Synthesis and Electrochemical and Electroluminescent Properties of N-Phenylcarbazole-Substituted Poly(p-phenylenevinylene)

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ABSTRACT: An N-phenylcarbazole-containing poly(p-phenylenevinylene) (PPV), poly [(2-(4'-carbazol-9-yl-phenyl)-5-octyloxy-1,4-phenylenevinylene)-alt-(2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene)] (Cz-PPV), was synthesized, and its optical, electrochemical, and electroluminescent properties were studied. The molecular structures of the key intermediates, the carbazole-containing boronic ester and the dialdehyde monomer, were crystallographically characterized. The polymer was soluble in common organic solvents and exhibited good thermal stability with a 5% weight loss at temperatures above 420 °C in nitrogen. A cyclic voltammogram showed the oxidation peak potentials of both the pendant carbazole group and the PPV main chain, indicating that the hole-injection ability of the polymer would be improved by the introduction of the carbazole-functional group. A single-layer light-emitting diode (LED) with a simple configuration of indium tin oxide (ITO)/Cz-PPV (80 nm)/Ca/Al exhibited a bright yellow emission with a brightness of 1560 cd/m² at a bias of 11 V and a current density of 565 mA/cm². A double-layer LED device with the configuration of ITO/poly(3,4-ethylenedioxy-2,5-thiophene):poly(styrenesulfonic acid) (60 nm)/Cz-PPV (80 nm)/Ca/Al gave a low turn-on voltage at 3 V and a maximum brightness of 6600 cd/m² at a bias of 8 V. The maximum electroluminescent efficiency corresponding to the double-layer device was 1.15 cd/A, 0.42 lm/W, and 0.5%. The desired electroluminescence results demonstrated that the incorporation of hole-transporting functional groups into the PPVs was effective for enhancing the electroluminescent performance. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 43: 5765–5773, 2005

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INTRODUCTION

Since polymeric light-emitting diodes (PLEDs) based on poly(p-phenylenevinylene) (PPV) were reported by the Cambridge group in 1990,1 considerable progress has been made in the development of π-conjugated polymers and the exploration of their possible applications in displays.2-4 PPV and its derivatives are some of the most frequently used conjugated polymers in the field of organic electroluminescence (EL) because of their good film-forming properties, high photoluminescence (PL) efficiency, and good color tunability through molecular structure designs.5 However, several issues still need to be improved, such as the low EL efficiency and undesired device operation stability.
The light emission of a PLED is produced by a recombination of the electron and hole injected into the emitting layer through the electrodes within. Employing an additional hole-injection/transport layer between the emitter and the anode and/or an electron-injection/transport layer between the emitter and the cathode has been successfully demonstrated to improve device efficiency and stability.6,7 There have been two strategies considered for the introduction of additional charge carrier molecules into light-emitting diode (LED) devices: physical blending or doping and chemical modification. The former has the parent problem of phase separation between different components. For chemists, it is their pursuit and challenge to molecularly design and synthesize light-emitting polymers containing hole- and/or electron-transporting groups by the latter method.

Small carbazole-containing molecules and polymers are known to be excellent hole-transporting materials because of the electron-donating capabilities associated with the nitrogen in the carbazole.8–11 Recently, some researchers reported the luminescent properties of polymers that had carbazole moieties in the main chain or as side pendants.11–15 In this study, we designed and synthesized a new N-phenylcarbazole-substituted PPV, poly[(2-(4-carbazol-9-yl-phenyl)-5-octyloxy-1,4-phenylenevinylene)-alt-(2-(2′-ethylhexyl-oxy)-5-methoxy-1,4-phenylenevinylene)] (Cz-PPV). The N-phenylcarbazole-functional group and the PPV main chain are expected to retain their respective hole-transporting and emitting properties simultaneously. In addition, the carbazole substituents are also anticipated to perform the functions of solubilization, aggregation suppression, and energy transfer.16 The structure of the polymer is depicted in Scheme 1. The synthesis and optical, electrochemical, and EL properties are presented here in detail.

