

## Research Article

# Photophysical Parameters, Excitation Energy Transfer, and Photoreactivity of 1,4-Bis(5-phenyl-2-oxazolyl)benzene (POPOP) Laser Dye

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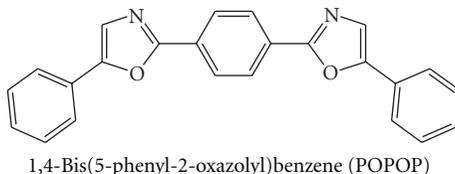
The effect of solvents on the absorption and emission spectra of 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP) laser dye has been studied in various solvents at 298 K. A bathochromic shift was observed in absorption and fluorescence spectra upon increase of solvent polarity, which indicates that this transition is  $\pi$ - $\pi^*$ . The ground and excited state dipole moments were calculated as 2.23 and 6.34 Debye, respectively. The dye solution in MeOH, *n*-heptane, and methyl isobutyl ketone gives laser emission in the blue region upon excitation by a 337.1 nm nitrogen pulse; the gain coefficient and emission cross section as well as normalized photostability have been determined. Excitation energy transfer from POPOP to rhodamine B and fluorescein was studied to improve the laser emission from these dyes. Such an energy transfer dye laser system (ETDL) obeys a long range coulombic energy transfer mechanism with a critical transfer distance,  $R_0$ , of 25 and 33 Å and  $k_q$  equal to  $10.4 \times 10^{12}$  and  $26.2 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$  for the POPOP/RB and POPOP/fluorescein pair, respectively. The POPOP dye is highly photostable in polar protic and polar aprotic solvents, while it displays photodecomposition in chloromethane solvent via formation of a contact ion pair. The photochemical quantum yield and rate of photodecomposition depend on the electron affinity of solvent.

## 1. Introduction

Fluorescent organic compounds possessing high Stokes shift values [1, 2] are prospective candidates for practical application in various fields of science and technology, where high concentrations or long optical paths are required [3, 4], for example, in scintillation techniques [5, 6], sunlight collection, and conversion of solar energy into electricity [7, 8], electroluminescent light sources (OLEDs) [9–11], and various biological applications, and so forth. Several physicochemical mechanisms can be applied to increase the fluorescence Stokes shift of organic compounds [12]; however, not all lead to emissions with high quantum yields [13].

The most popular and most studied is the excited state proton transfer reaction [14, 15]; however, it is usually connected with high radiationless excitation energy losses [16]. To our understanding, excited state conformational transformations resulting in the formation of more planar molecular structures [17–19] have several advantages in producing high Stokes shifted fluorescence emissions [20] over the alternative twisting mechanisms [21], which also induce radiationless excited state deactivation in most of the known cases [22].

Derivatives of 1,2-bis-(5-phenyloxazol-2-yl)benzene [23–25] are ortho analogs of the well-known scintillation luminophore POPOP [1,4-bis-(5-phenyloxazol-2-yl)benzene].



SCHEME 1

They belong to the class of efficient fluorescent organic compounds with abnormally high Stokes shifts [26]. In contrast to their planar paraisomers [27], molecules of the title series are characterized by essential nonplanarity caused by the steric repulsion of two bulky heterocyclic moieties introduced into the orthopositions of the central benzene ring [28]. The resulting disruption of intramolecular conjugation shifts the electronic absorption spectra of ortho-POPOPs towards the shorter-wavelength region with respect to the absorption of their planar paraisomers.

Further increase of the Stokes shift values is possible by combination of several photophysical mechanisms in one molecule: for example, excited state planarization and solvatochromic effects. Asymmetrization of the electronic density distribution by introduction of highly electron-donating and/or electron-withdrawing substituents into the ortho-POPOP molecule leads to a significant rise in its excited state dipole moment, increased sensitivity to solvent polarity, and thus enlarges the fluorescence Stokes shift in polar media [29]. In the present we report photophysical parameters, excitation energy transfer, and photoreactivity of POPOP laser dye (Scheme 1).

## 2. Experimental

1,4-Bis(5-phenyl-2-oxazolyl)benzene (POPOP), fluorescein, and rhodamine B (Aldrich) were used without further purification. All solvents used in this work were of spectroscopic grade and were preliminary checked for the absence of absorbing or fluorescent impurities within the scanned spectral ranges. UV-Visible electronic absorption spectra were recorded on a Shimadzu UV-Vis 1650-PC spectrophotometer and steady state fluorescence spectra were measured using a rectangular quartz cell of 0.2 cm path length to minimize the reabsorption of emitted photons; the emission was monitored at 90°. The fluorescence quantum yield ( $\phi_f$ ) was measured using the optically diluted solution to avoid reabsorption effects (absorption at excitation wavelength  $\leq 0.1$ ) relative method with solution of 9,10-diphenylanthracene as reference standard [30–32]. Using the same excitation wavelength, the unknown quantum yield is calculated using the following [33–35]:

$$\phi_u = \phi_s \times \frac{I_u}{I_s} \times \frac{A_s}{A_u} \times \frac{n_u^2}{n_s^2}, \quad (1)$$

where  $\phi_u$ ,  $\phi_s$  are the fluorescence quantum yield of the unknown and standard, respectively,  $I$  is the integrated emission intensity,  $A$  is the absorbance at excitation wavelength, and  $n$  is the refractive index of the solvent. The oscillator

strength ( $f$ ) of electronic transition and the transition dipole moment ( $\mu_{12}$ ) from ground to excited state was calculated in different solvents using (2) and (3) [36]:

$$f = 4.32 \times 10^{-9} \int \varepsilon(\tilde{\nu}) d\tilde{\nu} \quad (2)$$

or  $f = 4.32 \times 10^{-9} \Delta\tilde{\nu}_{1/2} \varepsilon_{\max}$ ,

$$\mu_{12}^2 = \frac{f}{4.72 \times 10^{-7} E_{\max}}, \quad (3)$$

where  $\varepsilon(\tilde{\nu})$  is the numerical value for the molar extinction coefficient measured in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  and  $\tilde{\nu}$  is the wavenumber value in  $\text{cm}^{-1}$  and  $E_{\max}$  is the energy maximum of absorption band in  $\text{cm}^{-1}$ . The radiative decay rate constant ( $k_r$ ) of a fluorophore (or fluorescence rate constant) presents a fundamental photophysical property, which determines, together with the rates for radiation less processes, the fluorescence life time; the rate of fluorescence resonance energy transfer (FRET) is also directly proportional to the radiative decay rates of the donor. The inverse of the fluorescence rate constant is the radiative (natural) life time ( $\tau_0$ ) of the excited state and corresponds to the lifetime expected in the absence of radiation less decay processes. The dependence of the radiative decay rate on the environment is significant; namely, it increases with its polarizability. It can be theoretically predicted from the well-known Strickler-Berg equation, which has its foundations in Einstein's spontaneous emission rate and Planck's black body radiation law [37]:

$$k_r = \frac{1}{\tau_0} = 2.88 \times 10^{-9} n^2 \frac{\int F(\tilde{\nu}) d\nu}{\int F(\tilde{\nu}) \tilde{\nu}^{-3} d\nu} \int \frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu}, \quad (4)$$

where  $F$  is the fluorescence intensity,  $\tilde{\nu}$  is the wave number, and  $\varepsilon(\tilde{\nu})$  is the molar extinction coefficient at a particular wave number  $\tilde{\nu}$ . For the ideal case of a negligible Stokes shift and a perfect mirror-image relationship of absorption and fluorescence spectrum, (4) simplifies to become the following [38]:

$$k_r = \frac{1}{\tau_0} = 2.88 \times 10^{-9} n^2 \langle \tilde{\nu} \rangle_{\text{av}}^2 \int \varepsilon(\tilde{\nu}) d\tilde{\nu}, \quad (5)$$

where  $\langle \tilde{\nu} \rangle_{\text{av}}$  is the average wave number corresponding to the 0-0 transition. Thus, according to (2) we can write

$$k_r = 0.668 \langle \nu \rangle_{\text{av}}^2 n^2 f. \quad (6)$$

The fluorescence life time can be calculated by using the equation:

$$\tau = \tau_0 \phi_f. \quad (7)$$

TABLE 1: Absorption and fluorescence properties of POPOP in different solvents.

Solvent	$\lambda_{\text{abs}}$ (nm)	$\lambda_f$ (nm)	$\epsilon \times 10^4$ $\text{mol}^{-1} \text{cm}^{-1} \text{dm}^3$	$f$	$k_r \times 10^8 \text{ s}^{-1}$	$\phi_f$	$\tau_f$ (ns)	$k_{\text{isc}} \times 10^8$	$\sigma_a \times 10^{-16} \text{ cm}^2$	$\sigma_e \times 10^{-16} \text{ cm}^2$
<i>n</i> -Heptane	362	416	5.65	1.00	9.79	0.76	0.78	3.02	1.34	2.96
Carbon tetra chloride	370	416	4.89	0.86	8.90	0.74	0.83	3.02	1.16	2.74
Benzene	365	411	5.73	1.02	11.48	0.74	0.65	3.88	1.36	2.56
Toluene	368	418	4.98	0.90	9.95	0.81	0.81	2.29	1.18	2.81
Diethyl ether	362	411	5.12	0.93	8.67	0.73	0.84	3.15	1.22	2.88
Methyl isobutyl ketone	365	418	4.81	0.80	7.93	0.68	0.86	3.63	1.14	2.46
Amyl alcohol	365	424	4.33	0.79	7.95	0.85	1.07	1.36	1.03	2.58
Cyclohexane	363	409	4.48	0.80	8.31	0.76	0.92	2.53	1.06	2.56
Acetone	362	415	5.17	0.93	8.78	0.69	0.78	3.88	1.23	2.88
Ethanol	363	424	4.92	0.97	9.15	0.75	0.82	2.98	1.17	3.03
Methanol	361	424	4.83	0.89	8.09	0.75	0.93	2.58	1.15	2.82
Diethyl formamide	368	425	5.00	0.95	9.62	0.77	0.80	2.83	1.19	2.89
Ethylene glycol	367	439	3.25	0.57	5.82	0.92	1.58	0.47	0.77	2.1
Propylene carbonate	365	430	4.87	0.94	9.58	0.82	0.85	2.10	1.16	3.12

The intersystem crossing rate constant ( $k_{\text{isc}}$ ) is related to the quantum fluorescence yield  $\phi_f$  for ( $\phi_f \approx 1$ ) by the approximate relationship:

$$k_{\text{isc}} = \frac{(1 - \phi_f)}{\tau_f}. \quad (8)$$

The photochemical quantum yield ( $\phi_c$ ) was calculated using the method that was previously described in detail [39] and light intensity was measured by using ferrioxalate actinometry [40].

### 3. Results and Discussion

**3.1. Optical Absorption and Emission Spectra in Different Solvents.** The steady state absorption and emission parameters of  $1 \times 10^{-5} \text{ mol dm}^{-3}$  POPOP were recorded in various non-polar, polar aprotic, and polar protic solvents and are summarized in Table 1. The absorption and emission spectrum of POPOP are shown in Figures 1 and 2, respectively. As shown in Figure 1, the solvent polarity shows a slight effect on the position of electronic absorption spectral maxima, indicating the polar character of POPOP in the ground state.

