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Journal of Photochemistry and Photobiology A: Chemistry 195 (2008) 89–98

Journal of Photochemistry and Photobiology A:Chemistry

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Photophysical properties, excitation energy transfer and laser activity of 3-(4′-dimethylaminophenyl)-1-(2-pyridinyl) prop-2-en-1-one (DMAPP)
A new potential laser dye

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Received 2 May 2007; received in revised form 18 September 2007; accepted 20 September 2007
Available online 29 September 2007

Abstract

The photophysical properties such as singlet absorption, molar absorptivity, fluorescence spectra, fluorescence quantum yield (ϕ_f) and transition dipole moment (μ_{12}) of 3-(4′-dimethylaminophenyl)-1-(2-pyridinyl) prop-2-en-1-one (DMAPP) were measured in different media. DMAPP dye exhibits a large red shift in both absorption and emission spectra as solvent polarity increases, indicating a large change in dipole moment of molecule upon excitation. Also, the fluorescence quantum yield is solvent dependent. A crystalline solid of DMAPP gives excimer like emission at 585 nm. Dye solution ca 1×10^{-3} mol dm^{-3} in $CHCl_3$ gives a good laser emission in the range 440–600 nm with emission maximum at 550 nm upon pumping by nitrogen laser ($\lambda_{ex} = 337.1$ nm). The excitation energy transfer from 7-dimethylamino-4-methyl coumarine (DMC) to DMAPP has also been studied in $CHCl_3$ and the value of energy transfer and critical transfer distance indicate a Főrster-type mechanism. The photochemical quantum yields (ϕ_c) of DMAPP in chloromethane solvents are also determined.

Keywords: 3-(4′-Dimethylaminophenyl)-1-(2-pyridinyl)prop-2-en-1-one; Laser dye; Effect of solvents; Fluorescence quantum yield and photoreactivity in chloromethane solvents

1. Introduction

The photophysical and spectroscopy of molecules with intramolecular charge transfer (ICT) properties are of containing theoretical and experimental intrest [1–4]. The spectral behavior such as electronic absorption and emission spectra as well as fluorescence quantum yield (ϕ_f) of such molecule are strongly affected by the microenvironment of dye [5]. The determination of photophysical properties of singlet excited state is very important for an understanding the behavior of dye molecules, such as twisted intramolecular charge transfer (TICT) phenomenon and the rotational relaxation dynamic of excited molecules [6–8], and also in synthesis of laser and fluorescence dye with desired properties [9–11], such as high fluorescence quantum yield, high molar absorptivity, large Stockes shift as well as high photostability.

Chalcones, the bichromophoric molecules separated by a keto-vinyl chain, are among those D–A compounds. The photophysical properties of several chalcones containing electron donor substituents have been studied [12–17]. These compounds have been extensively used for various optical applications including photo-alignment layer of liquid crystals display [18], photorefractive polymers [19] and fluorescent probes for sensing of DNA [20] or metal ions [17,21–23]. In addition, it is well known that chalcones posses many biological activities [24–26].

In the present paper we study the photophysical properties and laser activity as well as photostability of

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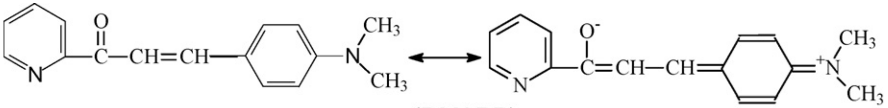
1010-6030/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jphotochem.2007.09.010

3-(4′-dimethylaminophenyl)-1-(2-Pyridyl) prop-2-en-1-one (DMAPP) in different media,



(DMAPP)

Resonance structure of DMAPP

2. Experimental details

2.1. Materials and methods

DMAPP was synthesized and purified as described previously [27,28] and its purity was confirmed by sharp melting point, TLC, IR, elemental analysis and ^{1}H NMR. All solvents used were of spectroscopic grade and were preliminarily checked for the absence of absorbing or fluorescent impurities within the scanned spectral ranges. UV–vis electronic absorption spectra were recorded on a Shimadzu UV-160 A spectrophotometer and the steady-state fluorescence spectra were measured using Shimadzu RF 510 spectrofluorophotometer. The fluorescence spectra were corrected for the machine response using 10^{-5} mol dm^{-3} anthracene solution in benzene [29]. The fluorescence quantum yield (ϕ_f) was measured using diluted solutions to avoid reabsorption effect (absorbance at excitation wavelength <0.2), relative to quinine sulphate ($\phi_f = 0.54$ in 0.1 M H_2SO_4), according to the following equation [30];

$$\phi_f = \phi_f^S \frac{\int_0^\infty I_F(\nu)\,d\nu}{\int_0^\infty I_F^S(\nu)\,d\nu}\left(\frac{1-10^{-A^S}}{1-10^{-A}}\right)\frac{n^2}{n_S^2} \qquad (1)$$

where ϕ_f^s is the quantum yield of standard and integrals are the area under fluorescence peaks. A and A^s are the absorbance of the dye and standard, respectively, at the excitation wavelength, n is the refractive index of the solvent. The photochemical quantum yields (ϕ_c) were calculated using the method that was described in details previously [31]. The light intensity was measured by using ferrioxalate actinometry [32].

The laser action of DMAPP was monitored using GL-302 dye laser, pumped by a nitrogen laser (GL-3300 nitrogen laser, PTI). The pump laser ($\lambda_{ex} = 337.1$ nm) was operated at repetition of 3 Hz with a pulse energy of 1.48 mJ and pulse duration of 800 Ps. The narrow-band output of the dye laser was measured with pyroelectric Joulemeter (ED 200, Gen-Tec Inc.).

The intrinsic radiative lifetime (τ_f^0) was calculated from the absorption spectra using the modified Strickler–Berg relation [33];

$$\frac{1}{\tau_f^0} = 3\times 10^{-9} n^2 \bar{\nu}_m^2 \int \varepsilon(\bar{\nu})\,d\bar{\nu} \qquad (2)$$

where n is the refractive index of the solvent, $\bar{\nu}_m^2$ is the energy of the absorption maximum (cm^{-1}) and the integration is the area under the absorption curve (plotted by the extinction coefficient versus the wavenumber in cm^{-1}). The fluorescence lifetime (τ_f) obtained from the product ($\phi_f \tau_f^0$).