**Scheme 1.** Synthetic route toward the monomer and the polymer.

![Scheme 1](image-url)
EXPERIMENTAL

Materials
2,5-Xylenol, carbazole, potassium tert-butoxide, triethyl phosphate, 2,2′-azobis(2-methylpropionitrile), pyridinium chlorochromate, n-butyllithium (1.6 M in hexane), tetrakis(triphenylphosphine) palladium, paraformaldehyde, and HBr (30 wt % in acetic acid) were purchased from Tokyo Kasei Co. and Kanto Chemical Co. and used without further purification. 2-Isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) were purchased from Aldrich Chemical Co. 2-Bromo-5-octyloxyterephthalaldehyde (I) was synthesized according to the Arbusov reaction of the corresponding azobis(2-methylpropionitrile) with hexane/dichloromethane (2/1) as an eluent to give a white solid (1.82 g, 32%).

9-(4-Bromophenyl)carbazole (1)
A mixture of carbazole (10 g, 60 mmol), dibromo-benzene (14.2 g, 60 mmol), CuI (1.14 g, 6 mmol), K2CO3 (16.6 g, 120 mmol), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (2 mL) was heated at 170 °C for 11 h under nitrogen. After cooling to room temperature, the mixture was filtered and washed with NH3·H2O and water. The grey solid was purified with column chromatography with hexane as an eluent (12.7 g, 66%).

mp: 146 °C. 1H NMR (CDCl3, 500 MHz, δ, ppm): 8.18 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.48–7.23 (m, 8H). 13C NMR (CDCl3, 125 MHz, δ, ppm): 140.7, 137.1, 133.1, 128.7, 126.1, 123.5, 121.0, 120.4, 120.2, 109.6. Electron-impact mass spectrometry (EIMS) m/e: 321 (M+), 323 [(M + 2)+], 321.02 (calcd.).

9-[4-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)phenyl]-9H-carbazole (2)
n-Butyllithium (10.6 mL, 17.0 mmol, 1.6 M in hexane) was added dropwise to 1 (5.0 g, 15.4 mmol) in dried tetrahydrofuran (THF; 154 mL, 0.1 M) at −78 °C and stirred for 15 min. A solution of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (10.6 g, 17.0 mmol, 1.1 equiv) in anhydrous THF (25 mL) was added slowly at −78 °C, and the reaction mixture was stirred for 2 h under this condition and then stirred overnight at room temperature. The solvent was evaporated, and the residue was dissolved in hexane/dichloromethane (2/1) and filtered. The crude product was purified by flash chromatography on the silica gel (deactivated with triethylamine) with hexane/dichloromethane (10/1) as an eluent to give a white solid (1.82 g, 32%).

mp: 181 °C. 1H NMR (CDCl3, 500 MHz, δ, ppm): 8.13 (d, J = 7.8 Hz, 2H), 8.04 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 2.0 Hz), 7.27 (t, J = 2.0 Hz), 1.40 (s, 12H). 13C NMR (CDCl3, 125 MHz, δ, ppm): 149.7, 141.0, 137.1, 135.5, 131.6, 130.9, 128.0, 127.1, 126.1, 123.6, 120.4, 120.3, 119.7, 69.3, 31.8, 29.3, 29.2, 29.0, 26.0, 22.6, 14.1. EIMS m/e: 503 (M+), 503.25 (calcd.). ELEM. ANAL. Calcd. for C24H24BNO2: C, 78.06%; H, 6.68%; N, 3.74%. Found: C, 77.78%; H, 6.53%; N, 3.74%.

4-[Carbazol-9-yl-4-octyloxy-biphenyl-2,5-dicarbaldehyde (4)]
To a dimethylformamide (10.0 mL) solution of 2 (0.333 g, 0.902 mmol), 3 (0.257 g, 0.752 mmol), and K2PO4 (0.24 g, 1.128 mmol) was added Pd(PPh3)4 (0.017 g, 0.015 mmol) at 60 °C under nitrogen. The mixture was stirred at 100 °C for 15 h and then extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated. The crude product was purified with a silica gel column with hexane/dichloromethane (4/1) as an eluent. Recrystallization from hexane gave monomer 4 (0.30 g, 79%).

