

Amplified spontaneous emission spectra of poly(9,9-dioctylfluorenyl-2,7-diyl) under pulsed laser excitation



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ABSTRACT

Photophysical parameters such as absorption, fluorescence spectra, Stokes' shift, fluorescence quantum yield and amplified spontaneous emission (ASE) of a soluble conducting polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) were measured in different solvents. The absorption spectra of PFO in tetrahydrofuran (THF) have shown two bands at 390 and 437 nm. The results showed that the optical density of the band 437 nm increased by increasing the concentration. This is a strong indication that PFO in solution aggregates at higher concentrations. On the other hand, at lower concentrations, the fluorescence spectra of PFO in THF have shown three bands; 422 (dominant), 445 (shoulder) and 470 nm (hump). For the higher concentrations, the band at 422 nm totally vanished while the band 470 nm became a dominant. Therefore, the band at 470 nm could be attributed to the dimer state. The ASE action was tested in a transverse pumping configuration where the conducting polymer was pumped by laser pulses from the third harmonic of an Nd:YAG laser (355 nm). It could be seen that there were three ASE peaks at 425, 450 and 475 nm. The spectral and ASE properties of PFO were compared with the conjugated polymer poly[9,9-di-(2'-ethylhexyl)fluorenyl-2,7-diyl] (PDHF) under the same operating conditions. The most important features are: (1) the ASE intensity and the photochemical stability of PDHF were remarkably high compared with PFO, (2) PFO has an ASE action even under low concentrations (3) and the ASE emission from PFO is tunable in the wavelength region between 425, 450 and 475 nm.

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1. Introduction

In the past few decades, conjugated polymers have fascinated many scientists in science and technology disciplines [1,2]. They have found potential applications in the fields like solar cells, bio-activators, super capacitors and molecular electronic device [3–5]. These conjugated polymers have been used as an active medium in several optoelectronic devices, such as field effect transistors, [6] photodiodes, light emitting diodes (LEDs) [7,8] and polymer light-emitting electrochemical cells (LECs).

The photo-physical properties of some conjugated polymers have been studied intensively during the last decades. These conjugated polymers became excellent laser media [9–15] because they have better photochemical stability and optical gain compared with conventional laser dyes such as coumarin and rhodamine derivatives.

Duarte et al. work in this area began with the demonstration of narrow-line-width laser emission using coumarin-tetramethyl dyes, as molecular gain media, [16,17] which offer high conversion efficiency and wide tunability in the green region of the electromagnetic spectrum [18].

Poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) is a prototypical main-chain liquid crystalline homopolymer that emits in the blue wavelength and exhibits polymorphic behavior, with striking implications for its photo-physical properties. Solid-state room temperature photo-luminescence quantum efficiencies of more than 60% have been measured for various thin phases of the polymer and very large stimulated emission cross-sections (10^{-15} cm^2) have been reported, making PFO a desirable laser medium [19].

The optical gain properties of a series of semiconductor polyfluorenes with photoluminescence emission spectra that span the entire visible spectrum have been investigated. The laser from distributed feedback (DFB) from poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(1,4-benzo-{2,1',3'}-thiadiazole)] in thin film was achieved [20]. The laser emission is centered at 569 nm with a full width at half maximum (FWHM) about 1.3 nm.

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The amplified spontaneous emission (ASE) and the spectral properties of poly[9,9-di-(2'-ethylhexyl)fluorenyl-2,7-diyl] (PDHF) in benzene under high concentration and pump power excitation of YAG laser (355 nm) have been studied. It was found that the fluorescence spectra of PDHF under low concentrations had two peaks; the dominant one due to monomer was around 415 nm, and the secondary band one attributed to the excimer was around 435 nm. By increasing the concentrations of PDHF, it could be seen that there was a new peak around 465 nm. This peak was being attributed to the double excimer. Under high power pulsed laser excitation, we observed amplified spontaneous emission (ASE) at 418 nm, 437 nm and 465 nm. These amplified spontaneous emission (ASE) peaks raised from the monomer, excimer and double excimer states of the macromolecule respectively [21].

The photoluminescence spectra of MEH-PPV deposited on glass substrates in different thickness have been investigated [22]. The results obtained were compared with the spectral properties of MEH-PPV in solution for different concentrations. From the absorptions and fluorescence spectra, the results showed that MEH-PPV could exist in excimer in both states thin film and solution.

In this study, the spectral and amplified spontaneous emission (ASE) properties of the polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) were demonstrated. The absorption, fluorescence and ASE properties of PFO in solution were dependent on the concentrations and solvents. When the laser pump power at 355 nm and concentration of above solution were suitably chosen, ASE at 425, 450 and 475 nm was observed. These ASE peaks could arise from the monomer, excimer and dimer states of the macromolecule, respectively. The results obtained were compared with another conjugated polymer PDHF under identical conditions.

