



Solvatochromic Study of Ground and Excited State Dipole moments of Pyrrromethene Laser Dyes

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Abstract

The photophysical properties of two commercial pyrrromethene dyes namely PM567 and PM580 are studied in a variety of solvents namely polar protic and polar aprotic at room temperature. The probes show bathochromic and hypsochromic shift in absorption and fluorescence spectra with increasing solvent polarity indicating $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. The solvatochromic correlations are used to obtain the ground and excited state dipole moments. The excited state dipole moments are greater than their ground state counterparts for the probes in the solvents studied indicating that the dyes are more polar in excited state than in ground state. The experimentally obtained difference of dipole moments are compared with those calculated using normalized polarity terms E_{N} from Reichardt equation.

Keywords: Pyrrromethene dyes, Dipole moment, Solvatochromic shift, Solvent polarity, Electrostatic potential.

1.0 INTRODUCTION

In recent years, the study of electric dipole moment of fluorophores in the excited state is gaining interest considerably. A molecule excited by a photon undergoes redistribution of electron density and correspondingly change in the dipole moment therein [1]. The ground and excited state dipole moments of organic molecules thus reveal information on the electronic and geometrical structure of the molecule in the excited state. Knowledge about the excited electronic state dipole moment of the solute molecule is quite useful not only in designing non linear materials and in elucidation of the nature of excited state. Though the ground state dipole moment of a chromophore can be measured, there is a lack of reliable technique for the estimation of short lived excited state dipole moment. Among the numerous ways of determining excited state dipole moment (μ_e), electro optical methods like electrochromism of absorption and fluorescence bands [2], the effect of an external electric field on the fluorescence anisotropy [3], Stark splitting of rotational levels of the 0-0 vibrational bands [4] etc., the solvatochromic method based on the spectral shift of absorption and fluorescence maxima caused by the solvent effects is the simplest and widely used [5]. The effect of the solvent on the UV-Vis absorption spectra can be used to determine the magnitude as well as the direction of electric dipole moment of solute in its first electronically excited

state. The excited state dipole moments of fluorescent dye molecules are useful to determine the tunability range of the emission energy as a function of polarity of the medium [6].

There is increased interest in the properties of pyrrromethene (PM) dyes due to their luminescence properties as an active media in tunable organic dye lasers. Dipyrrromethene-BF₂ (PM) fluorophores are highly fluorescent dyes and used for such diverse applications as bio labels, artificial light harvesters, sensitizers for solar cells, fluorescent sensors, molecular fluorescent wires and electron transfer reagents. Further these dyes are also very useful for laser applications since they have a low intersystem crossing rate and low triplet excitation coefficients over the laser spectral region and often possess a triplet-triplet absorption coefficient about one-fifth that of the rhodamin dyes [7]. Pyrrromethene compounds are the ionic dyes exhibiting good solubility in many organic solvents and even in methyl methacrylate (MMA) that is useful for solid state dye laser applications. Some of the PM dyes outperform the widely used laser dye rhodamine 6G. However the small Stokes shift often hinders the use of PM dyes as active lasing media due to the ground state absorption at the lasing wavelength. This problem has been partially resolved by incorporating bicyclic rigid aryl substitutes at the 8th position of the molecule [8]. PM dyes absorb and fluoresce strongly in the yellow-green region and are characterised by a high fluorescent quantum yield

[9, 10]. While the laser characteristics of PM dyes have been extensively studied [11-14], still some of their photo physical properties have to be explored. Arbeloa et al. [15] have summarized the photo physical information of PM dyes and studied the influence of structural and environmental factors on their photo physics. Soumyaditya Mula et al. [7] have added some structural groups at the 8th position of the dye molecule to enhance the photo stability and lasing efficiency. There are many reports on the photo stability of PM567 and PM 597 in liquid and solid gel media [16-21].

