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New light-emitting hyperbranched polymers prepared from tribromoaryls and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate)

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Abstract

Three new hyperbranched polymers (**P1–P3**) were prepared by copolymerization of tribromoaryl moieties (triphenylamine, carbazole and fluorene moieties) with 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) from "$A_2 + B_3$" approach based on Suzuki polycondensation reaction. They are soluble in common organic solvents, and exhibit good thermal stable luminescence. Interestingly, unlike most of fluorene-containing polymeric materials, **P3** emits strong green light due to its special structure. Double-layer devices with configurations ITO/PEDOT/Polymer (50 nm)/TPBI(50 nm)/LiF(0.5 nm)/Al(80 nm) were fabricated and emitted blue or green light, with maximum luminance in the range of 25–142 cd/m^2 and the current efficiency up to 0.18 cd/A.

Keywords: Fluorene; Hyperbranched polymers; Luminescence

1. Introduction

In the past decade, considerable interests have been shown in the development of light-emitting diodes (LEDs) based on conjugated polymers due to their wide-ranging applications [1–5]. And many studies were focused on exploring efficient, stable and pure blue light-emitting polymers, which still remain a challenge [6] though red (orange) and green PLEDs have sufficient efficiencies and lifetimes to be of commercial value. Among the different kinds of blue light-emitting polymers, polyfluorene derivatives (PFs) are considered as very promising blue light-emitting materials for their excellent chemical and thermal stabilities besides exceptionally high efficiencies both in photoluminescence (PL) and in electroluminescence (EL) not achieved by other polymers [7–11]. However, PFs are likely to form excimers or ketonic defect sites in solid states during either annealing or passage of current, directly leading to blue–green emission and fluorescence quenching, hence inhibiting their prospective utilization. Many attempts were used to solve the problems, including the introduction of longer or bulky side groups, the copolymerization with suitable comonomers, introducing cross-linking moieties, or adjusting the structure by linking sterically end groups [12–20]. And most of these PFs are linear conjugated polymers. Recently, PF backbones were even encapsulated into dendritic or hyperbranched polymers [21–24]. The highly branched and globular features help to depress the possible aggregation and excimer formation, enhance the thermal stability and improve the light-emitting efficiency, also make the materials forming good quality amorphous films. However, in comparison with the large number of light-emitting dendrimers, the light-emitting hyperbranched polymers are still scarce though hyperbranched polymers demonstrate many advantages, and generally there are branched units between the PF backbone or fluorene moieties as reported in the literatures.

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In this paper, the concept of our work is to prepare hyperbranched light-emitting polymers (**P1**–**P3**) by copolymerization of tribromoaryl moieties with 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) from "$A_2 + B_3$" approach based on Suzuki polycondensation reaction. Totally, three tribromoaryl moieties containing triphenylamine, carbazole and fluorene groups were used. **P1** and **P2** emit strong blue light upon excitation; interestingly, **P3** exhibits green luminescence, not like other PF derivatives with blue emissions. And the structural characterization indicated that **P3** was constructed only by fluorene moieties without bulky groups between each two fluorene groups. Herein, we would like to present the syntheses, structural characterization, thermal stabilities and the optical properties of the polymers in detail. Also, double-layer LEDs using these polymers as emissive layers demonstrate bright EL, making them potential candidates for practical applications.

2. Experimental section

2.1. Materials

Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. 3,6-Dibromocarbazole (**1**) and tris(4-bromophenyl)amine (**7**) were synthesized according to the literature method [28,29]. 9-Hydroxymethylfluorene (**4**) was bought from Acros. 9,9-Dihexylfluorene-2,7-bis(trimethyleneborate) (**8**) was purchased from Aldrich. All other reagents were used as received.

2.2. Instrumentation

^{1}H, ^{13}C NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer-2 spectrometer in the region of 3000–400 cm^{-1} on KBr pellets. UV–visible spectra were obtained using a Shimadzu UV-2550 spectrometer. FAB-MS spectra were recorded with a VJ-ZAB-3F-Mass spectrometer. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent and the flow rate was 1.0 mL/min. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 20 °C/min in nitrogen at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSC822e under nitrogen at a scanning rate of 10 °C/min. The thermometer for measurement of the melting point was uncorrected. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

2.3. Synthesis of **2** [30]

3,6-Dibromocarbazole (**1**) (0.97 g, 3.0 mmol) was dissolved in DMF (8 ml) and then powdered potassium hydroxide (1.77 g, 31.6 mmol) was added. After the mixture was stirred for 1 h, 2-chloroethanol (0.48 g, 6.0 mmol) was added slowly. After stirring for 24 h at room temperature, the mixture was poured into ice water (200 mL), then filtered and washed with water. The crude product was purified by recrystallization from ethanol/water to afford white powder. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.05 (t, $J = 4.8$ Hz, 2H, $-N-CH_2-$), 4.44 (t, $J = 4.8$ Hz, 2H, $-O-CH_2-$), 7.35 (d, $J = 9.0$ Hz, 2H, ArH), 7.43 (d, $J = 8.7$ Hz, 2H, ArH), 8.15 (s, 2H, ArH).

2.4. Synthesis of **3**

Compound **2** (0.50 g, 1.36 mmol), 4-(*N*,*N*-dimethyl)aminopyridine (10 mg), 4-bromo-benzoic acid (0.54 g, 2.70 mmol), and dicyclohexylcarbodiimine (0.42 g, 2.00 mmol) were dissolved in proper dry THF and stirred at room temperature for 48 h. The precipitate was filtered. After removal of the solvent, the resulting solid was washed with 0.5 M hydrochloride acid, a diluted aqueous solution of sodium bicarbonate and water. The crude product was purified by column chromatography on silica gel using chloroform/hexane (1:1) as eluent to afford white powder **3** (0.61 g, 80.6%). Mp = 196 °C. IR (thin film), ν (cm^{-1}): 1723 cm^{-1} (C=O), 1587 cm^{-1} (–C=C–). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.68 (br, d, 4H, $-CH_2CH_2-$), 7.34 (d, $J = 8.7$ Hz, 2H, ArH), 7.59 (m, 6H, ArH), 8.15 (s, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 42.2, 62.7, 110.5, 112.9, 123.7, 124.0, 128.4, 128.8, 129.5, 131.3, 132.0, 139.6, 165.8. MS (FAB), *m/z* [M$^+$]: 551.7, calcd: 550.9. $C_{21}H_{14}Br_3NO_2$ (EA) (%, found/calcd): C, 45.04/45.69; H, 2.52/2.56; N, 2.53/2.54.

2.5. Synthesis of **5**

The synthetic procedure was similar as that of **3** [**4** (0.98 g, 5.00 mmol), 4-bromo-benzoic acid (2.00 g, 10.00 mmol)]. White powder **5** was purified by column chromatography on silica gel using chloroform/hexane (1:1) as eluent (1.30 g, 68.6%). Mp = 101 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.38 (t, $J = 7.2$ Hz, 1H, $-CH-$), 4.63 (d, $J = 7.2$ Hz, 2H, $-CH_2-$), 7.33 (t, 2H, ArH), 7.43 (t, 2H, ArH), 7.63 (d, 4H, ArH), 7.81 (d, $J = 7.8$ Hz, 2H, ArH), 7.93 (d, $J = 8.4$ Hz, 2H, ArH).

