INVESTIGATION OF POLARITY EFFECT OF SOLVENTS ON PHOTOPHYSICAL PROPERTIES OF IODINATED 4-ARYLOXYMETHYL COUMARIN DYE

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ABSTRACT *The polarity effect of solvents on the photophysical properties of newly synthesized biologically active iodinated coumarin derivative 4-(2-iodo phenoxymethyl)-6-methoxy-chromen-2-one (4IP6MC) is studied using absorption and fluorescence spectroscopy. The polarity effect on the photophysical properties of the dye is analyzed using Lippert–Mataga polarity function, Reichardt's microscopic solvent polarity parameter, Kamlet's and Catalan's multiple linear regression approaches. The excited state dipole moment is estimated using the ground state dipole moment obtained from Gaussian 09 software. The excited state dipole moment is found to be more than the ground state dipole moment.*

KEYWORDS *Coumarin, solvent effect, dipole moment, quantum yield, intramolecular charge transfer.*

INTRODUCTION:

Coumarin dyes are an important class of dyes, which are extensively studied owing to their applications as biological and chemical sensors, fluorescent probes for biological imaging, light harvesting and laser dyes [1-3]. Coumarins are used as non-linear optical chromophores and as a probe for study of solvation dynamics in homogeneous solutions as well as organized media [4–10]. It is reported in literature that 4-aryloxymethyl coumarins exhibited antimicrobial activity, long range coupling and centrosymmetric nature [11,12] and newly synthesized 4-aryloxymethyl coumarin 4-(2-iodo phenoxymethyl)-6-methoxy-chromen-2-one (4IP6MC) exhibited better anti-cancer and anti mycobacterial activities [13]. The investigation of photophysical properties like absorption and fluorescence spectral shift, fluorescence decay time, quantum yield, ground and excited state dipole moments of organic molecules has been a major area of discussion [14–20]. In the present investigation, the polarity effect of solvents on the photophysical properties of the dye 4IP6MC is studied and the data is used to estimate excited state dipole moments of singlet state. The experimental results are studied using Lippert and Mataga bulk solvent polarity parameter [21, 22], Reichardt's microscopic solvent polarity parameter [23], solvatochromic parameters proposed by Kamlet et al. [24–26] and Catalan and coworkers [27]. The ground state dipole moment of the dye was obtained using quantum chemical method [28]. The excited state dipole moment was estimated using Bakshiev's [29], Bilot-Kawski [30–31] equations and equation based on Reichardt's microscopic solvent polarity parameter E_T^N [32]. However, no reports are available in literature on the photophysics the coumarin

derivative derivative 4-(2-iodo phenoxymethyl)-6-methoxy-chromen-2-one (4IP6MC). This prompted us to investigate the photophysical properties of the dye 4IP6MC.

MATERIALS AND METHODS

The coumarin dye 4IP6MC was synthesized by our research group [13]. The molecular structure of 4IP6MC is given in   **Fig. 1**. The spectroscopic grade solvents used in the present investigation were procured from S.D. Fine Chemicals Ltd., India. The absorption and fluorescence spectra were recorded using UV-VIS spectrophotometer (Model: Shimadzu UV-1800) and fluorescence spectrophotometer (Model: Agilent Technologies Carry Eclipse-60) respectively at room temperature. The dye concentration was maintained at 10^{-5} M in all solvents in order to reduce the effect of self absorption and aggregation formation. Parker's method [33] was used to determine relative fluorescence quantum yield, in which quinine sulphate in 0.1 M H_2SO_4 was used as standard ($\Phi_f = 0.54$).

The bulk solvent polarity parameter ($\Delta f(\varepsilon, n)$ of solvents was determined using Eq. (1) [29, 30].