3. Results and discussion

3.1. Spectral behavior of DMAPP in different media

The normalized absorption and emission spectra of DMAPP in some solvents having different polarity are shown in Fig. 1a and b and the corresponding spectral data are summarized in Table 1. The highly intense long-wavelength absorption band of DMAPP ($\varepsilon_{max} = 27 - 47 \times 10^3$ M^{-1} cm^{-1}) undergoes large red-shifts with increasing the solvent polarity (ca. 40 nm on going from n-heptane to DMSO). These features indicate a strongly allowed π–π* transition with charge transfer characters. This absorption band should attribute to the charge transfer from the dimethylamino group to the keto-pyridyl moiety. Such behavior is consistent with the restriction of charge transfer process from the dimethyl amino group due to the hydrogen bonding interactions between solvent molecules and the electron lone pair on the donor group. As shown in Fig. 1b, the fluo-

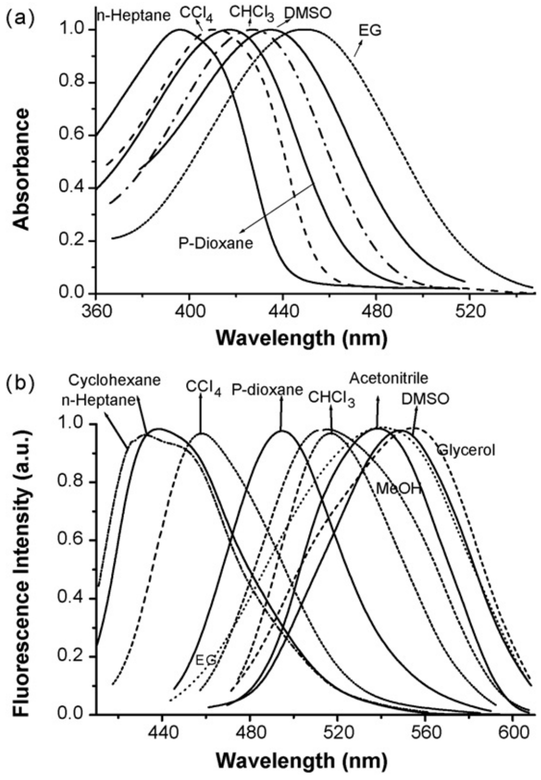


Fig. 1. (a) Normalized electronic absorption spectra in different solvents of DMAPP [1×10^{-5} mol dm^{-3}]; (b) normalized fluorescence spectra of 1×10^{-5}M of DMAPP in different solvents. ($\lambda_{ex} = 370$ nm.)

Table 1
Photo physical parameters of DMAPP in different solvents

Solvents	E_T (30) (kcal/mol)	Δf	λ_a (nm)	λ_f (nm)	$\Delta\bar{\upsilon}$ (cm^{-1})	ε_{max} (M^{-1} cm^{-1})	ϕ_f	μ_{12} (Debye)	τ (ns)
Cyclohexane	30.9	0.098	397	433	2094	30000	0.005	6.6	0.027
n-Heptane	31.1	0.095	395	428	1952	28400	0.002	7.2	0.010
CCl_4	32.4	0.115	410	455	2412	39600	0.037	8.0	0.156
p-Dioxan	36	0.121	413	495	4011	40200	0.339	8.4	1.554
$CHCl_3$	39.1	0.251	425	512	3998	41600	0.319	8.1	1.690
CH_2Cl_2	40.7	0.319	424	512	4054	38200	0.320	7.8	1.849
Acetone	42.2	0.374	420	538	5222	47000	0.008	8.9	0.038
Acetonitrile	45.6	0.393	419	538	5279	47400	0.008	8.9	0.040
DMF	43.8	0.377	427	538	4832	34600	0.103	7.9	0.645
DMSO	45.1	0.374	435	547	4707	42600	0.114	8.9	0.599
MeOH	55.4	0.393	430	510	3648	38600	0.009	8.8	0.039
EtOH	51.9	0.379	431	510	3594	29800	0.010	8.0	0.054
isoprOH	49.2	0.367	429	508	3625	33000	0.010	8.1	0.052
n-BuOH	50.2	0.36	430	508	3571	32200	0.011	7.9	0.060
EG	56.3	0.377	445	540	3953	27200	0.019	7.4	0.145

rescence spectrum suffers a strongly bathochromic shift as the solvent polarity is increased. This red-shift in the emission maximum from 428 nm in *n*-heptane to 547 nm in DMSO observably indicates that intensively photoinduced intramolecular charge transfer takes place within the molecule in the singlet excited state [34]. The peak wavenumbers in the fluorescence spectrum of the compound in different solvent polarity can correlated with the empirical Dimroth polarity parameter E_T (30) [35] of the solvents (refer to Fig. 2), except for strongly H-bonding solvents like methanol and ethanol, a very good linear correlation was obtained, implying potential application of this emission parameter to probe the local microenvironment of DMAPP [34].

Analysis of the solvatochromic behavior allows to estimate the difference in the dipole moment between the excited singlet and the ground state ($\Delta\mu = \mu_e - \mu_g$). This was achieved by applying the simplified Lippert–Mataga equation [35,36];

$$\Delta\bar{\upsilon}_{st} = \frac{(\mu_e - \mu_g)^2}{hca^3}\Delta f + \text{Const.} \qquad (3)$$

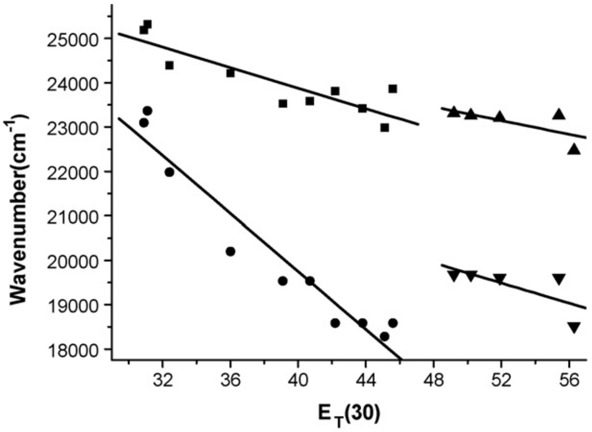


Fig. 2. Dependence of the absorption ($\bar{\upsilon}_{abs}$ aprotic [■] and alcoholic [▲]) and fluorescence ($\bar{\upsilon}_{em}$aprotic [●] and alcoholic [▼]) wavenumbers on the empirical solvent polarity parameter E_T(30).