2.6. Synthesis of **6**

To a solution of **5** (0.76 g, 2.00 mol) in $CHCl_3$ (10 ml) at 0 °C were added little ferric chloride and 0.23 ml (4.38 mmol) of bromine. The reaction proceeded in the dark for 12 h at room temperature. The resultant mixture was then poured into water and washed with sodium thiosulfate until the red color disappeared. The aqueous layer was extracted with chloroform. The combined organic layer was dried over magnesium sulfate overnight. After removal of the solvent, the crude product was purified by recrystallization from ethyl acetate to afford white powder (0.80 g, 74.5%). Mp = 185 °C. IR (thin film), ν (cm^{-1}): 1723 cm^{-1} (C=O), 1591 cm^{-1} (–C=C–). ^{1}H NMR (CDCl$_3$) δ (ppm): 4.35 (t, $J = 7.2$ Hz, 1H, –CH–), 4.60 (d, $J = 6.6$ Hz, 2H, –CH$_2$–), 7.58 (m, 6H, ArH), 7.74 (s, 2H, ArH), 7.90 (d, $J = 8.7$ Hz, 2H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 47.0, 66.5, 121.6, 121.7, 128.7, 131.3, 131.5, 132.2, 136.6, 145.5, 165.8. MS (FAB), *m/z* [M$^+$]: 536.6, calcd: 535.8. $C_{21}H_{13}Br_3O_2$ (EA) (%, found/calcd): C, 46.94/46.97; H, 2.44/2.46.

2.7. General procedure for synthesis of *P1–P3*

A mixture of compound **7**, **3** or **6** (1.00 equiv), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) **8** (Aldrich) (1.5 equiv), sodium carbonate (10.0 equiv), THF (monomer concentration is about 0.025 M)/water (3:1 in volume), and Pd(PPh$_3$)$_4$ (6 mol%) was carefully degassed and charged with nitrogen. Then the reaction mixture was stirred at 60 °C, and was stopped in a proper time. A lot of methanol was poured into the mixture and then filtered. The obtained solid was dissolved in THF and the insoluble solid was filtered out. After removal of the solvent, the residue was further purified by several precipitations from THF into methanol, and dried under vacuum overnight.

Compound **P1**: A mixture of compounds **7** (151.1 mg, 0.31 mmol) and **8** (240.2 mg, 0.47 mmol) was reacted, the reaction was stopped after 28 min. **P1** was obtained as a yellow solid (0.18 g, 71.1%). $M_w = 3454$, $M_w/M_n = 1.48$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 2800–3000 cm^{-1} (–C–H), 1598 cm^{-1} (–C=C–). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.6–1.0 (–CH$_3$), 1.0–1.2 (–CH$_2$–), 1.9–2.2 (–C–CH$_2$–), 7.0 (ArH), 7.1–7.2 (ArH), 7.3–7.4 (ArH), 7.5–7.8 (ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 14.0, 22.6, 23.8, 29.7, 31.5, 40.5, 55.3, 115.7, 120.0, 121.0, 121.5, 124.6, 125.5, 126.1, 128.0, 132.4, 136.5, 139.3, 140.0, 140.5, 146.4, 146.7, 151.7, 152.0.

Compound **P2**: A mixture of compounds **3** (165.5 mg, 0.30 mmol) and **8** (225.9 mg, 0.45 mmol) was reacted, the reaction was stopped after 30 min. **P2** was obtained as a gray solid (0.17 g, 65.4%). $M_w = 3770$, $M_w/M_n = 1.39$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 2800–3000 cm^{-1} (–C–H), 1721 cm^{-1} (C=O), 1605 cm^{-1} (–C=C–). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.6–1.0 (–CH$_3$), 1.0–1.2 (–CH$_2$–), 1.9–2.2 (–C–CH$_2$–), 4.6–4.9 (–N–CH$_2$–CH$_2$–), 7.3–7.4 (ArH), 7.5–8.0 (ArH), 8.1–8.2 (ArH), 8.3 (ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 14.2, 22.8, 24.0, 29.9, 31.7, 40.6, 42.4, 55.7, 62.8, 109.2, 110.4, 110.7, 112.8, 119.4, 120.1, 120.6, 121.8, 123.7, 124.0, 126.6, 127.3, 128.1, 128.7, 129.5, 130.5, 139.5, 139.7, 141.0, 146.6, 152.2, 166.7.

Compound **P3**: A mixture of compounds **6** (161.1 mg, 0.30 mmol) and **8** (225.9 mg, 0.45 mmol) was reacted, the reaction was stopped after 312 min. **P3** was obtained as a green solid (0.08 g, 31.3%). $M_w = 4300$, $M_w/M_n = 1.69$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 2800–3000 cm^{-1} (–C–H), 1721 cm^{-1} (C=O), 1610 cm^{-1} (–C=C–). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.6–1.0 (–CH$_3$), 1.0–1.4 (–CH$_2$–), 1.9–2.2 (–C–CH$_2$–), 5.0 (ArH), 6.2–6.4 (–C=CH$_2$–), 6.8–6.9 (ArH), 7.0 (ArH), 7.5–7.9 (ArH), 7.9–8.1 (ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 13.0, 21.6, 22.8, 23.4, 27.0, 27.9, 28.4, 28.7, 29.3, 30.5, 32.9, 33.2, 39.5, 54.4, 109.2, 118.9, 119.1, 120.4, 121.7, 123.4, 124.5, 125.1, 126.1, 127.1, 134.8, 138.0, 139.2, 139.8, 142.2, 143.0, 145.4, 150.8.

2.8. Synthesis of *9*

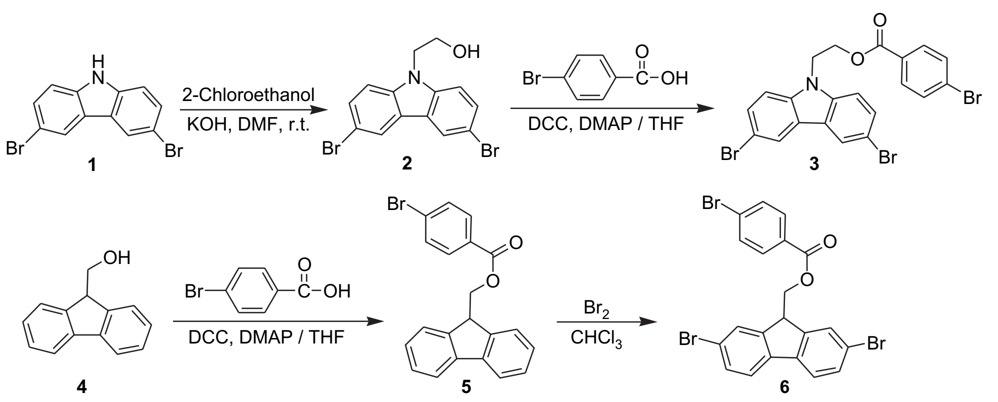
A mixture of compound **6** (0.10 g, 0.19 mmol), sodium carbonate (0.20 g, 1.90 mmol), THF (12 ml), and water (4 ml) was degassed and charged with nitrogen. Then the reaction mixture was stirred at 60 °C for 312 min, then cooled and extracted with CHCl$_3$. The combined organic layer was dried over magnesium sulfate overnight. After removal of the solvent, the crude product was washed with hexane, and filtered to afford white powder (39.8 mg, 62.9%). ^{1}H NMR (CDCl$_3$) δ (ppm): 6.10 (s, 2H, –C=CH$_2$–), 7.26–7.54 (m, 4H, ArH), 7.83 (s, 2H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 109.4, 120.1, 120.3, 123.4, 130.7, 137.0, 138.5, 140.4. MS (FAB), *m/z* [M$^+$]: 336.0, calcd: 335.9 (100%).

