Articles

Facile Synthesis of Carbazole-Containing Semiladder Polyphenylenes for Pure-Blue Electroluminescence

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ABSTRACT: A type of soluble and thermally stable semiladder polyphenylenes containing carbazole moieties (SLPFCs) have been prepared with a facile and short synthetic route. The full characterizations of structures and properties as well as the performances of electroluminescence devices of the new polymers are presented. The conjugated backbone of the SLPFCs contained three kinds of constituents: fluorene, ladder-type tetraphenylene, and ladder-type hexaphenylene. The SLPFCs exhibit pure-blue fluorescence (λ_{max} = 445 nm) with high efficiency up to 90% in solution. Electrochemical studies indicate that the introduction of carbazole moieties raises the HOMO energy levels. Furthermore, the single-layer light-emitting devices using the SLPFCs as the active layer show pure-blue emission (λ_{max} = 447 nm, CIE coordinates: 0.15, 0.05) with maximum luminescence of 5500 cd/m^2 and maximum luminance efficiency of 0.556 cd/A. The attractive properties exhibited by the new semiladder polymers establish them as good candidates for active layers in stable pure-blue light-emitting devices.

Introduction

Conjugated polymers have attracted much attention because of their potential application to large-area flat-panel displays at low power consumption.[1] One of the most important goals of research on conjugated polymers is the obtaining of a stable blue emission,[2] which is particularly required for full-color displays. Much research into blue-emitting conjugated polymer materials has centered on phenylene-based polymers such as polyfluorenes (PF),[3] ladder-type polyphenylenes,[4] and semiladder polyphenylenes[5] because of their wide band gap, well-defined structures, high-luminescence quantum yield, and color tunability. In the past few decades, Grimsdale and Mullen developed a series of semiladder polyphenylenes with a structure intermediate between PF and ladder-type polyphenylenes. These semiladder polyphenylenes with the repeat units from indenofluorene to bridged pentaphenylene show the emission color from 430 to 460 nm, which red-shifts with increasing the rigidity of the polymer chains. Among them, the polymer of bridged pentaphenylene (Chart 1 a) can give the emission maximum of 445 nm that has the optimized pure-blue observable by the human eye.[5d]

However, polyfluorene derivatives often show a tailed emission band at long wavelengths in solid-state or light-emitting devices, leading to both color instability and reduced efficiency.[3] The source of this long wavelength emission was initially attributed to the formation of an excimer, owing to interchain interactions and $\pi-\pi$ stacking interactions between the planar-conjugated main chains,[3b,6] but more recently, it has been confirmed that the long-wavelength emission arises from ketone defects formed by oxidative electro- and photodegradation at the methine bridge when nonsubstituted or monosubstituted fluorene units are present in the polymer main chain.[7]

As an alternative, increasing interest has been paid to 2,7-substituted carbazole building blocks. In 2001, Leclerc reported the first syntheses of 2,7-carbazole-based conjugated polymers. After that, many studies have been devoted to the development of novel 2,7-carbazole-based homopolymers,[8,9] copolymers,[10] and oligomers[11] as potential active materials in electronic applications such as organic light-emitting diodes (OLEDs), field-effect transistors, and photovoltaic devices. 2,7-Substituted carbazoles contain a rigid biphenyl unit like fluorene that can lead to a large band gap with efficient blue emission and improves the hole-accepting and transporting properties. The nitrogen bridge is not oxidizable to a carbonyl like fluorene and facile substitution to improving the solubility and processability of polymers. Several conjugated ladder-type polyphenylenes containing carbazole moieties have been present recently (Chart 1b).[12] These polymers show blue-green or yellow-green emission and obviously aggregation behavior, leading to both color instability and reduced efficiency.[12b]

In this paper, we present a novel kind of semiladder poly(*p*-phenylene)s containing carbazole and fluorene moieties (SLPFCs) with a facile and short synthetic strategy. The conjugated backbone of the polymers contained three kinds of constituents: fluorene, ladder-

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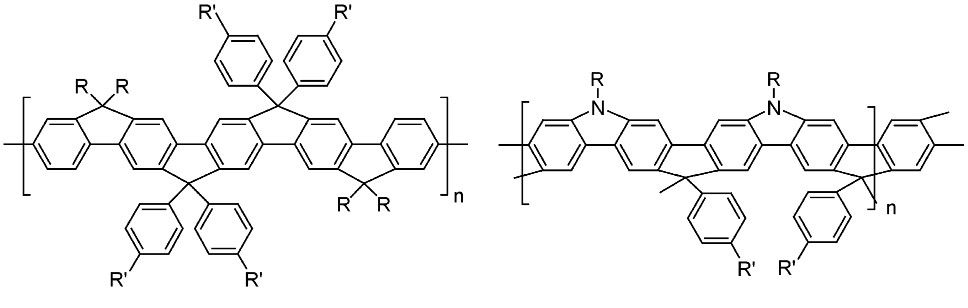
Chart 1



