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Polymer Communication

Hyperbranched triazine-containing polyfluorenes: Efficient blue emitters for polymer light-emitting diodes (PLEDs)

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Abstract

A series of hyperbranched triazine-containing polyfluorenes were synthesized by an "$A_2 + A'_2 + B_3$" approach based on Suzuki polycondensation. The polymers showed pure blue emission and the maximum emissions red-shifted in polar solvents and in solid film. By introducing triazine into polyfluorene, the electron injection and transport properties were improved and green emission was suppressed. PLED devices fabricated with the polymers showed reasonably high external quantum efficiencies.

Keywords: Conjugated polymer; Hyperbranched; Polymer light-emitting diodes

1. Introduction

Polymer light-emitting diodes (PLEDs) have attracted a great deal of attention recently due to their academic interests and potential utility of this technology in a wide variety of applications such as flat-panel displays and solid-state lighting [1]. However, the realization of potential uses is limited by their low quantum efficiency. To improve the quantum efficiency, it is critical to achieve both efficient charge injection and balanced mobility of both charge carriers inside the electroluminescent polymers. It can be obtained by multi-layer PLEDs fabricated with the additional hole-transporting and electron-transporting layer besides the electroluminescent polymer layer. Alternatively, conjugated polymers with transport-balance properties of electrons and holes could be developed so as to obtain the single-layer PLEDs. Introducing electron-deficient unit into the conjugated polymers has been studied intensively. The frequently used electron-deficient units are the nitrogen-containing heterocyclo-rings such as 1,3,4-oxadiazole [2], pyridine [3], thiadiazole [4], benzothiadiazole [5], etc. In our previous work, by introducing oxadiazole to the backbone of conjugated polymers, we have developed a series of p–n diblock conjugated copolymers with improved EL properties and these polymers showed unique and interesting optical and electrochemical properties [6].

Polyfluorene (PFs) derivatives are promising blue light-emitting materials because they exhibit excellent chemical stabilities and produce light with high quantum yields [7]. However, a big problem encountered with these materials is the appearance of green emission when thermally annealed or the current passed through the polyfluorenes-based devices [8]. Until now the origin of this phenomenon is still a very hot topic – the tendency to aggregate or the formation of excimers is one of the causes [9]. To overcome this drawback, several approaches [10] have been developed to use longer and

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branched side chains or bulky substituents, copolymerization techniques, dendrimer attachment, endcapping of PFs with bulky groups, cross-linking of PFs, oligomer approach, etc.

Recently, electroactive and light-emitting dendrimers and hyperbranched polymers are of interest for developing efficient electroluminescent devices for displays and lightings and other photonic devices [11], since highly branched and globular features can reduce or even eliminate strong intermolecular interactions and aggregation. Moreover, the EL devices fabricated by such three-dimensional polymers have shown the improved efficiency and high thermal stability [12]. In this communication, for the improvement of EL efficiency of polyfluorenes, 1,3,5-triazine units were introduced into the polyfluorenes, which act as the branch units of the hyperbranched structure. 1,3,5-Triazine is also an electron-deficient group with high electron-affinity [13], which is higher than that of 1,3,4-oxadiazoles (PBD) and 1,2,4-triazoles [14]. To the best of our knowledge, until now there was no polymer containing 1,3,5-triazine units has been reported as light-emitting materials for PLEDs except for several reported small molecules [15]. In the present work, a series of hyperbranched triazine-containing polyfluorenes were synthesized by an "$A_2 + A'_2 + B_3$" approach based on Suzuki polycondensation. The PLED devices have been fabricated based on the resulting copolymers and the EL characteristics have been investigated. The resulting hyperbranched triazine-containing polyfluorenes and their PLEDs show good blue light emission with the remarkably improved EL efficiency.

