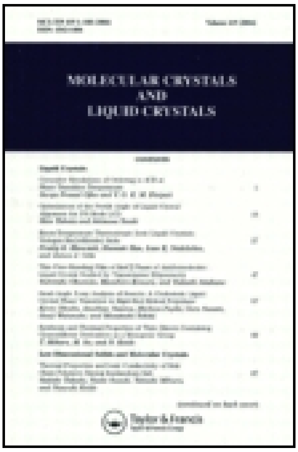

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Synthesis and Photophysical Properties of a Blue Light-Emitting Hyperbranched Poly(fluorene)

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*A novel hyperbranched conjugated poly(fluorene) (Hyper-PDHF) was obtained through the Suzuki coupling polymerization. Hyper-PDHF has good solubility in common organic solvents and showed good thermal stability up to 428°C with less than 5 wt% weight loss. The photophysical properties of Hyper-PDHF in solution and net solid film are inspected and compared with poly(di-*n*-hexylfluorene) (PDHF) having linear structure. An absorption maximum of Hyper-PDHF film was determined at 334 nm which was far blue shifted than that of linear PDHF film (381 nm). Hyper-PDHF showed absolute blue photoluminescence (PL) peak at 418 nm with 394 and 444 nm as shoulder peaks. Hyper-PDHF showed also high fluorescence quantum yield as about $\Phi_{sol} = 0.81$. In addition, Hyper-PDHF film exhibited almost no longer wavelength emission peaks even the film was annealed at 80°C for 1 hr with illuminating UV (365 nm) in air condition. The high PL efficiency and no aggregate or excimer emission of Hyper-PDHF results from the inhibition of intramolecular or intermolecular interaction by the introduction of the hyperbranched network into the poly(fluorene) backbone.*

Keywords Hyperbranched polymer; poly(fluorene); blue light-emitting polymer

Introduction

Conjugated polymers have emerged as viable electronic materials for numerous applications. In particular, the current activities in the development of light-emitting diode (LED)-based conjugated polymers have attracted much attention. Numerous kinds of conjugated polymers such as poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenylene) (PPP), poly(fluorene) (PF), and poly(thiophene) (PT) have been developed for efficient light emission, color tuning or charge transfer [1–3]. Among them, poly(fluorene) (PF) derivatives have been intensively studied recently as the blue light-emitting materials due to its good thermal stability and high photoluminescence (PL) efficiency [4]. However, the appearance of additional long wavelength emissions caused by aggregate or excimer formations in the PF film after thermal annealing is a big problem to be used as a blue light-emitting material [5,6]. To overcome such undesirable emissions of PF derivatives by aggregates or excimers, Miteva *et al.*, have reported end-capped PF homopolymer with triphenylamine (TPA) moieties and Ego *et al.*, also have studied bulky TPA substituted PF derivatives at 9-position to increase solubility and suppress aggregation or excimer formations in PF films [7,8].

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So far, the majority of synthesis on polymers LEDs has been focused on linear one-dimensional conjugated polymer. Although a few of two-dimensional conjugated polymer, such as hyperbranched conjugated polymer have been reported to exhibit comparable charge transferring and processing properties to their linear counterparts, two-dimensional conjugated polymeric light materials have been less discussed in the literature [9–11]. The new structure of hyperbranched polymer is expected to produce superior color tunability, charge transferring efficiency and processing properties than conventional linear emitting polymers.

In this paper, we report on the synthesis and light-emitting properties of novel hyperbranched poly(fluorene) (Hyper-PDHF) end-capped by the triphenylamine (TPA) group. Through the hyperbranched network of PF polymer, we successfully obtained pure blue PL and electroluminescene (EL) emission without aggregate or excimer emissions.

