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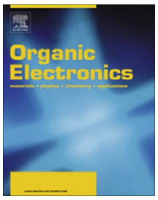

# The influence of residue aggregation in solution on photoluminescence and electroluminescence of polyoctylfluorene thin film

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## ABSTRACT

PFO thin films made of toluene solution dissolved for 12, 30 and 80 min at 55 °C were prepared and then treated by solvent vapor annealing or thermal annealing. Their absorption, photoluminescence, electroluminescence and morphology were characterized. The results show that the thin film made of solution dissolved for short time contains trace β phase PFO that lead to unusual emission. After solvent vapor annealing or thermal annealing, luminescence of such thin film is lower than that made of solution dissolved for long time. The surface morphology shows that such thin film contains large aggregations with size of 120 × 80 nm, which is in line with the light scattering results of 120 nm large particles in the solution, indicating the difference of luminescence originate from the residue aggregations. Such aggregations will lead to stronger diffraction peak in the in-plane GIXRD and weaker diffraction peak in the out-of-plane GIXRD, which indicates they have more ordered structure in main chain direction that will hinder the formation of ordered packing of PFO molecular chains in out-of-plane direction. These results demonstrate that the PFO solution needs to be dissolved for enough time to realize repeatment of high quality light-emitting device for actual massive application.

## 1. Introduction

Polymer light emitting diode (PLED) has attracted more and more attention because it can fabricate large area flexible device that will be applied in display and illumination [1–4]. Among the PLED materials, polyfluorene is a kind of widely used conjugated polymer due to its high photoluminescence efficiency, high hole mobility, good solubility and wide energy band gap, which can be used as blue-light-emitting material or host material [5–10]. Incorporating narrow bandgap unit into main chain or side chain of polyfluorene, the emission color can be tuned to green, red or white, which can be applied in full color display or lighting [5,11–15]. Another interesting characteristic of polyfluorene is its polymorphism. For example, poly(9,9-dioctylfluorene) (PFO) has amorphous, α, α′, β and nematic phase. In particular, the β phase of PFO has been most focused because of its pure blue emission and specific physical properties. The β phase of PFO can be achieved by the several methods: casting from the PFO solution using solvent with low solvent power; exposure PFO thin film to solvent vapor (solvent vapor annealing); cooling and reheating PFO thin film to room temperature; dipping in mixed solvent/nonsolvent; end-capping PFO with electron-deficient moieties [6,7].

However our previous work found that sometimes trace β phase even present in the thin film spin-coated from fresh solution in good solvent, which usually is amorphous [16]. After thermal annealing or solvent vapor annealing, the photoluminescence of such thin film is weaker than

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that of amorphous thin film. This phenomenon is harmful for actual massive application because it will affect the reproduction of device performance. Characterization using atomic force microscope found that there are some larger aggregations in the PFO thin films made of its solution prepared at low temperature for short time. The aggregations are suspected of originating from the residue gel in the solution, which need to be proved by more detailed evidences. In this work, we study PFO toluene solution prepared in different condition by light scattering to investigate the origin of aggregations in the thin film. The surface morphology and nanostructure of corresponding thin film were characterized by using atomic force microscope and grazing incident X-ray diffraction to reveal the mechanism of the influence of aggregations on photoluminescence and electroluminescence.

## 2. Material and methods

PFO was purchased from Aldrich Company and was dissolve in toluene with a concentration of 5 mg/ml at 55 °C. The films were obtained by spin-coating from the solution dissolved for various time (12, 30 and 80 min). For the solvent vapor annealing, the film was put into a container fill with saturated toluene vapor for 30 min. For the thermal annealing, the film was heated at 120 °C for 30 min under $N_2$ atmosphere. The UV–visible (UV) absorption spectrum was test from 300–500 nm with a Persee TU-1901 UV–Vis spectrophotometer. The photoluminescence (PL) spectrum was measured from 400–600 nm with an excitation of 380 nm by using a Shimadzu RF 5301 spectrofluorophotometer. The photoluminescence quantum efficiency was calculated in the reference method reported in Refs. [17,18]. The as-spin-coating PFO thin film made of solution dissolved for 80 min was used as standard and its quantum efficiency (53.5%, in line with reference 18) was calibrated by using an integrating sphere. Light-emitting devices (ITO/PEDOT:PSS/PFO/Ca/Al) were fabricated as follows: firstly spin-coating a hole-injection layer (PEDOT:PSS) onto transparent conductive indium tin oxide (ITO) glass, then spin-coating an active layer (PFO) on top of the PEDOT:PSS layer, followed by solvent vapor annealing or thermal annealing, finally the combination of calcium and aluminum was thermally evaporated as the cathode. The luminance-current–voltage characteristics of the devices were recorded using a combination of Keithley 2400 sourcemeter and Spectra Scan PR650 spectrophotometer.

