ORIGINAL ARTICLE

Synthesis and characterization of polycyclopentaphenanthrene with carbazole or oxidiazole pendant units

Suhee Song¹, Changyoon Kim¹, Sung Heum Park², Il Kim³, Kwanghee Lee⁴, Youngeup Jin⁵ and Hongsuk Suh¹

Poly(2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)) is a blue light emitting conjugated polymer that is stable even after annealing at 150 °C or operation of the electroluminescence (EL) device in air. Polymers with carbazole or oxadiazole units have been synthesized by Yamamoto polymerization. The photoluminescence (PL) emission spectra of the polymers in chloroform solutions exhibit maximum peaks at 384–398 nm. The PL emission spectra of polymer films exhibit maximum peaks at 419–425 nm and additional peaks at around 530 nm. The EL emission maxima of the polymers appear at 538–543 nm, as carbazole or oxadiazole pendants induce inter-molecular interactions.

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Keywords: carbazole; conjugated polymer; cyclopentaphenanthrene; light emitting diodes (LEDs); oxadiazole

INTRODUCTION

Conjugated polymers have attracted scientific and industrial interest as a result of their applications in electronic and optoelectronic devices such as organic light-emitting diodes,¹⁻² thin film transistors³⁻⁴ and photovoltaic cells.⁵ Many conjugated polymers have been studied because of their desirable features, such as low-driving voltages and simple manufacturing processes.⁶ In particular, fluorine-based conjugated polymers have several advantages, including a high photoluminescence (PL) quantum efficiency, good thermal stability and easy functionalization at the nine-position of the fluorene unit.7-8 However, a major disadvantage of polyfluorenes is that thermal annealing or the application of current induces red-shift and diminished emission. Previously, we reported the synthesis and properties of new electroluminescence (EL) polymers utilizing a new poly(2,6-(4,4bis(2-ethylhexyl)-4H-cyclopenta-[def]phenanthrene)) (PCPP) backbone with stabilized blue emission.9-13 The PL and EL spectra of PCPP do not show any peaks in the long wavelength region around 550 nm even after prolonged annealing or the application of current.9

Many conjugated polymers are not well matched to the electronic structure of devices This generally results in an imbalance of charge transport and poor device efficiency. Techniques used to overcome the imbalance of charge carrier transport¹⁴ include the

synthesis of copolymers incorporating a hole-transport moiety or electron-transport moiety, blending and the use of multi-layer devices. Whereas oxadiazole-based polymers¹⁵ have been widely used to improve electron transport,¹⁶ the carbazole¹⁵ unit is a well-known hole-transporting group because of its electron-donating capabilities.¹⁷ To improve the charge carrier transport, we have reported conjugated polymers containing a polyfluorene backbone with carbazole or oxadiazole pendants.¹⁴ We synthesized a polymer, PCPP, which has a rigid backbone and generates stabilized and efficient blue EL without exhibiting any peaks in the long-wavelength region. Here we report new conjugated polymers, BC-PCPP, CO-PCPP and BO-PCPP, synthesized through Yamamoto condensafrom 9-(6-(2,6-dibromo-4-(6-(9H-carbazol-9-yl)hexyl)-4Htion cyclopenta[def]phenanthren-4-yl)hexyl)-9H-carbazlole (4), 9-(6-(2,6dibromo-4-(6-(4-(5-phenyl-2,5-dihydro-1,3,4-oxadiazol-2-yl)phenyl)hexyl)-4H-cyclopenta[def]phenanthren-4-yl)hexyl)-9H-carbazlole (5) and 2-(4-((6-(2,6-dibrmo-4-(6-(4-(5-phenyl-2,5-dihydro-1,3,4-oxadiazol-2-yl)phenoxy)hexyl)-4H-cyclopenta[def]phenanthren-4-yl)hexyl) oxy)phenyl)-5-phenyl-2,5-dihydro-1,3,4-oxadiazole (6). The electrontransporting moiety, 2,5-diphenyl-1,3,4-oxadiazole-diyl (Oxd), and/or the hole-transporting moiety, N-carbazolyl (Cz), were introduced with a flexible carbon chain spacer of sufficient length as the side chain at the C-4 position of cyclopentaphenanthrene.

