

INFLUENCE OF THE ORGANIC SOLVENTS ON THE α AND β PHASES OF A CONJUGATED POLYMER (PFO)

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Optical properties of a conjugated polymer of poly[9, 9-dioctylfluorenyl-2, 7-diyl] – End capped with 2,5-diphenyl-1,2,4-oxadiazole (PFO-1) have been thoroughly studied in different organic solvents and concentrations. The spectral properties of PFO-1 were compared with the conjugated polymer of poly (9,9-dioctyl fluorenyl-2,7-diyl) (PFO-2) under the same operation conditions. The absorption spectra of PFO-1 in tetrahydrofuran (THF), under different concentrations, exhibited only one broad band at 390 nm. This broadband (390 nm) comprises two bands at 380 and 400 nm. At higher concentrations, there was no band detected at the end of the spectrum. Under identical operational conditions, PFO-1 exhibited a new band at 437 nm at the end of the spectrum for some other organic solvents. The new band (437 nm) increases rapidly with increasing the concentration. According to our knowledge, the bands at 390 and 437 nm are attributed to alpha (α) and beta (β) phases, respectively. On the other hand, the fluorescence spectra of PFO-1 in THF, for low concentrations, showed four bands; around 422, 445, 468 and 505 nm. At higher concentrations, the fluorescence spectra were drastically changed. It can be seen that the bands at 422 and 445 nm were totally disappeared, and there were two bands; one at 468 nm (dominant) and another at 505 nm (shoulder). For benzene and toluene, the band at 505 nm was not detected. Under pulsed laser excitation of Nd: YAG laser (λ_{ex} =355 nm), PFO-1 produced dual amplified spontaneous emission (ASE) peaks at 425 and 445 nm for low and high concentrations.

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1. Introduction

In the past few decades, conjugated polymers have drawn attention many scientists in science, solar cells and bio-activators[1, 2]. The main advantages of conjugated polymers as compared with traditional organic dye materials for optical applications are: these polymers can emit light across the visible spectrum; they have very strong absorption and an emission cross section. Moreover, have broad spectra suitable for tuneable lasers[3-5]. The implementation of conjugated polymers was reported by studying the electrical characterization of poly-acetylene[6]. The mechanical characteristics of conjugated polymer and its substantial processing quality, combined with its electronic properties, make it especially fetching materials for new electronics manufacturer. Thus; these new materials were used as great activity medium in various optics and electronic equipment, such as photodiodes[7, 8], LEDs [9-13], and field effect transistors[14-17]. It is well known that the molecular

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synthesis of conjugated polymer gives a higher quantum yield in the fluorescence and long range in Stokes shift [17-19], compared to those ones who have small organic molecule such like laser dyes. At a recent time, the optical possessions of conjugated polymer have been studied. They have shown a high photochemical stability, facility of processing, lower cost and high optical gain compared with laser dyes [20, 21]. The Amplified Spontaneous Emission (ASE) and spectral characterization of PFO in several solvents at various concentrations and pumped power YAG laser excitation (355nm) have been accomplished. These materials produce a powerful optical gain and generate a very confined spectral emission [12]. Also the dimer synthesis of PFO in the oleic acid has been studied before [22]. Not so many studies about the photoluminescence in solution and in thin films, made by spin coating solutions, were previously performed [23]. We report here, for the first time, the spectral characterization of poly (9,9- dioctyl fluorenyl-2,7-diyl) (PFO-1) in three solvents (benzene, toluene and tetrahydrofuran), at different concentrations.

In this paper, the optical and amplified spontaneous emission properties of the polymer PFO-1 in different solvents and concentrations were recorded. Under optimum concentrations and organic solvents, PFO showed dual absorption bands at 390 and 437 nm. These bands were attributed to the alpha and beta phases. The fluorescence spectra of PFO-1 in different solvents and concentrations showed four bands at 425, 445, 472 and 503 nm. The obtained results were compared with that of PFO-2. Under sufficient concentration and pump power energy, PFO-1 just exhibits dual ASE around 425 and 450 with FWHM of 4 nm even at higher concentrations and pump power energy; whereas PFO-2 showed ASE peaks in four wavelength regions (425, 450, 470 and 505 nm).