2.9. Synthesis of *P4*

A mixture of compound **9** (28.8 mg, 0.086 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (**8**) (Aldrich) (43.0 mg, 0.086 mmol), sodium carbonate (91.1 mg, 0.86 mmol), THF (monomer concentration is about 0.025 M)/water (5.1:1.7 ml in volume), and Pd(PPh$_3$)$_4$ (6 mol%) was carefully degassed and charged with nitrogen. Then the reaction mixture was stirred for 12 h at 60 °C. A lot of methanol was poured into the mixture and then filtered. The obtained solid was dissolved in THF and the insoluble solid was filtered out. After removal of the solvent, the residue was further purified by precipitation from THF into methanol, and dried under vacuum overnight. **P4** was obtained as a green solid (24.0 mg, 55.0%). $M_w = 5132$, $M_w/M_n = 2.88$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 2800–3000 cm^{-1} (–C–H), 1610 cm^{-1} (–C=C–). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.6–0.9 (–CH$_3$), 1.0–1.4 (–CH$_2$–), 1.8–2.0 (–C–CH$_2$–), 2.3 (–C–CH$_2$–), 5.0 (ArH), 6.2–6.4 (–C=CH$_2$–), 7.0 (ArH), 7.5–7.9 (ArH), 7.9–8.1 (ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 13.0, 21.6, 22.8, 28.7, 29.3, 30.5, 33.2, 39.5, 54.4, 107.1, 118.8, 119.1, 120.5, 123.9, 124.5, 125.1, 127.1, 134.8, 138.0, 139.3, 142.5, 150.8.

2.10. Synthesis of *P5*

The synthetic procedure was similar as that of **P4** but without **8** present [compound **9** (8.0 mg) was used only]. The reaction was stopped after 300 min. **P5** was obtained as a white solid (7 mg, 87.5%). $M_w = 1074$, $M_w/M_n = 1.37$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 2800–3000 cm^{-1} (–C–H), 1609 cm^{-1} (–C=C–). ^{1}H NMR (CDCl$_3$) δ (ppm): 2.3 (–C–CH$_2$–), 5.0 (ArH), 7.0 (ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 16.7, 29.7, 120.0, 123.7, 131.2, 147.0.



Scheme 1.

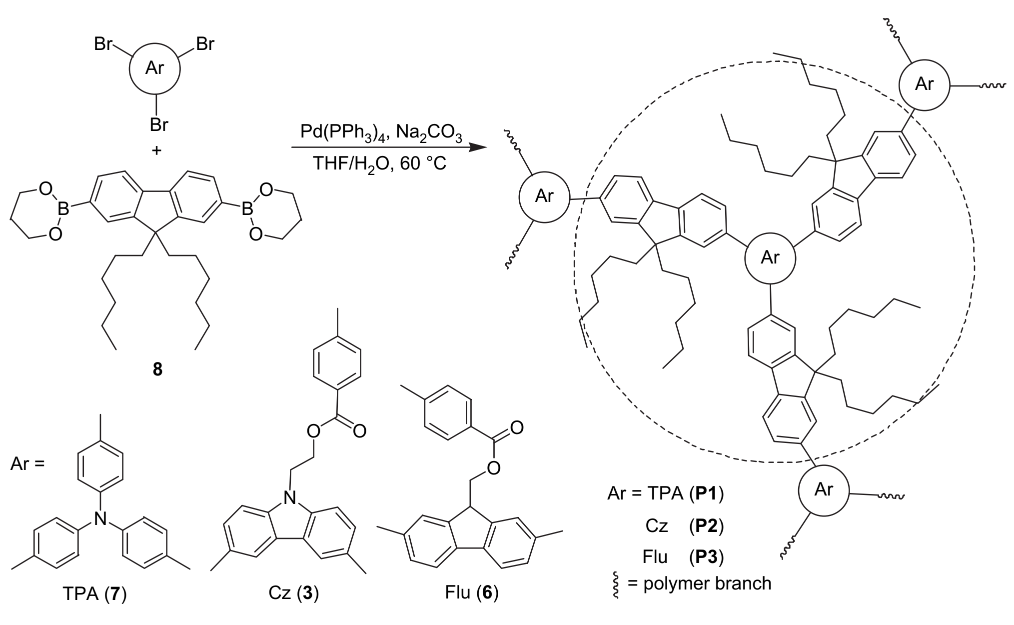
2.11. LED devices

LED devices were fabricated on indium–tin oxide (ITO, sheet resistance 30 Ω/γ) coated glass substrates. ITO glass was orderly cleaned by detergent, deionized water, acetone, and ethanol in ultrasonic baths and then was dried in an oven. Polymer used as an emissive layer was spin-casted onto an ITO glass. Deposition of the other organic layers, LiF, and Al layer was performed using a thermal evaporation system at a base pressure of 4×10^{-4} Pa. A quartz crystal oscillator placed near the substrates was used to monitor the thickness of the thin films, which were calibrated ex situ using an Ambios Technology XP-2 surface profilometer. The emitting area of the OLED devices was 4 mm^2. The luminescence output and current–voltage characteristics were recorded with a Newport 2835-C multifunction optical meter and a Hewlett–Packard 4140B semiconductor parameter analyzer. PL and EL spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. UV absorption spectrum was recorded on a Hitachi U-3010 UV spectrophotometer. All of the measurements were performed under ambient atmosphere at room temperature.

3. Results and discussion

3.1. Synthesis and structural characterization

The synthetic routes for **P1–P3** and their corresponding monomers were shown in Schemes 1 and 2. Compound **2** was easily synthesized from the reaction of 3,6-dibromocarbazole (**1**) with 2-chloroethanol in the solvent of DMF in the presence of potassium hydroxide as the base similar to previous cases [31,32]. Under the normal ester reaction condition [33], monomer **3** and compound **5** were prepared from their corresponding alcohols. Monomer **6** was obtained by the reaction of **5** with bromine in chloroform using a little ferric chloride as catalyst [34]. **P1–P3** were obtained from the typical Suzuki coupling reaction with THF and water as the solvents



Scheme 2.

