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Fluorene-based hyperbranched copolymers with spiro[3.3]heptane-2,6-dispirofluorene as the conjugation-uninterrupted branching point and their application in WPLEDs

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Abstract: A series of white light-emitting hyperbranched copolymers (**P2-P5**) consisting of polyfluorene (**PF**)/4,7-dithienyl-2,1,3-benzothiadiazole (**DBT**) branches and spiro[3.3]heptane-2,6-dispirofluorene (**SDF**) conjugated branching point have been synthesized and fully characterized. The effects of the branching degree on the thermal, photoluminescent (PL) and electroluminescent (EL) properties of the copolymers were investigated. The results suggest that the branching point helps to enhance both the thermal and spectral stabilities of the hyperbranched copolymers, and remain the energy transfer efficiency from fluorene to **DBT** unit. Efficient hyperbranched copolymer-based single layer devices are achieved with CIE coordinates located at near (0.33, 0.33).

Especially, a device based on **P4** (10 mol% of **SDF**) exhibits a doubled efficiency and 5.5-fold luminance compared to the device based on the linear reference.

Keywords: white-light emission; hyperbranched structure; copolymer; spiro[3.3]heptane-2,6-dispirofluorene

1. Introduction

Hyperbranched polymers have recently received considerable interest as light-emitting materials[1-8]. Their unique three-dimensional structure can help to reduce the aggregation of the polymer chains, make the material form amorphous films with good quality, and increase the glass transition temperature (T_g) of the polymers[9-14]. A number of hyperbranched electroluminescent polymers have been synthesized, and both emission efficiency and thermal stability were effectively improved with respect to their linear analogies[15]. However, the introduction of branching point, which decreases the conjugation length of the main chain, had significant influence on their photoelectronical properties, such as blue-shifted emission spectra and reduced Förster energy transfer (FET) efficiency[16-20]. The branching point which does not interrupt the linear π-system of the polymer chain is expected to overcome these drawbacks.

In the meantime, white polymer light-emitting diodes (WPLEDs) have attracted great attention owing to their potential applications in full-color displays combined with a color filter, and solid lighting sources[21-27]. Among the WPLEDs fabrication techniques, compared with the blending or doping system, white-light emitting from a single molecule has great advantages such as high color stability, low price, as well as easy fabrication process[28-30]. Polyfluorenes (**PFs**) are the most promising blue light-emitting materials because of high photoluminescence quantum efficiency, and relatively good chemical and thermal stabilities[31-36]. In our previous research[37], copolymers based on 9,9-dioctylfluorene and 4,7-dithienyl-2,1,3-benzothiadiazole (**DBT**) were synthesized, and white-light emission was obtained by the combination of blue light-emitting from **PF** and orange light-emitting from **DBT** through the incomplete FET from the fluorene segment to **DBT** unit[38]. To further improve the electroluminescent (EL) performance of the copolymers, molecular structure modification would be a promising strategy.

In this study, spiro[3.3]heptane-2,6-dispirofluorene) (**SDF**) was introduced as the conjugation-uninterrupted branching point with different contents (1-20 mol%) into the **PF-DBT** copolymer to construct the hyperbranched structures. The 2,7- substituted fluorenes of **SDF** are incorporated into the π-system of the **PF** branches, which could remain the blue-light emission from the **PF** segments, and efficient FET from fluorene to **DBT** unit. Moreover, the density functional theory (DFT) calculation on conformer optimization reveals that **SDF** branching point could block the aggregation of the polymer chains effectively. Thus, enhanced spectral and thermal stability, better film-forming property, and further improved EL performance of the material could be anticipated by employing this novel **SDF**-centered hyperbranched three-dimensional structure. On the basis of the synthesized copolymers, the effects of branching degree on their thermal, photoluminescent (PL), film-forming and EL properties were demonstrated.

2. Experimental Section

2.1 Materials and Characterization. 2,7-Dibromo-9,9-dioctylfluorene (**M1**, 99.8%) and 9,9-Dioctylfluorene-2,7-bis(boronic acid pinacol ester) (**M2**, 99.5%) were purchased from Energy Chemical and Synwitech, respectively. Tetrahydrofuran (THF) and toluene were distilled using standard procedures. Other solvents were used without further purification unless otherwise specified. All reactions were carried out using Schlenk techniques under dry nitrogen atmosphere. ^{1}HNMR spectra were measured on a Bruker DRX 600 spectrometer, and chemical shifts were reported in ppm using tetramethylsilane as an internal standard. Mass spectra were obtained on a Bruker autoflex MALDI-TOF/TOF mass spectrometer with anthralin (DI) as the matrix. Elemental analysis (EA) was performed by determined with an Vario EL elemental analyzer. Molecular weights and polydispersities of the copolymers were determined using gel permeation chromatography (GPC) on an HP1100 HPLC system equipped with a 410 differential refractometer, and a refractive index (RI) detector, with polystyrenes as the standard and THF as the eluent at a flow rate of 1.0 mL/min at 30 ℃. The UV-visible absorption spectra were determined on a Hitachi U-3900 spectrophotometer and the PL emission spectra were obtained using a Horiba FluoroMax-4 spectrophotometer at room temperature. Thermogravimetric analysis (TGA) of the copolymers was conducted on a Setaram thermogravimetric analyzer at a heating rate of 10 ℃/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed at both heating and cooling rates of 5 ℃/min under nitrogen atmosphere, using DSC Q100 V9.4 Build 287 apparatus. Atomic force microscopy (AFM) measurements were performed on a SPA-300HV from Digital Instruments Inc. (Santa Barbara, CA) at a tapping mode.