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

where the symbols ε and n represent dielectric constant and refractive index of solvents respectively. The values of ε and n of solvents were obtained from literature [34]. The E_T^N values of solvents were also taken from literature [23].
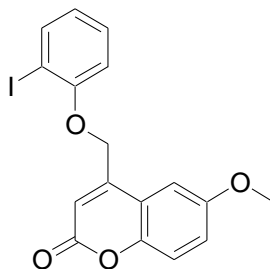

Fig 1: Molecular structure of 4IP6MC

The ability of solvents to stabilise a charge or dipole through non-specific dielectric interactions (π*), indices of hydrogen-bond donor (HBD) strength (α) and hydrogen-bond acceptor (HBA) strength (β) has been measured by correlating the spectral properties of the dye with an index of solvent's dipolarity/polarizability using multiple linear regression method proposed by Kamlet and co-workers [24-26)] according to Eq. (2) [35].

$$y = y_0 + a\alpha + b\beta + c\pi^* \tag{2}$$

where y is the spectroscopic property of interest, y_0 is the respective spectroscopic property in gas phase and a, b and c are the measures of solvents HBD ability, HBA ability and non-specific dielectric interactions respectively. This approach includes dipolarity and polarisability of solvent in single parameter π* [36], limiting understanding individual parameter contribution.   In recent times, Catalan [27] proposed another method based on four empirical scales namely dipolarity (SdP, a new scale, polarizability (SP)), solvent acidity (SA) and basicity (SB) of the medium. This method is based on Eq. (3).

$$y = y_0 + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SdP}SdP \tag{3}$$

where y and y0 have their usual meanings, aSA , bSB , cSP and dSdP are the measures of solvents SA, SB, SP and SdP respectively. Using this method, it is possible to break up the relative contributions of dipolarity, polarizability, acidity and basicity of the medium.

In order to obtain theoretical ground state dipole moment (µg) of dyes, quantum chemical computation carried out using Gaussian 09 program [28] on a Pentium – 4 PC with method B3LYP and built-in basis set 3-21G was used. The excited state dipole moment of dye was estimated using Bakshiev's, Kawski-Chamma-Viallet equations and also by the equation based on E_T^N . According to Bakshiev [29] and Kawski-Chamma-Viallet [37-42] for a spherical molecule with the isotropic polarizability, the following Eqs. (4) and (5) hold good:

$$\bar{v}_a - \bar{v}_f = m_1 F_1(\varepsilon, n) + \text{constant} \qquad (4)$$

$$\frac{\bar{v}_a + \bar{v}_f}{2} = -m_2 F_2(\varepsilon, n) + \text{constant} \qquad (5)$$

where $\bar{v}_a$ and $\bar{v}_f$ are the absorption and fluorescence maxima wavenumbers in cm^{-1} respectively, and F_1 & F_2 are solvent polarity functions given by Eqs. (6) and (7) respectively.

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \frac{(2n^2 + 1)}{(n^2 + 2)} \qquad (6)$$

$$F_2(\varepsilon, n) = \left[\frac{(2n^2 + 1)}{2(n^2 + 2)} \left(\frac{\varepsilon - 1}{\varepsilon + 1} - \frac{n^2 - 1}{n^2 + 1} \right) + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \right] \qquad (7)$$

where ε and n have their usual meanings. The plots of $(\bar{v}_a - \bar{v}_f)$ versus $F_1(\varepsilon, n)$, and $(\bar{v}_a + \bar{v}_b)/2$ versus $F_2(\varepsilon, n)$ for different solvents yield the slopes m_1 and m_2 respectively and are given below:

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

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \qquad (9)$$

where h, c and a are Planck's constant, velocity of light and Onsager radius of a molecule respectively. μ_g and μ_e are the ground and excited state dipole moments respectively. The Onsager radius of the dye was estimated according to the method suggested by J T Edward [43].

If the ground and excited state dipole moments are parallel, and the symmetry of the investigated solute molecule remains unchanged upon electronic transition, the following equations are obtained [44] based on Eqs. (8) and (9).