2. Experimental section

2.1. Materials

All reagents were purchased from Acros, Fluka or Aldrich Chemical Co. and were used without further purification. All solvents were dried under standard conditions. 2,7-Dibromo-9,9-dioctylfluorene (**1**), 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) (**2**), 2,4,6-tris(*p*-bromophenyl)-1,3,5-triazine (**3**), 2-bromo-9,9-dioctylfluorene (**4**), 9,9-dioctylfluorene-2-boronic acid (**5**) were synthesized by the literature methods [15a,16].

2.2. Instruments

All NMR spectra were recorded on a NMR spectrometer, Varian Mercury plus 400 at 295 K. GPC results were obtained on Shimadzu Lc-VP. The DSC and TG scans were performed on Shimadzu DSC-60A and DTG-60A equipment, respectively. The heating rate was 10 K/min. Nitrogen was used as the protective and purge gas. Elemental analysis was performed on a CHNS–O (Elementar Co.). Cyclic voltammetry (CV) was performed at a scanning rate of 100 mV/s on an AUTOLAB.PGSTAT30 potentiostat/galvanostat system (Ecochemie, Netherlands). UV–vis absorption spectra were recorded on Shimadzu UV-3150. Fluorescence spectra were measured on Shimadzu RF-5300PC. The absolute quantum efficiency of solid materials was measured by utilizing an integrating sphere. The EL spectra were collected by a CCD Instapec 4 (Oriel). The $I-V$, $B-V$ and QE curves were characterized by a computerized Keithley 236 source meter and a calibrated silicone photodiode.

2.3. Hyperbranched polymer synthesis: general procedure

To solutions of **1**, **2** and **3** in different molar ratios of 5:6.5:1 (abbreviated as $\mathbf{PTF_5}$) and 10:11.5:1 (abbreviated as $\mathbf{PTF_{10}}$) in toluene were added $Pd(PPh_3)_4$ and 2 M aqueous Na_2CO_3 solution. The mixtures were degassed and stirred at 85 °C for 5 days. Then compounds **4** and **5** were added to the reaction mixtures together with additional $Pd(PPh_3)_4$ and the reactions were continued for further 2 days. After cooling to room temperature, the reaction mixtures were washed with 2 M HCl solution and water. Then the mixtures were extracted with toluene and were poured into 200 ml of methanol to give precipitates. The obtained solids were redissolved in toluene and reprecipitated from methanol, followed by Soxhlet extraction with acetone for 5 days to give yellow powders.