2.2 Device Fabrication and Characterization. Patterned glass substrates coated with indium tin oxide (ITO) (20 Ω square^{-1}) were cleaned by a surfactant scrub, washed successively with deionized water, acetone and isopropanol in an ultrasonic bath, and then dried at 120 ℃ in a heating chamber for 8 h. A 40-nm-thick poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonic acid) (PEDOT:PSS) hole injection layer was spin-coated on top of ITO and baked at 120 ℃ for 20 min. Thin films (50 nm thick) of the copolymers as the emitting layer were deposited on top of the PEDOT:PSS layer by spin-coating the chlorobenzene solution of **P1-P5**, followed by thermal annealing at 110 ℃ for 20 min. Then an electron-transporting layer of 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI, 35 nm) and LiF (1 nm) and Al (150 nm) as the cathode were deposited by vacuum evaporation under a base pressure of 5 $\times 10^{-4}$ Pa[39]. The EL spectra and CIE coordinates were measured with a PR-655 spectra colorimeter. The current-voltage-forward luminance curves were measured using a Keithley 2400 source meter and a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions.

2.3 DFT Calculation. Geometry optimization for **SDF** was carried out using Gaussian 03. The results were obtained by DFT calculation using B3LYP functional and the 6-31G (d, p) basis.

2.4 Syntheses. *Synthesis of Spiro[3.3]heptane-2,6-di-(2',2'',7',7''-tetrabromospirofluorene) (**TBrSDF**)*[40, 41] To a solution of 2,7-dibromofluorene (3.24 g, 10 mmol) in 100 mL of THF was added NaH (0.6 g, 25 mmol) in portions at 50 ℃. After stirring for 1 h, a suspension of pentaerythrityl tetrabromide (0.86 g, 2.21 mmol) in THF was added dropwise within 2 h. The mixture was stirred for another 12 h at 65 ℃, and then cooled to room temperature. The solvent was removed under reduced pressure, and the residue was hydrolyzed with H_2O (100 mL). The mixture was extracted with CH_2Cl_2 (3×50 mL), and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was recrystallized from dichloromethane to afford **TBrSDF** as colorless crystal (1.42 g, 40 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.71 (d, J =1.8 Hz, 4H, Ph), 7.53 (d, J = 8.4 Hz, 4H, Ph), 7.49 (dd, J_1 = 1.8 Hz, J_2 = 7.8 Hz, 4H, Ph), 3.06 (s, 8H, CH_2); ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 156.548, 140.452, 133.454, 129.261, 124.716, 124.022, 49.648, 49.418, 33.759; MS (MT): m/z 752.6 [M+K^+]. Elemental Anal. Calcd. for $C_{31}H_{20}Br_4$: C 52.29, H 2.83; found: C 52.64, H 2.98.

General Procedure for the Synthesis of Copolymers ***P1-P5***. To a solution of predetermined amount of monomers (**M1**, **M2**, **TBrSDF** and **DBrDBT**) in toluene (20 mL) was added an aqueous solution (5 mL) of potassium carbonate (2 M) and a catalytic amount of $Pd(PPh_3)_4$ (2.0 mol%). Aliquat 336 (1 mL) in toluene (5 mL) was added as the phase transfer catalyst. The mixture was vigorously stirred at 90 ℃ for 4 days. Phenylboronic acid was then added to the reaction mixture followed by stirring at 90 ℃ for an additional 12 h. Finally, bromobenzene was added in the same way by heating for 12 h again. When cooling to room temperature, the reaction mixture was washed with 2 M HCl and water. The organic layer was separated, and the solution was added dropwise to excess methanol. The precipitated polymers were collected by filtration, and dried under vacuum. The solid was Soxhlet extracted with acetone for 72 h and then passed through a short chromatographic column using toluene as the eluent to afford the polymers.

