Highly Efficient Light-Emitting Polymers Composed of Both Hole and Electron Affinity Units in the Conjugated Main Chain

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ABSTRACT: Two new fully conjugated alternating copolymers containing both carbazole and oxadiazole units were prepared through the Wittig condensation polymerization (carbazole units were linked with oxadiazole units by meta and para). The polymers with the para linkage (PPOX−CAR) and the meta linkage (PMOX−CAR) in the main chain were soluble in common organic solvents and thermally stable on heating (the weight loss was less than 5% on heating to about 400 °C under nitrogen atmosphere). The maximum photoluminescence and the electroluminescence wavelengths of PPOX−CAR and PMOX−CAR were varied from 495 nm in the greenish-blue emission region to 450 nm in the blue emission region depending on the kink structure. The turn-on voltages of PPOX-CAR and PMOX-CAR were 7.5 and 10.5 V, respectively, when the single-layer light-emitting diodes of Al/PPOX-CAR or PMOX-CAR/ITO glass were fabricated. The maximum brightness of the Al/PPOX-CAR/ITO single-layer device was 500 cd/m^2 at 20 V.

Introduction

Research concerning electroluminescence (EL) of π-conjugated polymers has rapidly developed since the demonstration of light emission from a poly(*p*-phenylenevinylene) (PPV) thin film sandwiched between hole- and electron-injecting electrodes.[1−4] Many research groups have tried to improve the quantum efficiency and to synthesize short-wavelength light-emitting polymers for blue light.[4−6]

To improve the device performance of organic light-emitting diodes (LEDs), it is necessary to balance the rate of injection of electrons and holes from opposite electrodes into the device. For PPV derivatives, the injection of holes predominates over the injection of electrons.[7] One method for balancing the rates of injected holes and electrons employs multilayer devices. Oxadiazole units are known as electron deficient groups and poor hole acceptors. Aromatic oxadiazole compounds, such as 2-(4-*tert*-butyl-phenyl)-5-biphenyl-1,3,4-oxadiazole (PBD), have been investigated as electron-conducting/hole-blocking (ECHB) materials within multilayer devices,[8−11] and poly(*N*-vinylcarbazole) compounds have been used as hole-transporting materials.[12] Although some polymer LEDs have shown high-enough efficiencies and long lifetimes, they are mainly multilayer LEDs, which involve complicated and difficult device fabrication processes, or single layer LEDs based on polymer blends, which have the disadvantage of phase separation. So, it is important to achieve conjugated polymers which have both functions of hole/electron affinity in the single layer LEDs. The bipolar transport characteristics of polymers are important for high EL efficiency, because the polymers offer good recombination sites for hole and electron charge carriers.[13,14]

Another need has been the achievement of short-wavelength light-emitting polymers in the field of polymer LEDs.[15−18] It was filled by the introduction of well-defined lumophores to the polymer main chains. However, these polymers contained nonconjugated spacer groups between the lumophores, leading to high threshold voltages that generally damage the polymeric material and the cathode metal.[18]

Our present work involves the synthesis of a new series of soluble emissive alternating copolymers containing both hole and electron affinity units in the conjugated main chain for pursuing efficient single-layer polymer LEDs. The alternating copolymers were prepared by the Wittig condensation polymerization between the oxadiazole unit and the carbazole unit. The oxadiazole unit was known to be an electron-transporting material as well as thermally, hydrolytically, and photolytically stable material.[19−24] The carbazole unit was also known as a hole-transporting and electroluminescent material.[25−27] In addition, we designed well-defined conjugated polymers by the kink structure for short-wavelength light-emitting polymers (blue and green emission). We synthesized poly[(2,5-di-phenyl-1,3,4-oxadiazole)-4-diylvinylene-*alt*-3,6-(9-(2-ethylhexyl)-carbazolenevinylene)] (PPOX-CAR) and poly[(2,5-di-phenyl-1,3,4-oxadiazole)-3-diylvinylene-*alt*-3,6-(9-(2-ethylhexyl)-carbazolenevinylene)] (PMOX-CAR) through the Wittig condensation polymerization. The synthetic route and details are given in the Schemes 1 and 2 and the Experimental Section.

