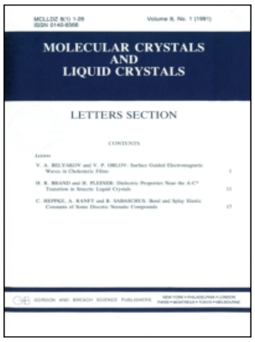

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# Synthesis and light-emitting properties of a fluorene containing hyperbranched conjugated poly(phenylene vinylene)

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**ABSTRACT**
A novel fluorene containing hyperbranched conjugated poly (phenylene vinylene) (Hyper-PFPPV) was obtained through the Wittig polycondensation polymerization. Hyper-PFPPV has good solubility in common organic solvents and showed good thermal stability up to 369°C with less than 5wt% weight loss. The photophysical properties of Hyper-PFPPV in solution and net solid film are inspected and compared with fluorene containing linear poly(1,4-phenylene vinylene) (PFPPV). An absorption maximum of Hyper-PFPPV film was determined at 385 nm which was far blue shifted than that of linear PFPPV film (425 nm). Hyper-PFPPV showed blue photoluminescence (PL) peak at 461 nm. In addition, Hyper-PFPPV film exhibited almost no long wavelength emission peaks even the film was annealed at 80°C for 1 hr in air condition. High PL efficiencies ($\Phi_{sol} = 0.78$ and $\Phi_{film} = 0.75$) and no aggregate or excimer emission of Hyper-PFPPV are due to the inhibition of intramolecular or intermolecular interaction by the introduction of the hyperbranched network into the fluorene containing poly(phenylene vinylene) backbone.

**KEYWORDS**
Hyperbranched polymer; fluorene; Wittig polycondensation

## Introduction

$\pi$-Conjugated polymers have attracted more considerable interest due to their electronic and photonic application, such as organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), photovoltaics, and organic lasers as well as other organic devices [1,2]. Numerous kinds of conjugated polymers such as poly(*p*-phenylene vinylene) (PPV) [3], poly(*p*-phenylene) (PPP) [4], poly(fluorene) (PF) [5], and poly(thiophene) (PT) [6] have been developed for efficient light emission, color tuning or charge transfer in OLED device applications. Among them, poly(*p*-phenylene vinylene) (PPV) and its derivatives are the most promising and extensively studied polymers due to their good mechanical and optical properties. However, PPV derivatives were usually limited as green or red-emitting materials due to their effective $\pi$-conjugation lengths. Therefore, the blue light-emitting polymers has been sought in conjugated polymers having a high HOMO-LUMO energy band gap, such as partially eliminated PPV [7], PPP, PF and copolymers containing confined conjugated segments [8]. Among them PFs and fluorene containing copolymers have extremely high luminescence efficiencies in solution, which are largely maintained in the polymer films [9]. As a result, PFs

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and fluorene containing copolymers haven been intensively studied recently as the blue light-emitting materials. But they showed rather poor processability and mechanical properties and high operating voltage in light emitting diode devices.

So far, the majority of synthesis on polymer 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 [10–12]. 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 the synthesis and light-emitting properties of a fluorene containing hyperbranched conjugated poly(phenylene vinylene) (Hyper-PFPPV) made by A2 and B3 type monomers. The photophysical properties of Hyper-PFPPV were systematically compared with the conjugated linear PFPPV polymer.