mp: 150 °C. 1H NMR (CDCl3, 500 MHz, δ, ppm): 10.63 (s, 1H), 10.16 (s, 1H), 8.16 (d, J = 8.0 Hz, 2H), 8.04 (s, 1H), 7.70 (d, J = 8.25 Hz, 2H), 7.65 (s, 1H), 7.59 (d, J = 8.25 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 4.0 Hz, 7.31 (t, J = 2.0 Hz), 4.24 (t, J = 2.0 Hz), 1.92 (m, 2H), 1.56–1.25 (m, 10H), 0.90 (t, J = 3.0 Hz). 13C NMR (CDCl3, 125 MHz, δ, ppm): 191.5, 189.3, 160.5, 140.7, 138.3, 138.0, 132.5, 131.6, 130.9, 128.0, 127.1, 126.1, 123.6, 120.4, 120.3, 111.1, 109.7, 69.3, 31.8, 29.3, 29.2, 29.0, 26.0, 22.6, 14.1. EIMS m/e: 503 (M+), 503.25 (calcd.). ELEM. ANAL. Calcd. for C24H23BNO2: C, 81.08%; H, 6.60%; N, 2.78%. Found: C, 81.19%; H, 6.68%; N, 2.76%.

Cz-PPV
To a xylene (6.0 mL) solution of 4 (0.2518 g, 0.5 mmol) and 5 (0.2683 g, 0.5 mmol) was added
solid potassium tert-butoxide (0.168 g, 1.5 mmol) at 60 °C. The solution was stirred at 100 °C for 5 h under nitrogen. The reaction mixture was extracted with chloroform. The organic layer was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated. The polymer, dissolved in a minimum amount of chloroform, was precipitated into methanol to give a bright orange-red powder (0.26 g, 71%).

$^{13}$C NMR (CDCl$_3$, 125 MHz, δ, ppm): 156.6, 152.5, 151.2, 140.8, 131.7, 131.5, 130.8, 130.1, 126.9, 126.8, 126.7, 126.5, 126.1, 126.0, 125.9, 123.6, 123.5, 120.4, 120.2, 120.0, 109.7, 109.1, 68.7, 61.9, 56.2, 39.7, 31.8, 30.9, 30.7, 29.4, 29.2, 26.2, 24.3, 24.0, 23.1, 22.9, 16.4, 14.1, 11.2.

$^{1}H$ NMR (CDCl$_3$, 500 MHz, δ, ppm): 8.15–6.80 (m, 20H), 4.21–3.49 (m, 7H), 1.95–0.67 (m, 29H).

Crystal Data for 2
$C_{24}H_{24}BNO_{2}$, molecular weight ($M$) = 369.27, crystal dimensions: 0.20 × 0.20 × 0.20, colorless, monoclinic, space group P2/a, $a = 19.241(6)$ Å, $b = 9.010(7)$ Å, $c = 25.245(5)$ Å, $β = 104.65(2)°$, $V = 4234(3)$ Å$^3$, $Z = 8$, Dcalcd = 1.158 Mg/m$^3$.

For $R$ significant reflections [$I > 3 σ(I)$], $R_1 = 0.066$, and $ωR_2 = 0.158$. The number of measured reflections was 4857, and the goodness of fit on $F^2$ was 1.095.

Crystal Data for 4
$C_{33}H_{33}NO_{3}$, $M = 503.64$, crystal dimensions: 0.80 × 0.10 × 0.10, yellow, triclinic, space group P-1, $a = 9.33(2)$ Å, $b = 10.36(1)$ Å, $c = 14.13(2)$ Å, $α = 94.49(6)^°$, $β = 105.91(7)^°$, $γ = 92.28(6)^°$, $V = 1306(3)$ Å$^3$, $Z = 2$, Dcalcd = 1.280 Mg/m$^3$.

For $R$ significant reflections [$I > 2 σ(I)$], $R_1 = 0.048$, and $ωR_2 = 0.114$. The number of measured reflections was 5870, and the goodness of fit on $F^2$ was 0.468.