Experimental Section

Instrumentation. The synthesized compounds were characterized by ^{1}H NMR and ^{13}C NMR spectra that were obtained using a Bruker AM 200 spectrometer. FT-IR spectra were obtained with Bomem Michelson series FT-IR spectrophotometer. Melting points were determined using an Electrothermal model 1307 digital analyzer. The elemental analyses were performed by the Seoul Branch Analytical Laboratory of the

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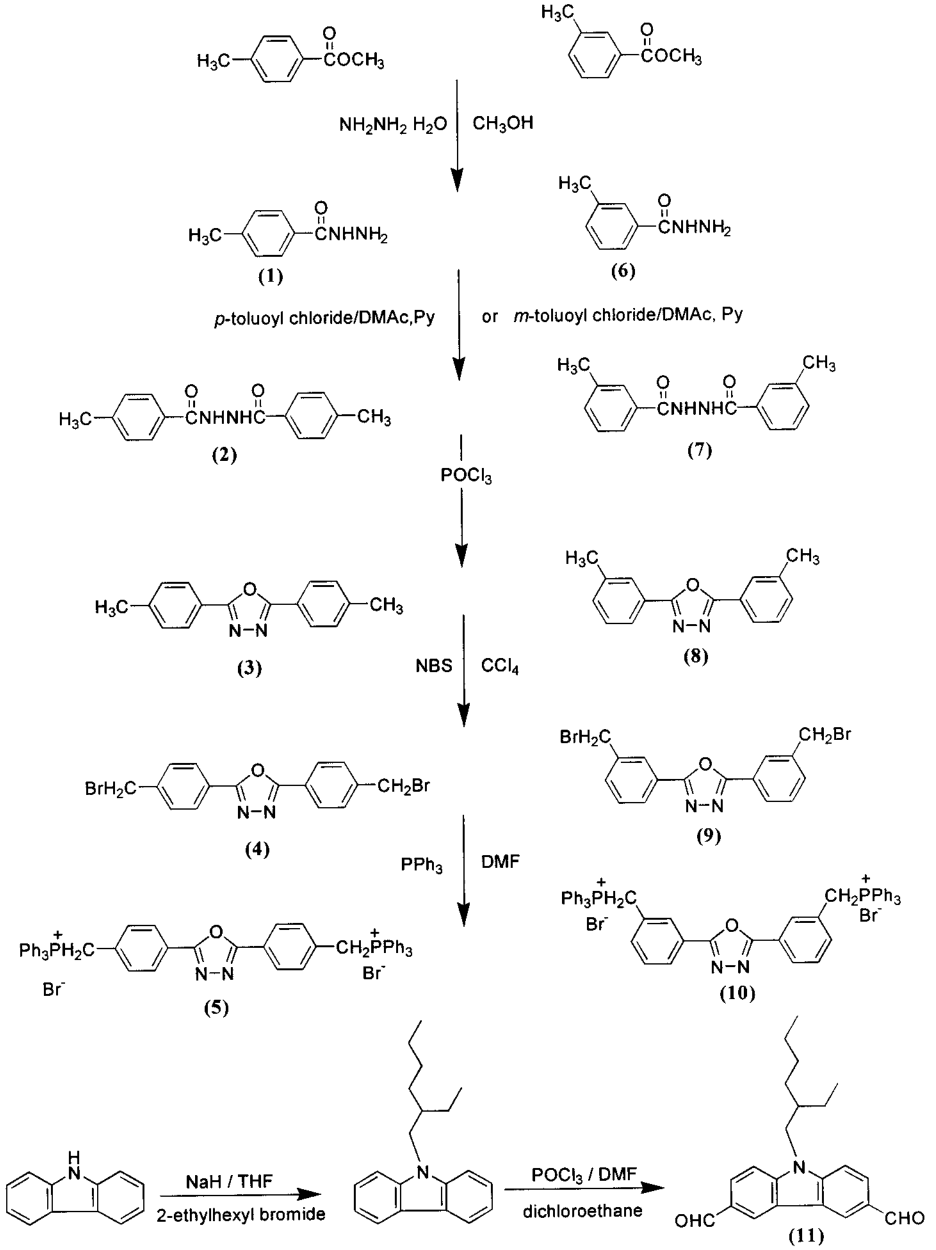
Scheme 1. Synthetic Routes to the Monomers

