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Synthesis and photoluminescence stability of non-conjugated polymers based on fluorene and benzoxazole

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ABSTRACT

A kind of non-conjugated blue luminescent polymer based on fluorene and benzoxazole was synthesized via solution condensation polymerization from 2,2-bis(3-amino-4-hydroxyphenyl)-propane and 2,7-dicarboxyl-9,9-dioctyl-fluorene and was characterized with H NMR, FT-IR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV–vis absorption and photoluminescence (PL) spectroscopy. The polymer displayed the maximum photoluminescence emission peak at 415 nm and showed high PL spectroscopic stability. The green-to-blue emission intensity ratio $I_{\mathrm{Green}}/I_{\mathrm{Blue}}$ is only 0.073 even after thermal annealing at 150 °C for 30 h. After being exposed to UV light for 30 min, no bathochromic emission or obvious crosslink is observed. The common phenomenon of greenish blue emission of fluorene-based polymer around 525 nm has been effectively restrained in this polymer by introducing the isopropylidene group into the backbone of polymer.

1. Introduction

Since the discovery of polymer-light-emitting diode (PLED) based on poly(*p*-phenylenevinylene) (PPV) [1], the light-emitting polymers have attracted great attention and have been extensively studied over the past decades because of their good processability, high flexibility, and the facility of fine-tune luminescence [2]. For materials required in commercial LED device applications, thermal and oxidative stability, color purity, luminance efficiency and balance of charge carrier mobility are of great importance. On the horizon, green- and red-light-emitting polymers have already basically met the requirements for commercial applications [3]. However, few blue-light-emitting materials can satisfy the demands. Among them, fluorene-based polymers are very promising candidates and have received broad interests due to large energy gap, the facility of modification, excellent thermal stability, high fluorescence quantum efficiency [4–6]. However, one major disadvantage of PFO-based LEDs is their poor spectral stability during operation, gradually revealing a low-energy emission band at 520–535 nm or 490–500 nm (green or blue–green) [7–9]. To clarify the origin of this long wavelength emissions, chemists have proposed many explanations including (I) the formation of fluorene-based aggregates and interchain excimers induced by heat or electric field [10–12], (II) interchain or intersegment interactions [13,14], (III) keto defects in the conjugated chain resulting from synthesis process, diode fabrication process and thermal/photo-oxidation in operation [15–19], and (IV) the cross linking that are formed upon thermal oxidation degradation in operation [20]. Many chemical and physical approaches have been used to strengthen the color stability of polyfluorenes with some progress, these approaches include: (I) introducing sterically hindered substituents at the 9-position of fluorene such as aryl substituent [21–24], (II) strictly control of the purity of monomers and polymers [25,26], (III) physical blending and end-capping with hole or electron transporting moie-

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ties [27–30], (IV) copolymerization with suitable comonomers [31–35]. Although much progress has been made, there is no accepted theory can explain solely the low-energy emission. What is certain is that the reasons are manifold and the gradual solution of the spectroscopic stability requires not only improvement of fabricating technique of PLED but also improvement of synthetic methods.

Recently, Huang et al. reported highly efficient and stable UV-blue PLEDs with emission peaking at 397 nm based on a non-conjugated fluorene-based polymer in which the conjugated units were interrupted by the ether linkage in the main chain [36]. List and coworkers investigated the influence of UV irradiation on keto defect emission in fluorene-based copolymers, finding that the UV irradiation can induce interruptions in the polymer backbone, which reduce the effective conjugation length and subsequently inhibit the energy transfer onto the keto defect sites [37]. In this way, the reduced emission intensity in the green spectral was achieved.

