

Studies of Green Emission in Polyfluorenes Using a Model Polymer

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(Received May 14, 2007; Accepted September 5, 2007; Published October 23, 2007)

ABSTRACT: The green emission (g-band) in polyfluorene-based conjugated materials is studied by various spectroscopic methods on defined poly(9,9'-dioctylfluorene) with one fluorenone unit (P₂₀), which can be seen as a model compound for polyfluorene emitting g-band. The absorption and emission properties of P₂₀ in the film and solution (room temperature) reveal the optical properties of the green emission emerging in polyfluorene-type polymer. All the experimental evidence obtained demonstrates that g-band in polyfluorene is attributed to the mono-chain fluorenone; and the aggregation of the chains further suppresses the blue emission and enhances g-band.

[doi:10.1295/polymj.PJ2007041]

KEY WORDS Polyfluorene / Conjugated Polymer / Membrane / Green Emission /

Conjugated polymers serving as emitters in light-emitting diodes (LEDs) are attractive to the display industry because of their potential ability for easy and cost-effective processing by solution casting, excellent mechanical properties and structure controllability to tune electro- and photophysical properties.^{1–6} Among the conjugated polymers considered for LED application, polyfluorenes (PFs) have been viewed as the most promising blue-light materials due to their extremely high solution and solid-state quantum efficiency, good charge transport, excellent chemical and thermal stabilities and tunability of physical parameters through chemical modification and copolymerization. However, a long-wave emission in the region of 490–550 nm,^{7–10} *i.e.* green emission (“g-band” for short), appears in the PFs spectra after ultraviolet light exposure, heating in the air or passage of current. The appearance of g-band is undesirable for two reasons: One is the reduction of the overall quantum efficiency, and the other is the impurity of the blue emission. Therefore, many research groups are studying the origin of g-band in order to suppress g-band. G-band had been early believed to originate from the aggregate of polyfluorene or polyfluorene-based excimer.^{11–13} But the PFs studied in the literatures are often synthesized *via* the Yamamoto route whose conditions are harsher than Suzuki coupling method and often result in production of fluorenone during and after the polymerization.^{14–16} Therefore, the origin of aggregate of polyfluorene cannot be accepted. Afterward, Sims *et al.* proposed a origin of fluorenone-based excimer.¹⁷ In their experiment, g-band was

not observed in PF/polystyrene blend film after UV-exposure, which was believed to be due to polystyrene blocking the formation of fluorenone-based excimer. But the inter-chain distance in PF film (about 1.28 nm¹⁷) is beyond the distance for excimer formation (about 0.3 nm or less¹⁸). It is difficult to form the fluorenone-based excimer in such a situation. And the theoretical calculation is also against the origin of the fluorenone-based excimer.¹⁹ List *et al.* presented a new origin of fluorenone defect.¹⁵ and other experimental evidence supported the opinion.^{20,21} But some experimental phenomena cannot be well explained by the opinion of fluorenone-defect yet.^{4,22–27}

Though the true origin of g-band (from fluorenone defect or fluorenone-based excimer) in the PF is not still clear, it is documented that the origin of g-band is related to the occurrence of the fluorenone.^{8,15,17,28–30} Therefore, a model molecule that is a copolymer of fluorene and fluorenone had been used to clarify the green emission in polyfluorene and the mechanism of fluorenone defect was proposed.⁸ But the occurrence of fluorenone segment (without alkyl substituent groups) in copolymer may allow the approach of aromatic groups to distance of 0.3 nm for excimer formation. Therefore, the validity of the model molecule was doubted.

In this work, a new model molecule that contains only one fluorenone unit in the midst of the PF chain (denoted as “P₂₀”) was designed to clarify the exact nature of g-band emission in the PF. The spectral properties of the model molecule in solution and film are investigated in detail. All the experimental evi-

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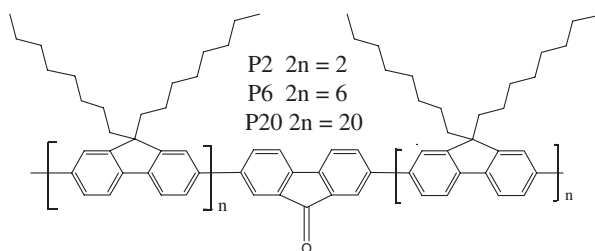


Figure 1. The structure formula of P_{2n}.

dence obtained demonstrates g-band in polyfluorene is attributed to the mono-chain fluorenone; more important, the aggregation of the chains suppresses the blue emission and enhances g-band.