2. Experimental procedures

A conducting polymer of PFO-1 and PFO-2 was purchased from American Dye Source and used as received with a molecular weights (MW) of 40,000 – 150,000 and 40,000 – 200,000, respectively. Its molecular structure is given in Fig.1a. PFO-1 and PFO-2 were dissolved in different organic solvents under wide range of concentrations. The absorption spectra of PFO-1 and PFO-2 were obtained using a thermo-scientific spectrometer (100 - 800nm). The fluorescence spectra recorded by the spectrometer of Perkin Elmer. The spectra for the solutions were measured in a small chamber. The dimension of this chamber is $1 \times 1 \times 4$. The chamber was pumped repetitively by light pulses generated from the third harmonic of a Q-switched Nd: YAG laser (wavelength: 355 nm, pulse width: 4 ns, repetition: 1 Hz). The pump light was focused onto the dye solution by a cylindrical lens ($f = 5\text{cm}$). Under suitable pump power and concentrations of PFO-1 and PFO-2 were excited. The amplified spontaneous emissions (ASE) were collected by a 1-mm entrance slit of an ICCD camera. It is important to note that these measurements were done under identical experimental conditions: only the dye cells were changed.

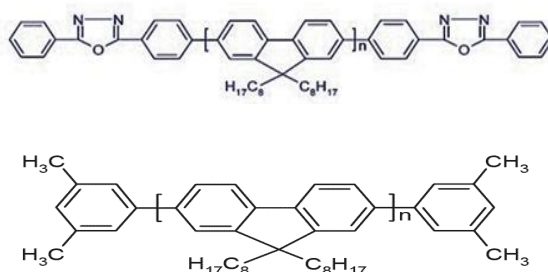


Fig. 1. (a) Chemical structure of conjugated polymer PFO-1;
(b) Chemical structure of conjugated polymer PFO-2.

3. Results and discussion

The absorptionspectra of the PFO-1 in tetrahydrofuran (THF) for different concentrations from 0.0025 to 0.1 mg/ml were recorded. Fig. 2 shows that PFO-1 has a broadband centered at 390 nm. When the concentration was increased, the spectrum did not change. It can be seen that the optical density increased by increasing the concentration. In addition, there was no band traced at the end of the spectrum. On the other hand, the fluorescence spectra of PFO-1 in THF, under the same operational conditions, were studied. At low concentrations (0.0025mg/ml), the spectrum exhibited four bands; 425, 445, 472 and 503 nm as shown in Fig.2.

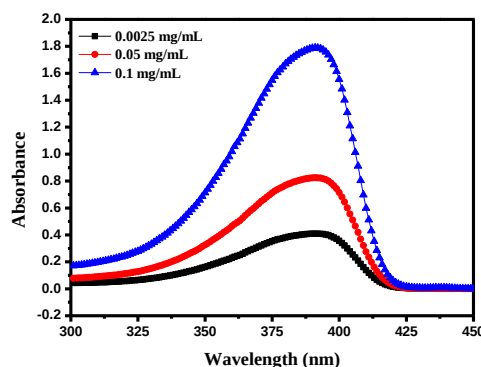


Fig. 2. Absorption of PFO-1 in THF at different concentrations.

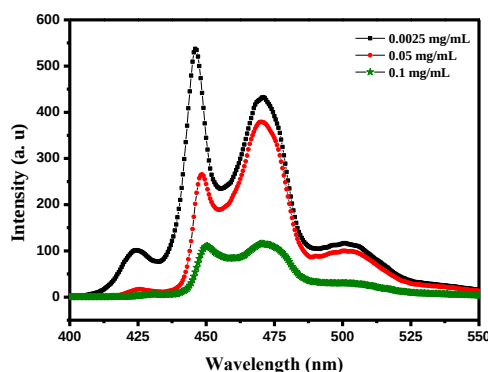


Fig. 3. Fluorescence of PFO-1 in THF at different concentrations.

When the concentration was increased to 0.05 mg/ml, the fluorescence spectrum was totally changed. One can see that the whole intensity of the spectrum was decreased. Besides that, the band at 425 nm almost vanished. Moreover, the dominant band at 445 nm became a shoulder, while the band at 472 nm which was a shoulder became dominant. At a concentration of 0.1mg/ml, the fluorescence spectrum dramatically changed. The results revealed that there the intensity of the bands of 445 and 472 nm became almost equal, and the intensity of the band 505 nm decreased rapidly (Fig. 3).

3.1. Influence of the solvents on the absorption and fluorescence spectra

The spectral properties of PFO-1 in toluene and benzene at a concentration of 0.05 mg/ml were investigated. The absorption spectra showed a small new band around 437 nm for each solution. The band at 390 and 437 nm are due to alpha (α) and beta (β) phases [20]. The optical density ratio between 390 nm to 437 nm for benzene and toluene were 35:1 and 108:1, respectively. That means that the nature of solvent species plays an important role in the β phase as in Fig.4 [20].