P1: M1 (0.274 g, 0.50 mmol), **M2** (0.322 g, 0.50 mmol), **DBrDBT** (0.2 mL, 2×10^{-3} mol/L). Light yellow powder, yield: 30.0 %. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.96-7.43 (-ArH-), 7.03-6.92 (-ArH-), 2.35-1.86 ($-C-CH_2-$), 1.18-1.02 ($-CH_2-$), 1.01-0.58 ($-CH_3-$).

P2：**M1** (0.266 g, 0.48 mmol), **M2** (0.325 g, 0.51mmol), **TBrSDF** (0.007 g, 0.01 mmol) and **DBrDBT** (0.2 ml, 2×10^{-3} mol/L). Light yellow powder, yield: 67.4 %. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.88-7.57 (-ArH-), 6.93-6.89 (-ArH-), 3.41-2.93 ($-CH_2-$), 2.21-1.89 ($-C-CH_2-$), 1.18-0.96 ($-CH_2-$), 0.93-0.55 ($-CH_3$).

P3：**M1** (0.233 g, 0.42 mmol), **M2** (0.338 g, 0.53 mmol), **TBrSDF** (0.036 g, 0.05 mmol) and **DBrDBT** (0.2 ml, 2×10^{-3} mol/L). Light yellow powder, yield: 40.0 %. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.89-7.56 (-ArH-), 6.93-6.81 (-ArH-), 3.42-2.93 ($-CH_2-$), 2.21-1.88 ($-C-CH_2-$), 1.19-0.98 ($-CH_2-$), 0.94-0.60 ($-CH_3$).

P4: M1 (0.192 g, 0.35 mmol), **M2** (0.354 g, 0.55 mmol), **TBrSF** (0.071 g, 0.1 mmol) and **DBrDBT** (0.2 ml, 2×10^{-3} mol/L). Green powder, yield:

41.3 %. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.06-7.42 (-ArH-), 6.94-6.77 (-ArH-), 3.45-3.02 ($-CH_2-$), 2.24-1.87 ($-C-CH_2-$), 1.19-0.95 ($-CH_2-$), 0.94-0.64 ($-CH_3$).

P5：**M1** (0.109 g, 0.20 mmol), **M2** (0.386 g, 0.60 mmol), **TBrSDF** (0.142 g, 0.20 mmol) and **DBrDBT** (0.2ml, 2×10^{-3}mol/L). Gray powder, yield: 50.0 %. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.98-7.48 (-ArH-), 6.93-6.78 (-ArH-), 3.39-3.02 ($-CH_2-$), 2.21-1.75 ($-C-CH_2-$), 1.22-0.88 ($-CH_2-$), 0.86-0.45 ($-CH_3$).

3. Results and discussion

3.1 DFT calculation

The molecular structure and the energy-minimized conformer of **SDF** obtained by DFT calculation are shown in Figure 1. The molecule adopts three-dimensional conformation because of the spiro[3.3]heptane segment. Therefore, the chain aggregation of the SDF-centered hyperbranched copolymer could be effectively hindered. On the other hand, the distance between the two fluorenes is 9.0 Å, which is smaller than Förster radius (R_0 = 65 Å)[42]. As a result, efficient interchain FET from fluorene segment to DBT unit could be expected.

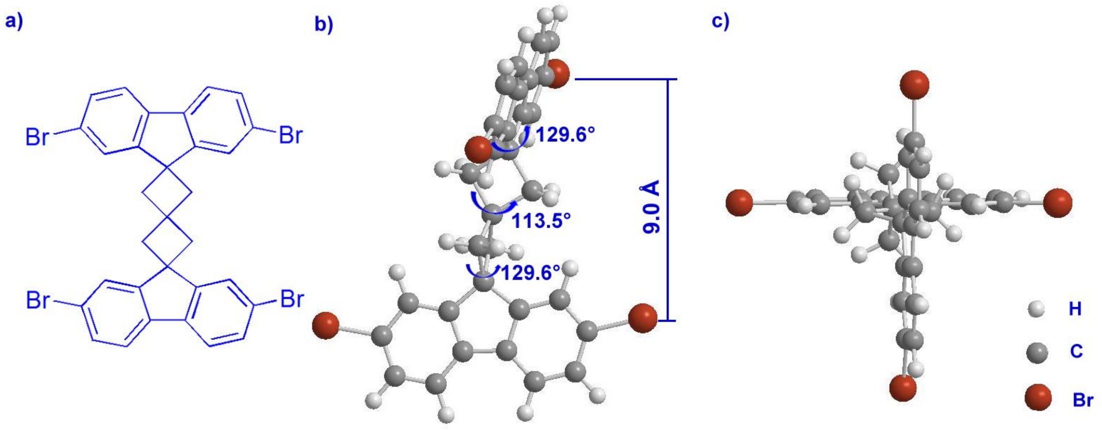


Figure 1. Molecular structure (a) and geometrically optimized 3D molecular model of **TBrSDF** from side view (b) and top view (c) by DFT B3LYP/6-31 G (d, p) calculation.