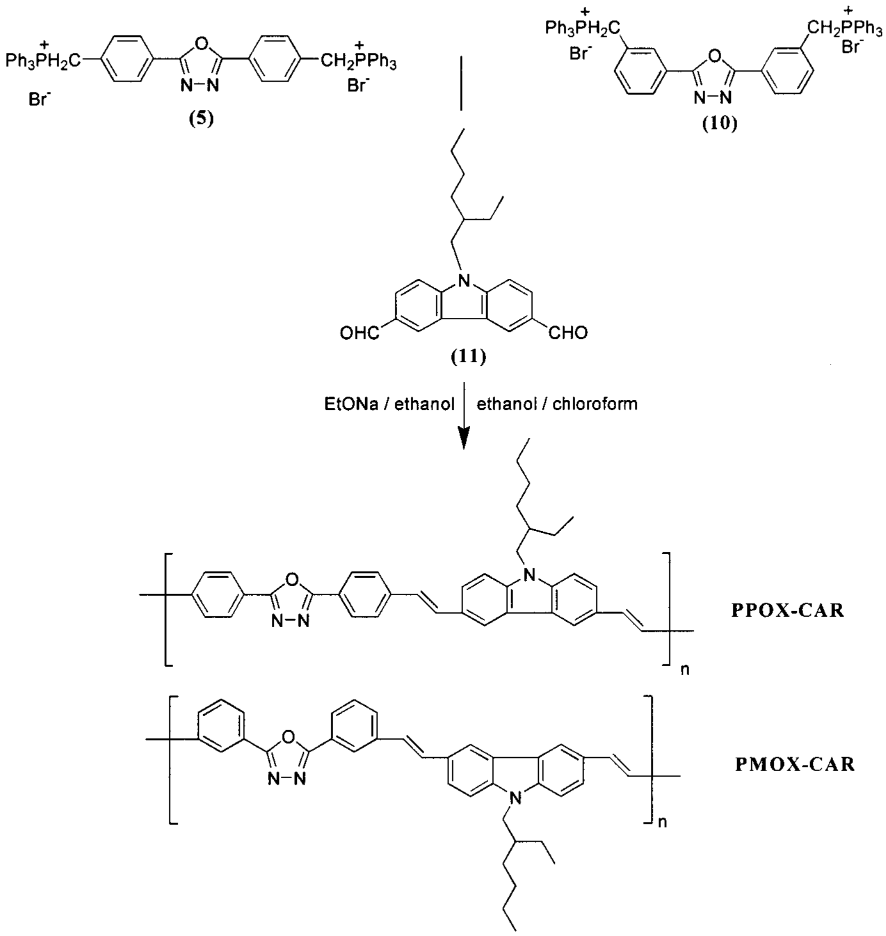


Korea Basic Science Institute. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymers were performed under nitrogen atmosphere at a heating rate of 10 °C/min with a DuPont 9900 analyzer. The UV−visible spectra of the polymers were measured using a Shimadzu UV-3100S. The photoluminescence (PL) spectra of the polymers were obtained using a Perkin−Elmer LS-50 luminescence spectrometer. The electroluminescence spectra were measured using a dual-grating monochromator (Spex 270M) with a photomultiplier tube (Hammamatzu R955) as a detector. The EL spectra were recorded at 3 nm resolution by computer through the photon counter (SR400) averaging the signal from PMT while applying a direct current from a current/voltage source (Keithley 238). The current/voltage ($I-V$) and light intensity−voltage ($L-V$) characteristics were measured using a current/voltage source and an optical powermeter (Newport 835). The injected current was measured by the voltage supply while applying forward bias. In addition, the emitted light was collected with a Si photodetector (Newport 818SL) placed in front of the device and recorded by computer. The brightness of the EL device was measured using a Minolta CS-1000 spectroradiometer. All of the measurements mentioned above were performed in air and at room temperature.

4-Methylbenzoichydrazide (1). A mixture of 20.0 g of methyl 4-methylbenzoate (133.2 mmol) and an excess amount of hydrazine monohydrate was dissolved in methanol, and then the mixture was heated at 80 °C for 30 h. After the reaction was finished, water was poured into the reaction mixture and extracted with ethyl acetate. The product yield was 18.6 g (93%). Mp: 121−123 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 9.9 (s, 1H), 7.6 (d, 2H), 7.1 (d, 2H), 4.6 (s, 2H), 2.3 (s, 3H). ^{13}C NMR (CDC13, ppm): δ 168.5, 142.2, 129.6, 129.2, 126.8, 21.3. FT-IR (KBr pellet, cm^{-1}): 3300~3223 (ν_{N-H}), 1661 ($\nu_{C=O}$), 1616 (δ_{N-H}). Anal. Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.76; H, 6.66; N, 18.59.

