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Optical Study of Poly (9,9-dioctylfluorene) Isolated by AlB_2OB_3 flat rafts

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Abstract. Nanocomposite films of poly (9,9-dioctylfluorene) (PFO)/Al_2O_3 have been prepared by blending the conjugated polymer solution with alumina nanoparticle dispersion in common organic solvent and investigated in terms of the optical property. A blue shift of the photoluminescence (PL) spectrum for the as fabricated PFO/Al_2O_3 nanocomposite film was observed as compared to the results obtained from the bulk PFO film, the maximum of the PL emission peaks occurs at 442 nm in the bulk film while after the incorporation of the alumina nanoparticles the maximum appears at 420 nm in the spectrum for PFO/Al_2O_3 nanocomposite film. The dependence of fluorescence blue shift of PFO on the concentration of Al_2O_3 was investigated. The isolation of the conjugated polymer chains by the flat rafts of alumina nanoparticles was shown to play a key role for the obtained blue shift.

Introduction

Conjugated polymers have been intensively studied during the last two decades mainly due to their semiconductor-like optical and electronic properties. These organic materials have the capability to be processed on a variety of substrates as well as to allow for a broad tunability of emission by controlling their chemical structure. As one of the attractive blue-light-emitting conjugated polymers, poly (fluorene)s are promising materials for light emitting diodes because these materials show extremely high photoluminescence (PL) quantum efficiencies and thermal stability [1]. However, study is still necessary to the modification of the conjugated polymer both chemically and physically for the optimization of its use in full color light-emitting devices.

Recently, the conjugated-polymer/inorganic nanocomposites have attracted a great deal of attention due to the novel synergy effects as well as their enhanced optical and electronic properties [2-10]. When the conjugated polymers are mixed with inorganic nanoparticles such as porous silica (SiO_2) [2,3], porous gallium phosphide (GaP) [4] or porous alumina (Al_2O_3) [5,8] to form nanocomposites, their optical properties are altered. These papers indicate that modification of the optical and electronic properties of conjugated polymers contribute to the isolation of polymer chains within inorganic materials.

In the present work, we demonstrated color-shift in the emission spectra of poly (9,9-dioctylfluorene) (PFO) based nanocomposites which could be simply prepared by blending the conjugated polymer solution with the inorganic material dispersion. Enhanced blue shift was observed for the nanocomposite samples. It was also found that the enhanced blue shift depends on the concentration of Al_2O_3 up to a certain value in polyfluorene. The effect of isolation of the conjugated polymer chains by Al_2O_3 nanosheets and the strong dependence of optical properties of conjugated polymers on chain conformation were also examined and are presented in this paper.

Experimental

Poly (9,9-dioctylfluorene) (PFO) (American Dye Source, Quebec, Canada) and Alumina nanoparticles (Condea-Vista Chemicals, Inc) were used as conjugated polymer and inorganic material. The weight-average molecular mass of PFO is 46 kDa and polydispersity index PDI = 4.2 as

determined via GPC using polystyrene standards. The Alumina nanoparticles are flat rafts with two dimensions in the range of 20-100 nm and one dimension of a few nanometers [11] when dispersed in the organic solvent, exhibiting a unique combination of purity and dispersibility. Al_2O_3 particles were first sonicated in chloroform ($CHCl_3$) solvent for 2 hours for completely dispersion before use. The conjugated polymer was dissolved in the same kind of solvent and then mixed with the Al_2O_3 dispersion. The mixture was sonicated at room temperature for several minutes.

The preparation of polymer film is described as follows. The substrates, cut into 1.2×2 cm^2 and carefully purified, were dipped into the polymer solution for some time to ensure the deposition of essential film on the supports. The polymer coating substrates were then withdrawn out of solution and dried in the air at room temperature. The fabricated film was denoted as PFO. The nanocomposite film was prepared via the same procedures, using PFO/ Al_2O_3 nanocomposite dispersion. The obtained film was named as PFO/ Al_2O_3.

Results and Discussion

Figure 1 (left) shows the photoluminescence (PL) spectra of conjugated polymer and nano-composite analyzed in $CHCl_3$ solution at an excitation wavelength of 320 nm. The weight ratio of Al_2O_3 versus PFO was controlled to be 280:1 (w/w). The two spectra display similar emitting from fluorene units at 421 nm, implying that the incorporation of alumina nanoparticle to the conjugated polymer solution rendered no change in the PL spectrum of polymer. Besides the maximum peak from the fluorene unit at 421 nm, two shoulders occur at 443 and 475nm, respectively.