The light scattering measurements were carried out using Malvern Zetasizer Nano ZS90 Zeta Potential and Size analyzer with a 633 nm He–Ne laser as the light source. AFM image was measured by using a Seiko SPI3800 N scanning probe microscope in tapping mode. For the out-of-plane grazing incident X-ray diffraction studies, a Bruker D8 discover diffractometer equipped with a copper target + Göbel mirror (Kα1 line, $\lambda = 0.15406$ nm), a motorized reflectometry sample stage and a multi-slit + Scintillation detector was used. The in-plane grazing incident X-ray diffraction was measured at Beijing Synchrotron Radiation Facility on beam line 1W1A ($\lambda = 0.154$ nm) with a Huber 5-circle diffractormeter and a point detector. Data are expressed as a function of the scattering vector, q, that has a magnitude of ($4\pi\sin\theta/\lambda$).

## 3. Results and discussion

Fig. 1a and b shows the photoluminescence and UV–Visible absorption spectra of the PFO thin films spin-coated from solution dissolved for 12, 30 and 80 min at 55 °C. The absorption spectrum of the thin film made of solution dissolved for 12 min has a small absorption peak at 430 nm beside main peak at 380 nm, which is consistent with that of the reported β phase PFO. Likewise, two emission peaks at 440 nm and 460 nm corresponding to β phase PFO appears in the photoluminescence spectrum. Another photoluminescence peak at 422 nm corresponding to amorphous PFO can also be observed, which means uncompleted energy transfer that indicates the content of β phase PFO is very low. As increasing the dissolving time to 30 min, the obtained film also shows luminescence peak similar to the above films. However, the intensity of photoluminescence peak at the 440 nm corresponding to the β phase PFO decreases from 420 to 263, while the intensity of peak at the 422 nm corresponding to amorphous PFO increases from 186 to 234. This is due to more uncompleted energy transfer caused by the reduction of content of β phase PFO, which is indicated by the smaller absorption peak at 430 nm. Keep increasing the dissolving time to 80 min, the absorption peak at 430 nm disappeared and the photoluminescence spectrum present three peak at 422, 457, and 479 nm, which is well agreed with the amorphous phase of PFO. The integrated areas of such three PFO thin film are 13191, 12050 and 13331 respectively and their absorptions at 380 nm are 0.291, 0.294 and 0.292 respectively. Thus their photoluminescence quantum efficiency can be calculated to be 53.1%, 48.0% and 53.5%. Because β phase PFO can lead to “self dopant” effect that will enhance quantum efficiency, such similar quantum efficiencies indicate the thin film containing trace β phase PFO must has some negative influence that reduce quantum efficiency.

The performance of electroluminescence device based on PFO thin film made of solution dissolved for 12 min (A) is almost same with that based on thin film made of solution dissolved for 80 min (B) (see Fig. 2a). Their onset voltage and breakthrough voltage are both 3.5 and 7.5 V. When the bias is less than 7.0 V the brightness of device A is lower than that of device B. Under 7.5 V their brightness of device A (2386 Cd/$m^2$) is higher than that (2271 Cd/$m^2$) of device B. However as shown in Fig. 2b the maximum efficiency of device A (0.86 Cd/A) is slightly higher than that of device B (0.61Cd/A), which may be due to the “self-dopant” effect of trace β phase PFO. Their electroluminescence spectra (shown in Fig. 3c) are similar with photoluminescence spectra. The EL spectrum of device A has a main peak at 440 nm corresponding to β phase PFO and a shoulder peak at 424 nm corresponding to amorphous PFO. Since the electroluminescence is the mixed emission, there should exits six peaks, which is overlapped and cannot be identified separately. As dissolved time increasing, mixed emission changes to single emission