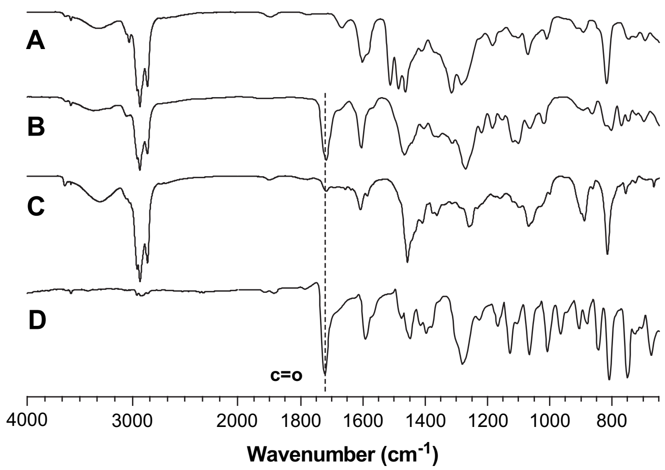


Fig. 1. IR spectra of polymers (A) **P1**, (B) **P2** and (C) **P3**. The spectrum of monomer **6** (D) is shown for comparison.

and sodium carbonate as the base. However, if the reaction time is too long or the polymerization degree is too high, cross-linking reactions would be favored and no soluble hyperbranched polymers could be obtained. This is unlike the reports in the literatures, in which the reaction time could be as long as 2 days, or even longer [24,27,35]. In our case, the reaction time was much shorter; the reason might be due to the different reacting activities existing in different aryl halides. For example, in the synthetic procedure of **P1**, if the reaction proceeded over 29 min, the whole reaction system became a big gel, thus, the reaction was stopped by injecting a lot of methanol after reacting for 28 min. Similar favorable time (30 min) was found for the preparation of **P2**, while it was much longer for that of **P3** (312 min). Also, we could control the progress of the polymerization by diluting the concentrations of the reaction reagents, or adding less catalyst, adjusting the feed ratios of the monomers.

The molecular structures of the monomers and polymers were characterized by spectroscopic methods, and all give satisfactory spectral data (see Section 2). Fig. 1 shows the IR spectra of **P1**–**P3**, and that of monomer **6** is also present for comparison. It is easily seen that the strong vibration band associated with C=O stretch at 1723 cm^{-1} is present in the spectrum of **P2**, indicating the successful incorporation of the carbazolyl unit similar to monomer **3** into the hyperbranched polymer. Unlike the case in **P2**, there is nearly no absorption attributed to the carbonyl groups in the spectrum of **P3**, though the absorption band of carbonyl groups is obvious in that of monomer **6** as shown in Fig. 1D. Also, there are nearly no peaks assigned to the methylene protons found in the ^{1}H NMR spectrum of **P3** (Fig. 2D) either. These points are very strange, indicating that the structure of monomer **6** might be damaged during the polymerization process. Thus, we conducted a control experiment (Scheme 3): monomer **6** underwent the whole reaction procedure just as the preparation of **P3**, all the conditions were the same but without the addition of monomer **8** and the [Pd] catalyst. After carefully analyzing the obtained product by the ^{1}H and ^{13}C NMR and mass spectra, we could confirm that the ester hydrolyzed and an elimination reaction occurred, as a result, monomer **6** was converted to compound **9** under the reaction conditions [36]. This point was further proved as reported in the literatures at even mild reaction conditions [37]. Then, we worried if monomer **3** underwent similar hydrolysis and elimination reactions during the polymerization procedure, though the spectra of **P2** are as good as its structure should be. Thus, we further did the similar control experiment of monomer **3** as that of monomer **6**, however, this time, there was no new point detected on the thin-layer chromatography (TLC) plates, and the product was the same as monomer **3** after the reaction. Thus, monomer **3** was stable during the preparation process of **P2**, and the structure of **P2** is shown in Scheme 2.

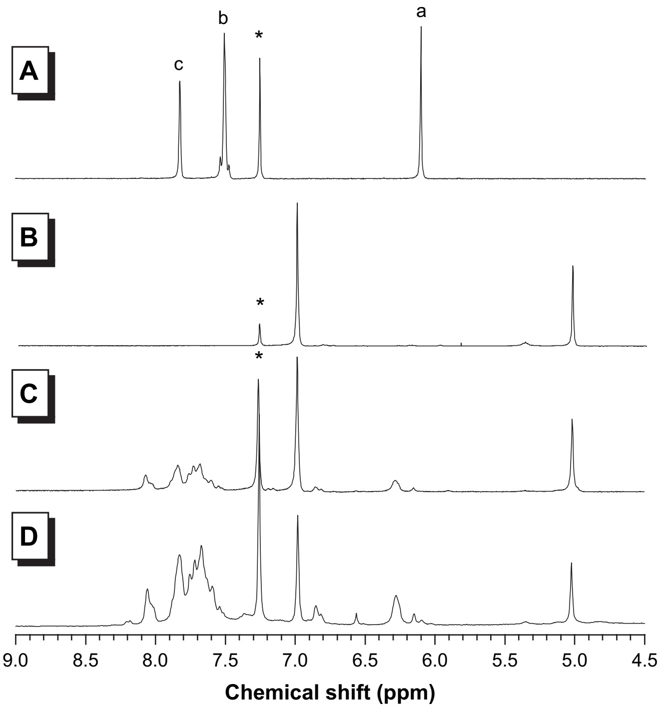
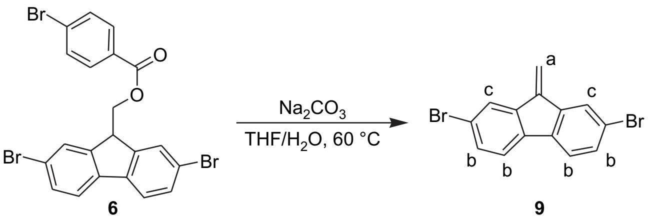
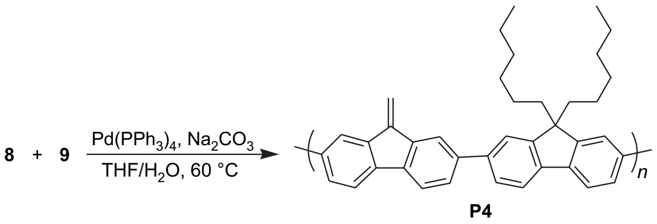


Fig. 2. ^{1}H NMR spectra of monomer **9** (A), and polymers **P5** (B), **P4** (C) and **P3** (D) in chloroform-*d*. The solvent peaks are marked with asterisks (*).

Since monomer **6** could be converted to the structure of compound **9** completely under the polymerization conditions, we used monomer **9** to run the copolymerization reaction instead of monomer **6** (Scheme 4), and really, **P4** was obtained and demonstrated similar spectroscopic data as those of **P3** (Fig. 2). This further proved the above discussion. However, it is still very strange that it would yield insoluble big gel if the copolymerization reaction of monomers **6** and **8** prolonged.



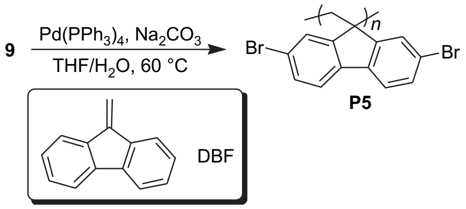
Scheme 3.



Scheme 4.

And the peaks at about 5.0 and 7.0 ppm in the ^{1}H NMR spectra of **P3** and **P4** (Fig. 2C and D, respectively) could not easily be assigned. So, further we did another experiment as shown in Scheme 5, and the resultant product is not soluble in methanol any more. The analysis results showed that monomer **9** underwent polymerization process just as dibenzofulvene (DBF) did in the literature [38,39]. Thus, the structure of **P3** and **P4** could be described as shown in Fig. 3. The ^{1}H NMR spectrum of **P5** is shown in Fig. 2B, two peaks at about 5.0 and 7.0 ppm appear. Similarly as reported in the literature, the peak at 5.0 ppm could be assigned to the signal of methylene groups on the main chain, while the aryl protons are responsible for the peak at 7.0 ppm. Thus, the two peaks at about 5.0 and 7.0 ppm in the ^{1}H NMR spectra of **P3** and **P4** are derived from the poly(dibenzofulvene) (poly(DBF)) structure, which further confirmed their structure shown in Fig. 3 to some degree.

