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Amplified Spontaneous Emission (ASE) Properties of a laser dye (LD-473) in solid state

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Abstract

The spectral characteristics of 1,2,3,8-tetrahydro-1,2,3,3,8-pentamethyl-5-(trifluoromethyl)-7H-pyrrolo[3,2-g]quinolin-7-one (LD-473) were demonstrated in liquid and solid states. For the liquid state, the absorption and fluorescence spectra of the LD-473 in Methyl Methacrylate showed bands at 385 and 420 nm, respectively. LD-473 in the solid state showed one absorption band at 530 nm, while the fluorescence spectra, under low concentration, showed one band at 615 nm. For higher concentrations, the fluorescence bands are shifted to the red. LD-473 in the solid state under an impulse of Nd: YAG laser showed dual amplified spontaneous emission (ASE) peaks at 605 and 650 nm. The longer wavelength coincided with a fluorescence peak while the shorter wavelength is an abnormal peak.

Keywords: Dye LD-473, Spectral properties, ASE, Solid state

Introduction

LD-473 is a type of laser dyes usually used to produce lasers light in the visible and infrared region of the spectrum [1–4]. When organic dyes like coumarins or rhodamines series dissolved in organic solvents and optically excited by laser source, the dye molecules strongly absorb the incident photons and emit high intense laser due to population inversion [5–8]. If the population inversion is very high, the optical gain should be so high and more enough to produce amplified spontaneous emission (ASE). ASE is a mirrorless laser without feedback, and is totally dependent on the active medium, as in coumarin and rhodamine laser dyes. However, any medium produced an ASE, has an ability to exhibit laser, although the reverse is not true [5, 9, 10]. Number of researches was done on rhodamine dye-doped polymers [8, 11–13]. A meager works have been done on blue green emitting solid-state dye lasers. The main purpose of this paper is to give an insight about the photo-physical properties of a LD-473 in solution. Previously,

we had been tried to observe this phenomenon in some other laser coumarin dyes in solutions. All these coumarin dyes exhibited superexciplex formation under suitable concentrations and pump pulse energies. In this work, the spectral and ASE properties of LD-473 in solution and solid states were investigated. The absorption, fluorescence and ASE properties of LD-473 in solution and solid states depended on the concentrations, solvent environments and pump pulse energies. When the pump pulses excitation (Nd: YAG laser of 355 or 532 nm) and the concentrations were suitably chosen, LD-473 showed an ASE around 475 nm; while LD-473 in PMMA exhibited dual ASE peaks at 605 and 640 nm, respectively.

Experimental

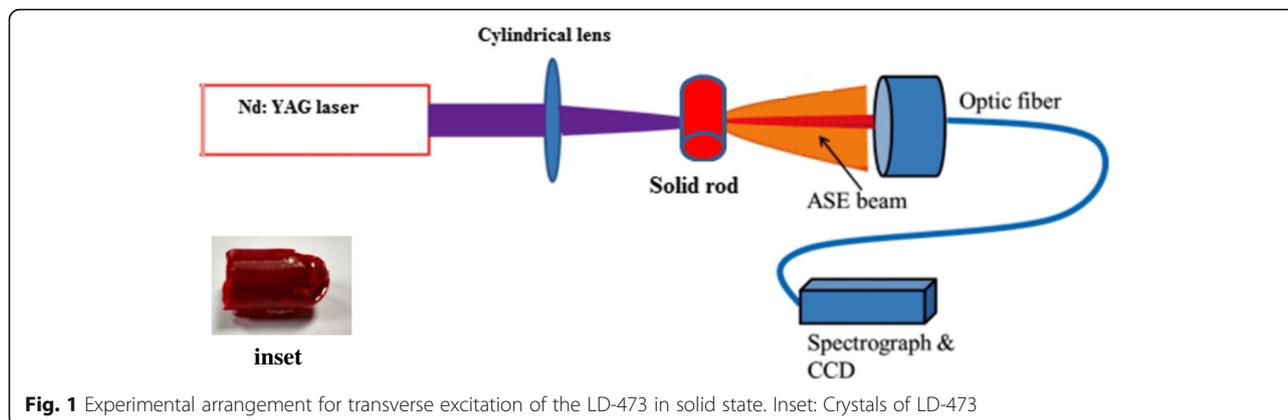
Methyl Methacrylate (MMA) and 2-hydroxyethyl methyl methacrylate (HMMA), dibenzoyl peroxide was obtained from Sigma-Aldrich and LD-473 from the *Exciton* Company was used in this work [14]. Solid-state rods with 7.0×10^{-3} , 4.5×10^{-3} and 1.8×10^{-3} M LD-473 were prepared by adding the exact masses of dye to 1:1 MMA to HMMA ratio. About 500 mg of the initiator was then added and the mixture was stirred at 50 °C for 15 min. The mixture was finally poured into a test tube of 1 cm

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diameter and left for 2 days at room temperature. A bright red solid was formed (inset Fig. 1).

