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Incident Laser Power and Concentration Effects on the Fluorescence of DCM Dye in PMMA Polymer

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Abstract: Incident laser power and concentration effects on fluorescence emission from DCM dye in PMMA polymer have been investigated. Different concentrations of the dye were used. It was found that the fluorescence intensity increased with increasing of the concentration of the dye, with a red shift. In addition, it was found that the fluorescence intensity increased with the increase of the incident laser power I_0.

Introduction

From the mid 60s, dye lasers were attractive sources of coherent tunable radiation because of their unique operational flexibility. The salient features of dye lasers are their tunability, with emission from near ultraviolet to the near infrared. Dyes have been demonstrated to lase in the solid, liquid and gas phases. From the early days of development of dye lasers, attempts were made to overcome the problems posed by dye solutions, by incorporating dye molecules into solid matrices [1].

Solid-state dye lasers, consisting of an organic dye dissolved in a solid matrix, have been the subject of much interest nearly four decades ago. The dyes, most commonly dissolved in sol gels or polymers. Solid-state dye lasers offer practical advantages such as compactness as well as alleviating some disadvantages associated with the flammable and volatile organic solvents used in liquid dye lasers. One way to form solid-state polymerization, often with additives to increase the solubility of the dye in the monomer or to improve the stability or physical properties of the final product [2]. The first observations of stimulated emission from solid matrices doped with organic dyes were reported as early as 1967 and 1968 by Soffer and McFarland [1] and Peterson and Snavely [3], respectively. Since laser dyes were in most cases merely dispersed, the results were not very encouraging due to the low lasing efficiencies and fast dye photo degradation. In recent years, the synthesis of high performance dyes and the implementation of new ways of incorporating the organic molecules into the solid matrix have resulted in significant advances towards the development of practical tunable solid-state lasers [4].

The use of a synthetic polymer host presents advantages as these materials show much better compatibility with organic laser dyes and is amenable to inexpensive fabrication techniques [5]. These polymers provide an opportunity for the production of active elements that can effectively control the characteristics of laser radiation. Hence, adequate knowledge of thermal and optical properties of dye-doped polymers is important in identifying suitable laser media.

Concentration effect on fluorescence of Rhoda mine B (RB) Rhoda mine 6G (R6G) have been studied by Binddhu and Harilal [6] and Kurian et al. [7] respectively. Effect of concentration on the lifetime and emission spectra of some dyes like R6G and RB and Com 102 have been studied by Al-Khafahji [8]. In the present work, the effects of concentration and incident laser power on fluorescence emission of DCM dye have been investigated.

Materials and Methods

The materials used were: DCM dye (4-dicyanomethylene-2-methyl-6-p-dimethylamin-ostyryl-4-4H-pyran, (LC 6500), spectroscopic standard, supplied from Lambda physiks, MMA (methylmethacrylate), (Fluka & Buchs, Switzerland), and methyl chloroform (Philip Harris, England).

Two kinds of solutions were prepared: The first using methanol as solvent with primary concentrations of DCM dye between 10^{-3}-10^{-5} M. The second using a mixture of MMA and methyl chloroform in ratio (1:1) (to form PMMA polymer later), and then adding the first solution to this mixture with different percentages (20%, 40%, and 60% by volume). The final concentrations of the mixtures were determined by multiplying the corresponding primary concentrations by the mixing ratios (e.g. 0.20, 0.40, and 0.60). The solutions were pour in identical cylindrical cells, 22 mm in diameter and kept under normal laboratory condition in dark room to avoid photo degradation of the dye.

During fluorescence measurements the cells were put in identical positions in front the entrance slit of the analyzing monochrometer (Fig.1). Fluorescence spectra of the DCM dye in PMMA polymer have been recorded through a designed spectrofluormeter using a diode pumped solid state CW green laser of 531 nm and 10mW power as a light source. The samples' emission spectra were detected through a Jarrell Ash monochrometer model 82-000, which operates in wavelength range from 190 nm to 910 nm with resolution 2 nm in the first order. The instrument has 0.5 meter focal length, with eight speed electric drive, plane reflection grating of 1180 groove/mm.

The detection unit was a photomultiplier PMT (type S666 Hamamatsa) which was connected to an X-Y recorder (Siemens)to detect the output signal .The power of the exciting laser light was reduced from 10mW to 8.7 mW and 3.2 mW using natural density filters. Fig. (1) shows the layout of the experimental setup.