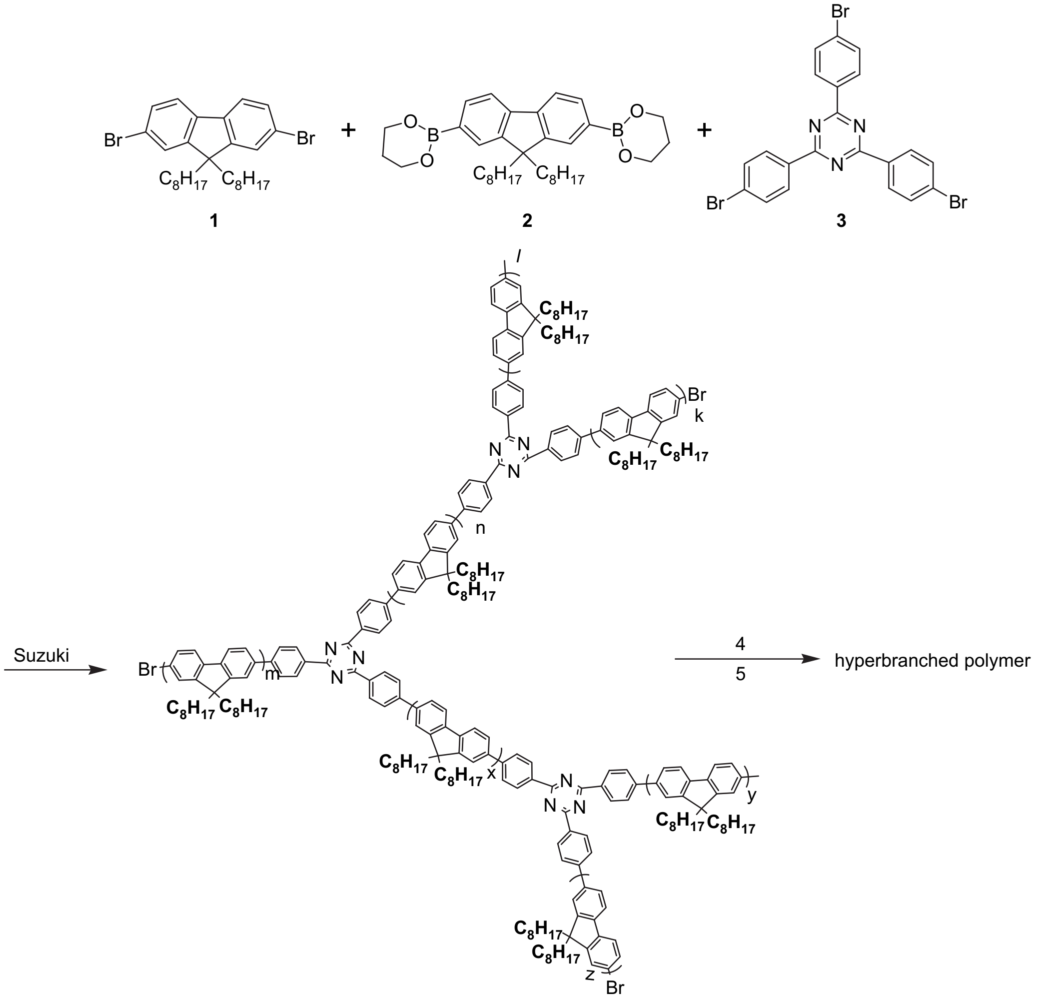
$\mathbf{PTF_5}$: **1** (0.75 g, 1.37 mmol), **2** (0.99 g, 1.79 mmol) and **3** (0.15 g, 0.27 mmol), toluene (30 ml), $Pd(PPh_3)_4$ (0.04 g, 0.034 mmol) and 2 M aqueous Na_2CO_3 solution (10 ml) were used. The obtained solid was a yellow powder (0.98 g, 76.3%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.89 (s), 7.88 (s), 7.71–7.85 (br), 7.54–7.70 (br), 7.40 (br), 2.05 (br), 1.07 (br), 0.74 (br); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.77, 139.45, 138.99, 131.16, 130.07, 127.75, 127.51, 127.39, 126.17, 125.13, 120.45, 118.94, 54.32, 39.37, 30.78, 29.02, 28.69, 28.21, 22.90, 13.06. $(C_{354}H_{469}N_3)_n$ $(4763.7)_n$ Calcd: C, 89.26; H, 9.86; N, 0.88. Found: C, 88.35; H, 9.44; N, 0.88.

$\mathbf{PTF_{10}}$: **1** (0.80 g, 1.46 mmol), **2** (0.94 g, 1.68 mmol) and **3** (0.08 g, 0.15 mmol), toluene (30 ml), $Pd(PPh_3)_4$ (0.04 g, 0.034 mmol) and 2 M aqueous Na_2CO_3 solution (10 ml) were used. The obtained solid was a yellow powder (1.05 g, 81.2%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.92 (s), 7.92 (s), 7.72–7.86 (br), 7.55–7.72 (br), 7.42 (br), 2.08 (br), 1.10 (br), 0.78 (br); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.04, 140.74, 140.25, 132.42, 132.33, 128.99, 128.73, 128.61, 127.42, 126.39, 121.73, 120.19, 55.57, 40.62, 32.02, 30.27, 29.45, 24.15, 22.83, 14.29. $(C_{644}H_{869}N_3)_n$ $(8647.7)_n$ Calcd: C, 89.44; H, 10.06; N, 0.49. Found: C, 88.26; H, 10.00; N, 0.52.