Comparing the synthetic conditions of **P4** with those of **P3**, there is a big difference present in the reaction time, 312 min for **P3** while 12 h for **P4**. This is understandable; in the polymerization process for **P3**, all the three bromine atoms in monomer **6** would surely react with monomer **8** obeying the Suzuki coupling manner, and at the same time, monomer **6** would undergo the hydrolysis and elimination procedures to give birth to double bonds, which could form the main chain of dibromo-substituted poly(dibenzofulvene) similar to that of poly(DBF). Although the carbonyl groups were nearly not detected in **P3**, there are still some present as confirmed by its IR spectrum. Thus, the copolymerization behavior of monomers **6** and **8** should be more complicated than those of monomers **8** and **9**, which directly led to the shorter reaction time. From these points, the actual structure of **P3** should not be as simple as that of **P4**, however, the main structure should be similar. And according to the signals at about 6.3 ppm in their ^{1}H NMR spectra, there should be unpolymerized double bonds in **P3** and **P4**.



Scheme 5.

3.2. Thermal analysis

The thermal properties of the polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. The results are shown in Table 1. All the polymers demonstrated no weight loss at low temperature, and the 5% weight loss temperatures are higher than 300 °C, indicating their good thermal stability.

3.3. Optical properties

The polymers **P1–P5** are easily soluble in common organic solvents, such as THF and chloroform. Figs. 4 and 5 show their UV–visible spectra tested in the diluted THF solutions. While those of **P1** and **P3** are 372 and 365 nm, respectively, the maximum absorption wavelength of **P2** is 338 nm, which might indicate the shorter effective conjugated length in the polymer, since the π–π conjugation is broken by the alkyl spacer in the moieties from monomer **3**. **P4** exhibits similar maximum absorption wavelength (367 nm) just like **P3**, further confirming their similar structure. And the peak in the spectrum of **P5** is 278 nm, longer than that reported for poly(DBF) (about 265 nm), mainly caused by the two bromine atoms linked on the fluorene ring.

P1 and **P2** emit strong blue light upon exciting, while **P3** is a good green luminophor. The photoluminescence spectra of **P1–P5** in dilute THF solutions are shown in Figs. 6 and 7. As a hyperbranched copolymer of triphenylamine and fluorene moieties, **P1** exhibited a very narrow emission band peaked at 436 nm with an fwhm of 57 nm, which is similar as reported in the literature though the synthetic method is different [40]. The emission peak of **P2** is also in the blue region (437 nm), however, with broader curve (fwhm = 75 nm). Interestingly, **P3** emits strong green luminescence, with the peaks at 472 and 494 nm. Generally, 9,9-disubstituted fluorene-containing polymers and oligomers (PFs) have been proven to be the most promising blue light-emitting materials. Also, the so far reported hyperbranched 9,9-disubstituted fluorene-containing polymers are blue-emitting polymers except some heterocyclic rings introduced [24–27,35,41]. As expected, the emission spectrum of **P4** is nearly the same as that of **P3**. We further tested the fluorescence behavior of **P5**, and it could emit weak luminescence with the peaks at 410 and 435 nm, a little red shifted comparing with that of poly(DBF) as there are two bromine atoms present. It is also noticed that there is a very small peak at about 411 nm in the curves of **P3** and **P4**, which should be the typical vibronic feature of polyfluorene homopolymers, indicating the presence of the polyfluorene chains in the hyperbranched polymers, **P3** and **P4**. Thus, the green emission of **P3** should be originated from the electronic interactions between the construction segments of polyfluorene and dibromo-substituted poly(dibenzofulvene). Another possibility is that the formed excimers of fluorene moieties since they are close enough in the hyperbranched polymers without isolation groups. But the former explanation should be more reasonable, and the related job is under way in our lab.

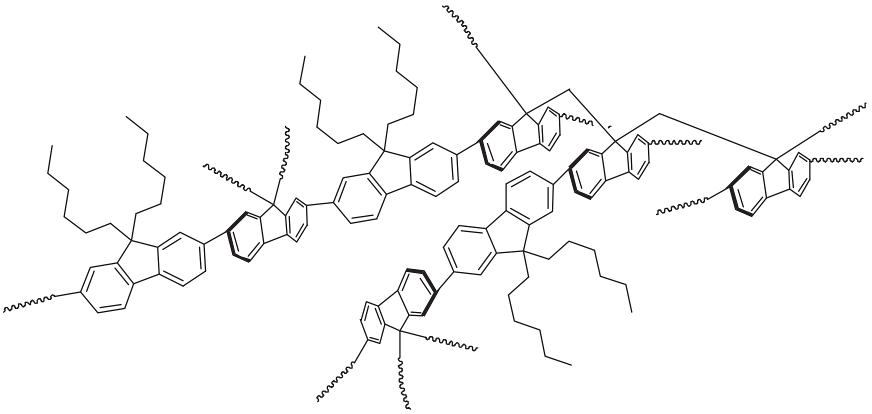


Fig. 3. The speculated structure of **P3** and **P4**.

The PL quantum yields (Φ_F) of the polymers in THF were also measured using 9,10-diphenylanthracene in cyclohexane ($\Phi_F = 90\%$) as a reference standard [42], and the results are presented in Table 1. The highest quantum yield is up to 0.70 (**P2**), and those of **P3** and **P4** are similar, with the data are 0.34 and 0.30, respectively, much lower than that of poly(2,7-(9,9-dioctyl)-fluorene)s ($\Phi_F = 0.78$).

To test the thermal spectral stability of the obtained polymers, we prepared their solid films on ITO glass by spin-coating using their diluted THF solutions (weight concentrations about 2%). The solid films were first baked at 150 °C for 30 min in air, then at 180 °C for another 30 min, followed by 200 and 225 °C. As to **P3** and **P4**, their films were further baked at 250 °C for another 30 min. Figs. 8–11 present the normalized PL emission spectra of the polymers after annealing in air. It was reported that thermal treatment of the film of poly(dihexylfluorene) at 100 °C would lead to a significant increase of the shoulder peak at about 460 nm due to the aggregation or keto effect formation in air. Our polymers (**P1**–**P3**), on the contrary, are very stable after baking at 150 °C for half an hour, and the PL spectra are almost the same as tested before annealing. With the temperature increased, there appears a new shoulder peak at about 550 nm in the spectra of **P1**, which is not obvious after annealing at 180 °C. Similar phenomena are found in the case of **P2**, however, the shoulder peak is insignificant, not so obvious as that of **P1**. Unlike **P1** and **P2**, no shoulder peak appeared while heating the solid films of **P3**, even at temperature as high as 250 °C. Alternatively, the PL emission spectra red shift, which might be ascribed to the prolonged effective conjugated length, was caused by the reaction of the remaining double bonds in the polymer under thermal treatment conditions. This point might also indicate that the green emission of **P3** should be caused by the electronic interactions between the construction segments of polyfluorene and dibromo-substituted poly(dibenzofulvene), but not from the possibly formed excimers of fluorene moieties. Thermal treatment of the films of **P4** gave the same trend as that of **P3**. Thus, the hyperbranched molecular structure really effectively hampers the aggregation formation of the polymer backbone or improves the resistance to the keto defect formation.

