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Luminescence Properties of Structurally Modified PPVs: PPV Derivatives Bearing 2-(4-*tert*-Butylphenyl)-5-phenyl-1,3,4-oxadiazole Pendants

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Two new poly(*p*-phenylenevinylene) (PPV) derivatives bearing 2-phenyl-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole pendants were prepared, and their photo- and electroluminescence properties were studied. The first polymer (**P-1**) is poly[2-{4-[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenyl}-1,4-phenylenevinylene], which is a PPV derivative having diphenyl-substituted 1,3,4-oxadiazole pendant that is known to be an excellent electron-transporting structure. The second polymer (**P-2**) is poly[2-{4-[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]-phenyl}-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]. The only structural difference between **P-1** and **P-2** is the presence of additional 2-ethylhexyloxy pendant groups in **P-2**. Both polymers were prepared by direct polymerization of the α,α′-dibromo-*p*-xylene monomers having the pendant group(s) in the presence of excess potassium *tert*-butoxide. Both polymers reveal much improved electroluminescence (EL) properties when compared with PPV. They emit luminescence light over the wavelength range from about 500 to 600 nm. The external quantum efficiencies of **P-1** and **P-2** were respectively 16 and 56 times the value for PPV when LED devices were fabricated using an indium−tin oxide (ITO) coated glass anode and the aluminum cathode. In particular, the EL device ITO/poly(3,4-ethylenedioxy-2,4-thienylene)/**P-2**/Al:Li geometry revealed a maximum luminance of 1090 cd/m^2 at the electric field of 2.36 MV/cm with the external quantum efficiency of 0.045%. The maximum brightness of the ITO/**P-2**/Ca/Al was 7570 cd/m^2 at the electric field of 2.80 MV/cm.

Introduction

Luminescence properties of poly(*p*-phenylenevinylene), PPV, and other conjugated polymers have been attracting a great deal of interests since the first light-emitting diodes (LEDs) based on PPV were reported a decade ago by the Cambridge group.[1] Electroluminescence (EL) efficiency of the devices, however, was far from satisfactory. And it soon was found that chemical modifications of PPV[2] and use of different electrodes[3] together with utilization of electron-[4] and/or hole-transporting[5] layers can improve the device efficiency to impressive extents.

It is understood that in LED devices electrons and holes are separately injected from an anode and a cathode, respectively, under a bias voltage into the light-emitting polymer layer where the injected negative and positive carriers form excitons.[6] The excitons can disappear via various mechanisms; one of them is luminescence decay or radiative decay. To improve devices' efficiency of LEDs there have been many attempts[7] to balance the injection of carriers from electrodes and also their mobility in the emitting polymer layer. Unfortunately, the hole mobility in PPV and its simple derivatives is typically higher than that of electron mobility.[8] This is one of the reasons why the LED devices

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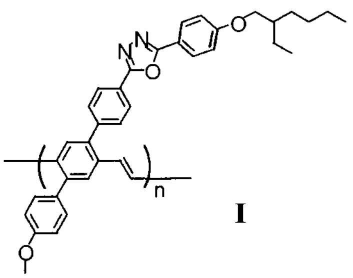
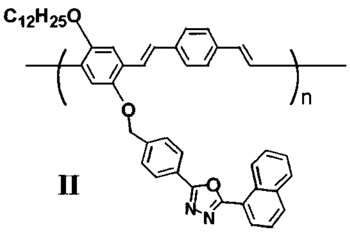
fabricated using these polymers exhibit rather unsatisfactory efficiencies.[9] Utilization of low work function metals as cathodes makes the electron injection easier.[3] Calcium and lithium are representative examples. Another approach for improving electron transporting is to use of additives of electron-deficient compounds such as 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD).[4] But their efficacy can be limited due to their crystallization and aggregation. This problem is mitigated by incorporating the electron-transporting units into the main chain[10] or as pendants attached to the backbone of a polymer.[11] Or they can be included both in the main chain and in the side group.[12]

Chen et al.[11a] recently prepared the polymer **I** that bears the oxadiazole moiety as a pendant, but it was not soluble in organic solvents. They had to include dialkoxyphenylenevinylene comonomer units to make the 1:1 alternating copolymer, which became soluble in organic solvents.



I

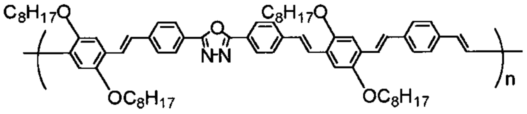
In comparison, Bao et al.[11b] prepared an organic soluble PPV derivative (**II**) bearing an electron-transporting pendant and an alkoxy group on the phenylene ring and also placed an oxymethylene spacer between the pendant and the backbone.



II

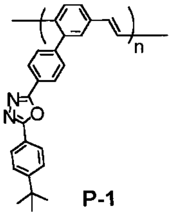
This polymer emits light at 580 nm, and the ITO/polymer/Al device exhibited an external quantum efficiency of 0.02% at a current density of about 8 mA/cm^2. PPV itself shows the external quantum efficiency of about 2.0×10^{-4} to 5.0×10^{-4} % for the ITO/PPV/Al device.[13]

Peng and Zhang[12] recently reported a polyconjugated polymer containing the oxadiazole electron-transporting structures both in the backbone and in the side chain. They reported the external quantum efficiency of 0.07% for the ITO/polymer/Al device and 0.15% for the device where the calcium cathode was used instead of the aluminum cathode. Peng et al.[10b] previously reported that polymer **III** showed an external efficiency 40 times higher than that of PPV.

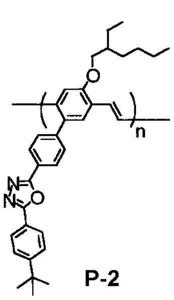


III

All the polymers described above are claimed to show enhanced electron injection and improved balance in carrier mobility. We[11c] also reported briefly the luminescence properties of the polymer **P-1** that bears the 2-(4-*tert*-butylphenyl)-5-phenyl-1,3,4-oxadiazole (BPD) pendants directly attached to the PPV backbone. Such a simple structural modification resulted in a much higher EL efficiency, 16 times the efficiency of PPV. The polymer is soluble at room temperature in organic solvents such as 1,1,2,2-tetrachloroethane and toluene. It is known that attachment of long alkoxy substituents on the phenylene rings increases the interchain distance giving rise to improved LED device efficiencies resulting from diminished formation of interchain polaron pairs.[14] Therefore, we became interested in a further modification of **P-1** with an additional alkoxy substituent (**P-2**) to compare its luminescence properties with **P-1** and also with PPV. This article describes the synthesis, structural analysis, and spectral and luminescence properties of **P-1** and **P-2**. LED devices were fabricated using the polymers, and the devices' characteristics also are discussed. For the purpose of comparison, data obtained for PPV in our laboratory also are included whenever necessary.