The absorption spectra were recorded for solid and liquid phases using a Perkin-Elmer lambda 950 spectrophotometer over the range from 100 to 1100 nm. The solid samples in a form of solid rods were prepared under same dimensions and different concentrations, and the fluorescence spectra were recorded using a Perkin Elmer LS 55 spectrofluorometer which has a scan range of 200 to 1000 nm, at room temperature. The excitation wavelengths were 355 and 532 nm.

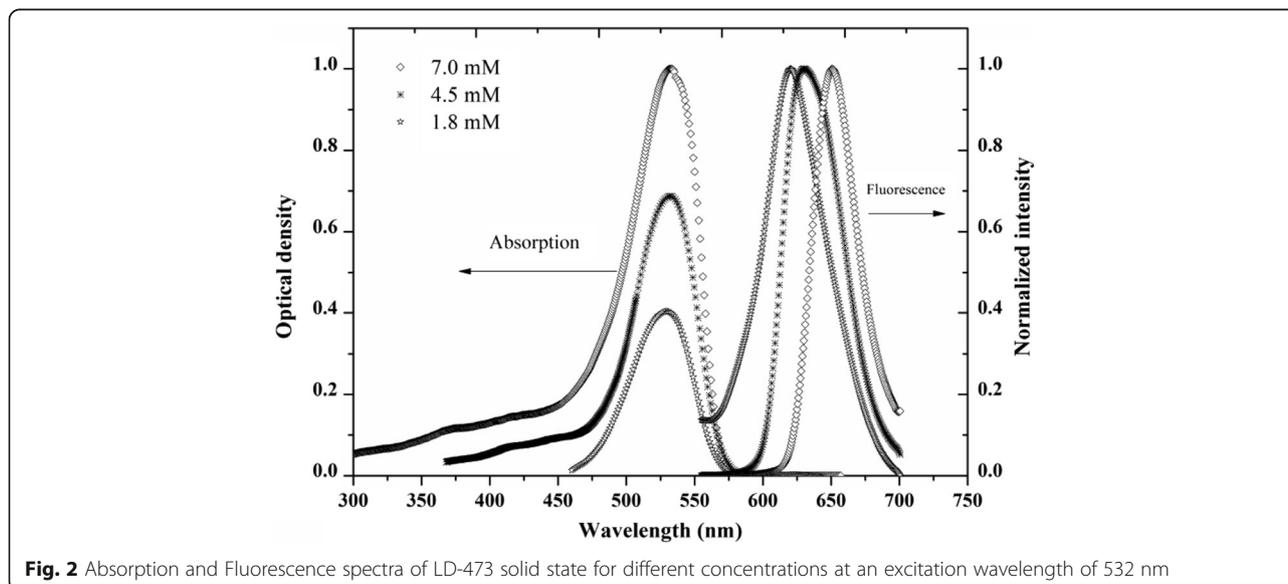
The ASE action was obtained by optically pumping the samples with an Nd: YAG laser emitting pulses at 355 and 532 nm with a 6 ns duration and 10 Hz repetition rate. A quartz cylindrical lens of focal length of 5 cm was used to focus the laser light beam. The focused pulse was transversely applied to excite the solid and liquid samples (Fig. 1). The cuvette was kept tilted for LD-473 in liquid state to avoid feedback [15, 16]. At a

