

## Stable blue light emitting polyfluorenes with good solution processibility

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### Abstract

New polyfluorene derivatives, poly[9,9-bis(4'-n-octyloxyphenyl)] fluorene (PAPF-8) and poly[9,9-bis(4'-(2'',7''-dimethyloxy)phenyl)] fluorene (PAPF-10) were synthesized from the monomers, 2,7-dibromo-9,9-bis[4' (2''-ethylhexyloxy)benzene] fluorene and 2,7-dibromo-9,9-bis[4' (2'',7''-dimethyloxy)benzene]fluorene through the Ni(0) mediated polymerization. The copolymers were characterized using FT-IR spectroscopy, UV-vis spectroscopy, TGA, photoluminescence (PL) & electroluminescence (EL) spectroscopy, elemental analysis, and molecular weight studies. The synthesized POPF-8 and POPF-10 showed a pure blue emission without any spectral change upon thermal annealing and EL device operation.

### 1. Introduction

Polyfluorenes are promising new materials for blue light emitting diodes because of their high photoluminescence (PL) quantum efficiencies and thermal stability.[1-3] However, troublesome long wavelength emission in polymer film of polyfluorenes on heating during device formation or operation has been the crucial problem for practical applications. Studies on the structures and the optical properties of polyfluorene derivatives have revealed that the long wavelength emission is originated from the excited state interaction (excimer) rather than ground state interaction (aggregate).[4, 5] There have been several approaches to suppress excimer emission including the copolymerization or the end-capping with anthracene, the attachment of bulky aryl groups at the 9-position of the fluorene, and so on.[4-6]

The spiro structure in spirobifluorene is also believed to be an effective way to reduce the interchain interaction which leads to broadening of emission spectrum. A 9,9-spirobifluorene based conjugated polymer, poly(9,9'-spirobifluorene-2,7-

diyl) has been reported by Kreuder *et al.*, to suppress the excimer emission.[7] Yu *et al.* have prepared the alternating copolymer of the 9,9'-spirobifluorene and the fluorene, which showed blue emission with improved solubility in common organic solvents.[8] M? len *et al.* also demonstrated the stable blue emission by attaching polyphenylene dendron side chains to PFs to prevent aggregation.[9] Carter *et al.* reported similar results by using dendron substituents.[10] Although the excimer emission became smaller than the previous results, it seems that the small excimer emission still looks troublesome to obtain a pure blue emission.

In this article, we introduced alkoxyphenyl groups in 9-position of fluorene to suppress the excimer emission. Alkoxyphenyl substituted polyfluorenes (PAPF)s, poly[9,9-bis(4-n-octyloxyphenyl)fluorene-2,7-diyl] (PAPF-8) and poly[9,9-bis(4-(3'',7''-dimethyloxy)phenyl)fluorene-2,7-diyl] (PAPF-10), as a blue light emitting polymer with high color purity and good solubility were synthesized and their light-emitting properties were characterized.

### Scheme

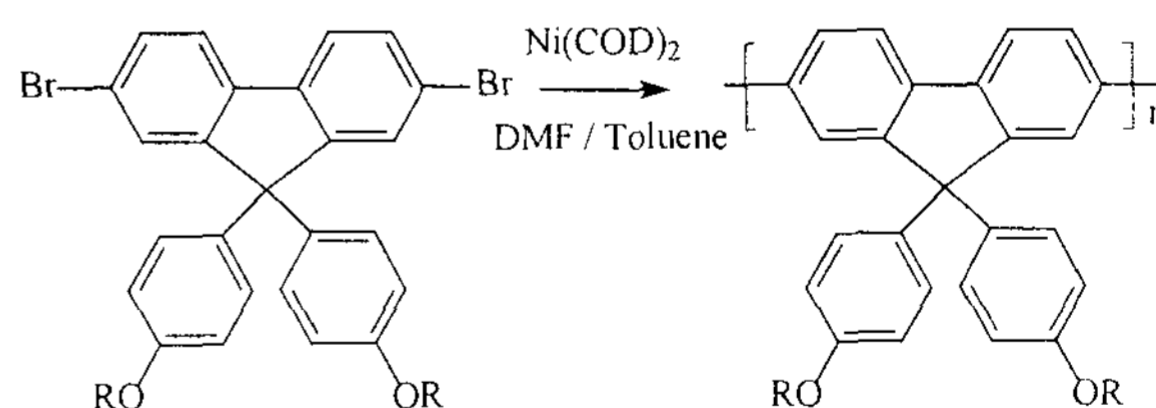


Figure 1. Polymer structures of PFV and copolymers.