P-1



P-2

Results and Discussion

Synthesis of Monomers, M-1 and M-2. P-1 and **P-2** were synthesized by polymerizing bis(bromomethyl)

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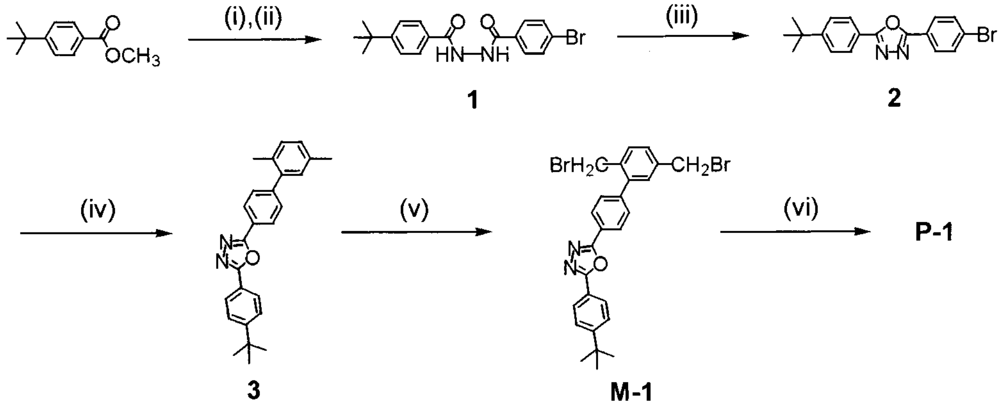
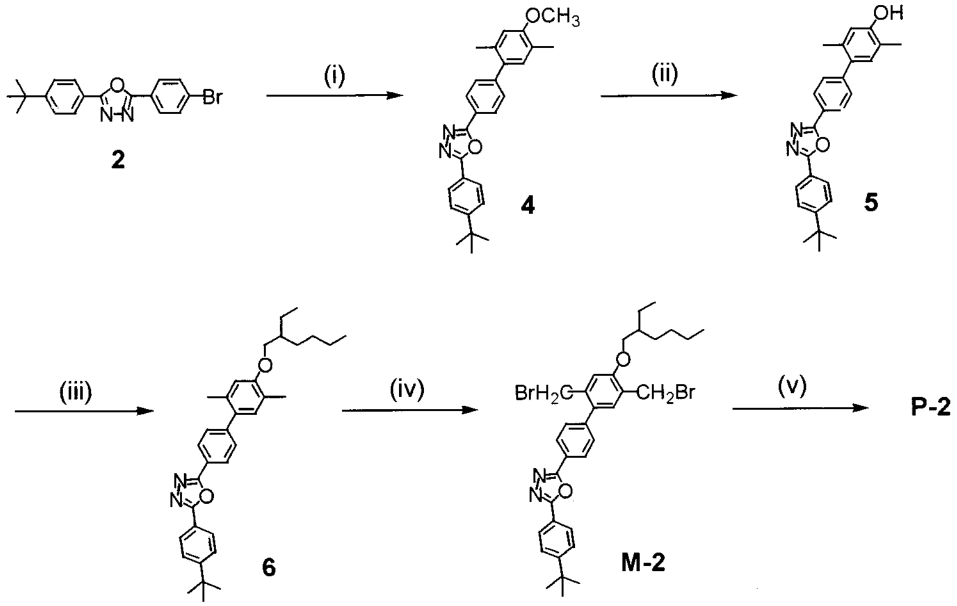
Scheme 1. Synthetic Route to M-1 and P-1[a]



[a]Reagents and conditions: (i) $NH_2NH_2{\cdot}H_2O$, ethanol, reflux, 6 h, 83%; (ii) 4-bromobenzoyl chloride, THF, pyridine, 0 °C, 1 h, 79%; (iii) $POCl_3$, reflux, 12 h, 84%; (iv) $(PPh_3)_4Pd$ (cat.), toluene/Na_2CO_3 (2 M in H_2O), 2,5-dimethylphenylboronic acid, 24 h, 73%; (v) *N*-bromosuccinimide (NBS), CCl_4, reflux, 2 h, 42%; (vi) $KOBu^t$, THF, 4 h, 43%.

Scheme 2. Synthetic Route to M-2 and P-2[a]



[a] Reagents and conditions: (i) $(PPh_3)_4Pd$ (cat.), toluene/Na_2CO_3 (2 M in H_2O), 2,5-dimethyl-4-methoxyphenylboronic acid, 24 h, 59%; (ii) BBr_3, methylene chloride, 0 °C, 3 h, 97%; (iii) 2-ethylhexyl bromide, K_2CO_3, tetrabutylammonium bromide, acetonitrile, 12 h, 92%; (iv) *N*-bromosuccinimide (NBS), CCl_4, reflux, 2 h, 40%; (v) $KOBu^t$, THF, 4 h, 40%.

monomers, **M-1** (2-[4-(2′,5′-bis(bromomethyl)biphenylyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) and **M-2** (2-[4-(2′,5′-bis(bromomethyl)-4′-(2-ethylhexyloxy))biphenylyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole), both of which prepared via multistep routes shown in Schemes 1 and 2, respectively. For the synthesis of **M-1**, we had to first synthesize 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, **2**, by dehydrative cyclization of the mixed hydrazide, 1-(4-bromobenzoyl)-2-(4-*tert*-butylbenzoyl) hydrazine (**1**), using $POCl_3$. Cyclization of hydrazides by $POCl_3$[15] is a very well-known method widely used in the synthesis of oxadiazoles. Compound **1** was obtained by condensing 4-*tert*-butylbenzoylhydrazide with 4-bromobenzoyl chloride in the presence of the HCl acceptor, pyridine. Compound **2** was reacted by a Suzuki reaction[16] with 2,5-dimethylphenylboronic acid in the presence of the tetrakis(triphenylphosphine)palladium(0) catalyst to produce 2-(4-*tert*-butylphenyl)-5-{4-(2′,5′-dimethyl)biphenylyl}-1,3,4-oxadiazole, **3**. Finally, compound **3** was brominated benzylically[17] using *N*-bromosuccinimide (NBS) and the free-radical generator, benzoyl peroxide. All of the synthetic steps produced products in 60−80% yield, with the exception of the last step that yielded the final product, **M-1**, only in the yield of 42%. Since several byproducts are formed in the final step which are not easily separable from one another, the crude product was purified using a silica gel column. The structures of intermediates and **M-1** were confirmed by elemental analysis and IR and ^1H NMR spectroscopy. The data are given in the Experimental Section.

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The second monomer, **M-2**, was synthesized in a similar fashion, but its synthesis is a little bit more complicated because the monomer bears the 2-ethylhexyloxy group on the phenylene ring. Compound **2** was coupled with the 2,5-dimethyl-4-methoxyphenylboronic acid via the Suzuki coupling reaction[16] as shown in Scheme 2. The methoxy group in the resulting product was deprotected by BBr_3[18] at 0 °C to give 2-(4-*tert*-butylphenyl)-5-{4-(2′,5′-dimethyl-4′-hydroxy)biphenylyl}-1,3,4-oxadiazole, **5**. After being purified by column chromatography and dried in a vacuum oven, compound **5** was reacted with 2-ethylhexylbromide using K_2CO_3 as base in acetonitrile to yield product **6**, i.e., 2-(4-*tert*-butylphenyl)-5-{4′-(4′-(2-ethylhexyloxy)-2′,5′-dimethyl)-biphenylyl}-1,3,4-oxadiazole. Finally, monomer **M-2** was synthesized via benzylic bromination[17] of **6** using *N*-bromosuccinimide (NBS) and benzoyl peroxide (BPO) as utilized in synthesis of **M-1**.