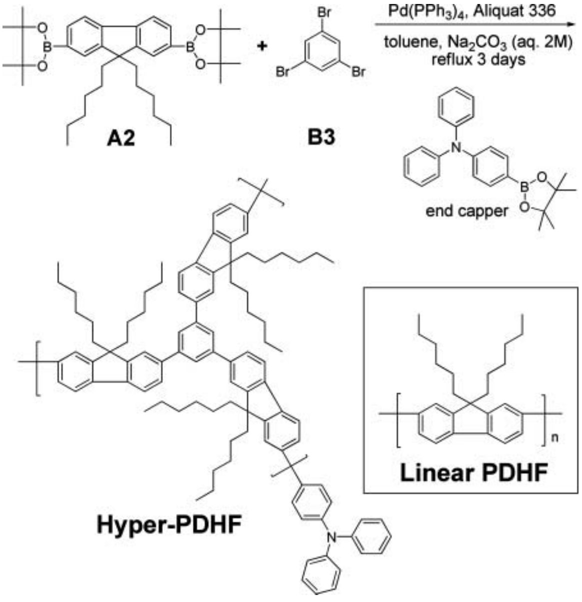
Experiments

Materials and Measurements

2,7-Dibromofluorene, 1-bromohexane, *t*-butyllithium (1.7 M in hexane), 1,3,5-tribromobenzene, 4-bromo-*N*,*N*-diphenylaniline, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Aliquat® 336 were purchased from Aldrich. Tetraki(triphenylphosphine)palladium (0) was obtained from DNF Solution Co. Solvents with analytical grade were used during the whole experiments and all chemical were used without further purification. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. The number- and weight-average molecular weight of the polymer was determined by gel permeation chromatography (GPC) on Waters GPC-150C instrument using tetrahydrofuran (THF) as an eluent. UV-vis spectra were measured by using a Jasco V-530 UV/vis Spectrometer. PL spectra were measured by using Spex Fluorolog-3 spectrofluorometer. For the polymer LED measurements, EL spectra were obtained with a Minolta CS-1000. The current-voltage-luminescence characteristics were measured with a current-voltage source (Keithley 238) and a luminescence detector (Minolta LC-100).

Polymerization of Hyperbranched Poly(Fluorene) (Hyper-PDHF)

An A2 type monomer, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-dihexylfluorene, was synthesized from 2,7-dibromofluorene by successive alkylation and boration reaction according to procedure outlined in the literature [12]. Into 100 mL two-neck flask 1.56 mmol of 1,3,5-tribromobenzene (B3 type monomer) and 1.56 mmol 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-dihexylfluorene in 25 mL of anhydrous toluene were added. Water soluble Pd(0) complex (0.02 g), tetrakis(triphenylphosphine)palladium (1 mol%) was transferred into the mixture in dry box. Subsequently, 2M aqueous sodium carbonate (5.4 mL, 10.7 mmol) and the phase transfer catalyst, Aliquat® 336 (several drops) in toluene purged under nitrogen for 1h was transferred via cannula. The reaction mixture was stirred at 80°C for 3 days and then the excess amount of *N*,*N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, the end capper, dissolved in 1 mL of anhydrous toluene was added and stirring continued for 12 h. The reaction mixture is cooled to about 50°C, added slowly to a vigorously stirred mixture of 200 mL of methanol. The polymers are collected by filtration and re-precipitation from methanol and acetone. The polymers are purified further by washing for 2 day in a Soxhlet apparatus with methanol and acetone to remove oligomers and catalyst residues. The polymer yield was 68%. ^{1}H-NMR ($CDCl_3$, ppm) δ 7.91–7.77 (br m, 6H, Ar H), 7.70–7.31 (br m, 3H, Ar H), 2.10–1.23 (br m, 4H, Aliphatic H), 1.21–0.50 (br m, 22H, Aliphatic H).



Scheme 1. A synthetic route of Hyper-PDHF and a chemical structure of linear PDHF.

Results and Discussion

A novel hyperbranched conjugated poly(fluorene) (Hyper-PDHF) was obtained through the Suzuki coupling polymerization using A2 type (2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-dihexylfluorene) and B3 type (1,3,5-tribromobenzene) monomers. To increase the hole transporting ability and efficiency of Hyper-PDHF, end-capping was done using triphenylamine moiety as shown in Scheme 1. To compare the property of Hyper-PDHF with poly(fluorene) having linear polymer structure, we also prepared the poly(di-*n*-hexylfluorene) (linear PDHF). Synthesized Hyper-PDHF showed good solubility in common organic solvents and exhibited good thermal stability up to 428°C with less than 5 wt% weight loss. In case of linear PDHF, T_g was measured as 92°C, which is well match to the previously reported data [6]. However Hyper-PDHF, no T_g was detected during DSC measurement up to 250°C. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of Hyper-PDHF was determined with GPC and found to be as 8,500 and 32,000, respectively, with polydispersity index (PDI) as 3.76. The optical properties of the newly synthesized Hyper-PDHF were investigated UV-vis absorption spectroscopy. Figure 1 shows the absorption spectra of Hyper-PDHF and linear PDHF films on quartz plates. Hyper-PDHF showed a strong absorption with λ_{max} at 334 nm, which was more than 50 nm blue-shifted from that of linear PDHF (λ_{max} at 381 nm). This kind of large shift of absorption peak from linear PDHF to Hyper-PDHF is clearly to be associated with inhibition of stacked structure assisted by hyperbranched structure of polymer backbone. Because the stacking of backbone of poly(fluorene) derivatives in the solid state can bring unwanted emissions at longer wavelength regions, the prevention of such