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

$$\mu_e = \frac{m_1 + m_2}{2} \left(\frac{hca^3}{2m_1} \right)^{1/2} \qquad (11)$$

If the dipole moments μ_g and μ_e are not parallel to each other and form an angle ϕ, the Eqs. (10) and (11) can be written as

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

(12)

The excited state dipole moment of dye was also estimated using the Eq. (13) which is based on E_T^N [32].

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

(13)

where $\Delta\mu_B$ and a_B are the change in dipole moment and Onsager radius of betaine dye respectively, 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 of Stokes shift versus E_T^N using the reported values $\Delta\mu_B$ = 9D of the betaine dye and its Onsager radius a_B = 6.2Å.

RESULTS AND DISCUSSION

(A) EFFECT OF PURE SOLVENTS ON ABSORPTION AND FLUORESCENCE SPECTRA

The absorption and fluorescence spectra of 4IP6MC in different solvents were recorded and typical spectra in toluene, acetonitrile and methanol solvennts are given in **Fig. 2.** The energies of absorption ($\bar{\nu}_a$) and emission transitions ($\bar{\nu}_f$), Stokes' shift ($\Delta\bar{\nu}$) and arithmetic mean of wavenumbers ($\bar{\nu}_a + \bar{\nu}_f$)/2 (in cm^{-1}) for different solvents are given in **Table 1.** It is observed from Table 1 that, when solvent is changed from non-polar toluene to a polar aprotic solvent acetonitrile and a polar protic solvent methanol, there is no appreciable spectral band shift in absorption spectra of 4IP6MC. But, when solvent is changed from non-polar toluene to a polar aprotic solvent acetonitrile and a polar protic solvent methanol, there is a spectral band shift of 12 nm in acetonitrile and 12 nm in methanol in the emission spectra. This implies that the ground state energy distribution of the dye is not much affected by change in polarity and hydrogen bonding characteristics of solvents [15, 16]. However, the excited state of the dye is influenced by change in polarity of solvents. Also, the comparison of emission maxima of the dye in acetonitrile and methanol suggests that the emission characteristics of the dye are also influenced by hydrogen bond characteristics of solvents. The Stokes' shift of 6476 cm^{-1}, 7090 cm^{-1} and 7090 cm^{-1} were observed in non polar solvent toluene, polar aprotic solvent acetonitrile and polar protic solvent methanol respectively indicating the increase in Stokes' shift with solvent polarity. Further, the fluorescence band maxima of 4IP6MC undergo red shift with increase in solvent polarity. The red shift with increase in solvent polarity indicates the involvement of $\pi \rightarrow \pi^*$ transition [15, 16]. The red shift with increase in solvent polarity could be due to the marked difference between the solute's excited state and ground state charge distribution, resulting in a stronger intermolecular interaction with polar solvents in the excited state [15, 16].

To get further insight on the solvatochromic behavior of the dye, spectroscopic properties were correlated with different solvent polarity scales. The spectroscopic properties $\bar{\nu}_f$ and $\Delta\bar{\nu}$ were plotted as a function of Δf (ϵ, n). The least square correlation analysis gave a moderate correlation in case of $\bar{\nu}_f$ (r = 0.67) and $\Delta\bar{\nu}$ (r = 0.51). The moderate correlation

of spectral properties with Δf (ε, n) implies that this is not a sufficiently valid polarity scale to explain solvent effect in 4IP6MC. This could be due to the reason that the polarity scale Δf(ε,n) does not consider specific solute–solvent interactions such as hydrogen bonding effect, charge transfer interactions, complex formation and ignores molecular aspects of solvation. Therefore, an attempt has been made to explain spectroscopic properties by solvent polarity parameter E_T^N. The values of $\overline{v}_f$ and $\Delta\overline{v}$ were correlated with E_T^N. The least square analysis gave once again a moderate correlation of r = 0.72 and r = 0.52 for $\overline{v}_f$ and $\Delta\overline{v}$ graphs respectively.
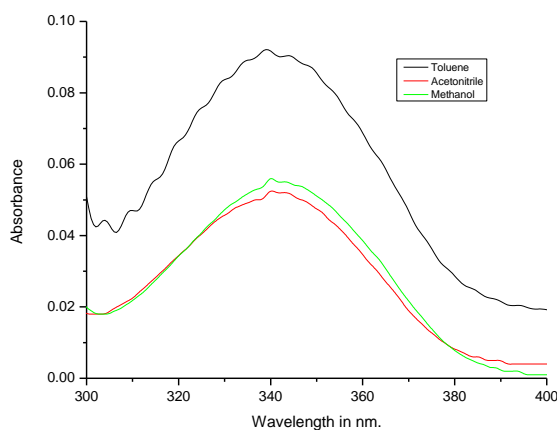

