SPECTRAL AND ASE PROPERTIES OF AN AMINO CHALCONE 1-(4-CHLOROPHENYL)-3-(4- N, N DIMETHYLAMINO PHENYL)-2-PROPEN-1-ONE

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Photophysical characteristics such as absorption, fluorescence spectra, stokes' shift, fluorescence quantum yield and amplified spontaneous emission (ASE) of a new chalcone laser dye material 1-(4-chlorophenyl)-3-(4- N, N dimethylamino phenyl)-2-propen-1-one (CPDAPP) were measured in different solvents and concentrations. Here, the ASE spectra of CPDAPP in acetone have been obtained using a transverse cavity configuration where the conjugated CPDAPP was pumped by laser pulses from the third harmonic of Nd: YAG laser (355 nm). The CPDAPP in acetone produces high intense ASE. The obtained results were compared with the 3-(4-(dimethylamino) phenyl)-1-phenyl-(2E)-propen-1-one (DMAPPP) under identical operational conditions.

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1. Introduction

Light-emitting organic materials are wieldy used in various field of science, medicine, and technology. Additionally, it has applications in printable electronics, such as conducting composites, and chemical sensor research [1]. There are a few kinds of laser are known; nevertheless most of them are expensive such as neodymium glass, ytterbium-doped glass and Cerium doped lithium [2]. On the other hand, dye lasing material, such as rhodamine and coumarin; have a disadvantage described in low lasing efficiency and fast photo-degradation [3-5]. Among the light emitting materials, organic compounds and their derivatives have newly fascinated many researcher owing to their unique optical homogeneity, easy to synthesis and design, costless, capability of light emission and the smoothness to govern their structure and fabrication management allow familiarizing controlled changes in development their properties. The interest in light-emitting organic materials as a new optical material has started before two decades by the scientist [6-10].

Although significant efforts were devoted to improve the performance and efficiency of light-emitting organic lasing materials; however, there are little information about laser damage threshold and photo-degradation of organic materials is still remaining as a challenge for many researchers [11-15]. The light-emitting organic lasing materials, which are going to be studied, are not investigated up to date [12]. The light emitting organic lasing materials under consideration

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have broad UV spectra, providing scope for making tunable lasers and high absorption coefficients, which means a greater possibility of achieving light amplification. According to the chemical structure of these organic materials under investigation, such materials are expected to produce tunable laser owing to their unique and excellent chemical and physical properties. The current study intended to fabricate new light emitting organic materials with noble future to address the problem associated with laser damage threshold and photo-degradation.

In the present study the photophysical characteristics and amplified spontaneous emission (ASE) behaviors of 1-(4-chlorophenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (CPDAPP) in different solvents and concentrations are reported. The obtained results have been compared with a 3-(4-(dimethyl amino) phenyl)-1-phenyl-(2E)-propen-1-one (DMAPPP) which has shown a distinguished optical properties compared with the conventional laser dyes [unpublished data]. It was found that the ASE of DMAPPP is more efficient that CPDAPP in different solvents under same identical conditions.

2. Experimental details

Light-emitting organic material 1-(4-chlorophenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (CPDAPP) was fabricated via simple reaction between 4-dimethyl aminobenzaldahyde (0.01 mole) and 4-chloroacetophenpne (0.01 mole) in the presence of NaoH (1.0 gm) and alcohol (CH3CH2OH 50ml). The mixture was placed in the glass vessel and left for steering at room temperature overnight, afterward the product recrystallized from ethanol and washed with distilled water in order to achieve pure final product. Another organic Light-emitting material 3-(4-(dimethylamino)phenyl)-1-phenyl-(2E)-propen-1-one (DMAPPP) was synthesized using same method mentioned above by adding 0.01 mole of acetophenone with 0.01 mole of 4-dimethylaminobenzaldehyde in basic condition of sodium hydroxide (1.0 gm), in ethanol (50ml). The mixture was left overnight under steering at room temperature and then the yield was recrystallized from ethanol. The crystal was washed with distilled water and it had been left to dry [16]. The CPDAPP and DMAPPP were characterized by FTIR, H1NMR and UV-Vis spectroscopy.

CPDAPP and DMAPPP were dissolved in different organic solvents (spectroscopic grade with purity 99.8%). The molecular structure of CPDAPP and DMAPPP are given in Fig.1. The absorption and fluorescence spectra of CPDAPP in acetone were studied under a wide range of concentrations. The spectra for the solutions measured using a small quartz cuvette with the dimensions 1×1×4 cm with an optical path length of 1 cm.

