Contents lists available at ScienceDirect



Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

Optical, photo physical parameters and photo stability of 6-Substituted-1, 2, 4-Triazine mono glucosyl derivative to act as a laser dye in various solvents



Mahmoud E.M. Sakr^{a,*}, Maram T.H. Abou Kana^{a,*}, Ahmed H.M. Elwahy^b, Hamed M. Kandel^a, Mohamed S. Abdelwahed ^c, Samy A. El-Daly ^c, El-Zeiny M. Ebeid ^{c,d}

^a Laser Sciences and Interactions Department, National Institute of Laser-Enhanced Sciences (NILES), Cairo University, Giza, Egypt

^b Chemistry Department, Faculty of Science, Cairo University, Egypt

^c Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

^d Misr University for Science and Technology (MUST), 6th of October City, Egypt

ARTICLE INFO

Article history: Received 6 December 2019 Received in revised form 30 January 2020 Accepted 9 February 2020 Available online 10 February 2020

Keywords: Photo physical properties 1, 2, 4-Triazine mono glucosyl derivative Photostability Fluorescence spectra Optical properties

ABSTRACT

The optical properties of a visible absorption range6-Substituted-1, 2, 4-Triazine mono glucosyl fluorescent derivative dye, such as absorption spectra, emission spectra in different solvents, were experimentally investigated. As well, some important photo physical parameters such as extinction coefficient (ε), cross-sections of the absorption (σ_a) and the emission (σ_e), quantum yield (ϕ_f), fluorescence lifetime, oscillator strength (*f*), the dipole moment (μ), decay rate radiative constant (k_r), energy yield of fluorescence (E_f) and the length of attenuation Λ (λ) were assessed. The ground-state (μ_g) and excited-state (μ_e) dipole moments by solvatochromic correlations method were reported. The dye amplified spontaneous emission (ASE) of 2×10^{-4} M with different input pumping energies of a continuous wave blue diode laser ($\lambda = 450$ nm) was studied. Photostability of dye was observed that was decreased to 53% of its initial energy by pumping with 100 mW of diode laser after exposure to 120 min.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

Development of organic luminophores has been of great significant, due to their wide applications in different fields such as optical storage. optoelectronics and bio-imaging [1-4]. In order to optimise the luminophores organic molecules for certain range of optical wavelength region, it is usually practice to control the length of the conjugation. As well, presence of both substituents donating electrons (D) and accepting (A) in a single molecule displays interesting spectral and optical properties due to intramolecular charge transfer (ICT). They change their photophysical characteristics, explicitly and large red shifts in their spectra of emission with respect to increase solvent polarity as shown in the Stokes shifts. The fluorescence lifetimes and quantum yields reduced with increasing the polarity of solvent [5]. The solvent type plays an imperative role in photo-physical properties of *p*-conjugated organic compounds. A change in solvent leads to a change in the surrounding medium polarity. Thus, changing of solvent will effect on the

Corresponding authors.

ground-state and excited-state differently. The dipolar molecules correlate with solvatochromic shifts much better with microscopic parameter of solvent polarity as E_T^N or $E_T(30)$ rather than the traditionally used solvent polarity bulk functions that including relative permittivity's and refractive indices [6,7]. The present investigations study the effect of different solvents on the various spectroscopic and photo-physical properties of dye samples to suggest its probability to act as laser dye.

2. Experimental

2.1. Materials and methods

Spectroscopic grade solvents and requested chemicals were obtained from Sigma Aldrich and used without further purification.

2.1.1. Samples preparation

2-(Acetoxymethyl)-6-(3-((4-amino-6-(4-methoxystyryl)-5-oxo-4,5-dihydro-1,2,4-triazin-3-yl)amino)-2,4-dioxo-3,4-

dihydroquinazolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate as compound (6) was prepared as outlined in Scheme 1. Thus,

E-mail addresses: m.sakr@niles.edu.eg (M.E.M. Sakr), mabou202@niles.edu.eg (M.T.H. Abou Kana).