¹Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan, Korea; ²Department of Physics, Pukyong National University, Busan, Korea; ³The WCU Center for Synthetic Polymer Bioconjugate Hybrid Materials, Department of Polymer Science and Engineering, Pusan National University, Busan, Korea; ⁴Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea and ⁵Department of Industrial Chemistry, Pukyong National University, Busan, Korea

Correspondence: Dr H Suh, Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Korea.

E-mail: hssuh@pusan.ac.kr or Professor Y Jin, Department of Industrial Chemistry, Pukyong National University, Busan 608-739, Korea.

E-mail: yjin@pknu.ac.kr

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EXPERIMENTAL PROCEDURE

Instrumental characterization

All reagents were purchased from Aldrich (St Louis, MO, USA) or TCI (Tokyo, Japan) and used without further purification. Solvents were purified by normal procedures and handled under a moisture-free atmosphere. ¹H and ¹³C NMR spectra were recorded with a Varian Gemini-300 (300 MHz) spectrometer (Varian, Palo Alto, CA, USA), and chemical shifts were recorded in p.p.m. units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (Merck, Whitehouse, KY, USA) (particle size 230~400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with UV254 fluorescent indicator. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer (JEOL, Tokyo, Japan) under electron impact (EI) or fast atom bombardment conditions at the Korea Basic Science Institute (Daegu, Korea). The molecular weights and polydispersities of the polymers were determined by gel permeation chromatography analyses with polystyrene standard calibration. The UV-vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer whereas the Oriel InstaSpec IV CCD detection system (Oriel, Irvine, CA, USA) with a xenon lamp was used for the PL and EL spectra measurements. The cyclic voltammetry was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu₄NBF₄; 0.10 M) in acetonitrile at a scan rate of 100 mV s⁻¹ at room temperature under the protection of argon. A platinum electrode ($\sim 0.05 \text{ cm}^2$) coated with a thin polymer film was used as the working electrode. Platinum wire and an Ag/AgNO3 electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO3 reference electrode (calibrated by the FC/FC⁺ redox system) was 4.8 eV below the vacuum level.

EL device fabrication and measurements

For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) was used as the hole-injection-transport layer and was introduced between the emissive layer and an indium tin oxide (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 a chlorobenzene solution of the polymer. The prepared emissive polymer thin film had a uniform surface with a thickness of about 110 nm. The emissive film was dried in a vacuum, and calcium (20 nm) and aluminum (100 nm) electrodes were deposited on top of the polymer films through a mask by vacuum evaporation at pressures below 10^{-7} Torr, yielding active areas of 4 mm². To determine the device characteristics, the current density-voltage (I-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 the monomers

A solution of 2,6-dibromo-4*H*-cyclopenta[*def*]phenanthrene (2) (500 mg, 1.15 mmol).⁹ and catalytic amounts of triethylbenzylammonium chloride in 20 ml of DMSO was heated at 60 °C After 1 h, the reaction mixture was treated with 9-(6-bromohexyl)-9*H*-carbazole (3),¹¹ 2-(4-((6-bromohexyl)oxy)phenyl)-5-phenyl-1,3,4-oxadiazole (1).¹¹ and 50% aqueous NaOH at room temperature. After 5 h, water and ethyl acetate were added. The organic phase was washed with 3×100 ml of water. The organic phase was concentrated under reduced pressure and purified by flash column chromatography to produce 260 mg (27%) of monomer (4), 340 mg (32%) of monomer (5) and 280 mg (24%) of monomer (6).