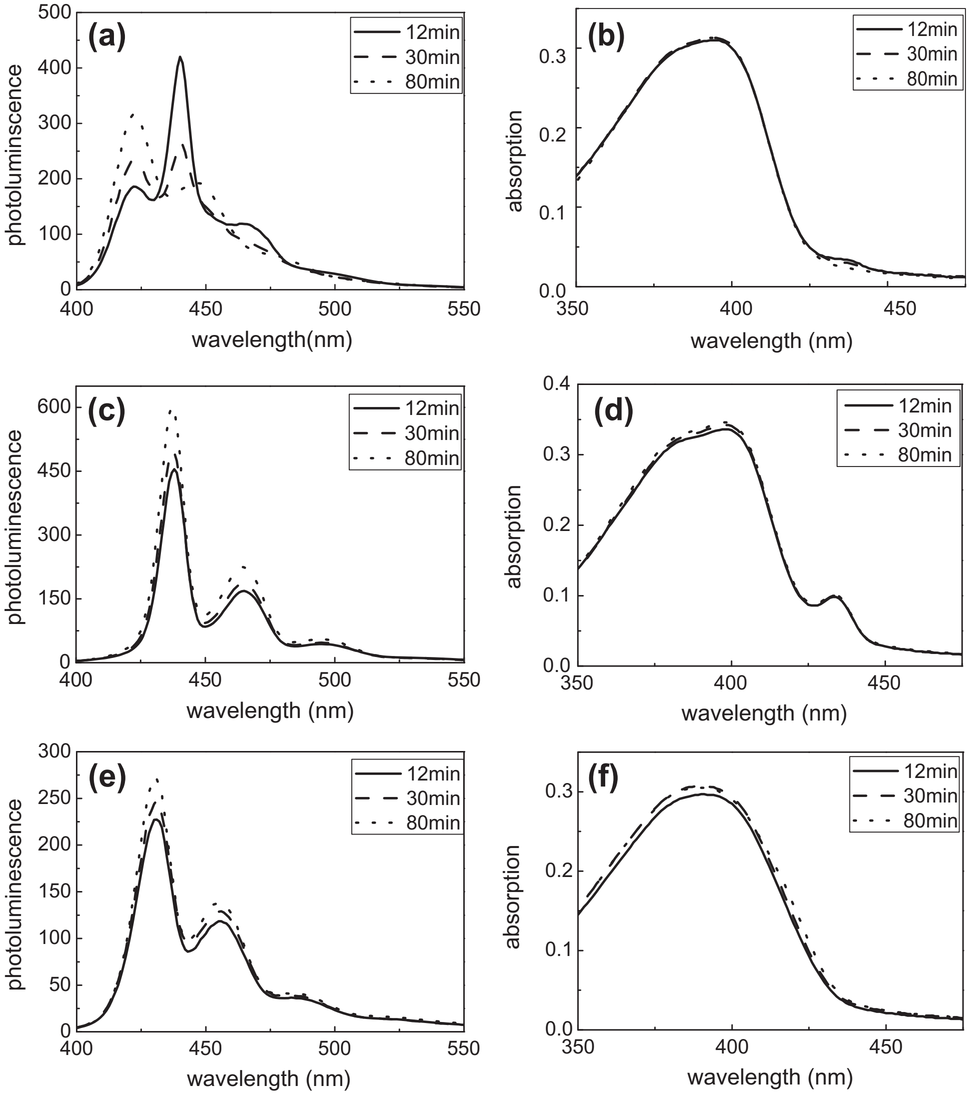

**Fig. 1.** Photoluminescence and absorption spectra of the as-spin-coating (a and b), solvent vapor annealed (c and d) and thermal annealed (e and f) PFO thin film made of toluene solution dissolved for 12, 30 and 80 min at 55 °C.

corresponding to amorphous PFO, which shows only three peaks at 424, 448 and 480 nm in the electroluminescence spectrum of device B.

To investigate whether the difference of luminescence can be eliminated by further treatment, such PFO thin films were solvent vapor annealed by exposure to toluene vapor for 30 min. In the UV absorption spectra shown in Fig. 1d, all the films show a small peak at 430 nm beside main peak at 380 nm and their intensities are almost same, which indicates the difference of content of β phase PFO is reduced. The photoluminescence spectra (shown in Fig. 1c) display three peaks at 438, 464, and 495 nm, which is corresponding to β phase PFO because of the efficient energy transfer from amorphous PFO to β phase PFO. The integrated area of photoluminescence peaks increase from 11734 to 12729 and 15104 and the quantum efficiency increase from 44.2% to 47.4% and 55.3% with the increasing dissolved time from 12 to 30 and 80 min respectively, which demonstrates that the difference of luminescence still exists. Although the maximum efficiency of device based on solvent annealed PFO thin film made of solution dissolved for 12 and 80 min are almost same, 2.29 and 2.15 Cd/A respectively (shown in Fig. 2d), the brightness of such two devices are 1764 and 3770 Cd/m$^2$ respectively (shown in Fig. 2c), demonstrating the difference of electroluminescence is enhanced after solvent vapor annealing.

