Solvatochromic and computational study of ground state and excited state dipole moments of coumarin dyes in polar and non-polar solvent environments

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Solvatochromic and computational study of ground state and excited state dipole moments of coumarin dyes in polar and non-polar solvent environments

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ABSTRACT

The solvent effect on the photophysical properties of two coumarin derivatives 4-Hydroxy-3-nitrocoumarin (C1) and 3-(Bromoacetyl)coumarin (C2) is examined using UV-VIS and fluorescence spectroscopic procedure in polar and non-polar solvent environments. Lippert, Bakhshiev and Kawaski-Chamma-Viallet correlations were evoked for the calculation of their excited state dipole moments as well as change in the dipole moment. Meanwhile Reichardt's microscopic solvent polarity parameter E_T^N is also used for the same. The ground state dipole moment is evaluated using Gaussian 16 program and geometry optimization using DFT method at 6–311++G (d, p)/B3LYP. The excited state dipole moments of both the compounds calculated from different equations are found to be higher than that of ground state indicating the intra molecular charge transfer (ICT) and twisted intra molecular charge transfer (TICT) in their emitting singlet states

Key words:

Coumarin derivatives, Solvatochromism, Dipole moments, Gaussian studies

1. INTRODUCTION

It is a well-known fact that the photo physical properties of organic compounds such as ground state dipole moment (μ_g), excited state dipole moment (μ_e), quantum efficiency, fluorescence quenching etc depend on solvent environment. In solvent environment, the initial and final state of a molecule is either steady or disturbed by *solvation energy*. The solvation energy differences between initial and excited states termed as Solvatochromic shift and it is one of the simplest and most widely used method to calculate μ_g and μ_e[1-6]

When EM radiation falls on the molecule, the electric vector present in it affects the charge distribution and hence the dipole moment of the molecule is altered. This change is also influenced by solvent parameters such as viscosity and polarity (as mentioned earlier). The knowledge of dipole moments and change in dipole moment is required to design optical sensors, dye lasers, to understand the charge distribution, and charge cloud distribution in singlet (S) and triplet (T) states.

Coumarins are well known laser dyes for the blue – green spectral region and exhibit a strong fluorescence in UV and VISIBLE region. They have widespread applications such as laser

dyes, fluorescent probes to determine the rigidity and fluidity of living cells and its surrounding medium, fluorescent indicators, estimation of enzymes, etc [3,7,8]

2. THEORY

Theories in solvatochromism for the estimation of μ_g and μ_e consider general solvent effects and they link the solvent effects to dielectric constant (ε) and refractive index (n) of the solvent [2,7]. The three linear equations used are [9-13]

Lippert-Mataga equation

$$(\bar{\nu}_a - \bar{\nu}_f) = S_1 \Delta f(\varepsilon, n) + const \qquad (1)$$

Bakshiev equation

$$(\bar{\nu}_a - \bar{\nu}_f) = S_2 f_1(\varepsilon, n) + const \qquad (2)$$

Kawski-Chamma-Viallet relation

$$\frac{1}{2}(\bar{\nu}_a + \bar{\nu}_f) = -S_3 f_2(\varepsilon, n) + const \qquad (3)$$

Here $(\bar{\nu}_a - \bar{\nu}_f)$ is stokes' shift,

Δf =Lippert-Mataga solvent polarity function

f_1 = Baksheiv solvent polarity function

f_2 =Kawski-Chamma-Viallet solvent polarity function. In terms of ε and n they can be written as.

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

$$f_1(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \qquad (5)$$

and

$$f_2(\varepsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] + \frac{3}{2}\left[\frac{n^4 - 1}{(n^2 + 2)^2}\right] \qquad (6)$$

S_1, S_2 and S_3 in the above equations are the slopes of linear fit of corresponding equations. They depend critically on the change of the solute's dipole moment upon excitation ($\Delta\mu = \mu_e - \mu_g$) and the size of the cavity radius (a). They are given by

$$S_1 = \frac{2}{hc}\frac{(\mu_e - \mu_g)^2}{a^3} \qquad (7)$$

$$S_2 = \frac{2}{hc}\frac{(\mu_e - \mu_g)^2}{a^3} \qquad (8)$$

$$S_3 = \frac{2}{hc}\frac{(\mu_e^2 - \mu_g^2)}{a^3} \qquad (9)$$

here 'a' is the Onsager radius and it is calculated by calculating the molecular volume [14]. The other terms have their usual meaning. μ_g and μ_e are calculated using equations

$$\mu_g = \frac{S_3 - S_2}{2}\left[\frac{hca^3}{2S_2}\right]^{1/2} \qquad (10)$$

$$\mu_e = \frac{S_3 + S_2}{2}\left[\frac{hca^3}{2S_2}\right]^{1/2} \quad (11)$$

$$\mu_e = \left[\frac{S_3 + S_2}{S_3 - S_2}\right]\mu_g \quad for\ (S_3 > S_2) \quad (12)$$