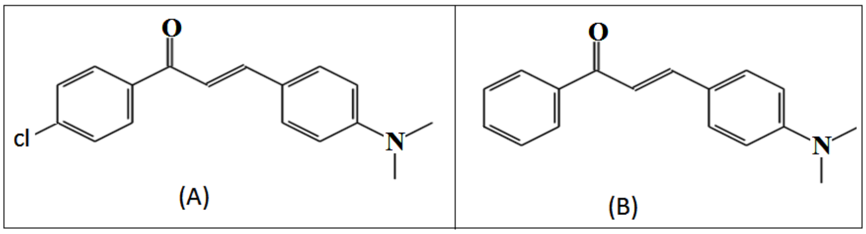

Fig.1. Molecular Structure of laser dyes (a) CPDAPP (b) DMAPPP

The absorption spectra were taken using a Perkin-Elmer lambda 590spectrophotometers over the range from 200 to 800 nm and the fluorescence spectra were recorded using a Perkin-Elmer LS55 Spectrofluorometer in the range from 200 to 900 nm, at room temperature. The excitation wavelength was 400 nm. The UV laser was focused by a quartz plano-cylindrical lens with a focal length of 5 cm. This was used to perform transverse excitation of the CPDAPP solution taken in a four-sided polished quartz cell, which was kept canted to avoid feedback [17]. Under optimum values of the pump power and concentrations of CPDAPP, the amplified spontaneous emission (ASE) was observed, 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 the spectral features of the amplified spontaneous emission as shown in Fig.2. To avoid saturation of CCD, we had used neutral density filters, as and when required. The ASE of the CPDAPP in solution was compared to that of DMAPPP. It is important to note that these measurements were done under identical experimental conditions: only the dye cells were changed.

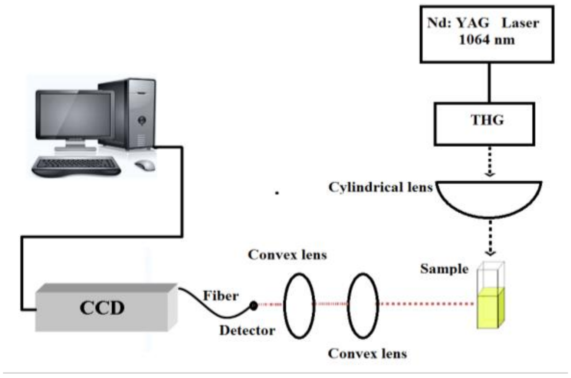

Fig. 2. Experimental arrangement for transverse excitation of CPDAPP and DMAPPP in solution

3. Result and discussion

3.1 Spectral properties of CPDAPP

The optical properties such as absorption and fluorescence of CPDAPP in acetone with different concentrations from 0.65 to 6.5mM were recorded. The absorption spectra showed only one peak at 420 nm. When the concentration was increased, there was no new absorption peak detected in the longer wavelength region. However, the optical density of the peak 420 nm increased monotonically with concentration. On the other hand, the fluorescence spectra of CPDAPP in acetone, for the same concentrations mentioned above, were recorded. The results showed only one peak at535 nm, the spectra profile did not change irrespective of concentration for this dye. Moreover, the intensity decreased with an increasing the concentration as shown in Fig.3.

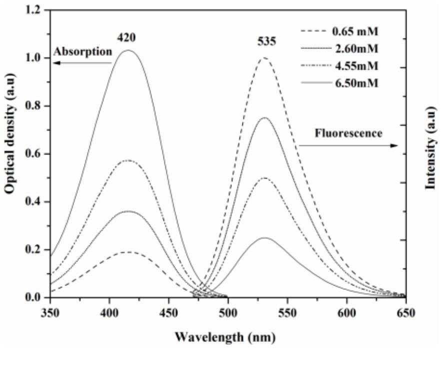

Fig.3.Absorption and fluorescence spectra of CPDAPP in acetone for different concentrations

The results obtained were compared with the spectral properties of DMAPPP. Fig.4 shows the absorption and fluorescence spectra of DMAPPP in acetone for different concentrations (as mentioned above). It showed an absorption band at 405 nm. By increasing the concentration, there was no new absorption peak observed, whereas, the fluorescence spectra of DMAPPP in acetone under an excitation wavelength of 355 nm for different concentrations were obtained as shown in Fig.4. The fluorescence spectra had one band, at 525nm.