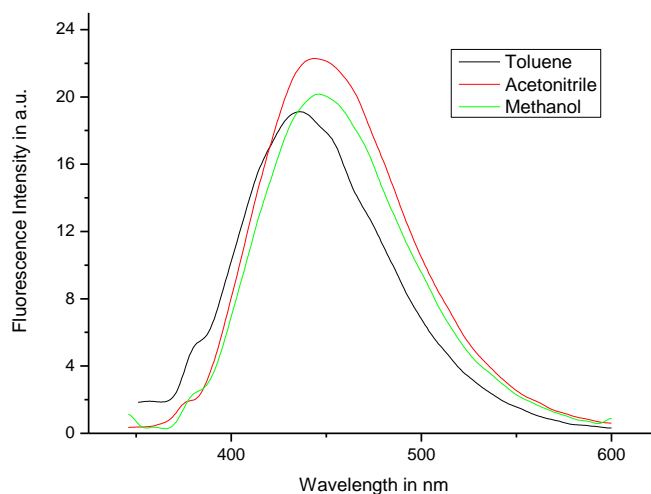**Fig 2(A): Absorption spectra of 4IP6MC in toluene, acetonitrile and   methanol**

Fig 2(B): Fluorescence spectra of 4IP6MC in toluene, acetonitrile and methanol

However, when $\overline{v}_f$ and $\Delta\overline{v}$ were correlated with E_T^N separately for alcoholic and non-alcoholic solvents, the correlation is found to be good. The least square correlation coefficient in case of $\overline{v}_f$ for non-alcoholic solvents is r = 0.89 and alcoholic solvents is r = 0.99. The least square correlation in case of $\Delta\overline{v}$ for non-alcoholic solvents is r = 0.86 and alcoholic solvents is r = 0.82 The double linear fits are shown in **Fig 3** and **Fig 4**. The

double linear correlation indicates that, solvent stabilization of excited states is due to a variety of solute-solvent interactions such as hydrogen bonding and dipole-dipole interactions [45]. In protic solvents, increasing polarity stabilizes 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 [46].

Table 1: Photophysical parameters of 4IP6MC in different solvents

Solvents[a]	E_T^N	λ_a (nm)	λ_f (nm)	$\Delta\bar{\nu}$ (cm^{-1})	$(\bar{\nu}_a + \bar{\nu}_f)/2$ (cm^{-1})	Φ_f
Cyclohexane	0.006	340	427	5993	26415	0.0838
Toluene	0.099	340	436	6476	26174	0.0125
Diethyl ether	0.117	340	433	6317	26253	0.0204
1,4 Dioxane	0.164	340	440	6684	26070	0.0134
THF	0.207	335	435	6862	26420	0.0156
EAC	0.228	340	437	6528	26148	0.0143
Chloroform	0.259	343	435	6166	26072	0.0154
Acetone	0.355	340	445	6940	25942	0.0274
DMF	0.386	345	441	6310	25831	0.0397
DMSO	0.444	343	445	6683	25813	0.0346
Acetonitrile	0.460	340	448	7090	25867	0.0224
Butanal	0.586	340	438	6581	26121	0.0263
Propanol	0.617	340	440	6684	26070	0.0238
Ethanol	0.654	343	441	6479	25915	0.0272
Methanol	0.762	340	448	7090	25867	0.0186