Synthesis of Polymers, P-1 and P-2. Both polymers were prepared by polymerization of respective monomers at room temperature in THF in the presence of a strong base, potassium *tert*-butoxide. This polymerization was first reported by Gilch and Wheelwright.[19] This method requires the use of excess strong alkali to ensure the formation of the fully eliminated structure as shown in Schemes 1 and 2. Therefore, the base acts not only as a condensing agent but also as a dehydrobrominating agent. The polymers obtained were purified by Soxhlet extraction for 3 days using methanol and acetone sequentially.

The polymers are soluble in organic solvents such as tetrahydrofuran and 1,1,2,2-tetrachloroethane. In particular, **P-2** shows a better solubility in these solvents. Molecular weights of **P-1** and **P-2** determined by gel-permeation chromatography against polystyrene standards are $\overline{M}_n = 24\,000$ and 12 500, respectively. Their polydispersity indices are 1.21 and 1.32. Relatively narrow molecular weight distribution must be brought about by removal of the low molar mass portion by the extraction process. Both polymers readily form free-standing films when cast from 1,1,2,2-tetrachloroethane solutions. We were not able to detect the glass transitions for these polymers up to 300 °C by differential scanning calorimetry. In TGA analyses, both polymers did not lose any weight up to 300 °C and started to undergo fast weight loss at 350 °C and a major decomposition at about 450 °C for **P-1** and at about 400 °C for **P-2**. The presence of the alkoxy substituent appears to cause a little diminished thermal stability for **P-2** when compared with **P-1**.

The wide-angle X-ray diffractograms (WAXD) of **P-1** and **P-2** obtained at room temperature tell us that both polymers are amorphous. The virgin sample of **P-2(0)** exhibits the same WAXD as the one obtained for the sample (**P-2(3)**) thermally treated for 3 h at 150 °C in vacuo. In other words, additional thermal elimination and annealing did not change the amorphous nature of the polymer.

UV−Vis Absorption and Photoluminescence Properties. Figure 1 compares the UV−vis spectra of **P-1**, **P-2,** and PPV films. PPV was prepared via the Wessling−Zimmerman[20] water-soluble precursor route and thermally treated at 270 °C in vacuo for 12 h. **P-1** and **P-2(3)** have a common feature in their spectra, a strong absorption centered around 300 nm ($\lambda_{max} = 300$ nm for **P-1** and 302 nm for **P-2(3)**) and a broader peak at about 330−510 nm for **P-1** and at about 370−530 nm for **P-2(3)**. In contrast, PPV absorbs broadly over the wavelength of 290−570 nm. The absorption by **P-1** and **P-2(3)** in the shorter wavelength region is attributed to the oxadiazole pendant,[21] and those in the longer wavelength region are attributed to the $\pi-\pi^*$ transitions of the main chains. The absorption position for the backbone $\pi-\pi^*$ transition of **P-1** is slightly blue-shifted as compared with PPV. This is ascribed to a partial destruction of the π-delocalization along the backbone by the bulky substituents that disrupt the coplanarity of the π-conjugated backbone. However, the same blue-shift is not observed for **P-2(3)** because of the presence of the electron-donating alkoxy substituent that usually causes a bathochromic shift.[22]

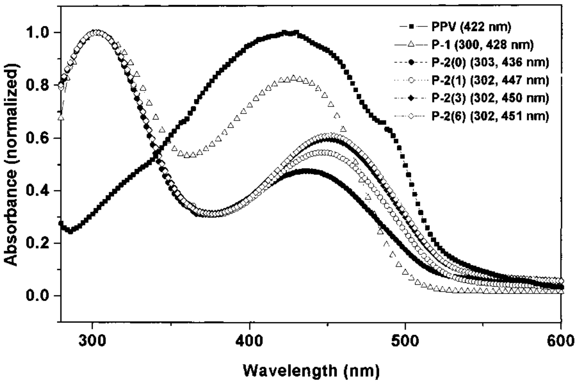

Figure 1. Comparison of UV−vis absorption spectra of **P-1**, **P-2**, and PPV. The numbers in the parentheses indicate the time (hours) of thermal treatment at 150 °C, 0.1 Torr.

The UV−vis spectrum of **P-2** is strongly dependent on thermal history as shown in Figure 1. It is evident that additional double bonds are formed when the polymer was thermally treated at 150 °C under a pressure of 0.1 Torr. Not only the absorption intensity of the $\pi-\pi^*$ transition grows but also the absorption position moves red as the period of thermal treatment lengthens up to 3 h. The virgin sample **P-2(0)** showed λ_{max} at 436 nm, which moved to 450 nm when it was heat-treated at 150 °C for 3 h under a vacuum. On the contrary, the spectrum of **P-1** exhibited very little dependence on thermal history, which suggests that conjugative backbone was more readily formed in **P-1** during polymerization than in **P-2**. The presence of the bulky electron-donating group on the phenylene rings of **P-2** appears to hinder the dehydrobromination reaction mentioned above. The λ_{max} value for the $\pi-\pi^*$ transition of the **P-1** backbone is 428 nm.

Photoluminescence (PL) spectra of **P-1**, **P-2**, and PPV are compared in Figure 2. The wavelength ranges of the

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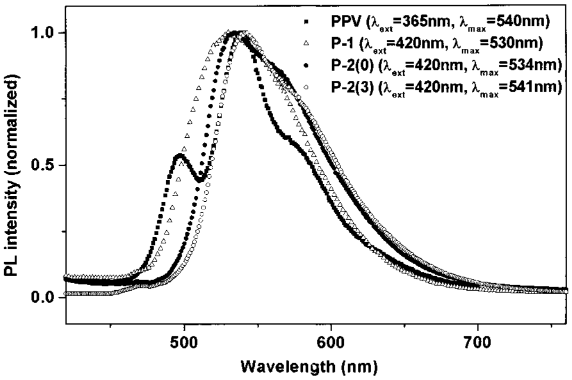

Figure 2. Comparison of PL spectra of **P-1**, **P-2**, and PPV.

emitted light by the three polymers are not much different from one another with **P-2** emitting light in the slightly longer wavelength. In contrast with PPV, **P-1** and **P-2** show structureless emission, although their PL spectra reveal shoulders in the longer wavelength side. As expected, thermally treated sample of **P-2(3)** luminesces in a very slightly longer wavelength region than the virgin sample, **P-2(0)**. PPV's spectrum is composed of well-resolved vibronic bands as reported earlier by many other groups.[23] This suggests that the pendants in **P-1** and **P-2** are involved in electronic interactions with the main chain, e.g., charge transfer interaction as reported recently by us.[24] Since the oxadiazole ring contains three electronegative atoms, it can act as a π-electron acceptor. The general feature of PL spectra of **P-1** and **P-2(3)** remains the same regardless the wavelength of excitation light, when the excitation wavelength is varied from 270 to 420 nm. As explained above, **P-1** and **P-2(3)** absorb strongly at $\lambda_{\max} = 300$ nm by the oxadiazole pendant and also at $\lambda_{\max} = 428$ or 450 nm by the backbone π-system. The PL spectra, for example, obtained at the excitation wavelength of 300 and 420 nm are exactly the same in the spectral feature. This is another indication for a facile electronic interactions between the pendant and the backbone. Another point to be noted is that, as one increases the wavelength of excitation beam, the PL intensity increases. Exceptions are for the wavelengths (360 and 390 nm) where **P-2(3)** absorbs only weakly.