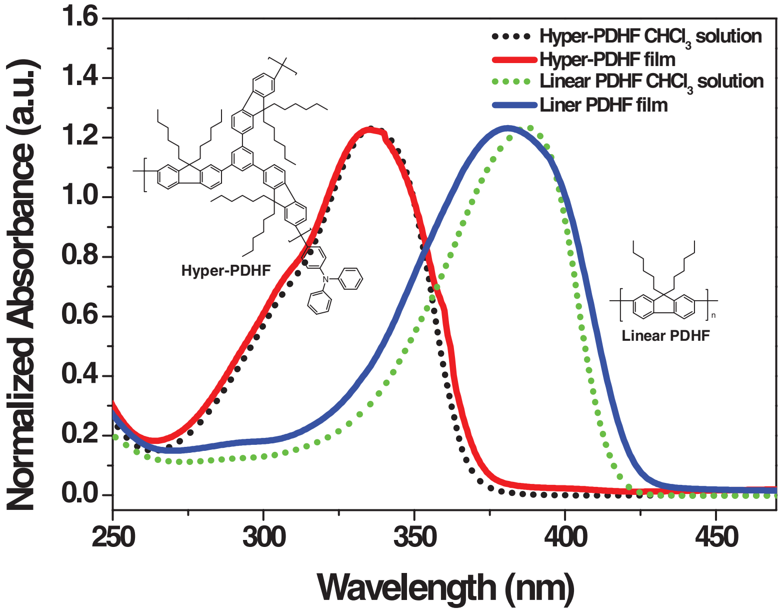


Figure 1. UV-vis absorption spectra of Hyper-PDHF and linear PDHF in the chloroform solution and in thin film.

packing in film state is important in achieving pure blue emission. The optical band-gap was estimated from the onset position of the absorption spectrum, and Hyper-PDHF and linear PDHF showed 3.28 and 2.93 eV, respectively. With the aid of hyperbranched network structure, the electron density of Hyper-PDHF polymer has decreased, and this increases the band-gap compared with its linear analogue, PDHF.

The photoluminescence (PL) spectra (Figure 2) showed a drastic change of emission color by the hyperbranched structure of poly(fluorene). Theses PL spectra were recorded with the excitation wavelength corresponding to the maximum absorption wavelength of the polymer. The PL spectrum of linear PDHF showed the emission maximum at 423 nm with shoulder peaks at 447 nm, 477 nm, and 510 nm, respectively, which is well matched with the previously reported data [6]. Such shoulder peaks caused by the aggregate or excimer formation from the interaction of the polymer chains. Problem is that the intensities of these longer wavelength emissions could be increased when the polymer film is annealed or is passed by current in EL device. The Hyper-PDHF film shows a maximum emission peak at about 418 nm, which is similar to that of linear PDHF. However, shoulder peaks of Hyper-PDHF were found to be at 394 nm (even blue shifted than emission maximum peak), 444 nm, and 478 nm, respectively. In addition, the intensities of shoulder peaks of Hyper-PDHF at longer wavelength are much weaker than that of linear PDHF. Overall, Hyper-PDHF exhibited more blue emission than linear PDHF. Clearly, the inhibition of excimer formation by the introduction of the hyperbranched network into the poly(fluorene) backbone brought about the pure blue emission. We also investigate the Hyper-PDHF whether it show both excimer and aggregate formation upon thermal annealing. The Hyper-PDHF film and linear PDHF film are heated at 80°C for 1 hr with illuminating UV (365 nm) and then, we measured the PL. We found that the dramatic effect of hyperbranched poly(fluorene) system from PL emissions of thermal and UV annealed samples as shown in Figure 2.

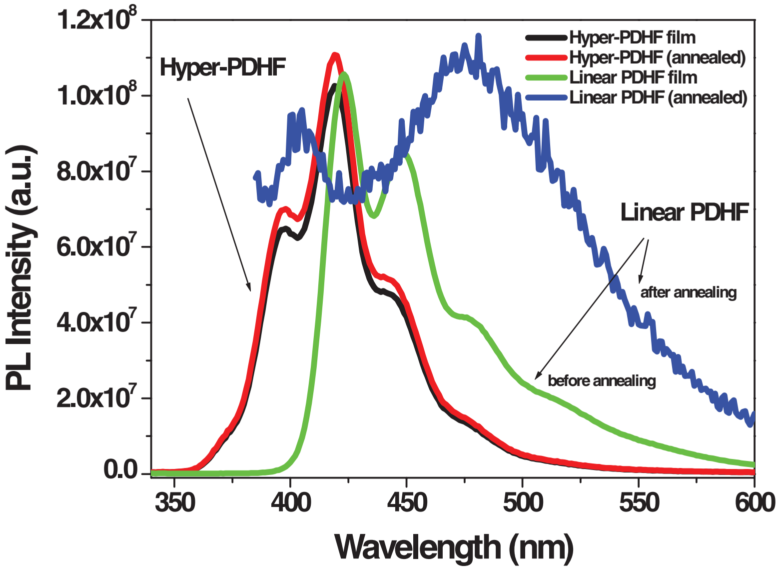


Figure 2. Photoluminescene (PL) spectra of Hyper-PDHF and linear PDHF thin films (pristine and annealed films at 80°C for 1 hr with illuminating UV (365 nm)).

