

## Desirable Amplified Spontaneous Emission(Ase) from a Conjugated Polymer Poly (9,9-Dioctylfluorenyl-2,7-Diyl) End Capped with 2,5-Diphenyl-1,2,4-Oxadiazole(Pfo) in Liquid and Solid State

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**Abstract:** Thin films of a conducting polymer, poly (9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) were prepared. PFO was dissolved in tetrahydrofuran (THF) with different concentrations to achieve thin films with different thicknesses. The solution was deposited by spin coating technique on glass substrates. The absorption spectrum has shown two distinguished peaks. The spectral and amplified spontaneous emission (ASE) properties of PFO thin films were recorded. The photoluminescence (PL) spectra at 0.0025mg/ml showed two clear peaks and a hump. These peaks could be attributed to PFO molecule, dimer, and excimer, respectively. Under suitable pump power excitation of Nd: YAG laser (355 nm) the amplified spontaneous emission spectrum was obtained at 462 nm. To the best of our knowledge, this perhaps is the first report on conjugated polymer PFO in solid state thin film producing ASE from the excimer state.

**Keywords:** Amplified spontaneous emission; Conjugated polymer PFO; Dimer; Excimer; Laser active medium; Thin film.

### 1. INTRODUCTION

Conjugated polymers were discovered in 1977 by Chiang et al (1). These materials have been used as an active medium in several optoelectronic devices, such as field effect transistors (2), photodiodes, and light emitting diodes (3). The molecular structure of conjugated polymer leads to a high fluorescence quantum yield and large Stokes shift, in comparison to those of small organic molecules such as laser dyes (4).

The photophysical properties of some conjugated polymers have been studied recently during the last decades; they have better photochemical stability and optical gain compared with conventional laser dyes, such as coumarin and rhodamine derivatives (5).

The amplified spontaneous emission (ASE) and spectral properties of ADS429BE in THF under high concentration and pump power excitation of YAG laser (355nm) have been studied. The ASE intensity depends on the solvent, concentration, and pump power (6).

The thin films of ADS429BE on a glass substrate in THF, toluene and benzene in different concentrations and different speeds have been prepared. The comparisons between absorption and photoluminescence (PL) in solutions and thin films have been made.

### 2. EXPERIMENTAL

In this work, we reported the photo-physical properties of conjugated polymer poly (9,9-dioctylfluorenyl-2,7-diyl) end-capped with 2,5-diphenyl-1,2,4-oxadiazole (ADS429BE) as shown in Fig.1.

## STRUCTURE

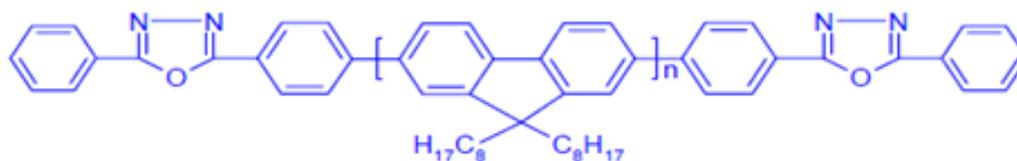


Fig1. Molecular structure of the polymer (PFO) ADS429BE

The sample molecular weight is in the range of (40000-120000). The absorption spectroscopy is obtained by using a thermo-scientific spectrometer, whereas the fluorescence spectroscopy obtained by the spectrometer of Perkin Elmer. The absorption and fluorescence of the PFO were checked in three solvents (benzene, toluene and tetrahydrofuran) at different concentrations. The sample of the PFO is prepared at American dye, the well-known company.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Absorption Spectra

The absorption and fluorescence of poly (9,9-dioctylfluorenyl-2,7-diyl) end-capped with 2,5-diphenyl-1,2,4-oxadiazole(ADS429BE) were obtained in concentration range of 0.0025-0.1 mg/ml. The absorption of ADS429BE in benzene, toluene, and tetrahydrofuran (THF) was recorded. It was found that at a concentration of 0.0025mg/ml, there were two peaks in benzene ( $C_6H_6$ ) and toluene ( $C_7H_8$ ), the dominant one around 390nm, and the second one around 438nm, which is attributed to aggregation of molecules in the ground state (dimer state) (7). On the other hand, there was one peak in THF ( $C_4H_8O$ ) at the same concentration (Fig.2).