Extensive experimental and theoretical study with different methods has been carried out by several researchers on the ground state and excited state dipole moments of various organic fluorescent compounds such as coumarins [1,22-25], indoles [26,27], purines [28,29], exalite dyes [30,31], curcuminoid dyes [32], hemi cyanine dyes [6], acridinedione dyes [33], hydroxycoumarin dyes [34], fluorescein [35], flavones [36], prodan, badan and acrylodan [37], quinazolines [38], acridines and phenazines [39], pyromethenes [40] and in some laser dyes [41,42].

In this paper, we have reported the determination of ground and excited state dipole moments of PM567 and PM580 from systematic experimental study of solvent effect on the absorption, emission and solvatochromic shift and have compared the results with the theoretically computed ground and excited state dipole moments from density functional theory (DFT) and configuration interaction singles (CIS) respectively.

1.1 Theory

In a solution the overall interaction between solute and solvent molecules is due to the dielectric property of the solvent medium. Therefore the shift between the absorption and emission spectra is related to the refractive index (n) and dielectric constant (ϵ) of the solvent [42,43].

In fluorescence spectroscopy, the equation developed by Lippert [44, 45] and Mataga et al, [46, 47] based on Onsager's reaction field theory, is the most commonly used. According to this theory, the fluorophore is a point dipole residing in the centre of a spherical cavity of radius a , in a homogeneous, isotropic dielectric with relative permittivity ϵ . In presence of specific interactions such as hydrogen bonding or electron pair donor /acceptor interactions, along with non-specific interactions the Lippert-Mataga equation is not applicable.

Based on quantum mechanical perturbation theory [48,49] of absorption and fluorescence band shift of a spherical solute in different solvents of varying permittivity (ϵ) and refractive index (n) relative to the band position of the solute molecule, the difference between the dipole moment

of ground and first excited singlet state describes the following equations [50].

$$v_a - v_f = m_1 f(\epsilon, n) + \text{const} \quad (1)$$

$$v_a + v_f = -m_2 [f(\epsilon, n) + 2g(n)] + \text{const} \quad (2)$$

where v_a and v_f are the steady state peak absorption and fluorescence frequencies, and

$$f(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (3)$$

is the solvent polarity parameter [49] and

$$g(n) = \frac{3}{2} \left[\frac{n^4 - 1}{(n^2 + 2)^2} \right] \quad (4)$$

with

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (5)$$

and

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (6)$$

where h is Plank's constant and c , the velocity of light in vacuum whereas μ_g and μ_e are the ground and excited state dipole moments respectively. The parameters m_1 and m_2 can be determined from equation (1) and (2) and values of μ_g and μ_e from equation (5) and (6) assuming that the symmetry of the probe molecule remains unchanged upon electronic transition, and the ground and excited state dipole moments are parallel [51],

$$\mu_g = \frac{|m_2 - m_1|}{2} \left[\frac{hca^3}{2m_1} \right]^{\frac{1}{2}} \quad (7)$$

$$\mu_e = \frac{|m_2 + m_1|}{2} \left[\frac{hca^3}{2m_2} \right]^{\frac{1}{2}} \quad (8)$$

$$\frac{\mu_e}{\mu_g} = \frac{|m_2 + m_1|}{|m_2 - m_1|} \quad (9)$$

Parameters m_1 and m_2 are linear functions of the solvent polarity parameters $f(\epsilon, n)$ and $f(\epsilon, n) + 2g(n)$ and can be determined from the slopes of straight lines. The Onsager cavity radius a can be determined by computational calculations.

Reichardt [52] proposed an empirical polarity scale, the method based on which gave better results of solvatochromic shift of dipolar molecules that correlates much better with microscopic solvent polarity E_T^N rather than traditionally used bulk solvent polarity functions involving ϵ and n . Accordingly the excited state dipole moment is determined using equation [53]

$$\nu_a - \nu_b = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_B} \right)^2 \left(\frac{a_B}{a} \right)^3 \right] E_T^N + \text{Constant} \quad (10)$$

where $\Delta\mu_B = 9D$ and $a_B = 6.2 \text{ \AA}$ are the change in dipole moment on excitation and Onsager radius respectively for betaine dye and also are the corresponding quantities for the molecule of interest.