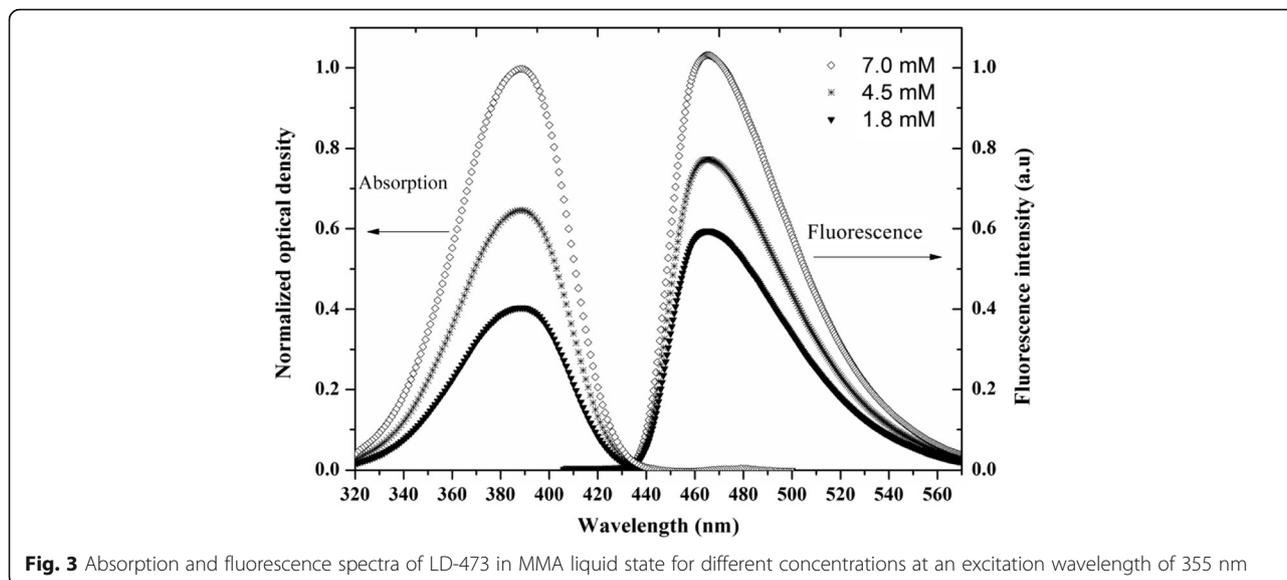
suitable pump power, we could achieve an ASE beam which excited as a cone-shaped light. The emanated light was collected by a 1-mm entrance slit of a spectrograph connected with a CCD camera to obtain the spectral features of the ASE.

Results and discussions:

Spectral properties of LD-473

The absorption spectra of LD-473 in solid state were recorded, with the dye concentrations from 1.8 to 7 mM. The absorption spectra showed only one band at 530 nm as shown in Fig. 2. On the other hand, the fluorescence spectrum of LD-473, at a concentration of 1.8 mM showed a fluorescence band at 615 nm. When the concentration increased, the fluorescence peak was red shifted. For example, at concentrations of 4.5 and 7 mM, the fluorescence bands were at 625 and 650 nm, respectively as illustrated in Fig. 2. At concentrations higher than 7 mM, there was no significant *red shift* observed.





Before the solidification, LD-473 in methyl methacrylate (MMA) was prepared. Figure 3 shows the absorption and fluorescence spectra of LD-473 for concentrations range from 1.8 to 7 mM. It was found that LD-473 has only one absorption band at 385 nm. On the other hand, the fluorescence spectra of LD-473 in MMA for all concentrations mentioned above showed only one band at 465 nm without changes in the shape of the fluorescence spectra.

Fluorescence quantum yield

The absorption and fluorescence spectra of LD-473 in different organic solvents were recorded. The fluorescence quantum yield (Φ_f) was measured using diluted solutions (1.8 mM) to avoid reabsorption effect. The fluorescence quantum yield (Φ_f) was calculated using the Eq. (1) [17]. It was found that the fluorescence quantum yield (Φ_f) around 0.72.

$$\Phi_f(s) = \Phi_f(r) \frac{A_r n_s^2 \int F_s(\bar{\nu}) d\bar{\nu}}{A_s n_r^2 \int F_r(\bar{\nu}) d\bar{\nu}} \tag{1}$$

where the subscripts s and r refer to sample and reference; respectively, the integrals over F represent the area of the corrected fluorescence spectrum; A is the absorbance

value of the excitation wavelength; and “n” the refractive index of the solvent.

Table 1 shows the strong dependence of Φ_f on the absorption cross section (σ_a), stimulated emission cross section (σ_e), and extinction coefficient (ϵ_{max}) [18]

$$\sigma_e = \frac{\lambda^5 \Phi_f}{8\pi c n^2 \tau_f} \times \frac{I(\lambda)}{\int I(\lambda) d\lambda} \tag{2}$$

