

Nondilute 1,2-Dichloroethane Solution of Poly(9,9-dioctylfluorene-2,7-diyl): A Study on the Aggregation Process*

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Abstract Molecular aggregates in conjugated polymer (CP) solution can propagate into mesoscale morphology of the relevant film and further dominate the optoelectronic property. Herein, we probed the aggregation behavior of poly(9,9-dioctylfluorene-2,7-diyl) (PFO) and studied its influence on the photophysical property in 1,2-dichloroethane (DCE) solution, where the contents of β -phase or -aggregates increased with prolonged aging time. Thereinto, high quality β -film was fabricated from DCE solution with critical aggregate time of 6 min. The film exhibited excellent surface morphology and characteristic emission of β -phase. Meanwhile, films prepared from aged DCE solutions exhibited high crystallinity, which was promising to obtain higher photoluminance efficiency and charge transport ability simultaneously. Therefore, it is significant to get deep insight into the aggregation behavior of CP, which is involved not only with the solution-processing technology of plastic device, but also with the optoelectronic property of CP.

Keywords: Poly(9,9-dioctylfluorene-2,7-diyl); Aggregation behavior; Film morphology; β -Phase.

INTRODUCTION

Conjugated polymer (CP) is an important family of organic optoelectronic materials for applications in polymer light-emitting diodes (PLEDs)^[1, 2], transistors^[3], organic lasers^[4] and photovoltaics^[5–7]. As the bridge between polymer chain and plastic device, film morphology plays a critical role in governing the fundamental exciton and

* This work was financially supported by the National Key Basic Research Program of China (973) (No. 2015CB932200), the National Natural Science Funds for Excellent Young Scholar (No. 21322402), the National Natural Science Foundation of China (Nos. 21504041, 21274064 and 61475074), University of Jiangsu Province Natural Science Foundation Project (No. 14KJB510027), Natural Science of the Education Committee of Jiangsu Province (No. 15KJB430019), Jiangsu Planned Projects for Postdoctoral Research Funds (No. 1501019B), China Postdoctoral Science Foundation (No. 2015M580419), SICAM Fellowship, Imperial College London and Open Project from State Key Laboratory of Supramolecular Structure and Materials at Jilin University (No. sklssm201612).

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Received May 4, 2016; Revised June 23, 2016; Accepted June 28, 2016

doi: 10.1007/s10118-016-1851-z

carrier behaviors in the film state, and further dominates the performance and stability of printed plastic devices^[8–12]. In this regard, studying on aggregate structures in CP solution becomes necessary, since the solution contains some “precursory structures” that would dominate the structural development in the film-casting process^[13–16]. The accepted definition of “aggregate”, a cluster of polymer chains, remains ambiguous in solution states. Under this circumstance, both the structures with amorphous state and some degree of crystallization are defined as aggregates, without taking into account of whether they influence the resulting optoelectronic properties. Therefore, to further gain insight into the aggregation behavior of CP in the solution states become imperative, so do the effect on the film morphology and optoelectronic property ultimately.

Among a wide variety of CP thus far studied, polyfluorenes (PFs) have been intensely investigated in PLEDs and organic lasers for their deep blue emission^[17, 18] and high photoluminance quantum yield (PLQY)^[19], which show polymorphic behaviors, including amorphous phase, β -phase, liquid crystalline, semi crystalline α and α' phases^[20, 21]. Particularly, β -phase shows a series of attractive features, such as higher charge-carrier mobility^[22], higher current efficiency and excellent spectral stability in PLEDs^[23–26], efficient amplified spontaneous emission (ASE) and low threshold lasers^[27–29]. Actually, molecular gelation processing is the most extensive self-aggregating strategy to induce the formation of β -phase in solution and gelation-film states^[29–31]. Our previous work indicated that poly(9,9-dioctylfluorene-2,7-diyl) (PFO) can form gel in 1,2-dichloroethane (DCE) solution^[30], which provided an effective way to fabricate high quality β -phase film for high efficiency and stable deep-blue PLEDs^[25]. In order to establish a research model, this work focuses on the influence of the aggregates in PFO-DCE solution on the morphology and optical property of corresponding spin-coated film. We systematically investigated the time-dependent aggregation behavior of PFO in DCE solution, and its effect on the optical property and morphology of relevant spin-coated films by dynamic light scattering (DLS), UV-Vis absorption and photoluminescence (PL), atom force microscope (AFM) and grazing incidence X-ray diffraction (GIXD).

