Syntheses and Characterization of the Alternating Polymers Based on Cyclopenta[*def*]phenanthrene Backbone with Spiro Group

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New electroluminescent spiro-PCPP copolymers, poly((2,6-(3′,6′-bis(2-ethylhexyloxy)-spiro(4*H*-cyclopenta[*def*]phenanthrene-4,9′-[9*H*]fluorene)))-*alt*-(2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene))) (spiro-PCPP-*alt*-PCPP) and poly((2,6-(3′,6′-bis(2-ethylhexyloxy)-spiro(4*H*-cyclopenta[*def*]phenanthrene-4,9′-[9*H*]fluorene)))-*alt*-(1,4-phenylene)) (spiro-PCPPP), have been synthesized by the Suzuki-Miyaura polymerization. Both of the PL emission spectra of the polymers in chloroform show the maximum peaks at 397 nm. The maximum peaks of the PL emission spectra of the polymers in solid thin films appeared at around 448 and 441 nm which are red-shifted over 40 nm as compared to those of the solution conditions, which is caused by the increased inter-chain interaction in solid state. Both of the EL spectra of the sprio-PCPP copolymers exhibited maximum peaks at 448 nm.
KEY WORDS: OLEDs / Cyclopenta[*def*]phenanthrene / Blue Emission / Spiro / Polymer /

Since the polymeric light-emitting diodes based on conjugated polymers[1] were reported, various kinds of conjugated polymers have been developed for electroluminescence (EL) because of the potential application in flat panel displays.[2] Among these conjugated polymers, the polyfluorenes (PFs)[1] and polycyclopenta[*def*]phenanthrenes (PCPPs)[3] for blue[4] and poly(*p*-phenylenevinylene) (PPVs) for green[5] or red[6] emission have obtained much attention due to their thermal and chemical stability, and exceptionally high solution and solid-state fluorescence quantum yield.

To be used as blue light sources in full-color displays or as the host materials for the generation of other colors through energy transfer to lower-energy fluorophores,[7] the conjugated polymers with blue light emission have been investigated intensively. Out of blue light emitting polymers, polyfluorenes (PFs) have emerged as the most attractive blue emitters due to their high luminescent efficiency and easy functionalization at the 9-position of the fluorene unit. However, a major trouble in obtaining blue EL from PFs is the unwanted long-wavelength emission caused by the aggregation,[8] originating from inter-chain attractions of the π-conjugated systems, or keto defects,[9] inducing an energy transfer of singlet excitons. In order to overcome the weak points of PFs, the stabilized blue emission with new EL polymer utilizing a new backbone, poly(2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)) (PCPP), has been demonstrated in our previous report. EL spectrum of dialkylated PCPP did not show any peak between 500–600 nm, which corresponds to keto defect sites or aggregates/excimers even after annealing the device at 150 °C or operation of the device in air.[3]

Since the distance between the polymer chains is expected to

be a crucial governing factor for the formation of aggregates,[10] several researchers have attempted to restrain the green emission by introducing a bulky end group[11] or a cross-linkable group.[12] Especially, spiro-shaped molecules based on 9,9′-spirobifluorene (spiro-PF),[13] have been introduced as EL materials to overcome the problem of the low energy emission.[14] A spiro-bifluorene, with two biphenylene units connected by a tetrahedrally bonded carbon atom, could minimize the π-staking of the conjugated polymer backbone by preventing the approach of other polymer.[15] As compared to the spiro-PF, the spiro(4*H*-cyclopenta[*def*]phenanthrene-4,9′-[9*H*]fluorene) (spiro-PCPP homopolymer), with the spiro moiety in the cyclopenta[*def*]-phenantherene (CPP) unit, showed some inter-chain interaction leading to the emission in the region of 450–500 nm.[16] As compared to the maximum peak of PL emission at 406 nm of the dialkylated PCPP,[3] that of spiro-PCPP homopolymer appeared at 451 nm caused by the inter-chain interaction in the solid thin film state. In case of spiro-PCPP homopolymer, it was concluded that the inter-chain interaction between aromatic spiro group and the backbone of PCPP induce the red-shifted color emission and reduce the luminescence efficiency.[16] Dialkylated cyclopenta-[*def*]phenanthrene unit of spiro-PCPP-*alt*-PCPP and phenylene unit of spiro-PCPPP could decrease the inter-chain interaction between aromatic spiro group and the backbone of PCPP. We present here the synthesis and characterization of new spiro-PCPP-*alt*-PCPP and spiro-PCPPP by Suzuki reaction.

