

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

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New poly(cyclopenta[*def*]phenanthrene) (PCPP)-based conjugated copolymers, containing carbazole units as pendants, were prepared as the electroluminescent (EL) layer in light-emitting diodes (LEDs) to show that most of them have higher maximum brightness and EL efficiency. The prepared polymers, Poly(2,6-(4-(6-(*N*-carbazolyl)-hexyl)-4-octyl-4*H*-cyclopenta[*def*]phenanthrene)) (CzPCPP10) and Poly(2,6-(4-(6-(*N*-carbazolyl)-hexyl)-4-octyl-4*H*-cyclopenta[*def*]phenanthrene))-*co*-(2,6-(4,4-dioctyl-4*H*-cyclopenta[*def*]phenanthrene)) (CzPCPP7 and CzPCPP5), were soluble in common organic solvents and used as the EL layer in light-emitting diodes (LEDs) of configuration with ITO/PEDOT/polymer/Ca/Al device. The polymers are thermally stable with glass transition temperature (T_g) at 77-100 °C and decomposition temperature (T_d) at 423-457 °C. The studies of cyclic voltammetry indicated same HOME levels in all polymers, although the ratios of carbazole units are different. 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.

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 There are a few appropriate polymers for fabricating PLEDs which emit green, orange, or red color.⁸⁻¹¹ A lot of attention has been paid to poly(9,9'-dialkylfluorene)s (PFs) as a prospective blue emitting layer for PLEDs,¹²⁻¹⁴ because they have a rigid biphenyl unit to obtain a large band gap for the efficient blue emission, and the remote C-9 position to provide the desirable solubility for the processability of polymers without appreciably increasing the steric interactions in the polymer backbone. However, in order to increase efficiency and remove the tendency of PFs to generate long wave length emission around 550 nm caused by the formation of keto defect sites¹⁵ or aggregates/excimers,¹⁶ many novel blue polymers containing new backbone was also reported.¹⁷⁻²⁰

Many of the conjugated polymers investigated as the light-emitting layer in OLEDs preferentially transport one of the injected charges. This generally results in an imbalance of charge transport and poor device efficiency. Many approaches have been taken to overcome the imbalance of charge carrier transport. The most frequent practices have been either to adjust the energy band of the polymer by introduction of electron-withdrawing groups as pendant groups or as part of the polymer backbone,²¹⁻²⁴ or to use additional

organic charge-transporting layers between the emissive layer and the electrodes.²⁵ According as poly(*N*-vinylcarbazole) (PVK) have been used as the charge-transporting materials in LEDs,^{26,27} carbazole units was applied to conjugated polymers, and many polymer derivatives with carbazole units as pendants were investigated to improve the charge carrier transport.²⁸⁻³⁰

In our previous contribution, synthesis and properties of new EL polymer utilizing a new backbone, poly(2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)) (PCPP) with stabilized pure blue emission and poly(9-(6-(*N*-carbazolyl)-hexyl)-9-hexyl)-fluorene-2,7-diyl) (Cz-PF) with carbazole units as pendants to improve the charge carrier transport, has been reported.^{19,30} 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, and the luminescence efficiency of Cz-PF was increased by the enhancement of hole transporting properties due to intra or inter chain interaction, which could be the reason of the low turn-on voltages and the high maximum luminescence,

In this work, we report the synthesis and electroluminescence properties of new EL polymer, Poly(2,6-(4-(6-(*N*-carbazolyl)-hexyl)-4-octyl-4*H*-cyclopenta[*def*]phenanthrene)) (CzPCPP10) and Poly(2,6-(4-(6-(*N*-carbazolyl)-hexyl)-4-octyl-4*H*-cyclopenta[*def*]phenanthrene))-*co*-(2,6-(4,4-dioctyl-4*H*-cyclopenta[*def*]phenanthrene)) (CzPCPP7 and CzPCPP5)

