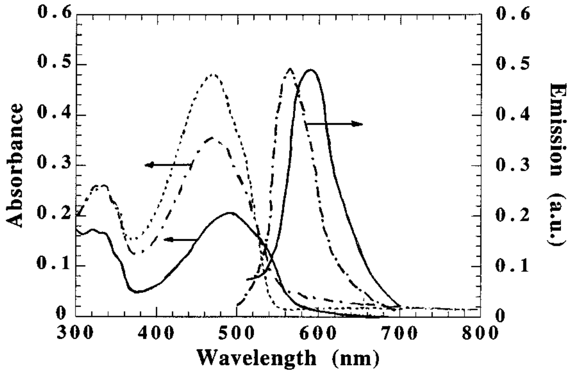

**Figure 1.** UV–vis and photoluminescence spectra of oxadiazole-containing polymers. (—) for **OXAPPT**, (-·-) for **OXAPPV1**, (- - -) for **OXAPPV2**.

using the palladium-catalyzed Heck reaction, and the PPTs are synthesized using the Stille reaction (Scheme 2).[28–31] **OXAPPV1** and **OXAPPV2** are partially soluble in warm toluene but completely soluble in warm 1,1,2,2-tetrachloroethane. **OXAPPT** is completely soluble in warm toluene. Gel permeation chromatography measurements were performed using *N*-methylpyrrolidinone as solvent at 85 °C calibrated with polystyrene standards. **OXAPPV1** has a weight-averaged molecular weight ($M_W$) of 28.5K Da with a polydispersity of 3.65; **OXAPPV2**, which is also prepared by the Heck reaction, has a $M_W$ similar to that of **OXAPPV1** of 29K Da and a polydispersity of 3.47. The Stille coupling reaction results in lower molecular weight polymers as previously reported.[31] For **OXAPPT**, $M_W$ is 8.1K Da and its polydispersity is 1.67. The elemental analyses of these polymers are given in ref 32.

The UV–vis spectra of all polymers, obtained with an HP 8453 UV/vis spectrometer, showed two strong absorption peaks (Figure 1). For **OXAPPV1** and **OXAPPV2**, an absorption peak at 330 nm from the oxadiazole side chain is observed in addition to the typical absorption of the **PPV8** backbone (ca. 460 nm). **OXAPPT** exhibits a similar spectrum except that the absorption of the **PPT8** backbone is slightly red-shifted to 480 nm. As a result **OXAPPT** is a red solid while **OXAPPV1** and **OXAPPV2** are both yellowish orange.