9,9'-9-(2,6-Dibromo-4*H*-cyclopenta[*def*]phenanthren-4-yl)di-6,1-hexyanediyl)bis-9*H*-carbazlole (4) has the following properties (R_f : 0.30 (SiO₂, MC/ Hexane=1/3)); ¹H-NMR (300 MHz, CDCl₃) δ (p.p.m.) 0.66–1.71(m, 16H), 1.99(t, 4H, *J*=4.5 Hz), 4.18(t, 4H, *J*=6.9 Hz), 7.20(t, 4H, *J*=7.5 Hz), 7.29(t, 4H, *J*=8.1 Hz), 7.42(t, 4H, *J*=8.1 Hz), 7.53(s, 2H), 7.72(s, 2H), 7.94(s, 2H), 8.10(d, 4H, *J*=8.1 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ (p.p.m.) 24.61, 27.25, 29.27, 30.13, 30.31, 39.37, 43.21, 59.99, 108.93, 119.02, 120.61, 122.37, 123.03, 123.80, 125.86, 126.23, 128.75, 135.10, 140.56 and 150.90. The HRMS (*m/z*, EI⁺) calculated for C₅₁H₄₆Br₂N₂ was 844.2028, and the HRMS found was 844.2036.

9-(6-(2,6-Dibromo-4-(6-(4-(5-phenyl-2,5-dihydro-1,3,4-oxadiazol-2-yl) phenyl)hexyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)hexyl)-9*H*-carbazlole (5) has the following properties (Rf: 0.60 (SiO2, EA/Hexane=1/3)); ¹H-NMR (300 MHz, CDCl₃) δ(p.p.m.) 0.70-1.72(m, 16H), 2.03-2.09(m, 4H), 3.90(t, 2H, J=6.3 Hz), 4.18(t, 2H, J=6.9 Hz), 6.95(d, 2H, J=8.7 Hz), 7.20(t, 2H, J=7.4 Hz), 7.30(d, 2H, J=8.1 Hz), 7.43(t, 2H, J=8.1 Hz), 7.52-7.54(m, 3H), 7.59(s, 2H), 7.75(s, 2H), 7.96(s, 2H), 8.02-8.04(m, 6H); ¹³C-NMR (75 MHz, CDCl₃) δ (p.p.m.) 24.57, 26.04, 27.21, 29.20, 29.36, 29.99, 30.09, 39.37, 39.46, 43.06, 43.20, 59.95, 68.33, 108.78, 115.11, 116.34, 118.86, 120.48, 122.18, 122.90, 123.66, 124.29, 125.71, 126.09, 126.98, 127.69, 128.62, 128.81, 129.12, 131.66, 135.02, 140.44, 150.75 and 161.91. The HRMS (m/z, EI⁺) calculated for C53H47Br2N3O2 was 915.2035, and the HRMS found was 915.2042. 2,2'-((2,6-Dibrmo-4H-cyclopenta[def]phenanthren-4-yl)bis(6,1-hexanediyloxy-4,1-phenylene))bis(5-phenyl-1,3,4-oxadiazole) (6) has the following properties $(R_{f}, 0.50 \text{ (SiO}_2, \text{EA/Hexane}=1/4)); ^{1}\text{H-NMR} (300 \text{ MHz}, \text{CDCl}_3) \delta(\text{p.p.m.})$ 0.76-1.65(m, 16H), 2.14(t, 4H, J=8.1 Hz), 3.90(t, 4H, J=6.3 Hz), 6.93(d, 4H, J=8.7 Hz), 7.49-7.52(m, 6H), 7.62(s, 2H), 7.75(s, 2H), 7.96(s, 2H), 7.98(d, 4H, J=8.7 Hz), 8.08-8.12(m, 4H); ¹³C-NMR (75 MHz, CDCl₃) δ (p.p.m.) 14.65, 21.49, 24.62, 26.04, 29.36, 30.00, 39.46, 60.04, 60.73, 68.32, 115.11, 116.31, 122.20, 123.70, 124.25, 125.70, 126.11, 126.97, 128.64, 128.81, 129.19, 131.70, 135.06, 150.80 and 161.92. The HRMS (m/z, EI⁺) calculated for C55H48Br2N4O4 was 986.2042, and the HRMS found was 986.2049.