In continuation of our interest in the synthesis and photophysics properties of polybenzobisoxazoles [38–40], in this paper we synthesized a novel kind of fluorene-based non-conjugated polymer based on fluorene and benzoxazole to investigate the effects of conjugation extent, thermal oxidation and UV irradiation on the fluorescent spectroscopic properties. It was worth mentioning that fluorene-based polymers studied in previous literatures were mostly synthesized via the Yamamoto or Suzuki coupling reactions which involved a nickel or palladium catalyzed reaction. There would be some residual transition metal catalysts reserved in polymers as free catalysts or plugged in polymer chain and these transition metal catalysts can effectively catalyze the formation of fluorenone and quench the emission of polyfluorene [16,41]. To exclude the interference of metal catalysts, in this paper, polymers were synthesized without metal catalysts. Meanwhile, the effects of thermal oxidation and UV irradiation on the photoluminescence properties of polymers were also discussed.

2. Experimental

2.1. Materials

Poly(phosphoric acid) (PPA), phosphorus pentoxide (P_2O_5), *n*-butyllithium solution (2.0 M in hexane) and sodium hypochlorite solution were purchased from Shanghai Lingfeng Chemical Corporation. Bisphenol A, fluorene and bromine liquid were purchased from Aldrich Chemical Company and used as received. Absolute ether is purified by tight drying and redistillation. Other solvents and reagents were used as received.

2.2. Measurements

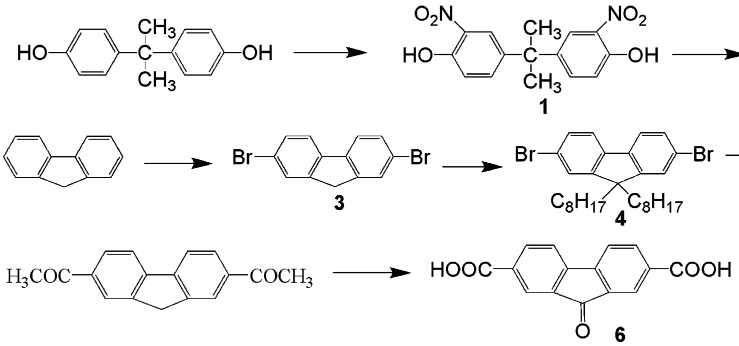
Fourier transform infrared (FT-IR) spectra were taken using a Nicolet Magna-IR 550 FT-IR spectrometer. ^1H NMR spectra were measured using a Bruker Avance DRX-500 (500 MHz) spectrometer with tetramethylsilane as the standard. Elementary analysis was done with elementar Vario EL III. The TGA and DSC were done using Du Pont Model 951 and Du Pont DSC-2000 respectively in flowing nitrogen at a heating rate of 10 °C/min. Intrinsic viscosities of all the samples were measured in *N*-methyl pyrrolidone (NMP) at 30 °C using the Ubbelohde capillary viscometer. UV–vis and photoluminescence spectra were recorded on a Varian Cary 500 UV–visible spectrophotometer and a Varian Cary Eclipse fluorescence spectrophotometer at room temperature, respectively. Thin polymer films were prepared by using Jenekhe's method [42], i.e., spin-coating of the polymer solution in nitromethane/$AlCl_3$ with a polymer concentration of 2–3 wt.% onto synthetic silica substrates.

2.3. Synthesis of monomers

The synthetic route of monomers is illustrated in Scheme 1.

2.3.1. Synthesis of 2,2-bis(3-nitro-4-hydroxyphenyl)-propane (**1**)

Bisphenol A (11.4 g, 50 mmol) powder was added to 17% (w/w) aqueous HNO_3 (150 ml) at 20 °C in three equal lots of 3.8 g each. The reaction mixture was stirred at 25 °C for 3 h and then poured into 300 ml of water. The resulting yellow acicular crystal was got by filtrating, rinsing and purifying by chromatography on silica using toluene as an eluent. Yield: 85.6%. mp: 120–122 °C. ^1H NMR (500 MHz, acetone-d_6) δ: 7.730, 7.738 (d, J = 4.0 Hz, 2H), 7.340, 7.347, 7.360, 7.372 (q, J = 11.0 Hz, 2H), 7.042, 7.068 (d, J = 13.0 Hz, 2H), 1.62 (s, 6H). FT-IR (KBr, cm^{-1}): 3340 (N—O), 3260 (O—H); 2983 (C—H); 1583, 1480 (C═C); 1428, 1335 (C—C). Anal.