[a]Abbreviations of the solvents: THF, Tetrahydrofuran; EAC, Ethylacetate; DMF, Dimethyl formamide; DMSO, Dimethyl sulfoxide
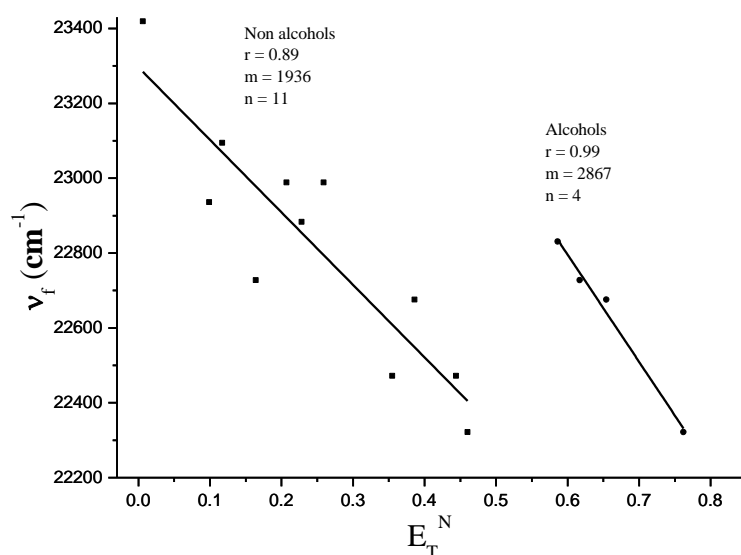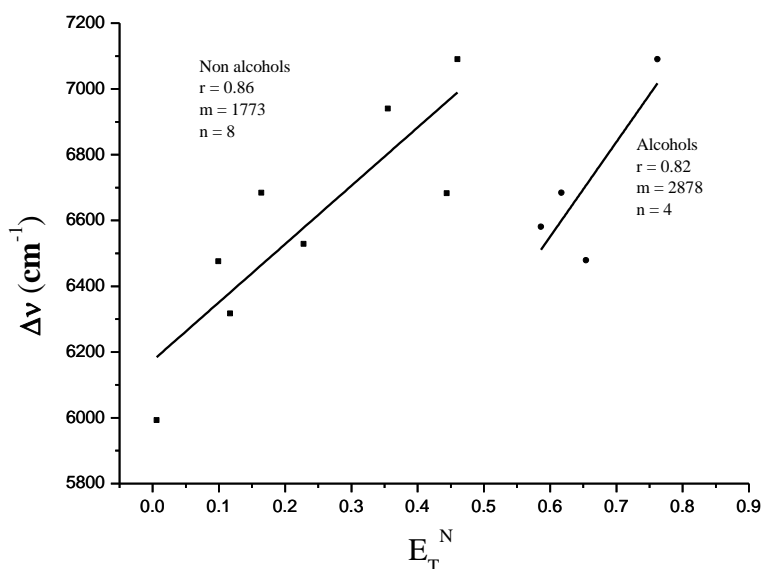

Fig 3: Plot of $\bar{\nu}_f$ versus E_T^N

Fig 4. Plot of Stokes' shift ($\Delta \bar{\nu}$) versus E_T^N

In order to get information about the individual contributions of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities of solvents on spectroscopic properties of the dye 4IP6MC, $\bar{\nu}_f$ and $\Delta \bar{\nu}$ were correlated with solvatochromic parameters α, β and π* using multiple regression. The multiple regression analysis data along with correlation coefficients is given below in Eqs. (14) and (15).

$$\bar{\nu}_f \text{ (cm}^{-1}) = 23533 - 279\ \alpha + 454\ \beta - 959\ \pi* \qquad r = 0.86 \qquad (14)$$

$$\Delta \bar{\nu} \text{ (cm}^{-1}) = 5971 - 141\ \alpha + 823\ \beta + 1416\ \pi* \qquad r = 0.84 \qquad (15)$$