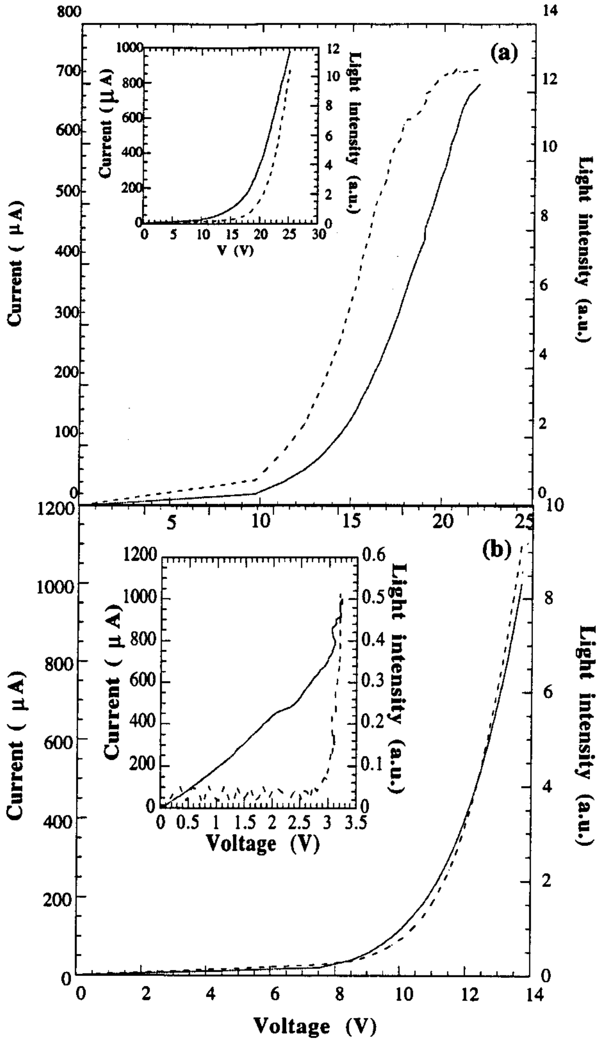

**Figure 2.** Current–light–voltage curve characteristics of oxadiazole-containing polymers (—) for current and (- - -) for light. (a) **OXAPPV1**, inset **PPV8**; (b) **OXAPPT**, inset **PPT8**.

When the polymer thin films were excited at 442 nm, the photoluminescence (PL) spectra showed only one emission peak at 580 nm for **OXAPPV1** and **OXAPPV2** and at 590 nm for **OXAPPT** (Figure 1). The same emission spectrum was obtained from a dilute **OXAPPV1** solution in tetrahydrofuran excited at either 320 or 470 nm. In addition, the excitation spectrum monitored at 504 nm is almost identical to the absorption spectrum. These results indicate that efficient energy transfer occurs from oxadiazole side chains to the PPV backbone. Emission spectrum from the oxadiazole moiety indeed overlaps well with the absorption spectrum of the PPV backbone which facilitates energy transfer.

The new polymers are good candidates for single-layer LED devices because they combine electron-transporting, hole-transporting, and light-emitting properties in a single species. Several different devices with vacuum-evaporated Al or Ca electrodes were prepared and tested. The typical LED size was 3–4 mm², and the thickness of the polymer layer was 100–150 nm. For all the devices, the forward bias current was obtained by applying a positive bias at the ITO electrode and a negative bias for Al or Ca electrode. The diodes exhibit typical rectification as measured by a Hewlett-Packard

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(27) Compund **2**, Calcd for $C_{19}H_{13}BrON_2$: C, 62.48; H, 3.59; N, 7.67. Found: C, 61.67; H, 3.22; N, 7.48. $^1$H NMR ($CDCl_3$) $\sigma$ 4.55 (s, $CH_2$Br, 2H), 7.58 (d, 7.84 Hz, phenyl, 2H), 7.62 (d, 7.78 Hz, naphthyl, 2H), 7.71 (dd, naphthyl, 1H), 7.94 (d, 8.14 Hz, naphthyl, 1H), 8.06 (d, 8.17 Hz, naphthyl, 1H), 8.18 (d, 8.14 Hz, phenyl, 2H), 8.27 (d, 7.16 Hz, naphthyl, 1H), 9.27 (d, 8.57 Hz, naphthyl, 1H) ppm. Compound **3** was synthesized according to the following reference: Peng, Z.; Gharavi, A.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 4622–4632. Monomer **1**, Calcd for $C_{37}H_{40}O_3N_2I_2$: C, 54.56; H, 4.95; N, 3.44. Found: C, 54.50; H, 4.78; N, 3.61. $^1$H NMR ($CDCl_3$) $\sigma$ 0.88 (t, $CH_3$, 3H), 1.27 (m, $CH_2$, 12H), 1.51 (m, $CH_2$, 6H), 1.81 (m, $CH_2$, 2H), 3.95 (t, $CH_2$-ph, 2H) 5.15 (s, $CH_2O$, 2H), 7.27 (d, 7.84 Hz, phenyl, 2H), 7.64 (m, naphthyl, 2H), 7.70 (s, phenyl, 2H), 7.72 (m, naphthyl, 1H), 7.95 (d, 8.04 Hz, naphthyl, 1H), 8.06 (d, 8.16 Hz, naphthyl, 1H), 8.24 (d, 9.36 Hz, phenyl, 2H), 8.29 (d, 7.15 Hz, naphthyl, 1H), 9.29 (d, 8.55 Hz, naphthyl, 1H) ppm.