EXPERIMENTAL

Instrumental Characterization

All reagents were purchased from Aldrich or TCI, and used

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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-300 (300 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 aluminum plates with fluorescent indicator UV254. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) or fast atom bombardment (FAB) conditions in the Korea Basic Science Institute (Daegu, Korea). Melting points were determined on an electrothermal model IA 9100 micro-melting point apparatus. Molecular weight and poly dispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. Differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at heating rates of 10 °C/min. Thermo gravimetric analysis (TGA) was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 800 °C. The UV-vis absorption spectra were recorded by a Varian Cary 1 spectrophotometer, while the Oriel InstaSpec IV CCD detection system with arc-xenon lamp was used for the photoluminescence and electroluminescence spectra measurements. Fluorescence quantum yields (Φ_f) are reported relative to 9,10-diphenylanthracene and calculated according to eq 1,[17] where funk is the fluorescence quantum yield of the sample, Φ_{std} is the quantum yield of the standard ($\Phi_f = 0.91$ in ethanol),[18] I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard, respectively, A_{unk} and A_{std} are the absorbances of the sample and the standard at the excitation wavelength, respectively, and η_{unk} and η_{std} are the refractive indexes of the corresponding solutions (pure solvents were assumed).

$$\Phi_{unk} = \Phi_{std}(I_{unk}/A_{unk})(A_{std}/I_{std})(\eta_{unk}/\eta_{std})^2 \qquad (1)$$

EL Device Fabrication and Measurements

For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. The solution of the PEDOT:PSS in aqueous isopropyl alcohol was spin-coated on the surface-treated ITO substrate and dried on a hot plate for 30 min at 110 °C. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting chlorobenzene 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 (20 nm) and aluminum (100 nm) 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 mm[2]. For the determination of device characteristics, current density-voltage (*J-V*) and luminance-voltage (*L-V*) characteristics of the devices were measured using a Keithley 2400 Source Measure Unit equipped with a calibrated photo-multiplier tube.

Synthesis of Polymer

Poly((2,6-(3′,6′-bis(2-ethylhexyloxy)-spiro(4*H*-cyclopenta-[*def*]phenanthrene-4,9′-[9*H*]fluorene)))-*alt*-(2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene))) (spiro-PCPP-*alt*-PCPP) (**4**). The mixture of 2,6-dibromo-(3′,6′-bis(2-ethylhexyloxy)-spiro(4*H*-cyclopenta[*def*]phenanthrene-4,9′-[9*H*]fluorene)) (**1**) (341 mg, 0.45 mmol), 2-(4,4-bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-cyclopenta-[*def*]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (301.9 mg, 0.45 mmol), and Pd(PPh₃)₄ (31.2 mg, 0.027 mmol) in 4 mL of toluene and 3 mL of aqueous 2 M K_2CO_3 was refluxed with vigorous stirring for 3 d under argon atmosphere. After cooling to room temperature, reaction mixture was poured into methanol. The resulting precipitate was reprecipitated using methanol several times to remove residual amount of catalyst. The obtained pale yellow solid was dried in vacuum to give 0.2 g: ^{1}H NMR (300 MHz, THF-d_8): δ (ppm) 0.48–0.49 (m, 12H), 0.72–0.99 (m, 36H), 1.36–1.51 (m, 12H), 2.33 (m, 4H), 3.82–3.98 (m, 4H), 6.23–6.66 (m, 4H), 7.41–7.46 (m, 2H), 7.56 (s, 2H), 7.73–8.10 (m, 8H), 8.24 (s, 2H).

