Study On Solvent Effect And Estimation Of Dipole Moments Of An Organic Fluorophore

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Abstract: The effect of solvents on spectroscopic properties of an organic fluorophore 2,5-di[(E)-1-(4-diphenylaminophenyl) methylidine]-1-cyclopentanone (2,5-DPHAPMC) belonging to a ketocyanine dye family is analyzed using Lippert-Mataga bulk polarity function, Reichardt's microscopic solvent polarity parameter and Kamlet's multiple linear regression approach. The spectroscopic properties better follows Reichardt's microscopic solvent polarity parameter than conventional Lippert-Mataga bulk polarity function. The double linear correlation of Stokes shift with Reichardt's microscopic solvent polarity parameter for non-alcohol and alcohol solvents is observed. This indicates that both general solute – solvent interactions and specific interactions are contributing to the resultant spectral changes. Kamlet's multiple linear regression approach indicates that polarizability/dipolarity solvent influences are dominating more compared to solvents hydrogen-bond donor and hydrogen-bond acceptor influences. The data on effect of solvents is used to estimate excited state dipole moment using the theoretically determined ground state dipole moment. The excited state dipole moment determined by different methods is compared and analysed. The excited state dipole moment of dye is found to be greater than its corresponding ground state counterpart and, ground and excited state dipole moments are almost perpendicular to each other.

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1 INTRODUCTION

The study of solvent effects in organic fluorophores has been the interesting area of research in recent years [1], [2], [3], [4], [5], [6]. Accordingly, photophysical properties like fluorescence quantum yield (Φ_f), fluorescence life time (τ_f), absorption and fluorescence spectral shift, etc., have been the subject of interesting investigations [7], [8]. These investigations have considerable importance in the fields of photophysics and photochemistry. The data from solvent effects can be used to estimate the electric dipole moment of molecules in the excited states. The knowledge of electric dipole moment of electronically excited molecules is useful in designing nonlinear optical materials [9], in elucidation of the nature of the excited states and also it reflects the charge distribution in the molecule. The photophysical properties of ketocyanine dyes have been the subject of intensive investigations in previous years [10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20]. The pronounced solvent effects in both absorption and emission spectra of these dyes make them promising probes for monitoring micro-polarity, hydrogen-bond donating interaction, metal ion sensing, investigation of the cell membrane structures, evaluating the micro-environmental characteristics of biochemical and biological systems and many others [21], [22], [23], [24]. Even though intensive investigations have been carried out on photophysics and photochemistry of a ketocyanine dye 2,5-di[(E)-1-(4-diphenylaminophenyl) methylidine] -1- cyclopentanone (2,5-DPHAPMC), there is a lack of information on the analysis of spectral properties in terms of different solvent polarity parameters and, estimation of ground and excited state dipole moments to the best of present knowledge.

This motivated me to carry out the present work. The aim of the present work is to analyse solvent effects on absorption transition energy, fluorescence transition energy and Stokes shift using different solvent polarity scales and, estimate ground and excited-state dipole moments of 2,5-DPHAPMC by different methods. The spectral properties are analyzed using Lippert and Mataga bulk solvent polarity parameter, Reichardt's microscopic solvent polarity parameter and solvatochromic parameters proposed by Kamlet et al. The ground state dipole moment of the dye was determined by quantum chemical method using Gaussian 09 program. The excited state dipole moment was estimated using Bakhshiev's, Kawaski-Chamma-Viallet equations and Richardt's microscopic solvent polarity parameter E_N^T .

2 THEORETICAL BACKGROUND

The Lipper-Mataga bulk solvent polarity parameter (F(ε,n)) values of solvents used in the present study were calculated using (1) [25], [26]

$$F(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (1)$$

where ε and n are respectively dielectric constant and refractive index of respective solvents. The microscopic solvent polarity parameter (E_N^T) values of solvents were taken from literature [21]. The multiple linear regression approach proposed by Kamlet and co-workers [27], [28], [29] has also been used to correlate absorption transition energy($\overline{\nu}_a$), fluorescence transition energy ($\overline{\nu}_f$) and Stokes shift($\overline{\Delta \nu}$) with an index of solvents dipolarity/polarizability which is a measure of the solvent's ability to stabilize a charge or dipole through nonspecific dielectric interactions (π*), and indices of the solvent's hydrogen-bond donor (HBD) strength (α) and hydrogen-bond acceptor (HBA) strength (β), according to (2);

