Synthesis and Properties of PCPP-Based Conjugated Polymers Containing Pendant Carbazole Units for LEDs

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In this work, we report the synthesis and electroluminescence properties of new EL polymers, Poly(2,6-(4-(6-(N-carbazolyl)-hexyl)-4-octyl-4H-cyclopenta[def]phenanthrene)) (CzPCPP10) and Poly(2,6-(4-(6-(N-carbazolyl)-hexyl)-4-octyl-4H-cyclopenta[def]phenanthrene)-co-(2,6-(4,4-dioctyl-4H-cyclopenta[def]phenanthrene))) (CzPCPP7 and CzPCPP5) which all of the maximum EL efficiency were 0.12 cd/A. The CIE coordinates of the EL spectrum of PLEDs using CzPCPP10 was (0.18, 0.08), which are quite close to that of the standard blue (0.14, 0.08) of NTSC.

Key Words: Light emitting diode, PCPP, Carbazole

Introduction

In the past few years, polymer light-emitting diodes (PLEDs) have been devoted in much research, which has been investigated to the design and synthesis of light-emitting polymers for practical applications.1-7 Many of the conjugated polymers investigated as the light-emitting materials in LEDs,8-11 or to use additional organic charge-transporting layers between the emissive layer and the electrodes.12 According as poly(N-vinylcarbazole) (PVK) have been used as the charge-transporting materials in LEDs,12,13 carbazole units was applied to conjugated polymers, and many polymer derivatives with carbazole units as pendants were investigated to improve the charge carrier transport.14-20

In our previous contribution, synthesis and properties of new EL polymer utilizing a new backbone, Poly(2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene)) (PCPP) with stabilized pure blue emission and poly(9-(6-(N-carbazolyl)-hexyl)-9-hexyl)-fluorene-2,7-diy) (Cz-PF) with carbazole units as pendants to improve the charge carrier transport, has been reported.19,20 EL spectra of PCPP did not show any peak in the long wavelength region which corresponded to keto defect sites or aggregates/excimers even after annealing the device for 18 h in air or operation of the device for 40 min. In this work, we report the synthesis and electroluminescence properties of new EL polymer, Poly(2,6-(4-(6-(N-carbazolyl)-hexyl)-4-octyl-4H-cyclopenta[def]phenanthrene)) (CzPCPP10) and Poly(2,6-(4-(6-(N-carbazolyl)-hexyl)-4-octyl-4H-cyclopenta[def]phenanthrene)-co-(2,6-(4,4-dioctyl-4H-cyclopenta[def]phenanthrene))) (CzPCPP7 and CzPCPP5).
with carbazole units as pendants. The hole transporting moiety, N-carbazolyl \( \text{Cz} \), were introduced with flexible spacer of sufficient length as the side chain at the C-4 position of PCPP. According to the ratio of Cz units, different copolymers were synthesized, and these polymers were investigated optical and EL properties.

**Experimental Section**

**General.** Used all reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. \(^1\)H and \(^{13}\)C NMR spectra were recorded with a Varian Gemini-200 (200 MHz), Unityplus-300 (300 MHz) and Inova-500 (500 MHz) spectrometer and chemical shifts were recorded in ppm units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230-400 mesh ASTM) with ethyl acetate/hexane or methyl alcohol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminium plates with fluorescent indicator UV254. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. The PL and EL spectra of the device were measured using an Oriel InstaSpec IV CCD detection systems. For PL spectrum measurements, xenon lamp was used as the excitation source, and incident beam took the maximum absorption peak of the polymers. For the determination of device characteristics, current-voltage (I-V) characteristics were measured using a Keithley 236 source measure unit. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s. The CV was performed in a solution of tetrabutylammonium tetrafluoroborate (Bu\(_4\)NBF\(_4\)) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under argon atmosphere. A platinum electrode (~0.05 cm\(^2\)) coated with a thin polymer film was used as the working electrode. A Pt wire and a Ag/AgNO\(_3\) electrode were used as the counter electrode and reference electrode, respectively. All measurements were calibrated against an internal standard, ferrocene (\( \text{Fc} \)), which has the IP value (~4.8 eV) for the \( \text{Fc}/\text{Fc}^+ \) redox system. Elemental analysis (Korea Basic Science Institute: Daegu) was observed towards identification of the structure of polymers. FAB Mass spectra were determined using at Korea Basic Science Institute Seoul Branch and Korea Basic Science Institute Daegu Branch.