Scheme 1. Preparation of a dye6 (R = 4-MeOC₆H₄CH=CH-).

hydrazinolysisof4-amino-3-thioxo-3, 4-dihydro-1, 2, 4-triazin-5(2H)one as compound (1) could be achieved by its treatment with a boiling mixture of hydrazine, MeOH/DMF to afford 4-amino-3-hydrazinyl-6methyl-1, 2, 4-triazin-5(4H)-one as compound (2). Condensation of 2 with isatoicanhydride as compound (3) in an hydrous boiling dioxane furnished 3-((4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3yl) amino) quinazoline-2,4 (1H,3H)-dione as compound (4). Compound (4) was elucidated by spectroscopic data. Thus, the IR spectrum of compound (4) showed absorption bands characteristic for carbonyl groups at 1500, 1595 and 1640 cm⁻¹. Its ¹HNMR spectrum showed a singlet at 6.18 ppm characteristic for the NH₂ protons. In addition, its mass spectrum showed the parent ion peak at m/z = 419. Coupling of compound (4) with 2-(acetoxymethyl)-6-bromotetrahydro-2H-pyran-3,4,5-triyl triacetate as compound (5) in pyridine at room temperature 2-(acetoxymethyl)-6-(3-((4-amino-6-methyl-5-oxo-4,5gave dihydro-1,2,4-triazin-3-yl) amino)-2,4-dioxo-3,4-dihydro quinazolin-1 (2H)-yl) tetrahydro-2H-pyran-3,4,5-triyl triacetate as compound (**6**). Orange colored powder of 50% yield; m.p. 269–270 °C was obtained. The ¹HNMR spectra of compound ($\mathbf{6}$) showed the position of the anomeric protons at 4.67 with $J_{1t} = 9.59$ Hz confirmed the β -N-structure of 6 in addition to the presence of OAc groups at the range 2.09-2.58 ppm. Its IR spectra showed bands at the range 1626-1750 cm⁻¹; IR (KBr), 1626 (CN), 1691 (C=O), 1748 (C=OO) cm $^{-1};\,^{1}$ HNMR (DMSO-d6) δ 2.09, 2.18, 2.23, 2.26 (4s, 12H, 4Ac), 3.14 (s, 3H, CH3O-4), 3.92 (s, 2H, NH2), 4.21, 4.36, 4.45, 4.59, 4.67 (5s, 7H, Hpyran, I1t = 9.59 Hz), 6.60–6.88 (m, 10H, H), 8.13 (s, 1H, NH). Anal. For C35H37N7O13 Calcd.: C, 55.04; H, 4.80; N, 12.84. Found: C, 55.11; H,4.69; N, 12.77.

2.2. Spectra measurements

Solutions of dye concentrations ranging from 4×10^{-5} M to 1×10^{-6} M were prepared for optical studies. The dye optimum concentration in ethanol was assessed from its absorption and emission spectra. The optimum concentration was 3×10^{-5} M in ethanol. Then, the same concentration of dye dissolved into different solvents like hexane, THF, DMF, DMSO, iso-propanol, ethanol, methanol and ethylene glycol. A Camspec M501 UV/Vis spectrophotometer and PF-6300 spectrofluorometer were used to measure the absorption and excitation-emission

spectra respectively. The wavelengths of excitation were adjusted according to the absorption maximum wavelengths for each fluorescence measurement of dye samples. The amplified spontaneous emission (ASE) of the dye, various with input pumping power, was measured using our previous experimental setup [8]. However, the dye samples were contained in 1 cm optical-path guartz cells that were transversely pumped by blue laser diode (450 nm). The exciting beam was directed towards the surface of cell sample with a combination of concave lens (f = 10 cm) and a cylindrical lens forming a line shape of 1 cm. The pumping energy (input energy) was measured via a beam splitter (4%) and the Gentec power meter (ModelQE50) detector head. The ASE output was focused by convex lens (f = 15 cm) onto Oplenic spectrophotometer which was connected to a computer unit for processing the spectrum. The samples were transversely pumped and were allowed to emit in the super radiant mode without employing a cavity mirror, since optical feedback were provided by reflection at host material air interface.

The photostability of a dye was also measured by using the same experimental setup. The input energy was kept constant at 100 mW of CW blue diode laser ($\lambda = 450$ nm) for 120 min.

2.3. Photophysical parameters calculations

For more deep clarification of the spectroscopic behavior of the dye and its performance to act as laser dye, some important photo-physical parameters should be assessed. These parameters such as; absorption cross section σ_a [9] and emission cross section σ_e [10], quantum yield [11,12]. Also, oscillator strength which is a function of molar absorption coefficient [13], the attenuation length Λ (λ) [14], the dipole moment transition (μ_{12}) [15], the decay of excited electrons either radiative and/or non-radiative [16], the excited state lifetime (τ_f) [17–19] should estimate.