$$\sigma_a = 0.385 \times 10^{-20} \epsilon \tag{3}$$

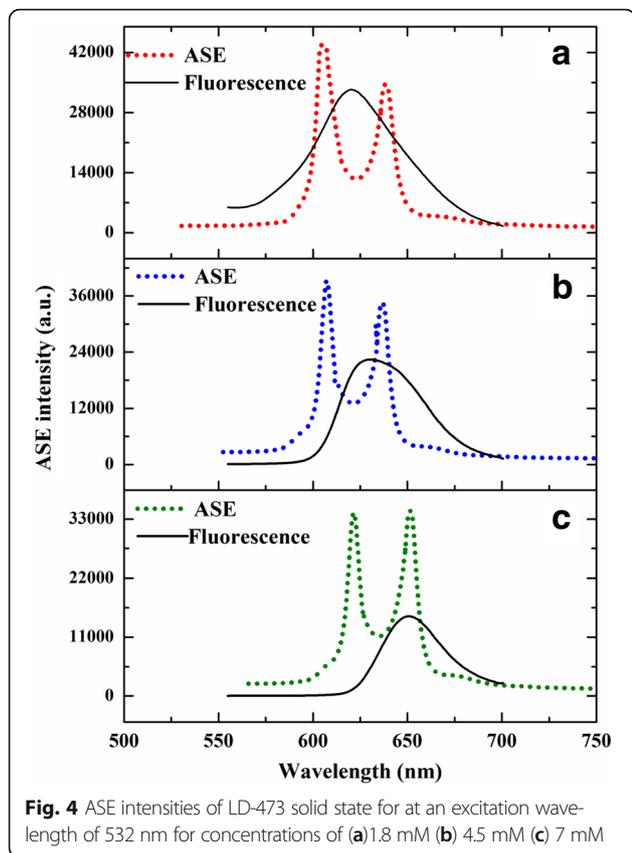
where λ is the wavelength, Φ_f is the quantum of the fluorescence, n is the index of refraction of the material, c is the speed of light in vacuum, τ is the fluorescent lifetime of the upper laser level, I(λ) is the fluorescent intensity at wavelength λ , and ϵ is an extinction coefficient.

ASE Spectrum of LD-473

1.8 mM of LD-473, as solid state rod, was transversely excited using an Nd: YAG laser pulses (532 nm) with sufficient energy of 6 mJ. Dual ASE peaks were observed in two narrow spectral regions; one at 605 nm, as a shorter wavelength (SW), and at 640 nm, as a longer wavelength peak (LW) as shown in Fig. 4a. The intensity ratio recorded between SW and LW was 4:3. By increasing the concentration

Table 1 The photophysical parameters; Fluorescence quantum yield (ϕ_f), extinction coefficient (ϵ), absorption cross section (σ_a), emission cross section (σ_e), fluorescence lifetime (τ_f), for LD-473 in different concentrations and matrixes

LD-473	Quantum Yield %	$\epsilon_{max} \times 10^5 (M.cm)^{-1}$	$\sigma_a \times 10^{-15} (cm^2)$	$\sigma_e \times 10^{-15} (cm^2)$	$\tau_f (ns)$
PMMA	59.57	3.67	1.41	1.37	5.6
MMA	71.94	5.56	2.14	2.07	4
Ethanol	93.3	22.22	8.55	5.44	3.5

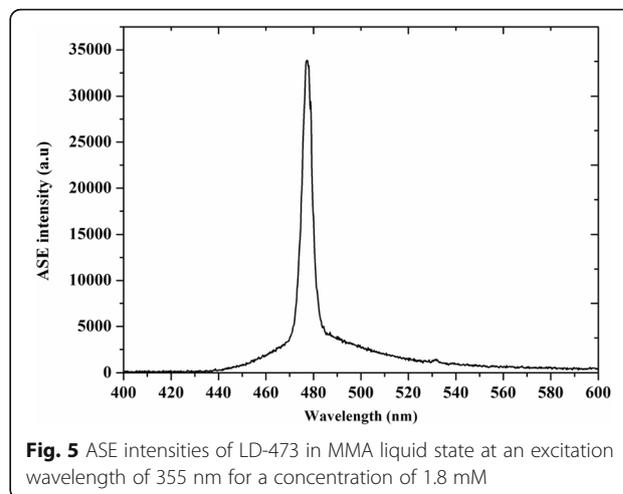


to 4.5 mM, the intensity ratio was changed to 4:3.6 (Fig. 4b). One can immediately observe a small red shift in the SW band. Further increase in the concentration to 7 mM; the ASE peaks were almost comparable as shown in Fig. 4c. Moreover, there was a large red shift observed for the SW and LW to 621 and 650 nm, respectively. It is important to note that corresponding to ASE around 650 nm, there is a fluorescence band around 650 nm, but there is no fluorescence band corresponding to ASE at 621 nm (see Figs. 4c and 2). It can be seen that, when the concentration was increased, the ASE intensity quenched due to the intermolecular interaction [19, 20] the ASE intensity was changed inversely with the concentration.