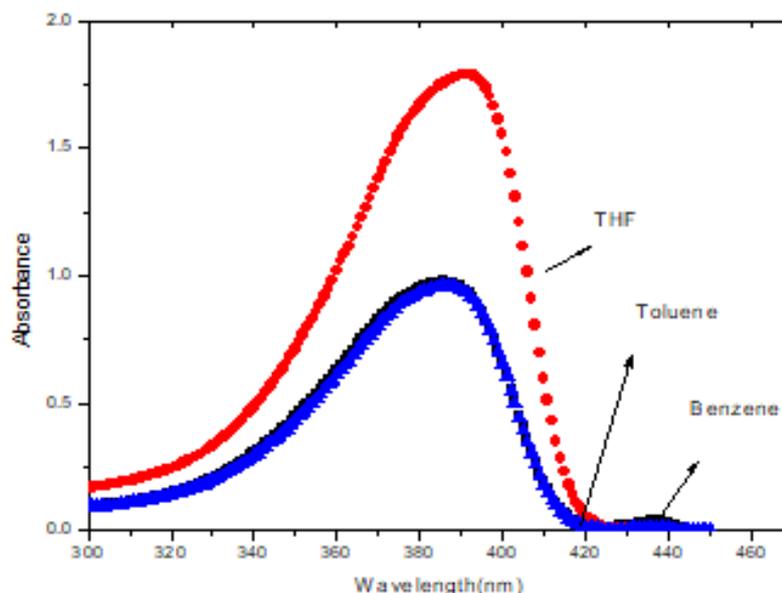


Fig2. Absorption of PFO at a concentration of .0025 mg/ml in different solvents.

The results showed that the greatest optical density of the dominant peak in THF, and the greatest optical density of the second peak in benzene. These results depend on the polarity of the solvent (8).

The absorption spectra of PFO (ADS429BE) in benzene, toluene, and THF in different concentrations have been recorded as shown in figures 3, 4, and 5 respectively. One can be seen that, by increasing the concentration the intensity increases. These results attributed to the dimer state.

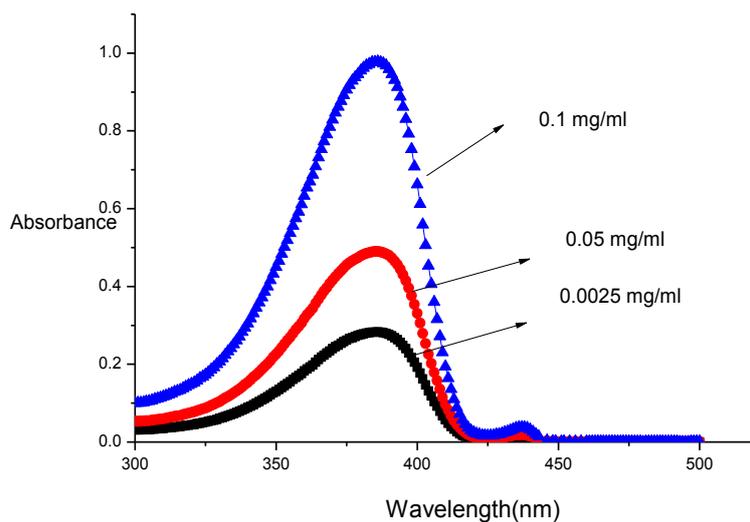


Fig3. Absorption of (PFO) ADS429BE in benzene in different concentrations.