Fluorescence spectra, on the other hand, are more sensitive to solvent polarity. As solvent polarity increases, the emission spectra become red-shifted, Figure 2. This indicates that the singlet excited state of the POPOP molecule is more polar than the ground state. There is also a good mirror image relationship between absorption and fluorescence spectra. These facts, together with high molar absorptivities ( $\epsilon = 32500\text{--}56500 \text{ mol dm}^{-3} \text{ cm}^{-1}$ ) and high oscillator strength ( $f = 0.57\text{--}1.02$ ), are consistent with a strong  $\pi\text{-}\pi^*$  transition with a small geometry change between electronic ground and excited states [41]. The fluorescence quantum yields  $\phi_f$  are slightly affected by solvent properties; the values of  $\phi_f$  in methyl isobutyl ketone ( $\phi_f = 0.68$ ) and acetone

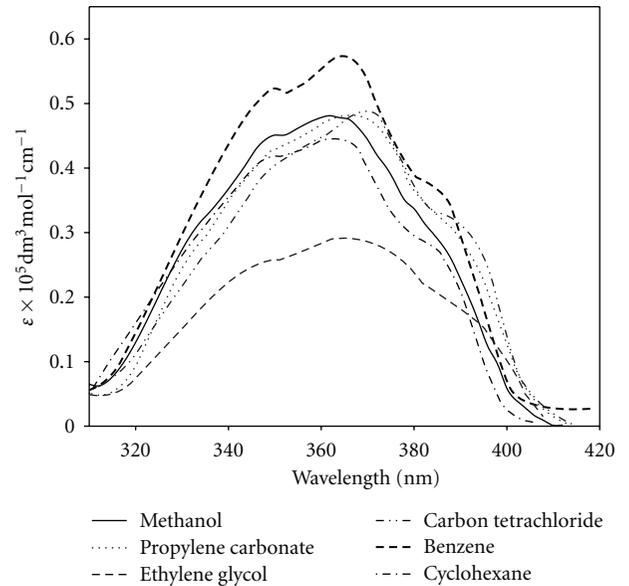


FIGURE 1: Absorption spectra of  $1 \times 10^{-5} \text{ mol dm}^{-3}$  (POPOP) in different solvents.

( $\phi_f = 0.69$ ) are low due to the carbonyl group quenching the singlet excited state via enhancement of intersystem crossing ( $S_1 \rightarrow T_1$ ), while the high value of fluorescence quantum yield in ethylene glycol ( $\phi_f = 0.92$ ) can be explained in term of a cage effect and the role of medium viscosity which decrease the stretching and twisting molecular motion in the excited state, thereby decreasing the nonradiative process [42]. As seen in Table 1, the calculated fluorescence lifetimes obtained using the Strickler-Berg equation are very similar to the measured values. This is expected because the electronic absorption and fluorescence spectrum are nearly mirror image.

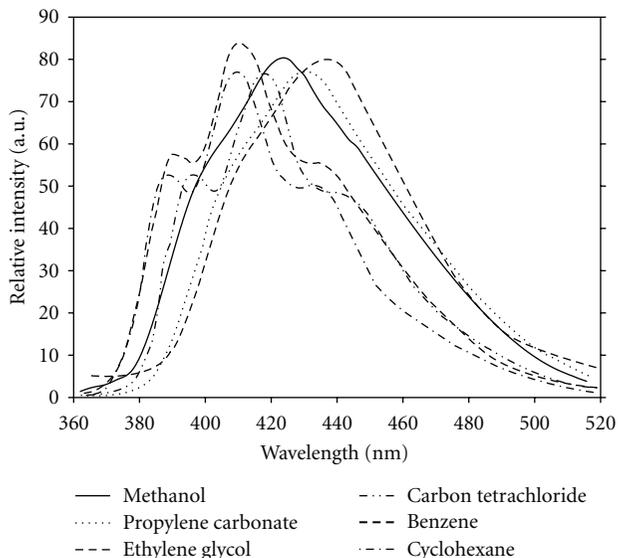


FIGURE 2: Emission spectra of  $1 \times 10^{-5} \text{ mol dm}^{-3}$  (POPOP) in different solvents ( $\lambda_{\text{ex}} = 380 \text{ nm}$ ).

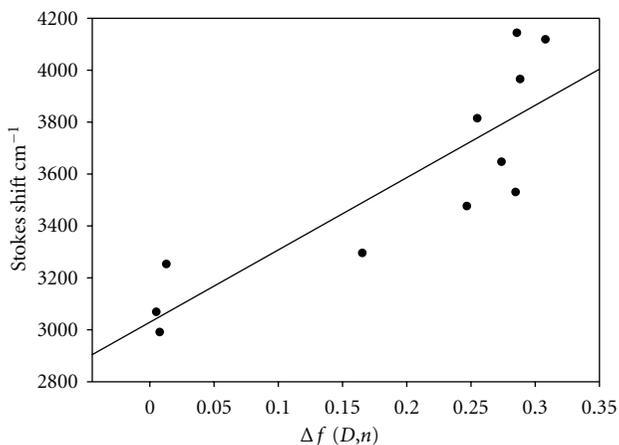


FIGURE 3: Stokes shift versus polarity  $\Delta f$  of POPOP.