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (4)$$

where $\Delta\bar{\upsilon}_{st}$ is the Stokes-shift [37], which increases with increasing the solvent polarity pointing to stronger stabilization of the excited state in polar solvents, h is Planck's constant, c is the speed of light and a is the Onsager cavity radius. ε and n are the dielectric constant and refractive index of the solvent, respectively. The Onsager cavity radius was taken as 40% of the distance between the two farthest atoms in the direction of charge separation within the molecule [38]. The estimated distance following geometry optimization equals 14.2 Å, consequently the value of the cavity radius is 5.7 Å.

Fig. 3 shows the plot of Stokes shift versus the orientation polarization (Δf). The data in polar protic solvents were excluded to avoid specific solute-solvent interactions (hydrogen bonding). The change of dipole moment upon excitation which was calculated from slope of the plot and the cavity radius is 12.75 Debye. This large change in dipole moment is caused by redistribution of atomic charges in the excited state as a result of charge transfer from the electron rich –$N(CH_3)_2$ group to the electron acceptor keto-pyridinyl.

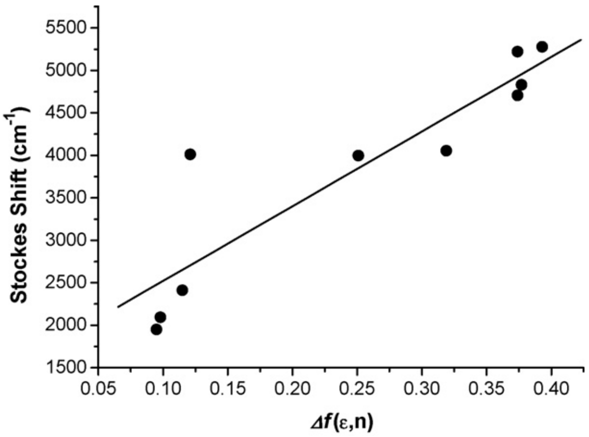


Fig. 3. Plot Stockes shift vs. polarity (Δf) of solvent for DMAPP.

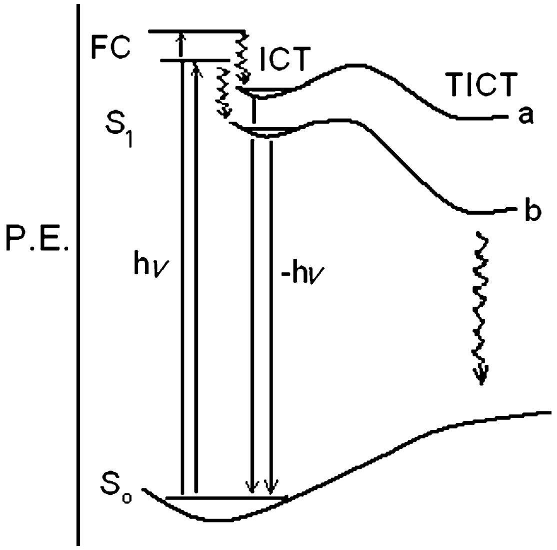


Fig. 4. Potential energy surfaces for rotation of the amine function depicting a Franck–Condon (FC) transition, relaxation involving coordinates for salvation, and evolution of the planar emissive intramolecular CT state (ICT) to the twisted conformation (TICT). Energy relationships, the barrier heights for rotation, and extent of stabilization of ICT and TICT are presented qualitatively for less polar (a) and more polar (b) solvents.

The transition dipole moment (μ_{12}) of DMAPP from ground to excited state was calculated in different solvents [39]

$$\mu_{12}^2 = \frac{f}{4.72 \times 10^{-7} E_{\max}} \tag{5}$$

where $E_{\max}$ is the energy maximum absorption in cm^{-1} and f is the oscillator strength which shows the effective number of electrons whose transition from ground to excited state gives the absorption area in the electron spectrum. Values of the experimental oscillator strength were calculated using the following equation [33,40]:

$$f = 4.32 \times 10^{-9} \int \varepsilon(\bar{\nu})\, \mathrm{d}\bar{\nu} \tag{6}$$

where ε is the numerical value of molar decadic extinction coefficient measured in $\text{dm}^3\,\text{mol}^{-1}$ and $\bar{\nu}$ is the numerical value of the wavenumber measured in cm^{-1}.

The integral is the experimental extinction coefficient; the values of μ_{12} are listed in Table 1.

The presence of a rotatable dimethyl aniline group in DMAPP opens the likeliness of a low-laying twisting intermolecular charge transfer (TICT) state through twisting of this group around the single bond. The planar intermolecular charge transfer (ICT) state and TICT state, on other hand, are highly polar states. For DMAPP increasing solvent polarity will therefore decrease ICT and TICT energy as shown in Fig. 4.

The emission spectrum of $1 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$ (DMAPP) has also measured in cetyltrimethyl ammonium bromide (CTAB), triton X-100 (TX-100) and in sodium dodecyl sulfate (SDS) micellar media, as shown in Fig. 5a–c. The emission intensity of dye increases as the concentration of surfactants increases, an abrupt change in fluorescence intensity is observed at surfactant concentration of 7.3×10^{-4}, 3.2×10^{-4} and $8.6 \times 10^{-3}\,\text{mol}\,\text{dm}^{-3}$ which very close to the critical micelle concentration of CTAB, TX-100 and SDS, respectively [41,42].

The emission spectra and quantum yield of DMAPP have been also measured in micro emulsion media containing CHCl_3 as the oil. Micro emulsions have been exploited as media capable of causing molecular dispersion with a subsequent decrease in molecular aggregation and bimolecular reactions [43,44].

As shown in Table 2, in oil–water (O/W) micro emulsion, the fluorescence maximum is red shifted (435 nm) compared with that in CHCl_3 and water–oil (W/O) ($\lambda_f = 512$ and 517 nm, respectively) see Fig. 6. The ϕ_f value of W/O is higher than that in O/W micro emulsion ($\phi_f = 0.045$ and