LD-473 in MMA at a concentration of 1.8 mM was studied under identical operating conditions. This was the minimum concentration for LD-473 to produce an ASE spectrum. Figure 5 shows an ASE peak around 475 nm. This peak is corresponding to the fluorescence band at 465 nm. For higher concentrations, there was no change in the ASE features (Table 2).

Here, the optical and laser properties of LD-473 showed a large red shift after solidification; while in the previous studies, no shift appears in the spectrum after solidification [5, 21, 22].

When 1.8 mM of LD-473 as solid state was excited by Nd: YAG laser pulse of 6 mJ pulse energy, it gives ASE



emission. The optical gain coefficient (γ) of LD-473 was calculated using measuring the intensity of ASE intensity for two lengths of excitation $l_1=1$ cm and $l_2 =0.5$ cm according to the following relation [23, 24]:

$$\gamma(\lambda) = \frac{2}{L} Ln\left(\frac{I_{l1}}{I_{l2}} - 1\right)$$

where, where L is the length of the irradiated dye in PMMA matrix rod, I_{l1} , and I_{l2} are the intensities of ASE at lengths of l_1 and l_2 , respectively.

Figure 6 illustrates the gain of LD-473 in solid state for different concentrations. For a length (L) of 10 mm, repetition rate of 10 Hz and pump pulse energy of 6 mJ, the gain (γ) was found to be concentration dependent where the optimum gain per unit length was 4.4 cm^{-1} for the concentration of 7 mM, 3.5 cm^{-1} for 4.5 mM and 2.8 cm^{-1} for 1.8 mM.

Conclusion

In this paper, the spectral characteristics of LD-473 in the liquid state showed only one fluorescence band in the blue region. After solidification, the optical and ASE spectra were totally changed. It could be seen that the

Table 2 The photophysical parameters; absorption peak (λ_a), fluorescence peak (λ_f) and wavelength max of laser emission (λ_l), for LD-473 in different concentrations and matrixes

LD-473	Concentration (mM)	λ_a (nm)	λ_f (nm)	λ_l (nm)		$\left(\frac{I_{sw}}{I_{lw}}\right)$
				SW	LW	
PMMA	1.8	530	615	605	640	1.33
	4.5	530	625	605	640	1.11
	7	530	650	605	640	1.00
MMA	1.8	408	465	471	---	---
Ethanol	1.8	390	440	473	---	---

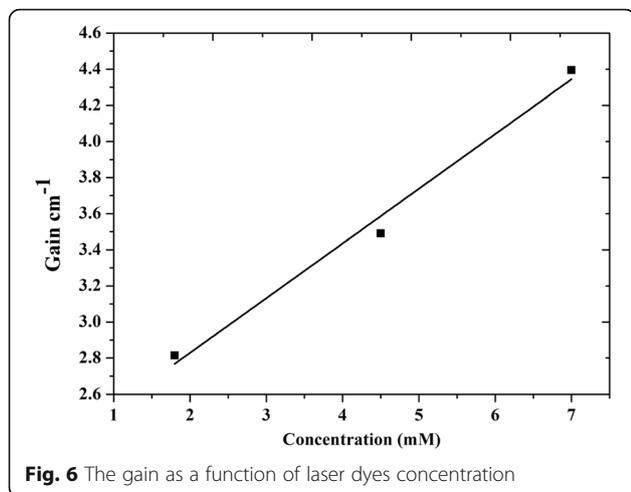


Fig. 6 The gain as a function of laser dyes concentration

whole spectrum was shifted to the red by 180 nm. Moreover, anomalous ASE band at 605 nm was observed. The ASE band at 650 nm coincides with fluorescence at steady state, while the ASE band at 605 nm is an abnormal peak.

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Availability of data and materials

None.

Authors' contributions

K.K. Taha and K.H. Ibnaouf designed the experiments; K.K. Taha, Hajo Idriss and K.H. Ibnaouf performed the experiments; K.H. Ibnaouf and K.K. Taha analyzed the data; K.H. Ibnaouf, K.K. Taha and Hajo Idriss and Aldaghri wrote and revised the paper. All authors read and approved the final manuscript.

Ethics approval and consent to participate

None.

Consent for publication

None.

Competing interests

The authors declare that they have no competing interests

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