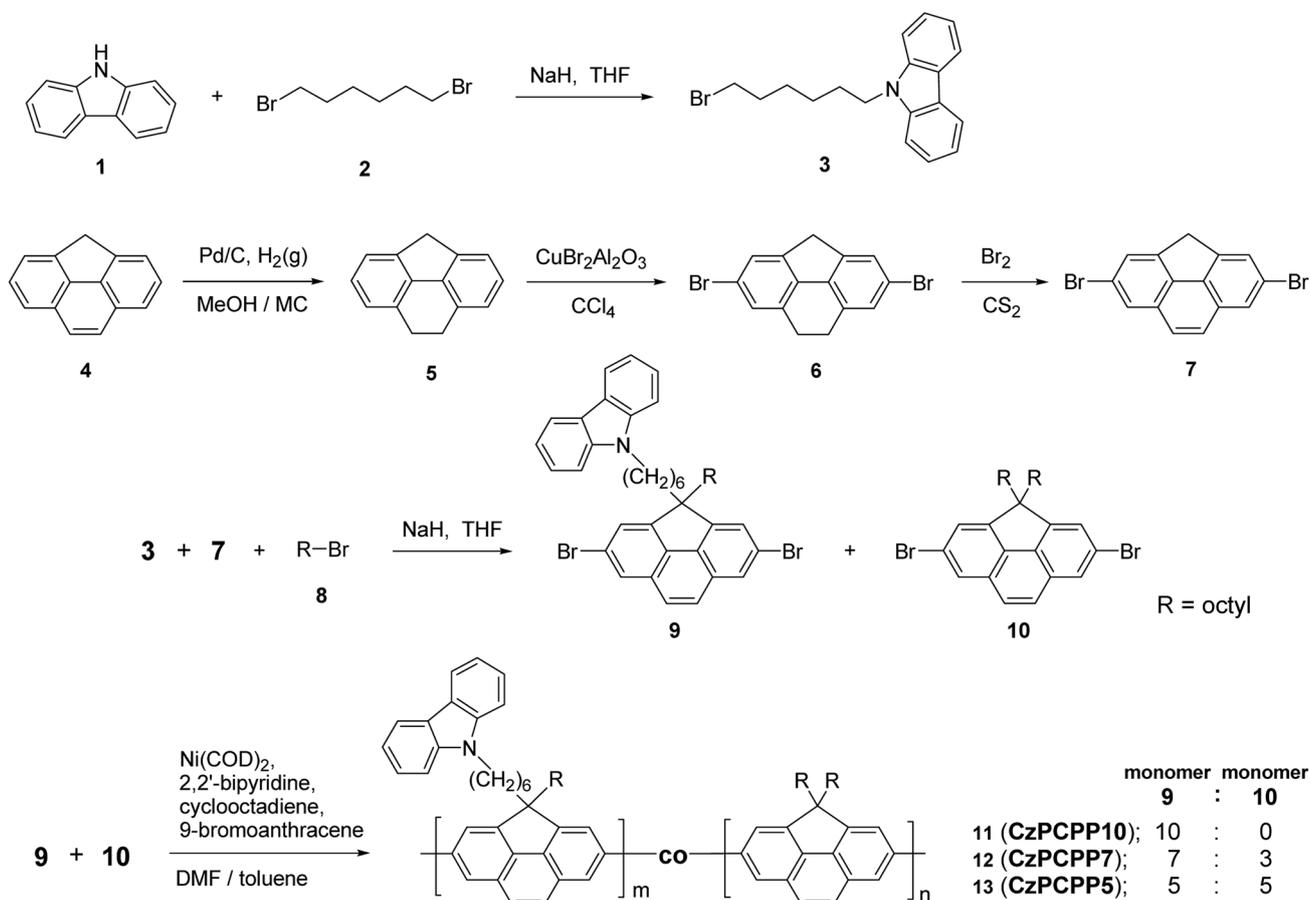
with carbazole units as pendants. The hole transporting moiety, *N*-carbazolyl (Cz), were introduced with flexible spacer of sufficient length as the side chain at the C-4 position of PCPP. According to the ratio of Cz units, different copolymers were synthesized, and these polymers were investigated 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. ^1H 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 methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated 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 Insta-Spec IV CCD detection systems. For PL spectrum measure-

ments, 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_4NBF_4) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under argon atmosphere. A platinum electrode ($\sim 0.05\text{ cm}^2$) 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 (Fc), which has the IP value (-4.8 eV) for the Fc/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)-9*H*-carbazole (3). To a stirred solution of 2.9 g (71.8 mmol) of NaH (60%) in 100



Scheme 1. Synthetic routes for the monomers and polymers.

mL of tetrahydrofuran (THF) at room temperature under argon was added 10 g (59.8 mmol) of 9*H*-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 (R_f = 0.30, methylene chloride (MC):hexane = 1:4) to give 12.68 g (64.2%) of 9-(6-bromohexyl)-9*H*-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 = 7.69 Hz). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 26.30, 27.77, 28.67, 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 C₁₈H₂₀BrN, 329.07; found, 329.

