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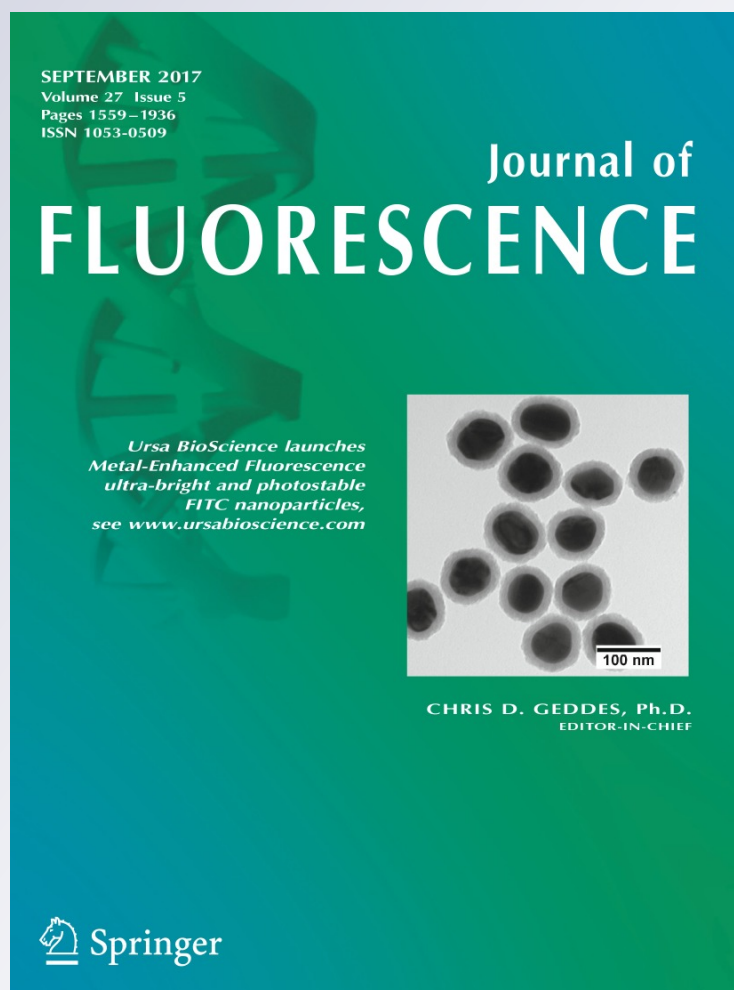
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Photophysical Properties of a Novel and Biologically Active 3(*2H*)-Pyridazinone Derivative Using Solvatochromic Approach

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Abstract Herein, we report photophysical properties of a novel and biologically active 3(*2H*)-pyridazinone derivative 5-(4-chloro-2-hydoxy-phenyl)-2-phenyl-*2H*-pyridazin-3-one [CHP] molecule using solvatochromic approaches. Absorption and fluorescence spectra of CHP molecule have been measured at room temperature in various solvents of different polarities. From this, it is observed that the positions, intensities and shapes of the absorption and emission bands are usually modified. Experimentally, the ground and excited state dipole moments are estimated using solvatochromic shift method which involves Lippert's, Bakshiev's and Kawski-Chamma-Viallet's equations. Theoretically, the ground state dipole moment was estimated using the Gaussian-09 program. The value of ground state dipole moment estimated using experimental and theoretical methods are well correlated. This inference that the molecular geometry is taken for CHP molecule under theoretical and experimental methods are similar. Further, we observed that the excited state dipole moment (μ_e) is greater than the ground state dipole moment (μ_g) which indicates that the excited state is more polar than the ground state. Furthermore, we have estimated an angle between the ground and excited state dipole moments. In addition, we have estimated the fluorescence quantum yield of CHP molecule using Rhodamine B as a standard reference in different solvents.

Introduction

The 3(*2H*)-pyridazinones are the pyridazine derivatives contain two adjacent nitrogen atoms at the one and second positions in a six-membered ring and a carbonyl group at the third position and they have different functionalities in their structure [1, 2]. These derivatives generally exhibit broad spectrum showing biological activities such as anticancer, antimicrobial, analgesic, anti-inflammatory, antituberculosis, antipyretic, antiplatelet, adrenoreceptor antagonist, antidiabetic, COX inhibitors and acetylcholinesterase activities [3]. They are also known as weedicidal and muticidal agents [4].