E_T^N is defined using water and tetra methyl silane (TMS) as extreme reference solvents with the equation

$$E_T^N = \frac{E_T(\text{Solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} = \frac{E_T(\text{Solvent}) - 30.7}{32.4} \quad (11)$$

Then the change in dipole moment is,

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{m \times 81}{\left(\frac{6.2}{a} \right)^3}} \times 11307.6 \quad (12)$$

where m is the slope of linear plot of E_T^N against Stokes shift.

2.0 MATERIALS AND METHODS

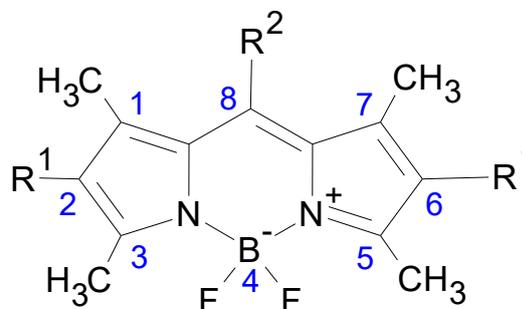
The commercially available laser dyes PM567 and PM580 were obtained from Lambda Chrome and were used as received. The solvents used for the study are of spectroscopic grade (HPCL, Fluka). Steady state absorption and fluorescence spectra (intrinsic photo physical properties) at room temperature were obtained using UV-

Vis ratio recording spectrophotometer (Hitachi, model U-2800) and fluorescence spectrofluorometer (JY Horiba, model Fluoromax-4) respectively, in dilute solutions using quartz cuvette. The concentration of the solutions was kept quite low ($\approx 10\mu\text{M}$ - $15\mu\text{M}$) in order to avoid self absorption and aggregation.

All of the studied dipyrromethene- BF_2 (4,4-difluoro-4-bora-3a,4a-diaza-5-indacene) fluorophores possessed methyl groups at the 1,3,5 and 7 positions and differ in the substitution at 2,6 and 8 positions. The commercially available laser grade PM dyes (Exciton, Chemical Co. USA) have alkyl groups, methyl at position 8, and ethyl (PM567) or butyl (PM580) at the 2 and 6 positions. Theoretical calculations were carried out using Gaussian-09 software.

3.0 RESULTS AND DISCUSSION

The structure of dyes PM567 and PM580 are shown in Fig. 1. The polarity of the molecule depends on its electron distribution. The absorption of an additional energy will cause the transition of an electron from HOMO to LUMO orbital. This will cause a change in dipole moment with respect to the ground state dipole moment [6]. For the estimation of excited state dipole moment we recorded the absorption and emission spectra of the two dye molecules in solvents of varying polarity with dielectric constant (ϵ) varying from 8 for decanol to 111 for formamide. The absorption spectra showed maxima at 517 nm and 519 nm for PM567 and PM580 respectively in ethanol, with a shift of the maxima depending on the polarity of the solvent used. The emission spectra have been recorded by exciting the sample at its absorption maximum. The shift in the absorption and emission maxima has been observed as a function of solvent polarity. The observed emission and absorption spectra of these dyes do not show much broadening. The spectral shift in absorption observed in all solvents is larger for PM567 compared to PM580 indicating large change in the energy distribution and more polar in ground state between two dyes.



	R ¹	R ²
PM567	C ₂ H ₅	CH ₃
PM580	(CH ₂) ₃ CH ₃	CH ₃

Fig. 1: Structure of Pyrromethene molecules.

The wave numbers (ν) of absorption and emission maxima along with solvent parameters refractive index (n), dielectric constant (ϵ) and the microscopic polarity scale $f(\epsilon, n)$, are summarized in Table 1 & 2 for the two dyes. In order to estimate the ground and excited state dipole moments of the solute molecules, the solvent polarity parameters $f(\epsilon, n)$ and $f(\epsilon, n) + 2g(n)$ were calculated (Table 2). Figs. 2 & 3 show the respective spectral shifts $\nu_a - \nu_f$ and $\nu_a + \nu_f$ for the dyes observed in alcohols and general solvents against the polarity function $f(\epsilon, n)$ and $f(\epsilon, n) + 2g(n)$ respectively. The plots show a linear correlation. The slopes m_1 and m_2 of the paired plots were used to estimate the ground and excited state dipole moments with the help of equation (7) and (8). The value of m_2 is usually observed to be negative; however it is observed to be positive in some cases of the present study as reported in the references [6,35,38]. The difference in the dipole moments was evaluated and compared with that calculated using equation (12). A small change in dipole moment for PM dyes was observed, which suggests that the emission from this dye originates from states which although more polar than ground state, are probably similar to the locally excited states [6].