By using solvatochromic methods, the dye dipole moments were estimated as follow: The solvatochromic method based on linear correlation between the absorption, fluorescence maxima and functions of solvent polarity [20,21], for determining the dipole moment of ground and excited state. Lippert–Mataga's Eqs. (1) and (2) [20,22], which is based on the correlation of difference in energy between both states (Stokes shift) with the solvent orientation polarizability (Δf), can



Fig. 1. Absorption spectra of $(3 \times 10^{-5} \text{M})$ dye in ethanol (inset figure is the dye absorption intensity in ethanol as function of different concentrations).

calculate the changing in the dye dipole moment between the both states as the following:

$$\Delta v = \frac{2(\mu e - \mu g)^2}{hca^3} \Delta f + Const$$
⁽¹⁾

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{2}$$

where, $\Delta \upsilon$ is the difference maxima between absorption and emission frequencies expressed in wave numbers (cm⁻¹). μ_e and μ_g are both states dipole moments, respectively, and Δf is the solvent orientation polarizability which measures both mobility of electron and the solvent molecule dipole moment.

From molecular volume of molecules the Onsager cavity radius (a) is calculated using Suppan's Eq. (3) [23],

$$a = \left(\frac{3M}{4\pi\delta N}\right)^{1/3} \tag{3}$$

where δ is the dye density, *M* is the dye molecular weight and *N* is Avogadro's number. The difference between both states which give dipole moment change ($\Delta\mu$) has been further investigated using the



Fig. 2. The dye absorption wavelength and intensity in various solvents (according to increasing the polarity of solvent).



Fig. 3. Emission spectra of the dye with different concentrations in ethanol (inset figure is the emission intensity with different concentration in ethanol).

solvatochromic shift method introduced by Reichardt [24]. The solvent polarity parameters dimension less microscopic E_T^{N} .

is given by the Eqs. (4) and (5),

$$E_T^N = \frac{E_T(solvent) - 30.7}{32.4}$$
(4)

$$E_T \text{solvent} = \frac{28.591}{\lambda_{\text{max}}} \text{nm}$$
(5)

This method has main disadvantage over the Lippert–Mataga method due to avoid incorporation of hydrogen bonding in addition on the solvent polarity into the solvent parameter. In this method, the dipole moment change is calculated by correlating the Stokes shift of the fluorophore to E_T^N according to Eq. (6),

$$\nu_a - \nu_b = 11307.6 \left[\left(\frac{\Delta \mu}{\Delta \mu_B} \right)^2 \left(\frac{a_B}{a} \right)^3 \right] E_T^N + const.$$
(6)

where $\Delta\mu$ is the dipole moments of the probe molecule between the both states and $\Delta\mu_B$ is the dipole moment change of the dye; a (taken as 4.34 Å) and the values of a_B and μ_B are known (6.2 Å and 9Debye, respectively) the dipole moment change is determined by Eq. (7),

$$\Delta \mu = \mu_e - \mu_g = \sqrt{\frac{m \times 81}{\left(\frac{6.2}{a}\right)^3 \times 11307.6}}$$
(7)



Fig. 4. Emission spectra of the dye of 3×10^{-5} M in different solvents.



Fig. 5. The dye emission wavelength and intensity in various solvents (according to increase the solvent polarity).

where, *m* is the slope of linear plot of E_T^N vs Stokes shift. The values of $\Delta \mu$ calculated by both methods are found closely and the higher value of $\Delta \mu$ may be attributed to the strong ICT character in some solvents.

3. Results and discussion

3.1. Solvents effect on optical spectra of dye

The UV–Vis absorption and fluorescence spectra of the dye as function of various solvents of different polarities were shown in Figs. 1–5. There is a minimum overlap between the dye absorption and emission spectra in various solvents. This is mainly important as far as reabsorption of emitted photons to be concerned.

Fig. 1 showed that, the absorption profiles of the dye at concentration 3×10^{-5} M in ethanol, while the inset figure in Fig. 1 showed the absorption intensities of the dye with different concentrations. The absorption intensities were increased as the dye samples became more concentrated. Fig. 2 shows the dye absorption wavelength and intensity in various solvents according to increase the polarity of solvents.

It noticed in absorption spectra of dye in different solvents that, in aprotic polar solvents the absorption energy corresponding to energy gap between ground state and excited state of dye decreased from 3.23 eV in case of hexane to 3.10 eV in case of DMSO with increasing solvent polarity. In protic polar solvent, the energy gap increases with the increasing solvent polarity from 3.15 eV in case of n-propanol to 3.22 eV in methanol. Also, the molar absorptivity of dye firstly increased gradually from the lowest polar solvent (hexane) to reach DMF as aprotic polar of high polarity. This molar absorptivity in protic solvents had opposite trend. In DMSO solvent as aprotic polar of higher polarity than DMF solvent, the molar absorptivity was dramatic decreased that might attribute to its high viscosity.