Bis(4-methylphenyl)hydrazine (2). A mixture of 6.0 g of 4-methylbenzoic hydrazide (40.0 mmol) and 5.3 mL of *p*-toluoyl chloride (1.0 equiv) was dissolved in *N*,*N*-dimethylacetamide (DMAc). The reaction was carried out at 0 °C for 3 h, and then pyridine (5.0 mL) was added. The reaction mixture was poured into cold water and precipitated. The precipitate was collected and dried in a vacuum oven. The pure white solid product was obtained by recrystallizing from methanol. The product yield was 9.5 g (89%). Mp: 257−258 °C. ^{1}H NMR (DMSO-d_6, ppm): δ 10.4 (s, 2H), 7.8 (d, 4H), 7.3 (d, 4H), 2.3 (s, 6H). ^{13}C NMR (DMSO-d_6, ppm): δ 165.8, 141.9, 129.8, 129.1, 127.5, 21.1. FT-

Scheme 2. Synthetic Routes to PPOX-CAR and PMOX-CAR



IR (KBr pellet, cm^{-1}): 3196 (ν_{N-H}), 1660 ($\nu_{C=O}$), 1627 (δ_{N-H}). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.29; H, 5.99; N, 10.44.

2,5-Bis(4-methylphenyl)-1,3,4-oxadiazole (3). A solution of bis(4-methylphenyl)hydrazine (5.0 g, 18.6 mmol) in $POCl_3$ (50.0 mL) was heated to 80 °C and kept at this temperature for 16 h. Excess $POCl_3$ was distilled off the reaction mixture, and then the residue was slowly poured into water and extracted with methylene chloride. Purification of crude product on methyl alcohol gave a white solid compound. The product yield was 4.0 g (85%). Mp: 164−166 °C. ^1H NMR ($CDCl_3$, ppm): δ 8.0 (d, 4H), 7.3 (d, 4H), 2.4 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 164.3, 142.0, 129.6, 126.7, 121.1, 21.5. FT-IR (KBr pellet, cm^{-1}): 1612 ($\nu_{C=N}$). Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.34; H, 5.64; N, 11.34.

2,5-Bis[4-(bromomethyl)phenyl]-1,3,4-oxadiazole (4). A mixture of 3.6 g of 2,5-bis(4-methylphenyl)-1,3,4-oxadiazole (14.4 mmol) and 5.5 g of *N*-bromosuccinimide (NBS) (2.2 equiv) was dissolved in carbon tetrachloride. A catalytic amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed at 120 °C for 5 h under nitrogen atmosphere. The completion of the reaction was indicated by the appearance of succinimide on the surface of the reaction solution. A yellow solution was obtained after filtration of the succinimide. The solution was then poured into water and extracted with methylene chloride. The organic layer was collected and dried using $MgSO_4$, and the solvent was removed using a rotary evaporator. The crude product was purified by recrystallization using methanol. The yield was 4.3 g (75%). Mp: 224−225 °C. ^1H NMR ($CDCl_3$, ppm): δ 8.1 (d, 4H), 7.5 (d, 4H), 4.5 (s, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 166.3, 143.2, 128.6, 125.6, 121.5, 33.4. FT-IR (KBr pellet, cm^{-1}): 1612 ($\nu_{C=N}$). Anal. Calcd for $C_{16}H_{14}N_2O$: C, 47.09; H, 2.96; N, 6.86. Found: C, 47.37; H, 3.09; N, 7.02.

2,5-Bis(4-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole (5). A solution of 3.0 g of 2,5-bis[4-(bromomethyl)phenyl]-1,3,4-oxadiazole (7.3 mmol) and 4.3 g (2.2 equiv) of triphenylphosphine in 30.0 mL of DMF was stirred and heated to reflux for 24 h. The resulting mixture was poured into diethyl ether. After filtration and being vacuum-dried, the monomer was obtained as a white powder. The product yield was 4.6 g (82%). Mp: 240−241 °C. ^1H NMR ($CDCl_3$, ppm): δ 7.8−7.5 (m, 34H), 7.1 (d, 4H), 5.1 (d, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 165.7, 134.9, 134.7, 134.2, 132.6, 132.2, 130.2, 129.9, 129.7, 118.4, 117.2, 30.6. FT-IR (KBr pellet, cm^{-1}): 1612 ($\nu_{C=N}$). Anal. Calcd for $C_{52}H_{42}Br_2N_2OP_2$: C, 66.97; H, 4.54; N, 3.00. Found: C, 66.88; H, 4.55; N, 3.12.