Poly((2,6-(3′,6′-bis(2-ethylhexyloxy)-spiro(4*H*-cyclopenta-[*def*]phenanthrene-4,9′-[9*H*]fluorene)))-*alt*-(1,4-phenylene)) (spiro-PCPPP) (**5**). Polymer **5** was prepared according to the modified procedure for the synthesis of compound **4**. The mixture of 2,6-dibromo-(3′,6′-bis(2-ethylhexyloxy)-spiro(4*H*-cyclopenta[*def*]phenanthrene-4,9′-[9*H*]fluorene)) (**1**) (350 mg, 0.46 mmol), 1,4-benzenediboronic acid bis(pinacol) ester (153 mg, 0.46 mmol), and Pd(PPh₃)₄ (31 mg, 0.027 mmol) in 4 mL of toluene and 3 mL of aqueous 2 M K_2CO_3 was refluxed with vigorous stirring for 3 d under argon atmosphere. After cooling to room temperature, reaction mixture was poured into methanol. The resulting precipitate was reprecipitated using methanol several times to remove residual amount of catalyst. The obtained pale yellow solid was dried in vacuum to give 0.15 g: ^{1}H NMR (300 MHz, THF-d_8): δ (ppm) 0.92–0.99 (m, 12H), 1.29–1.51 (m, 18H), 3.96 (s, 4H), 6.46–6.52 (m, 2H), 6.63 (m, 2H), 7.24–7.28 (m, 2H), 7.53–7.63 (m, 6H), 7.90–8.14 (m, 4H).

RESULTS AND DISCUSSION

Synthesis and Characterization

The general synthetic routes toward the polymers are outlined in Scheme 1. 2,6-Dibromo-(3′,6′-bis(2-ethylhexyl-oxy)-spiro(4*H*-cyclopenta[*def*]phenanthrene-4,9′-[9*H*]fluorene)) (**1**)[19] and 2-(4,4-bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-cyclopenta[*def*]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**)[20] were synthesized by following the previous literature. The Suzuki-Miyaura coupling reaction[21] were employed for the synthesis of spiro-PCPP-*alt*-
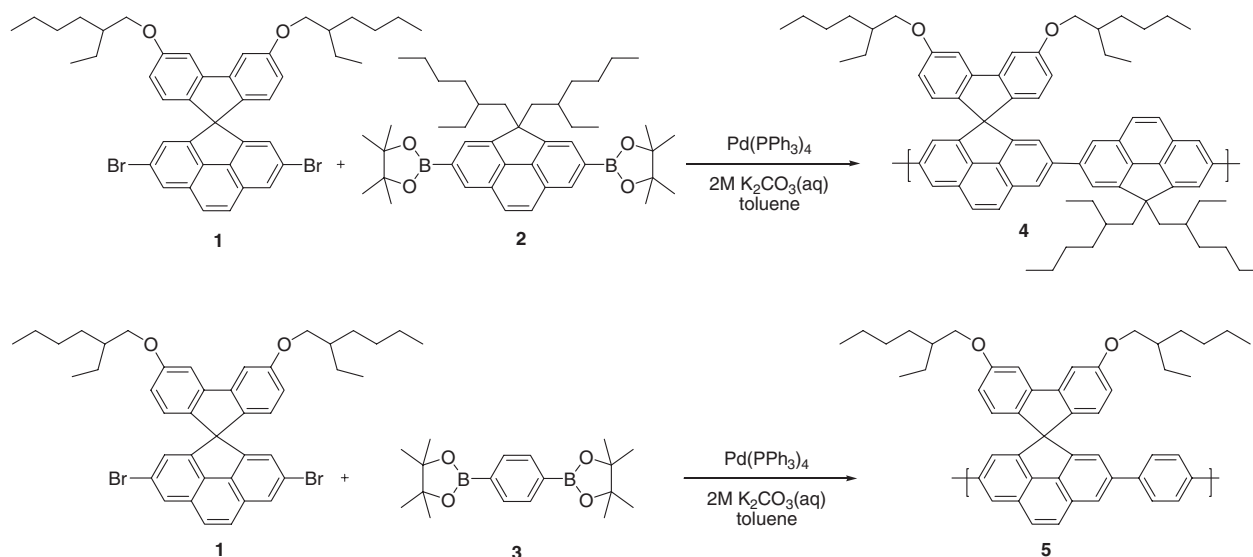
**Scheme 1.** Synthetic routes for the alternating copolymers.