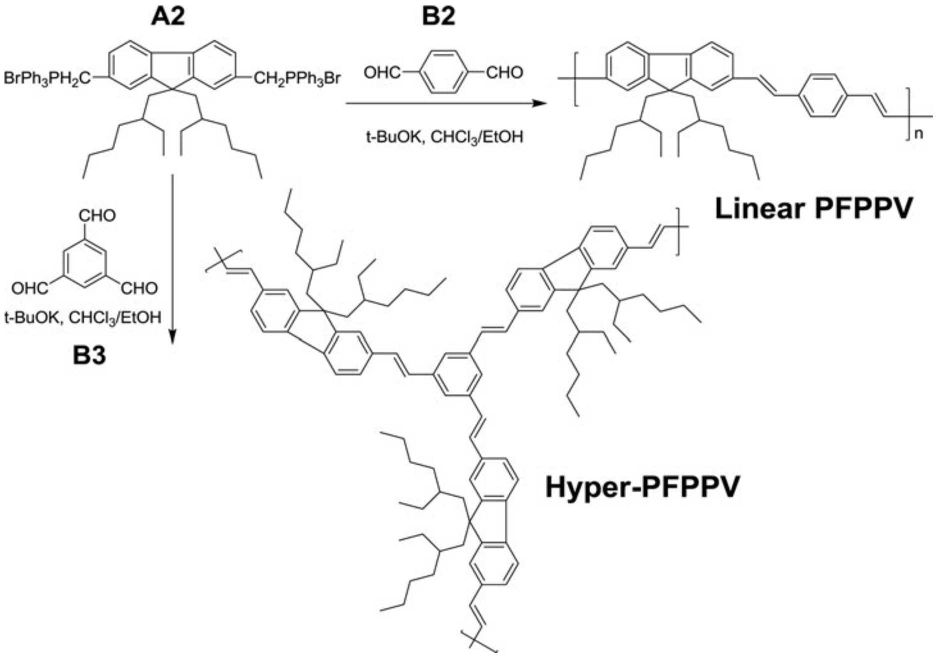
## Experiments

### Materials and measurements

Fluorene, 2-ethylhexyl bromide, triphenylphosphine ($PPh_3$), benzene-1,3,5-tricarbaldehyde, terephthalaldehyde, paraformaldehyde, hydrogen bromide solution, potassium *tert*-butoxide and *n*-butyl lithium were purchased from Aldrich. 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 JEOL JNM-ECX 400 spectrometer. Thermogravimetric analysis (TGA) was performed under nitrogen at a heating rate of 10°C/min with SINCO TGA N-1500 analyzer. The number- and weight-average molecular weight of the polymer was determined by gel permeation chromatography (GPC) on YOUNGLIN GPC-9100 instrument using tetrahydrofuran (THF) as an eluent. UV-vis spectra were measured by using a HITACHI U-300 UV-vis spectrometer. PL spectra were measured by using SHIMADZU RF-5300 spectrofluorometer. For the polymer LED measurements, electroluminescence (EL) spectra were obtained with a Konica Minolta CS-1000. The current-voltage-luminescence characteristics were measured with a current-voltage source (Keithley 2400) and a luminescence color meter (Konica Minolta CS-100a).

### Polymerization of Hyper-PFPPV

An A2 type monomer, ((9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis(methylene))bis(bromotriphenylphosphorane) was synthesized from fluorene by successive 2-ethylhexyl alkylation, bromomethylation and bisphosphonium salt formation reaction according to procedure outlined in the literature [9]. A solution of 1.0 g (0.9 mmol) of ((9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis(methylene))bis(bromotriphenylphosphorane) (A2) and 0.15 g (0.9 mmol) of benzene-1,3,5-tricarbaldehyde (B3) in 10 mL of chloroform was prepared. Potassium *ter*-butoxide (0.62 g, 5.5 mmol) was dissolved in 10 mL of ethanol, and this base solution was carefully dropped into the solution of monomers. After 48 h, the polymer product was precipitated from methanol. The crude polymer was filtered and then purified by a Soxhlet extraction in methanol for 3 days. The polymer yield was 0.67 g (53.2%). $^1$H-NMR ($CDCl_3$, ppm) $\delta$ 8.03–7.88, 7.77–7.03 (br m, 9H, aromatic H), 6.91 (br d, 2H, vinylic H), 2.14 (br s, 1H aliphatic H), 1.61–0.36 (br m, 32 H, aliphatic H).