$$y = y_0 + a\alpha + b\beta + c\pi* \qquad (2)$$

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where y is the spectroscopic property under consideration, y_0 is respective spectroscopic property in gas phase, a, b, and c are respectively measures of solvents HBD, HBA and dipolarity/polarisability. The theoretical ground state dipole moment (μ_g) of dye was obtained by quantum chemical calculations. The B3LYP model which is based on density functional theory was used. The 6-31G(d) basis set was employed in the calculation. All the computations were carried out using Gaussian 09 program [30] on a Pentium – 4 PC. The effect of solvents on absorption and fluorescence spectra of dye was used to estimate the excited-state dipole moment and is determined according to Bakshiev's and Kawski-Chamma-Viallet's [31], [32], [33], [34], [35], [36], [37] (3) and (4) as given below:

$$\overline{\nu}_a - \overline{\nu}_f = m_1 F_1(\varepsilon, n) + \text{constant} \qquad (3)$$

$$\frac{\overline{\nu}_a + \overline{\nu}_f}{2} = -m_2 F_2(\varepsilon, n) + \text{constant} \qquad (4)$$

where $\overline{\nu}_a$ and $\overline{\nu}_f$ are the absorption and fluorescence maxima wavenumbers in cm^{-1} respectively, and

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \frac{(2n^2 + 1)}{(n^2 + 2)} \qquad (5)$$

$$F_2(\varepsilon, n) = \left[\frac{(2n^2 + 1)}{2(n^2 + 2)} \left(\frac{\varepsilon - 1}{\varepsilon + 1} - \frac{n^2 - 1}{n^2 + 1} \right) + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \right] \qquad (6)$$

From (3) & (4), the plots of ($\overline{\nu}_a - \overline{\nu}_f$) versus $F_1(\varepsilon, n)$ and ($\overline{\nu}_a + \overline{\nu}_f$)/2 versus $F_2(\varepsilon, n)$ are linear with slopes m_1 and m_2 respectively and are given by (7) and (8):

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \qquad m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3}$$
$$(7) \qquad\qquad\qquad\qquad (8)$$

where μ_g and μ_e are ground and excited dipole moments of a molecule respectively, h is Planck's constant, c is the velocity of light and a is Onsager cavity radius of a molecule. In the present study, the Onsager cavity radius of 2,5-DPHAPMC was estimated using the method suggested by J. T. Edward [38]. If the ground and excited state dipole moments are parallel, the following expressions can be obtained on the basis of above equations [39]

$$\mu_g = \frac{m_2 - m_1}{2} \left(\frac{hca^3}{2m_1} \right)^{1/2} \qquad (9)$$

$$\mu_e = \frac{m_1 + m_2}{2} \left(\frac{hca^3}{2m_1} \right)^{1/2} \qquad (10)$$

If dipole moments μ_e and μ_g are not parallel to each other, but form an angle ϕ, then ϕ can be calculated using (11)

$$\cos\phi = \frac{1}{2\mu_g\mu_e} \left[(\mu_g^2 + \mu_e^2) - \frac{m_2}{m_1} (\mu_e^2 - \mu_g^2) \right] \qquad (11)$$

The excited dipole moment was also estimated by the method based on empirical solvent polarity parameter E_T^N. This method correlates the spectral shift better than the traditionally used bulk solvent polarity functions. Also, this polarity scale includes intermolecular solute/solvent hydrogen bond donor/acceptor interactions along with solvent polarity. The theoretical basis for the correlation of the spectral band shift with E_T^N is according to (12) [40]

$$\overline{\nu}_a - \overline{\nu}_f = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_B} \right)^2 \left(\frac{a_B}{a} \right)^3 \right] E_T^N + \text{constant} \qquad (12)$$

where $\Delta\mu_B$ and a_B are the change in dipole moment and Onsager cavity radius respectively of the Betaine dye, and $\Delta\mu$ and a are the corresponding quantities of the molecule of interest. The change in dipole moment $\Delta\mu$ can be extracted from the slope of the plot ($\overline{\nu}_a - \overline{\nu}_f$) versus E_T^N using the reported values of $\Delta\mu_B$ = 9D and a_B = 6.2Å.