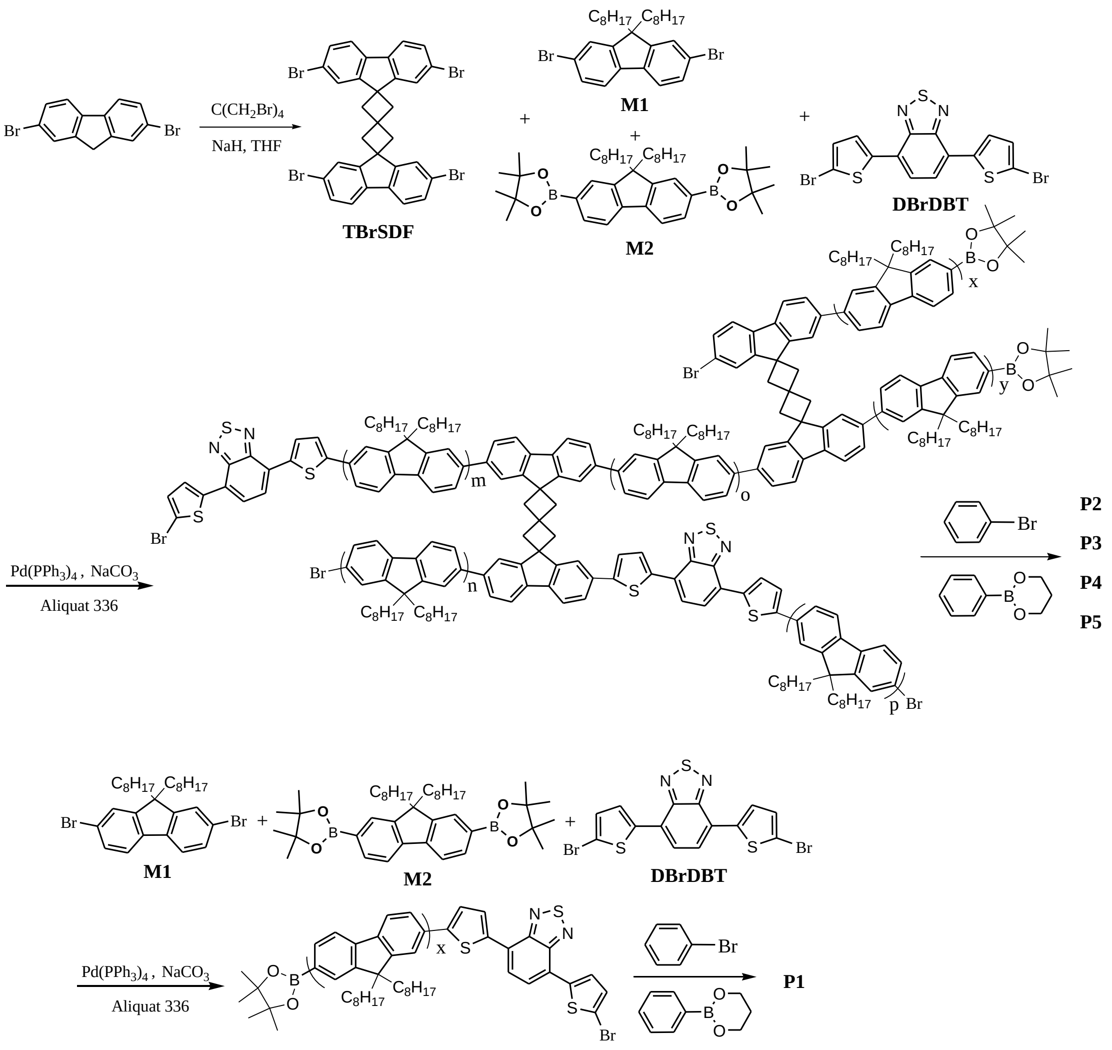
3.2 Synthesis and characterization

The branching point **TBrSDF** was prepared via cyclization of 2,7-dibromofluorene and pentaerythrityl tetrabromide in THF under base conditions in a 40 % yield. Monomer 4,7-bis(2-bromo-5-thienyl)-2,1,3-benzothiadiazole (**DBrDBT**) was synthesized according to the literature[43-45]. The hyperbranched copolymers **P2-P5** with 9,9-dioctylfluorene/**DBT** as the branches and **SDF** as the branching point were prepared by Suzuki polycondensation (Scheme 1). To obtain white-light emission, the organe-light-emitting unit **DBT** was incorporated into the framework in a 0.05 mol% feed ratio relative to the blue-light-emitting groups for all the polymers[37]. The feed ratios of **SDF** were 1 mol% (**P2**), 5 mol% (**P3**), 10 mol% (**P4**), and 20 mol% (**P5**). For comparison, linear copolymer **P1** was also prepared. The yields of the copolymers ranged from 30% to 67%. The synthetic and structural results of **P1-P5** were summarized in Table 1.