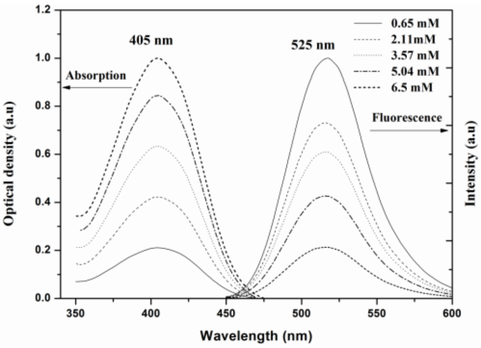

Fig. 4. Absorption and fluorescence spectra of DMAPPP in acetone for different concentrations

The difference between CPDAPP and DMAPPP in their chemical structures is a chlorine group attached to para-position to ring A, the chlorine is acting as electron acceptor. The addition of chlorine group to DMAPPP dye leads to increase the fluorescence wavelength by 20 nm to red shift, whereas the absorption peak shifted by 15 nm to the red.

3.2 Stokes' shift

CPDAPP was dissolved in various organic solvents that have different dielectric constants. The concentration was kept at 0.65mM. It was observed that there are very small changes in the absorption and fluorescence spectra, the only difference being a small shift in the peaks of the absorption and the fluorescence wavelengths. The Stokes’ shift has a linear variation with the dipole factor [18].

Fig.5 shows a plot of the Stokes’ shift as a function of dipole factor for representative solvents, as defined by Metaga [19]. This dipole factor is a measure of dipole-dipole interaction between the solvents and the solute. It could be seen that CPDAPP is slightly less polar than DMAPPP. These results indicate that all of these dyes exhibit large changes in the dipole moment in the excited state.

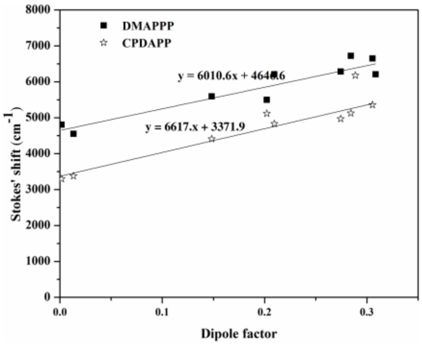

Fig. 5. Variation in the Stokes’ shift of CPDAPP and DMAPPP in solution with a dipole factor for different solvents

3.3 Quantum yield of fluorescence

Rhodamine 6G (Rh 6G) in methanol has a known fluorescence quantum yield (ΦF) of 0.94. Rh 6G in methanol at a concentration of 0.65mM of was taken as the standard for measurement of quantum yields for CPDAPP in different solvents. The quantum yield can be measured using known equation [20,21].

The fluorescence spectra of CPDAPP in different organic solvents were recorded. The concentration was kept at 0.65mM. The fluorescence spectra were recorded at the excitation wavelength of 355 nm. The quantum yield of these solutions was calculated as seen in the table.1

(a &b).The results obtained was compared with the quantum yield of DMAPPP. The results showed that the quantum yield depends on the solvent and the chemical structure of the dye.

Table.1: The spectral and ASE properties of and CPDAPP in different solvents

Solvent	Dielectric constant (ε)	CPDAPP λ_{max}			ϕ_F
		Absorption	Fluorescence	ASE	
Benzene	2.27	420	487.5	----	0.13
Toluene	2.38	413	480	----	0.11
Chloroform	4.81	424	521.5	----	0.89
Acetic acid	6.15	429	520.5	----	0.20
Tetrahydrofuran	7.58	413	516	538	0.86
Acetone	20.7	418	532	547	0.66
Ethanol	24.5	425		----	0.44
Methanol	32.7	427		----	0.22
Dimethylformamide	36.7	427	541.5	566	0.96
Acetonitrile	37.5	417	538	563	0.40

3.4 Amplified spontaneous emission (ASE)

To study the ASE properties of CPDAPP under high power laser excitation; DMAPMPP was dissolved in acetone, the concentration fixed at 1 mM. This solution was transversely excited with a UV laser at 355 nm. At a pump power of 3 mJ, the ASE spectrum was recorded. Note that this was the minimum concentration and the minimum pump power excitation for CPDAPP to produce an ASE spectrum at 550 nm with a full width at half maximum (FWHM) of 6 nm as shown in Fig.6 (a). At higher concentrations, under identical operational conditions, the ASE spectrum did not change. Note the one-to- one correspondence between the steady-state fluorescence shown in Fig.2 and the ASE spectrum, also shown in Fig.6 (b).The results obtained were compared with that DMAPPP under the same operating conditions. It was found that the ASE of CPDAPP in acetone was shifted 20 nm to the red region with regard to DMAPPP. This could be due the effect of the chlorine group of CPDAPP.