The dye emission intensity in ethanol at concentrations from 1×10^{-6} M to 4×10^{-5} Mare shown in Fig. 3. The optimum concentration of dye in ethanol was found to be 3×10^{-5} M. So, 3×10^{-5} M of dye was dissolved in various solvents and their emission spectra were monitored and represented in Fig. 4. It showed that, the different solvents played a critically role in the optical and consequently the photophysical properties of the dye.

As shown in Fig. 4, the different solvents affected on the dye spectroscopic spectra. The fluorescence intensities which represent the radiative decay efficiency of dye increased with the increasing of solvent polarity. The lowest fluorescence efficiency was obtained in case of using hexane (has the lowest polarity) as solvent. The fluorescence intensity increased to its maximum value in case of DMF as aprotic solvent. It also noticed that, although the polarity of DMSO as aprotic polar solvent is higher than that of DMF (0.444 and 0.386 respectively), the dye fluorescence has lower intensity which may be attributed to high viscosity of DMSO. This high viscosity of medium plays significant effect on electronic transitions of fluorophore. In protic polar solvent, 2propanol, ethanol, methanol and ethylene glycol of polarity 0.546, 0.654, 0.762 and 0.792 respectively, the fluorescence intensity decrease with increasing polarity of solvent molecules. In case of ethylene glycol as the highest polarity polar solvent, although its molecule is polar, it is symmetrical. Since it contains internal dipoles, but contains no net dipole moment because its internal dipoles oppose each other. So ethylene glycol contains both polar and nonpolar parts with strong hydrogen bond formation through its diols with electronegativity of oxygen and nitrogen atoms exist in dye resulting in abnormal fluorescence trend at higher wavelength ($\lambda_f = 502 \text{ nm}$).

Fig. 5 is represented the emission wavelength and intensity of the dye in various solvent according to increase the solvents polarity.

Figs. 2–5 showed that, the solvent played an important role in the dye optical properties. Fig. 2 represented the absorption intensities of the dye at concentration 3×10^{-5} M in various solvents as function of solvent polarity increase that represented in x-axis. Also Fig. 5 represented the emission intensities and wavelengths of the dye at concentration 3×10^{-5} Min different solvents according to increase the polarity. It was found that in Figs. 3–5, the emission peaks tended to shift to the long-wavelength (red shift) of the spectra with increasing broadening of the fluorescence band as the solvent polarity increased, suggesting that the singlet higher excited state is more polar than the



Fig. 6. A) Absorption and emission frequency (Cm^{-1}) versus $\Delta f(n, D)$ parameter of different solvents. B) Stokes shifts versus $\Delta f(n, D)$ parameter that is dye polarity parameter of different solvents 1) Hexane 2) THF 3) Chloroform 4) DMF 5) DMSO 6) Propanol 7) Ethanol 8) Methanol (______).



Fig. 7. A) Stokes shift of the dye versus $E_T^N \cdot B$) Fluorescence quantum yields versus E_T^N that is the dye solvent Polarity Microscopic parameter in various solvents. 1) Hexane 2) THF 3) chloroform 4) DMF 5) DMSO 6) 2-propanol 7) ethanol 8) methanol (—).

lower ground state. Thus the emission spectra are more effected by the polarity of solvent than the absorption spectra, which indicate that a large charge transfer taking place in excited state.

Since the solvent changing lead to the emission wavelength change, this can attribute to effect of other properties of the fluid due to the interaction between solvent molecules and dye molecules. Thus, the solvent has a large effect in photophysical properties of the dye depending on their other properties such as refractive index, dielectric constant....etc. Also, the electronic energy states difference of the dye between excited state and ground state is sensitive to the different solvents properties. These changes may be attributed to the dye structure and its orientation in various solvents. The spectral changes of the dye may also due to the changing in the dielectric constant of the respective solvents. The absorption and fluorescence peak frequencies (abs and fl respectively in cm^{-1}) of the dye had plotted with polarity of solvent parameter Δf . As seen in Fig. 6a. The *abs.* and *fl* values follow relationship linearly with Δf . The negative slope of emission relation with increasing f(D,n) parameter of solvent is higher than that of the same respective absorption relation. This higher negative slope behavior indicates that the emission state is strongly dipolar in nature due to strong ICT [25,26].