**Synthesis of 9-(6-bromohexyl)-9H-carbazole (3).** To a stirred solution of 2.9 g (71.8 mmol) of NaH (60%) in 100 mL of THF

![Scheme 1](image-url)
mL of tetrahydrofuran (THF) at room temperature under argon was added 10 g (59.8 mmol) of 9H-carbazole (1) in 100 mL of THF. After 10 min at room temperature, the reaction mixture was treated with 19 mL (119.6 mmol) of 1,6-dibromohexane (2). After stirring overnight at reflux, the reaction mixture was quenched with 200 mL of water. The aqueous layer was separated and extracted with 3 × 100 mL of methylene chloride. The combined organic layer was dried over MgSO₄ and concentrated in vacuo. The oily residue was purified by flash column chromatography (Rf = 0.30, methylene chloride (MC):hexane – 1:4) to give 12.68 g (51.7% yield) of 9-(6-bromohexyl)-9H-carbazole (2) as white solid.

1H NMR (200 MHz, CDCl₃): δ (ppm) 1.39-1.55 (m, 4H), 1.74-1.96 (m, 4H), 3.36 (t, 2H, J = 7.33 Hz), 4.31 (t, 2H, J = 7.51 Hz), 7.21 (t, 2H, J = 6.04 Hz), 7.27-7.52 (m, 4H), 8.10 (d, 2H, J = 6.79 Hz). 13C NMR (75 MHz, CDCl₃): δ (ppm) 29.36, 32.44, 33.63, 42.66, 108.51, 118.70, 120.25, 122.73, 125.52, 140.28. LRMS-EI (m/z): [M⁺] calcd. for C₁₅H₁₃Br₂, 345.90; found, 346.

Synthesis of 8,9-dihydro-4H-cyclopenta[def]phenanthrene (5). The reaction mixture of 4 g (21.03 mmol) of 4H-cyclopenta[def]pentaphenanthrene (4), 800 mg of 10% palladium-charcoal, 40 mL of methylene chloride, and 40 mL of ethanol was shaken in the Parr shaker for 14 h at room temperature under a hydrogen atmosphere. After removal of the catalyst by filtration, the ethanol and methylene chloride were evaporated under reduced pressure. The residue was purified by flash column chromatography (Rf = 0.64, 100% MC) to give 3.5 g (86.57%) of compound 5 as white powder (mp: 161 °C).

1H NMR (200 MHz, CDCl₃): δ (ppm) 3.16 (s, 2H), 3.88 (s, 2H), 7.31 (s, 2H), 7.50 (s, 2H). 13C NMR (75 MHz, CDCl₃): δ (ppm) 37.16, 125.31, 125.62, 126.41, 127.97, 128.97, 136.91, 139.51, 140.53. LRMS-EI (m/z): [M⁺] calcd. for C₁₃H₁₂Br₂, 192.09; found, 192.

Synthesis of 2,6-dibromo-8,9-dihydro-4H-cyclopenta[def]phenanthrene (6). To a stirred solution of 50 g of copper(II) bromide in 30 mL of distilled water was added 60.25 g of neutral alumina (Merck: Aluminium oxide 90 active neutral) at room temperature. The water was evaporated at 80 °C under reduced pressure. The resulting reagent was then dried under vacuum (4 Torr) at 100 °C for 15 h. The prepared reagent was added to a stirred solution of 2.8 g (14.42 mmol) of octyl bromide (1) at room temperature. After 2 h at 60 °C, the reaction mixture was treated with 474 mg (1.43 mmol) of compound 3 and 3.2 mL of 4% aqueous NaOH at room temperature. After refluxed for overnight, the reaction mixture was poured into 500 mL of ethyl acetate and 500 mL of water. The aqueous layer was separated and washed with 3 × 500 mL of water, the combined organic layer was dried by MgSO₄ and concentrated under reduced pressure. The oily layer was purified by flash column chromatography to give 3.5 g (86.57%) of compound 6 as white crystal (mp: 165 °C). H NMR (200 MHz, CDCl₃): δ (ppm) 0.71-1.69 (m, 23H), 2.02-2.07 (m, 4H), 4.18 (t, 2H, J = 6.9 Hz), 7.19 (dd, 2H, J = 6.9 Hz). 13C NMR (75 MHz, CDCl₃): δ (ppm) 26.65, 37.81, 122.85, 124.81, 127.40, 130.65, 139.51, 140.53. LRMS-EI (m/z): [M⁺] calcd. for C₁₃H₁₂Br₂, 192.09; found, 192.