Table I. Characterization of the polymers

polymers	yield (%)	$M_n{}^a$	$M_w{}^a$	PDI[a]	$T_g{}^b$ (°C)	$T_d{}^c$ (°C)
spiro-PCPP-*alt*-PCPP	22	25,600	42,900	1.67	89	380
spiro-PCPPP	32	22,200	37,500	1.69	84	372

[a]Molecular weight and Polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. [b]Glass transition temperature measured by DSC under N_2. [c]Onset decomposition temperature (5% weight loss) measured by TGA under N_2.

PCPP (**4**) and spiro-PCPPP (**5**) using Pd(PPh₃)₄, K₂CO₃ and corresponding monomers. The remaining bromine-end groups of the polymers may cause the fluorescence quenching. The structures of the intermediates, monomers, and the resulting polymers were determined with ¹H, ¹³C NMR spectroscopy and high resolution mass spectrum.

The resulting polymers were soluble in common organic solvents such as chloroform, chlorobenzene, tetrahydrofuran (THF), dichloromethane and *o*-dichlorobenzene. Table I summarizes the polymerization results including molecular weights, polydispersity indexes (PDI, M_w/M_n) and thermal stability of the polymers. The number-average molecular weight (M_n) of spiro-PCPP-*alt*-PCPP and spiro-PCPPP, determined by gel permeation chromatography using mono-disperse polystyrene as calibration standard, are 25600 and 22200, respectively, with PDI around 1.7. The thermal properties of the polymers were evaluated by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) under nitrogen atmosphere. All of the polymers show good thermal stability, with glass transition temperature (T_g) of polymers at around 89 and 84 °C, respectively, using DSC, performed in the temperature range from 30 to 250 °C. As shown in Figure 1, their decomposition temperatures (T_d), which correspond to a 5% weight loss upon heating during TGA, are 380 and 372 °C for polymers, respectively. The polymers exhibit good thermal stability which is important for the application of the copolymers in organic light emitting diodes.
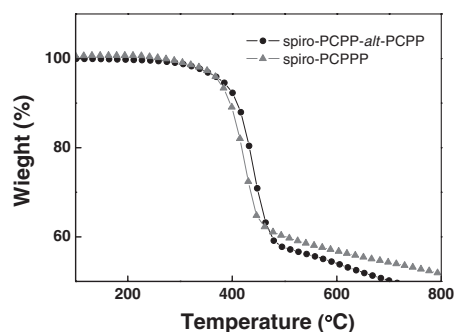

Figure 1. Thermogravimetric analysis of the polymers under N_2.

