Time-resolved photoluminescence study of low-energy emission mechanisms in oligofluorene and polyfluorene films

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ABSTRACT

We report time-resolved photoluminescence (PL) spectroscopy study of solutions and thin films of pure penta-fluorenes with varying alkyl side-chain structures. While no low-energy green emissions were observed in solutions, spin-cast and vacuum dried initial films exhibited low-energy emission in time-delayed PL spectra, centered at 490 nm, whose intensity varied strongly with the side-chain structure. In comparison, the films annealed at 170 °C in air showed nearly identical low-energy emission in time-delayed PL spectra, centered at 520 nm, regardless of the side-chain structures. Therefore, our experimental results obtained for pure penta-fluorenes provided clear evidence that the mechanism of the green emission of oligofluorene and polyfluorene films includes both the intermolecular aggregate/excimer formation, emitted around 490 nm, and fluorenone-type chemical defects, emitted around 520 nm.

1. Introduction

During the past decade, extensive studies have been carried out on polyfluorenes as promising blue-light emitting materials for organic light emitting diodes (OLEDs), due to their high quantum yield, good hole transport mobility, solution processability, and thermotropic liquid crystallinity [1–4]. However, the emissions from polyfluorenes are well known to exhibit unwanted color changes into low-energy green, when they are used as light emitting materials, and a large number of investigations have been carried out to understand and suppress this phenomenon [5–9]. Initially, the low-energy green emission from polyfluorenes was attributed to excimer formation in aggregates, which was inferred from the related studies of conjugated polymers such as poly(para-phenylene)s [7,10]. Subsequently, fluorenone chemical defect in polyfluorene molecule was strongly proposed as the most likely source for the degradation of blue emission in polyfluorene and related polymer films [11–13]. This argument was further supported by the fact that synthetically prepared cooligomers and copolymers containing fluorenone moiety showed green emission characteristics similar to those of degraded emission in polyfluorenes [14,15]. On the other hand, recent studies on polyfluorenes provided the evidence that the thin film morphology and the related intermolecular interactions also have a strong influence on the degradation of the blue emission [5,16,17]. However, the difficulty of preparing chemically pure materials devoid of chemical defects, such as fluorenone, and the inevitable polydispersity of chain lengths make the extensive experimental studies on polyfluorenes subject to serious uncertainties. This is because the emission properties are significantly influenced by the presence of residual emission quenchers and the morphology-dependent intra- and intermolecular energy transfer processes [18–21].

In comparison to polyfluorenes, oligofluorenes are prepared by well-controlled and rigorous synthetic and purification procedures [22]. Hence, oligofluorenes have not only uniform chain length but also much lower probability of containing chemical defects. Moreover, one can systematically vary the side-chain substituents and thus the resultant aggregation and packing effects of fluorene chromophores on the emission characteristics. In this work, we employed the pure oligofluorenes with various alkyl side-chain substituents as model compounds of polyfluorenes, and carried out detailed time-resolved photoluminescence (PL) experiments on their dilute solutions and solid films in order to study the mechanisms of the low-energy emissions in oligofluorene and polyfluorene films.

2. Experimental

2.1. Sample preparation

The synthesis of the oligofluorenes has been described in detail elsewhere [22].

Dilute solutions of the oligofluorenes for spectroscopic measurements were prepared using distilled MTHF solvent to obtain a concentration of 5 μg/ml, and prior to the solution preparation, the solvent was degassed by purging with Ar.

Thin films of the oligofluorenes were prepared by spin casting onto cleaned quartz substrate from 1 mg/ml toluene solutions, resulting in ca. 50 nm final thicknesses. The initial pristine films were prepared by removing the solvent in a vacuum oven at room temperature for 24 h after spin casting. The air-annealed films were prepared by annealing the initial films at 170 °C for 2 h under ambient air.

2.2. Measurements

For the time-resolved PL measurements, we used a frequency-doubled mode locked Ti:sapphire laser operating at 380 nm supplying 80 MHz repetition, which produced c.a. 200 fs pulses. The spectra and PL transients were recorded with Hamamatsu 4742 streak camera system with the time resolution of 4 ps. When the laser power was varied from 100 μW to 1 mW, the spectra showed the same shape and differed only in the intensity, which varied linearly with the excitation intensity. Since this result indicated no discernible effect of photo-oxidation or non-linear effect such as singlet–singlet annihilation during the PL measurements, all the data were obtained with the excitation intensity of 500 μW. All the measurements were carried out at 25 °C, and the films were kept under dynamic vacuum in the order of 10^{-5} mbar during the time-resolved PL measurements. The experimentally measured lifetime, $\tau_{1/e}$, was obtained for each sample to compare the exciton lifetimes.

