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Highly Efficient Novel Poly(*p*-phenylenevinylene) Derivative with 1,3,4-Oxadiazole Pendant on a Vinylene Unit

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Since the first report of the polymer light-emitting diode (PLED) based on poly(*p*-phenylenevinylene) (PPV) by Cambridge group,[1] many research groups have tried to improve the efficiency of LED. PPV derivatives with linear or branched alkoxy substituents (ROPPV) have low efficiency because the injection of holes is much more favorable than the injection of electrons. One of the strategies of improving the efficiency of PLED is to develop new polymers. It is desirable to synthesize new polymers with HOMO and LUMO levels such that the number of electrons and holes from the electrodes are nearly the same. It has been continuously reported that PPV derivatives containing electron-withdrawing groups such as cyano (CN),[2,3] 1,3,4-oxadiazole (OXD),[4−8] fluoroaryl,[9] or quinoline[10] in the main chain or side chains can be used as electron-transporting materials in PLEDs. In MEH−PPV-based polymers, incorporation of OXD units enhances the electron-injection rate while lowering the hole-injection rate because their HOMO and LUMO energy levels are lower than those of ROPPV. Oxidation of the vinyl groups of the PPV derivatives is one of the major causes which lower the efficiency and stability.[11,12] Introduction of electronegative OXD units in the polymer chain lowers the electron density in the vinyl group, leading to enhancement of stability and efficiency of the EL device.[13]

To synthesize a novel highly luminescent polymer, we take advantage of electron-transporting properties of OXD, which is substituted on the vinyl unit of the PPV main chain. In addition, the polymer is expected to have highly twisted chain conformations because of the bulky OXD units. Such chain confirmations are expected to minimize interchain interactions, which are well-known to lower the efficiency of EL and PL.[14] Thus, the designed polymer structure (Scheme 1) is aimed for highly efficient and stable EL devices. In this communication, we report the synthesis, optical properties, and electroluminescent (EL) properties of a novel PPV derivative, poly{1,4-phenylene-1,2-ethenediyl-2′-[2″-(4‴-octyloxyphenyl)−(5″-yl)-1″,3″,4″-oxadiazole]-1,4-phenylene-1,2-ethenediyl-1′-[2″-(4‴-octyloxyphenyl)-5″-yl-1″,3″,4″-oxadiazole]-1,4-phenylene-1,2-ethenediyl-2,5-bis-dodecyloxy-1,4-phenylene-1,2-ethenediyl} (OXD−PPV), which has OXD pendant on the vinyl unit. To the best of our knowledge, PPV derivatives with an OXD pendant on the vinyl unit have never been reported before.

The synthetic route of the key monomer, compound **5**, is shown in Scheme 1. The first step is a simple synthetic procedure of ether in which methyl 4-hydroxybenzoate reacts with 1-bromooctane to form **1** in a high yield of over 90%. Amidization of **1** with hydrazine leads to **2**. Reaction of **2** with 1,4-phenylenediacetic acid in the presence of 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI), a well-known amide coupling agent, gives **3**. Cyclization of **3** by $POCl_3$ leads to **4**, which is a well-known method for the synthesis of oxadiazole. As the NMR peak of the benzylic proton in **4** appeared at 4.24 ppm[15] and the peak of benzylic proton in phenylacetonitrile appears approximately at 3.7 ppm, one can assume that the acidity of the two protons are comparable. It is well-known that phenylacetonitrile undergoes condensation reaction with 4-bromobenzaldehyde. Thus, it is expected that **4** can also undergo condensation reaction with 4-bromoaldehyde. In fact, it was possible to obtain **5** by condensation reaction between compound **4** and 4-bromobenzaldehyde in the presence of a catalytic amount (10 mol %) of tetrabutylammonium hydroxide in relatively high yield (85.3%) and purity. Polymerization was conducted by the well-known palladium-catalyzed Heck coupling reaction between **5** and 1,4-bis-dodecyloxy-2,5-divinylbenzene in DMF at 140 °C (Scheme 1). The number average molecular weight of the polymer was 1.4×10^4 with a polydispersity index of 4.70 as determined by GPC. The point of 5% weight loss in the TGA thermogram of OXD−PPV appeared at 397 °C. The polymer was readily soluble in chloroform, THF, or toluene and formed good transparent film on the surface of ITO-coated glass.