## 2. Experimental

UV-vis and PL spectra were recorded on Jasco V-530 and Spex Fluorolog-3 spectrofluorometers. FT-IR spectra were recorded using an EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) was performed on a DuPont 9900 analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. The number and weight average molecular weight of polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150C instrument, using tetrahydrofuran (THF) as eluent and polystyrene as standard.

## 3. Results and discussion

A series of polyfluorene derivatives containing spiro groups or dendron side chains has been known as good blue light emitting materials as mentioned above, but their solubility in common organic solvents is too low, especially for high molecular weight compounds to be used for practical applications. We expected that the alkoxyphenyl group help to give much better solubility than the previously reported materials. The PAPP-8 and PAPP-10 synthesized in this work were readily soluble in common organic solvents such as THF, chloroform, toluene etc. The molecular weight was measured by gel permeation chromatography (GPC) with THF eluent. The Mw of PAPP-8 and PAPP-10 were 21,000 and 44,000 with polydispersity indices of 1.97 and 1.96, respectively. The glass transition temperatures ( $T_g$ ) of the PAPP-8 and PAPP-10 were determined by differential scanning calorimetry (DSC) with 10 °C/min under a nitrogen atmosphere to be about 108 °C and 98 °C, respectively. The glass transition temperatures of the polymers are higher than the  $T_g$  of poly(9,9-di-*n*-octylfluorene-2,7-diyl) which is about 75 °C according to the previous report. The alkoxyphenyl group may contribute to increase the glass transition temperature. Some poly(alkylfluorene)s have been reported to form stable liquid crystals. For example Gnell *et al.* found that poly(di-*n*-octyl)fluorenes have very stable liquid crystalline states and Bernius *et al.* observed polarized light emission from poly(alkylfluorene)s with a liquid crystalline structure.[9,10]

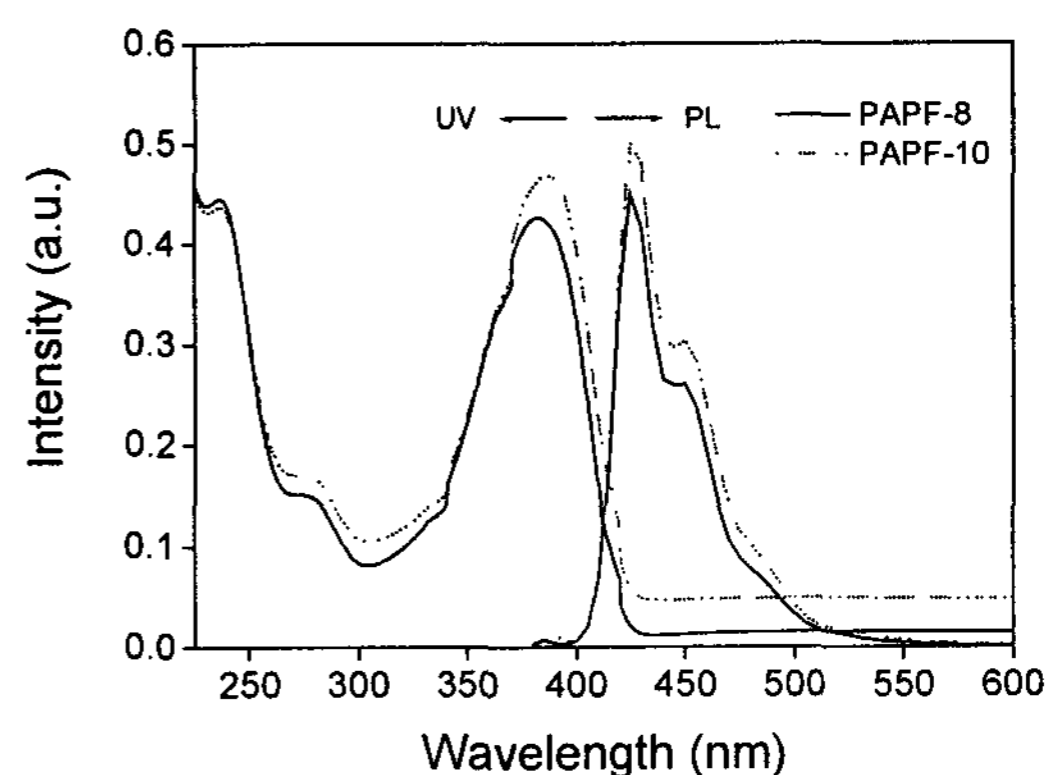


Figure 1. UV-visible absorption and PL emission spectra of the polymer films.

