

# Alkoxyphenyl-substituted polyfluorene: a stable blue-light-emitting polymer with good solution processability

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A new alkoxyphenyl-substituted poly(fluorene) was synthesized to suppress the emission of long-wavelength radiation. The polymer emitted pure blue light, the characteristics of which did not change upon thermal annealing or normal operation of the EL device.

Conjugated polymers have attracted much research interest in science and technology during the past few decades as semiconductors and electro-active materials in diverse applications such as transistors, photovoltaic devices, nonlinear optical devices, and light-emitting diodes. In particular, interest in light-emitting diodes constructed from conjugated polymers<sup>1–3</sup> has increased in recent years since poly(1,4-phenylenevinylene) (PPV) was first employed in a polymer electroluminescent (EL) device in 1990,<sup>1</sup> because they have many advantages in flat-panel displays due to their good processability, low operating voltage, fast response time, and easy color tunability over the full visible range. The development of new materials displaying colors correctly with high efficiency and stability is essential for the development of a full-color display. Poly(fluorene)s (PFs) are promising materials for blue-light-emitting diodes because of their high photoluminescence quantum efficiency, thermal stability, and also easy color tuning by introducing low-band-gap comonomers.<sup>4–7</sup> However, the emission of long-wavelength radiation by polymer films comprising PFs upon heating during device formation or operation has been the crucial problem for practical applications.

These long-wavelength emissions may be attributable to the formation of excimers.<sup>8–10</sup> Several approaches have been used to suppress the emission of excimers, including the copolymerization or end capping with anthracene, and the attachment of bulky aryl groups at the 9-position of the fluorene.<sup>9,10</sup> Spiro-substitution is also believed to provide an effective way for reducing interchain interactions that leads to broadening of the emission spectrum. Kreuder *et al.* have reported that a 9,9'-spirobifluorene-based conjugated polymer, poly(9,9'-spirobifluorene-2,7-diyl), suppresses excimer emissions.<sup>11</sup> Yu *et al.* prepared a copolymer with alternating 9,9'-spirobifluorene and fluorene, which exhibited the emission of blue light and improved solubility in common organic solvents.<sup>12</sup> Müllen *et al.* also produced stable blue radiation by attaching polyphenylene dendron side chains to PFs to prevent aggregation.<sup>13</sup>

More recently, List *et al.* have claimed another origin of the long-wavelength emissions of poly(alkylfluorene) derivatives:<sup>14</sup> keto-defects on the polymer chain. However, the origin of long-wavelength emissions of poly(alkylfluorene) is not yet clear. Both the excimer and keto-defects may be responsible for the long-wavelength emissions, but regardless of the underlying mechanism, the importance of synthesizing stable blue-light-emitting poly(fluorene) with good processability is crucial to the realization of polymer EL displays.

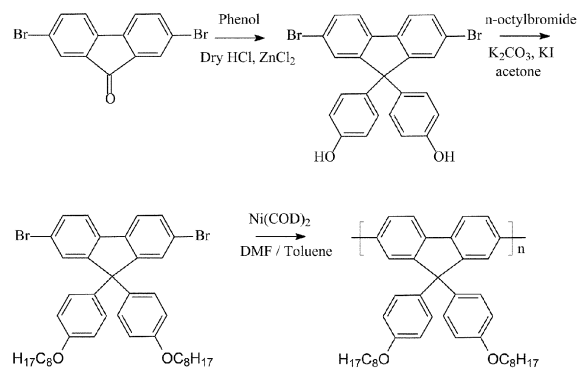
In the study reported here, we introduced alkoxyphenyl groups on the 9-position of fluorene to suppress the additional long-wavelength emissions. An alkoxyphenyl-substituted PF,

poly[9,9-bis(4'-*n*-octyloxyphenyl)fluorene-2,7-diyl] (PBOPF), has been synthesized as a blue-light-emitting polymer with high color purity and good solubility, and its light-emitting properties have been characterized.

The new PF was successfully synthesized *via* only three simple reaction steps. The synthetic scheme of the polymer is shown in Scheme 1. The PBOPF synthesized in this work was readily soluble in common organic solvents such as THF, chloroform, and toluene. The molecular weight was measured by gel-permeation chromatography with THF eluent. The weight average molar mass of PBOPF was 40000, with a polydispersity index of 1.97.

The glass transition temperature of PBOPF was found to be about 108 °C when using differential scanning calorimetry at a rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. This temperature is higher than that of poly(9,9-di-*n*-octylfluorene-2,7-diyl) (PDOF), which has been reported to be about 75 °C.<sup>15</sup>

The absorption and emission spectra of PBOPF are very similar to those of poly(alkylfluorene)s, indicating that the introduction of the alkoxyphenyl group does not change the optical properties of the poly(alkylfluorene)s. Fig. 1 shows UV-



Scheme 1

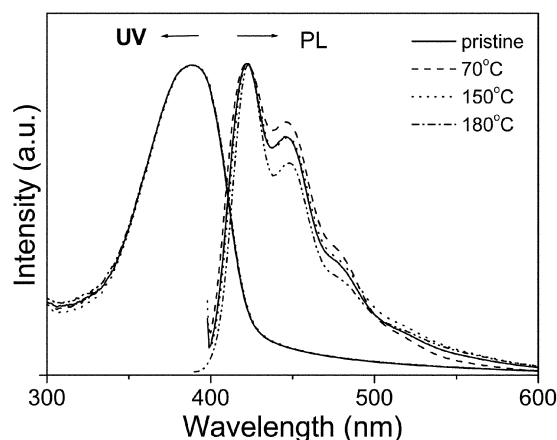


Fig. 1 UV-visible and PL emission spectra of the PBOPF film after thermal annealing at different temperatures under air.