The UV−vis and photoluminescence (PL) spectra of the polymer film are shown in Figure 1. The polymer film shows two absorption bands. An absorption maximum at 356 nm is attributable to OXD units while the

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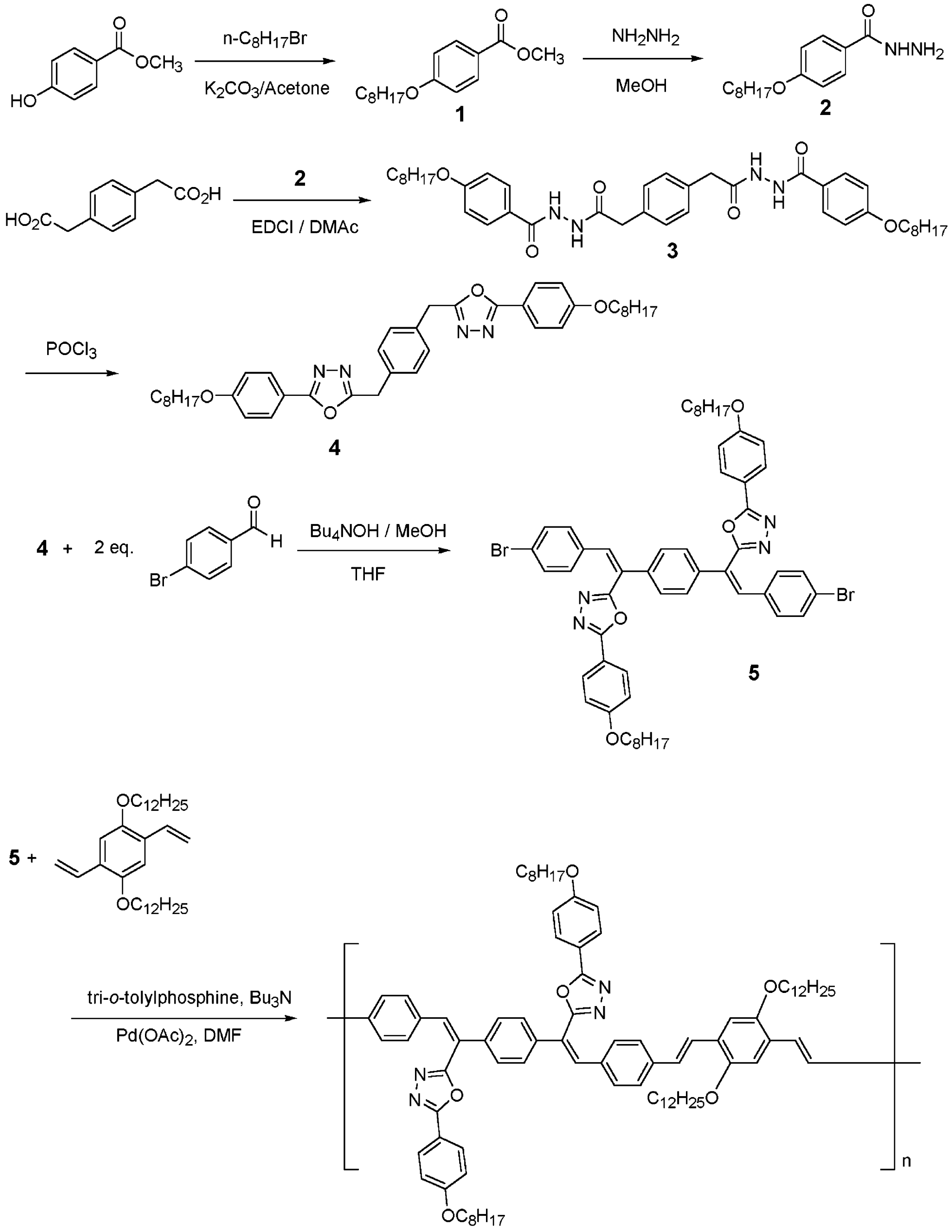
Scheme 1. Synthesis of Monomer and Polymer