Synthesis of the polymers

A solution of Ni(COD)₂ (1.5 mmol), 2,2'-dipyridyl (1.5 mmol) and cyclooctadiene (1.5 mmol) in 5 ml of DMF was heated at 80 °C After 30 min, the reaction mixture was treated with one of 0.75 mmol of 9-(6-(2,6-dibromo-4-(6-(9*H*carbazol-9-yl)hexyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)hexyl)-9*H*-carbazlole (4), 9-(6-(2,6-dibromo-4-(6-(4-(5-phenyl-2,5-dihydro-1,3,4-oxadiazol-2-yl) phenyl)hexyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)hexyl)-9*H*-carbazlole (5) or 2-(4-((6-(2,6-dibromo-4-(6-(4-(5-phenyl-2,5-dihydro-1,3,4-oxadiazol-2-yl) phenoxy)hexyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)hexyl)oxy)phenyl)-5-phenyl-2,5-dihydro-1,3,4-oxadiazole (6) in 5 ml of toluene and heated at 80 °C for 3 days. After cooling to room temperature, the mixture was poured into methanol. After filtration, the resulting solid material was precipitated again using 1.01 of methanol several times to remove catalyst residues. The resulting polymers were soluble in THF, CHCl₃, *o*-dichlorobenzene (ODCB) and toluene.

RESULTS AND DISCUSSION

Synthesis and characterization

The general synthetic routes toward the monomers and polymers are outlined in Schemes 1 and 2. To prepare PCPPs, three types of monomers (4, 5 and 6) were first synthesized from 2,6-dibromo-4H-cyclopenta[def]phenanthrene (2), 9-(6-bromohexyl)-9H-carbazole (3) and 2-(4-((6-bromohexyl)oxy)phenyl)-5-phenyl-1,3,4-oxadiazole (1) with a NaOH solution and a catalytic amount of triethyl-benzylammonium chloride. The polymerizations of the monomers 4, 5 and 6 were conducted under Yamamoto conditions¹⁸ using bis(1,5-cyclooctadiene) nickel(0) (Ni(COD)₂), 2,2'-dipyridyl and cyclooctadiene to generate the desired polymers BC-PCPP, CO-PCPP and BO-PCPP, respectively. All of the polymers demonstrated good solubility at room temperature in organic solvents such as chloroform, THF, chlorobenzene and ODCB. Table 1 summarizes the polymerization results including the molecular weight, polydispersity index and thermal stability of each polymer. Using gel permeation chromatography, the number-average molecular weight $(M_{\rm n})$ of the resultant polymers was found to be $14\,000 \sim 15\,000$, the weight-average molecular weight (M_w) was $39\,000 \sim 84\,000$ and the polydispersity index (M_w/M_n) was 2.6 ~ 5.6.

The thermal properties of the polymers were characterized by thermal gravimetric analysis (TGA). The TGA data of the polymers are summarized in Table 1. TGA was performed with TGA 2950 TGA instrument in a nitrogen atmosphere at a heating rate of $10 \,^{\circ}\text{C}\,\text{min}^{-1}$



Scheme 1 Synthetic routes for monomers.



Scheme 2 Synthetic routes for polymers.

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to a final temperature of 600 °C. TGA showed that BC-PCPP, CO-PCPP and BO-PCPP are thermally stable, with only about a 5% weight loss in air at temperatures of 400 °C, 386 °C and 353 °C, respectively. The high-thermal stability of the resulting polymers prevents the deformation of the polymer morphology and is important for organic light-emitting diode. The polymers showed no glass transition temperature ($T_{\rm g}$) using differential scanning calorimetry performed at a temperature range of 30–250 °C.

Optical properties

The solution of the synthesized polymers were prepared using chloroform as a solvent. Polymer thin films were prepared by spin-coating the solution in ODCB on quartz plates. The UV-vis absorption spectra of the polymers in solution and as thin films are shown in Figures 1 and 2 and summarized in Table 2. The polymer solutions presented absorption bands with maximum peaks at about 303 and 370 nm, similar to those of PCPP.9 The peaks at 303 nm were caused by the $\pi - \pi^*$ transition of cyclopenta[*def*]phenanthrene units, and the peaks at about 370 nm were due to the $\pi - \pi^*$ transition of the conjugated main chains. The polymer thin films exhibited absorption spectra with two maximum peaks at around $232 \sim 298$ and $350 \sim 356$ nm. The PL emission spectra of the BC-PCPP, CO-PCPP and BO-PCPP in chloroform solutions exhibited maximum peaks at 398, 387 and 384 nm, respectively, similar to that of PCPP. Maximum peaks for the polymer thin films appeared at $419 \sim 425$ nm. These peaks were red-shifted by about 25-40 nm compared with those of polymers in solution. Although carbazole and oxadiazole pendants were introduced to the polymer backcone for high efficiency, the polymers exhibited additional peaks at 530 nm in PL spectra. The polymer with two carbazole units, BC-PCPP, displayed an additional, lower peak compared with