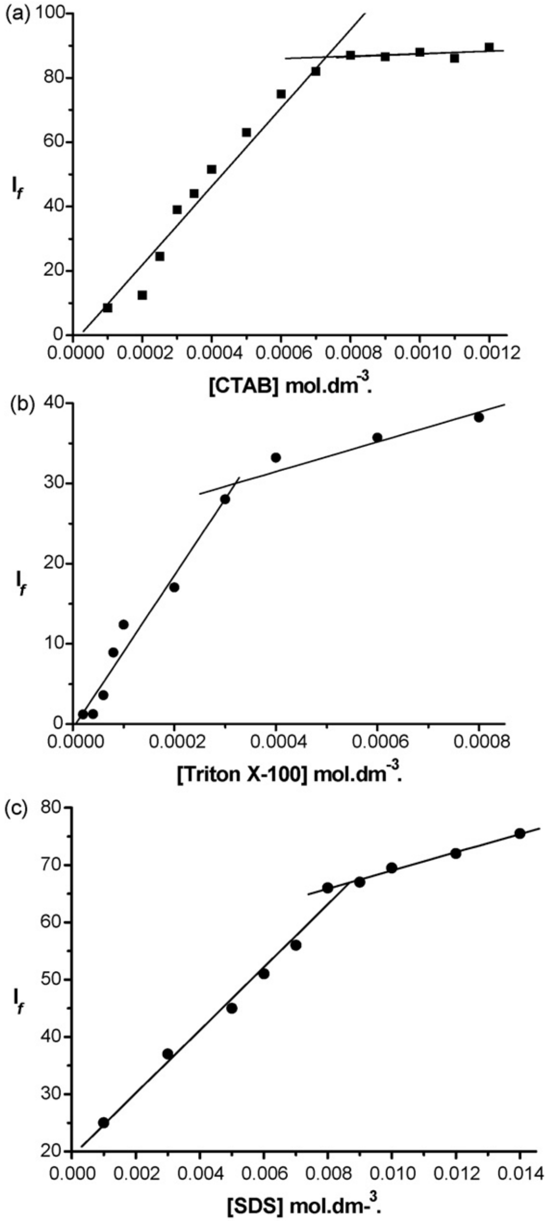


Fig. 5. Emission intensity of $1 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$ (DMAPP) in different concentrations of (a) CTAB, (b) TX-100 and (c) SDS.

Table 2
Spectral properties and fluorescence quantum yield (ϕ_f) of DMAPP in micro-emulsions

Medium	λ_{abs}^{max} (nm)	ε_{max} (M^{-1} cm^{-1})	λ_{em}^{max} (nm)	ϕ_f
$CHCl_3$	425	23529	512	0.319
W/O	429	23310	517	0.045
O/W	434	23041	535	0.021

0.021, respectively). However, these values are less than that measured in bulk $CHCl_3$ ($\phi_f = 0.319$) indicating that DMAPP is solubilized in the oil phase. The relatively lower ϕ_f value in W/O and O/W medium may be due to the quenching role of H-bond formation with the dominant water molecules.

The effect of medium acidity on the electronic absorption and fluorescence spectra has been studied. The electronic absorption and emission spectra of DMAPP in $CHCl_3$ were measured at different hydrogen ion concentrations (H_0). In acidic medium a new absorption band develops at 546 nm with an isosbestic point at 480 nm as shown in Fig. 7a–c. The fluorescence spectral pattern has not change in acidic media, only quenching occurs (due to formation of non-emissive protonated form). The change in absorption spectra of DMAPP in acidic media is obviously due to protonation of heterocyclic nitrogen with subsequent development of spectral pattern. The protonation constant of the ground state (pK_a) was determined by UV-spectrophotometric titration according to half-height method. The value of pK_a was determined as 1.73 from absorption and 1.77 from the emission spectra. The excited state protonation constant pK_a^* were calculated by using the following relation [45,46]:

$$\mathrm{p}K_a - \mathrm{p}K_a^* = 2.10 \times 10^{-3}(\bar{\upsilon}_{BH^+} - \bar{\upsilon}_B) \qquad (7)$$

The quantities ($\bar{\upsilon}_{BH^+} - \bar{\upsilon}_B$) represent the difference between the wave number of pure electronic transition in acidic and conjugate base, respectively. The pK_a^* value is 12.7 which consistent with the earlier observation that the pyridine nitrogen atom becomes more basic on excitation to S_1 state.

Solid crystals of DMAPP exhibit intense orange photoluminescence with maximum at 586 nm upon excitation at 470 nm. Such a behavior was attributed to excimer like formation whose fluorescence is 76 and 38 nm red-shifted compared to the emission from diluted and concentrated methanolic solutions, respectively, Fig. 8. This property is interesting since most solutions of DMAPP, which have been investigated, are weakly fluorescent. For many fluorophores the opposite behavior is the typical, that is to say, despite of intense fluorescence is obtained in solutions, radiationless deactivation predominates in the crystalline state. These properties are influenced considerably by the packing effects [47], which have a decisive influence on the relaxation pathways of the excitation energy. Solid state photoluminescent substances are very interesting for several high-technology applications such as the fabrication of light emitting diodes [48].

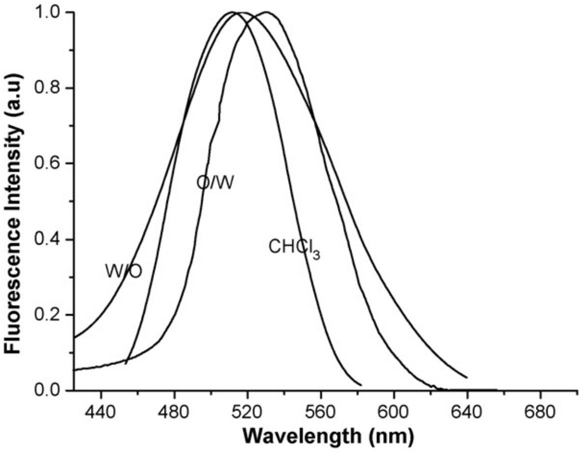


Fig. 6. Emission spectrum of DMAPP $CHCl_3$, W/O and O/W micro emulsions.