As mentioned earlier specific effects of solvents such as polarization and hydrogen bonding effect on spectroscopic properties are not included in these theories. Hence for better understanding of the dipole moment change, microscopic solvent polarity parameter (E_T^N) is employed as suggested by Reichardt [15] and adopted by many researchers in their work [16-18]. The corresponding linear equation is

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2\left(\frac{a_B}{a}\right)^3\right]E_T^N + const \quad (13)$$

Here $\Delta\mu_B$ (9D) and a_B (6.2A^0) are the difference in dipole moment and Onsager radius of betaine dye, respectively. The change in dipole moment ($\Delta\mu$) can be obtained from the slope (S) of the Stokes' shift versus E_T^N graph and it is given by

$$\Delta\mu = \left(\mu_e - \mu_g\right) = \sqrt{\frac{S \times 81}{\left(6.2/a\right)^3 11307.6}} \quad (14)$$

3. EXPERIMENTAL METHODS

Two coumarin derivatives namely 4-Hydroxy-3-nitrocoumarin ($C_9H_5NO_5$.)(C1) and 3-(Bromoacetyl)coumarin($C_{11}H_7BrO_3$.)(C2) are used in this study. Their structures are given in Fig-1. They are procured from Sigma Aldrich

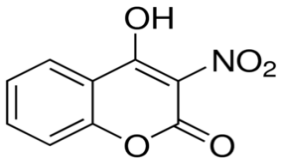


Fig 1-(a) Molecular structure of 4-Hydroxy-3-nitrocoumarin (C1)

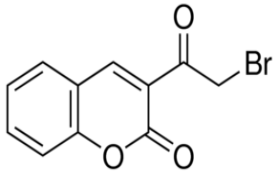
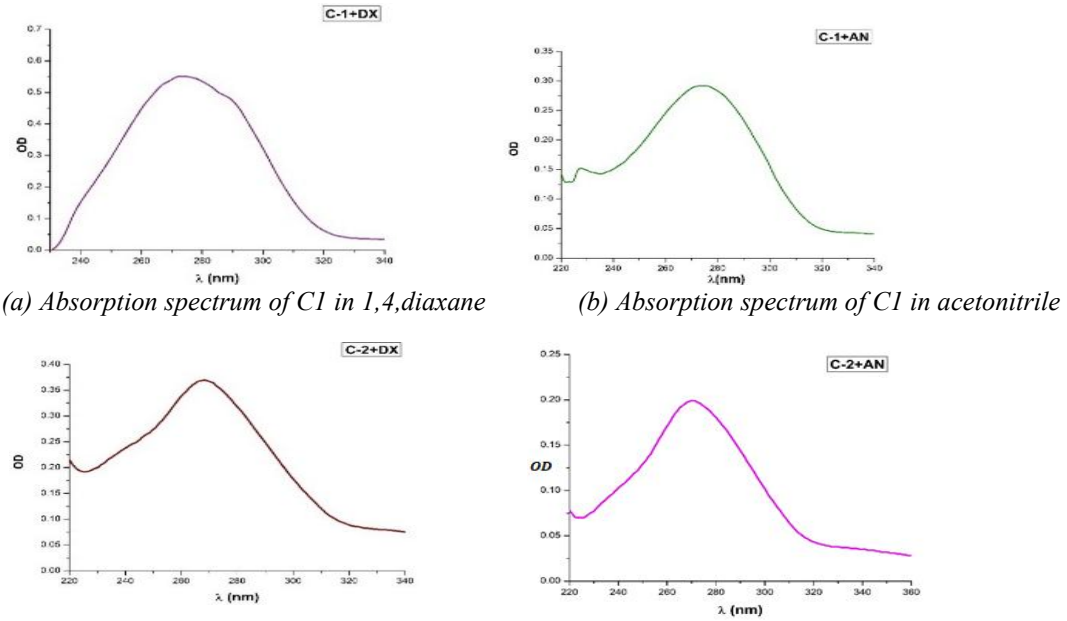