Thermal annealing was also used to treat PFO thin film because it can rearrange the packing of molecular chain more easily, which may eliminate the luminescence difference. Fig. 1e and f show the photoluminescence and absorption spectra of the thin films thermal annealed at 120 °C for 30 min. The UV absorption spectra of all the films show a similar pattern with a broader peak at 380 nm with an edge at 440 nm, which is consistent with

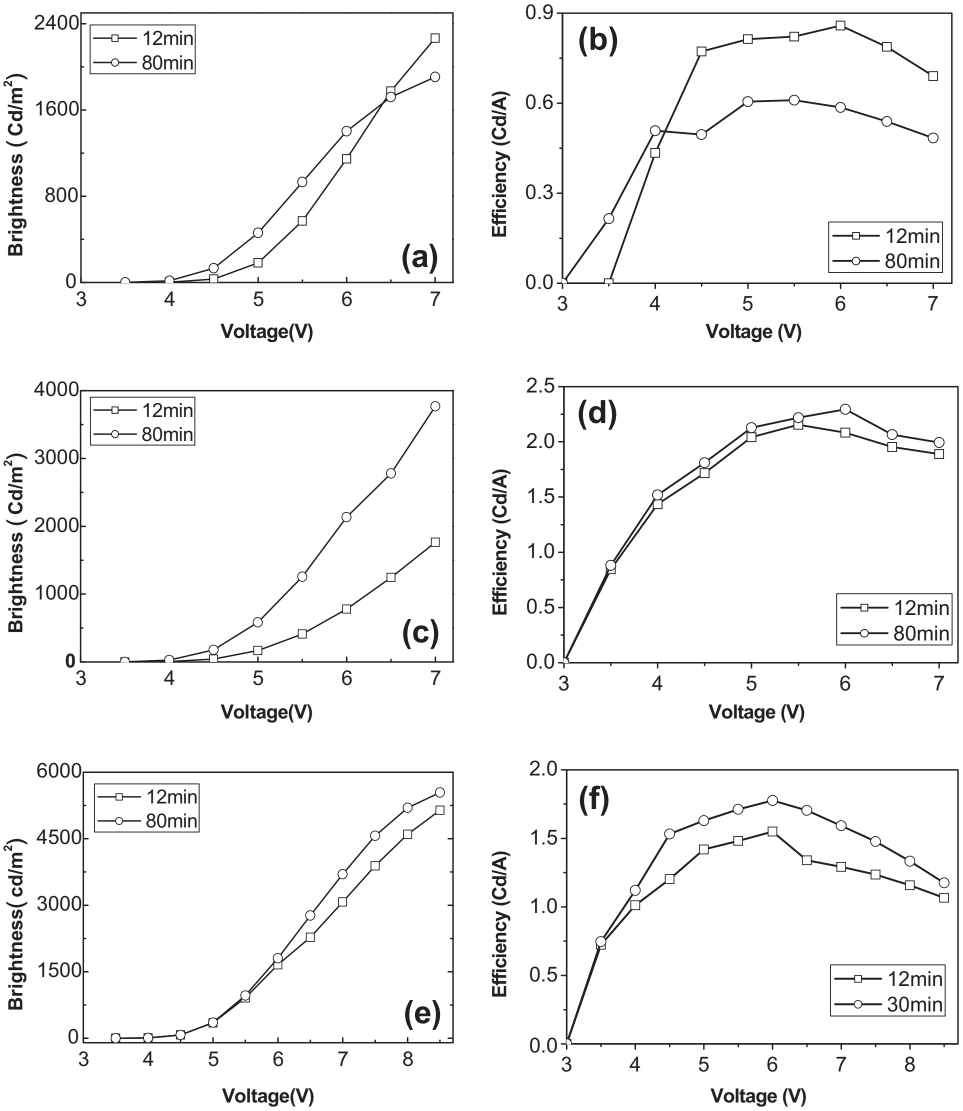

**Fig. 2.** Brightness–voltage curve and efficiency–voltage curve of the electroluminescence device based on the as-spin-coating (a and b), solvent vapor annealed (c and d) and thermal annealed (e and f) PFO thin film made of toluene solution dissolved for 12 and 80 min at 55 °C.

the reported absorption of α phase of PFO. The same peak intensities indicate that the content of α phase PFO are almost same. The PL spectrum of all films also exhibit similar shape with three typical peaks at 431, 455 and 485 nm, consistent with that of α phase of PFO. However, the integrated area of photoluminescence peaks increase from 8849 to 9492 and 10197 and the quantum efficiency increase from 36.5% to 37.6% and 40.5% with the increasing dissolved time from 12 to 30 and 80 min respectively, which demonstrates that the photoluminescence is enhanced with increasing dissolving time. The brightness and the maximum efficiency of related electroluminescence device (shown in Fig. 2e and f) also slightly increases from 5142 (12 min) to 5542 Cd/m$^2$ (80 min) and 1.55 to 1.77 Cd/A. These results demonstrate that the difference of luminescence is reduced but still exists after thermal annealing.