**3.2. Determination of Dipole Moments.** Analysis of the solvatochromic effect allows the estimation of difference in the dipole moment ( $\Delta\mu$ ) between the excited singlet and the ground state. This was achieved by applying the simplified Lippert-Mataga equation [43–45]

$$\Delta\tilde{\nu}_{\text{st}} = (\tilde{\nu}_{\text{abs}} - \tilde{\nu}_{\text{em}}) = \frac{2(\mu_e - \mu_g)^2}{hca^3} \Delta f + \text{Constant}, \quad (9)$$

$$\Delta f = \frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1},$$

where  $h$  is the Planck's constant,  $c$  is the velocity of light in vacuum,  $\mu_g$  and  $\mu_e$  are the dipole moments in the ground and excited states, and  $a$  is the Onsager cavity radius of POPOP (taken to be between 4.2–4.7 Å [46]),  $D$ ,  $n$  are the dielectric and refractive index of the solvent, and  $\Delta\tilde{\nu}_{\text{st}}$  is the Stokes shift in  $\text{cm}^{-1}$ , which increases with increase in solvent polarity, pointing to stabilization of excited state in polar

solvents. Figure 3 shows a plot of Stokes shift versus the orientation polarizability ( $\Delta f$ ). The change in dipole moment upon excitation was calculated from the slope of the plot (slope =  $902 \text{ cm}^{-1}$ ) and the cavity radius is  $\Delta\mu = 2.45$  Debye, indicating the polar nature of the excited singlet state.

Bakhshiev's and Kawski-Chamma-Viallet equations [47–51] have been used for the treatment of observed spectral shifts to determine the ground and excited state dipole moments of POPOP.

Bakhshiev's formula is given in

$$\tilde{\nu}_{\text{abs}} - \tilde{\nu}_{\text{em}} = S_1 F_1(D, n) + \text{const.}, \quad (10)$$

where  $\tilde{\nu}_{\text{abs}}$  and  $\tilde{\nu}_{\text{em}}$  are the absorption and fluorescence maxima in wavenumber ( $\text{cm}^{-1}$ ), respectively,  $F_1$  (solvent polarity function) and  $S_1$  are defined as follows:

$$F_1(D, n) = \frac{2n^2 + 1}{n^2 + 2} \left[ \frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right], \quad (11)$$

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3}. \quad (12)$$

Kawski-Chamma-Vaillet's formula is given in

$$\frac{\tilde{\nu}_{\text{abs}} + \tilde{\nu}_{\text{em}}}{2} = -S_2 F_2(D, n) + \text{const.} \quad (13)$$

$F_2$  and  $S_2$  are defined as

$$F_2(D, n) = \frac{1}{2} F_1(D, n) + \frac{3}{2} \left( \frac{n^4 - 1}{(n^2 + 2)^2} \right), \quad (14)$$

$$S_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3}, \quad (15)$$

where the symbols have their usual meaning as given in (9). The parameters  $S_1$  and  $S_2$  can be calculated from (12) and (15); they are the slope of straight lines Figure 4, and the values of  $\mu_g$  and  $\mu_e$  can be obtained from (8) and (10)

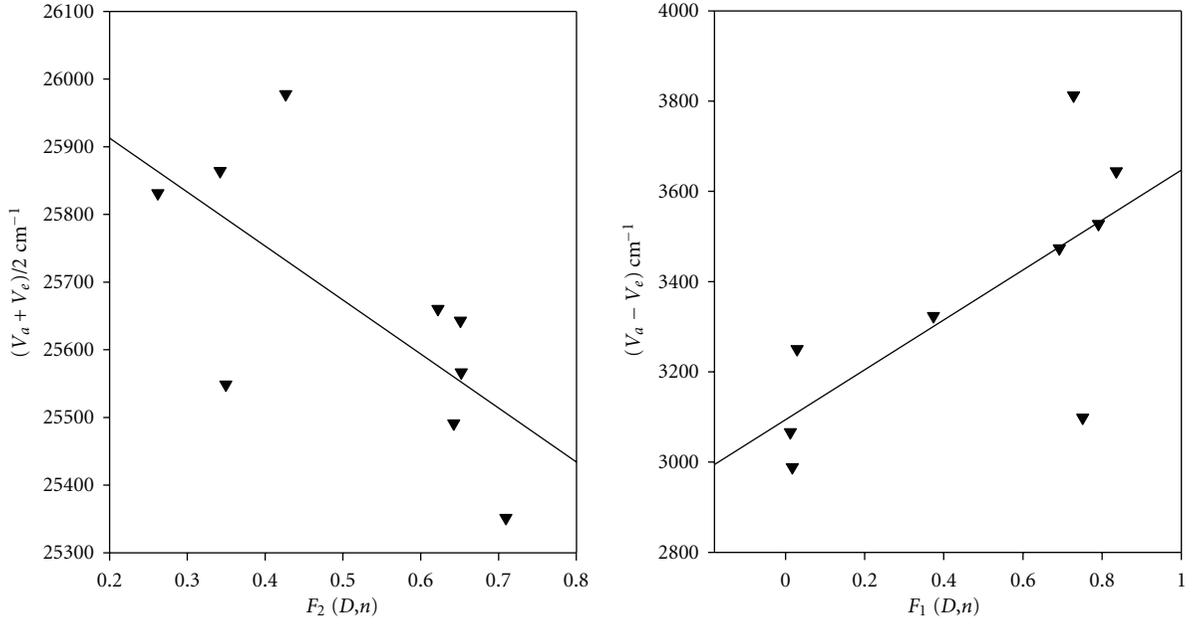
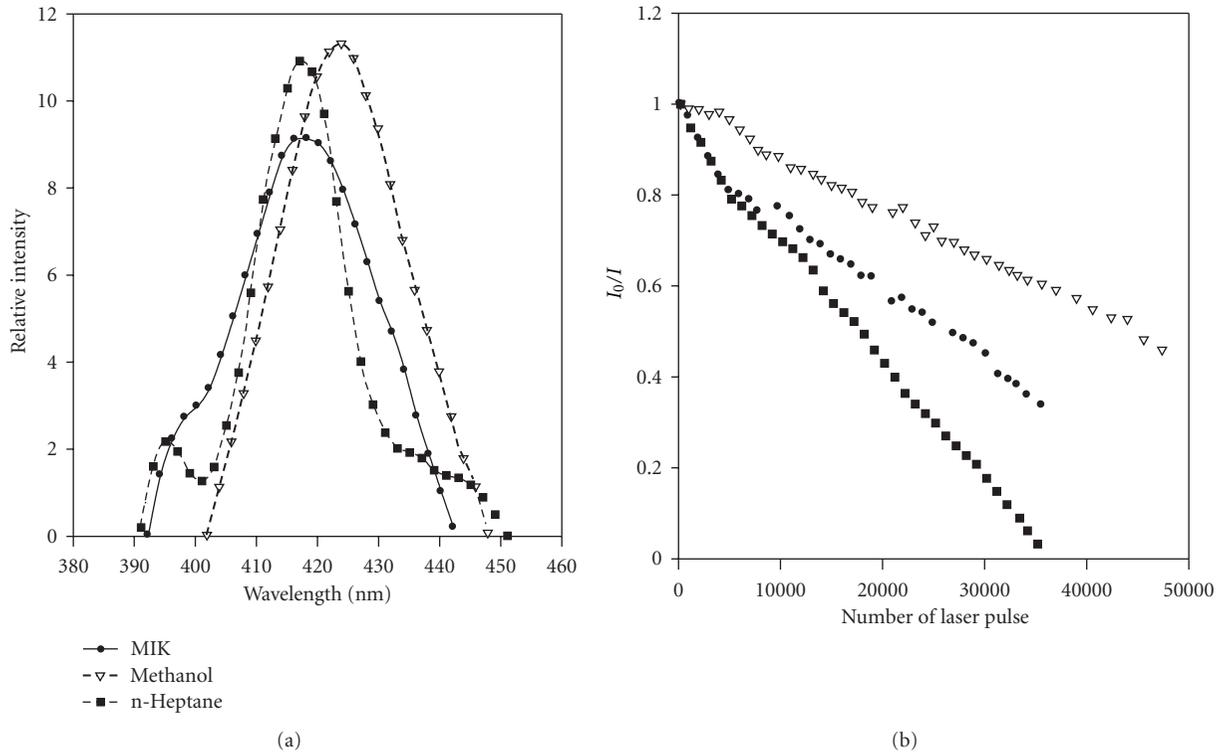
$$\mu_g = \frac{(S_2 - S_1)}{2} \left[ \frac{hca^3}{2S_1} \right]^{1/2},$$