Synthesis of 8,9-dihydro-4*H*-cyclopenta[def]phenanthrene (5**).** The reaction mixture of 4 g (21.03 mmol) of 4*H*-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 was evaporated under reduced pressure. The residue was purified by flash column chromatography (R_f = 0.64, 100% MC) to give 3.5 g (86.57%) of compound **5** as white powder (mp: 106 °C). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 3.16 (s, 4H), 3.90 (s, 2H), 7.11 (d, 2H, J = 6.9 Hz), 7.19 (dd, 2H, J = 6.9 Hz), 7.34 (d, 2H, J = 7.5 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 C₁₅H₁₂, 192.09; found, 192.

Synthesis of 2,6-dibromo-8,9-dihydro-4*H*-cyclopenta[def]phenanthrene (6**).** To a 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.³¹ This prepared reagent of 46.89 g of copper(II) bromide adsorbed on alumina was added to a stirred solution of 2.8 g (14.42 mmol) of 8,9-dihydro-4*H*-cyclopenta[def]phenanthrene (**5**) in 200 mL of carbon tetrachloride at room temperature. After 4 h at 60 °C, the reaction mixture was filtered and washed with 5 × 30 mL of carbon tetrachloride. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (R_f = 0.58, 100% MC) to give 4.45 g (88.70%) of compound **6** as pale yellow powder (mp: 161 °C). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 3.13 (s, 4H), 3.88 (s, 2H), 7.31 (s, 2H), 7.50 (s, 2H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 26.15, 37.51, 121.28, 126.38, 128.37, 131.85, 137.85, 141.71. LRMS-EI (m/z): [M^+] calcd. for C₁₅H₁₀Br₂, 347.91; found, 348.

Synthesis of 2,6-dibromo-4*H*-cyclopenta[def]phen-

anthrene (7**).** To a stirred solution of 4.45 g (12.79 mmol) of 2,6-dibromo-8,9-dihydro-4*H*-cyclopenta[def]phenanthrene (**6**) in 100 mL of carbon disulfide at room temperature was added dropwisely 0.79 mL (15.35 mmol) of Br₂ in 50 mL of carbon disulfide over 3 h. The reaction mixture was stirred additional hour and concentrated under reduced pressure, and the residue was purified by flash column chromatography (R_f = 0.44, 100% MC) to give 4.203 g (95.0%) of compound **7** as yellowish white crystal (mp: 165 °C). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 4.32 (s, 2H), 7.75 (s, 2H), 7.80 (s, 2H), 7.99 (s, 2H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 37.16, 125.31, 125.62, 126.41, 127.97, 128.97, 136.91, 143.03. LRMS-EI (m/z): [M^+] calcd. for C₁₅H₈Br₂, 345.90; found, 346.

Synthesis of monomers (9** and **10**).** A solution of 1 g (2.9 mmol) of 2,6-dibromo-4*H*-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 (4.4 mmol) of octyl bromide (**8**), and 1 mL of 50% 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 578 mg (28.1%) of Cz monomer **12** (mp: 93 °C, R_f = 0.44, EtOAc:hex = 1:10) and 725 mg (43.7%) of dioctyl monomer **13** (mp: 76 °C, R_f = 1.63, 100% Hex).

9-[6-(2,6-Dibromo-4-octyl-4*H*-cyclopenta[def]phenanthren-4-yl)hexyl]-9*H*-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, 29.92, 30.09, 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, 135.02, 140.42, 150.95. HRMS-EI (m/z): [M^+] calcd. for C₄₁H₄₀NBr₂, 707.1762; found, 707.17557.

2,6-Dibromo-4,4-dioctyl-4*H*-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) 14.30, 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 C₃₁H₄₀Br₂, 570.1497; found, 570.1497.