These results indicate that the state of solution has a dramatically influence on the luminescence properties of PFO thin film, although all the solutions are look as clear. To reveal the origin of the difference of luminescence, the PFO solutions dissolved for various time were characterized using light-scattering and the results are shown in Fig. 3a. For the solution dissolved 12 min, it mainly contains two kinds of particles with the size of 24 and 120 nm respectively. As the dissolved time lengthened to 30 min, the amount of particles with size of 120 nm is decreased. For the solution dissolved for 80 min, only particle with size of 24 nm can be observed. These imply that the difference come from the large particles remain in the solution dissolved for shorter time, which cannot be observed by the naked eye. Because the dissolving process of PFO includes swelling at beginning, followed gelation and final dispersion, the large particles should be the

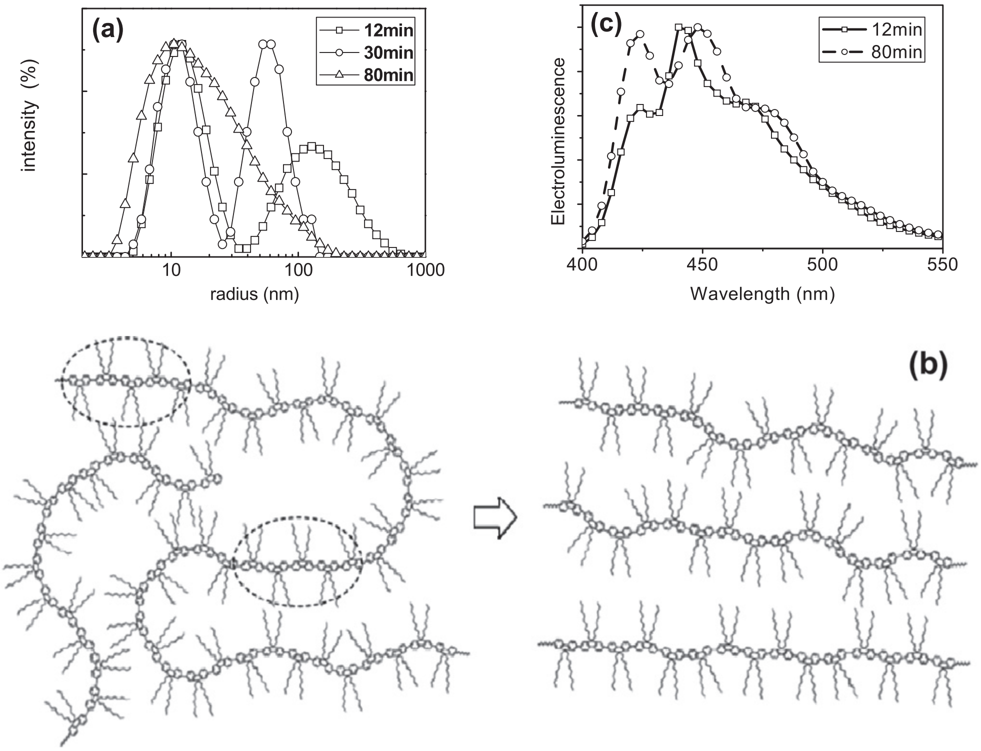

**Fig. 3.** (a) Light scattering intensity distribution for PFO solution dissolved for 12, 30 and 80 min at 55 °C. (b) Schematic illustration of the structural modification from residue aggregations to well dispersed state. (c) Electroluminescence spectra of device based on PFO thin film made of solution dissolved for 12, and 80 min at 55 °C.