Differential scanning calorimetry (DSC) (TA Instruments) was employed to obtain the thermograms under nitrogen atmosphere. The solid powder samples precipitated from solutions were first heated to 200 °C and cooled back to room temperature in the first heating/cooling cycle, and the DSC thermograms were recorded in the second heating cycle which remained nearly the same in the subsequent heating runs.

3. Results and discussion

The materials employed for this study are penta-fluorenes whose 9-positions are substituted with di-butyl (But5FL), di-hexyl (Hex5FL), di-octyl (Oct5FL), and di-2-ethylhexyl (EH5FL) groups, as drawn schematically in Fig. 1a. The systematic change in the alkyl side-chains is expected to result in varying local packing characteristics and interactions of the fluorene chromophores as well as the macroscopic morphology in thin films. As indicated by the DSC heating traces in Fig. 1b, only But5FL with the shortest side-chain shows definite crystallization and melting characteristics while the other samples show no such features. It is also interesting to note that although all the samples show the glass transition, only EH5FL exhibits a nematic–isotropic transition (see the curve D), which occurs at 105 °C [22]. Therefore, only But5FL with the shortest side-chain shows a strong tendency of crystallizing in bulk state.

As shown in Fig. 2a, the prompt PL spectra of the dilute solutions of penta-fluorenes with different alkyl side-chains are identical. That is, the various side-chains give rise to no detectable differences in the PL spectra in the solution state. Since the intermolecular interactions are negligible in the dilute solutions, such PL characteristics indicate that the conformational structure and the electronic structure of the fluorene chromophores in isolated molecules are hardly affected by the alkyl side-chains. In comparison, the PL spectra of the solid films are generally red-shifted from the solution spectra, as shown in Fig. 3a. This has been attributed to the intra-chain conformational change and the resultant increase in the conjugation length [23]. As the alkyl side-chain structure changes, the position of the first vibronic emission peaks is seen to be more

red-shifted as the size (or the volume) of the side-chain is decreased: i.e., 427 nm for But5FL, 425 nm for Hex5FL, 422 nm for Oct5FL, and 420 nm for EH5FL. This result shows that the characteristics of side-chains have a direct influence on the intrachain conformational structure in the solid films.