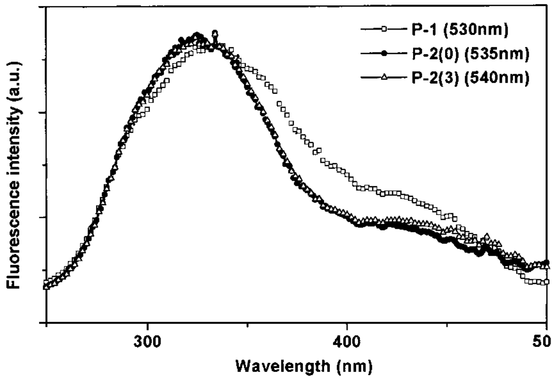

Figure 3. Comparison of excitation spectra of **P-1**, **P-2(0)**, and **P-2(3)**. All spectra were obtained at their maximum emission wavelengths indicated in the figure.

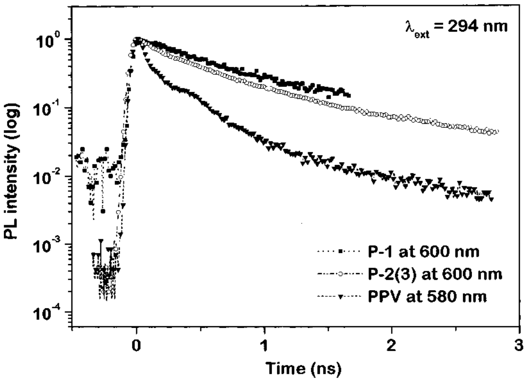

Figure 4. Time-resolved PL spectra of **P-1**, **P-2**, and PPV.

Figure 3 supports this supposition very clearly. The excitation spectra shown in Figure 3 were obtained for emitting wavelengths of maximum fluorescence intensities of **P-1** and **P-2(3)**. In other words, they are for $\pi-\pi^*$ transitions of the backbones only. Comparison of these excitation spectra with the corresponding absorption spectra given in Figure 1 strongly suggests that absorption by BPD pendants makes a significant contribution to the emission by the backbone. This will be possible only when the singlet excitons formed by pendants migrate to the backbones and undergo radiative decay. In other words, the excited energy transfer from the pendants to the backbone occurs readily. The spectral feature of the excitation spectra of **P-1** and **P-2(3)** for different wavelengths of emitted light (530−620 nm) was all the same, which is as expected since all of them are for emission from the π-electron systems of polymer backbones.

Figure 4 compares the time-resolved PL spectra of **P-1**, **P-2**, and PPV obtained by a pico-second laser at the excitation wavelength of 300 nm. As one can see from the figure, PL decays of **P-1** and **P-2(3)** are much slower than that of PPV. But the difference between **P-1** and **P-2(3)** is not significant. The presence of bulky substituents in **P-1** and **P-2(3)** appears to slow PL decay by stabilizing the intrachain excitons formed and also by reducing the formation of interchain excitons due to increased interchain distances.[14]

Electroluminescence Properties. Light-emitting diode (LED) devices were prepared from **P-1** and **P-2** using the indium−tin oxide (ITO) coated glass anode and the aluminum or aluminum:lithium alloy or calcium cathode. Polymers (ca. 15 mg/mL) were dissolved in 1,1,2,2-tetrachloroethane and spin coated on an ITO-coated glass, and the metal cathode was vapor deposited. The surfaces of the spin-coated films were very smooth, and the average surface roughness measured by the AFM analysis is only 12.9 and 12.1 Å respectively for **P-2(0)** and **P-2(3)**. Thermal treatment of **P-2(0)** for 3 h at 150 °C did not change the surface roughness to any significant extent.

The EL spectra given in Figure 5 were obtained for ITO/polymer/Al devices at the operating electric field of 1.4, 3.8, and 3.6 MV/cm respectively for PPV, **P-1**, **P-2(0)**, and **P-2(3)**. The EL spectra are much the same as their corresponding PL spectra shown above in Figure 2. This fact indicates that light-emitting mech-

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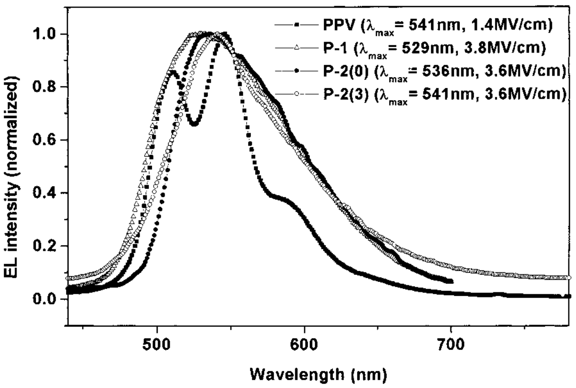

Figure 5. Comparison of EL spectra of **P-1**, **P-2**, and PPV.

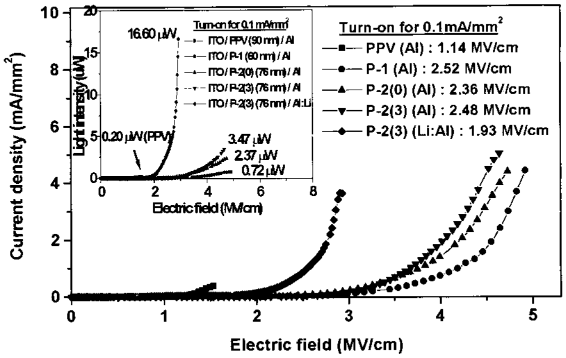

Figure 6. Comparison of *I*−*V* and light intensity−*V* curves for **P-1**, **P-2**, and PPV.

anisms and the nature of so-called excitons are the same for both cases.

The current/emitted light intensity-electric field curves of the LED devices are shown in Figure 6. According to the figure, the turn-on electric field for the ITO/**P-2(3)**/Al:Li device is the lowest (1.93 MV/cm for the current density of 0.1 mA/mm^2) and the value for the ITO/**P-1**/Al device is the highest (2.52 MV/cm for the current density of 0.1 mA/mm^2). Evidently, the cathode prepared from the Al:Li alloy facilitates the electron injection when compared with the aluminum electrode. It is well-known that the work function of lithium is much lower than that of aluminum, 2.9 vs 4.2 eV. Another important point to note for the device of **P-2** for which the Al:Li alloy was utilized as the cathode is that not only the turn-on electric field for current is the same as that for light emission but also the dependence of light-emission on the electric field closely follows the current−electric field curve (see the inset in Figure 6). This strongly indicates an equally efficient injection and transport of the both carriers, i.e., holes and electrons. On the other hand, for the devices where the aluminum electrode was used, current increases much more rapidly than the emitted light intensity does as the electric field increases. This may due to an unbalanced injection of the carriers. Most probably, despite the presence of the oxadiazole pendants, electron injection is less efficient than hole injection. Moreover, hole mobility through the polymers (**P-1** and **P-2**) may still be much faster than electron mobility. But this point still has to be experimentally verified. The maximum brightness observed for the ITO/**P-2(3)**/Al:Li device was 415 cd/m^2 at the electric field of 2.93 MV/cm for the current density of 3.62 mA/mm^2.

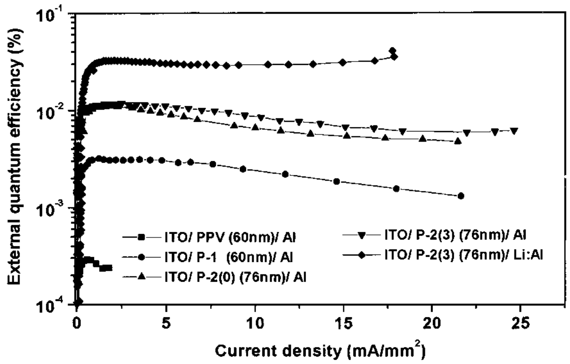

Figure 7. Comparison of current density−external quantum efficiency curves for **P-1**, **P-2**, and PPV.