Fig 1-(b) Molecular structure of 3-(Bromoacetyl)coumarin (C2)

Spectroscopic properties of these solutes are examined in both polar and non-polar solvents environment. Spectroscopic grade Polar solvents like water, acetone, acetonitrile, DMF, DMSO etc have large dipole moment and have considerable charge separation. On the other hand non polar solvents such as alkanes, benzene, toluene, diethylether, pyridine etc have very low dipole moment and do not have appreciable charge separation. 1,4,diaxne (DX), diethylether (DEE), tetrahedrofuran (THF), dichloromethane(DCM), dimethylsulfoxide (DMSO), acetonitrile (ACN), Toluene(TOL), butanol (BU)and methanol(ME) are used for the study. The concentration of the solution was maintained at 1×10^{-4} M to satisfy Beer-Lambert's law and to nullify the self-absorption [2]. The absorption spectrum of sample at 300K is recorded using UV–Visible Spectrophotometer (Hitachi UH5300) keeping scanning wavelength in the range is 200 nm-500 nm at 0.5 nm scanning speed. The absorption spectra of C1 and C2 in 1,4,diaxane and acetonitrile are given in Fig-2.

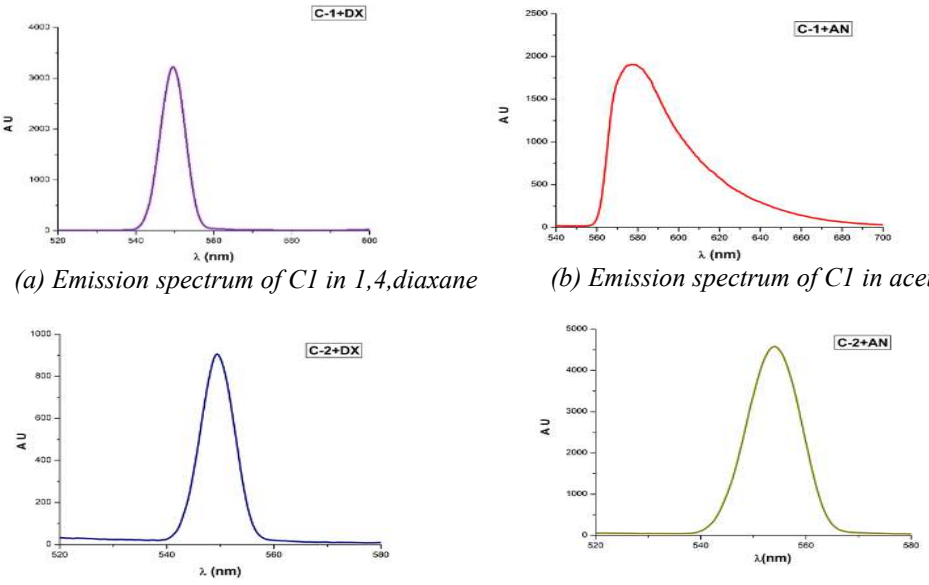
The emission spectra at 300K is taken using F-2700 Spectrophotometer keeping the slit width at 5 nm and operating voltage 700 V. The wavelength corresponds to absorption peak is taken as excitation wavelength. The emission spectra of C1 and C2in 1,4 diaxane and acetonitrile are given in Fig-3



(a) Absorption spectrum of C1 in 1,4,diaxane *(b) Absorption spectrum of C1 in acetonitrile*

(c) Absorption spectrum of C2 in 1,4,diaxane *(d) Absorption spectrum of C2 in acetonitrile*

Fig.2. The absorption spectra of C1 and C2 in 1,4,diaxane and acetonitrile



(a) Emission spectrum of C1 in 1,4,diaxane *(b) Emission spectrum of C1 in acetonitrile*

(c) Emission spectrum of C2 in 1,4,diaxane *(d) Emission spectrum of C2 in acetonitrile*

Fig.3. The fluorescence spectrum of C1 and C2 in 1,4,diaxane and acetonitrile

4. RESULTS AND DISCUSSIONS

4.1 Solvatochromic study

The solvatochromic data such as absorption and emission peak (in *nm*), absorption and emission wavenumber (in cm^{-1}), Stokes shift and arithmetic mean of wavenumbers of both C1 and C2 are given in Table-1 and Table-2. The solvent polarity and E_T^N values of the chosen solvents are given in Table-3. While Δf, f_1 and f_2 are calculated from equations (4) (5) & (6) E_T^N are chosen from literature [3, 18]

We noticed a small shift in the absorption peak towards longer wavelength as the solvent polarity increases. However emission peak shifts by 28nm in C1 and 16nm in C2. This indicates possible $\pi \rightarrow \pi^*$ transitions.