**Scheme 1.** A synthetic route of Hyper-PFPPV and linear PFPPV.

## Results and discussion

A novel fluorene containing hyperbranched conjugated poly(phenylene vinylene) (Hyper-PFPPV) was obtained through the Wittig polycondensation polymerization using A2 type ((9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis(methylene))-bis(bromotriphenylphos phorane) and B3 type (benzene-1,3,5-tricarbaldehyde) monomers. To compare the property of Hyper-PFPPV with linear conjugated polymer, we have prepared the poly[9,9-di(2-ethylhexyl)-2,7-fluorenediylvinylene-*alt*-1,4-phenylene vinylene] (linear PFPPV) as shown in Scheme 1. Hyper PFPPV showed excellent solubility in common organic solvents and exhibited good thermal stability up to 369°C with less than 5wt% weight loss from TGA study. The number-average molecular weight ($M_n$) and the weight-average molecular weight ($M_w$) of Hyper-PFPPV were determined by GPC and found to be as 5,700 and 14,000, respectively, with polydispersity index (PDI) as 2.54. Figure 1 shows the FT-IR spectra of Hyper-PFPPV and linear PFPPV. Sharp absorption peaks at 960–963 $cm^{-1}$ corresponding to the out-of-plane bending mode of the trans-vinylene in both PFPPV polymers have appeared [9]. This proves the formation of a vinylene double bond, and consequently the polymerization reactions have been successful. The optical properties of Hyper-PFPPV and linear PFPPV were investigated UV-vis absorption spectroscopy. Figure 2 shows the absorption spectra of Hyper-PFPPV and linear PFPPV in the chloroform solution and in thin film on quartz plates. Hyper-PFPPV exhibited a strong absorption at 385 nm, which was more than 40 nm blue shifted from that of linear PFPPV ($\lambda_{max}$ at 425 nm). This kind of large shift of absorption peak of Hyper-PFPPV is clearly caused by the inhibition of stacked structure assisted by hyperbranched structure of polymer backbone. Because the packing of the conjugated polymer backbone in the solid state can bring the unwanted emission such as excimer or aggregate emission, the prevention of such packing in film state is important in achieving the pure emission. The optical bandgap was calculated from the onset position of the absorption spectrum. Hyper-PFPPV and linear PFPPV showed 2.86 and 2.58 eV, respectively. Due to the hyperbranched structure, the

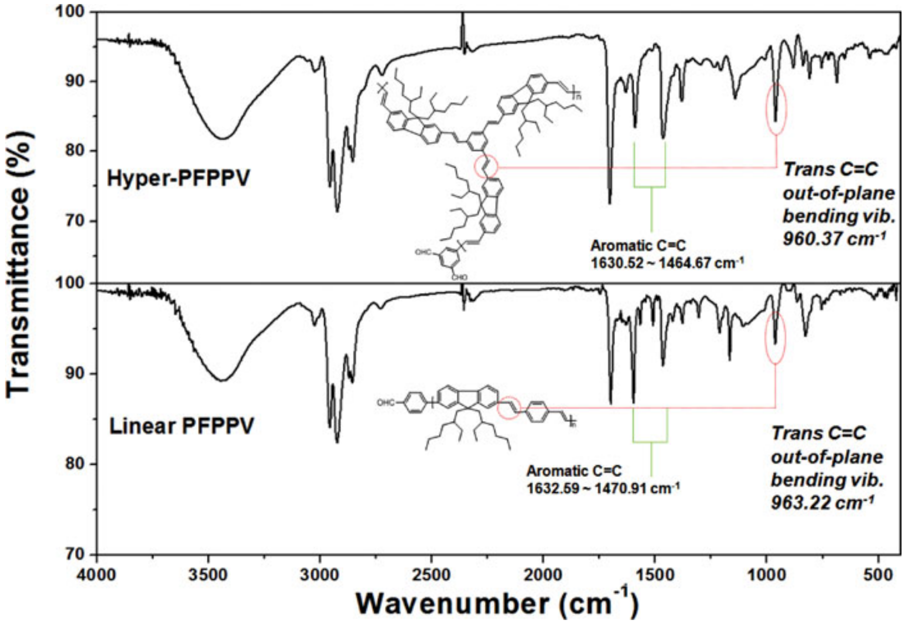


**Figure 1.** FT-IR spectra of Hyper-PFPPV and linear PFPPV in KBr pellets.

electron density of Hyper-PFPPV polymer has decreased, therefore the band-gap of Hyper-PFPPV is increased compared with that of linear PFPPV. The PL spectra (Figure 3 (a) and (b)) showed a drastic change of emission color by the hyperbranched structure of Hyper-PFPPV. The PL spectrum of linear PFPPV film showed the emission at 509 nm with a shoulder peak at 547 nm. Such a shoulder peak is usually happened by the aggregate or excimer formation through the interaction of the polymer chains. Problem is that the intensity of these undesired emissions could be increased when the polymer film is thermally annealed. In addition, PL emission maximum of linear PFPPV film is considerably shifted to the longer wavelength regions than that of PFPPV solution sample. This also means that intermolecular stacking of