absorption maximum at 426 nm corresponds to the $\pi-\pi^*$ transition of the main chain. The band gap energy and PL maximum of the polymer film are 2.20 eV and 561 nm ($\lambda_{ex} = 450$ nm), respectively. Very often the tail appearing in the long wavelength region of PL spectra of the π-conjugated polymers are attributed to the interchain interactions.[16] It is known that interchain interactions tend to lower PL efficiency.[14,16] There was no tail in the long wavelength region of the PL spectrum of OXD−PPV. The PL quantum yield of OXD−PPV film was 6.5 times higher than that of MEH−PPV film. In addition, the PL decay time of OXD−PPV film was 790 ps, which is slower than that of MEH−PPV.[15] We can think of two reasons for this. First, because the OXD unit is attached to the vinyl unit in the main chain, the dihedral angle between the phenyl ring in the main chain and the vinyl group is greater than that in MEH−PPV, the π-conjugation length would become shorter. Second, OXD units would stick out almost perpendicularly to the phenyl ring in the main chain. In this case, chances of interactions between the main chains would be extremely low compared to the case of polymers with the substituents on the phenyl ring.[7]

Cyclic voltammetry (CV) was used to investigate the redox behavior of the polymer and to assess the HOMO and LUMO energy levels. The oxidation and reduction potentials were compared with a reduction potential of ferrocene/ferrocenium (FOC). The onset potentials for oxidation and reduction appeared at 0.50 and −1.69 V vs FOC, respectively. The HOMO and LUMO energy levels obtained from cyclic voltammetry and UV−vis spectroscopy were −5.30 and −3.10 eV, respectively. The band gap energy measured from the CV was 2.19 eV, which agrees very well with the value obtained from UV−vis spectroscopy (2.10 eV). The HOMO and LUMO energy levels support the argument that the injection

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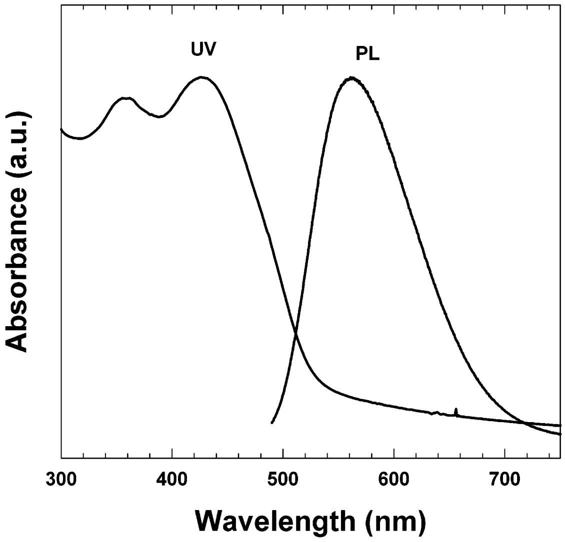

Figure 1. UV−vis and PL spectra of OXD−PPV film.

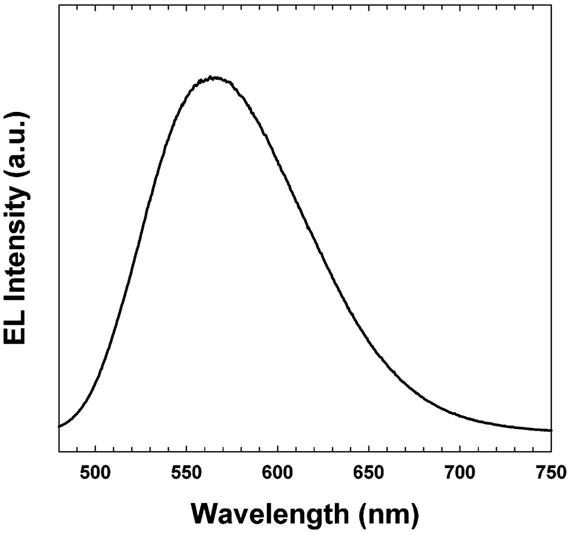

Figure 2. EL spectrum of ITO/PEDOT/OXD−PPV/Al.

of holes and electrons in the polymer is more balanced than in MEH−PPV (−4.98 eV, −2.89 eV).[17]

