Origin of Green Emission in Extremely Pure Oligofluorene Films: Effect of Molecular Packing

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Introduction

Tremendous efforts have been devoted to polyfluorenes as promising blue-light emitting materials for organic light emitting diodes (OLEDs), due to their high quantum yield, good thermal stability, and good solubility. They also show thermotropic liquid crystalline properties which allow the macroscopic molecular alignment. The fact that this oriented liquid crystalline phase can be quenched into a glass or crystallized allows the highly polarized emitting device making them potential candidate for backlight illumination in LC displays. However, the emissions from polyfluorenes and related copolymers are known to be very sensitive to changes in thermal history, morphology, and purity, etc. When they are used as light-emitting materials, it is well known that they suffer from unwanted color change due to the emergence of red-shifted green emission. This emergence of green emission band was initially attributed to aggregate formation or excimer formation, which was inferred from the related studies of conjugated polymers such as poly(para-phenylene)s.[1] To suppress this undesirable red-shifted green emission, a large number of efforts have been made, which include substitution of bulky side chains, copolymerization, and end-capping, etc. Recently, it was reported that the introduction of chemical defects into polyfluorene backbone leads to the undesirable color change, and that keto-type defects are responsible for the red-shifted green emission. Moreover, Lupton et al. reported that almost identical green emissions were observed in both dilute solution and thin film samples of polymers by using time-resolved spectroscopy.[2] In most experiments, however, the difficulty of preparing extremely pure samples without keto-defect sites which can be formed during synthesis, or during thermal-, photo- or electro-degradation, and the inevitable polydispersity of chain length make the detailed study of polyfluorenes subject to uncertainty.

In contrast to polyfluorenes, the oligofluorenes are prepared by well-controlled and rigorous synthetic and purification procedures. Hence, the oligofluorenes have uniform chain length and extremely lower probability of having chemical defects in the molecule.[3] At the same time, by introducing various side chains and end-capping group, one can systematically control the intermolecular interactions and packing in oligofluorene films. So, oligofluorenes are very promising model compounds for detailed study of spectroscopic properties of polyfluorenes.

Experimental

In this work, we have performed time-resolved photoluminescence spectroscopy experiment with oligofluorenes with diffent alkyl chains and end-capping groups to examine the origin of low-energy emissions. The materials employed in this study are penta-fluorenes whose 9-positions are substituted with various alkyl groups, and penta-fluorenes with end-capping groups which can induce high-order liquid crystalline phase.

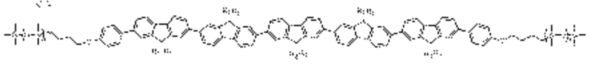

Figure 1. chemical structures of oligofluorenes studied in this work

The synthetic and purification route of preparing oligofluorenes employed in this study has been reported elsewhere.[3]

Time resolved photoluminescence measurements were made using a frequency doubled mode locked titanium-sapphire laser and Hamamatsu C4742 streak camera. The laser operates at 377 nm supplying 80 MHz pulses. The dilute solutions of oligofluorenes samples were prepared to concentration of 5 μg/ml in distilled 2-methylhydrofuran. The film samples were prepared by spin coating on quartz substrates (for PL and UV spectrcoscopy).

Results and discussion

Time-resolved spectroscopy is a useful tool to study the decay mechanism of excited state.[4] One can observe the spectra of short-lived fluorescent species and the long-lived species, separately. With oligofluorenes, delayed spectra were exactly identical with prompt spectra in solution state, which reflects the purity of used material is extremely high. On the other hand, the films of oligofluorenes showed unstructured broad emission around 500 nm in the delayed spectra. With pristine films and air-annealed films (at 170 ℃), two different kinds of green emissions were observed, which can be attributed to the different origins of green emissions that are keto-defects and aggregate formation. The green emissions around 490 nm were largely affected by intermolecular interactions which results from the bulkiness of alkyl side chains.

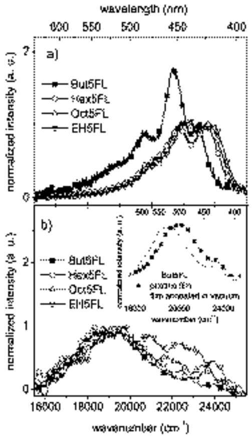

Figure 2. Normalized PL spectra of air-annealed film (at 170℃) of penta-fluorenes at prompt (a) and at 2000 ps after excitation (b) in 500 ps time window. Delayed spectra (at 2000 ps) of pristine and air-annealed film are compared in the inset.

Oligofluorenes with siloxane end-capping groups showed high-ordered liquid crystalline phase such as smectic phase. By controlling thermal history of the films of these oligofluorenes, one could have various films which have different packing states. The annealed films, whose high-ordered packing state was quenched to glassy state, showed less green emission at time-delayed spectra compared with nematic films.

Conclusions

The red-shifted green emission of highly pure oligofluorene was studied using time-resoled photoluminescence spectroscopy. In delayed spectra, we could observe two different kinds of green emissions around 490 nm and 520 nm which originate from aggregate formation and keto-defect site, respectively. Particularly, the green emissions around 490 nm were dependent upon the intermolecular interactions of oligofluorenes. Moreover, the red-shifted emission was observed to be strongly dependent upon molecular packing in solid films.

References

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