3 RESULTS AND DISCUSSION

3.1 Analysis of Solvent Effects

The absorption (λ_a) and emission maxima (λ_f), Stokes shift ($\overline{\nu}_a - \overline{\nu}_f$) and arithmetic mean of wavenumbers ($\overline{\nu}_a + \overline{\nu}_f$)/2 (in cm^{-1}) for 2,5-DPHAPMC dye in different solvents are given in Table 1. Absorption and emission maxima were taken from [17]. From Table 1, it is observed that when solvent is changed from non-polar toluene to acetonitrile which is a polar aprotic solvent, there is 4nm spectral band shift in the absorption spectrum, whereas it is 15nm for methanol which is polar protic solvent. Also, when solvent is changed from non-polar toluene to a polar aprotic solvent acetonitrile, there is a spectral band shift of 139nm in the fluorescence spectrum, whereas it is 166nm for polar protic solvent methanol. This implies that the ground state energy distribution of 2,5-DPHAPMC is less influenced by change in polarity and hydrogen bonding property of solvent compared to excited state. The Stokes shift increases with increase in solvent polarity. The Stokes shift of 4730cm^{-1} is observed in polar protic solvent methanol and 4480cm^{-1} in case of polar aprotic solvent acetonitrile. These observations indicate the good response of 2,5-DPHAPMC to the polarity and hydrogen bonding characters of the solvents. The observed solvatochromic behavior could be due to the presence of two tautomeric forms of 2,5-DPHAPMC (keto and charged enol forms, Fig. 1). The degree of contribution of both tautomers in solution is governed by the nature and polarity of the solvents used.

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The less polar keto form contributes mainly in non- and less polar solvents. In contrast the highly polar enol form predominates in polar and strong hydrogen bonding donor solvents, thus, causing a larger spectral shifts [1]. Further, both absorption and fluorescence band maxima undergoes pronounced red shift with increase in solvent polarity. The observed solvent sensitivity is understandable in terms of π →π* with intramolecular charge transfer (ICT) from diphenyl amino group to the carbonyl oxygen.

Table 1. Spectral Data of Dye in Different Solvents[a]

Solvent	E_T^N	λ_a (nm)	λ_f (nm)	$(\bar{\nu}_a - \bar{\nu}_f)$ (cm⁻¹)	$(\bar{\nu}_a + \bar{\nu}_f)/2$ (cm⁻¹)
Toluene	0.099	463	502	1680	20759
Dioxane	0.164	459	545	3440	20067
BA	0.241	456	559	4020	19909
DMF	0.386	467	630	5540	18643
	0.6	486	641		

[a] *Absorption and fluorescence maxima were taken from [17]. BA:Butyl Acetate;DMF:Dimethyl formamide, ACN:Acetonitrile, IP-nol:Isoproponol, E-nol: Ethanol, M-nol:Methanol*

To get further insight on the solvatochromic behavior of 2,5-DPHAPMC, spectroscopic properties are correlated with relevant solvent polarity scales. The spectroscopic properties $\bar{V}_a$, $\bar{V}_f$ and $\Delta\bar{\nu}$ are plotted as a function of Lipper-Mataga solvent polarity parameter $F(\varepsilon, n)$. The least square correlation analysis gave a better correlation in case of $\bar{V}_f$ (r = 0.96) and $\Delta\bar{\nu}$ (r = 0.95) as compared to $\bar{V}_a$ (r = 0.58). The average correlation in case of absorption implies that Lippert-Mataga solvent polarity parameter is not a complete valid polarity scale to explain solvent effect in the present case. This could be due to the reason that this method not consider specific solute – solvent interactions such as hydrogen bonding effect, complex formation and also ignore molecular aspects of solvation. The average correlation of absorption transition energies with $F(\varepsilon, n)$ indicates the role of specific solvent effects like hydrogen bonding effect in the present case, as is evident from very large spectral shifts in polar protic solvents. Therefore, an attempt has been made to explain spectroscopic properties by solvent polarity parameter E_T^N.