(a) Ladder poly-pantaphenylenes

(b) Ladder polycarbazole

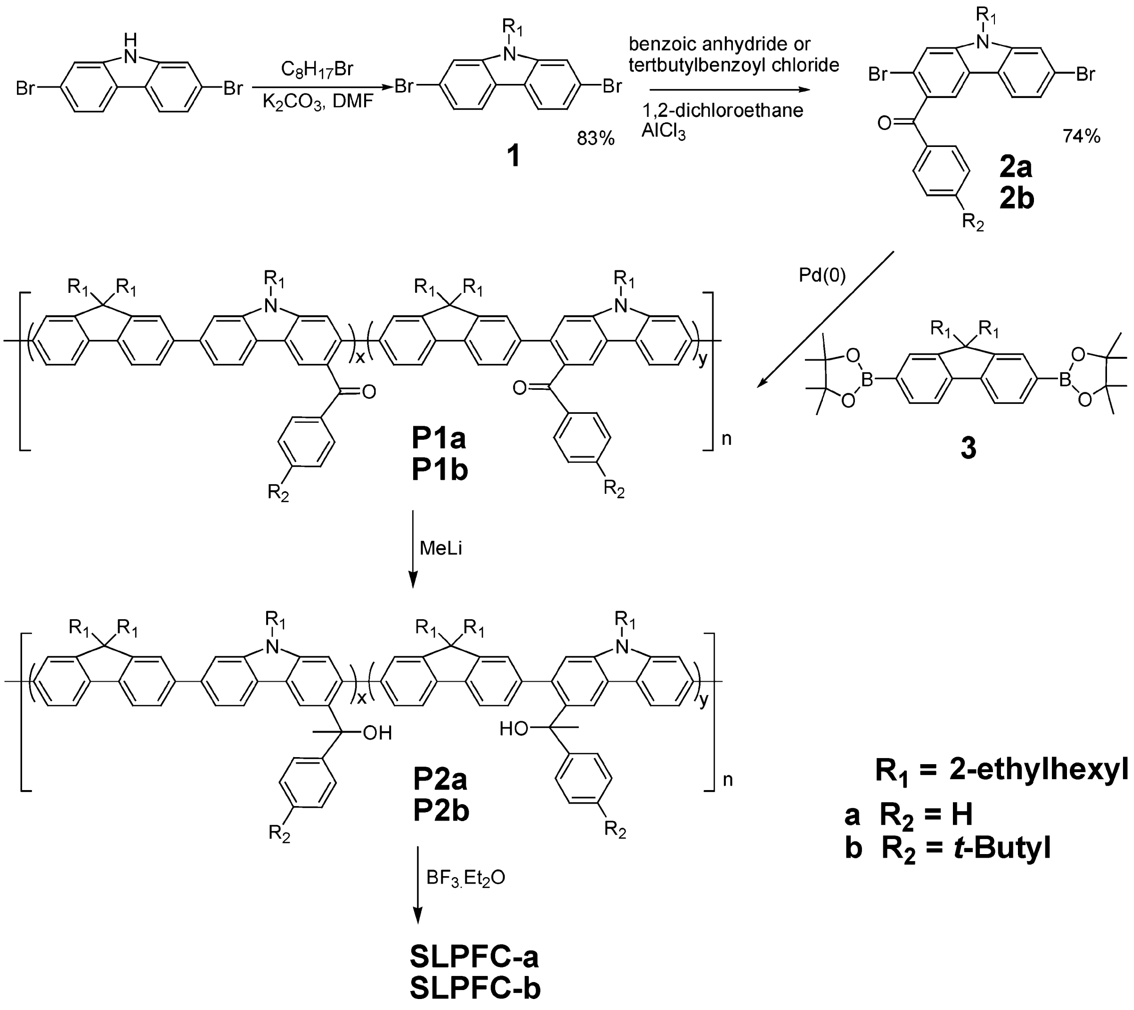
type tetraphenylene, and ladder-type hexaphenylene. The polymer backbone with such multiform constituents is expected to be useful for inhibiting the aggregation of planar-conjugated polymers such as the corresponding ladder polymers. The full characterizations of structures and properties as well as the performances of electroluminescence devices of the SLPFCs are presented. The attractive properties of this class of new semiladder polymers establish them as good candidates for active materials in stable pure-blue polymer light-emitting diodes and other polymer-based optical and electrooptical applications.