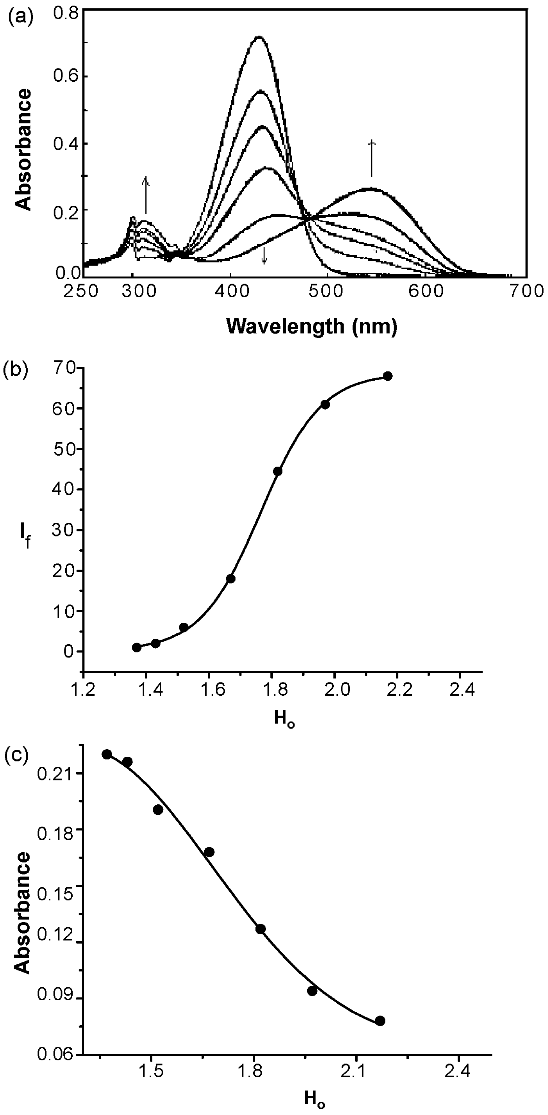


Fig. 7. (a) Effect of pH on the electronic absorption spectrum of DMAPP in $CHCl_3$ as a solvent by using trichloroacetic acid by adding the following conc.0.0, 0.5, 1, 2, 4, 8 × 10^{-3} mol dm^{-3}. (b) Effect of [H^+] on the absorption Spectrum of DMAPP in $CHCl_3$, use different concentrations of TCA. (c) Effect of [H^+] on the emission. Spectrum of DMAPP in $CHCl_3$, use different concentrations of TCA.

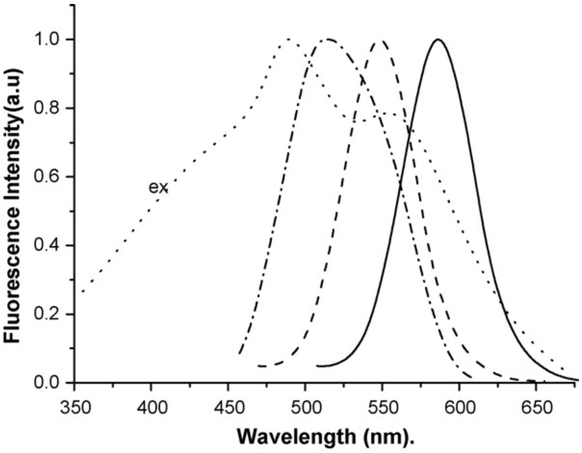


Fig. 8. Normalized emission spectra of DMAPP in (-·-·-) MeOH 10^{-5} mol dm^{-3}; (- - -) 10^{-3} mol dm^{-3}; (—) in crystalline solid and (···) excitation spectra.

3.2. *Fluorescence quantum yield in different media*

The fluorescence quantum yield (ϕ_f) of DMAPP, Table 1, depends strongly on the solvent properties. As illustrated in Fig. 9, the ϕ_f—value increases largely with decreasing the solvent polarity (expressed as $E_T(30)$ [49] which measures both the solvent polarizability and hydrogen bond donating ability) in aprotic solvents reaching a maximum value in *p*-dioxane. Further increase in the $E_T(30)$ leads to a decrease in the fluorescence yield. Several mechanisms such as; biradicaloid charge transfer, proximity effect and conformational changes have been proposed to explain the increase of ϕ_f with a suitable enhancement of the ICT (planar state) character (negative solvatokinetic effect). The reduction in ϕ_f on going from *p*-dioxane to DMF (positive solvatokinetic effect) can be attributed to the strong ICT interaction. In contrast, in non-polar solvents like cyclohexane the emitting state (with dipolar characters) is significantly destabilized to experience perturbation by the proximity effect and vibronic coupling to an energetically close lying n–π* state. This opens an effective non-radiative deactivation pathway for the excited singlet state, which explains the observed negative solvatokinetic effect.

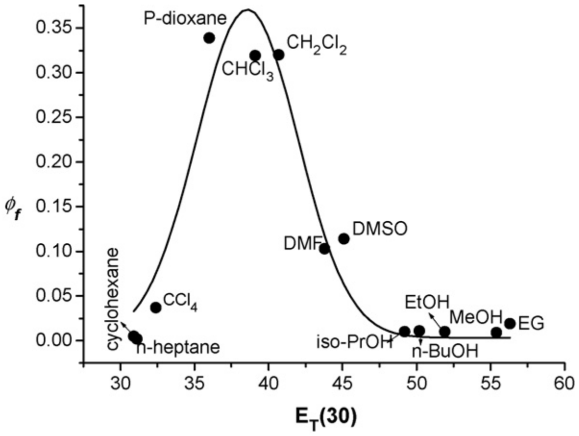


Fig. 9. Plot fluorescence quantum yield of DMAPP as a function of $E_T(30)$ of solvent.

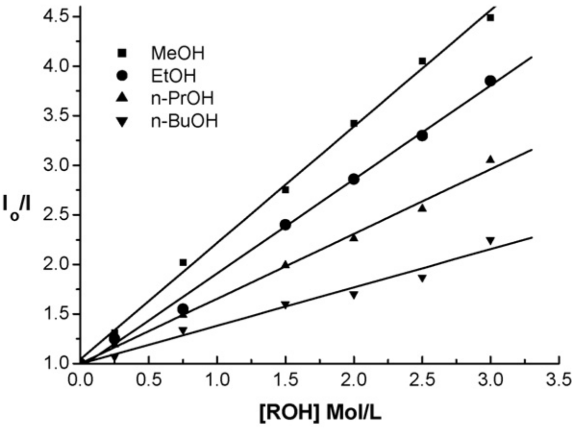


Fig. 10. Stern–Volmer plots of the quenching of DMAPP in DMF by alcoholic solvents.

The non-radiative deactivation of DMAPP dye has attributed to the formation of the so-called twisted intramolecular charge transfer (TICT) state from singlet excited state [50–52]. The population probability of this state depends on the electron donor–acceptor capacities of involved partners and on the solvent polarity which would stabilize the highly polar structure. The concept of TICT state was first proposed by Grabowski [53] to explain the fluorescence of *N*,*N*-dimethylamino benzonitrile derivatives in polar solvent.

However, the ϕ_f decreases strongly in highly polar proton donor solvents such as alcohols, Table 1. This effect is due to efficient hydrogen bonding interactions between the solvent molecules and the carbonyl group of the fluorophore. The carbonyl group of DMAPP becomes more negatively charged upon excitation. So, it was concluded that hydrogen-bonding interaction is playing a key role in enhancing the radiationless deactivation of the excited singlet state of DMAPP.