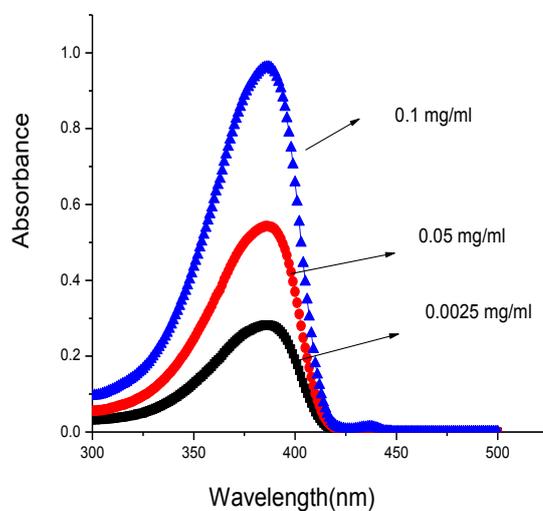


Fig4. Absorption of (PFO) ADS429BE in toluene in different concentrations.

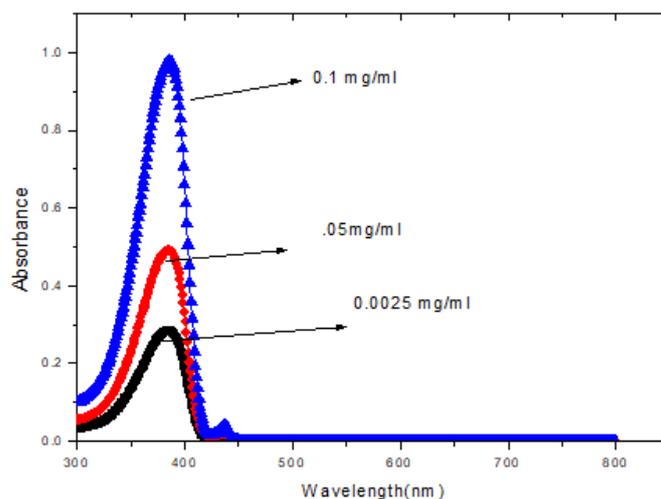
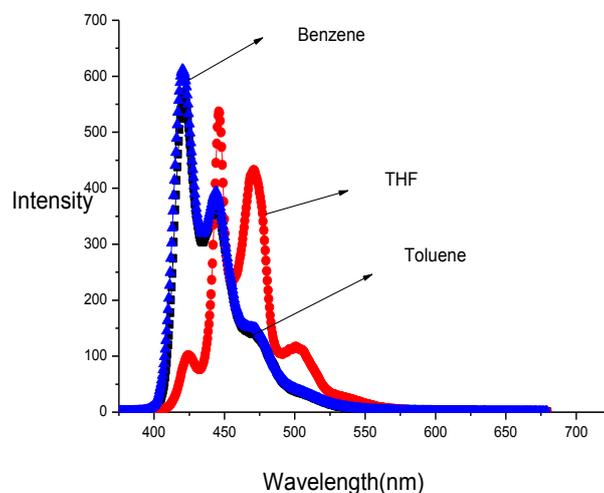


Fig5. Absorption of ADS429BE in THF in different concentrations.

### 3.2. Fluorescence Spectra

Fig.6 shows the fluorescence of PFO in different solvents at a concentration of 0.0025 mg/ml. There were three peaks at 425, 450, and 475nm, in benzene, and toluene. On the other hand, there were four peaks (425,450,475, and 510 nm) in THF, at the same operational conditions. These results depend on the solvent polarity (Table.1).