Table 1. Polymerization results and characterization of the copolymers

Copolymers	$n_{\mathbf{M1}}$	$n_{\mathbf{M2}}$	$n_{\mathbf{TBrSDF}}$		$n_{\mathbf{DBrDBT}}$	Yield	GPC	
			feed	found		(%)	M_n	PDI
P1	0.5	0.5	0	0	5×10^{-4}	30	7965	1.33
P2	0.4847	0.5053	0.01	0.0124	5×10^{-4}	44	7414	1.46
P3	0.4245	0.5255	0.05	0.063	5×10^{-4}	40	9222	1.46
P4	0.35	0.55	0.10	0.1243	5×10^{-4}	41	13252	1.78
P5	0.20	0.60	0.20	0.2016	5×10^{-4}	50	24992	3.27

The actual contents of **SDF** calculated from the high-resolution NMR spectroscopy (Figure S3 and Table 1) are close to the feed ratios, showing the similar reactivity of bromines in **TBrSDF** and **M1**[46]. The number-average molecular weights (M_n) of the copolymers determined by GPC range from 7504 to 24992 with a polydispersity index (PDI) from 1.33 to 3.27. It is noted that the M_n increases with increasing **SDF** contents from **P2** to **P5**, suggesting that the degree of polymerization of the hyperbranched copolymers can be efficiently increased by the increase of branching degree[47]. Except for **P5**, the copolymers are readily soluble in common organic solvents such as $CHCl_3$, THF and toluene. The poor solubility of **P5** is probably due to its rigid framework.



Scheme 1. Synthesis of the white-light-emitting copolymers.

3.3 Thermal properties

The TGA and DSC data are shown in Figure 2 and Table 2. All of the copolymers exhibit good thermal stability with the onset decomposition temperatures (T_d, measured at a 5 % weight loss) from 373 to 409 ℃. The glass transition temperatures (T_g, inset of Figure 1) of the copolymers are closely correlated to the density of the branching point. With the highest content of branching point, **P5** has the highest T_g at 182 ℃, which is 88 ℃ higher than that of the linear polymer **P1**. This result suggests that the segmental mobility decreases with the increasing content of the branching core, and thus the morphological stability of the copolymers can be greatly enhanced by the introduction of high content of **SDF**.

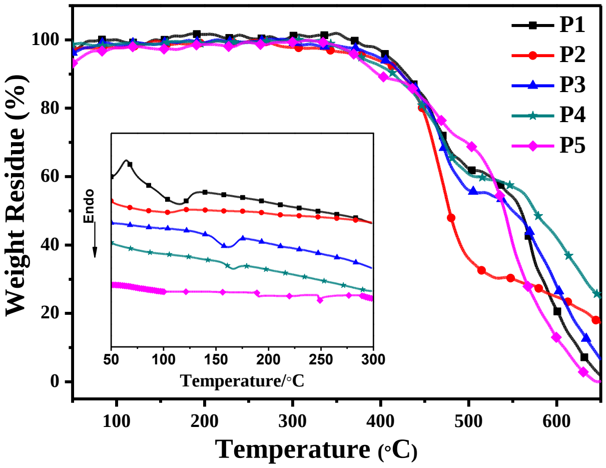


Figure 2. TGA and DSC (insert) curves of **P1-P5** in nitrogen atmosphere with a heating rate of 10 ℃/min and 5 ℃/min, respectively.

3.4 Photophysical properties

The normalized UV-vis absorption and PL spectra of the copolymers in dilute solution are shown in Figure 3a. With the increase of branching degree of the copolymers, the absorption peaks are slightly blue-shifted gradually from **P1** at 386 nm to **P5** at 377 nm (Table 2). As the introduction of the branching point does not interrupt the conjugation of the backbone of the copolymers, this hypsochromic shift may be attributed to the more twisted molecular conformation with the increasing ratio of the spiro-structured **SDF**. In the PL spectra, all of the copolymers exhibit typical emission peaks of polyfluorene at 420, 442, and a shoulder peak at 468 nm. This suggests that the chain structure and conformation of the hyperbranched copolymers are quite similar in the excited state despite the difference in the branching density. The absorption and emission bands of **DBT** are not observable in the spectra owing to its comparatively low content (0.05 mol %) in the copolymers and the FET is exclusively intrachain in dilute solution.