The annealed linear PDHF shows severe longer wavelength emissions might be caused by aggregate or excimer formation. However, Hyper-PDHF shows almost no changes of emission spectra after the annealing treatments except a little bit increased intensities of shoulder peaks.

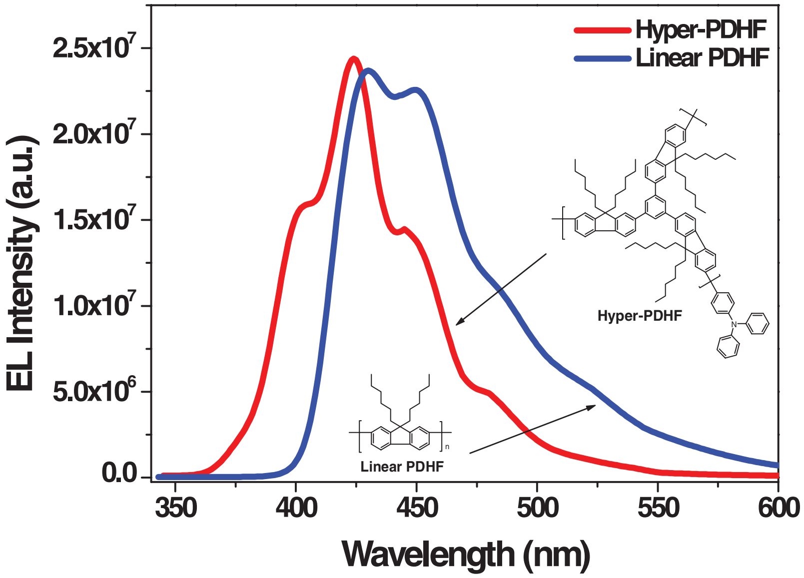


Figure 3. Electroluminescence (EL) spectra of LED devices of Hyper-PDHF and linear PDHF with a configuration of ITO/PEDOT/polymer/Al.

To test the effect of hyperbranched system in real devices, we fabricated EL devices with ITO/PEDOT (40 nm)/polymer (80 nm) (Hyper-PDHF or linear PDHF)/Al (100 nm) configuration. Firstly, a cleaned ITO glass was coated with PEDOT as a hole-injection layer. The remaining water and solvent were removed in vacuum at 150°C for 1hr. Each polymer solution (15 mg/mL in anhydrous toluene) was then spin-coated onto ITO glass coated with PEDOT and polymer layer was annealed at 80°C for 1 hr to remove the residual solvent. Finally, Al was thermally evaporated as a cathode. The EL spectra of the Hyper-PDHF and linear PDHF are shown in Figure 3. The EL emission maximum of the Hyper-PDHF appears at about 426 nm (with shoulder peaks at 396 nm and 446 nm). The EL spectrum of the Hyper-PDHF is nearly same as compared the PL spectrum of the polymer. However, linear PDHF exhibit significantly increased longer wavelength emissions due to aggregate or excimer formations. These results indicate that the hyperbranched structure of poly(fluorene) could be a good candidate for the stable blue-emitting material. Device optimizations by replacing the cathode electrode as LiF/Al or Ca/Al enable us to increase the EL efficiency of Hyper-PDHF polymer and the study of long term stability of EL devices are in progress and will be published elsewhere.

Conclusion

In this paper, we have synthesized the novel hyperbranched poly(fluorene) (Hyper-PDHF) through the Suzuki coupling polymerization. To inhibit the longer wavelength emissions of blue-emitting poly(fluorene)s caused by aggregate or excimer formation, the hyperbranched structure was introduced into poly(fluorene) backbone by using A2 and B3 type monomers. Prepared Hyper-PDHF showed good solubility in common organic solvents and also exhibited excellent thermal stability up to 428°C. Most importantly, Hyper-PDHF exhibited almost no longer wavelength emissions by aggregate or excimer formation even when its film was annealed at 80°C for 1 hr with illuminating UV (365 nm). The maximum emission peak of Hyper-PDHF was found at 418 nm as pure blue light. However, linear type of poly(fluorene), PDHF, showed critical longer wavelength emissions due to aggregate or excimer formation. We strongly propose that the hyperbranched poly(fluorene) system provides good opportunities to solve the low solubility and longer wavelength emissions of linear poly(fluorene) derivatives.

Acknowledgement

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