Fig. 6b shows that the relation between Stokes shift versus the orientation and polarization (Δf), The linear correlation of Lippert–Mataga plot supports the occurrence of photo induced intra molecular charge transfer. The dye dipole moment change calculated from the slope of this plot and cavity radius ($a = 4.6 \times 10^{-9}$) which found to be 6.55D. The data in polar protic solvents were excluded from the Fig. 6b which show Stokes shift against Δf , to avoid specific solute-solvent interactions (hydrogen bonding). The values of Stokes shift and absorption maximum and maximum emission is indication of charge transfer during excitation. Larger Stokes shift magnitude of compound 6 $(\Delta \lambda > 100 \text{ nm})$ can minimize cross-talk between the excitation source and the fluorescent emission [27]. Typical fluorophore dyes such as fluorescein dyes [28], rhodamine dyes [29], cyanine dyes [30] and BODIPY dyes [31] exhibit small Stokes shifts ($\Delta\lambda < 70$ nm) [32]which can reabsorb emitted photons leading to undesired background interferences. To address this issue, great effects have been dedicated and a number of noted fluorophore dyes with large Stokes shift ($\Delta\lambda$ > 80 nm) are focused by researchers [33].

From Fig. 7A which show Stokes shift against E_T^N and the value of $\Delta \mu$ is found to be 6.58D. The values of $\Delta \mu$ calculated by both methods are found closely and the higher value of $\Delta \mu$ may be attributed to the strong ICT character in some solvents.

Fig. 7B shows that, the dye fluorescence quantum yield (Φ_f) is strongly influenced by the polarity and hydrogen bonding ability of the different solvents. It also shows Φ_f values increases and then decreases with increasing polarity of solvent E_T^N , where E_T^N is the polarity of solvent parameter that considers interactions such as solvent polarizability and hydrogen bonding besides those of a specific nature. This may be attributed to efficient intersystem crossing by extensive mixing between the close lying π - π^* and n- π^* states. In addition the nonradiative rate increases markedly in solvents with strong hydrogen bond character such as alcoholic solvents and competes with fluorescence emission due to the enhancement of intersystem crossing, strong internal conversion and vibrational deactivation [34–36].

3.2. Laser-induced fluorescence of 6-Substituted-1,2,4-Triazine mono glucosyl derivative

The 6-Substituted-1,2,4-Triazine mono glucosyl derivative dye in ethanol was pumped by continuous wave blue diode laser for monitoring the amplified spontaneous fluorescence with excitation wavelength ($\lambda = 450$ nm). The spontaneous fluorescence intensities varied with input pumping power of 450 nm wavelength of diode laser as shown in Fig. 8.

By pumping using blue diode laser ($\lambda = 450 \text{ nm}$) the emission maximum peak wavelength of dye in ethanol ($\lambda_f = 522 \text{ nm}$) has been showed. The pump energy was controlled and varied between 20 and 250 mW as in the inset Fig. 8. In general, the output energy increased slowly then after threshold energy increased rapidly with increasing the pumping energy for the sample. The photostability can be studied by the evolution of the fluorescence output versus the exposure time,



Fig. 8. The fluorescence spectra of the dye in ethanol and the inset figure represent peak power (μ W) of ASE of dye as function of input pumping powers (mW) of diode laser.



Fig. 9. Normalized output fluorescence of the dye as a function of exposure time using pumping power 100 mW of (450 nm wavelength) diode laser.

in the same position of the samples, as plotted in Fig. 9. This study was carried out for the dye sample examined by blue diode laser (450 nm) of 100 mW as in Fig. 9. The time exposure was exactly 120 min.

Due to the progressive photodegradation and thermo degradation of the dye molecules, a gradual decreasing in the output fluorescence energy was observed for the sample. This decreasing occurred for the dye in ethanol and ASE peak dropped to 53% of the initial ASE value of the dye. Since the mechanism of photodegradation occurs by the interaction of the dye molecules in the excited state with other species such as impurities, other dye molecules and singlet oxygen. Movable molecules, as in solution, will be more likely to encounter oxygen molecules and undergo degradation. Less freedom, as defined by the restrictive pores of the matrix, may make the dye molecules less likely to interact with molecular oxygen leading to photo degradation or fluorescence This quenching behavior may attribute quenching. to paramagneticnature of oxygen molecules which well known as fluorescence quencher [37].

Finally, some important photo-physical parameters of the dye were calculated and summarized in Table 1, which proved their future applicable action in advanced optical applications. However, absorption cross section (σ_a) is the ability of the molecule to absorb a photon of a certain polarization and wavelength. Emission cross section (σ_e) measure the rate of optical transitions (per active ion) starting from a certain electronic level times the photon flow. The attenuation length(Λ) (called absorption length) is the distance into a material when the probability has dropped to¹/_e that a particle has not been absorbed.