Table 2. Thermal and photophysical properties of the copolymers

Polymer	T_d	T_g	Dilute Solution		Solid Film	
	(℃)	(℃)	λ_{abs} (nm)	λ_{PL} (nm)	λ_{abs} (nm)	λ_{PL} (nm)
P1	408	94	386	422, 444	385	434, 450, 605
P2	387	104	384	422, 443	385	420, 444, 603
P3	397	143	382	422, 444	383	420, 445, 603
P4	378	156	380	421, 443	382	421, 445, 604
P5	373	182	377	421, 442	384	420, 436, 515

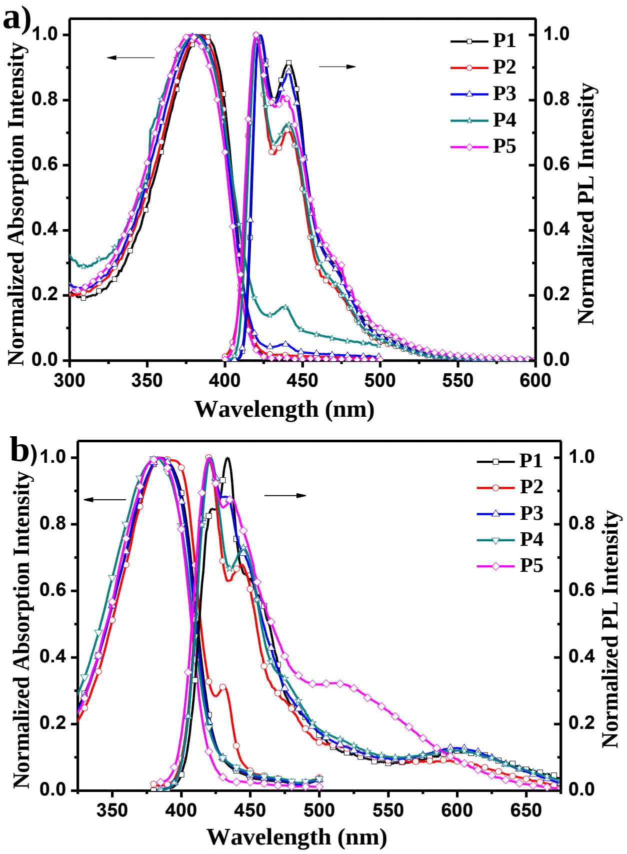


Figure 3. UV-vis absorption and PL spectra of **P1-P5**: (a) in $CHCl_3$ solution (10^{-5} M) and (b) in solid film.

In films, all of the copolymers exhibite similar UV-vis absorption pattern with a typical PF absorption maximum at around 384 nm (Figure 3b and Table 2). In the PL spectra, the emission peaks of **P1** show a bathochromic shift about 10 nm with respect to those in dilute solution. On the contrary, there are no obvious bathochromic shifts for the spectra of copolymers **P2-P5**. This result indicates that the hyperbranched structure can prevent the aggregation of the polymer chain efficiently. The emission bands assigned to **DBT** centered at 605 nm are observed for all of the copolymers, which is the result of both intra- and interchain FET from fluorene to **DBT** unit. Given the equal emission intensities from **DBT** for **P1-P4**, and the same content of **DBT** in the copolymers, this hyperbranched structure with **SDF** branching point does not affect the efficiency of FET. The emission band around 515 nm for **P5** could not be explained clearly at this stage, and we guess it might be attributed to the complex chain configuration and disordered chain conformation of **P5** with ultrahighly branched to slightly crosslinked structure.

3.5 Film morphology

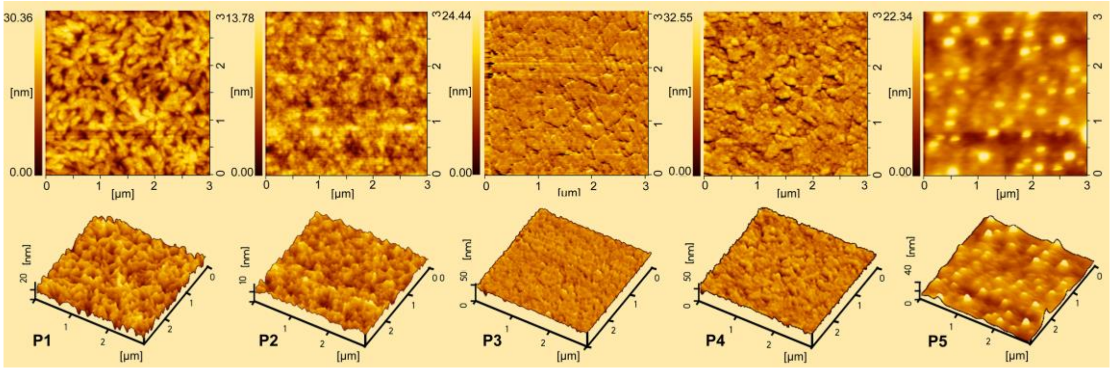


Figure 4. AFM images (3×3 μm) of the copolymer films.