Time-delayed PL spectra of the solutions and thin films at various delay times were measured for detailed comparison of emission characteristics and exciton dynamics. Figs. 2b and 3b show the normalized PL spectra of the penta-fluorenes at 2000 ps time-delayed regions. In solutions, the normalized PL spectra at prompt and at 2000 ps delay after excitation are identical. More importantly, no sign of green emission (with longer lifetime) is observed at all, indicating the high purity of the employed penta-fluorenes, devoid of (fluorenone-type) chemical defects generally found in polyfluorenes. In contrast, the 2000 ps time-delayed regions for the initial pristine films exhibit well-distinguishable, broad green emission as seen in Fig. 3b. The intensity of this green emission relative to that of the vibronic singlet emission in the delayed spectra is found to increase as the size of the alkyl side-chain of penta-fluorenes decreases. The maximum peak of this green emission is positioned around 490 nm (2.53 eV) for But5FL and Hex5FL films, but it cannot be precisely determined for Oct5FL and EH5FL films due to the weak intensity and the overlap with the vibronic emission. UV–vis absorption spectra confirmed that the low-energy emission has no correlation with reabsorption of the emission, since the intensities of the absorption tails in the initial pristine films are nearly identical. The possibility of generating chemical defects by photo-oxidation during the time-resolved PL measurements was eliminated as discussed above. Hence, the green emissions in the time-delayed PL spectra in Fig. 3b, which last longer than singlet emission, most likely originate from the intermolecular species, such as excimer or aggregate, induced by the interactions between the molecules in the solid state. Therefore, our results indicate that as the size of the alkyl side-chains of the penta-fluorenes decreases, the tendency to form aggregates or excimers of fluorene chromophores becomes more favorable, consistent with the strong tendency for crystallization in bulk But5FL (see Fig. 1).
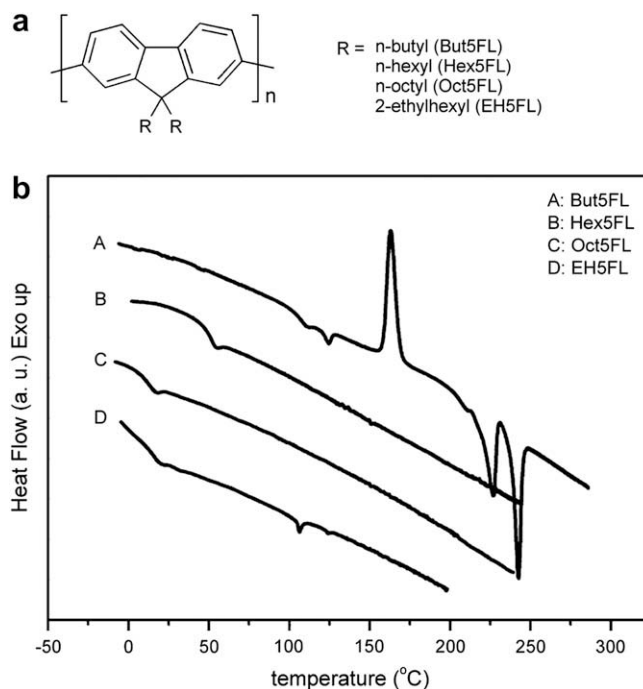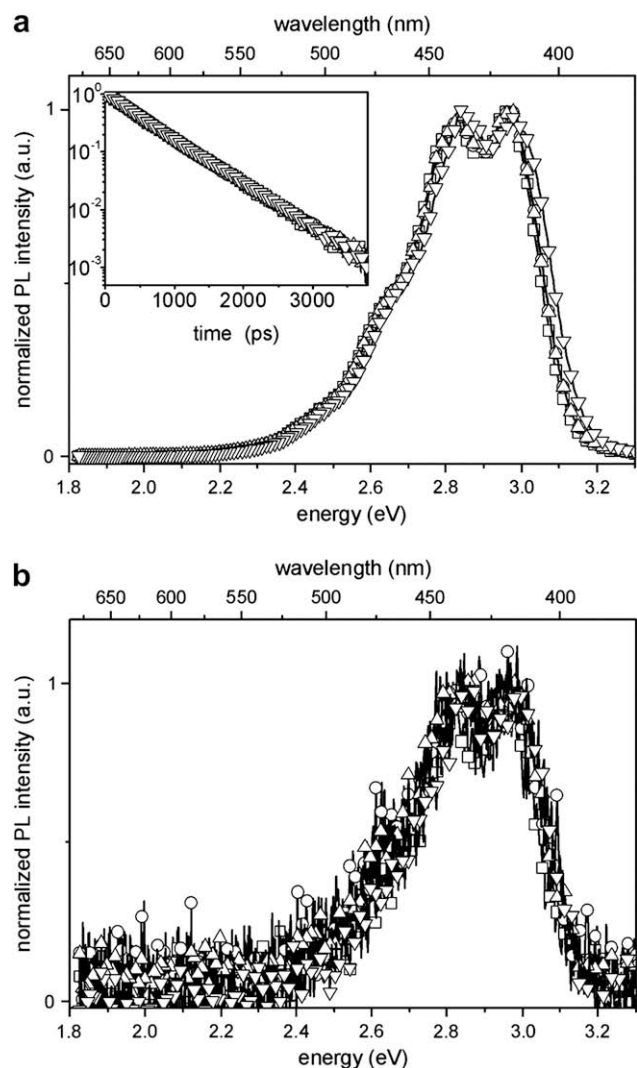

Fig. 1. (a) Chemical structure of 4 different penta-fluorenes. (b) DSC heating traces of penta-fluorenes, measured at the heating rate of 10 °C/min.

Fig. 2. Time-resolved PL spectra of But5FL (rectangle), Hex5FL (circle), Oct5FL (triangle), and EH5FL (inverted triangle) in dilute solutions at (a) prompt and (b) approximately 2000 ps after excitation pulses with integration window of 500 ps. For all the spectra, the intensity was normalized to match the first vibronic peak in each PL spectrum. The PL decay transients for first vibronic emissions are shown in inset (a).