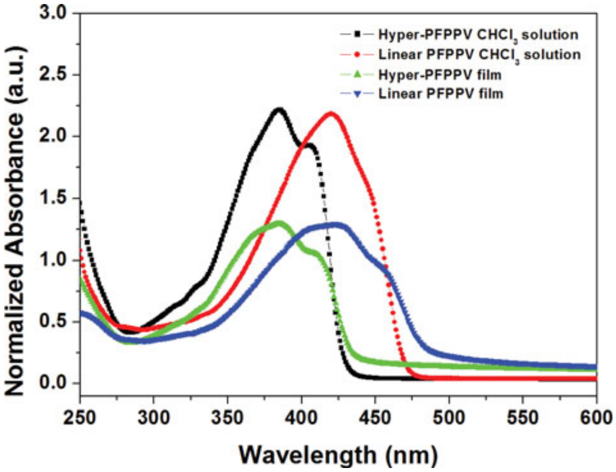


**Figure 2.** UV-vis absorption spectra of Hyper-PFPPV and linear PFPPV in the chloroform solution and in thin film.

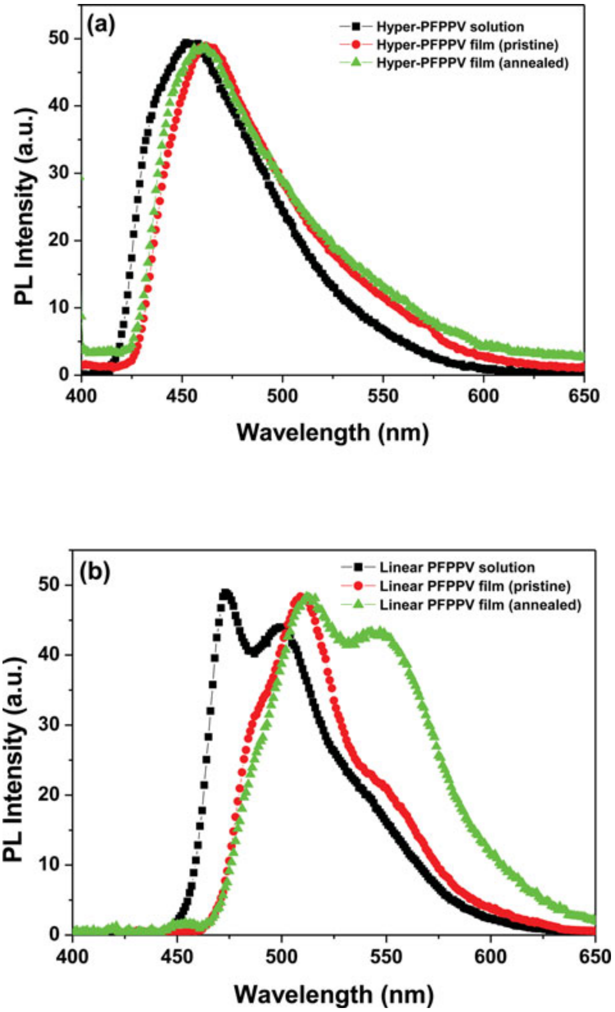


**Figure 3.** PL spectra of (a) Hyper-PFPPV and (b) linear PFPPV in the chloroform solution and thin films (pristine and annealed films at 80°C for 1 hr).

linear PFPPV in film state is happened significantly. However, Hyper-PFPPV shows a maximum emission peak at about 461 nm, which is far more blue-shifted than that of linear PFPPV. Shoulder peaks were not observed in Hyper-PFPPV film. This proves that the inhibition of excimer or aggregate formation by the introduction of the hyperbranched network into the fluorene based poly(phenylene vinylene) backbone brought about the such blue emission. The emission maximum differences between Hyper-PFPPV solution and film are much smaller than that of linear PFPPV about less than 10 nm. This also support that intermolecular stacking is really interrupted in Hyper-PFPPV polymer.

Hyper-PFPPV also showed highly fluorescent emissions in both solution and film state. Therefore, we have investigated PL quantum efficiencies of Hyper-PFPPV and linear PFPPV to compare their relationships between polymer structure and PL efficiency. The PL quantum efficiency of Hyper-PFPPV in chloroform solution was determined twice more, using a dilute quinine sulfate as a standard (ca. $1 \times 10^{-5}$ M solution in 0.10 M $H_2SO_4$) [13]. The measured values were then averaged. The PL efficiency of quinine sulfate in 0.1 $H_2SO_4$ solution was taken to be 0.55 at 365 nm excitation, and the refractive indices of the dilute polymer solutions in chloroform and 0.10 M $H_2SO_4$ were taken to be 1.45 and 1.33, respectively. Using these values, the quantum yields of Hyper-PFPPV was determined as $\Phi_{sol} = 0.78$ which are higher than linear PFPPV ($\Phi_{sol} = 0.62$) and those of other linear PPV derivatives. In considering the utility of Hyper-PFPPV for applications in thin film devices, the film PL quantum efficiency is more meaningful than the solution value. The film PL quantum efficiencies were measured using an optically dense configuration, and diphenyl anthracene (dispersed in a PMMA film at a concentration of less than $10^{-3}$ M, assuming a PL efficiency of 0.83) as the standard [14]. Hyper-PFPPV showed very high film PL quantum efficiency of $\Phi_{film} = 0.75$. This value is much higher than linear PFPPV ($\Phi_{film} = 0.51$) and those of other linear PPV derivatives. Chain packing and conjugation are more effectively interrupted in the hyperbranched structure than linear system, which results in the formation of amorphous polymer thin films for an increased luminescence.