"residue aggregation" that has not well dispersed in the solution. To study the influence of such aggregations on the corresponding PFO thin film, the surface morphologies of as-spin-coating and treated PFO thin film were characterized by using atomic force microscope (AFM). For as-spin-coating films, short dissolved time lead to a film contained large islands with an average size of 120 × 80 nm (Fig. 4a), which is consistent with the large particles in the solution. As the dissolved time increased to 30 min, the islands gradually become long and narrow with an average size of 140 × 40 nm, in addition with lots of small islands with an average size of 40 × 40 nm (Fig. 4b). The thin film obtained from solution dissolved 80 min only present small islands with an average size of 40 × 40 nm (Fig. 4c), which is larger than the particle size in the solution. This is because light scattering measure the well dispersed PFO molecular chain in the solution while AFM measure the aggregation of PFO molecular chain in the thin film. After solvent vapor annealing, in the PFO thin films made of solution dissolved for short time the large islands become smaller (Fig. 4d–f). In the PFO thin films made of solution dissolved for long time the boundaries of small islands become obscure while the surface roughness increase. After thermal annealing, both large islands and small islands become larger due to the formation of α phase PFO crystallites (Fig. 4g–i). The crystallite sizes of PFO thin films made of solution dissolved for 12, 30 and 80 min are 230 × 170, 120 × 100 and 110 × 40 nm respectively.

In order to get a deep insight of the origin of the influence of aggregations, the nanostructure of the PFO thin films was characterized by using grazing incident X-ray diffraction. For the as spin coating PFO thin film, there are only a broad and weak diffraction peaks at 14.5 nm$^{-1}$ in out-of-plane GIXRD (Fig. 5a) and no obvious diffraction peak in in-plane GIXRD (Fig. 5b). Although absorption and photoluminescence spectra indicates the exits of β phase PFO, diffraction peak of β phase does not appear because its content is very low. After solvent vapor annealing, an obviously diffraction peak at 14.5 nm$^{-1}$ corresponding to intramolecular chain ordered structure appears in the in-plane GIXRD (Fig. 5d) of the PFO thin film made of solution dissolved for 12 min. As dissolved time increase, such diffraction peak becomes weak and broad, indicating the decrease of content of β phase PFO, which is in line with the results of absorption spectra. This shows PFO aggregations have more ordered structure in main chain direction. The out-of-plane GIXRD (Fig. 5c) of the PFO thin films made of different solution all have two more diffraction peaks at 5.0 and 10.0 nm$^{-1}$, corresponding to intermolecular chain ordered structure. They are so weak that no obvious difference can be observed and thus the difference of ordered structure in out-of-plane direction cannot be estimated. After thermal annealing, PFO convert to α phase, which has obvious diffraction peaks. In the out-of-plane diffraction patterns (Fig. 5e) of the three films after thermal annealing, three diffraction peak at 4.8, 7.5 and 14.8 nm$^{-1}$ can be observed, which are corresponding to