Excitation of a molecule by photon causes a redistribution of charges leading to conformational changes in the excited state. This can result in increase or decrease of the dipole moment of the excited state as compared to the ground state. The dipole moment of an electronically excited state of a molecule is an important property that provides information on the electronic and geometrical structures of the molecule in the short-lived state. Knowledge of the excited state dipole moment of electronically excited molecules is quite useful in designing nonlinear optical materials [5]. A number of techniques e.g. electronic polarization of fluorescence, electric-dichroism and microwave conductivity [6–8] were available for estimation of excited-state dipole moment, but their use is limited because they are considered equipment sensitive and studies have been related to very simple molecules. As the solvatochromic method does not use any external field, it is experimentally much simpler and widely accepted. The solvatochromic method is based on the shift of absorption

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and fluorescence maxima in different solvents of varying polarity. Using solvatochromic shift method dipole moment in the ground and excited states have been determined for a variety of dyes namely coumarin [9–11], benzimidazolone [12], pyridazinone [13, 26], quinoline [14], acridine, phenazine [15] and exalite [16].

Fluorescence quantum yields are among the most important parameters in spectroscopic analysis. Fluorescence quantum yield is a direct measure of the fraction of excited molecules that return to the ground state with emission of fluorescence photons. In other words, it is the ratio of the number of emitted photons to the number of absorbed photons and it is given by Eq. 1

$$\phi = \frac{Number\ of\ emitted\ photons\ (S_1 \rightarrow S_0 - h\upsilon)}{Number\ of\ absorbed\ photons\ (S_0 + h\upsilon \rightarrow S_1)} \quad (1)$$

Quantum yield provides important information regarding excited states, radiationless transitions and coupling of electronic to vibronic states. Moreover, they are used in the estimation of chemical structures, sample purity and appropriateness of laser media. Several researchers have calculated quantum yields of different fluorescence molecules in order to explore various aspects like solute-solvent interactions, solvent polarity induced structural changes and their use as standards [17–19]. The fluorescence quantum yield can be classified as absolute and relative. While measuring absolute quantum yield they required more sophisticated instrumentation. It is easy to measure the fluorescence quantum yield using a relative method. In this method, the fluorescence quantum yield of molecule is calculated by comparing it to a standard reference (with a known fluorescence quantum yield). There are two types in the relative method for the estimation of fluorescence quantum yield namely; single point method and comparative method. Here, we used single point method for our study. The single point method involves comparison of the integrated spectrally corrected fluorescence intensity of a dilute fluorescence solution with that of standard reference under same experimental conditions.

In the present work, we have reported the estimation of ground and excited state dipole moments of CHP molecule using solvatochromic approach. The ground state dipole moment is also estimated theoretically using the Gaussian-09 program. Further, we have estimated an angle between the ground and excited state dipole moments. In addition, we have estimated the fluorescence quantum yield of CHP molecule using Rhadamine-B as a standard reference in different solvents.

Materials and Methods

The 3(*2H*)-pyridazinone derivative 5-(4-chloro-2-hydroxyphenyl)-2-phenyl-*2H*-pyridazin-3-one [CHP] was synthesized according to reference [20] and its molecular structure is
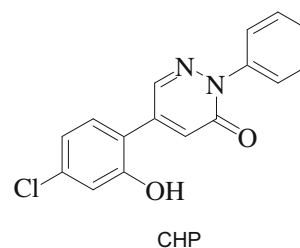
Fig. 1 The molecular structure of CHP

shown in Fig. 1. The spectroscopic grade solvents methanol, ethanol, acetonitrile, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), propan-2-ol, ethyl acetate, tetrahydrofuran (THF), 1, 4-dioxane and toluene were obtained from S.D. Fine Chemicals Ltd. India. Rhodamine B was purchased from HIMEDIA Laboratories Pvt. Ltd. India. Required solutions were prepared at fixed solute concentration in all solvents. In order to achieve the optical density [OD] value less than 0.1, the solute concentrations were taken from the order of 1×10^{-5} M/L in all solvents.

The absorption and emission spectra of CHP molecule were recorded using the UV-visible spectrophotometer [Model: Hitachi U-3310, USIC, K U Dharwad, India] and fluorescence spectrophotometer [Model: Hitachi F-7000, USIC, K U Dharwad, India] respectively. The refractive index of the CHP molecule is measured using Abbe's refractometer. All these measurements were carried out at room temperature.

Solvatochromic Approach

The ground and excited state dipole moments were estimated using solvatochromic approach which involves Lippert's, Bakshiev's and Kawski-Chamma-Viallet's equations.