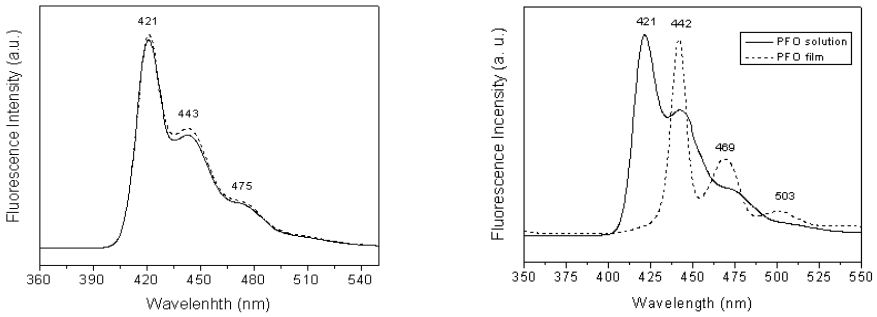

Fig. 1 The fluorescence spectra of PFO solution (solid line) and nanocomposite solution (dashed line) the spectra have been normalized to the same maximum for better comparison (left); Fluorescence spectra of PFO in chloroform solution (solid line) and in solid film (dashed line) (right)

However, the emissions of PFO in chloroform solution and in solid film are different (Figure 1 (right)). The photoluminescence (PL) spectrum for the polymer chloroform solution shows three vibronic peaks at 421, 443 and 475 nm. In the spectrum obtained from the film sample fabricated from the PFO chloroform dispersion, the emission is red-shifted and shows more highly resolved vibronic structure with three clear peaks at 442, 469 and 503 nm, followed by a long featureless tail extending into the red. In the solid film, molecular packing favors more planar molecular orientations, and the more planar orientations lead to an increase in effective conjugation length and a resultant red shift. Thus the lower π-π^* band gap of the conjugated polymer in thin film resulted in the suppression of the peak at 421 nm and the increase of the one at 442 nm to be the maximum. The weak shoulder at 469 nm and 503 nm in the PL spectrum from the chloroform solution has also been intensified in solid film. Therefore with the red-shifted emission one can speculate on the possession of a modified physical structure of conjugated polymer chain with a longer efficient conjugation length in the solid film of PFO.

To investigate the effect of nanoparticles on the optical properties of conjugated polymer in nanocomposite film, we characterized the emission of two film samples prepared from PFO solution and PFO/Al_2O_3 dispersion (the weight ratio of Al_2O_3 versus PFO was also controlled to be 280:1) at

the excitation wavelength of 320 nm. Figure 2a shows the PL spectra of the thin films of the bulk and the composite coated on glass slide. The PL spectrum of pure PFO film exhibits the emission maximum at 442 nm with shoulders at 420 and 469 nm. While the fabricated PFO/Al_2O_3 nanocomposite film shows the main emission peak at 421 nm, blue-shifted by about 22 nm. The weak shoulder at 420 nm in the PL spectrum of pure polyfluorene is greatly intensified, while the peak at 442 nm shrinks a little and the one at 469 nm almost disappears. When the nanocomposite film was excited at 340 nm, i.e. at a wavelength within the absorption peak, essentially the same emission spectrum was observed. Similar results were observed in the samples prepared from three different kinds of substrates, glass slide (Figure 2a), Al foil (Figure 2b) and filter paper (Figure 2c). The position of the emission peaks as well as the construction of the spectra are nearly identical, indicating that the blue-shift was not affected by the substrate, but the interaction between Al_2O_3 nanoparticals and PFO chains.