EXPERIMENTAL

Materials

The model polymer (denoted as “P₂₀”) was polyfluorene containing one fluorenone unit in the chain, which was synthesized and characterized in our laboratory. The detailedly synthetical procedure was introduced in our previous literature.³¹ The ratio of fluorenone unit to fluorene unit in P₂₀ was around 1:20 according to the fed ratio and there is only one fluorenone unit in each P₂₀ chain. Other two oligofluorenes containing one fluorenone unit (denoted as “P₂” and “P₆”) were also synthesized and studied in order to compare with P₂₀. The P₂₀, P₆ and P₂ (the figure is the number of repeat fluorene units) were called P_{2n} by a joint name. The structure formula of P_{2n} is shown in Figure 1. The poly(9,9'-dioctylfluorene) (PF) was synthesized according to Suzuki polycondensation method.³² The molecular weight ($M_n = 9000$, $M_w/M_n = 2.6$) of PF was determined by gel permeation chromatography (GPC) calibrated with polystyrene standard.

Solution Preparation

All solutions were prepared by first dissolving the appropriated amount of polymer into a solvent and

then heated in oil bath at 50 °C with stirring for 24 h to fully dissolve.

Spectral Characterization

The UV-vis absorption spectra were recorded by a spectrophotometer of SHIMADZU, UV-1601PC. Steady state photo-luminescent (PL) spectra were recorded by a fluorescence photometer (VARIAN, Cary Eclipse, FLR025). The photo-luminescent lifetime measurements were performed with an Edinburgh Analytical Instruments (FLS-920). All spectral characterizations were carried out at room temperature.

RESULTS AND DISCUSSION

Spectral Characterization of P₂₀ Film and PF Film After UV-light Exposure for 24 h

There are two reasons to choose P₂₀ molecule as the model molecule. Firstly, the structure of P₂₀ is nearly identical to that of the PF except one fluorenone unit, which makes the P₂₀ well miscible with the PF. Secondly, the interaction between fluorenone units will be restricted because the fluorenone unit is packed by fluorene units, which is different the random copolymers of fluorene and fluorenone reported in literatures.⁸

In order to ensure that P₂₀ is a valid model polymer for the PF emitting green band, the spectral studies of the pure PF exposed to UV-light have been firstly carried out. It is found that a new emission peak at 530 nm appears when PF film is exposed to UV-light for 1 h. There is no emission peak at 530 nm in PF film before exposing (in the insert of Figure 2a). And the strength of g-band increases with increasing UV-light exposure time, which is identical to the phenomena reported by List *et al.*¹⁵ Figure 2 shows the PL and absorption spectra of PF film after UV-light exposure for 24 h (denoted as “PF-UV-24h”) and the blend film containing 75% P₂₀ and 25% PF (denoted as “P₂₀PF25”). The PL spectra of the two films have weak peaks at 424 nm and strong peaks at 532 nm.

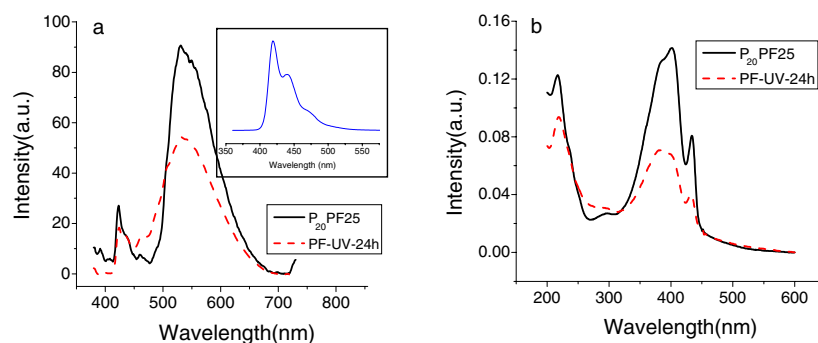


Figure 2. The emission (a) and absorbance (b) of PF-UV-24 h (dash) and P₂₀PF25 film (solid). The insert in (a) is the emission of pure PF before UV-exposure.