Table 1 Polymerization results and thermal properties of polymers

Polymer	Yield (%)	<i>M</i> _n ^a	M_w^a	PDI ^a	TGA (T _d) ^b
BC-PCPP	62	15000	39000	2.6	400
CO-PCPP	45	15000	84000	5.6	386
BO-PCPP	42	14000	42000	3.0	353

^aMolecular weight (M_w) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. ^bOnset decomposition temperature (5% weight loss) measured by TGA under N₂.



Figure 1 UV-vis absorption and PL spectra of polymers in chloroform solution.

CO-PCPP and BO-PCPP. This additional peak suggests that the carbazole unit decreases the interchain interaction of the polymer backbones.¹⁹

Electrochemical properties

The oxidation potentials derived from the onset of electrochemical p-doping and the optical band gaps estimated from the absorption onset of the polymers are summarized in Table 3. HOMO levels were calculated according to the empirical formula $(E_{HOMO} =$ $-([E_{onset}]^{ox}+4.8)$ eV). During the anodic scan, the oxidation onset potentials of the polymers were in the range of $0.47 \sim 0.56$ V and exhibited an irreversible p-doping process. HOMO energy levels of the BC-PCPP, CO-PCPP and BO-PCPP were about -5.27, -5.28 and $-5.36 \,\mathrm{eV}$, respectively. The absorption onset wavelengths of the polymers were $410 \sim 420$ nm, which correspond to band gaps of $3.02 \sim 2.95$ eV. The LUMO energy levels were calculated from the values of the band gap and the HOMO energy levels and were determined to be about $-2.25 \sim -2.38$ eV. The HOMO energy levels of the polymers were similar to that of PCPP $(-5.54 \text{ eV})^9$ because there is no conjugation between the polymer backbone and the substituents of carbazole pendants or oxadiazole pendants. Figure 3 illustrates the energy levels of the polymers compared with that of ITO, PEDOT:PSS, and aluminum used in polymer light emitting diods devices.

Electroluminescent properties

The EL properties of the polymers were investigated by fabricating devices with a ITO/PEDOT/polymer/Al configuration. The EL spectra of the devices are shown in Figure 4 and Table 4. The emission maxima of the BC-PCPP, CO-PCPP and BO-PCPP appeared at 540, 543 and 538 nm, respectively. CIE coordinates of the devices were in the range of $x=0.37 \sim 0.39$ and $y=0.50 \sim 0.52$. Compared with PCPP, the EL spectra of the polymers were red-shifted because the substituents of carbazole and oxidaizole were introduced to the cyclopentaphenanthrene backbone as pendants, inducing intermolecular interaction.

The current density-voltage (J-V) and luminescence-voltage (L-V) characteristics of ITO/PEDOT/polymer/Ca/Al devices are shown in Figures 5 and 6. The turn-on voltages of BC-PCPP, CO-PCPP and BO-PCPP were about 5, 4.5 and 6.5 V, respectively. The luminescence



Figure 2 UV-vis absorption and PL spectra of polymers in thin film.

Table 2 Characteristics of the UV-vis absorption and photoluminescence

	Solu	tion	Film		
Polymers	Abs λ_{max} (nm)	PL λ_{max} (nm)	Abs λ_{max} (nm)	PL λ_{max} (nm)	
PCPP	357	403	359	413	
BC-PCPP	303, 371	398	232, 350	419	
CO-PCPP	303, 370	387	297, 350	425	
BO-PCPP	303, 369	384	298, 356	425	



Figure 3 Energy-level diagram showing the HOMO and LUMO energy levels of polymers.