To confirm this conclusion, the fluorescence quenching of DMAPP in DMF was studied by using some protic solvents as quenchers. These solvents are methanol, ethanol, *n*-propanol and *n*-butanol which have different acidities. The Stern–Volmer constants (K_{SV}) were calculated from the Stern–Volmer plots shown in Fig. 10. The K_{SV} constant (K_{SV} = 1.17, 0.95, 0.65 and 0.39 M^{-1} in methanol, ethanol, *n*-PrOH and *n*-BuOH, respectively) increases linearly with the acidity constant of the solvent (α) as shown by the following regression;

$$K_{SV} = -1.42 + 2.65\alpha \quad (r = 0.966)$$

This indicates that the quenching mechanism is governed by hydrogen bond formation between the solvent molecules and the excited DMAPP*.

3.3. *Laser activity of DMAPP*

DMAPP is characterized by a relatively high fluorescence quantum yield ($\phi_f = 0.32$) and high photostability in CHCl$_3$. In addition, the dye is free from molecular aggregation either in the

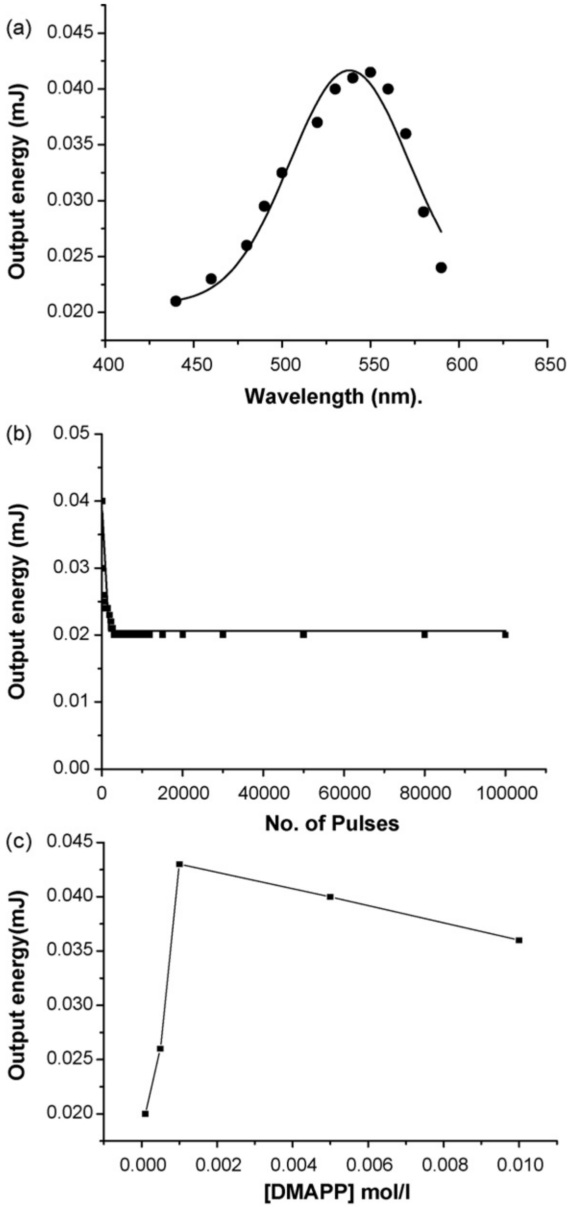


Fig. 11. (a) Tuning curve of laser emission from DMAPP in $CHCl_3$. (b) Output energy versus the number of pulses. (c) Effect of concentration on laser output energy.

ground or in the excited state since the emission spectrum suffers no shift as the concentration is raised up to 5×10^{-3} mol dm^{-3}. Such properties render DMAPP as a suitable candidate for dye lasers. When 5×10^{-3} M solution of DMAPP in $CHCl_3$ was excited by nitrogen laser pulses ($\lambda_{ex} = 337.1$ nm) of 800 ps duration and 1.48 mJ pulse energy, it gives good laser emission in the wavelength range 440–600 nm with an emission maximum at 550 nm (Fig. 11a) and band width equal 78 nm. The gain coefficient $\alpha(\lambda)$ of the laser emission of DMAPP was calculated by measuring the intensity of laser emission from the entire cell length and that from the cell half-length (I_L and $I_{L/2}$, respectively) according to the following relation [54];

$$\alpha(\lambda) = \frac{2}{L} \ln \left[\frac{I_L}{I_{L/2}} - 1 \right] \tag{8}$$

The value of α obtained at $\lambda = 550$ nm is 0.67 cm^{-1}, the low value of gain coefficient can be attributed to the remarkable overlap between electronic absorption and emission spectra of DMAPP as well as excited state absorption ($S_1 \rightarrow S_n$) of laser emission. The cross section for stimulated laser dye emission σ_e was calculated at the laser emission maximum ($\lambda = 550$ nm) according to the equation [55];

$$\sigma_e = \frac{\lambda_e^4 E(\lambda) \phi_f}{8\pi C n^2 \tau_f} \tag{9}$$

where λ_e is the emission wavelength, n is the refractive index of the solution, C is the velocity of light and $E(\lambda)$ is the normalized fluorescence line-shape function. This is correlated with fluorescence quantum yield by the equation [55,56],

$$\int_0^\infty E(\lambda)\, d\lambda = \varphi_f \tag{10}$$

$E(\lambda)$ is obtained from solution whose absorbance is low to avoid reabsorption processes (optical density at absorption maximum ≤ 0.1.

For an efficient laser dye the fluorescence quantum yield ϕ_f ≈ 1 [55].

For DMAPP a value of $\sigma_e = 4.2 \times 10^{-16}$ cm^2 was obtained at 550 nm, which is in close agreement with the values reported for good laser dyes [56,57].

The photochemical stability of laser dye was determined as the half-life energy ($E_{1/2}$) which the amount of total absorbed pump energy until the dye laser energy has dropped to 50% of its out put initial value. By knowing concentration of the laser dye and the photon energy of the nitrogen laser used (as shown in Fig. 11b) the value of $E_{1/2}$ was calculated as 3070 J/l, the $E_{1/2}$ value can be expressed in a physically more meaningful as the number of photons absorbed per laser dye molecule when the output energy of the dye laser has dropped to half of its initial energy output [58], the $E_{1/2}$ (photons/molecule) value for DMAPP was found to be 4607 photons/molecule.