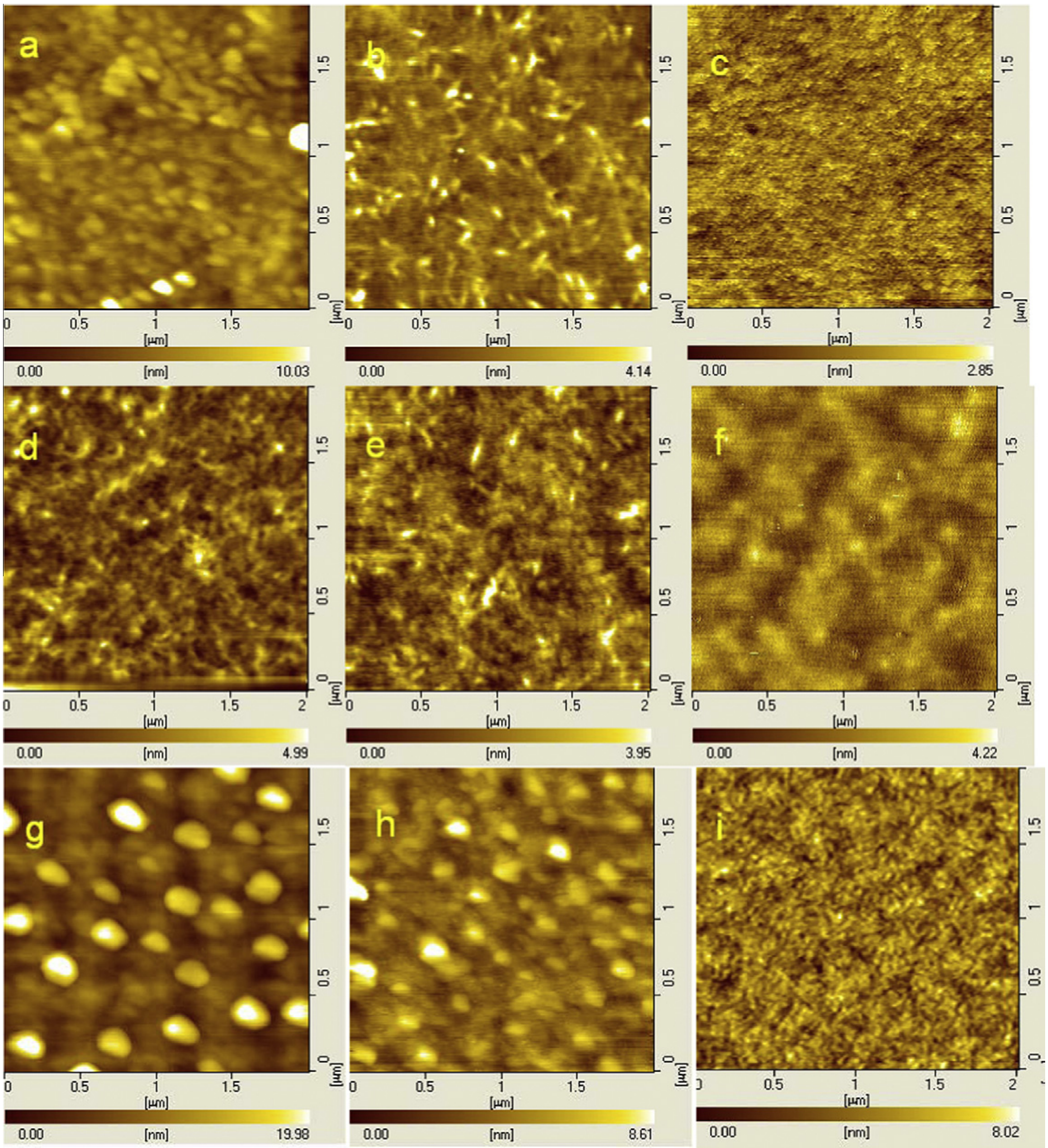

**Fig. 4.** Surface morphology of the as-spin-coating (a, b and c), solvent vapor annealed (d, e and f) and thermal annealed (g, h and i) PFO thin film made of toluene solution dissolved for 12, 30 and 80 min at 55 °C.

(200), (310) and (008) of α phase PFO. The intensities of main (200) peak, which corresponding to intermolecular chain ordered structure, increase from 2960 to 3230 and 4200 counts as dissolving time increasing from 12 to 30 and 80 min respectively, demonstrating that PFO aggregations have less ordered structure in side chain direction. On the contrary in the in-plane diffraction patterns (Fig. 5f) only one (008) diffraction peak, which corresponding to intramolecular chain ordered structure, can be observed and its intensities decrease from 160 to 140 and 115, also demonstrating that PFO aggregations have more ordered structure in main chain direction.

Because the aggregations originate from the large particles (residue gel) in solution, these results indicate that the large particles should have some ordered structure in main chain direction. On the other hand, the island-like morphology indicates they also have some bend molecular chains. Thus the large particles maybe have the coil-like structure containing some ordered rod-like segment (shown in Fig. 3b). Such structure will be kept in the corresponding thin film and hinder the formation of ordered packing of PFO molecular chains in out-of-plane direction (side chain direction). As dissolving time increase and the residue gel well disperse, such structure will disappear