Fig. 1. Keto and charged enol forms of 2,5-
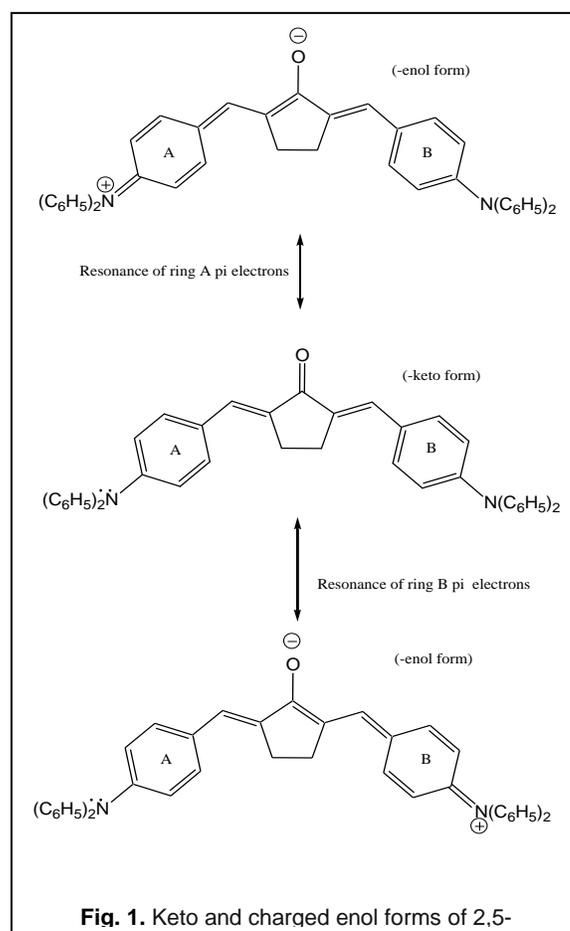
The $\bar{V}_a$, $\bar{V}_f$ and $\Delta\bar{\nu}$ are correlated with the microscopic solvent polarity parameter E_T^N. The least square correlation analysis gave a better correlation for all the three spectral properties $\bar{V}_a$ (r = 0.83), $\bar{V}_f$ (r = 0.92) and $\Delta\bar{\nu}$ (r = 0.84). However, the correlation was very good, when $\Delta\bar{\nu}$ was correlated with E_T^N separately for non-alcohol and alcohol solvents (For non-alcohols r = 0.98 and For alcohols r = 0.99). This double linear correlation of $\Delta\bar{\nu}$ with E_T^N is shown in Fig. 2. A double linear correlation indicates that solvent stabilization of ground and excited states are due to a variety of solute-solvent interactions such as hydrogen bonding and dipole-dipole interactions [5]. In protic solvents, increasing polarity stabilize the molecule through hydrogen bonding. On the other hand, in aprotic solvents dipole-dipole and dipole-induced dipole forces are assumed to be the predominant interactions.

Fig. 2. A plot of $(\overline{\nu}_a - \overline{\nu}_f)(cm^{-1})$ versus E_N^T
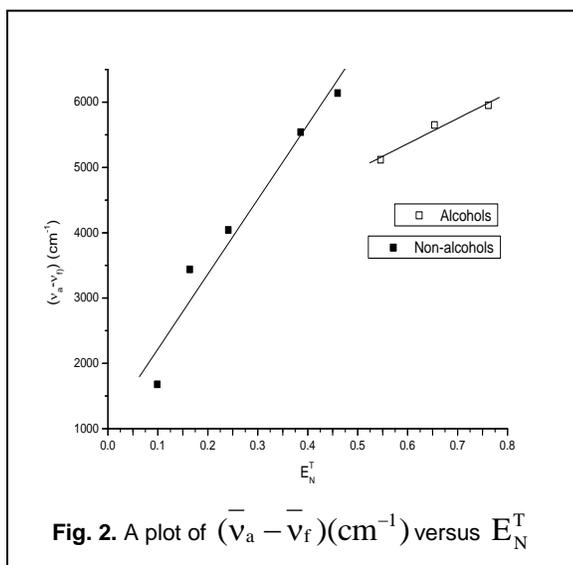
In order to get information about the individual contributions of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities of the solvents on the spectroscopic properties, $\overline{\nu}_a$ $\overline{\nu}_f$ and $\Delta\overline{\nu}$ are correlated with solvatochromic parameters α, β and π* using multiple regression method. The multiple regression analysis data along with correlation coefficients is given in (13).