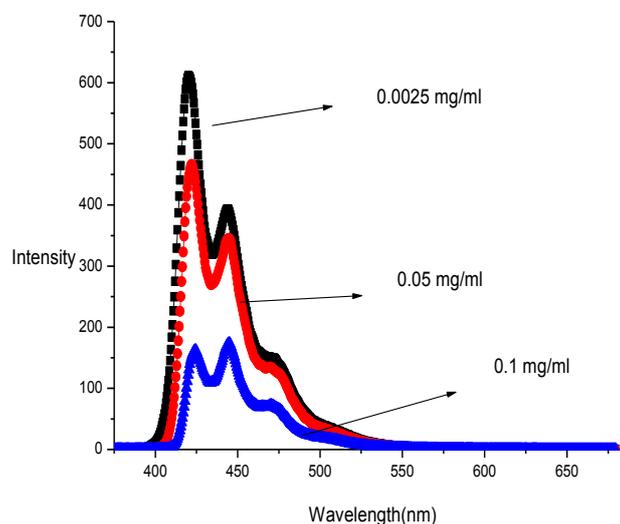


**Fig6.** Fluorescence of ADS429BE at a concentration of 0.0025mg/ml in different solvents

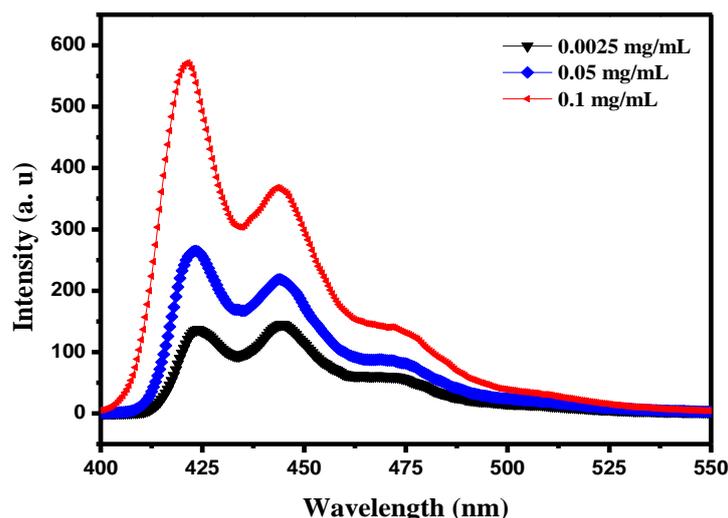
The fluorescence spectra of PFO in benzene and toluene in different concentrations have been studied. At a concentration of 0.0025mg/ml, the results showed that each solution has three fluorescence bands around 422, 445 and 468 nm as shown in Fig. 7 and Fig. 8. When the concentration was increased to 0.05 mg/ml, the intensity was decreased rapidly for each solution. Further, increase the concentration to 0.1 mg/ml, the band at 445 nm became a dominant for benzene. Similarly, in toluene, the intensity was decreased again and the intensity of the bands 422 and 445 nm was almost comparable.

**Table1.** The spectral properties of PFO in different solvents.

Solvent	Dielectric constant( $\epsilon$ )	$\lambda$ max Absorption	$\lambda$ max Fluorescence
Benzene	2.27	390	425
Toluene	2.38	390	425
Tetrahydrofuran(THF)	7.58	390	450



**Fig7.** Fluorescence of ADS429BE in benzene in different concentrations.

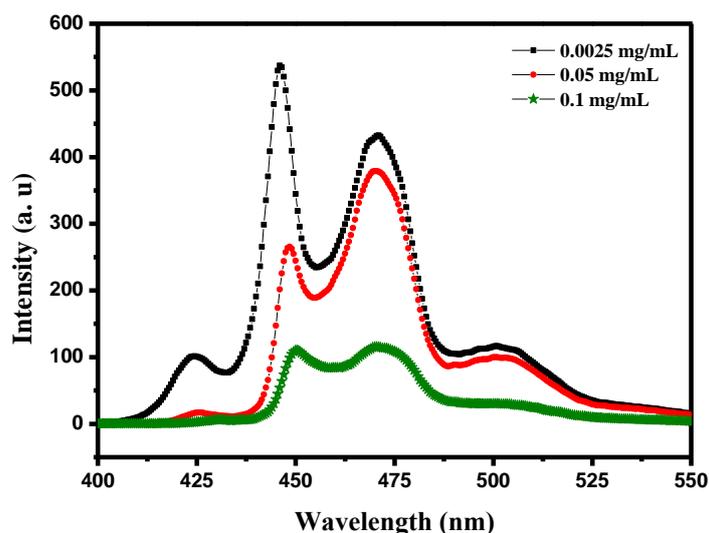


**Fig8.** Fluorescence of PFO in toluene in different concentrations.

The fluorescence spectra of PFO 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 F.g.9.