EXPERIMENTAL

Chemicals

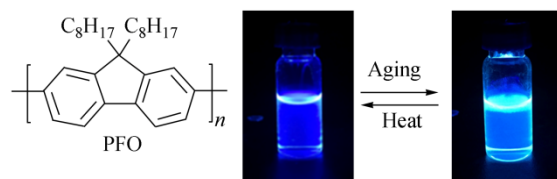
PFO was synthesized according to our previous work^[31]. DCE was received from Aldrich Chemicals and used without further purification.

Characterization

Dynamic light scattering measurements were carried out using an ALV/CGS-3 light scattering spectrometer equipped with an ALV/LSE-7004 multiple- τ digital correlator over the time range of 10^{-8} – 10^3 s. JDS-Uniphase solid-state He-Ne laser, which has the output power of about 22 mW at the operating wavelength of 632.8 nm, was used as the light source. The light scattering (LS) cell is held in a thermostat refractive index matching vat filled with purified and dust-free toluene. Absorption spectra were measured with a Perkin-Elmer UV/VIS spectrometer (Lambda 650 S), and the PL spectra were recorded by using a Perkin-Elmer LS55 fluorescence spectrometer. Quartz cells of 10 mm thickness were used to measure the spectra. AFM images of polyfluorenes films spin-coated on silicon chips were obtained by using a Dimension 3100 (Veeco, CA) in tapping model with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N·m⁻¹) at a scanning rate of 1 Hz. Grazing incidence X-ray diffraction (GIXD) measurements were performed on Beamline 7.3.3 at the Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory.

Preparation of PFO DCE Solutions and Film

The chemical structure of PFO and the photographs of PFO aggregation processing in DCE solution under UV lamp with the irradiation wavelength of 365 nm are shown in Scheme 1. PFO was prepared *via* Yamamoto-type polymerization and the corresponding number average molecular weight (M_n) was measured to be about 62.1 kDa with polydispersity index (PDI) of 1.7. DCE solutions of PFO were prepared by stirring their mixtures at about 80 °C for 3 h, leaving it to stand and cooling to room temperature, where macroscopically homogeneous solutions were observed by naked eyes. PFO films were obtained *via* spin-coating from DCE solution at various aging time with a spin-coating speed of 1000 r/min.



Scheme 1 Chemical structure of PFO and photographs of PFO aggregation processing in DCE solution under UV lamp with irradiation wavelength of 365 nm

RESULTS AND DISCUSSION

Dynamic Light Scattering Measurements

DLS was utilized to probe the aggregation behavior of PFO during gelation process^[32, 33]. The dispersion state of polymer chains in the solution can be reflected directly by its dynamics. Figure 1 presents the normalized intensity correlation function, $g^2(t)-1$, and the hydrodynamic radius (R_h) distribution of 1 mg/mL PFO/DCE solution as a function of aging time at 25 °C at scattering angle $\theta = 90^\circ$. For these experiments, the solutions were constantly stirred at 80 °C prior to DLS measurements, followed by quick transfer to sample cells for DLS experiments. Then we conducted the time-resolved DLS experiments. It can be seen that the intensity of the correlation function grew with increasing aging time. The average R_h also increased with aging time, showing coarsening or clustering of aggregates in the solution upon aging. Three regimes are seen in Fig. 1. In about 10 min, the intensity correlation function did not shift obviously with the increase in aging time and displayed the fast mode, which was attributed to the motion of the flexible side chains and the translational diffusion of individual PFO chain^[33]. Moreover, the R_h distribution also revealed that the molecular chains were in stretch states in DCE. The intensity correlation function started to exhibit strong time dependence upon aging for 15 min and the R_h distribution showed a bimodal mode, which indicated coexisting single chain and aggregation in the solvent. When exceeding 25 min, the correlation function grew in intensity and shifted to longer time with increasing aging time. In this case, the slow mode is considered as a measure of the dynamics of the aggregates formed by the segmental association of PFO. The fact that the slow mode dominates the relaxation spectra implies that the majority of PFO chains form aggregates in the solution and the R_h distribution also proves the existence of aggregates. The original solution was found to become a sol after 45 min of aging and displayed the average R_h of about ~ 800 nm, *i.e.*, the slowest mode. The sol-gel thus obtained was visually opaque,