2,5-bis(3-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole was prepared by the same method (same scale) as 2,5-bis(4-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole except for the starting materials (methyl 3-methylbenzoate and *m*-toluoyl chloride).

3-Methylbenzoic Hydrazide (6). The product yield was 19.0 g (95%). Mp: 100−101 °C. ^1H NMR ($CDCl_3$, ppm): δ 9.5 (s, 1H), 7.5 (m, 2H), 7.2 (m, 2H), 5.4 (s, 2H), 2.3 (s, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 168.8, 138.5, 132.5, 128.5, 127.7, 127.5, 123.6, 21.2. FT-IR (KBr pellet, cm^{-1}): 3296 (ν_{N-H}), 1677 ($\nu_{C=O}$), 1622 (δ_{N-H}). Anal. Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.68; H, 6.61; N, 18.61.

Bis(3-methylphenyl)hydrazine (7). The product yield was 9.2 g (82%). Mp: 224−225 °C. ^1H NMR (DMSO-d_6, ppm): δ 10.4 (s, 2H), 7.7 (m, 4H), 7.4 (m, 4H), 2.3 (s, 6H). ^{13}C NMR (DMSO-d_6, ppm): δ 166.0, 137.9, 132.6, 132.4, 128.1, 127.7, 124.6, 21.0. FT-IR (KBr pellet, cm^{-1}): 3212 (ν_{N-H}), 1672 ($\nu_{C=O}$), 1637 (δ_{N-H}). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.25; H, 5.97; N, 10.47.

2,5-Bis(3-methylphenyl)-1,3,4-oxadiazole (8). The product yield was 4.3 g (91%). Mp: 83−84 °C. ^1H NMR ($CDCl_3$, ppm): δ 7.9 (m, 4H), 7.4 (m, 4H), 2.4 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 164.5, 138.8, 132.4, 128.9, 127.4, 127.2, 123.8, 21.1. FT-IR (KBr pellet, cm^{-1}): 1594 ($\nu_{C=N}$). Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.25; H, 5.62; N, 11.36.

2,5-Bis[3-(bromomethyl)phenyl]-1,3,4-oxadiazole (9). The product yield was 4.3 g (75%). Mp: 162−164 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 8.1 (m, 4H), 7.5 (m, 4H), 4.5 (s, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 163.5, 143.0, 138.9, 132.4, 129.7, 127.4, 127.2, 32.1. FT-IR (KBr pellet, cm^{-1}): 1617 ($\nu_{C=N}$). Anal. Calcd for $C_{16}H_{12}Br_2N_2O$: C, 47.09; H, 2.96; N, 6.86. Found: C, 47.28; H, 2.99; N, 6.87.

2,5-Bis(3-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole (10). The product yield was 4.5 g (80%). Mp: 197−198 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.8−7.5 (m, 34H), 7.2 (m, 4H), 5.6 (d, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 163.6, 135.1, 134.5, 134.4, 130.3, 130.1, 129.4, 129.0, 128.9, 126.6, 123.7, 117.6, 116.7, 38.8. FT-IR (KBr pellet, cm^{-1}): 1612 ($\nu_{C=N}$). Anal. Calcd for $C_{52}H_{42}Br_2N_2OP_2$: C, 66.97; H, 4.54; N, 3.00. Found: C, 66.62; H, 4.55; N, 3.11.

3,6-Diformyl-9-(2-ethylhexyl)-carbazole (11). 3,6-Diformyl-9-(2-ethylhexyl)-carbazole was synthesized by the previous work.[28]

Polymerization. PPOX-CAR and the PMOX-CAR were synthesized through the Wittig condensation polymerization between 3,6-diformyl-9-(2-ethylhexyl)-carbazole and either 2,5-bis(4-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole or 2,5-bis(3-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole, respectively.