Scheme 1. Synthetic route for the monomers.

calcd for $C_{15}H_{14}N_2O_6$: C, 56.80; H, 4.46; N, 8.90. Found: C, 56.76; H, 4.51; N, 8.86.

*2.3.2. Synthesis of 2,2-bis(3-amino-4-hydroxyphenyl)-propane (**2**)*

2,2-Bis(3-amino-4-hydroxyphenyl)-propane (**2**) was synthesized and purified according to the method reported in reference [43]. Yield: 95.4%. mp: 249–250 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 8.715 (s, 2H), 6.491, 6.517 (d, J = 13.0 Hz, 2H), 6.402, 6.409 (d, J = 3.5 Hz, 2H), 6.268, 6.276, 6.288, 6.295 (q, J = 10.0 Hz, 2H), 4.304 (s, 4H), 1.443 (s, 6H). FT-IR (KBr, cm^{-1}): 3420 (N—H); 3323 (O—H); 2983 (C—H); 1863, 1295 (C—N); 1595, 1508 (C=C); 1448, 1355 (C—C); 1190 (C—O). Anal. calcd for $C_{15}H_{18}N_2O_2$: C, 72.21; H, 6.92; N, 11.12. Found: C, 72.20, H, 6.96, N, 11.08.

*2.3.3. Synthesis of 2,7-dibromofluorene (**3**) and 2,7-dibromo-9,9-dioctylfluorene (**4**)*

2,7-Dibromofluorene (**3**) and 2,7-dibromo-9,9-dioctylfluorene (**4**) were prepared according to the reference [44]. The compound **3** was purified by recrystallization from ethyl acetate to yield a white acicular crystal product. Yield: 88.3%. mp: 160–161 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ: 7.63 (m, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.46 (m, 2H), 3.91 (s, 2H). Anal. calcd for $C_{13}H_8Br_2$: C, 48.19; H, 2.49. Found: C, 48.17; H, 2.48.

The compound **4** was purified via recrystallization from hexane and ethanol to yield a white crystalline product. Yield: 82.6%. mp: 45–47 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ: 7.62 (d, J = 12.4 Hz, 2H), 7.44–7.47 (m, 4H), 1.91 (m, 4H), 1.09–1.24 (m, 20H), 0.83 (t, J = 5.6 Hz, 6H), 0.59 (m, 4H). Anal. calcd for $C_{29}H_{40}Br_2$: C, 63.51; H, 7.35. Found: C, 63.55; H, 7.26.

*2.3.4. Synthesis of 2,7-dicarboxyl-9,9-dioctylfluorene (**5**)*

2,7-Dibromo-9,9-dioctylfluorene (4.1 g, 7.5 mmol) was put into a 250 ml flask with 120 ml of absolute ether under argon. Then *n*-butyllithium solution (2.0 M in hexane, 30 ml) was added dropwise at −78 °C. The mixture was stirred for 2 h at room temperature and then cooled to −78 °C. After 4 h of carbon dioxide injection, the reaction mixture was heated slowly to room temperature to get white serosity. The resulting white solid was collected by acidifying with hydrochloric acid, extracting from ether, recrystallizing from toluene, and drying in vacuo. Yield: 60.5%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.12 (s, 2H), 8.09 (dd, J = 9.2 Hz, 2H), 8.02 (d, J = 6.0 Hz, 2H), 2.16 (m, 4H), 1.00–1.12 (m, 20H), 0.72 (t, J = 8.4 Hz, 6H), 0.54–0.60 (m, 4H). FT-IR (KBr, cm^{-1}): 3042 (Ar—H); 2500–3000 (O—H); 1706 (C=O); 1608, 1509 (C=C); 1468, 1377 (C—H). Anal. calcd for $C_{31}H_{42}O_4$: C, 77.82; H, 8.79. Found: C, 77.85; H, 8.77.