Synthesis of monomers (9 and 10). A solution of 1 g (2.9 mmol) of 2,6-dibromo-4H-cyclopenta[def]phenanthrene (7) and catalytic amounts of triethylbenzylammonium chloride in 200 mL of DMSO was stirred at 60 °C under Ar condition. After 2 h at 60 °C, the reaction mixture was treated with 474 mg (1.43 mmol) of compound 3 and 3.2 mL of 4% aqueous NaOH at room temperature. After refluxed for overnight, the reaction mixture was poured into 500 mL of ethyl acetate and 500 mL of water. The aqueous layer was separated and extracted with 3 × 500 mL of ethyl acetate. After the total extract was washed with 3 × 500 mL of water, the combined organic layer was dried by MgSO₄ and concentrated under reduced pressure. The oily layer was purified by flash column chromatography to give 758 mg (28.1%) of Cz monomer 12 (mp: 93 °C, Rf = 0.44, EtOAc:hex = 1:10) and 725 mg (43.7%) of dioctyl monomer 13 (mp: 76 °C, Rf = 1.63, 100% Hex).

9-6-(2,6-Dibromo-4-octyl-4H-cyclopenta[def]phenanthrene[4-yl]hexyl)-9H-carbazole (9): 1H NMR (300 MHz, CDCl₃): δ (ppm) 0.71-1.69 (m, 23H), 2.02-2.07 (m, 4H), 4.18 (t, 2H, J = 5.9 Hz), 7.23 (t, 2H, J = 6.7 Hz). 7.32 (d, 2H, J = 7.9 Hz), 7.45 (t, 2H, J = 7.2 Hz), 7.59 (d, 2H, J = 1.1 Hz). 7.76 (s, 2H), 7.97 (d, 2H, J = 1.3 Hz). 8.1 (d, 2H, J = 7.8 Hz). 13C NMR (75 MHz, CDCl₃): δ (ppm) 14.31, 22.79, 24.28, 24.37, 26.97, 28.97, 29.36, 29.41, 29.22, 30.92, 31.09, 31.93, 39.08, 39.30, 42.93, 59.82, 108.74, 118.83, 120.48, 122.17, 122.85, 123.67, 125.64, 125.71, 126.01, 128.57, 135.09, 151.18. HRMS-EI (m/z): [M⁺] calcd. for C₃₉H₃₉Br₂, 707.1762; found, 707.1755.

2,6-Dibromo-4,4-dioctyl-4H-cyclopenta[def]phenanthrene (10): 1H NMR (300 MHz, CDCl₃): δ (ppm) 0.82-1.58 (m, 30H), 2.06-2.12 (m, 4H), 7.62 (d, 2H, J = 1.4 Hz). 7.77 (s, 2H), 7.97 (d, 2H, J = 1.2 Hz). 13C NMR (75 MHz, CDCl₃): δ (ppm) 14.31, 22.80, 24.44, 29.38, 29.42, 30.14, 31.94, 39.26, 59.97, 122.17, 123.76, 125.64, 125.96, 128.60, 135.09, 151.18. HRMS-EI (m/z): [M⁺] calcd. for C₃₉H₄₀Br₂, 750.1497; found, 750.1497.

Synthesis of Polymers (11, 12 and 13). The polymers were synthesized by using monomer 9 and 10 of different proportion (10:0, 7:3, 5:5). In a two neck flask was placed Ni(COD)₂ (528 mg, 1.92 mmol), 2,2’-dipyridyl (299 mg, 1.92 mmol) as catalyst, cyclooctadiene (0.23 mL, 1.92 mmol), and...
DMF (8 mL) by using Atmos Bag (Aldrich) under argon. After the reaction mixture of the catalyst was heated to 80 °C for half an hour to form the purple complex, the monomers 9 and 10 (0.96 mmol) in 8 mL of toluene were added to the solution and heated at 80 °C for 3 days. The polymer reaction mixtures were treated to 500 mg of 9-bromoanthracene, the end capper, dissolved in 5 mL of anhydrous toluene, and further heated at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into the solution of 100 mL HCl, 100 mL of acetone and 200 mL of methanol. After stirring for 3 h, the solid were filtered, redissolved in chloroform, and precipitated in large amount methanol. The pale yellow solid was purified by soxhlet extraction with methanol and dried in vacuum for 48 h to generate the polymers (CzPCPP10 (11), CzPCPP7 (12), CzPCPP5 (13)) as white powder.