From above equations, it is clear that non-specific dielectric interaction (π*) has a major solvent influence, with minor contribution from HBD and HBA. Further, spectroscopic properties of 4IP6MC $\bar{\nu}_f$ and $\Delta \bar{\nu}$ were also correlated with solvatochromic parameters SA, SB, SP and SdP proposed by Catalan. The linear correlation analysis along with correlation coefficients is shown in Eqs. (16) and (17) respectively.

$$\bar{\nu}_f \text{ (cm}^{-1}) = 23150 - 16\ SA + 453\ SB + 1546\ SP - 1039\ SdP \qquad r = 0.95 \qquad (16)$$

$$\Delta \bar{\nu} \text{ (cm}^{-1}) = 4427 + 258\ SA + 356\ SB + 5684\ SP + 1519\ SdP \qquad r = 0.81 \qquad (17)$$

From above equations, it is observed that influence of polarizability (SP) and dipolarity (SdP) parameters is more. However, the contributions of solvent influences due to acidity and basicity cannot be neglected. The solvent acidity (SA) influences less than solvent basicity (SB). This is in good agreement with the results obtained by Kamlet analysis.

The relative quantum yield of 4IP6MC was estimated in different solvents and is given in Table 1. The relative quantum yield varies from 0.0125 to 0.0838 depending on the nature of solvents. The general observation is that, the relative quantum yield value does not change much with solvent polarity.

   ESTIMATION OF GROUND AND EXCITED STATE DIPOLE MOMENTS

The ground state dipole moment of 4IP6MC was obtained using quantum chemical calculation following geometry optimisation and is given in **Table 2** (μ_g^a). The optimized molecular geometry of 4IP6MC is shown in **Fig. 5**. This kind of calculation assumes that

molecules involved are in gas phase and does not include solvent interactions. The ground state dipole moment was also calculated using equation (10) and is also given in Table 2 (μ_g^b). From **Table 2**, it is clear that ground state dipole moment obtained using quantum chemical calculations (μ_g^a) is more than the ground state dipole moment (μ_g^b) obtained using equation (10). The ground state dipole moment obtained using quantum chemical calculations is used for further calculations, as equation (10) is based on the assumption that dipole moment are parallel in ground and excited states, which may not be true.

Fig. 6 shows the plots $\Delta\bar{\nu}$ versus $F_1(\varepsilon, n)$ and $(\bar{\nu}_a + \bar{\nu}_b)/2$ versus $F_2(\varepsilon, n)$. The linear progression was done and the data was fit to a straight line. The corresponding values of the slopes (m), correlation coefficients (r) and number of data points (n) are mentioned on respective plots. In both the plots good linearity was obtained for selected number of data points. The excited state dipole moments (μ_e) were calculated from the slopes of the respective plots and are given in **Table 2** (μ_e^c and μ_e^d).

Table 2: Onsager radius, ground-state and excited-state dipole moments in Debye (D).

Dye	Radius(Å)	μ_g^a (D)	μ_g^b (D)	μ_e^c(D)	μ_e^d(D)	μ_e^e(D)	μ_e^h(D)
4IP6MC	**3.99**	**7.575**	**0.21**	**9.87**	**7.97**	**9.41** f **9.92** g	**2.51**

a The ground state dipole moment from quantum chemical calculations.

b The ground state dipole moment calculated using Eq. (10).

c The excited state dipole moment calculated from Bakshiev's equation.

d The excited state dipole moment calculated from Kawski-Chamma-Viallet's equation.

e The excited state dipole moment calculated from microscopic solvent polarity parameter function.

f The excited state dipole moment calculated from microscopic solvent polarity parameter function for non alcohols.

g The excited state dipole moment calculated from microscopic solvent polarity parameter function for alcohols.