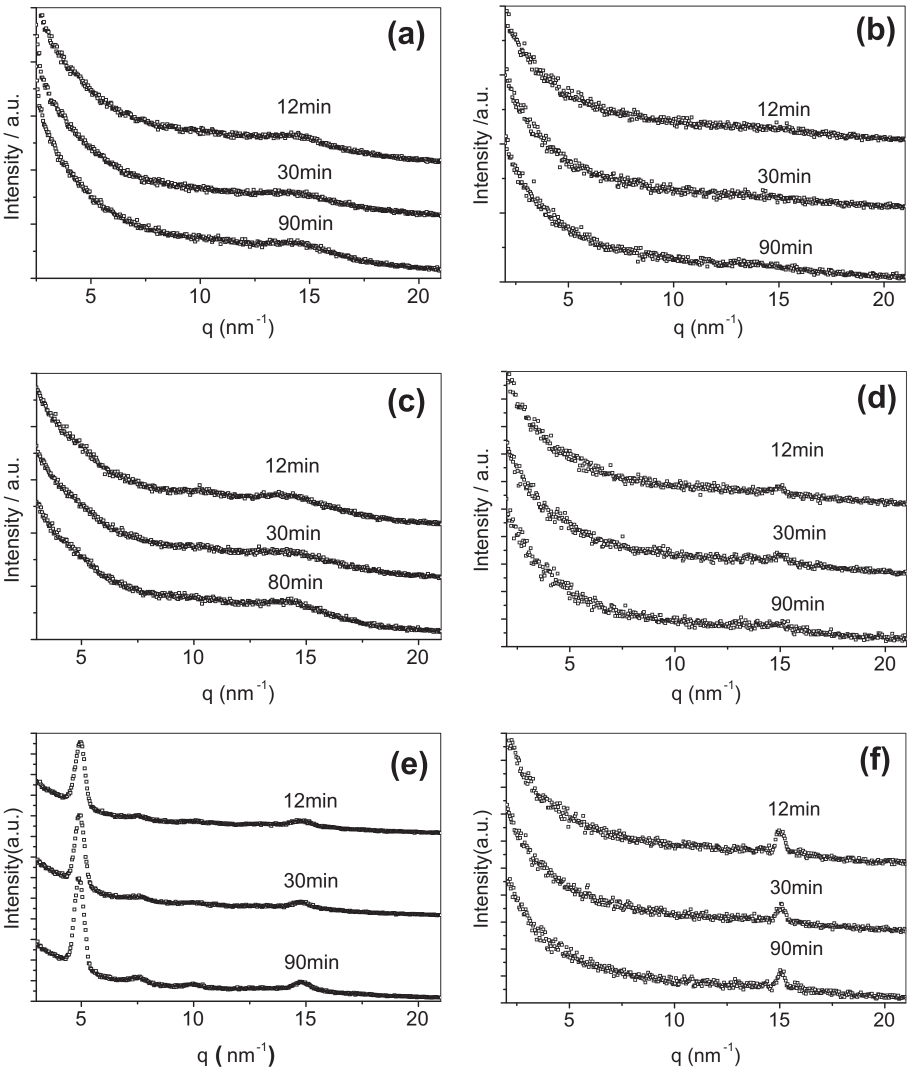

**Fig. 5.** (a, c and e) Out-of-plane and (b, d and f) in-plane grazing incident X-ray diffraction pattern of as-spinning coating, solvent vapor annealed, thermal annealed PFO thin film made of toluene solution dissolved for 12, 30 and 80 min at 55 °C.

and disordered rod-like structure (shown in Fig. 3b) appears. Although more vacancy defects will exist in thin film containing aggregations, its luminescence is not reduced by quenching and efficiency is even higher, which is due to the "dopant-effect" of trace β phase PFO. After solvent vapor annealing, "dopant-effect" occurs in both devices and thus their efficiency are almost the same. However the worse packing cannot be significantly ameliorated because the movement ability of PFO molecular chains is low and meanwhile more defects generates due to the formation of crystallites, the quenching effect appears and lead to the enlargement of the difference of luminescence. After thermal annealing the quenching effect is reduced because molecular chains can rearrange during annealing and eliminate some vacancy defects, resulting in the less difference of luminescence and efficiency.

Actually the influence of residue aggregation still exist even when its size is very small, which is demonstrated by the various luminescence of PFO thin film if the solution was not carefully prepared. In order to totally eliminate the effect of residue aggregation the solution need to be prepared for enough long time or high temperature. On the other hand, even after the PFO molecular chains are well dispersed in solution, they will aggregate again in the solution, which is also demonstrated by the variation of luminescence of PFO thin film made of solution aged for different time. Further research will be focused on the influence the aggregations formed during aging.

## 4. Conclusion

We have studied the influence of preparation condition of polyoctylfluorene solution on the luminescence of corresponding thin film and reveal its origin. Light scattering characterization shows that the solution dissolved for short time contains large particles with size of 120 nm, which come from the residue aggregations and transform to small particles with size of 24 nm when dissolving time increase. The PFO thin film made of solution containing large particles has aggregations with size of 120 × 80 nm, which still remain even after solvent vapor annealing or thermal annealing. The aggregations leads to partly emission of β phase PFO in as-spin-coating thin film and will reduce the luminescence contrasting to that without aggregations after solvent vapor annealing or thermal annealing. Characterizing the nanostructure using GIXRD indicates that the large particle has more ordered structure in molecular main chain direction because of residue aggregation structure, which is kept in the thin film and hinder the formation of ordered packing of PFO molecular chains in out-of-plane direction while enhance the content of ordered structure in in-plane direction. Such nanostructure will lead to more defects that will reduce the luminescence. These results demonstrate that the PFO solution dissolved for enough time will lead to repeatable high quality light-emitting device after totally eliminating the influence of residue aggregation.

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