Results and Discussion

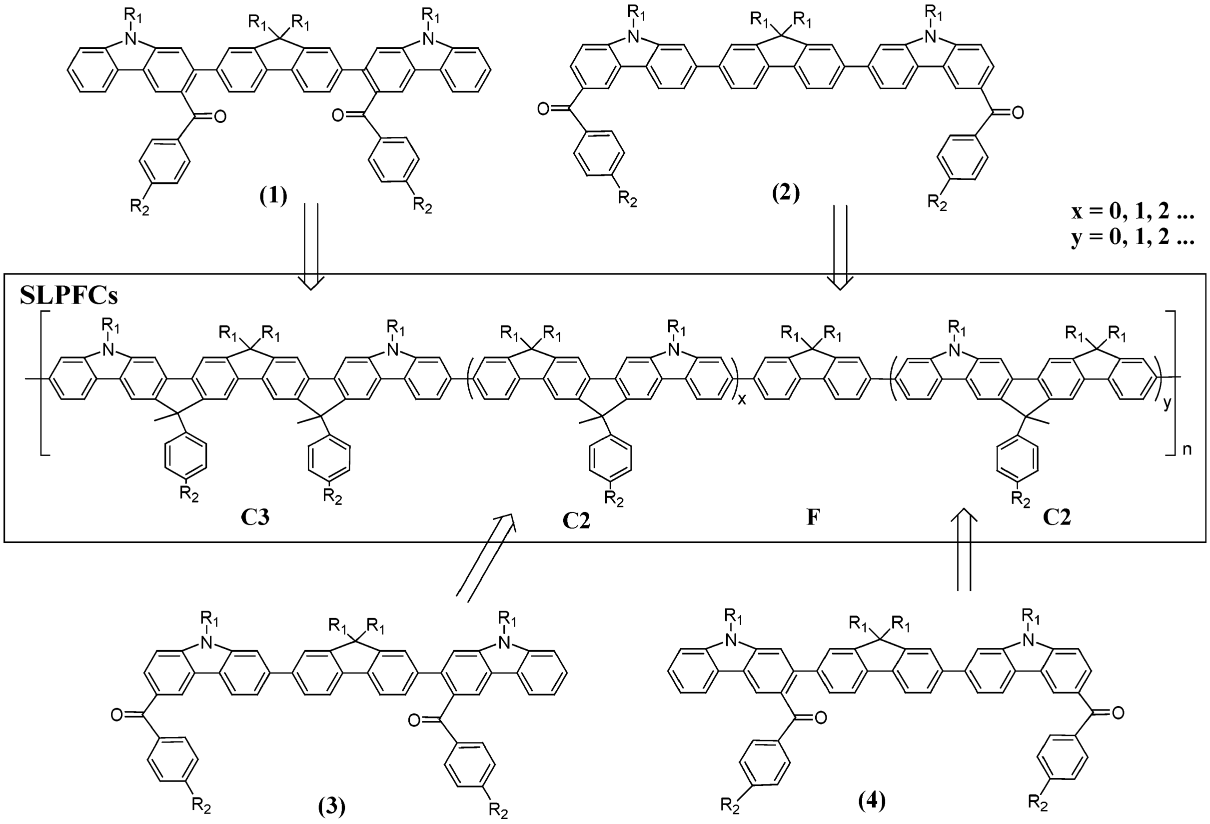
Synthesis and Characterization. The synthetic procedures used to prepare the monomers and polymers are outlined in Scheme 1. We prepared 2,7-dibromo-carbazole with an efficient route developed by Dierschke et al.[13] The N-alkylation of the 2,7-dibromo-carbazole in *N,N*-dimethylformamide (DMF) by K_2CO_3 and 2-ethylbromohexane leads to 2,7-dibromo-9-ethylhexylcarbazole (**1**) in 78% yield. Then, a Friedel−Crafts acylation of compound **1** with benzoic anhydride or 4-*tert*-butylbenzoyl chloride using an $AlCl_3$ catalyst in 1,2-dichloroethane gives monoacylation products **2a** and **2b** in good yields by a rigorous 1:1 feed rate. The copolymerized monomer 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(2-ethylhexyl)-fluorene (**3**) was prepared according to the literature.[14]

To prepare the novel carbazole-based semiladder polymers, we adapted the synthetic approach developed by Scherf.[4] The first step is a Pd^0-catalyzed Suzuki

Scheme 1. Synthesis of Semiladder Polymers (SLPFCs)



Scheme 2. Structure Analysis of Semiladder Polymers SLPFCs



cross-coupling for the synthesis of the precursor alternating copolymer **P1**. Then the precursor **P1** was transformed into the polyalcohol **P2** with methyllithium. The final semiladder polymers (SLPFCs) were obtained by the ring-closure reaction of **P2** with boron trifluoride etherate via a polymer-analogous intramolecular Friedel–Crafts alkylation. Immediately after the addition of boron trifluoride, a strong blue fluorescent solution is obtained, indicating the formation of the SLPFCs.

Polymer **SLPFC-a** is readily dissolved in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran (THF), and toluene, while the polymer **SLPFC-b** can only be readily dissolved in chloroform and partially dissolved in THF. The number-average molecular weights (M_n) and the weight-average molecular weights (M_w) of the polymers were measured by gel-permeation chromatography (GPC) using polystyrene as a standard. The M_n and M_w of **SLPFC-a** are estimated to be 7895 and 10339, respectively, corresponding to about 44 benzene rings in the backbone. The M_n of **SLPFC-b** is 6677, indicating that the *tert*-butyl group is useless for increasing the solubility and molecular weights of the polymer.