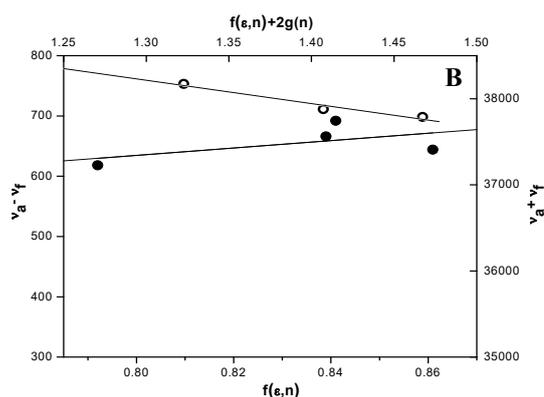
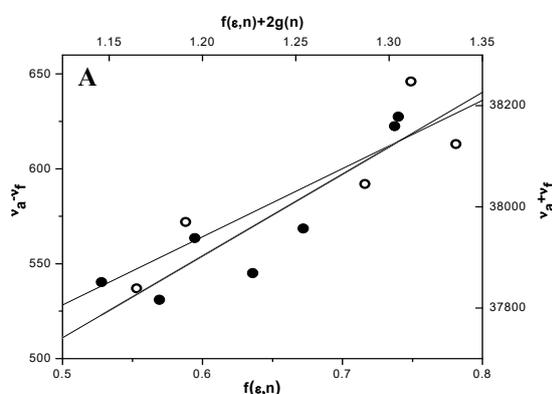


Fig. 2: Plot of $\nu_a - \nu_f$ vs. $f(\epsilon, n)$ and $\nu_a + \nu_f$ vs. $f(\epsilon, n) + 2g(n)$ of PM567 in (A) alcohols and (B) general solvents.

Kemlet-Taft solvent properties namely π^* , α , β , refractive index (n) and dielectric constant (ϵ) [54,55] are used along with the spectral positions of the dye solutions in all the solvents, to study the solvent effect on the ground and excited state dipole moment. The total dipole moment of the molecule in the given excited state is the sum of the initial dipole moment and an induced dipole contribution associated with the solvent reaction field, which is proportional to polarizability (α) of the solute in that state. Thus it follows that $\alpha_e \gg \alpha_g$.

At the simplest level, solvent dependent shifts of the fluorescence emission spectra are interpreted in terms of Lippert-Mataga equation, which describes the Stokes shift $\Delta\nu = \nu_a - \nu_f$ as a function of interaction between the change of dipole moment upon excitation and the dipoles in solvents of different dielectric constants and refractive indices [44,46,47]. The model used to derive the equation is based on a point dipole in a spherical cavity of solvent, resulting in a net stability in their ground state. During electronic transition, if the dipole moment of solute increases, the excited state is formed inside the cavity which is surrounded by partly oriented solvent dipoles. The net stabilization of excited state as compared to ground state results in bathochromic shift with $\mu_e > \mu_g$. A decrease of dipole moment of solute during electronic excitation results in an excited state with strained solvent cavity of oriented dipoles not correctly disposed for its efficient stability. Thus the energy of the ground state is lowered more than that of the excited state with increasing solvent polarity resulting in a hypsochromic shift. Consequentially ground state in this case is more dipolar than excited state with $\mu_g > \mu_e$ [52]. A general observation thus is, an increase in Stokes shift with increasing solvent polarity, indicates increased dipole moment on excitation. In such cases the relaxed excited state S_1 will be at equilibrium with respect to ground state S_0 and hence a significant red shift of fluorescence is observed [6,25].