3.4. Electroluminescence properties

To study the electroluminescence properties of **P1**–**P3**, we prepared double-layer devices using the polymers as the emitting layers. The active area of the device was about 4 mm^2. Similar as their PL emission, the devices based on

Table 1
Polymerization results and characterization data

No.	Yield (%)	M_w[a]	M_w/M_n[a]	λ_{max}[b] (nm)	T_g[c] (°C)	T_d[d] (°C)	Φ_F[e]	V_{on}[f] (V)	B[g] (cd/m^2)	CD[h] (mA/cm^2)	CE[i] (cd/A)
P1	71.1	3454	1.48	436	236	320	0.67	5.0	93 (15)	201.8	0.18 (10.0)
P2	65.4	3770	1.39	437	263	316	0.70	7.5	25 (19.5)	165	0.06 (14.5)
P3	31.3	4300	1.69	472, 494	148		0.34	5.0	142 (15.5)	204	0.15 (10.5)
P4	55.0	5132	2.88	472, 495	129		0.30				
P5	87.5	1074	1.37	435							

[a] Determined by GPC in THF on the basis of a polystyrene calibration.
[b] The maximum emission wavelength of polymer solutions in THF.
[c] Glass transition temperature (T_g) of polymers detected by the DSC analyses under nitrogen at a heating rate of 10 °C/min.
[d] The 5% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 20 °C/min.
[e] Quantum yields in THF solution using 9,10-diphenylanthracene in cyclohexane ($\Phi_F = 90\%$) as standard.
[f] Turn-on voltage.
[g] Maximum luminescence, while the corresponding operating voltage is given in the parentheses.
[h] Current density at the maximum luminescence, also the maximum current density.
[i] Maximum current efficiency, while the corresponding operating voltage is given in the parentheses.

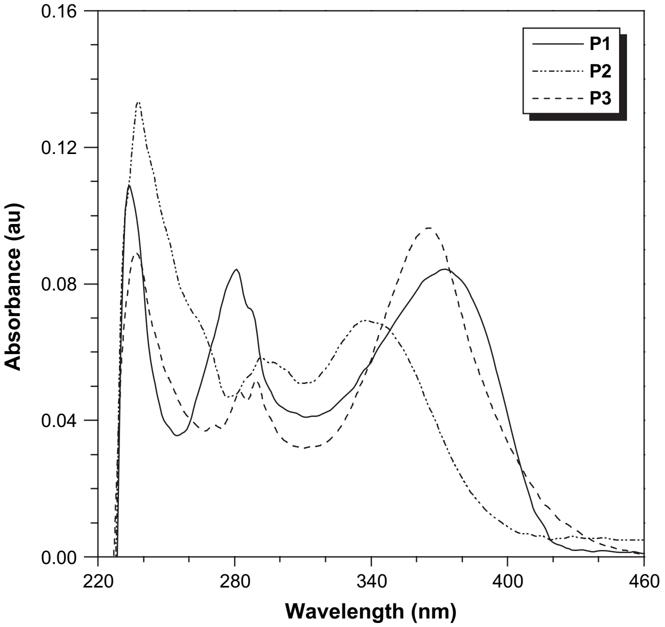


Fig. 4. UV–visible spectra of polymers **P1**–**P3** tested in their THF solutions. Concentration (mg/mL): 1.2×10^{-3} mg/mL.

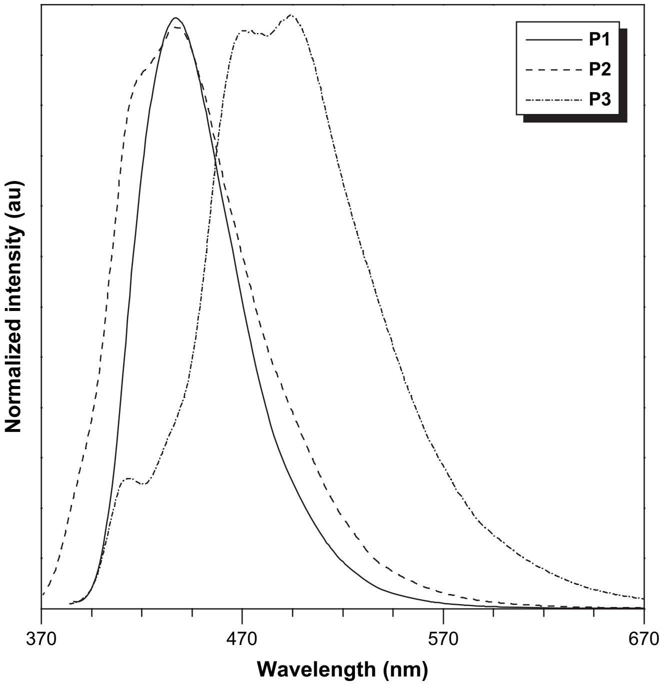


Fig. 6. PL spectra of polymers **P1**–**P3** tested in their THF solutions. Concentration (mg/mL): 1.2×10^{-3} mg/mL. Excited wavelength (nm): 380 for **P1**, 355 for **P2** and 370 for **P3**.

P1 and **P2** emit blue light, while green light is observed from the device of **P3**. Fig. 12 shows the PL and EL spectra of the device based on **P3**. The EL spectrum corresponds well with the PL curve, indicating that the same excited states were involved in the two processes. There are no obvious shoulder peaks observed in both of PL and EL spectra, indicating that the intermolecular interactions of the polymer are very weak, thanks to the hyperbranched structure.

All the device performance data are listed in Table 1. The current–voltage and luminance–voltage characteristics of the device of **P3** are shown in Fig. 13, as an example. The device emits bright green light starting at about 5.0 V, and reaches a brightness of 142 cd/m^2 at a bias of 15.5 V. The obtained maximum current efficiency was 0.15 cd/A (at 10.5 V with current density of 12.7 mA/cm^2 and a brightness of 19 cd/m^2). As discussed above in the PL emission, the green

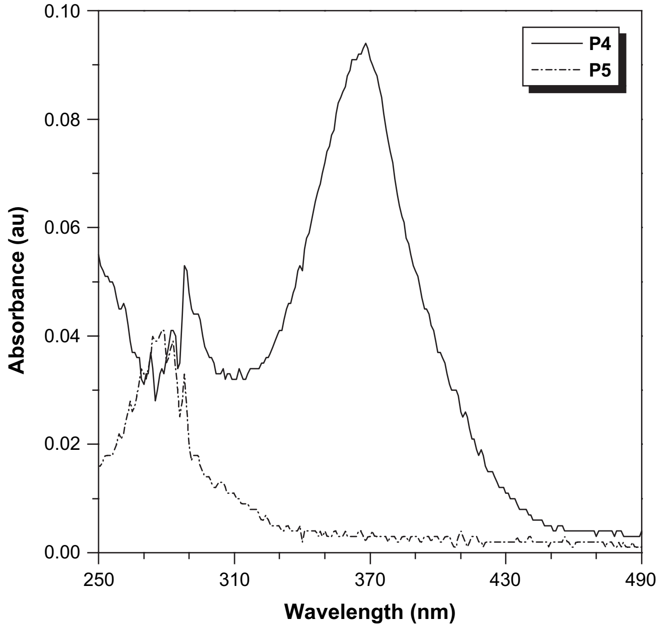


Fig. 5. UV–visible spectra of polymers **P4** and **P5** tested in their THF solutions. Concentration (mg/mL): 1.2×10^{-3} mg/mL.