As reported earlier by us,[11c] data obtained from ultraviolet photoelectron spectroscopy (UPS) and UV−vis spectrum of **P-1** indicate that the ionization potential (IP) or the HOMO level and electron affinity (EA) or the LUMO level are 6.42 and 3.93 eV, respectively. The EA values were evaluated from the optical band gaps estimated from UV−vis spectra and the IP values obtained from the UPS data. The corresponding values for **P-2(3)** are 6.32 and 3.98 eV, respectively. Therefore, it can be conjectured that hole and electron injections are slightly more favored in **P-2(3)** than in **P-1**.

External quantum efficiencies (number of photons emitted per electron injected) of the devices constructed are compared in Figure 7. The highest efficiency was attained from the ITO/**P-2(3)**/Al:Li device and is about 0.04%, which is greater by more than 2 orders of magnitude when compared with the ITO/PPV/Al device. With aluminum as the cathode, the device prepared from **P-2(3)** exhibits the external quantum efficiency of about 0.015%. The efficiency (3×10^{-3}%) of the ITO/**P-1**/Al device lies inbetween **P-2(3)** and PPV devices. The presence of the 2-ethylhexyloxy substituent in **P-2** definitely improves the EL efficiency when compared with **P-1** that does not bear the substituent. It is very well documented[25] that the presence of long or bulky substituents enhances the device efficiency by reducing the possibility for the formation of interchain polaron pairs. The bulky substituents are expected to increase the interchain distance. And the efficiency for **P-2(3)** is slightly higher than for **P-2(0)**.

According to the present results, attachment of the electron-withdrawing and electron-transporting BPD pendant on the PPV backbone definitely improves the device efficiency to about the same extent reported by Bao et al.,[11b] who prepared PPV derivatives carrying similar pendants. These polymers, however, exhibit lower EL efficiencies than the polymer[12] containing the oxadiazole moieties both in the backbone and side chain. Having the additional oxadiazole structure along the main chain appears further help balancing the charge injection and transport by its ability to block hole transport. Song et al.[10a] recently reported improved EL efficiencies for the devices prepared from blends consisting of a polymer containing the oxadiazole unit in the main chain and a dialkoxy-substituted PPV.

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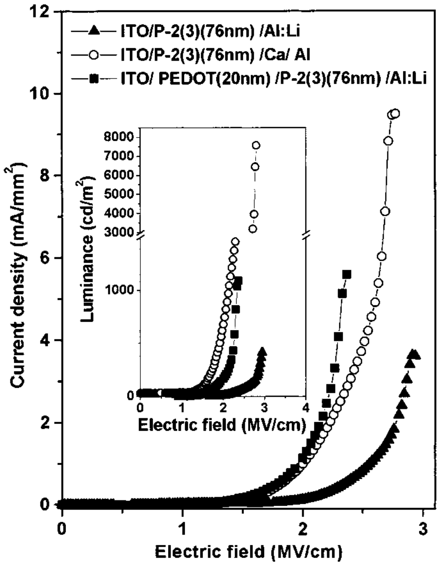

Figure 8. Comparison of $I-V$ curves and brightness of **P-2(3)** devices.

Highly Light-Emitting Devices. Although **P-2** exhibits a much enhanced EL efficiency when compared with unsubstituted PPV, there are many aspects that still require much further improvement to serve in practical applications. Too high a turn-on and operating electric fields, relatively low brightness of emitted light, and poor long-term stability are some of the most important drawbacks that need much more studies for improvement. Especially, contact barrier or poor contact between the inorganic electrodes and organic emitting layer appears to be one of the most difficult technical problems to overcome when one is to design efficient EL devices based on organic light-emitting polymers. One of the approaches being employed is to apply an organic conducting layer between the ITO-coated glass anode and the organic light-emitting layer.[26−28] Polyanilines[26] and polythiophenes[27] are some of the organic conducting polymers frequently utilized for this purpose. Copper phthalocyanine[28] is another conducting organometallic compounds employed for the same purpose.

We have fabricated a device using a poly(3,4-ethylenedioxythiophene) (PEDOT) doped with a sulfonated polystyrene in order to construct an ITO-coated glass anode/PEDOT/**P-2(3)**/Al:Li cathode structure. Figure 8 shows the characteristics of the device thus constructed. For comparison, the results obtained from the device of ITO/**P-2(3)**/Al:Li structure are also shown. As one can see from Figure 8, the turn-on electric field has been significantly reduced to 1.35 MV/cm that is about two-thirds of the value for the ITO/**P-2(3)**/Al:Li device described above, and the maximum brightness (Figure 8 inset) attainable was about 1090 cd/m^2 at the electric field of 2.36 MV/cm. As described above, the device without the PEDOT layer revealed the maximum brightness of 415 cd/m^2 at the field of 2.93 MV/cm.

Finally, we constructed a device having the ITO/**P-2(3)**/Ca/Al geometry and the device performance was studied. The current vs electric field and intensity of emitted light vs electric field characteristics are shown in Figure 8. Calcium was deposited onto the light-emitting layer first, and then an aluminum layer was deposited onto it in order to protect the calcium cathode. Even without the PEDOT layer, the turn-on electric field, arbitrarily taken as the field for the current density of 0.1 mA/mm^2, is 1.46 MV/cm. Moreover, comparison of the $I-V$ curves given in Figure 8 implies that use of the calcium cathode leads to more efficient carrier injection and flow than the Al:Li alloy cathode. The two metals (Li and Ca) are known to have almost the same value of work function (2.90 and 2.87 eV, repectively).[29] It is conjectured that the calcium cathode gives rise to a better contact between the electrode and the organic polymer emitting layer. Moreover, when the Al:Li alloy was utilized for deposition of the metal cathode, the lithium layer might have not been effectively protected by aluminum. The maximum brightness (Figure 8 inset) attainable was 7570 cd/m^2 at the current density of 9.50 mA/mm^2 and the electric field of 2.80 MV/cm. The efficiency of the device was 0.13 lm/W at the current density of 2−9 mA/mm^2.

Since, in our initial studies, **P-2(3)** was found to be much superior to **P-1** in the external quantum efficiency for the ITO/polymer/Al device, we did not study the performance of **P-1** in other devices. It, however, is our belief that a similar improvement in device performance can be achieved even for **P-1** if we used Al:Li or Ca cathode together with the PEDOT layer.