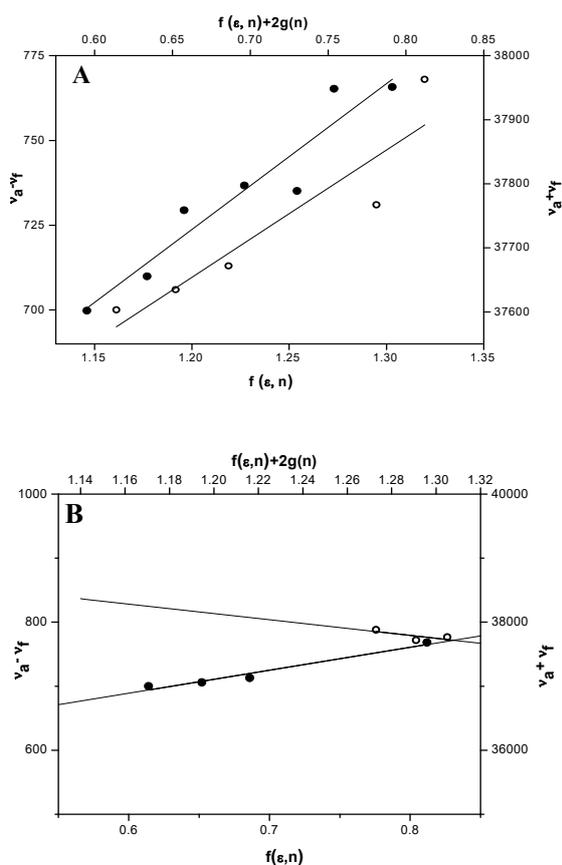


Fig. 3: Plot of $\nu_a - \nu_f$ vs. $f(\epsilon, n)$ and $\nu_a + \nu_f$ vs. $f(\epsilon, n) + 2g(n)$ of PM580 in (A) alcohols and (B) general solvents

Use of Lippert-Metaga equation is limited to transitions where the excited state reached after absorption is also the emissive state and where the excited state dipole moment is independent of solvent polarity [56]. For polar solutes like PM567 and PM580 the interaction with non polar solvents (alkanes) depends on the dipole- induced dipole force, while with polar aprotic solvents the solute solvent interaction depends on stronger dipole- dipole forces. In protic solvents like alcohols we find specific interaction such as hydrogen bonding along with strong dipole-dipole interaction as the hydroxyl group in alcohol forms the hydrogen bond due to inter molecular charge transfer (ICT). Hydrogen bonding interaction puts a severe limitation on the validity of eqn. (1) and (2). It is therefore useful to use the solvent polarity function $E_T(30)$ [57] for understanding the polarization dependence of spectral characteristics. $E_T(30)$ with unit kcal /mole is not used in SI units, and the normalized E_T^{21} values given by eqn. (11) are recommended.

Table 1: Spectral data of PM567 & PM580 in various solvents.

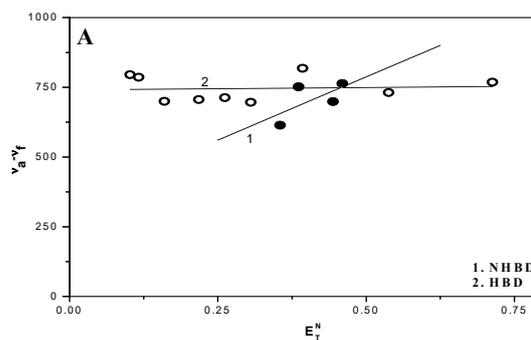
Solvent	ν_a/cm^{-1}		ν_f/cm^{-1}		$\Delta\nu/\text{cm}^{-1}$	
	PM 567	PM 580	PM 567	PM 580	PM 567	PM 580

Methanol	19380	----	18798	-----	582	----
Ethanol	19361	19286	18798	18518	563	768
Propanol	19305	19249	18692	18518	613	731
Butanol	19268	19268	18622	18450	646	818
Pentanol	19249	19249	18657	18553	592	696
Hexanol	19231	19231	18726	18518	505	713
Heptanol	19212	19231	18657	18525	555	706
Octanol	19212	19212	18726	18512	486	700
Nonanol	19194	19212	18622	18426	572	786
Decanol	19194	19194	18657	18399	537	795
DMF	19361	19305	18695	18553	666	752
DMSO	19342	19286	18650	18587	692	699
Acetone	19380	19342	18762	18734	618	608
Acetntrle	19455	19399	18811	18636	644	763

---- Dyes insoluble.