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.

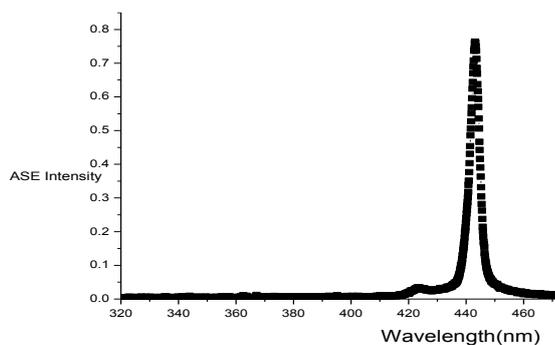
Moreover, the dominant band at 445 nm became a shoulder, while the band at 472 nm which was a shoulder became dominant. At a concentration of 0.1mg/ml, the fluorescence spectrum dramatically changed. The result revealed that there the intensity of the bands of 445 and 472 nm became almost equal, and the intensity of the band 503 nm decreased rapidly.



**Fig9.** The Fluorescence of ADS429BE in THF in different concentrations.

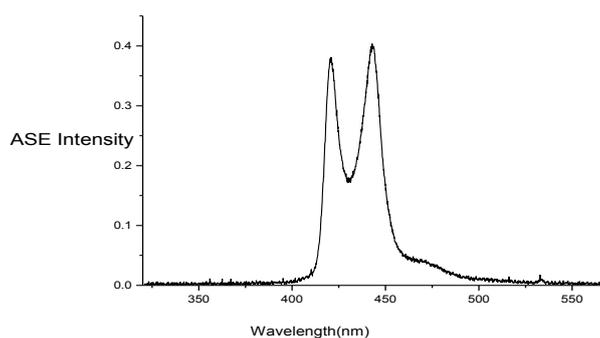
### 3.3. Amplified Spontaneous Emission (ASE) of PFO

PFO was dissolved in benzene, toluene, and THF with the concentration fixed at 0.1 mg/ml. This solution was transversely excited with a UV laser at 355 nm. At a pump power of 2 mJ, the ASE spectrum was recorded. Note that this was approximately the minimum concentration and the minimum pump power excitation for PFO to produce an ASE spectrum. Fig.10 shows ASE in benzene. The result showed that there were two peaks around 425 and 445 nm, with a narrow spectral bandwidth (full width at half maximum (FWHM)) 5 nm. The maximum peak is coinciding with the maximum of the fluorescence emission spectrum at this concentration.

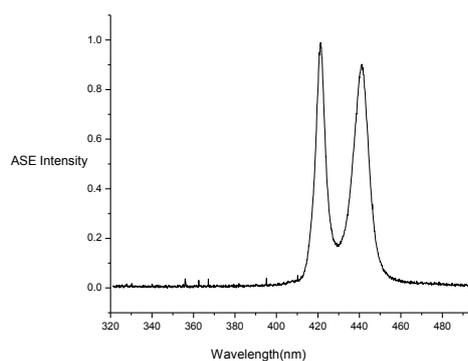


**Fig10.** ASE in benzene at a concentration of 0.1 mg/ml.

Figures 11 and 12 show the ASE spectrum in toluene and THF. One can be seen that the ASE spectrum in toluene has comparable peaks around 425 and 440nm. ASE in THF in the same operation conditions has a maximum peak around 425nm. These differences due to the dielectric constant ( $\epsilon$ ) of the solvents.