It noticed from photo-physical parameters of dye in different solvents as shown in Table 1 that; 1) the dye in hexane, as non-polar of the lowest polarity, has a moderate molar absorptivity and absorption cross section but has the highest rate of intersystem crossing leading to have the lowest quantum yield. 2) The dye in DMF, as aprotic of the highest polarity, has the highest absorptivity and oscillator strength but has very low non-radiative decay resulting in the dye quantum yield has the highest value. 3) The dye in DMF, DMSO (the highest aprotic polar solvents) has the highest dipole moment. 4) In case of ethylene glycol as the highest polarity polar solvent, it contains internal dipoles, but contains no net dipole moment because its internal dipoles oppose each other. So ethylene glycol contains both polar and nonpolar parts with strong hydrogen bond formation through its diols with electronegativity of oxygen and nitrogen atoms exist in dye resulting in abnormal trend. However, the dye has the highest dipole moment, attenuation length and quantum yield.

4. Conclusion

This paper discussed a visible 6-Substituted-1, 2, 4-Triazine mono glucosyl derivative, dye2-(Acetoxymethyl)-6-(3-((4-amino-6-(4methoxystyryl)-5-oxo-4,5-dihydro-1,2,4-triazin-3-yl)amino)-2,4dioxo-3,4-dihydroguinazolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5trivl triacetate, to be able to act as a laser dye in various solvents as hexane, THF, DMF, DMSO, iso-propanol, ethanol, methanol, and ethylene glycol. The optical properties and photo-physical parameters of dye as function of different solvents are strongly dependent. The fluorescence intensities gradually increased with the increasing of solvent polarity in non-polar and aprotic type solvents such as hexane, THF, DMF and DMSO. However, it decreased in solvents of protic type such as isopropanol, ethanol and methanol. The reason for these different solvent effects on fluorescence intensity may be due hydrogen bond effect on the radiation less deactivation process. The emission peaks tended to shift to the long-wavelength (red shift) of the spectra with broadening in the fluorescence band as the solvent polarity increased, suggesting that the singlet excited state is more polar than the ground state. Thus the emission spectra are more sensitive to polarity of solvent than the absorption spectra, which indicate that a large charge transfer taking place in excited state more than the lower ground state. In case of ethylene glycol as the highest polarity polar solvent, although its polarity molecule, it is symmetrical. Since it contains internal dipoles, but contains no net dipole moment because its internal dipoles oppose each other. So ethylene glycol contains both polar and nonpolar parts with strong hydrogen bond formation through its diols with electronegativity of oxygen and nitrogen atoms exist in dye resulting in abnormal fluorescence trend at higher wavelength ($\lambda_f = 502 \text{ nm}$).

On the same concurrent objective, increasing of some photophysical parameters such as molar absorptivity, oscillator strength, absorption and emission cross sections as well as radiative rate decay had a positive effect on quantum yield of dye consequently, lasing behavior. While,

Table 1

The dye photo-physical parameters in different solvents; (ϵ) molecular extinction coefficient; σ_a and σ_e : absorption and emission cross section; (Λ) the attenuation length, (τ_f) fluorescence life time, (τ_0) calculated fluorescence life time, μ_{12} (D) the dipole moment transition, (E_f) energy yield of fluorescence, (K_r) the radiative decay rate, (K_{isc}) the rate of intersystem crossing, (f) oscillator strength, ϕ_f fluorescence quantum yield, indifferent solvents.

Sample/solvent	$^{\epsilon}_{L\cdot M^{-1}\cdot cm^{-1}}$ (10 ⁴)	$\sigma_a \ (10^{-16}) \mathrm{cm}^2$	$\sigma_{e} \ (10^{-17}) \ {\rm cm}^2$	Λ (cm)	$ au_{f}$ (ns)	τ ₀ (1/k _r) (ns)	μ ₁₂ (D)	E _f	K _r (10 ⁹) s ⁻¹	$\begin{matrix} K_{isc} \\ (10^9) \\ s^{-1} \end{matrix}$	F	ϕ_{f}
Hexane	16.76	6.452	2.079	0.086	0.05	0.157	8.50	0.34	6.36	13.53	0.44	0.32
Tetrahydrofuran	18.02	6.937	1.634	0.080	0.06	0.178	9.39	0.39	5.62	9.56	0.54	0.37
Chloroform	17.03	6.556	1.521	0.085	0.11	0.222	8.94	0.51	4.52	4.15	0.48	0.52
DMF	19.09	7.349	1.103	0.075	0.17	0.251	9.82	0.72	3.98	1.87	0.58	0.68
Dimethyl sulfoxide	16.40	6.314	1.100	0.088	0.15	0.252	9.63	0.64	3.97	2.53	0.55	0.65
2-Propanol	16.33	6.287	1.086	0.088	0.16	0.271	8.72	0.63	3.70	2.46	0.46	0.63
Ethanol	17.09	6.579	1.675	0.084	0.10	0.220	8.81	0.46	4.54	5.12	0.49	0.47
Methanol	18.26	7.030	2.025	0.079	0.07	0.183	8.74	0.42	5.46	7.54	0.47	0.42
Ethylene glycol	8.03	3.091	1.127	0.180	0.27	0.387	9.60	0.66	2.58	1.05	0.56	0.70