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**Table 1. Quantum Efficiencies of LED Devices with ITO Anodes and Al (1100 Å) or Ca (500 Å)/Al (500 Å) Cathodes**

| | | Al | | Ca | |
|---|---|---|---|---|---|
| entry | polymer | $\eta$% | $V_{on}$ (V) | $\eta$% | $V_{on}$ (V) |
| **1** | **PPT8** | 0.0002 | 2.8 | 0.0005 | 2.6 |
| **2** | **OXAPPT** | 0.0019 | 7 | 0.0017 | 7 |
| **3** | **PPV8** | 0.002 | 14 | 0.007 | 10 |
| **4** | **OXAPPV1** | 0.020 | 9.8 | 0.015 | 10 |
| **5** | **OXAPPV2** | 0.003 | 12 | 0.022 | 10 |
| **6** | **OXAPPV1/PBD** | 0.013 | 13 | NA | NA |
| **7** | **OXAPPT/PBD** | 0.0015 | 8 | NA | NA |

4155A semiconductor parameter analyzer. The forward current was observed to increase dramatically after the turn-on voltage was exceeded. Yellowish orange light was observed from **OXAPPV1** and **OXAPPV2** EL devices operated under a continuous dc mode, while reddish orange light was seen for **OXAPPT** devices.

Figure 2a shows a typical current−light−voltage curve for an ITO/**OXAPPV1**/Al device. Similar turn-on voltages for both current and light are observed, indicating balanced charge injection from the cathode and anode. These results are in contrast to **PPV8** devices, in which hole injection and transport is much easier than electron injection and transport (Figure 2a inset). The external quantum efficiency for an ITO/**OXAPPV1**/Al device without any correction is ca. 0.02% at a current density of about 8 mA/cm$^2$. This value is 1 order of magnitude higher than the **PPV8** polymer prepared and purified using the same procedure and fabricated into the same device configuration (Table 1, entries 3 and 4). For ITO/**PPV**/Al devices, imbalanced charge injection is indicated by different turn-on voltages for light (16 V) and current (10 V) (Figure 2a inset). In addition, the quantum efficiencies for **OXAPPV1** are similar when Al and Ca are used as the cathode (Table 1, entry 4). The attempt to make a single-layer LED with a blend of **PPV8** and 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) with the same oxadiazole content as that of **OXAPPV1** failed since PBD crystalizes out (phase separates) from the **PPV8** polymer matrix after Al electrodes are vacuum deposited.

**OXAPPT** polymer, on the other hand, makes less efficient devices compared to **OXAPPV1**. Nevertheless, its quantum efficiency is still 1 order of magnitude higher than the **PPT** polymer without any oxadiazole side chains (Table 1, entries 1 and 2). The very low turn-on voltage for **PPT8** may be attributed to impurities that cause partial doping of the polymer. This has previously been reported for PPV polymers.[33]

An additional layer of electron-transporting and hole-blocking layer of PBD (100 Å) was vacuum evaporated onto the polymer layer before Al electrodes were deposited. The EL quantum efficiencies of these devices were similar to those without a PBD layer, indicating that a sufficient concentration of electron-transporting groups is incorporated (Table 1, entries 6 and 7). When the amount of oxadiazole side chains in **OXAPPV2** is reduced by half as compared to that in **OXAPPV1**, the turn-on voltage is slightly increased whereas the quantum efficiency is dramatically decreased (Table 1, entry 5). This might be due to the increasing difficulties in electron injection evidenced by the higher efficiency of the Ca device compared to the Al device (Table 1, entry 5). In addition, electron transport is less efficient in **OXAPPV2** since a minimum concentration of oxadiazole is needed to form an electron transport pathway (percolation threshold).

In summary, we have synthesized and characterized new conjugated polymers with electron-deficient oxadiazole side chains. These polymers show enhanced electroluminescence efficiencies and better charge injection properties as compared to the corresponding conjugated backbone polymers. In addition, better LED performance is obtained with polymers having a higher concentration of electron-transporting molecules. This approach should be a general method to achieve high-efficiency single-layer organic and polymer LEDs.

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