The PL peaks at 424 nm come from PF or PF segment and the peaks at 532 nm are g-band mentioned above. The absorption spectra of the two films have π - π^* transitions at 400 nm with shoulder peaks at 433 nm. It is suggested that the PL and absorption spectra of the PF-UV-24h film are the same as those of the P₂₀PF25 film.

Figure 3 shows the PL decays for g-band emissions of the PF-UV-24h film and the P₂₀PF25 film. Their decay curves are measured by exciting at 450 nm with 200 ps pulses and can be fit with single exponentials,¹⁷ yielding time constants of 6.656 ns for PF-UV-24h and 6.464 ns for P₂₀PF25. From above experiment results, we believe that the P₂₀ is a valid polymer for clarification of the exact nature of g-band emission in the PF.

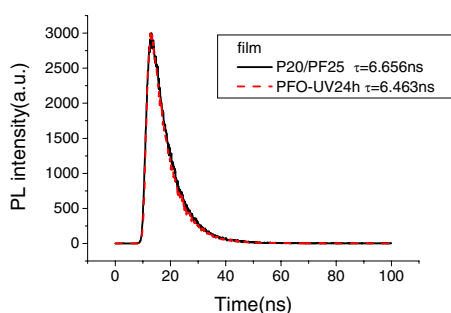


Figure 3. PL decays for g-band emission of PF-UV-24h film and P₂₀PF25 film (excited at 450 nm).

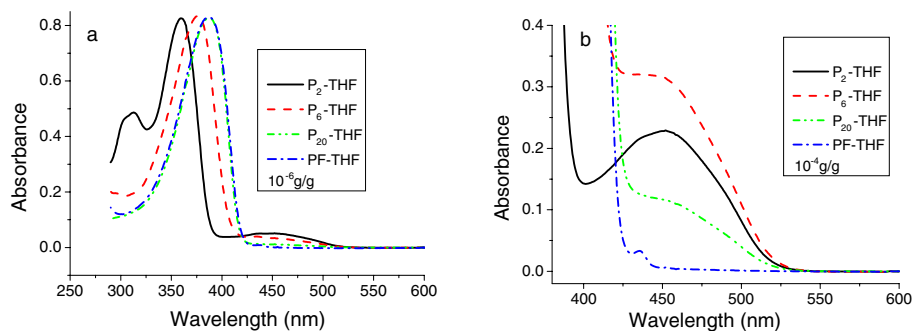


Figure 4. The absorption spectra of P_{2n} and PF in THF. a, π - π^* transition; b, CT π - π^* transition.

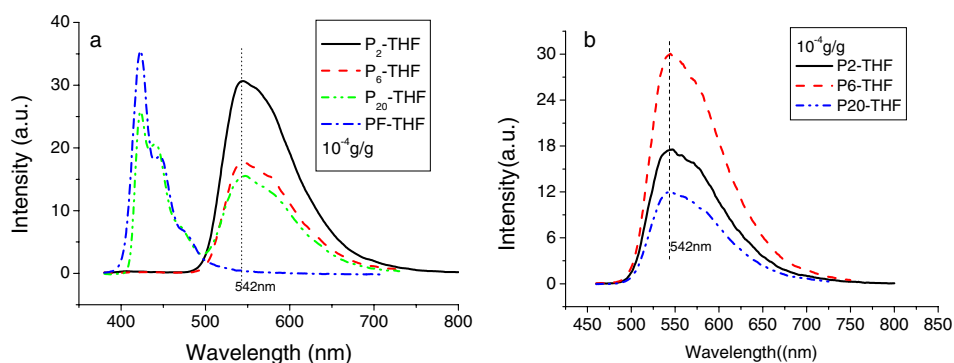


Figure 5. The PL spectra of P_{2n} and PF in THF at the concentration of 10⁻⁴ g/g. a, excited at 370 nm; b, excited at 450 nm.