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), 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)-9*H*-carbazole (**3**) and 2,6-dibromo-4*H*-cyclopenta[*def*]phenanthrene (**7**) were synthesized and coupled with octyl bromide (**8**) to generate carbazole substituted monomer **9** and dioctyl 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

Table 1. Polymerization results and thermal properties of the polymers

polymer	feed ratio (monomer 9 : 10)	M_n^a	M_w^a	PDI ^a	T_g^b (°C)	T_d^c (°C)
CzPCPP10	10:0	20,000	100,000	4.9	77	457
CzPCPP7	7:3	30,000	140,000	4.5	99	450
CzPCPP5	5:5	60,000	270,000	4.5	100	423

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

Table 2. Optical properties of the polymers

polymer	solution (nm)			film λ_{max} (nm)		
	Abs λ_{max}	PL λ_{max}^a	fwhm ^b	Abs λ_{max}	PL λ_{max}^a	fwhm ^b
CzPCPP10	293, 365	396	38	297, 359	451	88
CzPCPP7	293, 362	396	38	296, 359	402, 425, 448	92
CzPCPP5	293, 359	396	42	296, 361	402, 431, 448	85

^aThe data in the parentheses are the wavelengths of shoulders and subpeaks. ^bFull width at half-maximum of the solution and film PL spectra.

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

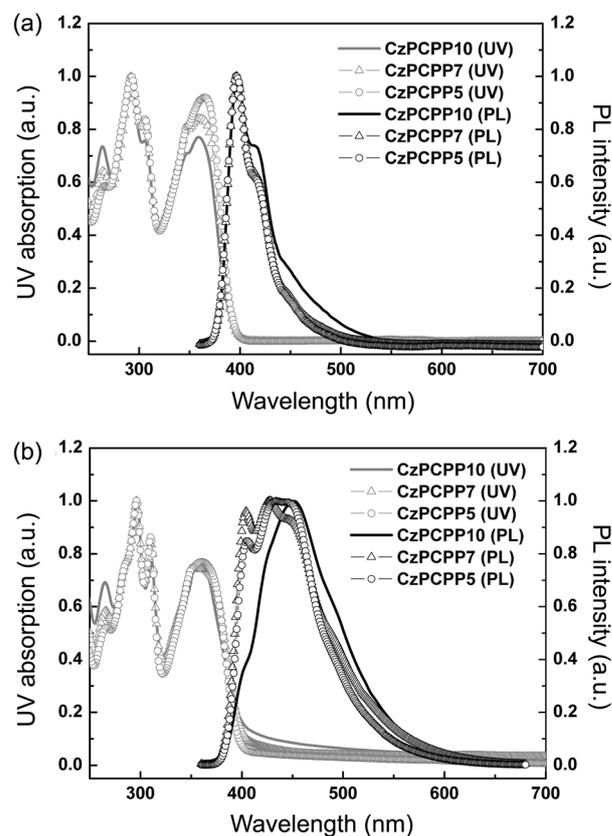
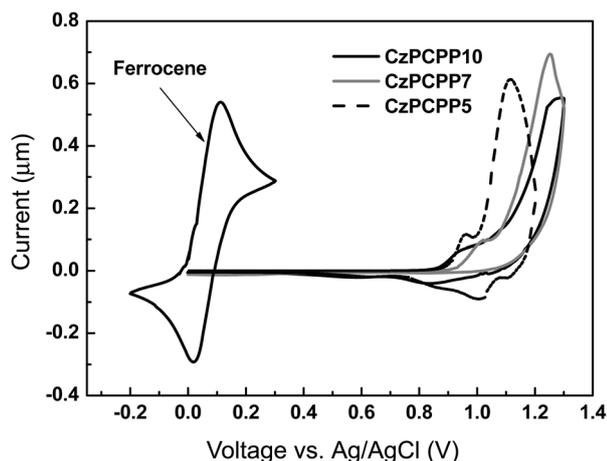


Figure 1. UV-visible absorption and PL spectra of CzPCPP10, CzPCPP7 and CzPCPP5 in solution (a) and in thin film state (b).

Table 3. Electrochemical potentials and energy levels of the polymers

polymer	E_{ox}^a (V)	HOMO ^b (eV)	LUMO ^c (eV)	E_g^d (eV)
CzPCPP10	0.85	5.65	2.65	3.0
CzPCPP7	0.85	5.65	2.65	3.0
CzPCPP5	0.85	5.65	2.65	3.0

^aOnset oxidation potential measured by cyclic voltammetry. ^bCalculated from the oxidation potentials. [$HOMO = 4.8 + (E_{ox} - E_{Fe})$]. ^cCalculated from the HOMO energy levels and E_g . ^dEnergy band gap was estimated from the onset wavelength of the optical absorption.

