Hyperbranched Oxadiazole-Containing Polyfluorenes: Toward Stable Blue Light PLEDs

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Introduction. The discovery of electroluminescent poly(p-phenylene) (PPV) in 1990¹ has attracted considerable interest for the application in the display tech $nology^2$ for their merits, such as low-cost solution processing, good thermal stability, flexibility, and so on. Polymer light-emitting diodes (PLEDs) will require high quantum efficiency so as to satisfy its future commercialization. For improving the quantum efficiency, it is critical to achieve both efficient charge injection and balanced mobility of both charge carriers inside the electroluminescent (EL) polymers. It can be obtained by multilayer PLEDs fabricated with the additional holetransporting and electron-transporting layer besides the electroluminescent polymer layer. Alternatively, conjugated polymers with transport-balance properties of electrons and holes should be developed so as to obtain the single-layer PLEDs. In previous work, our group has developed a series of p-n diblock conjugated copolymers³ with improved EL properties by introducing a heteroaryl moiety, oxadiazole, to the backbone of conjugated polymers, and these polymers showed unique and interesting optical and electrochemical properties.⁴

Oligo- and polyfluorene (PFs) derivatives are promising blue light-emitting materials, for they exhibit excellent chemical and thermal stabilities and produce light with high quantum yields.⁵ Problems encountered with these materials are their tendency to aggregate and formation of excimers in the solid state leads to bluegreen emission and fluorescence quenching and the decrease in electroluminescence efficiency.⁶ To minimize this tendency for aggregation and avoid this detrimental excimer emission, several attempts have been made to use longer and branched side chains or bulky substituents,⁷ copolymerization techniques,⁸ dendrimer attachment,⁹ the end-capping of PFs with bulky groups,¹⁰ the cross-linking of PFs,¹¹ an oligomer approach,^{8,12} etc.

Since the highly branched and globular features can reduce or eliminate strong intermolecular interactions and aggregation, electroactive and light-emitting dendrimers and hyperbranched polymers are of current interest for developing efficient electroluminescent devices for displays and lighting and other photonic devices.¹³ Moreover, it is likely that PLEDs made of three-dimensional polymers should have improved stability and efficiency and also make the materials form good quality amorphous films.¹⁴ In this communication, to avoid the excimer formation and to improve the charge transport-balance properties of PFs, we introduce a heteroaryl moiety, oxadiazole, as a branching unit into the PF to make the polymers with hyperbranched structure. A novel " $A_2 + A'_2 + B_3$ " approach based on Suzuki polycodensation was developed for the hyperbranched polymer synthesis. The conventional methods to synthesize the hyperbranched polymers are the AB₂ and A₂ + B₃ approaches.¹⁵ The resulting hyperbranched oxadiazole-containing polyfluorenes show stable blue light emission even in the air at the elevated temperatures. Moreover, the PLED devices have been fabricated on the basis of the resulting copolymers, and the EL characteristics have been investigated.

Results and Discussion. a. Synthesis and Structural Characterization. A novel " $A_2 + A'_2 + B_3$ " Suzuki polycondensation was developed to synthesize the hyperbranched polymers (see Scheme 1).¹⁶ Since it has been 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. The Suzuki coupling polycondensation reaction is much better to be carried out in a dilute solution and relatively low temperature to reduce the possible crosslinking between branches; thus, the poor solubility of the polymer should be avoided. Three monomers, 2,7dibromo-9,9-dioctylfluorene (2), 9,9-dioctylfluorene-2,7bis(trimethylene boronate) (4), and 2-(4-bromophenyl)-5-(3,5-dibromophenyl)-1,3,4-oxadiazole (12), were synthesized according to literature procedures.¹⁷ The polymers were obtained in toluene with $Pd(PPh_3)_4$ (0.5 mol %) by taking 2, 4, and 12 in different molar ratios. Because random hyperbranched polymer synthesized by the one-pot Suzuki approach has a large number of bromo- and boronic ester end groups which are detrimental for light-emitting applications, the monofunctional monomers 2-bromo-9,9-dioctylfluorene (6) and 9,9-dioctylfluorene-2-boronic acid (7) were therefore used to cap the end groups. The reaction mixture containing monomers 2, 4, and 12 was stirred and refluxed for 5 days at the polymerization stage. Compounds 6 and 7 were then added to the reaction mixture together with additional $Pd(PPh_3)_4$ (0.5 mol %). The reaction was continued for further 2 days. Slightly yellow amorphous materials were obtained through standard workup. The molar ratio was found to be a key factor on the solubility of hyperbranched products. The solubility was poor in common organic solvents for hyperbranched polymers with higher contents of 12. The polymers in the molar ratios (monomer 2/4/12) of 5:6.5:1 (POF_5) and 10:11.5:1 (POF_{10}) are soluble in common organic solvents, e.g., toluene, THF, chloroform, and methylene chloride. However, under molar ratios of 0:3:2 (POF) and 3:3.5:1 (POF₃), the polymers cannot be soluble or soluble partially in common organic solvents.