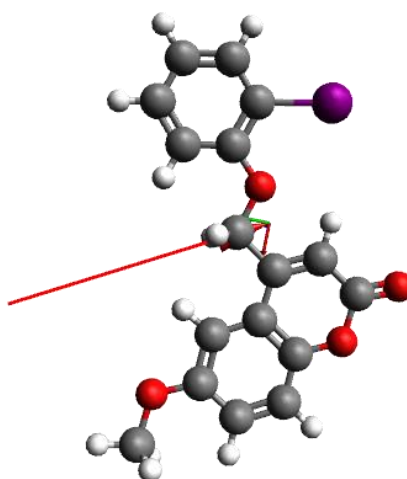h The excited state dipole moment calculated using Eq. (11).

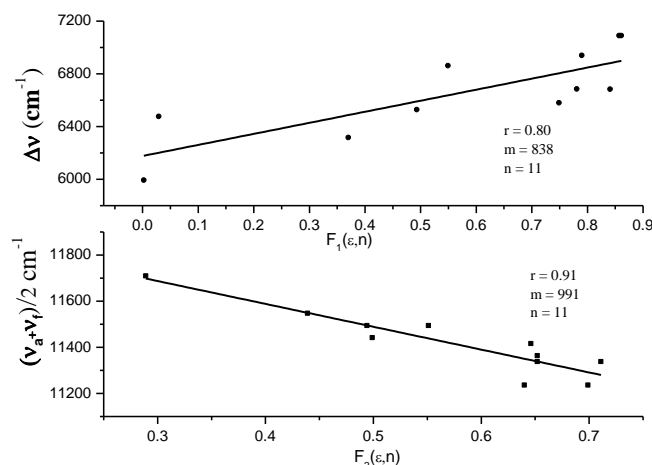**Fig 5: Ground state optimized molecular geometry of 4IP6MC.**

Fig 6: (A) Plot $\Delta\bar{\nu}$ **versus** $F_1(\varepsilon, n)$ **and (B) Plot of** $(\bar{V}_a + \bar{V}_f)/2$ **versus** $F_2(\varepsilon, n)$.

The double linear correlation of Stokes' shift with E_T^N prompted us to calculate excited dipole moments separately for non- alcoholic and alcoholic solvents according to **Fig**. **3** and **Fig 4**. These values are also collected in Table 2 (μ_e^e). The values of excited state dipole moments determined from different methods are slightly different. This could be due to difference in type of solute – solvent interactions considered.

The excited state dipole moment of 4IP6MC was also estimated assuming that they are parallel using Eqs. (11). The estimated value is also given in **Table 2** (μ_e^h). The major difference in value μ_e with this assumption compared to respective values from other methods (Table 2) suggests that μ_g and μ_e are not parallel. This prompted us to estimate the angle between μ_g and μ_e according to Eq. (12). The estimated value is found to be 19.79 ^{0}.

From **Table 2**, it is clear that the dipole moment of 4IP6MC   is higher in the first excited-state compared to ground-state. This indicates the existence of a more relaxed excited state, due to intramolecular charge transfer (ICT).

CONCLUSION

The polarity effect of solvents on the photophysical properties of biologically active coumarin dye 4IP6MC was studied using absorption and fluorescence spectroscopy. Solvent polarity parameters have been used to analyse the experimental results. A bathochromic shift with increase in polarity of solvent for 4IP6MC dye indicates the involvement of π

→π* transition. The double linear correlation of spectral properties with E_T^N indicates the role of solute-solvent interactions such as hydrogen bonding and dipole-dipole interactions. The contribution of general solute-solvent and hydrogen bonding interactions were quantified using Kamlet's and Catalan's multiple linear regression approach. The contribution of dielectric interactions is more compared to hydrogen bonding interactions. The dipole moment of the dye is more in the first excited singlet state than in the ground state. This indicates the existence of a more relaxed excited state, due to ICT. As per our knowledge, this is the first report on extensive study of photophysical characteristics of biologically active 4-aryloxymethyl coumarin 4IP6MC and it would help to understand the usage of the dye in various chemical and biological applications.

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