1. Lippert's Eq. [21] is Given by

$$\overline{\upsilon_a} - \overline{\upsilon_f} = S_1 F(\varepsilon, n) + Constant \quad (2)$$
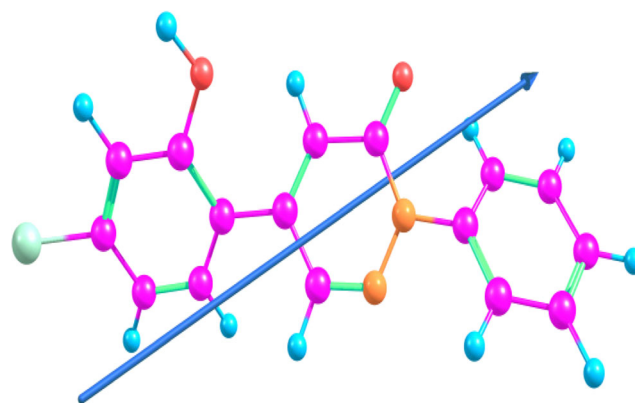
Fig. 2 The ground state optimized geometry of CHP molecule

Table 1 The solvatochromic data and calculated polarity function used for the estimation of dipole moments

Solvent	λ_a (nm)	λ_f (nm)	$\overline{v_a}$ (cm^{-1})	$\overline{v_f}$ (cm^{-1})	$\overline{v_a}-\overline{v_f}$ (cm^{-1})	$\frac{\overline{v_a}+\overline{v_f}}{2}$ (cm^{-1})	$F(\varepsilon,n)$	$F_1(\varepsilon,n)$	$F_2(\varepsilon,n)$
1. Methanol	246	399	40,650.41	25,062.66	15,587.75	32,856.53	0.309	0.857	0.652
2. Ethanol	256	352	39,062.5	28,409.09	10,653.41	33,735.80	0.288	0.811	0.651
3. Acetonitrile	273	329	36,630.04	30,395.14	6234.90	33,512.59	0.304	0.861	0.664
4. DMSO	262	382	38,167.94	26,178.01	11,989.93	32,172.97	0.841	0.744	0.440
5. DMF	287	363	34,843.21	27,548.21	7294.99	31,195.71	0.275	0.839	0.711
6. Propan-2-ol	279	378	35,842.29	26,455.03	9387.26	31,148.66	0.276	0.780	0.646
7. Ethyl acetate	256	356	39,062.50	28,089.89	10,972.61	33,576.19	0.200	0.492	0.499
8. THF	289	360	34,602.08	27,777.78	6824.29	31,189.93	0.209	0.547	0.207
9. 1,4-Dioxane	214	391	46,728.97	25,575.45	21,153.52	36,152.21	0.029	0.061	0.316
10. Toluene	286	340	34,965.03	29,411.76	5553.27	32,188.40	0.015	0.033	0.359

2. Bakhshiev's Eq. [22] is Given by

$$\overline{v_a}-\overline{v_f} = S_2 F_1(\varepsilon, n) + Constant \tag{3}$$

3. Kawski-Chamma-Viallete's Eq. [23] is Given by

$$\frac{\overline{v_a}+\overline{v_f}}{2} = -S_3 F_2(\varepsilon, n) + Constant \tag{4}$$

where,

$F(\varepsilon,n) = \left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{\varepsilon-1}{2\varepsilon+1}\right]$ is Lippert's polarity function

$F_1(\varepsilon,n) = \frac{2n^2+1}{n^2+2}\left[\frac{2n^2+1}{n^2+2} - \frac{2n^2+1}{n^2+2}\right]$ is Bakhshiev's polarity function

$F_2(\varepsilon,n) = \left[\frac{2n^2+1}{2(n^2+2)}\left(\left[\frac{2n^2+1}{2(n^2+2)} - \frac{2n^2+1}{2(n^2+2)}\right]\right) + \frac{2n^2+1}{2(n^2+2)}\right]$ is KCV polarity function
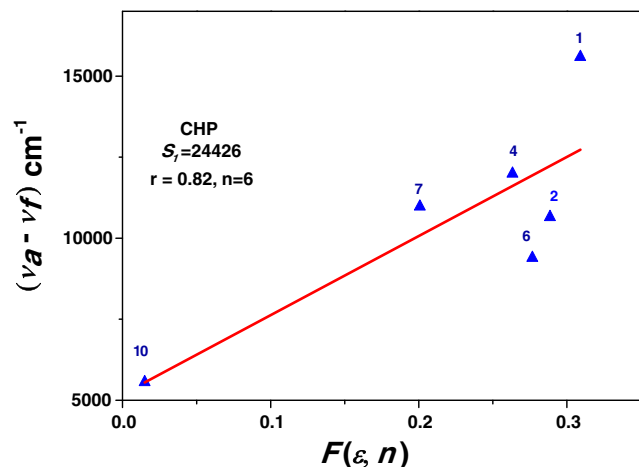
The plot of ($\overline{v_a}-\overline{v_f}$) versus $F(\varepsilon, n)$ for different solvents gives the slope S_1, given by