## Results and Discussion

### Synthesis and Characterization.

The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. By using analogous methods as were reported, 9-(6-bromohexyl)-9H-carbazole (3) and 2,6-dibromo-4H-cyclopenta[def]phenanthrene (7) were synthesized and coupled with octyl bromide (8) to generate carbazole substituted monomer 9 and diocyl substituted monomer 10. The polymerizations for the copolymers containing these monomers of different ratios were generated under Yamamoto conditions using Ni(0) catalysis to obtain CzPCPP10 (11), CzPCPP7 (12) and CzPCPP5 (13).

The resulting CzPCPPs, brittle white polymers were soluble in organic solvents such as chloroform, chlorobenzene, THF, MC and o-dichlorobenzene (ODCB). The emissive polymer films were obtained by spin-casting an ODCB solution of the polymers. The results of polymerization of CzPCPPs are summarized in Table 1. The number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$), and the polydispersities (PDI) of CzPCPPs were in the range of 30000-60000, 100000-270000, and 4.5-4.9, respectively, as determined by GPC using THF as the eluant and polystyrene as the standard. The thermal properties of polymers were identified by TGA, and DSC thermograms. The weight losses of CzPCPPs were less than 5% in heating to about 423-457 °C. The $T_g$ values for CzPCPPs were observed to be 77-100 °C.

### Optical Properties.

Figure 1 shows the absorption and photoluminescence (PL) (exciting wavelength, 380 nm) spectra for CzPCPPs in solution and thin film which are summarized in Table 2. The solution was prepared using THF as solvent and the thin film was prepared by spin-coating on quartz plates from the polymer solutions in ODCB. The maximum absorption peaks of CzPCPPs appeared at around 293 and 362 nm in THF solution. The

### Table 1. Polymerization results and thermal properties of the polymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>feed ratio (monomer 9 : 10)</th>
<th>$M_n$ a</th>
<th>$M_w$ a</th>
<th>PDI b</th>
<th>$T_g$ c (°C)</th>
<th>$T_d$ c (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CzPCPP10</td>
<td>10:0</td>
<td>20,000</td>
<td>100,000</td>
<td>4.9</td>
<td>77</td>
<td>457</td>
</tr>
<tr>
<td>CzPCPP7</td>
<td>7:3</td>
<td>30,000</td>
<td>140,000</td>
<td>4.5</td>
<td>99</td>
<td>450</td>
</tr>
<tr>
<td>CzPCPP5</td>
<td>5:5</td>
<td>60,000</td>
<td>270,000</td>
<td>4.5</td>
<td>100</td>
<td>423</td>
</tr>
</tbody>
</table>

* $M_n$, $M_w$, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards. $T_g$ were determined by DSC. $T_d$ were measured at a temperature of 5% weight loss for the polymers by TGA. Calculated from the results of NMR.

### Table 2. Optical properties of the polymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>solution (nm)</th>
<th>film $\lambda_{max}$ (nm)</th>
<th>fwhm a</th>
<th>solution (nm)</th>
<th>film $\lambda_{max}$ (nm)</th>
<th>fwhm a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abs $\lambda_{max}$</td>
<td>PL $\lambda_{max}$ a</td>
<td>fwhm a</td>
<td>Abs $\lambda_{max}$</td>
<td>PL $\lambda_{max}$ a</td>
<td>fwhm a</td>
</tr>
<tr>
<td>CzPCPP10</td>
<td>293, 365</td>
<td>396</td>
<td>38</td>
<td>297, 359</td>
<td>451</td>
<td>88</td>
</tr>
<tr>
<td>CzPCPP7</td>
<td>293, 362</td>
<td>396</td>
<td>38</td>
<td>206, 359</td>
<td>402, 425, 448</td>
<td>92</td>
</tr>
<tr>
<td>CzPCPP5</td>
<td>293, 359</td>
<td>396</td>
<td>42</td>
<td>206, 361</td>
<td>402, 431, 448</td>
<td>85</td>
</tr>
</tbody>
</table>