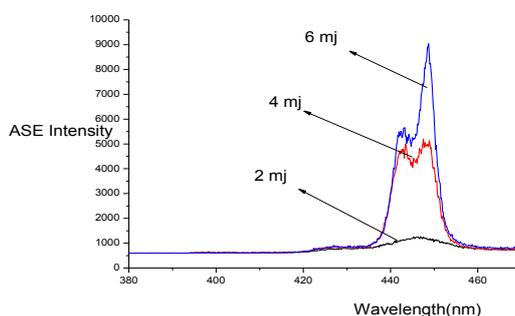


**Fig11.** ASE in Toluene at a concentration of 0.1 mg/ml.



**Fig12.** ASE spectrum in THF at a concentration of 0.1 mg/ml.

Figures 13 and 14 show the ASE in toluene and THF at a concentration 0.1mg/ml in different powers. The result shows there were two peaks, the dominant peak in toluene at 450nm. On the other hand, the dominant peak in THF at 445nm. The intensity of ASE increased with increasing pump power (9).



**Fig13.** ASE spectrum in Toluene in different powers at a concentration of 0.1 mg/ml.

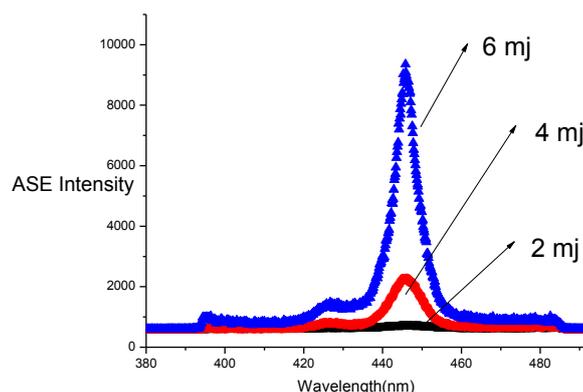


Fig14. ASE spectrum in THF at a concentration of 0.1 mg/ml In different powers.

### 3.4. Comparison between Absorption of PFO in Benzene in Thin Film and in Solution

The emitting polymer layer was spin-coated from solution at various concentrations and various spin speeds in order to achieve a range of film thicknesses. Fig.15-a shows thin film absorption in benzene in different concentrations. There were two peaks around 395 and 440nm. When the concentration was further increased, the optical density of the peak 440nm increased rapidly. The band at 440 could be due to the ground state aggregation. Fig.15-b shows absorption of PFO in solution in different concentrations. There were two peaks (390 and 438nm). The results showed that there was a redshift between two spectra (Fig.15-a and Fig.15-b). This result could be attributed to more aggregation in a solid state.

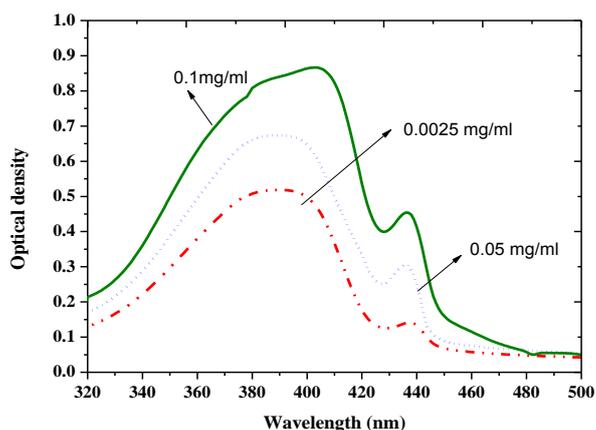


Fig15(a). Thin film absorption in benzene at speed of 500 rpm in different concentrations.

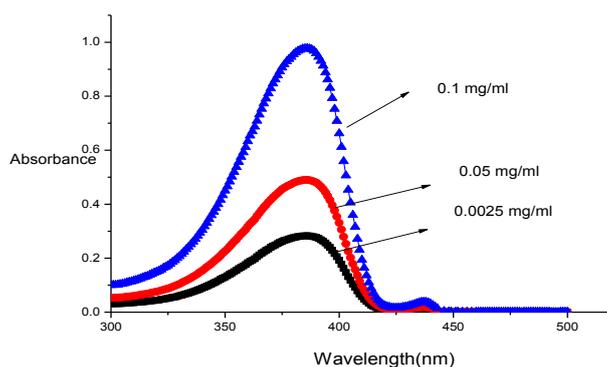


Fig15(b). Absorption spectrum of PFO (ADS429BE) in benzene in solution in different concentrations.