3.4. Excitation energy transfer

The excitation energy transfer from DMC ($\lambda_{ex} = 337.1$ nm) as a donor to DMAPP as an acceptor has been studied in $CHCl_3$ to improve the laser emission of DMAPP when excited by the nitrogen laser. The DMC/DMAPP pair represents an efficient energy transfer laser system achieving better harvesting of light photons at 337.1 nm. Fig. 12 shows the increase in the output energy of the laser emission from DMAPP at 550 nm as the concentrations of DMC increases, indicating a non-radiative energy transfer from the excited DMC* to the ground state DMAPP.

To determine the rate constant of the energy transfer process and ascertain its nature, the fluorescence quenching of DMC has been studied in $CHCl_3$ by using DMAPP as a quencher. The emission intensity ($\lambda_{ex} = 337$ nm) of DMC decreases with increasing the concentration of DMAPP quencher. Following the well known Stern–Volmer relation [59] Fig. 13a;

$$\frac{I_0}{I} = 1 + k_{ET} \tau_f [A] \tag{11}$$

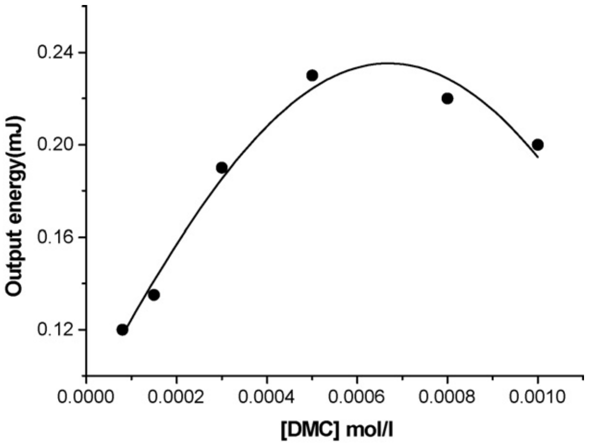


Fig. 12. The output energy (mJ/pulse) of DMAPP as a function of concentration of donor (DMC).

where, I_0 and I represent the fluorescence intensity of the donor in the absence and presence of quencher of concentration $[Q]$ in mol dm^{-3}, k_{ET} ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) is the rate constant of the energy transfer and τ_{f} is the fluorescence lifetime of DMC (=4.2 ns in $CHCl_3$). From the slope of Fig. 13a, k_{ET} has been calculated as $k_{\mathrm{ET}} = 13 \times 10^{12}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$. This value is much higher than the diffusion rate constant in $CHCl_3$ ($k_{\mathrm{diff}} = 17 \times 10^{9}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$) at room temperature, indicating a diffusionless energy transfer from DMC to DMAPP. This is further supported by the strong overlap between the electronic absorption spectrum of DAMPP and the emission spectrum of DMC, Fig. 13b. The critical transfer distance, R_0, for energy transfer within the DMC/DMAPP pair has been calculated using the Főrster formulation [60];

$$R_0^6 = 1.25 \times 10^{-25} \frac{\phi_{\mathrm{D}}}{n^4} \int_0^{\infty} F_{\mathrm{D}}(\bar{\upsilon})\varepsilon_{\mathrm{A}}(\bar{\upsilon}) \frac{\mathrm{d}\bar{\upsilon}}{\bar{\upsilon}^4} \tag{12}$$

where R_0 is the distance at which energy transfer and emission processes are equally probable, ϕ_{D} is the emission quantum yield of donor in absence of acceptor, n the solvent refractive index and the integral is the overlap integral for the fluorescence spectrum of donor normalized to unity (F_{D}) and the absorption spectrum of the acceptor (ε_{A}) divided by the fourth power of wavenumber ($\bar{\upsilon}$). Accordingly the critical transfer distance (R_0) was found as 71.3 Å. This value is longer than that for collisional energy transfer for which R_0 values are in the range of 4–6 Å [61].

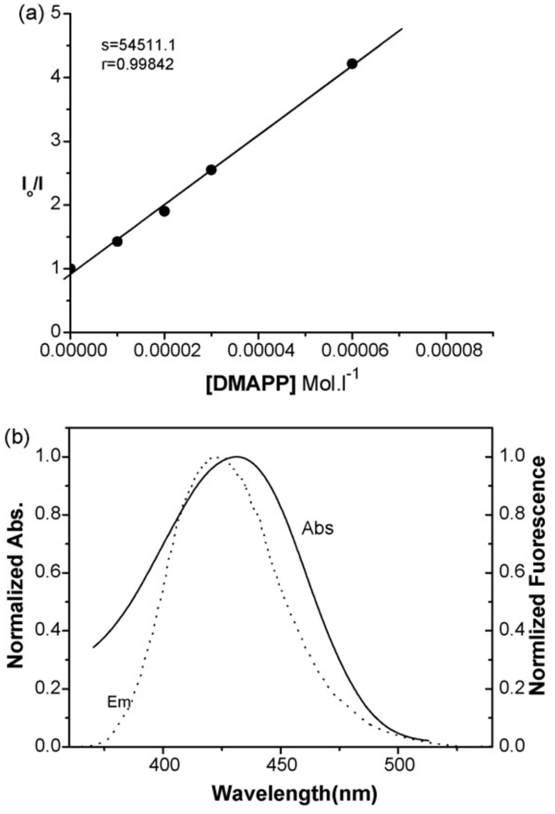
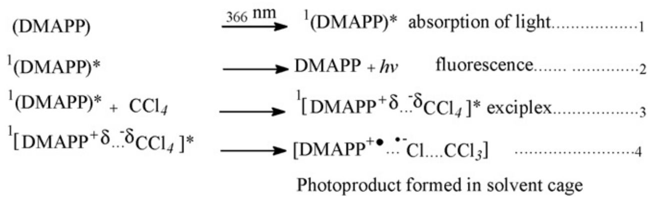


Fig. 13. (a) Stern–Volmer plot of fluorescence quenching of 1×10^{-5} mol dm^{-3} DMC in $CHCl_3$ by DMAPP ($\lambda_{\mathrm{ex}} = 337$ nm). (b) Shows the overlap between emission (· · ·) spectra of DMC and absorption (- - -) of DMAPP.

The higher values of critical transfer distance and the quenching rate constant indicate that the underlying mechanism of energy transfer is that of resonance energy transfer due to long-range dipole–dipole interaction between excited DMC as a donor and the ground state DMAPP as an acceptor.