* The data in the parentheses are the wavelengths of shoulders and subpeaks. *Full width at half-maximum of the solution and film PL spectra.
PCPP-Based PLEDs with Pendant Carbazole Units

Table 3. Electrochemical potentials and energy levels of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{ox}}$ (V)</th>
<th>HOMO $^a$ (eV)</th>
<th>LUMO $^b$ (eV)</th>
<th>$E_g$ $^d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CzPCPP10</td>
<td>0.85</td>
<td>5.65</td>
<td>2.65</td>
<td>3.0</td>
</tr>
<tr>
<td>CzPCPP7</td>
<td>0.85</td>
<td>5.65</td>
<td>2.65</td>
<td>3.0</td>
</tr>
<tr>
<td>CzPCPP5</td>
<td>0.85</td>
<td>5.65</td>
<td>2.65</td>
<td>3.0</td>
</tr>
</tbody>
</table>

$^a$Onset oxidation potential measured by cyclic voltammetry. $^b$Calculated from the oxidation potentials. $[\text{HOMO} = 4.8 + (E_{\text{ox}} - E_{\text{Fc}})]$. $^c$Calculated from the HOMO energy levels and $E_g$. $^d$Energy band gap was estimated from the onset wavelength of the optical absorption.

Figure 2. Cyclic voltammogram of CzPCPP10, CzPCPP7 and CzPCPP5.

spectra of all polymers were exhibited almost similarly. The maximum absorption peak of CzPCPPs in solid thin film is a little shifted to around 297 and 360 nm. The absorption onset wavelengths of all polymers were around 415 nm, which correspond to band gaps of 3.0 eV. Because all polymers have the same PCPP back-bone, the absorption spectra of these polymers were all similar.

The PL emission spectra of CzPCPPs in THF solution show a maximum peak at 396 nm and a shoulder peak at around 415 nm. In case of solid thin film, they are more red-shifted over 30-50 nm than solution conditions, and the full width at half maximum (FWHM) was increased, which can be contributed to the increased $\pi-\pi^*$ interaction. The PL spectra of CzPCPPs in the solid film consist of a multiple structured band comprising three maxima at around 402, 430 and 450 nm. The maximum of CzPCPP10 at 451 nm was occurred mainly. In case of CzPCPP7 and CzPCPP5, the peaks at 448 nm was increased such as CzPCPP10, however, the peaks of at 402 and around 430 nm, which correspond to maximum and shoulder peaks in solution respectively, were remained.

This indicate that CzPCPPs have more red-shifted emission peaks than PCPP in solid thin film by raising aggregation among polymer backbone, which can be attributed to the $\pi-\pi^*$ interaction between the conjugated main chains and carbazole units.

Electrochemical Properties of the Polymers. The energy band diagrams of the polymers were determined from the band gaps which were estimated from the absorption edges, and the HOMO energy levels which were estimated from the cyclic voltammetry. Electrochemical properties of the polymers were measured to show that all of the polymers exhibit irreversible processes in an oxidation scan. As shown in Figure 2, the oxidation onsets were estimated to be 8.5 V for CzPCPPs, which correspond to HOMO energy level of 5.65 eV. The LUMO energy levels of polymers were calculated with the HOMO and optical band gap. The LUMO energy levels of CzPCPPs were thus determined to be 2.65 eV. The electrochemical measurements reveal that the main chain determines their own electronic characteristics in the polymers, since Cz group is connected for pendant type although the electron-rich Cz group may lead to an improvement in charge injection of the polymer.

Electroluminescent Properties and Current-Voltage-Luminance. For the EL experiment of PLEDs with configuration of ITO/PEDOT/polymers/Ca/Al, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced.

Table 4. Device performance characteristics of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$V_{\text{on}}$ $^a$ (V)</th>
<th>$V_{\text{max}}$ $^b$ (V)</th>
<th>Current density $^c$ (mA/cm$^2$)</th>
<th>Luminance $^c$ (cd/m$^2$)</th>
<th>$L_{\text{max}}$ $^d$ (cd/A)</th>
<th>CIE $^e$ ($x$, $y$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CzPCPP10</td>
<td>448</td>
<td>6.0</td>
<td>6.5</td>
<td>23.3</td>
<td>4481</td>
<td>0.12</td>
<td>(0.18, 0.06)</td>
</tr>
<tr>
<td>CzPCPP7</td>
<td>450</td>
<td>6.5</td>
<td>7.5</td>
<td>33.2</td>
<td>3262</td>
<td>0.12</td>
<td>(0.19, 0.09)</td>
</tr>
<tr>
<td>CzPCPP5</td>
<td>450</td>
<td>6.0</td>
<td>11.0</td>
<td>302.5</td>
<td>302.5</td>
<td>0.12</td>
<td>(0.18, 0.06)</td>
</tr>
</tbody>
</table>