Conclusion

New chemically modified PPV derivatives bearing the 2-(4-*tert*-butylphenyl)-5-(4-phenyl)-1,3,4-oxadiazole (BPD) substituents directly attached to the phenylene rings of the PPV main chain were synthesized and characterized for photo- and electroluminescence properties. The two polymers described in this work are simple homopolymers and are readily soluble in various organic solvents. They emit yellowish-green color light in PL and EL. Especially, attachment of the electron-withdrawing BPD pendant and a bulky, branched alkoxy group onto the PPV backbone results in much improved EL performance of the LED devices. Due to electronic interactions between the BPD pendant and the backbone, fluorescence lifetime is lengthened significantly when compared with PPV, which is related to enhanced EL devices' external quantum efficiencies of **P-1** and **P-2**. The presence of the BPD pendant is expected to increase its electron-transport ability resulting in the more favorable balance in injection and transport of holes and electrons, as shown by us in the recent report on the transient EL[30] behavior of **P-1** and also by the

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device characteristics of **P-1** and **P-2** described in the present investigation. In the light of less than satisfactory device performance of **P-1** and **P-2**, it is conjectured that the BPD pendants are not so effective as a hole blocker although it increases electron transport. The presence of the bulky alkoxy pendant provides a further increase in EL performance, which is explained by the increased interchain distance by their presence resulting in less probability for the formation of interchain polaron pairs claimed to give rise to a low quantum efficiency due to their tendency to undergo radiationless decay. Promotion of a better contact between the inorganic electrode and organic light-emitting layer and utilization of a low work function metal cathode vastly improve the LED device efficiency.

Experimental Section

Measurements. ^{1}H NMR (300 MHz) and IR spectra were recorded on a Varian AM 300 spectrometer and on a Bomem MB FT-IR instrument, respectively. Elemental analyses were performed by the Center for Organic Reactions, Sogang University, Seoul, Korea, using an Eager 200 elemental analyzer. The purity of products was also determined by a combination of TLC on silica gel plates (MERCK, silica gel 60 F_{254}) with UV lamp (254 or 365 nm) and a visualization reagent. Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821^e instrument. Thermogravimetric analysis (TGA) was also performed under a nitrogen atmosphere at the heating/cooling rate 10 °C/min on a DuPont 9900 thermogravimetric analyzer. GPC analysis was conducted with a Waters GPC 410 system equipped with five Ultra-μ-stragel columns (2×10^5, 10^4, 10^3, 500 Å) in THF at a flow rate of 1.0 mL/min at 30 °C using polystyrene as the calibration standard. The UV−vis spectra of the polymer films were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. The thickness of polymers were determined by a TENCOR P-10 surface profiler. The ultraviolet photoelectron spectroscopy (UPS) data were acquired at room temperature with a VG ESCALab 220i spectrometer (Manchester, U.K.) with a VG UV lamp. UPS analysis was performed using He I (21.2 eV) photons. The base pressure of the analysis chamber was lower than 1×10^{-10} Torr, and the combined instrumental resolution was about 0.1 eV. Atomic force microscopy (AFM) was conducted on a AutoProbe CP (Park Scientific Instruments) by the Korea University Engineering Laboratory Center, Seoul, Korea.

The luminescence spectra for the polymers were recorded on an AMINCO-Bowman Series 2 luminescence spectrometer at room temperature. The current and luminescence intensity as a function of applied field were measured using an assembly consisting of PC-based dc power supply (HP 6623A) and a digital multimeter (HP 34401), and also a light power meter (Newport Instruments, model 818-UV) was used to measure the device light output in microwatts. Luminance was measured by a Minolta LS-100 luminance meter. A picosecond time-correlated single photon counting (TCSPC) system was employed for the time-resolved fluorescence decay measurements. The system was consisted of cavity dumped dual-jet dye laser (700 series, coherent) that was synchronously pumped by Nd:YAG laser (Antares 76-YAG, coherent). The full width at half-maximum of the instrumental response function was 67 ps. The fluorescence decays were measured at magic angle emission polarization, and their exponential fittings were performed by the least-squares deconvolution fitting method.

Materials. All the compounds were purchased from Aldrich, TCI, or Fluka chemicals, and thionyl chloride, tetrahydrofuran, pyridine, toluene, *N*-bromosuccinimide, benzoyl peroxide, 1,1,2,2-tetrachloroethane, and acetonitrile were purifed by the method in ref 31. All other compounds were used as received.

Synthesis. *1-(4-Bromobenzoyl)-2-(4-tert-butylbenzoyl)hydrazine (**1**). Method i*. The mixture of methyl 4-*tert*-butylbenzoate (30.0 g, 156 mmol) and hydrazine monohydrate (31.2 g, 624 mmol) was refluxed for 24 h in 600 mL of ethanol. After the reaction was completed, the mixture were cooled to room temperature and then poured into cold water to precipitate the white solid, which was collected on a filter and washed with hexane and small amount (ca. 100 mL) of cold water to remove the unreacted starting materials. The product, 4-*tert*-butylbenzylhydrazide, was dried for 1 h by vacuum filtration followed by drying in a vacuum oven for 1 day. The product yield was 83% (24.9 g). Mp: 126 °C.

Method ii. To 18.5 g (104 mmol) of 4-bromobenzoic acid, 50 mL of $SOCl_2$ was added, and the mixture was refluxed for 6 h with a catalytic amount of purified pyridine to give 4-bromobenzoyl chloride. The excess $SOCl_2$ was removed by vacuum distillation, and the reaction mixture was cooled to room temperature. After 30 min, 20.0 g of 4-*tert*-butylbenzylhydrazide and 8.4 mL (104 mmol) of pyridine dissolved in 100 mL THF were added to the reaction flask containing 4-bromobenzoyl chloride through a dropping funnel over a period of 20 min. White precipitates were generated immediately. After being stirred for 2 h, the reaction mixture was poured into distilled water. The product was collected on a filter and washed with water and then dried in a vacuum oven. The yield was 79% (30.8 g). Mp: 224 °C. ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 1.31 (s, 9H, $-C(CH_3)_3$), 7.54 (d, 2H, Ar-*H*), 7.75 (d, 2H, Ar-*H*), 7.86 (d, 2H, Ar-*H*), 7.87 (d, 2H, Ar-*H*), 10.48 (s, 1H, $-NHNH-$), 10.62 (s, 1H, $-NHNH-$). Anal. Calcd for $C_{18}H_{19}BrN_2O_2$: C, 57.6; H, 5.1; N, 7.5. Found: C, 57.6; H, 5.2; N, 7.5.

*2-(4-Bromophenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (**2**)*. Compound **1** (30.0 g, 80.0 mmol) was placed in a 500 mL two-necked round-bottomed flask. $POCl_3$ (250 mL) was added to the flask. The mixture were refluxed for 6 h under a nitrogen atmosphere. After the completion of the reaction was confirmed by TLC, the reaction mixture was slowly poured into cold water in a ice bath and 0.5 M NaOH solution was added to neutralize the reaction mixture. Then the precipitate was collected on a filter, washed with distilled water, and finally recrystallized from ethanol/water = 3:1 (v/v). The yield was 84% (24.0 g). Mp: 134 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.37 (s, 9H, $-C(CH_3)_3$), 7.50 (d, 2H, Ar-*H*), 7.73 (d, 2H, Ar-*H*), 8.01 (d, 2H, Ar-*H*), 8.05 (d, 2H, Ar-*H*). Anal. Calcd for $C_{18}H_{17}BrN_2O$: C, 60.5; H, 4.8; N, 7.8. Found: C, 60.2; H, 4.9; N, 7.6.