$$\mu_e = \frac{(S_2 + S_1)}{2} \left[ \frac{hca^3}{2S_1} \right]^{1/2}, \quad (16)$$

$$\mu_e = \frac{S_1 + S_2}{S_2 - S_1} \mu_g \quad (S_2 > S_1).$$

The values of  $S_1$  and  $S_2$  were found to be 553 and  $1152 \text{ cm}^{-1}$ , respectively. Thus the calculated values of  $\mu_g$  and  $\mu_e$  were found to be 2.23 and 6.34, respectively.

**3.3. Lasing Action and Fluorescence Quenching of POPOP.** POPOP is characterized by a high fluorescence quantum yield, high molar absorptivity, large Stokes shift, and high photostability in most organic solvents. A solution  $2 \times 10^{-3} \text{ mol dm}^{-3}$  of POPOP in methanol,  $n$ -heptane, and methyl isobutyl ketone (MIK) gives laser emission when using


 FIGURE 4: Stokes shift versus the functions  $F_1(D, n)$  and  $F_2(D, n)$  for POPOP in different solvents.

 FIGURE 5: (a) Lasing range, (b) number of laser pulse versus  $(I_0/I)$  of POPOP in different solvents using nitrogen pulsed laser ( $\lambda = 337$  nm).

a nitrogen pulsed laser ( $\lambda_{\text{ex}} = 337.1$  nm) of 800 ps duration and 1.48 mJ pulse energy. The solution was taken in oscillator and amplifier cuvettes of 10 mm path length. The output energy of the laser dye was measured as a function of wavelength to determine the lasing range in different solvents Figure 5(a). The maximum gain coefficient ( $\alpha$ ) was

calculated at the maximum laser emission by measuring the intensity  $I_L$  of laser emission from the entire cell length  $L$  and the intensity from the cell half length  $I_{L/2}$ . One can calculate the laser gain emission from the following [52]:

$$\alpha(\lambda) = \frac{2}{L} \ln \left[ \frac{I_L}{I_{L/2}} - 1 \right]. \quad (17)$$

It is well known that gain occurs when the stimulated emission of photons exceeds the reabsorption or loss due to scattering. Therefore, gain is the increase in the number of emitted photons and is dependent on both wavelength and incident intensity. The cross section for the stimulated laser emission ( $\sigma_e$ ) of the dye was calculated at the laser emission maximum according to [53]

$$\sigma_e = \frac{\lambda^4 F(\lambda) \phi_f}{8\pi c n^2 \tau_f}. \quad (18)$$

Here  $\lambda$  is the emission wavelength,  $n$  is the refractive index of the solvent,  $c$  is the velocity of light, and  $F(\lambda)$  is the normalized fluorescence line-shape function [54]. The normalized photostability is defined as the accumulated pump energy absorbed by the system per mole of dye molecules before the output energy falls to one half of its initial value using the following relation [55–57]:

$$\begin{aligned} & \text{Normalized photostability (MJ/mol)} \\ &= \frac{E_{\text{pulse}} N_{1/2}}{\pi \times r^2 \times l \times C \times 10^6}, \end{aligned} \quad (19)$$

where  $E_{\text{pulse}}$  is the pulse energy in Joules,  $N_{1/2}$  is the number of pulses to get the half of initial emission intensity Figure 5(b),  $r$  is the radius of the laser beam on surface of sample in cm and  $l$  is the sample thickness in cm ( $l = 1$  cm) and  $c$  is the dye concentration mol·dm<sup>-3</sup>. The laser parameters and normalized photostability of POPOP are listed in Table 2.