$^a$Voltages required to achieve a brightness of 1 cd/m$^2$. $^b$Measured under the condition of maximum luminescence efficiency. $^c$Maximum luminescence efficiency. $^d$Measured under the condition of maximum brightness. $^e$Calculated from the EL spectrum.
between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. Isopropyl solution of the PEDOT/PSS was spin-coated on the surface-treated ITO substrate. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting ODCB (o-dichlorobenzene) solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in vacuum, and calcium and aluminum electrodes were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below 10⁻⁷ Torr, yielding active areas of 4 mm².

Figure 3 shows the EL spectra of ITO/PEDOT/CzPCPPs/Ca/Al devices. These spectra exhibited maximum peaks at around 450 nm, which correspond to blue light. The EL spectra of the device using all CzPCPPs were similar to the PL spectrum of CzPCPP10 through vacuum evaporation at pressures below 10⁻⁷ Torr, yielding active areas of 4 mm².

Figure 4. Current density-voltage-luminescence (J-V-L) characteristics of PLEDs with the configuration of ITO/PEDOT/polymer/Ca/Al by using CzPCPP10, CzPCPP7 and CzPCPP5.

Figure 5. Current density-efficiency (cd/A) of PLEDs with the configuration of ITO/PEDOT/polymer/Ca/Al (b) by using CzPCPP10, CzPCPP7 and CzPCPP5.

L'Eclairage (CIE) coordinates of the CzPCPPs were shown in Table 4. The emission colors of the device with the configuration of ITO/PEDOT/CzPCPPs/Ca/Al was blue with the CIE coordinates of x = 0.18, y = 0.06 and x = 0.19, y = 0.09.

The current density-voltage and luminescence-voltage characteristics of ITO/PEDOT/polymer/Ca/Al devices are shown in Figure 4. All processing steps and measurements mentioned above were carried out under air and at room temperature. The turn-on voltages of devices were about 6.0-6.5 V, which the luminescence intensities of the polymers are exponentially enhanced with an increase of voltage. Especially, the maximum luminescence of PLED device using CzPCPP with Al electrode were over 4400 cd/m² at 9 V, the maximum EL efficiencies of CzPCPPs are shown in Figure 5, which all of the maximum luminescence efficiency of CzPCPPs are 0.12 cd/A at 6.5-11.0 V.

Conclusion

In order to improve the charge carrier transport, we have synthesized, new fully conjugated polymers, CzPCPPs containing PCPP backbone with pendants of carbazole moiety by the Yamamoto polymerization. The carbazole moieties may provide highly increased intra or inter chain interaction between PCPP backbone. As increased the ratio of carbazole moiety, the red-shifted peaks by aggregation was raised in solid thin film state. In case of EL spectra, all PLEDs with configuration of ITO/PEDOT/CzPCPPs/Ca/Al device exhibited only red-shifted peaks by aggregation. The electrochemical measurements reveal that the main chain determines their own electronic characteristics in the polymers, although the electron-rich carbazole moiety may lead to an improvement in charge injection of the polymers. The difference of the ratios of carbazole moiety does not affect the effective conjugation length of the polymers, since the carbazole moieties were introduced as pendants using non-conjugated chain. These polymers, which have quite good thermal stability, include similar electrical and optical properties. In case of PLEDs with configuration of ITO/PEDOT/CzPCPPs/Ca/Al device, The EL maximum peaks were around 450 nm, which the turn-on voltages were about 6.0-6.5 V. The maximum luminescence of PLEDs using CzPCPP10 was over 4400 cd/m² at 6.5 V, which all of the maximum EL efficiency were 0.12 cd/A. The CIE coordinates of the EL spectrum of PLEDs using CzPCPP10 was (0.18, 0.08), which are quite close to that of the standard blue (0.14, 0.08) of NTSC.

Acknowledgement. This work was supported by the Ministry of Information & Communication, Korea, under the Information Technology Research Center (ITRC) Support Program.

References and Notes