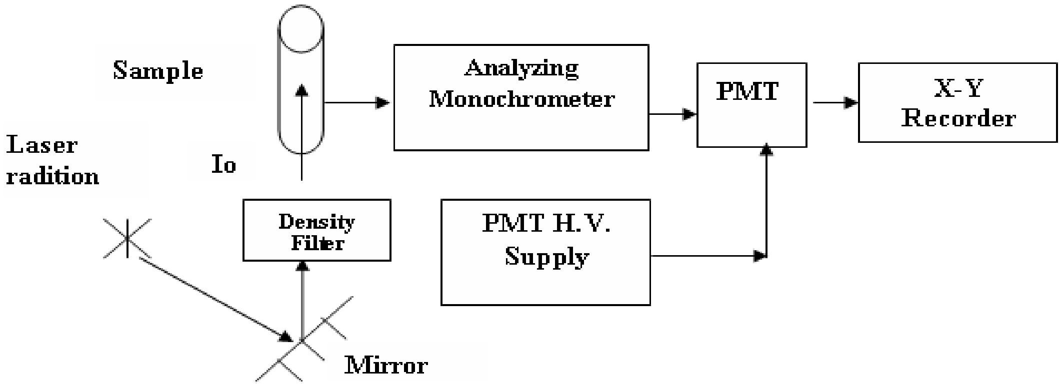

Fig. (1): Schematic diagram of fluorescence spectra system.

Results and Discussion

The measured fluorescence spectra of the solid samples of DCM dye in PMMA polymer with different primary concentrations, mixing ratios, and incident laser powers are shown in Figs. (2-4).

It has been found that fluorescence intensity of DCM dye increases with the increase of the incident laser power. Typical example is shown in Fig. (5), for 10^{-5}M-10^{-3}M primary concentrations and 20% mixing ratio of the dye in the polymer. This can be explained as follows:

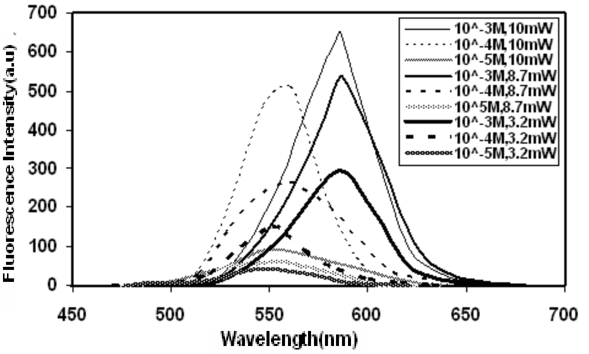

Fig. (2): Fluorescence intensity vs. wavelength of DCM dye in PMMA polymer of 20% mixture ratio using different primary concentrations and incident laser powers.

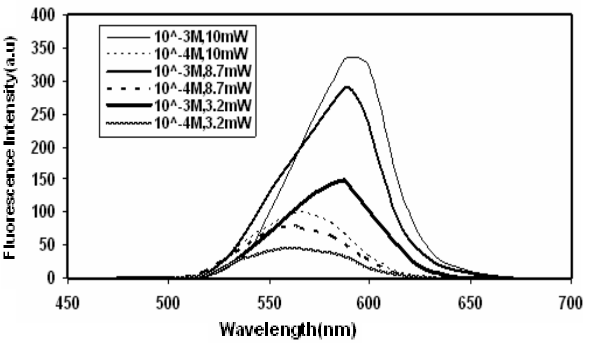

Fig. (3): Fluorescence intensity vs. wavelength DCM the dye solution in PMMA polymer of 40% mixture using different primary concentrations and incident laser power.

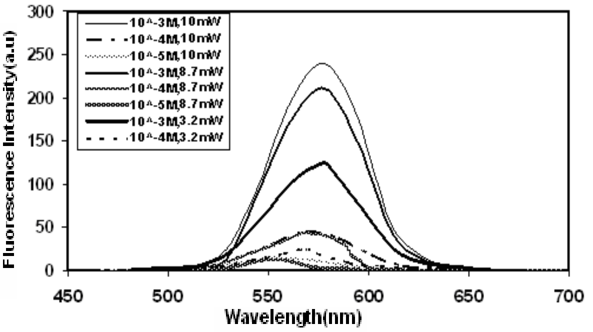

Fig. (4): Fluorescence intensity vs. wavelength of DCM dye solution in PMMA polymer mixture using different primary concentrations and incident laser powers.

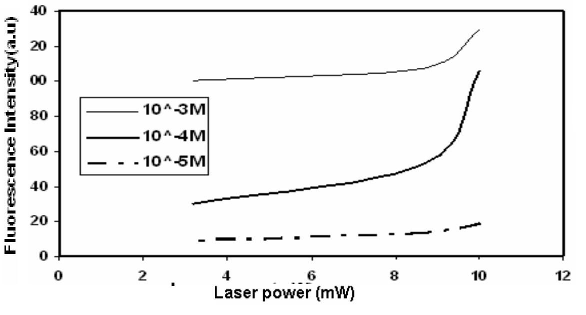

Fig. (5): Peak fluorescence intensity vs. incident laser power (I_0) of DCM Dye in PMMA polymer of 20% mixture ratio using different primary concentrations.