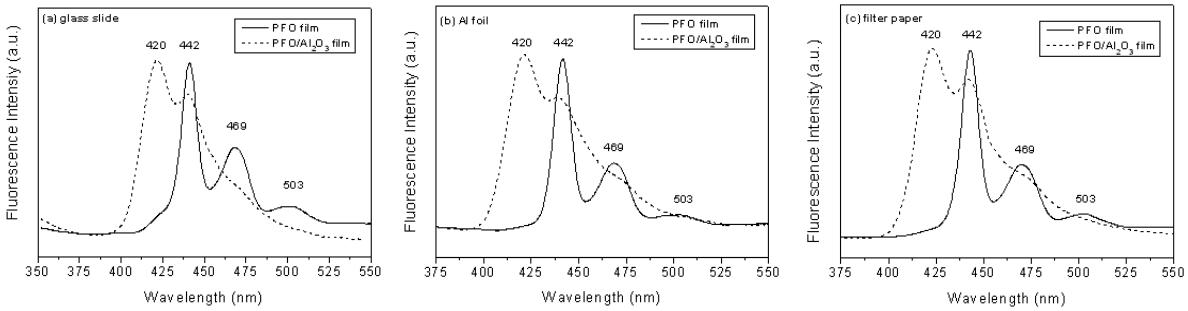

Fig. 2 Fluorescence Spectrophotometer of PFO film (solid line) and PFO/ Al_2O_3 film (dashed line) coated on (a) glass slide, (b) Al foil, (c) filter paper

The interference effect of the conjugated polymer on the alumina nanoparticles in PFO/Al_2O_3 nanocomposite can also be partially verified by the typical absorption spectra. Figure 3 shows the absorption spectra of Al_2O_3 film, PFO film and PFO/Al_2O_3 nanocomposite film in air at room temperature. The absorption of PFO film consists of a strong featureless π-π transition that peaks at 398 nm and a vibronic sideband at 437 nm. The Al_2O_3 film shows high optical transparency at the PL wavelength of PFO (442 nm) due to the very thin film. But the spectral shape of PFO/Al_2O_3 nanocomposite film is different from that of PFO or Al_2O_3 film, the absorption maximum of which shifts to 391 nm with respect to that of the polymer bulk film. The fluorescence maximum of PFO film, occurring at 442 nm, is widely separated from the absorption maximum, giving a large value of the Stoke's shift. This Stoke's shift is also observed for the spectra of PFO/Al_2O_3 nanocomposite film, the PL spectrum of which has a maximum at 420 nm, while the maximum of absorption spectrum locals at 391 nm. Since polymer with longer effective polymer chains may exhibit UV-vis peaks at higher wavelength, the observed blue shift both in the absorption spectrum and emission spectrum of composite film signifies that the effective π-conjugation length of PFO was shortened in the PFO/Al_2O_3 nanocomposite. We speculate that the Al_2O_3 nanolayers' modification on nanoscopic structure of PFO led to more intrachain disorder.

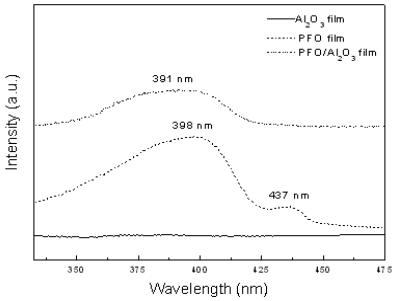

Fig. 3 The UV-vis spectra of PFO / Al_2O_3 film (solid line), PFO film (dashed line) and Al_2O_3 film (dash-dot-dotted line)

As presented in Figure 4, the weight ratio increasing from 0:1 to 280:1 shifts the emission maximum from 442.2 nm to 420.0 nm. The most intense fluorescence peaks of PFO/Al_2O_3 nanocomposite are 442.2 nm for 0:1, 439.2 nm for 40:1, 438.4 nm for 80:1, 437.8 nm for 160:1, 436.8 nm for 180:1, 423.4 nm for 200:1, 420.8nm for 240:1 and 420.0 nm for 280:1, respectively, indicating that an enhanced blue shift dependent on the increasing amount of Al_2O_3 added into the polyfluorene. However, above the ratio of 280:1 the blue shift is not enlarged any more. The blue shift occurring to the solid state of nanocomposite films was not observed in their emission spectra of nanocomposite solution containing different concentration of Al_2O_3. Since polymer with shorter effective conjugated polymer chains may display PL emission at lower wavelength, our results indicate that the efficient conjugation length of the PFO chains decreases as the concentration of Al_2O_3 is increased.

