

Note

BLUE LIGHT-EMITTING POLY(FLUORENE-CO-BENZENE) CONTAINING AN OXADIAZOLE MOIETY*

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Abstract A new kind of polyfluorene containing oxadiazole as the side chain was synthesized. The introduction of oxadiazole moiety as more bulky group prevents the aggregation and reduces the crystallinity of the polymers. Efficient intramolecular energy transfer from oxadiazole moiety to the conjugated backbone has been realized, leading to 70% improvement of photoluminescence quantum efficiency of the designed polymers. Compared with PAF, the PFOXD exhibits significant improvement in electroluminescence properties, with luminous efficiency of 0.8 cd/A and maximum luminance of 1800 cd/m².

Keywords Polyfluorenes, Oxadiazole, Intramolecular energy transfer, Photoluminescence quantum efficiency

Poly(9,9-dialkylfluorene)s (PAF) and their derivatives have attracted much attention in the development of polymer-based optoelectronic devices and in particular for the fabrication of blue light-emitting diodes^[1]. To achieve high efficiency for the polymer light-emitting diodes (PLED), it is desirable to develop an effective methods for improving the photoluminescence quantum efficiency of PAF by using intramolecular energy transfer, by balancing electron- and hole injections in the main chain and side chain, and by reducing the aggregation^[2–4].

In this note, we report a new kind of polyfluorene with pendant oxadiazole group (as a example of PFOXD) having improved photoluminescence quantum efficiency. The oxadiazole moiety has been incorporated into polymers because of its electron-deficient property, which will improve the electron transporting ability of the polymers. More importantly, the introduction of oxadiazole moiety as the more bulky group attached by flexible spacer into the PAF-based conjugated polymer backbone is expected to realize efficient intramolecular energy transfer from oxadiazole moiety to polymer backbone, to prevent the aggregation and to reduce the crystallinity, resulting in an improvement of photoluminescence quantum efficiency of the desired polymers.

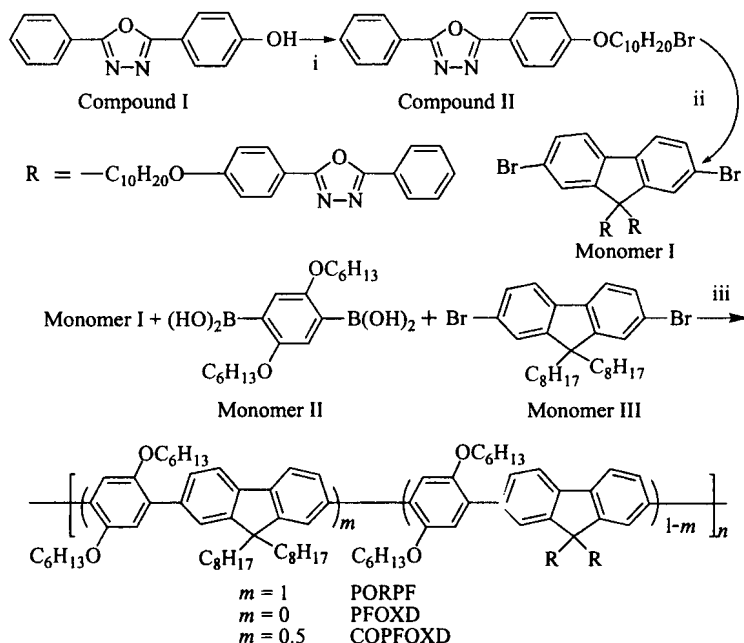
The synthetic route to PFOXD is shown in Scheme 1. Compound I is used as the starting material and is prepared according to the procedure described in literature^[5]. Compound II is synthesized by the reaction of compound I with 1,10-dibromodecane in the presence of KOH (with 95% yield). Treatment of compound II with 2,7-dibromofluorene affords monomer I (with 75% yield). Monomer II is synthesized according to the literature procedure^[6]. Polymerization reaction between monomer I, II, and III was performed via the Suzuki coupling

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reaction^[6]. PFOXD is obtained from the reaction of monomer I and monomer II as yellowish powder with a yield of 55% and is characterized by NMR. PFOXD is soluble in common organic solvents such as chloroform and tetrahydrofuran and emits intense blue light on irradiation with UV light. It has molecular weight (M_n) of 19 000, with a polydispersity index (PDI) of 2.4, as determined by gel permeation chromatography (GPC) with THF as eluent and polystyrene as the standard. Differential scanning calorimetry (DSC) measurement of PFOXD shows two phase transitions at 89 °C and 228 °C, respectively. As polarizing optical microscopy does not show evidence for a thermotropic liquid crystalline phase, hence we can attribute them to two glass transitions, corresponding to the side chains and the main chains, respectively. COPFOXD (obtained from the reaction of monomers I, II and III) and PORPF formed by the reaction of monomers II and III have also been synthesized for comparison (in Scheme 1). And the details of the resulting polymer are shown in Table 1.