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

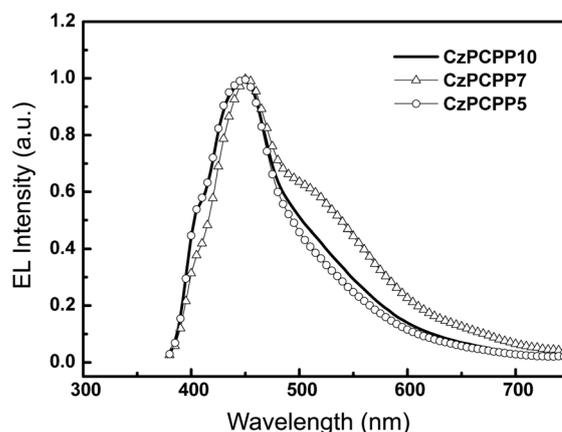
spectra of all polymers were exhibited almost similarly. The maximum absorption peak of CzPCPPs in solid thin film is a little shifted to around 297 and 360 nm. The absorption onset wavelengths of all polymers were around 415 nm, which correspond to band gaps of 3.0 eV. Because all polymers have the 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 π - π^* 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 π - π^* 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.³² 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

**Figure 3.** Electroluminescence spectra of PLEDs with the configuration of ITO/PEDOT/polymer/Ca/Al by using CzPCPP10, CzPCPP7 and CzPCPP5.**Table 4.** Device performance characteristics of the polymers

polymer	EL λ_{max} (nm)	turn-on voltage ^a (V)	voltage ^b (V)	current density ^b (mA/cm ²)	luminance ^c (cd/m ²)	LE _{max} ^d (cd/A)	CIE (x,y) ^e
CzPCPP10	448	6.0	6.5	23.3	4481	0.12	(0.18, 0.06)
CzPCPP7	450	6.5	7.5	33.2	3262	0.12	(0.19, 0.09)
CzPCPP5	450	6.0	11.0	302.5	3025	0.12	(0.18, 0.06)

^aVoltages required to achieve a brightness of 1 cd/m². ^bMeasured under the condition of maximum luminescence efficiency. ^cMeasured under the condition of maximum brightness. ^dMaximum luminescence efficiency. ^eCalculated from the EL spectrum.

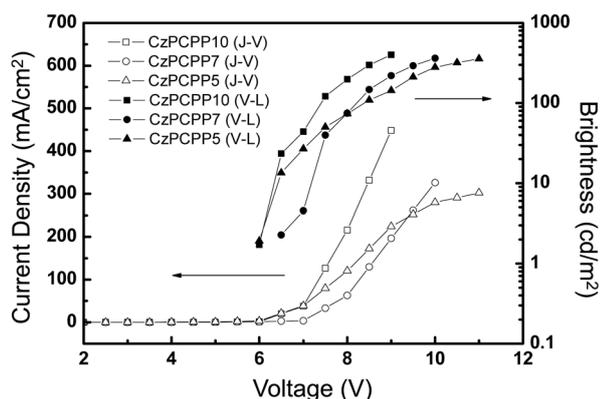


Figure 4. Current density-voltage-luminescence (J - V - L) characteristics of PLEDs with the configuration of ITO/PEDOT/polymer/Ca/Al by using CzPCPP10, CzPCPP7 and CzPCPP5.

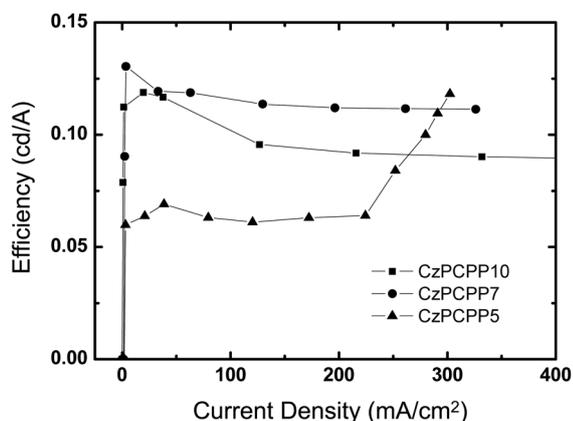


Figure 5. Current density-efficiency (cd/A) of PLEDs with the configuration of ITO/PEDOT/polymer/Ca/Al (b) by using CzPCPP10, CzPCPP7 and CzPCPP5.

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 with the largest ratio of Cz group. We can guess that the red-shift in EL spectrum by aggregation among polymer backbone, which can be attributed to the π - π^* interaction between the conjugated main chains and carbazole units, is easier than PL in solid thin film, since even the EL spectrum of CzPCPP5 with the smallest ratio of Cz group exhibited only maximum peak in around 450 nm. The 1931 Commission Internationale de

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/polymers/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.

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