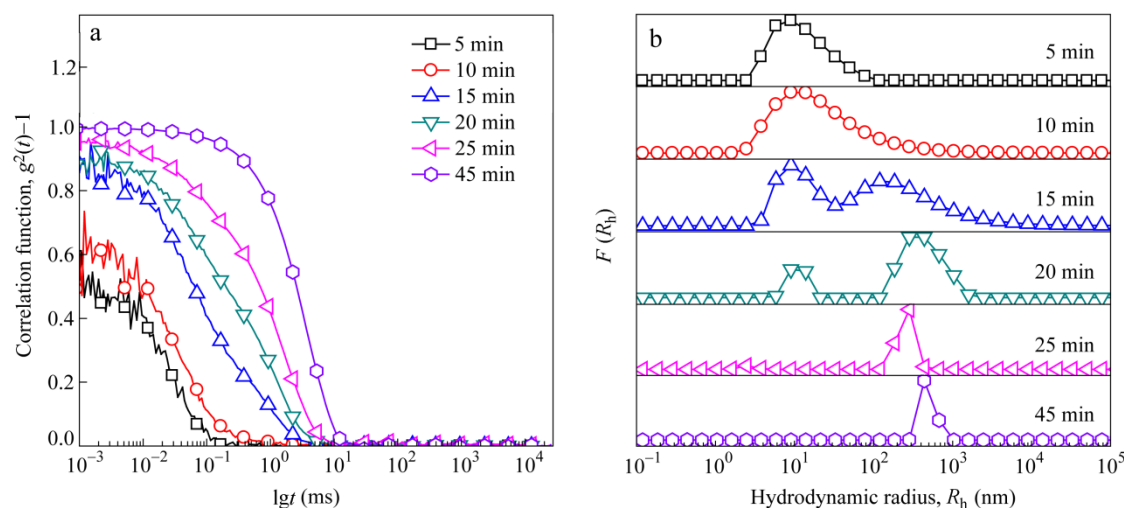


Fig. 1 (a) Normalized intensity correlation function, $g^2(t)-1$, and (b) the hydrodynamic radius (R_h) distribution of 1 mg/mL PFO/DCE solution as a function of aging time at 25 °C at scattering angle $\theta = 90^\circ$

which indicated the occurrence of phase separation and/or the formation of mesomorphic phase. Therefore, to some sense, critical aggregate time existed in the aggregation process of PFO in DCE solution.

Optical Property of PFO in Various States

PL spectra were employed to investigate the optical properties and to explore further the aggregation process of PFO in DCE solution at excitation wavelength of 390 nm. Here, the time-dependent PL spectra of 5 mg/mL PFO/DCE solution (the same as that sample for preparation of spin-coated film) were obtained at 1 min of time interval at 25 °C. The effect of aggregation on the optical property is demonstrated in Figs. 2(a) and 2(b), where PL spectra change significantly with extended aging time. The intensities of the emission peak at 422 nm decreased remarkably, while the emission peaks at 440, 465 and 499 nm grew progressively with increasing aging time. The observed variation of the spectral features upon aging time attested that aggregation process of PFO/DCE solution was accompanied by the formation of β -phase. Firstly, PL spectrum showed an emission peak at 422 nm at 0 min, attributed to the 0-0 transition of the intra-chain singlet transition. Moreover, the shoulder emission at 440 nm was assigned to 0-0 transition of β -phase, suggesting the existence of β -phase but insufficient energy transfer from amorphous phase to β -phase. When exceeding 2 min, the characteristic emission bands of β -phase appeared, where the intensity of emission at 422 nm decreased strongly, and peaks at 440, 465 and 499 nm significantly increased. Finally, the disappearance of 422 nm (10–12 min) indicated that the content of β -phase was high enough to quench the high-energy emission from the isotropic phase through effective energy transfer. In this work, two critical transition times were observed: formation of β -phase (2–6 min) and β -aggregate (10–15 min). Therefore, this time-dependent model definitely demonstrated that aggregation behavior played a critical role in determining the photo-physical property of conjugated polymer.