Spectra of P_{2n} Solutions

Figure 4 shows the absorption spectra of P_{2n} and PF in tetrahydrofuran (THF). The maximum absorptions at 360, 376, 387 nm are assigned to π - π^* transition of main chain of P₂, P₆, P₂₀, respectively, and a long-wave absorption peak at 453 nm is all clearly observed in P₂, P₆, P₂₀ spectra and no absorption at 453 nm is observed in PF. The π - π^* transitions are red shifted with increasing the conjugated length of P_{2n} molecular chains (from P₂, to P₆, and to P₂₀), which is the same as those of oligofluorene with comparative number of repeat unit.³³ It is suggested that the fluorenone unit in P_{2n} cannot destroy the conjugation along the PF backbone. The long-wave absorptions of P_{2n} assigned to CT π - π^* transition are unchanged with the conjugated length, which is consistent with the result of the quantum chemical calculation.¹⁹

The effect of the conjugated length of the P_{2n} chains on g-band emission is shown in Figure 5. Through exciting at 370 nm (in Figure 5a), the emission spectra only contain g-band and without blue emission for the P₂, P₆ samples. This is because that the excitation of the fluorene can entirely transfer to the fluorenone moieties.³¹ And for the P₂₀ sample, the emission spectrum displays the regular PF feature except the long-wave emission at 542 nm. No emission at 542 nm is observed in PF. Exciting at 450 nm, only g-band with maximum at 542 nm is observed. The position and the

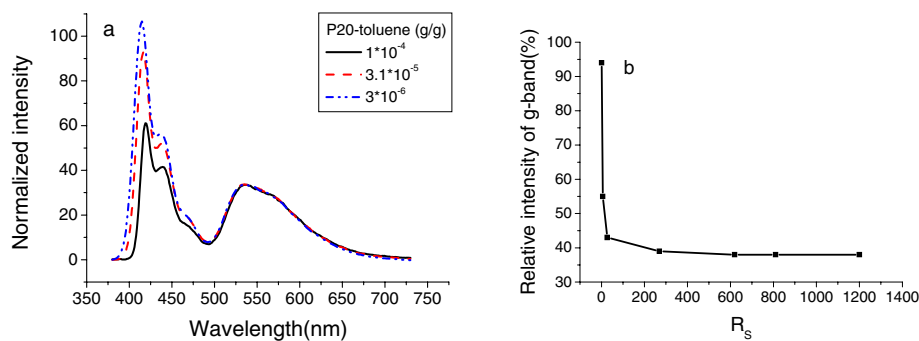


Figure 6. (a) The normalized PL spectra at different concentrations of P₂₀/toluene solution and (b) the relative strength of g-band at different multiple of dilution.

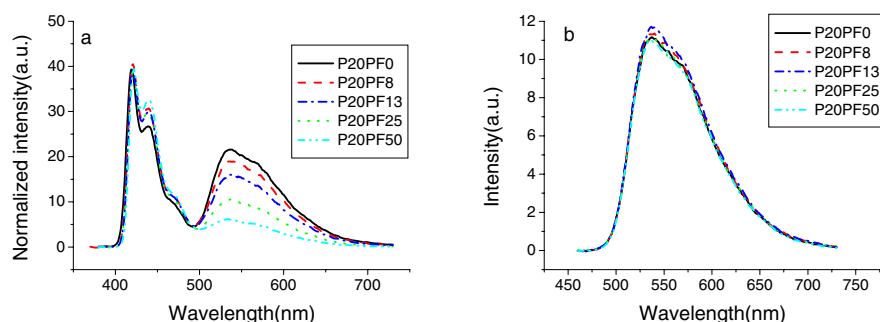


Figure 7. PL spectra of P₂₀/PF in toluene. a, excited at 370 nm, normalized spectra at 420 nm; b, excited at 450 nm. The concentration of P₂₀ in solution is fixed at 10⁻⁴ g/g. the number '0, 8, 13, 25, 50' in inset is the percentage of PF in P₂₀/PF blend.

shape of g-bands are identical for the three samples (in Figure 5b). It is suggested g-band emission is localized in fixed conjugated length, which is consistent with the quantum-chemical calculation.¹⁹

The changes of the emission spectra and the relative strength of g-band with the change of the concentration of the P₂₀/toluene solution are shown in Figure 6. The emission spectra are normalized at 530 nm. The blue band and g-band are observed in the emission spectra. The blue band is blue shifted from 419 nm to 414 nm when the concentration changes from 1 × 10⁻⁴ to 3 × 10⁻⁶ g/g. This suggests the interaction of chains decreases and blue-emission efficiency will improve. But g-band is not shifted with changing the concentration and shows the identical shape and location, which suggests that the decrease of interaction of chains does not affect the emission properties of g-band. It can also be observed from the Figure 6b, that the relative strength of g-band is quickly decreased firstly and then keeps unchanged when the solution is diluted. The relative strength of g-band is 93% at the concentration of 10⁻³ g/g PF in toluene. And when the solution concentration is decreased to lower than 5 × 10⁻⁶, the relative strength is rapid decreased to 38%, and then keeps unchanged when the concentration is further decreased. The rapid decrease of the relative strength of g-band is possibly due to the fast increase of the blue-emission efficiency of PF seg-