The fluorescence intensity (I_F) is proportional to the fluorescence quantum efficiency (q_F) and the absorbed light intensity (I_A), namely [9]

$$I_F= q_F\, I_A \qquad (1)$$

From Beer-Lambert law, I_A is proportional to the incident light intensity (I_0), and given by

$$I_A= I_0(1-10^{-\varepsilon\, c\, d)} \qquad (2)$$

where ε is the extinction coefficient, c is the concentration, and d is the sample thickness. Hence,

$$I_F = q_F\, I_0(1-10^{-\varepsilon\, c\, d)} \qquad (3)$$

As can be seen from Eq. (3), that I_F increases linearly with I_0 when other quantities are fixed, which is clear from Fig. (5).

From these figures, we notice that fluorescence intensity increases with the increasing of the concentration. This behavior is shown in Fig. (6), where the peak fluorescence intensity is plotted against the concentration.

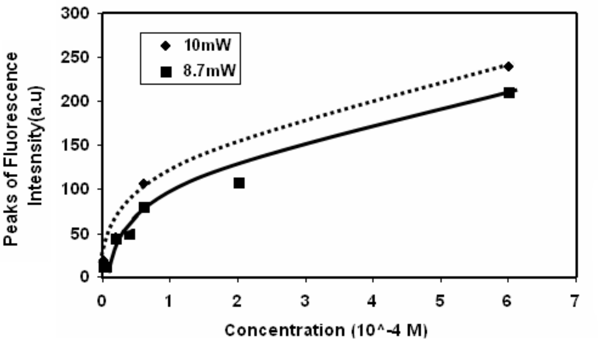

Fig. (6): Peak fluorescence intensity vs. the concentration of DCM in PMMA, using 10 mW and 8.7 mW incident laser powers.

The increase of fluorescence intensity with the increase of concentration is expected from Eq. (3) in the absence of other competing processes. We noticed a red shift of the fluorescence spectra, which increases as the concentration of DCM dye increases. This red shift of the fluorescence spectra may be attributed to self-absorption.

When the fluorescence spectra were measured for DCM dye in methanol using different concentrations (first solution), it has found that at low concentrations, the fluorescence intensity increases with the increase of the dye concentration. But at higher concentrations the intensity reaches a limiting maximum value, and then decreases with further increase of the concentration. This behavior is illustrated in Fig. (7).

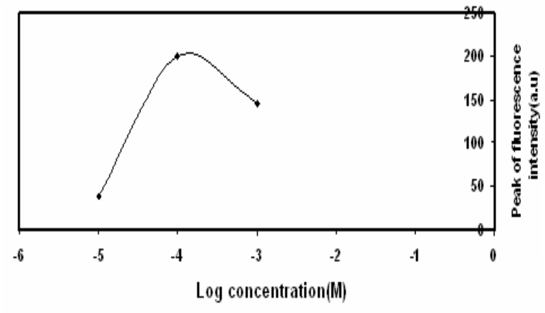

Fig. 7: Concentration effects on the fluorescence intensity of DCM dye in methanol.

The dependence of the fluorescence intensity, I_F, on the concentration, in liquid methanol, may be explained as follows: at low concentrations, where the bimolecular competing processes are negligible, the fluorescence intensity, I_F, increases as the concentration, c, increases. This is clear from Eq. (3) (keeping other factors fixed, e.g., I_0, ε and d). But at higher concentrations, the bimolecular competing processes to the molecular fluorescence, such as self-absorption (re-absorption and re-emission of emitted fluorescent photons), and dimmer (and possibly higher aggregates) formation of the dye molecules, play more important rule. This will ultimately reduce the fluorescence emission. Hence the formation of dimmers and higher aggregates, and the resulting decrease of fluorescence intensity, put an upper limit to the concentration used. A red shift was also observed, which increases as the concentration of DCM dye increases. This red shift can be attributed to the self-absorption which modifies the observed (technical) fluorescence spectrum by reducing the intensity of the short wavelength region of the spectrum (due to overlap with the absorption spectrum) and enhancing the intensity of the long wavelength region [9,10]. One can see from Figs. (6) and (7) that the fluorescence intensity of DCM in PMMA increases monotonically with the increase of the concentration(up to 6×10^{-4}M), while the fluorescence intensity decreases for concentration above 10^{-4}M in methanol. This may be attributed to the caging effect of the solid PMMA on the DCM molecules, which hinder the dimmer and higher aggregates formation.

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تأثيرات قدرة الليزر والتركيز على تألق صبغة DCM في بوليمر البولي مثيل ميثا أكرليت

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الخلاصة

تمت دراسة تاثيرات قدرة الليزر والتركيز على انبعاث التألق من صبغة DCM في بوليمر البولي مثيل ميثا أكرليت . استخدمت تراكيز مختلفة من الصبغة ووجد ان شدة التألق تزداد بزيادة تركيز الصبغة مع ظهور أزاحة حمراء ، كما تزداد مع زيادة قدرة الليزر الساقط .