$$\overline{\nu}_a (cm^{-1}) = 23307 - 989\alpha - 75\beta - 1066\pi^* \quad (r = 0.96)$$

$$\overline{\nu}_f (cm^{-1}) = 23432 - 1407\alpha - 1023\beta - 2716\pi^* \quad (r = 0.93) \qquad (13)$$

$$\Delta\overline{\nu}(cm^{-1}) = 1755 + 1823\alpha + 3806\beta + 4737\pi^* \quad (r = 0.78)$$

From (13), it is clear that non-specific dielectric interaction (π*) has the major solvent influence compared to HBD and HBA. However, the contribution of HBD and HBA parameters cannot be neglected. It is clear from $\overline{\nu}_a$ and $\overline{\nu}_f$ multiple regression analyses with better correlation coefficients, HBD(α) influence is more than HBA(β).

3.2 Estimation of Ground and Excited state dipole moments

The ground state dipole moment of 2,5-DPHAPMC was obtained using quantum chemical calculation following geometry optimisation and is found to be 4.07 D. The optimized molecular geometry with the direction of dipole moment is shown in Fig. 3.

Fig. 3. Optimized molecular geometry of 2,5-DPHAPMC
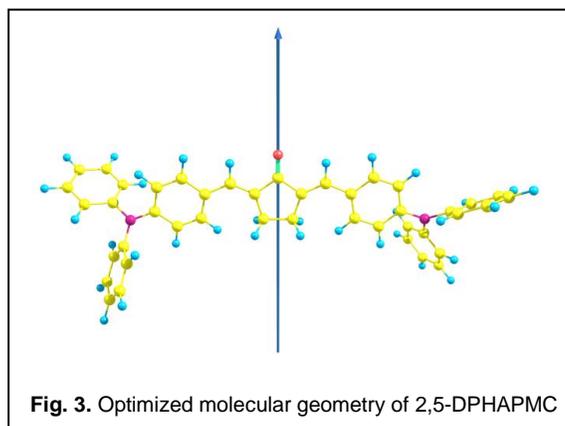
Fig. 4 shows the plots of $(\overline{\nu}_a - \overline{\nu}_f)$ versus $F_1(\varepsilon, n)$ (Fig. 4(a)) and $(\overline{\nu}_a + \overline{\nu}_f)/2$ versus $F_2(\varepsilon, n)$ (Fig. 4(b)). The linear progression was done and the data was fit to a straight line. The corresponding values of slopes, intercepts and correlation coefficients are collected in Table 2. In both the cases the correlation coefficients are more than 0.90 with selected number of data points. The excited state dipole moment (μ_e) was calculated from the slopes of respective plots and is given in Table 3. From Table 3, it is clear that calculated excited state dipole moments from Bakshiev's (μ_e^b) and Kawski-Chamma-Viallet's (μ_e^c) equations are slightly different because of the difference in assumptions in obtaining those equations.