ments with dilution of the solution. When the solution is very dilute, the PF segments blue-emission luminescent efficiency is unchanged any more with dilution of the solution. Therefore, the relative strength of g-band is unchanged during further diluting. The results are different from the phenomena common to excimer emission that can be vanished in very dilute solution,^{17,18} which further support the origin of mono-chain fluorenone of g-band emission.

Spectra of PF/P₂₀ Blends

The emission properties of the PF/P₂₀ blends in toluene are shown in Figure 7a. In order to fix the concentration of the P₂₀ in the solution, the different amount of PF powder is added into the P₂₀/toluene solution with the concentration of 10⁻⁴ g/g. And the concentrations of the PF in the solutions are 0, 8 × 10⁻⁶, 1.3 × 10⁻⁵, 2.5 × 10⁻⁵ and 5.0 × 10⁻⁵ g/g, which are denoted as the P₂₀PF0, P₂₀PF8, P₂₀PF13, P₂₀PF25 and P₂₀PF50, respectively. The emission spectra excited as 370 nm are normalized at 420 nm. It can be found that the relative strength of g-band is decreased with increasing the content of the PF in Figure 7a. However, the strengths of g-band are identical when exciting 450 nm as shown in Figure 7b, that is, the strength of g-band is actually independent on the PF and depends on the fluorenone content when exciting at 450 nm. The above results demonstrate that

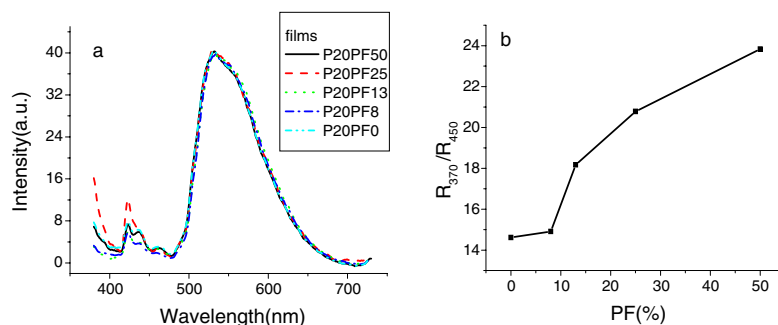


Figure 8. The emission spectra (a) and the intensity ratio of g-band strength excited at 370 nm to that excited at 450 nm (b) of P₂₀/PF blend films.

no interaction of fluorenone units occurs, which is because fluorene units closely pack the fluorenone unit, prevent approach of fluorenones. These phenomena are also different from those common to excimer emission.

The spectra of the P₂₀/PF blending films are shown in Figure 8a. In the film, the spectra show very strong g-bands and very weak blue emissions, that is, the blue emission is suppressed and g-band is enhanced in the aggregated state when comparing with the emission properties in the corresponding solutions. This may be due to the decrease of blue-emission efficiency and the enhancement of the inter-chain energy transfer from PF segments to fluorenone units in the film. It can be also found that the strength of g-band excited at 370 nm (R_{370}) is much higher than that excited at 450 nm (R_{450}). The ratio of R_{370}/R_{450} is above 14 when there is no dissociative PF in the system and is increased with increasing the PF content in the P₂₀/PF blend films, which is possibly due to more energy transferring from PF chains to fluorenone units (Figure 8b). This is different from the experimental phenomenon that demonstrated the origin of g-band of the fluorenone excimer.¹⁷

CONCLUSIONS

The origin of g-band in the PF is studied by using P₂₀ as a model polymer. The experiments rule out the fluorenone-based excimer origin and demonstrate the mono-chain fluorenone origin as the origin of g-band. The aggregation of the conjugated polymer suppresses the blue emission and enhances g-band emission. This conclusions will provide a clear direction for future material research to minimize the formation of the fluorenone defect.

Acknowledgment. The financial support by National Natural Science Foundation of China (Grant No. 50473057, 20374055, 50521302) and Chinese Academy of Sciences (Grant No. KJCX2-SW-H07) is greatly appreciated.

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