3. Results and discussion

3.1. Synthesis and structural characterization

Hyperbranched polymers were synthesized by an "$A_2 + A'_2 + B_3$" approach based on Suzuki polycondensation (see Scheme 1) [17]. Since it is well established that it tends to produce insoluble cross-linked polymers in the step-growth polymerization, the reaction conditions such as temperature, time, concentration and solvent, which will influence the polymerization process should be considered. Suzuki coupling



Scheme 1. General procedure for hyperbranched triazine-containing polyfluorenes.

polycondensation reaction is much better to be carried out in a dilute solution and relatively low temperature to reduce possible cross-linking between branches, and thus the poor solubility of the polymer could be avoided. Because random hyperbranched polymer synthesized by one-pot Suzuki approach has a large number of bromo- and boronic ester-end groups which are detrimental for light-emitting applications, monobromo- and monoboronic acid-substituted monomers were therefore used to cap the end groups. Three monomers, 2,7-dibromo-9,9-dioctylfluorene (**1**), 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) (**2**) and 2,4,6-tris(*p*-bromophenyl)-1,3,5-triazine (**3**), in different molar ratios and $Pd(PPh_3)_4$ (0.5 mol%) were added in toluene. The mixtures were stirred and refluxed for 5 days at the polymerization stage. 2-Bromo-9,9-dioctylfluorene (**4**) and 9,9-dioctylfluorene-2-boronic acid (**5**) were added to the reaction mixtures together with additional $Pd(PPh_3)_4$ (0.5 mol%), and the reaction was continued for further 2 days. The amorphous polymers with slightly yellow color were obtained through standard workup. The results show that the molar ratio is a key factor for the solubility of hyperbranched products. The solubility was poor in common organic solvents for hyperbranched polymers with higher contents of **3**. Thus, $\mathbf{PTF_5}$ and $\mathbf{PTF_{10}}$ are soluble in common organic solvents.

The molecular structures of the polymer were characterized with NMR spectroscopy and elemental analysis. In the proton NMR spectra, the characteristic signals of the branching units and fluorene units were observed at around $\delta = 8.9$ and 7.7 ppm, respectively. The ratio between the branching unit and fluorene of these two polymers can be estimated from NMR spectra, i.e. 1:8 for $\mathbf{PFT_5}$ and 1:17 for $\mathbf{PTF_{10}}$, respectively, as shown in Fig. 1. The number-average molecular weight and the weight-average molecular weight were determined by gel permeation chromatography (GPC) with THF as the eluting solvent, against the calibration with standard polystyrene (molecular weight ranging from 500 to 1,000,000). The former for the polymers were 19,600 and 20,100, while the latter for the polymers were 52,600 and 48,200. The thermal properties of the hyperbranched polymers were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). No distinct glass transition was observed for polymers in the DSC curve. TGA reveals good thermal stabilities of these polymers with the onset decomposition temperature (T_d) of 385.8 and 407.6 °C under nitrogen, respectively.