The insignificant shift in absorption spectra is because of the less polar nature of the ground states of studied compounds and hence ground state energy distribution is not affected. On the other hand substantial shift of emission peak shows that excited states interact more strongly with polar solvents and obviously the excited state dipole moment is greater than ground state dipole moment.

The linear plots of Lippert's and Bakshiev's polarity function versus Stokes shift, Kawski-Chamma-Viallet's polarity function versus arithmetic mean Stokes shift and Microscopic solvent polarity parameter versus Stokes shift are plotted. These plots, represented in Fig-4 and Fig.5,are having an excellent correlation. The slopes, number of data points and correlation (R^2) are presented in Table.4.

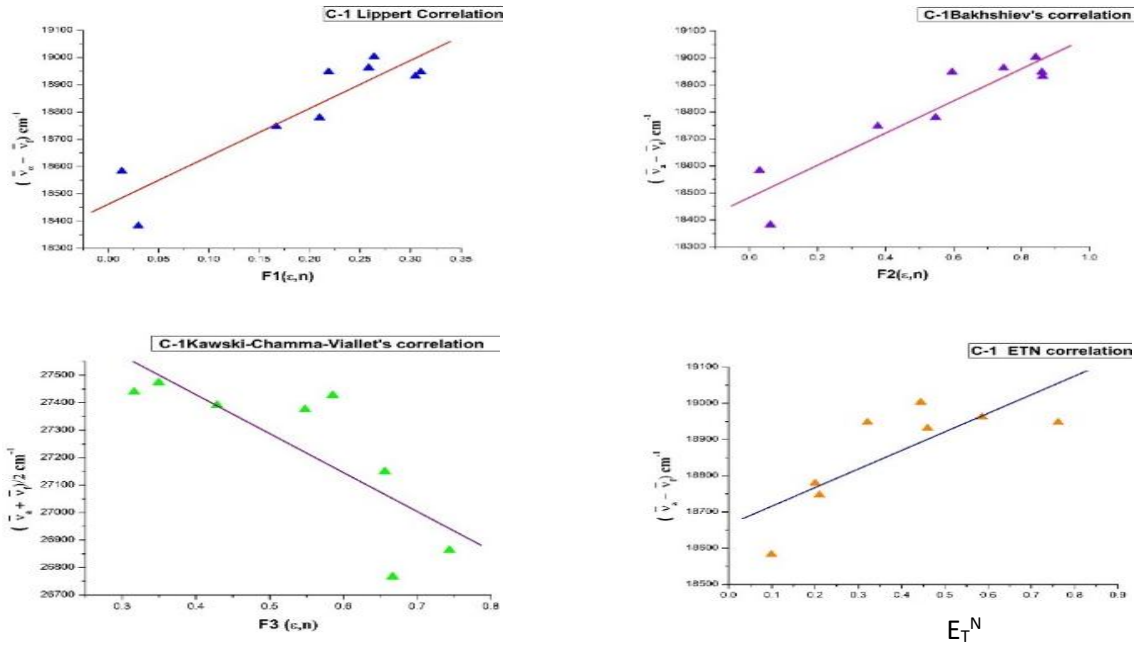