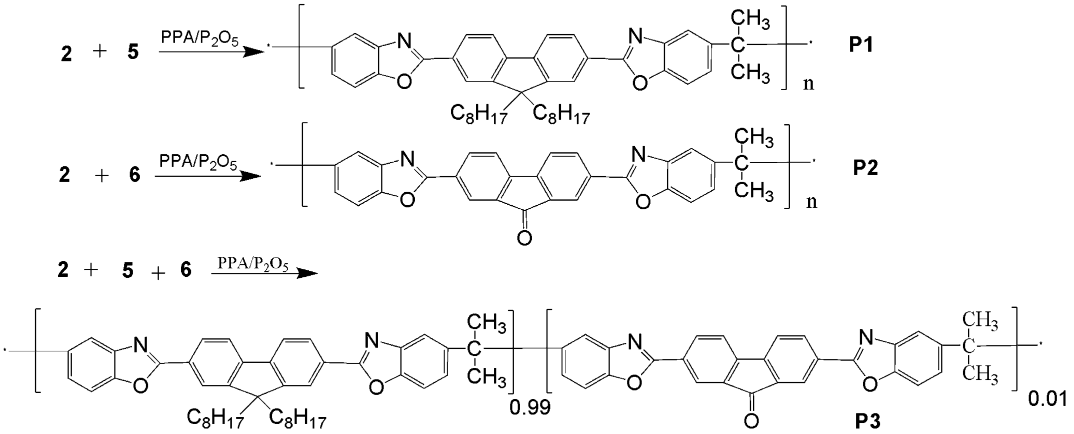
*2.3.5. Synthesis of 2,7-dicarboxyl fluorenone (**6**)*

To a 500 ml three-neck flask charged with dimethyl sulfoxide (DMSO, 200 ml), 2,7-diacetylfluorene (5.0 g, 0.02 mol), sodium hydroxide (8.0 g, 0.20 mol) and tetrabutylammonium bromide (TBAB, 0.5 g), sodium hypochlorite solution (50.0 g, activated chlorine content = 10%) was added slowly at 10 °C. The mixture was stirred for 2 h at room temperature and then heated to 70 °C for 4 h. The sodium hyposulfite was added to destroy the excess sodium hypochlorite, and then the concentrated hydrochloric acid (37%, 30 ml) was added. The resulting yellow solid was collected by filtrating, rinsing, recrystallizing from ethanol and drying in vacuo.

Yield: 85.4%. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.54 (m, 2H), 8.38 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 7.5 Hz, 2H). FT-IR (KBr, cm^{-1}): 2500–3100 (O—H); 1705 (C=O); 1609, 1473 (C=C). Anal. calcd for $C_{15}H_8O_5$: C, 67.17; H, 3.01. Found: C, 67.21; H, 3.02.

*2.3.6. Synthesis of polymers (**P1**, **P2** and **P3**)*

The fluorene-based polymer **P1**, fluorenone-based **P2** and copolymer **P3** were prepared via a facile one-step condensation reaction. The structures and synthetic routes for the **P1**, **P2** and **P3** are shown in Scheme 2. Take **P1** as an example, the synthesis is as the follows. The 2,2-bis(3-amino-4-hydroxyphenyl)-propane (0.2583 g, 1.0 mmol), 2,7-dicarboxyl-9,9-dioctylfluorene (0.4787 g, 1.0 mmol), PPA (21.0 g) and P_2O_5 (8.4 g) is added into a glass reactor vessel under argon at room temperature. After a half-hour of stirring at 80 °C, the mixture is heated at 100 °C for 6 h, then



Scheme 2. The structure and synthetic route for the **P1**, **P2** and **P3**.