Fig. 4 (A) and (B) show the plots of Stokes shift as a function of E_T^{21} in all solvents for PM567 and PM580. The linear dependence of E_T^{21} on Stokes shift shows the existence of general type of solute solvent interaction in which the Stokes shift depends on refractive index n , and dielectric constant ϵ of the solvents.

The Onsager cavity radius a_0 is evaluated by three methods. In the first, a_0 is determined by the relation $a_0 = \left[\frac{3V}{4\pi} \right]^{1/3}$ where V is the Van der Waal volume of the probe molecule obtained from Edward's atomic increment method. Secondly a_0 is taken as equal to the semi major axis. Cavity radius is also obtained from computational calculation using GAUSSIAN 09 software [58]. The ground and excited state dipole moments evaluated using different values of cavity radius are listed in Table 3. The slopes m_1



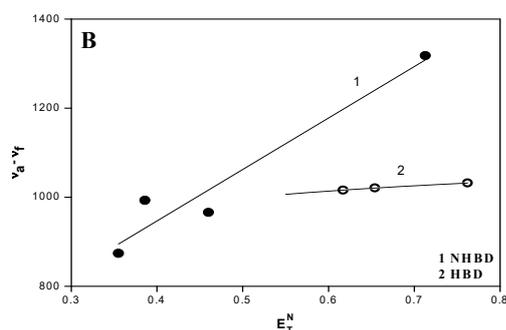


Fig. 4: Plot of $\nu_g - \nu_f$ vs. E_T^N for (A) PM567 and (B) PM580 in general solvents (NHBD) & alcohols (HBD).

and m_2 obtained from the plots of solvent shift vs solvent polarity functions function along with ground and excited state dipole moments calculated using these values are summarised in Table 4. The difference in dipole moments calculated using eqn. (12) and obtained from the listed values are reasonably in good agreement for all solvents used. The ground and excited state dipole moments for

Table 2: Some solvent polarity parameters with physical constants of different solvents.

Solvent	n^a	ϵ^a	E_T^N (a)	$f(\epsilon, n)$	$2g(n)$	$\varphi(n)$
Methanol	1.329	33.7	0.762	0.857	0.448	1.305
Ethanol	1.361	24.3	0.654	0.812	0.491	1.303
Propanol	1.385	20.6	0.617	0.781	0.524	1.304
Butanol	1.399	17.4	0.586	0.749	0.542	1.296
Pentanol	1.410	14.8	0.568	0.716	0.557	1.277
Hexanol	1.418	13.0	0.559	0.686	0.568	1.254
Heptanol	1.424	11.3	0.549	0.652	0.575	1.236
Octanol	1.429	9.8	0.537	0.614	0.582	1.209
Nonanol	1.434	9.0	0.528	0.588	0.589	1.172
Decanol	1.437	8.0	0.525	0.553	0.593	1.143
DMF	1.430	38.2	0.386	0.839	0.583	1.423
DMSO	1.479	47.2	0.444	0.841	0.648	1.489
Acetone	1.359	21.0	0.355	0.792	0.489	1.281
Acetntrle	1.344	36.6	0.460	0.861	0.469	1.330

^a taken from ref. 52 and $\varphi(\epsilon, n) = f(\epsilon, n) + 2g(n)$

PM567 and PM580 were also determined from basis set B3LYP/6-31+G(d) and CIS/6-31+G(d) [58] and are shown in Fig 5. (a) and (b). The arrow in the figure indicates the direction of transition dipole moment in the ground state and excited state. The ground and excited state dipole moments for PM567 and PM580 calculated from

Table 4: Slopes (m_1 and m_2), Dipole moments (μ_g and μ_e) in Debye (D), $\Delta\mu$, correlation factor (r) and Number of data (n).

solvatochromic shift and computational methods agree fairly well.