In the backbone of the precursor **P1**, the acyl groups randomly locate at the 3- or 6-position of carbazole moieties, and there are four kinds of different arrangement conformations as shown in Scheme 2. As a result, the polymer SLPFCs present a very complex structure with four kinds of constituents in the backbone after the ring-closure reaction of **P2**. Two of these constituents (**C2**) are mirror images of each other with the structure of ladder-type tetraphenylene. The other two constituents (**F** and **C3**) are fluorene and ladder-type hexaphenylenes, respectively. If the acyl groups in carbazole moieties are a totally random presence, the proportion of the four constituents of SLPFCs will be 25% each. Neither constituents **C3** nor **F** can continuously present with itself in the SLPFC's backbone because the fluorene and carbazole moieties have to be the adjoining moieties defined by the Suzuki polymerization reaction. The constituents **C2** can continuously present and occupy the half proportion of SLPFCs; as a result, the properties of final product SLPFCs will be analogous to that of the polymer of ladder-type tetraphenylenes (**C2**). Such an irregular conjugated backbone will inhibit the formation of aggregation like the corresponding ladder polymers.[4,12]

The structures of the polymers were characterized by NMR, FT-IR, and elemental analysis. ^{1}H NMR spectra of **P1** are consistent with the structure. But the well-resolved ^{1}H NMR spectra of SLPFCs were not obtainable because of the complex structure. FT-IR spectra can help us to confirm the complete reaction of the intramolecular ring closure. As shown in Figure 1, the keto group in 1660 cm^{-1} almost disappears when comparing the **SLPFC-a** with the precursor polymer **P1**, while the fluorenone defect or hydroxyl groups in 1716 cm^{-1} or 3420 cm^{-1} were not observed, indicating that the incomplete ring closure reaction or defects were not found in SLPFCs.

SLPFCs exhibit good thermal stability measured by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The polymers both have the onset degradation temperatures (T_d) above 370 °C (Figure 2). The phase transitions of the polymers were determined by differential scanning calorimetry (DSC) in a nitrogen atmosphere at a heating rate of 5 K/min, but we observed neither a glass transition process (T_g) nor other thermal processes (such as liquid-crystal phase) from 20 °C to 300 °C.

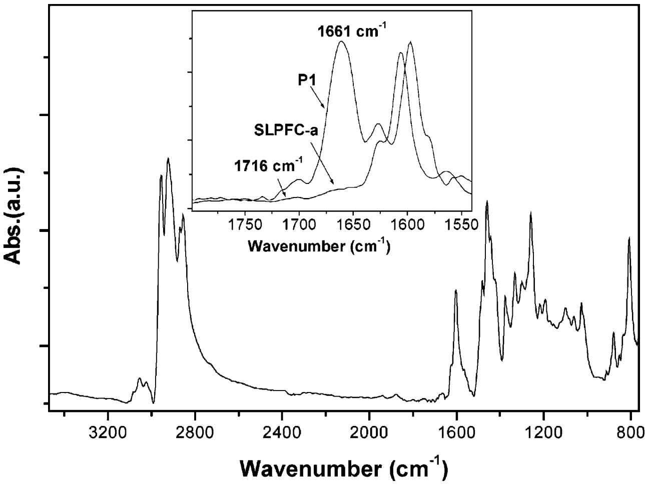


Figure 1. FT-IR spectra of **SLPFC-a**. Inset: the detailed spectra of **P1** and **SLPFC-a** in the region of 1800−1550 cm^{-1}.

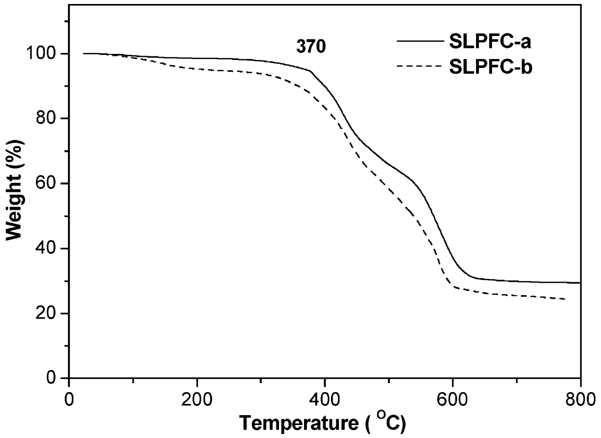


Figure 2. thermogravimetric analysis (TGA) of **SLPFC-a** and **SLPFC-b**.

Spectroscopic Properties. The UV−vis absorption and photoluminescence (PL) data of polymers are shown in Table 1, Figure 3, and Figure 4. The optical properties of the precursor **P1a** and the semiladder polymer **SLPFC-a** present enormous differences that can be attributed to the change in the conformation. The absorption of **P1a** in THF shows an unstructured broad peak centered at 365 nm, while **SLPFC-a** showed as distinctly shifted toward low energy. The shape and peak value of **P1a** in the PL spectrum is very similar to those of PF, but the PL quantum efficiency of **P1a** is very low.

According to expectation, the absorption spectra of SLPFCs in THF display broad absorption bands peaking around 382, 411, and 426 nm without the well-resolved vibrational energy bands, which generally appear in the spectra of the other semiladder or ladder-type polymers with the well-defined structure. At the same time, a steep absorption edge and a very small Stokes shift less than 17 nm is observed, which indicates that SLPFCs mostly remain the character of a rigid, planar, one-dimensional π-system.