The fluorescence quenching of POPOP has also been studied using rhodamine B (RB) and fluorescein as a quencher in methanol. Figure 6 shows the Stern-Volmer plot of POPOP using RB and fluorescein as a quencher by applying the Stern-Volmer relation in the form [58, 59]:

$$\begin{aligned} \frac{I_0}{I} &= 1 + k_{\text{ET}} \tau_f [A] \\ &= 1 + k_q [A], \end{aligned} \quad (20)$$

where  $k_{\text{ET}}$  is the bimolecular quenching rate parameter,  $\tau_f$  is the fluorescence lifetime of the donor in the absence of the acceptor taken as 0.93 ns in MeOH,  $I_0$  and  $I$  are the fluorescence intensities in the absence and in the presence of quencher of concentration  $[A]$  in mol dm<sup>-3</sup>. A plot of  $((I_0/I) - 1)$  versus acceptor concentration  $[A]$  is given in Figure 6. From the slope of Figure 6,  $k_{\text{ET}}$  has been calculated as  $26.2 \times 10^{12}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>,  $10.4 \times 10^{12}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for the POPOP/RB and POPOP/fluorescein systems, respectively. These values are much higher than the diffusion controlled rate constant ( $k_{\text{diff}}$ ) in methanol. We determine the value of  $k_q$  as  $24.4 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup>,  $9.66 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> for the POPOP/RB and POPOP/fluorescein system, and we can calculate the quenching sphere by using the quenching sphere of action model [60, 61]:

$$\ln \frac{I_0}{I} = V N_A [A], \quad (21)$$

where  $V$  the volume of the transient quenching sphere and  $N_A$  the Avogadro's number, the radius of quenching sphere calculated to be 17.9 Å for RB and 13.99 Å for fluorescein.

TABLE 2: Laser parameters of POPOP.

Solvent	$\sigma_e \times 10^{-16}$ cm <sup>2</sup>	Lasing range	$\lambda_{\text{max}}^L$ nm	$\alpha$ cm <sup>-1</sup>	Normalized photostability
Methanol	2.82	408–450	424	1.25	20.94 MJ/mol
<i>n</i> -Heptane	2.96	400–450	417	0.89	8.41 MJ/mol
MIK	2.46	395–440	418	0.58	12.62 MJ/mol

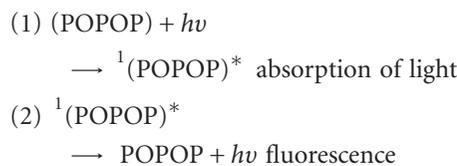
From spectral data it is seen that there is a significant overlap between electronic absorption of acceptor (RB, fluorescein) and the emission spectrum of donor (POPOP) Figures 7(a) and 7(b). Applying Forester's resonance energy transfer mechanism, the critical transfer distance  $R_0$  has been calculated for POPOP/RB and POPOP/fluorescein pair using the following relation [62]:

$$\begin{aligned} R_0^6 &= \frac{9000(\ln 10)k^2 \phi_f J}{128\pi^5 n^4 N_A}, \\ J &= \frac{\int F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda}{\int F_D(\lambda) d\lambda}, \\ R_0^6 &= 1.25 \times 10^{-25} \frac{\phi_f}{n^4} J, \end{aligned} \quad (22)$$

where  $F_D(\lambda)$  is the corrected normalized fluorescence intensity of donor in the absence of the acceptor at wavelength  $\lambda$ , and  $\epsilon_A(\lambda)$  is the molar absorption coefficient of the acceptor at  $\lambda$ ,  $N_A$  Avogadro's number, the orientation factor  $k^2 = 2/3$  was taken to be a reference state. Accordingly, the critical transfer distance  $R_0$  was found as 25 and 33 Å for POPOP/RB and POPOP/fluorescein pair, respectively. This value is higher than that for collision energy transfer in which  $R_0$  values are in the range of 4–6 Å [63]. The high value of the critical transfer distance as well as the quenching rate constant indicates that the underlying mechanism of energy transfer is that of resonance energy transfer due to long-range dipole-dipole interaction between excited donor and ground state acceptor.

#### 3.4. Photoreactivity of POPOP in Chloromethane Solvents.

The photoreactivity of POPOP was studied in CCl<sub>4</sub>, CHCl<sub>3</sub> and CH<sub>2</sub>CH<sub>2</sub> solvents. Upon irradiation of a  $2 \times 10^{-5}$  mol dm<sup>-3</sup> solution of POPOP at 366 nm ( $I_0 = 4 \times 10^{-6}$  Einstein min<sup>-1</sup>), the absorbance of dye decreases upon increasing the irradiation time and a new absorption peak appears at 260 nm Figure 8. This indicates the formation of photoproduct in a solvent cage. The net photochemical quantum yields of the underlying reaction were calculated as 0.61, 0.103, and 0.067 for CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>, respectively (Figure 9). The formation of photoproduct is a one photon process as represented by the well-known mechanism [64–67]:



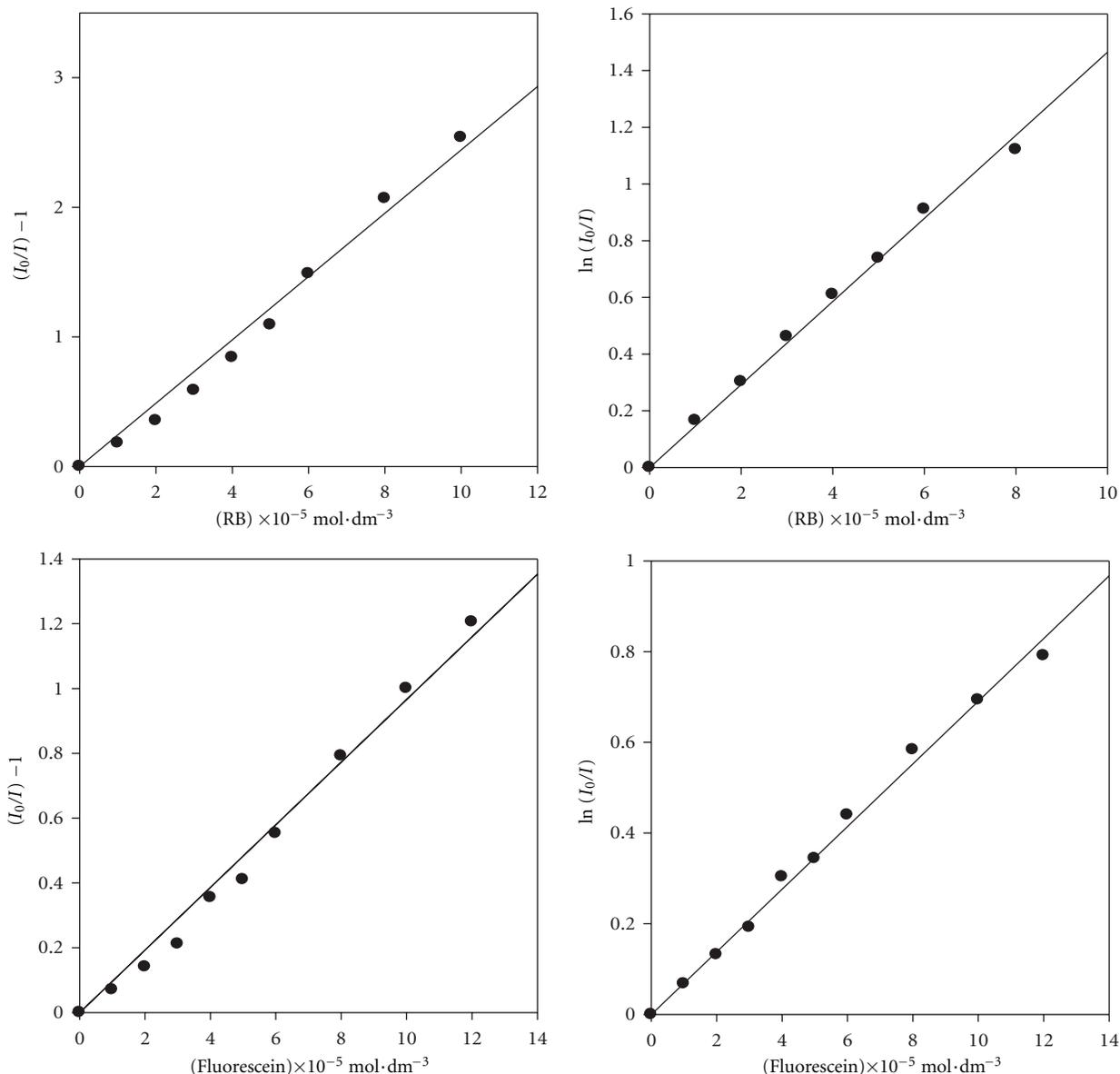
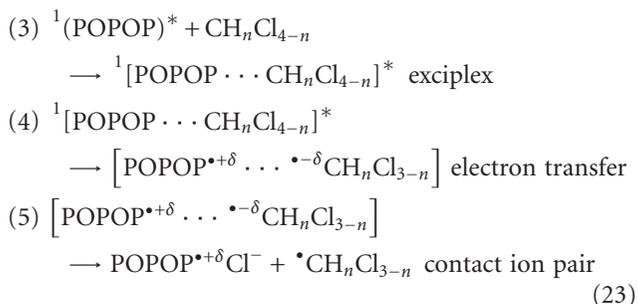


FIGURE 6: Stern-Volmer plots for fluorescence quenching of  $1 \times 10^{-5} \text{ mol dm}^{-3}$  POPOP by RB and fluorescein in methanol ( $\lambda_{\text{ex}} = 337 \text{ nm}$ ).



It was proposed that the electron transfer from the excited singlet POPOP to  $\text{CH}_n\text{Cl}_{4-n}$  within the transient excited charge transfer complex (exciplex) is the main primary photochemical process. This leads to the POPOP radical cation,

a chloride ion and a chloromethyl radical in the solvent cage Step (5).

The formation of constant ion pair usually occurs by electron transfer from excited donor molecule ( $\text{POPOP})^*$  to the acceptor ( $\text{CH}_n\text{Cl}_{4-n}$ ). The rate constant of photoreactivity of POPOP was calculated by applying the simple first order rate equation:

$$\ln \frac{A_0 - A_\infty}{A_t - A_\infty} = kt, \tag{24}$$

where  $A_0$ ,  $A_t$ , and  $A_\infty$  are the initial absorbance, absorbance at time ( $t$ ), and infinity, respectively. The rate constant was found to be 0.024, 0.011, and  $0.005 \text{ min}^{-1}$  in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$ , respectively. It was found that the net photochemical quantum yield ( $\phi_c$ ) and the observed rate constant