Polymer PPOX-CAR or PMOX-CAR. A solution of sodium ethoxide (2.7 g, 39.7 mmol) in 15.0 mL of absolute ethanol was added to 15.0 mL of anhydrous chloroform/ethanol solution of 0.53 g (0.4 equiv) of the dialdehyde monomer **11** and 1.47 g (0.4 equiv) of the salt monomer **5** or **10** at room temperature. The mixture was stirred for 24 h at room temperature under N_2 atmosphere. The reaction mixture was extracted with excess dichloromethane and water. After being dried and having the solvent removed, a crude polymer product was obtained. Then, the polymer was dissolved in dichloromethane and precipitated in methanol several times. After filtration and being vacuum-dried, yellow PPOX-CAR or PMOX-CAR was obtained. The product yields of PPOX-CAR and PMOX-CAR were 0.5 g (58%) and 0.4 g (46%), respectively. Thin films of the polymers could be obtained with excellent reproducibility by being spin-cast from a 1,2-dichloroethane solution. The EL device structures consist of an aluminum rectifying contact on the polymers that were coated on the ITO electrode acting as a hole-injecting contact. The film thickness measured using a Tencor Alpha-Step 500 profiler was about 100 nm. Electron-injecting aluminum contacts were formed by vacuum evaporation at pressures below 10^{-6} Torr, giving active areas of 0.2 cm^2.

Results and Discussion

The synthetic routes to PPOX-CAR and PMOX-CAR are a little bit complicated, but we could obtain all of the intermediate compounds in high yields, over 75%, and these compounds were well-characterized through the data from melting points, ^{1}H NMR, ^{13}C NMR, FT-IR, and elemental analyses. Both of the intermediate compounds (**1**−**5** for PPOX-CAR and **6**−**10** for PMOX-CAR) showed almost the same ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analyses data, except for the melting points. The intermediates toward PMOX-CAR showed lower melting points due to their nonlinear kinked structures compared with those of PPOX-CAR. Figure 1 shows the FT-IR spectra of the dialdehyde monomer **11** and the PPOX-CAR on the KBr pellet. The FT-IR spectrum of the dialdehyde monomer **11** exhibited a strong peak of the aldehyde carbonyl group at 1686 cm^{-1} and the characteristic peak of aldehydic hydrogen at 2719 cm^{-1}. However, the FT-IR spectrum of PPOX-CAR did not exhibit the strong peak at 1686 cm^{-1} nor the aldehydic hydrogen peak after polymerization. At the same time, a weak but sharp peak at 961 cm^{-1} corresponding to the out-of-plane bending mode of the *trans*-vinylene groups appeared, suggesting that the generated double bonds are mainly in the trans configuration.

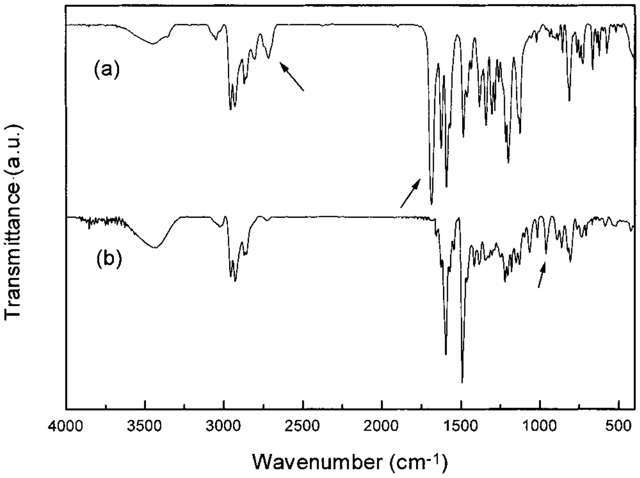


Figure 1. FT-IR spectra of (a) monomer **11** and (b) PPOX-CAR.

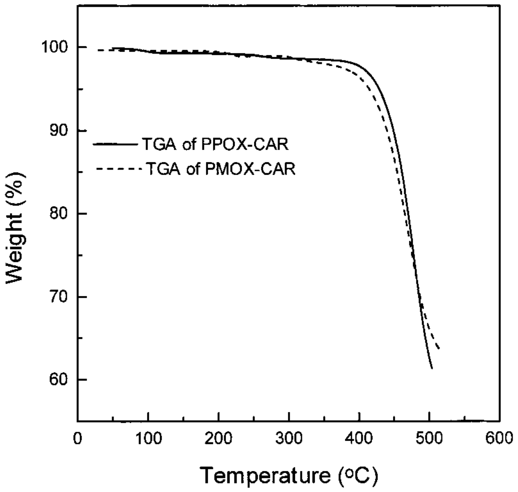


Figure 2. TGA thermograms of PPOX-CAR and PMOX-CAR.