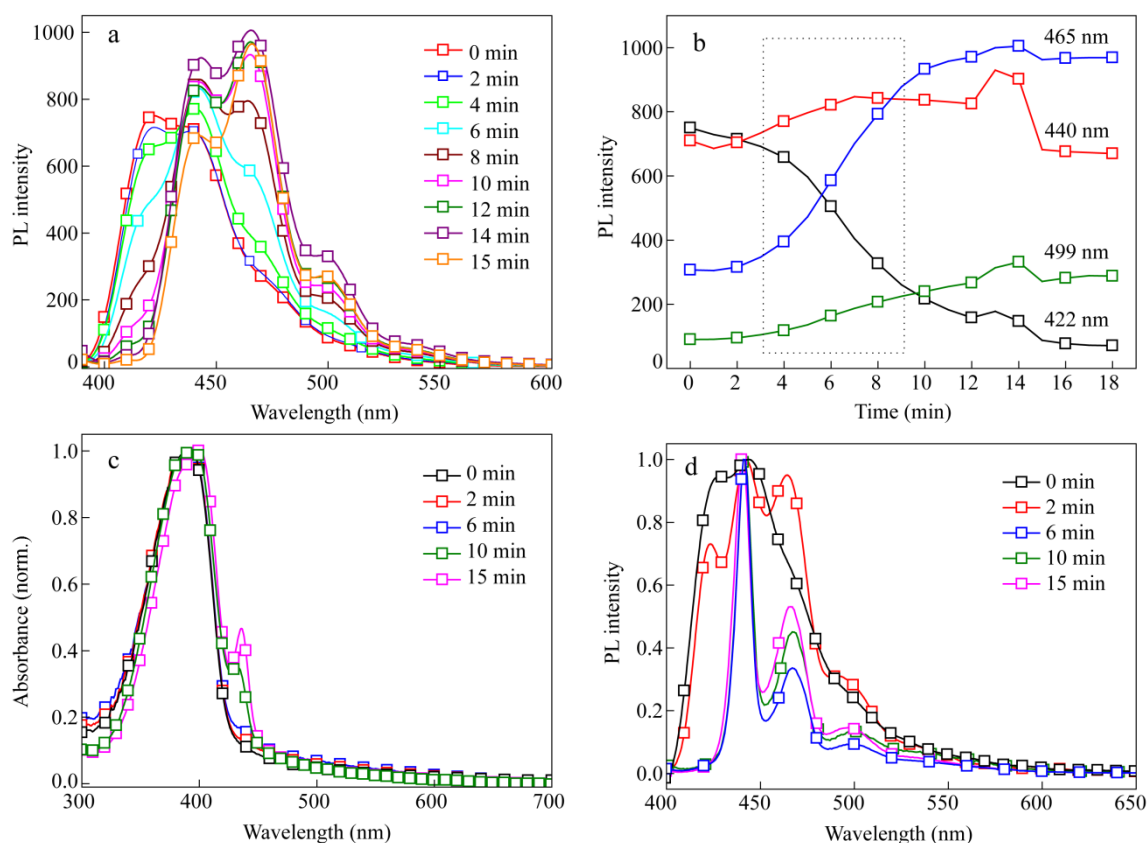


Fig. 2 (a) Time-dependent PL spectra of 5 mg/mL PFO/DCE solution (It can be seen that the emission intensities at 440, 465 and 499 nm increase while that at 422 nm decreases progressively with the increase in aging time.); (b) Plot of PL intensities at 422, 440, 465 and 499 nm versus aging time; (c) Absorbance and (d) PL spectra of PFO films spin-coated from DCE solution (5 mg/mL) at various time intervals

As we know that aggregates in precursor solution may propagate into corresponding spin-coated film. Subsequently, we investigated the effect of the aggregation behavior on the optical property of PFO films spin-coated from DCE solution (Figs. 2c and 2d). The absorption spectrum of the pristine film (0 min) showed a maximum at 392 nm, and the corresponding emission peaks appeared at 422, 440 nm with a long emission tail to 550 nm, suggesting a minor content of β -phase in the film. When the holding time was prolonged to 6 min, an extra absorption peak at 436 nm appeared and attributed to the formation of β -phase. Moreover, the maximum emission peak at 440 nm with shoulder emission at 422 nm suggested insufficient energy transfer from amorphous to the β -phase. Meanwhile, a stronger peak at 436 nm appeared in the absorbance spectra when the aging time was over 6 min, and the corresponding PL showed feature emission of β -phase. It was obviously that the contents of β -phase increased with prolonged aging time.

Morphology of PFO β -Phase Film

As shown in Fig. 3, AFM images indicate that the root mean square (RMS) roughness of PFO films increased from 0.414 to 7.99, 21.1, and 28.1 nm with the aging time increased from 2 min to 6 min, 10 min, and 15 min, respectively. In addition, at the same aging time, it was also observed that the spin-coating speed (associated to centrifugal force at the axial direction) was an important factor but not the key solution-processing parameter in determining film morphology. While the film casted from DCE solution with aging time of 15 min showed a significantly rougher topography and more nano-dots in comparison with the films casted from a shorter aging time, and the β -phase content was much higher as well. The increased roughness of films was ascribed to the aggregation tendency of solvated polymer chains in the solution state after long aging time. In this regard, one can conclude that the optimized aging time for fabricating high quality β -phase film of PFO was about 6 min, since a higher roughness was not beneficial to fabricate devices.