increasing of excited state-lifetime, intersystem crossing rate and nonradiative rate decay had a negative effect on quantum yield of dye. The further lasing properties of the dye will depend mainly on the sum of these photophysical parameters of dye in each solvent.

Good photostability of dye was observed that its fluorescence energy was decreased to 53% of its initial value by pumping with 100 mW of blue diode laser ($\lambda = 450$ nm) for 120 min time exposure.

CRediT authorship contribution statement

Mahmoud E.M. Sakr: Methodology, Writing - review & editing. Maram T.H. Abou Kana: Conceptualization, Investigation, Supervision. Ahmed H.M. Elwahy: Conceptualization, Supervision, Investigation. Hamed M. Kandel: Writing - original draft. Mohamed S. Abdelwahed: Resources. Samy A. El-Daly: Supervision. El-Zeiny M. Ebeid: Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- A.C. Grimsdale, K.L. Chan, R.E. Martin, P.G. Jokisz, A.B. Holmes, Synthesis of lightemitting conjugated polymers for applications in electroluminescent devices, Chem. Rev. 109 (2009) 897.
- [2] D. Braga, G. Horowitz, High-performance organic field-effect transistors, Adv. Mater. 21 (2009) 1473.
- [3] R.J. Radford, W. Chyan, S.J. Lippard, Peptide-based targeting of fluorescent zinc sensors to the plasma membrane of live cells, Chem. Sci. 4 (2013) 3080.
- [4] A. Facchetti, π-Conjugated polymers for organic electronics and photovoltaic cell applications, Chem. Mater. 23 (2011) 733.
- [5] T.H.N. Pham, R.J. Clarke, Solvent dependence of the photochemistry of the styrylpyridinium dye RH421, J. Phys. Chem. B 112 (2008).
- [6] A. Belay, E. Libnedenge, H.K. Kim, Y.H. Hwang, Effects of solvent polarity on the absorption and fluorescence spectra of chlorogenic acid and caffeic acid compounds: determination of the dipole moments, Luminescence 31 (2016) 118–126.
- [7] N.R. Patil, R.M. Melavanki, S.B. Kapatkar, N.H. Ayachit, J. Saravanan, Solvent effect on absorption and fluorescence spectra of three biologically active carboxamides (C1, C2 and C3). Estimation of ground and excited state dipole moment from solvatochromic method using solvent polarity parameters, J. Fluoresc. 21 (2011) 1213–1222.
- [8] D.M. AL-Aqmar, H.I. Abdelkader, M.H. AbouKana, Spectroscopic properties and amplified spontaneous emission of fluorescein laser dye in ionic liquids as green media, Opt. Mater. 47 (2015) 573.
- [9] S.A. El-Daly, Photophysical properties: laser activity of and energy transfer from 1,4bis[β-(2-benzothiazolyl)vinyl]benzene (BVB), J. Photochem. Photobiol. A Chem. 124 (1999) 127.
- [10] B.B. Raju, T.S. Varadrajan, Photophysical properties and energy transfer dye laser characteristics of 7-diethylamino-3-heteroaryl coumarin in solution, Laser Chem. 16 (1995) 109.