### 3.5. Comparison between Fluorescence of PFO in Thin Film and in Solution

Figures 4.16-a and 4.16-b show the fluorescence spectra of PFO in benzene in different concentrations in a thin film, and in solution respectively. At a concentration of 0.1 mg/ml, the results showed only two bands In the solid state, one around 480nm (dominant) and another around 510 nm, These peaks in the solid state were analogue to the absorption bands of 395 and 440nm in absorption spectrum (Fig.15-a). In liquid state (at the same concentration) there were three bands 425, 450, and 475nm (Fig. 16-b). These peaks may be attributed to the PFO molecule (10-13).

At a concentration of 0.05 mg/ml, fluorescence spectrum (thin film) has dramatically changed as shown in fig.4.16-a. There was a shoulder at 460nm and dominant peak around 480nm. In liquid state also there were three peaks around 430, 450, and 475 nm. Further decrease the concentration to 0.0025mg/ml, in the solid state, there were three peaks 435 450, and 480 nm (shoulder), and in liquid, there were also three peaks at 425,450 and 475nm and the intensity of the peak 475 nm was increased.

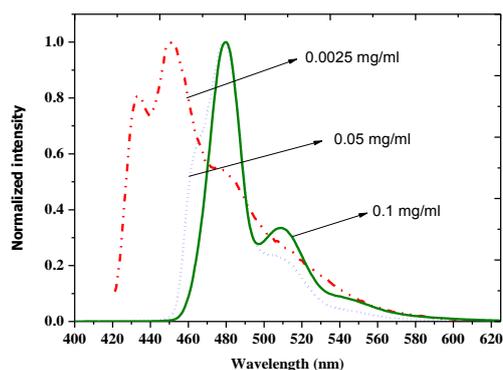


Fig16(a). Fluorescence of ADS429BE in benzene thin film at speed of 500 rpm in different concentrations.

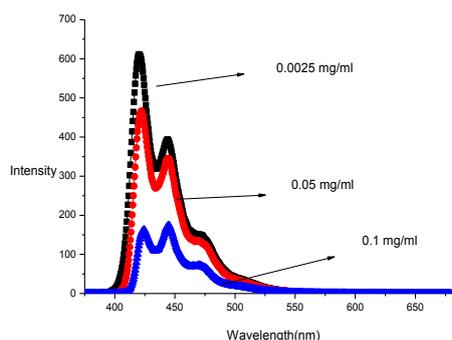


Fig16(b). Fluorescence of PFO in benzene (solution) in different concentrations.

Table2. Comparison Between the Absorption of PFO in Solution and thin film in different solvents.

Solvent	$\lambda$ max Absorption of PFO in Solution	$\lambda$ max Absorption of PFO in thin film
Benzene	390	395
Toluene	390	395
THF	390	430

Table3. Comparison between Fluorescence and Stokes shift of PFO in Solution and thin film in different solvents.

Solvent	$\lambda$ max Fluorescence of PFO in Solution	$\lambda$ max Fluorescence of PFO in thin film	Stoke,s shift
Benzene	425	450	25
Toluene	425	450	25
THF	440	450	10

#### 4. CONCLUSION

To conclude, the authors stressed that thin films of a conducting polymer, poly (9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) were prepared and examined. The absorption spectrum has shown two distinguished peaks. The spectral and amplified spontaneous emission (ASE) properties of PFO thin films were recorded. The photoluminescence (PL) spectra at 0.0025mg/ml showed two clear peaks and a hump. These peaks could be attributed to PFO molecule, dimer, and excimer, respectively. Under suitable pump power excitation of Nd: YAG laser (355 nm) the amplified spontaneous emission spectrum was obtained at 462 nm. To the best of our knowledge, this perhaps is the first report on conjugated polymer PFO in solid state thin film producing ASE from the excimer state.

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