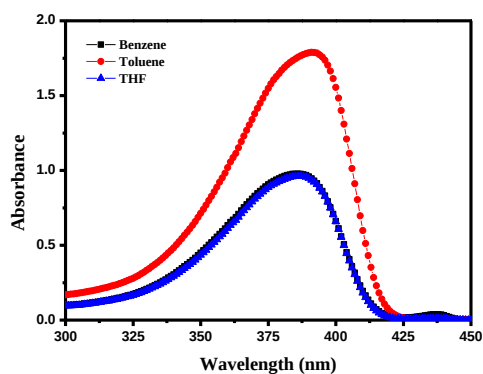


Fig.4. Absorption spectra of PFO-1 at a concentration of 0.05 mg/ml in different solvents.

The influence of the concentrations of PFO-1 in benzene and toluene was examined under identical operational conditions. Fig. 5 showed that the band at 437 nm, which is due to beta phase, is more pronounced in benzene solvent compared with THF (Fig. 2) and toluene as illustrated in Fig. 6.

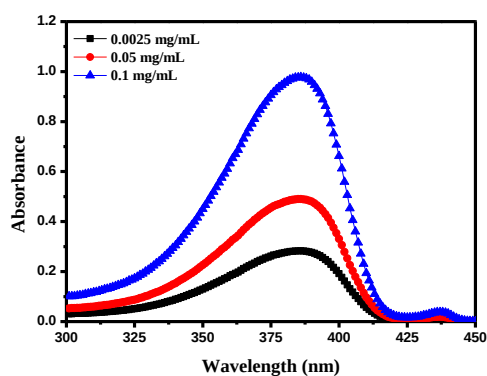


Fig.5. Absorption of PFO-1 in benzene in different concentrations.

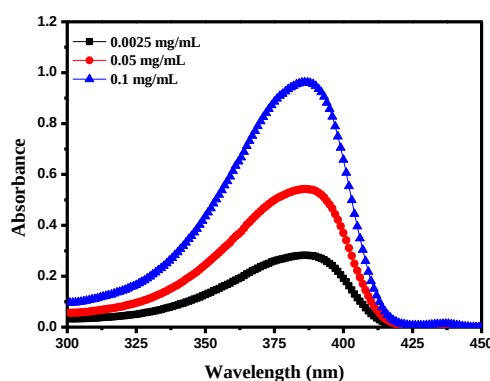


Fig.6. Absorption of PFO-1 in Toluene in different concentrations.

The fluorescence spectra of PFO-1 in benzene and toluene in different concentrations have been studied. At a concentration of 0.0025 mg/ml, the results showed that each solution has three fluorescence bands around 422, 445 and 468 nm as shown in Fig. 7 and Fig. 8. When the concentration was increased to 0.05 mg/ml, the intensity was

decreased rapidly for each solution. Meanwhile, the bands 422 and 445 nm became comparable in benzene, while the band 422 nm was still dominant in toluene (Fig. 7 and Fig. 8). Further increase the concentration to 0.1 mg/ml, the band at 445 nm became a dominant for benzene and the band at 468 nm grew up. Similarly, in toluene the intensity was decreased again and the intensity of the bands 422 and 445 nm was almost comparable.

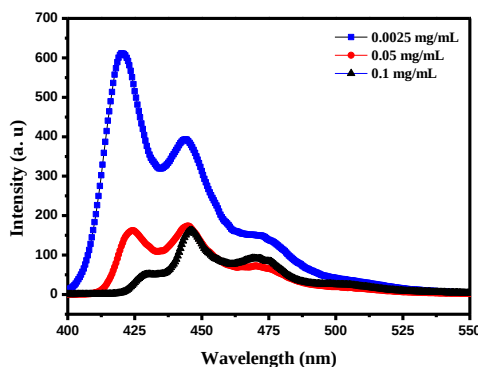


Fig.7. Fluorescence of PFO-1 in benzene in different concentrations.

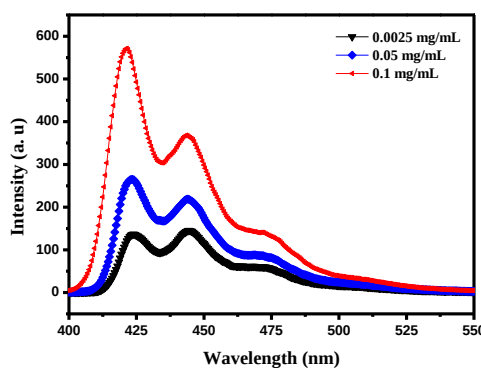


Fig. 8. Fluorescence of PFO-1 in toluene in different concentrations.