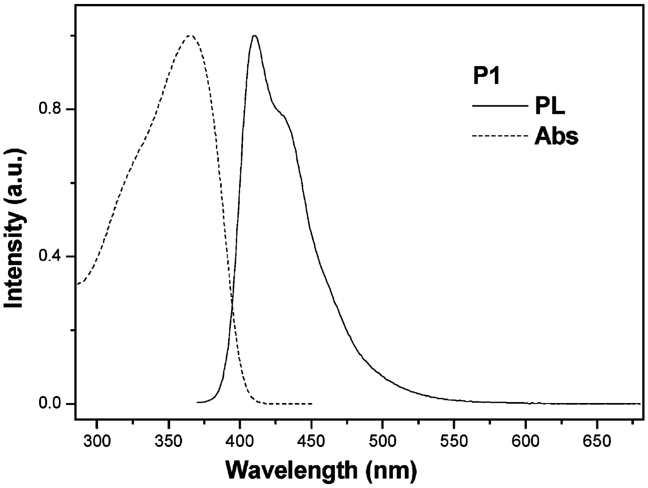


Figure 3. Absorption and emission spectra of polymer **P1** in THF.

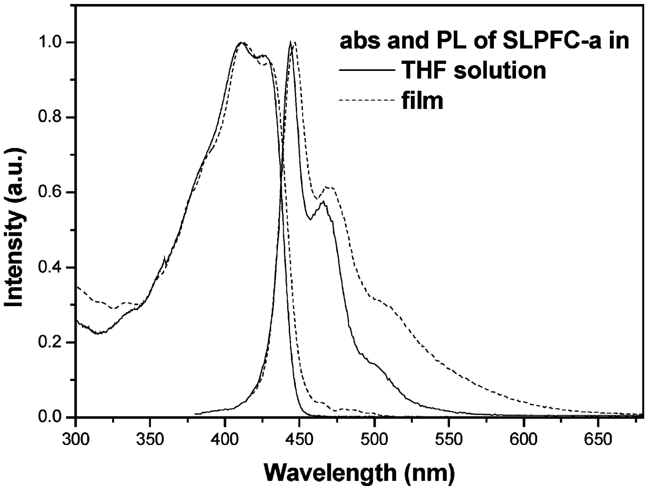


Figure 4. Absorption and emission spectra of polymer **SLPFC-a** in solution (THF) and film.

The PL spectrum of **SLPFC-a** in THF shows a pure-blue emission with a sharp peak centered at 443 nm and a shoulder peak at 465 nm. The position of the emission maximum is very close to that of ladder-type pantaphenylenes (445 nm) and lies between PIF (430 nm)[5b] and MeLPF (460 nm).[4c] The absorption and PL spectra of **SLPFC-a** in film are almost identical with those in solution, and no bathochromic shift is observed, which indicates that there is almost no change in the conformation of the SLPFCs' backbone from the solution to the solid state. The slight increase in relative intensity around 500-nm emissions in films may be ascribed to the stronger self-absorption effects than that in solution. Generally, the low-energy emission from the fluorenone defects around 550−570 nm was enhanced in the film compared to the corresponding solution because of the increased interchain energy transfer. However, in the PL spectra of **SLPFC-a** in solid film, no low-energy tailed peak is found. From

Table 1. Spectral Properties of Polymers

polymer	abs (in THF) λ_{max} (nm)	PL (in THF)[a] λ_{max} (nm)	PL of film[a] λ_{max} (nm)	PL efficiency in THF (Φ_{PL})[b]	EL λ_{max} (nm)
P1	365	410		< 2%	
SLPFC-a[c]	411 (426)	442 (466)	445 (470)	93%	447 (473)
SLPFC-b	410 (425)	442 (466)	445 (470)	89%	447 (473)

[a] Excited at 380 nm. [b] Calculated by relative method.[15] [c] Peaks that appear as shoulders or weak bands shown in parentheses.

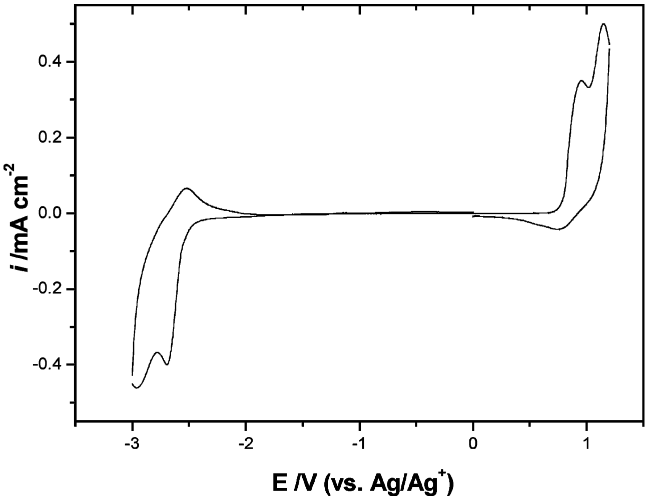


Figure 5. Cyclic voltammetry curves of the drop-cast films of **SLPFC-a** measured in 0.1 M Bu_4NBF_4 acetonitrile solution at a scan rate of 100 mV/s at room temperature (vs an Ag quasireference electrode).