$$S_1 = \left[\frac{2\left(\mu_e-\mu_g\right)^2}{hca^3}\right] \tag{5}$$

The plot of ($\overline{v_a}-\overline{v_f}$) versus $F_1(\varepsilon, n)$ for different solvents gives the slope S_2, given by

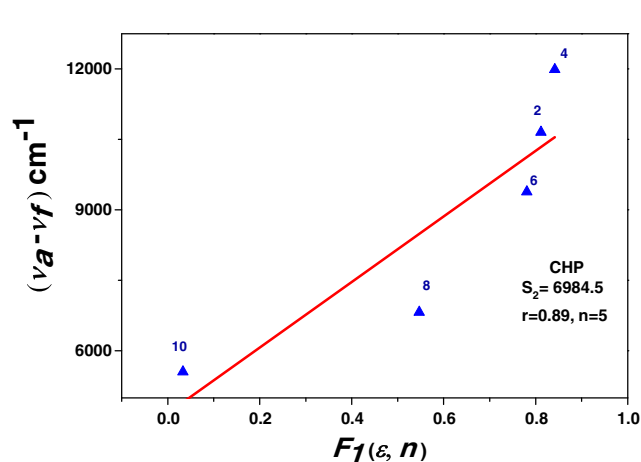$$S_2 = \left[\frac{2\left(\mu_e-\mu_g\right)^2}{hca^3}\right] \tag{6}$$

The plot of $\left(\frac{\overline{v_a}+\overline{v_f}}{2}\right)$ versus $F_2(\varepsilon, n)$ for different solvents gives the slope S_3, given by
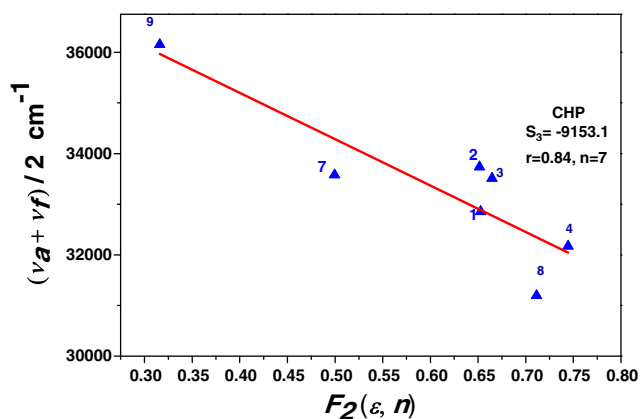

Fig. 3 The graph of ($\overline{v_a}-\overline{v_f}$) versus $F(\varepsilon, n)$. 1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9.1,4-Dioxane and 10.Toluene

Fig. 4 The graph of ($\overline{v_a}-\overline{v_f}$) versus $F_1(\varepsilon, n)$. 1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9.1, 4-Dioxane and 10.Toluene

Fig. 5 The graph of $(\frac{\overline{v_a}+\overline{v_f}}{2})$ versus $F_2\,(\varepsilon, n)$. 1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9.1, 4-Dioxane and 10.Toluene

$$S_3 = \left[\frac{2\left(\mu_e^2 - \mu_g^2\right)}{hca^3}\right] \qquad (7)$$

where, μ_g and μ_e are the ground and excited state dipole moments of the solute molecule. ε and n are the dielectric constant and refractive index of the respective solvents used in the experiment. The symbols h, c and a are the Planck's constant, velocity of light in vacuum and Onsager cavity radius of the solute molecule respectively. Onsager cavity radius of the molecule was estimated using the method as suggested by Edward [24].