We also investigate the Hyper-PFPPV film whether it show excimer or aggregate formation upon thermal annealing. The Hyper-PFPPV and linear PFPPV film are heated at 80°C for 1 hr, respectively and then we measured the PL spectra again. We found that the dramatic effect of hyperbranched backbone system from PL emissions of thermal annealed samples as shown in Figure 3 (a) and (b). The annealed linear PFPPV shows a severe unwanted emission might be caused by aggregate or excimer formation. However, Hyper-PFPPV shows almost no change of a emission spectrum even after the thermal treatment except a little bit increased peak intensity.

To test the effect of hyperbranched structure in real devices, we fabricated LEDs with ITO/PEDOT (40 nm)/polymer (80 nm) (Hyper-PFPPV or linear PFPPV)/LiF/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 1 hr. 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-PFPPV and linear PFPPV are shown in Figure 4. Unexpectedly, the EL spectrum of the Hyper-PFPPV is completely different from PL spectrum. Usually, EL spectrum of conjugated polymer is nearly same as compared the PL spectrum of the polymer. In our previous work, hyperbranched

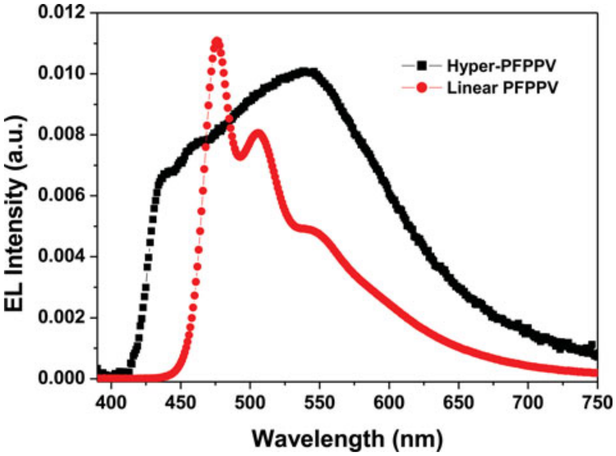


**Figure 4.** EL spectra of LED devices of Hyper-PFPPV and linear PFPPV with a configuration of ITO/PEDOT/polymer/LiF/Al.

polyfluorene showed almost similar EL spectrum as compared with PL spectrum [12]. However, Hyper-PFPPV showed extremely red-shifted EL maximum at 541 nm and very broad emission even cover the whole visible spectrum ranges. It looks like almost white emission to naked eyes. We fabricated same LED devices more than three times using Hyper-PFPPV. All EL spectra from each LED devices shows very similar maximum emission peak with broad pattern as in Figure 4. The origin of this big difference between PL and EL spectra of Hyper-PFPPV is still ambiguous. Deep investigations about the conditions of Hyper-PFPPV film fabrication are currently in progress to reveal the reason of almost white EL spectrum of Hyper-PFPPV in LED devices.

## Conclusion

We have synthesized a novel fluorene containing Hyper-PFPPV through the Wittig polycondensation route. To inhibit excimer or aggregate emissions caused by the polymer chain interaction, the hyperbranched structure was designed by using A2 and B3 type monomers. Hyper-PFPPV showed good solubility in common organic solvents and also exhibited excellent thermal stability up to 369°C. Hyper-PFPPV showed larger band gap as 2.86 eV than that of linear PFPPV (2.58 eV). The maximum emission peak of Hyper-PFPPV was found at 461 nm as almost pure blue light. In addition, Hyper-PFPPV exhibited no undesired emissions by aggregate or excimer formation even when its film was annealed at 80°C for 1 hr. We propose that the fluorene containing hyperbranched poly(phenylene vinylene) system is a good candidate as a highly luminescent conjugated polymer without unwanted emissions caused by excimer or aggregate formation.

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