130 °C for 8 h, finally 160 °C for 8 h. After being cooled to 60 °C, 200 ml of deionized water is added and the mixture is stirred for 1 h. Then filtering and washing are done to remove the residual PPA completely. Polymer **P1** is obtained as a brown powder after drying in vacuo in 80 °C to give a yield of 99.9% (0.6710 g). The polymers **P2** and **P3** are synthesized by similar methods. FT-IR (KBr, cm^{-1}): with **P1**: 3068 (Ar—H); 2926, 2854 (—H); 1609, 1509 (C═H); 1460, 1373 (C—H); 1245, 1159 (C═N). Anal. calcd: C, 83.09; H, 7.88; N, 4.21. Found: C, 83.04; H, 7.92; N 4.20. FT-IR (KBr, cm^{-1}): with **P2**: 3064 (Ar—H); 1707 (C═O); 1605, 1509 (C═H); 1373 (C—H); 1245, 1159 (C═N). Anal. calcd: C, 79.28; H, 3.99; N, 6.16. Found: C, 79.21; H, 3.98; N 6.10. FT-IR (KBr, cm^{-1}): with **P3**: 3072 (Ar—H); 2928, 2856 (C—H); 1608, 1505 (═H); 1460, 1372 (C—H); 1245, 1160 (C═N). Anal. calcd: C, 83.05; H, 7.84; N, 4.23. Found: C, 83.06; H, 7.83; N 4.25.

3. Results and discussion

3.1. Characterization of polymers

The intrinsic viscosities ([η]) of **P1**, **P2** and **P3** are in the range of 0.92–1.05 dL/g (Table 1). The fluorenone-based polymer **P2** can dissolve in strong polar organic solvents, such as DMF, DMAC, DMSO and so on. The polymers **P1** and **P3** dissolve in most organic solvents at room temperature, such as dioxane, DMF, DMAC, DMSO and so on. Compared with most aromatic polybenzoxazoles, such as PBO and PBZT which only dissolve in strong protonic acid, fluorene-based polymer **P1** and **P3** show improved solubility. The improved solubility is attributed to the introduction of fluorene with alkyl groups along the polymer backbones. The existence of two bulky flexible octyl groups prevent the close chain packing and allow solvent molecules to diffuse into the polymer chains easily.

Table 1
Characterization of the polymers.

	[η][a] g/dL	T_g[b] (°C)	T_d[c] (°C)
P1	1.03	118	390
P2	1.05	146	421
P3	0.92	117	393

[a] Intrinsic viscosities in NMP measured at 30.0 °C.

[b] Glass transition temperature was determined by a second heating DSC curve in N_2, 10 °C/min.

[c] Decomposition temperature determined by TGA in N_2 on 5% weight loss.

The thermal properties of polymers are investigated by TGA and DSC measurement in flowing nitrogen at a heating rate of 10 °C/min. The 5% weight loss temperatures (T_d) in N_2 is 390 °C for **P1** and 393 °C for **P3**, and the glass transition temperatures (T_g) of **P1** and **P3** are 118 and 117 °C, respectively, both showing excellent thermal stabilities compared conventional fluorene-based conjugated polymers. This is advantageous to light-emitting polymers. Meanwhile, the overall weight loss for fluorenone-based polymer **P2** is higher than that observed for fluorene-based polymers **P1** and **P3**, which probably attributable to the absence of octyl groups at 9 positions.

3.2. Role of thermal oxidation on the photoluminescence stability

The normalized UV–vis absorption spectra and the PL emission spectra of polymers in thin films are shown in Fig. 1. The spectral data are listed in Table 2. The optical band gaps (E_g) of the polymers are calculated from the onset wavelength of their UV–vis spectra according to the empirical equation ($E_g = 1240/\lambda_{onset}$ eV). It can be seen from the Fig. 1 that the absorption spectra reveal general blue-shifts of λ_{max} compared with the ordinary conjugated fluorene-based polymers. For polymer **P1**, absorption profile is featured with two main peaks at 328 and 370 nm. While the fluorenone-based polymer **P2** shows single peak at 474 nm. In contrast, the copolymer **P3** exhibits similar absorption bands except for a very weak flat hump at around 460 nm.