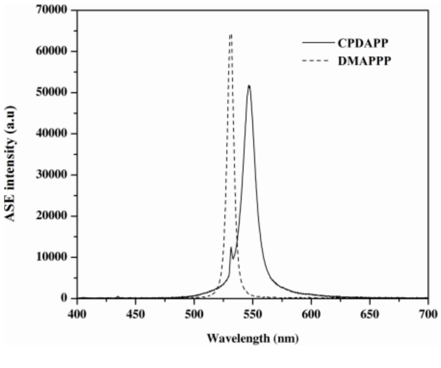

Fig. 6. ASE spectra of CPDAPP and DMAPPP in acetone eat a concentration of 1mM

The ASE spectra of CPDAPP and DMAPPP dissolved in different solvents under identical conditions; the concentration and pump power were kept at 6.5mM and 9 mJ for each solution, respectively. The ASE in acetic acid, methanol, benzene and toluene was not detected even at high pump power energy and concentration. In toluene and benzene this may be due to the lowest solubility of the CPDAPP and DMAPPP. The absence of the ASE spectra in acetic acid could be attributed to the protonation of N-dimethylamino group of CPDAPP and DMAPPP with responsible for their photo properties. For CPDAPP and DMAPPP in methanol, the ASE was not observed. This may be the solvent plays similar role by deactivation of the lone pair of N-dimethylamino group by hydrogen bonding. On the other hand, CPDAPP in chloroform the ASE was not noted nevertheless DMAPPP in chloroform gives highly intense ASE, this refers to the chlorine group in CPDAPP.

Fig.6 shows the variation in the ASE intensities of CPDAPP and DMAPMPP in DMF was studied in different concentrations from 2 to 6mM. The pump power was fixed at 9 mJ. It was found that, when the concentration increased, the ASE intensity decrease. However, ASE did not reach saturation even at high concentrations.

Fig.7 shows the comparison of the ASE intensity of CPDAPP and DMAPPP in DMF. The concentration was kept at 6mM for each dye; and the pump power was taken from 3 to 15 mJ. It was found that as the pump power was increased, the ASE intensity of CPDAPP and DMAPPP increases.

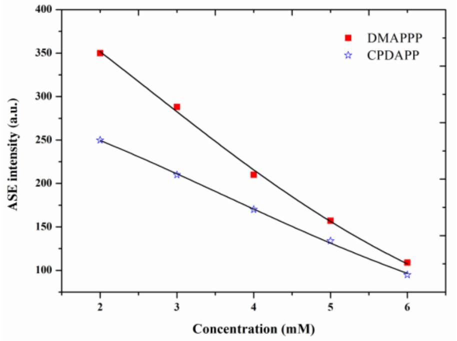

Fig. 7. ASE intensities of CPDAPP and DMAPPP in THF as a function of the concentration

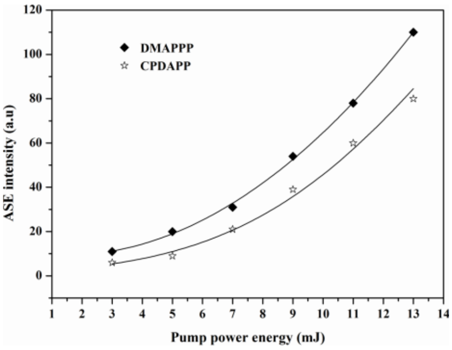

Fig. 8. ASE intensities of CPDAPP and DMAPPP in THF as a function of pulse energy at a concentration of 6 mM

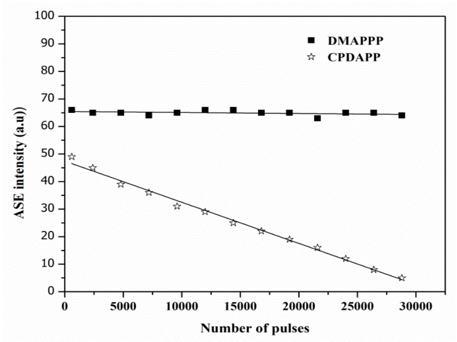

Fig. 9. The photochemical stability of CPDAPP and DMAPPP in DMF at a concentration of 6mM

The photochemical stability of the CPDAPP in DMF at a concentration of 6.5mM was compared to that of DMAPPP in DMF at 6.5mM. These solutions were pumped by the third harmonic (355 nm) of Nd: YAG with pulse energy of 6 mJ and a repetition rate of 1 HZ. After 3×103 pulses, the DMAPPP ASE intensity unchanged whereas, CPDAPP dropped to 50% of its initial intensities after 150×102 pulses. Note that the solutions were never circulated or stirred to simulate the condition of a solid-state laser.

5. Conclusions

The ASE behaviors of CPDAPP and DMAPPP were studied under the influence of solvent environments and laser power excitation levels. Quantum yield, stokes' shift and ASE have been studied. The study reveals that such kinds of compounds (amino chalcones) will be promising as laser materials in the future.

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