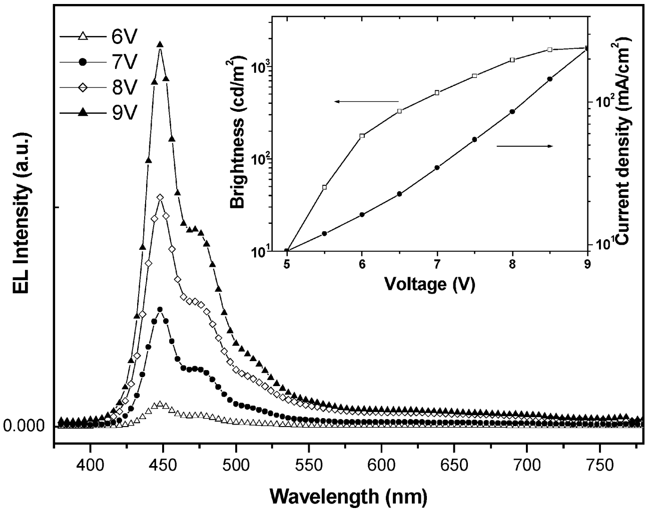


Figure 6. Electroluminescent spectra of **SLPFC-a** (ITO/PEDOT/**SLPFC-a**/Ba/Ag) at different voltages. Inset: Current−brightness−voltage characteristics of the device.

these results, no evidence indicates that there is any fluorenone defect or aggregation in the semiladder polymers.

The PL efficiency (Φ_{PL}) of the polymers in THF was measured and compared to quinine sulfate (2×10^{-5} M, assuming Φ_{PL} of 0.546 at 365 nm excitation in 1 N H_2SO_4)[15] as a standard. SLPFCs exhibited very high PL efficiencies in THF in the range of 89−93% (Table 1), corresponding to few routes existing for nonradiative deactivation.

Electrochemical Study. The electrochemical behavior and the electrochemical stability of these polymers was investigated by cyclic voltammetry (CV). The CV measurement on drop-cast polymer film was conducted in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate as an electrolyte at room temperature. The CV curves were referenced to an Ag quasireference electrode, which was calibrated using an internal standard, ferrocene/ferrocenium redox couple (0.35 V vs Ag/$AgNO_3$).

As shown in Figure 5, the **SLPFC-a** shows typical reversible p-doping patterns similar to those reported for the alternative copolymers of fluorene and 3,6-carbazole.[17] The onsets for reduction and oxidation occurred at 0.786 and −2.543 V, from which we estimate the lowest unoccupied and highest occupied molecular orbital (LUMO and HOMO) energy levels to be 2.06 and 5.39 eV (vs SCE), respectively, given an energy level of 4.6 eV for Ag/Ag$^+$. This corresponds to an electrochemical band gap of 3.3 eV. Compared with poly(9,9-dioctylfluorene) ($I_p = 5.7$ eV),[16] the **SLPFC-a** has the higher HOMO levels, so that efficient hole injection should occur from ITO anodes (work function 5.0 eV) or the PEDOT layer (5.2 eV). The high value of HOMO can be attributed to the electron-donating effect of the nitrogen atom in carbazole moieties.

Device Characteristics. The single-layer polymer light-emitting diodes (PLEDs) with the configuration of ITO/PEDOT:PSS/**SLPFC-a**/Ba/Ag were fabricated to investigate the electroluminescent properties of the SLPFCs. As shown in Figure 6, the EL spectra of **SLPFC-a** show pure-blue emission (CIE coordinates[18] 0.15, 0.05) with a peak wavelength around 447 nm and a shoulder around 472 nm, which are similar to the PL spectra of the corresponding polymer film. The shape of the spectra is very stable in different voltages, and no emission of the oxidative degradation of the polymers or the ketone defects around 540−570 nm are observed. The control of emissive layer thickness is important for the shape of EL spectra. The thicker emissive layer (more than 120 nm) will cause rather strong self-absorption, resulting in a blue-green emission.[19] The best devices with the emissive layer of ca. 70−80 nm were obtained by controlling the concentration of the solution and the speed of the spin coating. Figure 6 shows the current−brightness−voltage curves for the device of ITO/PEDOT:PSS/**SLPFC-a**/Ba/Ag. With the increase of forward-bias voltage, the current and brightness in the devices increase. Light emitting is observed with a turn-on voltage of 5.5 V and the maximum brightness over 5500 cd/m^2 in the best devices. The maximum luminance efficiency of 0.56 cd/A is achieved at a brightness of 830 cd/m^2. Further improvement in device efficiency and brightness can be obtained by adjusting the device structure and electrode metals with more efficient injection and balanced transport of both charge carriers.