The PL emission spectrum of polymer **P1** displays the maximum wavelength λ_{max} at 415 nm and a shoulder at 438 nm. Compared with most of conjugated fluorene-based

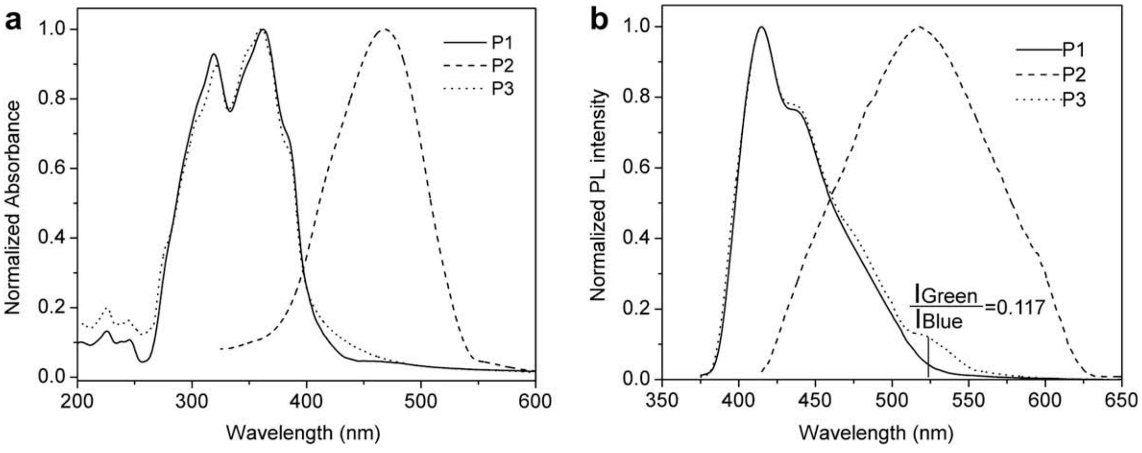


Fig. 1. The normalized absorbance spectra of polymers in solution (a) and the normalized PL emission spectra in films (b).

Table 2
Spectral properties of the polymers.

	Absorption λ_{max} (nm) (energy, eV)	Emission λ_{max} (nm) (energy, eV)	E_g[a] (eV)	PL quantum yields[c]
P1	328, 370 (3.78, 3.35)	415, 438 (2.99, 2.83)	2.88	0.80
P2	474 (2.62)	520 (2.38)	2.27	0.41
P3	333, 373 (3.72, 3.33)	415, 439, 525[b] (2.99, 2.82, 2.36)	2.85	0.73

[a] Determined from the UV–vis absorption onset in the solid state.

[b] A weak hump.

[c] Solution fluorescence quantum yields was measured in DMF relative to 9,10-diphenylanthracene. **P1** and **P3** were excited at 365 nm; **P2** was excited at 400 nm.

polymers, **P1** shows a blue shift of about 10–20 nm. The hypsochromic shift is attributed to the reduction of effective conjugation length in the polymer backbone by the interruption of the isopropylidene group. Similar result was reported on another fluorene-based non-conjugated polymer [36]. The PL spectrum of fluorenone-based polymer **P2** is characterized by single broad peak around 520 nm. Copolymer **P3** which contains 1 mol.% fluorenone shows a similar spectrum with **P1** except a very weak band around 525 nm. Considering the spectrum of the fluorenone-based polymer **P2**, it is reasonable that the faint band around 525 nm of **P3** is assigned to the emission of fluorenone fragments incorporated deliberately into main chain. For convenience, we use I_{Green}/I_{Blue} to indicate the intensity ratio of the long wavelength emission at about 525 nm to the strongest blue emission at around 415 nm. The I_{Green}/I_{Blue} ratio for **P3** is only 0.117 and this differs with the previous literatures concerning conjugated fluorene-based polymers which find even minimal keto defects can induce strong long wavelength emission because of efficient energy migration between fluorene chromophores and energy transfer from fluorene chromophores to keto defects [45]. The reason will be discussed in the following.