The knowledge about delocalization of electron in the molecule is of great importance as it gives rise to the electric dipole moment. The possible resonance structures of dyes under study are shown in Fig. 6. The lone pair electrons of sp^3 hybridized ring Nitrogen atoms can delocalize throughout aromatic rings. Further, electrostatic potential map provides visualization of the electron delocalization in dyes (Fig. 7a&7b), in which red coloured regions indicate the most negative electrostatic potential and the blue coloured region represents the most positive electrostatic potential. Other colours indicate intermediate levels of attraction.

Table 3: Calculated values of dipole moments for different values of cavity radius of the two dye molecules in alcohols

- ^a van der Waal's radius calculated using atomic increment method
- ^b Suppan equation
- ^c from Gaussian 09.
- ^d Semimajor axis
- ^e Calculated from DFT with basis set B3LYP/6-31+G(d).
- * Calculated using eqn. (12).

Mole cule	Radius (Å)	μ_g (D)	μ_e (D)	μ_e/μ_g	$\Delta\mu$ (D)	$\Delta\mu^*$
PM 567	4.68 ^a	4.78	6.69	1.4	1.912	0.84
	4.65 ^b	4.74	6.63	1.4	1.894	0.83
	5.61 ^c	6.28	8.79	1.4	2.509	1.10
	7.3 ^d	10.93	15.29	1.4	4.362	1.63
		4.44 ^e	4.92 ^e	1.1	0.48	
PM 580	5.31 ^a	5.62	7.73	1.38	2.11	0.61
	4.88 ^b	4.91	6.75	1.38	1.85	0.53
	5.88 ^c	7.00	8.54	1.22	1.54	0.71
	9.16 ^d	12.72	17.5	1.38	4.78	1.38
		4.40 ^e	4.88 ^e	1.11	0.48	---

4.0 CONCLUSION

We have estimated the dipole moments of two dipolar laser dyes namely PM567 and PM580 in various solvents in the ground and excited states as a function of solute solvent interaction by solvatochromic shift method. The bathochromic and hypsochromic shift observed in the absorption and fluorescence spectra indicates $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. We have observed a

Probe molecule	Radius ^b (Å)	solvents	m ₁	m ₂	μ _g (D)	μ _e (D)	μ _e /μ _g	Δμ (D)	r	n
PM567	4.68	i. Alcohols	126	1705	5.14	7.17	1.40	2.03(0.84) ^a	0.90:0.75	9:9
		ii. General solvents	703	1758	2.34	4.83	2.07	2.50(0.77) ^a	0.97:0.92	3:3
PM580	5.31	i. Alcohols	300	1896	5.62	7.73	1.38	2.11(0.61) ^a	0.81:0.90	5:7
		ii. General solvents	2178	1118	1.61	5.02	3.11	3.41(0.71) ^a	0.76:0.75	4:3

^a Calculated using Eqn.(12)

^b Van der Waal radius

Parameter	PM567	PM580
Ground state		
Excited state		

Fig. 5: Gaussian optimised ground and excited state structures with dipole moment direction.