2. Experimental

The polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and polymer poly[9,9-di-(2'-ethylhexyl)fluorenyl-2,7-diyl] (PDHF) were purchased from American Dye Source (ADS) and Sigma-Aldrich, respectively and they were used as received. The molecular mass of PFO and PDHF were 120,000 and 7264, respectively. The purity of the samples was examined using thin layer chromatography (TLC). The results showed that the purity for the two polymers was more than 95%. The molecular structures of these polymers are given in Fig. 1(a and b). PFO and PDHF were dissolved in different organic solvents (spectroscopic grade with purity 99.8%). The absorption and fluorescence spectra of these polymers in THF were studied under a wide range of concentrations. The absorption, fluorescence and amplified spontaneous emission (ASE) were measured using a small quartz cuvette with the dimensions $1 \times 1 \times 4$ cm with an optical path length of 1 cm.

The absorption spectra were recorded using a PerkinElmer lambda 950 spectrophotometer over the range from 330 to 550 nm. The fluorescence spectra were recorded using a PerkinElmer LS55 spectrofluorometer in the range from 380 to 700 nm, at room temperature. The excitation wavelength was 355 nm.

The third harmonic (355 nm) of an Nd:YAG laser (Brilliant B from Quantel) with a pulse width of 6 ns was used as the excitation source. The UV laser was focused by a quartz cylindrical lens with a focal length of 5 cm. This was used to perform transverse excitation of the HOTS solution taken in a four-sided polished quartz cell, which was kept canted to avoid feedback (see Ref. [21]). At the optimum values of the pump power and concentration, we could achieve an ASE beam coming out as a cone of light. This was collected by an optical fiber and fed into the 1-mm entrance slit of a spectrometer followed by a CCD camera (Ocean Optics) to obtain

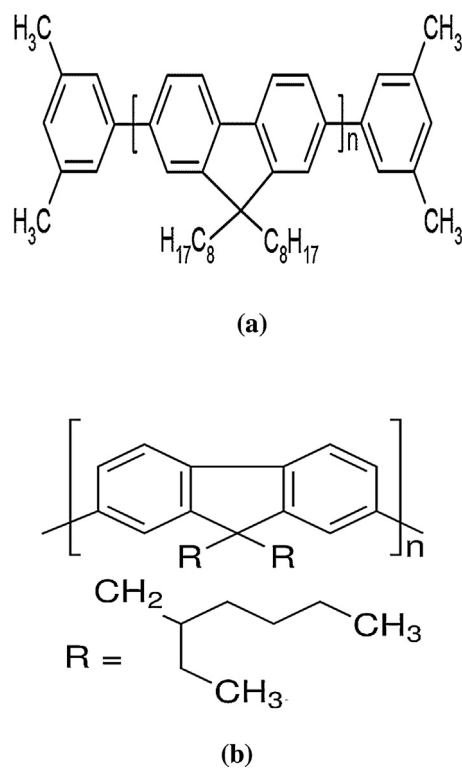


Fig. 1. Molecular structure of polymers (a) PFO and (b) PDHF.

the spectral features of the amplified spontaneous emission. To avoid saturation of CCD camera, neutral density filter was used as and when required. It is important to note that these measurements were done under identical experimental conditions: only the dye cells were changed.

3. Results and discussion

3.1. Spectral properties of PFO

The steady state absorption and fluorescence spectra of poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) in tetrahydrofuran (THF) under different concentrations ranging from 0.0002 to 0.06 mol/m³ were recorded. At lower concentration (0.0002 mol/m³), the absorption spectrum exhibited only one band at 390 nm. When the concentration was increased to 0.002 mol/m³, a new band of absorption at 437 nm appeared. When the concentration was further increased, the optical density of the band 437 nm increased rapidly as shown in Fig. 2. This is a strong indication of dimer formation of PFO in THF.

On the other hand, the fluorescence spectrum of PFO in THF at a concentration of 0.0002 mol/m³ showed three distinct bands at 422, 445 and 470 nm as shown in Fig. 2. At a concentration of 0.002 mol/m³, the intensity of the band 422 nm was decreased, whereas the bands 445 and 470 nm became comparable. When the concentration was increased to 0.06 mol/m³, the peak at 422 nm was entirely absent, and the band at 445 nm became a shoulder, whereas the band 470 nm became a dominant. According to results obtained, it could be seen that the band 437 nm, in the absorption spectra, is attributed to ground state aggregation. When the concentration increased, the number of dimer formations increased. So the intensity of the band 470 nm is proportional to the absorption band of 437 nm. Hence, the band at 470 nm could be attributed to dimer formation in a highly excited state (see Fig. 2).

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