To discuss the role of thermal oxidation on the photoluminescence properties of **P1**, we did the experiments on PL spectra for (1) fresh films, (2) films annealed in nitrogen at 150 °C (over the T_g of **P1**) for 8 and 30 h, (3) films annealed in air at 150 °C for 8, 12, 20 and 30 h. Fig. 2 shows the PL spectra of **P1** at different conditions and the related data are listed in Table 3. It can be seen from Fig. 2 and Table 3 that the PL spectra of the fresh film and the film annealed in N_2 are almost the same and dominated by emission at 415 nm, suggesting that heating alone cannot weaken the spectra stability of polymer. Different with the spectrum of **P1** annealed in N_2, the spectra of air-annealed films display an additional weak green emission around 525 nm. Combined with the emission spectrum of fluorenone-based polymer **P2**, it is believed that the green emission is attributed to fluorenone-like defects due to oxidative degradation of the film. To confirm the existence of fluorenone defect, transmission FT-IR spectroscopy was used to grope the structure varieties of these films (Fig. 3).

What puzzled us is that no signal for carbonyl groups was found in films of **P1** even air-annealed at 150 °C for 30 h. It is worth mentioning that the film of copolymer **P3** which contains 1 mol% of fluorenone shows a weak carbonyl IR signal at 1707 cm^{-1}, implying that even if the carbonyl groups formed in the annealing process, their content are much less than 1 mol% and could not be detected.

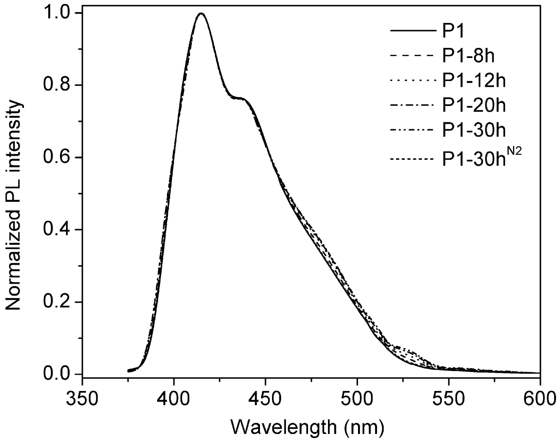


Fig. 2. The normalized PL emission spectra of films annealed in air.

Table 3
Intensity ratios (I_{Green}/I_{Blue}) of the blue emission (525 nm) to the strongest blue emission (415 nm) at different annealing process.

Samples	Annealing time (h)	Ambience	I_{Green}/I_{Blue}
P1	–	–	0.040
P1-8 h	8	Air	0.051
P1-12 h	12	Air	0.060
P1-20 h	20	Air	0.067
P1-30 h	30	Air	0.073
P1-30 h^{N2}	30	N_2	0.041

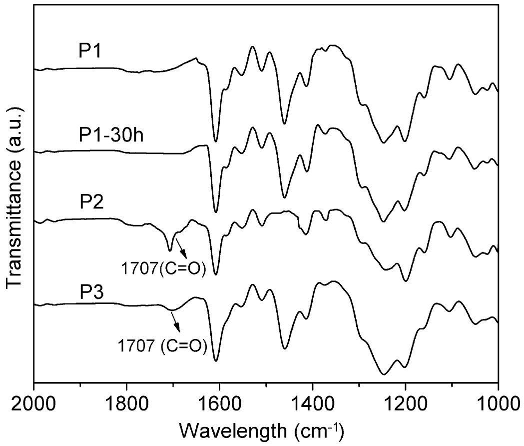


Fig. 3. FT-IR spectra of polymer films.