*2-(4-tert-Butylphenyl)-5-{4-(2,5-dimethyl)biphenylyl}-1,3,4-oxadiazole (**3**)*. To compound **2** (17.7 g, 50.0 mmol) dissolved in 150 mL of toluene was added $(PPh_3)_4Pd$ (2.89 g, 2.50 mmol) and 50 mL of 2 M Na_2CO_3 (100 mmol). The mixture was stirred for 5 min under a nitrogen atmosphere. 2,5-Dimethylphenylboronic acid (9.0 g, 60 mmol) dissolved in 10 mL of ethanol was added to the reaction pot, and the mixture was refluxed for 24 h. And then, the reaction mixture was cooled to room temperature. Dark impurities were removed by filtration using Celite and charcoal as a filter aids. Solvents were removed by evaporation under a reduced pressure, and the crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate = 1/6 (v/v) as an eluent. The product is viscous liquid. The yield was 73% (14.0 g). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.39 (s, 9H, $-C(CH_3)_3$,), 2.31 (s, 3H, $Ar-CH_3$), 2.38 (s, 3H, $Ar-CH_3$), 7.04−7.24 (m, 3H, Ar-*H*), 7.48 (d, 2H, Ar-*H*), 7.59 (d, 2H, Ar-*H*), 8.12 (d, 2H, Ar-*H*), 8.20 (d, 2H, Ar-*H*). Anal. Calcd for $C_{26}H_{26}N_2O$: C, 81.6; H, 7.0; N, 7.3. Found: C, 81.6; H, 6.9; N, 7.3.

*2-[4-{2,5-Bis(bromomethyl)biphenylyl}]-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (**M-1**)*. A mixture of compound **3** (8.00 g, 20.9 mmol), *N*-bromosuccinimide (8.18 g, 46.0 mmol), and benzoyl peroxide (1.00 g, 4.18 mmol) was dissolved in 200 mL of CCl_4, and the mixture was refluxed for 2 h under nitrogen atmo-

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sphere. The mixture was cooled to room temperature, and insolubles were removed by filtration. The solvent was removed by evaporation under a reduced pressure to obtain white crystals. The crude product was washed with 200 mL of *n*-hexane and further purified by column chromatography on a silica gel column using *n*-hexane/ethyl acetate = 5/1 (v/v) as an eluent. The yield was 42% (4.74 g). Mp: 115 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.39 (s, 9H, $-C(CH_3)_3$,), 4.42 (s, 2H, $Ar-CH_2Br$), 4.53 (s, 2H, $Ar-CH_2Br$), 7.25 (s, 1H, Ar-*H*), 7.37−7.49 (m, 2H, Ar-*H*), 7.59 (d, 2H, Ar-*H*), 7.64 (d, 2H, Ar-*H*), 8.10 (d, 2H, Ar-*H*), 8.27 (d, 2H, Ar-*H*). Anal. Calcd for $C_{26}H_{24}Br_2N_2O$: C, 57.4; H, 4.5; N, 5.2. Found: C, 57.8; H, 4.6; N, 5.2.

*Poly[2{4-[5-(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenyl}-1,4-phenylenevinylene] (***P-1***).* Monomer **M-1** (1.00 g, 1.85 mmol) was dissolved in 100 mL of THF, and the polymerization flask was charged with argon. After the inner atmosphere was fully refreshed with argon, 11.1 mL of potassium *tert*-butoxide (1.0 M solution in THF, 11.1 mmol) was added dropwisely over a period of 5 min. After the reaction proceeded 4 h, the reaction mixture was poured into a 5:1 mixture of methanol and distilled water not only to precipitate the polymer but also to remove the unreacted base and produced salts. The precipitated polymer was collected on a filter. The polymer was dissolved in 1,1,2,2-tetrachloroethane and reprecipitated in methanol, and this dissolution−precipitation process was repeated twice more. Finally, the polymer solid was ground and low molecular weight materials were removed by Soxhlet extraction using methanol and acetone for 2 days, respectively. The product has orange color, and the recovery yield was 43% (0.30 g). ^{1}H NMR (300 MHz, 1,1,2,2-tetrachloroethane-d_2, ppm): 1.22 (s, 9H, $-C(CH_3)_3$,), 6.90−7.11 (br m, 2H, $-CH{=}CH-$), 7.25−8.23 (m, 11H, Ar-*H*). Anal. Calcd for $C_{26}H_{22}N_2O$: C, 82.5; H, 5.9; N, 7.4. Found: C, 82.3; H, 6.0; N, 7.3.

*2-(4-tert-Butylphenyl)-5-{4-(2,5-dimethyl-4-methoxy)biphenylyl}-1,3,4-oxadiazole (***4***).* Compounds **4**−**6** and **M-2** were synthesized as shown in Scheme 2. Compound **2** (14.2 g, 40.0 mmol) dissolved in 150 mL of toluene was mixed with $(PPh_3)_4Pd$ (2.89 g, 2.50 mmol) and 40 mL of 2 M Na_2CO_3 under nitrogen atmosphere. 2,5-Dimethyl-4-methoxyphenylboronic acid (10.8 g, 60.0 mmol) dissolved in 10 mL of ethanol was charged into the reaction flask. The reaction mixture was refluxed for 24 h. Dark impurities formed were removed by filtration using Celite and charcoal as a filter aids. Then, solvents in the filtrate were evaporated out under a reduced pressure and the crude product was purified by column chromatography on a silica gel column using *n*-hexane/ethyl acetate = 1/5 (v/v) as an eluent. The yield was 59% (12.17 g). Mp: 149 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.38 (s, 9H, $-C(CH_3)_3$), 2.24 (s, 3H, $Ar-CH_3$), 2.31 (s, 3H, $Ar-CH_3$), 3.88 (s, 3H, $-OCH_3$), 6.76 (s, 1H, Ar-*H*), 7.06 (s, 1H, Ar-*H*), 7.48 (d, 2H, Ar-*H*), 7.56 (d, 2H, Ar-*H*), 8.09 (d, 2H, Ar-*H*), 8.17 (d, 2H, Ar-*H*). Anal. Calcd for $C_{27}H_{28}N_2O_2$: C, 78.6; H, 6.8; N, 6.8; O, 7.8. Found: C, 78.4; H, 6.9; N, 7.3.

*2-(4-tert-Butylphenyl)-5-{4-(2,5-dimethyl-4-hydroxy)biphenylyl}-1,3,4-oxadiazole (***5***).* Compound **4** (10.0 g, 24.2 mmol) was dissolved in 50 mL of methylene chloride, and the solution was cooled to −20 °C. BBr_3 solution (1.0 M in methylene chloride, 45.0 mL, 45.0 mmol) was added dropwise to the reaction flask over a period of 30 min while the temperature was maintained at −20 °C for 1 h. Then the bath was warmed to 0 °C. After the mixture was kept at 0 °C for 2 h, when the completion of the reaction was confirmed by TLC, the mixture was poured into the distilled water to quench the excess BBr_3. The product formed was extracted with methylene chloride three times (150 mL × 3). After the extraction solution washed with water and brine sequentially, the solution was dried over 15 g of $MgSO_4$ for 2 h. And then the drying agent was removed by filtration. Removal of the solvent by evaporation at a reduced pressure produced a white solid, which was purified by column chromatography on a silica gel using methylene chloride as an eluent. Mp: 237 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.38 (s, 9H, $-C(CH_3)_3$,), 2.24 (s, 3H, $Ar-CH_3$), 2.29 (s, 3H, $Ar-CH_3$), 5.82−6.09 (br s, 1H, $Ar-OH$), 6.78 (s, 1H, Ar-*H*), 7.04 (s, 1H, Ar-*H*), 7.47 (d, 2H, Ar-*H*), 7.57 (d, 2H, Ar-*H*), 8.09 (d, 2H, Ar-*H*), 8.16 (d, 2H, Ar-*H*). Anal. Calcd for $C_{26}H_{26}N_2O_2$: C, 78.3; H, 6.6; N, 7.0. Found: C, 78.1; H, 6.6; N, 7.1.