Table 3 Electrochemical potentials and energy levels of the polymers

Optical band gap (eV)ª	E _{ox} (V) ^b	HOMO (eV) ^c	LUMO (eV) ^d
2.98	0.77	-5.57	-2.59
3.02	0.47	-5.27	-2.25
2.95	0.48	-5.28	-2.33
2.98	0.56	-5.36	-2.38
	Optical band gap (eV) ^a 2.98 3.02 2.95 2.98	Optical band gap (eV) ^a E_{ox} (V) ^b 2.98 0.77 3.02 0.47 2.95 0.48 2.98 0.56	Optical band gap (eV)a E_{ox} (V)bHOMO (eV)c2.98 0.77 -5.57 3.02 0.47 -5.27 2.95 0.48 -5.28 2.98 0.56 -5.36

^aOptical energy band gap was estimated from the onset wavelength of the optical absorption. The data in the parentheses are the wavelengths of absorption onset of the polymers. ^bOnset oxidation and reduction potential measured by cyclic voltammetry. ^cCalculated from the oxidation potentials

^dCalculated from the HOMO energy levels and optical band gap.





Figure 5 (a) Current density-Voltage (J-V) and (b) Voltage-Luminescence (V-L) characteristics of organic light-emitting diode with a ITO/PEDOT/ polymer/Al configuration.

Table 4	Device	performance	characteristics (of devices	with the	configuration	of ITO/PFDOT/	oolymer/Al
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Polymers	EL λ _{max} (nm)	Turn-on voltage (V)ª	Voltage (V) ^b	<i>Current density (mA cm⁻²)</i> ^b	Luminance (cd m ^{-2)b}	LE _{max} (cd A ⁻¹) ^c	CIE (x,y) ^d
BC-PCPP	540	5	10	703	142	0.023	(0.37, 0.52)
CO-PCPP	543	4.5	14.5	689	93	0.035	(0.39, 0.50)
BO-PCPP	538	6.5	16	361	97	0.032	(0.38, 0.50)

Abbreviations: AI, aluminium; EL, electroluminescence; ITO, indium tin oxide; PEDOT, poly(3,4-ethylenedioxythiophene). ^aVoltages required to achieve a brightness of 1 cd m⁻².

^bMeasured under the condition of maximum brightness.

^cMaximum luminescence efficiency. ^dCalculated from the EL spectrum.



Figure 6 Efficiencies of organic light-emitting diodes of polymers with a ITO/PEDOT/polymer/Al configuration.

intensities of BC-PCPP, CO-PCPP and BO-PCPP increased as the applied voltage increased, and the maximum luminescence (L_{max}) of the polymer devices was 93 ~ 142 cd m⁻². The maximum luminescence efficiencies of BC-PCPP, CO-PCPP and BO-PCPP at room temperature were 0.023, 0.035 and 0.032 cd A⁻¹, respectively. The highest maximum luminescence efficiency of CO-PCPP was 0.035 cd A⁻¹ because of the charge balance of the hole-transporting ability of the carbazole and the electron transporting ability of the oxadiazole in the EL devices.²⁰ As shown in Figure 6, the maximum luminescence efficiencies of BC-PCPP, CO-PCPP and BO-PCPP at room temperature were 0.023, 0.035 and 0.032 cd A⁻¹, respectively.

CONCLUSION

The present investigation pertains to the synthesis, characterization and EL properties of several new polymers (BC-PCPP, CO-PCPP and BO-PCPP) synthesized by Yamamoto polymerization. These polymers, with pendants of carbazole or oxadiazole, were synthesized to improve the efficiency of the EL devices. The polymer solutions presented absorption bands with maximum peaks at about 303 and 370 nm. The PL emission spectra of BC-PCPP, CO-PCPP and BO-PCPP in chloroform solution displayed maximum peaks at 398, 387 and 384 nm, respectively, similar to that of PCPP. The polymer films displayed maximum peaks at 419, 425 and 425 and additional peaks at around 530 nm in PL spectra. The EL emission maxima of BC-PCPP, CO-PCPP and BO-PCPP appeared at 540, 543 and 538 nm, respectively, as carbazole or oxadiazole pendants induce inter-molecular interactions. The maximum luminescence efficiencies of BC-PCPP, CO-PCPP and BO-PCPP at room temperature were 0.023, 0.035 and $0.032 \text{ cd } \text{A}^{-1}$, respectively.

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