Scheme 1. Regent and conditions

i) 1,10-dibromodecane, 5% KOH aqueous solution, TBABr, 80 °C, 12 h

ii) DMSO, KOH, KI, 2,7-dibromofluorene, 10 h

iii) THF/aqueous potassium carbonate solution, Pd (PPh₃)₄, reflux, 2 days

Table 1. Molecular weight and optical properties of PFOXD, COPFOXD and PORPF

Polymer	M_n (10 ⁴)	PDI	PL (nm) S/F ^a	UV (nm) S/F	PLE (nm) S/F	ETE ^b S/F
PFOXD	1.9	2.4	417 / 423	300, 375/ 310, 380	300, 375/ 285, 380	80%/ 85%
COPFOXD	2.1	2.6	417 / 424	295, 375/ 305, 375	300, 380/ 295, 380	90%/ >95%
PORPF	1.8	2.2	413, 425	375/385	375/375	

^a In solution (S) and in film (F); ^b Energy transfer efficiency (ETE)

Figure 1 shows the UV-Vis absorption spectra and photoluminescence excitation spectra of PORPF and PFOXD in solutions (chloroform) and as thin films, respectively. The absorption spectrum of PORPF in solution shows one main peak at 375 nm contributed by the conjugated polymer backbone, while the absorption spectrum of PFOXD in solution exhibits two absorption peaks at 300 and 375 nm, which can be attributed to the oxadiazole moiety and conjugated main chain. The same spectral features are also observed for PORPF and PFOXD as solid films, as shown in Fig. 1(b).

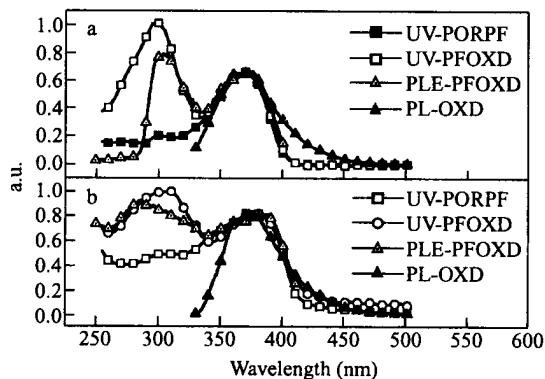


Fig. 1 (a) The UV-Vis absorption spectra and photoluminescence excitation spectra of PORPF and PFOXD in solution (5×10^{-9} g/mL) (b) The UV-Vis absorption spectra and photoluminescence excitation spectra of PORPF and PFOXD in thin films

The photoluminescence (PL) spectra of PFOXD appear at 417 nm in solution and 423 nm as thin film, indicating that PFOXD emits blue light. The photoluminescence excitation spectra (PLE) of PFOXD in solution and as thin film are measured at the $\lambda_{\max}$ of its emission spectrum (in Fig. 1). The excitation spectrum of PFOXD is similar to its absorption spectrum. It should be pointed out that no peak of the emission from the oxadiazole moiety (at 375 nm, as shown in Table. 1) appeared in PL spectra of PFOXD when excited at 300 nm, which is the absorption wavelength of oxadiazole moieties. This indicates that there is excellent energy transfer from OXD to the main chain in this polymer^[7]. The emission maximum of PFOXD as solid film is red-shifted by 6 nm in comparison to the maximum wavelength of PFOXD in solution. In contrast to PFOXD, the emission spectra of PORPF film exhibits 12 nm red-shift in comparison to that of PORPF in solution and appears as a long tail from 500 nm to 600 nm. This result is consistent with that of poly(9,9-dioctylfluorene) reported by Bradley *et al.*^[8] and suggests that the introduction of oxadiazole moiety into the polymer reduces the aggregation of PFOXD compared with PORPF. This is also supported by polarizing optical microscopy measurements. In the control experiments, PORPF shows the existence of thermotropic liquid crystalline phase, while no thermotropic liquid crystalline phase is observed in PFOXD, as described above. The absence of a thermotropic liquid crystalline phase indicates that the oxadiazole moiety as more bulky group restricts the orientation and the packing of the resulting polymer.