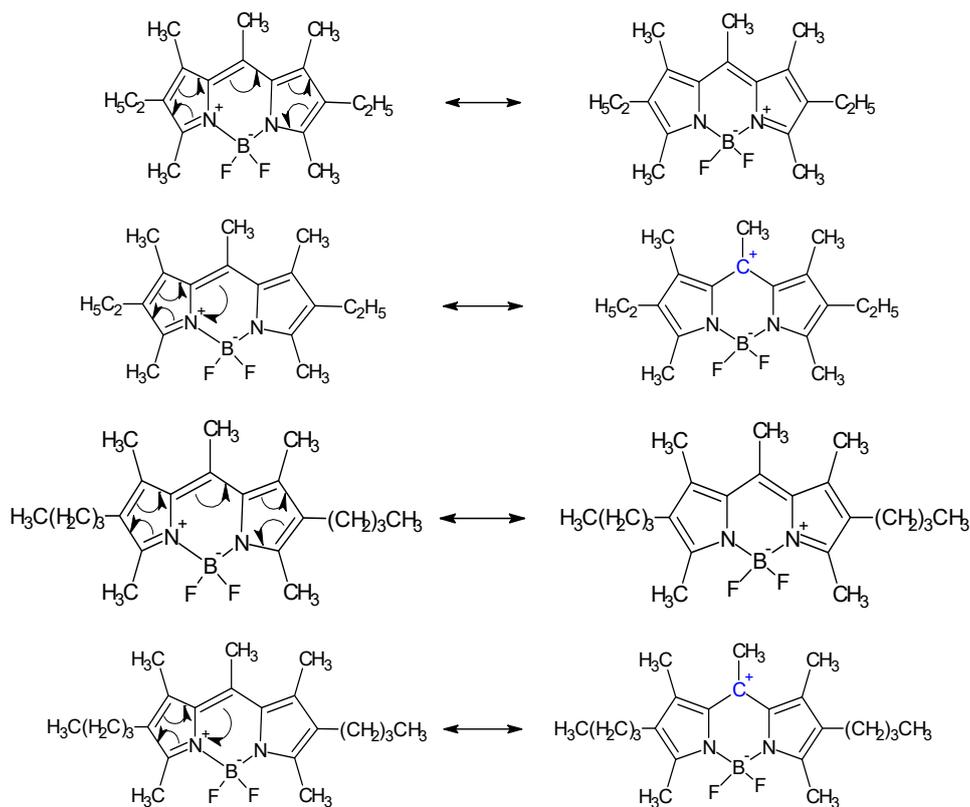


Fig. 6: Possible resonance structure of (a) PM567 and (b) PM580.

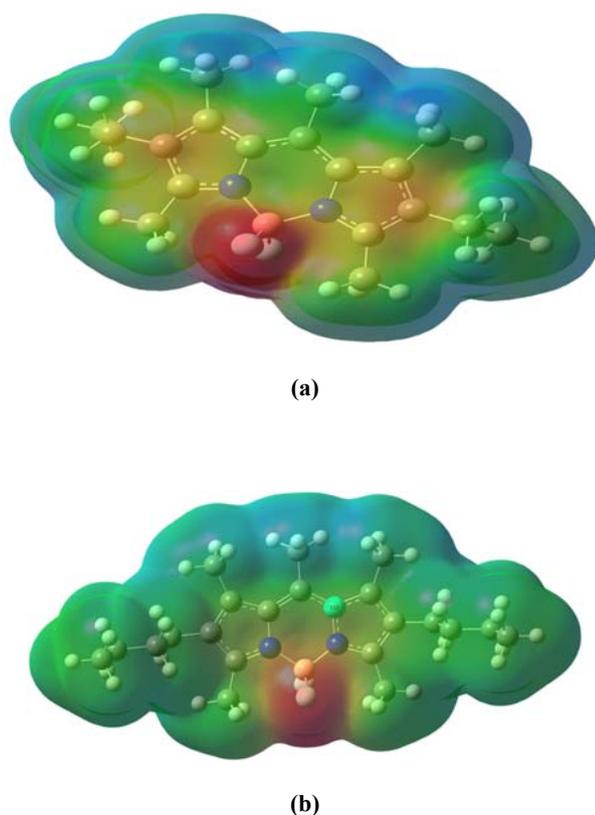


Fig. 7: Electrostatic potential maps of (a) PM 567 and (b) PM 580.

larger excited state dipole moment than ground state for both the dyes in all solvents. This change in dipole moment on excitation may be due to the nature of emitting state or intramolecular charge transfer. Also the change in dipole moment on excitation as in PM580 can be explained as nature of excited state is twisted intramolecular charge transfer. Thus change in planarity and presence of large twisted intramolecular charge transfer on excitation suggests that the molecule is more polar in excited state than in ground state.

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