Fig. 4. Plots of (a) $(\overline{\nu}_a - \overline{\nu}_f)(cm^{-1})$ versus F₁(ε,n) and (b) plot of $(\overline{\nu}_a + \overline{\nu}_f)/2(cm^{-1})$ versus F₂(ε,n)
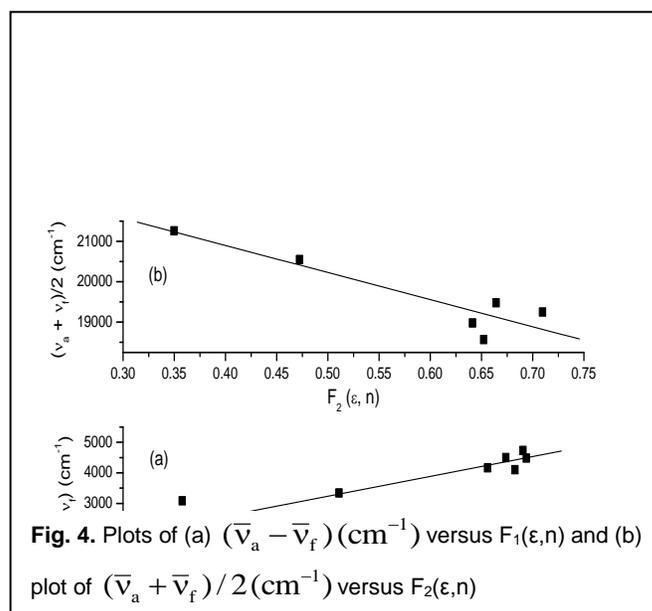
Table 2: The slope (m), correlation coefficient (r) and number of data points (n) corresponding to linear fit of spectral shifts with F₁, F₂ and E_T^N parameters

Function	m	r	n
F₁	3990	0.95	8
F₂	5972	0.91	6
E_T^N	11451	0.98	5
	(3861)	(0.99)	(3)

Table 3: The Onsager cavity radius and, Ground-state and Singlet excited state dipole moments (in Debye, D)

Radius ($\mathring{A}$)	μ_g^a	μ_e^b	μ_e^c	μ_e^d
5.09	4.07	11.30	9.75	10.78[*] (7.98)[**]

[a] Ground state dipole moment estimated by Gaussian software.
[b] Excited – state dipole moment calculated from (3).
[c] Excited – state dipole moment calculated from (4).
[d] Excited – state dipole moments calculated from (12) (*: non-alcohols, **:alcohols).

The excited state dipole moment is also calculated using polarity parameter E_T^N according to (12) and Fig. 2, separately for non-alcohol and alcohol solvents. The value of excited state dipole moment calculated from this method is represented as μ_e^d and is also collected in Table 4. This value is slightly different from one calculated from Bakshiev's and Kawski-Chamma-Viallet's equations. This could be due to the fact that, methods based on Bakshiev's and Kawski-Chamma-Viallet's equations not consider specific solute – solvent interactions such as hydrogen bonding effect, complex formation and also ignore molecular aspects of solvation, whereas these aspects are incorporated in the method based on E_T^N [21]. The difference in excited dipole moment in non-alcohol and alcohol solvents is also the indicative of hydrogen bonding effect. The ground and excited state dipole moments of 2,5-DPHAPMC were also estimated with the assumption that they are parallel using (9) and (10). The estimated values are μ_g = 1.80D and μ_e =9.03D. The difference in these values of μ_g and μ_e compared to respective values from other methods (Table 4) suggest that μ_g and μ_e are not parallel. This prompted to estimate the angle between μ_g and μ_e according to (11) and the value is found to be 94[0]. It means that μ_g and μ_e are almost perpendicular to each other. From Table 3, it is clear that the dipole moment of 2,5-DPHAPMC is higher in the first excited-state as compared to the ground-state. The dipole moment increases almost twice on excitation. This indicates the existence of a more relaxed excited state, due to ICT favoured by the cooperative effects of the diphenyl aniline moieties as donors and the carbonyl group as an acceptor, and suggests that the present dye can serve as good candidate component of non-linear optical materials [1].

4. CONCLUSION

The solvent effect on spectroscopic properties of 2,5-DPHAPMC has been analysed using different polarity parameters. The spectral properties of this dye are influenced more by dipolarity/polarizability of solvents. However, the contributions from solvents HBD and HBA cannot be ignored. HBD influences are more than HBA. The dye has higher dipole moment in the excited state than in the ground state. This clearly indicates that dye has more relaxed excited state due to ICT and suggests that it can serve as good candidate component of nonlinear optical materials. To the present day knowledge, this is the first report on detailed analysis of effect of solvents and

estimation of dipole moments of 2,5-DPHAPMC, and would be of great help in many fields as discussed in the introduction.

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