Light-Emitting Device Fabrication and Testing
The EL devices were fabricated on ITO substrates ultrasonicated sequentially in detergent, methanol, 2-propanol, and acetone and treated with O$_2$ plasma for 10 min under UV light before use. A hole-injecting layer, poly(3,4-ethylenedioxy-2,5-thiophene), was spin-coated at a spin rate of 1550 rpm from its water solution (1.3 wt %) onto the ITO substrates and annealed at 110 °C for 60 min in vacuo. The emissive layers were prepared via spin casting from the solution in chloroform (10 mg/mL, 2500 rpm) and then annealed at 80 °C for 60 min in vacuo. Before spin coating, the polymer solution was filtered with a 0.45-μm membrane filter. The metal electrodes Ca and Al were deposited onto the surface of the spin-coated polymer film by a thermal evaporation technique at 10$^{-6}$ Torr through a shadow mask. The typical active area of the LEDs was 5 mm$^2$. The EL spectra were measured on a Hamamatsu photonic multichannel analyzer. The current–voltage characteristics and luminance were measured with a
Keithley 2400 source meter and a Topcon BM-8, respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic routes of the monomers and the corresponding polymers are shown in Scheme 1. A bromo-substituted N-phenylcarbazole (1) was synthesized with a coupling reaction between carbazole and 1,4-dibromobenzene with the catalyst Pd₂(dba)₃. The pinacol borate ester (2) was prepared by the lithiation of 1 and then reacted with 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. The key monomer for the synthesis of the target polymer was the carbazole-containing 1,4-phenylenedialdehyde (4), which was prepared by Suzuki coupling of the carbazole-containing boronic ester (2) and 3.

The Wittig–Horner type polymerization of 4 and 5 was carried out in an m-xylene solution in the presence of potassium tert-butoxide at 110 °C. Cz-PPV was obtained as a bright orange-red powder in a greater than 71% yield. The polymer showed good solubility in common organic solvents, such as chloroform, toluene, and THF.

The molecular structures of the monomers and the corresponding polymers were identified by ¹H NMR, ¹³C NMR, and elemental analysis. The structures of the carbazole-containing boronic ester (2) and dialdehyde monomer (4) were further confirmed by single-crystal X-ray diffractions. The Oak Ridge thermal ellipsoid plot (ORTEP) diagrams of 2 and 4 are shown in Figure 1. Obviously, because of the steric effect caused by the large volume of the N-phenylcarbazole substituent, the intermolecular/intramolecular...
lar aggregation among PPV main chains was expected to be diminished.

The molecular weights were determined by GPC with polystyrene as the standard. The weight-average molecular weight and polydispersity of Cz-PPV were found to be 15,100 and 1.32. The thermal properties of the polymers were determined by thermogravimetric analysis measurements (heating at 10 °C/min in nitrogen). Thermogravimetric analysis showed a 5% weight loss at 420 °C. The glass-transition temperature could not be measured by differential scanning calorimetry (DSC).

Optical Properties

Figure 2 shows the UV–vis absorption and PL spectra of Cz-PPV in a CHCl₃ solution and in a thin film, respectively. Two absorption bands around 328 and 342 nm in the CHCl₃ solution can be attributed to the absorption of the carbazole segment;²⁰,²¹ the 455-nm peak in solution is associated with the absorption of the \( \pi-\pi^* \) transition derived from the conjugated PPV main chain. In the solid film, the carbazole moiety shows absorption characteristics similar to those in the solution. In contrast to the absorption in the solution, the absorption of the PPV main chain in the solid film (482 nm) shifts bathochromically because of the aggregation effect. Cz-PPV shows a PL emission maximum in the solution at 537 nm but in the solid film state at 586 nm (ca. 50-nm redshift). No emission from the carbazole segment was detected. This suggests the existence of energy transfer from the \( N \)-phenylecarbazole segment to the PPV main chain. Similar phenomena have been observed in molecular systems based on PPVs containing triarylamine groups in our study.¹⁶,¹⁷

Electrochemical Properties

The electrochemical behavior of the polymers was investigated by CV. The polymer films deposited on ITO glass were scanned both positively and negatively separately in a 0.10 M anhydrous acetonitrile solution of \( n \)-BuNBF₄ against Ag/AgCl calibrated with ferrocene (Fc/Fc⁺). As depicted in Figure 3, upon the anodic scan, Cz-PPV gives two electrochemical oxidation peaks, which indicate the existence of two oxidation procedures. The electrochemical behavior is quite similar to that of PPVs bearing triarylamine pendant in our recent report¹⁶ and other molecular systems, such as copolymers consisting of fluorene units and triphenylamine units.²²,²³ The first oxidation potential with a peak value around 1.24 V can be attributed to the \( p \)-doping of the carbazole segments.¹¹ The second oxidation peak with a peak value at 1.69 V is assigned to the PPV main chain. Upon the cathodic scan, an irreversible reduction peak with a peak potential at −1.77 V was observed, which corresponds to the reduction process of the PPV main chain. The oxidation peaks were not well separated, so it seems that the onset values corresponding to the oxidation potentials cannot be determined directly from the electrochemical diagram. It is concluded from the electrochemical properties of Cz-PPV that the hole injection in organic light-emitting diode
(OLED) is from ITO (−5.0 eV) to the highest occupied molecular orbital (HOMO) level of carbazole and then from carbazole to the HOMO level of the PPV backbone, which is more favorable than directly from ITO to that of PPV. This suggests that the hole-injection ability of the explored polymer was improved upon the incorporation of the carbazole group into PPV.