Further, it was noted in Bakhshiev's and Kawski-Chamma-Viallete's equations, if the ground and excited state dipole moments are parallel and the symmetry of the investigated solute molecule remains unchanged upon electronic transition, then the following expressions may be obtained

$$\mu_g = \frac{S_3 - S_2}{2}\left[\frac{hca^3}{2S_2}\right]^{\frac{1}{2}} \qquad (8)$$

$$\mu_e = \frac{S_3 + S_2}{2}\left[\frac{hca^3}{2S_2}\right]^{\frac{1}{2}} \qquad (9)$$

An angle between the ground and excited state dipole moments were estimated using an Eq. (10)

$$\cos\theta = \frac{1}{2\mu_g\mu_e}\left[\left(\mu_g^2 + \mu_e^2\right) - \frac{S_2}{S_3}\left(\mu_e^2 - \mu_g^2\right)\right] \qquad (10)$$

Gaussian-09 Program

The theoretical value of ground state dipole moment (μ_g) of CHP molecule was estimated using a Gaussian-09 program [basis set: 6-31G and method: B3LYP] [25]. The corresponding optimized molecular geometry is used as shown in Fig. 2. The arrow in molecular geometry indicates the direction of dipole moment.
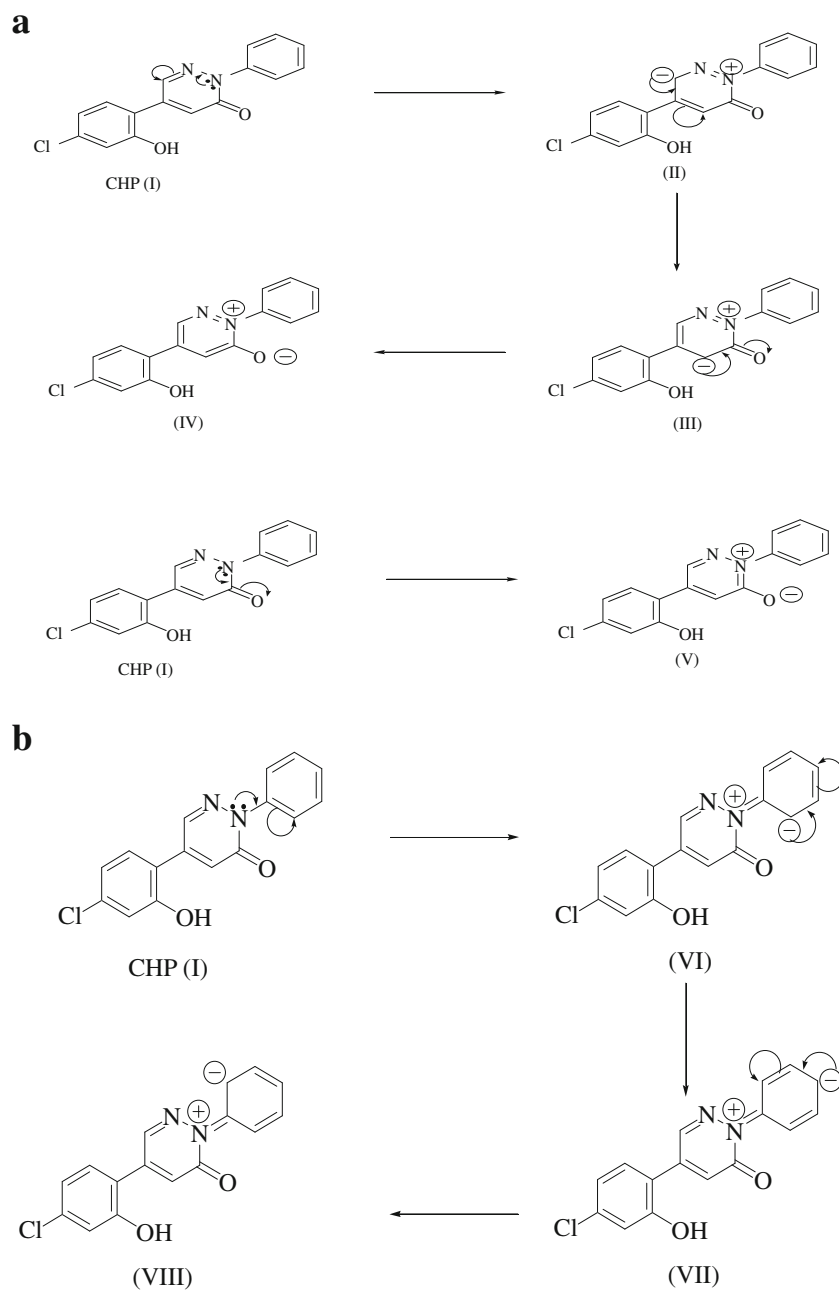
2.3 Relative Method

The fluorescence quantum yield has been measured using the relative method in which the quantum yield is obtained by comparing the fluorescence intensity of sample solution with that of standard solution. The fluorescence quantum yield is calculated using an Eq. (11)

$$\Phi_f = \Phi_r \left(\frac{F_f}{F_r}\right)\left(\frac{A_r}{A_f}\right)\left(\frac{n_f^2}{n_r^2}\right) \qquad (11)$$

where f and r stand for the sample and standard reference respectively. F is the integrated fluorescence intensity. A is the absorbance of the solution.