In the dilute solutions of penta-fluorenes with different side-chains, the decay of the first vibronic emissions shows mono-exponential behavior with identical lifetimes ($\tau_{1/e} = 540$ ps) regardless of the size of side-chains, as seen in the inset of Fig. 2a. This indicates the unimolecular decay process which does not vary with the size of alkyl side-chains. In the pristine films, the exciton lifetimes are generally decreased from the solution values as expected. More interestingly, the observed lifetimes are found to decrease significantly as the size of the side-chain decreases, as shown in the inset of Fig. 3a and denoted in the figure caption. At the same time, the deviation from the mono-exponential decay becomes more significant as the size of the side-chain decreases and hence the observed lifetime decreases, as shown in Fig. 4. This result indicates an increasing occurrence of bimolecular decay processes, as the size of the side-chain decreases.

The slight decrease of lifetime in EH5FL film (515 ps) as compared with the dilute solution (540 ps) indicates a near absence of intermolecular processes in solid films. Therefore, the increasing low-energy emission around 490 nm in the time-delayed PL spectra of But5FL and Hex5FL films is corroborated by the increased intermolecular processes in solid films, as reflected in the lifetimes and the deviation from the mono-exponential decay characteristics.
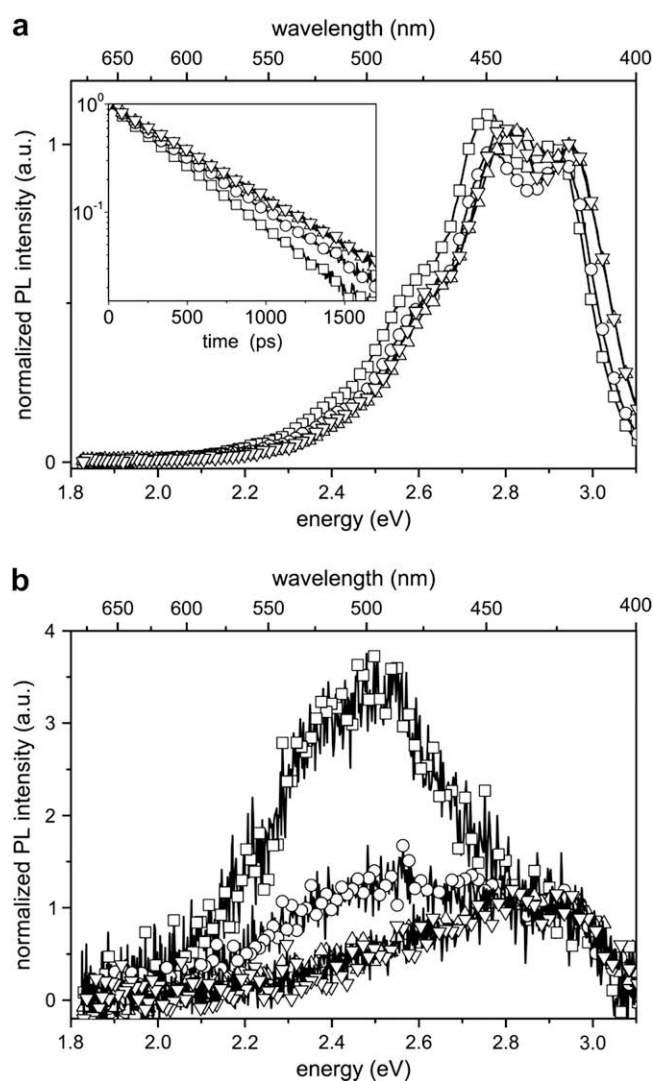
Fig. 3. Time-resolved PL spectra of But5FL (rectangle), Hex5FL (circle), Oct5FL (triangle), EH5FL (inverted triangle) in the initial pristine films at (a) prompt with 500 ps integration window, and (b) 2000 ps after excitation pulses with 1000 ps integration window. All spectra are normalized to match the intensity of the first vibronic peak. The first vibronic emission decay transients are shown in inset (a). The measured lifetimes, $\tau_{1/e}$, of the blue (400–420 nm) are 377 ps for But5FL, 443 ps for Hex5FL, 485 ps for Oct5FL, and 515 ps for EH5FL.

In this regard, our result is consistent with the previous work by Lim et al., who found that the green emission was suppressed by reducing the close packing of molecular segments in polyfluorene copolymers [24].