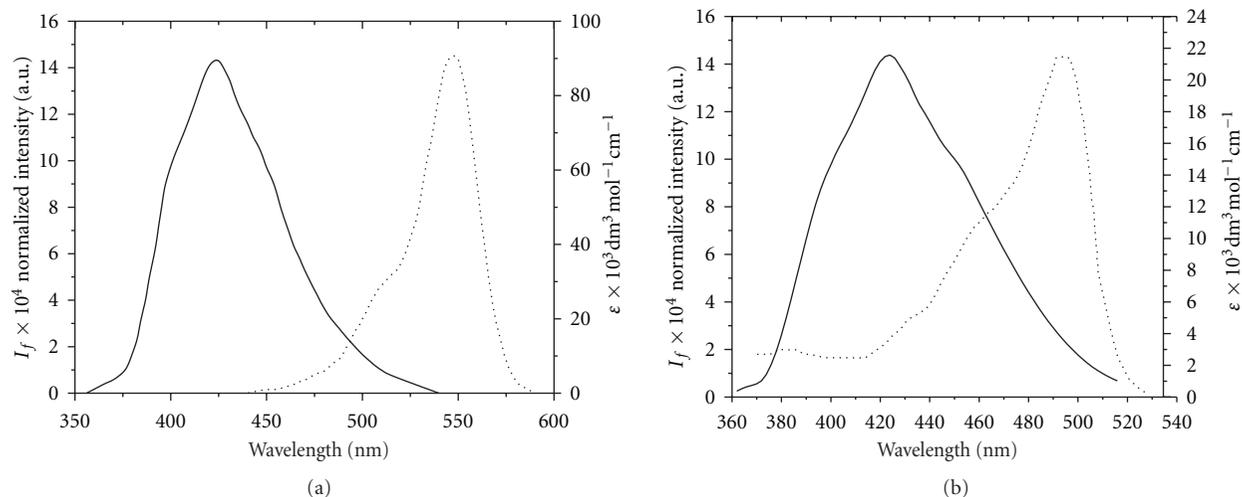


FIGURE 7: (a) Normalized emission spectrum of  $1 \times 10^{-5} \text{ mol dm}^{-3}$  of POPOP (—) and absorption spectrum ( $\cdots$ ) of  $1 \times 10^{-5} \text{ mol dm}^{-3}$  of RB in methanol, (b) normalized emission spectrum of  $1 \times 10^{-5} \text{ mol dm}^{-3}$  of POPOP (—) and absorption spectrum ( $\cdots$ ) of  $1 \times 10^{-5} \text{ mol dm}^{-3}$  of fluorescein in methanol.

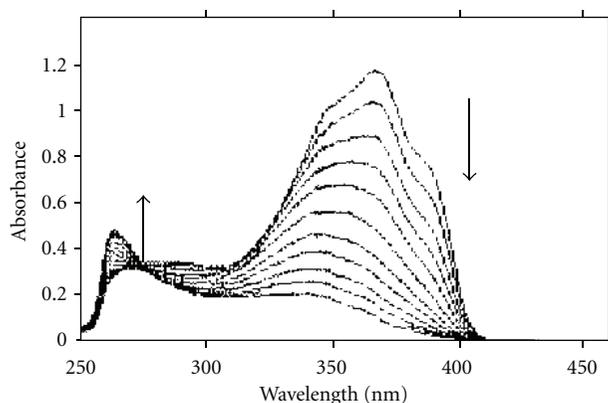


FIGURE 8: The change in absorption spectra of  $2 \times 10^{-5} \text{ mol dm}^{-3}$  of POPOP in  $\text{CCl}_4$  as a result of UV irradiation ( $\lambda_{\text{ex}} = 366 \text{ nm}$ ). The irradiation times at decreasing absorbance are 0.0, 1, 2, 3, 4, 5, 6, 7, 8, 10, and 11 min.

(*k*) increases with increase in the electron affinity ( $E_A$ ) of chloromethane solvents ( $E_A$  equal 2.12, 1.75 and 1.36 eV for  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , resp.), indicating that the electron affinity of the solvent plays a role in the photoreactivity and controls the photochemical reaction. The POPOP dye is highly photostable in polar protic and aprotic solvents, since no change in absorbance of dye was observed upon prolonged irradiation by using either 336 or 254 nm light for about 24 hours.

#### 4. Conclusion

The ground and excited state dipole moments of POPOP were determined as 2.3 and 6.34 Debye, respectively. The dye solution in methanol, *n*-heptane, and methyl-isobutyl ketone

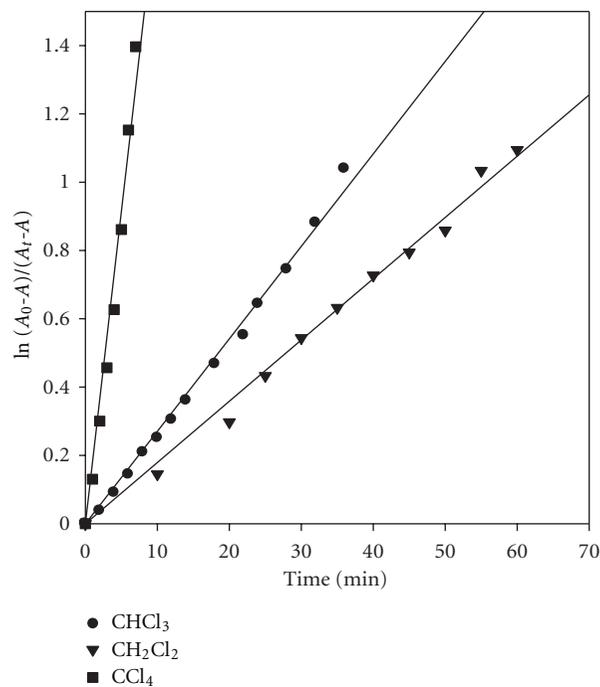


FIGURE 9: First order plots of photoreactivity of POPOP in chloromethane solvents.

gives laser emission in blue region with emission maximum in the range 417–450 nm upon pumping by nitrogen laser pulse. POPOP act as a good energy donor for rhodamine B and fluorescein laser dyes, the energy transfer rate constant and critical transfer distance are determined. POPOP dye is highly photostable in polar solvents but displays photodecomposition in chloromethane solvents via electron transfer from excited dye to solvent molecules.

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