Here we have chosen Rhodamine B as a standard reference.

Table 2 Radius, statistical correlation values and dipole moments of CHP molecule in the ground and excited states

Molecule	Radius (a) A°	Statistical correlation			Dipole moment						θ
		Slope (cm^{-1})	Correlation co-efficient	Number of points	μ_g^a (D)	μ_g^b (D)	μ_e^c (D)	μ_e^d (D)	μ_e^e (D)	μ_e^f (D)	0
CHP	3.89	$S_1 = 24{,}426$	0.82	6	0.99	2.93	7.38	12.43	7.38	7.38	
		$S_2 = 6984.5$	0.89	5							
		$S_3 = -9153.1$	0.84	7							

1 Debye = 3.33564×10^{-30} cm = 10^{-18} esu cm

[a] The ground state dipole moment calculated from the Eq. (8)

[b] The ground state dipole moment calculated Gaussian-09 program

[c] The excited state dipole moment calculated from the Eq. (9)

[d] The excited state dipole moment calculated from Lippert's Eq. (5)

[e] The excitede state dipole moment calculated from Bakshiev's Eq. (6)

[f] The excited state dipole moment calculated from KCV Eq. (7)

θ An angle between the ground state and excited state dipole moments calculated from Eq. (10)

Fig. 6 Resonance structures of CHP

$$\Phi_r = 0.31$$
$$F_r = 2362484.255$$
$$A_r = 0.094$$
$$n_r = 1.3625$$

Results and Discussion

The steady-state absorption and fluorescence measurements of CHP molecule were made in different solvents of different polarities at room temperature. Based on these studies, the absorption maxima wave number ($\overline{v_a}$), fluorescence maxima

wave number ($\overline{v_f}$), Stokes shift ($\overline{v_a} - \overline{v_f}$), arithmetic mean of wave number ($\frac{\overline{v_a} + \overline{v_f}}{2}$) for CHP molecule were obtained and are shown in Table 1. Solvent polarity functions F (ε, n), F_1 (ε, n) and F_2 (ε, n) in different solvents are also shown in Table 1. From the Table 1, it is observed that the Stokes shift increases with solvent polarity, this may be due to $\pi \rightarrow \pi^*$ transition. The graphs of ($\overline{v_a} - \overline{v_f}$) versus F (ε, n), ($\overline{v_a} - \overline{v_f}$) versus F_1 (ε, n) and ($\frac{\overline{v_a} + \overline{v_f}}{2}$) versus F_2 (ε, n) were plotted and are shown in Fig. 3, Fig. 4 and Fig. 5 respectively. Using the ORIGIN 8 software the data fitted to a straight line. The values of slope, intercept, correlation coefficient and the number of data points
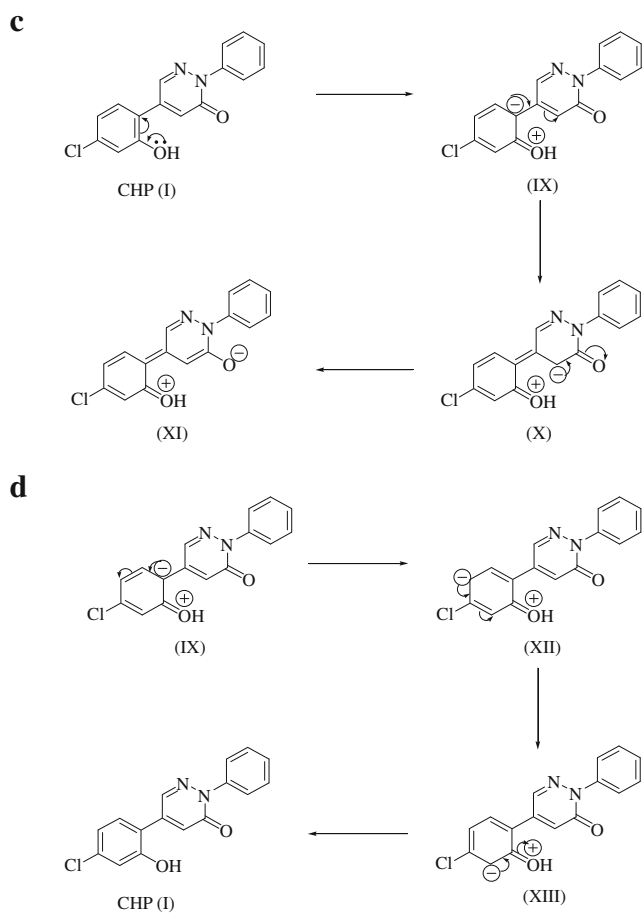
c