The weight-average molecular weights (M_w) of PMOX-CAR and PPOX-CAR were in the range of 5 000−15 000, with a polydispersity index of about 1.5. Both polymers were soluble in common organic solvents such as chloroform, THF, and 1,2-dichloroethane. The polymers with the para linkage (PPOX-CAR) and the meta linkage (PMOX-CAR) in the main chain showed glass-transition temperatures (T_g) at 130 and 98 °C, respectively. The kinked meta-linked PMOX-CAR showed lower T_g because of its poor chain packing compared to the linear para-linked polymer. Both PPOX-CAR and PMOX-CAR showed good thermal stability (Figure 2) as weight loss was less than 5% on heating to about 400 °C under nitrogen atmosphere. The linear para-linked PPOX-CAR polymer showed a slightly higher decomposition temperature compared to that of kinked PMOX-CAR.

The UV−visible absorption spectra of PPOX-CAR and PMOX-CAR are shown in Figure 3. The characteristic maximum absorption of PPOX-CAR was shown at around 390 nm, which is a characteristic of conjugated polymers, and 300 and 250 nm, which originated from carbazole and oxadiazole units. The absorption edge of

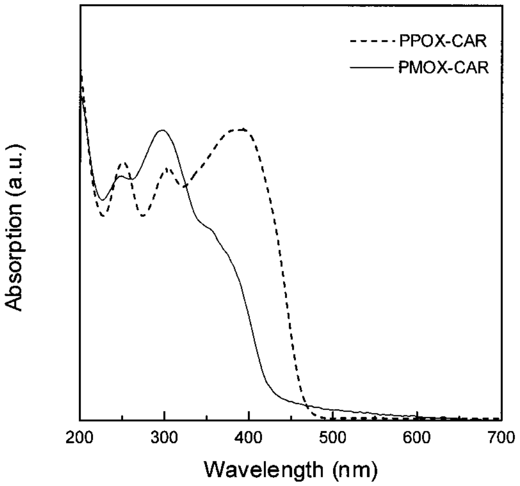


Figure 3. UV−vis absorption spectra of PPOX-CAR and PMOX-CAR.

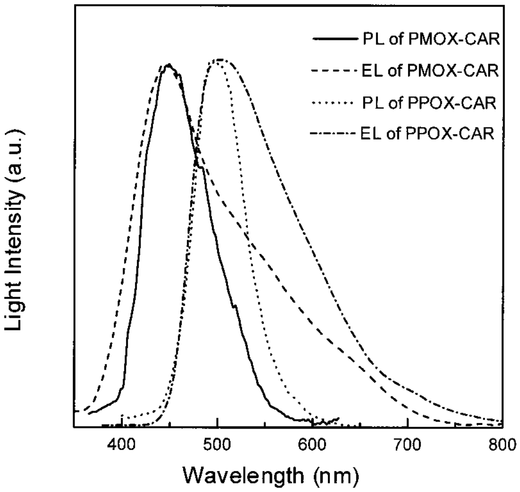


Figure 4. Photoluminescence, and electroluminescence spectra of PPOX-CAR, and the PMOX-CAR.

PPOX-CAR was shown at around 470 nm. The UV−visible absorption spectrum of PMOX-CAR is similar to that of PPOX-CAR, but the absorption maximum and the edge were shown at around 300 nm and 450 nm, respectively. This blue shift was caused by the kink structure of meta-linked PMOX-CAR, because the meta linkage between oxadiazole and carbazole unit shortened the effective conjugation length by restriction of the fully conjugated polymer structure.[29]

Table 1. Comparison of Relative EL Quantum Efficiency, Turn-On Voltage, and Emissive Wavelength among PPV, PPOX-CAR, and PMOX-CAR

light-emitting polymer	relative EL quantum efficiency	turn-on voltage [electric field (V/m)]	emissive wavelength (nm)
PPV	1	5.0×10^7	540
PPOX-CAR	36	7.5×10^7	495
PMOX-CAR	2	10.5×10^7	450

Figure 4 shows the photoluminescence, and electroluminescence spectra of PPOX-CAR, which has para linkage in the main chain, and meta-linked PMOX-CAR. The PL spectrum of PPOX-CAR has a maximum peak at 495 nm, corresponding to greenish-blue light emission. The EL spectrum also showed a maximum peak at 495 nm, when the LED was composed of Al/PPOX-CAR/ITO. The PL and EL spectra of PMOX-CAR exhibited a maximum emission peak at 450 nm, indicating a pure blue light emission. It is clear that the PMOX-CAR polymer in the meta linkage was less conjugated because of its poor π-electron delocalization than was the case for the PPOX-CAR polymer.