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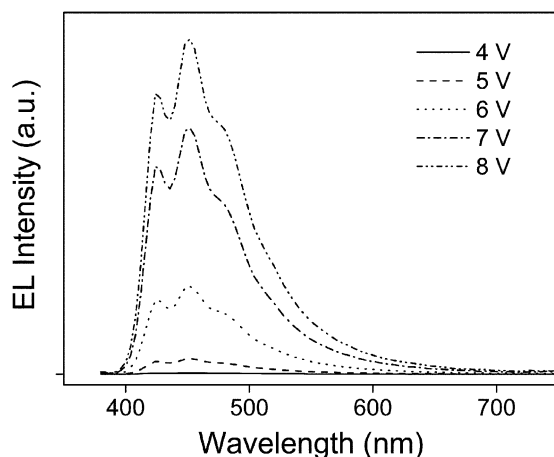
visible absorption and PL emission spectra of thin films of PBOPF coated onto fused quartz plates before and after thermal annealing at 70 °C, 150 °C, and 180 °C for 2 h under air. PBOPF exhibits peak absorption and an absorption edge at 388 nm and 430 nm, respectively, and no spectral changes even after thermal annealing, suggesting that PBOPF does not form aggregates in the ground state. The emission stability on thermal annealing was confirmed to verify the effects of the sterically hindered alkoxyphenyl group on the formation of excimers. Long-wavelength emissions at 500–600 nm are barely observable, suggesting that the introduction of the sterically hindered alkoxyphenyl group suppresses such emissions in PFs.

We obtained FT-IR spectra of the PDOF and PBOPF films before and after thermal annealing at 70 °C, 150 °C, and 180 °C for 2 h under air to detect the formation of keto-defects. The PDOF did not show any carbonyl peak up to 150 °C, but showed a small carbonyl peak at 1715  $\text{cm}^{-1}$  after thermal annealing at 180 °C. In contrast, the PBOPF film did not show any carbonyl peak even after thermal annealing at 180 °C, suggesting that PBOPF is more resistant against oxidation and the formation of keto-defects.

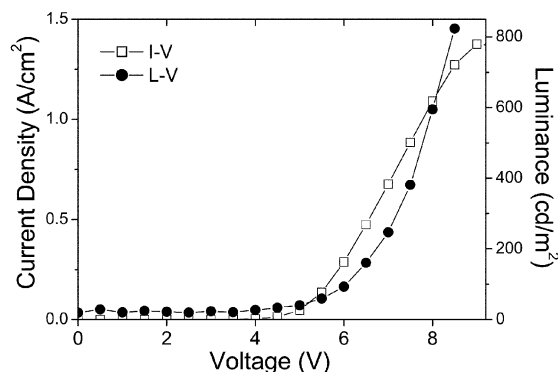
A double-layered EL device with an ITO/PEDOT : PSS (50 nm)/PBOPF (80 nm)/Ca (50 nm)/Al (200 nm) configuration was fabricated, and characterized as a function of applied voltage. Usually, poly(alkylfluorene) EL devices show an intense additional band between 500 and 600 nm.<sup>16</sup> However, the device constructed with PBOPF did not exhibit any significant long-wavelength emission in the EL spectrum. Fig. 2 demonstrates that the device exhibited a voltage-independent and stable EL spectrum.

Fig. 3 shows the current–voltage and luminance–voltage characteristics of the EL devices. Light emission from this device was observable at voltages greater than 3.7 V ( $\sim 1 \text{ cd m}^{-2}$ ). The EL device constructed from PBOPF exhibits a maximum brightness of  $820 \text{ cd m}^{-2}$  and an efficiency of  $0.03 \text{ cd A}^{-1}$ . The CIE 1931 coordinates of the devices measured at a brightness of  $100 \text{ cd m}^{-2}$  are  $x = 0.136$  and  $y = 0.162$ .

In conclusion, a new alkoxyphenyl-substituted poly(fluorene) was synthesized to suppress the emission of long-wavelength radiation. The polymer emitted pure blue light, the



**Fig. 2** EL spectra of the ITO/PEDOT/PBOPF/Ca/Al device at various voltages.



**Fig. 3** *I-V* and *L-V* curves of the EL device constructed with a ITO/PEDOT/PBOPF/Ca/Al configuration.

characteristics of which did not change upon thermal annealing or normal operation of the EL device. It is suggested that introduction of the alkoxyphenyl group on the 9-position of fluorene is an effective way to obtain stable blue-light emission in a polymer exhibiting good processability.

We are currently endeavoring to further improve the performance of PBOPF-based copolymers with charge-transporting comonomers. The significantly enhanced device efficiency and brightness obtained with these devices will be reported in future papers.

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