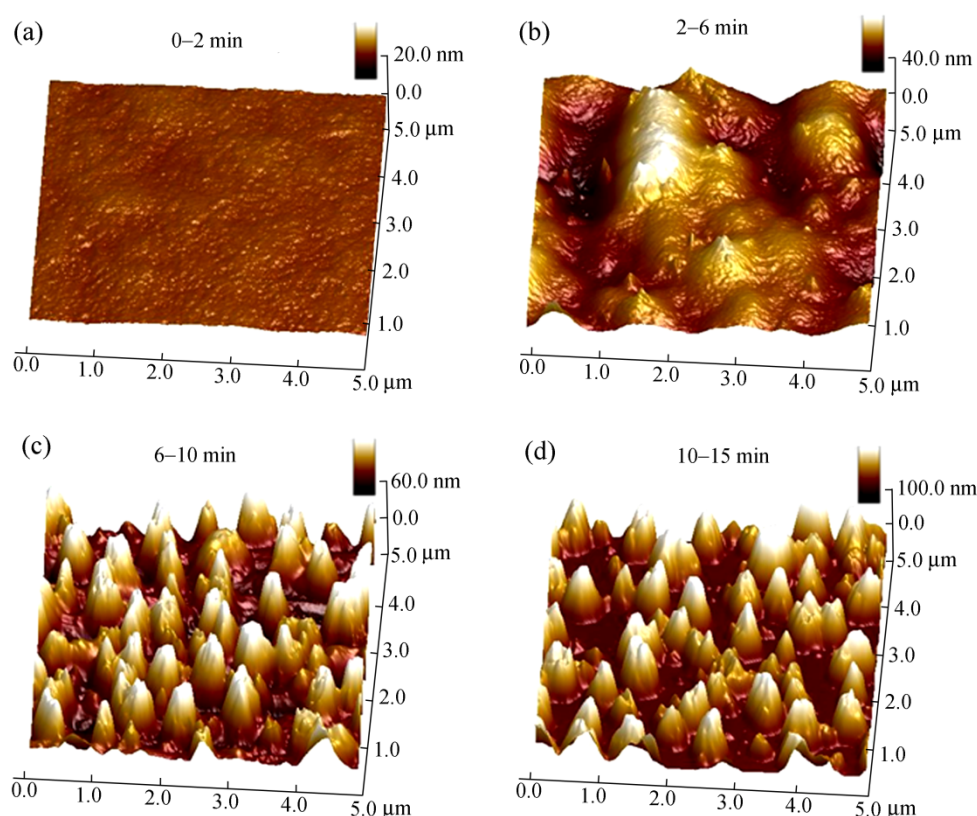


Fig. 3 AFM images of PFO film spin-coated from DCE solution with various aging time: (a) 0–2 min, (b) 2–6 min, (c) 6–10 min and (d) 10–15 min

During spin-coating process from DCE solution, flat PFO chain was readily to form cofacial π - π stacking to reduce systematic energy, leading to high crystallization, which was well tracked by GIXD. Figure 4 displays 2D GIXD pattern of the PFO film, spin-coated from DCE solution after 6 min of aging. Previously, Yan *et al.* proposed an orthorhombic unit cell with the lattice parameters $a = 1.32$ nm, $b = 2.10$ nm, and $c = 3.36$ nm for the β -phase of PFO^[34]. In this work, we indexed the most of diffractions of the GIXD pattern according to this unit cell, and the detailed indexes were marked in Fig. 4. It was seen from the diffraction pattern that a series of strong diffraction peaks showed up along out-of-plane direction, and were assigned to (200), (400) and (600). The sharp peak located at 15.1 nm^{-1} along the in-plane direction, giving a d -space of 0.415 nm corresponding to half size of fluorene monomer, was assigned to (008). Also, the diffractions in the off-axis were indexed according to the unit cell owing to the orthorhombic unit cell. As we know, spin-coating process is usually completed in a short time without self-assemble of polymer chains, so we believe that the high quality crystalline structure of PFO may be formed as early at the stage of solution state. It is noteworthy that such a high crystalline thin film maintained a high fluorescence quantum yield of 55%. Therefore, ordered chains in bulk films would help enhance the potential application in organic electronic devices.