Photophysical Properties

The linear UV-vis absorption and photoluminescence (PL) emission spectra of polymers as solution and thin film are shown in Figure 2 and Figure 3. The solution was prepared using chloroform as solvent and the thin film was prepared by spin-coating on quartz plates from the polymer solutions in chlorobenzene. The absorption peaks originating from the conjugated backbone of spiro-PCPP-*alt*-PCPP and spiro-PCPPP appeared at around 363 and 345 nm, respectively, in the solution with chloroform as the solvent. The corresponding absorption peaks of the polymers in solid thin film appeared at around 359 and 349 nm, respectively. The spiro-PCPP copoly-
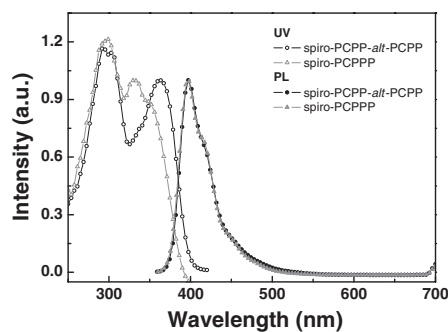
Figure 2. UV-vis absorption and photoluminescence spectra of ploymers in the THF solutions.
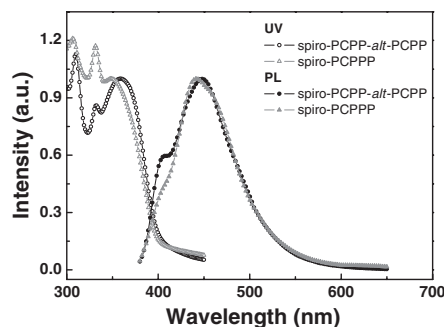
Figure 3. UV-vis absorption and photoluminescence spectra of polymers in the solid state.

Table II. Characteristics of the UV-vis absorption, photoluminescence, and electroluminescence spectra

polymers	solution				film			diviece	
	Abs λ_{max} (nm)	PL λ_{max} (nm)	fwhm[a] of PL	QE_{PL} (%)	Abs λ_{max} (nm)	PL λ_{max} (nm)	fwhm[a] of PL	EL λ_{max} (nm)	fwhm[a] of PL
spiro-PCPP-*alt*-PCPP	363	397	39	70.4	359	407, 448	105	448	91
spiro-PCPPP	345	397	41	62.0	349	441	78	448	64

[a]Full width at half-maximum of PL and EL spectra.

mers exhibit additional absorption peak at 306 nm due to the π-π^* transition of cyclopenta[*def*]phenanthrene units[4] and the peak at 331 nm is originating from the aromatic spiro-portion. In case of spiro-PCPP homopolymer, it was concluded that the inter-chain interaction between aromatic spiro group and the backbone of PCPP induce the red-shifted color emission and reduce the luminescence efficiency.[16] Dialkylated cyclopenta-[*def*]phenanthrene unit of spiro-PCPP-*alt*-PCPP and phenylene unit of spiro-PCPPP could decrease the inter-chain interaction between aromatic spiro group and the backbone of PCPP. Caused by the decrease of the inter-chain interaction, the absorption maxima of the copolymers were blue-shifted by 10–25 nm as compared with that of spiro-PCPP homopolymer.[22] The PL emission spectra of the two copolymers in chloroform solution show maximum peaks at 397 nm. The emission peaks in solution are nearly identical with that of dialkylated PCPP. In solid thin films, the maximum peaks of PL emission spectra of spiro-PCPP-*alt*-PCPP and spiro-PCPPP appeared at around 448 and 441 nm, respectively. The PL spectra in solid thin films display a vibronic fine structure, which are also red-shifted over 40 nm than solution conditions, which is caused by the increased inter-chain interaction in solid state.

As listed in Table II, the quantum efficiencies of the spiro-PCPP-*alt*-PCPP and spiro-PCPPP are 70 and 62% in solution, respectively. Quantum efficiency in solution was determined in chloroform, relative to 9,10-diphenylanthracene as standard ($\Phi_{PL} = 0.91$ in ethanol).