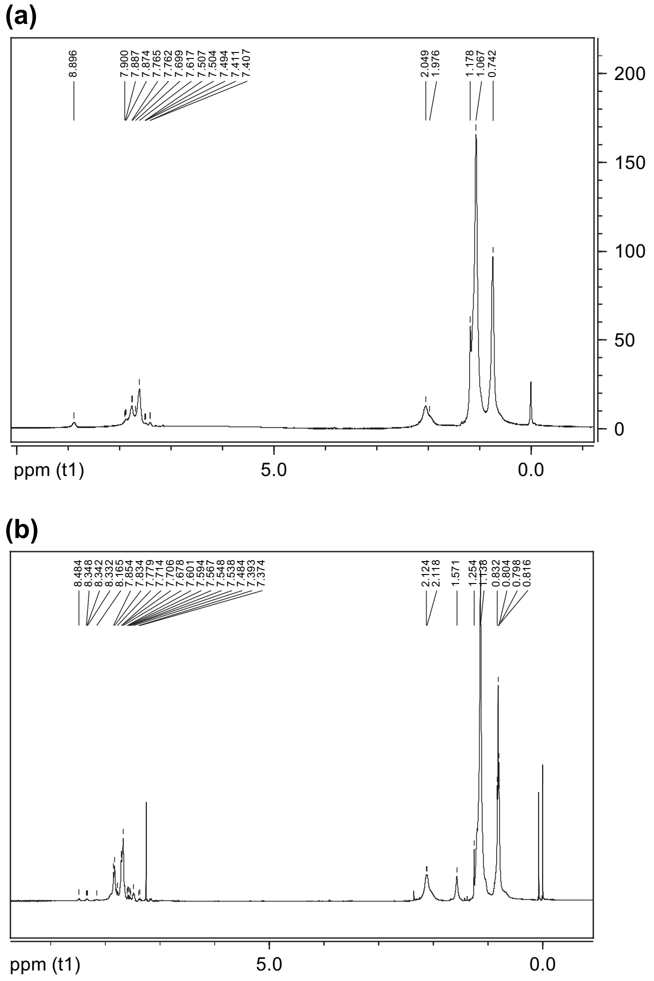


Fig. 1. ^{1}H NMR spectra of **PTF$_5$** (a) and **PTF$_{10}$** (b).

3.2. Optical properties

The spectroscopic characteristics of the polymers were investigated in solutions and in the thin films. The UV–vis absorption and photoluminescence (PL) spectra for **PTF$_{10}$** in toluene, $CHCl_3$, and in films spin-coated from toluene, $CHCl_3$ are shown in Fig. 2. Solid films on quartz plates used for fluorescence were prepared by spin-coating with 10^{-3} M toluene solution at 1500 rpm. The polymer shows the maximum absorption at 386 nm in toluene, attributed to $\pi-\pi^*$ transition of the polymer. Interestingly, it was found that these polymers exhibit solvatochromism on the fluorescence spectra in different solutions. With the increasing polarity of the solutions, the maximum emissions of the polymers show red-shift apparently and the emission patterns become broader. The PL spectra of **PTF$_{10}$** in toluene and $CHCl_3$ are peaked at 418 and 444 nm, respectively. Compared to the emission in solutions, the emission in solid films show also red-shift phenomena, attributed to the change in the conformation of the polymer. The spectroscopic results of **PTF$_5$** are almost the same.

The PL quantum yields (Φ_F) of **PTF$_5$** and **PTF$_{10}$** in toluene were measured with 9,10-diphenylanthracene as a reference standard (cyclohexane solution, $\Phi_F = 0.9$) [18]. The quantum efficient yield reaches 0.40 and 0.53, respectively, which is similar to the hyperbranched polyfluorene in the previous report [19]. The absolute quantum efficiencies (η_{qe}) of solid films were measured by the integrating sphere, which reach 0.26 and 0.32 for **PTF$_5$** and **PTF$_{10}$**, respectively.

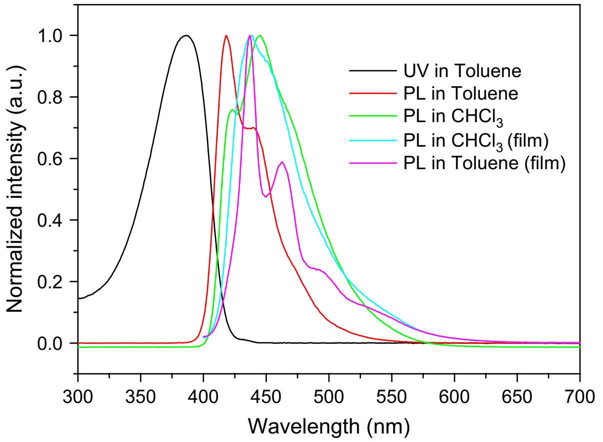


Fig. 2. UV and PL spectra of the **PTF$_{10}$** in toluene, $CHCl_3$ and in films spin-coated from toluene, $CHCl_3$.