A double-layer EL device with the configuration of ITO/PEDOT:PSS/OXD−PPV/Al gave bright yellow emission with an EL maximum (Figure 2) at 563 nm, which is almost the same as the PL maximum. In fact, the shape of the EL spectrum is almost identical to the PL spectrum (Figure 1b and Figure 2). This indicates that the emission mechanism in EL is very similar to PL. The EL spectra did not change significantly in a wide bias range, that is, from 6 to 14 V. Figure 3 shows the current density (J) vs applied voltage and brightness (B) vs applied voltage characteristics of the EL devices based on OXD−PPV. The maximum quantum efficiency of the device with Al cathode was 0.34% at 11.0 V and 0.077 A/cm^2 and the maximum luminance was 1457 cd/m^2 at 13.0 V and 0.22 A/cm^2. The device with an Al cathode showed a high EL efficiency. When a Ca cathode was used in place of an Al cathode, the maximum external quantum efficiency was 0.43% at 11.0 V (0.25 A/cm^2) and the maximum luminance was 5140 cd/m^2 at 12.5 V (0.61 A/cm^2) with the turn-on voltage of 5.5 V. Interestingly, despite a lower work function (2.9 eV) of Ca than that of Al (4.2 eV), we observed no significant improvement in EL efficiency by replacing the Al cathode with a Ca cathode. This implies that the electron-transporting property has already been improved by the presence of OXD units in the polymer. The device based on a Ca cathode has lower turn-on voltage and higher brightness than that of the device based on an Al cathode. The lower turn-on voltage and higher brightness achieved in the Ca-cathode-based device is due to the more improved injection ability of electrons.

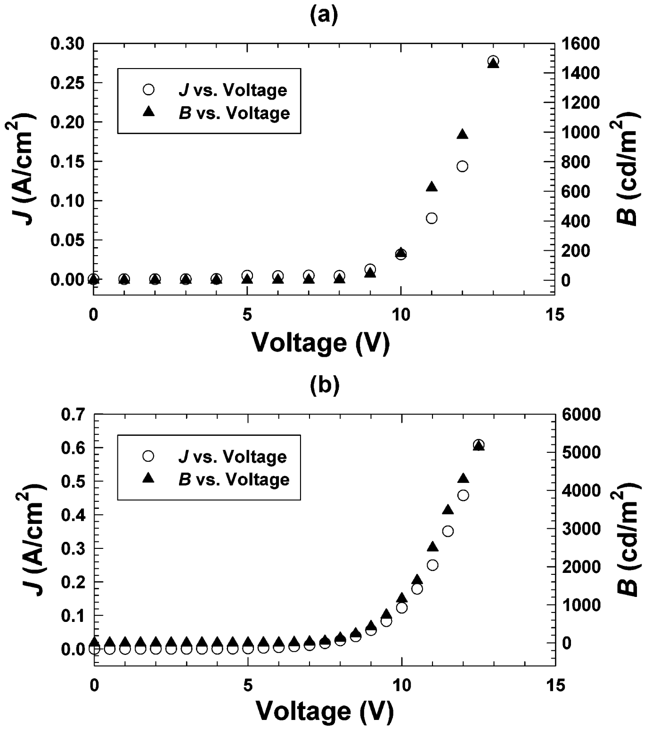

Figure 3. $J-V-B$ curves of (a) ITO/PEDOT/OXD−PPV/Al and (b) ITO/PEDOT/OXD−PPV/Ca/Ag.

In conclusion, a new and highly efficient OXD−PPV with OXD units on the vinyl unit was synthesized by the palladium-catalyzed Heck coupling polymerization reaction. The incorporation of electron-withdrawing OXD groups lead to an increase in electron affinity and decrease in interchain interaction. The device based on the polymer fabricated with Al or Ca cathode show bright yellow emission and significantly high efficiency with a relatively low turn-on voltage.

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Supporting Information Available: Detailed experimental methods, the synthetic procedure, and spectral data of compounds **1**−**5** and the polymer. ^{1}H NMR, FT-IR spectrum, time-resolved PL decay curve, and TGA thermogram of OXD−PPV. This material is available free of charge via the Internet at http://pubs.acs.org.

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