Conclusion

We prepared a novel kind of semiladder poly(*p*-phenylene) containing carbazole moieties with a facile and short synthetic strategy. The backbone of the polymer contained three kinds of constituents: fluorene, ladder-type tetraphenylene, and ladder-type hexaphenylene. The polymer backbones with such multiform constituents inhibit the aggregation of planar-conjugated polymers. The high-efficiency pure-blue emission in photoluminescence spectra is observed from the polymer both in the solution and in the solid film. Electrochemical studies indicate that the introduction of carbazole moieties raises the HOMO energy levels. The single-layer light-emitting devices using the polymers as the active layer show stable pure-blue emission with maximum luminescence of 5500 cd/m^2 and maximum luminance efficiency of 0.556 cd/A. The attractive properties of this class of new semiladder polymers establish them as good candidates for active materials in stable pure-blue polymer light-emitting diodes and other polymer-based optical and electrooptical applications.

Experimental Section

Measurement. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCZ 500 MHz spectrometer with chloroform-*d* as solvent and tetramethylsilane (TMS) as the internal standard. FT-IR spectra were recorded on a Bruker IFS66V FT-IR spectrometer in the 800−4000 cm^{-1} region by casting the solution of polymers on a CaF_2 substrate. UV−vis and fluorescence spectra were obtained on a Shimadzu UV-3100 spectrophotometer and a Shimadzu RF-5301PC spectrophotometer, respectively. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer Thermal Analysis system under a heating rate of 20 K/min and a nitrogen flow rate of 80 mL/min. Differential scanning calorimetry (DSC) was also run on a Perkin-Elmer thermal analysis system. Elemental analysis was performed on a Flash EA 1112, CHNSO instrument. Number-average and weight-average molecular weights of polymer products were determined by gel-permeation chromatography (GPC) with a HPLC Waters 510 using a series of monodisperse polystyrene as standards in THF (HPLC grade) at 308 K. Cyclic voltammetry (CV) measurements were performed on a BAS100W with a three-electrode cell in a 0.1-M *n*-Bu_4NBF_4 solution in acetonitrile at a scan rate of 100 mV/s at room temperature under nitrogen. A silver wire (2-mm diameter) sealed in a soft glass rod, a platinum wire (0.5-mm diameter), and a platinum disk (1-mm diameter) were used as the quasireference electrode, counter electrode, and working electrode, respectively. The Ag quasireference electrode was calibrated using a ferrocene/ferrocenium redox couple as an external standard prior to measurements.

LED Device Fabrication and Characterization. PLED devices were fabricated on glass substrates coated with ITO. The substrate was cleaned by a general procedure, which included sonication in detergent followed by repeated rinsing in deionized water, acetone, and ethanol, and, prior to use, placed in boiling H_2O_2 for 5 min. A conducting polymer dispersion of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS) was obtained from Bayer Corp. The hole injection layer of PEDOT: PSS was prepared from a water dispersion with the thickness of 50 nm and baked at 170 °C for 20 min under N_2 atmosphere. The emitting layer of the polymer was spin coated from an oxygen-free toluene solution onto the hole injection layer with a thickness of 100 nm. Finally, a Ba and Ag cathode was vacuum deposited onto the polymer layers at a pressure below 5×10^{-6} Torr. The emitting areas of the EL devices were 2×2 mm^2. EL spectra of the devices were measured by a PR650 fluorescence spectrophotometer. Luminance−current density−voltage ($L-I-V$) curves were recorded with a Keithley 2400 instrument. All measurements were carried out at room temperature under ambient conditions.

Materials. Tetrahydrofuran (THF) for spectral study was distilled over sodium/benzophenone, and toluene was distilled over P_2O_5. Other solvents were used as commercial p.a. quality. 2,7-Dibromo-9H-carbazole was prepared according to literature procedures. All other chemicals were purchased from Aldrich and Acros and used without any further purification.

Synthesis. 2,7-Dibromo-*N*-(2-ethylhexyl)carbazole (1). To a solution of 2,7-dibromo-carbazole (2.0 g, 6.15 mmol) in 20 mL of DMF was added anhydrous K_2CO_3 (1.8 g, 13.0 mmol). The solution was stirred at 80 °C for 2 h under N_2, and then 2-ethylhexybromide (2.3 g, 12.0 mmol) was added. The mixture was stirred at 80 °C for 24 h and then quenched with 30 mL water. The aqueous layer was extracted with diethyl ether three times. The organic fractions were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, 10% $CHCl_3$ in cyclohexane) to give 2.01 g of **1** as a white crystal; mp 99−100 °C (Yield: 78%). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.90 (d, 2H, $J = 9$ Hz), 7.51 (s, 2H), 7.35 (d, 2H, $J = 9$ Hz), 4.09 (m, 2H), 2.03 (m, 1H), 1.38−1.28 (m, 8H), 0.94−0.86 (m, 6H).

3-Benzoyl-2,7-dibromo-*N*-(2-ethylhexyl)carbazole (2a). To a mixture of compound **2** (200 mg, 0.458 mmol) and $AlCl_3$ (150 mg, 1.13 mmol) in 1,2-dichloroethane (3 mL) was added benzoic anhydride (104 g, 0.46 mmol) slowly at 0 °C. The mixture was stirred for 8 h at room temperature and then quenched with ice. The inorganic precipitate was dissolved in 2 M HCl, and the product was extracted with CH_2Cl_2. The organic fractions and the solvent were dried under reduced pressure. The product was purified by column chromatography (silica gel, 2% EtOAc in petroleum ether) to give 181 mg of **2a** as a white crystal; mp 95−96 °C (Yield: 73%). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.06 (s, 1H), 7.87 (m, 3H), 7.64 (s, 1H), 7.61 (t, 1H, $J = 7.5$ Hz), 7.55 (s, 1H), 7.48 (t, 2H, $J = 7.5$ Hz), 7.37 (d, 1H, $J = 8.5$ Hz), 4.13 (m, 2H), 2.06 (m, 1H), 1.43−1.27 (br m, 8H), 0.95 (t, 3H, $J = 7.5$ Hz), 0.90 (t, 3H, $J = 7.0$ Hz).