The molecular structures of the polymers were characterized with high-resolution NMR spectroscopy and elemental analysis (see Supporting Information). In the proton NMR spectra, the characteristic signals of the branching units and fluorene units were observed at around $\delta = 8.3$ and 7.7 ppm, respectively. The ratios

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between the branching unit and fluorene of these two polymers can be estimated from NMR spectra, that is 9:1 for POF_5 and 17:1 for POF_{10} , respectively. The number-average molecular weight and the weightaverage molecular weight were determined by gel permeation chromatography (GPC) against standard polystyrene. The former for the polymers were 18 000 and 15 200, while the latter for the polymers were 47 000 and 37 000. The thermal properties of the hyperbranched polymers were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). No distinct glass transitions were observed for the polymers in the DSC curve (10 °C/min). TGA reveals good thermal stabilities of these polymers with the onset decomposition temperature (T_d) of 424.8 and 425.6 °C under nitrogen, respectively. They are much higher than those for the linear polyfluorene.¹⁸

b. Optical Properties. The photophysical characteristics of the polymers were investigated in solution and in the thin film. The UV-vis absorption and photoluminescence (PL) spectra for POF_{10} in toluene and in the film are shown in Figure 1. Solid films on quartz plates used for fluorescence were prepared by spin-coating with 10^{-3} mol/L CHCl₃ solution at 1500 rpm. The polymer shows the maximum absorptions in 376 nm, attributed to $\pi - \pi^*$ transition of the polymer. The PL spectrum in solution peaked at 418 nm. When in film, there is a slight red shift by about 7 nm, and the PL spectral pattern is similar to the one for polymer in solution. The spectroscopic results of POF₅ are almost the same. Figure 2 shows the normalized PL emission spectra of POF₁₀ in the film annealed at room temperature, 100, 150, and 200 °C for 1 and 3 h under a nitrogen atmosphere. After the polymers annealing at different temperatures for 1 h, there is nearly no change in the PL spectra. With the annealing time prolonged, the PL spectra show a little change at the range of above 460 nm at 150 and 200 °C. However, there was no additional band emerged, which would change the pure blue emission to an undesirable blue-green color.¹⁹ The

same phenomena were observed for POF_5 under the same condition. Interestingly, similar results can be seen after annealing in the air, shown in Figure 3. The normalized PL emission spectra of POF_{10} show very little characteristic broad band for the aggregation in the film annealed at room temperature, 100, 150 and 200 °C for 0.5 and 1 h in the air. To our best of knowledge, no similar stable polyfluorene derivatives annealed in the elevated temperatures in the air have been reported. Apparently, with the introduction of oxadiazole ring as the branching unit, the red-shift phenomena of polyfluorenes are reduced markedly, and the aggregation and excimer-forming of polymer chains can be avoided in the hyperbranched fluorene–oxadiazole copolymers.

The PL quantum yields ($\Phi_{\rm F}$) of POF₅ and POF₁₀ in toluene were measured with 9,10-diphenylanthracene as a reference standard (cyclohexane solution, $\Phi_{\rm F} =$ 0.9).²⁰ The quantum efficient yield reaches 0.46 and 0.54, respectively, which is similar to the hyperbranched polyfluorene in the previous report.²¹ The absolute quantum efficiencies ($\eta_{\rm qe}$) of solid films were measured



Figure 1. Absorption and emission spectra of the POF_{10} in solution (toluene) and in thin film.



Figure 2. Photoluminescent spectra of POF₁₀ in thin films annealing at 100, 150, and 200 °C: (a) for 1 h; (b) for 3 h (under N₂).



Figure 3. Photoluminescent spectra of POF₁₀ in thin films annealing at 100, 150 and 200 °C: (a) for 0.5 h; (b) for 1 h (in air).

Table 1. EL Performances of POF10 and	and PUF5
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device structure	$\lambda_{\max} \left[nm \right]$	voltage [V]	current density [mA/cm ²]	brightness [cd/cm ²]	QE max [%]
ITO/PEDOT/POF ₁₀ /Ba/Al	423	10.4	24.9	63	0.44
ITO/PEDOT/PVK/POF ₁₀ /Ba/Al	446	9.6	6.0	51	1.5
ITO/PEDOT/POF ₅ /Ba/Al	423	11.0	179.1	150	0.15
ITO/PEDOT/PVK/POF ₅ /Ba/Al	446	8.6	1.2	7	1.0

by the integrating sphere, which reaches 0.32 and 0.42 for POF_5 and $\mathrm{POF}_{10}.$

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/Ba (4 nm)/Al (150 nm). The EL spectra of the two polymers are almost similar to the PL spectra of the corresponding polymer films. The EL performances of both POF₁₀ and POF₅ are concluded in Table 1. For POF₁₀ the maximum brightness is 165 cd/m² at 12 V, while it reaches 1150 cd/m² at 14 V after adding PVK layer. POF₅ has similar results. Apparently, when the hole-transporting layer PVK was deposited on the PEDOT, the external maximum quantum efficiencies improved a lot.

Conclusion. A novel " $A_2 + A'_2 + B_3$ " approach based on Suzuki polycodensation was developed for the hyperbranched polymer synthesis. The polymer films exhibited very stable blue light emission even after being annealed in the elevated temperatures in the $N_{\rm 2}$ and air.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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