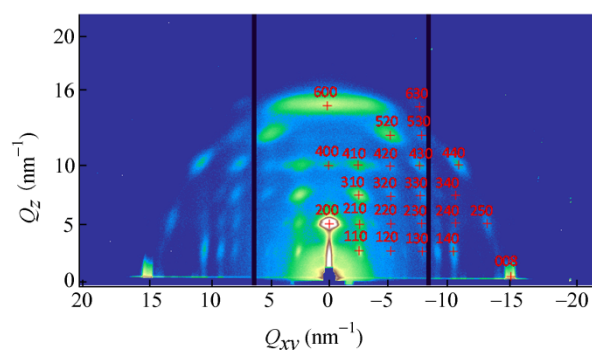
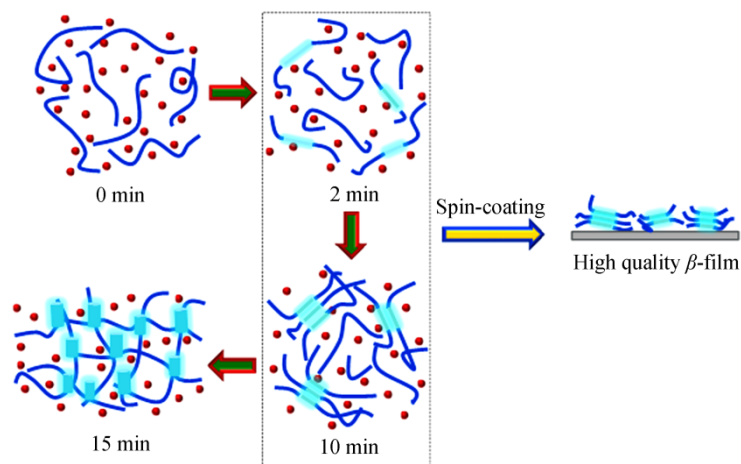


Fig. 4 GIXD pattern of PFO film spin-coated from DCE solution (5 mg/mL) of 6 min. Indexing corresponds to the proposed orthorhombic structure. Polymer layers stack along the out-of-plane direction and aromatic fluorenes stack along the in-plane direction.

Tentative Aggregation Behavior of PFO in DCE Solution

A proposed model of PFO/DCE aggregation process is given in Scheme 2. PFO powder is difficult to be dissolved in DCE with a concentration of 5 mg/mL at room temperature. After heating at 80°C for 3 h, PFO was dissolved in DCE with extended wormlike conformation, or linear rod-like chains^[16]. A portion of PFO chains



Scheme 2 Schematic model of PFO aggregation process in solution and film states

transformed from amorphous state to β -phase during the aging process (0–2 min), with the corresponding PL spectra showing an inconspicuous feature emission peak of β -phase (stronger emission at 440 nm). With the aging time increasing from 2 min to 10 min, a small fraction of chain aggregates gradually appeared, and single chains and β -sheet and -aggregates coexisted in the solution. If the aging time (10–15 min) was further extended, the majority of PFO chains self-assembled into cylinder clusters in the solution^[30]. Low-energy emission peak at 540 nm was probably ascribed to the aggregation or excimer emission of π -stacked fluorene segments at that time. And the aggregates in solution would also propagate into the film and to determine therefore their morphology and optoelectronic property.

CONCLUSIONS

We have systemically investigated the effect of aggregation behavior of PFO in DCE solution on β -phase formation and corresponding spin-coated film morphology. Critical aggregate time is observed by DLS according to the variation of R_h during the aging process of PFO/DCE solution, which can be used as a detection method to optimize the film spin-coating technology. Time-dependent PL spectra of PFO solutions and corresponding spin-coated films indicated that the optimized critical aggregate time of PFO/DCE solution (5 mg/mL) to obtain high-quality β -phase film is about 6 min, when the corresponding film showed the feature emission of β -phase and excellent film morphology. Chain aggregation induces PFO backbone transformed from amorphous to β -phase, which exhibited highly regular arrangement in the β -phase film by simple spin-coating technology. Our observation supported that the aggregation behavior in the solution can propagate into the mesoscale morphology in the spin-coated film. Therefore, to uncover molecular aggregation behavior in the solution state is prerequisite to control over the optoelectronic property of CP spin-coated film.

ACKNOWLEDGMENTS We sincerely thank Professor Donal D.C. Bradley (University of Oxford) for valuable discussions.

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