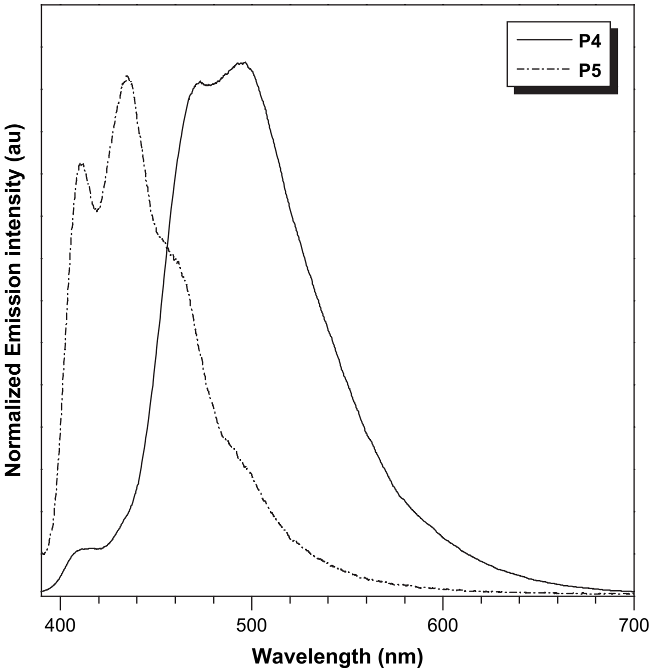


Fig. 7. PL spectra of polymers **P4** and **P5** tested in their THF solutions. Concentration (mg/mL): 1.2×10^{-3} mg/mL. Excited wavelength (nm): 371 for **P4** and 377 for **P5**.

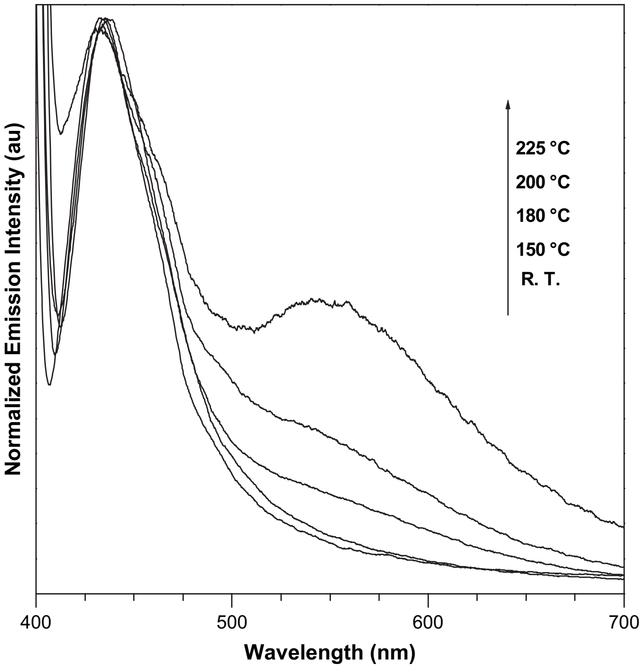


Fig. 8. Photoluminescent spectra of the film of **P1** before and after annealing at different temperatures for 30 min in air.

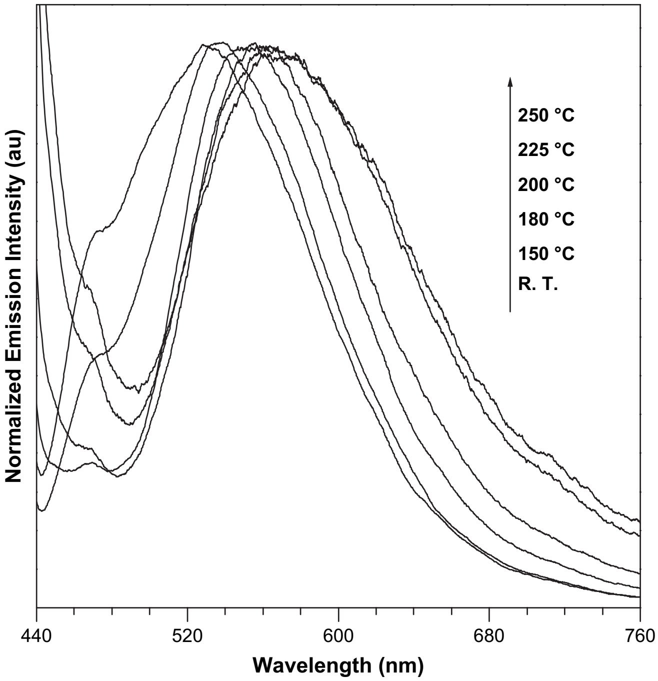


Fig. 10. Photoluminescent spectra of the film of **P3** before and after annealing at different temperatures for 30 min in air.

light emission of **P3**, not blue one as reported in nearly all the literatures concerned with fluorene-containing polymers (no matter linear, dendritic or hyperbranched polymers), should be ascribed to the special structure of **P3**, perhaps mainly due to the presence of the dibromo-substituted poly(dibenzofulvene) chains in the hyperbranched structure. Actually, poly(dibenzofulvene) is considered as a π-stacked structure, which is responsible for its high hole mobility; as to the PL emission, this π-stacked structure directly leads to the red-shifted emission from 305 to 320 nm of monomer to about 400 nm of the polymer [38,39]. Here, in our case, the PL emissions of **P5** at 410 and 435 nm are also caused by the

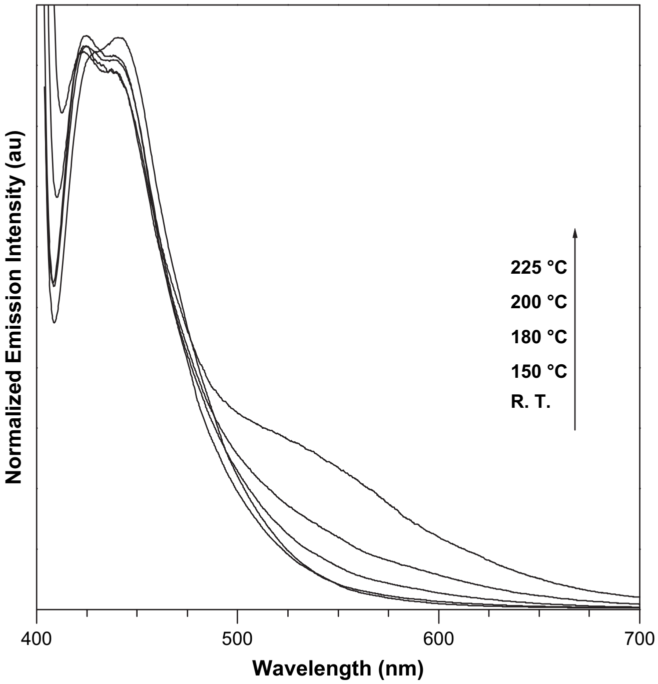


Fig. 9. Photoluminescent spectra of the film of **P2** before and after annealing at different temperatures for 30 min in air.