Next, we annealed the initial pristine films at 170 °C for 2 h in ambient air to intentionally generate some chemical defect sites. For such air-annealed films, the vibronic PL intensity is reduced considerably when compared to the spectra of the pristine films, and the broad, featureless green band occurs in the delayed-time region (see Fig. 5). The red-shifted prompt spectrum in the But5FL film is possibly due to the high crystallinity and the increased reabsorption after annealing [25]. Most importantly, the green emissions appeared in the time-delayed spectra for all the air-annealed films, regardless of the alkyl side-chains. While the green emission in the pristine films shows a maximum intensity around 490 nm (2.53 eV), the maximum of the green emission in the air-annealed films is shifted to around 520 nm (2.38 eV) (see the inset of Fig. 5b). More-over, it is important to note that the prompt PL spectra in the air-annealed films are nearly identical to those of the pristine films except But5FL, demonstrating that the fluorene chromophore
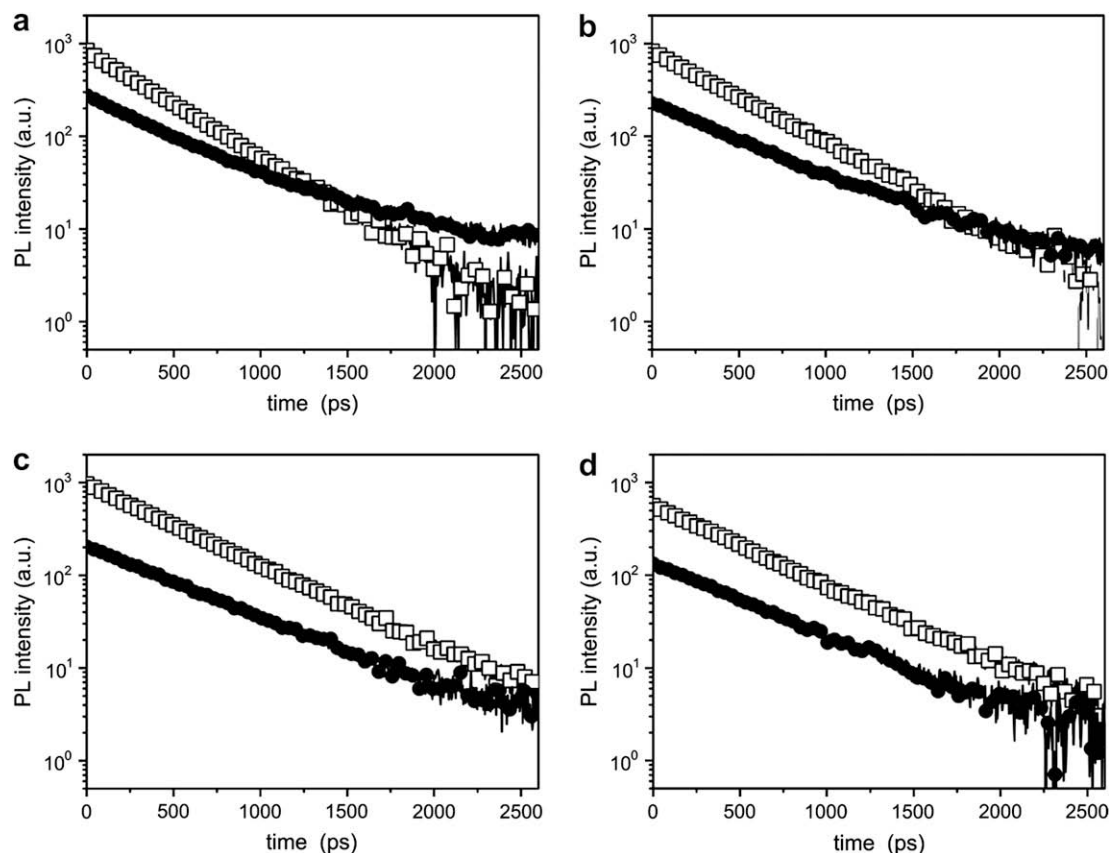
Fig. 4. PL transients of the blue (open rectangle, 400–440 nm) and the lower energy (solid circle, 460–560 nm) emissions in the initial pristine films of (a) But5FL, (b) Hex5FL, (c) Oct5FL, and (d) EH5FL.

environments and conformations in other penta-fluorenes were hardly changed by the annealing at 170 °C for 2 h in ambient air. Therefore, the green emission from the air-annealed films around 520 nm is most likely due to a different mechanism, for example, the fluorenone-type chemical defects formed by thermal oxidation.