On the basis of these previous results, it might be expected that the PAPP-8 and PAPP-10 synthesized in the present work, which has a highly rigid backbone and long flexible alkoxyphenyl groups on the side chain, would form a liquid crystalline structure. However, no evidence of a significant mesophase or liquid crystalline texture was found in DSC measurements and polarized microscopy examinations. All of the polymers exhibit good thermal stabilities, losing less than 5% of their weight on heating to approximately 400 °C.

Figure 1 shows UV-Vis absorption and PL emission spectra of thin films of PAPP-8 and PAPP-10 coated onto fused quartz plates. The absorption and the emission spectra of PAPP-8 and PAPP-10 are very similar to those of poly(alkylfluorene)s, which indicates that the introduction of alkoxyphenyl group do not change the optical properties of poly(alkylfluorene)s. PAPP-8 and PAPP-10 shows the peak absorption and absorption edge at 388 nm and 430 nm, respectively. The maximum photoluminescence of PAPP-8 and PAPP-10 films appears at 425 nm when it is excited at 350 nm with a Xenon lamp. The emission stability on thermal annealing was confirmed to verify the effects of the sterically hindered alkoxyphenyl substituted on the excimer formation.

Figure 2 shows the emission spectra of thin films of PAPP-8 after thermal annealing at 70 °C, 100 °C, 150 °C and 180 °C for 2 hours.

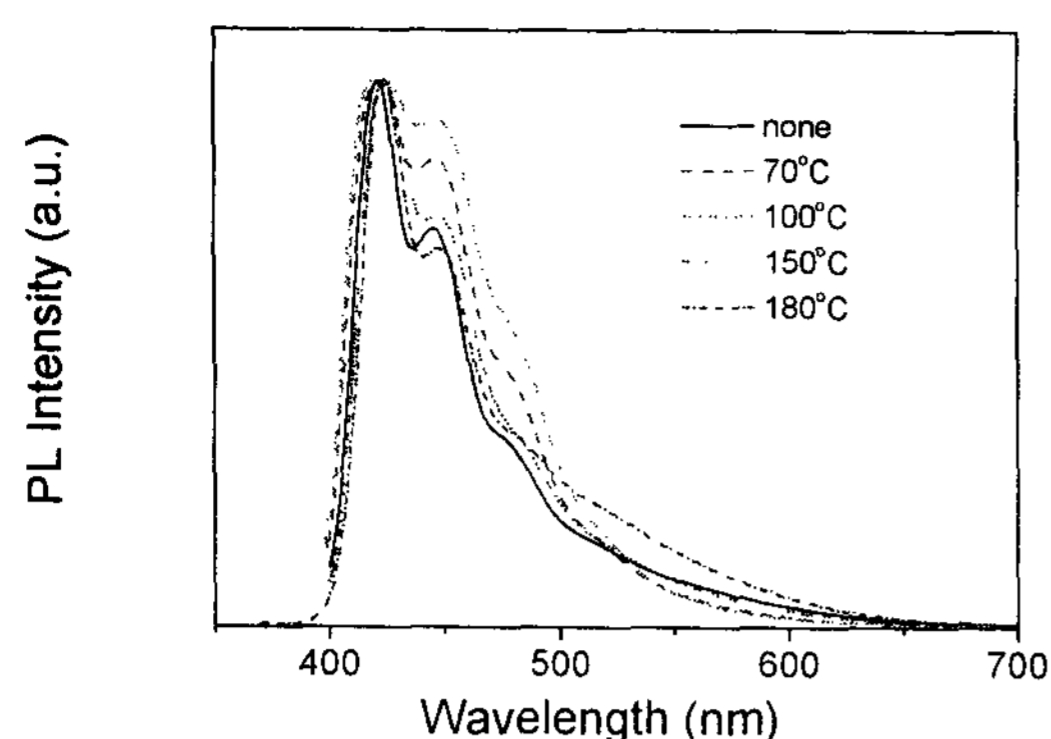


Figure 2. PL spectra of PAPP-8 film before and after thermal annealing.

We have hardly observed the development of long wavelength emission at 500~600 nm and therefore, the introduction of the sterically hindered alkoxyphenyl group is believed to be successful to suppress the excimer emission in polyfluorenes.

In conclusion, we have synthesized the polymer based on alkoxyphenyl substituted fluorene to suppress the excimer emission of polyfluorene with good solution processibility. A pure blue emission was obtained, which did not show spectral change upon thermal annealing and EL device operation. We believe that the alkoxyphenyl substituted fluorene is an effective way to obtain pure blue light emission without excimer formation and with good processibility

#### 4. Acknowledgements

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