Fig.4. Plots of solvent polarity v/s spectroscopic data for C1

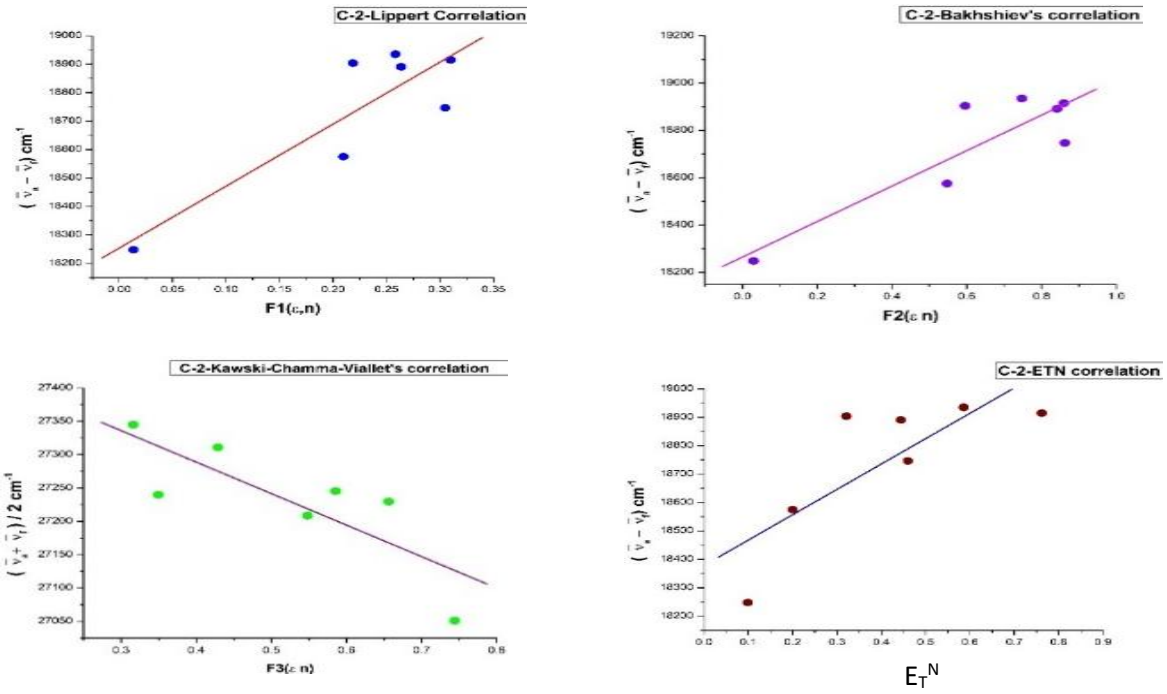


Fig.5. Plots of solvent polarity v/s spectroscopic data for C2

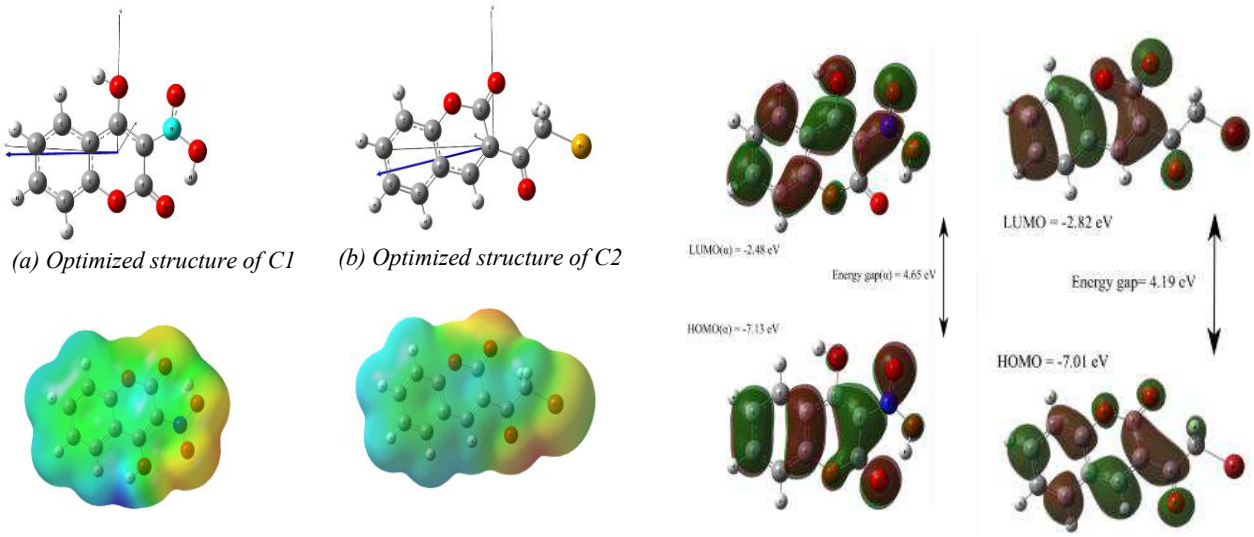
The theoretically estimated ground state dipole moment using Gaussian 16 program, B3LYP hybrid functional and the 6-311 G ++(d,p)[19,20] basis set, excited state dipole moments calculated using Lippert equation, Bakhsiev equation and Kawaski-Chamma-Viallet equations for both the compounds are given in Table.5. Ground state and excited state dipole moment for C1 are also calculated using equation (10) and equation (11). For C2 this exercise is not performed because of $S_3 < S_2$. The change in dipole moment is evaluated from microscopic solvent polarity parameter versus Stokes shift graph as well as from equations (10) and (11) and the data is presented in Table.5.