- [11] H.M. Fahmy, N.A. Negm, A.H.M. Elwahy, M.T.H. Abou Kana, Laser induced fluorescence, photo-physical parameters and photostability of new fluorescein derivatives, J. Mol. Liq. 229 (2017) 31.
- [12] M.A.S. Sakr, E.-S.A. Abdel Gawad, M.T.H. Abou Kana, E.-Z.M. Ebeid, Photophysical, photochemical and laser behavior of some diolefinic laser dyes in sol- gel and methyl methacrylate/2-hydroxyethyl methacrylate copolymer matrices, Opt. Laser Technol. 71 (2015) 78.
- [13] V. Bojinov, I. Grabchev, Synthesis and photophysical investigations of novel combined benzo[de]anthracen-7-one/2,2,6,6-tetramethylpiperidines as fluorescent stabilisers for polymer materials, Polym. Degrad. Stab. 85 (2004) 789.
- [14] F. Masetti, F. Elisei, U. Mazzucato, Optical study of a large-scale liquid-scintillator detector, J. Lumin. 68 (1996) 15.
- [15] E.M. Ebeid, S.M. Alhazmy, Photophysical and Laser-based Techniques Chemistry, Biology and Medicine, Book Surge Publisher, Charleston, SCUSA, 2006.
- [16] T.G. Pavlopoulos, Scaling of dye lasers with improved laser dyes, Prog. Quantum Electron. 26 (2002) 193.
- [17] S.G. Schulman, Fluorescence and Phosphorescence Spectroscopy; Physicochemical Principles and Practice, Pergmon press, Oxford, 1976.
- [18] J.B. Birks, J.B. Birks, Photophysics of aromatic molecules, Wiley Interscience, Wiley, London 1970, p. 880rganic Molecular Photophysics. , John Wiley and Sons, New York, 1970.
- [19] S.J. Strickler, R.A. Berg, Relationship between absorption intensity and fluorescence lifetime of molecules, J. Chem. Phys. 37 (1962) 814.
- [20] E. Lippert, Z. Naturforsch. 10 (1955) 541.
- [21] A. Chamma, P. Viallet, C. R., Determination dipoloment dipolaired une molecule dansunetat excite singulet, Acad. Sci., Ser. C 270 (1970) 1901.
- [22] N. Mataga, T. Kubota, Molecular Interactions and Electronic Spectra, Marcel Dekker New York, 1970 371.
- [23] P. Suppan, Excited-state dipole moments from absorption/fluorescence solvatochromic ratios, Chem. Phys. Lett. 94 (1983) 272.
- [24] C. Reichardt, Solvatochromic dyes as solvent polarity indicators, Chem. Rev. 94 (1994) 2319.
- [25] J.R. Lakowicz, Principle of Fluorescence Spectroscopy, Plenum Press, NewYork, 2006.
- [26] P. Dahiya, S.D. Choudhury, D.K. Maity, T. Mukherjee, H. Pal, Solvent polarity induced structural changes in 2,6-diamino-9,10-anthraquinone dye, Spectrochim. Acta A 69 (2008) 134.
- [27] X. Wu, X. Sun, Z. Guo, J. Tang, Y. Shen, T.D. James, H. Tian, W. Zhu, J. Am. Chem. Soc. 136 (2014) 3579.
- [28] Y. Duan, M. Liu, W. Sun, M. Wang, S. Liu, Q.X. Li, Mini-Rev. Org. Chem. 6 (2009) 35.
- [29] M. Beija, C.A.M. Afonso, J.M.G. Martinho, Chem. Soc. Rev. 38 (2009) 2410.
- [30] J.L. Bricks, A.D. Kachkovshii, Y.L. Slominskii, A.O. Gerasov, S.V. Popov, Dyes Pigments 121 (2015) 238.
- [31] Y. Ni, J. Wu, Org. Biomol. Chem. 12 (2014) 3774.
- [32] Y. Hayashi, N. Obata, M. Tamaru, S. Yamaguchi, Y. Matsuo, A. Saeki, S. Seki, Y. Kureishi, S. Saito, S. Yamaguchi, H. Shinokubo, Org. Lett. 14 (2012) 866.
- [33] M.M. Bishop, J.D. Roscioli, S. Ghosh, J.J. Mueller, N.C. Shepherd, W.F. Beck, J. Phys. Chem. B 119 (2015) 6905.
- [34] T. Shim, M.H. Lee, D. Kim, Y. Ouchi, Comparison of photophysical properties of the hemi cyanine dyes in ionic and nonionic solvents, J. Phys. Chem. B 112 (2008) 1906.
 [35] J.B. Birks, Organic Molecular Photophysics, John Wiley and Sons, New York, 1973.
- [36] A.C. Bhasikuttan, R.N. Rajule, V.S. Satam, S.R. Bendre, V.R. Kanetkar, H. Pal, Contrasting solvent polarity effect on the photophysical properties of two newly synthesized aminostyryl dyes in the lower and in the higher solvent polarity regions, J. Phys. Chem. A 114 (2010) 4507.
- [37] T. Suratwala, Z. Gardlund, K. Davidson, D.R. Uhlmann, Photostability of silylated coumarin dyes in polycerams hosts, J. Sol-Gel Sci. Technol. 8 (1997) 973.