The impact of branching degree on the film morphology of the copolymers was investigated by atomic force microscopy (AFM) at a tapping mode. Figure 4 shows the AFM images of **P1-P5** films prepared by spin-coating $CHCl_3$ solutions of the copolymers (10^{-5} M) on the ITO substrates. Generally, all of the films are amorphous without any pinhole defects. **P2-P4** films show smoother surface than **P1** film, suggesting the hyperbranched copolymers possess good film-forming ability[48]. The surface of the **P5** film appears to be rougher than those of **P1-P4**, which should be attributed to its rigid, and twisted molecular configuration. The difference in film morphology of the copolymers may have influence on their EL performances, which will be discussed below.

3.6 Electroluminescent properties

Using the copolymers as emitting materials, single-layer PLEDs were fabricated with a configuration of ITO/PEDOT:PSS (40 nm)/polymers (50 nm)/TPBI(35 nm)/LiF(1 nm)/Al(40 nm). The electroluminescent (EL) performances are summarized in Table 3.

Table 3. EL Performances of the PLEDs

Polymer	$V_{on}{}^{a}$(V)	$L_{max}{}^{b}$(cd/m^2) (at the voltage (V))	CE$_{max}$(cd/A)	LE$_{max}$(lm/W)	CIE(x,y)
P1	4.6	1224.7(7.7)	1.52	0.75	(0.33,0.37)
P2	4.5	2282.9(8.5)	1.85	0.76	(0.26,0.32)
P3	4.5	4614.3(9.0)	2.57	0.91	(0.34,0.35)
P4	4.7	6768.6(9.5)	3.23	1.00	(0.32,0.33)
P5	4.7	5035.2(8.7)	1.79	0.95	(0.31,0.35)

[a] Turn-on voltage (at 1 cd/m^2).

[b] Maximum luminance at applied voltage.

Figure 5 shows the electroluminescence (EL) spectra of copolymers **P1-P5** at 12 V and the photo of device **P4** at the maximum luminance. The EL spectra ranged from 420 to 750 nm and white-light emission was obtained with CIE coordinates located near (0.33, 0.33) (Table 3). The current density-voltage (I-V) and luminance-voltage (L-V) characteristics of the devices are shown in Figure 6. The hyperbranched copolymers **P2-P5** exhibit better performance than their linear reference **P1,** and **P2-P4** show enhanced performance with the increase of branching degree in terms of maximum luminance, luminance efficiency and power efficiency. The **P4-**based device acquires a maximum luminance of 6768.6 cd/m^2 (at 9.5 V), a maximum current efficiency of 3.23 cd/A, and a maximum power efficiency of 1.00 lm/W. The dropped performance of **P5-**based device may be attributed to the poor film morphology of **P5**, as mentioned above. The current efficiency (CE)-current density (J) characteristics of the devices show that the efficiencies decrease very slowly with increasing current density, indicating that all of the copolymers and devices have good stability (Figure 7). All of the results suggest that the EL performance of the copolymers can be effectively improved by introducing **SDF** branching point with a proper branching degree. Further investigations on the optimization of the device performance are ongoing in our laboratory.

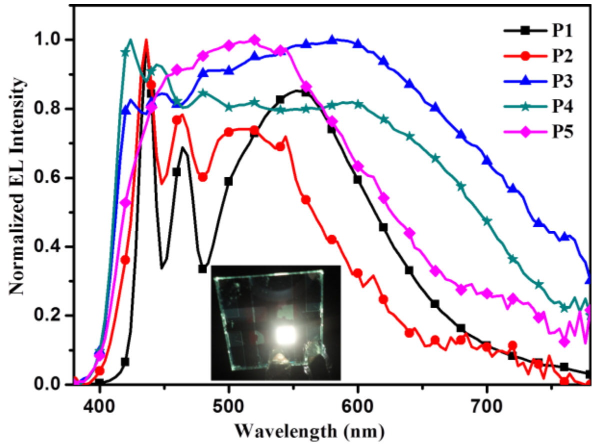


Figure 5. Electroluminescence spectra of **P1-P5** at 12 V and the photo of **P4**-device at the maximum luminance (inset).