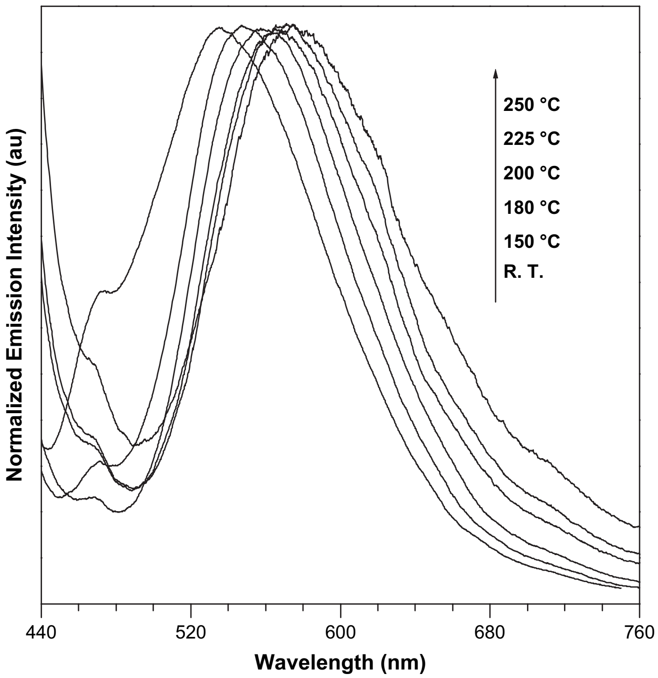


Fig. 11. Photoluminescent spectra of the film of **P4** before and after annealing at different temperatures for 30 min in air.

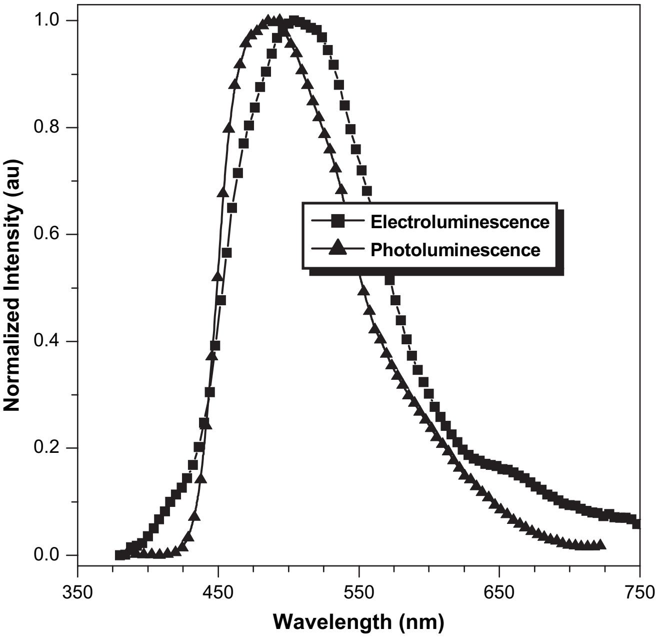


Fig. 12. The EL and PL spectra of an LED device of **P3**.

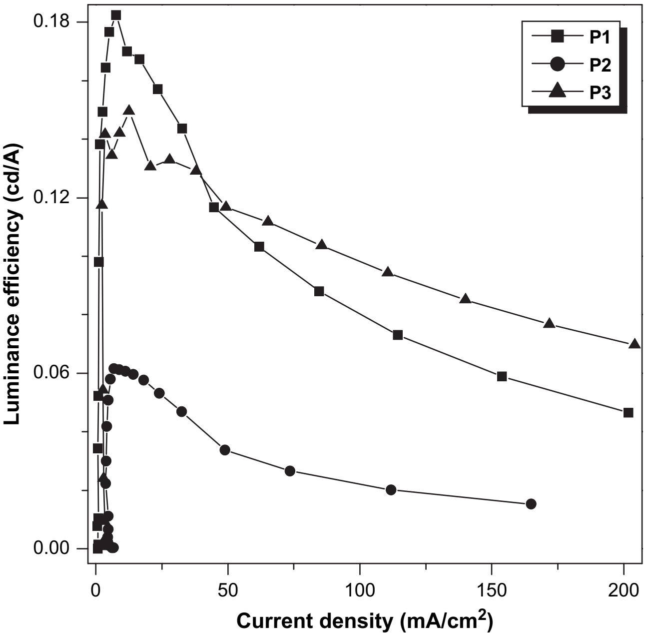


Fig. 14. Current efficiencies of LED devices of **P1**–**P3**.

π-stacked structure. Without the π-stacked structure, **P1** and **P2** are blue luminophors, just like other fluorene-containing hyperbranched polymers. Thus, our study may provide another approach to tune the color of the emission light by controlling the structure of materials.

The luminescence efficiency–current characteristics of the devices are shown in Fig. 14. The efficiencies quickly increase while the current density increase, then gradually decrease with a further increase in the current density, which imply that the recombination of electrons and holes is not as effective as before, possibly caused by the unbalanced injection of electrons and holes under a higher voltage. The relatively low efficiency of **P2** might be due to its bad conjugation structure.

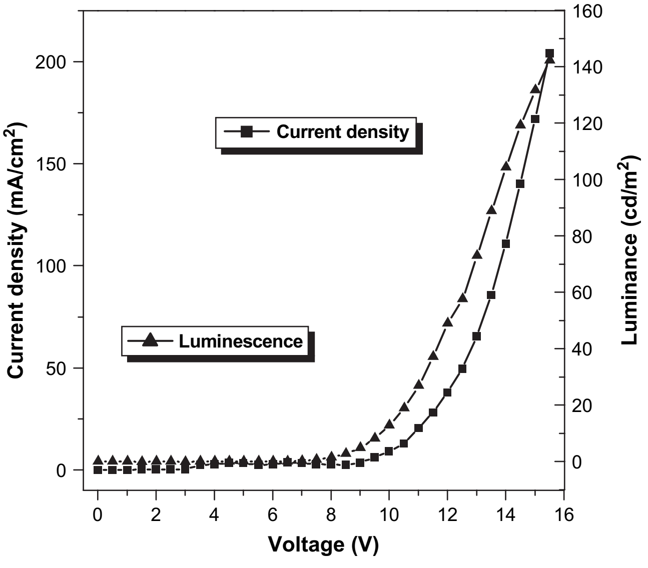


Fig. 13. *I*–*V*–*B* curve of an LED device of **P3**.

4. Conclusions

We report in this paper the syntheses of three hyperbranched alternation copolymers (**P1**–**P3**) from tribromoaryl moieties with 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) from "$A_2 + B_3$" approach based on Suzuki polycondensation reaction. The polymers are easily soluble in common solvents, and can form solid films with good quality. Interestingly, **P3** emits strong green light, unlike the reported blue ones of fluorene-containing hyperbranched polymers, which might be due to the presence of the π-stacked structure of poly(dibenzofulvene). Also, all the polymers demonstrate good luminescent stabilities: shoulder peak emission in long wavelength was not observed in their film after annealing at 150 °C for half an hour, and **P3** exhibits much better stable emission even annealed at 250 °C for half an hour.

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