3.3. Electrochemical properties

The CV investigations of **PTF$_5$** and **PTF$_{10}$** were performed in a solution of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in acetonitrile at a scan rate of 100 mV/s, using a Pt wire as counter electrode and a $Ag/AgNO_3$ (0.1 M) electrode as reference electrode. On sweeping anodically, **PTF$_5$** and **PTF$_{10}$** display reversible oxidation processes. The HOMO levels are calculated according to an empirical formula, $E_{HOMO} = -e(E_{ox} + 4.70)$ (eV) [20]. The LUMO levels are calculated through the formula, E_{LUMO} = optical band gap − E_{HOMO}. The optical band gaps are determined from onset absorptions of the polymers. Therefore, the values of E_{red} are obtained from an empirical formula, $E_{LUMO} = -e(E_{red} + 4.70)$ (eV). The data are listed in Table 1. The HOMO and LUMO levels of linear PF have been reported [21], which are 5.58 and 2.25 eV, respectively. It can be seen that the values of the LUMO level increase from 2.25 to 2.60 eV upon the introduction of triazine units into polyfluorene. With increasing the ratio of triazine unit in the hyperbranched polymers, the LUMO energy level increases. This effect brings the LUMO levels of the polymers close to the work function of typical cathode materials, as shown in Fig. 3. Consequently, a significant enhancement can be expected for the injection of electrons from the cathode to the polymer layer.

Table 1
Electrochemical properties of **PTF$_5$** and **PTF$_{10}$**

Polymers	Optical band gap (eV)	E_{ox} (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)
PTF$_5$	3.00	0.90	−2.10	5.60	2.60
PTF$_{10}$	3.09	0.89	−2.20	5.59	2.50

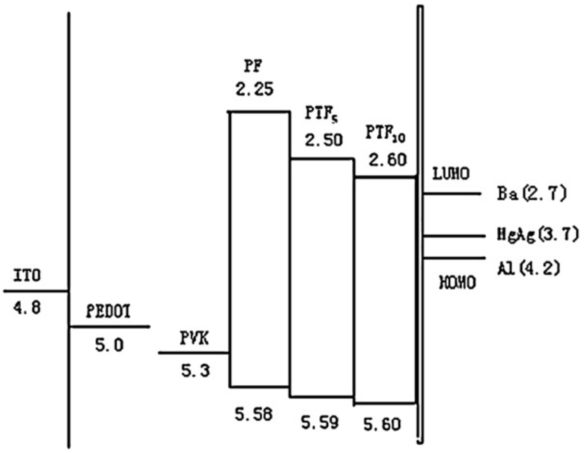


Fig. 3. Comparison of the energy levels of PF, **PTF$_5$** and **PTF$_{10}$** with the work functions of the electrodes.

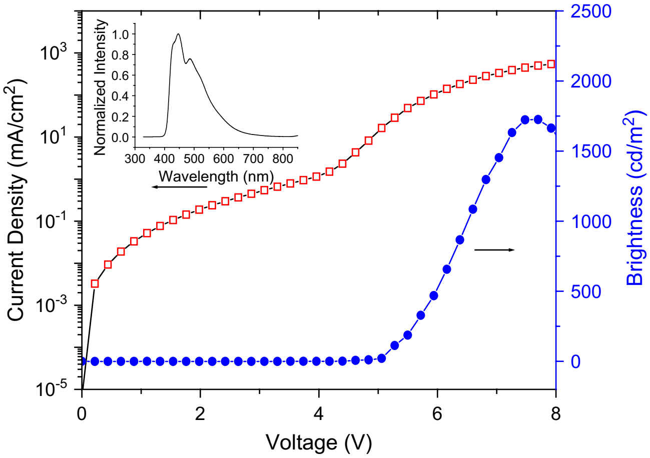


Fig. 4. EL spectrum, *I*–*V* curve and light output of **PTF$_{10}$** in ITO/PEDOT/**PTF$_{10}$**/Ba/Al.