**EL Properties**

A concise sandwiched LED with the configuration of ITO/Cz-PPV/Ca/Al was initially fabricated. The purpose was to simplify the device structure and to emphasize the function of the carbazole moiety by a comparison of the EL performance with commercially available MEH-PPV. The thicknesses were about 100 nm for the polymer film, 20 nm for calcium, and 100 nm for aluminum. From the device, a bright yellow light was observed, and the EL spectra, which are independent of the different driving currents, are shown in Figure 4. The whole spectra appear broader than the PL spectrum in the film state. A similar phenomenon has been reported in the literature. The maximum emission wavelength is located at 609 nm with a red-shift of ~20 nm in comparison with the wavelength maximum in film PL emission. One possible reason is that the EL emission is composed of two segments. One emission is from the polymer Cz-PPV itself (~590 nm), and the other is from the electroplex emission between the carbazole moieties or between the carbazole and PPV main chain (peak above 600 nm). Figure 5(a) shows the typical current–luminance–voltage characteristics. The turn-on voltage is 5 V, and the brightness of the device increases with the current density. The maximum brightness is 1560 cd/m² at a bias of 11 V and a current density of 565 mA/cm². In our previous article, we described the EL performance of commercially available MEH-PPV. From a comparison of Cz-PPV, which is a characteristic hole-transporting carbazole-functionalized PPV, and MEH-PPV, it was found that the device of Cz-PPV gave a brightness of 1560 cd/m² at 11 V, which was much higher than that of the MEH-PPV device (250 cd/m² at 11 V). The efficiencies of the device based on Cz-PPV were 0.37 cd/A and 0.13 lm/W, respectively. A twofold enhancement was realized in comparison with the controlled MEH-PPV device. It was thus concluded that the introduction of the carbazole substitution on the PPV improved the EL performance. The result indicated the dual function of...
the polymer Cz-PPV for both hole injection/transport and light emission.

Double-layer LED devices with the configuration of ITO/poly(3,4-ethylenedioxy-2,5-thiophene): poly(styrenesulfonic acid) (PEDOT:PSS; 60 nm)/Cz-PPV (80 nm)/Ca/Al, were also examined. The device exhibited a pronounced enhancement in performance in comparison with the corresponding single-layer device. The turn-on voltage was as low as 3 V. The maximum brightness reached up to 6600 cd/m² at a bias of merely 8 V [see Fig. 5(b)]. The maximum current efficiency was 1.15 cd/A, and the maximum power efficiency was estimated to be 0.42 lm/W. The maximum external quantum efficiency was estimated to be 0.5% (see Fig. 6). The improved EL performance of the double-layer device in comparison with the single-layer device is probably attributable to the fact that PEDOT:PSS spin-coated on ITO could improve the surface quality and modify the interface between inorganic ITO and organic light-emitting materials.25,26

CONCLUSIONS

We synthesized and characterized, for the first time, a new PPV derivative with a directly attached N-phenylcarbazole moiety. The obtained polymer, Cz-PPV, showed good solubility, good film quality, and high thermal stability. On the basis of an electrochemical study, the oxidation peaks from the carbazole segment and PPV main chain were detected separately, and this indicated that the hole-injection ability of the polymer would be improved by the introduction of the carbazole-functional group. A single-layer light-emitting device made from Cz-PPV emitted bright yellow light with a maximum brightness of 1560 cd/m² at a bias of 11 V. The double-layer LED devices gave a low turn-on voltage at 3 V and a maximum brightness of 6600 cd/m² at a bias of 8 V. The experimental results demonstrated that the incorporation of hole-transporting functional groups into the PPVs was effective for enhancing the EL performance.

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REFERENCES AND NOTES