Electrochemical Properties of the Polymers

The electrochemical properties of the polymer were determined from the band gaps which were estimated from the absorption onset wavelength, and the HOMO energy levels

**Table III.** Electrochemical potentials and energy levels of the polymers

polymers	E_{onset}[a] (V)	HOMO[b] (eV)	LUMO[c] (eV)	E_g[d] (eV)
spiro-PCPP-*alt*-PCPP	1.10	−5.90	−2.82	3.08
spiro-PCPPP	1.20	−6.00	−2.89	3.11

[a]Onset oxidation potential measured by cyclic voltammetry. [b]Calculated from the oxidation potentials. [c]Calculated from the HOMO energy levels and E_g. [d]Energy band gap was estimated from the onset wavelength of the optical absorption.

which were estimated from the cyclic voltammetry (CV). The CV was performed with 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 the protection of argon. A platinum electrode ($\sim$0.05 cm^2) coated with a thin polymer film was used as the working electrode. Pt wire and Ag/AgNO$_3$ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO$_3$ reference electrode (calibrated by the FC/FC$^+$ redox system) was 4.80 eV below the vacuum level. The oxidation potentials derived from the onset of electrochemical p-doping are summarized in Table III. HOMO levels were calculated according to the empirical formula ($E_{HOMO} = -([E_{onset}]^{ox} + 4.80)$ eV). The optical band gaps estimated from absorption onset of the copolymers are listed in Table III. As shown in Figure 4, the oxidation onset potentials of polymers are 1.10 and 1.20 V. HOMO energy levels of polymers are −5.90 and −6.00 eV. The LUMO energy level was estimated from the respective optical bandgap and HOMO energy level. The values of the LUMO energy levels of the spiro-PCPP-*alt*-PCPP and spiro-PCPPP are calculated to be −2.82 and −2.89 eV, respectively.
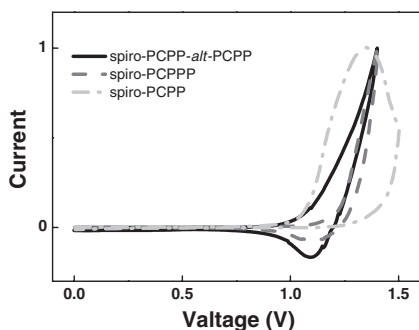
Figure 4. Cyclic voltammetry curves of the polymers in 0.1 M Bu$_4$NBF$_4$ acetonitrile solution at a scan rate of 100 mV/s at room temperature (*vs.* an Ag quasi-reference electrode).
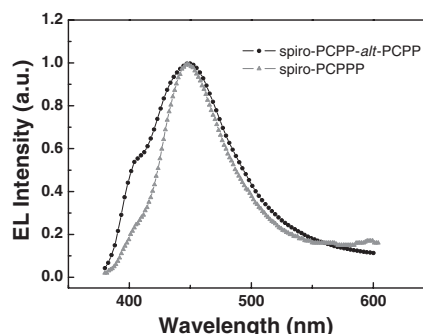
Figure 5. Electroluminescence spectra of devices with the configuration of ITO/PEDOT/polymer/Ca:Al.

Table IV. Device performance characteristics of polymers

polymers	turn-on voltage[a] (V)	voltage[b] (V)	current density[b] (mA/cm^2)	luminance[b] (cd/m^2)	LE$_{max}$[c] (cd/A)	CIE (x, y)[d]
spiro-PCPP-*alt*-PCPP	9	13	274.5	61.6	0.025	(0.22, 0.22)
spiro-PCPPP	9	18	210.2	15.9	0.009	(0.41, 0.39)

[a]Voltages required to achieve a brightness of 1 cd/m^2. [b]Measured under the condition of maximum brightness. [c]Maximum luminescence efficiency. [d]Calculated from the EL spectrum.

Electroluminescent Properties

Figure 5 shows the EL spectra of ITO/PEDOT/polymer/Ca:Al devices. The EL spectra of spiro-PCPP copolymers are similar to the PL spectra. Both of the EL spectra of spiro-PCPP-*alt*-PCPP and spiro-PCPPP show maximum peaks at 448 nm. The results indicate that the EL and PL phenomena are originated from the same excited state. As compared to the PL spectrum of the thin film, the EL spectrum of the polymer showed smaller fwhm. Although spiro-PCPP has the maximum peak of EL at 463 nm, the alternating copolymers, spiro-PCPP-*alt*-PCPP and spiro-PCPPP, show blue shifted EL with maximum peaks at 448 nm. Inter-chain interaction was reduced by using comomoners, such as dialkylcyclopenta[*def*]phenanthrene or phenylene.[16] The emission color of the device with the configuration of ITO/PEDOT/polymer/Ca:Al has the CIE coordinates of $x = 0.22$ and 0.41, $y = 0.22$ and 0.39, respectively.