Figure 5 shows the characteristics of the current and emission-light intensity against voltage. The PPOX-CAR polymer has turn-on voltage for current at 7.5 V and the PMOX-CAR polymer at 10.5 V (both polymer films have almost the same thickness, around 100 nm). It is clear that the kink structure has high turn-on voltage because of shorter conjugation length and less effective π-electron delocalization through the kinked polymer chain. The relatively low turn-on voltage compared to other green and blue light emission polymers[30,31] was caused by the effect of the carbazole unit as a hole transporting material.

At relatively low operating voltages, the light intensity of PPOX-CAR is much stronger than that of PMOX-CAR, as shown in Figure 5b. So, it is believed that the PPOX-CAR polymer can be used as a excellent greenish-blue light-emitting layer. We investigated the relative EL quantum efficiencies of PPV and both polymer devices in the same device condition (shown in Table 1).

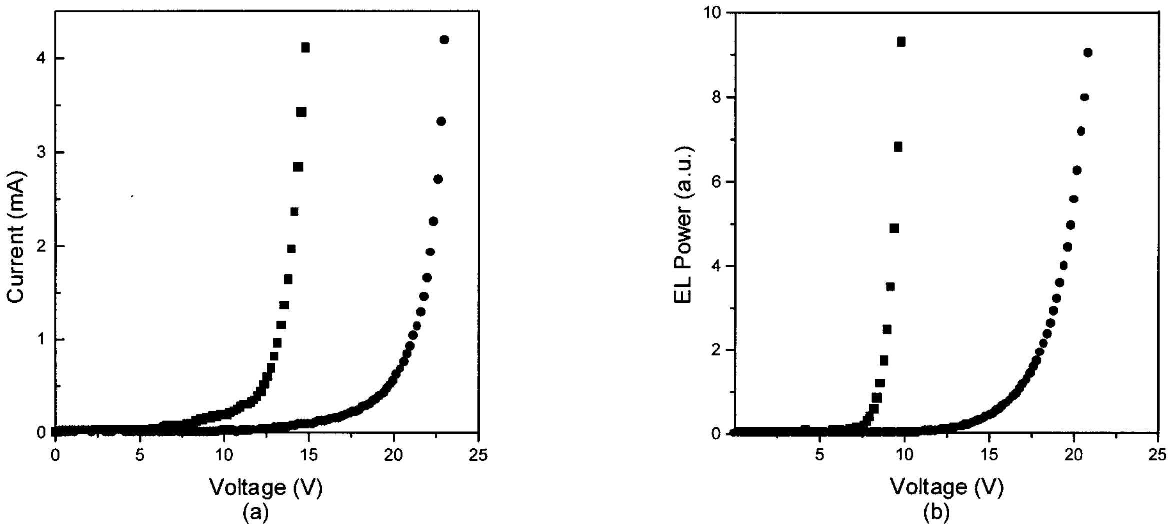


Figure 5. EL characteristics of PPOX-CAR (■) and PMOX-CAR (●) with an ITO/polymers/Al structure. (a) Current vs voltage and (b) EL power vs voltage.

We synthesized PPV by the method of a previous work.[32] The PPOX-CAR polymer exhibited 36 times higher EL quantum efficiency compared to PPV. On the other hand, the EL quantum efficiency of PMOX-CAR was increased just 2-fold. This means that the PPOX-CAR polymer in the para linkage more easily forms balanced injections of holes and electrons from opposite electrodes because the fully and linearly conjugated structures improve the balance of charged carriers. The brightness of the Al/PPOX-CAR/ITO single-layer device was measured, and the maximum brightness of the device was 500 cd/m^2 at 20 V. By introduction of the electron affinitive oxadiazole moiety into the conjugation segment, the electron density may shift away from the vinyl bond, which could increase the stability of resulting LED devices because oxidation of the vinyl group is a primary reason for the loss of efficiency.[33,34]

Conclusion

Two new fully conjugated oxadiazole- and carbazole-based alternating copolymers were synthesized by condensation polymerization. The emissive light of the PPOX-CAR and PMOX-CAR polymers showed greenish-blue and pure blue lights, respectively. The polymers based on the electron-facilitated oxadiazole unit and the hole-facilitated carbazole unit exhibited high EL quantum efficiency at low turn-on voltage, as well as in the shorter emission wavelength region. Studies on multilayer LED device fabrications and their luminances are under investigation. We expect that the PPOX-CAR and PMOX-CAR polymers can be used in double-layer diodes to block passage of holes toward the cathode.

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