3-(4-*tert*-Butyl-benzoyl)-2,7-dibromo-*N*-(2-ethylhexyl)-carbazole (2b). The procedure was the same as that performed on **3a**. The product was isolated as a white crystal; mp 120−122 °C. (Yield: 70%). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.04 (s, 1H), 7.86 (d, 1H, $J = 8.5$ Hz), 7.82 (d, 2H, $J = 8.5$ Hz), 7.64 (s, 1H), 7.55 (d, 1H, $J = 1.5$ Hz), 7.49 (d, 2H, $J = 8.5$ Hz), 7.36 (dd, 1H, $J = 8.5$ Hz and $J = 1.5$ Hz), 4.13 (m, 2H), 2.06 (m, 1H), 1.40−1.28 (br m, 17H), 0.95 (t, 3H, $J = 7.5$ Hz), 0.90 (t, 3H, $J = 7.0$ Hz).

Polymer P1a. A mixture of **2a** (111.0 mg, 0.205 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)-9,9-bis(2-ethylhexyl)fluorene (131.9 mg, 0.205 mmol), tetrakis(triphenylphosphino)-palladium(0) (8 mg), 3 mL of toluene, 1 mL of 1-butanol and 1 mL of aqueous K_2CO_3 (2 M) was refluxed for 48 h under nitrogen. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine and water, then dried over $MgSO_4$ and concentrated, then the polymer was precipitated into methanol, and the crude product was dissolved in dichloromethane and reprecipitated into methanol to give **P1a** of 102.0 mg as a yellow-green solid (Yield: 65%). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.23−8.03 (m, 2H), 7.89−7.29 (br m, 14H), 4.31 (d, 2H), 2.25−1.80 (br m, 5H), 1.50−1.27 (br m, 8H), 1.03−0.45 (br m, 36H). M_n 7121, M_w 8693, M_w/M_n 1.13 (GPC, PS calibration).

Polymer P1b. Yellow-green solid (Yield: 67%). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.31−8.02 (m, 2H), 7.89−7.36 (br m, 13H), 4.31(d, 2H), 2.24−1.79 (br m, 5H), 1.46−1.30 (br m, 17H), 1.01−0.48 (br m, 36H). M_n 6602, M_w 7527, M_w/M_n 1.24 (GPC, PS calibration).

Polymer P2a (Polymer P2b). A solution of polymer **P1a** (**P1b**) (100 mg) in 40 mL of toluene was treated with a solution of 1.6 M methyllithium in diethyl ether (1 mL, 1.6 mmol). The mixture was stirred for 30 min at room temperature and carefully quenched with ethanol, water, and dilute hydrochloric acid. The organic layer was washed with water and dried with $MgSO_4$, and the solvent was removed under reduced pressure to give light-yellow solid (Yield: 90.2−92.1%).

Polymer SLPFC-a. A solution of polymer **P2a** (100 mg) in 20 mL of methylene chloride was treated with boron trifluoride etherate (300 mg, 2.11 mmol). After stirring for 5 min at room temperature, 10 mL of ethanol was added to the mixture to destroy the catalyst. The organic layer was then carefully washed with water, dried, and concentrated. Precipitation in methanol gave 89.0 mg **SLPFC-a** as a yellow-green powder (Yield: 89.2%). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.09−7.16 (br m), 4.33(d, 2H), 2.24−2.02 (br m, 8H), 1.53−0.56 (br m). $(C_{57}H_{69}N)_n$: Calcd C 89.12, H 9.05, N 1.82; Found C 86.82, H 9.05, N 1.37. FTIR(KBr): 2923, 2855, 1599, 1456, 1372, 1332, 1257, 1190, 1024, 877, 809, 695. M_n 7895, M_w 10339, M_w/M_n 1.310 (GPC, PS calibration).

Polymer SLPFC-b. Precipitation in methanol gave **SLPFC-b** as a yellow-green powder (Yield: 86%). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.13−7.24 (br m), 4.33 (d, 2H), 2.25−2.02 (br m, 8H), 1.53−0.56 (br m). $(C_{61}H_{77}N)_n$: Calcd C 88.88, H 9.42, N 1.70; Found C 85.96, H 9.66, N 1.33. FTIR(KBr): 2925, 2860, 1604, 1458, 1376, 1333, 1257, 1193, 1014, 879, 807, 577. M_n 6677, M_w 7920, M_w/M_n 1.186 (GPC, PS calibration).

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Supporting Information Available: ^{1}H NMR spectra of all the new compounds synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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