Standard PLED devices were fabricated with the configuration of ITO/PEDOT (50 nm)/polymer (70 nm)/Ba (4 nm)/Al (150 nm) and ITO/PEDOT (50 nm)/PVK (40 nm)/polymer (70 nm)/Ba (4 nm)/Al (150 nm). The polymer films were spun from the toluene solutions, if not specially stated. The shape of the EL spectra of the two polymers is almost the same as that of the PL spectra of the corresponding polymer films, no additional band emerged [8]. It demonstrates that under electric field, the aggregation and excimer-forming of polymer chains can be remarkably avoided by introduction of triazine as the branching unit. Strangely, PTF5-based device exhibits longer-wavelength maximum emission than PTF10. Since the phenomenon is inconsistent with that from the aggregation and excimer-forming of polymer chains, we are seeking for others reasonable reason. The EL performances of both **PTF$_{10}$** and **PTF$_5$** are summarized in Table 2. Fig. 4 shows the EL spectrum, *I*–*V* curve and light output of **PTF$_{10}$** in ITO/PEDOT/**PTF$_{10}$**/Ba/Al. For **PTF$_{10}$** the maximum brightness is 1750 cd/m^2 at 7.8 V, while it reaches 1950 cd/m^2 at 13.5 V after adding PVK layer. **PTF$_5$** shows the similar results. We note that the device efficiency was enhanced for the hyperbranched polymers when the hole-transporting layer PVK was coated on top of the PEDOT. This result is consistent with the electrochemical data from which HOMO levels were determined as ca. 5.60 eV (Table 1). A big hole injection barrier is expected between the hyperbranched polymer and the PEDOT, which has the HOMO level typically about 5.0 eV. However, the addition of PVK layer will increase the resistance of the device, and thus results in the decrease of the current passing through the device. It is well known that the brightness is proportion to the current density.

Table 2
EL performances of **PTF$_{10}$** and **PTF$_5$**

Device structure	λ_{max} (nm)	Voltage (V)	Current density (mA/cm^2)	Brightness (cd/cm^2)	QE$_{max}$ (%)
ITO/PEDOT/**PTF$_5$**/Ba/Al	463	6.8	59.2	202	0.60
ITO/PEDOT/PVK/**PTF$_5$**/Ba/Al	469	10.4	35.5	247	1.2
ITO/PEDOT/**PTF$_{10}$**/Ba/Al	446	6.4	182.3	867	0.83
ITO/PEDOT/PVK/**PTF$_{10}$**/Ba/Al	444	10.2	39.8	312	1.4

4. Conclusion

A series of hyperbranched triazine-containing polyfluorenes were synthesized by an "$A_2 + A'_2 + B_3$" approach based on Suzuki polycodensation. The increasing content of triazine branching unit is detrimental to the solubility of the hyperbranched products. The resulting polymers exhibit solvatochromism on the fluorescence spectra. Compared with linear polyfluorenes, the LUMO levels of the polymers were closer to the work function of typical cathode materials. External quantum efficiencies of 1.2% and 1.4% were achieved for **PTF$_5$** and **PTF$_{10}$** with the devices configuration of ITO/PEDOT/PVK/polymer/Ba/Al. These hyperbranched triazine-containing polyfluorenes, showing improved efficiencies and the distinct suppression of aggregation-induced green emission, are promising for blue light-emitting PLEDs application.

Acknowledgments

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