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Dual ASE from the monomeric and excimeric states of a conjugated-polymer (PDHF) in solution

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ABSTRACT

In this work, the spectral and amplified spontaneous emission (ASE) properties of a conjugated polymer poly [9, 9-di-(2′-ethylhexyl) fluorenyl-2, 7-diyl] (PDHF) in tetrahydrofuran (THF) have been studied. Our results showed that the absorption spectra of PDHF in THF have only one peak under wide range of concentrations (0.012 mol/m^3 to 0.39 mol/m^3), it could be seen that the shape of the absorption did not change; this indicates no dimer formation in these solutions for all concentrations mentioned above. On the other hand, the fluorescence spectra of PDHF in THF, at low concentration, showed two peaks, the primary at 415 nm and the secondary at 435 nm. The effects of concentration and the temperature on PDHF in THF under same conditions were studied. For example, the intensity of the peak at 435 nm became increasingly stronger for higher concentration and lower temperature. These are analogs to the excimeric behavior of organic molecules. Under high power pulsed laser excitation, we observed ASE at 418 nm and 437 nm. These ASE peaks could arise from the monomer and excimer states of the macromolecule respectively. The ASE spectra of PDHF were compared with the rhodamine 6 G (Rh 6 G). The most important and distinguishing features are that PDHF has a two times better photochemical stability than rhodamine 6 G and high optical gain compared with the conventional laser dyes.

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1. Introduction

In the past few decades, conjugated polymers have attracted much attention in science and technology [1–5]. The conjugated polymers have found applications in fields like biosensors, bioactivators, supercapacitors and molecular electronic devices [3–5]. These materials have been used as a kind of active medium in several optoelectronic devices, such as field effect transistors, photodiodes, light emitting diodes (LEDs) [6,7] and polymer light-emitting electrochemical cells (LECs). Many conjugated polymers have properties such as high electroluminescence efficiency, low operating voltage, good mechanical flexibility and ease of fabrication as initially demonstrated by Pei and co-workers [8].

The photo-physical properties of this kind of conjugated polymers are yet to be fully understood; yet in recent years, conducting conjugated polymers have emerged as an attractive new gain medium for lasers and optical amplifiers that are tunable throughout the visible spectrum [9–13]. The ASE from liquid solution of poly [2-methoxy-5-(2′-ethylhexyloxy)-1, 4-phenylene vinylene] (MEH-PPV) by optically pumped was first reported by Moses [14].

The laser and the spectral properties of conjugated MEH-PPV in benzene under high concentrations and pump power excitation of Nd: YAG laser (355 nm) have been studied. The results showed that the fluorescence spectra of MEH-PPV under low concentrations had two peaks: the dominant one due to monomer was around 560 nm, and the shoulder one attributed to the excimer was around 600 nm. Under higher concentrations, it was found that there was only one band around 600 nm due to the excimeric state. By increasing the concentrations of MEH-PPV, it could be seen that there was a new band around 640 nm. This band is being attributed to the double excimer. Under high power pulsed laser excitation, we observed amplified spontaneous emission (ASE) at 570 nm, 605 nm and 650 nm. These ASE peaks could arise from the monomer, excimer and ***double excimer*** states of the macromolecule respectively [15].

The amplified spontaneous emission (ASE) from the excimeric state of MEH-PPV in liquid solution was earlier reported by Masilamani et al [16]. In this work presented here, the spectral properties of another such conjugated polymer, poly [9, 9-di-(2′-ethylhexyl) fluorenyl-2, 7-diyl] (PDHF) in tetrahydrofuran (THF) with different concentrations and temperatures are described. The results show that under sufficient concentration this conjugated polymer could exhibit excimer formation with a fluorescence peak at 435 nm. At this concentration, with sufficient pump power, the ASE with peaks 418 nm and 437 nm with the full width at half maximum (FWHM) of 7 nm also could be obtained. These ASE peaks could arise from the monomer and excimer states of the macromolecule. The ASE spectra of PDHF in THF were compared with the rhodamine 6 G (Rh 6 G) in methanol.

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2. Experimental

The polymer Poly [9, 9-di-(2′-ethylhexyl) fluorenyl-2, 7-diyl] (PDHF) was purchased from Sigma-Aldrich. The purity of the sample was examined using thin layer chromatography (TLC) and the results showed that the purity is more than 96%. The molecular structure of which is given in Fig. 1. This is a macromolecule with a molecular mass of 7264. PDHF was dissolved in tetrahydrofuran (THF) (spectroscopic grade with purity 99.8%). The absorption and fluorescence spectra of PDHF in THF were studied under wide range of concentrations. The spectra for the solutions measured using a small quartz cuvette with the dimensions $1 \times 1 \times 4\ cm^3$ with an optical path length of 1 cm.

The absorption spectra were taken using ***a Perkin Elmer lambda 40 spectrophotometer*** over the range from 200 to 800 nm and the fluorescence spectra were recorded using ***a Perkin Elmer LS45 spectrofluorometer*** in the range from 200 to 900 nm, at room temperature. The excitation wavelength was 355 nm.

The third harmonic (355 nm) of Nd: YAG laser, with a pulse width of 11 ns, was used as the excitation source. The UV laser was focused by a quartz cylindrical lens of focal length of 5 cm. This was used to do transverse excitation of the PDHF solution taken in a four-side polished quartz cell, which was kept canted to avoid feedback as shown in Fig. 2. At optimum values of the pump power and concentration of PDHF, we could achieve an amplified spontaneous emission (ASE) beam coming out as a cone of light. This was collected by a 1-mm entrance slit of an ICCD camera, to obtain the spectral features of the ASE.