3.5. *Photoreactivity of DMAPP in chloromethane solvents*

The photoreactivity of DMAPP has been studied in chloromethane solvents namely; CH_2Cl_2, $CHCl_3$ and CCl_4. Upon irradiation of 1×10^{-5} molar solution of the pyridylchalcone derivative at 366 nm ($I_0 = 3.6 \times 10^{-6}$ Ein/min), the absorbance of DMAPP in CH_2Cl_2 and $CHCl_3$ decreases with increasing the irradiation time till reaching a photostationary state as shown in Fig. 14a. This indicates the formation of a photoproduct which has significant absorption around 480 nm in such diluted solutions. The net photochemical quantum yield of the underlying reaction is 0.007 and 0.009 in CH_2Cl_2 and $CHCl_3$, respectively. In contrast, in CCl_4 the absorbance of DMAPP solution decreases with irradiation time till complete disappearance after 171 min, indicating a photodecomposition of DMAPP in such solvent Fig. 14b, The photochemical quantum yield of the photoproduct formed in solvent cage which has absorbance at about 330 nm is 0.041. The formation of photoproduct is a one-photon process as represented by the following scheme;



It was proposed that the electron transfer from the excited singlet DMAPP to CCl_4 within the transient excited charge transfer complex (exciplex) is the main primary photochemical process. It leads to the DMAPP radical cation, a chloride ion and a trichloromethyl radical in solvent cage step 4. The formation of a contact ion pair [DMAPP$^{+\bullet}$−Cl] usually occurs by electron transfer from excited donor molecule [DMAPP]* to the acceptor (CCl_4). In order to for such a compound to be formed

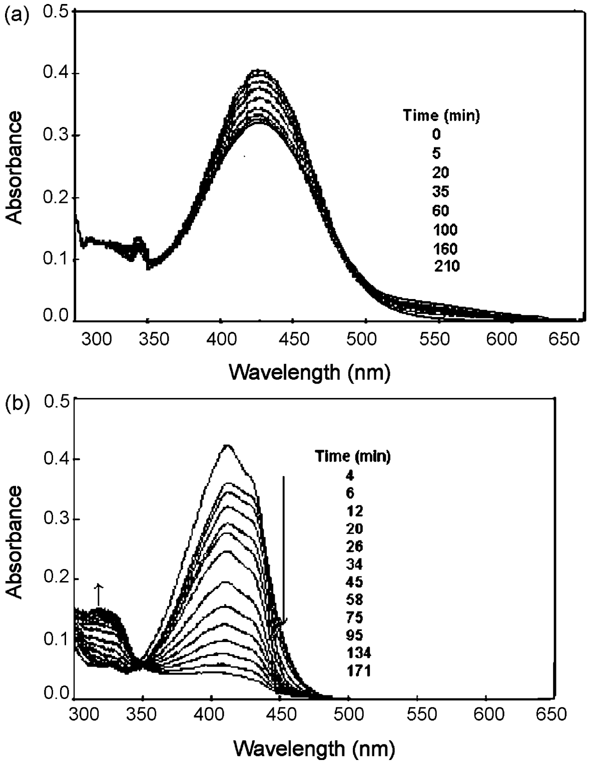


Fig. 14. Effect of irradiation ($\lambda_{ex} = 366$ nm, $I_0 = 3.6 \times 10^{-6}$ Ein/min) of the electronic absorption spectrum of a 1×10^{-5} mol dm^{-3} (a) in CH_2Cl_2 and (b) in CCl_4. The irradiation time are seen in figures.

a low ionization potential of the donor and high electron affinity of the acceptor are necessary.

The rate constant of photoreactivity of DMAPP was calculated by applying the simple first-order rate equation as follows:

$$\ln \frac{A_0 - A_\infty}{A_t - A_\infty} = kt \qquad (13)$$

where A_0, A_t and A_∞ are the initial absorbance, absorbance at time (t) and infinity, respectively. k is the rate constant. The rate constants were found to be 0.007, 0.01 and 0.02 min^{-1} in CH_2Cl_2, $CHCl_3$ and CCl_4, respectively Fig. 15. It was observed that the rate constant of photoreactivity of DMAPP increases with the electron affinity of chloromethane solvents ($E_A = 1.36$, 1.75 and 2.12 eV for CH_2Cl_2, $CHCl_3$ and CCl_4, respectively) [62,63] indicating that the electron affinity of solvent play a role in the photoreactivity and control the photochemical reaction.

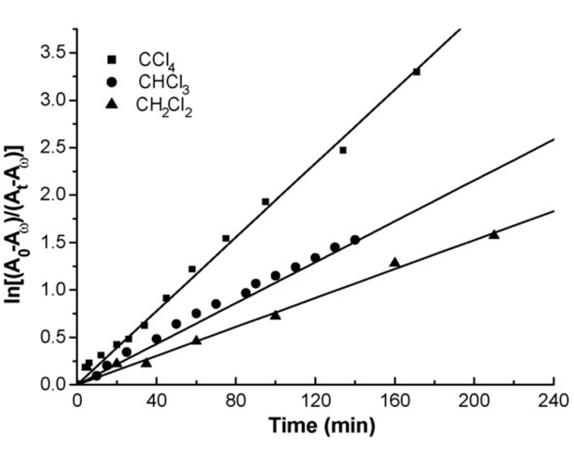


Fig. 15. First order plots of photoreactivity of DMAPP in chloromethane solvents.

It is worth while to mention that, DMAPP is highly photostable in polar and aprotic solvents, since no change in absorbance of this dye was observed upon prolonged irradiation by using either 365 or 254 nm for about 24 h.

4. Conclusion

The following conclusion can be arrived to from the above studies. DMAPP dye has high extinction coefficient, large difference in dipole moment between ground and singlet excited state (S_1), the fluorescence quantum yield dependent on the polarity of solvent as well as specific solute–solvent interaction such as hydrogen bond and high photostability when excited by 337 nm. These properties make DMAPP a good laser dye. The dye gives laser emission at 530 nm upon pumping with nitrogen laser pulse ($\lambda_{ex} = 337.1$ nm). DMAPP may be used in the determination CMC of surfactants (e.g. SDS, CTAB and TX-100). The excited state prtenationconstant (pK_a^*) is large than that the ground state protenation constant (pK_a), indicating the basicity of dye increases upon excitation. DMAPP act as a good energy acceptor for laser dyes which have high molar absorptivity at 337 nm such as DMC dye. DMAPP display a photodecomposition with low photochemical quantum yield in chloromethane solvents.

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