To determine the intramolecular energy transfer efficiency, the absorption spectra and excitation spectra of PFOXD in solution and in the form of thin solid film are normalized at $\lambda_{\max}$ (375 nm), as depicted in Fig. 1. By comparing the peaks at 300 nm of the excitation spectrum with that of the absorption spectrum, the energy transfer efficiency was estimated to be about 80% in solution and 85% in thin film, respectively. This clearly indicates that the designed polymer PFOXD is a highly efficient intramolecular energy transfer material. It can also be seen that the overlap between the emission spectrum of oxadiazole moieties and the absorption spectrum of the conjugated main chains are excellent, as shown in Fig. 1. This is responsible for the high efficiency value for PFOXD in both solution and thin film^[7]. The energy transfer efficiency values of COPFOXD are also obtained by the same method as for PFOXD. The efficiency values can reach up to 90% in solution and nearly 100% in thin film. It can be seen that the efficiency values are improved with the decrease of Monomer I in the polymer. A thin film was made from a blend of oxadiazole itself and PORPF with the same ratio as that of PFOXD. When the film was treated at 95 °C after spin-coating, the efficiency value decreased from 80% to 60%. This indicates the occurrence of phase-separation in the blend after being heated. However, no change happens in the thin film of PFOXD after being heated at the same temperature. These results demonstrate that there is no phase-separation in PFOXD thin film and the introduction of OXD through a flexible spacer with conjugated backbone results in the formation of a molecular dispersion of OXD in the designed polymer film, which is

responsible for the improvement of photoluminescence quantum efficiency^[5].

The PL efficiencies of PORPF and PFOXD in 200 nm thickness films were measured on excitation at 325 nm (HeCd laser). PORPF and PEOXD have a photoluminescence quantum efficiency of 17% and 30%, respectively. The PL efficiency of PFOXD is 70% higher than that of PORPF, implying that both the intramolecular energy transfer and the reducing of aggregation induced by oxadiazole moiety are responsible for the improvement of PL efficiency of the designed polymers.

The single layer devices with the structure of ITO/PEDOT (poly(3,4-alkylenedioxythiophene))/polymer/Ca/Al were fabricated to investigate their electroluminescence properties. Figure 2 shows the current-brightness-voltage characteristics of the devices for PFOXD and PORPF, respectively. For the device containing PORPF, its luminous efficiency is about 0.03 cd/A with the maximum brightness of 45 cd/m². In the case of PFOXD, its luminous efficiency can reach 0.8 cd/A with a maximum luminance of 1800 cd/m². These results demonstrate that the introduction of oxadiazole moiety results in a significant improvement in the electroluminescence properties of the resulting polymers.

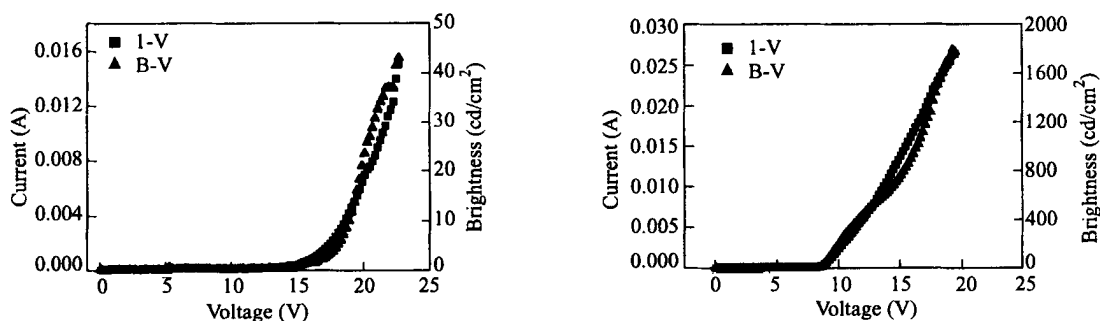


Fig. 2 Current-brightness-voltage characteristics for PORPF (left) and PFOXD (right); I-V, Current-Voltage; B-V, Brightness-Voltage

In conclusion, we have synthesized and characterized some new blue light-emitting polyfluorenes containing an oxadiazole moiety as the side chain. These polymers have realized efficient intramolecular energy transfer from oxadiazole moiety to the conjugated backbone and reduced the aggregation, leading to the improvement of photoluminescence quantum efficiency of the designed polymers. Further work on the fabrication of device and electron-transporting properties is in progress.

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