From the calculated values of μ_g & μ_e we can make out that the excited state dipole moment of both the compounds is larger than the ground state value. This is because of more polar nature of the excited states, intramolecular charge transfer (ICT) and twisted intramolecular charge transfer (TICT)[21,22]

4.2 Computational study

The structures of C1 and C2 underwent optimization through density functional theory(DFT), employing the B3LYP hybrid functional and the 6-311 G ++(d,p) basis set. The resulting optimized structure of C1 achieved a minimum energy of -777.32645 Hartree (-21.15 keV). It exhibited a dipole moment of 7.063 Debye and a polarization of 139.06533 atomic units. For C2 the resulting optimized structure achieved a minimum energy of -3220.779038 Hartree (-87.64 keV). It exhibited a dipole moment of 6.73 Debye and a polarization of 147.52 atomic units. The ground state dipole moments obtained from computational studies are normally on higher side because calculation of this type assumes that molecules are involved in the gas phase and does not

include solvent interactions [23]. Optimized geometries, ESP maps and HOMO-LUMO surfaces of C1 and C2 are as shown in Fig-6



(a) Optimized structure of C1 *(b) Optimized structure of C2*

(c) ESP map of C1 *(d) ESP map of C2* *(e) HOMO-LUMO of C1* *(f) HOMO-LUMO of C2*

Fig.6. Images of optimized structure, ESP and HOMO-LUMO for C1 and C2

5. CONCLUSIONS

From the solvatochromic and computational studies photophysical properties of two coumarin derivatives in different solvent environment we have arrived at certain conclusions. The insignificant shift in the absorption peaks and significant shifts in emission peaks denotes the possible $\pi \rightarrow \pi^*$ transitions and also stresses the fact that the ground states are less affected and excited states are more affected due to interaction of solute with the solvents. The higher values of excited state dipole moments the high polar nature of the compounds in excited state and the high polar nature is attributed to ICT and TICT. It is believed that the experimental results presented in this article may be useful for designing of newer molecules and sensors for explicit applications

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1: Absorption peak, emission peak, absorption wavenumber ($\bar{\nu}_a$), emission wave number ($\bar{\nu}_f$), Stokes shift ($\Delta\bar{\nu}$) and arithmetic mean of wavenumbers of C1

Solvent	λ_a (nm)	λ_f (nm)	$\overline{\nu_a}$ (cm^{-1})	$\overline{\nu_f}$ (cm^{-1})	$\Delta\bar{\nu} = \overline{\nu_a} - \overline{\nu_f}$ (cm^{-1})	$\frac{\overline{\nu_a} + \overline{\nu_f}}{2}$ (cm^{-1})
TOL	272	550	36764.71	18181.82	18582.89	27473.26
DX	273	548	36630.04	18248.18	18381.86	27439.11
DEE	272	555	36764.71	18018.02	18746.69	27391.36
THF	272	556	36764.71	17985.61	18779.09	27375.16
DCM	271	557	36900.37	17953.32	18947.05	27426.85
BU	273	566	36630.04	17667.84	18962.19	27148.94
DMSO	275	576	36363.64	17361.11	19002.53	26862.37
ACN	276	578	36231.88	17301.04	18930.85	26766.46
ME	271	557	36900.37	17953.32	18947.05	27426.85

Table 2: Absorption peak, emission peak, absorption wavenumber ($\overline{\nu_a}$), emission wave number ($\overline{\nu_f}$), Stokes shift ($\Delta\bar{\nu}$) and arithmetic mean of wavenumbers of C2