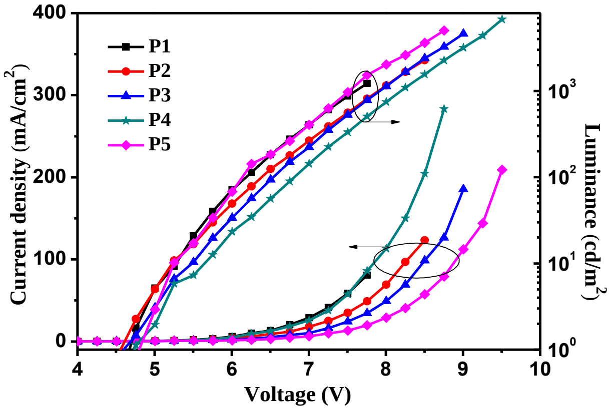


Figure 6. Current-voltage (left) and luminance-voltage (right) curves of **P1-P5** PLEDs. .

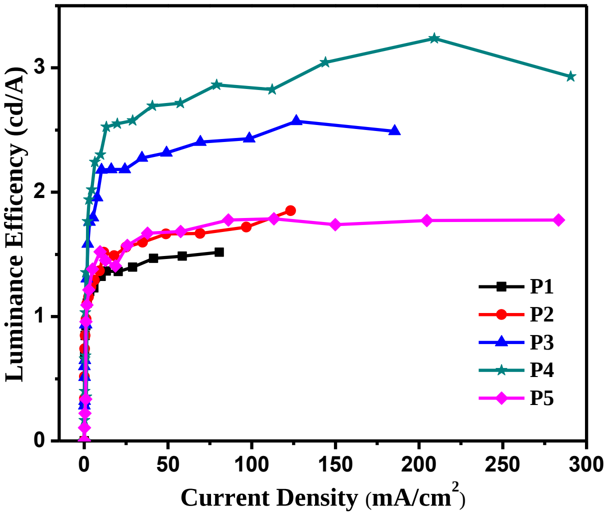


Figure 7. Current efficiency-current density characteristics of **P1-P5** PLEDs .

4. Conclusions

Hyperbranched white-light-emitting copolymers based on polyfluorene/4,7-dithienyl-2,1,3-benzothiadiazole as the branches and spiro[3.3]heptane-2,6-dispirofluorene as the branching point with branching degrees varying from 1 mol% to 20 mol% have been synthesized through Suzuki coupling reaction. Compared with their linear reference, the hyperbranched copolymers show enhanced thermal stability with T_gs ranging from 104 ℃ to 182 ℃ with the increase of the branching degree. As the introduction of spiro[3.3]heptane-2,6-dispirofluorene does not interrupt the conjugation of the copolymer chains, the copolymers exhibit typical polyfluorene emission patterns, with no obvious bathochromic shift observed in solid films because of the hyperbranched structure. Furthermore, the FET efficiency from fluorene segment to 4,7-dithienyl-2,1,3-benzothiadiazole unit remains in the hyperbranched systems, and white-light emission is acquired in the single-layer devices. The efficiency, luminance and stability are efficiently improved in the hyperbranched copolymer-based devices. A maximum luminance of 6768.6 cd/m^2 (at 9.5 V), and a maximum current efficiency of 3.23 cd/A with a Commission Internationale de l’Eclairage coordinate at (0.32, 0.33) are obtained using the hyperbranched copolymer with an spiro[3.3]heptane-2,6-dispirofluorene content of 10 mol%, which is doubled in efficiency and 5.5-fold in luminance compared with the linear copolymer-based device. The results indicate that the polyfluorene-4,7-dithienyl-2,1,3-benzothiadiazole based hyperbranched polymers with spiro[3.3]heptane-2,6-dispirofluorene branching point could be attractive candidates as white-light-emitting materials with high efficiency and stability.

Associated content

Supplementary Information

^{1}H NMR, ^{13}C NMR and MS characterization of **TBrSDF** and ^{1}H NMR characterization of the copolymers. This material is available free of charge via the Internet at http://pubs.rsc.org

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Notes

The authors declare no competing financial interest.

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Graphical Abstract

Fluorene-based hyperbranched copolymers with spiro[3.3]heptane-2,6-dispirofluorene as the conjugation-uninterrupted branching point and their application in WPLEDs

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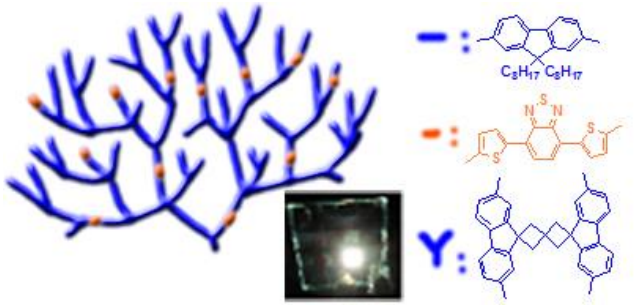

Spiro[3.3]heptane-2,6-dispirofluorene as the three-dimensional, conjugation-uninterrupted branching point helps to enhance the electroluminescent performance of polyfluorene based white-light-emitting hyperbranched copolymers.