3. Results and discussions

3.1. Spectral properties of PDHF

The absorption spectra of polymer Poly [9, 9-di-(2′-ethylhexyl) fluorenyl-2, 7-diyl] (PDHF) in THF at room temperature for

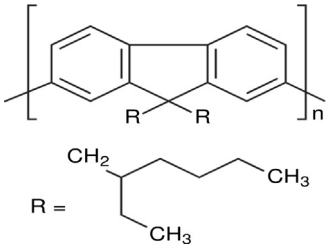

Fig. 1. Molecular structures of polymer of PDHF.

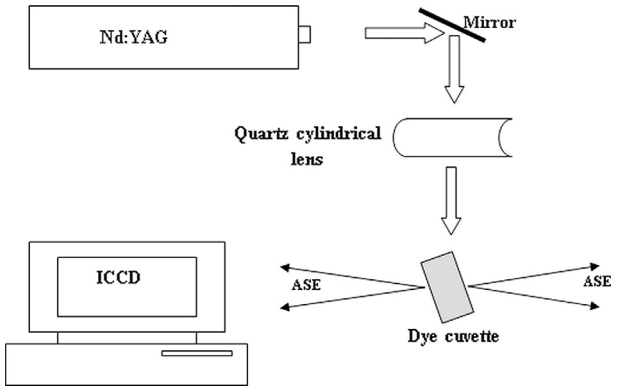

Fig. 2. Experimental arrangement for transverse excitation of the PDHF in solution.

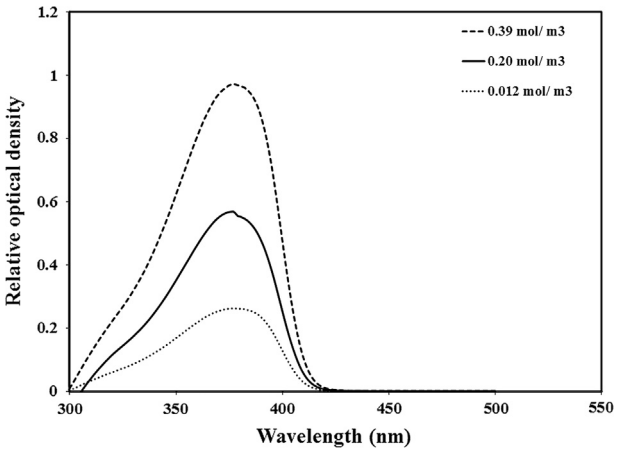

Fig. 3. Absorption spectra of PDHF in THF at different concentrations.

different concentrations from 0.012 mol/m^3 to 0.39 mol/m^3 were recorded. Fig. 3 shows that there is only one absorption band in the UV region around 380 nm. The shape of the absorption spectra remained the same, although optical density increases as the concentration is increased. This indicates the absence of any dimer (aggregation) in the ground state over all of concentrations used. PDHF was dissolved in various organic solvents with different concentration (0.012 mol/m^3 to 0.39 mol/m^3). It was found that the shape of the absorption spectra remained the same with a small peak shift due to the polarity of the solvent. Note that the optical density was not to the scale.

The fluorescence spectra of PDHF in THF at concentration 0.012 mol/m^3 were recorded for two different excitation wavelengths: 355 nm and 380 nm. The results showed for each excitation wavelength, there were two peaks of the fluorescence; one at 415 nm and the other at 435 nm and the peak at 415 nm had higher intensity than the peak at 435 nm. It can be seen that the shape of the fluorescence spectra did not change for either of the excitation wavelengths indicating that there is only one type of emitting species for PDHF in THF at low concentrations, as shown in Fig. 4.

The solvents influence upon the spectral properties is the Stokes′ shift, which is a measure of changes in the dipole movement of the species when it goes from the ground state to the excited state.

PDHF was dissolved in various organic solvents that have different dielectric constants with a fixed concentration of 0.012 mol/m^3. We observed very small changes in the absorption and fluorescence spectra (the fluorescence spectra were recorded at the excitation wavelength of 355 nm), the only difference being a small shift in the peaks of the absorption and the fluorescence wavelengths. Fig. 5 gives the variation of the Stokes′ shift as a function of the dipole factor of the solvent, as defined by Metaga and Tsuno. [17]. It can be seen that PDHF in solution undergoes significant changes in the electron delocalization and becomes more polar in the excited state than in the ground state. The Stokes, shift has a linear variation with the dipole factor, given within square brackets in the expression:

$$\nu_a - \nu_f \approx \left[\frac{(\varepsilon-1)}{(2\varepsilon+1)} - \frac{(n^2-1)}{(2n^2+1)}\right] \frac{(\mu_e-\mu_g)^2}{a^3 hc} \tag{3.1a}$$

Dipole factor

$$D_f = \left[\frac{(\varepsilon-1)}{(2\varepsilon+1)} - \frac{(n^2-1)}{(2n^2+1)}\right] \tag{3.1b}$$

Here ν_a and ν_f are the absorption and fluorescence peaks in wave numbers, ε is the dielectric constant and $\boldsymbol{n}$ is the refractive index

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