The fluorescence spectra of PFO-1 for different solvents were investigated. The concentration was kept at 0.05 mg/ml for each solution. The results revealed that the fluorescence spectra of benzene and toluene were identical; whereas the spectrum of PFO-1 in THF was totally different as displayed in Fig. 9. One can see that the band 422 nm which was dominant in benzene and toluene became a tiny band in THF. Moreover, the band 468 nm which was a shoulder in benzene or toluene became a pronounced band in THF. In addition, PFO-1 in THF there was a clear band at 505 nm which have never appeared in benzene and toluene.

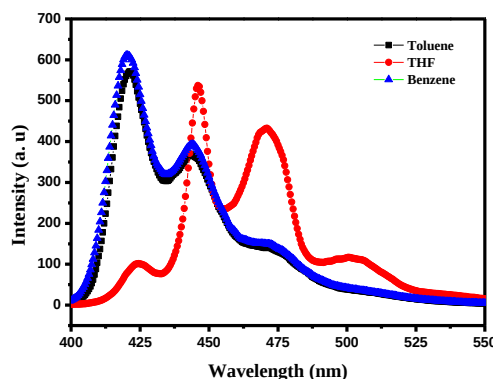


Fig.9. Fluorescence of PFO-1 at a concentration of 0.05 mg/ml in different solvents.

Having discussed the effect of the solvents and concentrations on the spectral properties of PFO-1 and PFO-2, here the influence of the molecular structure on the absorption and fluorescence spectra will be discussed. In our previous study, a new type of PFO of poly (9,9-dioctyl fluorenyl-2,7-diyl) (PFO-2) has been investigated[19]. The only difference between the two compounds is that the PFO-1 contains additional functional groups of 2,5-diphenyl-1,2,4-oxadiazole (Fig.1). The absorption spectra of PFO-1 and PFO-2 in THF were investigated. The concentration was fixed to be 0.05 mg/ml. The results showed that PFO-2 has a clear band at 437 nm (due to beta phase), whereas, the band did not detected for PFO-1 under same conditions. This indicates that the additional functional group in PFO-1 plays an important role for beta phase; see Fig.10(a-b).

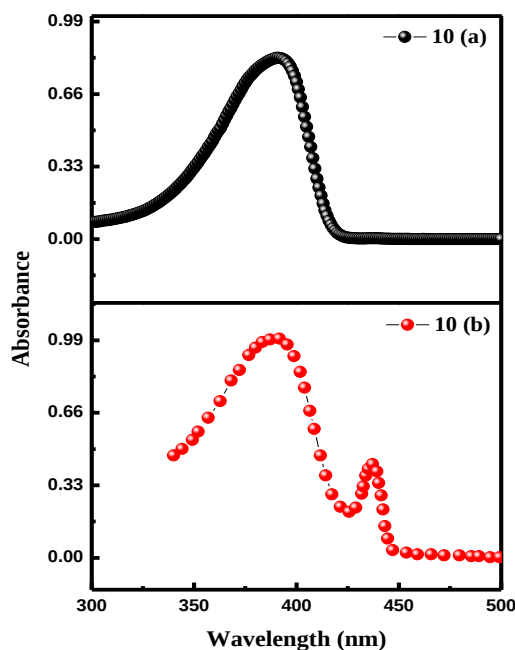


Fig.10. (a) Absorption of PFO-1 in THF at a concentration of 0.05 mg/ml. and (b) Absorption of PFO-2 in THF at a concentration of 0.05 mg/ml.

On the other hand, the fluorescence spectra of these polymers were studied in THF at a concentration of 0.05 mg/ml. It was clear that the two spectra were almost identical as illustrated in (Fig.11).

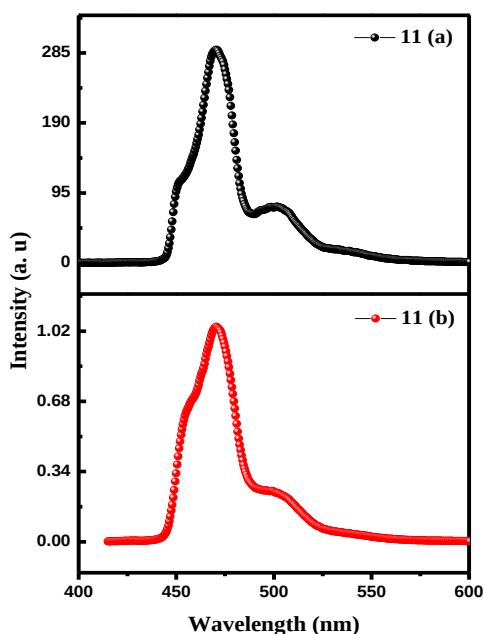


Fig.11.(a) Fluorescence of PFO-1 and (b) PFO-2 at a concentration of .05 mg/ml.