The various characteristics of the green emission spectra of polyfluorene films and their possible origins were extensively discussed in previous publications [17,26,27]. While the emission around 520 nm is generally accepted to be related to the fluorenone

moiety, there have been conflicting explanations concerning the emission around 490 nm. In this regard, it is important to note the previous report indicating that the low-energy green emission of polyfluorenes arises from both "physical" and "chemical" defects [28]. Also, Chen et al. proposed a green emission mechanism from the intermolecular species, based on their observation of enhanced green emission around 507 nm from the polyfluorene samples without end-group capping that impeded the aggregation [29]. Such previous results supporting the "physical" origin of the green
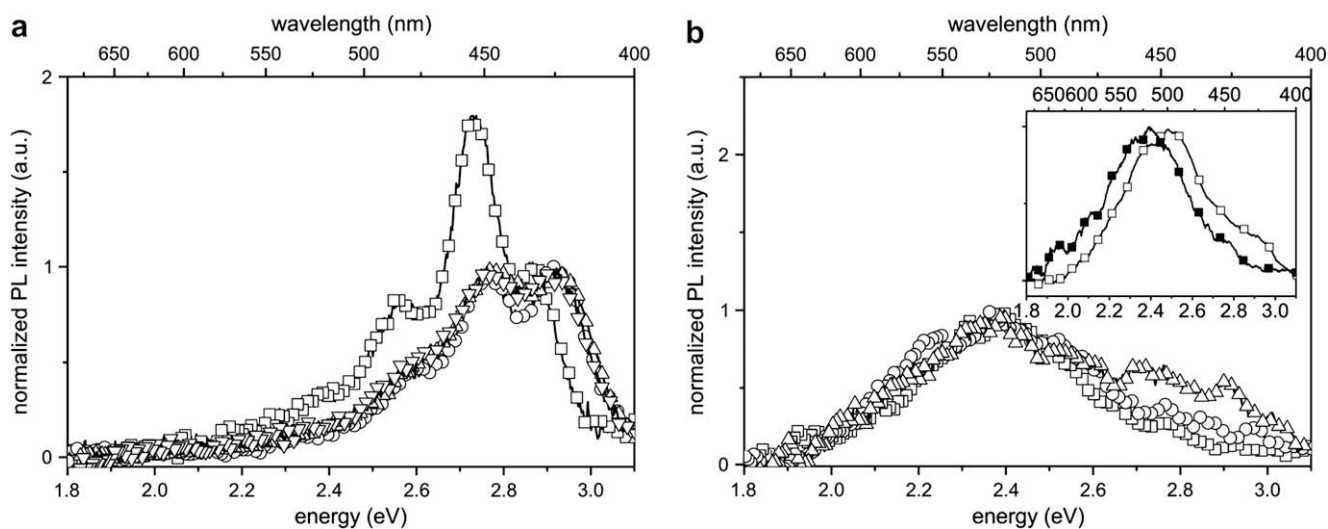
Fig. 5. Time-resolved PL spectra of But5FL (rectangle), Hex5FL (circle), Oct5FL (triangle), EH5FL (inverted triangle) in the air-annealed films at (a) prompt with 500 ps integration window, and (b) approximately 1500 ps after excitation pulses with 1000 ps integration window. For all the spectra, normalization was performed for comparison. Comparison of the delayed spectra of But5FL in the pristine film (open rectangle) and the air-annealed film (solid rectangle) is shown in inset (b).

emission of polyfluorenes have been questioned due to the lack of chemical purity of the samples. In this regard, our results based on chemically pure penta-fluorenes represent a more plausible evidence in support of the contribution from the physical inter-molecular species, in addition to the well-known chemical species.

4. Conclusions

In summary, we performed time-resolved photoluminescence spectroscopy with pure monodisperse penta-fluorenes with various alkyl side-chains as model compounds for polyfluorenes. For such highly pure oligofluorenes, no green emissions in the time-delayed spectra were observed in dilute solutions. However, the initial pristine films showed increased green emissions around 490 nm in the time-delayed region as the size of the side-chain becomes smaller. Since the existence of chemical impurity in our oligo-fluorenes can be ruled out, the 490 nm green emission from the pristine film is most likely to arise from the intermolecular species. This proposal is also consistent with the decreased lifetime and the increased deviation from the mono-exponential time decay of the first vibronic singlet emission as the size of the side-chain decreases. Upon annealing the pristine films at 170 °C in ambient air, shifted green emissions were observed whose maximum intensities occur around 520 nm, which is attributed to the fluorenone-type chemical defects generated by thermal oxidation. Therefore, our experi-mental results obtained for pure penta-fluorenes provided clear evidence that the mechanism of the green emission of oligofluorene and polyfluorene films includes both the intermolecular aggregate/excimer formation, emitted around 490 nm, and fluorenone-type chemical defects, emitted around 520 nm.

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