Table IV shows the characteristics of EL spectra of ITO/PEDOT/polymer/Ca:Al devices. The current density-voltage and luminescence-voltage characteristics of the devices with the same configuration are shown in Figure 6. The turn-on voltage of spiro-PCPP-*alt*-PCPP device is about 9 V. The maximum luminescence of spiro-PCPP-*alt*-PCPP device is 61.6 cd/m^2 at 13 V. The maximum luminescence efficiency of the device with spiro-PCPP-*alt*-PCPP is 0.025 cd/A at current density of 184 mA/cm^2.

CONCLUSION

We present here the synthesis and characterization of new spiro-PCPP copolymers by Suzuki-Miyaura reaction. To remove the inter-chain interaction of spiro-PCPP homopolymers, spiro-PCPP-*alt*-PCPP with dialkylated cyclopenta[*def*]-
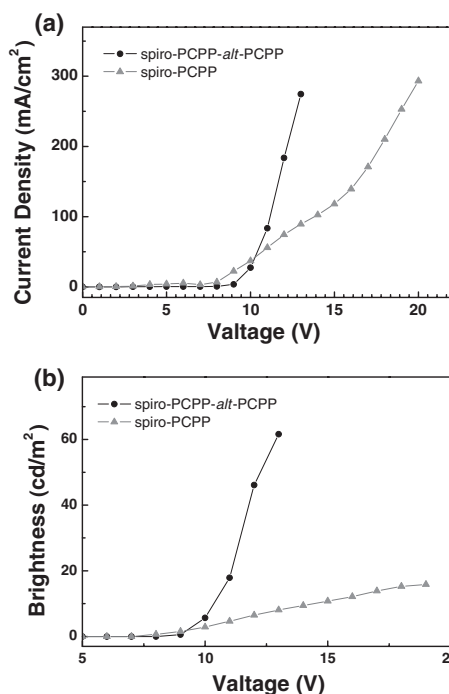
Figure 6. (a) Current-Voltage (I-V) and (b) Voltage-Luminescence (V-L) characteristics of OLED with the configuration of ITO/PEDOT/polymer/Al.

phenanthrene unit and spiro-PCPPP with phenylene unit were synthesized. spiro-PCPP-*alt*-PCPP and spiro-PCPPP showed the maximum absorption peaks at around 363 and 345 nm with the solutions of chloroform and at 359 and 349 nm with the solid films, respectively. PL emission spectra of the copolymers in chloroform show the maximum peaks at 397 nm. The PL emissions of the copolymers in solution
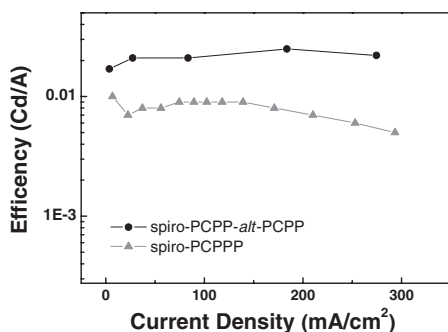
Figure 7. Efficiency of OLEDs of polymer with the configuration of ITO/PEDOT/polymer/Ca:Al.

were quite similar as compared with that of dialkylated PCPP. The maximum peaks of the PL emission spectra of the copolymers in solid thin films appeared at around 448 and 441 nm which are red-shifted over 40 nm as compared to those of the solution conditions, which is caused by the increased inter-chain interaction in solid state. The EL spectrum of sprio-PCPP copolymers show identical maximum peaks at 448 nm.

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