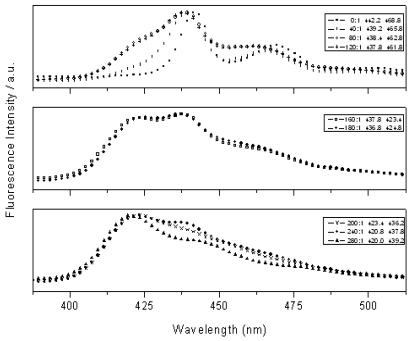

Fig. 4 The fluorescence spectra of PFO/Al_2O_3 prepared from different weight ratio of Al_2O_3 versus PFO. (The Maxima of the emission spectra are normalized to the same value, following the weight ratios in the inset are the values of the most intense two peaks in the emission spectra.)

The experiment also shows a new method of controlling the morphology of polymer chains by incorporating alumina nanoparticles to the conjugated polymer, resulting in the emission maximum shift toward blue region in the spectrum for polyfluorene. In the chloroform dispersion of PFO and alumina, PFO chains exist in a free isolated state affected by the nanosheets of Al_2O_3 as is illustrated in Figure 5 (left). The solid lines correspond to the nanosheets of alumina viewed from their side directions, while the coils are the conjugated polymer chains. However in the thin film, the flat rafts would pack irregularly on the substrate after the volatilization of solvent. The attachment of the flat rafts results in the isolation of polymer chains. As showed in Figure 5 (right), different conformations of conjugated polymer chains depend on diverse contents of Al_2O_3 in PFO/Al_2O_3 nanocomposite. Figure 5a (right) displays the morphology of pure polymer film. Figure 5b (right) indicates that when a small amount of Al_2O_3 is added into the conjugated polymer (the weight ratio was lower than 160:1), the aggregation of the polymer chains is little affected, partially crystalline region still existed in the composite film, the interaction between the surface of Al_2O_3 nanosheet and polyfluorene chain was low, few polymer was absorbed on the surface of the Al_2O_3 raft flats, corresponding to a small blue shift in the emission spectrum. Further increasing the content of Al_2O_3 (intermediate between 160:1 and 200:1), an increased fraction of polymer chains would be absorbed on the surface of inorganic material and the crystalline region of polyfluorene would be disturbed, resulting in the coiling of the polymer chains (see Figure 5c (right)). When the weight ratio approaches 200:1, the polymer molecule appears as random coils being isolated from each other by the Al_2O_3 nanosheets as presented in Figure 5d (right). In the experiment, the blue-shifted phenomena would reach the maximum only when the weight ratio of Al_2O_3 versus PFO was enhanced up to 280:1, which might result in full isolation of polymer chains and completely absorption of polyfluorene on the surface of Al_2O_3 flat rafts.

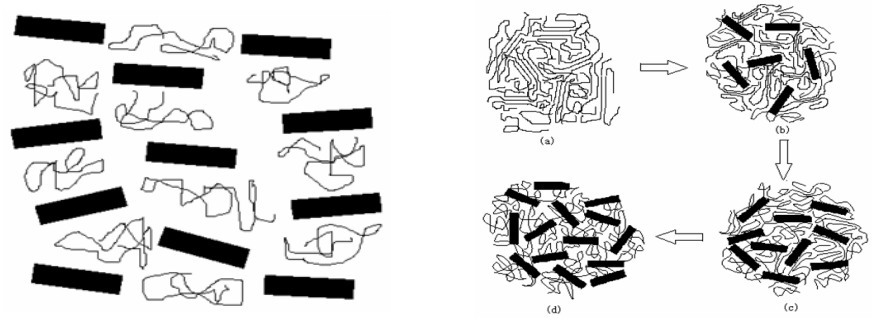

Fig. 5 Schematic illustration of PFO/Al_2O_3 nanocomposite silution (solid line: the flat raft of alumina nanoparticle; coil: conjugated polymer) (left); Schematic illustration of the effect of increasing alumina content on the conformation of polyfluorene chains in PFO/Al_2O_3 nanocomposite. (thick black lines: the flat raft of alumina nanosheets viewed from a direction paralled to the planes of the sheets; coils: conjugated polymer chains) (right)

Conclusions

We have investigated a new type of composite material prepared by blending the PFO solution with the modified alumina dispersion. The nanocomposite as fabricated showed a 22 nm blue-shift of PL emission as compared to the bulk polymer. This suggests the significant potential for modifying the optical emission properties of PFO by isolating the polymer within the inorganic materials and provides valuable information for the optimization devices based on conjugated polymers.

Acknowledgments

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