d

Fig. 6 (continued)

of fitted lines are shown in Table 2. In almost all cases, the correlation coefficient value indicates the good linearity. The ground and excited state dipole moments were estimated using Eqs. (8) and (9) are shown in Table 2.
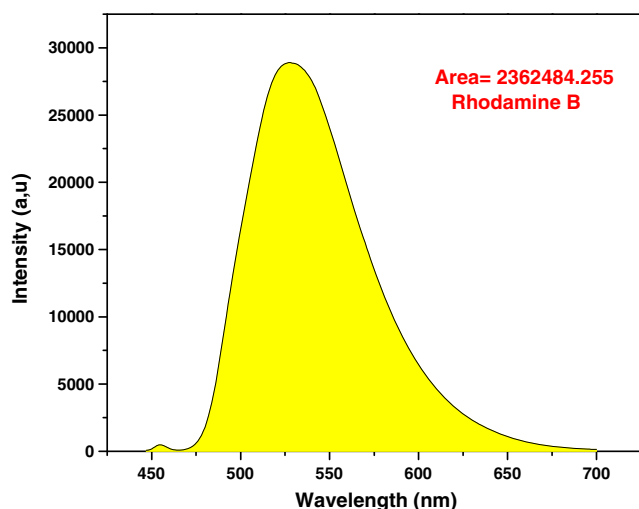

Fig. 7 Fluorescence spectrum of Rhodamine B along with the integrated area in ethanol solvent

In order to verify the some of the inferences discussed above the excited state dipole moment was calculated using Lippert's, Bakshiev's and Kawski-Chamma-Viallet's equations. In these equations, ground state dipole moment calculated from Eq. (8) is used and these values are shown in Table 2, from this it is clear that the dipole moment of CHP molecule is higher in the first excited state as compared to the ground state. Theoretically, the ground state dipole of CHP molecule is estimated using the Gaussian-09 program and this value is shown in Table 2. From above results, it is observed that the value of the excited state dipole moment of CHP molecule is found to be greater than the ground state dipole moment. Thus, it may be inferred that the excited state is more polar than the ground state. Further, an angle between the ground and excited state dipole moments is found to be 0°. This inference that the ground and excited state dipole moments are parallel. The variation in dipole moment value can be explained in terms of possible resonance structures of the molecule. The resonance structures of CHP molecule is shown in Fig. 6 (a-d). These resonance structures arise due to delocalization of π electrons. The fluorescence spectrum of Rhodamine-B along with the integrated area in ethanol solvent is shown in Fig. 7. Fluorescence spectra of CHP molecule along with their corresponding integrated area in different solvents are shown in Fig. 8. The values of OD, integrated fluorescence area, the refractive index of solute in different solvents are shown in Table 3. Using values of refractive index, the optical density of absorption spectra and fluorescence integrated area of CHP molecule in different solvents and corresponding values of standard reference the fluorescence quantum yield for CHP molecule in different solvents is calculated and these values are also shown in Table 3.