Solvent	λ_a (nm)	λ_f (nm)	$\overline{\nu_a}$ (cm^{-1})	$\overline{\nu_f}$ (cm^{-1})	$\Delta\bar{\nu} = \overline{\nu_a} - \overline{\nu_f}$ (cm^{-1})	$\frac{\overline{\nu_a}+\overline{\nu_f}}{2}$ (cm^{-1})
TOL	275	552	36363.64	18115.94	18247.69	27239.79
DX	271	560	36832.41	17857.14	18975.27	27344.78
DEE	272	560	36764.71	17857.14	18907.56	27310.92
THF	274	558	36496.35	17921.15	18575.20	27208.75
DCM	272	562	36697.25	17793.59	18903.65	27245.42
BU	272	563	36697.25	17761.99	18935.26	27229.62
DMSO	274	568	36496.35	17605.63	18890.72	27050.99
AN	272	555	36764.71	18018.02	18746.69	27391.36
ME	271	556	36900.37	17985.61	18914.76	27442.99

Table 3: Values of Solvent polarity parameters and ETN

Solvent	Δf	f_1	f_2	E_T^N	Solvent	Δf	f_1	f_2	E_T^N
BU	0.2584	0.7475	0.6562	0.586	BU	0.2584	0.7475	0.6562	0.586
DMSO	0.2637	0.8417	0.7440	0.444	DMSO	0.2637	0.8417	0.7440	0.444
AN	0.3047	0.8625	0.6669	0.46	AN	0.3047	0.8625	0.6669	0.46
ME	0.31	0.86	0.65	0.762	ME	0.31	0.86	0.65	0.762

Table.4: Types of Correlations, Slope, Correlation value and Number of data points for C1 and C2

Correlations	Compound	Slope (S)	Correlation (R^2)	No. of data
Lippert Correlation (S_1)	C1	1759.147	0.9170	9
	C2	2178.622	0.8657	7
Bakhshiev's correlation (S_2)	C1	594.807	0.9291	9
	C2	749.847	0.8795	7
Kawski-Chamma-Viallet's correlation (S_3)	C1	-1419.044	-0.7969	8
	C2	-472.538	-0.8058	7
E_T^N correlation (S)	C1	512.757	0.7824	8
	C2	893.271	0.7954	7

Table 5: The calculated values of radius (*a*), μ_g, μ_e and dipole moment change ($\Delta\mu$) for C1 & C2

Compound2	*a (Å)*	μ_g [a] *(D)*	μ_g [b] *(D)*	μ_e [c] *(D)*	μ_e [d] *(D)*	μ_e [e] *(D)*	μ_e [f] *(D)*	μ_e [g] *(D)*	$\Delta\mu$ [h] *(D)*	$\Delta\mu$ [i] *(D)*
C1	3.3678	7.0630	1.0409	2.5432	9.6472	8.5657	7.4345	7.8300	1.5023	0.7673
C2	3.5180	6.7300	---	---	9.8004	8.5310	6.8800	7.8111	---	1.0811

D = Debye = 3.33564×10⁻³⁰ Cm = 10⁻¹⁸ esu cm

[a] ground state dipole moment using Gaussian 16 program, B3LYP hybrid functional and the 6-311 G ++(d,p)[19,20] basis set

[b] Experimental ground state dipole moments calculated from Eq. (10)

[c] Experimental excited-state dipole moments calculated from Eq. (11)

[d] Excited state dipole moments calculated from Lippert's Eq. (7)

[e] Excited state dipole moments calculated from Bakshiev's Eq. (8)

[f] Excited state dipole moments calculated from Kawaski-Chamma-Viallet parameter Eq.(9)

[g] Excited state dipole moments calculated from E_T^N parameter Eq.(14)

[h] Change in dipole moments for μ_e and μ_g from Eq. (10) & (11)

[i] Change in dipole moments calculated from E_T^N parameter Eq. (14)

DATA AVAILABILITY

Data used in this work is available with the corresponding author and will be provided on responsible request

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AUTHOR CONTRIBUTION

Geethanjali H S: Supervision of work, data analysis and original script writing.
Nagasree G: Conceptualization and execution of experimental work.
Nagaraja D: Result analysis, computational calculation, review and editing the script.
Chaluvaraju. B V: Execution of experimental work and editing the script
Raghavendra U P: Execution of experimental work, computational calculation and result analysis