*2-(4-tert-Butylphenyl)-5-[4-{4-(2-ethylhexyloxy)-2,5-dimethyl}-biphenylyl]-1,3,4-oxadiazole (***6***).* A mixture of 8.70 g of 2-ethylhexyl bromide (45.2 mmol), compound **5** (9.00 g, 22.6 mmol), and K_2CO_3 (6.32 g, 45.2 mmol) in 150 mL of acetonitrile was refluxed for 12 h to give compound **6**. After completion of reaction was confirmed by TLC, the reaction mixture was filtered to remove undissolved K_2CO_3, and the filtrate was evaporated at a reduced pressure. The crude product was purified by column chromatography on a silica gel column using *n*-hexane/ethyl acetate = 4/1 (v/v) as an eluent. The product is viscous liquid. The yield was 92% (10.61 g). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.88−1.00 (m, 6H, $-CH_3$), 1.37 (s, 9H, $-C(CH_3)_3$), 1.35−1.60 (m, 8H, $-CH(CH_2CH_3)CH_2CH_2CH_2$-$CH_3$), 1.78−1.84 (m, 1H, $-CH_2CH(CH_2-)CH_2-$), 2.24 (s, 3H, $Ar-CH_3$), 2.29 (s, 3H, $Ar-CH_3$), 3.90 (d, 2H, $-OCH_2CH-$), 6.75 (s, 1H, Ar-*H*), 7.05 (s, 1H, Ar-*H*), 7.47 (d, 2H, Ar-*H*), 7.55 (d, 2H, Ar-*H*), 8.08 (d, 2H, Ar-*H*), 8.16 (d, 2H, Ar-*H*). Anal. Calcd for $C_{34}H_{42}N_2O_2$: C, 80.0; H, 8.3; N, 5.5. Found: C, 79.9; H, 8.3; N, 5.4.

*2-[4-{2,5-Bis(bromomethyl)-4-(2-ethylhexyloxy)}biphenylyl]-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (***M-2***).* A mixture of compound **6** (5.11 g, 10.0 mmol), *N*-bromosuccinimide (3.92 g, 22.0 mmol), and benzoyl peroxide (0.48 g, 2.0 mmol) was dissolved in 200 mL of CCl_4, and the mixture was heated slowly to and kept at 76 °C under nitrogen atmosphere for 4 h. After the completion of the reaction was confirmed by TLC, the mixture was cooled to room temperature. And the insolubles were removed by filtration. The CCl_4 solvent was removed by evaporation under a reduced pressure to obtain a crude product. It was first purified by recrystallization from methylene chloride/methanol = 1/5 (v/v) twice. Finally, the product was purified by column chromatography on a silica gel column using *n*-hexane/ethyl acetate = 5/1 (v/v) as an eluent. The yield was 40% (2.67 g). Mp: 132 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.87−1.04 (m, 6H, $-CH_2CH_3$), 1.38 (s, 9H, $-C(CH_3)_3$), 1.43−1.64 (m, 8H, $-CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 1.78−1.89 (m, 1H, $-CH_2CH(CH_2-)CH_2-$), 4.10 (d, 2H, $-OCH_2CH-$), 4.43 (s, 2H, $Ar-CH_2Br$), 4.56 (s, 2H, $Ar-CH_2Br$), 7.03 (s, 1H, Ar-*H*), 7.26 (s, 1H, Ar-*H*), 7.57 (d, 2H, Ar-*H*), 7.61 (d, 2H, Ar-*H*), 8.18 (d, 2H, Ar-*H*), 8.22 (d, 2H, Ar-*H*). Anal. Calcd for $C_{34}H_{40}Br_2N_2O_2$: C, 61.1; H, 6.0; N, 4.2. Found: C, 61.1; H, 6.0; N, 4.2.

*Poly[2-{4-[5-(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenyl}-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (***P-2***).* Polymer **P-2** was synthesized as the same manner as used in the synthesis of **P-1**. The product has orange color, and the recovery yield was 40% (0.30 g). ^{1}H NMR (300 MHz, 1,1,2,2-tetrachlorothane-d_2, ppm): 0.69−0.98 (br, 6H, $-CH_2CH_3$), 1.08−1.80 (br, 18H, $-C(CH_3)_3$, $-CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$,), 3.80−4.13 (br d, 2H, $-OCH_2CH_3$), 6.93−7.76 (br m, 6H, $-Ar-CH{=}CH-Ar$),7.90−8.19 (br m, 2H, Ar-*H*). Anal. Calcd for $C_{34}H_{38}N_2O_2$: C, 80.1; H, 7.6; N, 5.5. Found: C, 80.7; H, 7.7; N, 5.5.

Device Fabrication. The ITO-coated glass (1.1 × 1.2 cm^2) with a sheet resistance of 25 Ω cm^{-1} (LG Co., Korea) was patterned by immersing into the concentrated HCl solution for 15 min and washed in the stream of water. The glass was further cleaned by sequential ultrasonication in acetone, methanol, distilled water, acetone, and 2-propanol for 10 min, respectively, and finally dried in a stream of dry nitrogen. The polymer solution in 1,1,2,2-tetrachloroethane (ca. 15 mg/mL) filtered through a syringe filter (Nalgene, 0.45 μm) was spin-coated onto the cleaned glass substrate under an argon atmosphere using a Laurell spin coater to obtain films about 600−800 nm thick. In the case of **P-2(3)**, the coated films were thermally treated at 150 °C for 3 h in a vacuum to the final polyconjugated polymers. For ITO/PEDOT/polymer/Li:Al device, PEDOT solution doped with polystyrenesulfonate (PSS) (Bayer; 10 S cm^{-1}) was spin coated onto the ITO-coated glass substrate preliminarily to obtain 20 nm thick films. Then, the Al or Al:Li electrode 1200 Å thick was vapor deposited on the polymer layer using a Leybold L560 (Kölm, Germany) apparatus at a deposition rate of 5 Å/s at pressure of 1.0 × 10^{-6} Torr. Deposition of the cathode electrodes were conducted by the Korea Basic Science Institute−Seoul Branch, Korea. The active layer of the device was 4.91 mm^2.

In the case of the ITO/polymer/Ca/Al devices, they were fabricated with ITO coated glass with a sheet resistance of 15 Ω cm^{-1}, and ITO layers were partially etched. After being etched, the glass substrates were cleaned by UVO (ultraviolet−ozone) cleaner in water first and then by ultrasonication in isopropyl alcohol and acetone sequentially for 13 min, respectively. And the **P-2** solutions in 1,1,2,2-tetrachloroethane (1.0 wt %) were spin coated to obtain 70 nm thick films. Finally, Ca and Al cathodes were vacuum deposited from the tungsten boat at deposition rates of 2 and 4 Å/s, respectively, at the pressure of 3.0 × 10^{-7} Torr. Luminescence properties were recorded on ISS PC1 (ISS Inc.) photon counting spectrofluorometer, and film thickness was determined by a Tencor P-10 surface profilmeter. Current−voltage ($I-V$) and luminance curves were obtained by Keithley 238 electrometer and Topcon BM-7 luminance colormeter (Topcon Technologies, Inc.), respectively. And all theses steps were conducted in an argon filled glovebox without exposing to air.

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