3.2. Amplified spontaneous emission (ASE)

The amplified spontaneous emission (ASE) of PFO-1 and PFO-2 at a concentration of 0.05 mg/ml in THF was transversely excited by Nd: YAG laser pulses ($\lambda_{\text{ex}} = 355$ nm). The pump power excitation was kept at 5 mJ. The results showed that PFO-1 has two ASE peaks at 425 nm as shorter wavelength (SW) and 450 nm as longer wavelength (LW) with a full width half maximum (FWHM) of 4 nm. The intensity ratio between these two ASE peaks was almost comparable (i.e. $\frac{I_{\text{LW}}}{I_{\text{SW}}} \approx 1$) as illustrated in Fig. 12. Under same operational conditions (concentration, solvent, temperature and pump power excitation) PFO-2 showed dual ASE peaks at 450 nm (SW) and 475 nm (LW). These peaks may be attributed to alpha and beta phases (Fig. 12)[24-27].

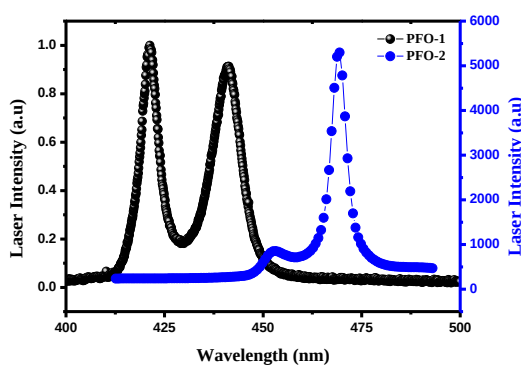


Fig.12.ASE of PFO-1 and PFO-2 in THF at a concentration of 0.05mg/ml.

Similarly, PFO-1 in toluene showed also two ASE peaks at 425 and 450 nm. The intensity ratio ($\frac{I_{\text{LW}}}{I_{\text{SW}}}$) was 1.04 as shown in Fig. 13. Similarly, the intensity ratio ($\frac{I_{\text{LW}}}{I_{\text{SW}}}$) for PFO-1 in benzene was 50 as seen in Fig. 14. This is a strong indication that the solvents play important role in the ASE spectra.

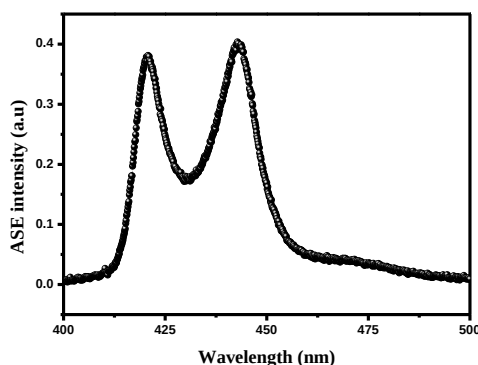


Fig. 13. ASE of PFO in toluene at a concentration of 0.1mg/ml.

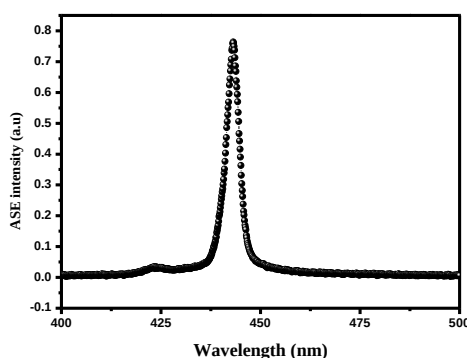


Fig.14. Amplified spontaneous emission (ASE) of PFO in benzene at a concentration of 0.1 mg/ ml.

4. Conclusions

To recapitulate this work, the spectral and amplified spontaneous emission of the conjugated polymer PFO-1 under the influence of the solvents and concentrations were reported in this paper.

The most important result is the demonstration of the beta phase of PFO-1 in some organic solvents. The influence of the organic solvents on the spectral properties was studied thoroughly. Under pulsed laser excitation, PFO-1 produced ASE peaks at 425 and 450 nm. In addition, the intensity ratio between these ASE peaks depends on the concentration and solvent nature. PFO-2 under the same operating conditions was examined and compared with that of PFO-1.

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