It is also found from the Table 3 that the I_{Green}/I_{Blue} ratio for air-annealed **P1** increases very slowly with increasing of annealing time. The I_{Green}/I_{Blue} air-annealed for 30 h at 150 °C is only 0.073, far below the values reported on the fluorene-based polymers [9,17]. The possible reason of good fluorescent spectroscopic stability of **P1** is that very few (far below 1 mol.%) keto defects produce in the process of thermal oxidation and this can be supported by the FT-IR spectra of **P1** and **P3** (Fig. 3). All the polymers reported in this paper are synthesized by the conventional condensation reaction without any metal catalysts and this can restrain the formation the keto defects in the process of thermal oxidation [16]. Secondly, the non-conjugated structure of **P1**, i.e. the interruption of the isopropylidene group in the polymer main chain, suppresses the energy transfer towards the keto defect sites. It is known that if the exciton reaches a conjugated segment with a fluorenone unit, it will be trapped there and the green emission occurs. But now the large bandgap due to the interruption of the isopropylidene group in the **P1** block the energy transfer both along backbone and between main chains. This is supported by the PL spectrum of copolymer **P3** (Fig. 1(b)). It was reported that incorporation of as little as 1 mol.% of fluorenone in conjugated polyfluorene can lead to strong green fluorescence and the I_{Green}/I_{Blue} ratio reached 0.9 [45]. But the non-conjugated copolymer **P3** which incorporates 1 mol.% fluorenone only shows a low I_{Green}/I_{Blue} ratio of 0.117 (Fig. 1(b)). It is considered that the interruption of the isopropylidene group in the main chain hinders the energy transfer along backbone. Similar phenomenon was reported in the fluorene-based conjugated polymer by appropriate UV-radiation [37]. Thirdly, we find that about 5–20% of the air-annealed films of **P1** are insoluble and these insoluble portions are thought to be cross-linking agents that can drive up the green emission [20]. The content of cross-linking agents for **P1** is only 5–20%, far below the value of 80% reported in the reference [20], and this may also help the polymer keeping good spectra stability.

3.3. Role of UV irradiation on the photoluminescence stability

To investigate the influence of UV irradiation on the photoluminescence properties of **P1**, we expose fresh films to intense UV-radiation of 300 W/m^2 xenon lamp (290–400 nm) for 15 and 30 min at room temperature. It is found that the green emission around 525 nm almost remain unchanged except the 4–6% decrease of the blue emission intensity at 415 nm (Fig. 4). Further investigation finds that there is hardly any crosslink in the films after irradiation. Transmission FT-IR spectroscopy does not show signal for carbonyl groups yet. The result indicates that UV irradiation has little influence on the long wavelength emission of **P1**.

4. Conclusion

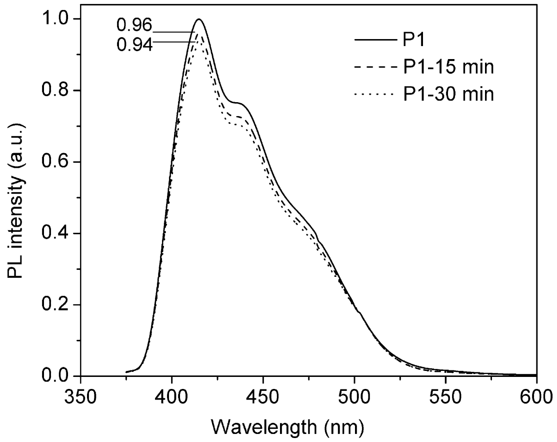


Fig. 4. PL emission spectra of films after UV irradiation.

In this paper, the stable blue luminescent non-conjugated polymers based on fluorene and benzoxazole are synthesized and characterized. The fluorene-based polymer **P1** shows a blue PL spectrum with the maximum emission peak at 415 nm. The influences of thermal annealing and UV irradiation on the photoluminescence properties of **P1** are investigated. This polymer displays excellent photoluminescence stability, and the green-to-blue emission intensity ratio I_{Green}/I_{Blue} is only 0.073 after annealing in air at 150 °C for 30 h. The photoluminescence spectra of **P1** almost remain unchanged after UV irradiation of 300 W for 30 min. The possible reasons for the excellent spectra stability of **P1** are the synthesis method without metal catalyst, the suppression of the energy transfer towards the keto defect sites due to the non-conjugated polymer structure, and the less crosslink after anneal.

Acknowledgments

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