4. Conclusion

The effect of solvents on absorption and emission spectra of newly synthesized CHP molecule was studied, it is observed that the absorption and fluorescence band maxima of CHP molecule shifts to lower wavelength it may be due to π → π* transition. Theoretically, the ground state dipole was estimated using the Gaussian-09 program. The value of μ_g obtained using these two methods is well correlated. This inference that the molecular geometry is taken for CHP molecule under theoretical and experimental methods are similar. The excited state dipole moment of CHP molecule was estimated using solvatochromic approach which involves three equations proposed by Lippert's, Bakshiev's and Kawski-Chamma-Viallet's. The value of excited state dipole moment calculated using these three equations is well correlated. It can be seen that the dipole moment is significantly higher in the excited state than in the ground state. This indicates that the CHP molecule is more polar in the excited state than in the
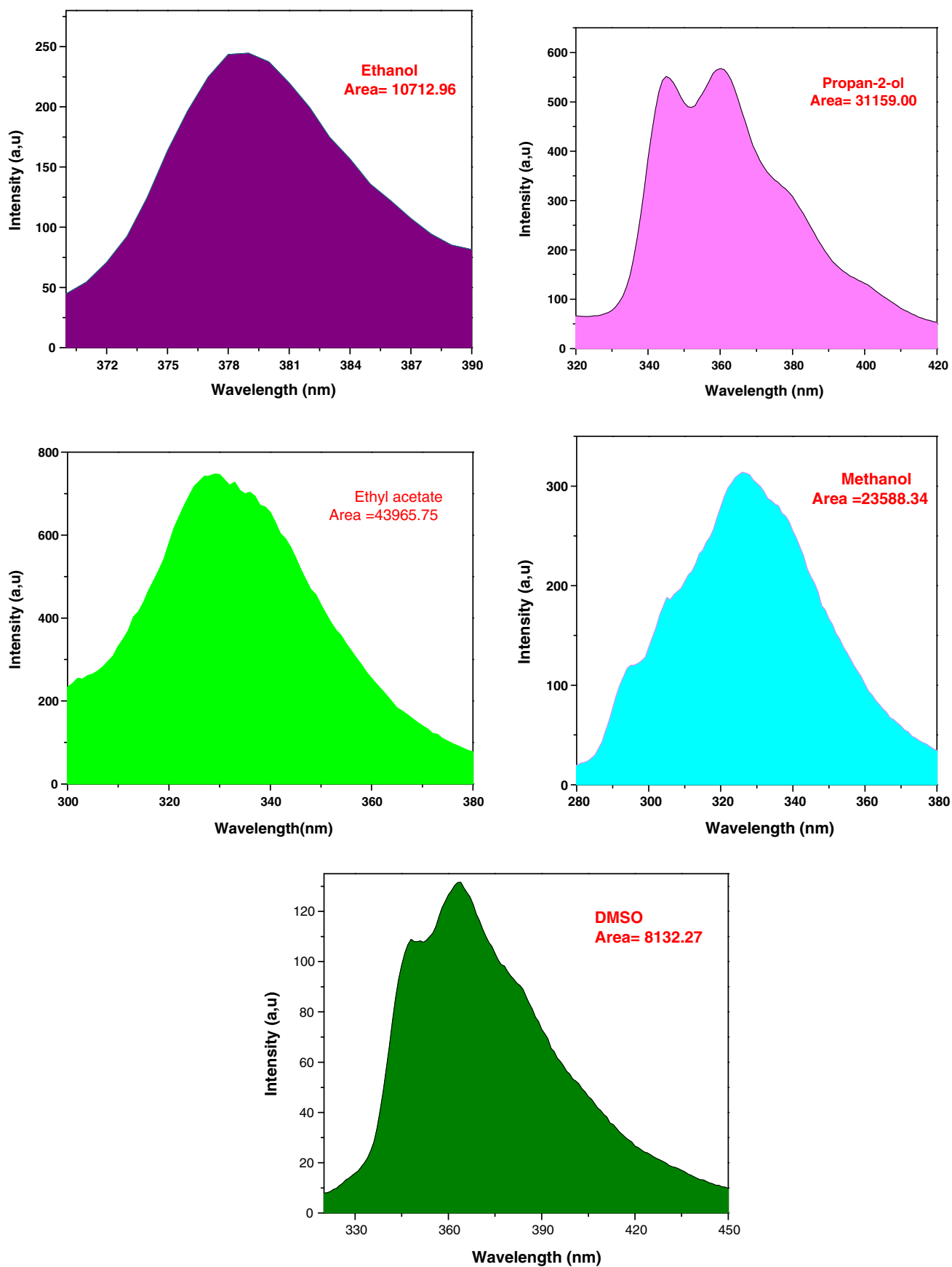
Fig. 8 Fluorescence spectra of CHP molecule along with the integrated area in different solvents

Table 3 Values of refractive index, optical density, integrated fluorescence area and quantum yield of CHP molecule in different solvents

Solvent	Refractive index	O.D	Integrated fluorescence area	Fluorescence quantum yield (%)
Ethanol	1.3620	0.0990	10,712.96	0.133
Methanol	1.3293	0.0822	23,588.34	0.337
Propan-2-ol	1.3775	0.0592	31,159.00	0.665
DMSO	1.4792	0.0521	8132.27	0.227
Ethyl acetate	1.3728	0.0314	43,965.73	1.750

ground state. Further, the angle between the ground and excited state dipole moments is found to be 0°. This inference that the ground and excited state dipole moments are parallel.

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